Electronic Supplementary Material (ESI) for ChemComm.

Nitrosoarene-Catalysed Regioselective Aromatic C–H Sulfinylation with Thiols under Aerobic Conditions

Suman Pradhan, Sandeep Patel and Indranil Chatterjee *

Indian Institute of Technology Ropar

Ropar, Punjab-140001, India

Indranil.chatterjee@iitrpr.ac.in

Supporting Information

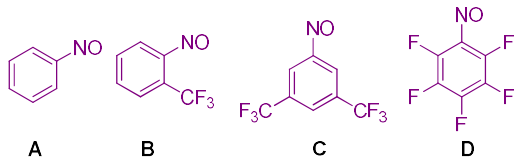
Table of Contents

1 General Information

Reactions were performed in flame-dried glassware under aerobic condition unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled prior to use. $CDCl_3$ was stored over 4Å molecular sieves. Used chemicals were purchased from *Sigma-Aldrich*, *TCI*, *A*lfa-*A*esar and *Sisco Research Laboratories (SRL)* used without further purification.1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was bought from *SRL* and prior to use distilled freshly and store at 4 °C. All the liquid chemicals and solvents were distilled freshly prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates from *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from *Merck* using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 unless otherwise stated on JEOL JNM ECS-400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for **^{1}H NMR** and $CDCl_3$: δ = 77.16 ppm for **^{13}C NMR**; DMSO-d_6: δ = 2.50 ppm for **^{1}H NMR** and DMSO-d_6: δ = 39.52 ppm for **^{13}C NMR**). Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2-XS QTOF. All the X-ray data were recorded on Bruker D8 venture instrument. All UV data were recorded using UV-2600 (UV-VIS spectrophotometer), SHIMADZU instrument. CV measurements were performed with the three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode, a platinum wire counter electrode, a Ag/AgCl as a reference electrode and tetabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte. The control of the measurement instrument, the acquisition and processing of the cyclic voltammetric data were performed with the software Metrohm Autolab NOVA 1.10.4.

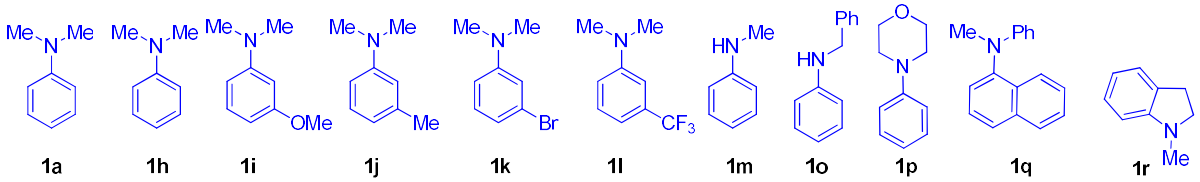
2. Synthetic Procedure for the Preparation of Starting Materials:

All the nitrosoarenes were synthesized following the previously reported literature.[S1-S8] All the amine starting materials **1i-1s**,[S9,S10] **1x, 1ad**,[S9] **3a'**,[S11] **1ah**,[S12] **1ai**[S13] and **4'**[S20]were synthesized according to a procedure in the literature.

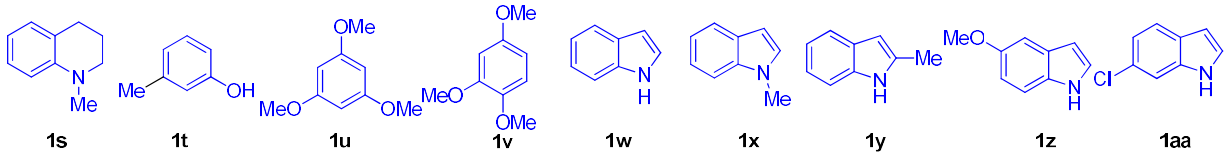


A B C D

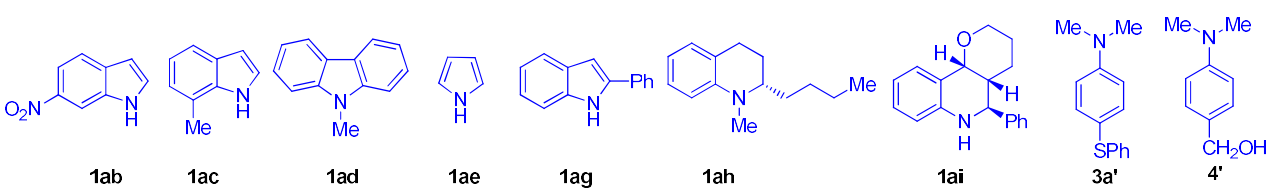
List of Catalysts Screened



1a 1h 1i 1j 1k 1l 1m 1o 1p 1q 1r

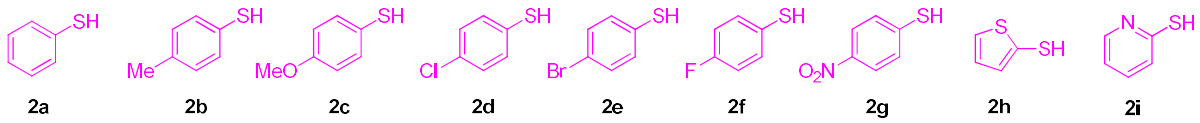


1s 1t 1u 1v 1w 1x 1y 1z 1aa



1ab 1ac 1ad 1ae 1ag 1ah 1ai 3a' 4'

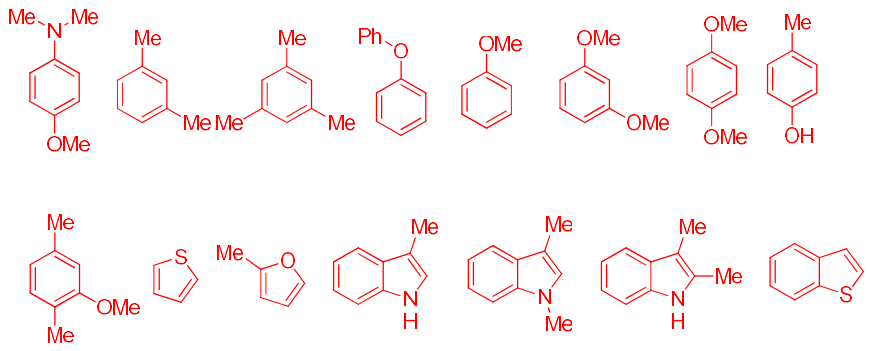
List of Amines Screened



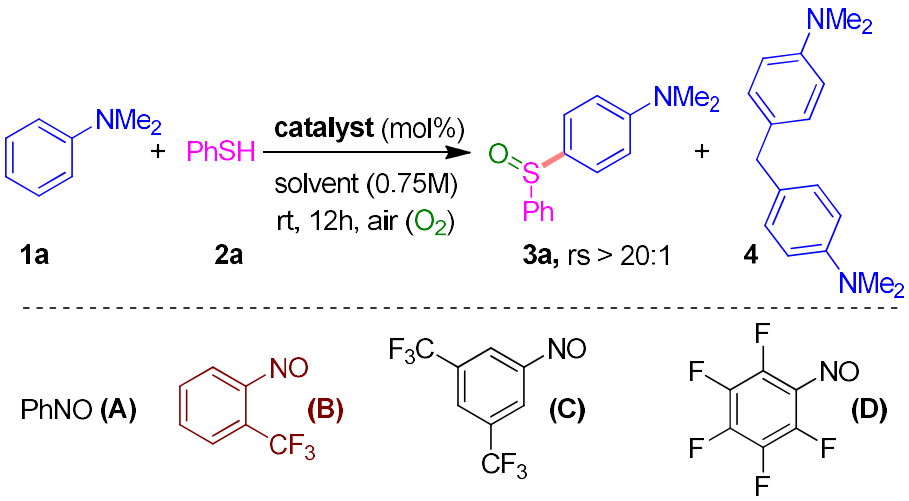
2a 2b 2c 2d 2e 2f 2g 2h 2i

List of Thiols Screened

3. List of Unsuccessful Substrates:



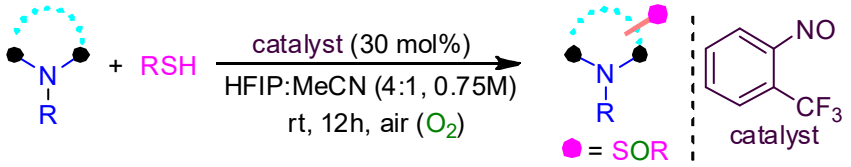
4. Optimization of C–H Sulfinylation



Entry	Solvent	Catalyst (mol%)	Isolated Yield **3a**/**4** (%)
1	MeCN	**A (40)**	<10/n.d.
2	MeOH	**A (40)**	<10/n.d.
3	Isopropanol	**A (40)**	<10/n.d.
4	TFE	**A (40)**	<10/n.d.
5	DCM	**A (40)**	<10/n.d.
6	HFIP	**A (40)**	50/4
7	HFIP	**B (30)**	64/5
8	HFIP	**C (30)**	64/6
9	HFIP	**D (30)**	55/5
10	HFIP	**no catalyst**	n.r.
11	**HFIP : MeCN (4:1)**	**B (30)**	**71/6**
12[a]	HFIP : MeCN (4:1)	**B (30)**	n.r.
13	HFIP : MeCN (4:1)	**B (25)**	56/5
14[b]	HFIP : MeCN (4:1)	**B (30)**	71/7

Table S1: Reaction condition **1a** (2.0 equiv, 0.3 mmol, 35.0 mg) and **2a** (1.0 equiv, 0.15 mmol, 16.0 mg) at room temperature for 12 h [a] Reaction carried out in degassed solvent under N_2 and freeze-pump-thaw (3 cycle). [b] in presence of O_2 balloon.; n.r. = no reaction.

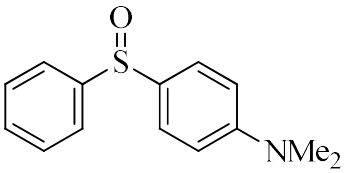
5. General Procedure for the Reaction of Amination and Iminoquinone (GP-1)



An oven-dried glass vial is charged with a magnetic stir bar, catalyst-**B** (30 mol%, 0.045 mmol, 8.0 mg), arene (2.0 equiv), and the corresponding thiol (0.15 mmol, 1.0 equiv). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) / MeCN (4:1) (0.75 M) is added to the mixture in aerobic atmosphere. The vial is maintained for 12 h at rt. The reaction mixture is then passed through a plug of silica. The vial is rinsed with CH_2Cl_2 (2 X 2 mL), and the collected organic phases are evaporated under reduced pressure. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

6. Experimental Details for the Synthesized Compounds

6.1 *N,N*-dimethyl-4-(phenylsulfinyl)aniline (3a)

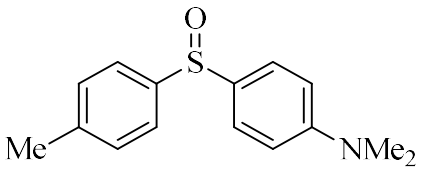


$C_{14}H_{15}NOS$
MW: 245.34 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1.5:1 v/v) as eluent afforded the sulfoxide **3a** (26.0 mg, 71%) as white solid. **Melting Point**: 118-119 °C. **HRMS (ESI):** for $C_{14}H_{16}NOS^+$ [(M+H)$^+$]: calculated 246.0953, found 246.0971. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.46-7.38 (m, 5H), 6.68-6.66 (m, 2H), 2.98 (s,

6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 146.2, 130.7, 130.3, 129.1, 127.9, 124.7, 112.0, 40.3.

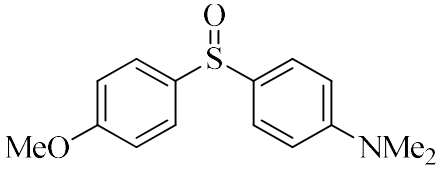
6.2 *N,N*-dimethyl-4-(*p*-tolylsulfinyl)aniline (3b)



$C_{15}H_{17}NOS$
MW: 259.36 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2b** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1.5:1 v/v) as eluent afforded the sulfoxide **3b** (26.0 mg, 67%) as white solid. **Melting Point**: 161-162 °C**. HRMS (ESI**): for $C_{15}H_{18}NOS^+$ [$(M+H)^+$]: calculated 260.1109, found 260.1104. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.43 (m, 4H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.69-6.66 (m, 2H), 2.98 (s, 6H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 143.0, 140.7, 131.0, 129.8, 127.7, 124.8, 112.0, 40.3, 21.5.

6.3 4-((4-methoxyphenyl)sulfinyl)-*N,N*-dimethylaniline (3c)

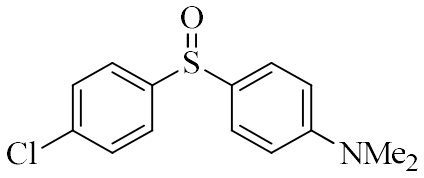


$C_{15}H_{17}NO_2S$
MW: 275.3660 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2c** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent

afforded the sulfoxide **3c** (30.5 mg, 74%) as colorless oily liquid. **HRMS (ESI**): for $C_{14}H_{18}NO_2S^+$ [$(M+H)^+$]: calculated 276.1058, found 276.1060. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.46-7.42 (m, 2H), 6.97-6.93 (m, 2H), 6.70-6.66 (m, 2H), 3.82 (s, 3H), 2.99 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) 161.5, 152.4, 137.5, 131.0, 127.5, 126.8, 114.6, 112.0, 55.6, 40.3.

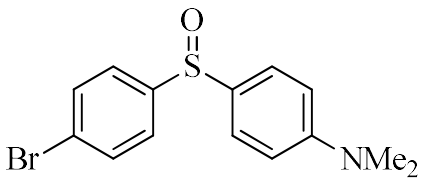
6.4 4-((4-chlorophenyl)sulfinyl)-*N,N*-dimethylaniline (3d)



$C_{14}H_{14}ClNOS$
MW: 279.78 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2d** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1.5:1 v/v) as eluent afforded the sulfoxide **3d** (28.0 mg, 68%) as colorless solid. **Melting Point**: 128-129 °C. **HRMS (ESI**): for $C_{14}H_{15}ClNOS^+$ [$(M+H)^+$]: calculated 280.0563, found 280.0559. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.46-7.40 (m, 4H), 6.69-6.66 (m, 2H), 3.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 144.9, 136.5, 130.2, 129.4, 127.9, 126.1, 112.1, 40.3.

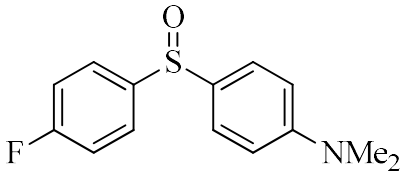
6.5 4-((4-bromophenyl)sulfinyl)-*N,N*-dimethylaniline (3e)



$C_{14}H_{14}BrNOS$
MW: 324.23 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2e** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1.5:1 v/v) as eluent afforded the sulfoxide **3e** (32.0 mg, 66%) as colorless solid. **Melting Point**: 108-109 °C. **HRMS (ESI**): for $C_{14}H_{15}BrNOS^+$ [$(M+H)^+$]: calculated 324.0058, found 324.0054. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.47-7.42 (m, 4H), 6.69-6.65 (m, 2H), 3.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 145.5, 132.3, 130.1, 128.0, 126.3, 124.7, 112.0, 40.3.

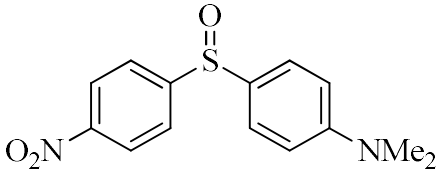
6.6 4-((4-fluorophenyl)sulfinyl)-*N,N*-dimethylaniline (3f)



$C_{14}H_{14}FNOS$
MW: 263.33 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2f** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3f** (20.0 mg, 51%) as pale yellow solid. **Melting Point**: 119-120 °C. **HRMS (ESI**): for $C_{14}H_{15}FNOS^+$ [$(M+H)^+$]: calculated 264.0858, found 264.0851. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.46-7.42 (m, 2H), 7.16-7.11 (m, 2H), 6.70-6.66 (m, 2H), 3.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.6, 141.8, 130.4, 127.8, 127.0 (q, *J* = 8.9 Hz), 116.5, 116.2, 112.0, 40.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.0 ppm.

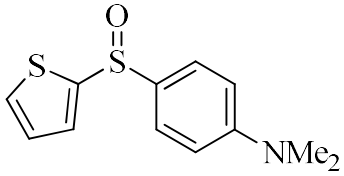
6.7 *N,N*-dimethyl-4-((4-nitrophenyl)sulfinyl)aniline (3g)



$C_{14}H_{14}N_2O_3S$
MW: 290.33 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2g** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1.5 v/v) as eluent afforded the sulfoxide **3g** (16.0 mg, 36%) as colorless solid. **Melting Point**: 159-160 ºC **HRMS (ESI**): for $C_{14}H_{15}N_2O_3S^+$ [(M+H)$^+$]: calculated 291.0803, found 291.0796. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30-8.27 (m, 2H), 7.77-7.74 (m, 2H), 7.47-7.43 (m, 2H), 6.69-6.65 (m, 2H), 3.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.0, 153.0, 148.9, 129.0, 128.3, 125.5, 124.2, 112.1, 40.2.

6.8 *N,N*-dimethyl-4-(thiophen-2-ylsulfinyl)aniline (3h)

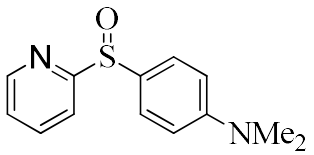


$C_{12}H_{13}NOS_2$
MW: 251.36 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2h** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (4:1 v/v) as eluent afforded the sulfoxide **3h** (23.0 mg, 61%) as colorless oily liquid. **HRMS (ESI**): for $C_{12}H_{14}NOS_2^+$ [(M+H)$^+$]: calculated 252.0517, found 252.0494. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.54-7.53 (m, 1H), 7.45-7.43 (m, 1H), 7.06-7.04 (m, 1H),

6.76-6.72 (m, 2H), 3.03 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.6, 149.6, 131.3, 130.2, 130.0, 127.4, 126.8, 111.9, 40.3.

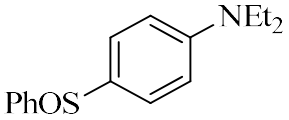
6.9 *N,N*-dimethyl-4-(pyridin-2-ylsulfinyl)aniline (3i)



$C_{13}H_{14}N_2OS$
MW: 246.32 g/mol

Prepared according to the GP-1, using **1a** (35.0 mg, 0.3 mmol, 2.0 equiv), **2i** (18.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / $CHCl_3$ (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3i** (18.0 mg, 50%) as colorless oily liquid. **HRMS (ESI**): for $C_{13}H_{15}N_2OS^+$ [(M+H)$^+$]: calculated 247.0905, found 247.0890. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54-8.53 (m, 1H), 8.12-8.10 (m, 1H), 7.92-7.87 (m, 1H), 7.56-7.54 (m, 1H), 7.29-7.28 (m, 2H), 6.70-6.68 (m, 2H), 2.98 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 152.5, 149.9, 138.0, 134.0, 127.9, 124.3, 118.8, 112.2, 40.3.

6.10 *N,N*-diethyl-4-(phenylsulfinyl)aniline (3j)

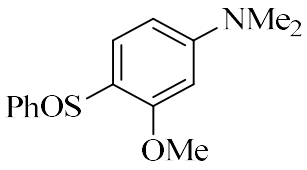


$C_{16}H_{19}NOS$
MW: 273.39 g/mol

Prepared according to the GP-1, using **1j** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3j** (29.0 mg, 71%) as pale yellow solid. **Melting Point**: 161-162 ^{o}C. **HRMS (ESI**) for $C_{16}H_{20}NOS^+$ [(M+H)]$^+$: calculated 274.1266 found 274.1260. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.47-7.38 (m, 5H), 6.65-6.61 (m, 2H), 3.35 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 146.2, 130.2, 129.6, 129.1, 128.4, 124.7, 111.4, 44.6, 12.5.

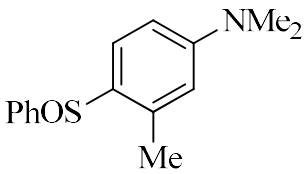
6.11 3-methoxy-*N,N*-dimethyl-4-(phenylsulfinyl)aniline (3k)



$C_{15}H_{17}NO_2S$
MW: 275.36 g/mol

Prepared according to the GP-1, using **1k** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3k** (29.0 mg, 70%) as white solid. **Melting Point**: 100-101 °C. **HRMS (ESI**) for $C_{15}H_{18}NO_2S^+$ $[(M+H)]^+$: calculated 276.1058 found 276.1050. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.43-7.37 (m, 3H), 6.35 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.09 (d, *J* = 2.3 Hz, 1H), 3.80 (s, 3H), 2.99 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 154.0, 146.4, 130.2, 128.9, 127.2, 125.1, 118.9, 105.10, 94.7, 55.6, 40.5.

6.12 *N,N*,3-trimethyl-4-(phenylsulfinyl)aniline (3l)

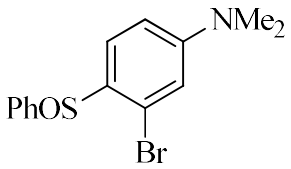


$C_{15}H_{17}NOS$
MW: 259.36 g/mol

Prepared according to the GP-1, using **1l** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column

chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3l** (21.0 mg, 55%) as white solid. **Melting Point**: 98-99 °C. **HRMS (ESI**) for $C_{15}H_{18}NOS^+$ [(M+H)]$^+$: calculated 260.1109, found 260.1120. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 3H), 7.45-7.37 (m, 3H), 6.60 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 2.98 (s, 6H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 145.9, 138.5, 130.3, 129.1, 128.7, 128.1, 125.3, 113.5, 110.4, 40.2, 19.3

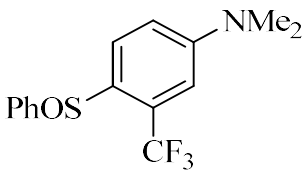
6.13 3-bromo-*N,N*-dimethyl-4-(phenylsulfinyl)aniline (3m)



$C_{14}H_{14}BrNOS$
MW: 324.23 g/mol

Prepared according to the GP-1, using **1m** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3m** (29.0 mg, 60%) as red solid. **Melting Point**: 110-111 °C. **HRMS (ESI**) for $C_{14}H_{15}BrNOS^+$ [(M+H)]$^+$: calculated 324.0058, found 324.0061. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.46-7.40 (m, 3H), 6.76 (d, *J* = 2.5 Hz, 1H), 6.72 (dd, *J* = 8.9, 2.6 Hz, 1H), 2.98 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9, 146.0, 130.8, 129.7, 129.2, 127.8, 125.5, 122.2, 115.1, 111.9, 40.3.

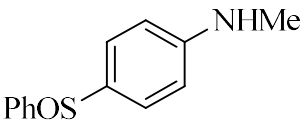
6.14 *N,N*-dimethyl-4-(phenylsulfinyl)-3-(trifluoromethyl)aniline (3n)



$C_{15}H_{14}F_3NOS$
MW: 313.33 g/mol

Prepared according to the GP-1, using **1n** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3n** (15.0 mg, 32%) as oily liquid. **HRMS (ESI**) for $C_{15}H_{15}F_3NOS^+$ $[(M+H)]^+$: calculated 314.0826 found 314.0820. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 1H), 7.62-7.59 (m, 2H), 7.46-7.40 (m, 3H), 6.87-6.84 (m, 2H), 3.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 146.3, 130.6, 129.7, 129.4, 129.2, 128.9, 124.9, 115.3, 108.0 (q, *J* = 5.3 Hz), 40.2. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –56.6 ppm.

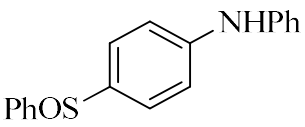
6.15 *N*-methyl-4-(phenylsulfinyl)aniline (3o)



$C_{13}H_{13}NOS$
MW: 231.31 g/mol

Prepared according to the GP-1, using **1o** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3o** (23.0 mg, 67%) as red solid. **Melting Point**: 121-122 °C. **HRMS (ESI**) for $C_{13}H_{14}NOS^+$ $[(M+H)]^+$: calculated 232.0796, found 232.0798. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.56 (m, 2H), 7.45-7.39 (m, 5H), 6.58-6.55 (m, 2H), 4.13 (s, 1H), 2.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 145.5, 131.2, 130.6, 129.2, 128.3, 124.8, 112.4, 30.3.

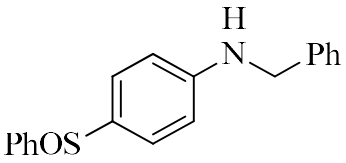
6.16 *N*-phenyl-4-(phenylsulfinyl)aniline (3p)



$C_{18}H_{15}NOS$
MW: 293.38 g/mol

Prepared according to the GP-1, using **1p** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3p** (30.0 mg, 69%) as white solid. **Melting Point**: 128-129 °C. **HRMS (ESI**): for $C_{18}H_{16}NOS^+$ [(M+H)$^+$]: calculated 294.0953, found 294.0965. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.49-7.43 (m, 5H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.06-7.00 (m, 3H), 3.62 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 145.9, 141.0, 135.3, 130.7, 129.7, 129.3, 127.7, 124.7, 123.2, 120.3, 116.1.

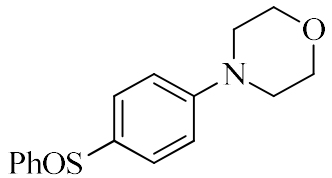
6.17 *N*-benzyl-4-(phenylsulfinyl)aniline (3q)



$C_{19}H_{17}NOS$
MW: 307.40 g/mol

Prepared according to the GP-1, using **1q** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3q** (33.0 mg, 72%) as oily liquid. **HRMS (ESI**) for $C_{19}H_{18}NOS^+$ [(M+H)]$^+$: calculated 308.1109, found 308.1104. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.53-7.50 (m, 2H), 7.48-7.39 (m, 3H), 7.29-7.25 (m, 5H), 7.20-7.16 (m, 1H), 6.95-6.90 (m, 1H), 6.61-6.57 (m, 2H), 4.24 (d, *J* = 6.0 Hz, 1H).**^{13}C NMR** (101 MHz, DMSO-D_6) δ 151.3, 146.6, 139.3, 130.5, 130.3, 129.2, 128.4, 127.1, 127.0, 126.8, 123.9, 112.2, 45.9.

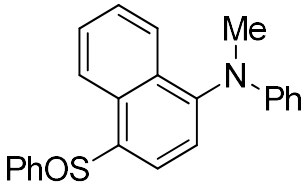
6.18 4-(4-(phenylsulfinyl)phenyl)morpholine (3r)



$C_{16}H_{17}NO_2S$
MW: 287.37 g/mol

Prepared according to the GP-1, using **1r** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3r** (23.0 mg, 66%) as colorless solid. **Melting Point**: 84-85 °C. **HRMS (ESI)**: for $C_{16}H_{18}NO_2S^+$ [(M+H)$^+$]: calculated 288.1058, found 288.1046. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.58 (m, 2H), 7.53-7.49 (m, 2H), 7.47-7.41 (m, 3H), 6.92-6.88 (m, 2H), 3.84-3.82 (m, 4H), 3.22-3.20 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 146.0, 134.7, 130.7, 129.3, 127.4, 124.7, 115.1, 66.7, 48.1.

