Exhaustive Reduction of Esters Enabled by Nickel Catalysis

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Supplementary information

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1. General considerations

1.1 General experimental details

Unless otherwise indicated, reactions were conducted under an atmosphere of nitrogen in 8 mL screw capped vials that were oven dried (120 °C). Column chromatography was either performed manually using Silicycle F60 40−63 μm silica gel or by using a Combiflash Rf+ automated chromatography system with commercially available Biotage normal-phase Silica Flash columns (35−70 μm). Analytical thin layer chromatography (TLC) was conducted with aluminum-backed EMD Millipore Silica Gel 60 F254 pre-coated plates. Unless otherwise noted, visualization of developed plates was performed under UV light (254 nm) and/or using $KMnO_4$ stain.

1.2 Instrumentation

^1H NMR and ^{13}C NMR were recorded on a Bruker AVANCE 400 MHz spectrometer. ^1H NMR spectra were internally referenced to the residual solvent signal (e.g., $CDCl_3$ = 7.27 ppm). ^{13}C NMR spectra were internally referenced to the residual solvent signal (e.g., $CDCl_3$ = 77.00 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (Hz), integration. NMR yields for optimization studies were obtained by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. GC data was obtained via a 5-point calibration curve using FID analysis on an Agilent Technologies 7890B GC with a 30 m x 0.25 mm HP-5 column. Accurate mass data (EI) was obtained from an Agilent 5977A GC/MSD using MassWorks 4.0 from CERNO Bioscience.

1.3 Materials

Organic solvents were purified by rigorous degassing with nitrogen before passing through a PureSolv solvent purification system. Low water content was confirmed by Karl Fischer titration (<20 ppm for all solvents). Unless otherwise noted, starting materials were obtained commercially from Sigma Aldrich, Alfa Aesar or Combi-Blocks and used as received. d_8-Toluene was purchased from Sigma Aldrich (99 %D). $Ni(cod)_2$ was purchased from Sigma Aldrich. $Ni(OTf)_2$ (96% purity) was purchased from Alfa Aesar. $NiBr_2$·glyme (97% purity) was purchased from Sigma Aldrich. Granulated Mn was purchased from Alfa Aesar (99.6% purity, < 10 micron). D_2 (g) was purchased as a 458 mL cylinder from Sigma Aldrich (99.8% D). ICy·HBF_4 was made according to the literature.[1]

2. Synthesis of starting materials

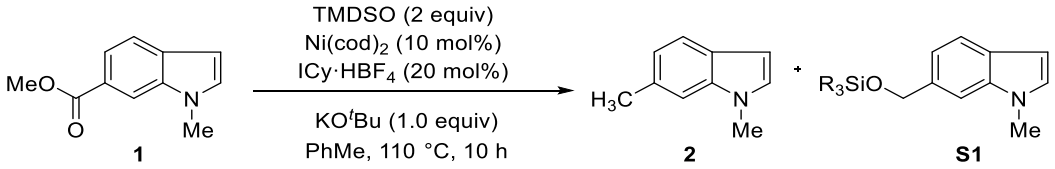
The following ester starting materials were prepared from the corresponding carboxylic acid through acid catalyzed esterification reactions: methyl [1,1'-biphenyl]-4-carboxylate (**3**), methyl 2-naphthoate (**4**), methyl phenanthrene-9-carboxylate (**5**), methyl 4-((1S,4R)-4-butylcyclohexyl)benzoate (**6**), methyl 4-(dimethylamino)benzoate (**7**), methyl 4-vinylbenzoate (**8**), trans-4-(methoxycarbonyl)stilbene (**9**), methyl 3,4,5-trimethoxybenzoate (**10**), methyl 3,5-di-*tert*-butyl-4-hydroxybenzoate (**15**), methyl 4-morpholinobenzoate (**22**), methyl 1-methyl-1*H*-indazole-3-carboxylate (**33**), methyl quinoline-6-carboxylate (**34**) and methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**39**).

Esters including 1-methyl-1*H*-indole-6-carboxylate (**25**), 1-methyl-1*H*-indole-3-carboxylate (**27**), 1-methyl-1*H*-indole-2-carboxylate (**28**), methyl 7-methoxybenzofuran-2-carboxylate (**35**), isochroman-1-one (**37**), Bifendatatum (**38**) and methyl (E)-3-([1,1'-biphenyl]-4-yl)acrylate (**45**) were purchased commercially and used as such for the reduction reaction.

The following ester starting materials were synthesized according to the noted citations: methyl 4-(phenoxy)benzoate (**11**),[2] methyl 4-(4-methoxyphenoxy)benzoate (**12**),[3] methyl 4-(4-phenoxyphenoxy)benzoate (**13**),[4] methyl 2'-hydroxy-[1,1'-biphenyl]-4-carboxylate (**14**),[5] methyl 6-phenylnicotinate (**17**),[6] methyl 6-(2-methoxyphenyl)nicotinate (**45**),[6] methyl 4-(pyridin-2-yl)benzoate (**18**),[6] methyl 4-(4-(pyridin-2-yl)piperazin-1-yl)benzoate (**19**),[7] methyl 6-morpholinonicotinate (**20**),[7] methyl 2-morpholinobenzoate (**21**),[8] methyl 2-(4-methylpiperidin-1-yl)benzoate (**23**),[8] methyl 4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)benzoate (**24**),[8] methyl 4-(1*H*-indol-1-yl)benzoate (**29**),[9] methyl 9-benzyl-9*H*-carbazole-3-carboxylate (**30**),[10] methyl 6-(*tert*-butyl)-9-methyl-9*H*-carbazole-3-carboxylate (**32**),[10] methyl 6-methoxy-9-methyl-9*H*-carbazole-3-carboxylate (**31**),[11] methyl 8-methoxydibenzo[*b,d*]furan-2-carboxylate (**36**)[12]. 4'-(methoxycarbonyl)biphenyl-4-carboxylic acid (**16**), methyl 4'-fluoro-1,1'-biphenyl-4-carboxylate (**40**),methyl 4'-trifluoromethylbiphenyl-4-carboxylate (**41**), methyl 4'nitro-4-

biphenylcarboxylate (**42**), 4-(3-pentyn-1-yloxy)-carboxylate (**43**), and 4-(2-furanyl)-methyl benzoate (**44**) were synthesized by Suzuki reactions according to literature precedent.[5]

3. Reaction optimization



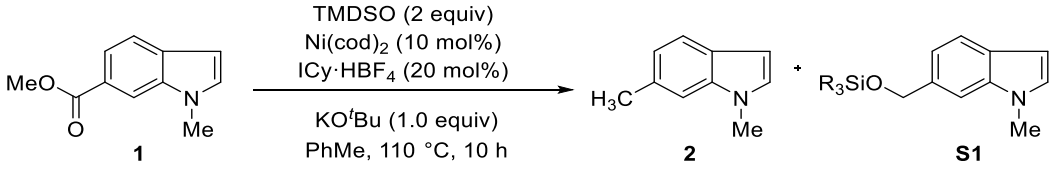
Scheme S1. General method for the reduction of esters

To an oven dried 8 mL screw-top test-tube, 0.20 mmol of methyl ester starting material is added alongside an oven dried micro-stir bar. The screw-top test-tube is subsequently brought into a nitrogen-filled glovebox. Once under the inert atmosphere, 0.04 mmol ICy·HBF_4, 0.02 mmol $Ni(cod)_2$ and 0.20 mmol of KO^tBu are added. 0.8 mL of toluene is added to the test-tube, followed by 0.4 mmol of 1,1,3,3-tetramethyldisiloxane. The reaction vessel is quickly sealed with a Teflon-septa equipped cap and brought outside of the glovebox, where it is stirred inside of a mineral-oil bath at 600 rpm for 10 hours at 110 °C. After 10 hours, the reaction vessel is allowed to come to room temperature before being opened to the atmosphere. 0.80 mmol of tetra-n-butylammonium fluoride is added slowly as a 1.0 M solution in tetrahydrofuran and the resulting solution is heated to 65 °C and stirred for 2 hours.* The reaction solution is filtered through a short plug of silica before 100 µL of 1,3,5-trimethoxybenzene in toluene is added to act as an internal standard. Solvent is removed via rotary evaporation, yielding crude product which is subsequently dissolved in 0.75 mL of $CDCl_3$ before being submitted for NMR analysis. All yields are obtained via ^{1}H-NMR, setting the integral value of the peak corresponding to the three methyl protons at 2.54 ppm to 3.00 and referencing it with respect to the peak at 6.08 ppm for 1,3,5-trimethoxybenzene.

* **S1** is initially formed as a mixture of silylated species – TBAF is added to the reaction solution in order to deprotect these species so that the alcohol can be quantified.

3.1 Control Experiments

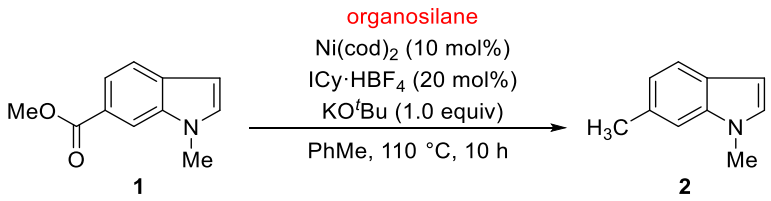
Table S1. Control experiments for the ester to methyl reduction



entry	deviation from standard conditions	yield 2 [%]	yield S1 [%]
1	No deviation	84	0
2	*remove* KO^tBu	0	0
3	*remove* TMDSO	0	0
4	*remove* $Ni(cod)_2$	trace	52
5	*remove* $ICy{\cdot}HBF_4$	14	0
6	*remove all except* TMDSO and KO^tBu	trace	66
7	*remove all except* $Ni(cod)_2$	0	0
8	room temperature	14	61
9	1 h	13	67

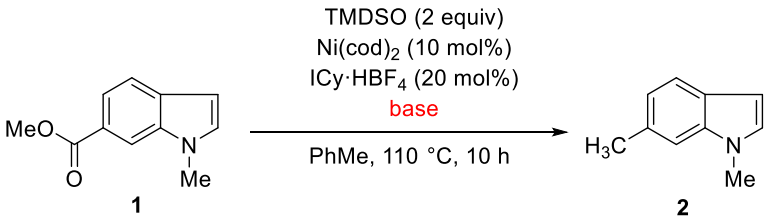
3.2 Optimization of reaction conditions

Table S2. Organosilane optimization for the ester to methyl reduction



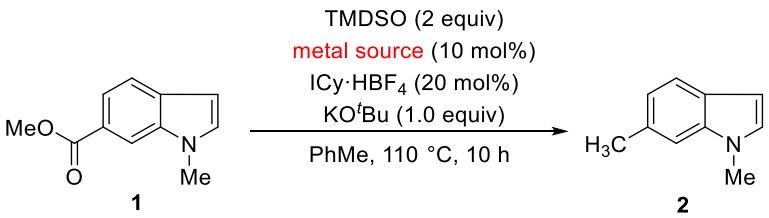
entry	organosilane	yield 2 [%]
1	Et_3SiH (4.0 equiv)	42
2	$^{i}Pr_3SiH$ (4.0 equiv)	5
3	$(EtO)_3SiH$ (4.0 equiv)	20
4	PMHS (10.0 equiv)	trace
5	$PhSiH_3$ (2.0 equiv)	trace
6	$[(Me_3SiO)_2SiHMe]$ (4.0 equiv)	48
7	$[(CH_3)_2SiHO)_2Si(CH_3)_2]$ (4.0 equiv)	65
8	TMDSO (1.0 equiv)	52
9	TMDSO (1.5 equiv)	76
10	TMDSO (2.0 equiv)	84
11	TMDSO (2.5 equiv)	74

Table S3. Base optimization for the ester to methyl reduction



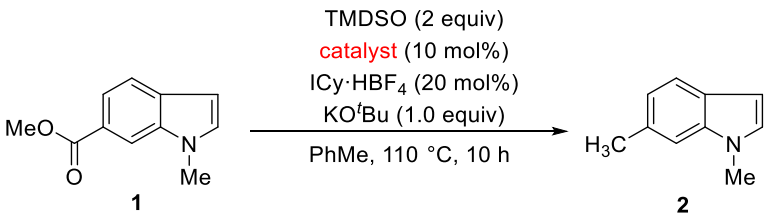
entry	base	yield, 2 [%]
1	NaOH (1.0 eq)	4
2	LiOH (1.0 eq)	0
3	KOH (1.0 eq)	12
4	Et_3N (1.0 eq)	0
5	Cs_2CO_3 (1.0 eq)	0
6	K_2CO_3 (1.0 eq)	3
7	$NMe_4OH{\cdot}5H_2O$ (1.0 eq)	37
8	KHF_2 (1.0 eq)	0
9	NaOMe (1.0 eq)	56
10	KOEt (1.0 eq)	51
11	LiO^tBu (1.0 eq)	trace
12	NaO^tBu (1.0 eq)	75
13	KO^tBu (1 eq)	78
14	KO^tBu (0.5 eq)	69
15	KO^tBu (1.5 eq)	74
16	KO^tBu (2.0 eq)	68

Table S4. Optimization of metal source for the ester to methyl reduction



entry	Metal source	yield, 2 [%]
1	$Ni(cod)_2$	84
2	$NiCl_2$	4
3	$Ni(P(OPh)_3)_4$	0
4	$NiCl_2(PCy_3)_2$	67
5	$Ni(OAc)_2$	trace
6	$Ni(OTf)_2$	5
7	$NiBr_2$·glyme	7
8	$PdCl_2$	29
9	$Pd(OAc)_2$	28
10	Pd_2dba_3	34
11	$RhCl(PPh_3)_3$	trace
12	Pt/C	11
13	$Ir(cod)_2Cl_2$	13
14	$[Ru(p\text{-cymene})Cl_2]_2$	7
15	CuI	0
16	$FeCl_3$	0
17	$Ni(cod)_2$ (5 mol%)	62
18	$Ni(cod)_2$ (20 mol%)	86
19	$Ni(cod)_2$ (30 mol%)	82

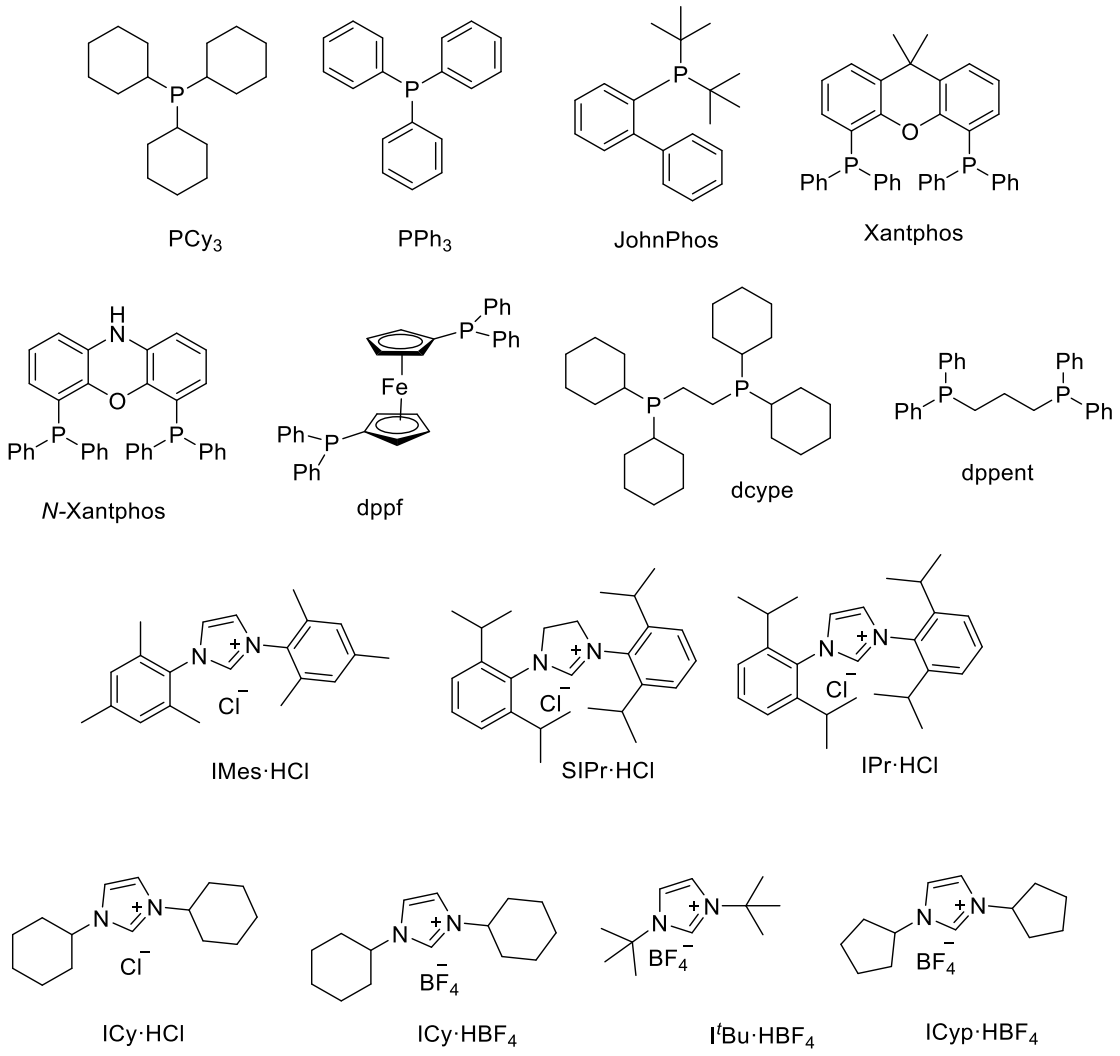
Table S5. Optimization of reaction with air stable Ni(II) salts



entry	**catalyst**	**deviation from standard procedure**	**yield, 2 [%]**
1	$Ni(OAc)_2$	none	trace
2	$Ni(OAc)_2$	added Mn (1 eq)	56
3	$Ni(OAc)_2$	added Mn (20 mol%)	13
5	$Ni(OAc)_2$	added Mn (1 eq)/*no TMDSO*	0
6	$Ni(OAc)_2$	added Mn (1 eq)/*no TMDSO/no base*	0
7	$Ni(OAc)_2$	added Mn (1 eq)/0.2 eq base	27
8	$Ni(OAc)_2$	added Mn (1 eq)/*no base*	trace
9	$Ni(OAc)_2$	added Mn (1 eq)/*no ICy*	33
10	$NiBr_2$·glyme	none	7
11	$NiBr_2$·glyme	added Mn (1 eq)	78
12	$NiBr_2$·glyme	added Mn (20 mol%)	35

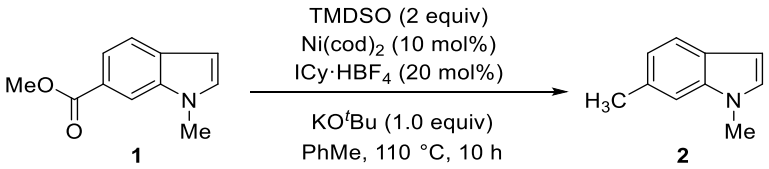
Table S6. Ligand optimization for the ester to methyl reduction

entry	ligand	yield, 2 [%]
1	PCy_3	53
2	PPh_3	15
3	JohnPhos	16
4	Xantphos	35
5	*N*-Xantphos	29
6	dppf	27
7	dcype	44
8	dppent	35
9	IMes·HCl	3
10	SIPr·HCl	53
11	IPr·HCl	70
12	ICy·HCl	77
13	ICy·HBF_4	84
14	I^{t}Bu·HBF_4	73
15	ICyp·HBF_4	60



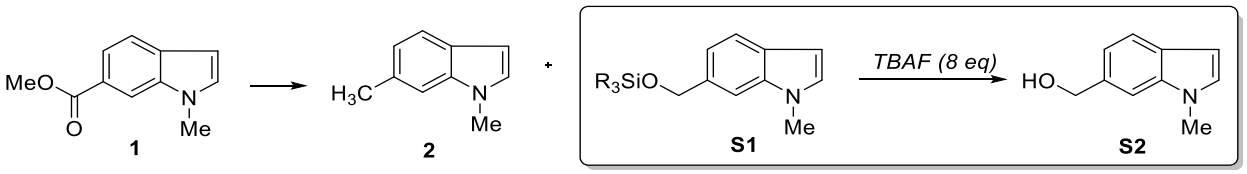
Scheme S2. Structures of ligands

Table S7. Miscellaneous optimization for the ester to methyl reduction



entry	deviation from standard conditions	yield, 2 [%]
1	temperature = 80 °C	51
2	temperature = 100 °C	71
3	temperature = 120 °C	81
4	temperature = 150 °C	67
5	reaction time = 3 h	25
6	reaction time = 6 h	54
7	reaction time = 9 h	79
8	reaction time = 10 h	84
9	reaction time = 16 h	81
10	solvent = xylene	71
11	solvent = DMF	0
12	solvent = benzene	78

3.3 Work-up



The major side products in the reduction of esters to tolyl derivatives are the corresponding silylated alcohol (e.g. **S1**) and various siloxane derivatives arising from the TMDSO. While the quantity of silylated alcohol is minimized by running the reaction to completion, purification can still be hindered by the siloxane byproducts. This is particularly true when purifying non-polar products by silica gel chromatography. We found that quenching the reaction with 8 equivalents of 1.0 M TBAF in THF and stirring for 2 h at 65 °C (or alternatively, 6 h at room temperature) prior to isolation was beneficial. While not mandatory, this work-up procedure was followed throughout to ensure the products obtained were spectroscopically pure.

4. Reaction scope

4.1. General procedures

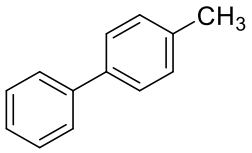
General procedure A

To an oven dried 8 mL screw-top test-tube, 0.20 mmol of methyl ester starting material is added alongside an oven dried micro-stir bar. The screw-top test-tube is subsequently brought into a nitrogen-filled glovebox. Once under the inert atmosphere, 0.04 mmol ICy·HBF_4, 0.02 mmol $Ni(cod)_2$ and 0.20 mmol of KO^{t}Bu are added. 0.8 mL of toluene is added to the test-tube, followed by 0.40 mmol of 1,1,3,3-tetramethyldisiloxane. The reaction vessel is quickly sealed with a Teflon-septa equipped cap and brought outside of the glovebox, where it is stirred inside of a mineral-oil bath at 600 rpm for 10 hours at 110 °C. After 10 hours, the reaction vessel is allowed to come to room temperature before being opened to the atmosphere. 0.80 mmol of tetra-n-butylammonium fluoride is added slowly as a 1.0 M solution in tetrahydrofuran and the resulting solution is heated to 65 °C and stirred for 2 hours. The crude reaction solution is subsequently added directly to a 10 g Biotage SNAP silica-packed column where it is purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate in hexanes.

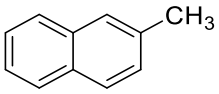
General procedure B – glovebox free conditions

To an 8 mL screw-top test-tube, 0.20 mmol of methyl ester starting material is added alongside a micro-stir bar. 0.20 mmol Mn, 0.02 mmol $NiBr_2$·glyme, 0.04 mmol ICy·HBF_4 and 0.20 mmol of KO^{t}Bu are subsequently added. 0.8 mL of toluene is introduced to the test-tube, followed by 0.40 mmol of 1,1,3,3-tetramethyldisiloxane. The reaction vessel is quickly sealed with a Teflon-septa equipped cap and stirred inside of a mineral-oil bath at 600 rpm for 10 hours at 110 °C. After 10 hours, the reaction vessel is allowed to come to room temperature before being opened to the atmosphere. 0.80 mmol of tetra-n-butylammonium fluoride is added slowly as a 1.0 M solution in tetrahydrofuran and the resulting solution is heated to 65 °C and stirred for 2 hours. The crude reaction solution is subsequently added directly to a 10 g Biotage SNAP silica-packed column where it is purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate in hexanes.

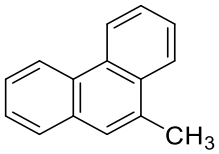
4.2 Reaction products and characterization data



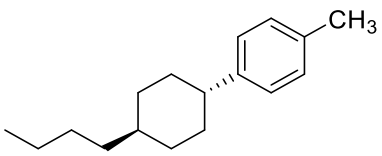
4-Methyl-1,1'-biphenyl (3) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**3**) as a yellow liquid (30 mg, 86% yield). The reaction was repeated according to general procedure B (24 mg, 73% yield). Characterization data matched those previously reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62-7.60 (d*, J* = 7.8 Hz, 2H), 7.54-7.42 (t, *J* = 8.4 Hz, 2H), 7.37-7.33 (d*, J* = 7.8 Hz, 2H), 7.29-7.27 (d, *J* = 7.8 Hz, 2H), 7.25 (m, 1H) 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): 141.1, 138.3, 136.9, 129.4, 127.6, 126.9, 126.8, 126.9, 21.0.



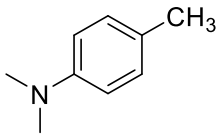
2-Methylnaphthalene (4) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**4**) as an off-white solid (26 mg, 76% yield). The reaction was repeated according to general procedure B (22 mg, 70% yield). Characterization data matched those previously reported.[14] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80-7.78 (d, *J* = 8.0 Hz, 3H), 7.79 (m, 1H), 7.45-7.41 (m, 2H), 7.37-7.34 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 135.4, 133.6, 131.7, 128.0, 127.6, 127.5, 127.1, 126.0, 125.7, 124.9, 21.6.



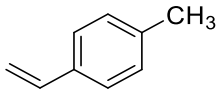
9-Methylphenanthrene (5) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**5**) as a faint yellow solid (32 mg, 73% yield). Characterization data matched those previously reported.[15] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 8.77-8.67 (m, 3H), 8.11-8.09 (m, 1H), 7.94-7.57 (m, 5H), 2.77 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 127.0, 21.1.



1-(*trans*-4-Butylcyclohexyl)-4-methylbenzene (6) was prepared according to general procedure A. Purification was done using a gradient of 1→5% EtOAc in hexane to afford (**6**) as colourless liquid (35 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11-7.10 (m, 4H), 2.46-2.39 (m, 1H), 2.32 (s, 3H), 1.90-1.85 (m, 4 H), 1.49-1.38 (m, 2H), 1.34-1.21 (m, 7H), 1.10-1.00 (m, 2H), 0.93-0.89 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 144.9, 135.1, 128.9, 126.7, 44.2, 37.3, 37.1, 34.4, 33.7, 29.2, 23.0, 20.9, 14.1; **Accurate mass (EI)**: Theoretical: 230.2035. Found: 230.2029. Spectral Accuracy: 98.5%. **Melting Point:** 164-167 °C.

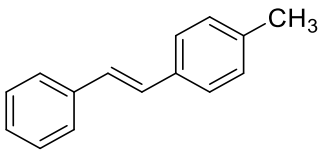


***N*,*N*,4-Trimethylaniline (7)** was prepared according to general procedure A. Purification was performed using a gradient of 1→15% ethyl acetate in hexanes to afford (**7**) as a yellow liquid (28 mg, 73% yield). The reaction was repeated in a 50 mL heavy-walled pressure tube using 5.58 mmol (1.0 g) methyl 4-(dimethylamino)benzoate, 11.2 mmol (1.97 mL) TMDSO, 5.58 mmol (626 mg) KO^{t}Bu, 0.167 mmol (46.0 mg) $Ni(cod)_2$ and 0.335 mmol (107 mg) ICy·HBF_4 in 22 mL toluene – purification was performed using column chromatography with a gradient of 1→15% ethyl acetate in hexanes to afford (**7**) as a white solid (761 mg, 77% yield). Characterization data matched those previously reported.[16] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.07-7.05 (d, J = 8.8 Hz, 2H), 6.79-6.68 (d, J = 8.8 Hz, 2H), 2.92 (s, 6H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 129.5, 129.2, 113.3, 41.1, 21.2, 21.1.

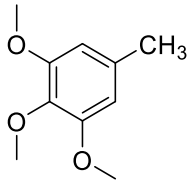


1-Methyl-4-vinylbenzene (8) was prepared according to a modified general procedure A using 1.5 equivalents of TMDSO, a reaction temperature of 90 °C and a reaction time of 6 h. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**8**) as a colourless liquid (26 mg,

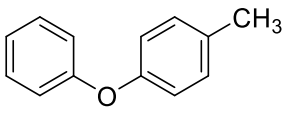
74% yield). Characterization data matched those previously reported.[17] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.36 (d, *J* = 8.2 Hz, 2H), 7.24-7.21 (d, *J* = 8.0 Hz, 2H), 6.79-6.72 (dd, *J* = 18.0, 11.4 Hz, 1H), 5.78-5.74 (dd, *J* = 18.0, 1.4 Hz, 1H), 5.26-5.23 (dd, *J* = 10.8, 1.4 Hz, 1H), 2.40 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): 137.6, 136.7, 134.9, 129.2, 126.1, 112.7, 21.2.



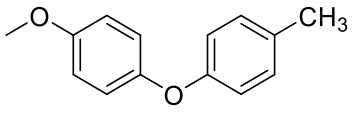
1-Methyl-4-(2-phenylethenyl)benzene (9) was prepared according to a modified general procedure A using 1.5 equivalents of TMDSO, a reaction temperature of 90 °C and a reaction time of 6 h. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**9**) as a white solid (22 mg, 71% yield). Characterization data matched those previously reported.[18] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 1H), 7.51-7.50 (m, 1H), 7.36-7.28 (m, 4H), 7.26-7.24 (m, 3H), 7.18-7.11 (m, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 131.1, 130.0, 129.0, 128.9, 128.7, 128.3, 127.5, 126.7, 126.3, 125.3, 21.4.



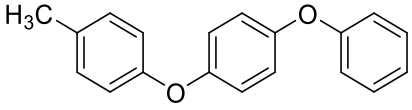
1,2,3-Trimethoxy-5-methylbenzene (10) was prepared according to general procedure A. Purification was done using a gradient of 1→5% EtOAc in hexane to afford (**10**) as colourless liquid (25 mg, 69% yield). Characterization data matched those previously reported.[19] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.40 (s, 2H), 3.82-3.79 (m, 9H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 152.9, 135.7, 133.5, 105.9, 60.8, 55.9, 21.8.



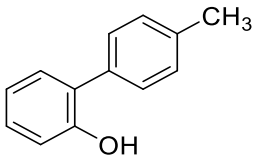
1-Methyl-4-phenoxybenzene (11) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexane to afford (**11**) as colorless solid (28 mg, 71% yield). Characterization data matched those previously reported.[20] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (t, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.13-7.10 (m, 3H), 6.91-6.88 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 158.8, 155.3, 132.4, 130.1, 129.8, 123.2, 120.4, 118.6, 20.7.



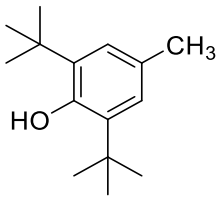
1-Methoxy-4-(*p*-tolyloxy)benzene (12) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexane to afford (**12**) as colourless liquid (26 mg, 63% yield). Characterization data matched those previously reported.[20] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10-7.07 (d, *J* = 8.2 Hz, 2H), 6.96-6.92 (d, *J* = 8.8 Hz, 2H), 6.87-6.82 (m, 4H), 3.78 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.0, 155.6, 150.7, 132.0, 130.0, 120.3, 117.8, 114.7, 55.6, 20.6.



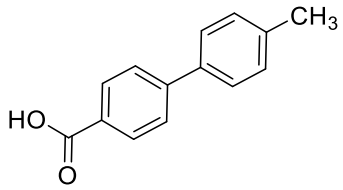
1-Methyl-4-(4-phenoxyphenoxy)benzene (13) was prepared according to general procedure A. Purification was performed using a gradient of 1→ 5% EtOAc in hexane to afford (**13**) as a colourless liquid (23 mg, 72% yield). The reaction was repeated according to general procedure B (17 mg, 64% yield). Characterization data matched those previously reported.[20] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 2H), 7.14-7.05 (m, 2H), 7.05 (t, *J* = 1.2 Hz, 1H), 7.01-6.95 (m, 6H), 6.93-6.89 (m, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 157.9, 155.2, 153.3, 152.3, 132.6, 130.2, 129.7, 122.9, 120.4, 119.9, 118.5, 118.1, 20.7.



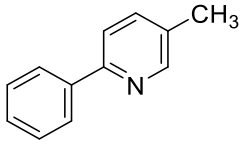
4'-Methyl-[1,1'-biphenyl]-2-ol (14) was prepared according to general procedure A. After the TBAF workup, the reaction solution was quenched with 1.0 M HCl. A liquid-liquid extraction was performed with 2 x 5 mL of ethyl acetate – the resulting organic fractions were collected and solvent was evaporated via rotary evaporation. The subsequent crude mixture was redissolved in 0.8 mL of dichloromethane and purified on a Combiflash Rf automated chromatography instrument using a gradient of 1→5% EtOAc in hexane to afford (**14**) as yellow liquid (19 mg, 66% yield). Characterization data matched those previously reported.[21] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.29-7.27 (m, 2H), 7.25-7.19 (m, 2H), 6.98-6.94 (m, 2H), 5.18 (s, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 152.4, 137.7, 133.9, 130.1, 130.0, 129.0, 128.9, 128.0, 120.7, 115.6, 21.2.



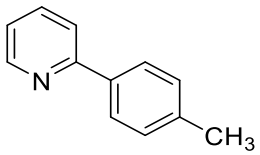
2,6-Bis(1,1-dimethylethyl)-4-methylphenol (15) was prepared according to the general procedure A, modified to use a reaction temperature of 90 °C and a reaction time of 6 h. After the TBAF workup, the reaction solution was quenched with 1.0 M HCl. A liquid-liquid extraction was performed with 2 x 5 mL of ethyl acetate – the resulting organic fractions were collected and solvent was evaporated via rotary evaporation. The subsequent crude mixture was dissolved in 0.8 mL of dichloromethane and purified on a Combiflash Rf automated chromatography instrument using a gradient of 1→5% EtOAc in hexanes to afford (**15**) as an off-white solid (23 mg, 81% yield). The reaction was repeated according to general procedure B (15 mg, 67% yield). Characterization data matched those previously reported.[22] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.06 (s, 2H), 5.08 (s, 1H), 2.36 (s, 3H), 1.52 (t, J = 7.8 Hz; 0.8 Hz, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$): 151.6, 135.8, 128.3, 125.6, 34.3, 30.4. 21.3.



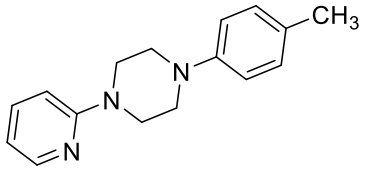
4'-Methyl-4-biphenylcarboxylic acid (16) was prepared according to a modified general procedure A, employing 2.2 equivalents of KO^{t}Bu rather than 1.0 equivalent. After the TBAF workup, the reaction solution was quenched with 1.0 M HCl. A liquid-liquid extraction was performed with 2 x 5 mL of ethyl acetate – the resulting organic fractions were collected and solvent was evaporated via rotary evaporation. The subsequent crude mixture was redissolved in 0.8 mL of dichloromethane and purified on a Combiflash Rf automated chromatography instrument using a gradient of 10→45% EtOAc in hexane to afford (**16**) as an off-white solid (29 mg, 82% yield). Characterization data matched those previously reported.[52] **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.00-7.97 (m, 2H), 7.77-7.68 (m, 2H), 7.64-7.51 (m, 2H), 6.97-6.95 (m, 2H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): 166.9, 141.7, 140.3, 138.1, 132.3, 130.4, 129.9, 127.4, 127.1, 20.4. **Accurate mass (EI)**: Theoretical: 212.0804. Found: 212.0794. Spectral Accuracy: 96.8%. **FT-IR**: ν (cm^{-1}) 2953, 2901, 1678, 1611, 1420, 1326, 1291. **mp:** 241-244 °C.



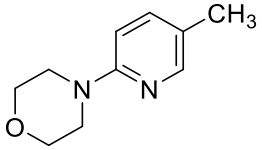
5-Methyl-2-phenylpyridine (17) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexane to afford (**17**) as colorless solid (29 mg, 73% yield). Characterization data matched those previously reported.[24] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 (d, J = 2.0 Hz, 1H), 7.95-7.92 (m, 2H), 7.62-7.60 (m, 1H), 7.55-7.53 (m, 1H), 7.46-7.41 (m, 2H), 7.39-7.34 (m, 1H), 2.35 (s, 3H); **13C NMR** (100 MHz, $CDCl_3$): 154.7, 150.0, 139.3, 137.4, 131.7, 128.7, 128.6, 126.7, 120.1, 18.2.



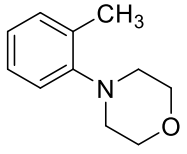
2-(*p*-Tolyl)pyridine (18) was prepared according to the general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexane to afford (**18**) as colorless liquid (26 mg, 78% yield). Characterization data matched those previously reported.[25] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.67-8.65 (d, J = 8.4 Hz, 1H), 7.89-7.86 (m, 2H), 7.77-7.67 (m, 2H), 7.27-7.24 (d, J = 8.0 Hz, 2H), 7.19-7.16 (m, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 157.4, 149.5, 138.9, 136.7, 136.6, 129.4, 126.7, 121.7, 120.2, 21.2.



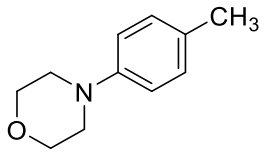
1-(4-Methylphenyl)-4-phenylpiperazine (19) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**19**) as a white solid (28 mg, 67% yield). Characterization data matched those previously reported.[26] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (m, 1H), 7.51-7.47 (m, 1H), 7.10-7.07 (m, 1H), 6.90-6.88 (m, 2H), 6.70-6.62 (m, 3H), 3.70-3.68 (m, 4H), 3.25-3.21 (m, 4H), 2.27 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): 159.4, 149.2, 147.9, 137.5, 129.7, 116.7, 113.5, 107.2, 49.8, 45.3, 30.9, 20.4.



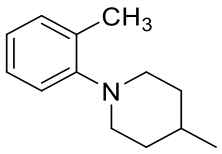
4-(5-Methyl-2-pyridinyl)-morpholine (20) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**20**) as a white solid (28 mg, 78% yield). Characterization data matched those previously reported.[26] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 (m, 1H), 7.35-7.32 (m, 1H), 6.68-6.56 (m, 1H), 3.81 (m, 4H), 3.43 (m, 4H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 158.1, 147.5, 138.4, 122.8, 106.8, 68.7, 46.1, 17.1.



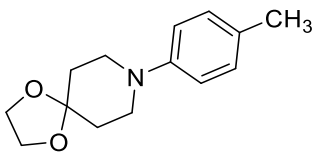
4-(2-Methylphenyl)-morpholine (21) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**21**) as a white solid (25 mg, 73% yield). Characterization data matched those previously reported.[27] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21-7.18 (m, 2H), 7.05-6.98 (m, 2H), 3.87-3.85 (m, 4H), 2.93-2.91 (m, 4H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 167.0, 153.9, 138.4, 137.6, 131.2, 120.1, 113.6, 107.1, 51.6, 47.2, 44.8.



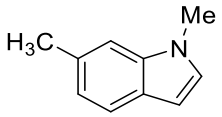
4-(*p*-Tolyl)morpholine (22) was prepared according to general procedure A. Purification was done using a gradient of 1→5% EtOAc in hexanes to afford (**22**) as off-white solid (27 mg, 77% yield). The reaction was repeated according to general procedure B (21 mg, 71% yield). Characterization data matched those previously reported.[27] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.08 (d, J = 6.8 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 3.85 (m, 4H), 3.10 (t, J = 4.8 Hz, 4H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.1, 129.6, 129.5, 115.9, 66.9, 49.8, 20.3.



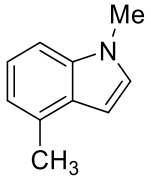
4-Methyl-1-(*o*-tolyl)piperidine (23) was prepared according to general procedure A. Purification was done a gradient of 1→5% EtOAc in hexane to afford (**23**) as colorless liquid (24 mg, 72% yield). Characterization data matched those previously reported.[28] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16-7.11 (m, 2H), 7.00-6.91 (m, 2H), 3.09-3.06 (t, J = 8.4 Hz, 2H), 2.64-2.57 (dt, J = 8.6, 3.4 Hz, 2H), 2.28 (s, 3H), 1.72-1.69 (m, 2H), 1.63-1.58 (m, 1H) 1.41-1.33 (m, 2H), 0.99-0.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 168.8, 152.9, 131.4, 123.8, 120.5, 118.7, 53.1, 51.9, 34.5, 30.7, 21.9.



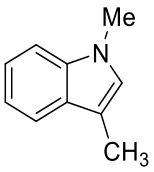
8-(4-Methylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane (24) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford **(24**) as a white solid (31 mg, 68% yield). Characterization data matched those previously reported.[29] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.07-7.06 (m, 2H), 6.89-6.87 (m, 2H), 3.99 (s, 4H), 3.29-3.26 (m, 4H), 2.28 (s, 3H), 1.87-1.84 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): 148.4, 129.5, 128.7, 116.3, 106.9, 65.3, 48.2, 24.5, 20.1.



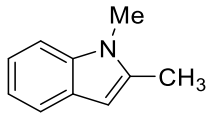
1,6-Dimethylindole (25) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**25**) as colorless liquid (26 mg, 79% yield). The reaction was repeated according to general procedure B (24 mg, 76% yield).Characterization data matched those previously reported.[30] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.55 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.15 (s, 1H), 7.00-6.98 (m, 2H), 6.48-6.46 (m, 1H), 3.77 (s, 3H) 2.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.0, 131.1, 128.1, 126.2, 121.0, 120.4, 109.1, 100.6, 32.6, 21.8.



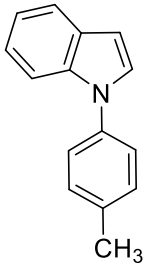
1,4-Dimethylindole (26) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**26**) as colorless liquid (22 mg, 70% yield). Characterization data matched those previously reported.[31] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.18-7.16 (m, 2H), 7.11-7.03 (d, *J* = 3.2 Hz, 1H), 6.92-6.89 (m, 1H), 6.50-6.49 (d, *J* = 3.2 Hz, 1H), 3.80 (s, 3H), 2.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 136.4, 130.3, 128.36, 128.12, 121.6, 119.5, 106.8, 99.4, 33.0, 18.7.



