Modular Cyclopentenone Synthesis through the Catalytic Molecular Shuffling of Unsaturated Acid Chlorides and Alkynes

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Supporting information

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1. General information

Unless otherwise noted, all reactions were carried out under argon in oven-dried 4 mL screw-top glass vials using anhydrous solvents. The anhydrous solvents were prepared by distillation over appropriate drying agents or by using solvent purification system (LC Technology Solutions, Inc.) under N_2 atmosphere (H_2O content: below 10 ppm, as determined by Karl Fischer titration) and stored over molecular sieves prior to use. All commercially available compounds were used as received from common suppliers (Sigma-Aldrich, Strem Chemicals, abcr, TCI, Fluorochem, Acros Organics, Alfa Aesar and Apollo Scientific).

Thin layer chromatography (TLC): Aluminum TLC plate, silica gel coated with fluorescent indicator F254 (TLC Silica gel 60 F254, Merck). Visualization was accomplished using UV light (254 nm) or $KMnO_4$ stain.

Flash column chromatography: SiliaFlash P60 silica gel (60 Å, 40−63 µm, SiliCycle Inc.) with reagent grade solvents.

NMR: Spectra were recorded on Bruker AVANCE III 400, Neo 400, Neo 500, or 600 spectrometers at room temperature, unless indicated otherwise; the chemical shifts are reported with respect to internal solvent: δH = 7.26 ppm, and δC = 77.16 (t) ppm ($CDCl_3$); δH = 7.16 ppm, and δC = 128.06 (t) ppm (C_6D_6); δH = 2.50 (p) ppm, and δC = 39.52 (hept) ppm (DMSO-d6). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (sextet), hept (septet), m (multiplet), br (broad), or combinations thereof. All 2D NMR measurements were performed by the NMR service in the Laboratorium für Organische Chemie at ETH Zürich.

GC/FID and GC/MS: Shimadzu GC-2025 (capillary column: Macherey-Nagel OPTIMA 5, 30.0 m × 0.25 mm × 0.25 µm; carrier gas: H_2); To determine GC yields, calibration curves were generated using *n*-dodecane as an internal standard. Agilent Intuvo 9000 GC (capillary column: Agilent HP-Chiral-20B (permethylated ß-cyclodextrin); 30.0 m × 0.25 mm × 0.25 µm; carrier gas: He). Shimadzu GCMS-QP2020 (capillary column: Macherey-Nagel OPTIMA 5, 30.0 m × 0.25 mm × 0.25 µm; carrier gas: He).

High-resolution MS (HRMS): Thermo scientific Q-Exactive GC Orbitrap for EI. Bruker Daltonics maXis ESI-QTOF or solariX ESI-FTICR-MS for ESI. HRMS data were obtained by the mass spectrometry service (MoBiAS, Molecular and Biomolecular Analysis Service) in the Laboratorium für Organische Chemie at ETH Zürich.

X-ray crystal structure: Bruker SMART Platform with Apex I CCD-detector, Bruker-Nonius Kappa-CCD, Bruker-Nonius Mach III/ Apex II CCD-detector, Rigaku Oxford Synergy with Dual-Microsource and Dectris Pilatus 300K. X-ray single crystal structure analyses were provided by the Small Molecule Crystallography Center (SMoCC) of Department of Chemistry and Applied Biosciences at ETH Zürich.

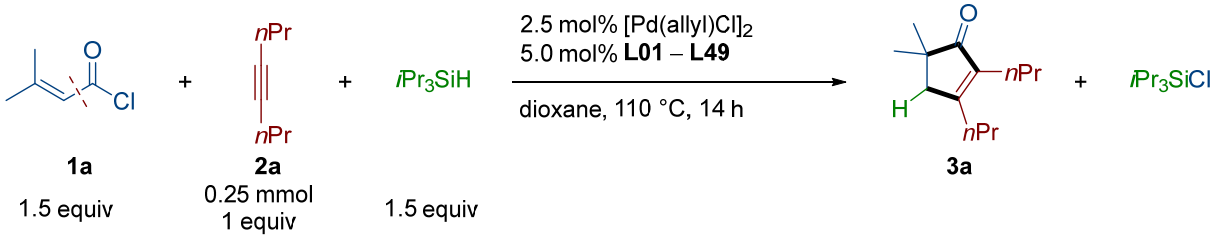
2. Reaction optimization

2.1. Phosphine Ligands

General procedure for ligand screening

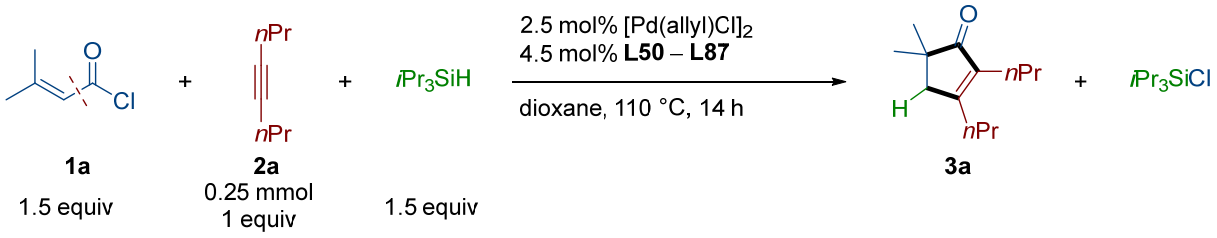
In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (2.5 mol%, 6.25 µmol, 2.29 mg) and the indicated monophosphine ligand (**L01-L49**, 5.0 mol%, 12.50 µmol) or the indicated bisphosphine ligand (**L50-L87**, 4.5 mol%, 11.25 µmol) and then dioxane (2 mL). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added 3,3-dimethylacryloyl chloride (**1a**, 1.5 equiv, 0.375 mmol), 4-octyne (**2a**, 1.0 equiv, 0.250 mmol) and triisopropylsilane (iPr$_3$SiH, 1.5 equiv, 0.375 mmol). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then diluted with DCM (2 mL) and *n*-dodecane was added as an internal standard. The resulting solution was filtered through a celite/silica plug and the filtrate was analyzed by GC/FID and GC/MS.

Eq. S1. Ligand screening – monophosphine ligands.



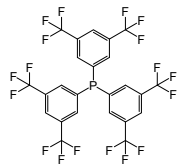
1a 1.5 equiv + **2a** 0.25 mmol 1 equiv + iPr$_3$SiH 1.5 equiv → **3a** + iPr$_3$SiCl

Eq. S2. Ligand screening – bisphosphine ligands.

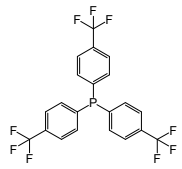


1a 1.5 equiv + **2a** 0.25 mmol 1 equiv + iPr$_3$SiH 1.5 equiv → **3a** + iPr$_3$SiCl

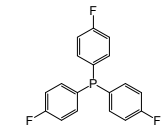
Table S1. Ligand screening – monophosphine ligands. [a]

99% yield 

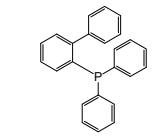
L01 Tris[3,5-bis(trifluoromethyl)phenyl]phosphine

98% yield 

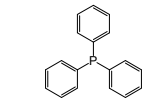
L02 Tris(4-trifluoromethylphenyl)phosphine

88% yield 

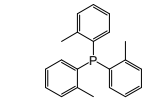
L03 Tris(4-fluorophenyl)phosphine

81% yield 

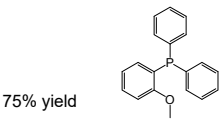
L04 2-(Diphenylphosphino)biphenyl

79% yield 

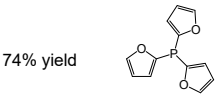
L05 Triphenylphosphine

77% yield 

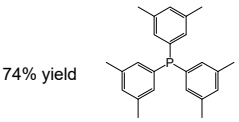
L06 Tri(o-tolyl)phosphine

75% yield 

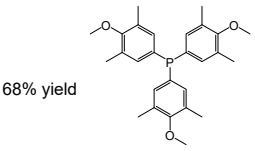
L07 Diphenyl(2-methoxyphenyl)phosphine

74% yield 

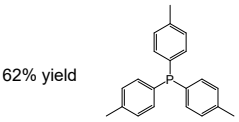
L08 Tri(2-furyl)phosphine

74% yield 

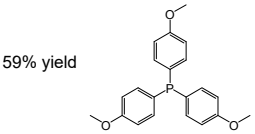
L09 Tris(3,5-dimethylphenyl)phosphine

68% yield 

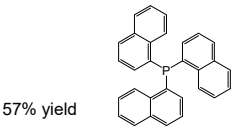
L10 Tris(4-methoxy-3,5-dimethylphenyl)phosphine

62% yield 

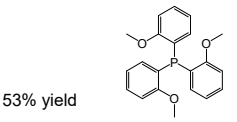
L11 Tri(p-tolyl)phosphine

59% yield 

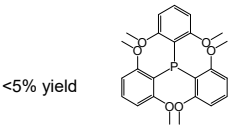
L12 Tris(4-methoxyphenyl)phosphine

57% yield 

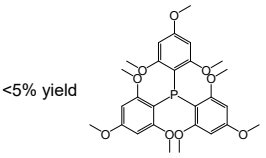
L13 Tri-1-naphthylphosphine

53% yield 

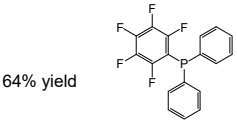
L14 Tris(o-methoxyphenyl)phosphine

<5% yield 

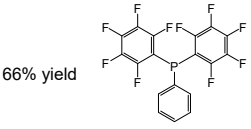
L15 Tris(2,6-dimethoxyphenyl)phosphine

<5% yield 

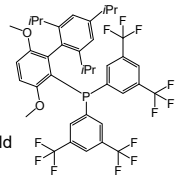
L16 Tris(2,4,6-trimethoxyphenyl)phosphine

64% yield 

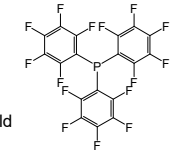
L17 (Pentafluorophenyl)diphenylphosphine

66% yield 

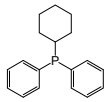
L18 Bis(pentafluorophenyl)phenylphosphine

12% yield 

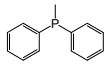
L19 Jackiephos

7% yield 

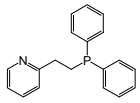
L20 Tris(pentafluorophenyl)phosphine

60% yield 

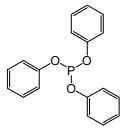
L21 Cyclohexyldiphenylphosphine

51% yield 

L22 Methyldiphenylphosphine

43% yield 

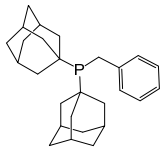
L23 2-(2-(Diphenylphosphino)ethyl)pyridine

85% yield 

L24 Triphenyl phosphite

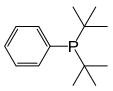
Table S1 (continued). Ligand screening – monophosphine ligands. [a]

52% yield



L25 Di(1-adamantyl)benzylphosphine

20% yield

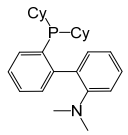


L31 Di-tert-butylphenylphosphine

18% yield

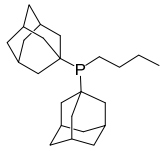
L37 Dicyclohexylphenylphosphine

32% yield



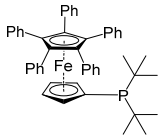
L43 DavePhos

45% yield



L26 Di(1-adamantyl)-n-butylphosphine

7% yield

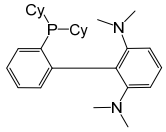


L32 QPhos

28% yield

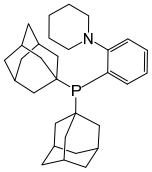
L38 Dicyclohexyl (2-methylphenyl)phosphine

24% yield



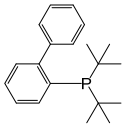
L44 Cphos

30% yield



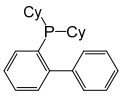
L27 Di(1-adamantyl)-1-piperidinylphenylphosphine

7% yield



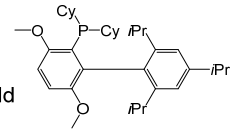
L33 JohnPhos

37% yield



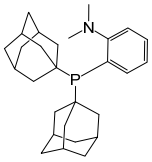
L39 CyJohnPhos

5% yield



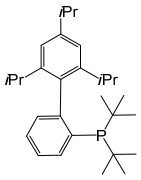
L45 BrettPhos

<5% yield



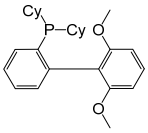
L28 Di(1-adamantyl)-2-dimethylaminophenylphosphine

<5% yield



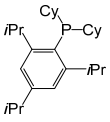
L34 tBuXPhos

38% yield



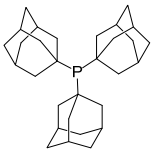
L40 Sphos

8% yield



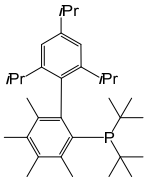
L46 Dicyclohexyl (2,4,6-triisopropylphenyl)phosphine

n.d.



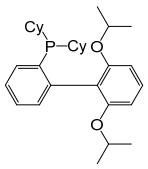
L29 Tris(1-adamantyl)phosphine

8% yield



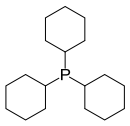
L35 Me4tButylXphos

32% yield



L41 RuPhos

5% yield

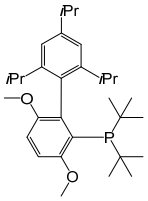


L47 Tricyclohexylphosphine

n.d.

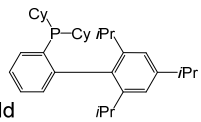
L30 Tri-tert-butylphosphine

<5% yield



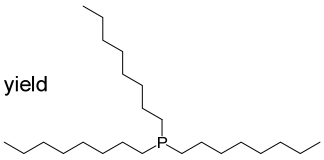
L36 tBuBrettPhos

30% yield



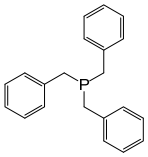
L42 Xphos

8% yield



L48 Trioctylphosphine

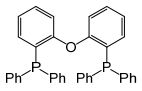
19% yield

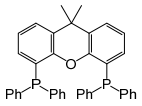


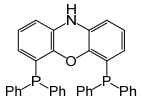
L49 Tribenzylphosphine

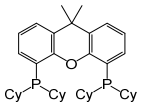
[a]The GC yields (**3a**) are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

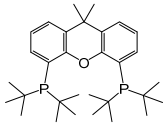
Table S2. Ligand screening – bisphosphine ligands.[a]

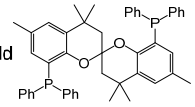
70% yield 
L50 DPEphos

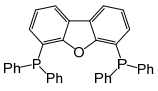
19% yield 
L51 Xantphos

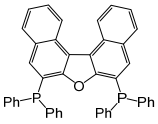
25% yield 
L52 4,6-Bis(diphenylphosphino)phenoxazine

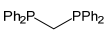
<5% yield 
L53 4,5-Bis(dicyclohexylphosphino)-9,9-dimethylxanthene

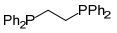
8% yield 
L54 9,9-Dimethyl-4,5-bis(di-t-butylphosphino)xanthene

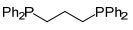
62% yield 
L55 SPANphos

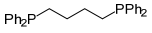
45% yield 
L56 DBFphos

38% yield 
L57 UDNFphos

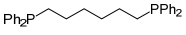
30% yield 
L58 dppm

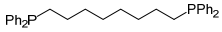
6% yield 
L59 dppe

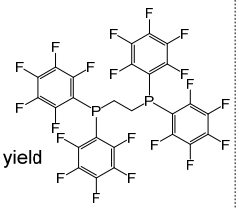
7% yield 
L60 dppp

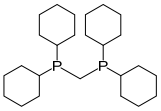
17% yield 
L61 dppb

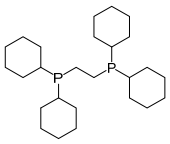
28% yield 
L62 dpppent

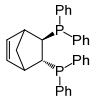
30% yield 
L63 dpphex

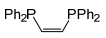
38% yield 
L64 dppoct

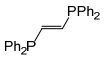
28% yield 
L65 dAr^{F}pe

<5% yield 
L66 dcypm

<5% yield 
L67 dcype

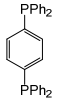
16% yield 
L68 (R,R)-NORPHOS, 71042-55-2

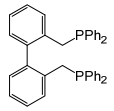
<5% yield 
L69
cis-1,2-Bis(diphenylphosphino)ethylene

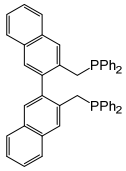
69% yield 
L70
trans-1,2-Bis(diphenylphosphino)ethylene

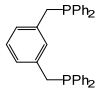
<5% yield 
L71 1,2-Bis(diphenylphosphino)benzene

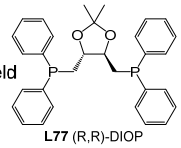
<5% yield 
L72 1,8-(Diphenylphosphino)naphthalene

79% yield 
L73
1,4-bis(diphenylphosphaneyl)benzene

75% yield 
L74 BISBI

67% yield 
L75 VNAphos

21% yield 
L76
1,3-Bis(diphenylphosphinomethyl)benzene

19% yield 
L77 (R,R)-DIOP

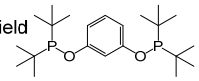
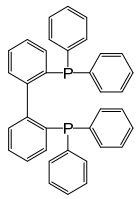
12% yield 
L78
1,3-Bis[(di-tert-butylphosphino)oxy]benzene

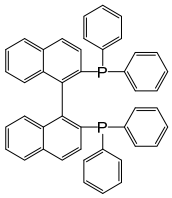
Table S2 (continued). Ligand screening – bisphosphine ligands.[a]

61% yield



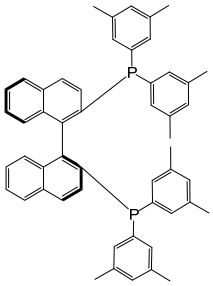
L79 BIPHEP

65% yield



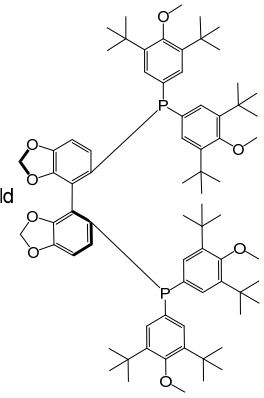
L80 rac-BINAP

58% yield



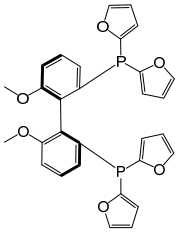
L81 (S)-(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl

57% yield



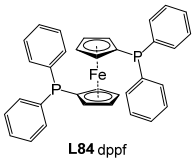
L82 (S)-DTBM-SEGPHOS

6% yield



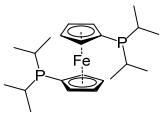
L83 (S)-(−)-2,2'-Bis(di-2-furylphosphino)-6,6'-dimethoxy-1,1'-biphenyl

37% yield



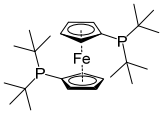
L84 dppf

7% yield



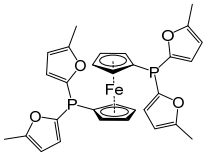
L85 1,1'-Bis(diisopropylphosphino)ferrocene

54% yield



L86 1,1'-Bis(di-t-butylphosphino)ferrocene

23% yield



L87 HiersoPHOS-3

[a]The GC yields (**3a**) are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

Figure S1. Ligand screening – electronics.

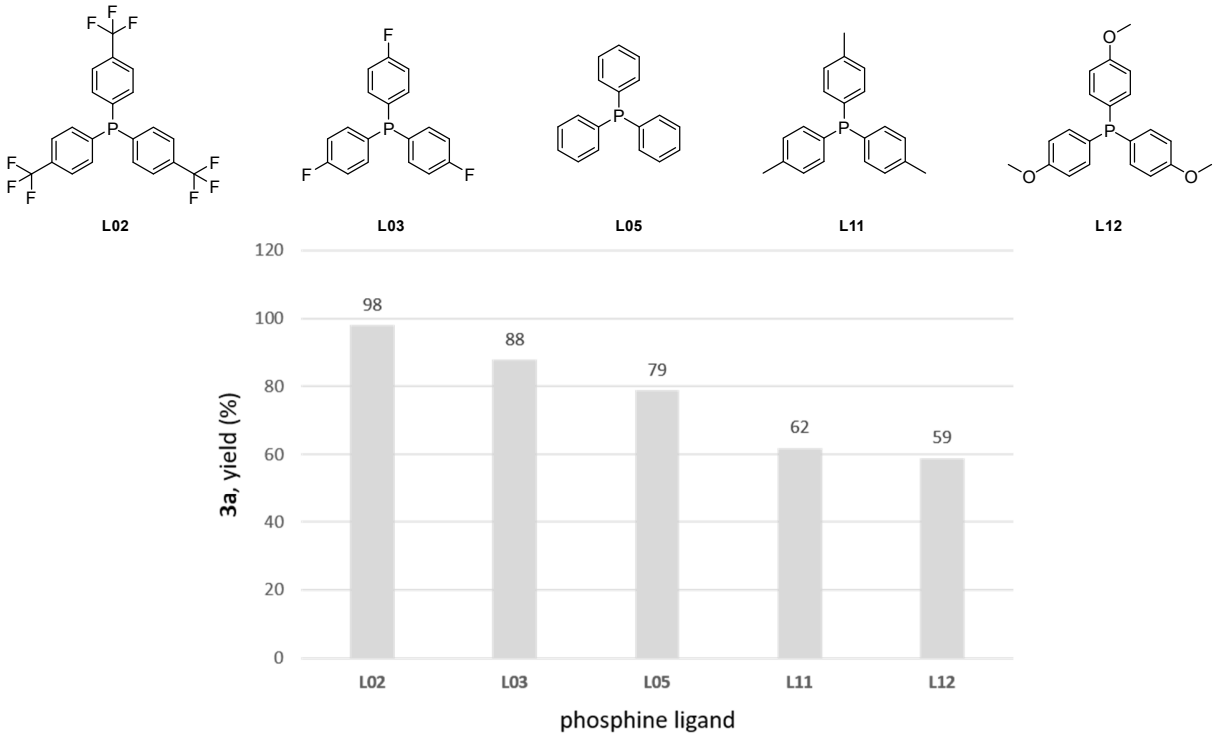


Figure S2. Ligand screening – electronics.

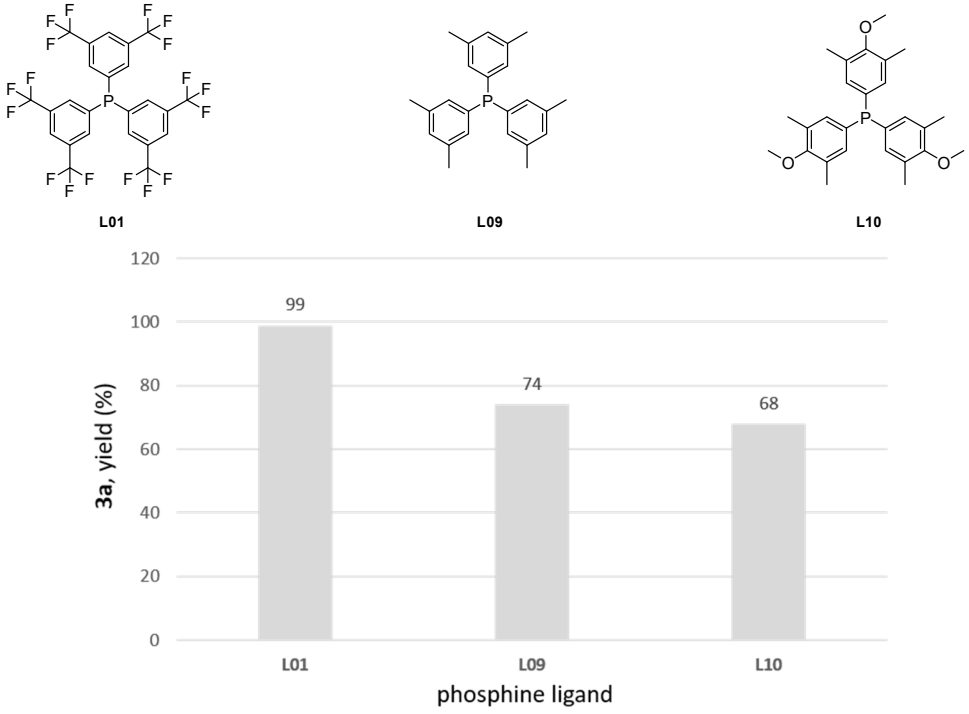
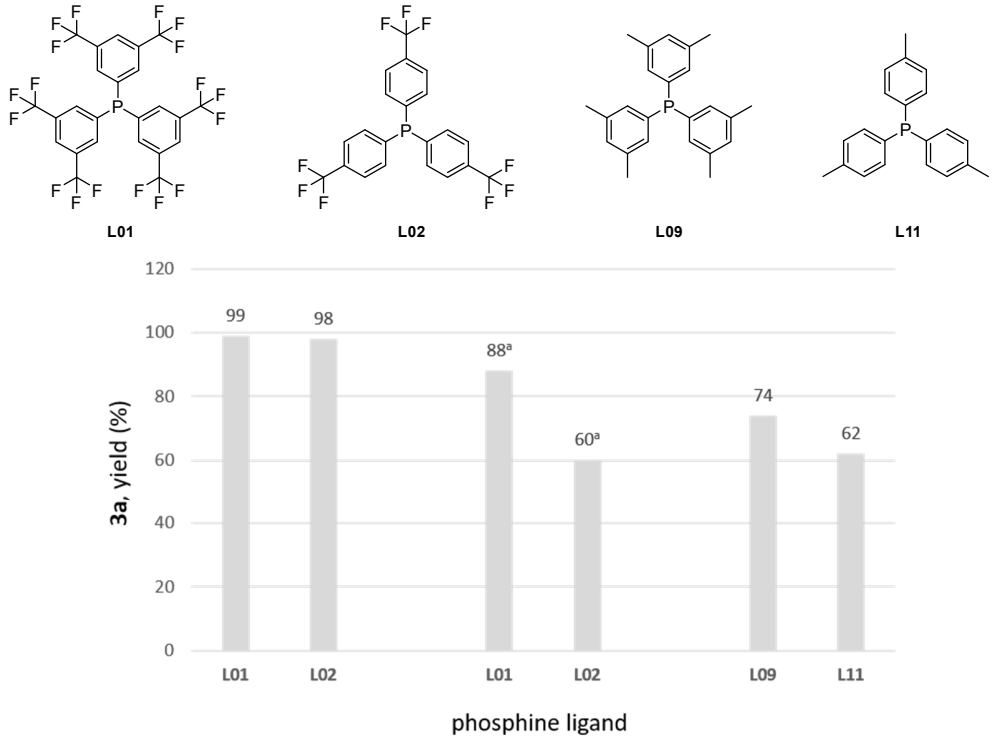


Figure S3. Ligand screening – cone angle.



[a]See Table S3, entries 2 and 4

Figure S4. Ligand screening – chelating and non-chelating.

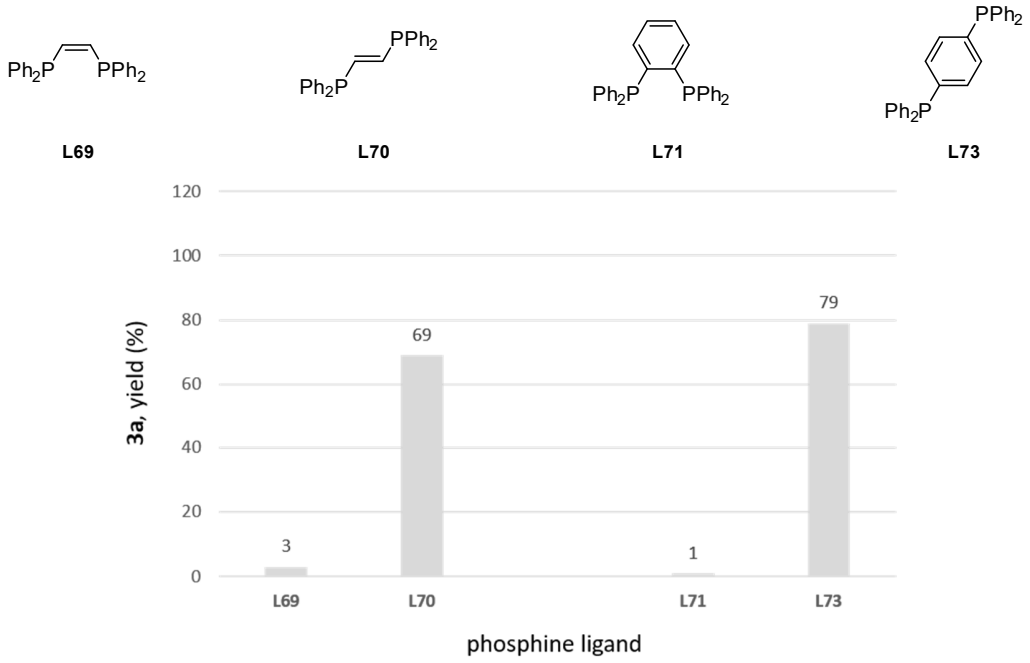
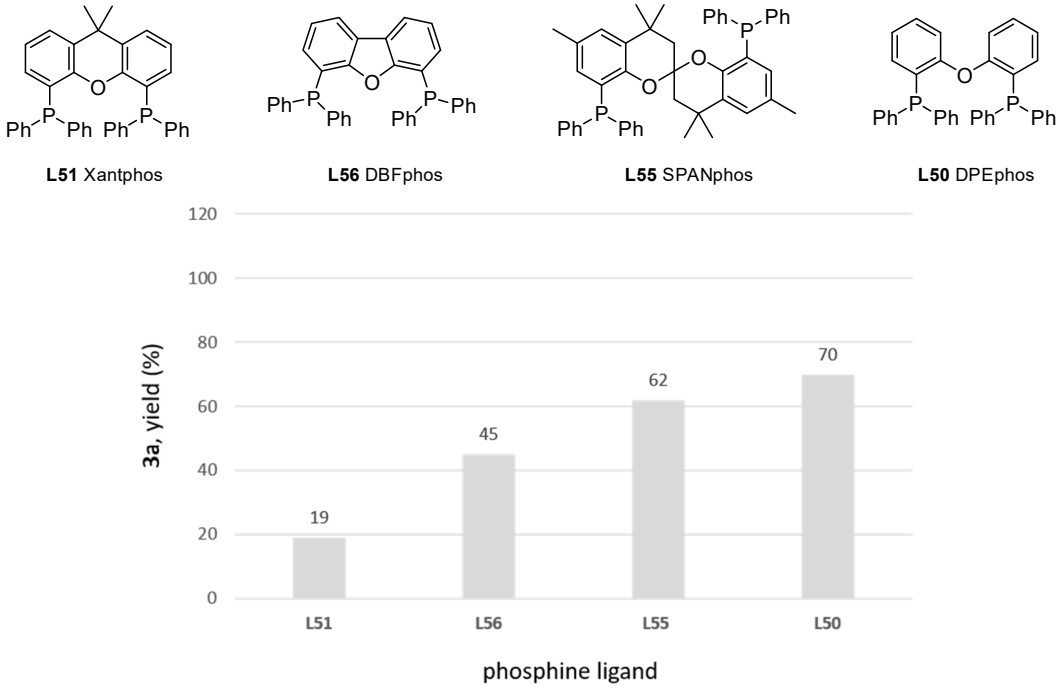
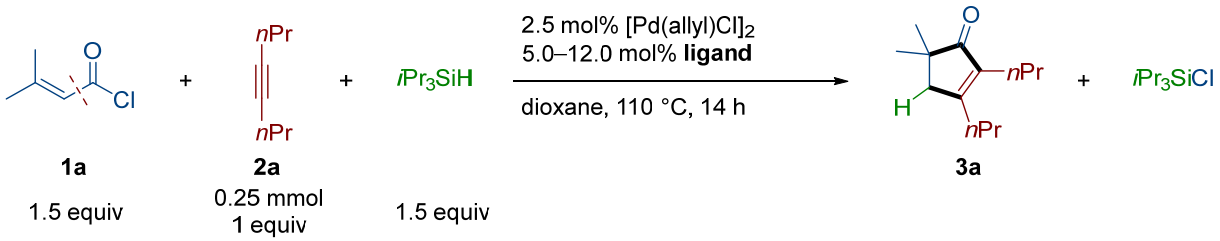


Figure S5. Ligand screening – bite angle and backbone rigidity.



2.2. P to Pd ratio

Eq. S3. P to Pd ratio screening.



1a 1.5 equiv

2a 0.25 mmol, 1 equiv

1.5 equiv

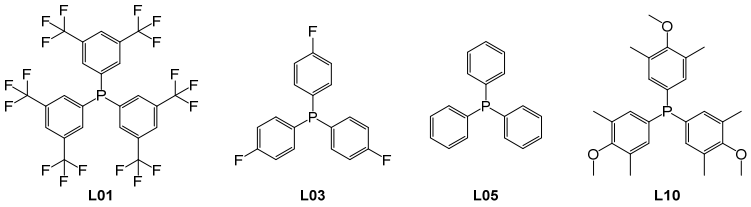
3a

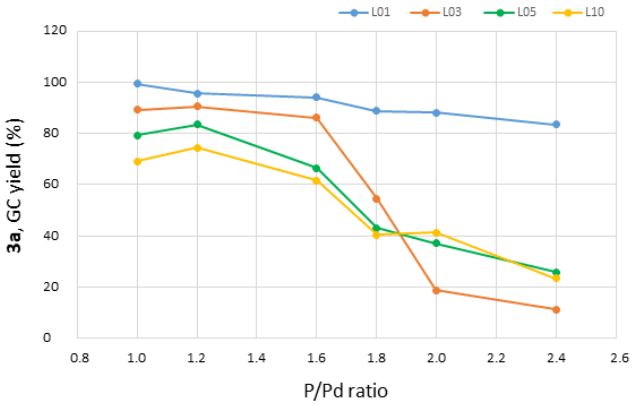
Table S3. P to Pd ratio screening - monophosphine ligands.[a]

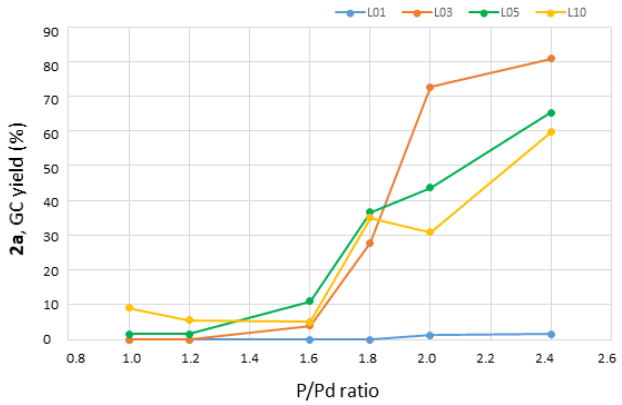
entry	ligand		mol%, ligand	P:Pd ratio	**2a** (unreacted), yield (%)	iPr$_3$SiH (unreacted), yield (%)	**3a**, yield (%)
1	**L01**	Tris[3,5-bis(trifluoromethyl)phenyl]phosphine	5	1.0	0	0	99
2	**L01**	Tris[3,5-bis(trifluoromethyl)phenyl]phosphine	10	2.0	<3	0	88
3	**L02**	Tris(4-trifluoromethylphenyl)phosphine	5	1.0	0	0	98
4	**L02**	Tris(4-trifluoromethylphenyl)phosphine	10	2.0	31	55	60
5	**L03**	Tris(4-fluorophenyl)phosphine	5	1.0	0	0	88
6	**L03**	Tris(4-fluorophenyl)phosphine	10	2.0	73	107	19
7	**L04**	2-(Diphenylphosphino)biphenyl	5	1.0	3	0	81
8	**L04**	2-(Diphenylphosphino)biphenyl	10	2.0	28	42	49
9	**L05**	Triphenylphosphine	5	1.0	<3	0	79
10	**L05**	Triphenylphosphine	10	2.0	44	70	37
11	**L08**	Tri(2-furyl)phosphine	5	1.0	<3	3	74
12	**L08**	Tri(2-furyl)phosphine	10	2.0	8	24	72
13	**L09**	Tris(3,5-dimethylphenyl)phosphine	5	1.0	7	0	74
14	**L09**	Tris(3,5-dimethylphenyl)phosphine	10	2.0	41	61	36
15	**L10**	Tris(4-methoxy-3,5-dimethylphenyl)phosphine	5	1.0	9	0	68
16	**L10**	Tris(4-methoxy-3,5-dimethylphenyl)phosphine	10	2.0	31	44	41
17	**L14**	Tris(o-methoxyphenyl)phosphine	5	1.0	14	<3	53
18	**L14**	Tris(o-methoxyphenyl)phosphine	10	2.0	32	24	35
19	**L24**	Triphenyl phosphite	5	1.0	<3	0	85
20	**L24**	Triphenyl phosphite	10	2.0	<3	0	90

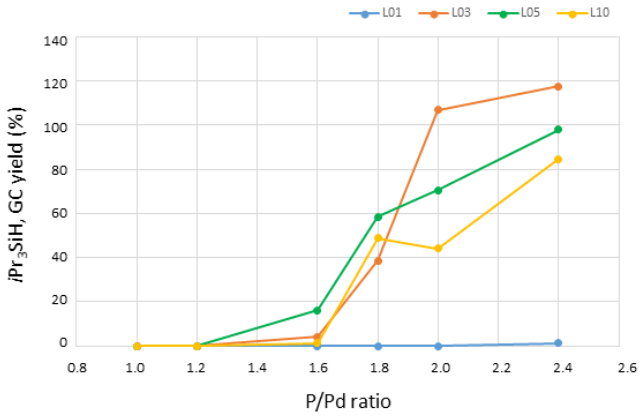
[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

Figure S6. P to Pd ratio screening - monophosphine ligands.[a]



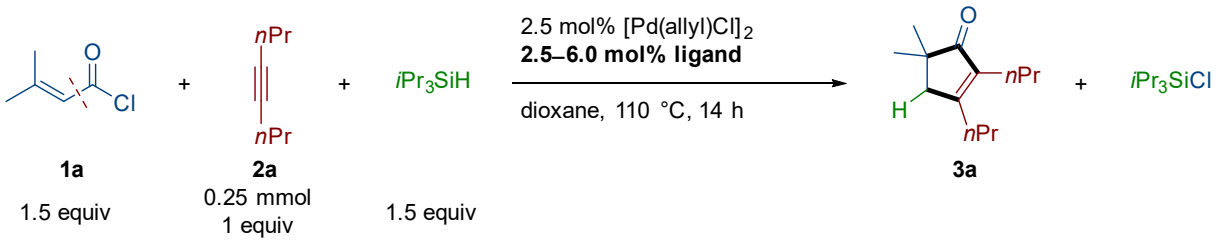






[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

Eq. S4. P to Pd ratio screening - bisphosphine ligands.



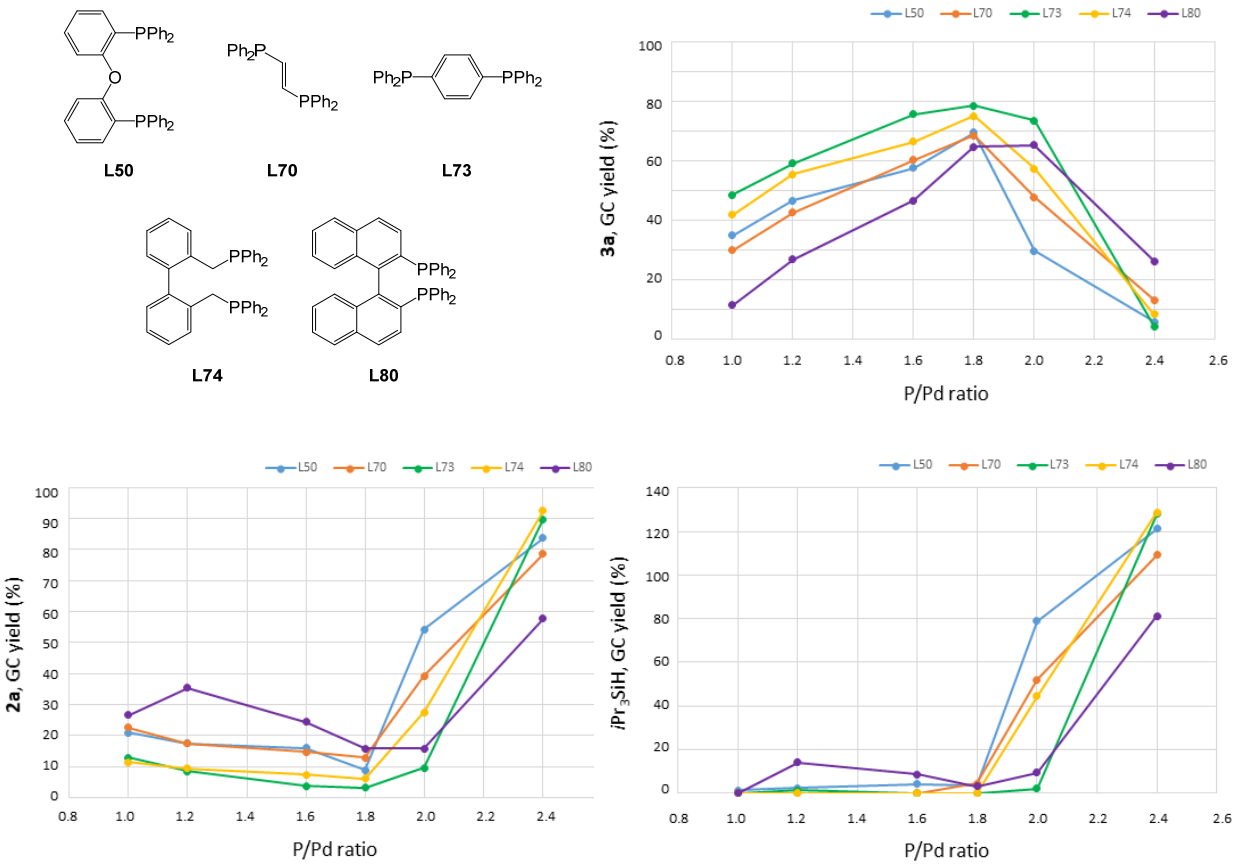
1a 1.5 equiv

2a 0.25 mmol, 1 equiv

1.5 equiv

3a

Figure S7. P to Pd atomic ratio screening - bisphosphine ligands.[a]



[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

2.3. Transition metal precursors

Eq. S5. Transition metal precursor screening.

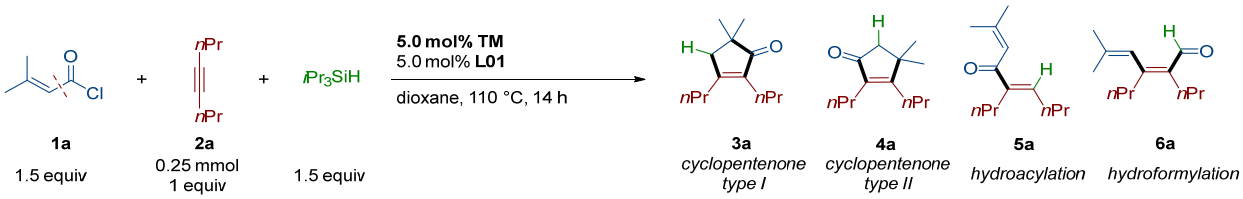


Table S4. Transition metal precursor screening**.**

Yield (%)[a,b]

entry	transition metal	**3a**	**4a**	**5a**	**6a**	iPr$_3$SiH (unreacted)	**2a** (unreacted)
1	$[Pd(allyl)Cl]_2$ (2.5 mol%)	99	n.d.	n.d.	n.d.	0	0
2	$Pd_2(dba)_3$ (2.5 mol%)	93	n.d.	n.d.	n.d.	0	0
3	$(PhCN)_2PdCl_2$ (5.0 mol%)	90	n.d.	n.d.	n.d.	0	0
4	$PdCl_2(cod)$ (5.0 mol%)	89	n.d.	n.d.	n.d.	0	0
5	$Pd(PPh_3)_4$ (5.0 mol%), no **L01**	8	n.d.	n.d.	n.d.	115	77
6	$[Pd(allyl)Cl]_2$ (2.5 mol%), no **L01**	n.d.	(19)	trace	n.d.	0	17
7	$Ni(cod)_2$ (5.0 mol%)	n.d.	n.d.	n.d.	n.d.	135	92
8	$[Ir(cod)Cl]_2$ (2.5 mol%)	n.d.	n.d.	n.d.	n.d.	0	52
9	$[Rh(cod)Cl]_2$ (2.5 mol%)	n.d.	n.d.	(59)	n.d.	0	8
10	$Co_2(CO)_8$ (2.5 mol%)	n.d.	n.d.	n.d.	n.d.	132	92
11	no transition metal	n.d.	n.d.	n.d.	n.d.	134	94

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.). [b]Yields of isolated product given in parentheses.

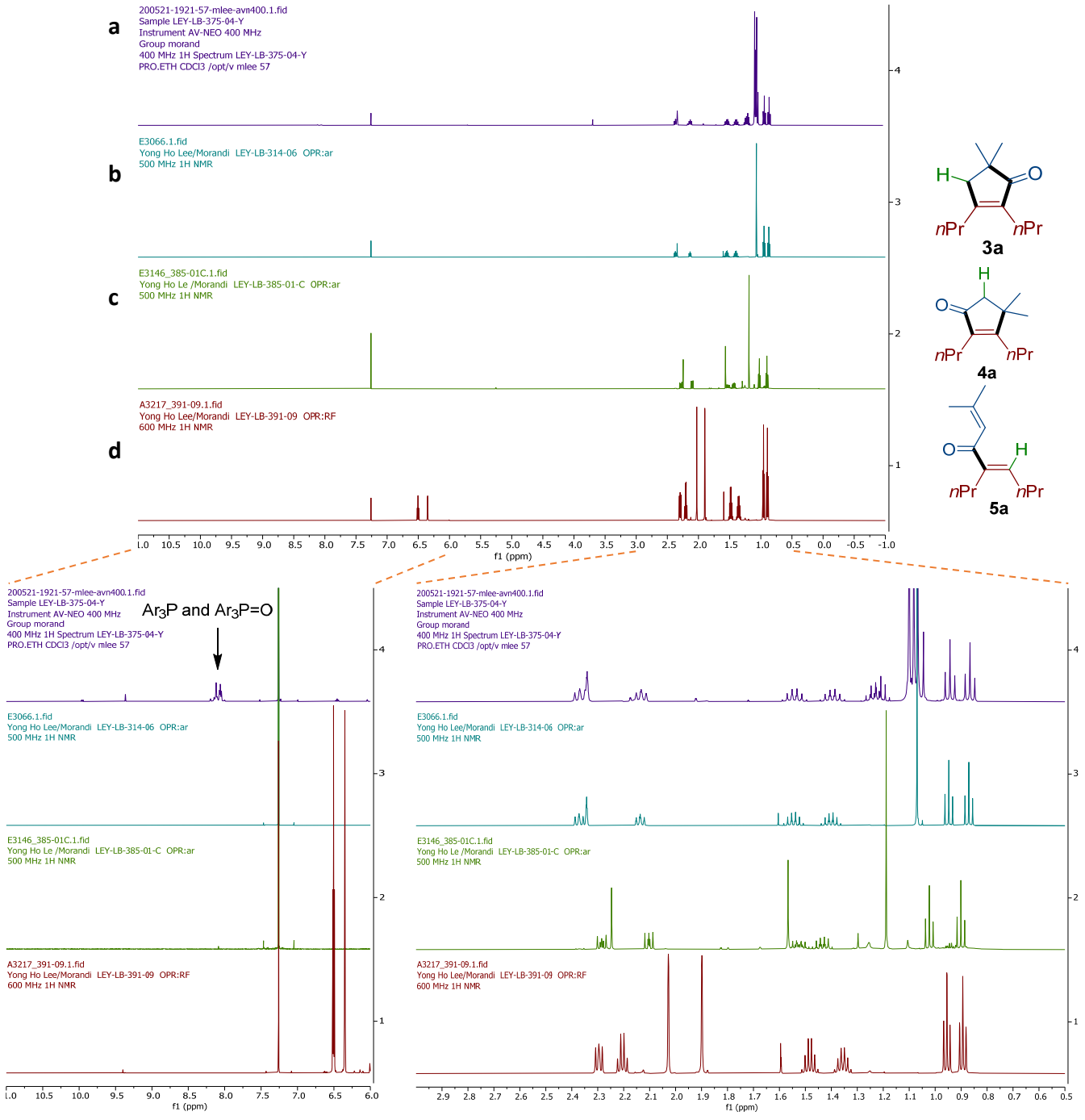
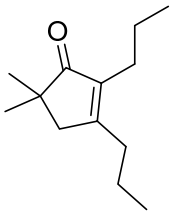


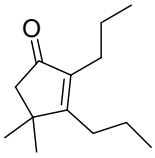
Figure S8. Comparison of ^{1}H NMR spectrum of the crude product mixture with ^{1}H NMR spectra of possible products **a,** ^{1}H NMR spectrum of the crude product mixture (Table S4. entry 1). **b,** ^{1}H NMR spectrum of compound **3a**. **c,** ^{1}H NMR spectrum of compound **4a** (Supplementary Table 4. entry 5). **d,** ^{1}H NMR spectrum of compound **5a** (Supplementary Table 4. entry 8).

5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one (**3a**). Pale yellow oil. **Method A**: 90% yield (44 mg).



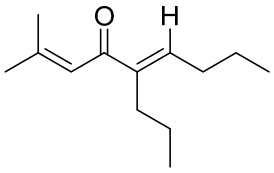
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (ddt, *J* = 7.7, 7.0, 0.9 Hz, 2H), 2.34 (p, *J* = 1.0 Hz, 2H), 2.14 (ddt, *J* = 8.8, 6.1, 1.2 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.45 – 1.36 (m, 2H), 1.07 (s, 6H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.2, 170.3, 137.8, 46.2, 42.7, 32.9, 25.4, 25.3, 22.0, 20.9, 14.2, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1745. The regiochemistry of the product was determined by 2D-NMR analysis. The ^{1}H-and ^{13}C-NMR data were consistent with the spectral data reported in literature.[1]

4,4-dimethyl-2,3-dipropylcyclopent-2-en-1-one (**4a**). Colorless oil. 19% yield (9 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 – 2.26 (m, 2H), 2.25 (s, 2H), 2.13 – 2.08 (m, 2H), 1.55 – 1.49 (m, 2H), 1.46 – 1.41 (m, 2H), 1.19 (s, 6H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.7, 180.6, 139.3, 51.1, 41.6, 29.5, 27.6, 25.8, 23.0, 21.7, 15.2, 14.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1740. The regiochemistry of the product was determined by 2D-NMR analysis and by analogy to previously reported literature.[2]

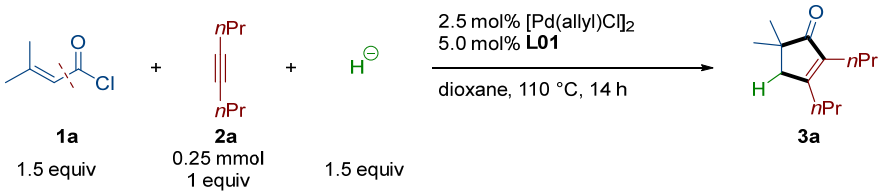
(*E*)-2-methyl-5-propylnona-2,5-dien-4-one (**5a**). Colorless oil. 59% yield (29 mg).



^{1}H NMR (600 MHz, $CDCl_3$) δ 6.50 (t, *J* = 7.3 Hz, 1H), 6.37 – 6.33 (m, 1H), 2.32 – 2.27 (m, 2H), 2.20 (q, *J* = 7.3 Hz, 2H), 2.04 – 2.02 (m, 3H), 1.91 – 1.89 (m, 3H), 1.48 (h, *J* = 7.3 Hz, 2H), 1.39 – 1.32 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.5, 152.1, 143.6, 142.1, 122.0, 31.0, 28.0, 27.6, 22.6, 22.4, 20.8, 14.3, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1746.

2.4. Hydride sources

Eq. 6. Hydride source screening.



1a 1.5 equiv + **2a** 0.25 mmol 1 equiv + $H^{\ominus}$ 1.5 equiv → **3a**

Table S5. Hydride source screening.

entry	hydrosilane, CAS no.	**3a** yield (%)[b]
1	tBu$_2$MeSiH, 56310-20-4	63
2	iPr$_3$SiH, 6485-79-6	99
3[a]	(iPr$_2$HSi)$_2$O, 18043-71-5	97
4	iBu$_3$SiH, 6485-81-0	93
5	tBu$_2$SiH$_2$, 30736-07-3	94
6	(iPr)$_2$OctSiH, 129536-19-2	82
7	tBuMe$_2$SiH, 29681-57-0	78
8	nOct$_3$SiH, 18765-09-8	40
9	nHex$_3$SiH, 2929-52-4	41
10	nBu$_3$SiH, 998-41-4	43
11	nPr$_3$SiH, 998-29-8	43
12	Et$_3$SiH, 617-86-7	30
13[a]	[(Me$_2$HSi)CH$_2$]$_2$, 20152-11-8	30
14[a]	(Me$_2$HSi)$_2$O, 3277-26-7	54
15	Ph$_2$$t$BuSiH, 33729-92-9	79
16	Ph$_3$SiH, 789-25-3	23
17	Ph$_2$MeSiH, 776-76-1	85
18	PhMe$_2$SiH, 766-77-8	41
19	Ph$_2$SiH$_2$, 775-12-2	30
20	(Me$_3$SiO)$_3$SiH, 1873-89-8	74
21	(EtO)$_3$SiH, 998-30-1	89
22	(EtO)$_2$MeSiH, 2031-62-1	91
23	tBu$_2$SiHCl, 56310-18-0	89
24	[Me$_3$Si]$_3$SiH, 1873-77-4	<3
25	nBu$_3$SnH, 688-73-3	30
26	Hantzsch ester, 1149-23-1	7
27	Potassium formate, 590-29-4	<3
28	Sodium formate, 141-53-7	<3
29	Ammonium formate, 540-69-2	n.d.

[a]0.75 equiv. of the silane was used.
[b]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

2.5. Solvents

Eq. S7. Solvent screening.

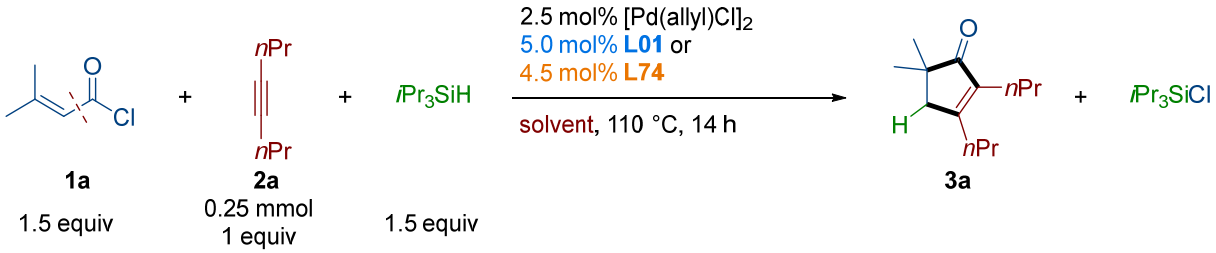
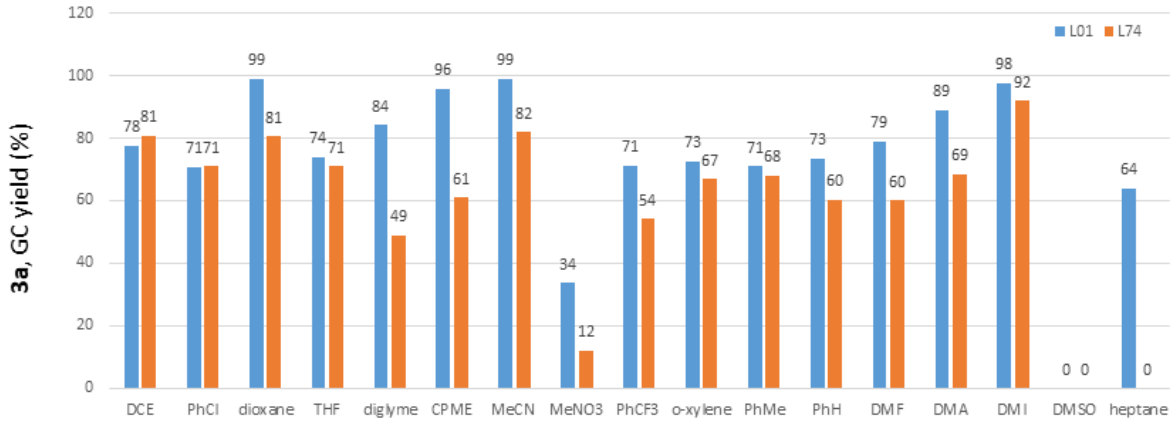


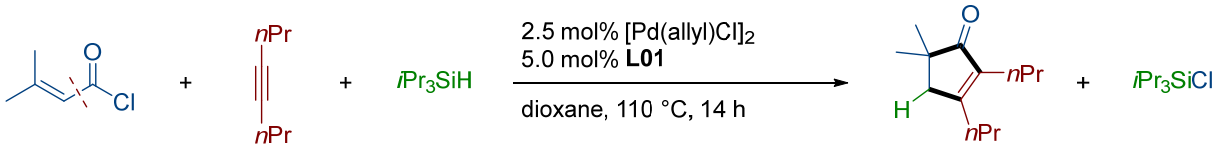
Figure S9. Solvent screening.



[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

2.6. Further optimization (other variations)

Eq. S8. Substrates equivalent ratio.



1a **2a** **3a**

1.0–1.5 equiv. **1.0–1.5 equiv.** **1.0–1.5 equiv.**

(1.0 equiv. = 0.25 mmol)

Table S6. Substrates equivalent ratio.

entry	acid chloride / alkyne / hydrosilane equivalent ratio	**3a**, yield (%)[a,e]
1	1.5 / 1.0 / 1.5	99
2[b,d]	1.5 / 1.0 / 1.5	95 (90)
3[b]	1.5 / 1.0 / 3.0	70
4	1.0 / 1.5 / 1.0	84
5[b]	1.0 / 1.5 / 1.0	84
6[c]	1.0 / 1.5 / 1.0	71
7	1.0 / 1.0 / 1.0	78

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).
[b][Pd(allyl)Cl]$_2$ (0.50 mol%), **L01** (1.0 mol%). [c][Pd(allyl)Cl]$_2$ (0.25 mol%), **L01** (0.5 mol%)
[d]Standard condition. [e]Yields of isolated product given in parentheses.

Eq. S9. Optimization, reaction temperature.

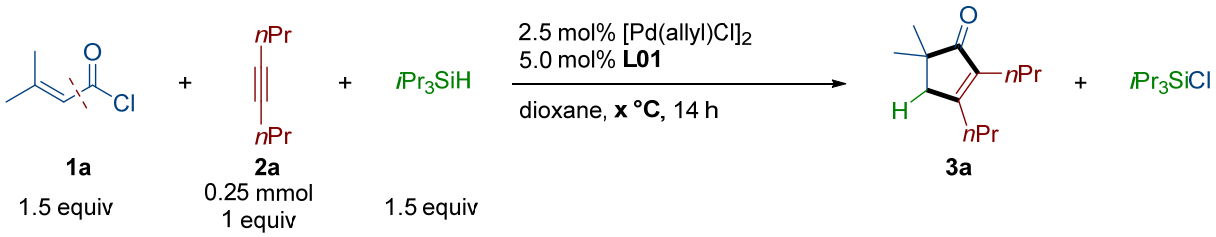


Table S7. Optimization, reaction temperature.

entry	reaction temperature	**3a**, yield (%)[a]
1	110 °C	99
2	90 °C	92
3	70 °C	75
4[b,c]	110 °C	95
5[b]	100 °C	93
6[b]	90 °C	85
7[b]	80 °C	71

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.). [b][Pd(allyl)Cl]$_2$ (0.50 mol%), **L01** (1.0 mol%). [c]Standard condition.

Eq. S10. Optimization, catalyst loading.

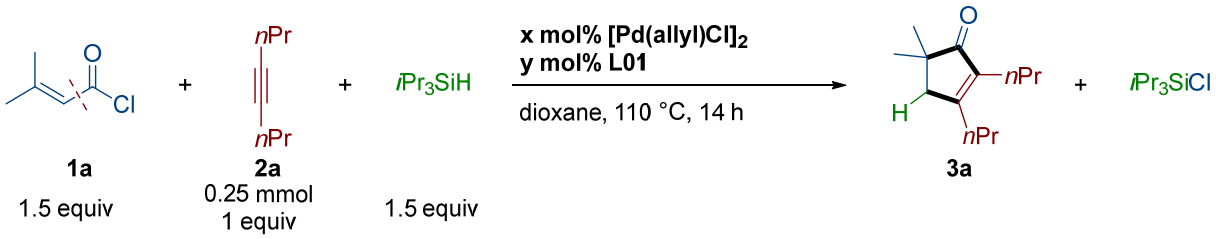


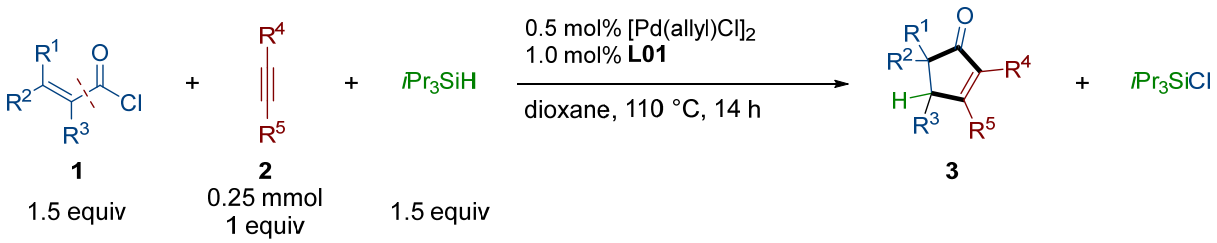
Table S8. Optimization, catalyst loading.

entry	catalyst loading	**3a**, yield (%)[a]
1	$[Pd(allyl)Cl]_2$ (2.50 mol%), **L01** (5.0 mol%)	99
2	$[Pd(allyl)Cl]_2$ (1.00 mol%), **L01** (2.0 mol%)	95
3[b]	$[Pd(allyl)Cl]_2$ (0.50 mol%), **L01** (1.0 mol%)	95
4	$[Pd(allyl)Cl]_2$ (0.25 mol%), **L01** (0.5 mol%)	82
5	$[Pd(allyl)Cl]_2$ (0.10 mol%), **L01** (0.2 mol%)	53

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.). [b]Standard condition.

3. Synthesis of polysubstituted cyclopentenones

Eq. S11. General procedure.

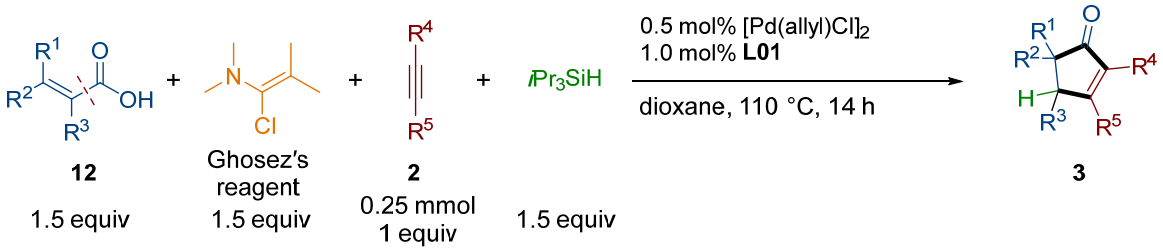


General procedure

Method A: In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (0.5 mol%, 1.25 µmol, 200 µL as 6.25 mM stock solution in dioxane) and **L01** (1.0 mol%, 2.50 µmol, 1.7 mg, or 16.8 mg as 10.0wt% stock solution in dioxane) and then dioxane (1.8 mL). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added acid chloride (**1**, 1.5 equiv, 0.375 mmol), alkyne (**2**, 1.0 equiv, 0.250 mmol) and *i*Pr$_3$SiH (1.5 equiv, 0.375 mmol, 59.4 mg). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then quenched with sodium methoxide (1.5 equiv, 0.375 mmol, 70 µL of 5.4M solution in MeOH, note: the quenching step could be omitted for substrates bearing a base-labile functional group) and diluted with DCM (2 mL). The resulting solution was filtered through a celite/silica plug and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/DCM, pentane/EA or pentane/MTBE). **Method A** was applied to all reactions unless otherwise stated.

Method B: In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (0.5 mol%, 1.25 µmol, 200 µL as 6.25 mM stock solution in dioxane) and **L01** (1.0 mol%, 2.50 µmol, 1.7 mg, or 16.8 mg as 10.0wt% stock solution in dioxane) and then dioxane (1.8 mL). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added acid chloride (**1**, 1.0 equiv, 0.250 mmol), alkyne (**2**, 1.5 equiv, 0.375 mmol) and *i*Pr$_3$SiH (1.0 equiv, 0.250 mmol, 39.6 mg). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then quenched with sodium methoxide (1.0 equiv, 0.250 mmol, 46 µL of 5.4M solution in MeOH, note: the quenching step could be omitted for substrates bearing a base-labile functional group) and diluted with DCM (2 mL). The resulting solution was filtered through a celite/silica plug and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/DCM, pentane/EA or pentane/MTBE).

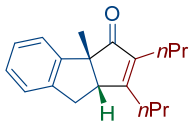
Eq. S12. General procedure using α,β-unsaturated carboxylic acid



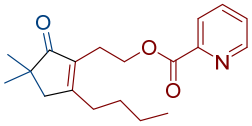
Method C: In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (0.5 mol%, 1.25 µmol, 200 µL as 6.25 mM stock solution in dioxane) and **L01** (1.0 mol%, 2.50 µmol, 1.7 mg, or 16.8 mg as 10.0wt% stock solution in dioxane) and then dioxane (1.8 mL). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added carboxylic acid (1.5 equiv, 0.375 mmol), Ghosez's reagent (1.5 equiv, 0.375 mmol, 50.1 mg, CAS Number: 26189-59-3), alkyne (1.0 equiv, 0.250 mmol) and *i*Pr_3SiH (1.5 equiv, 0.375 mmol, 59.4 mg). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then quenched with sodium methoxide (1.5 equiv, 0.375 mmol, 70 µL of 5.4M solution in MeOH, note: the quenching step could be omitted for substrates bearing a base-labile functional group) and diluted with DCM (2 mL). The resulting solution was filtered through a celite/silica plug and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/DCM, pentane/EA or pentane/MTBE).

Table S9. Examples using modified conditions of **Method A**.[a]

3al
34%[b]

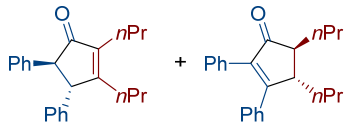


3ap
20%[b]



3ca
76% (*rr* = 68:32)[b,c]

isomerization



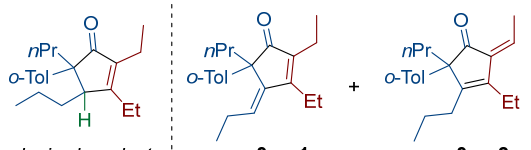
3ao-1
17%[b]
desired product

3ao-2
25%[b]

[a]All yields are isolated as a single regioisomer unless otherwise stated. [b][Pd(allyl)Cl]$_2$ (2.5 mol%), **L01** (5.0 mol%). [c]Isolated as an inseparable mixture of regioisomers.

Table S10. Examples using **Method B**.[a]

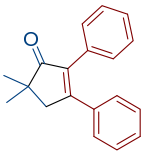
β-H elimination



desired product: not observed

3aq-1
21%[b,c]

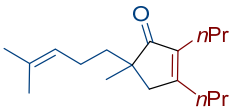
3aq-2
10%[b,c]



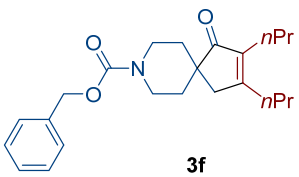
3bf
Method A: 27%
Method B: 39%

[a]All yields are isolated as a single regioisomer unless otherwise stated. [b][Pd(allyl)Cl]$_2$ (5.0 mol%), **L01** (10.0 mol%), 120 °C. [c]3-hexyne (1.5 equiv.) was used instead of **2a**.

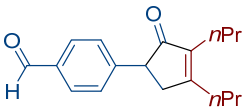
Table S11. Examples using **Method C**.[a]



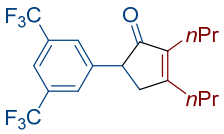
3d
70%[b]



3f
87%



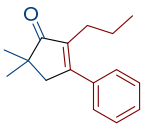
3x
57%



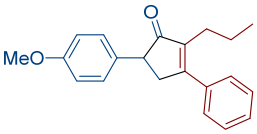
3ae
Method A: 62%
Method C: 73%[b]

[a]All yields are isolated as a single regioisomer unless otherwise stated. [b][Pd(allyl)Cl]$_2$ (2.5 mol%), **L01** (5.0 mol%).

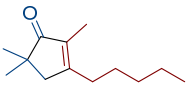
Table S12. Comparison between the ratio of isomeric products isolated separately and GC ratio of the crude mixture.



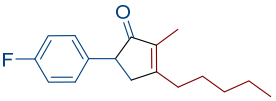
3bi
53% (*rr* = 57:43)
Crude GC (*rr* = 56:44)



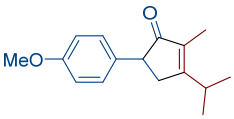
3bj
46% (*rr* = 58:42)
Crude GC (*rr* = 61:39)



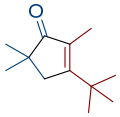
3bq
74% (*rr* = 58:42)
Crude GC (*rr* = 56:44)



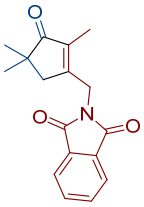
3br
69% (*rr* = 55:45)
Crude GC (*rr* = 56:44)



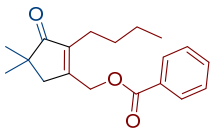
3bs
76% (*rr* = 59:41)
Crude GC (*rr* = 59:41)



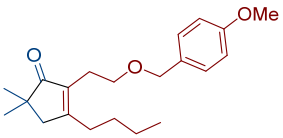
3bt
64% (*rr* = 73:27)
Crude GC (*rr* = 71:29)



3bu
67% (*rr* = 63:37)
Crude GC (*rr* = 63:37)

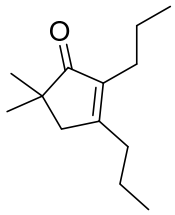


3bv
61% (*rr* = 56:44)
Crude GC (*rr* = 59:41)



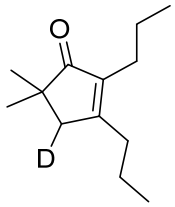
3by
56% (*rr* = 66:34)
Crude GC (*rr* = 66:34)

5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one (**3a**). Pale yellow oil. 90% yield (44 mg).



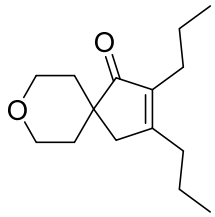
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (ddt, *J* = 7.7, 7.0, 0.9 Hz, 2H), 2.34 (p, *J* = 1.0 Hz, 2H), 2.14 (ddt, *J* = 8.8, 6.1, 1.2 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.45 – 1.36 (m, 2H), 1.07 (s, 6H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.2, 170.3, 137.8, 46.2, 42.7, 32.9, 25.4, 25.3, 22.0, 20.9, 14.2, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1745. The regiochemistry of the product was determined by 2D-NMR analysis. The ^{1}H-and ^{13}C-NMR data were consistent with the spectral data reported in literature.[1]

5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3a-*d***, 94%[D]). Pale yellow oil. 91% yield (45 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (ddd, *J* = 8.8, 6.4, 1.0 Hz, 2H), 2.35 – 2.30 (m, 1H), 2.13 (ddd, *J* = 8.9, 6.2, 1.1 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.44 – 1.36 (m, 2H), 1.07 (s, 6H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.2, 170.3, 137.8, 46.2, 45.8 (t, *J* = 19.9 Hz), 42.7, 32.9, 25.4 (t, *J* = 2.6 Hz), 25.3, 22.0, 20.9, 14.2, 14.2. **^{2}H NMR** (77 MHz, $CDCl_3$) δ 2.34, 2.31. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{22}DO$, 196.1806; found 196.1808. The regiochemistry of the product was determined by 2D-NMR analysis.

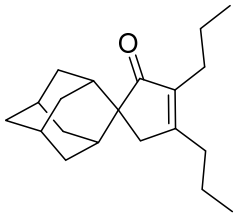
2,3-dipropyl-8-oxaspiro[4.5]dec-2-en-1-one (**3b**). Colorless oil. 92% yield (55 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.02 – 3.97 (m, 2H), 3.52 (td, *J* = 11.8, 2.4 Hz, 2H), 2.45 (s, 2H), 2.40 (ddt, *J* = 8.8, 7.1, 1.0 Hz, 2H), 2.14 (ddt, *J* = 8.9, 6.2, 1.2 Hz, 2H), 1.95 (ddd, *J* = 13.7, 11.9, 4.5 Hz,

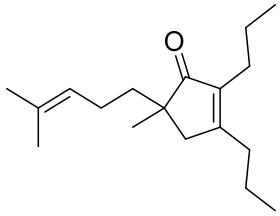
2H), 1.62 – 1.53 (m, 2H), 1.45 – 1.34 (m, 2H), 1.12 (dq, *J* = 13.7, 2.6 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.0, 170.5, 138.7, 65.1, 45.1, 42.4, 33.8, 33.0, 25.2, 21.9, 21.0, 14.2, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{15}H_{25}O_2$, 237.1849; found 237.1848. The regiochemistry of the product was determined by 2D-NMR analysis.

(1r,3r,5r,7r)-3',4'-dipropylspiro[adamantane-2,1'-cyclopentan]-3'-en-2'-one (**3c**). Colorless oil. 75% yield (54 mg).



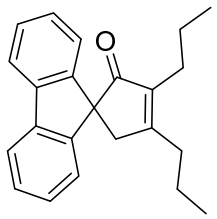
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 – 2.71 (m, 2H), 2.49 (s, 2H), 2.38 – 2.31 (m, 2H), 2.09 (ddt, *J* = 8.8, 7.4, 1.2 Hz, 2H), 1.93 – 1.81 (m, 4H), 1.76 – 1.66 (m, 4H), 1.61 – 1.44 (m, 6H), 1.41 – 1.31 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.6, 168.2, 138.8, 51.8, 44.0, 38.8, 36.2, 34.4, 32.8, 32.0, 27.4, 27.0, 25.2, 22.0, 21.0, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{20}H_{31}O$, 287.2369; found 287.2371. The regiochemistry of the product was determined by 2D-NMR analysis.

5-methyl-5-(4-methylpent-3-en-1-yl)-2,3-dipropylcyclopent-2-en-1-one (**3d**). Colorless oil. **Method C**: 70% yield (46 mg).



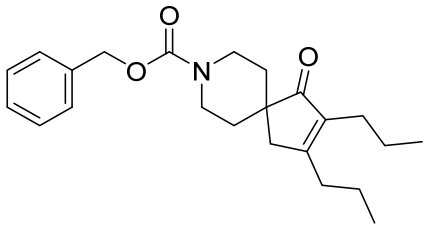
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (tp, *J* = 7.1, 1.5 Hz, 1H), 2.48 (dp, *J* = 18.1, 1.0 Hz, 1H), 2.43 – 2.33 (m, 2H), 2.22 (dp, *J* = 18.1, 1.0 Hz, 1H), 2.18 – 2.08 (m, 2H), 1.88 – 1.67 (m, 2H), 1.64 (d, *J* = 1.1 Hz, 3H), 1.67 – 1.53 (m, 2H), 1.54 (d, *J* = 0.9 Hz, 3H), 1.53 – 1.46 (m, 1H), 1.45 – 1.35 (m, 3H), 1.05 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.9, 171.0, 139.0, 131.7, 124.3, 46.2, 43.4, 38.4, 33.0, 25.8, 25.3, 24.2, 23.5, 22.0, 21.0, 17.7, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{18}H_{30}NaO$, 285.2189; found 285.2185. The regiochemistry of the product was determined by 2D-NMR analysis.

3,4-dipropylspiro[cyclopentane-1,9'-fluoren]-3-en-2-one (**3e**). Yellow solid. 87% yield (69 mg).



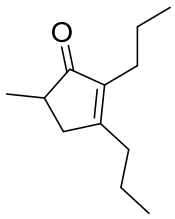
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dt, *J* = 7.6, 1.0 Hz, 2H), 7.36 (td, *J* = 7.5, 1.2 Hz, 2H), 7.25 (td, *J* = 7.5, 1.2 Hz, 2H), 7.12 (dt, *J* = 7.6, 1.0 Hz, 2H), 3.16 – 3.08 (m, 2H), 2.68 – 2.60 (m, 2H), 2.30 (ddt, *J* = 8.8, 6.1, 1.2 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.58 – 1.44 (m, 2H), 1.10 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 173.3, 147.7, 141.7, 140.5, 127.8, 127.8, 122.1, 120.4, 62.8, 43.2, 33.3, 25.8, 21.9, 21.1, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{23}H_{25}O$, 317.1900; found 317.1902. The configuration of the product was determined by 2D-NMR analysis and X-ray crystallography.

benzyl 1-oxo-2,3-dipropyl-8-azaspiro[4.5]dec-2-ene-8-carboxylate (**3f**). Colorless oil. **Method C**: 87% yield (80 mg).



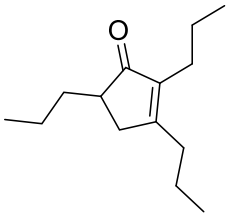
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 5.14 (s, 2H), 4.13 (br, 2H), 3.00 (br, 2H), 2.46 – 2.35 (m, 4H), 2.14 (ddd, *J* = 8.8, 7.4, 1.1 Hz, 2H), 1.87 – 1.74 (m, 2H), 1.62 – 1.50 (m, 2H), 1.45 – 1.33 (m, 2H), 1.25 (br, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.1, 170.6, 155.4, 138.6, 136.9, 128.6, 128.1, 128.0, 67.2, 45.6, 41.8, 41.2, 33.1, 33.0, 25.2, 21.9, 21.0, 14.2, 14.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{23}H_{31}NNaO_3$, 392.2196; found 392.2191. The regiochemistry of the product was determined by 2D-NMR analysis.

5-methyl-2,3-dipropylcyclopent-2-en-1-one (**3g**). pale yellow oil. 85% yield (38 mg).



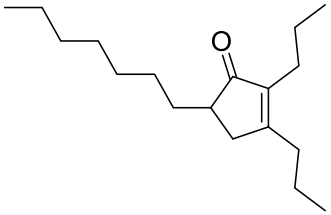
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.77 – 2.70 (m, 1H), 2.41 – 2.36 (m, 2H), 2.36 – 2.30 (m, 1H), 2.14 (ddt, *J* = 8.1, 7.0, 1.1 Hz, 2H), 2.07 (ddq, *J* = 18.0, 2.2, 1.0 Hz, 1H), 1.60 – 1.52 (m, 2H), 1.44 – 1.35 (m, 2H), 1.15 (d, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.6, 172.0, 139.3, 39.6, 38.2, 33.1, 25.3, 22.0, 21.0, 16.9, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{12}H_{21}O$, 181.1587; found 181.1586. The regiochemistry of the product was determined by 2D-NMR analysis. The ^{1}H-and ^{13}C-NMR data were consistent with the spectral data reported in literature.[1]

2,3,5-tripropylcyclopent-2-en-1-one (**3h**). Colorless oil. 79% yield (41 mg).



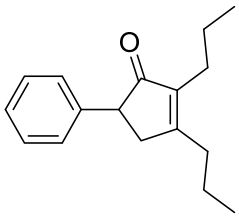
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.65 (dddd, *J* = 18.2, 7.9, 2.1, 1.0 Hz, 1H), 2.41 – 2.35 (m, 2H), 2.30 (dddd, *J* = 9.3, 6.6, 4.3, 2.4 Hz, 1H), 2.17 – 2.10 (m, 3H), 1.81 – 1.72 (m, 1H), 1.60 – 1.51 (m, 2H), 1.43 – 1.31 (m, 4H), 1.31 – 1.21 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.2, 172.3, 139.9, 45.0, 36.1, 34.1, 33.2, 25.2, 22.0, 21.0, 20.6, 14.3, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{14}H_{25}O$, 209.1900; found 209.1896. The regiochemistry of the product was determined by 2D-NMR analysis.

5-heptyl-2,3-dipropylcyclopent-2-en-1-one (**3i**). Colorless oil. 85% yield (56 mg).



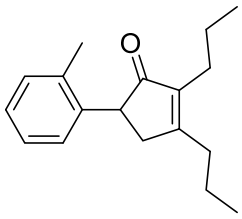
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 18.0, 6.7 Hz, 1H), 2.38 (t, *J* = 7.7 Hz, 2H), 2.33 – 2.23 (m, 1H), 2.19 – 2.07 (m, 3H), 1.83 – 1.72 (m, 1H), 1.56 (h, *J* = 7.4 Hz, 2H), 1.45 – 1.34 (m, 2H), 1.34 – 1.18 (m, 11H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.2, 172.3, 139.9, 45.2, 36.2, 33.2, 32.0, 31.9, 29.8, 29.3, 27.4, 25.2, 22.8, 22.0, 21.0, 14.3, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{33}O$, 265.2526; found 265.2523. The regiochemistry of the product was determined by 2D-NMR analysis.

5-phenyl-2,3-dipropylcyclopent-2-en-1-one (**3j**). Colorless oil. 78% yield (47 mg).



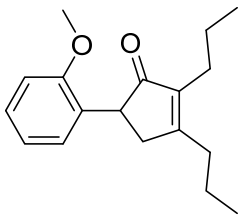
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.22 (ddt, *J* = 8.3, 6.6, 1.3 Hz, 1H), 7.13 – 7.09 (m, 2H), 3.54 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.04 (ddtd, *J* = 18.4, 7.2, 1.8, 0.9 Hz, 1H), 2.59 (ddt, *J* = 18.4, 2.5, 1.1 Hz, 1H), 2.55 – 2.42 (m, 2H), 2.27 – 2.16 (m, 2H), 1.63 (h, *J* = 7.7 Hz, 2H), 1.45 (h, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.9, 173.0, 140.7, 139.9, 128.9, 127.6, 126.8, 51.1, 39.3, 33.2, 25.4, 22.0, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{23}O$, 243.1743; found 243.1742. The regiochemistry of the product was determined by 2D-NMR analysis and by analogy to previously reported literature.[3,9]

2,3-dipropyl-5-(*o*-tolyl)cyclopent-2-en-1-one (**3k**). Pale yellow oil. 87% yield (56 mg).



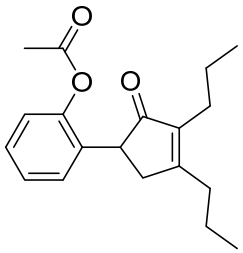
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 6.89 – 6.84 (m, 1H), 3.76 (dd, *J* = 7.3, 2.9 Hz, 1H), 3.09 – 3.02 (m, 1H), 2.52 – 2.41 (m, 3H), 2.33 (s, 3H), 2.29 – 2.18 (m, 2H), 1.65 – 1.56 (m, 2H), 1.51 – 1.43 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.7, 172.5, 140.4, 139.5, 136.8, 130.7, 126.9, 126.8, 126.5, 48.4, 38.9, 33.2, 25.5, 22.0, 21.0, 20.1, 14.4, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O$, 257.1900; found 257.1900. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(2-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one (**3l**). White solid. 94% yield (64 mg).



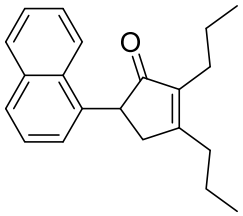
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.89 (td, *J* = 7.4, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.72 (s, 3H), 3.66 (dd, *J* = 7.2, 3.2 Hz, 1H), 2.97 – 2.89 (m, 1H), 2.56 – 2.49 (m, 1H), 2.49 – 2.37 (m, 2H), 2.29 – 2.17 (m, 2H), 1.65 – 1.54 (m, 2H), 1.54 – 1.41 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.9, 171.3, 157.5, 139.8, 129.9, 129.5, 128.1, 120.9, 111.0, 55.4, 47.7, 38.4, 33.0, 25.5, 22.1, 21.0, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O_2$, 273.1849; found 273.1850. The regiochemistry of the product was determined by 2D-NMR analysis and X-ray crystallography.

2-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)phenyl acetate (**3m**). Pale yellow oil. 90% yield (68 mg).



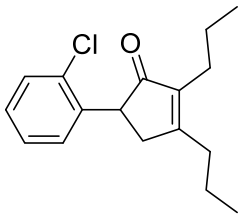
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.17 (td, *J* = 7.6, 1.3 Hz, 1H), 7.07 (ddd, *J* = 12.8, 7.9, 1.5 Hz, 2H), 3.63 (dd, *J* = 7.4, 3.2 Hz, 1H), 3.00 – 2.93 (m, 1H), 2.50 – 2.39 (m, 3H), 2.29 – 2.16 (m, 2H), 2.21 (s, 3H), 1.62 – 1.54 (m, 2H), 1.51 – 1.42 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.4, 172.3, 169.3, 149.0, 140.1, 132.8, 129.3, 128.0, 126.5, 122.9, 46.6, 38.7, 33.2, 25.5, 22.1, 21.1, 21.0, 14.4, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{25}O_3$, 301.1798; found 301.1795. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(naphthalen-1-yl)-2,3-dipropylcyclopent-2-en-1-one (**3n**). Pale yellow oil. 88% yield (65 mg).



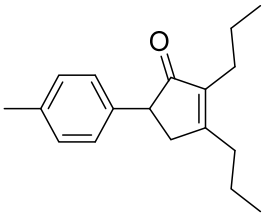
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 1H), 7.84 – 7.78 (m, 1H), 7.75 (dt, *J* = 8.3, 1.2 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.40 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 7.3, 3.1 Hz, 1H), 3.22 (ddt, *J* = 18.3, 7.3, 1.1 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.56 – 2.45 (m, 2H), 2.38 – 2.27 (m, 2H), 1.66 – 1.51 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.6, 172.3, 140.6, 137.3, 134.3, 132.1, 129.1, 127.6, 126.2, 125.7, 125.7, 125.4, 123.6, 48.8, 39.5, 33.2, 25.5, 22.0, 21.0, 14.3, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{25}O$, 293.1900; found 293.1897. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(2-chlorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3o**). Pale yellow oil. 93% yield (64 mg).



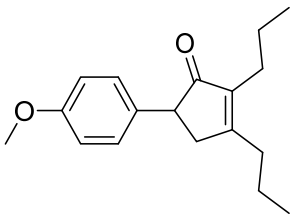
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 1H), 7.21 – 7.14 (m, 2H), 7.03 – 6.99 (m, 1H), 3.92 (dd, *J* = 7.3, 3.2 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.54 – 2.39 (m, 3H), 2.25 (ddq, *J* = 9.7, 7.1, 1.2 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.53 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.4, 172.2, 140.4, 138.8, 134.5, 129.9, 129.4, 128.2, 127.3, 49.3, 38.5, 33.1, 25.5, 22.0, 20.9, 14.3, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}ClO$, 277.1354; found 277.1353. The regiochemistry of the product was determined by 2D-NMR analysis.

2,3-dipropyl-5-(*p*-tolyl)cyclopent-2-en-1-one (**3p**). Pale yellow oil. 79% yield (51 mg).



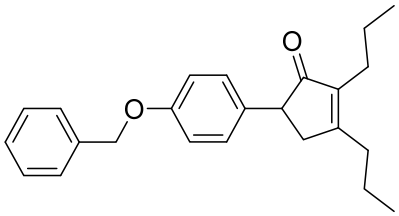
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 2H), 7.02 – 6.96 (m, 2H), 3.50 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.07 – 2.97 (m, 1H), 2.57 (ddt, *J* = 18.5, 2.4, 1.2 Hz, 1H), 2.54 – 2.40 (m, 2H), 2.31 (s, 3H), 2.26 – 2.15 (m, 2H), 1.62 (h, *J* = 7.6 Hz, 2H), 1.44 (h, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.1, 172.9, 139.8, 137.6, 136.4, 129.6, 127.5, 50.7, 39.3, 33.2, 25.4, 22.0, 21.2, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O$, 257.1900; found 257.1899. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one (**3q**). Pale yellow oil. 78% yield (53 mg).



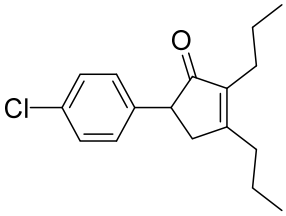
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 – 7.00 (m, 2H), 6.87 – 6.81 (m, 2H), 3.78 (s, 3H), 3.48 (dd, *J* = 7.2, 2.7 Hz, 1H), 3.06 – 2.98 (m, 1H), 2.55 (ddt, *J* = 18.3, 2.4, 1.2 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.27 – 2.15 (m, 2H), 1.66 – 1.58 (m, 2H), 1.44 (h, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.2, 172.8, 158.5, 139.8, 132.8, 128.6, 114.3, 55.4, 50.3, 39.3, 33.2, 25.4, 22.0, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O_2$, 273.1849; found 273.1847. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-(benzyloxy)phenyl)-2,3-dipropylcyclopent-2-en-1-one (**3r**). Yellow oil. 35% yield (31 mg).



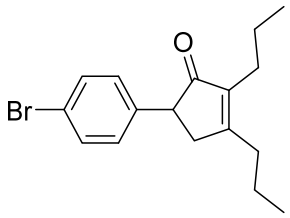
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.38 (tq, *J* = 8.1, 1.1 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.05 – 7.01 (m, 2H), 6.94 – 6.90 (m, 2H), 5.04 (s, 2H), 3.49 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.02 (ddtd, *J* = 18.5, 7.2, 1.8, 1.0 Hz, 1H), 2.55 (ddt, *J* = 18.3, 2.5, 1.1 Hz, 1H), 2.46 (tdt, *J* = 13.6, 8.2, 6.5 Hz, 2H), 2.21 (qt, *J* = 7.3, 1.2 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.44 (h, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.2, 172.9, 157.8, 139.8, 137.2, 133.0, 128.7, 128.6, 128.0, 127.6, 115.3, 70.2, 50.3, 39.3, 33.2, 25.4, 22.0, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{24}H_{28}NaO_2$, 371.1982; found 371.1979. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-chlorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3s**). Colorless oil. 78% yield (54 mg).



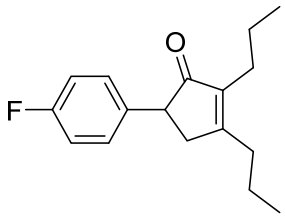
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.06 – 7.02 (m, 2H), 3.51 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.07 – 3.01 (m, 1H), 2.54 (ddt, *J* = 18.5, 2.6, 1.2 Hz, 1H), 2.52 – 2.42 (m, 2H), 2.25 – 2.16 (m, 2H), 1.62 (dtd, *J* = 8.2, 7.3, 0.9 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.3, 173.0, 139.9, 139.0, 132.6, 129.0, 50.4, 39.0, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}ClO$, 277.1354; found 277.1349. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-bromophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3t**). Pale yellow oil. 66% yield (53 mg).



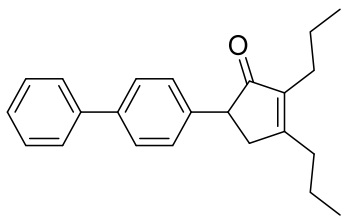
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.02 – 6.95 (m, 2H), 3.50 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.04 (dddt, *J* = 18.4, 7.2, 2.2, 1.1 Hz, 1H), 2.59 – 2.41 (m, 3H), 2.20 (tdt, *J* = 8.0, 2.3, 1.2 Hz, 2H), 1.67 – 1.56 (m, 2H), 1.43 (h, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.3, 173.1, 139.9, 139.5, 131.9, 129.4, 120.7, 50.4, 38.9, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}BrO$, 321.0849; found 321.0844. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-fluorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3u**). Pale yellow oil. 79% yield (52 mg).



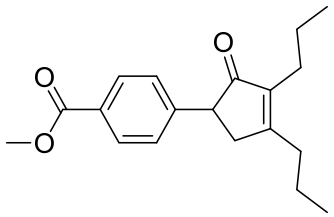
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.04 (m, 2H), 7.01 – 6.96 (m, 2H), 3.52 (dd, *J* = 7.2, 2.7 Hz, 1H), 3.09 – 2.99 (m, 1H), 2.57 – 2.52 (m, 1H), 2.52 – 2.42 (m, 2H), 2.27 – 2.15 (m, 2H), 1.67 – 1.58 (m, 2H), 1.44 (h, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.7, 172.9, 161.9 (d, *J* = 244.7 Hz), 139.9, 136.3 (d, *J* = 3.2 Hz), 129.1 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 21.3 Hz), 50.3, 39.2, 33.2, 25.4, 22.0, 21.0, 14.4, 14.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.4. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{17}H_{21}FNaO$, 283.1469; found 283.1470. The regiochemistry of the product was determined by 2D-NMR analysis.

5-([1,1'-biphenyl]-4-yl)-2,3-dipropylcyclopent-2-en-1-one (**3v**). White solid. 50% yield (40 mg).



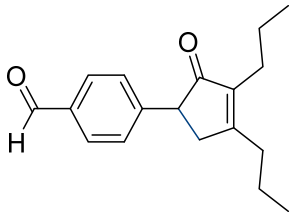
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 4H), 7.42 (dddd, *J* = 7.9, 6.7, 1.2, 0.6 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.21 – 7.17 (m, 2H), 3.59 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.07 (dddd, *J* = 18.5, 7.2, 2.1, 1.2 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.56 – 2.44 (m, 2H), 2.29 – 2.18 (m, 2H), 1.69 – 1.60 (m, 2H), 1.47 (h, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.8, 173.1, 141.1, 139.9, 139.8, 139.7, 128.9, 128.0, 127.7, 127.3, 127.2, 50.8, 39.2, 33.3, 25.5, 22.0, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{23}H_{27}O$, 319.2056; found 319.2050. The regiochemistry of the product was determined by 2D-NMR analysis and X-ray crystallography.

methyl 4-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)benzoate (**3w**). Pale yellow oil. 72% yield (54 mg).



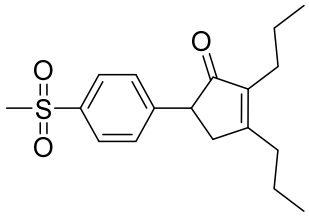
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.20 – 7.16 (m, 2H), 3.89 (s, 3H), 3.61 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.09 – 3.03 (m, 1H), 2.60 (ddt, *J* = 18.5, 2.5, 1.0 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.26 – 2.17 (m, 2H), 1.63 (h, *J* = 7.4 Hz, 2H), 1.44 (hd, *J* = 7.3, 1.0 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.0, 173.1, 167.1, 145.9, 140.0, 130.2, 128.8, 127.7, 52.2, 51.1, 38.9, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{25}O_3$, 301.1798; found 301.1796. The regiochemistry of the product was determined by 2D-NMR analysis.

4-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)benzaldehyde (**3x**). **Method C**: pale yellow oil. 57% yield (39 mg).



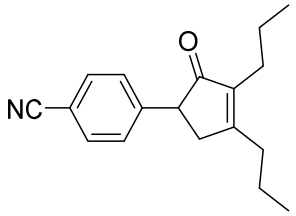
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.85 – 7.80 (m, 2H), 7.30 – 7.26 (m, 2H), 3.64 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.66 – 2.58 (m, 1H), 2.56 – 2.44 (m, 2H), 2.27 – 2.17 (m, 2H), 1.68 – 1.60 (m, 2H), 1.49 – 1.39 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.7, 192.0, 173.2, 147.6, 140.0, 135.2, 130.4, 128.4, 51.2, 38.8, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{23}O_2$, 271.1693; found 271.1689. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-(methylsulfonyl)phenyl)-2,3-dipropylcyclopent-2-en-1-one (**3y**). White solid. 66% yield (53 mg).



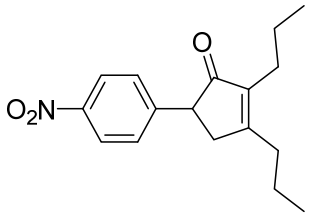
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.33 – 7.29 (m, 2H), 3.64 (dd, *J* = 7.2, 2.7 Hz, 1H), 3.09 (dddt, *J* = 18.6, 7.3, 2.2, 1.0 Hz, 1H), 3.02 (s, 3H), 2.60 (dqd, *J* = 18.5, 2.1, 1.1 Hz, 1H), 2.57 – 2.45 (m, 2H), 2.22 (dddt, *J* = 7.8, 6.6, 2.2, 1.2 Hz, 2H), 1.63 (h, *J* = 7.5 Hz, 2H), 1.49 – 1.40 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.5, 173.5, 146.9, 139.9, 139.0, 128.7, 128.0, 50.9, 44.7, 38.7, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O_3S$, 321.1519; found 321.1515. The regiochemistry of the product was determined by 2D-NMR analysis.

4-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)benzonitrile (**3z**). Pale yellow oil. 42% yield (28 mg).



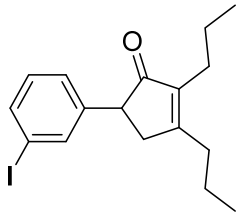
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.24 – 7.20 (m, 2H), 3.60 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.07 (dddt, *J* = 18.3, 7.2, 2.1, 1.0 Hz, 1H), 2.58 (dtd, *J* = 18.5, 2.1, 1.1 Hz, 1H), 2.55 – 2.43 (m, 2H), 2.21 (dddt, *J* = 7.8, 6.6, 2.2, 1.1 Hz, 2H), 1.63 (h, *J* = 7.6 Hz, 2H), 1.48 – 1.39 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.3, 173.2, 145.9, 140.0, 132.7, 128.5, 119.0, 110.8, 51.0, 38.6, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{22}NO$, 268.1696; found 268.1696. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-nitrophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3aa**). Yellow oil. 44% yield (32 mg).



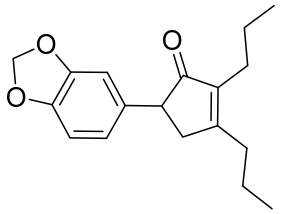
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 2H), 7.30 – 7.26 (m, 2H), 3.67 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.10 (ddq, *J* = 18.5, 7.3, 1.0 Hz, 1H), 2.61 (dqd, *J* = 18.5, 2.1, 1.1 Hz, 1H), 2.56 – 2.45 (m, 2H), 2.22 (dddt, *J* = 7.8, 6.6, 2.2, 1.2 Hz, 2H), 1.64 (h, *J* = 7.6 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.1, 173.3, 148.0, 147.0, 140.0, 128.6, 124.1, 50.9, 38.6, 33.2, 25.5, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}NO_3$, 288.1594; found 288.1593. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(3-iodophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3ab**). Pale brown oil. 37% yield (34 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.46 (t, *J* = 1.7 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 3.47 (dd, *J* = 7.2, 2.7 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.58 – 2.52 (m, 1H), 2.52 – 2.42 (m, 2H), 2.21 (dddt, *J* = 7.7, 6.5, 2.2, 1.2 Hz, 2H), 1.62 (h, *J* = 7.4 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.0, 173.1, 142.9, 139.9, 136.7, 135.9, 130.6, 126.9, 94.9, 50.5, 39.0, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}IO$, 369.0710; found 369.0710. The regiochemistry of the product was determined by 2D-NMR analysis.

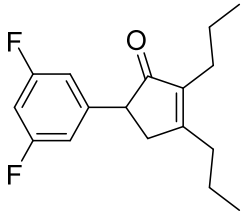
5-(benzo[d][1,3]dioxol-5-yl)-2,3-dipropylcyclopent-2-en-1-one (**3ac**). Pale yellow oil. 72% yield (52 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (d, *J* = 8.0 Hz, 1H), 6.59 (ddd, *J* = 8.0, 1.8, 0.6 Hz, 1H), 6.56 – 6.54 (m, 1H), 5.92 – 5.90 (m, 2H), 3.45 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.01 (ddq, *J* = 18.4, 7.2, 1.1 Hz, 1H),

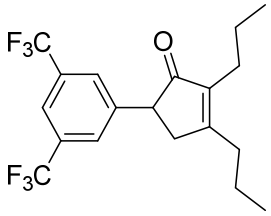
2.56 – 2.41 (m, 3H), 2.25 – 2.15 (m, 2H), 1.65 – 1.57 (m, 2H), 1.44 (h, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.9, 173.0, 148.1, 146.5, 139.8, 134.4, 121.0, 108.6, 107.8, 101.1, 50.7, 39.4, 33.2, 25.4, 22.0, 21.0, 14.4, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{23}O_3$, 287.1642; found 287.1641. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(3,5-difluorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3ad**). Pale yellow oil. 65% yield (46 mg).



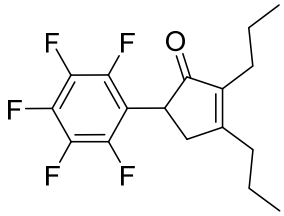
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 – 6.62 (m, 3H), 3.52 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.58 – 2.53 (m, 1H), 2.53 – 2.43 (m, 2H), 2.26 – 2.16 (m, 2H), 1.62 (h, *J* = 7.5 Hz, 2H), 1.44 (h, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.3, 173.1, 163.3 (dd, *J* = 248.4, 13.1 Hz), 144.2 (t, *J* = 9.2 Hz), 139.9, 110.8 – 110.5 (m), 102.4 (t, *J* = 25.3 Hz), 50.6 (t, *J* = 2.0 Hz), 38.7, 33.2, 25.4, 21.9, 21.0, 14.4, 14.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.8. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{21}F_2O$, 279.1555; found 279.1554. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(3,5-bis(trifluoromethyl)phenyl)-2,3-dipropylcyclopent-2-en-1-one (**3ae**). Colorless oil. **Method A**: 62% yield (58 mg). **Method C**: 73% yield (69 mg).



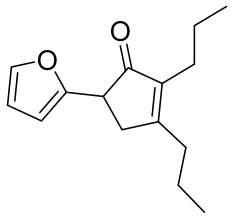
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dp, *J* = 1.6, 0.7 Hz, 1H), 7.57 (dp, *J* = 1.2, 0.6 Hz, 2H), 3.68 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.16 – 3.10 (m, 1H), 2.60 (dqd, *J* = 18.5, 2.1, 1.0 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.28 – 2.19 (m, 2H), 1.65 (h, *J* = 7.4 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 173.2, 142.7, 140.0, 132.1 (q, *J* = 33.3 Hz), 128.0 (q, *J* = 3.9 Hz), 123.4 (q, *J* = 272.7 Hz), 121.0 (hept, *J* = 3.9 Hz), 50.5, 38.5, 33.2, 25.5, 21.9, 21.0, 14.3, 14.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.9. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{21}F_6O$, 379.1491; found 379.1492. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(perfluorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3af**). Colorless oil. 89% yield (74 mg).



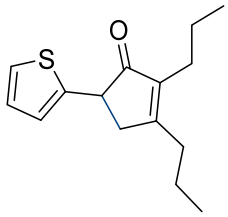
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (dd, *J* = 7.6, 3.7 Hz, 1H), 3.02 (ddt, *J* = 18.1, 7.7, 1.0 Hz, 1H), 2.58 (ddq, *J* = 18.0, 3.4, 1.1 Hz, 1H), 2.54 – 2.40 (m, 2H), 2.23 (ddt, *J* = 8.8, 6.2, 1.1 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.50 – 1.42 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.7, 171.8, 146.7 – 144.2 (m), 141.6 – 139.2 (m), 139.6, 138.9 – 136.5 (m), 114.1 (td, *J* = 17.4, 3.9 Hz), 40.4 (d, *J* = 1.4 Hz), 36.9, 33.0, 25.5, 21.8, 20.9, 14.2, 14.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -142.7, -156.1 (t, *J* = 20.8 Hz), -162.3 (m). **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{18}F_5O$, 333.1272; found 333.1268. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(furan-2-yl)-2,3-dipropylcyclopent-2-en-1-one (**3ag**). Pale yellow oil. 62% yield (36 mg).



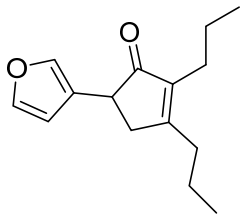
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 1.9, 1.0 Hz, 1H), 6.30 (dt, *J* = 3.1, 1.5 Hz, 1H), 6.17 (dt, *J* = 3.1, 0.9 Hz, 1H), 3.66 (dd, *J* = 7.3, 3.1 Hz, 1H), 2.93 (ddq, *J* = 18.2, 7.3, 1.0 Hz, 1H), 2.73 (dtt, *J* = 18.2, 2.1, 1.1 Hz, 1H), 2.51 – 2.39 (m, 2H), 2.19 (tt, *J* = 7.8, 1.2 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.48 – 1.38 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.0, 172.7, 152.6, 141.9, 139.3, 110.5, 106.4, 44.8, 35.8, 33.2, 25.4, 21.9, 20.9, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{15}H_{20}NaO_2$, 255.1356; found 255.1356. The regiochemistry of the product was determined by 2D-NMR analysis.

2,3-dipropyl-5-(thiophen-2-yl)cyclopent-2-en-1-one (**3ah**). Yellow oil. 55% yield (34 mg).



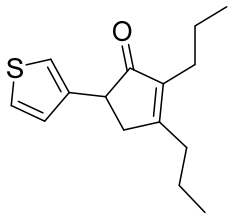
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.92 (dt, *J* = 3.5, 1.1 Hz, 1H), 3.80 (ddd, *J* = 7.2, 2.9, 1.1 Hz, 1H), 3.09 (ddq, *J* = 18.2, 7.2, 1.0 Hz, 1H), 2.72 (dqd, *J* = 18.1, 2.1, 1.0 Hz, 1H), 2.53 – 2.40 (m, 2H), 2.25 – 2.15 (m, 2H), 1.66 – 1.57 (m, 2H), 1.44 (h, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.8, 172.2, 142.3, 139.0, 126.9, 124.5, 124.0, 46.1, 39.2, 33.1, 25.4, 21.9, 20.9, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{15}H_{21}OS$, 249.1308; found 249.1308. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(furan-3-yl)-2,3-dipropylcyclopent-2-en-1-one (**3ai**). Colorless oil. 67% yield (39 mg).



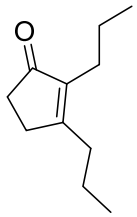
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 1.6, 0.7 Hz, 2H), 6.30 – 6.29 (m, 1H), 3.46 (ddd, *J* = 7.2, 2.9, 0.5 Hz, 1H), 2.97 (ddq, *J* = 18.0, 7.2, 1.0 Hz, 1H), 2.51 (ddq, *J* = 18.0, 2.9, 1.0 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.18 (ddq, *J* = 9.1, 7.8, 1.2 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.46 – 1.39 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.2, 172.3, 143.3, 139.5, 139.4, 123.4, 109.7, 41.7, 37.5, 33.2, 25.4, 21.9, 21.0, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{15}H_{21}O_2$, 233.1536; found 233.1538. The regiochemistry of the product was determined by 2D-NMR analysis.

2,3-dipropyl-5-(thiophen-3-yl)cyclopent-2-en-1-one (**3aj**). Colorless oil. 51% yield (32 mg).



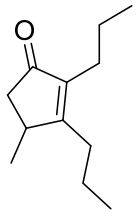
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.09 – 7.08 (m, 1H), 6.95 – 6.93 (m, 1H), 3.66 (dd, *J* = 7.2, 2.8 Hz, 1H), 3.02 (ddq, *J* = 18.3, 7.2, 1.0 Hz, 1H), 2.61 (dqd, *J* = 18.2, 2.1, 1.0 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.25 – 2.15 (m, 2H), 1.65 – 1.56 (m, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.1, 172.3, 140.0, 139.5, 126.8, 126.0, 121.0, 46.3, 38.2, 33.2, 25.4, 21.9, 21.0, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{15}H_{21}OS$, 249.1308; found 249.1309. The regiochemistry of the product was determined by 2D-NMR analysis.

2,3-dipropylcyclopent-2-en-1-one (**3ak**). Pale yellow oil. 41% yield (17 mg).



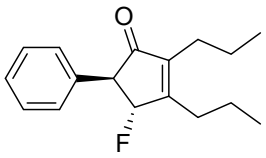
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.50 – 2.47 (m, 2H), 2.42 – 2.38 (m, 2H), 2.37 – 2.34 (m, 2H), 2.17 – 2.12 (m, 2H), 1.61 – 1.54 (m, 2H), 1.43 – 1.36 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 210.3, 174.0, 140.6, 34.4, 33.3, 29.1, 25.3, 22.0, 21.0, 14.3, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{11}H_{19}O$, 167.1430; found 167.1428. The configuration of the product was determined by 2D-NMR analysis and by analogy to previously reported literature.[4,5,6]

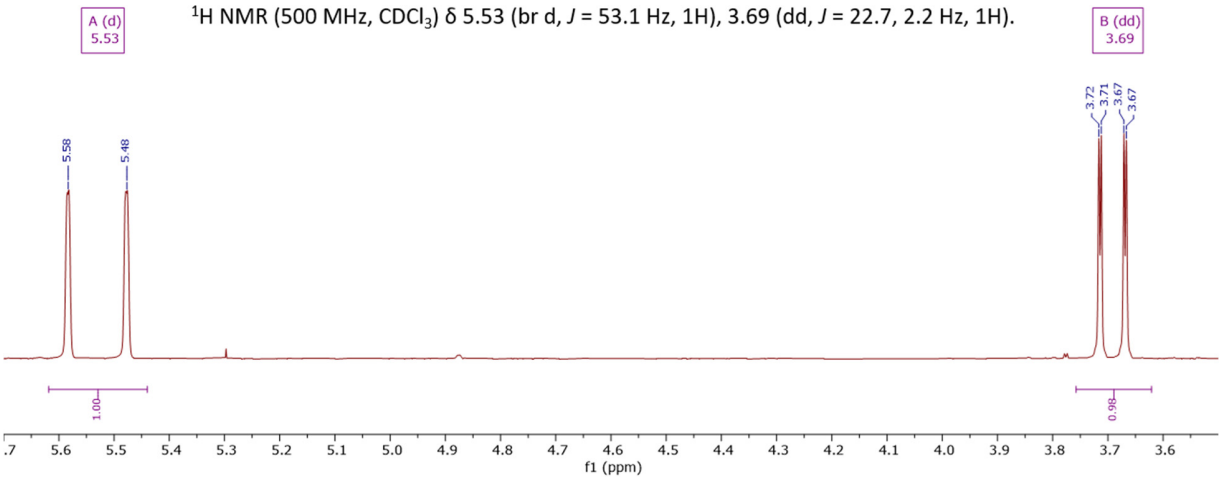
4-methyl-2,3-dipropylcyclopent-2-en-1-one (**3al**). Colorless oil. 34% yield (16 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.87 – 2.78 (m, 1H), 2.59 (ddd, *J* = 18.5, 6.5, 0.8 Hz, 1H), 2.46 (ddd, *J* = 13.6, 9.4, 6.8 Hz, 1H), 2.31 (ddd, *J* = 13.8, 9.4, 5.3 Hz, 1H), 2.17 – 2.07 (m, 2H), 1.94 (dd, *J* = 18.6, 2.2 Hz, 1H), 1.68 – 1.57 (m, 1H), 1.49 – 1.35 (m, 3H), 1.15 (d, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.2, 177.8, 140.2, 43.3, 34.7, 30.5, 25.3, 22.0, 20.9, 19.5, 14.5, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{12}H_{21}O$, 181.1587; found 181.1587. The regiochemistry of the product was determined by 2D-NMR analysis and by analogy to previously reported literature.[7]

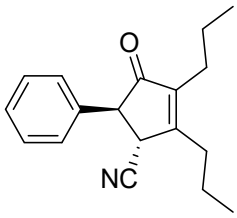
trans-4-fluoro-5-phenyl-2,3-dipropylcyclopent-2-en-1-one (**3am**). Colorless oil. 47% yield (30 mg).



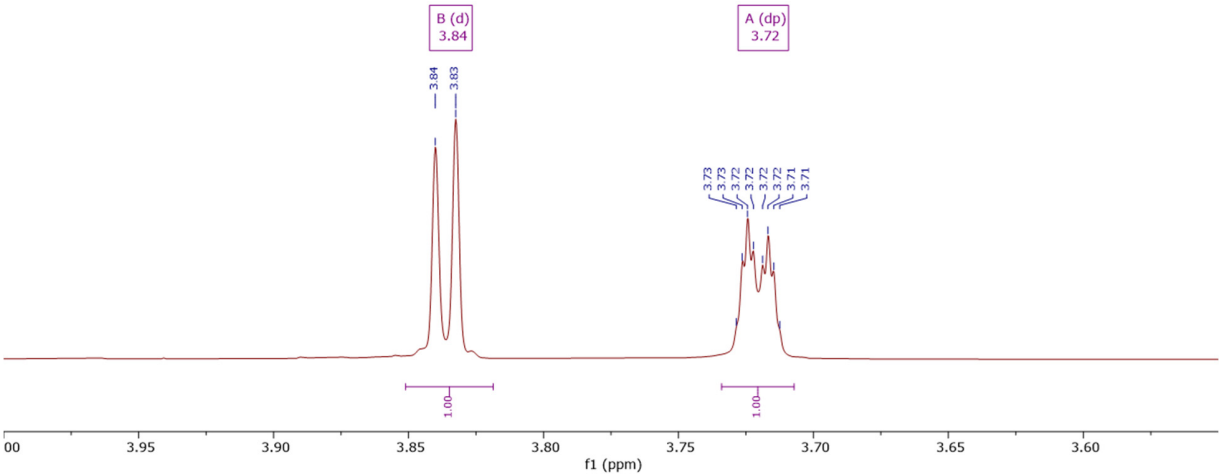


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.14 – 7.09 (m, 2H), 5.53 (dddd, *J* = 53.1, 1.7, 1.3, 0.7 Hz, 1H), 3.69 (dd, *J* = 22.7, 2.2 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.35 – 2.22 (m, 2H), 1.80 – 1.67 (m, 1H), 1.67 – 1.56 (m, 1H), 1.50 (h, *J* = 7.5 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.6 (d, *J* = 4.3 Hz), 166.2 (d, *J* = 16.0 Hz), 144.5 (d, *J* = 4.2 Hz), 137.1 (d, *J* = 1.4 Hz), 129.1, 128.1, 127.6, 97.2 (d, *J* = 181.8 Hz), 58.2 (d, *J* = 18.8 Hz), 29.7, 25.4 (d, *J* = 1.7 Hz), 21.7 (d, *J* = 3.1 Hz), 20.9, 14.5, 14.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -175.8. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{17}H_{21}FNaO$, 283.1469; found 283.1472. The configuration of the product was determined by 2D-NMR analysis and by analogy to the coupling constants of the vicinal H–F and H_4–H_5 previously reported literature.[8,9]

4-oxo-5-*trans*-phenyl-2,3-dipropylcyclopent-2-ene-1-carbonitrile (**3an**). Pale yellow oil. 30% yield (20 mg).

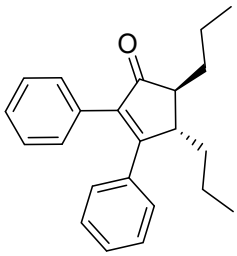


^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (d, *J* = 3.8 Hz, 1H), 3.72 (dp, *J* = 3.2, 1.1 Hz, 1H).

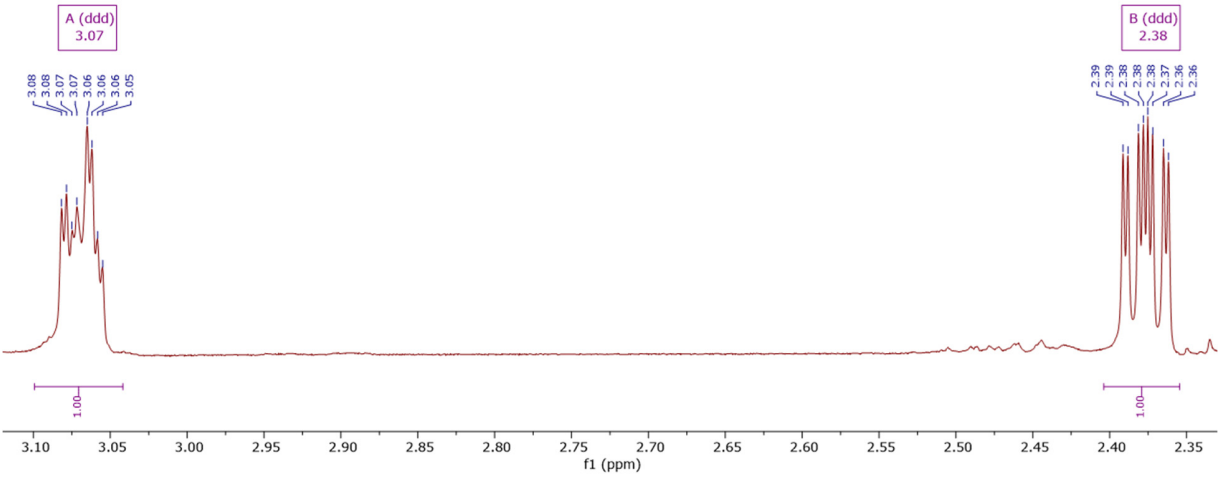


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 3H), 7.12 – 7.09 (m, 2H), 3.84 (d, *J* = 3.8 Hz, 1H), 3.72 (dp, *J* = 3.2, 1.1 Hz, 1H), 2.70 (dddd, *J* = 14.1, 9.3, 7.1, 0.9 Hz, 1H), 2.59 (dddd, *J* = 14.2, 9.3, 5.5, 1.1 Hz, 1H), 2.31 – 2.26 (m, 2H), 1.83 – 1.71 (m, 1H), 1.66 – 1.54 (m, 1H), 1.53 – 1.44 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 203.5, 163.8, 142.8, 136.9, 129.4, 128.2, 127.7, 118.3, 55.8, 40.7, 31.4, 25.8, 21.7, 21.0, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{22}NO$, 268.1696; found 268.1692. The configuration of the product was determined by 2D-NMR analysis and by analogy to the coupling constants of vicinal H_4–H_5 previously reported literature.[9]

2,3-diphenyl-4,5-*trans*-dipropylcyclopent-2-en-1-one (**3ao-2**, major). Yellow oil. 25% yield (20 mg).

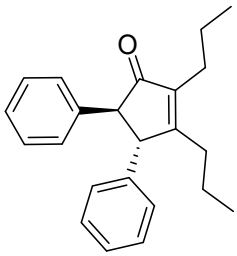


^{1}H NMR (500 MHz, $CDCl_3$) δ 3.07 (ddd, *J* = 8.4, 3.4, 1.6 Hz, 1H), 2.38 (ddd, *J* = 8.2, 5.1, 1.6 Hz, 1H).

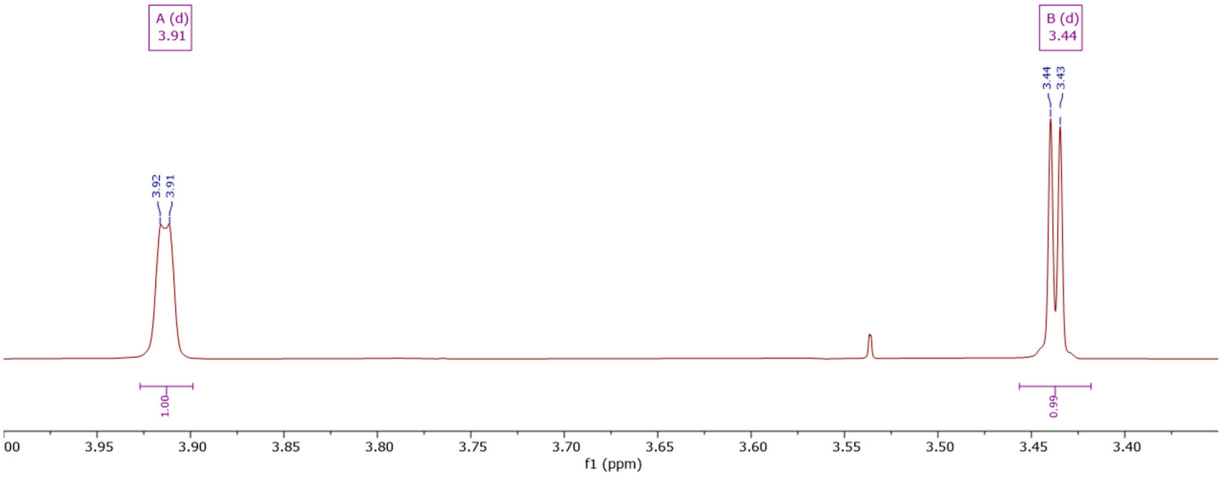


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 3H), 7.27 – 7.20 (m, 5H), 7.18 – 7.15 (m, 2H), 3.07 (ddd, *J* = 8.4, 3.4, 1.6 Hz, 1H), 2.38 (ddd, *J* = 8.2, 5.1, 1.6 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.68 – 1.59 (m, 1H), 1.56 – 1.46 (m, 2H), 1.37 – 1.23 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.5, 171.9, 139.0, 135.4, 132.1, 129.7, 129.3, 128.6, 128.4, 128.3, 127.7, 51.7, 47.9, 35.9, 35.3, 20.5, 20.1, 14.5, 14.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{23}H_{27}O$, 319.2056; found 319.2053. The configuration of the product was determined by 2D-NMR analysis and by analogy to the coupling constants of vicinal H_4–H_5 previously reported literature .[9,10]

4,5-*trans*-diphenyl-2,3-dipropylcyclopent-2-en-1-one (**3ao-1**, minor). Pale yellow oil. 17% yield (14 mg).

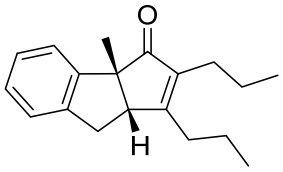


^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91 (d, *J* = 2.6 Hz, 1H), 3.44 (d, *J* = 2.6 Hz, 1H).



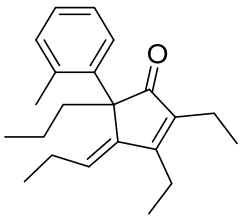
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 6H), 7.09 – 7.02 (m, 4H), 3.91 (d, *J* = 2.6 Hz, 1H), 3.44 (d, *J* = 2.6 Hz, 1H), 2.50 (dddd, *J* = 13.6, 9.2, 7.1, 0.7 Hz, 1H), 2.38 – 2.27 (m, 2H), 2.08 – 2.01 (m, 1H), 1.61 – 1.50 (m, 3H), 1.46 – 1.35 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.4, 174.5, 141.7, 141.3, 139.9, 129.1, 129.0, 127.8, 127.7, 127.3, 127.0, 62.1, 57.3, 31.1, 25.6, 22.2, 20.9, 14.3, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{23}H_{27}O$, 319.2056; found 319.2056. The configuration of the product was determined by 2D-NMR analysis and by analogy to the coupling constants of vicinal H_4–H_5 previously reported literature.[9] In addition, the ^{1}H-and ^{13}C-NMR data were consistent with the spectral data reported in literature.[3,11,12]

(3a,8a-*cis*)-3a-methyl-1,2-dipropyl-8,8a-dihydrocyclopenta[a]inden-3(3a*H*)-one (**3ap**). Pale yellow oil. 20% yield (14 mg).



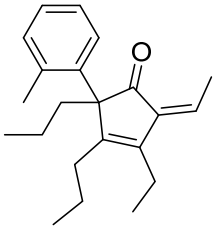
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.08 (m, 1H), 3.33 (ddq, *J* = 16.6, 10.4, 0.8 Hz, 1H), 3.24 (dqd, *J* = 10.4, 2.0, 0.9 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.55 (dddd, *J* = 14.1, 9.5, 7.2, 0.8 Hz, 1H), 2.35 (dddd, *J* = 14.0, 9.4, 5.2, 0.9 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.78 – 1.65 (m, 1H), 1.57 – 1.48 (m, 1H), 1.46 (s, 3H), 1.38 – 1.28 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.0, 172.8, 144.7, 141.1, 138.0, 127.8, 127.1, 125.0, 124.3, 60.0, 52.6, 33.8, 31.1, 25.5, 22.6, 21.9, 21.1, 14.4, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{25}O$, 269.1900; found 269.1897. The configuration of the product was determined by 2D-NMR analysis.

(*Z*)-2,3-diethyl-5-propyl-4-propylidene-5-(*o*-tolyl)cyclopent-2-en-1-one (**3aq-1**, major). Pale yellow oil. **Method B**: 21% yield (17 mg).



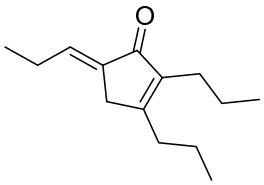
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.11 (td, *J* = 7.4, 1.4 Hz, 1H), 7.00 – 6.97 (m, 1H), 5.69 (t, *J* = 7.9 Hz, 1H), 2.59 (qd, *J* = 7.6, 1.1 Hz, 2H), 2.39 – 2.29 (m, 2H), 2.22 (td, *J* = 12.0, 5.0 Hz, 1H), 2.05 (td, *J* = 12.0, 4.6 Hz, 1H), 1.94 (s, 3H), 1.82 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.72 – 1.61 (m, 1H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.11 – 0.99 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.65 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.5, 167.1, 142.5, 141.9, 140.4, 137.1, 131.7, 127.9, 127.5, 126.7, 125.9, 57.1, 39.2, 21.7, 20.9, 19.2, 17.8, 17.0, 15.0, 13.8, 13.4, 13.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{31}O$, 311.2369; found 311.2371. The configuration of the product was determined by 2D-NMR analysis.

(*Z*)-4-ethyl-5-ethylidene-2,3-dipropyl-2-(*o*-tolyl)cyclopent-3-en-1-one (**3aq-2**, minor). Pale yellow oil. **Method B**: 10% yield (8 mg).



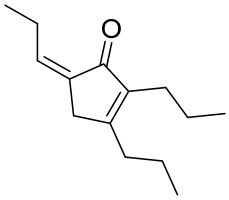
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.19 (tdd, *J* = 8.0, 1.6, 0.7 Hz, 1H), 7.12 (td, *J* = 7.4, 1.4 Hz, 1H), 7.04 – 6.99 (m, 1H), 5.96 (q, *J* = 7.7 Hz, 1H), 2.36 (q, *J* = 7.6 Hz, 2H), 2.26 (d, *J* = 7.6 Hz, 3H), 2.11 – 1.94 (m, 5H), 1.86 (dddd, *J* = 34.8, 13.5, 11.1, 5.3 Hz, 2H), 1.21 – 1.07 (m, 6H), 0.93 – 0.79 (m, 4H), 0.76 – 0.70 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.0, 141.3, 140.6, 139.7, 139.0, 137.6, 131.8, 127.9, 127.6, 127.0, 125.8, 62.8, 38.5, 28.9, 22.7, 21.3, 18.4, 17.1, 15.0, 14.9, 14.1, 12.9. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{22}H_{30}NaO$, 333.2189; found 333.2189. The configuration of the product was determined by 2D-NMR analysis.

(*E*)-2,3-dipropyl-5-propylidenecyclopent-2-en-1-one (**3ar-1**, major). Pale yellow oil. 42% yield (22 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (tt, *J* = 7.5, 1.7 Hz, 1H), 3.01 (dq, *J* = 2.0, 0.9 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.25 – 2.18 (m, 4H), 1.63 – 1.54 (m, 2H), 1.48 – 1.40 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.8, 166.4, 142.6, 134.8, 134.3, 32.7, 32.6, 25.6, 23.0, 22.0, 21.1, 14.3, 14.3, 13.3. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{14}H_{22}NaO$, 229.1563; found 229.1563. The regio- and stereochemistry of the product was determined by 2D-NMR analysis.

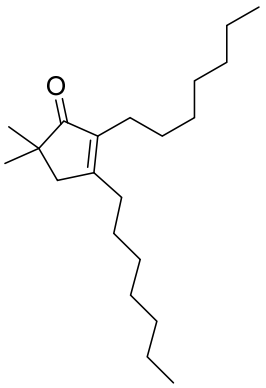
(*Z*)-2,3-dipropyl-5-propylidenecyclopent-2-en-1-one (**3ar-2**, minor). Pale yellow oil. 9% yield (5 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (tt, *J* = 7.5, 1.3 Hz, 1H), 3.00 (h, *J* = 1.1 Hz, 2H), 2.82 (pt, *J* = 7.5, 1.0 Hz, 2H), 2.39 (ddt, *J* = 8.7, 7.0, 1.0 Hz, 2H), 2.23 – 2.15 (m, 2H), 1.60 – 1.51 (m, 3H), 1.48 – 1.38 (m, 3H), 1.04 (t, *J* = 7.6 Hz, 4H), 0.96 (t, *J* = 7.4 Hz, 4H), 0.90 (t, *J* = 7.4 Hz, 4H). **^{13}C NMR** (126 MHz,

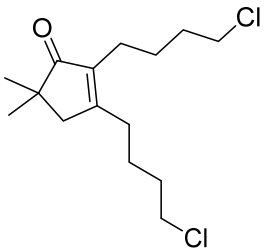
$CDCl_3$) δ 197.8, 166.1, 144.0, 140.4, 132.5, 35.8, 32.6, 25.5, 22.0, 21.1, 21.0, 14.3, 14.3, 14.0. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{14}H_{23}O$, 207.1743; found 207.1743. The regio- and stereochemistry of the product was determined by 2D-NMR analysis.

2,3-diheptyl-5,5-dimethylcyclopent-2-en-1-one (**3ba**). Colorless oil. 87% yield (67 mg).



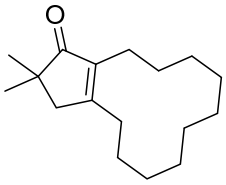
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.37 (t, *J* = 7.9 Hz, 2H), 2.34 (s, 2H), 2.14 (t, *J* = 7.5 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.39 – 1.20 (m, 18H), 1.07 (s, 6H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 214.2, 170.4, 137.8, 46.3, 42.7, 32.0, 31.9, 31.0, 29.7, 29.7, 29.3, 29.2, 28.8, 27.6, 25.4, 23.4, 22.8, 22.8, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{39}O$, 307.2995; found 307.2993. The regiochemistry of the product was determined by 2D-NMR analysis.

2,3-bis(4-chlorobutyl)-5,5-dimethylcyclopent-2-en-1-one (**3bb**). Colorless oil. 85% yield (62 mg).



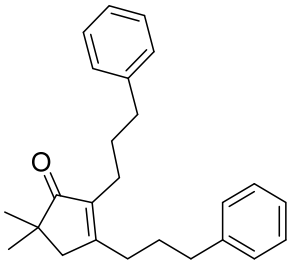
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.57 (t, *J* = 6.3 Hz, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.46 – 2.41 (m, 2H), 2.37 (p, *J* = 1.0 Hz, 2H), 2.18 (tt, *J* = 7.7, 1.1 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.77 – 1.65 (m, 4H), 1.56 – 1.49 (m, 2H), 1.08 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.9, 169.7, 137.5, 46.2, 44.9, 44.7, 42.9, 32.4, 32.4, 30.2, 26.0, 25.3, 24.8, 22.5. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{15}H_{24}Cl_2NaO$, 313.1096; found 313.1097. The regiochemistry of the product was determined by 2D-NMR analysis.

2,2-dimethyl-2,3,4,5,6,7,8,9,10,11,12,13-dodecahydro-1*H*-cyclopenta[12]annulen-1-one (**3bc**). Pale yellow oil. 90% yield (56 mg).



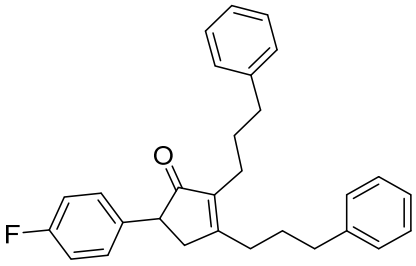
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 – 2.39 (m, 2H), 2.35 (p, *J* = 1.1 Hz, 2H), 2.23 (tt, *J* = 6.6, 1.2 Hz, 2H), 1.69 – 1.56 (m, 4H), 1.46 – 1.29 (m, 10H), 1.19 – 1.12 (m, 2H), 1.07 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.6, 170.8, 137.4, 46.0, 42.6, 27.8, 25.6, 25.5, 25.4, 25.2, 25.0, 24.7, 23.9, 23.0, 22.1, 20.8. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{29}O$, 249.2213; found 249.2207. The regiochemistry of the product was determined by 2D-NMR analysis.

5,5-dimethyl-2,3-bis(3-phenylpropyl)cyclopent-2-en-1-one (**3bd**). Colorless oil. 89% yield (77 mg).



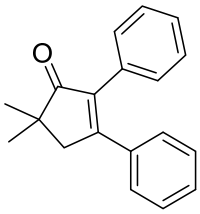
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 4H), 7.24 – 7.14 (m, 6H), 2.65 – 2.60 (m, 2H), 2.60 – 2.55 (m, 2H), 2.41 – 2.36 (m, 2H), 2.35 (s, 2H), 2.22 – 2.16 (m, 2H), 1.86 – 1.78 (m, 2H), 1.73 – 1.65 (m, 2H), 1.07 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.0, 170.1, 142.4, 141.6, 137.7, 128.6, 128.5, 128.5, 128.4, 126.2, 125.9, 46.3, 42.8, 36.0, 36.0, 30.6, 30.4, 29.4, 25.3, 23.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{25}H_{30}NaO$, 369.2189; found 369.2181. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-fluorophenyl)-2,3-bis(3-phenylpropyl)cyclopent-2-en-1-one (**3be**). Colorless oil. 57% yield (59 mg).



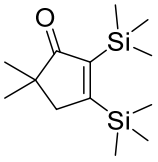
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.25 – 7.15 (m, 6H), 7.08 – 7.04 (m, 2H), 7.02 – 6.96 (m, 2H), 3.51 (dd, *J* = 7.2, 2.7 Hz, 1H), 3.03 (ddt, *J* = 18.5, 7.2, 1.1 Hz, 1H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.55 (ddt, *J* = 18.5, 2.6, 1.2 Hz, 1H), 2.52 – 2.42 (m, 2H), 2.30 – 2.20 (m, 2H), 1.94 – 1.83 (m, 2H), 1.78 – 1.68 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.4, 172.7, 161.9 (d, *J* = 244.9 Hz), 142.2, 141.4, 139.7, 136.1 (d, *J* = 3.2 Hz), 129.1 (d, *J* = 8.0 Hz), 128.7, 128.5, 128.5, 128.5, 126.3, 125.9, 115.7 (d, *J* = 21.3 Hz), 50.2, 39.2, 36.0, 36.0, 30.8, 30.3, 29.4, 23.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{29}H_{30}FO$, 413.2275; found 413.2273. The regiochemistry of the product was determined by 2D-NMR analysis.

5,5-dimethyl-2,3-diphenylcyclopent-2-en-1-one (**3bf**). White solid. **Method A**: 27% yield (18 mg). **Method B**: 39% yield (25 mg).



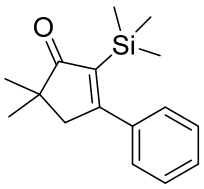
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 8H), 7.25 – 7.22 (m, 2H), 2.93 (s, 2H), 1.29 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.8, 164.7, 137.2, 135.9, 132.7, 129.9, 129.7, 128.5, 128.5, 128.3, 127.9, 46.8, 43.6, 25.6. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{19}H_{18}NaO$, 285.1250; found 285.1248. The regiochemistry of the product was determined by 2D-NMR analysis. The ^{1}H- and ^{13}C-NMR data were consistent with the spectral data reported in literature.[13,14]

5,5-dimethyl-2,3-bis(trimethylsilyl)cyclopent-2-en-1-one (**3bg**). Colorless oil. 38% yield (24 mg).



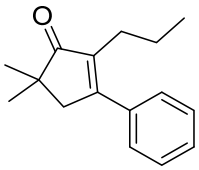
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 2H), 1.03 (s, 6H), 0.25 (s, 9H), 0.24 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 218.8, 187.0, 151.9, 53.4, 42.3, 25.2, 0.5, -0.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{13}H_{26}NaOSi_2$, 277.1414; found 277.1414. The regiochemistry of the product was determined by 2D-NMR analysis.

5,5-dimethyl-3-phenyl-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bh**). White solid. 69% yield (45 mg).



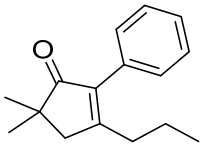
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 3H), 7.28 – 7.25 (m, 2H), 2.78 (s, 2H), 1.17 (s, 6H), 0.02 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 217.6, 181.5, 139.6, 139.1, 129.1, 128.3, 127.1, 51.9, 44.7, 25.4, -0.4. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{16}H_{22}NaOSi$, 281.1332; found 281.1335. The regiochemistry of the product was determined by 2D-NMR analysis.

5,5-dimethyl-3-phenyl-2-propylcyclopent-2-en-1-one (**3bi-1**, major). Colorless oil. 30% yield (17 mg).



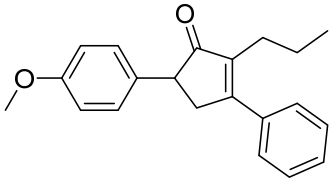
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 4H), 7.42 – 7.38 (m, 1H), 2.76 (t, *J* = 1.2 Hz, 2H), 2.36 (ddt, *J* = 9.1, 6.9, 1.2 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.18 (s, 6H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 214.0, 163.7, 138.5, 136.9, 129.3, 128.7, 127.4, 47.1, 42.8, 26.3, 25.5, 21.7, 14.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{21}O$, 229.1587; found 229.1584. The regiochemistry of the product was determined by 2D-NMR analysis and by analogy to previously reported literature.[14]

5,5-dimethyl-2-phenyl-3-propylcyclopent-2-en-1-one (**3bi-2**, minor). Colorless thick oil. 23% yield (13 mg).



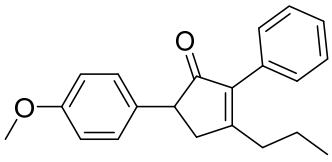
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 1H), 7.27 – 7.24 (m, 2H), 2.53 (t, *J* = 1.0 Hz, 2H), 2.51 (ddt, *J* = 8.8, 6.7, 1.0 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.19 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 212.1, 172.2, 137.9, 132.5, 129.4, 128.3, 127.6, 46.3, 43.3, 33.5, 25.5, 21.1, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{21}O$, 229.1587; found 229.1588. The regiochemistry of the product was determined by 2D-NMR analysis and by analogy to previously reported literature.[15]

5-(4-methoxyphenyl)-3-phenyl-2-propylcyclopent-2-en-1-one (**3bj-1**, major). Yellow oil. 27% yield (21 mg).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.50 – 7.46 (m, 2H), 7.46 – 7.42 (m, 1H), 7.14 – 7.10 (m, 2H), 6.89 – 6.85 (m, 2H), 3.79 (s, 3H), 3.66 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.42 (ddt, *J* = 18.0, 7.3, 1.2 Hz, 1H), 2.98 (ddt, *J* = 18.0, 2.5, 1.2 Hz, 1H), 2.47 – 2.38 (m, 2H), 1.59 – 1.49 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.0, 166.0, 158.6, 140.3, 136.6, 132.3, 129.6, 128.9, 128.7, 127.4, 114.4, 55.4, 50.3, 40.0, 26.4, 21.7, 14.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{23}O_2$, 307.1693; found 307.1691. The regiochemistry of the product was determined by 2D-NMR analysis.

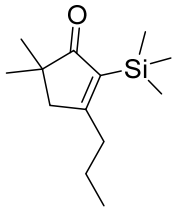
5-(4-methoxyphenyl)-2-phenyl-3-propylcyclopent-2-en-1-one (**3bj-2**, minor). Yellow oil. 19% yield (15 mg).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.35 – 7.31 (m, 1H), 7.30 – 7.27 (m, 2H), 7.15 – 7.11 (m, 2H), 6.89 – 6.86 (m, 2H), 3.79 (s, 3H), 3.71 – 3.66 (m, 1H), 3.20 (ddt, *J* = 18.8, 7.5, 1.0 Hz, 1H), 2.73 (ddt, *J* = 18.8, 2.9, 1.0 Hz, 1H), 2.65 – 2.54 (m, 2H), 1.71 – 1.62 (m, 2H), 0.98 (t, *J* = 7.3

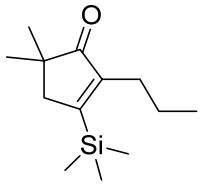
Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 174.5, 158.6, 139.7, 132.3, 132.1, 129.4, 128.7, 128.4, 127.8, 114.4, 55.4, 50.6, 39.2, 33.7, 21.2, 14.3. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{23}O_2$, 307.1693; found 307.1691.

5,5-dimethyl-3-propyl-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bk-1**, major, **88**:12 inseparable mixture). Colorless oil. 92% yield (52 mg).



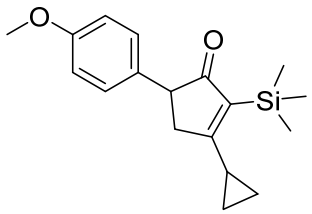
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.48 – 2.42 (m, 4H), 1.59 – 1.51 (m, 2H), 1.06 (s, 6H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.21 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 218.3, 186.1, 136.8, 49.6, 44.2, 35.9, 25.4, 21.9, 14.2, -0.2. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{13}H_{24}NaOSi$, 247.1489; found 247.1486. The regiochemistry of the product was determined by 2D-NMR analysis.

5,5-dimethyl-2-propyl-3-(trimethylsilyl)cyclopent-2-en-1-one (**3bk-2**, minor, 88:**12** inseparable mixture).



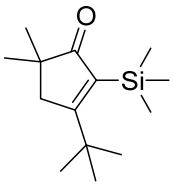
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.46 (s, 2H), 2.24 (ddt, *J* = 9.1, 6.9, 1.2 Hz, 2H), 1.43 – 1.37 (m, 2H), 1.04 (s, 6H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.22 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 214.9, 169.6, 150.9, 48.1, 42.5, 28.1, 25.4, 22.9, 14.3, -1.2. The regiochemistry of the product was determined by 2D-NMR analysis.

3-cyclopropyl-5-(4-methoxyphenyl)-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bl**). Pale yellow oil. 66% yield (50 mg).



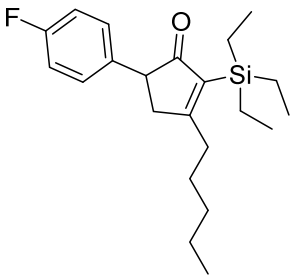
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 – 6.98 (m, 2H), 6.85 – 6.81 (m, 2H), 3.77 (s, 3H), 3.43 (dd, *J* = 7.6, 3.2 Hz, 1H), 2.73 (ddd, *J* = 18.3, 7.7, 0.7 Hz, 1H), 2.31 – 2.25 (m, 2H), 1.07 – 1.02 (m, 2H), 1.00 – 0.95 (m, 2H), 0.28 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.3, 188.9, 158.5, 138.2, 132.7, 128.6, 114.3, 55.4, 51.2, 37.0, 16.0, 8.8, 8.8, -0.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O_2Si$, 301.1618; found 301.1618. The regiochemistry of the product was determined by 2D-NMR analysis.

3-(*tert*-butyl)-5,5-dimethyl-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bm**). Colorless oil. 48% yield (29 mg).



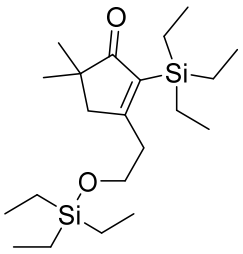
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53 (s, 2H), 1.23 (s, 9H), 1.04 (s, 6H), 0.27 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 218.4, 193.1, 135.9, 48.4, 43.3, 36.6, 30.2, 25.1, 1.9. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{14}H_{26}NaOSi$, 261.1645; found 261.1645. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-fluorophenyl)-3-pentyl-2-(triethylsilyl)cyclopent-2-en-1-one (**3bn**). Yellow oil. 68% yield (61 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 – 7.03 (m, 2H), 7.01 – 6.95 (m, 2H), 3.52 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.14 (ddt, *J* = 18.8, 7.6, 0.7 Hz, 1H), 2.68 (ddt, *J* = 18.8, 3.2, 0.8 Hz, 1H), 2.64 – 2.50 (m, 2H), 1.64 – 1.56 (m, 2H), 1.43 – 1.33 (m, 4H), 0.96 – 0.89 (m, 12H), 0.82 – 0.75 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.0, 190.1, 161.8 (d, *J* = 244.6 Hz), 136.3 (d, *J* = 3.2 Hz), 136.3, 129.0 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 21.3 Hz), 52.0, 42.6, 34.4, 32.3, 28.5, 22.7, 14.1, 7.6, 3.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.5. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{22}H_{33}FNaOSi$, 383.2177; found 383.2174. The regiochemistry of the product was determined by 2D-NMR analysis.

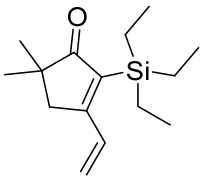
5,5-dimethyl-2-(triethylsilyl)-3-(2-((triethylsilyl)oxy)ethyl)cyclopent-2-en-1-one (**3bo-1**, major). Colorless oil. 40% yield (38 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79 (t, *J* = 6.6 Hz, 2H), 2.72 (tt, *J* = 6.7, 0.9 Hz, 2H), 2.53 (t, *J* = 0.8 Hz, 2H), 1.06 (s, 6H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.93 – 0.88 (m, 9H), 0.81 – 0.74 (m, 6H), 0.59 (q, *J* = 8.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 218.4, 184.6, 135.8, 61.5, 50.4, 44.2, 37.4, 25.4, 7.6, 6.9, 4.4, 3.6. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{21}H_{42}NaO_2Si_2$, 405.2616; found 405.2613. The regiochemistry of the product was determined by 2D-NMR analysis.

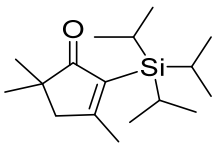
Besides the desired product (**3bo-1**), a side product (**3bo-2**) was isolated, which presumably results from the basic quench after the reaction.

5,5-dimethyl-2-(triethylsilyl)-3-vinylcyclopent-2-en-1-one (**3bo-2**, minor). Colorless oil. 14% yield (9 mg).



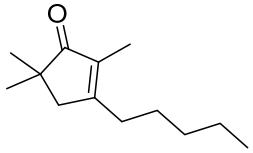
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (ddt, *J* = 17.4, 10.8, 0.9 Hz, 1H), 5.73 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.49 (dd, *J* = 10.6, 1.2 Hz, 1H), 2.64 (d, *J* = 1.0 Hz, 2H), 1.11 (s, 6H), 0.94 – 0.89 (m, 9H), 0.84 – 0.77 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 218.1, 175.6, 137.7, 134.3, 121.7, 45.0, 43.7, 25.6, 7.6, 3.9. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{15}H_{26}NaOSi$, 273.1645; found 273.1643. The regiochemistry of the product was determined by 2D-NMR analysis.

3,5,5-trimethyl-2-(triisopropylsilyl)cyclopent-2-en-1-one (**3bp**). Colorless oil. 31% yield (22 mg).



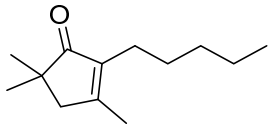
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (q, *J* = 0.9 Hz, 2H), 2.18 (t, *J* = 0.9 Hz, 3H), 1.51 (hept, *J* = 7.5 Hz, 3H), 1.07 (s, 6H), 1.04 (d, *J* = 7.5 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 218.5, 183.4, 133.4, 53.0, 44.4, 25.5, 21.3, 19.0, 11.8. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{17}H_{32}NaOSi$, 303.2115; found 303.2112. The regiochemistry of the product was determined by 2D-NMR analysis.

2,5,5-trimethyl-3-pentylcyclopent-2-en-1-one (**3bq-1**, major). Colorless oil. 42% yield (21 mg).



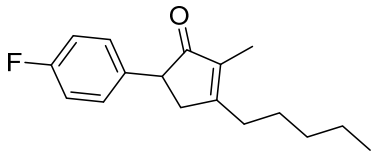
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 – 2.36 (m, 2H), 2.35 (qd, *J* = 2.0, 0.9 Hz, 2H), 1.68 (tt, *J* = 2.0, 0.6 Hz, 3H), 1.54 – 1.47 (m, 2H), 1.37 – 1.25 (m, 4H), 1.07 (s, 6H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.5, 170.8, 133.3, 46.5, 42.8, 31.8, 31.0, 27.0, 25.4, 22.6, 14.1, 8.4. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1742. The regiochemistry of the product was determined by 2D-NMR analysis.

3,5,5-trimethyl-2-pentylcyclopent-2-en-1-one (**3bq-2**, minor). Colorless oil. 31% yield (15 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (h, *J* = 1.1 Hz, 2H), 2.18 – 2.11 (m, 2H), 2.00 (dq, *J* = 1.2, 0.5 Hz, 3H), 1.40 – 1.19 (m, 6H), 1.07 (s, 6H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.9, 166.5, 138.1, 48.8, 42.9, 31.9, 28.2, 25.3, 23.2, 22.6, 17.1, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1745. The regiochemistry of the product was determined by 2D-NMR analysis.

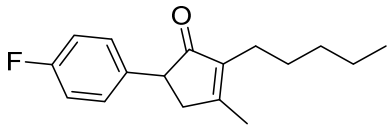
5-(4-fluorophenyl)-2-methyl-3-pentylcyclopent-2-en-1-one (**3br-1**, major). Pale yellow oil. 38% yield (25 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.05 (m, 2H), 7.01 – 6.96 (m, 2H), 3.54 (dd, *J* = 7.1, 2.7 Hz, 1H), 3.09 – 3.00 (m, 1H), 2.55 (dddt, *J* = 18.4, 2.9, 2.1, 1.0 Hz, 1H), 2.48 (h, *J* = 6.4 Hz, 2H), 1.75 (t, *J* = 2.0 Hz, 3H), 1.61 – 1.55 (m, 2H), 1.41 – 1.32 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126

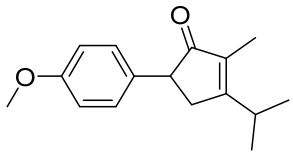
MHz, $CDCl_3$) δ 208.9, 173.1, 161.9 (d, *J* = 244.7 Hz), 136.1 (d, *J* = 3.2 Hz), 135.4, 129.2 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 21.5 Hz), 50.3, 39.4, 31.9, 31.3, 27.1, 22.6, 14.1, 8.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.3. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{17}H_{21}FNaO$, 283.1469; found 283.1470. The regiochemistry of the product was determined by 2D-NMR analysis.

5-(4-fluorophenyl)-3-methyl-2-pentylcyclopent-2-en-1-one (**3br-2**, minor). Pale yellow oil. 31% yield (20 mg).



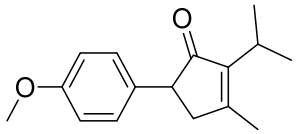
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.05 (m, 2H), 7.01 – 6.96 (m, 2H), 3.52 (dd, *J* = 7.2, 2.8 Hz, 1H), 3.04 (dddt, *J* = 18.4, 7.3, 2.3, 1.2 Hz, 1H), 2.54 (ddt, *J* = 18.5, 2.6, 1.2 Hz, 1H), 2.22 (td, *J* = 7.4, 3.8 Hz, 2H), 2.12 (s, 3H), 1.45 – 1.37 (m, 2H), 1.34 – 1.24 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.3, 169.0, 161.9 (d, *J* = 244.7 Hz), 140.1, 136.2 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 21.3 Hz), 50.4, 41.7, 31.9, 28.1, 23.3, 22.6, 17.3, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}FO$, 261.1649; found 261.1649. The regiochemistry of the product was determined by 2D-NMR analysis.

3-isopropyl-5-(4-methoxyphenyl)-2-methylcyclopent-2-en-1-one (**3bs-1**, major). Pale yellow oil. 45% yield (28 mg).



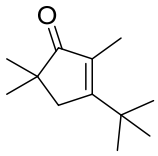
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 – 7.01 (m, 2H), 6.87 – 6.82 (m, 2H), 3.78 (s, 3H), 3.48 (dd, *J* = 7.2, 2.5 Hz, 1H), 3.11 (dtd, *J* = 7.7, 7.0, 6.1 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.58 – 2.49 (m, 1H), 1.76 (t, *J* = 2.0 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.6, 177.8, 158.5, 133.9, 132.6, 128.6, 114.3, 55.4, 49.9, 35.2, 29.5, 20.5, 20.3, 8.3. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{16}H_{20}NaO_2$, 267.1356; found 267.1360. The regiochemistry of the product was determined by 2D-NMR analysis.

2-isopropyl-5-(4-methoxyphenyl)-3-methylcyclopent-2-en-1-one (**3bs-2**, minor). Pale yellow oil. 31% yield (19 mg).



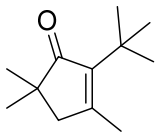
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 2H), 6.86 – 6.82 (m, 2H), 3.78 (s, 3H), 3.43 (dd, *J* = 7.2, 3.1 Hz, 1H), 2.98 (ddq, *J* = 18.3, 7.3, 1.2 Hz, 1H), 2.84 (p, *J* = 7.0 Hz, 1H), 2.52 (ddq, *J* = 18.3, 2.3, 1.2 Hz, 1H), 2.13 (q, *J* = 1.1 Hz, 3H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.5, 167.7, 158.5, 144.0, 132.7, 128.6, 114.3, 55.4, 50.4, 41.9, 25.1, 20.5, 20.4, 17.5. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{21}O_2$, 245.1536; found 245.1537. The regiochemistry of the product was determined by 2D-NMR analysis.

3-(*tert*-butyl)-2,5,5-trimethylcyclopent-2-en-1-one (**3bt-1**, major). Pale yellow oil. 47% yield (21 mg).



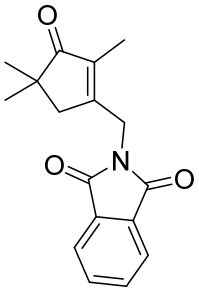
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (q, *J* = 2.0 Hz, 2H), 1.85 (t, *J* = 2.1 Hz, 3H), 1.23 (s, 9H), 1.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 215.1, 176.8, 131.9, 45.4, 41.8, 35.6, 28.9, 25.4, 10.5. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{12}H_{21}O$, 181.1587; found 181.1587. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(*tert*-butyl)-3,5,5-trimethylcyclopent-2-en-1-one (**3bt-2**, minor). Pale yellow oil. 17% yield (8 mg).



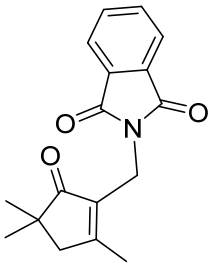
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (q, *J* = 1.0 Hz, 2H), 2.16 (t, *J* = 1.0 Hz, 3H), 1.27 (s, 9H), 1.03 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.0, 163.7, 142.8, 50.8, 42.5, 33.7, 29.9, 29.8, 25.3, 19.6. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{12}H_{21}O$, 181.1587; found 181.1589. The regiochemistry of the product was determined by 2D-NMR analysis.

2-((2,4,4-trimethyl-3-oxocyclopent-1-en-1-yl)methyl)isoindoline-1,3-dione (**3bu-1**, major). White solid. 42% yield (30 mg).



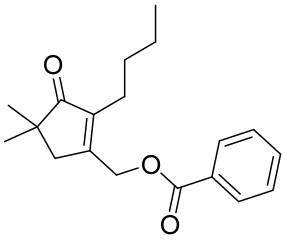
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.79 – 7.74 (m, 2H), 4.65 (h, *J* = 0.9 Hz, 2H), 2.31 (dhept, *J* = 2.2, 1.1 Hz, 2H), 1.85 (td, *J* = 2.2, 1.1 Hz, 3H), 1.05 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 213.6, 168.0, 161.6, 135.7, 134.5, 132.0, 123.8, 44.9, 43.0, 37.4, 25.2, 8.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{18}NO_3$, 284.1281; found 284.1281. The configuration of the product was determined by 2D-NMR analysis and X-ray crystallography.

2-((2,4,4-trimethyl-5-oxocyclopent-1-en-1-yl)methyl)isoindoline-1,3-dione (**3bu-2**, minor). Pale yellow oil. 25% yield (18 mg).



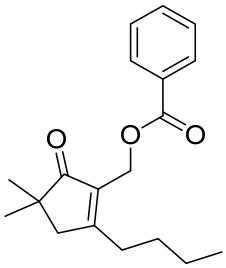
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.70 – 7.66 (m, 2H), 4.47 (dq, *J* = 1.5, 0.7 Hz, 2H), 2.41 (h, *J* = 1.0 Hz, 2H), 2.17 (q, *J* = 0.9 Hz, 3H), 1.05 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 211.8, 171.0, 168.0, 134.0, 132.2, 131.4, 123.4, 49.1, 43.1, 31.7, 25.1, 17.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{18}NO_3$, 284.1281; found 284.1276. The regiochemistry of the product was determined by 2D-NMR analysis.

(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)methyl benzoate (**3bv-1**, major). Colorless oil. 34% yield (26 mg).



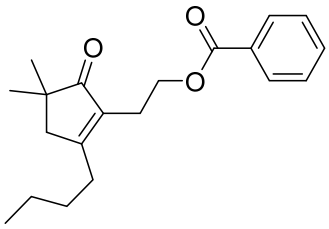
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H), 7.61 (ddt, *J* = 7.8, 7.0, 1.3 Hz, 1H), 7.50 – 7.45 (m, 2H), 5.21 (t, *J* = 1.2 Hz, 2H), 2.51 (p, *J* = 1.2 Hz, 2H), 2.30 – 2.24 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 – 1.26 (m, 2H), 1.11 (s, 6H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 213.4, 166.3, 161.7, 139.7, 133.6, 129.8, 129.7, 128.7, 62.3, 44.4, 43.0, 30.8, 25.3, 23.3, 22.8, 14.0. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{19}H_{24}NaO_3$, 323.1618; found 323.1609. The regiochemistry of the product was determined by 2D-NMR analysis.

(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)methyl benzoate (**3bv-2**, minor). Colorless oil. 27% yield (20 mg).



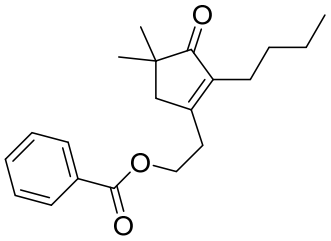
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.56 – 7.52 (m, 1H), 7.44 – 7.39 (m, 2H), 4.99 (t, *J* = 1.0 Hz, 2H), 2.57 (ddt, *J* = 8.8, 6.7, 0.9 Hz, 2H), 2.48 (p, *J* = 1.0 Hz, 2H), 1.55 – 1.49 (m, 2H), 1.38 – 1.30 (m, 2H), 1.14 (s, 6H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 212.3, 177.6, 166.6, 133.1, 132.2, 130.3, 129.8, 128.4, 55.9, 46.8, 43.2, 31.2, 29.9, 25.2, 22.9, 14.0. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{19}H_{24}NaO_3$, 323.1618; found 323.1614. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl benzoate (**3bw-1**, major, **65**:35 inseparable mixture). Colorless oil. 86% yield (68 mg).



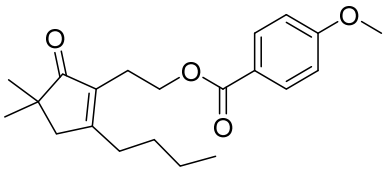
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.59 – 7.52 (m, 1H), 7.46 – 7.39 (m, 2H), 4.36 (t, *J* = 6.8 Hz, 2H), 2.67 (tt, *J* = 6.8, 1.2 Hz, 2H), 2.45 – 2.39 (m, 2H), 2.38 (p, *J* = 1.1 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.37 – 1.24 (m, 2H), 1.08 (s, 6H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.7, 173.2, 166.6, 133.3, 133.0, 130.4, 129.7, 128.4, 63.2, 46.5, 42.8, 30.9, 29.8, 25.3, 23.2, 22.9, 14.0. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{20}H_{26}NaO_3$, 337.1774; found 337.1774. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl benzoate (**3bw-2**, minor, 65:**35** inseparable mixture).



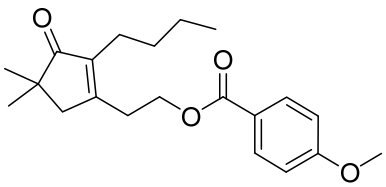
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.59 – 7.52 (m, 1H), 7.46 – 7.39 (m, 2H), 4.52 (t, *J* = 6.5 Hz, 2H), 2.88 (tt, *J* = 6.6, 1.0 Hz, 2H), 2.46 (p, *J* = 1.2 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.37 – 1.24 (m, 4H), 1.08 (s, 6H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.8, 166.5, 164.9, 140.1, 133.4, 129.9, 129.6, 128.6, 62.1, 46.2, 43.0, 31.0, 30.4, 25.3, 23.2, 22.9, 14.0. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl 4-methoxybenzoate (**3bx-1**, major, **65**:35 inseparable mixture). Pale yellow oil. 87% yield (75 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 6.96 – 6.88 (m, 2H), 4.34 (t, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 2.68 (tt, *J* = 7.0, 1.2 Hz, 2H), 2.47 – 2.42 (m, 2H), 2.40 (s, 2H), 1.52 – 1.44 (m, 2H), 1.40 – 1.25 (m, 2H), 1.10 (s, 6H), 0.93 – 0.89 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.7, 173.1, 166.4, 163.4, 133.5, 131.7, 122.8, 113.7, 62.9, 55.5, 46.5, 42.8, 30.9, 29.8, 25.3, 23.2, 22.9, 14.0. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{29}O_4$, 345.2060; found 345.2057. The regiochemistry of the product was determined by 2D-NMR analysis.

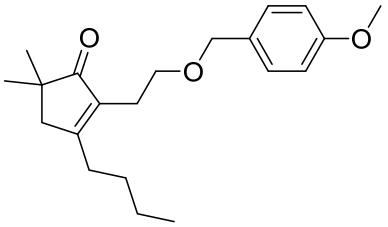
2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl 4-methoxybenzoate (**3bx-2**, minor, 65:**35** inseparable mixture).



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 6.96 – 6.88 (m, 2H), 4.51 (t, *J* = 6.6 Hz, 2H), 3.88 (s, 3H), 2.89 (tt, *J* = 6.5, 1.0 Hz, 2H), 2.48 (s, 2H), 2.24 – 2.19 (m, 2H), 1.40 – 1.25 (m, 4H), 1.10 (s,

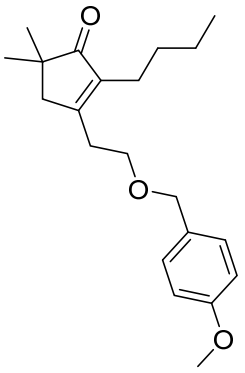
6H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.8, 166.2, 165.1, 163.7, 140.0, 131.7, 122.3, 113.8, 61.8, 55.6, 46.2, 43.0, 31.0, 30.5, 25.3, 23.2, 22.9, 14.0. The regiochemistry of the product was determined by 2D-NMR analysis.

3-butyl-2-(2-((4-methoxybenzyl)oxy)ethyl)-5,5-dimethylcyclopent-2-en-1-one (**3by-1**, major). Colorless oil. 37% yield (31 mg).



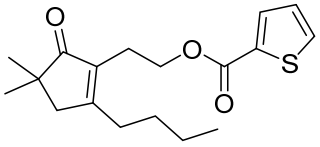
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.87 – 6.83 (m, 2H), 4.41 (s, 2H), 3.79 (s, 3H), 3.47 (t, *J* = 7.2 Hz, 2H), 2.50 (tt, *J* = 7.1, 1.2 Hz, 2H), 2.41 (ddt, *J* = 8.8, 6.6, 1.0 Hz, 2H), 2.36 (p, *J* = 1.1 Hz, 2H), 1.49 – 1.42 (m, 2H), 1.36 – 1.28 (m, 2H), 1.07 (s, 6H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.0, 172.8, 159.2, 134.2, 130.8, 129.3, 113.8, 72.6, 68.4, 55.4, 46.5, 42.8, 30.9, 29.8, 25.3, 24.3, 22.9, 14.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{21}H_{30}NaO_3$, 353.2087; found 353.2085. The regiochemistry of the product was determined by 2D-NMR analysis.

2-butyl-3-(2-((4-methoxybenzyl)oxy)ethyl)-5,5-dimethylcyclopent-2-en-1-one (**3by-2**, minor). Colorless thick oil. 19% yield (16 mg).



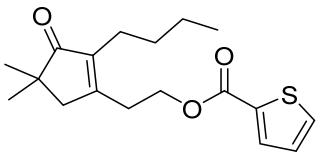
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 6.91 – 6.84 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.70 (tt, *J* = 6.7, 1.0 Hz, 2H), 2.36 (t, *J* = 0.9 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.38 – 1.22 (m, 4H), 1.06 (s, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.0, 167.0, 159.4, 139.2, 130.2, 129.4, 114.0, 72.8, 67.4, 55.4, 46.6, 42.8, 31.5, 30.9, 25.3, 23.2, 22.9, 14.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{21}H_{30}NaO_3$, 353.2087; found 353.2086. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl thiophene-2-carboxylate (**3bz-1**, major, **66**:34 inseparable mixture). Pale yellow oil. 86% yield (69 mg).



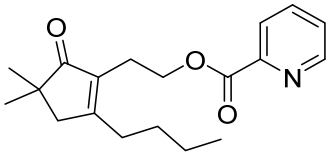
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.53 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.09 – 7.07 (m, 1H), 4.33 (t, *J* = 6.8 Hz, 2H), 2.64 (tt, *J* = 6.8, 1.1 Hz, 2H), 2.43 (ddt, *J* = 8.8, 6.6, 1.0 Hz, 2H), 2.38 (p, *J* = 1.0 Hz, 2H), 1.50 – 1.42 (m, 2H), 1.38 – 1.24 (m, 2H), 1.08 (s, 6H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.6, 173.3, 162.2, 133.8, 133.5, 133.2, 132.4, 127.8, 63.3, 46.5, 42.9, 30.9, 29.8, 25.3, 23.2, 22.9, 14.0. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{25}O_3S$, 321.1519; found 321.1518. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl thiophene-2-carboxylate (**3bz-2**, minor, 66:**34** inseparable mixture).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.11 – 7.09 (m, 1H), 4.49 (t, *J* = 6.5 Hz, 2H), 2.86 (tt, *J* = 6.4, 1.0 Hz, 2H), 2.46 (p, *J* = 1.1 Hz, 2H), 2.22 – 2.15 (m, 2H), 1.38 – 1.24 (m, 8H), 1.08 (s, 6H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.8, 164.8, 162.1, 140.2, 134.0, 133.3, 132.9, 128.0, 62.3, 46.3, 43.0, 30.9, 30.4, 25.3, 23.2, 22.9, 14.0. The regiochemistry of the product was determined by 2D-NMR analysis.

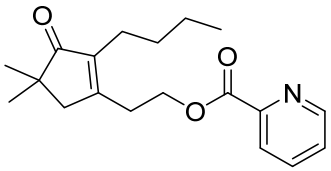
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl picolinate (**3ca-1**, major, **68**:32 inseparable mixture). Yellow oil. 76% yield (60 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 – 8.73 (m, 1H), 8.10 – 8.07 (m, 1H), 7.84 – 7.80 (m, 1H), 7.48 – 7.43 (m, 1H), 4.43 (t, *J* = 7.1 Hz, 2H), 2.71 (tt, *J* = 7.1, 1.2 Hz, 2H), 2.42 (ddt, *J* = 8.7, 6.5, 0.9 Hz, 2H), 2.37 (p, *J* = 1.1 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.34 – 1.22 (m, 2H), 1.07 (s, 6H), 0.86 (t, *J* = 7.3

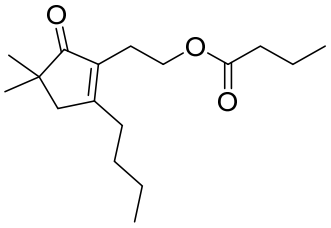
Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.6, 173.5, 165.1, 150.0, 148.2, 137.1, 133.1, 126.9, 125.3, 64.1, 46.5, 42.8, 30.9, 29.8, 25.3, 23.2, 22.9, 14.0. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{26}NO_3$, 316.1907; found 316.1908. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl picolinate (**3ca-2**, minor, 68:**32** inseparable mixture).



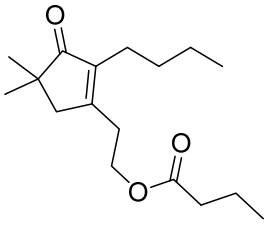
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 – 8.74 (m, 1H), 8.08 – 8.05 (m, 1H), 7.87 – 7.82 (m, 1H), 7.51 – 7.47 (m, 1H), 4.59 (t, *J* = 7.0 Hz, 2H), 2.93 (tt, *J* = 7.0, 1.0 Hz, 2H), 2.47 (p, *J* = 1.1 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.34 – 1.22 (m, 4H), 1.07 (s, 6H), 0.83 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.7, 165.1, 164.3, 150.1, 147.8, 140.3, 137.2, 127.2, 125.3, 63.0, 46.3, 43.0, 30.9, 30.5, 28.7, 25.2, 22.9, 14.0. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl butyrate (**3cb-1**, major, **62**:38 inseparable mixture). Colorless oil. 83% yield (59 mg).



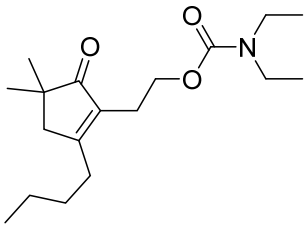
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (t, *J* = 7.0 Hz, 2H), 2.51 (tt, *J* = 7.0, 1.2 Hz, 2H), 2.44 – 2.40 (m, 2H), 2.38 (p, *J* = 1.1 Hz, 2H), 2.23 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.53 – 1.46 (m, 2H), 1.40 – 1.25 (m, 2H), 1.07 (s, 6H), 0.96 – 0.87 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.6, 173.7, 173.1, 133.4, 62.5, 46.5, 42.8, 36.3, 30.9, 29.8, 25.3, 23.1, 22.9, 18.5, 14.0, 13.8. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{17}H_{28}NaO_3$, 303.1931; found 303.1927. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl butyrate (**3cb-2**, minor, 62:**38** inseparable mixture).



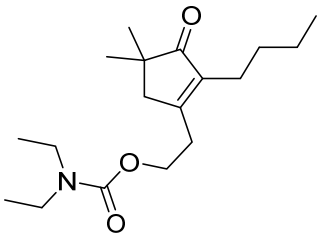
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (t, *J* = 6.6 Hz, 2H), 2.74 (tt, *J* = 6.6, 1.0 Hz, 2H), 2.39 (p, *J* = 1.2 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.66 – 1.57 (m, 2H), 1.40 – 1.25 (m, 4H), 1.07 (s, 6H), 0.96 – 0.87 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.7, 173.6, 165.0, 140.0, 61.4, 46.2, 42.9, 36.2, 30.9, 30.3, 25.3, 23.1, 22.8, 18.5, 14.1, 13.8. The regiochemistry of the product was determined by 2D-NMR analysis.

2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl diethylcarbamate (**3cc-1**, major, **59**:41 inseparable mixture). Colorless oil. 81% yield (63 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (t, *J* = 6.9 Hz, 2H), 3.36 – 3.11 (br, 4H), 2.53 (tt, *J* = 7.0, 1.3 Hz, 2H), 2.42 (t, *J* = 7.8 Hz, 2H), 2.37 (t, *J* = 1.1 Hz, 2H), 1.52 – 1.45 (m, 2H), 1.39 – 1.25 (m, 2H), 1.15 – 1.01 (m, 12H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.6, 172.9, 156.0, 133.7, 63.2, 46.5, 42.8, 41.3, 30.8, 29.8, 25.3, 23.5, 22.9, 14.1, 14.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{18}H_{31}NNaO_3$, 332.2196; found 332.2191. The regiochemistry of the product was determined by 2D-NMR analysis.

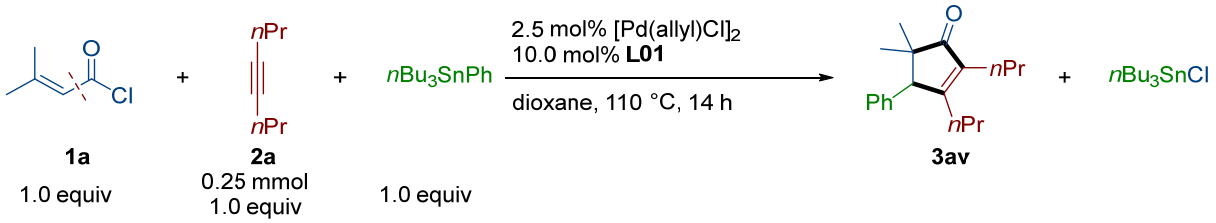
2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl diethylcarbamate (**3cc-2**, minor, 59:**41** inseparable mixture).



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.28 (t, *J* = 6.4 Hz, 2H), 3.36 – 3.11 (br, 4H), 2.79 – 2.71 (m, 2H), 2.41 (t, *J* = 1.1 Hz, 2H), 2.20 – 2.13 (m, 2H), 1.39 – 1.25 (m, 4H), 1.15 – 1.01 (m, 12H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.8, 165.8, 155.7, 139.8, 62.2, 46.0, 42.9, 41.8, 31.0, 30.8, 25.3, 23.1, 22.9, 14.1, 13.6. The regiochemistry of the product was determined by 2D-NMR analysis.

4. Synthesis of polysubstituted cyclopentenones using a carbon nucleophile

Eq. S13. General procedure.



1a 1.0 equiv

2a 0.25 mmol 1.0 equiv

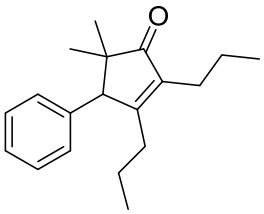
1.0 equiv

3av

General procedure

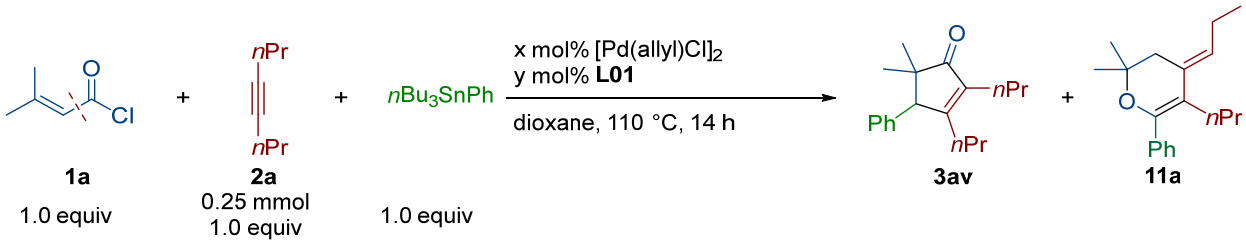
In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (2.5 mol%, 6.25 µmol, 2.29 mg or 1000 µL as 6.25 mM stock solution in dioxane) and **L01** (10.0 mol%, 25.00 µmol, 16.76 mg) and then dioxane (2 mL, or 1 mL when stock solutions were used). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added acid chloride (1.0 equiv, 0.25 mmol), alkyne (1.0 equiv, 0.25 mmol) and *n*Bu_3SnPh (1.0 equiv, 0.25 mmol). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then diluted with DCM (2 mL). The resulting solution was filtered through a celite/silica plug and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/DCM).

5,5-dimethyl-4-phenyl-2,3-dipropylcyclopent-2-en-1-one (**3av**). Colorless oil. 58% yield (39 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (td, *J* = 7.4, 1.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.19 – 6.71 (br, 2H), 3.67 (s, 1H), 2.50 (dddd, *J* = 13.7, 9.0, 7.2, 0.8 Hz, 1H), 2.34 – 2.22 (m, 2H), 2.11 – 2.03 (m, 1H), 1.56 – 1.45 (m, 3H), 1.37 (ddp, *J* = 13.4, 9.0, 7.4 Hz, 1H), 1.19 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.57 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.7, 171.2, 139.7, 139.6, 128.5, 127.0, 60.3, 47.7, 31.1, 28.2, 25.5, 22.2, 21.7, 20.7, 14.3, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{27}O$, 271.2056; found 271.2058. The regiochemistry of the product was determined by 2D-NMR analysis.

Eq. S14. Reaction optimization.



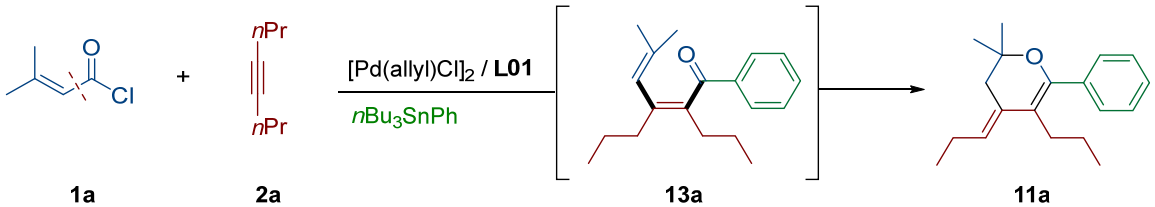
1a 1.0 equiv + **2a** 0.25 mmol 1.0 equiv + *n*Bu$_3$SnPh 1.0 equiv → **3av** + **11a**

Table S13. Reaction optimization

entry	[Pd(allyl)Cl]$_2$, **x** mol%	**L01** **y** mol%	P/Pd ratio	**3av**/**11a** ratio (by GC analysis of the crude mixture)
1	0.5	1.0	1.0	58 : 42
2	0.5	2.0	2.0	72 : 28
3[a]	2.5	10.0	2.0	93 : 7
4	2.5	12.5	2.5	95 : 5
5	2.5	15.0	3.0	96 : 4

[a]Standard condition.

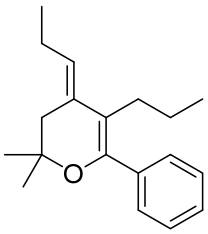
When the reaction conditions for the carbonylative carbocyclization using hydrosilane was applied to the reaction by using an aryl stannane reagent as a carbon nucleophile in place of the silane, non-negligible amount of an another carbonylated addition product (**11a**) with an alkyne was accompanied with the desired product (**3av**) (Table S13, entry 1). Next, when additional phosphine ligand was employed versus Pd, the competing formation of **11a** was dramatically suppressed. It was postulated that the initially formed carboacylated product (**13a**) further reacts to furnish **11a**, which was isolated as a single stereoisomer (Table S13, entry 1).[18]



1a + **2a** → **13a** → **11a**

carboacylation

(*E*)-2,2-dimethyl-6-phenyl-5-propyl-4-propylidene-3,4-dihydro-2H-pyran (**11a**). 18% yield (12 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 5.46 (tt, *J* = 7.3, 1.7 Hz, 1H), 2.41 – 2.38 (br, 2H), 2.18 – 2.11 (m, 4H), 1.51 – 1.43 (m, 2H), 1.32 (s, 6H), 1.02 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 137.9, 129.2, 129.0, 128.0, 127.8, 123.7, 111.5, 74.3, 36.8, 29.7, 26.5, 23.4, 21.1, 15.0, 14.4. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{27}O$, 271.2056; found 271.2056. The stereo-and regiochemistry of the product was determined by 2D-NMR analysis.

5. Additional control experiments

5.1. Control reaction using other acid chlorides

Eq. S15. Control reaction using 4-phenylbut-3-enoyl chloride instead of α,β-unsaturated acid chloride.

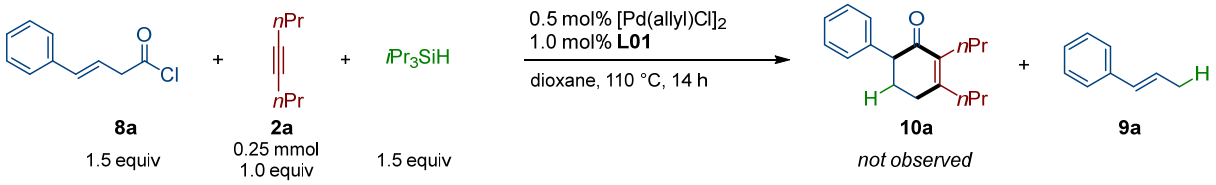
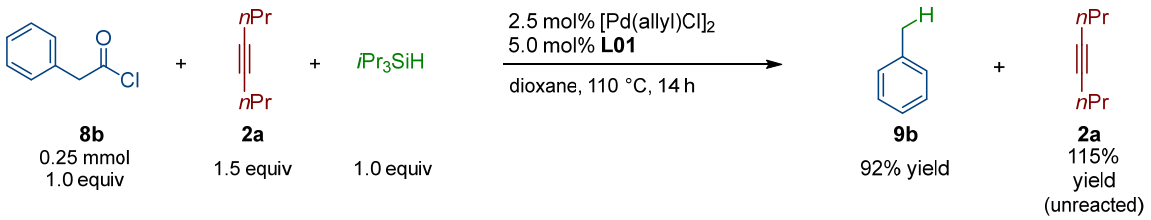


Table S14. Control reaction using 4-phenylbut-3-enoyl chloride instead of α,β-unsaturated acid chloride.

	Yield (%)[a]		
entry	**10a**	**9a**	**2a** (unreacted)
1	n.d.	148	91

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.).

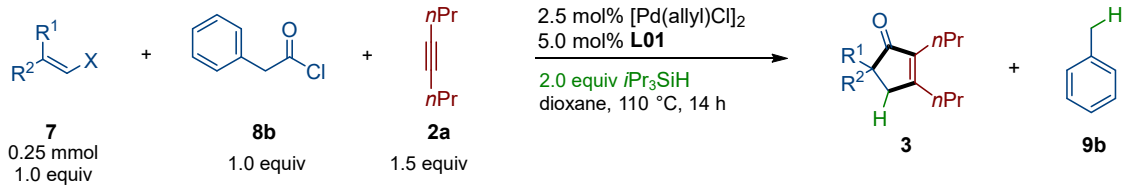
Eq. S16. Control reaction using phenylacetyl chloride instead of α,β-unsaturated acid chloride.

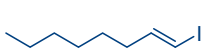


[a]The GC yields are based on the moles of a limiting reagent, phenylacetyl chloride (0.25 mmol, 1 equiv.).

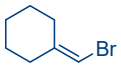
5.2. Divergent reaction using other alkenyl electrophiles

Table S15. Divergent reaction using other alkenyl electrophiles with CO surrogate.[a]





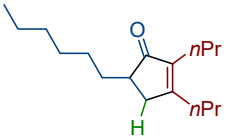
7a



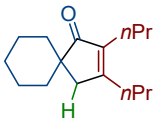
7b

7c

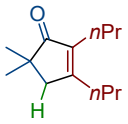
7d



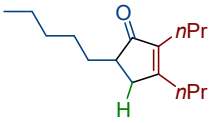
3as
39% yield



3at
34% yield[c]



3a
n.d.[c]



3au
n.d.[c]
13% yield[c,e]

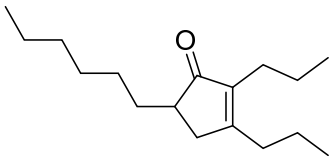
entry	alkenyl electrophiles (**7**)	products (**3**)	**3**, yield (%)[a]	**9b**, yield (%)[b]	iPr$_3$SiH (unreacted), yield (%)[b]	**2a** (unreacted), yield (%)[b]
1	**7a**	**3as**	39	84	0	30
2[c]	**7b**	**3at**	34	97	42	95
3	**7c**	**3a**	n.d.	93	79	130
4[c]	**7c**	**3a**	n.d.	98	71	130
5[d]	**7c**	**3a**	n.d.	95	-[f]	126
6[c]	**7d**	**3au**	n.d.	97	62	126
7[c,e]	**7d**	**3au**	13	98	57	104

[a]Isolated yields as a single regioisomer. [b]The GC yields are based on the moles of a limiting reagent, **7** (0.25 mmol, 1 equiv.). [c]130 °C. [d]150 °C in diglyme. [e]LiCl (2 equiv.) was added. [f]The GC retention time overlapped with the solvent.

General procedure

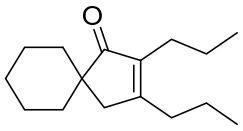
In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (2.5 mol%, 6.25 µmol, 2.29 mg or 1000 µL as 6.25 mM stock solution in dioxane) and **L01** (5.0 mol%, 12.50 µmol, 8.38 mg or 83.8 mg as 10.0wt% stock solution in dioxane) and then dioxane (1.8 mL). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added phenylacetyl chloride (1.0 equiv, 0.250 mmol), an alkenyl electrophile (1.0 equiv, 0.250 mmol), **2a** (1.5 equiv, 0.375 mmol) and *i*Pr_3SiH (2.0 equiv, 0.500 mmol, 79.18 mg). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then quenched with sodium methoxide (2.0 equiv, 0.500 mmol, 93 µL of 5.4M solution in MeOH) and diluted with DCM (2 mL). The resulting solution was filtered through a celite/silica plug and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/DCM, pentane/EA or pentane/MTBE).

5-hexyl-2,3-dipropylcyclopent-2-en-1-one (**3as**). Pale yellow oil. 39% yield (25 mg).



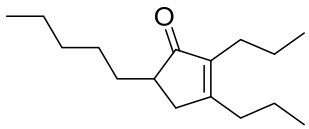
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.65 (dddd, *J* = 18.2, 5.6, 2.1, 1.1 Hz, 1H), 2.42 – 2.36 (m, 2H), 2.29 (dddd, *J* = 9.0, 6.6, 4.4, 2.5 Hz, 1H), 2.14 (dddd, *J* = 15.5, 6.6, 2.2, 1.1 Hz, 3H), 1.83 – 1.74 (m, 1H), 1.61 – 1.52 (m, 2H), 1.43 – 1.35 (m, 2H), 1.35 – 1.21 (m, 9H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.90 – 0.85 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.2, 172.3, 139.9, 45.2, 36.2, 33.2, 32.0, 31.9, 29.5, 27.4, 25.3, 22.8, 22.0, 21.0, 14.3, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{31}O$, 251.2369; found 251.2368. The regiochemistry of the product was determined by 2D-NMR analysis.

2,3-dipropylspiro[4.5]dec-2-en-1-one (**3at**). Colorless oil. 34% yield (20 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (ddt, *J* = 8.7, 7.1, 1.0 Hz, 2H), 2.35 (s, 2H), 2.13 (ddt, *J* = 8.8, 6.1, 1.2 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.69 – 1.63 (m, 1H), 1.61 – 1.52 (m, 4H), 1.44 – 1.23 (m, 5H), 1.23 – 1.17 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.2, 170.9, 138.3, 47.9, 42.6, 33.6, 33.0, 25.5, 25.2, 23.3, 22.0, 21.0, 14.2, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{27}O$, 235.2056; found 235.2058. The regiochemistry of the product was determined by 2D-NMR analysis.

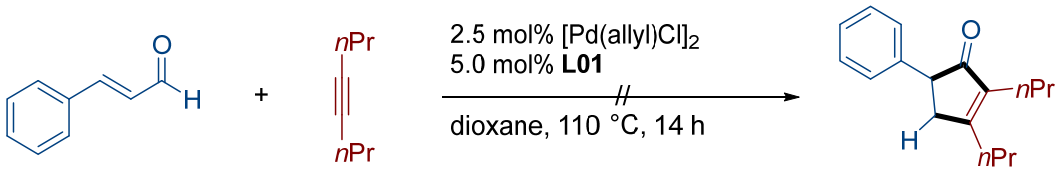
5-pentyl-2,3-dipropylcyclopent-2-en-1-one (**3au**). Colorless oil. 13% yield (8 mg).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (ddt, *J* = 18.3, 6.9, 1.2 Hz, 1H), 2.42 – 2.34 (m, 2H), 2.34 – 2.24 (m, 1H), 2.20 – 2.08 (m, 3H), 1.85 – 1.72 (m, 1H), 1.63 – 1.49 (m, 2H), 1.44 – 1.35 (m, 2H), 1.34 – 1.25 (m, 7H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.90 – 0.85 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.3, 172.4, 139.9, 45.2, 36.1, 33.2, 32.0, 31.9, 27.1, 25.2, 22.7, 22.0, 21.0, 14.3, 14.2, 14.2. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{29}O$, 237.2213; found 237.2211. The regiochemistry of the product was determined by 2D-NMR analysis.

5.3. Control reaction using *trans*-3-phenyl-2-propenal

Eq. S17. Control reaction using *trans*-3-phenyl-2-propenal instead of *trans*-3-phenylacryloyl chloride.



14a
1.5 equiv

2a
0.25 mmol
1 equiv

3j
not observed

Table S16. Control reaction using *trans*-3-phenyl-2-propenal instead of *trans*-3-phenylacryloyl chloride.

		Yield (%)[a]	
entry	**3j**	**14a** (unreacted)	**2a** (unreacted)
1	n.d.	149	84
2[b]	n.d.	142	77
3[c]	n.d.	139	92

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.). [b]*i*Pr$_3$SiH (1.5 equiv.) was added. [c]*i*Pr$_3$SiCl (1.5 equiv.) was added.

5.4. Reactions using chiral phosphine ligands

Eq. S18. Chiral ligand screening – β-aryl substituted enoyl chloride.

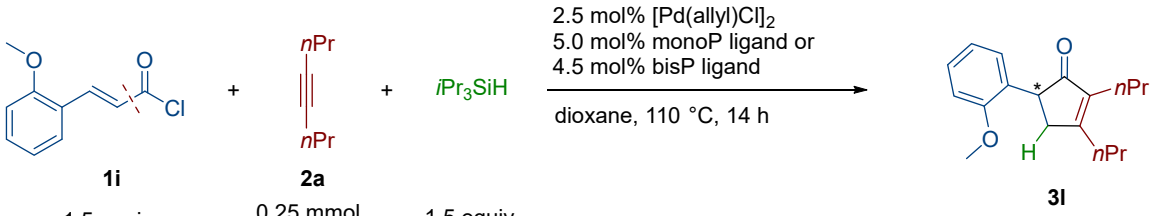
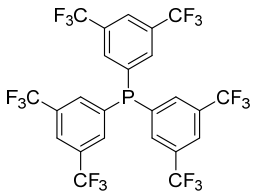
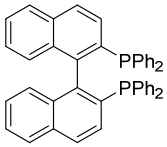


Table S17. Chiral ligand screening – β-aryl substituted enoyl chloride.[a]



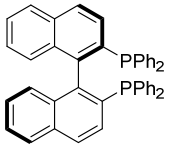
L01

3l: 94% yield (**Method A**)



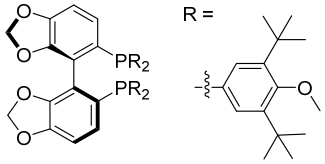
L80: rac-BINAP

3l: 39% yield
e.r. = 50:50



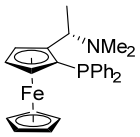
L88 (*R*)-BINAP

3l: 38% yield
e.r. = 49:51



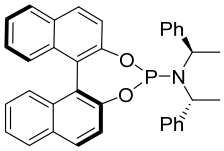
L82 (S)-DTBM-SEGPHOS

3l: 43% yield
e.r. = 50:50



L89, CAS Number 55650-58-3

3l: 36% yield
e.r. = 50:50



L90, CAS Number 415918-91-1 (DCM adduct)

3l: 66% yield
e.r. = 49:51

[a]Isolated yields as a single regioisomer. The e.r. was determined by GC using a chiral stationary phase.

Eq. S19. Chiral ligand screening – β-alkyl substituted enoyl chloride.

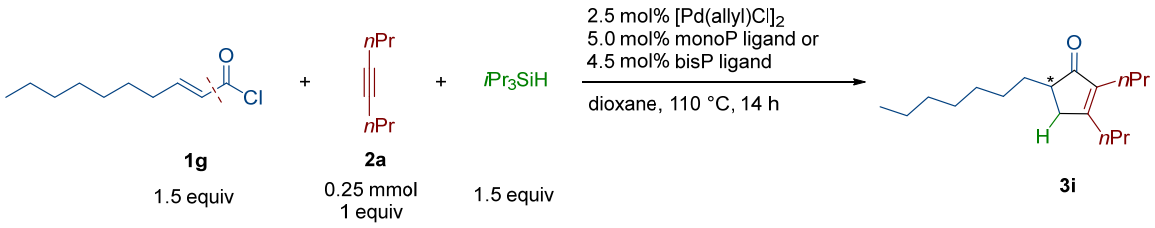
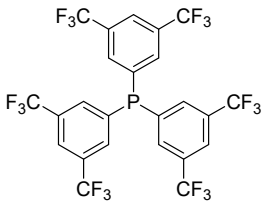
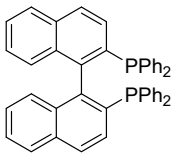


Table S18. Chiral ligand screening – β-alkyl substituted enoyl chloride.[a]



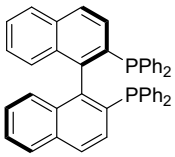
L01

3i: 85% yield (**Method A**)[b]
e.r. = 50:50



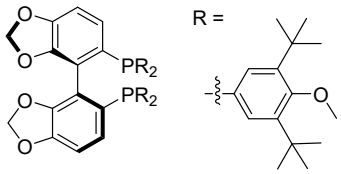
L80: rac-BINAP

3i: 31% yield
e.r. = 50:50



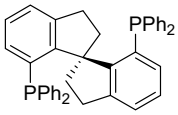
L88 (*R*)-BINAP

3i: 30% yield
e.r. = 50:50



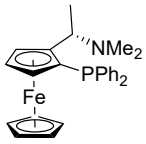
L82 (S)-DTBM-SEGPHOS

3i: 26% yield
e.r. = 50:50



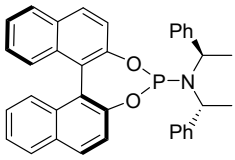
L91, (S)-SDP, CAS Number 528521-86-0

3i: 25% yield
e.r. = 50:50



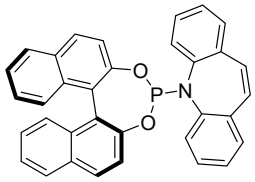
L89, CAS Number 55650-58-3

3i: 32% yield
e.r. = 51:49



L90, CAS Number 415918-91-1 (DCM adduct)

3i: 42% yield
e.r. = 48:52



L92, CAS Number 942939-38-0

3i: 44% yield
e.r. = 49:51

[a]The GC yields are based on the moles of a limiting reagent, **2a** (0.25 mmol, 1 equiv.). The e.r. was determined by GC using a chiral stationary phase. [b]Isolated yields as a single regioisomer.