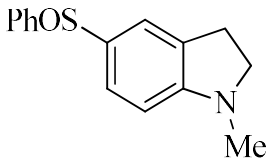
6.19 *N*-methyl-*N*-phenyl-4-(phenylsulfinyl)naphthalen-1-amine (3s)



$C_{23}H_{19}NOS$
MW: 357.46 g/mol

Prepared according to the GP-1, using **1s** (70.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1 v/v) as eluent afforded the sulfoxide **3s** (29.0 mg, 54%) as oily liquid. **HRMS (ESI)**: for $C_{23}H_{20}NOS^+$ [(M+H)$^+$]: calculated 358.1266, found 358.1249. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.60-7.57 (m, 2H), 7.53-7.48 (m, 2H), 7.45-7.41 (m, 4H), 7.39-7.37 (m, 2H), 7.33 (d, *J* = 6.6 Hz, 1H), 6.58-6.54 (m, 2H), 3.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 146.0, 143.7, 135.3, 132.0, 130.8, 130.4, 129.1, 128.8, 127.8, 127.0, 126.7, 126.6, 125.8, 124.7, 123.4, 113.2, 40.3.

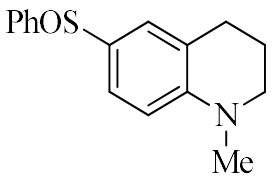
6.20 1-methyl-5-(phenylsulfinyl)indoline (3t)



$C_{15}H_{15}NOS$
MW: 257.35 g//mol

Prepared according to the GP-1, using **1t** (40.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1 v/v) as eluent afforded the sulfoxide **3t** (28.0 mg, 72%) as oily liquid. **HRMS (ESI)**: for $C_{15}H_{16}NOS^+$ [(M+H)$^+$]: calculated 258.0953, found 258.0946. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.47-7.43 (m, 2H), 7.42-7.38 (m, 2H), 7.20 (q, J = 1.5 Hz, 1H), 6.37 (d, J = 8.1 Hz, 1H), 3.43-3.39 (m, 2H), 2.92 (t, J = 8.4 Hz, 2H), 2.78 (d, J = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 146.2, 132.1, 131.8, 130.3, 129.1, 128.0, 124.7, 121.9, 105.5, 55.4, 34.9, 28.2.

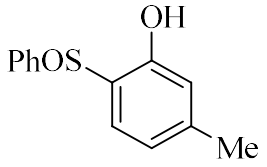
6.21 1-methyl-6-(phenylsulfinyl)-1,2,3,4-tetrahydroquinoline (3u)



$C_{16}H_{17}NOS$
MW: 271.37 g/mol

Prepared according to the GP-1, using **1u** (44.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1 v/v) as eluent afforded the sulfoxide **3u** (29.5 mg, 73%) as oily liquid. **HRMS (ESI)**: for $C_{16}H_{18}NOS^+$ [(M+H)$^+$]: calculated 272.1109, found 272.1117. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.46-7.38 (m, 3H), 7.31 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.15-7.14 (m, 1H), 6.51 (d, *J* = 8.6 Hz, 1H), 3.29-3.27 (m, 2H), 2.91 (s, 3H), 2.72-2.69 (m, 2H), 1.92 (dt, *J* = 12.1, 6.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 146.2, 130.2, 129.1, 126.5, 124.7, 123.4, 110.1, 51.1, 38.9, 27.9, 21.8.

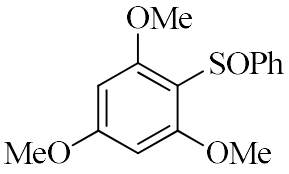
6.22 3-methyl-2-(phenylsulfinyl)phenol (3v)



$C_{13}H_{12}O_2S$
MW: 232.29 g/mol

Prepared according to the GP-1, using **1v** (32.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3v** (9.0 mg, 27%) as white solid, **Melting Point**: 160-162 °C. **HRMS (ESI)**: for $C_{13}H_{13}O_2S^+$ [$(M+H)^+$]: calculated 233.0636, found, 233.0623. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 3H), 7.48-7.42 (m, 3H), 6.75 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.63 (d, *J* = 2.0 Hz, 1H), 2.34 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 144.2, 139.2, 132.9, 131.0, 129.4, 128.2, 125.6, 118.2, 114.7, 18.8.

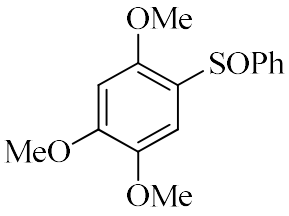
6.23 1,3,5-trimethoxy-2-(phenylsulfinyl)benzene (3w)



$C_{15}H_{16}O_4S$
MW: 292.35 g/mol

Prepared according to the GP-1, using **1w** (50.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3w** (27.0 mg, 61%) as white solid. **Melting Point**: 114-116 °C. **HRMS (ESI)**: for $C_{15}H_{17}O_4S^+$ [$(M+H)^+$]: calculated 293.0848, found 293.0865. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.42-7.38 (m, 2H), 7.36-7.32 (m, 1H), 6.05 (s, 2H), 3.82 (s, 3H), 3.70 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 161.6, 145.5, 129.0, 128.2, 124.4, 91.3, 56.1, 55.6.

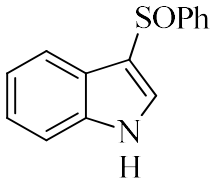
6.24 1,2,4-trimethoxy-5-(phenylsulfinyl)benzene (3x)



$C_{15}H_{16}O_4S$
MW: 292.35 g/mol

Prepared according to the GP-1, using **1x** (50.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3x** (24.0 mg, 55%) as white solid. **Melting Point**: 100-101 °C. **HRMS (ESI**): for $C_{15}H_{17}O_4S^+$ [(M+H)$^+$]: calculated 293.0848, found 293.0847. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.45-7.40 (m, 3H), 7.36 (s, 1H), 6.47 (s, 1H), 3.89 (d, *J* = 1.3 Hz, 6H), 3.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 150.6, 146.1, 144.4, 130.8, 129.1, 125.1, 123.3, 107.1, 97.2, 56.7, 56.4.

6.25 3-(phenylsulfinyl)-1*H*-indole (3y)

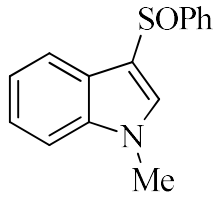


$C_{14}H_{11}NOS$
MW: 241.30 g/mol

Prepared according to the GP-1, using **1y** (35.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3y** (25.0 mg, 69**%**) as orange solid. **Melting Point**: 126-127 °C. **HRMS (ESI**): for $C_{14}H_{12}NOS^+$ [(M+H)$^+$]: calculated 242.0640, found 242.0616. **^{1}H NMR**

(400 MHz, DMSO-D_6) δ 11.95 (s, 1H), 8.12 (d, *J* = 2.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.48-7.43 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 137.2, 130.4, 130.2, 129.1, 125.1, 123.6, 123.5, 121.6, 119.4, 116.2, 112.6.

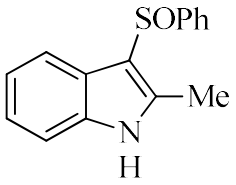
6.26 1-methyl-3-(phenylsulfinyl)-1*H*-indole (3z)



$C_{15}H_{13}NOS$
MW: 255.33 g/mol

Prepared according to the GP-1, using **1z** (40.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1.5:1 v/v) as eluent afforded the sulfoxide **3z** (30.0 mg, 78%) as pale yellow solid. **Melting Point**: 120-121 ^{o}C. **HRMS (ESI**): for $C_{15}H_{14}NOS^{+}$ [$(M+H)^{+}$]: calculated 256.0797, found 256.0796. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73-7.70 (m, 2H), 7.52 (s, 1H), 7.49-7.41 (m, 4H), 7.34-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.10-7.06 (m, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 137.9, 133.0, 130.2, 129.0, 125.1, 124.6, 123.5, 121.6, 120.1, 116.7, 110.3, 33.6.

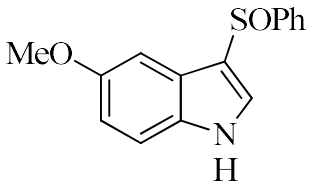
6.27 2-methyl-3-(phenylsulfinyl)-1*H*-indole (3aa)



$C_{15}H_{13}NOS$
MW: 255.33 g/mol

Prepared according to the GP-1, using **1aa** (40.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3aa** (24.0 mg, 63%) as red solid. **Melting Point**: 123-124 °C. **HRMS (ESI**): for $C_{15}H_{14}NOS^+$ [(M+H)$^+$]: calculated 256.0796, found 256.0773. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 10.87 (s, 1H), 7.71 (d, *J* = 1.1 Hz, 1H), 7.50-7.43 (m, 2H), 7.22 (t, *J* = 8.9 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 145.0, 141.8, 135.7, 129.7, 128.9, 124.4, 124.2, 122.0, 120.3, 118.3, 112.1, 111.6, 11.7.

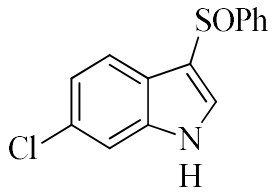
6.28 5-methoxy-3-(phenylsulfinyl)-1*H*-indole (3ab)



$C_{15}H_{13}NO_2S$
MW: 271.33 g/mol

Prepared according to the GP-1, using **1ab** (44.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3ab** (30.0 mg, 75**%**) as colorless oil. **Melting Point**: 144-145 °C. **HRMS (ESI**): for $C_{15}H_{14}NO_2S^+$ [(M+H)$^+$]: calculated 272.0745, found 272.0749. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 11.81 (s, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 6.78 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.59 (d, *J* = 2.3 Hz, 1H), 3.54 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 154.1, 144.8, 131.9, 131.3, 129.9, 129.0, 124.5, 123.9, 115.9, 113.5, 112.7, 100.6, 55.1.

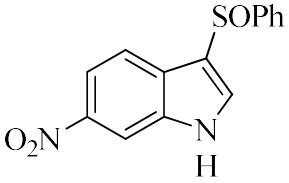
6.29 6-chloro-3-(phenylsulfinyl)-1*H*-indole (3ac)



$C_{14}H_{10}ClNOS$
MW: 275.75 g/mol

Prepared according to the GP-1, using **1ac** (45.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded **3ac** (30.0 mg, 72%) the sulfoxide as colorless oil. **HRMS (ESI**): for $C_{14}H_{11}ClNOS^+$ [(M+H)$^+$]: calculated 276.0250, found 276.0255. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 12.05 (s, 1H), 8.16 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.54-7.50 (m, 3H), 7.48-7.44 (m, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 144.8, 137.5, 131.8, 130.1, 129.1, 127.6, 124.4, 121.9, 121.1, 120.3, 116.7, 112.4.

6.30 6-nitro-3-(phenylsulfinyl)-1*H*-indole (3ad)

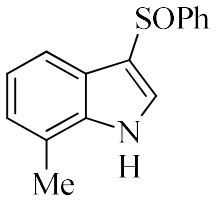


$C_{14}H_{10}N_2O_3S$
MW: 286.30 g/mol

Prepared according to the GP-1, using **1ad** (48.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by

column chromatography on silica gel using petroleum ether/ethyl acetate (1:1.5 v/v) as eluent afforded the sulfoxide **3ad** (27.0 mg, 64%) as red oily liquid. **HRMS (ESI,)**: for $C_{14}H_{11}N_2O_3S^+$ [(M+H)$^+$]: calculated 287.0490, found 287.0483. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 11.99 (s, 1H), 8.47 (s, 1H), 8.39 (d, *J* = 2.2 Hz, 1H), 7.89-7.86 (m, 1H), 7.69-7.66 (m, 2H), 7.56-7.52 (m, 2H), 7.50-7.46 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 144.6, 143.2, 135.9, 135.7, 130.4, 129.2, 128.0, 124.3, 119.3, 117.9, 115.8, 109.4.

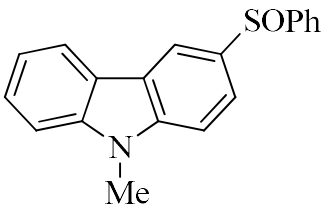
6.31 7-methyl-3-(phenylsulfinyl)-1*H*-indole (3ae)



$C_{15}H_{13}NOS$
MW: 255.33 g/mol

Prepared according to the GP-1, using **1ae** (40.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3ae** (27.0 mg, 70%) as white solid. **Melting Point**: 123-124 ^{o}C. **HRMS (ESI**): for $C_{15}H_{14}NOS^+$ [(M+H)$^+$]: calculated 256.0796, found 256.0792. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.96 (s, 1H) 8.12 (d, *J* = 3.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.1 Hz, 1H), 6.86-6.82 (m, 1H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 145.0, 136.6, 130.6, 129.9, 129.0, 124.4, 123.3, 122.9, 122.1, 120.9, 116.7, 116.6, 16.7.

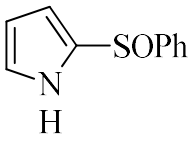
6.32 9-methyl-3-(phenylsulfinyl)-9*H*-carbazole (3af)



$C_{19}H_{15}NOS$
MW: 305.39 g/mol

Prepared according to the GP-1, using **1af** (54.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1 v/v) as eluent afforded the sulfoxide **3af** (18.5 mg, 41%) as white solid. **Melting Point**: 102-103 °C. **HRMS (ESI)**: for $C_{19}H_{16}NOS^+$ [(M+H)$^+$]: calculated 306.0953, found 306.0931. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.69-7.65 (m, 3H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47-7.39 (m, 5H), 7.29 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 142.6, 141.6, 135.1, 130.7, 129.3, 126.9, 124.8, 123.3, 123.0, 122.4, 120.9, 120.1, 118.6, 109.6, 109.1, 29.5.

6.33 2-(phenylsulfinyl)-1*H*-pyrrole (3ag)

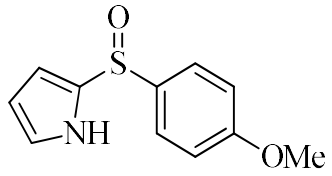


$C_{10}H_9NOS$
MW: 191.24 g/mol

Prepared according to the GP-1, using **1ag** (20.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3ag** (18.5 mg, 65%) as white solid. **Melting Point**: 92-93 °C. **HRMS (ESI)**: for $C_{10}H_{11}NOS^+$ [(M+H)$^+$]: calculated 192.0483, found 192.0475. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.61-7.58 (m, 2H), 7.50-7.45 (m, 3H), 6.95-6.93

(m, 1H), 6.67-6.65 (m, 1H), 6.23-6.21 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 130.9, 129.6, 129.3, 124.9, 124.3, 115.0, 109.7.

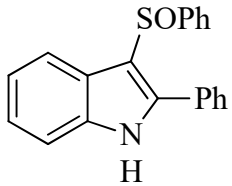
6.34 2-((4-methoxyphenyl)sulfinyl)-1*H*-pyrrole (3ah)



$C_{11}H_{11}NO_2S$
MW: 221.27 g/mol

Prepared according to the GP-1, using **1ah** (35.0 mg, 0.3 mmol, 2.0 equiv), **2c** (21.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3ah** (22.5 mg, 68%) as yellow solid. **Melting Point**: 105-106 ºC. **HRMS (ESI**): for $C_{11}H_{12}NO_2S^+$ [$(M+H)^+$]: calculated 222.0589, found 222.0582. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.56-7.52 (m, 2H), 7.00-6.96 (m, 2H), 6.95-6.94 (m, 1H), 6.54-6.52 (m, 1H), 6.21-6.19 (m, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9, 134.6, 129.8, 126.9, 124.2, 114.8, 114.3, 109.5, 55.7.

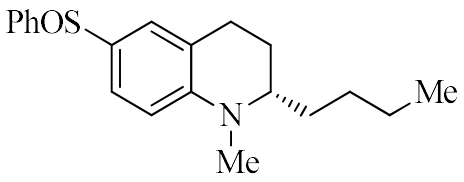
6.35 2-phenyl-3-(phenylsulfinyl)-1*H*-indole (3ai)



$C_{20}H_{15}NOS$
MW: 317.40 g/mol

Prepared according to the GP-1, using **1ai** (26.0 mg, 0.15 mmol, 1.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / $CHCl_3$ (4:1) (0.4 ml, 0.375 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluent afforded the sulfoxide **3ai** (30.0 mg, 63%) as white solid. **Melting Point**: 97-98 °C. **HRMS (ESI**): for $C_{20}H_{16}NOS^+$ [(M+H)$^+$]: calculated 318.0953, found 318.0939. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.77-7.75 (m, 2H), 7.68-7.66 (m, 2H), 7.51-7.50 (m, 3H), 7.46-7.38 (m, 4H), 7.30-7.28 (m, 1H), 7.20-7.16 (m, 1H), 7.00-6.96 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 144.1, 136.3, 130.0, 129.9, 129.8, 129.4, 129.1, 129.0, 125.2, 125.1, 123.8, 121.9, 120.5, 113.3, 111.8.

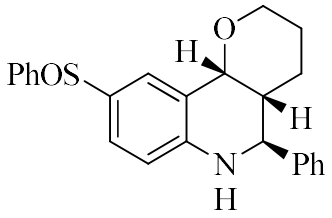
6.36 (2S)-2-butyl-1-methyl-6-(phenylsulfinyl)-1,2,3,4-tetrahydroquinoline (3aj)



$C_{20}H_{25}NOS$
MW: 327.48 g/mol

Prepared according to the GP-1, using **1ah** (60.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1.5:1 v/v) as eluent afforded the sulfoxide **3ah** (24.5 mg, 50%) as oily liquid. **HRMS (ESI**): for $C_{20}H_{26}NOS^+$ [(M+H)$^+$]: calculated 328.1735, found 328.1734. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.60 (m, 2H), 7.47-7.38 (m, 3H), 7.33-7.29 (m, 1H), 7.17-7.16 (m, 1H), 6.46 (d, *J* = 8.6 Hz, 1H), 3.28-3.23 (m, 1H), 2.94 (m, 3H), 2.78-2.68 (m, 1H), 2.64-2.56 (m, 1H), 1.91-1.85 (m, 1H), 1.82-1.72 (m, 1H), 1.61-1.53 (m, 1H), 1.46-1.18 (m, 5H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.0, 130.2, 129.2, 129.0, 126.6, 124.8, 122.6, 122.5, 110.0, 59.3, 38.3, 31.6, 28.3, 23.7, 23.4, 22.9, 14.2.

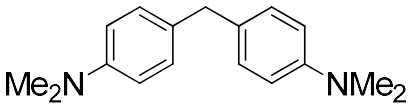
5.37 (4aR,5S,10bR)-5-phenyl-9-(phenylsulfinyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline (3ak)



$C_{24}H_{23}NO_2S$
MW: 389.50 g/mol

Prepared according to the GP-1, using **1ai** (80.0 mg, 0.3 mmol, 2.0 equiv), **2a** (16.0 mg, 0.15 mmol, 1.0 equiv) and HFIP / CH_2Cl_2 (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1.5 v/v) as eluent afforded the sulfoxide **3ai** (26.0 mg, 45%) as oily liquid. **HRMS (ESI**): for $C_{24}H_{24}NO_2S^+$ [(M+H)$^+$]: calculated 390.1528, found 390.1522. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.61-7.59 (m, 2H), 7.55-7.51(m, 2H), 7.49-7.45 (m, 1H), 7.41-7.32 (m, 6H), 7.26 (ddd, *J* = 7.9, 5.5, 2.2 Hz, 1H), 6.91 (s, 1H), 6.68 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.54 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.31 (dd, *J* = 7.9, 2.7 Hz, 1H), 3.87 (t, *J* = 12.5 Hz, 1H), 3.63-3.56 (m, 1H), 1.92-1.89 (m, 1H), 1.80-1.70 (m, 1H), 1.64-1.56 (m, 1H), 1.28-1.20 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 148.3, 148.2, 146.7, 146.6, 142.1, 142.0, 130.4, 130.0, 129.9, 129.3, 128.5, 128.3, 127.8, 126.7, 126.4, 123.9, 119.7, 119.6, 114.1, 114.0, 73.1, 73.0, 67.4, 67.3, 53.6, 37.5, 37.4, 23.3, 23.3, 21.5, 21.4.

5.38 4,4'-methylenebis(*N,N*-dimethylaniline) (4)

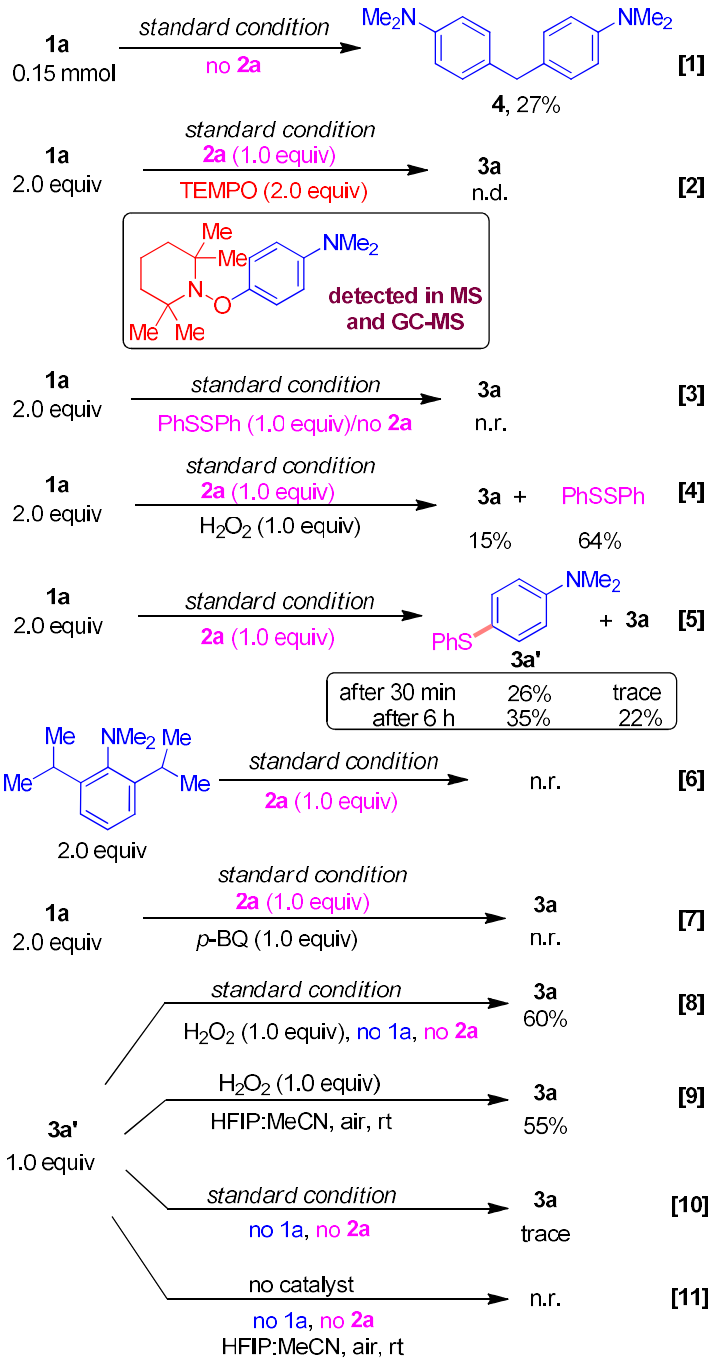


$C_{17}H_{22}N_2$
MW: 254.37 g/mol

Prepared according to GP-1, using **1a** (17.0 mg, 0.15 mmol), catalyst **B** (8.0 mg, 0.045 mmol, 30 mol%) and HFIP / MeCN (4:1) (0.2 ml, 0.75 M). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1 v/v) as eluent afforded the sulfoxide **4** (14.0 mg, 35%) as white solid. **HRMS (ESI)**: for $C_{17}H_{23}N_2^+$ [(M+H)$^+$]: calculated 390.1528, found 390.1522. **Melting Point**: 90-91 ^{o}C. **^{1}H NMR** (400

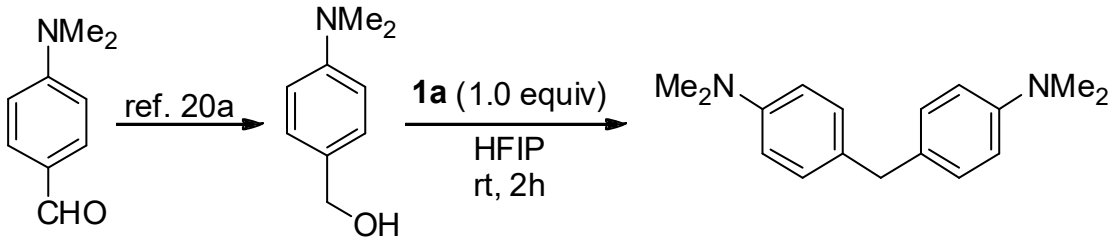
MHz, $CDCl_3$): δ 7.08-7.05 (m, 4H), 6.71-6.68 (m, 4H), 3.81 (s, 2H), 2.91 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 130.5, 129.5, 113.2, 41.1, 40.0.

7. Control Experiments



8. Mechanistic Evidences

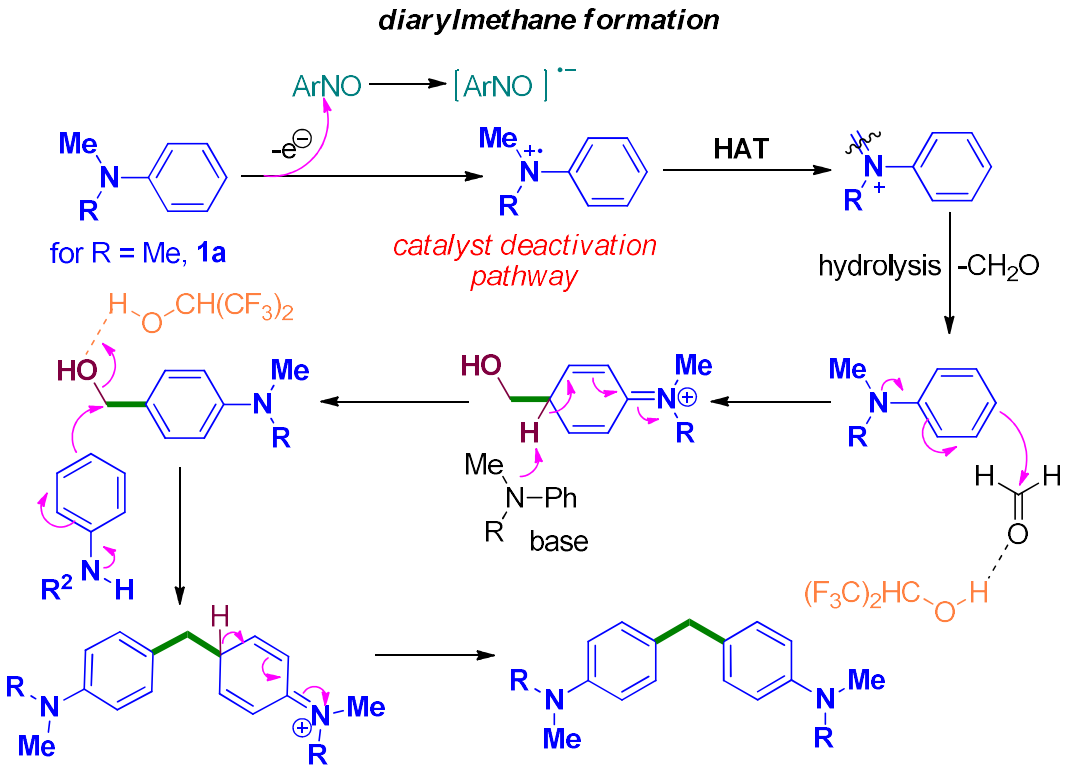
8.1 Mechanistic Rationale for the diarylmethane formation



4': 95%
1.0 equiv

4: 83%

Procedure: An oven-dried glass vial is charged with a magnetic stir bar, **1a** (1.0 equiv, 0.15 mmol, 35.0 mg), **4'** (1.0 equiv, 0.15 mmol, 23.0 mg) and 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) (0.75 M) is added to the mixture in aerobic atmosphere. The vial is maintained for 2 h at rt. The reaction mixture is then passed through a plug of silica. The vial is rinsed with CH_2Cl_2 (2 X 2 mL), and the collected organic phases are evaporated under reduced pressure. The analytically pure product **4** is obtained by column chromatography on silica gel using petroleum ether and ethyl acetate (20:1; v/v) as eluent.



