

Synthesis of Vinyl Cyclopropanes via Anion Relay Cyclization

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Supporting Information

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General Information

All reactions were performed in flame dried glassware under an argon atmosphere unless otherwise noted. THF was dried over sodium in the presence of benzophenone.

Cyanoketones were prepared according to a literature procedure.¹ Preparation of 2-aryl-3-vinyl oxiranes was accomplished according to a literature procedures.^{2,3,4,5,6,7,8}

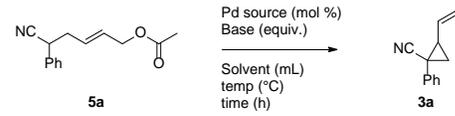
All other materials were obtained from Sigma-Aldrich, Acros Organics, Alfa Aesar or Fisher Scientific and were used without further purification. Reactions were monitored using either GC/MS on a Shimadzu GCMS-QP2010 SE or TLC on silica gel HL TLC plates w/UV254 from Sorbent Technologies. Compound purification was affected by flash chromatography using 230x400 mesh, 60 A porosity silica, using mixtures of hexane (Hex) and ethyl acetate (EA) as eluent as noted. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker Avance 400 or a Bruker Avance 500 DRX spectrometer equipped with a QNP Cryoprobe and referenced to residual protio solvent signals. Structural assignments are based on ¹H, ¹³C, DEPT135, COSY and NOESY techniques. J values are reported in Hz. High resolution mass spectral analysis was done on a Waters LCT Premeir mass spectrometer with a quadrupole and time of flight tandem mass analyzer and an electrospray ion source, or via LCMS using a Waters Q-ToF Premier in tandem with an Aquity UPLC using toluene assisted atmospheric pressure chemical ionization (TAPCI), as noted. Infrared analysis was performed on a Shimadzu FTIR-8400S infrared spectrometer. Melting points were obtained on a Digimelt MPA160 melting point apparatus.

Optimization of Reaction Conditions

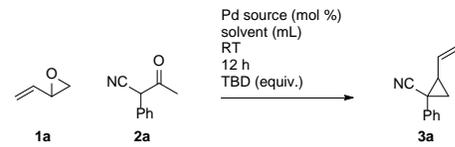
Initial experiments (shown in table 1A), revealed that formation of the vinyl cyclopropane was feasible starting from the corresponding allyl ester in the presence of palladium(0). Attention was then turned to optimization of the one-pot sequential allylation, retro-Claisen, cyclopropanation (table 1 B, C). When TBD was omitted, the reaction stopped at the allyl alcohol intermediate (entry 3). When TBD and palladium were added together with the vinyl epoxide, the reaction proceeded, albeit with unsatisfactory yield. (entry 4). Gratifyingly, when TBD was added in a second step after the formation of the allyl alcohol intermediate, the product was formed in appreciable yield (table 1 C, entry 5). Further optimization was conducted, exploring different solvents, temperatures, catalyst loading and base loading, but ultimately the optimal conditions were determined to be those shown in entry 5.

Table S1 – Reaction Optimization

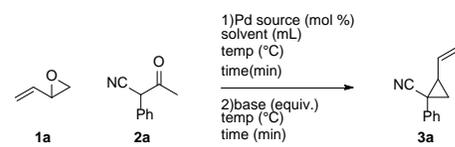
A^a



B^b



C^c



Entry	Time (h)	Pd Source (mol %)	Ligand (mol %)	temp. (°C)	solvent (mL)	Base (equiv.)	conversion to 3a (%)
1	2	Pd(PPh ₃) ₄ (10)	n/a	50	THF (5)	TBD (2)	75%
2	0.5	Pd(PPh ₃) ₄ (10)	n/a	80	Dioxane (2.5)	TBD (2)	62%

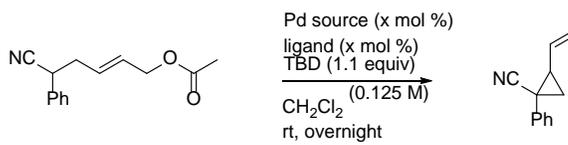
Entry	Time (h)	Pd Source (mol %)	Ligand (mol %)	temp. (°C)	solvent (mL)	Base (equiv.)	conversion to 3a (%)
3	12	Pd(PPh ₃) ₄ (2.5)	n/a	RT	DCM (2)	TBD (0)	0% ^d
4	12	Pd(PPh ₃) ₄ (2.5)	n/a	RT	DCM (2)	TBD (1.1)	14%

Entry	time step 1 (min) time step 2 (min)	Pd Source (mol %)	Ligand (mol %)	temp. step 1 (°C) temp. step 2 (°C)	solvent (mL)	Base (equiv.)	conversion to 3a (%)
5	30 60	Pd(PPh ₃) ₄ (2.5)	n/a	RT RT	DCM (2)	TBD (1.1)	75%
6	5 30	Pd(PPh ₃) ₄ (10)	n/a	RT 80	Dioxane (2.5)	TBD (2)	36%
7	5 30	Pd(PPh ₃) ₄ (10)	n/a	RT 80	Dioxane (1.5)	TBD (2)	0%
8	10 30	Pd(PPh ₃) ₄ (10)	n/a	RT 80	Dioxane (2.5)(2.5)	TBD (2)	0%
9	10 30	Pd(PPh ₃) ₄ (10)	n/a	RT 80	DMSO (2.5)(2.5)	TBD (2)	0%
10	10 120	Pd(PPh ₃) ₄ (10)	n/a	RT 50	THF (1)(1)	TBD (2)	12%
11	5 240	Pd(PPh ₃) ₄ (10)	n/a	RT RT	Dioxane (1)(1)	TBD (1.1)	42%
12	5 120	Pd(PPh ₃) ₄ (10)	n/a	RT RT	DCM (1)(1)	TBD (1.1)	30%
13	5 120	Pd ₂ (dba) ₃ (5)	PPh ₃ (30)	RT RT	THF (2.5)(2.5)	TBD (1.1)	24%
14	30 120	Pd(PPh ₃) ₄ (1)	n/a	RT RT	DCM (2)	TBD (1.1)	0%
15	10 30	Pd(PPh ₃) ₄ (5)	n/a	RT RT	DCM (2)	TBD (1.1)	75%

a. Ester (**5a**, 0.25 mmol), Pd source, base, and solvent were mixed and allowed to stir at indicated temperature for the indicated amount of time. b. Nitrile (**2a**, 0.25 mmol), Pd source, TBD, solvent and vinyl oxirane (**1a**, 1 equiv.) were mixed in that order and allowed to stir at the indicated temperature for the indicated amount of time. c. Nitrile (**2a**, 0.25 mmol), Pd source, solvent and vinyl oxirane (**1a**, 1 equiv.) were mixed in that order and allowed to stir at the temperature indicated and for the amount of time indicated for the

first step. Then TBD was added and the reaction was allowed to stir at the temperature indicated and for the amount of time indicated for the second step. d. 89% of the alcohol intermediate was formed, but no vinyl cyclopropane was observed. RT = room temperature ~22 °C.

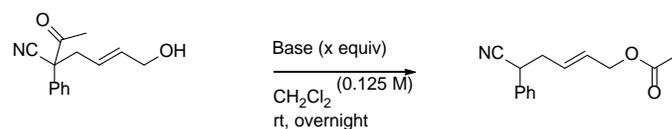
Table S2 – Ligand Screening Results



Pd source (x mol %)
ligand (x mol %)
TBD (1.1 equiv)
————— (0.125 M)
CH₂Cl₂
rt, overnight

Entry	Pd Source (mol %)	Ligand (mol %)	Yield (%)	dr (cis:trans)
1	Pd(dba) ₂ (2.5)	n/a	no rxn	n/a
2	Pd(dba) ₂ (2.5)	PPh ₃ (6)	38	76:24
3	Pd(dba) ₂ (5)	PBu ₃ (3.4)	69	80:20
4	Pd(dba) ₂ (5)	DPPF (3.4)	8	63:38
5	Pd(dba) ₂ (2.5)	PBu ₃ (10)	37	81:19
6	Pd(dba) ₂ (2.5)	DPPE (10)	1	n/a
7	Pd(dba) ₂ (2.5)	2-picoline (10)	no rxn	n/a
8	Pd(dba) ₂ (2.5)	2-methoxy pyridine (10)	no rxn	n/a
9	Pd(dba) ₂ (2.5)	DPPM (10)	23	74:26
10	Pd(dba) ₂ (2.5)	DPPBz (10)	no rxn	n/a
11	Pd(dba) ₂ (2.5)	DavePhos (10)	60	72:28
12	Pd(dba) ₂ (2.5)	XantPhos (10)	11	64:36

Table S3 – Base Screening



Base (x equiv)
————— (0.125 M)
CH₂Cl₂
rt, overnight

NB#	Entry	Base (equiv)	yield %
KA6_036	1	DABCO (1.1)	no rxn
KA6_037	2	NaH (2)	17%
KA6_040	2	Imidazole (1)	no rxn
KA6_041	2	Benzimidazole (1)	no rxn

General procedure for the formation of vinyl cyclopropanes:

In a flame dried 20 mL sealable flask or vial Pd(PPh₃)₄ (7.2 mg, 2.5 mol%), nitrile, (0.25 mmol, 1 equiv.), and 1.9 mL of DCM were combined in the glove box. In a separate vial 38.2 mg (0.275 mmol, 1.1 equiv.) of TBD was added and sealed. A 2.5 M solution of vinyl epoxide in DCM was prepared in a resealable container under argon (*Note*: the exact concentration of the vinyl epoxide solution was unimportant as long as the molar quantity used in the next step was consistent). Under an argon atmosphere, 100 μ L of the 2.5 M solution (0.25 mmol, 1 equiv.) was added and the reaction was allowed to stir for 30 to 60 min. or until all starting material was consumed (observed by GC/MS). TBD (1.1 equiv.) was then added to the reaction mixture and allowed to stir for 60 min. or until all of the intermediate was consumed. The reaction was quenched by filtering through a 1" plug of silica in a pipette and washing the plug with ethyl acetate. The crude product was then purified by flash chromatography on silica using an eluent of 1-5% ethyl acetate (EA) in hexanes.

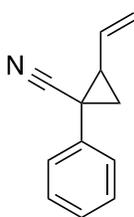
Larger scale synthesis of Product 3a

1a (0.675 g, 4.24 mmol) and Pd(PPh₃)₄ (0.12g, 0.107 mmol, 2.5 mol %) were dissolved in 20 mL DCM (0.212 M) in a flame dried Schlenk flask under argon. **2a** was then added directly by syringe (0.308 g, 4.38 mmol, 1.03 equiv.) and the resulting solution was allowed to stir at room temperature for 30 minutes. Next, TBD (0.682 g, 4.91 mmol, 1.16 equiv.) was added and the resulting solution was allowed to stir for 1 hour at room temperature. The solvent was evaporated under reduced pressure until it was nearly dry, and the resulting oil was directly loaded onto a silica column. The product was eluted using an eluent of 5% ethyl acetate (EA) in hexanes.

Characterization of vinyl cyclopropanes

Product **3a**

1-phenyl-2-vinylcyclopropane-1-carbonitrile

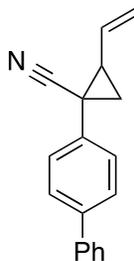


32.7 mg, colorless oil, yield: 75%, d.r.: 85:15. Purified by flash chromatography on silica with 5% EA:Hexane. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 5H, overlapping major and minor, aromatic), 5.80 (ddd, $J = 16.9, 10.3, 8.3$ Hz, 1H major, alkene *CH*), 5.40 – 5.25 (m, overlapping 2H major alkene *CH*₂, 1H minor alkene *CH*₂), 5.04 (ddd, $J = 10.3, 1.4, 0.6$ Hz, 1H minor, alkene *CH*₂), 4.87 (ddd, $J = 17.0, 10.3, 8.8$ Hz, 1H minor alkene *CH*), 2.56 – 2.50 (m, 1H minor, cyclopropane *CH*), 2.24 – 2.16 (m, 1H major, cyclopropane *CH*), 1.92 (dd, $J = 9.2, 5.9$ Hz, 1H minor, cyclopropane *CH*₂), 1.83 (dd, $J = 8.6, 5.9$ Hz, 1H major, cyclopropane *CH*₂), 1.76 (dd, $J = 7.3, 5.9$ Hz, 1H major, cyclopropane *CH*₂), 1.65 (dd, $J = 7.0, 5.9$ Hz, 1H minor cyclopropane *CH*₂). ^{13}C NMR (126 MHz, CDCl₃) δ 135.9, 134.5, 133.9, 133.5, 130.4, 129.7, 129.2, 129.1, 128.8, 128.6, 128.0, 125.8, 120.5, 119.0, 34.2, 31.9, 30.0, 23.5, 22.2, 19.4. IR ($\bar{\nu} - \bar{\nu}_{\text{IR}}$, neat) 3063, 3030, 2236, 1723, 1694, 1640, 1601, 1493, 1451, 1111, 986, 953, 918, 754, 696. HRMS (TAPCI, *m/z*) calcd. for C₁₂H₁₁N [M-H] 168.0813; found 168.0801.

Product **3a** (0.717 g) was obtained in 81% yield and 81:19 d.r. when the reaction was conducted on a 4.38 mmol scale.

Product **3b**

1-([1,1'-biphenyl]-4-yl)-2-vinylcyclopropane-1-carbonitrile from 2-([1,1'-biphenyl]-4-yl)-3-oxobutanenitrile.

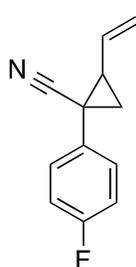


55.1 mg, white solid, m.p.: 86.0-91.4 °C, yield: 90%, d.r.: 80:20. Purified by flash chromatography on silica with 5% EA:Hexane. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.54 (m, 4H overlapping major and minor aromatic), 7.48 – 7.34 (m, 5H overlapping major and minor aromatic), 5.82 (ddd, $J = 17.0, 10.3, 8.3$ Hz, 1H major alkene *CH*), 5.39 (dt, $J = 17.0, 0.9$ Hz, 1H major alkene *CH*₂), 5.36 – 5.29 (m, 1H overlapping major and minor alkene *CH*₂), 5.08 (dd, $J = 10.4, 1.4$ Hz, 1H minor alkene *CH*₂), 4.94 (ddd, $J = 16.9, 10.3, 8.7$ Hz, 1H minor alkene *CH*), 2.56 (td, $J = 9.0, 7.0$ Hz, 1H minor cyclopropane *CH*), 2.24 (td, $J = 8.5, 7.5$ Hz, 1H major cyclopropane *CH*), 1.96 (dd, $J = 9.2, 5.9$ Hz, 1H minor cyclopropane *CH*₂), 1.88 (dd, $J = 8.6, 5.9$ Hz, 1H major cyclopropane

CH_2), 1.80 (dd, $J = 7.4, 5.9$ Hz, 1H major cyclopropane CH_2), 1.69 (dd, $J = 7.0, 5.9$ Hz, 1H minor cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 141.0, 140.4, 140.4, 134.9, 134.4, 133.5, 131.3, 130.1, 129.1, 129.1, 127.9, 127.9, 127.8, 127.3, 127.3, 126.2, 123.1, 120.5, 119.2, 119.1, 34.4, 32.1, 23.6, 22.0, 19.9, 19.5. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3086, 3057, 3032, 2922, 2236, 1638, 1601, 1524, 1487, 1447, 1408, 1109, 986, 916, 847, 762, 729, 698. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N$ [$M+Na$] 268.1102, [$M-CN$] 219.1179; found 268.1112, 219.117

Product 3c

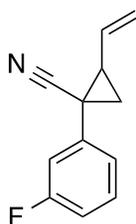
1-(4-fluorophenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(4-fluorophenyl)-3-oxobutanenitrile.



38.3 mg yellow oil, yield: 82%, d.r.: 76:24. Purified by flash chromatography on silica with 5% EA:Hexane. 1H NMR (500 MHz, Chloroform- d) δ 7.34 – 7.24 (m, 2H overlapping major and minor aromatic), 7.09 – 7.01 (m, 2H overlapping major and minor aromatic), 5.78 (ddd, $J = 17.0, 10.3, 8.3$ Hz, 1H major alkene CH), 5.38 (dt, $J = 17.0, 0.9$ Hz, 1H major alkene CH_2), 5.33 (dt, $J = 10.4, 0.8$ Hz, 1H major alkene CH_2), 5.28 (ddd, $J = 17.0, 1.4, 0.7$ Hz, 1H minor alkene CH_2), 5.06 (ddd, $J = 10.3, 1.4, 0.6$ Hz, 1H minor alkene CH_2), 4.85 (ddd, $J = 17.0, 10.3, 8.7$ Hz, 1H minor alkene CH), 2.56 – 2.48 (m, 1H minor cyclopropane CH), 2.19 – 2.11 (m, 1H major cyclopropane CH), 1.93 (dd, $J = 9.2, 5.9$ Hz, 1H minor cyclopropane CH_2), 1.81 – 1.69 (m, 2H major cyclopropane CH_2), 1.63 – 1.57 (m, 1H minor cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 163.4, 161.8, 161.5, 134.3, 133.3, 131.8, 131.8, 131.7, 131.6, 128.27, 128.25, 128.0, 127.9, 122.9, 120.4, 119.3, 119.2, 116.3, 116.2, 116.10, 116.06, 33.8, 31.7, 30.0, 23.3, 21.5, 19.7, 19.4. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 3013, 2990, 928, 2857, 2236, 1640, 1605, 1514, 1449, 1412, 1236, 1165, 1109, 988, 921, 837, 808, 723, 700. HRMS (TAPCI, m/z) calcd. for $C_{12}H_{11}FN$ [$M+H$] 188.0876; found 188.0874

Product 3d

1-(3-fluorophenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(3-fluorophenyl)-3-oxobutanenitrile.

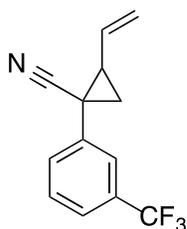


36.1 mg, yellow solid, m.p.: 38.0-43.2 °C, yield: 77%, d.r.: 81:19. Purified by flash chromatography on silica with 5% EA:Hexane. 1H NMR (500 MHz, Chloroform- d) δ 7.37 – 7.29 (m, 1H overlapping major and minor aromatic), 7.17 – 7.08 (m, 1H overlapping major and minor aromatic), 7.07 – 6.95 (m, 2H overlapping major and minor aromatic), 5.78 (ddd, $J = 16.9, 10.3, 8.2$ Hz, 1H major alkene CH), 5.39 (dt, $J = 17.0, 0.9$ Hz, 1H major alkene CH_2), 5.35 (dt, $J = 10.4, 0.8$ Hz, 1H major alkene CH_2), 5.30 (ddd, $J = 16.9, 1.3, 0.8$ Hz, 1H minor alkene CH_2), 5.08 (ddd, $J = 10.4, 1.3, 0.6$ Hz, 1H minor alkene CH_2), 4.90 (ddd, $J = 16.9, 10.3, 8.7$ Hz, 1H minor alkene CH), 2.59 – 2.51 (m, 1H minor cyclopropane), 2.25 – 2.16 (m, 1H major cyclopropane), 1.94 (dd, $J = 9.2, 6.0$ Hz, 1H minor cyclopropane), 1.85 – 1.77 (m, 2H major cyclopropane), 1.65 (dd, $J = 7.1, 6.0$ Hz, 1H minor cyclopropane). ^{13}C

NMR (126 MHz, CDCl₃) δ 164.3, 164.0, 162.3, 162.0, 138.6, 138.5, 134.81, 134.75, 134.0, 132.9, 130.8, 130.8, 130.7, 130.6, 125.44, 125.41, 122.6, 121.44, 121.42, 120.0, 119.6, 119.5, 116.9, 116.7, 115.9, 115.7, 115.1, 114.9, 113.0, 112.8, 34.5, 32.2, 23.8, 21.97, 21.95, 19.90, 19.88, 19.5. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3090, 3015, 2990, 2926, 2846, 2238, 1640, 1616, 1589, 1495, 1451, 1275, 1244, 1190, 1167, 1109, 988, 924, 876, 858, 777, 708, 687. HRMS (TAPCI, m/z) calcd. for C₁₂H₁₁FN [M+H] 188.0876; found 188.0876

Product 3e

1-(3-(trifluoromethyl)phenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(3-(trifluoromethyl)phenyl)-3-oxobutanenitrile.

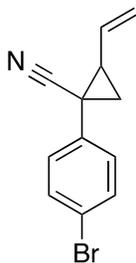


34.5 mg, yellow oil, yield: 58% d.r.: 81:19. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.46 (m, 5H overlapping major and minor aromatic), 5.80 (ddd, *J* = 17.0, 10.3, 8.2 Hz, 1H major alkene *CH*), 5.41 (dt, *J* = 17.0, 1.0 Hz, 1H major alkene *CH*₂), 5.37 (dt, *J* = 10.3, 0.8 Hz, 1H major alkene *CH*₂), 5.31 (dt, *J* = 17.0, 1.0 Hz, 1H minor alkene *CH*₂), 5.09 (dt, *J* = 10.4, 0.9 Hz, 1H minor alkene *CH*₂), 4.86 (ddd, *J* = 17.0, 10.3, 8.6

Hz, 1H minor alkene *CH*), 2.60 (td, *J* = 9.0, 7.3 Hz, 1H minor cyclopropane), 2.24 (td, *J* = 8.4, 7.5 Hz, 1H major cyclopropane), 1.99 (dd, *J* = 9.2, 6.1 Hz, 1H minor cyclopropane), 1.91 – 1.81 (m, 2H major cyclopropane), 1.69 (dd, *J* = 7.1, 6.1 Hz, 1H minor cyclopropane) ¹³C NMR (126 MHz, CDCl₃) δ 137.2, 133.8, 133.6, 133.31, 132.6, 131.9, 131.6, 129.8, 129.7, 129.4, 126.41, 126.38, 125.59, 125.56, 125.0, 124.91, 124.88, 124.85, 124.82, 122.9, 122.42, 122.39, 122.36, 122.33, 120.0, 119.8, 119.1, 34.5, 32.1, 23.7, 22.0, 19.9, 19.6. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3090, 3019, 2994, 2928, 2857, 2238, 1491, 1449, 1437, 1344, 1331, 1260, 1171, 1128, 1076, 988, 922, 808, 791, 700. HRMS (TAPCI, m/z) calcd. for C₁₃H₁₁F₃N = [M+H] 238.0844; found 238.0849

Product 3f

1-(4-bromophenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(4-bromophenyl)-3-oxobutanenitrile.



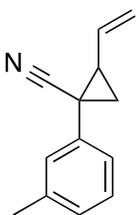
42.1 mg, yellow solid, m.p. 82.6-84.7 °C, yield: 67%, d.r.: 79:21. Purified by flash chromatography on silica with 2% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 2H overlapping major and minor aromatic), 7.24 – 7.12 (m, 2H overlapping major and minor aromatic), 5.78 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 1H major alkene *CH*), 5.38 (dt, *J* = 17.0, 1.0 Hz, 1H major alkene *CH*₂), 5.34 (dt, *J* = 10.4, 0.9 Hz, 1H major alkene *CH*₂), 5.28 (ddd, *J* = 17.0, 1.3, 0.7 Hz, 1H minor alkene *CH*₂), 5.07 (ddd, *J* = 10.3, 1.4, 0.6 Hz, 1H minor alkene *CH*₂), 4.86 (ddd, *J* = 17.0, 10.4, 8.7 Hz, 1H minor alkene *CH*),

2.57 – 2.49 (m, 1H minor cyclopropane *CH*), 2.16 (tdd, *J* = 8.3, 7.6, 0.8 Hz, 1H major cyclopropane *CH*), 1.93 (dd, *J* = 9.2, 6.0 Hz, 1H minor cyclopropane *CH*₂), 1.84 – 1.74 (m, 2H major cyclopropane *CH*₂), 1.61 (dd, *J* = 7.1, 6.0 Hz, 1H minor cyclopropane *CH*₂). ¹³C NMR (126 MHz, CDCl₃) δ 135.1, 134.0, 133, 132.31, 132.29, 131.5, 131.4, 127.5, 122.8,

122.6, 121.9, 120.0, 119.6, 119.4, 34.3, 32.0, 30.0, 23.5, 21.8, 19.5. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 2963, 2926, 2853, 2236, 1640, 1491, 1447, 1400, 1261, 1109, 1076, 1011, 986, 920, 827, 789, 712 HRMS (TAPCI, m/z) calcd. for C₁₂H₁₀BrN [M-H] 245.9918; found 245.9911

Product 3g

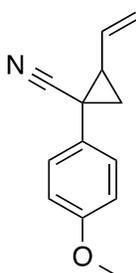
1-(*m*-tolyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(*m*-tolyl)-3-oxobutanenitrile.



38.1 mg, brown oil, yield: 83%, d.r.: 80:20. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 1H overlapping major and minor aromatic), 7.17 – 7.04 (m, 3H overlapping major and minor aromatic), 5.79 (ddd, $J = 17.0, 10.3, 8.4$ Hz, 1H major alkene CH), 5.37 (dt, $J = 17.0, 1.0$ Hz, 1H major alkene CH₂), 5.32 (dt, $J = 10.4, 0.8$ Hz, 1H major alkene CH₂), 5.28 (ddd, $J = 16.9, 1.5, 0.7$ Hz, 1H minor alkene CH₂), 5.04 (dd, $J = 10.3, 1.4$ Hz, 1H minor alkene CH₂), 4.88 (ddd, $J = 16.9, 10.3, 8.8$ Hz, 1H minor alkene CH), 2.51 (td, $J = 8.9, 6.9$ Hz, 1H minor cyclopropane CH), 2.38 – 2.33 (m, 3H overlapping major and minor CH₃), 2.23 – 2.14 (m, 1H major cyclopropane CH), 1.90 (dd, $J = 9.2, 5.9$ Hz, 1H minor cyclopropane CH₂), 1.82 (dd, $J = 8.6, 5.8$ Hz, 1H major cyclopropane CH₂), 1.74 (dd, $J = 7.3, 5.9$ Hz, 1H major cyclopropane CH₂), 1.64 (dd, $J = 7.0, 5.9$ Hz, 1H minor cyclopropane CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 139.0, 138.9, 135.8, 134.6, 133.6, 132.2, 130.5, 129.4, 129.1, 128.9, 128.7, 126.6, 123.3, 122.6, 120.7, 118.93, 118.86, 34.1, 31.9, 23.4, 22.1, 21.7, 21.6, 20.1, 19.3. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 2988, 2922, 2862, 2234, 1640, 1609, 1589, 1493, 1447, 986, 916, 795, 773, 708, 696 HRMS (ESI, m/z) calcd. for C₁₃H₁₃N, [M⁺] 183.1048, [M+H] 184.1126, [M+Na] 206.0946; found 183.1040, 184.1130, 206.0953

Product 3h

1-(4-methoxyphenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(4-methoxyphenyl)-3-oxobutanenitrile.

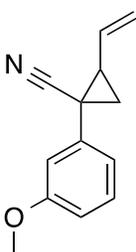


37.3 mg, yellow oil, yield: 75%, d.r.: 66:34. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.27 – 7.20 (m, 2H overlapping major and minor aromatic), 6.90 – 6.86 (m, 2H overlapping major and minor aromatic), 5.78 (ddd, $J = 17.0, 10.3, 8.4$ Hz, 1H major alkene CH), 5.36 (dt, $J = 17.0, 1.0$ Hz, 1H major alkene CH₂), 5.31 (ddd, $J = 10.3, 1.2, 0.6$ Hz, 1H major alkene CH₂), 5.27 (ddd, $J = 16.9, 1.5, 0.7$ Hz, 1H minor alkene CH₂), 5.04 (ddd, $J = 10.4, 1.5, 0.6$ Hz, 1H minor alkene CH₂), 4.87 (ddd, $J = 17.0, 10.3, 8.8$ Hz, 1H minor alkene CH), 3.80 (s, 3H overlapping major and minor CH₃), 2.48 (td, $J = 9.0, 6.9$ Hz, 1H minor cyclopropane CH), 2.13 (tdt, $J = 8.6, 7.3, 0.8$ Hz, 1H major cyclopropane CH), 1.89 (dd, $J = 9.2, 5.8$ Hz, 1H minor cyclopropane CH₂), 1.75 (dd, $J = 8.6, 5.8$ Hz, 1H major alkene CH₂), 1.69 (dd, $J = 7.3, 5.8$ Hz, 1H major alkene CH₂), 1.57 (dd, $J = 6.9, 5.8$ Hz, 1H minor alkene CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 159.8, 159.4, 134.7, 133.8, 131.1, 127.9, 127.6, 124.31,

123.3, 120.9, 118.7, 114.6, 114.5, 55.63, 55.55, 33.4, 31.7, 23.0, 21.5, 19.7, 19.4. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 3009, 2961, 2831, 2234, 2048, 1640, 1613, 1582, 1514, 1464, 1454, 1444, 1306, 1258, 1184, 1113, 1031, 988, 831, 786. HRMS (ESI, m/z) calcd. for C₁₃H₁₃NO [M+H] 199.0997; found 199.0997.

Product 3i

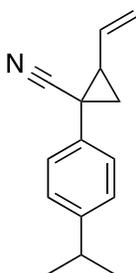
1-(3-methoxyphenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(3-methoxyphenyl)-3-oxobutanenitrile.



37.0 mg, brown oil, yield: 74%, d.r.: 80:20. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 1H overlapping major and minor aromatic), 6.94 – 6.80 (m, 3H overlapping major and minor aromatic), 5.79 (ddd, $J = 16.9, 10.3, 8.3$ Hz, 1H major alkene *CH*), 5.37 (dt, $J = 17.0, 1.0$ Hz, 1H major alkene *CH*₂), 5.32 (dt, $J = 10.3, 0.8$ Hz, 1H major alkene *CH*₂), 5.28 (ddd, $J = 16.9, 1.5, 0.7$ Hz, 1H minor alkene *CH*₂), 5.05 (dd, $J = 10.4, 1.4$ Hz, 1H minor alkene *CH*₂), 4.90 (ddd, $J = 17.0, 10.3, 8.8$ Hz, 1H minor alkene *CH*), 3.82 (s, 3H major OCH₃), 3.81 (s, 3H minor OCH₃), 2.52 (td, $J = 9.0, 7.0$ Hz, 1H minor cyclopropane *CH*), 2.23 – 2.15 (m, 1H major cyclopropane *CH*), 1.90 (dd, $J = 9.2, 5.9$ Hz, 1H minor cyclopropane *CH*₂), 1.82 (dd, $J = 8.6, 5.9$ Hz, 1H major cyclopropane *CH*₂), 1.74 (dd, $J = 7.4, 5.9$ Hz, 1H major cyclopropane *CH*₂), 1.64 (dd, $J = 7.1, 5.8$ Hz, 1H minor cyclopropane *CH*₂). ¹³C NMR (126 MHz, CDCl₃) δ 160.3, 160.0, 137.5, 134.4, 133.8, 133.5, 130.3, 130.1, 123.1, 121.9, 120.5, 119.1, 119.0, 117.9, 115.5, 114.0, 113.2, 111.9, 55.59, 55.55, 34.2, 32.0, 29.9, 23.6, 22.2, 20.2, 19.5. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 3009, 2961, 2940, 2837, 2236, 1603, 1584, 1493, 1454, 1435, 1288, 1219, 1051, 988, 920, 790, 773, 708, 692. HRMS (TAPCI, m/z) calcd. for C₁₃H₁₄NO [M+H] 200.1075; found 200.1083.

Product 3j

1-(4-isopropylphenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(4-isopropylphenyl)-3-oxobutanenitrile.

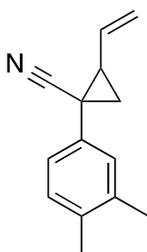


35.2 mg, yellow oil, yield: 61%, d.r.: 80:20. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, $J = 18.6$ Hz, 4H overlapping major and minor aromatic), 5.83 (ddd, $J = 16.9, 10.3, 8.3$ Hz, 1H major alkene *CH*), 5.39 (dt, $J = 17.0, 0.9$ Hz, 1H major alkene *CH*₂), 5.37 – 5.30 (m, 1H overlapping major and minor alkene *CH*₂), 5.08 (dd, $J = 10.3, 1.4$ Hz, 1H minor alkene *CH*₂), 4.93 (ddd, $J = 17.0, 10.3, 8.9$ Hz, 1H minor alkene *CH*), 2.94 (pd, $J = 6.9, 1.8$ Hz, 1H overlapping major and minor *CH*), 2.54 (td, $J = 9.0, 6.9$ Hz, 1H minor cyclopropane *CH*), 2.21 (q, $J = 8.2$ Hz, 1H major cyclopropane *CH*), 1.93 (dd, $J = 9.2, 5.8$ Hz, 1H minor cyclopropane *CH*₂), 1.84 (dd, $J = 8.6, 5.8$ Hz, 1H major cyclopropane *CH*₂), 1.76 (dd, $J = 7.3, 5.8$ Hz, 1H major cyclopropane *CH*₂), 1.65 (dd, $J = 7.0, 5.8$ Hz, 1H minor cyclopropane *CH*₂), 1.29 (s, 3H overlapping major and minor *CH*₃), 1.27 (s, 3H overlapping major and minor *CH*₃). ¹³C NMR (126 MHz, CDCl₃) δ 149.4, 148.8, 134.1, 133.8, 133.3, 129.7, 129.6, 127.3, 127.1,

125.8, 123.3, 120.7, 118.82, 118.75, 34.0, 34.0, 31.9, 30.0, 24.2, 24.11, 24.08, 23.4, 21.9, 19.8, 19.5. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 3051, 3028, 2963, 2930, 2872, 2236, 1629, 1516, 1458, 1438, 1420, 1120, 1057, 1018, 986, 918, 843. HRMS (ESI, m/z) calcd. for C₁₅H₁₇N [M-CN] 185.1336; found 185.1343.

Product 3k

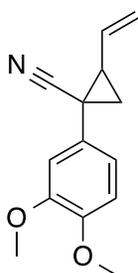
1-(3,4-dimethylphenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(3,4-dimethylphenyl)-3-oxobutanenitrile.



38.0 mg, yellow solid, m.p.: 43.0-49.0°C, yield: 77%, d.r.: 79:21. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.14 – 7.07 (m, 2H overlapping major and minor aromatic), 7.02 (ddd, $J = 17.1, 7.8, 2.2$ Hz, 1H overlapping major and minor aromatic), 5.79 (ddd, $J = 17.0, 10.3, 8.4$ Hz, 1H major alkene *CH*), 5.36 (dt, $J = 17.0, 1.0$ Hz, 1H major alkene *CH*₂), 5.33 – 5.30 (m, 1H major alkene *CH*₂), 5.27 (dd, $J = 16.6, 1.4$ Hz, 1H minor alkene *CH*₂), 5.04 (dd, $J = 10.4, 1.5$ Hz, 1H minor alkene *CH*₂), 4.89 (ddd, $J = 17.0, 10.4, 8.8$ Hz, 1H minor alkene *CH*), 2.49 (td, $J = 9.0, 6.9$ Hz, 1H minor cyclopropane), 2.26 (d, $J = 9.7$ Hz, 6H), 2.15 (td, $J = 8.4, 7.4$ Hz, 1H major cyclopropane) 1.88 (dd, $J = 9.2, 5.8$ Hz, 1H minor cyclopropane), 1.79 (dd, $J = 8.6, 5.8$ Hz, 1H major cyclopropane), 1.71 (dd, $J = 7.3, 5.8$ Hz, 1H major cyclopropane), 1.62 (dd, $J = 7.0, 5.8$ Hz, 1H minor cyclopropane). ¹³C NMR (126 MHz, CDCl₃) δ 137.6, 137.4, 137.1, 136.5, 134.7, 133.8, 133.3, 130.9, 130.3, 130.2, 129.6, 127.3, 126.9, 123.4, 123.0, 120.8, 118.7, 118.7, 33.9, 31.8, 23.2, 21.8, 20.05, 20.02, 19.8, 19.7, 19.6, 19.3. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3086, 3015, 2972, 2922, 2864, 2234, 1638, 1616, 1506, 1450, 1136, 986, 916, 824, 787, 718, 704. HRMS (ESI, m/z) calcd. for C₁₄H₁₅N [M+Na] 220.1102, [M-CN] 171.1179; found 220.1109, 171.1174.

Product 3l

1-(3,4-dimethoxyphenyl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(3,4-dimethoxyphenyl)-3-oxobutanenitrile.

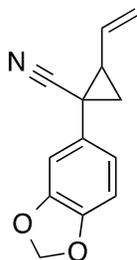


48.6 mg, brown oil, yield: 85%, d.r.: 75:25. Purified by flash chromatography on silica with 10% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 6.89 – 6.76 (m, 3H overlapping major and minor aromatic), 5.79 (ddd, $J = 17.2, 10.4, 8.5$ Hz, 1H major alkene *CH*), 5.37 (dt, $J = 17.0, 0.9$ Hz, 1H major alkene *CH*₂), 5.32 (dd, $J = 10.3, 1.0$ Hz, 1H major alkene *CH*₂), 5.30 – 5.26 (m, 1H minor alkene *CH*₂), 5.04 (dd, $J = 10.3, 1.3$ Hz, 1H minor alkene *CH*₂), 4.88 (ddd, $J = 17.0, 10.3, 8.9$ Hz, 1H minor alkene *CH*), 3.93 – 3.85 (m, 6H overlapping major and minor OCH₃), 2.48 (td, $J = 9.0, 6.9$ Hz, 1H minor cyclopropane *CH*), 2.14 (q, $J = 8.2$ Hz, 1H major cyclopropane *CH*), 1.89 (ddd, $J = 9.1, 5.8, 0.8$ Hz, 1H minor cyclopropane *CH*₂), 1.77 (dd, $J = 8.6, 5.8$ Hz, 1H major cyclopropane *CH*₂), 1.69 (dd, $J = 7.2, 5.8$ Hz, 1H major cyclopropane *CH*₂), 1.57 (dd, $J = 6.9, 5.8$ Hz, 1H minor cyclopropane *CH*₂). ¹³C NMR (126 MHz, CDCl₃) δ 149.5, 149.3, 149.3, 149.0, 134.6, 133.8, 128.4, 124.7, 123.3, 122.1, 120.9, 118.8, 118.7, 118.3, 113.0, 111.5, 111.2,

110.0, 56.3, 56.23, 56.21, 56.1, 33.5, 31.7, 22.9, 21.8, 19.81, 19.76. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3007, 2961, 2938, 2839, 2234, 1605, 1591, 1520, 1464, 1454, 1416, 1250, 1223, 1177, 1150, 1026, 990, 920, 851, 810, 766, 708. HRMS (TAPCI, m/z) calcd. for $C_{14}H_{15}NO_2$ [M-H] 228.1025, [M+H] 230.1181; found 228.1029, 230.1175

Product 3m

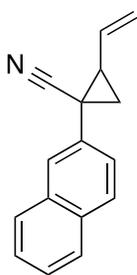
1-(benzo[d][1,3]dioxol-5-yl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(benzo[d][1,3]dioxol-5-yl)-3-oxobutanenitrile.