Eq. S20. Chiral ligand screening – β-dialkyl substituted enoyl chloride.

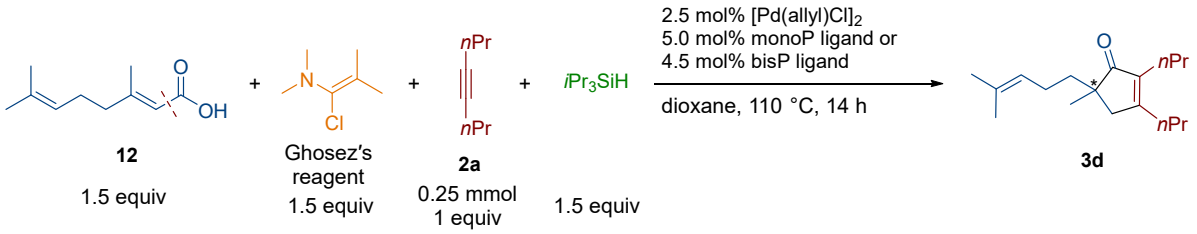
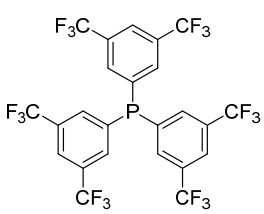
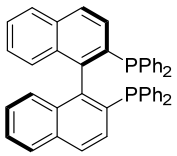


Table S19. Chiral ligand screening – β-dialkyl substituted enoyl chloride.[a]



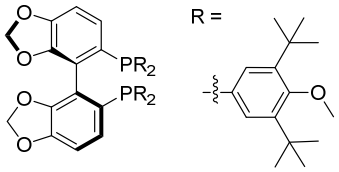
L01

3d: 70% yield (**Method C**)
e.r. = 50:50



L88 (*R*)-BINAP

3d: 10% yield
e.r. = 50:50



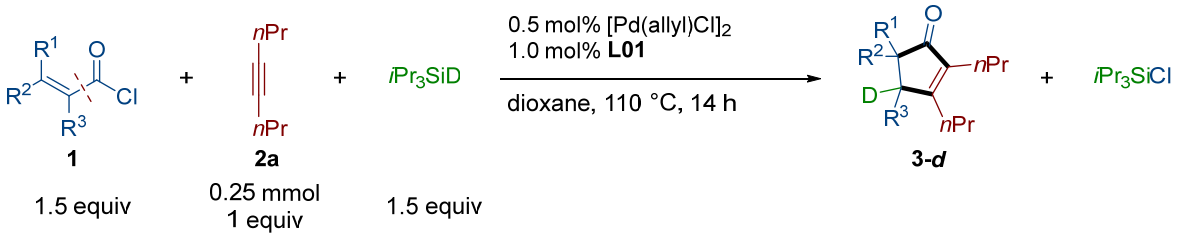
L82 (S)-DTBM-SEGPHOS

3d: traces

[a]Isolated yields as a single regioisomer. The e.r. was determined by GC using a chiral stationary phase.

6. D-isotope-labeling experiments and the proposed mechanism

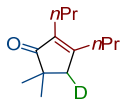
Eq. S21. Carbonylative carbocyclization reactions using D-labeled silanes.



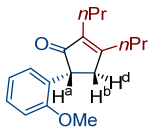
General procedure

In a glovebox, a 4 mL screw-cap vial equipped with a stirring bar was charged with $[Pd(allyl)Cl]_2$ (0.5 mol%, 1.25 µmol, 200 µL as 6.25 mM stock solution in dioxane) and **L01** (1.0 mol%, 2.50 µmol, 1.7 mg, or 16.8 mg as 10.0wt% stock solution in dioxane, and then dioxane (1.8 mL). The solution was stirred at room temperature for 10 min. To a pre-mixed solution were added acid chloride (1.5 equiv, 0.375 mmol), 4-octyne (**2a**, 1.0 equiv, 0.250 mmol) and iPr$_3$SiH (1.5 equiv, 0.375 mmol, 59.4 mg). The reaction mixture was stirred at 110 °C for 14 h. The reaction was cooled to room temperature then diluted with DCM (2 mL). The resulting solution was filtered through a celite/silica plug and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/DCM, pentane/EA or pentane/MTBE).

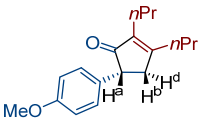
Table S20. Scope.[a]



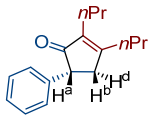
3a-*d*
91% yield, 94%[D]



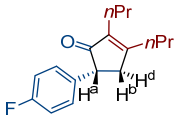
3l-*d*
93% yield, H^a = 6%[D], H^b = 44%[D], H^d = 45%[D]



3q-*d*
70% yield, H^a = 9%[D], H^b = 38%[D], H^d = 41%[D]



3j-*d*
78% yield, H^a = 4%[D], H^b = 34%[D], H^d = 34%[D]



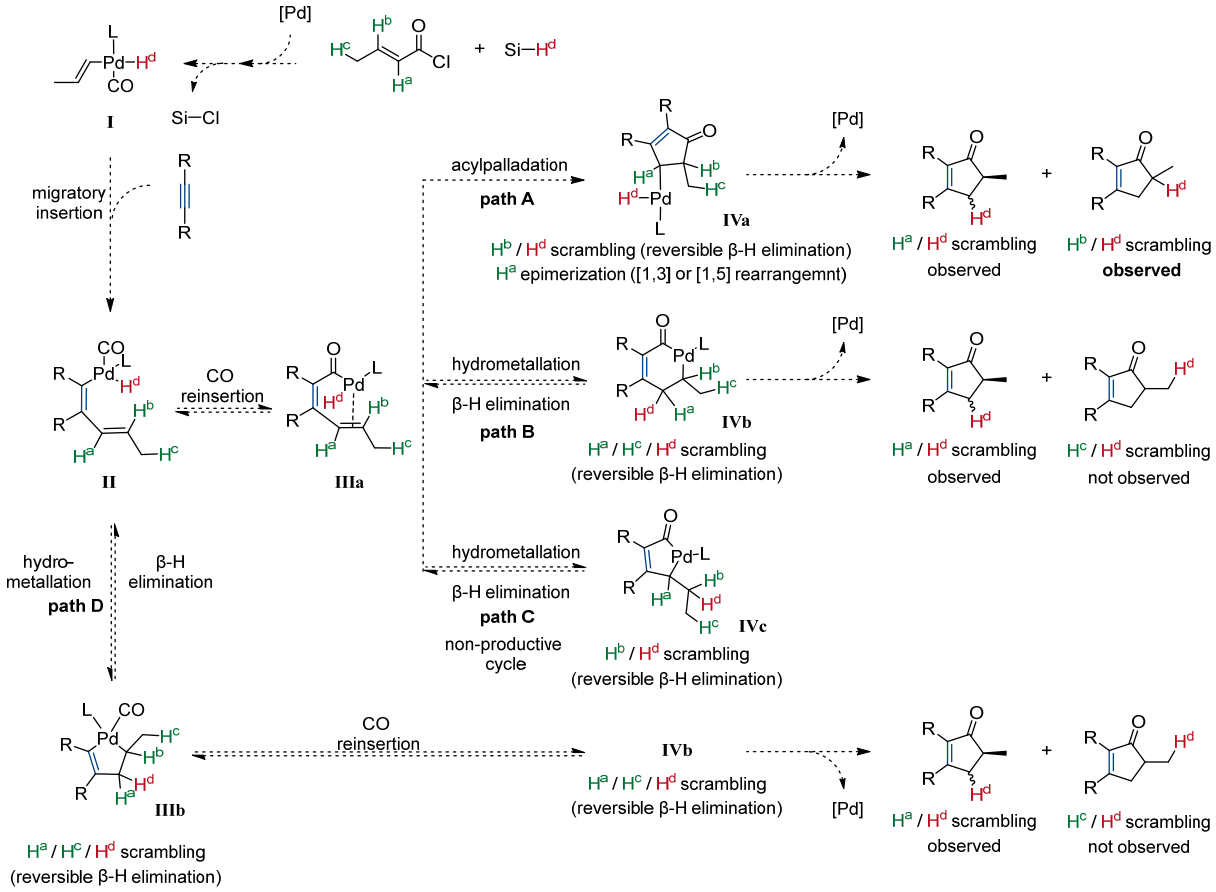
3u-*d*
83% yield, H^a = 6%[D], H^b = 39%[D], H^d = 42%[D]

[a]Isolated yields

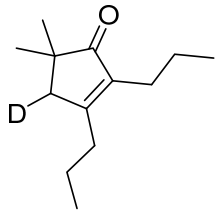
To elucidate some plausible mechanistic pathways, isotope labelling experiments were performed using a deuterium labeled silane under standard conditions. A set of α,β-unsaturated acid chlorides were tested (Table S17). While **3a-*d*** showed 94% of deuterium incorporation at the anticipated 4-position of the cyclopentenone, by contrast, other substrates which bear electronically and sterically differentiated mono aryl substituents resulted in a mixture of deuterium-scrambling products on the 4- and 5-position of the cyclopentenones. This result led us to consider four hypothetical pathways to figure out the origin of the deuterium scrambling (Figure S10). Because it is unclear, at which stage of the reaction, the transmetallation between the Pd–Cl and Si–H bonds occurs, it was assumed that the H/Cl exchange was occurred at the early stage of the elemental steps for the clarification of the illustration. The pathways for the intramolecular cyclization step from the intermediate **IIIa** can be divided by the acylpalladation (**path A**) and the hydropalladation path (**path B**). While the intramolecular acylpalladation of alkenes has been well-established in many tandem and cascade reactions, the dominance between acyl- and hydropalladation of alkenes from a plausible acyl–Pd–H species has been underexploited. The patterns of deuterium incorporation shown in **3l-*d***, **3q-*d***, **3j-*d***, and **3u-*d*** are consistent with the products accessed by **path A**. In addition, the deuteration at the 5-position does not seem viable through **path B**, **C**, and **D**. The formation of both **3aq-1** and **3aq-2** shown in the scope (Table 2) also can be accounted for by **path A**. Those acyl Mizoroki-Heck-type products are likely generated from the analogous **IVa** intermediate via β-H elimination. The other three paths involving hydropalladation from the comparable **IIIa** intermediate cannot afford either **3aq-1** of **3aq-2**. Although **path A** is likely the most plausible, there is not enough evidence to unambiguously differentiate between **path A** and other paths.

Recently, the reactivity priority between intermolecular hydrometallation and carbometallation of Aryl–Pd(II)–H toward activated olefin was studied by Engle and coworkers.[16] Interestingly, although analogous system involving a Pd catalyst, an electron poor monophosphine ligand, and a hydride source were employed, the tendency of carbometallation to prevail over hydrometallation was observed in our reaction system, contrary to the results obtained by Engle et al. Overall, the differences between the two systems might arise from either the carbopalladation of an aryl or acyl group, or the inter- or intramolecular process.

Figure S10. Plausible mechanistic pathways.



5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3a-*d***). 91% yield (45 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (ddd, *J* = 8.8, 6.4, 1.0 Hz, 2H), 2.35 – 2.30 (m, 1.06H), 2.13 (ddd, *J* = 8.9, 6.2, 1.1 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.44 – 1.36 (m, 2H), 1.07 (s, 6H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{2}H NMR** (77 MHz, $CDCl_3$) δ 2.34, 2.31. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{22}DO$, 196.1806; found 196.1808.

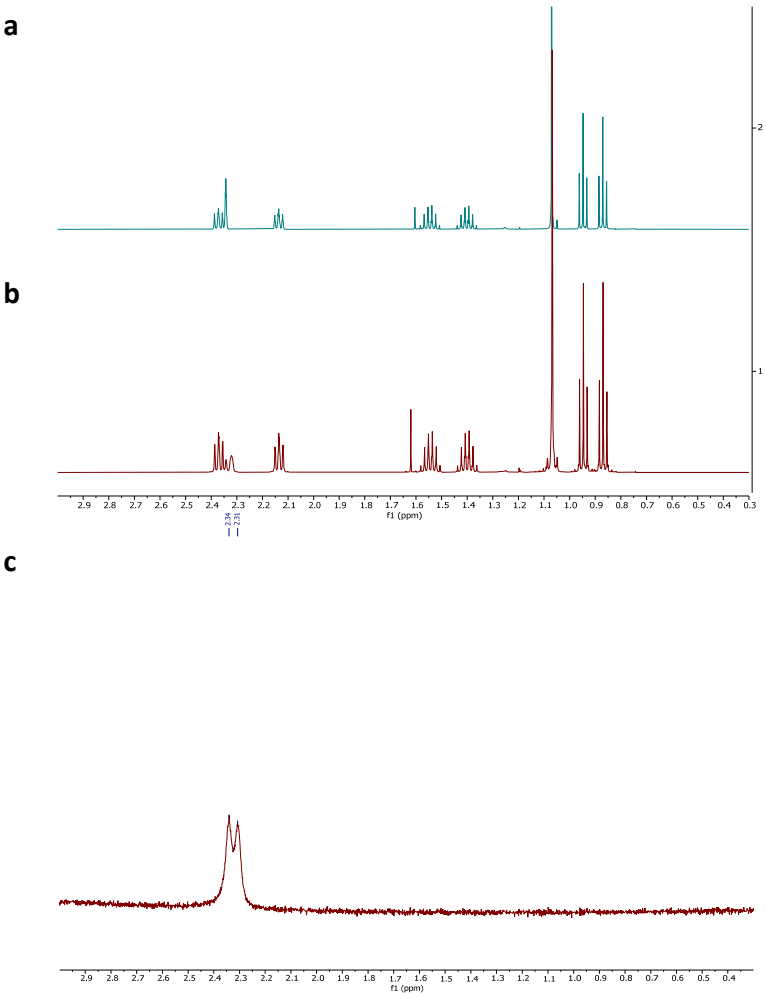
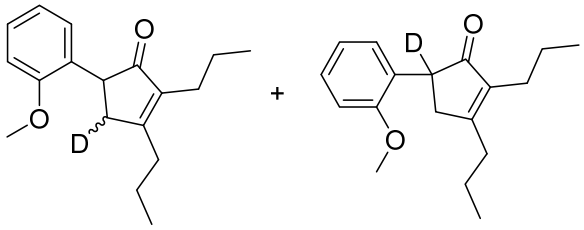


Figure S11. Comparison of ^{1}H NMR spectrum of the cyclocarbonylation product (**3a**) using unlabeled and D-labeled silanes. **a,** ^{1}H NMR spectrum of compound **3a**. **b,** ^{1}H NMR spectrum of compound **3a-*d***. **c,** ^{2}H NMR spectrum of compound **3a-*d***.

5-(2-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3l-*d***). 93% yield (63 mg).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (ddd, *J* = 8.2, 7.3, 1.8 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.89 (td, *J* = 7.4, 1.1 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.72 (s, 3H), 3.68 – 3.63 (m, 0.94H), 2.97 – 2.89 (m, 0.56H), 2.55 – 2.50 (m, 0.55H), 2.50 – 2.44 (m, 1H), 2.44 – 2.37 (m, 1H), 2.29 – 2.17 (m, 2H), 1.62 – 1.54 (m, 2H), 1.53 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{2}H NMR** (92 MHz, $CDCl_3$) δ 3.64, 2.93, 2.51. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{24}DO_2$, 274.1912; found 274.1913.

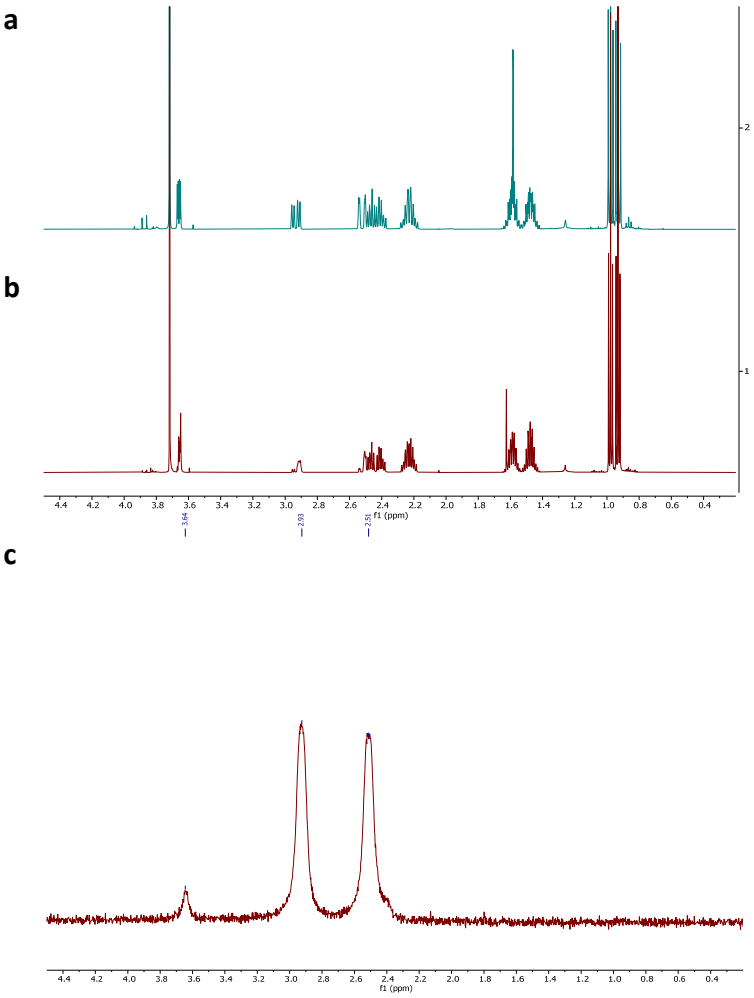
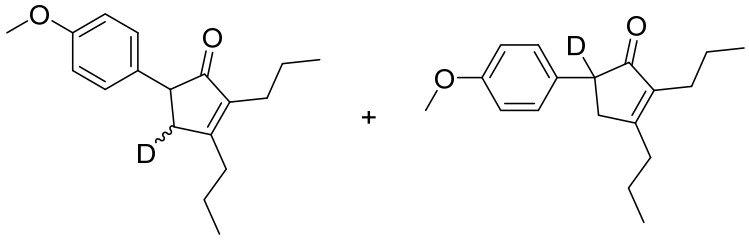


Figure S12. Comparison of ^{1}H NMR spectrum of the cyclocarbonylation product (**3l**) using unlabeled and D-labeled silanes. **a,** ^{1}H NMR spectrum of compound **3l**. **b,** ^{1}H NMR spectrum of compound **3l-*d***. **c,** ^{2}H NMR spectrum of compound **3l-*d***.

5-(4-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3q-*d***). 70% yield (48 mg).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 2H), 6.86 – 6.82 (m, 2H), 3.78 (s, 3H), 3.50 – 3.46 (m, 0.91H), 3.05 – 2.97 (m, 0.62H), 2.58 – 2.52 (m, 0.59H), 2.52 – 2.41 (m, 2H), 2.25 – 2.16 (m, 2H), 1.66 – 1.57 (m, 2H), 1.44 (h, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{2}H NMR** (92 MHz, $CDCl_3$) δ 3.48, 3.02, 2.55. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{24}DO_2$, 274.1912; found 274.1909.

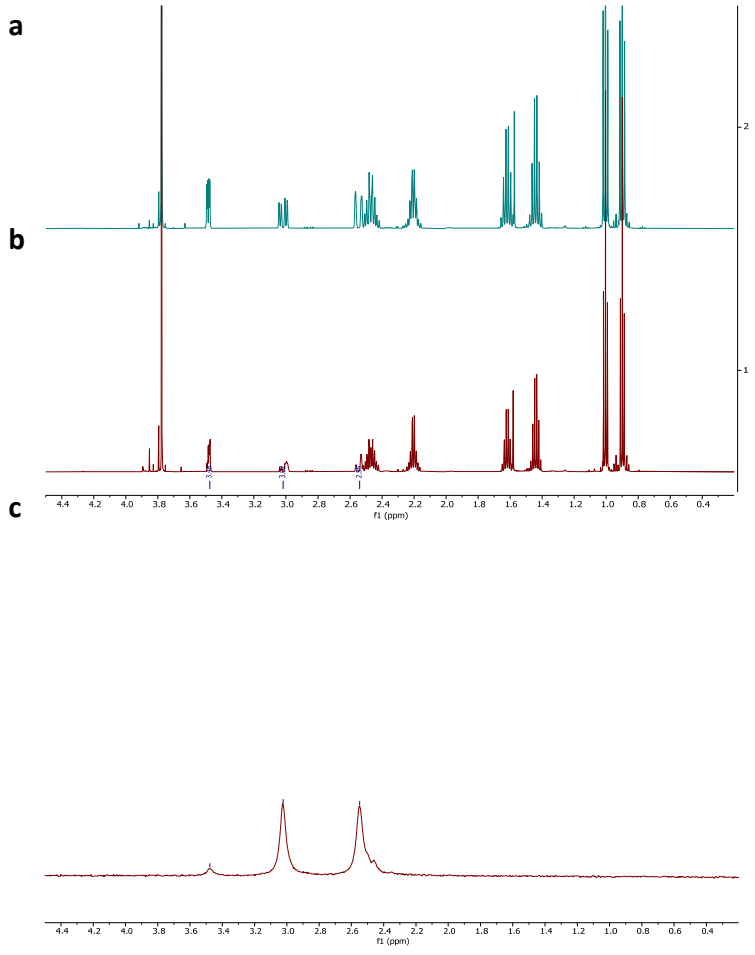
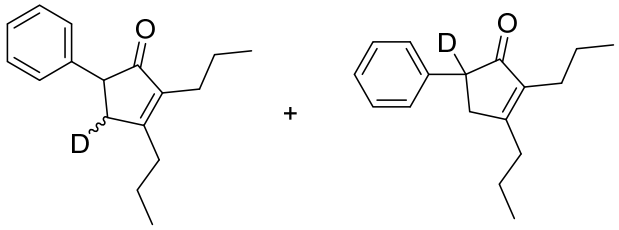


Figure S13. Comparison of ^{1}H NMR spectrum of the cyclocarbonylation product (**3q**) using unlabeled and D-labeled silanes. **a,** ^{1}H NMR spectrum of compound **3q**. **b,** ^{1}H NMR spectrum of compound **3q-*d***. **c,** ^{2}H NMR spectrum of compound **3q-*d***.

5-phenyl-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3j-*d***). 78% yield (47 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.13 – 7.09 (m, 2H), 3.56 – 3.51 (m, 0.96H), 3.08 – 2.99 (m, 0.66H), 2.63 – 2.56 (m, 0.66H), 2.55 – 2.42 (m, 2H), 2.27 – 2.16 (m, 2H), 1.63 (h, *J* = 7.3 Hz, 2H), 1.45 (h, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{2}H NMR** (77 MHz, $CDCl_3$) δ 3.52, 3.04, 2.60. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}DO$, 244.1806; found 244.1802.

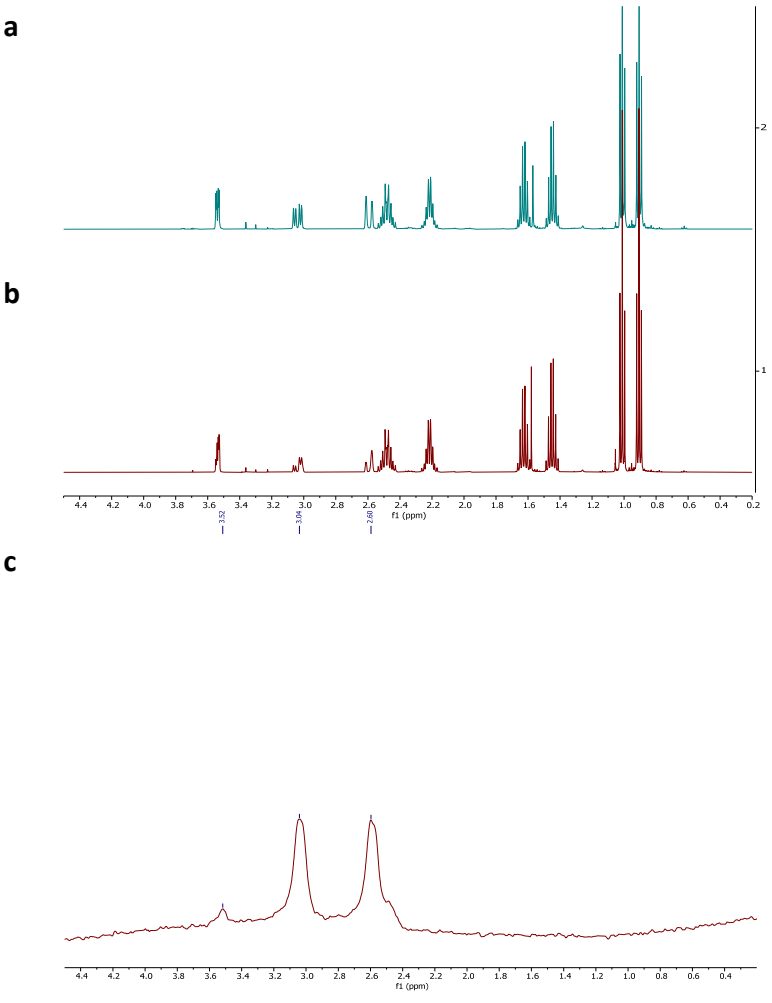
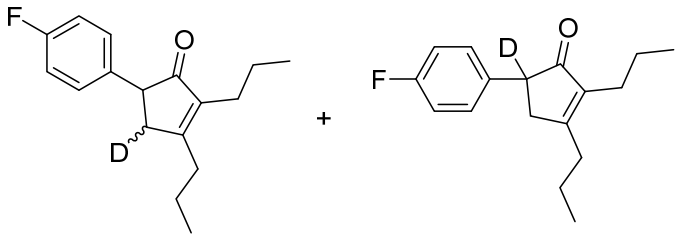


Figure S14. Comparison of ^{1}H NMR spectrum of the cyclocarbonylation product (**3j**) using unlabeled and D-labeled silanes. **a,** ^{1}H NMR spectrum of compound **3j**. **b,** ^{1}H NMR spectrum of compound **3j-*d***. **c,** ^{2}H NMR spectrum of compound **3j-*d***.

5-(4-fluorophenyl)-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3u-*d***). 83% yield (54 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.04 (m, 2H), 7.01 – 6.95 (m, 2H), 3.55 – 3.49 (m, 0.94H), 3.08 – 2.98 (m, 0.61H), 2.58 – 2.52 (m, 0.58H), 2.52 – 2.42 (m, 2H), 2.26 – 2.15 (m, 2H), 1.66 – 1.58 (m, 2H), 1.44 (h, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{2}H NMR** (77 MHz, $CDCl_3$) δ 3.49, 3.04, 2.55. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{21}DFO$, 262.1712; found 262.1710.

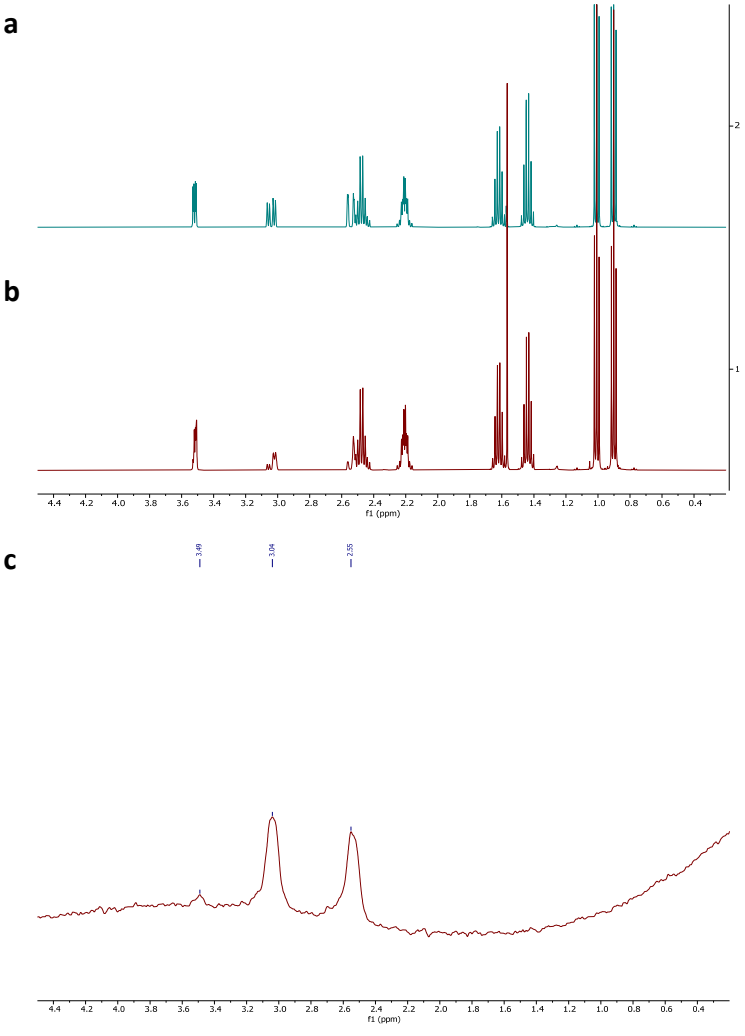
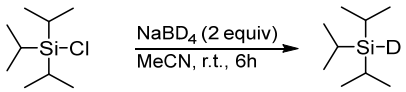


Figure S15. Comparison of ^{1}H NMR spectrum of the cyclocarbonylation product (**3u**) using unlabeled and D-labeled silanes. **a,** ^{1}H NMR spectrum of compound **3u**. **b,** ^{1}H NMR spectrum of compound **3u-*d***. **c,** ^{2}H NMR spectrum of compound **3u-*d***.

Synthesis of triisopropylsilane-*d* (*i*Pr$_3$SiD).

A deuterated triisopropyl silane was synthesized following the reported procedure.[17,18] ^{1}H and ^{13}C NMR data were consistent with the spectral data reported in literature.[17,18]

Eq. S22.

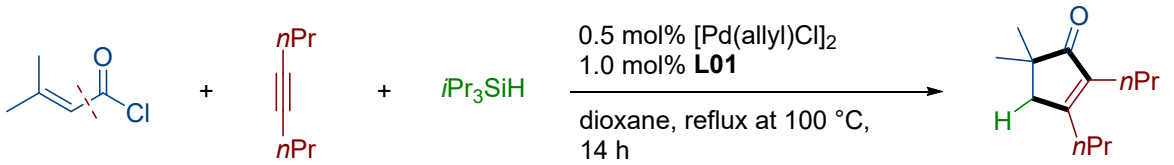


Triisopropylsilane-*d* (*i*Pr$_3$SiD). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 19.5, 10.3.

7. Large scale experiment

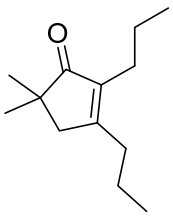
Eq. S23. Large scale experiment under open system.[19]



1a 1.3 equiv | **2a** 50 mmol, 1.0 equiv | iPr$_3$SiH 1.3 equiv | **3a** 73% yield (7.1 g)

In a glovebox, a 1 L-two neck flask equipped with a stirring bar was charged with [Pd(allyl)Cl]$_2$ (0.5 mol%, 0.25 mmol, 91.5 mg) and **L01** (1.0 mol%, 0.50 mmol, 335.2 mg). The flask was capped with a rubber septum, and was removed from the glovebox. To the flask was transferred dioxane (400 mL) using a cannula under N_2 atmosphere. The solution was stirred at room temperature for 20 min. To a pre-mixed solution were added 3,3-dimethylacryloyl chloride (**1a**, 1.3 equiv, 65 mmol, 7.24 mL), 4-octyne (**2a**, 1.0 equiv, 50 mmol, 7.34 mL) and iPr$_3$SiH (1.3 equiv, 65 mmol, 13.32 mL). The septum on top of the flask was pierced by a needle connected to an oil bubbler-attached manifolder under weak N_2 flow, for releasing the pressure. The reaction mixture was refluxed at 100 °C for 14 h under oil bath. The reaction was cooled to room temperature then quenched with sodium methoxide (1.3 equiv, 65 mmol, 12.04 mL of 5.4 M solution in MeOH) and diluted with DCM (200 mL). The resulting solution was filtered through a column packed with celite and silica (height 10 cm) and washed with DCM (100 mL) four times. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (pentane/EA = 70:1). Pale yellow oil. 73% yield (7.1 g).

5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one (LB-379-24). Pale yellow oil. **Method A**: 90% yield (44 mg). **73% yield (7.1 g, 50 mmol scale).**



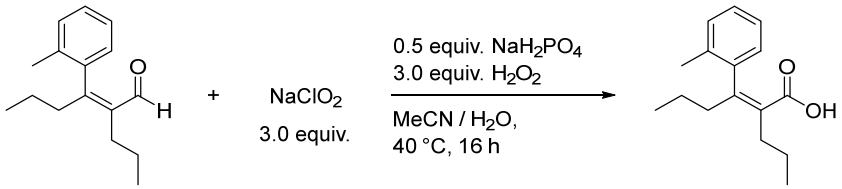
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (ddt, J = 7.7, 7.0, 0.9 Hz, 2H), 2.34 (p, J = 1.0 Hz, 2H), 2.14 (ddt, J = 8.8, 6.1, 1.2 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.45 – 1.36 (m, 2H), 1.07 (s, 6H), 0.95 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 214.2, 170.3, 137.8, 46.2, 42.7, 32.9, 25.4, 25.3, 22.0, 20.9, 14.2, 14.1. **HRMS** (ESI, m/z): $[M+H]^+$ calcd. for $C_{13}H_{23}O$, 195.1743; found 195.1745.

8. Synthesis of substrates

8.1. Synthesis of acid chloride substrates

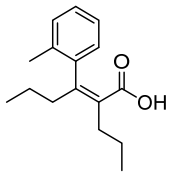
(*Z*)-2-propyl-3-(o-tolyl)hex-2-enal was synthesized following the reported procedures.[18]

Eq. S24. Oxidation of a tetrasubstituted α,β-unsaturated aldehyde.



(Z)-2-propyl-3-(o-tolyl)hex-2-enoic acid was synthesized in a similar manner according to the reported procedures.[20] To a 100 mL flask was added (Z)-2-propyl-3-(o-tolyl)hex-2-enal (1.84 g, 8.0 mmol), MeCN (30 mL), H_2O (20 mL), NaH_2PO_4 (0.5 equiv, 4.0 mmol, 0.48 g), H_2O_2 (3.0 equiv, 24.0 mmol, 2.06 mL, 2.33 g as 35wt% aqueous solution) and NaClO2 (3.0 equiv, 24.0 mmol, 2.71 g) sequentially. The reaction mixture was stirred at 40 °C for 16 h. The reaction was cooled to room temperature then quenched with 10wt% citric-acid aqueous solution (100 mL) and then extracted with EA (3 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (pentane/EA = 10:1). 76% yield (1.49 g).

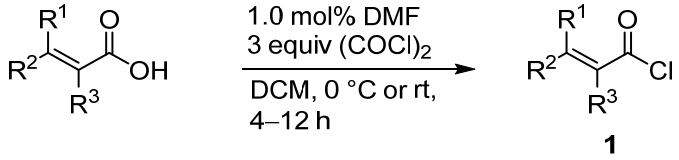
(*Z*)-2-propyl-3-(*o*-tolyl)hex-2-enoic acid (**12a**). Beige crystalline solid. 76% yield (1.49 g).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 6.91 – 6.87 (m, 1H), 2.52 – 2.40 (m, 3H), 2.22 – 2.14 (m, 4H), 1.60 – 1.44 (m, 2H), 1.44 – 1.22 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 149.4, 141.9, 134.9, 130.6, 129.9, 127.7, 127.0, 125.3, 37.1, 31.5, 22.5, 20.8, 19.6, 14.5, 14.1. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{16}H_{22}NaO_2$, 269.1512; found 269.1512.

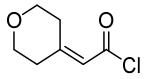
Acid chlorides were synthesized following the reported procedures[18,21] and used without further purification.

Eq. S25. Preparation of acid chlorides



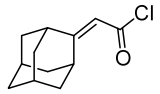
1

2-(tetrahydro-4*H*-pyran-4-ylidene)acetyl chloride (**1c**). Pale brown oil. Quantitative yield.



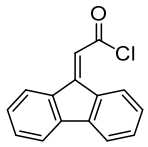
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 – 5.88 (m, 1H), 3.80 (td, *J* = 5.5, 1.9 Hz, 2H), 3.75 (td, *J* = 5.6, 1.9 Hz, 2H), 2.87 (td, *J* = 5.7, 1.2 Hz, 2H), 2.41 – 2.33 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0, 164.0, 120.9, 68.9, 68.3, 37.5, 32.2.

2-((1r,3r,5R,7S)-adamantan-2-ylidene)acetyl chloride (**1d**). Yellow solid. Quantitative yield.



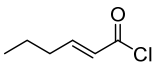
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 1H), 3.78 (s, 1H), 2.48 (s, 1H), 2.06 – 1.93 (m, 7H), 1.93 – 1.72 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.4, 163.9, 115.3, 41.6, 40.5, 39.6, 36.6, 34.5, 27.7.

2-(9*H*-fluoren-9-ylidene)acetyl chloride (**1e**). Orange colored solid. Quantitative yield.



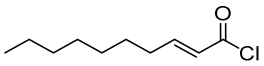
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.62 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.55 (tdd, *J* = 7.5, 1.2, 0.7 Hz, 2H), 7.42 (qd, *J* = 7.5, 1.1 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 6.89 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 152.1, 143.4, 141.7, 138.0, 134.3, 132.9, 132.4, 128.9, 128.8, 128.1, 122.3, 120.3, 120.2, 117.3.

(*E*)-hex-2-enoyl chloride (**1f**). Pale yellow oil. Quantitative yield.



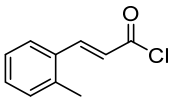
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dt, *J* = 15.3, 7.0 Hz, 1H), 6.06 (dt, *J* = 15.1, 1.6 Hz, 1H), 2.30 – 2.24 (m, 2H), 1.53 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 157.3, 126.5, 34.5, 21.1, 13.7.

(*E*)-dec-2-enoyl chloride (**1g**). Pale yellow oil. Quantitative yield.



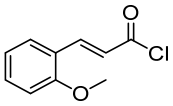
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dt, *J* = 15.3, 7.0 Hz, 1H), 6.06 (dt, *J* = 15.2, 1.6 Hz, 1H), 2.29 (qd, *J* = 7.2, 1.6 Hz, 2H), 1.57 – 1.42 (m, 2H), 1.42 – 1.20 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 157.6, 126.4, 32.6, 31.8, 29.2, 29.1, 27.8, 22.7, 14.2.

(*E*)-3-(o-tolyl)acryloyl chloride (**1h**). Pale yellow oil. Quantitative yield.



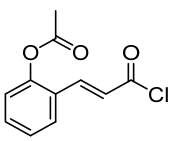
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 15.5, 0.8 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.26 (td, *J* = 7.5, 1.4 Hz, 1H), 7.15 (dddt, *J* = 7.2, 3.5, 2.2, 0.7 Hz, 2H), 6.46 (d, *J* = 15.5 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 148.2, 139.1, 131.9, 131.9, 131.3, 127.0, 126.7, 123.1, 19.8.

(*E*)-3-(2-methoxyphenyl)acryloyl chloride (**1i**). Yellow oil. Quantitative yield.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 6.99 (td, *J* = 7.6, 1.5 Hz, 1H), 6.95 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 159.2, 146.6, 133.6, 130.2, 122.5, 121.9, 121.0, 111.5, 55.6.

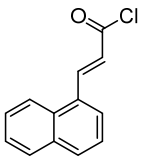
(*E*)-2-(3-chloro-3-oxoprop-1-en-1-yl)phenyl acetate (**1j**). White solid. Quantitative yield.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 15.7 Hz, 1H), 7.65 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.50 (ddd, *J* = 8.1, 7.4, 1.6 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.19 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.67 (d, *J* = 15.7 Hz, 1H),

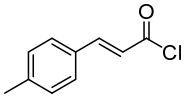
2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 166.2, 150.1, 143.9, 133.0, 128.3, 126.7, 125.8, 124.3, 123.6, 21.1.

(*E*)-3-(naphthalen-1-yl)acryloyl chloride (**1k**). Yellow solid. Quantitative yield.



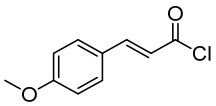
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 15.4 Hz, 1H), 8.16 (dq, *J* = 8.5, 1.1 Hz, 1H), 7.99 (dt, *J* = 8.2, 1.3 Hz, 1H), 7.91 (ddt, *J* = 8.1, 1.4, 0.7 Hz, 1H), 7.82 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.64 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.55 – 7.50 (m, 1H), 6.76 (d, *J* = 15.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 147.6, 133.9, 132.6, 131.7, 130.2, 129.1, 127.7, 126.8, 126.2, 125.6, 124.5, 123.0.

(*E*)-3-(*p*-tolyl)acryloyl chloride (**1l**). White solid. Quantitative yield.



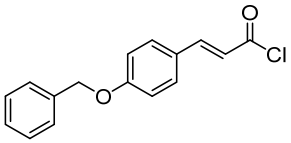
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.27 – 7.22 (m, 2H), 6.60 (d, *J* = 15.5 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.3, 151.0, 143.1, 130.5, 130.1, 129.3, 121.3, 21.8.

(*E*)-3-(4-methoxyphenyl)acryloyl chloride (**1m**). Pale yellow solid. Quantitative yield.



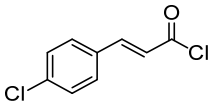
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 6.96 – 6.92 (m, 2H), 6.50 (d, *J* = 15.4 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 163.0, 150.7, 131.3, 125.9, 119.6, 114.9, 55.6.

(*E*)-3-(4-(benzyloxy)phenyl)acryloyl chloride (**1n**). Pale yellow solid. Quantitative yield.



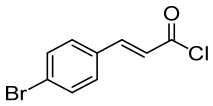
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.4 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.47 – 7.33 (m, 5H), 7.05 – 7.00 (m, 2H), 6.51 (dd, *J* = 15.4, 0.8 Hz, 1H), 5.13 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 162.1, 150.7, 136.2, 131.3, 128.8, 128.4, 127.6, 126.1, 119.7, 115.7, 70.3.

(*E*)-3-(4-chlorophenyl)acryloyl chloride (**1o**). White solid. Quantitative yield.



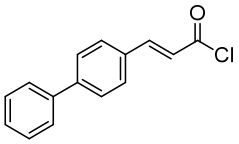
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 15.5, 0.5 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.44 – 7.39 (m, 2H), 6.62 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 149.2, 138.3, 131.6, 130.3, 129.7, 123.0.

(*E*)-3-(4-bromophenyl)acryloyl chloride (**1p**). White solid. Quantitative yield.



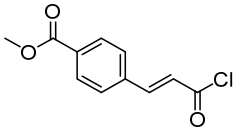
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.6 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.44 – 7.39 (m, 2H), 6.62 (d, *J* = 15.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 149.2, 132.6, 131.9, 130.4, 126.7, 123.0.

(*E*)-3-([1,1'-biphenyl]-4-yl)acryloyl chloride (**1q**). Beige solid. Quantitative yield.



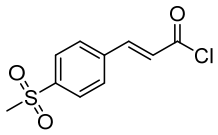
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.5 Hz, 1H), 7.71 – 7.61 (m, 6H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H), 6.69 (d, *J* = 15.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 150.4, 144.9, 139.8, 132.1, 129.8, 129.1, 128.4, 127.9, 127.2, 122.2.

methyl (*E*)-4-(3-chloro-3-oxoprop-1-en-1-yl)benzoate (**1r**). White solid. Quantitative yield.



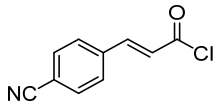
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.84 (dt, *J* = 15.6, 0.4 Hz, 1H), 7.65 – 7.62 (m, 2H), 6.72 (d, *J* = 15.6 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 166.1, 149.0, 137.1, 133.0, 130.5, 129.0, 124.7, 52.6.

(*E*)-3-(4-(methylsulfonyl)phenyl)acryloyl chloride (**1s**). Beige solid. Quantitative yield.



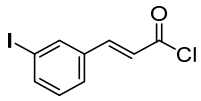
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.79 – 7.74 (m, 2H), 6.76 (d, *J* = 15.7 Hz, 1H), 3.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 147.6, 143.0, 138.1, 129.7, 128.4, 126.1, 44.5.

(*E*)-3-(4-cyanophenyl)acryloyl chloride (**1t**). Beige solid. Quantitative yield.



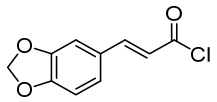
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.7 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.69 – 7.66 (m, 2H), 6.73 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.8, 147.7, 137.2, 133.0, 129.4, 125.8, 118.1, 115.0.

(*E*)-3-(3-iodophenyl)acryloyl chloride (**1u**). Brown oil. Quantitative yield.



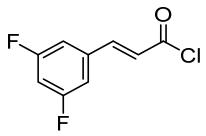
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (tt, *J* = 1.7, 0.5 Hz, 1H), 7.80 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.53 (dddd, *J* = 7.8, 1.7, 1.0, 0.5 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 148.8, 140.7, 137.7, 135.2, 130.9, 128.3, 123.7, 95.0.

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)acryloyl chloride (**1v**). Pale yellow solid. Quantitative yield.



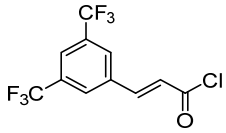
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dt, *J* = 15.4, 0.6 Hz, 1H), 7.08 (ddd, *J* = 8.1, 1.8, 0.6 Hz, 1H), 7.05 (dt, *J* = 1.8, 0.5 Hz, 1H), 6.85 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.45 (d, *J* = 15.4 Hz, 1H), 6.05 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 151.4, 150.6, 148.8, 127.6, 126.8, 120.1, 109.0, 107.0, 102.1.

(*E*)-3-(3,5-difluorophenyl)acryloyl chloride (**1w**). Beige solid. Quantitative yield.



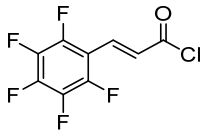
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 15.6 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.93 (tt, *J* = 8.5, 2.3 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.81, 163.42 (dd, *J* = 250.7, 12.6 Hz), 147.55 (t, *J* = 3.0 Hz), 136.19 (t, *J* = 9.5 Hz), 125.19, 111.89 – 111.62 (m), 107.16 (t, *J* = 25.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -108.0.

(*E*)-3-(3,5-bis(trifluoromethyl)phenyl)acryloyl chloride (**1x**). Yellow oil. Quantitative yield.



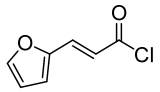
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.98 – 7.94 (m, 1H), 7.87 (dt, *J* = 15.7, 0.6 Hz, 1H), 6.80 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.65, 146.32, 135.21, 133.07 (q, *J* = 33.9 Hz), 128.62 (dq, *J* = 3.7, 1.2 Hz), 126.38, 124.98 (p, *J* = 3.8 Hz), 122.95 (q, *J* = 273.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.2, -63.2.

(*E*)-3-(perfluorophenyl)acryloyl chloride (**1y**). Yellow oil. Quantitative yield.



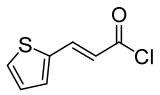
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.1 Hz, 1H), 6.97 (dd, *J* = 16.1, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.19, 147.87 – 144.59 (m), 144.59 – 141.43 (m), 139.67 – 136.52 (m), 133.37 (dt, *J* = 3.1, 1.7 Hz), 129.92 (td, *J* = 9.3, 2.8 Hz), 108.89 (td, *J* = 13.3, 4.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.58 – -137.72 (m), -147.59 (tt, *J* = 20.8, 4.3 Hz), -160.39 – -160.58 (m).

(*E*)-3-(furan-2-yl)acryloyl chloride (**1z**). Brown solid. Quantitative yield.



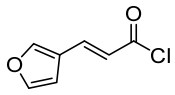
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 6.84 (dq, *J* = 3.5, 0.6 Hz, 1H), 6.57 – 6.54 (m, 1H), 6.49 (dq, *J* = 15.1, 0.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 149.9, 146.9, 136.1, 119.4, 119.3, 113.4.

(*E*)-3-(thiophen-2-yl)acryloyl chloride (**1aa**). Pale yellow solid. Quantitative yield.



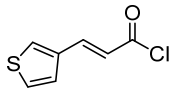
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 15.2, 0.8 Hz, 1H), 7.55 (dt, *J* = 5.0, 1.0 Hz, 1H), 7.42 (ddt, *J* = 3.7, 1.1, 0.5 Hz, 1H), 7.13 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.42 (d, *J* = 15.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 143.0, 138.2, 134.2, 131.7, 128.9, 120.6.

(*E*)-3-(furan-3-yl)acryloyl chloride (**1ab**). Grey solid. Quantitative yield.



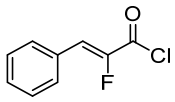
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (tp, *J* = 1.0, 0.5 Hz, 1H), 7.76 (dp, *J* = 15.3, 0.6 Hz, 1H), 7.49 (tq, *J* = 1.4, 0.7 Hz, 1H), 6.61 (ddq, *J* = 1.4, 0.9, 0.5 Hz, 1H), 6.36 (dt, *J* = 15.3, 0.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 147.1, 145.3, 141.1, 122.1, 122.0, 107.4.

(*E*)-3-(thiophen-3-yl)acryloyl chloride (**1ac**). Pale grey solid. Quantitative yield.



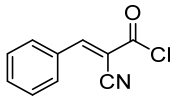
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dt, *J* = 15.3, 0.6 Hz, 1H), 7.69 (dd, *J* = 2.9, 1.5 Hz, 1H), 7.40 (ddd, *J* = 5.1, 2.9, 0.7 Hz, 1H), 7.32 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.46 (d, *J* = 15.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 144.0, 136.5, 131.9, 127.9, 125.3, 121.9.

(*Z*)-2-fluoro-3-phenylacryloyl chloride (**1ad**). Yellow oil. Quantitative yield.



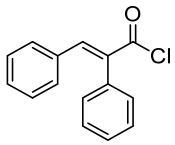
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.50 – 7.43 (m, 3H), 7.23 (d, *J* = 32.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.06 (d, *J* = 38.9 Hz), 147.93 (d, *J* = 268.3 Hz), 131.54 (d, *J* = 2.9 Hz), 131.36 (d, *J* = 8.5 Hz), 130.28 (d, *J* = 5.0 Hz), 129.30, 123.79 (d, *J* = 6.1 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.6.

(*E*)-2-cyano-3-phenylacryloyl chloride (**1ae**). Pale brown solid. Quantitative yield.



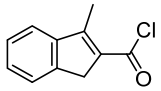
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.09 – 8.04 (m, 2H), 7.70 – 7.63 (m, 1H), 7.57 (tt, *J* = 7.6, 1.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.8, 158.9, 135.3, 132.3, 130.6, 129.8, 114.6, 107.8.

(*E*)-2,3-diphenylacryloyl chloride (**1af**). Grey solid. Quantitative yield.



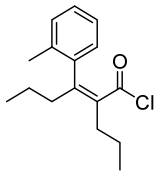
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.46 – 7.42 (m, 3H), 7.34 – 7.28 (m, 1H), 7.28 – 7.19 (m, 4H), 7.13 – 7.08 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 148.0, 136.2, 134.8, 133.5, 131.5, 130.8, 129.8, 129.2, 128.9, 128.6.

3-methyl-1*H*-indene-2-carbonyl chloride (**1ag**). Pale brown solid. Quantitative yield.



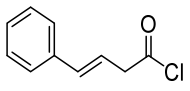
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.54 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.47 (td, *J* = 7.4, 1.5 Hz, 1H), 7.43 (td, *J* = 7.4, 1.6 Hz, 1H), 3.86 (q, *J* = 2.6 Hz, 2H), 2.59 (t, *J* = 2.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 159.0, 144.5, 144.5, 132.7, 129.9, 127.4, 124.4, 122.7, 41.1, 13.5.

(*Z*)-2-propyl-3-(*o*-tolyl)hex-2-enoyl chloride (**1ah**). Yellow oil. Quantitative yield.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 2H), 7.15 – 7.11 (m, 1H), 6.97 – 6.92 (m, 1H), 2.64 – 2.52 (m, 2H), 2.51 – 2.42 (m, 1H), 2.25 – 2.18 (m, 4H), 1.68 – 1.52 (m, 2H), 1.47 – 1.28 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.1, 148.4, 140.1, 136.8, 135.2, 130.2, 128.4, 127.8, 125.6, 36.5, 31.5, 22.1, 20.9, 19.6, 14.4, 13.9.

(*E*)-4-phenylbut-3-enoyl chloride (**8a**). Pale brown solid. Quantitative yield.

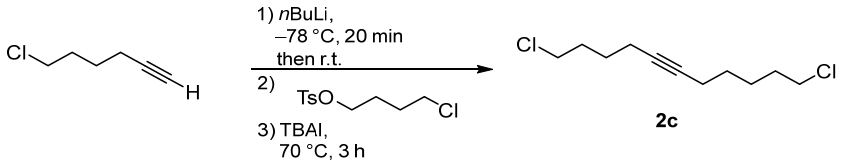


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 6.58 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.25 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.78 (dd, *J* = 7.1, 1.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.0, 136.1, 135.9, 128.8, 128.3, 126.6, 118.8, 50.3.

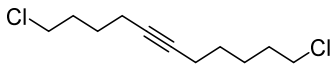
8.2. Synthesis of alkyne substrates

Alkynes were synthesized following the reported procedures[18,22] unless otherwise stated. ^{1}H and ^{13}C NMR data were consistent with the spectral data reported in literature.[18]

Eq. S26. Synthesis of 1,10-dichlorodec-5-yne (**2c**).

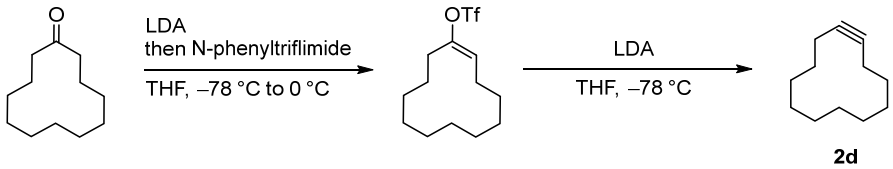


1,10-dichlorodec-5-yne (**2c**). Colorless oil.



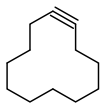
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (t, *J* = 6.60 Hz, 4H), 2.21–2.17 (tt, *J* = 6.99, 1.71 Hz, 4H), 1.92–1.85 (m, 4H), 1.67–1.60 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 80.1, 44.8, 31.7, 26.3, 18.2.

Eq. S27. Synthesis of cyclododecyne (**2d**).



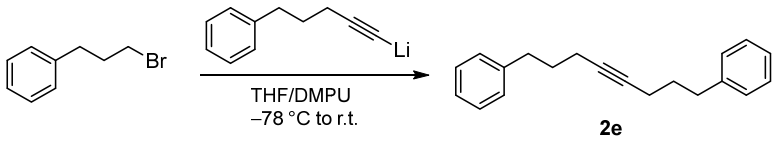
A cyclododecyne were synthesized following the reported procedures.[23]

Cyclododecyne (**2d**). Colorless oil.



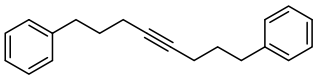
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 – 2.14 (m, 4H), 1.59 – 1.49 (m, 8H), 1.48 – 1.38 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 81.7, 25.8, 25.7, 25.0, 24.7, 18.6.

Eq. S28. Synthesis of 1,8-diphenyloct-4-yne (**2e**).



2e

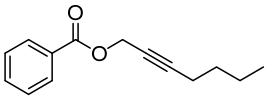
1,8-diphenyloct-4-yne (**2e**). Colorless oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.19 (m, 10H), 2.76 (t, *J* = 7.62 Hz, 4H), 2.24–2.20 (tt, *J* = 7.04, 1.80 Hz, 4H), 1.88–1.81 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 128.7, 128.5, 126.0, 80.5, 35.0, 30.9, 18.4.

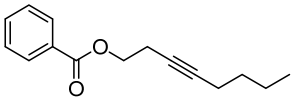
Eq. S29. Synthesis of alkynes bearing an ester group (**2f** to **2l**).

hept-2-yn-1-yl benzoate (**2f**). Colorless oil.



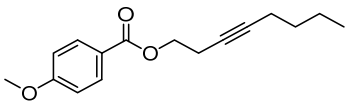
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.06 (m, 2H), 7.59–7.55 (m, 1H), 7.46–7.42 (m, 2H), 4.92 (t, *J* = 2.2 Hz, 2H), 2.27–2.22 (tt, *J* = 7.10, 2.22 Hz, 2H), 1.54–1.48 (m, 2H), 1.46–1.37 (m, 2H), 0.91 (t, *J* = 7.25, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 133.3, 130.0, 129.9, 128.5, 88.0, 74.1, 53.5, 30.6, 22.1, 18.6, 13.7. **HRMS** (ESI, m/z):$[M+Na]^+$ calcd. for $C_{14}H_{16}O_2Na$ 239.1043; found 239.1043.

oct-3-yn-1-yl benzoate (**2g**). Colorless oil.



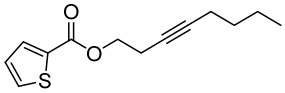
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.05 (m, 2H), 7.58–7.54 (m, 1H), 7.47–7.42 (m, 2H), 4.40–4.37 (t, *J* = 6.99 Hz, 2H), 2.65–2.60 (m, 2H), 2.18–2.13 (m, 2H), 1.49–1.34 (m, 4H), 0.90–0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 133.1, 130.3, 129.8, 128.5, 82.3, 75.6, 63.5, 31.1, 22.0, 19.5, 18.5, 13.7. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{15}H_{18}O_2Na$; 253.199, found 253.1197.

oct-3-yn-1-yl 4-methoxybenzoate (**2h**). Colorless oil.



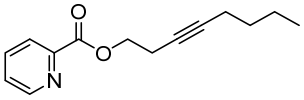
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 6.96 – 6.87 (m, 2H), 4.35 (t, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 2.61 (tt, *J* = 7.0, 2.4 Hz, 2H), 2.15 (tt, *J* = 6.9, 2.4 Hz, 2H), 1.51 – 1.32 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 163.5, 131.8, 122.7, 113.7, 82.2, 75.7, 63.2, 55.6, 31.1, 22.0, 19.6, 18.5, 13.7.

oct-3-yn-1-yl thiophene-2-carboxylate (**2i**).



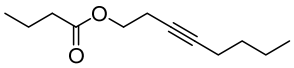
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.35 (t, *J* = 7.1 Hz, 2H), 2.60 (tt, *J* = 7.1, 2.4 Hz, 2H), 2.15 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.49 – 1.33 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 133.8, 133.7, 132.6, 127.9, 82.4, 75.4, 63.6, 31.1, 22.0, 19.5, 18.5, 13.7.

oct-3-yn-1-yl picolinate (**2j**). Yellow oil.



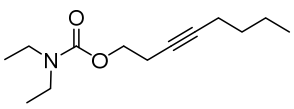
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.14 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.84 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 4.48 (t, *J* = 7.3 Hz, 2H), 2.68 (tt, *J* = 7.4, 2.4 Hz, 2H), 2.14 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.49 – 1.32 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 150.1, 148.1, 137.1, 127.1, 125.4, 82.6, 75.1, 64.3, 31.1, 22.0, 19.5, 18.5, 13.7.

oct-3-yn-1-yl butyrate (**2k**). Colorless oil.



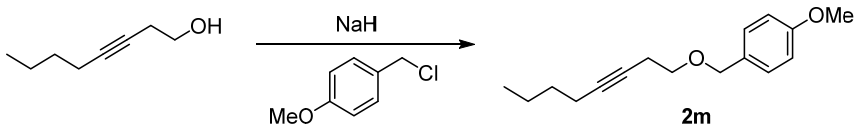
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (t, *J* = 6.97 Hz, 2H), 2.50–2.45 (m, 2H), 2.30 (t, *J* = 7.33 Hz, 2H), 2.16–2.11 (m, 2H), 1.70–1.61 (m, 2H), 1.49–1.34 (m, 4H), 0.95 (t, *J* = 7.41 Hz, 3H), 0.90 (t, *J* = 7.20 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 82.1, 75.7, 62.8, 36.3, 31.1, 22.0, 19.4, 18.6, 18.5, 13.8, 13.7. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{12}H_{20}O_2Na$ 219.1356; found 219.1356.

oct-3-yn-1-yl diethylcarbamate (**2l**). Pale yellow oil.

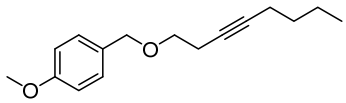


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15–4.11 (t, *J* = 6.82 Hz, 2H), 3.27 (br, 4H), 2.50–2.45 (m, 2H), 2.16–2.11 (m, 2H), 1.49–1.34 (m, 4H), 1.14–1.10 (t, *J* = 7.11 Hz, 6H), 0.91–0.88 (t, *J* = 7.14 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.8, 81.8, 76.2, 63.6, 42.0, 31.2, 22.0, 19.9, 18.5, 13.8, 13.8. **HRMS** (ESI, m/z): $[M+Na]^+$ calcd. for $C_{13}H_{23}O_2NNa$ 248.1621; found 248.1622.

Eq. S30. Synthesis of methoxy-4-((oct-3-yn-1-yloxy)methyl)benzene (**2m**)



methoxy-4-((oct-3-yn-1-yloxy)methyl)benzene (**2m**).

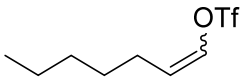


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 6.91–6.89 (m, 2H), 4.50 (s, 2H), 3.83 (s, 3H), 3.55 (t, *J* = 7.16 Hz, 2H), 2.50–2.45 (m, 2H), 2.19–2.15 (m, 2H) 1.52–1.39 (m, 4H), 0.92 (t, *J* = 7.19, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 130.5, 129.4, 113.9, 81.6, 76.8, 72.7, 68.8, 55.4, 31.2, 30.3, 22.1, 18.6, 13.8.

8.3. Synthesis of alkenyl triflates

A hept-1-en-1-yl trifluoromethanesulfonate was synthesized following the reported procedure.[24] ^{1}H and ^{13}C NMR data were consistent with the spectral data reported in literature.[24]

hept-1-en-1-yl trifluoromethanesulfonate (**7d**). Colorless oil (an inseparable mixture of *Z*/*E* isomers, *Z*/*E* = 84:16).

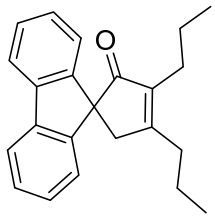


Z isomer, major: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.53 (dtd, *J* = 5.6, 1.6, 0.5 Hz, 1H), 5.26 (td, *J* = 7.6, 5.6 Hz, 1H), 2.19 (qd, *J* = 7.5, 1.6 Hz, 2H), 1.45 – 1.37 (m, 2H), 1.37 – 1.24 (m, 4H), 0.92 – 0.88 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.3, 121.1, 118.8 (q, *J* = 320.6 Hz), 31.3, 28.3, 24.2, 22.5, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.9.

E isomer, minor: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 – 6.48 (m, 1H), 5.77 (dt, *J* = 11.8, 7.7 Hz, 1H), 2.04 (qd, *J* = 7.5, 1.5 Hz, 2H), 1.46 – 1.24 (m, 6H), 0.92 – 0.85 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.0, 123.1, 31.2, 28.5, 26.7, 22.5, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.4.

9. X-ray structure analysis

3,4-dipropylspiro[cyclopentane-1,9'-fluoren]-3-en-2-one (**3e**).



Experimental

Single crystals of $C_{23}H_{24}O$ (compound **3e**, [bm010720_1_1]). A suitable crystal was selected on a Bruker/Nonius Kappa Apex2 diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2,[25] the structure was solved with the SHELXT[26] structure solution program using Intrinsic Phasing and refined with the SHELXL[27] refinement package using Least Squares minimisation.

Crystal structure determination of 3e

Crystal Data for $C_{23}H_{24}O$ (M =316.42 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.6463(12) Å, b = 11.9141(12) Å, c = 12.9699(14) Å, V = 1799.6(3) Å^3, Z = 4, T = 100.0(1) K, μ(MoKα) = 0.069 mm^{-1}, *Dcalc* = 1.168 g/cm^3, 33464 reflections measured (4.642° ≤ 2Θ ≤ 56.652°), 4473 unique (R_{int} = 0.0544, R_{sigma} = 0.0399) which were used in all calculations. The final R_1 was 0.0394 (I > 2σ(I)) and wR_2 was 0.0902 (all data).

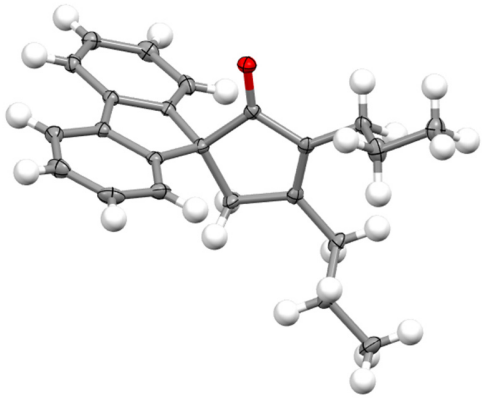
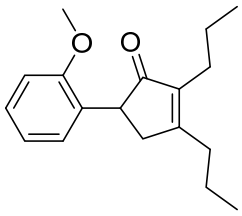


Figure S16. X-ray structure of compound **3e**. Thermal ellipsoids are drawn at the 50% probability level.

Table S21. Crystal data and structure refinement for **3e** (bm010720_1_1, 389-08).

Identification code	bm010720_1_1
Empirical formula	$C_{23}H_{24}O$
Formula weight	316.42
Temperature/K	100.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.6463(12)
b/Å	11.9141(12)
c/Å	12.9699(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1799.6(3)
Z	4
ρ_{calc}g/cm^3	1.168
μ/mm^{-1}	0.069
F(000)	680.0
Crystal size/mm^3	0.16 × 0.12 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.642 to 56.652
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 17
Reflections collected	33464
Independent reflections	4473 [R_{int} = 0.0544, R_{sigma} = 0.0399]
Data/restraints/parameters	4473/0/219
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0843
Final R indexes [all data]	R_1 = 0.0511, wR_2 = 0.0902
Largest diff. peak/hole / e Å^{-3}	0.21/-0.19
Flack parameter	-0.3(7)

5-(2-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one (**3l**).



Experimental

Single crystals of $C_{18}H_{24}O_2$ (compound **3l**, [bm131020_1_1]). A suitable crystal was selected on a XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2,[25] the structure was solved with the SHELXT[26] structure solution program using Intrinsic Phasing and refined with the SHELXL[27] refinement package using Least Squares minimisation.

Crystal structure determination of 3l

Crystal Data for $C_{18}H_{24}O_2$ (*M* =272.37 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 5.28116(5) Å, *b* = 21.9803(2) Å, *c* = 13.24729(16) Å, *β* = 100.3949(10)°, *V* = 1512.52(3) Å^3, *Z* = 4, *T* = 100.0(1) K, μ(Cu Kα) = 0.593 mm^{-1}, *Dcalc* = 1.196 g/cm^3, 40291 reflections measured (7.888° ≤ 2Θ ≤ 160.11°), 3258 unique (R_{int} = 0.0416, R_{sigma} = 0.0176) which were used in all calculations. The final R_1 was 0.0376 (I > 2σ(I)) and wR_2 was 0.1026 (all data).

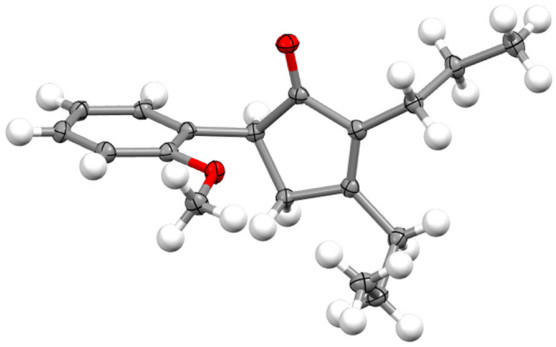
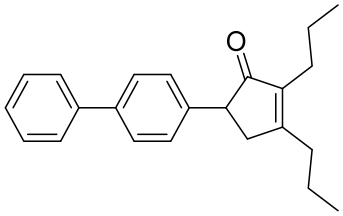


Figure S17. X-ray structure of compound **3l**. Thermal ellipsoids are drawn at the 50% probability level.

Table S22. Crystal data and structure refinement for **3l** (bm131020_1_1).

Identification code	bm131020_1_1
Empirical formula	$C_{18}H_{24}O_2$
Formula weight	272.37
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.28116(5)
b/Å	21.9803(2)
c/Å	13.24729(16)
α/°	90
β/°	100.3949(10)
γ/°	90
Volume/Å^3	1512.52(3)
Z	4
ρ_{calc}g/cm^3	1.196
μ/mm^{-1}	0.593
F(000)	592.0
Crystal size/mm^3	0.283 × 0.129 × 0.017
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.888 to 160.11
Index ranges	-6 ≤ h ≤ 6, -27 ≤ k ≤ 27, -14 ≤ l ≤ 16
Reflections collected	40291
Independent reflections	3258 [R_{int} = 0.0416, R_{sigma} = 0.0176]
Data/restraints/parameters	3258/0/184
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0996
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1026
Largest diff. peak/hole / e Å^{-3}	0.28/-0.23

5-([1,1'-biphenyl]-4-yl)-2,3-dipropylcyclopent-2-en-1-one (**3v**).



Experimental

Single crystals of $C_{23}H_{26}O$ (compound **3v**, [bm121020_1_2]). A suitable crystal was selected on a XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2,[25] the structure was solved with the SHELXT[26] structure solution program using Intrinsic Phasing and refined with the SHELXL[27] refinement package using Least Squares minimisation.

Crystal structure determination of 3v

Crystal Data for $C_{23}H_{26}O$ (*M* =318.44 g/mol): monoclinic, space group C2/c (no. 15), *a* = 40.4087(8) Å, *b* = 5.73700(10) Å, *c* = 19.0339(4) Å, *β* = 125.118(3)°, *V* = 3609.31(16) Å^3, *Z* = 8, *T* = 100.0(1) K, μ(Cu Kα) = 0.529 mm^{-1}, *Dcalc* = 1.172 g/cm^3, 22908 reflections measured (5.348° ≤ 2Θ ≤ 160.03°), 3846 unique (R_{int} = 0.0290, R_{sigma} = 0.0185) which were used in all calculations. The final R_1 was 0.0458 (I > 2σ(I)) and wR_2 was 0.1234 (all data).

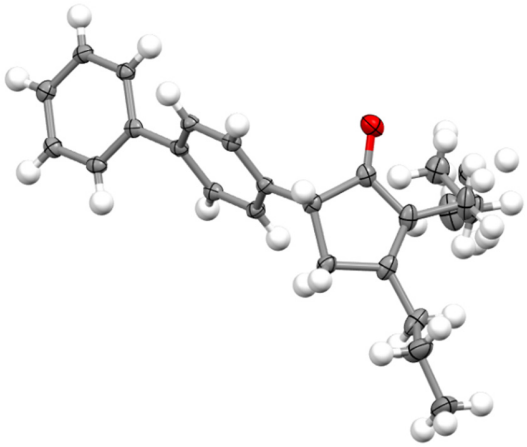
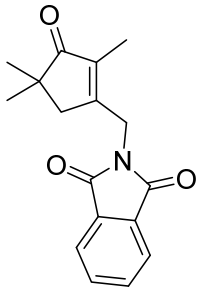


Figure S18. X-ray structure of compound **3v**. Thermal ellipsoids are drawn at the 50% probability level.

Table S23. Crystal data and structure refinement for **3v** (bm121020_1_2).

Identification code	bm121020_1_2
Empirical formula	$C_{23}H_{26}O$
Formula weight	318.44
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	C2/c
a/Å	40.4087(8)
b/Å	5.73700(10)
c/Å	19.0339(4)
α/°	90
β/°	125.118(3)
γ/°	90
Volume/Å^3	3609.31(16)
Z	8
ρ_{calc}g/cm^3	1.172
μ/mm^{-1}	0.529
F(000)	1376.0
Crystal size/mm^3	0.3 × 0.269 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.348 to 160.03
Index ranges	-46 ≤ h ≤ 51, -6 ≤ k ≤ 7, -24 ≤ l ≤ 21
Reflections collected	22908
Independent reflections	3846 [R_{int} = 0.0290, R_{sigma} = 0.0185]
Data/restraints/parameters	3846/30/239
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1212
Final R indexes [all data]	R_1 = 0.0486, wR_2 = 0.1234
Largest diff. peak/hole / e Å^{-3}	0.49/-0.39

2-((2,4,4-trimethyl-3-oxocyclopent-1-en-1-yl)methyl)isoindoline-1,3-dione (**3bu-1**).



Experimental

Single crystals of $C_{17}H_{17}NO_3$ (compound **3bu-1**, [bm240620_1_1]). A suitable crystal was selected on a Bruker/Nonius Kappa Apex2 diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2,[25] the structure was solved with the SHELXT[26] structure solution program using Intrinsic Phasing and refined with the SHELXL[27] refinement package using Least Squares minimisation.

Crystal structure determination of 3bu-1

Crystal Data for $C_{17}H_{17}NO_3$ (*M* =283.31 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 11.8424(6) Å, *b* = 10.6222(6) Å, *c* = 11.5154(6) Å, *β* = 95.133(2)°, *V* = 1442.74(13) Å^3, *Z* = 4, *T* = 100.0(1) K, μ(MoKα) = 0.090 mm^{-1}, *Dcalc* = 1.304 g/cm^3, 10645 reflections measured (3.454° ≤ 2Θ ≤ 56.562°), 3525 unique (R_{int} = 0.0277, R_{sigma} = 0.0377) which were used in all calculations. The final R_1 was 0.0433 (I > 2σ(I)) and wR_2 was 0.1124 (all data).

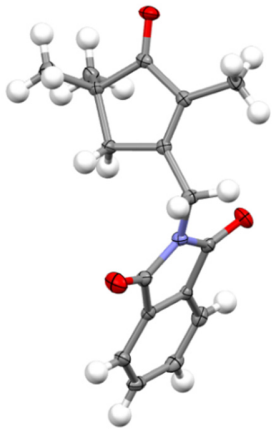


Figure S19. X-ray structure of compound **3bu-1**. Thermal ellipsoids are drawn at the 50% probability level.

Table S24. Crystal data and structure refinement for **3bu-1** (bm240620_1_1, 384-13-A).

Identification code	bm240620_1_1
Empirical formula	$C_{17}H_{17}NO_3$
Formula weight	283.31
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.8424(6)
b/Å	10.6222(6)
c/Å	11.5154(6)
α/°	90
β/°	95.133(2)
γ/°	90
Volume/Å^3	1442.74(13)
Z	4
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	0.090
F(000)	600.0
Crystal size/mm^3	0.24 × 0.16 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.454 to 56.562
Index ranges	-15 ≤ h ≤ 15, -13 ≤ k ≤ 14, -15 ≤ l ≤ 10
Reflections collected	10645
Independent reflections	3525 [R_{int} = 0.0277, R_{sigma} = 0.0377]
Data/restraints/parameters	3525/0/193
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1015
Final R indexes [all data]	R_1 = 0.0644, wR_2 = 0.1124
Largest diff. peak/hole / e Å^{-3}	0.33/-0.27

10. References

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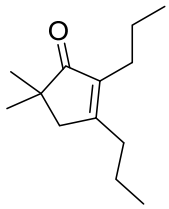
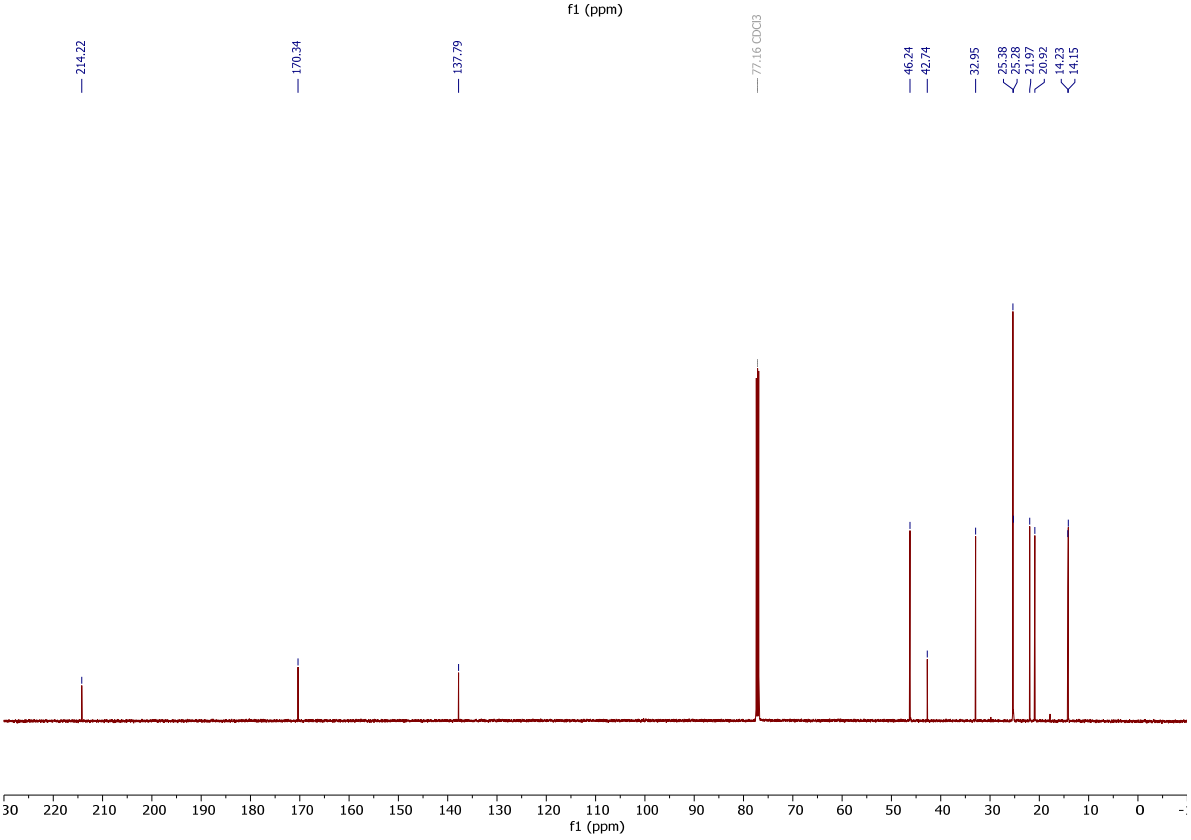
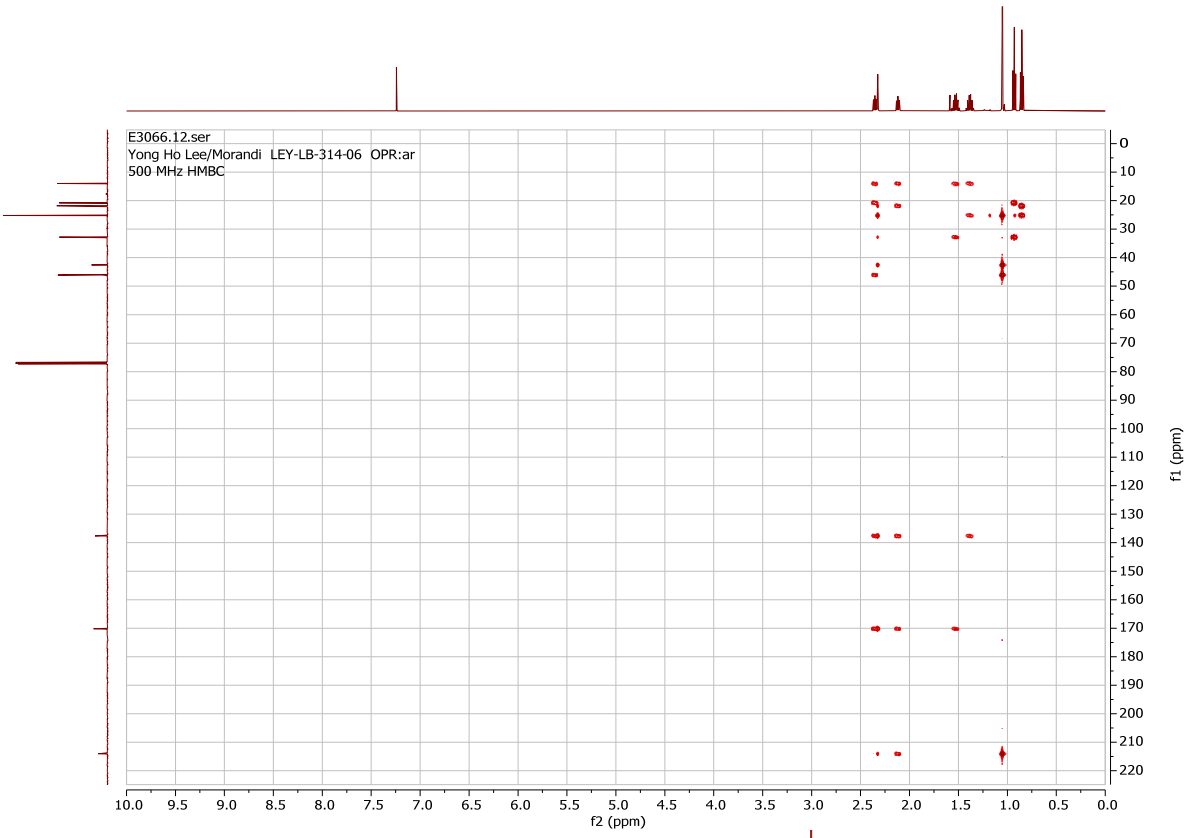
11. NMR spectra

11.1. Carbonylative carbocyclization

5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one (**3a**).



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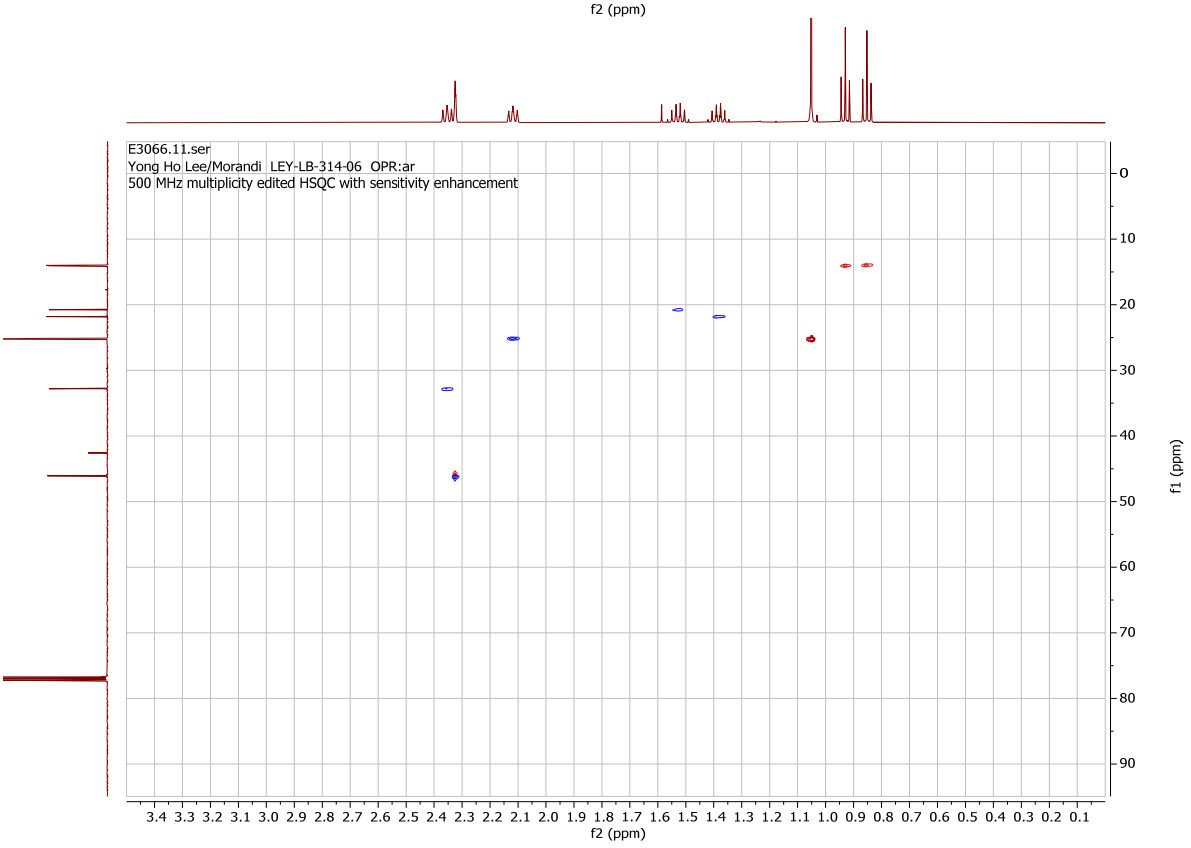
f1 (ppm)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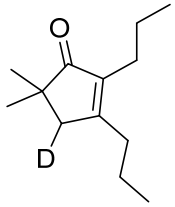
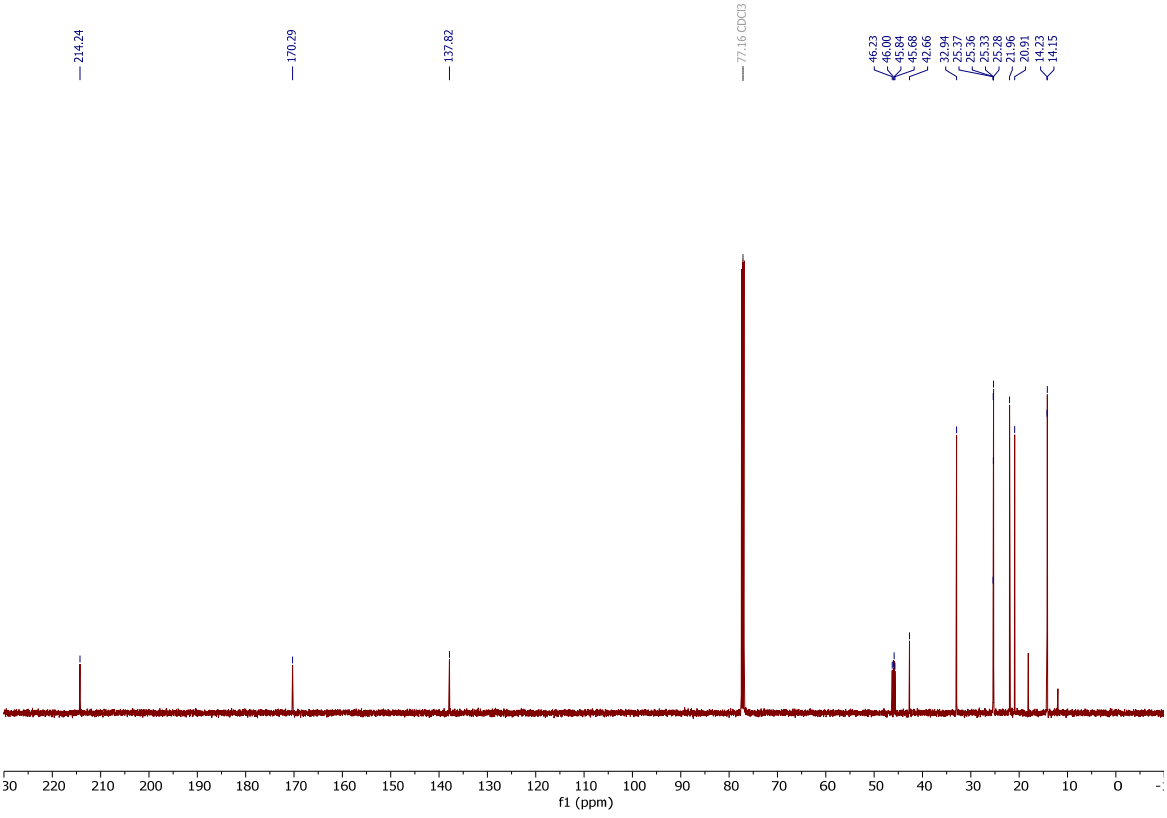
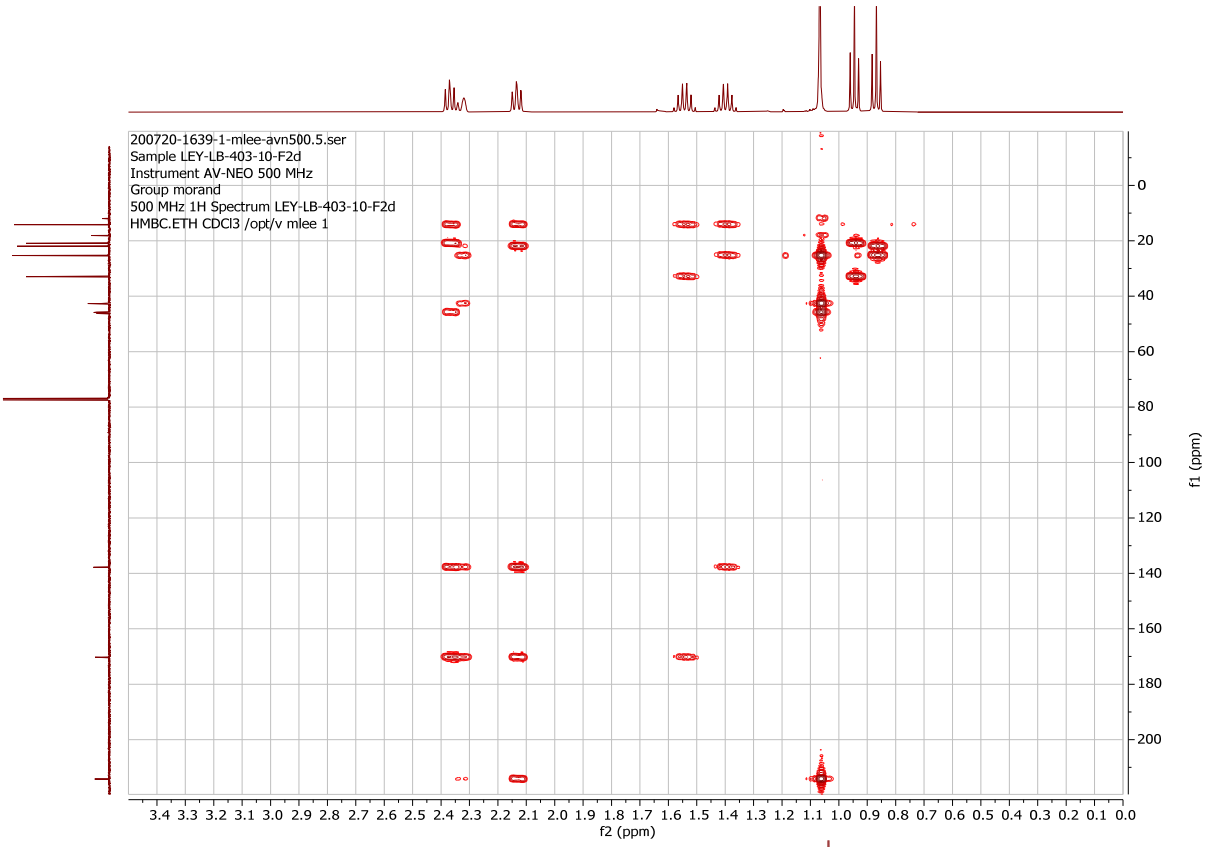
f2 (ppm)
f1 (ppm)

5,5-dimethyl-2,3-dipropylcyclopent-2-en-1-one-4-*d* (**3a-*d***, 94%[D]).



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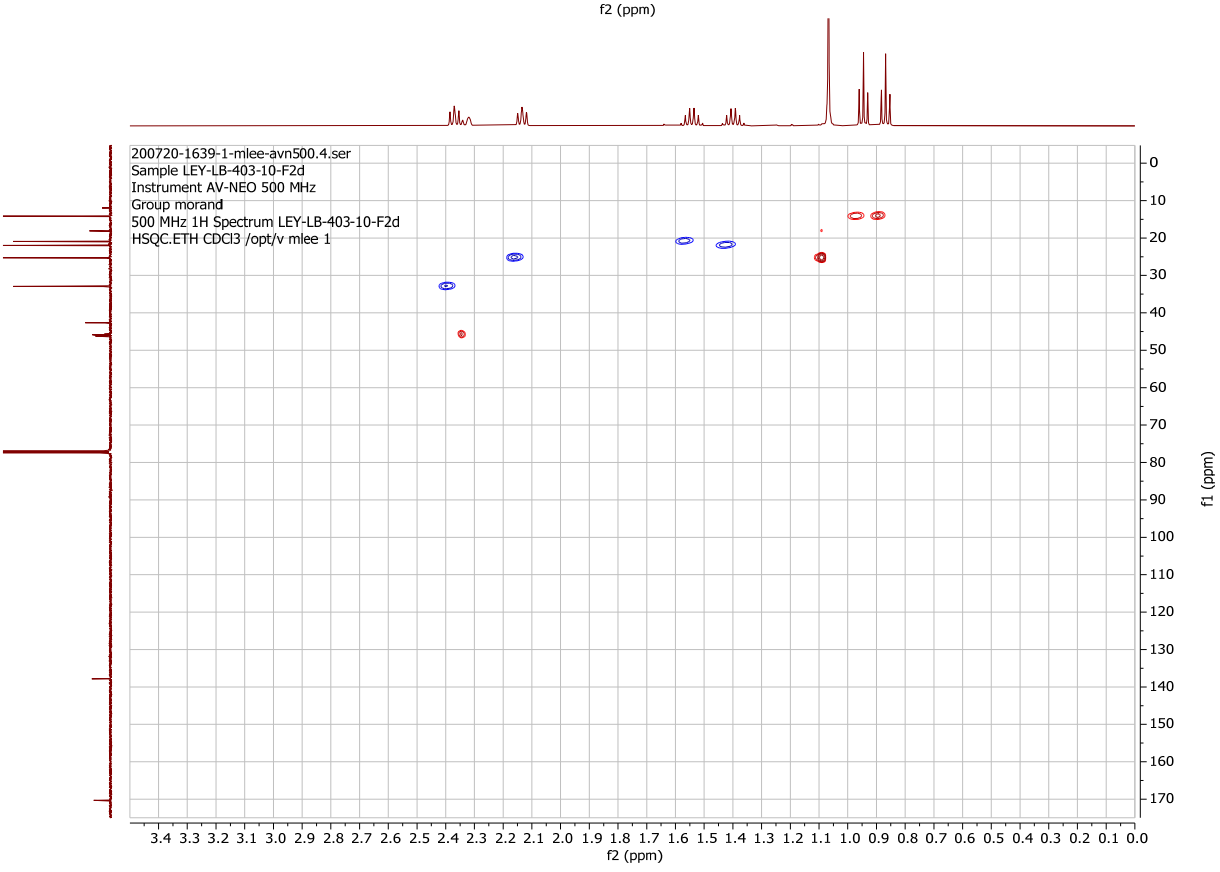
f1 (ppm)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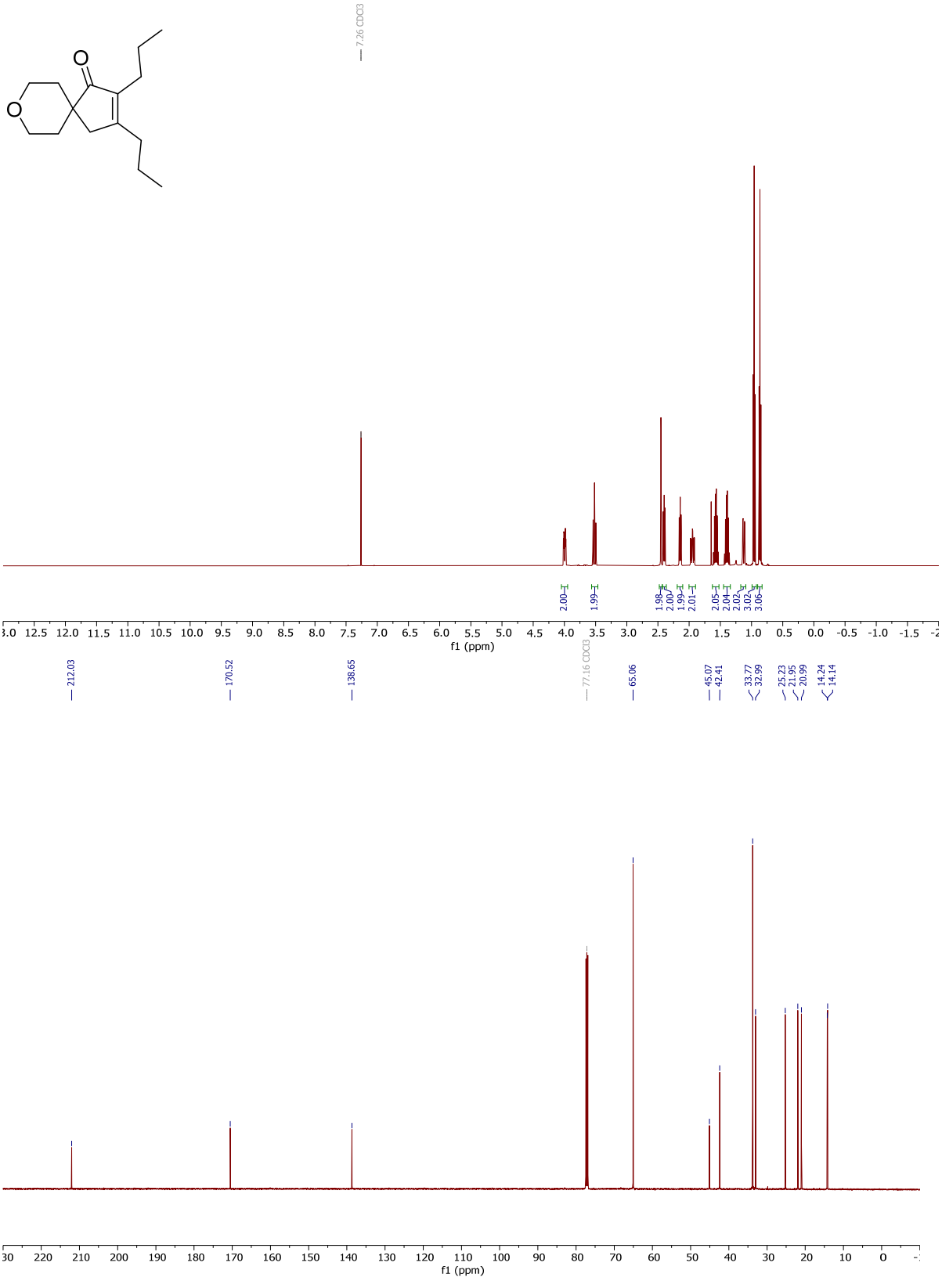
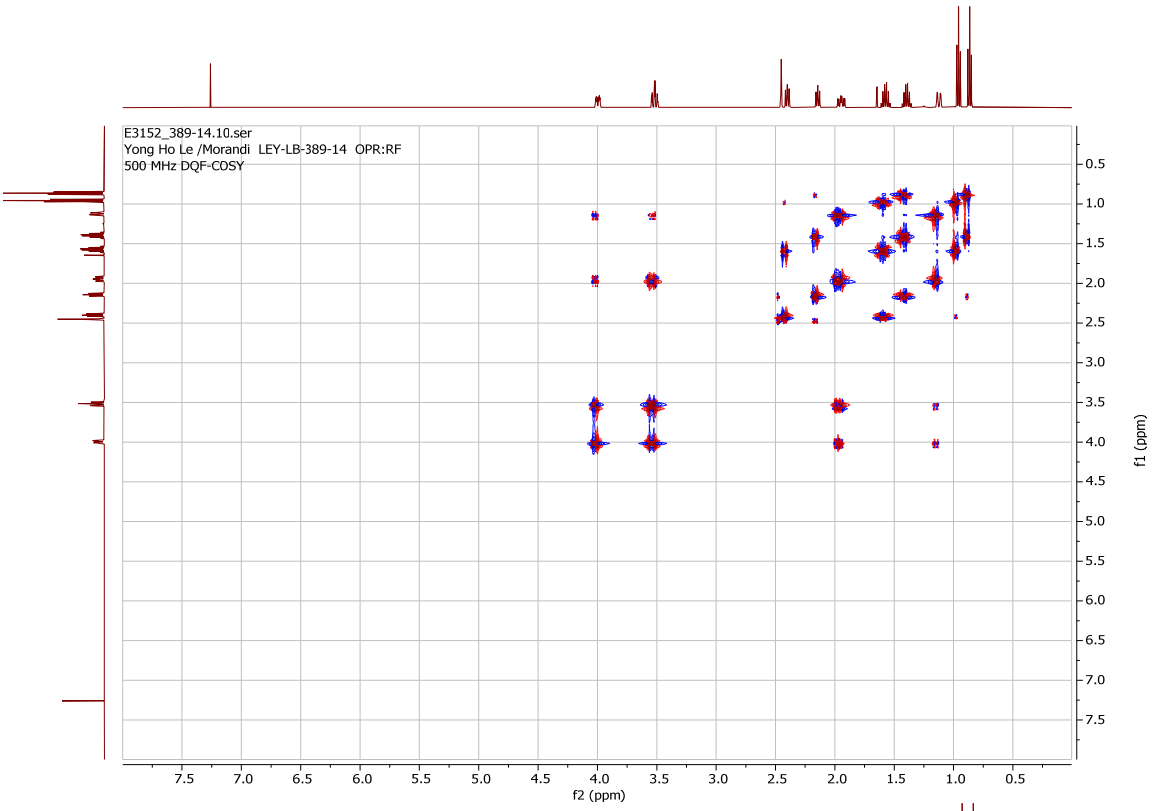
f2 (ppm)
f1 (ppm)

2,3-dipropyl-8-oxaspiro[4.5]dec-2-en-1-one (**3b**).

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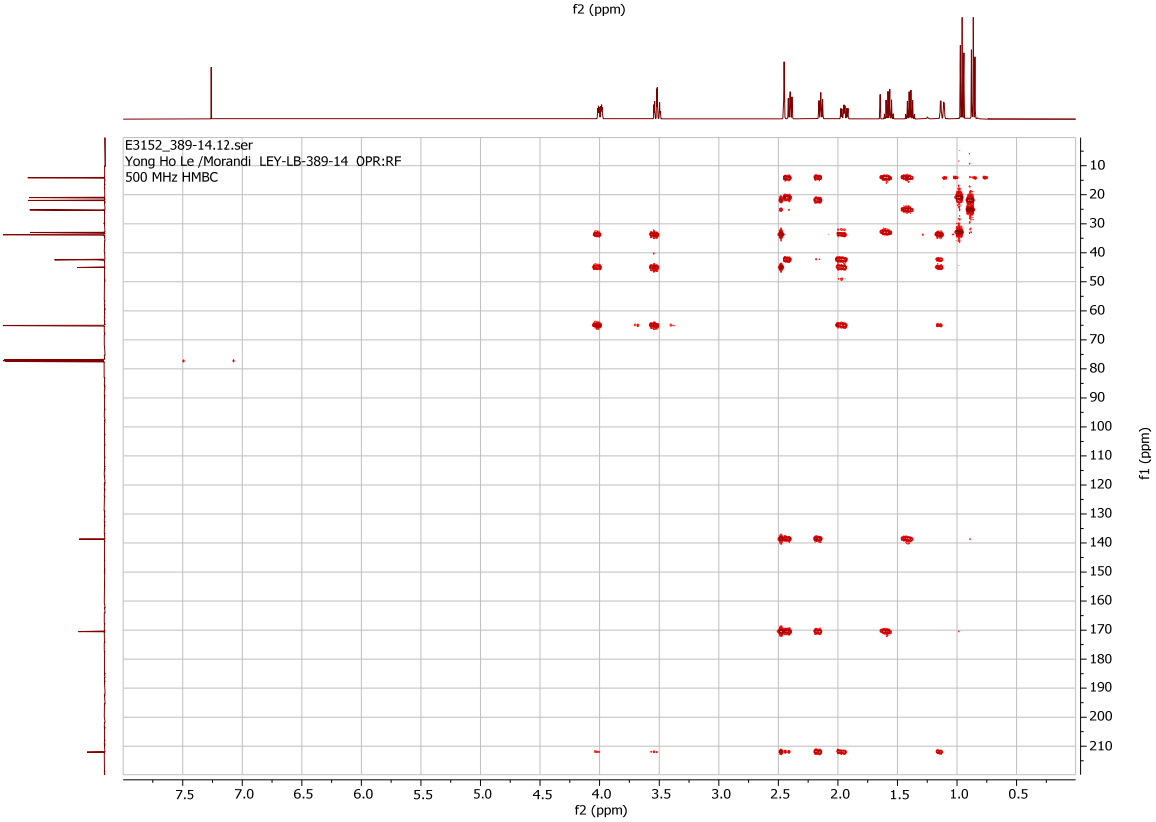
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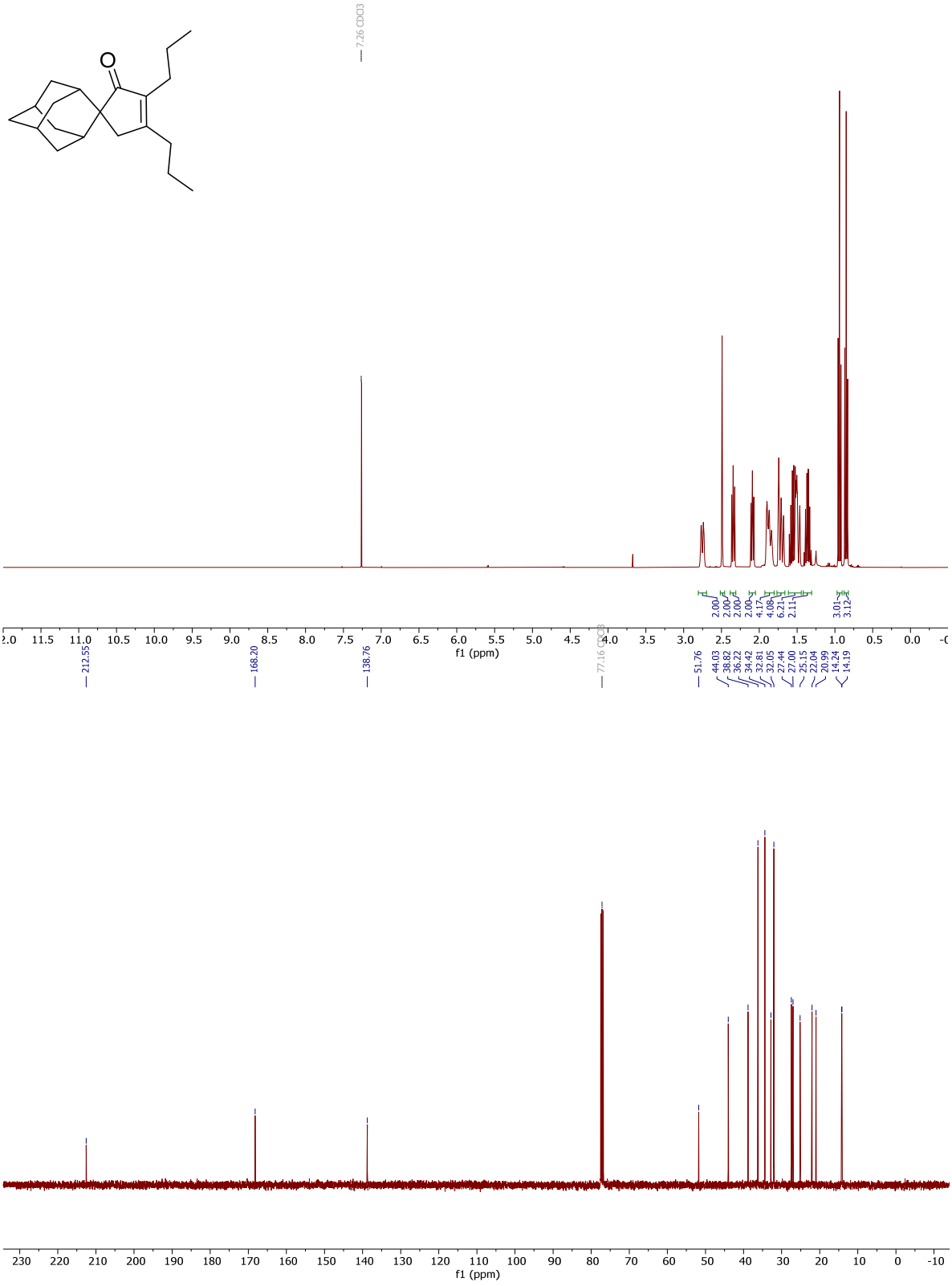
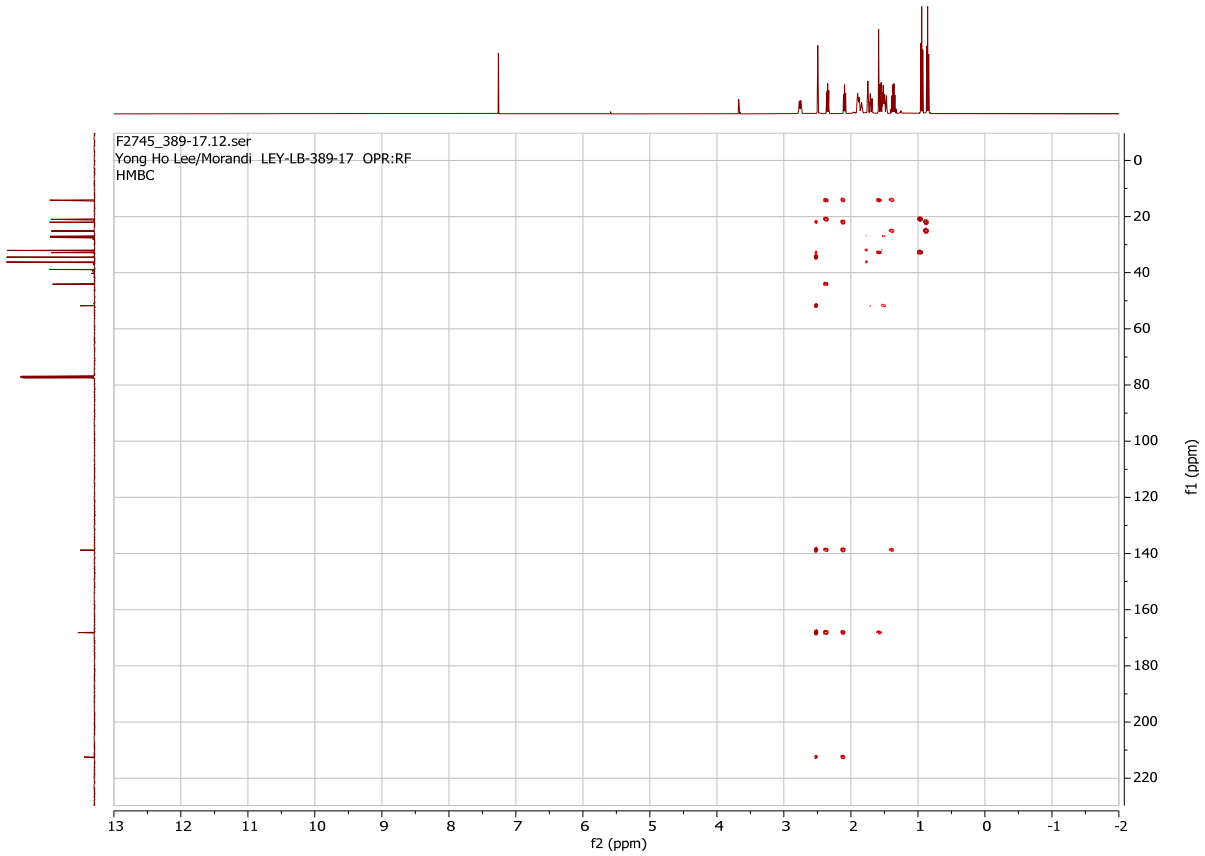
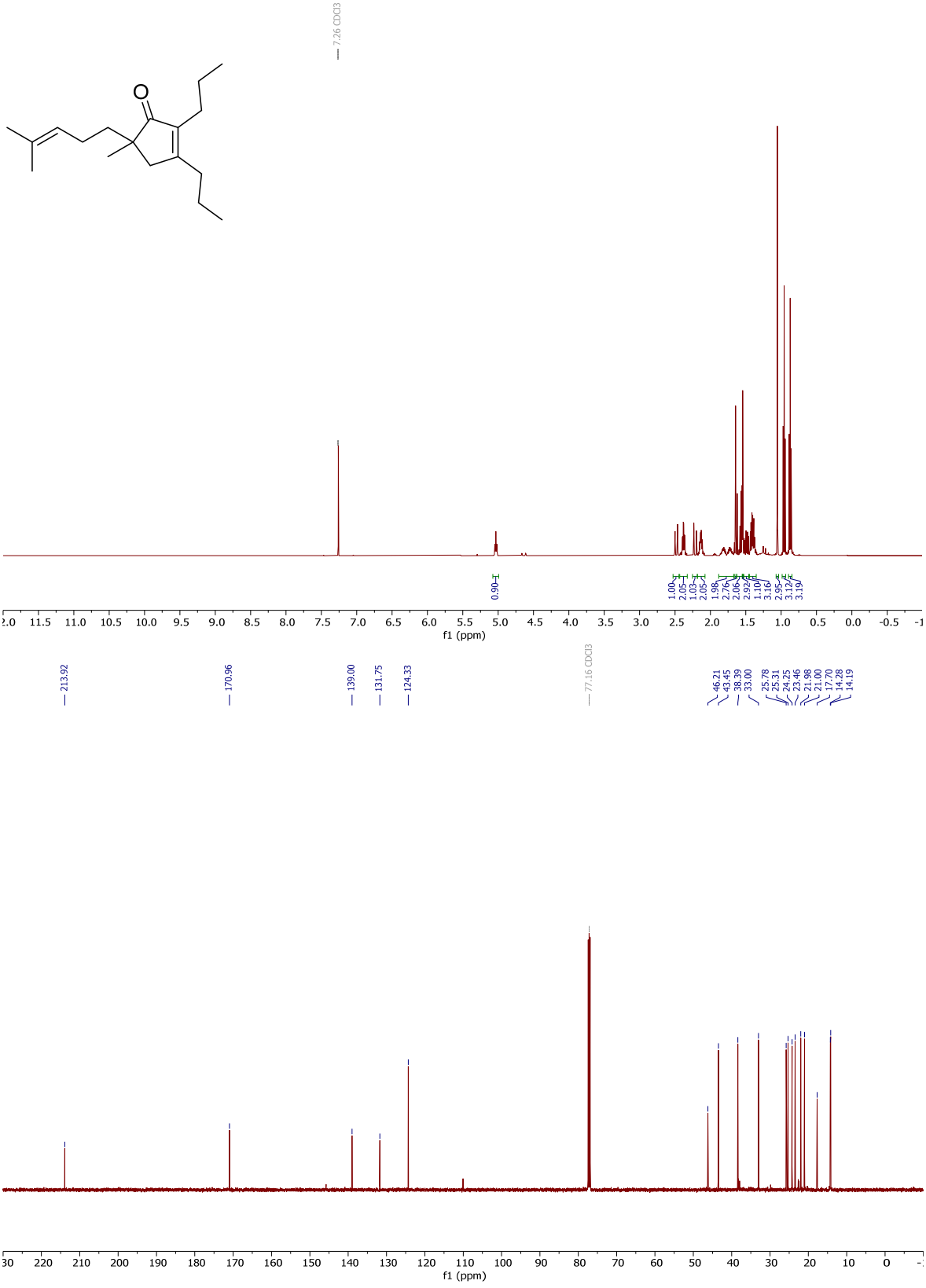
f1 (ppm)

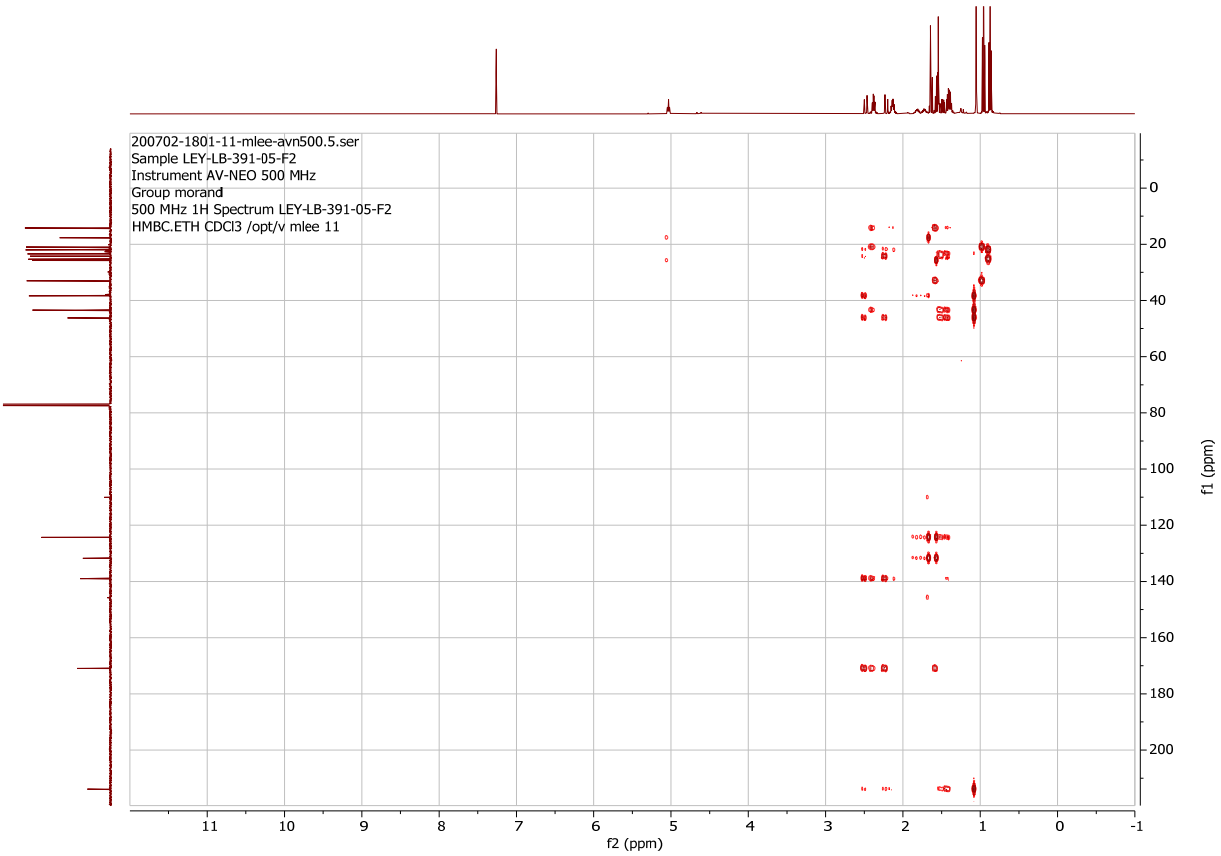
(1r,3r,5r,7r)-3',4'-dipropylspiro[adamantane-2,1'-cyclopentan]-3'-en-2'-one (**3c**).



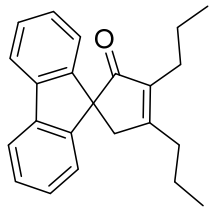

F2745_389-17.12.ser
Yong Ho Lee/Morandi LEY-LB-389-17 OPR:RF
HMBC
f2 (ppm)
f1 (ppm)

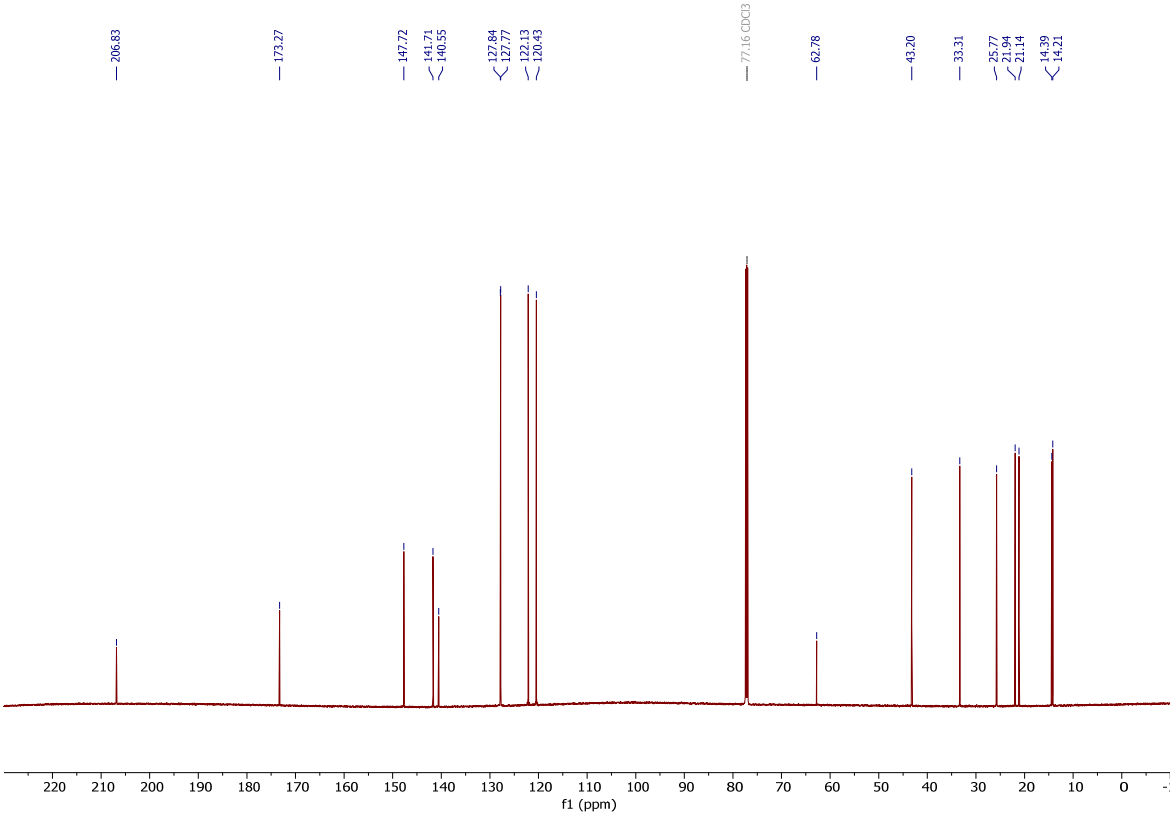
5-methyl-5-(4-methylpent-3-en-1-yl)-2,3-dipropylcyclopent-2-en-1-one (**3d**).

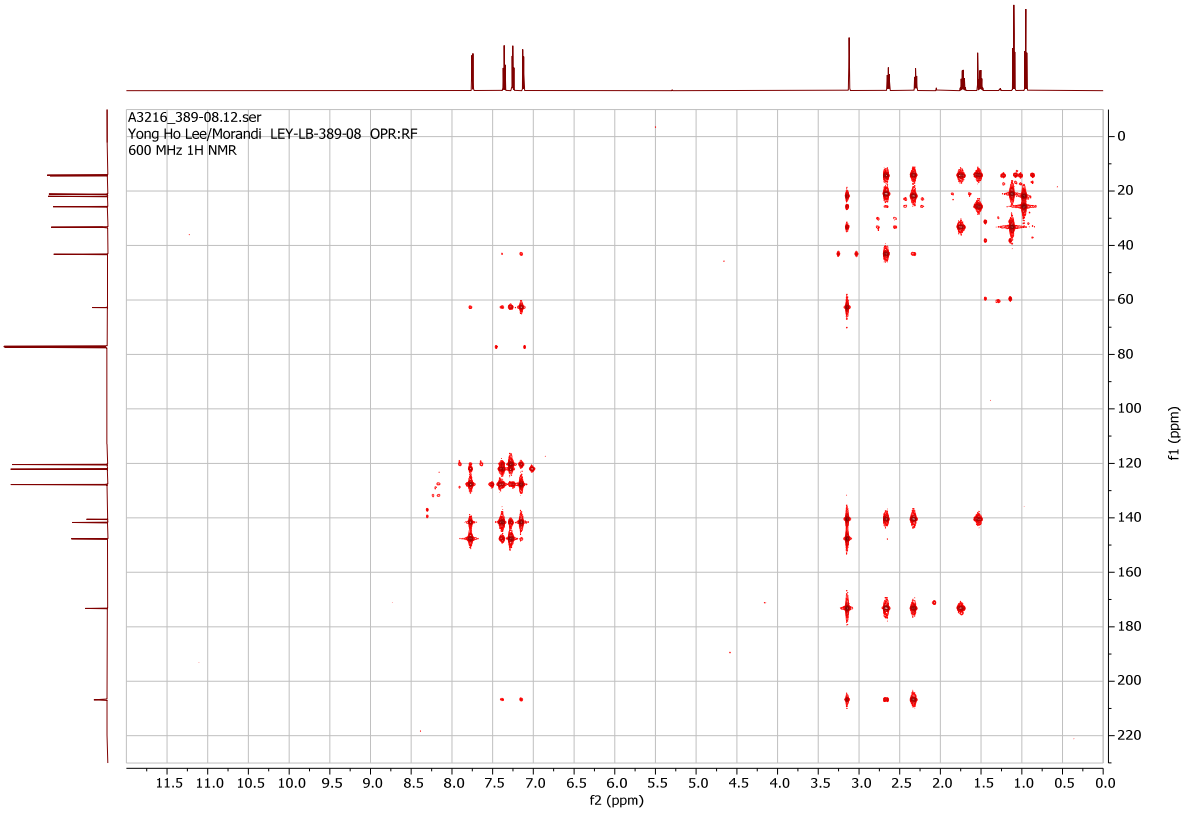



200702-1801-11-mlee-avn500.5.ser
Sample LEY-LB-391-05-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-391-05-F2
HMBC.ETH CDCl3 /opt/v mlee 11
f2 (ppm)
f1 (ppm)

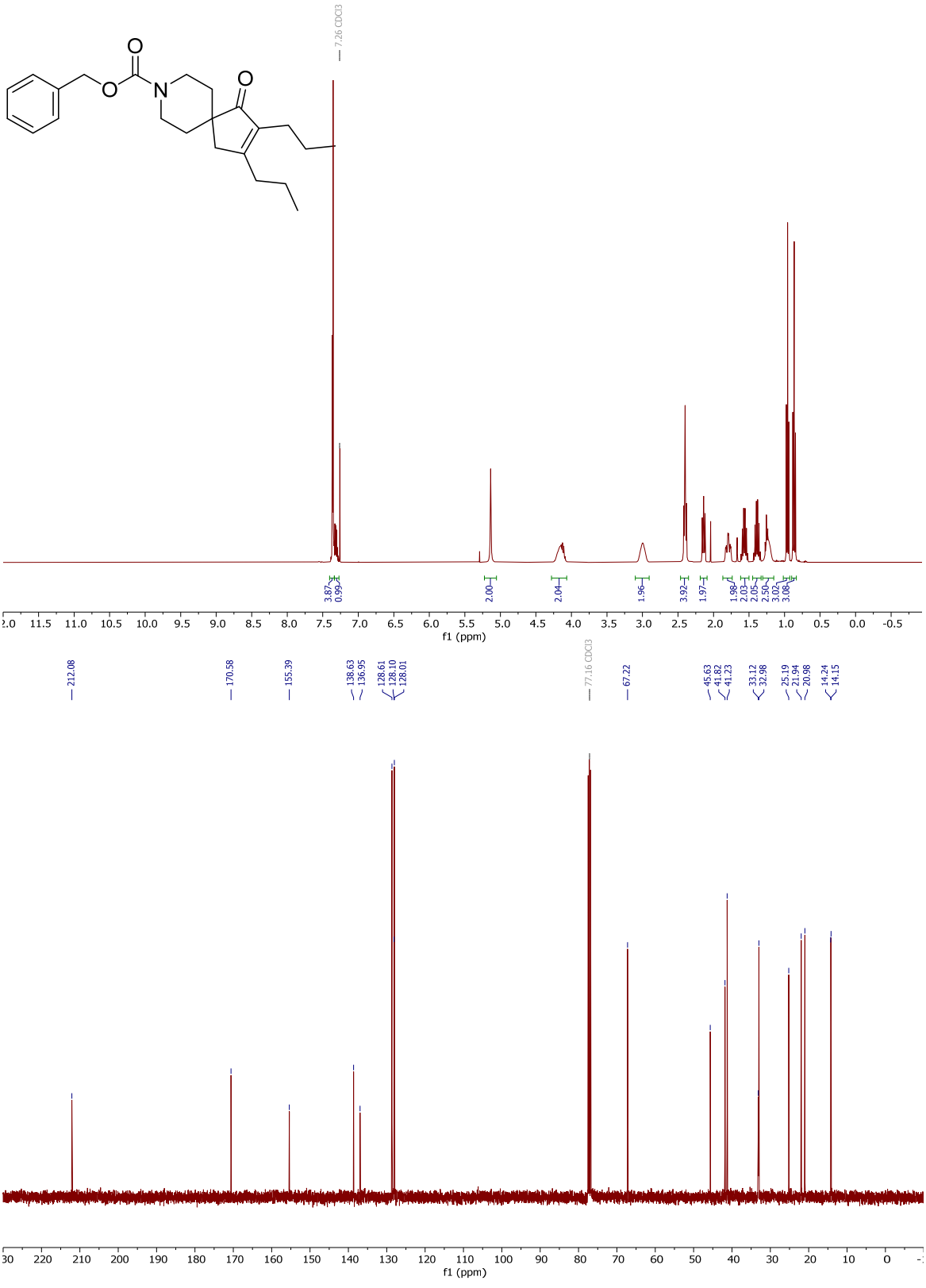
3,4-dipropylspiro[cyclopentane-1,9'-fluoren]-3-en-2-one (**3e**).

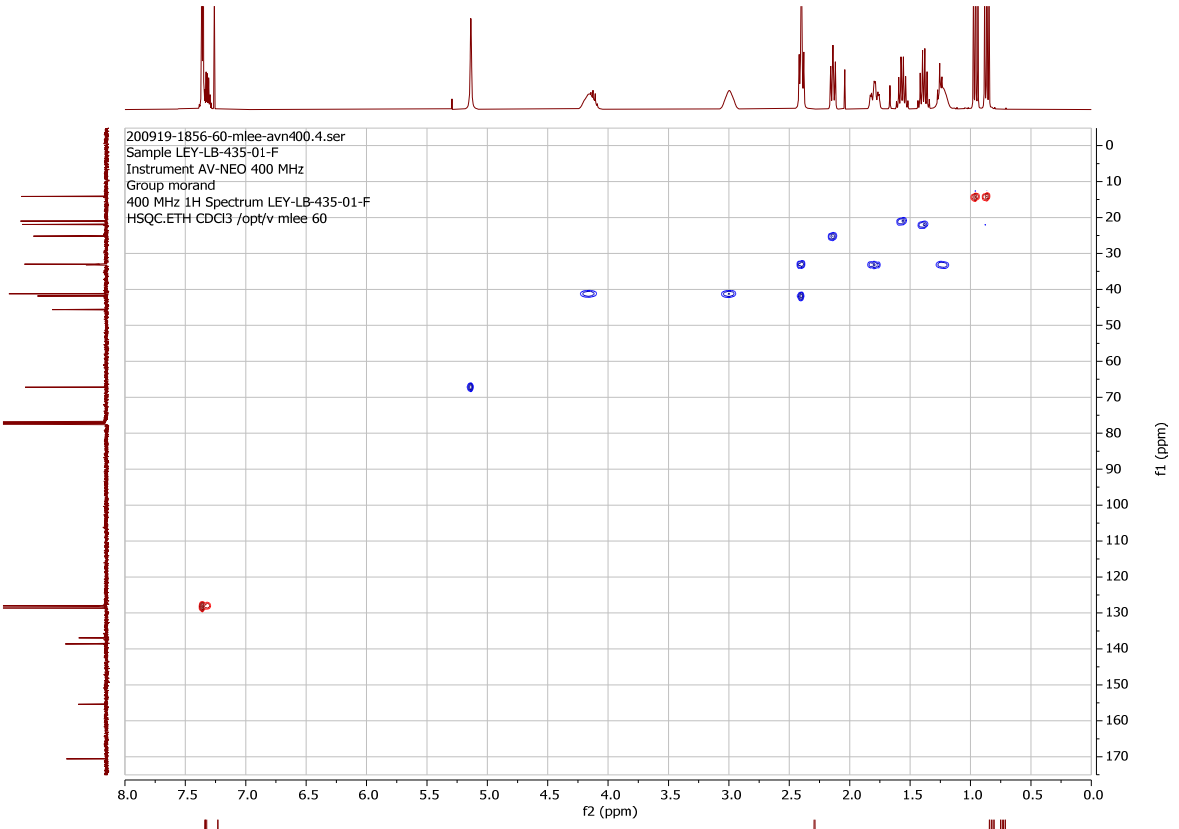


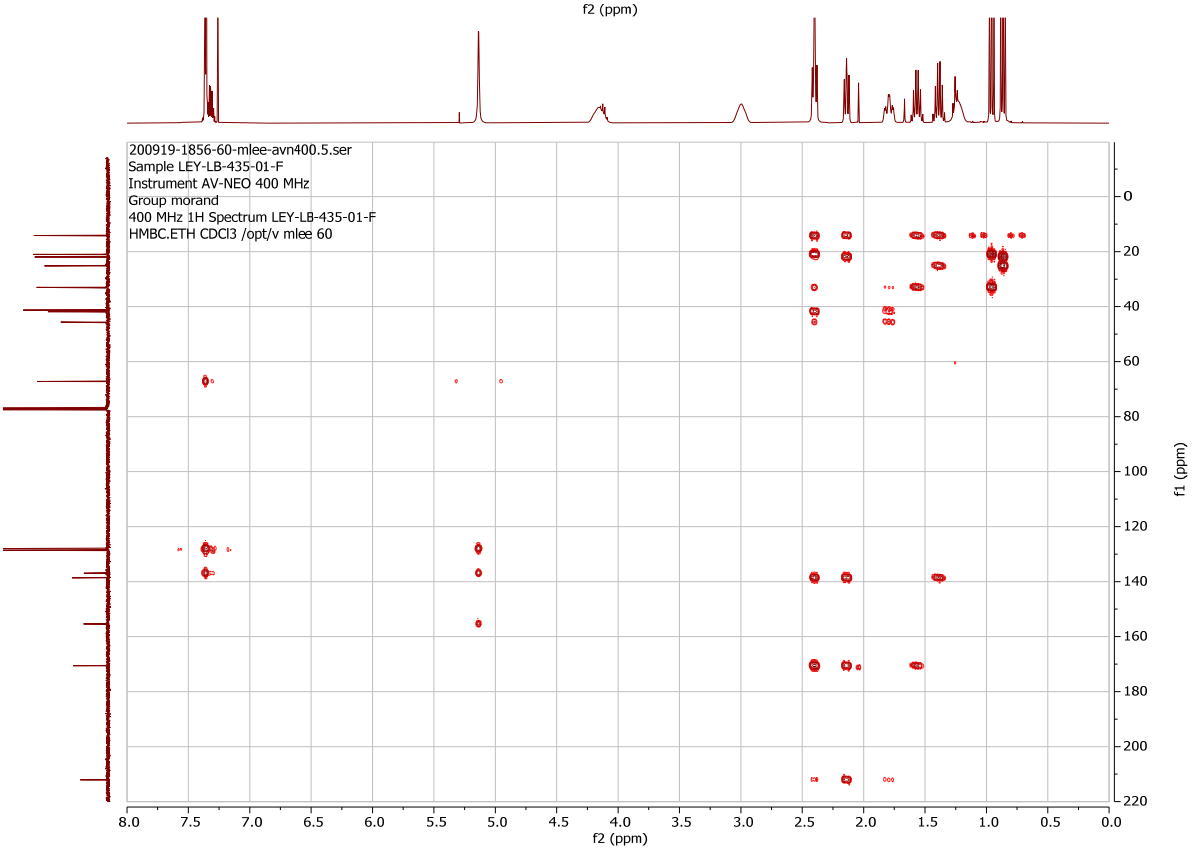


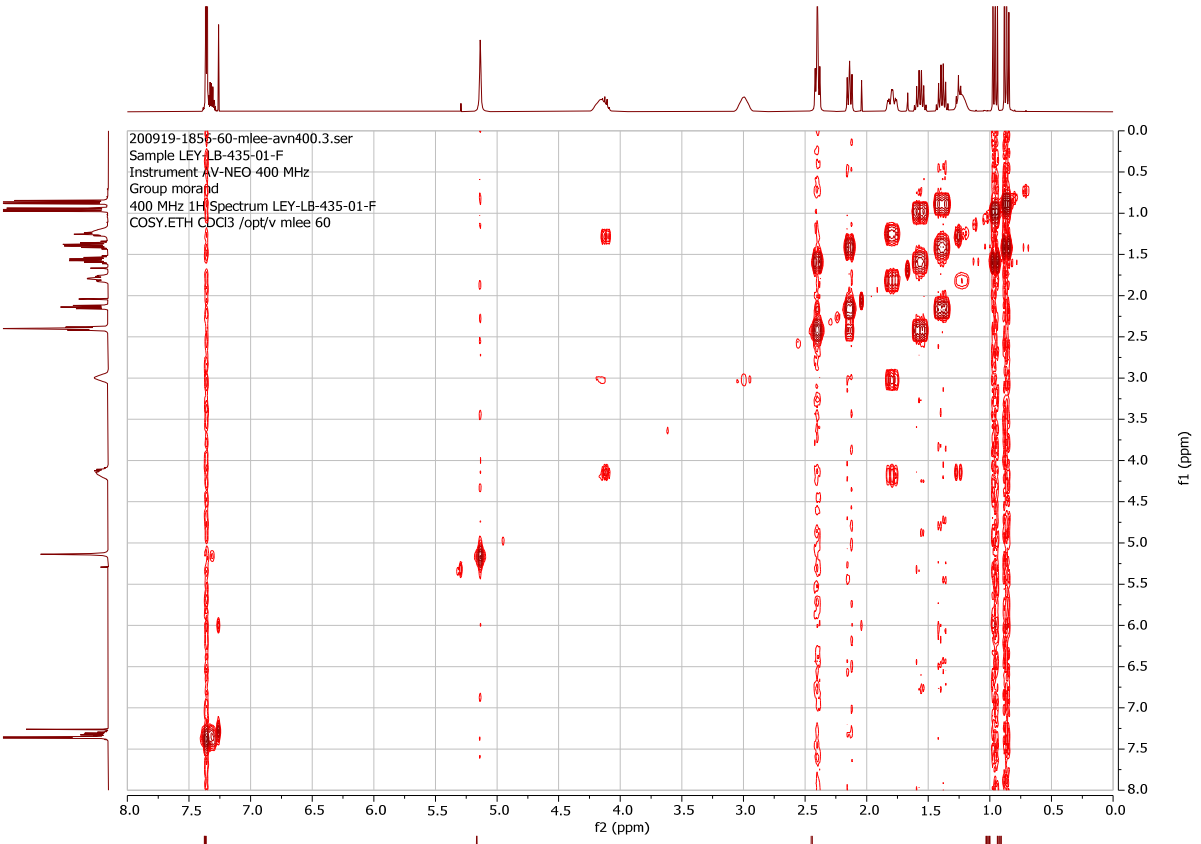

A3216_389-08.12.ser
Yong Ho Lee/Morandi LEY-LB-389-08 OPR:RF
600 MHz 1H NMR
f2 (ppm)
f1 (ppm)

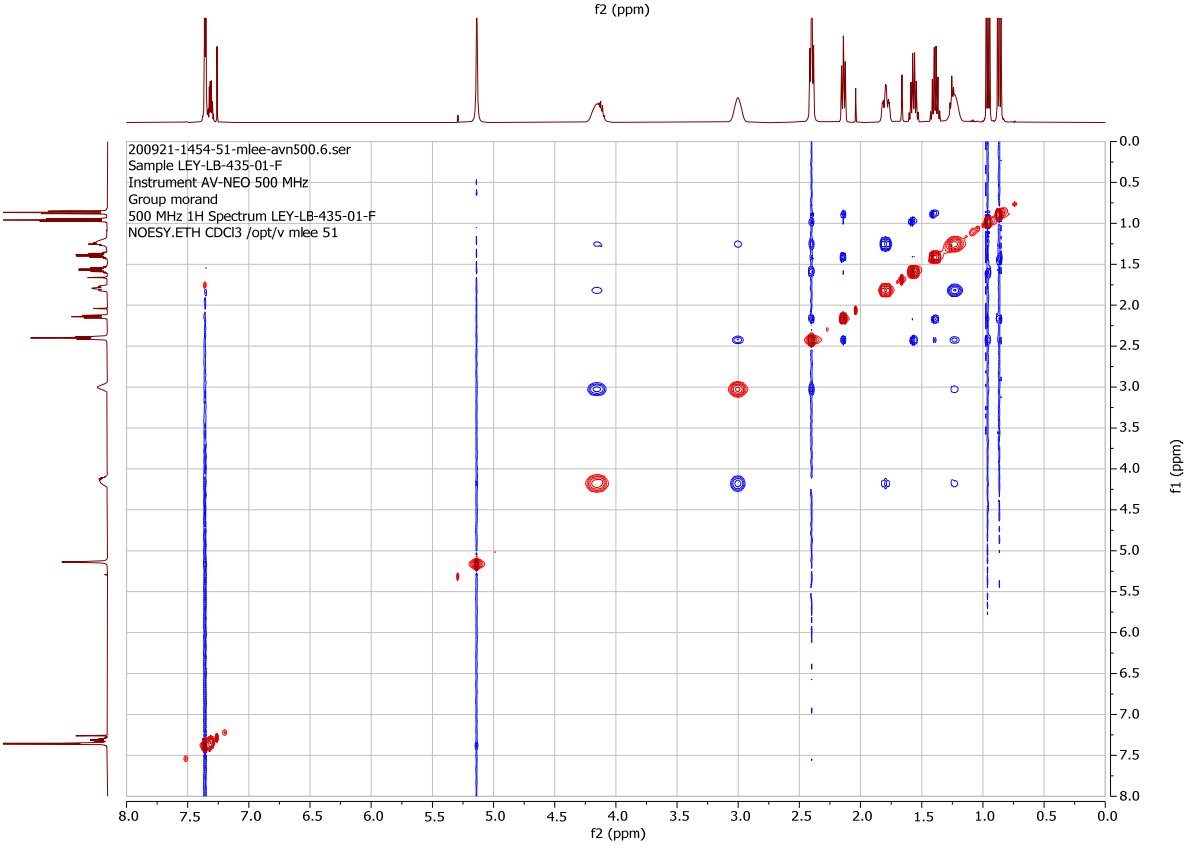
benzyl 1-oxo-2,3-dipropyl-8-azaspiro[4.5]dec-2-ene-8-carboxylate (**3f**).



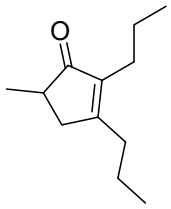

200919-1856-60-mlee-avn400.4.ser
Sample LEY-LB-435-01-F
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-435-01-F
HSQC.ETH CDCl3 /opt/v mlee 60
f2 (ppm)
f1 (ppm)

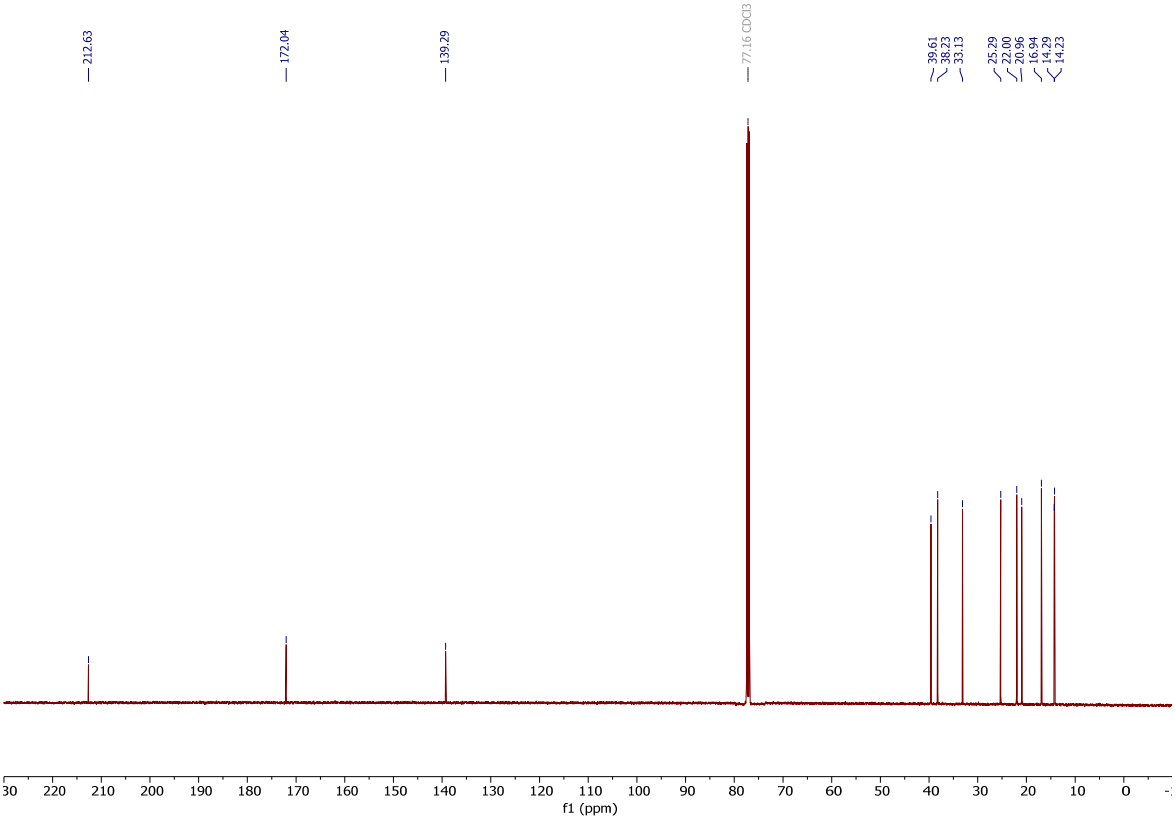

200919-1856-60-mlee-avn400.5.ser
Sample LEY-LB-435-01-F
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-435-01-F
HMBC.ETH CDCl3 /opt/v mlee 60
f2 (ppm)
f1 (ppm)

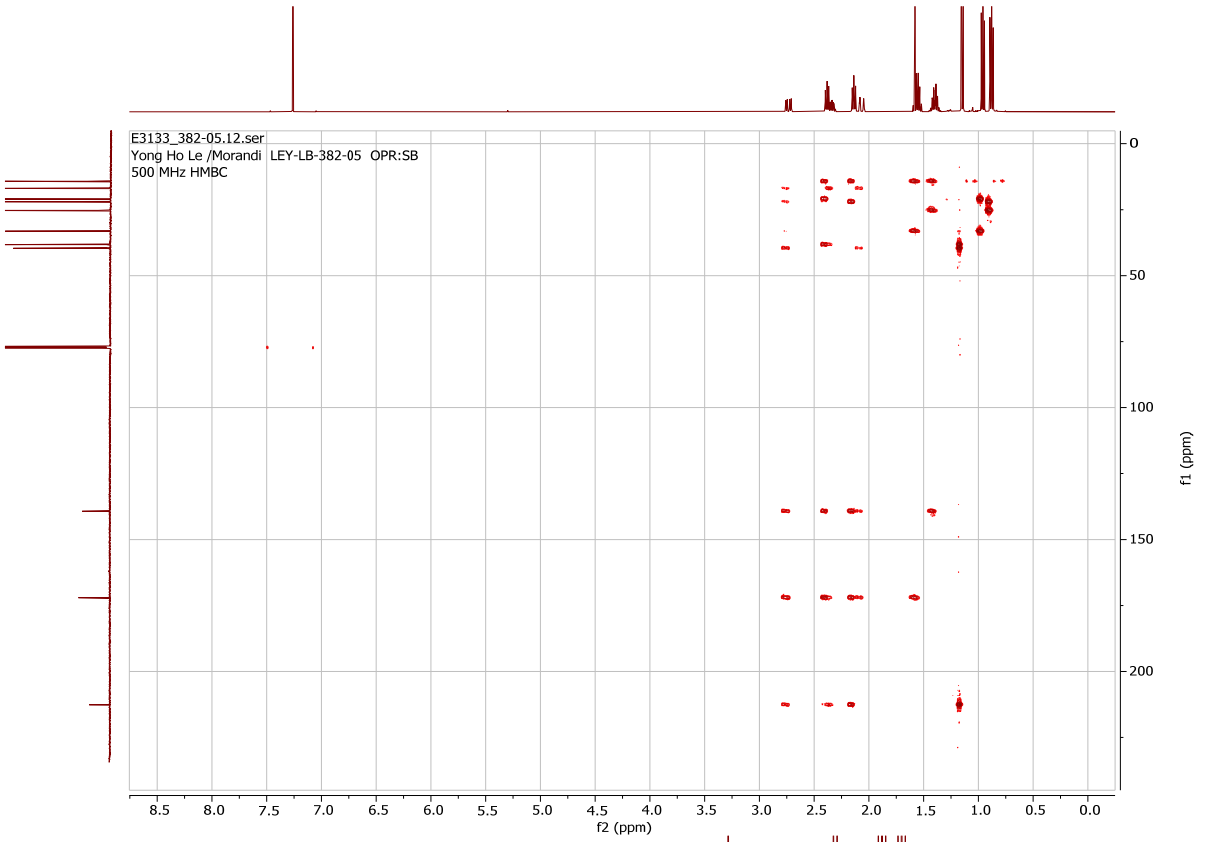

200919-1856-60-mlee-avn400.3.ser
Sample LEY-LB-435-01-F
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-435-01-F
COSY.ETH CDCl3 /opt/v mlee 60
f2 (ppm)
f1 (ppm)

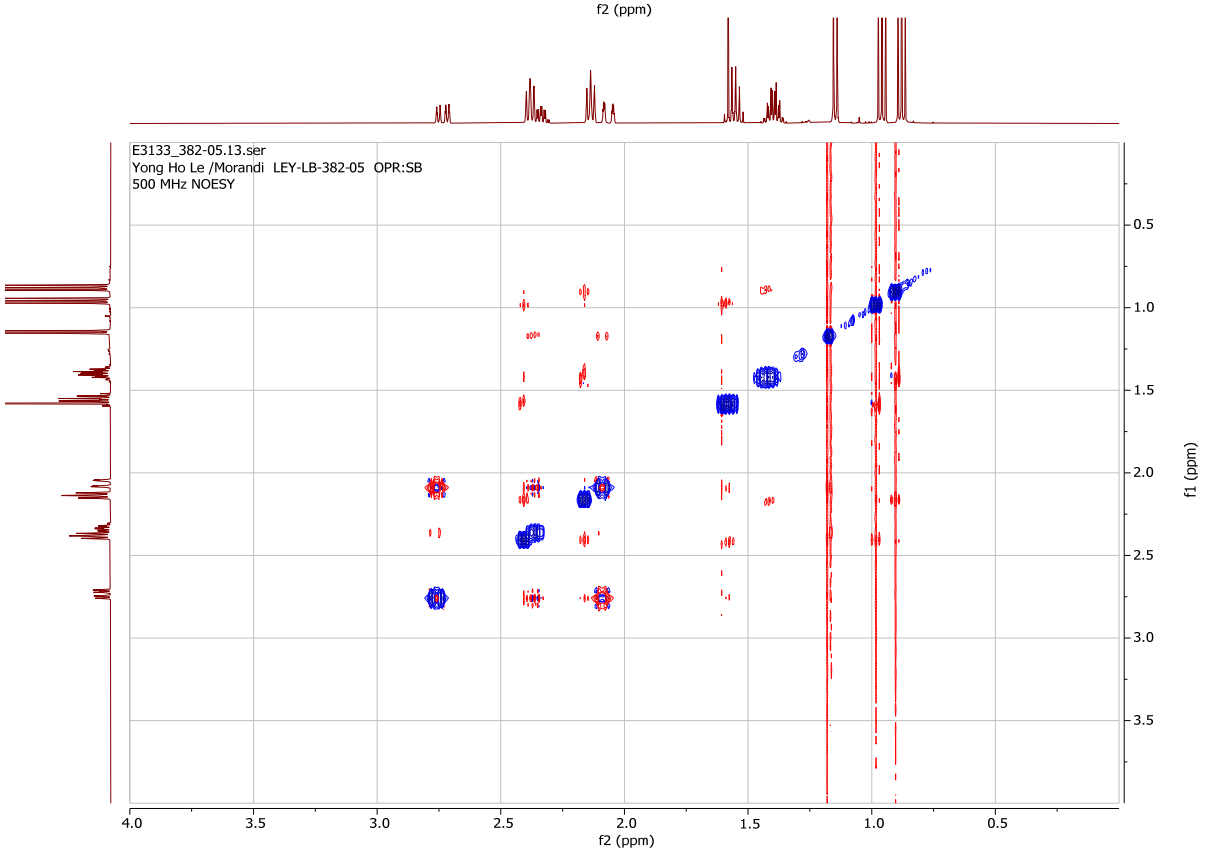

200921-1454-51-mlee-avn500.6.ser
Sample LEY-LB-435-01-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-435-01-F
NOESY.ETH CDCl3 /opt/v mlee 51
f2 (ppm)
f1 (ppm)

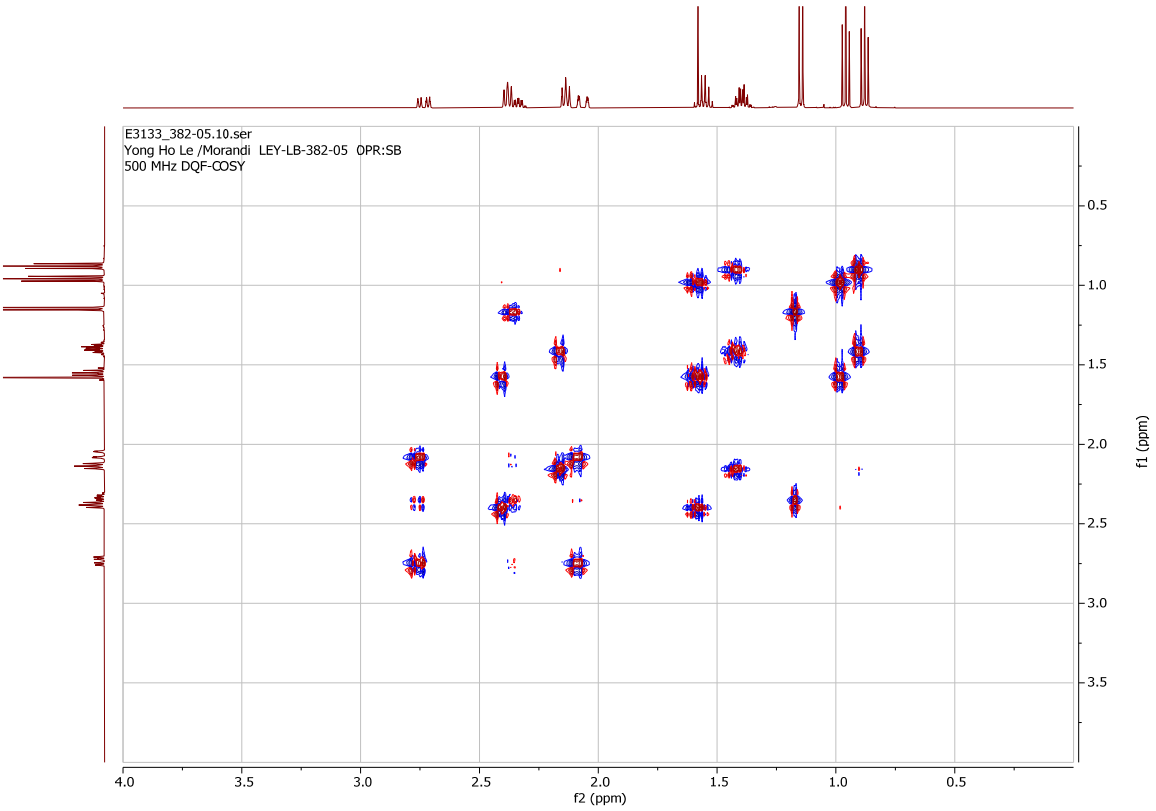
5-methyl-2,3-dipropylcyclopent-2-en-1-one (**3g**).

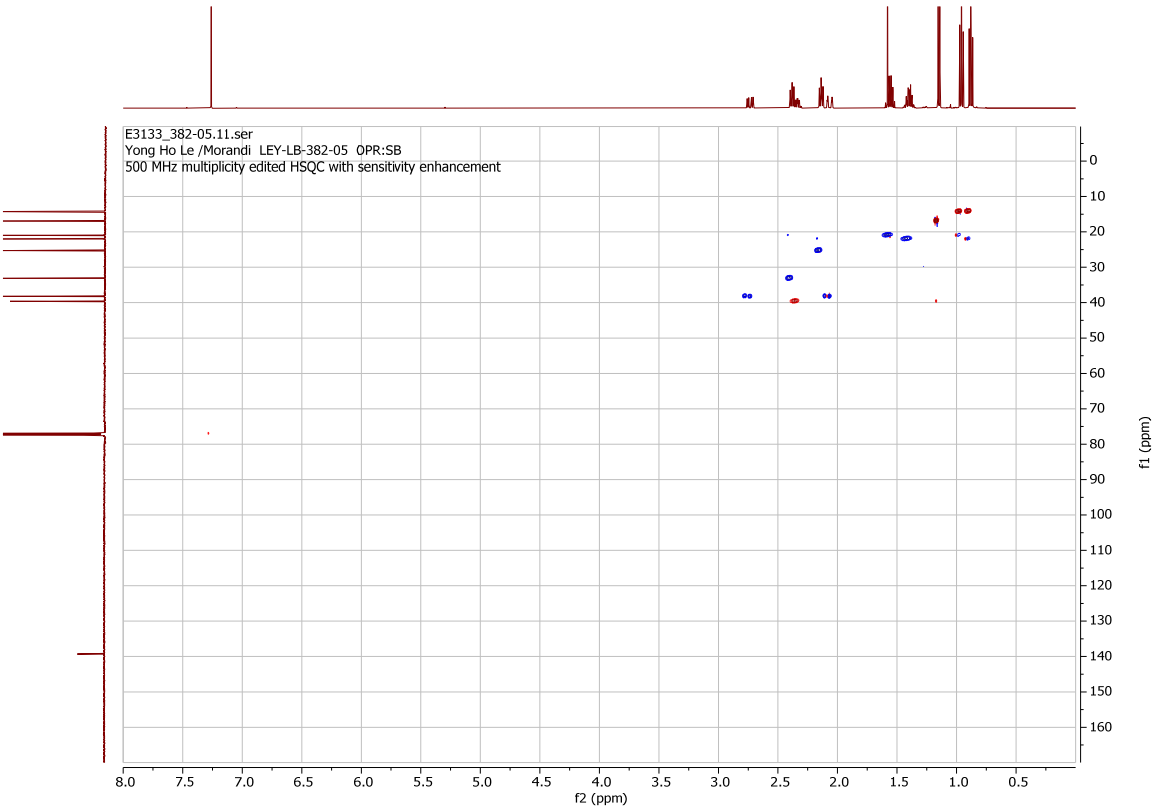




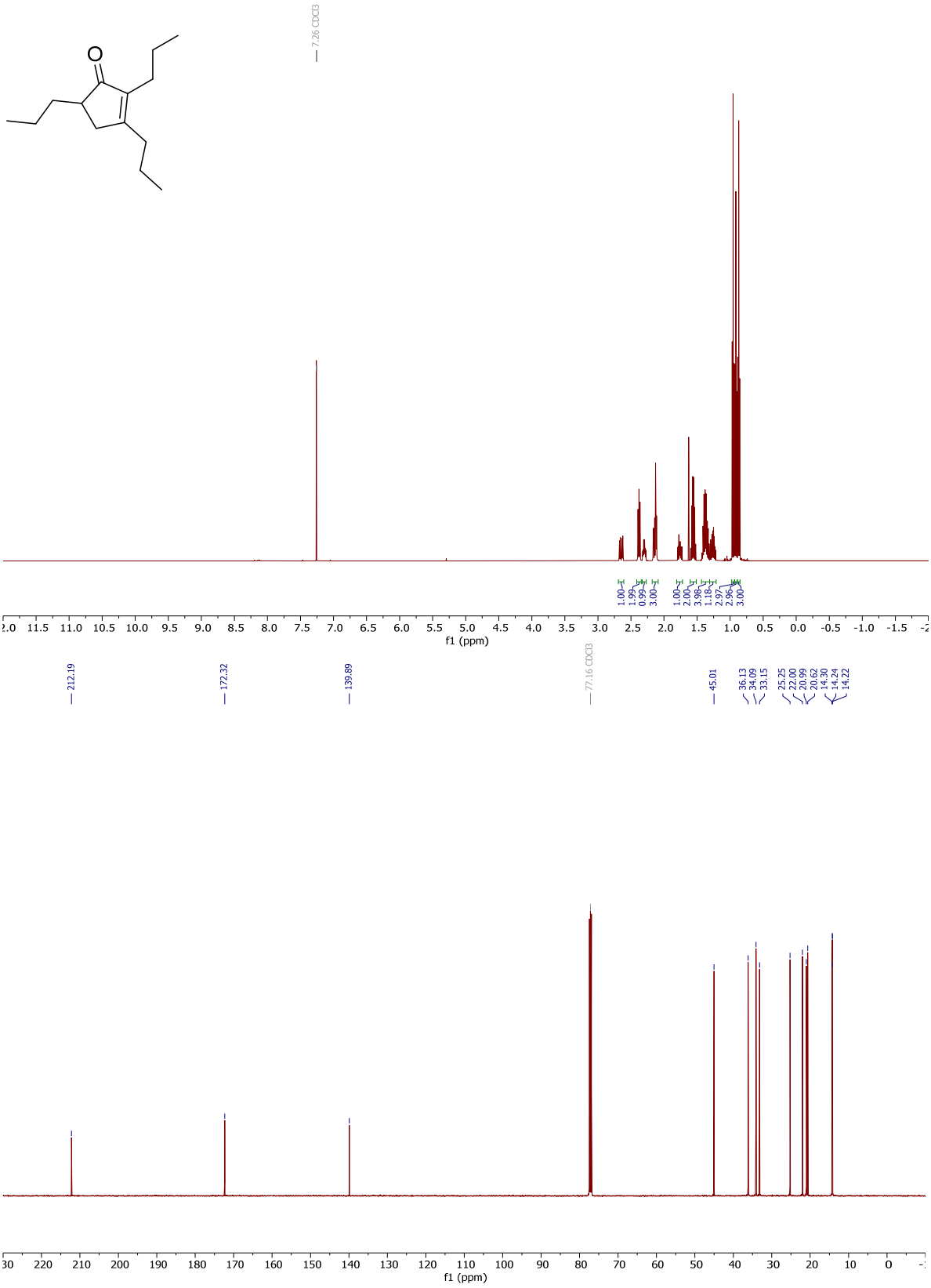

E3133_382-05.12.ser
Yong Ho Le /Morandi LEY-LB-382-05 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

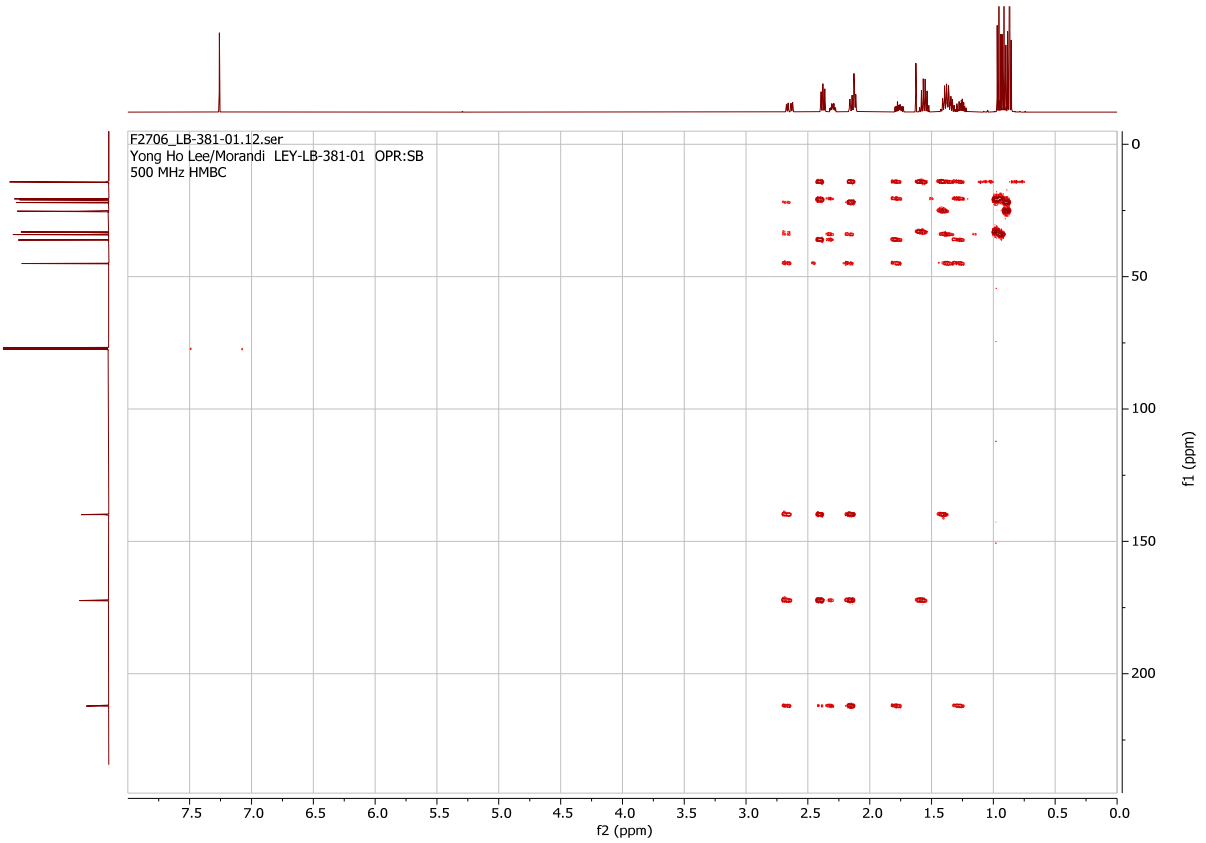

E3133_382-05.13.ser
Yong Ho Le /Morandi LEY-LB-382-05 OPR:SB
500 MHz NOESY
f2 (ppm)
f1 (ppm)


E3133_382-05.10.ser
Yong Ho Le /Morandi LEY-LB-382-05 0PR:SB
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

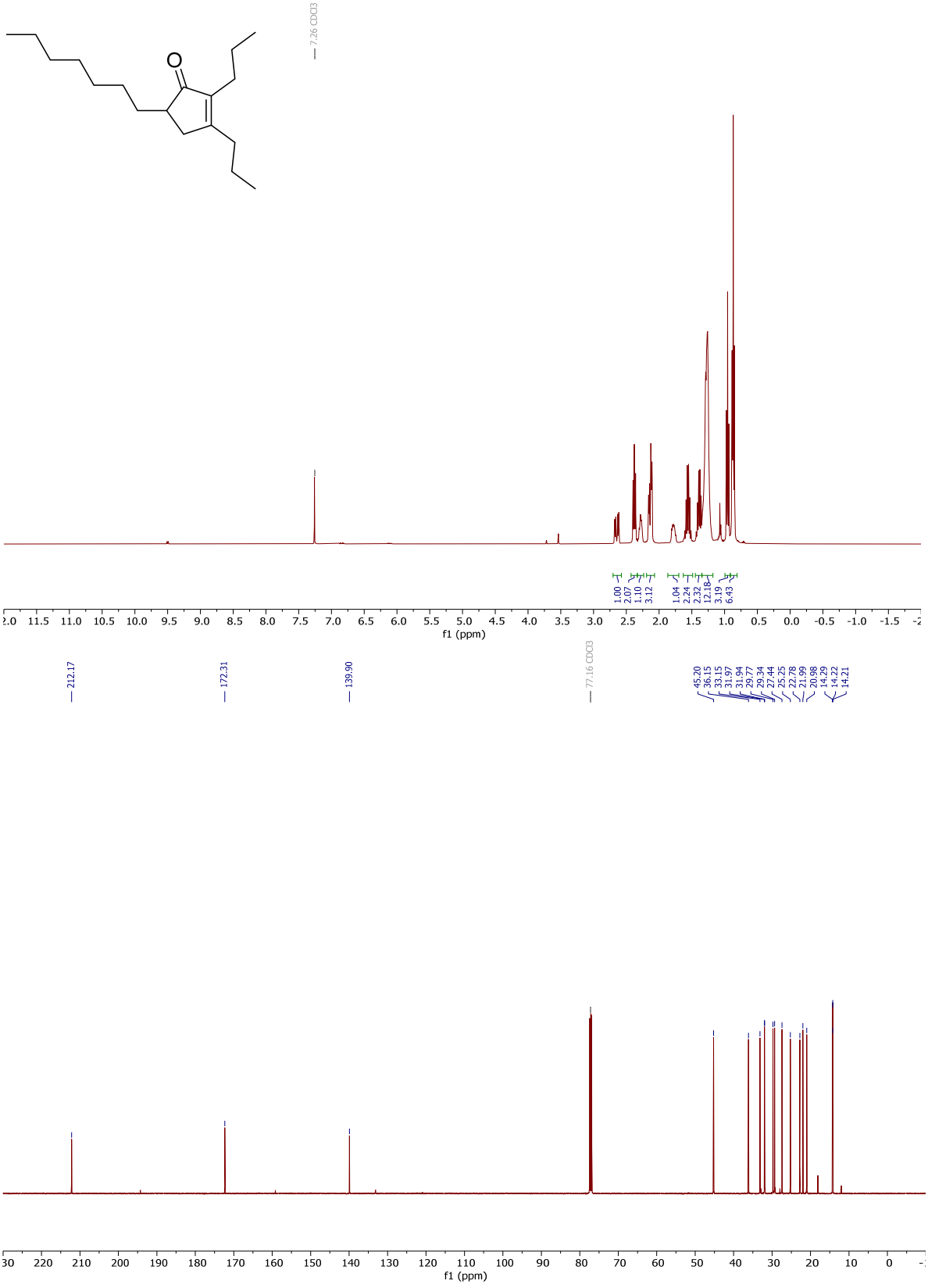

E3133_382-05.11.ser
Yong Ho Le /Morandi LEY-LB-382-05 0PR:SB
500 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

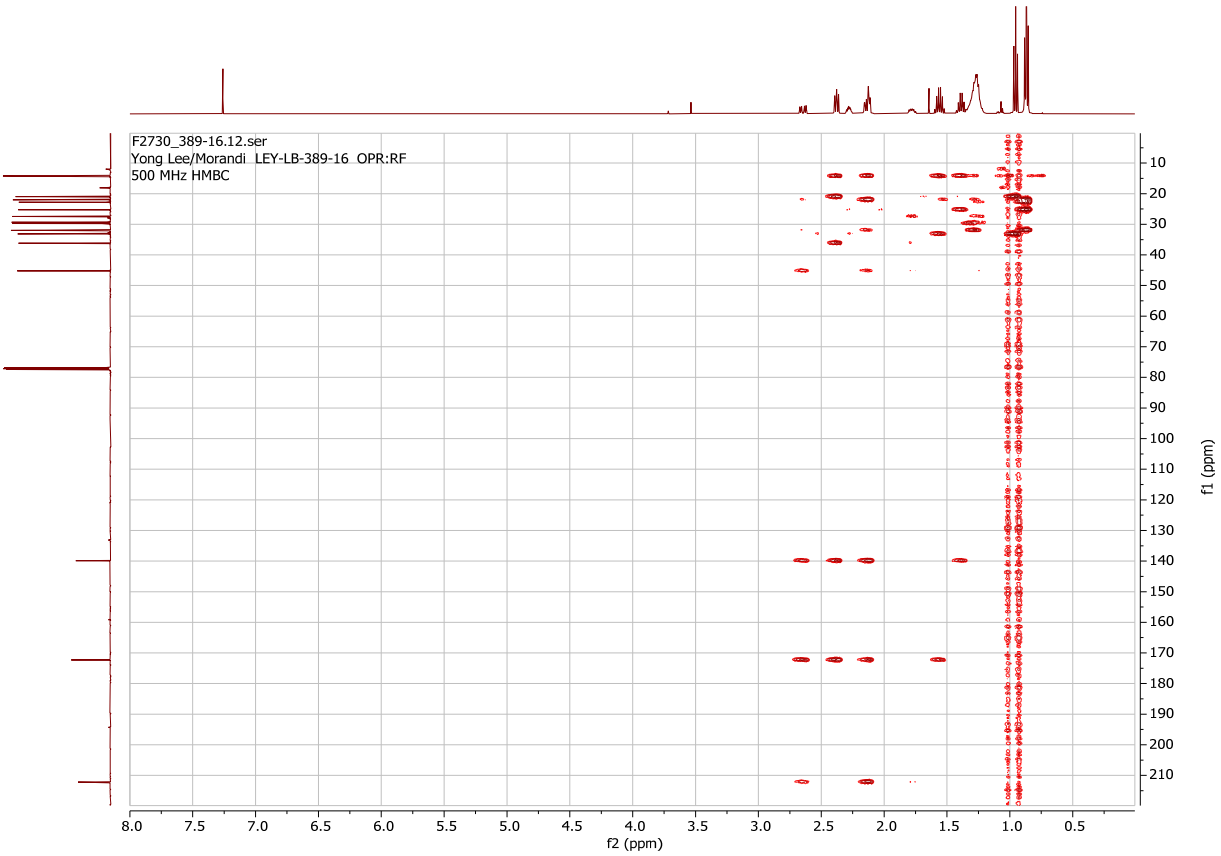
2,3,5-tripropylcyclopent-2-en-1-one (**3h**).



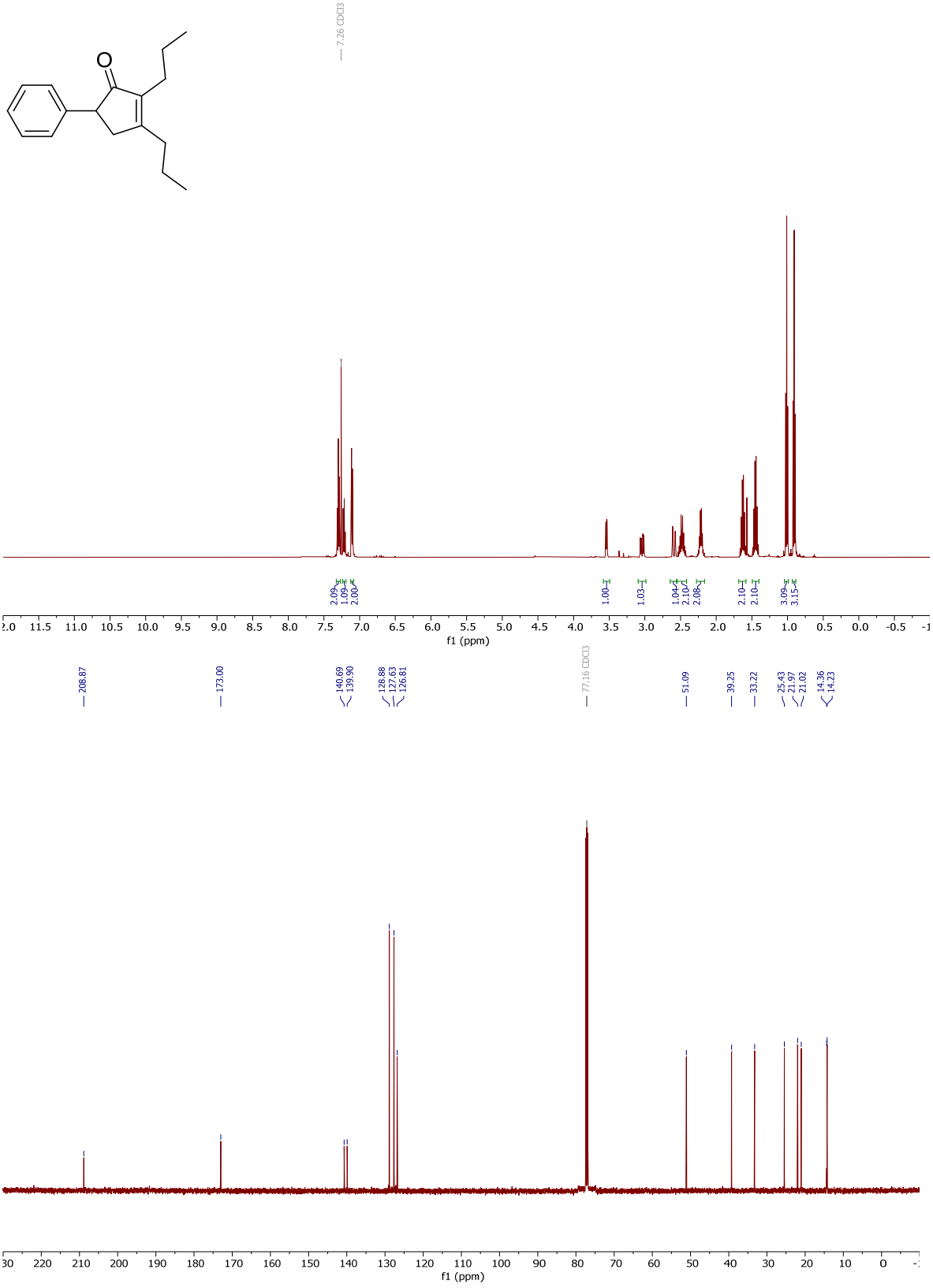

F2706_LB-381-01.12.ser
Yong Ho Lee/Morandi LEY-LB-381-01 OPR:SB
500 MHz HMBC
0
50
100
150
200
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

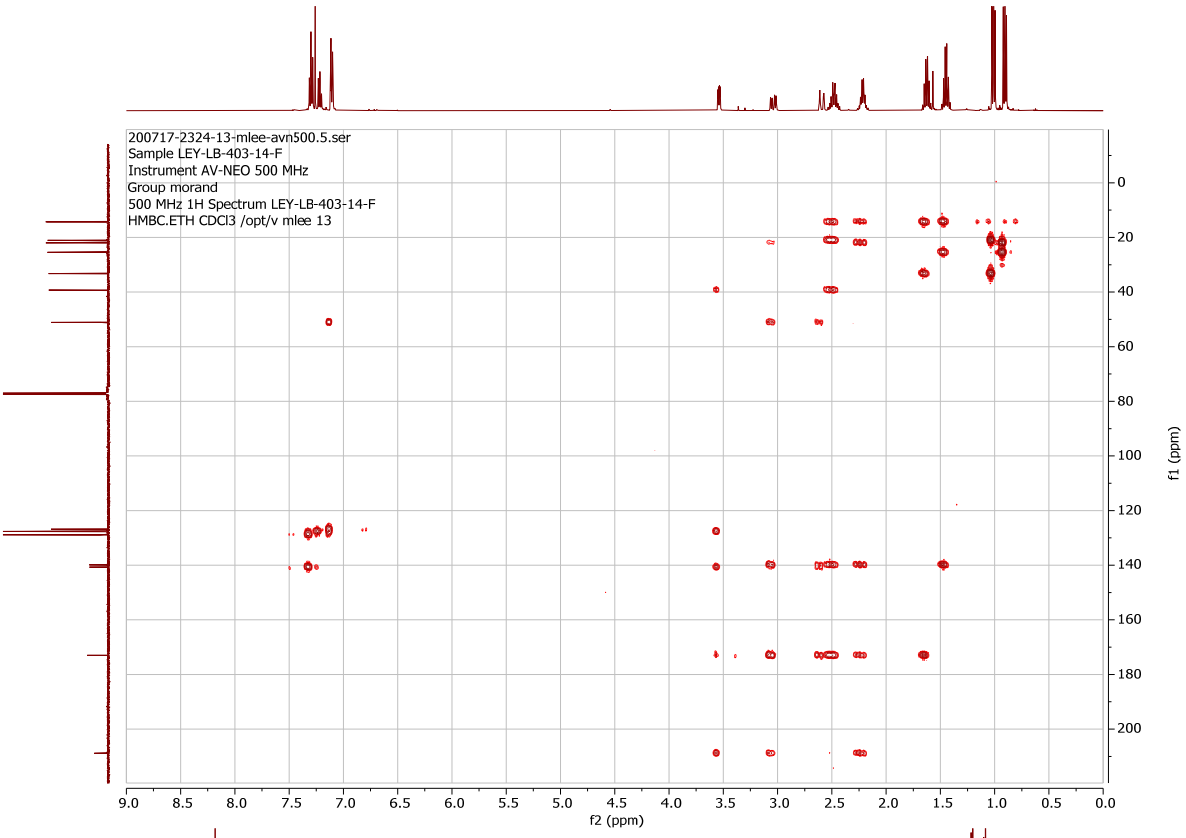
5-heptyl-2,3-dipropylcyclopent-2-en-1-one (**3i**).

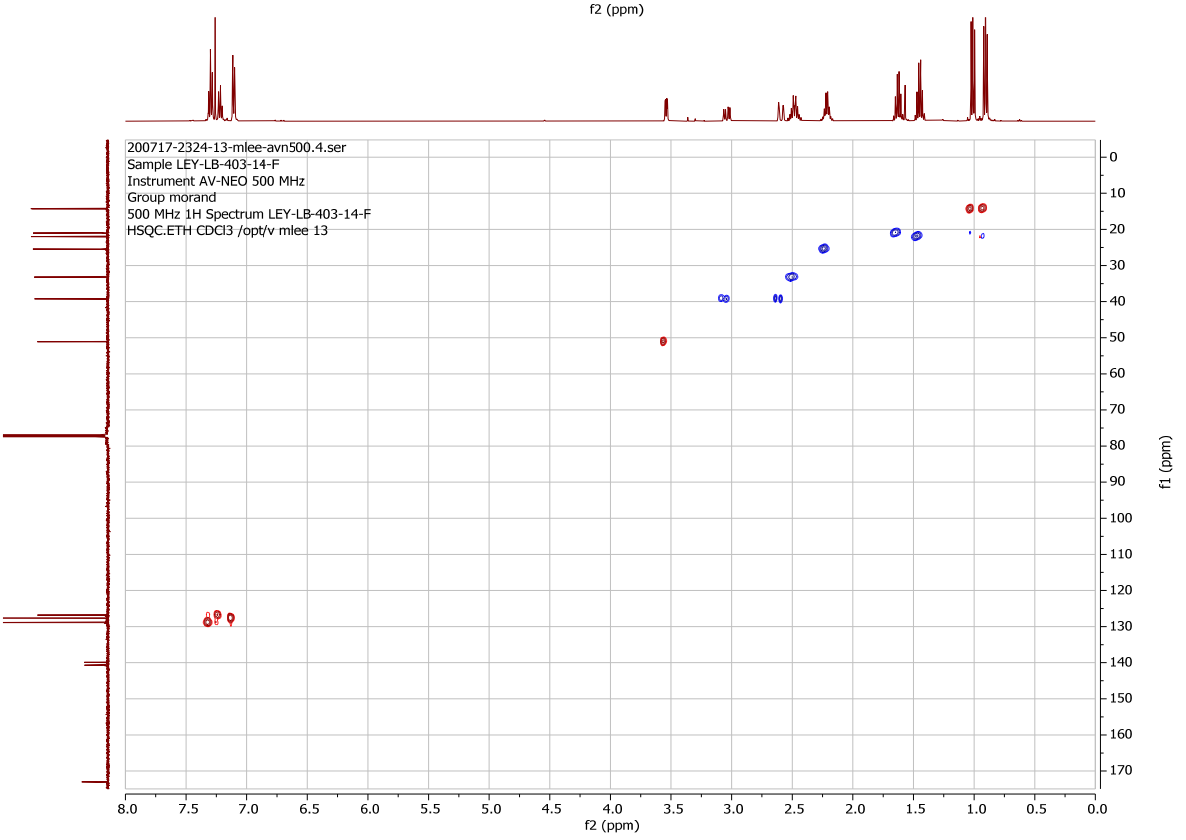



F2730_389-16.12.ser
Yong Lee/Morandi LEY-LB-389-16 OPR:RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

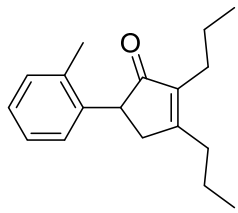
5-phenyl-2,3-dipropylcyclopent-2-en-1-one (**3j**).

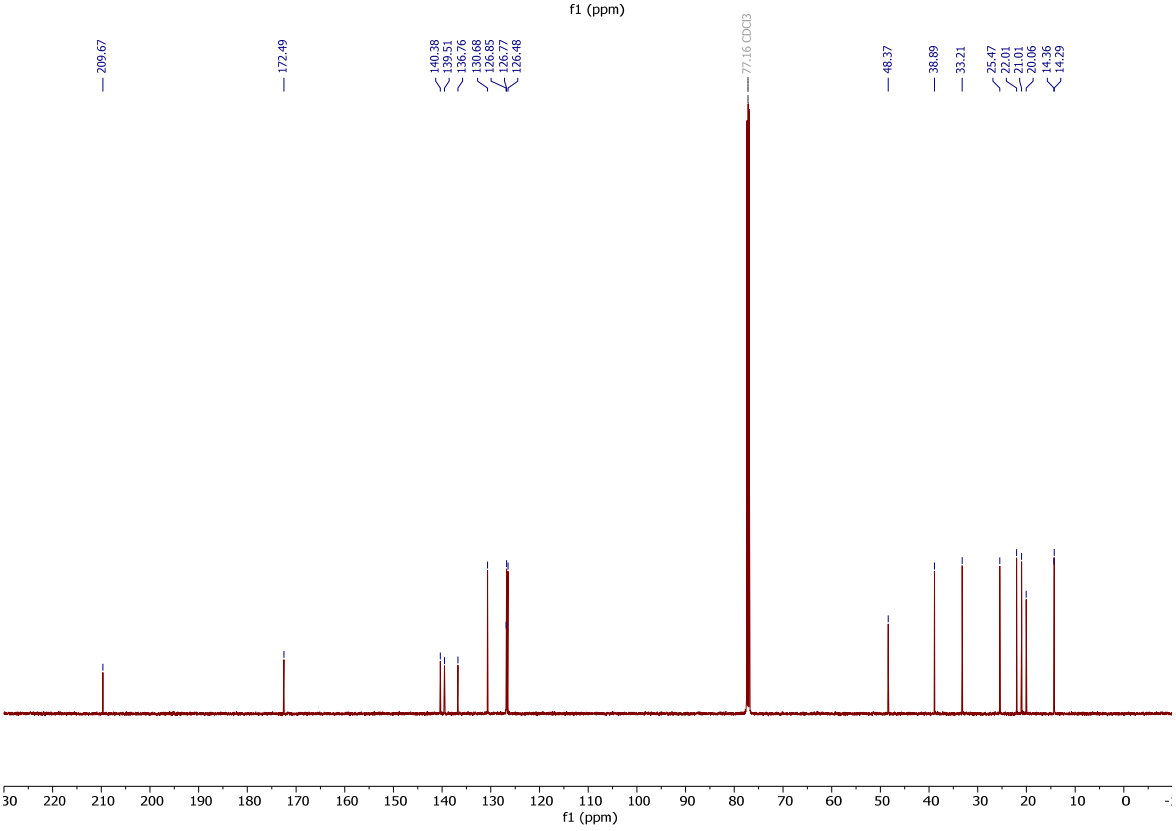


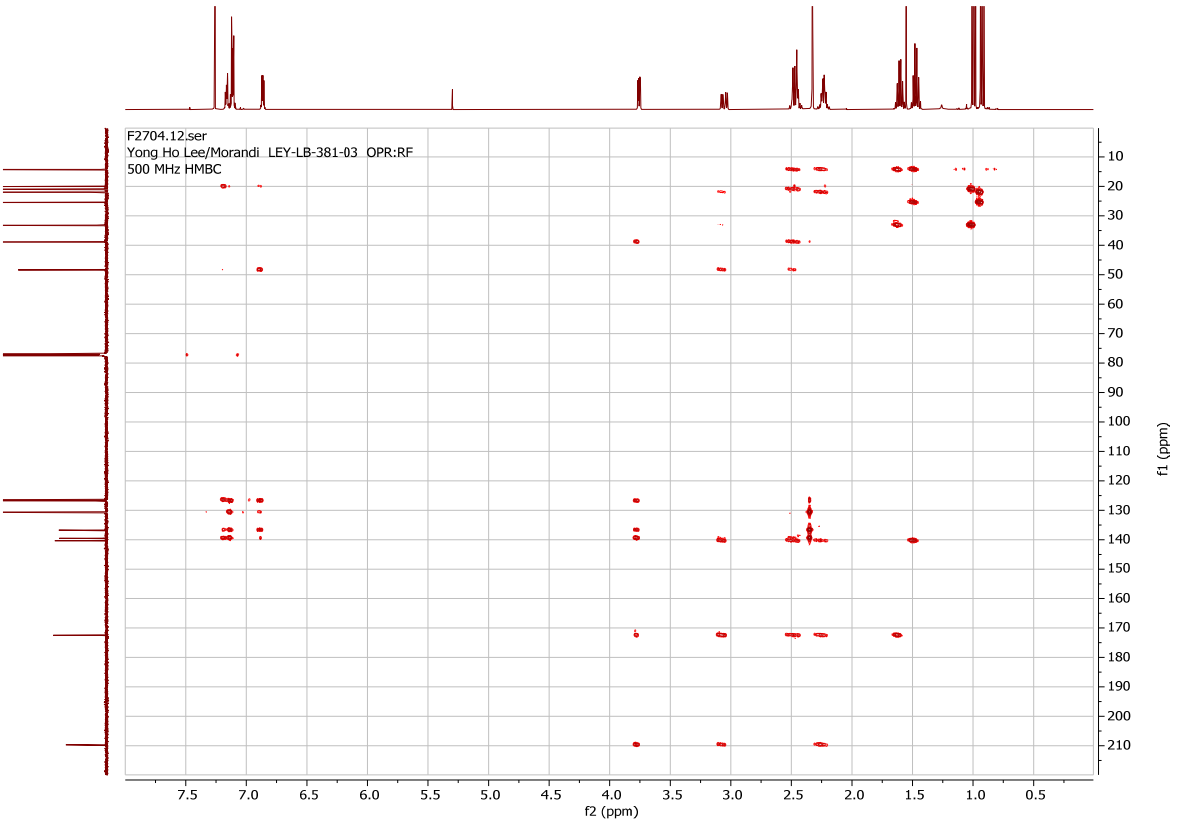

200717-2324-13-mlee-avn500.5.ser
Sample LEY-LB-403-14-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-403-14-F
HMBC.ETH CDCl3 /opt/v mlee 13
f2 (ppm)
f1 (ppm)


200717-2324-13-mlee-avn500.4.ser
Sample LEY-LB-403-14-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-403-14-F
HSQC.ETH CDCl3 /opt/v mlee 13
f2 (ppm)
f1 (ppm)

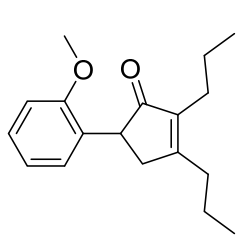
2,3-dipropyl-5-(*o*-tolyl)cyclopent-2-en-1-one (**3k**).