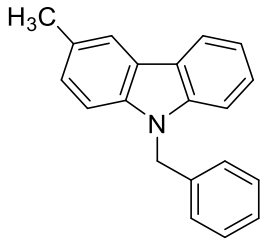
1,3-Dimethylindole (27) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**27**) as colorless liquid (16 mg, 53% yield). Characterization data matched those previously reported.[31] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65-7.62 (d, *J* = 7.5 Hz, 1H), 7.34 (m, 1H), 7.34-7.29 (m, 1H), 7.21-7.18 (t, *J* = 6.4 Hz, 1H), 6.87 (m, 1H), 3.79 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.1, 128.9, 126.7, 121.5, 119.2, 118.4, 110.1, 109.4, 32.4, 9.5.



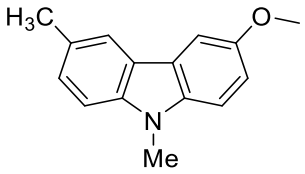
1,2-Dimethylindole (28) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**28**) as colorless liquid (12 mg, 41% yield). Characterization data matched those previously reported.[31] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 5.4 Hz, 1H), 7.21-7.16 (m, 2H), 6.34-6.31 (s, 1H), 3.71 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.4, 136.8, 127.8, 120.4, 119.7, 119.4, 108.7, 99.7, 29.5, 12.7.



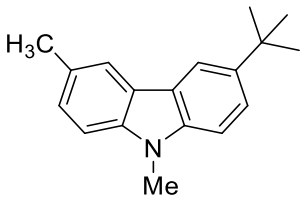
1-(*p*-Tolyl)-indole (29) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexane to afford (**29**) as yellow liquid (28 mg, 67% yield). Characterization data matched those previously reported.[32] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.40-7.38 (m, 2H), 7.32-7.30 (m, 3H), 7.23-7.14 (m, 2H), 6.67 (d, *J* = 3.2 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.2, 136.2, 135.9, 130.1, 129.1, 128.0, 124.3, 122.1, 121.0, 120.1, 110.4, 103.1, 21.0.



9-Benzyl-3-methylcarbazole (30) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**30**) as white solid (39 mg, 72% yield). Characterization data matched those previously reported.[33] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.6 Hz, 1H), 7.91 (s, 1H), 7.41-7.36 (m, 1H), 7.33-7.30 (m, 1 H), 7.25-7.18 (m, 6H), 7.12-7.10 (m, 2H), 5.48 (s, 2H), 2.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 140.8, 138.9, 137.3, 128.7, 128.5, 127.3, 127.1, 126.3, 125.6, 123.1, 122.8, 120.3, 120.2, 118.9, 108.8, 108.5, 46.5, 21.3.

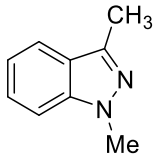


3-Methoxy-6,9-dimethyl-9H-carbazole (31) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**31**) as off-white solid (29 mg, 65% yield). Characterization data matched those previously reported.[34] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.28-7.23 (m, 3H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 3.92 (s, 2H), 3.77 (s, 3H), 2.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.4, 139.9, 136.4, 127.5, 127.0, 122.8, 122.6, 120.1, 114.6, 109.0, 108.2, 103.3, 56.1, 29.2, 21.3.

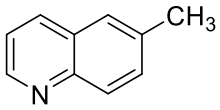


3-(*tert*-Butyl)-6,9-dimethyl-carbazole (32) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**32**) as brown solid (35 mg, 68% yield). Characterization data matched those previously reported.[34] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, J

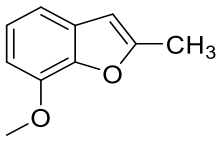
= 2.0 Hz, 1H), 7.89 (s, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.25 (s, 2H), 3.79 (s, 3H), 2.53 (s, 3H), 1.43 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): 141.5, 139.7, 139.4, 127.7, 126.7, 123.3, 123.0, 122.2, 120.1, 116.3, 108.0, 107.8, 34.6, 32.0, 29.1, 21.4.



1,3-Dimethylindazole (33) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**33**) as yellow liquid (17 mg, 59% yield). Characterization data matched those previously reported.[35] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.63 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.37-7.28 (m, 2H), 7.11-7.07 (m, 1H), 3.98 (s, 3H) 2.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 141.2, 140.8, 126.1, 123.2, 120.3, 119.5, 108.7, 35.0, 11.8.

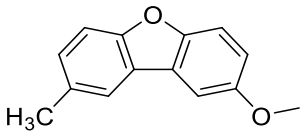


6-Methylquinoline (34) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**34**) as a yellow-green oil (23 mg, 63% yield). Characterization data matched those previously reported.[23] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 8.86 (m, 1H), 8.08-8.01 (m, 2H), 7.58-7.55 (m, 2H), 7.38-7.35 (m, 1H), 2.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.1, 146.7, 136.3, 135.1, 130.2, 128.1, 127.5, 125.9, 120.8, 21.6.

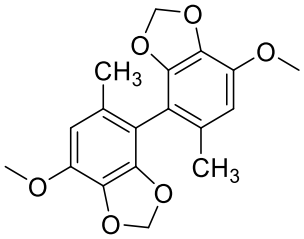


7-Methoxy-2-methylbenzofuran (35) was prepared according to a modified general procedure A using a reaction temperature of 90 °C and a reaction time of 6 h Purification was done by CombiFlash column

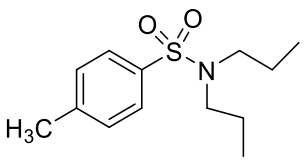
chromatography followed by preparatory TLC using a gradient of 1→5% EtOAc in hexanes to afford (**35**) as colourless liquid (21 mg, 63% yield). Characterization data matched those previously reported.[36] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.10-7.04 (m, 2H), 6.71 (dd, *J* = 7.2, J = 1.6 Hz, 1H), 6.34 (s, 1H), 3.98 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 155.5, 144.8, 143.7, 130.7, 123.0, 112.6, 105.3, 102.9, 55.9, 14.0.



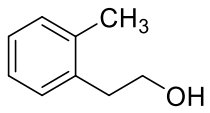
2-Methoxy-8-methyl-dibenzofuran (36) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**36**) as a white solid (26 mg, 81% yield). Characterization data matched those previously reported.[37] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.71-7.69 (s, 2H), 7.46-7.38 (m, 3H), 7.06-7.01 (m, 1H), 3.91 (s, 3H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 155.7, 155.2, 151.1, 131.8, 128.2, 124.6, 124.4, 120.5, 114.9, 112.0, 111.2, 103.6, 56.0, 21.3.



7,7'-Dimethoxy-5,5'-dimethyl-4,4'-bibenzo[d][1,3]dioxole (37) was prepared according to a modified general procedure A using 4.0 equivalents of TMDSO and 2.0 equivalents of KO^{t}Bu. Purification was performed using a gradient of 1→10% ethyl acetate in hexanes to afford (**37**) as a white solid (38 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.43-7.31 (m, 2H), 6.08-6.07 (m, 4H), 3.82 (s, 6H), 2.51 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 147.1, 142.3, 138.1, 137.7, 110.9, 102.2, 56.3, 51.7, 21.3. **Accurate mass (EI)**: Theoretical: 212.0832. Found: 212.0837. Spectral Accuracy: 96.3%. **FT-IR**: *ν* (cm^{-1}) 1718, 1626, 1489, 1422, 1389, 1220, 1085, 1010. **mp:** 148-151 °C.



4-Methyl-*N*,*N*-dipropylbenzenesulfonamide (38) was prepared according to general procedure A. Purification was done using a gradient of 5→10% EtOAc in hexane to afford (**38**) as yellow liquid (19 mg, 36% yield). Characterization data matched those previously reported.[39] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 2H), 7.26 (dd, J = 8.4, 0.2 Hz, 2H), 3.05-3.01 (m, 4H), 1.57-1.47 (m, 4H), 0.84 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 142.8, 137.2, 129.5, 127.0, 50.0, 22.0, 21.4, 11.1.

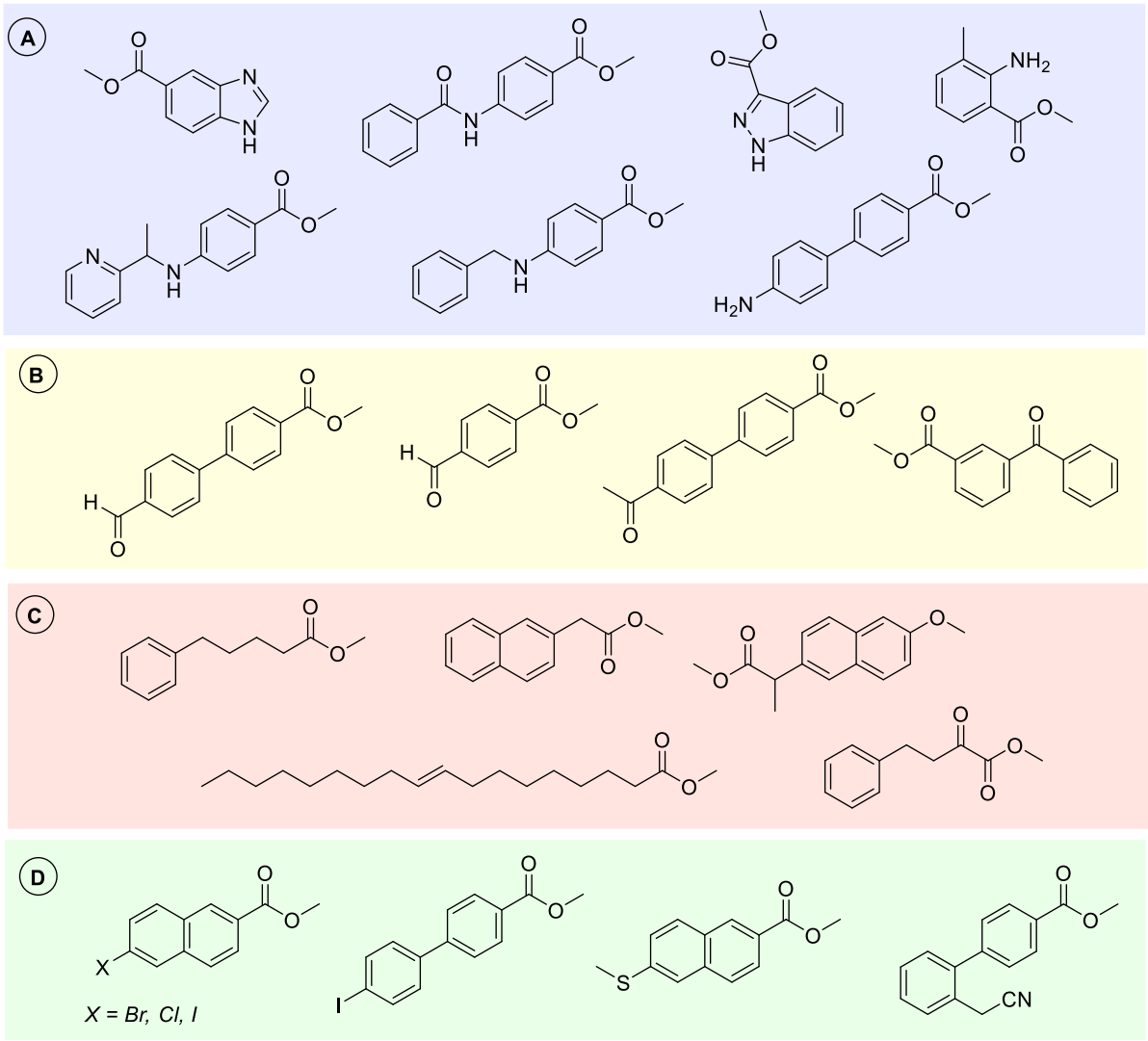


2-(Methylbenzene)ethanol (39) was prepared according to a modified general procedure A using 0.2 mmol of iso-chromanone as the starting material, a reaction temperature of 90 °C and a reaction time of 6 h. After the TBAF workup, the reaction solution was quenched with 1.0 M HCl. A liquid-liquid extraction was performed with 2 x 5 mL of ethyl acetate – the resulting organic fractions were collected and solvent was evaporated via rotary evaporation. The subsequent crude mixture was redissolved in 0.8 mL of dichloromethane and purified on a Combiflash Rf automated chromatography instrument using a gradient of 1→5% EtOAc in hexanes to afford (**39**) as an off-white solid (21 mg, 74% yield). Characterization data matched those previously reported.[38] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29-7.17 (m, 4H), 3.71-3.66 (m, 2H), 3.22 (m, 2H), 2.37(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.7, 128.9, 128.8, 128.1, 125.9, 125.1, 57.7, 21.2, 18.0.

5. Troubleshooting

5.1. Scope Limitations

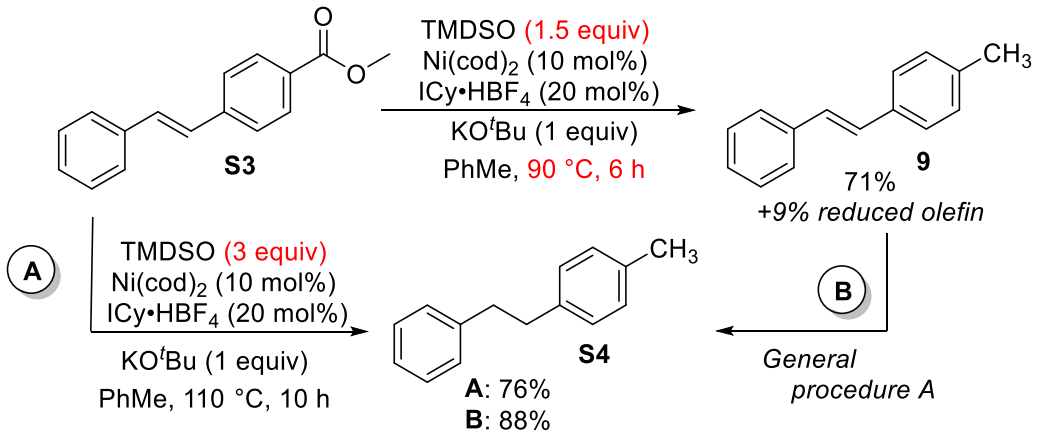
Several substrates, particularly those with free NH bonds, were found to be inert to the reaction conditions, instead giving recovery of starting material (Scheme S3A). Substrates with other carbonyl functionalities such as aldehydes and ketones were found to over-reduce to the corresponding methyl or methylene-containing products (Scheme S3B). Further, substrates bearing aliphatic esters, rather than aryl esters, were only found to reduce to the alcohol oxidation state (Scheme S3C). Lastly, esters bearing carbon-halogen bonds, carbon-sulfur bonds and select other functional groups were found to give intractable mixtures of products (Scheme S3D).



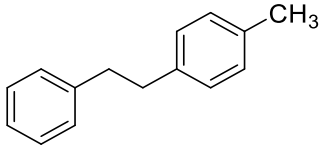
Scheme S3. Unsuccessful scope examples

5.2. Improving moderate yields

Several substrates afforded relatively low yields when subjected to the 'optimal' conditions. In general, yields could be improved by increasing the catalyst loading. In many cases, substrate-specific optimization resulted in improved yields without necessitating more catalyst. For instance, Substrate **S3**, bearing a stilbene backbone, was found to give desired product **9** upon reaction with 1.5 equivalents TMDSO at 90 °C for 6 h. Upon treatment with the general reaction conditions, product **S4** could be recovered. Further, **S4** could be recovered from substrate **S3** upon reaction with 3 equivalents of TMDSO.

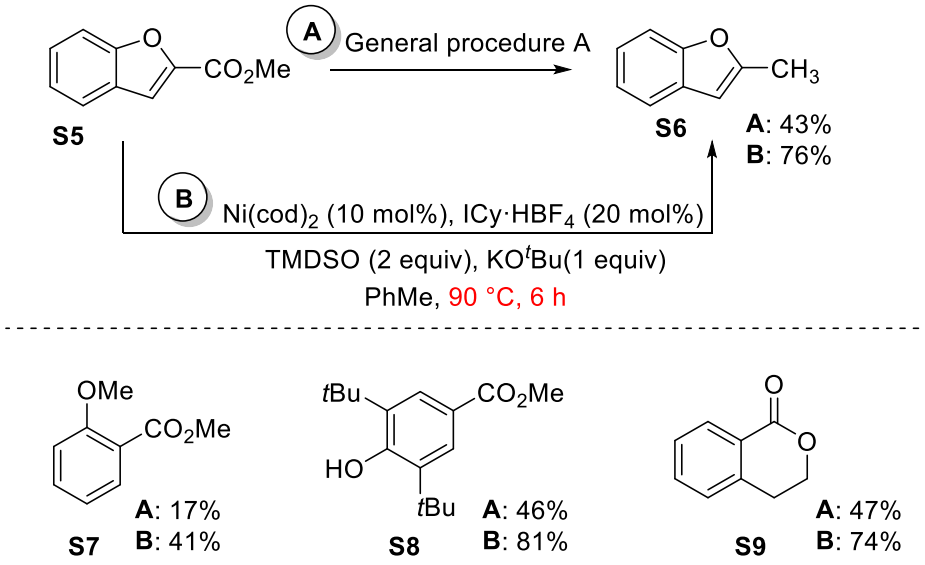


Scheme S4. Depicting control over olefin-containing ester substrates



1-Methyl-4-(2-phenethyl)benzene (**S4**) was prepared according to general procedure A. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**S4**) as a white solid (22 mg, 61% yield). Characterization data matched those previously reported.[40] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.44 (d, J = 8.2 Hz, 2H), 7.34-7.32 (d, J = 8.0 Hz, 2H), 7.14-7.11 (m, 3H), 7.01-6.93 (m, 2H), 2.92-2.89 (m, 4H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 143.4, 137.6, 134.3, 128.3, 128.1, 127.3, 125.7, 39.4, 36.1, 20.5.

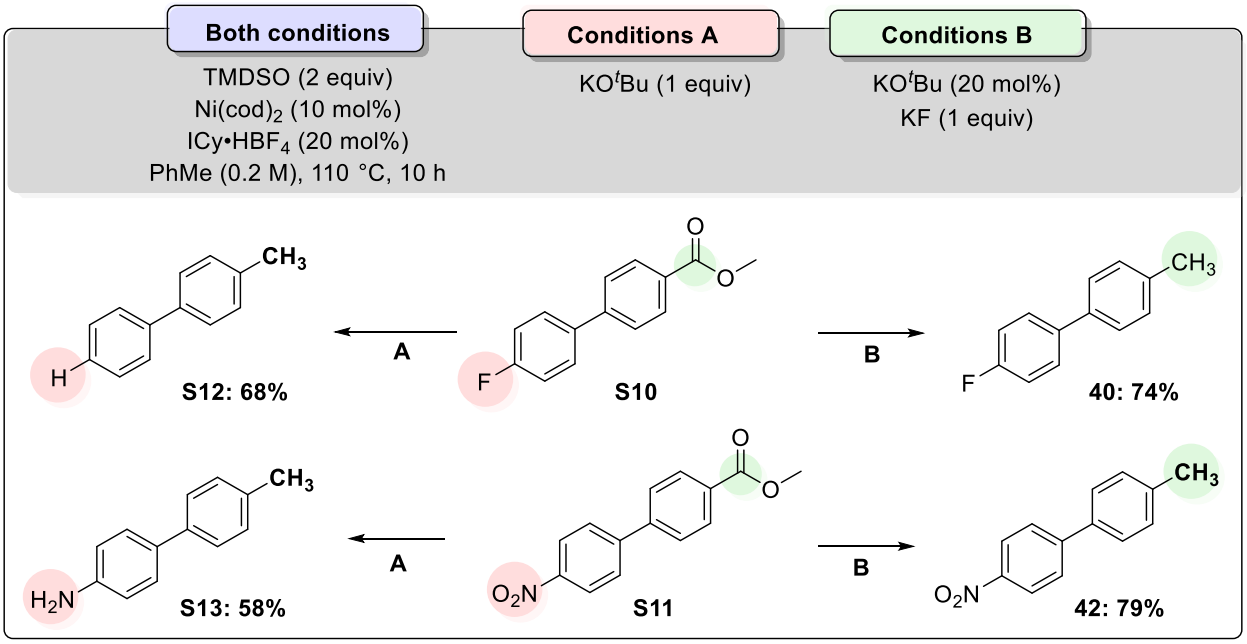
Substrate-specific optimization was performed on esters **S5**, **S7**, **S8** and **S9** after noting their modest yields upon exposure to the general procedure A. Higher yields could be obtained upon lowering the reaction temperature to 90 °C and shortening the reaction time to 6 h.



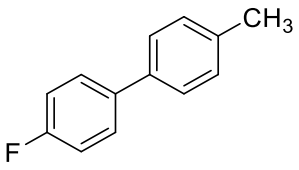
Scheme S5. Improved yields at reduced temperature and time

5.3. Employing a "weaker" reducing agent

Products **40-45** were obtained upon substituting KF (1 eq) + KO^{t}Bu (20 mol%) for KO^{t}Bu (1 eq). Under our original conditions, we tentatively propose that 20 mol% KO^{t}Bu was used to deprotonate the ICy·HBF$_4$ while the remainder went towards the formation of an activated, hypervalent siloxane reducing agent. Under these modified conditions, we propose that the KO^{t}Bu (20 mol%) was used to deprotonate the ICy·HBF$_4$ ligand while the KF was used to activate the siloxane species. Results obtained upon exposing substrates **S10** and **S11** bearing nitro groups and C-F bonds lead us to believe that combining TMDSO and KF creates a weaker reducing agent than does the combination of TMDSO and KO^{t}Bu.

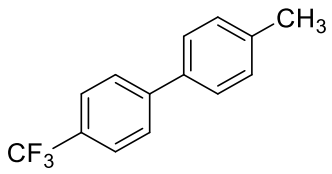


Scheme S6. Illustrating the deviations between using KF + KO^{t}Bu or using only KO^{t}Bu

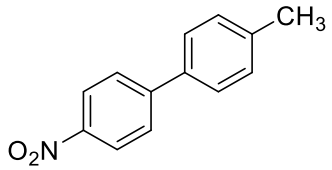


4-Fluoro-4'-methylbiphenyl (**40**) was prepared according to a modified general procedure A, employing 1.0 equivalent of KF and 20 mol% KO^{t}Bu in place of 1.0 equivalent KO^{t}Bu. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**40**) as a white solid (25 mg, 74% yield). Characterization data matched those previously reported.[53] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.38 (m,

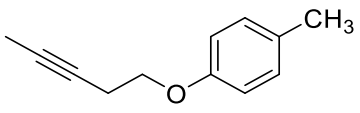
2H), 7.36-7.34 (m, 2H), 7.30-7.28 (m, 2H), 7.20-7.07 (m, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 161.9, 161.7, 136.2, 130.3, 129.1, 128.2, 123.9, 115.4, 20.8. **Accurate mass (EI)**: Theoretical: 186.0813. Found: 186.0816. Spectral Accuracy: 97.4%. **mp:** 79-81 °C.



4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (**41**) was prepared according to a modified general procedure A, employing 1.0 equivalent of KF and 20 mol% KO^{t}Bu in place of 1.0 equivalent KO^{t}Bu. Purification was performed using a gradient of 1→25% ethyl acetate in hexanes to afford (**41**) as an off-white solid (28 mg, 84% yield). Characterization data matched those previously reported.[54] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.54 (m, 2H), 7.49-7.47 (m, 2H), 7.45-7.42 (m, 2H), 7.38-7.36 (m, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 142.1, 138.2, 136.8, 129.2, 128.7, 126.8, 125.9, 124.3, 123.9, 21.4. **Accurate mass (EI)**: Theoretical: 236.0846. Found: 236.0839. Spectral Accuracy: 94.6%. **mp:** 119-122 °C.

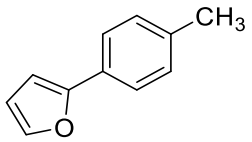


4-Methyl-4'-nitrobiphenyl (**42**) was prepared according to a modified general procedure A, employing 1.0 equivalent of KF and 20 mol% KO^{t}Bu in place of 1.0 equivalent KO^{t}Bu. Purification was performed using a gradient of 10→45% ethyl acetate in hexanes to afford (**42**) as a white solid (26 mg, 79% yield). Characterization data matched those previously reported.[55] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33-8.28 (m, 2H), 7.65-7.63 (m, 2H), 7.55-7.48 (m, 2H), 7.34-7.30 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 147.6, 138.8, 129.9, 128.7, 127.8, 127.4, 124.1, 21.2. **Accurate mass (EI)**: Theoretical: 213.0789 Found: 236.0806. Spectral Accuracy: 96.6%. **mp:** 139-142 °C.

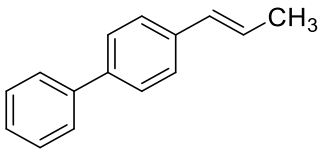


1-Methyl-4-(3-pentyn-1-yloxy)-benzene (**43**) was prepared according to a modified general procedure A, employing 1.0 equivalent of KF and 20 mol% KO^{t}Bu in place of 1.0 equivalent KO^{t}Bu. Purification was performed using a gradient of 1→25% ethyl acetate in hexanes to afford (**43**) as a white solid (20 mg, 68%

yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58-7.41 (m, 2H), 7.39-7.23 (m, 2H), 3.68-3.64 (m, 4H), 2.41-2.37 (m, 3H), 1.79 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 140.7, 137.9, 136.6, 129.0, 128.3, 126.5, 75.3, 61.0, 22.6, 20.6, 3.0. **Accurate mass (EI)**: Theoretical: 174.1340. Found: 174.1321 Spectral Accuracy: 97.1%. **mp:** 121-124 °C.



2-(4-Methylphenyl)furan (**44**) was prepared according to a modified general procedure A, employing 1.0 equivalent of KF and 20 mol% KO^{t}Bu in place of 1.0 equivalent KO^{t}Bu. Purification was performed using a gradient of 1→15% ethyl acetate in hexanes to afford (**44**) as a white solid (24 mg, 71% yield). Characterization data matched those previously reported.[56] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59-7.57 (d, J = 8.2 Hz, 2H), 7.48-7.37 (m, 3H), 6.95-6.93 (m, 1H), 6.47-6.46 (m, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 143.5, 140.1, 137.4, 137.3, 137.2, 131.2, 131.2, 113.4, 99.5, 90.2, 20.1. **FT-IR**: ν (cm^{-1}) 3286, 1634, 1440, 1344, 1280, 1130, 1092, 1068, 630. **Accurate mass (EI)**: Theoretical: 158.0731. Found: 158.0727. Spectral Accuracy: 95.6%.



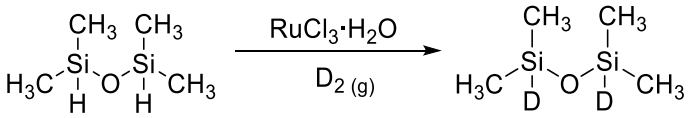
4-(1-Propen-1-yl)-1,1'-biphenyl (**45**) was prepared according to a modified general procedure A, employing 1.0 equivalent of KF and 20 mol% KO^{t}Bu in place of 1.0 equivalent KO^{t}Bu. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**45**) as an off-white solid (17 mg, 48% yield). Characterization data matched those previously reported.[57] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 2H), 7.43-7.36 (m, 2H), 7.24-7.18 (m, 2H), 7.07-7.05 (m, 3H), 6.32-6.28 (m, 2H), 2.16 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 144.8, 136.2, 134.4, 130.9, 130.3, 130.2, 128.8, 128.2, 128.0, 117.7, 18.8. **Accurate mass (EI)**: Theoretical: 194.1124. Found: 194.1181. Spectral Accuracy: 96.2%. **mp:** 90-94 °C.

5.4 General comments

The quality of reagents was observed to be particularly important for reproducibly obtaining the yields reported. In the conditions using $Ni(cod)_2$, any exposure to oxygen was highly detrimental. The age of the $Ni(cod)_2$ was also found to be important – in one instance, replacing an old (>6 month) bottle of $Ni(cod)_2$ with a new source resulted in substantially improved yields. While somewhat lower yielding, reactions performed using general procedure B ($NiBr_2$·glyme/Mn) were found to be more robust.

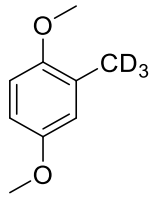
6. Additional experimental information

6.1. Catalytic deuteration



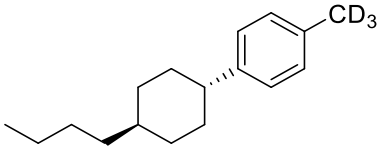
***d*$_2$-TMDSO**

In order to transform TMDSO into its deuterated analog, a modified literature procedure was used.[41] Inside of a nitrogen-filled glovebox, 10 mg $RuCl_3 \cdot H_2O$ is crushed into a fine powder and added alongside 3.0 mL of TMDSO to a 25 mL heavy-walled vacuum Schlenk tube. The tube is connected to a Buchi "tinyclave" pressure reactor and sealed. The reaction vessel is subsequently brought outside of the glovebox and equipped with a deuterium gas regulator as well as to a vacuum pump via a T-shaped vacuum stopcock. The reaction vessel placed in a liquid nitrogen bath for 5 minutes, until it is frozen. It is subsequently placed under vacuum for 20 seconds, at which point the vacuum is removed and the reaction mixture is allowed to come to room temperature. After the mixture turns back into liquid, D_2 (g) is introduced to the pressure tube to a gauge pressure of 10-12 psi. The reactor is sealed and stirred rapidly for 1 h at room temperature. After 1 h, the reaction vessel is placed in a liquid nitrogen bath until the TMDSO solution freezes, at which point the vessel was placed under vacuum for 10 seconds. After evacuating, the pressure tube is brought out of the liquid nitrogen bath and allowed to return to room temperature. Once at room temperature, D_2 was reapplied at the same pressure. This cycle (pressurize vessel, stir, freeze-pump-thaw) was repeated 6 times, until analysis of an aliquot by ^{1}H NMR showed >95% deuterium incorporation. The spectroscopically pure *d*$_2$-TMDSO (61% yield) can be purified by distillation to remove remaining $RuCl_3$;[41] however, this was not found to be necessary. The crude material was thus used in subsequent reduction reactions without further purification as a black, translucent liquid.

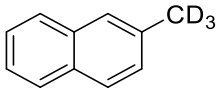


1,4-dimethoxy-2-(methyl-d_3)benzene

1,4-Dimethoxy-2-(methyl-d_3)benzene (46) was prepared according to general procedure B using d_2-TMDSO in d_8-toluene (use of non-deuterated toluene provides slightly reduced deuterium incorporation). Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**46**) as a white solid (23 mg, 68% yield, >95% D). Characterization data matches the literature for the analogous non-deuterated compound.[42] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.69-6.59 (m, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 2.26 (s, <0.08 H); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.1, 152.8, 152.7, 129.2, 114.5, 110.7, 58.3, 58.2, 18.6 (m, CD_3).

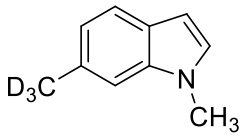


(d_3)-1-(*trans*-4-Butylcyclohexyl)-4-methylbenzene (**47**) was prepared according to general procedure B using d_2-TMDSO in d_8-toluene. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**47**) as a white solid (31 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11-7.10 (m, 4H), 2.46-2.39 (m, 1H), 2.32 (s, <0.08 H) 1.90-1.85 (m, 4 H), 1.49-1.38 (m, 2H), 1.34-1.21 (m, 7H), 1.10-1.00 (m, 2H), 0.93-0.89 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 144.9, 135.1, 128.9, 126.7, 44.2, 37.3, 37.1, 34.4, 33.7, 29.2, 23.0, 20.9, 14.1 (m, CD_3).



(d_3)-2Methylnapthalene (**48**) was prepared according to general procedure B using d_2-TMDSO in d_8-toluene. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**48**) as a white solid (23 mg, 68% yield). Characterization data matches the literature for the analogous non-deuterated compound.[14] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80-7.78 (d, J = 8.0 Hz, 3H), 7.79 (m, 1H), 7.45-7.41

(m, 2H), 7.37-7.34 (d, J = 8.4 Hz, 1H), 2.51 (s, <0.07 M); **^{13}C NMR** (100 MHz, $CDCl_3$): 135.4, 133.6, 131.7, 128.0, 127.6, 127.5, 127.1, 126.0, 125.7, 124.9, 21.6 (m, CD_3).



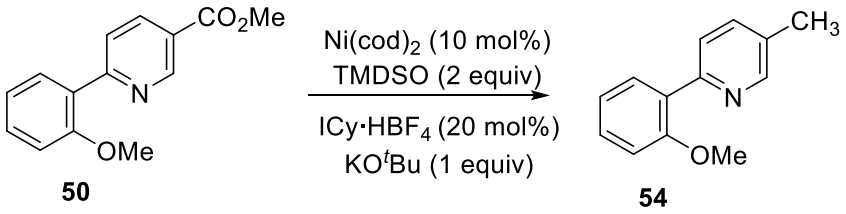
(*d*$_3$)-*N*-Methyl-6-methylindole (**49**) was prepared according to general procedure B using d_2-TMDSO in d_8-toluene. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**49**) as a white solid (23 mg, 65% yield). Characterization data matches the literature for the analogous non-deuterated compound.[30] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.15 (s, 1H), 7.00-6.98 (m, 2H), 6.48-6.46 (m, 1H), 3.77 (s, 3H), 2.53 (s, <0.07 H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.0, 131.1, 128.1, 126.2, 121.0, 120.4, 109.1, 100.6, 32.6, 21.8 (m, CD_3).

6.2. Chemoselectivity between ester reduction and ethereal cleavage

Ester reduction using the Ni/TMDSO/ICy/KO^{t}Bu system was done according to a modified general procedure A using 0.20 mmol of starting material, 0.4 mL of toluene and a reaction time of 12 h, affording products **54-57**.

General Procedure C (adopted from the method used by Martin and coworkers[43])

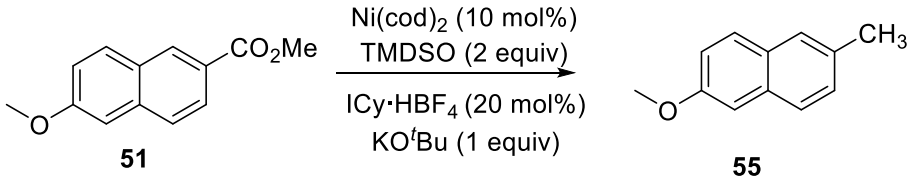
To an oven dried 8 mL screw-top test-tube, 0.20 mmol of starting material is added alongside an oven dried micro-stir bar. The screw-top test-tube is subsequently brought into a nitrogen-filled glovebox. Once under the inert atmosphere, 0.04 mmol PCy_3 and 0.02 mmol $Ni(cod)_2$ are added. 0.4 mL of toluene is added to the test-tube, followed by 0.20 mmol of 1,1,3,3-tetramethyldisiloxane. The reaction vessel is quickly sealed with a Teflon-septa equipped cap and brought outside of the glovebox, where it is stirred inside of a mineral-oil bath at 600 rpm for 12 hours at 110 °C. After 12 hours, the reaction vessel is allowed to come to room temperature before being opened to the atmosphere. 0.80 mmol of tetra-n-butylammonium fluoride is added slowly as a 1.0 M solution in tetrahydrofuran and the resulting solution is heated to 65 °C and stirred for 2 hours. The crude reaction solution is subsequently added directly to a 10 g Biotage SNAP silica-packed column where it is purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate in hexanes, affording products **58-60**.



50 **54**

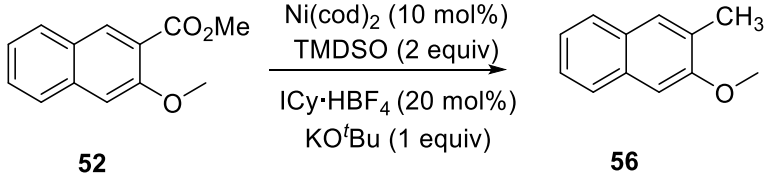
2-(2-Methoxyphenyl)-5-methylpyridine (54) was prepared according to a modified general procedure A using 0.2 mmol of starting material, 0.4 mL of toluene and a reaction time of 12 h. Purification was performed using a gradient of 1%→5% EtOAc in hexane to afford (**54**) as colorless solid (23 mg, 69% yield [76% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[44] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 (d, J = 2.4 Hz, 1H), 7.72-7.66 (m, 2H), 7.49 (dd, J = 8.4, 2.4 Hz, 1H), 7.35-7.31 (m, 1H), 7.04

(t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.9, 153.4, 149.8, 136.3, 131.1, 131.0, 129.6, 129.2, 124.5, 121.0, 111.3, 55.6, 18.2.



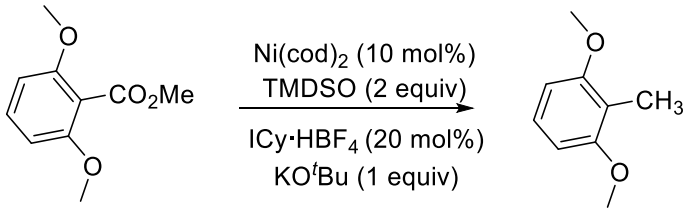
51 **55**

2-Methoxy-6-methylnaphthalene (55) was prepared according to a modified general procedure A using 0.2 mmol of starting material, 0.4 mL of toluene and a reaction time of 12 h. Purification was done a gradient of 1→5% EtOAc in hexanes to afford (**55**) as off-white solid (27 mg, 73% yield [88% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[45] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.64 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.54 (s, 1H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.13-7.10 (m, 2 H), 3.90 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 157.0, 133.0, 132.6, 129.1, 128.7, 128.5, 126.7, 126.5, 118.6, 105.6, 55.2, 21.4.



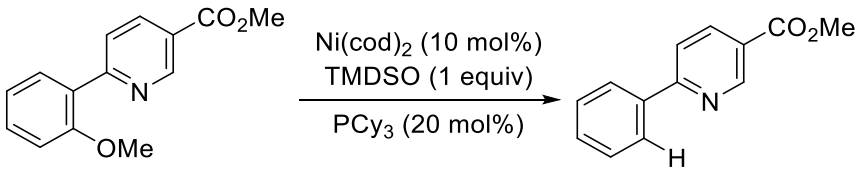
52 **56**

2-Methoxy-3-methylnapthalene (56) was prepared according to a modified general procedure A using 0.2 mmol of starting material, 0.4 mL of toluene and a reaction time of 12 h. Purification was performed using a gradient of 1→5% ethyl acetate in hexanes to afford (**56**) as an off-white solid (19 mg, 63% yield [78% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[46] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.73-7.69 (dd, *J* = 8.2, 3.4 Hz, 2H), 7.58 (m, 1H), 7.41-7.33 (m, 2H), 7.10-7.08 (m, 1H) 3.95 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 155.8, 131.1, 128.7, 126.8, 126.1, 125.3, 123.4. 104.3, 55.2, 16.8.



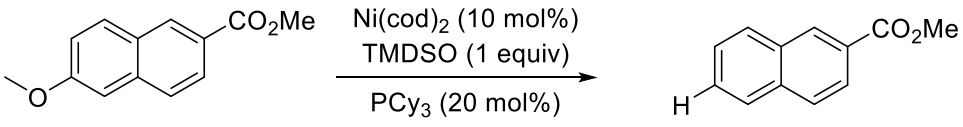
53 **57**

1,3-Dimethoxy-2-methylbenzene (57) was prepared according to a modified general procedure A using 0.2 mmol of starting material, 0.4 mL of toluene and a reaction time of 12 h. Purification was performed using a gradient of 1→5% EtOAc in hexanes to afford (**57**) as colourless solid (19 mg, 62% yield [73% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[47] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.12-7.08 (m, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 6H), 2.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 158.3, 126.1, 114.5, 103.5, 55.7, 8.1.



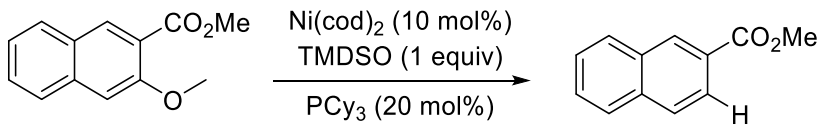
50 **58**

Methyl 5-phenylpyridine-3-carboxylate (58) was prepared according to general procedure C to afford (**58**) (25 mg, 68% yield [76% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[48] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 9.30 (s, 1H), 8.38-8.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.08-8.02 (dd, *J* = 9.0, 1.6 Hz, 2H), 7.83-7.80 (d, *J* = 8.4 Hz, 1H), 7.53-7.48 (m, 3H), 3.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 166.0, 160.8, 150.9, 138.1, 137.7, 129.8, 127.9, 124.1, 119.7, 52.3.



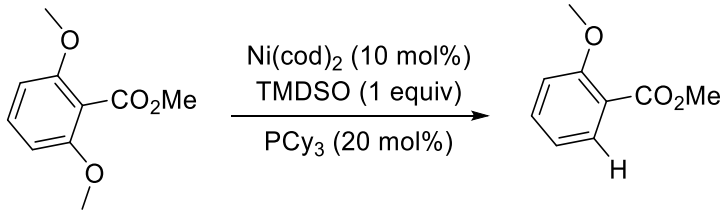
51 **59**

Methyl-2-napthoate (59) was prepared according to general procedure C to afford (**59**) (15 mg, 57% yield [60% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[43] **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 8.62 (s, 1H), 8.08-8.04 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.58-7.53 (m, 2H), 3.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 167.1, 135.3, 132.4, 129.2, 128.0, 127.7, 126.3, 124.8, 51.7.



52 **59**

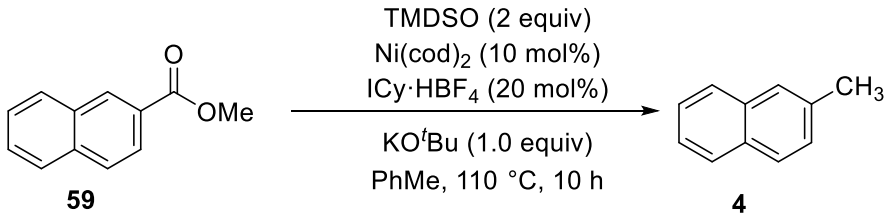
Methyl-2-napthoate (59) was prepared according general procedure C to afford (**59**) (28 mg, 79% yield [90% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[43] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.08-8.04 (dd, J = 8.6, 1.6 Hz, 1H), 7.58-7.53 (m, 2H), 3.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 167.1, 135.3, 132.4, 129.2, 128.0, 127.7, 126.3, 124.8, 51.7.