45.2 mg, brown solid, m.p.: 53.6-56.0 °C, yield: 85%, d.r.: 76:24. Purified by flash chromatography on silica with 10% EA:Hexane. 1H NMR (500 MHz, Chloroform-*d*) δ 6.85 – 6.73 (m, 3H overlapping major and minor aromatic), 6.00 – 5.95 (m, 2H overlapping major and acetal CH_2), 5.77 (ddd, $J = 16.9, 10.3, 8.4$ Hz, 1H major alkene CH), 5.36 (dt, $J = 17.0, 1.0$ Hz, 1H major alkene CH_2), 5.33 – 5.25 (m, 1H overlapping major and minor alkene CH_2), 5.06 (ddd, $J = 10.4, 1.4, 0.5$ Hz, 1H minor alkene CH_2), 4.90 (ddd, $J = 17.0, 10.3, 8.8$ Hz, 1H minor alkene CH), 2.47 (td, $J = 9.0, 7.0$ Hz, 1H minor cyclopropane CH), 2.15 – 2.08 (m, 1H major cyclopropane CH), 1.88 (dd, $J = 9.2, 5.8$ Hz, 1H minor cyclopropane CH_2), 1.73 (dd, $J = 8.6, 5.8$ Hz, 1H major cyclopropane CH_2), 1.68 (dd, $J = 7.3, 5.8$ Hz, 1H major cyclopropane CH_2), 1.54 (dd, $J = 7.0, 5.8$ Hz, 1H minor cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 148.2, 148.0, 147.6, 134.5, 133.6, 129.7, 126.0, 123.6, 123.1, 120.7, 120.2, 118.9, 118.9, 110.3, 108.72, 108.68, 107.1, 101.7, 33.4, 31.1, 23.0, 21.9, 19.9, 19.8. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3086, 3011, 2988, 2903, 2780, 2235, 1682, 1640, 1613, 1504, 1445, 1233, 1039, 932, 920, 815. HRMS (ESI, m/z) calcd. for $C_{13}H_{11}NO_2$ [M+Na] 236.0687; found 236.0696.

Product 3n

1-(naphthalen-2-yl)-2-vinylcyclopropane-1-carbonitrile was prepared from 2-(naphthalen-2-yl)-3-oxobutanenitrile.

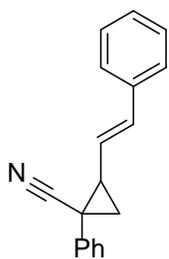


42.0 mg, brown oil, yield: 77%, d.r.: 78:22. Purified by flash chromatography on silica with 5% EA:Hexane. 1H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.79 (m, 3H aromatic), 7.56 – 7.45 (m, 2H aromatic), 7.33 (dd, $J = 8.6, 2.0$ Hz, 1H aromatic), 7.25 – 7.11 (m, 3H aromatic, minor), 6.75 – 6.64 (m, 2H aromatic, minor), 5.85 (ddd, $J = 17.0, 10.3, 8.3$ Hz, 1H, alkene CH , major), 5.70 (ddtd, $J = 13.5, 8.4, 2.6, 1.8$ Hz, 1H alkene CH_2 minor), 5.56 (ddt, $J = 11.4, 5.5, 2.7$ Hz, 1H alkene CH_2 , minor), 5.41 (dt, $J = 17.0, 1.0$ Hz, 1H, alkene CH_2 , major), 5.36 (dt, $J = 10.3, 0.8$ Hz, 1H alkene CH_2 , major), 4.66 (dd, $J = 12.6, 3.5$ Hz, 1H alkene CH , minor), 3.56 (dtt, $J = 18.0, 5.1, 2.9$ Hz, 1H cyclopropane CH_2 , minor), 2.74 (ddd, $J = 17.8, 8.5, 1.0$ Hz, 1H cyclopropane CH_2 , minor), 2.46 – 2.33 (m, 1H cyclopropane CH , minor), 2.36 – 2.24 (m, 1H cyclopropane CH , major), 1.96 (dd, $J = 8.7, 5.9$ Hz, 1H, cyclopropane CH_2 , major), 1.84 (dd, $J = 7.4, 6.0$ Hz, 1H cyclopropane CH_2 , major). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 138.4, 134.5, 133.4, 133.2, 132.8, 131.2, 129.9, 129.2, 129.1, 128.08, 128.05, 128.0, 127.9, 127.5, 127.1, 126.7,

125.2, 124.7, 123.4, 123.2, 120.6, 119.3, 119.1, 109.2, 40.4, 36.4, 34.1, 28.9, 23.4, 22.4. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3084, 3059, 3025, 2924, 2851, 2236, 1634, 1601, 1510, 1435, 1354, 1200, 988, 737, 704. HRMS (TAPCI, m/z) calcd. for C₁₆H₁₃N [M+Na] 242.0946; found 242.0945.

Product 3o

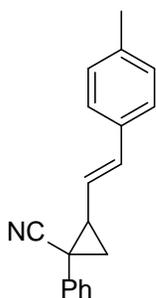
(E)-1-phenyl-2-styrylcyclopropane-1-carbonitrile was prepared from 2-phenyl-3-vinyloxirane.



44 mg, colorless oil, yield: 72%, d.r.: 80:20. Purified by flash chromatography on silica with 2% EA:Hexane. Major diastereomer (syn) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.29 (m, 10H aromatic), 6.71 (d, *J* = 15.8 Hz, 1H alkene CH), 6.14 (dd, *J* = 15.7, 8.7 Hz, 1H alkene CH), 2.35 (ddd, *J* = 9.0, 8.1, 7.1 Hz, 1H cyclopropane CH), 1.95 (dd, *J* = 8.6, 6.0 Hz, 1H cyclopropane CH₂), 1.87 (dd, *J* = 7.3, 5.9 Hz, 1H cyclopropane CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 136.6, 135.9, 134.2, 129.2, 128.9, 128.1, 128.0, 126.5, 126.1, 125.7, 120.6, 34.4, 24.1, 22.5. Minor diastereomer (anti) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.31 (m, 5H aromatic), 7.25 – 7.15 (m, 3H aromatic), 7.13 – 7.08 (m, 2H aromatic), 6.63 (d, *J* = 15.8 Hz, 1H alkene CH), 5.21 (dd, *J* = 15.8, 9.1 Hz, 1H alkene CH), 2.69 (tdd, *J* = 9.1, 7.0, 0.7 Hz, 1H cyclopropane CH), 2.02 (dd, *J* = 9.2, 5.9 Hz, 1H cyclopropane CH₂), 1.74 (dd, *J* = 7.0, 5.9 Hz, 1H cyclopropane CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 136.7, 133.9, 132.4, 129.8, 129.2, 128.8, 128.7, 127.0, 126.3, 125.1, 123.1, 31.9, 20.5, 20.1. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3082, 3059, 3028, 2932, 2228, 1599, 1497, 1448, 959, 748, 696. HRMS (ESI, m/z) calcd. for C₁₈H₁₅N [M+H] 246.1283, [M-CN] 219.1179; found 246.1287, 219.1173.

Product 3p

(E)-2-(4-methylstyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(*p*-tolyl)-3-vinyloxirane.

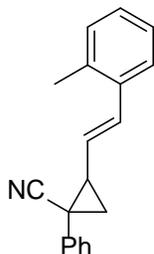


major (syn): white solid, m.p.: 91.0-95.2 °C, minor (anti): white solid, m.p.: 95.0-97.4 °C. 47 mg, yield: 72%, d.r.: 79:21 Purified by flash chromatography on silica with 2% EA:Hexane. Major (syn) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.29 (m, 5H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 15.7 Hz, 1H), 6.09 (dd, *J* = 15.7, 8.8 Hz, 1H), 2.35 (s, 3H), 2.33 (dd, *J* = 7.6, 0.9 Hz, 1H), 1.94 (dd, *J* = 8.6, 5.9 Hz, 1H), 1.85 (dd, *J* = 7.4, 5.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 138.0, 136.0, 134.0, 133.8, 129.6, 129.2, 127.9, 126.4, 125.7, 125.0, 120.7, 34.6, 24.1, 22.4, 21.5. Minor (trans) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 5H), 7.06 – 6.97 (m, 4H), 6.59 (d, *J* = 15.8 Hz, 1H), 5.16 (dd, *J* = 15.8, 9.1 Hz, 1H), 2.68 (tdd, *J* = 9.0, 7.0, 0.7 Hz, 1H), 2.28 (s, 3H), 2.01 (dd, *J* = 9.2, 5.9 Hz, 1H), 1.72 (dd, *J* = 7.0, 5.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 137.8, 133.9, 133.8, 132.5, 129.8, 129.5, 129.1, 128.7, 126.2, 124.0, 123.2, 32.0, 21.4, 20.4, 20.1. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3086, 3026,

2920, 2860, 2228, 1601, 1514, 1448, 960, 800, 764, 698. HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N$ 260.1441 [M+H], 2802.1266 [M+Na], 233.1336 [M-CN]; found 260.1441, 282.1266, 233.1336

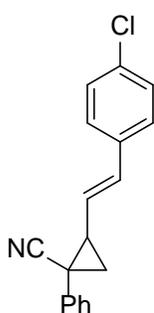
Product 3q

(E)-2-(2-methylstyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(*m*-tolyl)-3-vinyloxirane.



30 mg, white solid, m.p.: 78.2-84.3 °C, yield: 46%, d.r.: 76:24. Purified by flash chromatography on silica with 2% EA:Hexane. 1H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 6.96 (m, 9H overlapping major and minor aromatic), 6.94 (d, $J = 15.6$ Hz, 1H major alkene *CH*), 6.83 (d, $J = 15.7$ Hz, 1H minor alkene *CH*), 6.05 (dd, $J = 15.6, 8.7$ Hz, 1H major alkene *CH*), 5.13 (dd, $J = 15.6, 8.9$ Hz, 1H minor alkene *CH*), 2.75 (tdd, $J = 9.1, 7.1, 0.8$ Hz, 1H minor alkene *CH*), 2.44 – 2.36 (m, 4H overlapping major CH_3 and cyclopropane *CH*), 2.30 (s, 3H minor CH_3), 2.05 (dd, $J = 9.1, 5.9$ Hz, 1H minor cyclopropane CH_2), 1.98 (dd, $J = 8.6, 6.0$ Hz, 1H major cyclopropane CH_2), 1.90 (dd, $J = 7.3, 5.9$ Hz, 1H major cyclopropane CH_2), 1.78 (dd, $J = 7.0, 5.9$ Hz, 1H minor cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.94, 135.88, 135.7, 135.4, 135.4, 132.4, 132.1, 131.9, 130.52, 130.48, 129.8, 129.2, 129.2, 128.7, 128.0, 127.9, 127.8, 127.4, 126.5, 126.4, 126.2, 126.1, 125.72, 125.66, 123.2, 120.6, 34.7, 32.0, 24.2, 22.6, 20.6, 20.10, 20.05, 20.0. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3011, 2928, 2868, 2234, 1946, 1915, 1800, 1601, 1381, 1265, 1192, 1159, 1113, 1080, 1055, 1038, 961, 909, 839. HRMS (TAPCI, m/z) calcd. for $C_{19}H_{17}N$ [M-H] 258.1283; found 258.1291

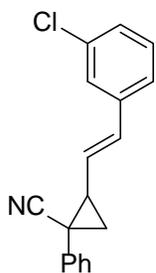
3r (E)-2-(4-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(4-chlorophenyl)-3-vinyloxirane.



55mg, white solid, m.p.: 78.2-89.3 °C, yield: 79%, d.r.: 79:21. Purified by flash chromatography on silica with 2-5% EA:Hexane. Major (syn) 1H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.34 (m, 2H aromatic), 7.38 – 7.25 (m, 7H aromatic), 6.65 (d, $J = 15.7$ Hz, 1H alkene *CH*), 6.11 (dd, $J = 15.7, 8.7$ Hz, 1H alkene *CH*), 2.33 (tdd, $J = 8.6, 7.3, 0.7$ Hz, 1H cyclopropane *CH*), 1.95 (dd, $J = 8.6, 6.0$ Hz, 1H cyclopropane CH_2), 1.86 (dd, $J = 7.3, 6.0$ Hz, 1H cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 135.1, 133.7, 132.9, 129.3, 129.0, 128.0, 127.7, 126.8, 125.8, 120.6, 34.2, 24.0, 22.6. Minor (anti) 1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.29 (m, 5H aromatic), 7.22 – 7.15 (m, 2H aromatic), 7.05 – 6.98 (m, 2H aromatic), 6.57 (d, $J = 15.8$ Hz, 1H alkene *CH*), 5.17 (dd, $J = 15.8, 9.1$ Hz, 1H alkene *CH*), 2.68 (tdd, $J = 9.2, 7.0, 0.7$ Hz, 1H cyclopropane *CH*), 2.07 – 1.96 (m, 1H cyclopropane CH_2), 1.74 (dd, $J = 7.0, 5.9$ Hz, 1H cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 133.5, 132.7, 132.3, 129.8, 129.2, 129.0, 128.8, 127.5, 125.9, 123.0, 31.7, 20.6, 20.1. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3090, 3063, 3030, 2930, 2233, 1601, 1492, 1450, 1089, 961, 812, 750, 696. HRMS (ESI, m/z) calcd. for $C_{18}H_{14}ClN$ 253.0787 [M-CN]; found 253.0787

Product 3s

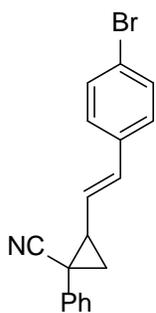
(E)-2-(3-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(3-chlorophenyl)-3-vinyloxirane.



37 mg, yellow oil, yield: 70%, d.r.: 78:22. Purified by flash chromatography on deactivated silica with 5% EA:Hexane containing 1% triethylamine. Major (syn) ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.18 (m, 9H aromatic), 6.64 (d, $J = 15.7$ Hz, 1H alkene *CH*), 6.14 (dd, $J = 15.7, 8.7$ Hz, 1H alkene *CH*), 2.33 (q, $J = 8.3$ Hz, 1H), 1.96 (dd, $J = 8.6, 6.0$ Hz, 1H), 1.87 (dd, $J = 7.3, 6.0$ Hz, 1H). Minor (anti) ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 5H aromatic), 7.18 – 7.10 (m, 2H aromatic), 7.07 (d, $J = 1.4$ Hz, 1H aromatic), 6.97 (td, $J = 4.6, 1.7$ Hz, 1H), 6.56 (d, $J = 15.7$ Hz, 1H alkene *CH*), 5.22 (dd, $J = 15.8, 9.1$ Hz, 1H alkene *CH*), 2.74 – 2.60 (m, 1H cyclopropane *CH*), 2.03 (dd, $J = 9.2, 5.9$ Hz, 1H cyclopropane *CH*₂), 1.74 (dd, $J = 7.0, 6.0$ Hz, 1H cyclopropane *CH*₂). ^{13}C NMR (126 MHz, CDCl₃) δ 138.5, 138.4, 135.6, 134.8, 134.7, 132.8, 132.6, 132.2, 130.1, 130.0, 129.8, 129.3, 129.2, 128.9, 128.1, 128.0, 127.8, 127.7, 126.8, 126.5, 126.2, 125.8, 124.7, 124.5, 122.9, 120.5, 34.2, 31.7, 24.0, 22.6, 20.7, 20.1. IR ($\bar{\nu} - \bar{\nu}_{\text{IR}}$, neat) 3088, 3061, 3030, 2937, 2233, 1682, 1593, 1566, 1497, 1450, another at about 1400, 1027, 1078, 959, 880, 779, 750, 696. HRMS (ESI, *m/z*) calcd. for C₁₈H₁₄ClN [M-CN] 253.0790; found 253.0791

Product 3t

(E)-2-(4-bromostyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(4-bromophenyl)-3-vinyloxirane.

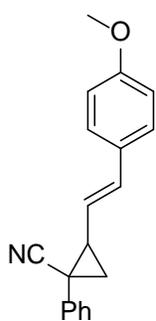


61 mg, white solid, m.p. 70.0-85.4 °C, yield: 80%, d.r.: 80:20. Purified by flash chromatography on silica with 2% EA:Hexane. Major (syn) ^1H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.24 (m, 9H aromatic), 6.63 (d, $J = 15.7$ Hz, 1H alkene *CH*), 6.12 (dd, $J = 15.7, 8.7$ Hz, 1H alkene *CH*), 2.36 – 2.28 (m, 1H cyclopropane *CH*), 1.96 (dd, $J = 8.6, 6.0$ Hz, 1H cyclopropane *CH*₂), 1.86 (dd, $J = 7.3, 6.0$ Hz, 1H cyclopropane *CH*₂). ^{13}C NMR (126 MHz, CDCl₃) δ 135.7, 135.5, 133.0, 132.0, 129.3, 128.1, 127.0, 126.9, 125.8, 121.9, 120.6, 34.3, 24.0, 22.5. Minor (anti) ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 7H aromatic), 6.99 – 6.94 (m, 2H aromatic), 6.56 (d, $J = 15.8$ Hz, 1H alkene *CH*), 5.19 (dd, $J = 15.8, 9.1$ Hz, 1H alkene *CH*), 2.67 (tdd, $J = 9.1, 6.9, 0.7$ Hz, 1H cyclopropane *CH*), 2.02 (dd, $J = 9.2, 5.9$ Hz, 1H cyclopropane *CH*₂), 1.74 (dd, $J = 7.0, 5.9$ Hz, 1H cyclopropane *CH*₂). ^{13}C NMR (126 MHz, CDCl₃) δ 135.5, 132.7, 132.3, 131.9, 129.8, 129.2, 128.8, 127.8, 126.0, 122.9, 121.7, 31.7, 20.6, 20.1. IR ($\bar{\nu} - \bar{\nu}_{\text{IR}}$, neat) 3088, 3061, 3028, 2234, 1601, 1487, 1448, 1404, 1072, 1009, 959, 808, 747,

969. HRMS (ESI, m/z) calcd. for $C_{18}H_{14}BrN$ [M^+] 323.310, [$M+Na$] 346.0207; found 323.0310, 346.0199

Product 3u

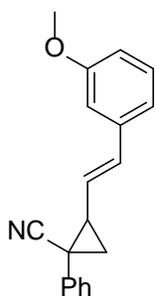
(E)-2-(4-methoxystyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(4-methoxyphenyl)-3-vinyloxirane.



44 mg, white solid, m.p: 68.1-75.6 °C, yield: 64%, d.r.: 82:18. Purified by flash chromatography on silica with 5% EA:Hexane. 1H NMR (500 MHz, Chloroform- d) δ 7.43 – 7.28 (m, overlapping 7H major, 5H minor, aromatic), 7.08 – 7.01 (m, 2H, aromatic, minor), 6.91 – 6.84 (m, 2H, aromatic, major), 6.76 (dd, J = 8.8, 2.0 Hz, 2H, aromatic, minor), 6.64 (d, J = 15.7 Hz, 1H, alkene CH , major), 6.57 (d, J = 15.7 Hz, 1H, alkene CH , minor), 6.00 (ddd, J = 15.8, 8.6, 1.8 Hz, 1H, alkene CH , major), 5.07 (ddd, J = 15.7, 9.0, 1.6 Hz, 1H, alkene CH , minor), 3.82 (s, 3H, CH_3 , major), 3.76 (s, 3H, CH_3 , minor), 2.67 (td, J = 9.0, 7.0 Hz, 1H, cyclopropane CH , minor), 2.32 (q, J = 8.2 Hz, 1H, cyclopropane CH , major), 2.00 (dd, J = 9.1, 5.9 Hz, 1H, cyclopropane CH_2 , minor), 1.93 (dd, J = 8.6, 6.0 Hz, 1H, cyclopropane, CH_2 , major), 1.84 (dd, J = 7.3, 6.0 Hz, 1H, cyclopropane, CH_2 , major), 1.71 (dd, J = 7.1, 5.9 Hz, 1H, cyclopropane, CH_2 , minor). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 159.5, 136.0, 133.6, 133.4, 132.5, 129.8, 129.5, 129.4, 129.2, 129.1, 128.6, 128.3, 127.87, 127.8, 127.5, 127.0, 125.7, 123.7, 123.2, 122.8, 120.7, 114.3, 114.2, 34.6, 32.0, 24.1, 22.4, 20.3, 20.1. IR ($\bar{\nu}_{IR}$, neat) 3061, 3030, 3007, 2957, 2936, 2837, 2234, 1607, 1514, 1450, 1304, 1252, 1178, 1109, 1031, 959, 818, 762, 741, 696. HRMS (TAPCI, m/z) calcd. for $C_{19}H_{17}NO$ [$M-H$] 274.1232; found 274.1234

Product 3v

(E)-2-(3-methoxystyryl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(3-methoxyphenyl)-3-vinyloxirane.

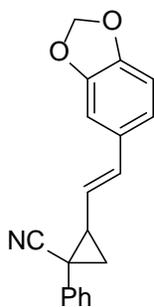


36 mg colorless oil, yield: 52%, d.r.: 78:22. Purified by flash chromatography on silica with 5% EA:Hexane. 1H NMR (500 MHz, Chloroform- d) δ 7.42 – 6.56 (m, 10H overlapping major and minor 9H aromatic, 1H alkene CH), 6.19 – 6.07 (m, 1H major alkene CH), 5.25 – 5.16 (m, 1H minor alkene CH), 3.83 (d, J = 1.5 Hz, 3H major OCH_3), 3.74 (d, J = 1.5 Hz, 3H minor OCH_3), 2.68 (td, J = 9.1, 8.6, 6.8 Hz, 1H minor cyclopropane CH), 2.39 – 2.29 (m, 1H major cyclopropane CH), 2.02 (dd, J = 9.2, 6.0 Hz, 1H minor cyclopropane CH_2), 1.98 – 1.92 (m, 1H major cyclopropane CH_2), 1.86 (td, J = 6.7, 5.8, 1.4 Hz, 1H major cyclopropane CH_2), 1.77 – 1.71 (m, 1H minor cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 159.9, 138.1, 138.0, 135.9, 134.1, 133.8, 132.4, 129.9, 129.8, 129.8, 129.3, 129.2, 128.8, 128.0, 126.4, 125.8, 125.6, 123.1, 120.6, 119.2, 118.9, 113.8, 113.2, 111.9, 111.8, 55.5,

55.4, 34.4, 31.8, 24.1, 22.5, 20.5, 20.2. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3061, 3028, 2957, 2940, 2835, 2234, 1599, 1580, 1495, 1452, 1290, 1267, 1157, 1040, 961, 777, 760, 694. HRMS (ESI, m/z) calcd. for C₁₉H₁₇NO [M+H] 276.1388, M-CN = 249.1285; found 276.1388, 249.1282

Product 3w

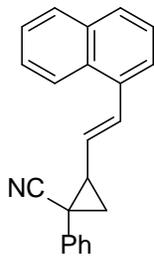
(E)-2-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)-1-phenylcyclopropane-1-carbonitrile was prepared from 5-(3-vinylloxiran-2-yl)benzo[d][1,3]dioxole.



52 mg, white solid, m.p.: 111.4-114.3 °C, yield: 73%, d.r.: 79:21. Purified by flash chromatography on silica with 5% EA:Hexane. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H overlapping major and minor aromatic), 6.98 – 6.49 (m, 4H overlapping major and minor 3H aromatic 1H alkene CH), 6.01 – 5.86 (m, 3H overlapping major and minor 2H acetal CH₂ and 1H major alkene CH), 5.03 (dd, *J* = 15.7, 9.0 Hz, 1H minor alkene CH), 2.65 (tdd, *J* = 9.1, 7.0, 0.7 Hz, 1H minor cyclopropane CH), 2.30 (tdd, *J* = 8.5, 7.3, 0.7 Hz, 1H major cyclopropane CH), 2.00 (dd, *J* = 9.2, 5.9 Hz, 1H minor cyclopropane CH₂), 1.93 (dd, *J* = 8.6, 6.0 Hz, 1H major cyclopropane CH₂), 1.84 (dd, *J* = 7.4, 6.0 Hz, 1H major cyclopropane CH₂), 1.71 (dd, *J* = 7.0, 6.0 Hz, 1H minor cyclopropane CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 148.3, 147.7, 135.9, 133.7, 133.5, 132.4, 131.2, 131.1, 129.8, 129.2, 129.1, 128.7, 127.9, 126.9, 125.7, 124.2, 123.2, 121.2, 121.1, 120.6, 108.54, 108.52, 108.45, 105.9, 105.4, 101.5, 101.4, 101.3, 34.5, 31.8, 24.0, 22.4, 20.4, 20.1. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3061, 3028, 3009, 2895, 2234, 1601, 1505, 1487, 1447, 1350, 1252, 1196, 1105, 1037, 959, 928, 802, 746, 696. HRMS (ESI, m/z) calcd. for C₁₉H₁₅NO₂ [M+Na] 312.1000; found 312.1002

Product 3x

(E)-2-(2-(naphthalen-1-yl)vinyl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(naphthalen-1-yl)-3-vinylloxirane.

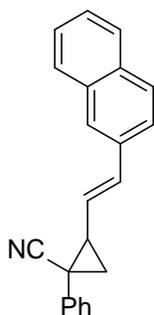


38mg, white solid, m.p.: 99.3-101.4 °C, yield: 61%, d.r.: 74:26. Purified by flash chromatography on silica with 2% EA:Hexane. Major (syn) ¹H NMR (500 MHz, Chloroform-*d*) δ 8.21 – 7.29 (m, 13H overlapping 12H aromatic and 1H alkene CH), 6.21 (ddd, *J* = 15.5, 8.7, 2.7 Hz, 1H alkene CH), 2.49 (q, *J* = 8.3 Hz, 1H cyclopropane CH), 2.00 (ddd, *J* = 8.4, 6.0, 1.5 Hz, 1H cyclopropane CH₂), 1.94 (t, *J* = 6.7 Hz, 1H cyclopropane CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 135.8, 134.3, 133.8, 131.4, 131.1, 129.24, 129.18, 128.79, 128.47, 127.96, 126.36, 126.03, 125.91, 125.68, 124.43, 123.86, 120.6, 34.6, 24.2, 22.6. Minor (anti) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.26 (m, 12H aromatic), 7.11 (dt, *J* = 7.2, 1.0 Hz, 1H alkene CH), 5.27 (dd, *J* = 15.6, 8.8 Hz, 1H alkene CH), 2.84 (tdd, *J* = 9.1, 7.0, 0.8 Hz, 1H cyclopropane CH), 2.08 (dd, *J* = 9.1, 6.0 Hz, 1H cyclopropane CH₂), 1.83 (dd, *J* = 7.0, 6.0 Hz, 1H cyclopropane CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 134.5, 133.7, 132.5, 131.4, 131.0, 129.9, 129.2, 128.8, 128.7, 128.4, 128.3, 126.3, 126.1,

125.7, 124.1, 123.9, 123.1, 32.0, 20.7, 20.0. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3061, 3046, 2955, 2236, 1601, 1503, 1451, 1398, 1265, 1173, 1111, 957, 797, 775, 756, 733, 696. HRMS (ESI, m/z) calcd. for $C_{22}H_{17}N$ $[M+Na]$ 318.1259; found 318.1265

Product 3y

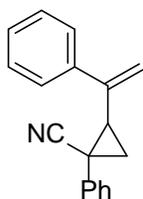
(E)-2-(2-(naphthalen-2-yl)vinyl)-1-phenylcyclopropane-1-carbonitrile was prepared from 2-(naphthalen-2-yl)-3-vinyloxirane.



39 mg, white solid, m.p.: 131.0-140.1 °C, yield: 62%, d.r.: 80:20. Purified by flash chromatography on silica with 2% EA:Hexane. 1H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.19 (m, 12H overlapping major and minor aromatic), 6.86 (d, $J = 15.7$ Hz, 1H major alkene *CH*), 6.79 (d, $J = 15.7$ Hz, 1H minor alkene *CH*), 6.26 (dd, $J = 15.7, 8.8$ Hz, 1H major alkene *CH*), 5.37 – 5.29 (m, 1H minor alkene *CH*), 2.75 (tdd, $J = 9.1, 7.0, 0.7$ Hz, 1H minor cyclopropane *CH*), 2.40 (tdd, $J = 8.6, 7.3, 0.7$ Hz, 1H major cyclopropane *CH*), 2.06 (dd, $J = 9.1, 6.0$ Hz, 1H minor cyclopropane CH_2), 1.99 (dd, $J = 8.6, 6.0$ Hz, 1H major cyclopropane CH_2), 1.91 (dd, $J = 7.3, 6.0$ Hz, 1H major cyclopropane CH_2), 1.78 (dd, $J = 6.9, 6.1$ Hz, 1H minor cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.9, 134.3, 134.0, 133.8, 133.3, 129.9, 129.3, 129.2, 128.8, 128.56, 128.4, 128.3, 128.2, 128.0, 127.94, 127.85, 126.60, 126.58, 126.45, 126.3, 126.24, 126.22, 125.8, 125.5, 123.7, 123.3, 123.1, 120.7, 100.2, 34.6, 32.0, 24.2, 22.6, 20.6, 20.3. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3088, 3053, 3028, 3003, 2236, 1599, 1505, 1452, 1265, 1109, 959, 812, 746, 735, 696. HRMS (ESI, m/z) calcd. for $C_{22}H_{17}N$ $[M+]$ 295.1361, $[M+H]$ 296.1439, $[M+Na]$ 318.1259; found 295.1357, 296.1435, 318.1263

Product 3z

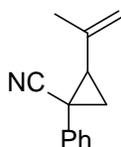
1-phenyl-2-(1-phenylvinyl)cyclopropane-1-carbonitrile was prepared from 2-phenyl-2-vinyloxirane.



15 mg, slightly yellow needles, m.p.: 118.4-122.6 °C, yield: 34%, d.r.: 77:23. Purified by flash chromatography on silica with 1% EA:Hexane. 1H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.27 (m, 8H overlapping major and minor aromatic), 7.20 – 7.13 (m, 1H overlapping major and minor aromatic), 5.76 (s, 1H major methylene CH_2), 5.39 (s, 1H minor methylene CH_2), 5.28 (d, $J = 1.4$ Hz, 1H major methylene CH_2), 4.90 (d, $J = 1.4$ Hz, 1H minor methylene CH_2), 2.98 (ddd, $J = 9.0, 7.6, 1.4$ Hz, 1H minor cyclopropane *CH*), 2.55 (td, $J = 8.2, 1.3$ Hz, 1H major cyclopropane *CH*), 2.13 (dd, $J = 7.8, 6.0$ Hz, 1H major cyclopropane CH_2), 2.04 (dq, $J = 9.1, 6.3$ Hz, 2H minor cyclopropane CH_2), 1.91 (dd, $J = 8.5, 6.1$ Hz, 1H major cyclopropane CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 140.4, 139.7, 139.6, 136.0, 131.2, 129.3, 128.80, 128.77, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 126.1, 126.0, 125.5, 123.4, 120.0, 115.4, 114.7, 35.7, 34.3, 23.9, 21.7, 21.1, 17.4. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3061, 2926, 2236, 1726, 1694, 1601, 1495, 1449, 1317, 1279, 1111, 1071, 1026, 910, 758, 698. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N$ $[M+H]$ 246.1283; found 246.1281

Product 3aa

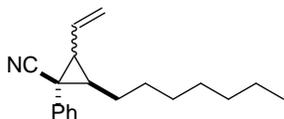
1-phenyl-2-(prop-1-en-2-yl)cyclopropane-1-carbonitrile was prepared from 2-methyl-2-vinylloxirane.



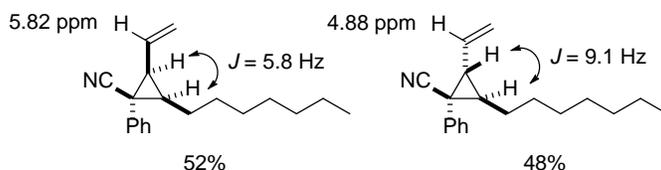
22 mg, yellow oil, yield: 48%, d.r.: 85:15. Purified by flash chromatography on silica with 1% EA:Hexane. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H aromatic), 5.12 (h, $J = 1.4$ Hz, 1H major alkene CH_2), 4.95 (q, $J = 1.1$ Hz, 1H major alkene CH_2), 4.83 – 4.78 (m, 1H minor alkene CH_2), 4.71 (q, $J = 1.3$ Hz, 1H minor alkene CH_2), 2.54 – 2.47 (m, 1H minor cyclopropane CH), 2.17 – 2.06 (m, 1H major cyclopropane CH), 2.04 – 1.92 (m, 1H), 1.89 (dd, $J = 7.7$, 6.2 Hz, overlapping 1H major cyclopropane CH_2 , 3H major CH_3), 1.83 (dd, $J = 9.2$, 6.2 Hz, 1H minor cyclopropane CH_2), 1.72 (dd, $J = 8.5$, 5.9 Hz, 1H minor cyclopropane CH_2), 1.43 (t, $J = 0.9$ Hz, 3H minor CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 139.9, 138.2, 136.5, 131.7, 129.3, 129.2, 128.63, 128.59, 128.2, 127.9, 126.0, 123.7, 120.4, 115.4, 114.2, 37.2, 36.1, 22.9, 22.5, 22.3, 21.6, 21.5, 19.9, 17.3. IR ($\bar{\nu} - \bar{\nu}_{\text{IR}}$, neat) 3061, 2974, 2939, 2234, 1651, 1601, 1497, 1451, 1385, 1234, 1196, 1119, 902, 760, 721, 696. HRMS (ESI, m/z) calcd. for $\text{C}_{13}\text{H}_{13}\text{N}$ [$\text{M}+\text{H}$] 184.1126; found 184.1123

Product 3ab

2-heptyl-1-phenyl-3-vinylcyclopropane-1-carbonitrile was prepared from (E)-2-(non-1-en-1-yl)oxirane.

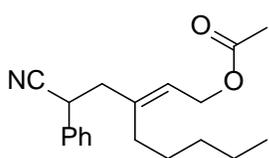


42 mg, yellow oil, yield: 62%, d.r.: 52:48. Purified by flash chromatography on silica with 0.5% EA:Hexane. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 5H aromatic), 5.82 (ddd, $J = 17.0$, 10.4, 9.4 Hz, 1H alkene CH), 5.41 (ddd, $J = 16.9$, 1.5, 0.7 Hz, 1H alkene CH_2), 5.35 (ddd, $J = 10.4$, 1.5, 0.6 Hz, 1H alkene CH_2), 5.24 (ddd, $J = 16.9$, 1.5, 0.6 Hz, 1H alkene CH_2), 5.05 – 4.98 (m, 1H alkene CH_2), 4.88 (ddd, $J = 16.9$, 10.3, 8.9 Hz, 1H alkene CH), 2.31 (t, $J = 9.1$ Hz, 1H cyclopropane CH), 2.19 (dd, $J = 8.9$, 5.8 Hz, 1H cyclopropane CH), 1.88 – 1.12 (m, 13H overlapping aliphatic CH_2 and cyclopropane CH), 0.89 (q, $J = 7.1$ Hz, 3H CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 136.9, 133.9, 133.3, 132.4, 132.3, 132.20, 132.18, 131.4, 129.9, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 127.8, 125.9, 121.6, 120.2, 119.2, 118.3, 38.9, 37.8, 34.7, 32.0, 32.0, 31.4, 30.8, 29.6, 29.5, 29.5, 29.4, 29.0, 28.9, 27.2, 26.5, 26.3, 22.90, 22.89, 14.4, 14.3. IR ($\bar{\nu} - \bar{\nu}_{\text{IR}}$, neat) 3086, 3061, 3030, 2928, 2857, 2230, 1715, 1634, 1601, 1495, 1449, 1377, 1298, 1175, 1120, 1030, 986, 912, 696. HRMS (TAPCI, m/z) calcd. for $\text{C}_{19}\text{H}_{25}\text{N}$ [$\text{M}-\text{H}$] 266.1909, [$\text{M}+\text{H}$] 268.2065; found 266.1907, 268.2062



Product 6

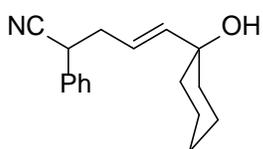
3-(2-cyano-2-phenylethyl)oct-2-en-1-yl acetate was prepared from 2-(hept-1-en-2-yl)oxirane at 0.75 mmol scale.



61mg, yellow oil, yield: 87%, E:Z: 53:47. Purified by flash chromatography on silica with 2-10% EA:Hexane. ^1H NMR (500 MHz, Chloroform- d) δ 7.43 – 7.29 (m, 5H aromatic), 5.51 (tt, J = 7.1, 1.3 Hz, 1H alkene CH, major), 5.46 (tt, J = 6.9, 1.0 Hz, 1H), 4.59 (d, J = 6.9 Hz, 1H), 4.47 – 4.32 (m, 2H, CH_2 , major), 3.89 (ddd, J = 8.7, 6.5, 5.0 Hz, 1H, CH, major), 2.80 (dd, J = 13.7, 8.7 Hz, 1H CH_2 , major), 2.68 – 2.49 (m, 3H overlapping 1H CH_2 , major and 2H CH_2 , minor), 2.15 (dt, J = 13.7, 7.7 Hz, 1H CH_2 , minor), 1.49 – 1.19 (m, 9H, overlapping 2H CH_2 , 3H CH_3 , major and 1H CH_2 minor 3H CH_3 , minor), 0.89 (td, J = 7.1, 2.5 Hz, 6H overlapping CH_3 major and minor). ^{13}C NMR (126 MHz, CDCl_3) δ 171.2, 171.0, 140.9, 140.5, 135.8, 135.6, 129.39, 129.35, 128.54, 128.45, 127.6, 127.5, 123.6, 123.3, 120.7, 120.6, 77.3, 60.9, 60.7, 43.1, 37.2, 36.9, 36.7, 36.7, 31.9, 31.7, 30.6, 28.4, 27.7, 22.7, 21.3, 21.2, 14.28, 14.25. IR ($\bar{\nu}$ – $\bar{\nu}_{\text{IR}}$, neat) 3065, 3032, 2957, 2932, 2861, 2241, 1732, 1667, 1601, 1497, 1454, 1374, 1233, 1078, 1024, 961, 754, 700, 608. LRMS (EI, m/z) parent mass 299.19 found 299.15 rel. intensity 0.06 HRMS via LCT ESI TOF MS and LC TAPCI QTOF MS was attempted

Product 7

(E)-5-(1-hydroxycyclohexyl)-2-phenylpent-4-enenitrile was prepared from 2-vinyl-1-oxaspiro[2.5]octane.



68 mg, yellow oil, yield >99%. Purified by flash chromatography on silica with 0-30% EA:Hexane. ^1H NMR (500 MHz, Chloroform- d) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 5.75 – 5.60 (m, 2H), 3.84 (dd, J = 7.7, 6.6 Hz, 1H), 2.68 – 2.56 (m, 2H), 1.70 – 1.40 (m, 9H), 1.34 – 1.19 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.2, 135.4, 132.4, 132.3, 129.3, 128.8, 128.7, 128.4, 127.6, 121.9, 120.6, 71.6, 38.8, 38.1, 38.1, 25.7, 22.3. IR ($\bar{\nu}$ – $\bar{\nu}_{\text{IR}}$, neat) 3452 (broad), 3063, 2932, 2857, 2241, 1601, 1497, 1454, 1346, 1261, 1173, 1055, 1034, 972, 754, 698. HRMS (TAPCI, m/z) calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}$ [M-H] 238.1596; found 238.1595

Equilibration of diastereomers under the reaction conditions.