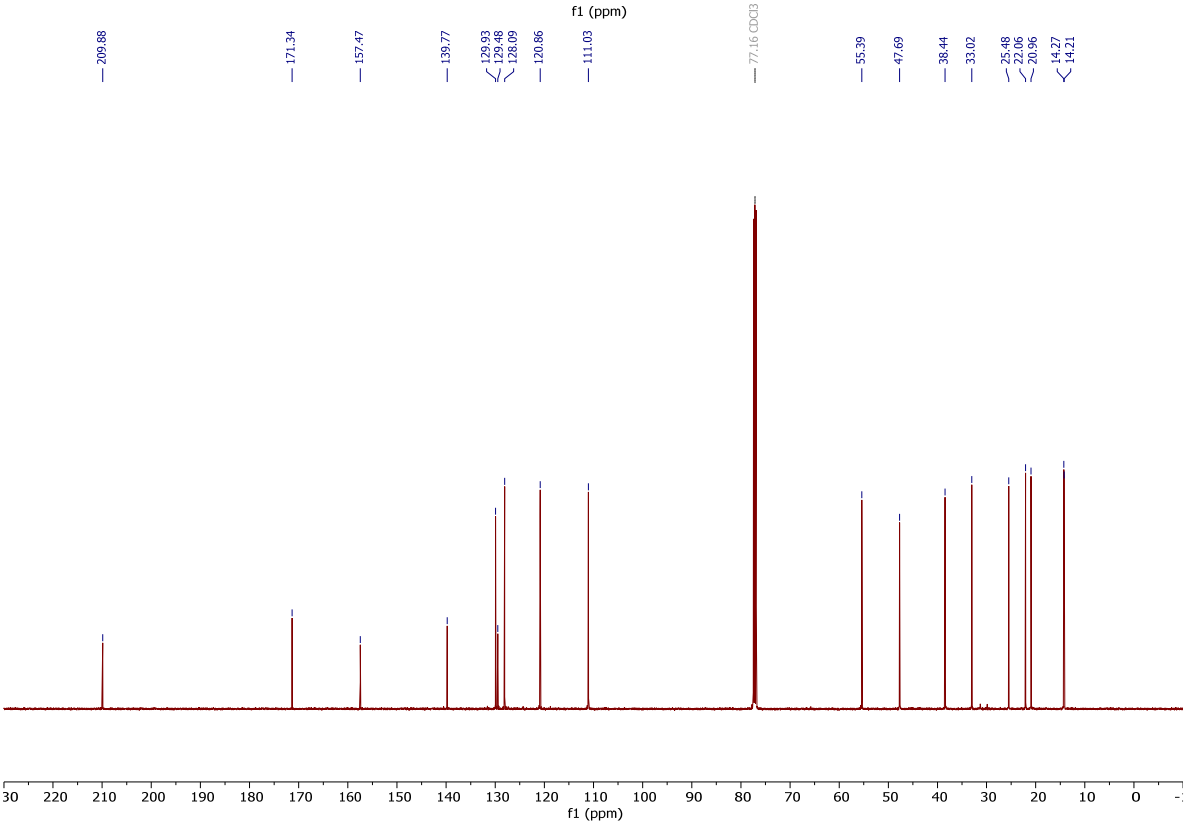


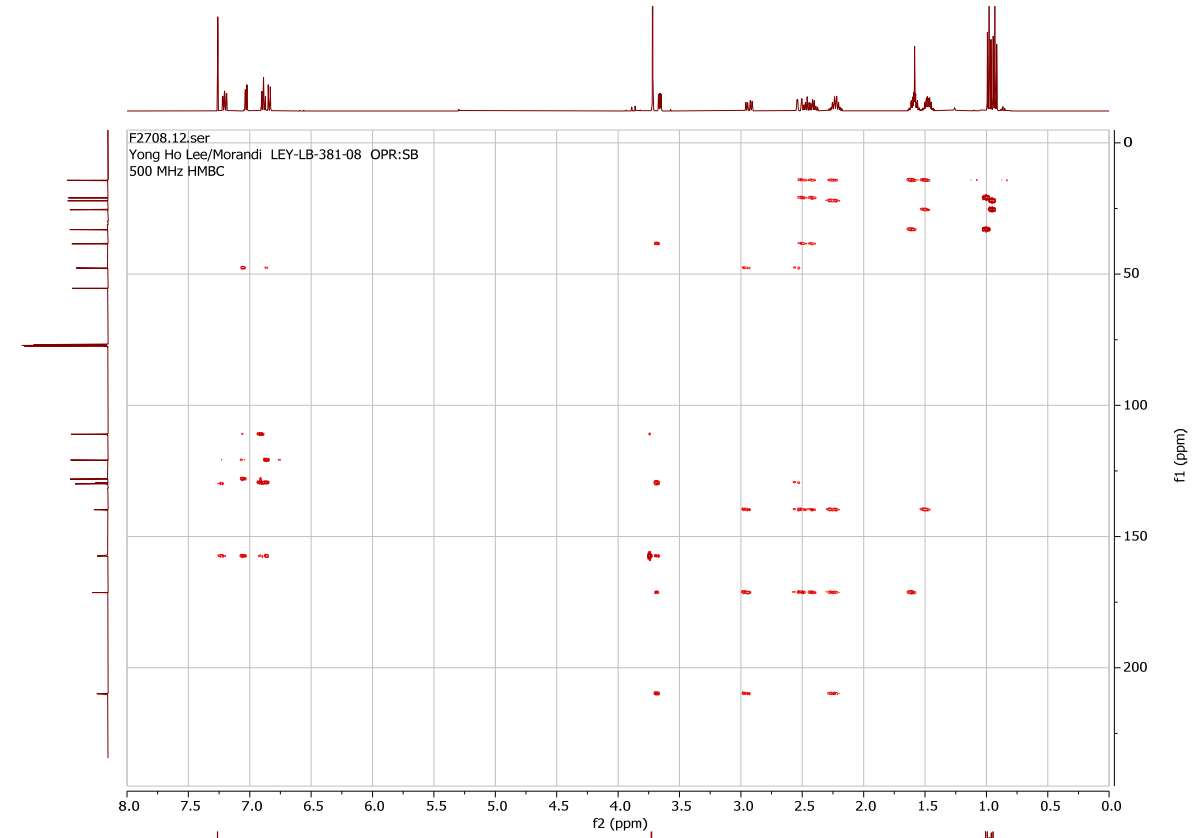


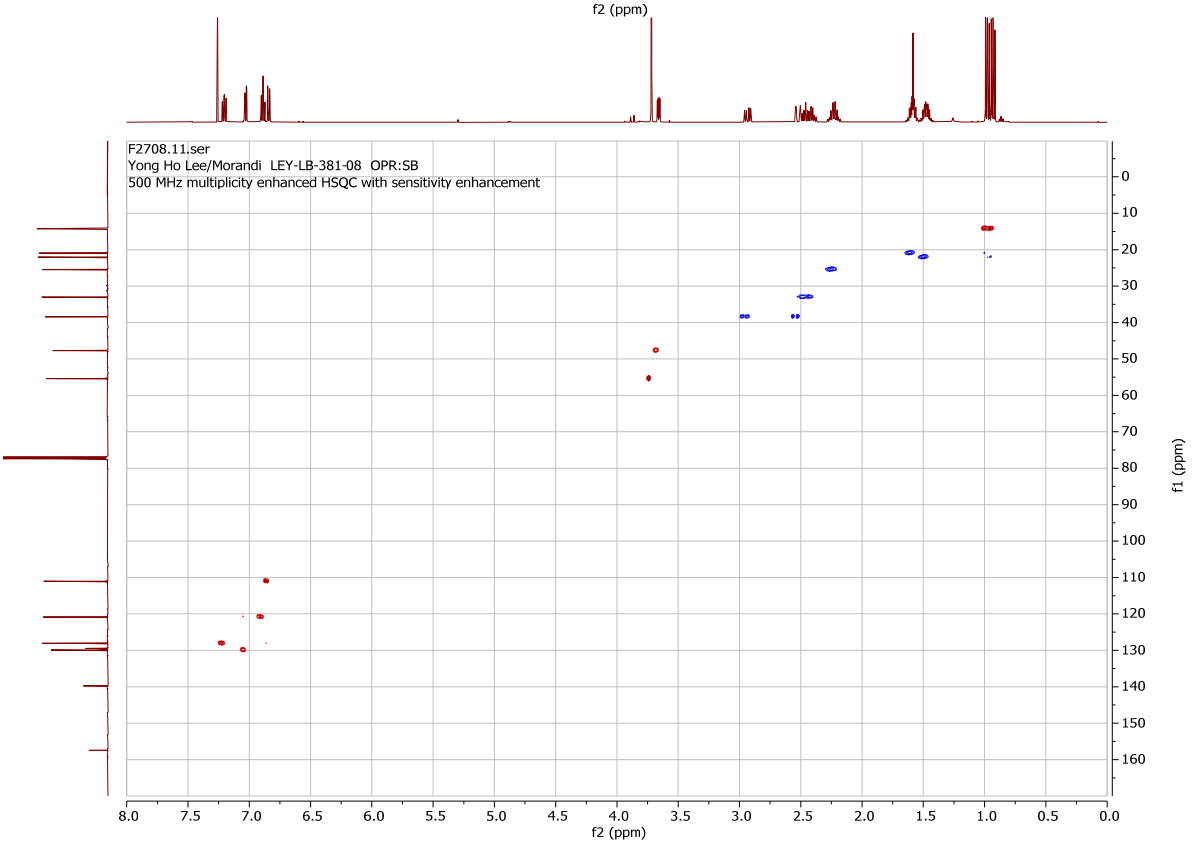

F2704.12.ser
Yong Ho Lee/Morandi LEY-LB-381-03 OPR:RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

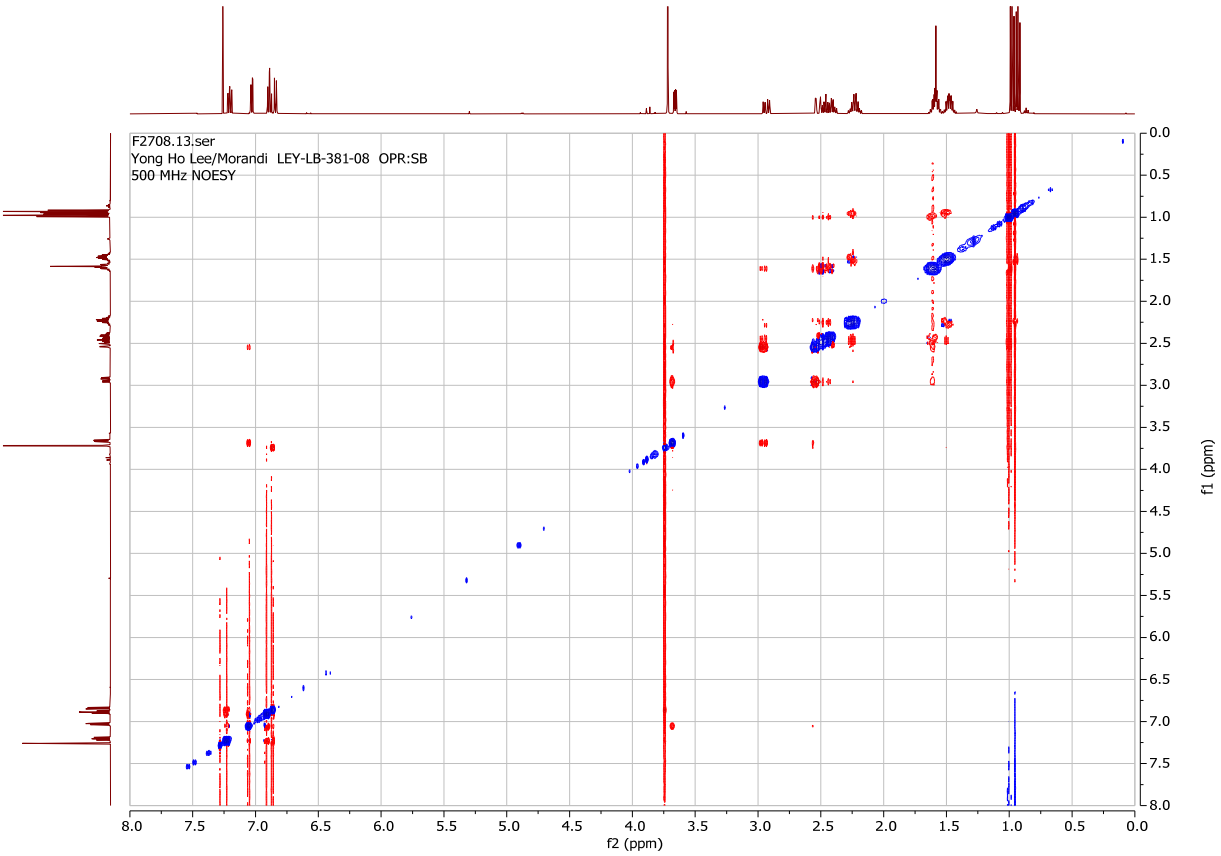
5-(2-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one (**3l**).



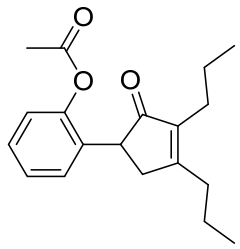


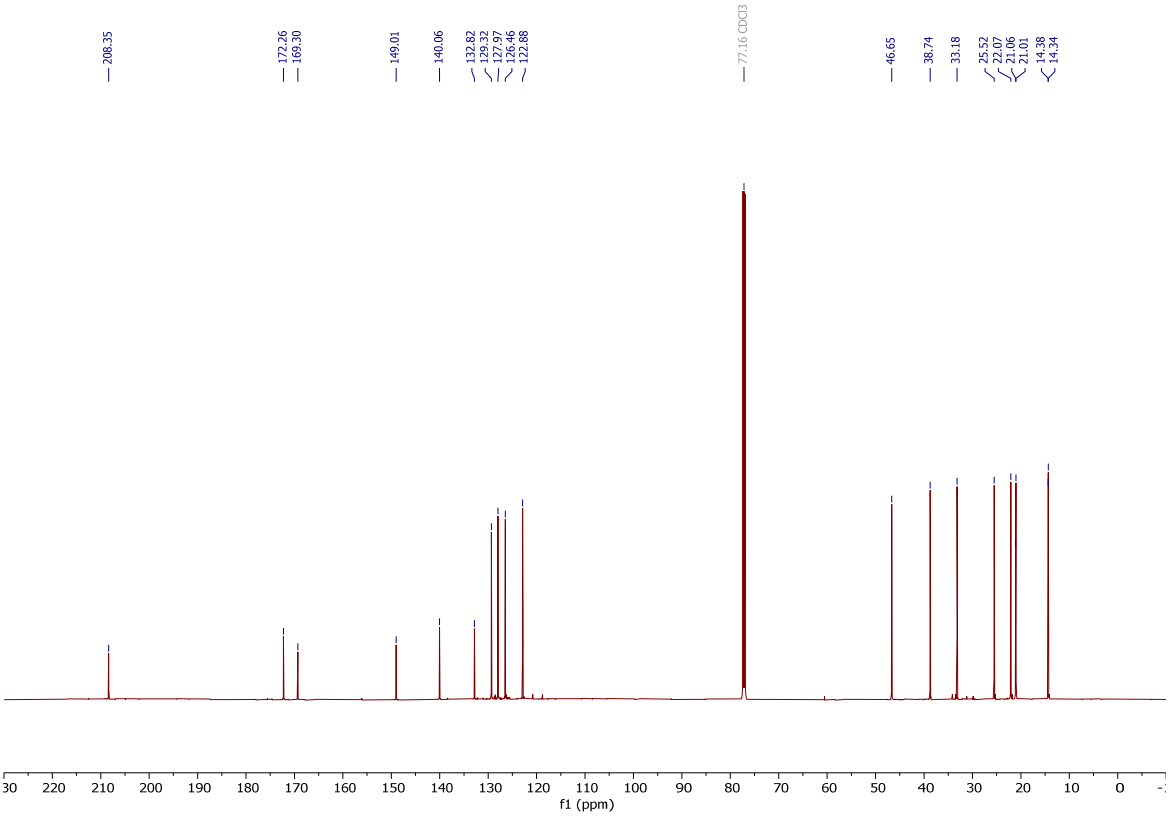

F2708.12.ser
Yong Ho Lee/Morandi LEY-LB-381-08 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

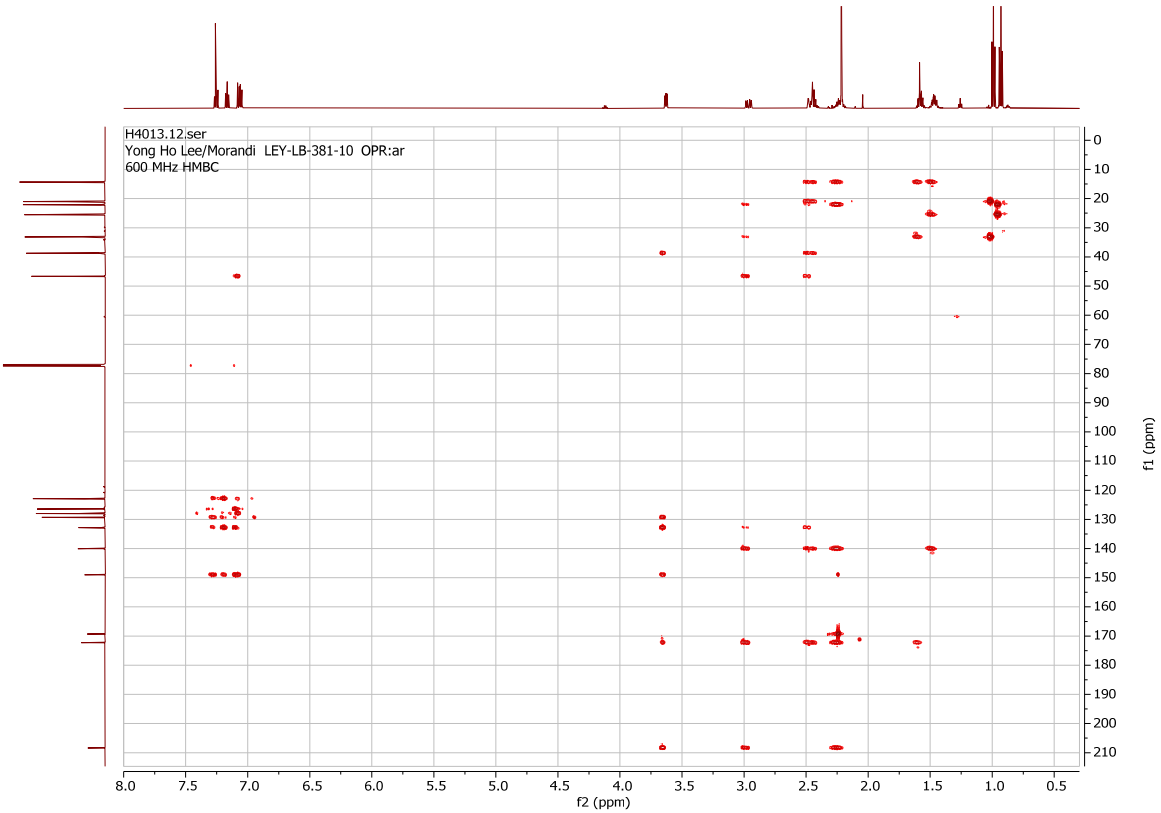

F2708.11.ser
Yong Ho Lee/Morandi LEY-LB-381-08 OPR:SB
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)


F2708.13.ser
Yong Ho Lee/Morandi LEY-LB-381-08 OPR:SB
500 MHz NOESY
f2 (ppm)
f1 (ppm)

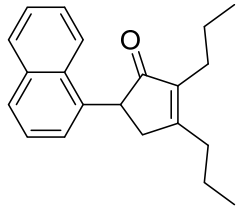
2-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)phenyl acetate (**3m**).

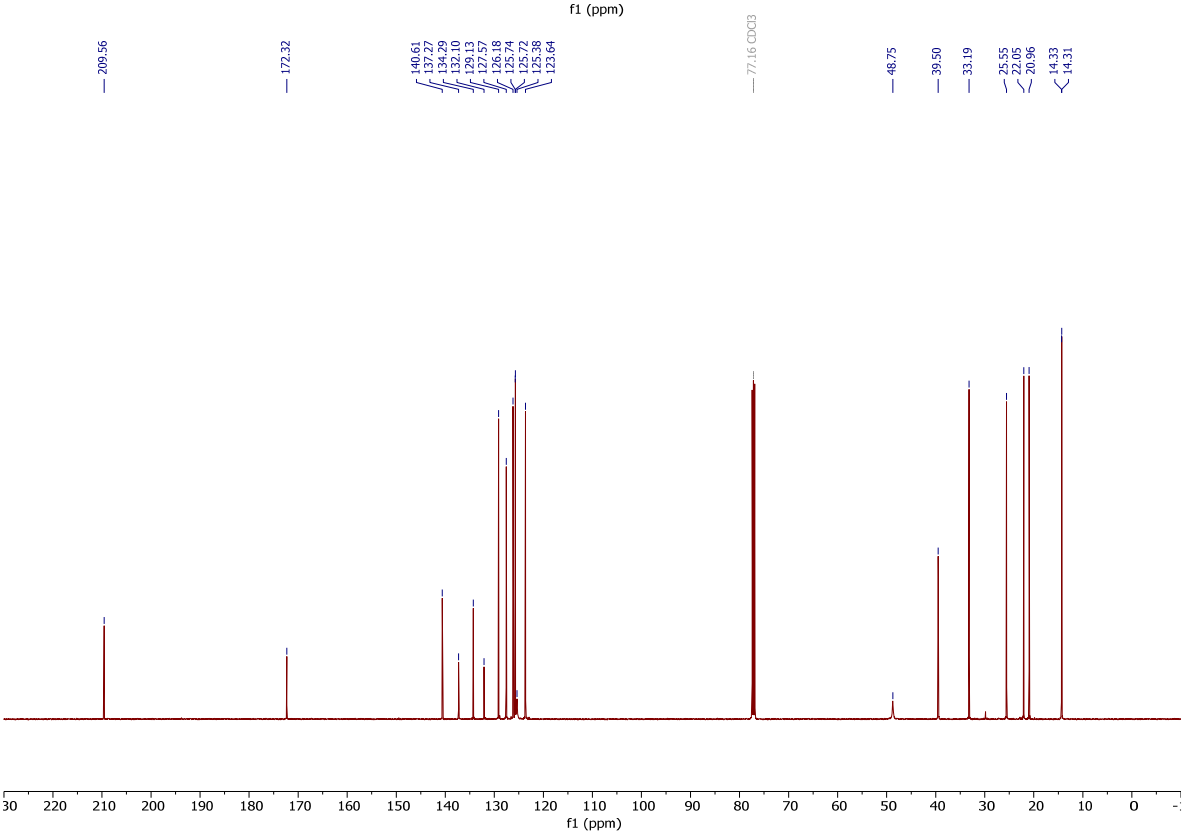


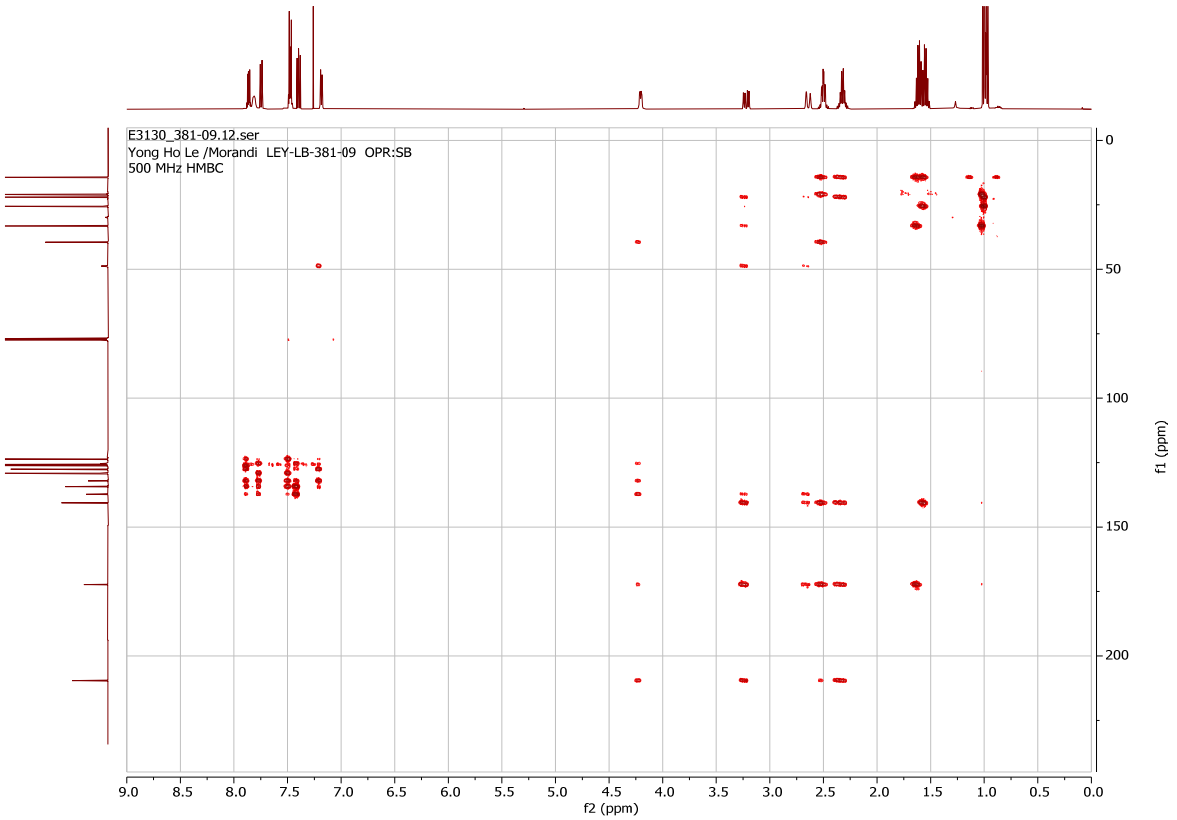



H4013.12.ser
Yong Ho Lee/Morandi LEY-LB-381-10 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

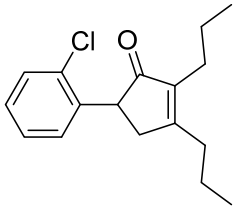
5-(naphthalen-1-yl)-2,3-dipropylcyclopent-2-en-1-one (**3n**).

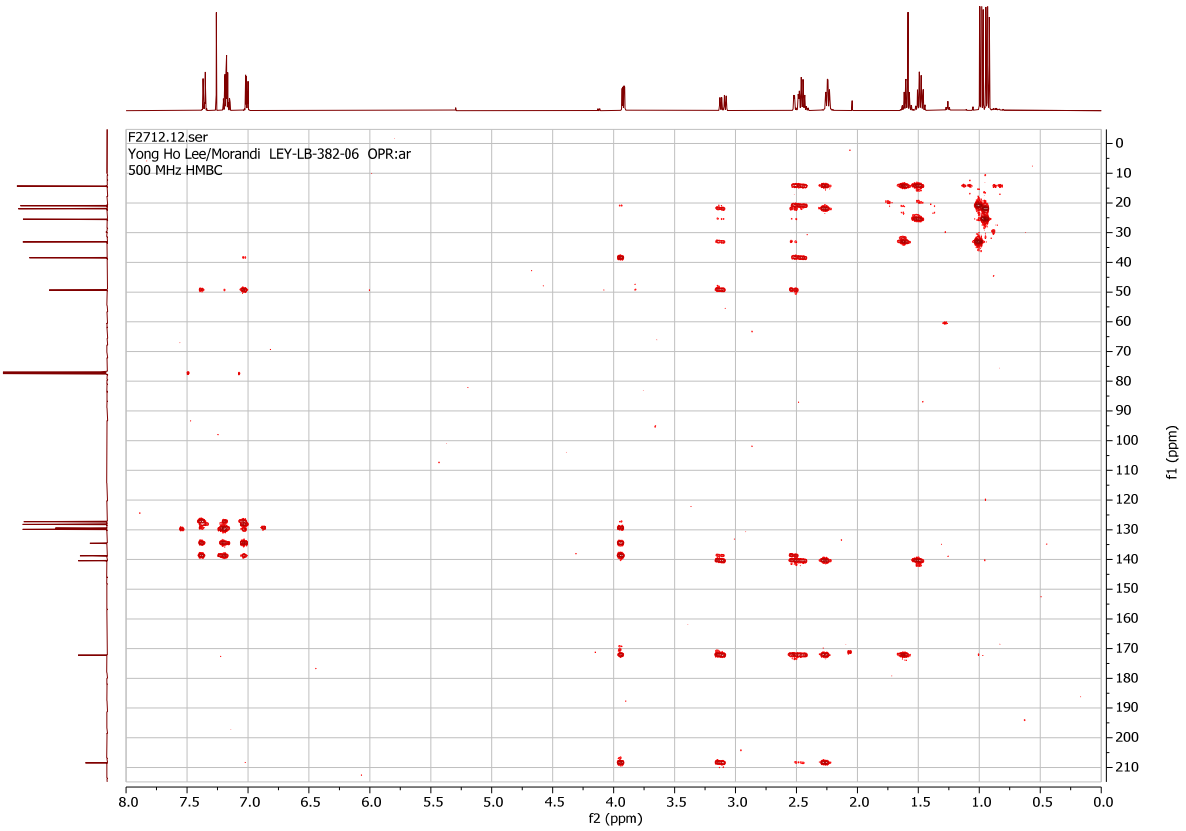




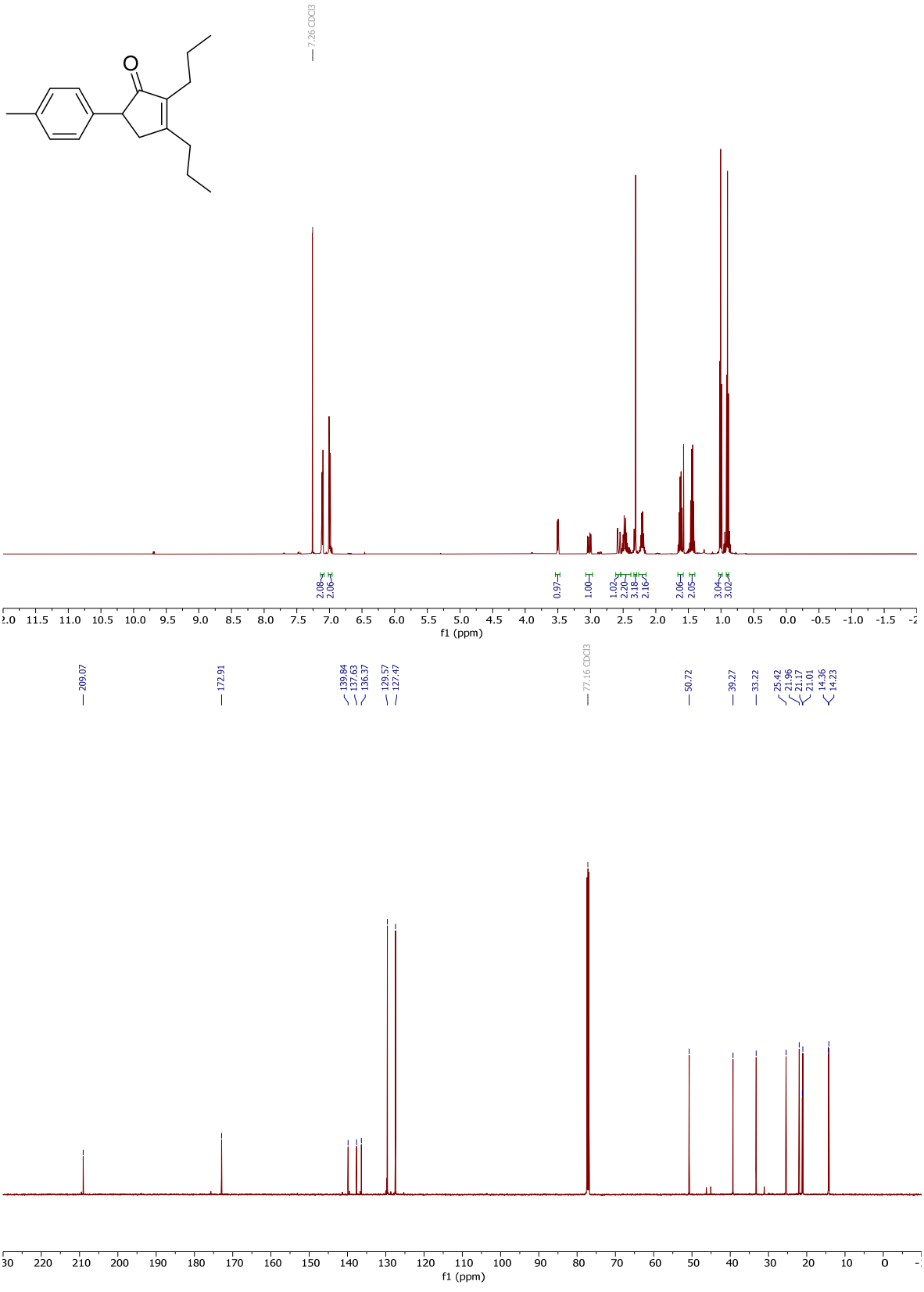

E3130_381-09.12.ser
Yong Ho Le /Morandi LEY-LB-381-09 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

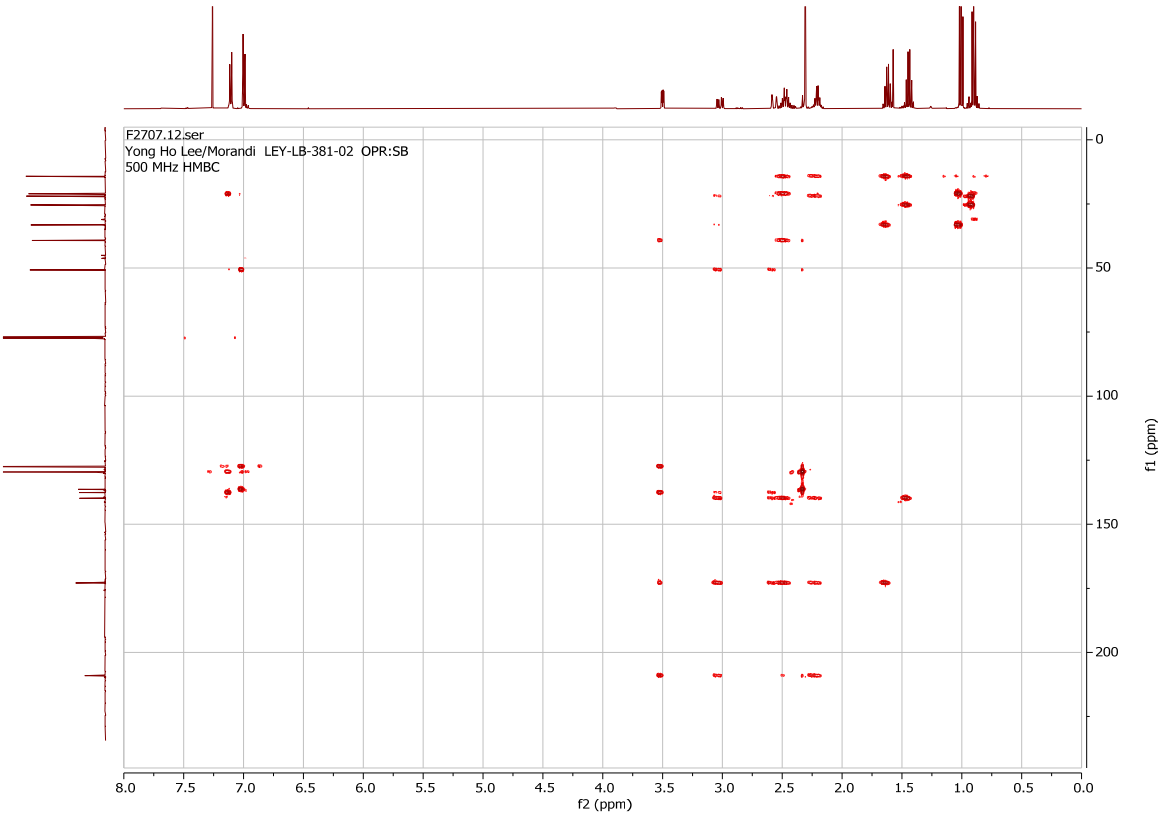
5-(2-chlorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3o**).



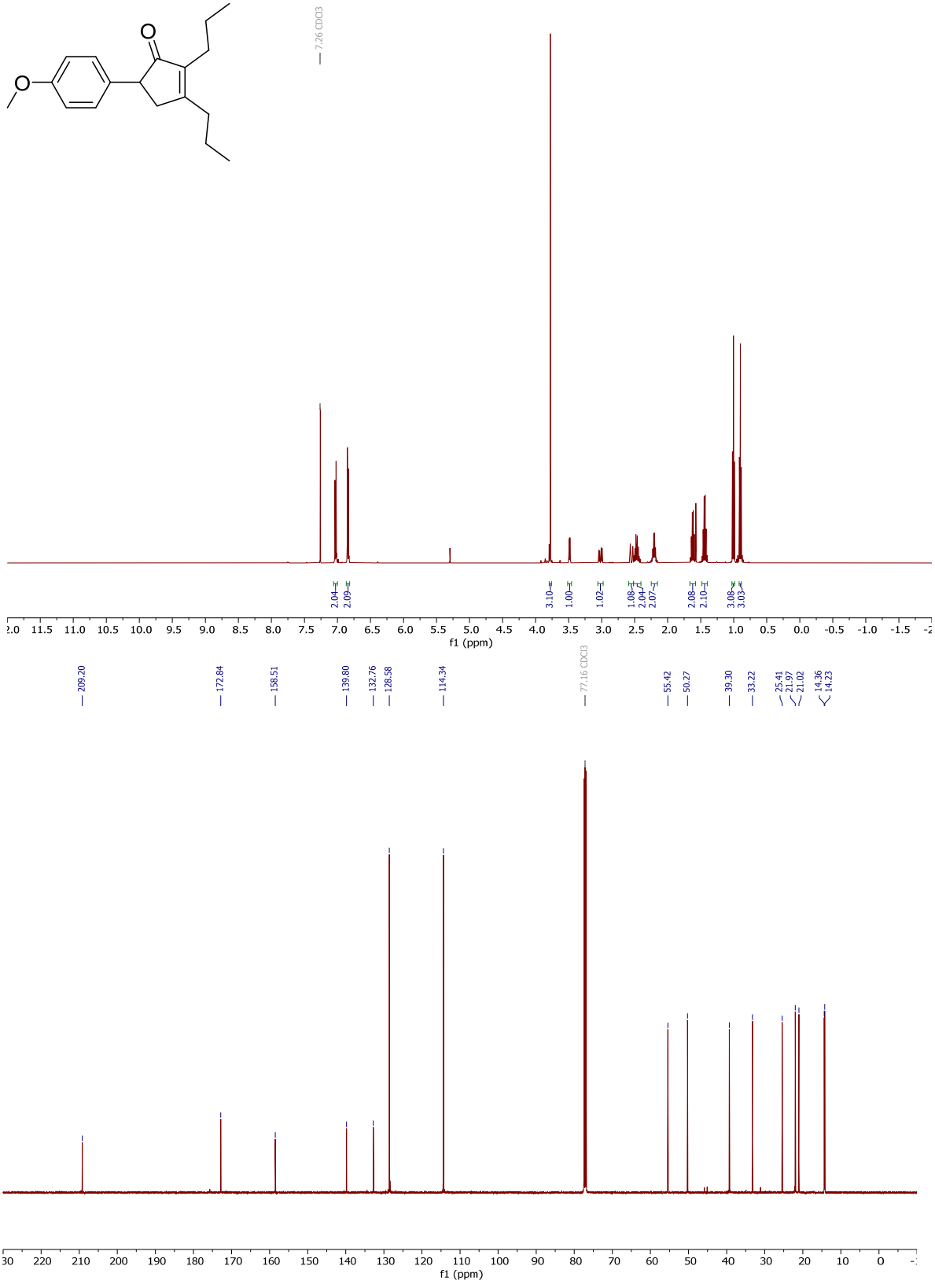

F2712.12.ser
Yong Ho Lee/Morandi LEY-LB-382-06 OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

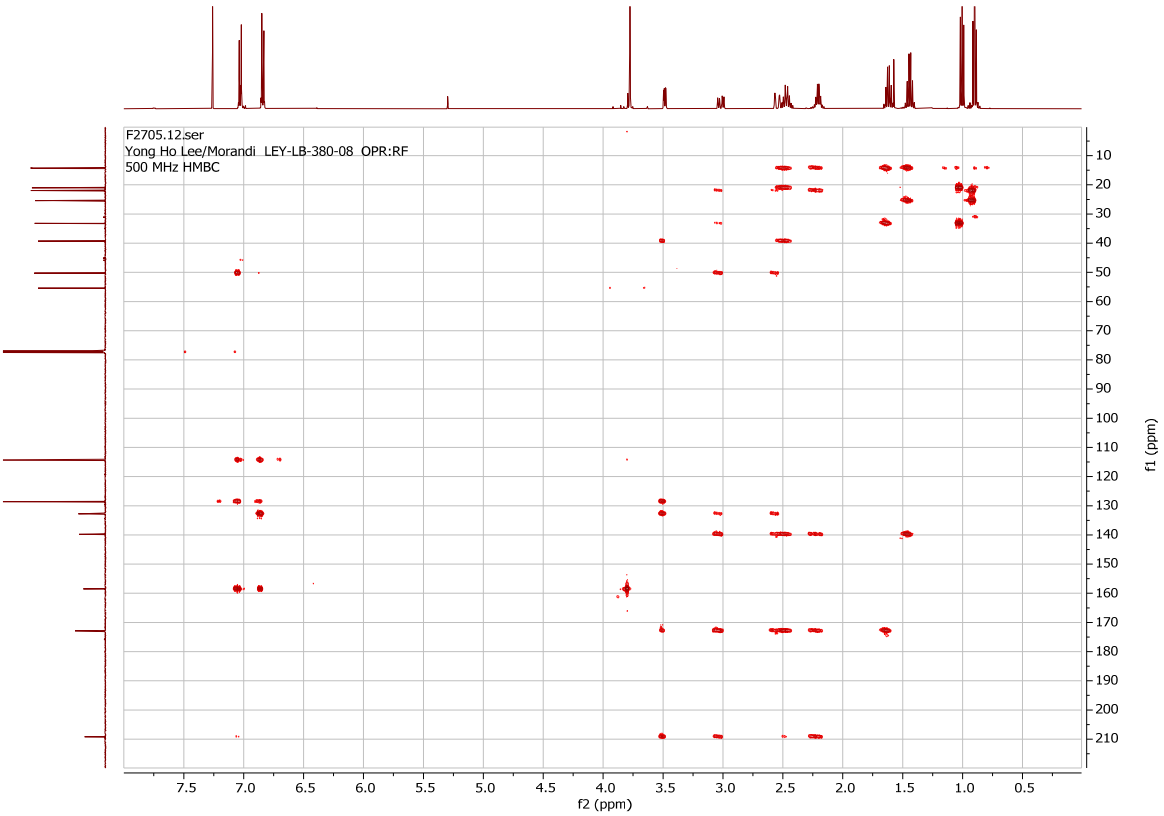
2,3-dipropyl-5-(*p*-tolyl)cyclopent-2-en-1-one (**3p**).



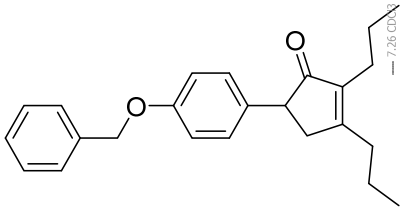

F2707.12.ser
Yong Ho Lee/Morandi LEY-LB-381-02 OPR:SB
500 MHz HMBC
f1 (ppm)
f2 (ppm)

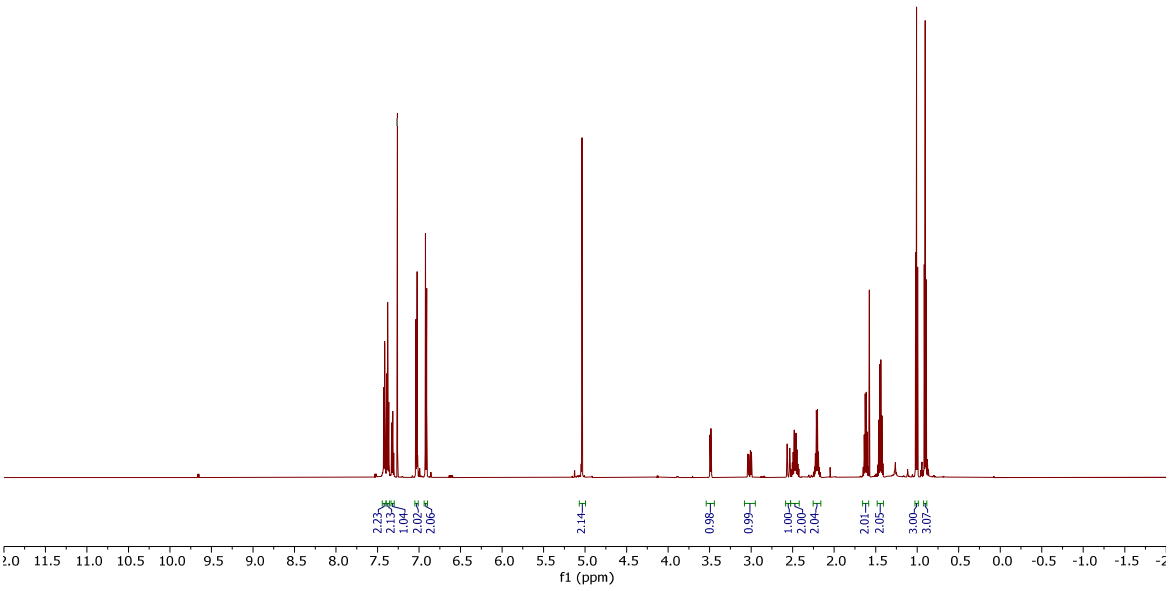
5-(4-methoxyphenyl)-2,3-dipropylcyclopent-2-en-1-one (**3q**).

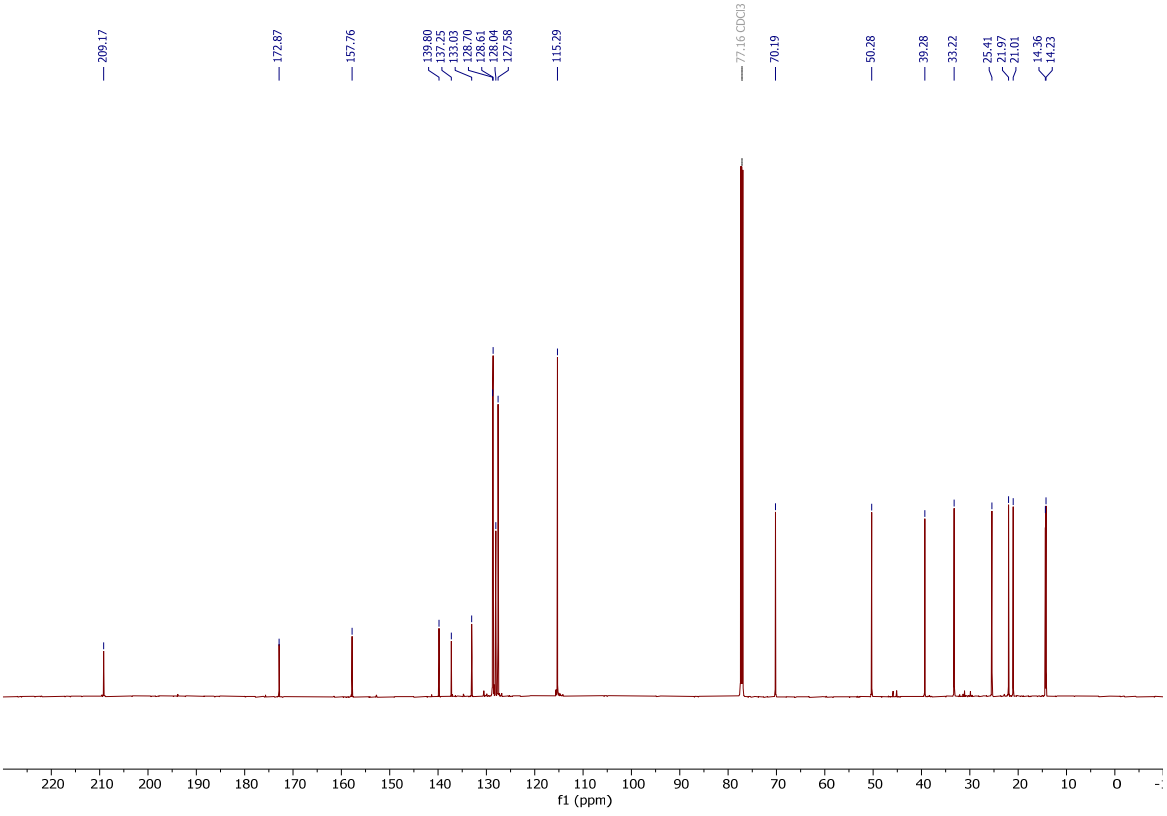


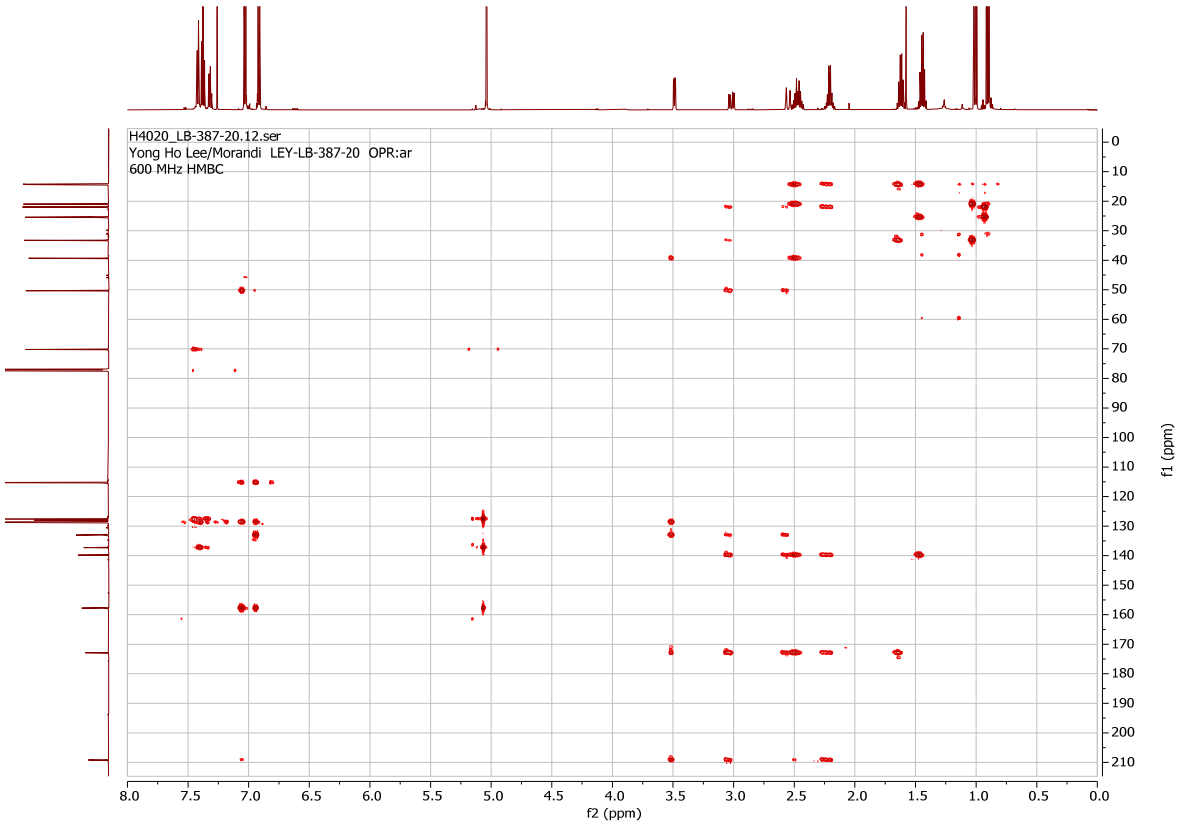

F2705.12.ser
Yong Ho Lee/Morandi LEY-LB-380-08 OPR:RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

5-(4-(benzyloxy)phenyl)-2,3-dipropylcyclopent-2-en-1-one (**3r**).

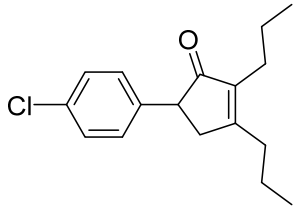


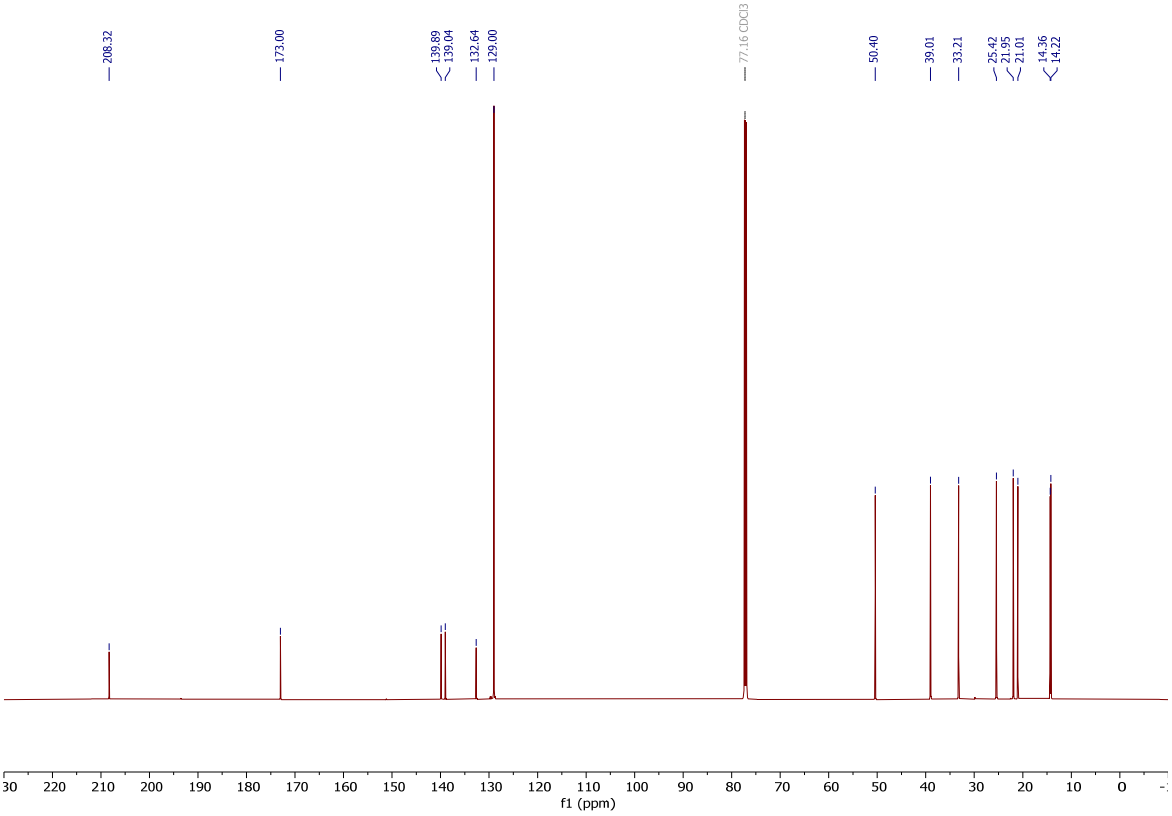


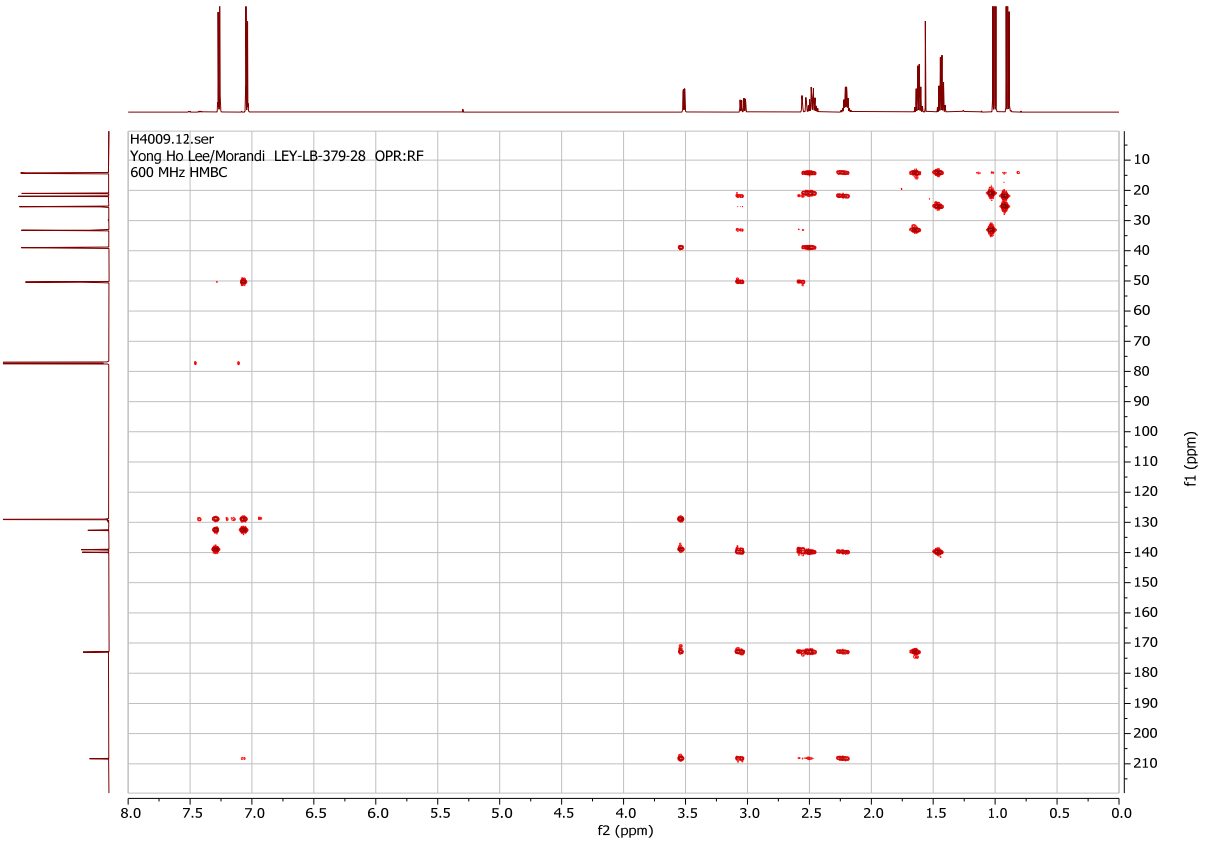



H4020_LB-387-20.12.ser
Yong Ho Lee/Morandi LEY-LB-387-20 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

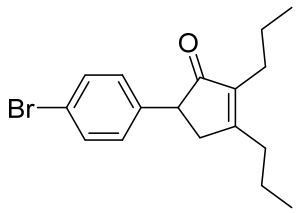
5-(4-chlorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3s**).

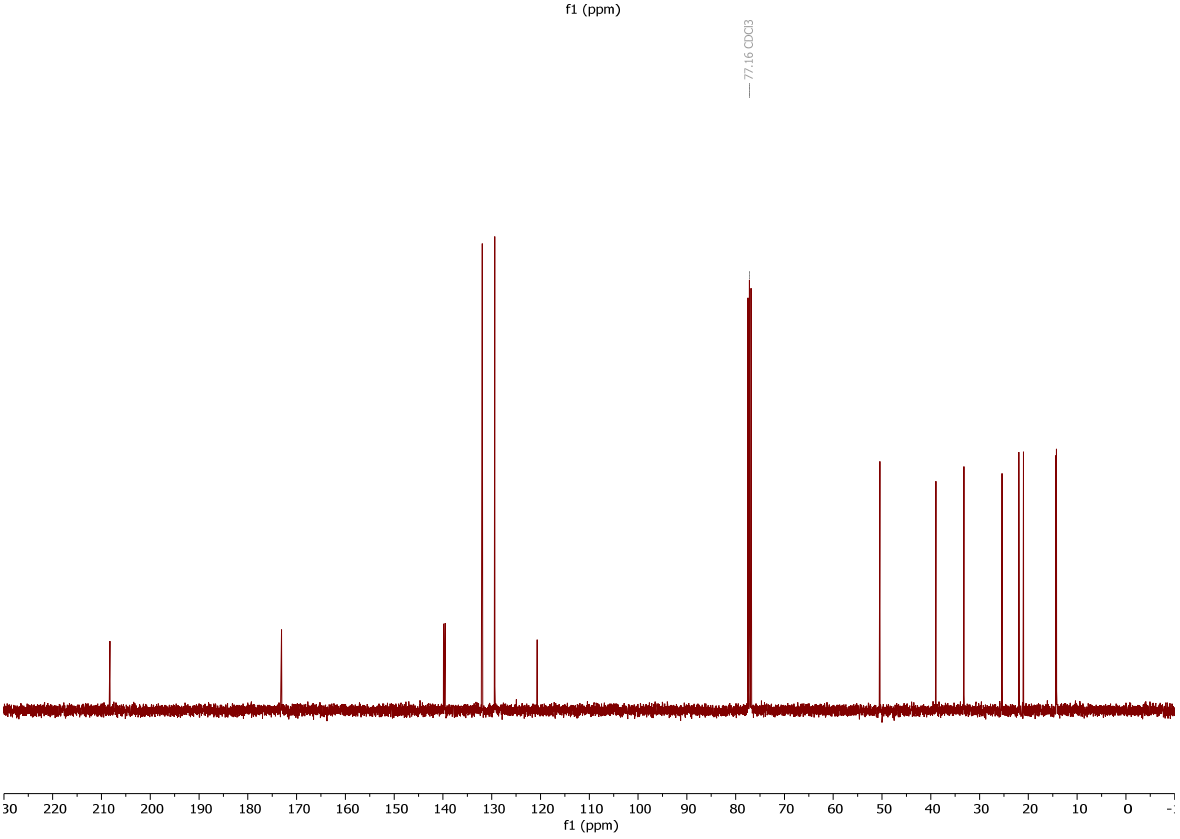


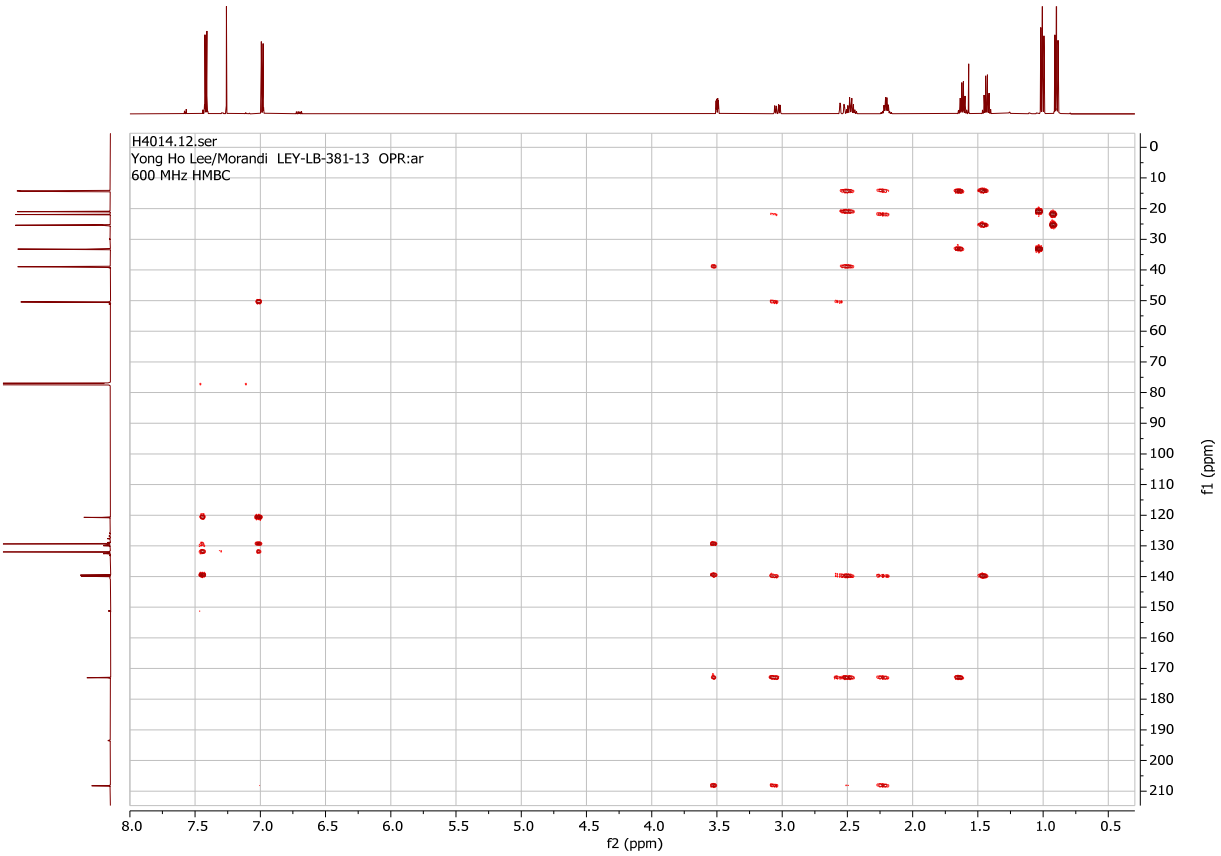



H4009.12.ser
Yong Ho Lee/Morandi LEY-LB-379-28 OPR:RF
600 MHz HMBC
f2 (ppm)
f1 (ppm)

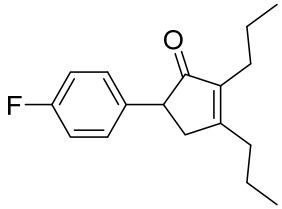
5-(4-bromophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3t**).

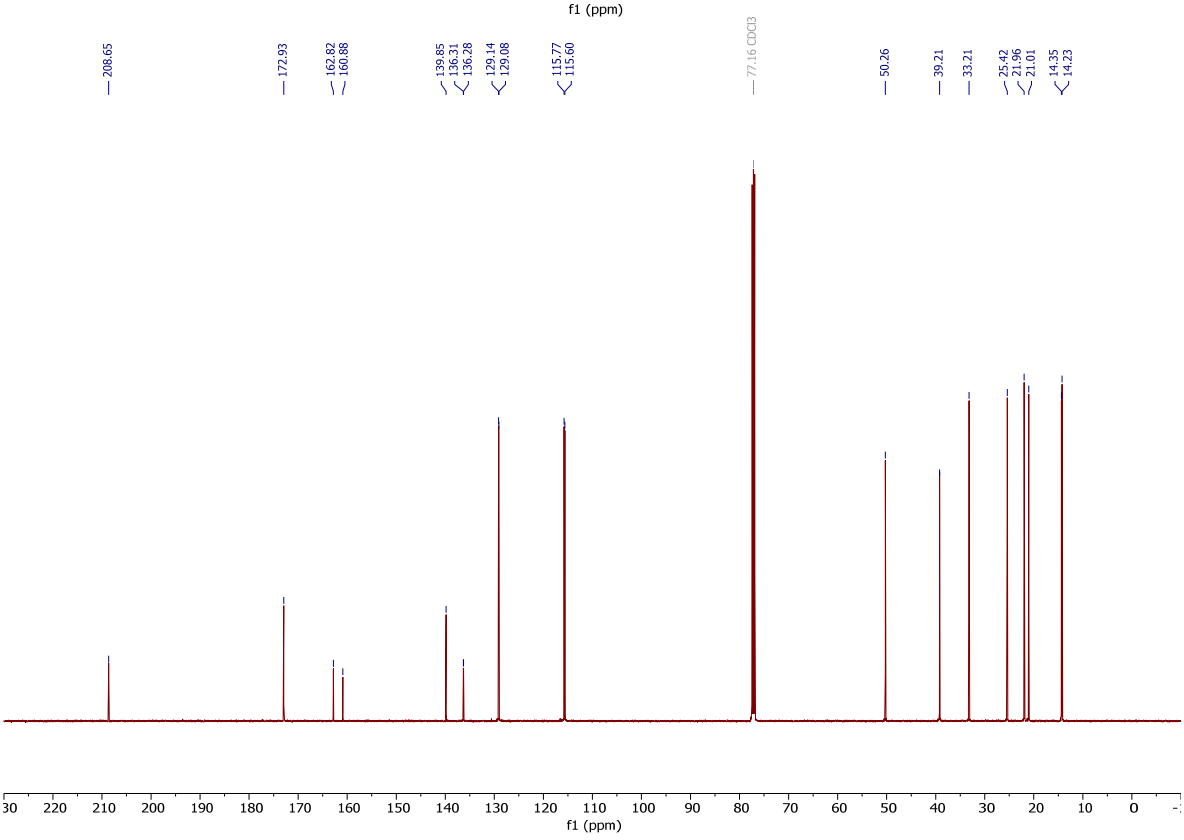


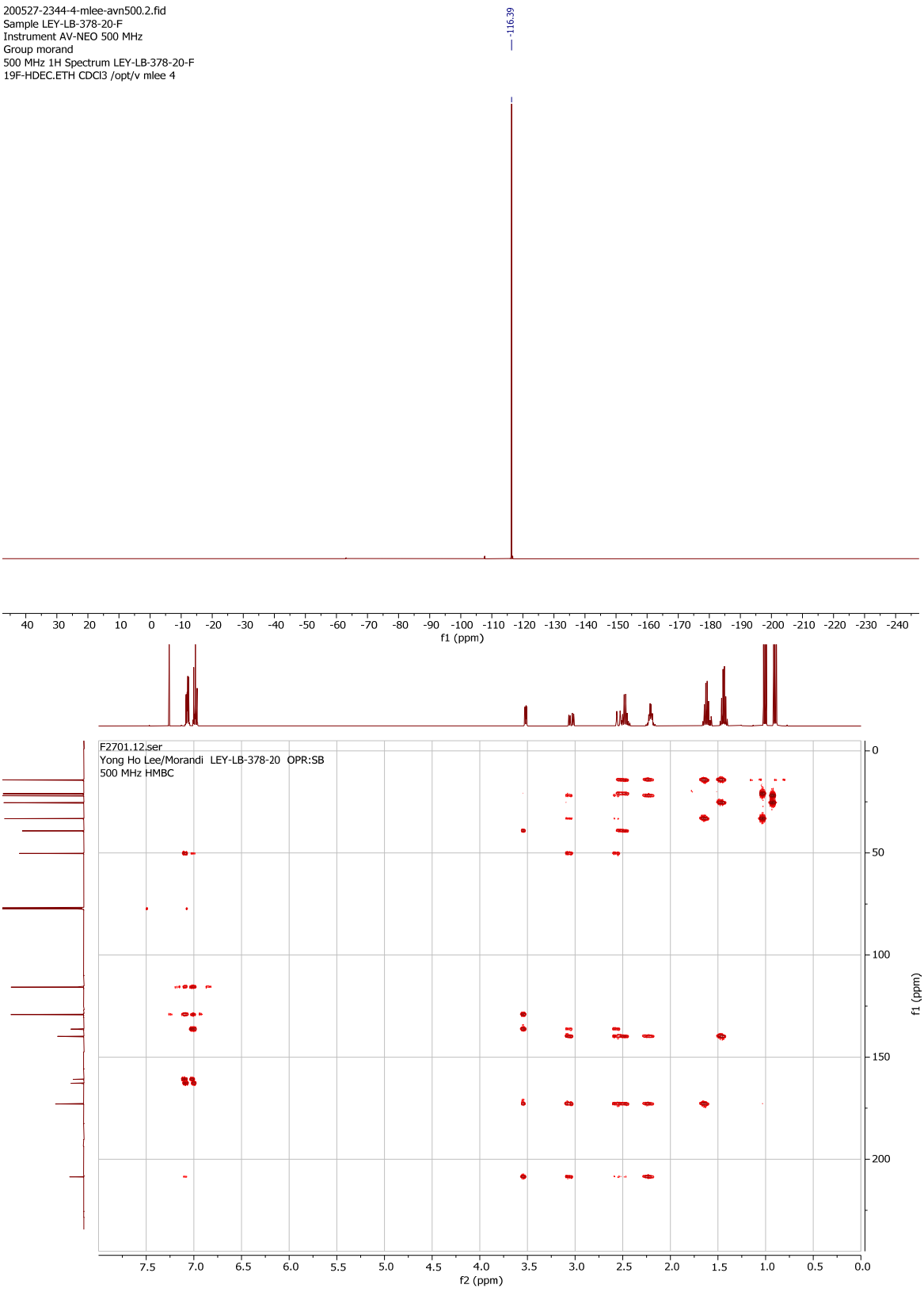



H4014.12.ser
Yong Ho Lee/Morandi LEY-LB-381-13 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

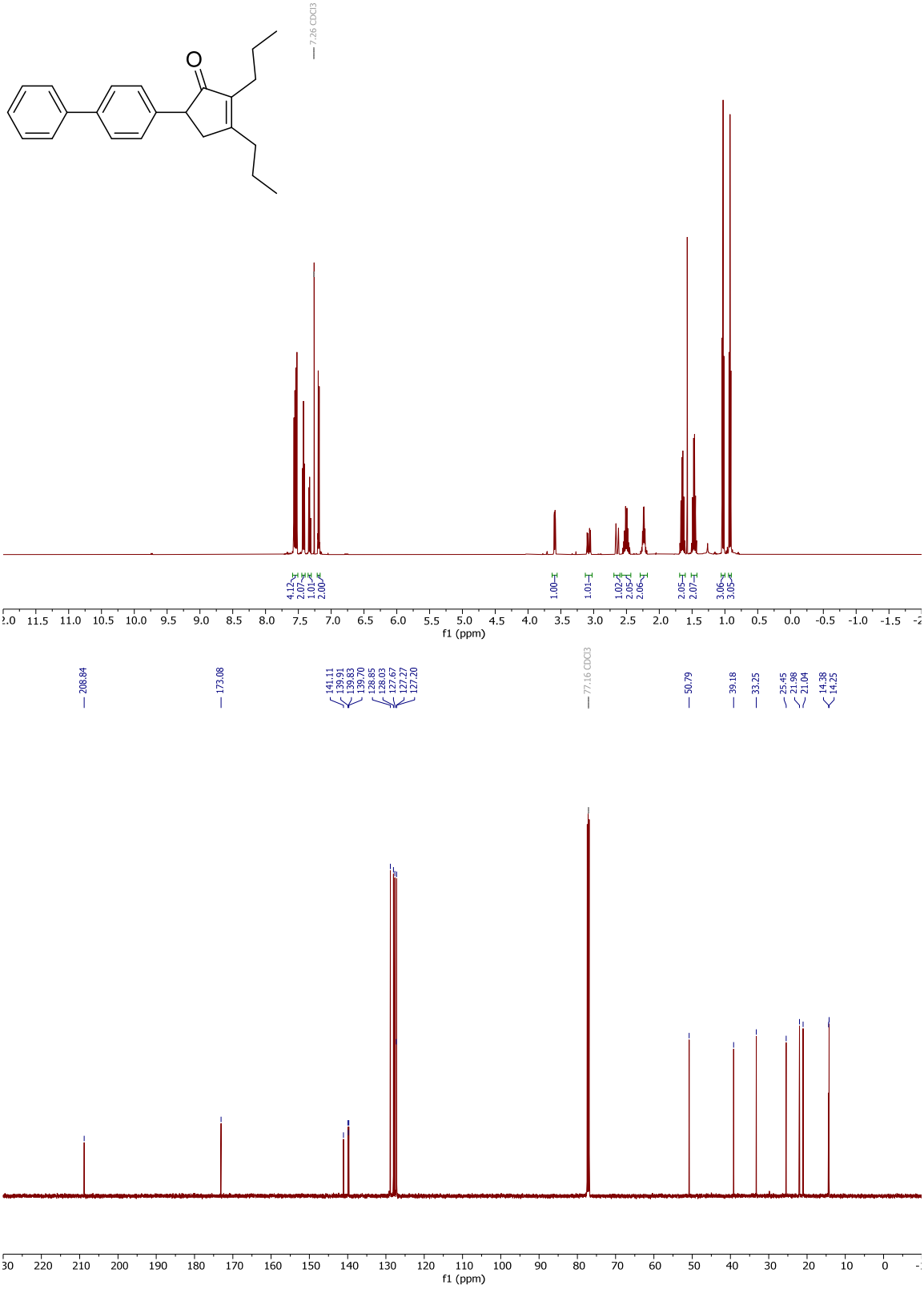
5-(4-fluorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3u**).

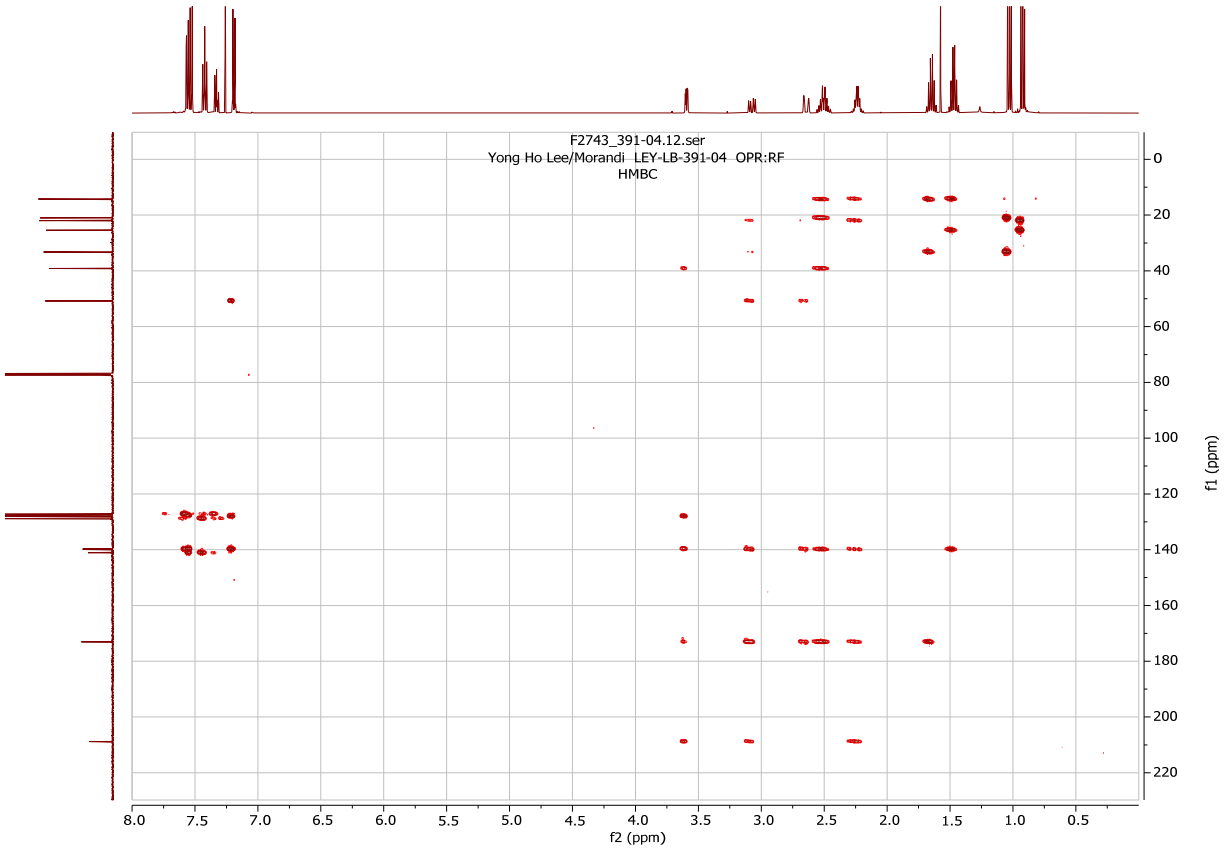




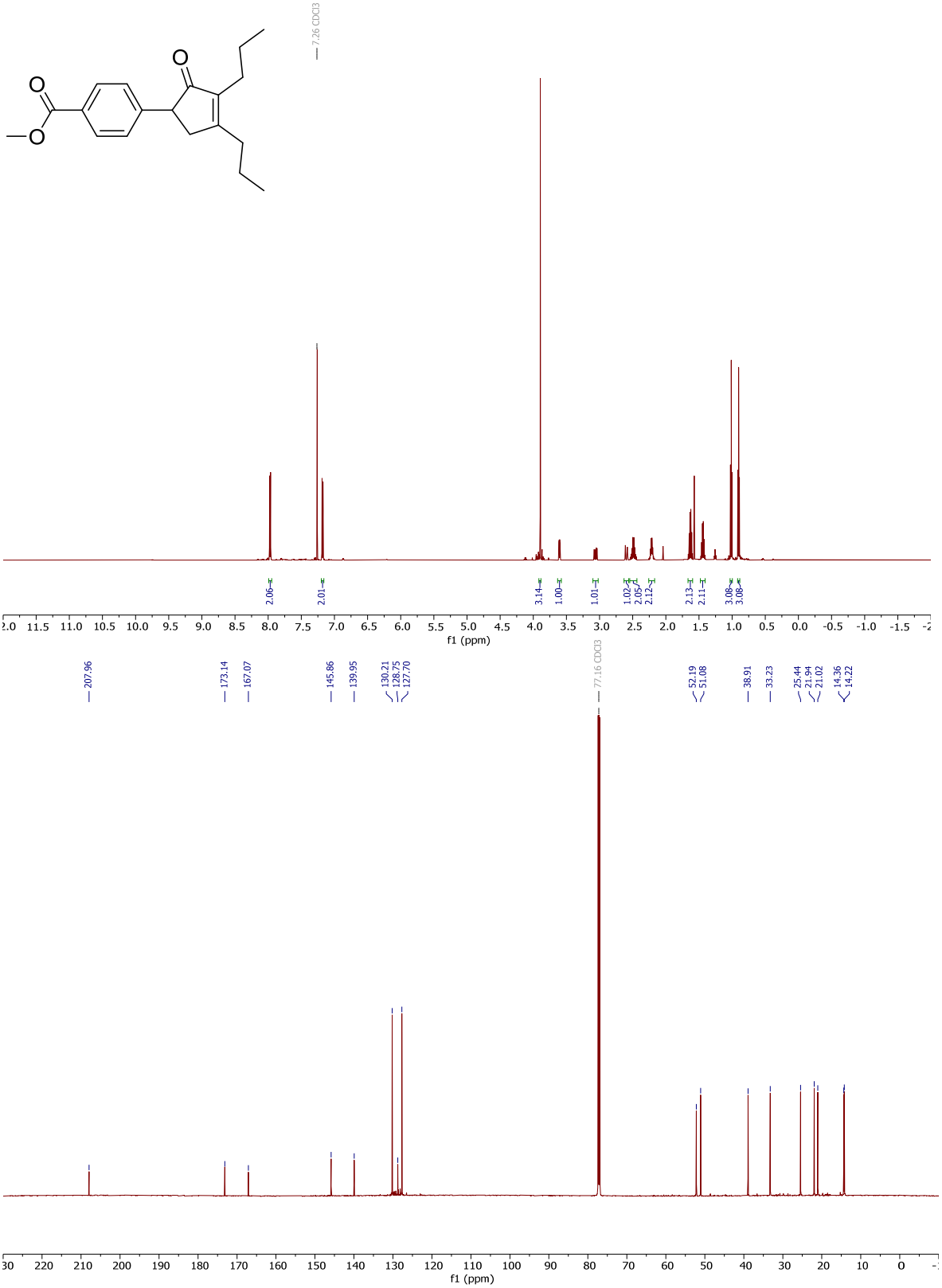

200527-2344-4-mlee-avn500.2.fid
Sample LEY-LB-378-20-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-378-20-F
19F-HDEC.ETH CDCl3 /opt/v mlee 4
-116.39
f1 (ppm)
F2701.12.ser
Yong Ho Lee/Morandi LEY-LB-378-20 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

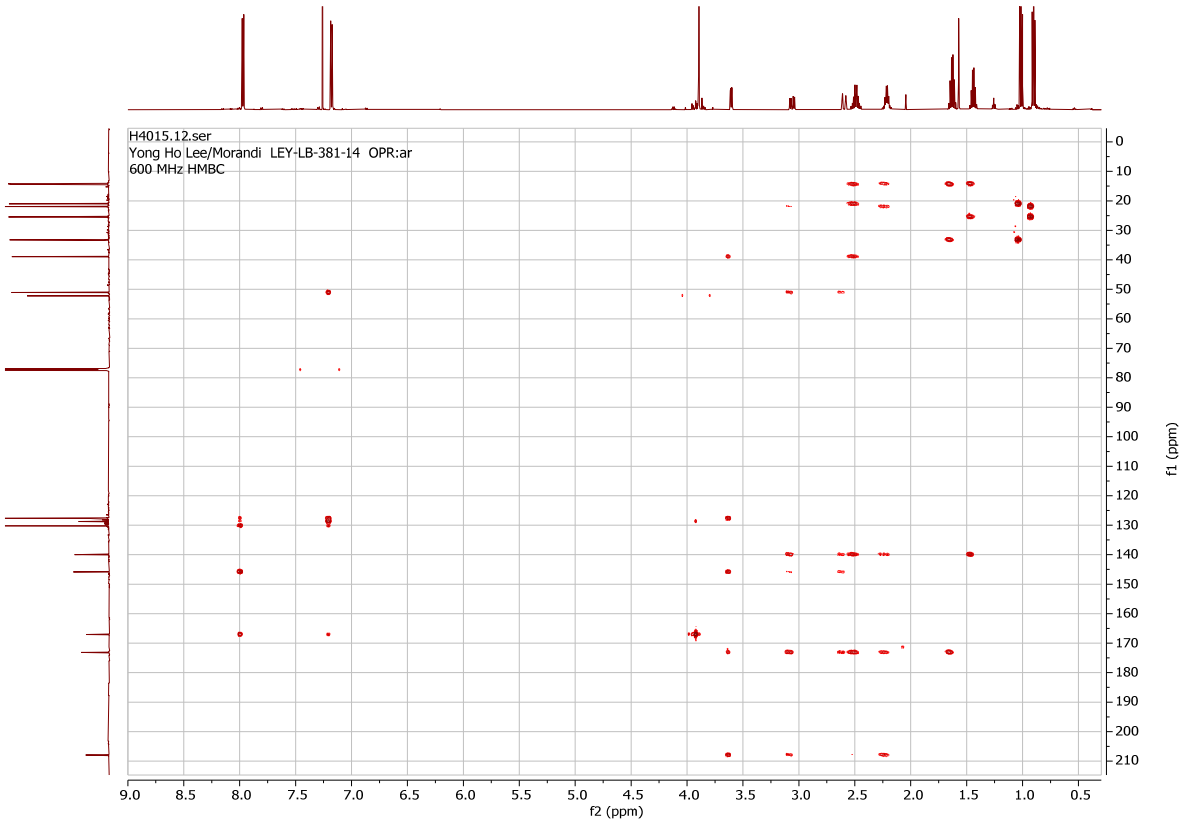
5-([1,1'-biphenyl]-4-yl)-2,3-dipropylcyclopent-2-en-1-one (**3v**).



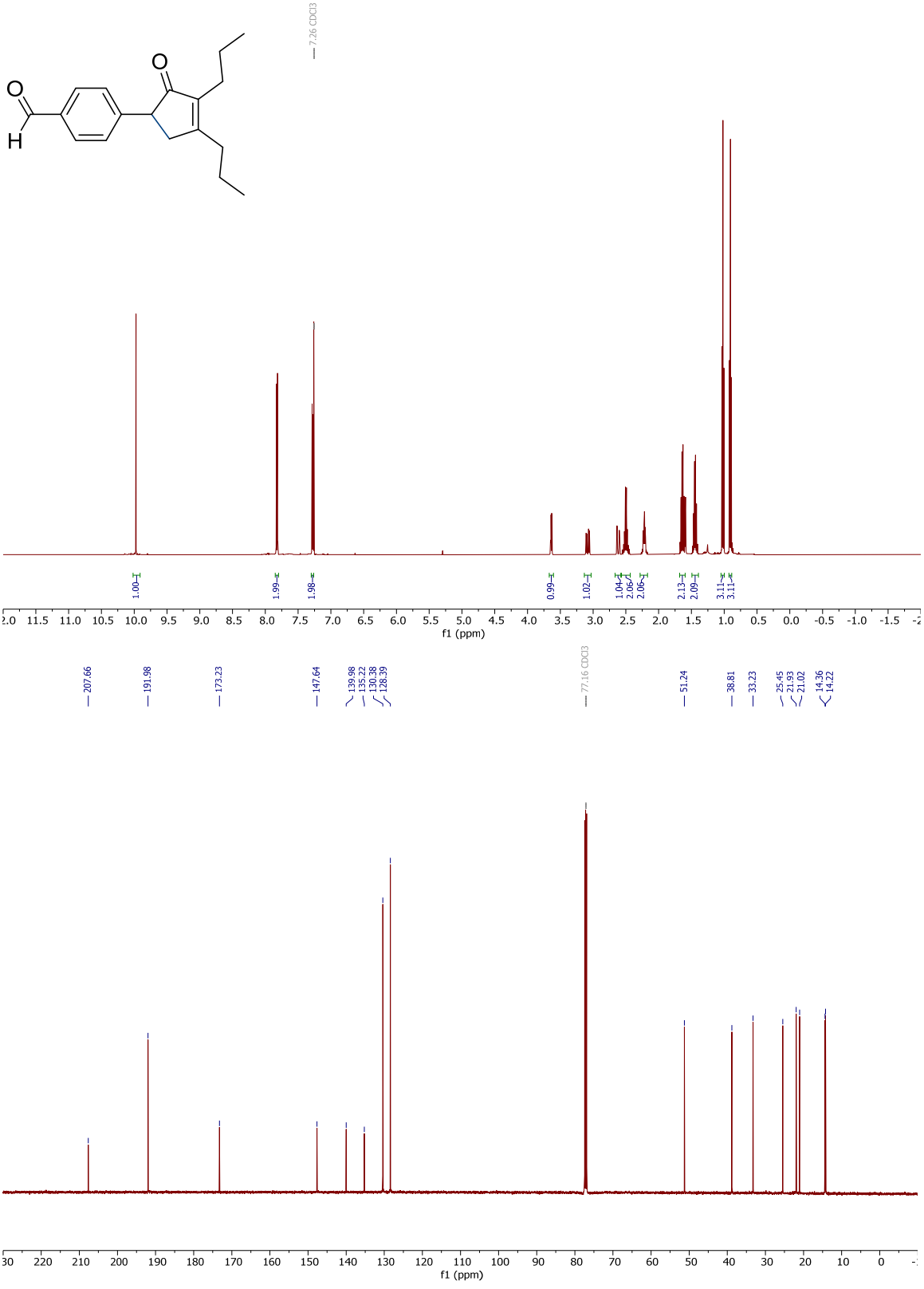

F2743_391-04.12.ser
Yong Ho Lee/Morandi LEY-LB-391-04 OPR:RF
HMBC
f2 (ppm)
f1 (ppm)

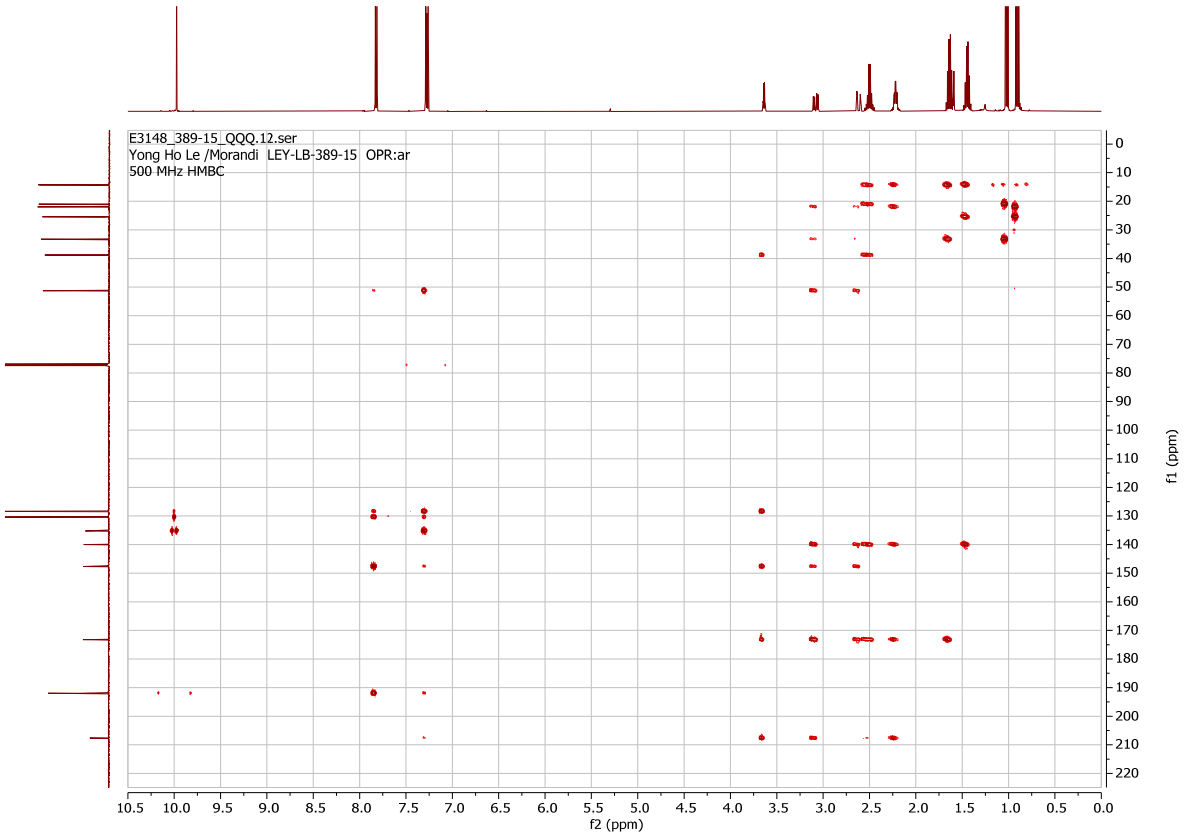
methyl 4-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)benzoate (**3w**).



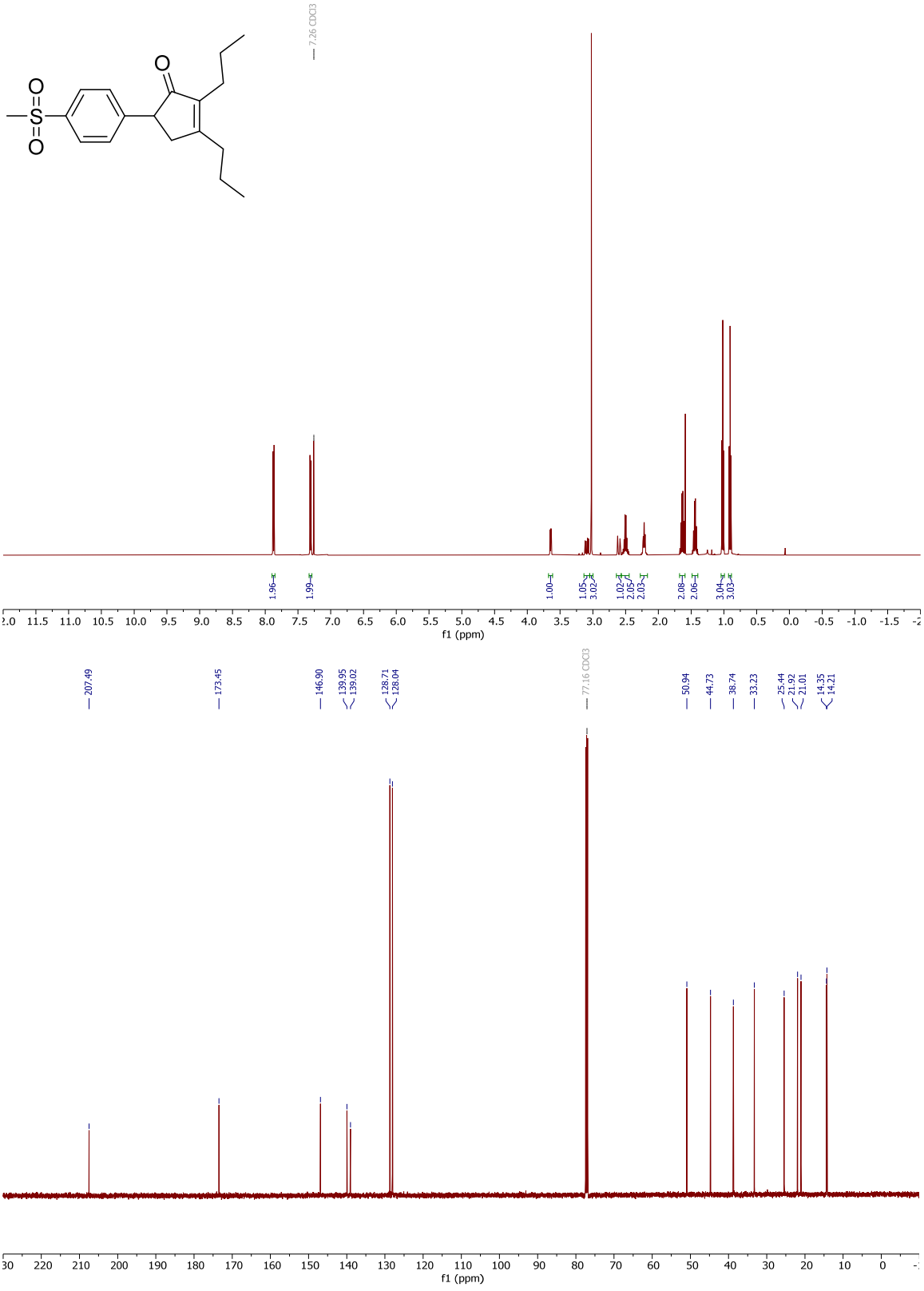

H4015.12.ser
Yong Ho Lee/Morandi LEY-LB-381-14 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

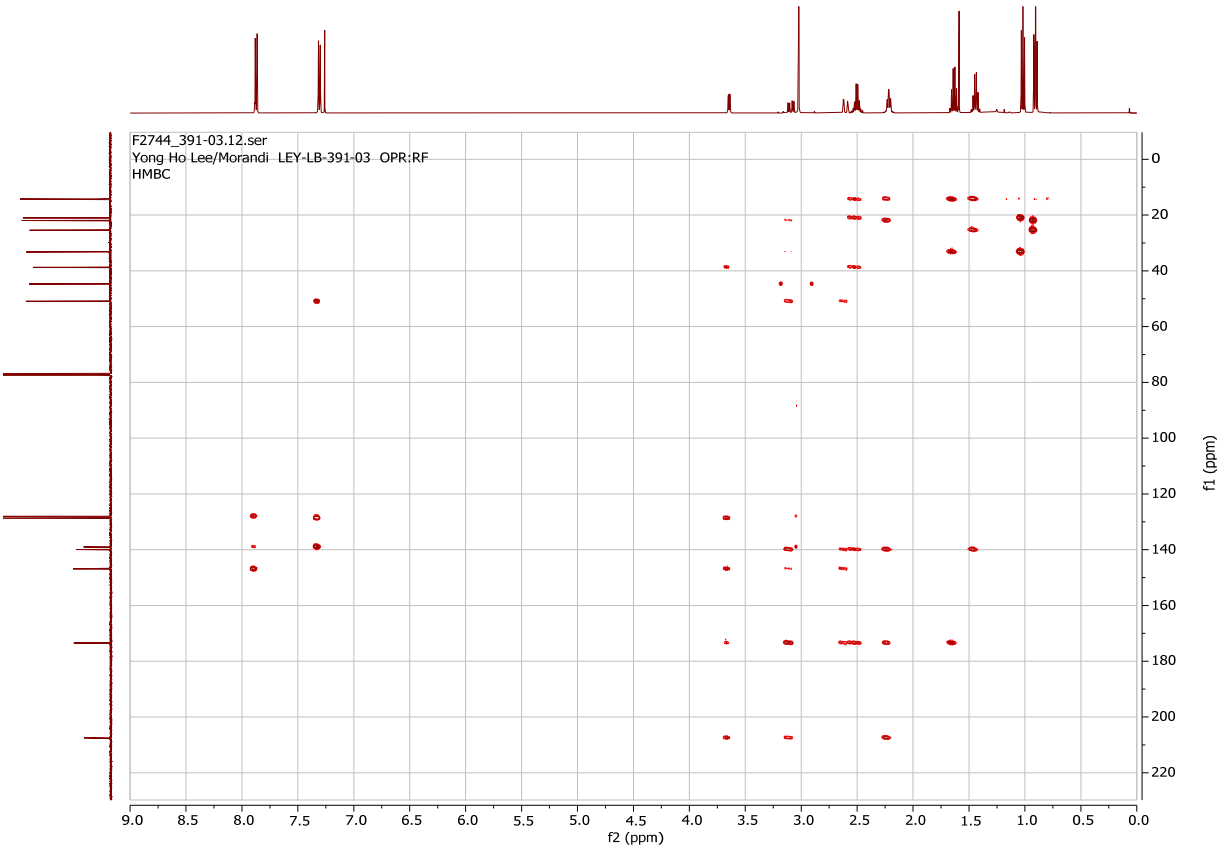
4-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)benzaldehyde (**3x**).



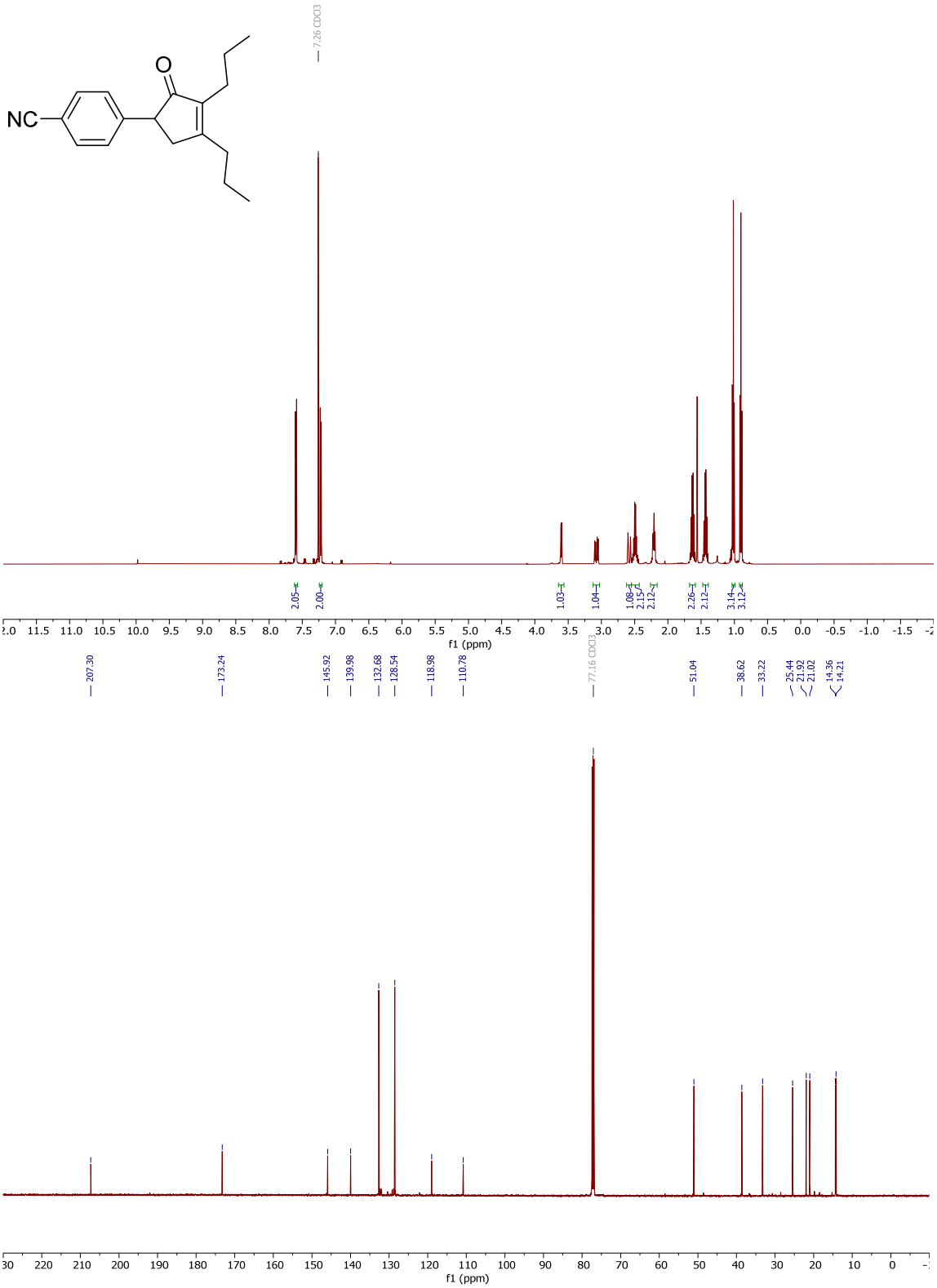

E3148_389-15_QQQ.12.ser
Yong Ho Le /Morandi LEY-LB-389-15 OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

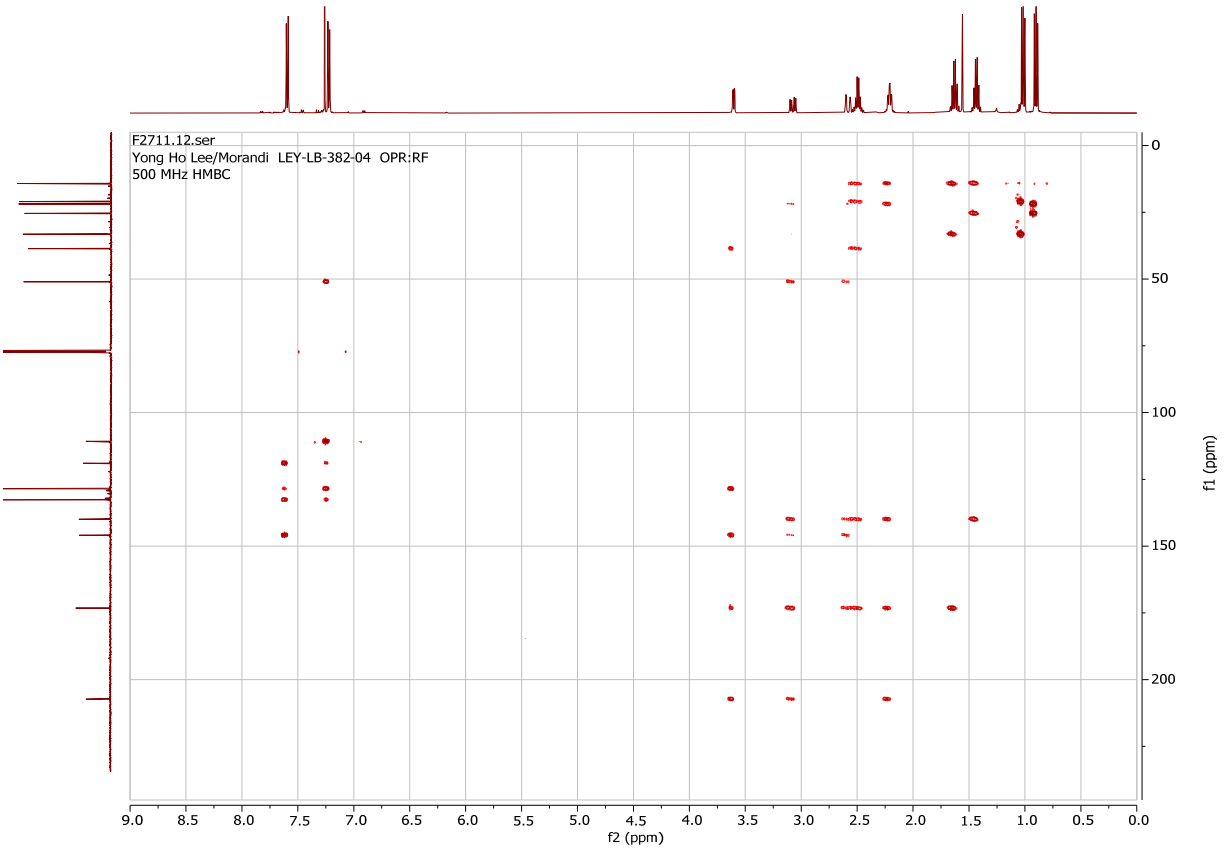
5-(4-(methylsulfonyl)phenyl)-2,3-dipropylcyclopent-2-en-1-one (**3y**).



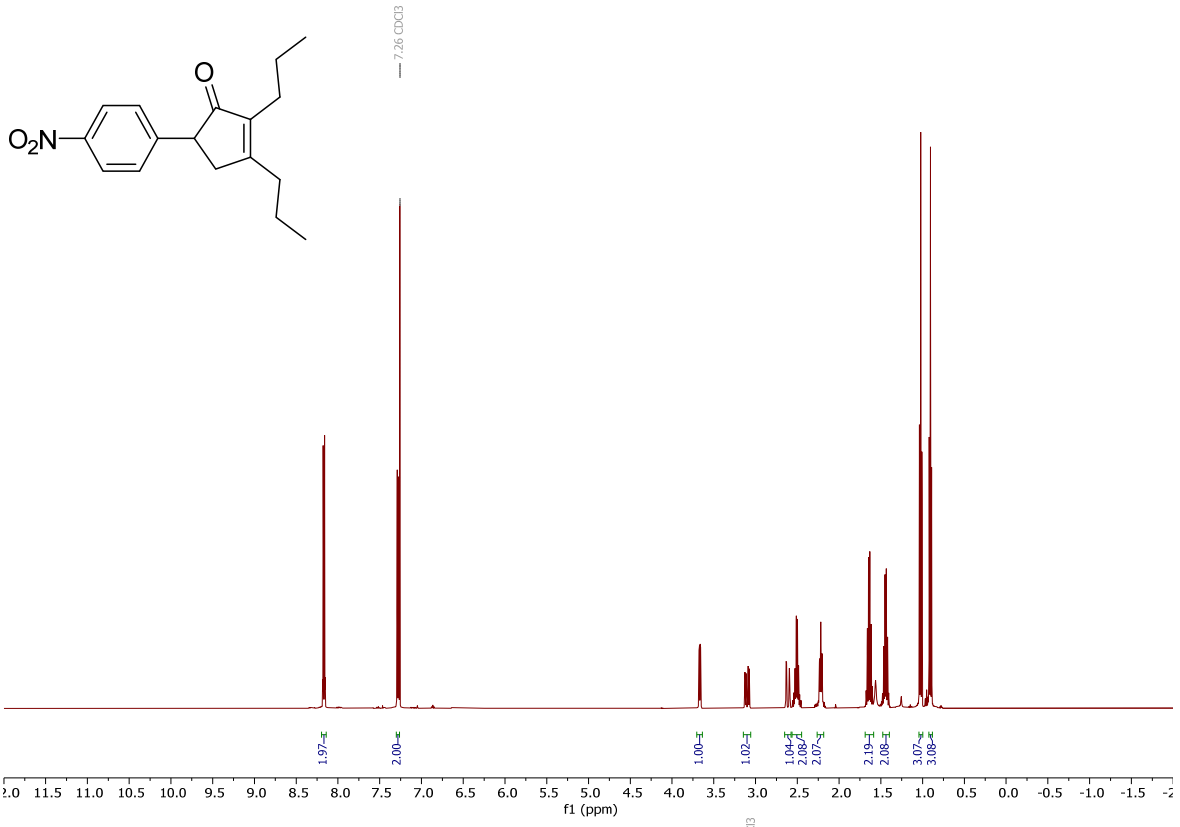

F2744_391-03.12.ser
Yong Ho Lee/Morandi LEY-LB-391-03 OPR:RF
HMBC
f2 (ppm)
f1 (ppm)

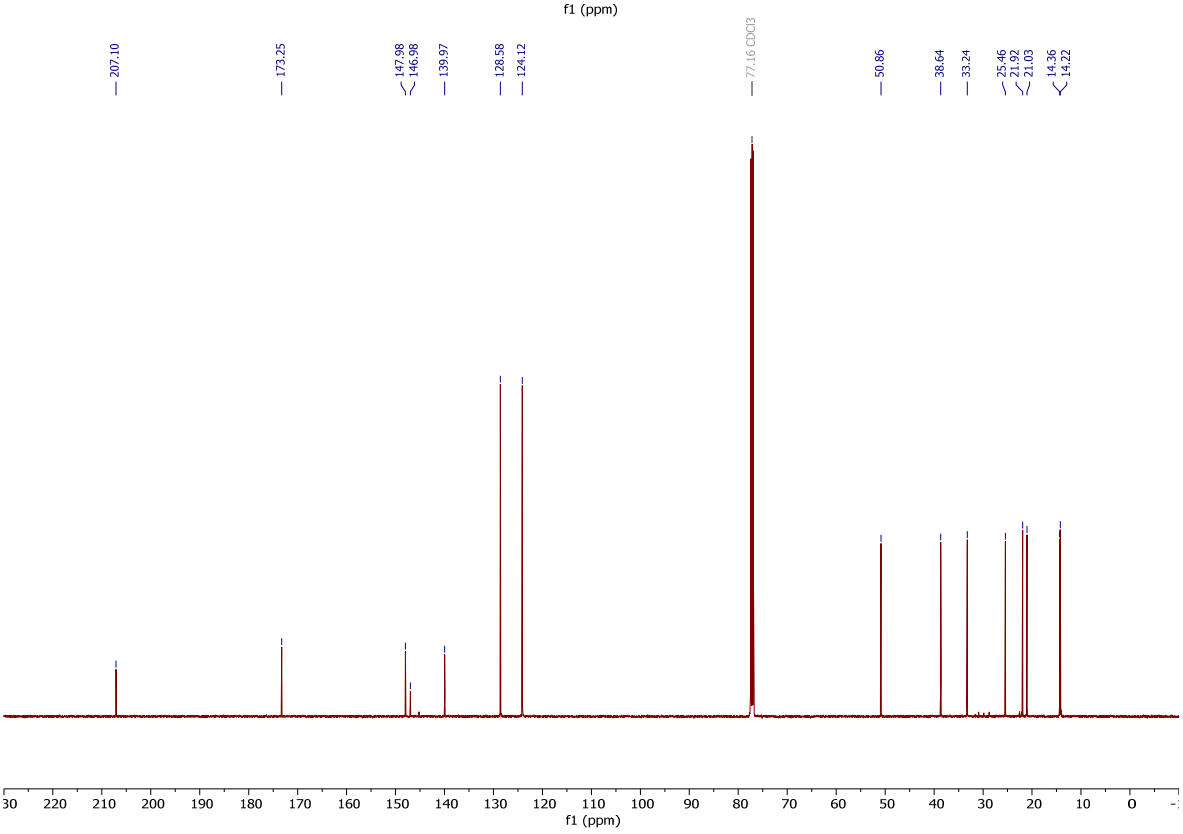
4-(2-oxo-3,4-dipropylcyclopent-3-en-1-yl)benzonitrile (**3z**).

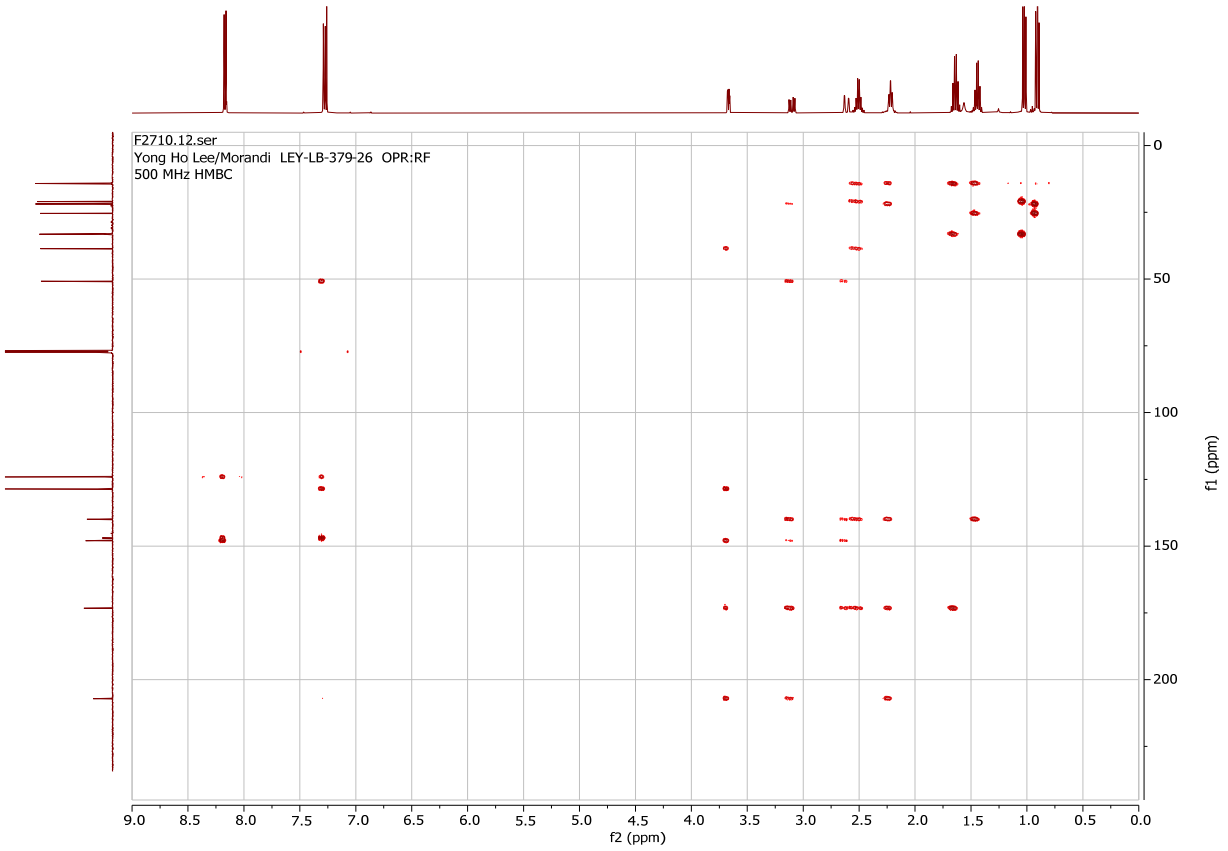



F2711.12.ser
Yong Ho Lee/Morandi LEY-LB-382-04 OPR;RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

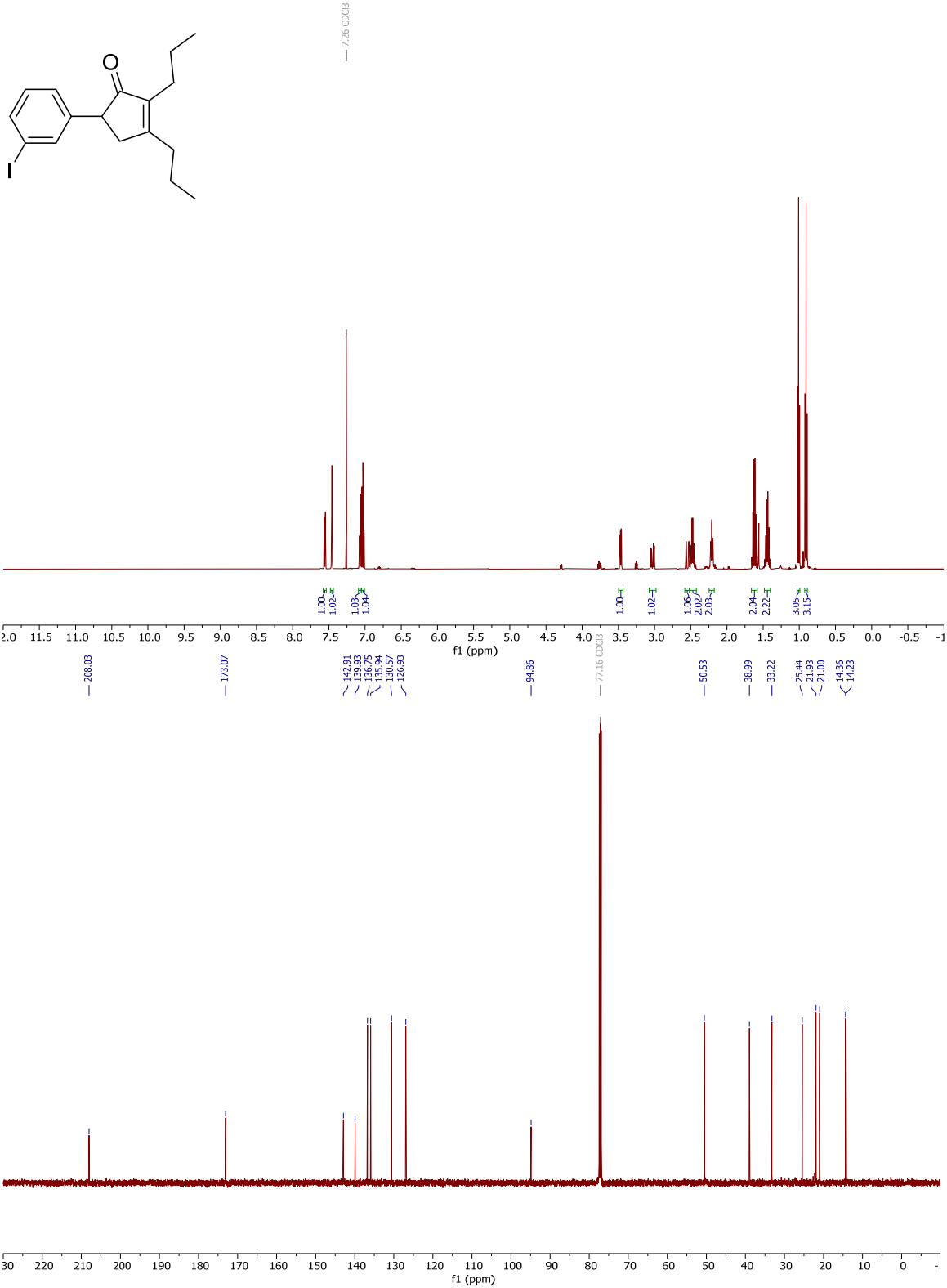
5-(4-nitrophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3aa**).

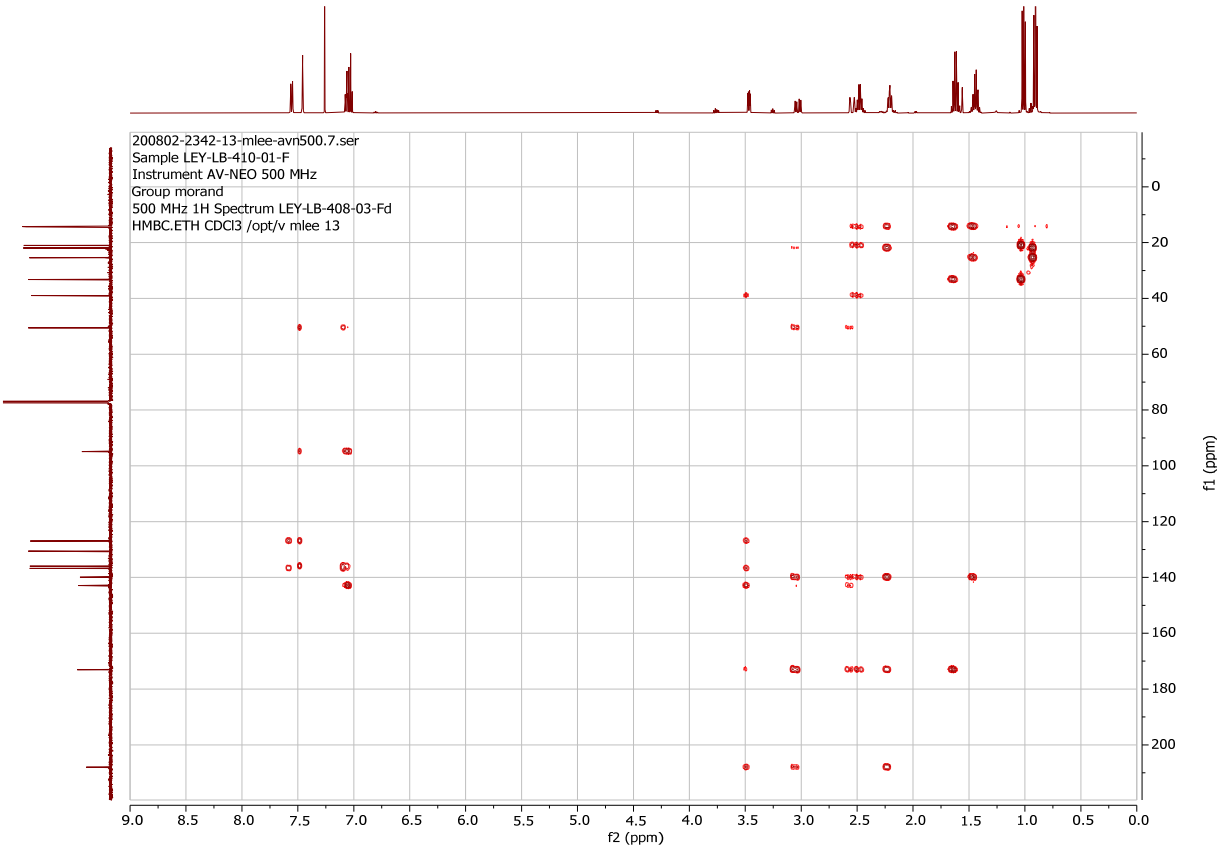




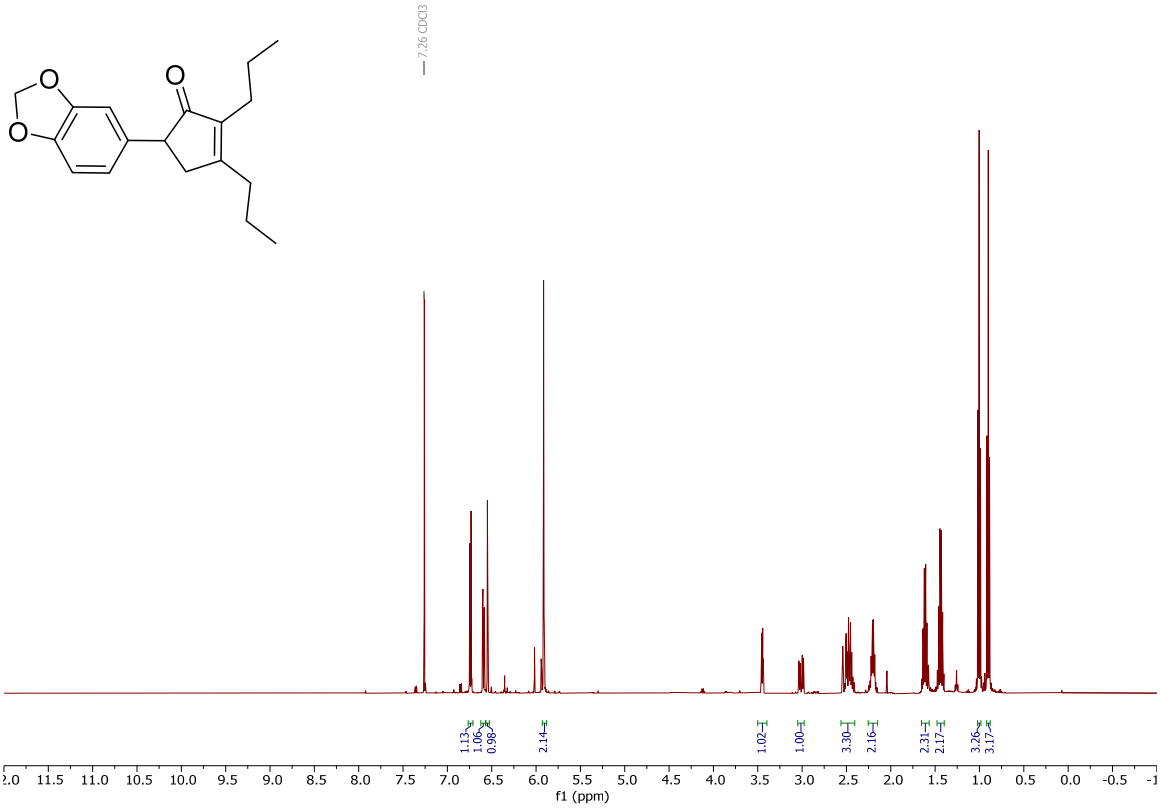

F2710.12.ser
Yong Ho Lee/Morandi LEY-LB-379-26 OPR:RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

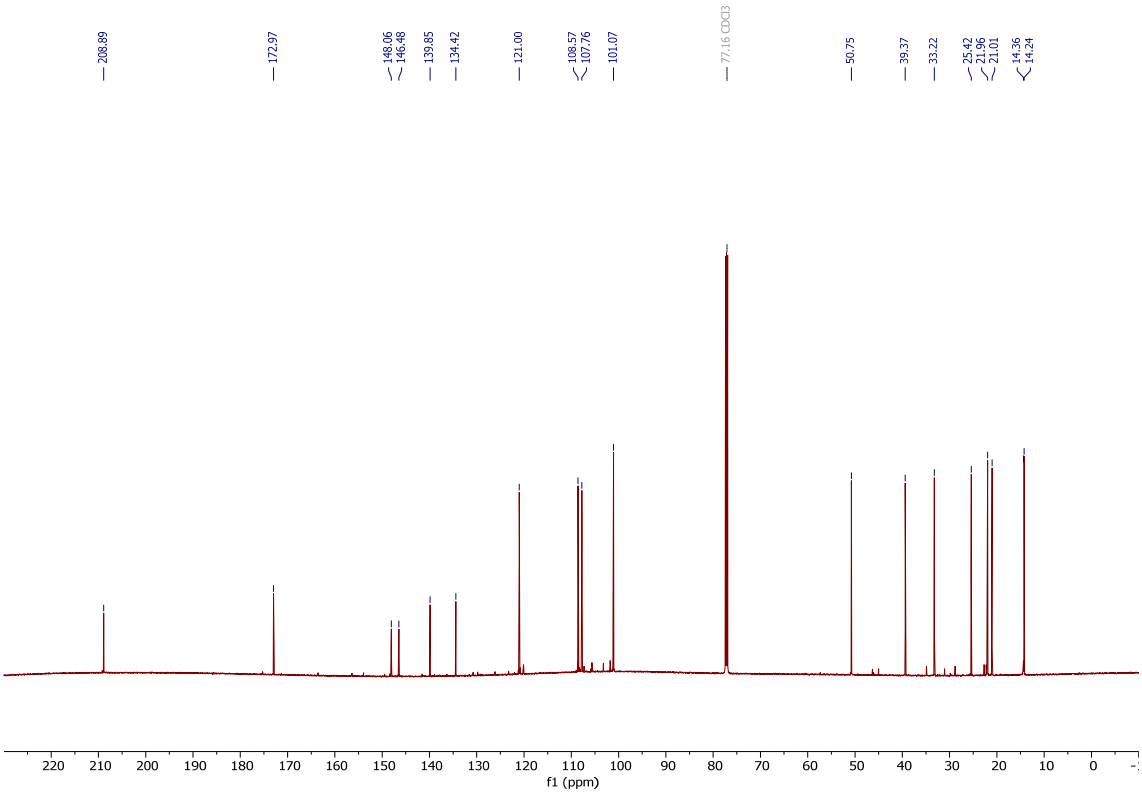
5-(3-iodophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3ab**).

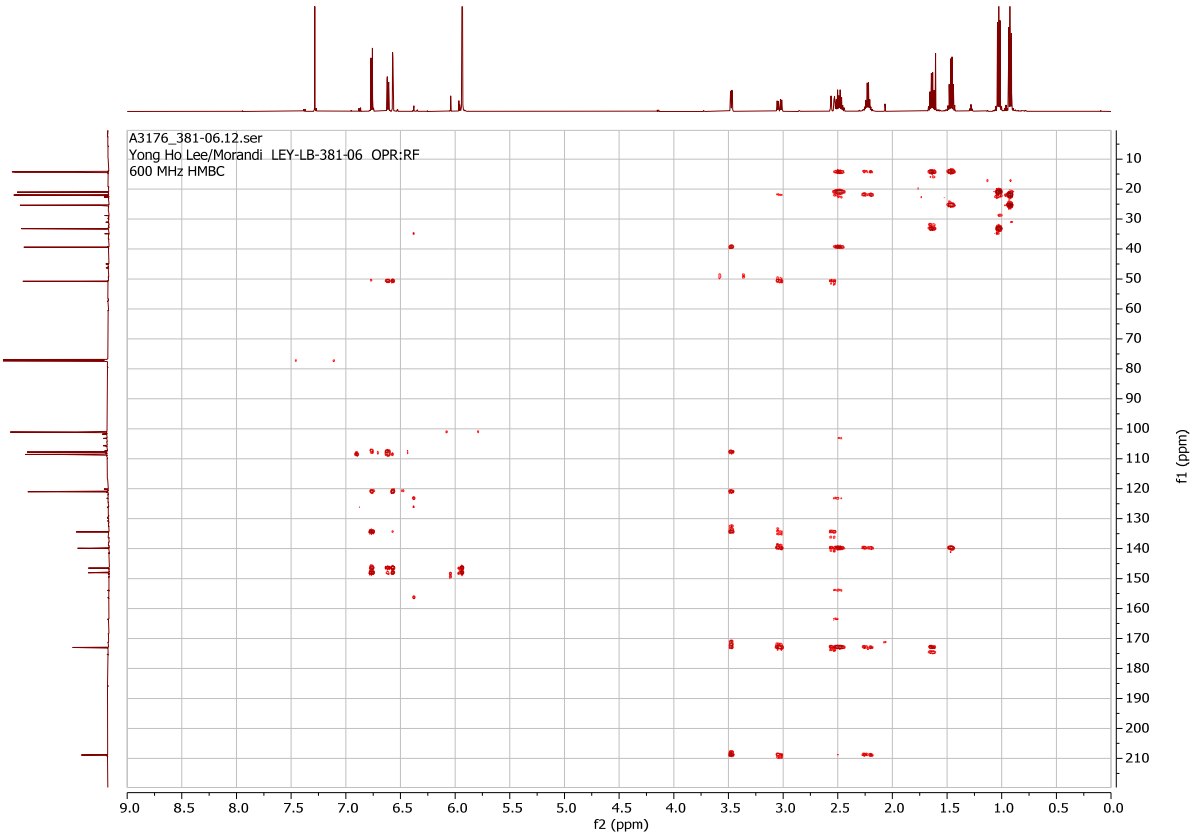



200802-2342-13-mlee-avn500.7.ser
Sample LEY-LB-410-01-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-408-03-Fd
HMBC.ETH CDCl3 /opt/v mlee 13
f2 (ppm)
f1 (ppm)

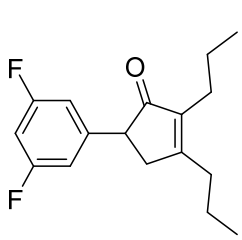
5-(benzo[d][1,3]dioxol-5-yl)-2,3-dipropylcyclopent-2-en-1-one (**3ac**).

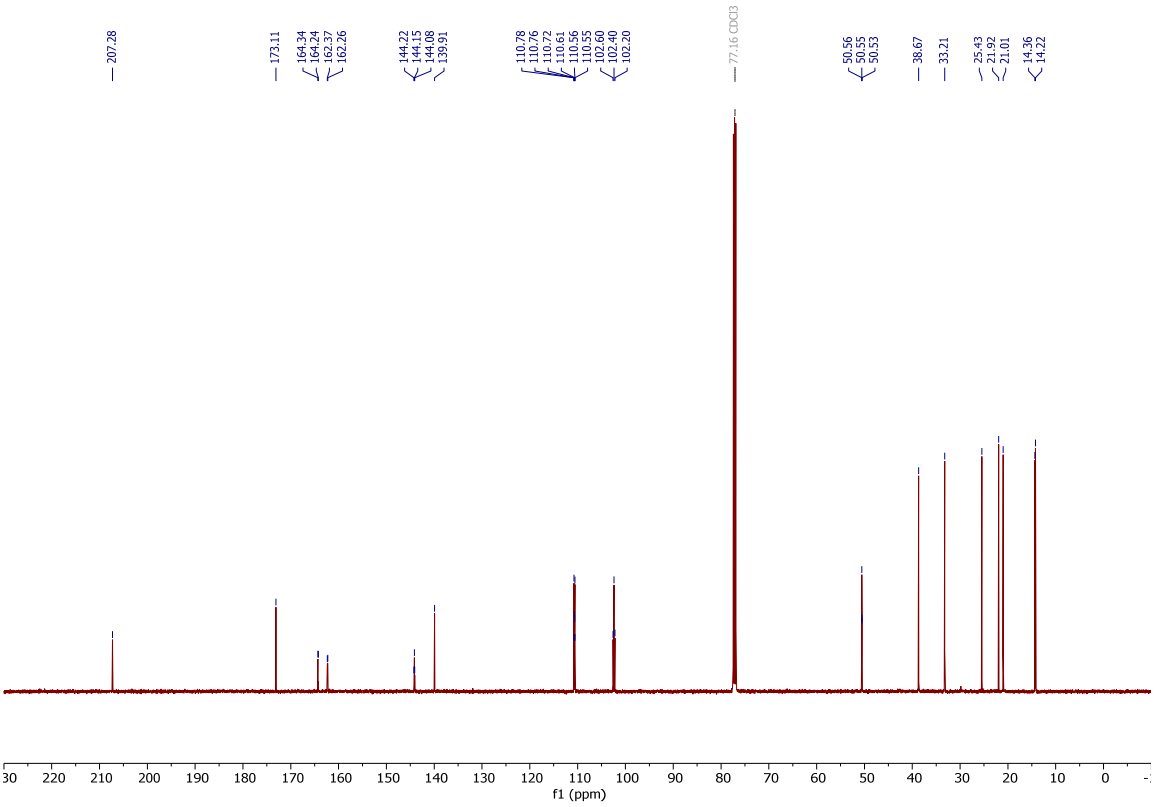


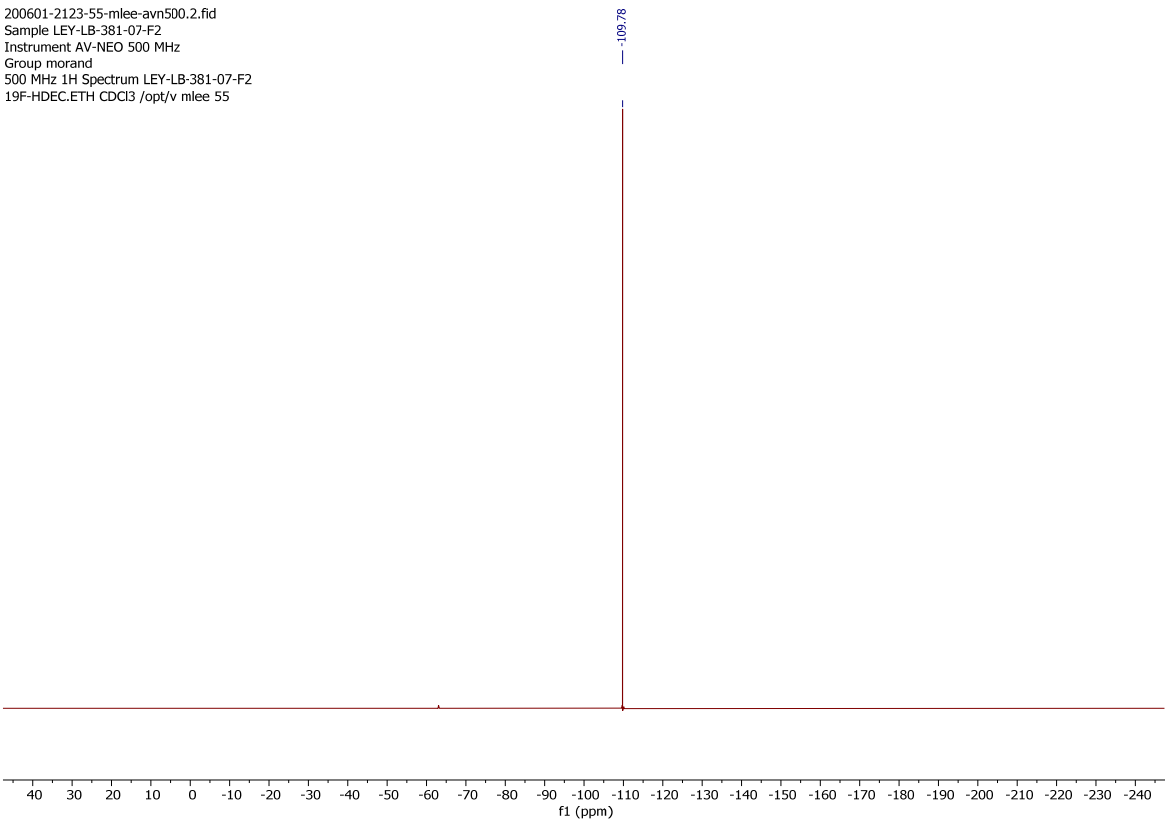


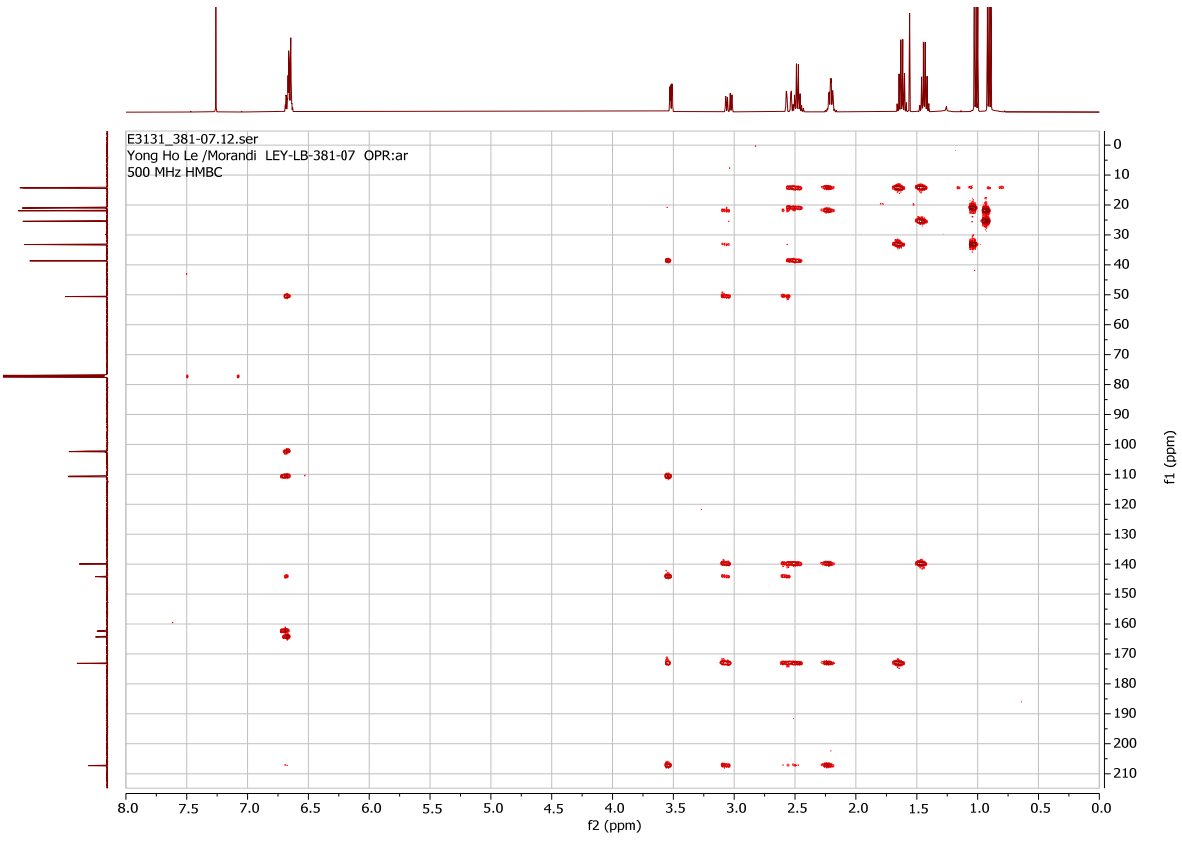

A3176_381-06.12.ser
Yong Ho Lee/Morandi LEY-LB-381-06 OPR:RF
600 MHz HMBC
f2 (ppm)
f1 (ppm)

5-(3,5-difluorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3ad**).

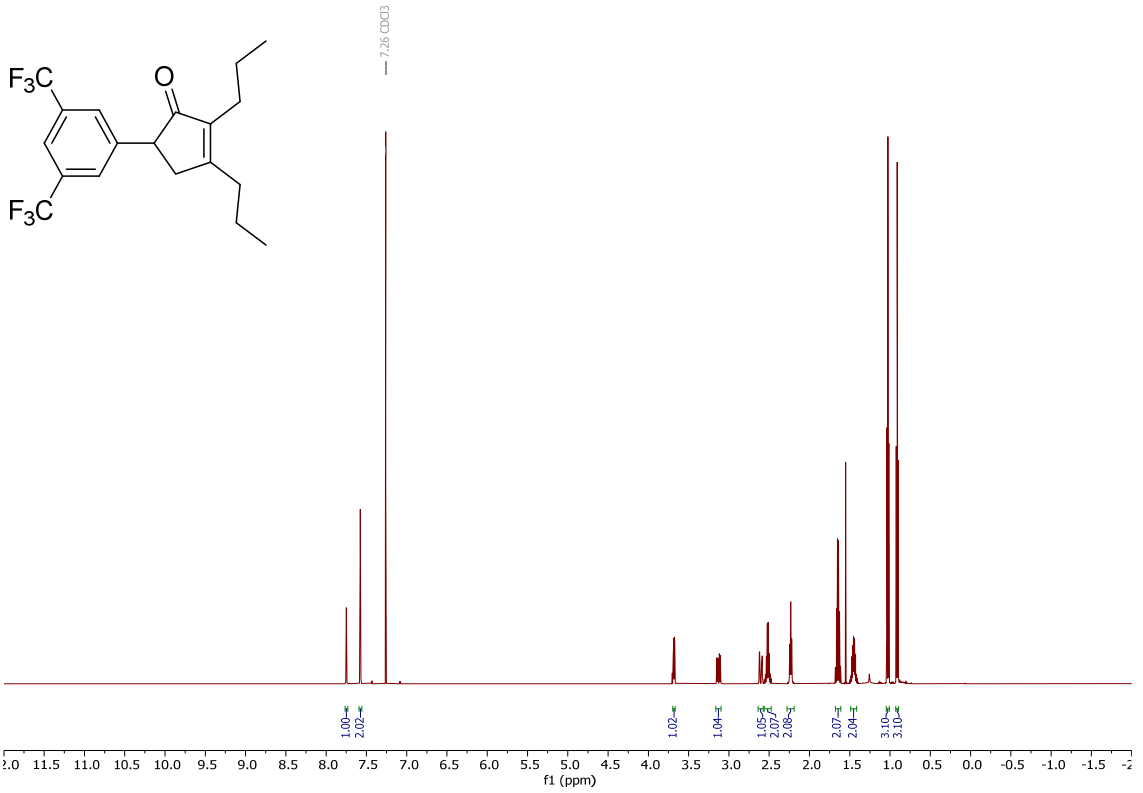


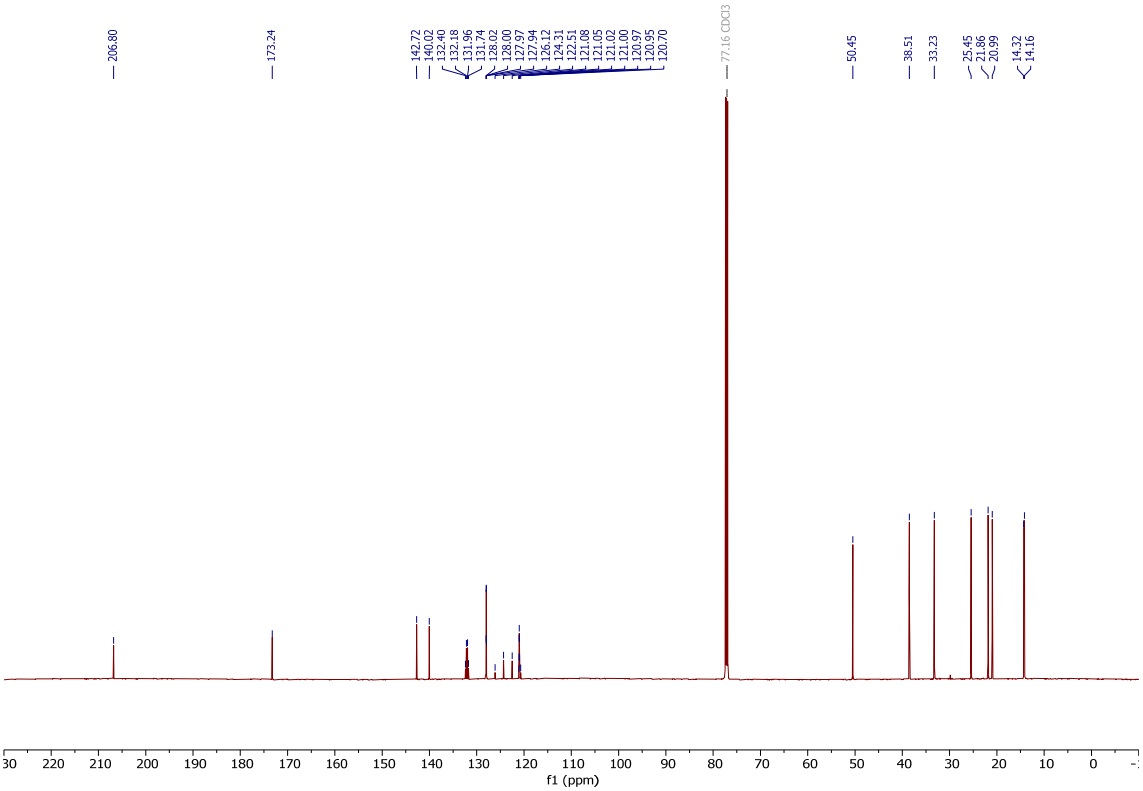


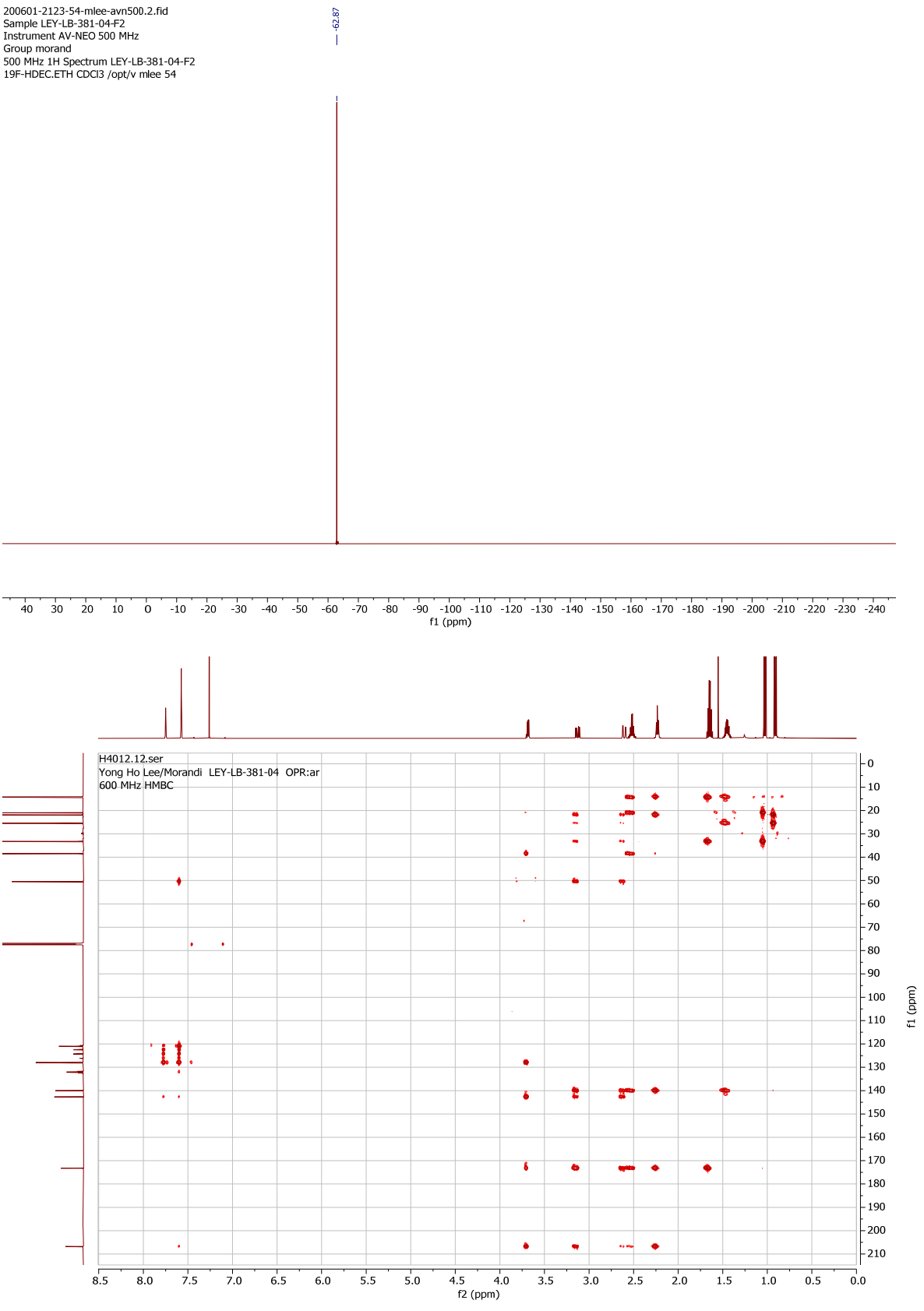

200601-2123-55-mlee-avn500.2.fid
Sample LEY-LB-381-07-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-381-07-F2
19F-HDEC.ETH CDCl3 /opt/v mlee 55
-109.78
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


E3131_381-07.12.ser
Yong Ho Le /Morandi LEY-LB-381-07 OPR:ar
500 MHz HMBC
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
f1 (ppm)

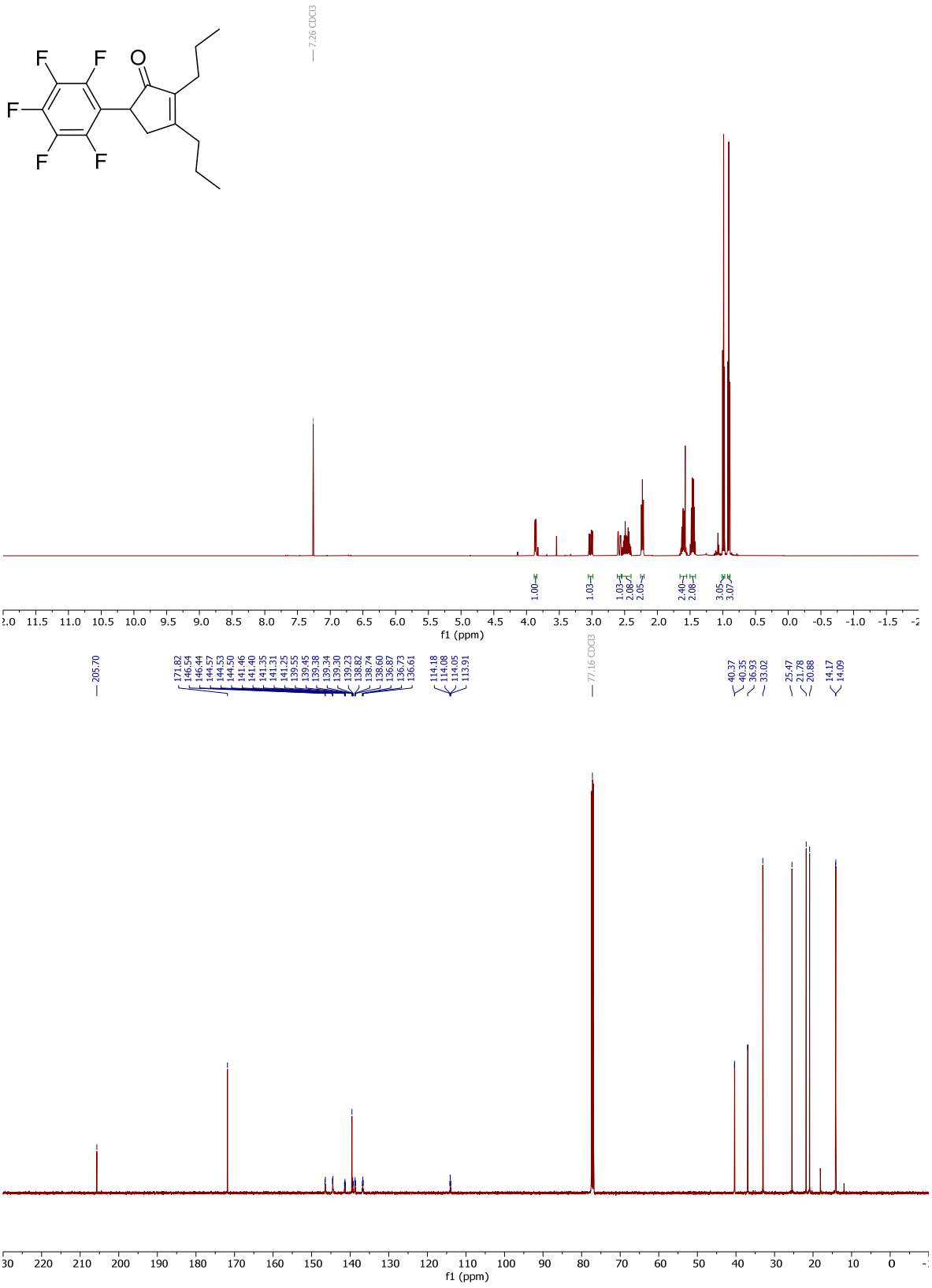
5-(3,5-bis(trifluoromethyl)phenyl)-2,3-dipropylcyclopent-2-en-1-one (**3ae**).

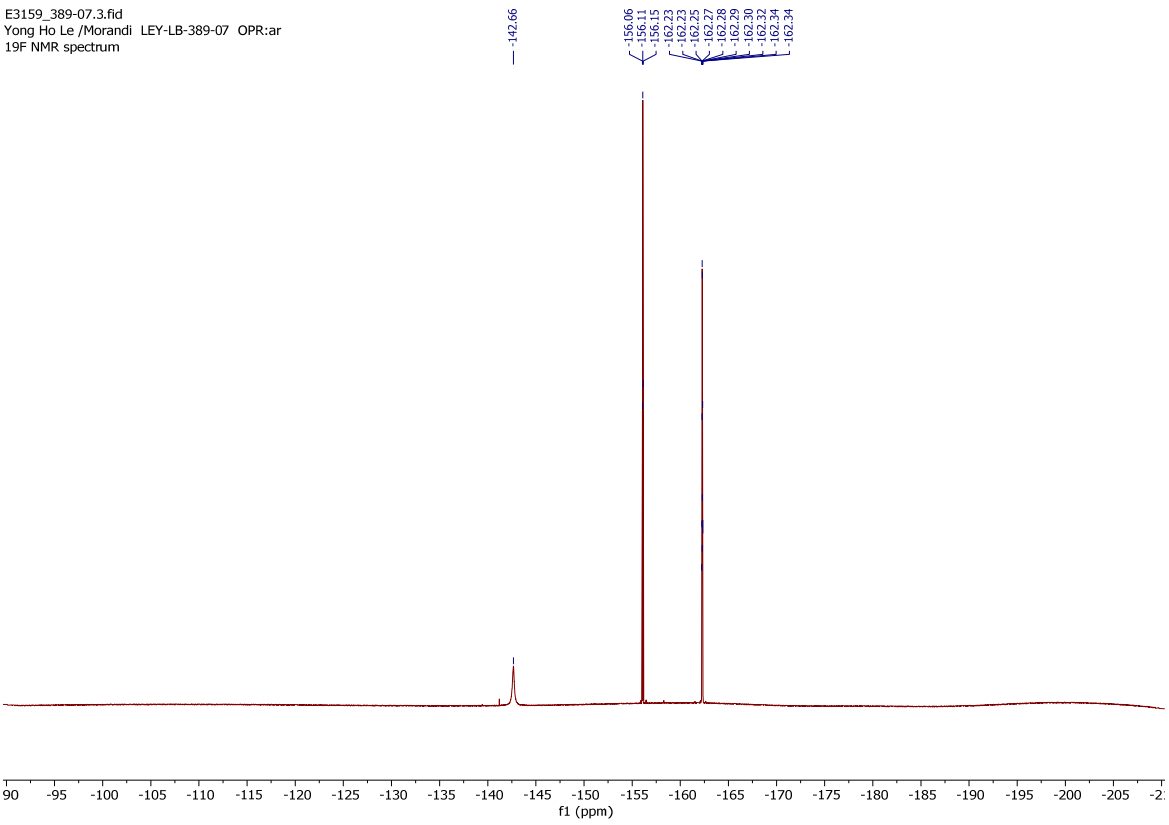


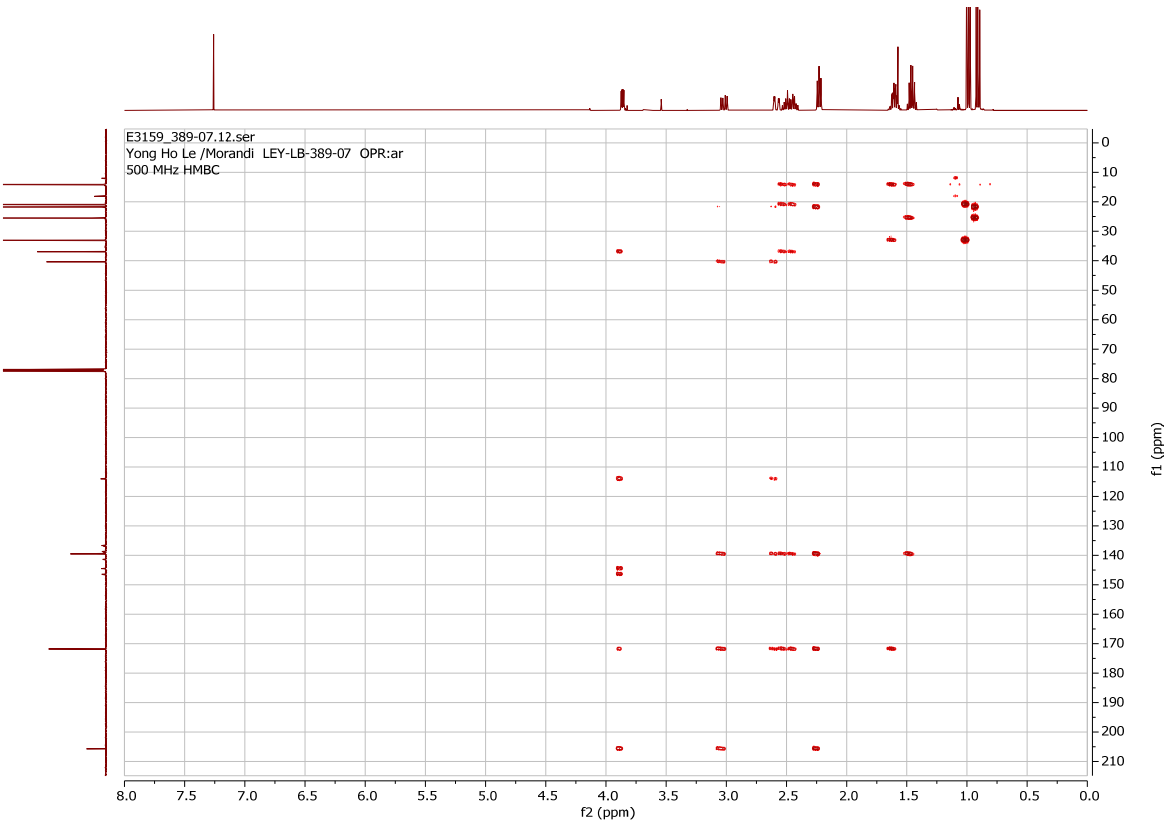



200601-2123-54-mlee-avn500.2.fid
Sample LEY-LB-381-04-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-381-04-F2
19F-HDEC.ETH CDCl3 /opt/v mlee 54
-62.87
f1 (ppm)
H4012.12.ser
Yong Ho Lee/Morandi LEY-LB-381-04 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

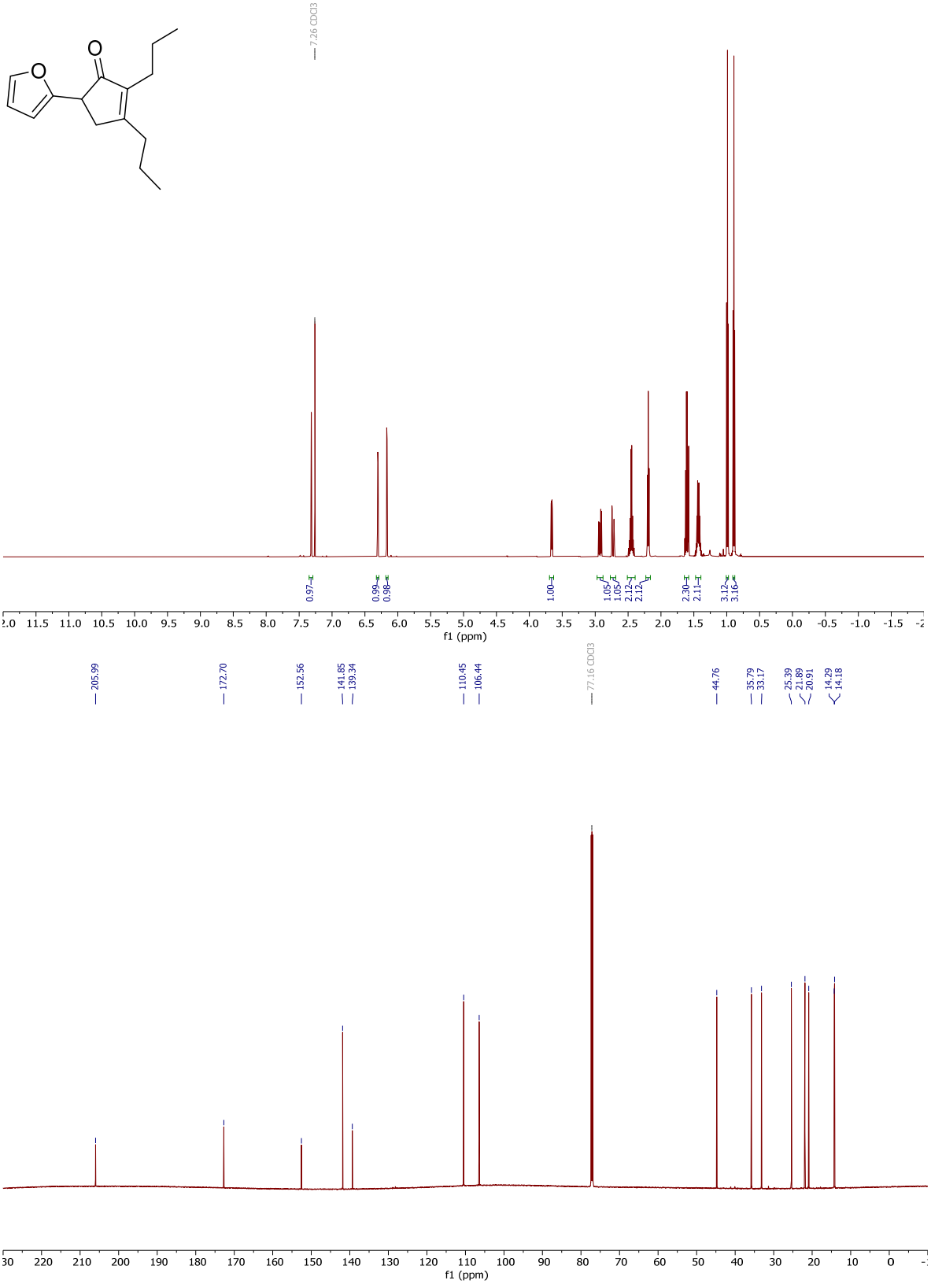
5-(perfluorophenyl)-2,3-dipropylcyclopent-2-en-1-one (**3af**).

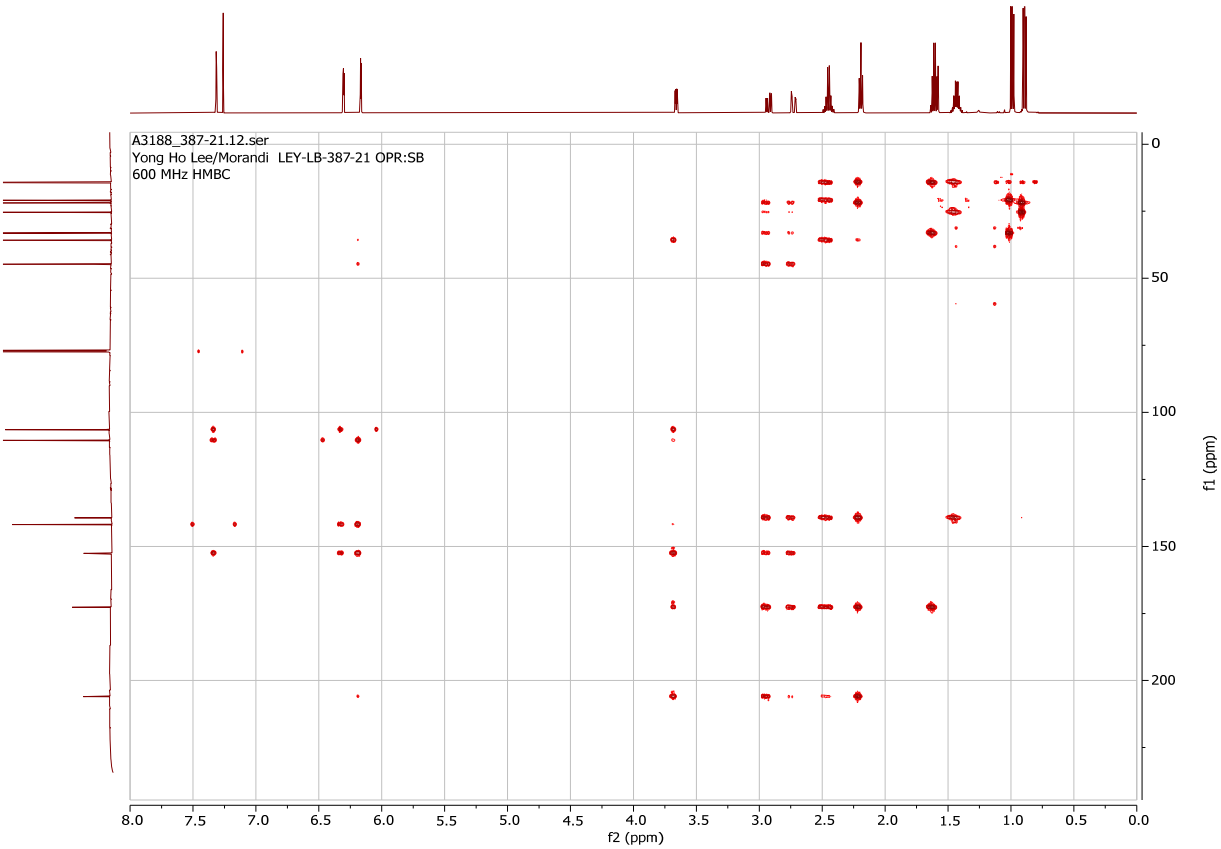



E3159_389-07.3.fid
Yong Ho Le /Morandi LEY-LB-389-07 OPR:ar
19F NMR spectrum
-142.66
-156.06
-156.11
-156.15
-162.23
-162.23
-162.25
-162.27
-162.28
-162.29
-162.30
-162.32
-162.34
-162.34
f1 (ppm)

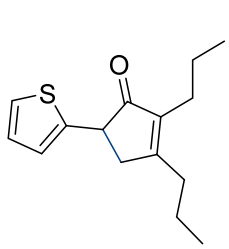

E3159_389-07.12.ser
Yong Ho Le /Morandi LEY-LB-389-07 OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

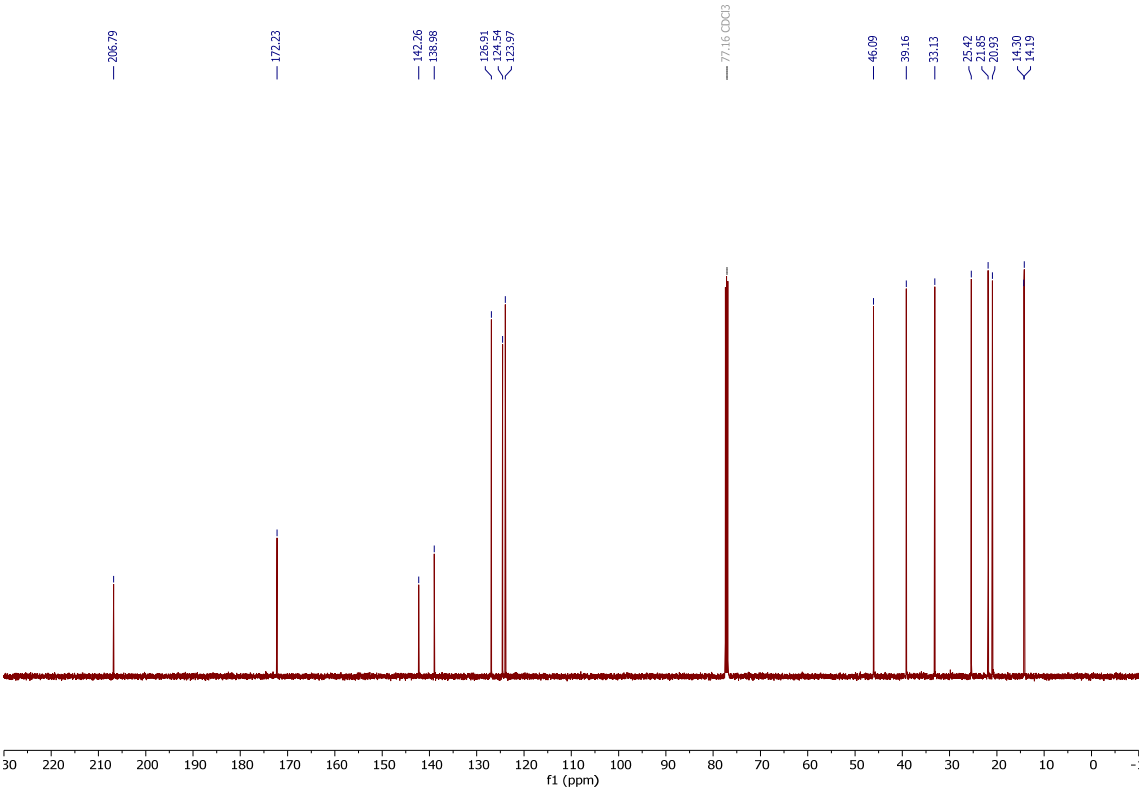
5-(furan-2-yl)-2,3-dipropylcyclopent-2-en-1-one (**3ag**).

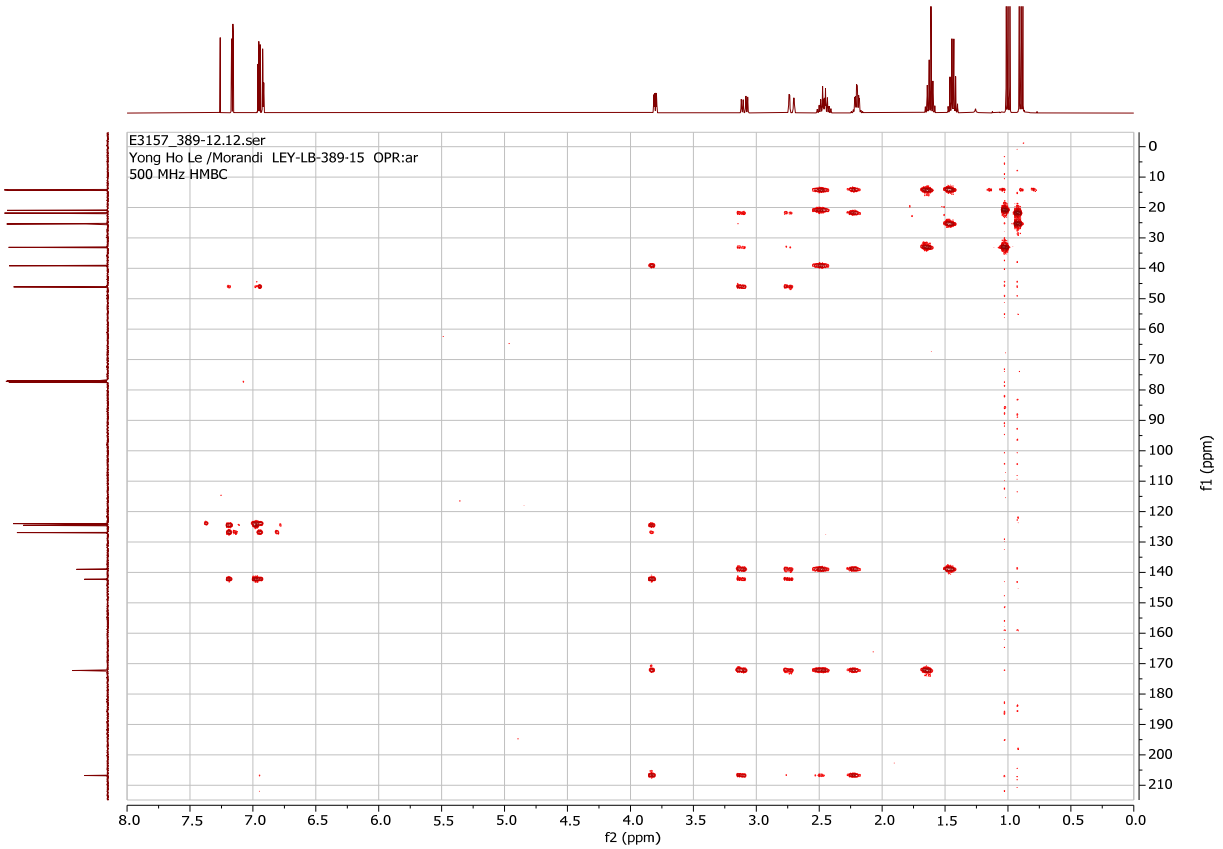



A3188_387-21.12.ser
Yong Ho Lee/Morandi LEY-LB-387-21 OPR:SB
600 MHz HMBC
f2 (ppm)
f1 (ppm)

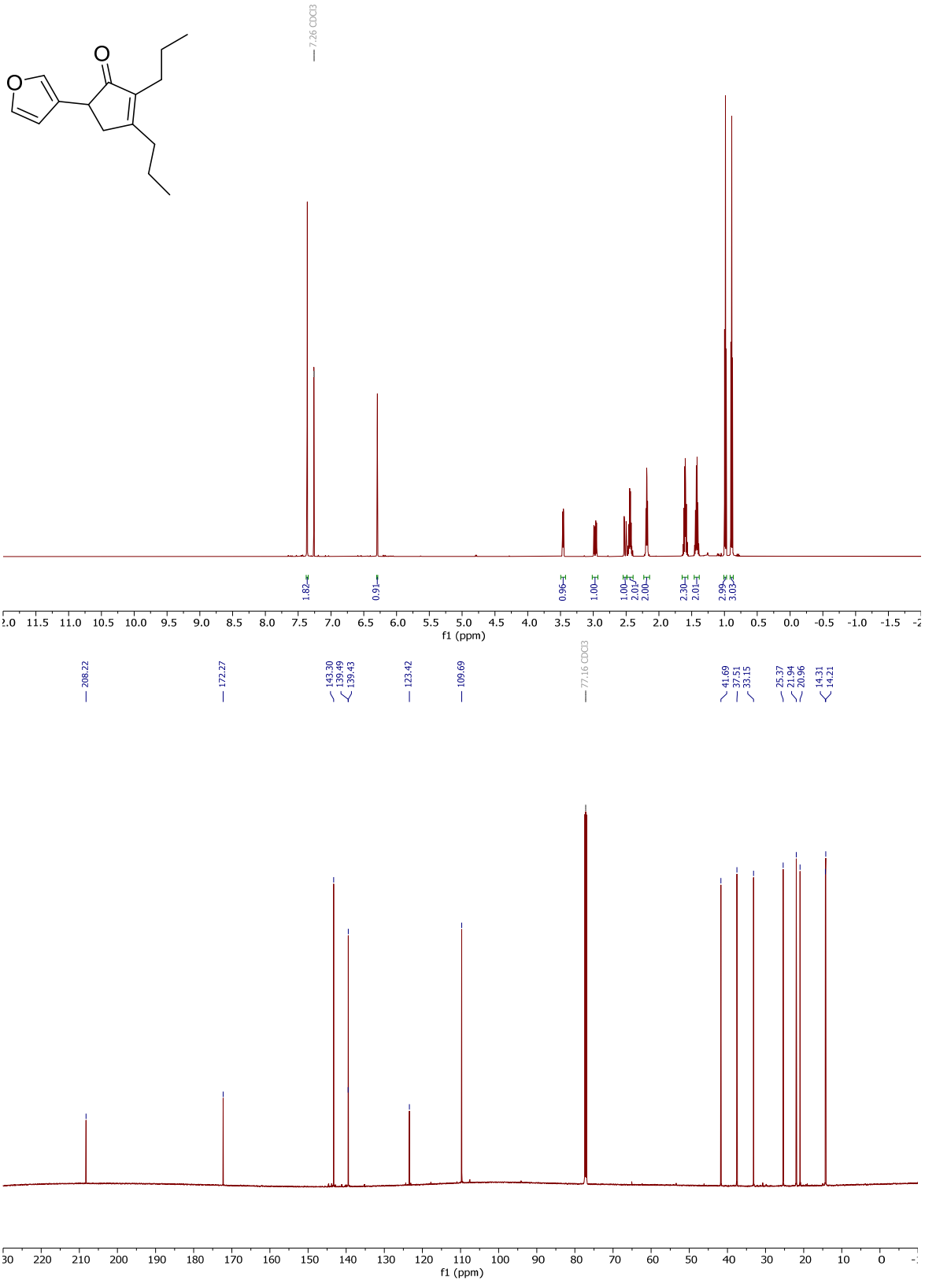
2,3-dipropyl-5-(thiophen-2-yl)cyclopent-2-en-1-one (**3ah**).

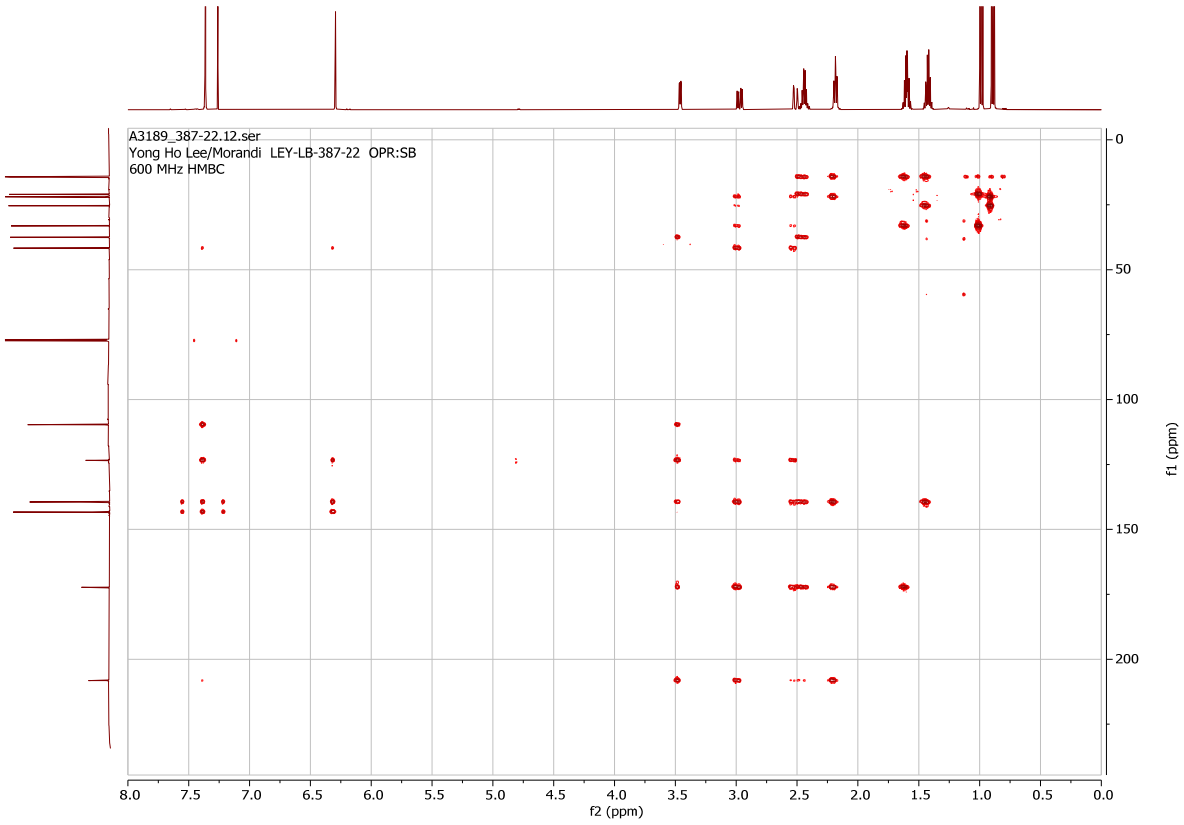




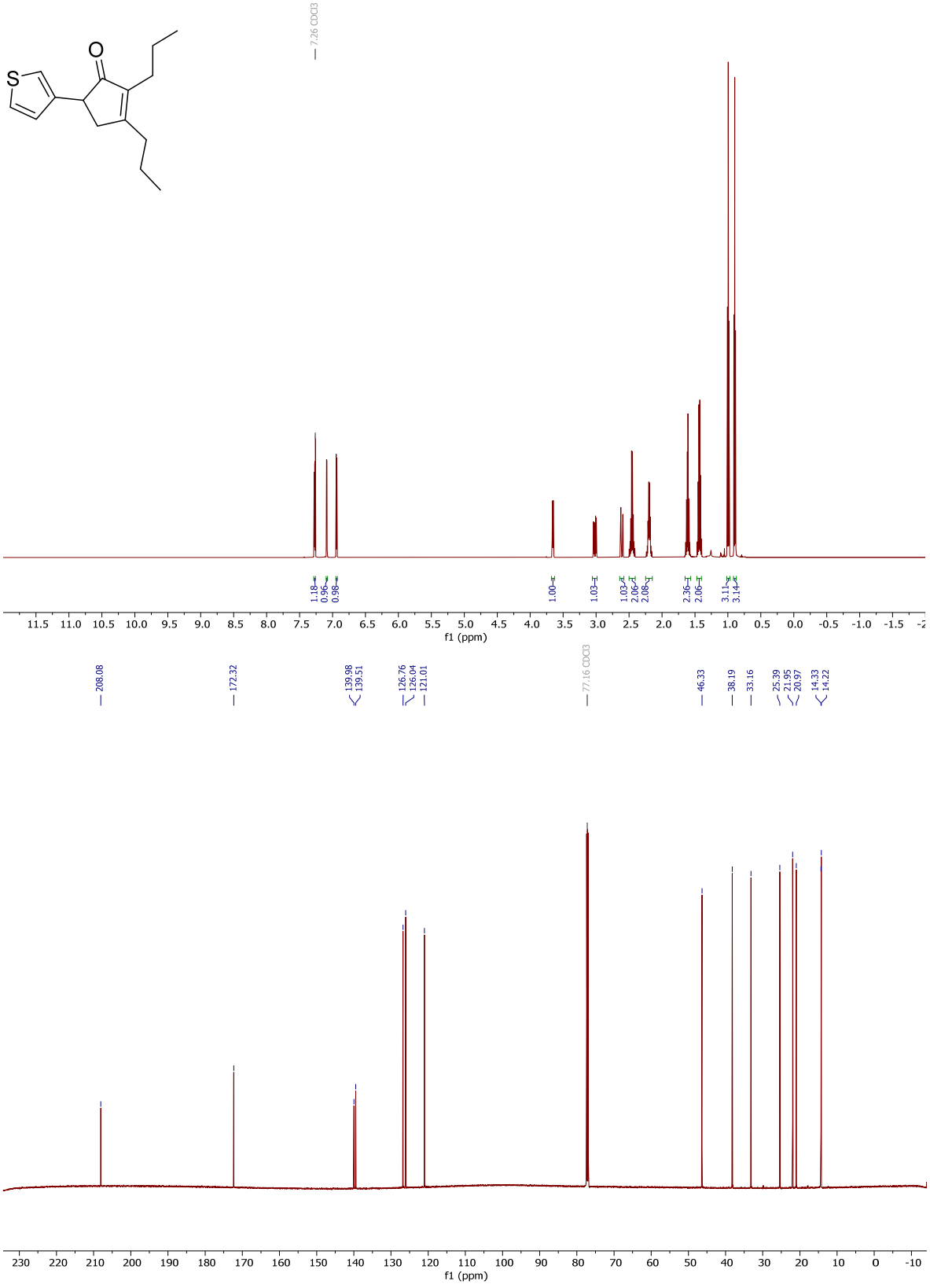

E3157_389-12.12.ser
Yong Ho Le /Morandi LEY-LB-389-15 OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

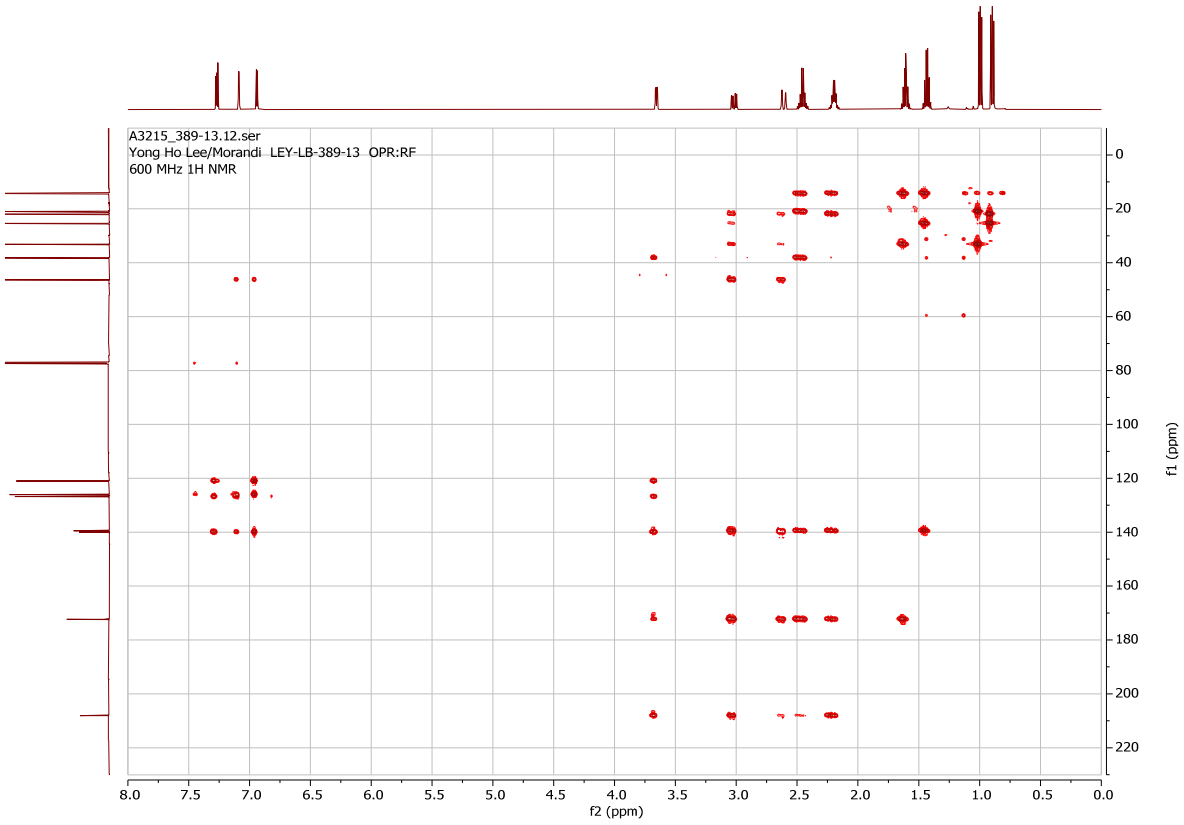
5-(furan-3-yl)-2,3-dipropylcyclopent-2-en-1-one (**3ai**).