53 **60**

Methyl-2-methoxybenzoate (60) was prepared according to general procedure C to afford (**60**) (21 mg, 68% yield [78% yield via ^{1}H-NMR]). Characterization data matched those previously reported.[49] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74-7.69 (dd, J = 7.5, 1.5 Hz, 1H), 7.44-7.38 (m, 1H), 6.97-6.93 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 164.7, 158.6, 133.1, 130.8, 118.9, 117.6, 111.3, 54.7, 51.4.

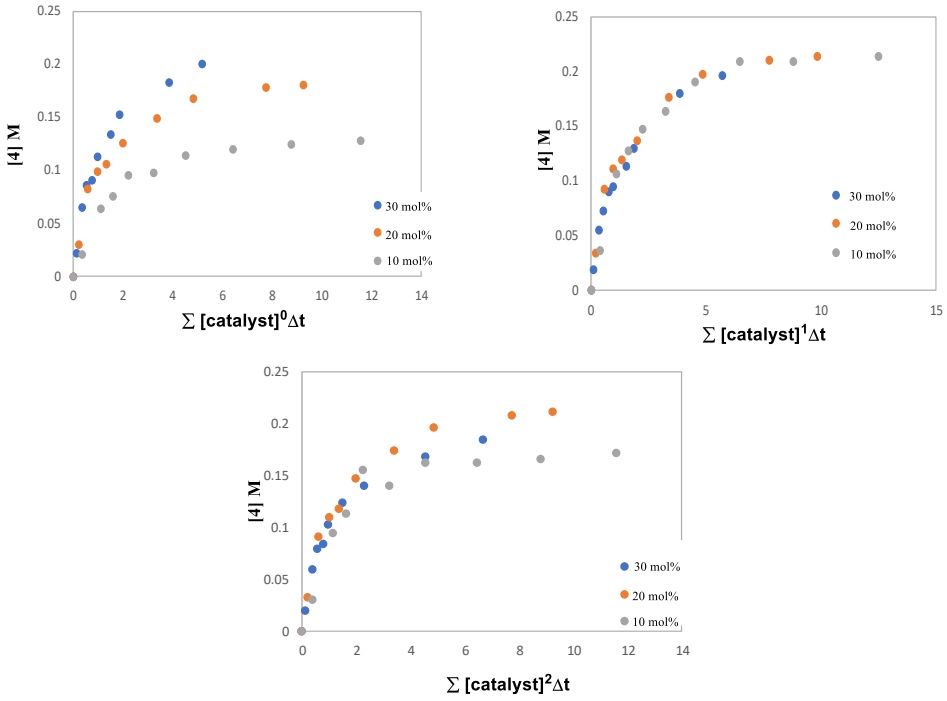
6.3. Kinetic experiments



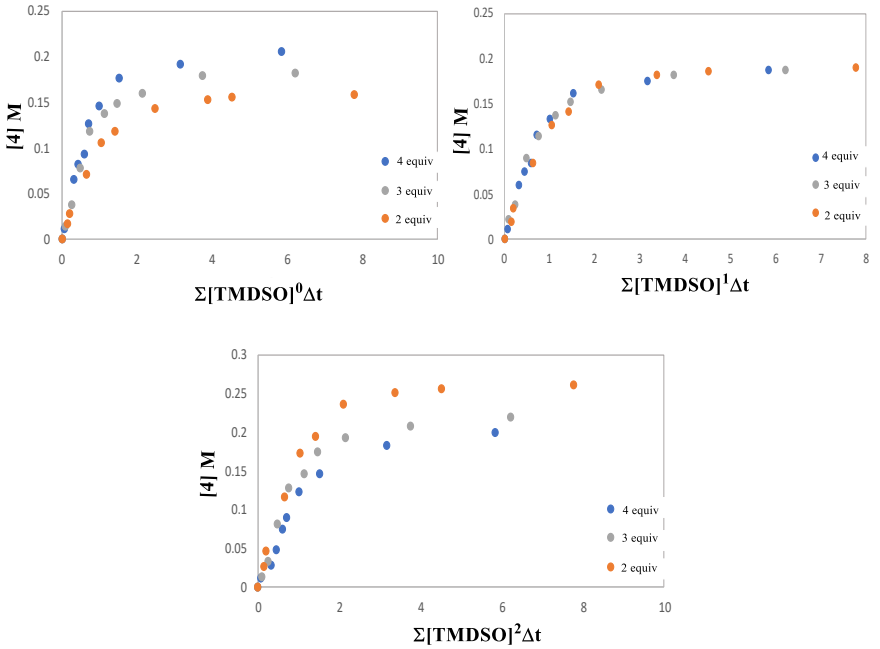
All individual kinetics experiments were performed according to general procedure A. Ten reactions were set up in parallel and stopped after 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 5 h, 7 h, 9 h and 10 h. Yields were obtained via ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. Variable time normalization analysis was conducted on the obtained time vs. yield data based on the method described by Bures and co-workers[51] in order to determine the observed rate equation.

Standard reaction conditions were 0.25 M 2-methyl naphthoate (**59**), 0.25 M KO^{t}Bu, 0.50 M TMDSO, 0.025 M Ni(cod)$_2$ and 0.05 M ICy·HBF$_4$. Scheme **S7** was generated by setting [catalyst] (Ni(cod)$_2$ + ICy·HBF$_4$, 1:2 ratio) to 0.025 M (standard conditions), 0.050 M and 0.075 M. Scheme **S8** was generated by varying [TMDSO], setting it to 0.50 M (standard conditions), 0.75 M, and 1.0 M. Scheme **S9** was generated by varying [**59**], setting it to 0.25 M (standard conditions), 0.5 M and 0.75 M. Scheme **S10** was generated by varying [KO^{t}Bu], setting it to 0.025 M (standard conditions), 0.038 M and 0.050 M.

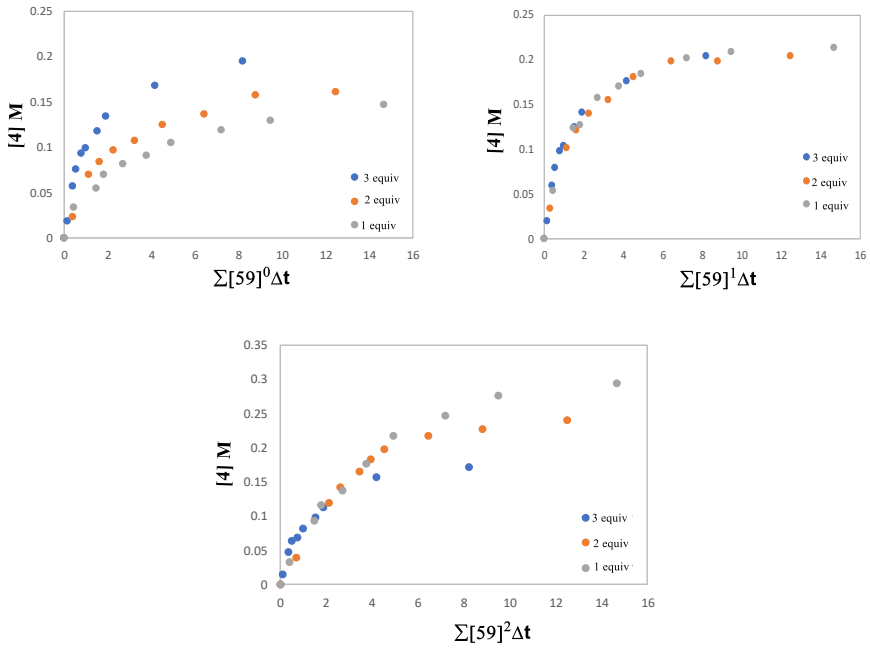
Results of these vTNA experiments indicate a positive order for all tested components, suggesting that each component plays a role in the rate-determining step. While good overlay was observed when normalizing the X axis assuming first order behavior, the current data cannot eliminate fractional orders between 0.5 to 1.5.



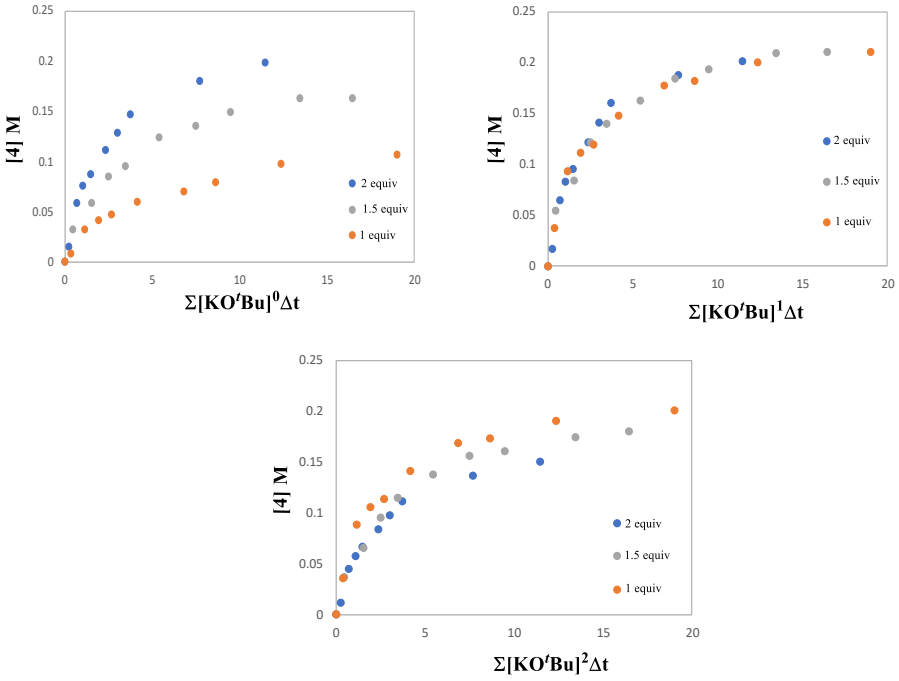
Scheme S7. Variation in catalyst: Variable time normalization plots illustrates positive order dependency.



Scheme S8. Variation in TMDSO: Variable time normalization plots illustrates positive order dependency.



Scheme S9. Variation in [59]: Variable time normalization plots illustrates positive order dependency.

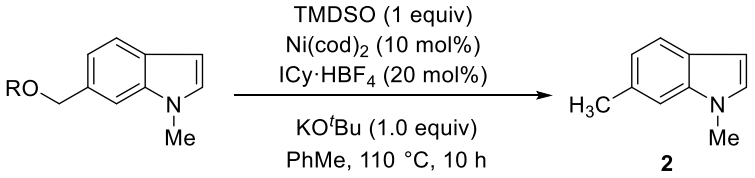


Scheme S10. Variation in KO^{t}Bu: Variable time normalization plots illustrates positive order dependency.

6.4. Reduction of proposed intermediates

To probe the catalytic reaction of benzyl alcohols, various indole-bearing alcohol derivatives were subjected to the reducing conditions to determine if this step of the reaction behaved differently in isolation (Table S8). Using 1.0 equivalents of TMDSO provided indole **2** in 58% yield (entry 1). Use of 0.6 equivalents TMDSO (formally 1.2 equivalents of hydride) gave a slightly lower yield (entry 2). As was the case in the direct reduction starting from the ester, both Ni and KO^{t}Bu were required for conversion (entries 3, 4). Removing the base from the reaction mixture failed to afford product (entry 5), however base was only required in catalytic quantity to afford product (entry 6), contrasting the results when the ester was used as starting material. Replacing KO^{t}Bu with KF failed to afford product (entry 7), presumably because KF is insufficiently basic to deprotonate the NHC ligand. Adding 20 mol% of KO^{t}Bu restored reactivity (entry 8), as did substituting KOH as the base (entry 9). Reactions performed using TBS, TMS, Me and Ph protected alcohols led to a higher yield than that which was obtained when using the unprotected analog (entries 10-19). These species are more analogous to the mixture of silyl-alcohol species that are believed to form in situ via ester hydrosilylation. Finally, the corresponding aldehyde underwent reduction upon exposure to our reaction conditions, confirming it as a viable intermediate in this reaction (entry 20).

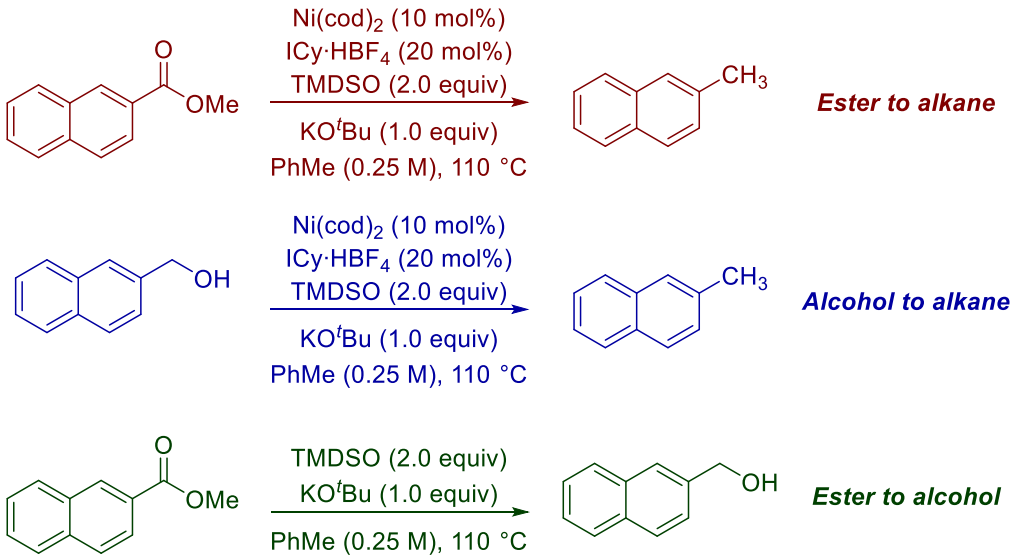
Table S8. Reduction of proposed intermediates

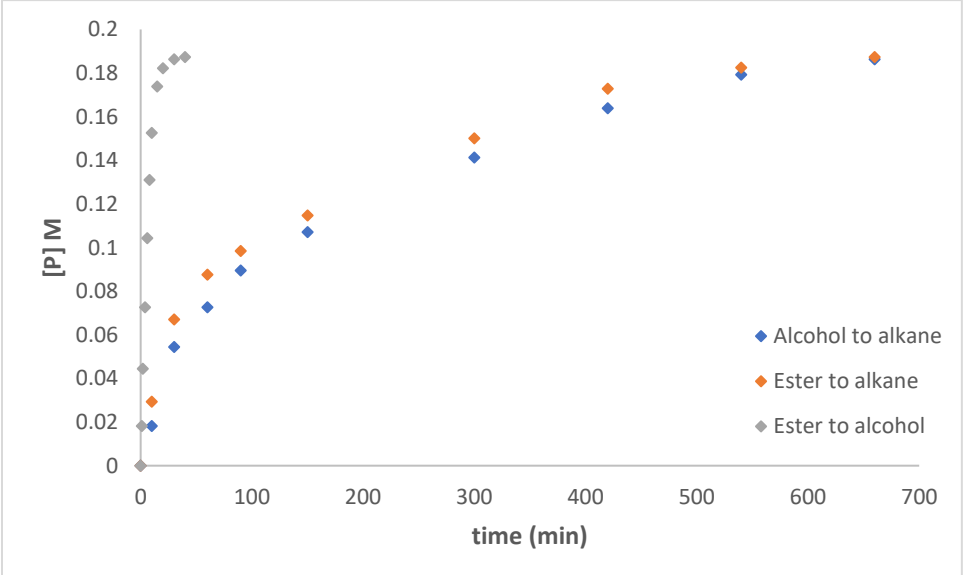


entry	R	deviation from standard conditions	yield, 2 [%]
1	R = H	none	53
2	R = H	0.6 equiv TMDSO	41
3	R = H	0.3 equiv TMDSO	18
4	R = H	No $Ni(cod)_2$	0
5	R = H	ICy (free), no base	0
6	R = H	20 mol% KO^{t}Bu	24
7	R = H	KF (1.0 equiv) *instead of KO^{t}Bu*	trace

8	R = H	KF (1.0 equiv) + 20 mol% KO^{t}Bu	47
9	R = H	KOH (1.0 equiv)	31
10	R = TBS	KF (1.0 equiv) *instead of KO*^{t}Bu	trace
11	R = TBS	KF (1.0 equiv) + 20 mol% KO^{t}Bu	74
12	R = TBS	none	74
13	R = TBS	0.6 equiv TMDSO	63
14	R = TBS	No $Ni(cod)_2$	0
15	R = TBS	ICy (free), no base	0
16	R = TMS	none	71
17	R = Me	none	77
18	R = Me	KF (1.0 eq) + 20 mol% KOtBu	70
19	R = Ph	none	51
20	-	aldehyde as starting material	73

Kinetic studies were performed in order to learn more about the fate of the methyl ester as it passes through the alcohol intermediate. Ester to alkane reduction was performed using general procedure A with methyl 2-naphthoate. Alcohol to alkane reduction was performed using general procedure A with napthalene-2-methanol as starting material. Ester to alcohol reduction was performed using a modified general procedure A, in which the catalyst and ligand were removed. The kinetic plots indicate that ester to alcohol reduction is exceptionally rapid relative to the subsequent steps.

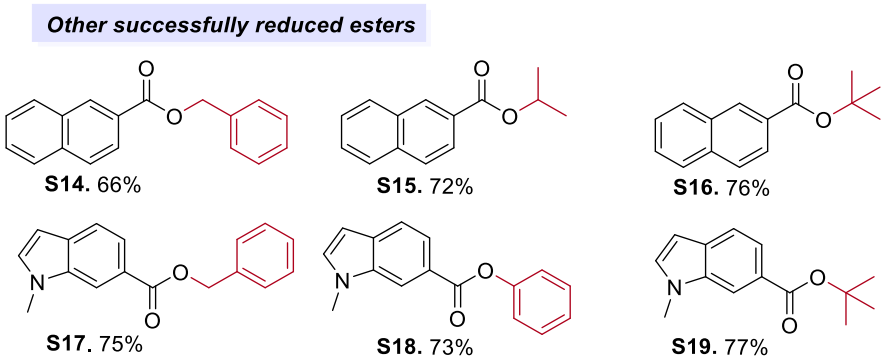




Scheme S11. Product vs. time curves for the reduction of methyl-2-napthoate and napthalene-2-methanol

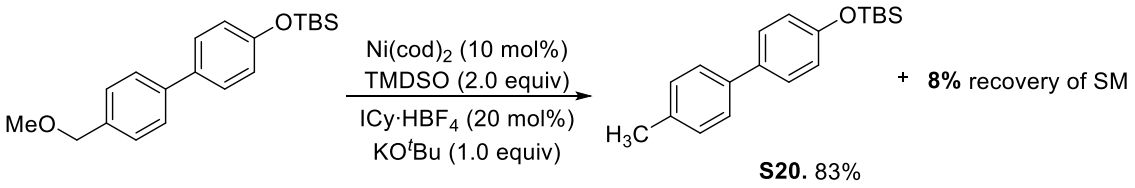
6.5. Reduction of other alkyl and aryl esters

The following esters were reduced according to general procedure A, confirming that the reaction is not limited to just the reduction of methyl esters (Scheme S10). Both ester-bearing naphthalene species (**S14-S16**) and ester-bearing indole species (**S17-S19**) were tested.



Scheme S12. Depicting the types of esters that could be reduced according to general procedure A

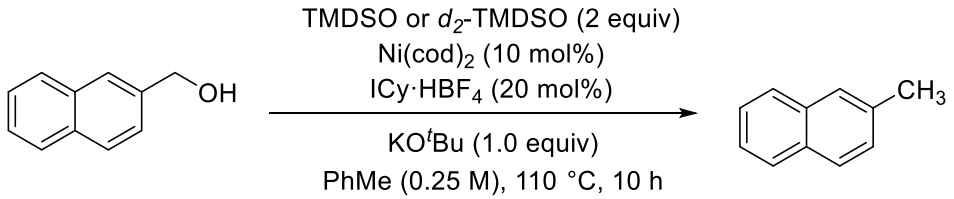
To further illustrate the selectivity of our method, we prepared **S20** from the corresponding arenol. Subjecting this compound to our reaction conditions led to selective reduction of the benzyl methyl ether in the presence of an aryl silyl ether.

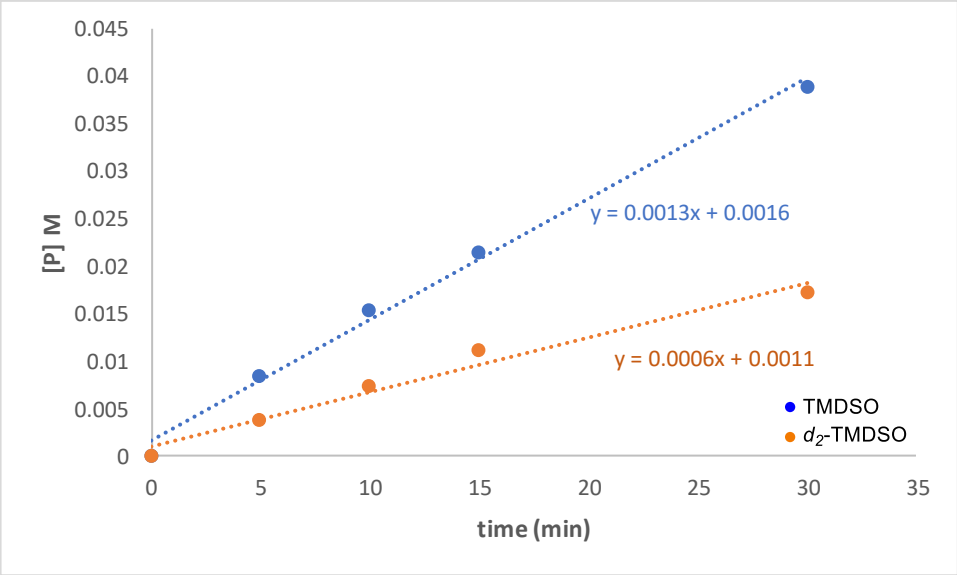


4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4'-methyl-1,1'-biphenyl (S20) was prepared according to general procedure A. Purification was performed using a gradient of 10 → 50% ethyl acetate in hexanes to afford (**S20**) (29 mg, 83% yield). Characterization data matched those previously reported.[50] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.51-7.47 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.26-7.25 (m, 1H), 2.41 (s, 3H), 0.99 (s, 9H), 0.38 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 141.1, 138.3, 137.0, 129.5, 128.7, 128.6, 127.0, 126.9, 25.3, 21.1, 19.1, 1.6. **Accurate mass (EI)**: Theoretical: 298.1804. Found: 298.1811. Spectral Accuracy: 96.8%.

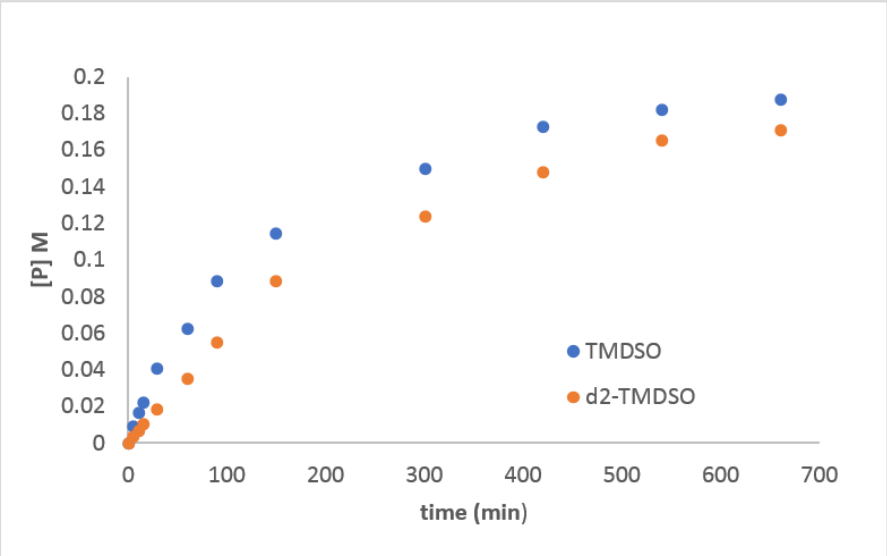
6.6. Kinetic isotope experiments

In order to determine the kinetic isotope effects of the reduction reaction, two parallel reductions of napthalene-2-methanol were set up – one with commercial TMDSO and one with d_2-TMDSO. Aliquots of each of these reactions were taken after 5, 10, 15, 30 and 60 minutes and subsequently analyzed by GC-FID. Product formation vs. time data was plotted and the initial rates were measured to determine a kinetic isotope effect of 2.24.



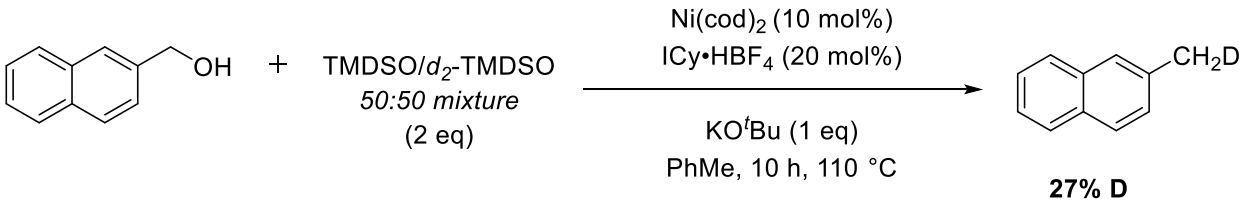


Scheme S13. Initial reaction progress in the presence of TMDSO or d_2-TMDSO



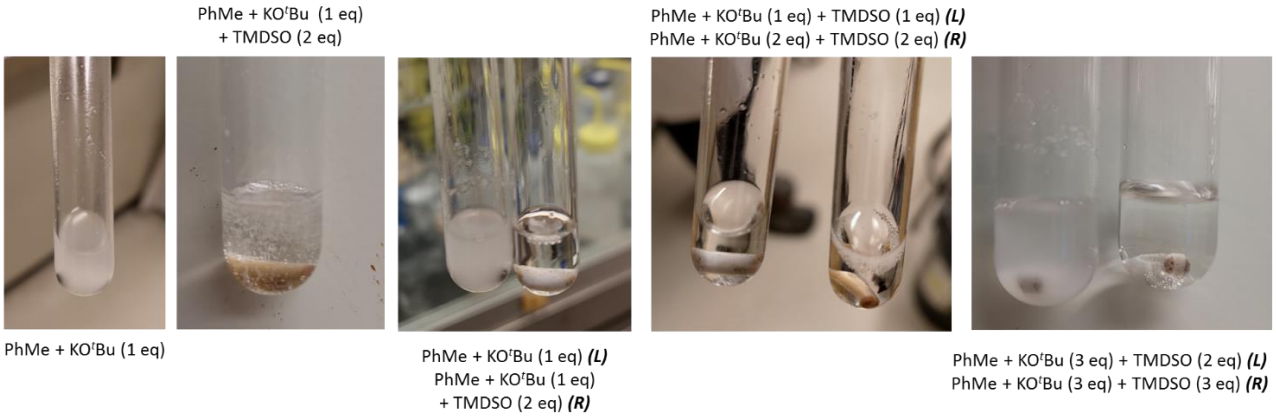
Scheme S14. Total reaction progress in the presence of TMDSO or d_2-TMDSO

Comparable results were obtained by intermolecular competition kinetic-isotope experiments performed using a 50:50 ratio of TMDSO to d_2-TMDSO. These experiments resulted in 27% deuterium incorporation in the methyl reduction product, providing further evidence for a primary-kinetic isotope effect.



6.7. Solubility of KO^{t}Bu

In the kinetic experiments detailed in Scheme S10, the amount of TMDSO was fixed at 2.0 equiv, while KO^{t}Bu varied from 1.0 to 2.0 equiv. Experiments with larger amounts of KO^{t}Bu showed a positive effect on the rate, but did not overlay with the kinetic plots normalized for first order behavior. Given the anticipated low solubility of KO^{t}Bu in toluene, we carried tested the homogeneity of different mixtures of KO^{t}Bu and TMDSO (Scheme **S15**). It was observed that TMDSO was able to solubilize KO^{t}Bu entirely, provided that it is TMDSO is in in equal-or-greater stoichiometric amounts relative to the KO^{t}Bu. Above that point, a slurry was observed. This suggests that the reaction is indeed positive order in KO^{t}Bu, but becomes heterogeneous and thus less kinetically tractable at high concentrations of KO^{t}Bu.



Scheme S15. Solubility of KO^{t}Bu in toluene upon mixing with TMDSO

7. Appendix

Data associated with the creation of the vTNA plots

Determining the order with respect to catalyst

First order:

time	tCAT^1	[product] mM	tCAT^1	[product] mM	tCAT^1	[product] mM
0m	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
10m	0.1193	0.0181	0.2126	0.0332	0.3738	0.0355
30m	0.3580	0.0543	0.5927	0.0923	1.1215	0.1065
60m	0.5374	0.0726	0.9769	0.1104	1.6124	0.1273
90m	0.7558	0.0894	1.3425	0.1185	2.2203	0.1474
2.5h	0.9694	0.0947	1.9901	0.1367	3.2260	0.1627
5h	1.5078	0.1132	3.3833	0.1755	4.5235	0.1901
7h	1.8736	0.1288	4.8469	0.1974	6.4453	0.2083
9h	3.8635	0.1792	7.7435	0.2101	8.7950	0.2084
11h	5.7179	0.1963	9.8457	0.2136	12.4875	0.2140

Zeroth order:

time	tCAT^0	[product] mM	tCAT^0	[product] mM	tCAT^0	[product] mM
10m	0.119	0.021	0.213	0.030	0.374	0.0212
30m	0.358	0.064	0.593	0.083	1.121	0.0636
60m	0.537	0.086	0.977	0.099	1.612	0.0761
90m	0.756	0.091	1.342	0.106	2.220	0.0951
2.5h	0.969	0.112	1.990	0.125	3.226	0.0972
5h	1.508	0.134	3.383	0.149	4.523	0.1135
7h	1.874	0.153	4.847	0.167	6.445	0.1194
9h	3.863	0.183	7.743	0.178	8.795	0.1245
11h	5.179	0.200	9.246	0.181	11.588	0.1278

Second order:

time	tCAT^2	[product] mM	tCAT^2	[product] mM	tCAT^2	[product] mM
0m	0.000	0.000	0.000	0.000	0.000	0.000
10m	0.119	0.020	0.213	0.033	0.374	0.030
30m	0.358	0.059	0.593	0.092	1.121	0.095
60m	0.537	0.079	0.977	0.110	1.612	0.114
90m	0.756	0.084	1.342	0.118	2.220	0.156
2.5h	0.969	0.103	1.990	0.147	3.226	0.141
5h	1.508	0.124	3.383	0.174	4.523	0.162
7h	2.274	0.141	4.847	0.196	6.445	0.162
9h	4.563	0.168	7.743	0.209	8.795	0.166
11h	6.679	0.184	9.246	0.212	11.588	0.172

Determining the order with respect to KO^tBu

First order:

time	tCAT^1	[product] mM	tCAT^1	[product] mM	tCAT^1	[product] mM
0m	0.000	0.0000	0.000	0.000	0.000	0.000
10m	0.255	0.0168	0.377	0.0371	0.490	0.0548
30m	0.716	0.0645	1.185	0.0927	1.541	0.0841
60m	1.075	0.0834	1.954	0.1109	2.540	0.1221
90m	1.512	0.0960	2.685	0.1190	3.490	0.1396
2.5h	2.376	0.1217	4.179	0.1485	5.433	0.1623
5h	3.016	0.1415	6.845	0.1781	7.490	0.1844
7h	3.747	0.1609	8.639	0.1820	9.478	0.1937
9h	7.727	0.1876	12.395	0.2006	13.490	0.2095
11h	11.484	0.2014	19.035	0.2111	16.490	0.2104

Zeroth order:

time	tCAT^0	[product] mM	tCAT^0	[product] mM	tCAT^0	[product] mM
0m	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
10m	0.2547	0.0153	0.4902	0.0324	0.3770	0.0082
30m	0.7159	0.0586	1.541	0.0578	1.185	0.0316
60m	1.075	0.0757	2.540	0.0848	1.954	0.0408
90m	1.512	0.0872	3.490	0.0947	2.685	0.0470
2.5h	2.376	0.1105	5.433	0.1240	4.179	0.0596
5h	3.016	0.1285	7.490	0.1348	6.845	0.0693
7h	3.747	0.1462	9.478	0.1487	8.639	0.0788
9h	7.727	0.1795	13.490	0.1624	12.395	0.0967
11h	11.484	0.1979	16.490	0.1631	19.035	0.1067

Second order:

time	tCAT^2	[product] mM	tCAT^2	[product] mM	tCAT^2	[product] mM
0m	0	0.0000	0	0	0	0
10m	0.255	0.0116	0.490	0.03654	0.3770	0.0352
30m	0.716	0.0445	1.541	0.0648	1.185	0.0880
60m	1.075	0.0575	2.540	0.09467	1.954	0.1052
90m	1.512	0.0663	3.490	0.11474	2.685	0.1129
2.5h	2.376	0.0840	5.433	0.1374	4.179	0.1409
5h	3.016	0.0976	7.490	0.1564	6.845	0.1690
7h	3.747	0.1110	9.478	0.161	8.639	0.1726
9h	7.727	0.1363	13.490	0.1746	12.395	0.1903
11h	11.484	0.1503	16.490	0.1796	19.035	0.2003

Determining the order with respect to TMDSO

First order:

time	tCAT^1	[product] mM	tCAT^1	[product] mM	tCAT^1	[product] mM
0m	0	0	0	0	0	0
10m	0.0675	0.0108	0.0847	0.02160	0.14582	0.01960
30m	0.3129	0.0592	0.2485	0.03749	0.203492	0.03384
60m	0.4380	0.0751	0.4856	0.08919	0.6427052	0.08468
90m	0.5901	0.0847	0.7479	0.1138	1.042	0.1263
2.5h	0.7092	0.1149	1.140	0.1377	1.412	0.1415
5h	1.002	0.1330	1.469	0.1520	2.090	0.1713
7h	1.529	0.1614	2.148	0.1649	3.367	0.1821
9h	3.164	0.1754	3.746	0.1813	4.520	0.1859
11h	5.847	0.1874	6.218	0.1877	7.782	0.1893

Zeroth order:

time	tCAT^0	[product] mM	tCAT^0	[product] mM	tCAT^0	[product] mM
0m	0	0	0	0	0	0
10m	0.0675	0.01181	0.0847	0.01378	0.14582	0.01642
30m	0.3129	0.06474	0.2485	0.03794	0.203492	0.02835
60m	0.4380	0.08214	0.4856	0.07840	0.6427052	0.07093
90m	0.5901	0.09267	0.7479	0.1184	1.042	0.1058
2.5h	0.7092	0.1256	1.140	0.1378	1.412	0.1185
5h	1.002	0.1455	1.469	0.1485	2.090	0.1435
7h	1.529	0.1765	2.148	0.1589	3.367	0.1526
9h	3.164	0.1918	3.746	0.1785	4.520	0.1557
11h	5.847	0.2050	6.218	0.1814	7.782	0.1586

Second order:

time	tCAT^2	[product] mM	tCAT^2	[product] mM	tCAT^2	[product] mM
0m	0	0	0	0	0	0
10m	0.0675	0.01162	0.0847	0.0141	0.14582	0.02703
30m	0.3129	0.02784	0.2485	0.03394	0.203492	0.04665
60m	0.4380	0.049	0.4856	0.0814	0.6427052	0.1167
90m	0.5901	0.0746	0.7479	0.1289	1.042	0.1742
2.5h	0.7092	0.08974	1.140	0.1475	1.412	0.1951
5h	1.002	0.1238	1.469	0.1748	2.090	0.2361
7h	1.529	0.1468	2.148	0.1938	3.367	0.2511
9h	3.164	0.1838	3.746	0.2090	4.520	0.2563
11h	5.847	0.1993	6.218	0.2194	7.782	0.2610

Determining the order with respect to methyl-2-benzoate

First order:

time	tCAT^1	[product] mM	tCAT^1	[product] mM	tCAT^1	[product] mM
0m	0.0000	0	0	0	0	0
10m	0.1193	0.01989	0.2768	0.03379	0.4195	0.0541
30m	0.3580	0.05967	1.121	0.1014	1.458	0.1234
60m	0.5374	0.07966	1.612	0.1212	1.785	0.1273
90m	0.7558	0.09818	2.220	0.1403	2.684	0.1579
2.5h	0.9694	0.1040	3.226	0.1549	3.749	0.17
5h	1.508	0.1243	4.523	0.1809	4.920	0.1846
7h	1.874	0.1415	6.445	0.1982	7.195	0.2018
9h	4.163	0.1757	8.795	0.1984	9.479	0.2084
11h	8.218	0.2046	12.49	0.2037	14.68	0.2140

Zeroth order:

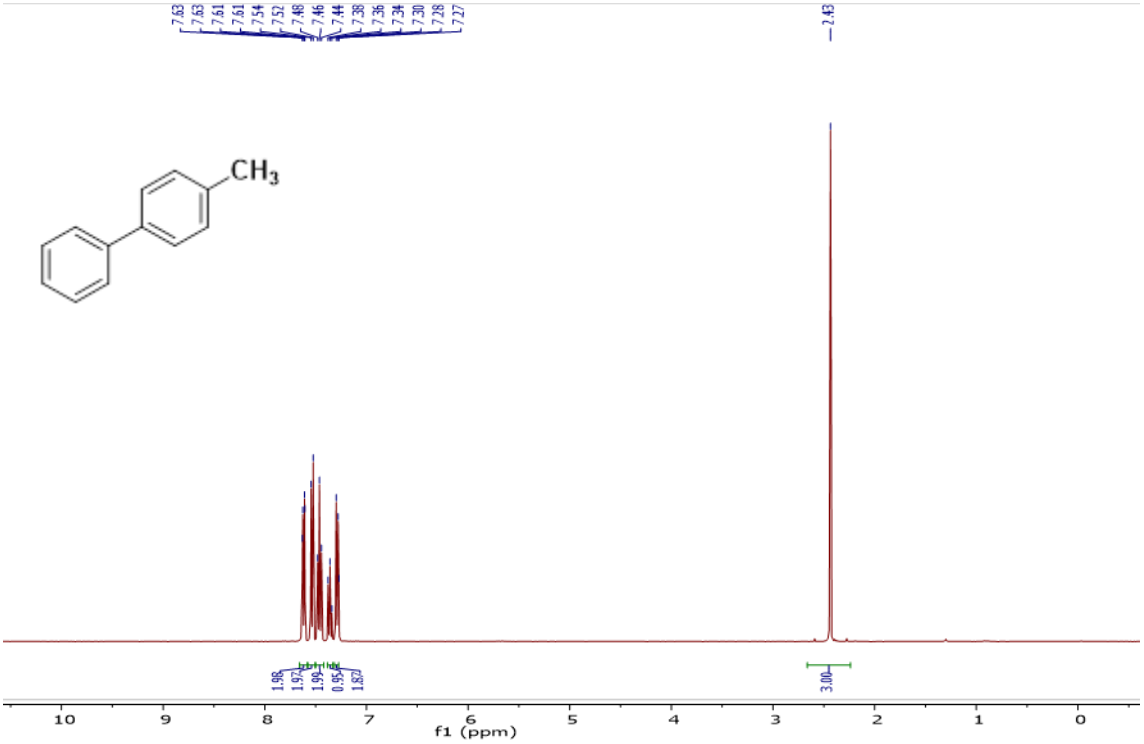
time	tCAT^0	[product] mM	tCAT^0	[product] mM	tCAT^0	[product] mM
0m	0.0000	0	0	0	0	0
10m	0.1193	0.01899	0.2768	0.08264	0.4195	0.034
30m	0.3580	0.05696	1.121	0.2479	1.458	0.0547
60m	0.5374	0.07604	1.612	0.3722	1.785	0.06998
90m	0.7558	0.09372	2.220	0.5235	2.684	0.08164
2.5h	0.9694	0.0993	3.226	0.6715	3.749	0.091
5h	1.508	0.1187	4.523	1.0444	4.920	0.1047
7h	1.874	0.1350	6.445	1.2977	7.195	0.1198
9h	4.163	0.1677	8.795	3.3001	9.479	0.1294
11h	8.218	0.1953	12.49	6.5138	14.68	0.1479

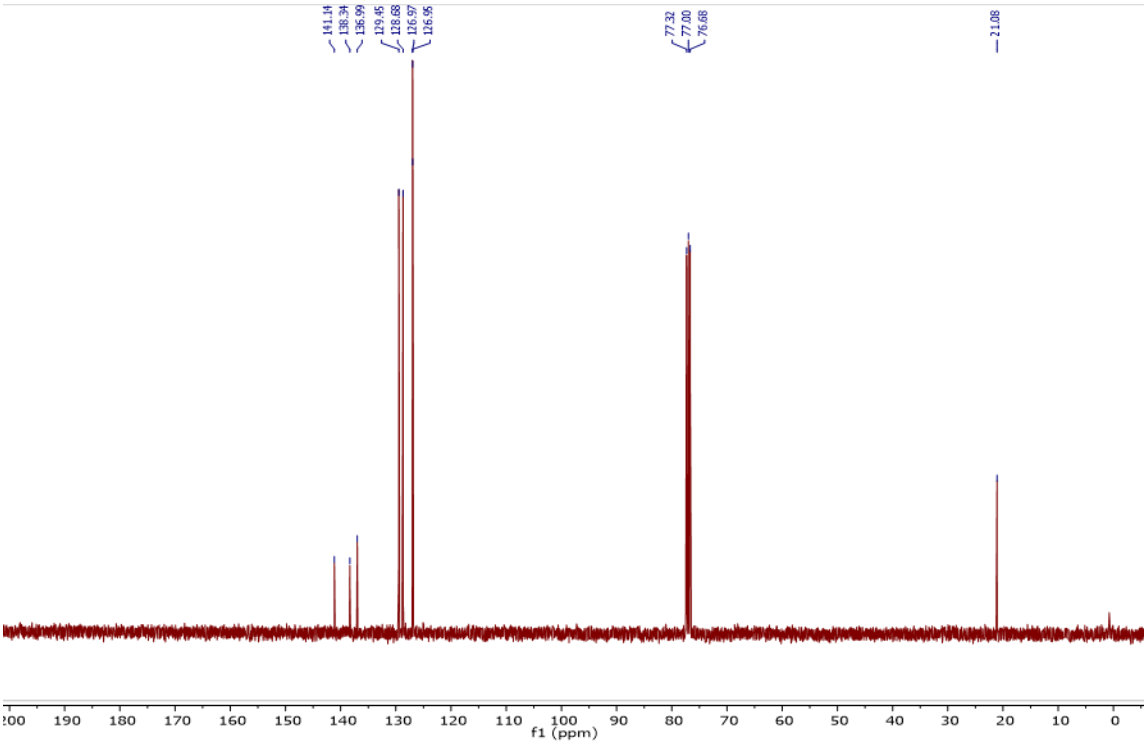
Second order:

time	tCAT^2	[product] mM	tCAT^2	[product] mM	tCAT^2	[product] mM
0m	0.0000	0	0	0	0	0
10m	0.1193	0.01591	0.2768	0.04003	0.4195	0.034
30m	0.3580	0.04772	1.121	0.1201	1.458	0.09367
60m	0.5374	0.06370	1.612	0.1436	1.785	0.1175
90m	0.7558	0.06957	2.220	0.1662	2.684	0.1374
2.5h	0.9694	0.0831	3.226	0.1835	3.749	0.18
5h	1.508	0.0994	4.523	0.1990	4.920	0.21847
7h	1.874	0.1131	6.445	0.2181	7.195	0.2477
9h	4.163	0.1573	8.795	0.2282	9.479	0.2765
11h	8.218	0.1724	12.49	0.2404	14.68	0.2947