Proposed Mechanistic Pathway for diarylmethane Formation

8.2 Mechanistic Evidence for the Radical Reaction

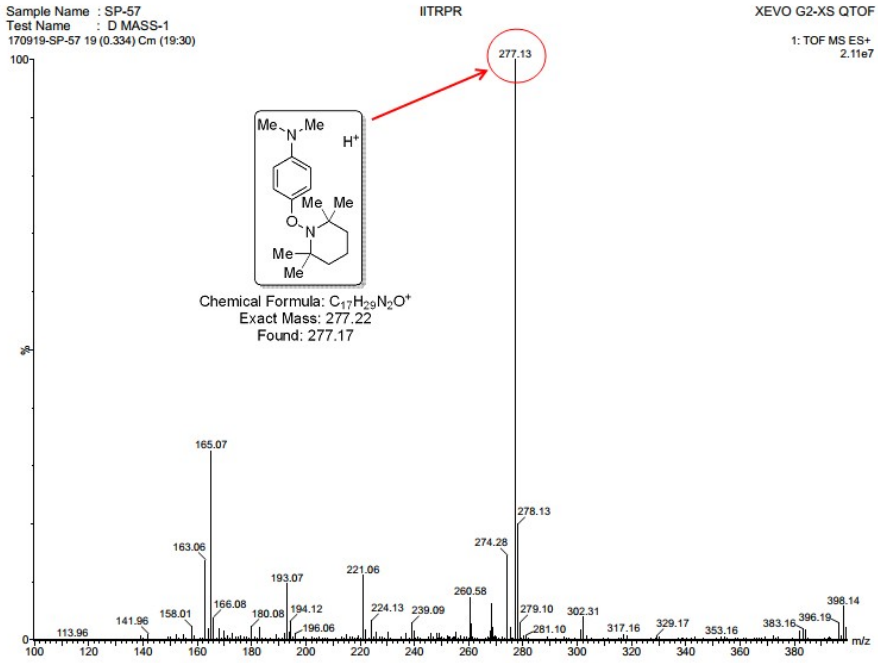


Figure S1: D-Mass data of **aryl-TEMPO** adduct.

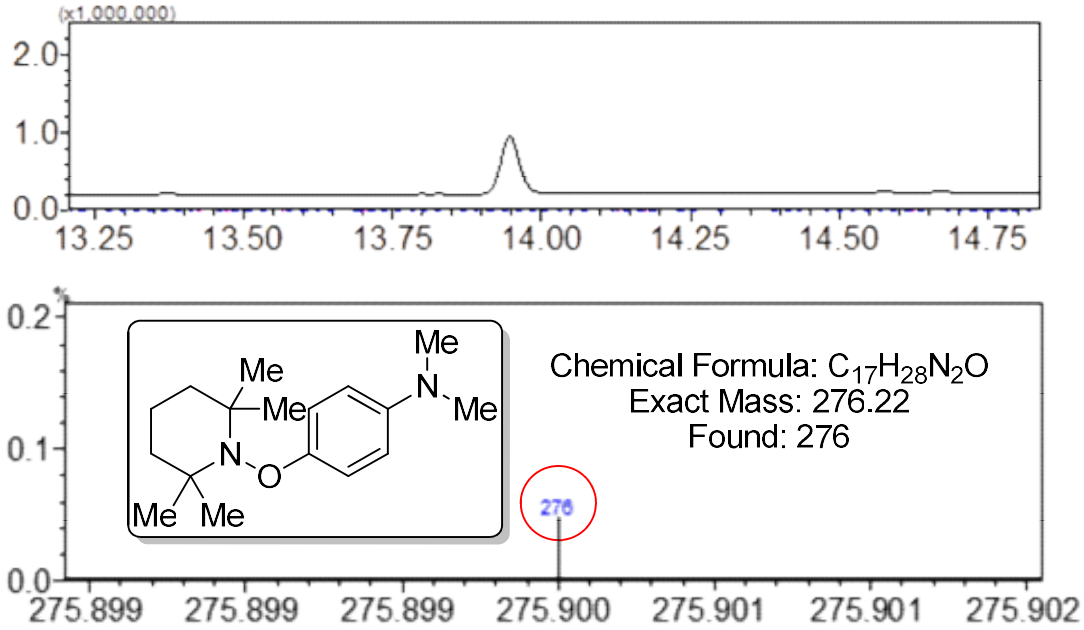


Figure S2: GC-MS data of of **aryl-TEMPO** adduct.

8.3. Mechanistic Evidences for the aryl-hydroxylamine formation

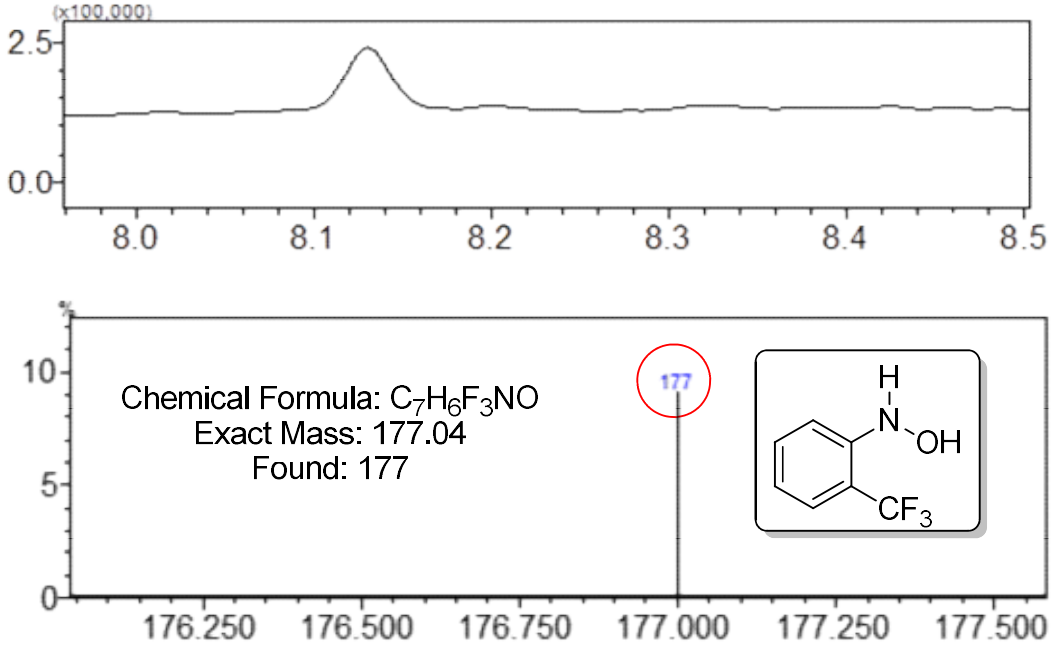


Figure S4: GC-MS data of **aryl-hydroxylamine** derivative

9. UV-visible Spectral Data

UV data suggests the electron transfer process from electro-rich aromatic amine to the nitrosoarene (**catalyst B**). **Figure S5** and **S6** represents the generation of Charge Transfer (CT) band around 500 nm regions in the presence of $PhNMe_2$ (**1a**) and **catalyst-B**.

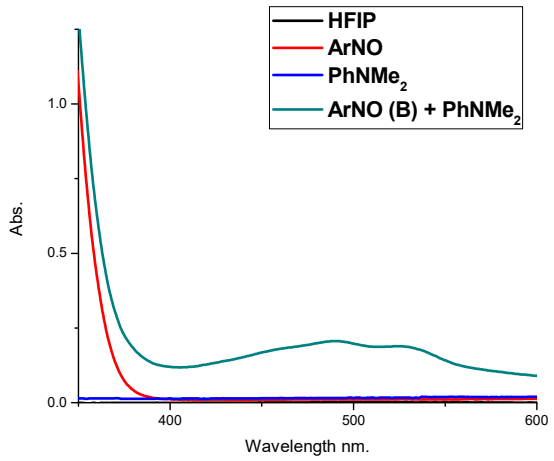


Figure S5

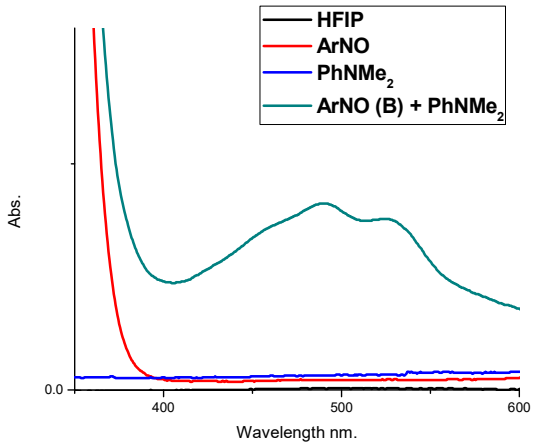


Figure S6 zoomed image of **S5**

Figure S5 and S6: UV-Vis spectra of 0.03 (M) $PhNMe_2$ **1a** (0.15 mmol) in freshly distilled HFIP in presence of ArNO (**catalyst B**) (0.045 mmol, 30 mol%).

10. Cyclic Voltammetric Study

The measurements were carried out as follows: a 0.1 (M) solution of tetrabutylammonium hexafluorophosphate in acetonitrile was added to the measuring cell and the solution was degassed by argon purge for 5 min. After recording the baseline the electroactive compound was added 0.01 (M) and the solution was again degassed with a stream of argon for 5 min. The cyclic voltammogram was recorded with one to two scans.

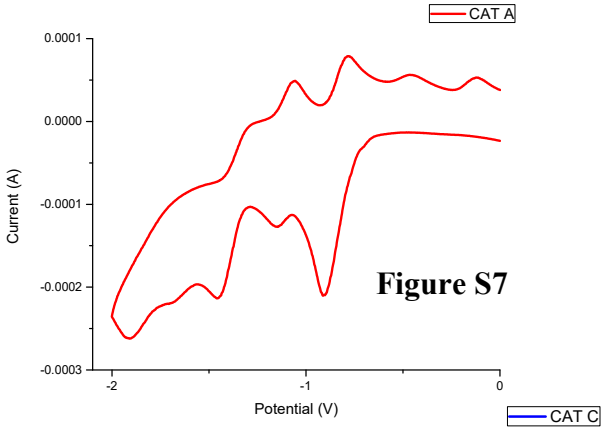


Figure S7

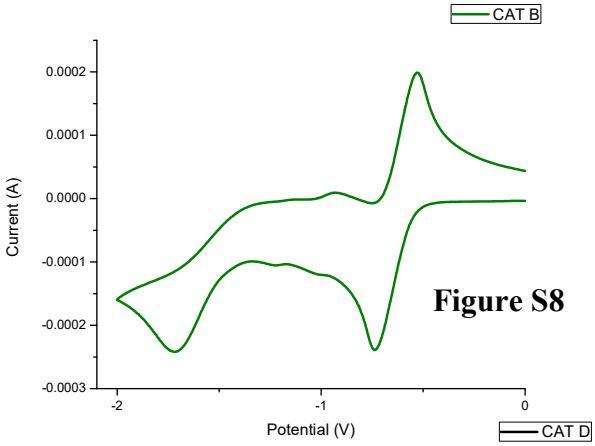


Figure S8

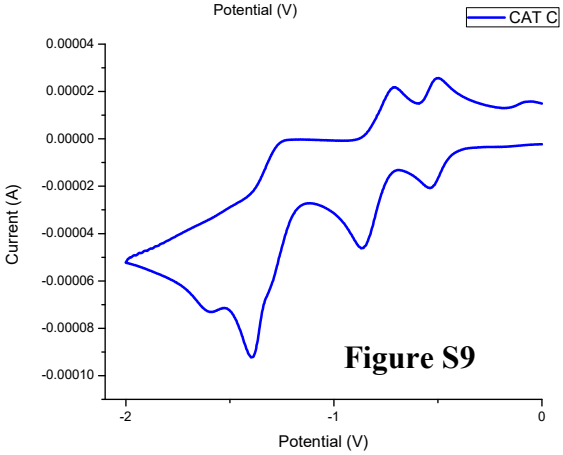


Figure S9

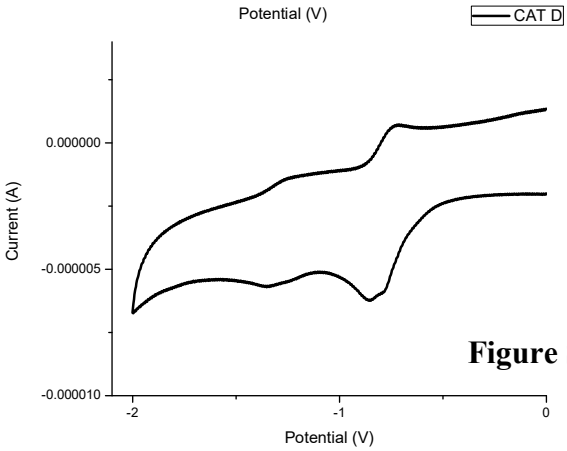


Figure S10

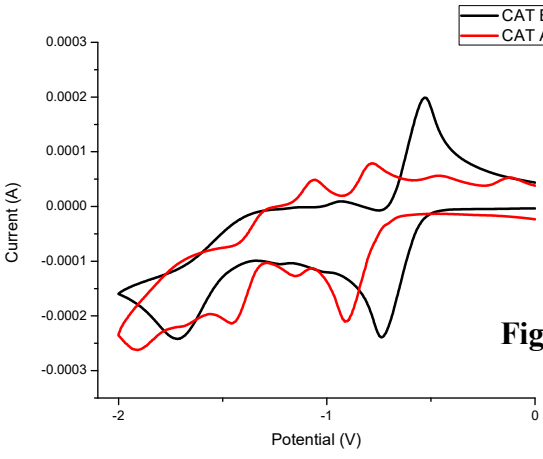


Figure S11

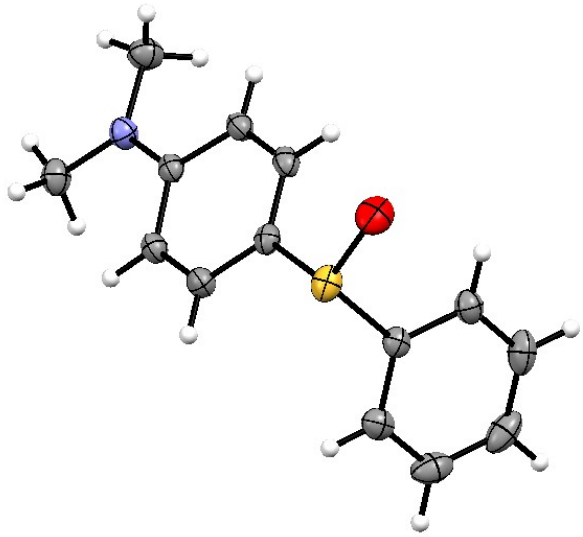
Cyclic voltammograms of 0.01 (M) solution of nitrosobenzene **catalyst A**, (Figure S7), 0.01 (M) solution of **catalyst B**, (Figure S8), 0.01 (M) solution of **catalyst C**, (Figure S9), and 0.01 (M) solution of **catalyst D**, (Figure S10), under argon. The measurements were performed with a scan rate of 100 mV/s and with tetabutylammonium hexafluorophosphate 0.1 (M) as supporting electrolyte. The comparison CV plot between catalyst A and catalyst B is shown in Figure S9.

The peak at -0.91 V, -0.74 V, -0.54 V and -0.85 V shows the reduction of **catalyst A, catalyst B, catalyst C,** and **catalyst D** respectively and corresponds to a potential vs Ag/AgCl.

11. X-Ray data of 3a and 3ac:

For the determination of X-ray crystal structures of **3a** and **3ac** a single crystal was selected and mounted with paratone oil on a glass fiber using gum. The data was collected at 293K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operation at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program[S14] was used. Absorption correction was done applying SADABS program.[S15] The crystal structure was solved by SIR 92[S16] and refined by full matrix least square method using SHELXL-97[S17] WinGX system, Ver 1.70.01.[S18] All the non-hydrogen atoms in the structure were located the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters. The crystal structure (excluding structure factor) has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number: **3a: CCDC 1965825** and **3ac: CCDC 1965821**.[S19]

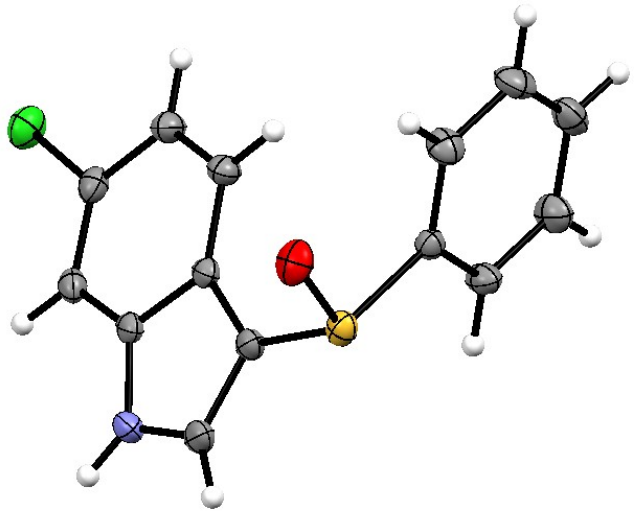
Crystal Data and Structure Refinement for Complex 3a (CCDC1965825)



Atom color code: grey = carbon atom, white = hydrogen atom, blue = nitrogen atom, yellow = sulfur atom and red = oxygen atom.

CCDC No.	CCDC 1965825
Formula	C14 H15 N O S
Formula weight	245.33
Crystal System	Monoclinic
Space group	P 21/c
a, b, c (Å)	14.275(2), 7.6981(10), 11.6398(17)
α, β, γ (°)	90, 101.250(5), 90
V ($Å^3$)	1254.5(3)
Z	4
Calculated Density (g/cm^3)	1.299
Absorption coefficient (mm^{-1})	0.241
F(000)	520.0
Crystal Size (mm^3)	0.30 x 0.36 x 0.40
Theta range for data collection:	2.9° to 26.4°
Data set	-17: 17 ; -9: 9 ; -14: 14
R indices [I>=2σ (I)] (all data)	R1 = 0.0692, wR2 = 0.2260
Reflection	12433
Independent refl.	4104, [R(int) = 0.020]
S	1.05
Min. and Max. Resd. Dens. ($e/Å^3$)	-0.45, and 0.53
Npar	154

Crystal Data and Structure Refinement for Complex 3ac (CCDC1965821)



Atom color code: grey = carbon atoms, white = hydrogen atoms, blue = nitrogen atom, red = oxygen atoms, yellow = sulfur atom and green = chlorine atom.

CCDC No.	CCDC 1965821
Formula	C14 H10 Cl N O S
Formula weight	275.74
Crystal System	Monoclinic
Space group	P 21/c
a, b, c (Å)	9.0173(7), 9.8035(10), 14.1588(13)
α, β, γ (°)	90, 95.552(3), 90
V ($Å^3$)	1245.8(2)
Z	4
Calculated Density (g/cm^3)	1.470
Absorption coefficient (mm^{-1})	0.459
F(000)	568.0
Theta range for data collection:	2.3° to 26.4°
Data set	-11: 11 ; -12: 12 ; -16: 17
R indexes [I>=2σ (I)] (all data)	R1 = 0.0504, wR2 = 0.1273
Reflection	11179
S	1.069
Min. and Max. Resd. Dens. ($e/Å^3$)	-0.38 and 0.24
Npar	163

12. References

S1. S1. D. J. Lippincott, R. T. H. Linstadt, M. R. Maser, F. Gallou, B. H. Lipshutz, *Org. Lett.,* 2018, **20**, 4719–4722.

S2. F. Tibiletti, M. Simonetti, K. M. Nicholas,; G. Palmisano,; M. Parravicini,; F. Imbesi, S. Tollari, A. Penoni, *Tetrahedron,* 2010, **66***,* 1280–1288.

S3. B. Priewisch, K. R. Braun, *J. Org. Chem.,* 2005, **70***,* 2350–2352.

S4. M. Dochnahl, G. C. Fu, *Angew. Chem. Int. Ed.,* 2009, **48**, 2391–2393.

S5. A. Jankowiak, E. Obijalska, P. Kaszynski, A. Pieczonka, V. G. Young, *Tetrahedron,* 2011, **67**, 3317–3327.

S6. Arcadi, A.; Chiarini, M.; Vecchio, L. D.; Marinelli, F.; Michelet, V. *Chem. Commun.,* 2016, **52**, 1458–1461.

S7. A. Defoin, *Synthesis,* 2004, **5**, 706–710.

S8. G. M. Min, S. Bang, H. Lee, B. C. Yu, *Chem. Commun*., 2010, **46**, 5232–5234.

S9. H. Kondo, N. Akiba, T. Kochi, F. Kakiuchi, *Angew. Chem. Int. Ed*., 2015, **54**, 9293–9297.

S10. M. Vellakkaran, K. Singh, D. Banerjee, *ACS Catal*., 2017, **7**, 8152−8158.

S11. H-H. Wang, T. Shi, W-W. Gao, Y-Q. Wang, J-F. Li, Y. Jiang, Y. S. Hou, C. Chen, X. Peng, Z. Wang, *Chem. Asian J*., 2017, **12**, 2675–2679.

S12. S. G. Davies, A. M. Fletcher, P. M. Roberts, J. E. Thomson, *Eur. J. Org. Chem*., 2019, 5093–5119.

S13 A. Semwal, S. K. Nayak, *Synthetic Communications*, 2006, **36**, 227–236,

S14. Bruker, *SAINT V7.68A*, Bruker AXS Inc., Madison (WI, USA), 2005.

S15. G. M. Sheldrick, *SADABS 2008/2*, Göttingen, 2008**.**

S16. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst*., 1993, **26**, 343–350.

S17. G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 1997.

S18. L. J. Farrugia, WinGX-A Windows Program for Crystal Structure Analysis, *J. Appl. Cryst*., 1999, **32**, 837–838.

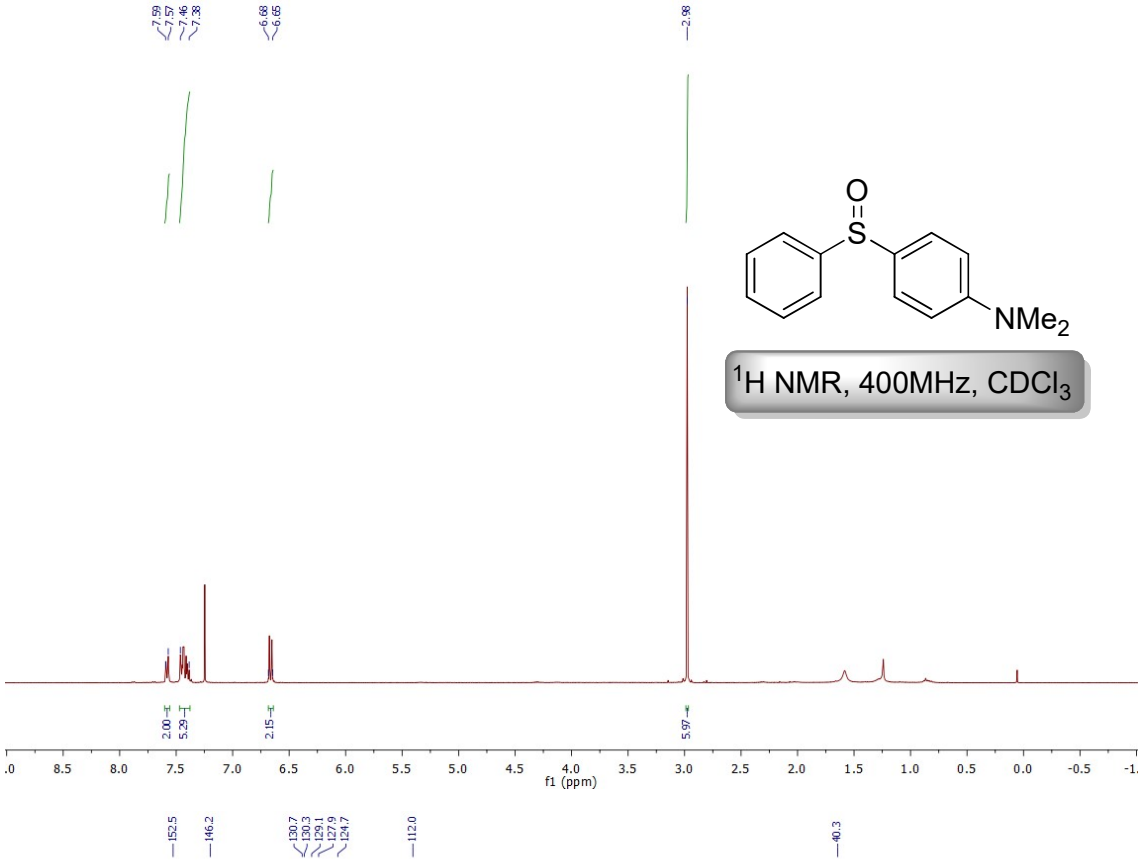
S19. (a) **CCDC 1965825** contains supplementary crystallographic data for the compound **3a**.

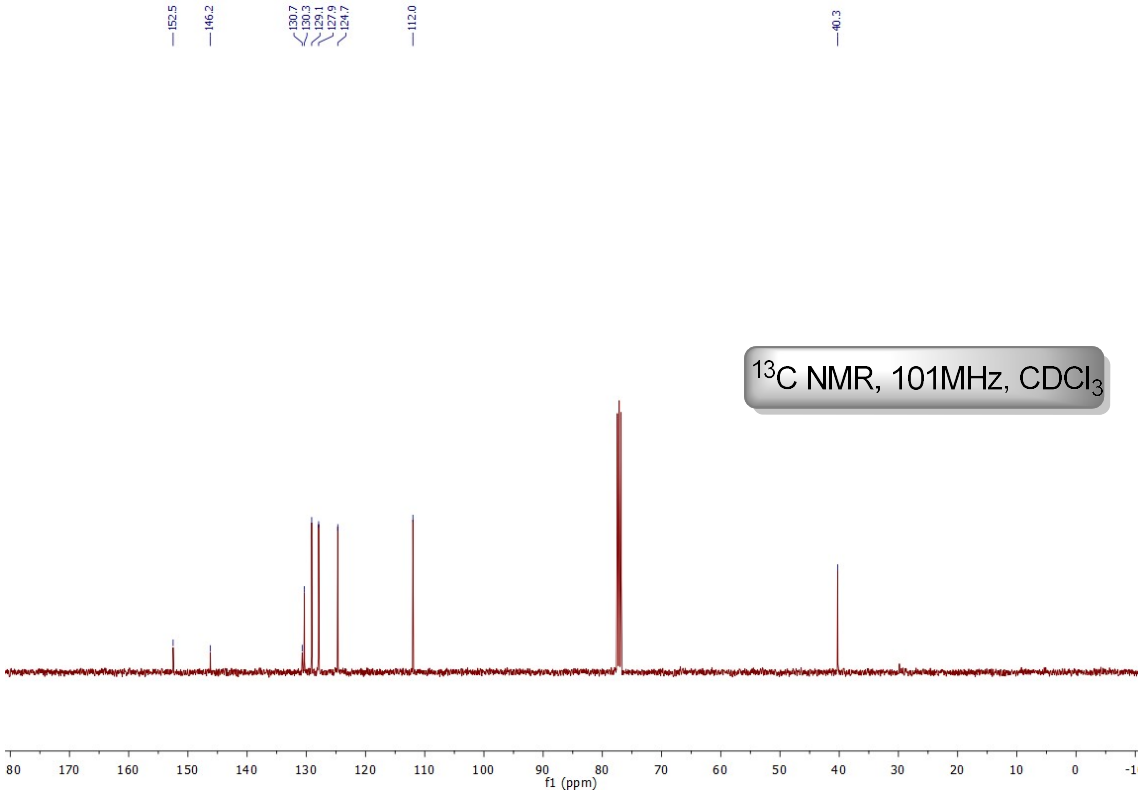
(b) **CCDC 1965821** contains supplementary crystallographic data for the compound **3ac**.