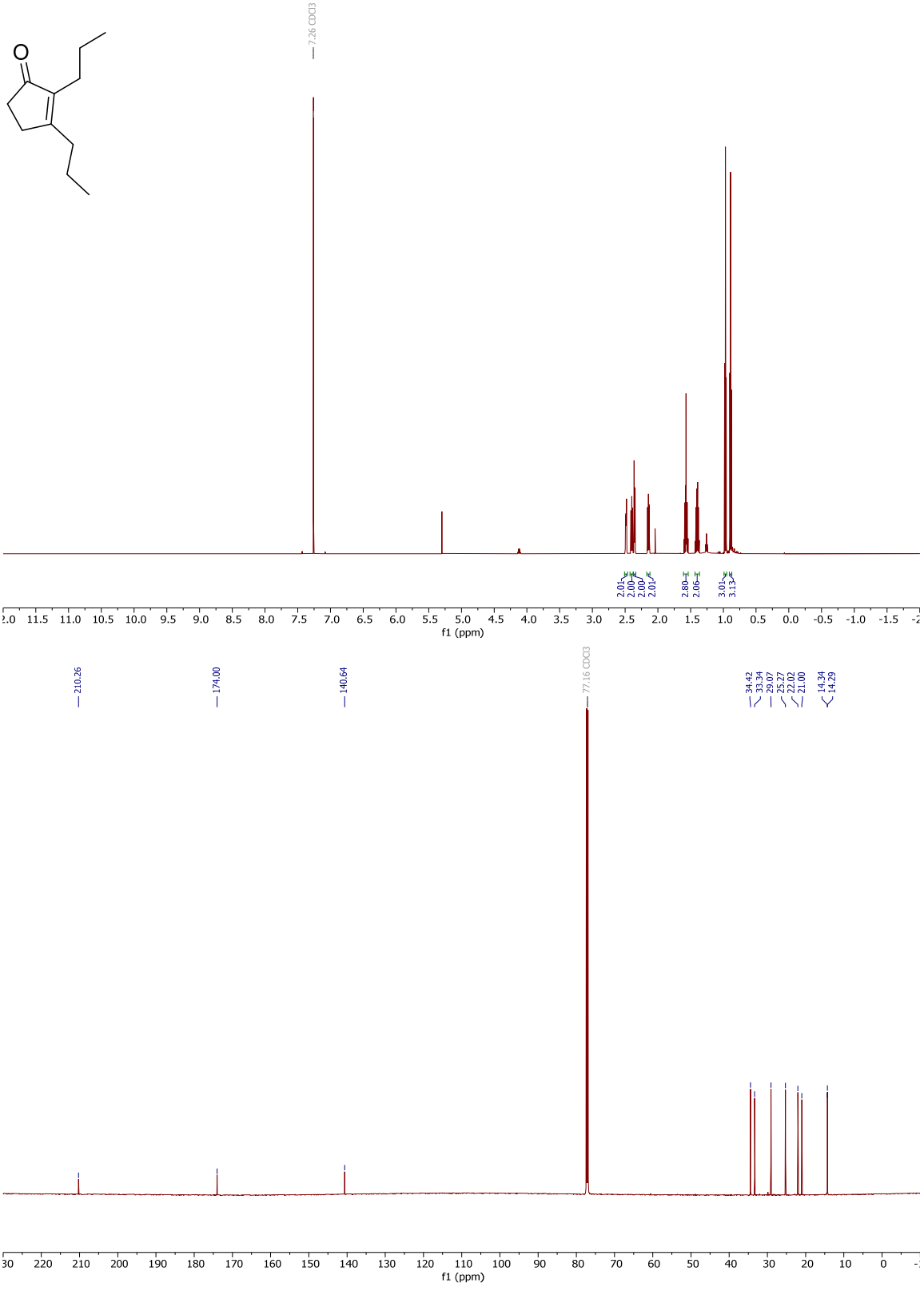

A3189_387-22.12.ser
Yong Ho Lee/Morandi LEY-LB-387-22 OPR:SB
600 MHz HMBC
f2 (ppm)
f1 (ppm)

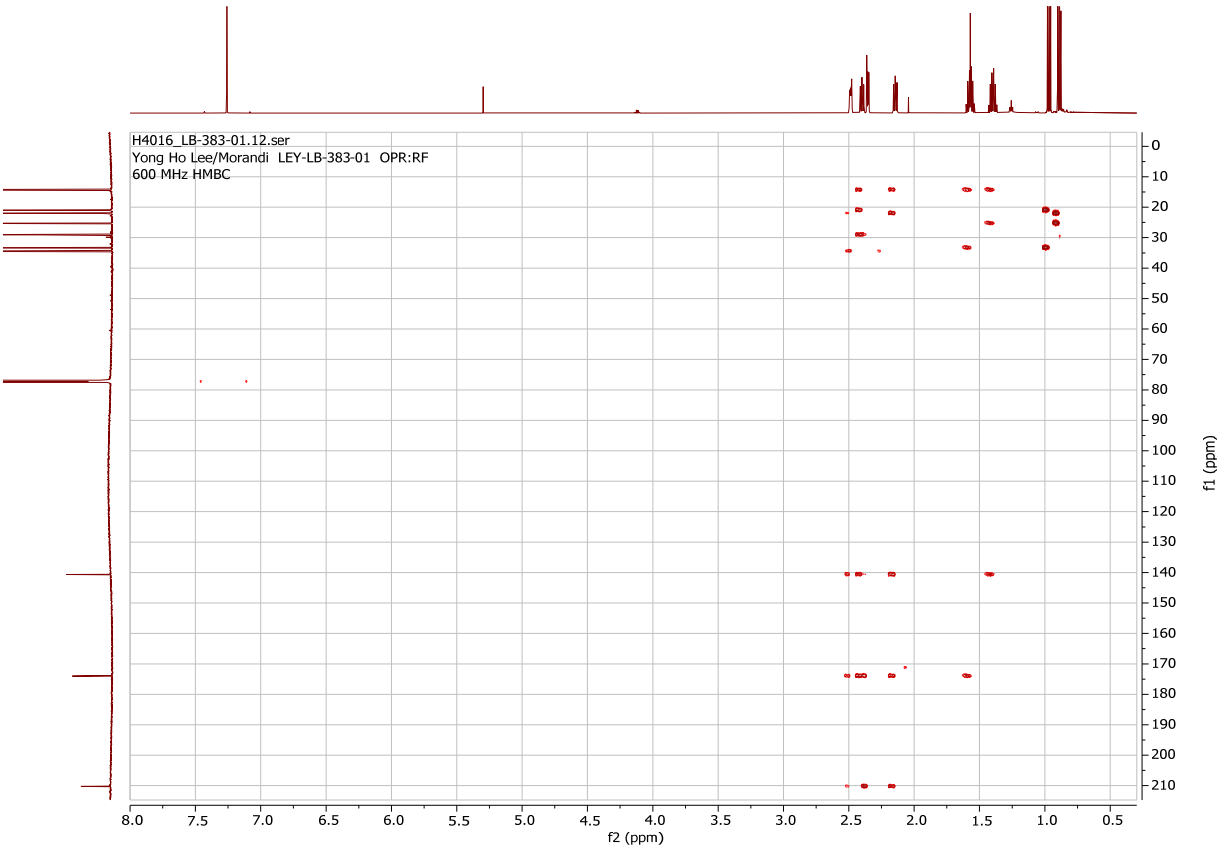
2,3-dipropyl-5-(thiophen-3-yl)cyclopent-2-en-1-one (**3aj**).



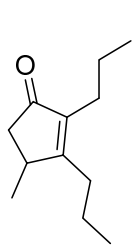

A3215_389-13.12.ser
Yong Ho Lee/Morandi LEY-LB-389-13 OPR:RF
600 MHz 1H NMR
f2 (ppm)
f1 (ppm)

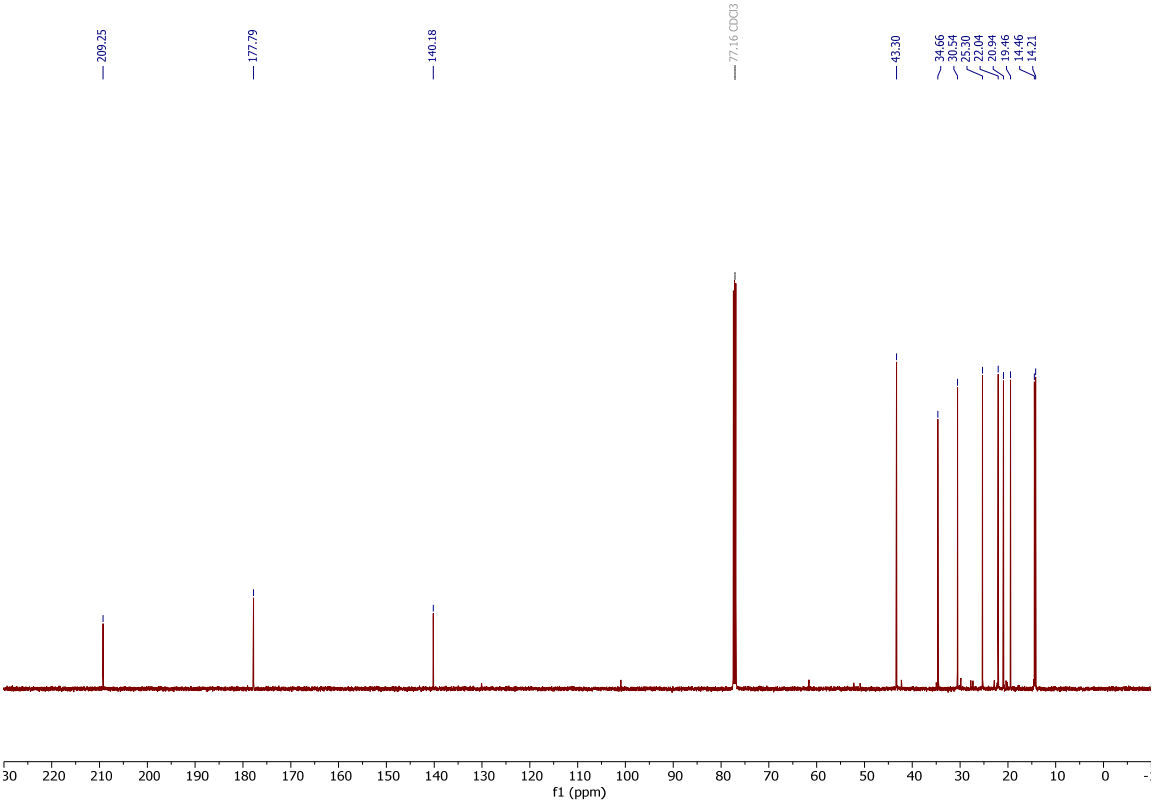
2,3-dipropylcyclopent-2-en-1-one (**3ak**).

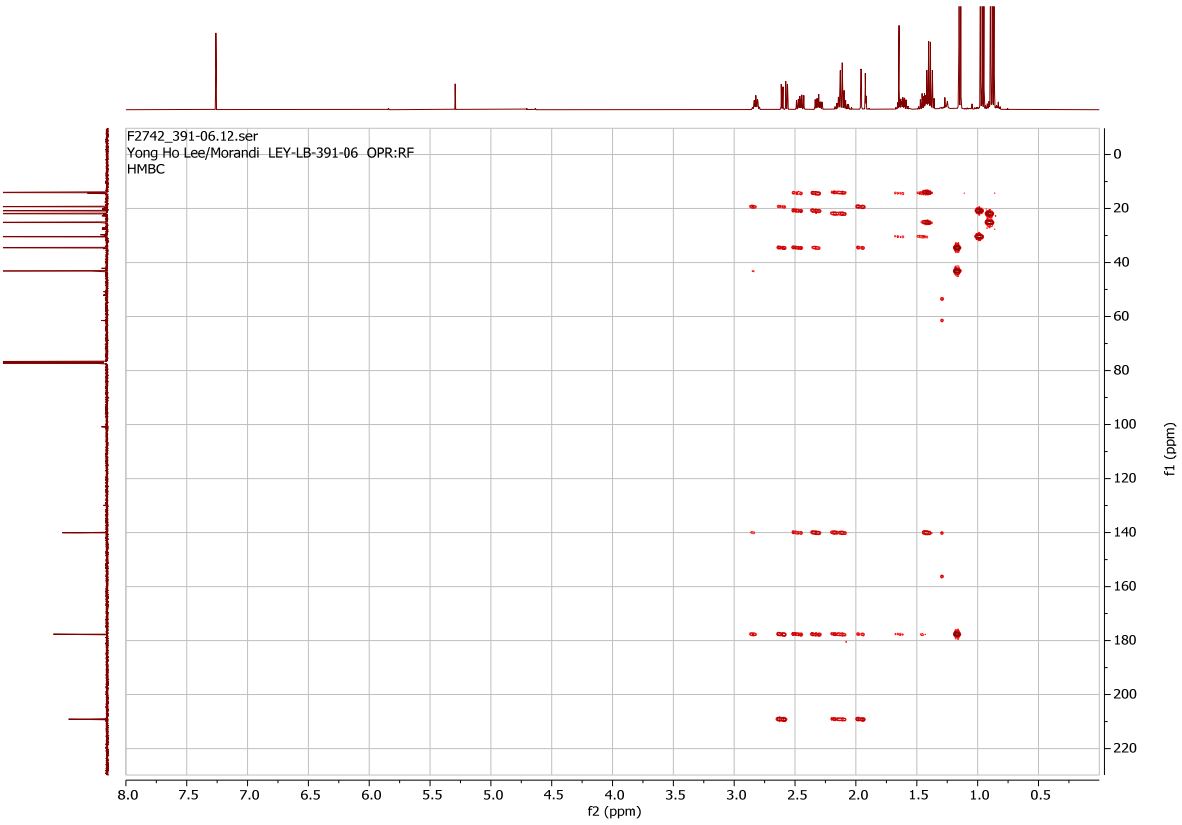


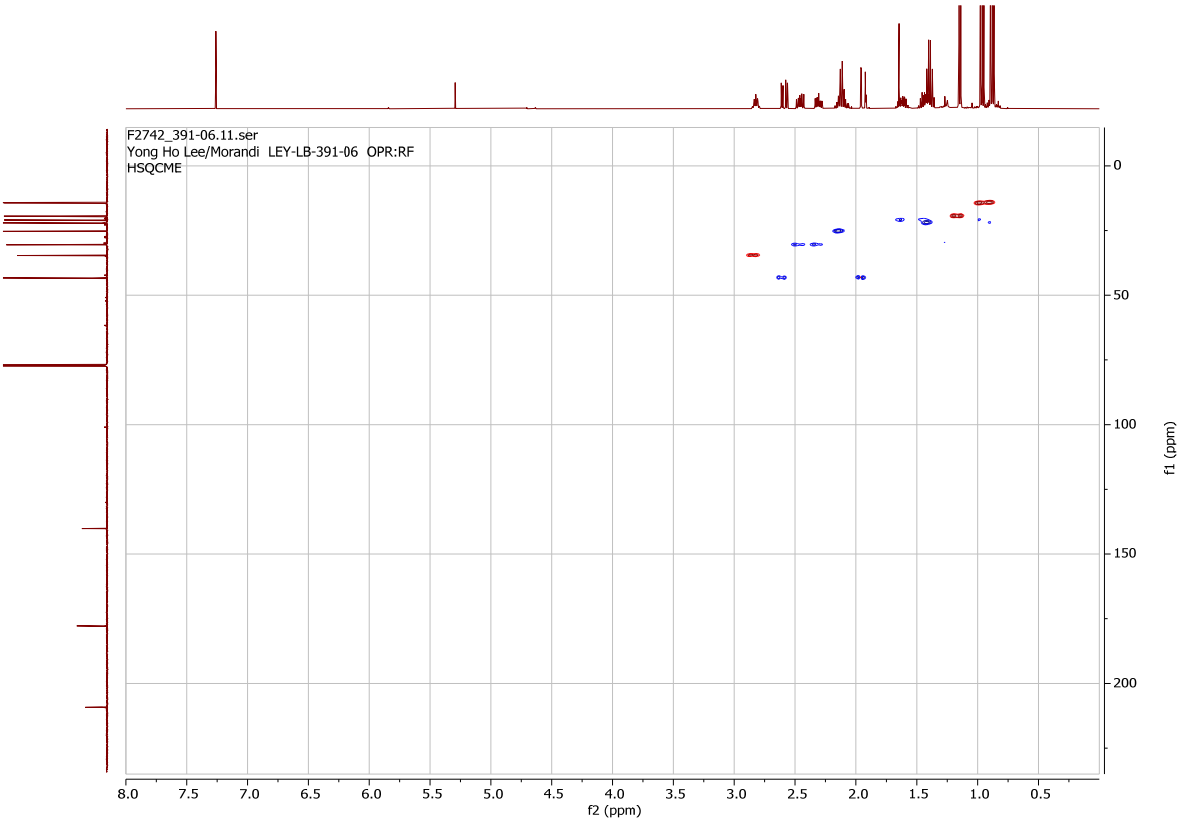

H4016_LB-383-01.12.ser
Yong Ho Lee/Morandi LEY-LB-383-01 OPR:RF
600 MHz HMBC
f2 (ppm)
f1 (ppm)

4-methyl-2,3-dipropylcyclopent-2-en-1-one (**3al**).

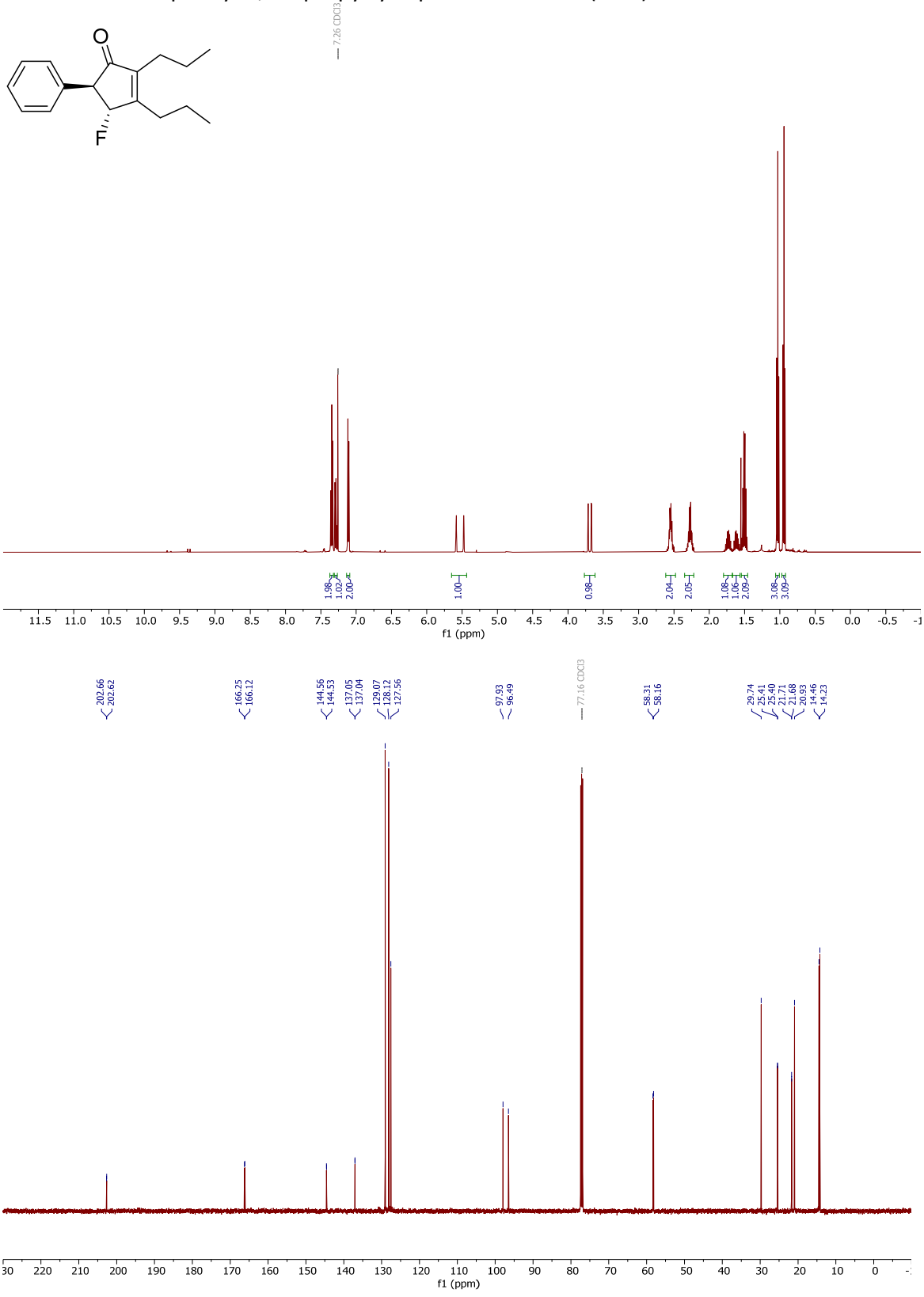


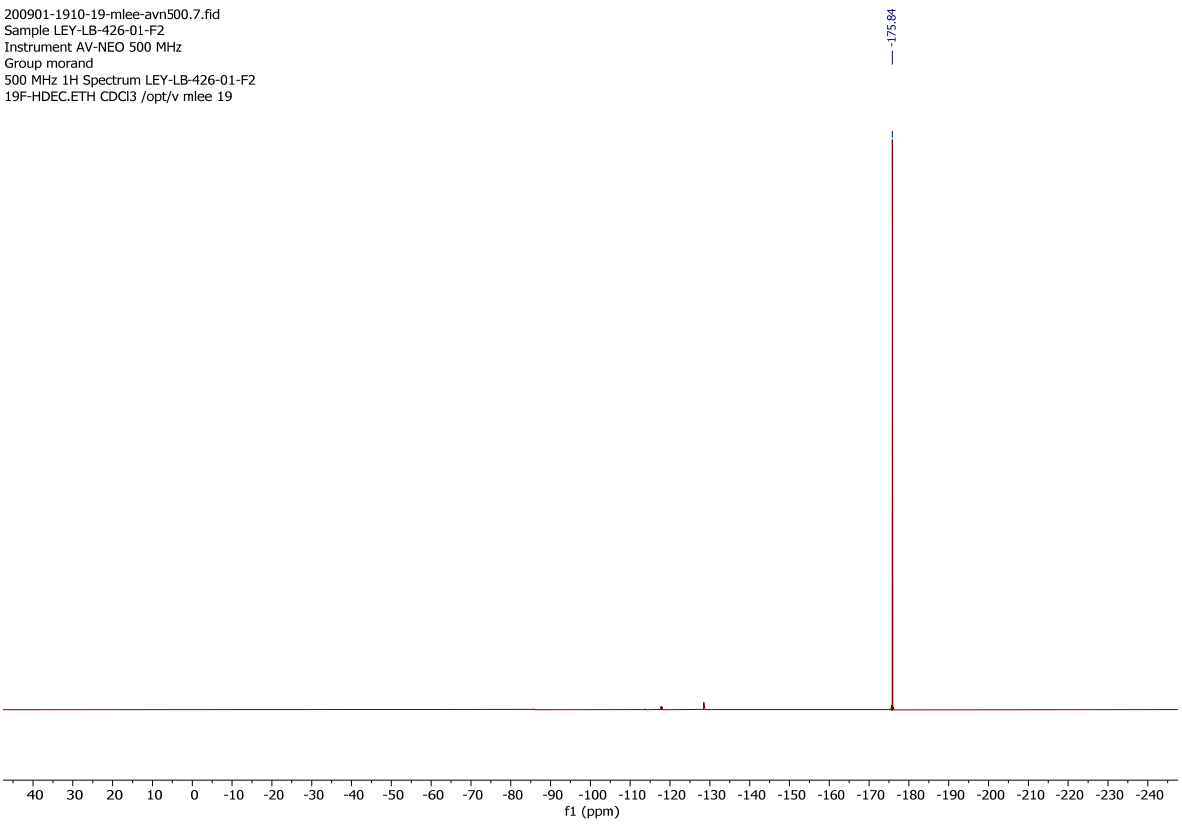


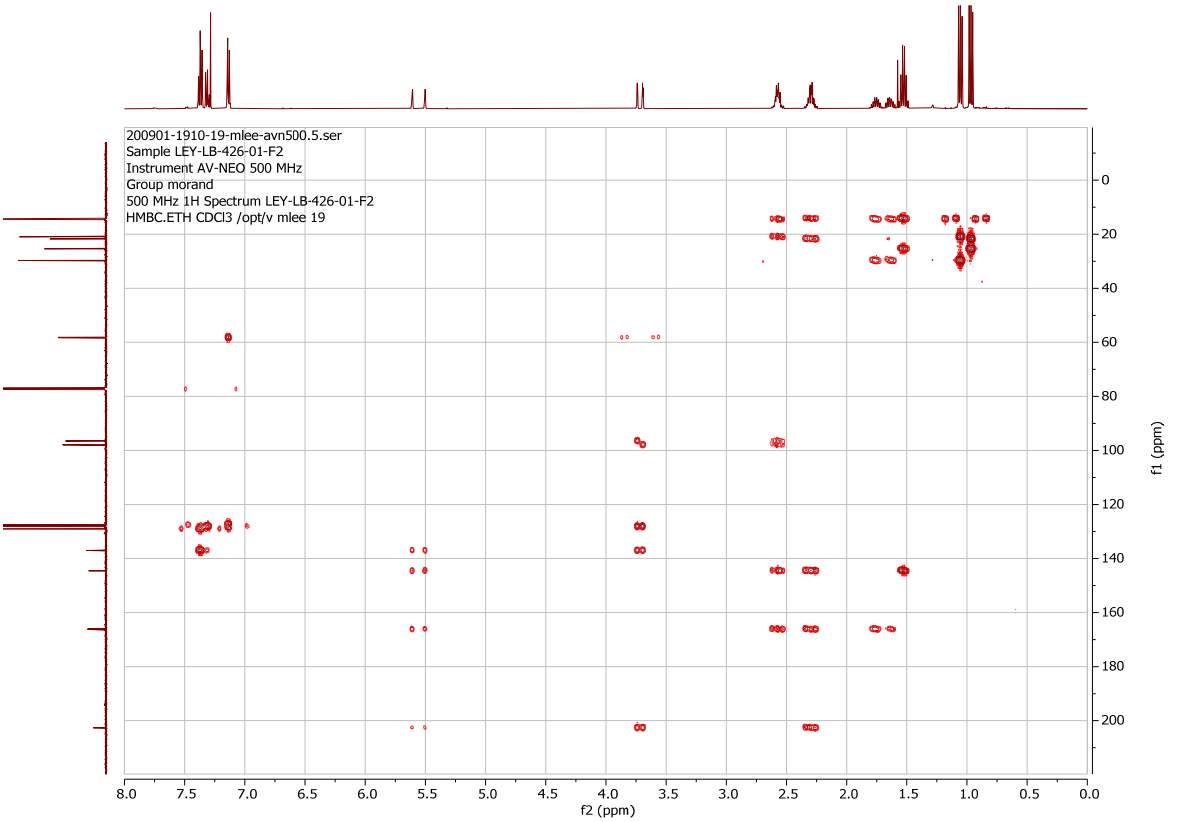

F2742_391-06.12.ser
Yong Ho Lee/Morandi LEY-LB-391-06 OPR:RF
HMBC
f2 (ppm)
f1 (ppm)

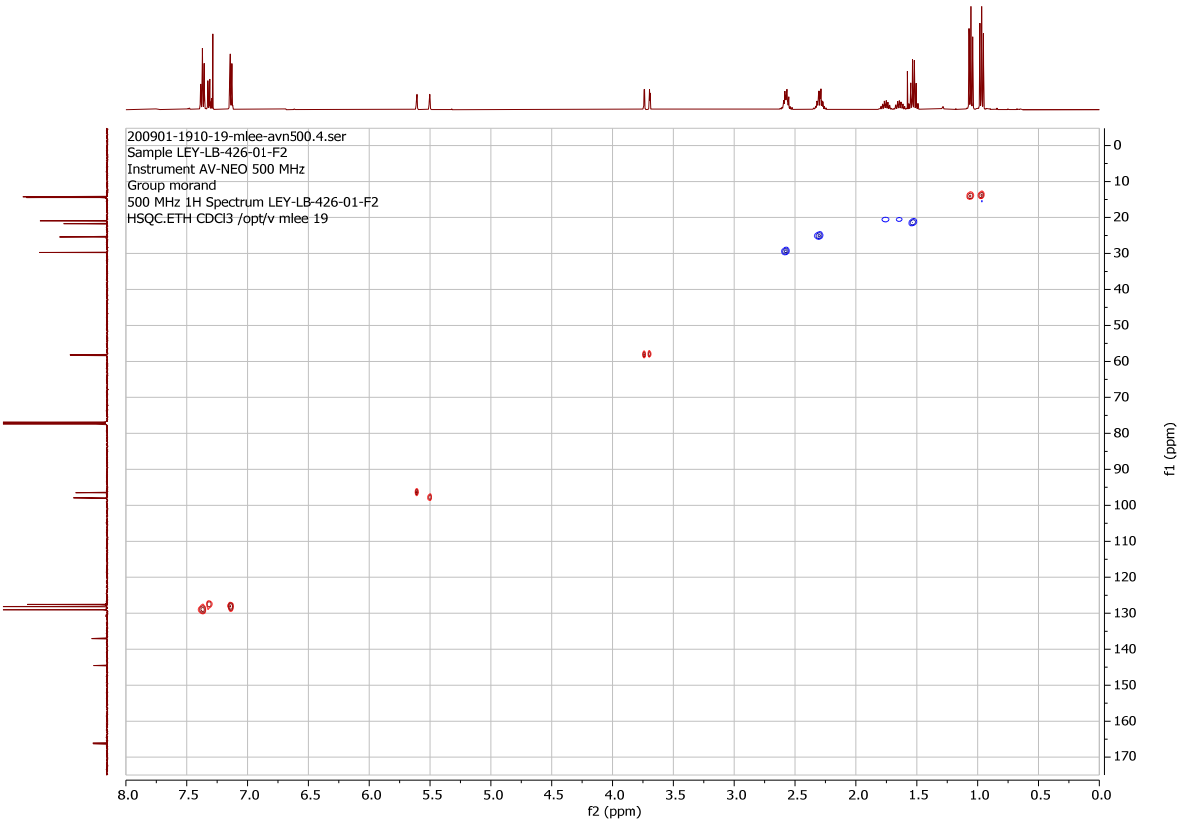

F2742_391-06.11.ser
Yong Ho Lee/Morandi LEY-LB-391-06 OPR:RF
HSQCME
f2 (ppm)
f1 (ppm)

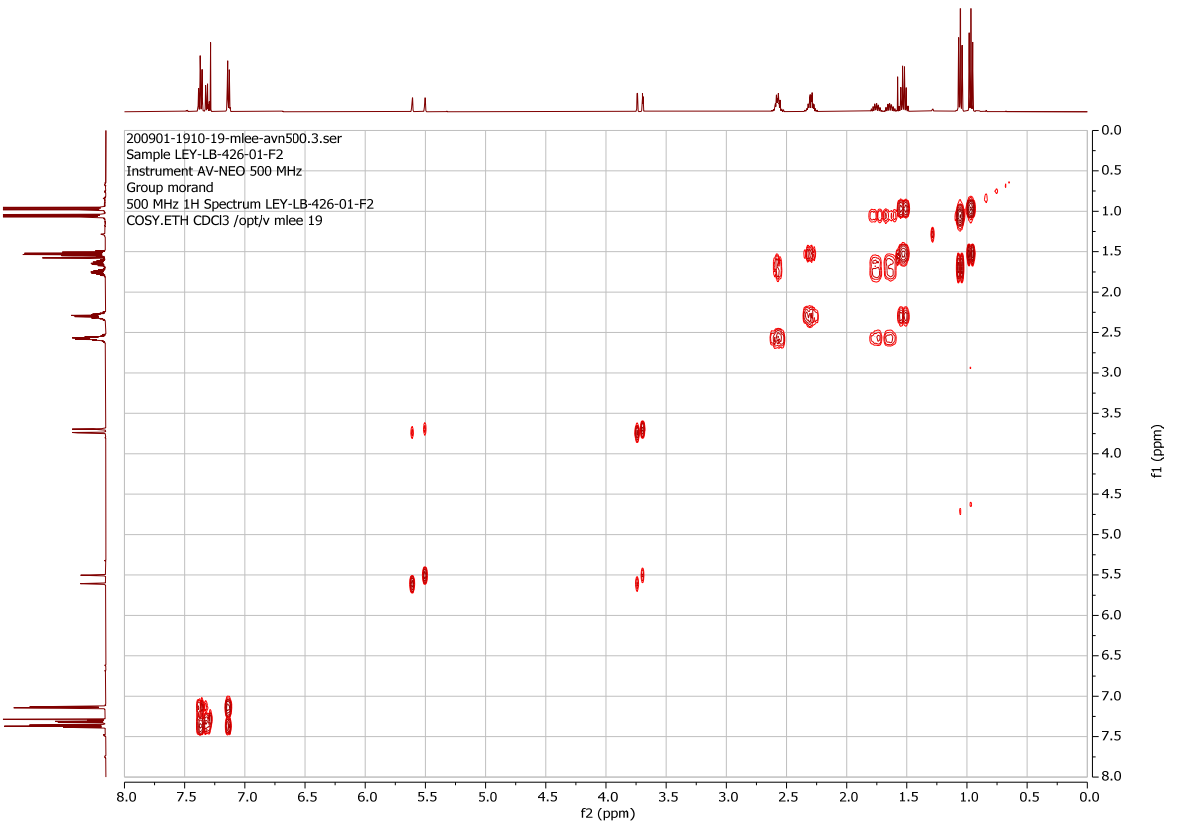
trans-4-fluoro-5-phenyl-2,3-dipropylcyclopent-2-en-1-one (**3am**).

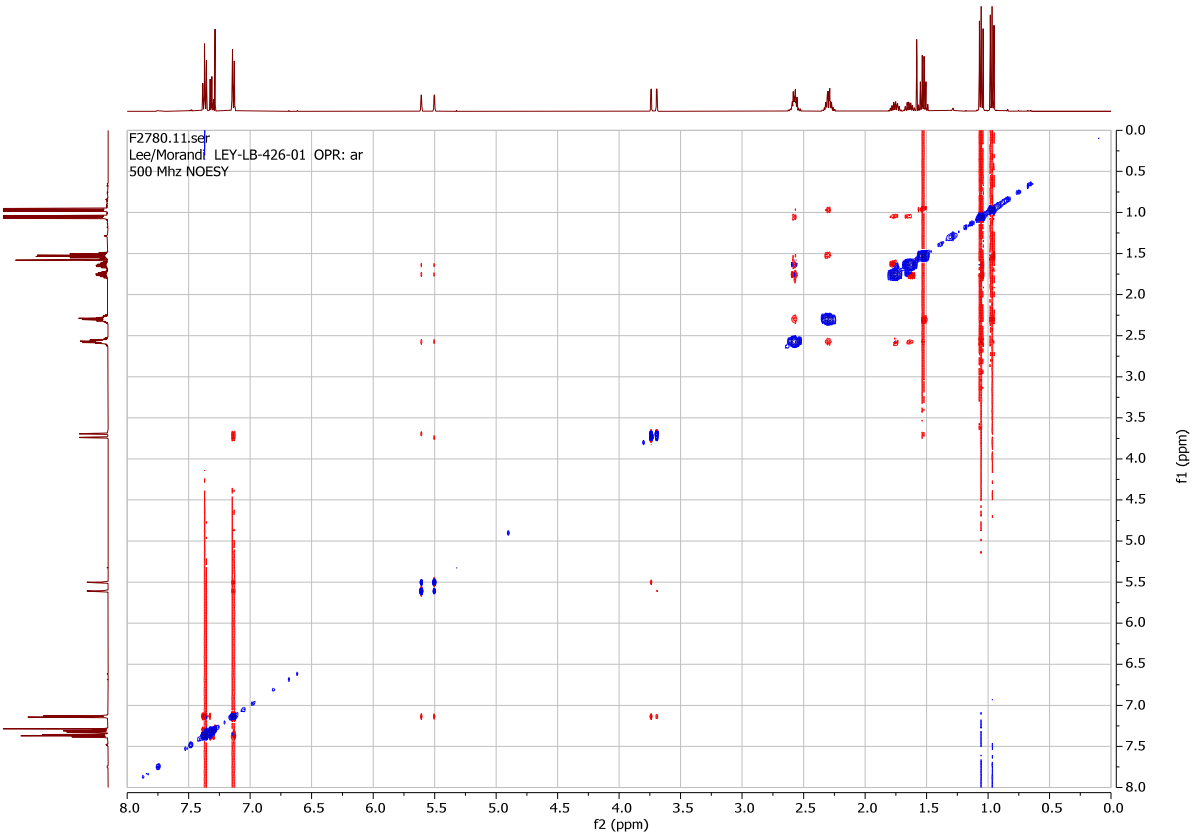


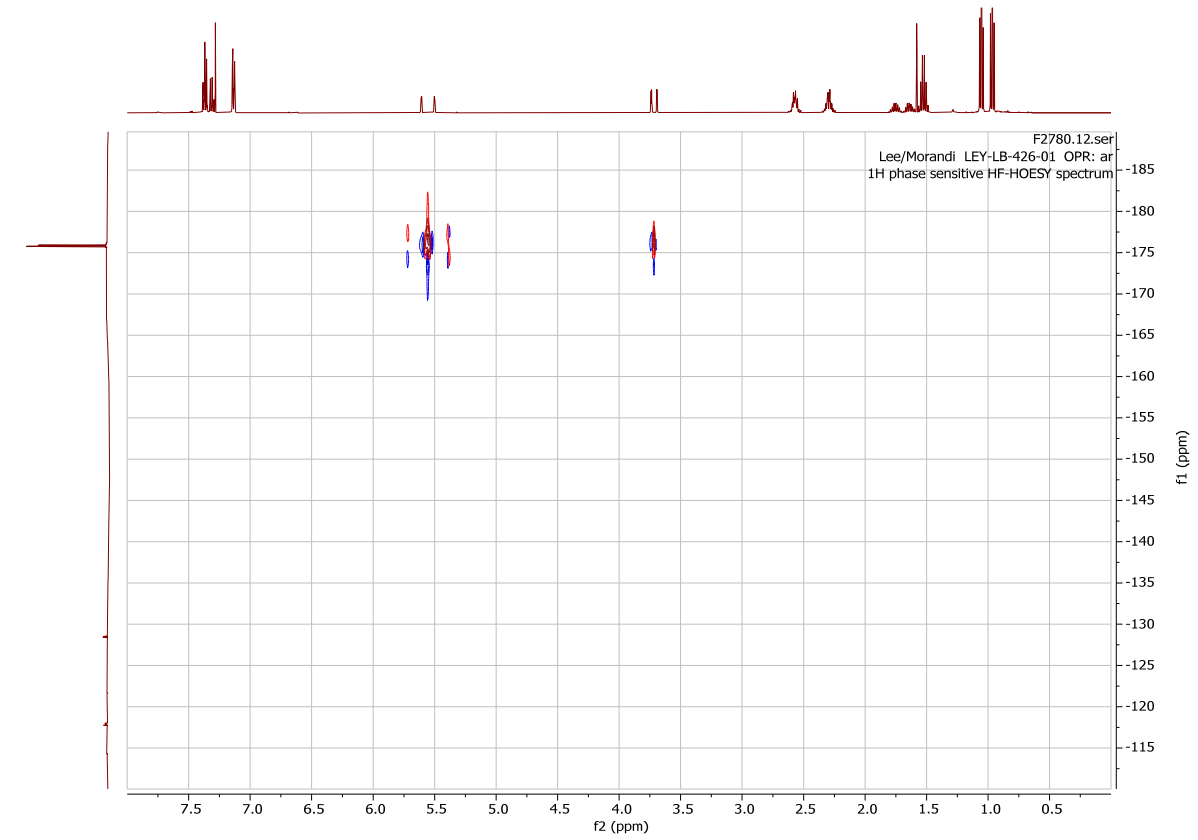

200901-1910-19-mlee-avn500.7.fid
Sample LEY-LB-426-01-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-426-01-F2
19F-HDEC.ETH CDCl3 /opt/v mlee 19
-175.84
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


200901-1910-19-mlee-avn500.5.ser
Sample LEY-LB-426-01-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-426-01-F2
HMBC.ETH CDCl3 /opt/v mlee 19
0 20 40 60 80 100 120 140 160 180 200
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

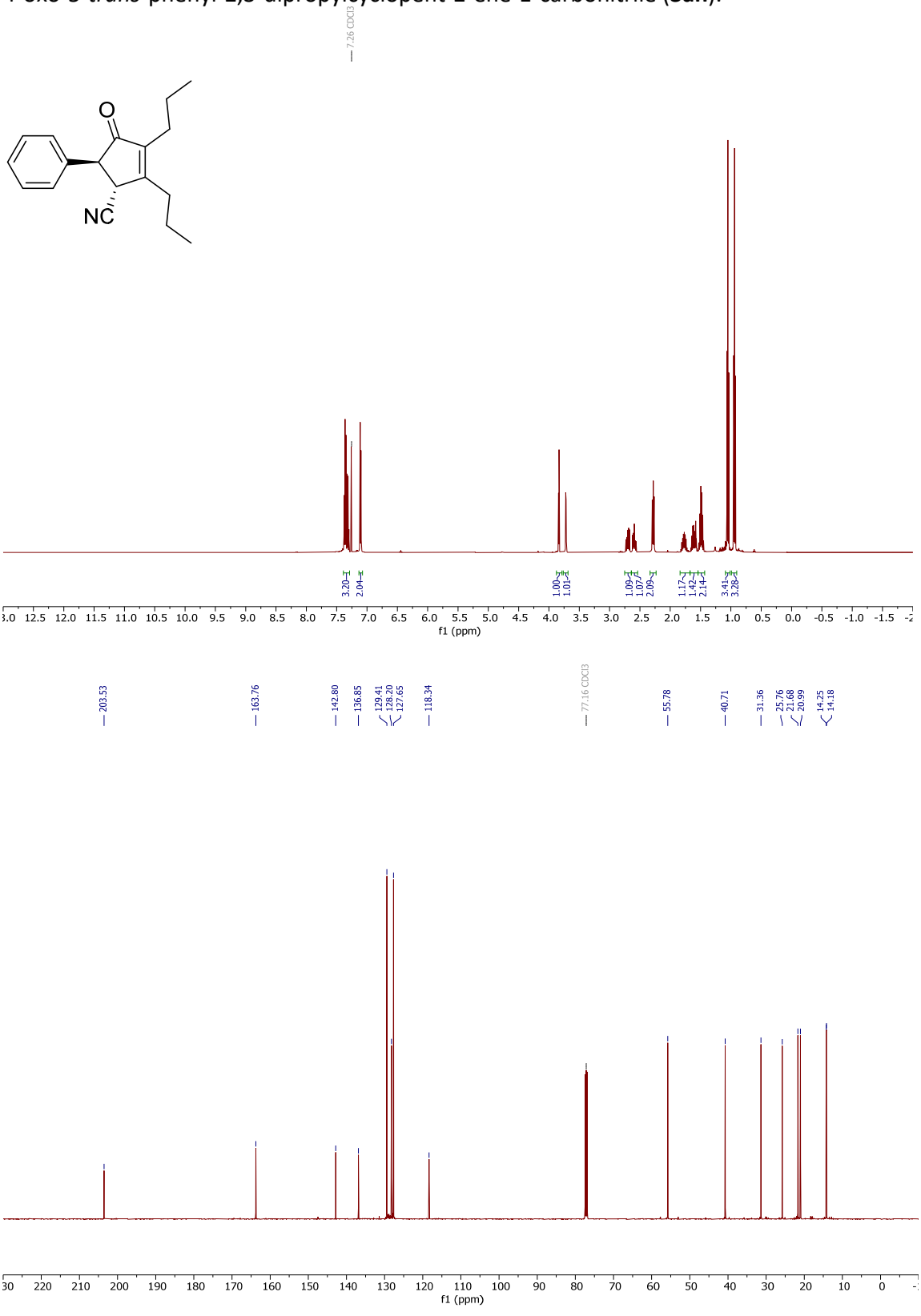

200901-1910-19-mlee-avn500.4.ser
Sample LEY-LB-426-01-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-426-01-F2
HSQC.ETH CDCl3 /opt/v mlee 19
f2 (ppm)
f1 (ppm)

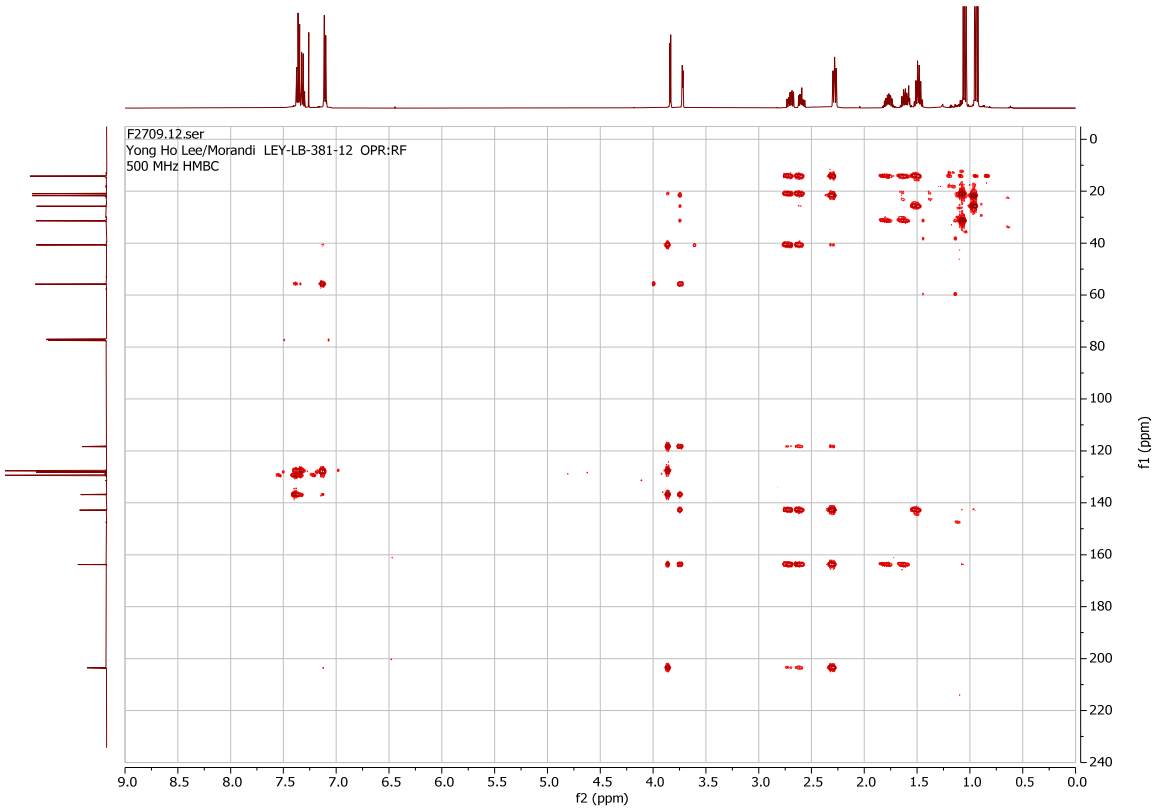

200901-1910-19-mlee-avn500.3.ser
Sample LEY-LB-426-01-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-426-01-F2
COSY.ETH CDCl3 /opt/v mlee 19
f2 (ppm)
f1 (ppm)

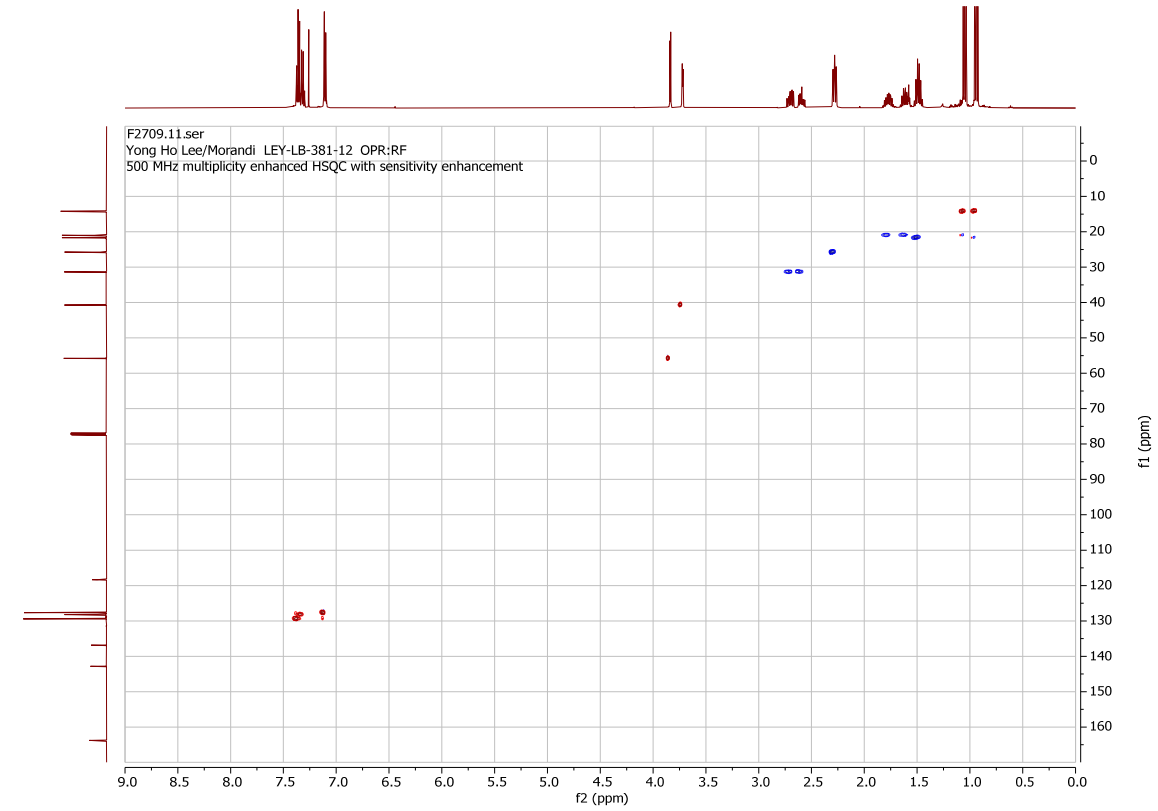

F2780.11.ser
Lee/Morandi LEY-LB-426-01 OPR: ar
500 Mhz NOESY
f2 (ppm)
f1 (ppm)

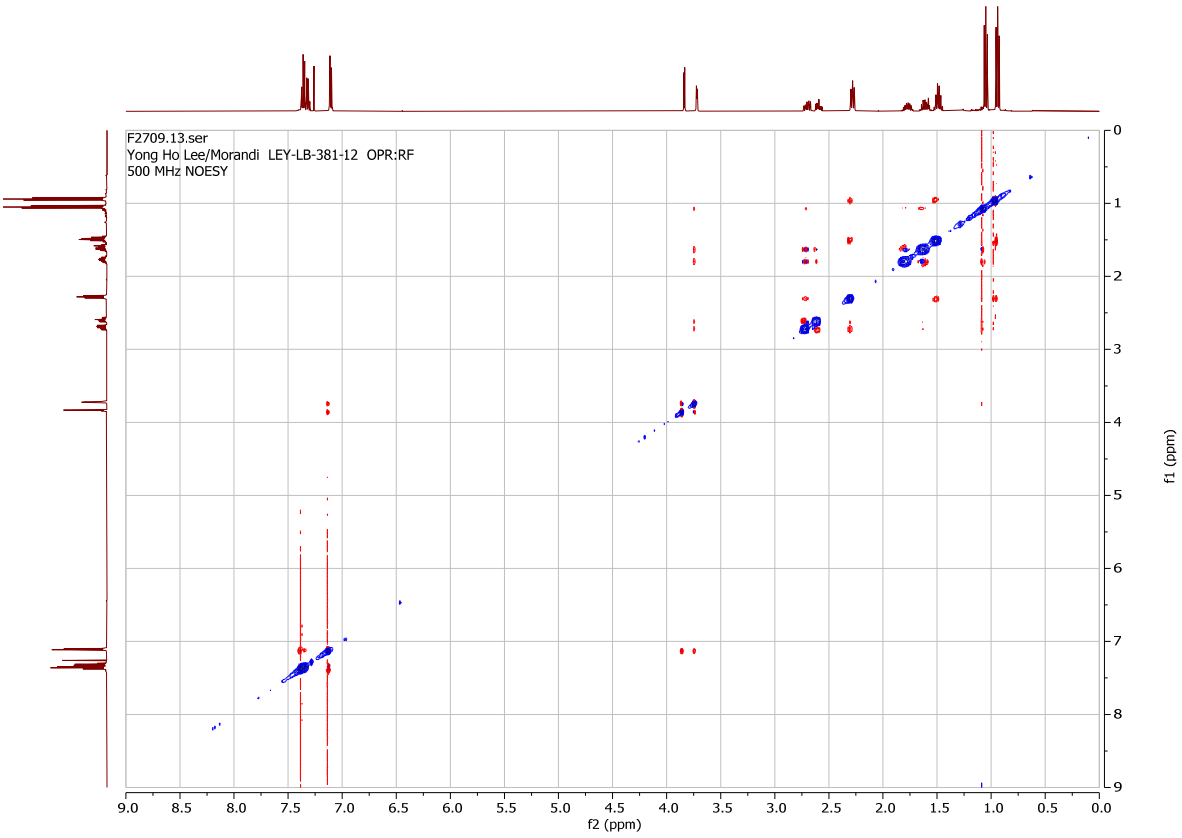

F2780.12.ser
Lee/Morandi LEY-LB-426-01 OPR: ar
1H phase sensitive HF-HOESY spectrum
f2 (ppm)
f1 (ppm)

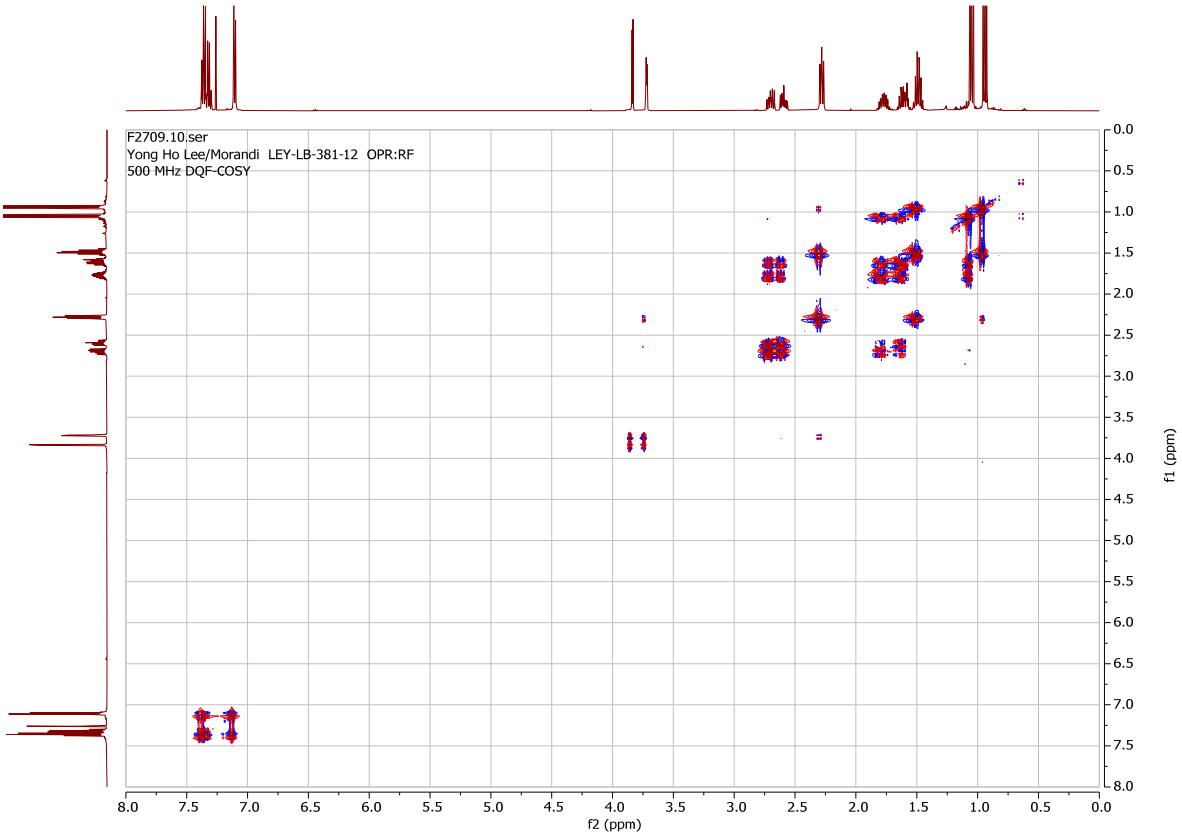
4-oxo-5-*trans*-phenyl-2,3-dipropylcyclopent-2-ene-1-carbonitrile (**3an**).



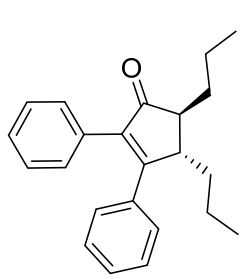

F2709.12.ser
Yong Ho Lee/Morandi LEY-LB-381-12 OPR:RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

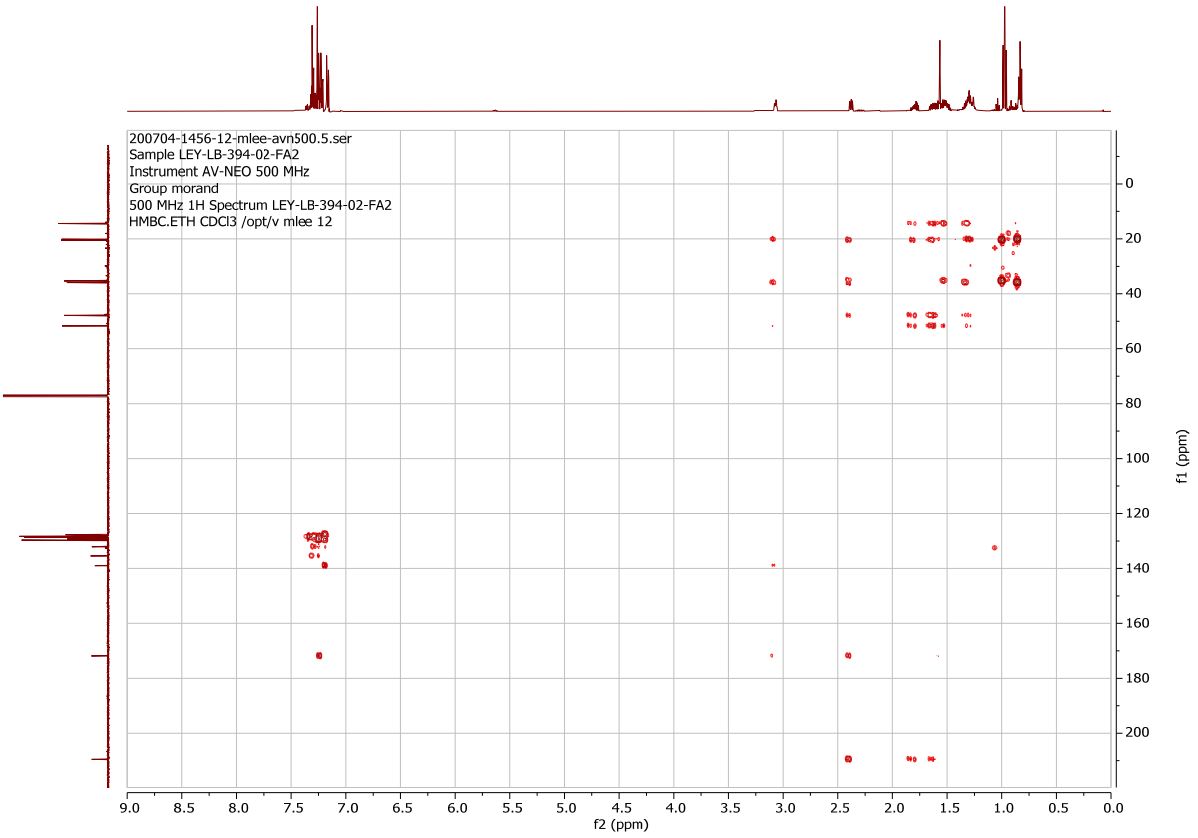

F2709.11.ser
Yong Ho Lee/Morandi LEY-LB-381-12 OPR:RF
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

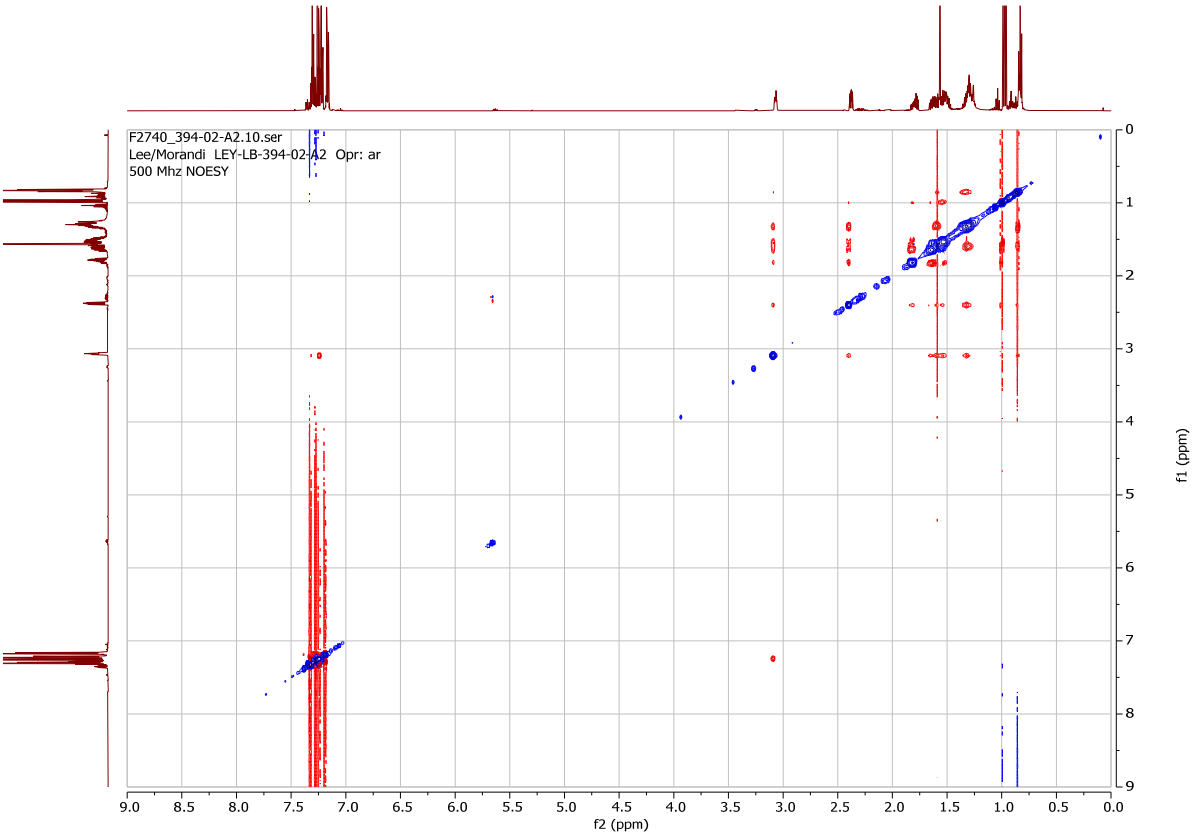

F2709.13.ser
Yong Ho Lee/Morandi LEY-LB-381-12 OPR:RF
500 MHz NOESY
f2 (ppm)
f1 (ppm)


F2709.10.ser
Yong Ho Lee/Morandi LEY-LB-381-12 OPR:RF
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

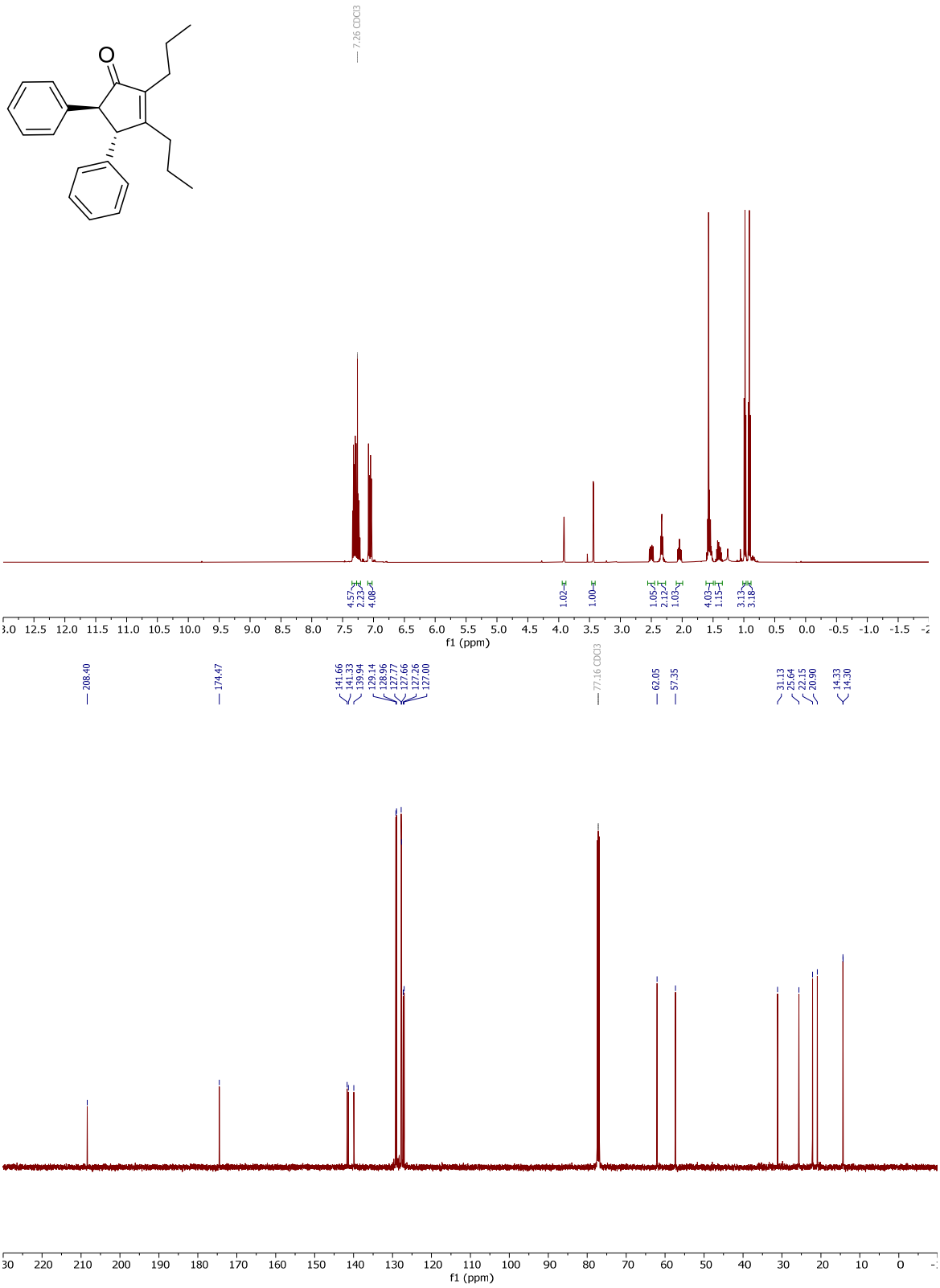
2,3-diphenyl-4,5-*trans*-dipropylcyclopent-2-en-1-one (**3ao-2**, major).

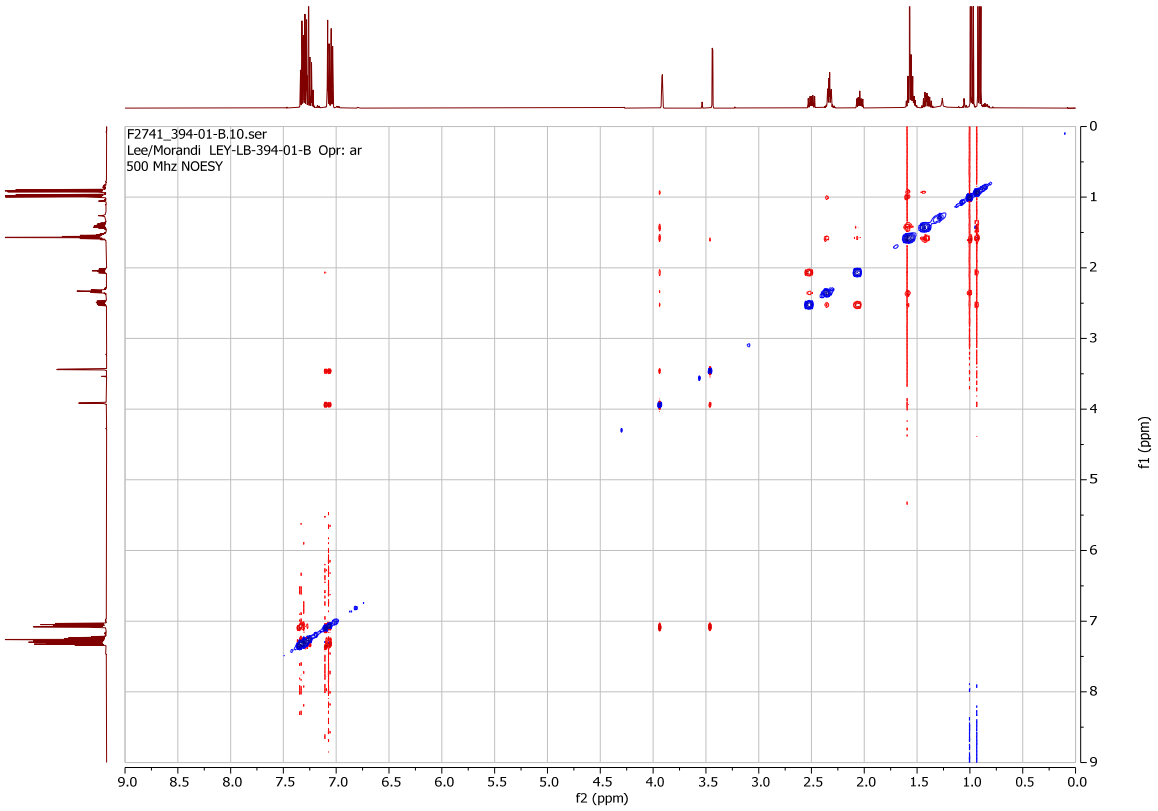


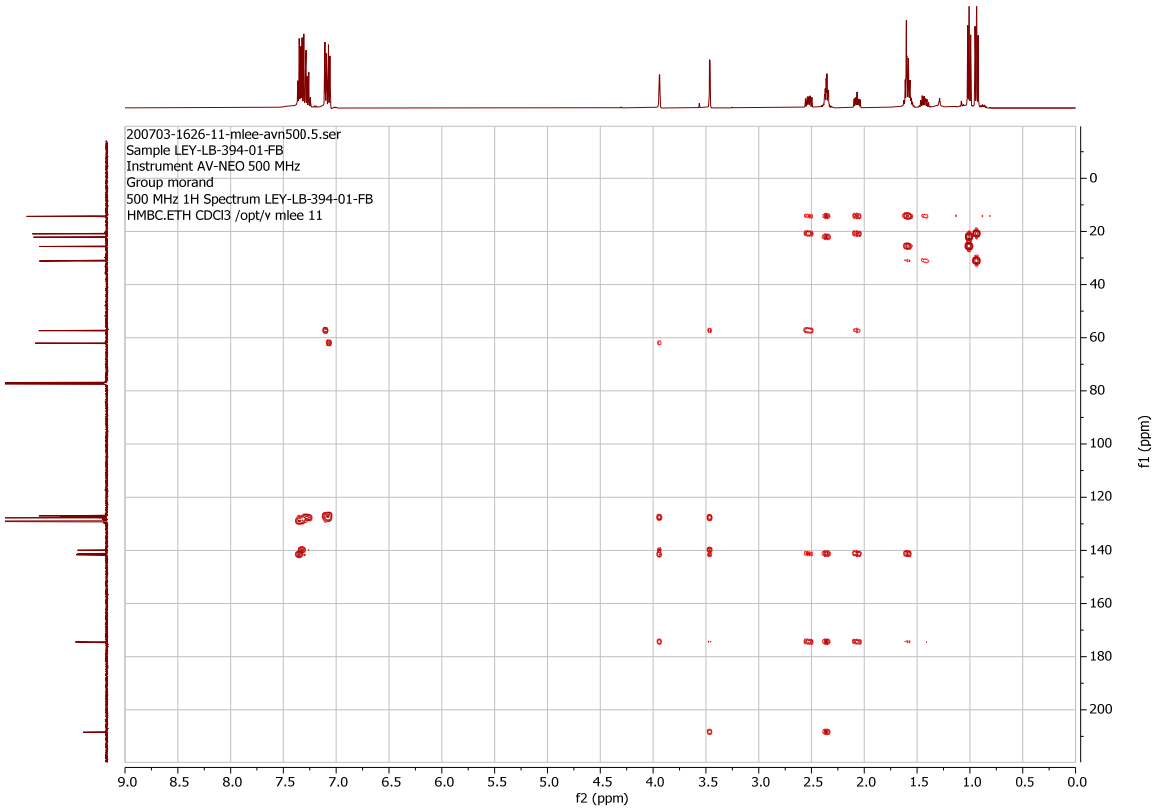

200704-1456-12-mlee-avn500.5.ser
Sample LEY-LB-394-02-FA2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-394-02-FA2
HMBC.ETH CDCl3 /opt/v mlee 12
f2 (ppm)
f1 (ppm)


F2740_394-02-A2.10.ser
Lee/Morandi LEY-LB-394-02-A2 Opr: ar
500 Mhz NOESY
f2 (ppm)
f1 (ppm)

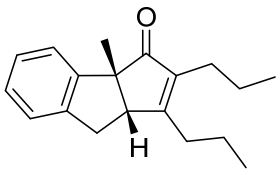
4,5-*trans*-diphenyl-2,3-dipropylcyclopent-2-en-1-one (**3ao-1**, minor).

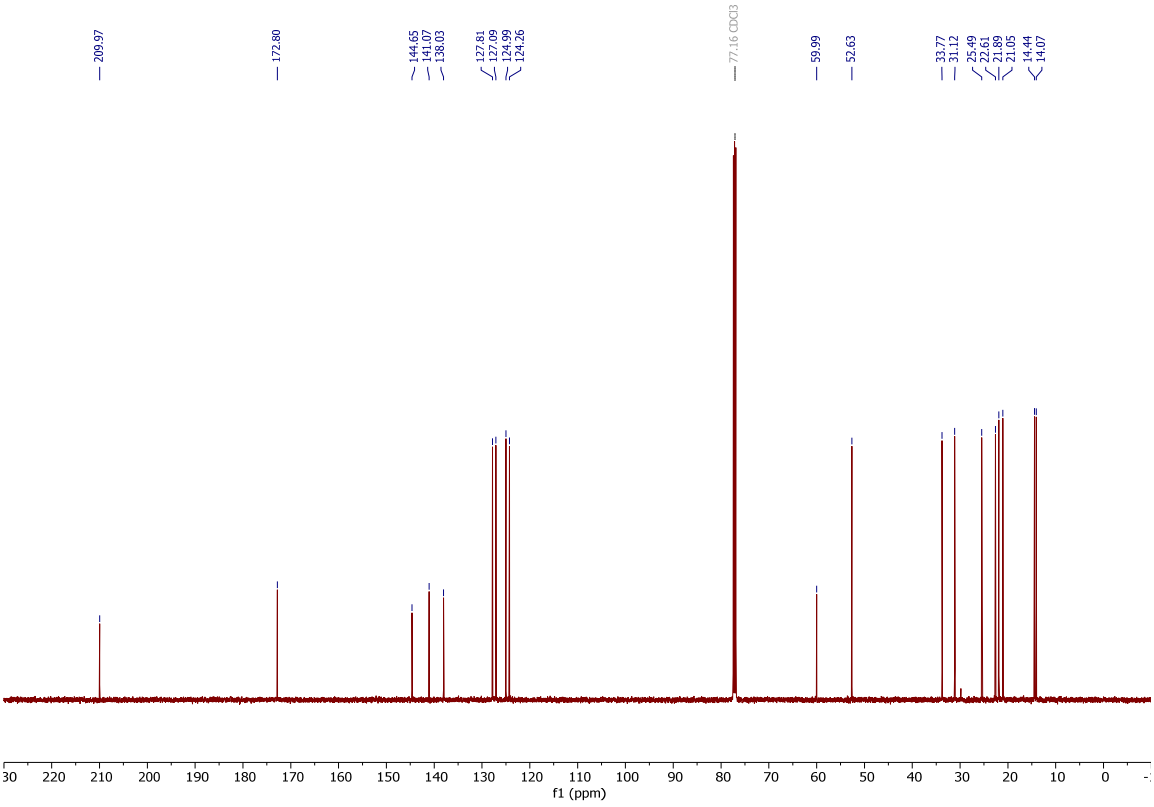


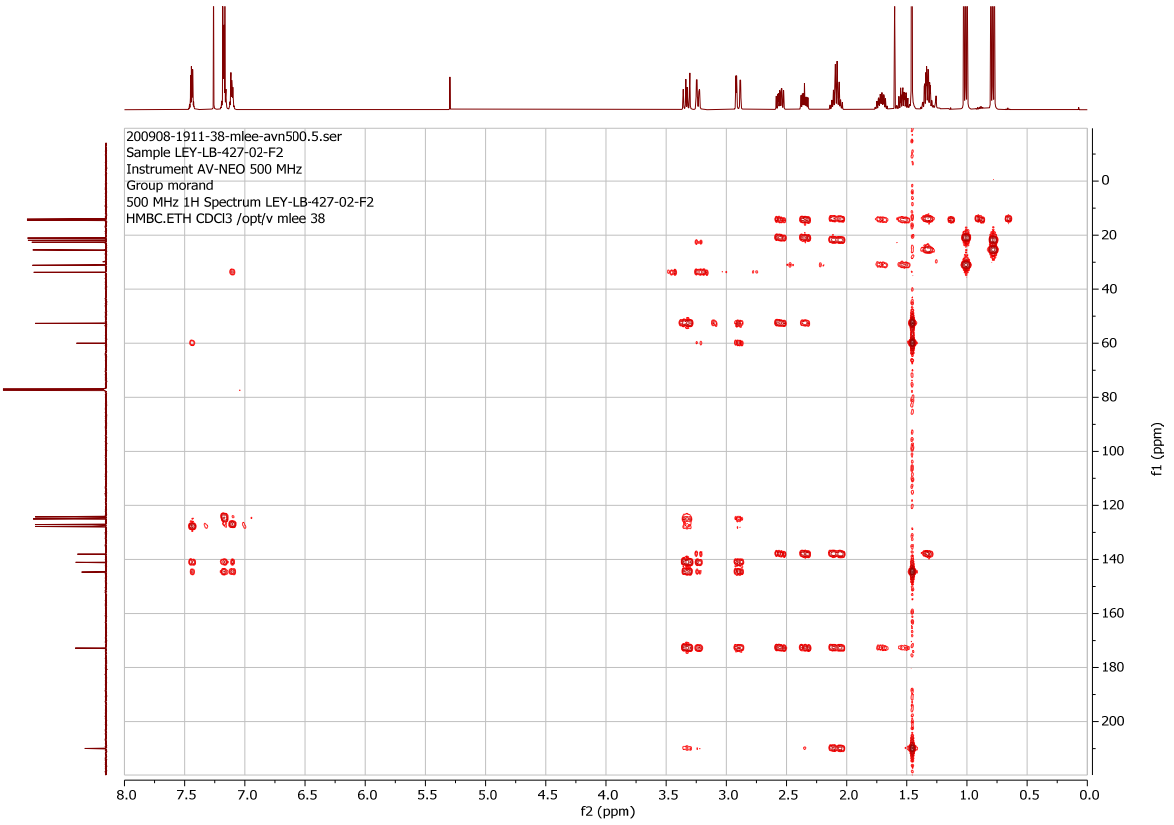

F2741_394-01-B.10.ser
Lee/Morandi LEY-LB-394-01-B Opr: ar
500 Mhz NOESY
f2 (ppm)
f1 (ppm)

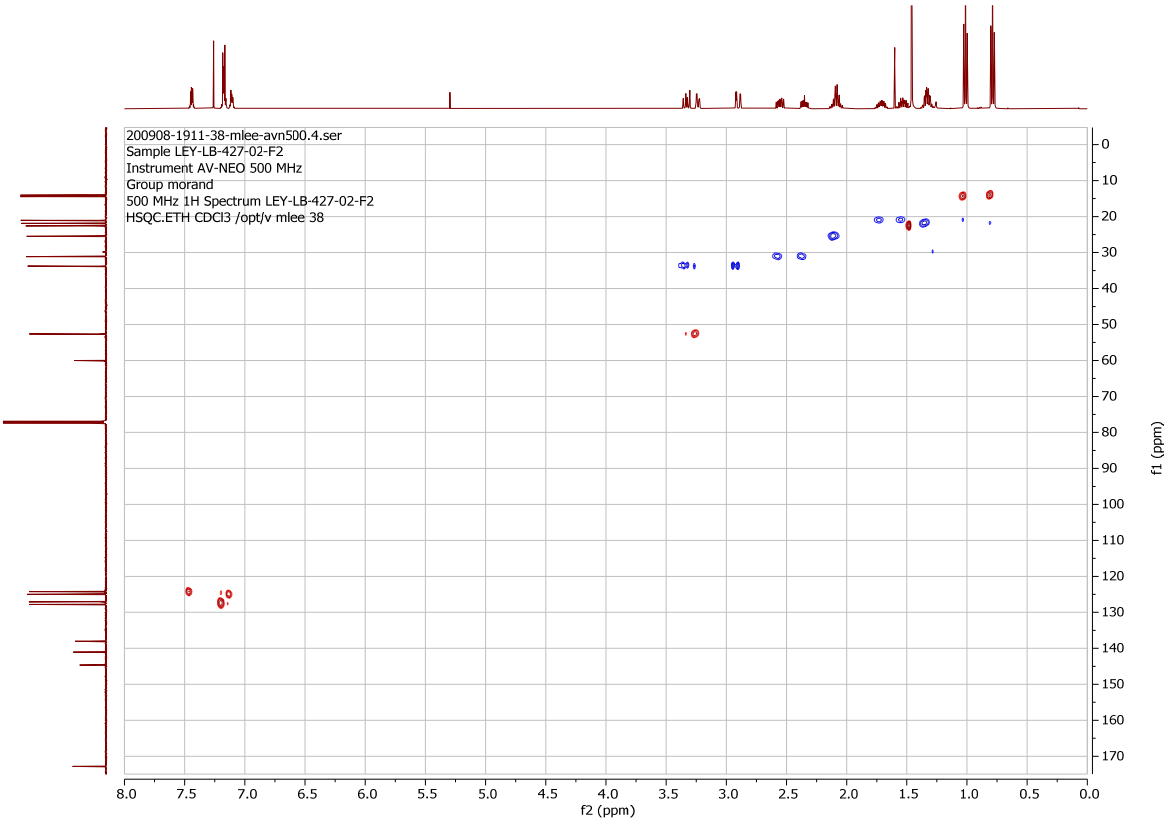

200703-1626-11-mlee-avn500.5.ser
Sample LEY-LB-394-01-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-394-01-FB
HMBC.ETH CDCl3 /opt/v mlee 11
f2 (ppm)
f1 (ppm)

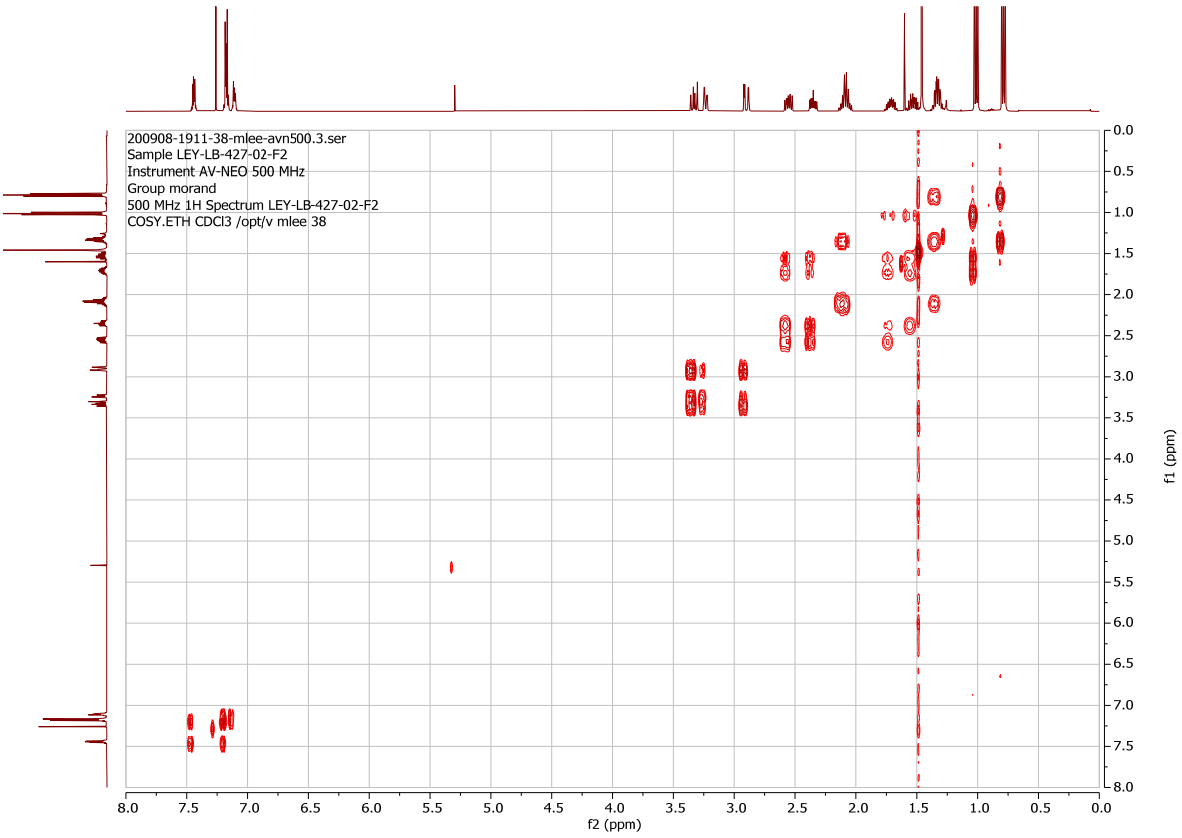
(3a,8a-*cis*)-3a-methyl-1,2-dipropyl-8,8a-dihydrocyclopenta[a]inden-3(3a*H*)-one (**3ap**).

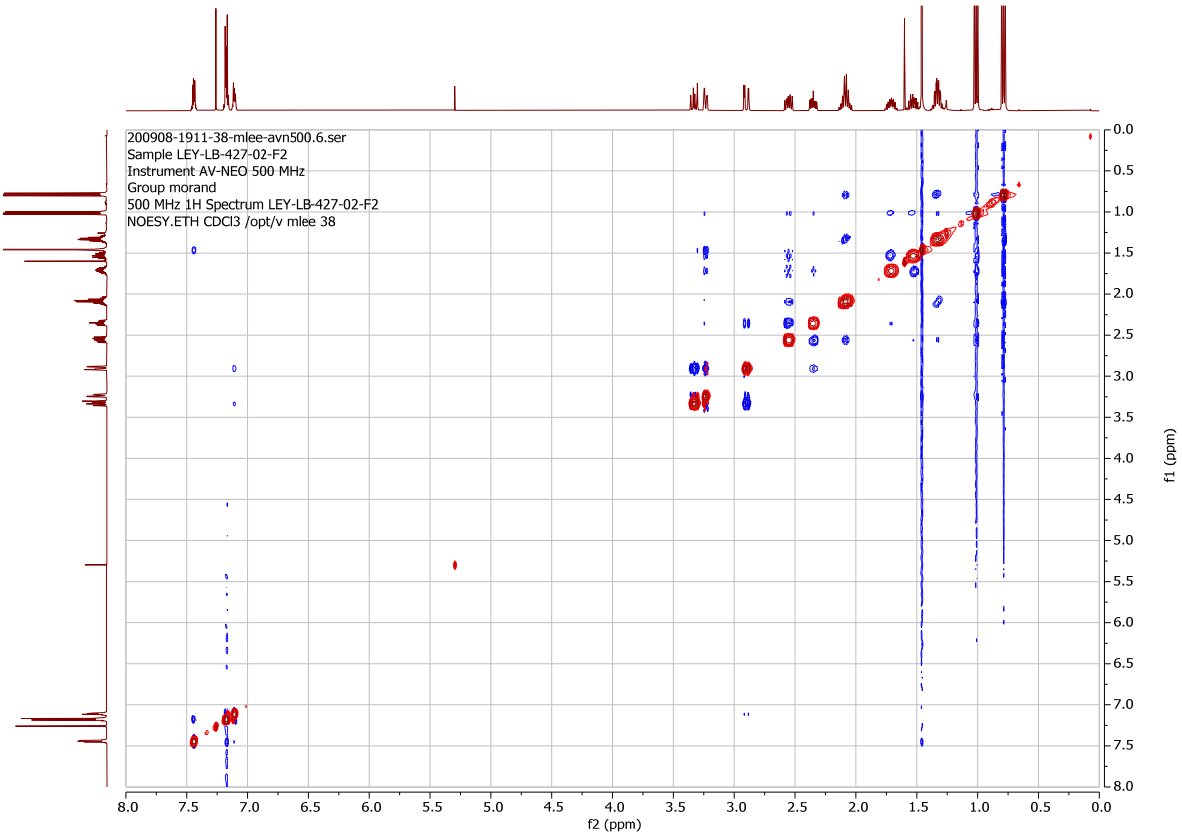


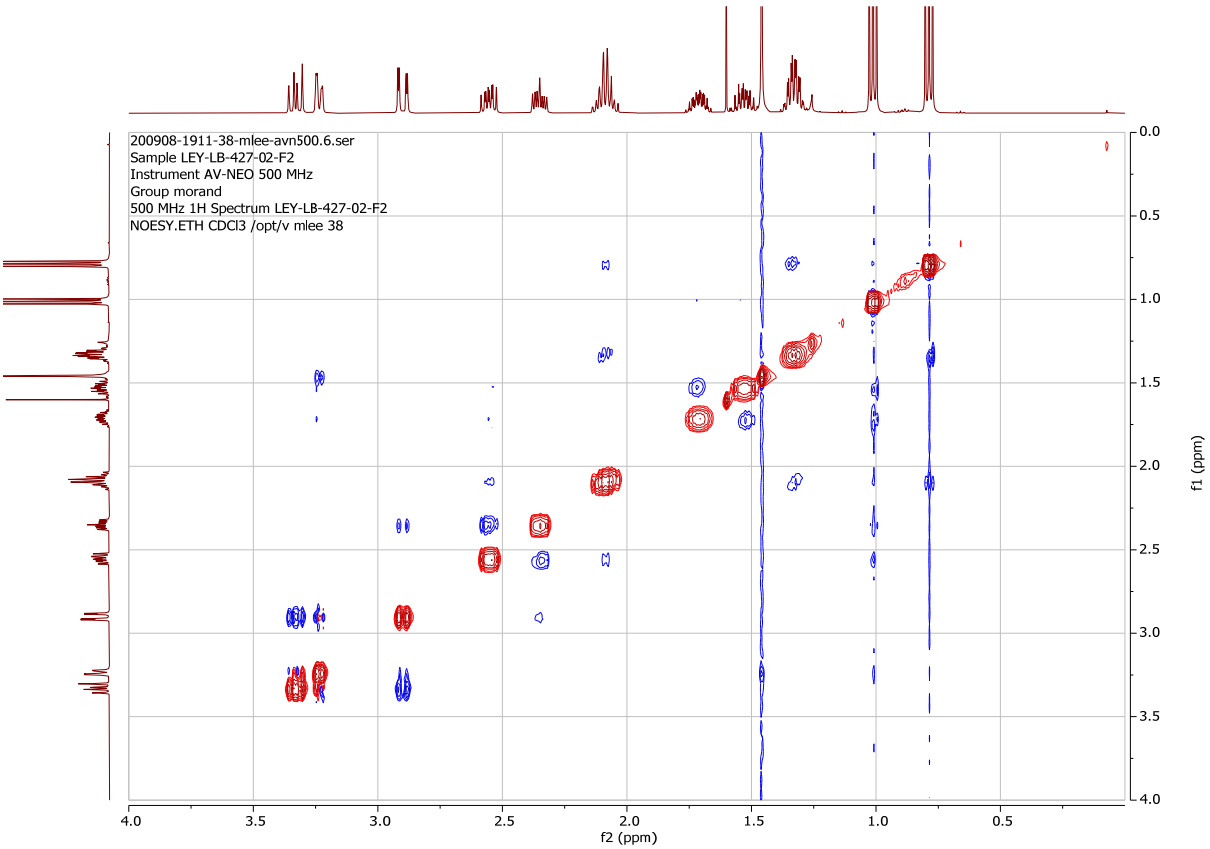



200908-1911-38-mlee-avn500.5.ser
Sample LEY-LB-427-02-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-02-F2
HMBC.ETH CDCl3 /opt/v mlee 38
f2 (ppm)
f1 (ppm)

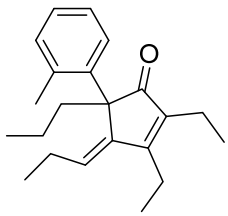

200908-1911-38-mlee-avn500.4.ser
Sample LEY-LB-427-02-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-02-F2
HSQC.ETH CDCl3 /opt/v mlee 38
f2 (ppm)
f1 (ppm)

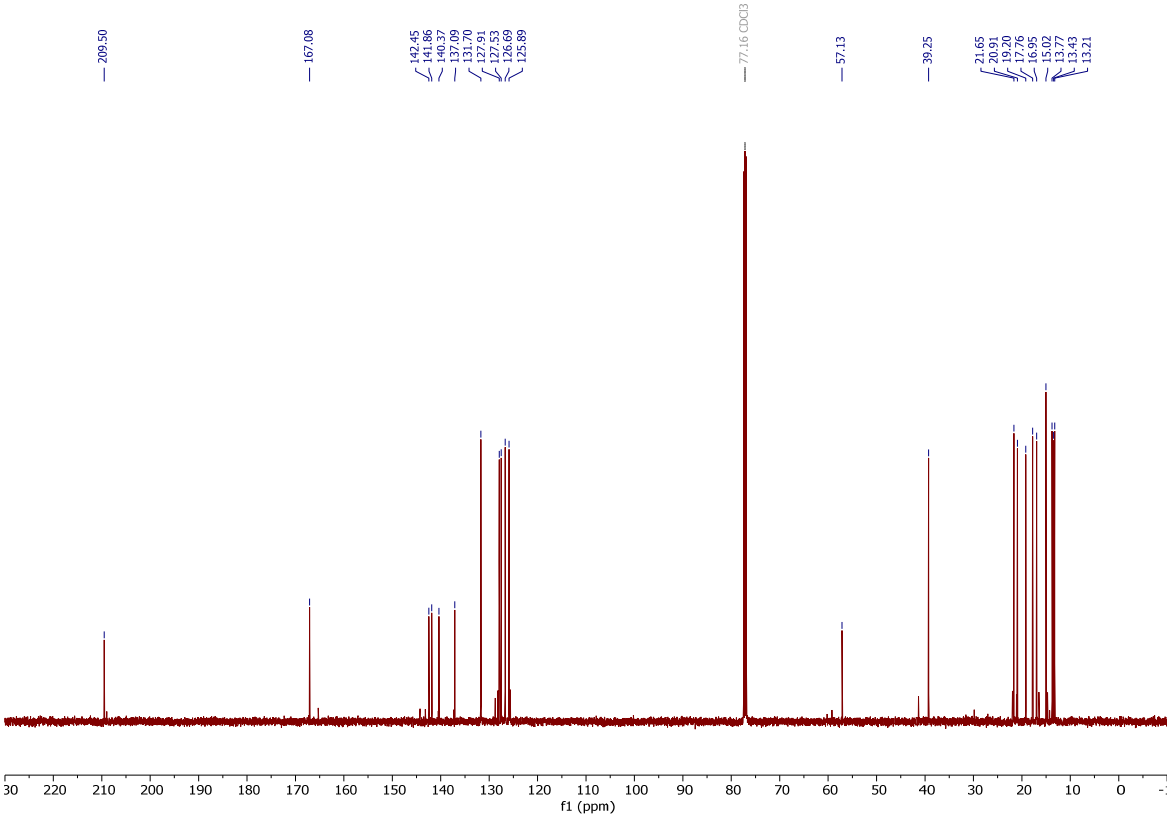

200908-1911-38-mlee-avn500.3.ser
Sample LEY-LB-427-02-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-02-F2
COSY.ETH CDCl3 /opt/v mlee 38
f2 (ppm)
f1 (ppm)

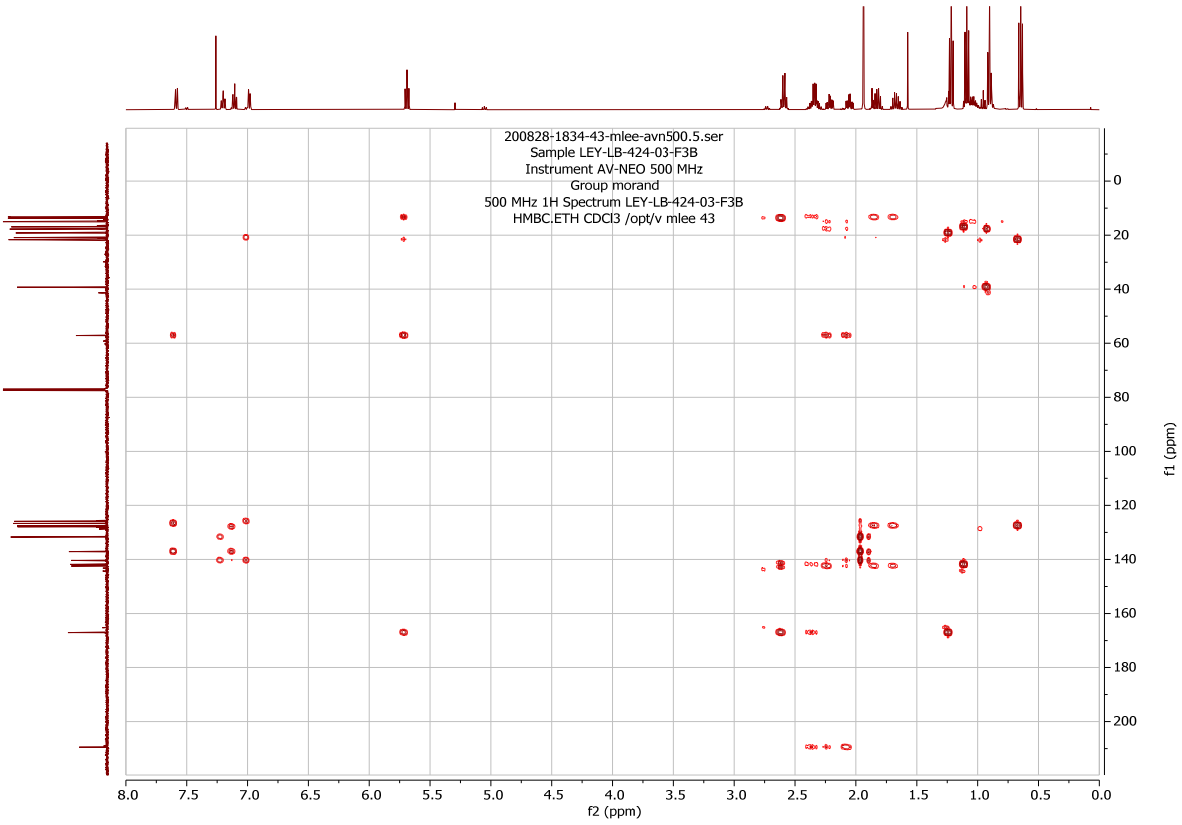

200908-1911-38-mlee-avn500.6.ser
Sample LEY-LB-427-02-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-02-F2
NOESY.ETH CDCl3 /opt/v mlee 38
f2 (ppm)
f1 (ppm)

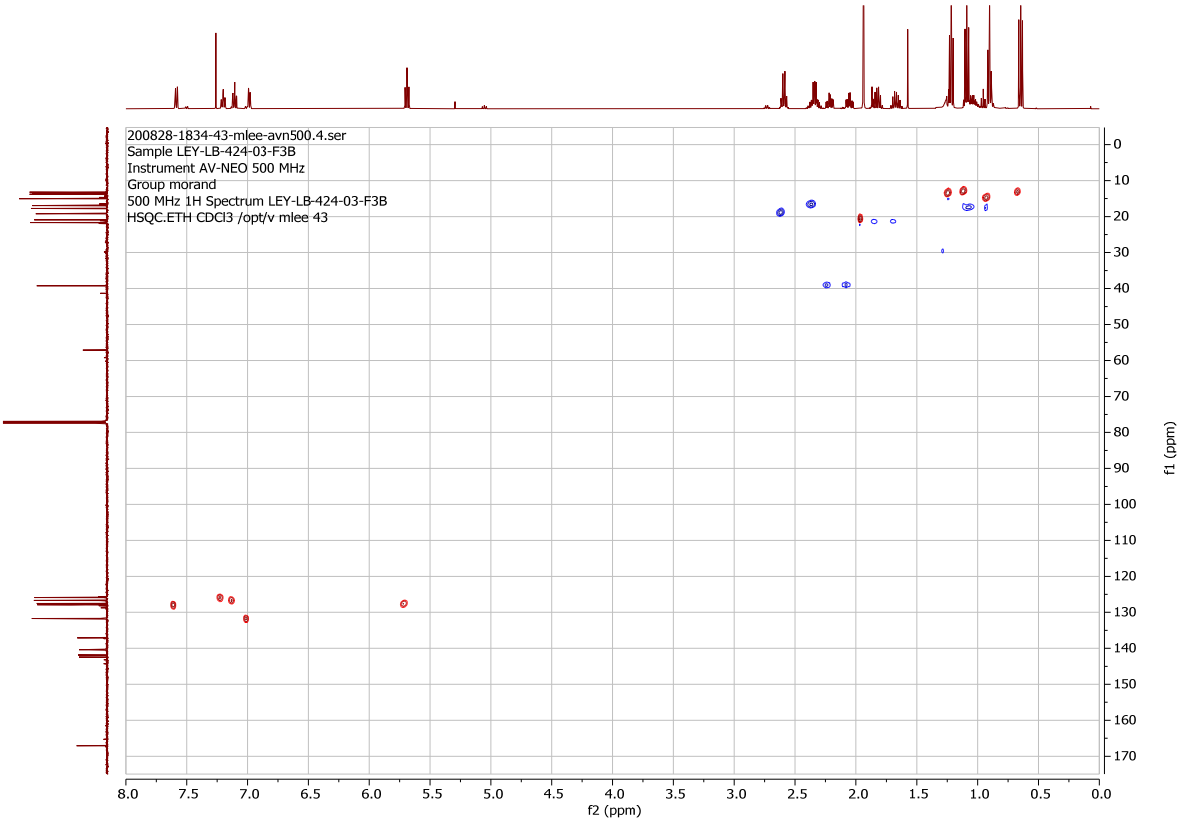

200908-1911-38-mlee-avn500.6.ser
Sample LEY-LB-427-02-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-02-F2
NOESY.ETH CDCl3 /opt/v mlee 38
f2 (ppm)
f1 (ppm)

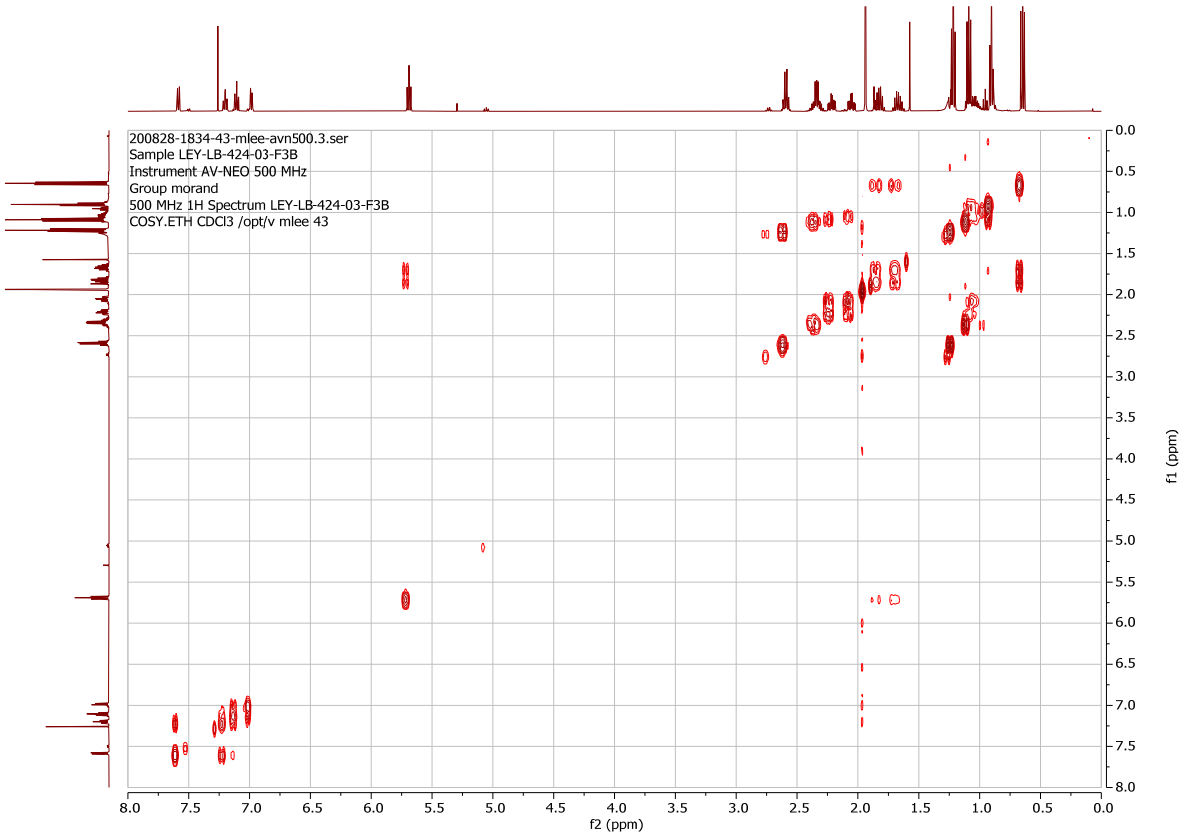
(*Z*)-2,3-diethyl-5-propyl-4-propylidene-5-(*o*-tolyl)cyclopent-2-en-1-one (**3aq-1**, major).

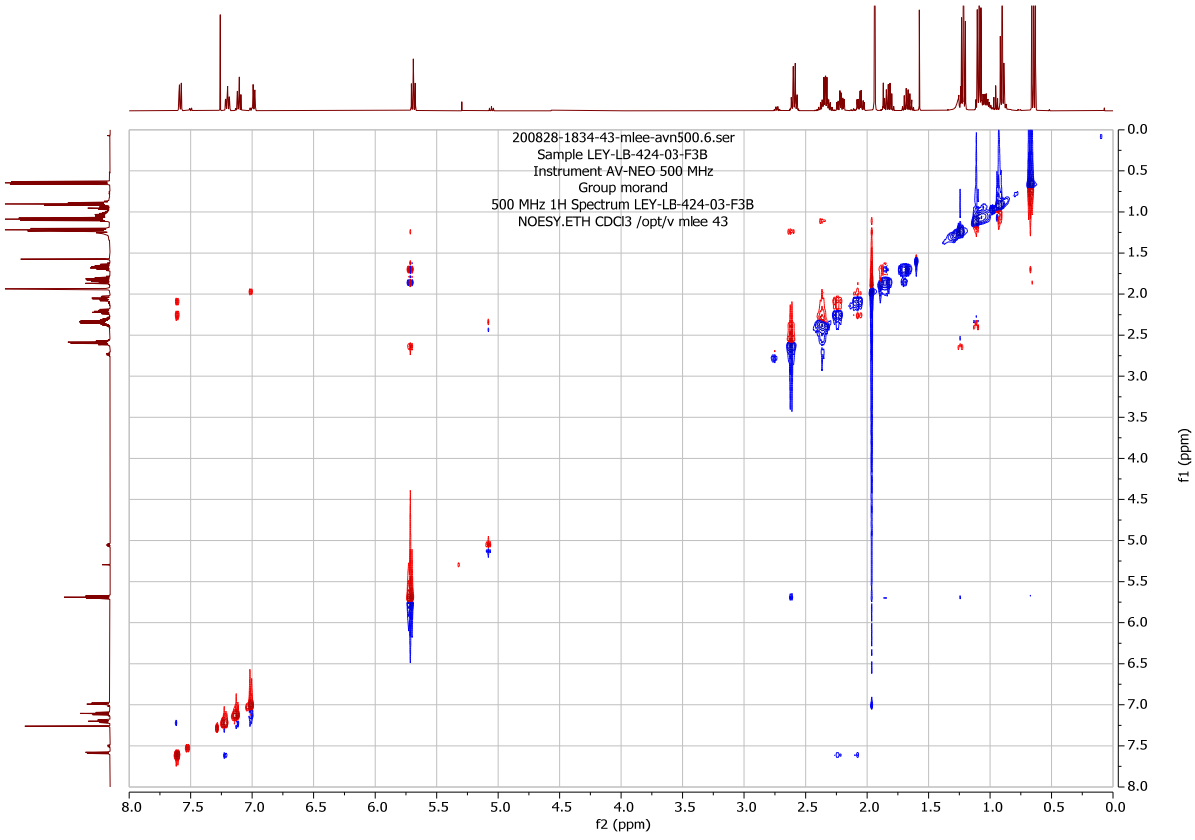




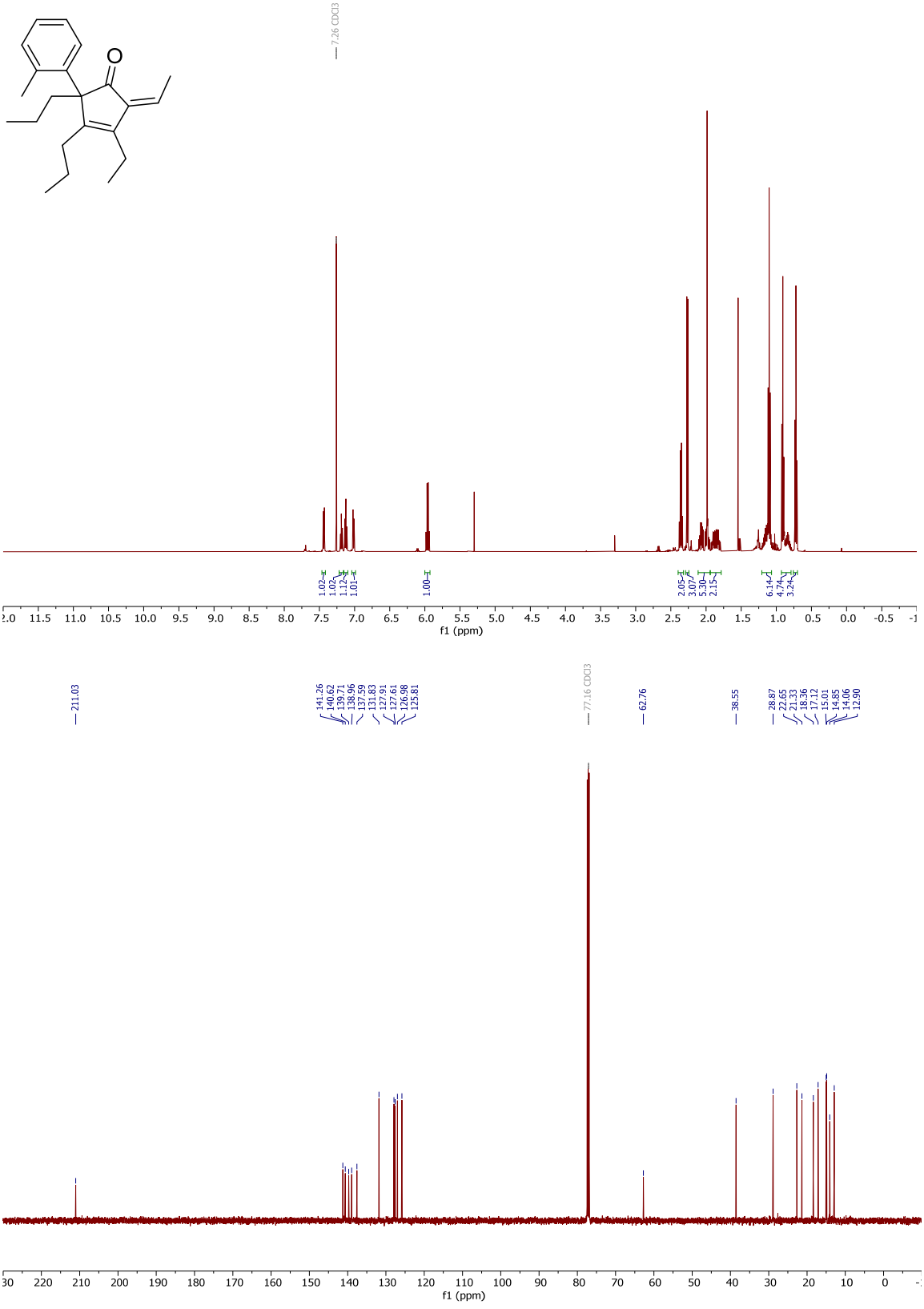

200828-1834-43-mlee-avn500.5.ser
Sample LEY-LB-424-03-F3B
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F3B
HMBC.ETH CDCl3 /opt/v mlee 43
f2 (ppm)
f1 (ppm)

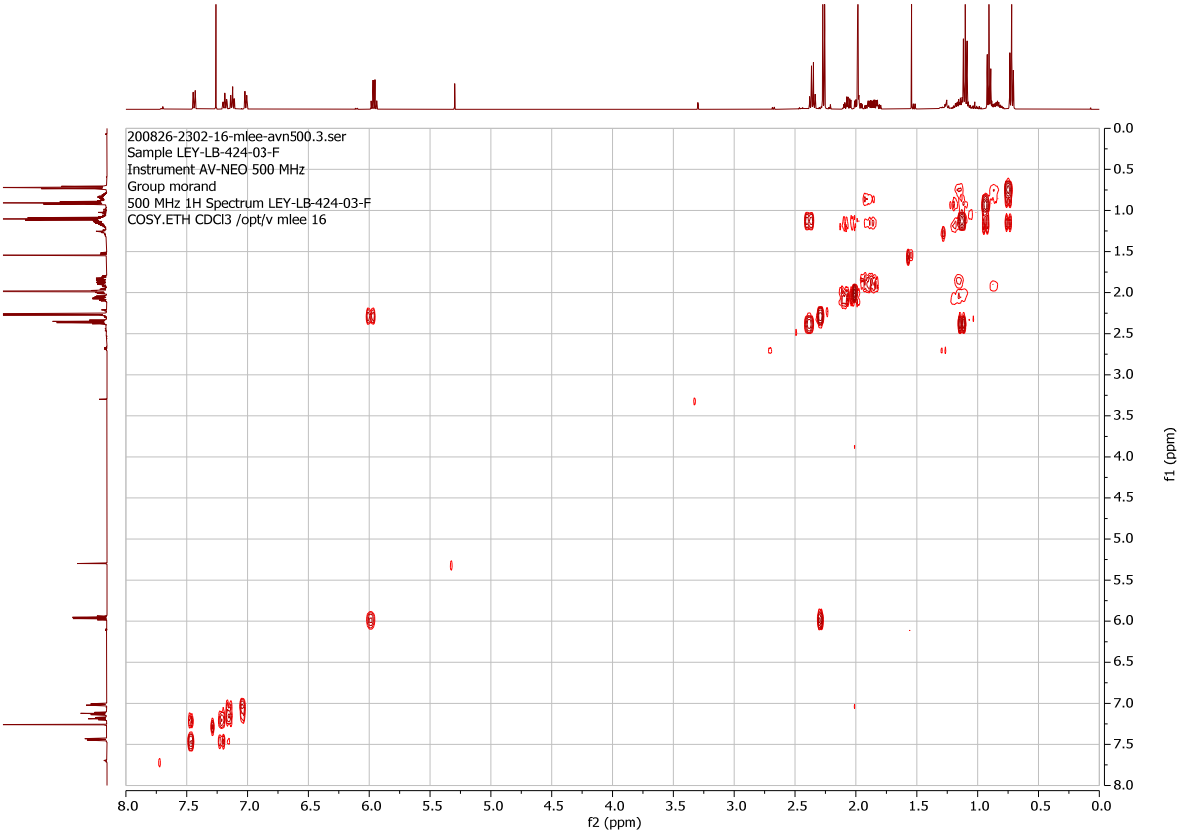

200828-1834-43-mlee-avn500.4.ser
Sample LEY-LB-424-03-F3B
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F3B
HSQC.ETH CDCl3 /opt/v mlee 43
f2 (ppm)
f1 (ppm)

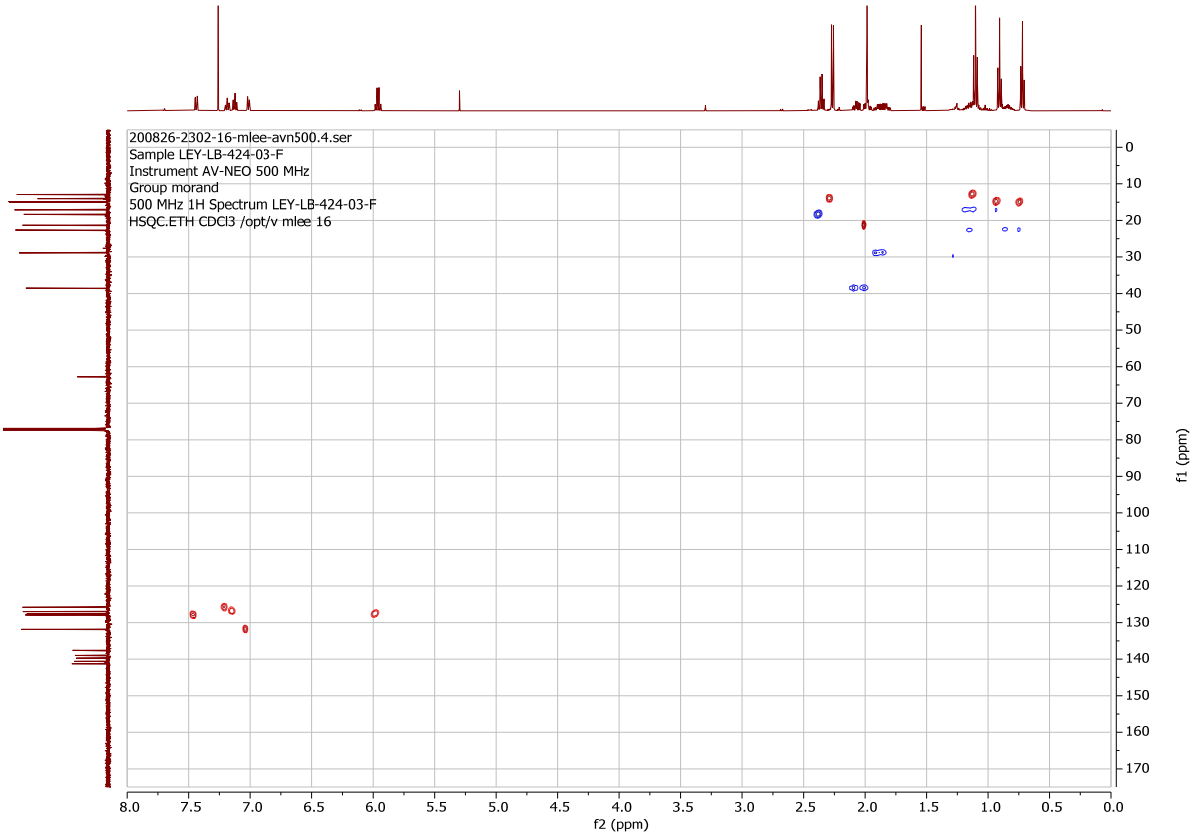

200828-1834-43-mlee-avn500.3.ser
Sample LEY-LB-424-03-F3B
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F3B
COSY.ETH CDCl3 /opt/v mlee 43
f2 (ppm)
f1 (ppm)

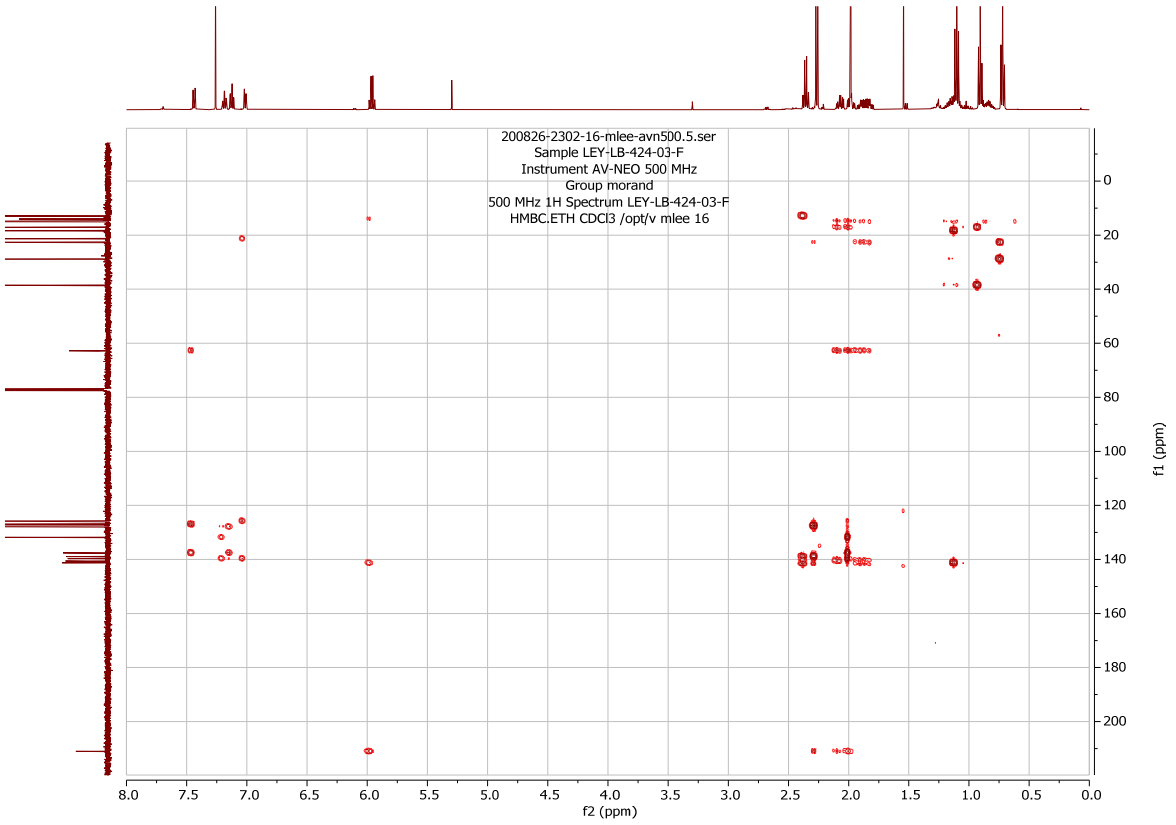

200828-1834-43-mlee-avn500.6.ser
Sample LEY-LB-424-03-F3B
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F3B
NOESY.ETH CDCl3 /opt/v mlee 43
f2 (ppm)
f1 (ppm)

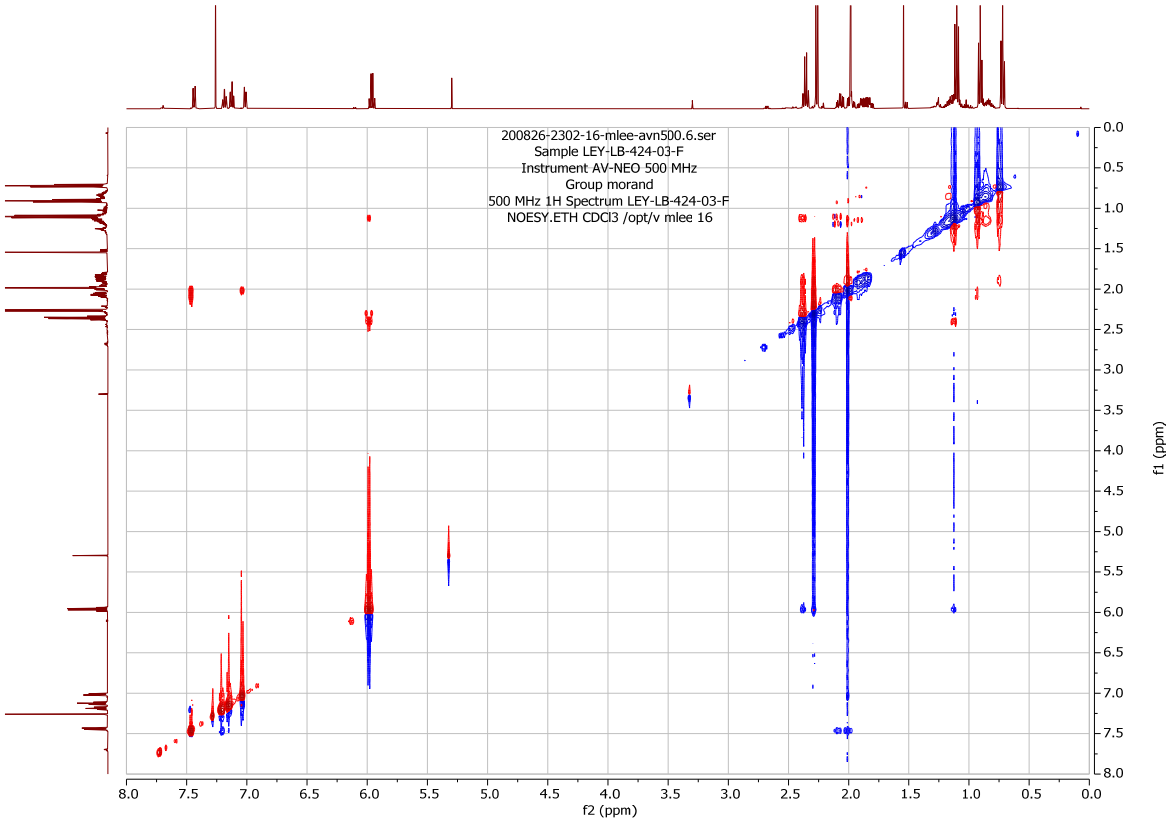
(*Z*)-4-ethyl-5-ethylidene-2,3-dipropyl-2-(*o*-tolyl)cyclopent-3-en-1-one (**3aq-2**, minor).



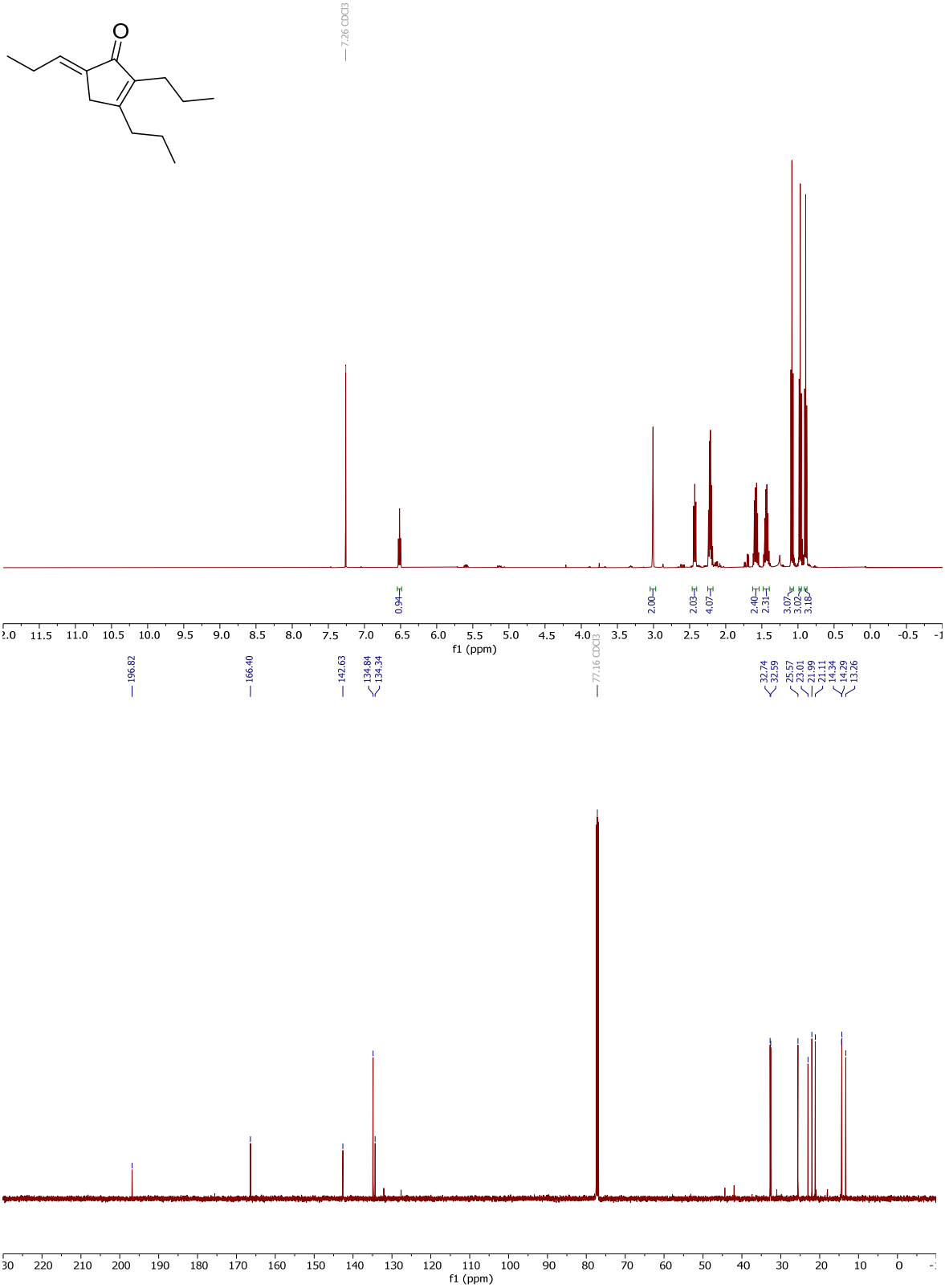

200826-2302-16-mlee-avn500.3.ser
Sample LEY-LB-424-03-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F
COSY.ETH CDCl3 /opt/v mlee 16
f2 (ppm)
f1 (ppm)

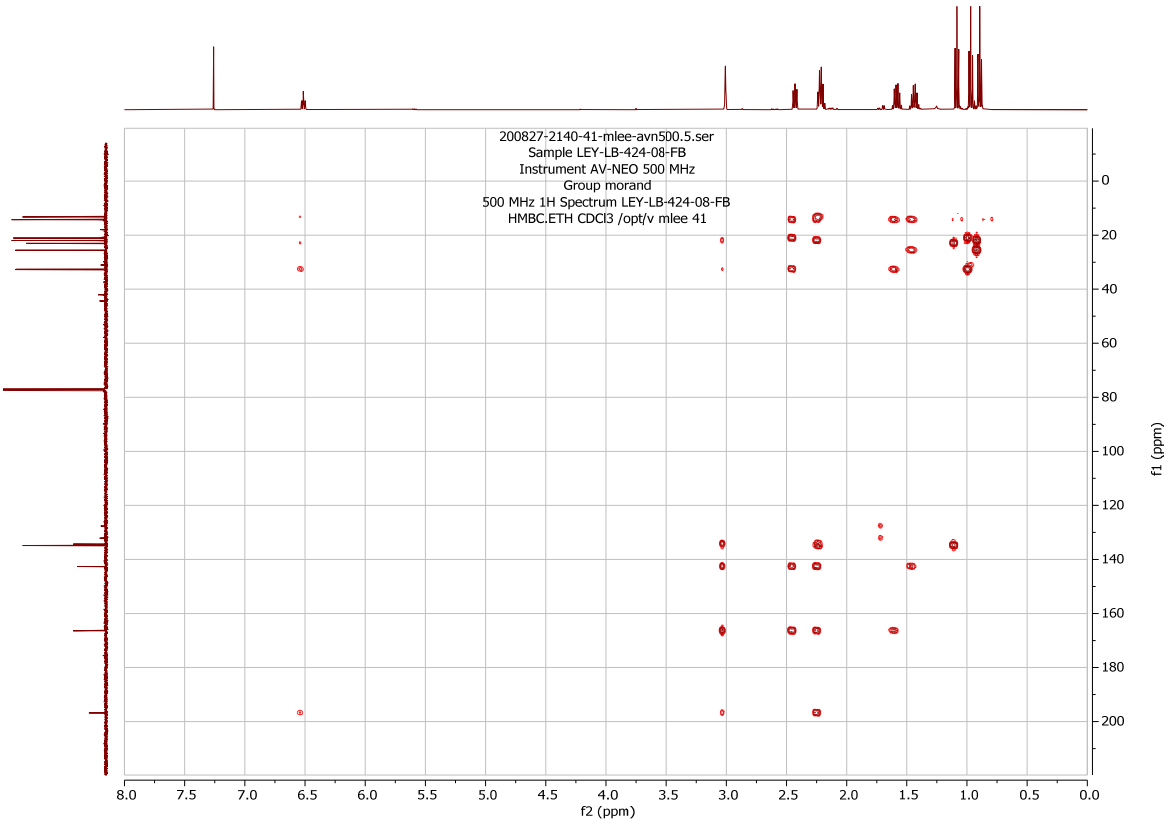

200826-2302-16-mlee-avn500.4.ser
Sample LEY-LB-424-03-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F
HSQC.ETH CDCl3 /opt/v mlee 16
f2 (ppm)
f1 (ppm)

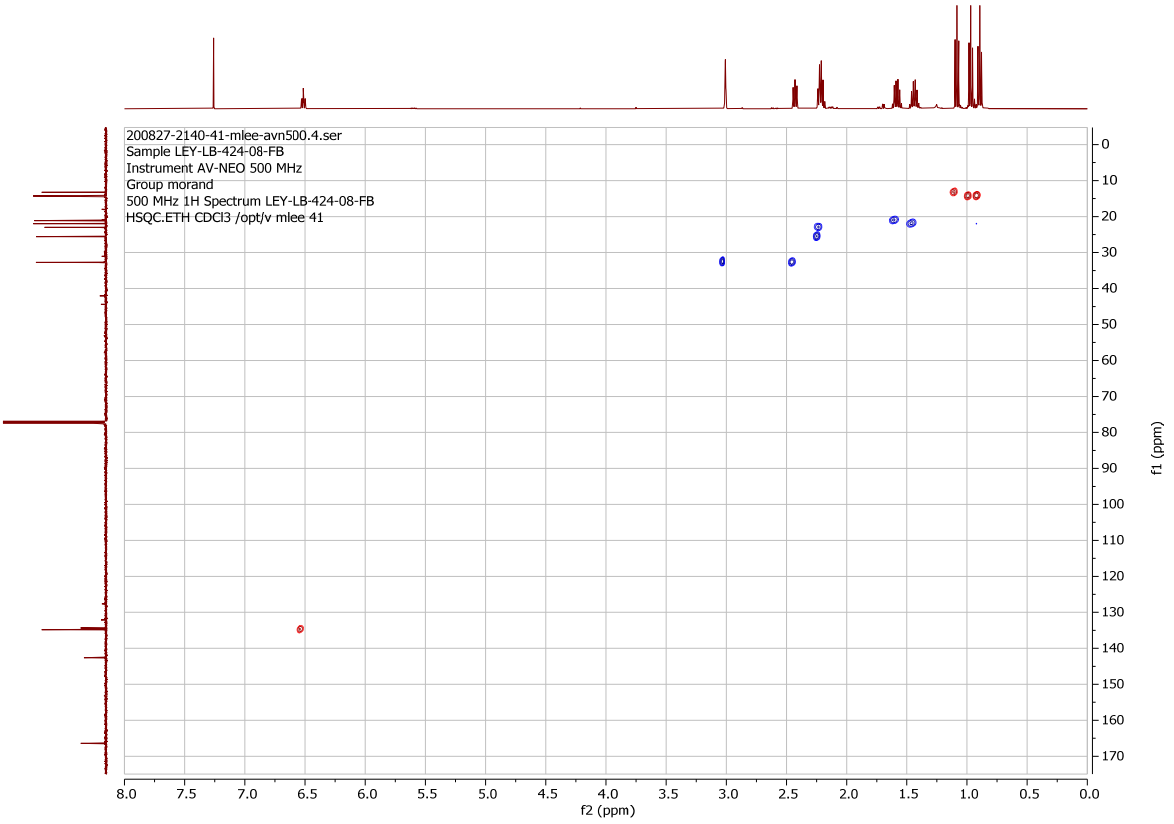

200826-2302-16-mlee-avn500.5.ser
Sample LEY-LB-424-03-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F
HMBC.ETH CDCl3 /opt/v mlee 16
f1 (ppm)
f2 (ppm)

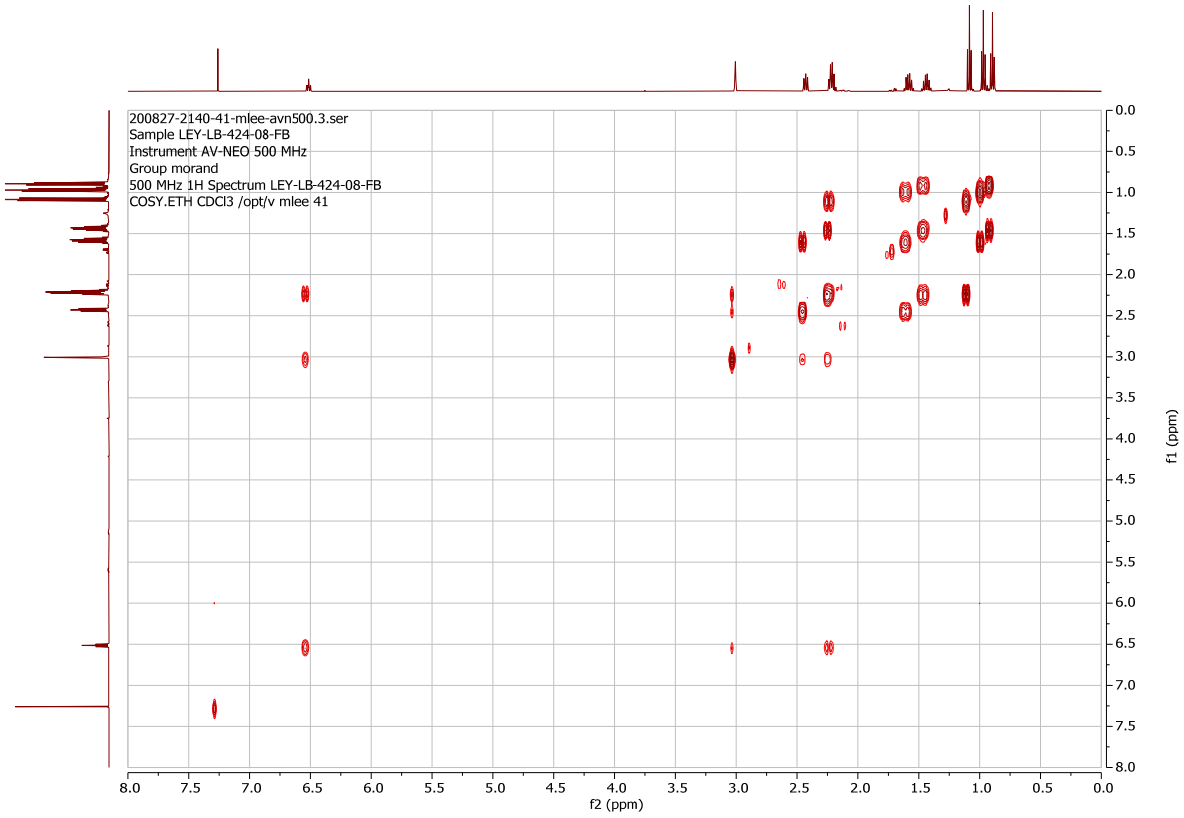

200826-2302-16-mlee-avn500.6.ser
Sample LEY-LB-424-03-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-03-F
NOESY.ETH CDCl3 /opt/v mlee 16
f1 (ppm)
f2 (ppm)

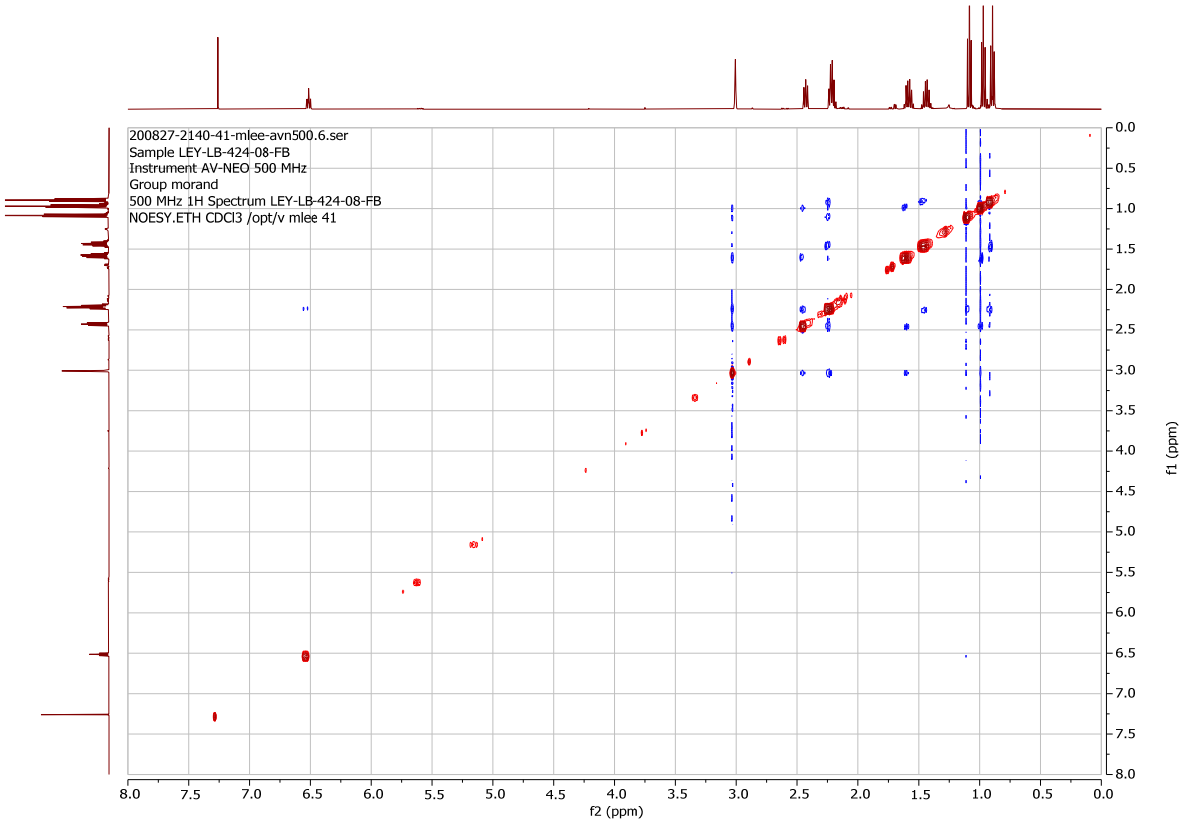
(*E*)-2,3-dipropyl-5-propylidenecyclopent-2-en-1-one (**3ar-1**, major).



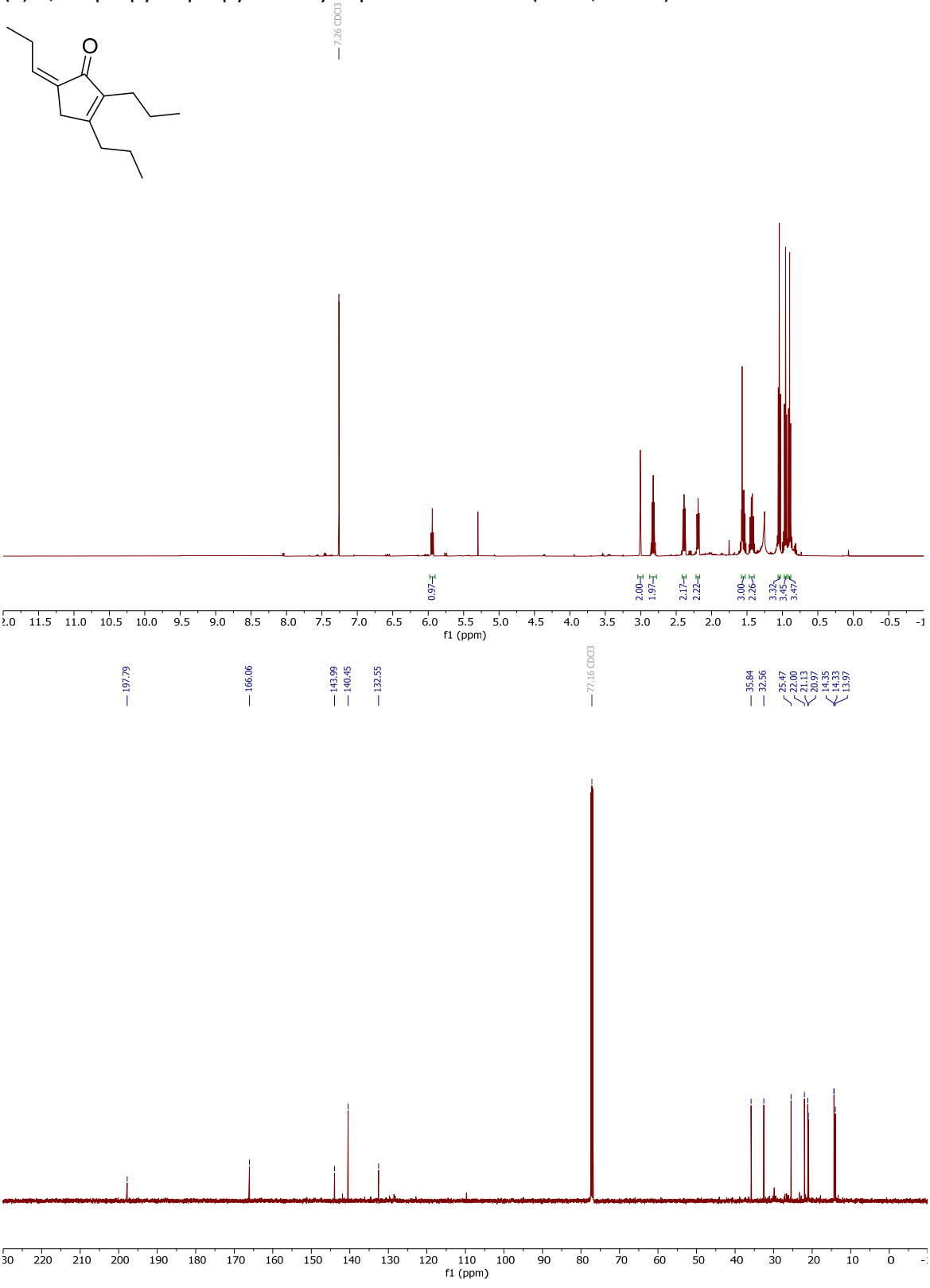

200827-2140-41-mlee-avn500.5.ser
Sample LEY-LB-424-08-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FB
HMBC.ETH CDCl3 /opt/v mlee 41
f1 (ppm)
f2 (ppm)

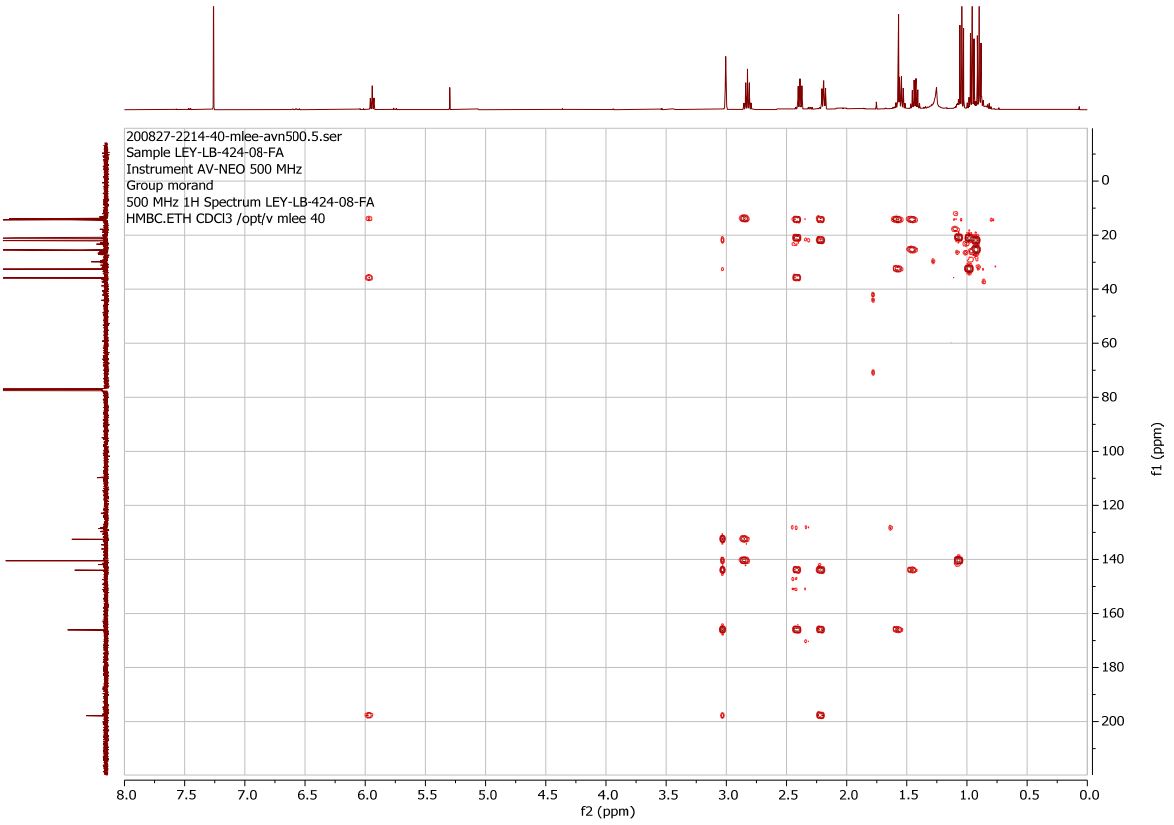

200827-2140-41-mlee-avn500.4.ser
Sample LEY-LB-424-08-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FB
HSQC.ETH CDCl3 /opt/v mlee 41
f1 (ppm)
f2 (ppm)

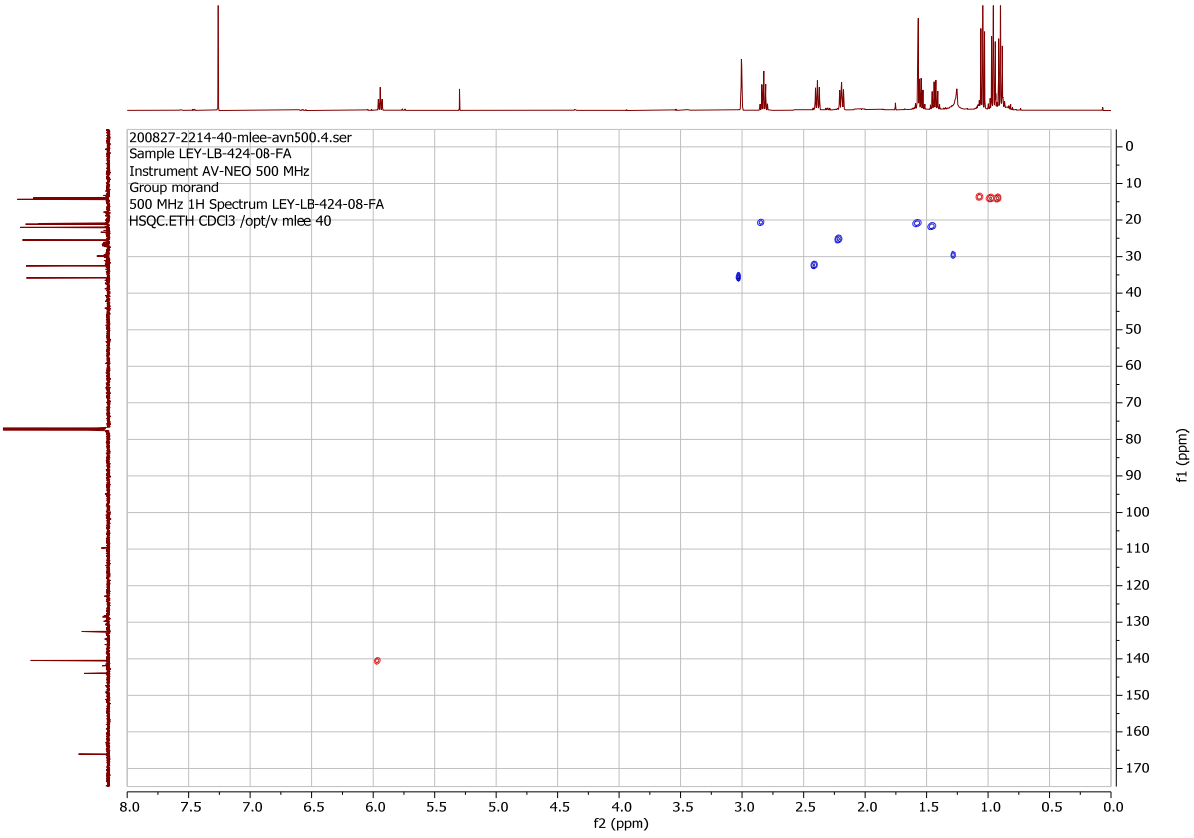

200827-2140-41-mlee-avn500.3.ser
Sample LEY-LB-424-08-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FB
COSY.ETH CDCl3 /opt/v mlee 41
f2 (ppm)
f1 (ppm)

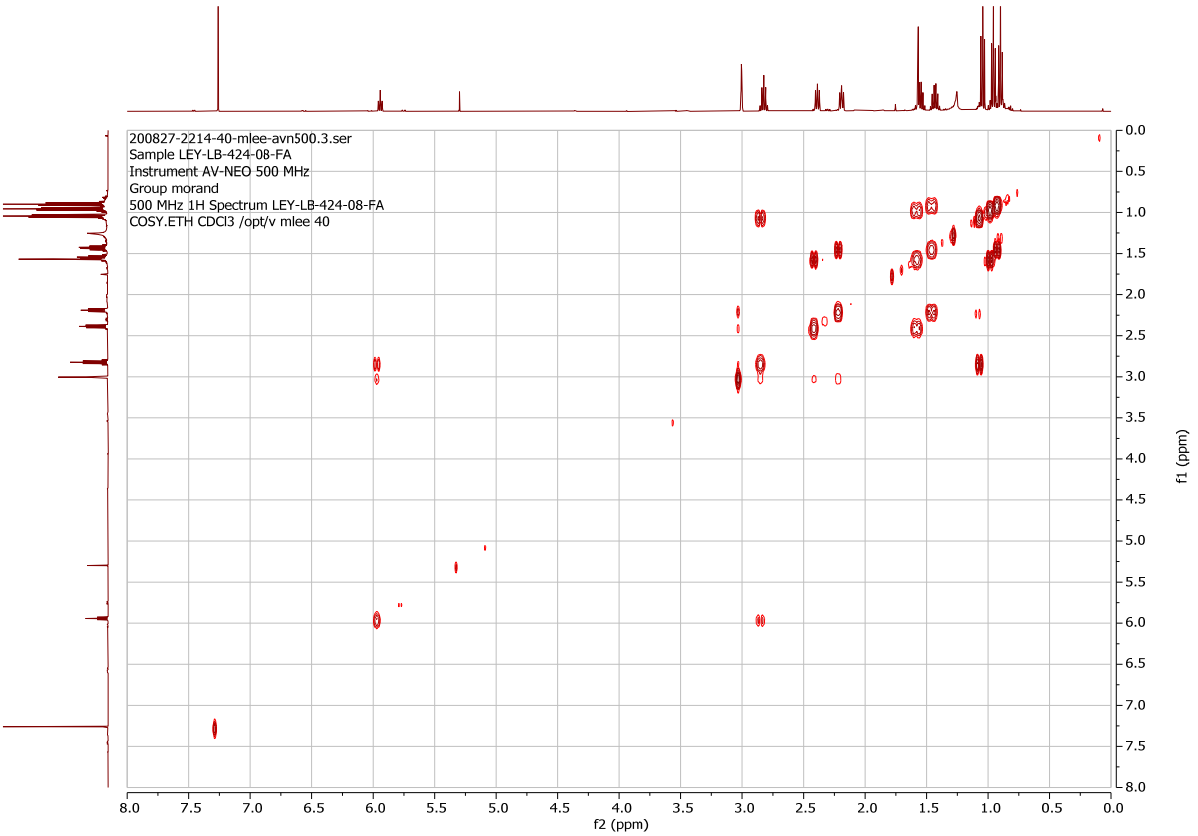

200827-2140-41-mlee-avn500.6.ser
Sample LEY-LB-424-08-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FB
NOESY.ETH CDCl3 /opt/v mlee 41
f2 (ppm)
f1 (ppm)

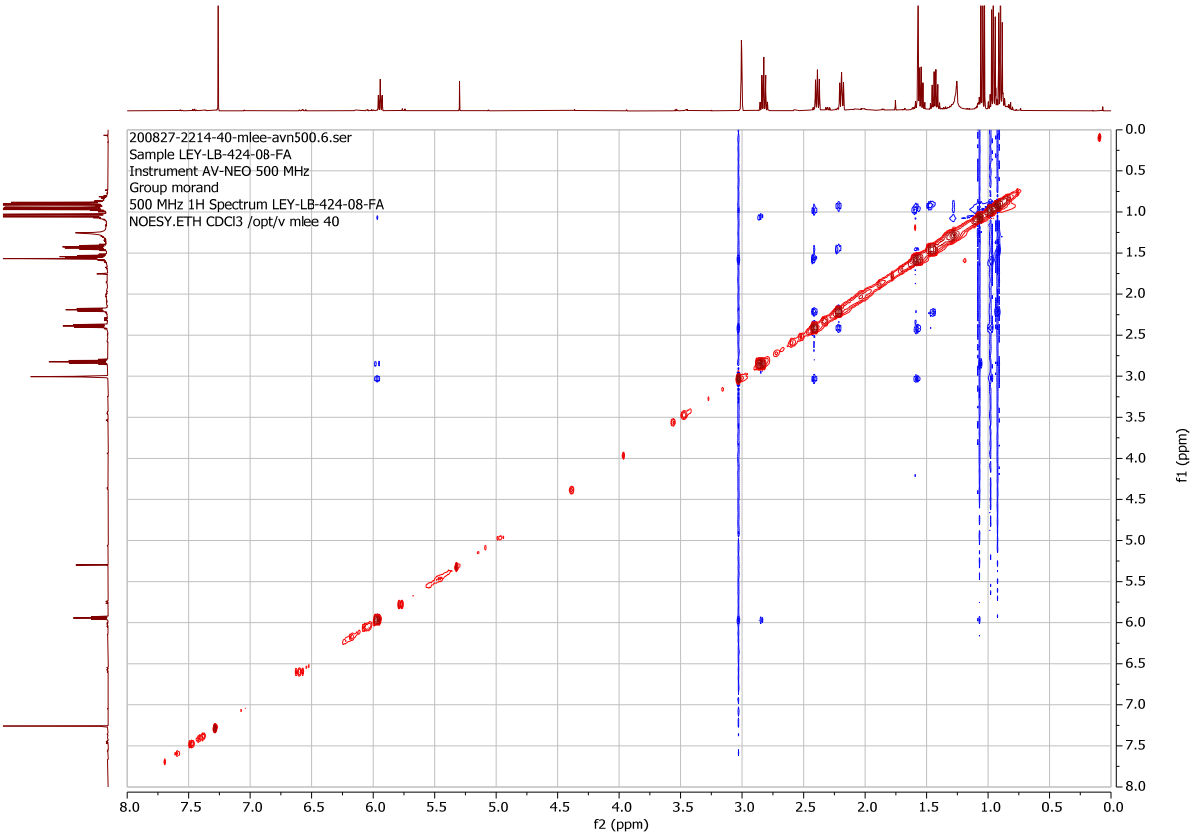
(*Z*)-2,3-dipropyl-5-propylidenecyclopent-2-en-1-one (**3ar-2**, minor).



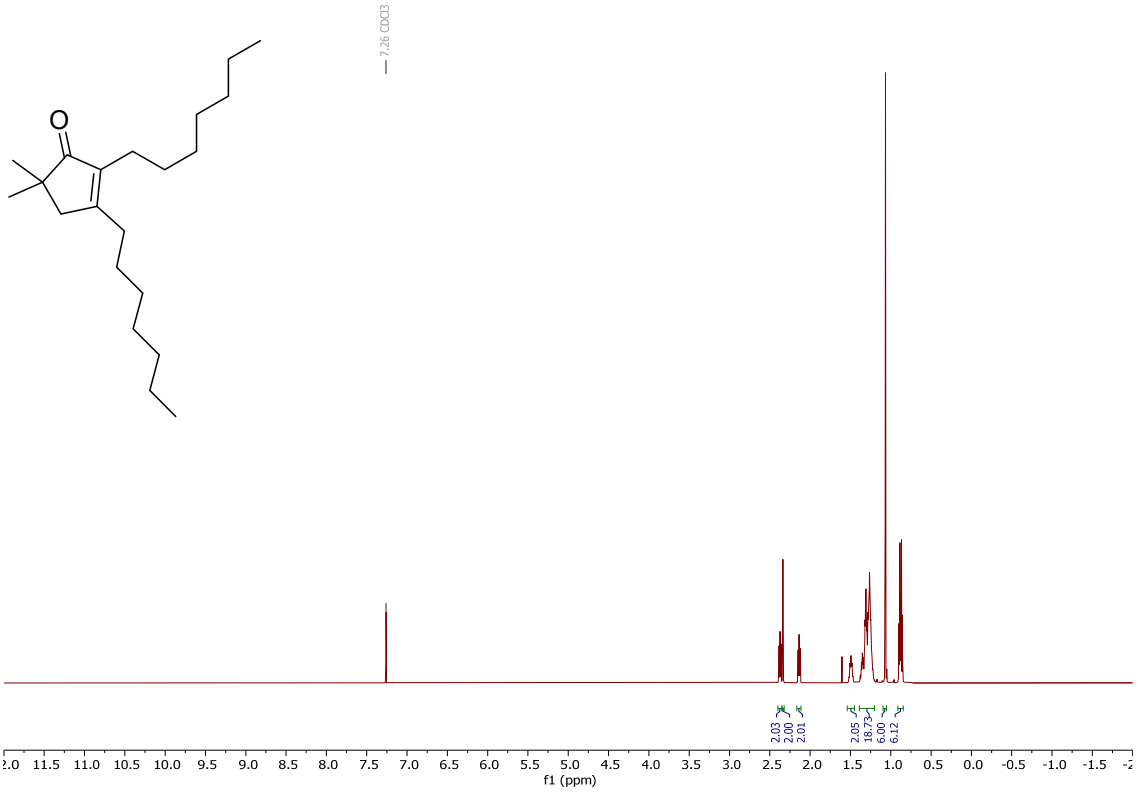

200827-2214-40-mlee-avn500.5.ser
Sample LEY-LB-424-08-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FA
HMBC.ETH CDCl3 /opt/v mlee 40
f2 (ppm)
f1 (ppm)

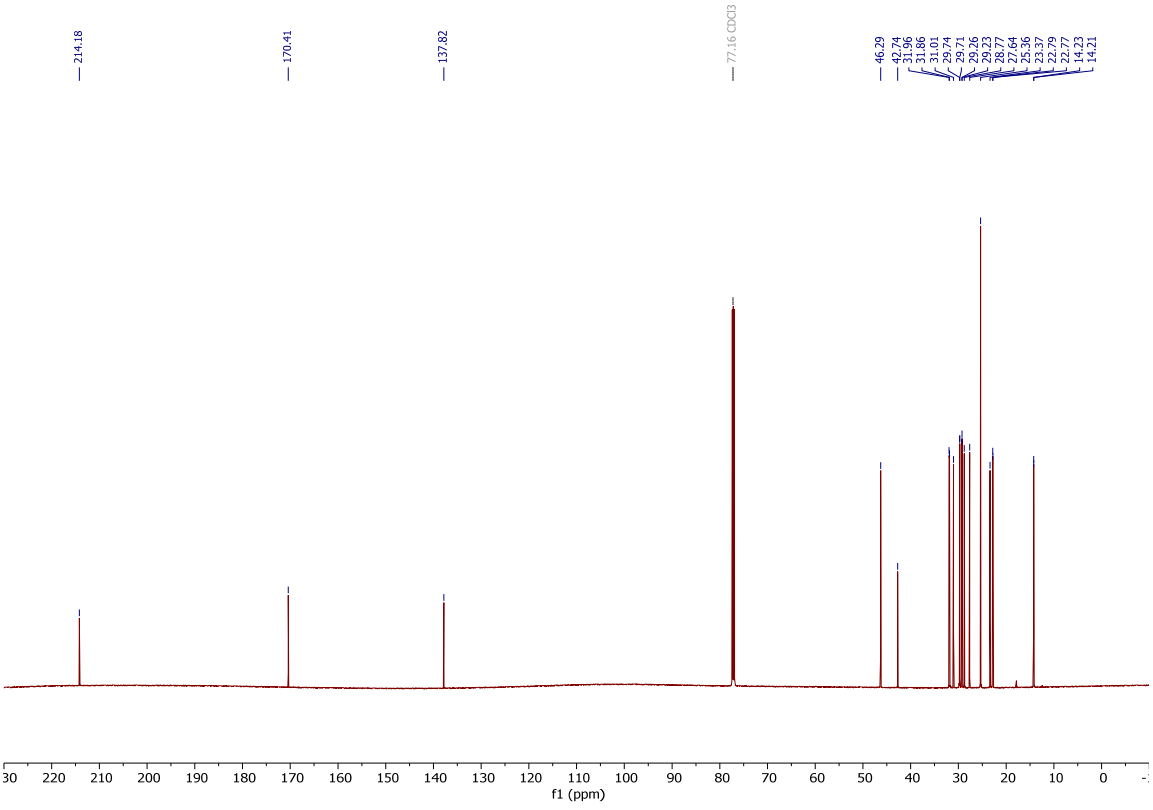

200827-2214-40-mlee-avn500.4.ser
Sample LEY-LB-424-08-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FA
HSQC.ETH CDCl3 /opt/v mlee 40
f2 (ppm)
f1 (ppm)

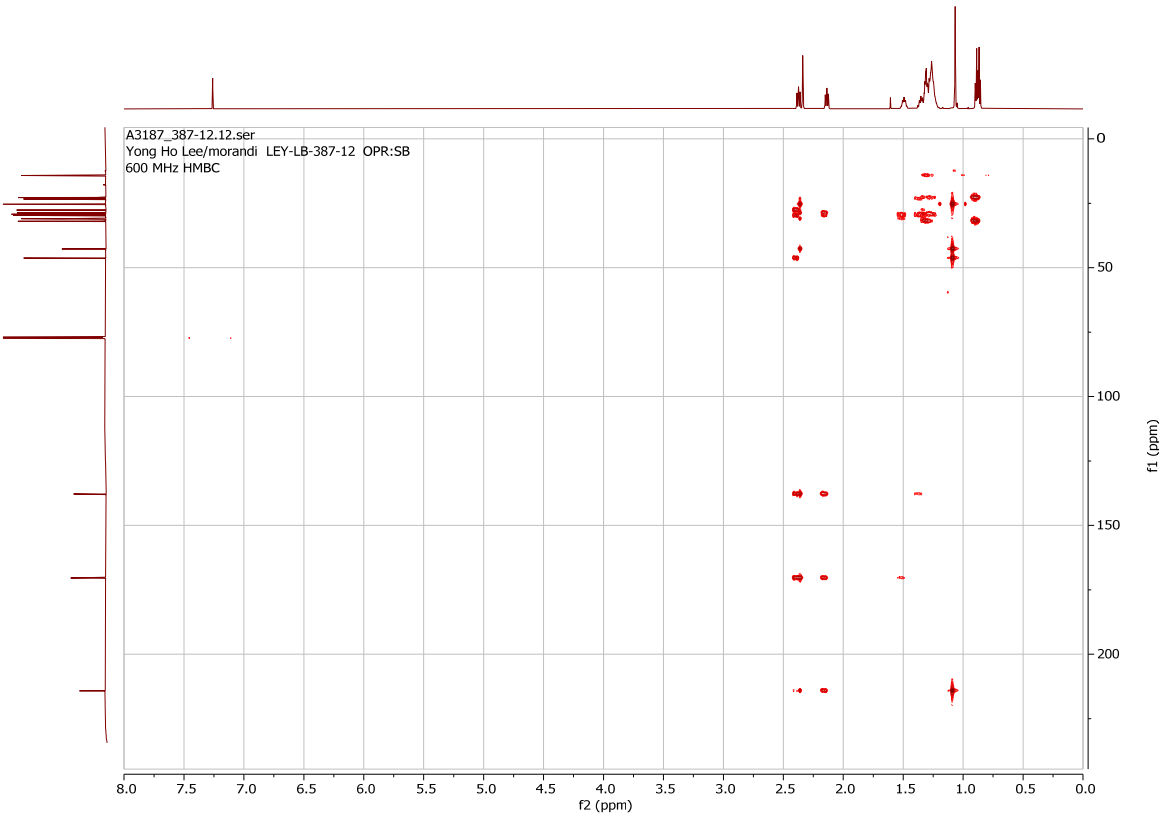

200827-2214-40-mlee-avn500.3.ser
Sample LEY-LB-424-08-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FA
COSY.ETH CDCl3 /opt/v mlee 40
f2 (ppm)
f1 (ppm)


200827-2214-40-mlee-avn500.6.ser
Sample LEY-LB-424-08-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-424-08-FA
NOESY.ETH CDCl3 /opt/v mlee 40
f2 (ppm)
f1 (ppm)

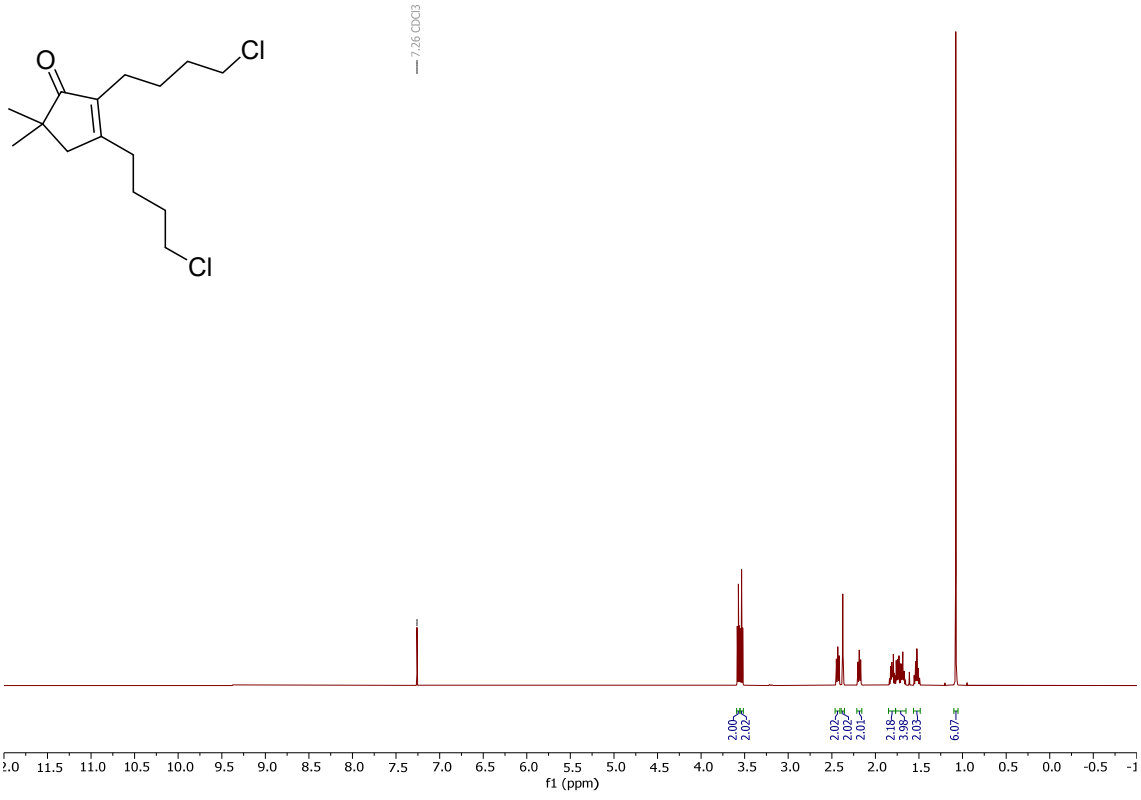
2,3-diheptyl-5,5-dimethylcyclopent-2-en-1-one (**3ba**).

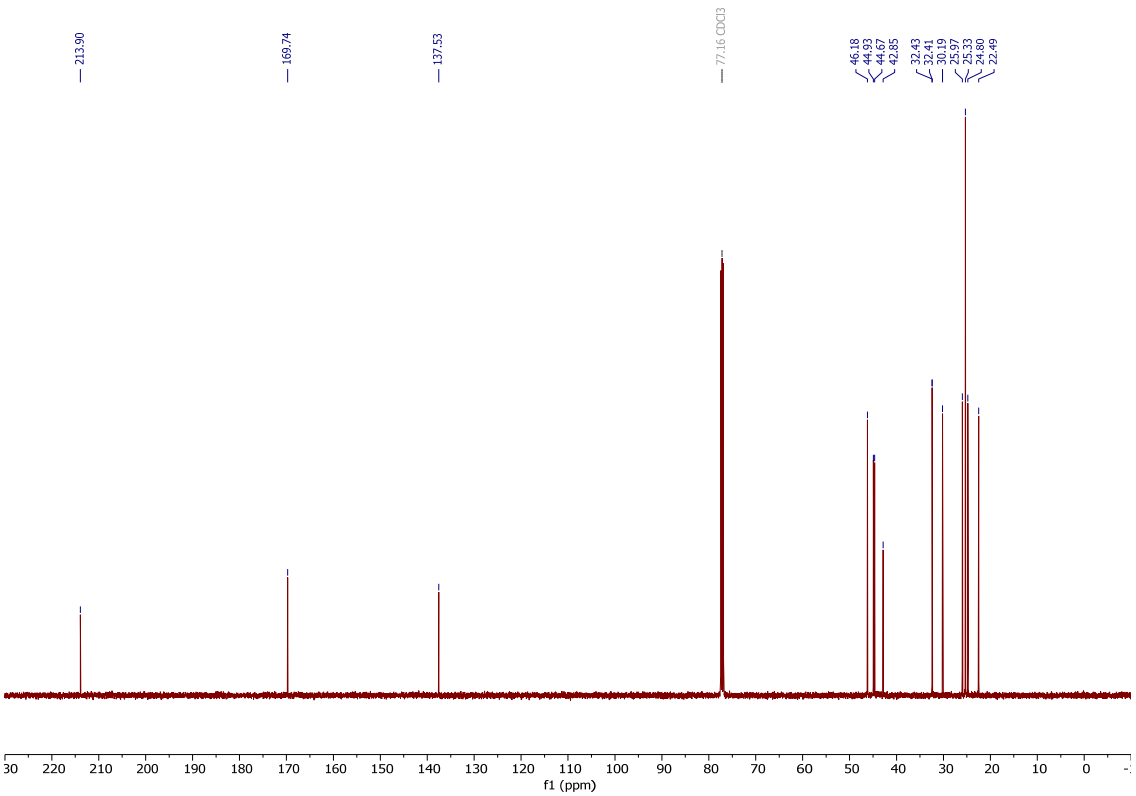


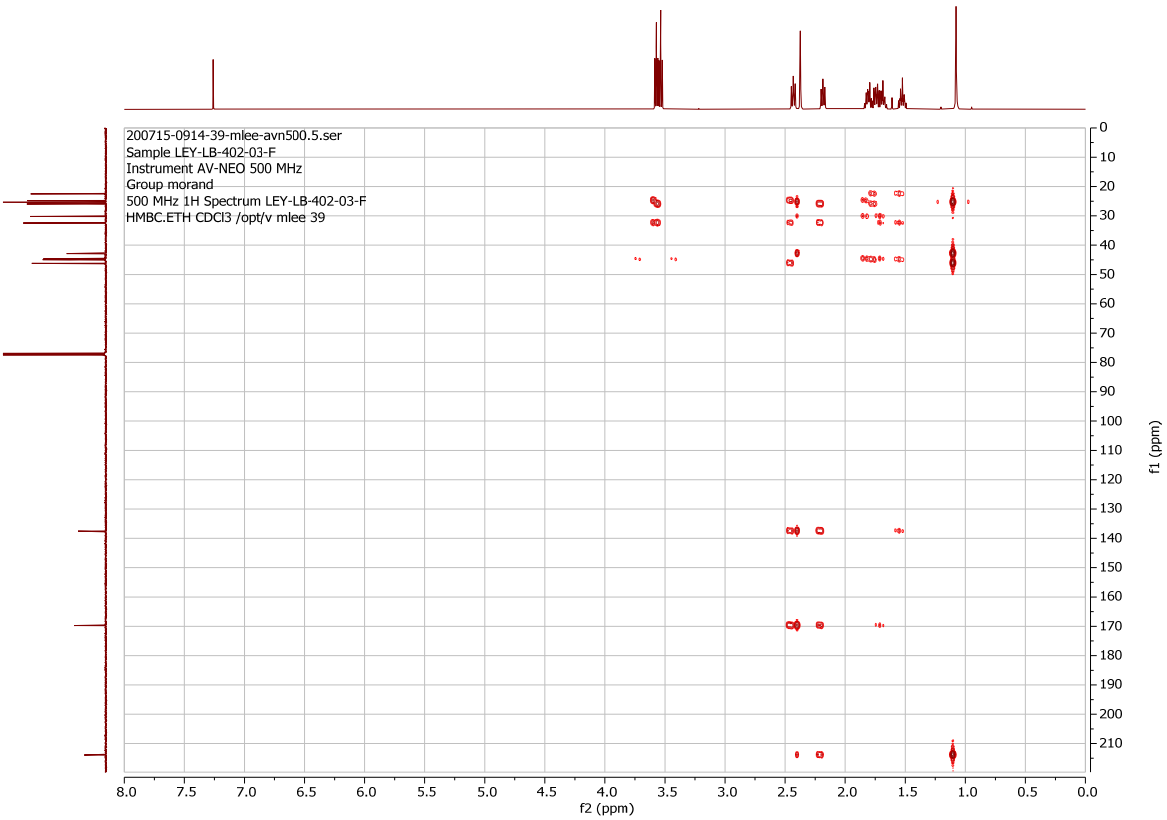



A3187_387-12.12.ser
Yong Ho Lee/morandi LEY-LB-387-12 OPR:SB
600 MHz HMBC
f2 (ppm)
f1 (ppm)

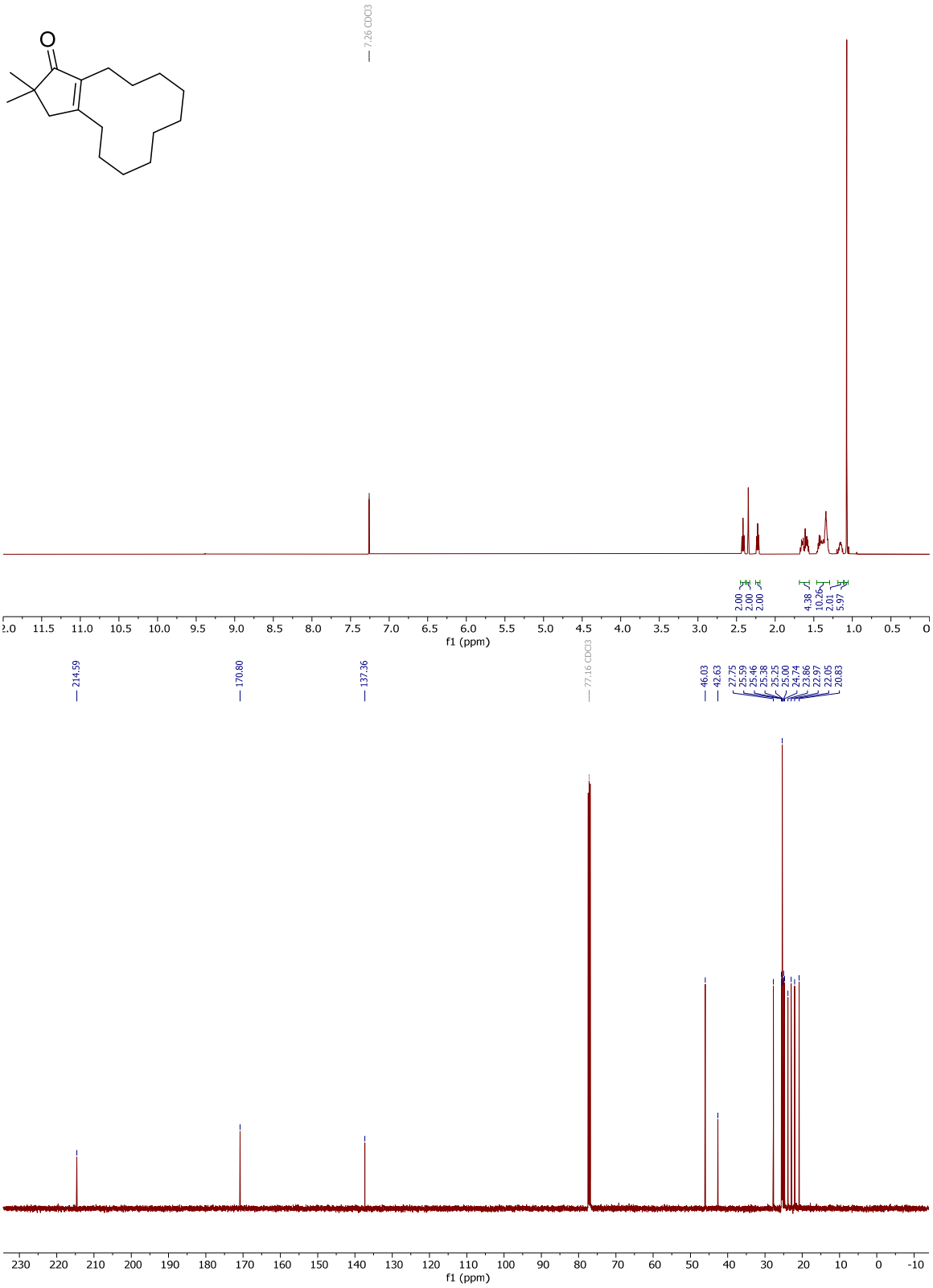
2,3-bis(4-chlorobutyl)-5,5-dimethylcyclopent-2-en-1-one (**3bb**).

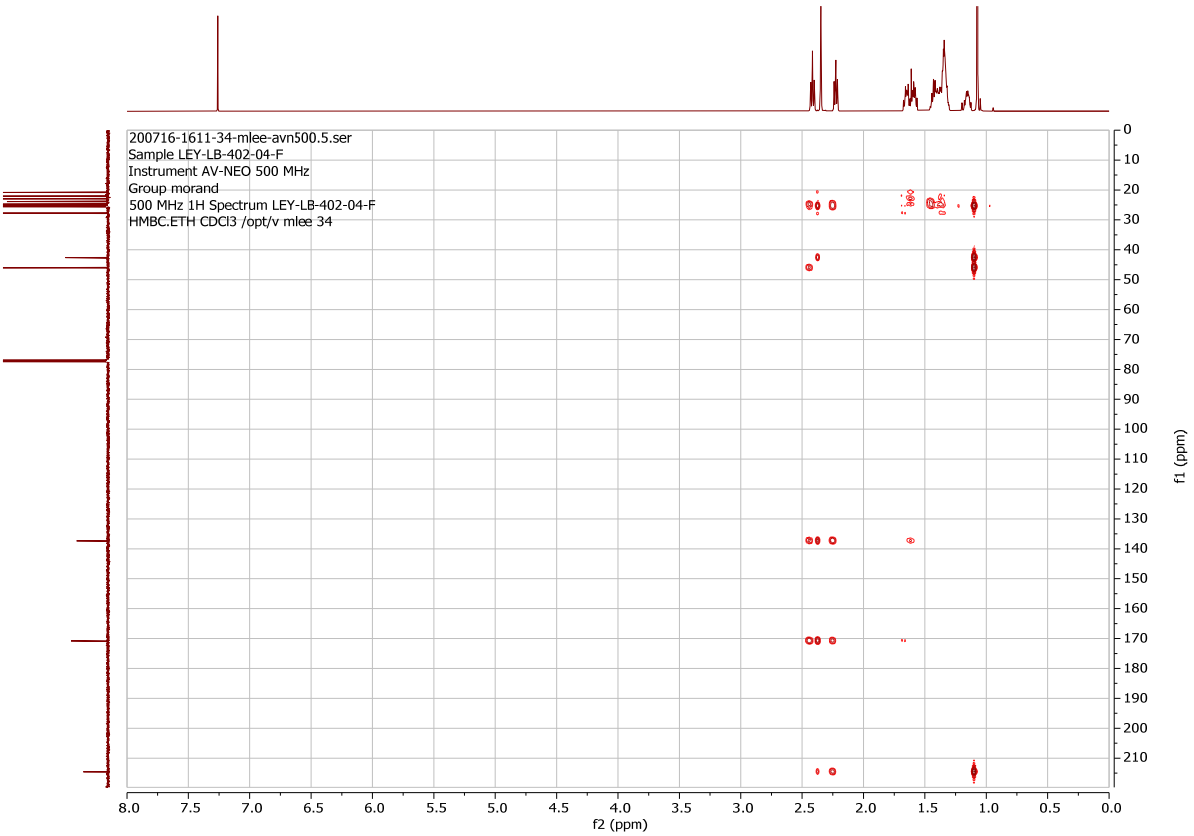




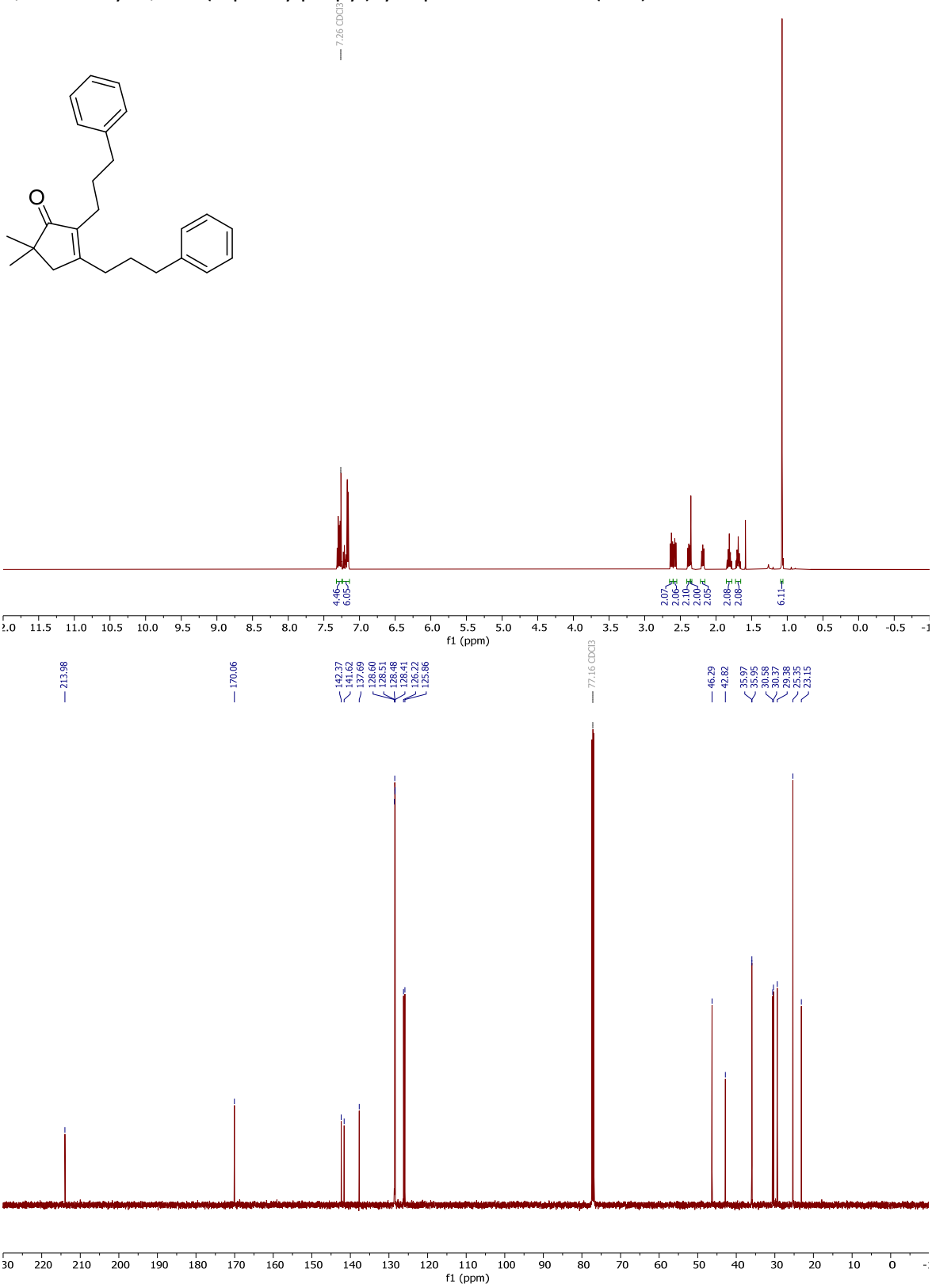

200715-0914-39-mlee-avn500.5.ser
Sample LEY-LB-402-03-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-402-03-F
HMBC.ETH CDCl3 /opt/v mlee 39
f2 (ppm)
f1 (ppm)

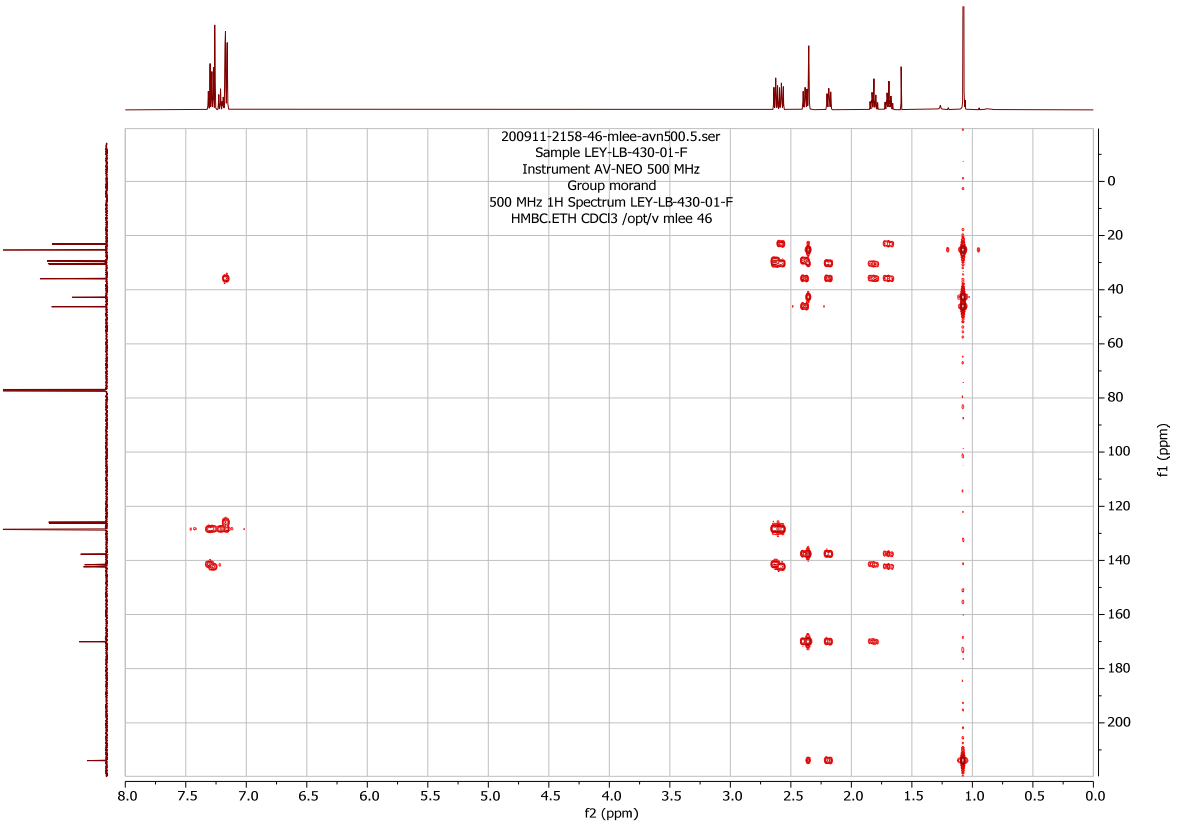
2,2-dimethyl-2,3,4,5,6,7,8,9,10,11,12,13-dodecahydro-1*H*-cyclopenta[12]annulen-1-one (**3bc**).