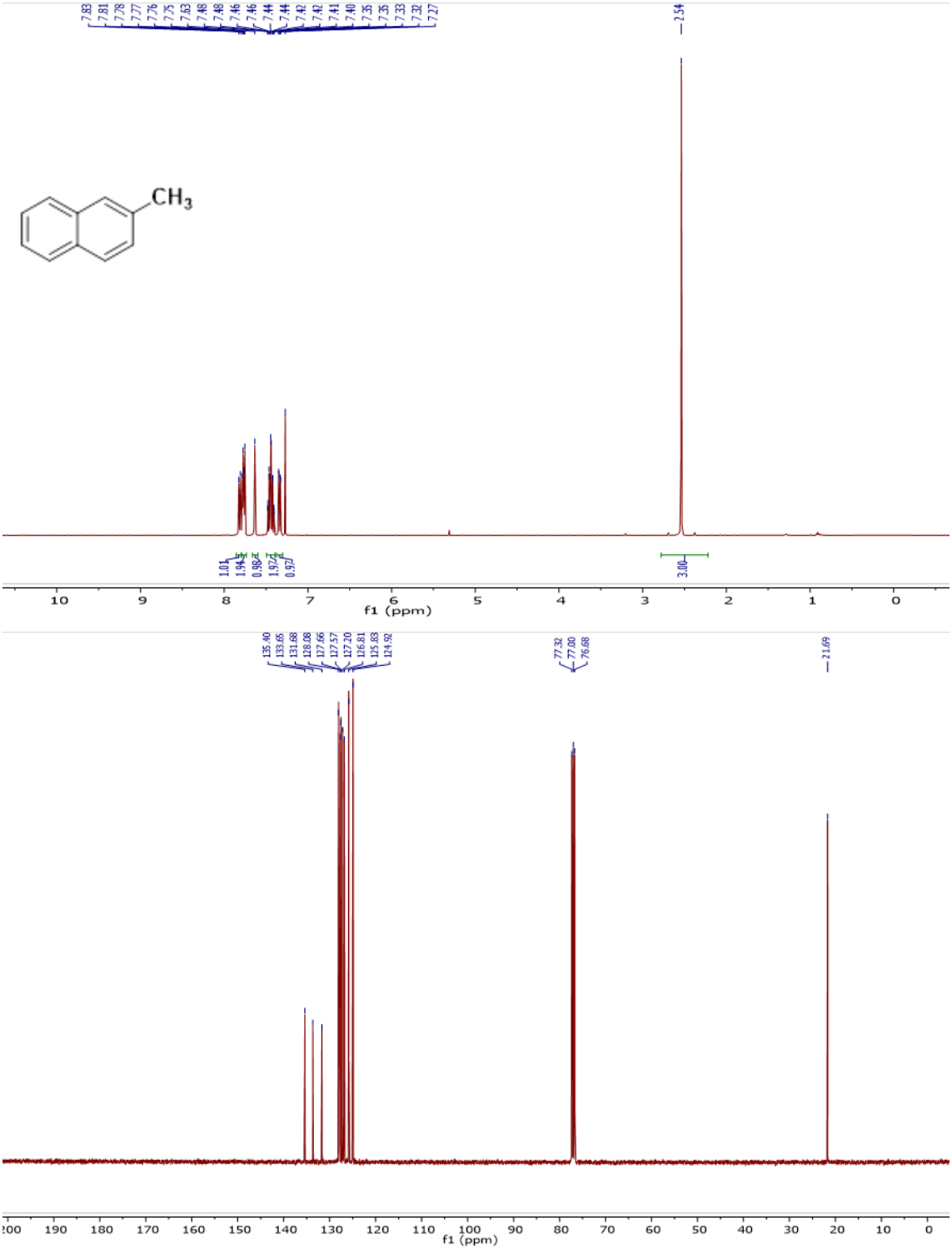
8. NMR Spectra

1-Methyl-4-phenylbenzene **3** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

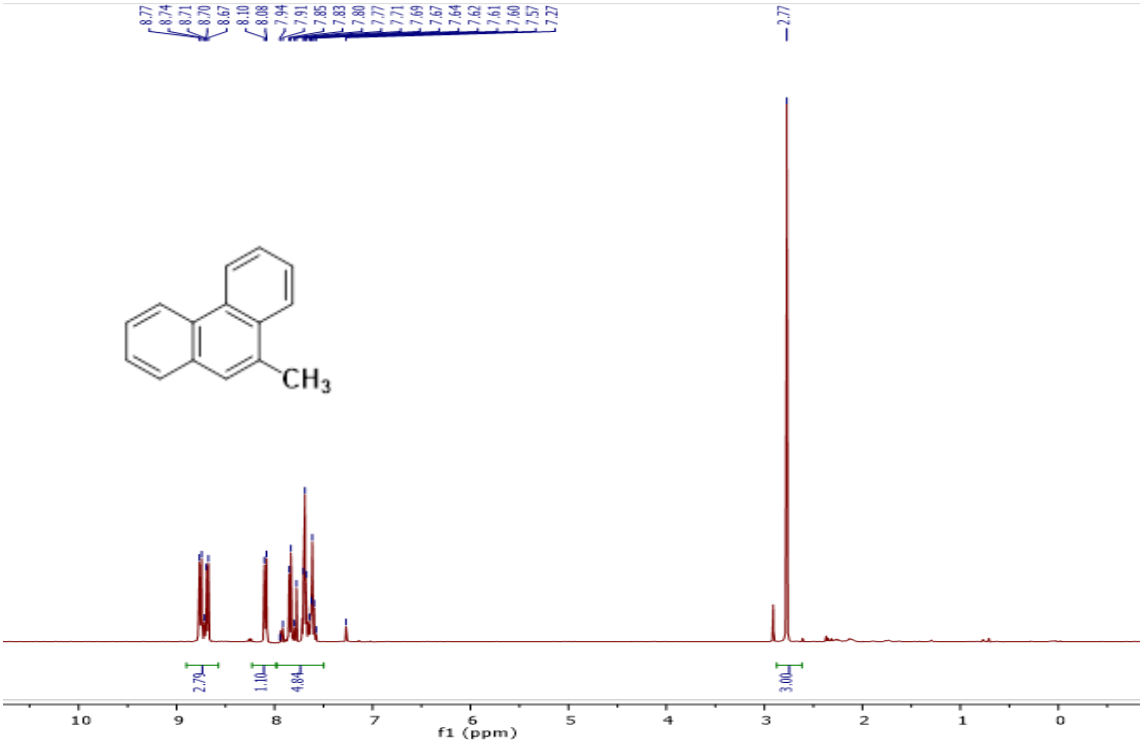


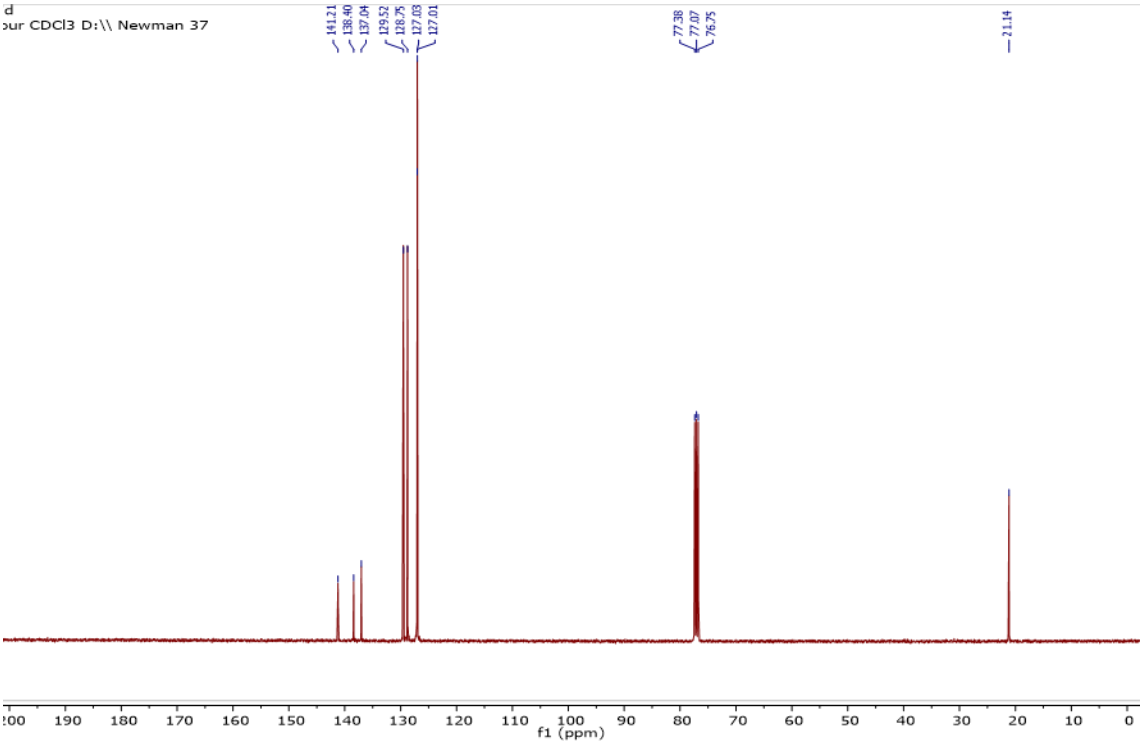


2-Methylnaphthalene **4** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

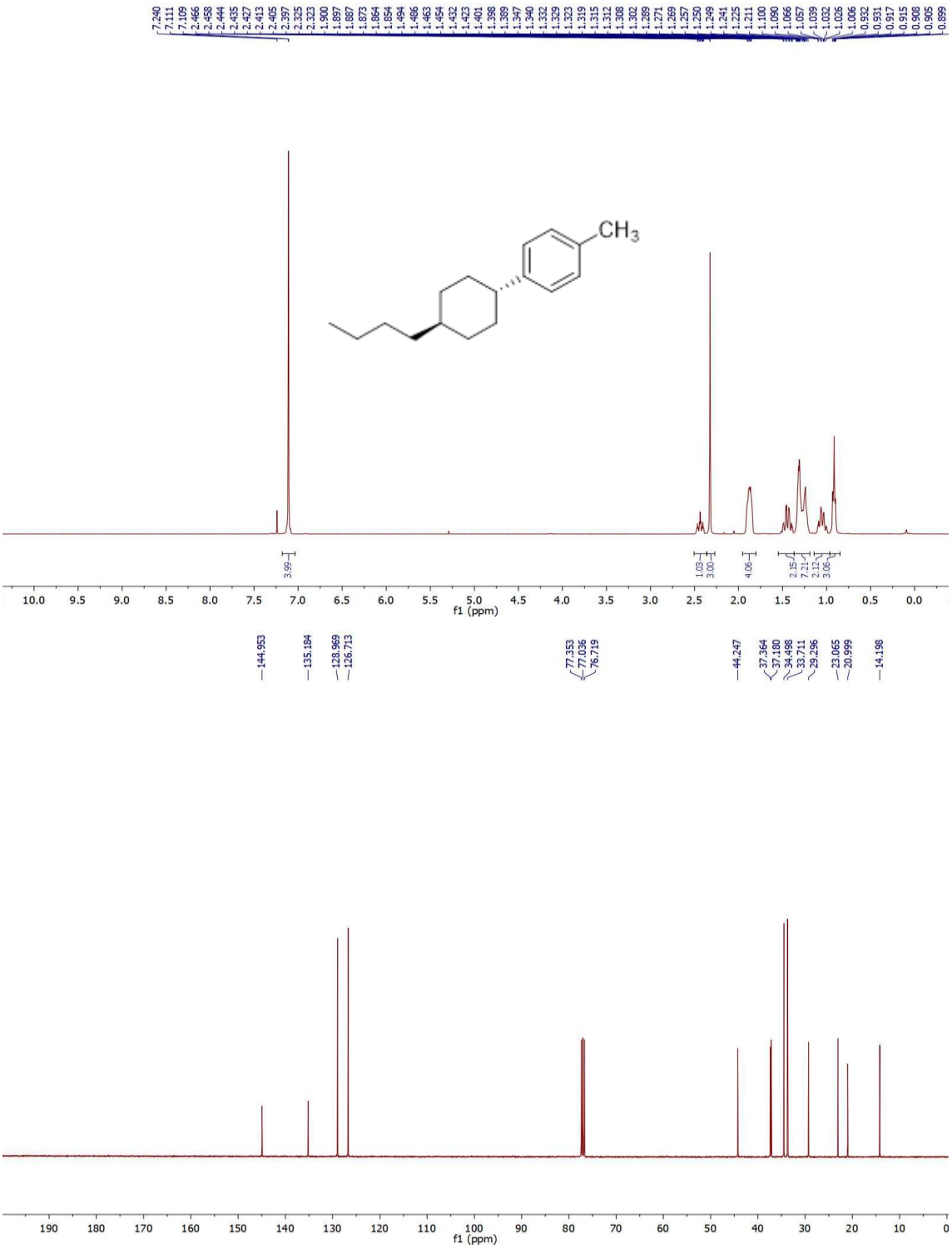


9-Methylphenanthrene **5** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

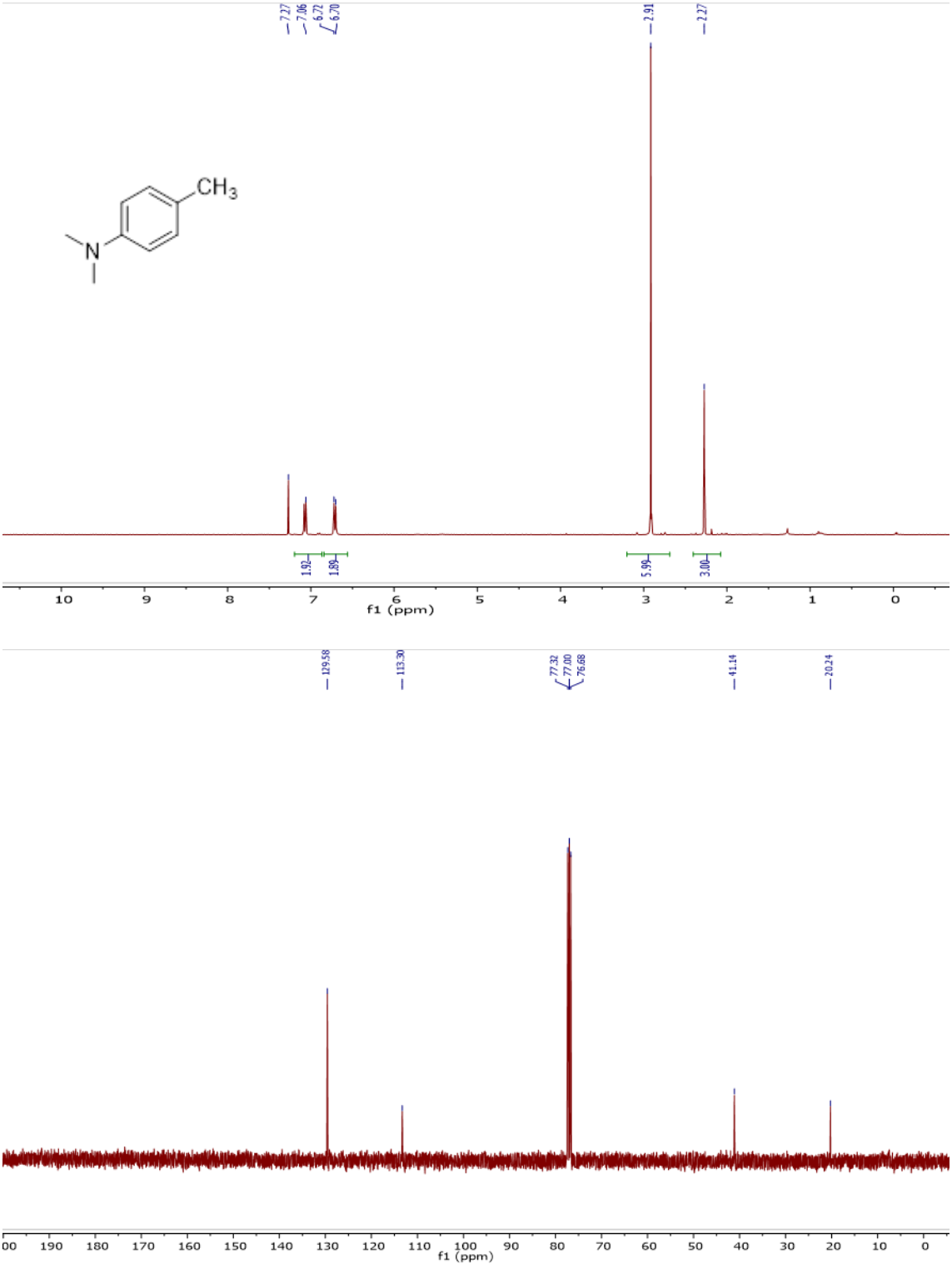




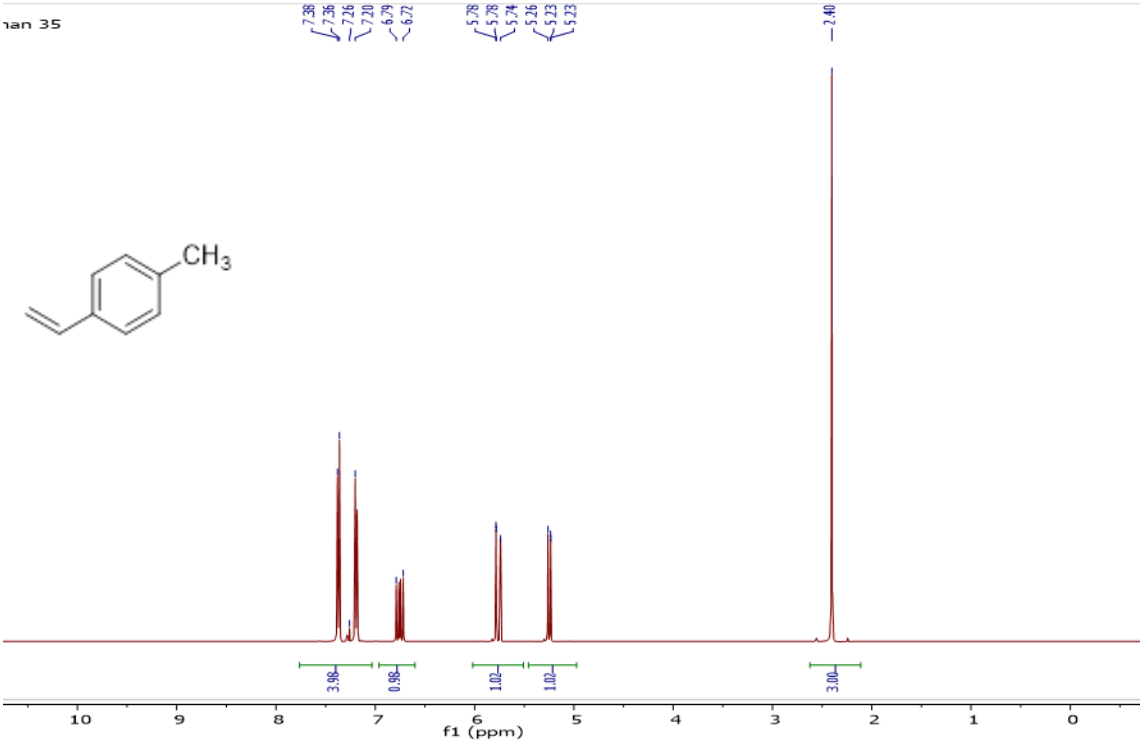
1-(*trans*-4-butylcyclohexyl)-4-methylbenzene **6** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

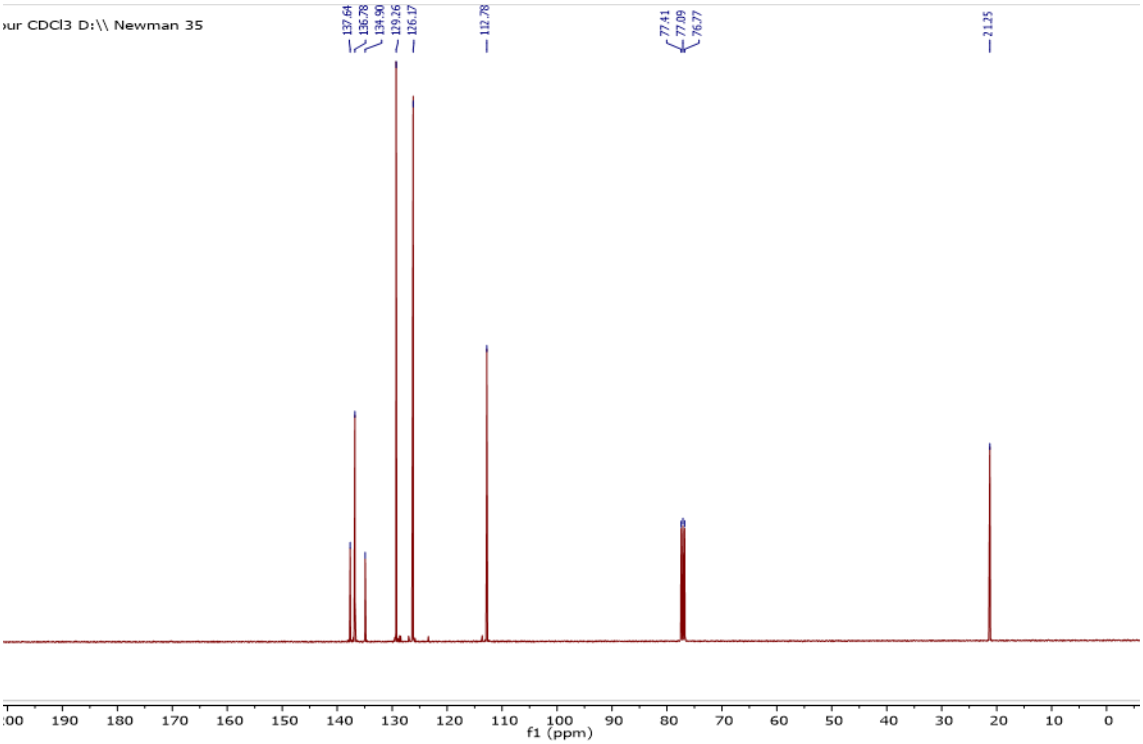


1-Methyl 4-dimethylamino benzene **7** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

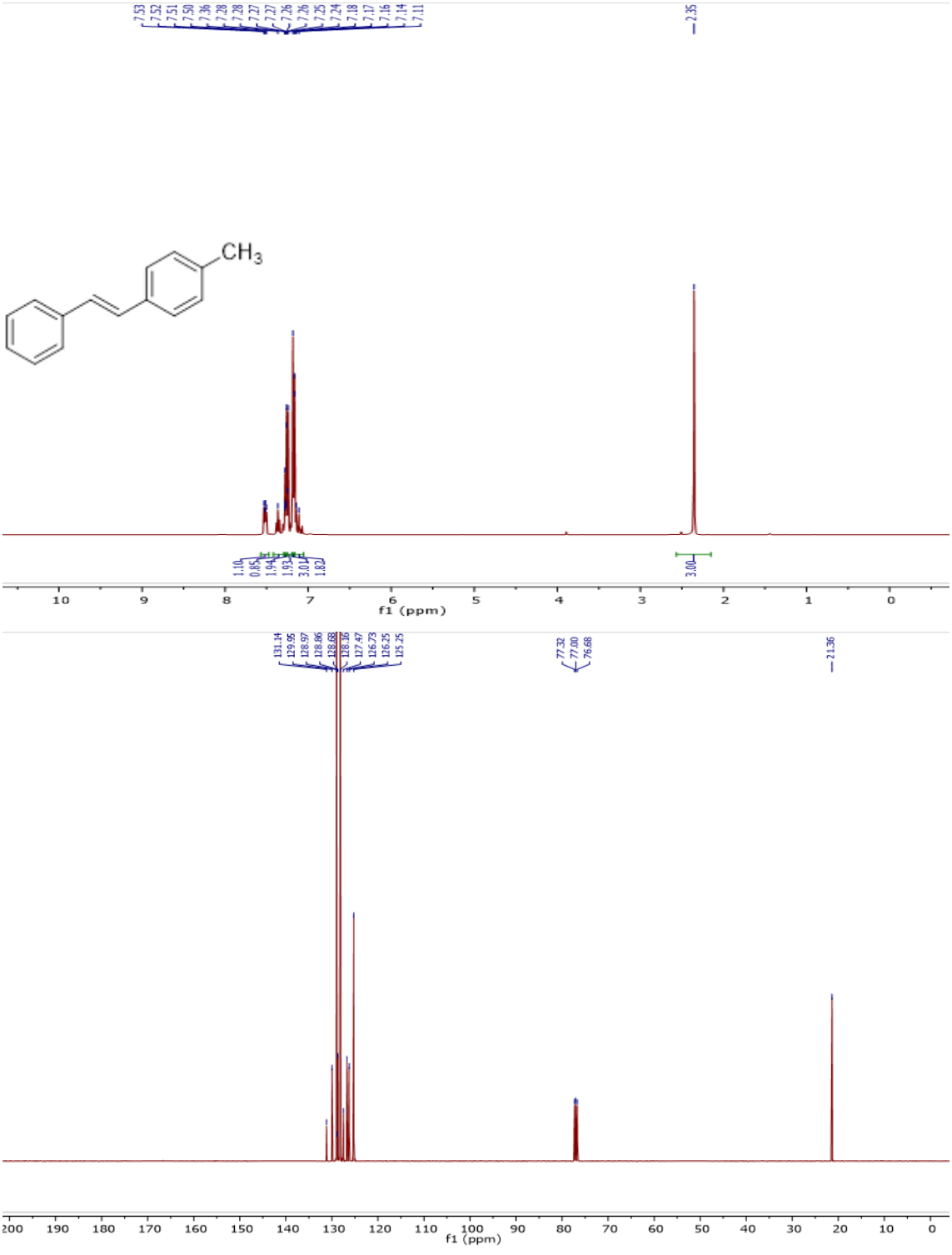


1-Methyl-4-vinylbenzene **8** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

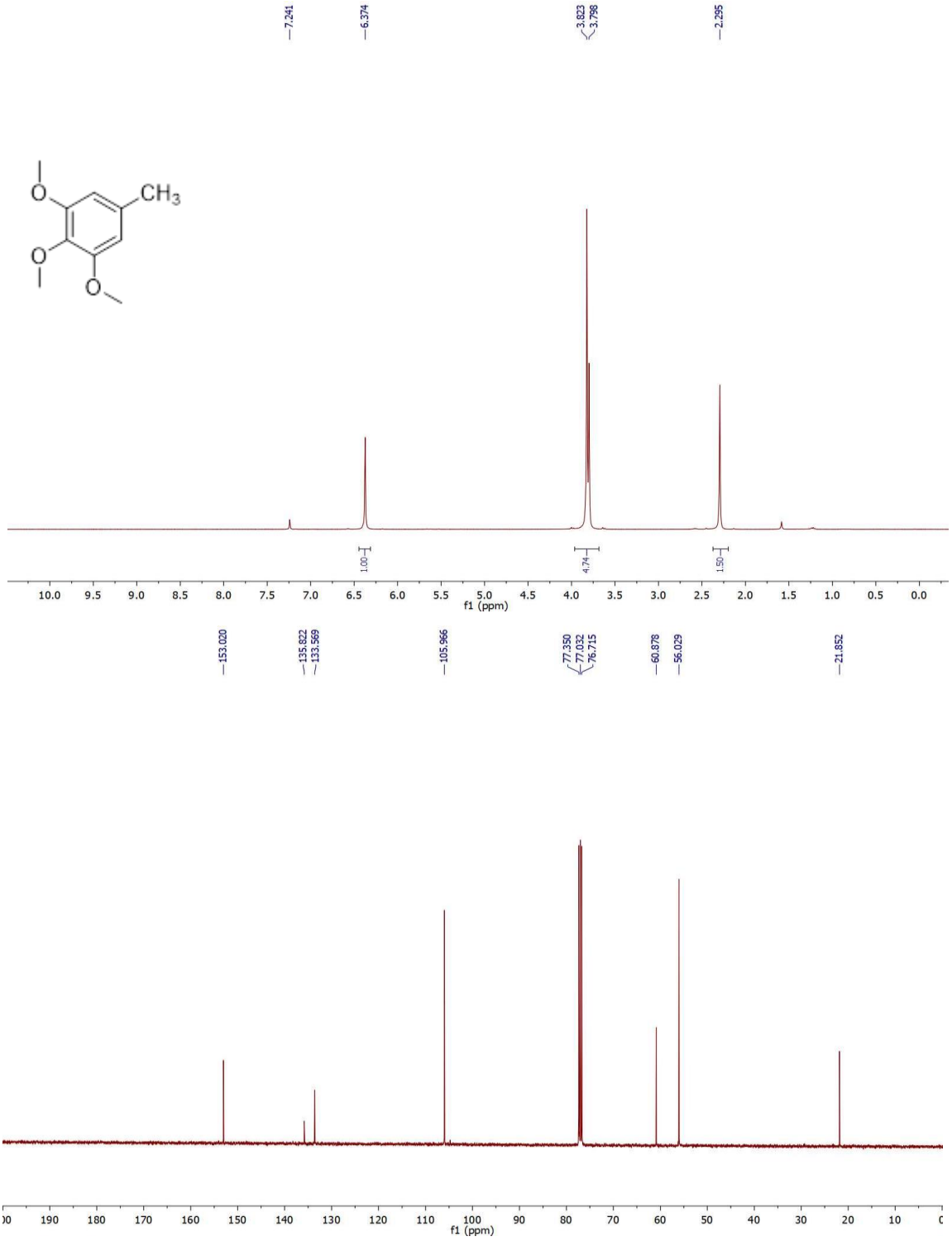




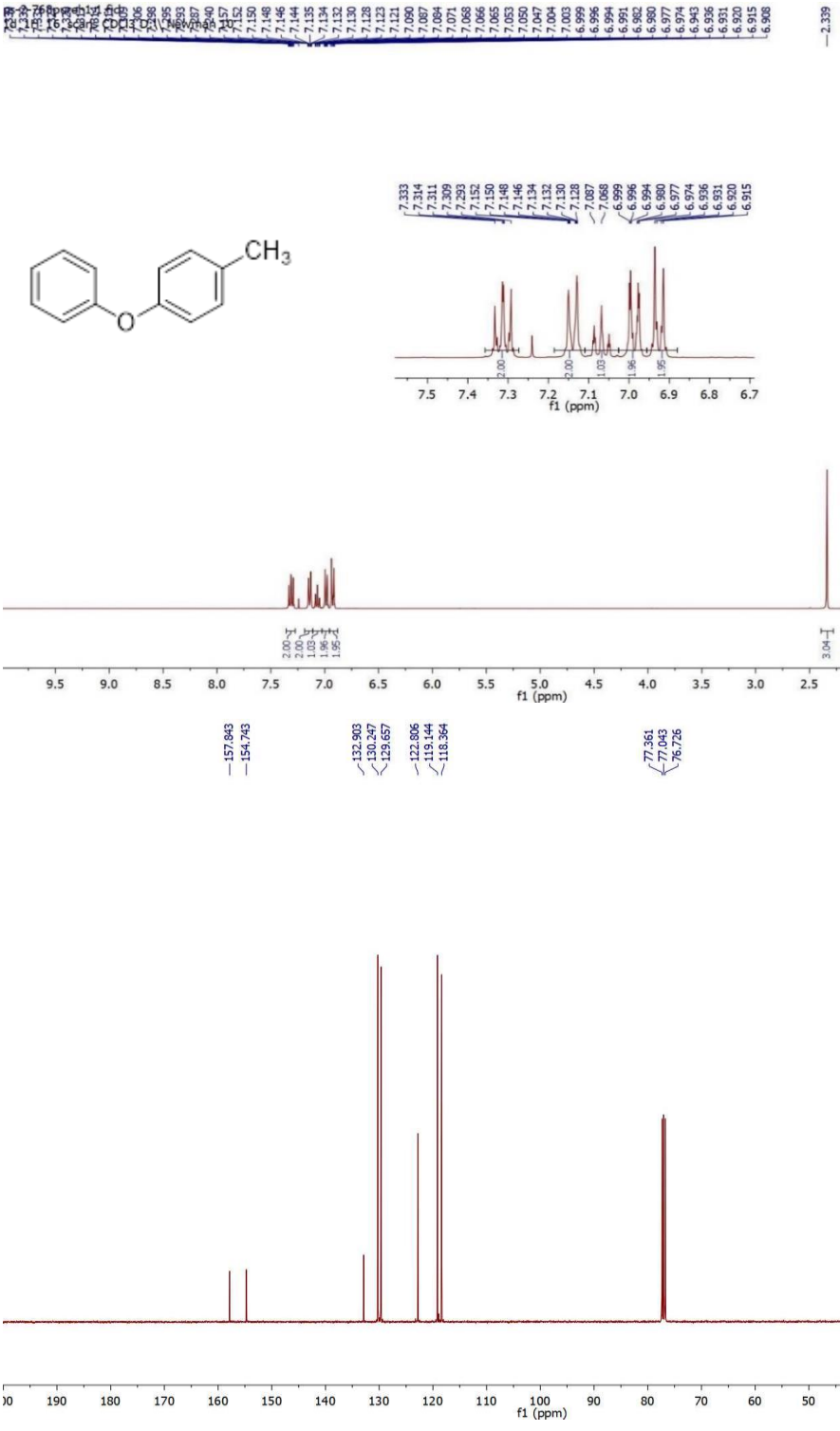
1-Methyl-4-(2-phenylethenyl)benzene **9** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



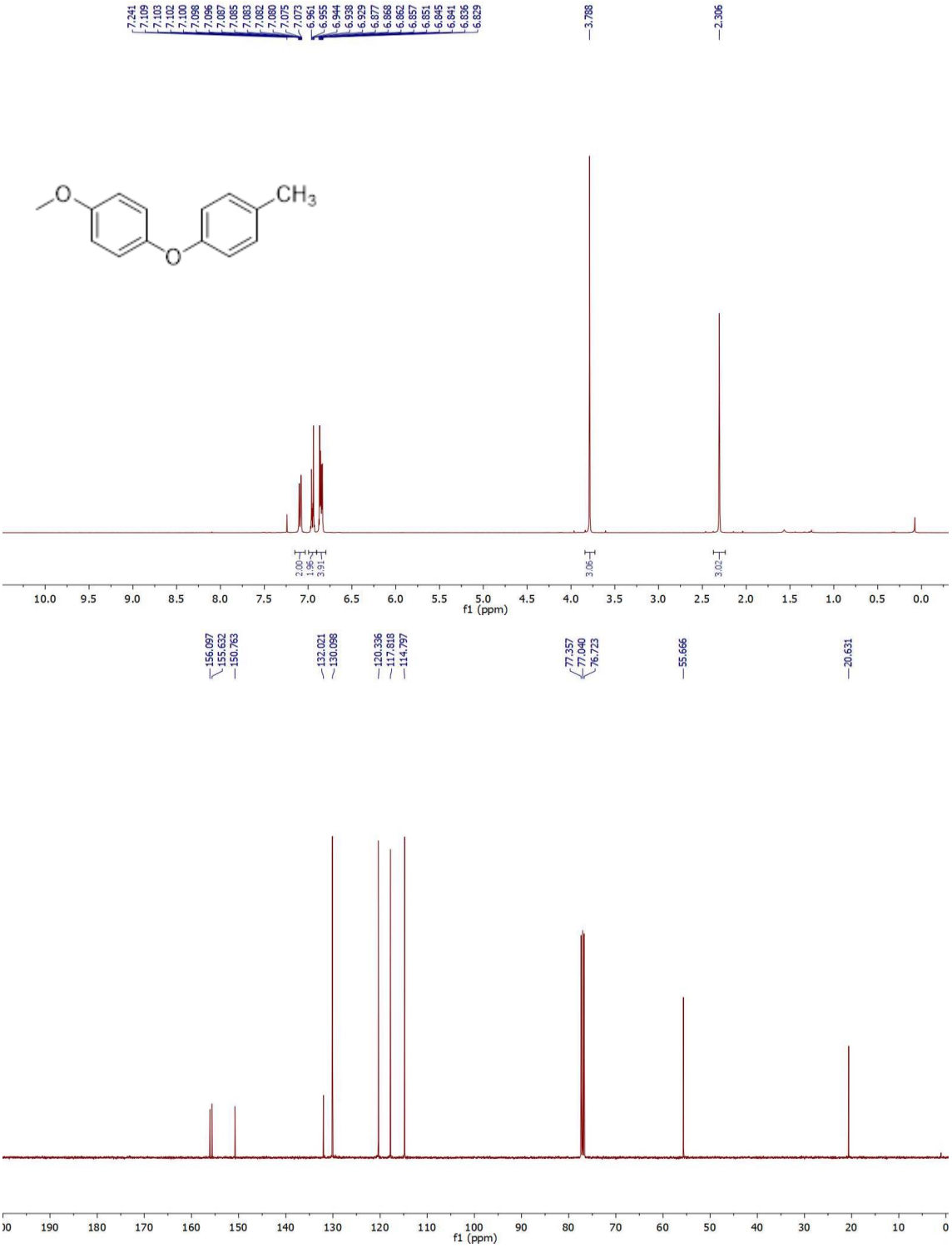
1,2,3-Trimethoxy-5-methylbenzene **10** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



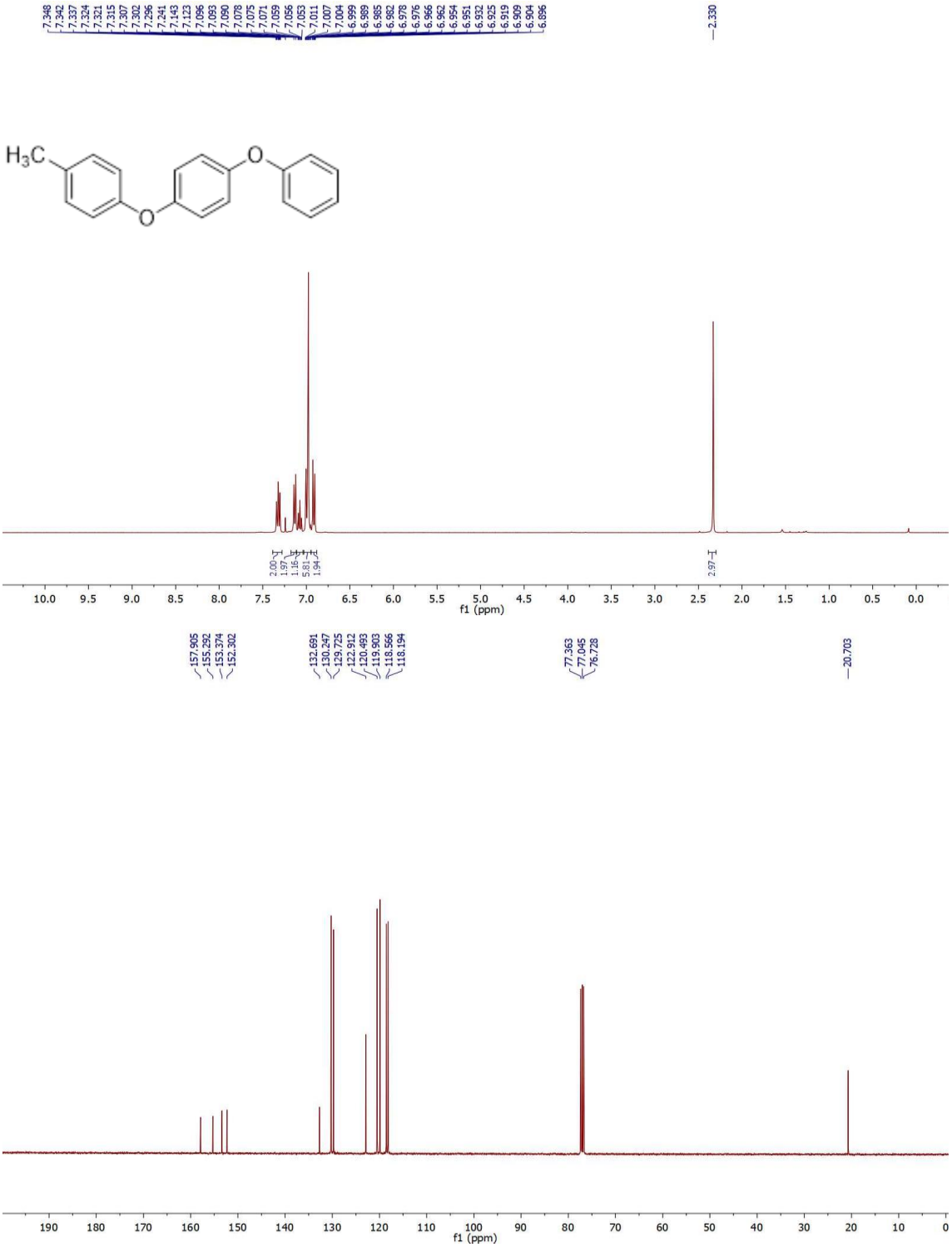
1-Methyl-4-phenoxybenzene **11** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