S20. a) M. J. Naimi-Jamal, J. Mokhtari, M. G. Dekamin, G. Kaupp, *Eur. J. Org. Chem.,* 2009, 3567–3572; b) V. D. Vuković, E. Richmond, E. Wolf, J. Moran, *Angew. Chem. Int. Ed.,* 2017, 56, 3085 –3089

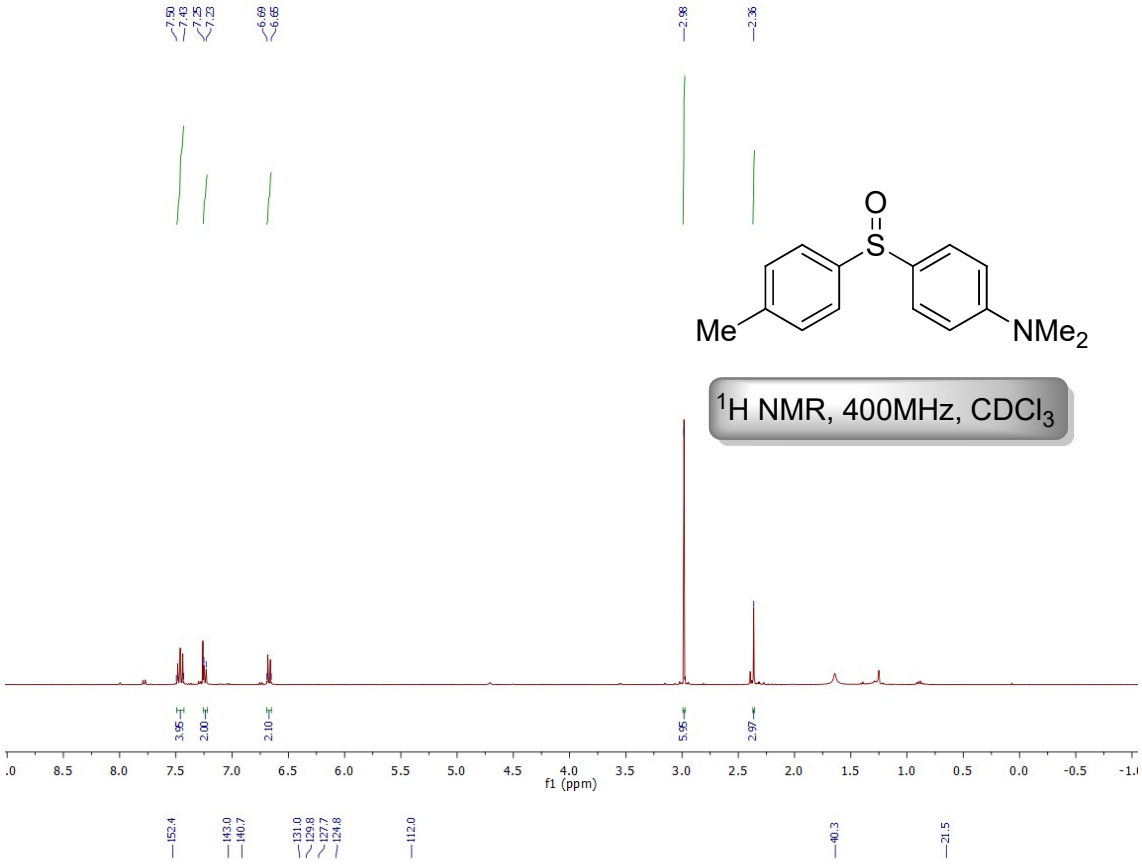
13. Experimental NMR Data

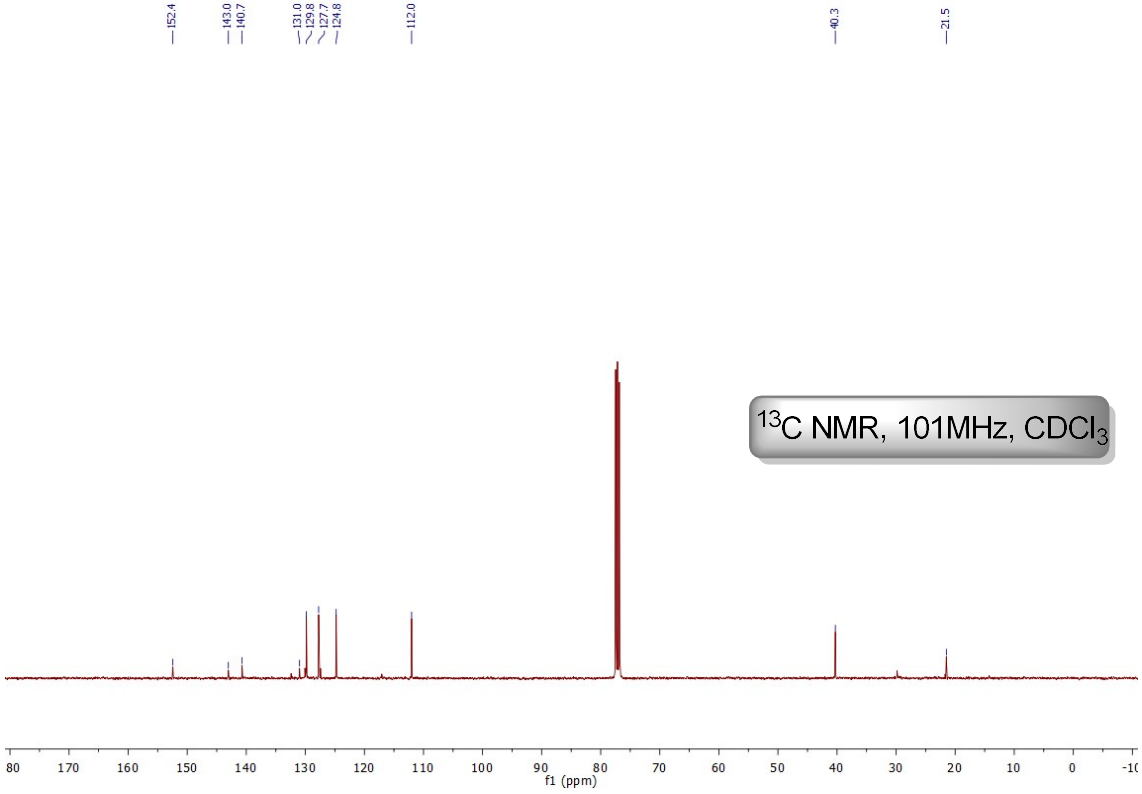
N,N-dimethyl-4-(phenylsulfinyl)aniline (3a)



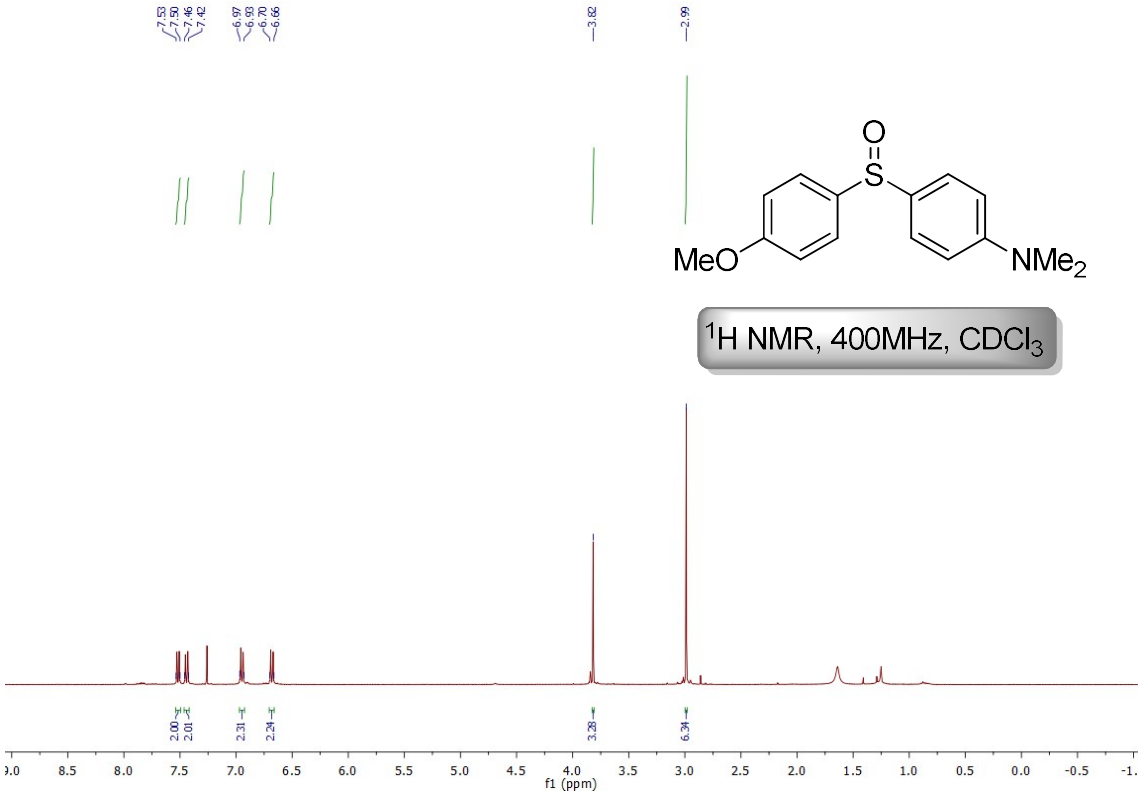


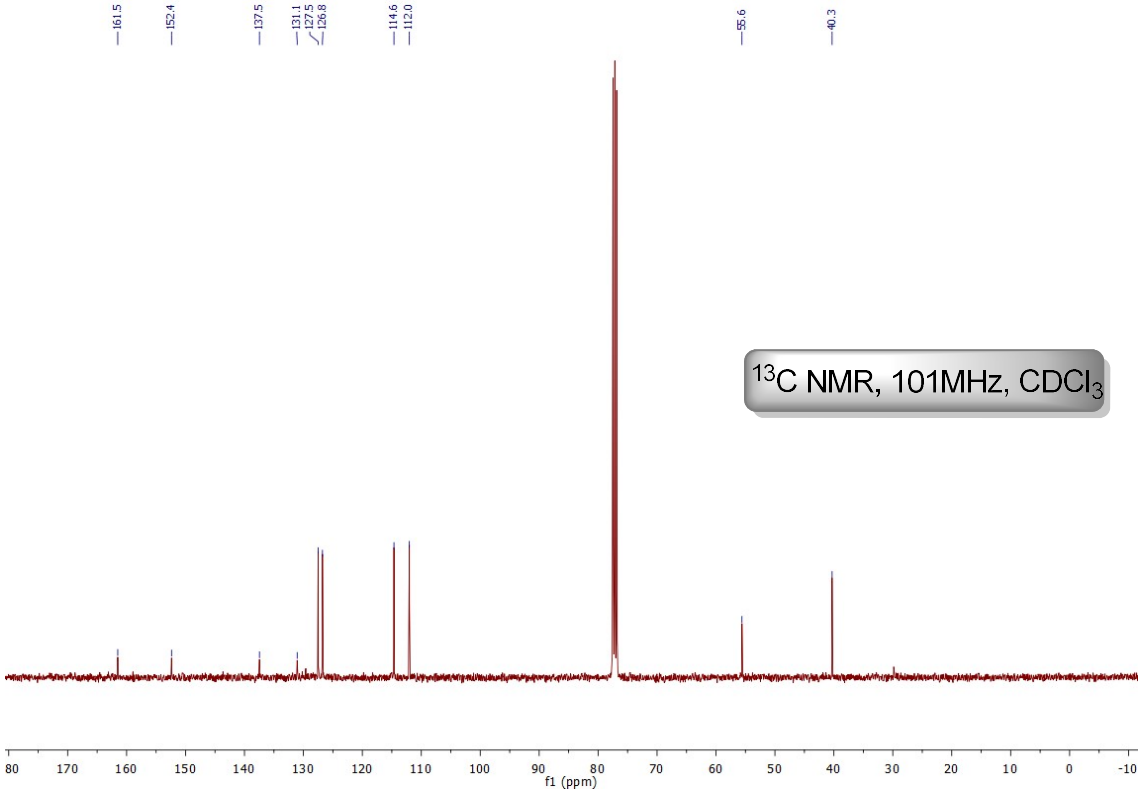
N,N-dimethyl-4-(*p*-tolylsulfinyl)aniline (3b)



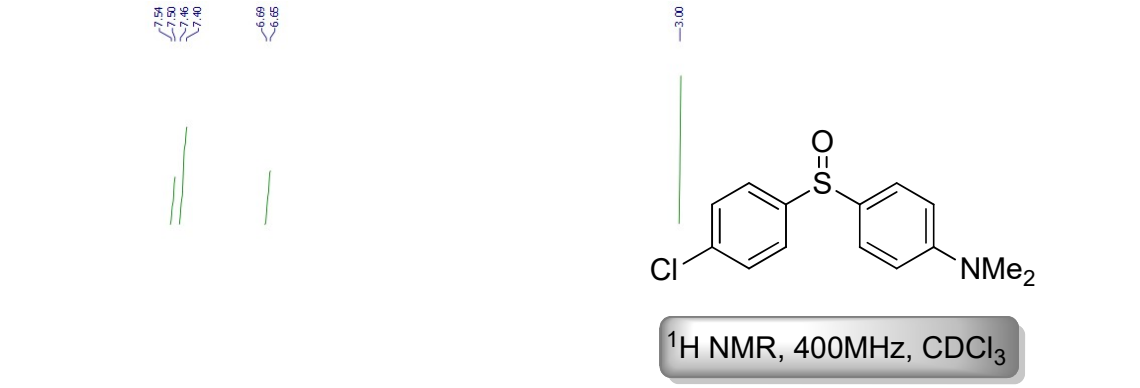


4-((4-methoxyphenyl)sulfinyl)-*N,N*-dimethylaniline (3c)

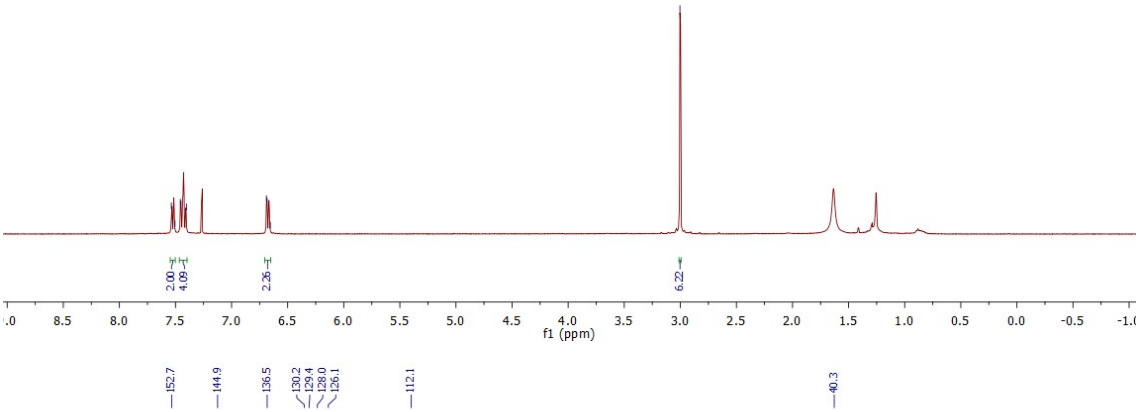




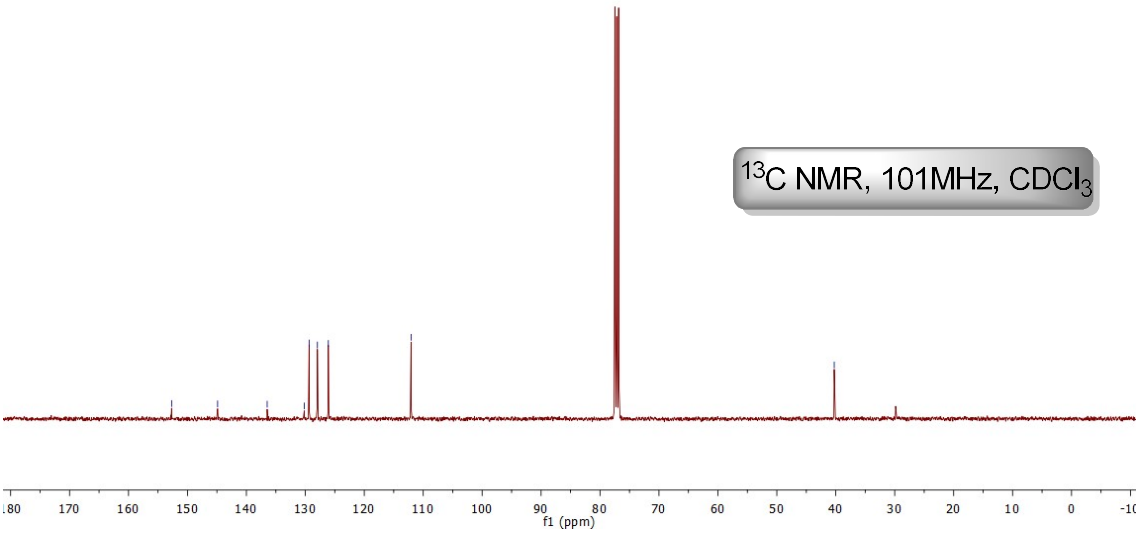
4-((4-chlorophenyl)sulfinyl)-*N,N*-dimethylaniline (3d)



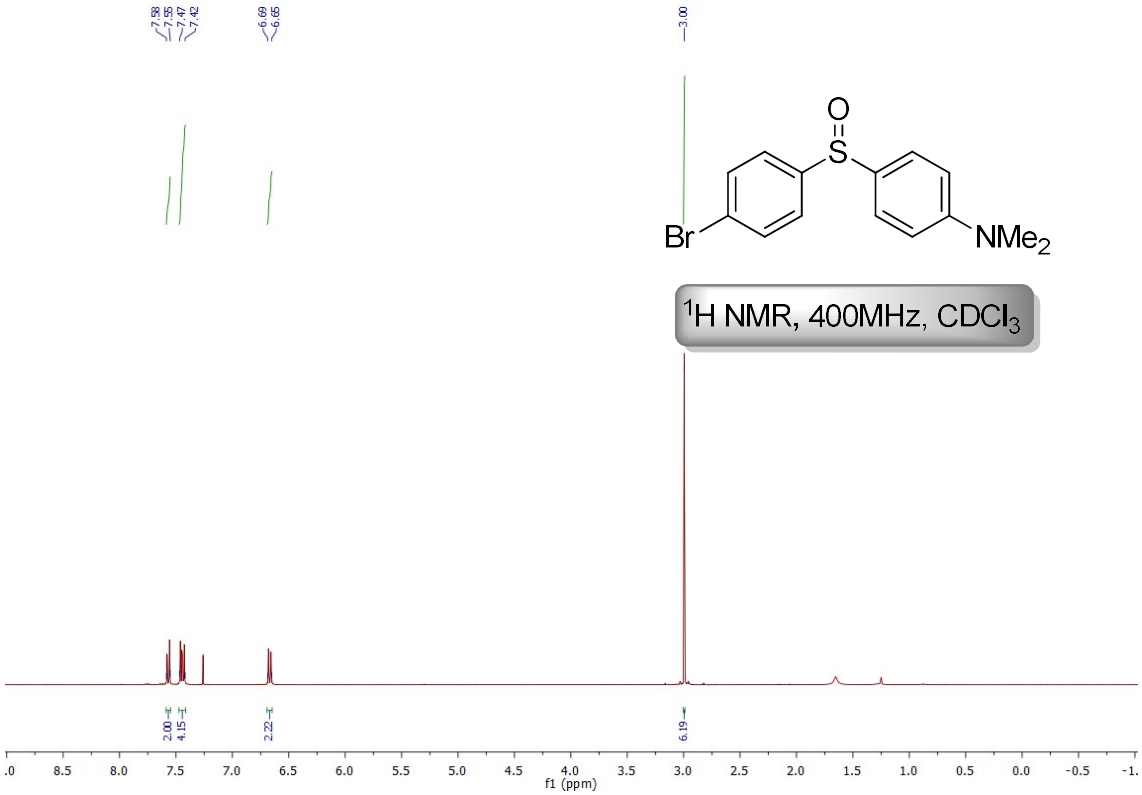
^{1}H NMR, 400MHz, $CDCl_3$

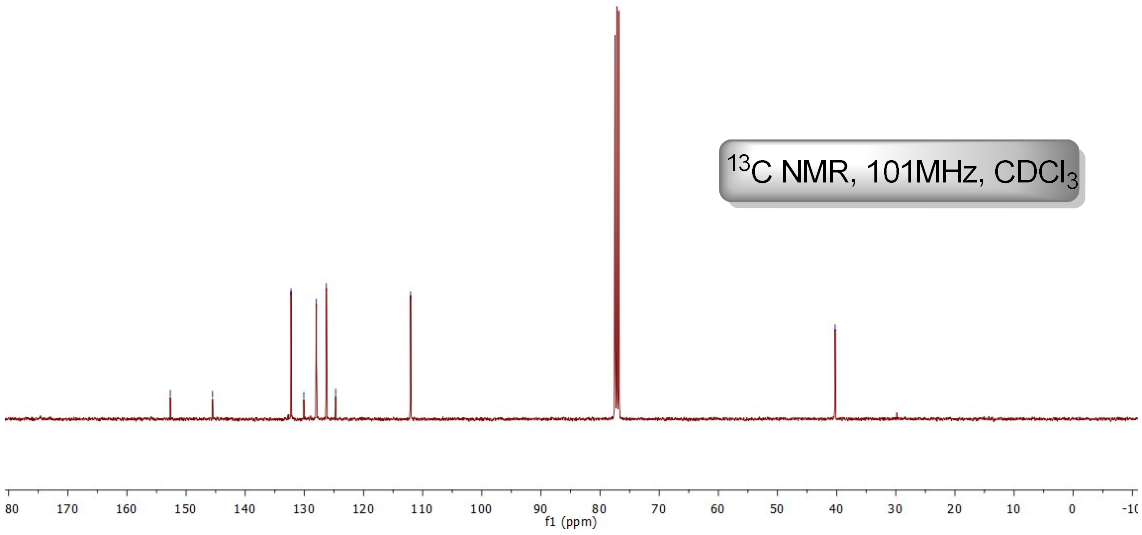


^{13}C NMR, 101MHz, $CDCl_3$

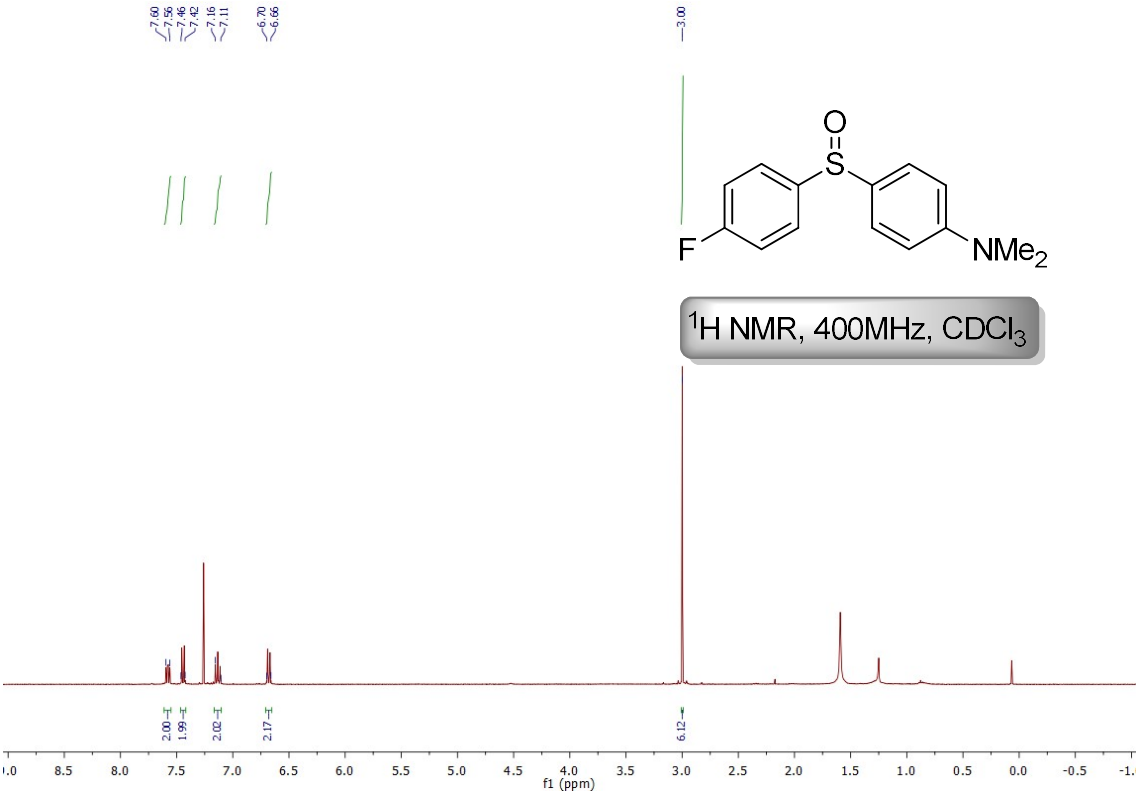


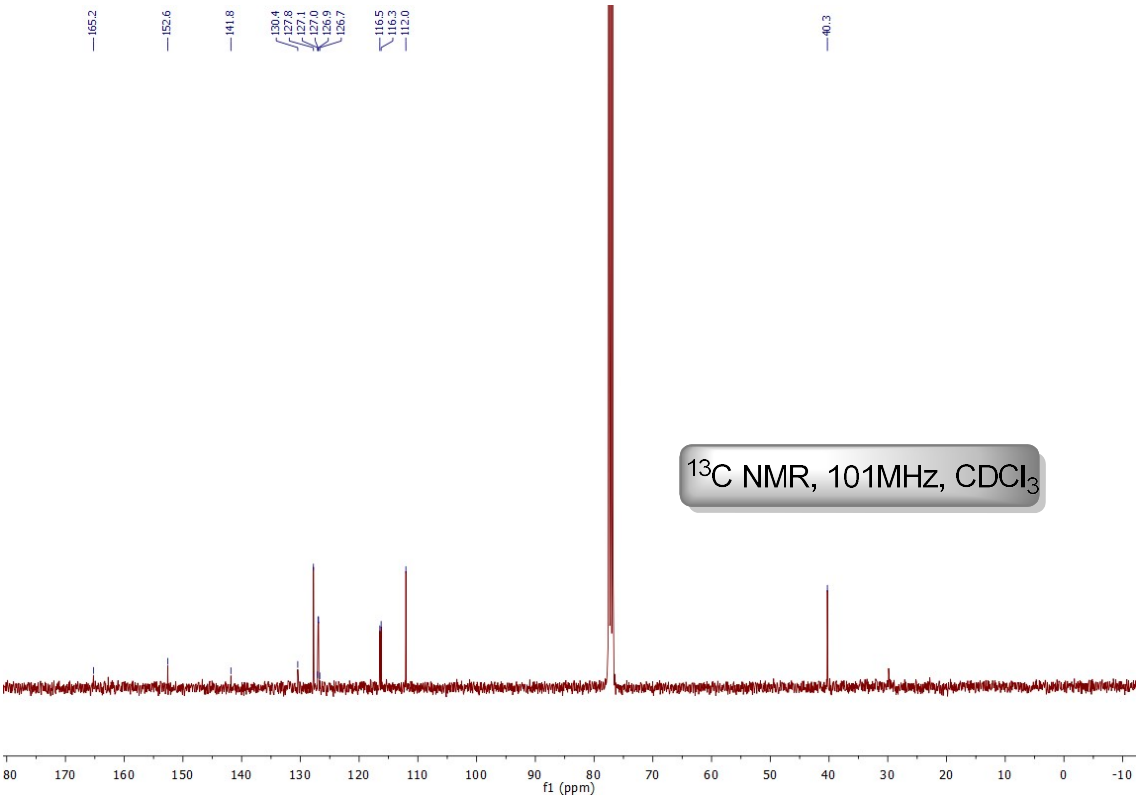
4-((4-bromophenyl)sulfinyl)-*N,N*-dimethylaniline (3e)