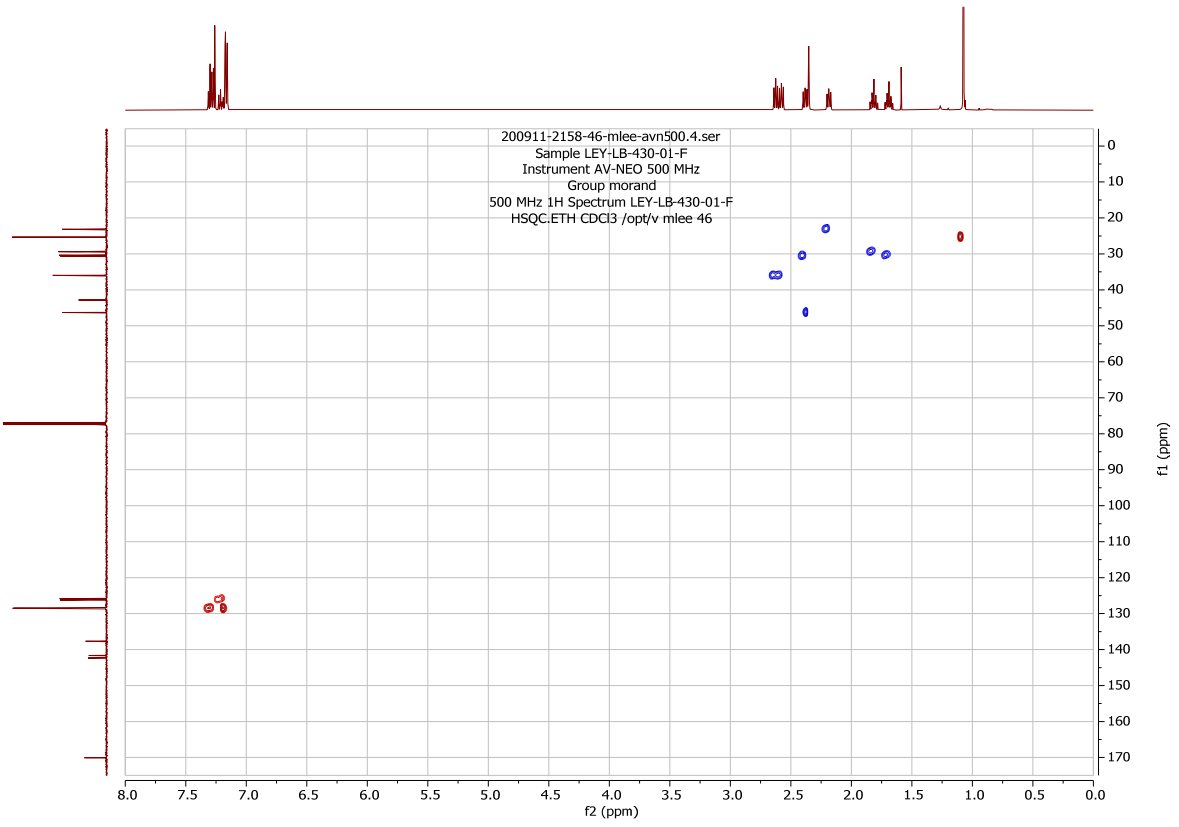


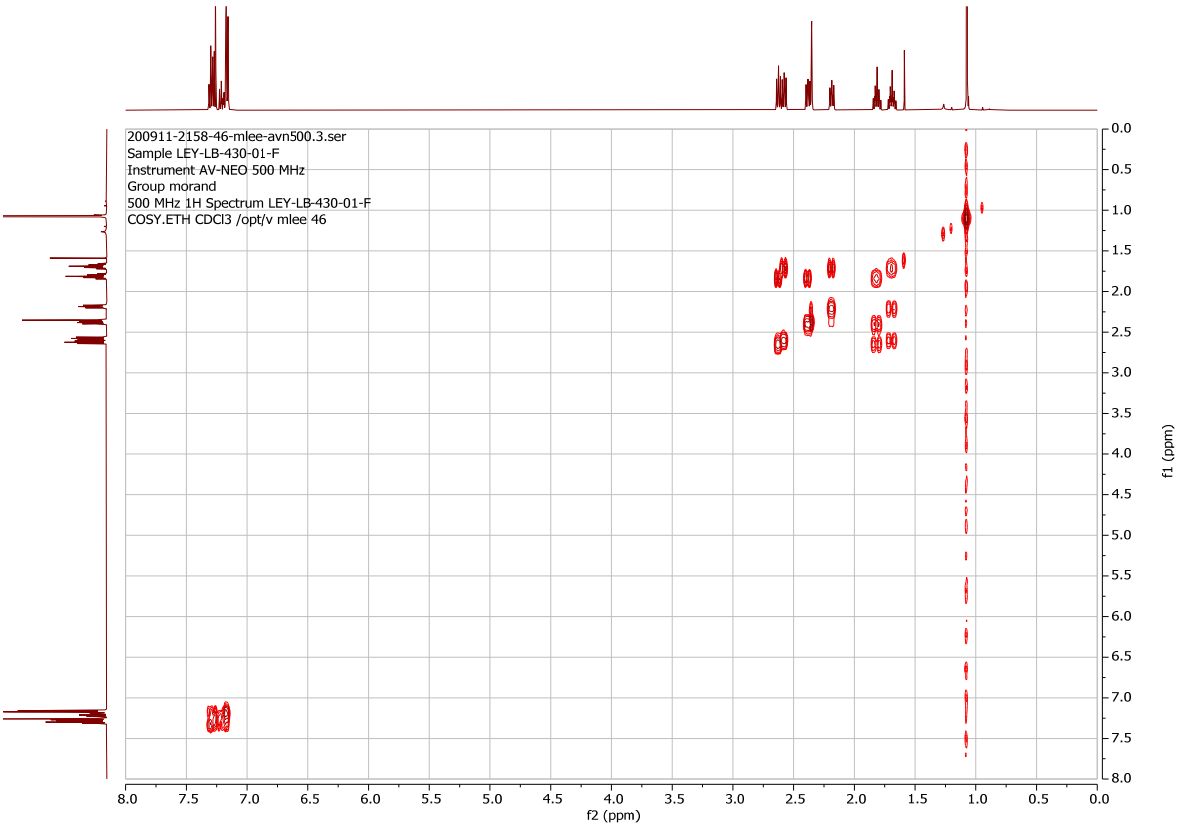

200716-1611-34-mlee-avn500.5.ser
Sample LEY-LB-402-04-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-402-04-F
HMBC.ETH CDCl3 /opt/v mlee 34
f2 (ppm)
f1 (ppm)

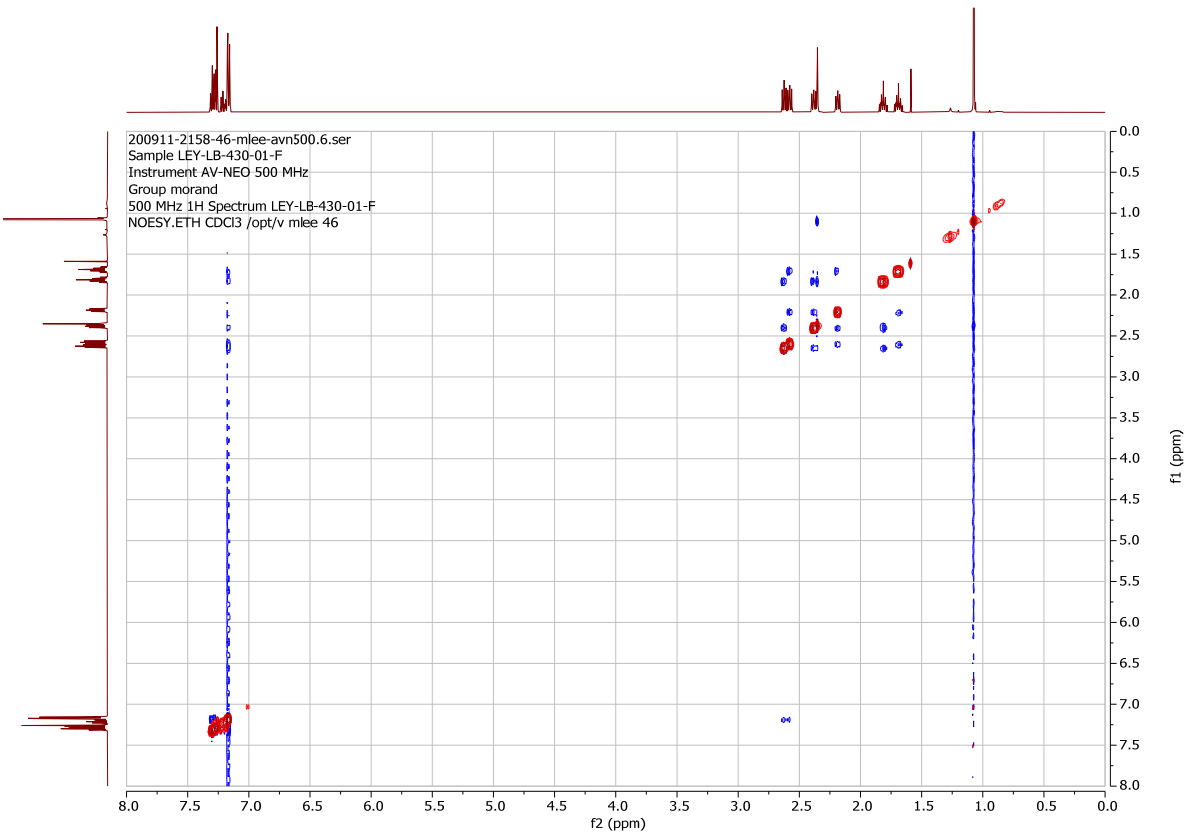
5,5-dimethyl-2,3-bis(3-phenylpropyl)cyclopent-2-en-1-one (**3bd**).



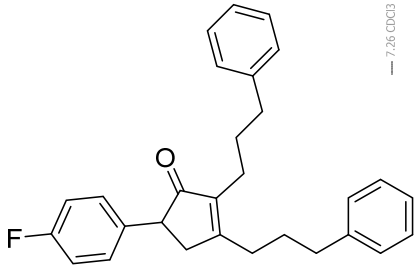

200911-2158-46-mlee-avn500.5.ser
Sample LEY-LB-430-01-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-01-F
HMBC.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

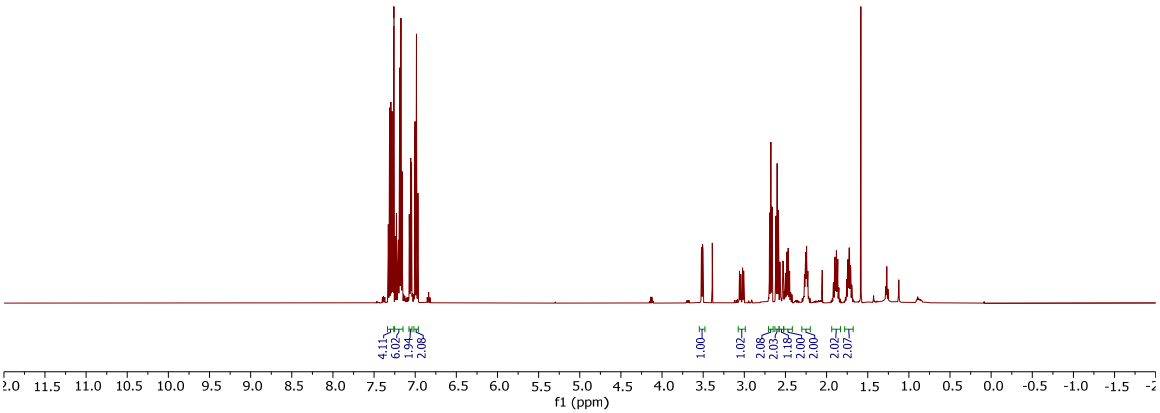

200911-2158-46-mlee-avn500.4.ser
Sample LEY-LB-430-01-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-01-F
HSQC.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

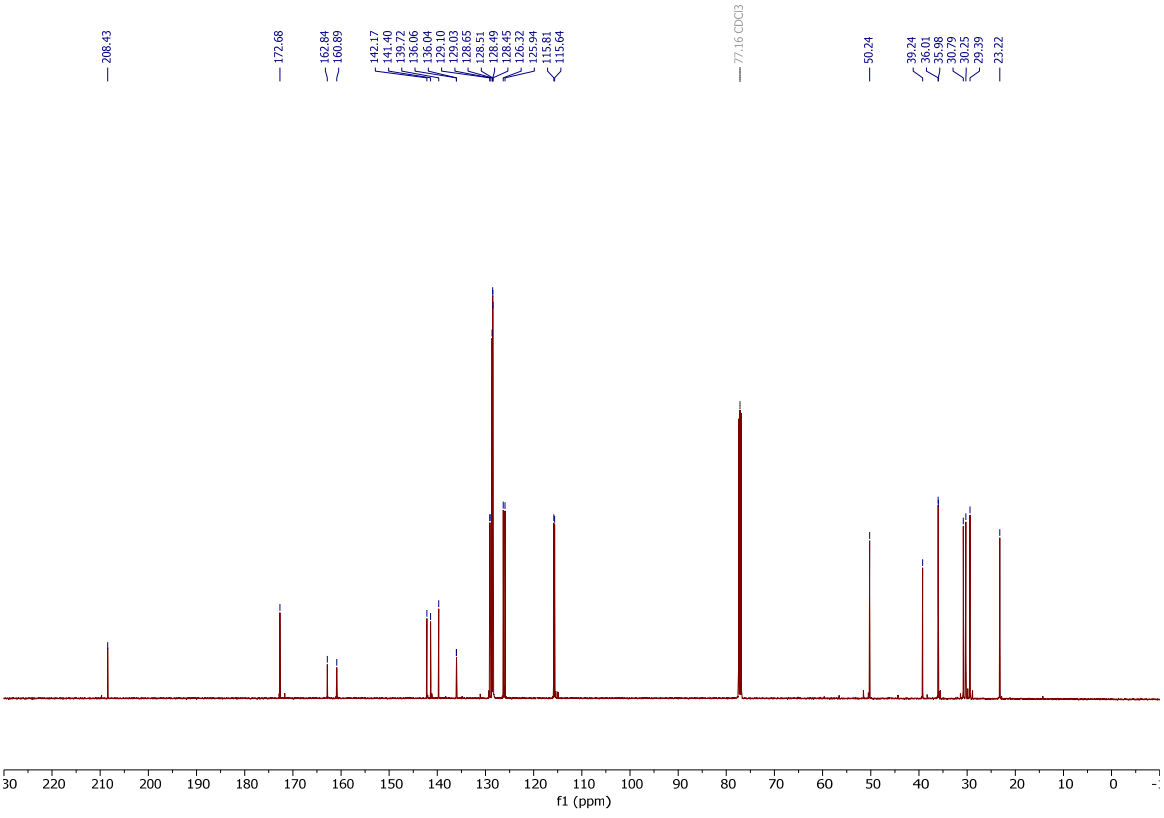

200911-2158-46-mlee-avn500.3.ser
Sample LEY-LB-430-01-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-01-F
COSY.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

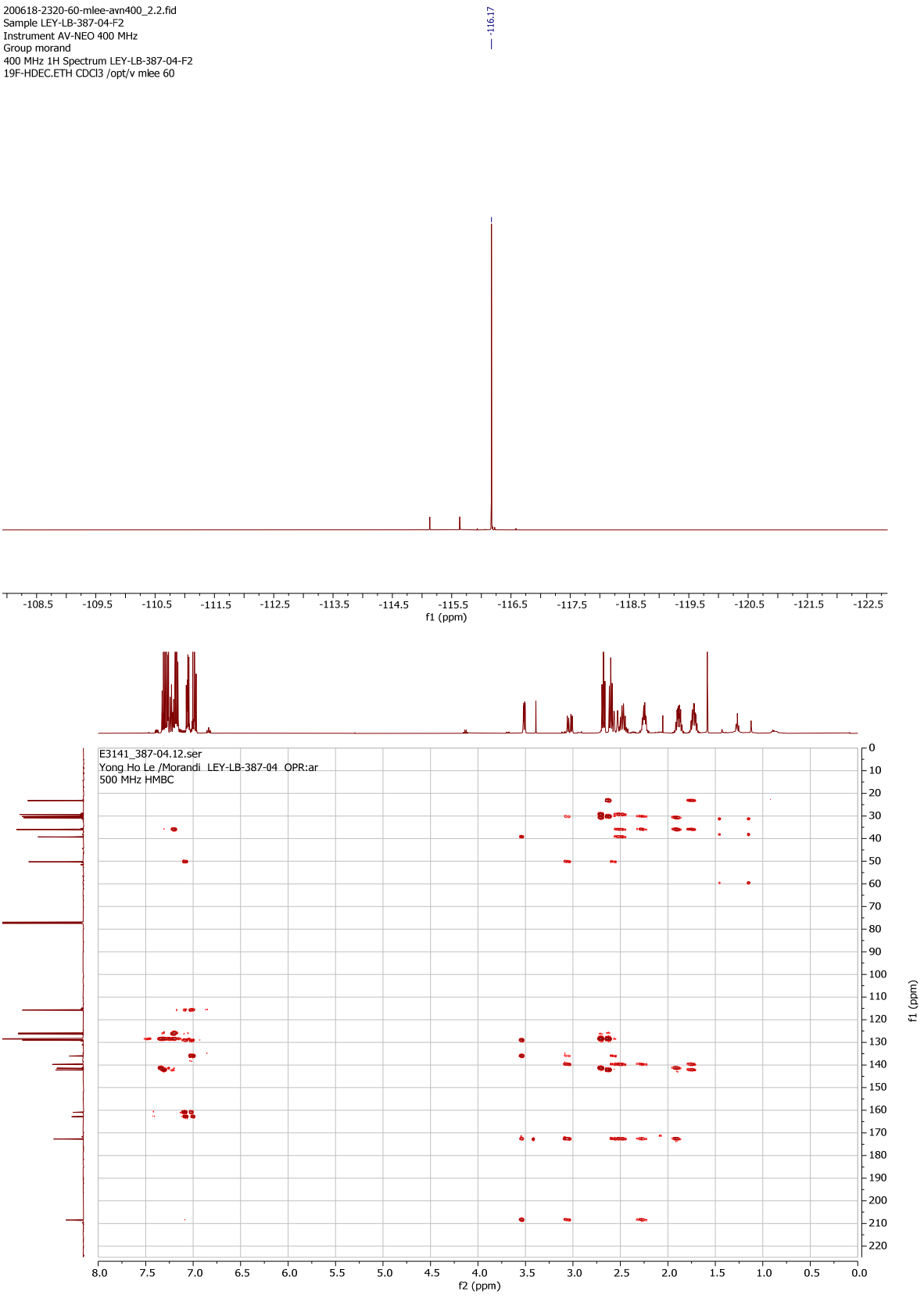

200911-2158-46-mlee-avn500.6.ser
Sample LEY-LB-430-01-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-01-F
NOESY.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

5-(4-fluorophenyl)-2,3-bis(3-phenylpropyl)cyclopent-2-en-1-one (**3be**).

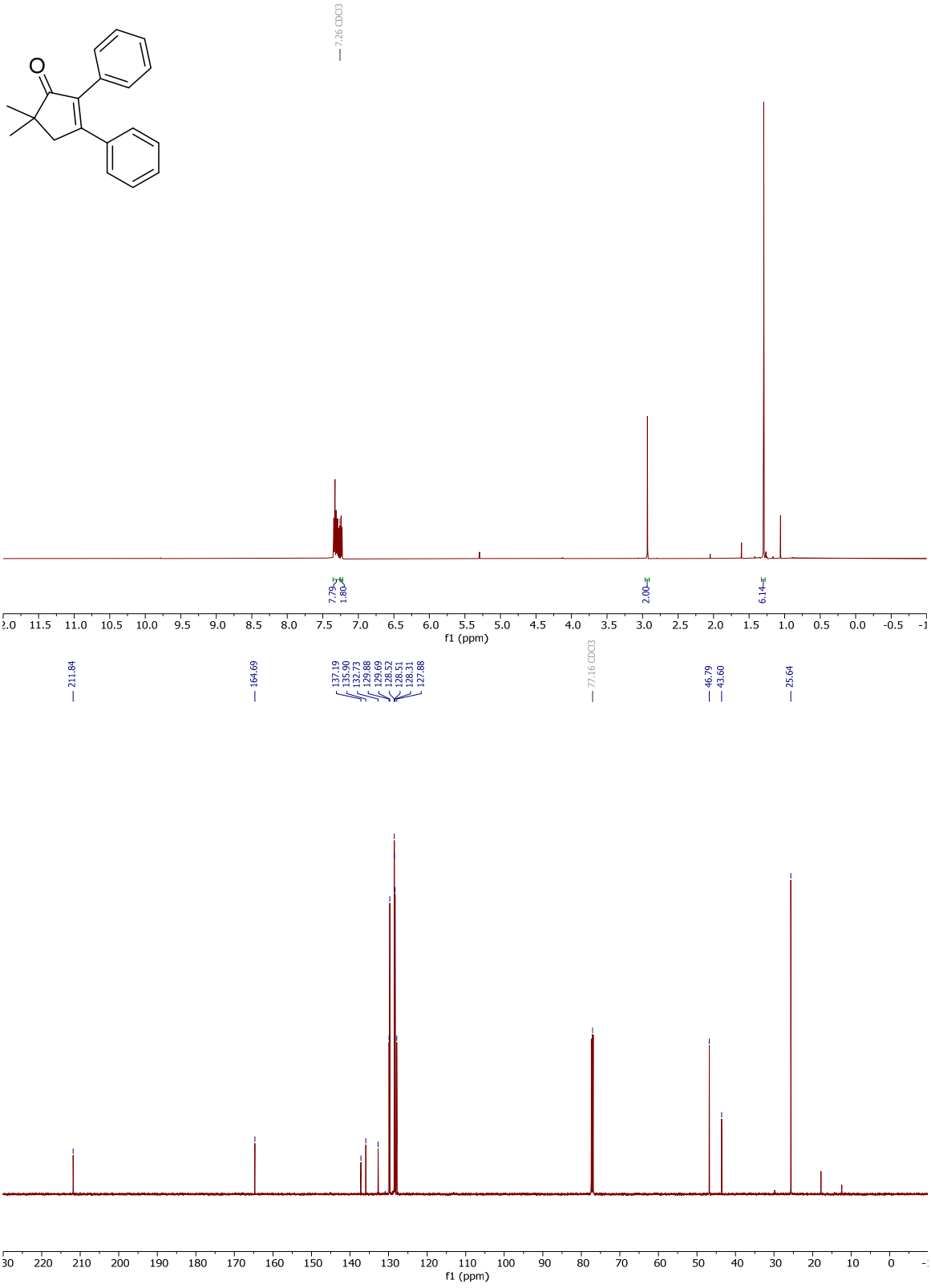


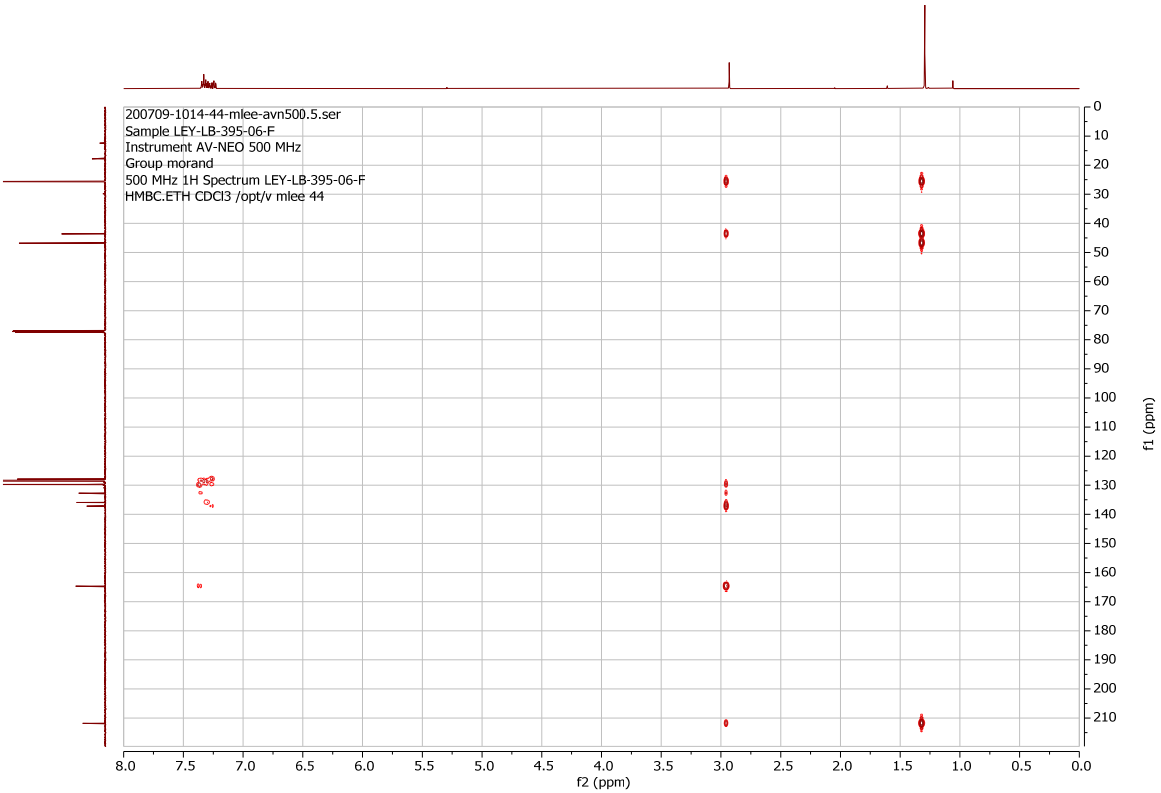




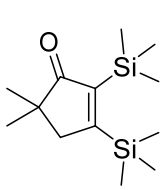

200618-2320-60-mlee-avn400_2.2.fid
Sample LEY-LB-387-04-F2
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-387-04-F2
19F-HDEC.ETH CDCl3 /opt/v mlee 60
-116.17
-108.5 -109.5 -110.5 -111.5 -112.5 -113.5 -114.5 -115.5 -116.5 -117.5 -118.5 -119.5 -120.5 -121.5 -122.5
f1 (ppm)
E3141_387-04.12.ser
Yong Ho Le /Morandi LEY-LB-387-04 OPR:ar
500 MHz HMBC
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220
f1 (ppm)

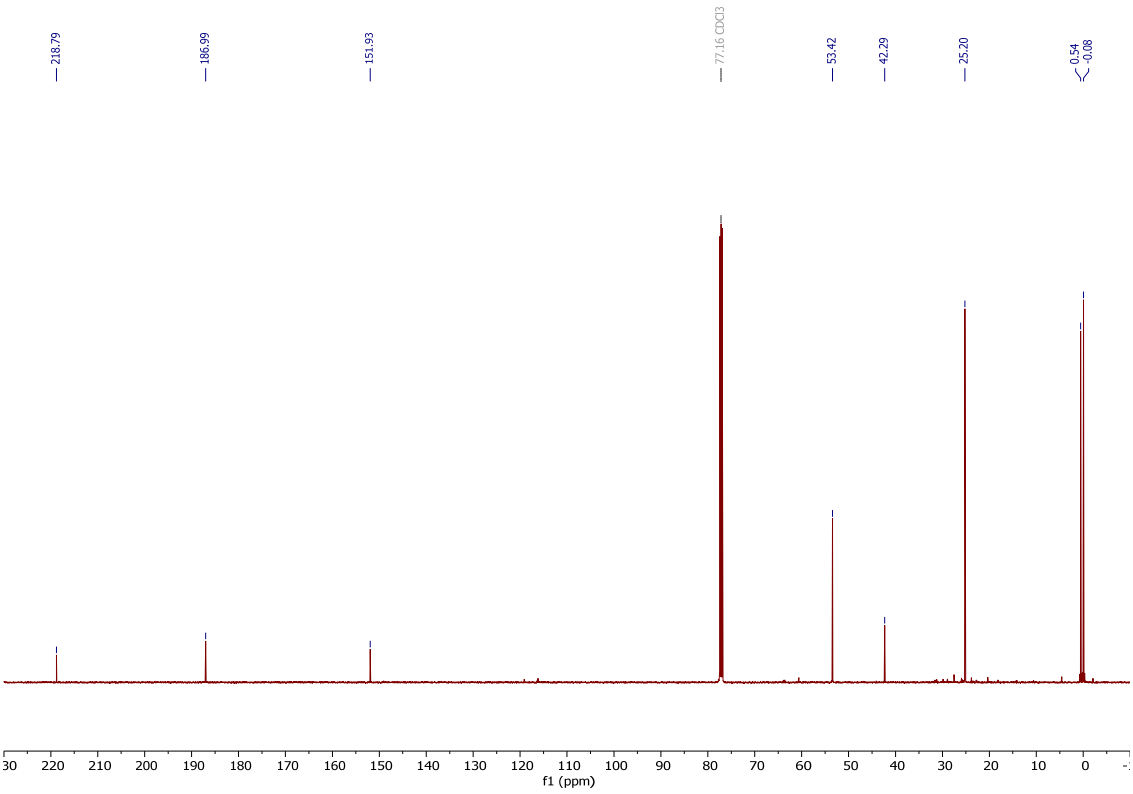
5,5-dimethyl-2,3-diphenylcyclopent-2-en-1-one (**3bf**).

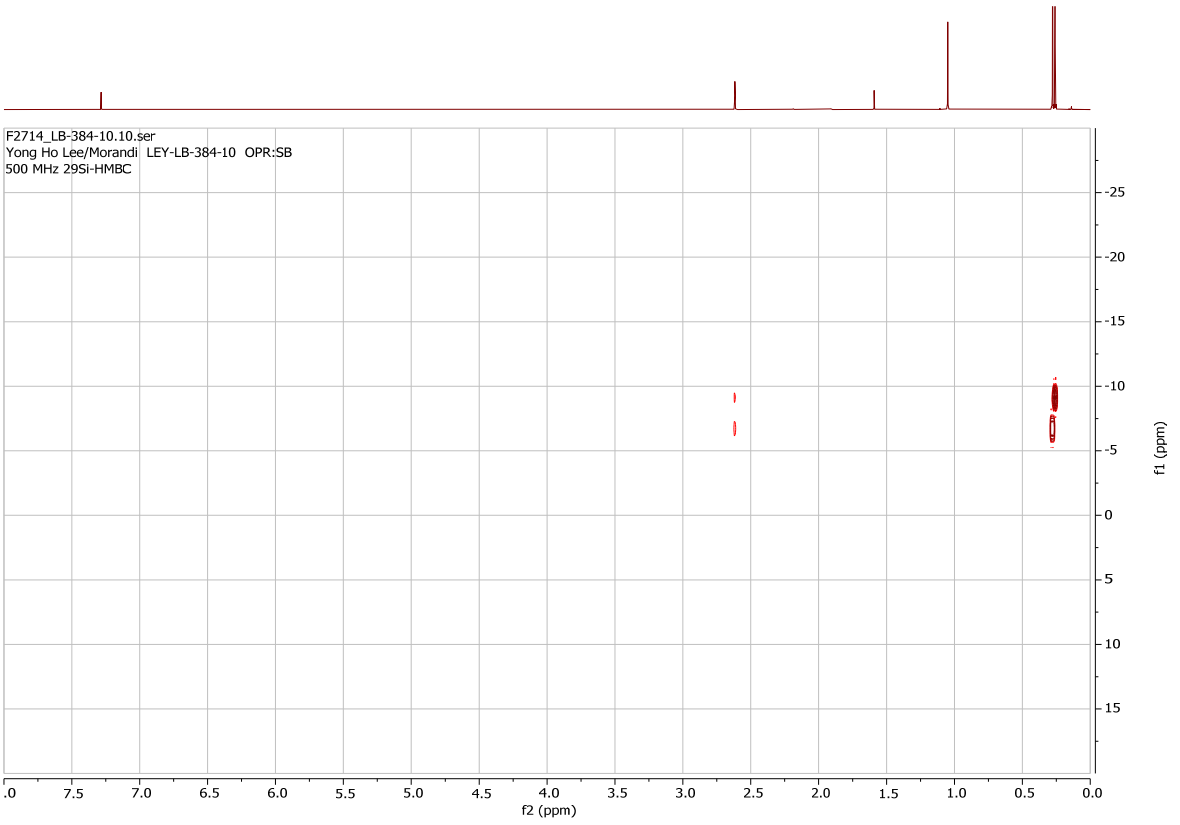


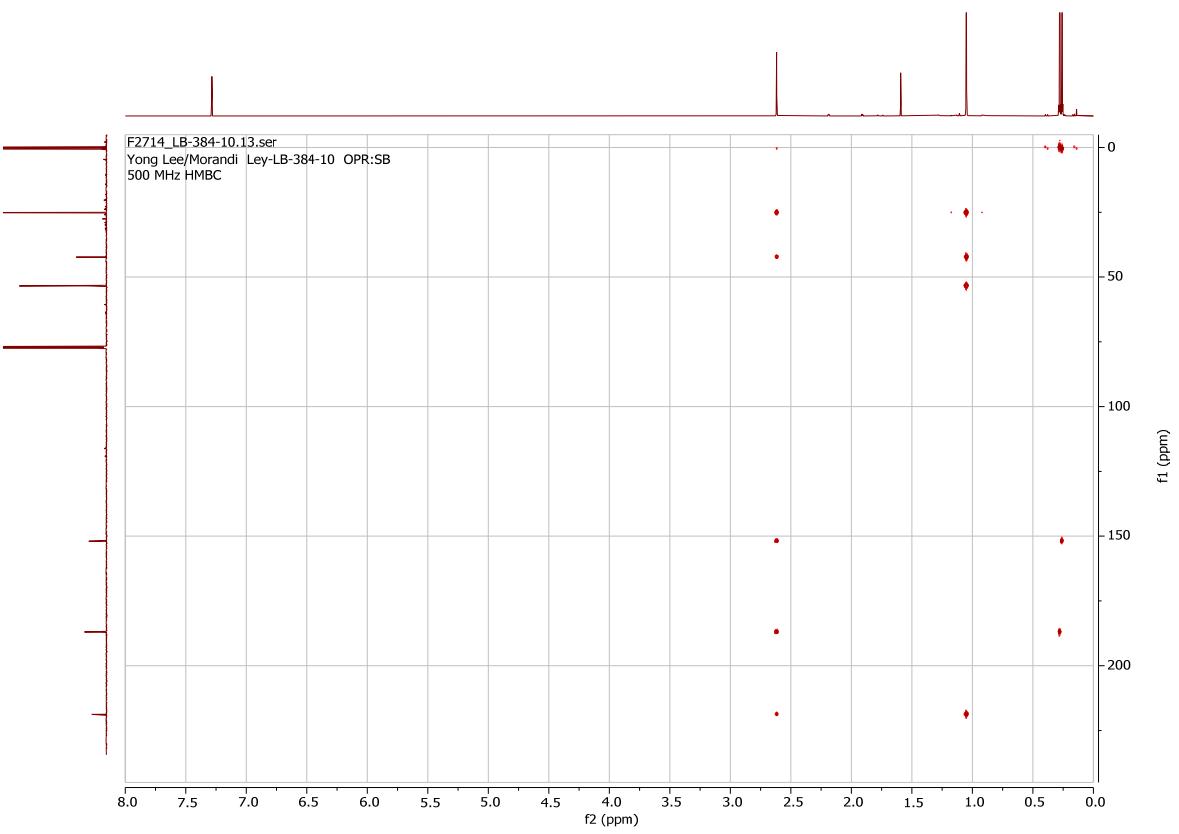

200709-1014-44-mlee-avn500.5.ser
Sample LEY-LB-395-06-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-395-06-F
HMBC.ETH CDCl3 /opt/v mlee 44
f2 (ppm)
f1 (ppm)

5,5-dimethyl-2,3-bis(trimethylsilyl)cyclopent-2-en-1-one (**3bg**).

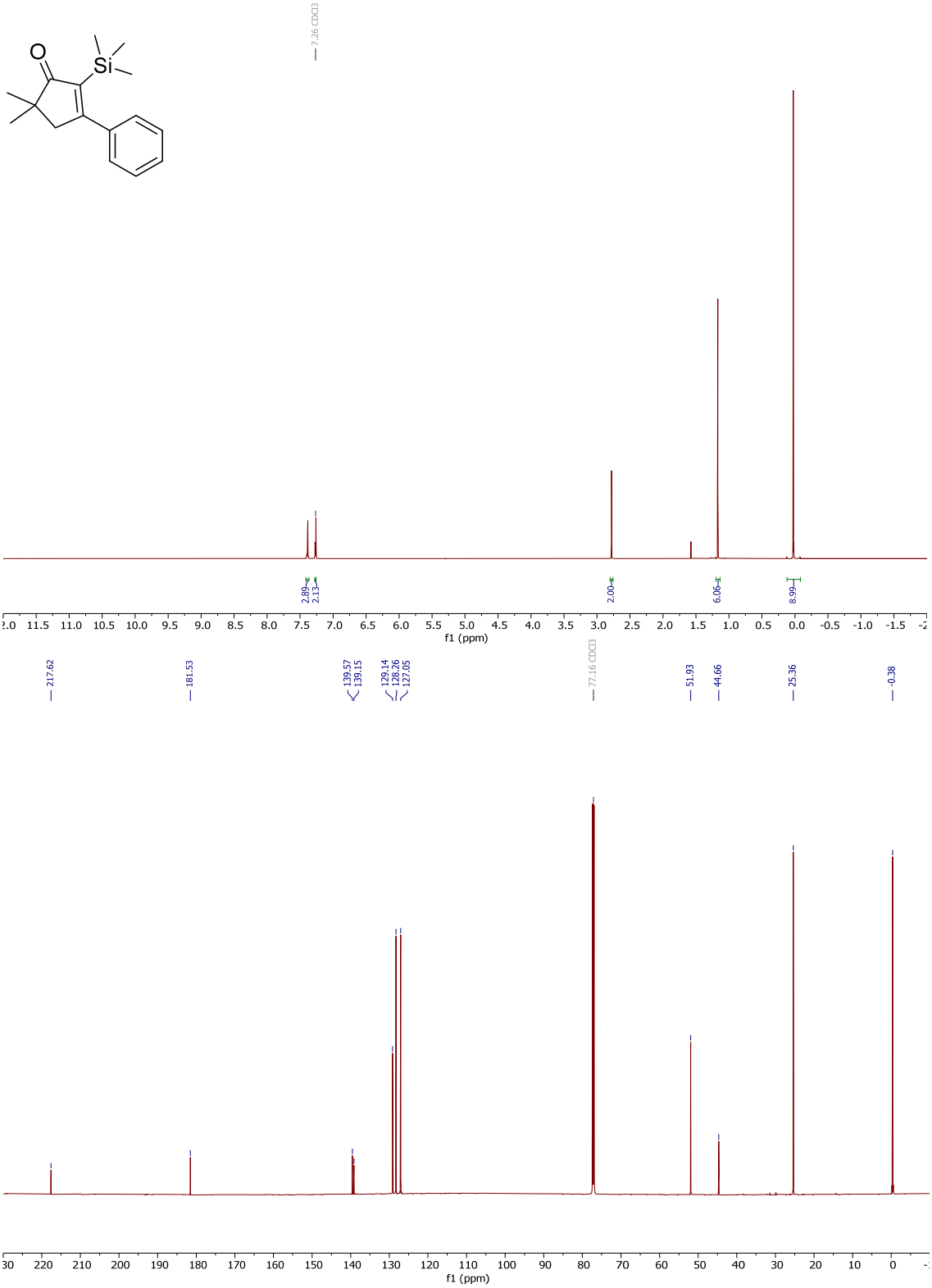


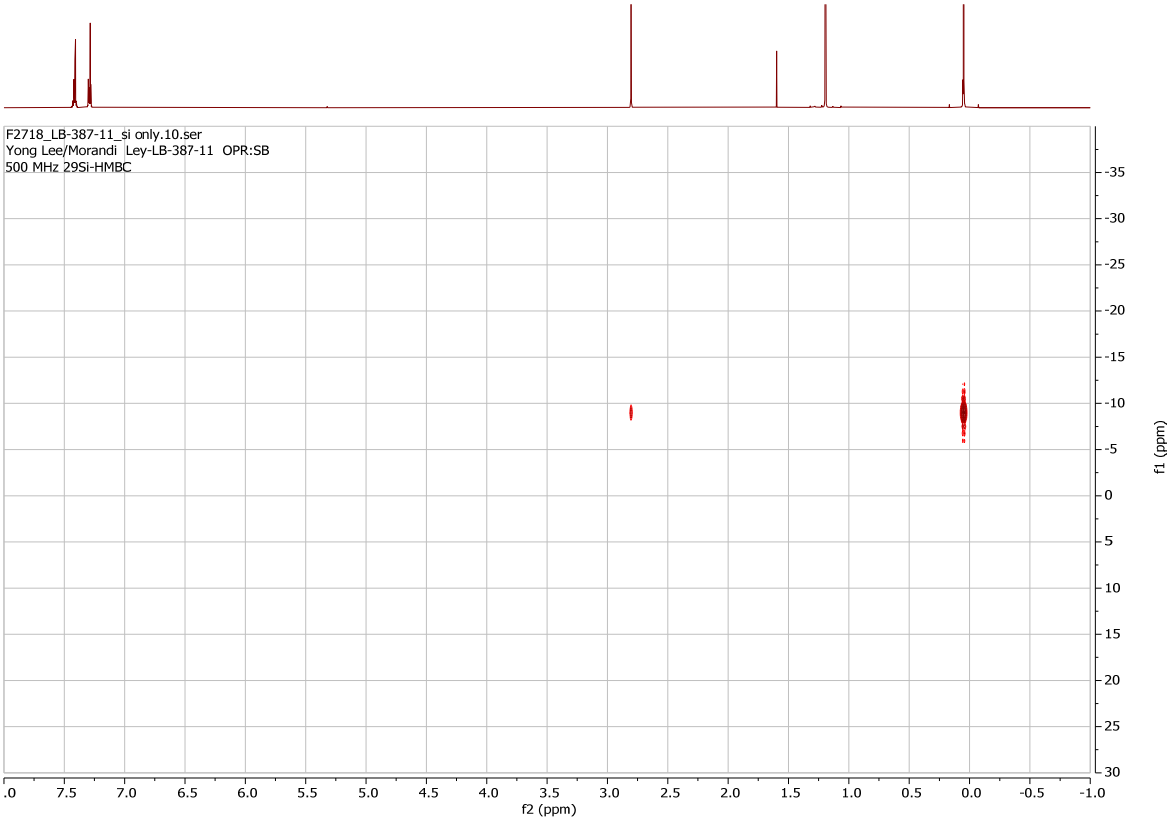


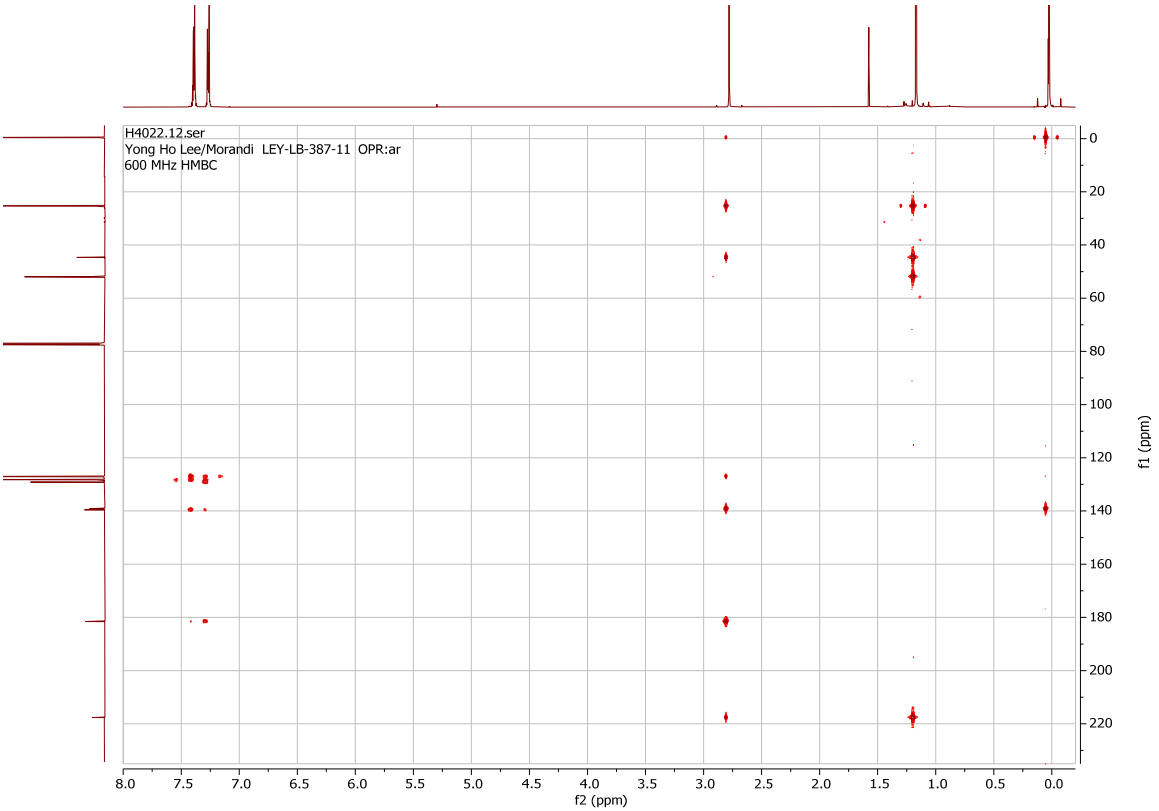

F2714_LB-384-10.10.ser
Yong Ho Lee/Morandi LEY-LB-384-10 OPR:SB
500 MHz 29Si-HMBC
f2 (ppm)
f1 (ppm)

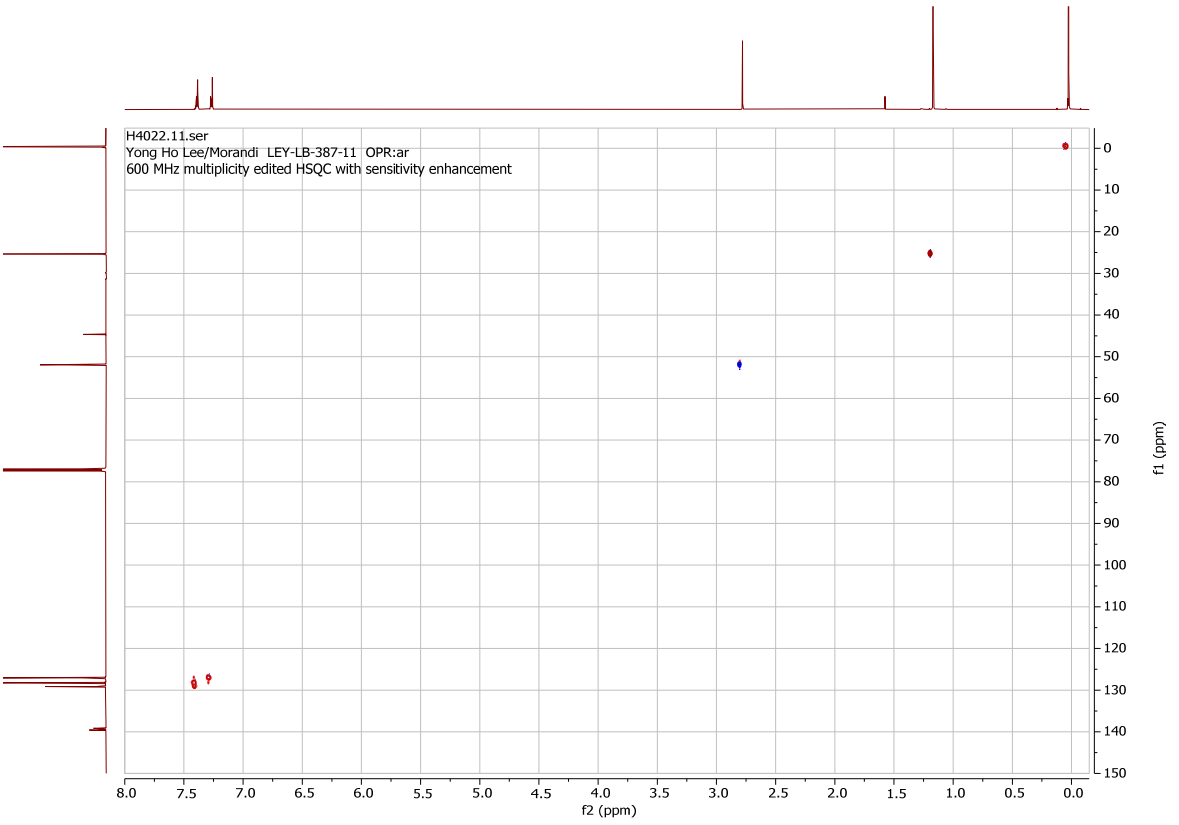

F2714_LB-384-10.13.ser
Yong Lee/Morandi Ley-LB-384-10 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

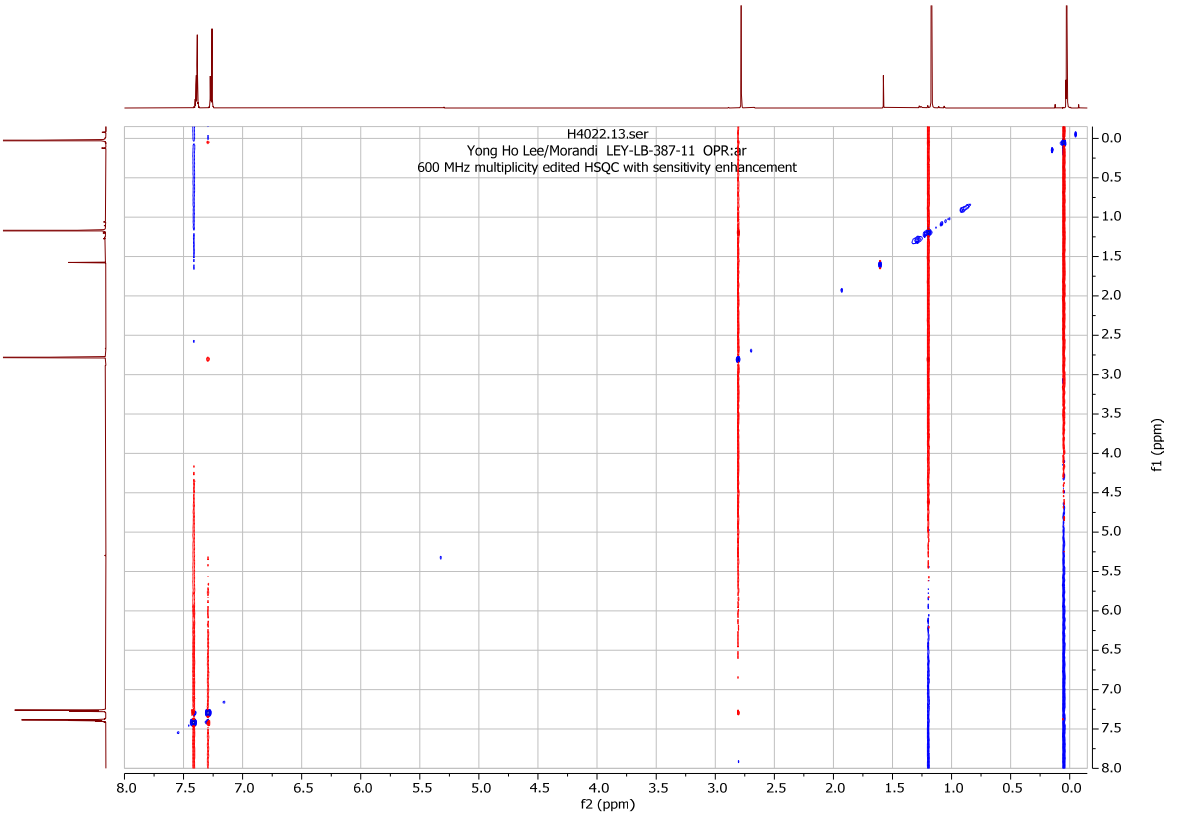
5,5-dimethyl-3-phenyl-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bh**).



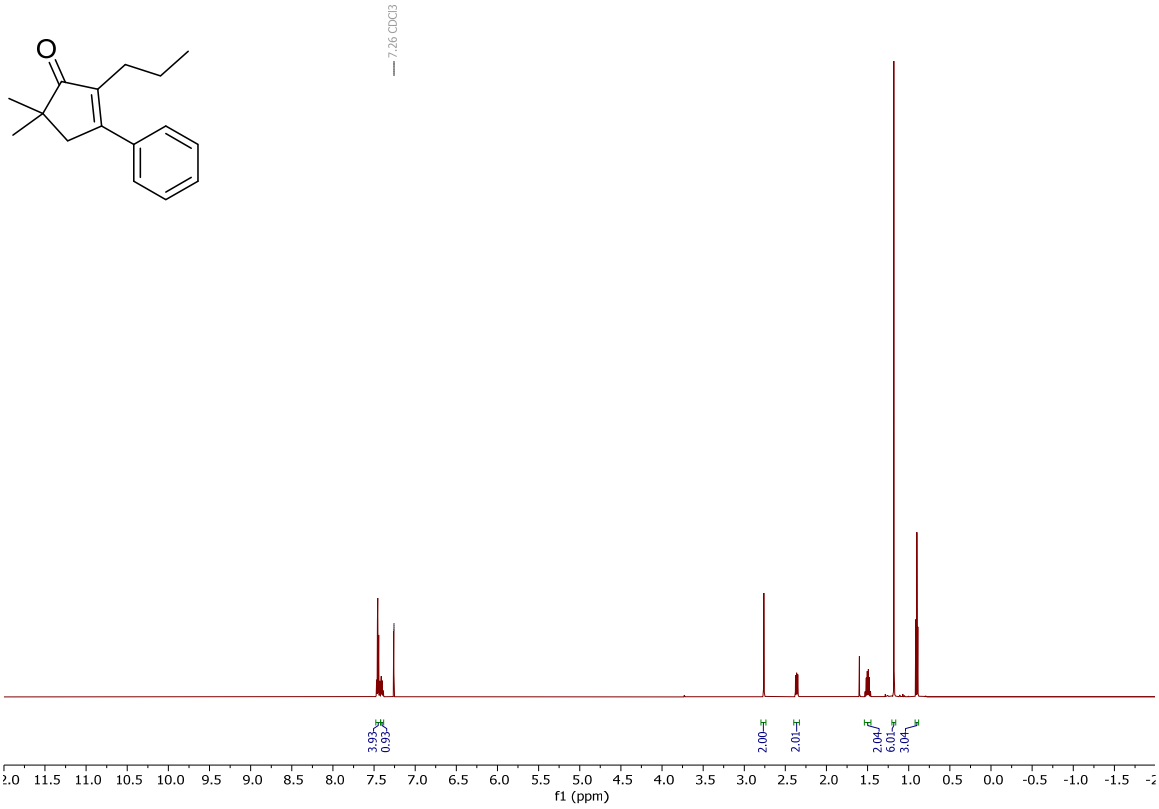

F2718_LB-387-11_si only.10.ser
Yong Lee/Morandi Ley-LB-387-11 OPR:SB
500 MHz 29Si-HMBC
f2 (ppm)
f1 (ppm)

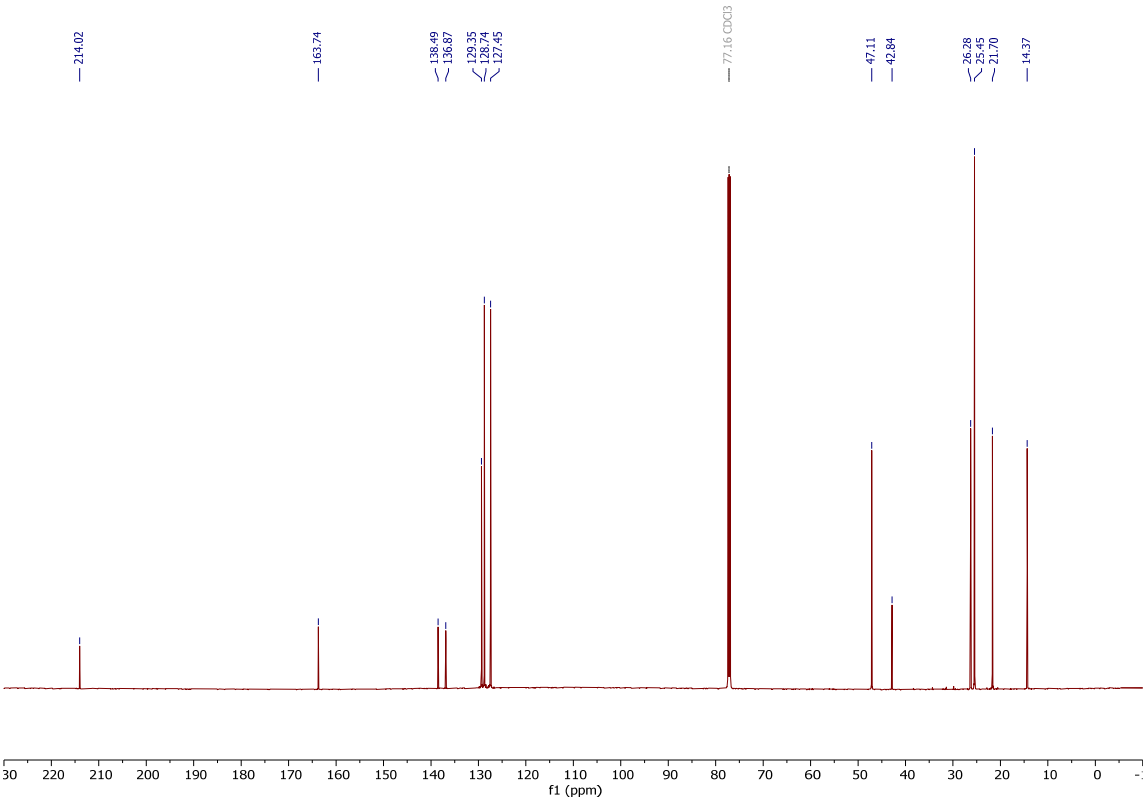

H4022.12.ser
Yong Ho Lee/Morandi LEY-LB-387-11 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

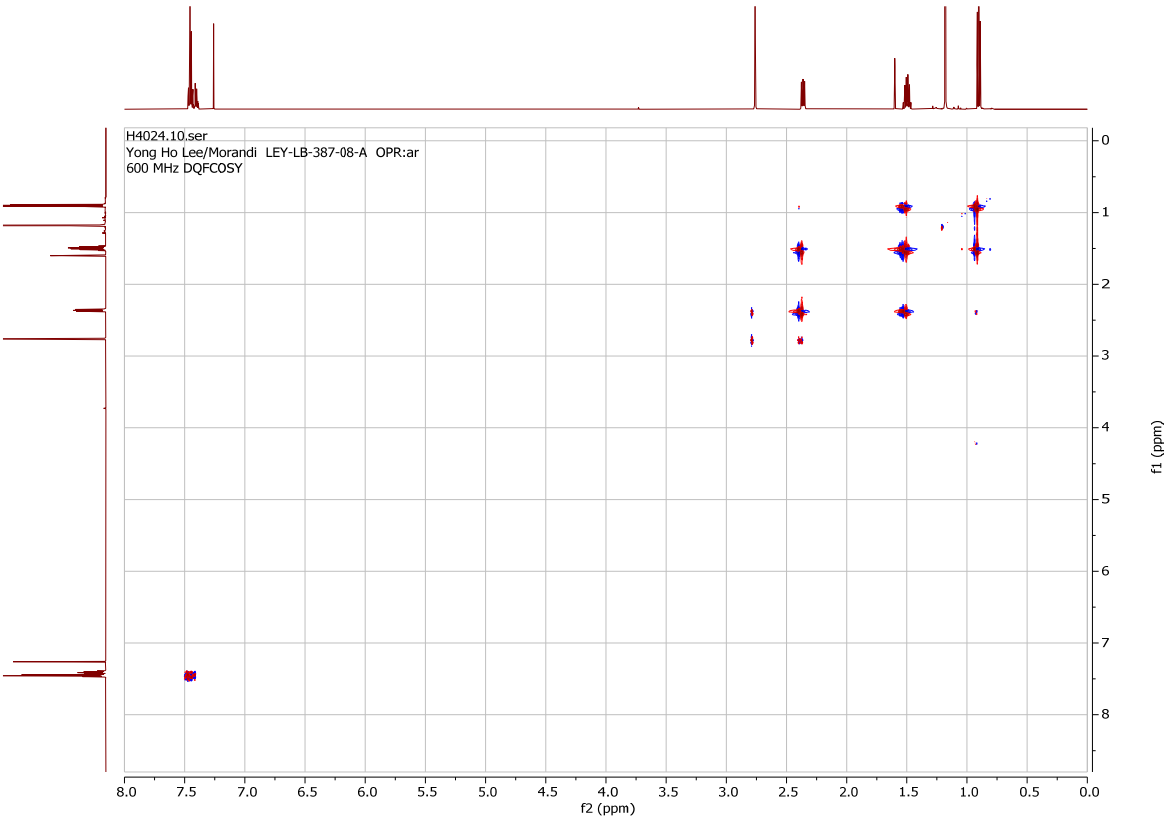

H4022.11.ser
Yong Ho Lee/Morandi LEY-LB-387-11 OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

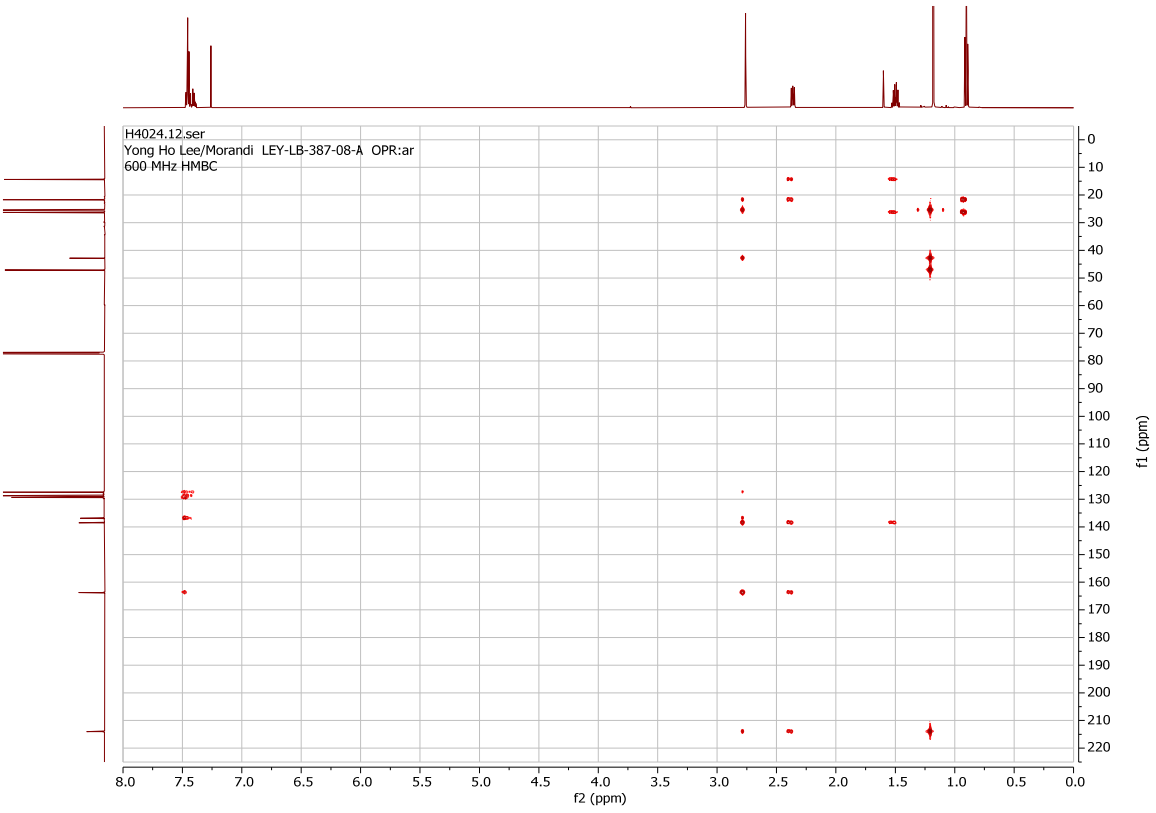

H4022.13.ser
Yong Ho Lee/Morandi LEY-LB-387-11 OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

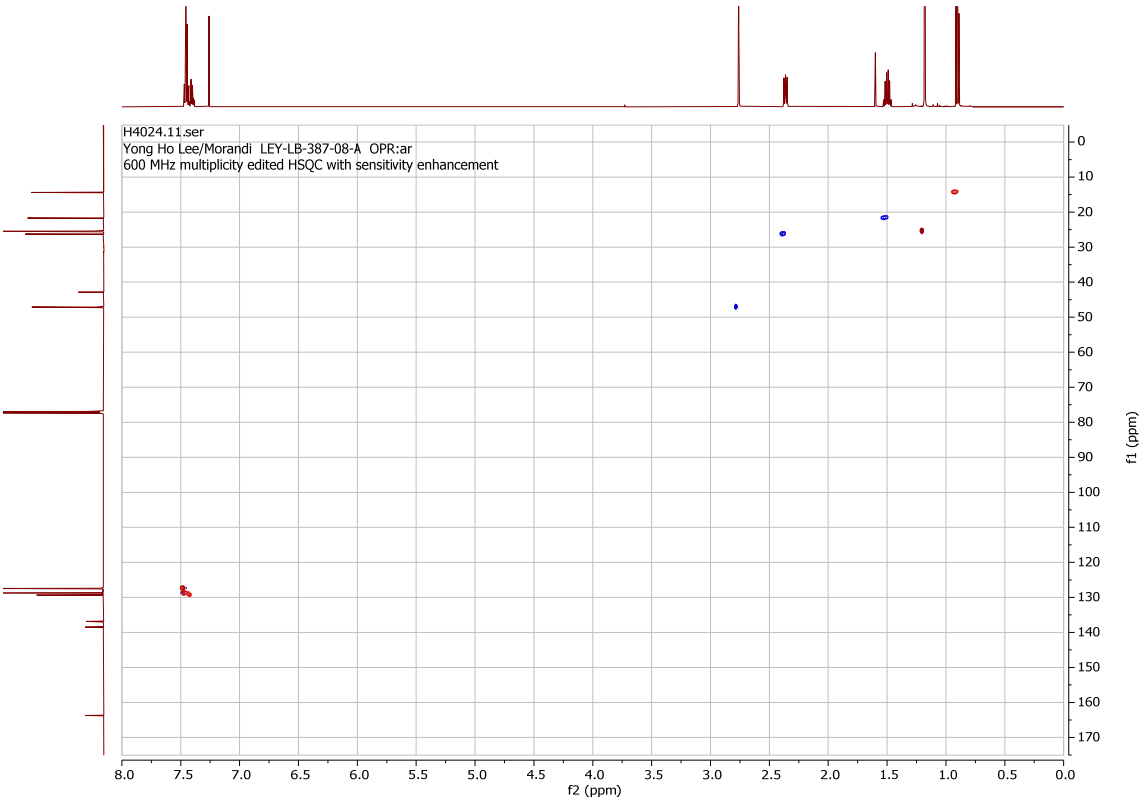
5,5-dimethyl-3-phenyl-2-propylcyclopent-2-en-1-one (**3bi-1**, major).

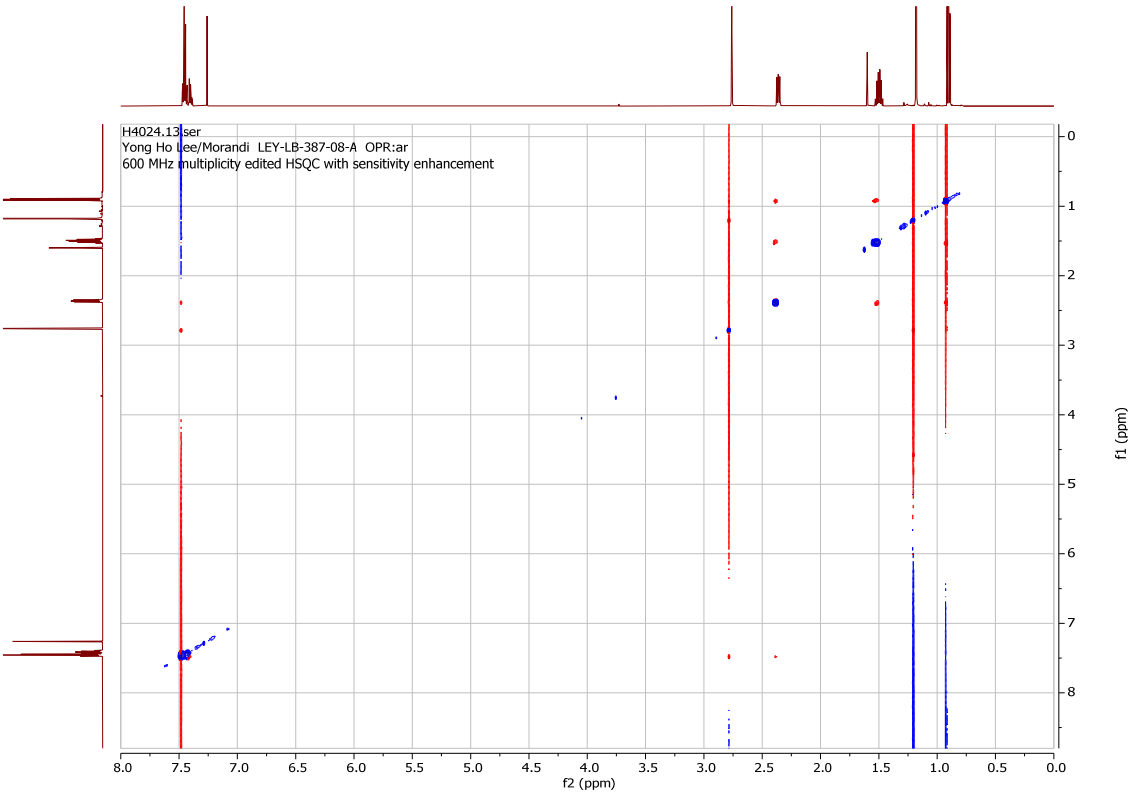




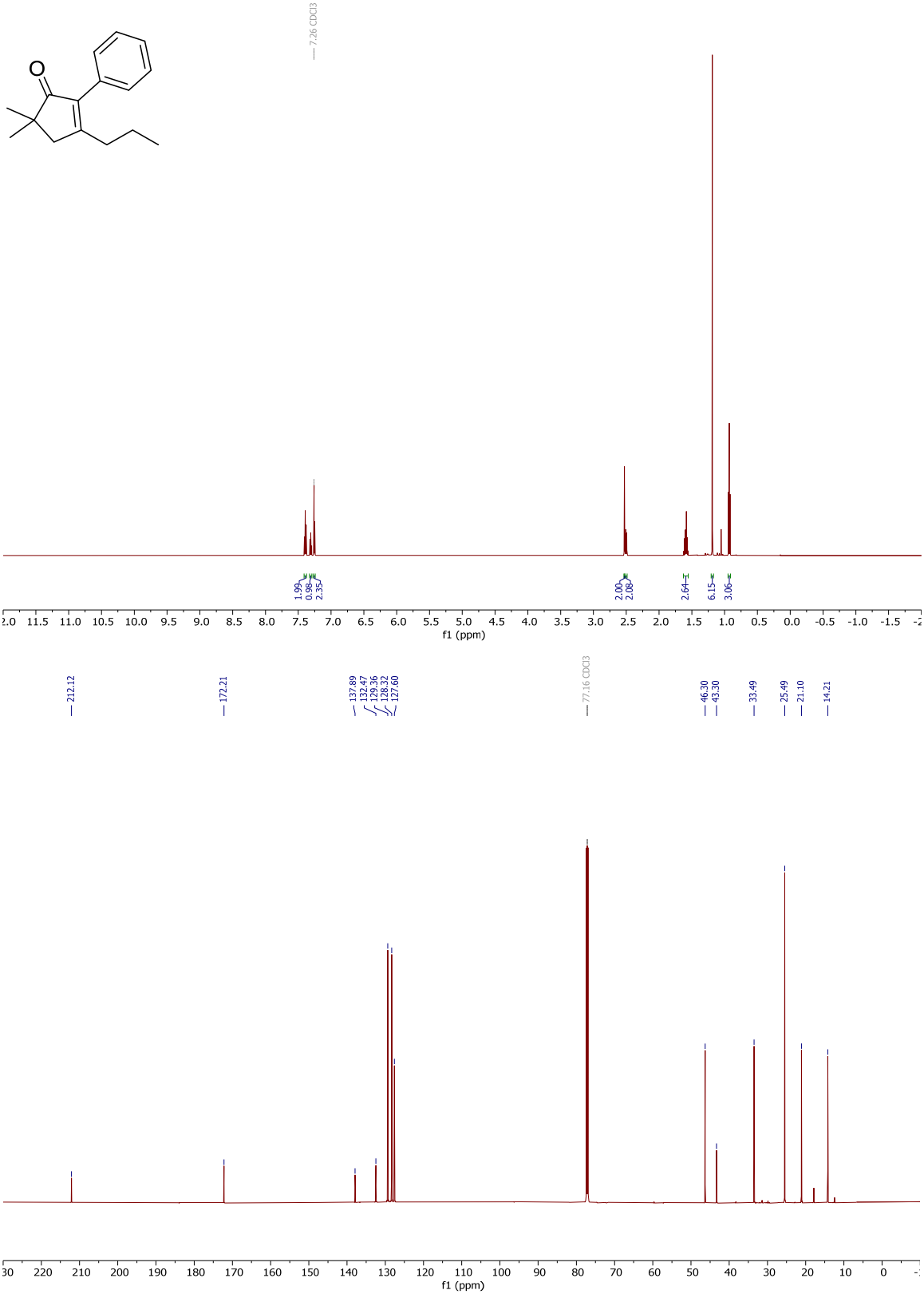

H4024.10.ser
Yong Ho Lee/Morandi LEY-LB-387-08-A OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

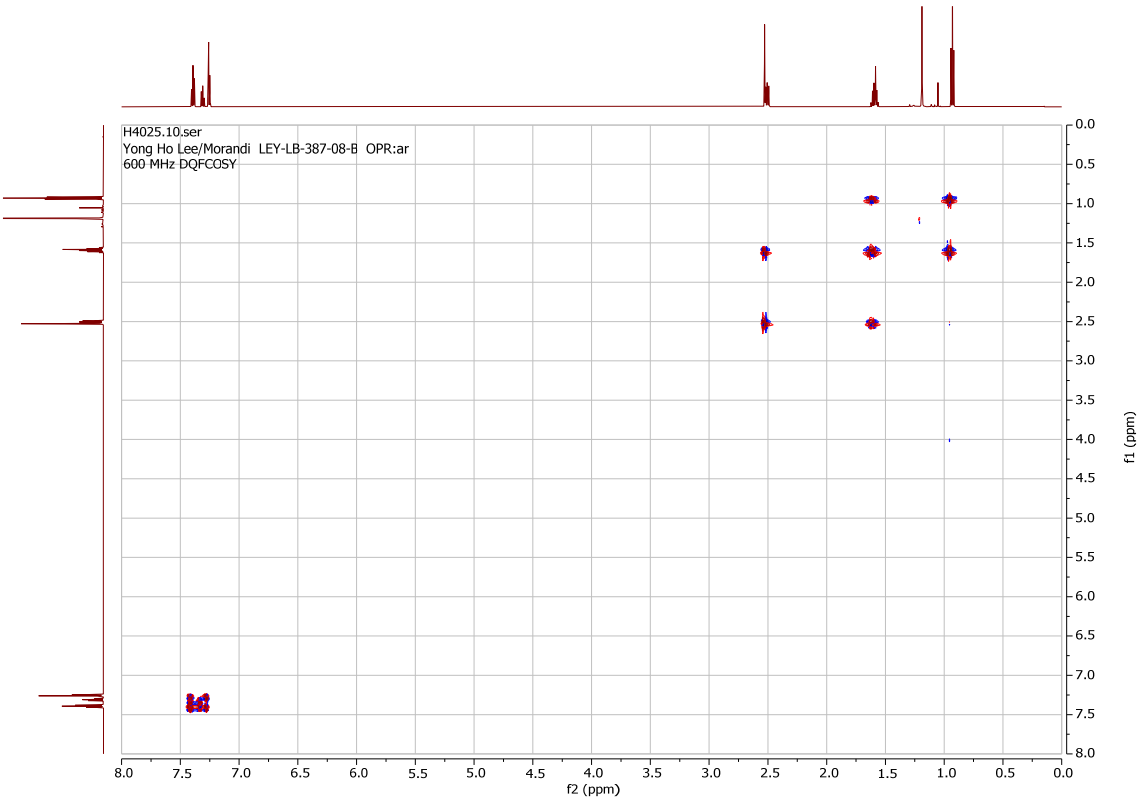

H4024.12.ser
Yong Ho Lee/Morandi LEY-LB-387-08-A OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

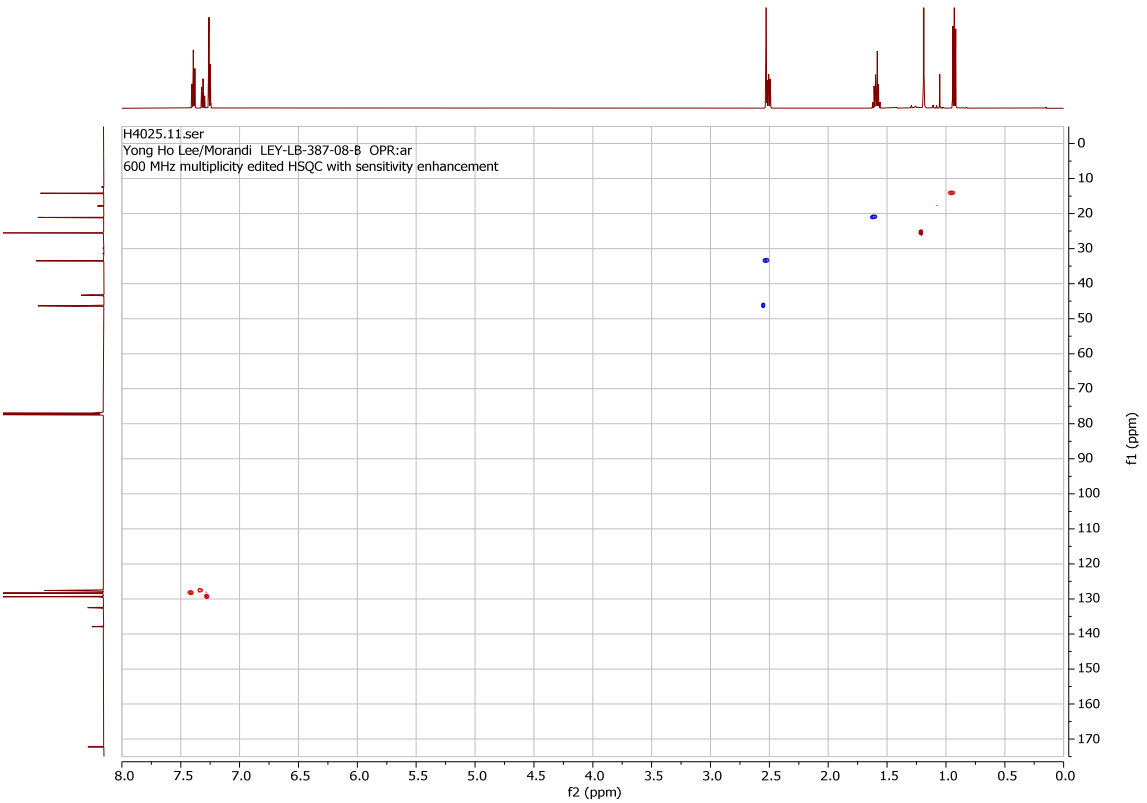

H4024.11.ser
Yong Ho Lee/Morandi LEY-LB-387-08-A OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

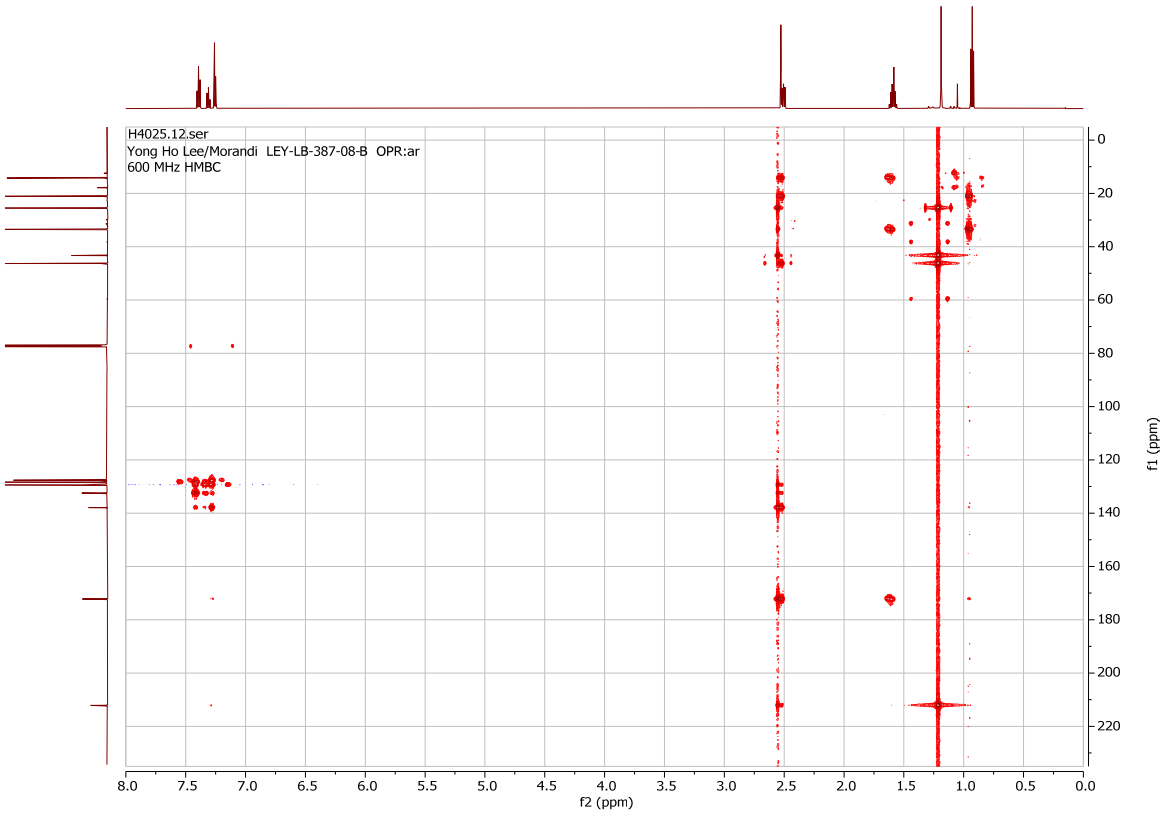

H4024.13.ser
Yong Ho Lee/Morandi LEY-LB-387-08-A OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

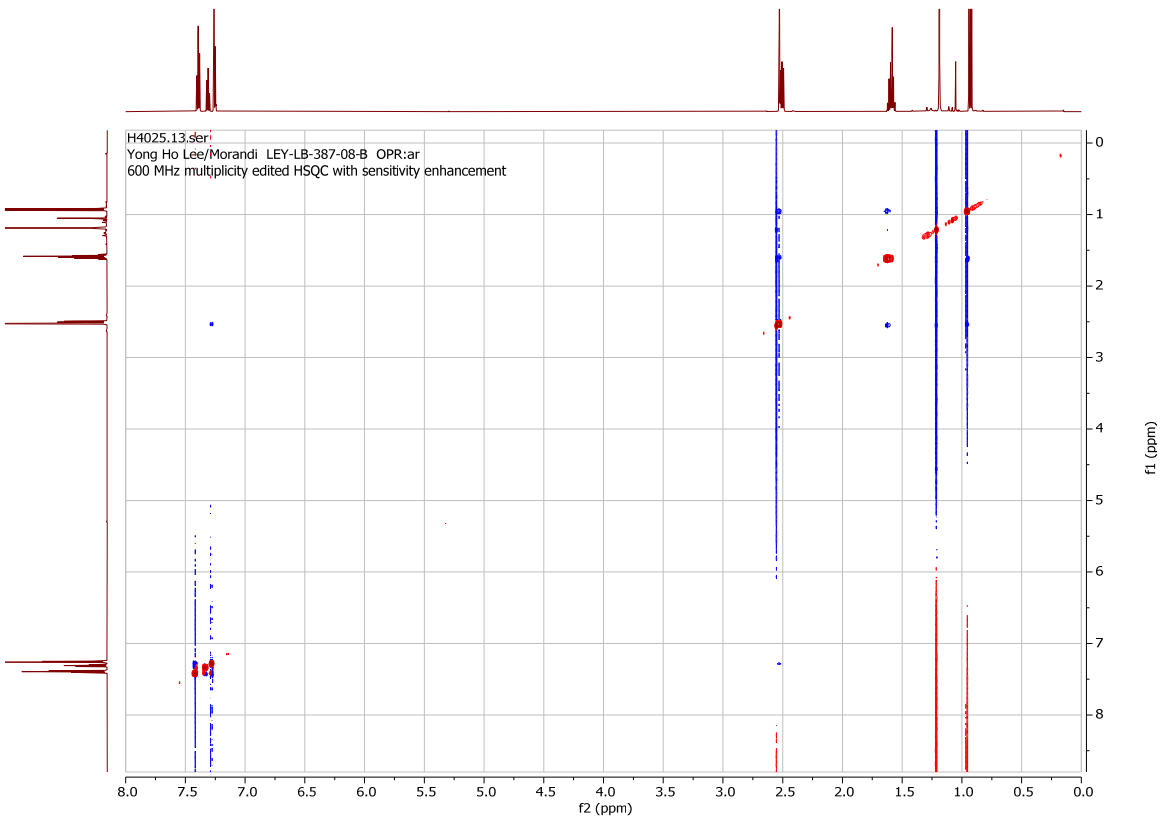
5,5-dimethyl-2-phenyl-3-propylcyclopent-2-en-1-one (**3bi-2**, minor).



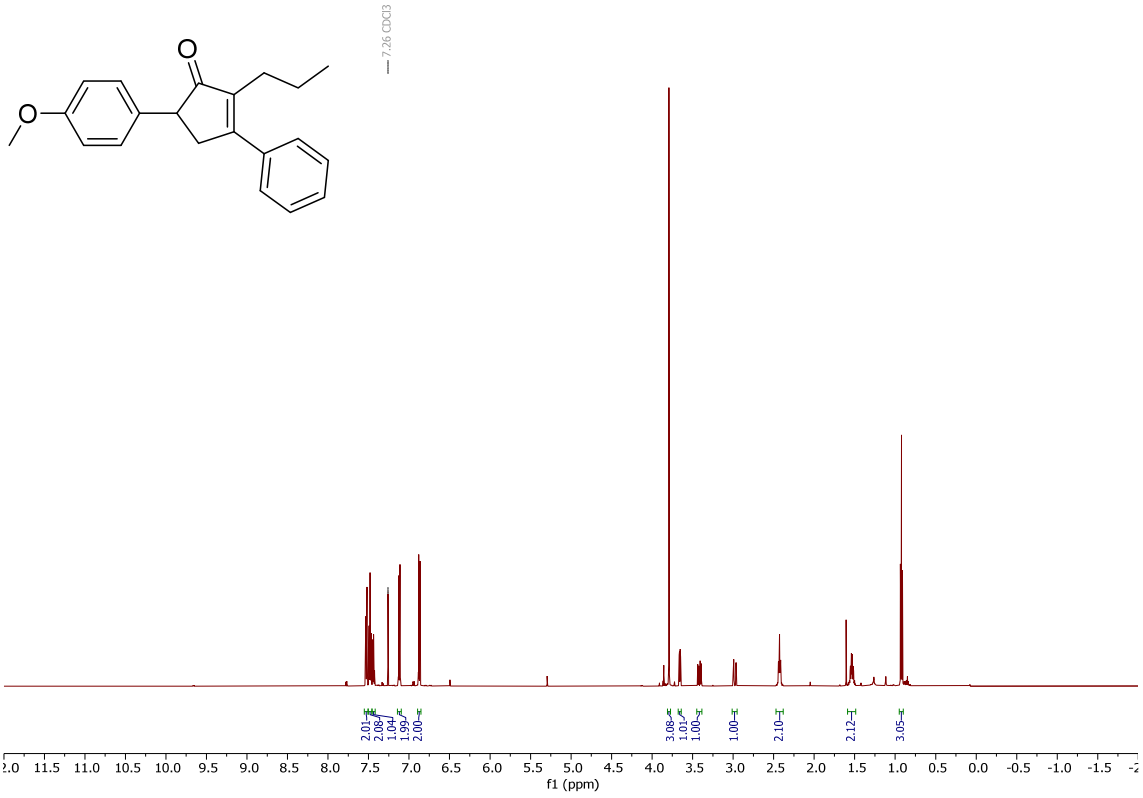

H4025.10.ser
Yong Ho Lee/Morandi LEY-LB-387-08-B OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

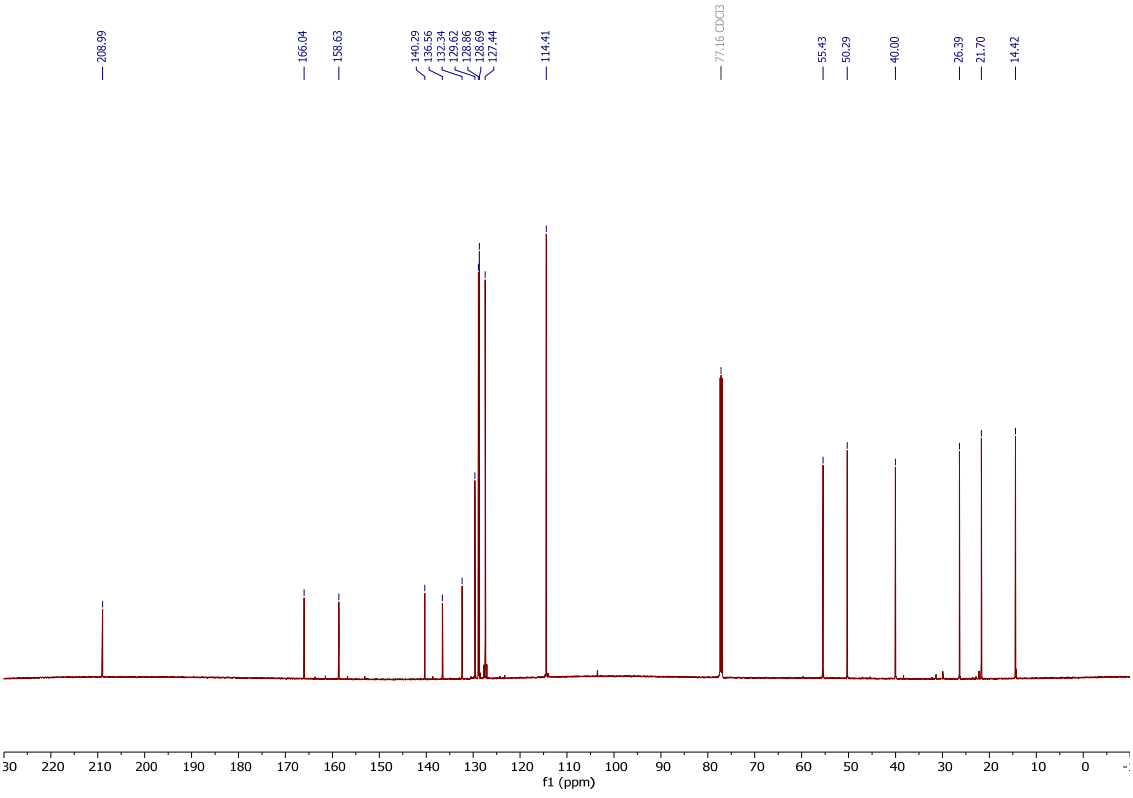

H4025.11.ser
Yong Ho Lee/Morandi LEY-LB-387-08-B OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)


H4025.12.ser
Yong Ho Lee/Morandi LEY-LB-387-08-B OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

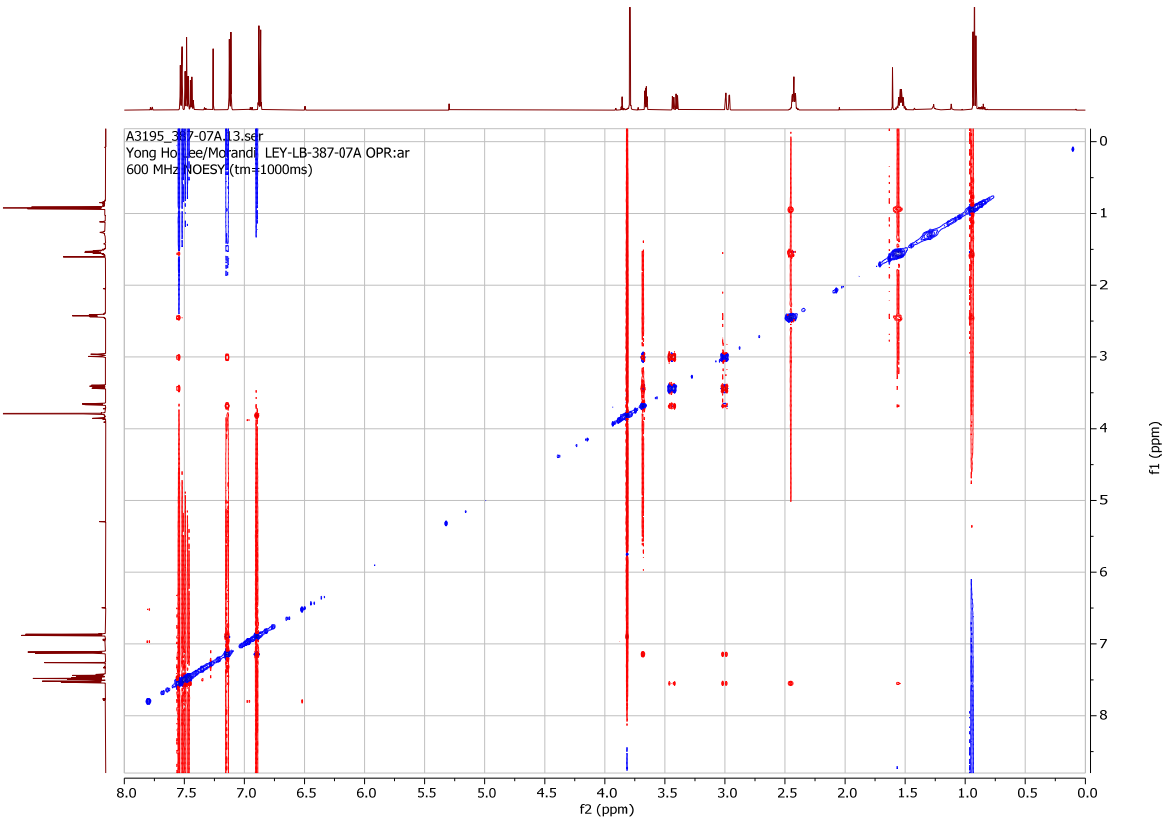

H4025.13.ser
Yong Ho Lee/Morandi LEY-LB-387-08-B OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

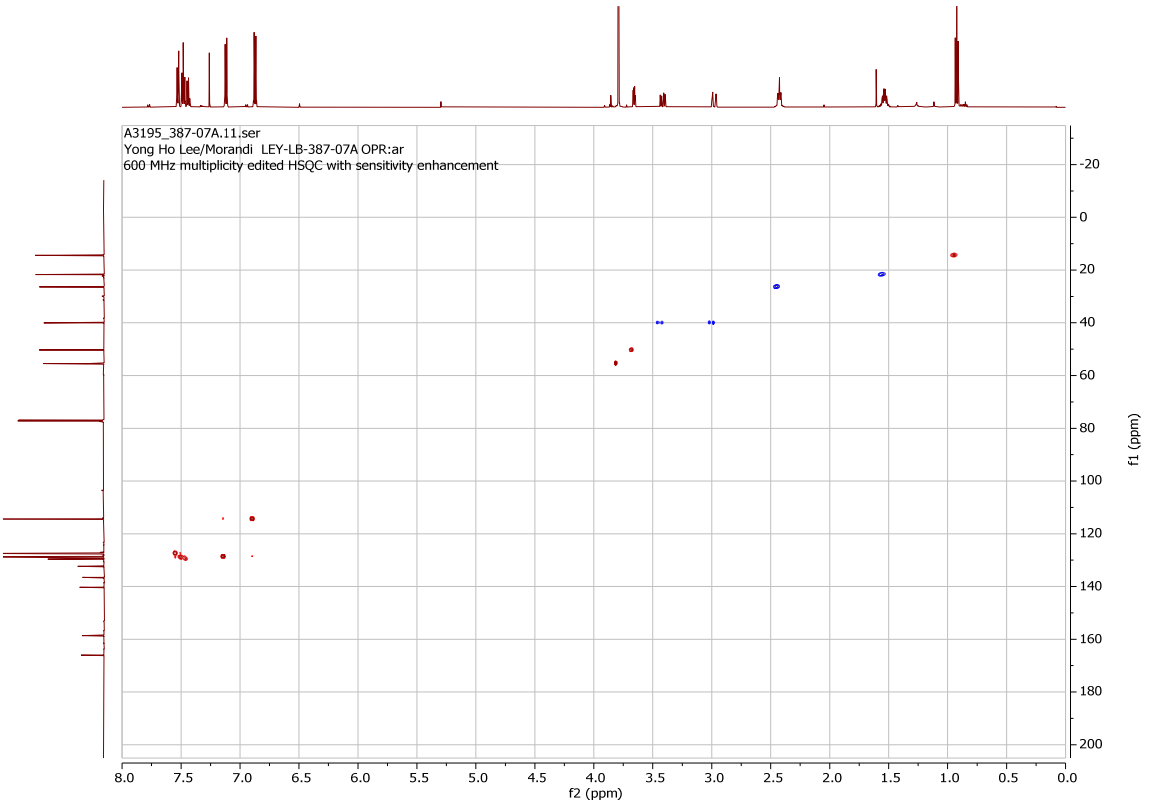
5-(4-methoxyphenyl)-3-phenyl-2-propylcyclopent-2-en-1-one (**3bj-1**, major).

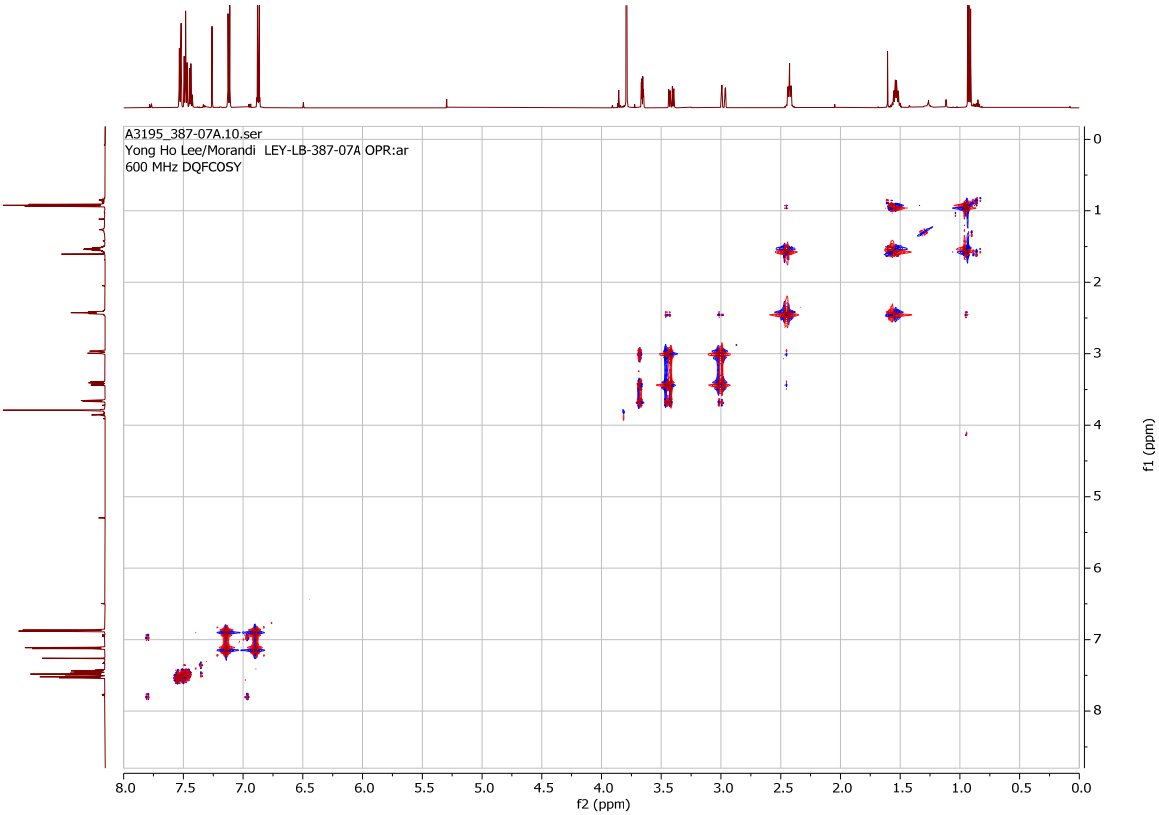




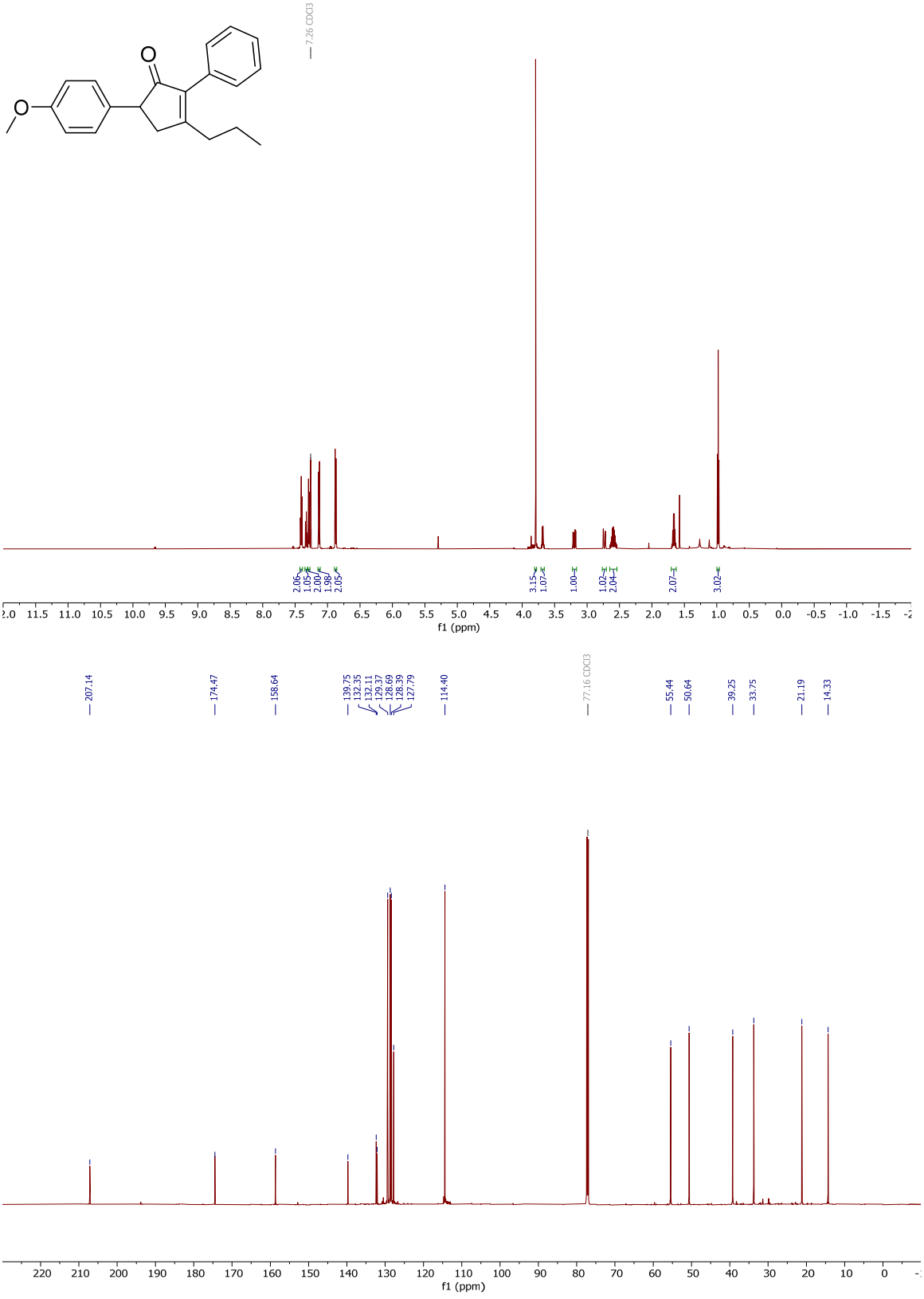

A3195_387-07A.12.ser
Yong Ho Lee/Morandi LEY-LB-387-07A OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)


A3195_387-07A.13.ser
Yong Ho Lee/Morandi LEY-LB-387-07A OPR:ar
600 MHz NOESY (tm=1000ms)
f2 (ppm)
f1 (ppm)

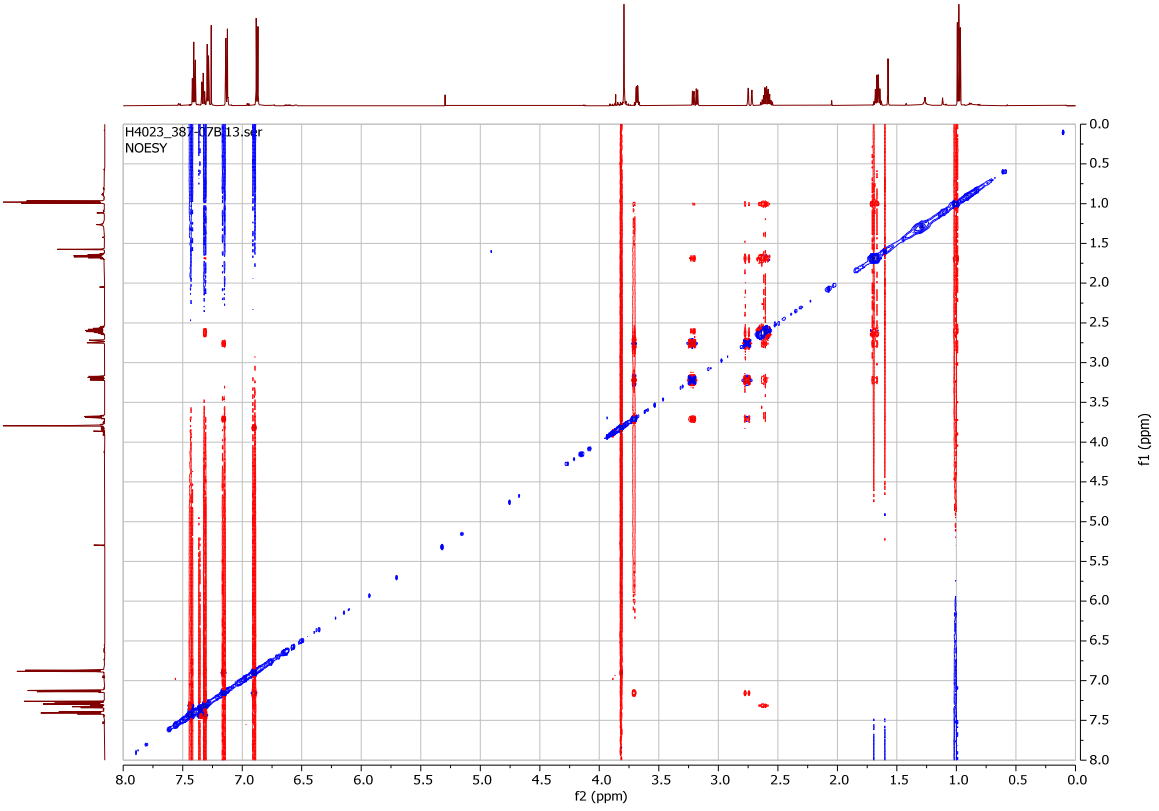

A3195_387-07A.11.ser
Yong Ho Lee/Morandi LEY-LB-387-07A OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

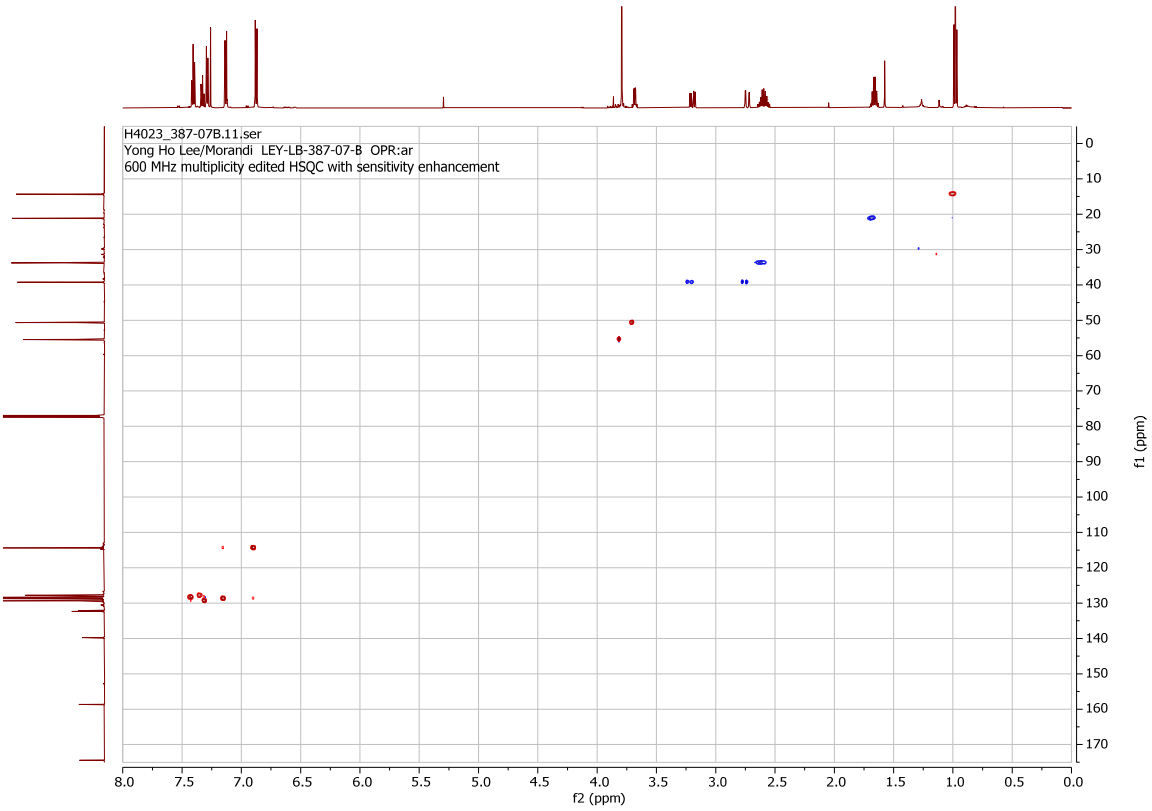

A3195_387-07A.10.ser
Yong Ho Lee/Morandi LEY-LB-387-07A OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

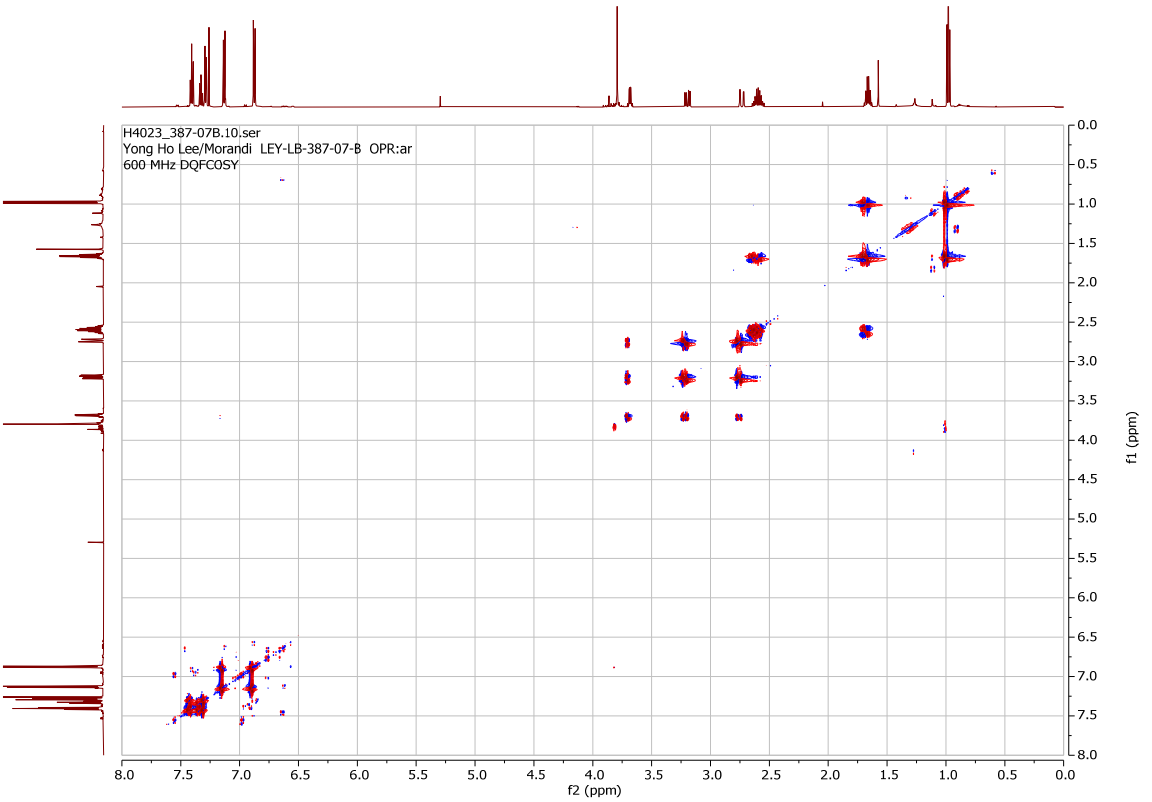
5-(4-methoxyphenyl)-2-phenyl-3-propylcyclopent-2-en-1-one (**3bj-2**, minor).



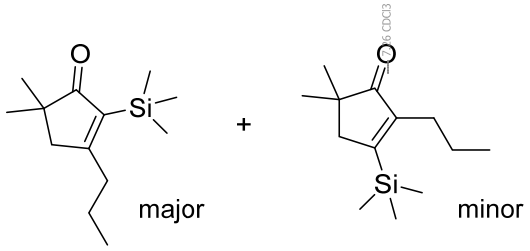

H4023_387-07B.12.ser
Yong Ho Lee/Morandi LEY-LB-387-07-B OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

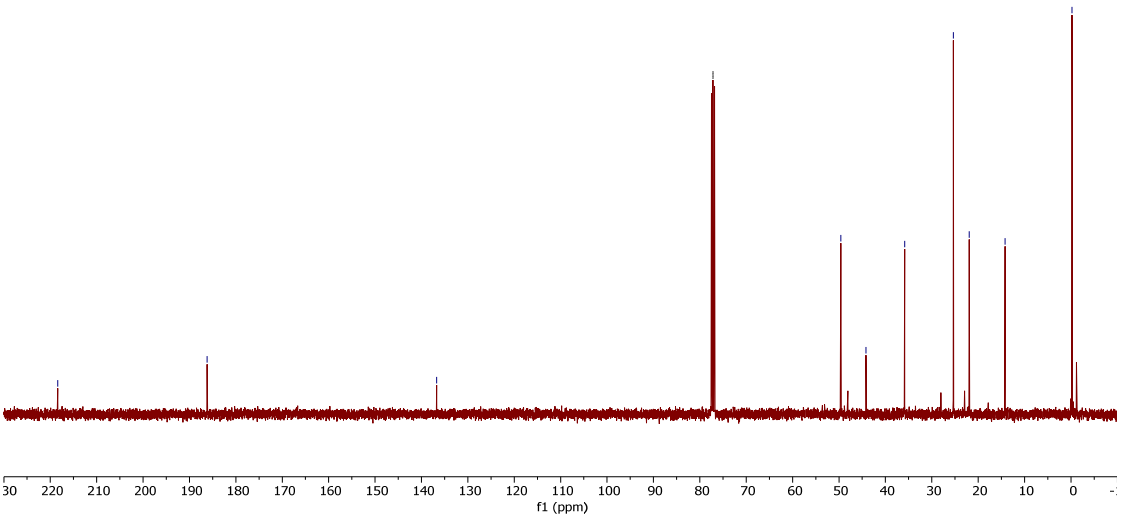

H4023_387-07B.13.ser
NOESY
f2 (ppm)
f1 (ppm)

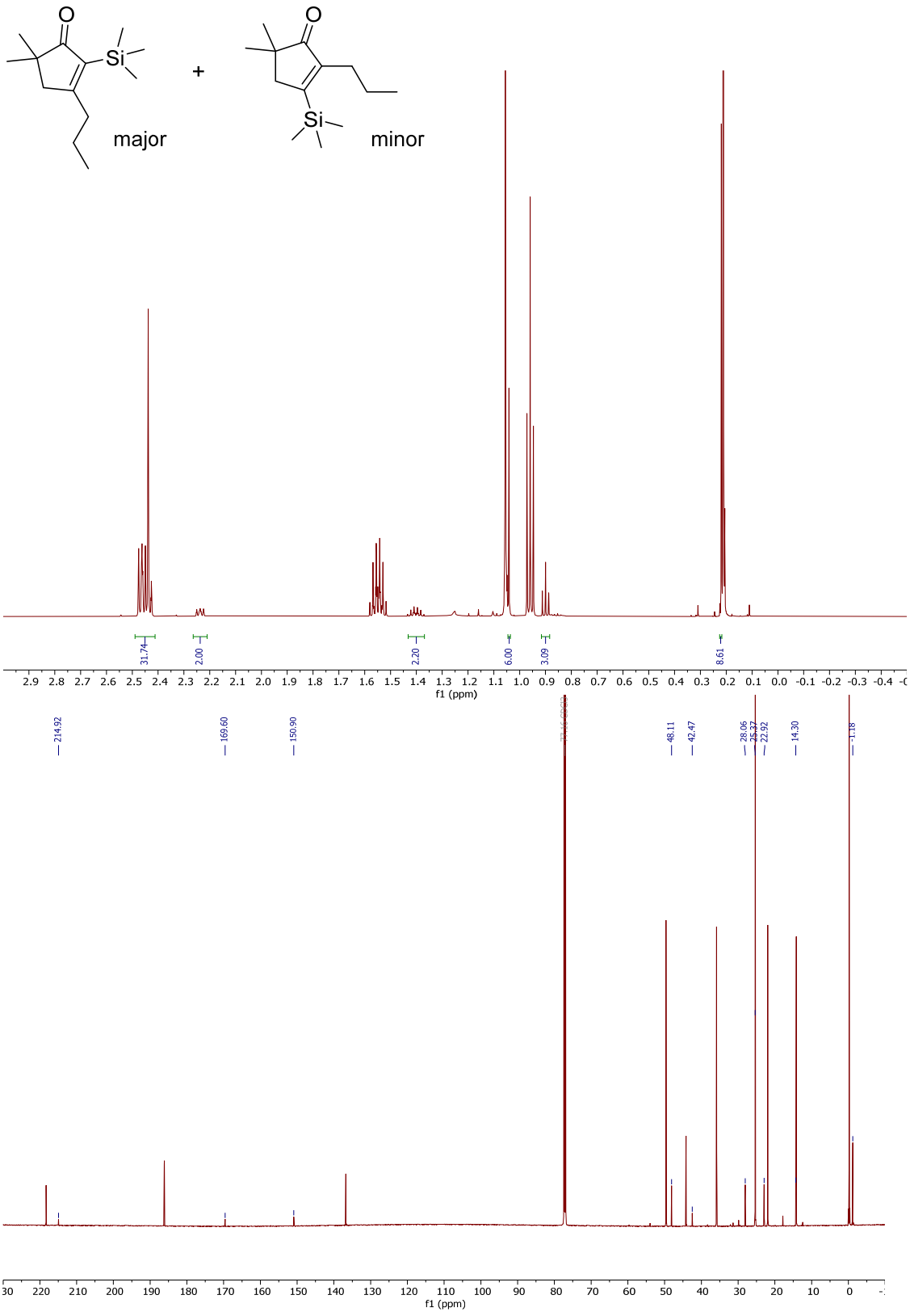

H4023_387-07B.11.ser
Yong Ho Lee/Morandi LEY-LB-387-07-B OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

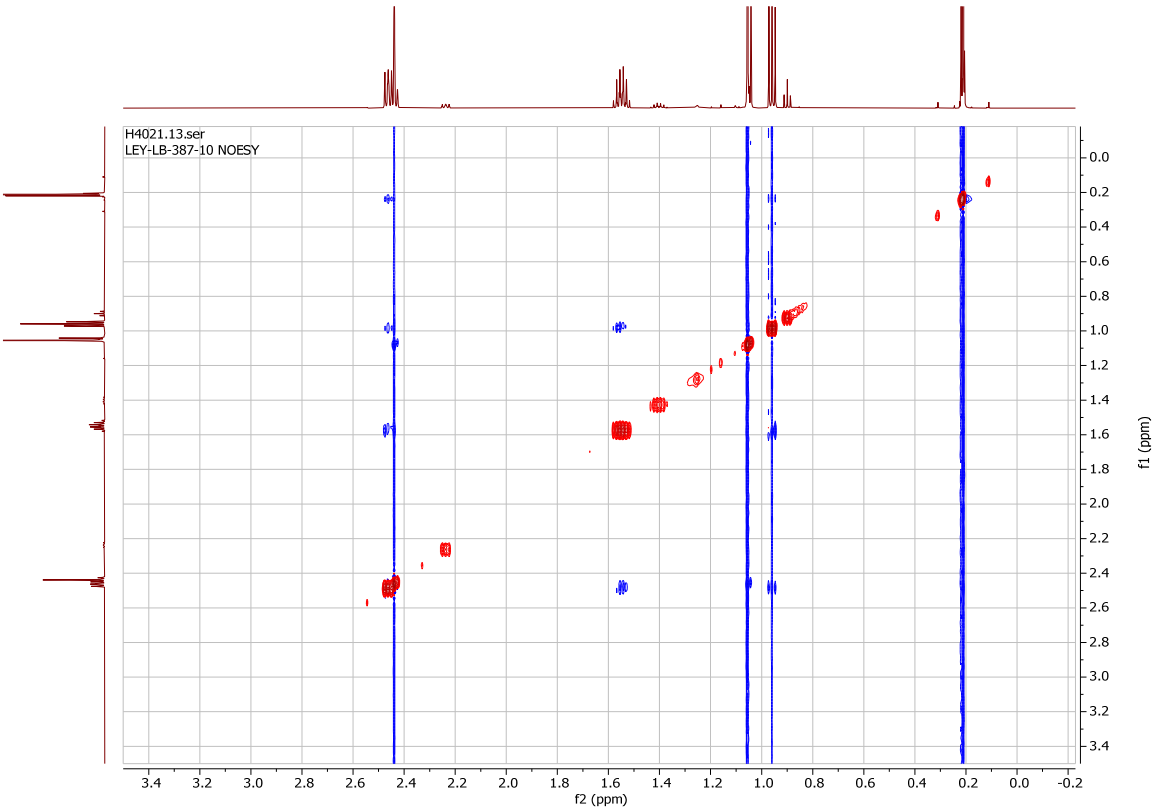

H4023_387-07B.10.ser
Yong Ho Lee/Morandi LEY-LB-387-07-B OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

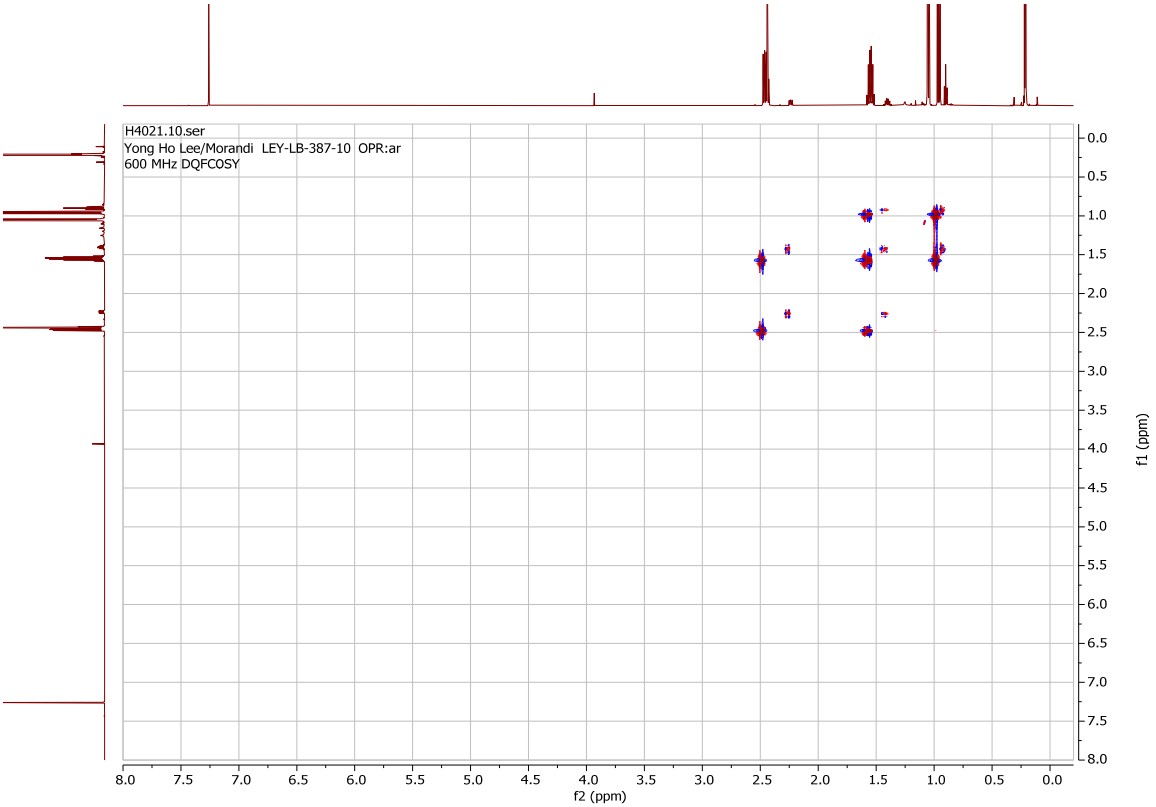
5,5-dimethyl-3-propyl-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bk-1**, major, **88**:12 mixture).
5,5-dimethyl-2-propyl-3-(trimethylsilyl)cyclopent-2-en-1-one (**3bk-2**, minor, 88:**12** mixture).

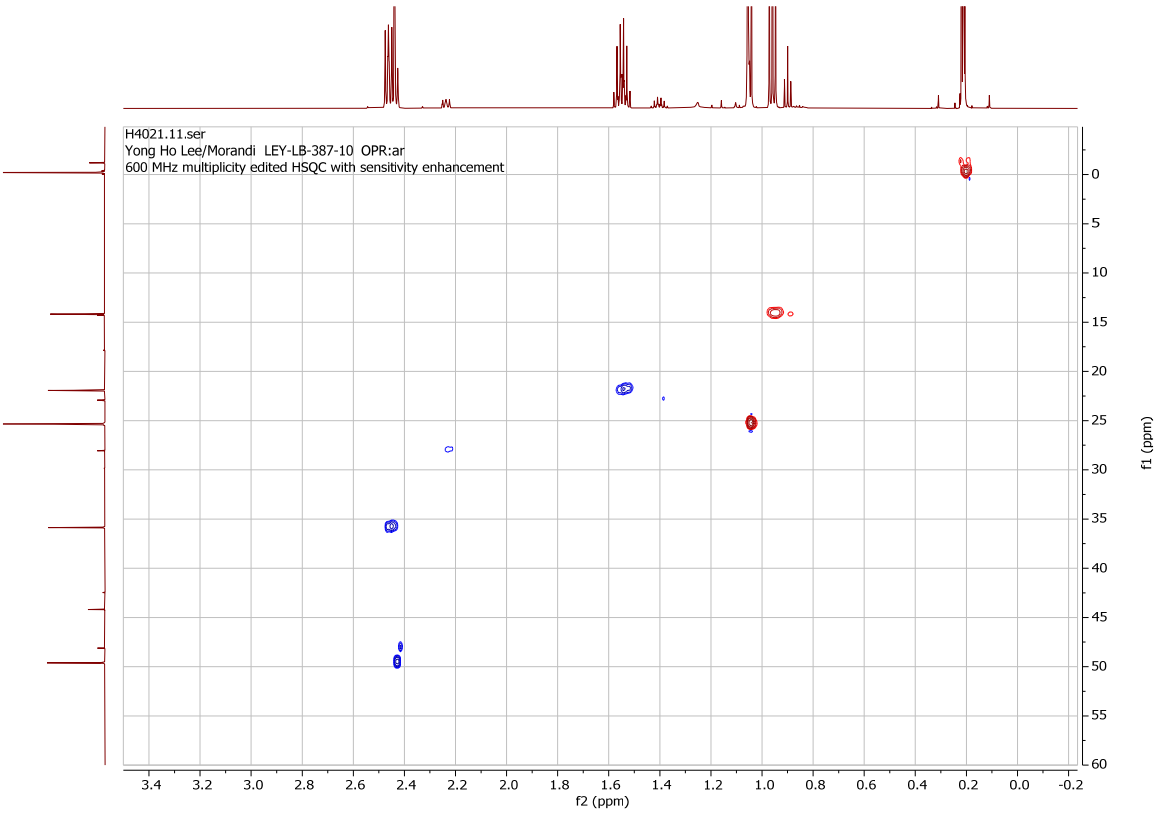


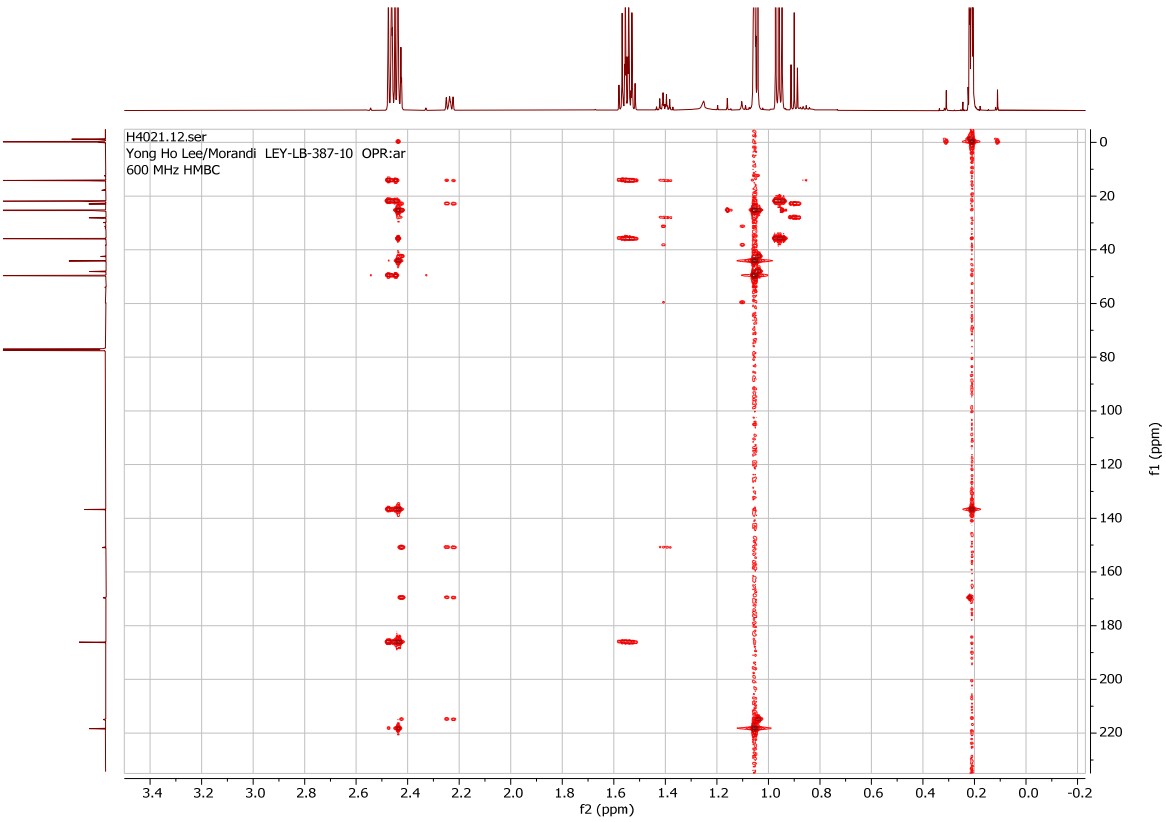


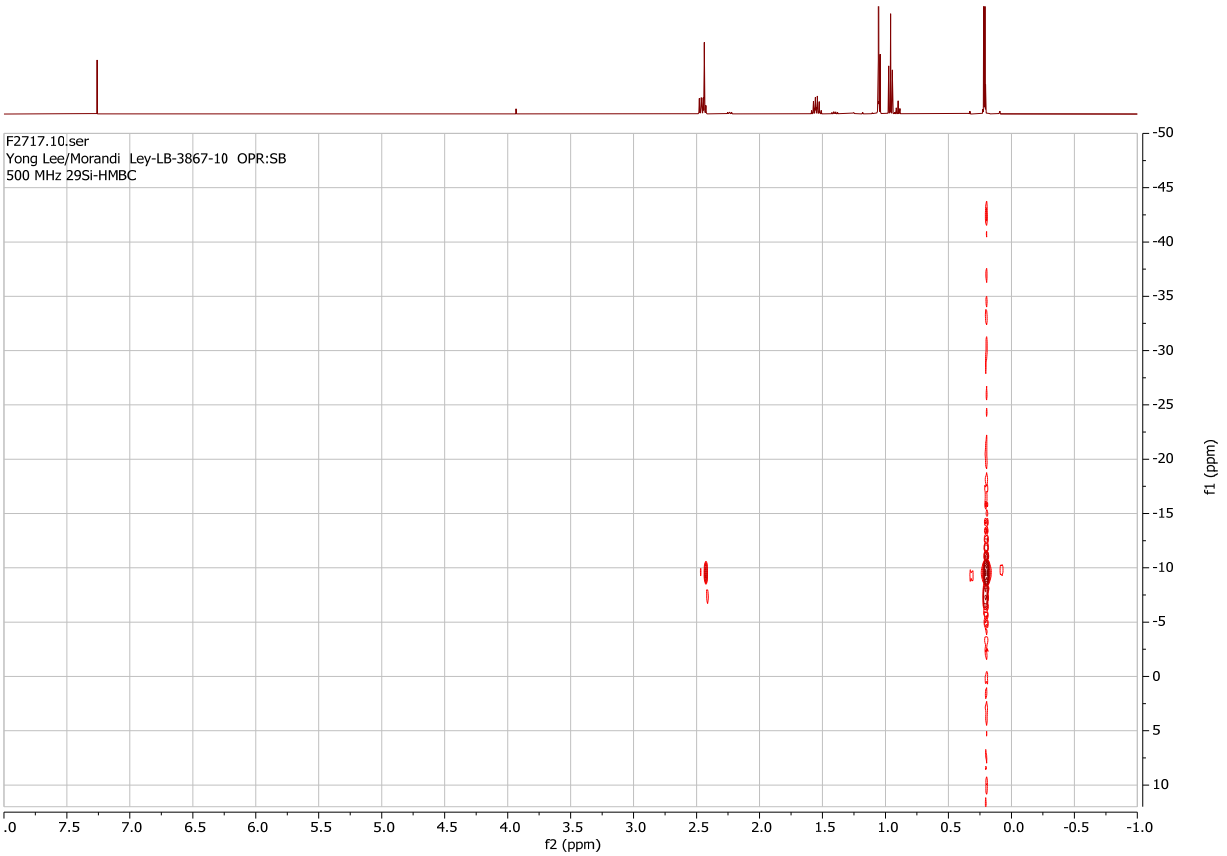

major
+
minor
31.74
2.00
2.20
6.00
3.09
8.61
f1 (ppm)
214.92
169.60
150.90
77.16
48.11
42.47
28.06
25.37
22.92
14.30
-1.18
f1 (ppm)


H4021.13.ser
LEY-LB-387-10 NOESY
f2 (ppm)
f1 (ppm)

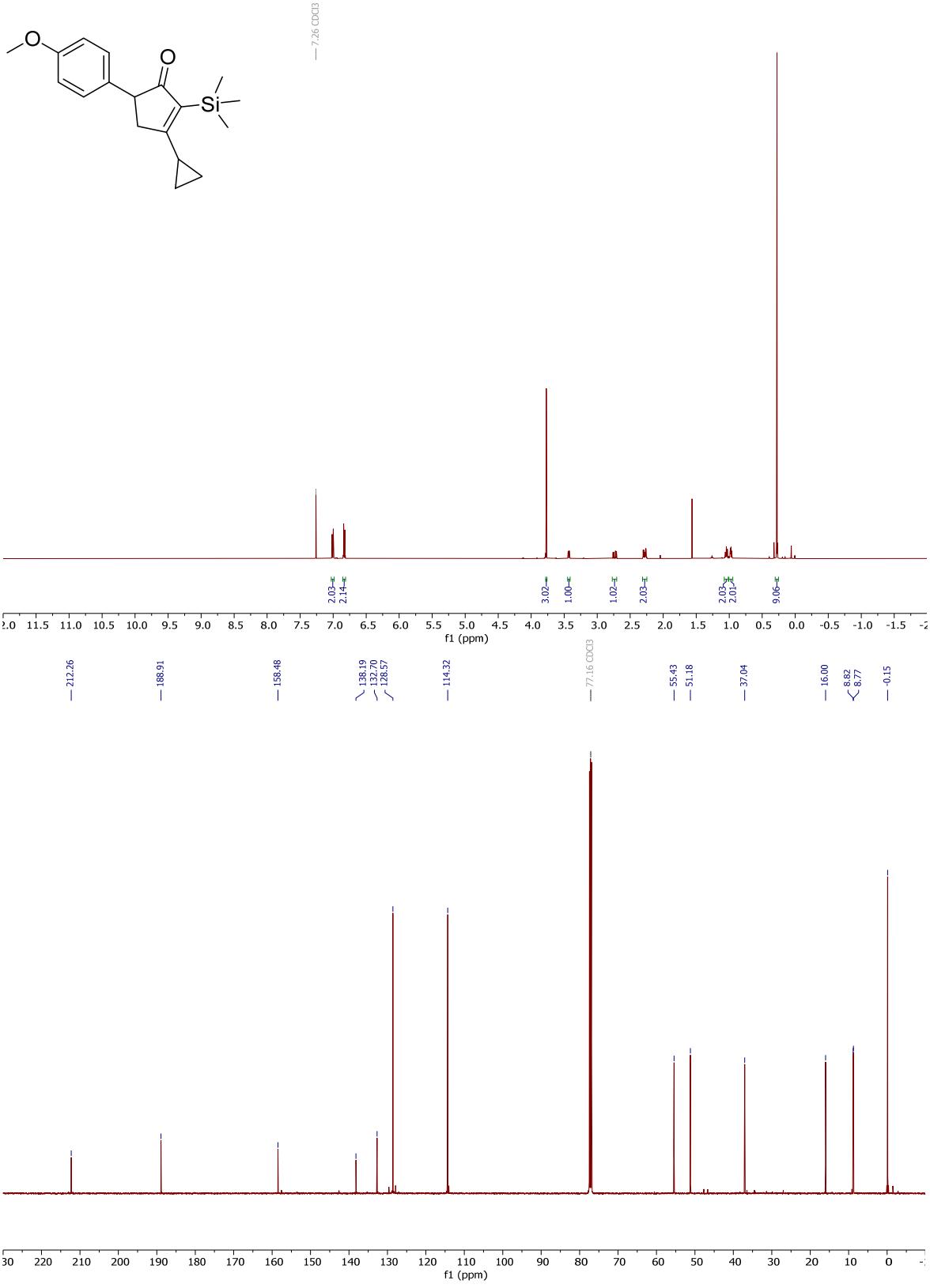

H4021.10.ser
Yong Ho Lee/Morandi LEY-LB-387-10 OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

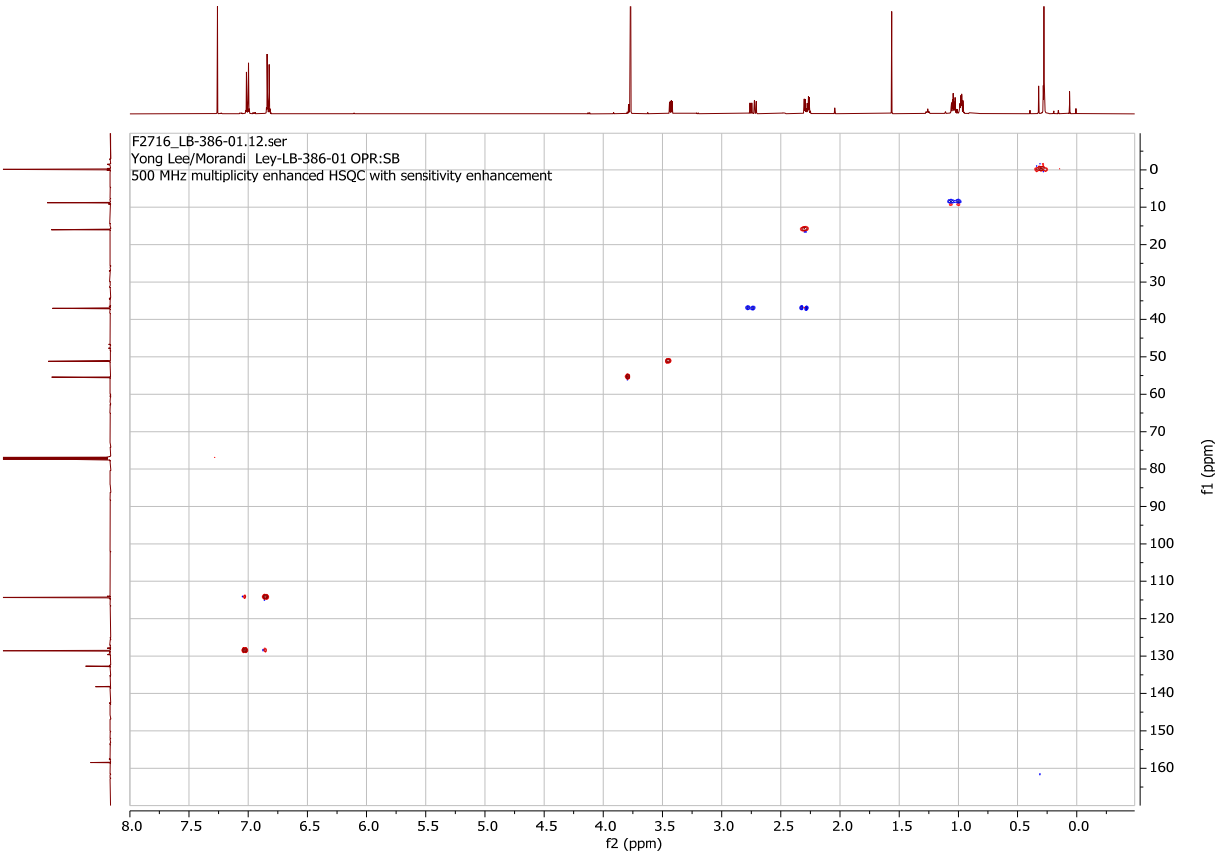

H4021.11.ser
Yong Ho Lee/Morandi LEY-LB-387-10 OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

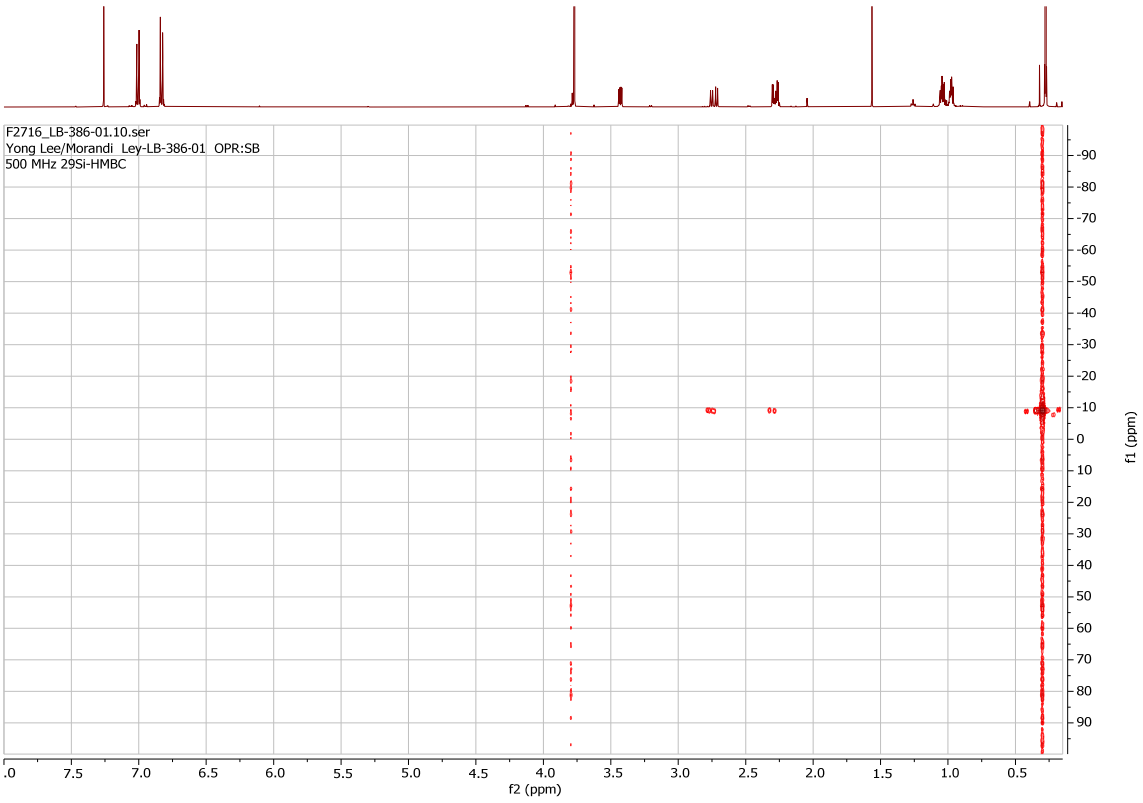

H4021.12.ser
Yong Ho Lee/Morandi LEY-LB-387-10 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

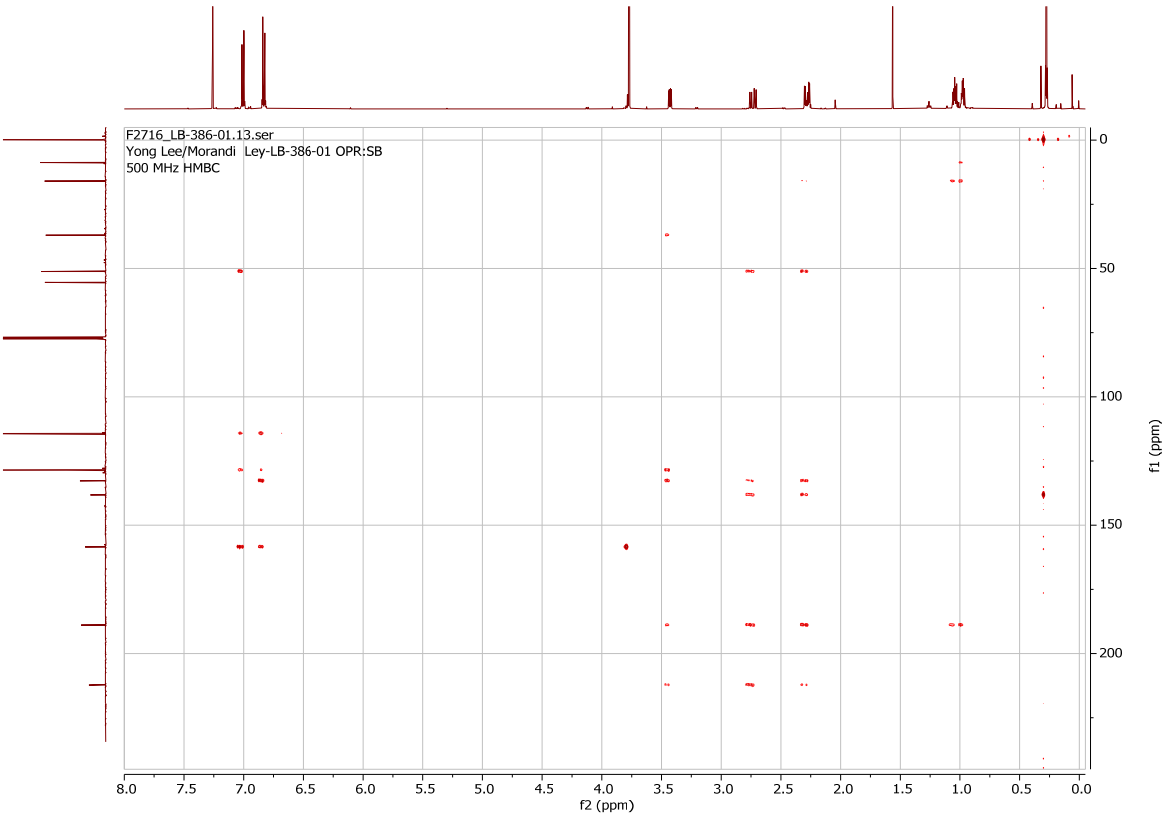

F2717.10.ser
Yong Lee/Morandi Ley-LB-3867-10 OPR:SB
500 MHz 29Si-HMBC
f2 (ppm)
f1 (ppm)

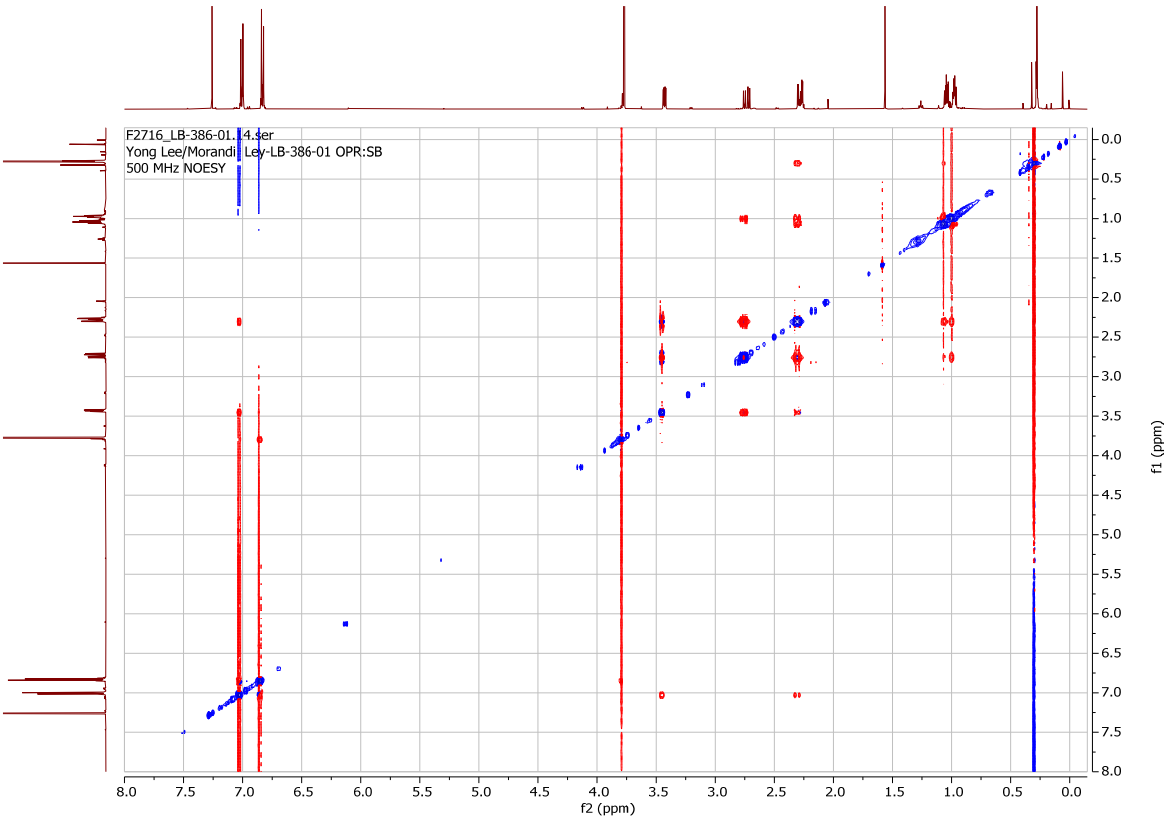
3-cyclopropyl-5-(4-methoxyphenyl)-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bl**).

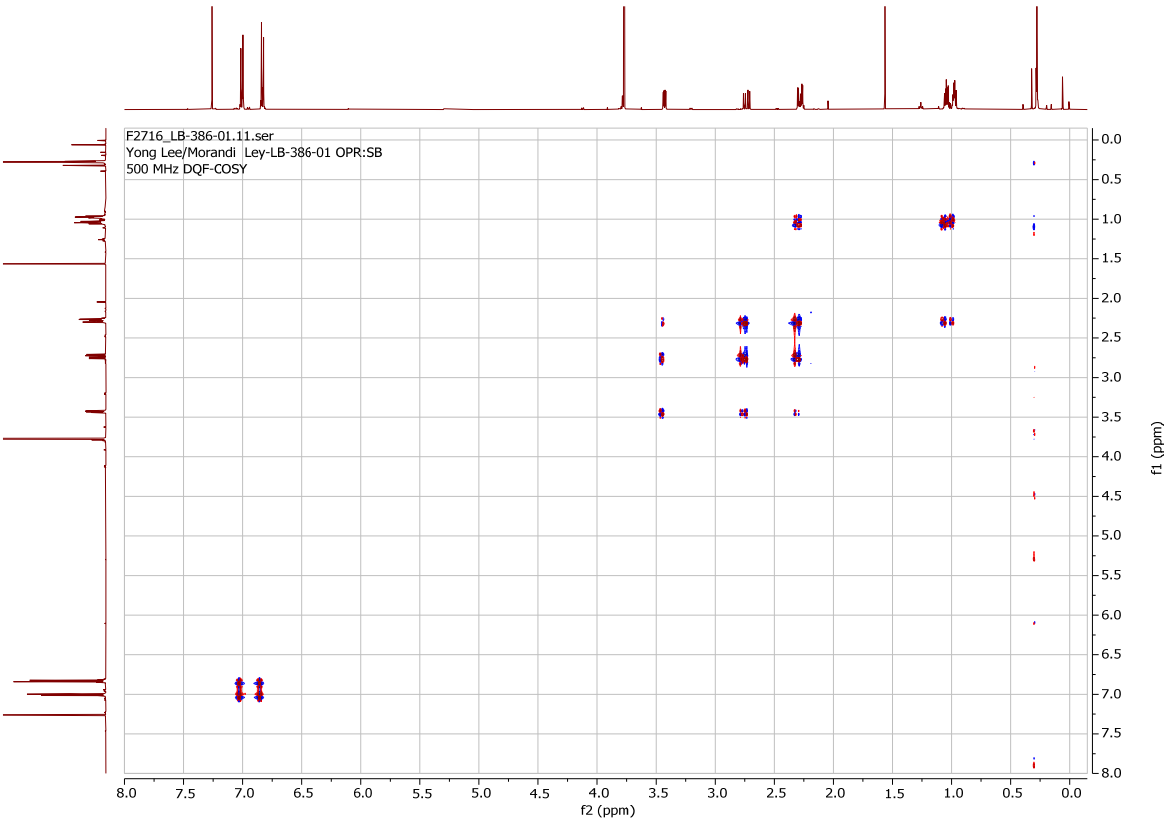



F2716_LB-386-01.12.ser
Yong Lee/Morandi Ley-LB-386-01 OPR:SB
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f1 (ppm)
f2 (ppm)

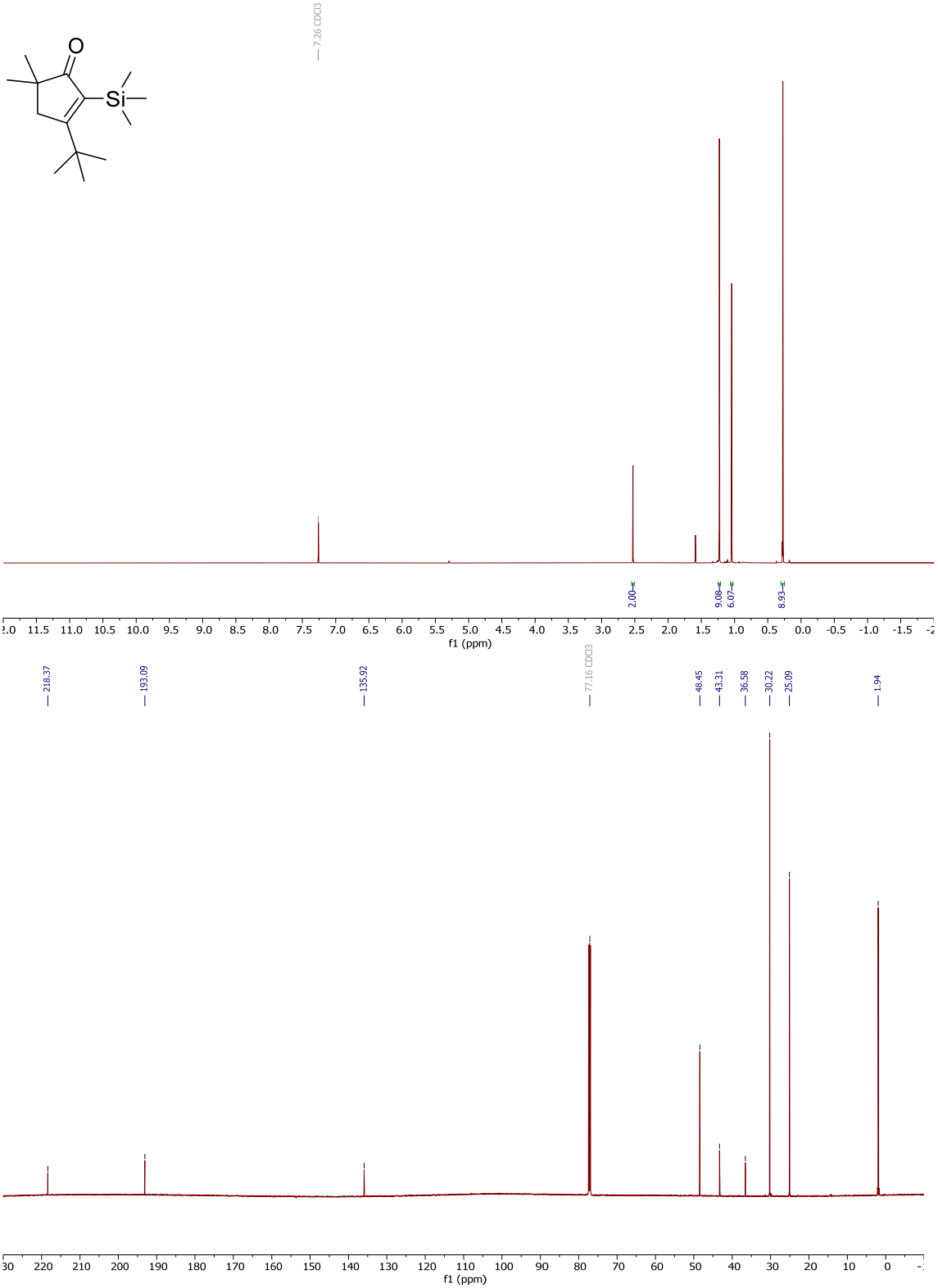

F2716_LB-386-01.10.ser
Yong Lee/Morandi Ley-LB-386-01 OPR:SB
500 MHz 29Si-HMBC
f1 (ppm)
f2 (ppm)

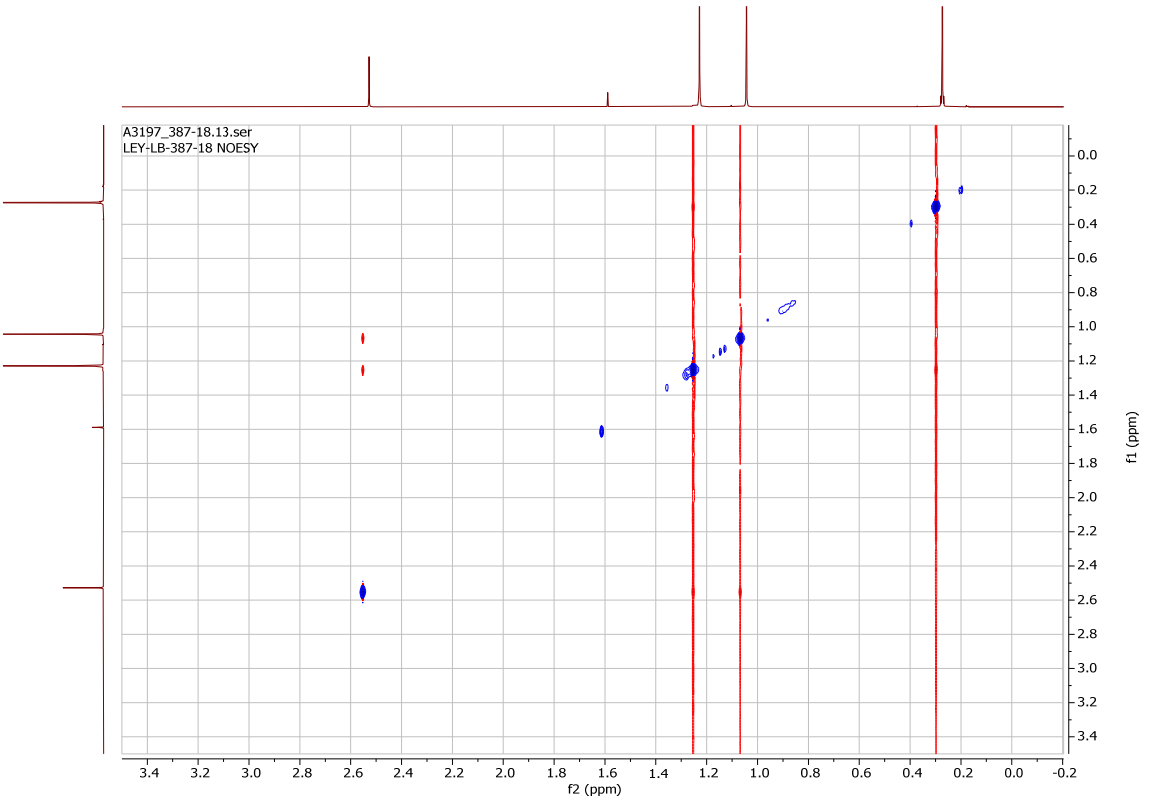

F2716_LB-386-01.13.ser
Yong Lee/Morandi Ley-LB-386-01 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

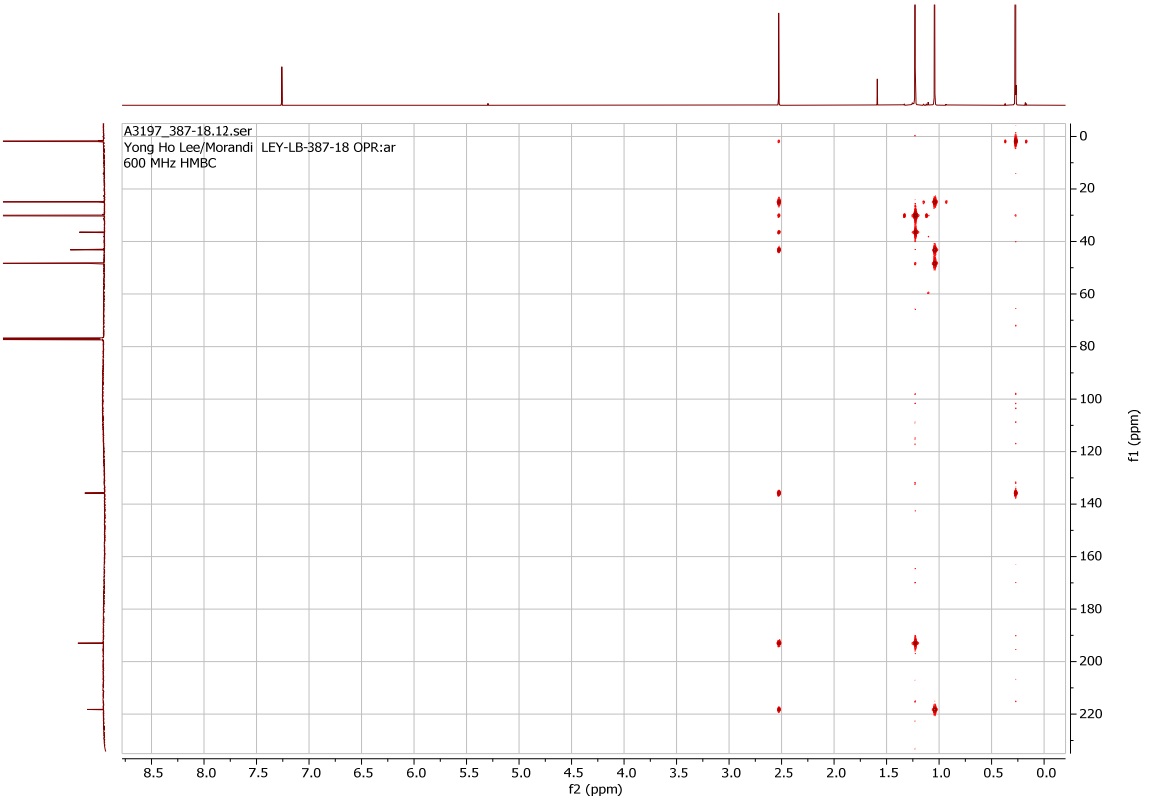

F2716_LB-386-01.14.ser
Yong Lee/Morandi Ley-LB-386-01 OPR:SB
500 MHz NOESY
f2 (ppm)
f1 (ppm)


F2716_LB-386-01.11.ser
Yong Lee/Morandi Ley-LB-386-01 OPR:SB
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

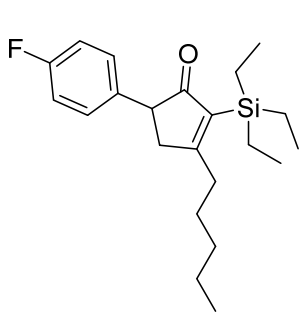
3-(*tert*-butyl)-5,5-dimethyl-2-(trimethylsilyl)cyclopent-2-en-1-one (**3bm**).

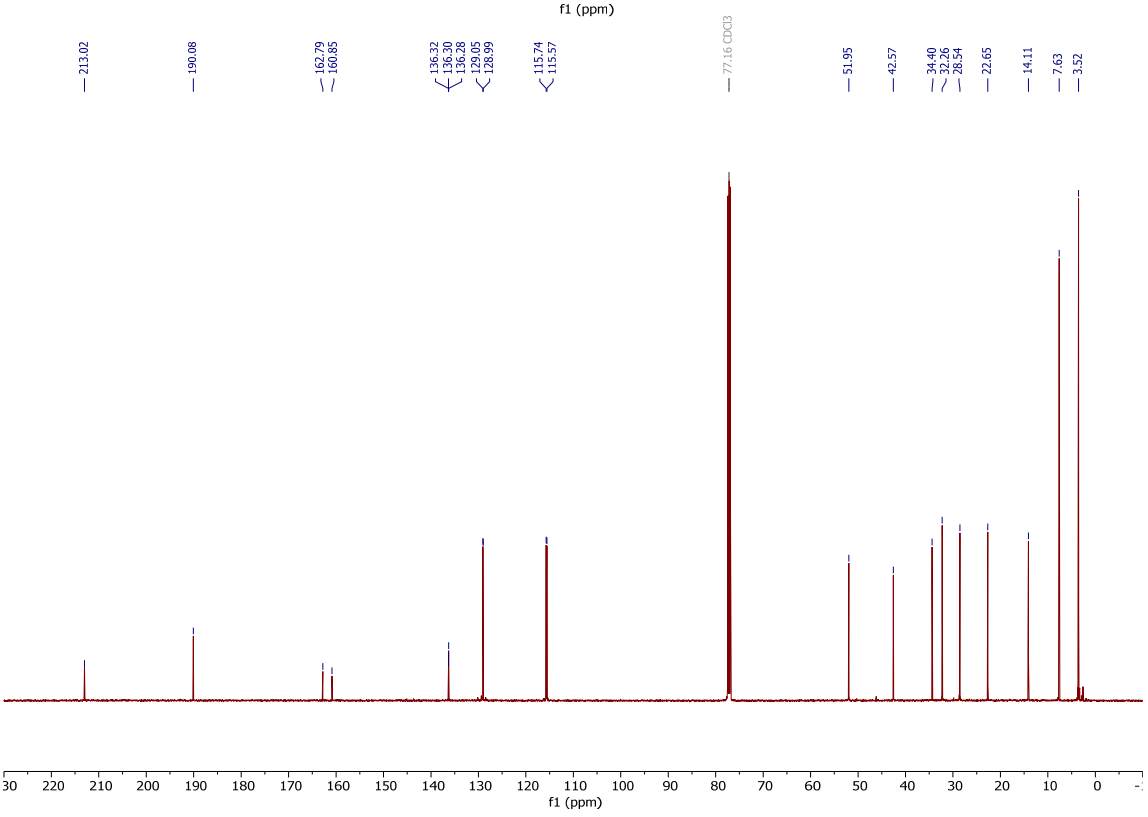



A3197_387-18.13.ser
LEY-LB-387-18 NOESY
f2 (ppm)
f1 (ppm)

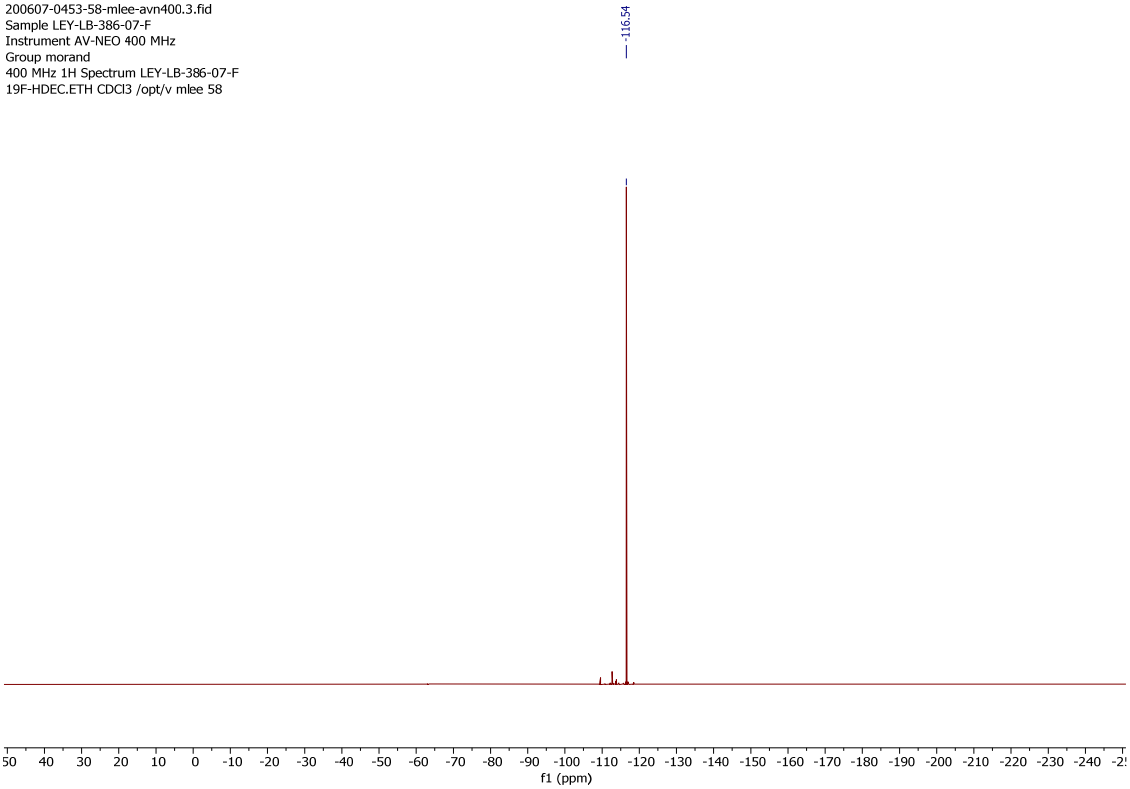

A3197_387-18.12.ser
Yong Ho Lee/Morandi LEY-LB-387-18 OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

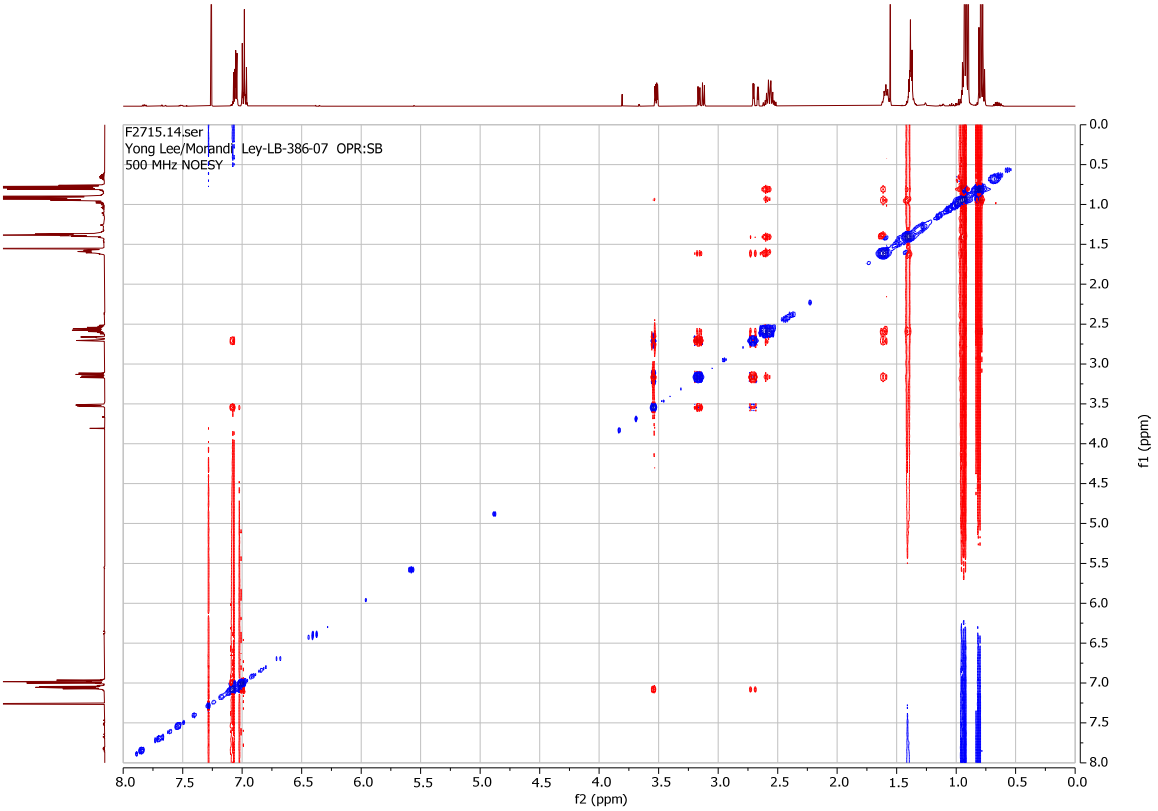
5-(4-fluorophenyl)-3-pentyl-2-(triethylsilyl)cyclopent-2-en-1-one (**3bn**).

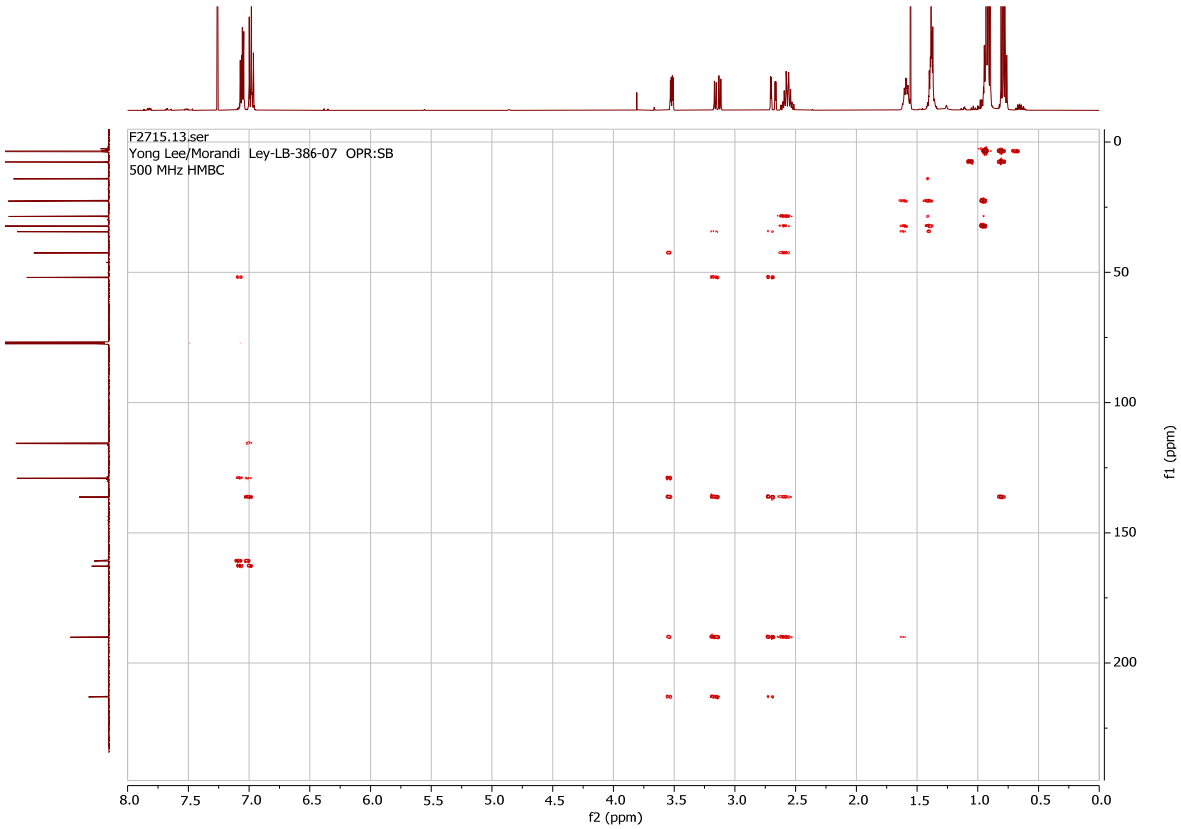




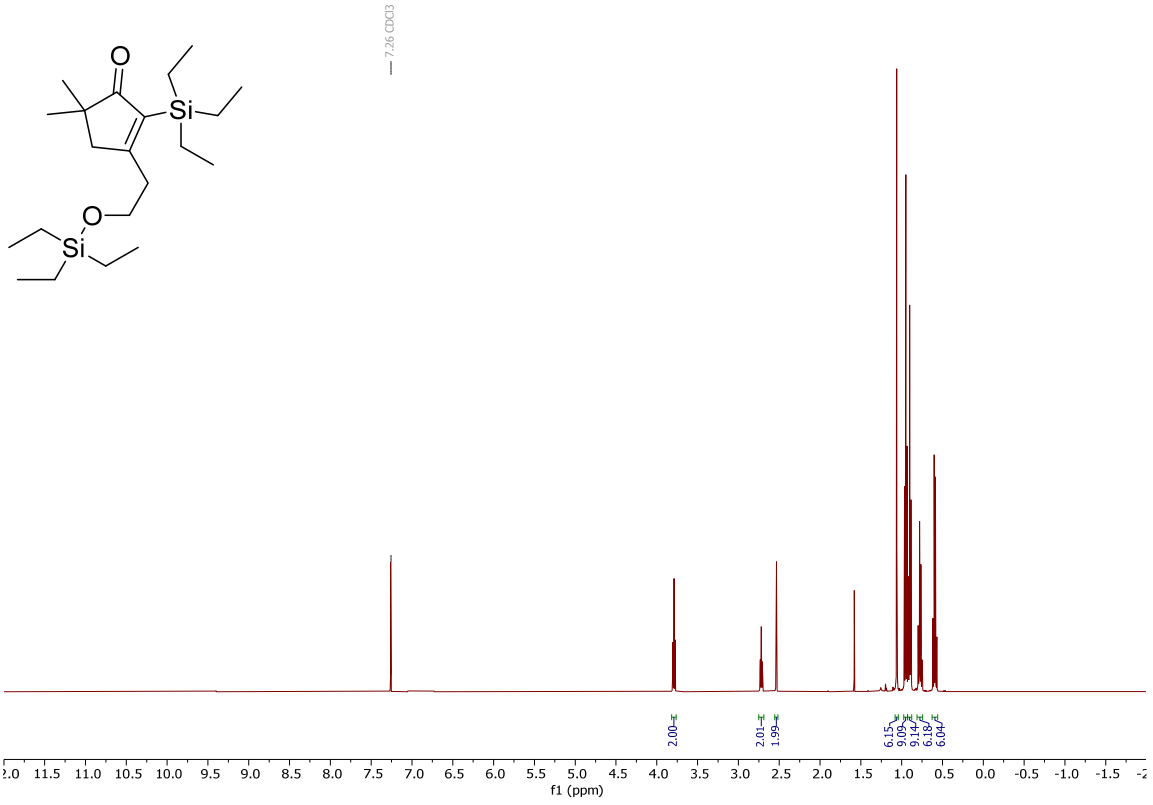
200607-0453-58-mlee-avn400.3.fid
Sample LEY-LB-386-07-F
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-386-07-F
19F-HDEC.ETH CDCl3 /opt/v mlee 58

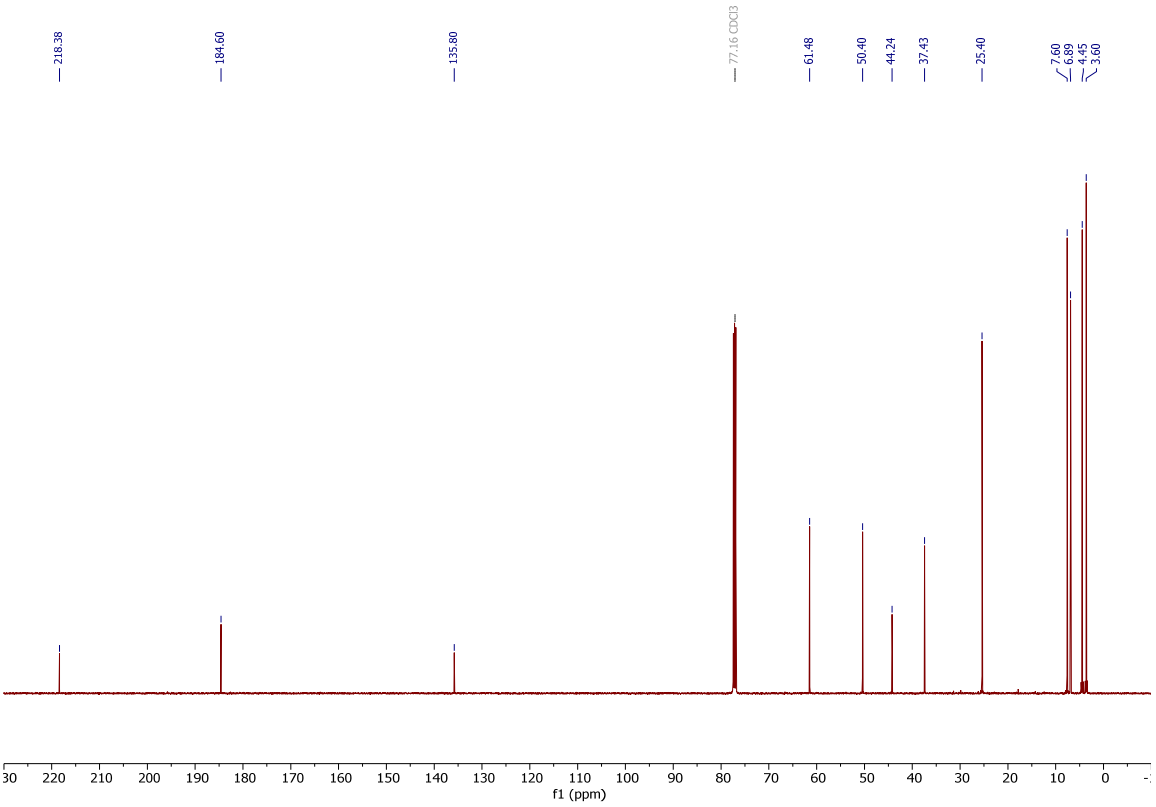


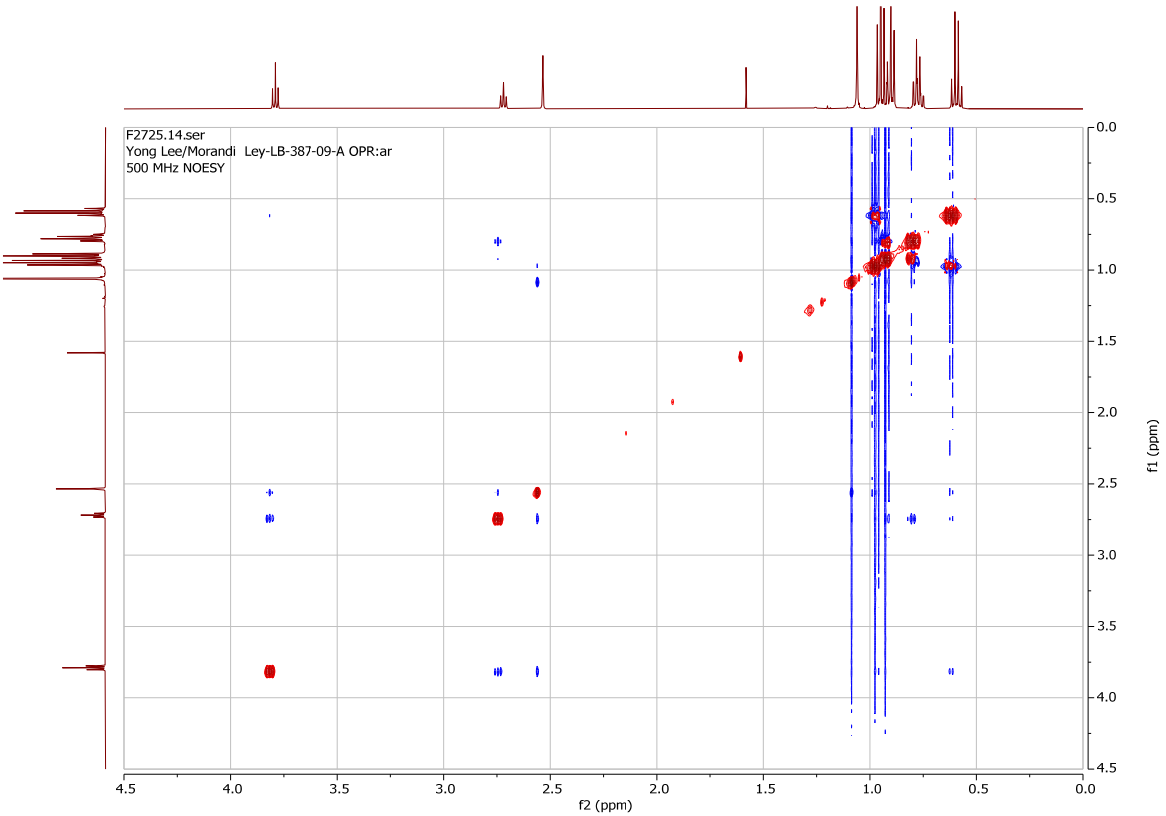


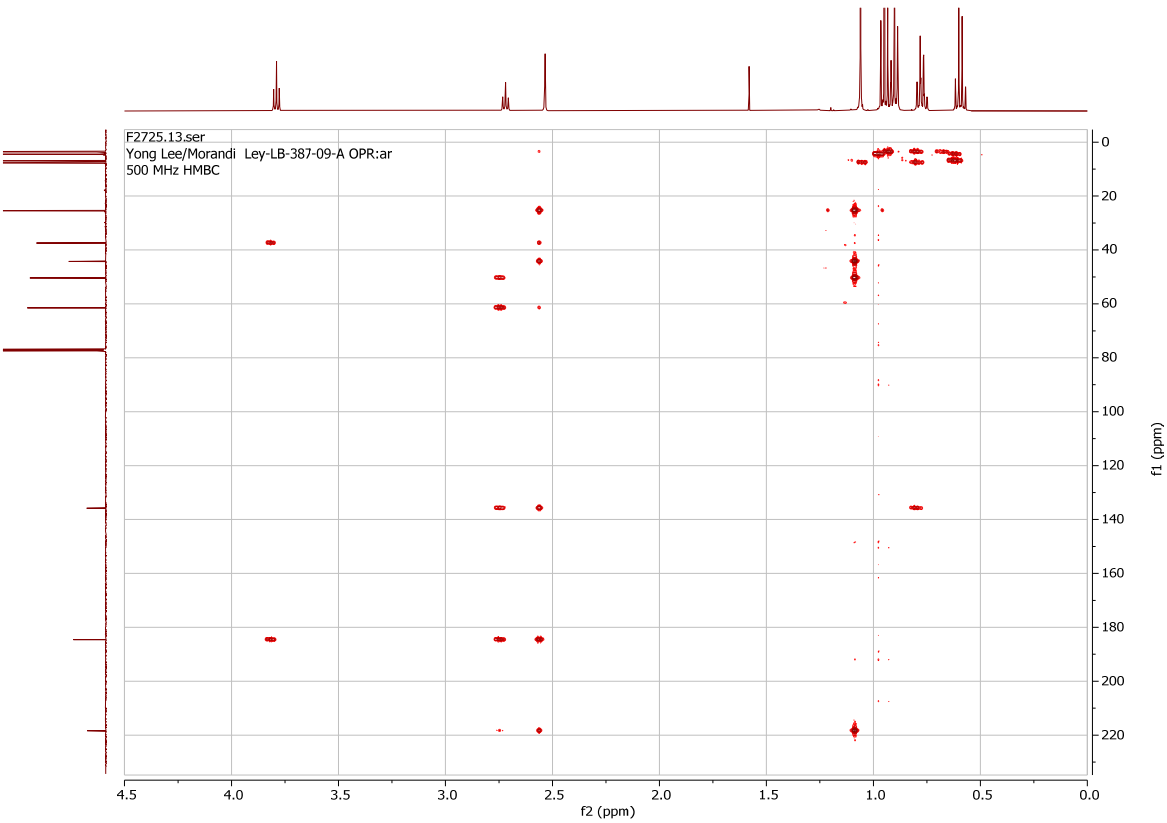

F2715.13.ser
Yong Lee/Morandi Ley-LB-386-07 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

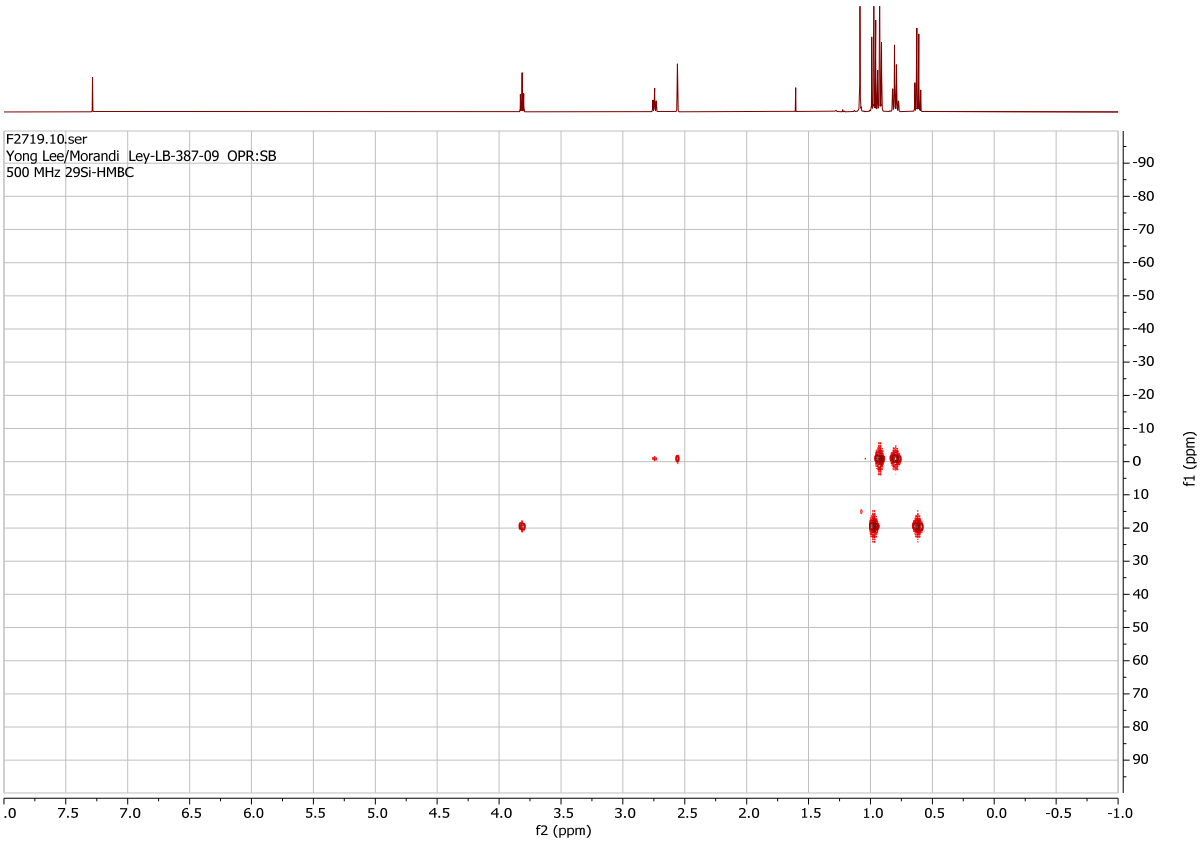
5,5-dimethyl-2-(triethylsilyl)-3-(2-((triethylsilyl)oxy)ethyl)cyclopent-2-en-1-one (**3bo-1**, major).