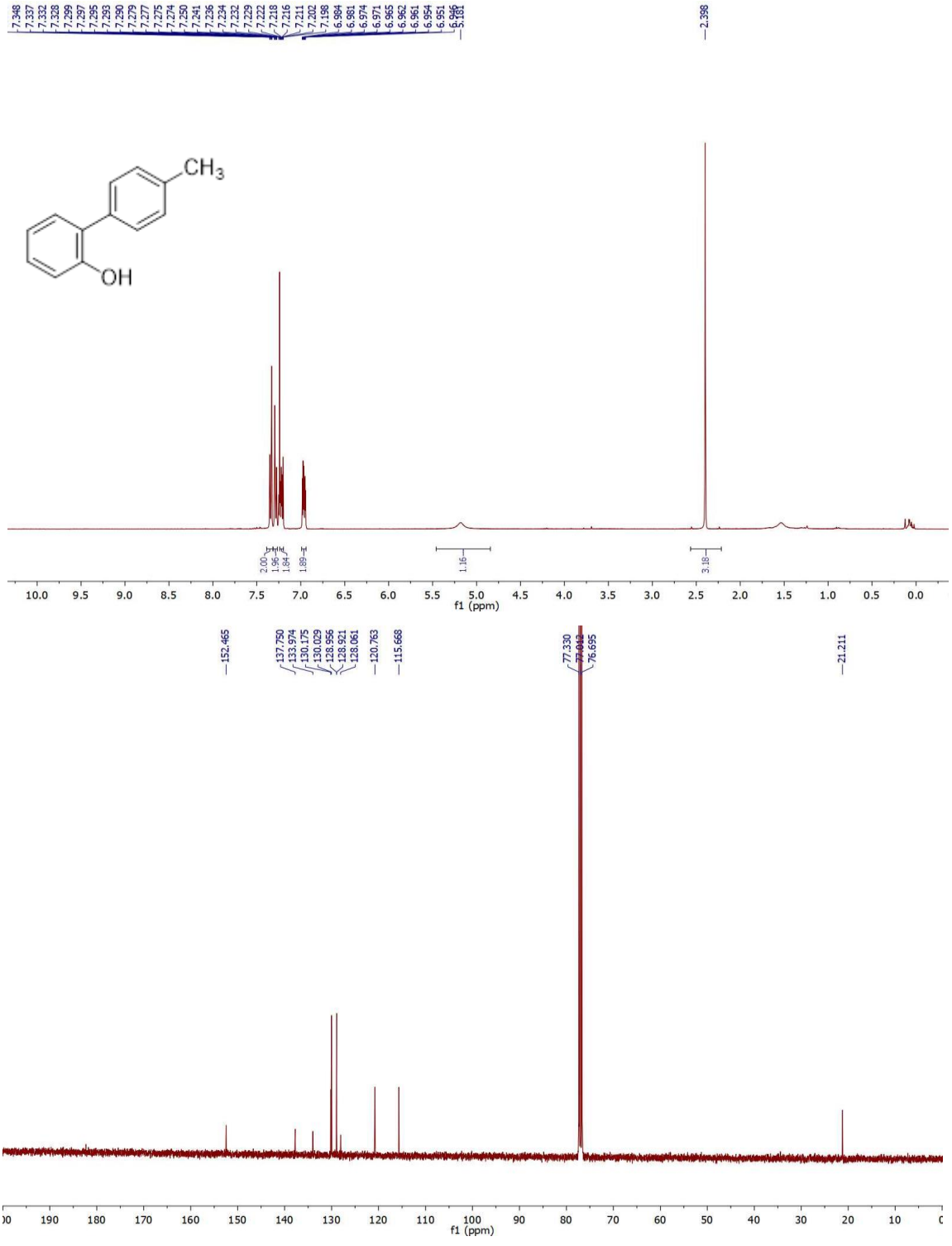
1-Methoxy-4-(4-methylphenoxy)benzene **12** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



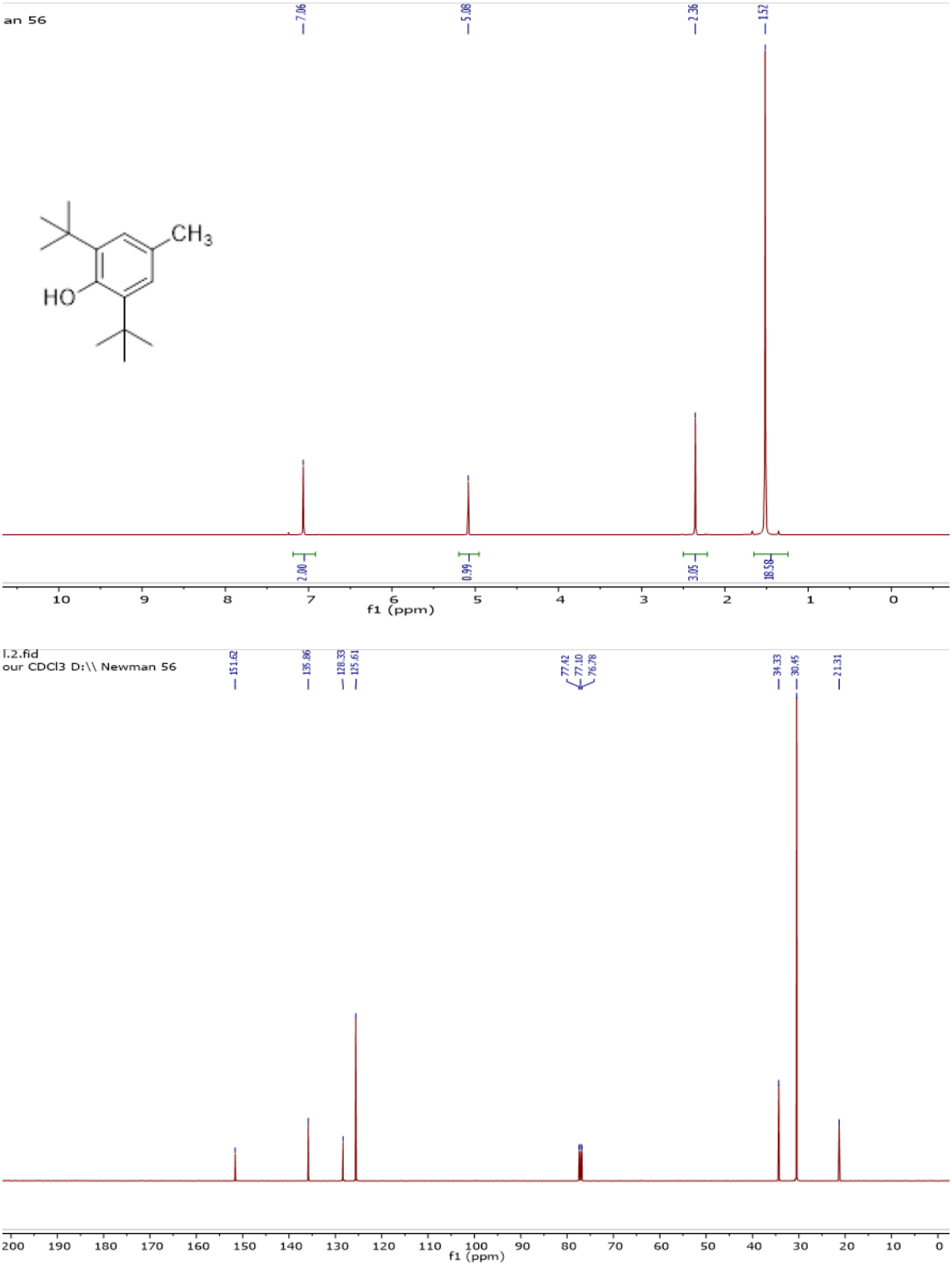
1-(4-Methylphenoxy)-4-phenoxybenzene **13** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



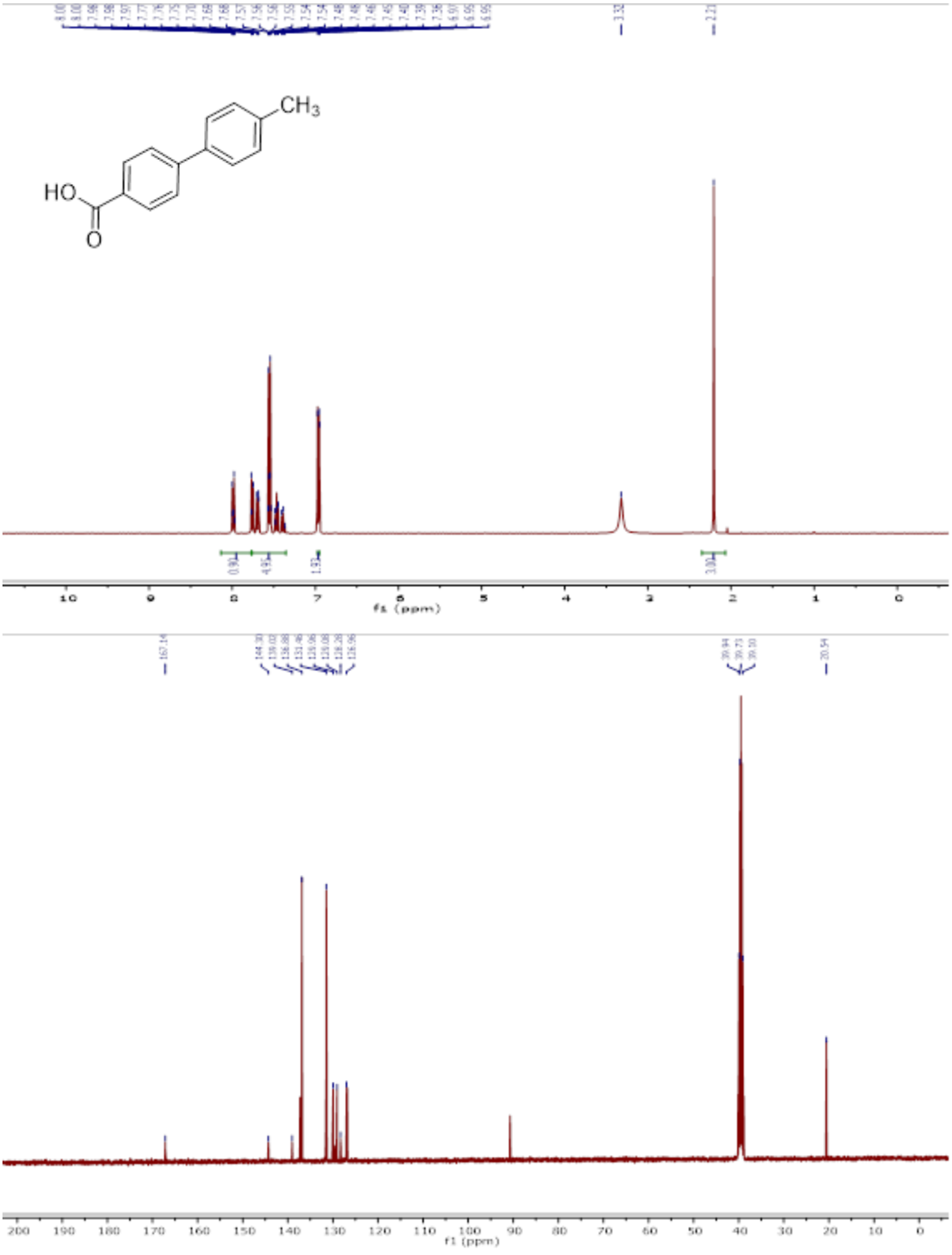
4'-Methyl-[1,1'-biphenyl]-2-ol **14** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



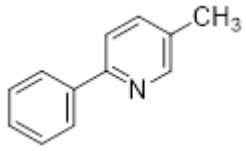
2,6-Bis(1,1-dimethylethyl)-4-methylphenol **15** ($CDCl_3$, 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR)

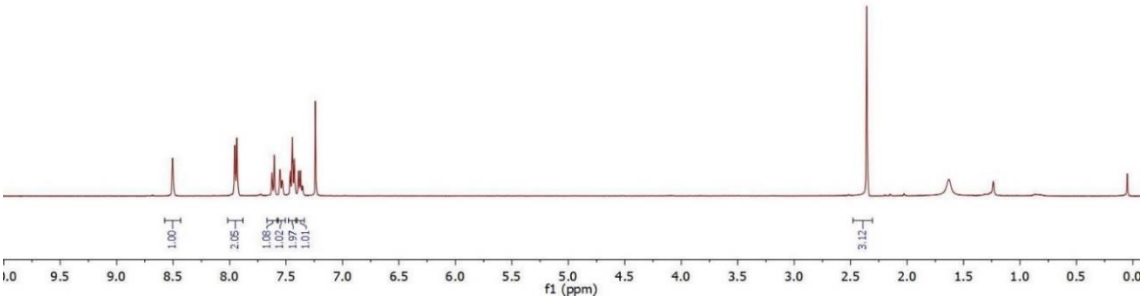


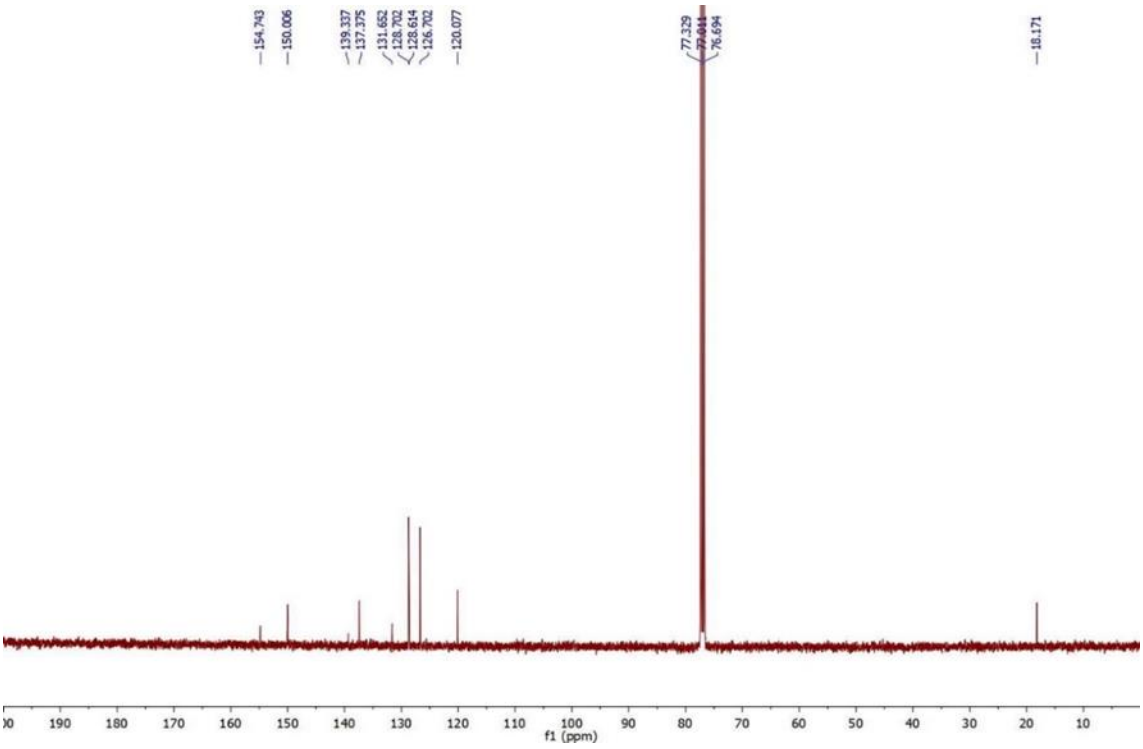
4'-Methyl-4-biphenylcarboxylic acid **16** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



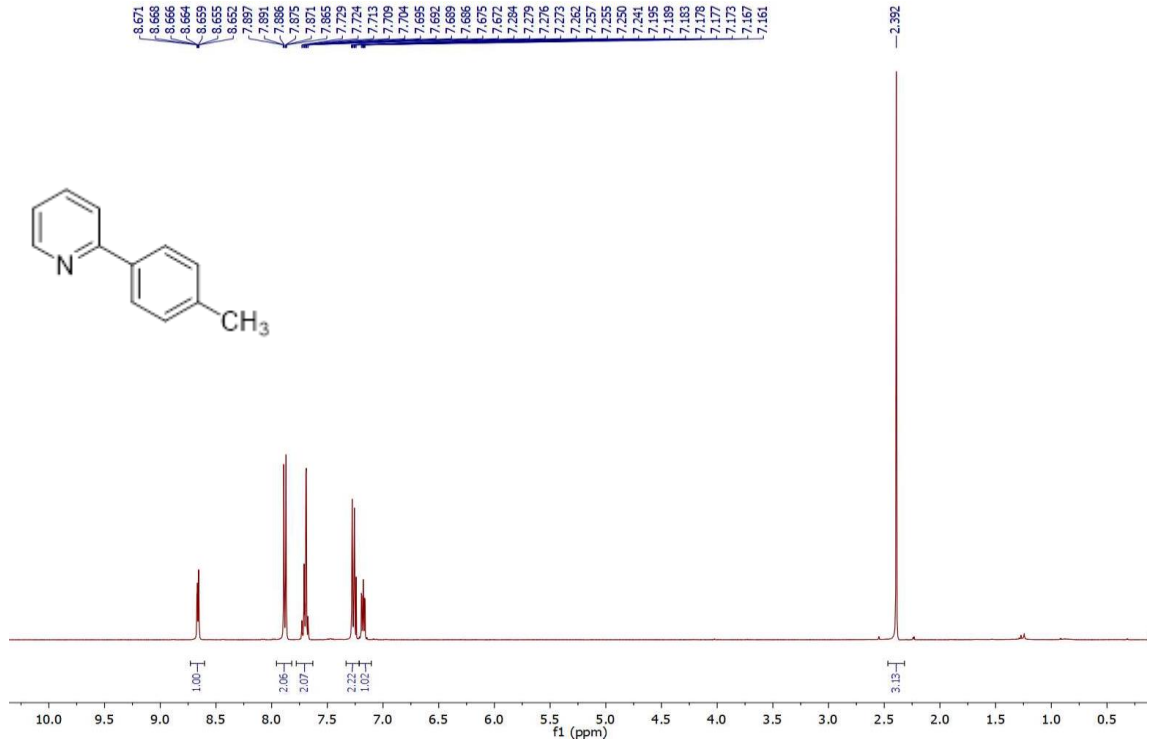
5-Methyl-2-phenylpyridine **17** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

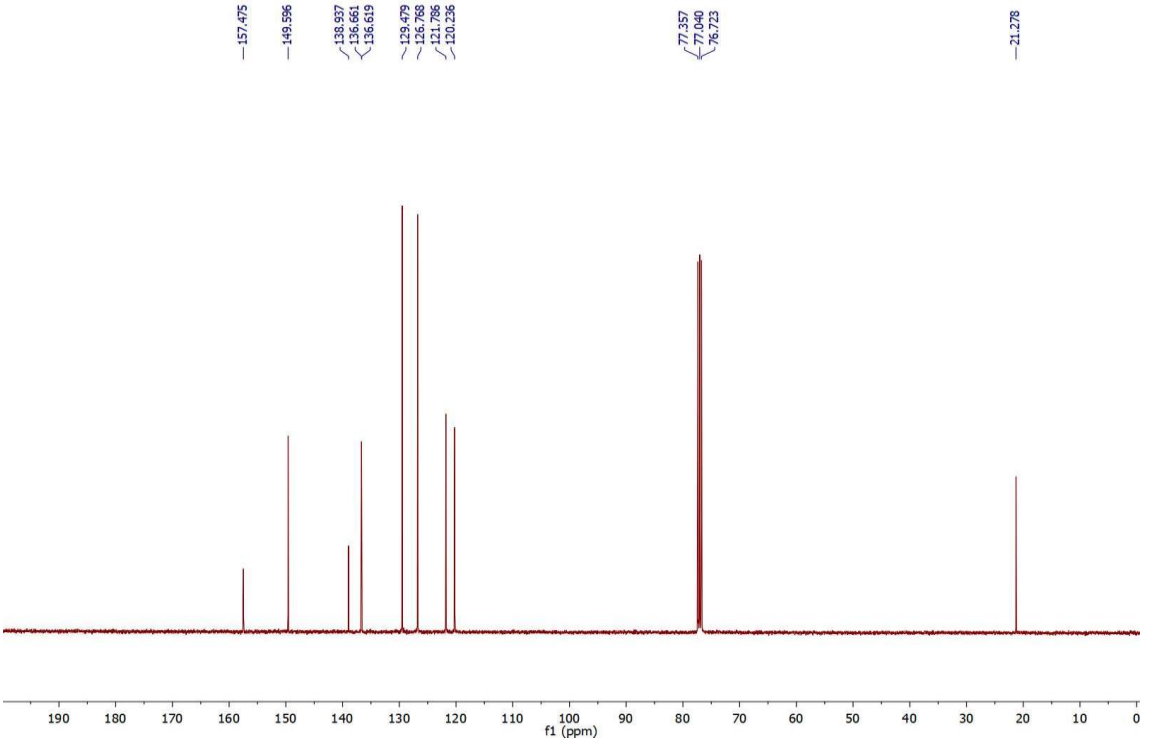




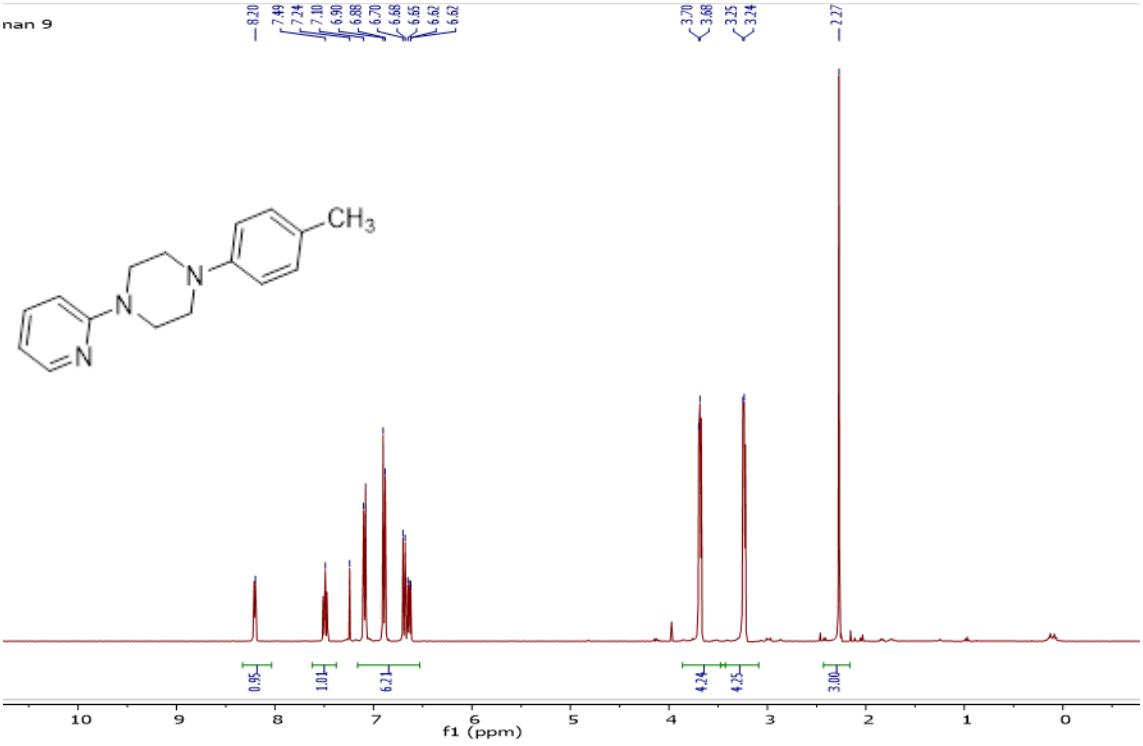


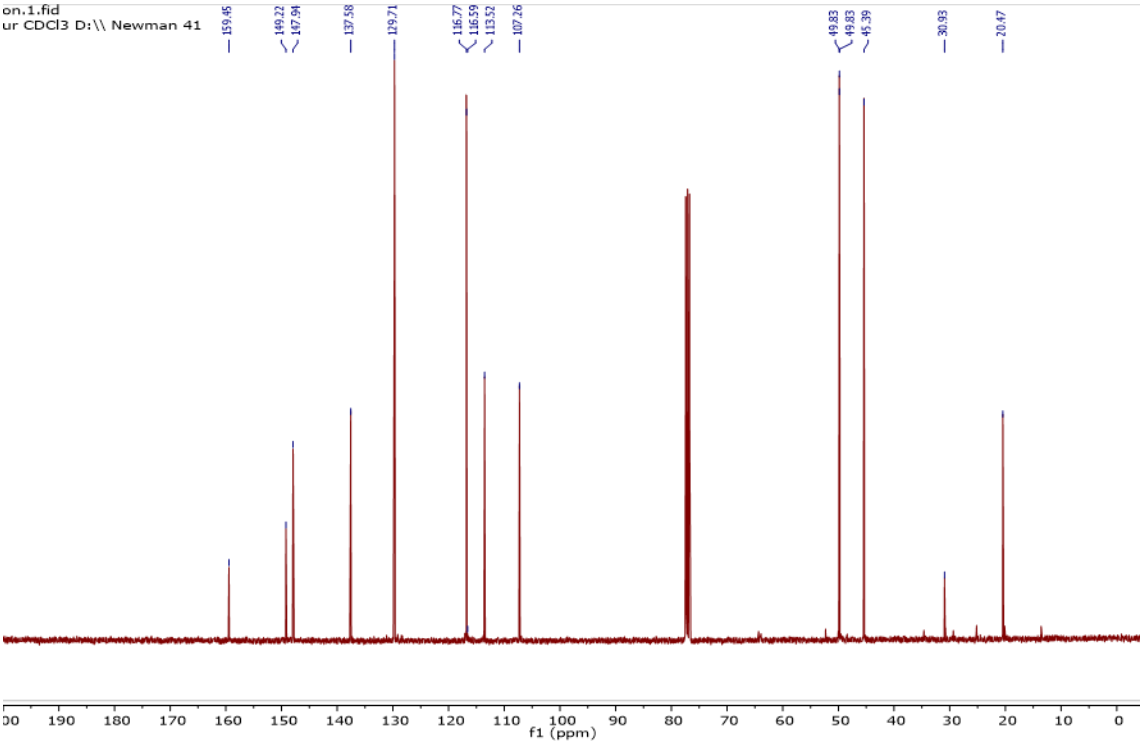
2-(p-Tolyl)pyridine **18** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



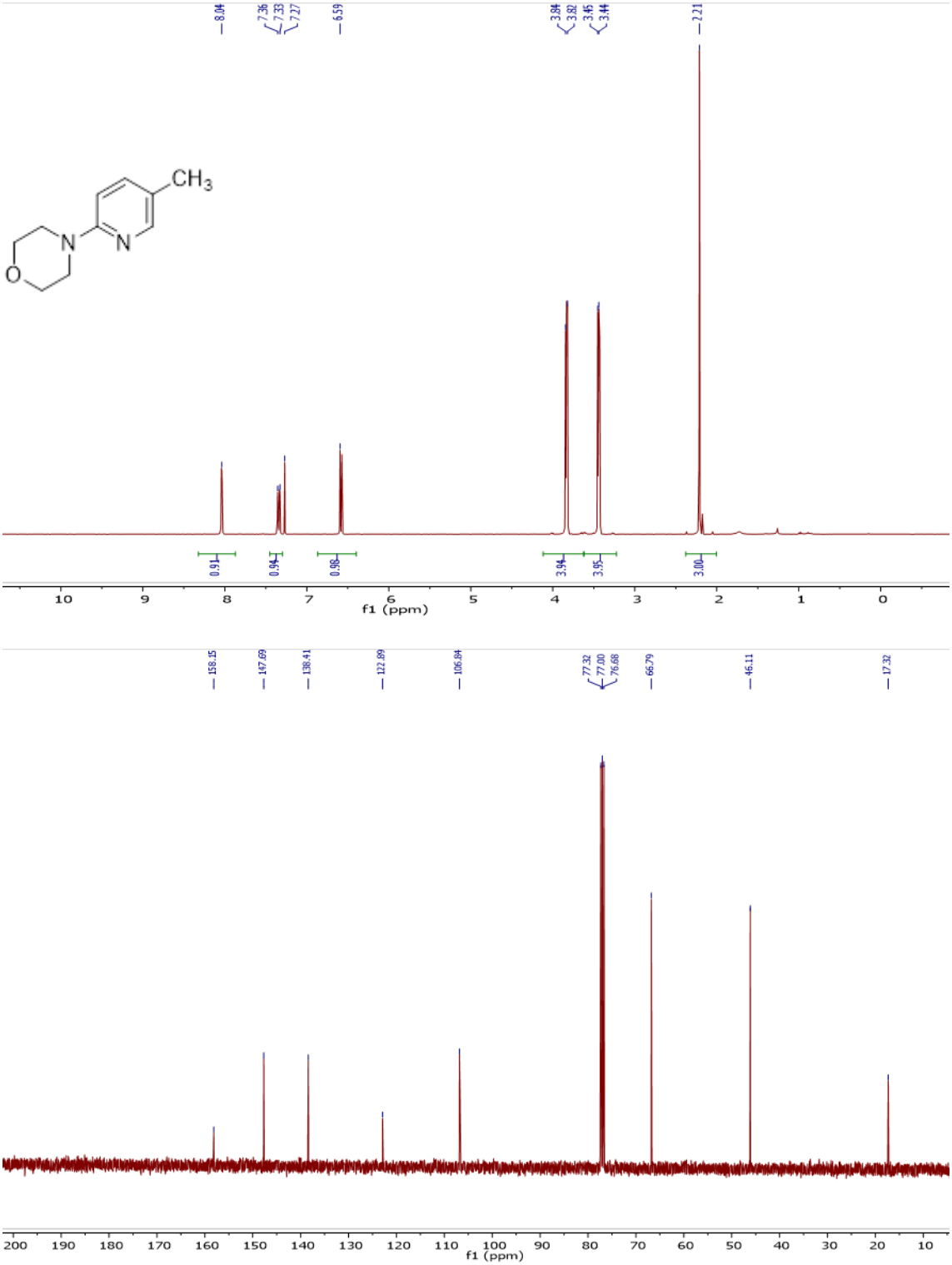


1-(4-Methylphenyl)-4-phenylpiperazine **19** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

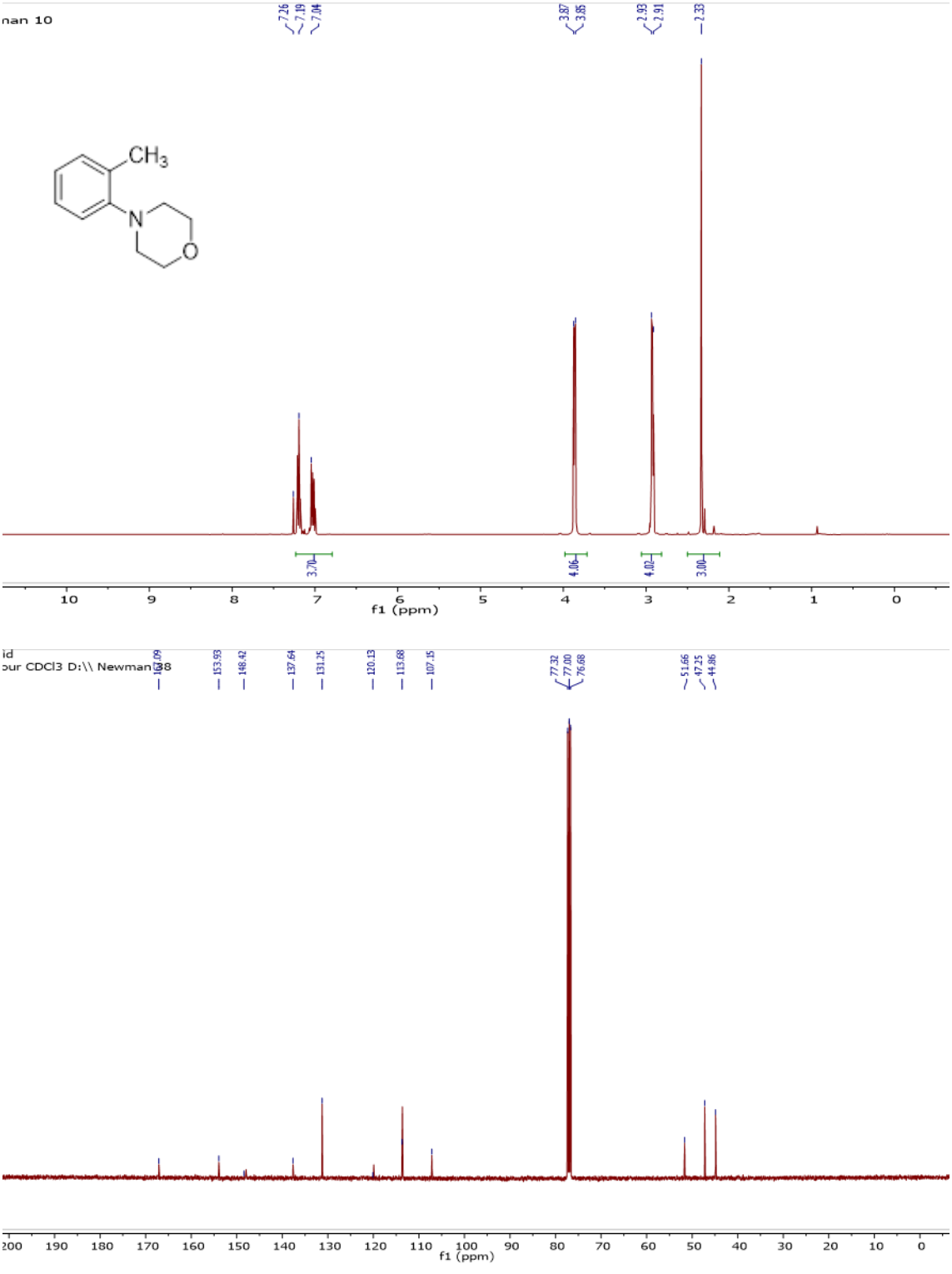




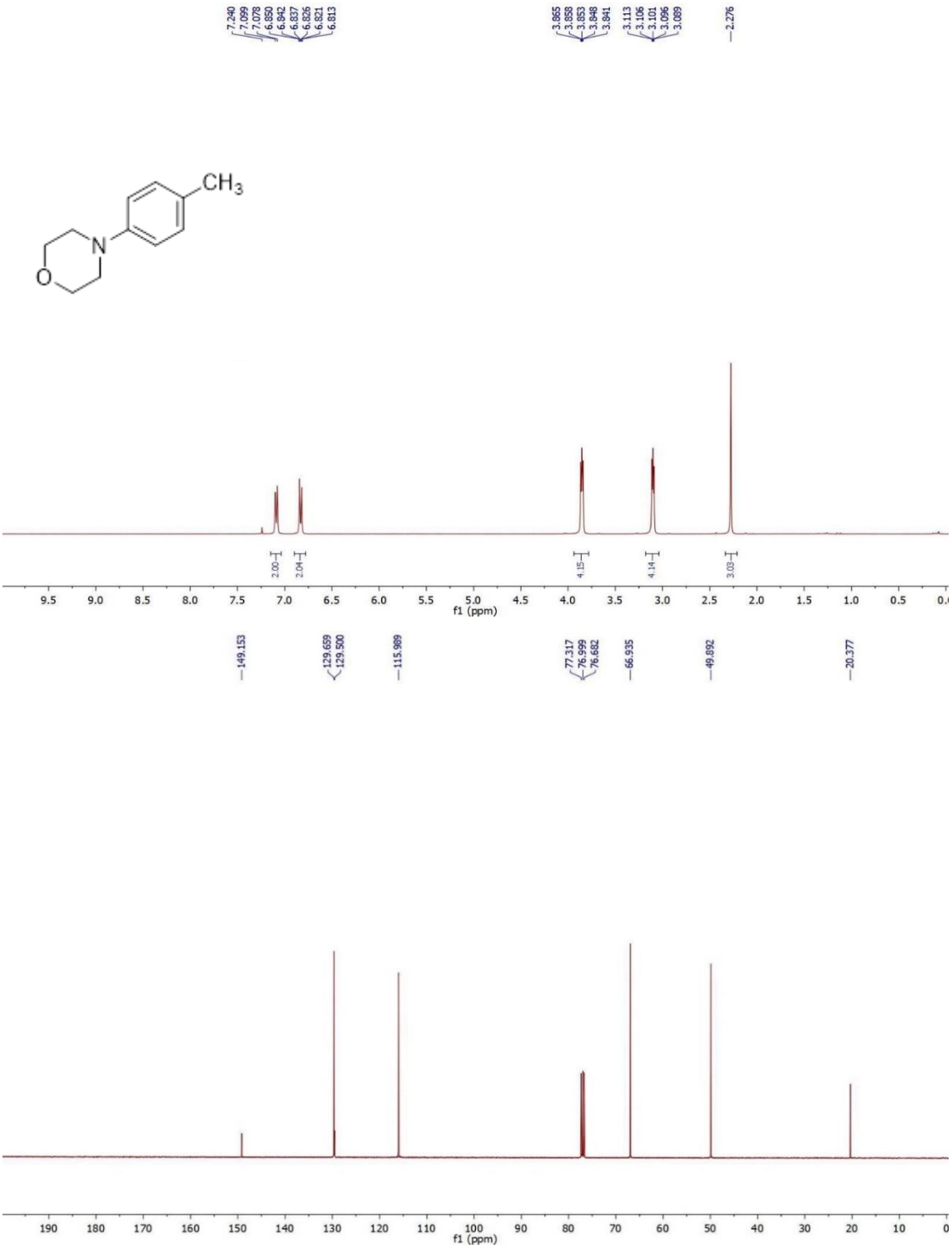
4-(5-Methyl-2-pyridinyl)-morpholine **20** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



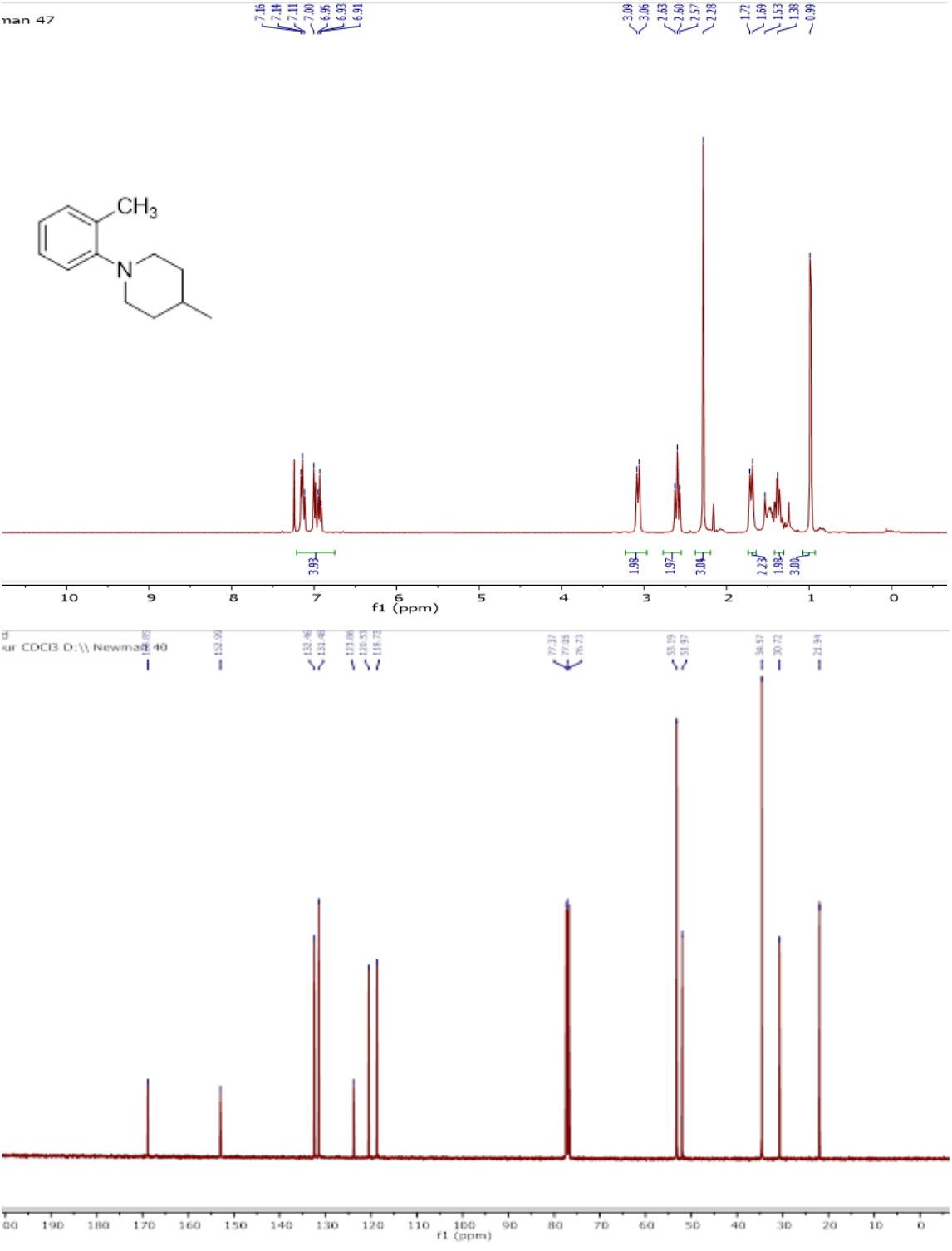
4-(2-Methylphenyl)-morpholine **21** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