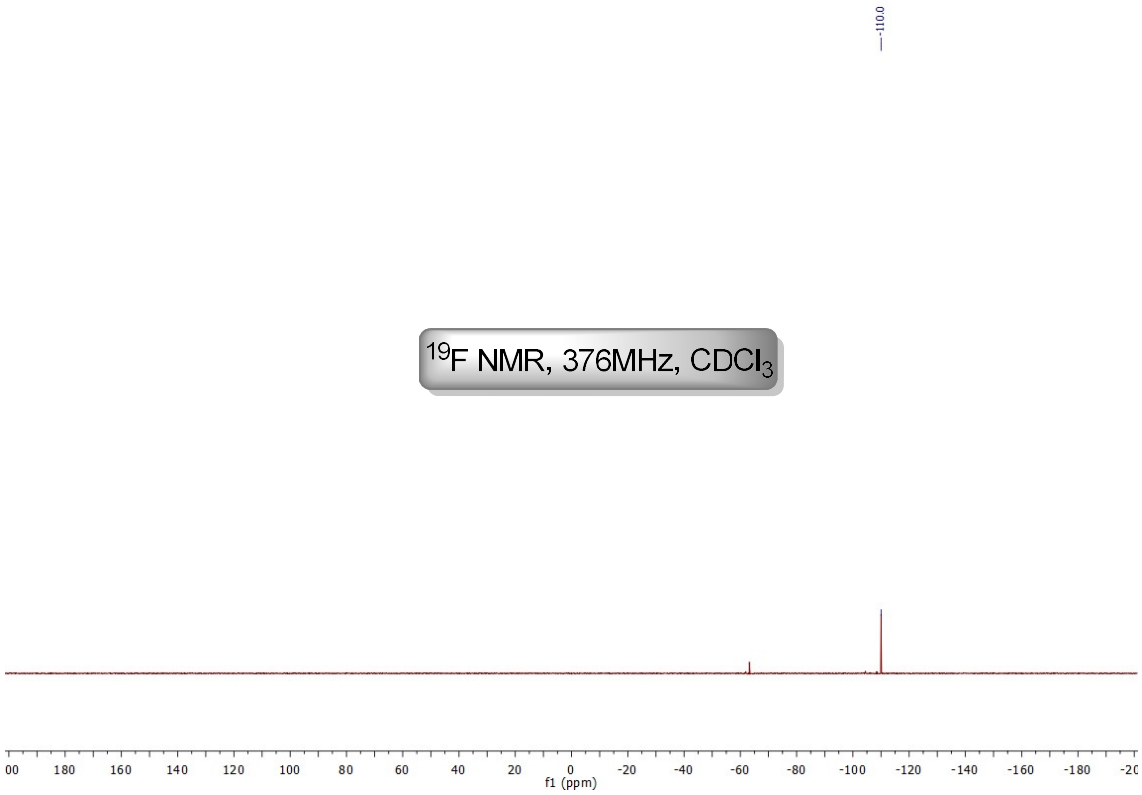




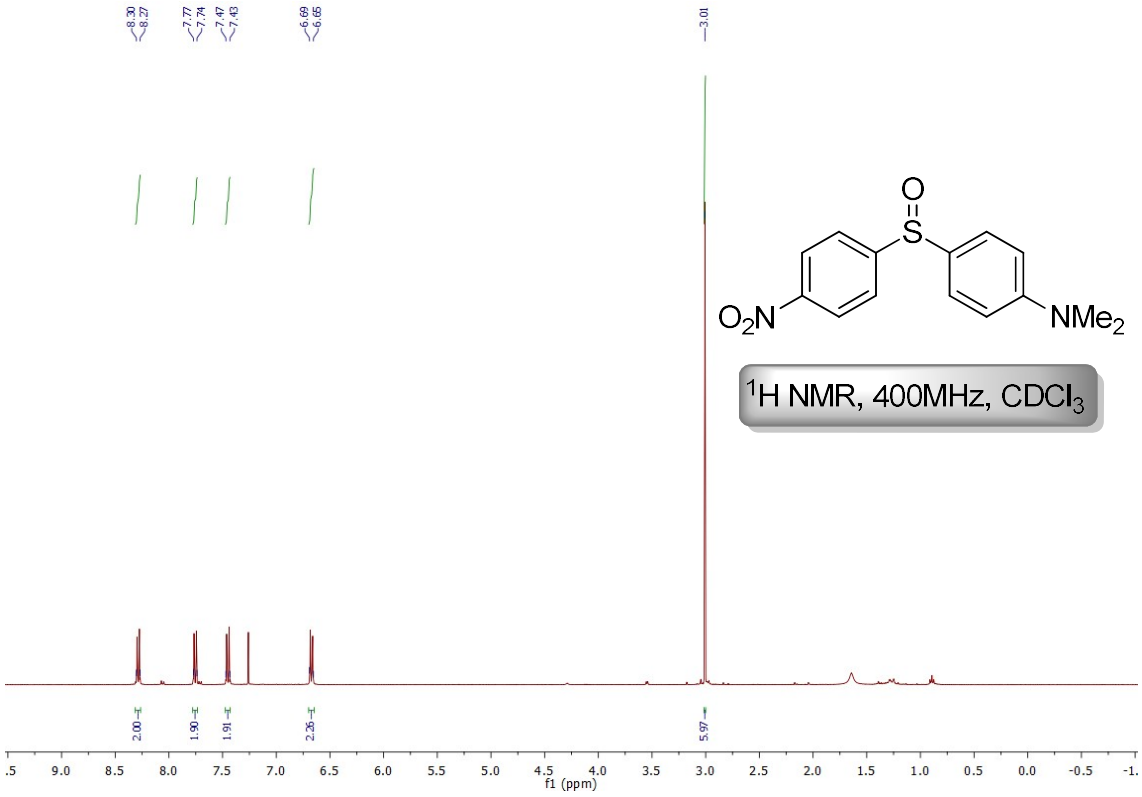
4-((4-fluorophenyl)sulfinyl)-*N,N*-dimethylaniline (3f)



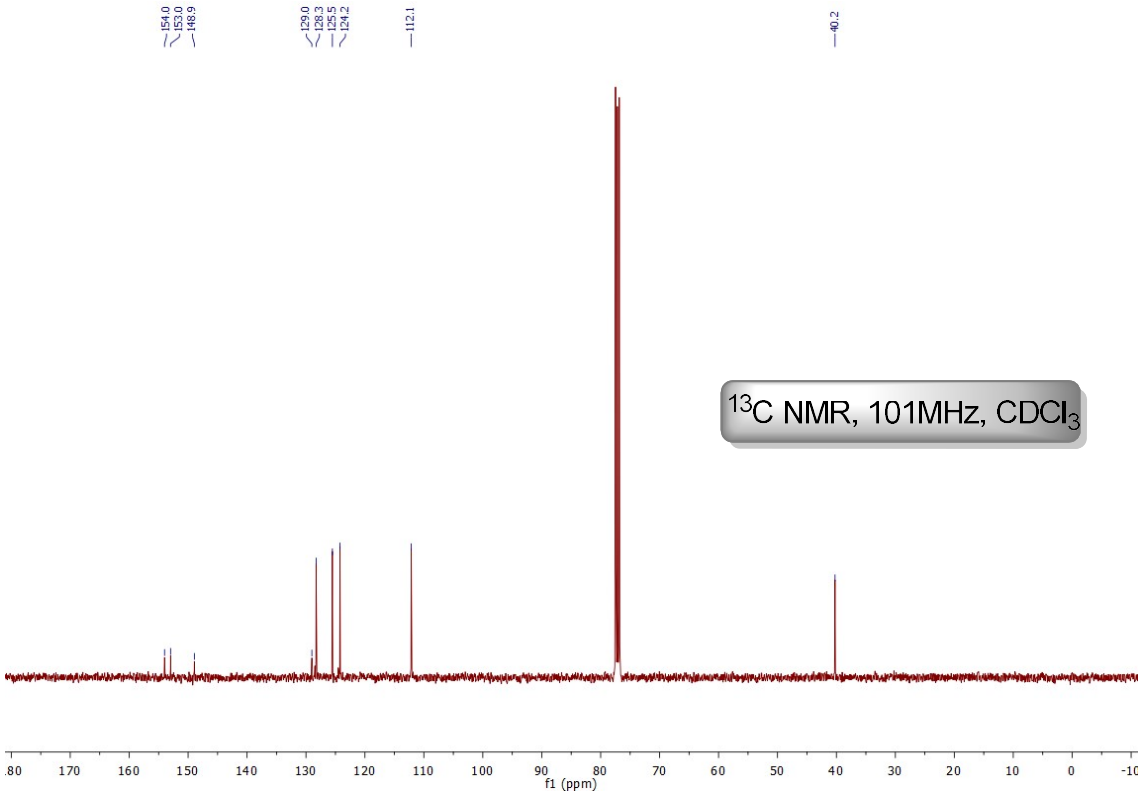



-110.0
^{19}F NMR, 376MHz, CDCl$_3$
00 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
f1 (ppm)

N,N-dimethyl-4-((4-nitrophenyl)sulfinyl)aniline (3g)

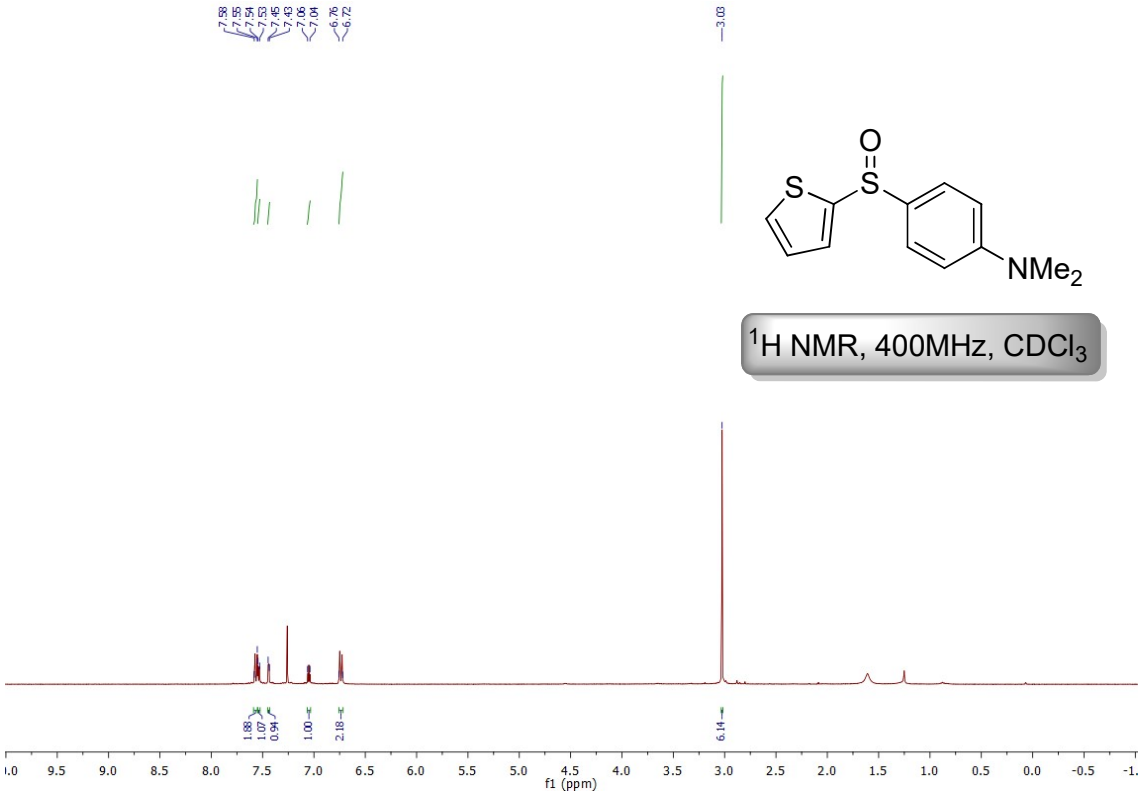


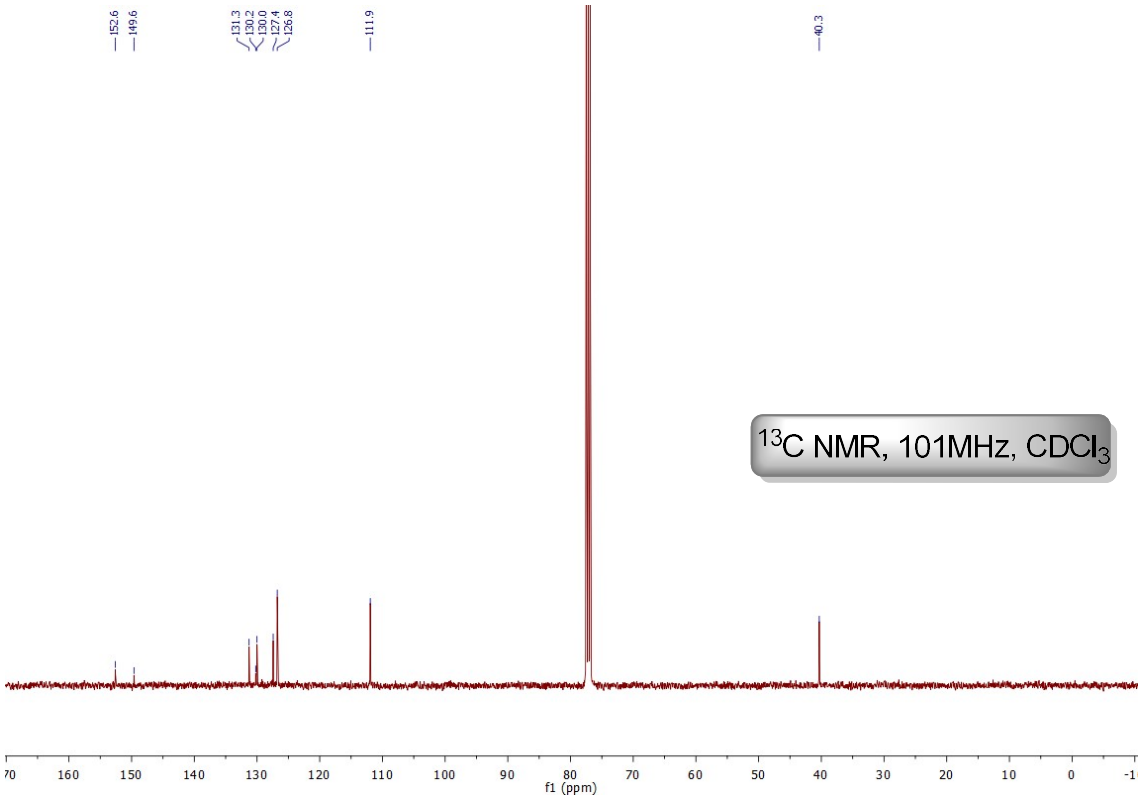
^{1}H NMR, 400MHz, $CDCl_3$



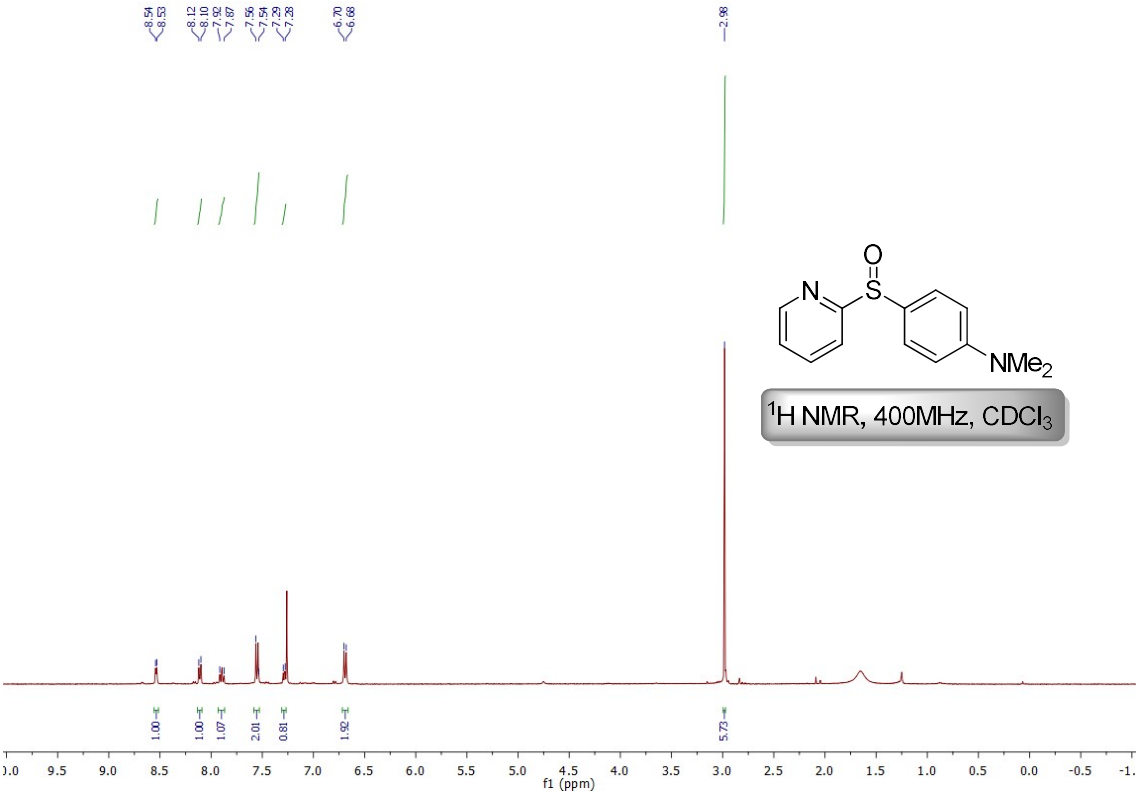
^{13}C NMR, 101MHz, $CDCl_3$

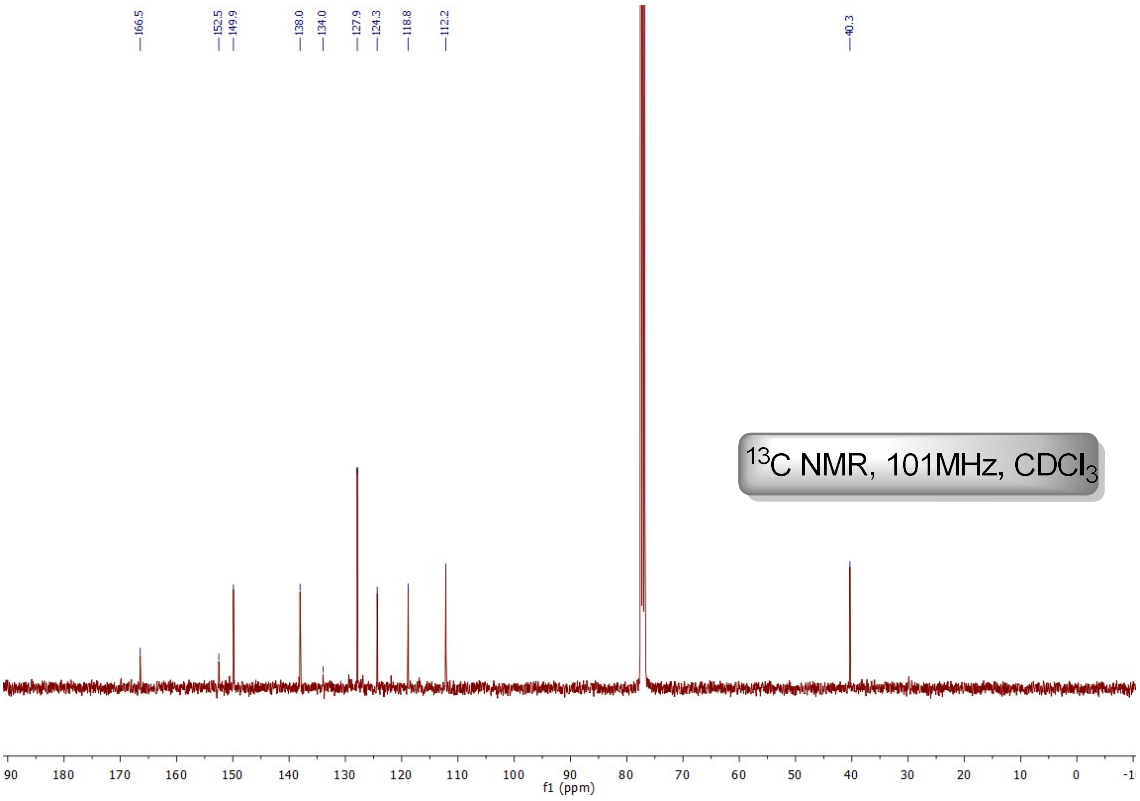
N,N-dimethyl-4-(thiophen-2-ylsulfinyl)aniline (3h)



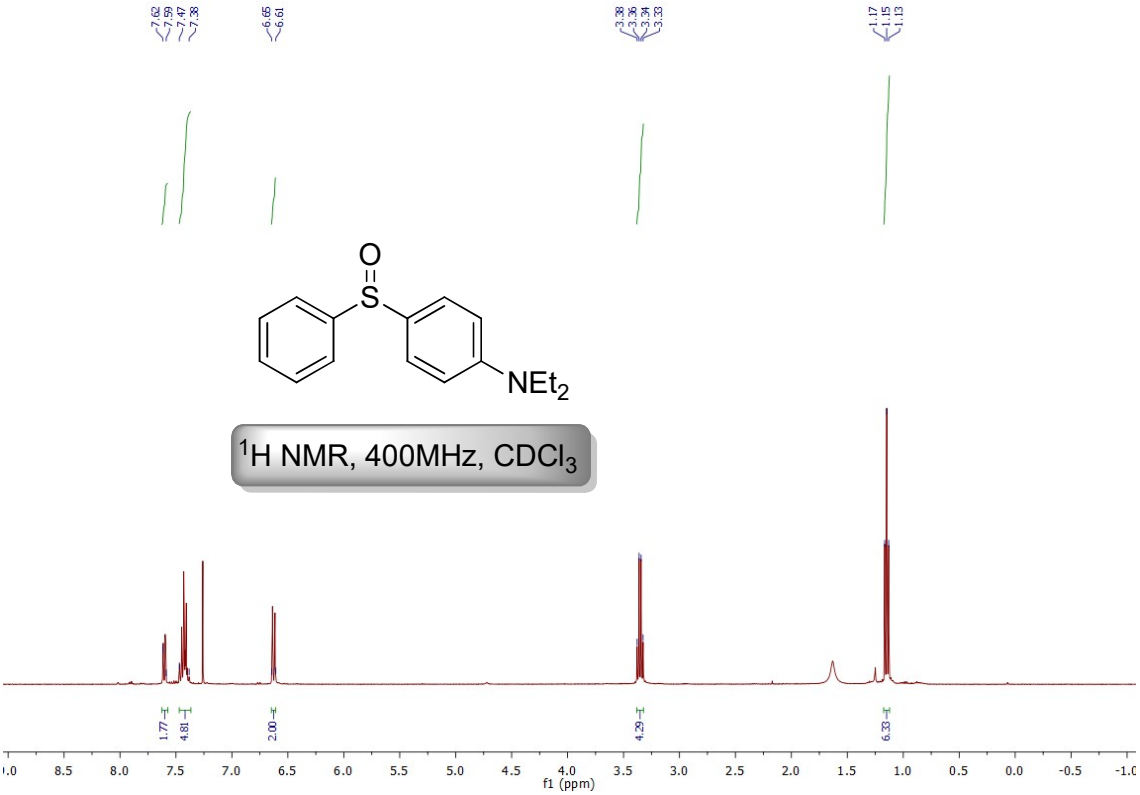


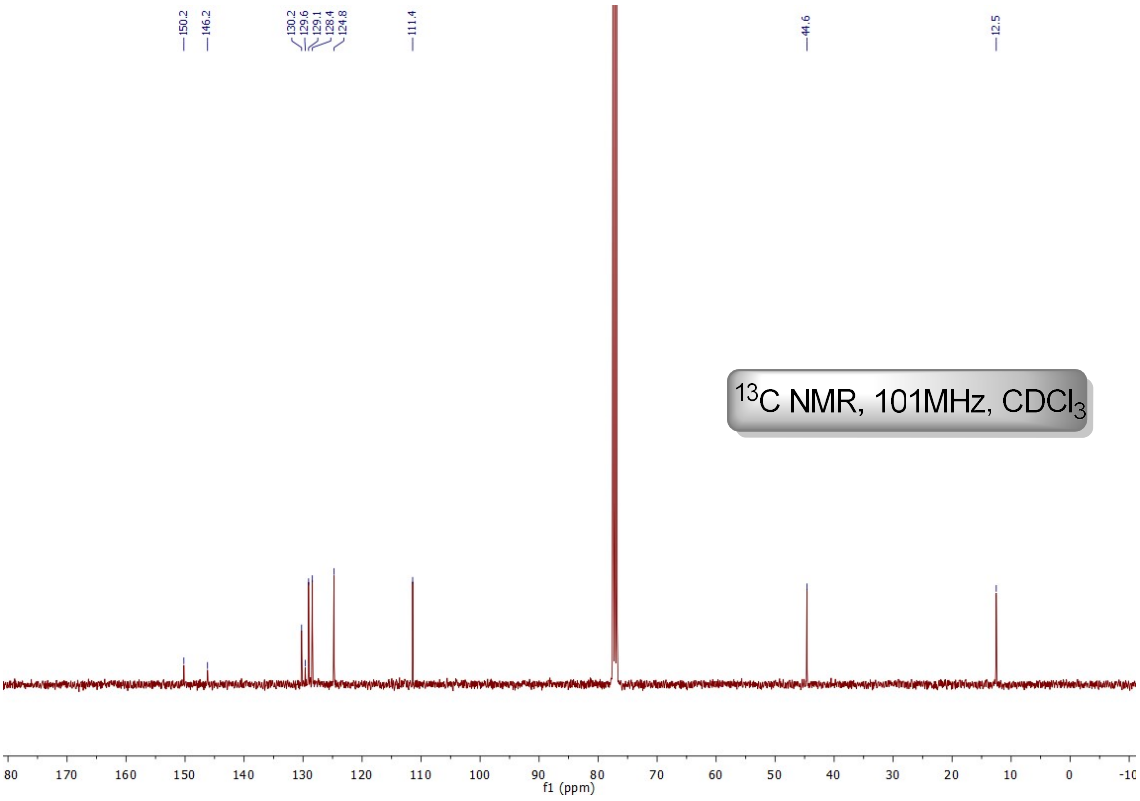
N,N-dimethyl-4-(pyridin-2-ylsulfinyl)aniline (3i)