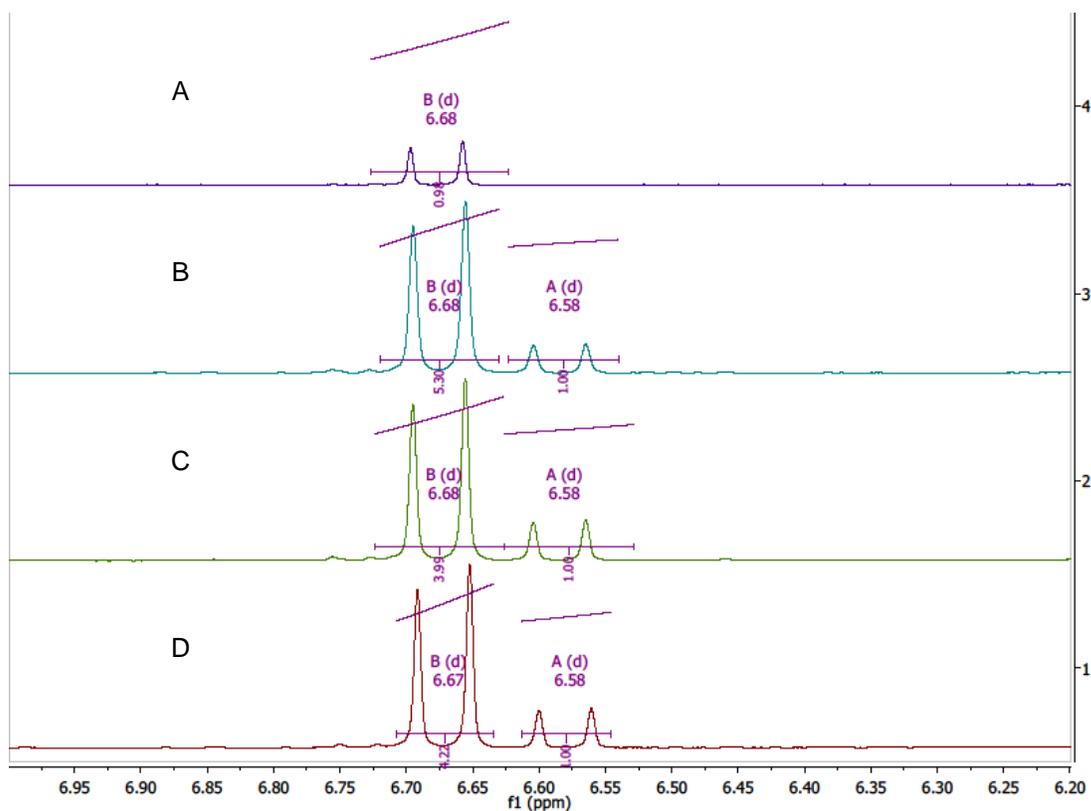
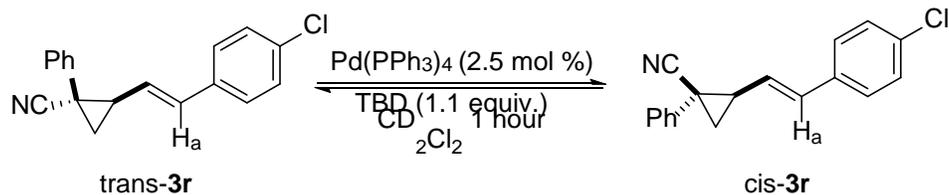


Figure S1. Isomerization of *cis-3r*. Reaction conditions: *cis*-(*E*)-2-(4-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile (17.9 mg, 0.064 mmol) was dissolved in CD_2Cl_2 (0.5 mL, 0.128 M). Tetrakis triphenylphosphine palladium(0) (1.8 mg, 1.6 μmol , 2.4 mol %) and TBD (9.8 mg, 0.070 mmol, 1.1 equiv) were added to an NMR tube under argon. The cyclopropane solution was added to the NMR tube and the reaction was monitored by NMR. A. the starting cyclopropane B. immediately after adding mixing. C. 1 h. D. 6 h.

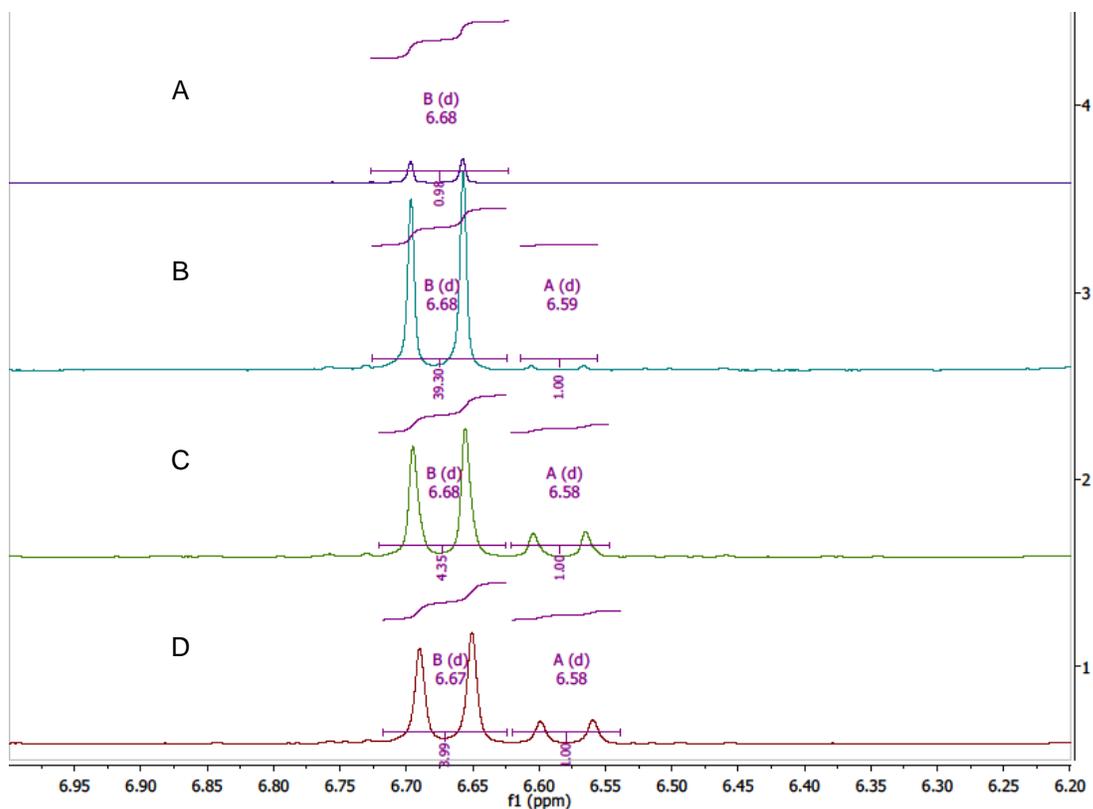


Figure S2. Isomerization of *cis*-3r without TBD. Reaction conditions: *cis*-(*E*)-2-(4-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile (17.5 mg, 0.063 mmol) was dissolved in CD₂Cl₂ (0.5 mL, 0.125 M). Tetrakis triphenylphosphine palladium(0) (1.9 mg, 1.6 μmol, 2.5 mol %) was added to an NMR tube under argon. The cyclopropane solution was added to the NMR tube and the reaction was monitored by NMR. A. the starting cyclopropane B. immediately mixing C. 1 h. D. 6 h.

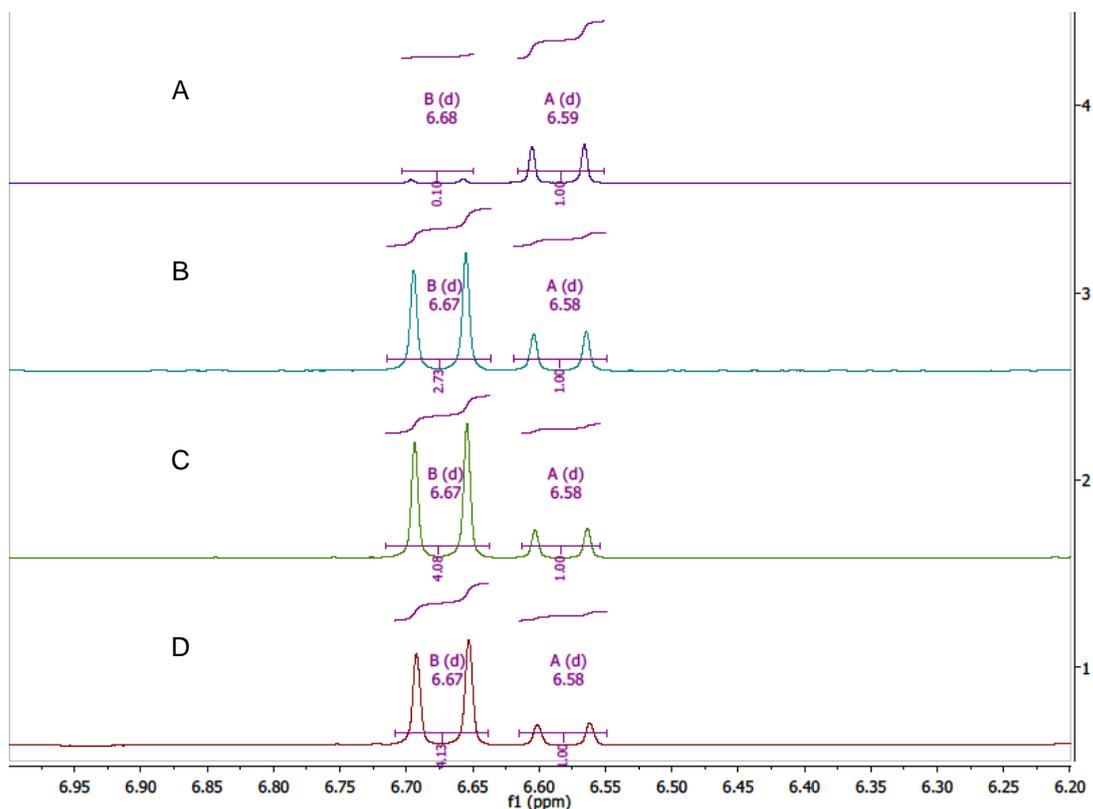


Figure S3. Isomerization of *trans*-3r. Reaction conditions: *trans*-(*E*)-2-(4-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile (17.5 mg, 0.063 mmol) was dissolved in CD₂Cl₂ (0.5 mL, 0.125 M). Tetrakis triphenylphosphine palladium(0) (1.8 mg, 1.6 μ mol, 2.4 mol %) and TBD (9.9 mg, 0.071 mmol, 1.1 equiv) were added to an NMR tube under argon. The cyclopropane solution was added to the NMR tube and the reaction was monitored by NMR. A. the starting cyclopropane B. immediately after mixing C. 1 h. D. 6 h.

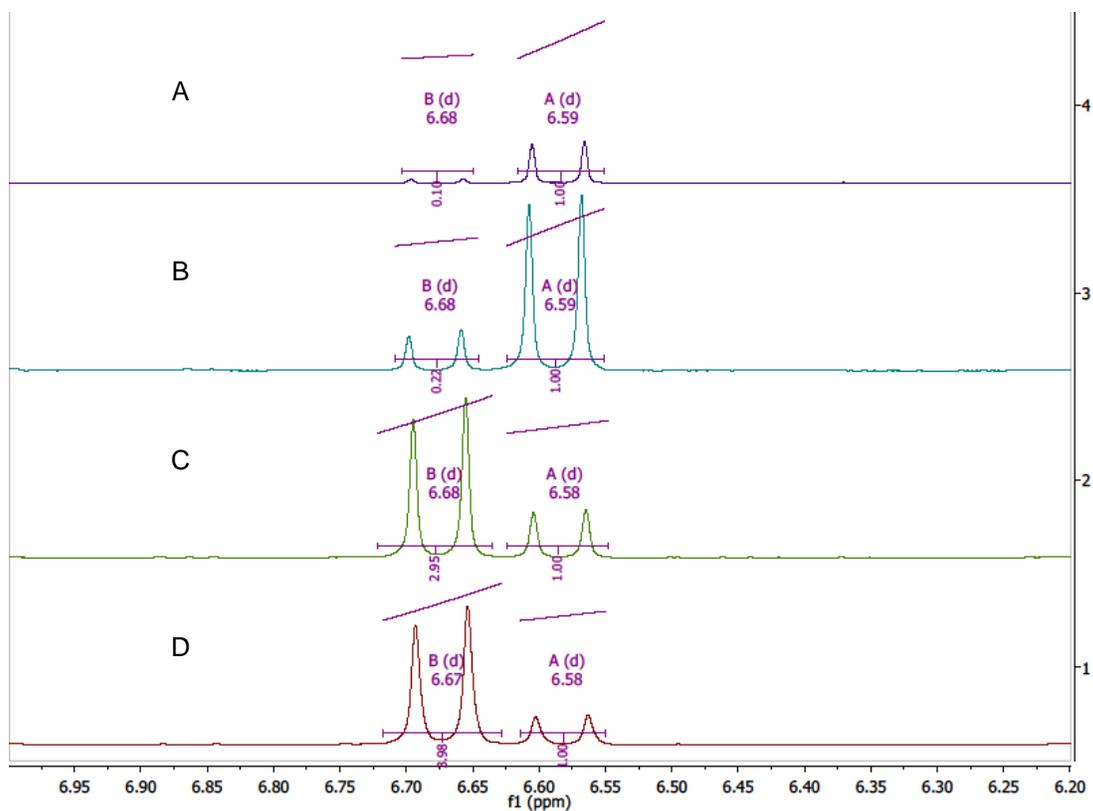
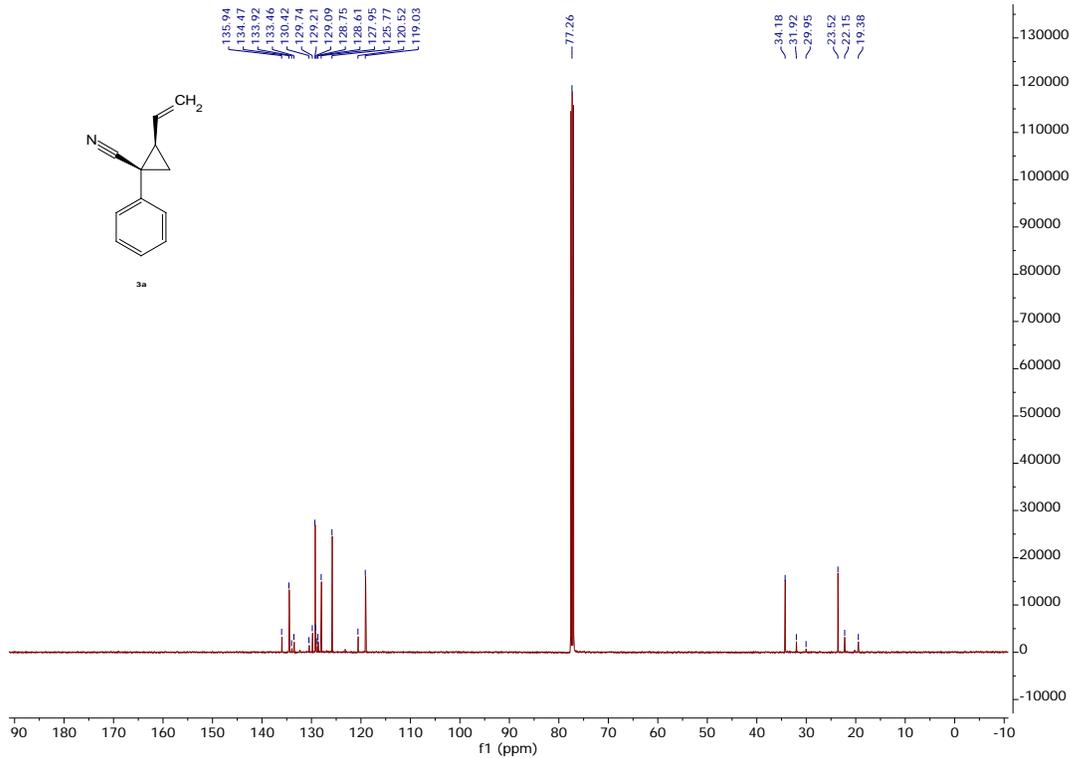
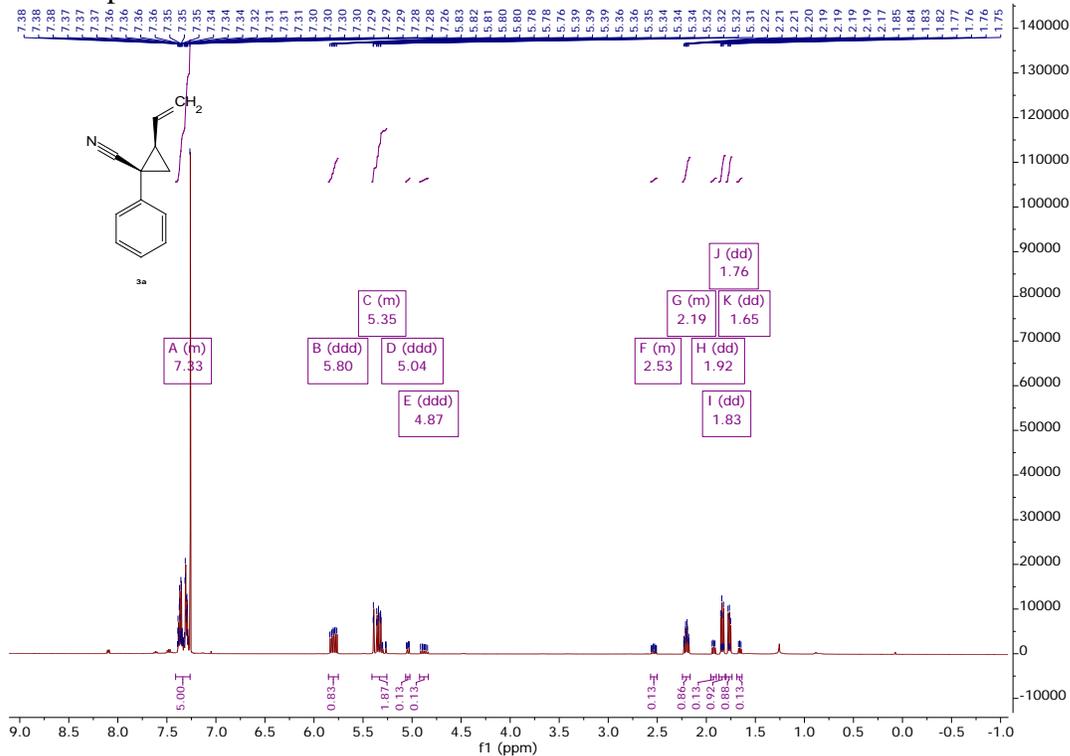
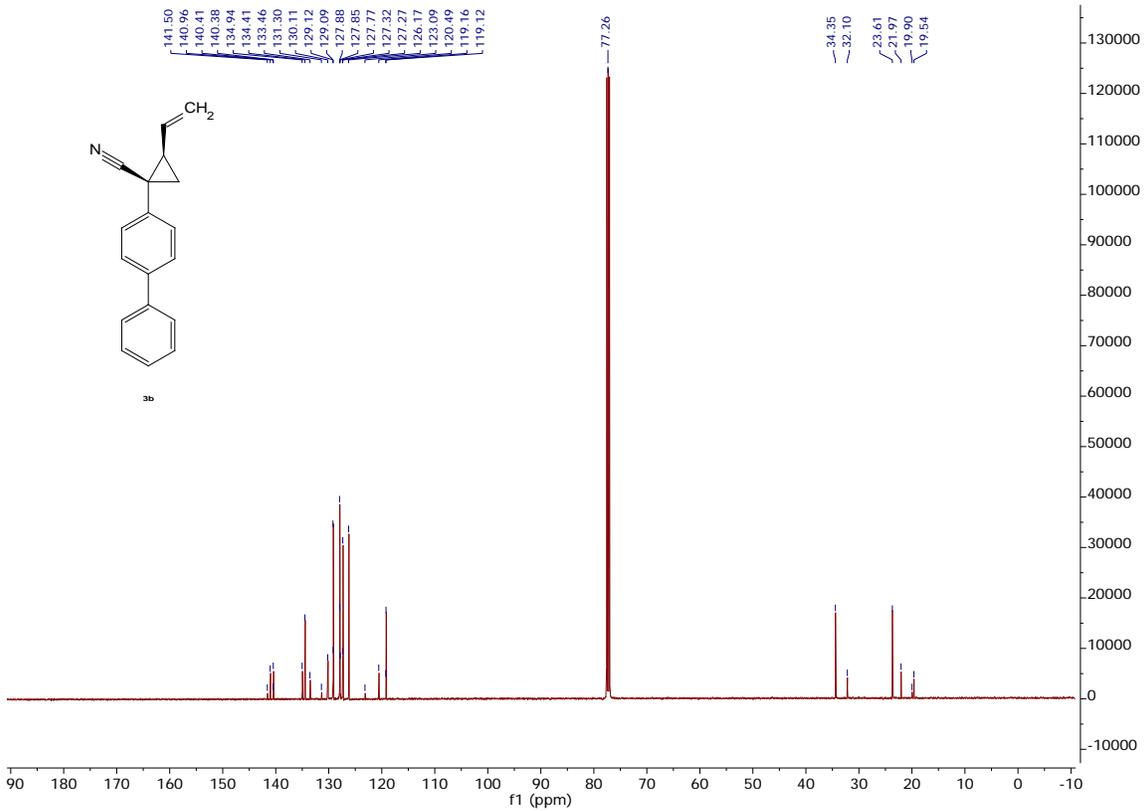
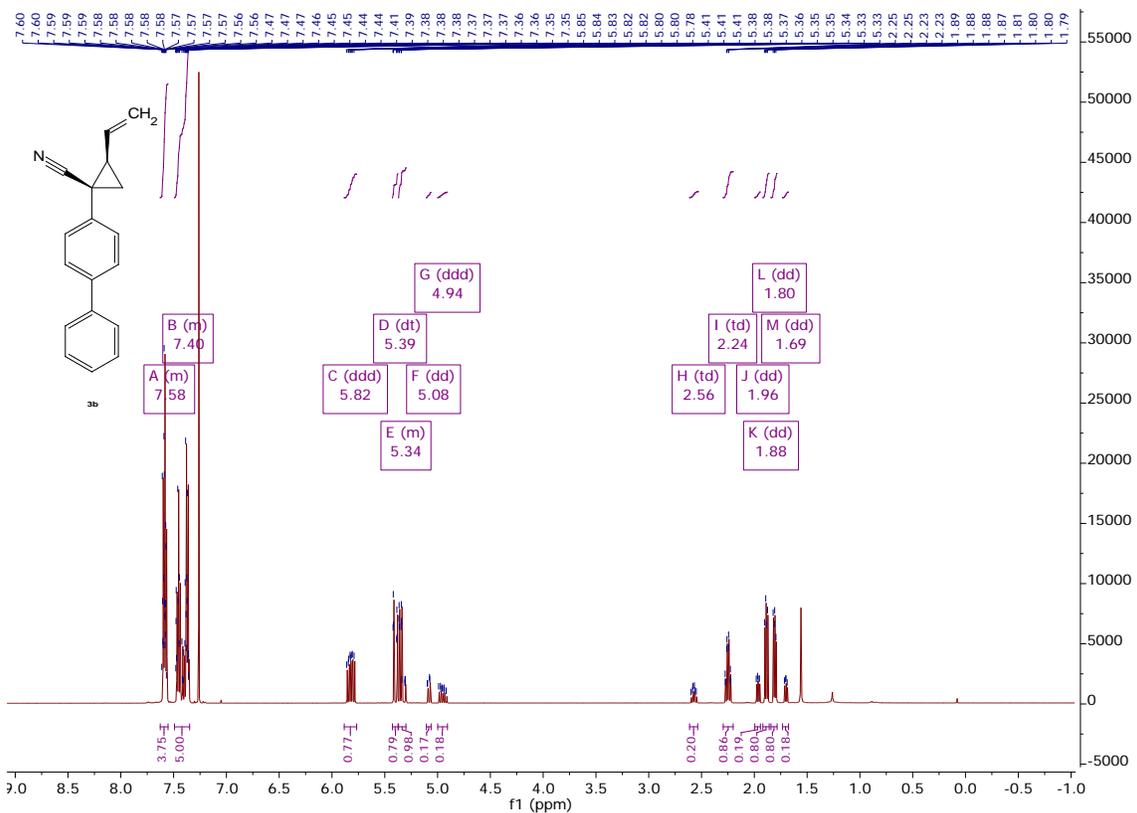


Figure S4. Isomerization of *cis*-3r without TBD. Reaction conditions: *trans*-(*E*)-2-(4-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile (17.7 mg, 0.063 mmol) was dissolved in CD₂Cl₂ (0.5 mL, 0.126 M). Tetrakis triphenylphosphine palladium(0) (1.8 mg, 1.6 μ mol, 2.5 mol %) was added to an NMR tube under argon. The cyclopropane solution was added to the NMR tube and the reaction was monitored by NMR. A. the starting cyclopropane B. immediately after mixing C. 1 h. D. 6 h.

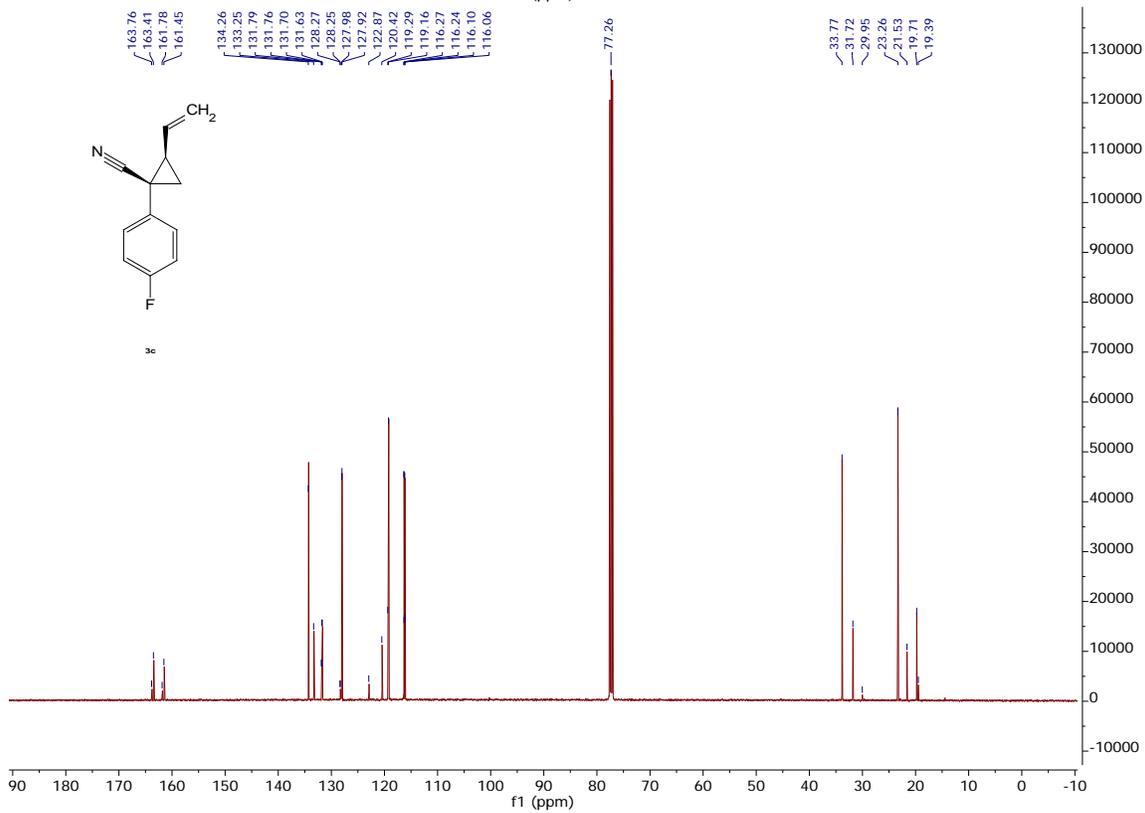
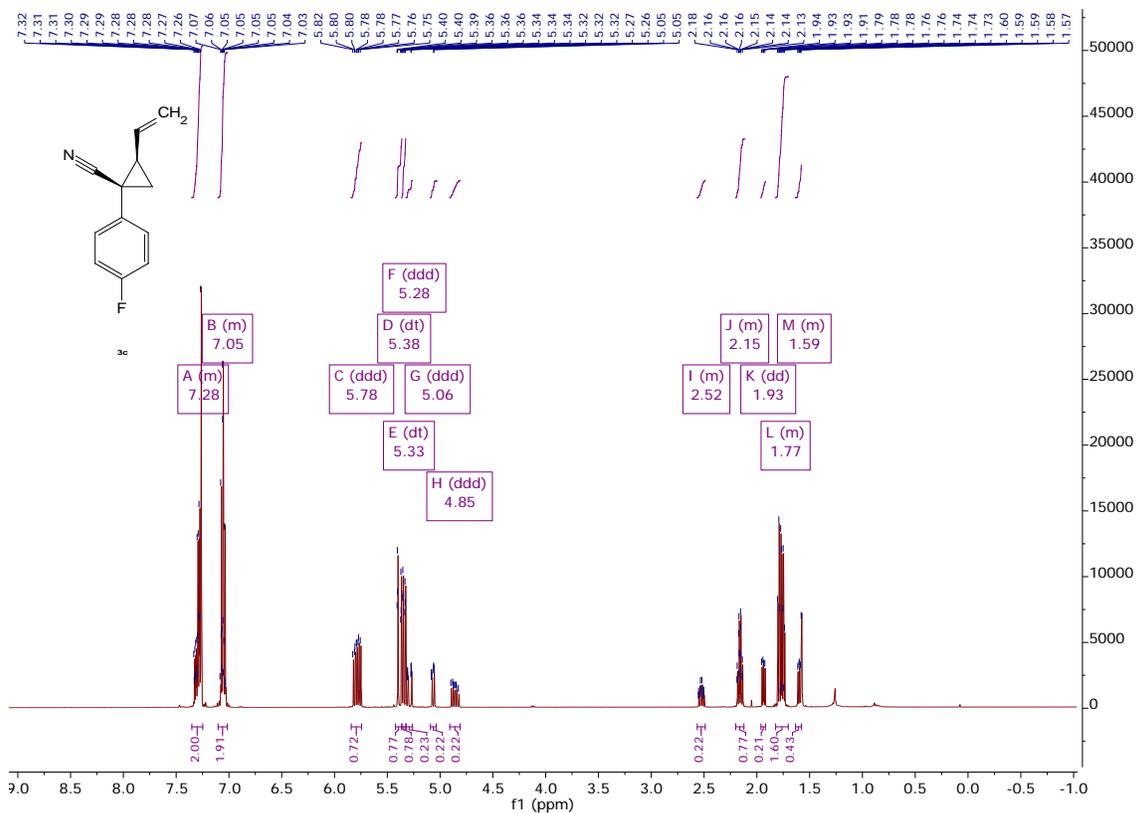
NMR Spectra



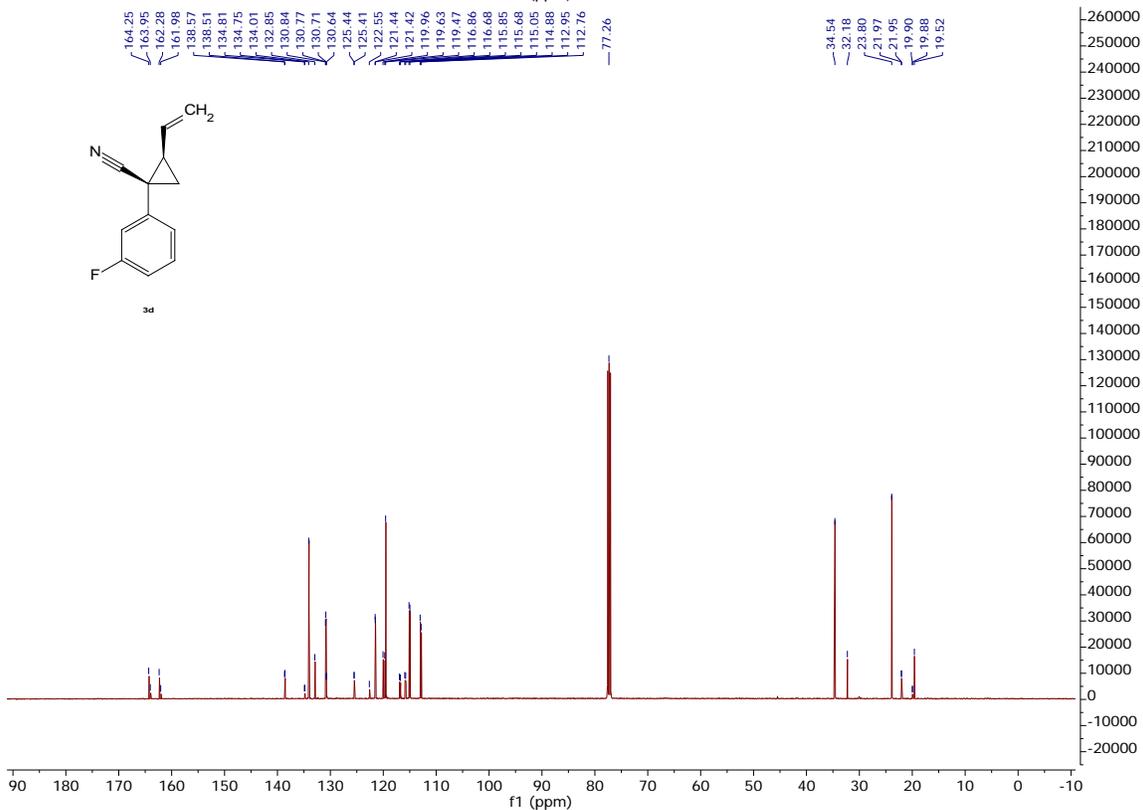
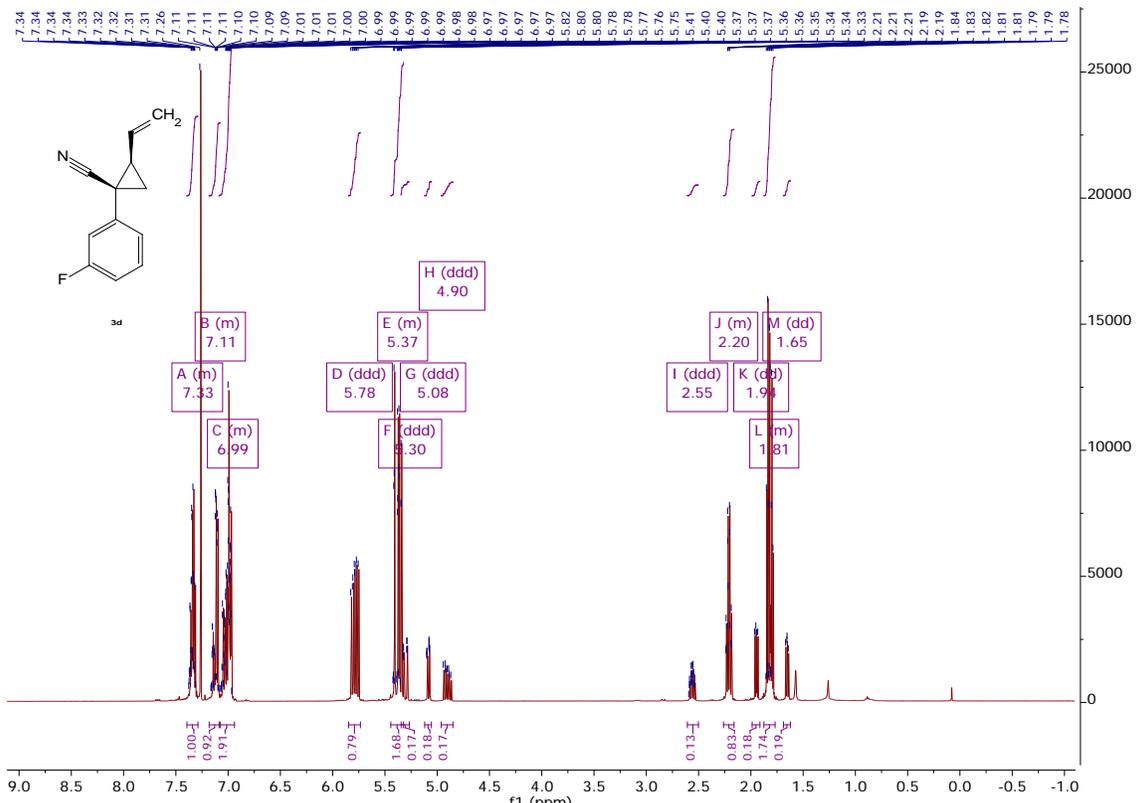
3a