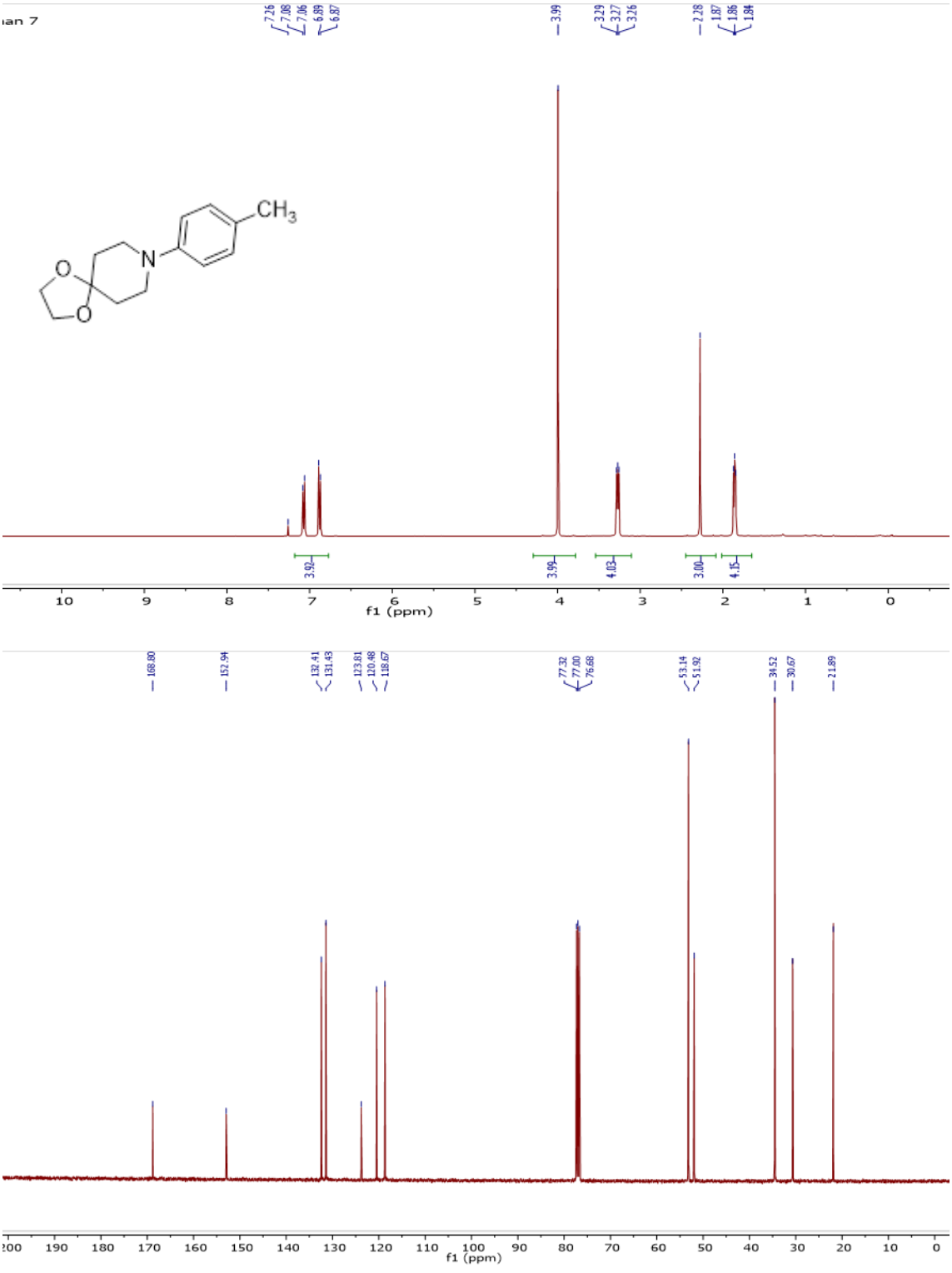
4-(p-Tolyl)morpholine **22** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



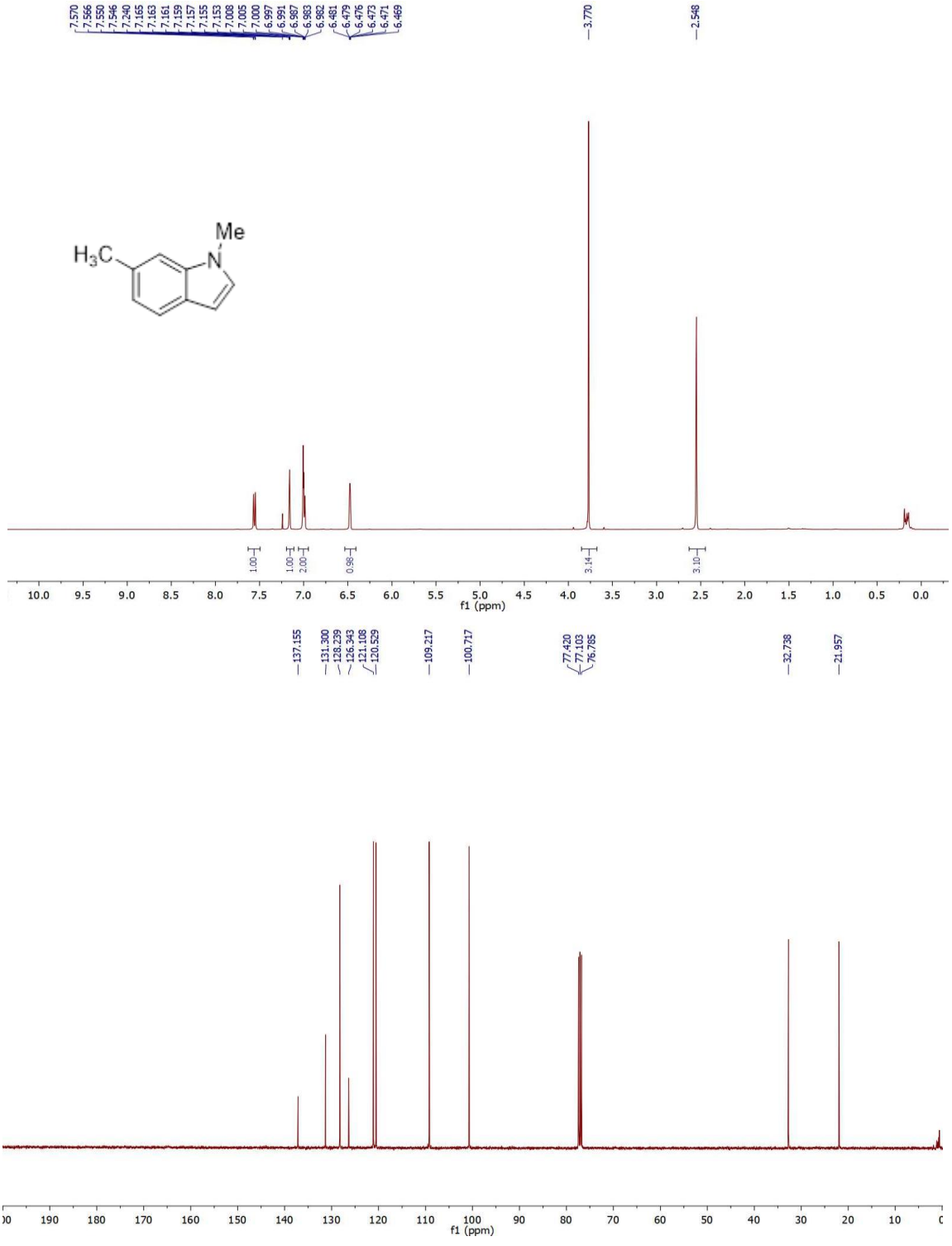
4-Methyl-1-(o-tolyl)piperidine **23** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



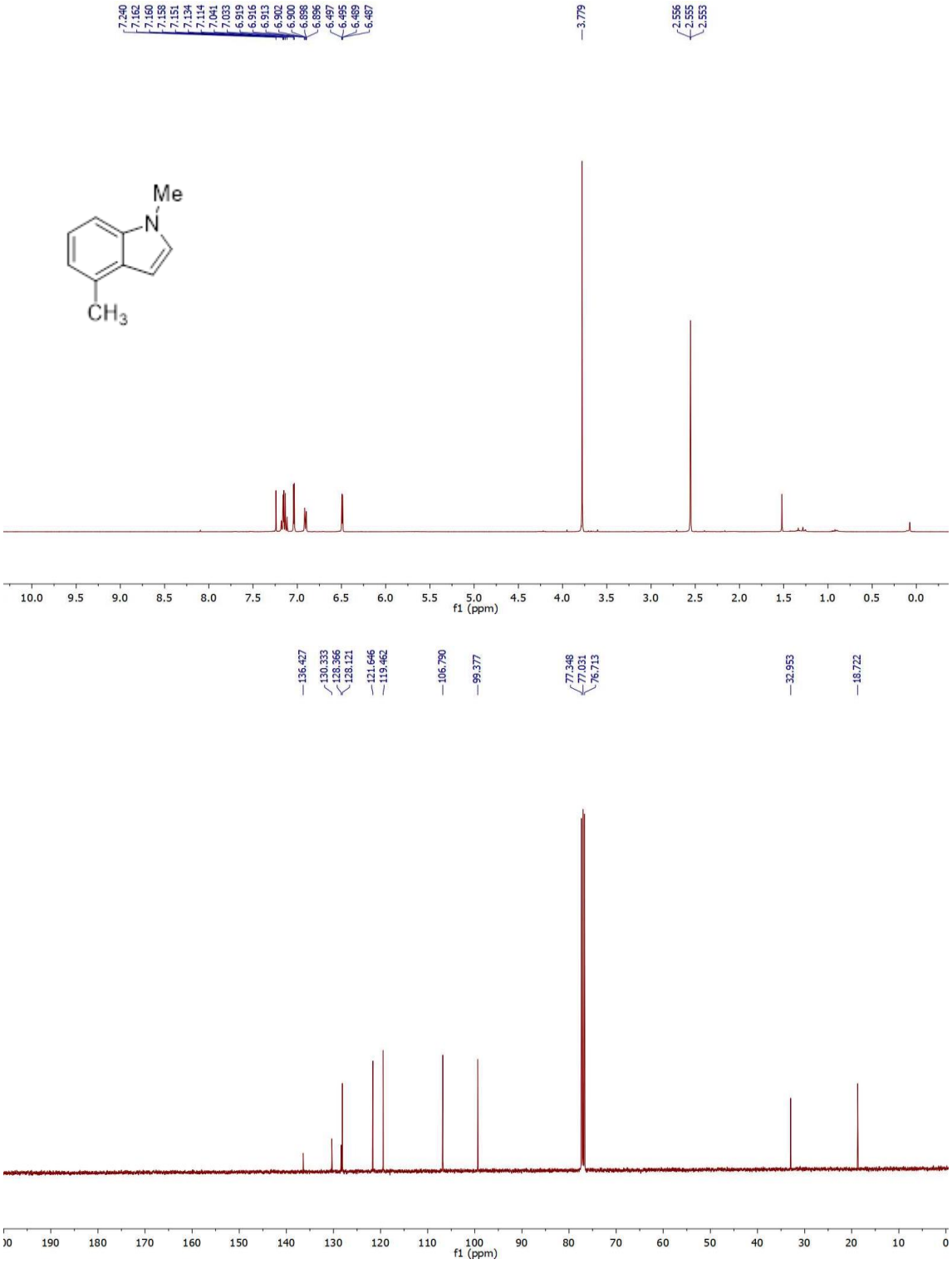
8-(4-Methylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane **24** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



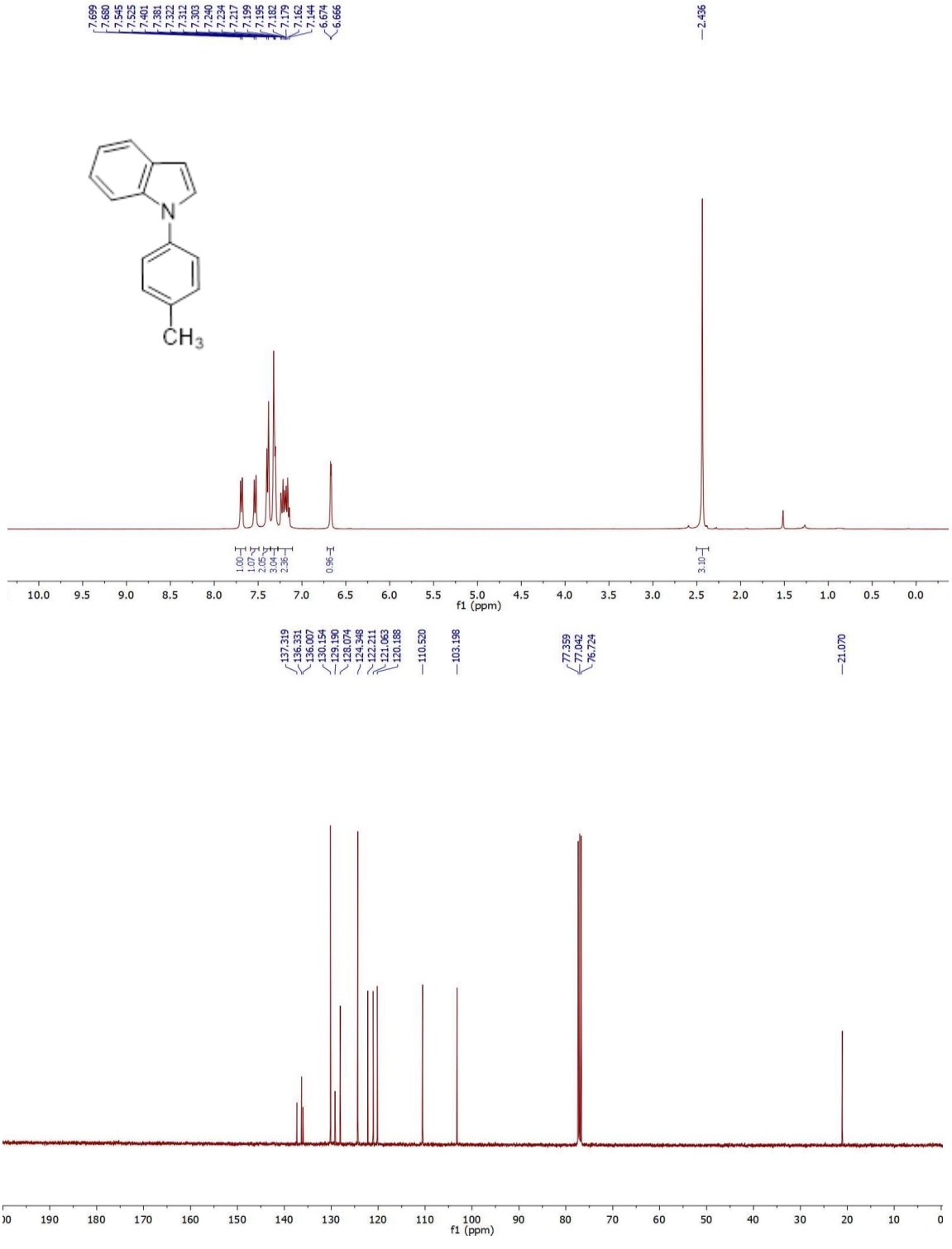
1,6-Dimethylindole **25** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



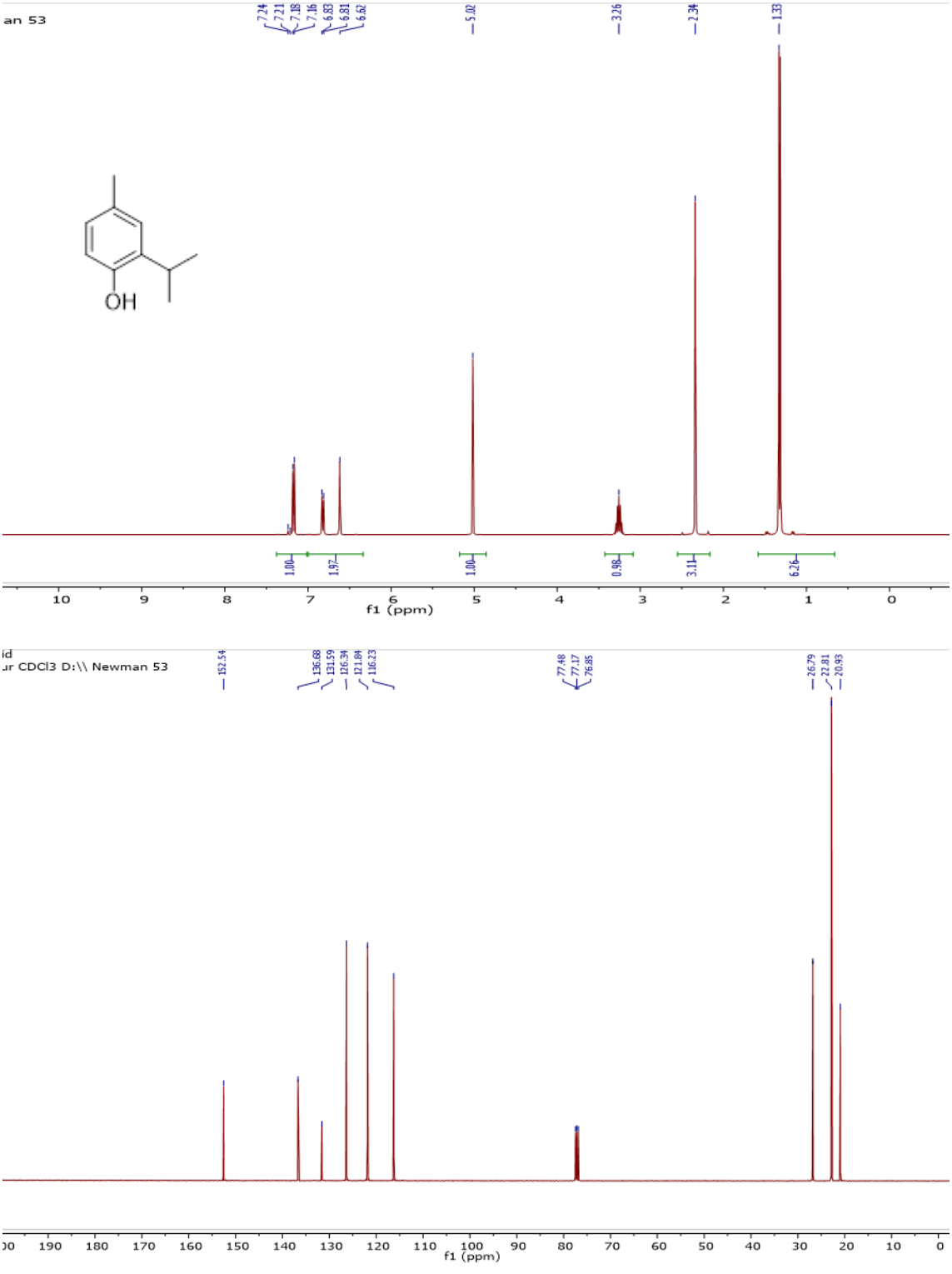
1,4-Dimethylindole **26** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



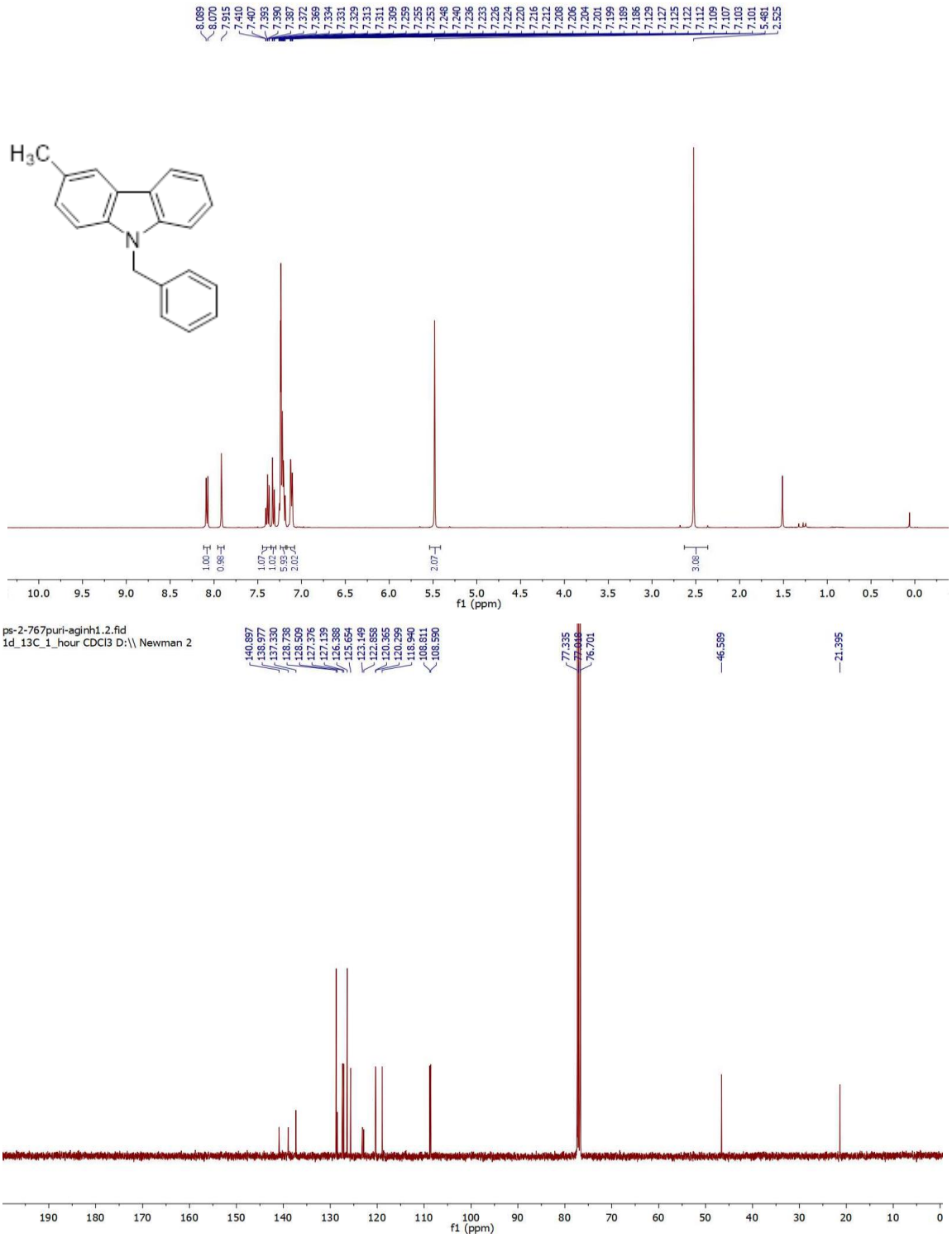
1-(p-Tolyl)-indole **27** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



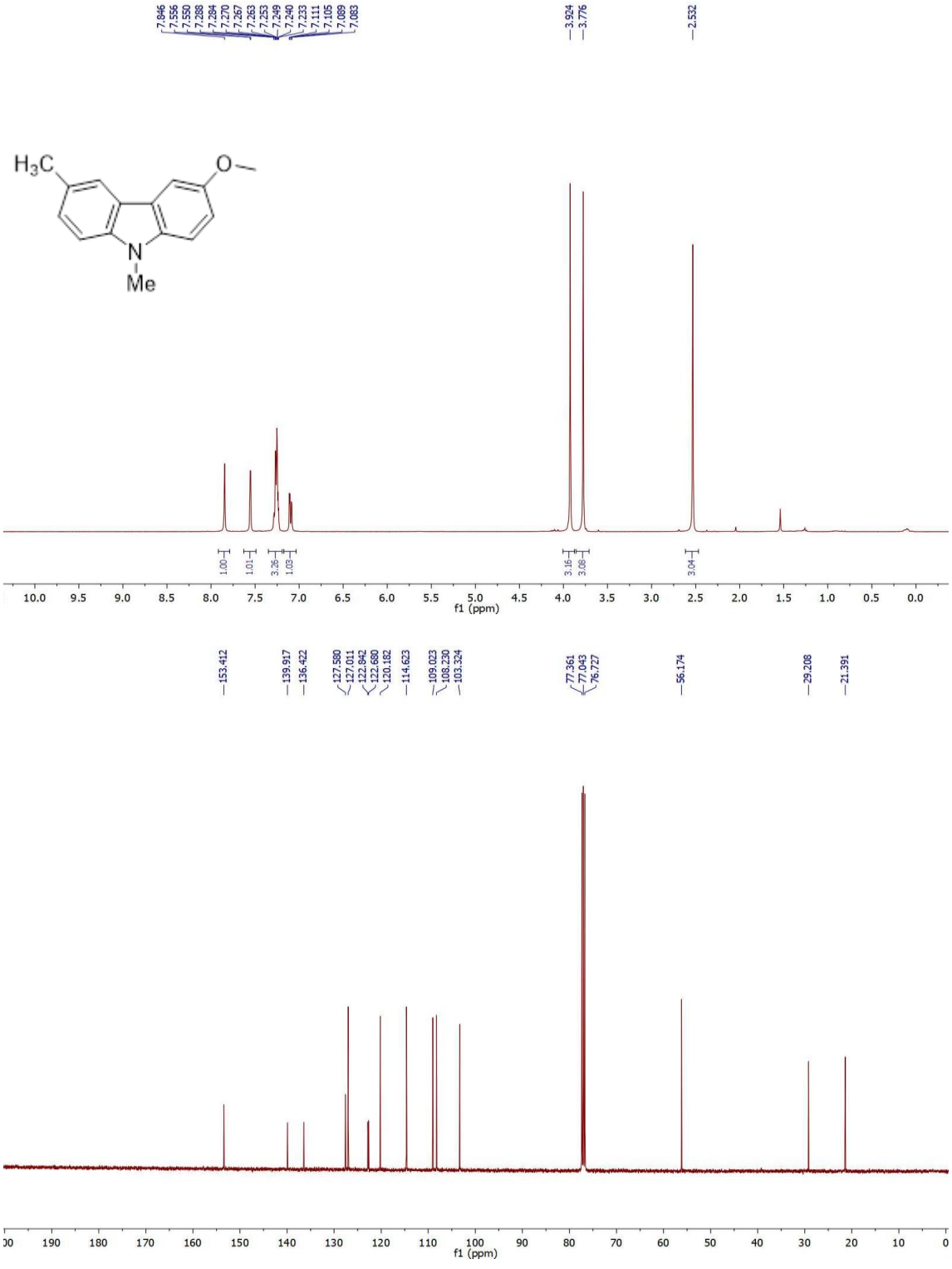
1-Methyl-3-hydroxy-4-isopropylbenzene **29** ($CDCl_3$, 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR)



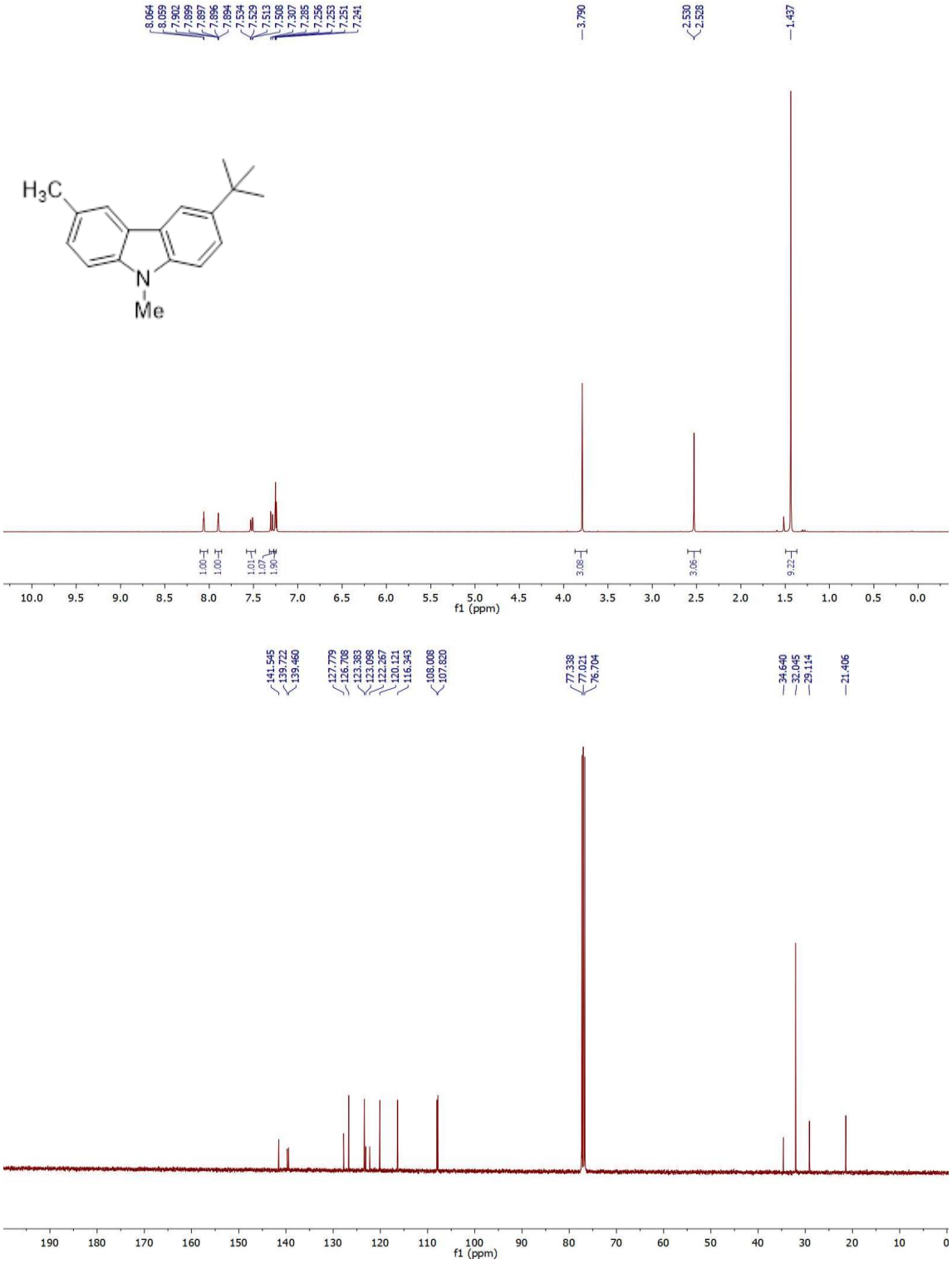
9-Benzyl-3-methylcarbazole **30** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



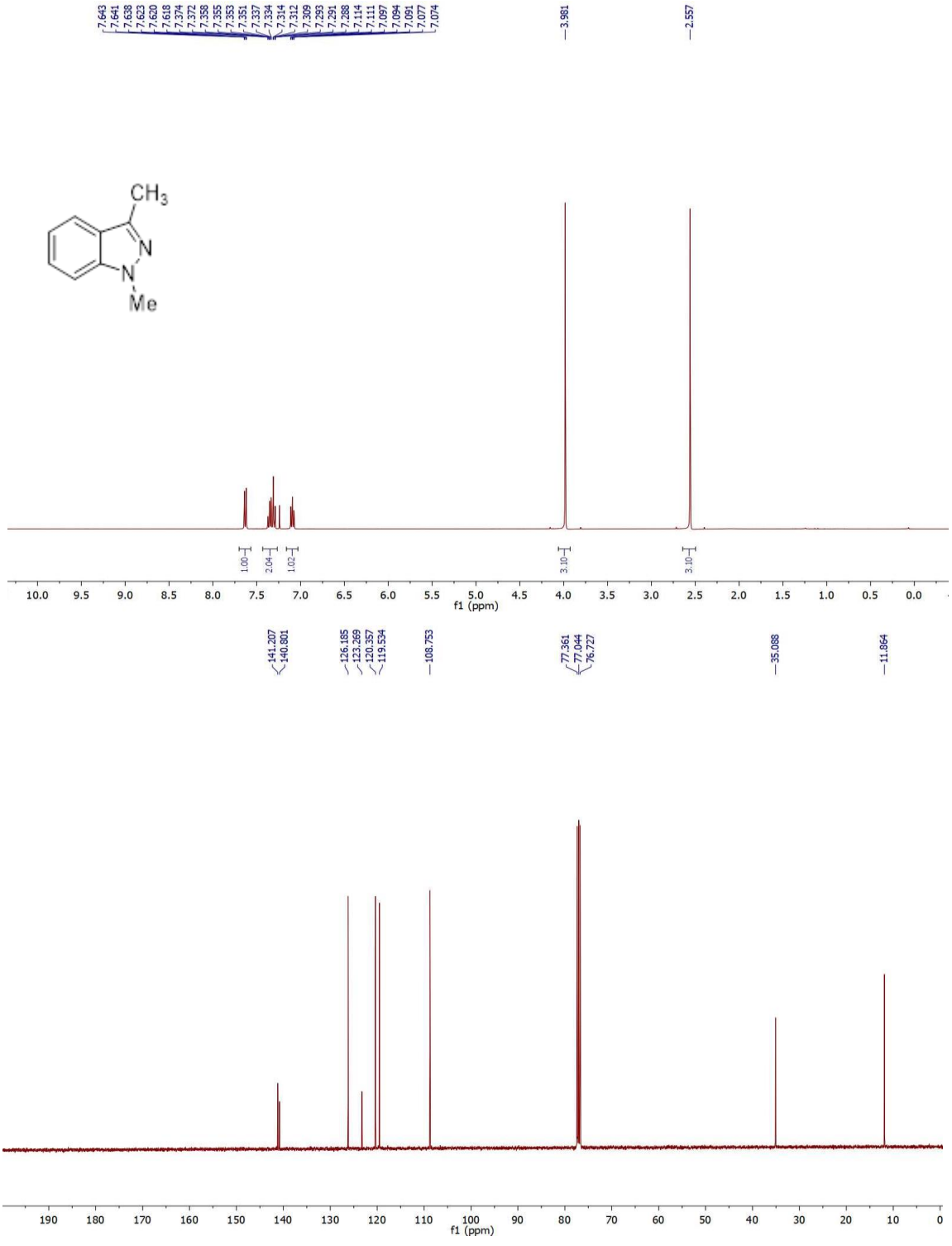
3-Methoxy-6,9-dimethyl-9-carbazole **31** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



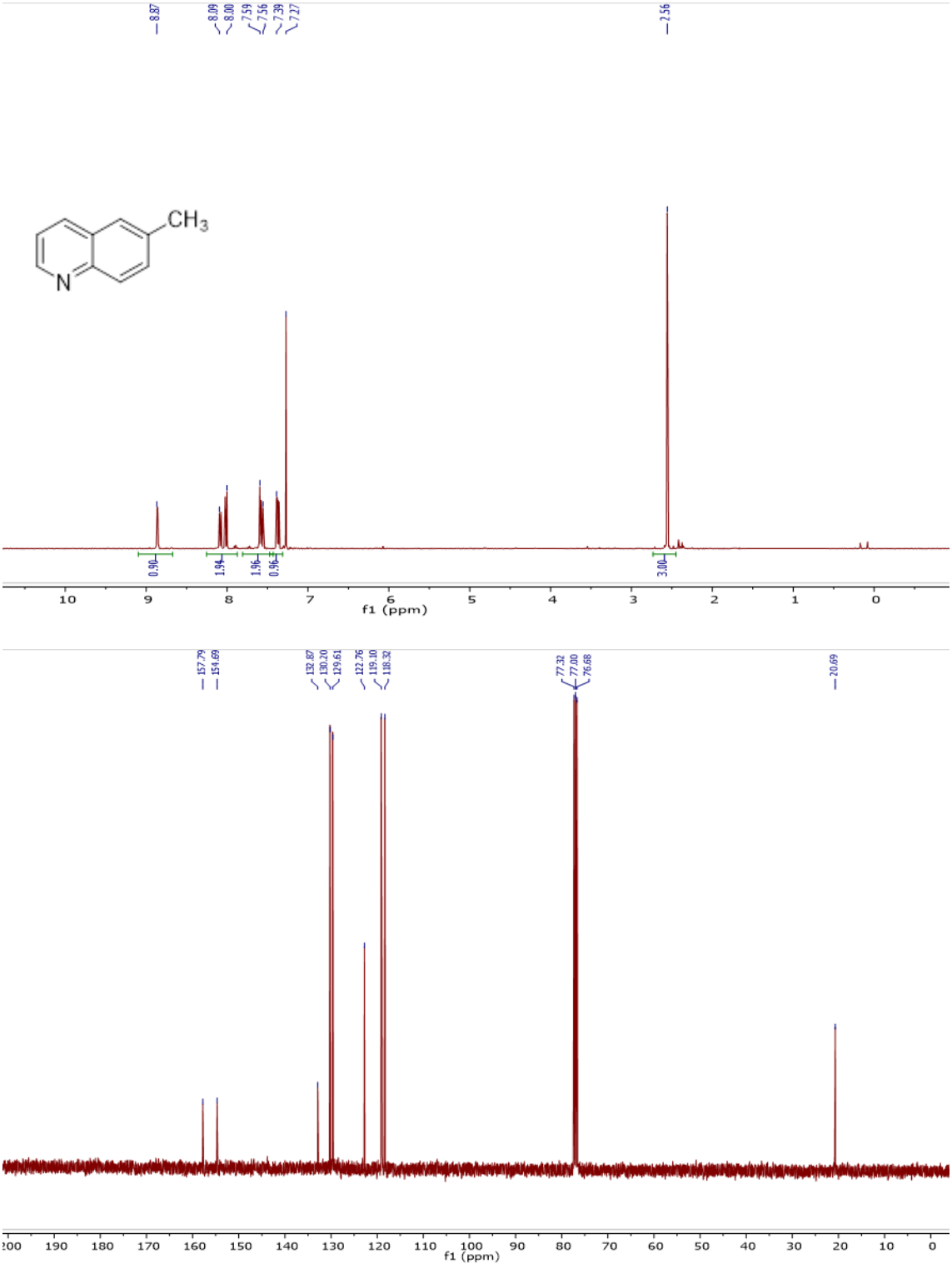
3-(*t*-Butyl)-6,9-dimethyl-carbazole **32** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



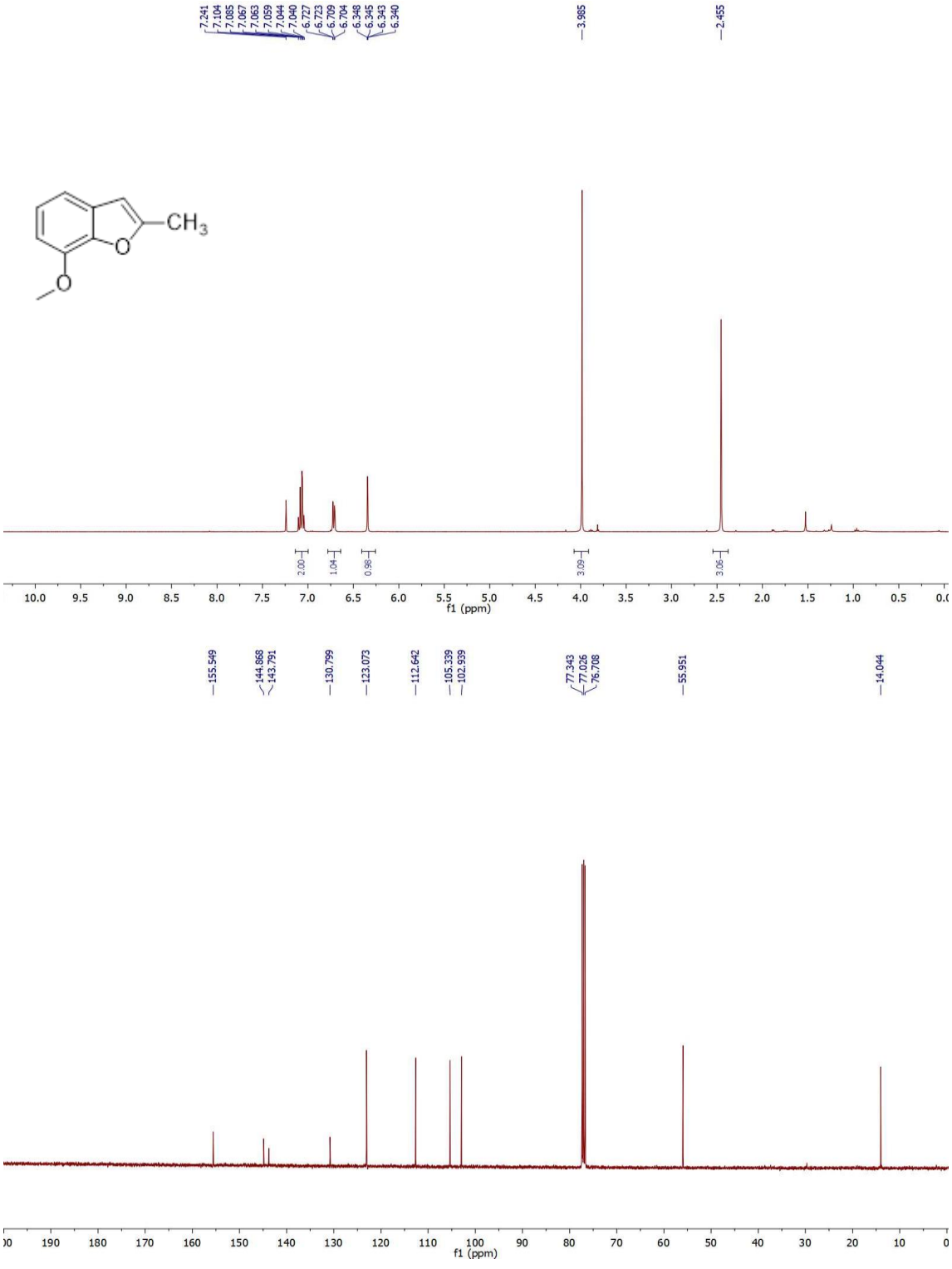
1,3-Dimethylindazole **33** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