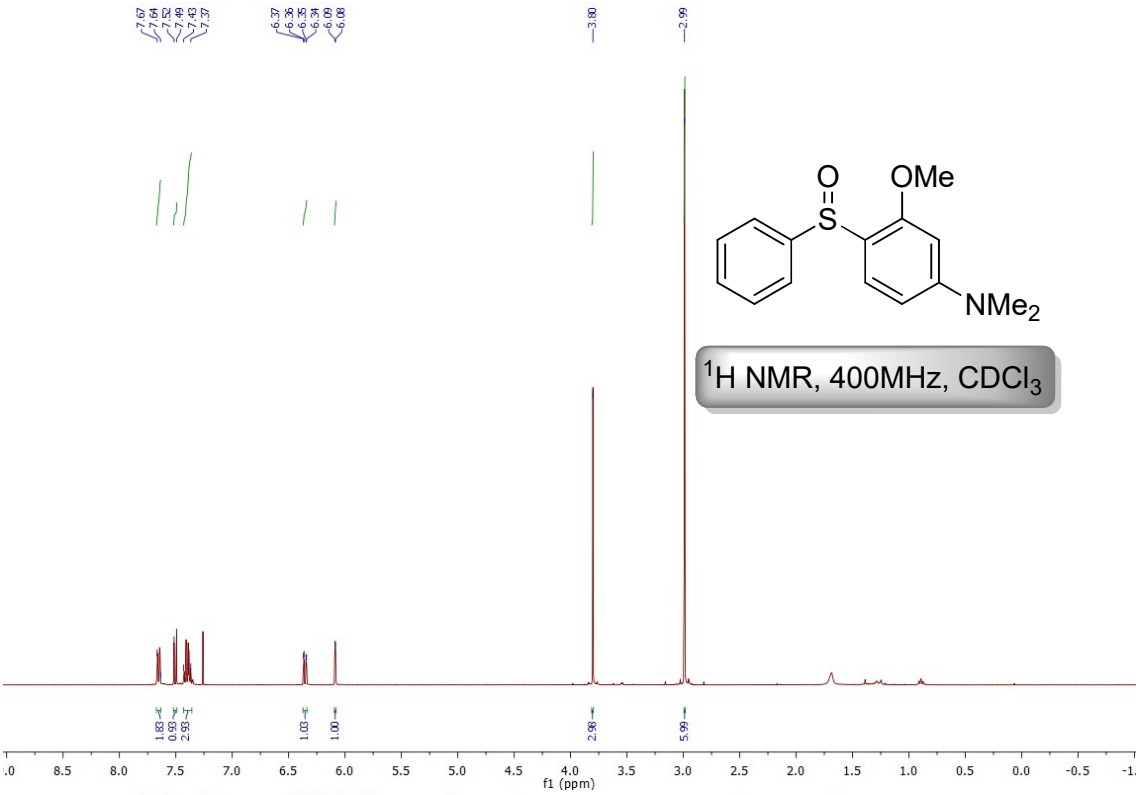


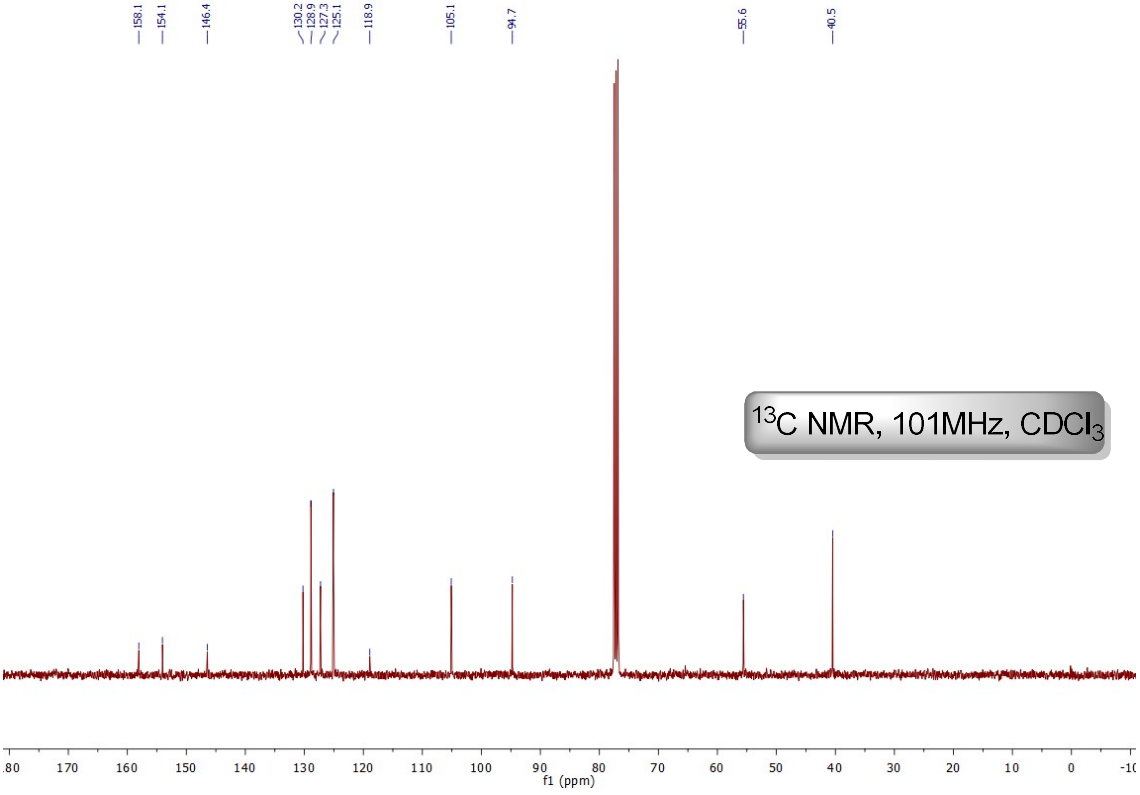
N,N-diethyl-4-(phenylsulfinyl)aniline (3j)



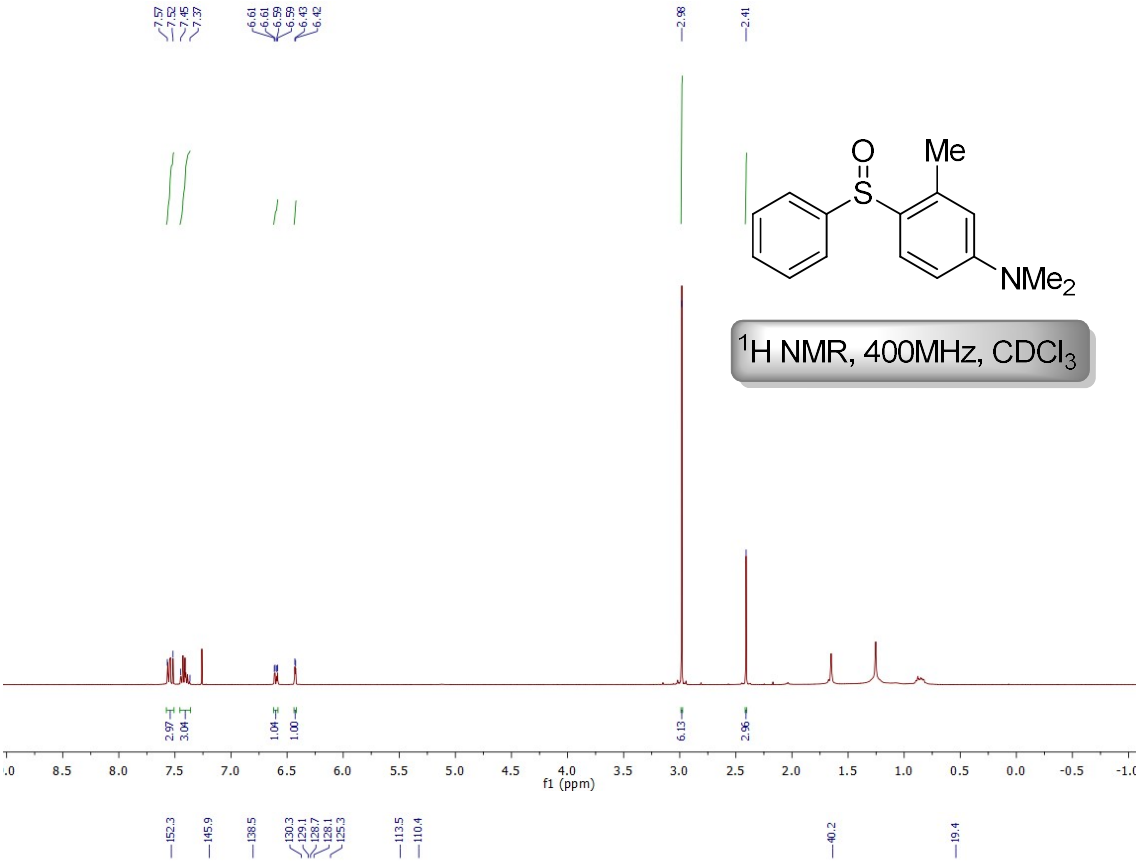


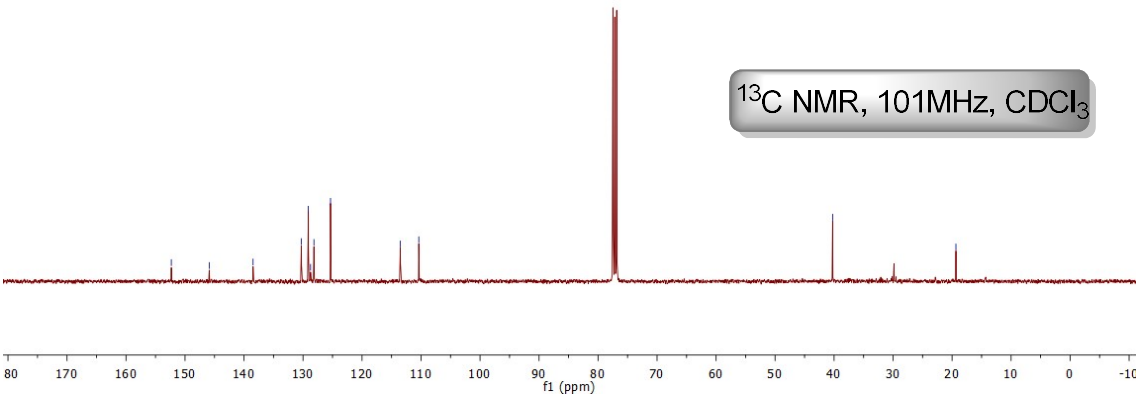
3-methoxy-*N,N*-dimethyl-4-(phenylsulfinyl)aniline (3k)



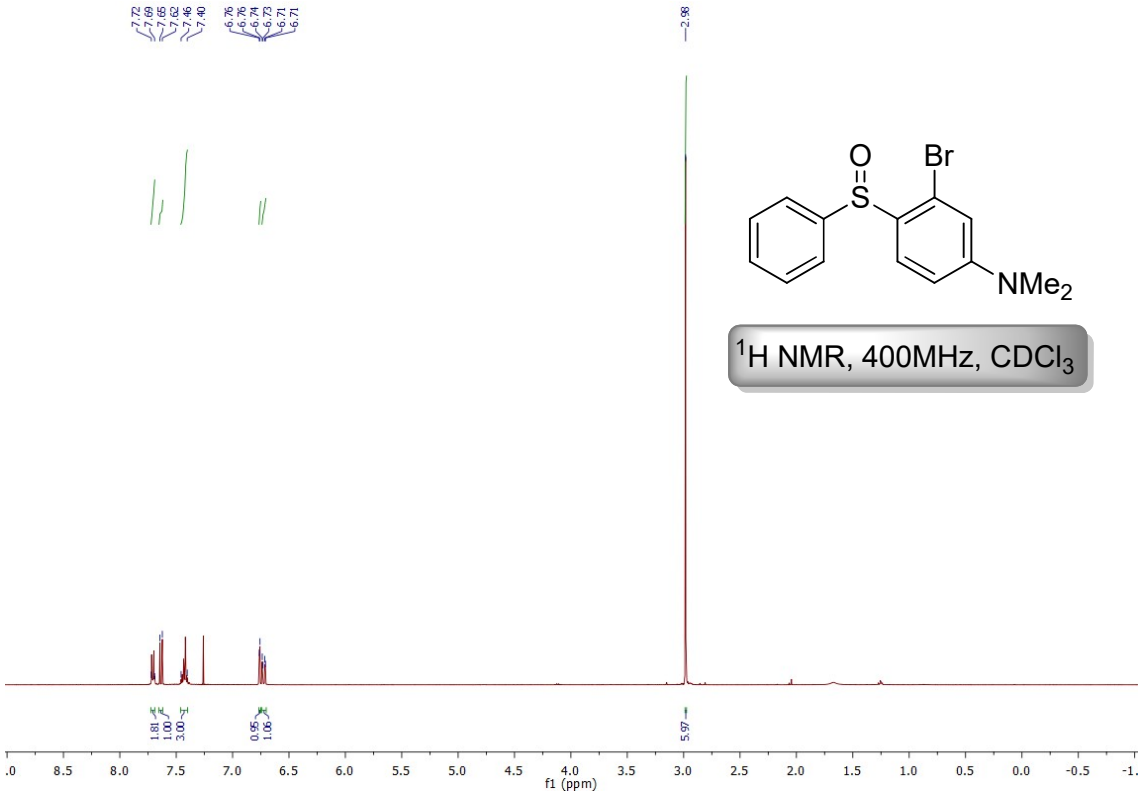


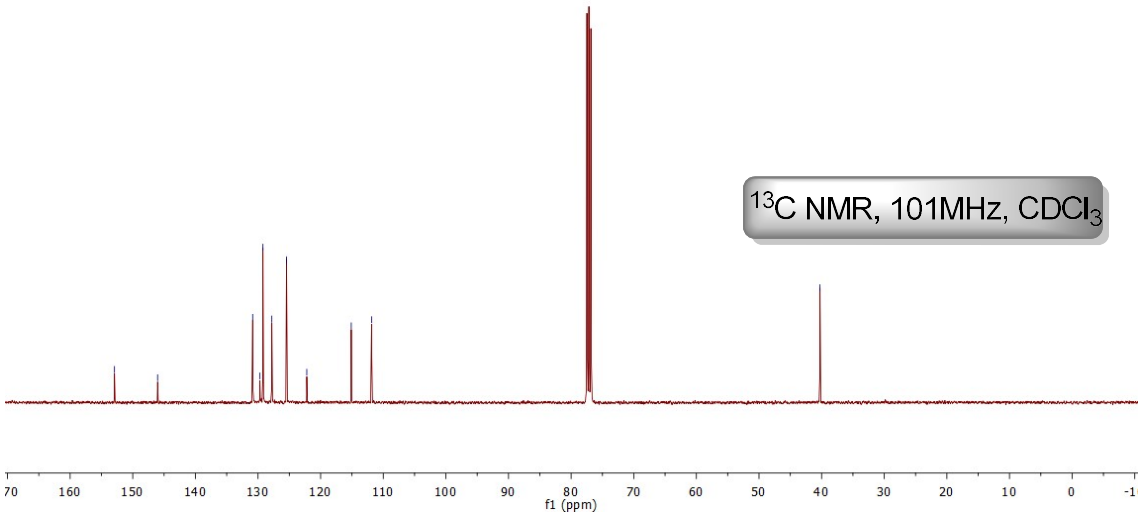
N,N,3-trimethyl-4-(phenylsulfinyl)aniline (3l)



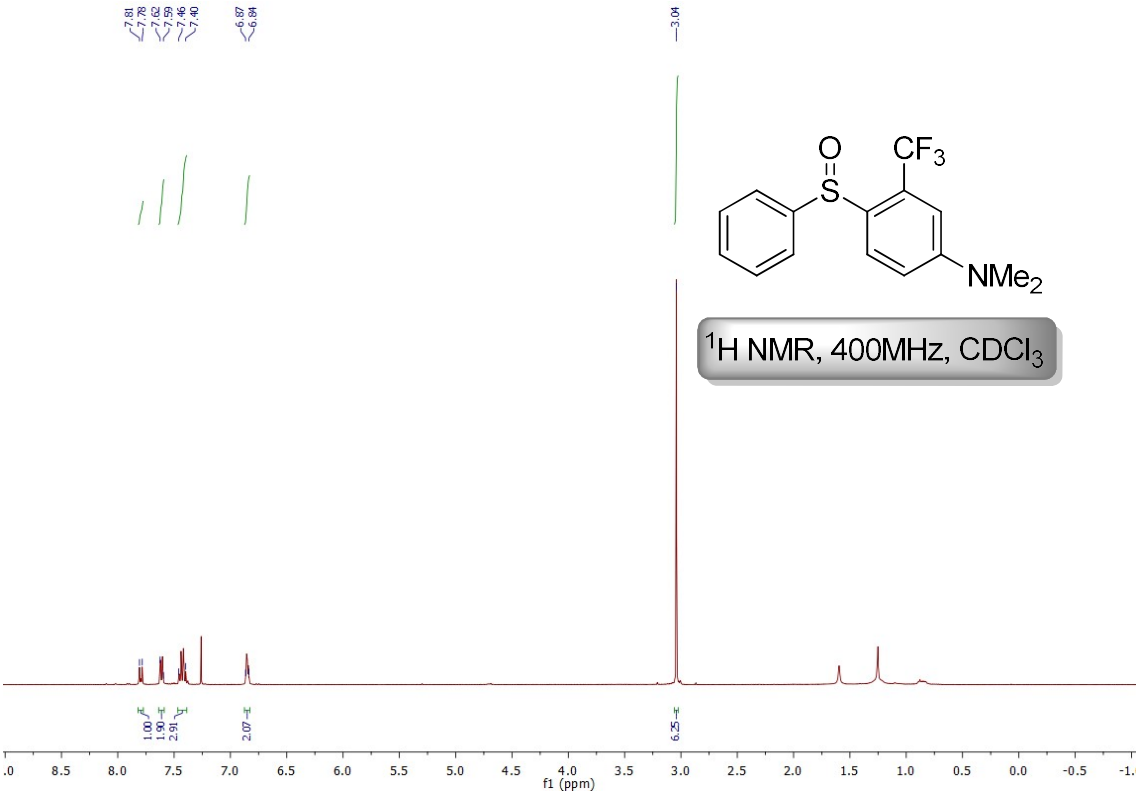


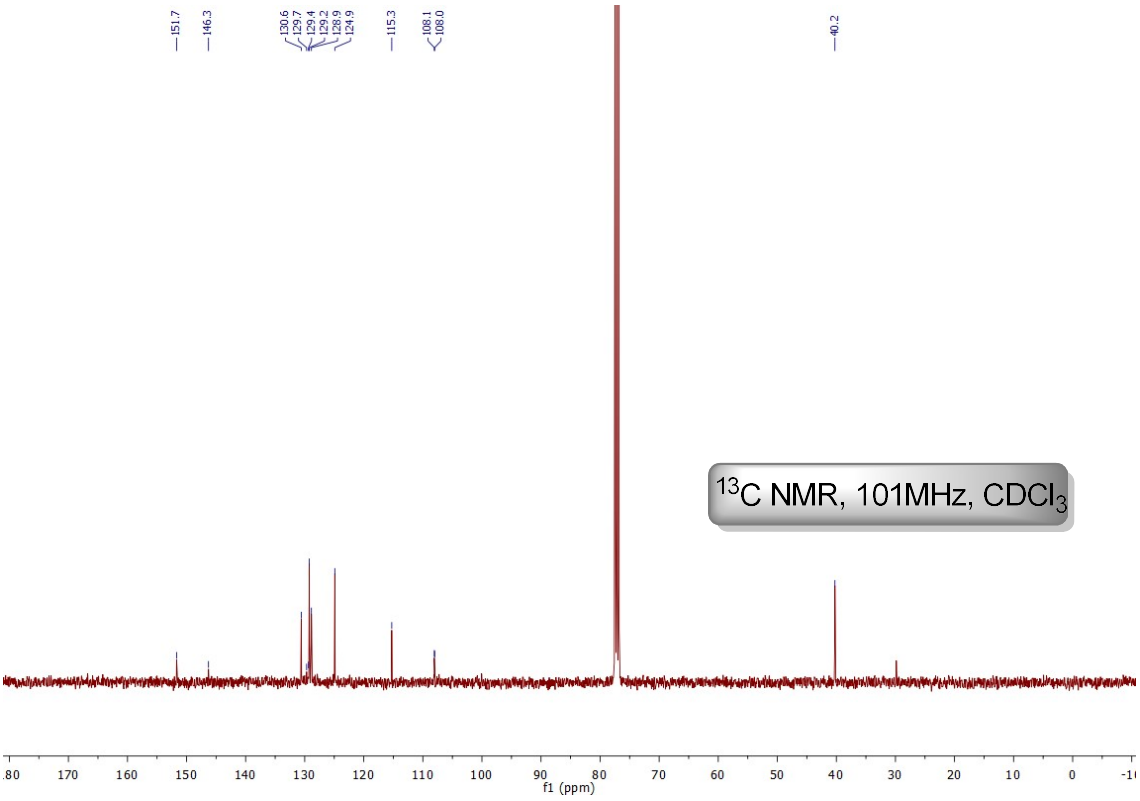
3-bromo-*N,N*-dimethyl-4-(phenylsulfinyl)aniline (3m)

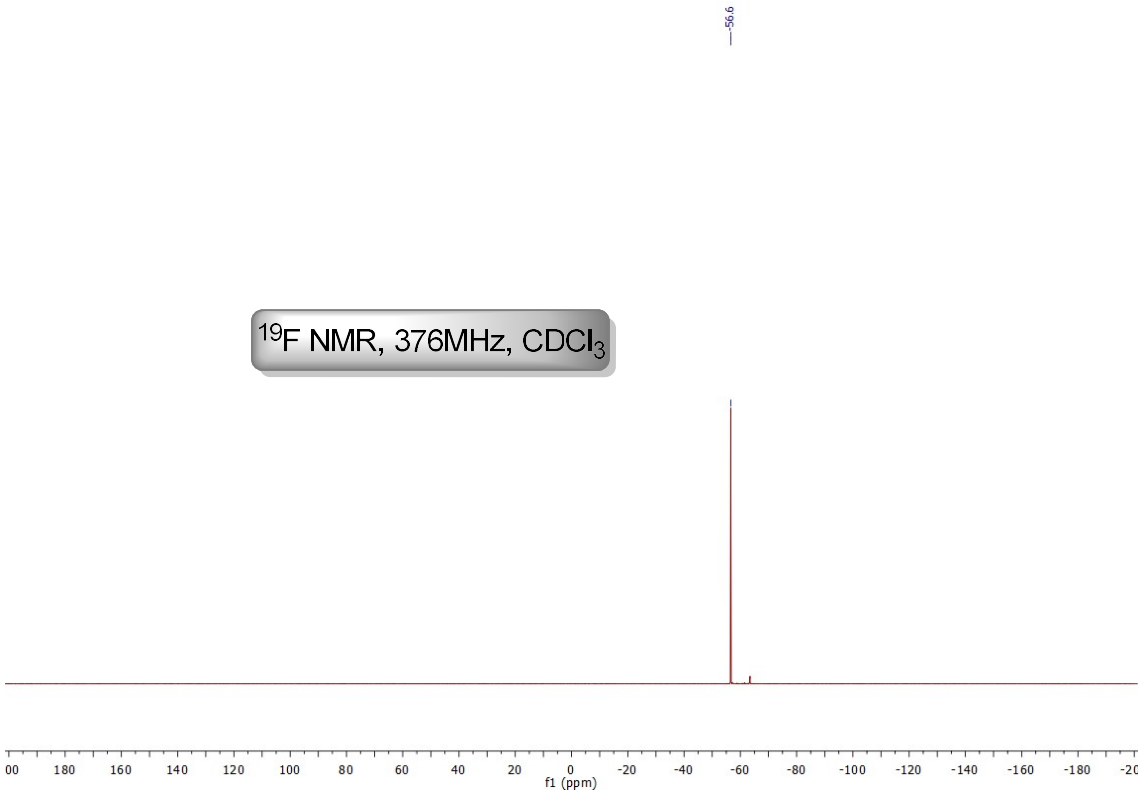




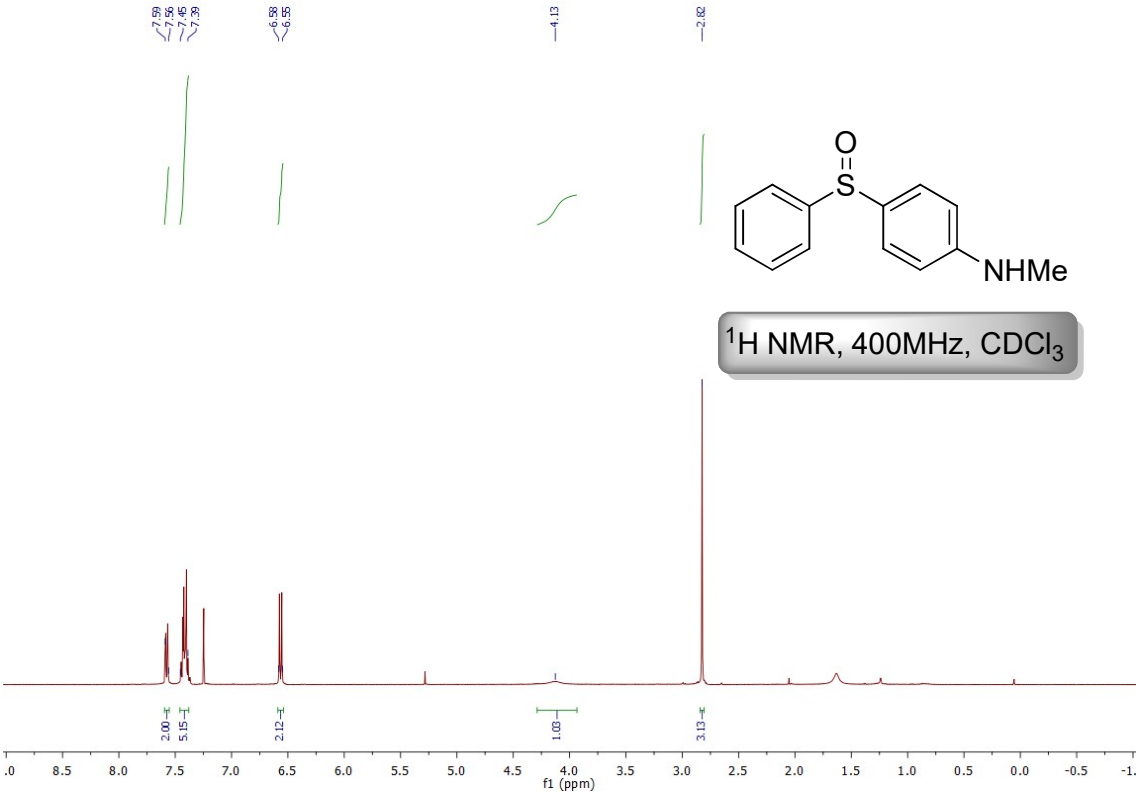
N,N-dimethyl-4-(phenylsulfinyl)-3-(trifluoromethyl)aniline (3n)