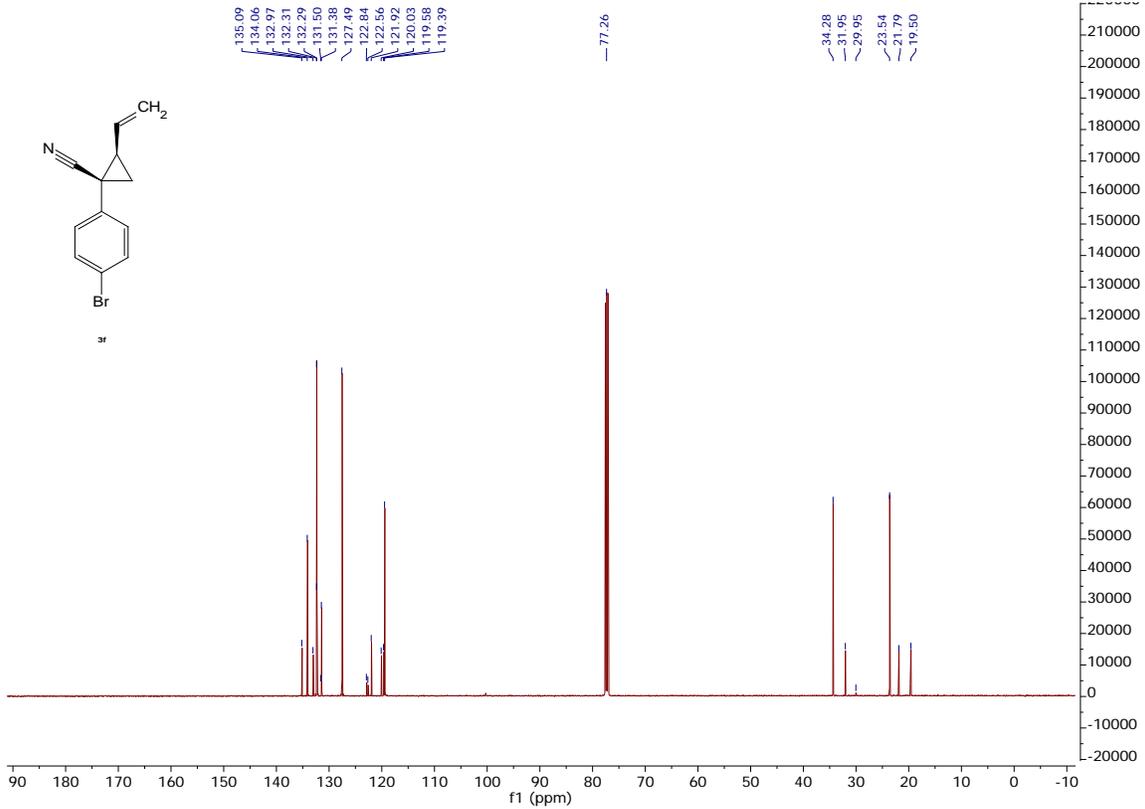
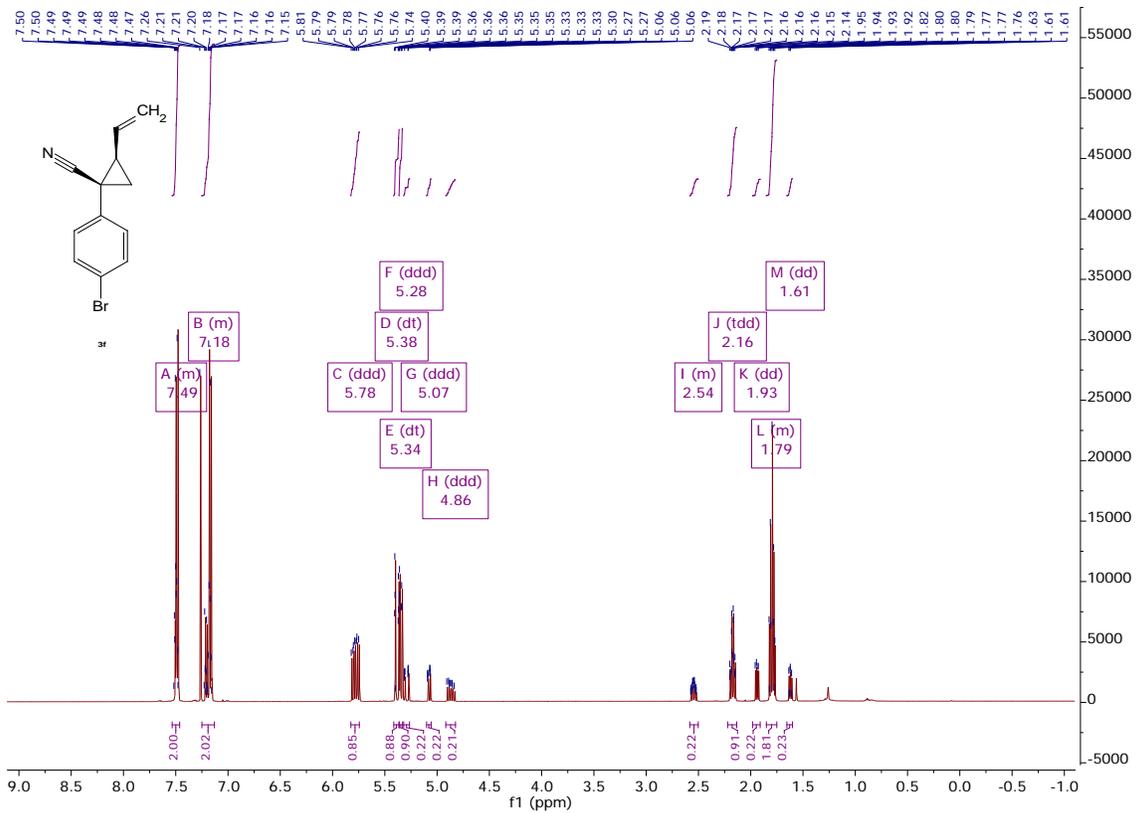
3b



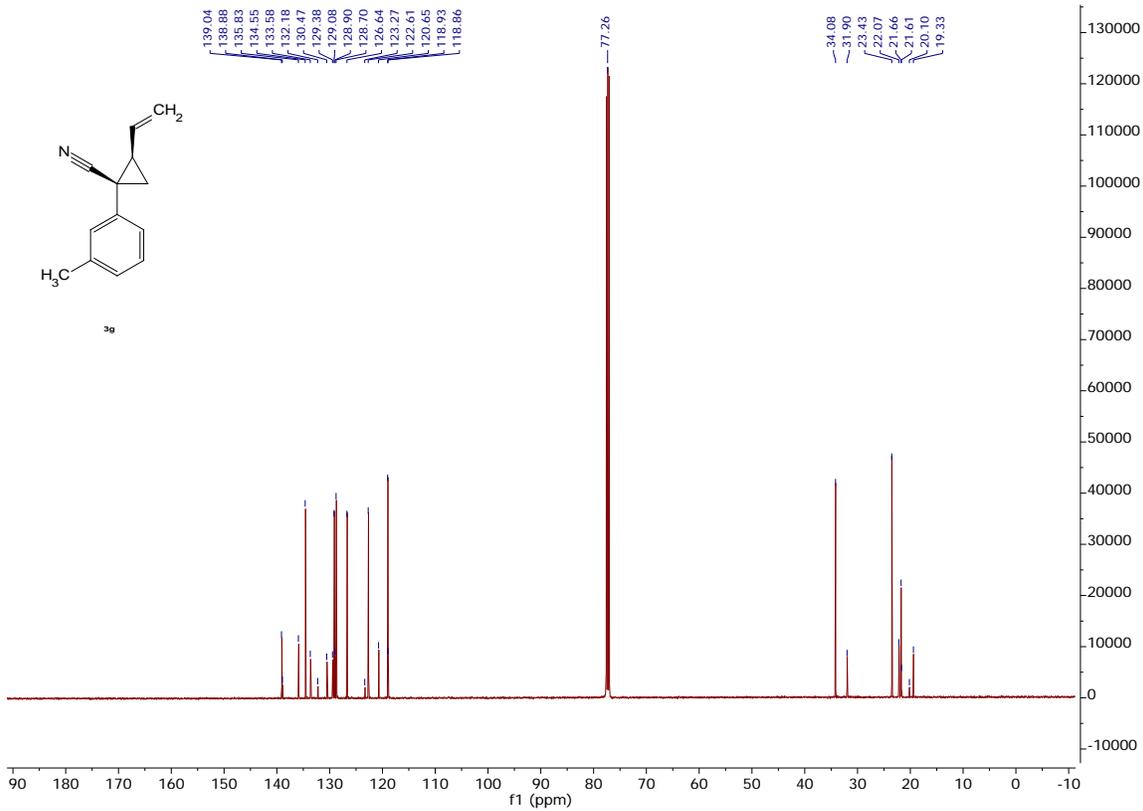
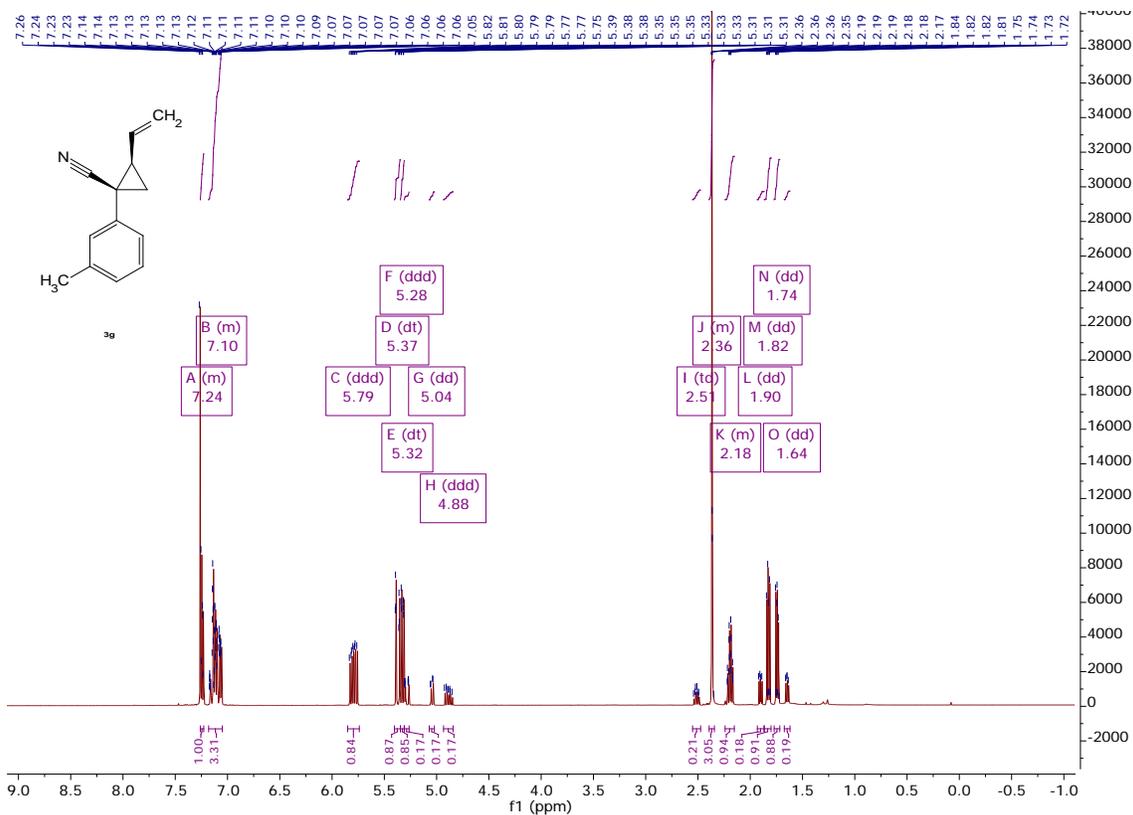
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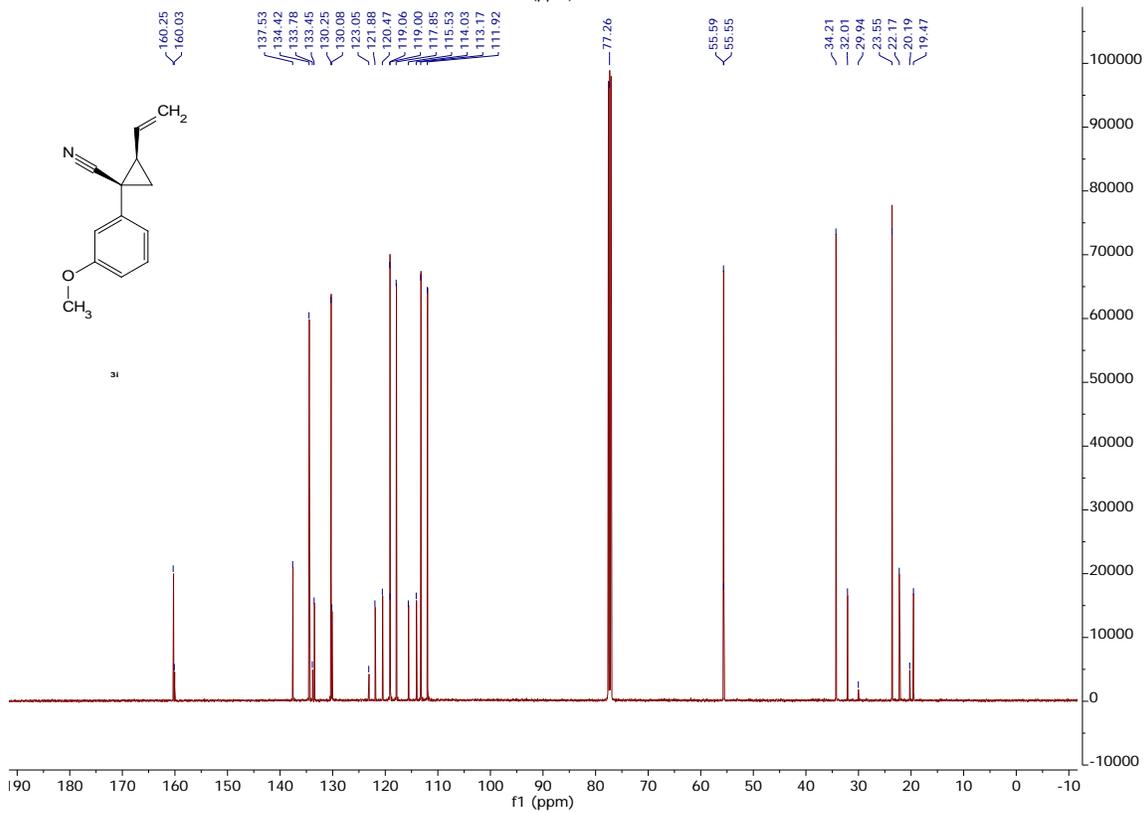
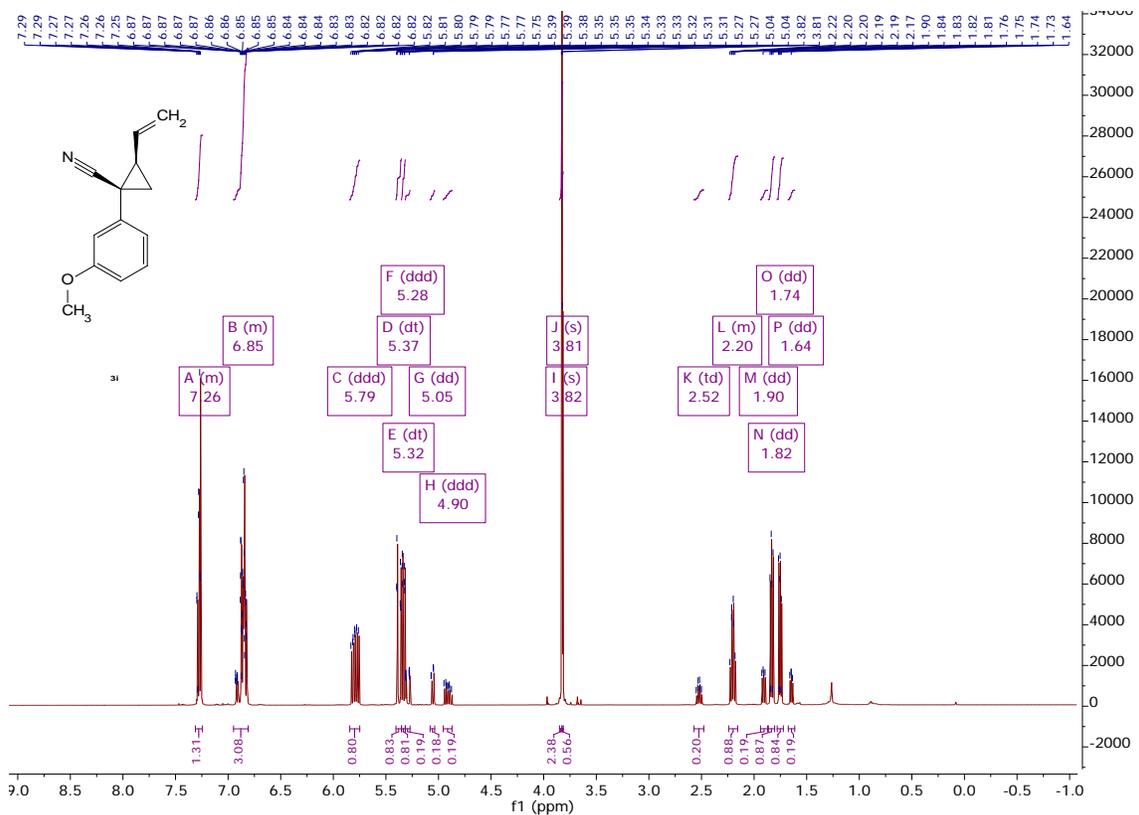
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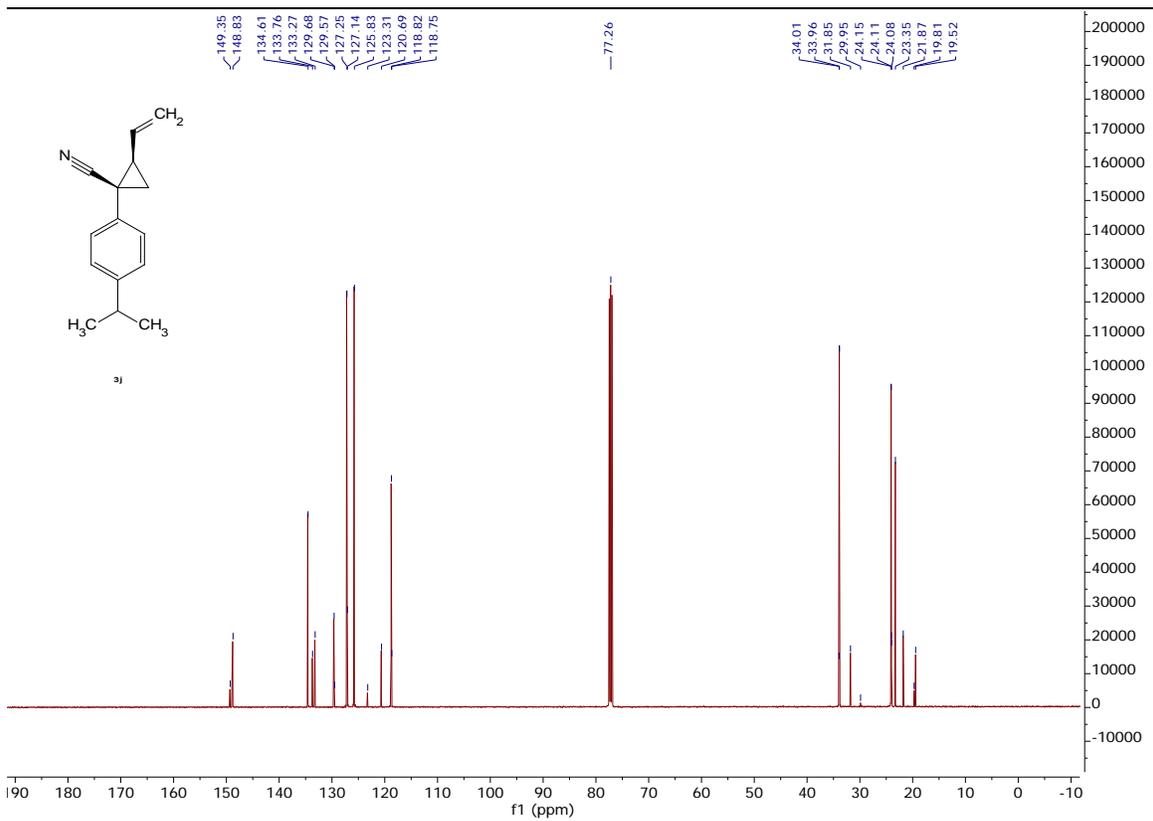
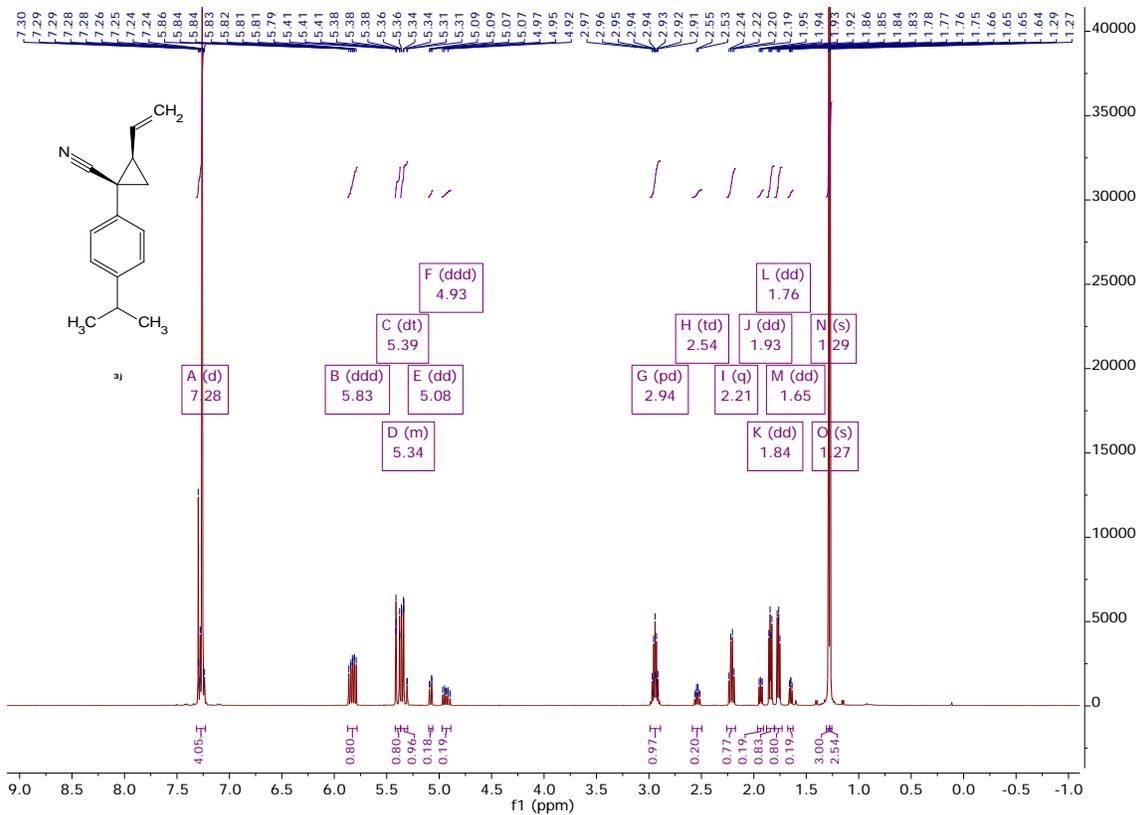
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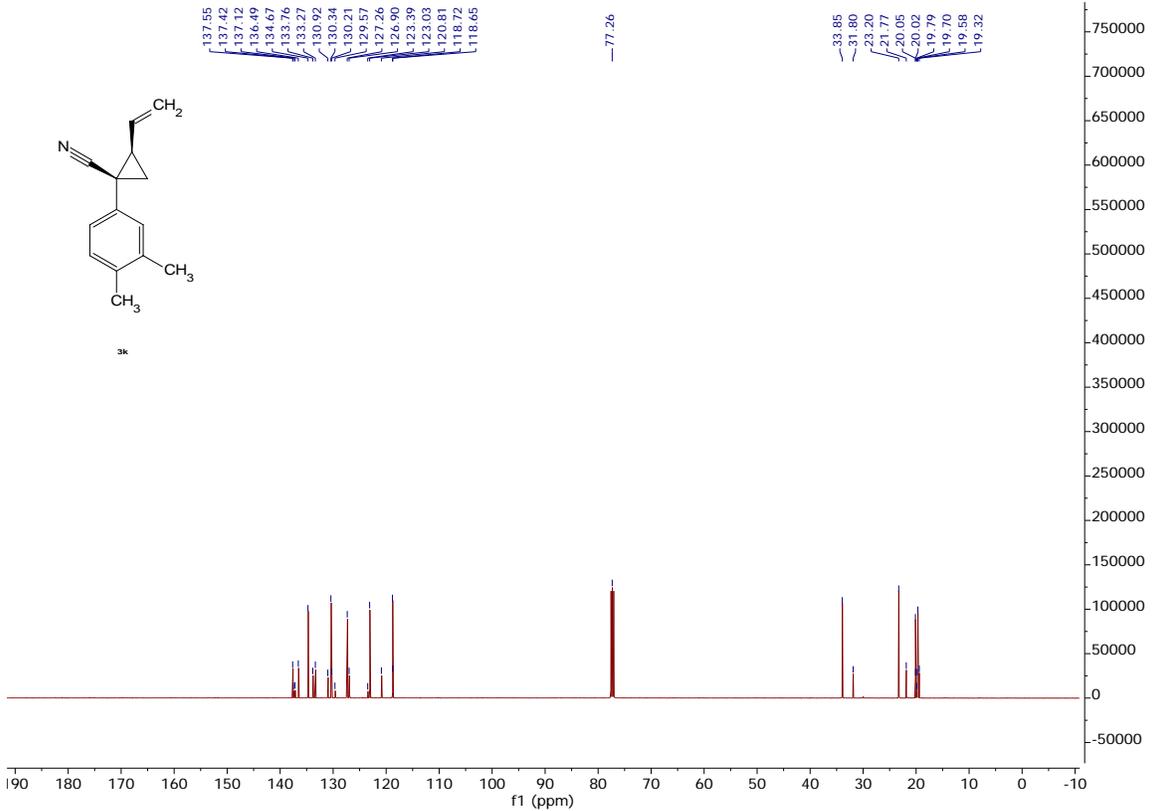
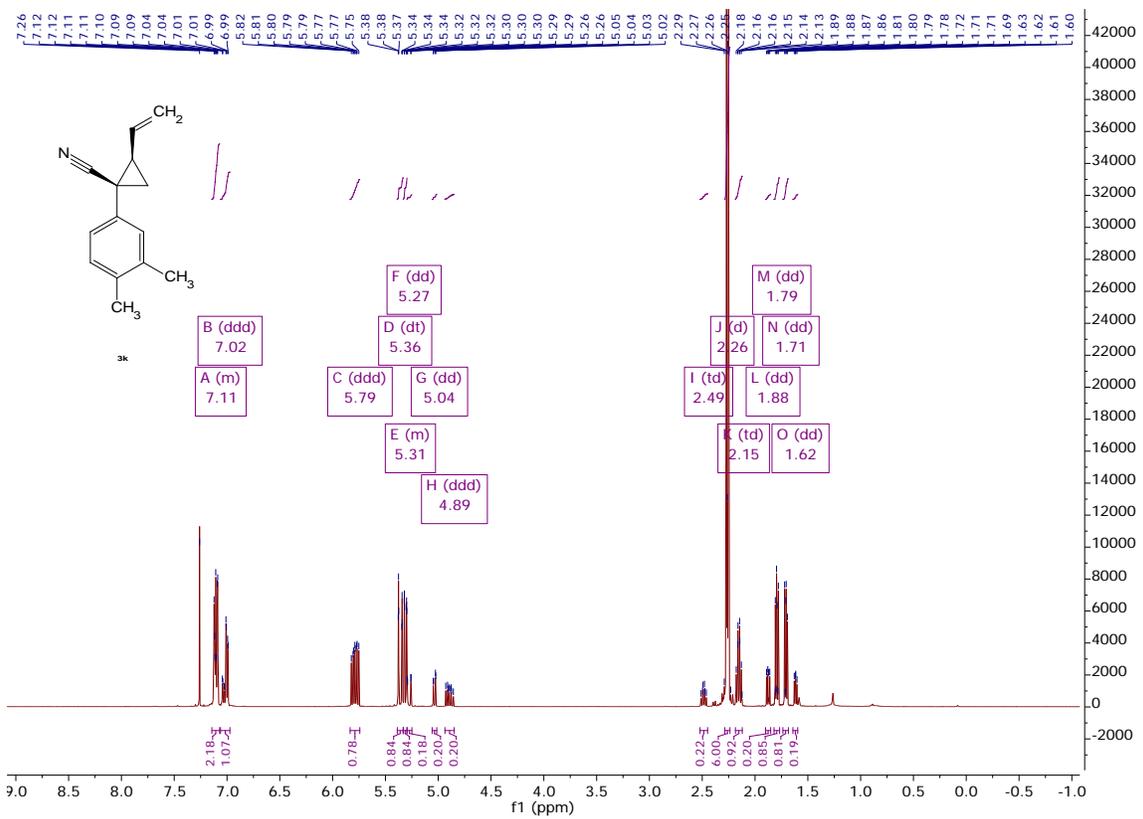


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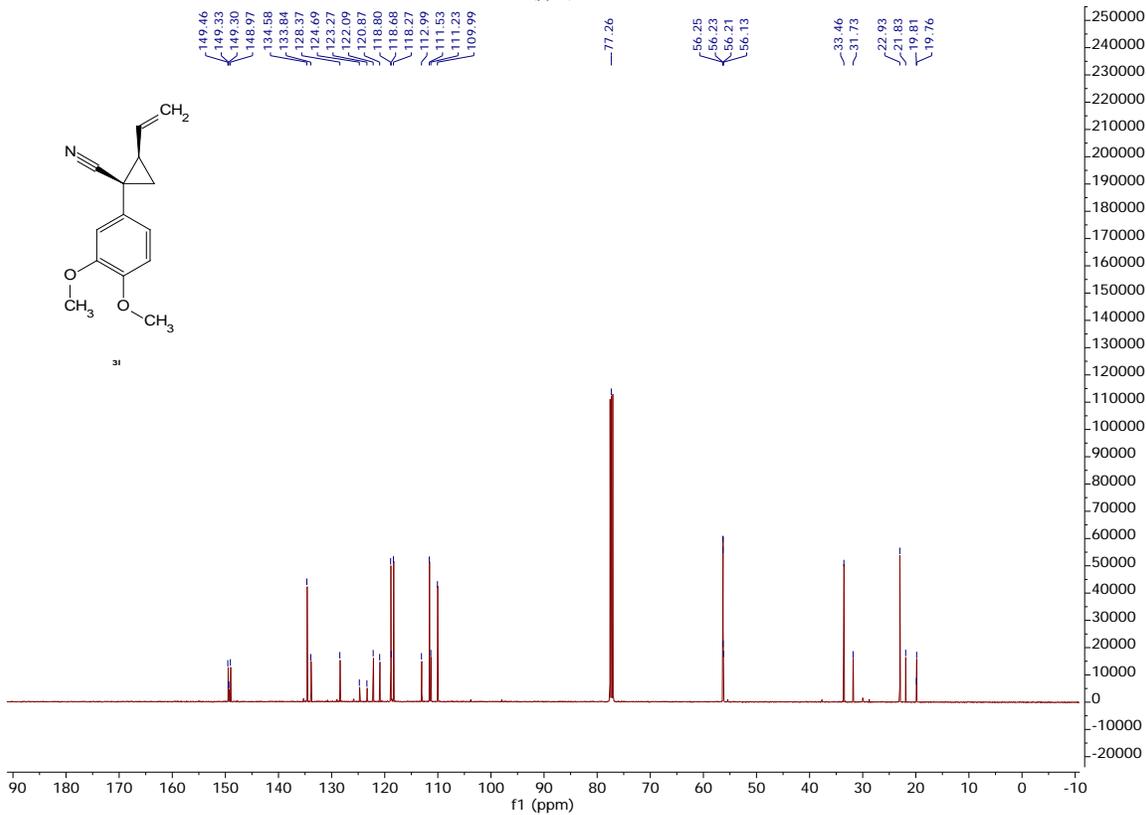
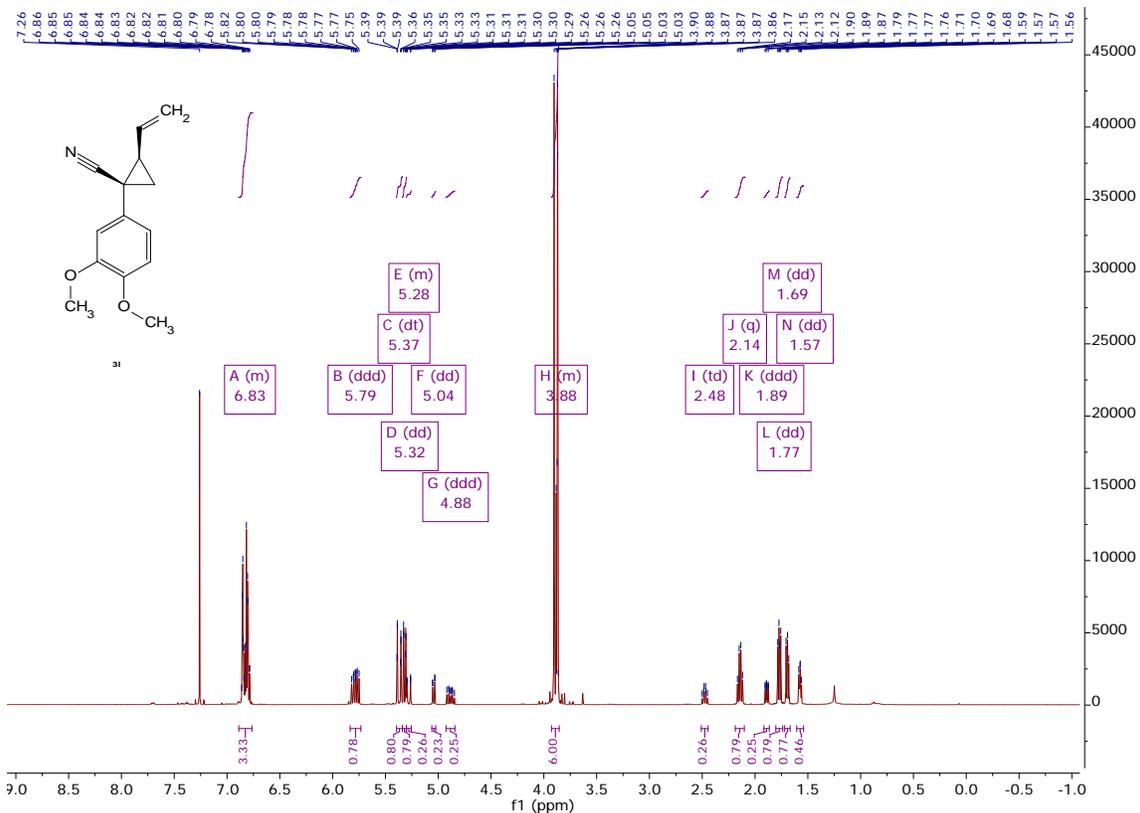


3i

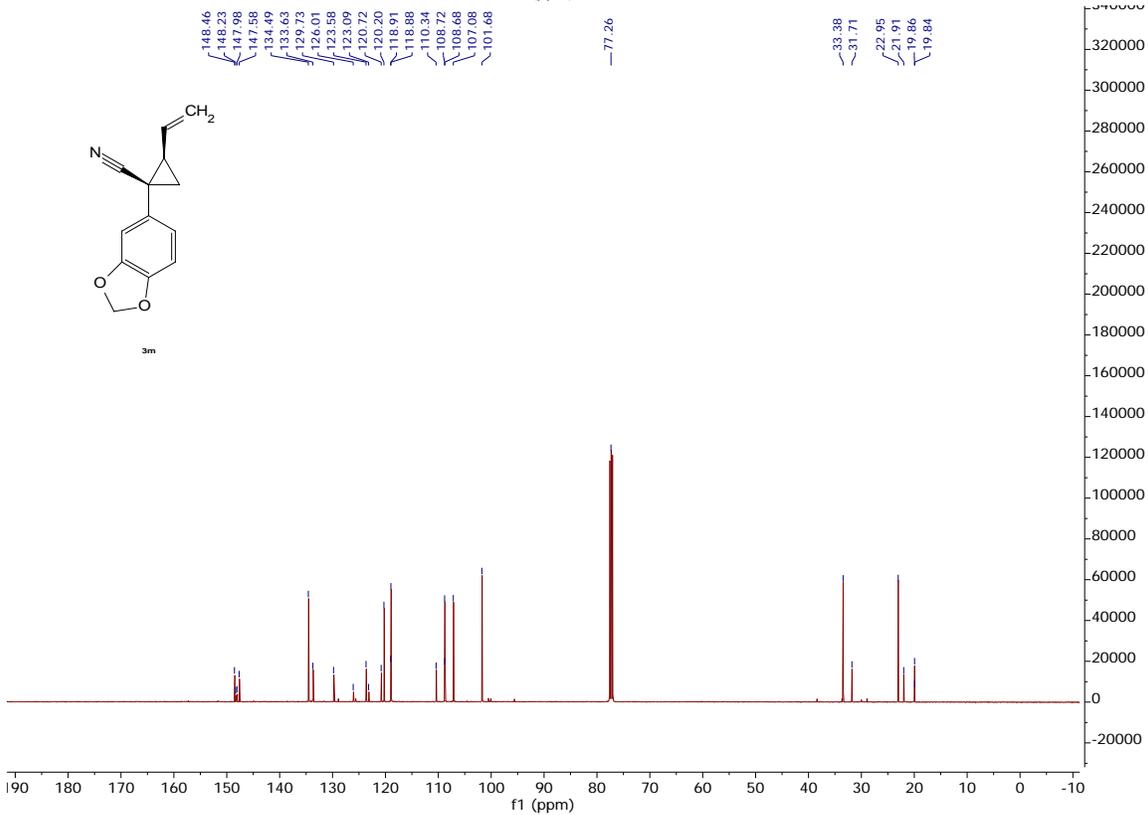
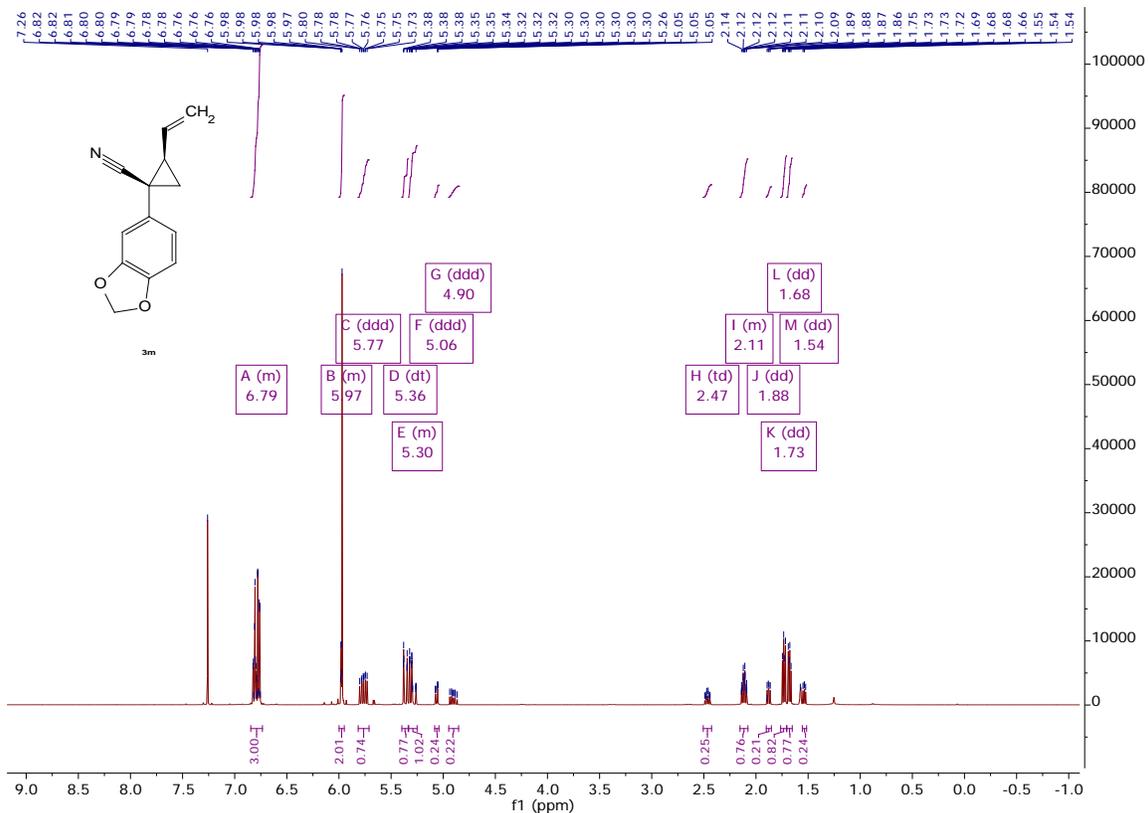