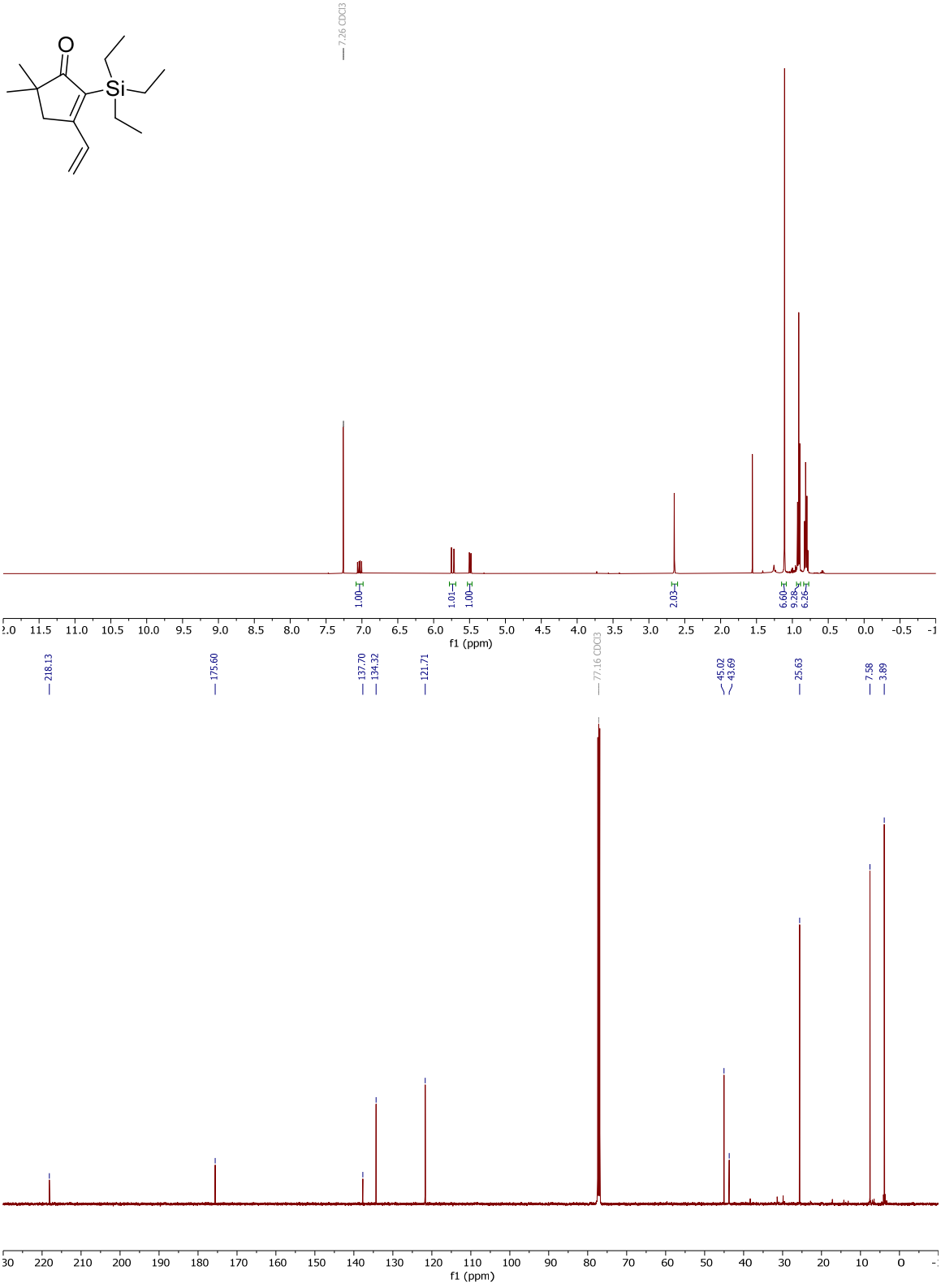


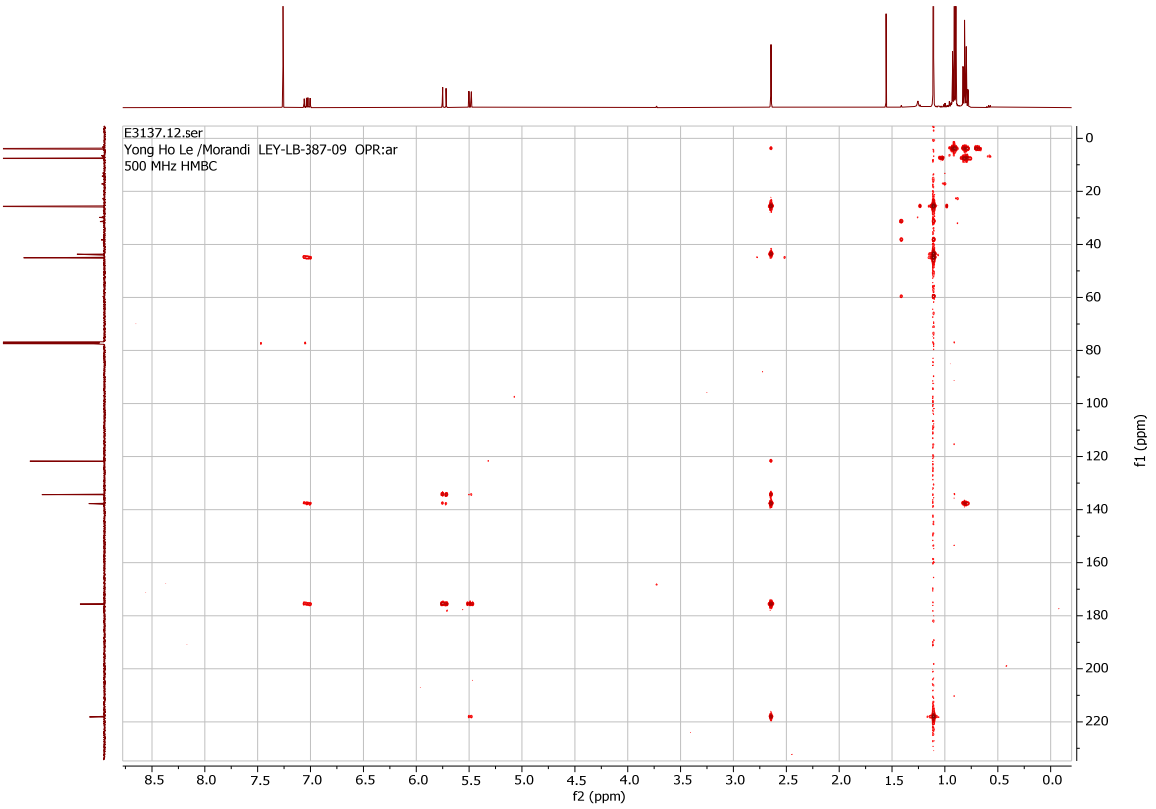

F2725.14.ser
Yong Lee/Morandi Ley-LB-387-09-A OPR:ar
500 MHz NOESY
f2 (ppm)
f1 (ppm)

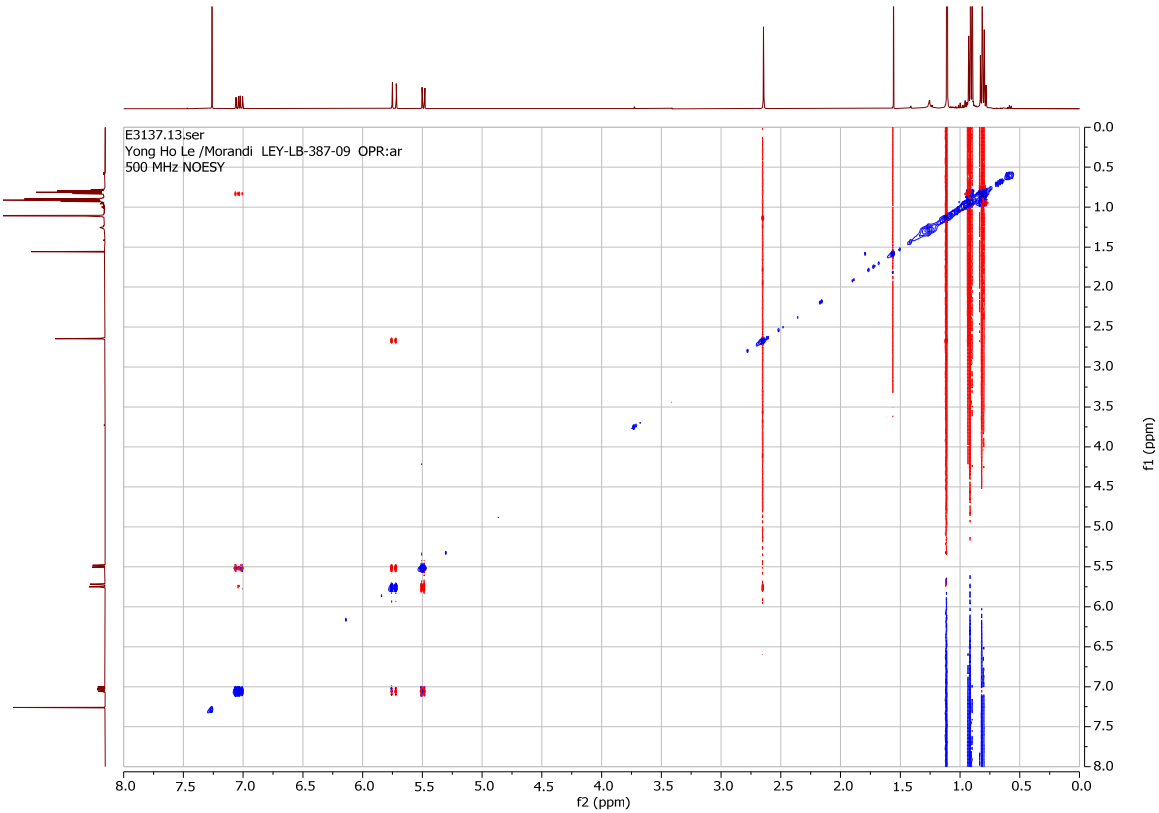

F2725.13.ser
Yong Lee/Morandi Ley-LB-387-09-A OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)


F2719.10.ser
Yong Lee/Morandi Ley-LB-387-09 OPR:SB
500 MHz 29Si-HMBC
f2 (ppm)
f1 (ppm)

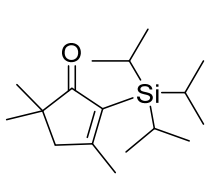
5,5-dimethyl-2-(triethylsilyl)-3-vinylcyclopent-2-en-1-one (**3bo-2**, minor).

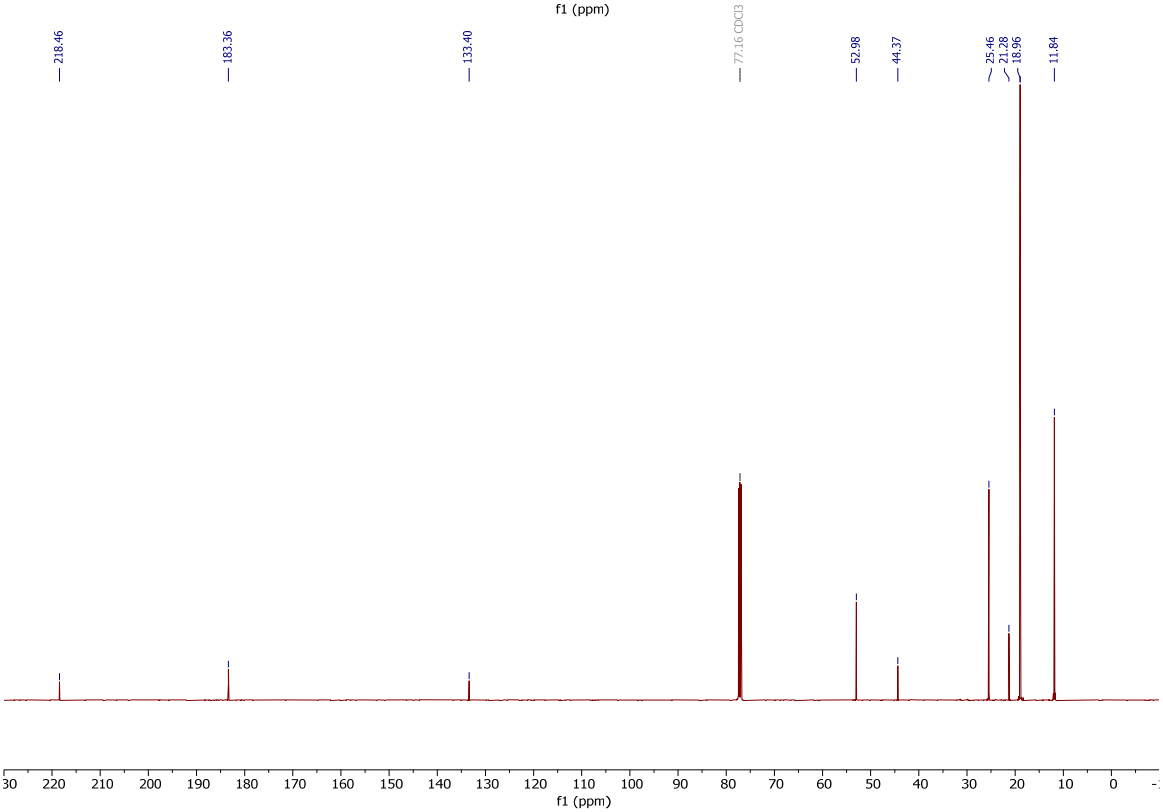


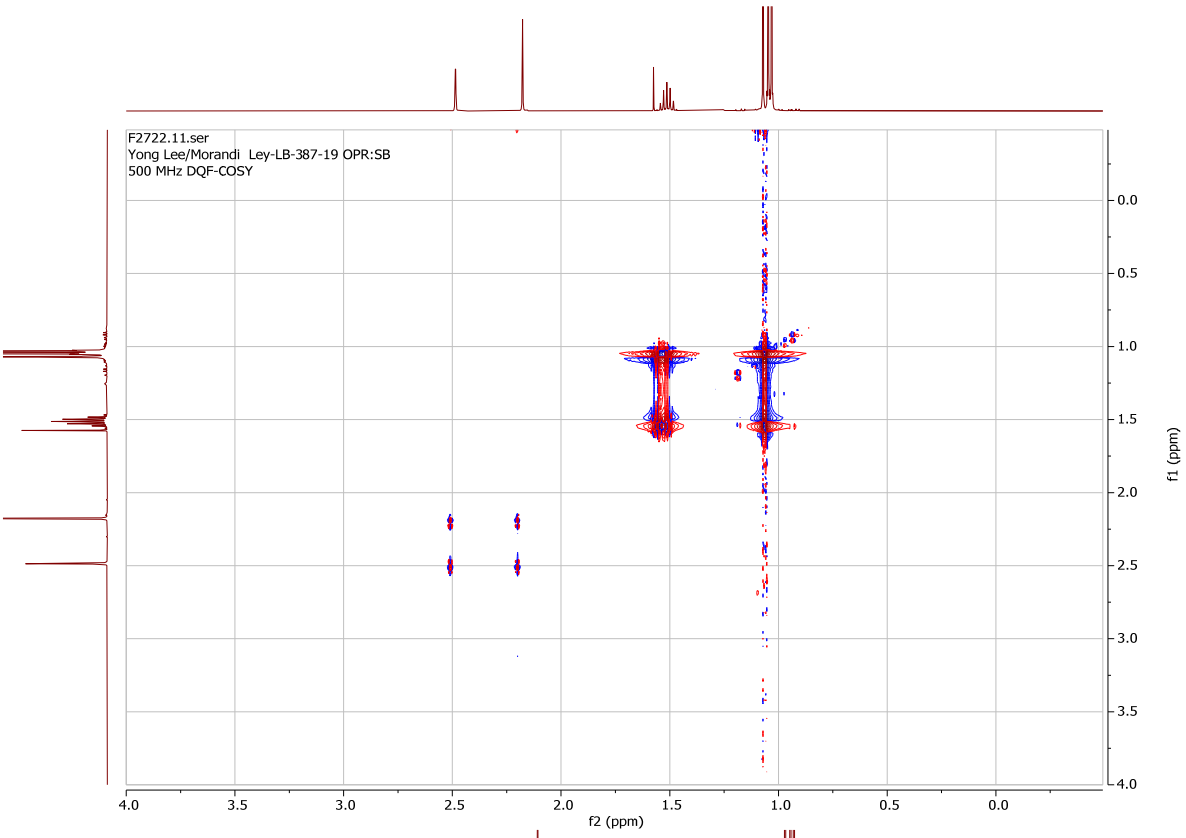

E3137.12.ser
Yong Ho Le /Morandi LEY-LB-387-09 OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

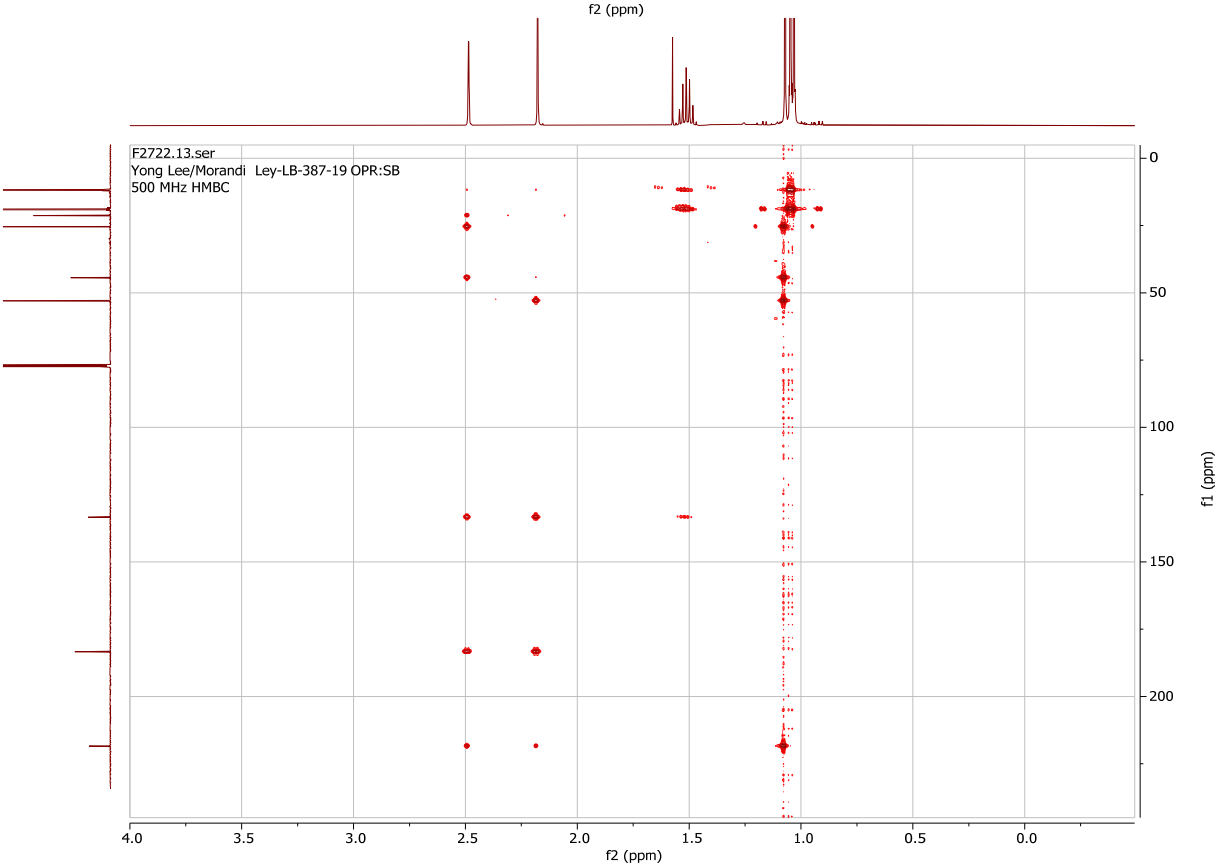

E3137.13.ser
Yong Ho Le /Morandi LEY-LB-387-09 OPR:ar
500 MHz NOESY
f2 (ppm)
f1 (ppm)

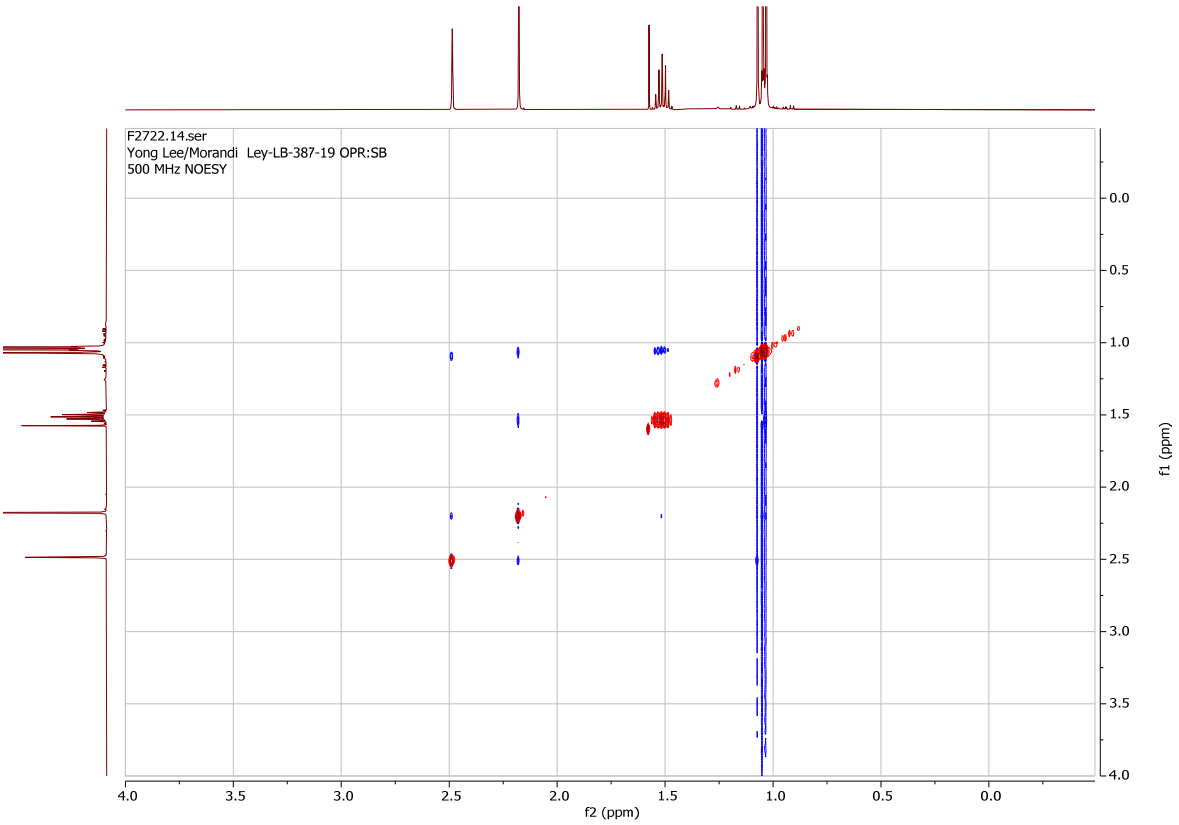
3,5,5-trimethyl-2-(triisopropylsilyl)cyclopent-2-en-1-one (**3bp**).



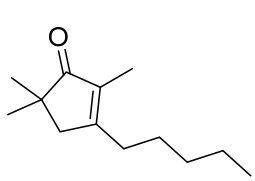


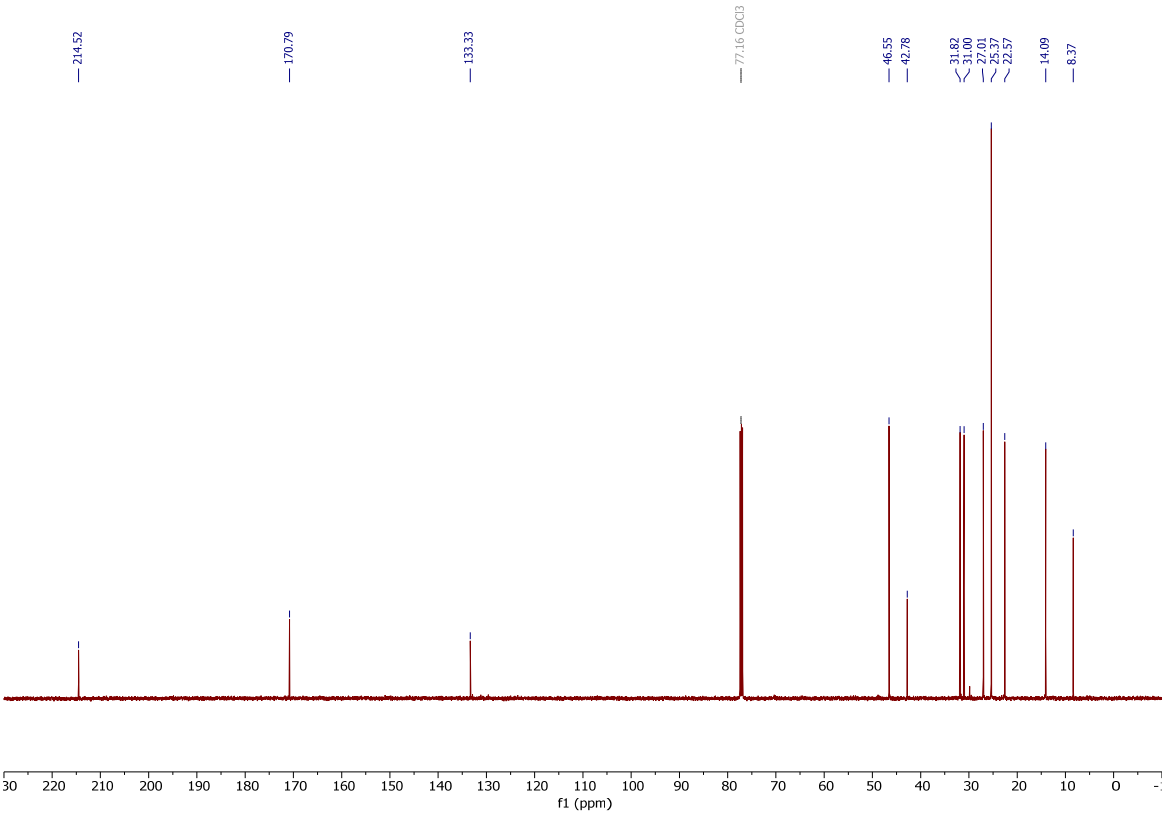

F2722.11.ser
Yong Lee/Morandi Ley-LB-387-19 OPR:SB
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

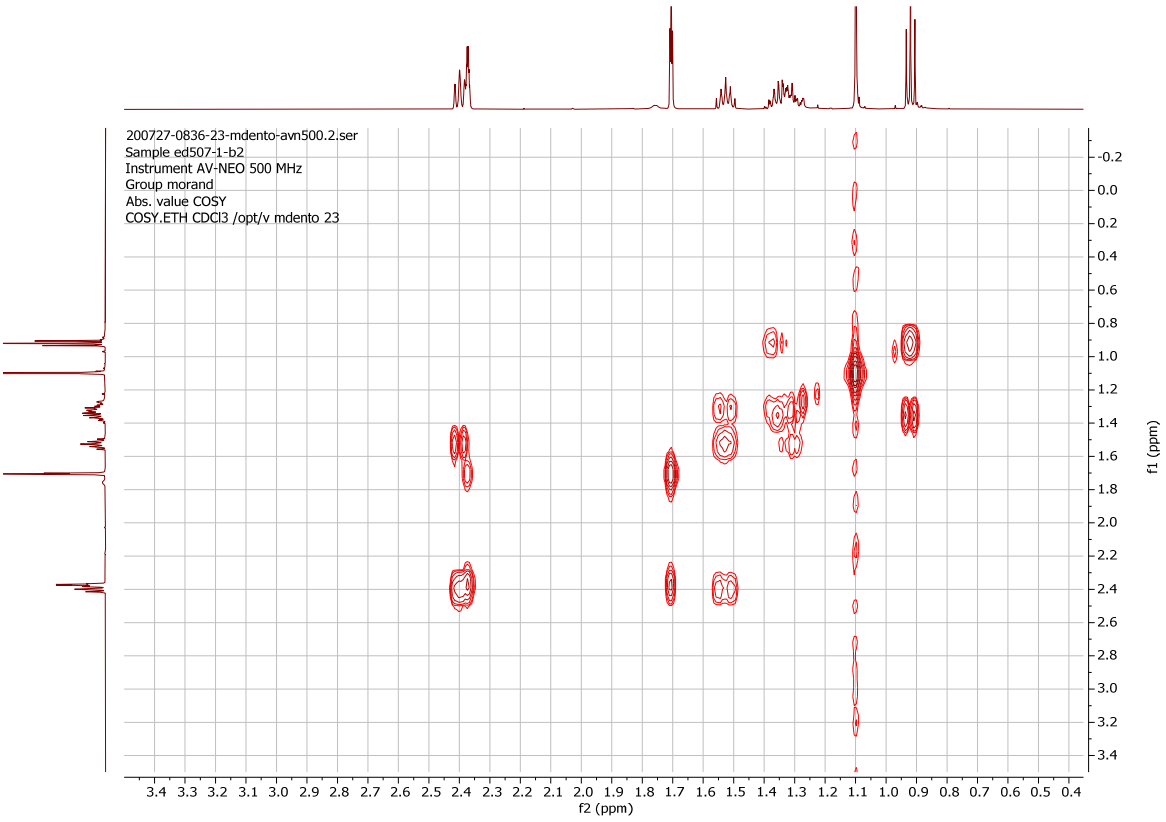

F2722.13.ser
Yong Lee/Morandi Ley-LB-387-19 OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

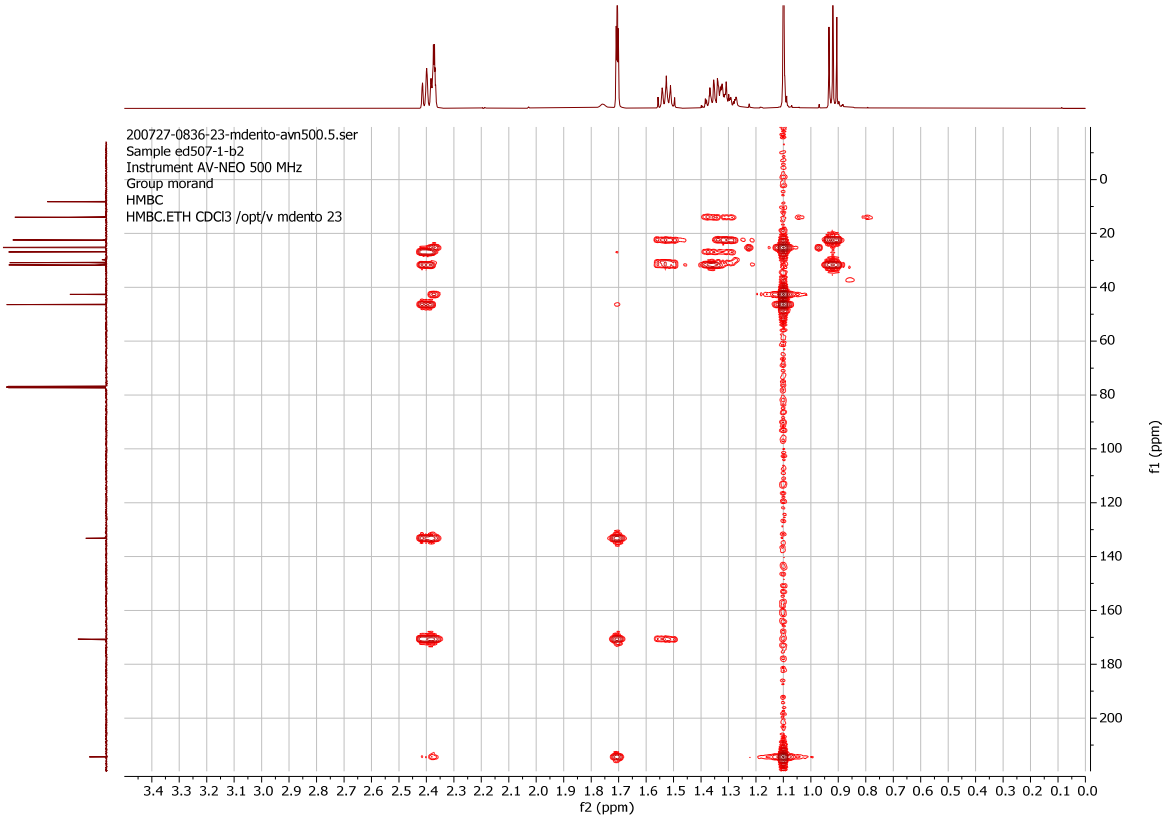

F2722.14.ser
Yong Lee/Morandi Ley-LB-387-19 OPR:SB
500 MHz NOESY
f2 (ppm)
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

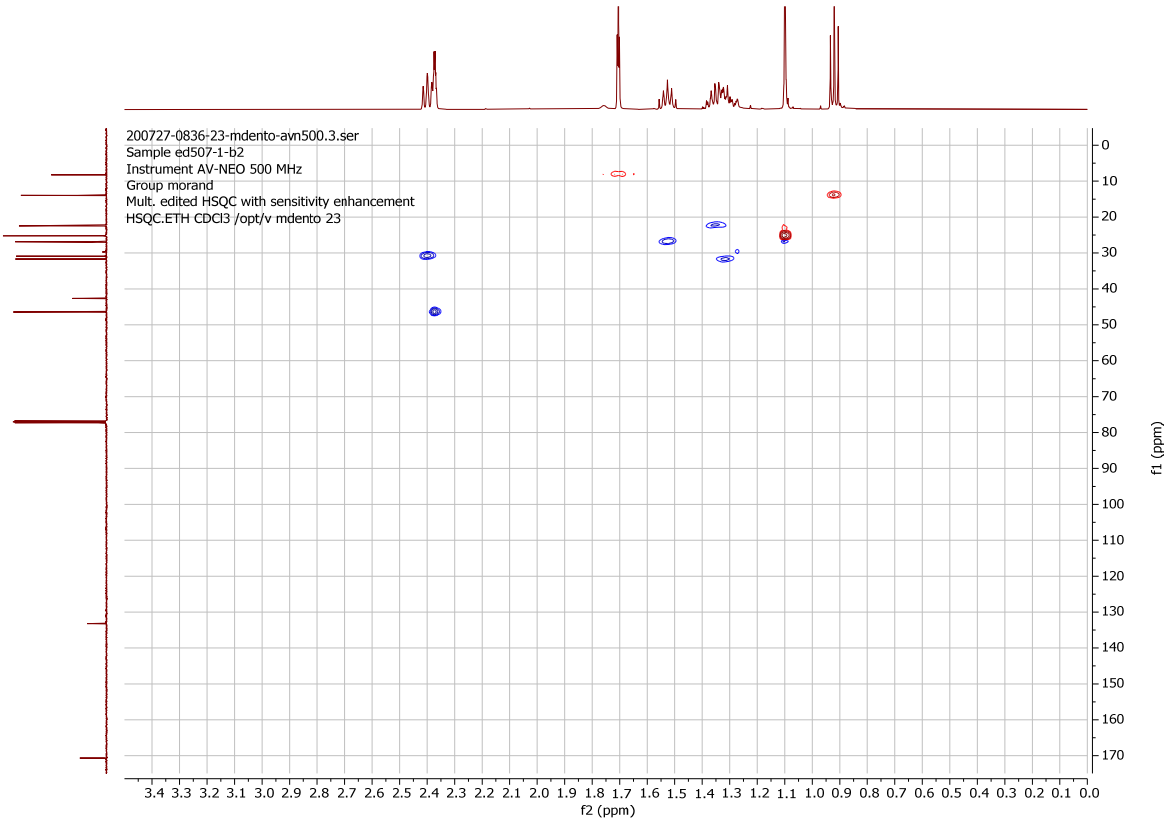
2,5,5-trimethyl-3-pentylcyclopent-2-en-1-one (**3bq-1**, major).



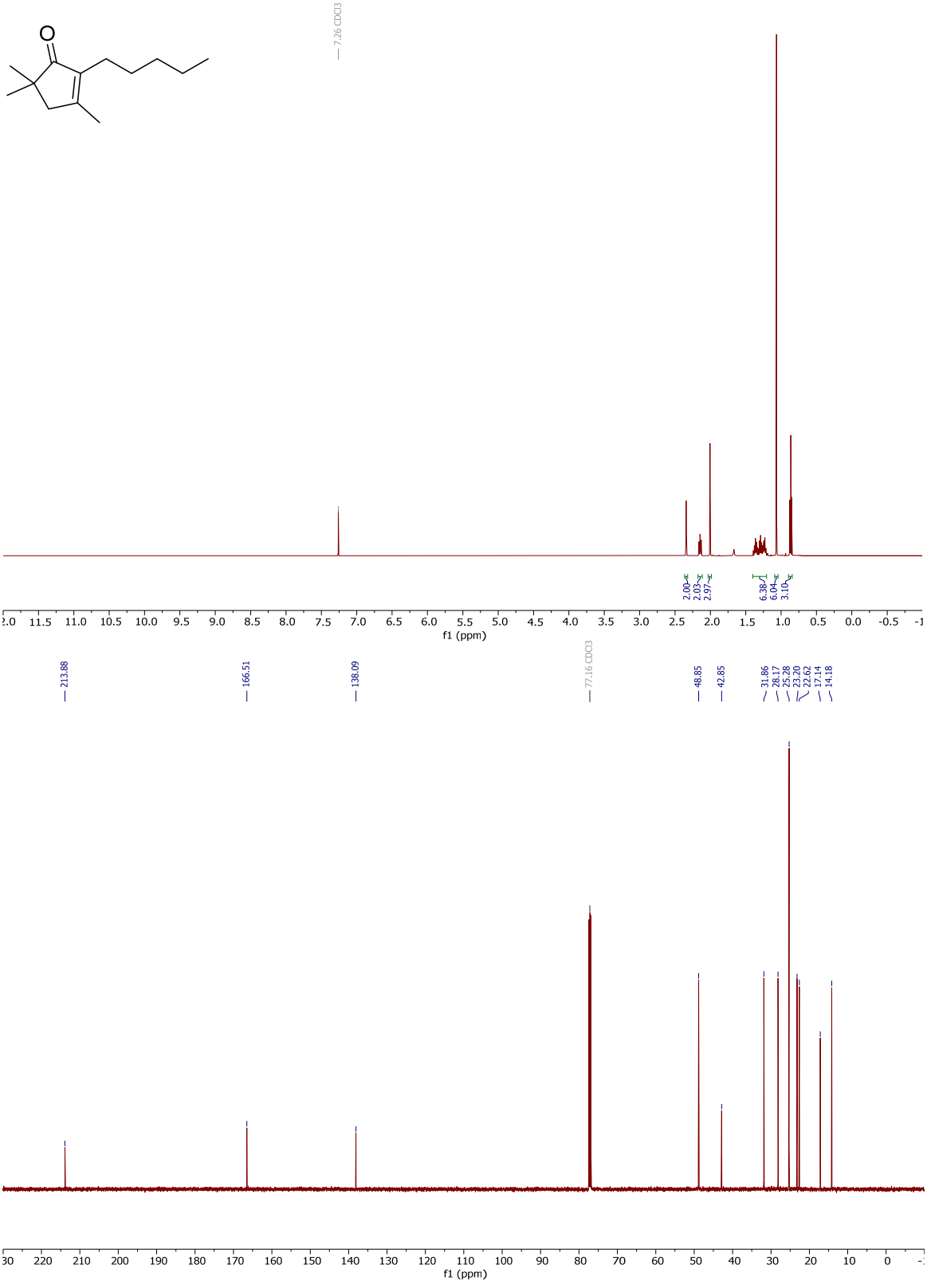


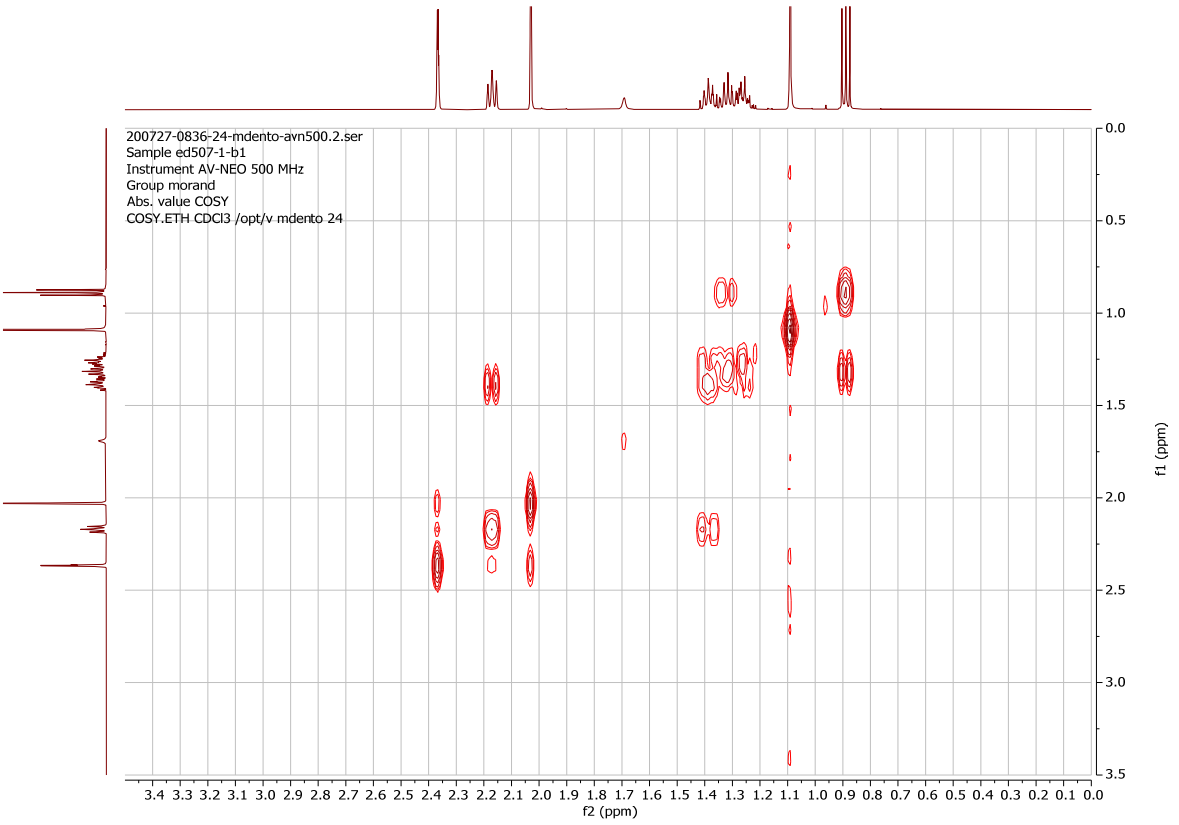

200727-0836-23-mdento-avn500.2.ser
Sample ed507-1-b2
Instrument AV-NEO 500 MHz
Group morand
Abs. value COSY
COSY.ETH CDCl3 /opt/v mdento 23
f2 (ppm)
f1 (ppm)

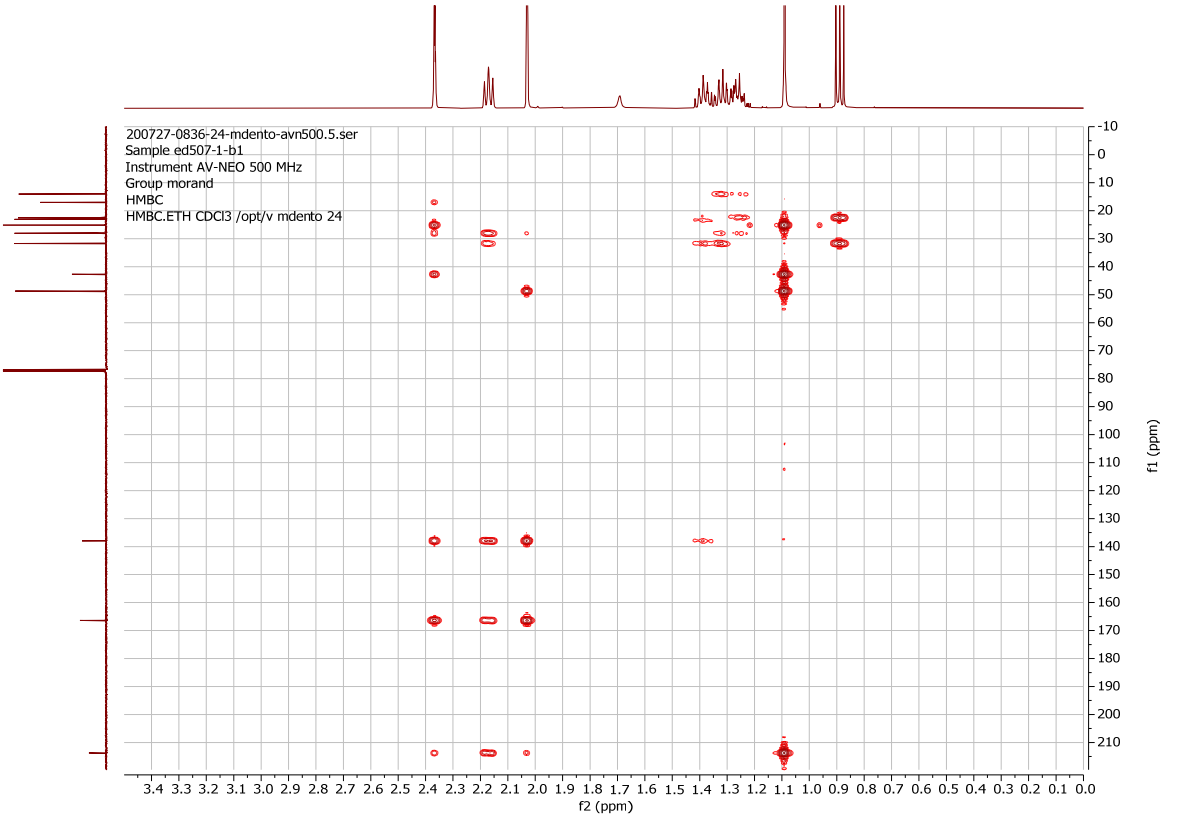

200727-0836-23-mdento-avn500.5.ser
Sample ed507-1-b2
Instrument AV-NEO 500 MHz
Group morand
HMBC
HMBC.ETH CDCl3 /opt/v mdento 23
f2 (ppm)
f1 (ppm)

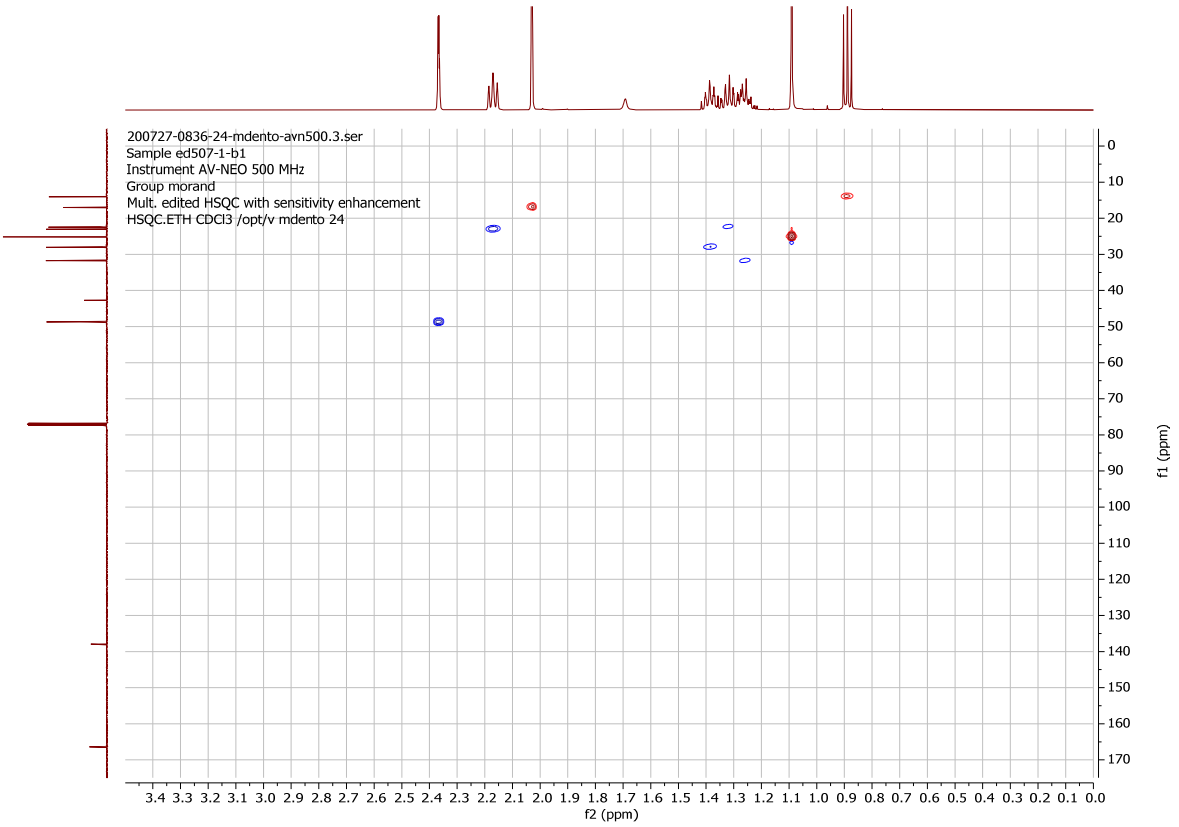

200727-0836-23-mdento-avn500.3.ser
Sample ed507-1-b2
Instrument AV-NEO 500 MHz
Group morand
Mult. edited HSQC with sensitivity enhancement
HSQC.ETH CDCl3 /opt/v mdento 23
f2 (ppm)
f1 (ppm)

3,5,5-trimethyl-2-pentylcyclopent-2-en-1-one (**3bq-2**, minor).

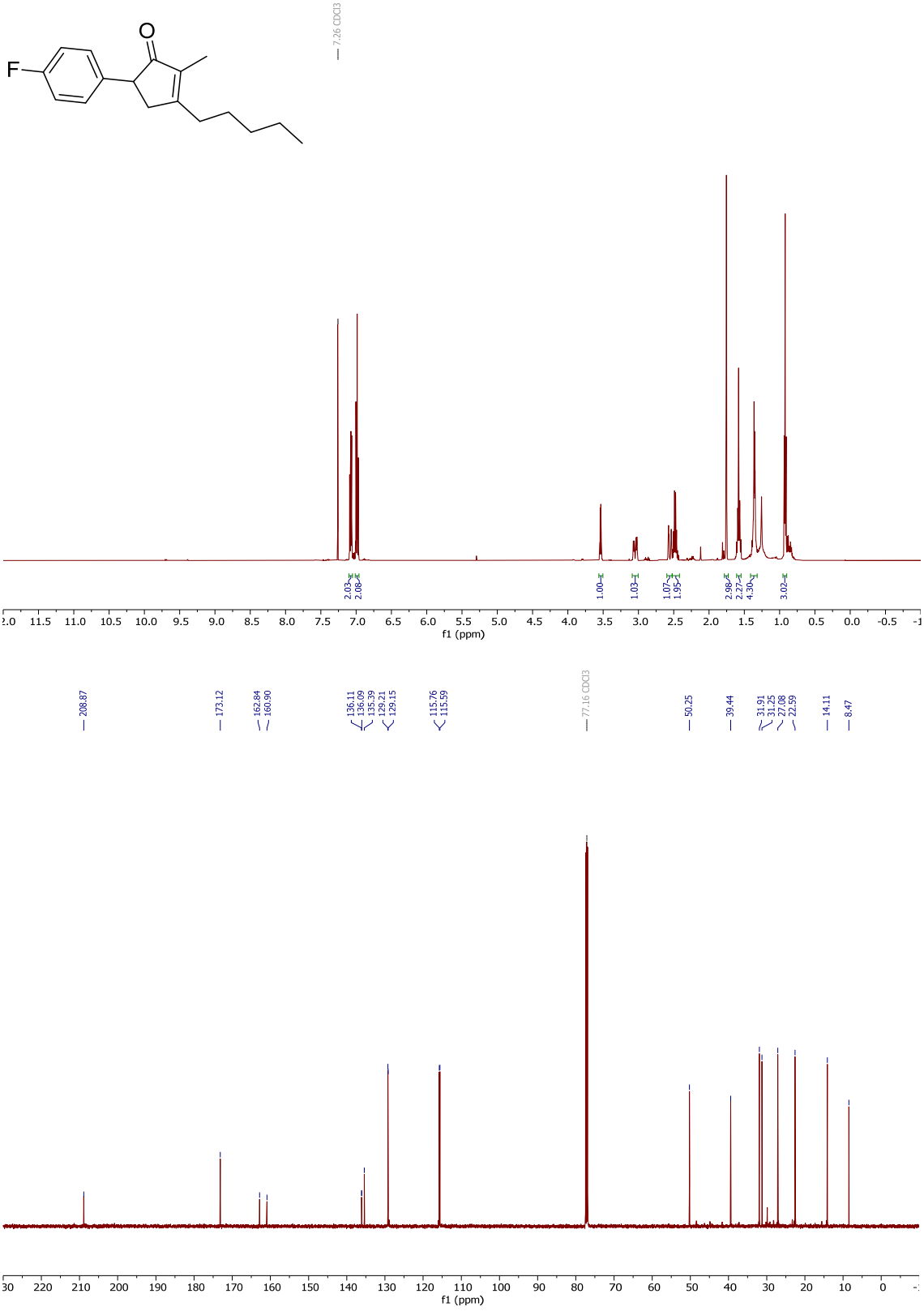


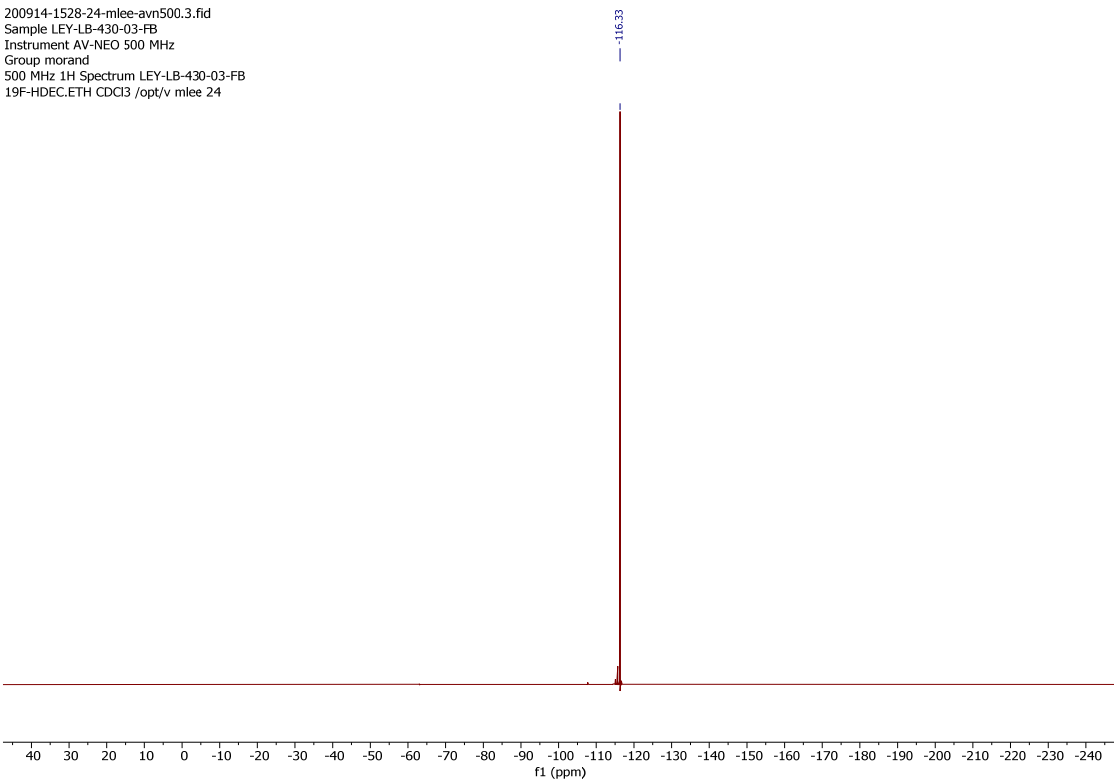

200727-0836-24-mdento-avn500.2.ser
Sample ed507-1-b1
Instrument AV-NEO 500 MHz
Group morand
Abs. value COSY
COSY.ETH CDCl3 /opt/v mdento 24
f1 (ppm)
f2 (ppm)

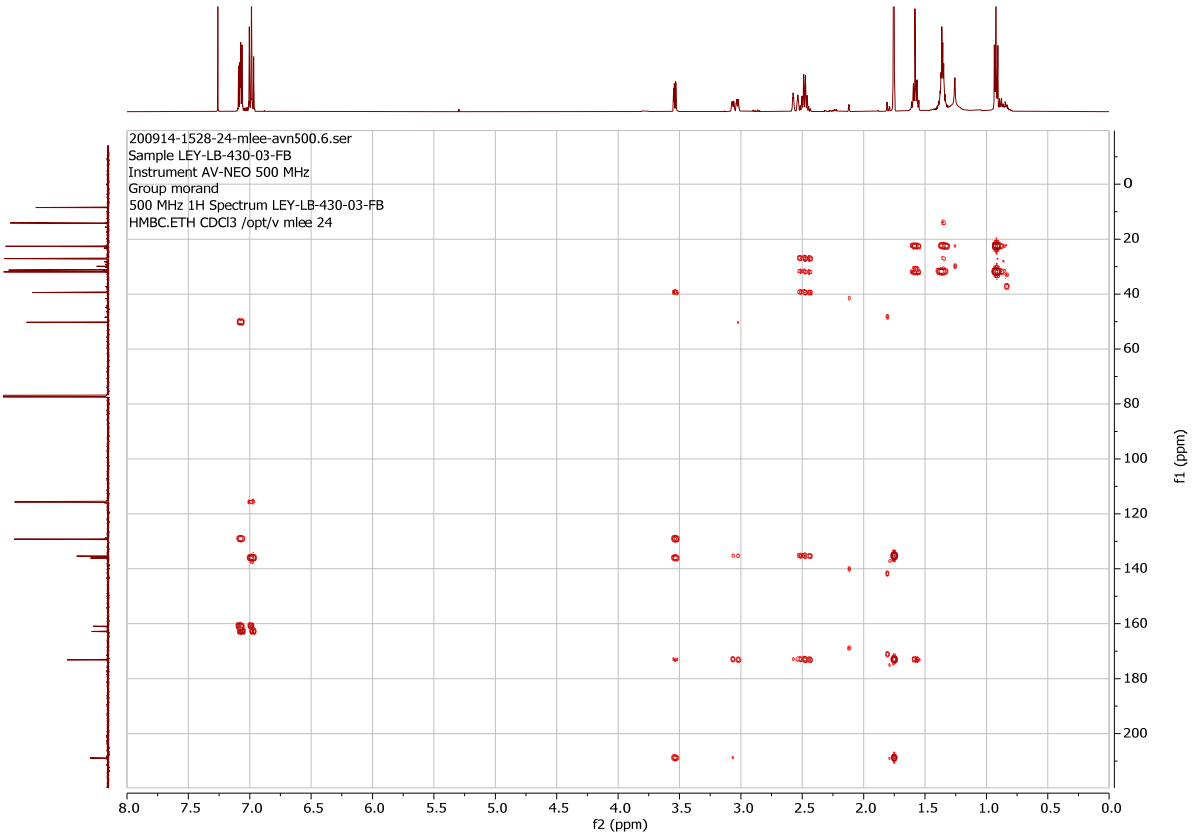

200727-0836-24-mdento-avn500.5.ser
Sample ed507-1-b1
Instrument AV-NEO 500 MHz
Group morand
HMBC
HMBC.ETH CDCl3 /opt/v mdento 24
f1 (ppm)
f2 (ppm)

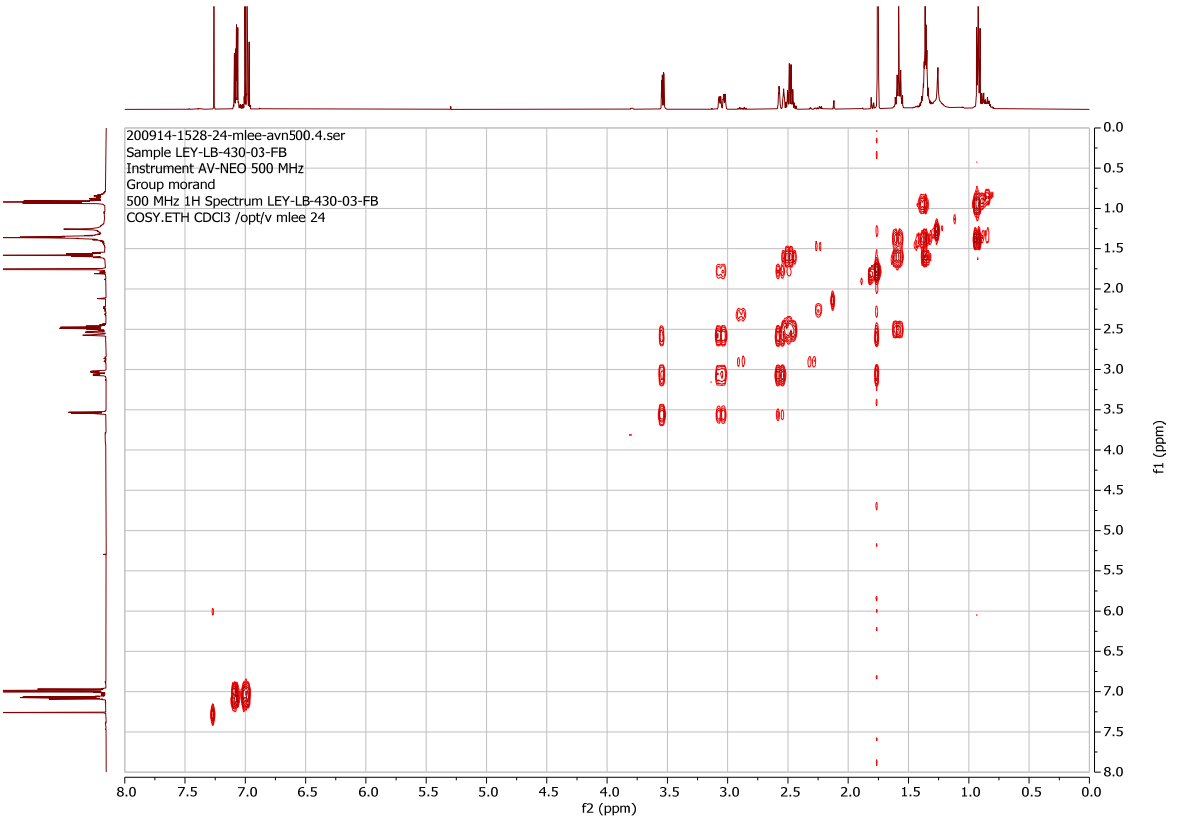

200727-0836-24-mdento-avn500.3.ser
Sample ed507-1-b1
Instrument AV-NEO 500 MHz
Group morand
Mult. edited HSQC with sensitivity enhancement
HSQC.ETH CDCl3 /opt/v mdento 24
f1 (ppm)
f2 (ppm)

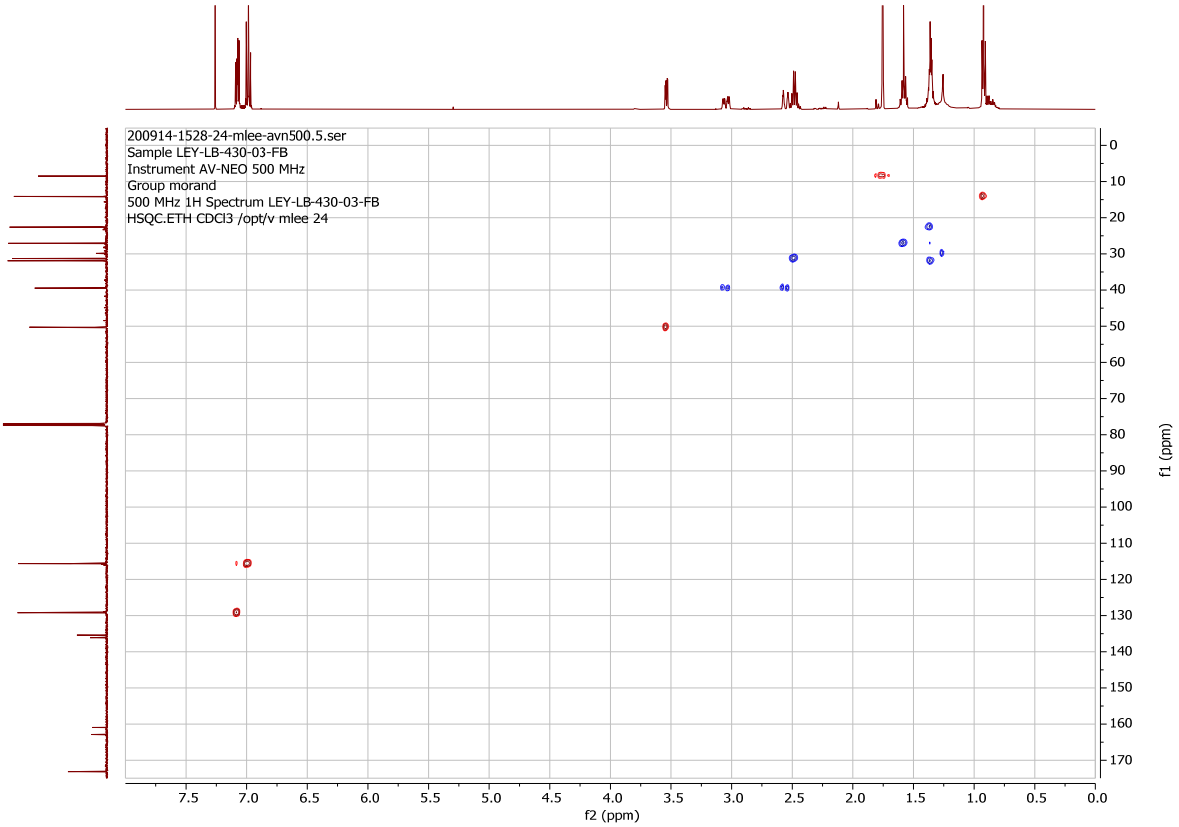
5-(4-fluorophenyl)-2-methyl-3-pentylcyclopent-2-en-1-one (**3br-1**, major).

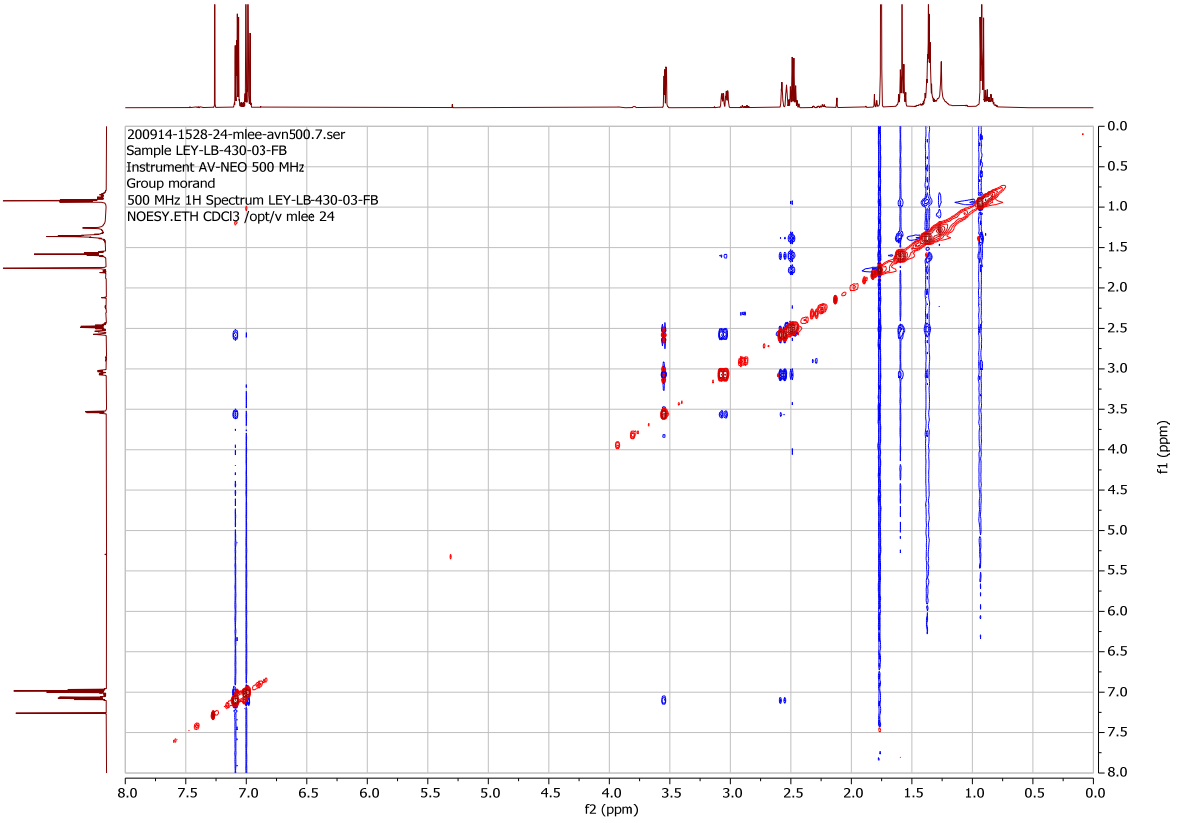



200914-1528-24-mlee-avn500.3.fid
Sample LEY-LB-430-03-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-03-FB
19F-HDEC.ETH CDCl3 /opt/v mlee 24
-116.33
f1 (ppm)

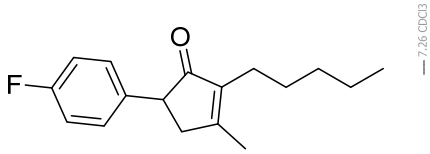

200914-1528-24-mlee-avn500.6.ser
Sample LEY-LB-430-03-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-03-FB
HMBC.ETH CDCl3 /opt/v mlee 24
f2 (ppm)
f1 (ppm)

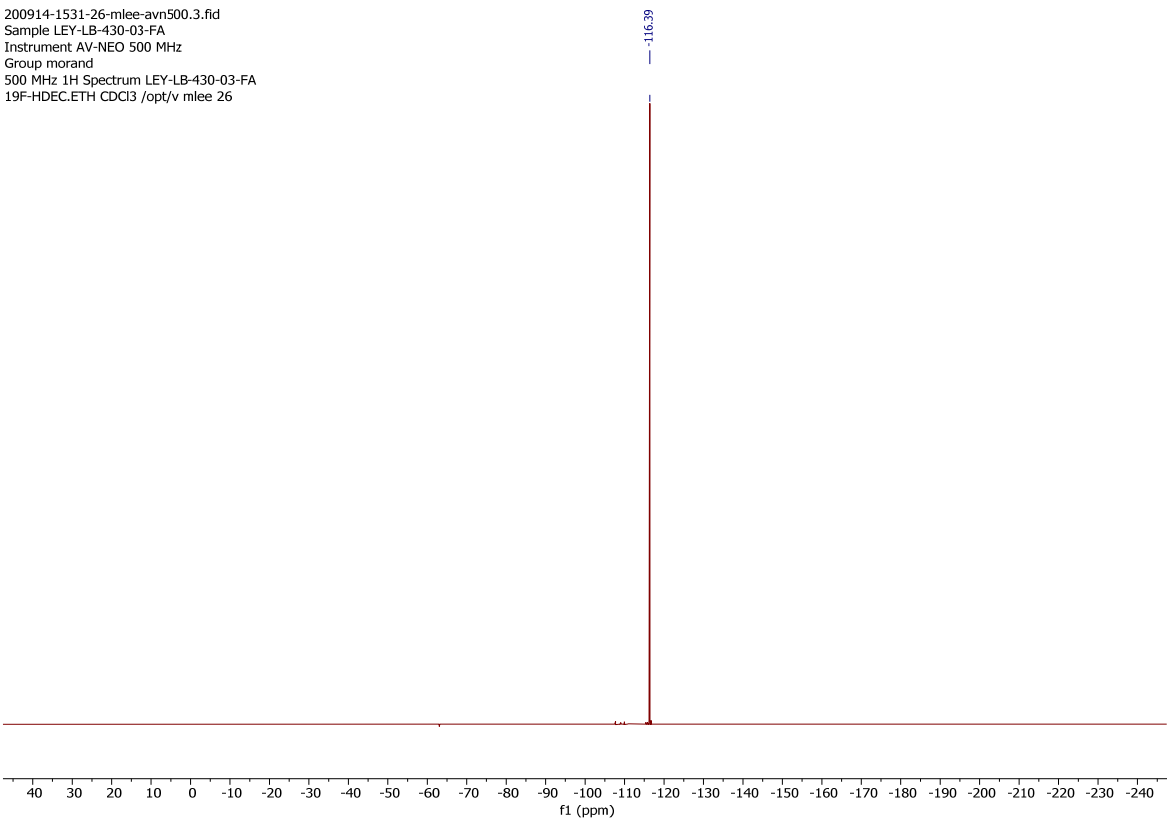

200914-1528-24-mlee-avn500.4.ser
Sample LEY-LB-430-03-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-03-FB
COSY.ETH CDCl3 /opt/v mlee 24
f2 (ppm)
f1 (ppm)

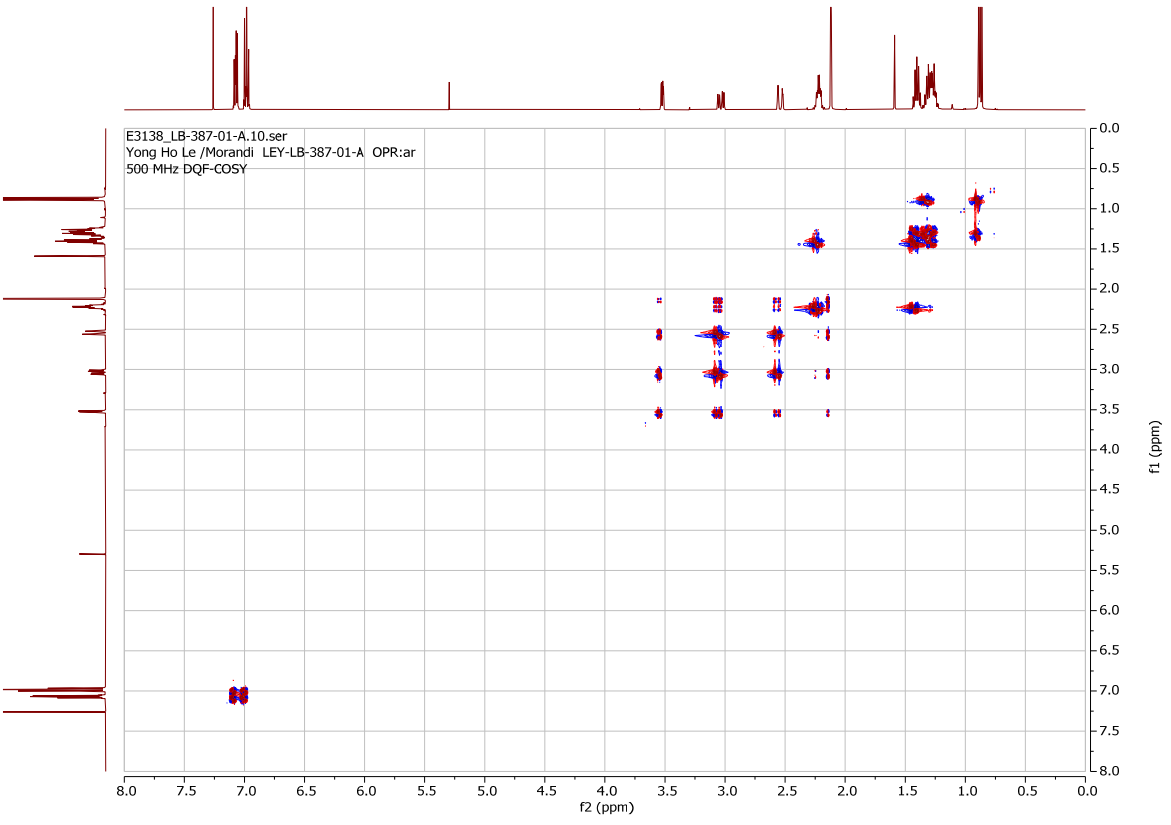

200914-1528-24-mlee-avn500.5.ser
Sample LEY-LB-430-03-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-03-FB
HSQC.ETH CDCl3 /opt/v mlee 24
f2 (ppm)
f1 (ppm)

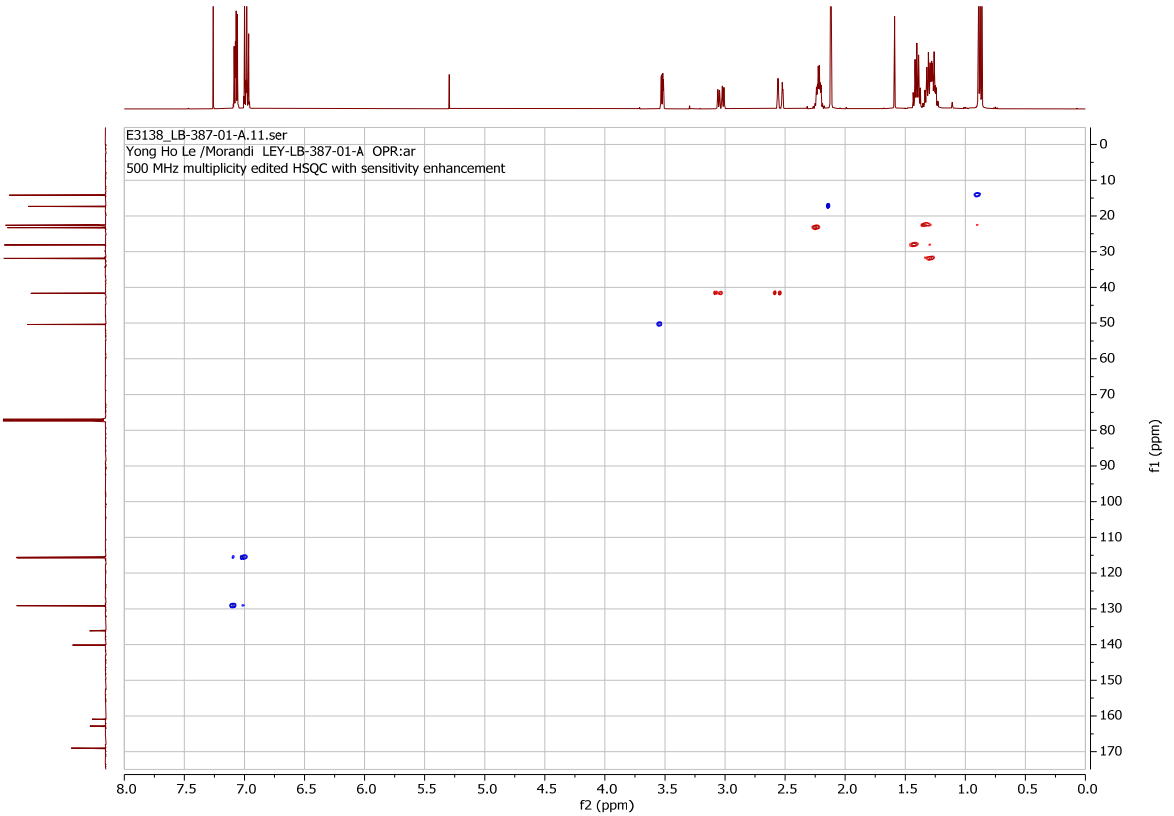

200914-1528-24-mlee-avn500.7.ser
Sample LEY-LB-430-03-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-03-FB
NOESY.ETH CDCl3 /opt/v mlee 24
f2 (ppm)
f1 (ppm)

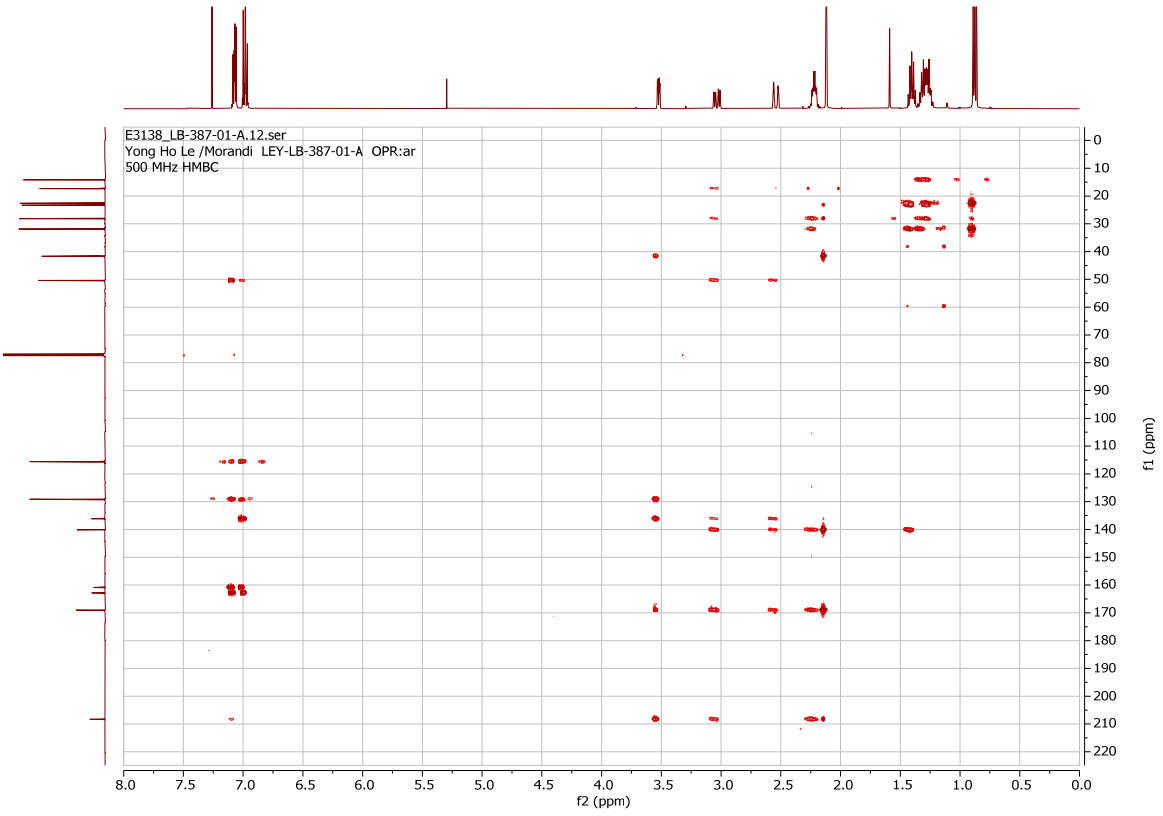
5-(4-fluorophenyl)-3-methyl-2-pentylcyclopent-2-en-1-one (**3br-2**, minor).

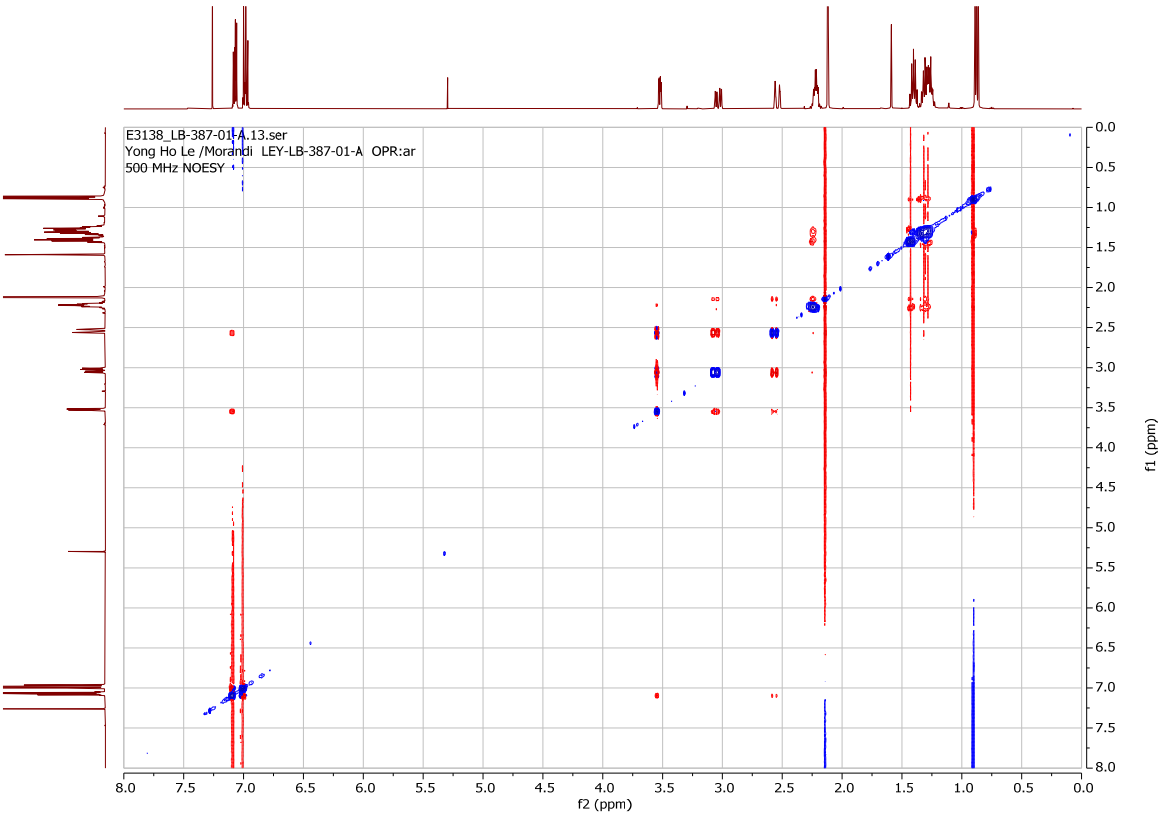



200914-1531-26-mlee-avn500.3.fid
Sample LEY-LB-430-03-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-03-FA
19F-HDEC.ETH CDCl3 /opt/v mlee 26
-116.39
f1 (ppm)

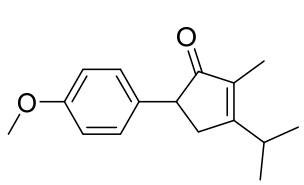

E3138_LB-387-01-A.10.ser
Yong Ho Le /Morandi LEY-LB-387-01-A OPR:ar
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

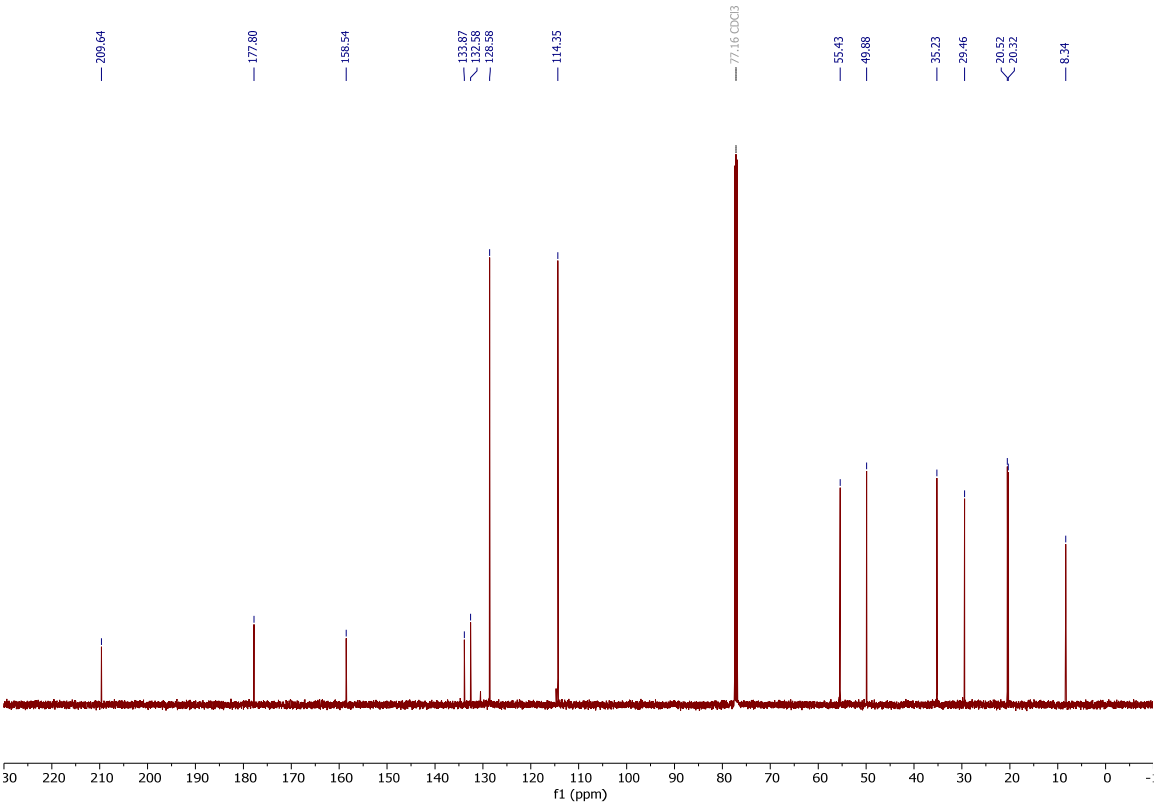

E3138_LB-387-01-A.11.ser
Yong Ho Le /Morandi LEY-LB-387-01-A OPR:ar
500 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

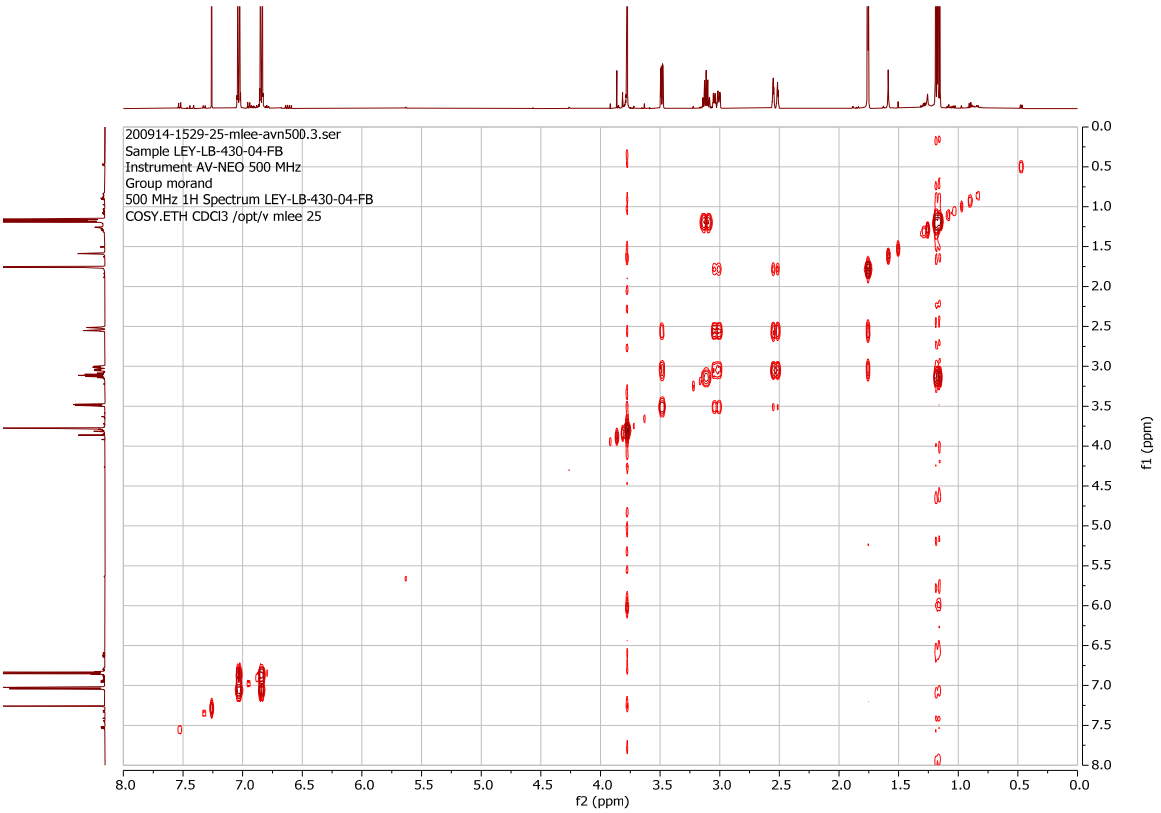

E3138_LB-387-01-A.12.ser
Yong Ho Le /Morandi LEY-LB-387-01-A OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

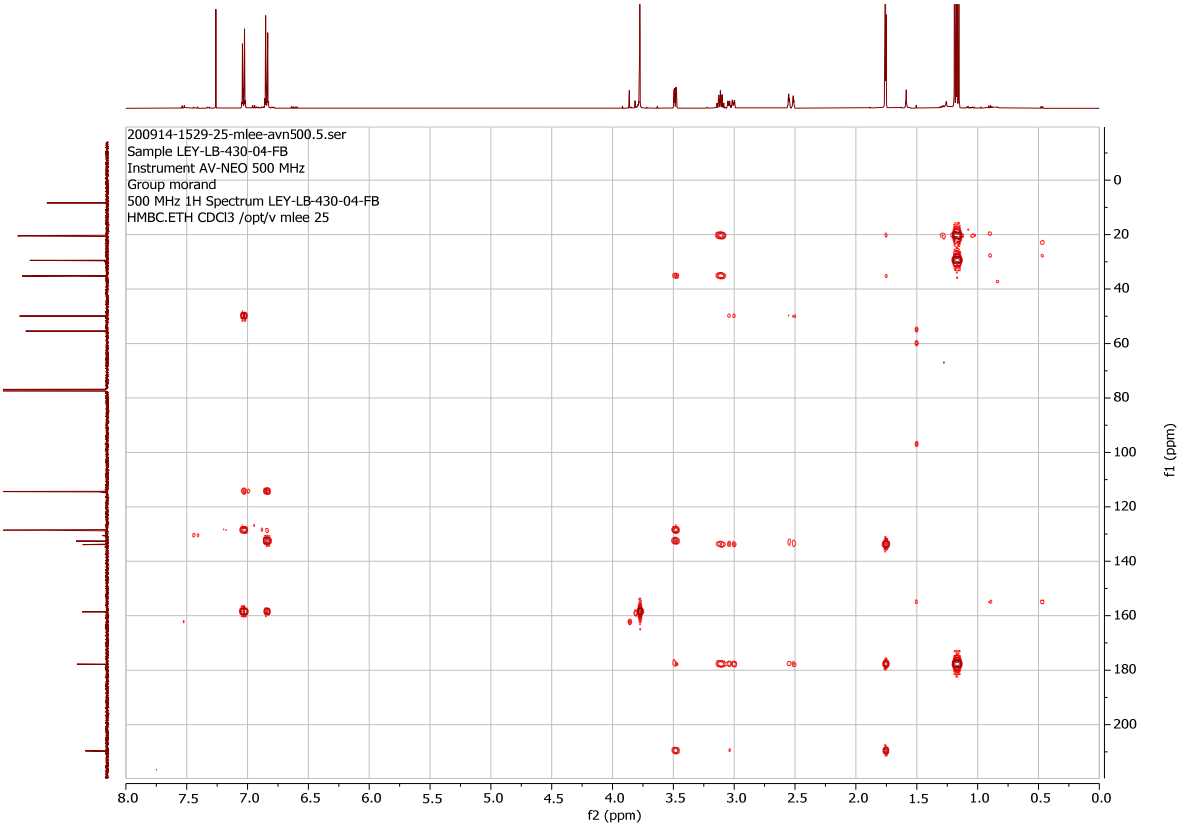

E3138_LB-387-01-A.13.ser
Yong Ho Le /Morandi LEY-LB-387-01-A OPR:ar
500 MHz NOESY
f2 (ppm)
f1 (ppm)

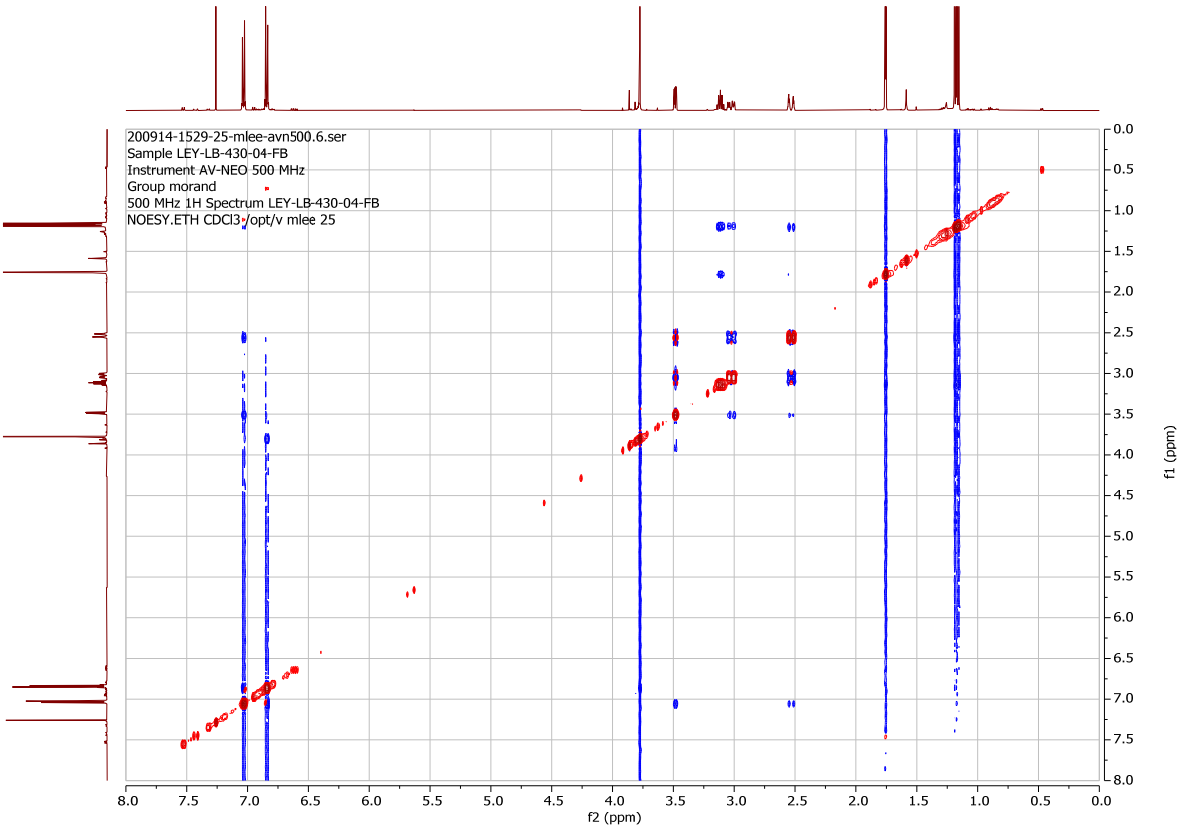
3-isopropyl-5-(4-methoxyphenyl)-2-methylcyclopent-2-en-1-one (**3bs-1**, major).

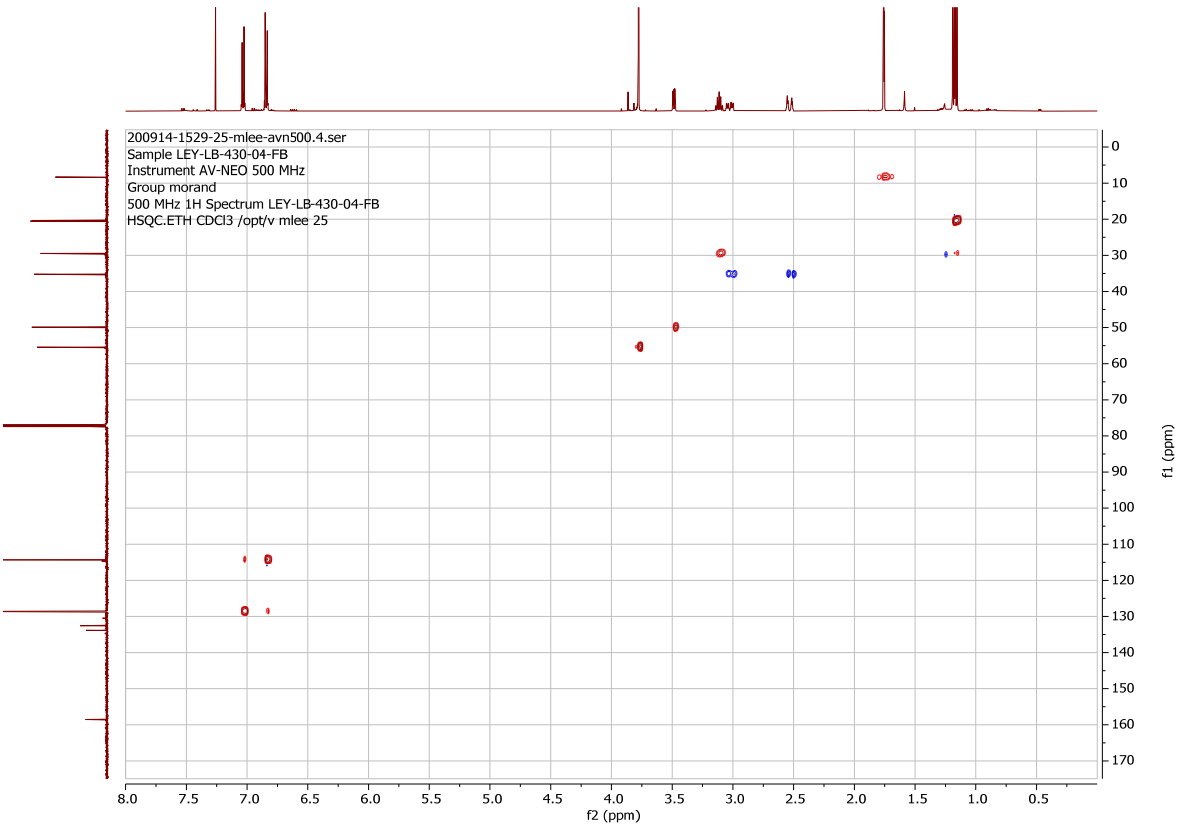




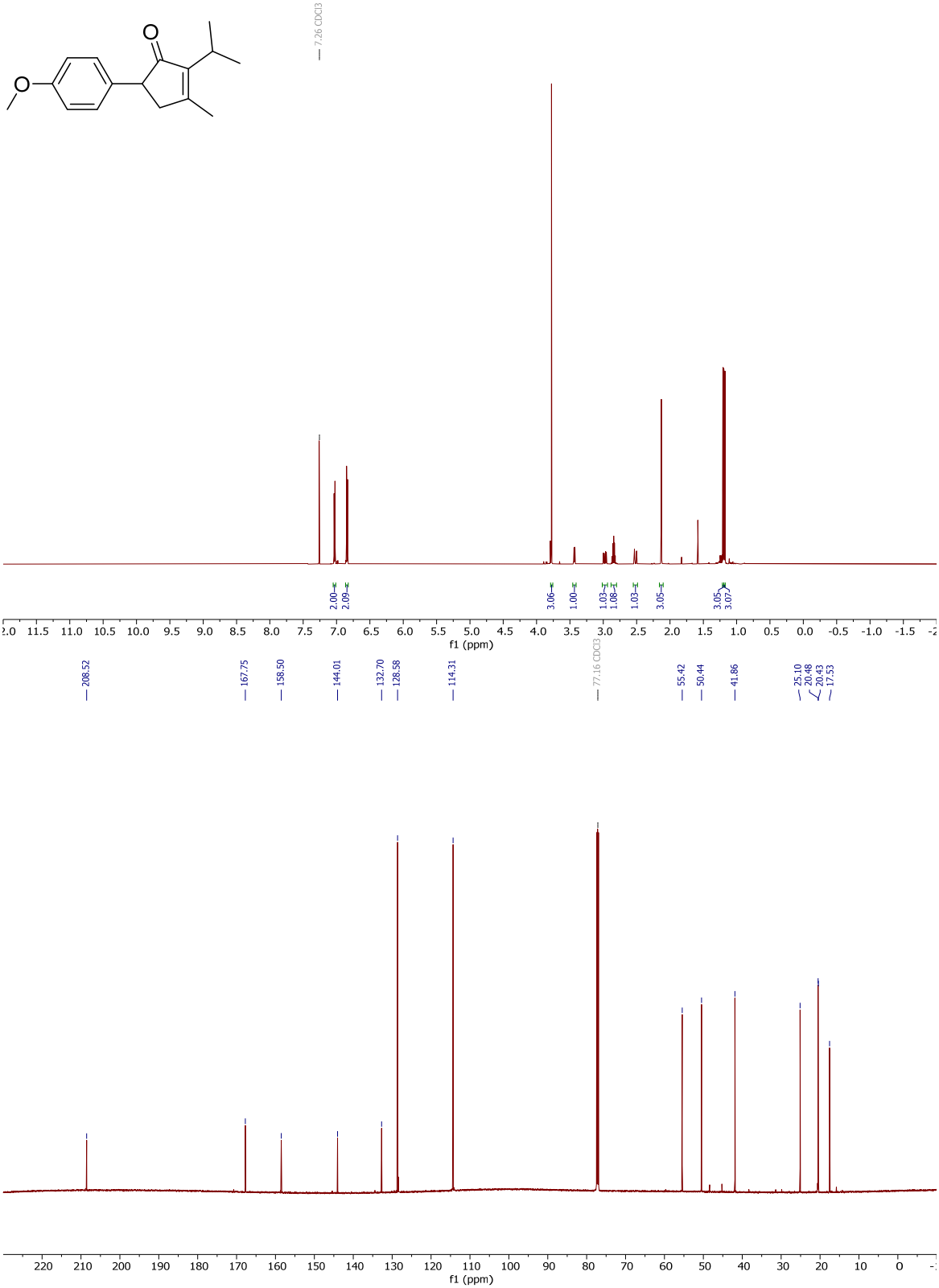

200914-1529-25-mlee-avn500.3.ser
Sample LEY-LB-430-04-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-04-FB
COSY.ETH CDCl3 /opt/v mlee 25
f2 (ppm)
f1 (ppm)

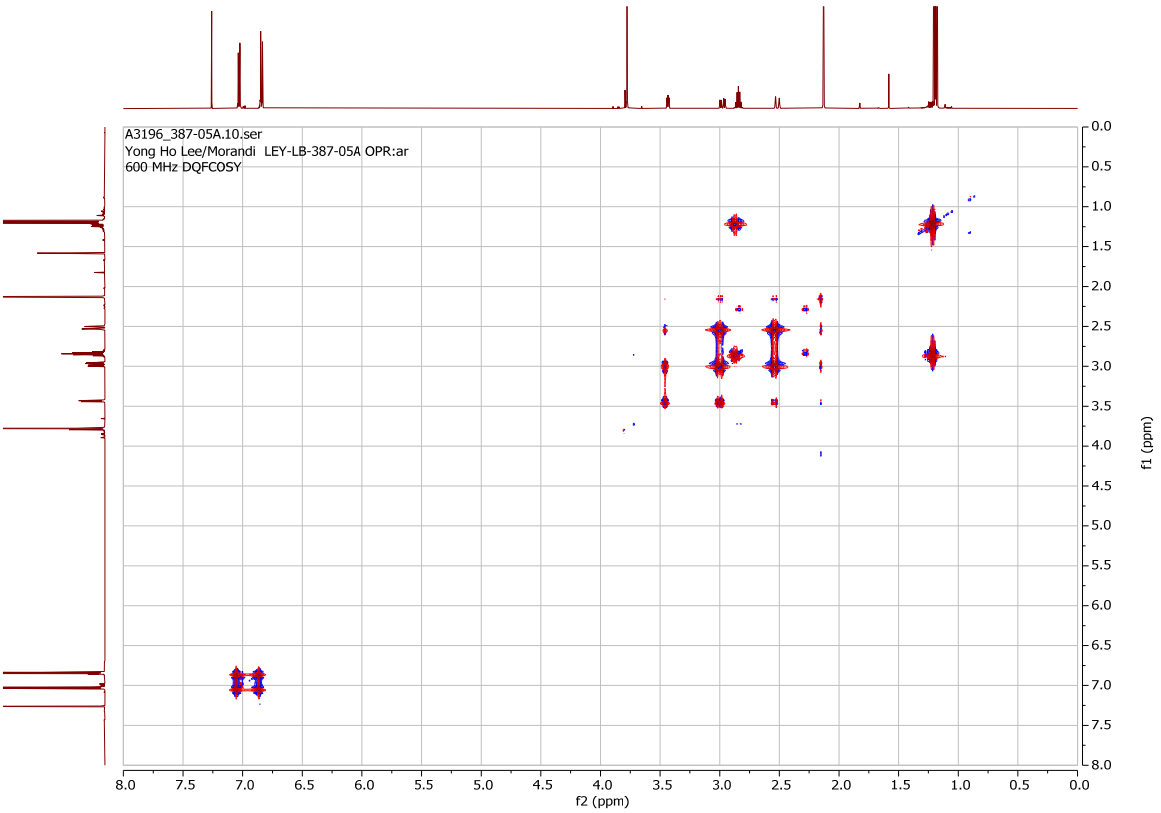

200914-1529-25-mlee-avn500.5.ser
Sample LEY-LB-430-04-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-04-FB
HMBC.ETH CDCl3 /opt/v mlee 25
f2 (ppm)
f1 (ppm)

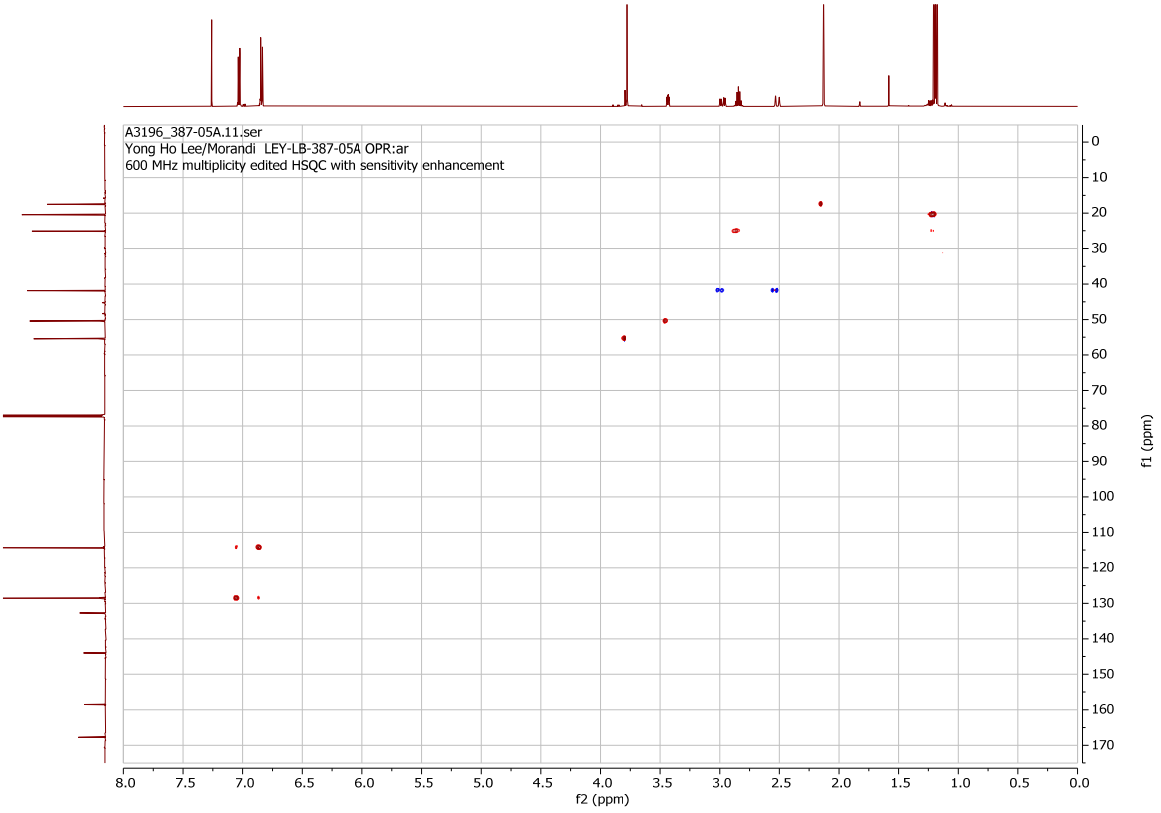

200914-1529-25-mlee-avn500.6.ser
Sample LEY-LB-430-04-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-04-FB
NOESY.ETH CDCl3 -/opt/v mlee 25
f2 (ppm)
f1 (ppm)

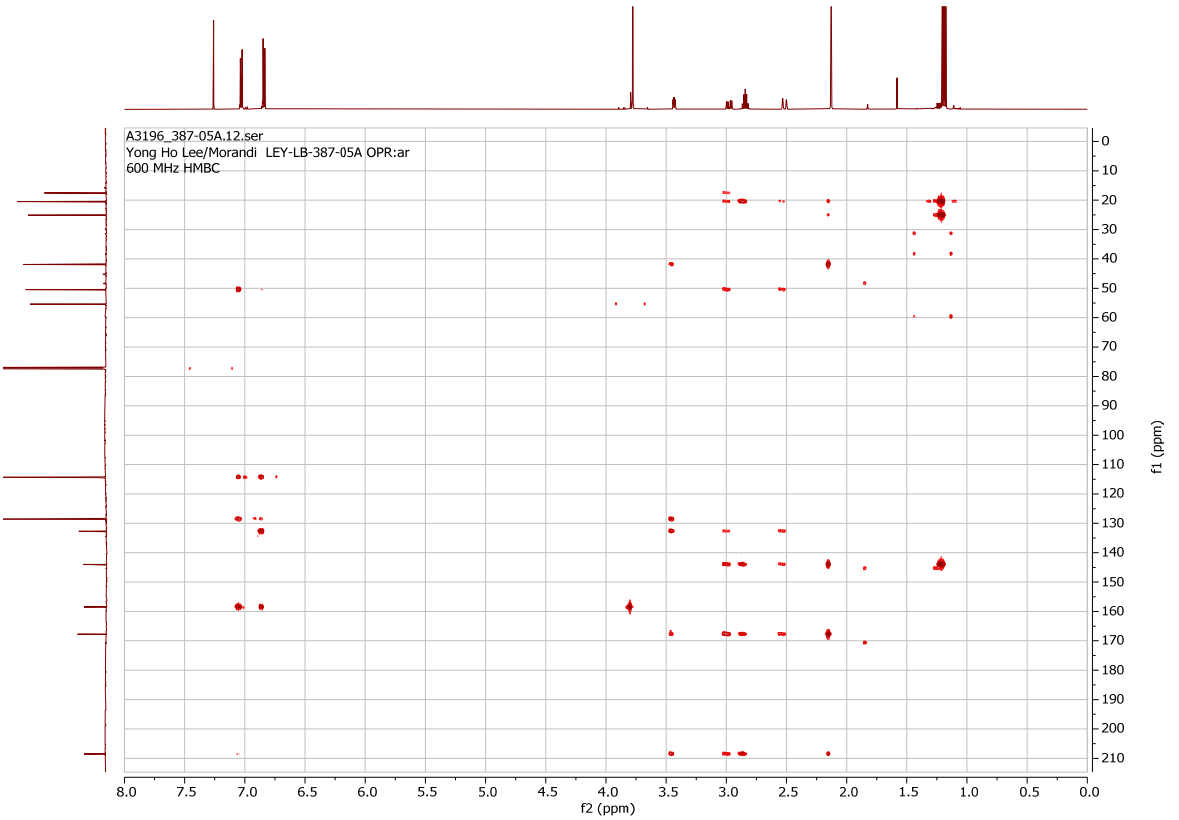

200914-1529-25-mlee-avn500.4.ser
Sample LEY-LB-430-04-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-04-FB
HSQC.ETH CDCl3 /opt/v mlee 25
f2 (ppm)
f1 (ppm)

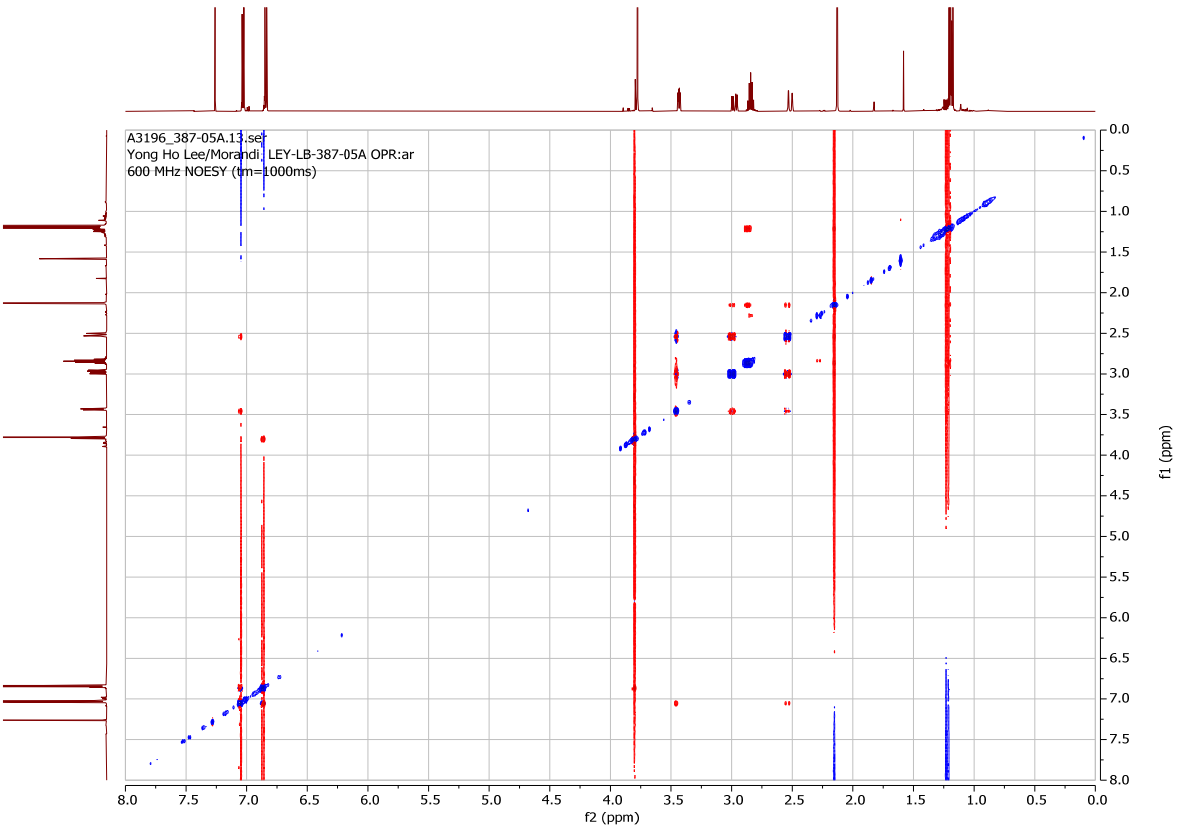
2-isopropyl-5-(4-methoxyphenyl)-3-methylcyclopent-2-en-1-one (**3bs-2**, minor).



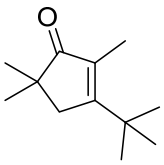

A3196_387-05A.10.ser
Yong Ho Lee/Morandi LEY-LB-387-05A OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

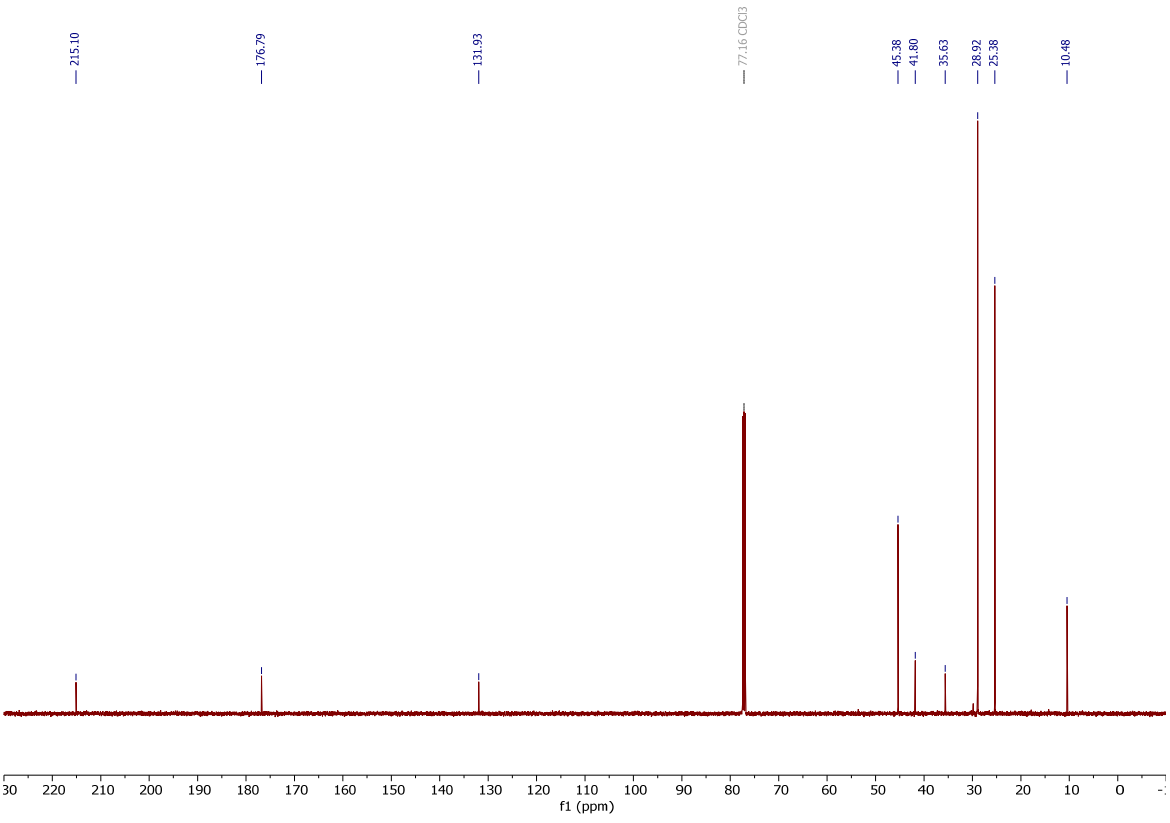

A3196_387-05A.11.ser
Yong Ho Lee/Morandi LEY-LB-387-05A OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

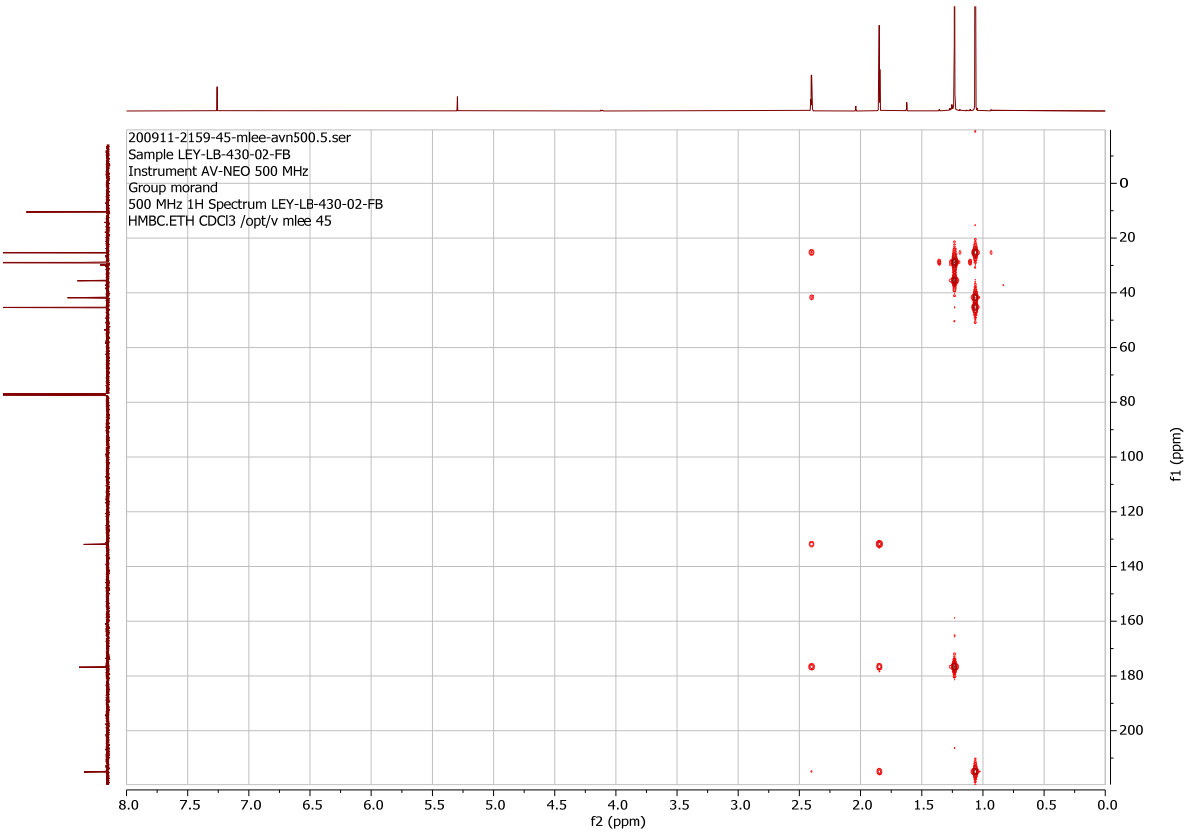

A3196_387-05A.12.ser
Yong Ho Lee/Morandi LEY-LB-387-05A OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

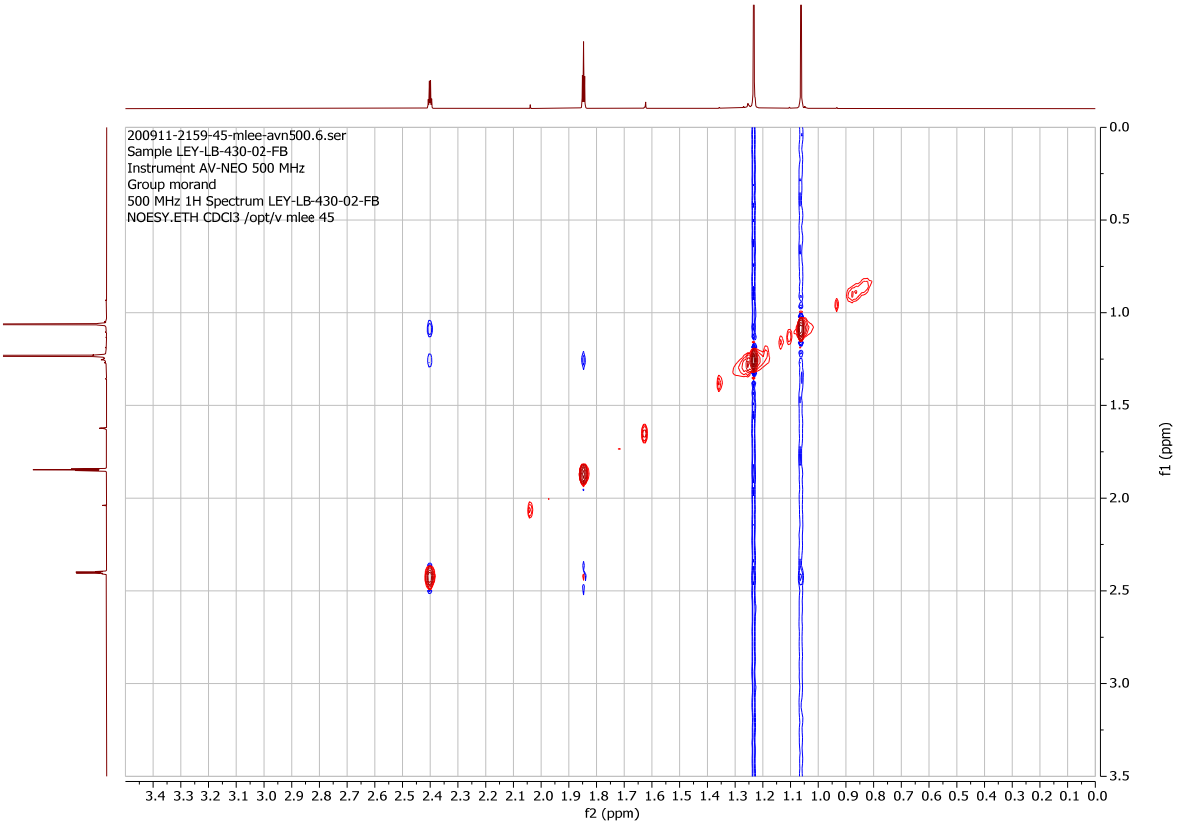

A3196_387-05A.13.ser
Yong Ho Lee/Morandi LEY-LB-387-05A OPR:ar
600 MHz NOESY (tm=1000ms)
f2 (ppm)
f1 (ppm)

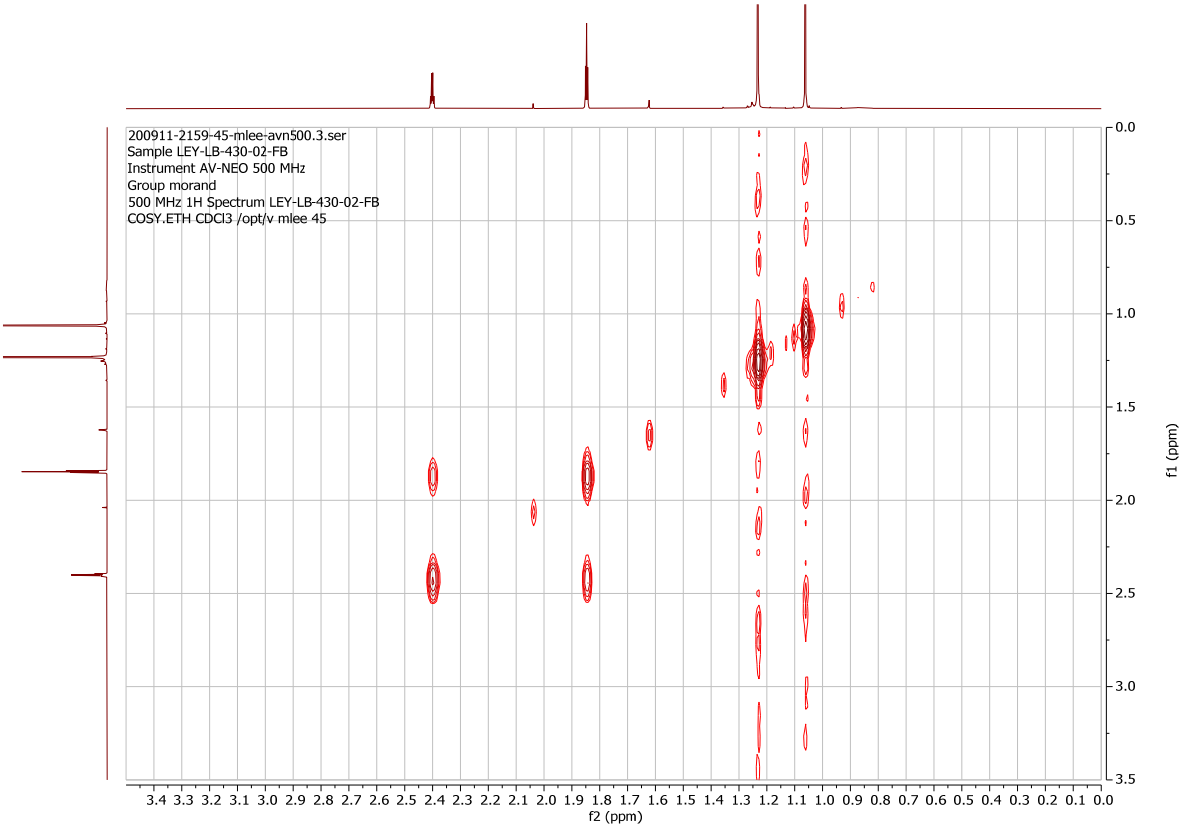
3-(*tert*-butyl)-2,5,5-trimethylcyclopent-2-en-1-one (**3bt-1**, major).

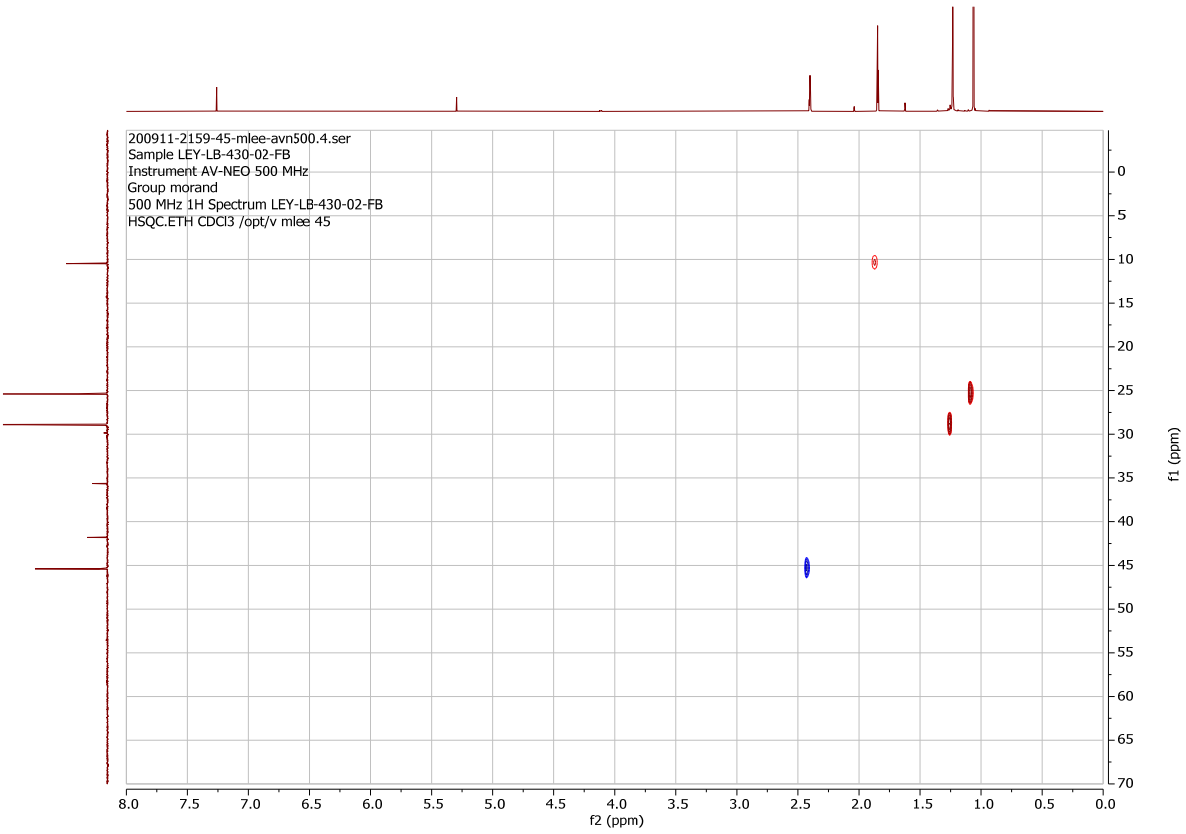




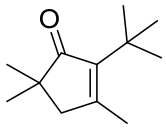

200911-2159-45-mlee-avn500.5.ser
Sample LEY-LB-430-02-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FB
HMBC.ETH CDCl3 /opt/v mlee 45
f2 (ppm)
f1 (ppm)

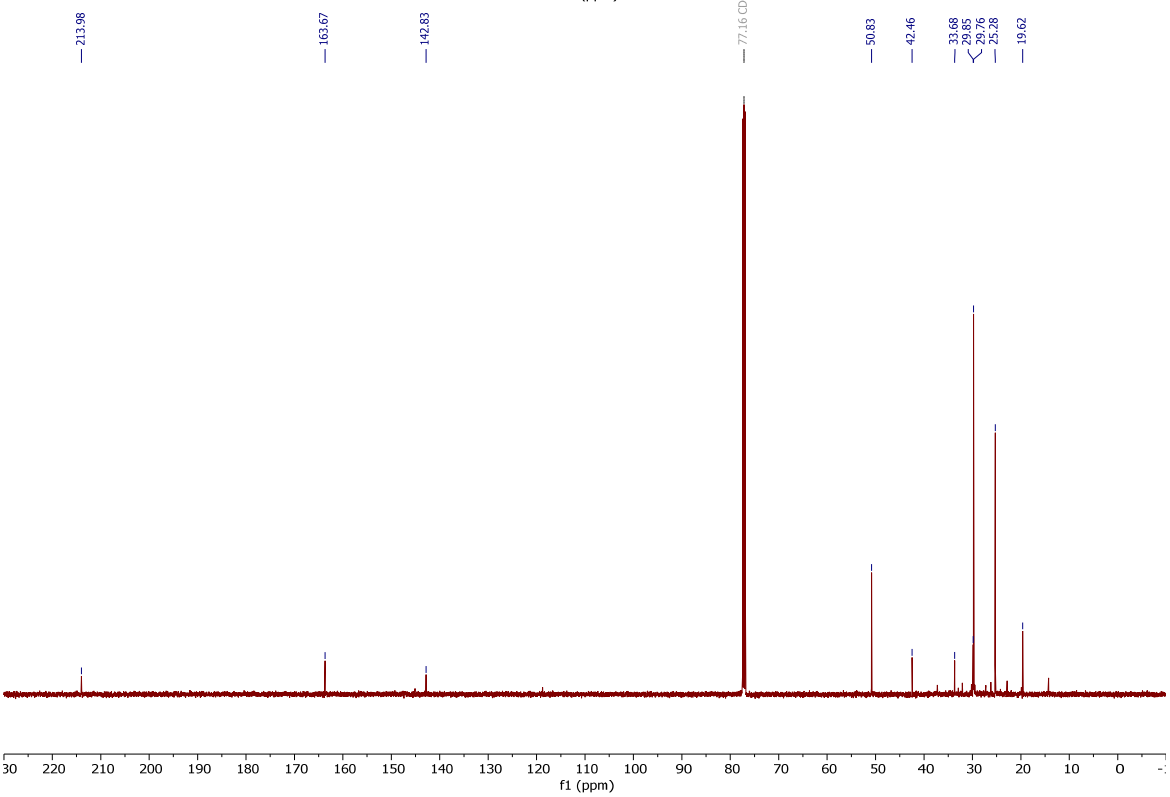

200911-2159-45-mlee-avn500.6.ser
Sample LEY-LB-430-02-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FB
NOESY.ETH CDCl3 /opt/v mlee 45
f2 (ppm)
f1 (ppm)

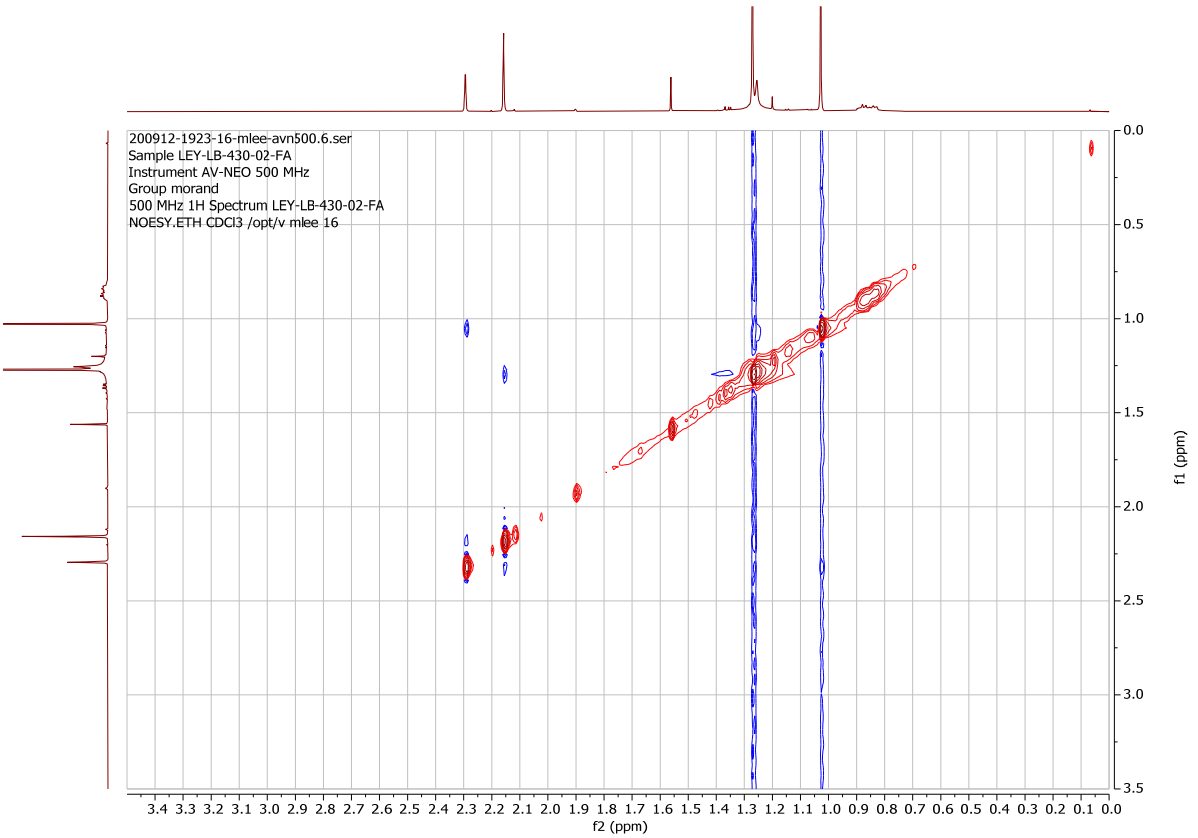

200911-2159-45-mlee-avn500.3.ser
Sample LEY-LB-430-02-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FB
COSY.ETH CDCl3 /opt/v mlee 45
f2 (ppm)
f1 (ppm)

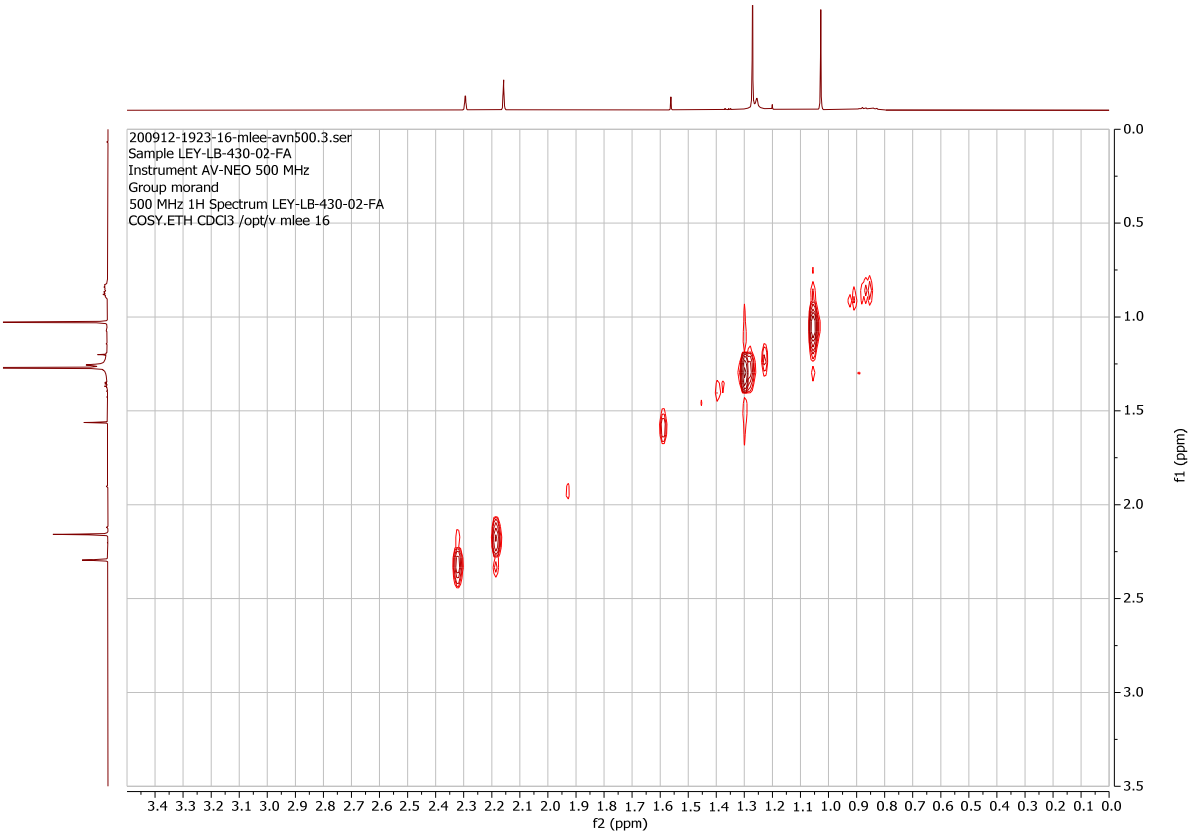

200911-2159-45-mlee-avn500.4.ser
Sample LEY-LB-430-02-FB
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FB
HSQC.ETH CDCl3 /opt/v mlee 45
f2 (ppm)
f1 (ppm)

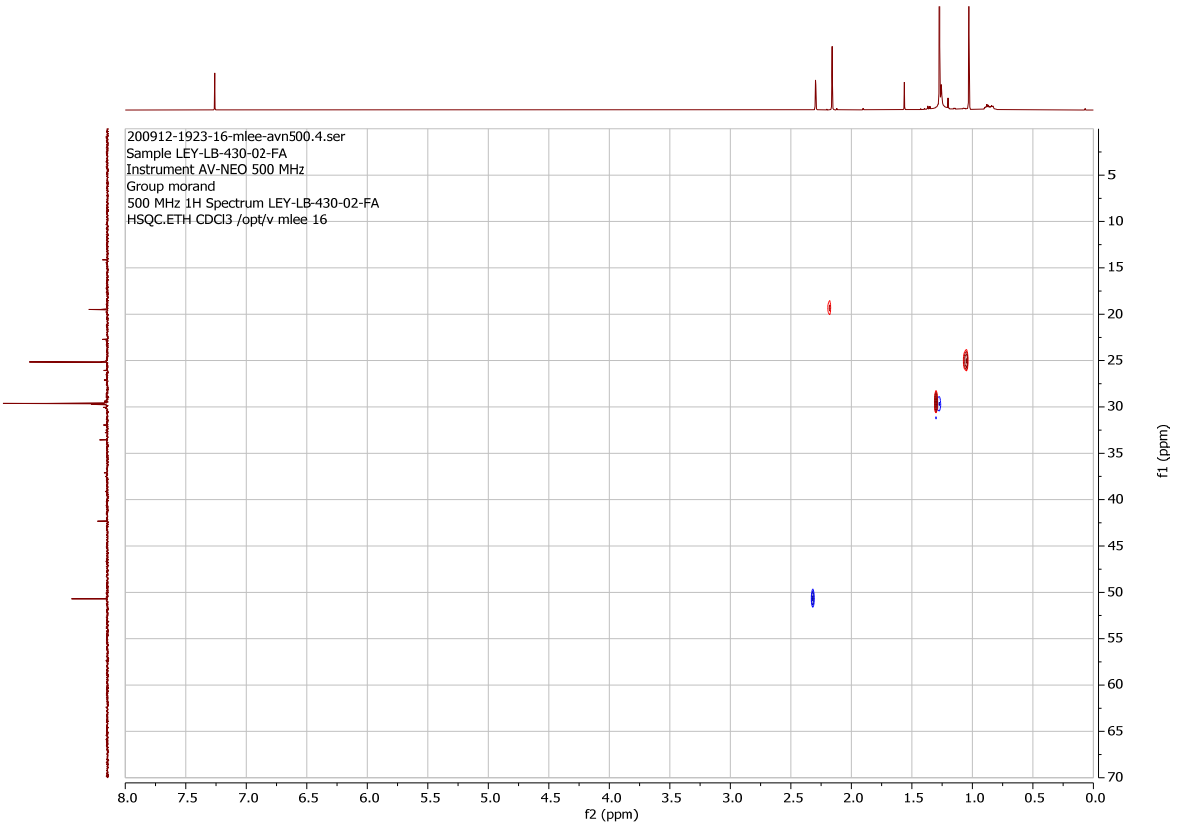
2-(*tert*-butyl)-3,5,5-trimethylcyclopent-2-en-1-one (**3bt-2**, minor).

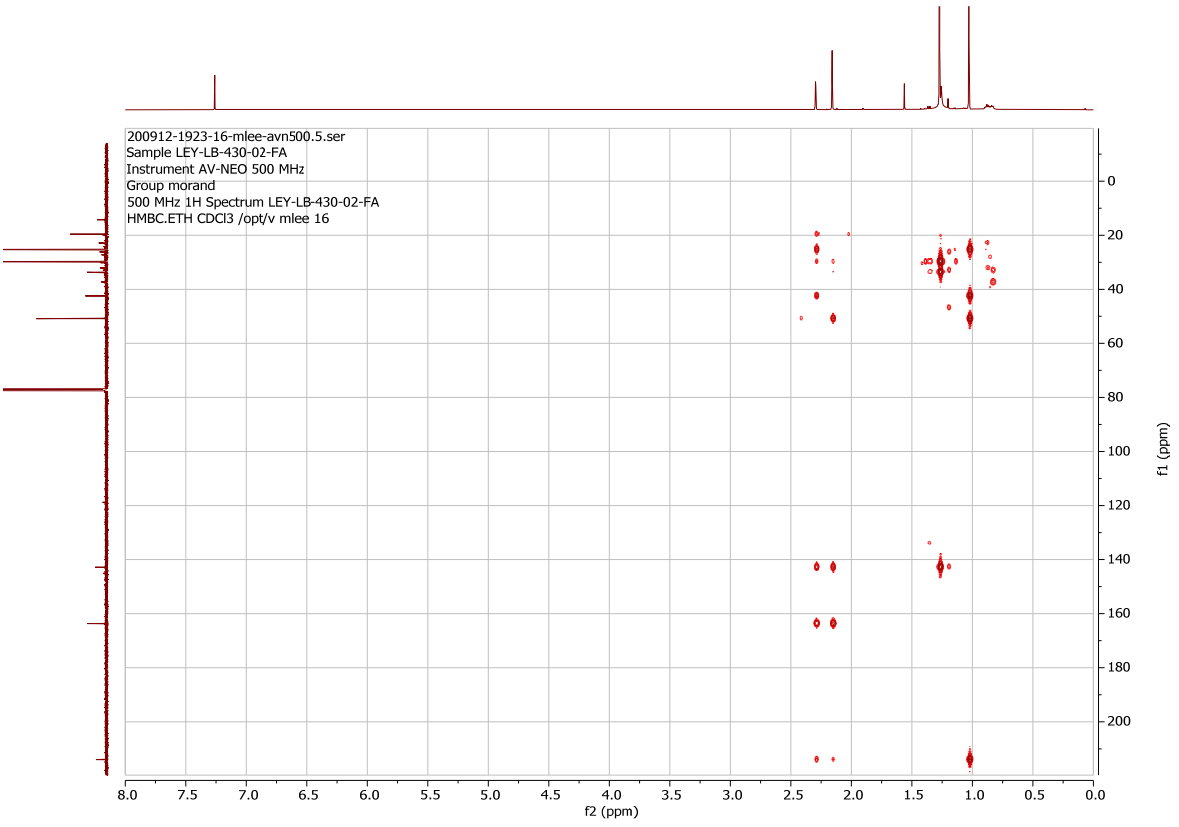




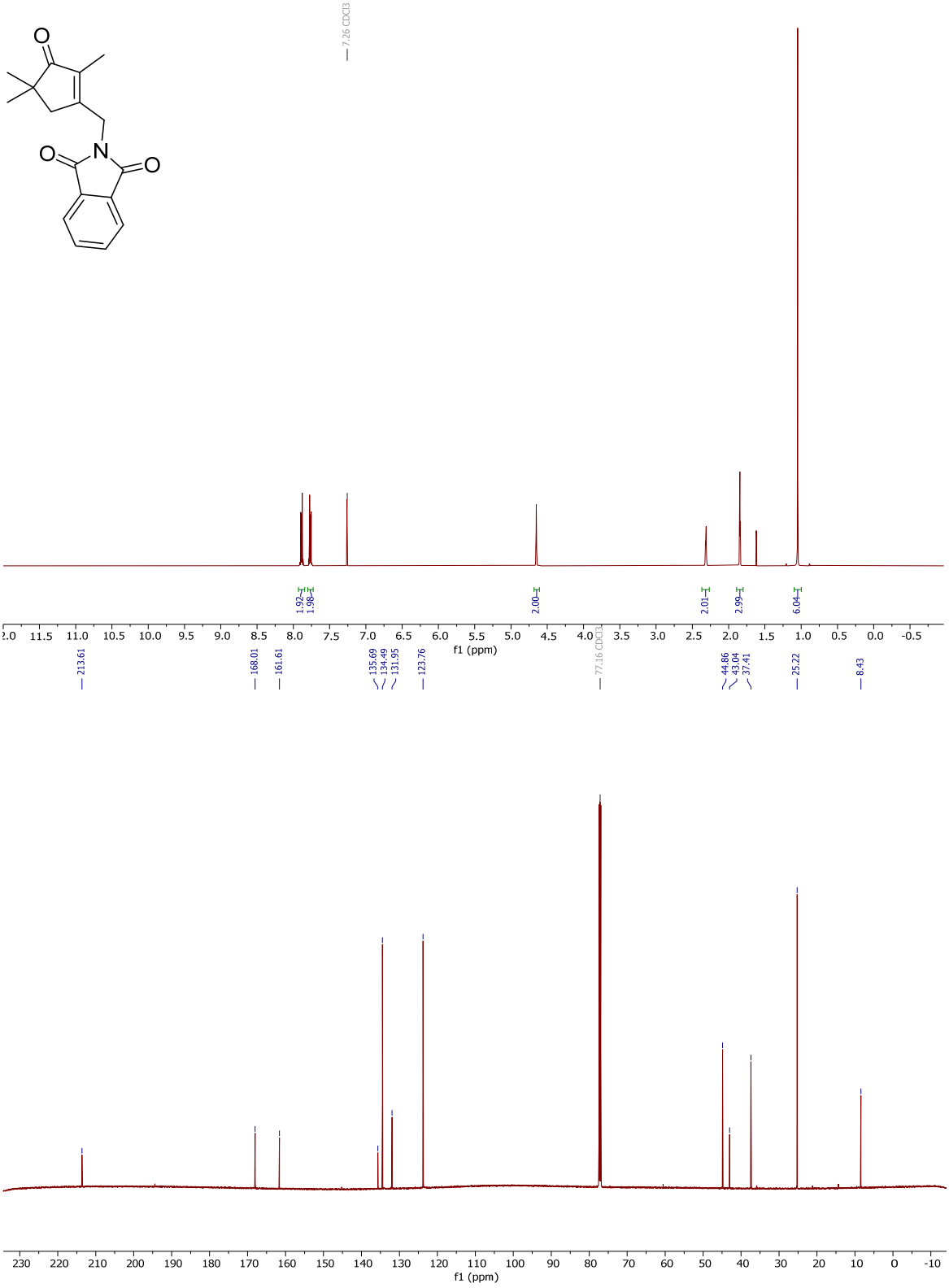

200912-1923-16-mlee-avn500.6.ser
Sample LEY-LB-430-02-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FA
NOESY.ETH CDCl3 /opt/v mlee 16
f2 (ppm)
f1 (ppm)

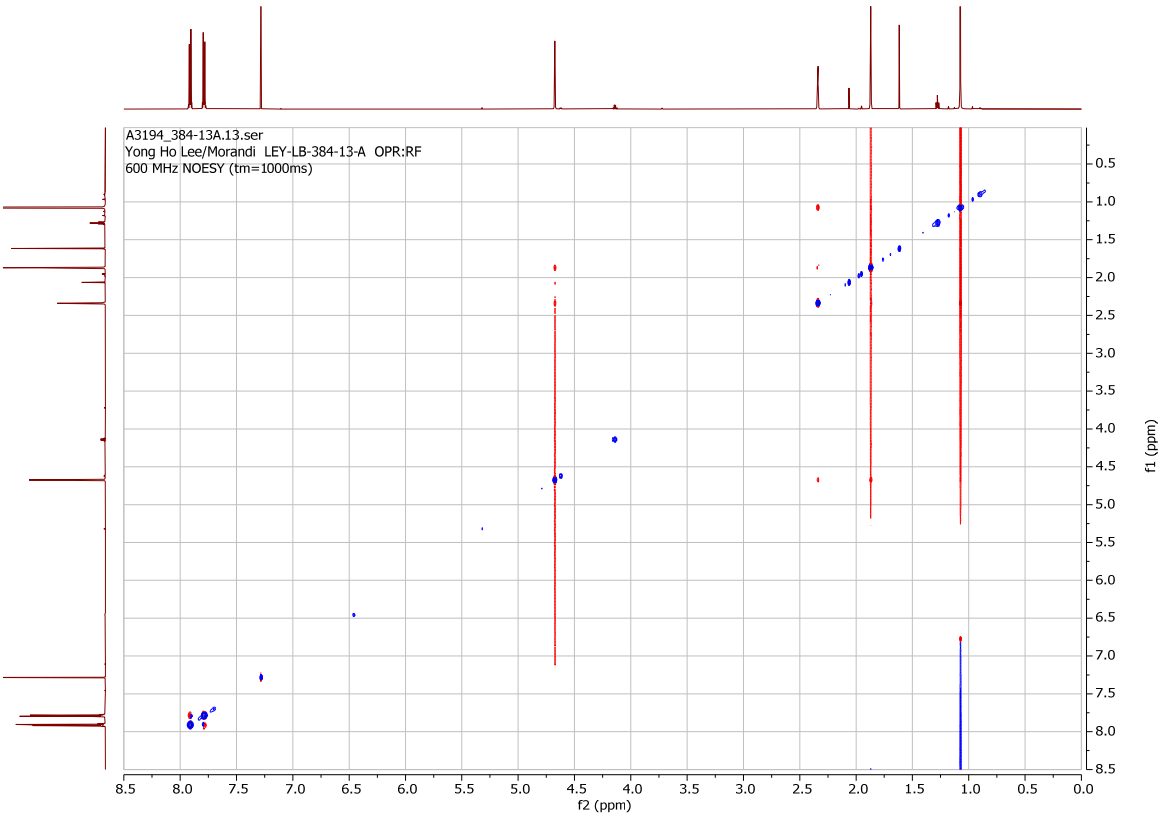

200912-1923-16-mlee-avn500.3.ser
Sample LEY-LB-430-02-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FA
COSY.ETH CDCl3 /opt/v mlee 16
f2 (ppm)
f1 (ppm)

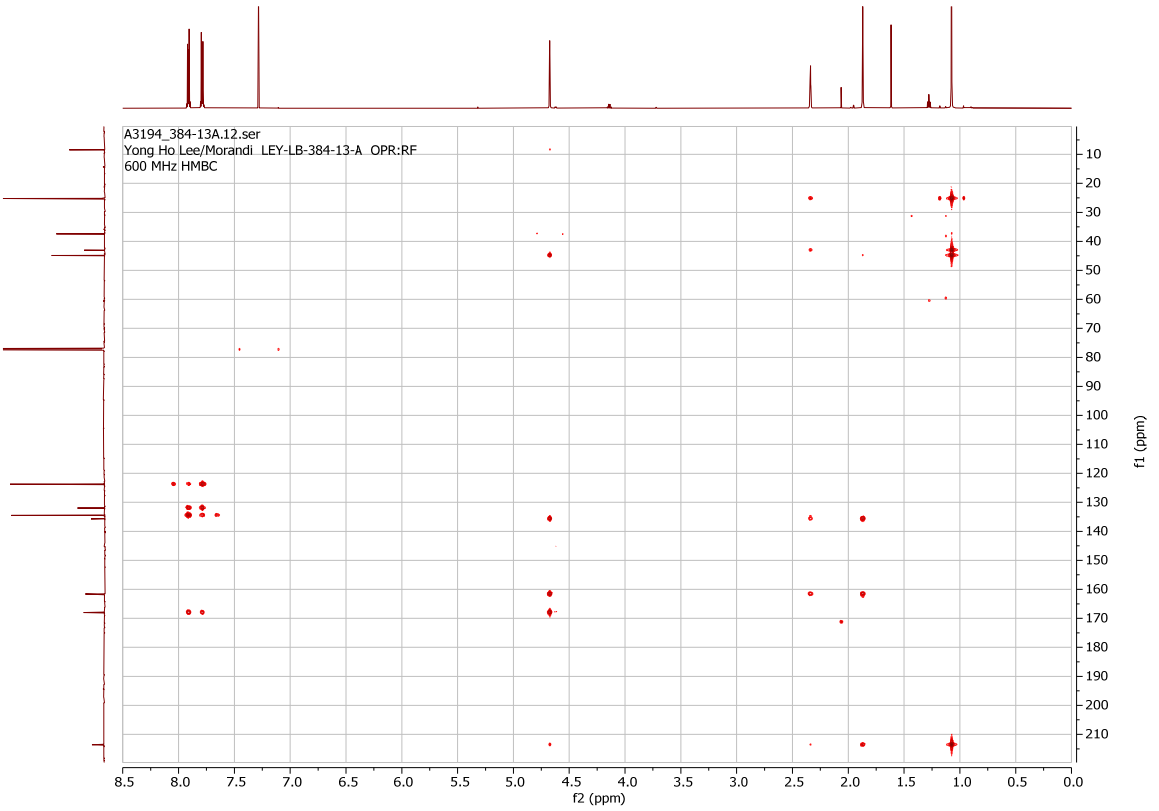

200912-1923-16-mlee-avn500.4.ser
Sample LEY-LB-430-02-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FA
HSQC.ETH CDCl3 /opt/v mlee 16
f2 (ppm)
f1 (ppm)

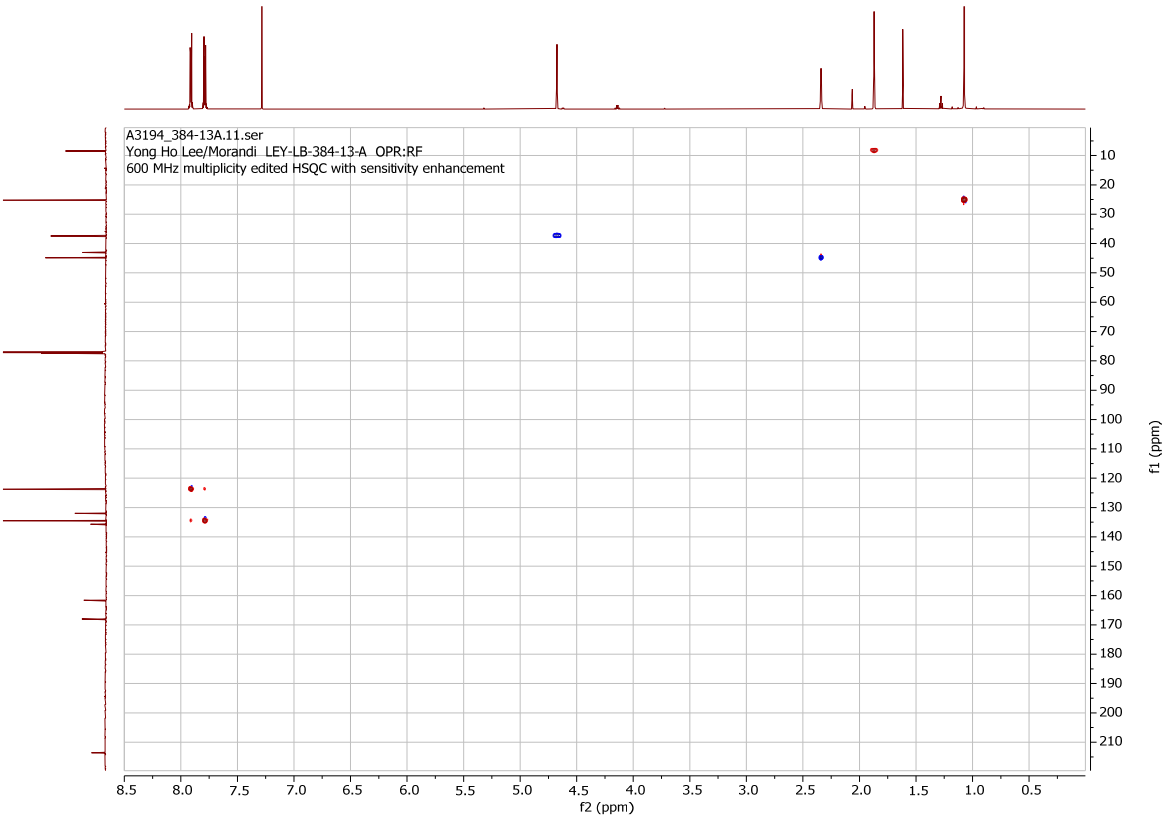

200912-1923-16-mlee-avn500.5.ser
Sample LEY-LB-430-02-FA
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-430-02-FA
HMBC.ETH CDCl3 /opt/v mlee 16
f2 (ppm)
f1 (ppm)

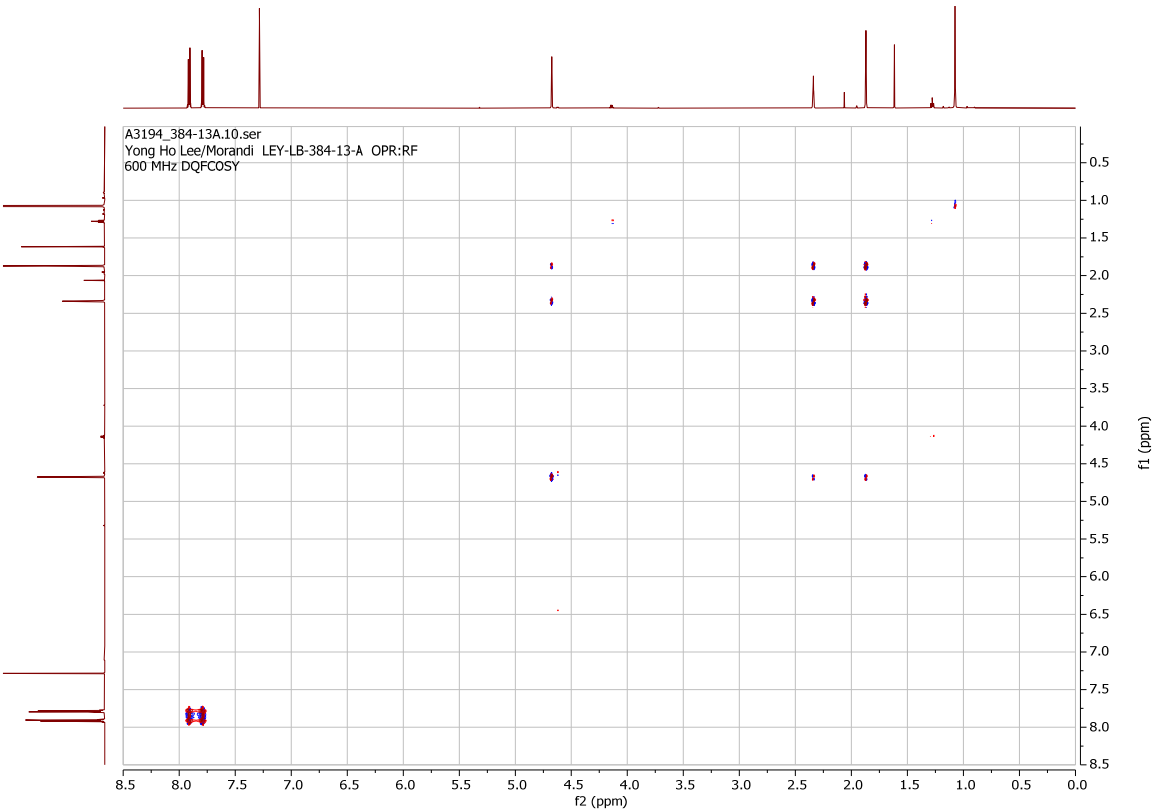
2-((2,4,4-trimethyl-3-oxocyclopent-1-en-1-yl)methyl)isoindoline-1,3-dione (**3bu-1**, major).



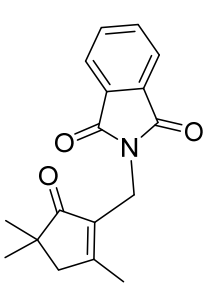

A3194_384-13A.13.ser
Yong Ho Lee/Morandi LEY-LB-384-13-A OPR:RF
600 MHz NOESY (tm=1000ms)
f2 (ppm)
f1 (ppm)

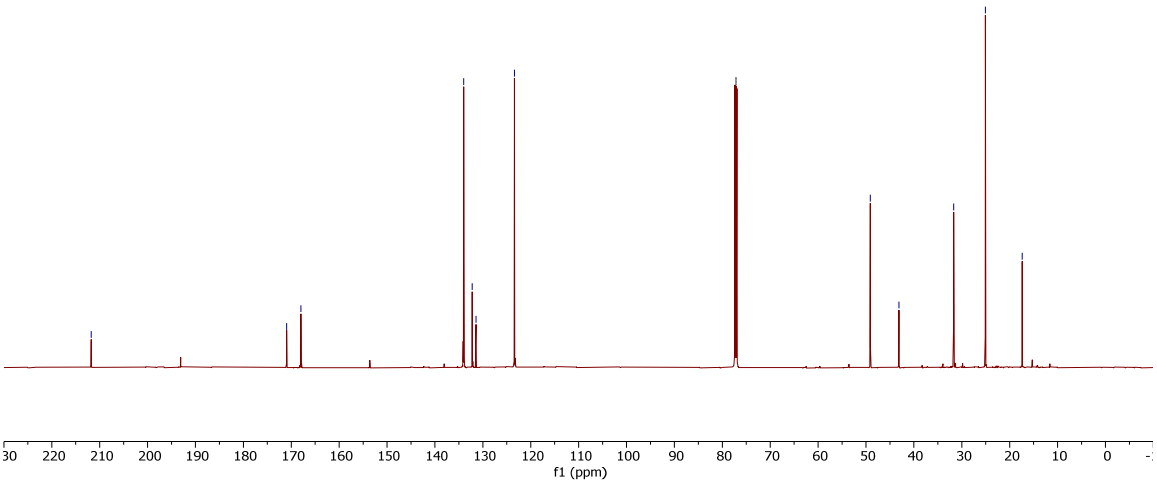

A3194_384-13A.12.ser
Yong Ho Lee/Morandi LEY-LB-384-13-A OPR:RF
600 MHz HMBC
f2 (ppm)
f1 (ppm)

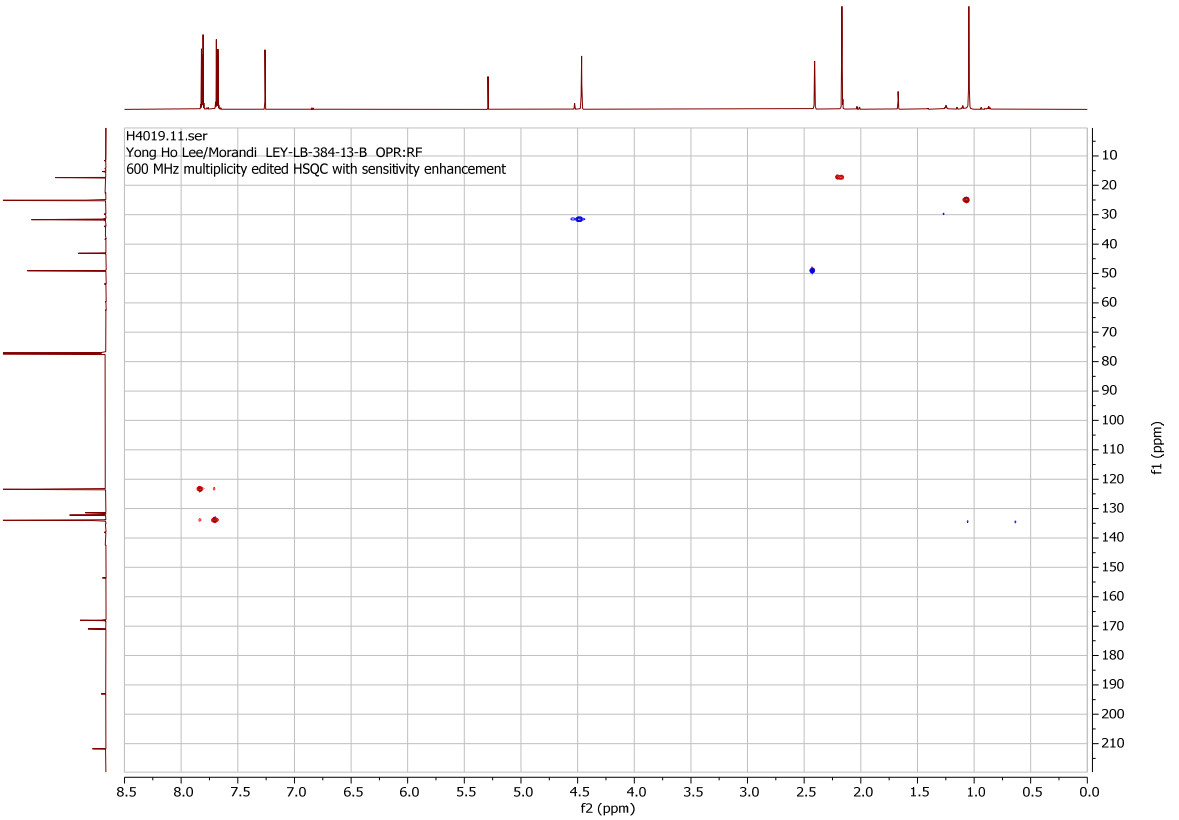

A3194_384-13A.11.ser
Yong Ho Lee/Morandi LEY-LB-384-13-A OPR:RF
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

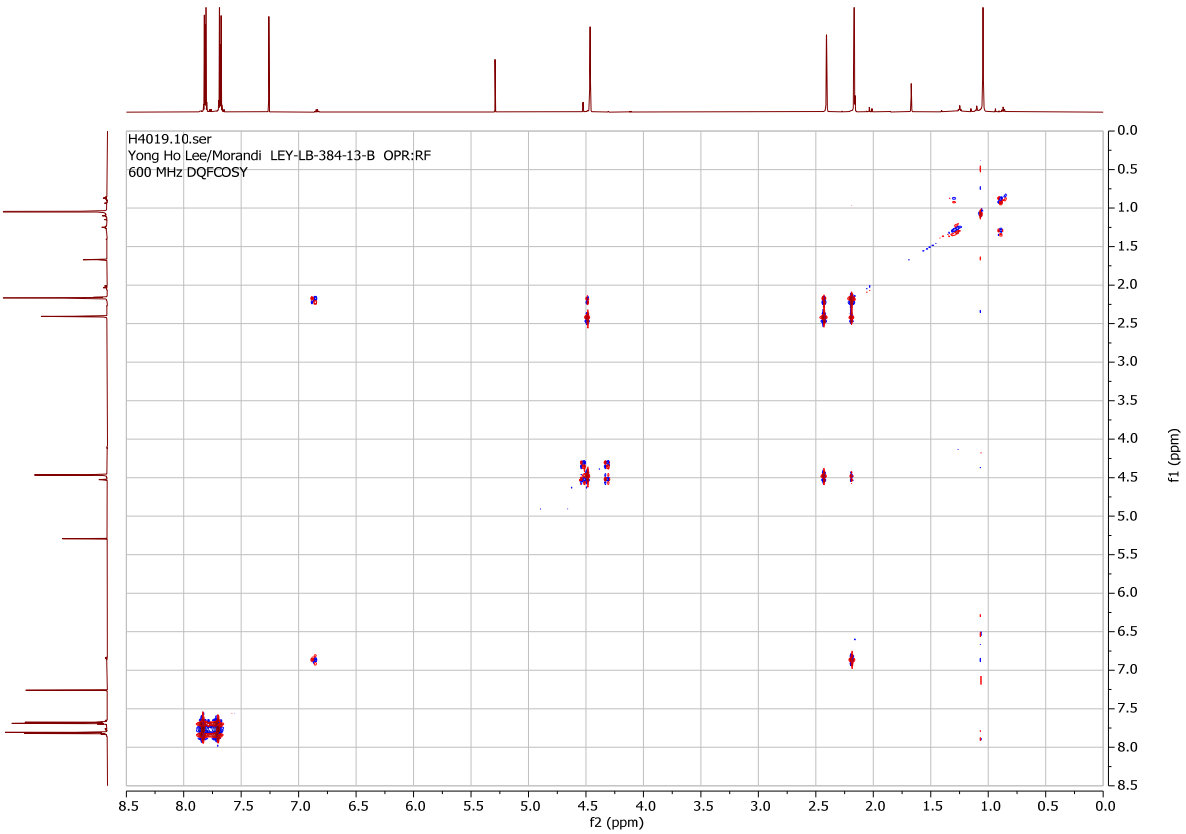

A3194_384-13A.10.ser
Yong Ho Lee/Morandi LEY-LB-384-13-A OPR:RF
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

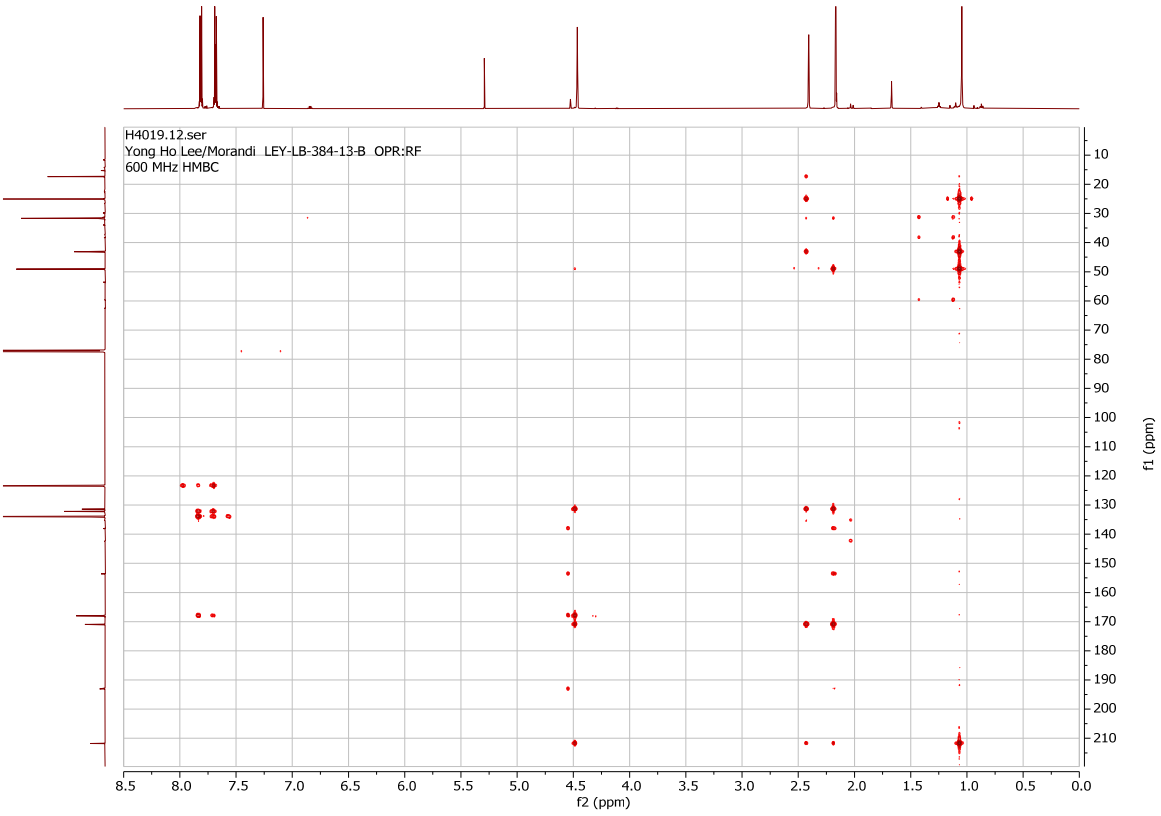
2-((2,4,4-trimethyl-5-oxocyclopent-1-en-1-yl)methyl)isoindoline-1,3-dione (**3bu-2**, minor).

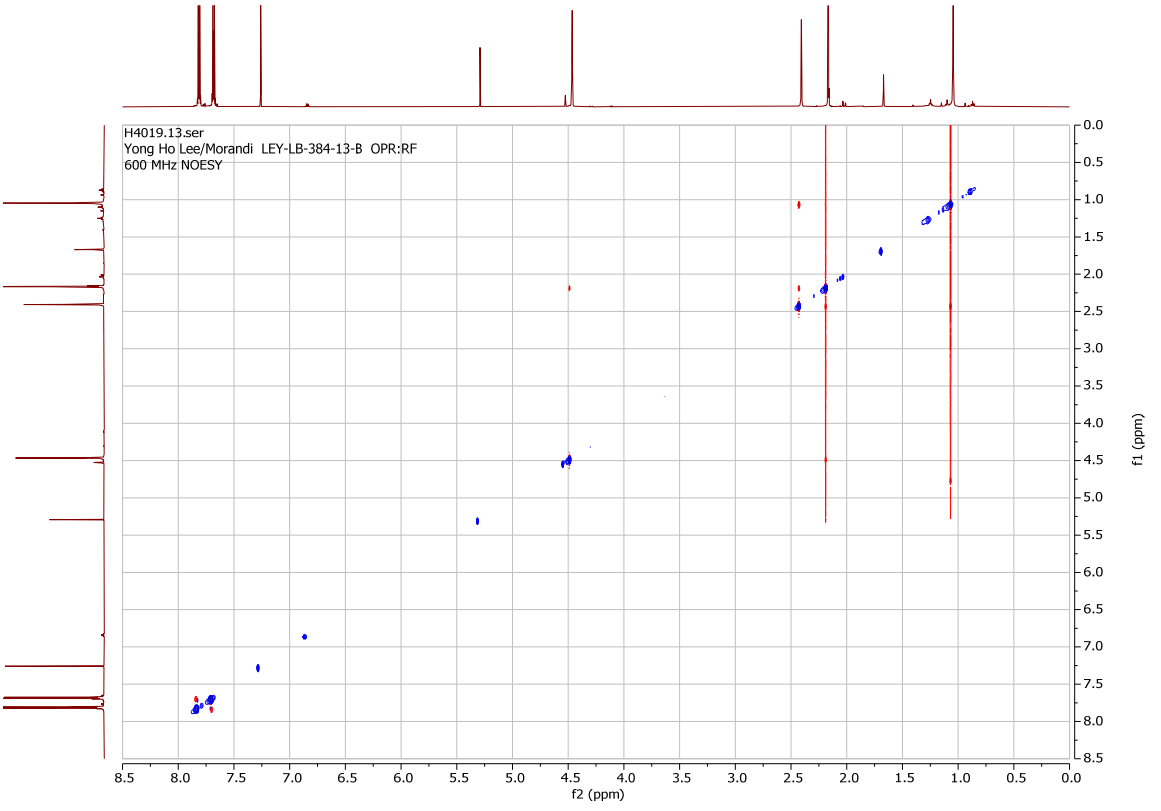




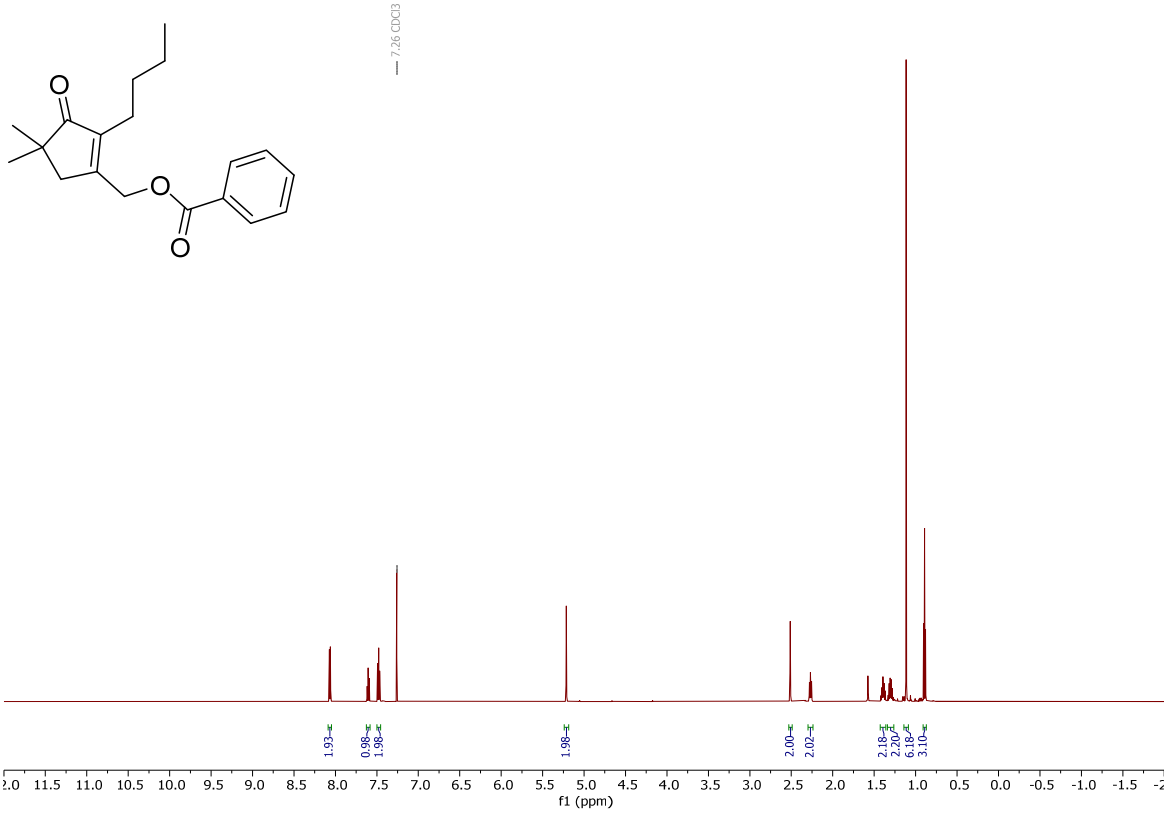

H4019.11.ser
Yong Ho Lee/Morandi LEY-LB-384-13-B OPR:RF
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

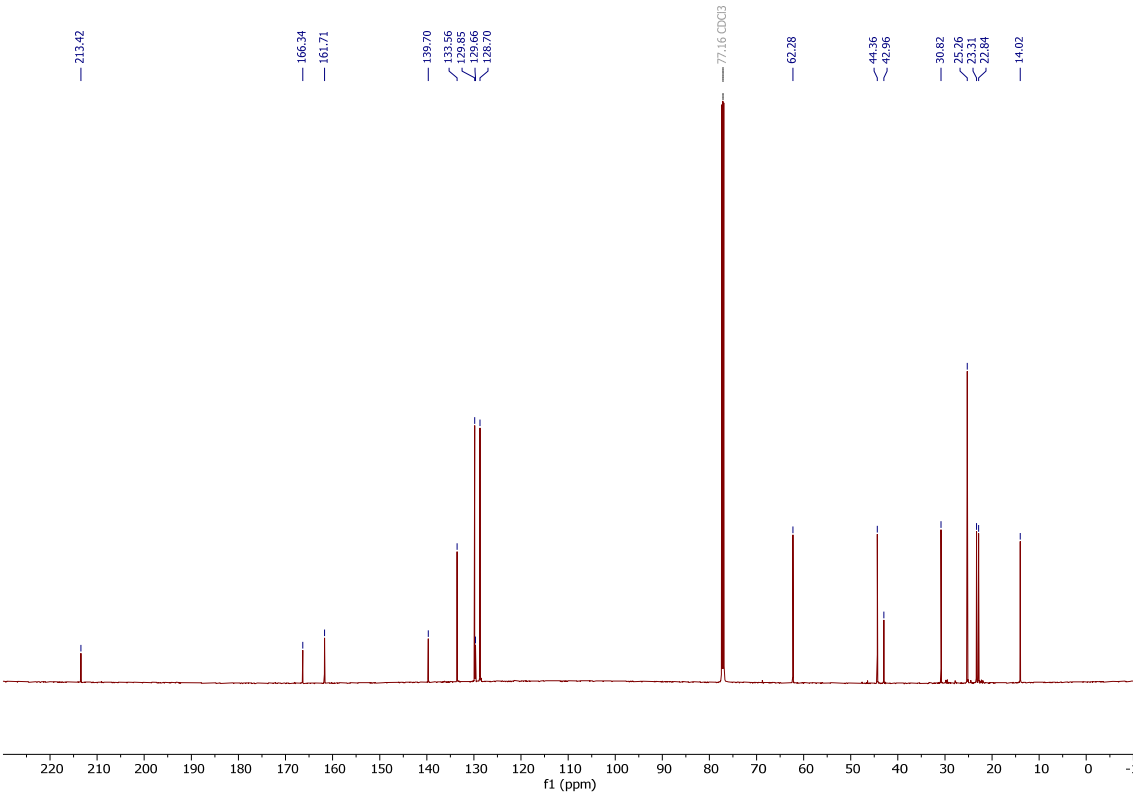

H4019.10.ser
Yong Ho Lee/Morandi LEY-LB-384-13-B OPR:RF
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

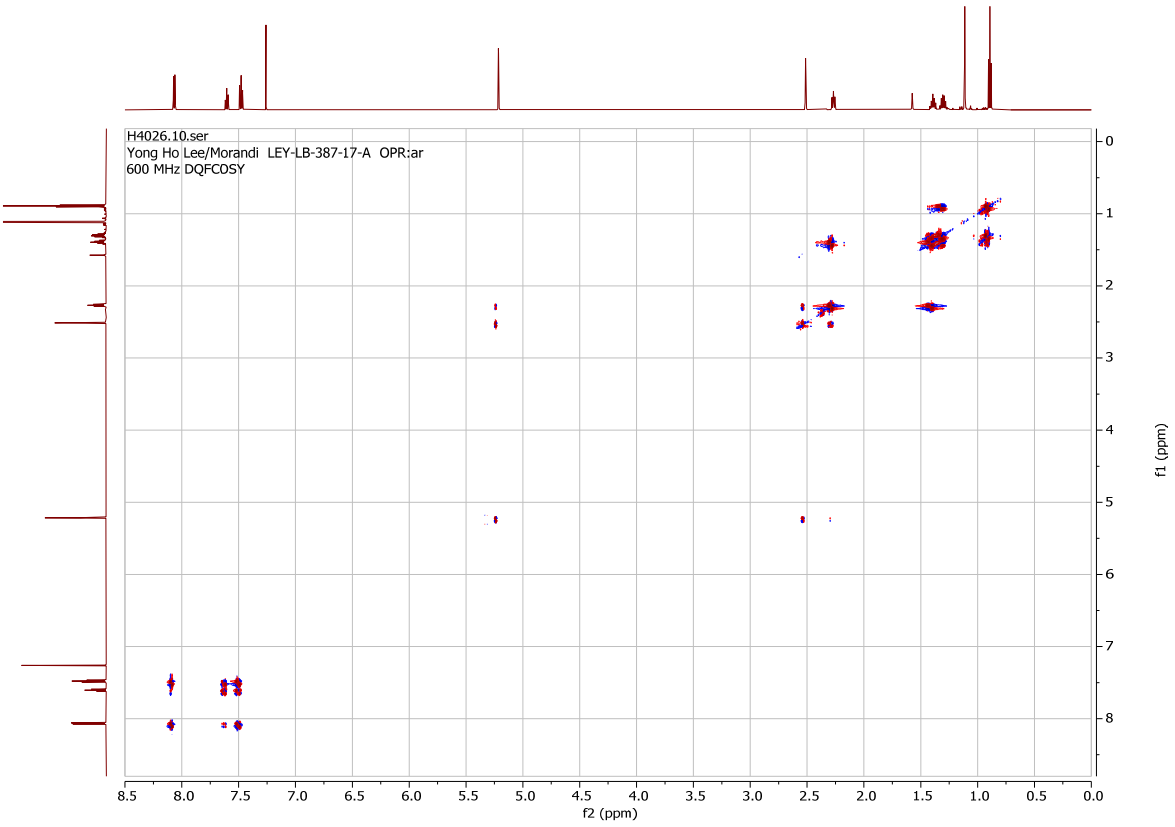

H4019.12.ser
Yong Ho Lee/Morandi LEY-LB-384-13-B OPR:RF
600 MHz HMBC
f2 (ppm)
f1 (ppm)

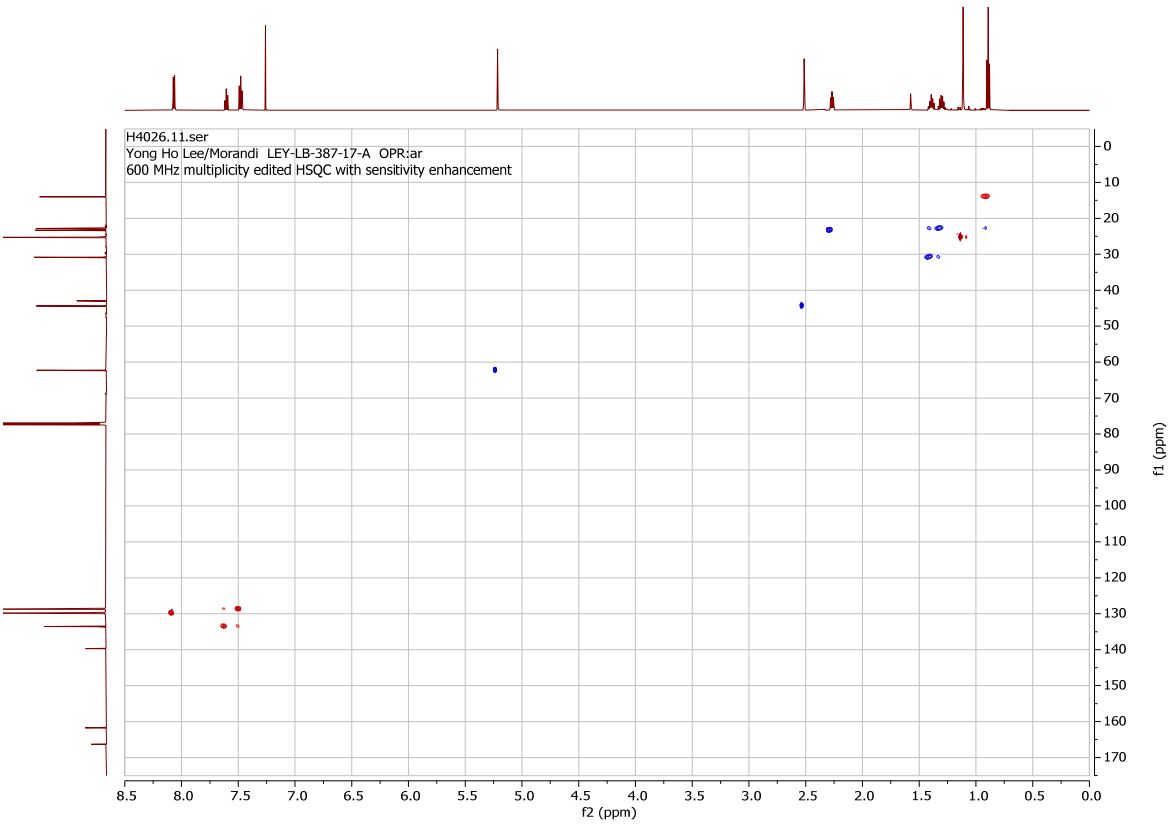

H4019.13.ser
Yong Ho Lee/Morandi LEY-LB-384-13-B OPR:RF
600 MHz NOESY
f2 (ppm)
f1 (ppm)

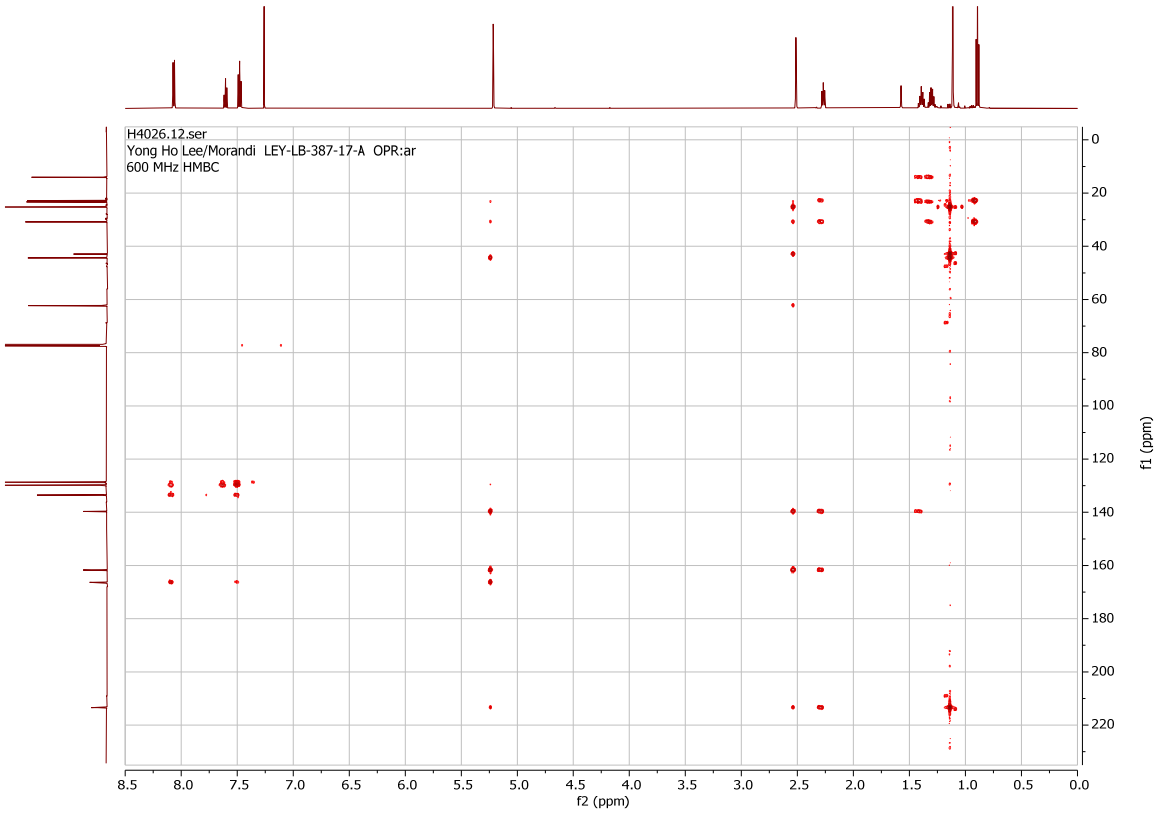
(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)methyl benzoate (**3bv-1**, major).