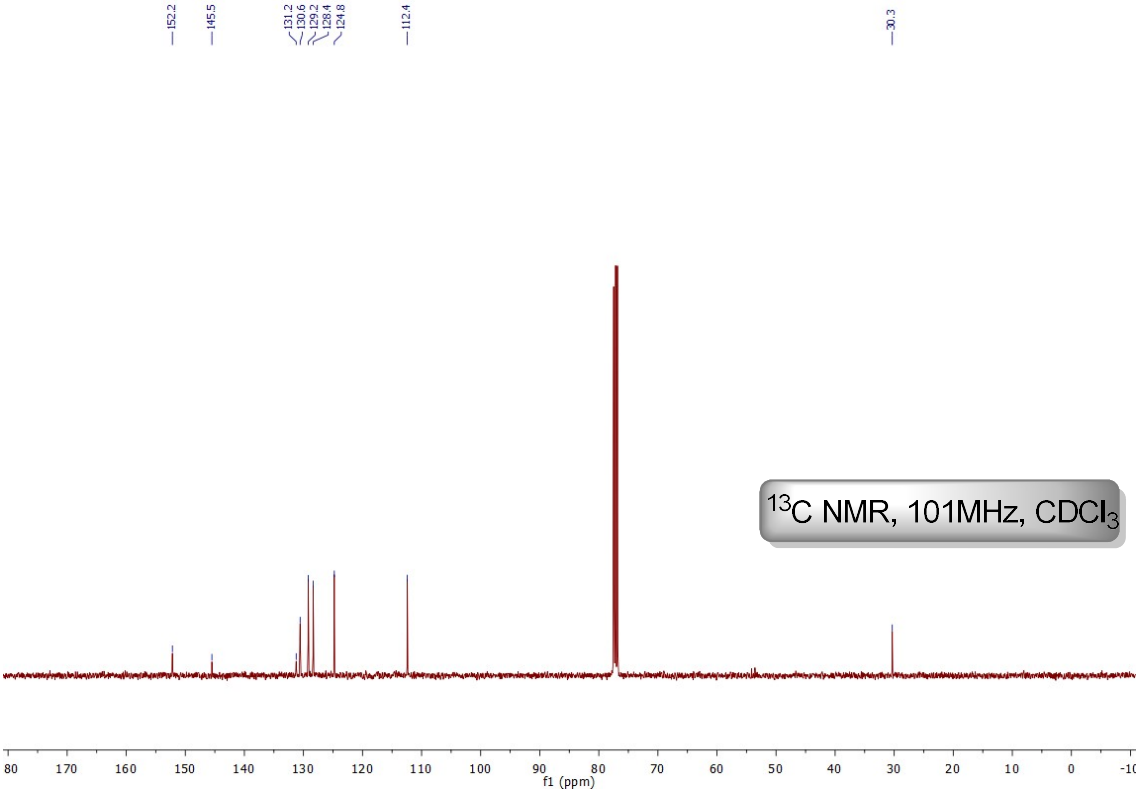




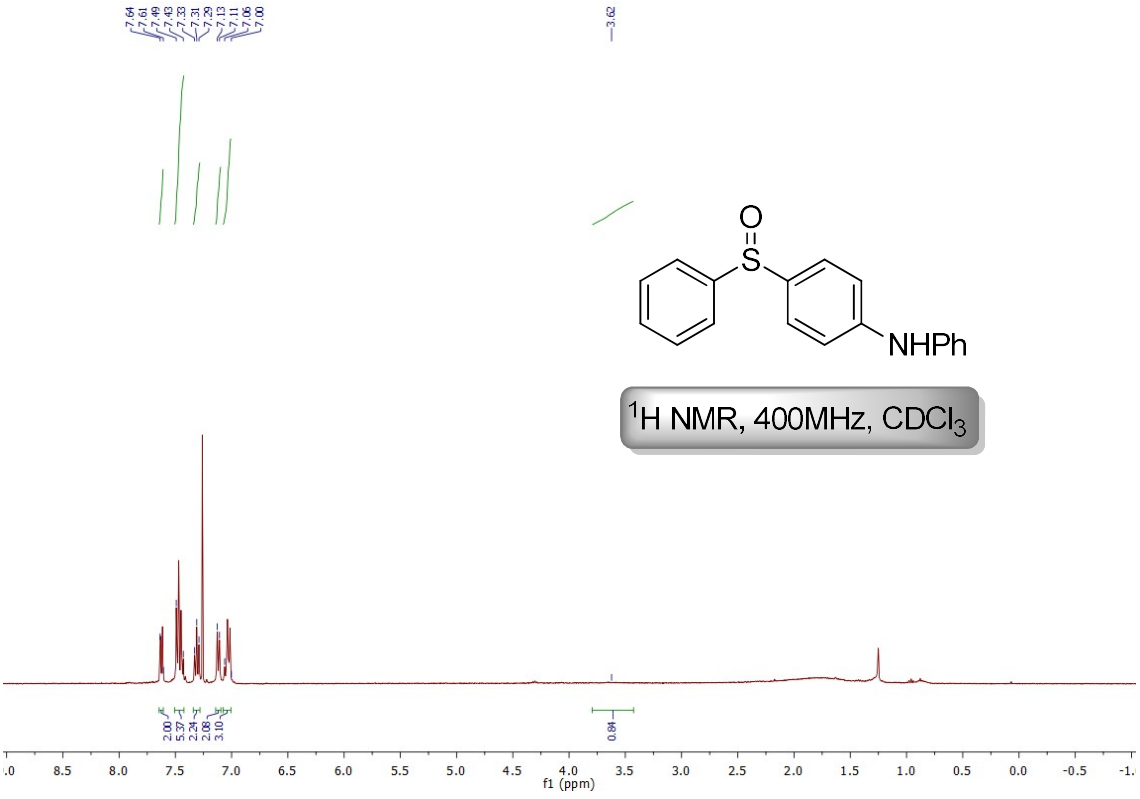

-56.6
^{19}F NMR, 376MHz, $CDCl_3$
00 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
f1 (ppm)

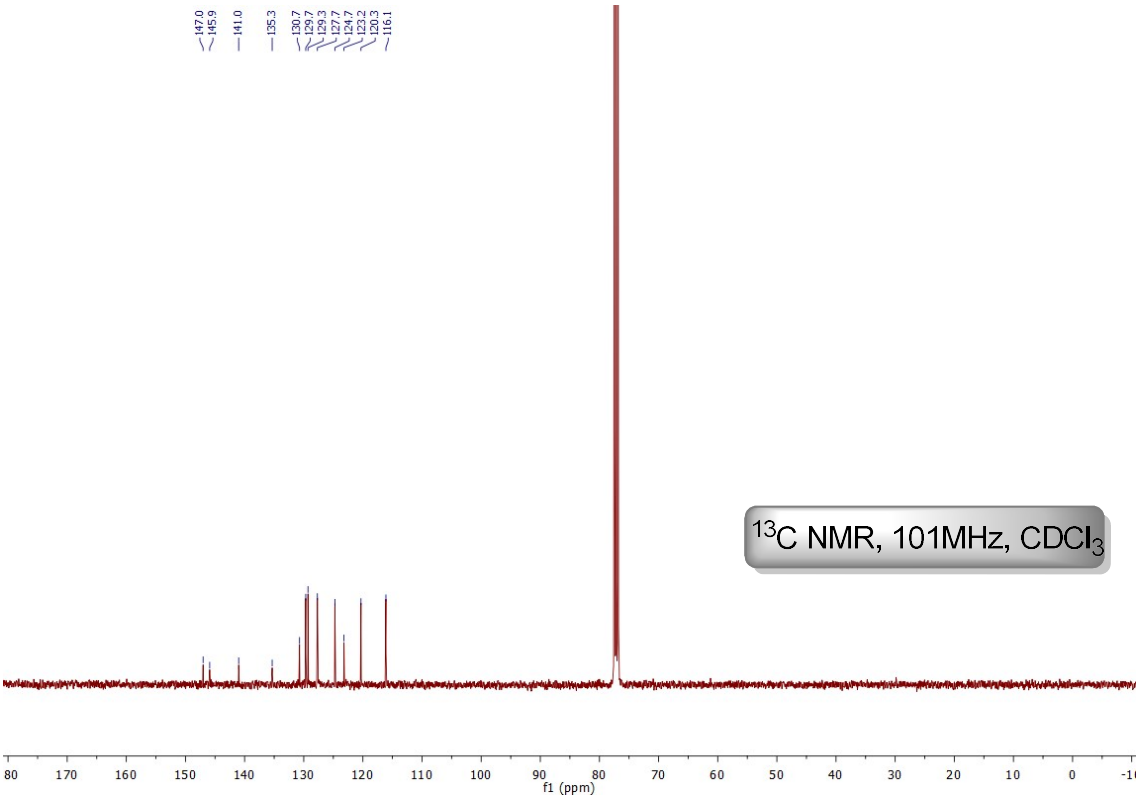
***N*-methyl-4-(phenylsulfinyl)aniline (3o)**



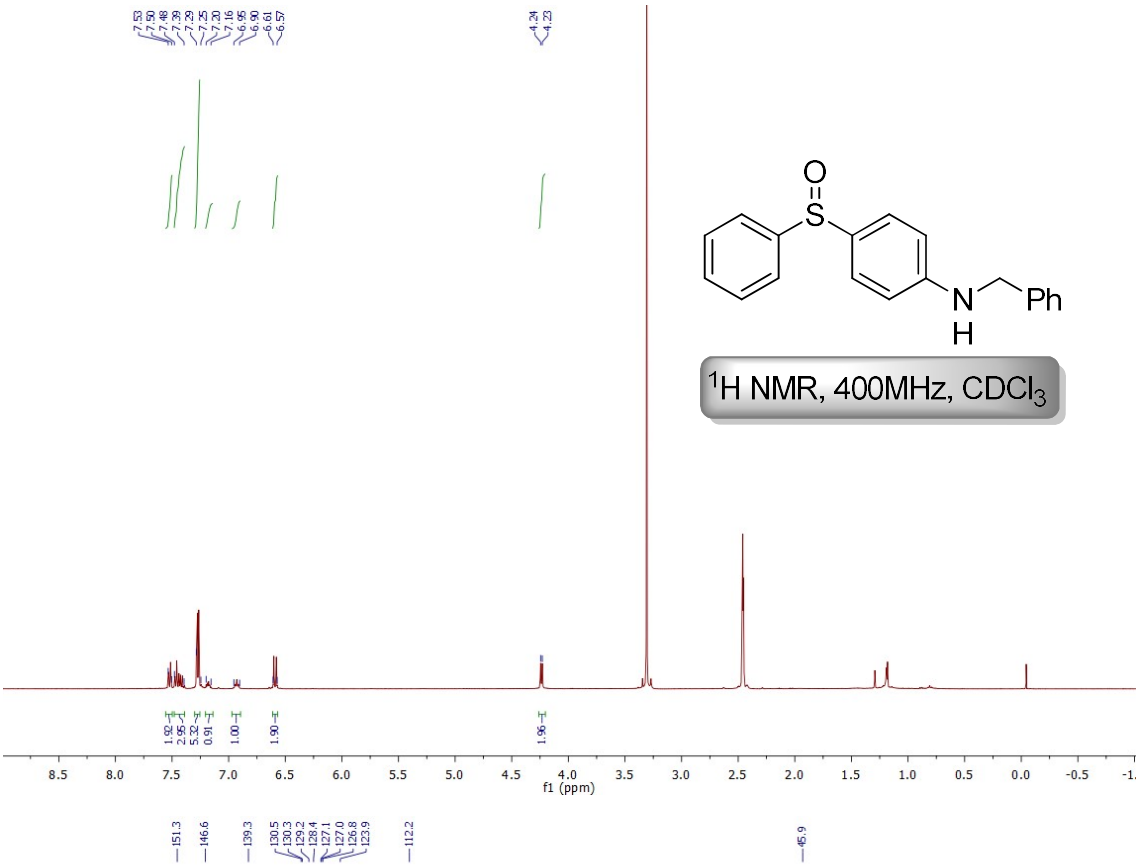


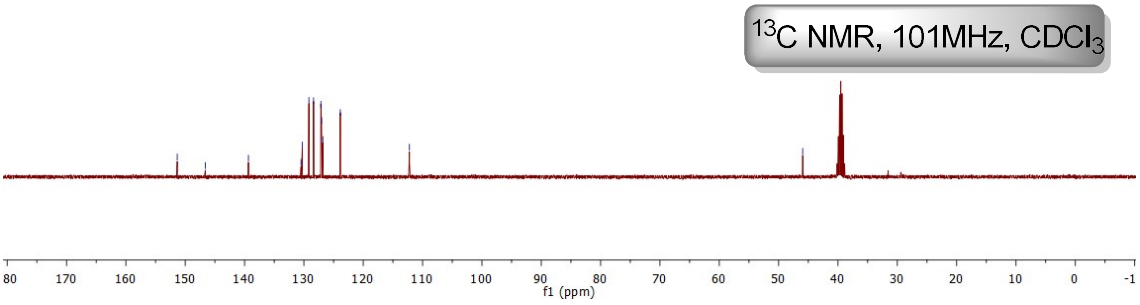
***N*-phenyl-4-(phenylsulfinyl)aniline (3p)**



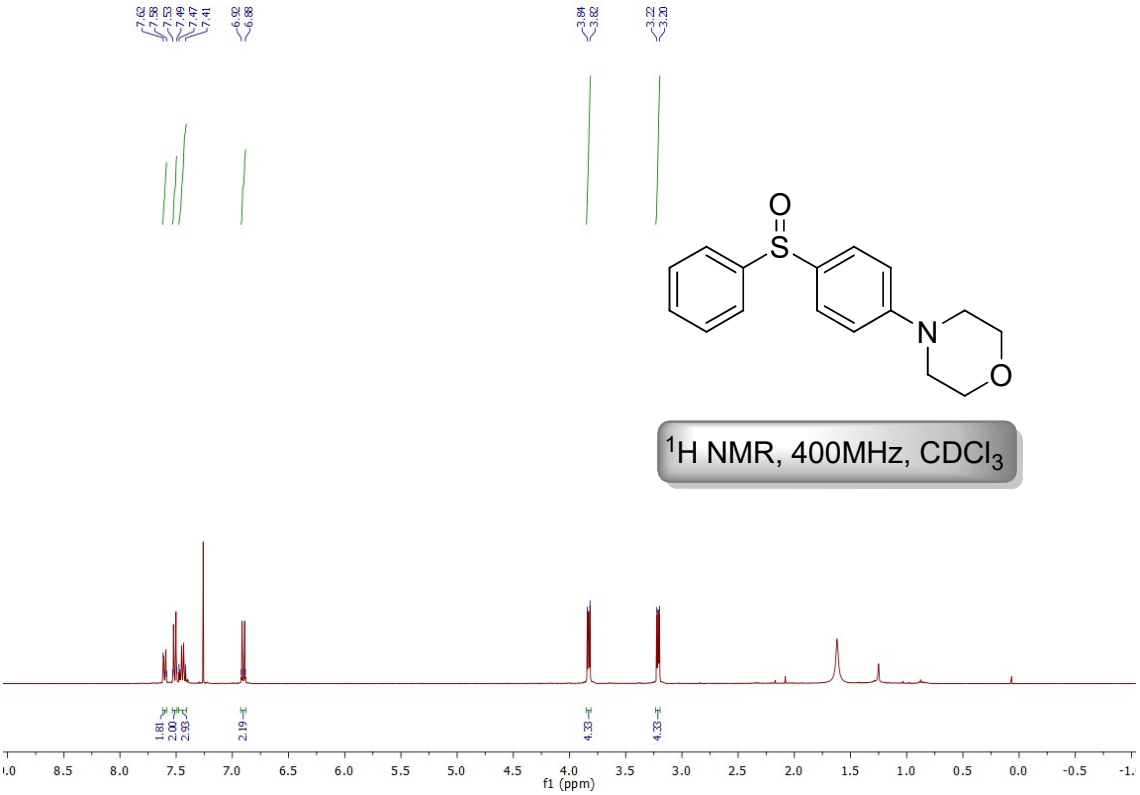


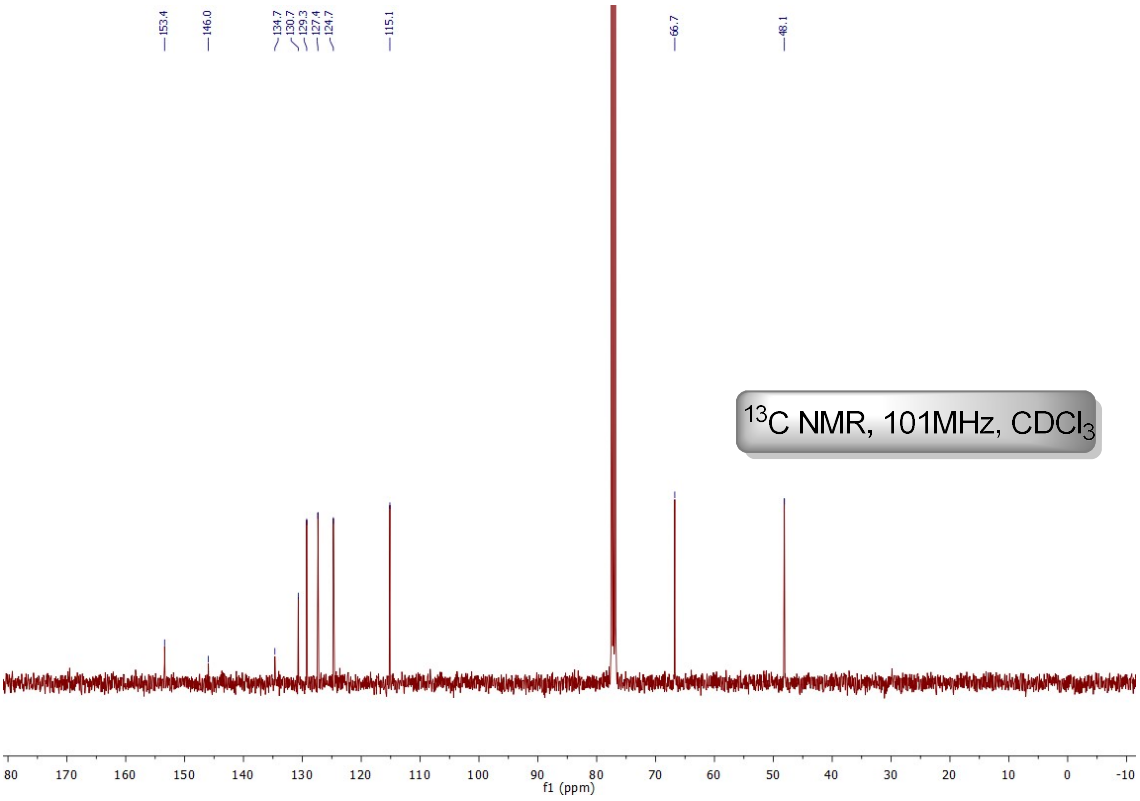
N-benzyl-4-(phenylsulfinyl)aniline (3q)



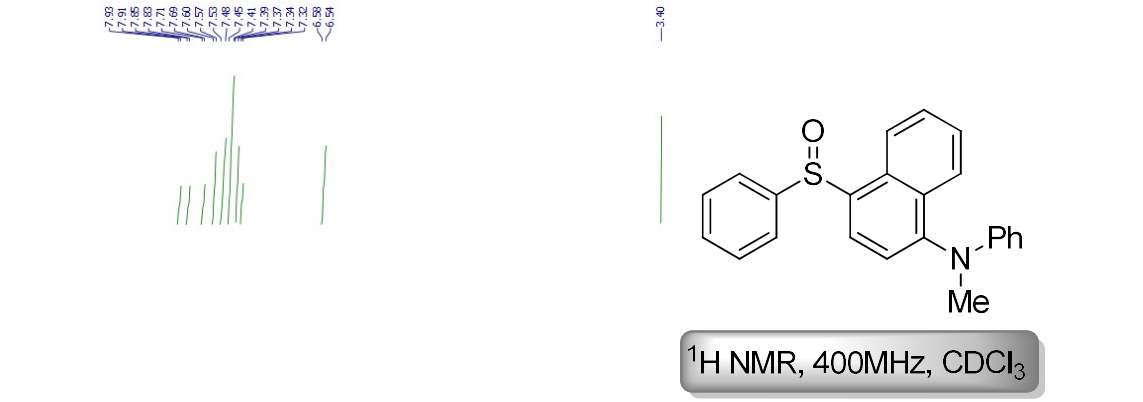


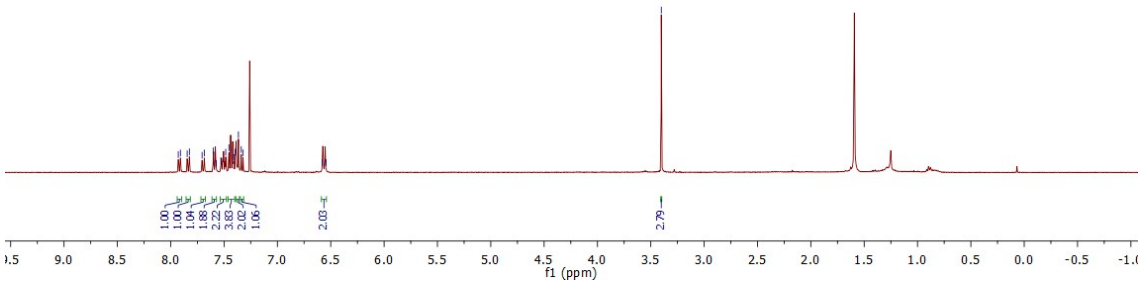
4-(4-(phenylsulfinyl)phenyl)morpholine (3r)

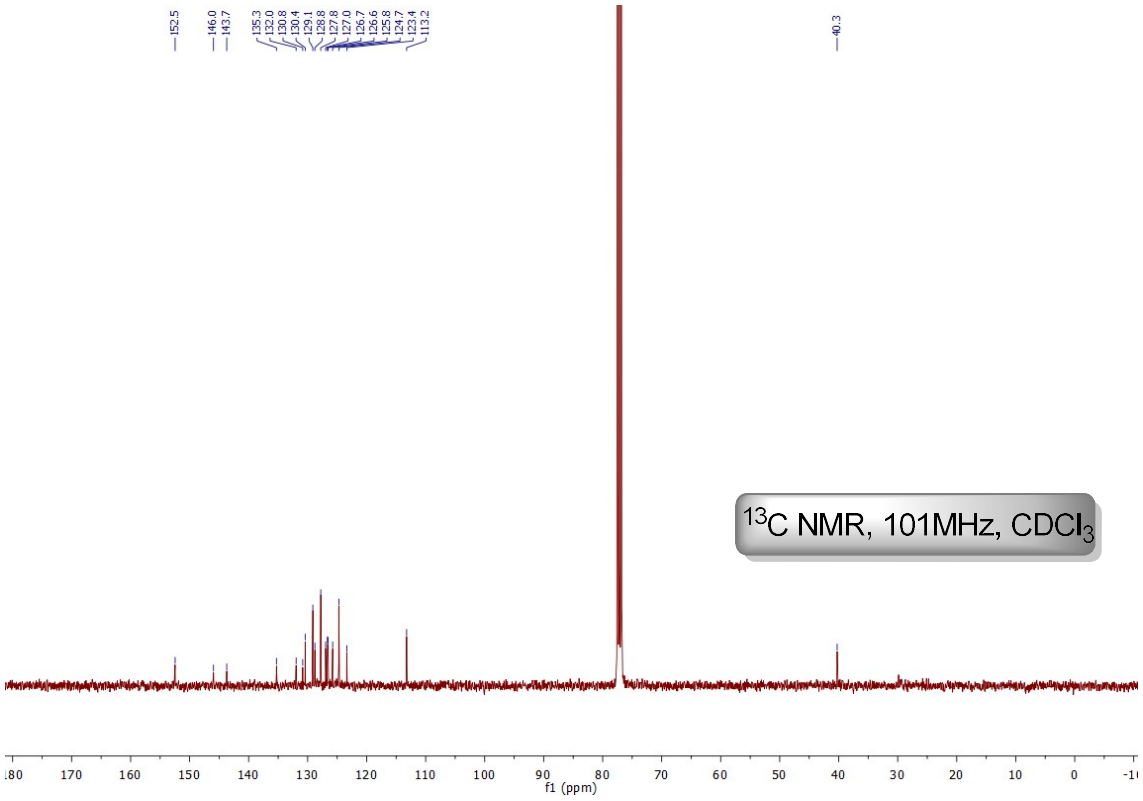




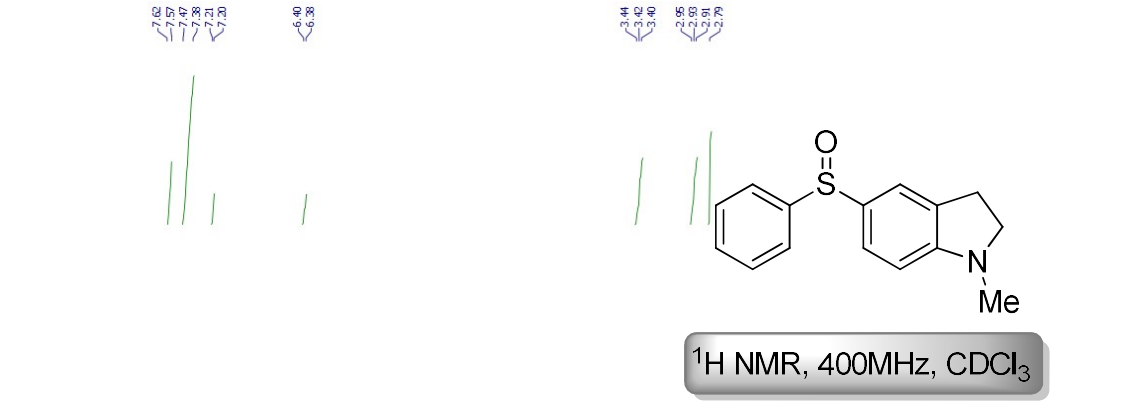
***N*-methyl-*N*-phenyl-4-(phenylsulfinyl)naphthalen-1-amine (3s)**