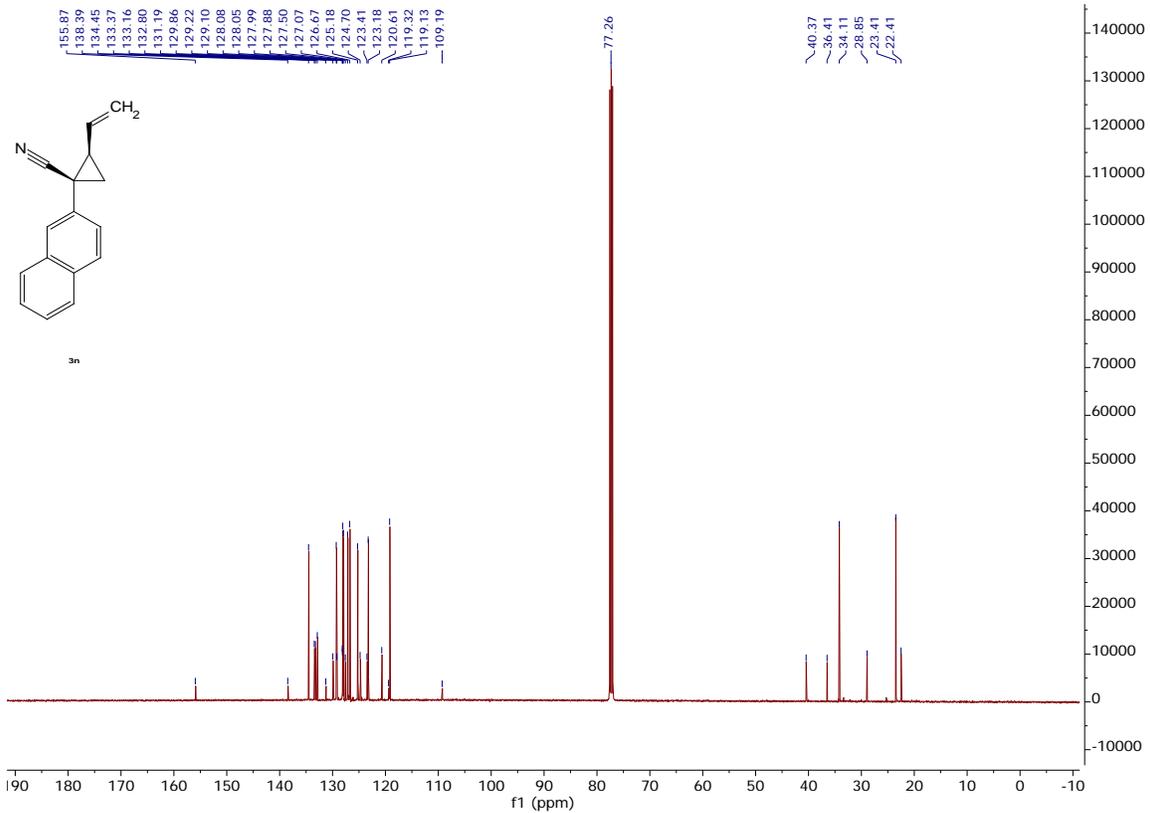
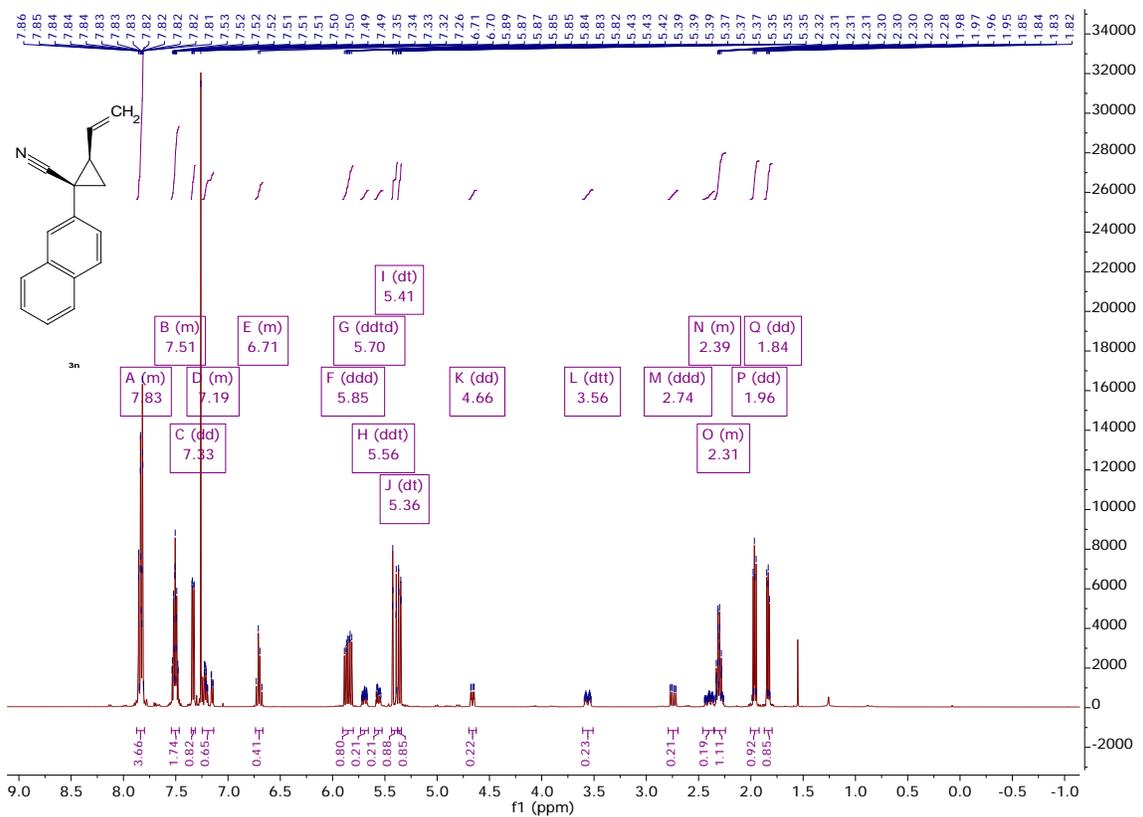


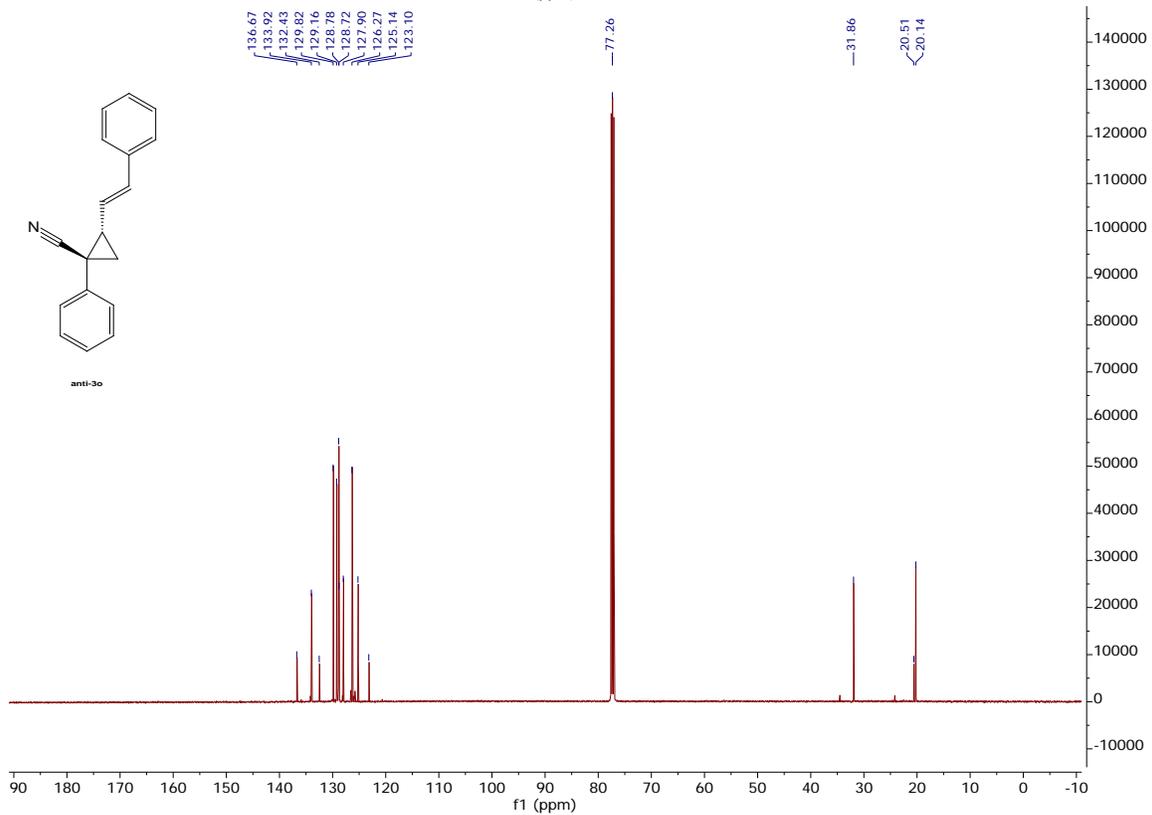
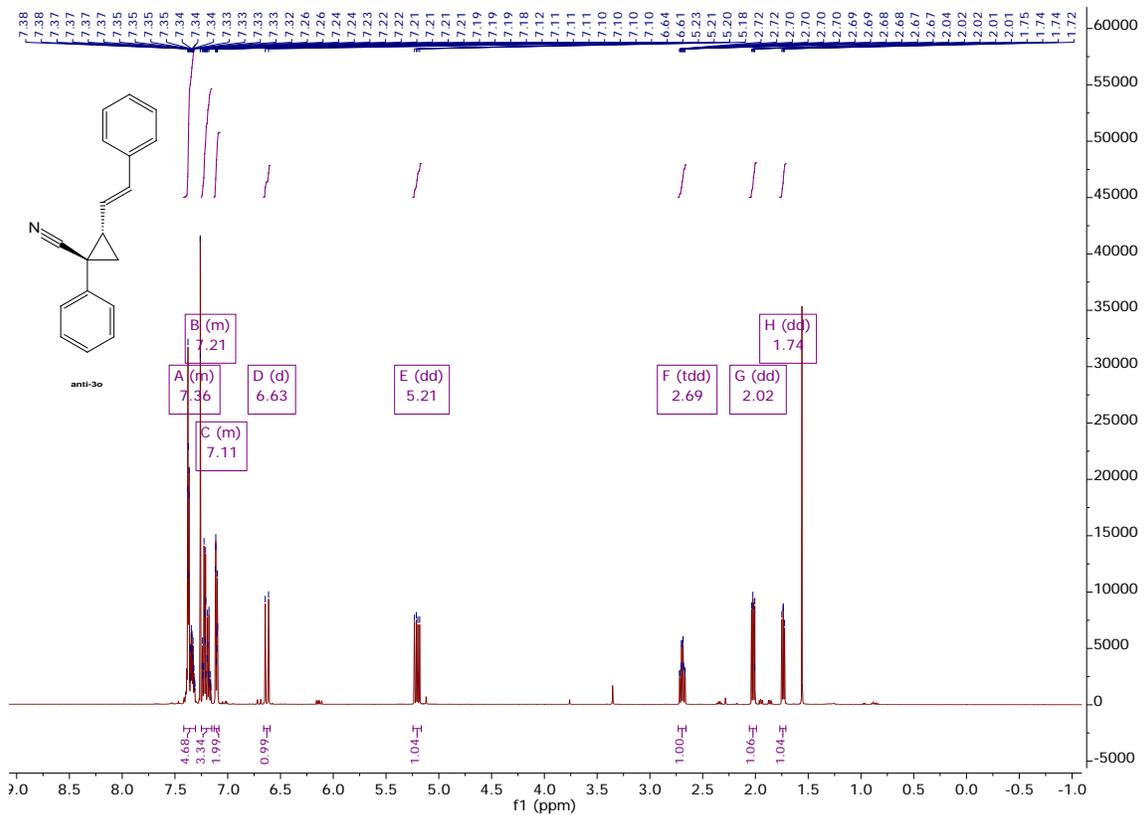
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31

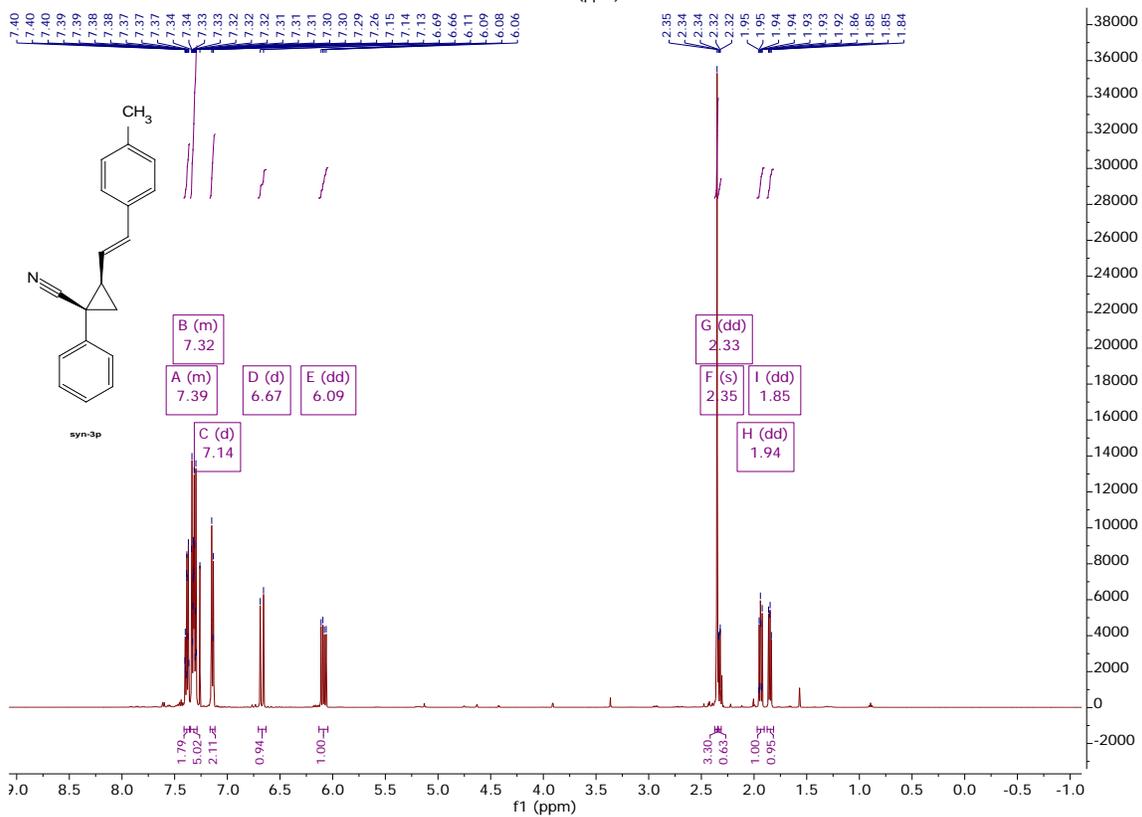
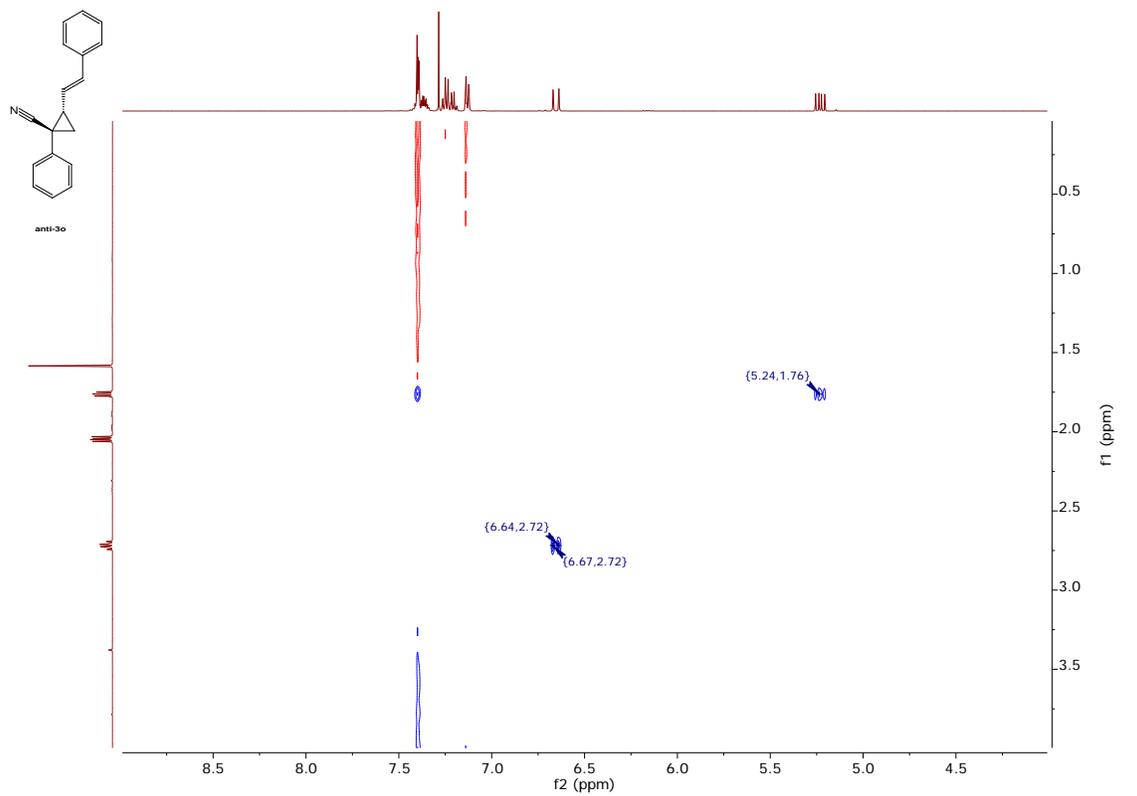


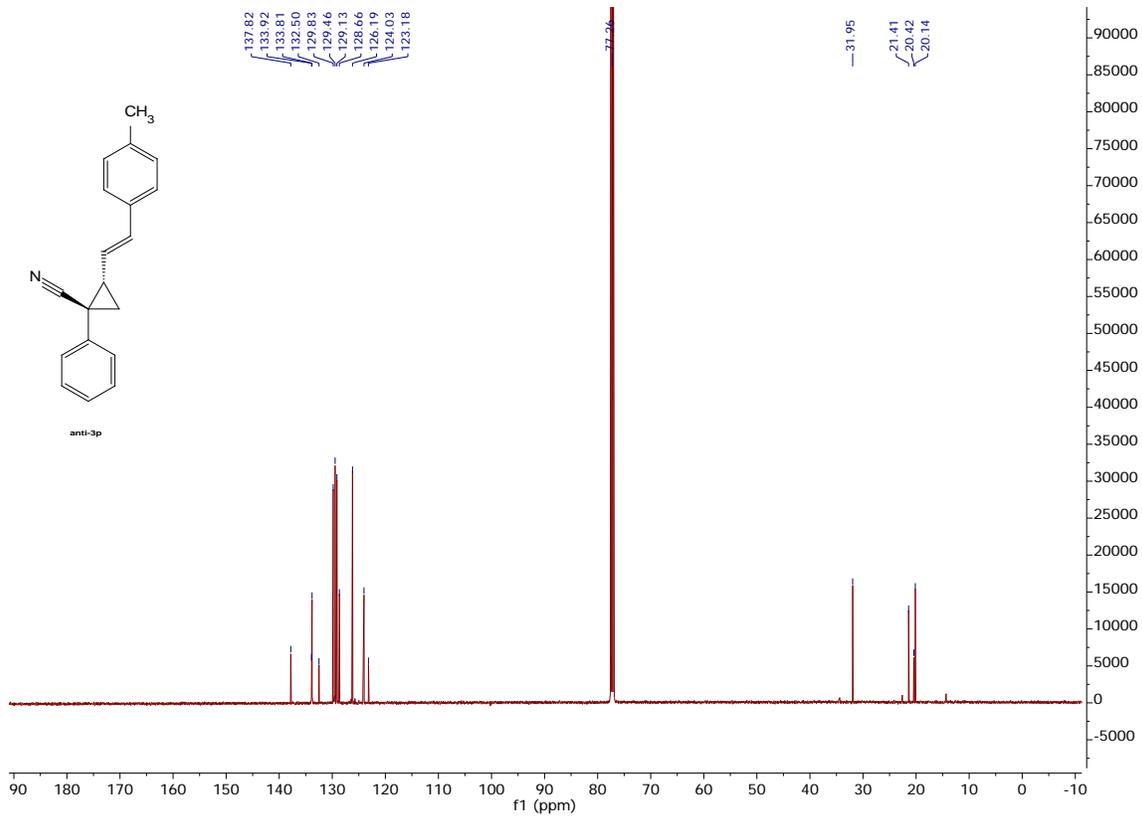


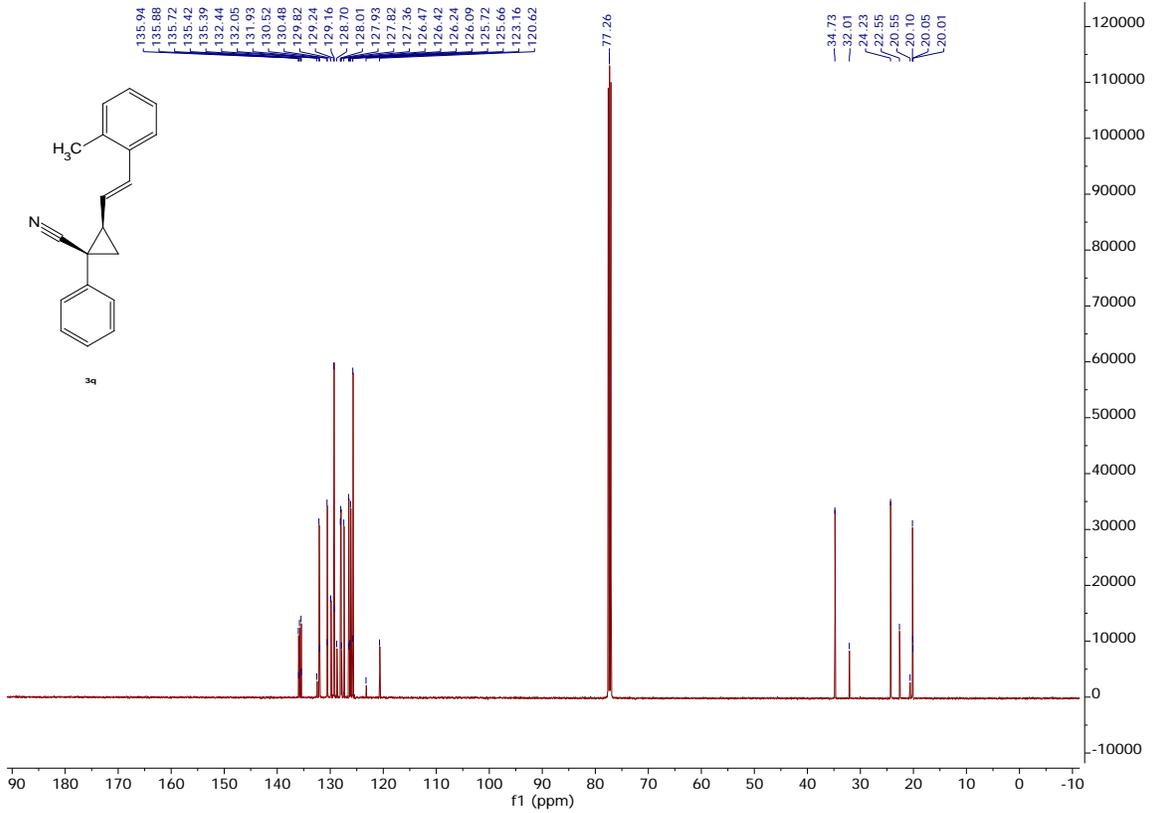
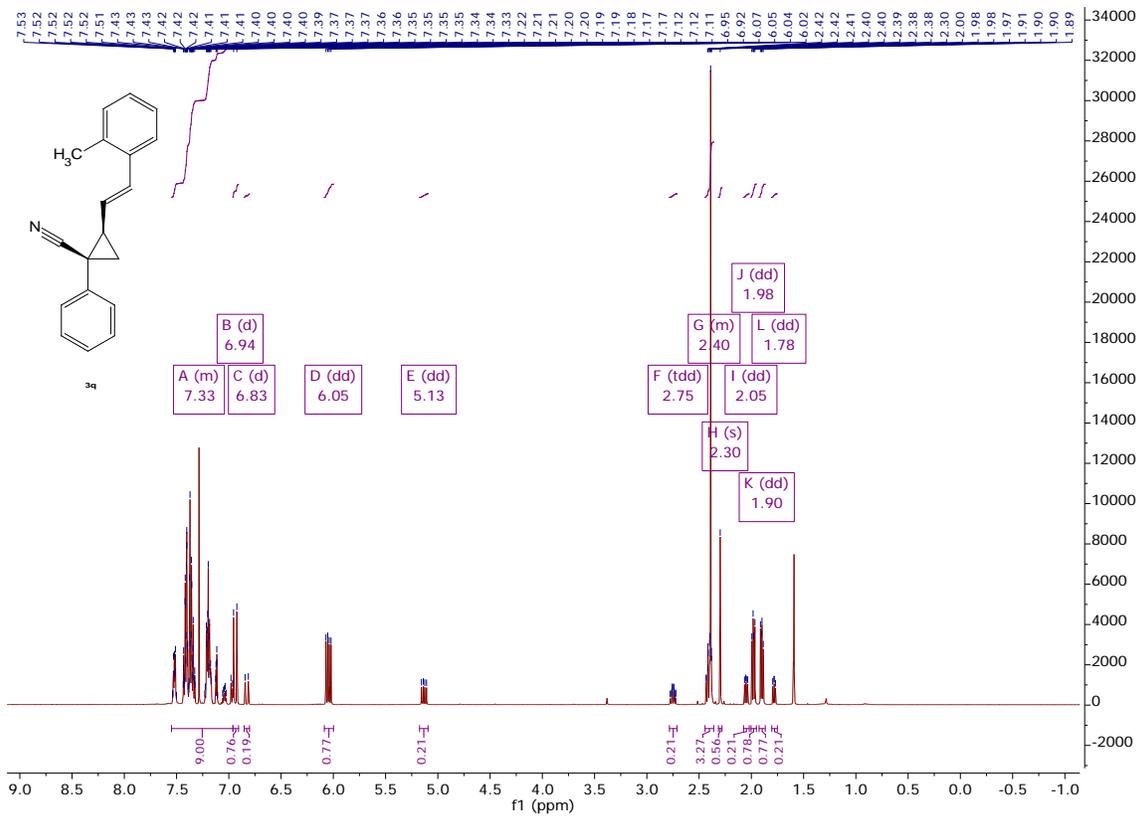


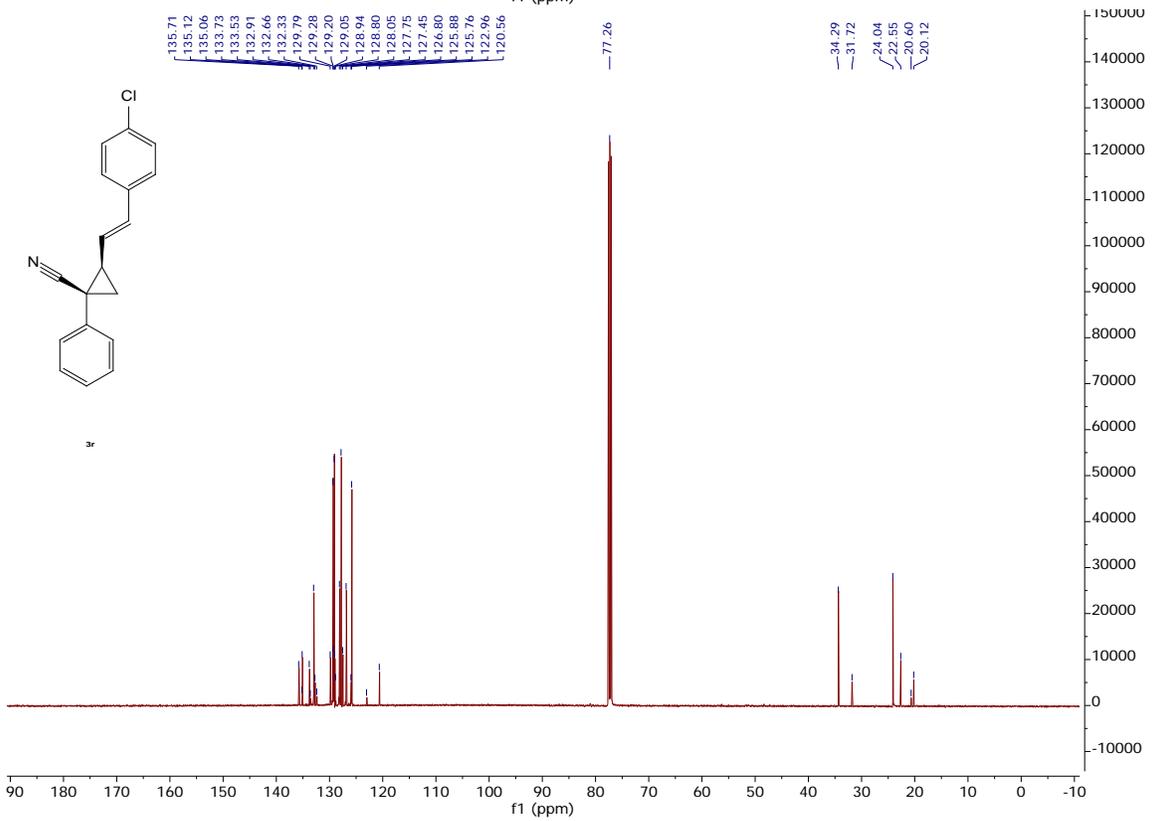
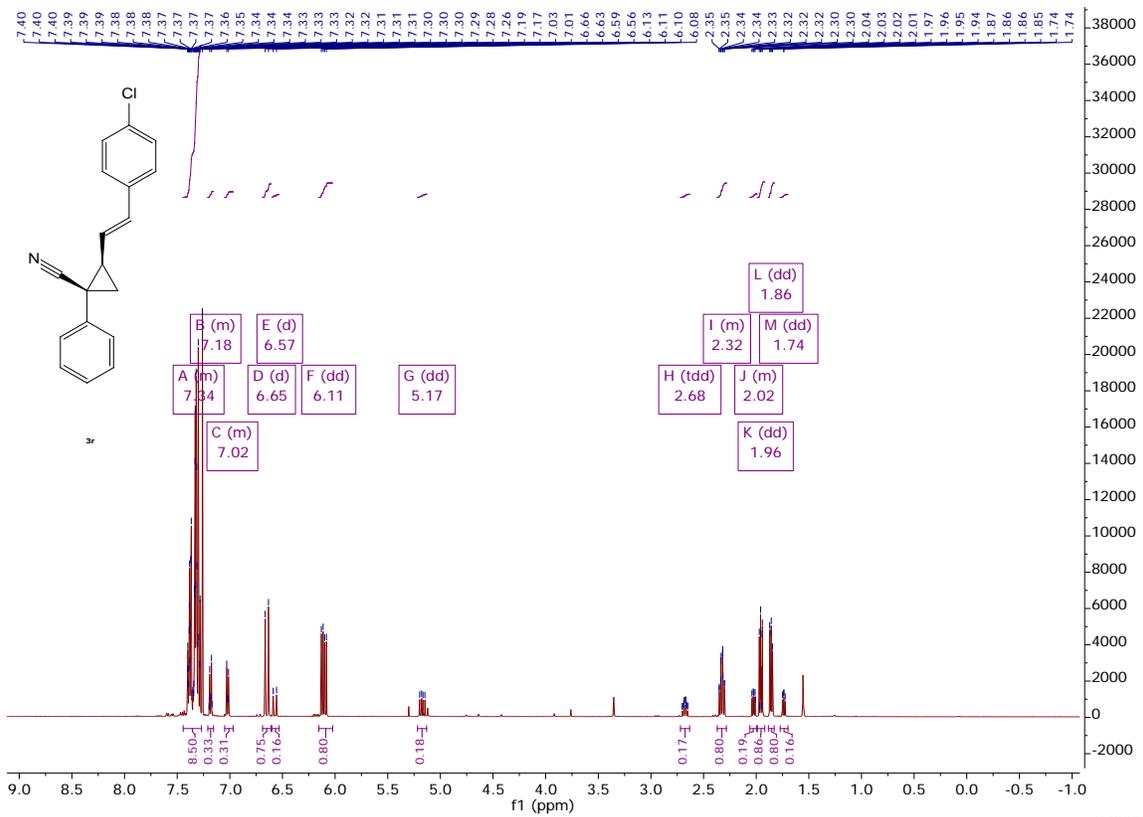
3o

NOESY 3o

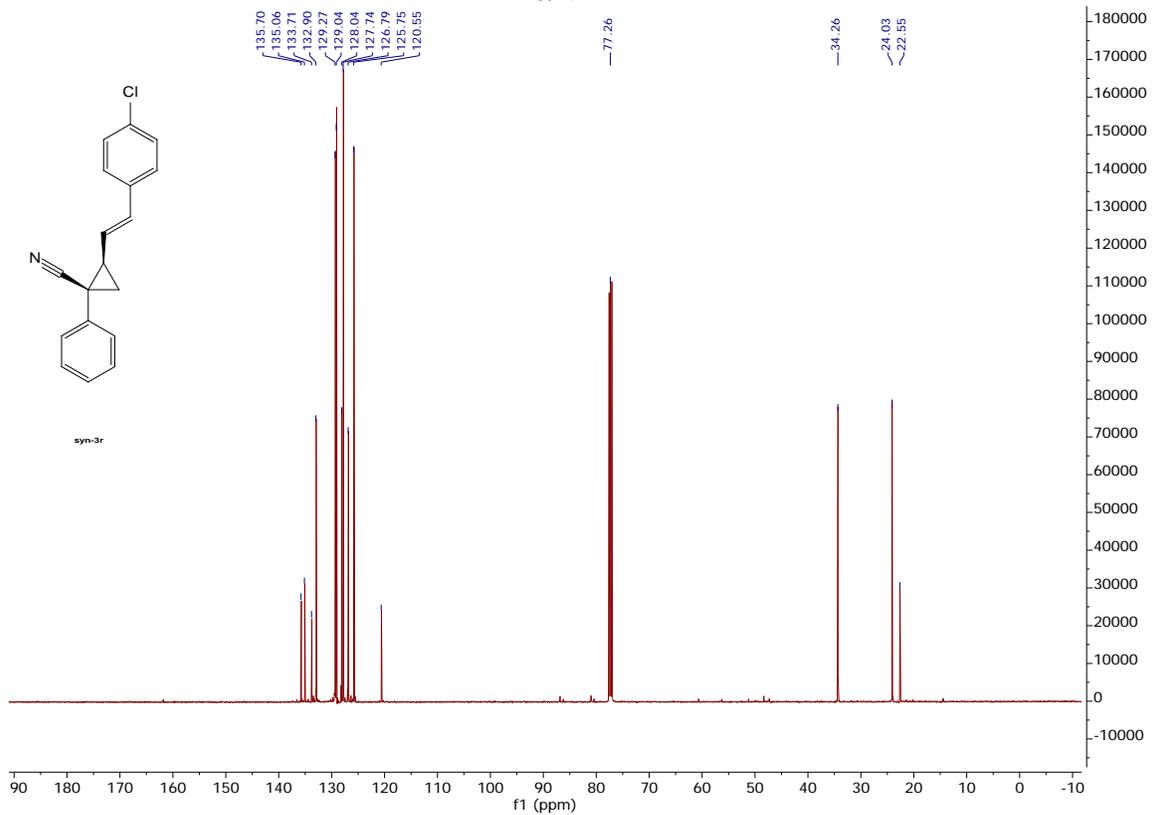
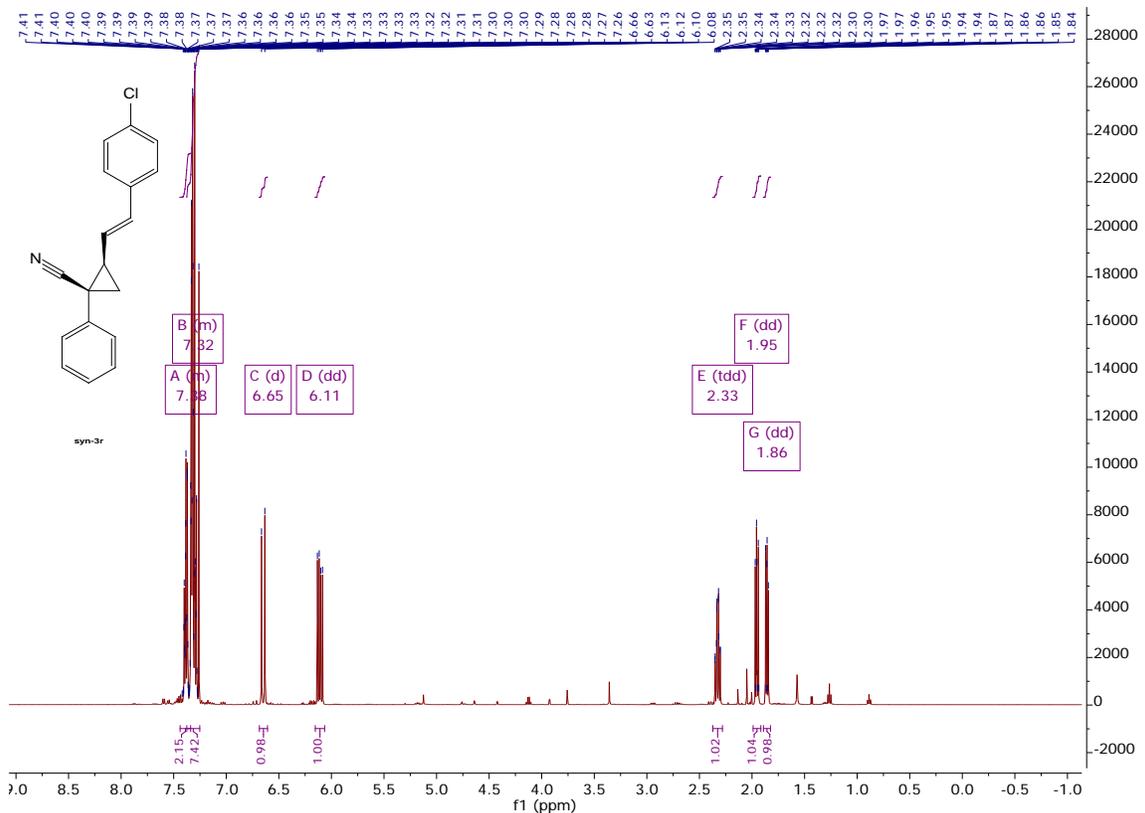