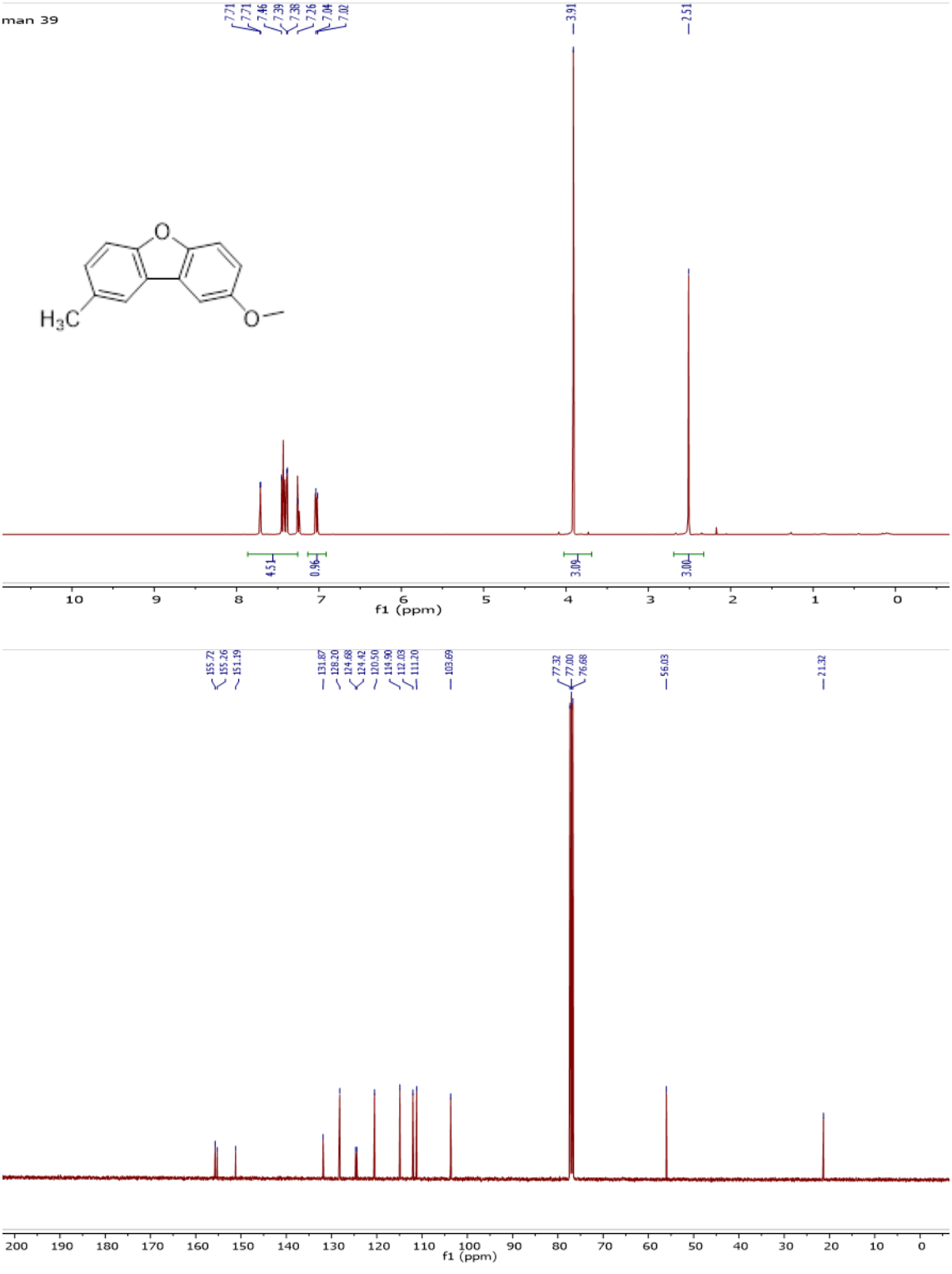
6-Methylquinoline **34** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



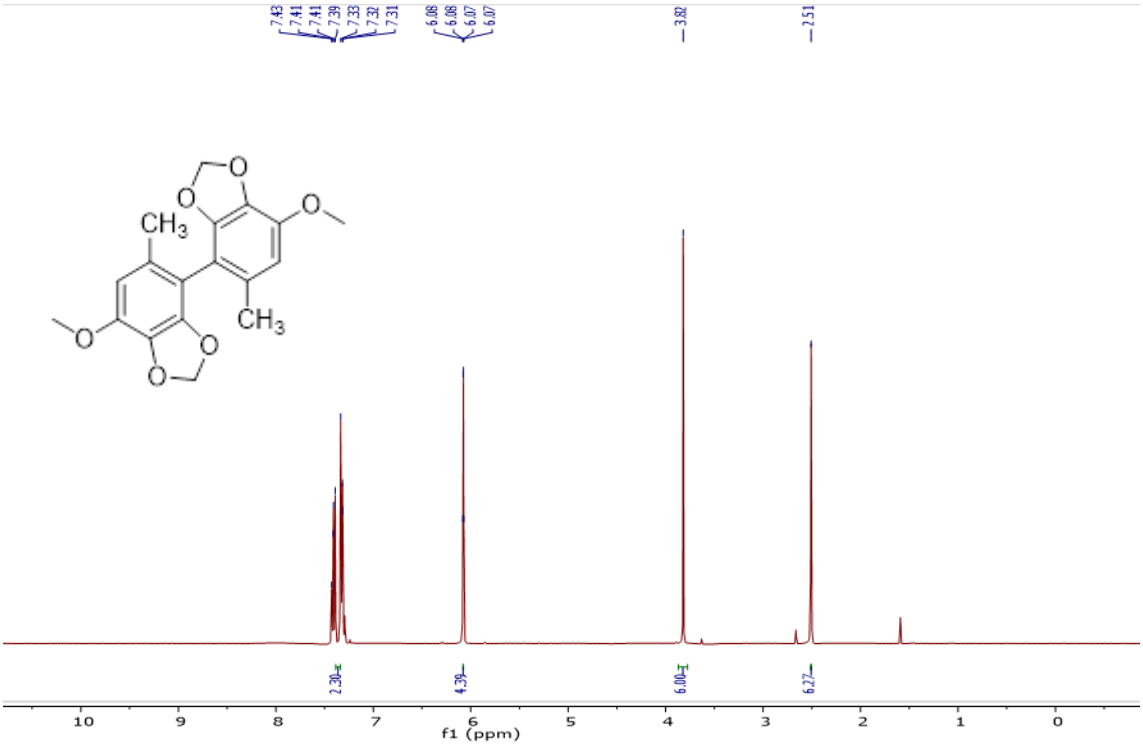
7-Methoxy-2-methylbenzofuran **35** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

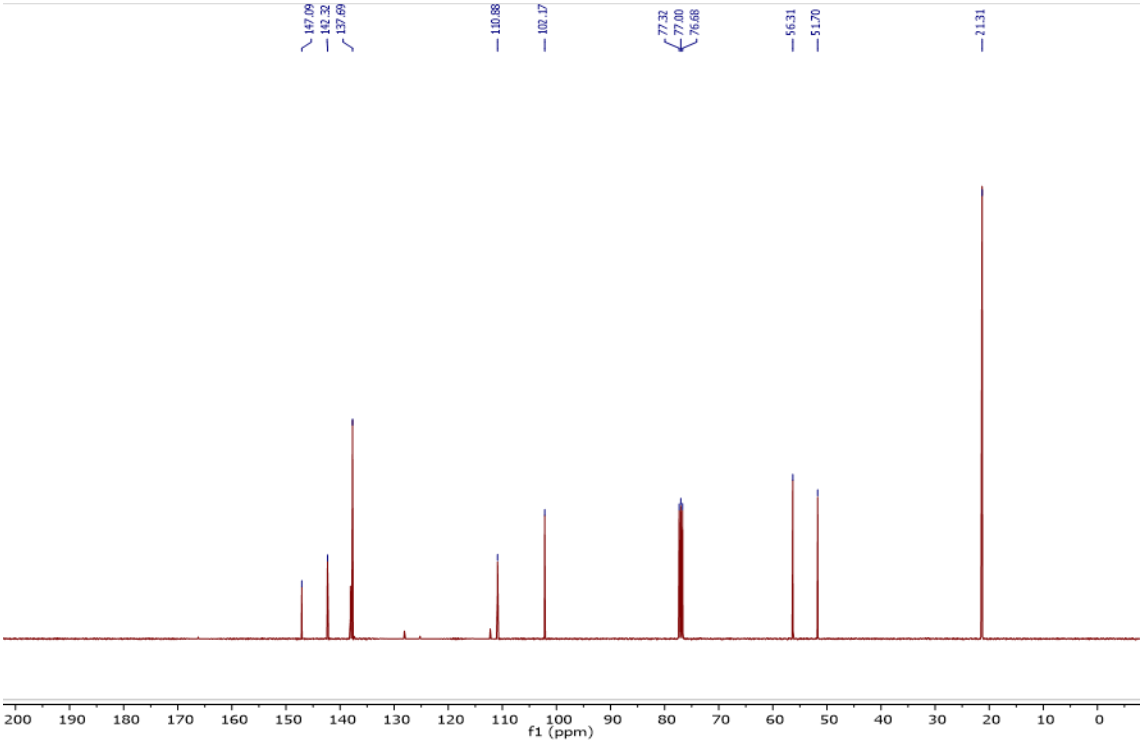


2-Methoxy-8-methyl-dibenzofuran **36** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

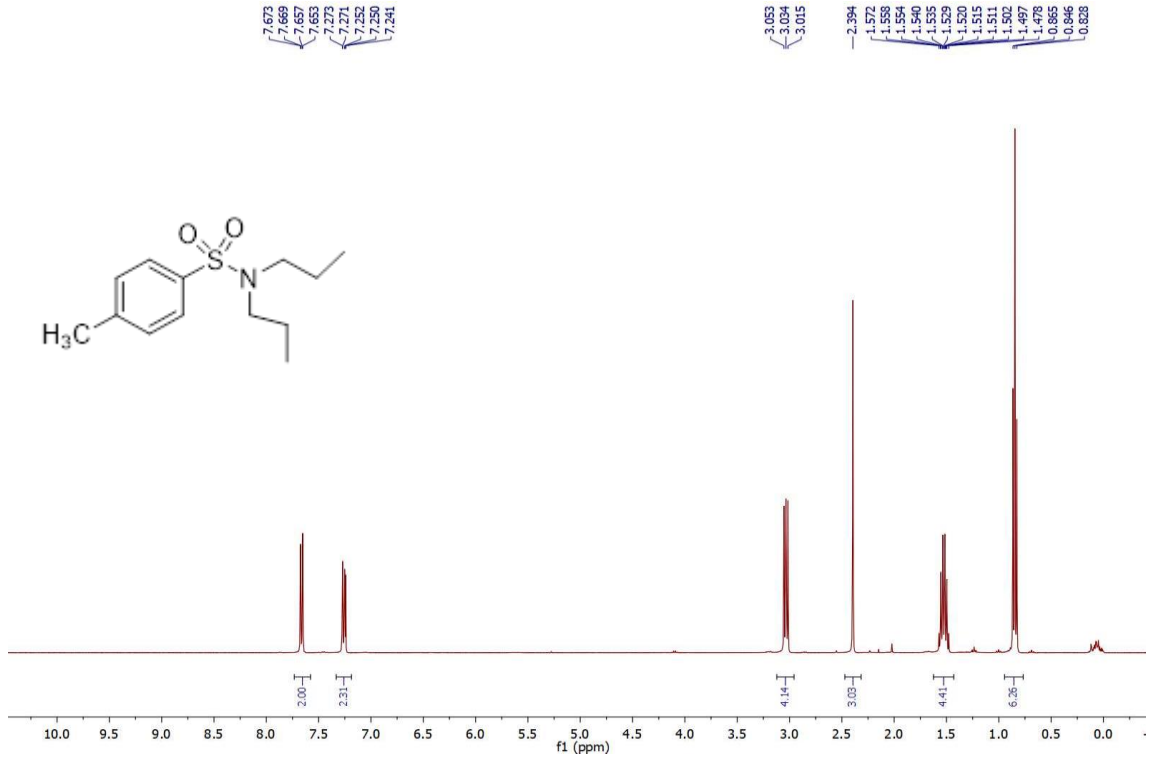


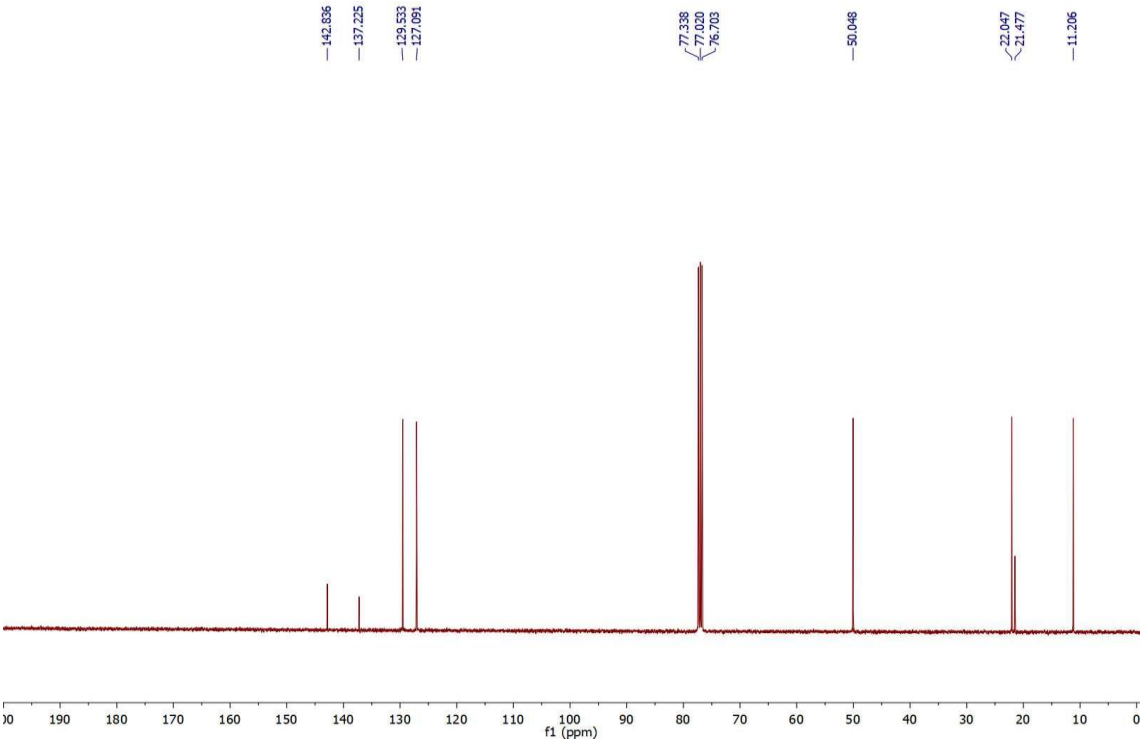
7,7'-Dimethoxy-5,5'-dimethyl-4,4'-bibenzo[d][1,3]dioxole **37** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



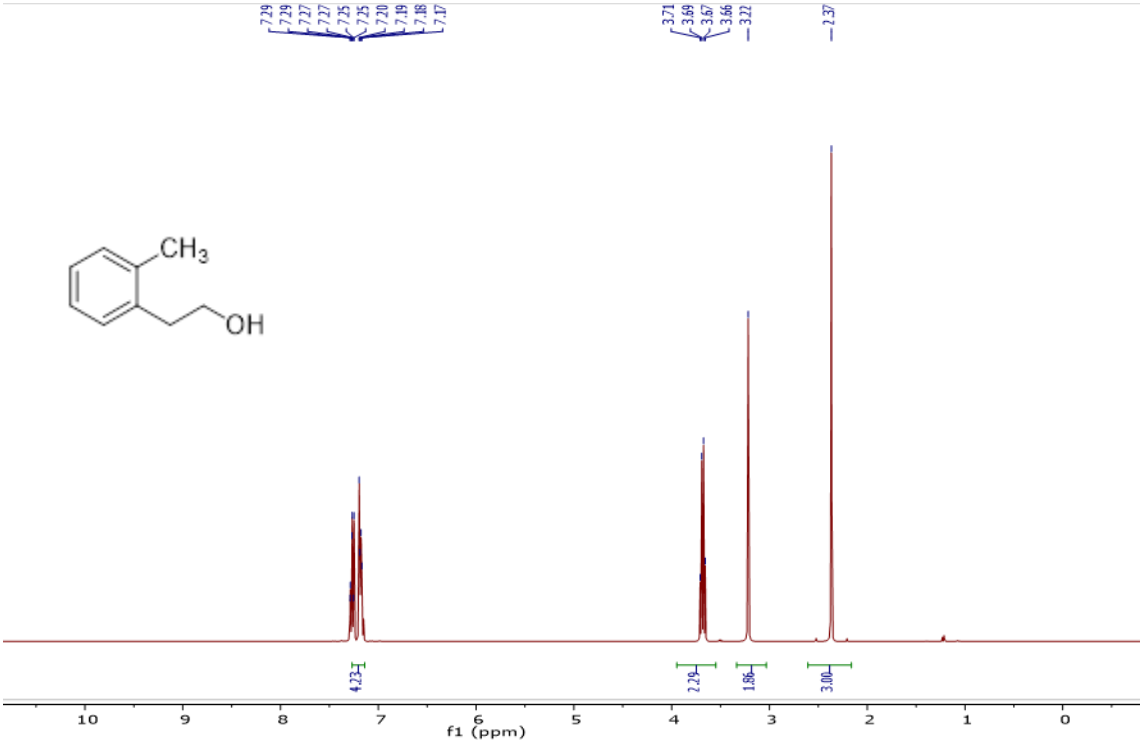


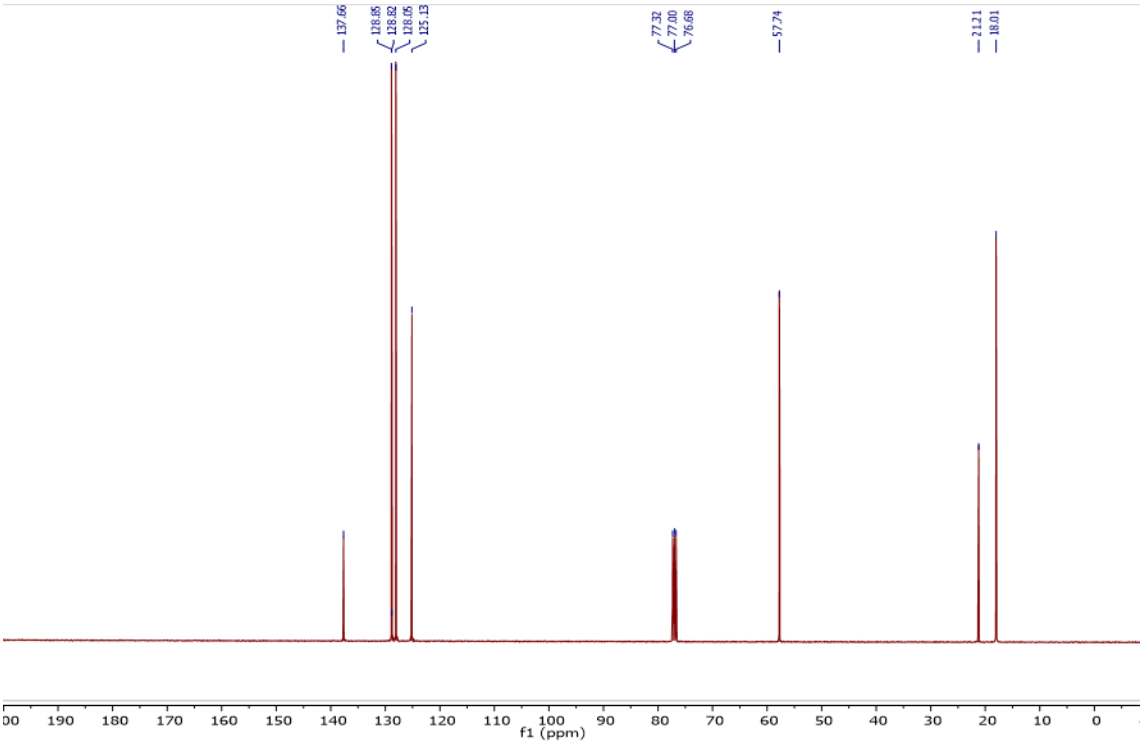
4-Methyl-*N,N*-dipropylbenzenesulfonamide **38** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



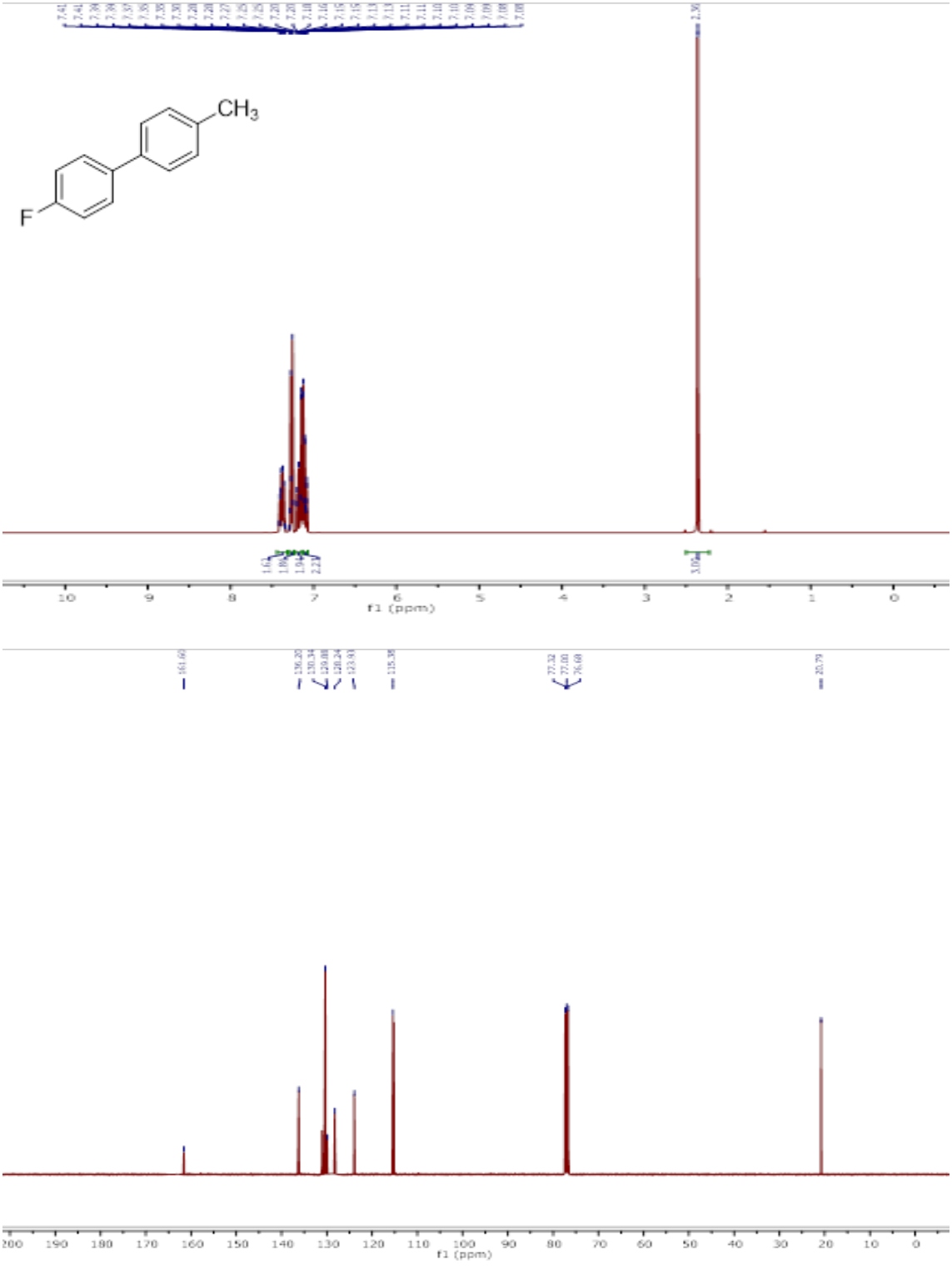


2-(Methylbenzene)ethanol **39** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

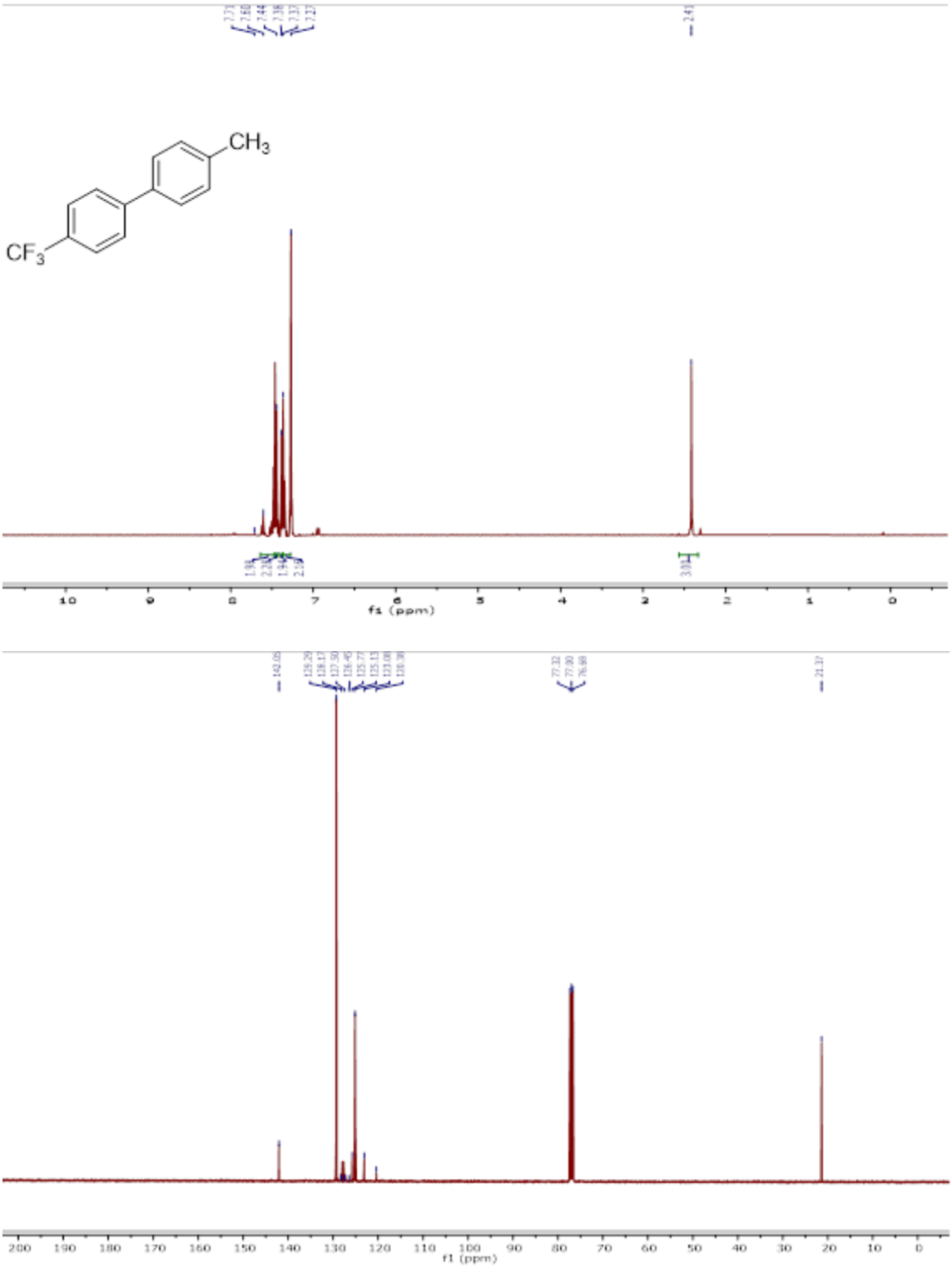




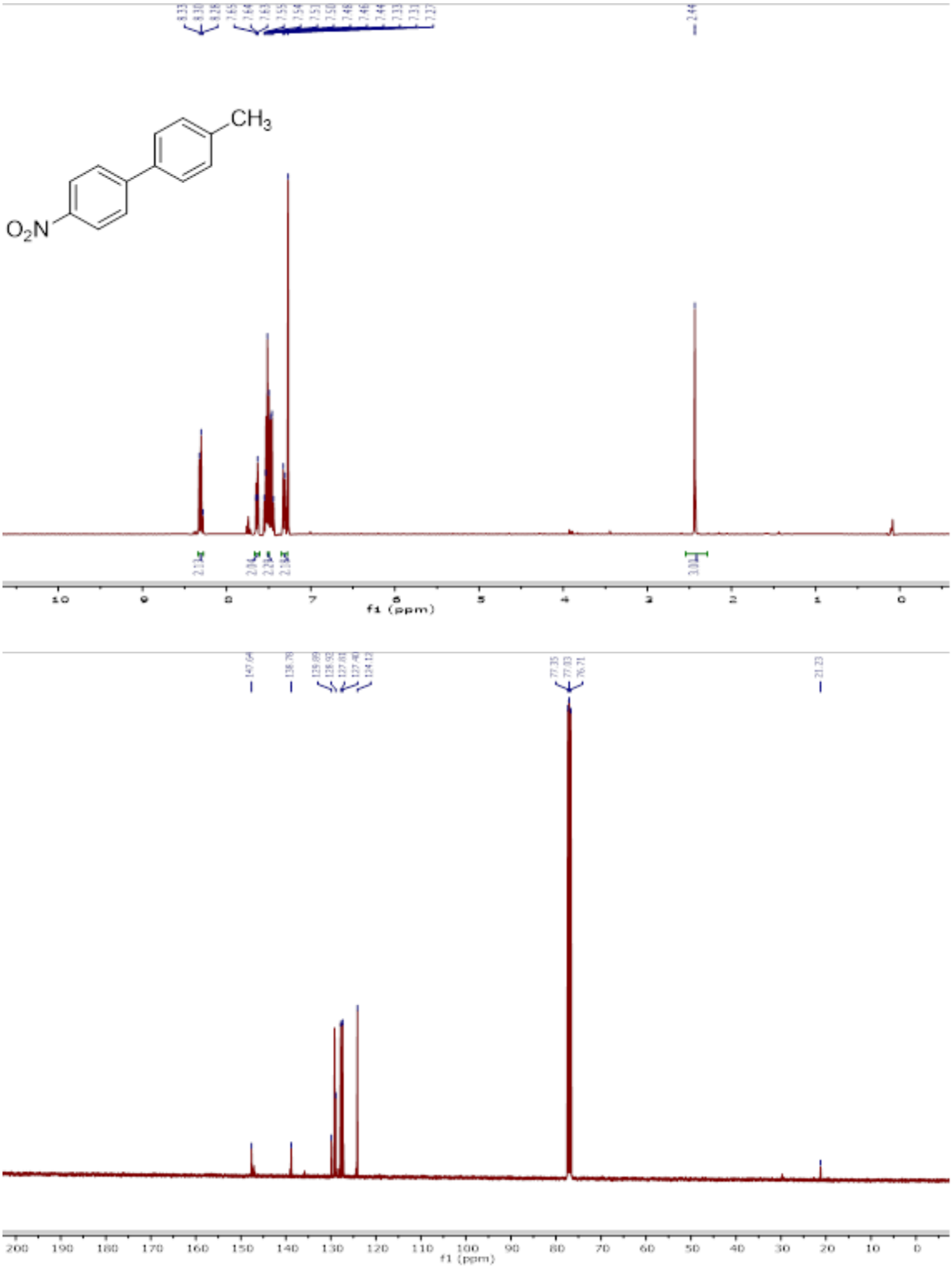
4-Fluoro-4'-methylbiphenyl **40** ($CDCl_3$, 400 MHz for ^1H NMR)



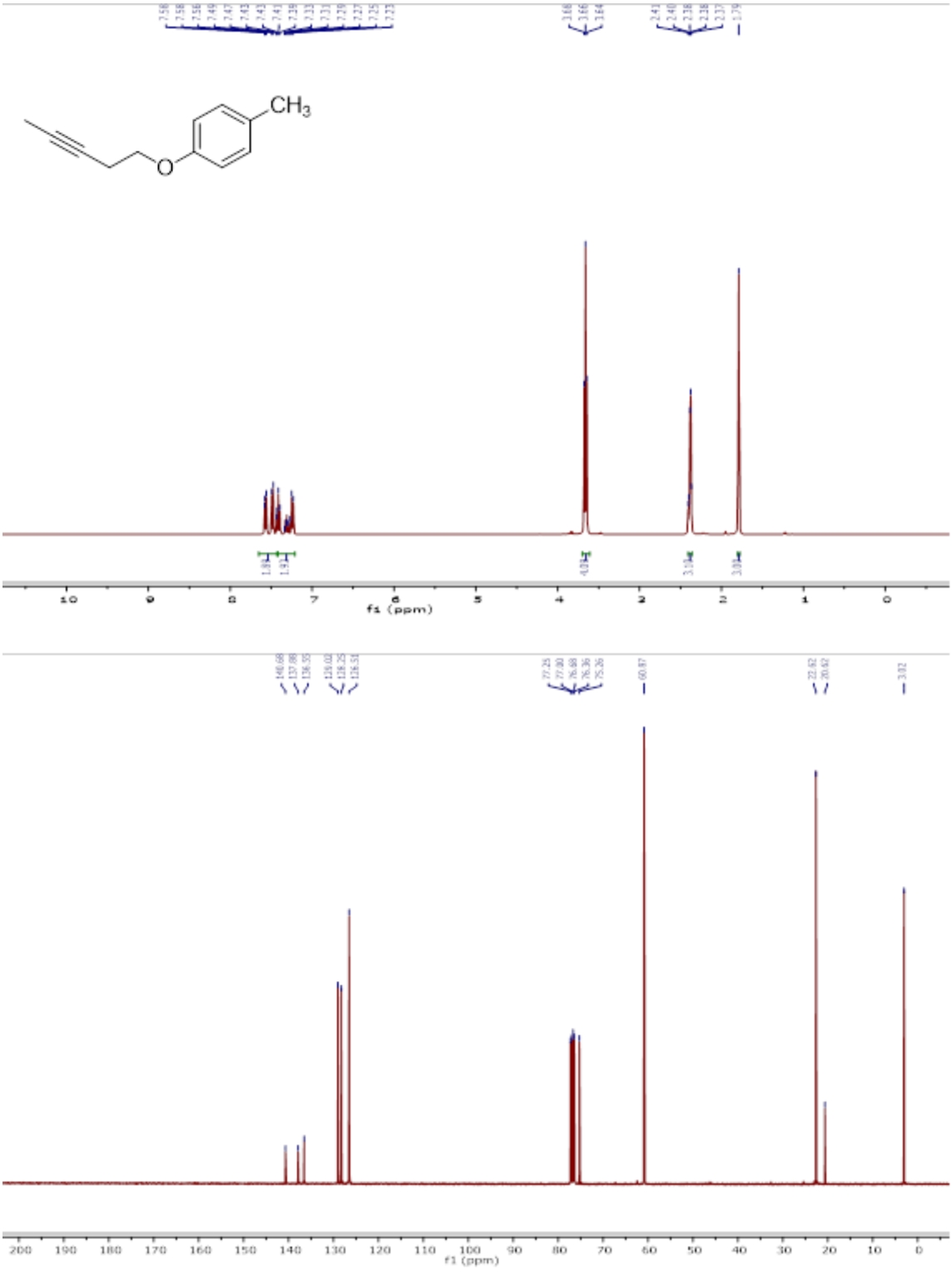
4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl **41** ($CDCl_3$, 400 MHz for ^1H NMR)



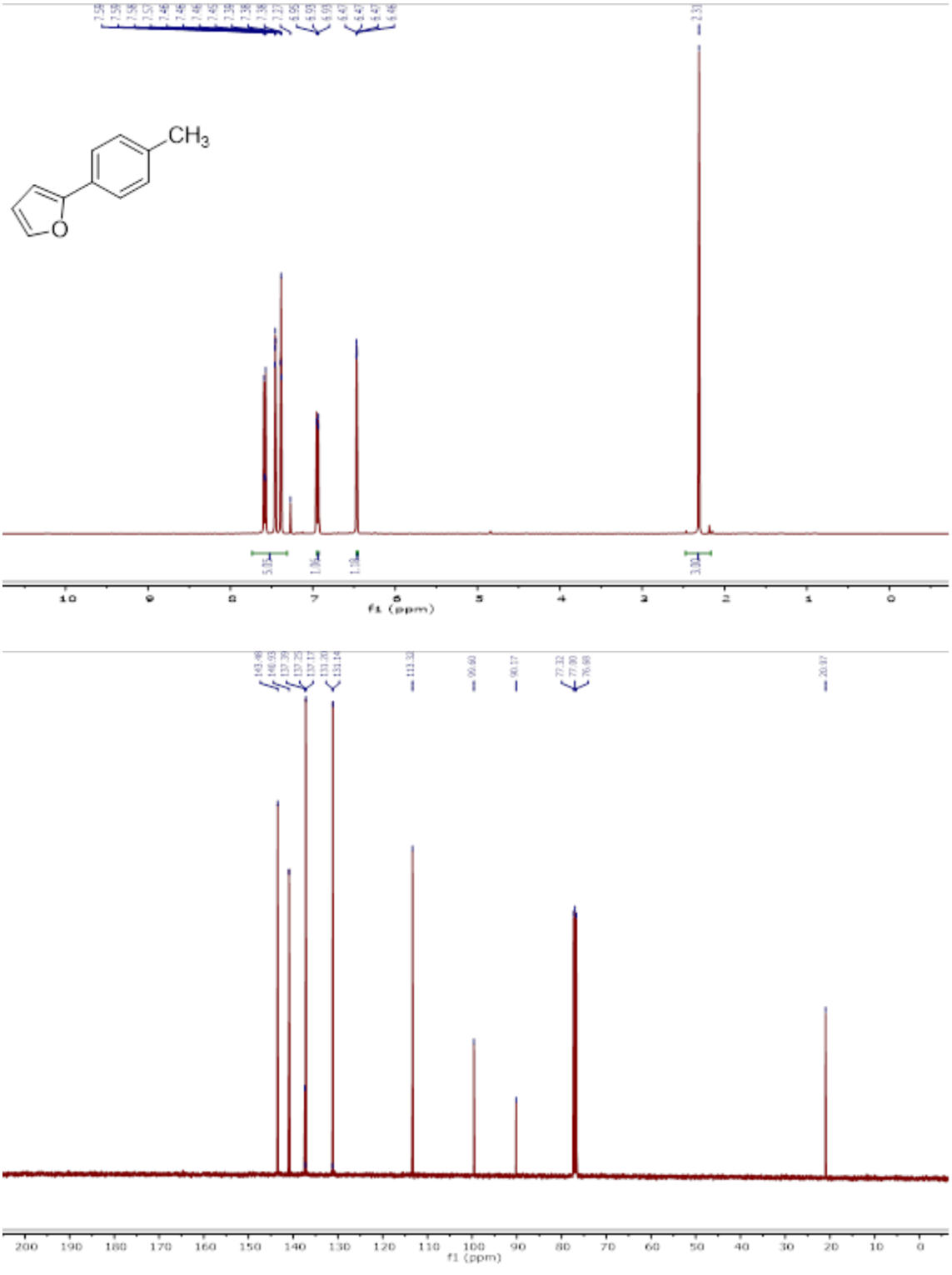
4-methyl-4’-nitrobiphenyl **42** ($CDCl_3$, 400 MHz for ^1H NMR)



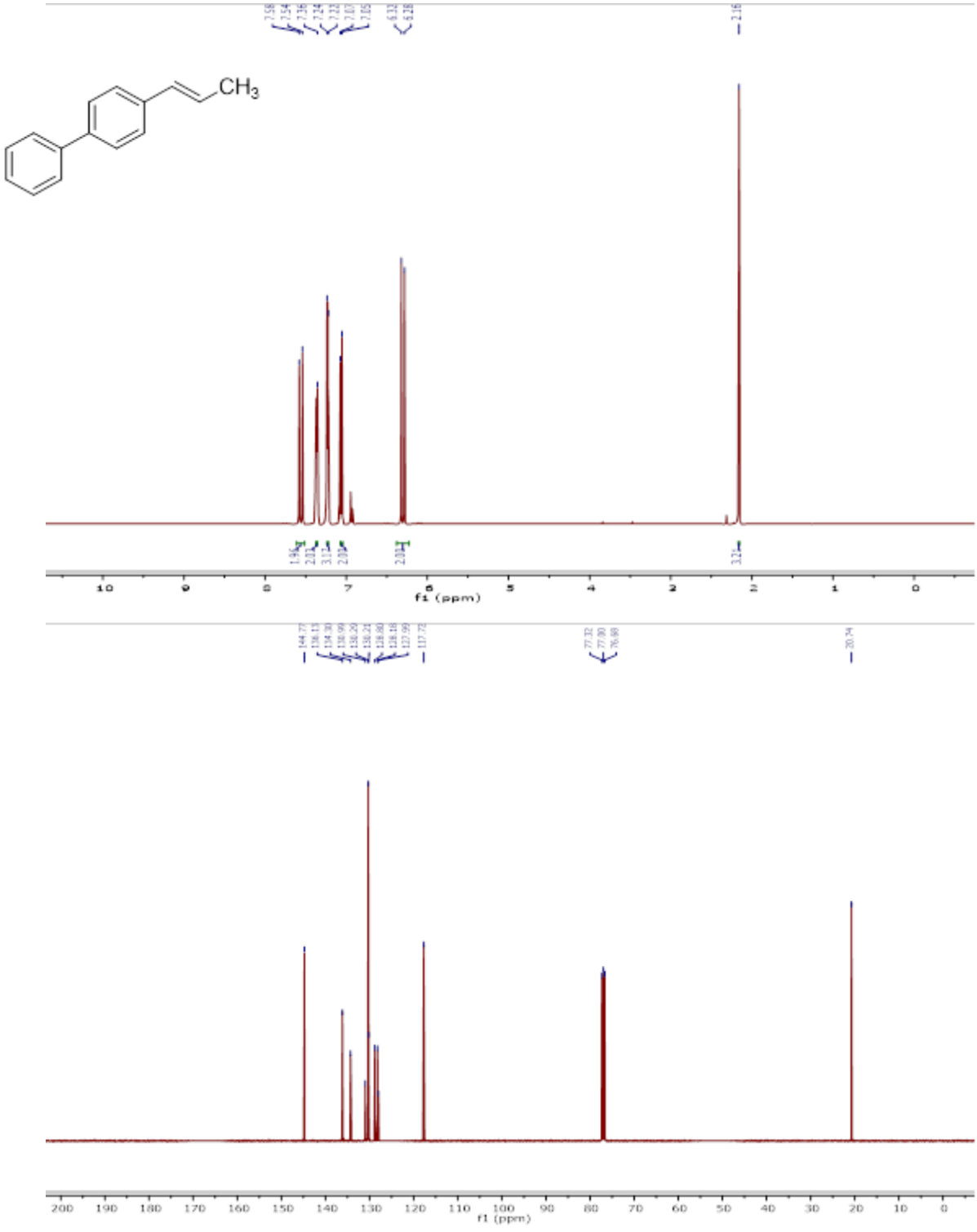
1-methyl-4-(3-pentyn-1-yloxy)-benzene **43** ($CDCl_3$, 400 MHz for ^1H NMR)