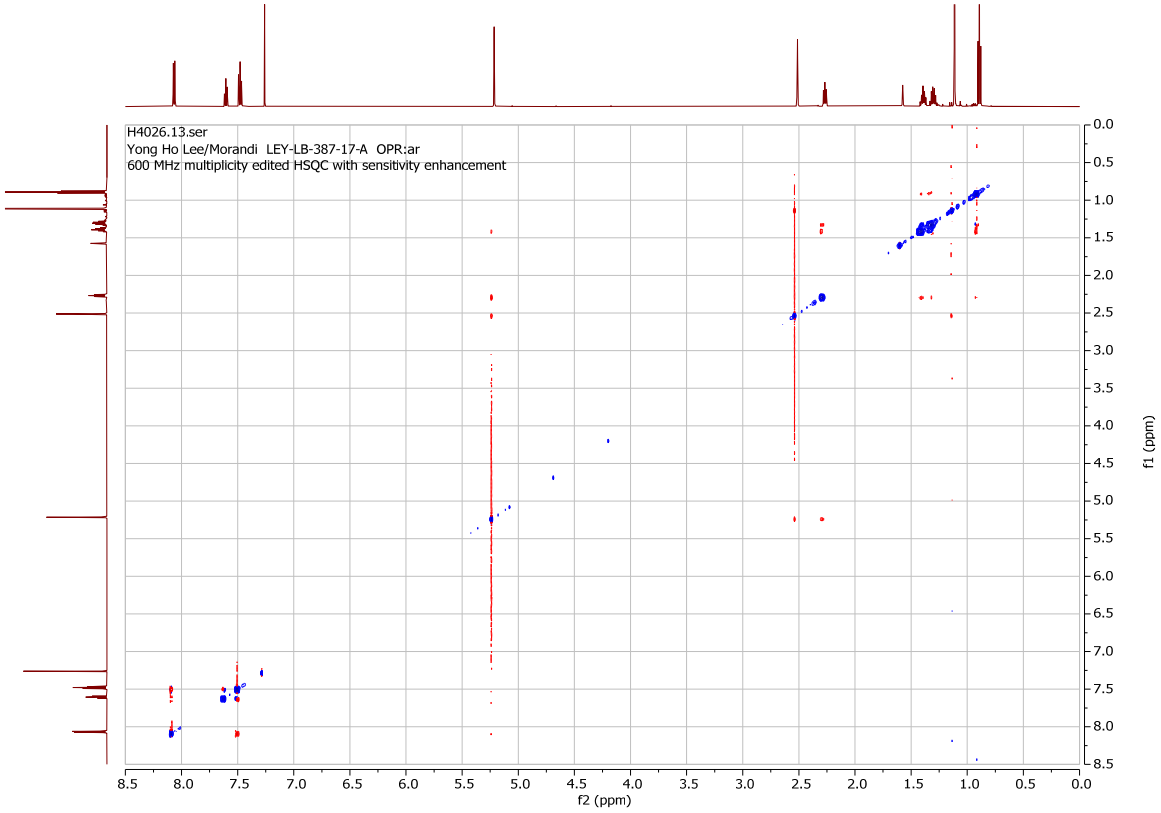




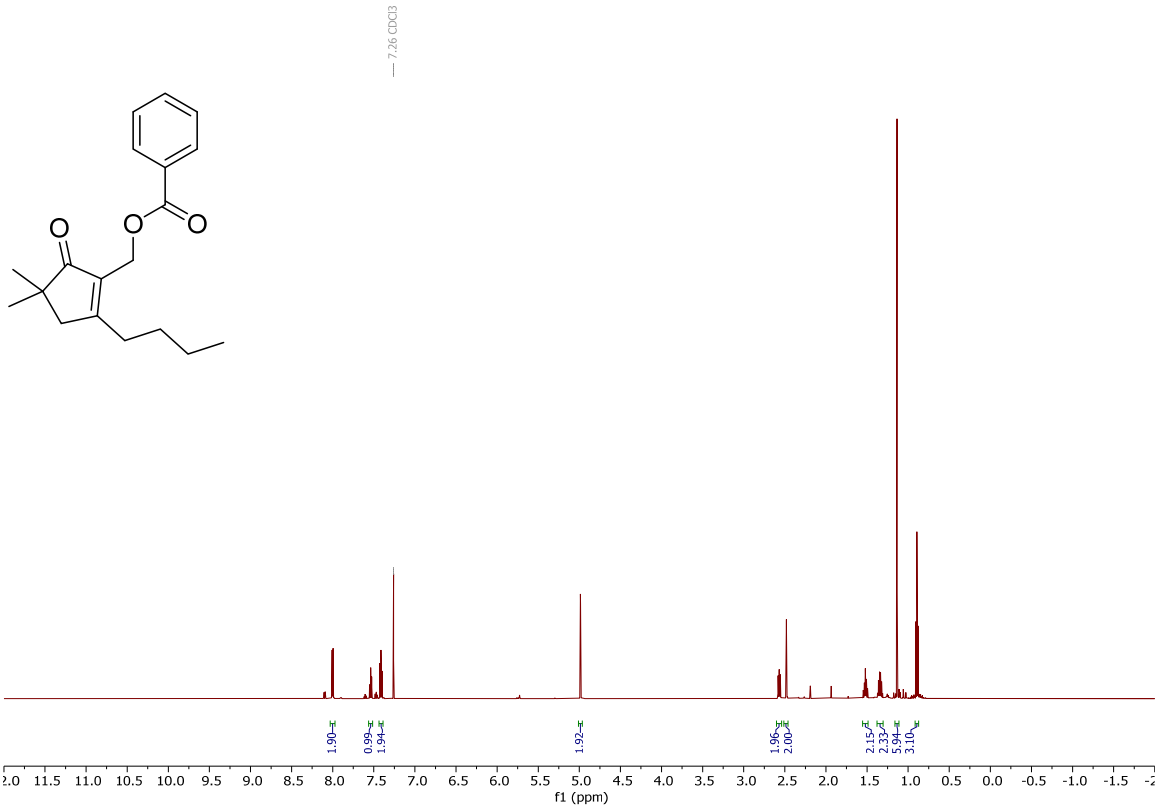

H4026.10.ser
Yong Ho Lee/Morandi LEY-LB-387-17-A OPR:ar
600 MHz DQFCOSY
f2 (ppm)
f1 (ppm)

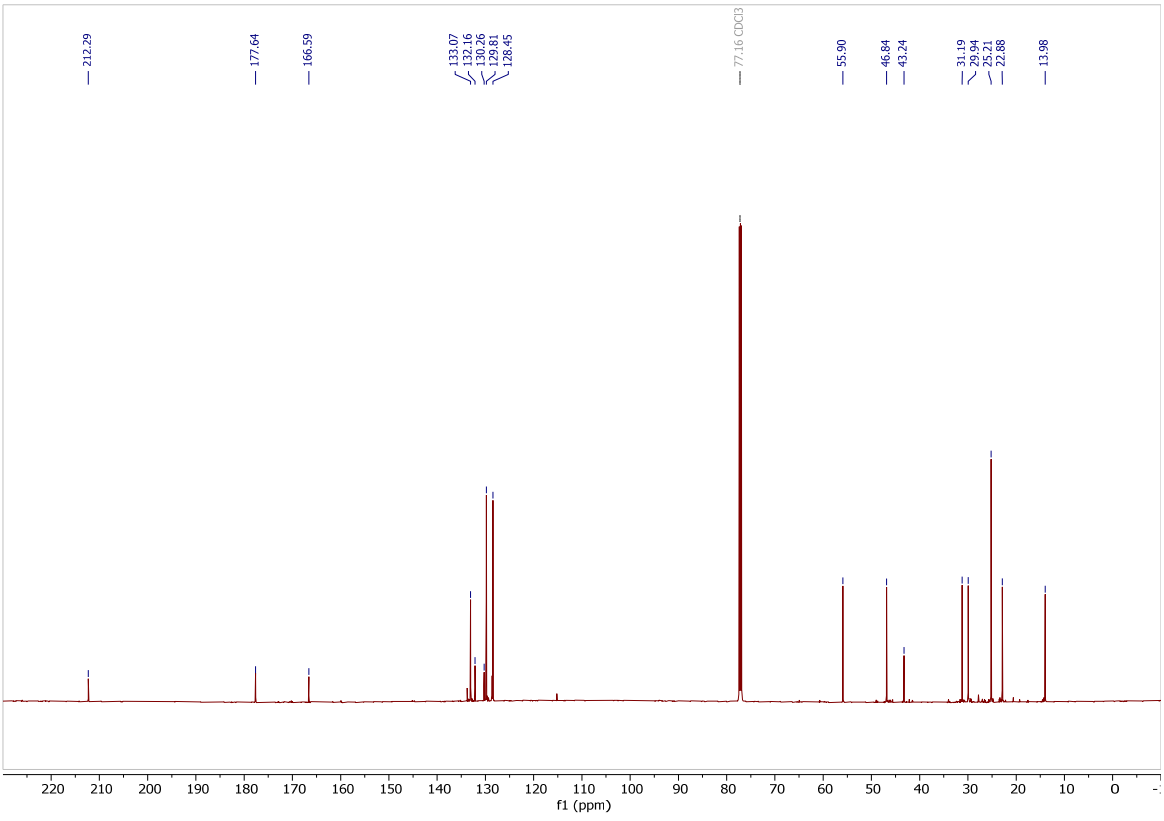

H4026.11.ser
Yong Ho Lee/Morandi LEY-LB-387-17-A OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

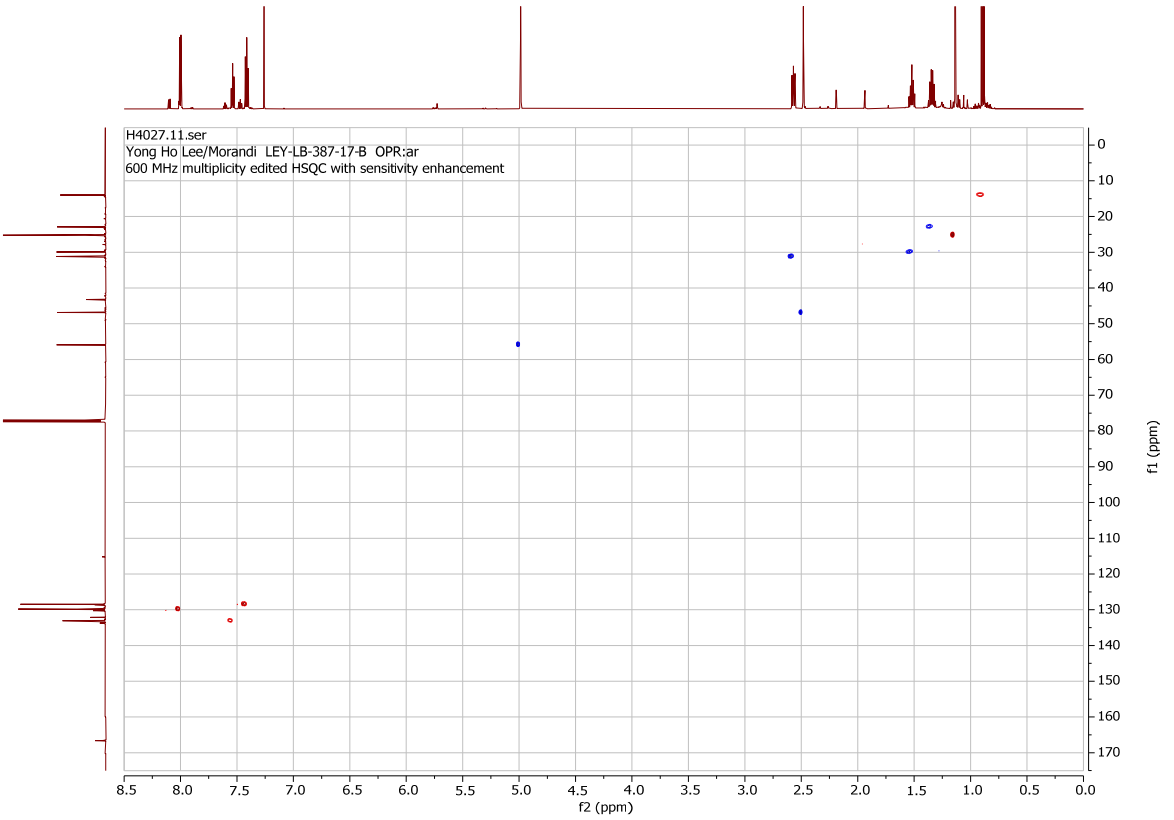

H4026.12.ser
Yong Ho Lee/Morandi LEY-LB-387-17-A OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

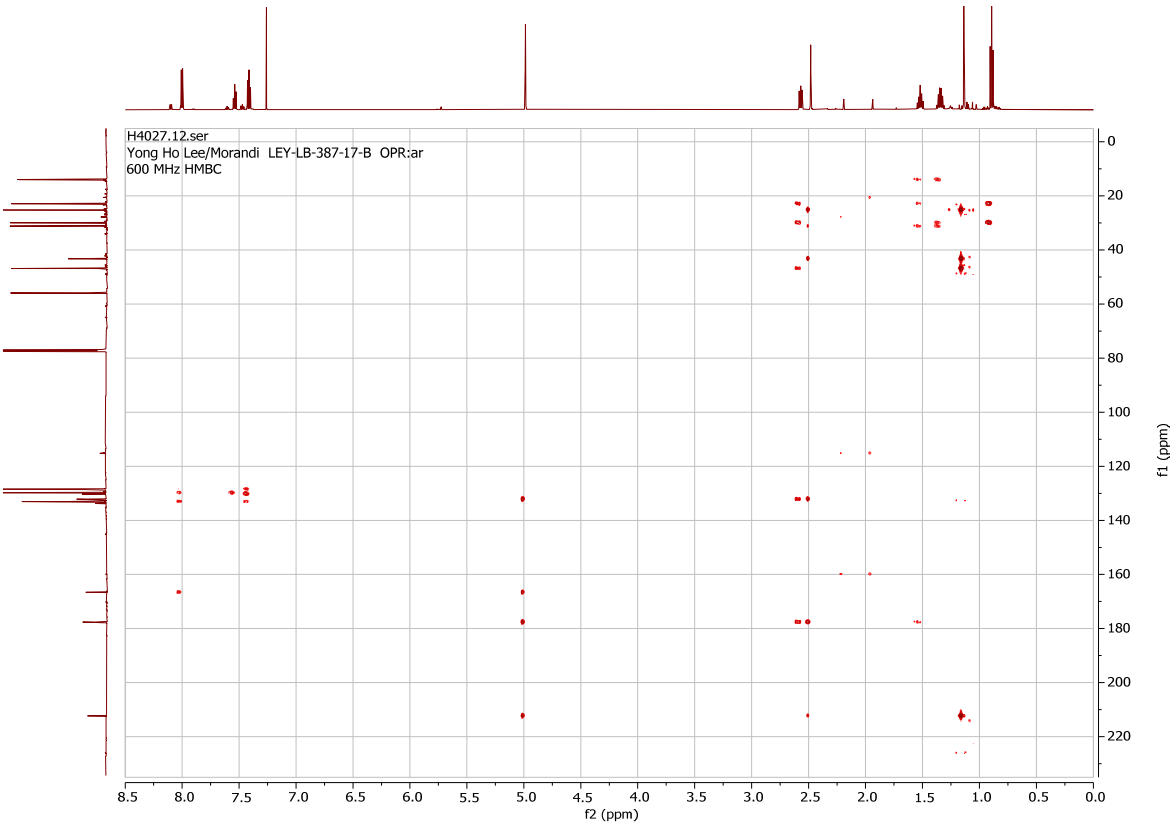

H4026.13.ser
Yong Ho Lee/Morandi LEY-LB-387-17-A OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)methyl benzoate (**3bv-2**, minor).

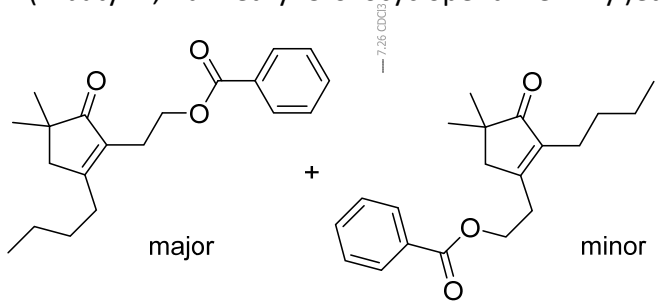


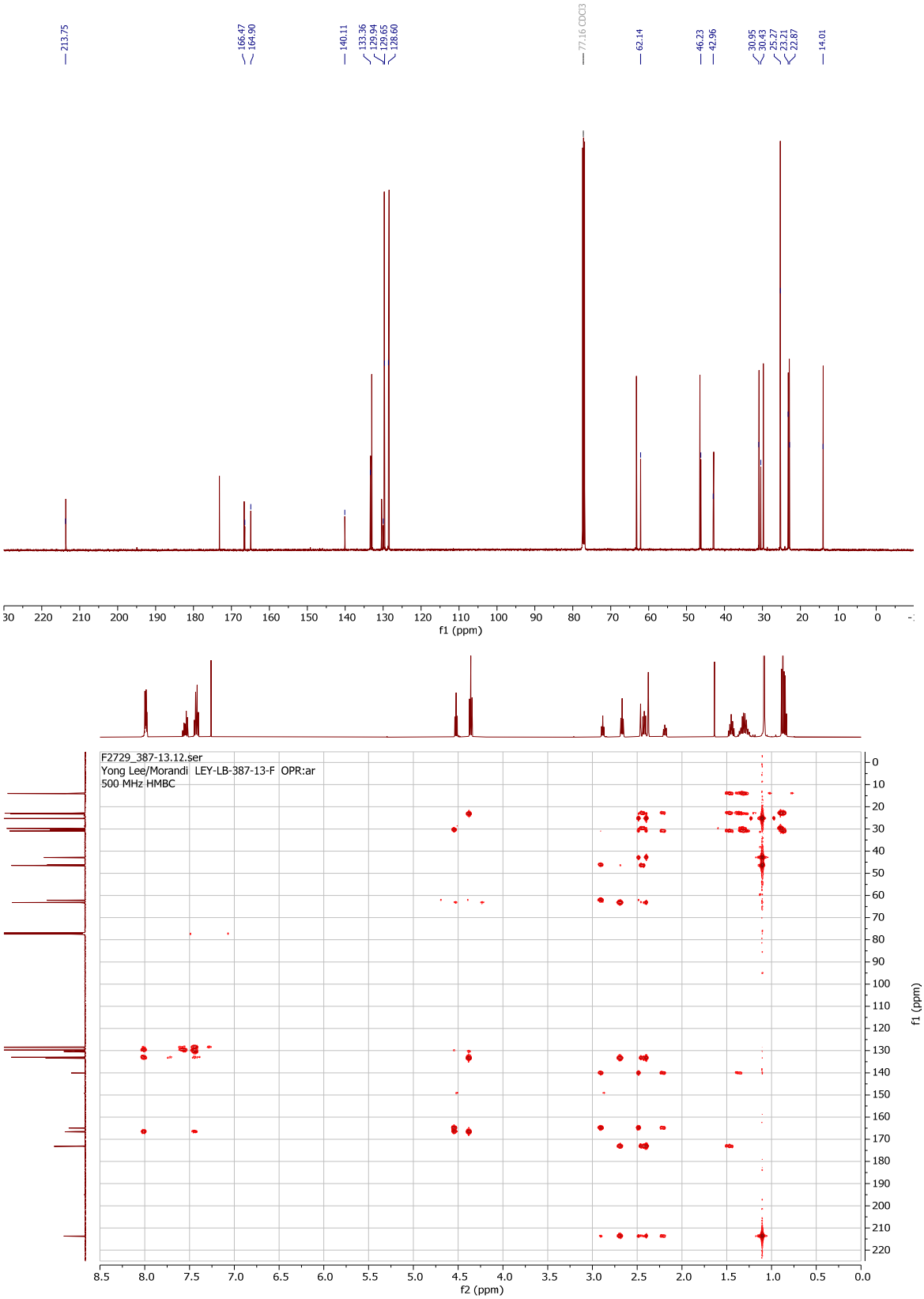


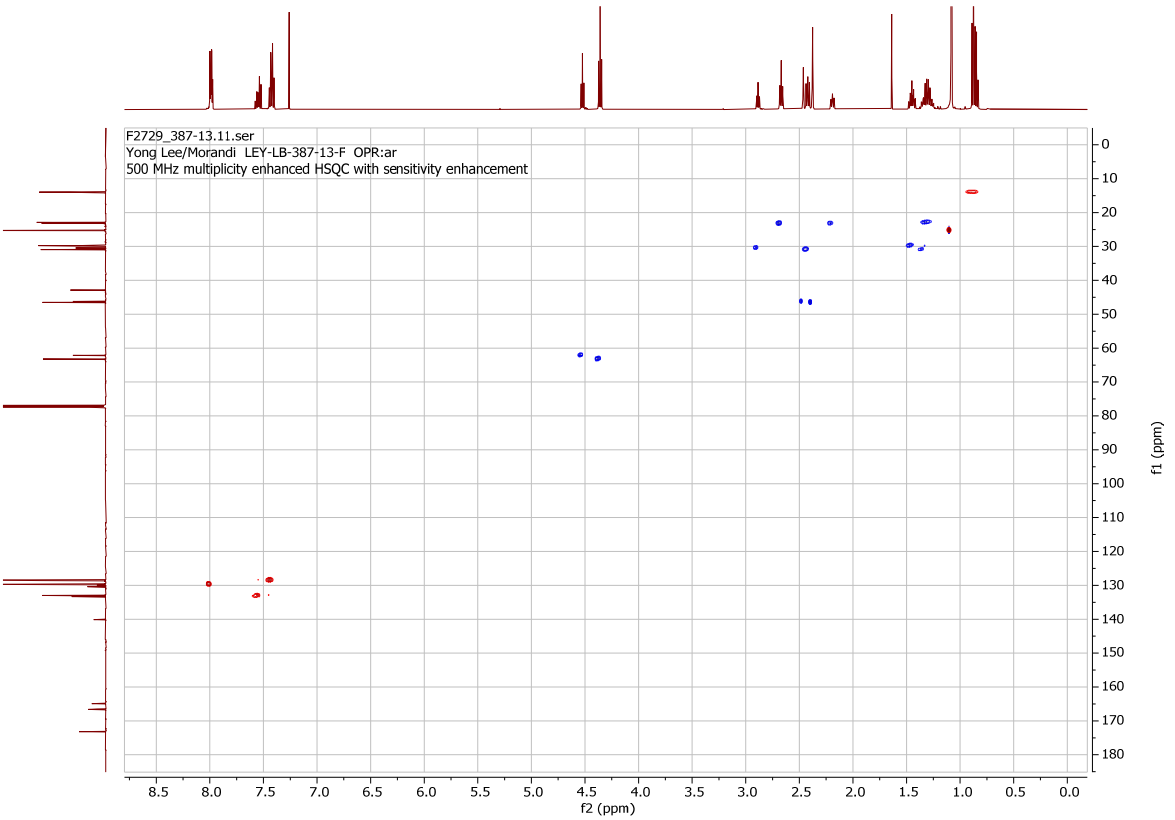

H4027.11.ser
Yong Ho Lee/Morandi LEY-LB-387-17-B OPR:ar
600 MHz multiplicity edited HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

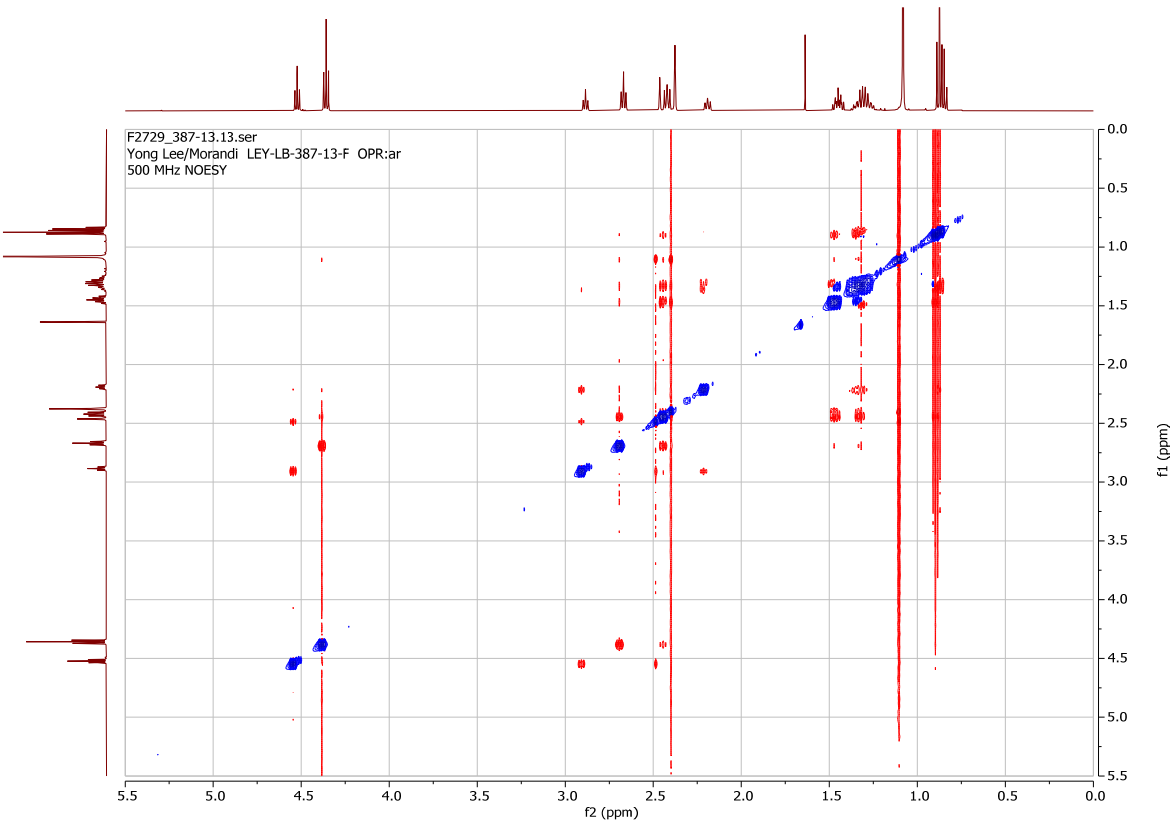

H4027.12.ser
Yong Ho Lee/Morandi LEY-LB-387-17-B OPR:ar
600 MHz HMBC
f2 (ppm)
f1 (ppm)

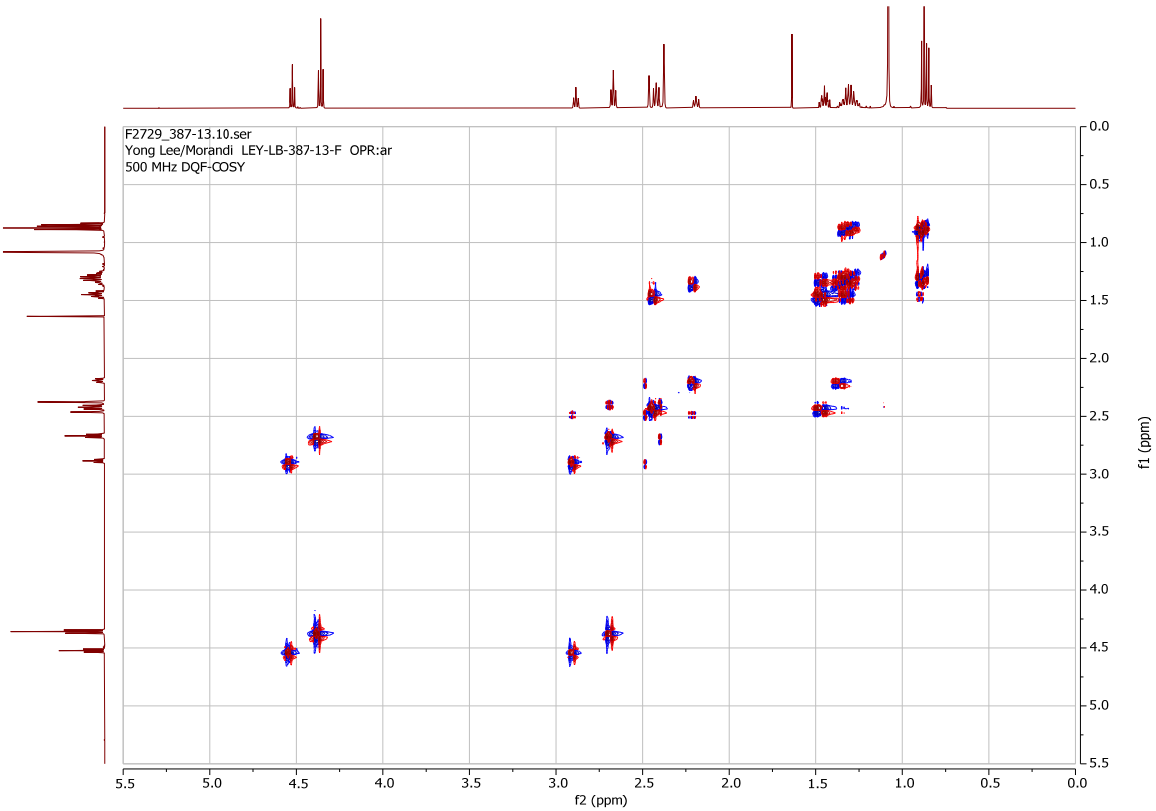
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl benzoate (**3bw-1**, major, **65**:35 mixture).
2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl benzoate (**3bw-2**, minor, 65:**35** mixture).



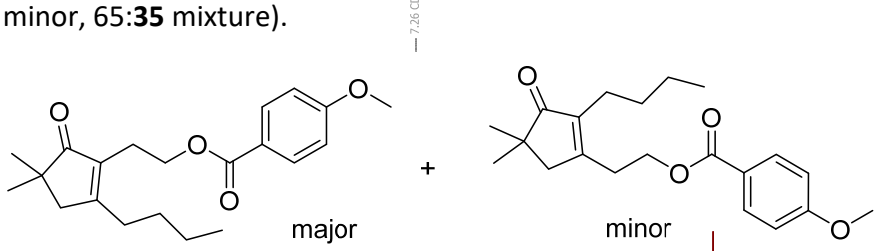

213.75
166.47
164.90
140.11
133.36
129.94
129.65
128.60
77.16 CDCl3
62.14
46.23
42.96
30.95
30.43
25.27
23.21
22.87
14.01
f1 (ppm)
F2729_387-13.12.ser
Yong Lee/Morandi LEY-LB-387-13-F OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

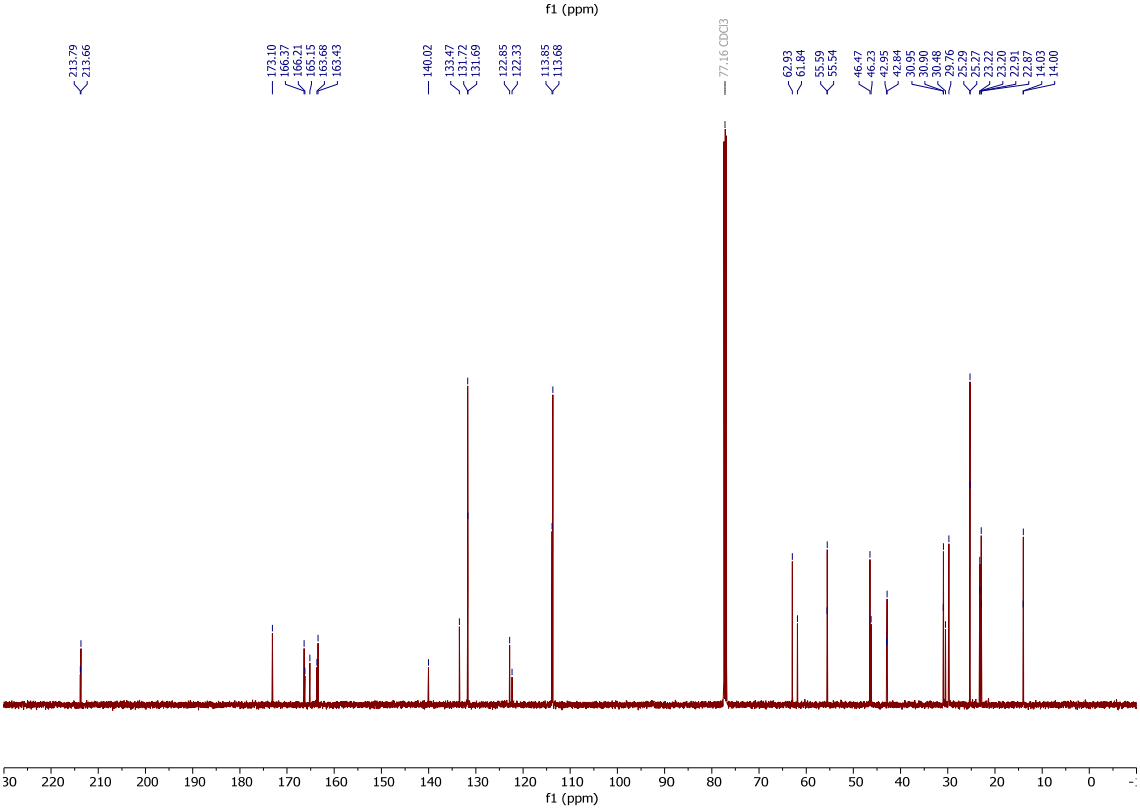

F2729_387-13.11.ser
Yong Lee/Morandi LEY-LB-387-13-F OPR:ar
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

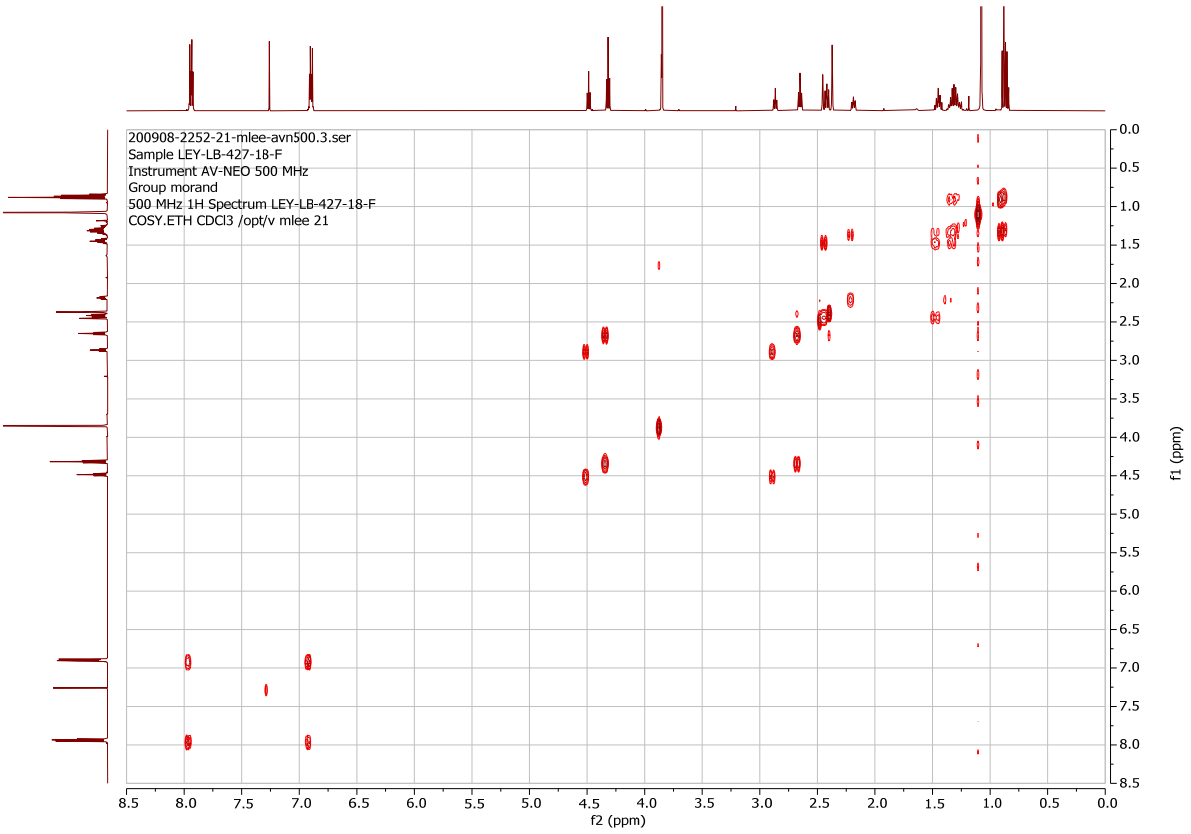

F2729_387-13.13.ser
Yong Lee/Morandi LEY-LB-387-13-F OPR:ar
500 MHz NOESY
f2 (ppm)
f1 (ppm)

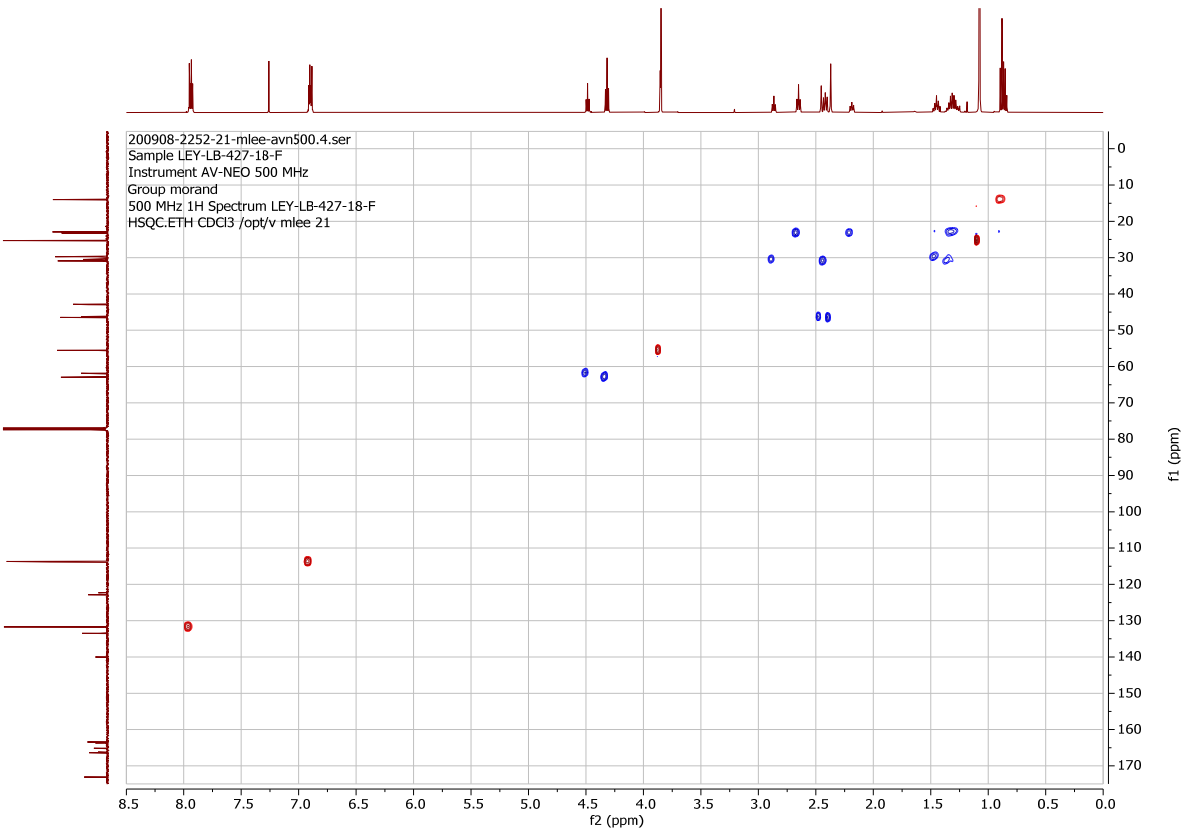

F2729_387-13.10.ser
Yong Lee/Morandi LEY-LB-387-13-F OPR:ar
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

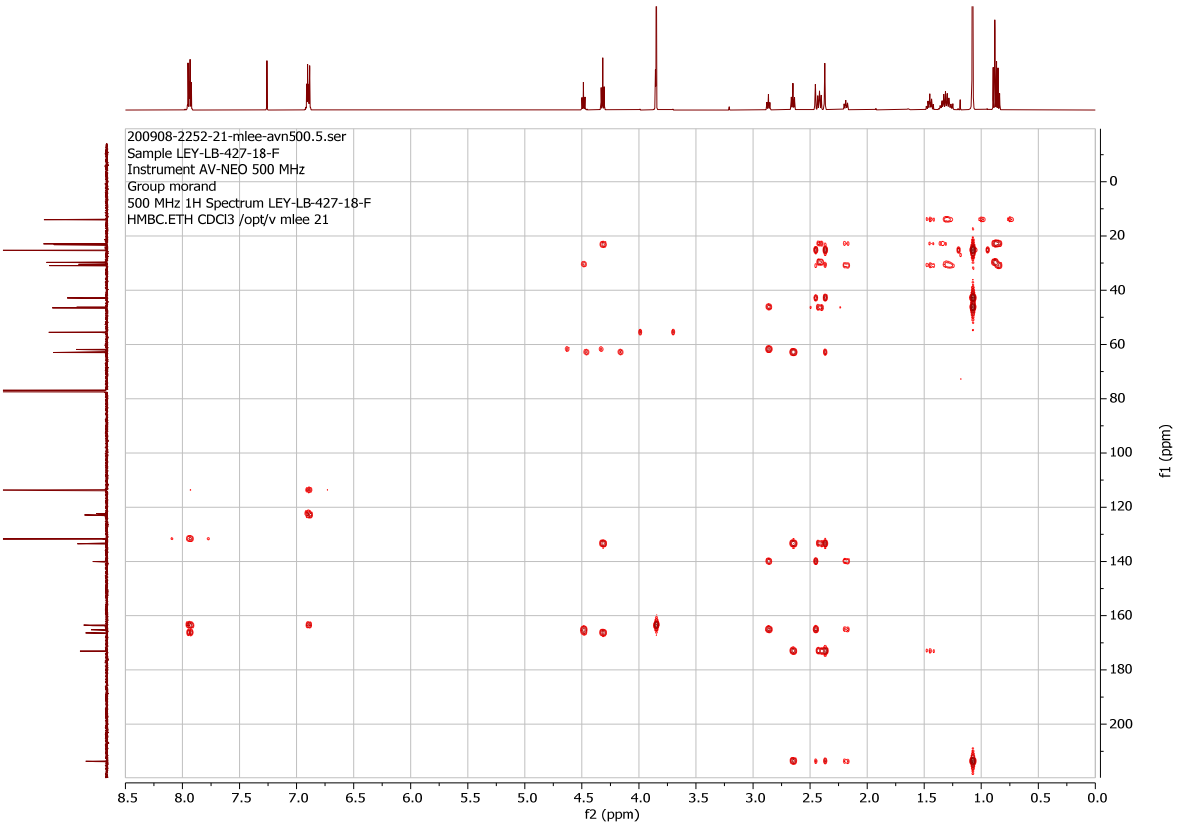
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl 4-methoxybenzoate (**3bx-1**, major, **65**:35 mixture). 2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl 4-methoxybenzoate (**3bx-2**, minor, 65:**35** mixture).

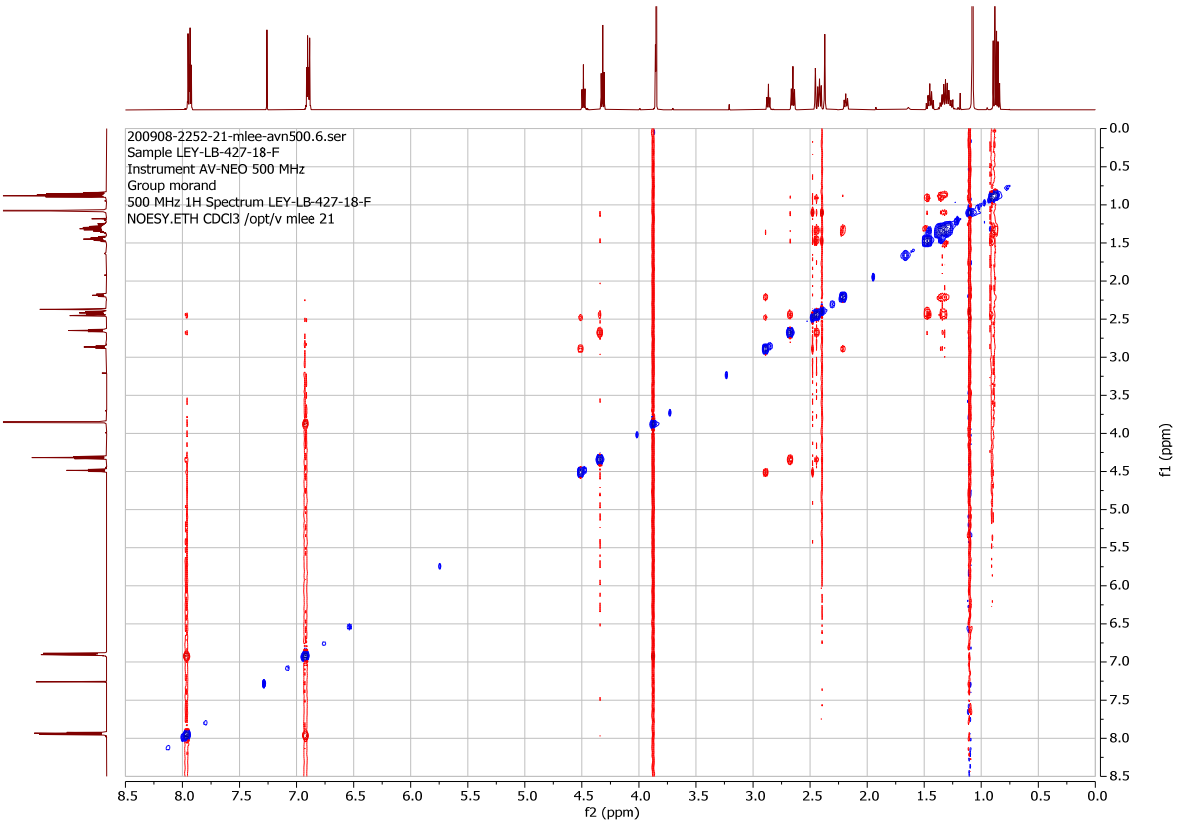




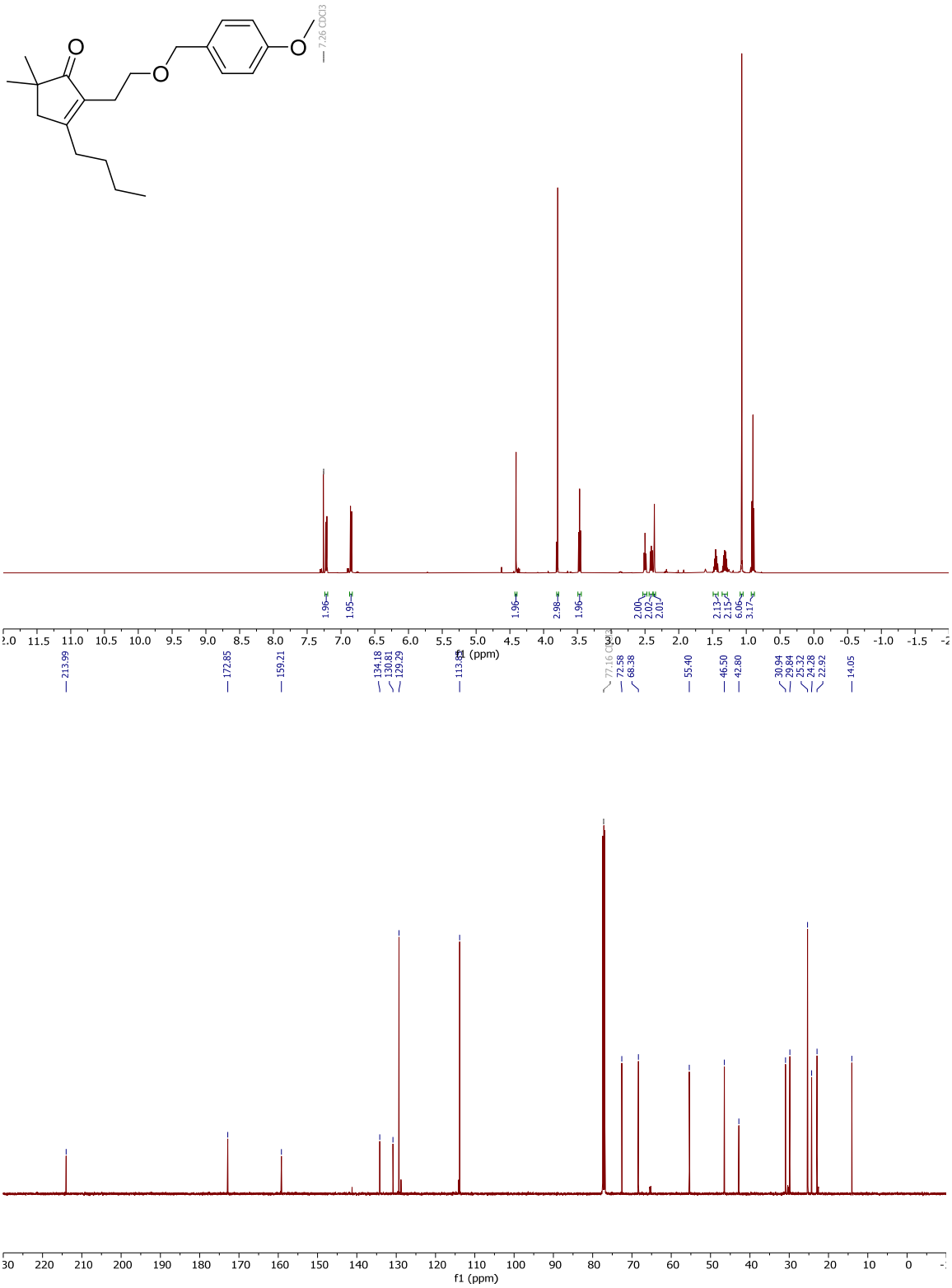

200908-2252-21-mlee-avn500.3.ser
Sample LEY-LB-427-18-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-18-F
COSY.ETH CDCl3 /opt/v mlee 21
f2 (ppm)
f1 (ppm)

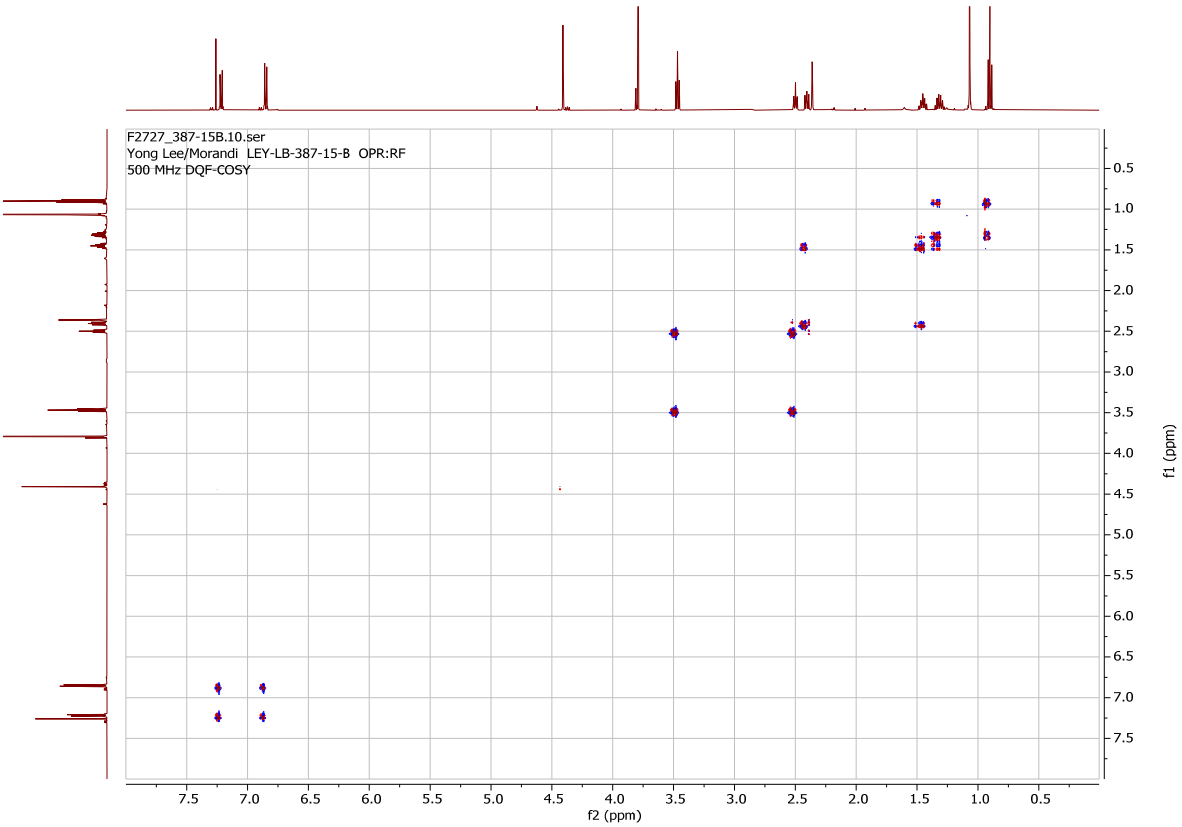

200908-2252-21-mlee-avn500.4.ser
Sample LEY-LB-427-18-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-18-F
HSQC.ETH CDCl3 /opt/v mlee 21
f2 (ppm)
f1 (ppm)

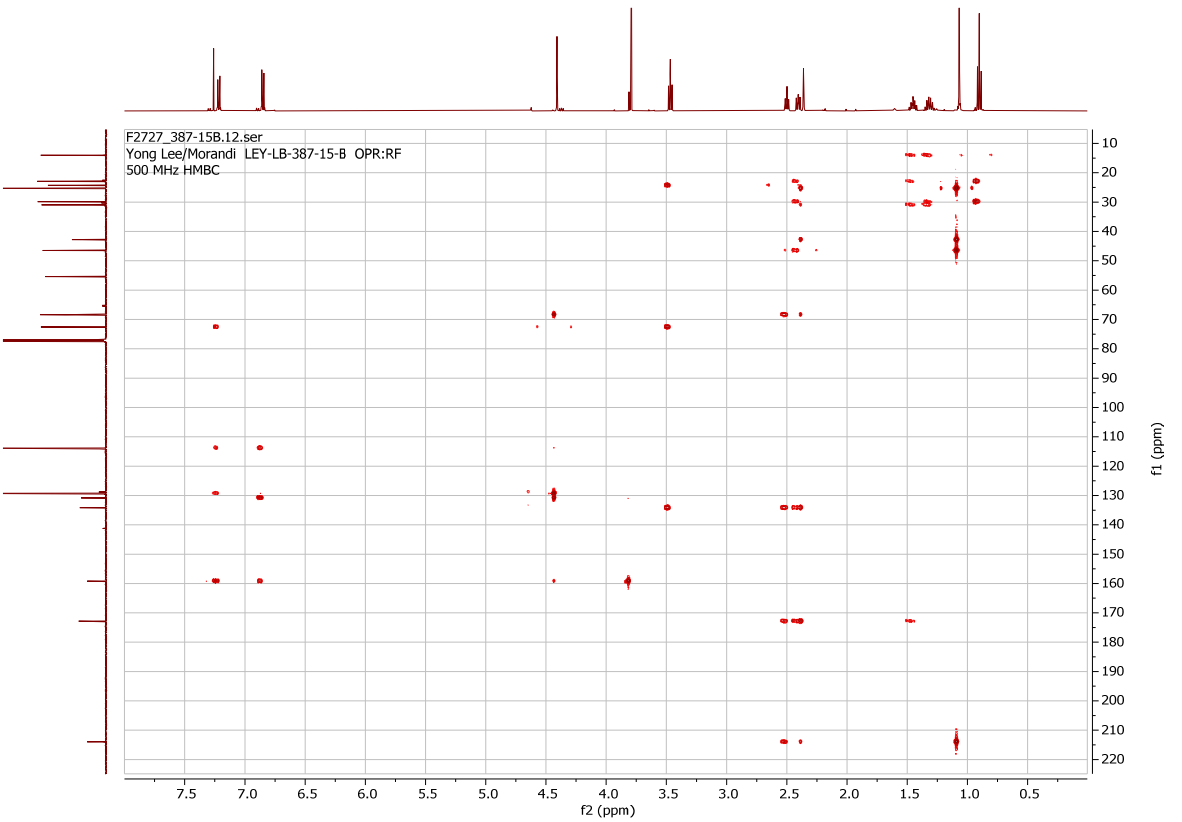

200908-2252-21-mlee-avn500.5.ser
Sample LEY-LB-427-18-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-18-F
HMBC.ETH CDCl3 /opt/v mlee 21
f2 (ppm)
f1 (ppm)

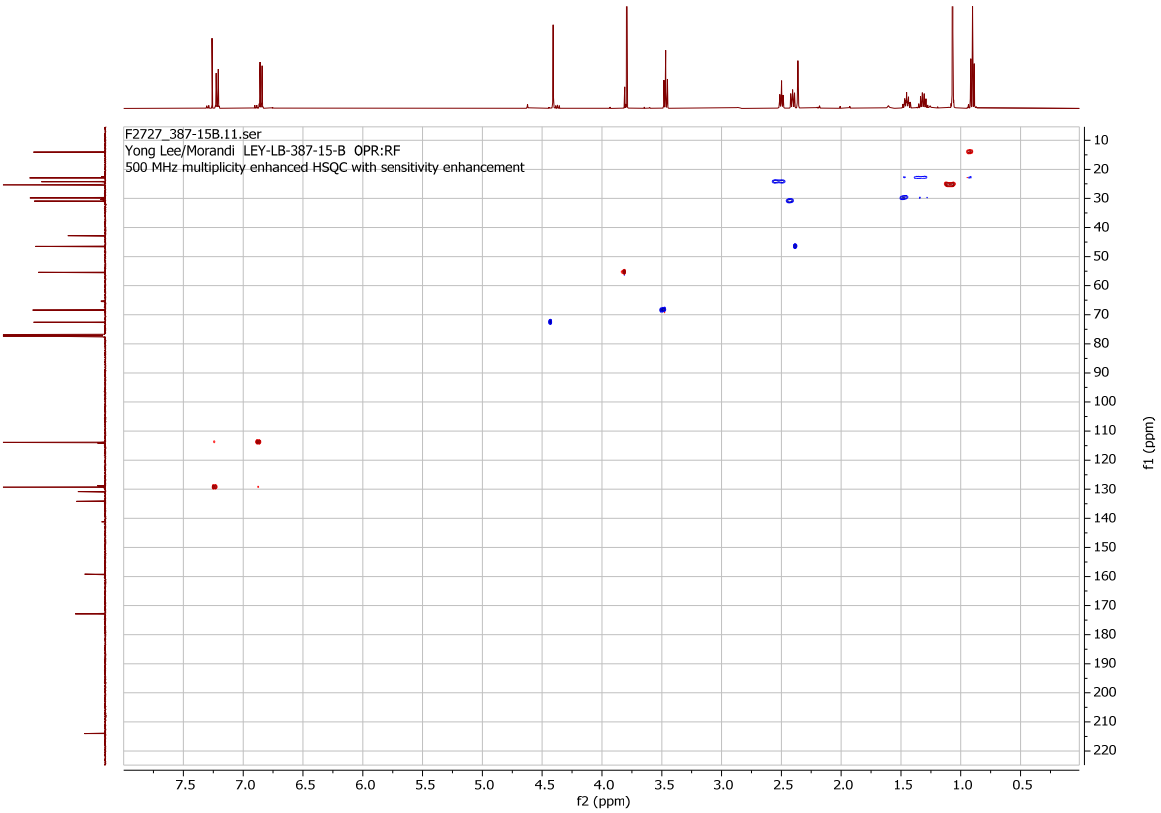

200908-2252-21-mlee-avn500.6.ser
Sample LEY-LB-427-18-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-18-F
NOESY.ETH CDCl3 /opt/v mlee 21
f2 (ppm)
f1 (ppm)

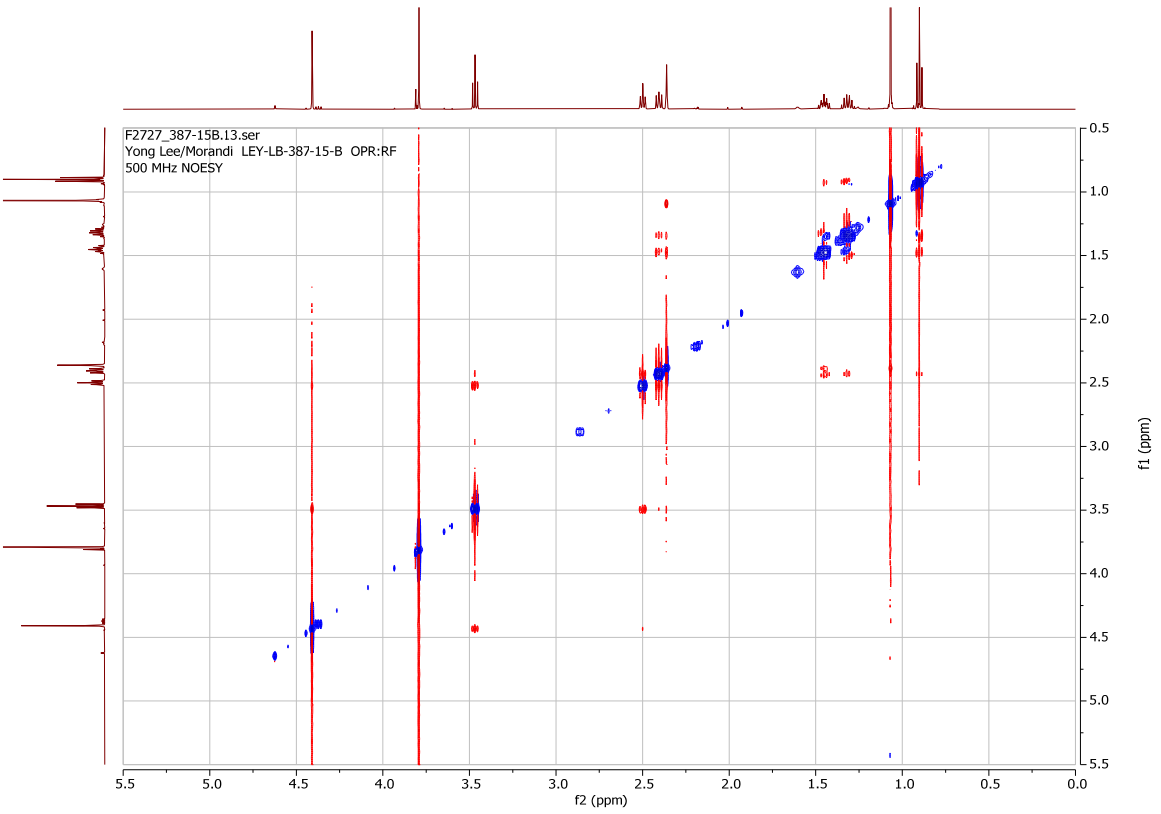
3-butyl-2-(2-((4-methoxybenzyl)oxy)ethyl)-5,5-dimethylcyclopent-2-en-1-one (**3by-1**, major).



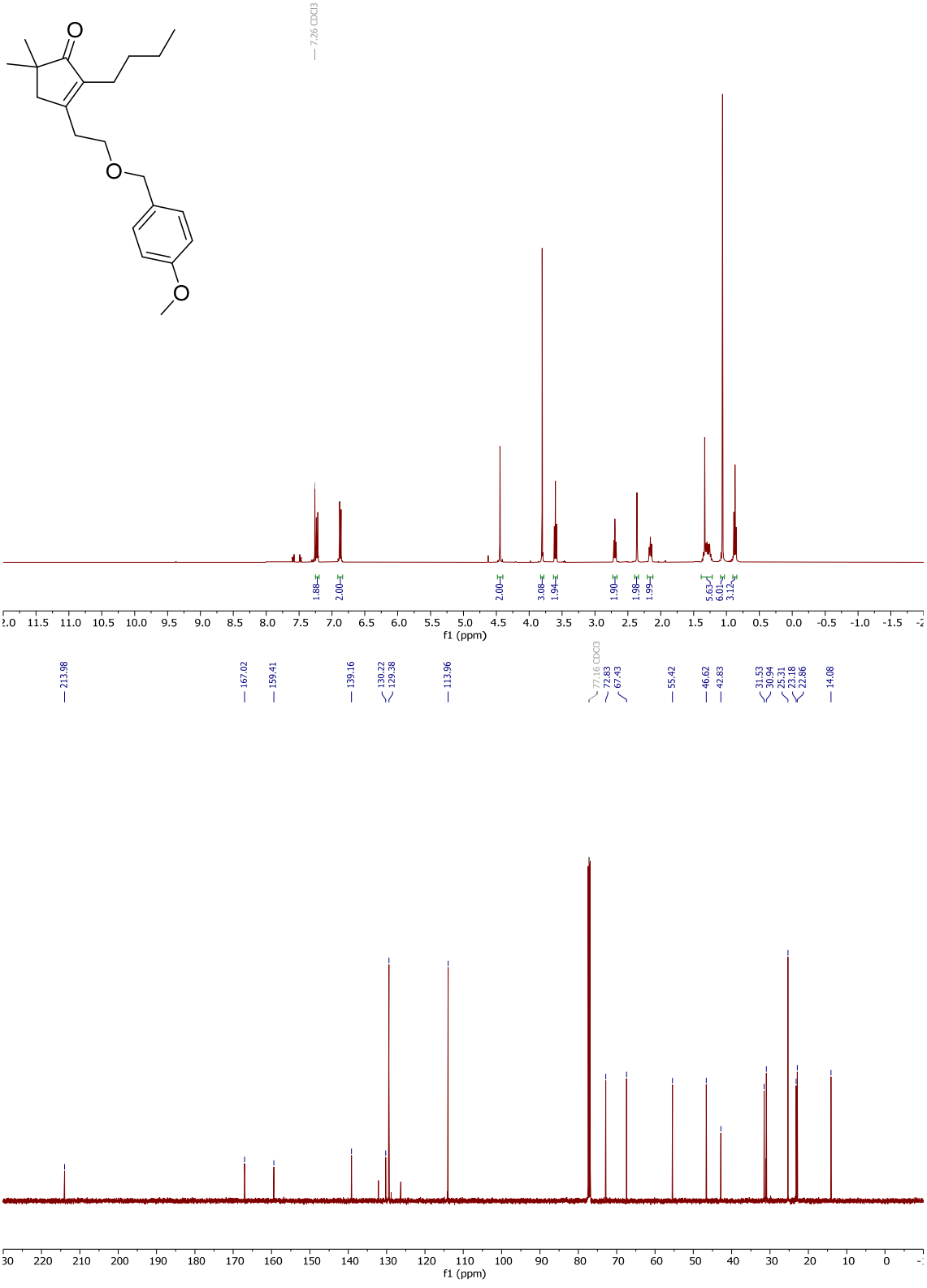

F2727_387-15B.10.ser
Yong Lee/Morandi LEY-LB-387-15-B OPR:RF
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

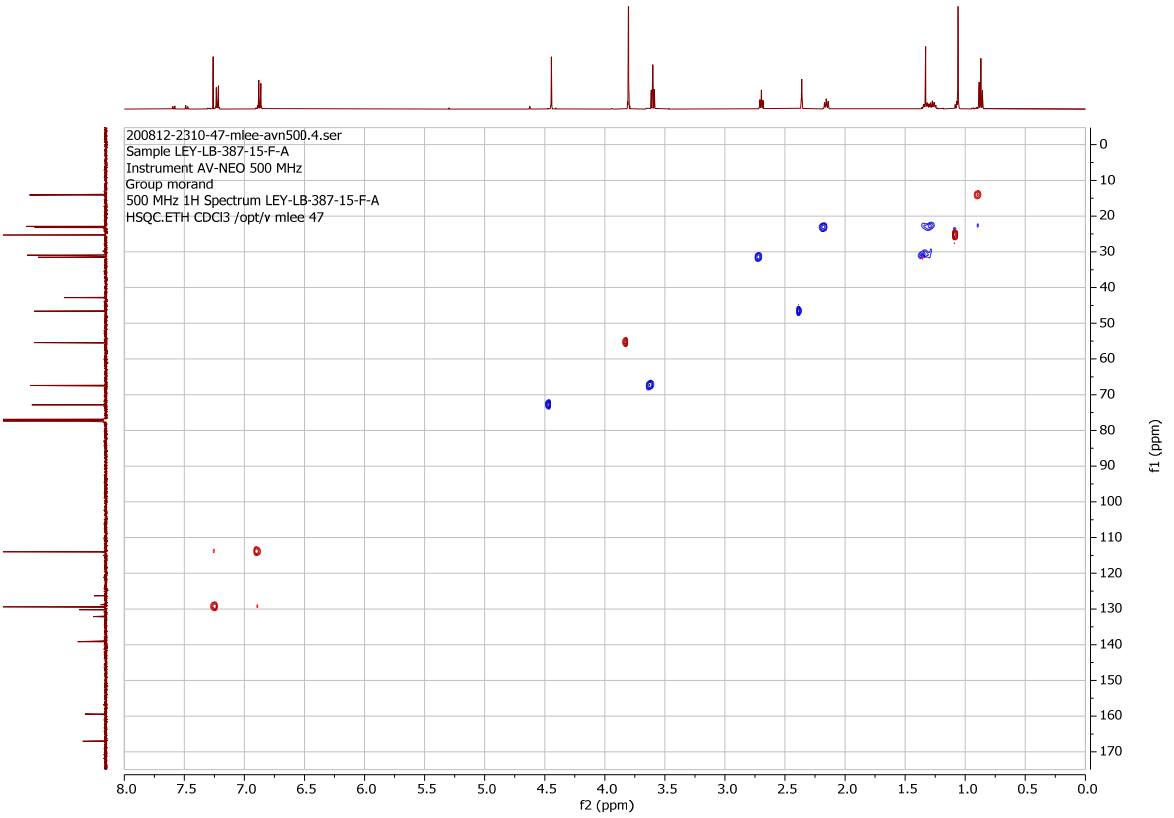

F2727_387-15B.12.ser
Yong Lee/Morandi LEY-LB-387-15-B OPR:RF
500 MHz HMBC
f2 (ppm)
f1 (ppm)

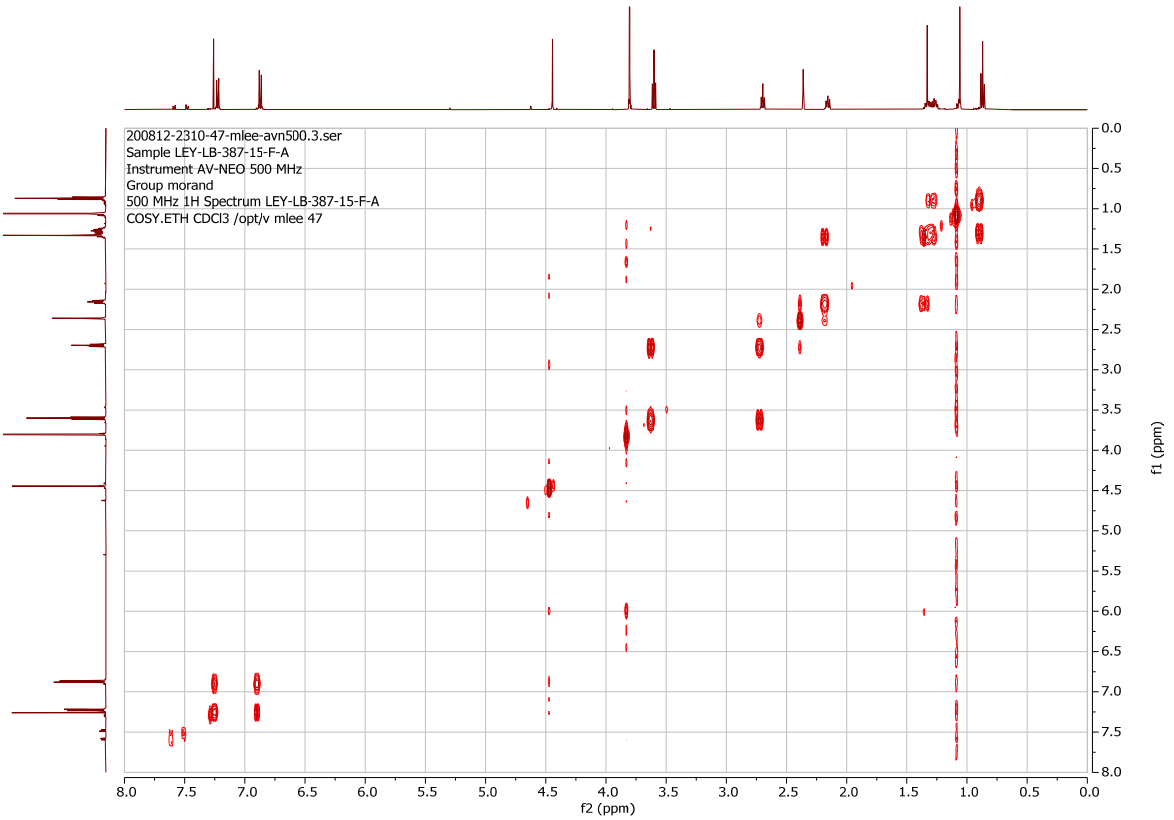

F2727_387-15B.11.ser
Yong Lee/Morandi LEY-LB-387-15-B OPR:RF
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

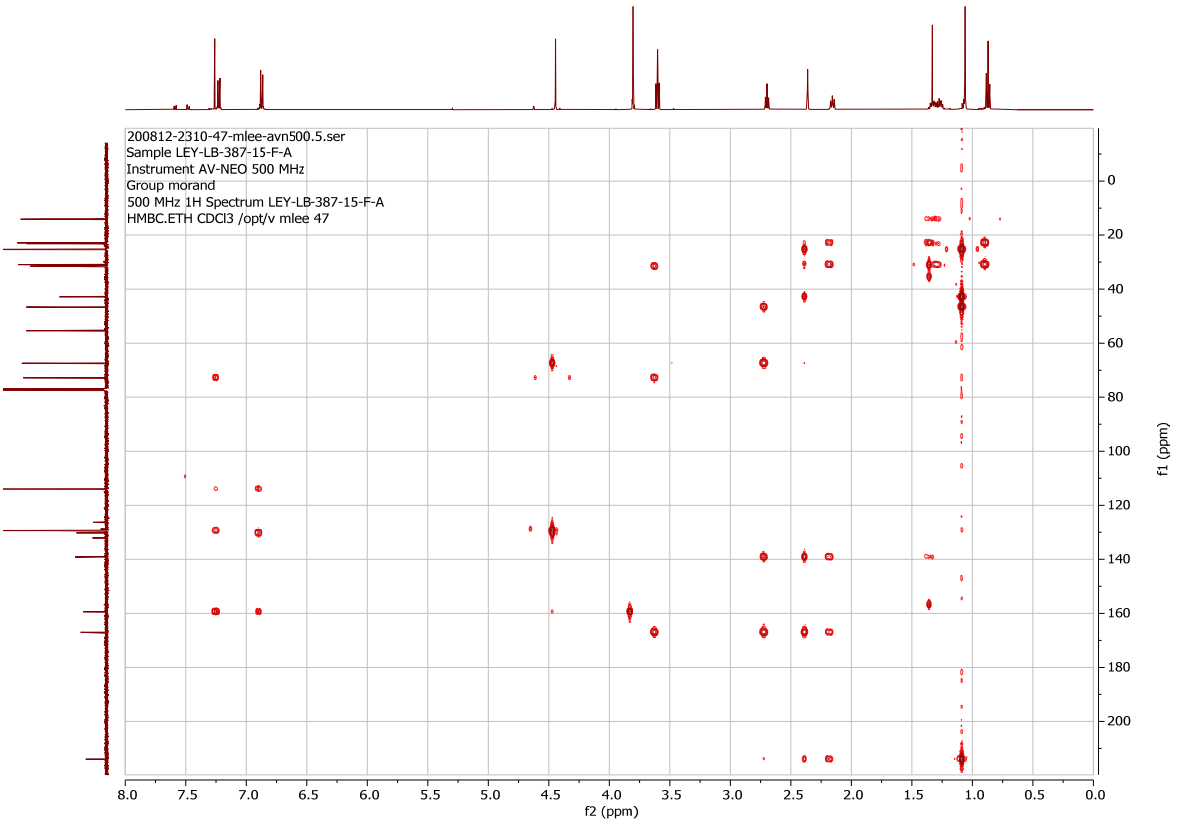

F2727_387-15B.13.ser
Yong Lee/Morandi LEY-LB-387-15-B OPR:RF
500 MHz NOESY
f2 (ppm)
f1 (ppm)

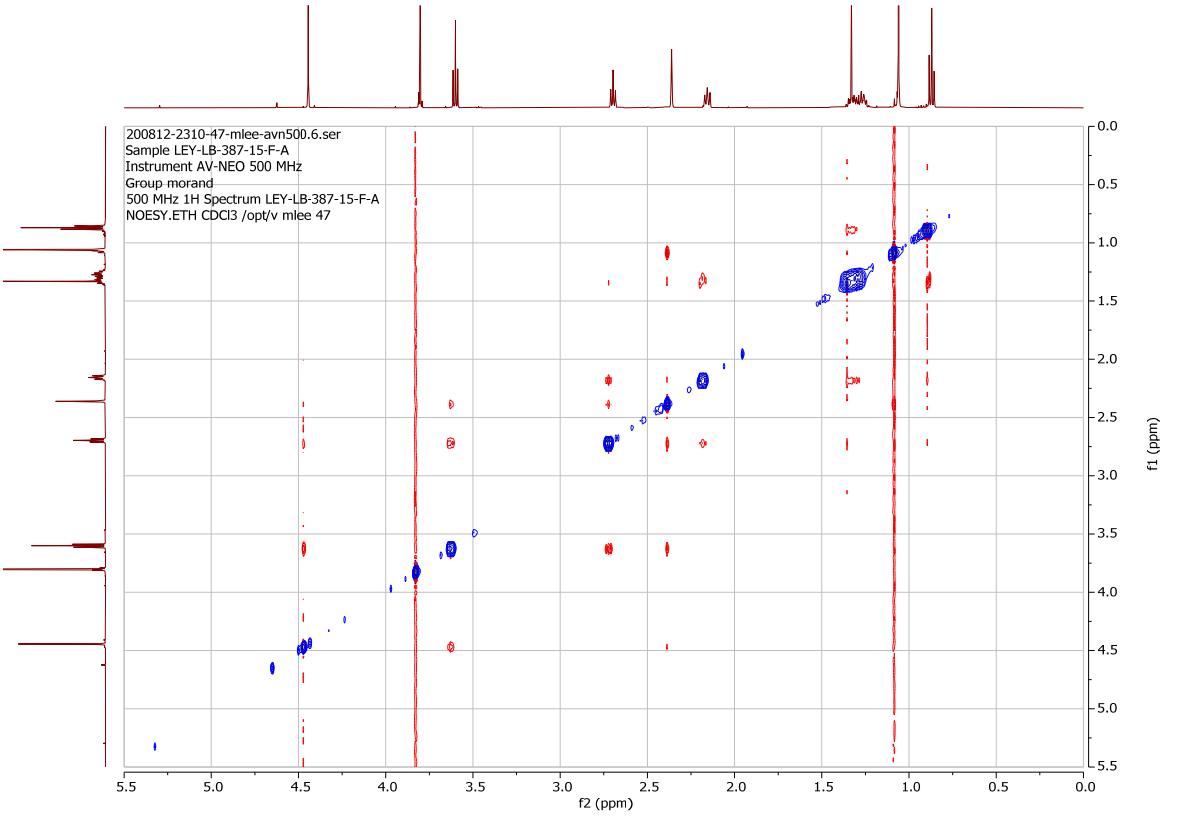
2-butyl-3-(2-((4-methoxybenzyl)oxy)ethyl)-5,5-dimethylcyclopent-2-en-1-one (**3by-2**, minor).



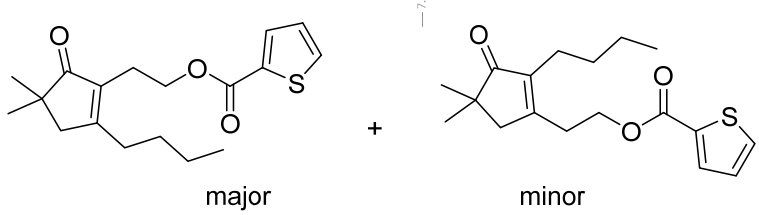

200812-2310-47-mlee-avn500.4.ser
Sample LEY-LB-387-15-F-A
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-15-F-A
HSQC.ETH CDCl3 /opt/v mlee 47
f2 (ppm)
f1 (ppm)

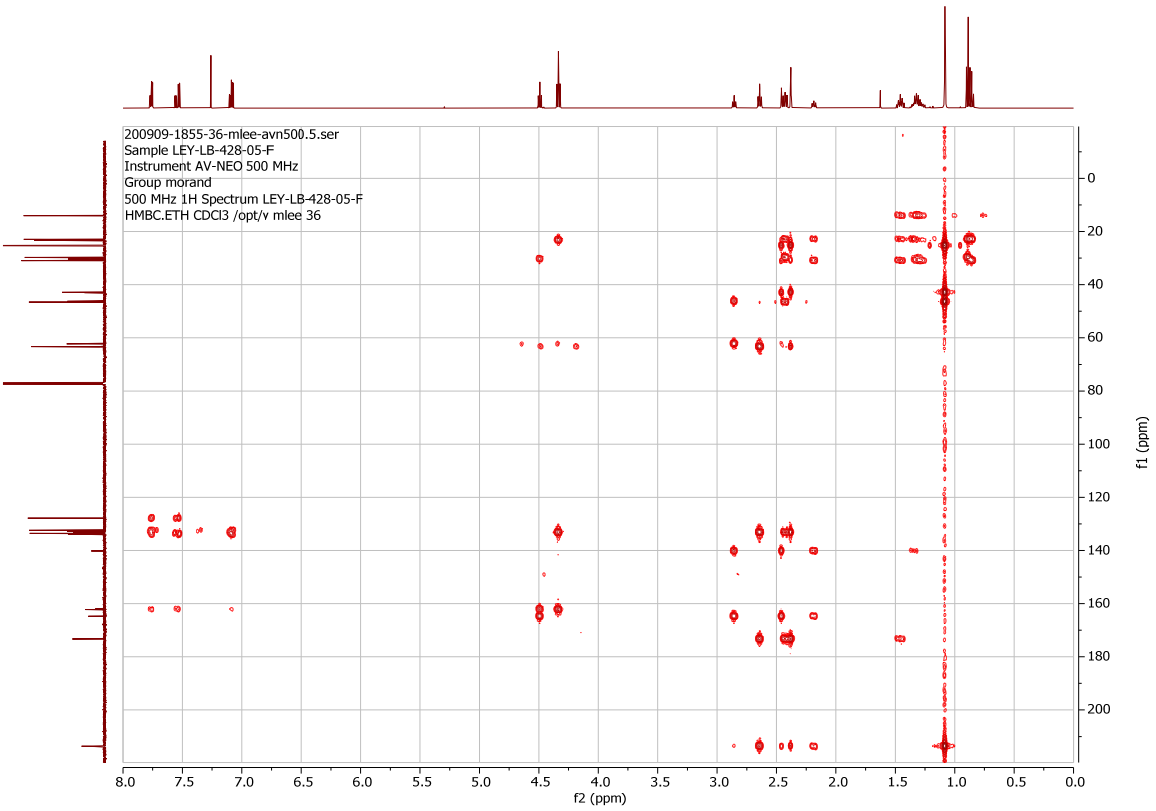

200812-2310-47-mlee-avn500.3.ser
Sample LEY-LB-387-15-F-A
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-15-F-A
COSY.ETH CDCl3 /opt/v mlee 47
f2 (ppm)
f1 (ppm)

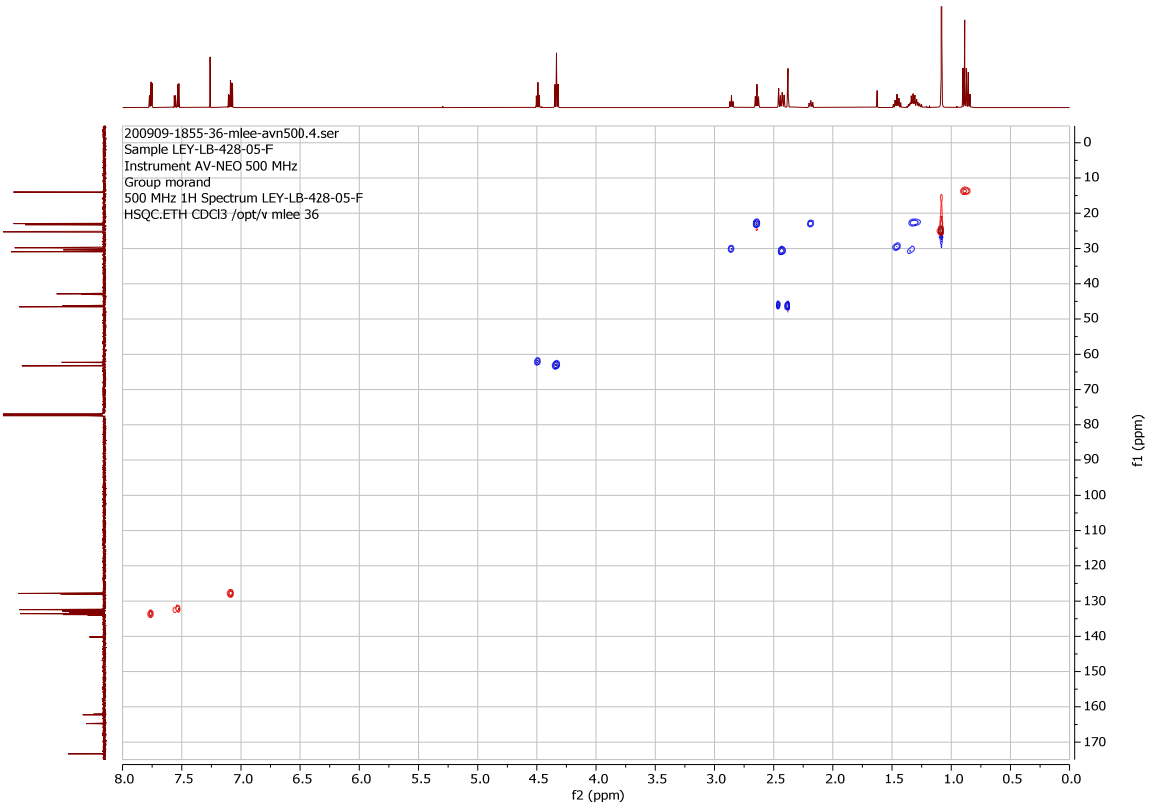

200812-2310-47-mlee-avn500.5.ser
Sample LEY-LB-387-15-F-A
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-15-F-A
HMBC.ETH CDCl3 /opt/v mlee 47
f1 (ppm)
f2 (ppm)

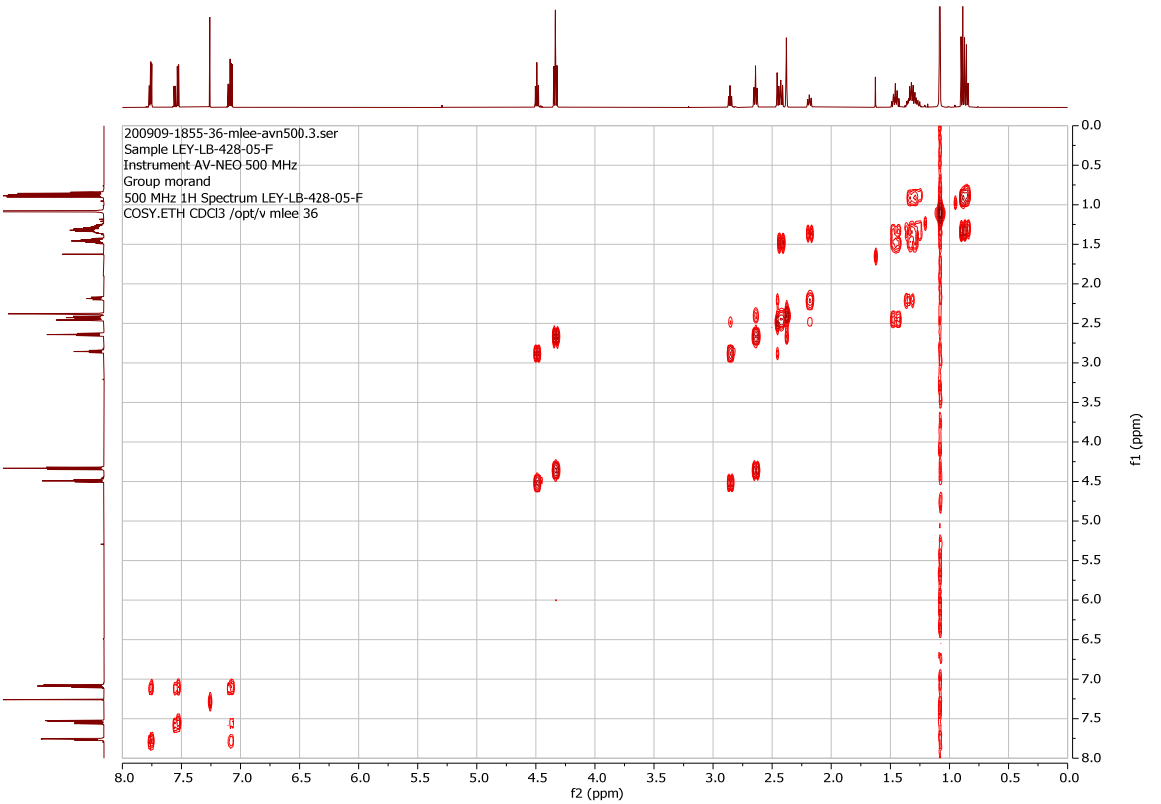

200812-2310-47-mlee-avn500.6.ser
Sample LEY-LB-387-15-F-A
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-15-F-A
NOESY.ETH CDCl3 /opt/v mlee 47
f1 (ppm)
f2 (ppm)

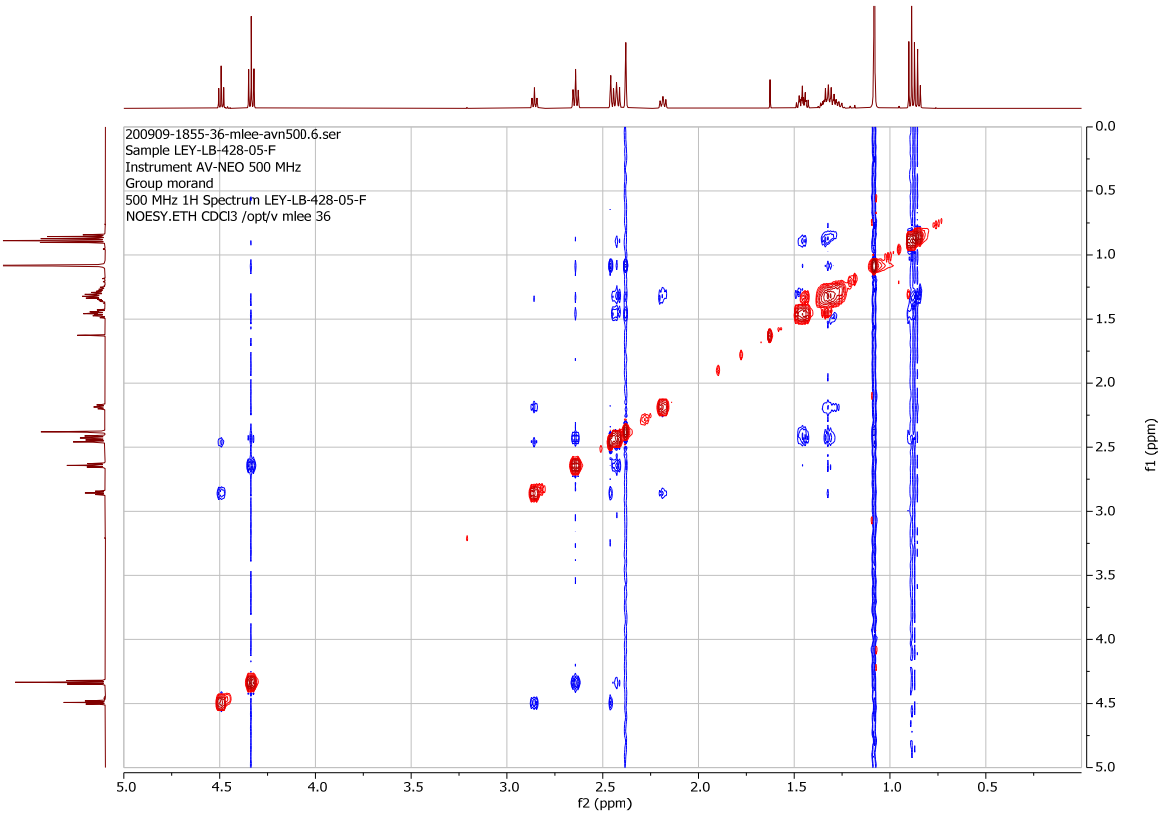
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl thiophene-2-carboxylate (**3bz-1**, major, **66**:34 mixture). 2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl thiophene-2-carboxylate (**3bz-2**, minor, 66:**34** mixture).



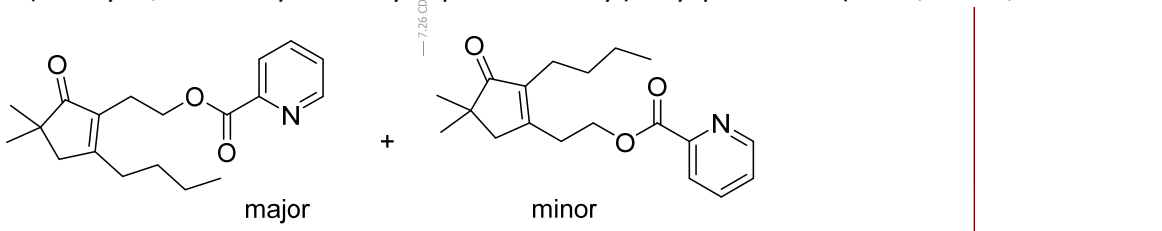

200909-1855-36-mlee-avn500.5.ser
Sample LEY-LB-428-05-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-428-05-F
HMBC.ETH CDCl3 /opt/v mlee 36
f2 (ppm)
f1 (ppm)

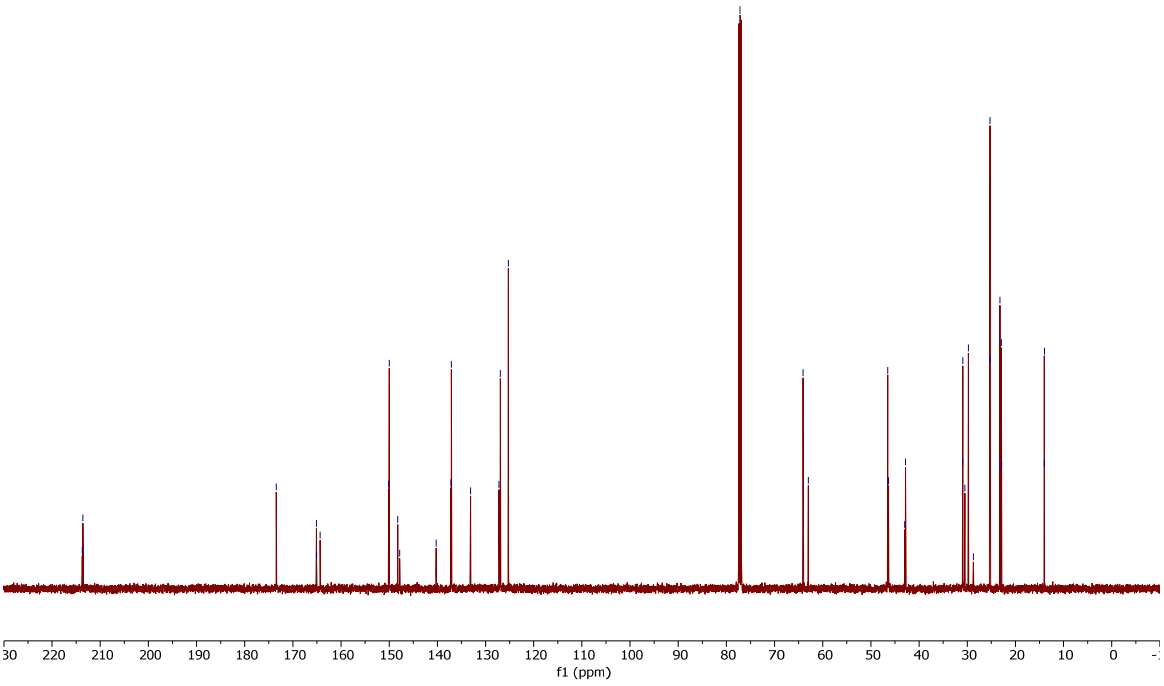

200909-1855-36-mlee-avn500.4.ser
Sample LEY-LB-428-05-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-428-05-F
HSQC.ETH CDCl3 /opt/v mlee 36
f2 (ppm)
f1 (ppm)

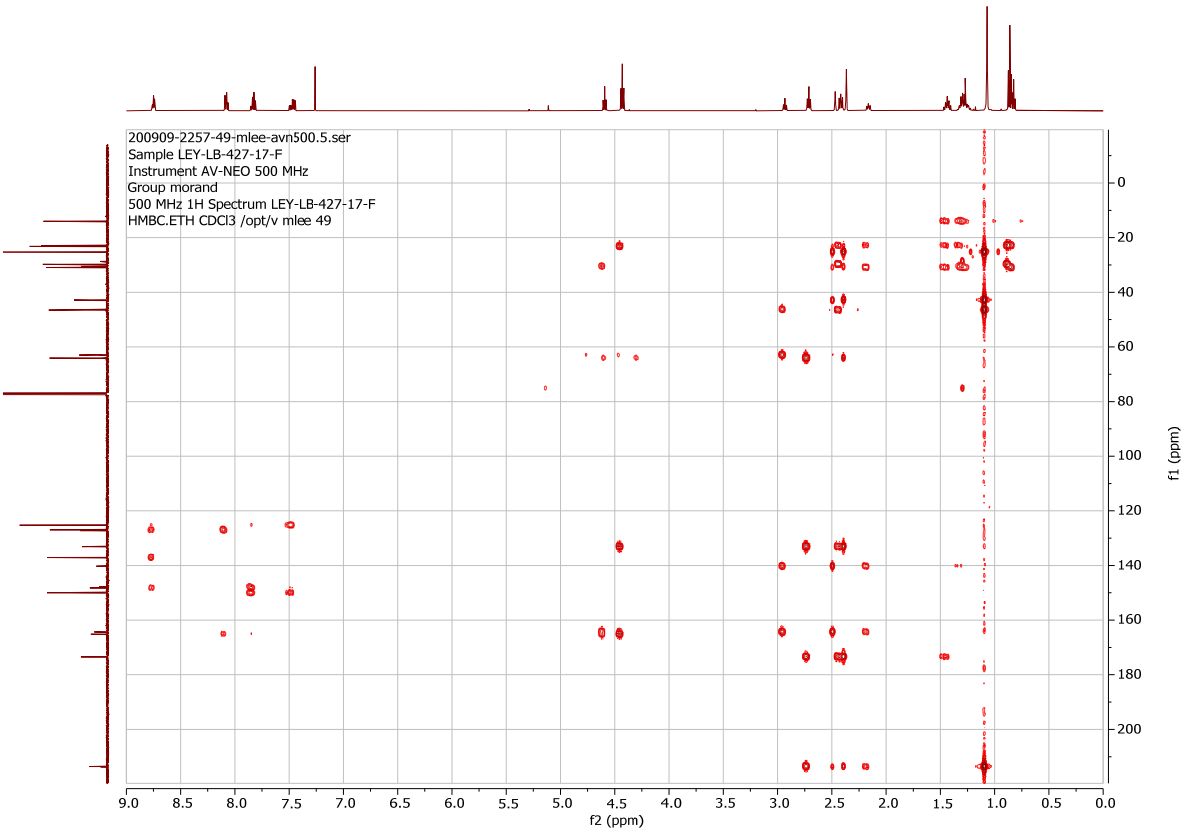

200909-1855-36-mlee-avn500.3.ser
Sample LEY-LB-428-05-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-428-05-F
COSY.ETH CDCl3 /opt/v mlee 36
f2 (ppm)
f1 (ppm)

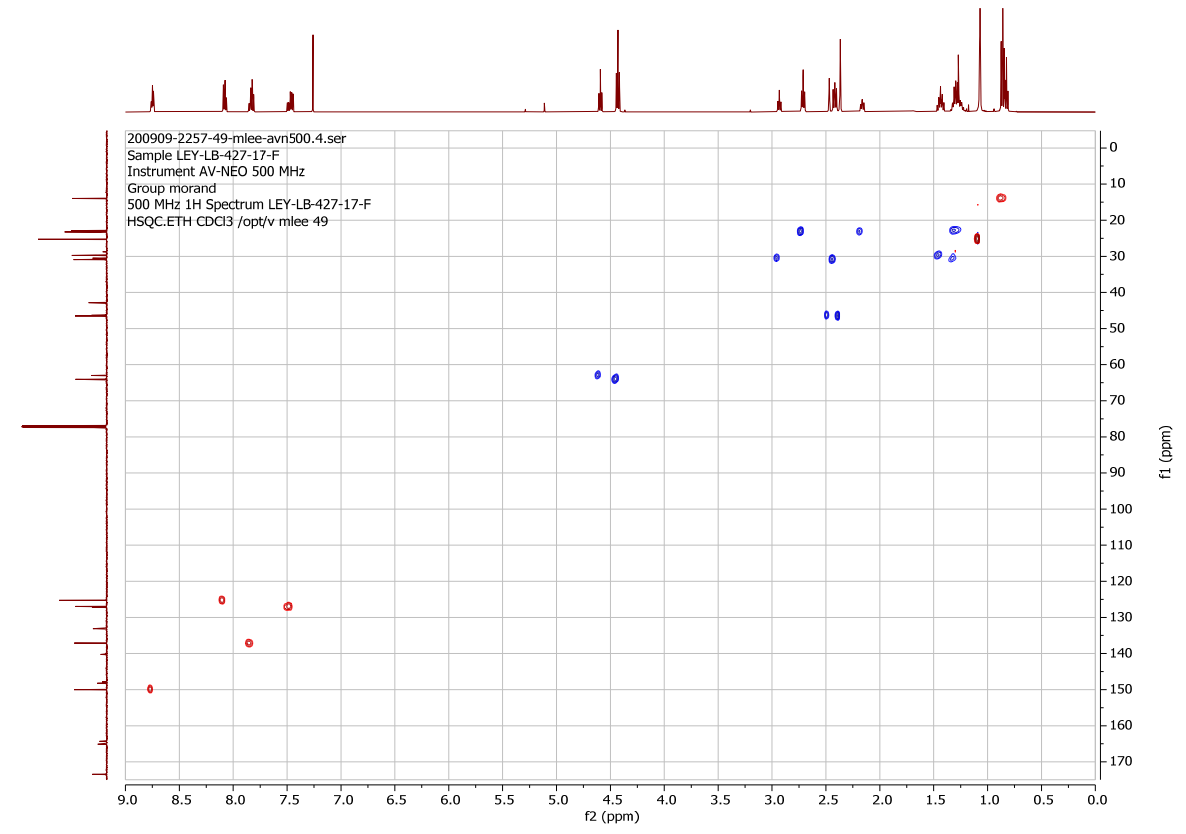

200909-1855-36-mlee-avn500.6.ser
Sample LEY-LB-428-05-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-428-05-F
NOESY.ETH CDCl3 /opt/v mlee 36
f2 (ppm)
f1 (ppm)

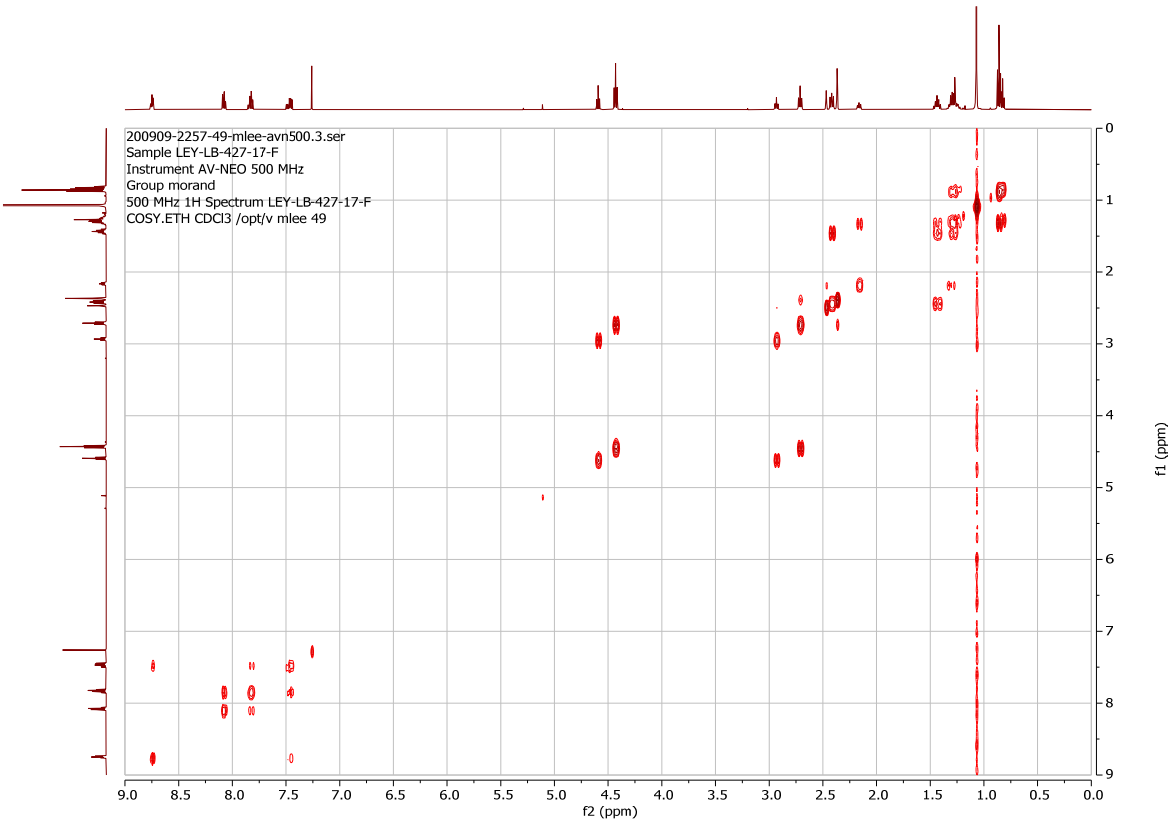
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl picolinate (**3ca-1**, major, **68**:32 mixture).
2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl picolinate (**3ca-2**, minor, 68:**32** mixture).

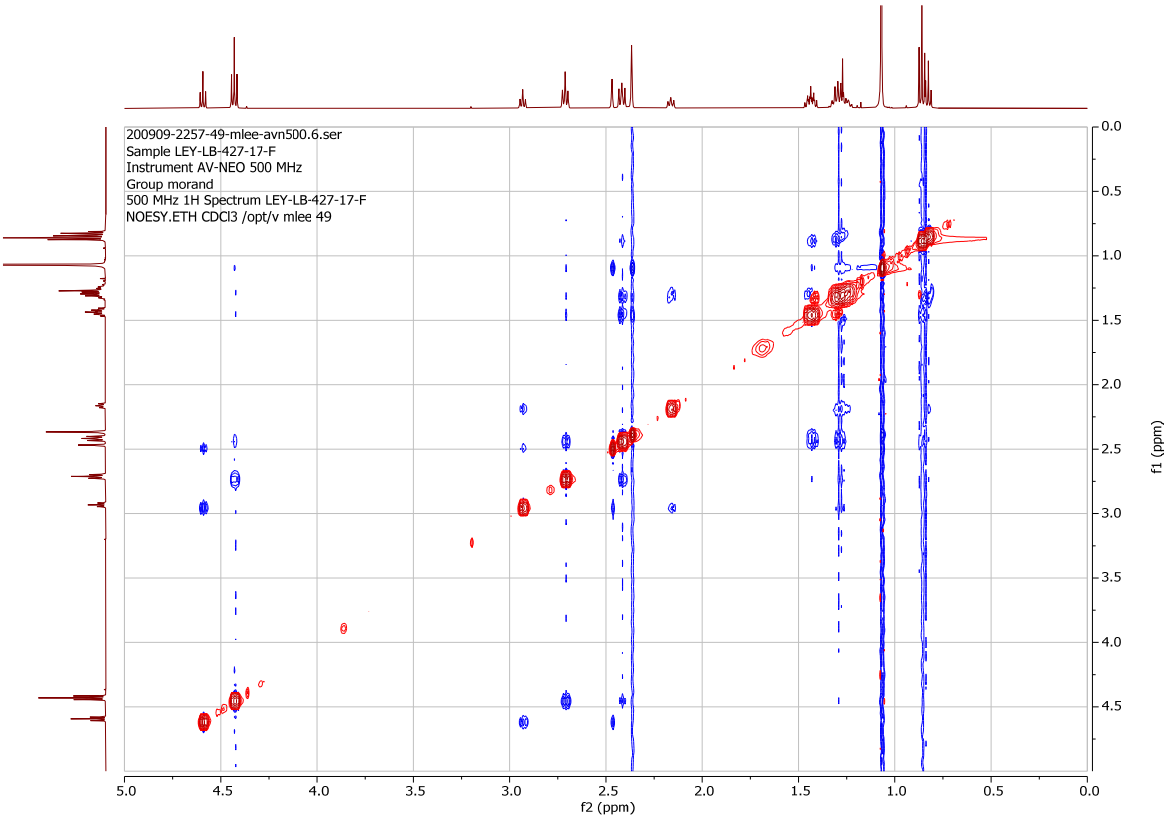




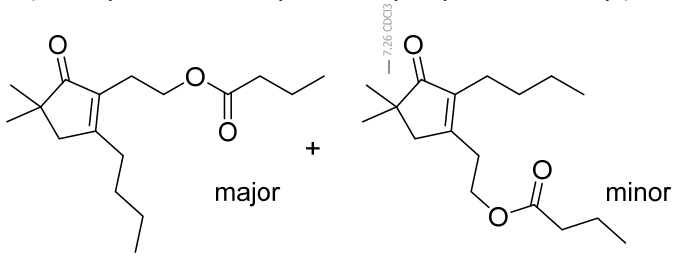

200909-2257-49-mlee-avn500.5.ser
Sample LEY-LB-427-17-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-17-F
HMBC.ETH CDCl3 /opt/v mlee 49
f2 (ppm)
f1 (ppm)

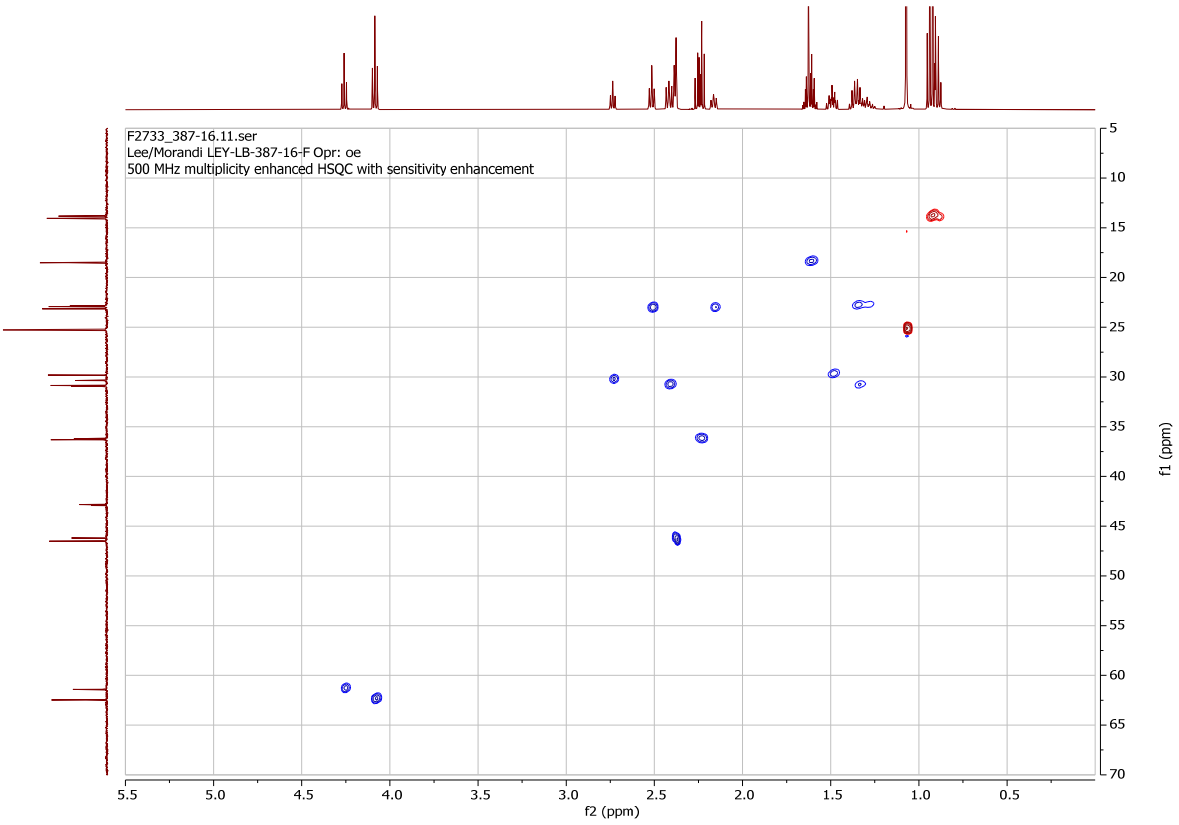

200909-2257-49-mlee-avn500.4.ser
Sample LEY-LB-427-17-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-17-F
HSQC.ETH CDCl3 /opt/v mlee 49
f2 (ppm)
f1 (ppm)


200909-2257-49-mlee-avn500.3.ser
Sample LEY-LB-427-17-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-17-F
COSY.ETH CDCl3 /opt/v mlee 49
f2 (ppm)
f1 (ppm)

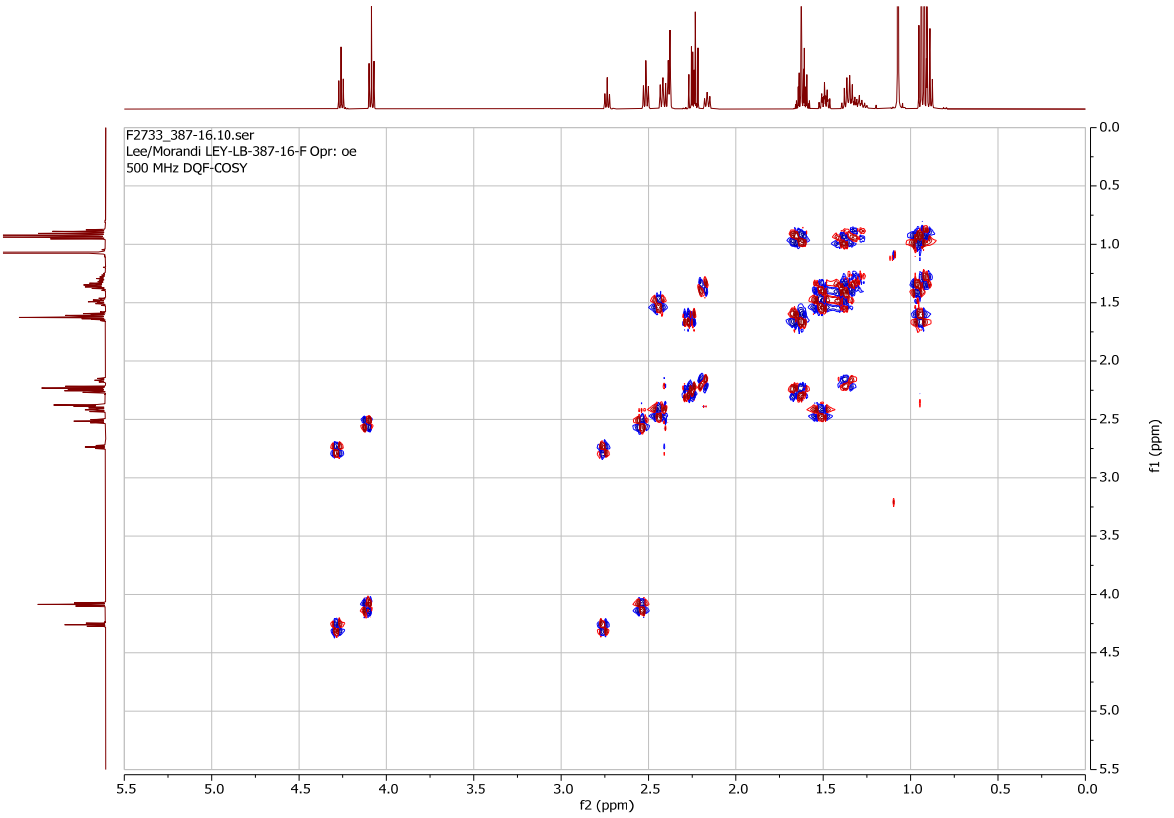

200909-2257-49-mlee-avn500.6.ser
Sample LEY-LB-427-17-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-427-17-F
NOESY.ETH CDCl3 /opt/v mlee 49
f2 (ppm)
f1 (ppm)

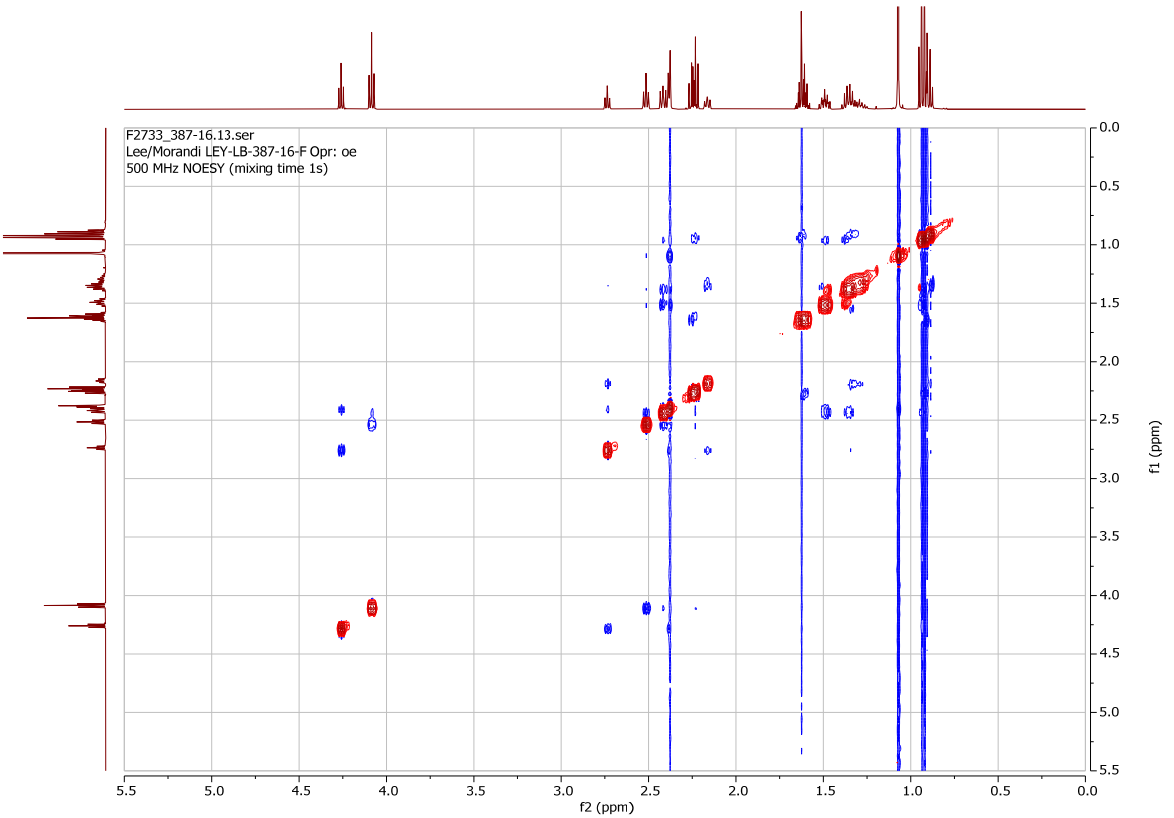
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl butyrate (**3cb-1**, major, **62**:38 mixture).
2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl butyrate (**3cb-2**, minor, 62:**38**, mixture).



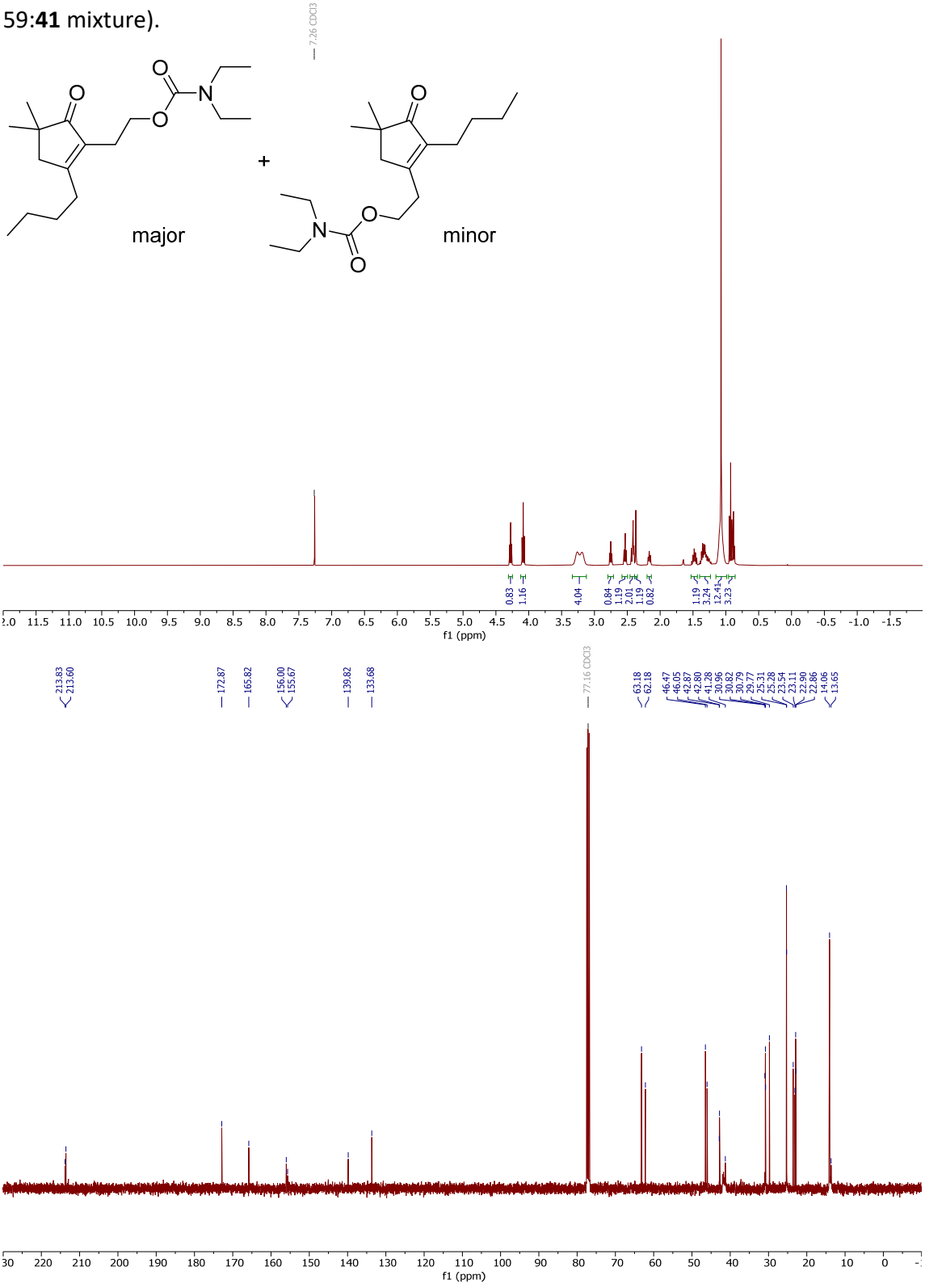

F2733_387-16.11.ser
Lee/Morandi LEY-LB-387-16-F Opr: oe
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

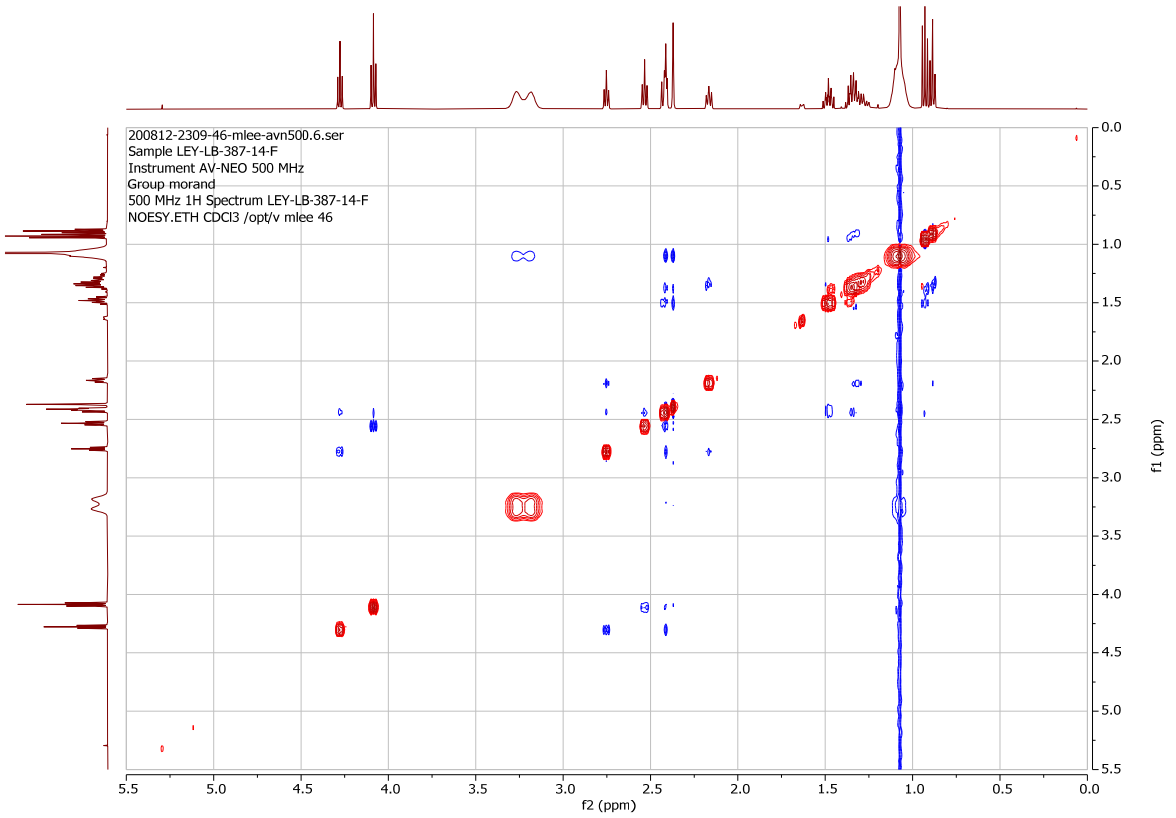

F2733_387-16.12.ser
Lee/Morandi LEY-LB-387-16-F Opr: oe
500 MHz HMBC
f2 (ppm)
f1 (ppm)

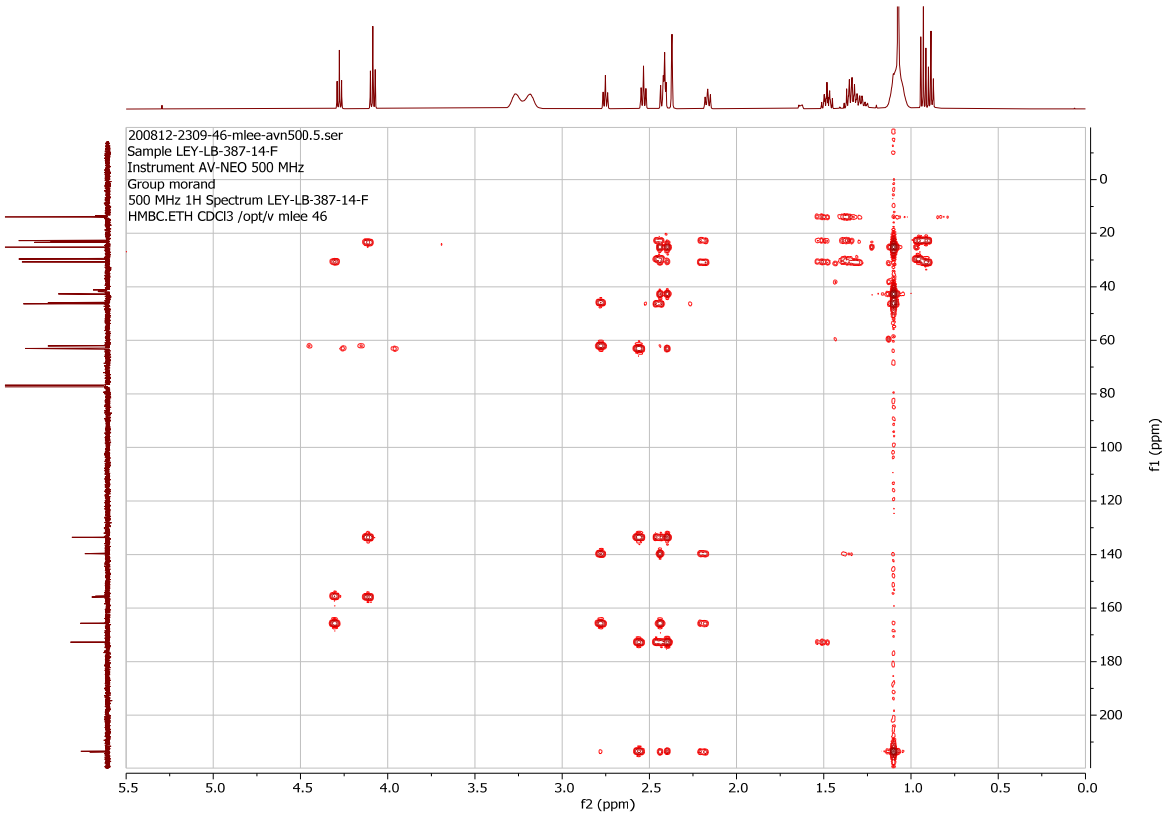

F2733_387-16.10.ser
Lee/Morandi LEY-LB-387-16-F Opr: oe
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

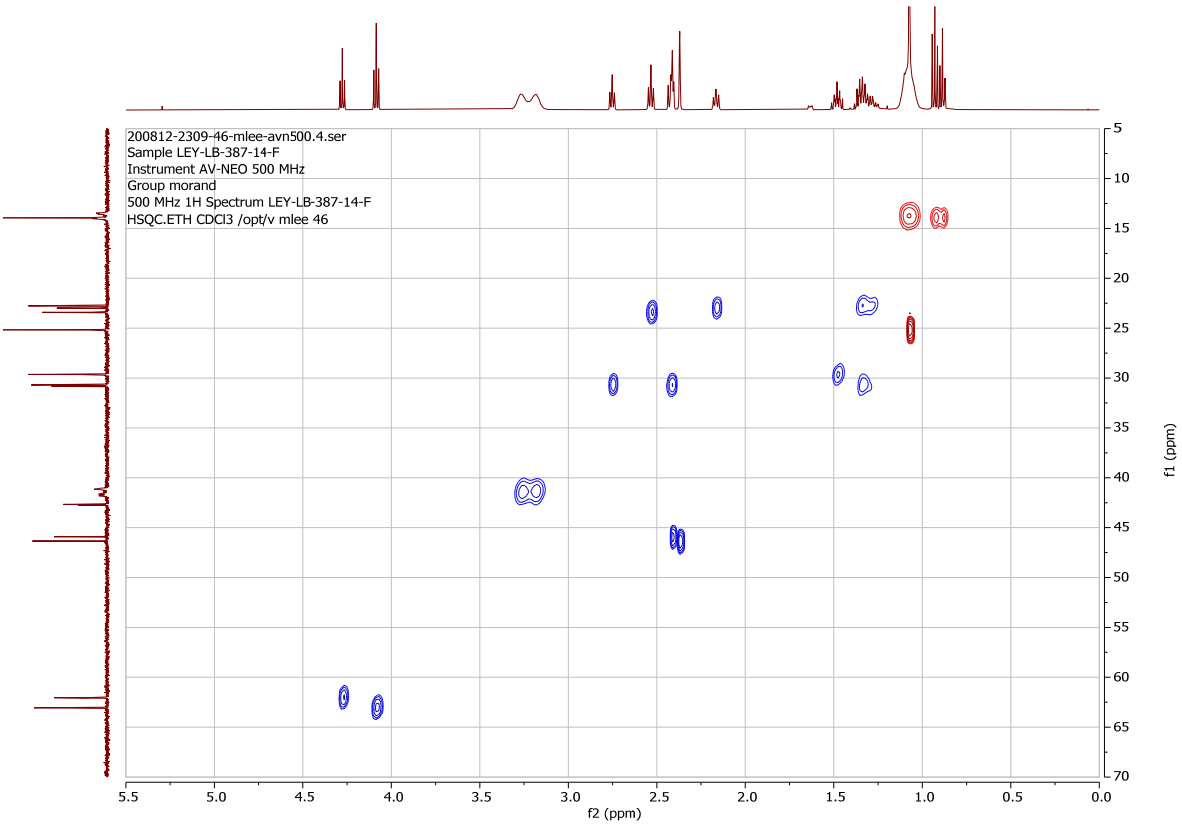

F2733_387-16.13.ser
Lee/Morandi LEY-LB-387-16-F Opr: oe
500 MHz NOESY (mixing time 1s)
f2 (ppm)
f1 (ppm)

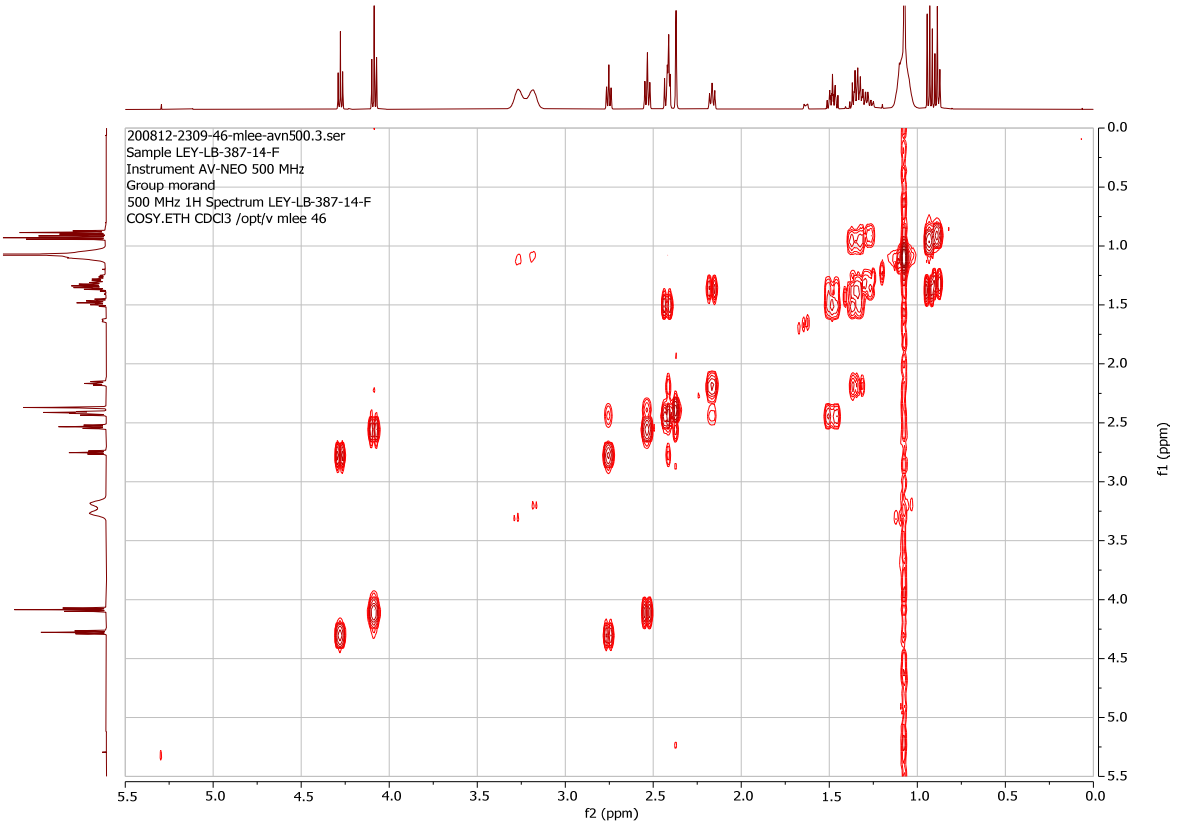
2-(2-butyl-4,4-dimethyl-5-oxocyclopent-1-en-1-yl)ethyl diethylcarbamate (**3cc-1**, major, **59**:41 mixture). 2-(2-butyl-4,4-dimethyl-3-oxocyclopent-1-en-1-yl)ethyl diethylcarbamate (**3cc-2**, minor, 59:**41** mixture).




200812-2309-46-mlee-avn500.6.ser
Sample LEY-LB-387-14-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-14-F
NOESY.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

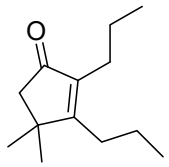

200812-2309-46-mlee-avn500.5.ser
Sample LEY-LB-387-14-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-14-F
HMBC.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

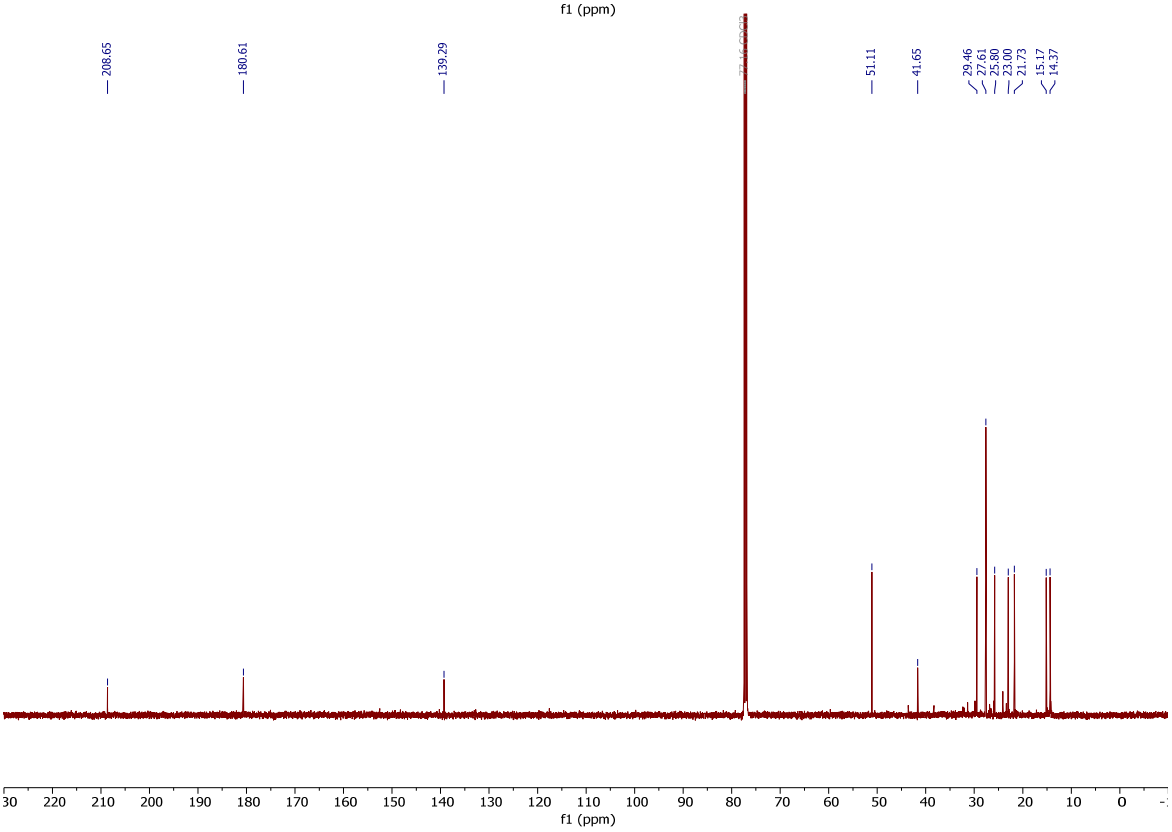

200812-2309-46-mlee-avn500.4.ser
Sample LEY-LB-387-14-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-14-F
HSQC.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

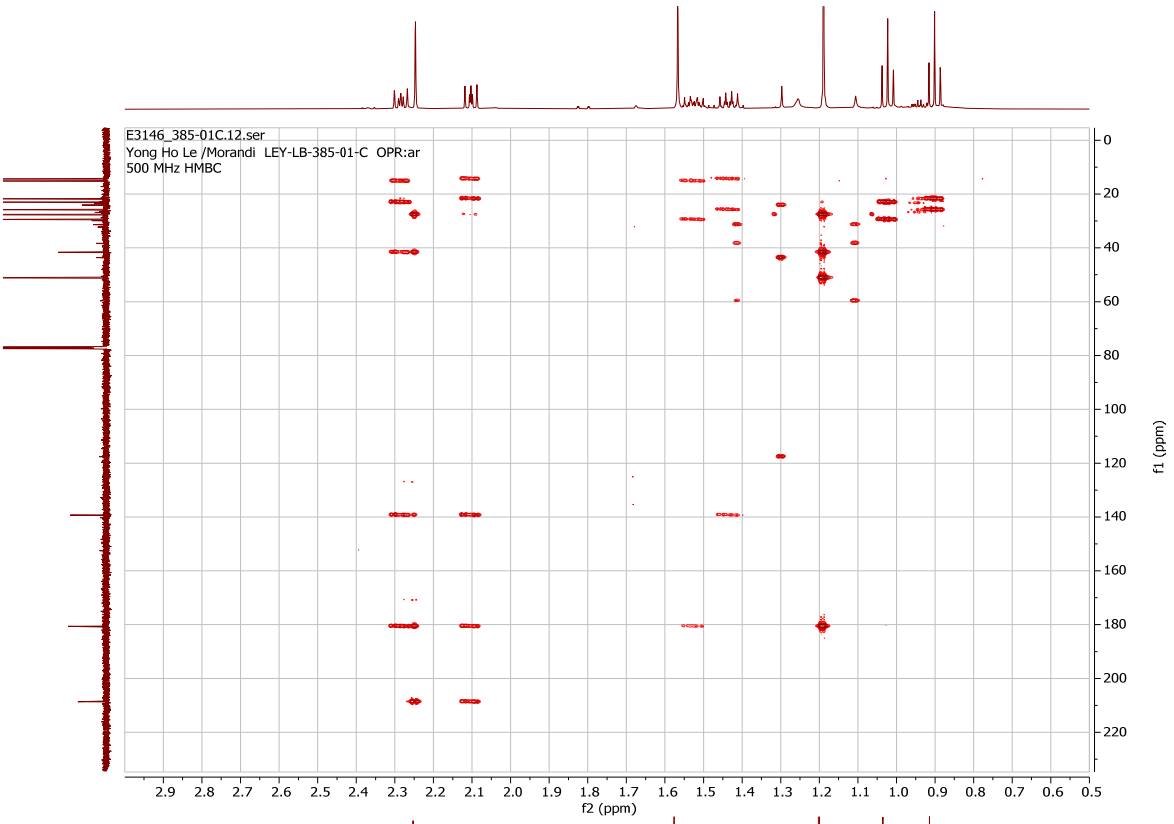

200812-2309-46-mlee-avn500.3.ser
Sample LEY-LB-387-14-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-387-14-F
COSY.ETH CDCl3 /opt/v mlee 46
f2 (ppm)
f1 (ppm)

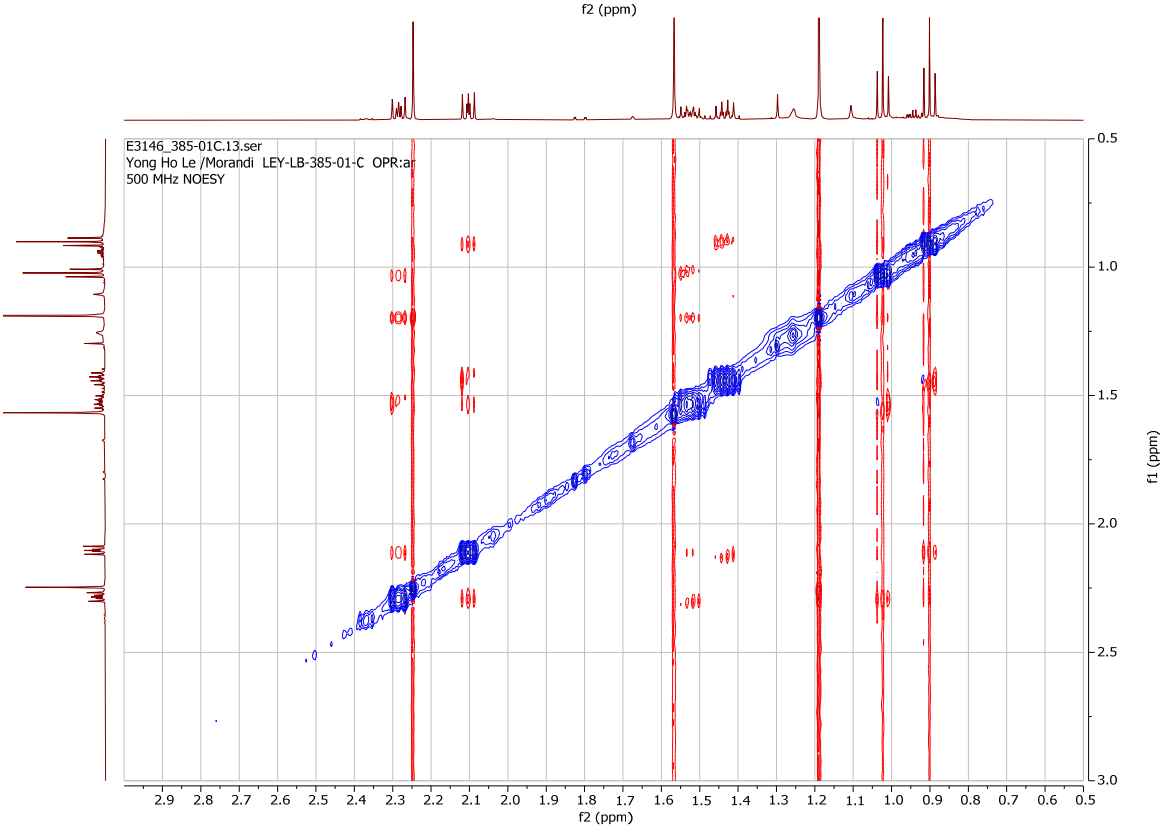
11.2. Carbonylative carbocyclization (other transition metals)

4,4-dimethyl-2,3-dipropylcyclopent-2-en-1-one (**4a**).

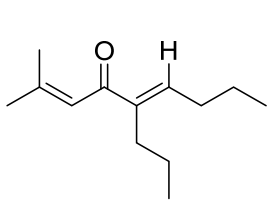


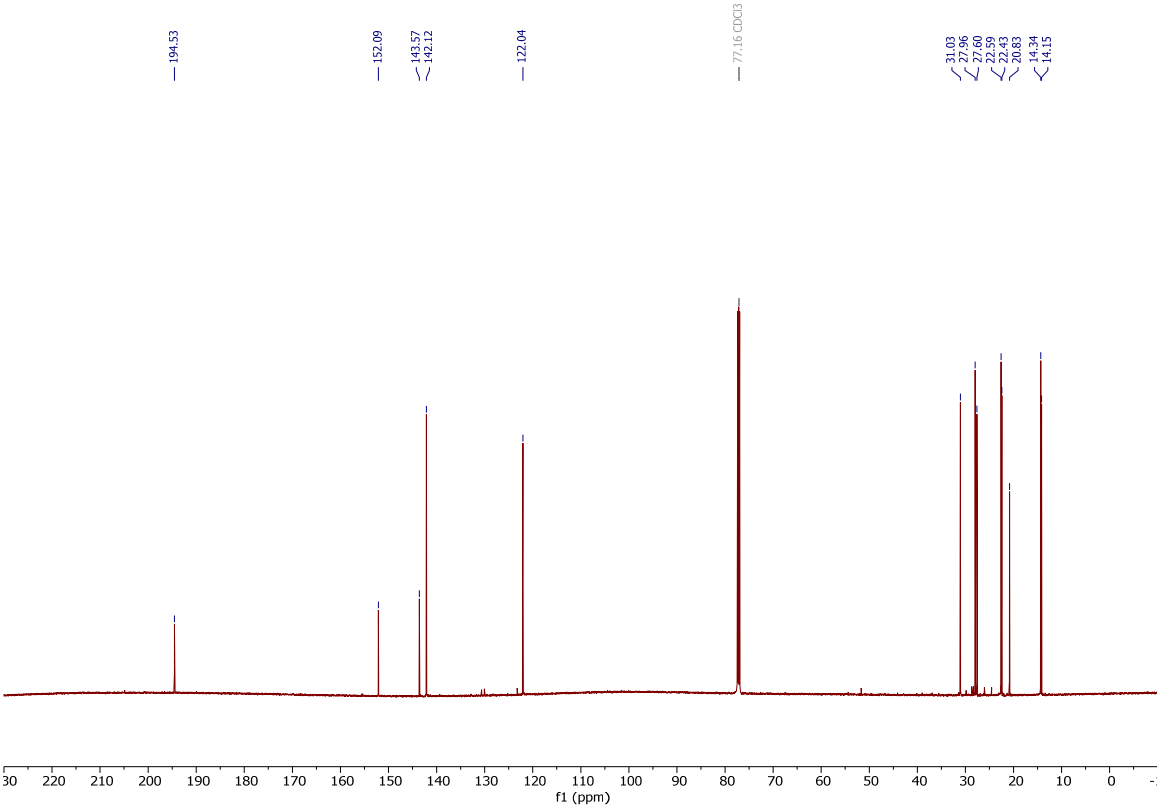


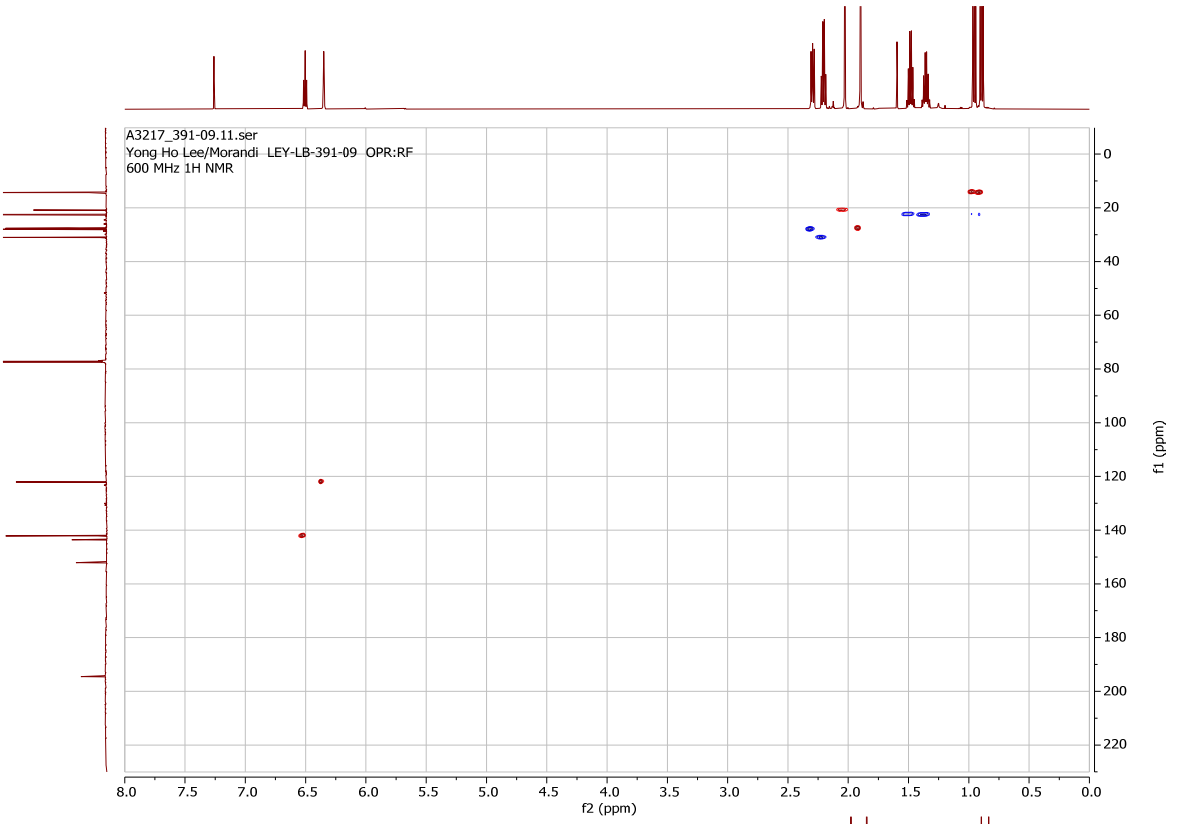

E3146_385-01C.12.ser
Yong Ho Le /Morandi LEY-LB-385-01-C OPR:ar
500 MHz HMBC
f2 (ppm)
f1 (ppm)

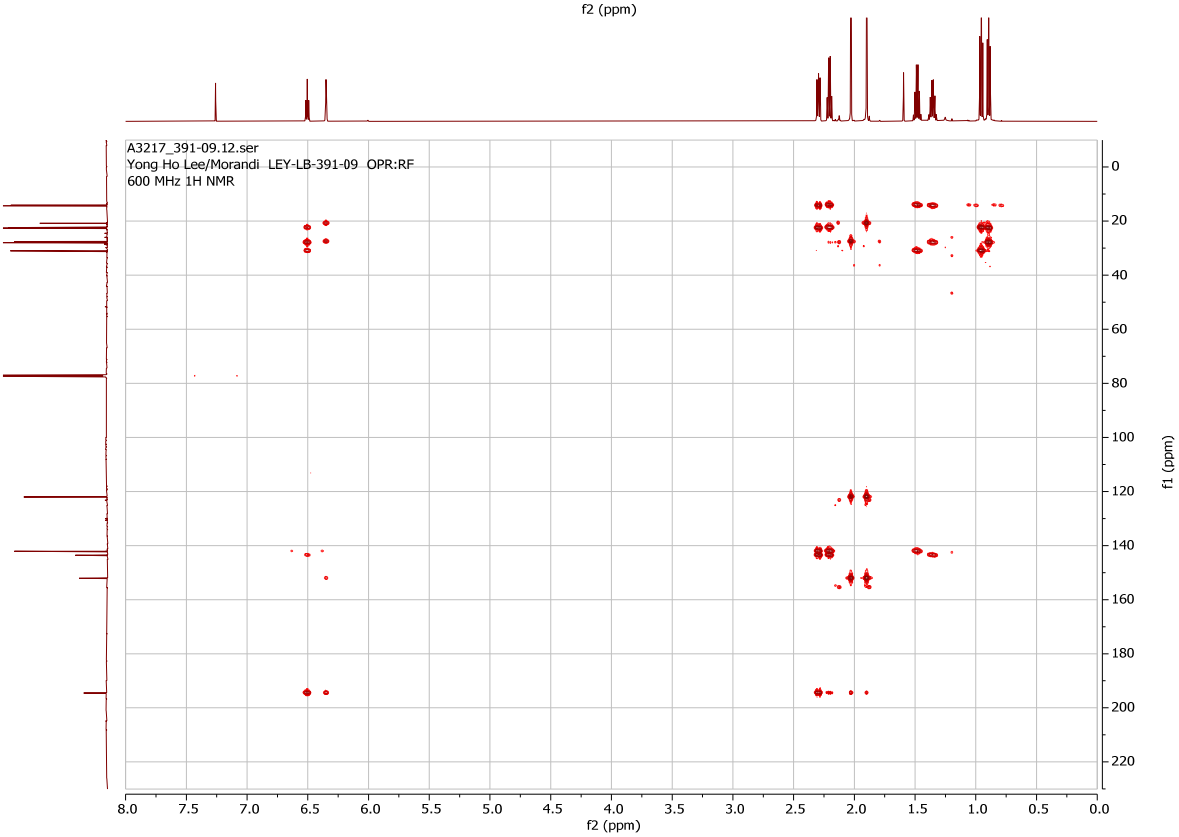

E3146_385-01C.13.ser
Yong Ho Le /Morandi LEY-LB-385-01-C OPR:ar
500 MHz NOESY
f2 (ppm)
f1 (ppm)

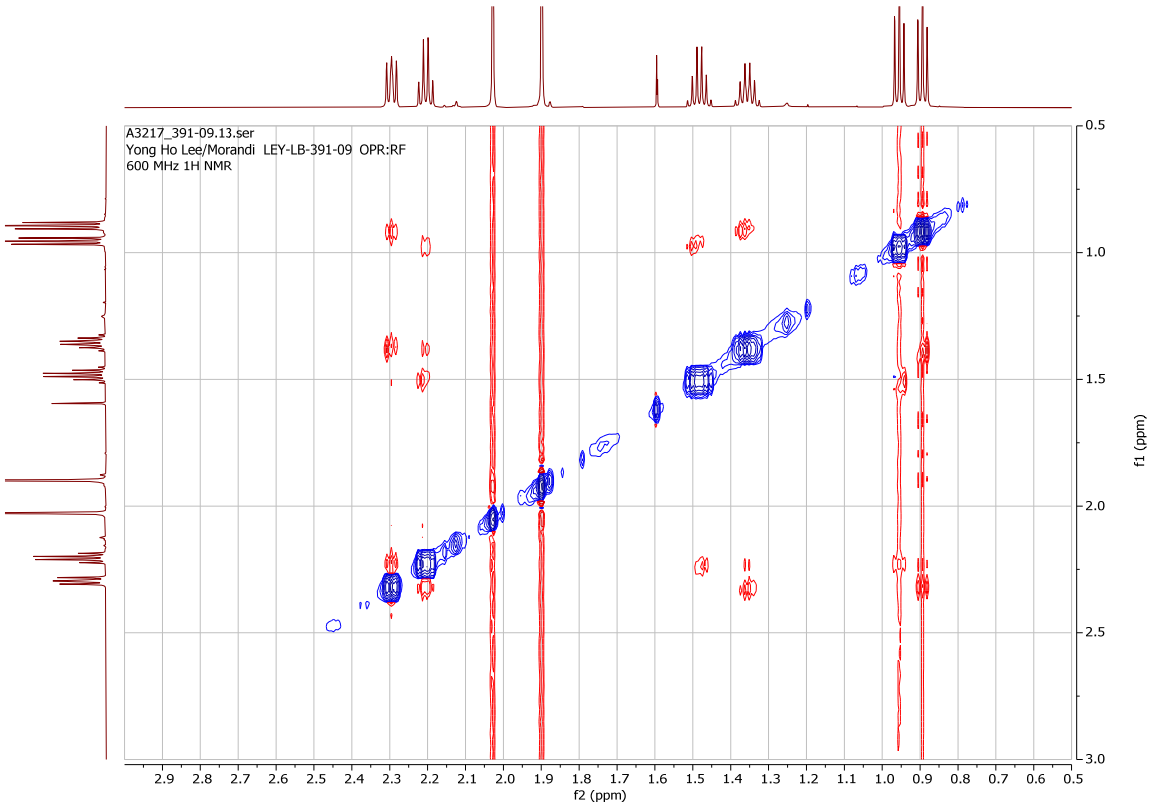
(*E*)-2-methyl-5-propylnona-2,5-dien-4-one (**5a**).





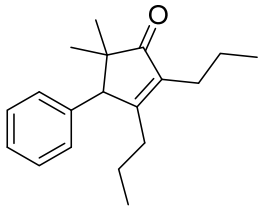

A3217_391-09.11.ser
Yong Ho Lee/Morandi LEY-LB-391-09 OPR:RF
600 MHz 1H NMR
f2 (ppm)
f1 (ppm)

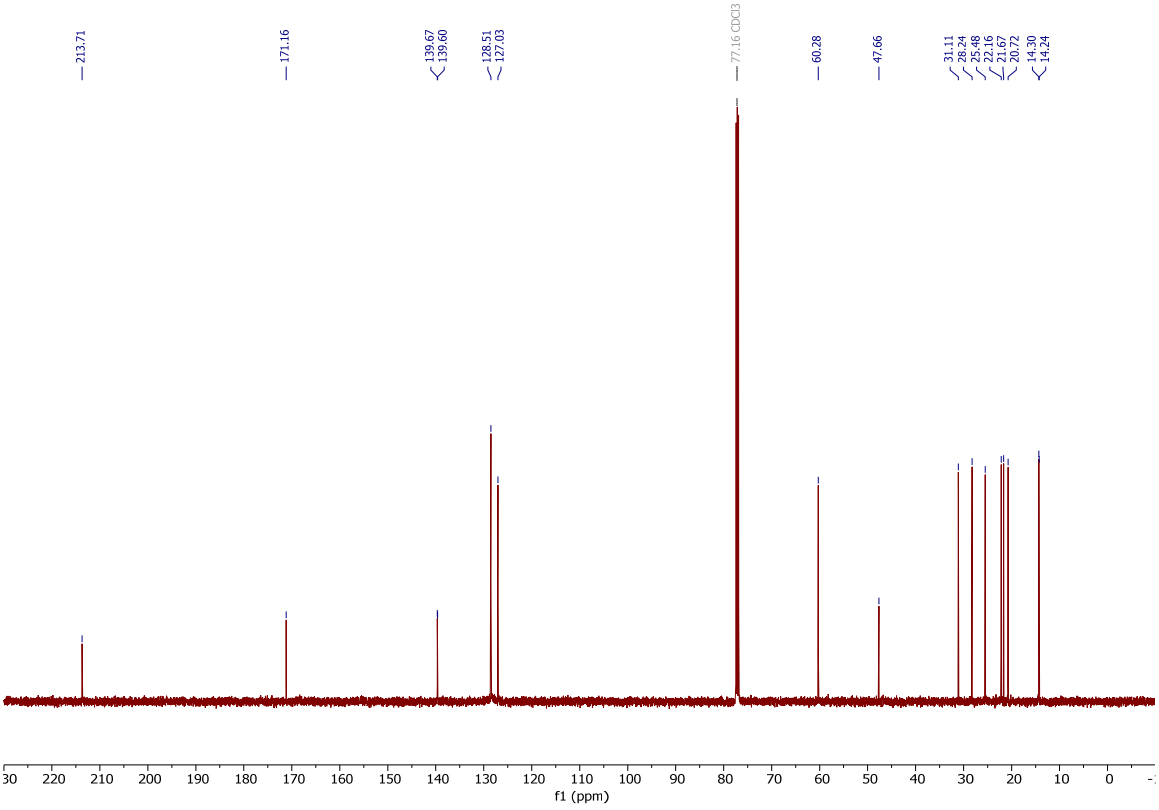

A3217_391-09.12.ser
Yong Ho Lee/Morandi LEY-LB-391-09 OPR:RF
600 MHz 1H NMR
f2 (ppm)
f1 (ppm)

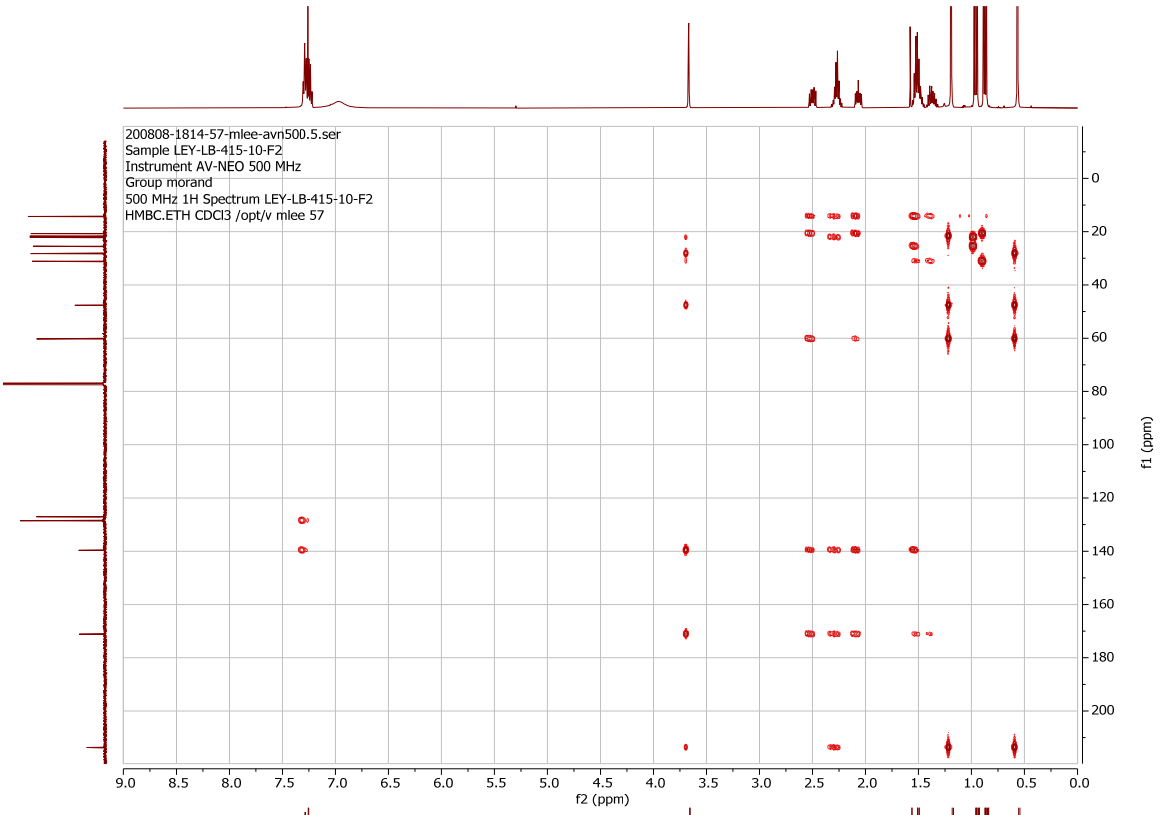

A3217_391-09.13.ser
Yong Ho Lee/Morandi LEY-LB-391-09 OPR:RF
600 MHz 1H NMR
f2 (ppm)
f1 (ppm)

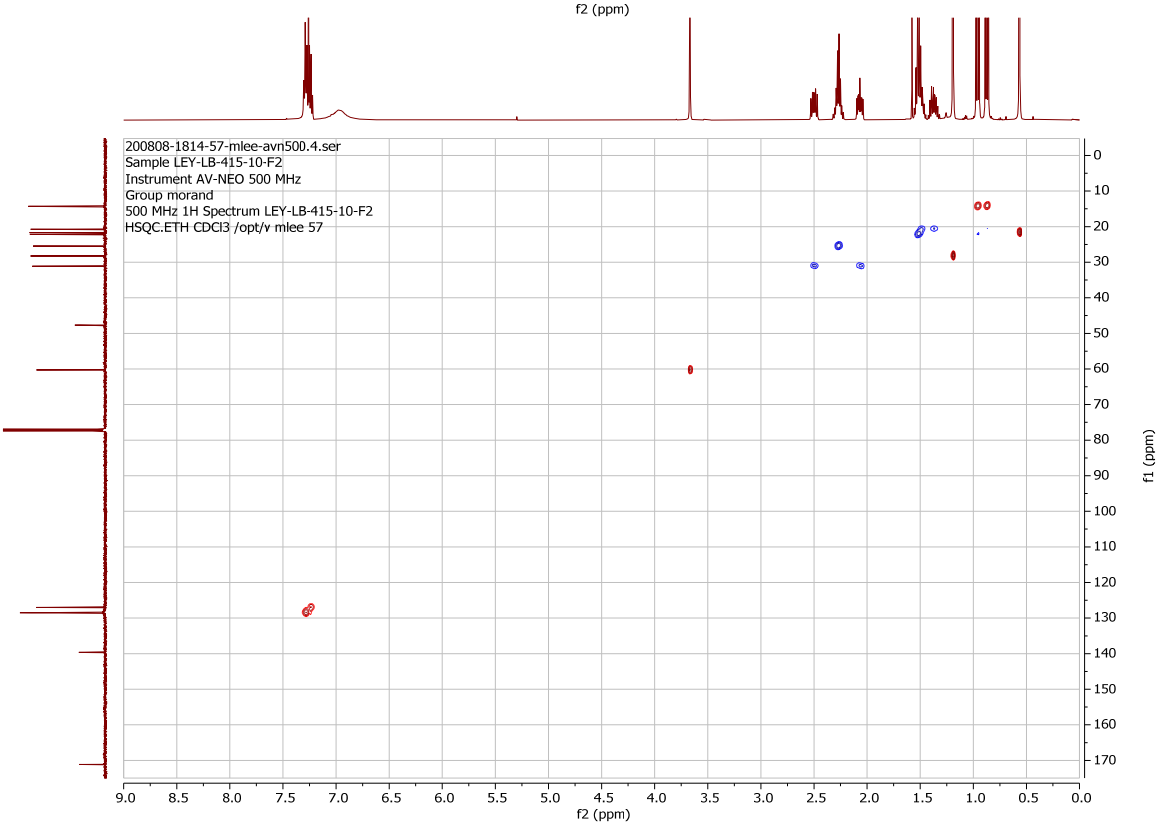
11.3. Carbonylative carbocyclization (using a tin reagent)

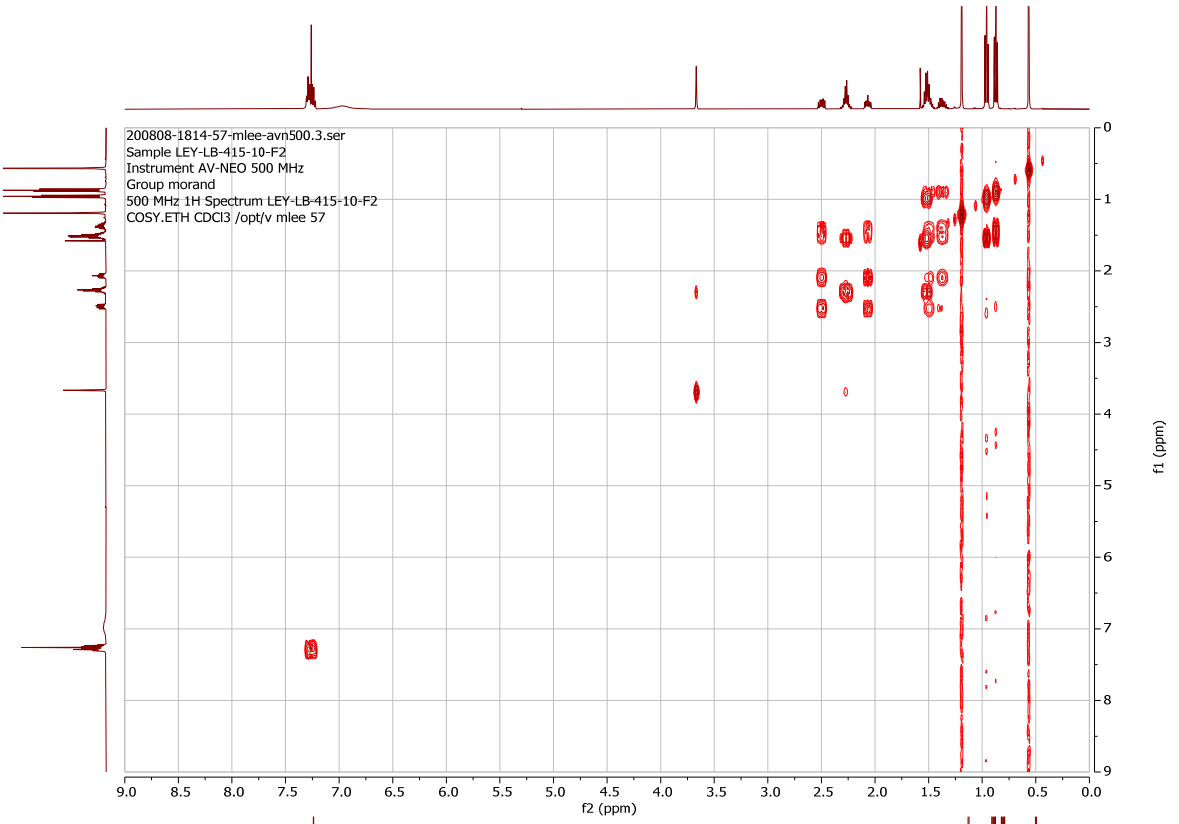
5,5-dimethyl-4-phenyl-2,3-dipropylcyclopent-2-en-1-one (**3av**).

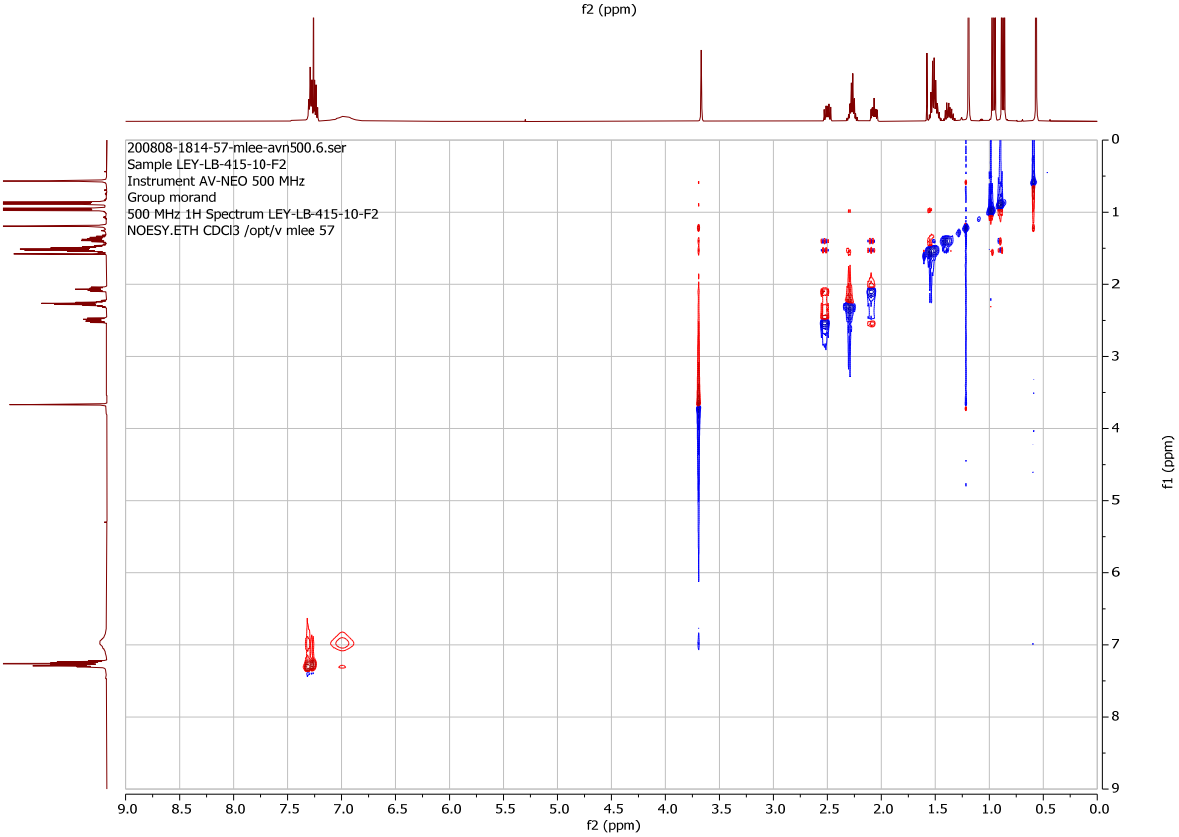




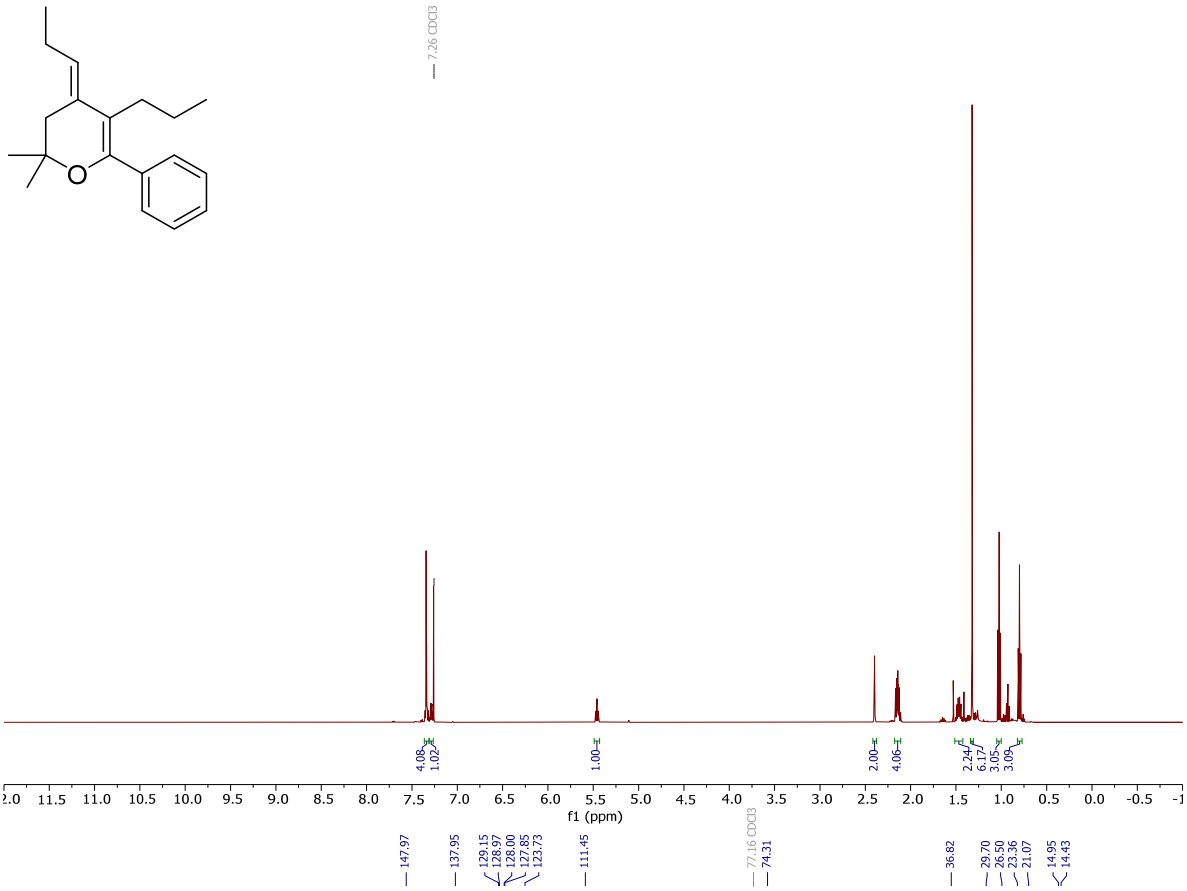

200808-1814-57-mlee-avn500.5.ser
Sample LEY-LB-415-10-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-415-10-F2
HMBC.ETH CDCl3 /opt/v mlee 57
f2 (ppm)
f1 (ppm)

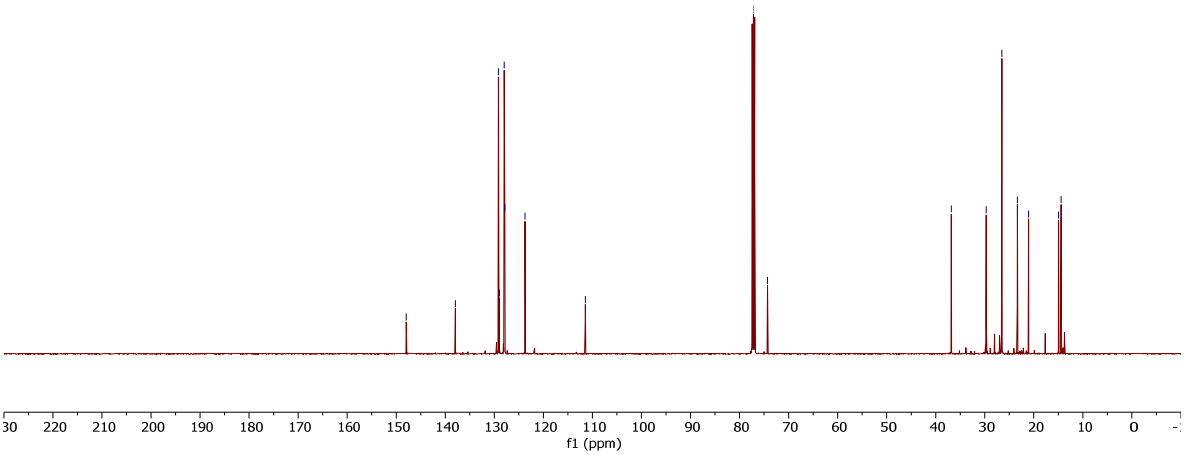

200808-1814-57-mlee-avn500.4.ser
Sample LEY-LB-415-10-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-415-10-F2
HSQC.ETH CDCl3 /opt/v mlee 57
f2 (ppm)
f1 (ppm)

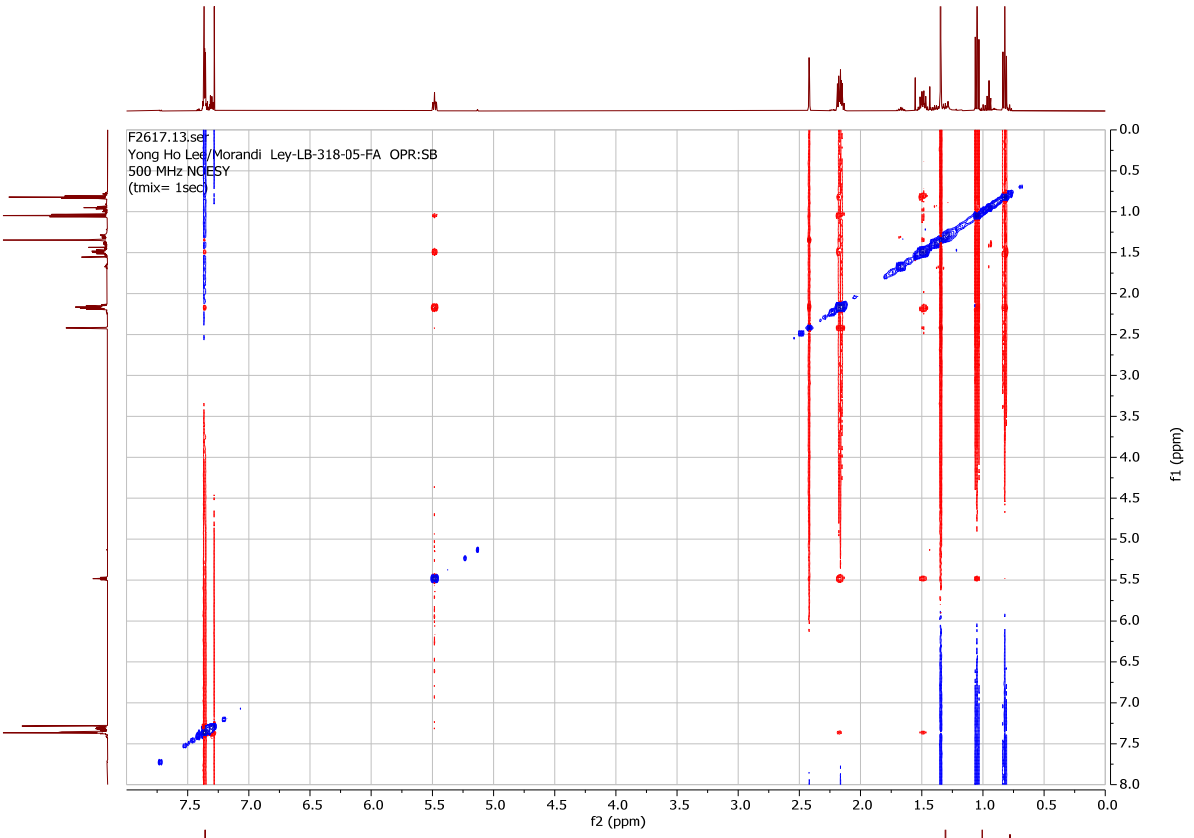

200808-1814-57-mlee-avn500.3.ser
Sample LEY-LB-415-10-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-415-10-F2
COSY.ETH CDCl3 /opt/v mlee 57
f2 (ppm)
f1 (ppm)

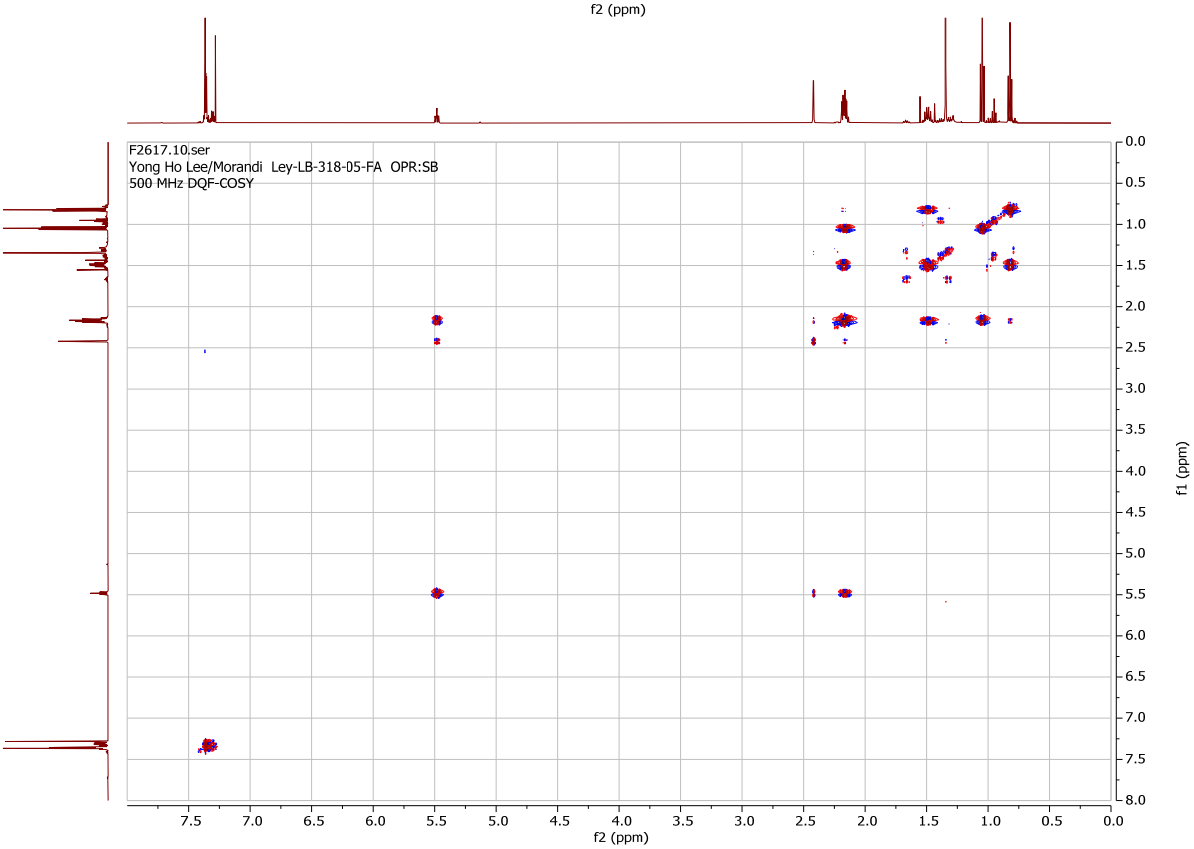

200808-1814-57-mlee-avn500.6.ser
Sample LEY-LB-415-10-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-415-10-F2
NOESY.ETH CDCl3 /opt/v mlee 57
f2 (ppm)
f1 (ppm)

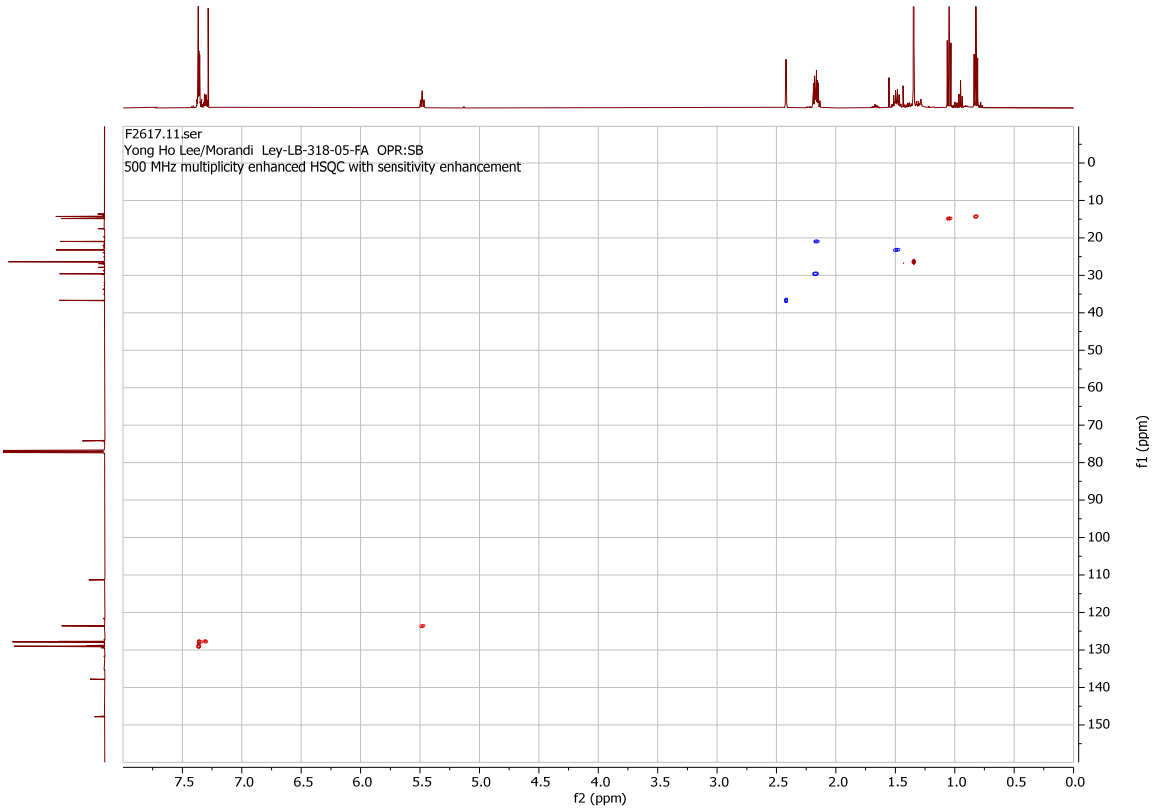
(*E*)-2,2-dimethyl-6-phenyl-5-propyl-4-propylidene-3,4-dihydro-2*H*-pyran (**11a**).