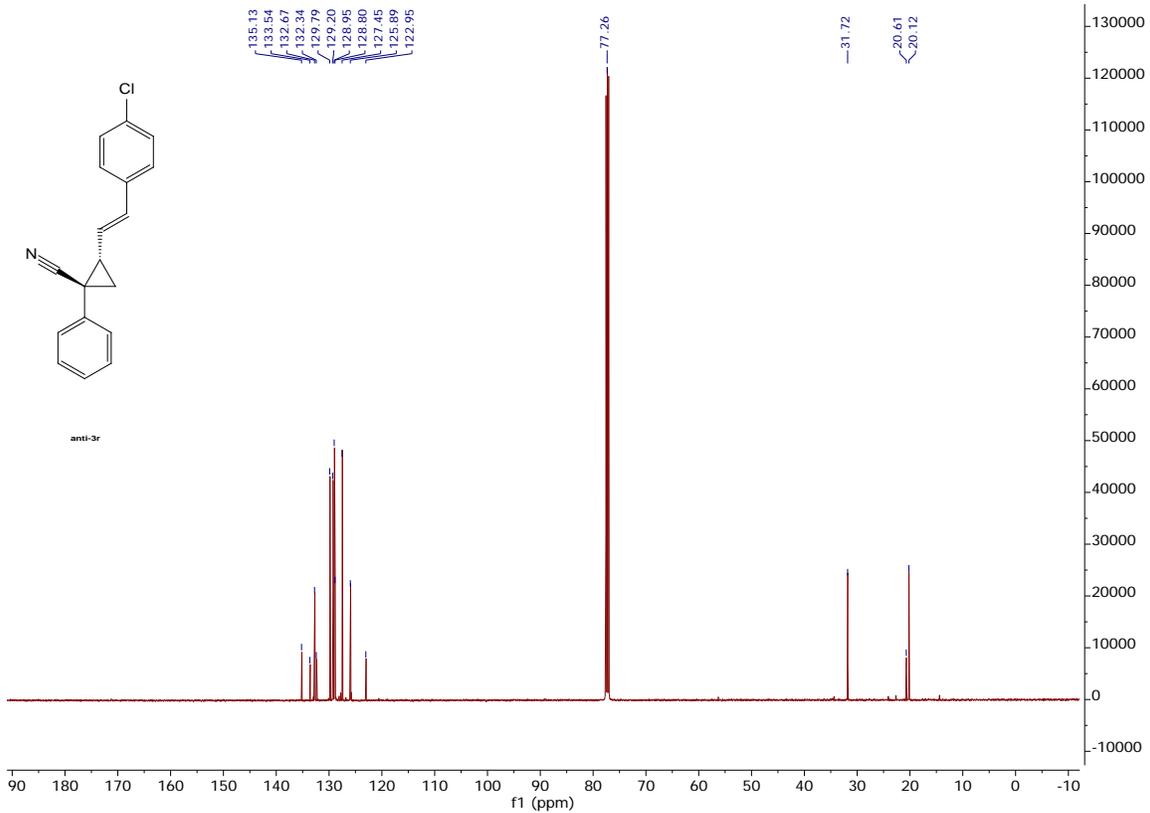
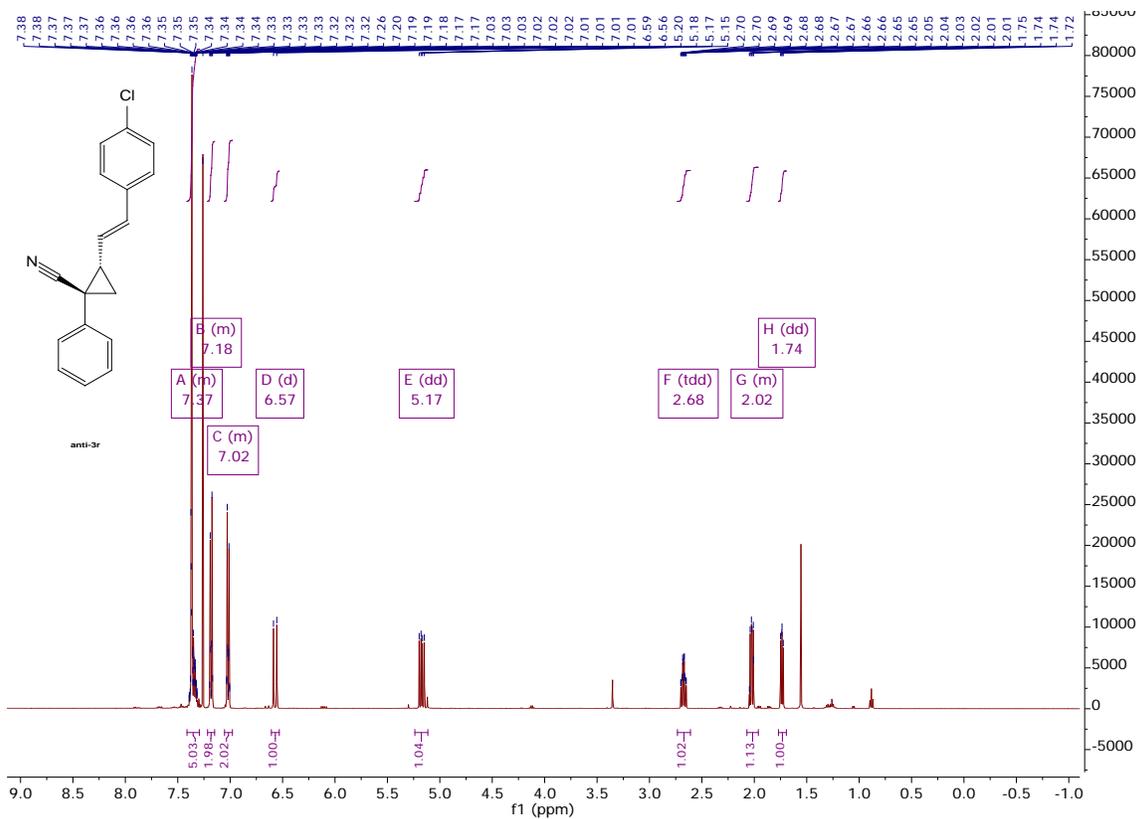


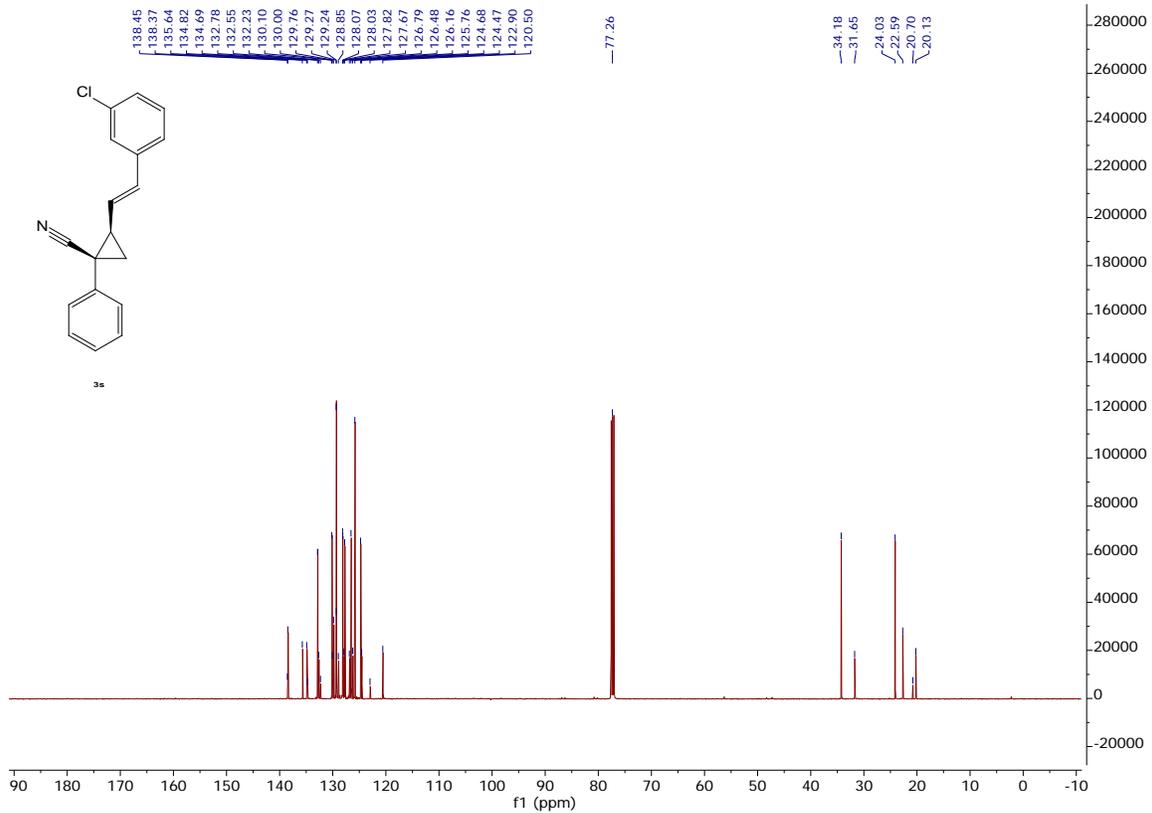
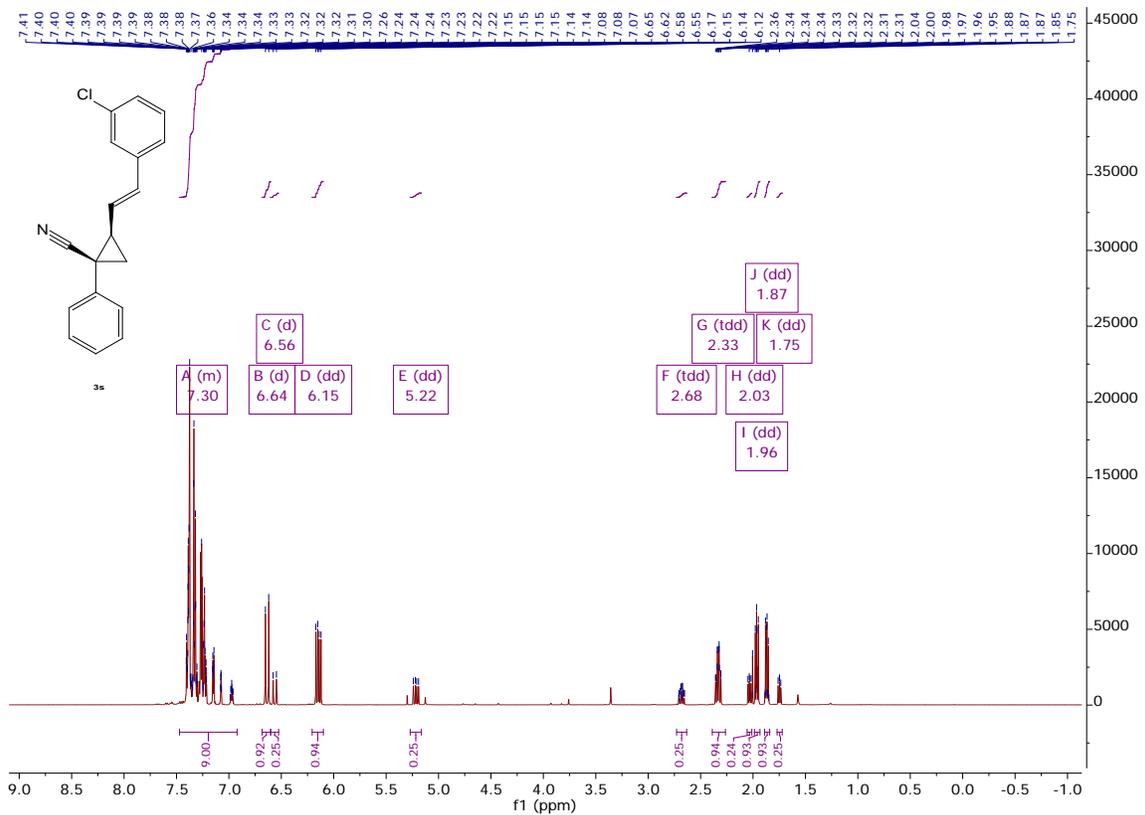




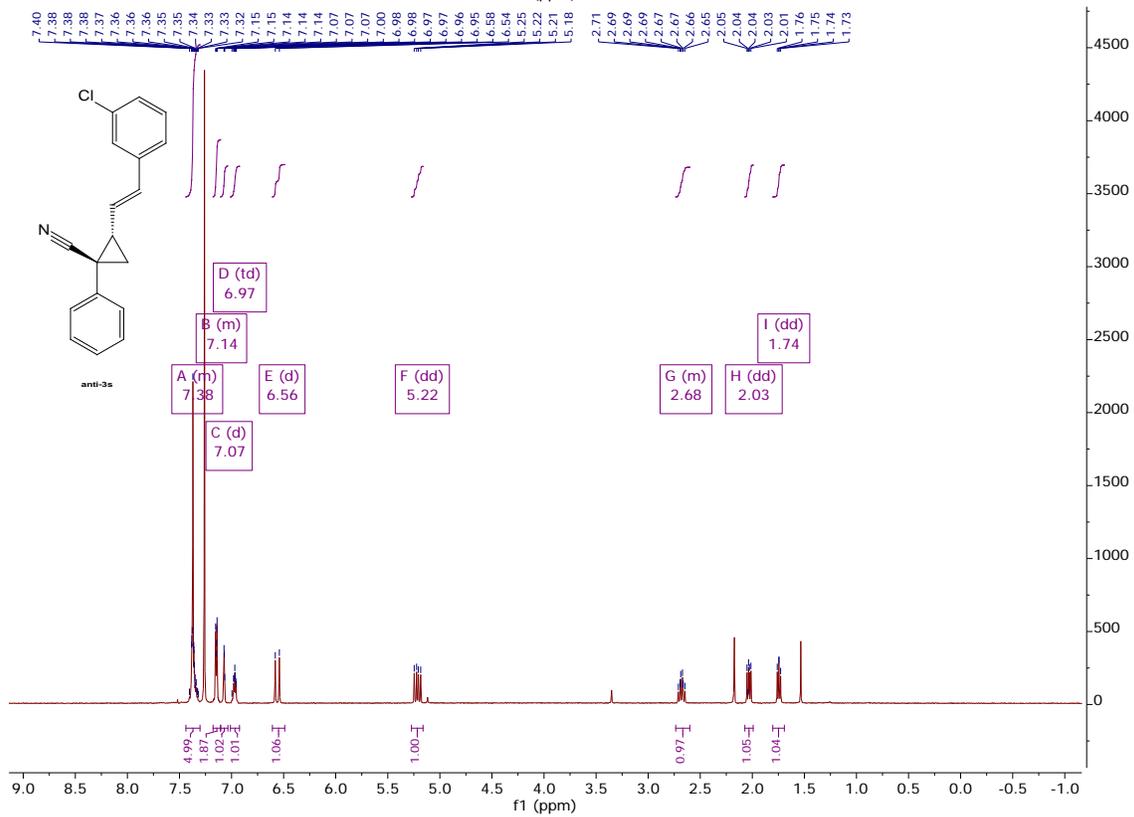
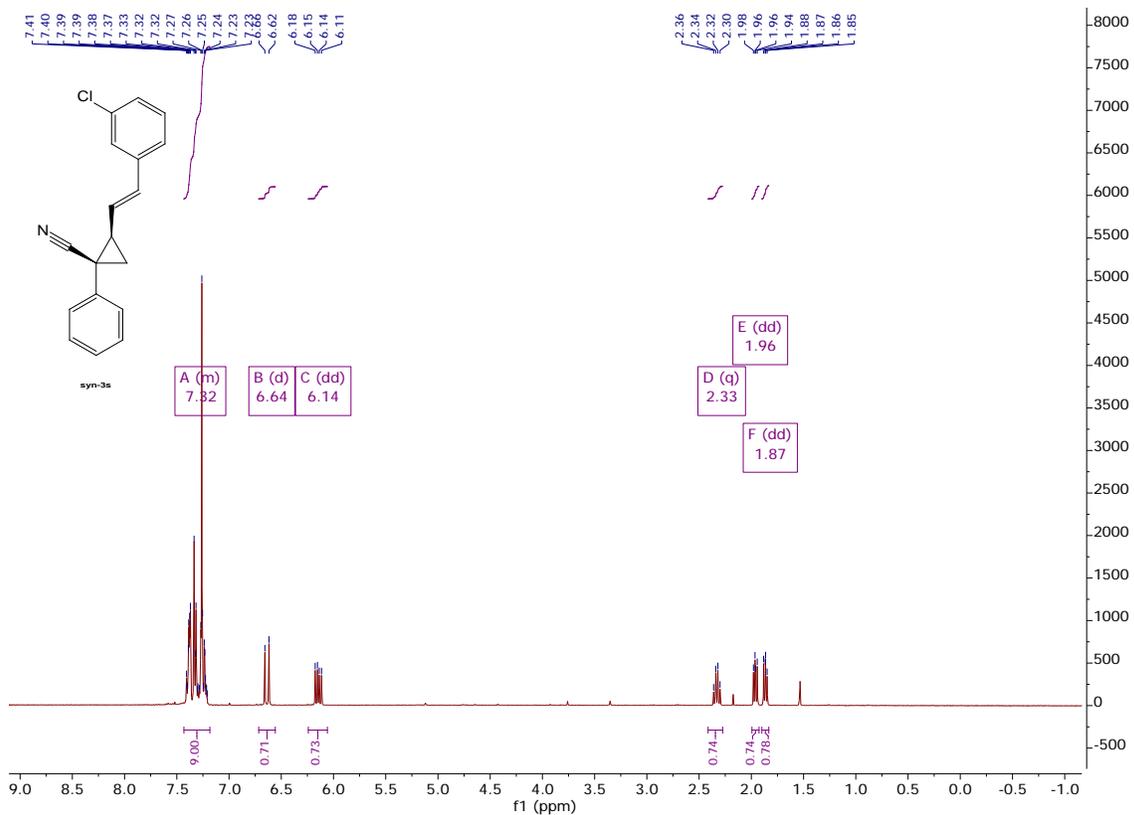
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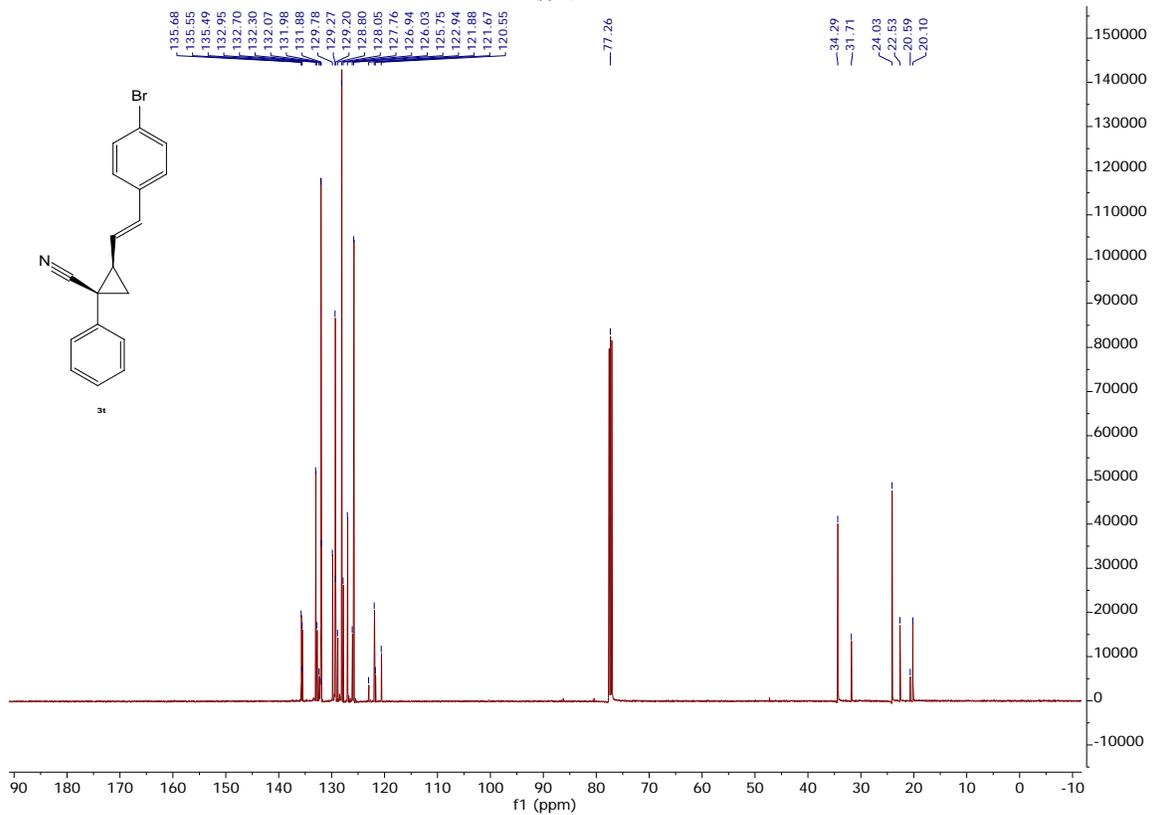
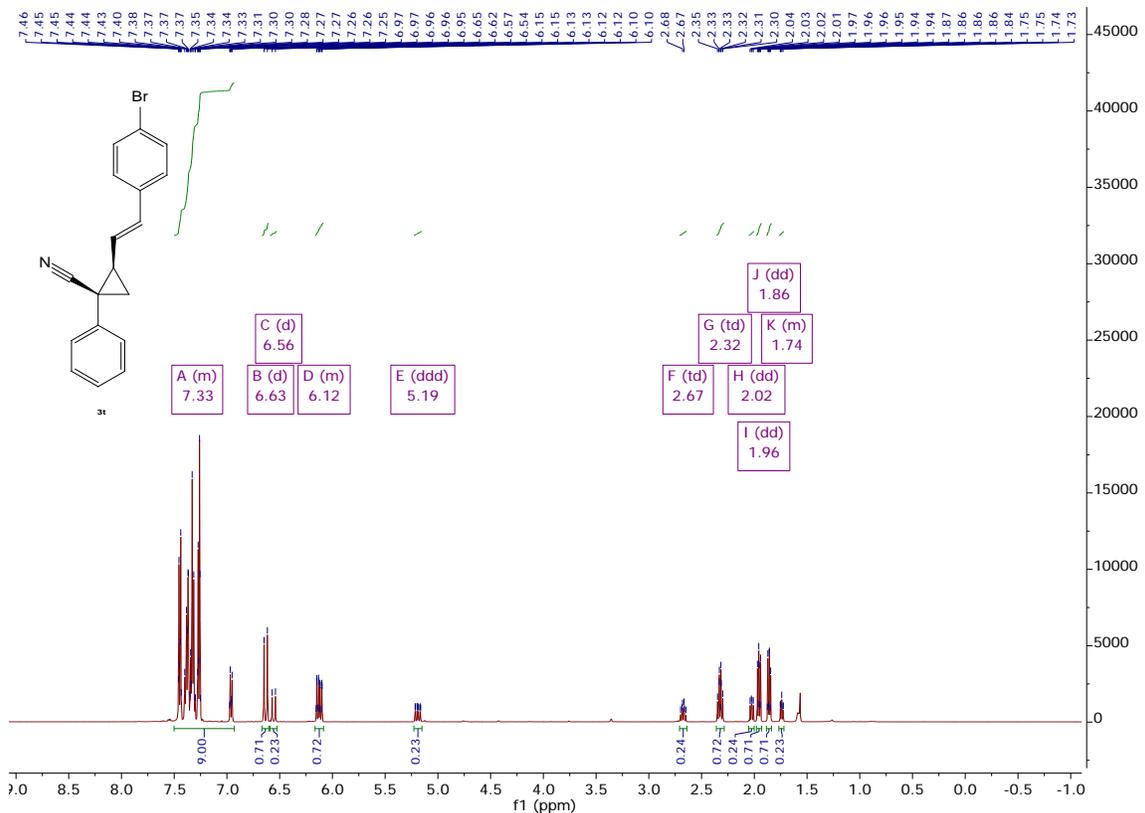


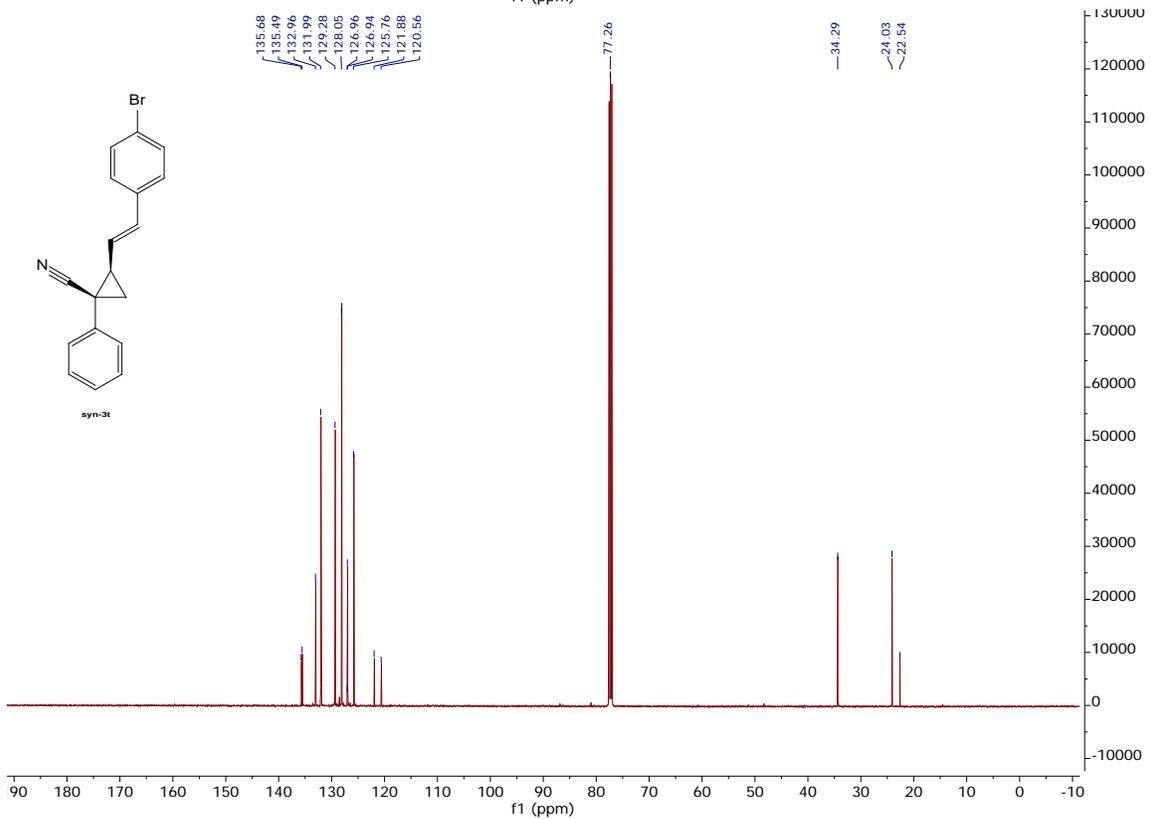
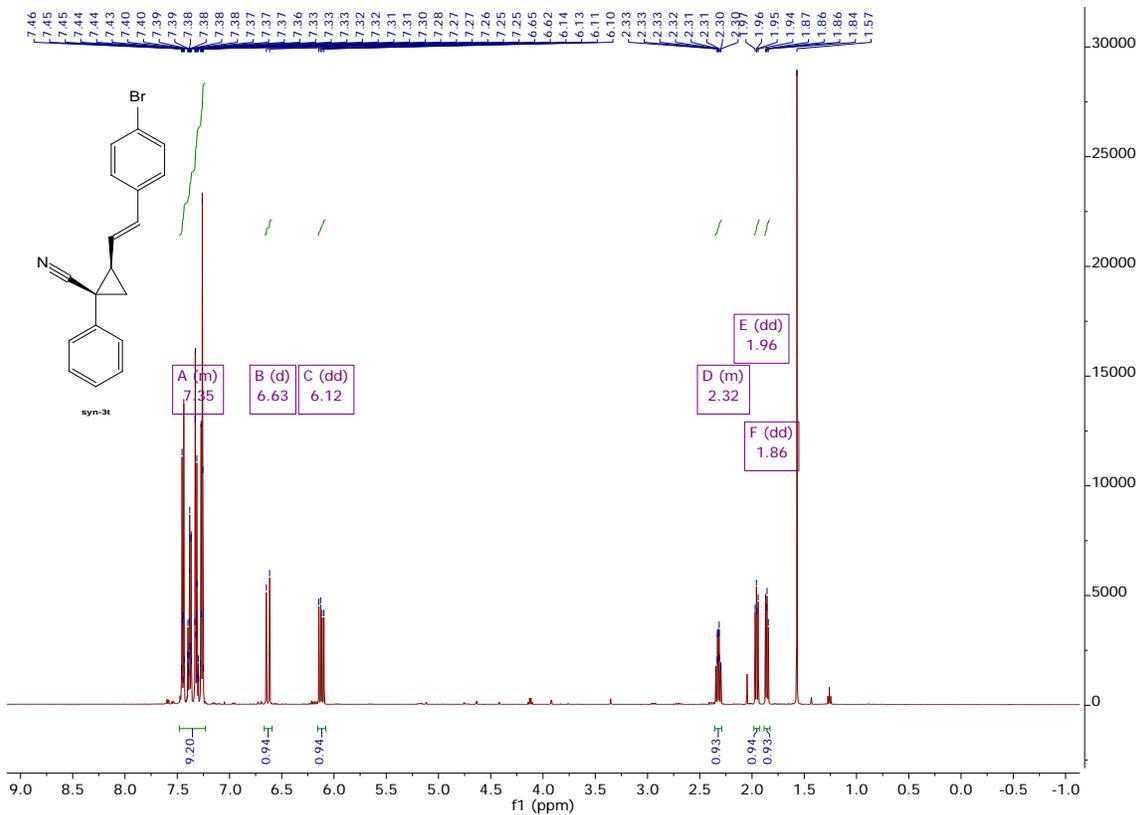


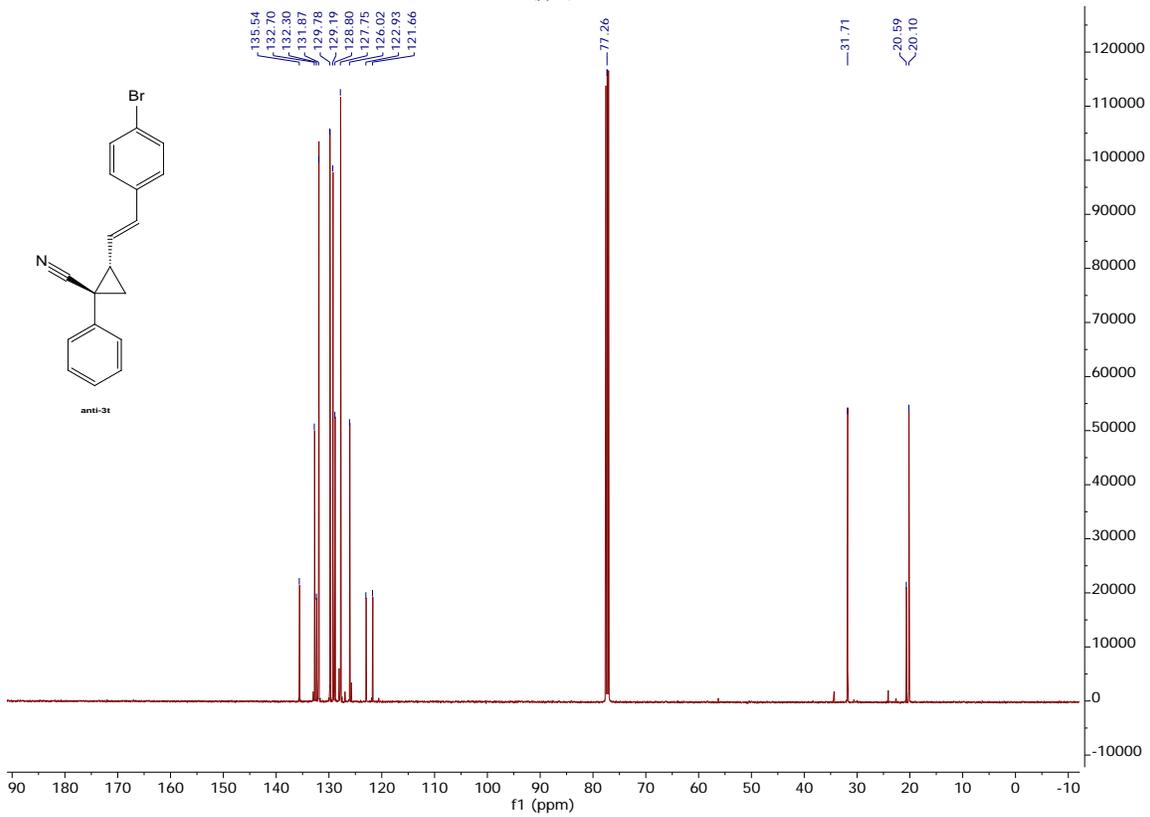
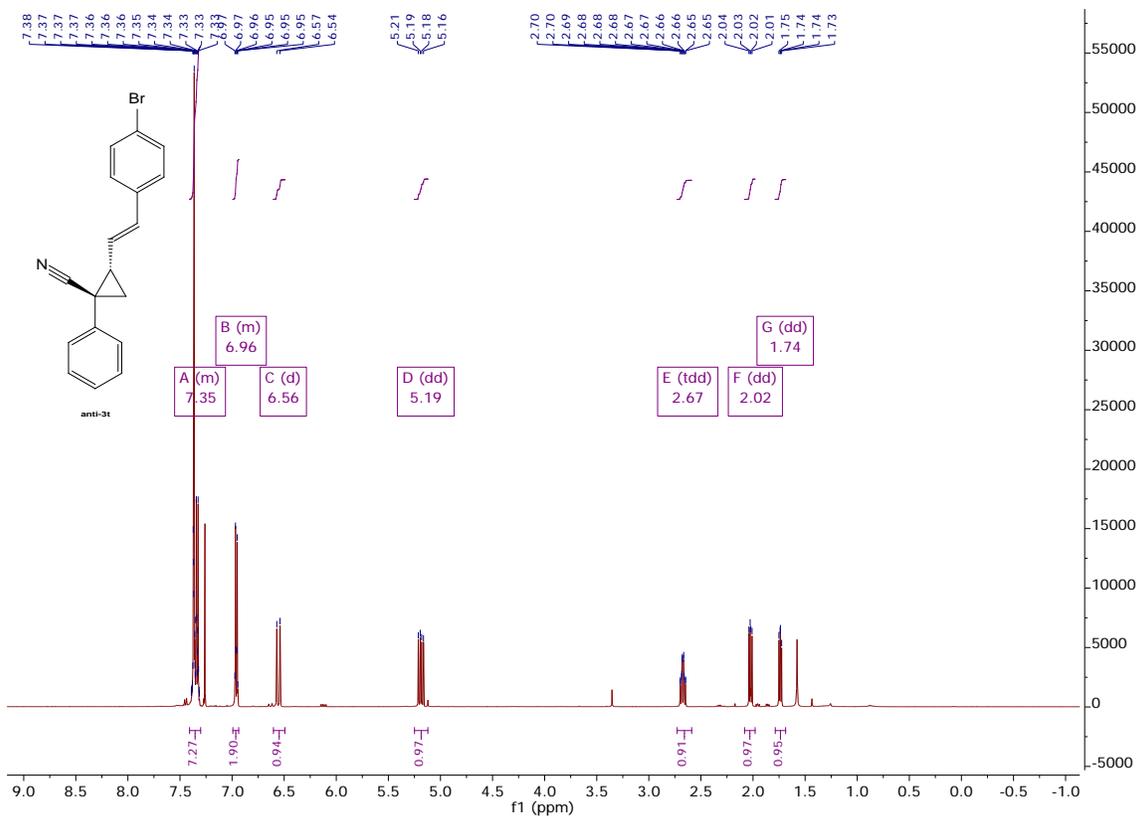