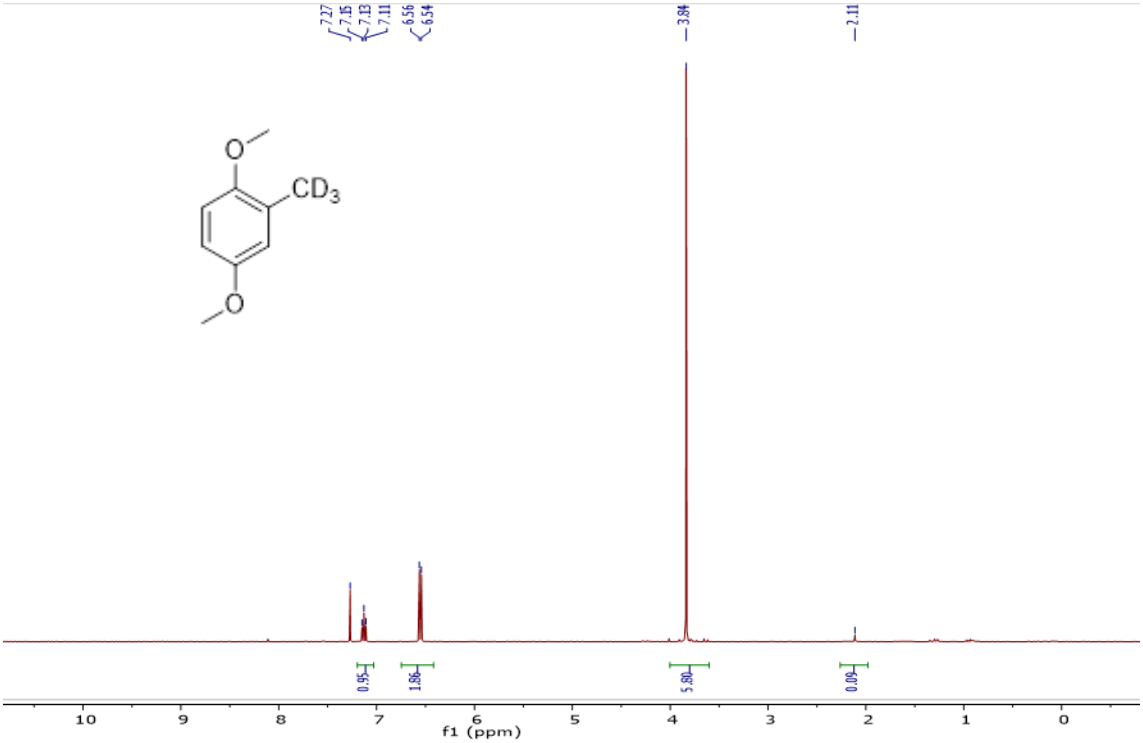
2-(4-Methylphenyl)furan **44** ($CDCl_3$, 400 MHz for ^1H NMR)



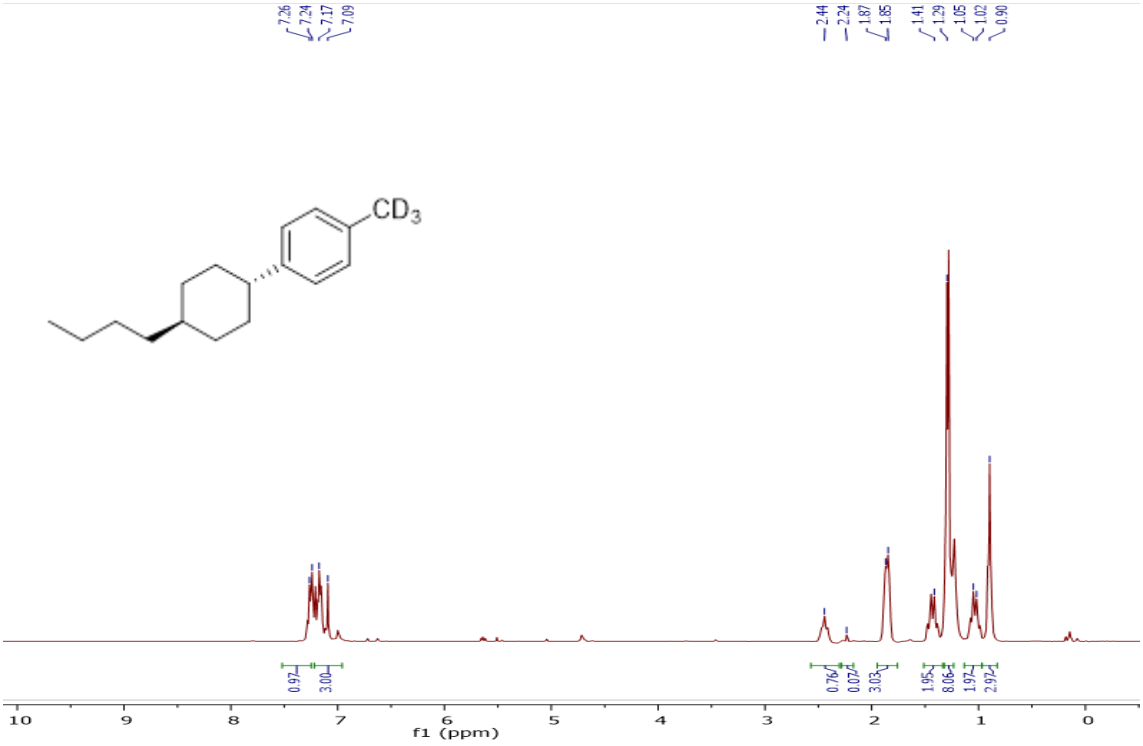
4-(1-propen-1-yl)-1,1’-biphenyl **45** ($CDCl_3$, 400 MHz for ^1H NMR)



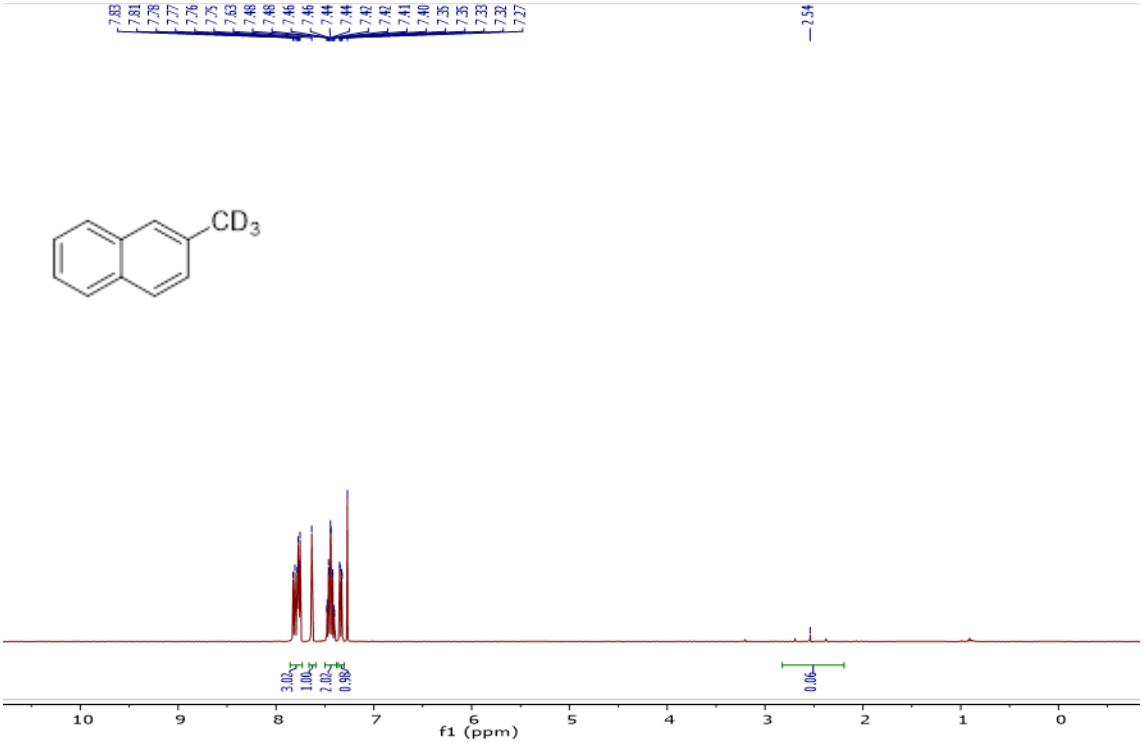
1,4-Dimethoxy-2-(methyl-d_3)benzene **46** ($CDCl_3$, 400 MHz for ^1H NMR)



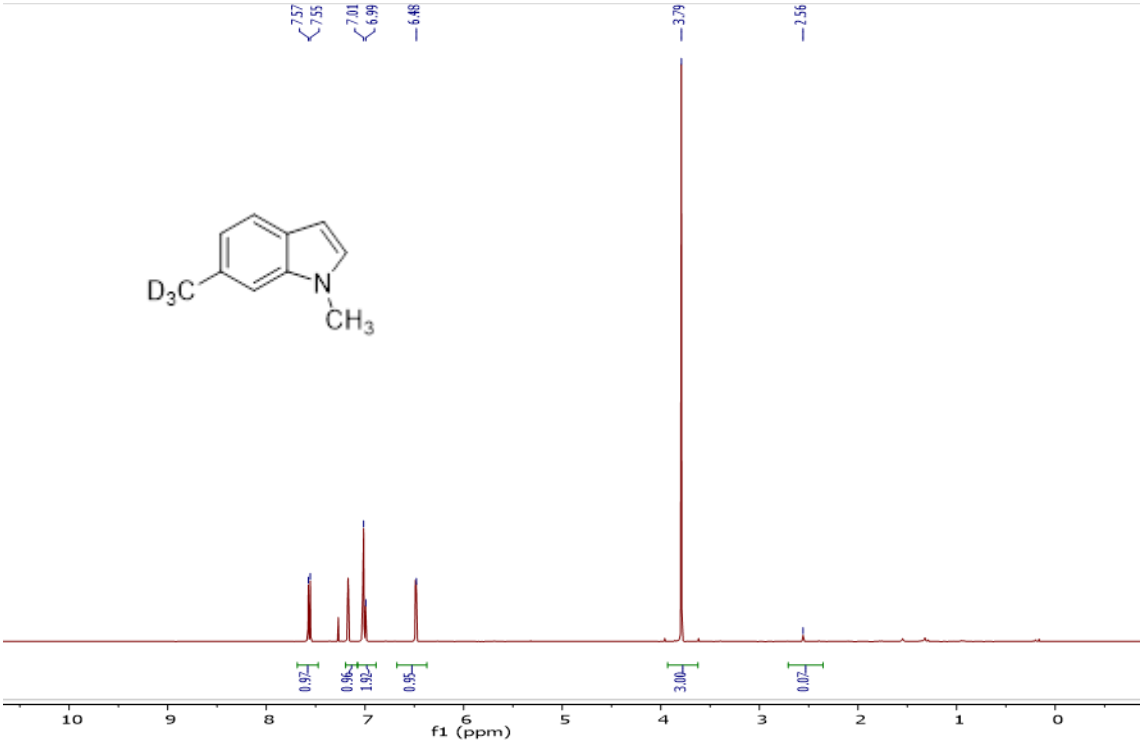
d^3-1-(*trans*-4-butylcyclohexyl)-4-methylbenzene **47** ($CDCl_3$, 400 MHz for ^1H NMR)



d^3-2-Methylnapthalene **48** ($CDCl_3$, 400 MHz for ^{1}H NMR)

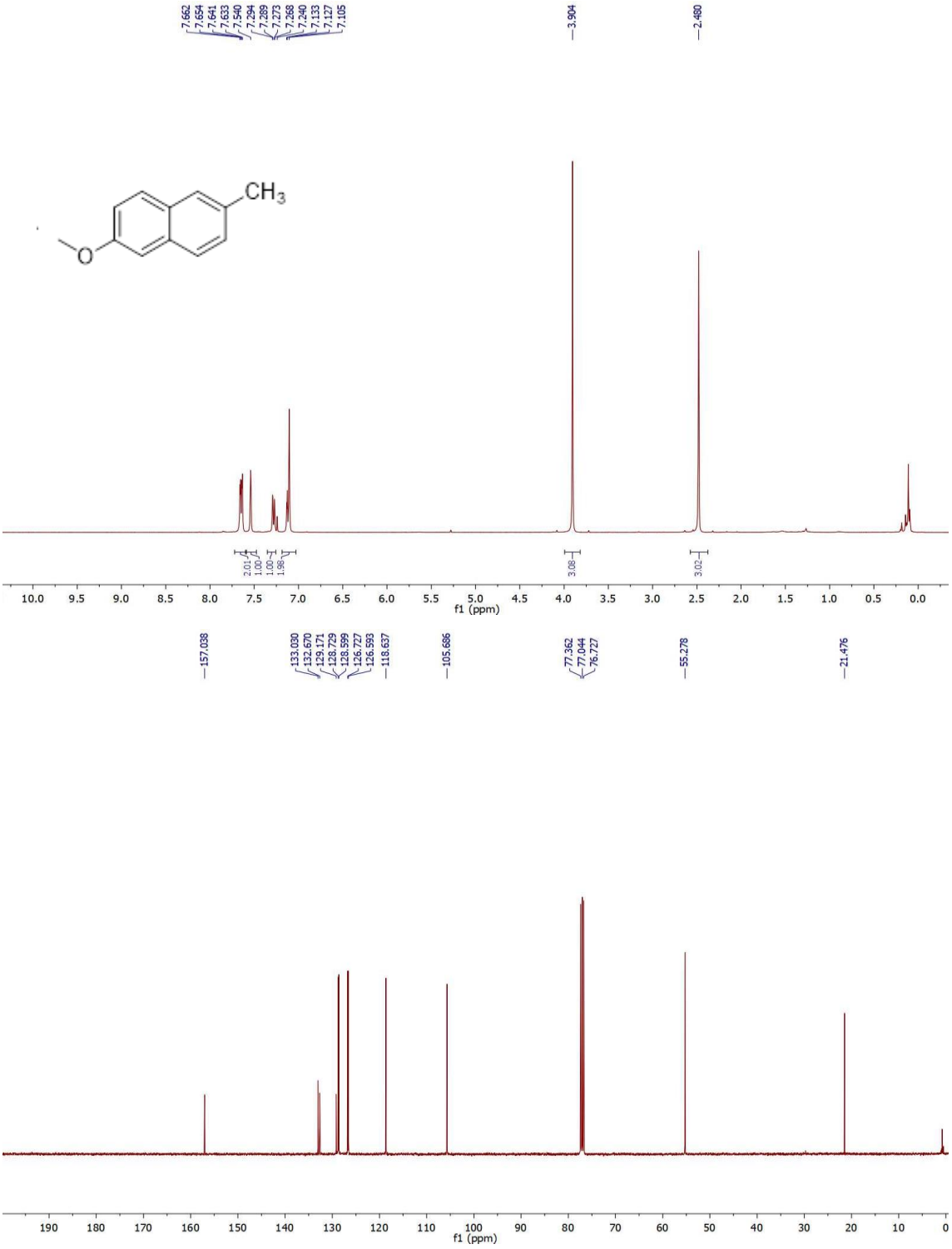


d^3-1,6-Dimethylindole **49** ($CDCl_3$, 400 MHz for ^{1}H NMR)

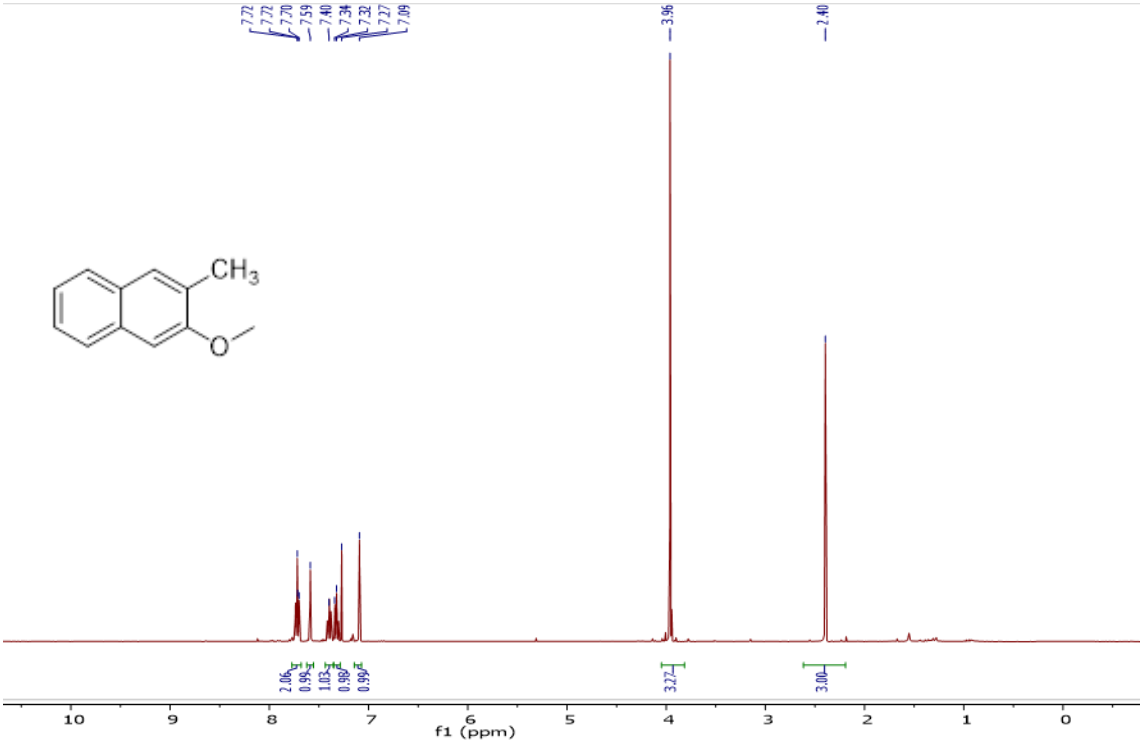


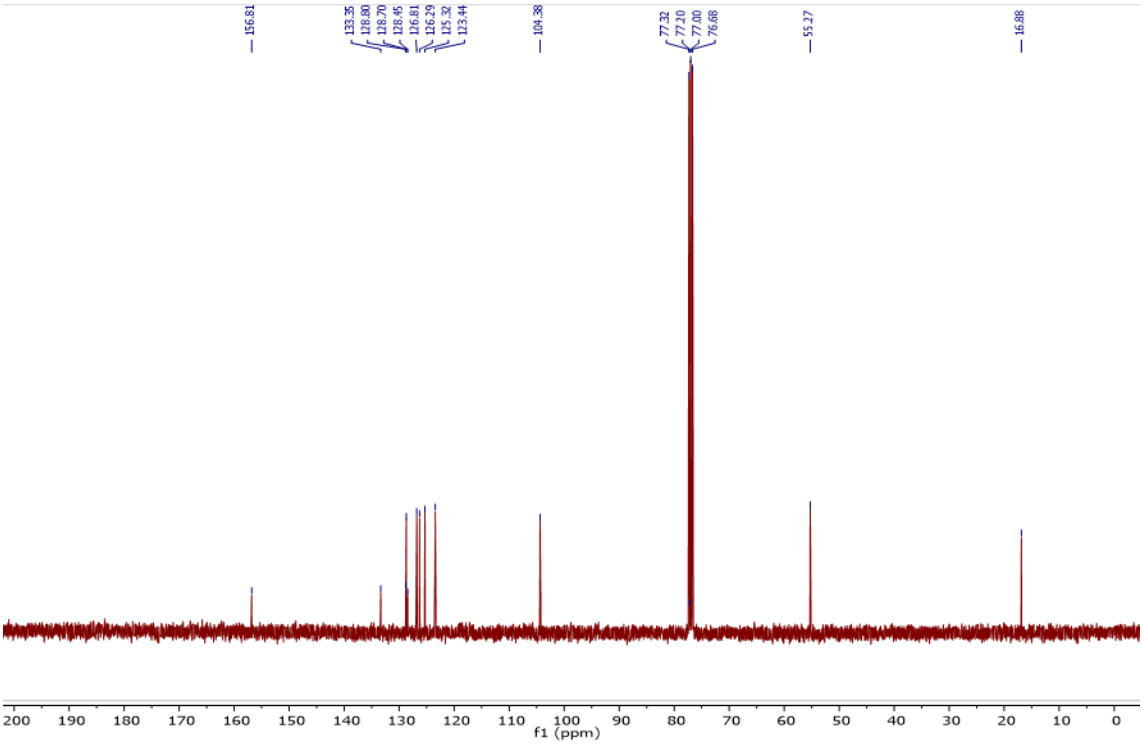
2-(2-Methoxyphenyl)-5-methylpyridine **54** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

2-Methoxy-6-methylnaphthalene **55** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

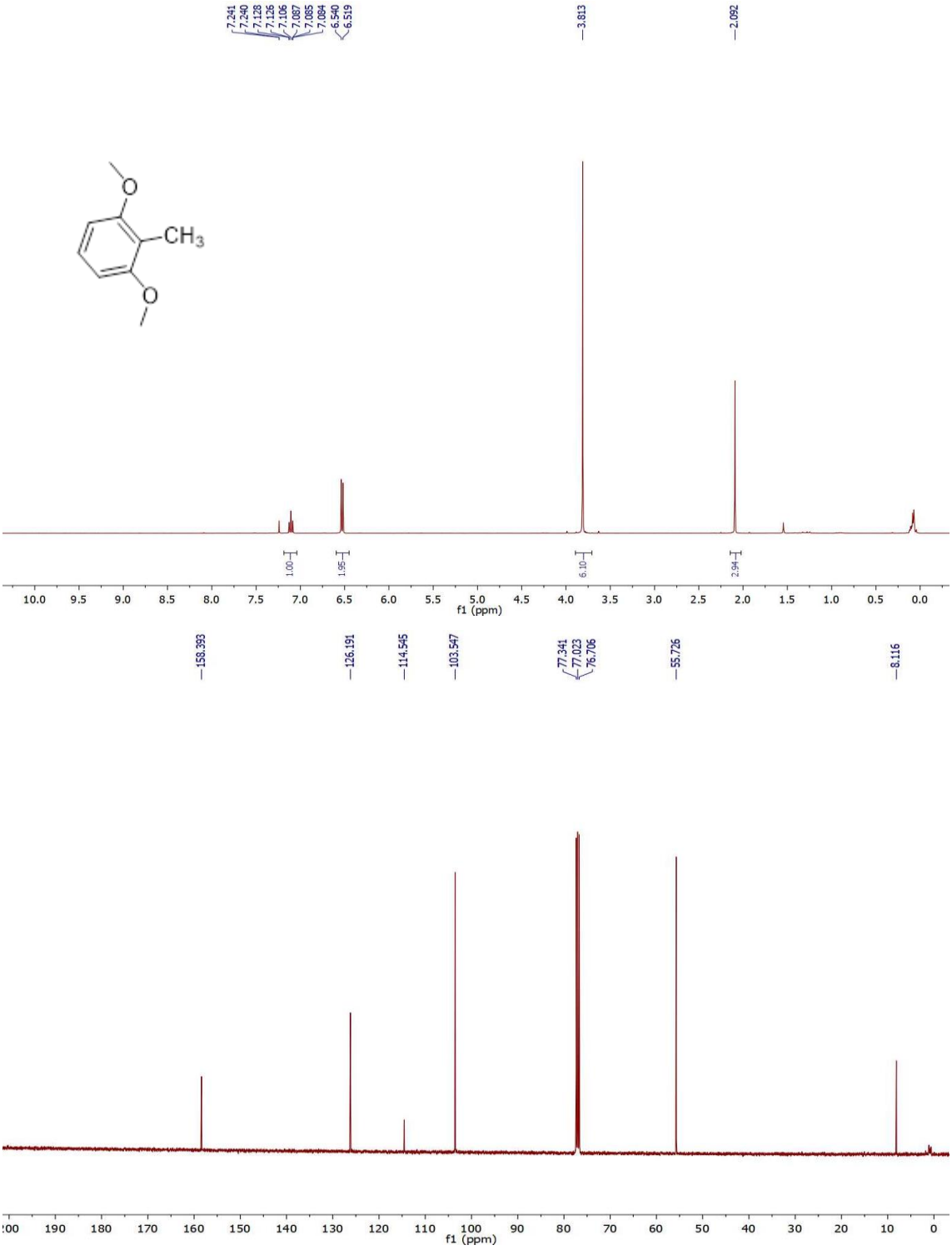


2-Methoxy-3-methylnapthalene **56** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

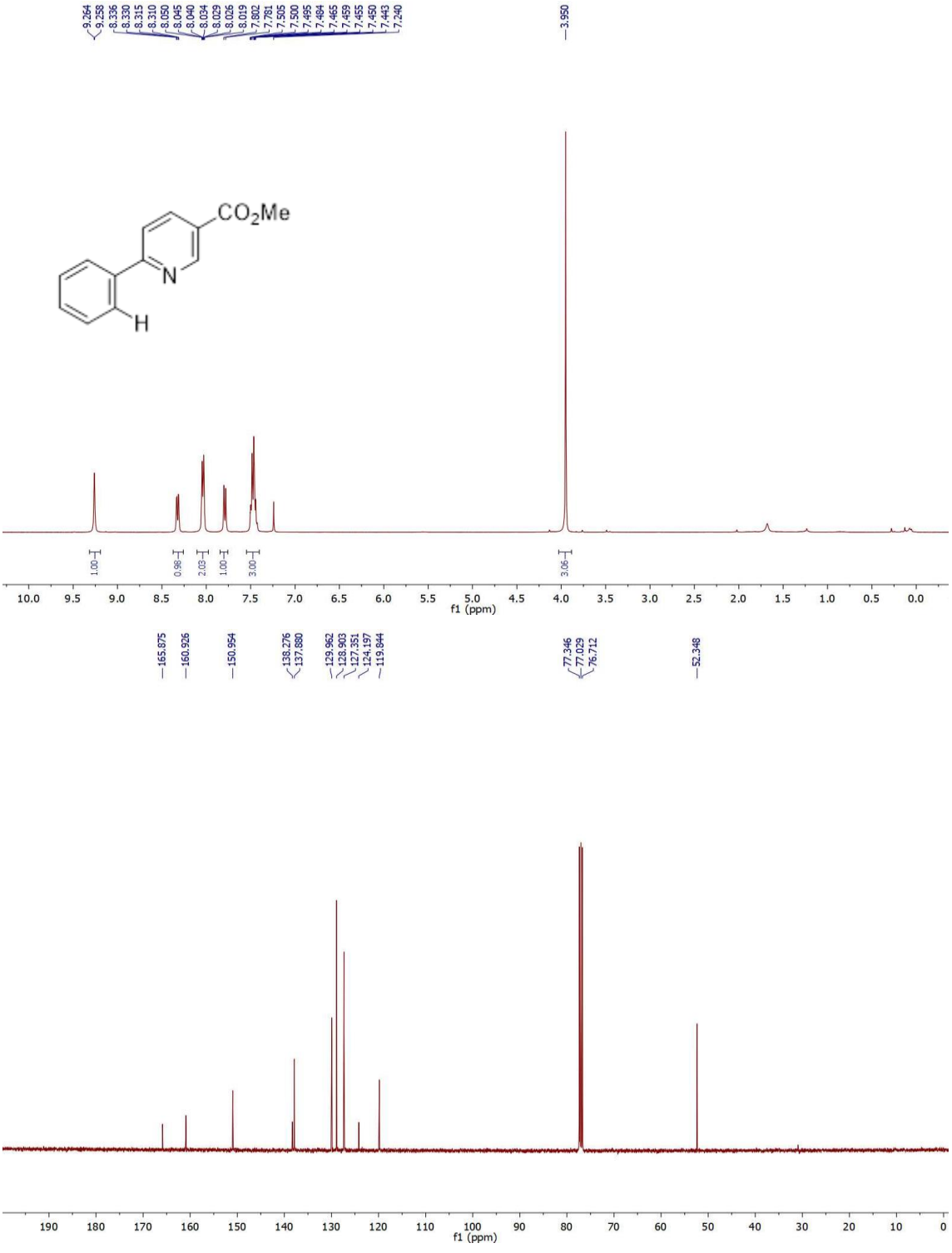




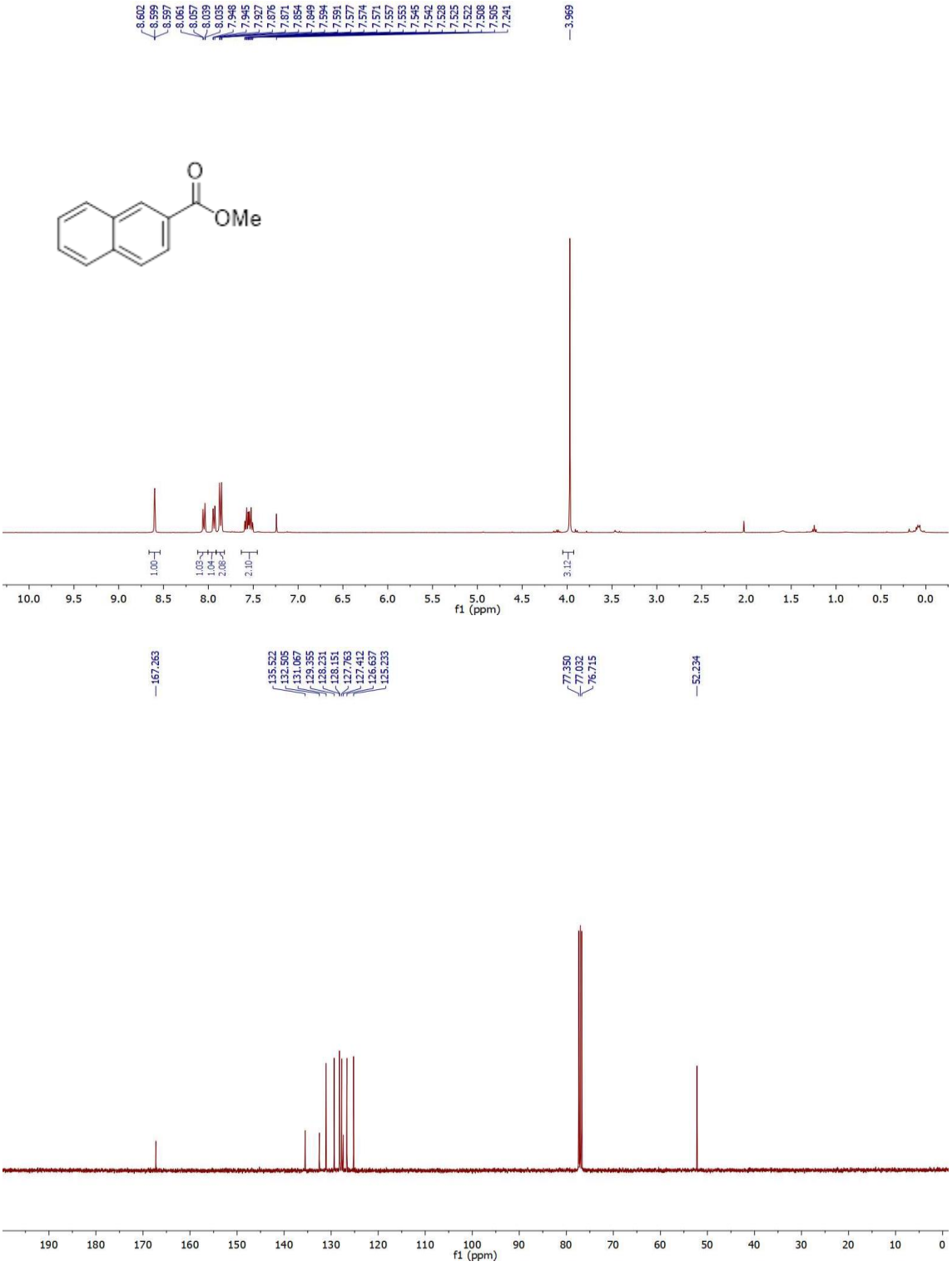
1,3-Dimethoxy-2-methylbenzene **57** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



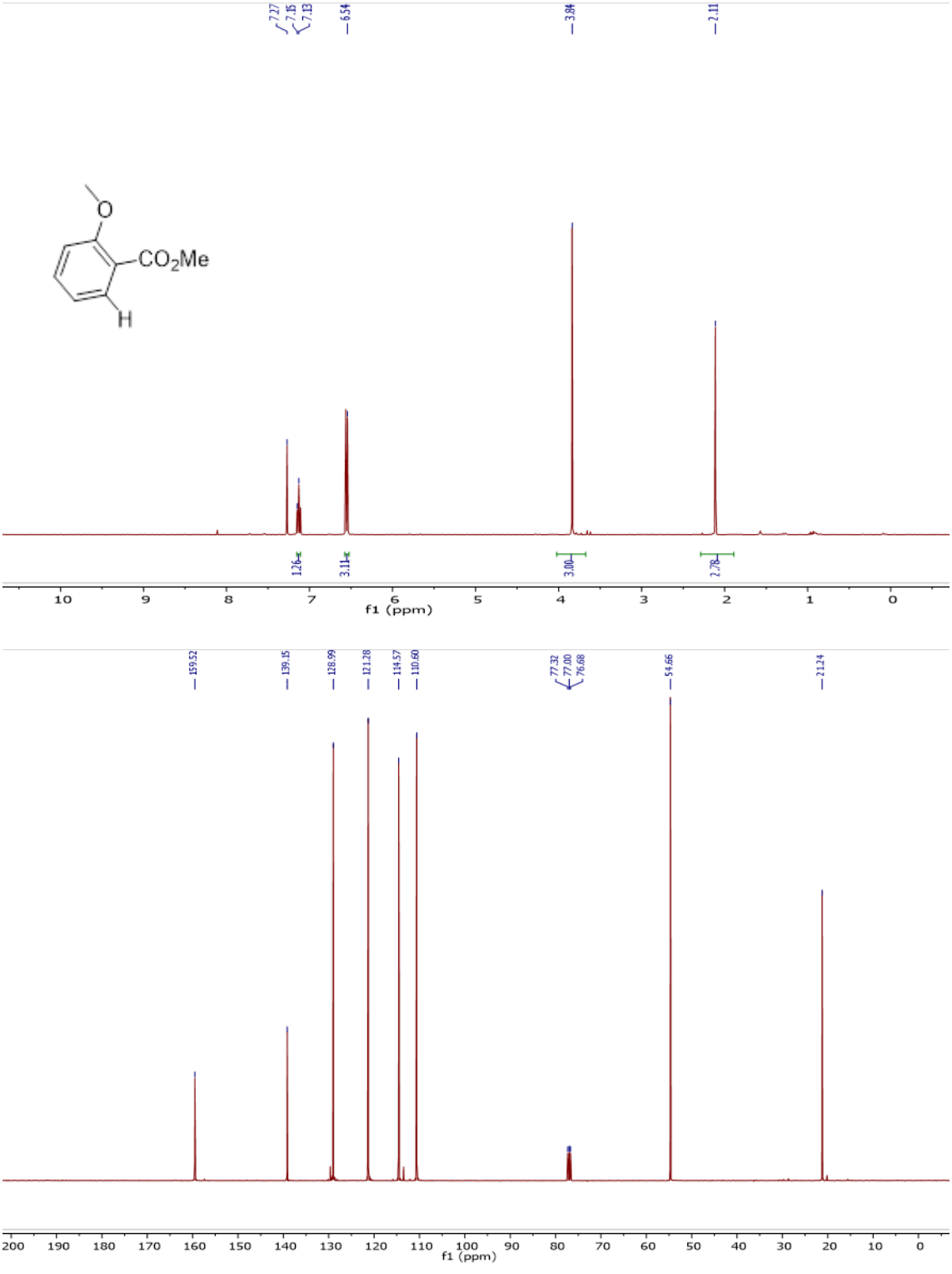
Methyl 5-phenylpyridine-3-carboxylate **58** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



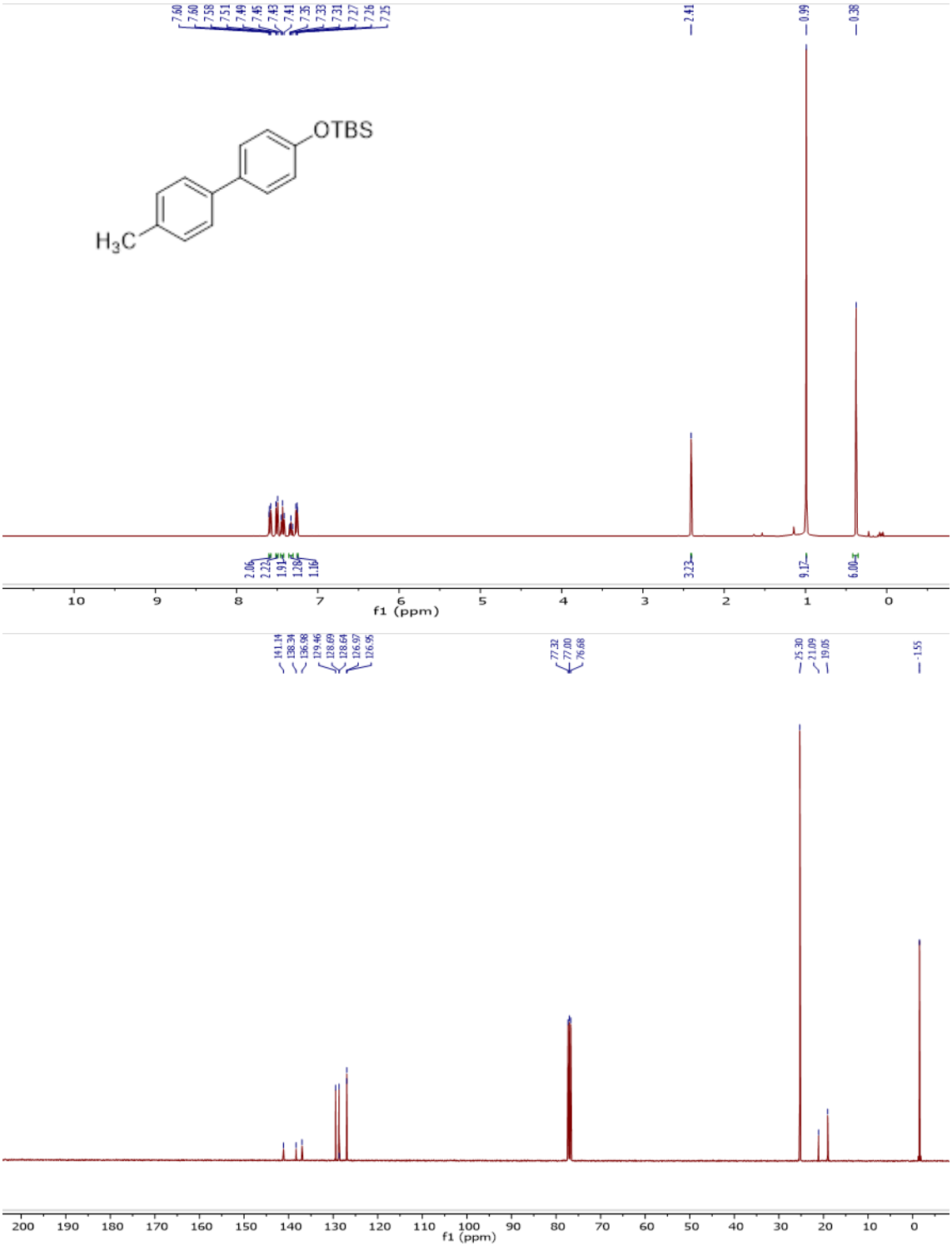
2-Methyl naphthoate **59** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



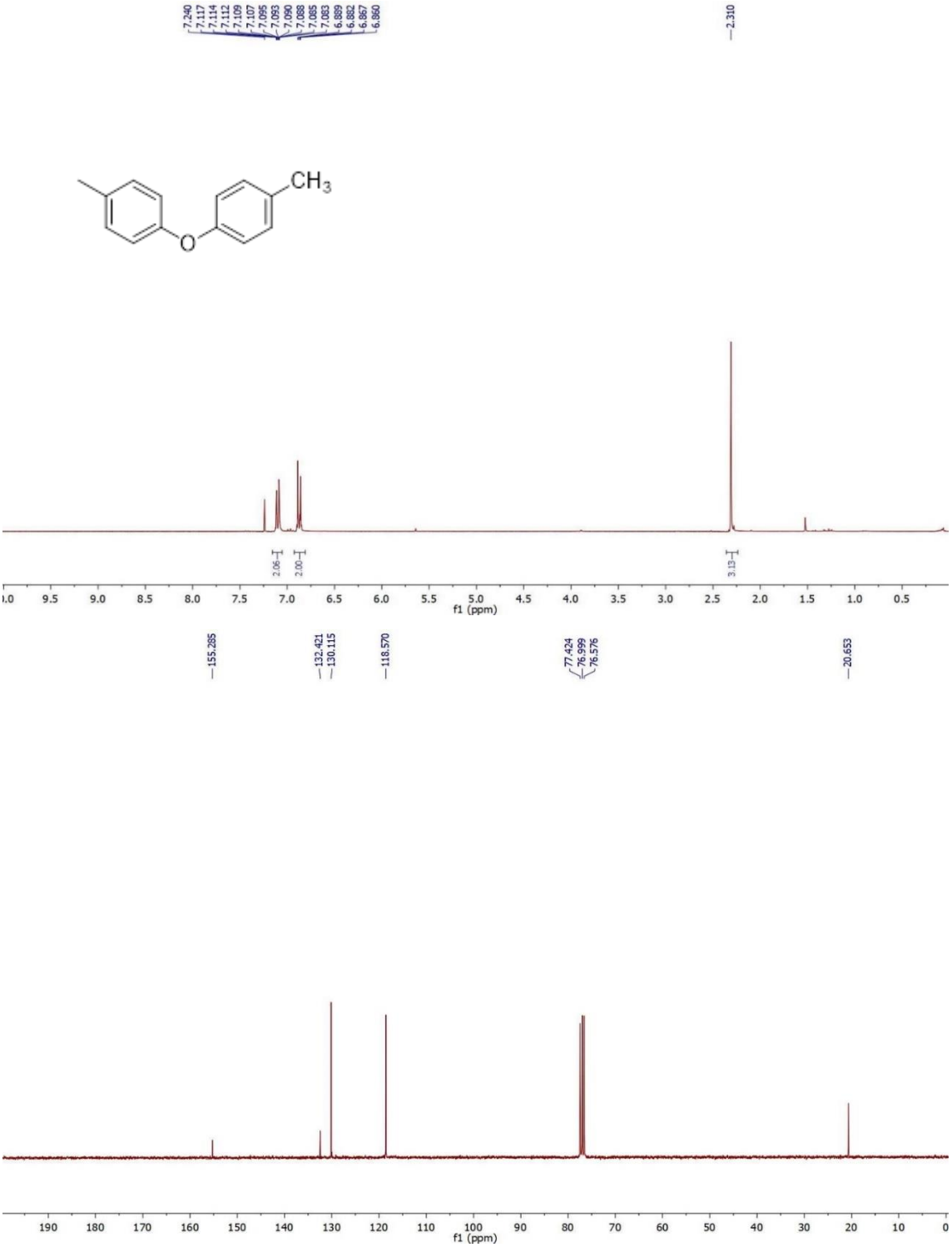
Methyl-2-methoxybenzoate **60** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-4'-methyl-1,1’-biphenyl **S20** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



4,4'-Oxybis(methylbenzene) **56** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



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