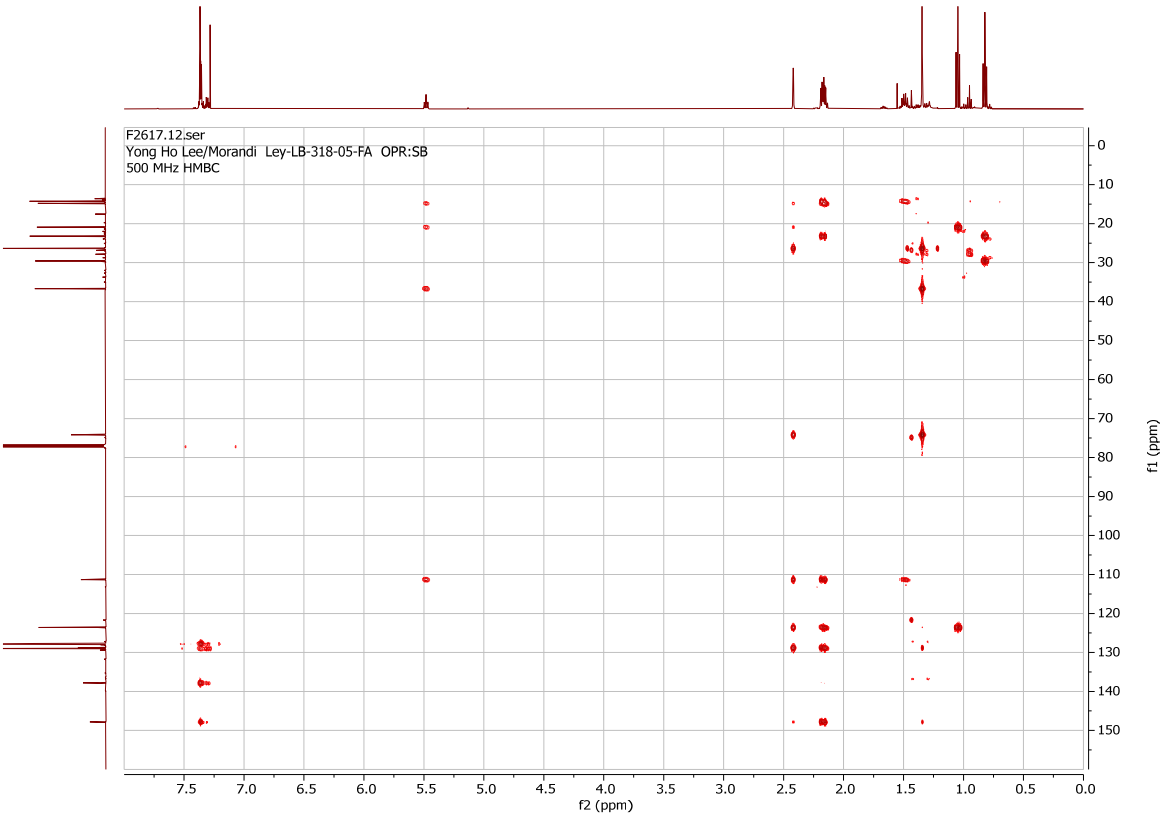





F2617.13.ser
Yong Ho Lee/Morandi Ley-LB-318-05-FA OPR:SB
500 MHz NOESY
(tmix= 1sec)
f2 (ppm)
f1 (ppm)

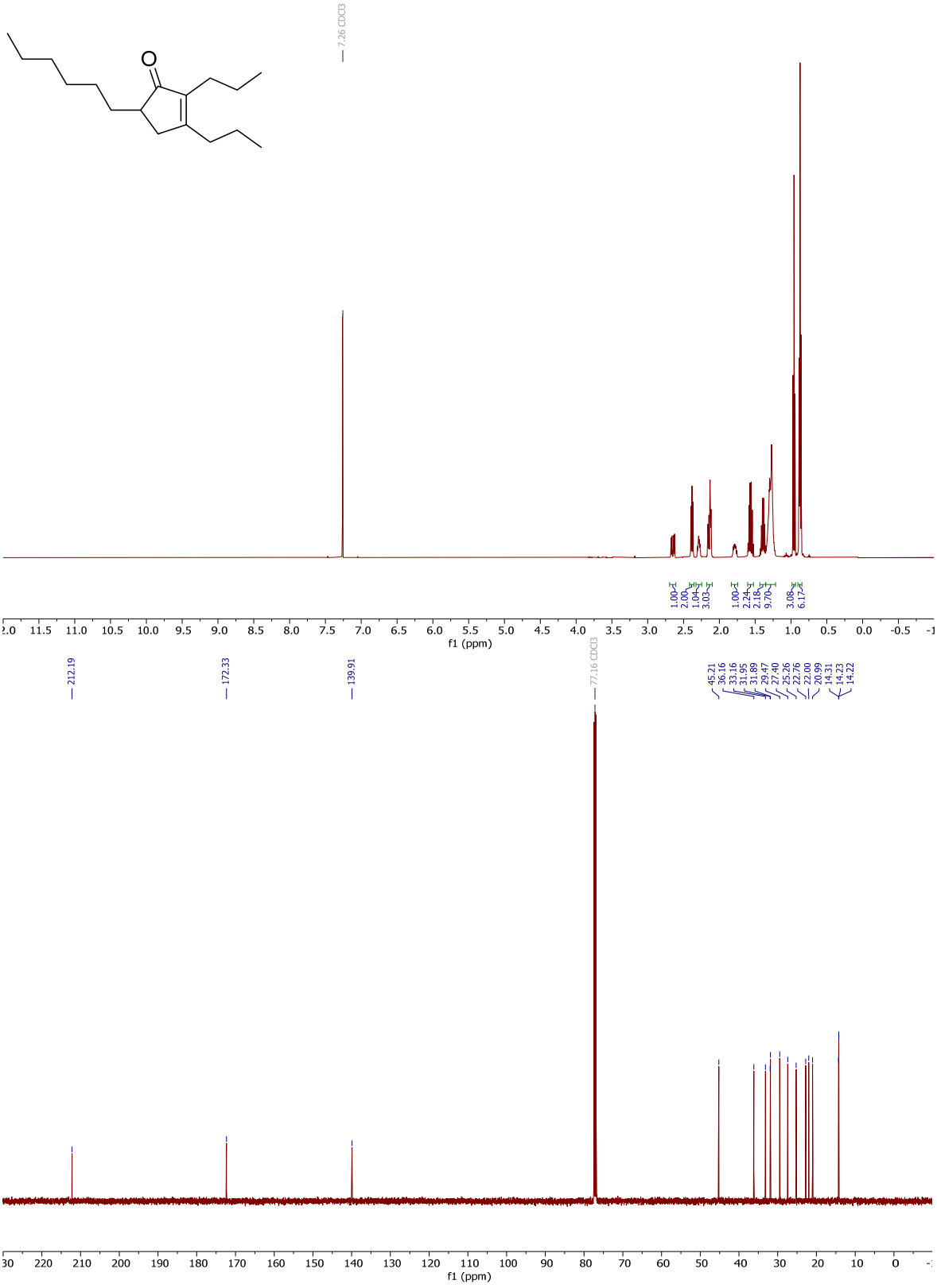

F2617.10.ser
Yong Ho Lee/Morandi Ley-LB-318-05-FA OPR:SB
500 MHz DQF-COSY
f2 (ppm)
f1 (ppm)

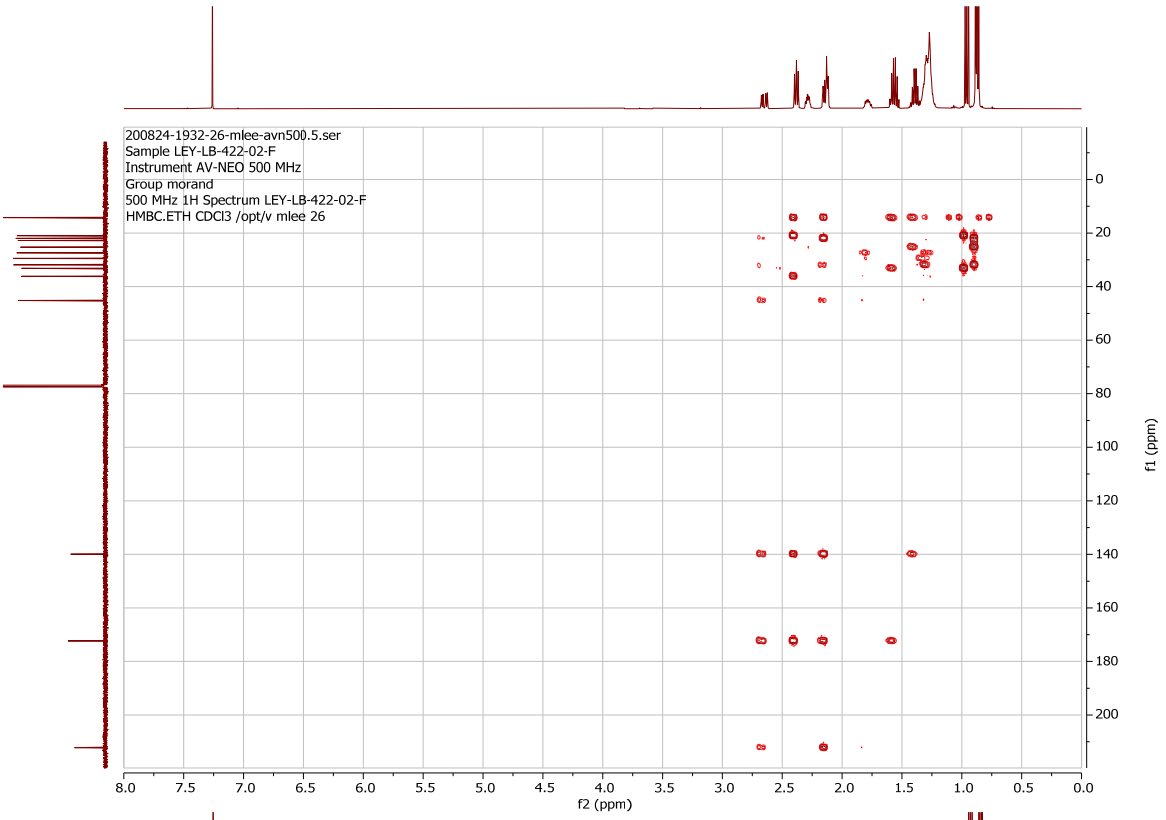

F2617.11.ser
Yong Ho Lee/Morandi Ley-LB-318-05-FA OPR:SB
500 MHz multiplicity enhanced HSQC with sensitivity enhancement
f2 (ppm)
f1 (ppm)

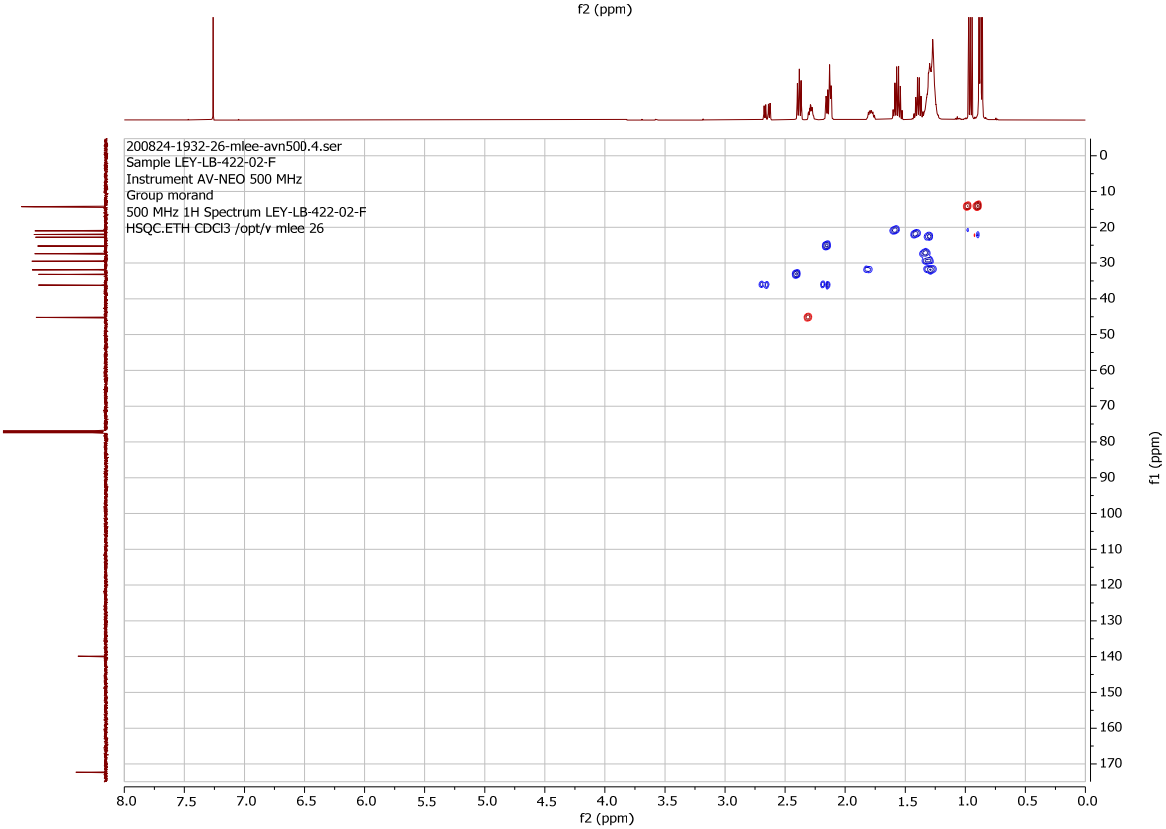

F2617.12.ser
Yong Ho Lee/Morandi Ley-LB-318-05-FA OPR:SB
500 MHz HMBC
f2 (ppm)
f1 (ppm)

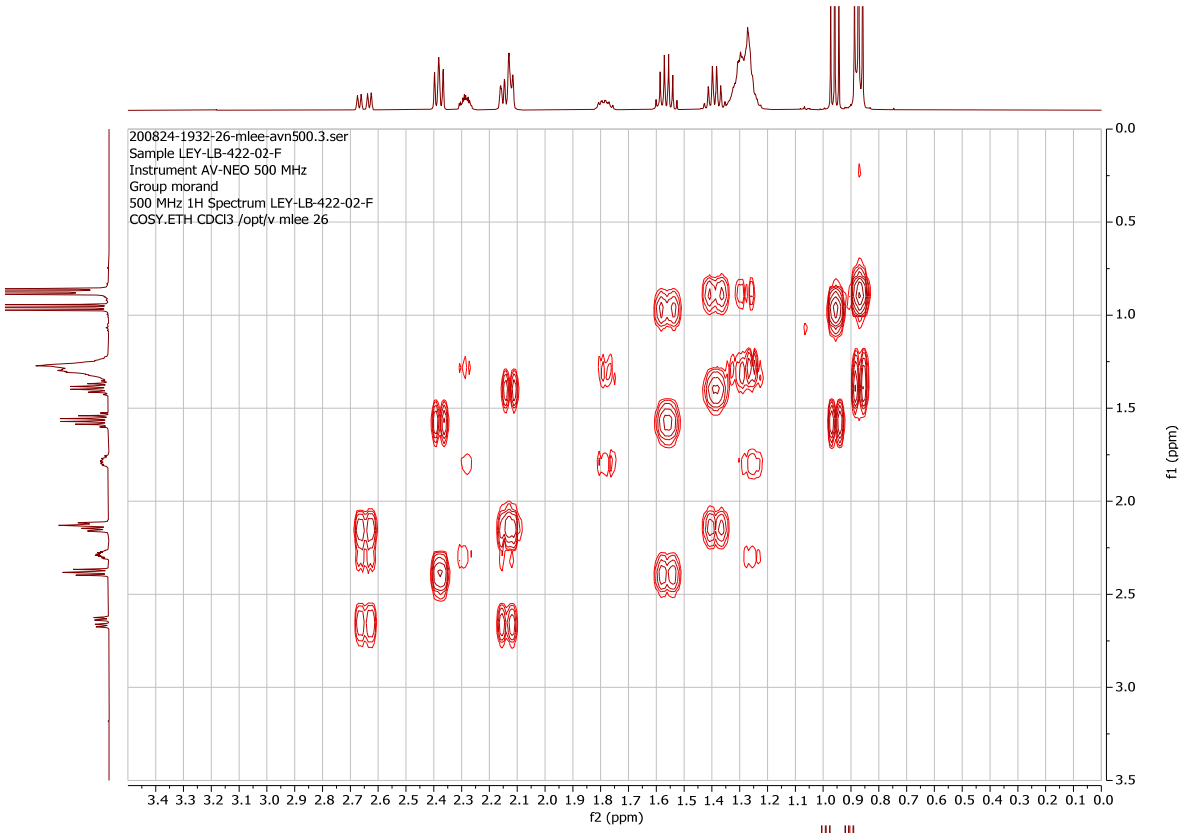
11.4. Carbonylative carbocyclization (from alkenyl electrophiles)

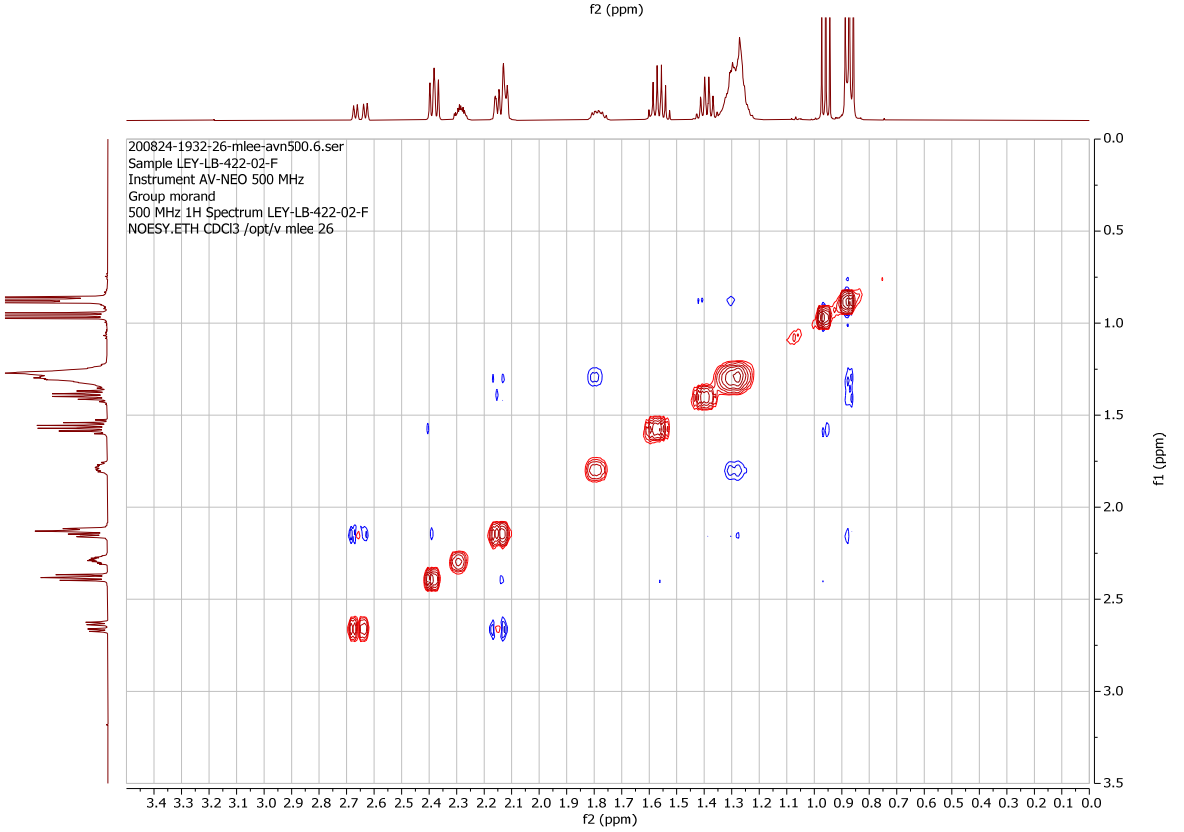
5-hexyl-2,3-dipropylcyclopent-2-en-1-one (**3as**).



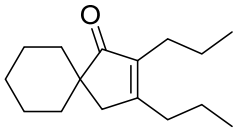

200824-1932-26-mlee-avn500.5.ser
Sample LEY-LB-422-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-422-02-F
HMBC.ETH CDCl3 /opt/v mlee 26
f2 (ppm)
f1 (ppm)

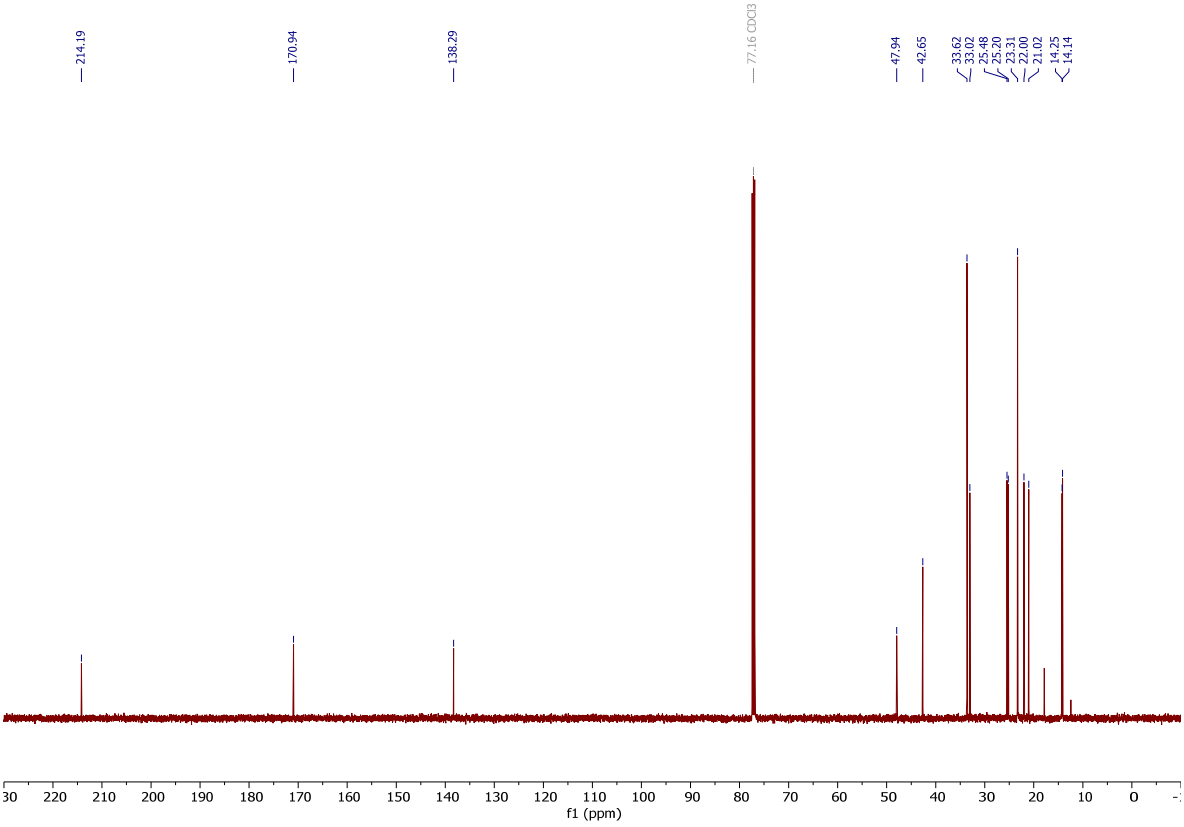

200824-1932-26-mlee-avn500.4.ser
Sample LEY-LB-422-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-422-02-F
HSQC.ETH CDCl3 /opt/v mlee 26
f2 (ppm)
f1 (ppm)

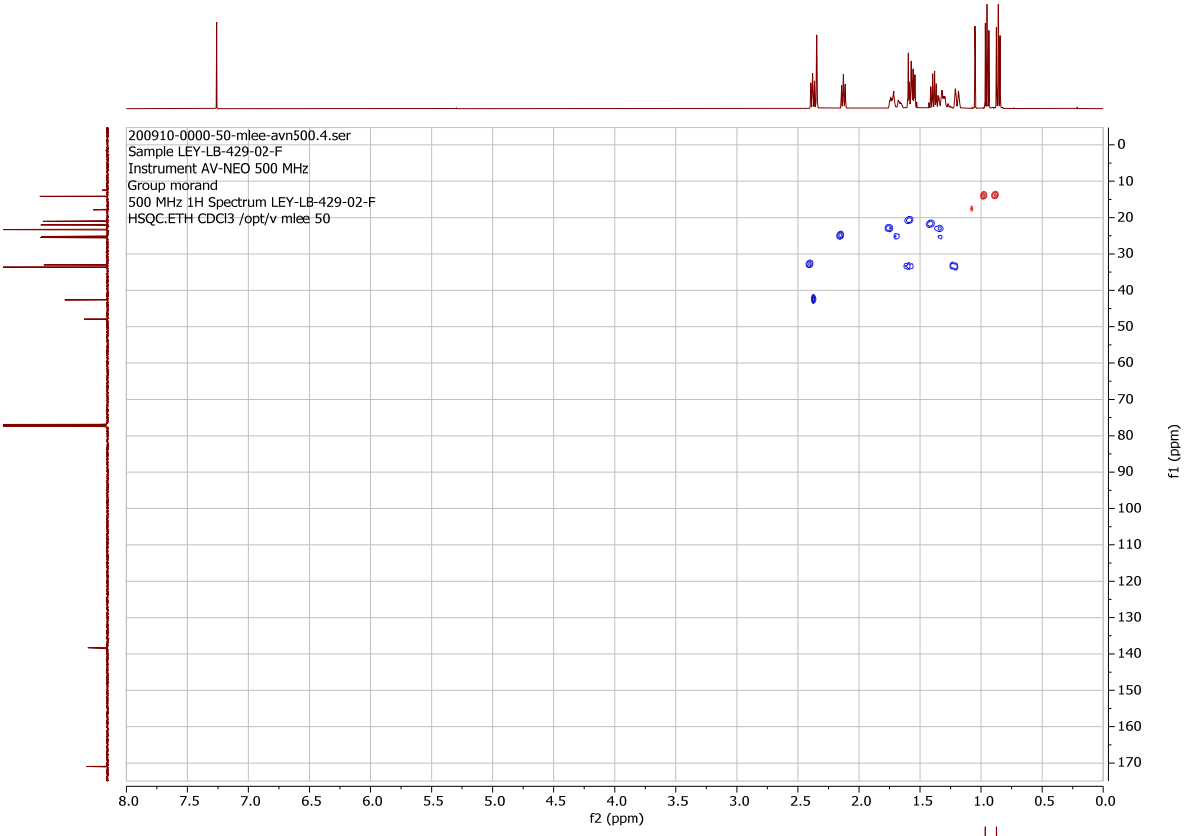

200824-1932-26-mlee-avn500.3.ser
Sample LEY-LB-422-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-422-02-F
COSY.ETH CDCl3 /opt/v mlee 26
f1 (ppm)
f2 (ppm)

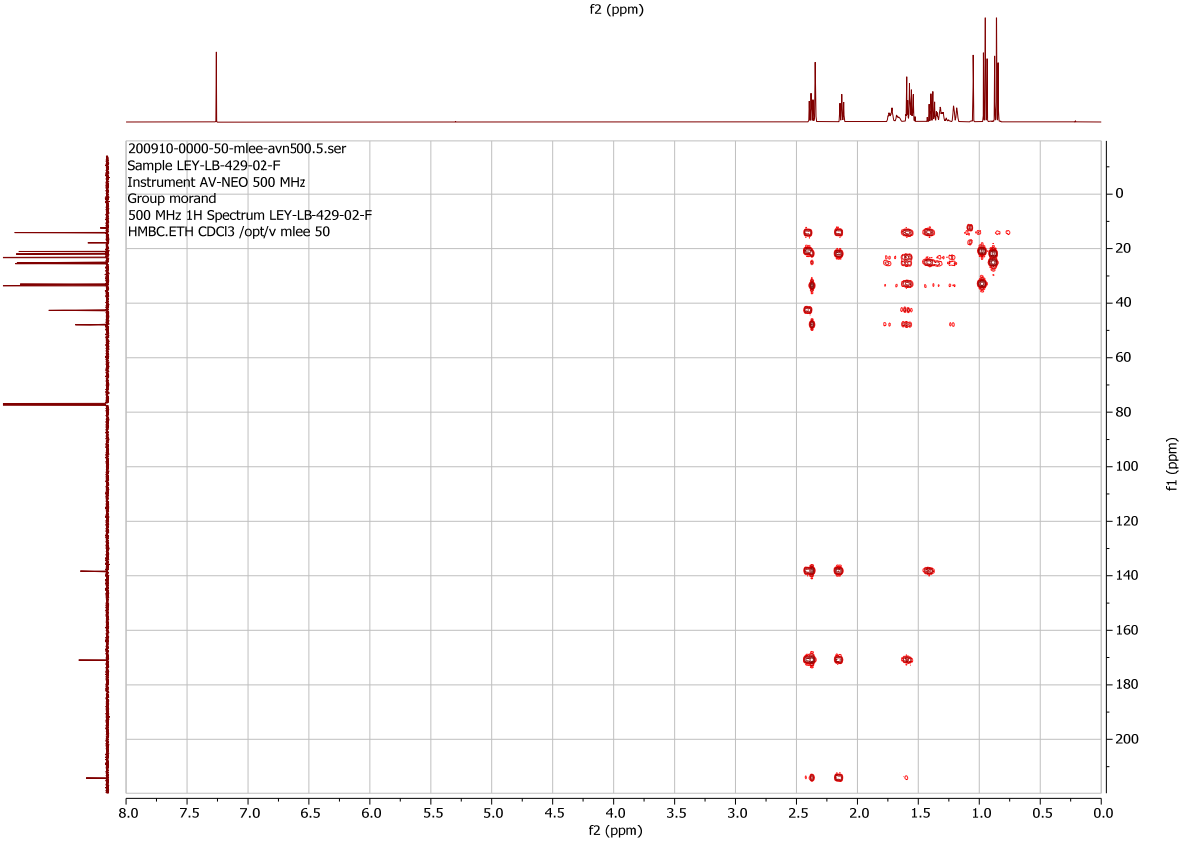

200824-1932-26-mlee-avn500.6.ser
Sample LEY-LB-422-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-422-02-F
NOESY.ETH CDCl3 /opt/v mlee 26
f1 (ppm)
f2 (ppm)

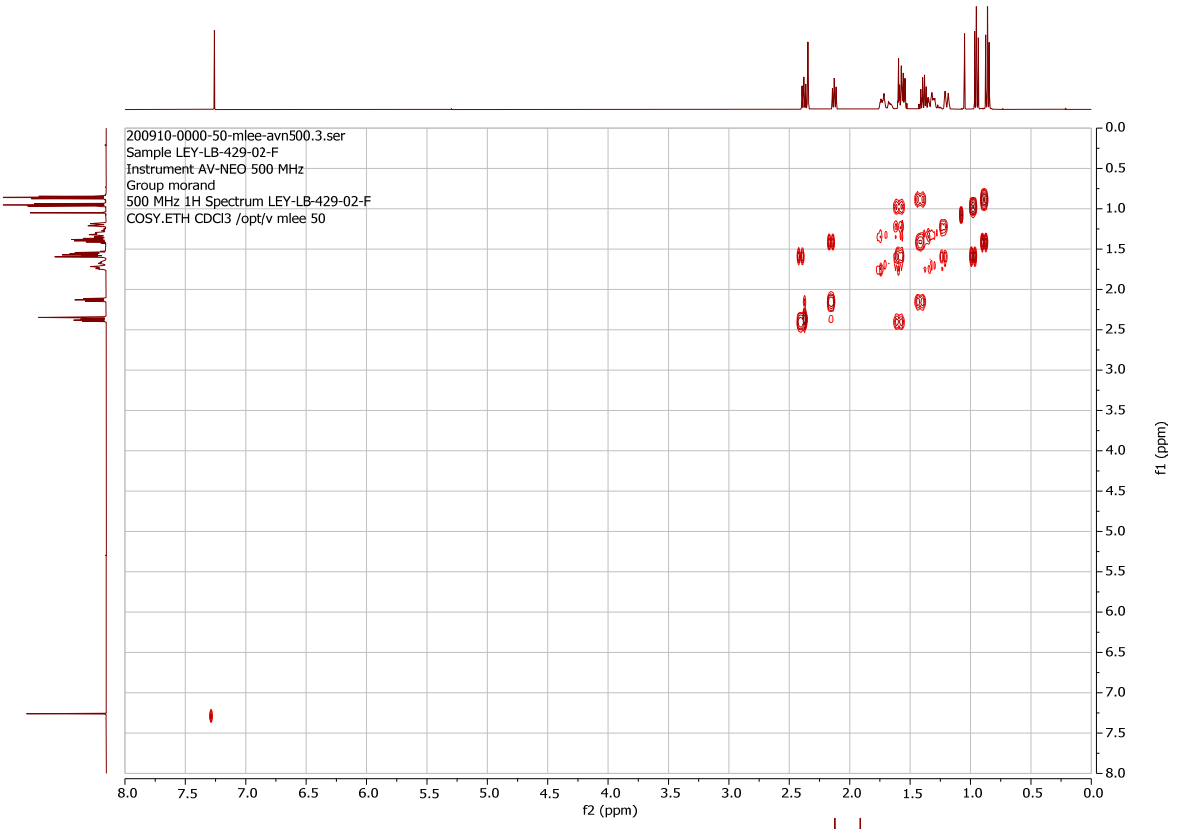
2,3-dipropylspiro[4.5]dec-2-en-1-one (**3at**).

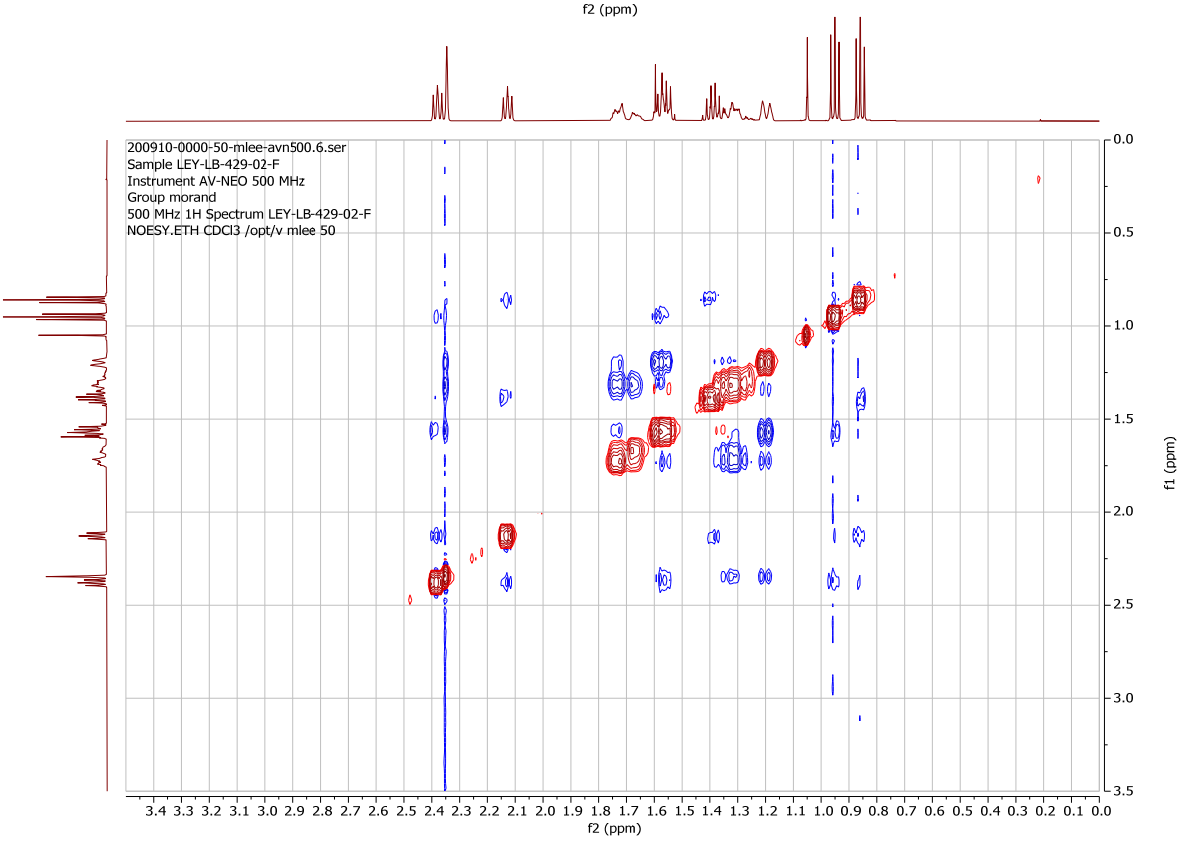




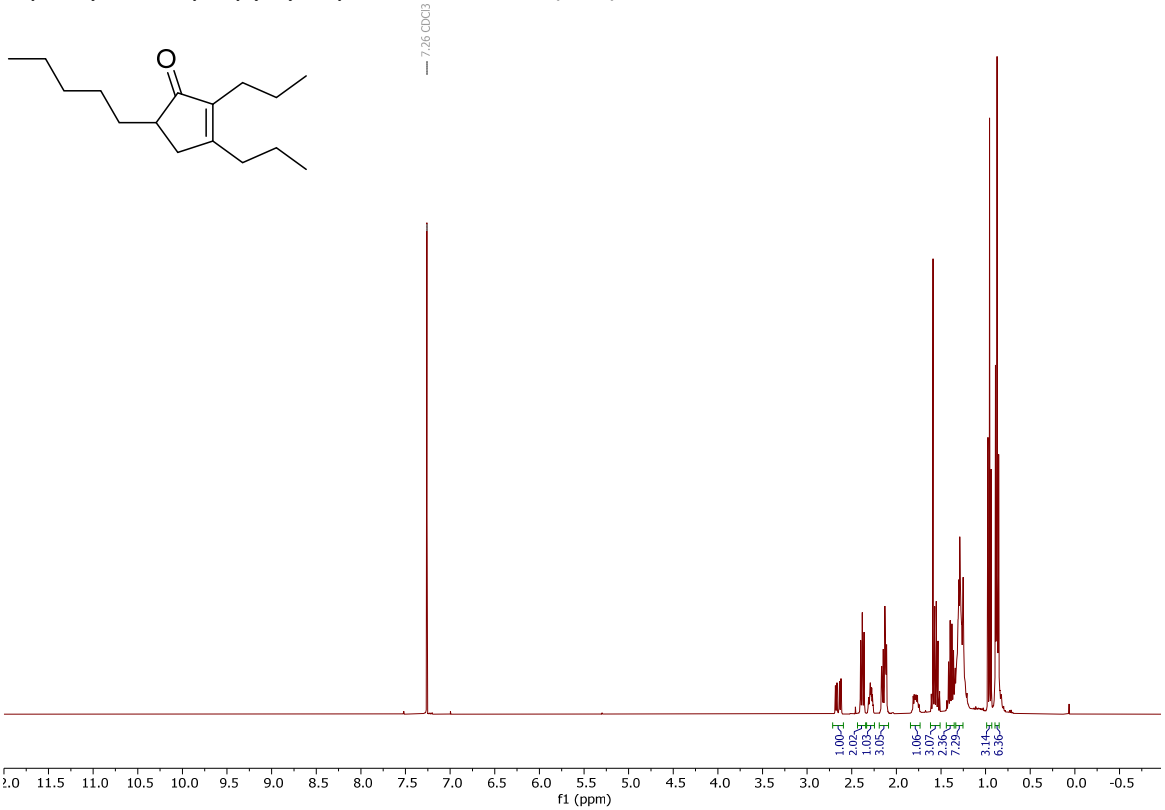

200910-0000-50-mlee-avn500.4.ser
Sample LEY-LB-429-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-429-02-F
HSQC.ETH CDCl3 /opt/v mlee 50
f2 (ppm)
f1 (ppm)

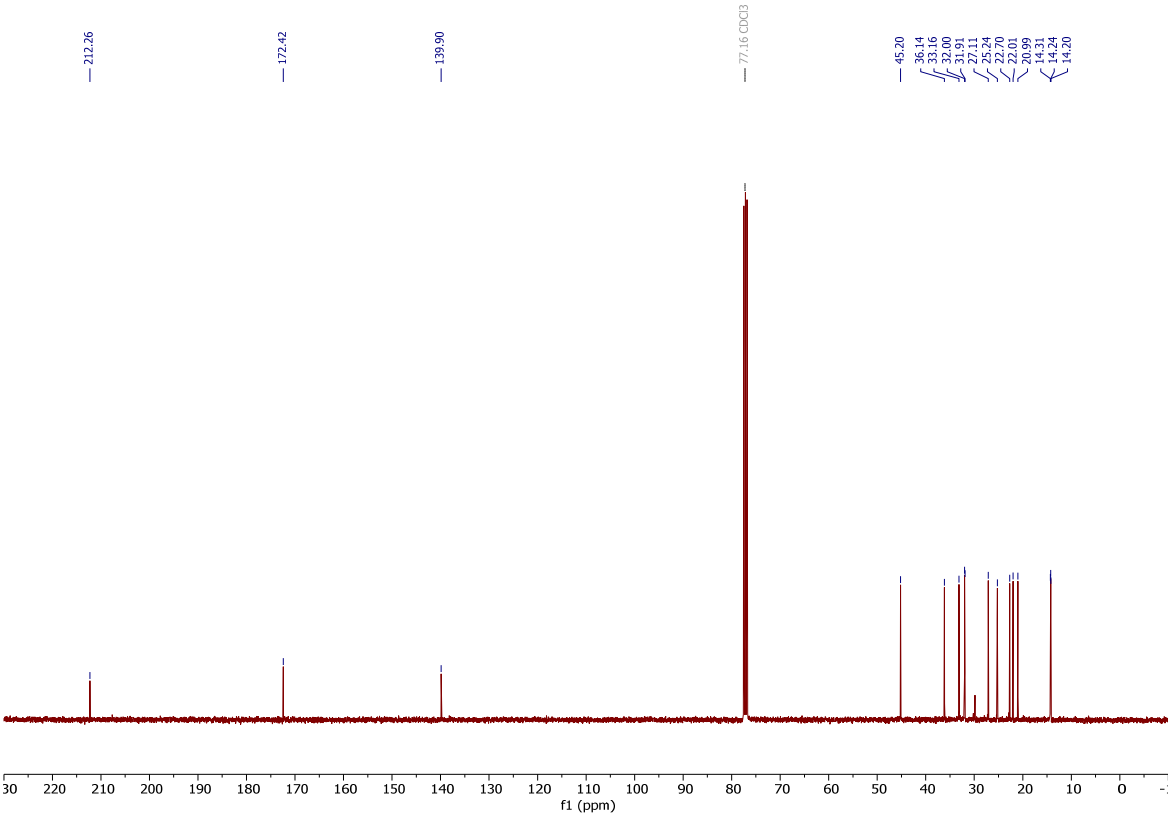

200910-0000-50-mlee-avn500.5.ser
Sample LEY-LB-429-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-429-02-F
HMBC.ETH CDCl3 /opt/v mlee 50
f2 (ppm)
f1 (ppm)

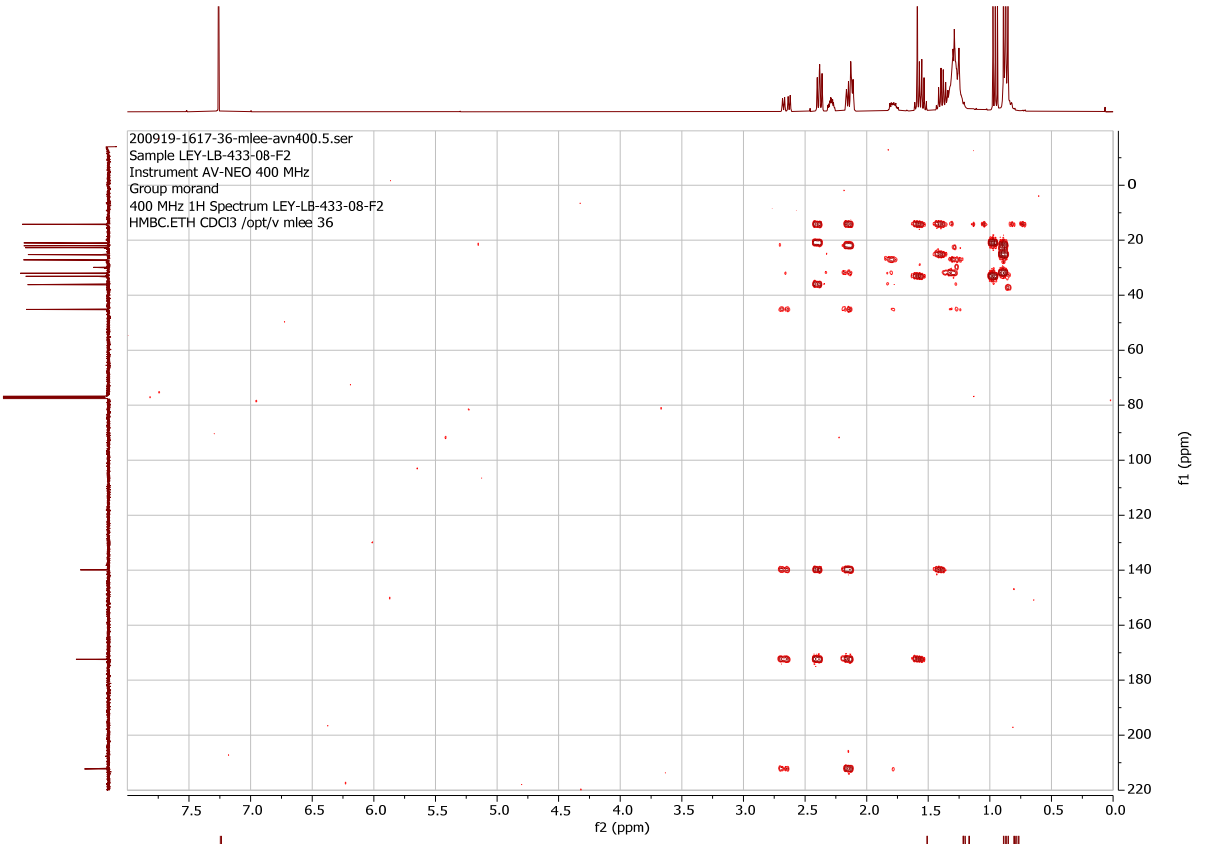

200910-0000-50-mlee-avn500.3.ser
Sample LEY-LB-429-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-429-02-F
COSY.ETH CDCl3 /opt/v mlee 50
f2 (ppm)
f1 (ppm)

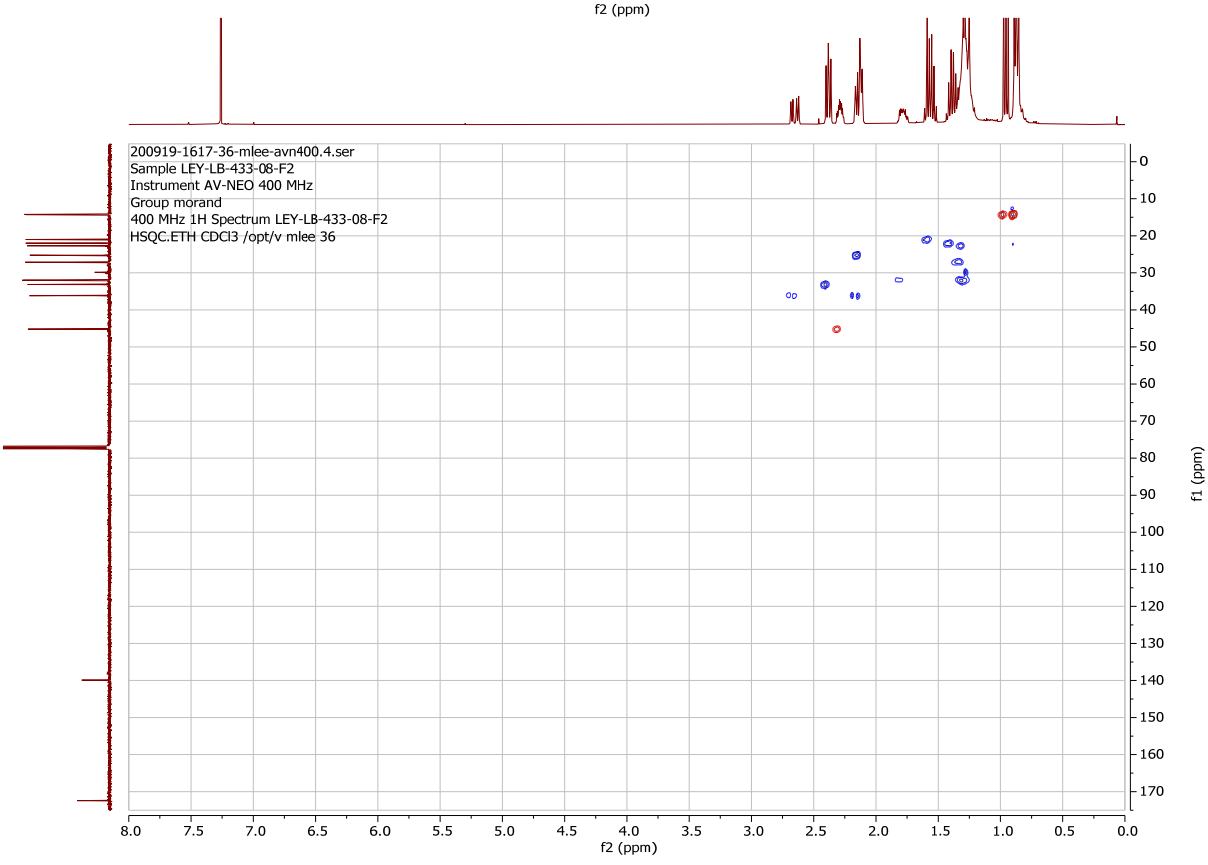

200910-0000-50-mlee-avn500.6.ser
Sample LEY-LB-429-02-F
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-429-02-F
NOESY.ETH CDCl3 /opt/v mlee 50
f2 (ppm)
f1 (ppm)

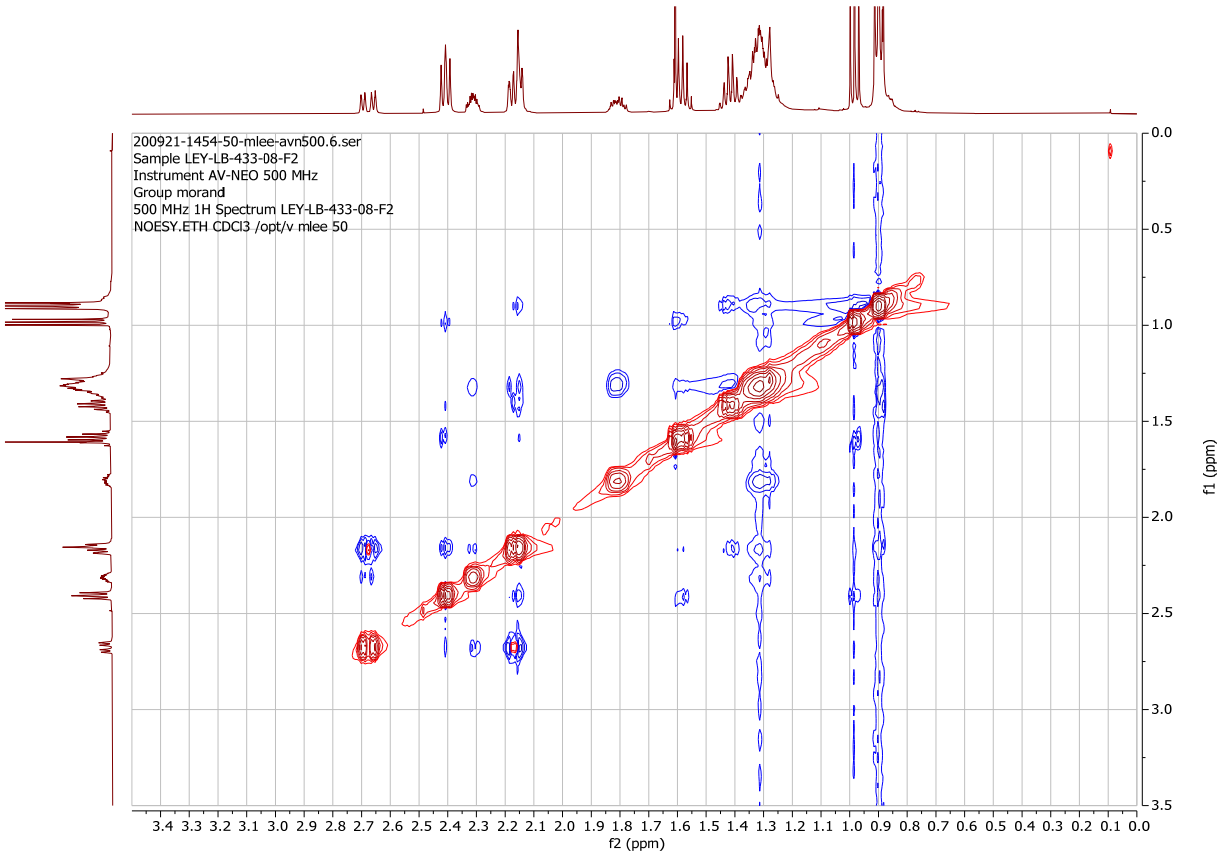
5-pentyl-2,3-dipropylcyclopent-2-en-1-one (**3au**).





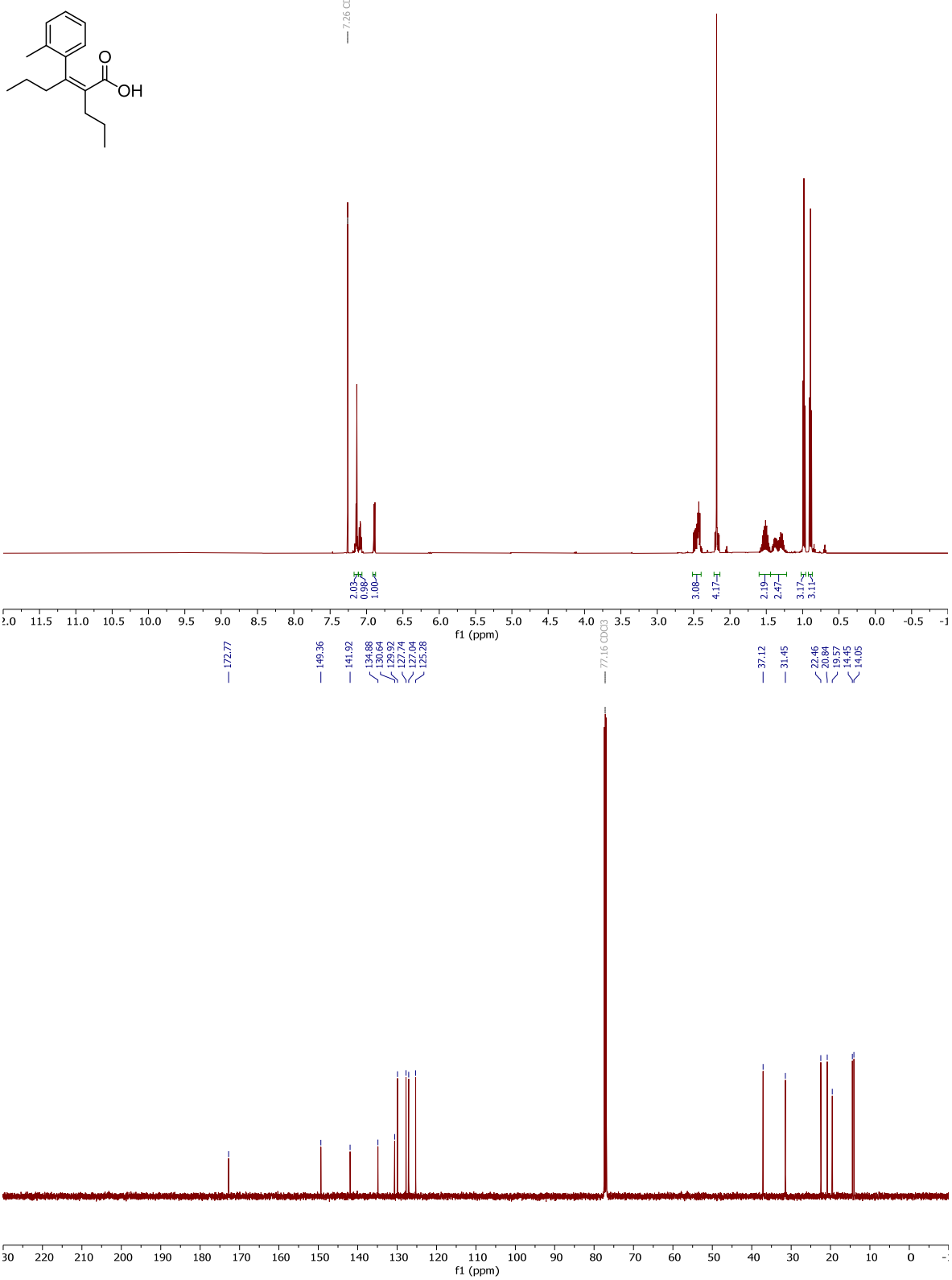

200919-1617-36-mlee-avn400.5.ser
Sample LEY-LB-433-08-F2
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-433-08-F2
HMBC.ETH CDCl3 /opt/v mlee 36
f2 (ppm)
f1 (ppm)

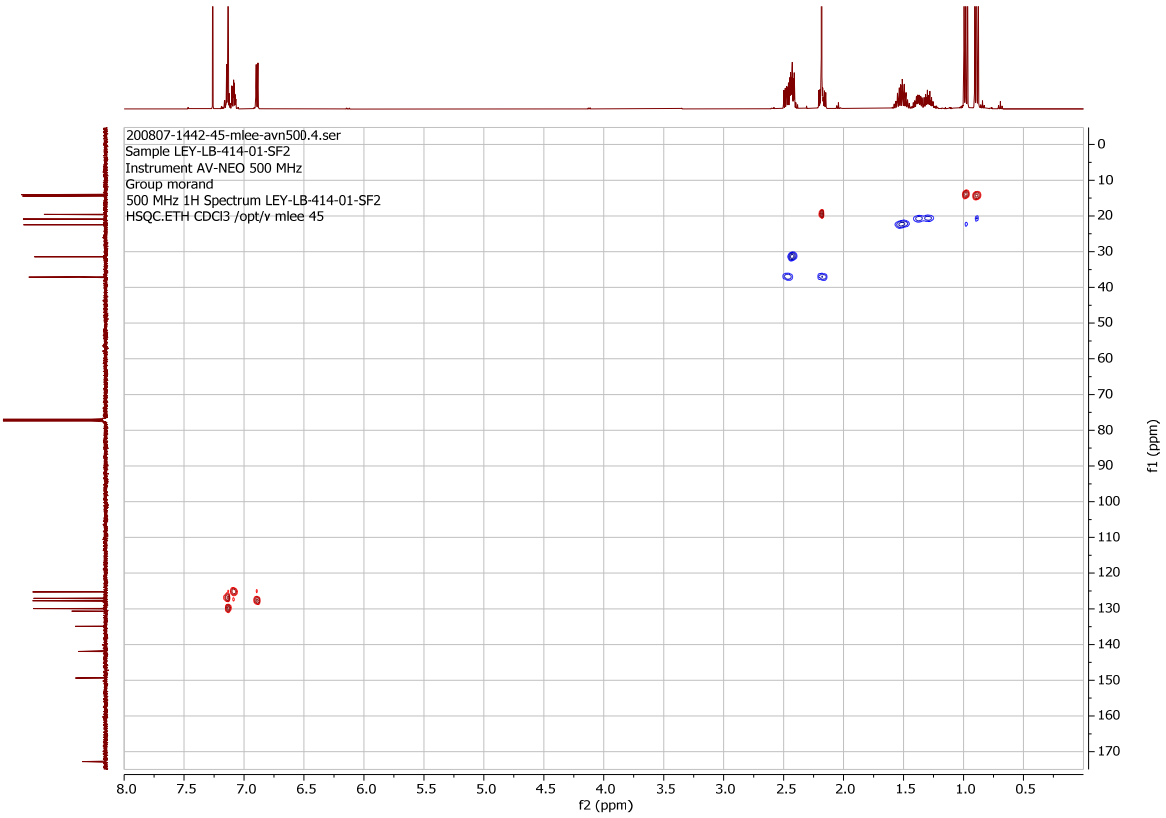

200919-1617-36-mlee-avn400.4.ser
Sample LEY-LB-433-08-F2
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-433-08-F2
HSQC.ETH CDCl3 /opt/v mlee 36
f2 (ppm)
f1 (ppm)


200921-1454-50-mlee-avn500.6.ser
Sample LEY-LB-433-08-F2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-433-08-F2
NOESY.ETH CDCl3 /opt/v mlee 50
f2 (ppm)
f1 (ppm)

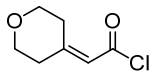
11.5. Acid chloride and alkyne substrates, etc.

(*Z*)-2-propyl-3-(*o*-tolyl)hex-2-enoic acid (**12a**).

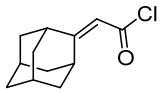


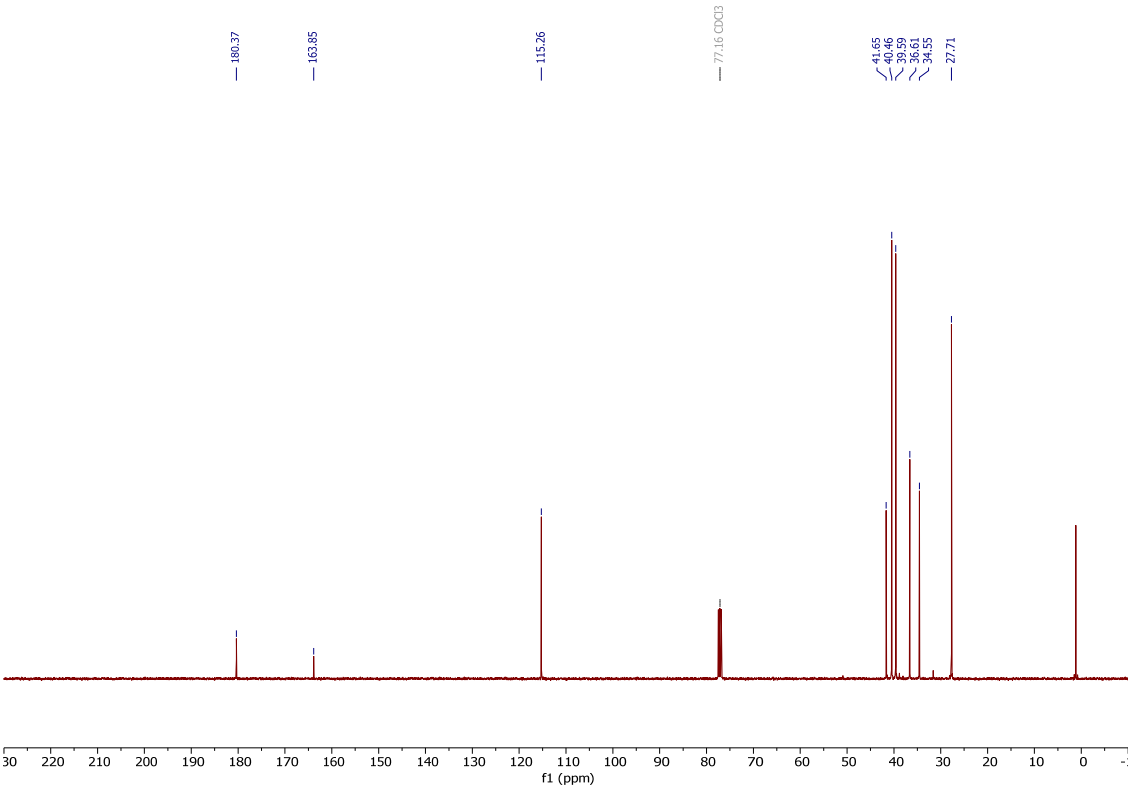

200807-1442-45-mlee-avn500.4.ser
Sample LEY-LB-414-01-SF2
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-414-01-SF2
HSQC.ETH CDCl3 /opt/v mlee 45
f2 (ppm)
f1 (ppm)

2-(tetrahydro-4*H*-pyran-4-ylidene)acetyl chloride (**1c**).

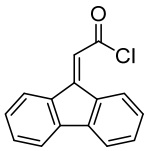


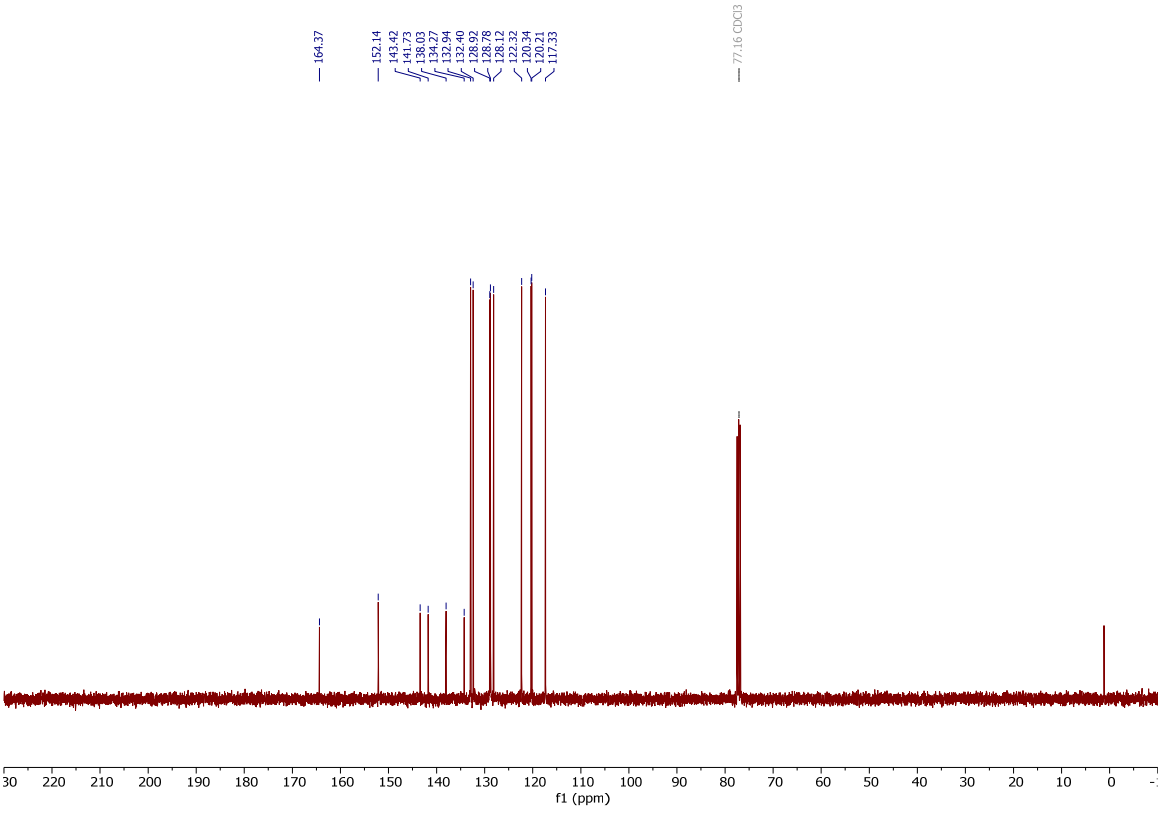
2-((1r,3r,5R,7S)-adamantan-2-ylidene)acetyl chloride (**1d**).



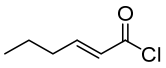


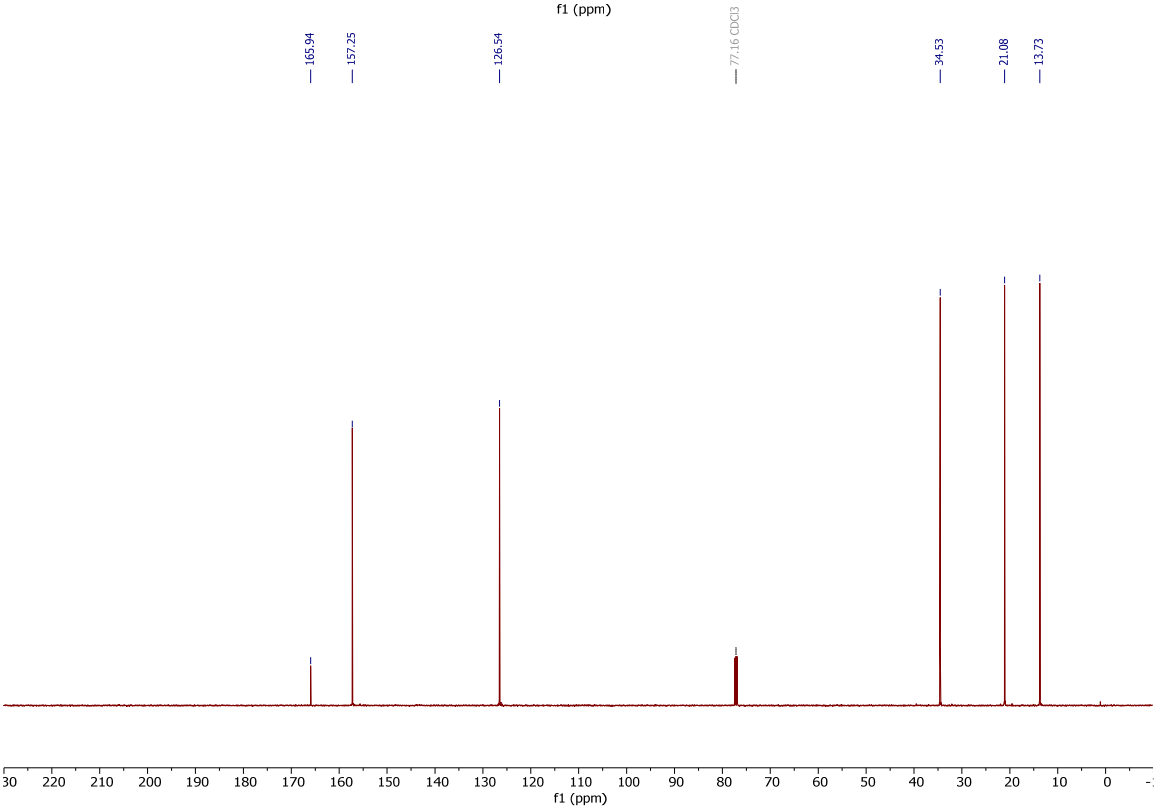
2-(9*H*-fluoren-9-ylidene)acetyl chloride (**1e**).



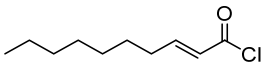


(*E*)-hex-2-enoyl chloride (**1f**).

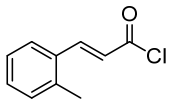


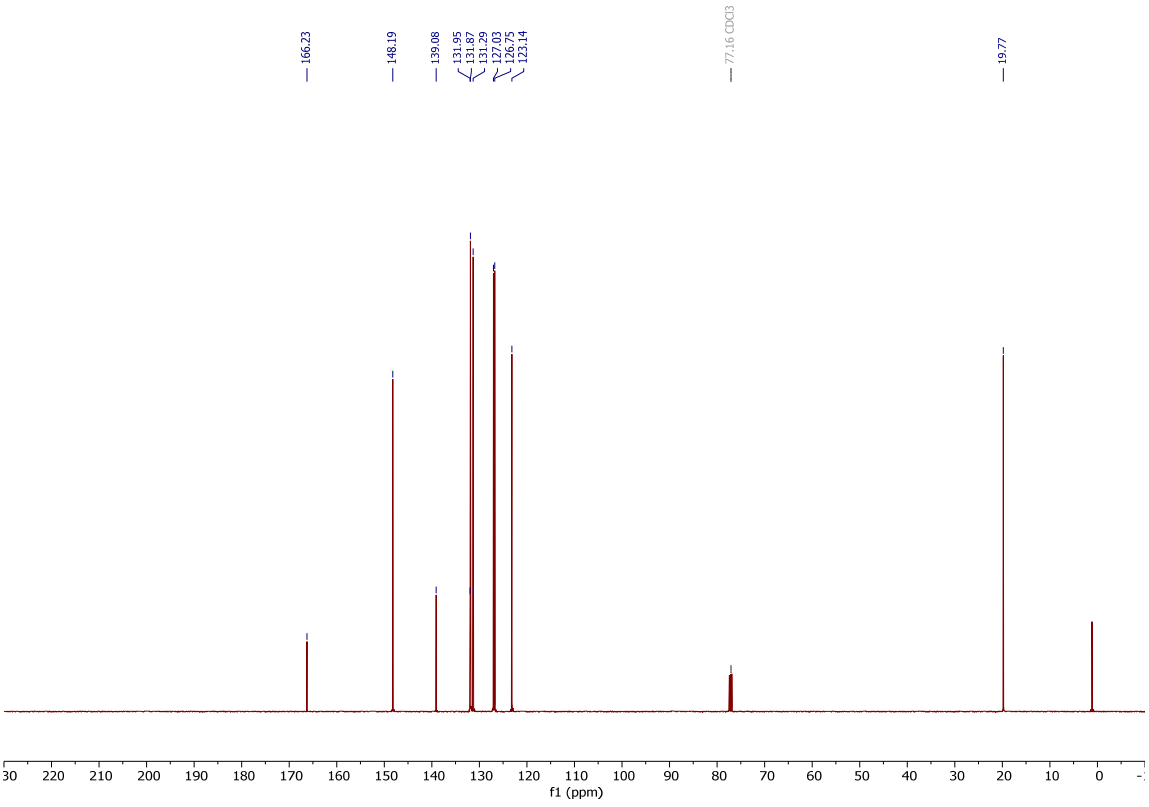


(*E*)-dec-2-enoyl chloride (**1g**).

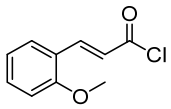


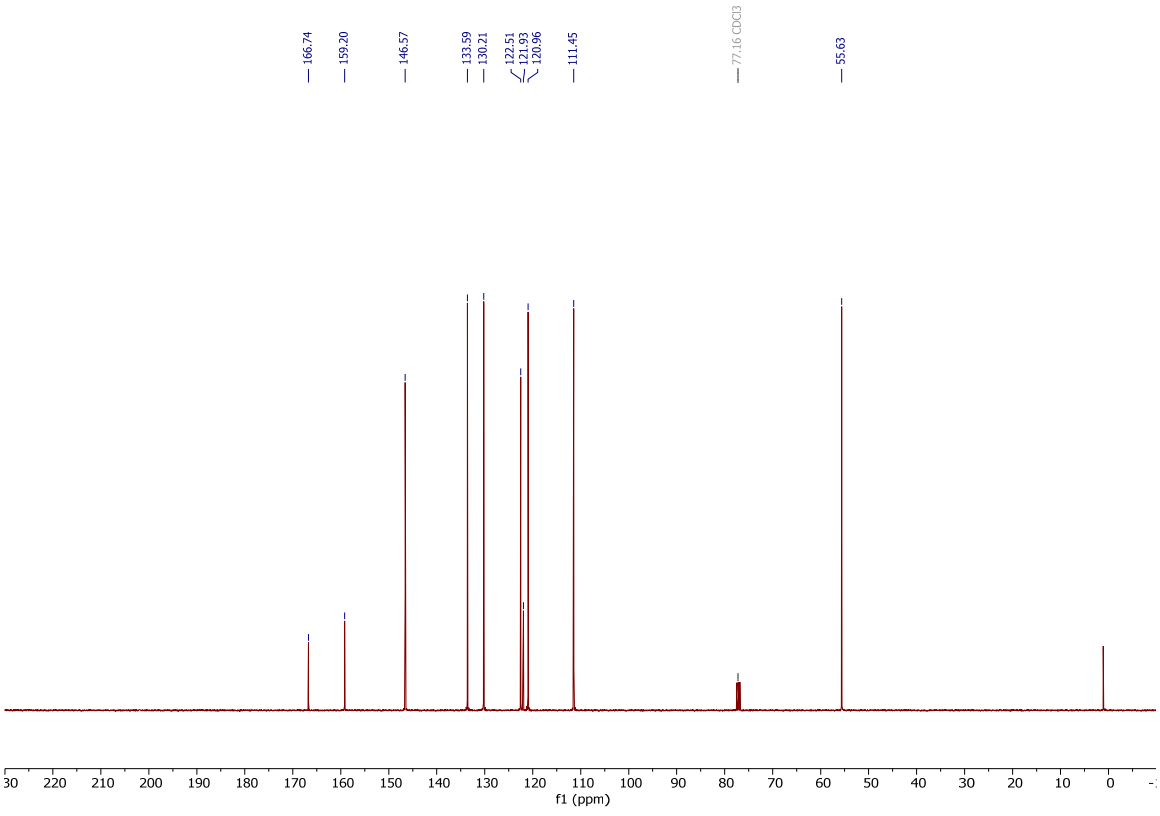
(*E*)-3-(*o*-tolyl)acryloyl chloride (**1h**).



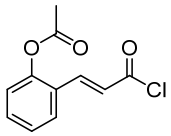


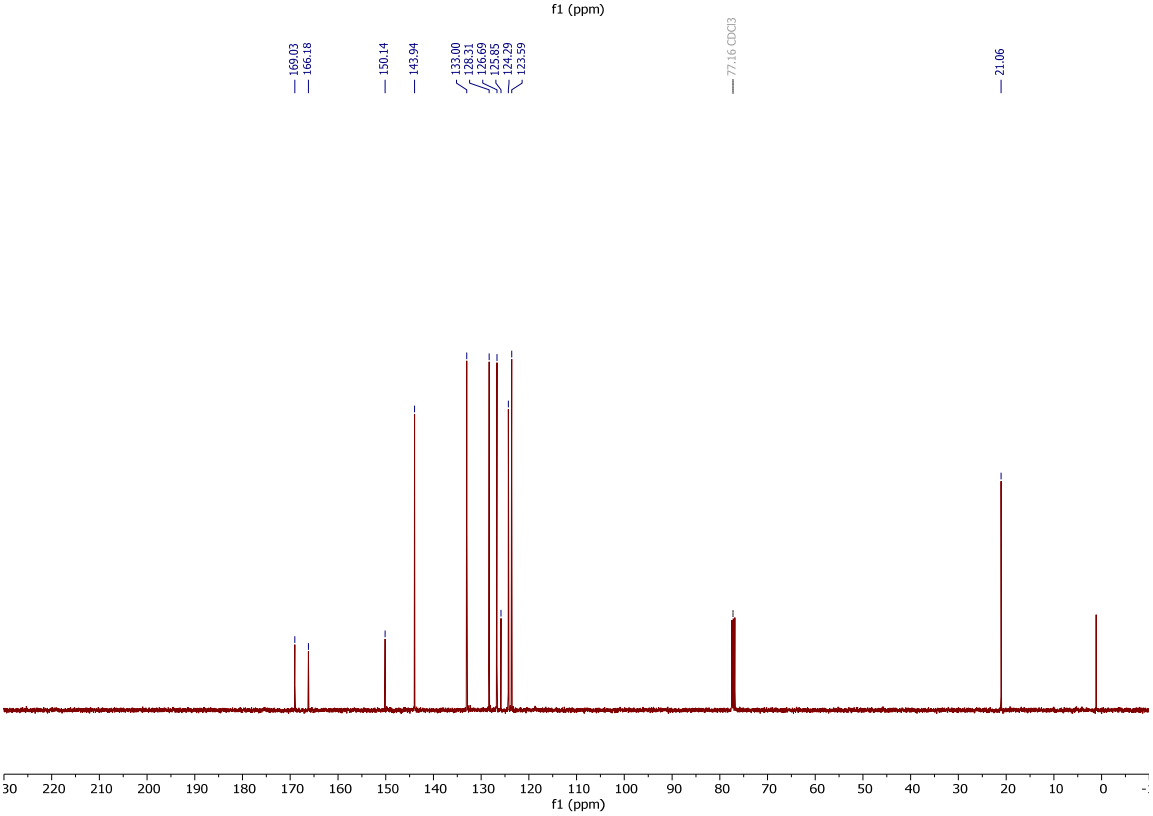
(*E*)-3-(2-methoxyphenyl)acryloyl chloride (**1i**).



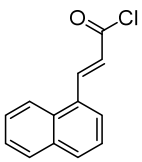


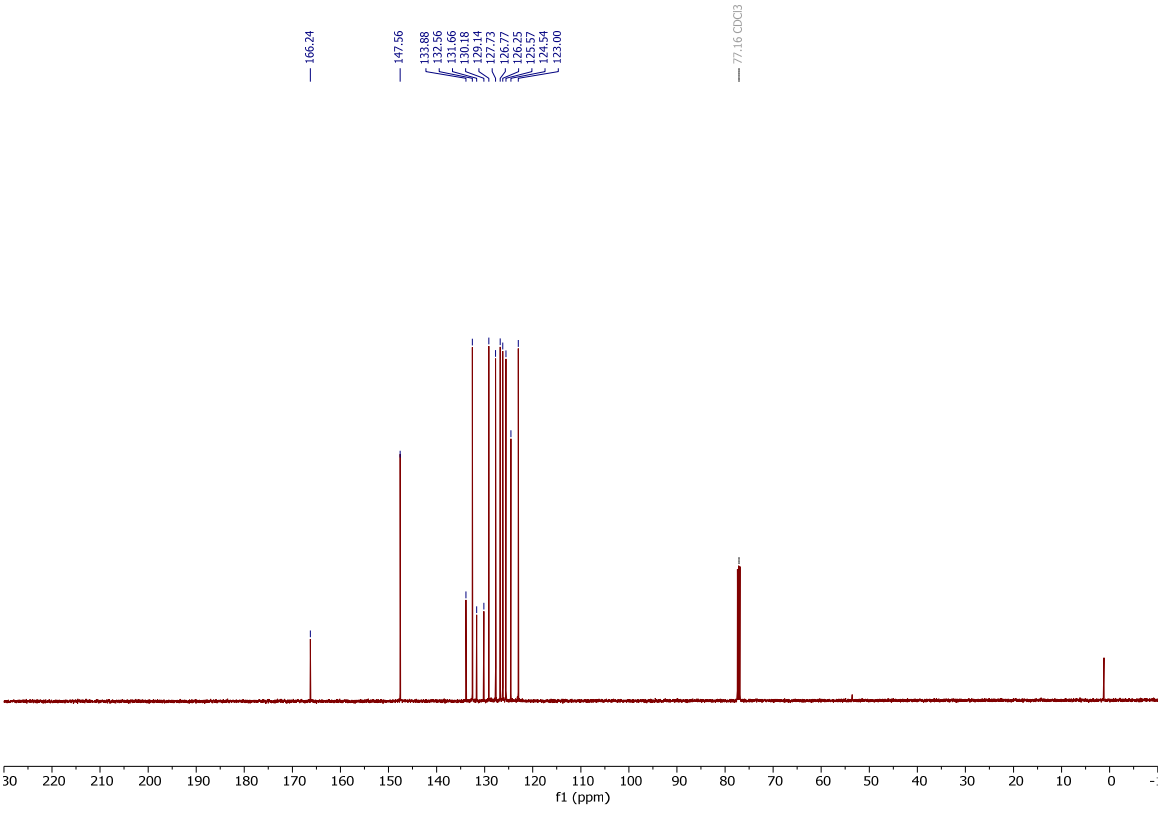
(*E*)-2-(3-chloro-3-oxoprop-1-en-1-yl)phenyl acetate (**1j**).



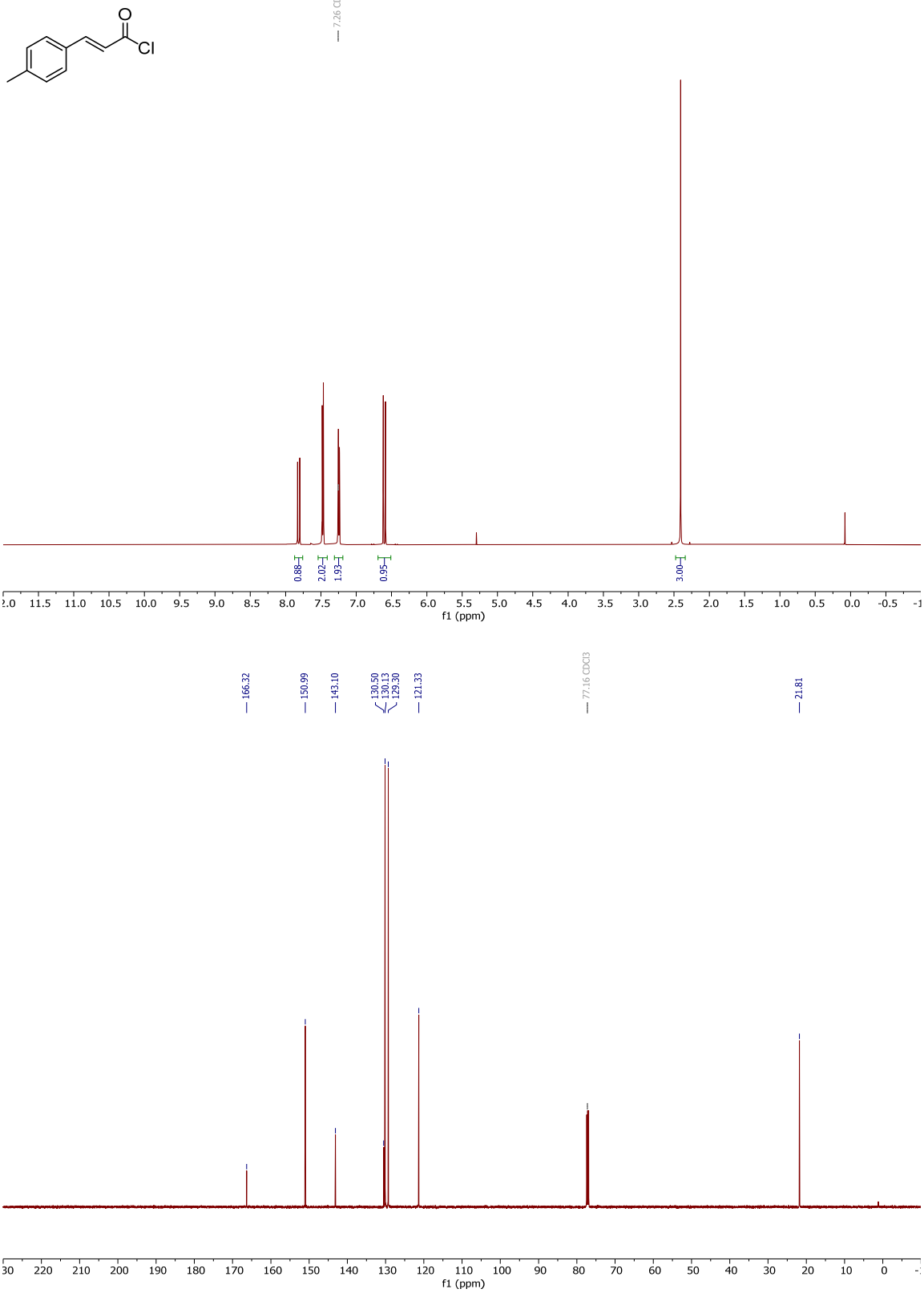


(*E*)-3-(naphthalen-1-yl)acryloyl chloride (**1k**).

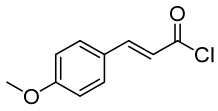


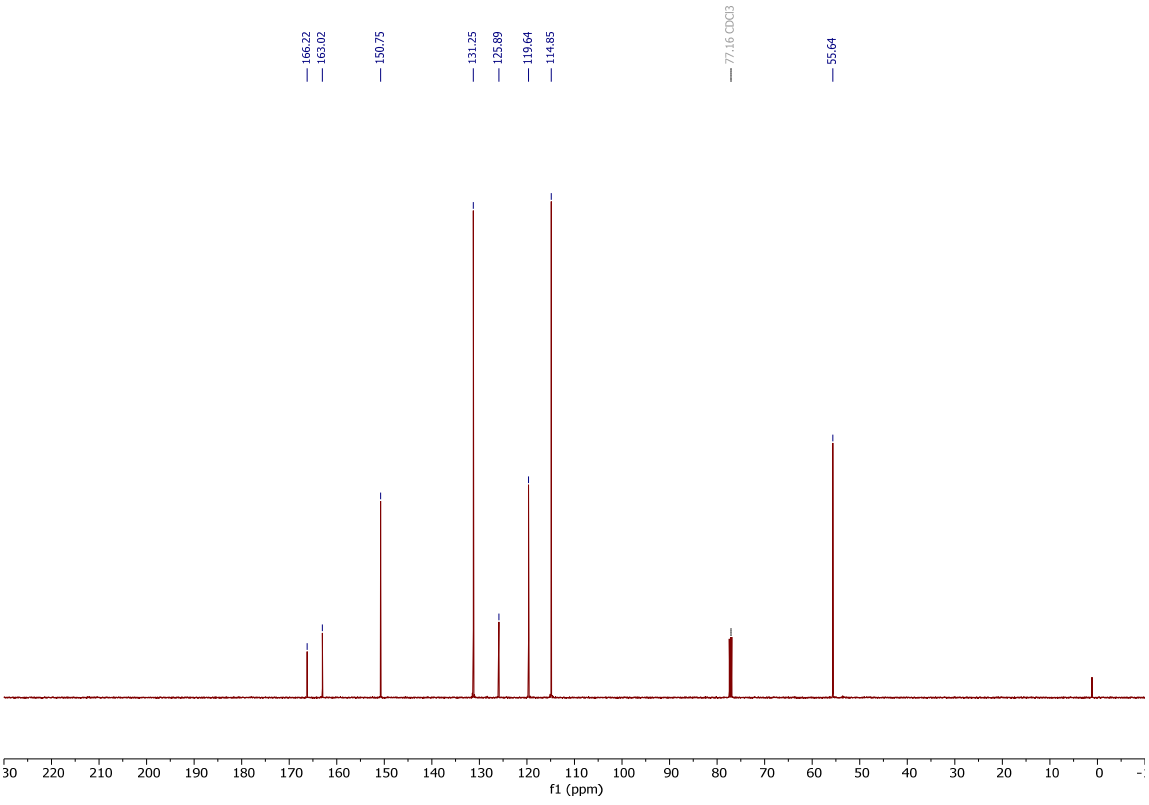


(*E*)-3-(*p*-tolyl)acryloyl chloride (**1l**).

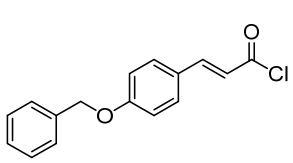


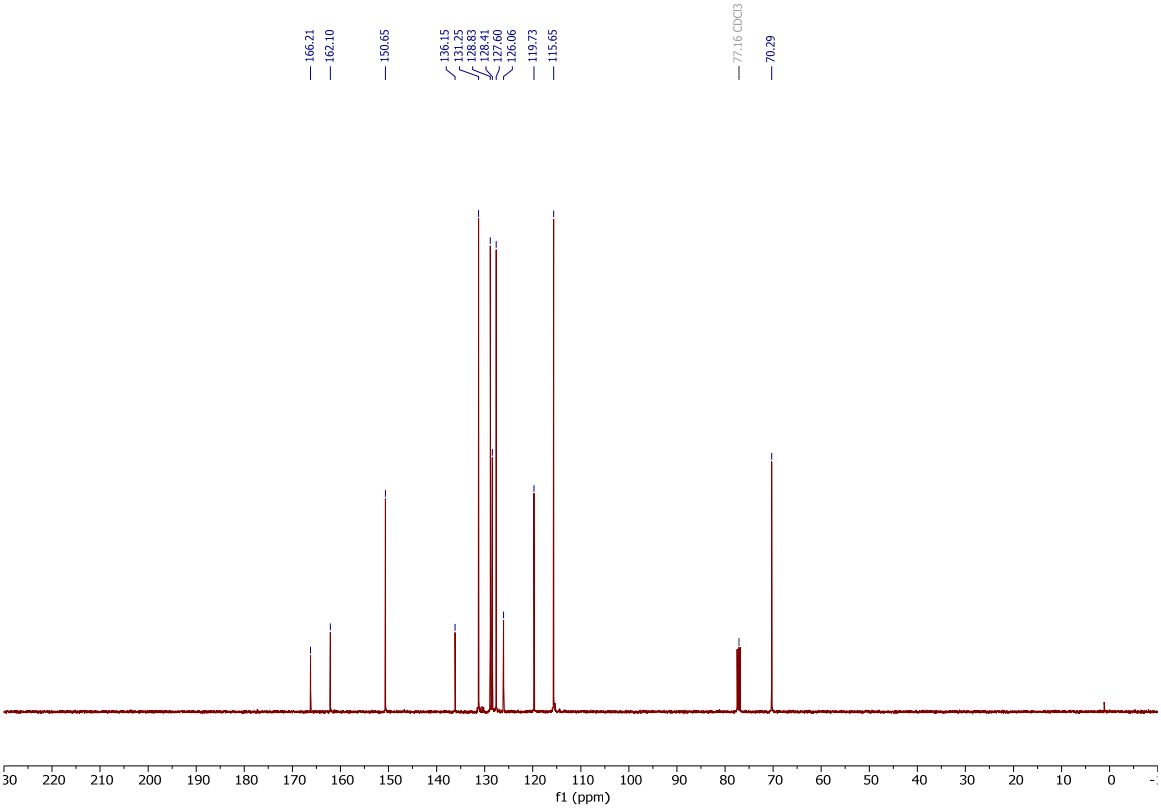
(*E*)-3-(4-methoxyphenyl)acryloyl chloride (**1m**).



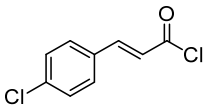


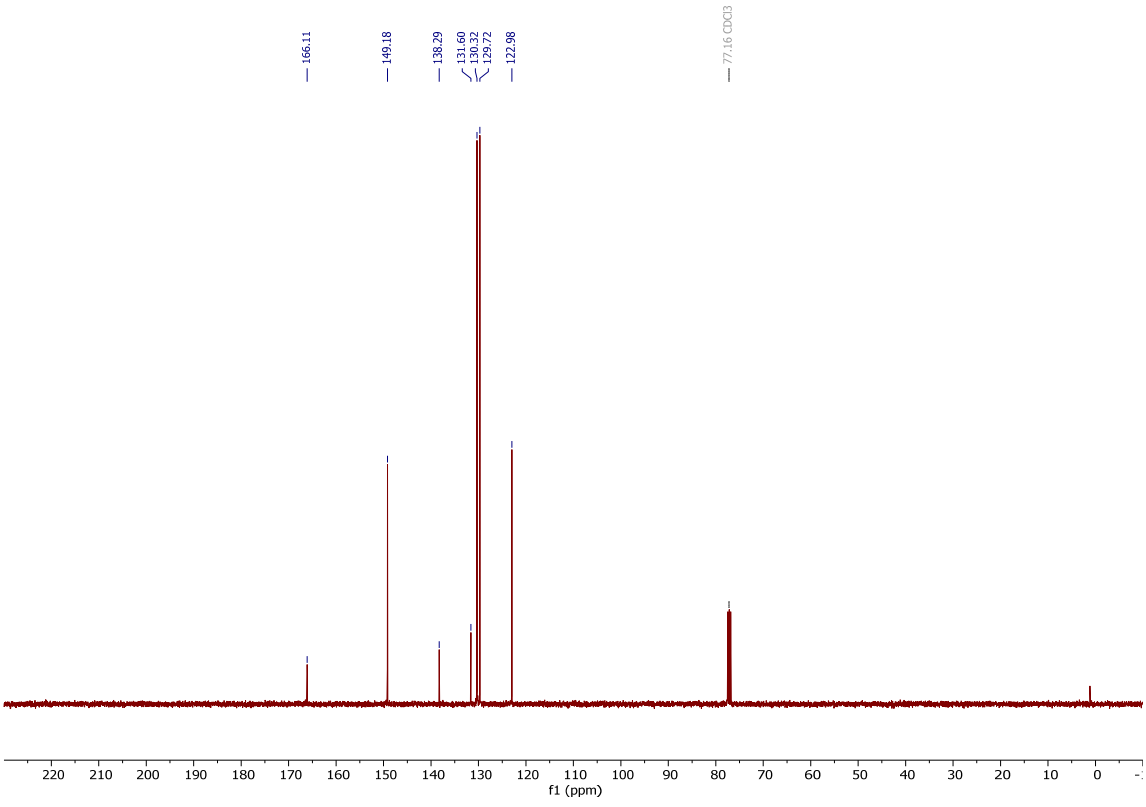
(*E*)-3-(4-(benzyloxy)phenyl)acryloyl chloride (**1n**).



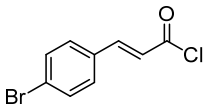


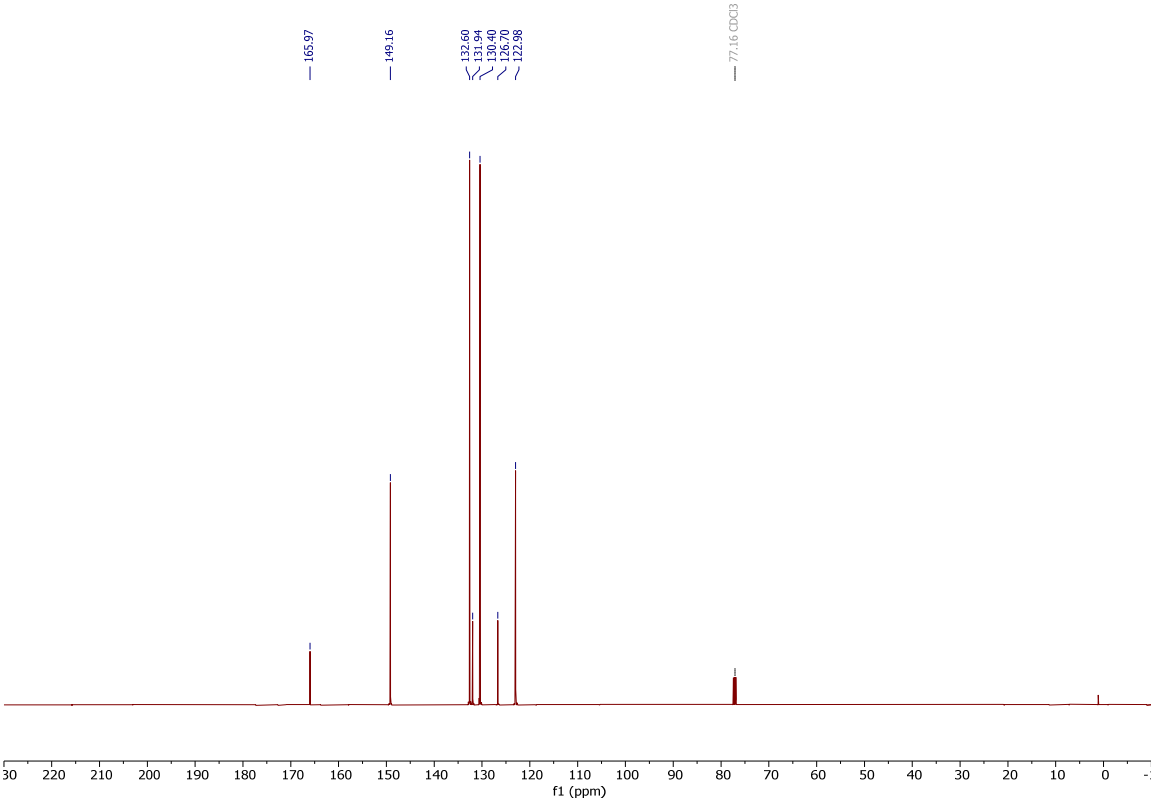
(*E*)-3-(4-chlorophenyl)acryloyl chloride (**1o**).



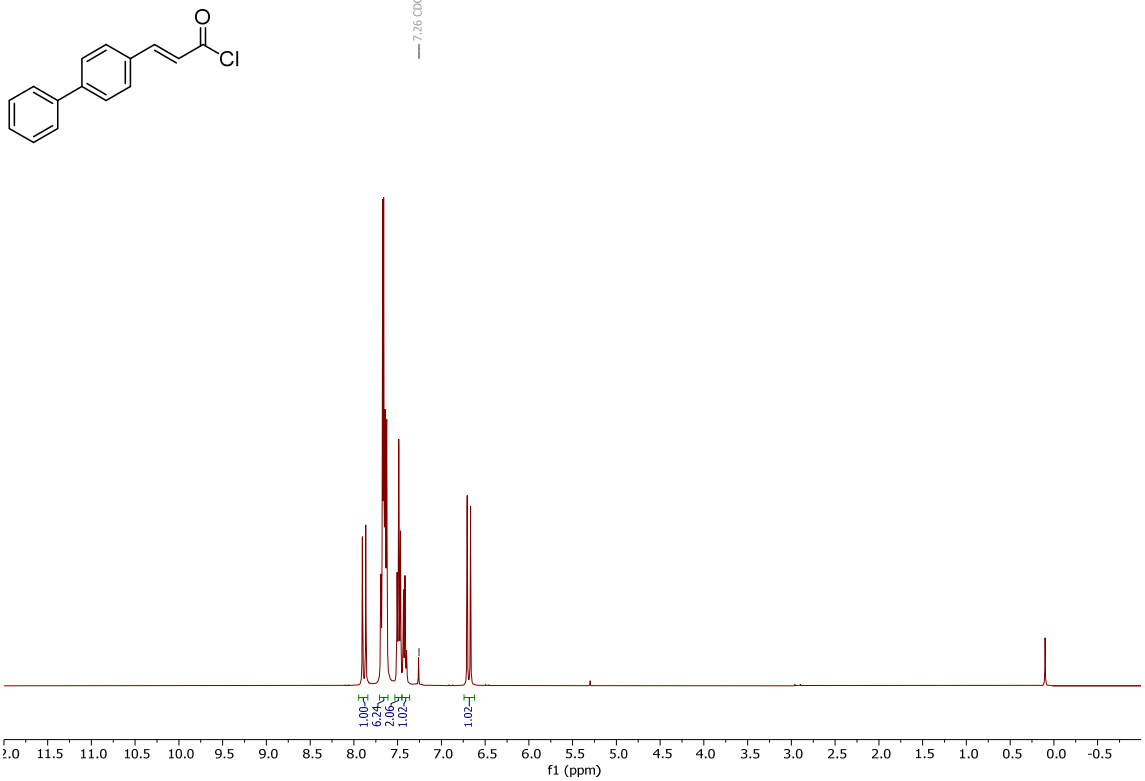


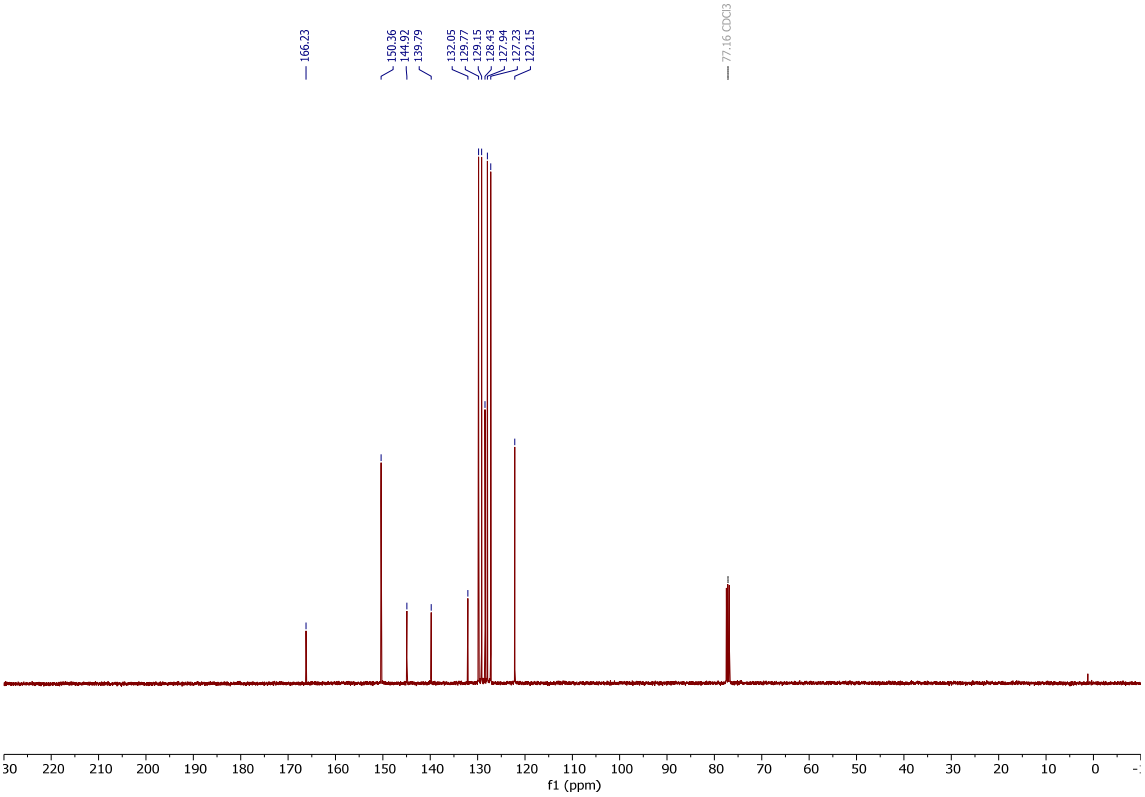
(*E*)-3-(4-bromophenyl)acryloyl chloride (**1p**).



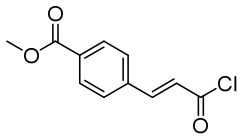


(*E*)-3-([1,1'-biphenyl]-4-yl)acryloyl chloride (**1q**).

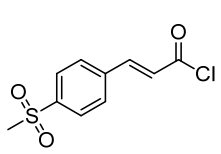


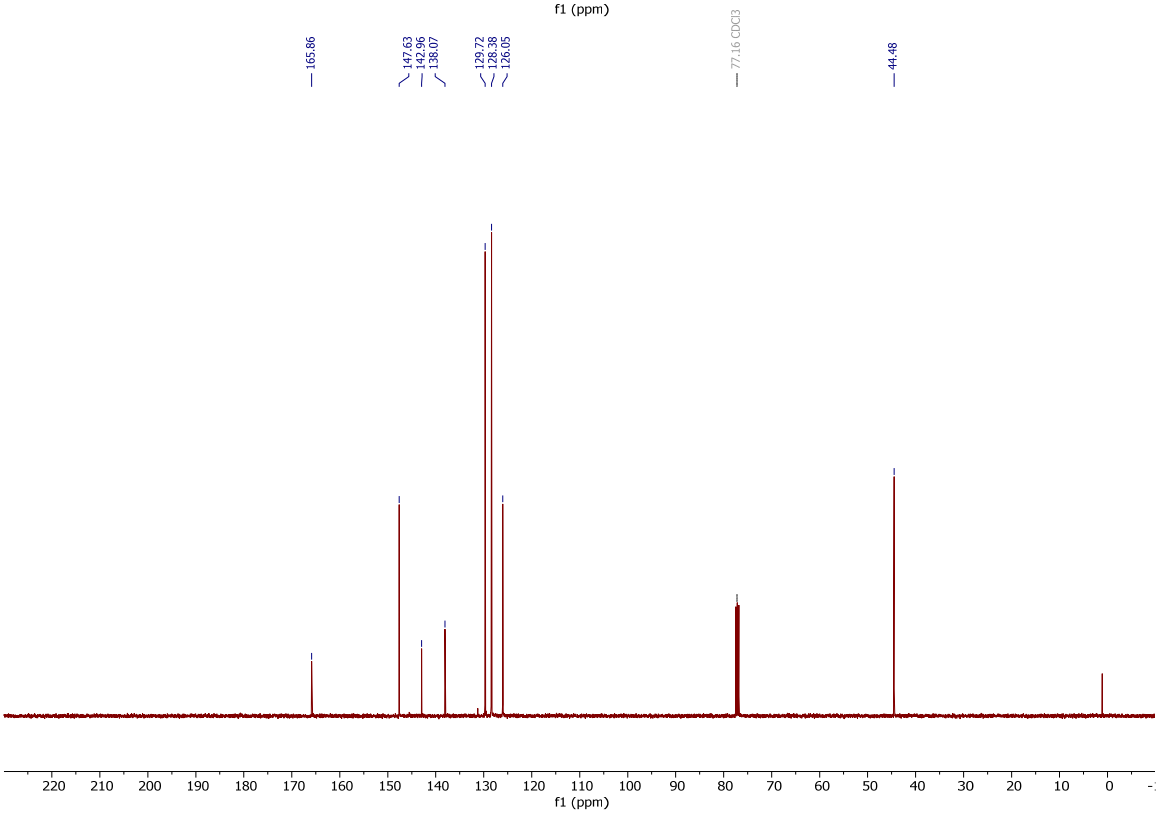


methyl (*E*)-4-(3-chloro-3-oxoprop-1-en-1-yl)benzoate (**1r**).

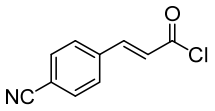


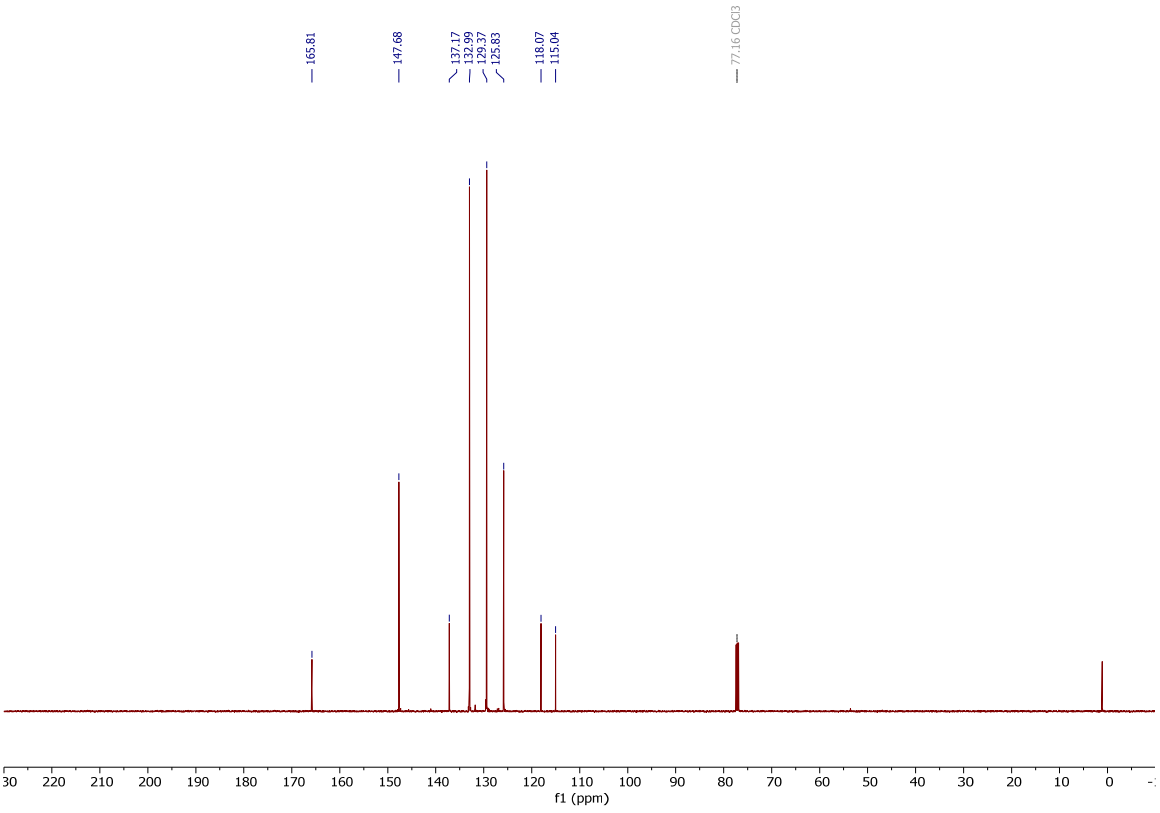
(*E*)-3-(4-(methylsulfonyl)phenyl)acryloyl chloride (**1s**).



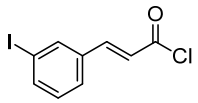


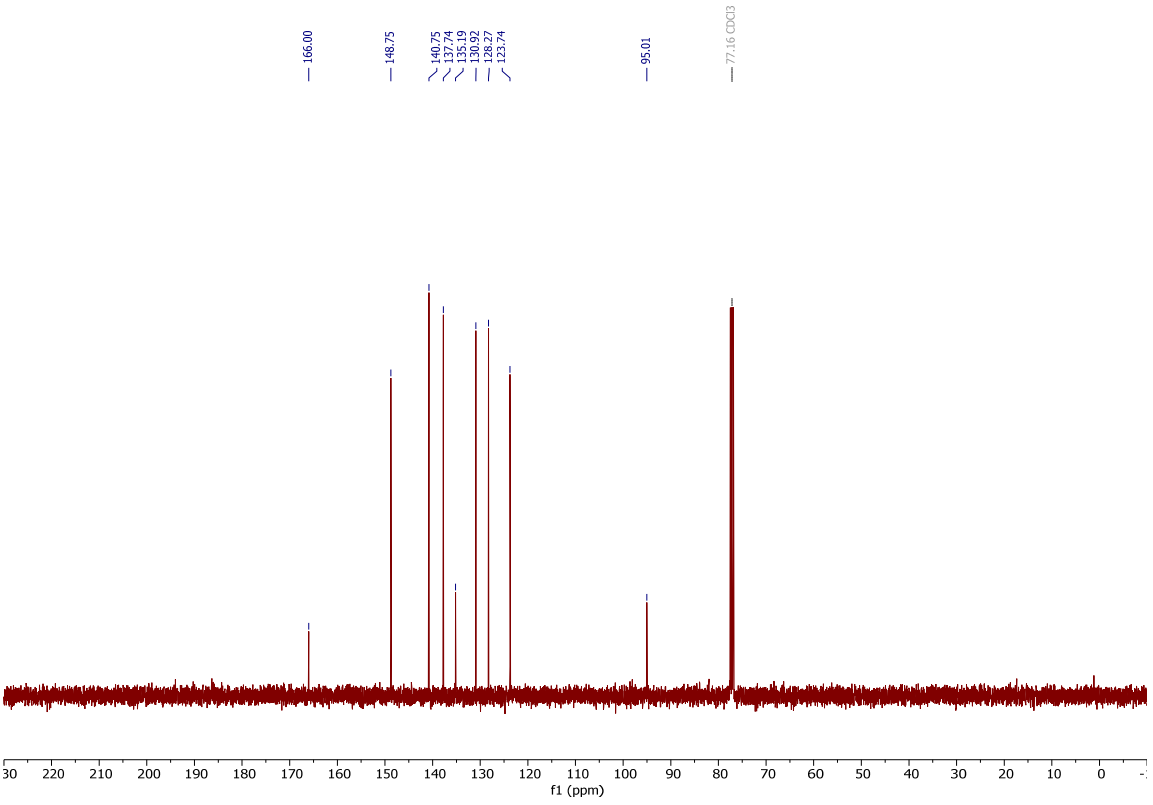
(*E*)-3-(4-cyanophenyl)acryloyl chloride (**1t**).



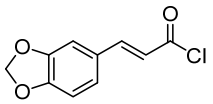


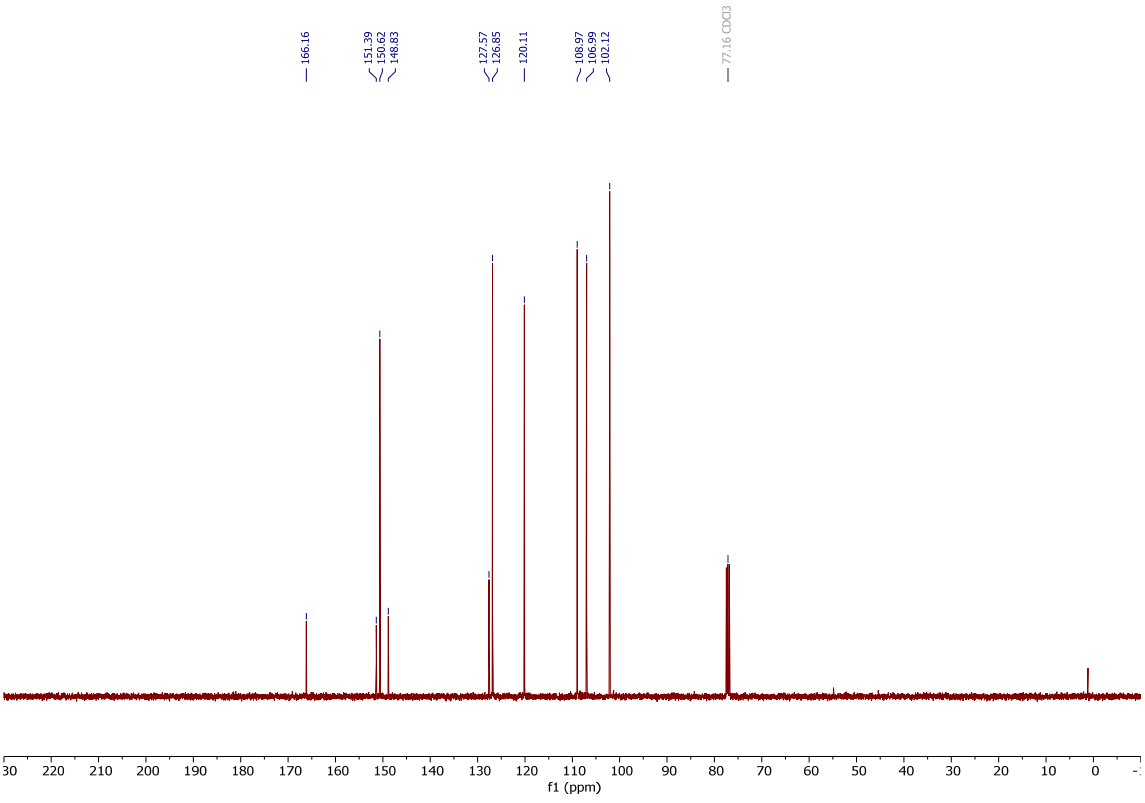
(*E*)-3-(3-iodophenyl)acryloyl chloride (**1u**).



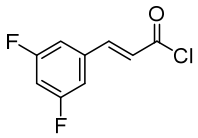


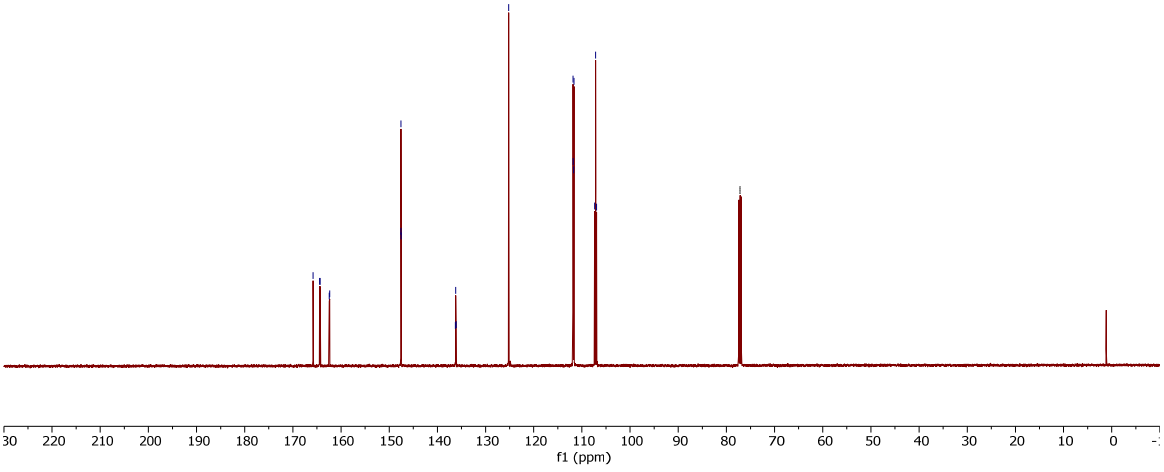
(*E*)-3-(benzo[d][1,3]dioxol-5-yl)acryloyl chloride (**1v**).

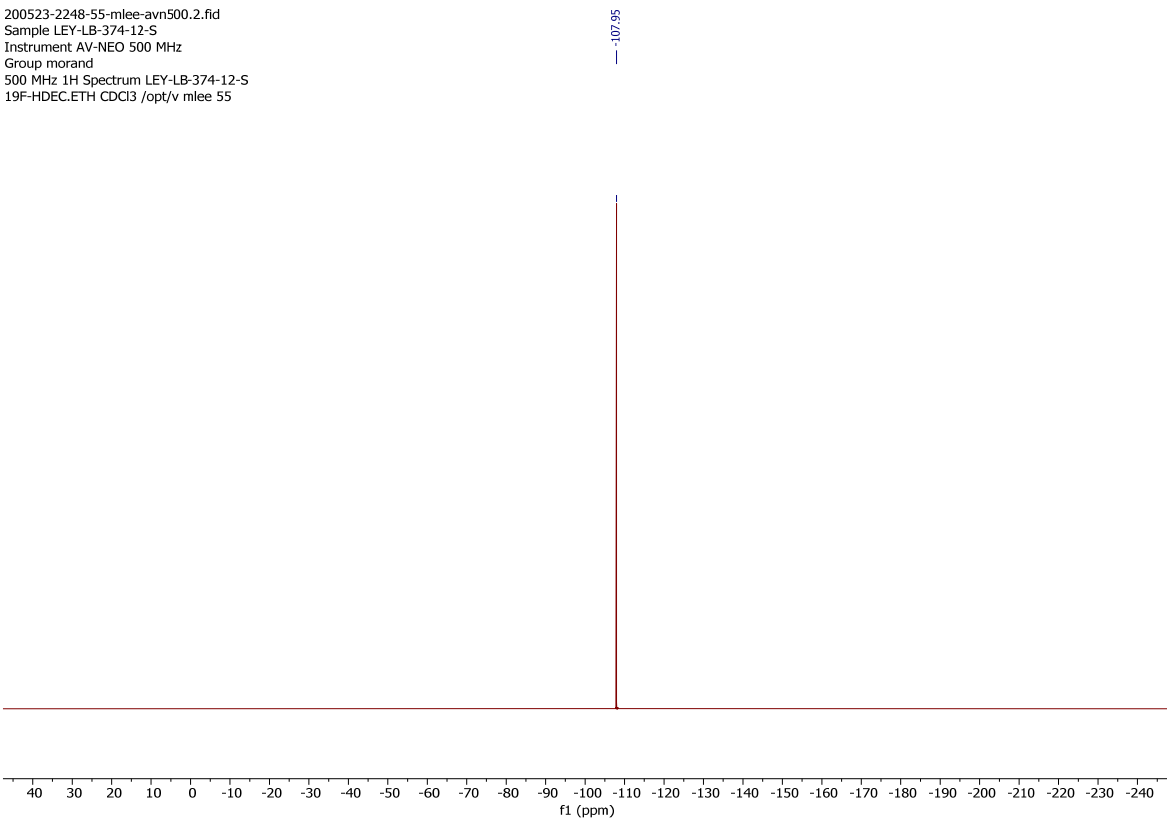




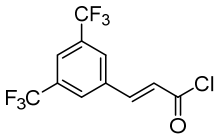
(*E*)-3-(3,5-difluorophenyl)acryloyl chloride (**1w**).

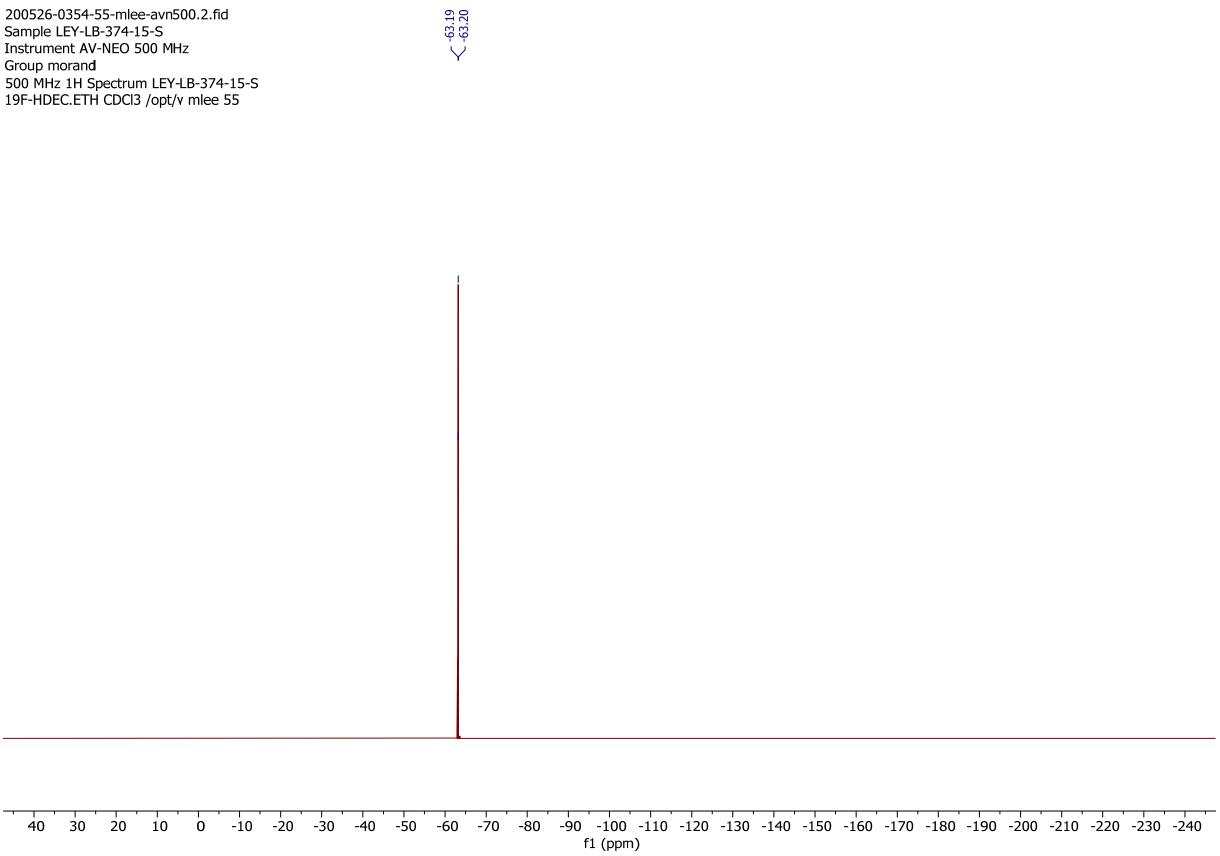




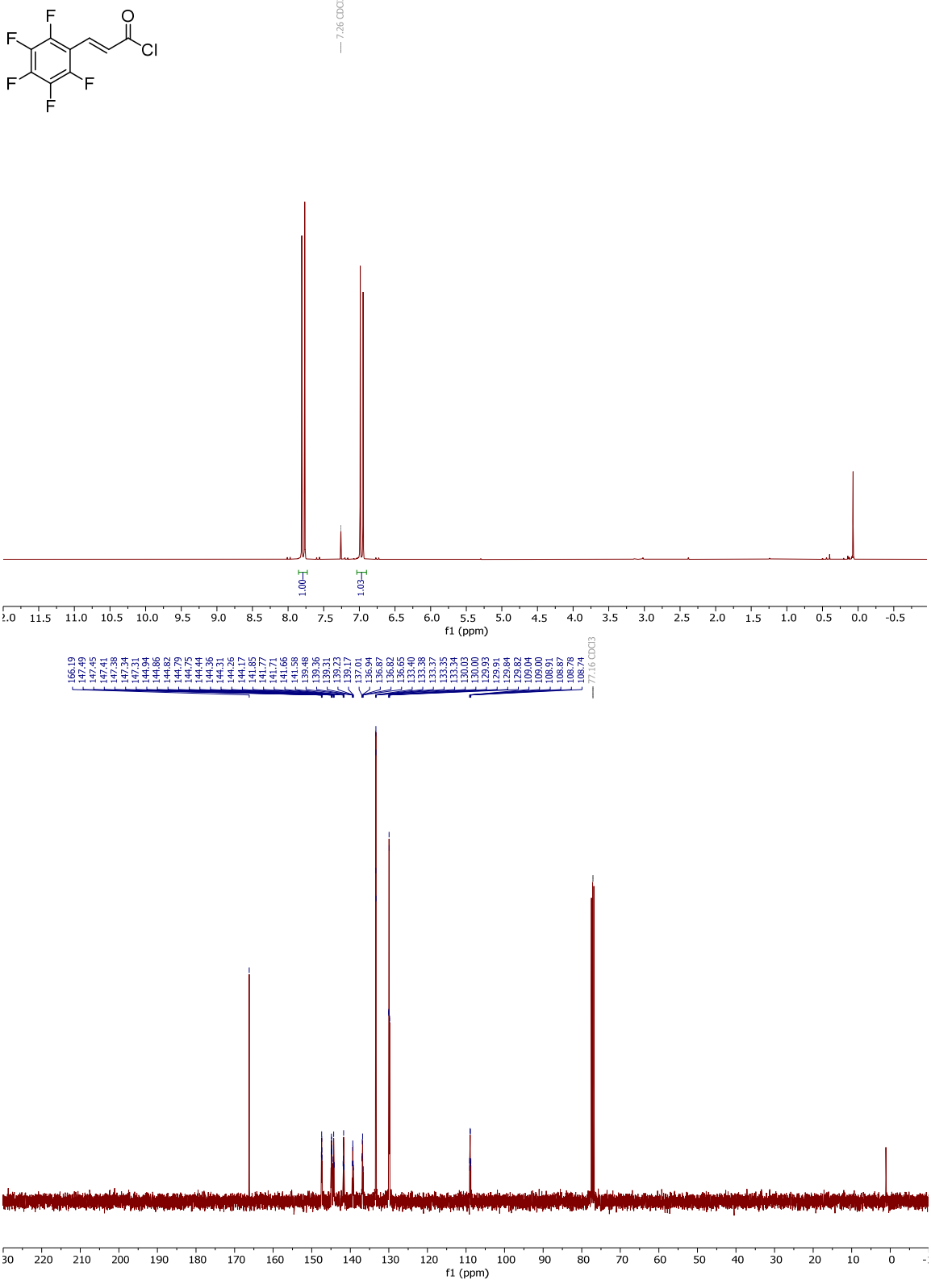

200523-2248-55-mlee-avn500.2.fid
Sample LEY-LB-374-12-S
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-374-12-S
19F-HDEC.ETH CDCl3 /opt/v mlee 55
-107.95
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

(*E*)-3-(3,5-bis(trifluoromethyl)phenyl)acryloyl chloride (**1x**).

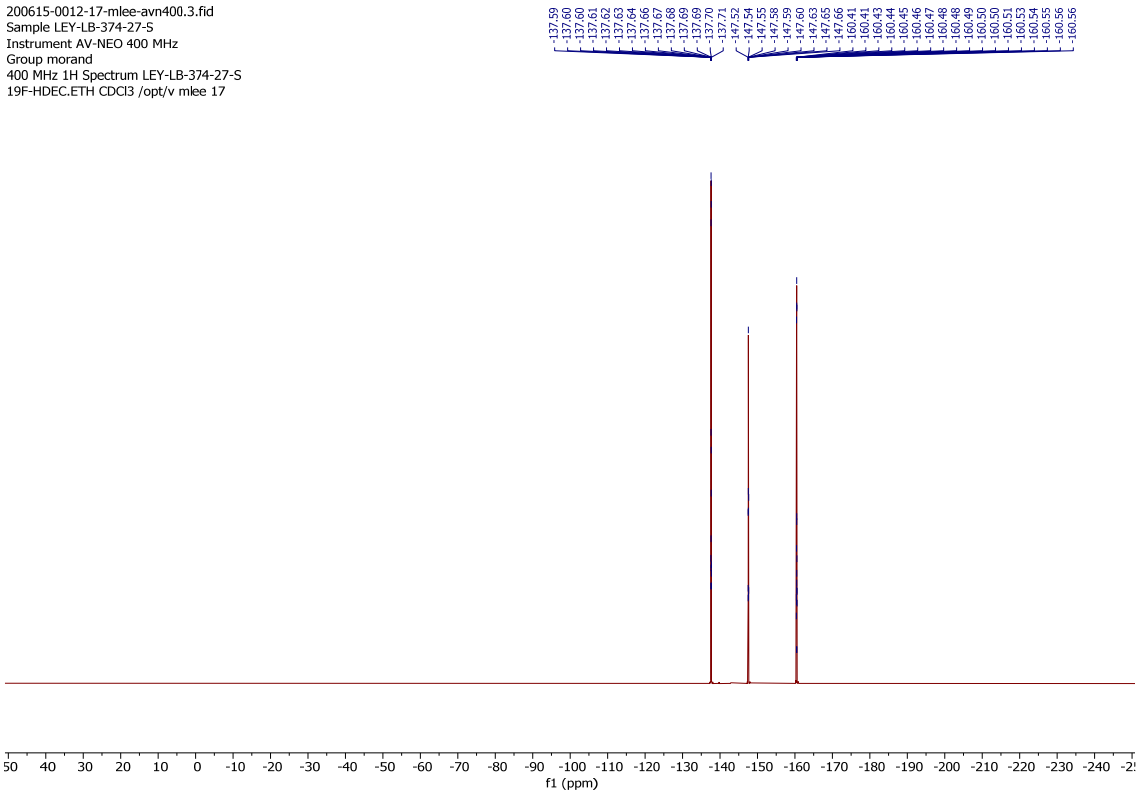



200526-0354-55-mlee-avn500.2.fid
Sample LEY-LB-374-15-S
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-374-15-S
19F-HDEC.ETH CDCl3 /opt/v mlee 55
-63.19
-63.20
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

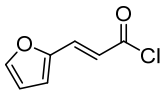
(*E*)-3-(perfluorophenyl)acryloyl chloride (**1y**).

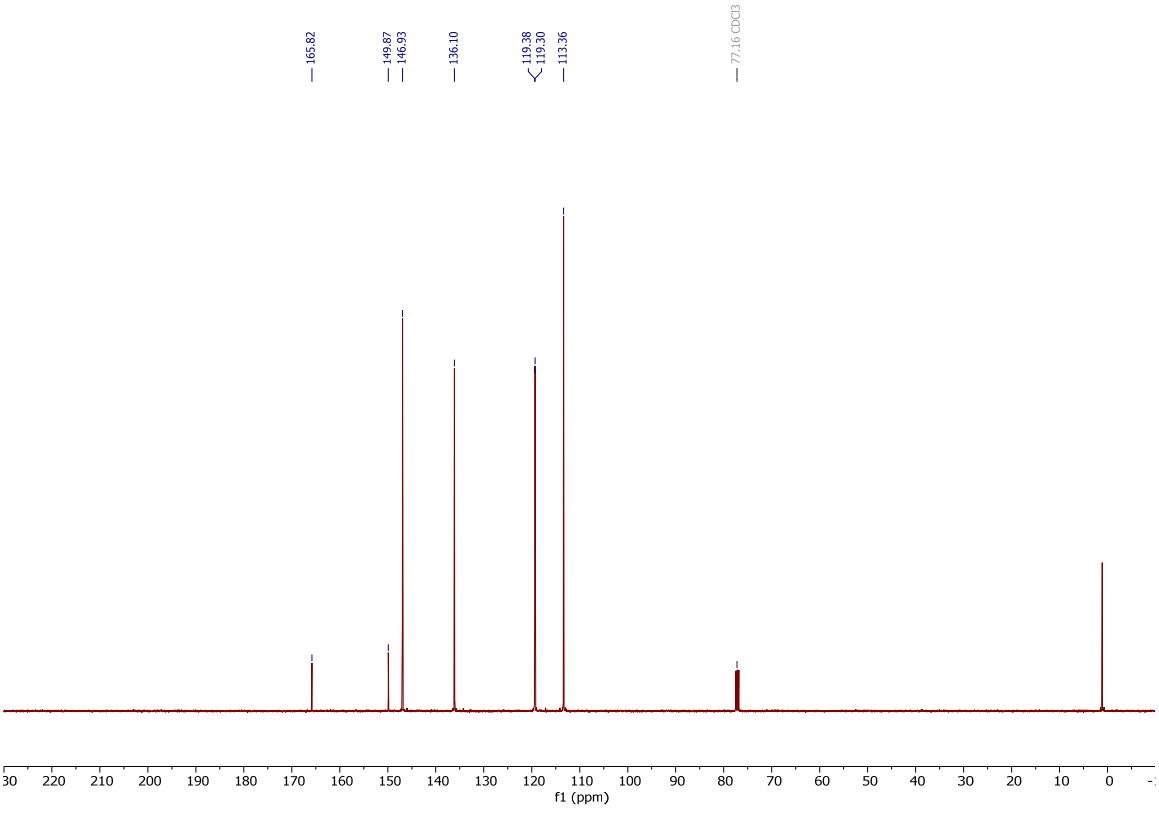


200615-0012-17-mlee-avn400.3.fid
Sample LEY-LB-374-27-S
Instrument AV-NEO 400 MHz
Group morand
400 MHz 1H Spectrum LEY-LB-374-27-S
19F-HDEC.ETH CDCl3 /opt/v mlee 17

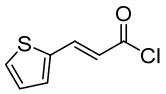


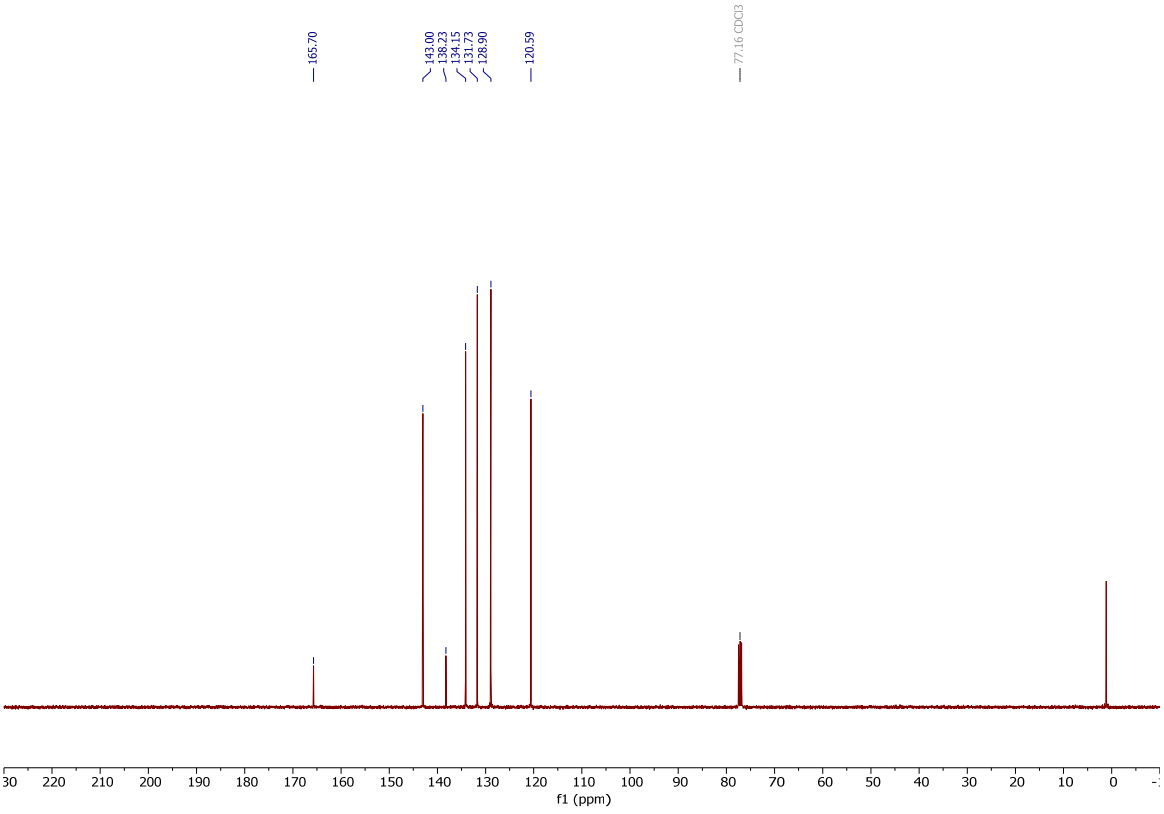
(*E*)-3-(furan-2-yl)acryloyl chloride (**1z**).



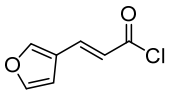


(*E*)-3-(thiophen-2-yl)acryloyl chloride (**1aa**).

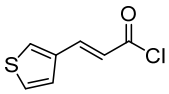


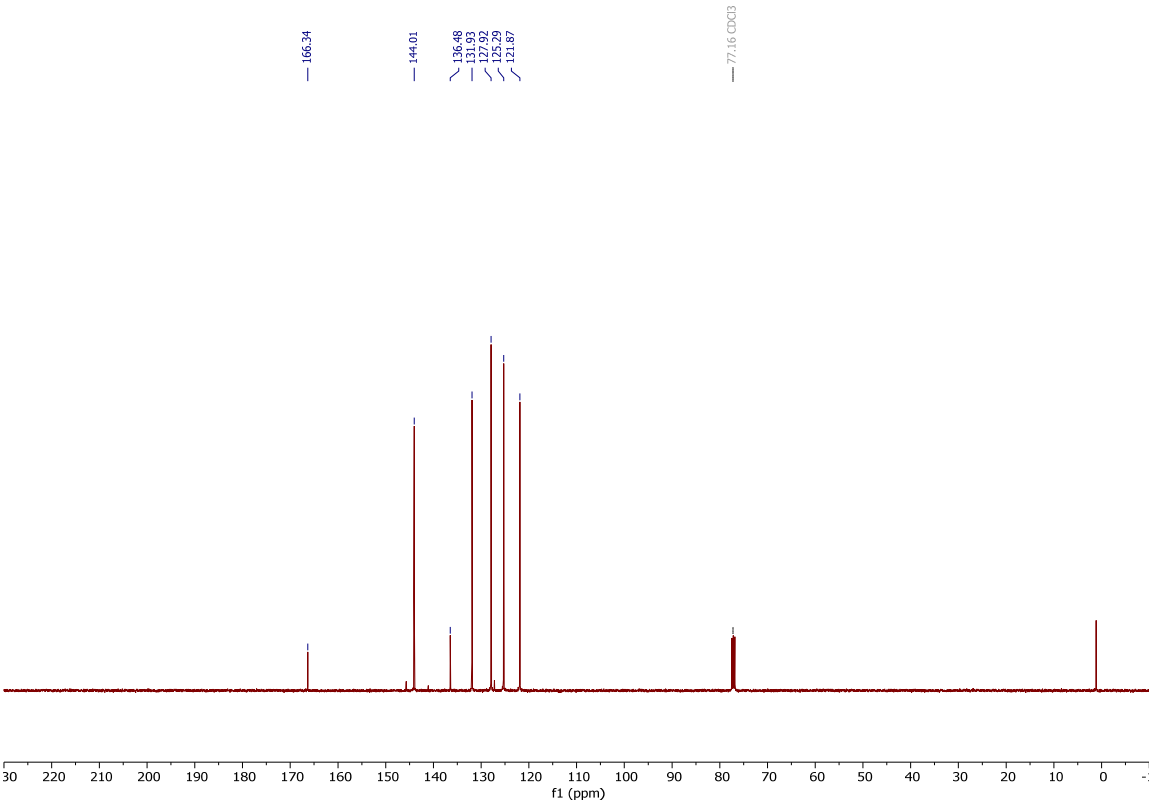


(*E*)-3-(furan-3-yl)acryloyl chloride (**1ab**).

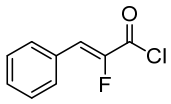


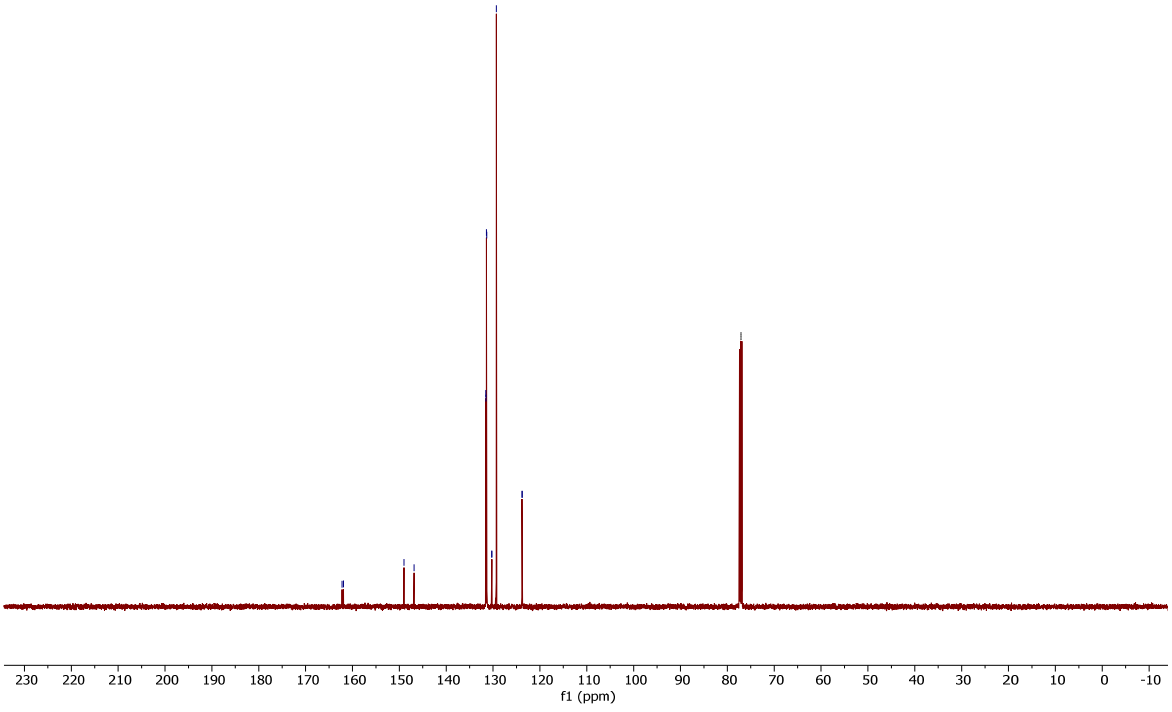
(*E*)-3-(thiophen-3-yl)acryloyl chloride (**1ac**).

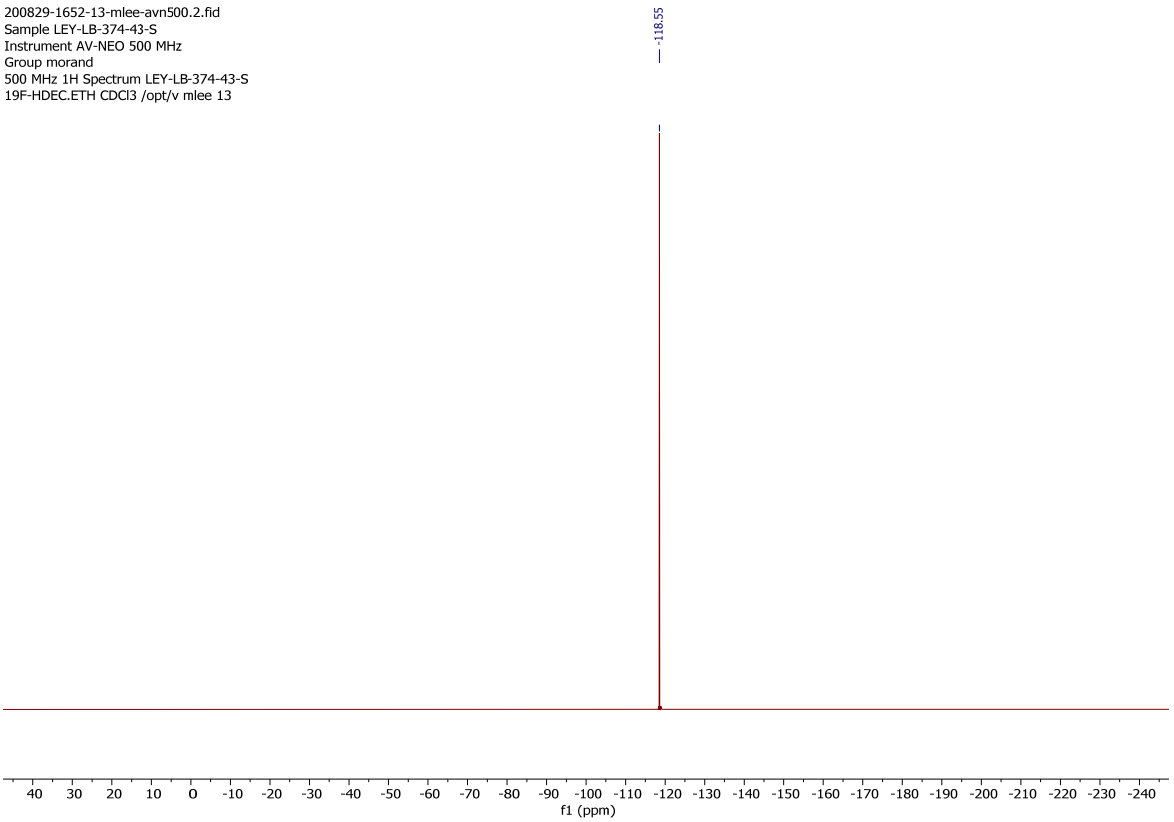




(*Z*)-2-fluoro-3-phenylacryloyl chloride (**1ad**).



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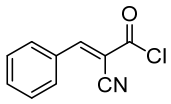
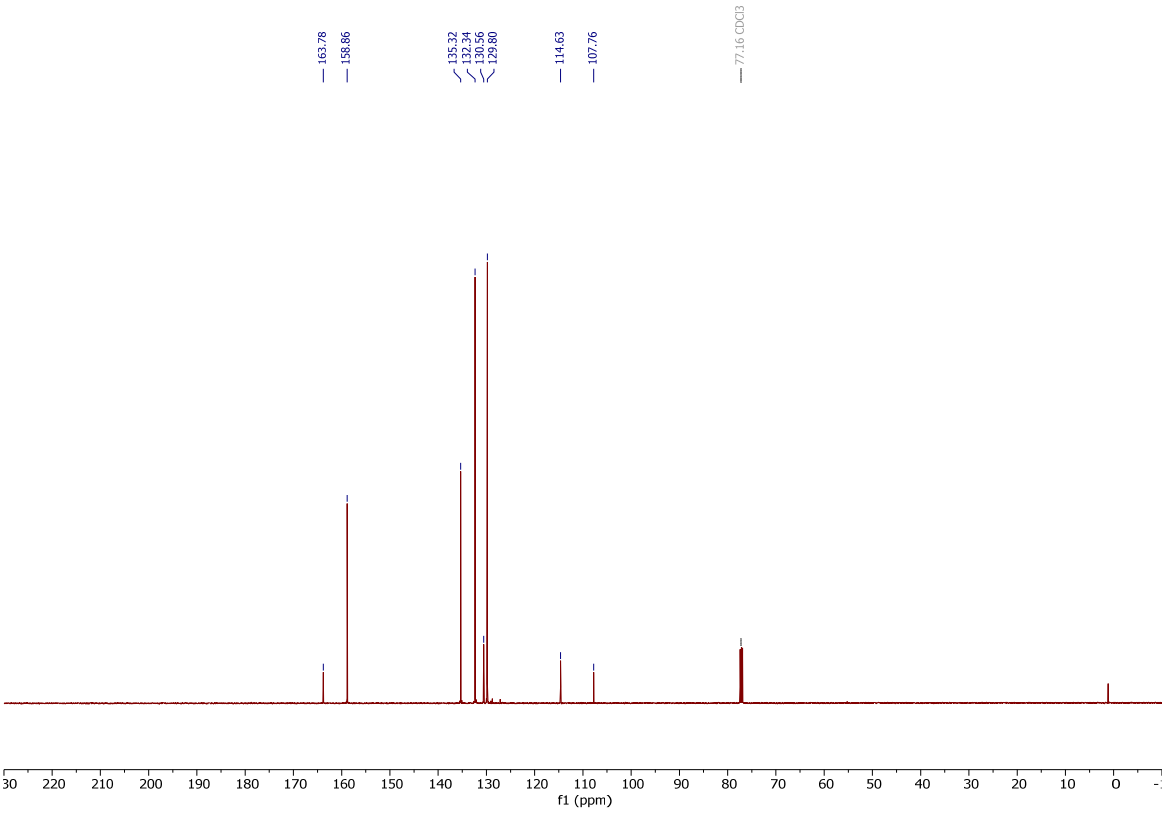
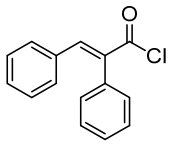
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-374-43-S
19F-HDEC.ETH CDCl3 /opt/v mlee 13
-118.55
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

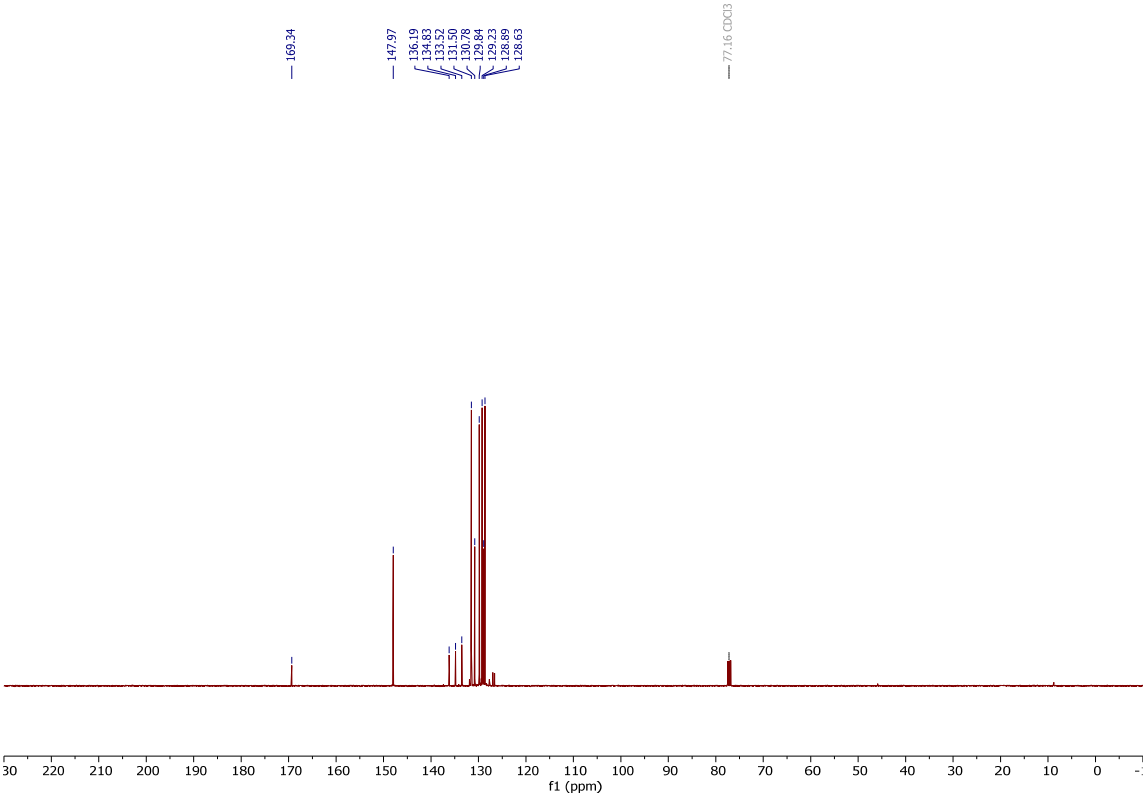
(*E*)-2-cyano-3-phenylacryloyl chloride (**1ae**).



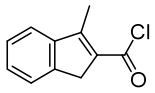


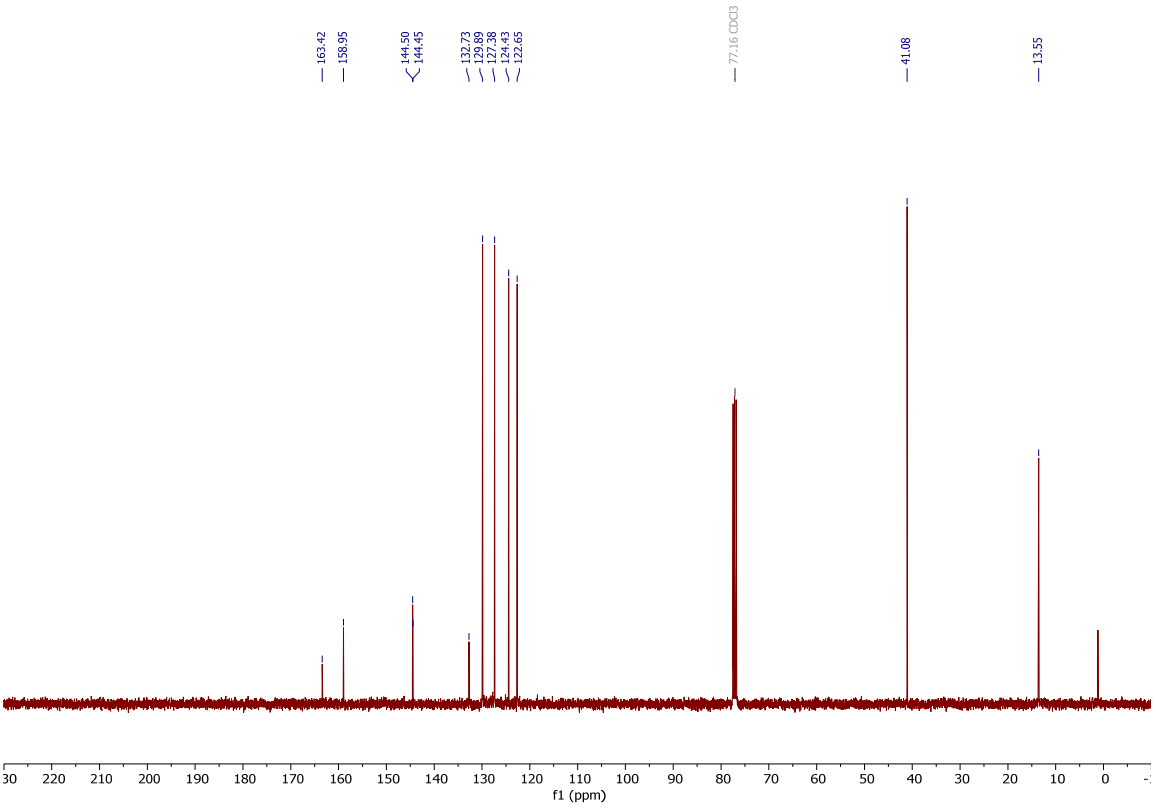
(*E*)-2,3-diphenylacryloyl chloride (**1af**).



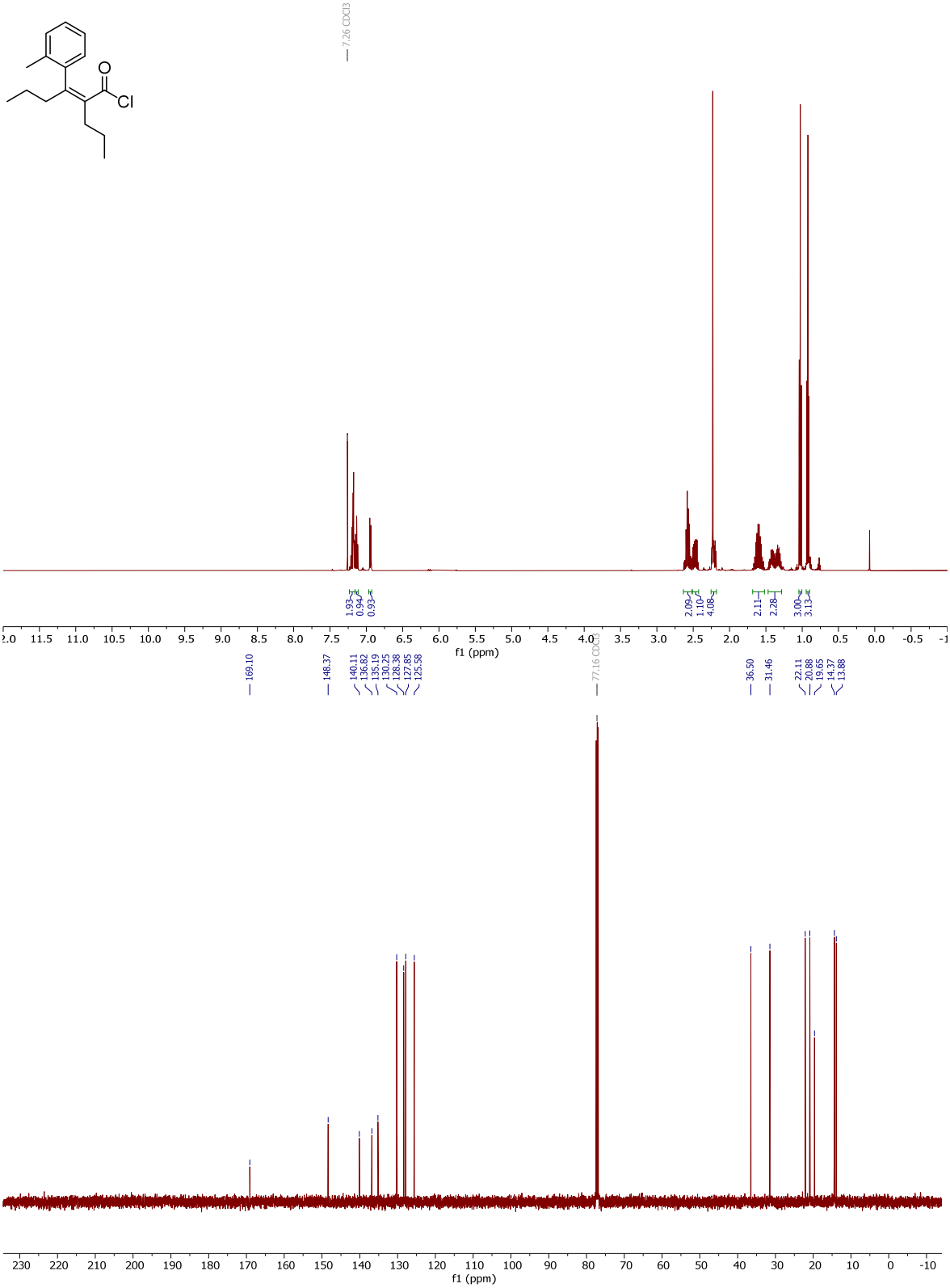


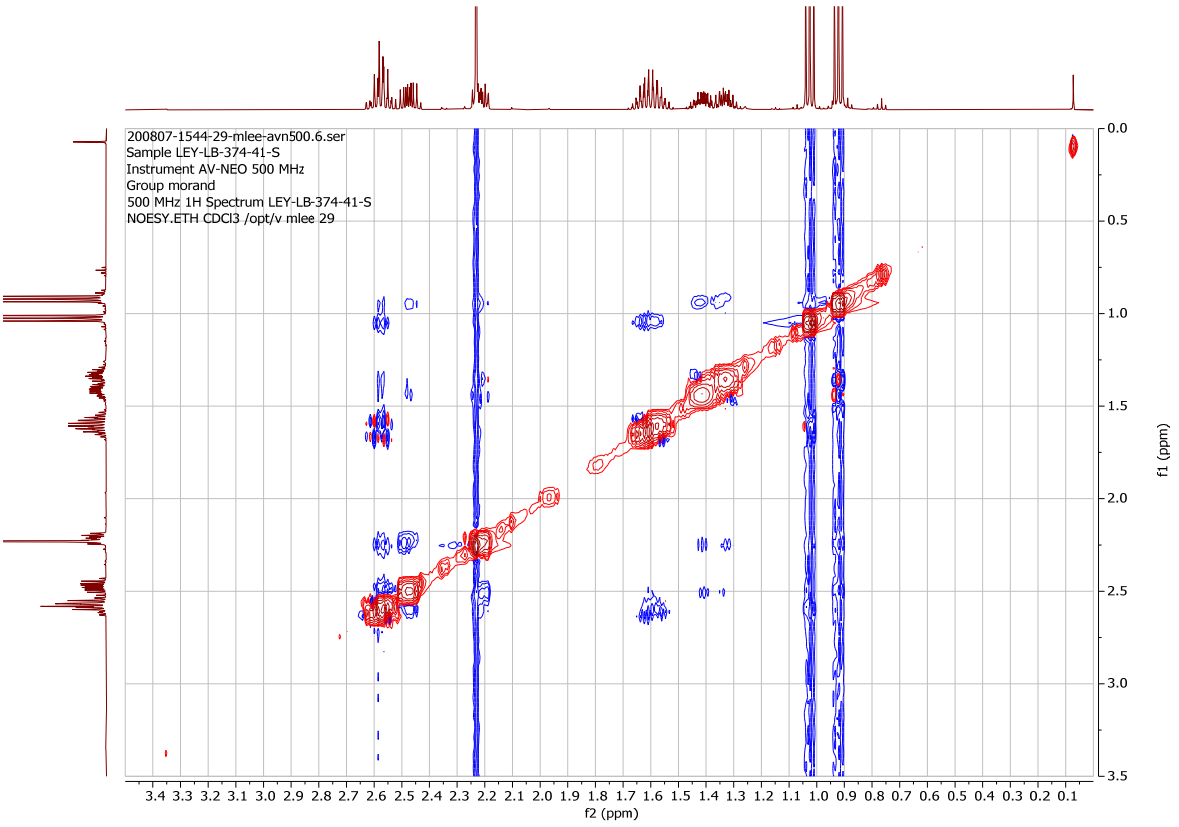
3-methyl-1*H*-indene-2-carbonyl chloride (**1ag**).





(*Z*)-2-propyl-3-(*o*-tolyl)hex-2-enoyl chloride (**1ah**).

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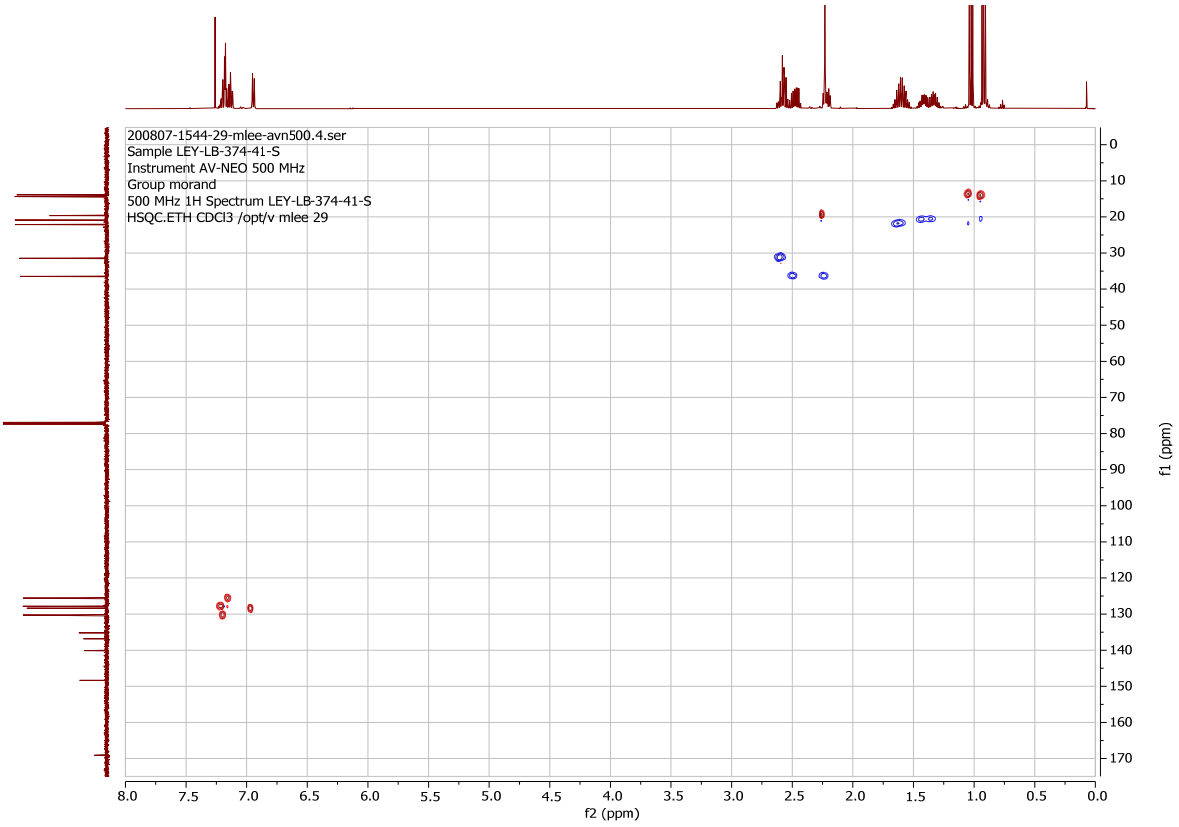
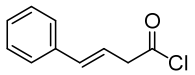
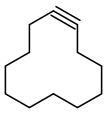
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-374-41-S
NOESY.ETH CDCl3 /opt/v mlee 29
f2 (ppm)
f1 (ppm)

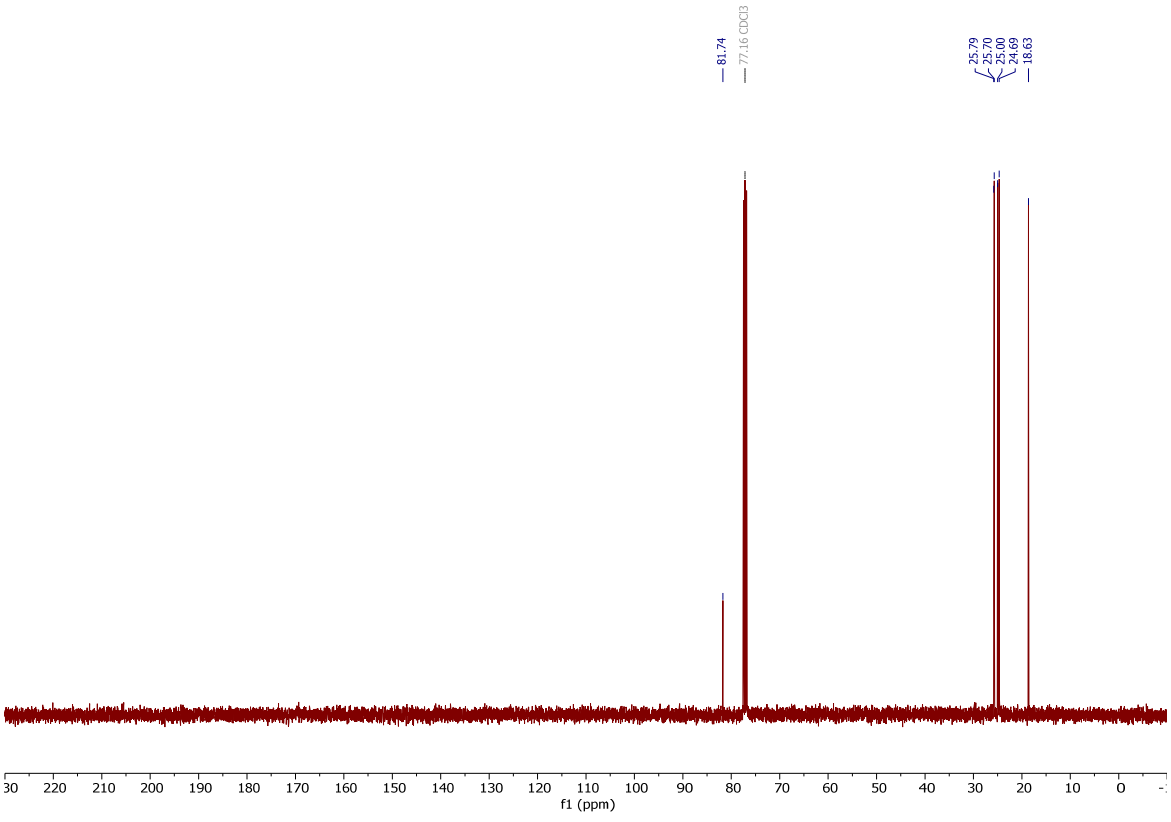

200807-1544-29-mlee-avn500.4.ser
Sample LEY-LB-374-41-S
Instrument AV-NEO 500 MHz
Group morand
500 MHz 1H Spectrum LEY-LB-374-41-S
HSQC.ETH CDCl3 /opt/v mlee 29
f2 (ppm)
f1 (ppm)

(*E*)-4-phenylbut-3-enoyl chloride (**8a**).

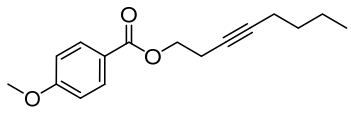


cyclododecyne (**2d**).

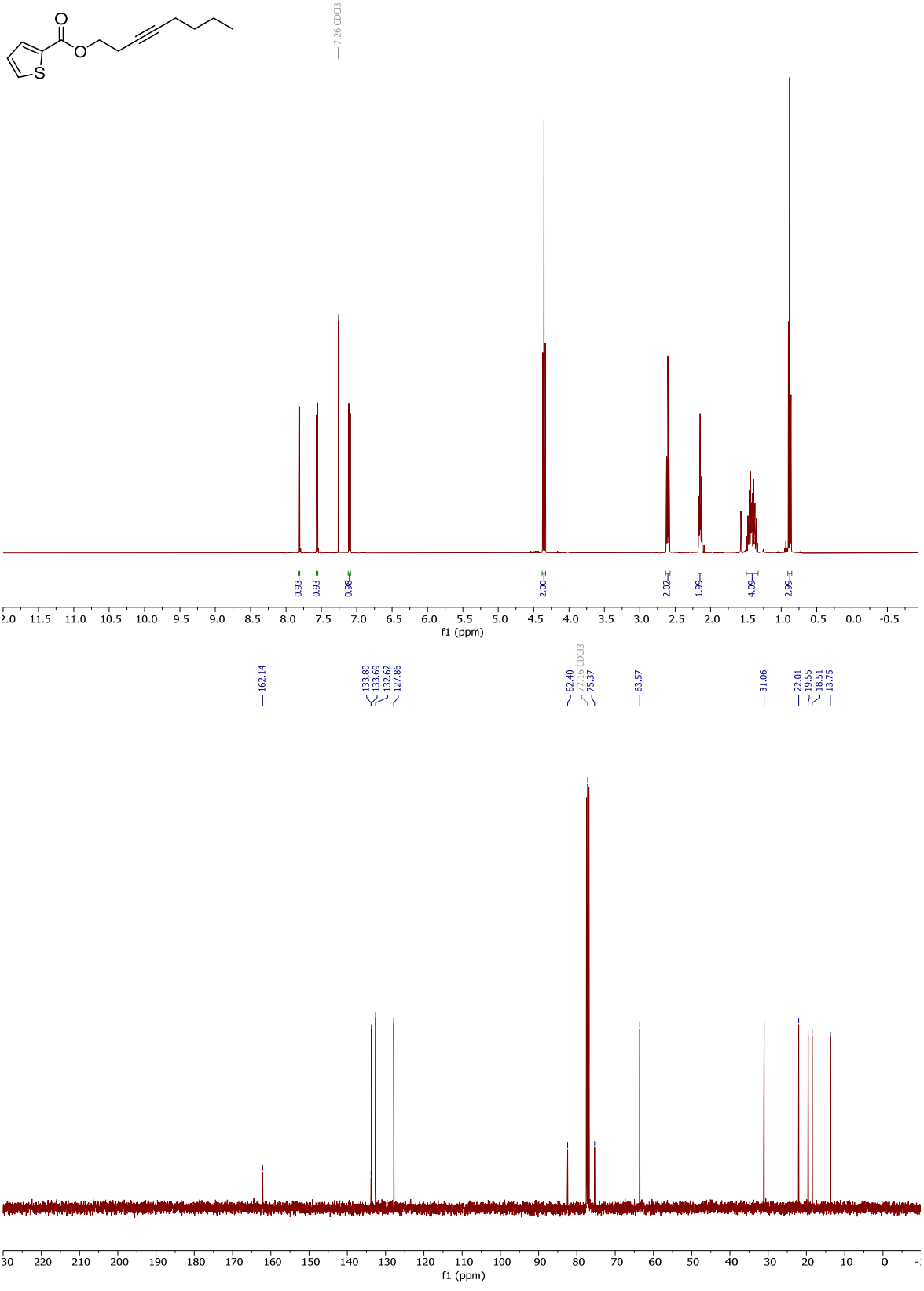




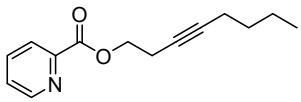
oct-3-yn-1-yl 4-methoxybenzoate (**2h**).

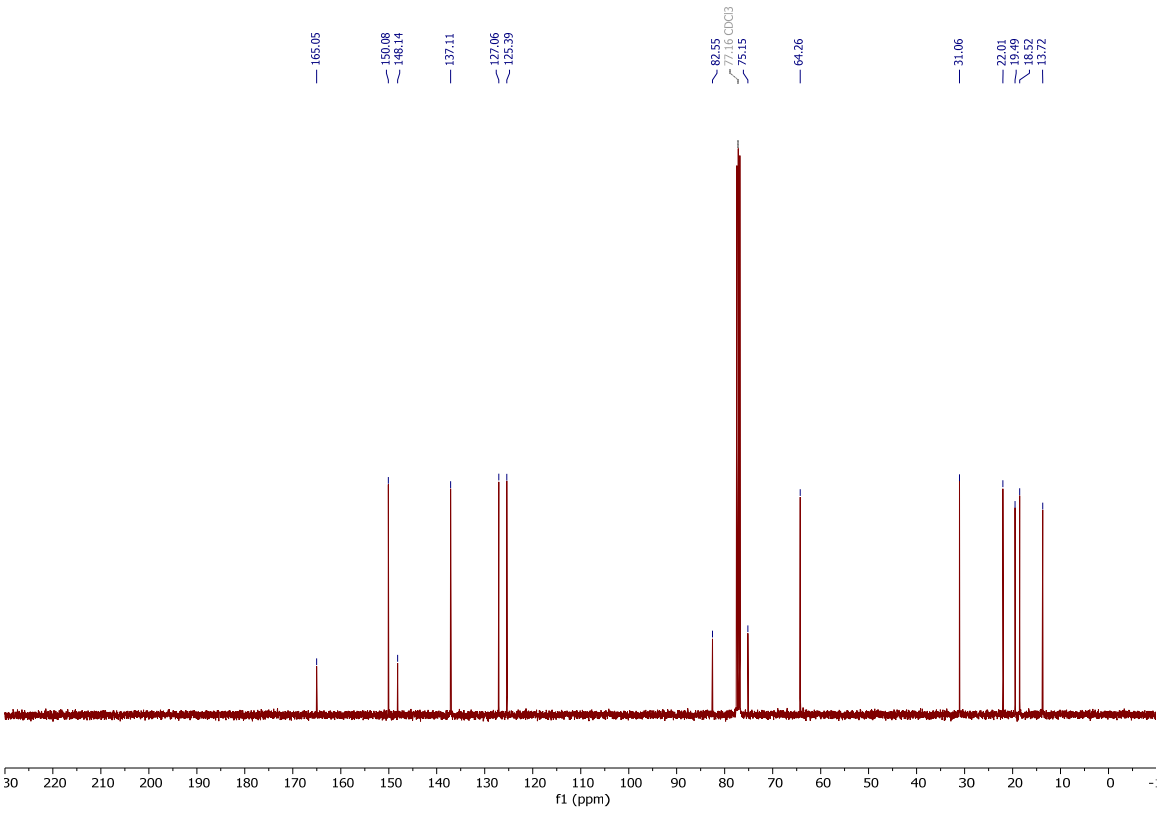


oct-3-yn-1-yl thiophene-2-carboxylate (**2i**).

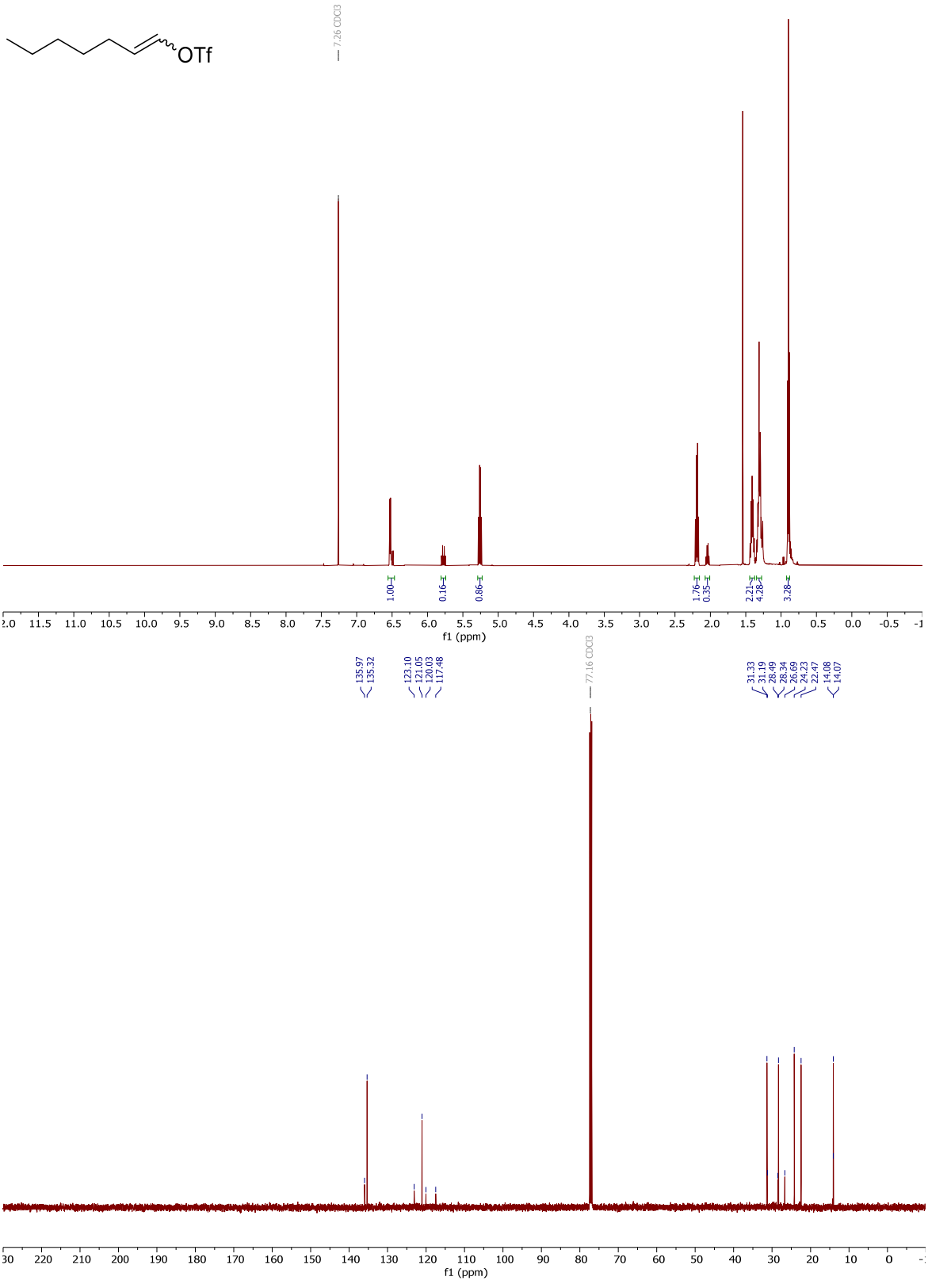


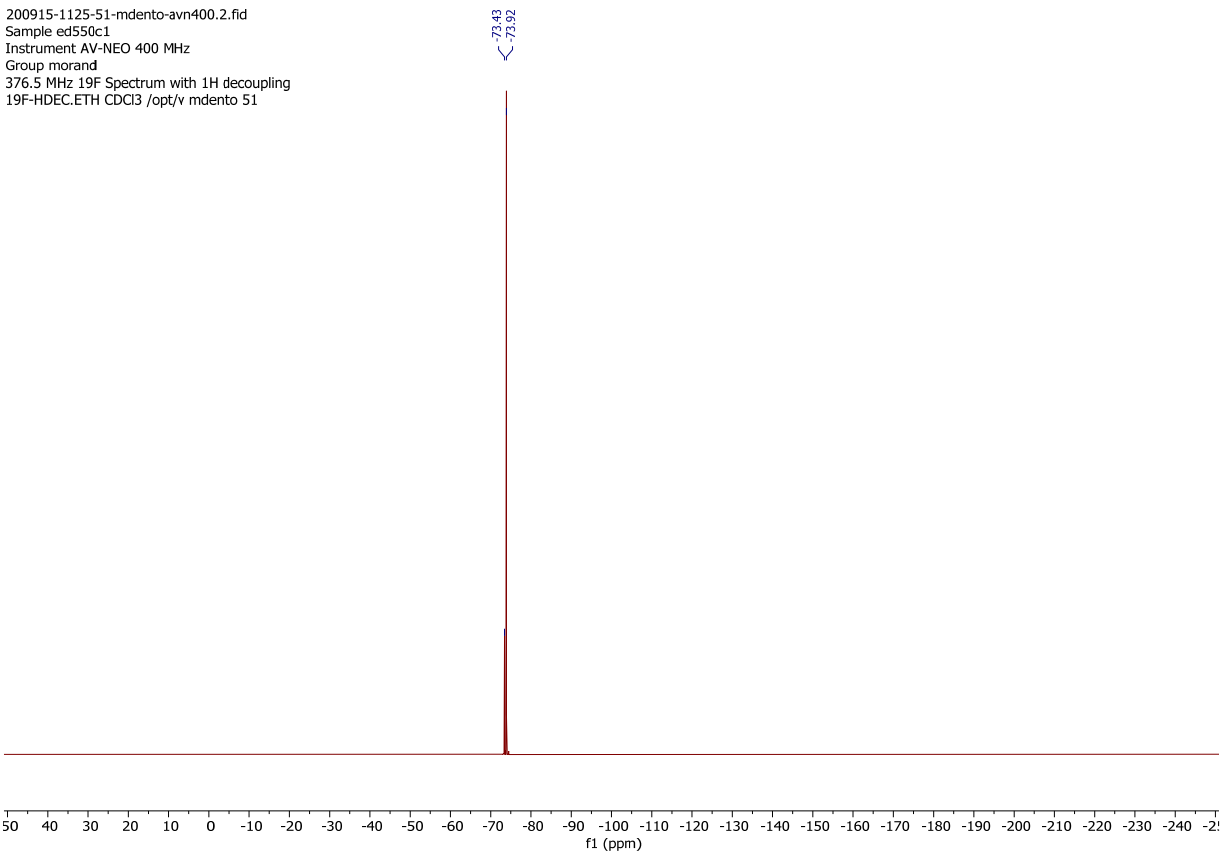
oct-3-yn-1-yl picolinate (**2j**).





hept-1-en-1-yl trifluoromethanesulfonate (**7d**).




200915-1125-51-mdento-avn400.2.fid
Sample ed550c1
Instrument AV-NEO 400 MHz
Group morand
376.5 MHz 19F Spectrum with 1H decoupling
19F-HDEC.ETH CDCl3 /opt/v mdento 51
-73.43
-73.92
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)