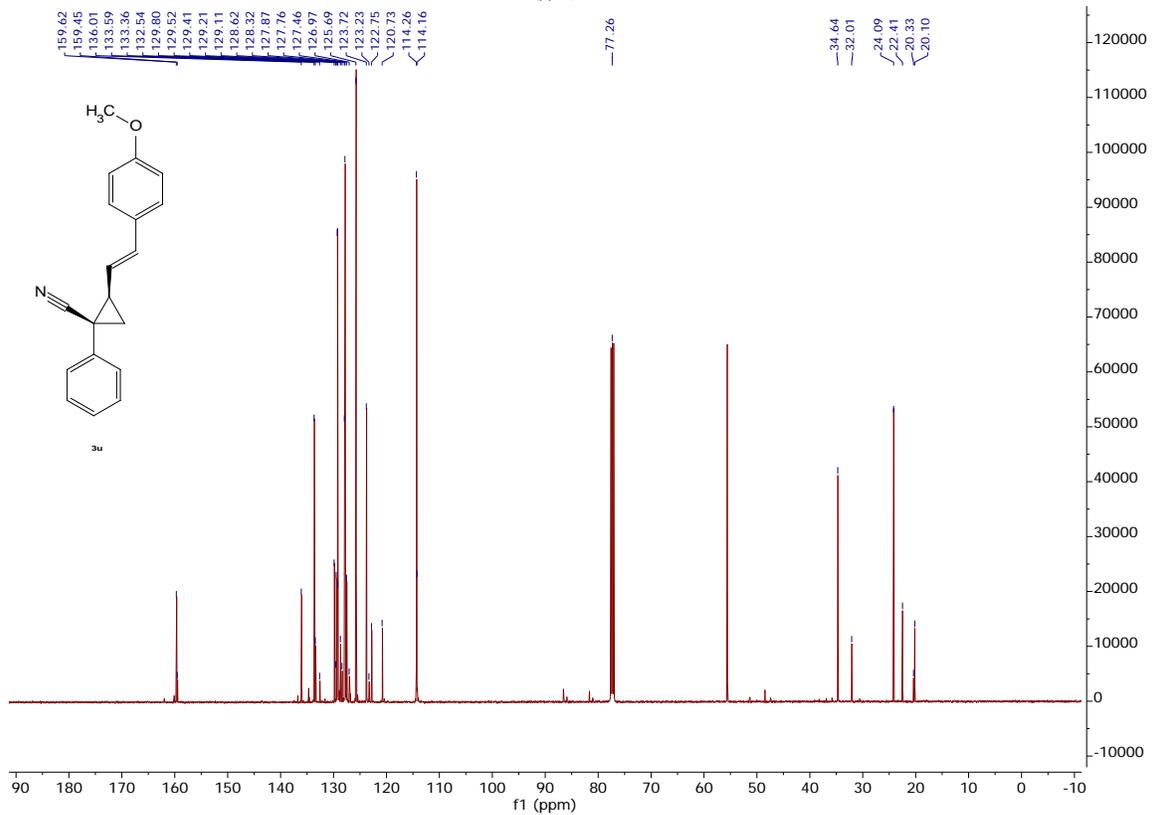
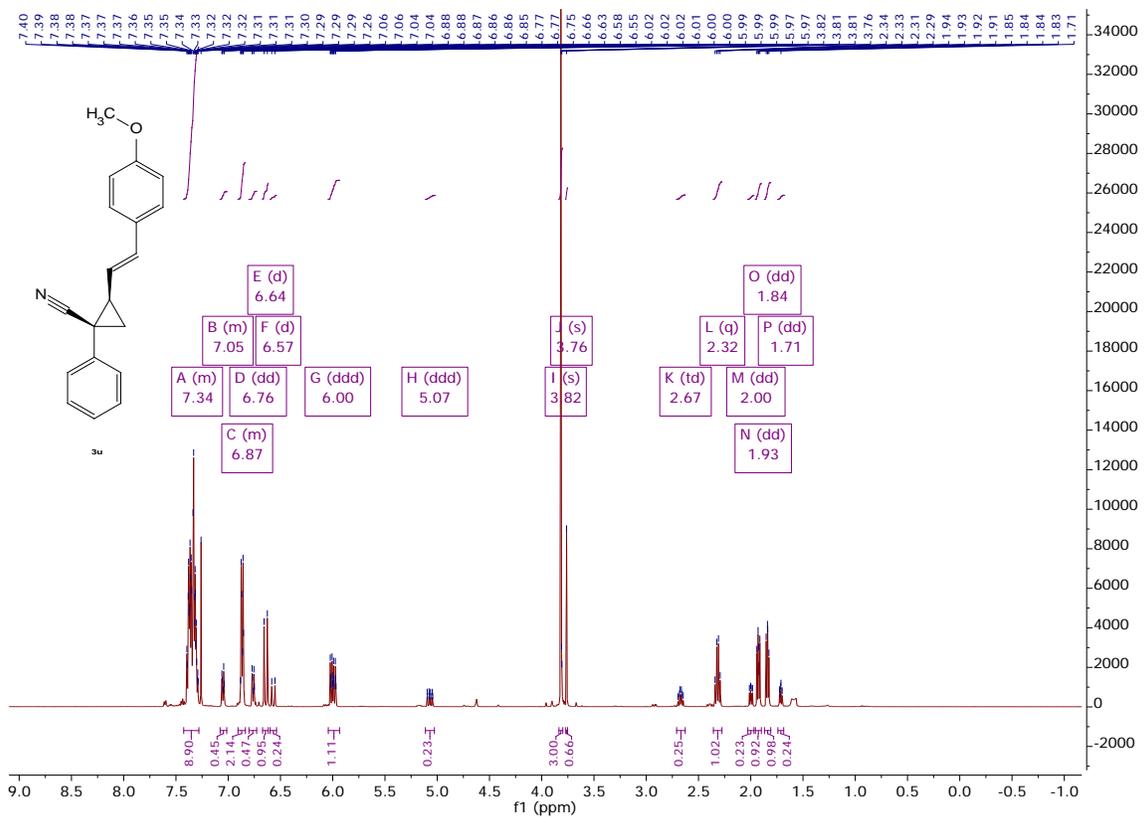
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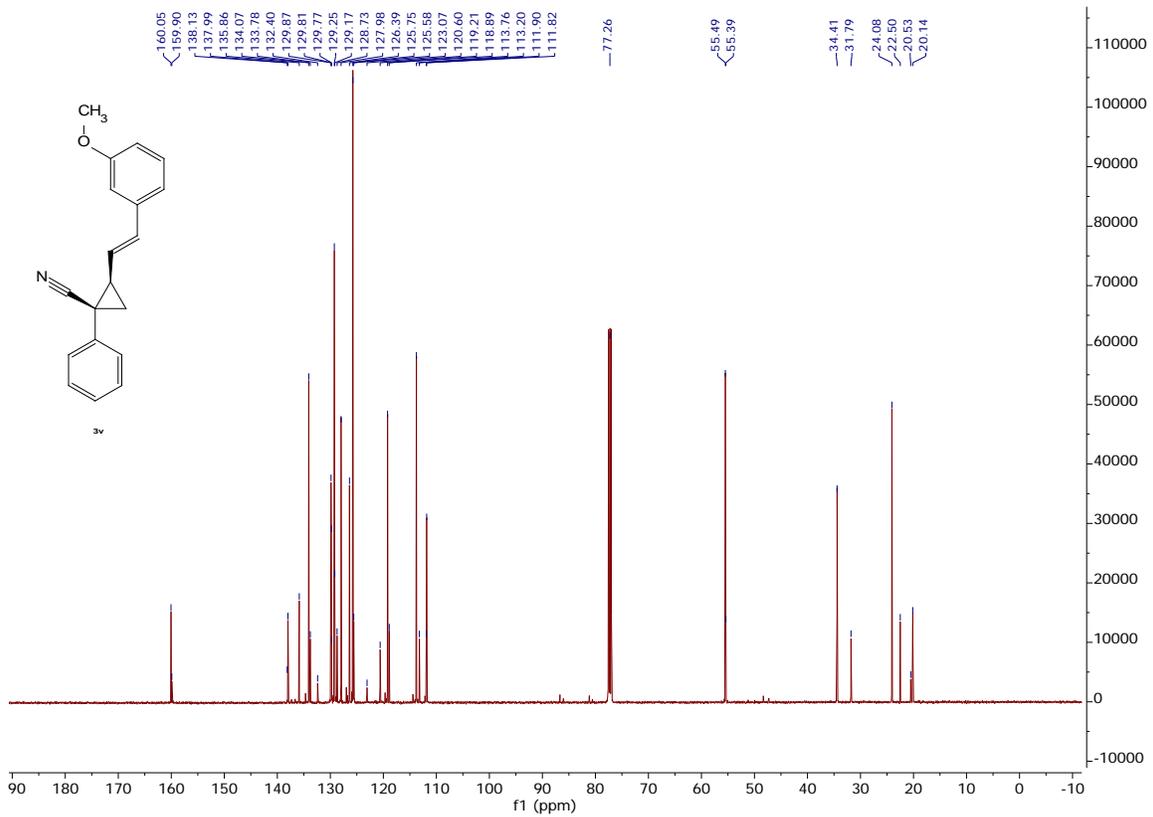
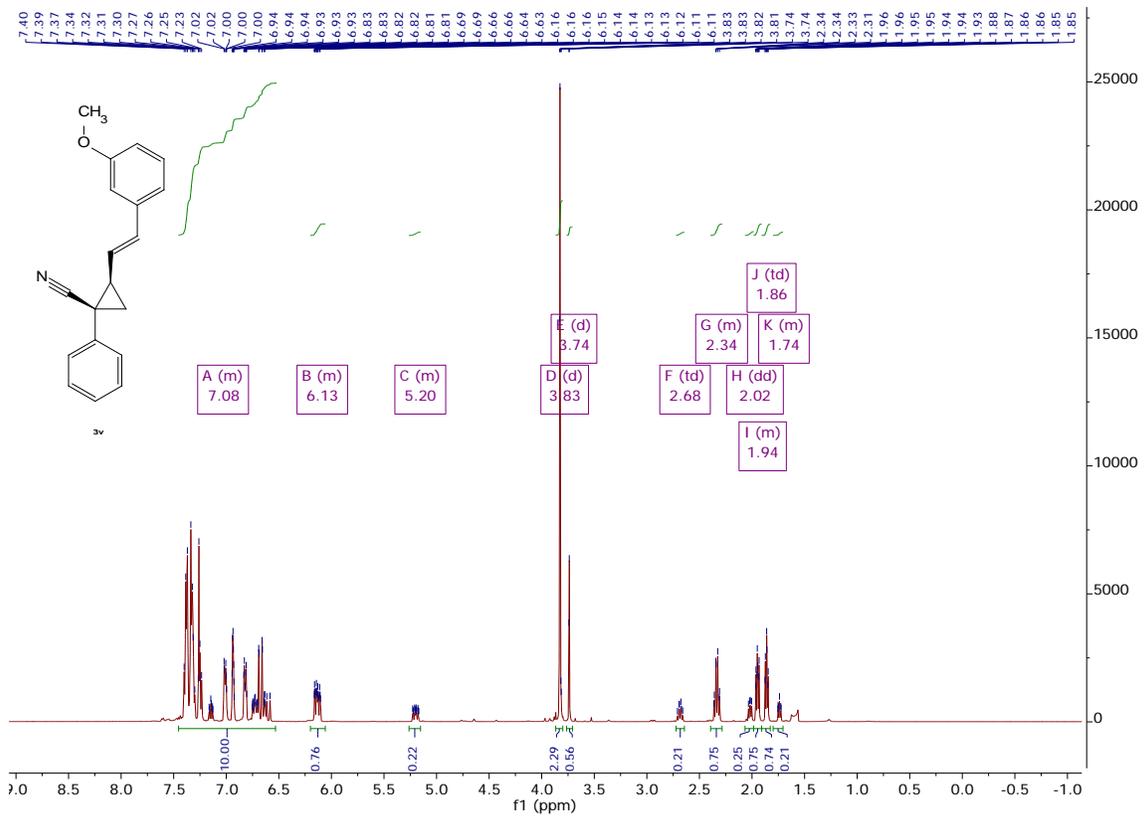




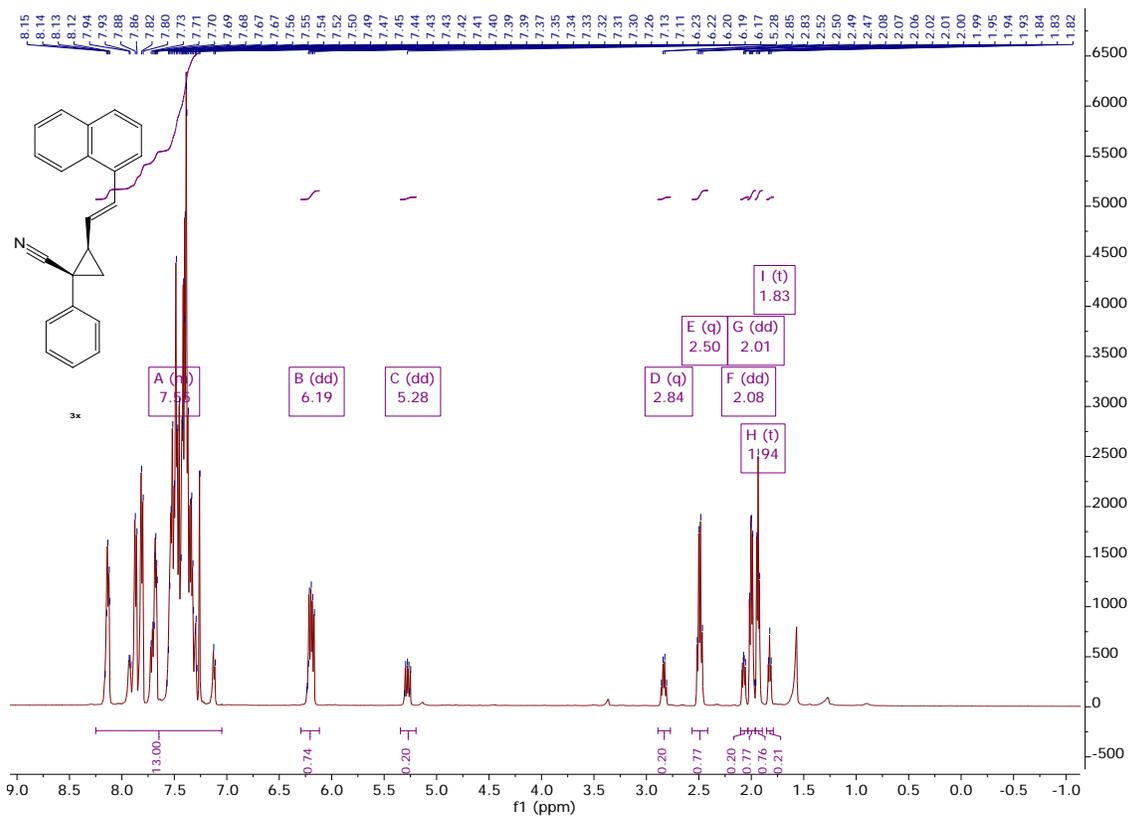


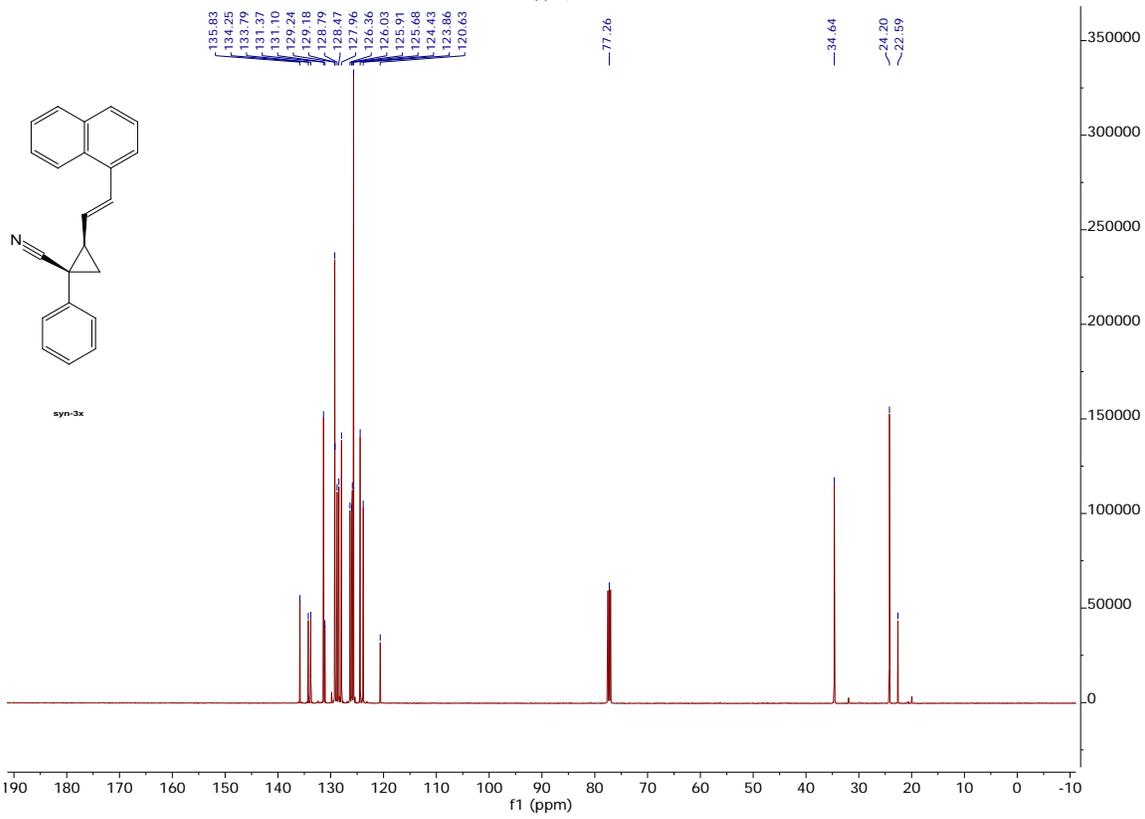
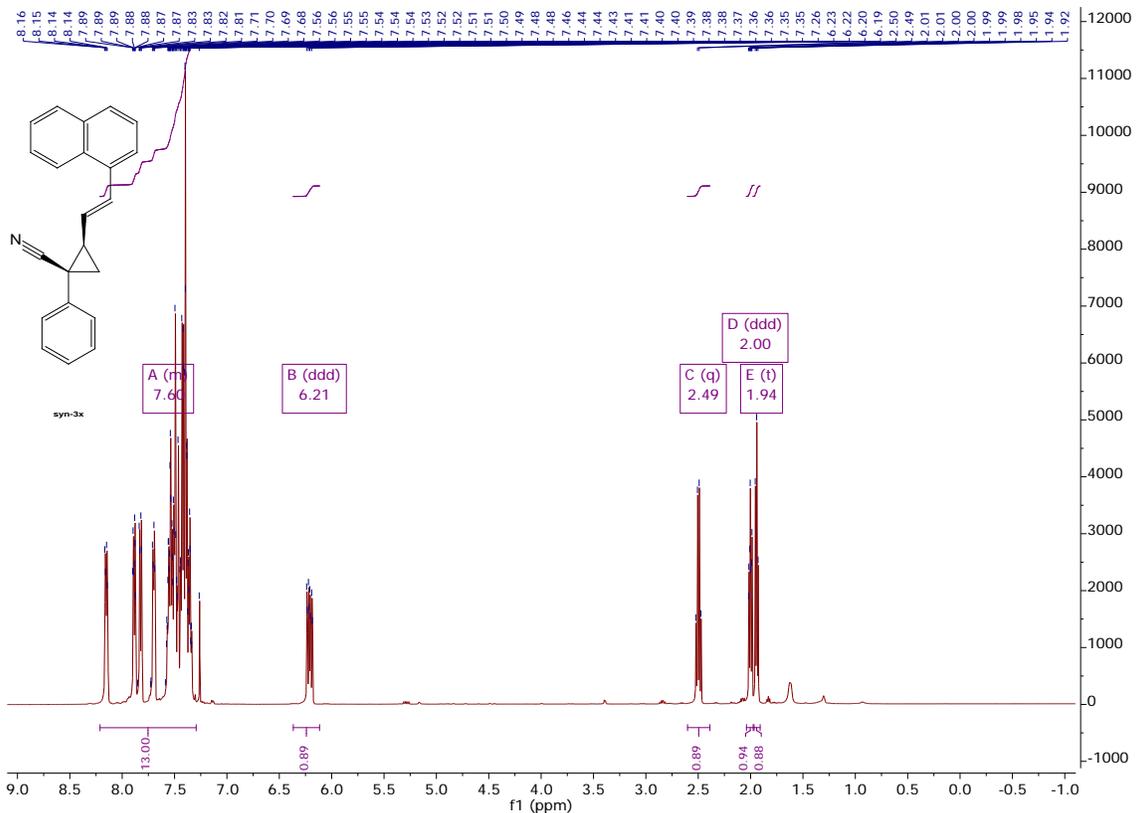


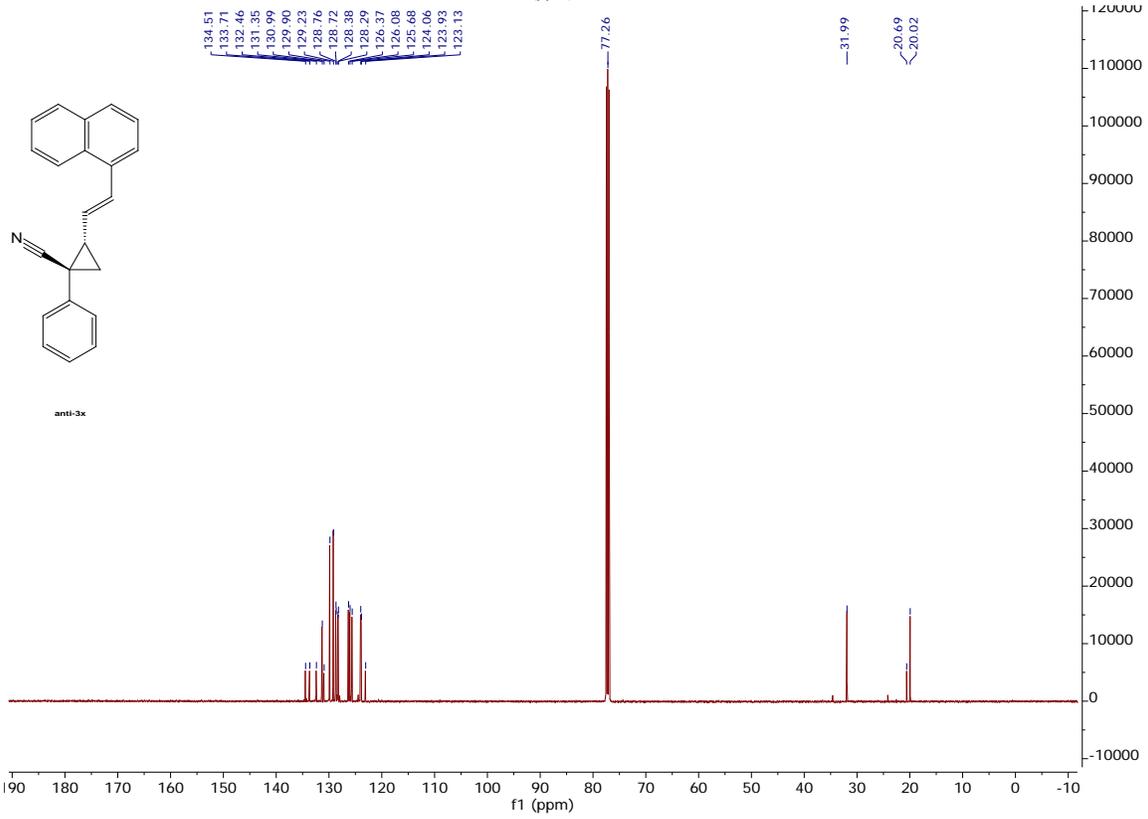
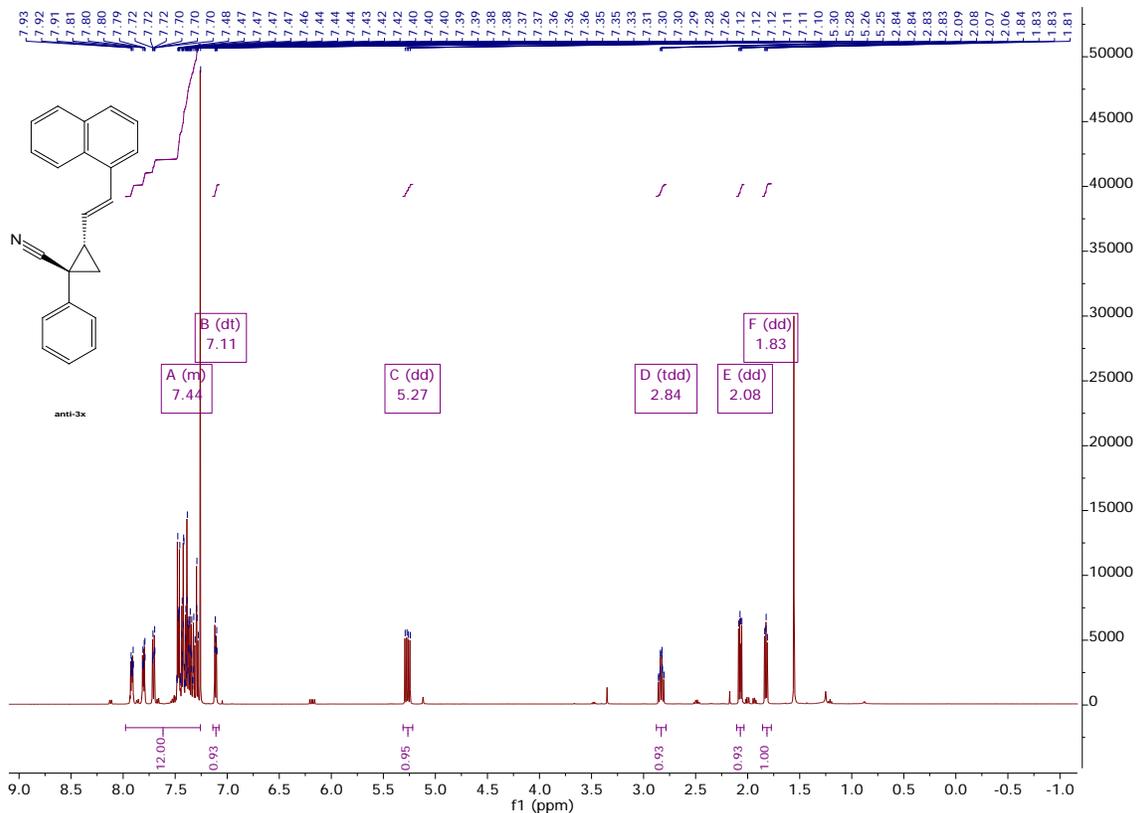
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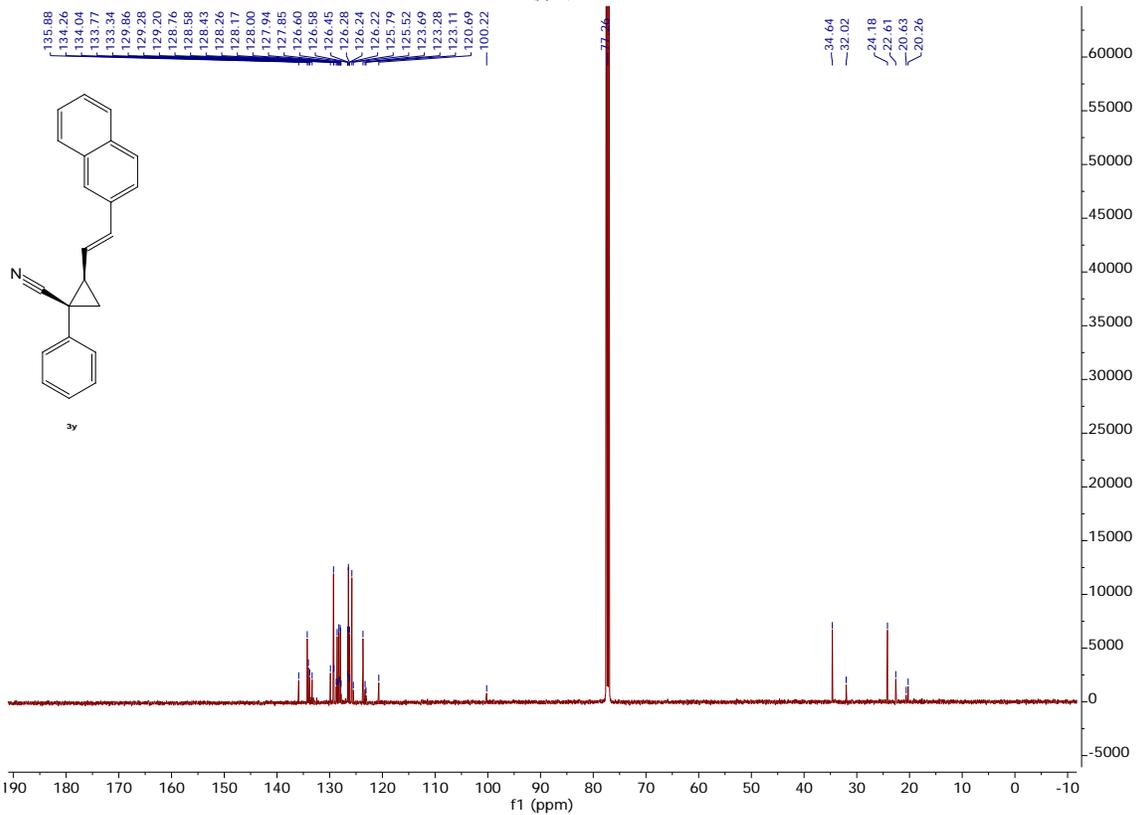
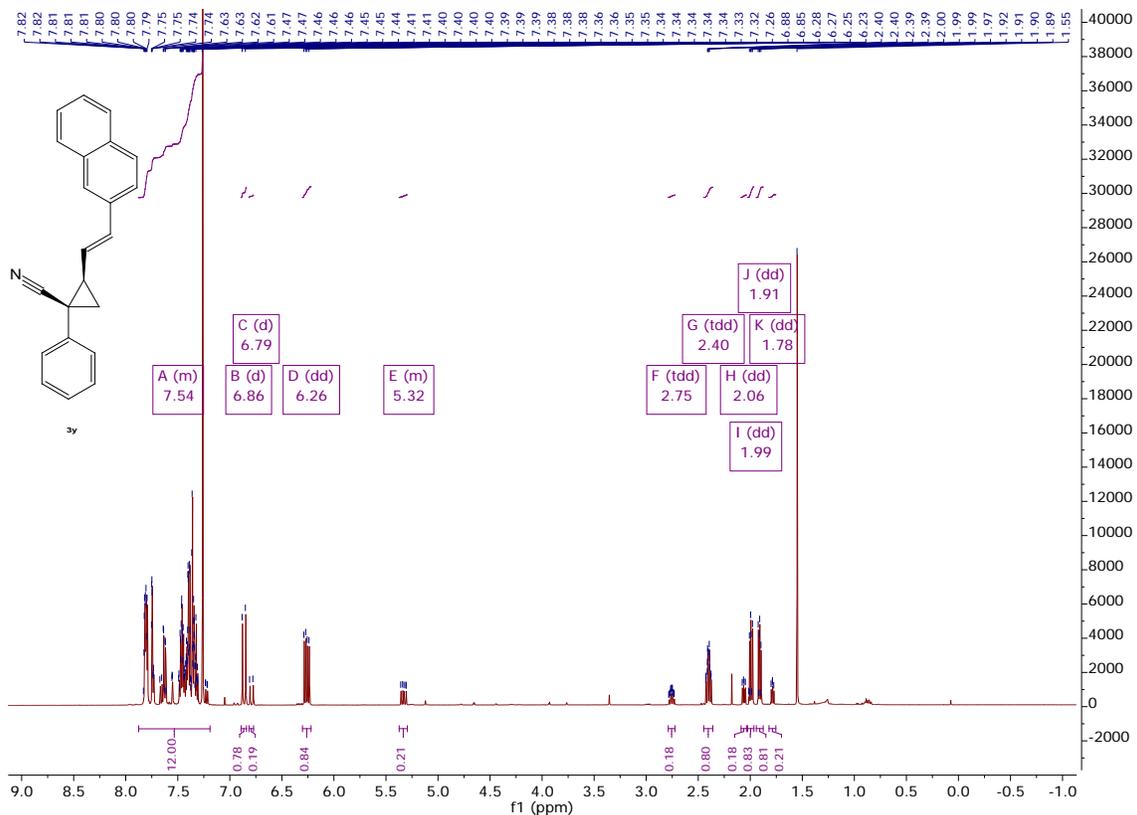
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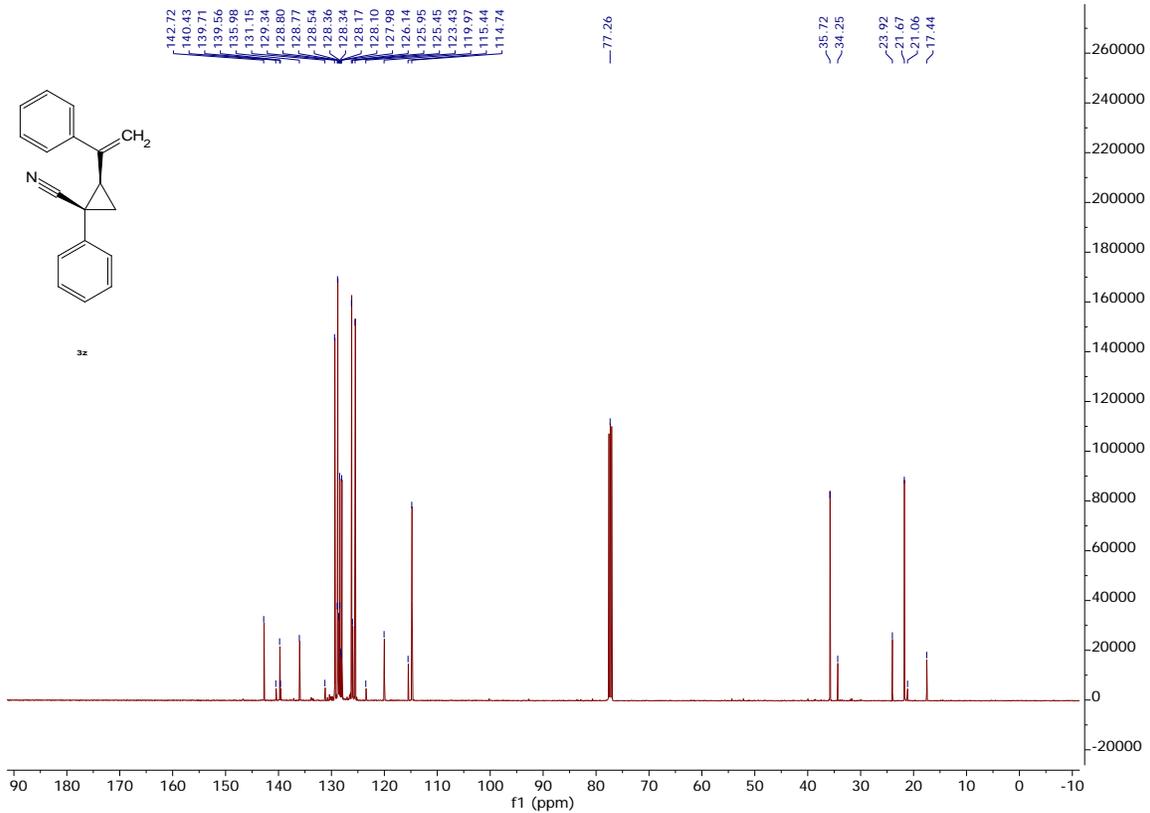
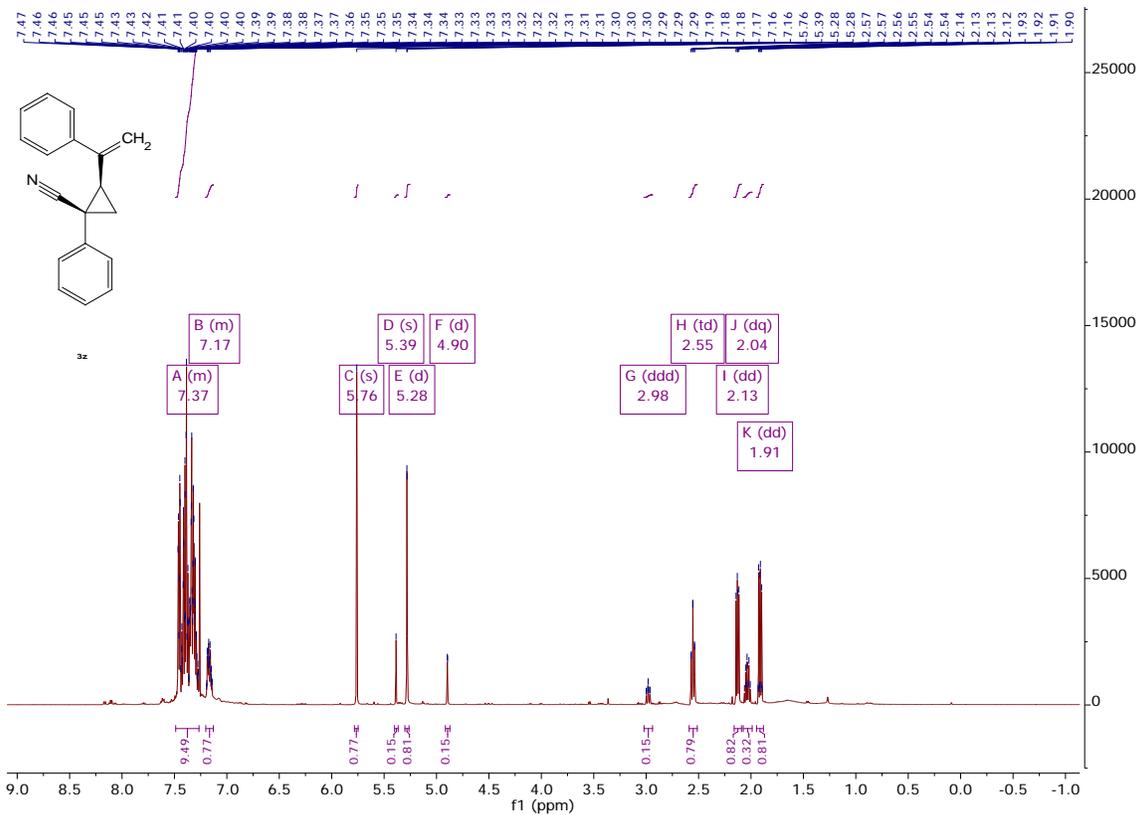


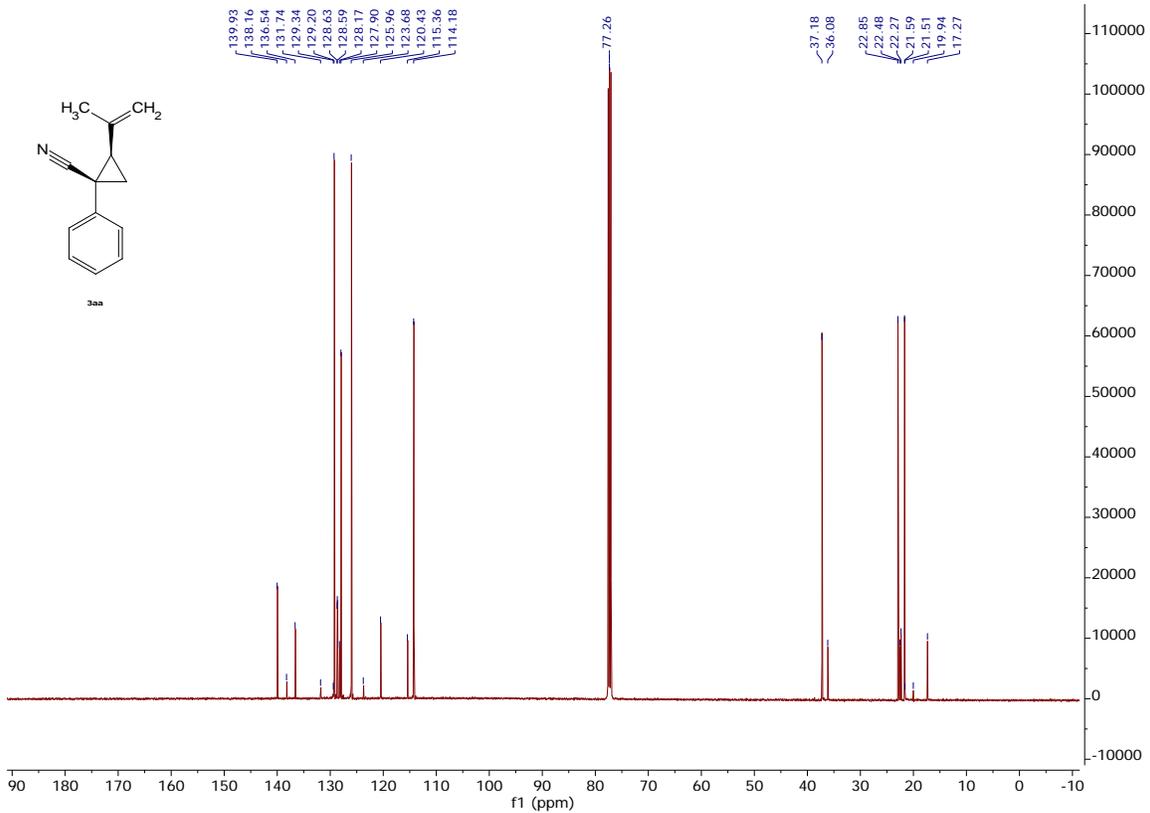
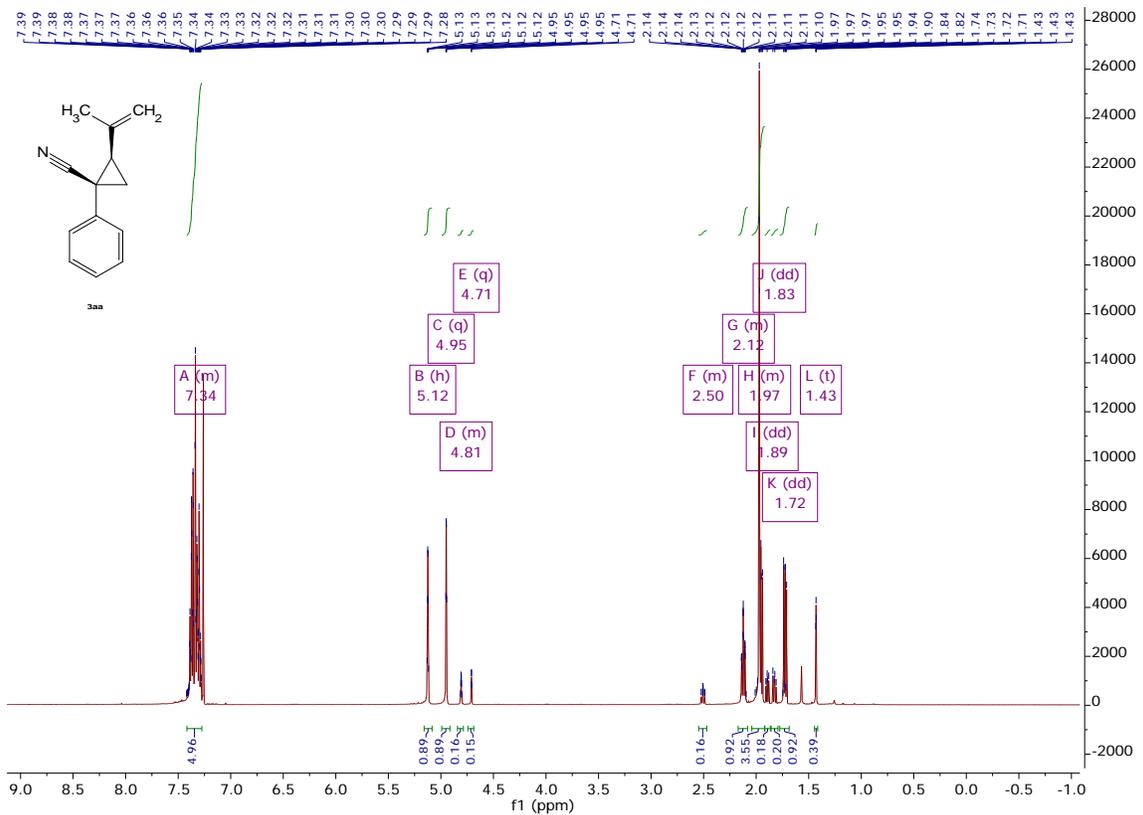


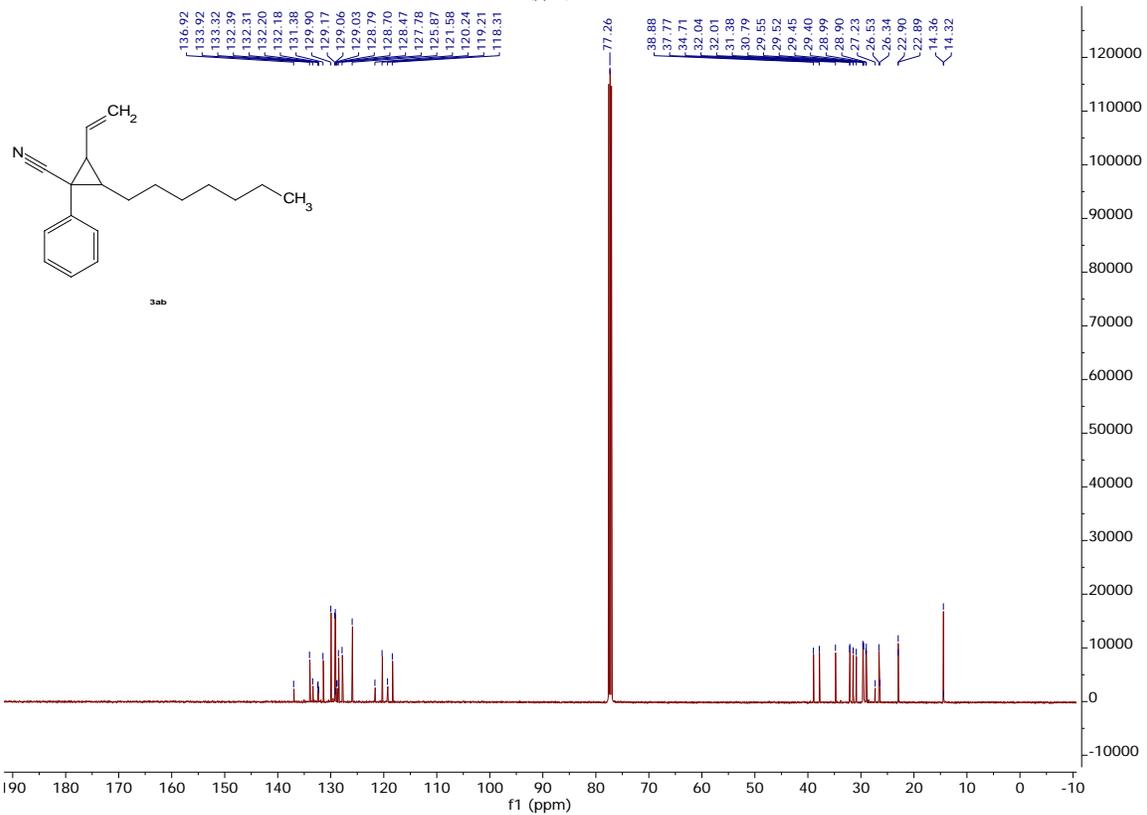
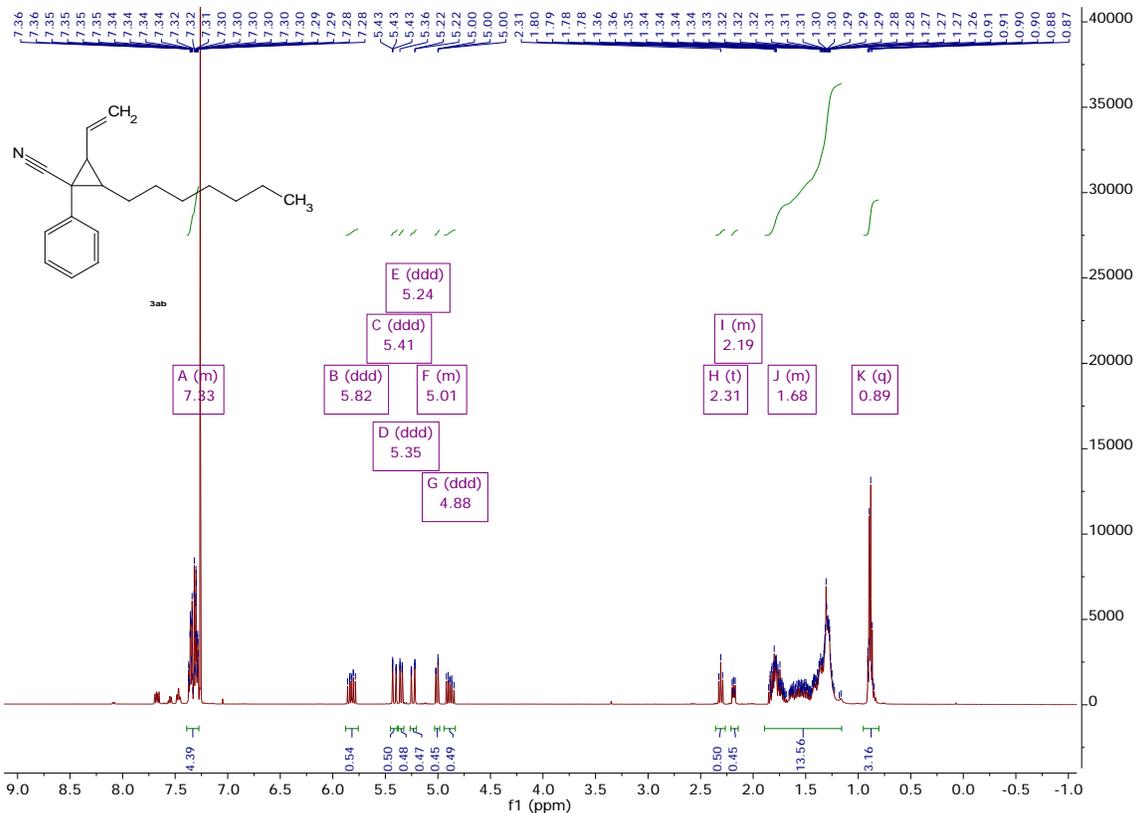
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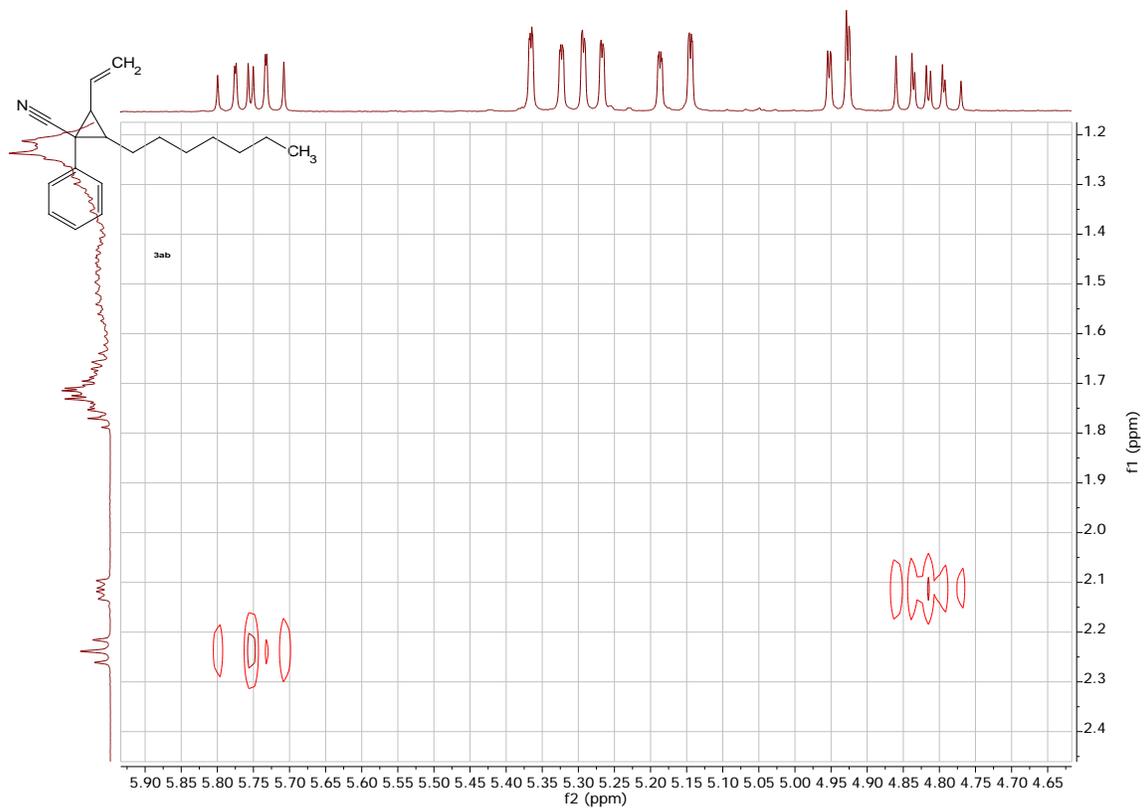
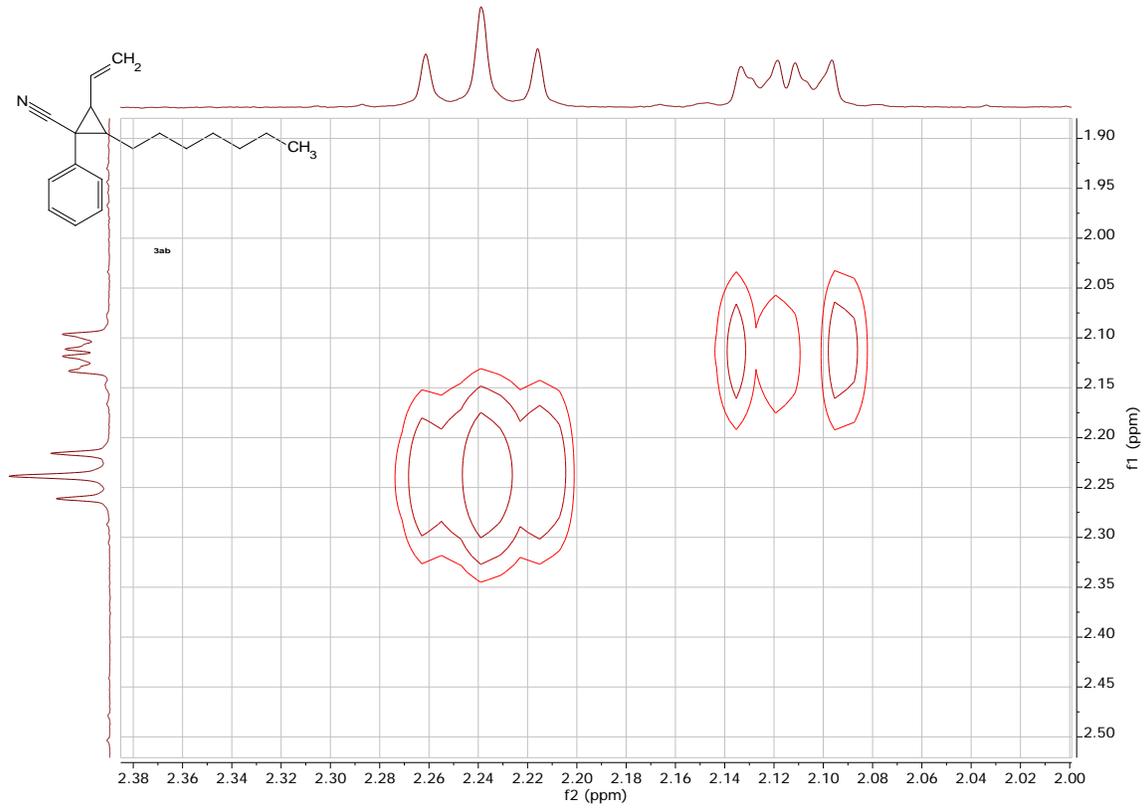


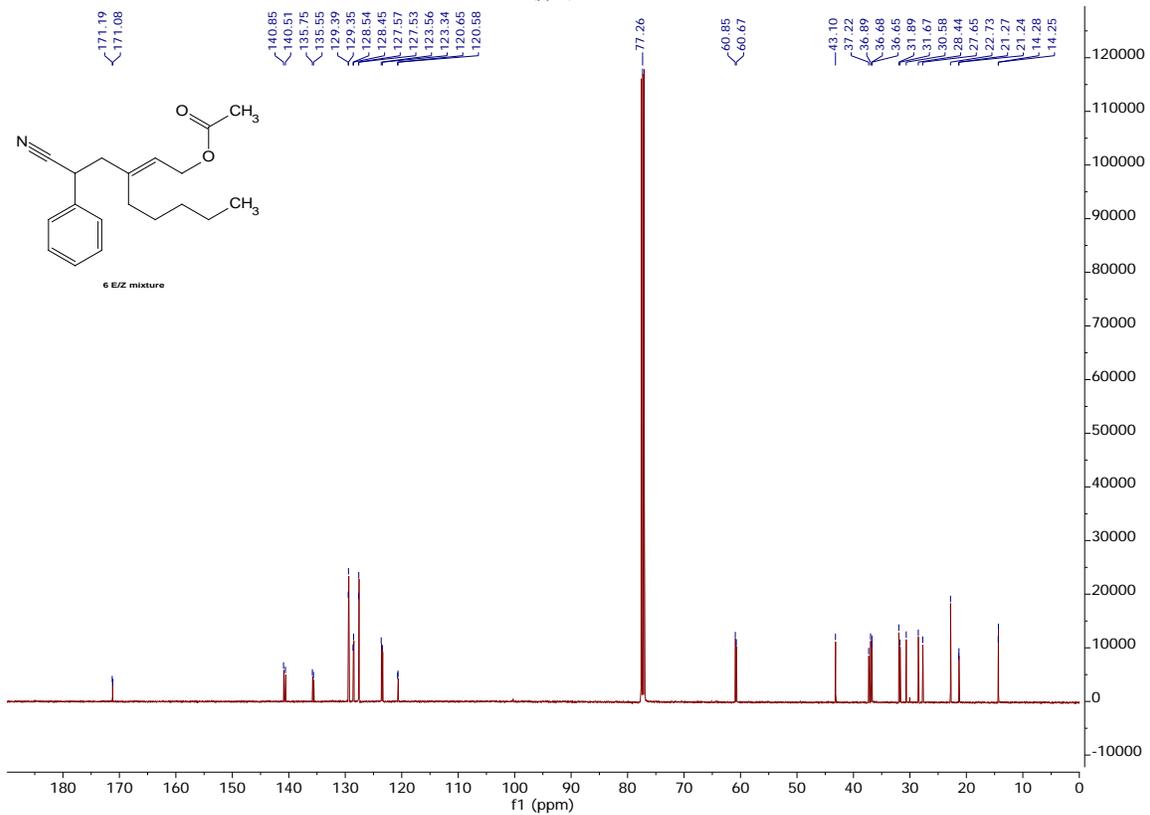
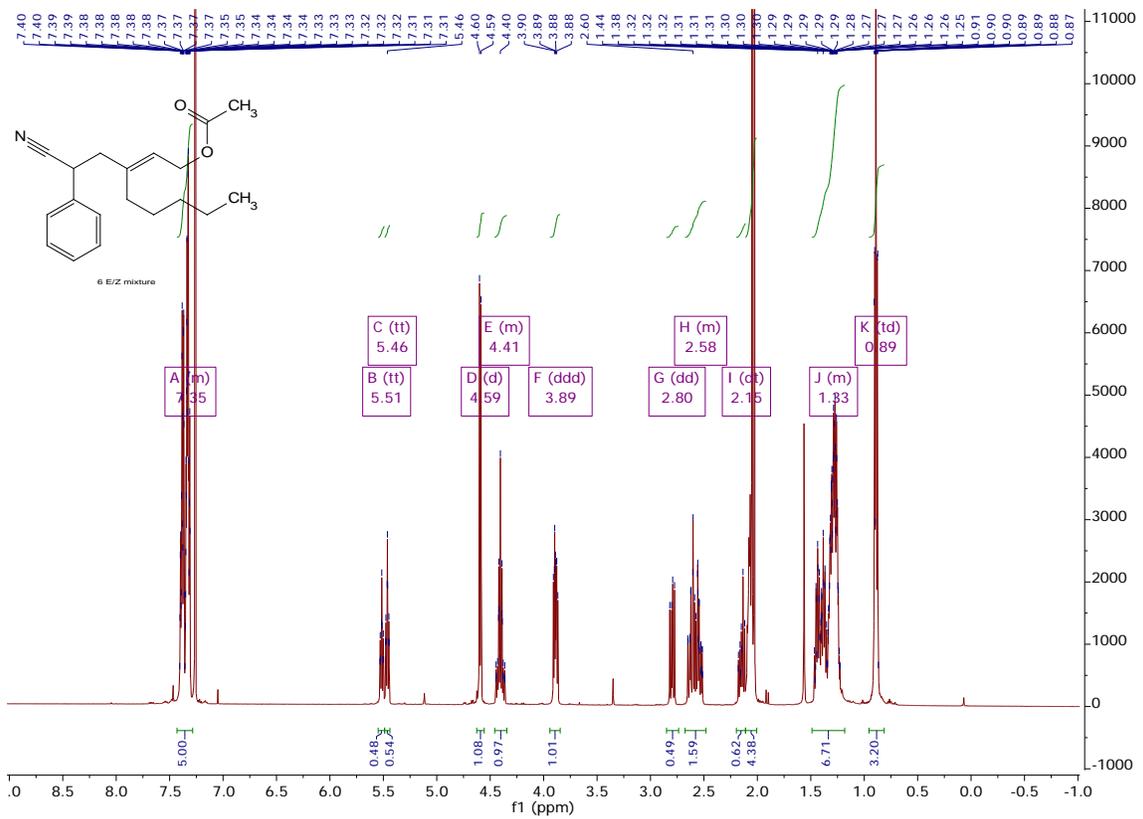




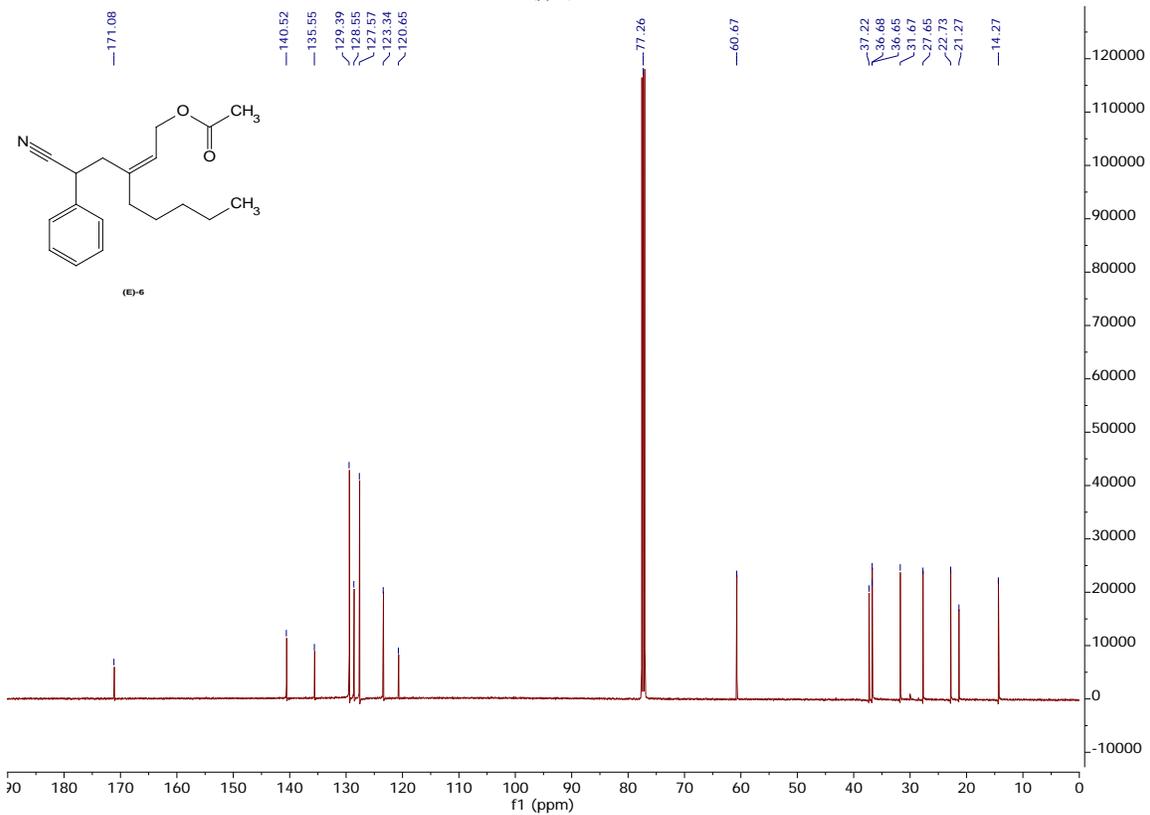
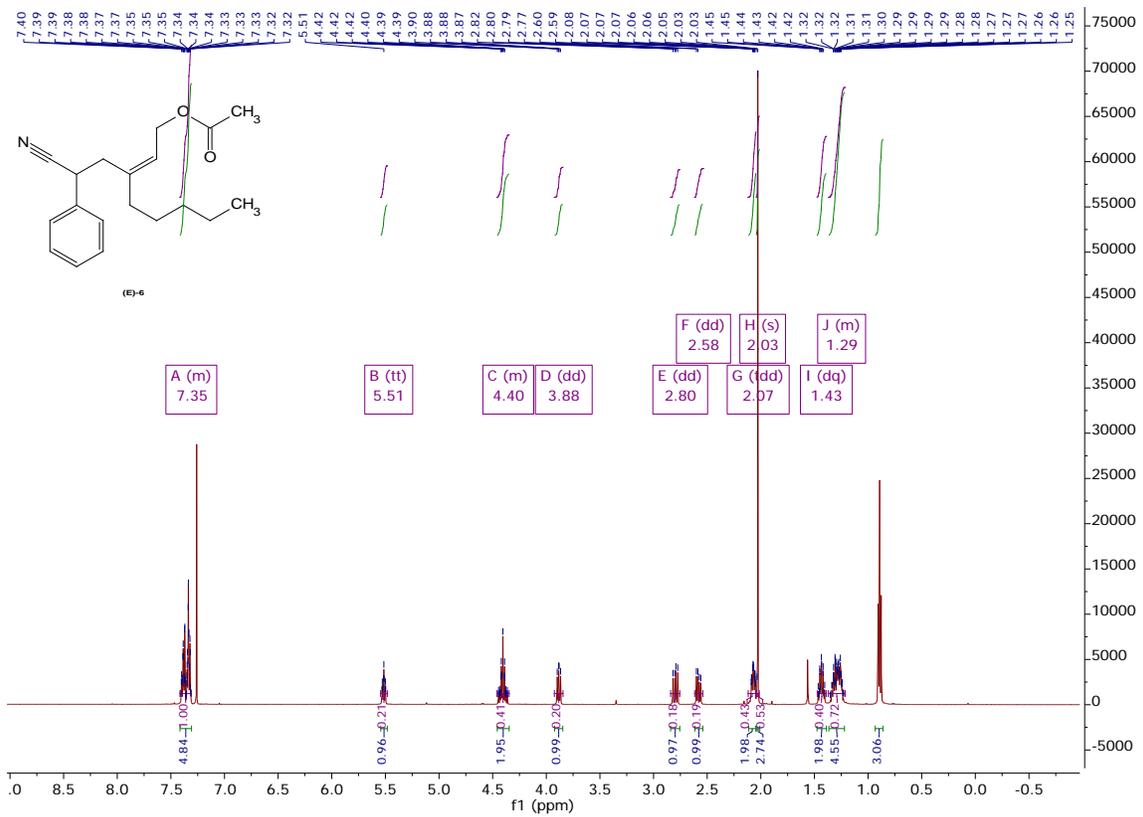
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COSY 3ab

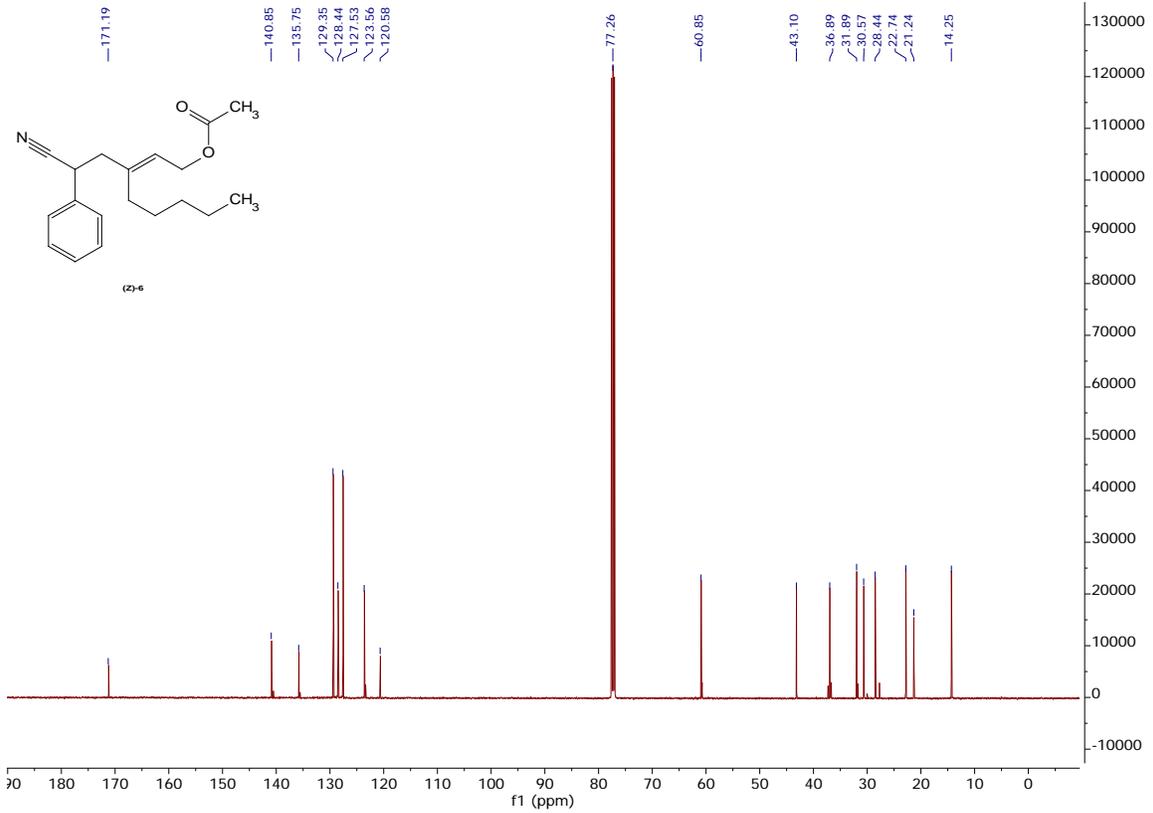
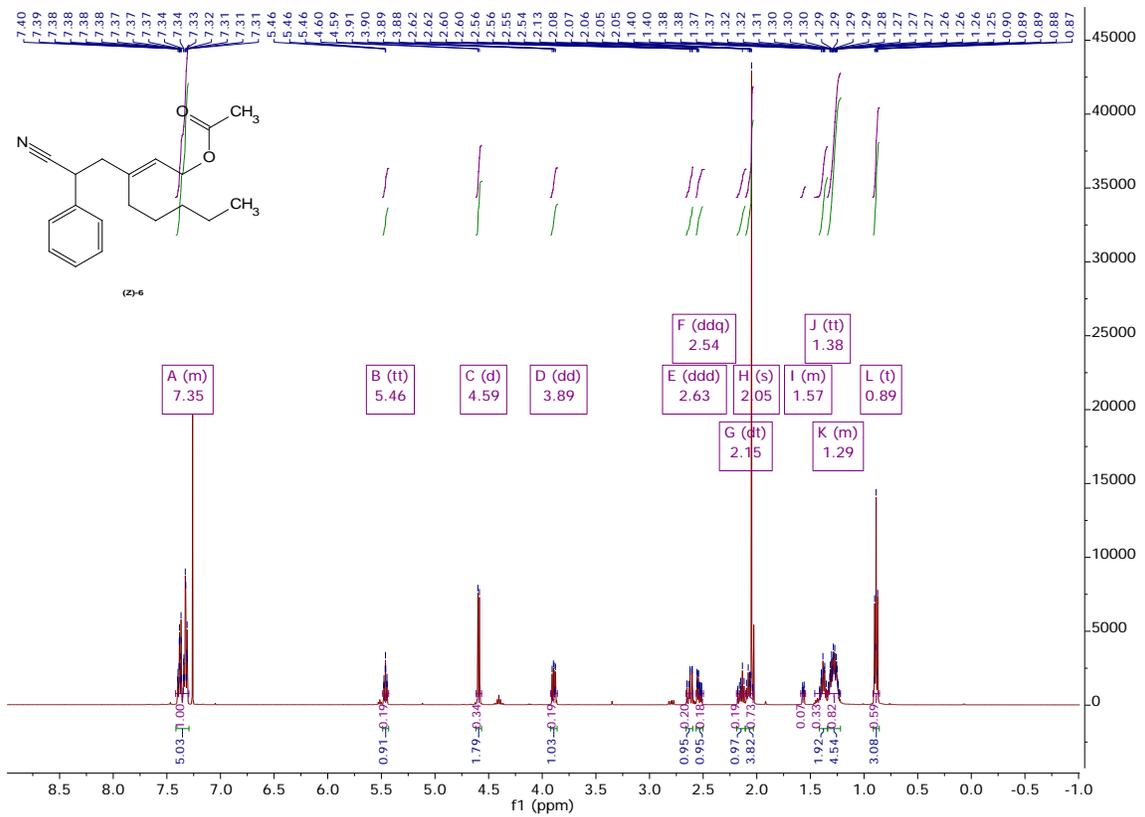


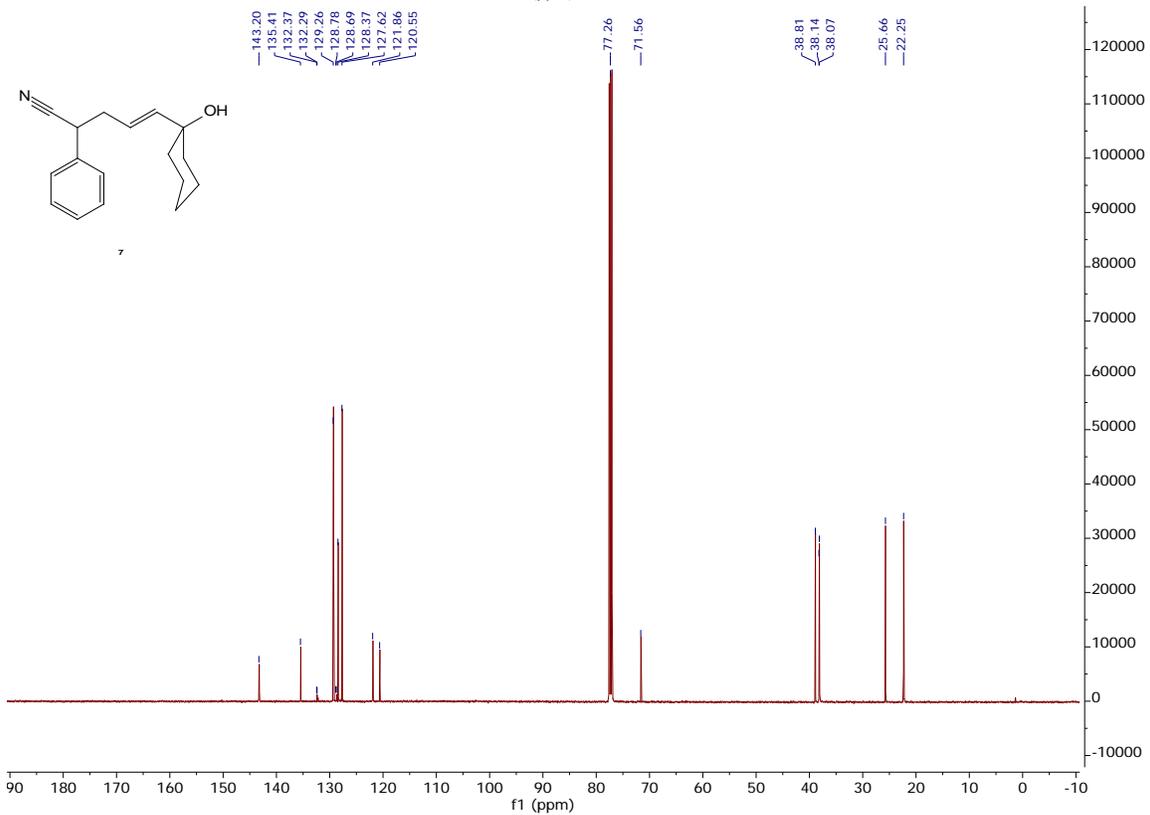
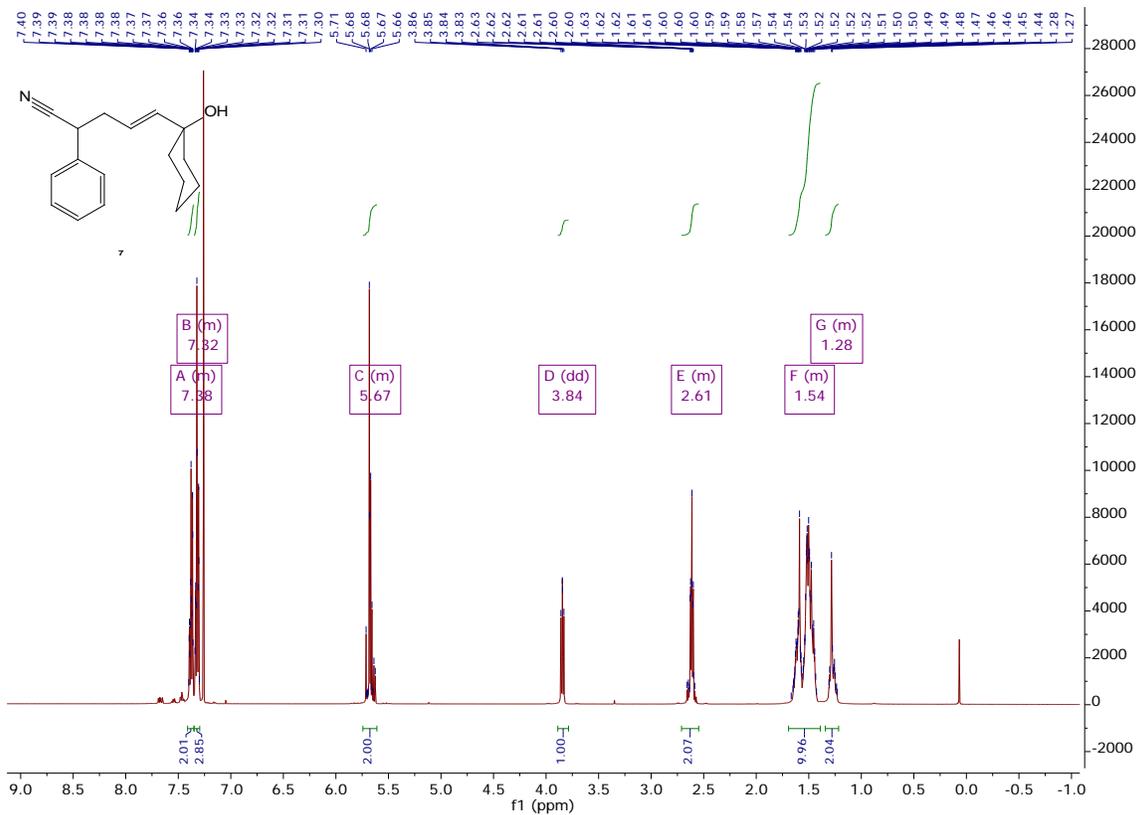


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