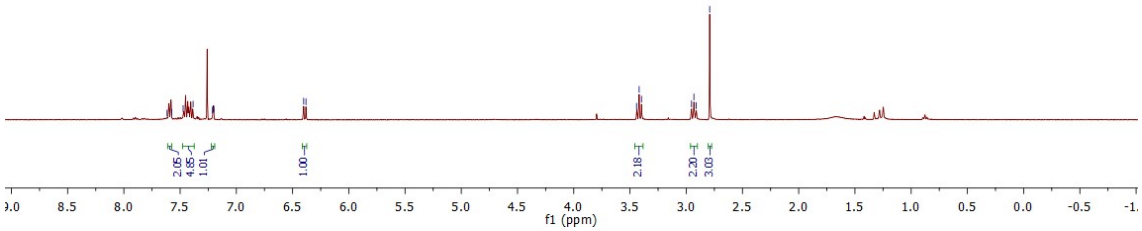


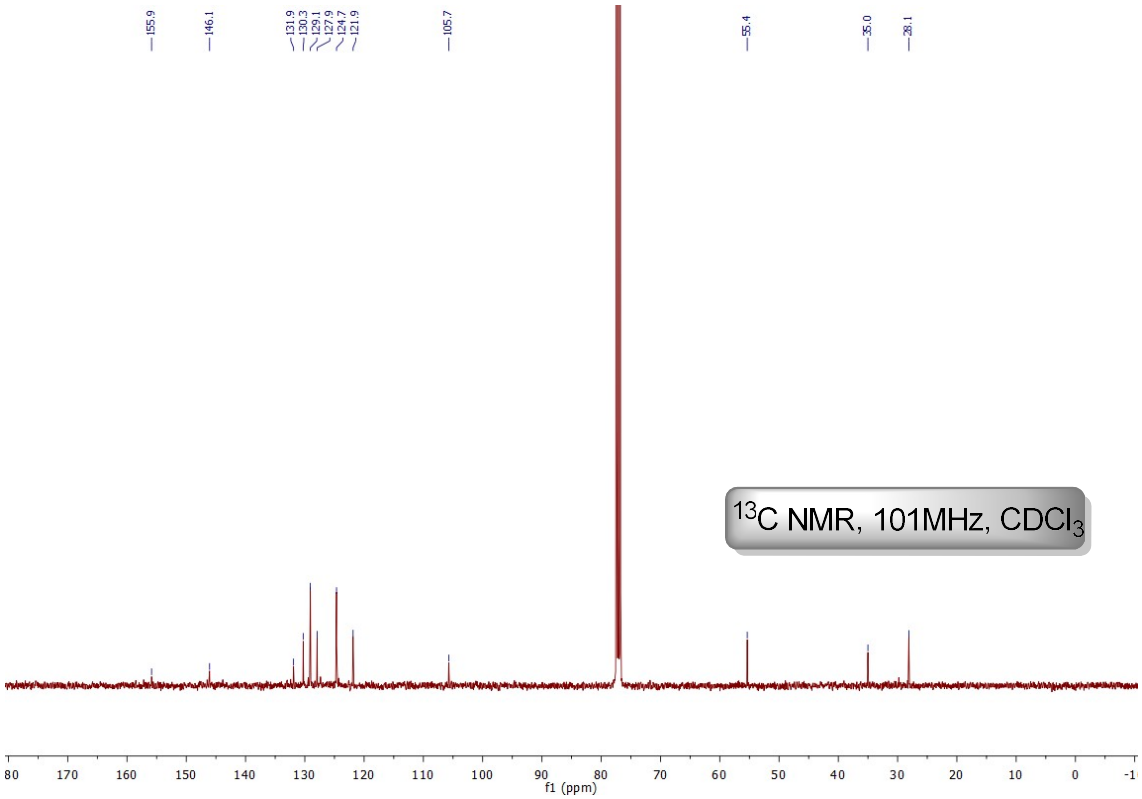


1-methyl-5-(phenylsulfinyl)indoline (3t)



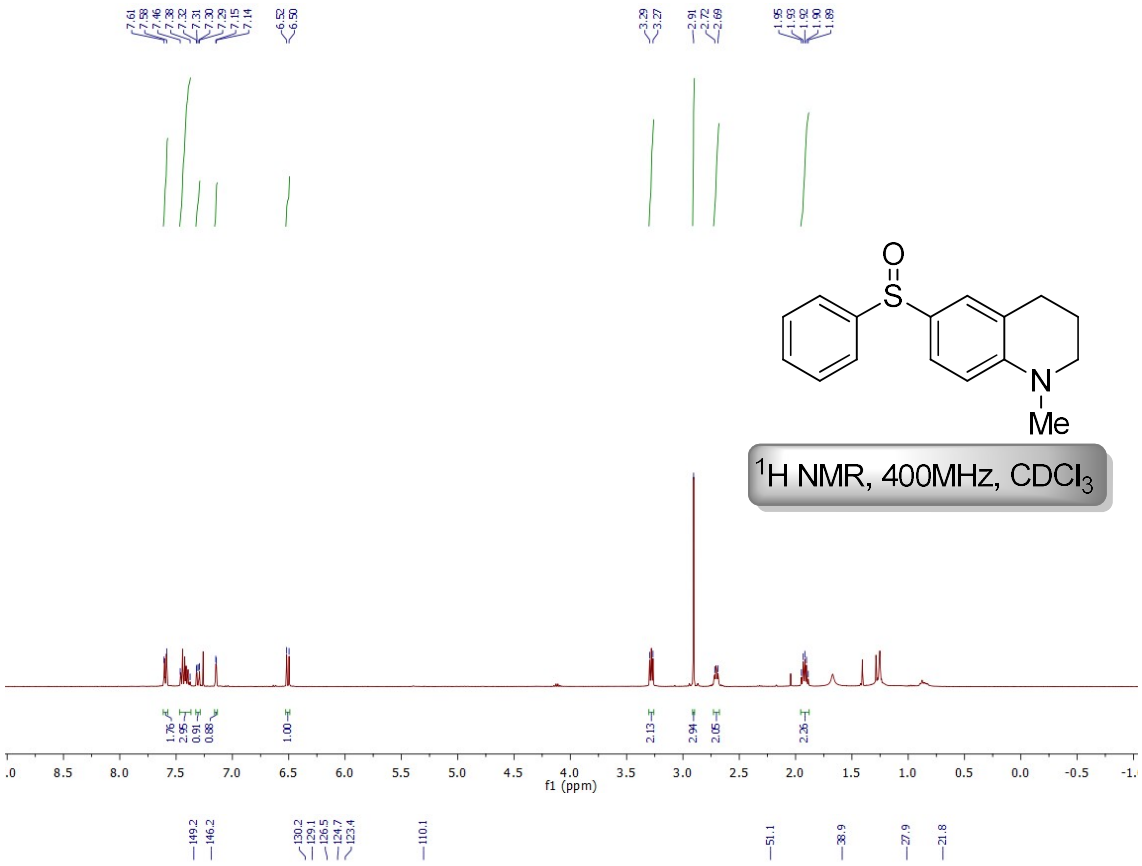
^{1}H NMR, 400MHz, $CDCl_3$

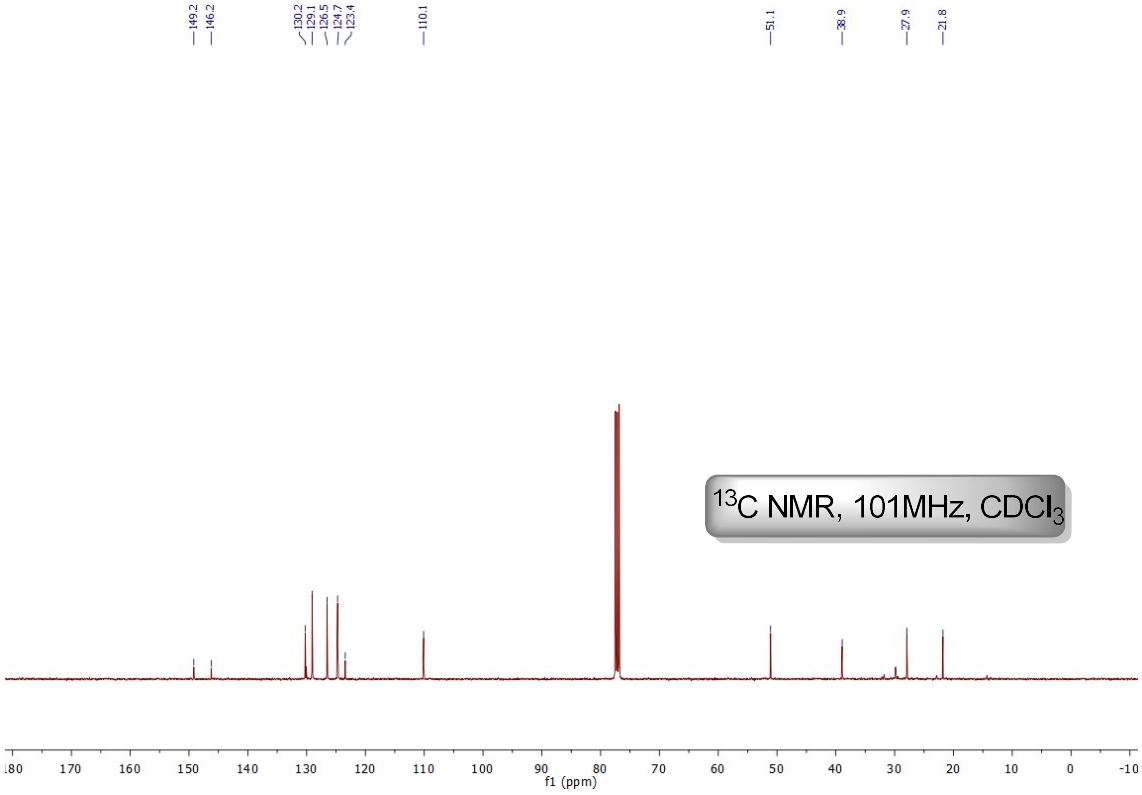




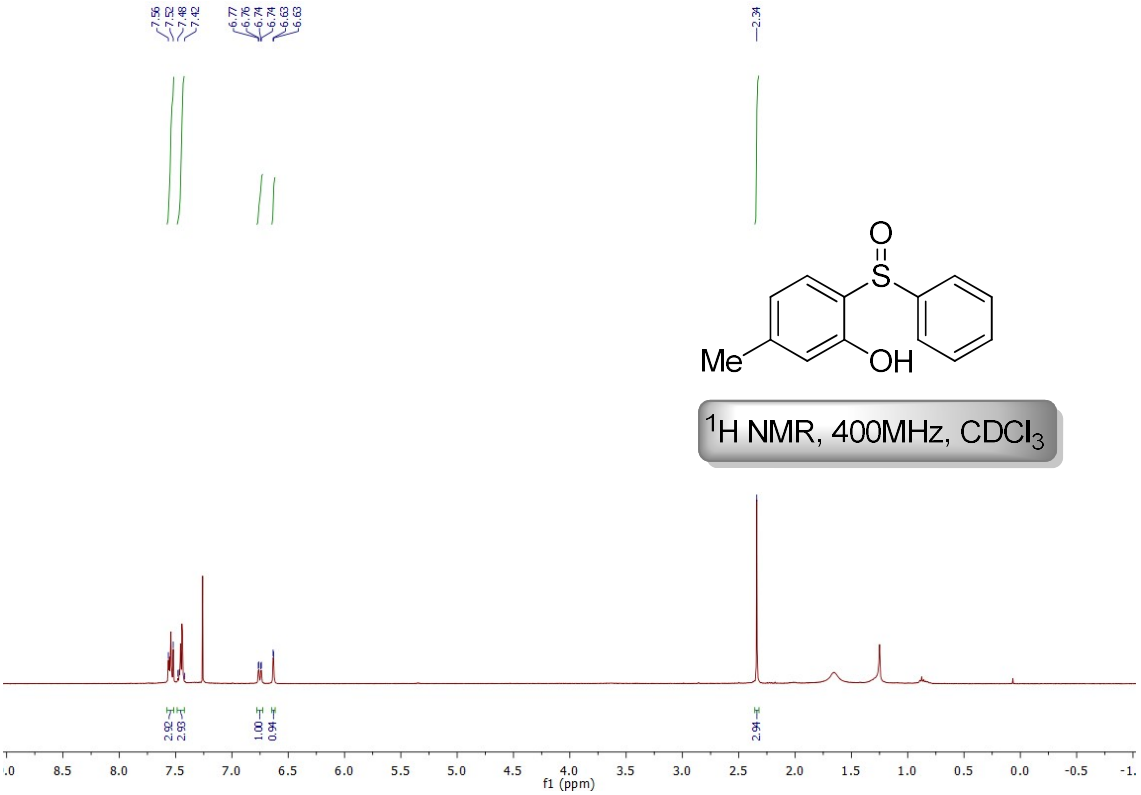
^{13}C NMR, 101MHz, $CDCl_3$

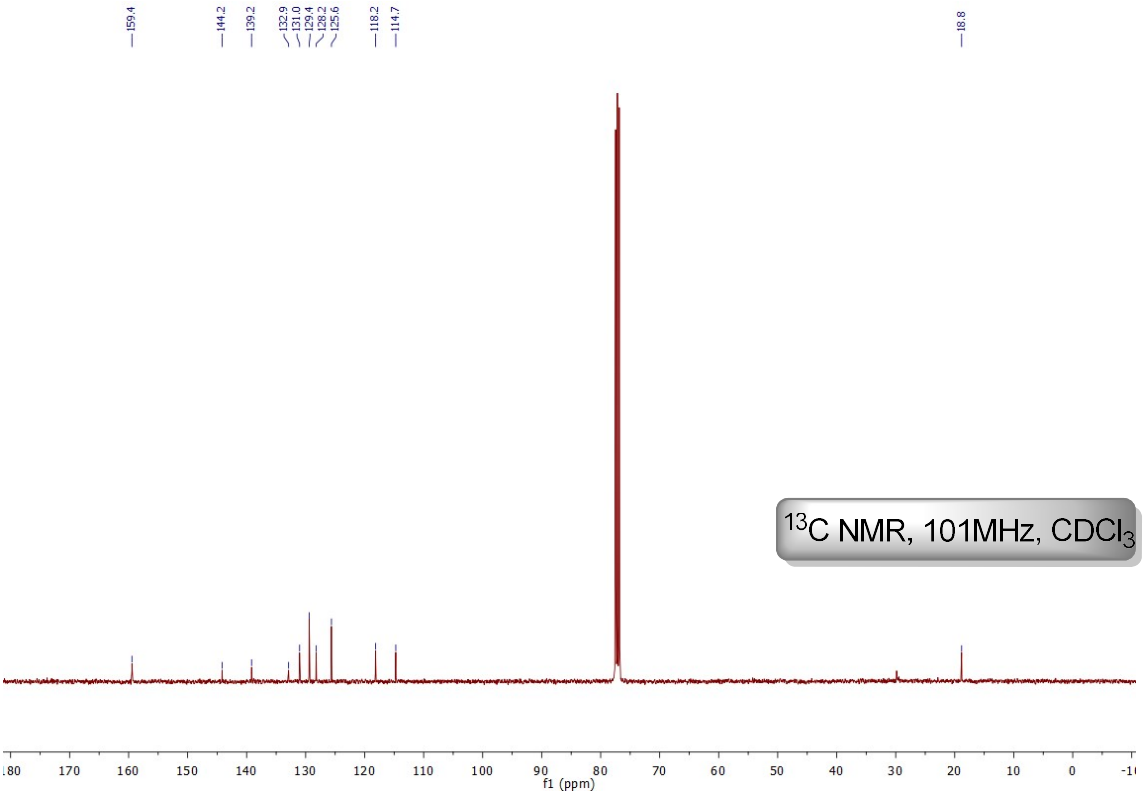
1-methyl-6-(phenylsulfinyl)-1,2,3,4-tetrahydroquinoline (3u)



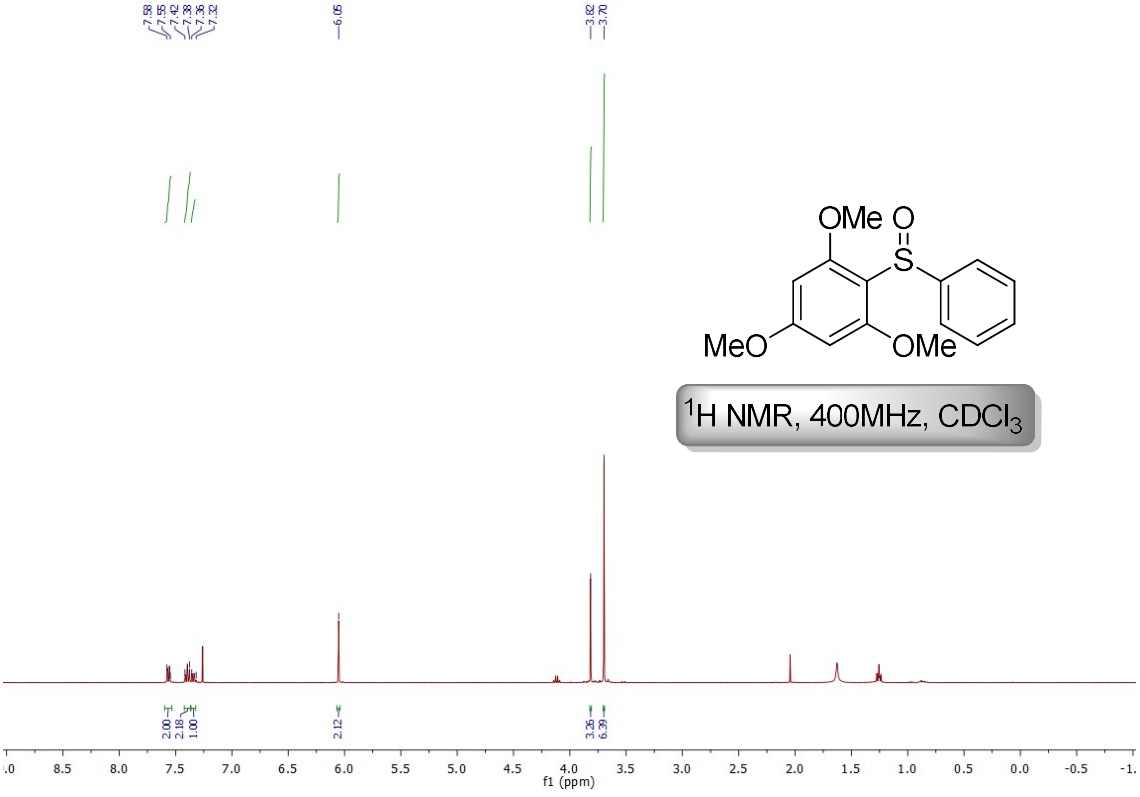


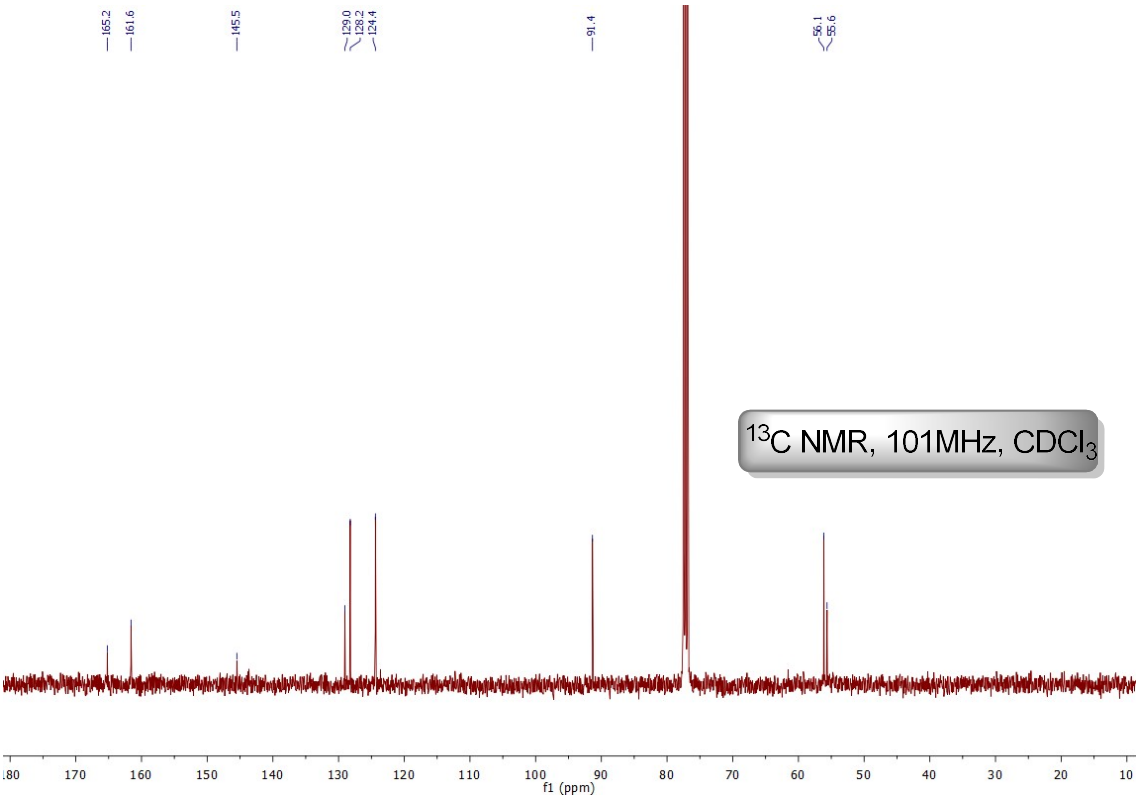
3-methyl-2-(phenylsulfinyl)phenol (3v)



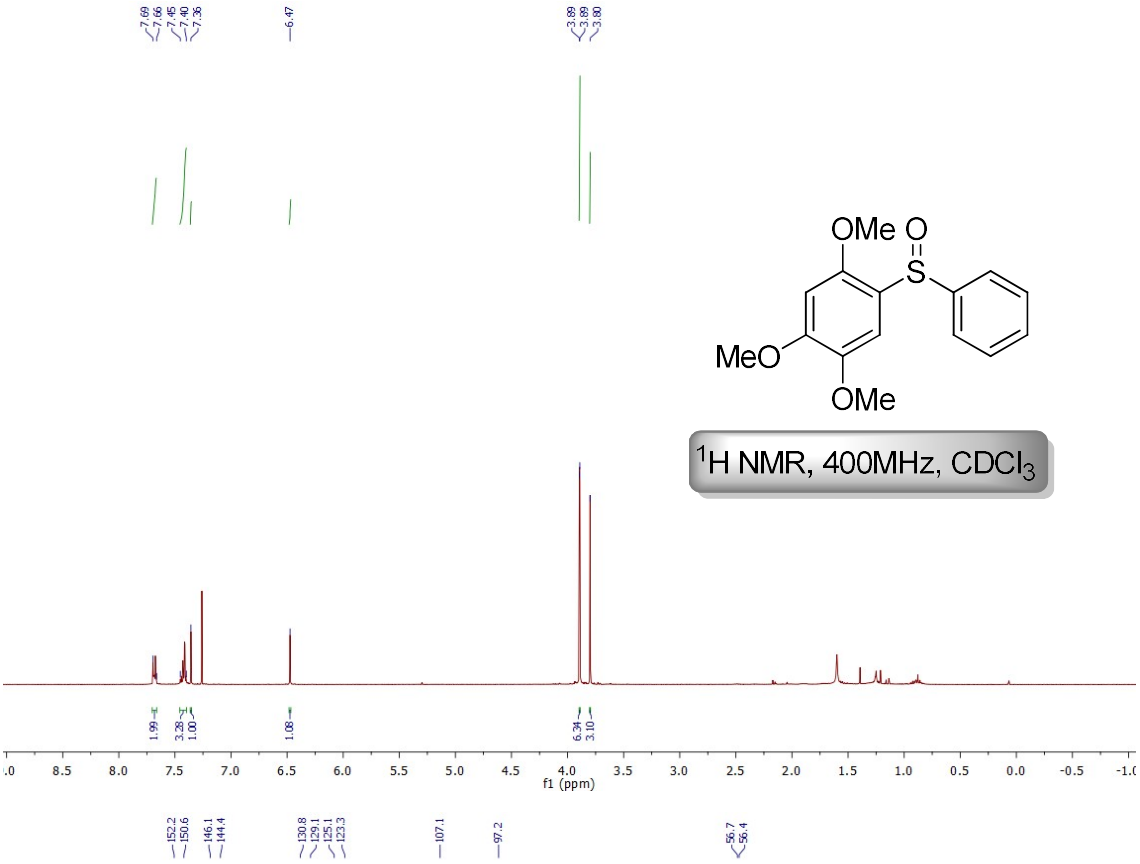


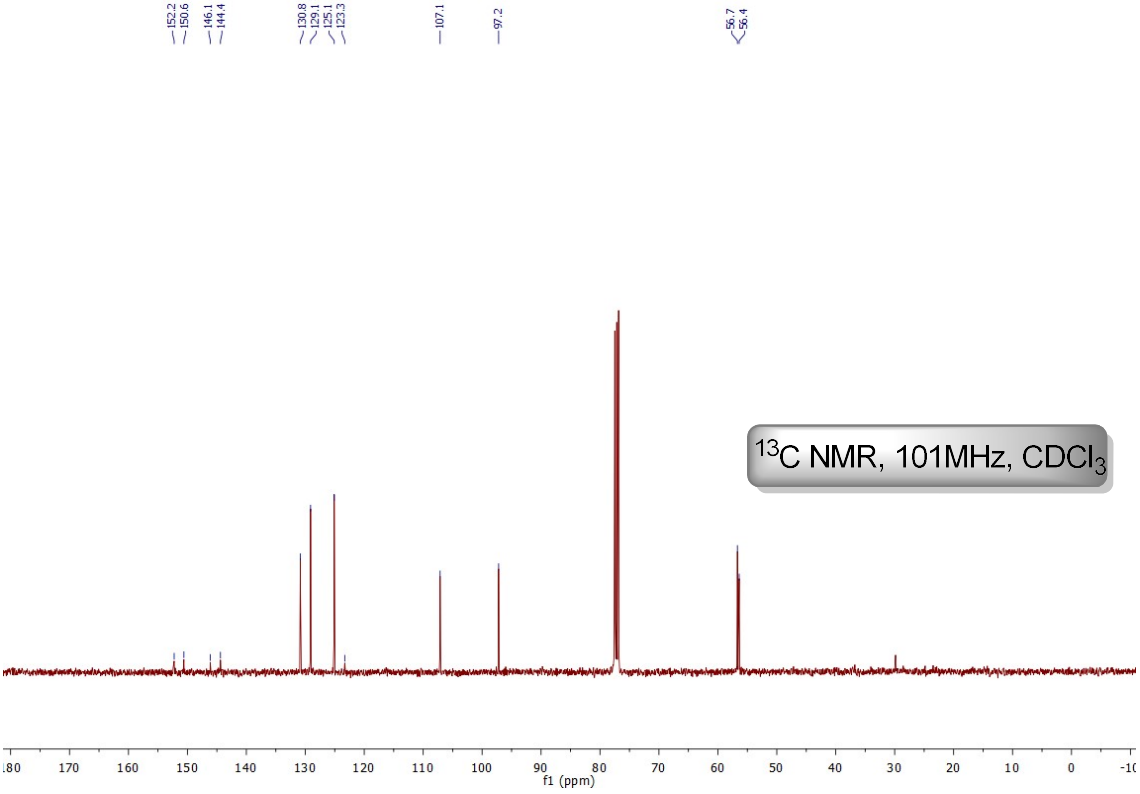
1,3,5-trimethoxy-2-(phenylsulfinyl)benzene (3w)



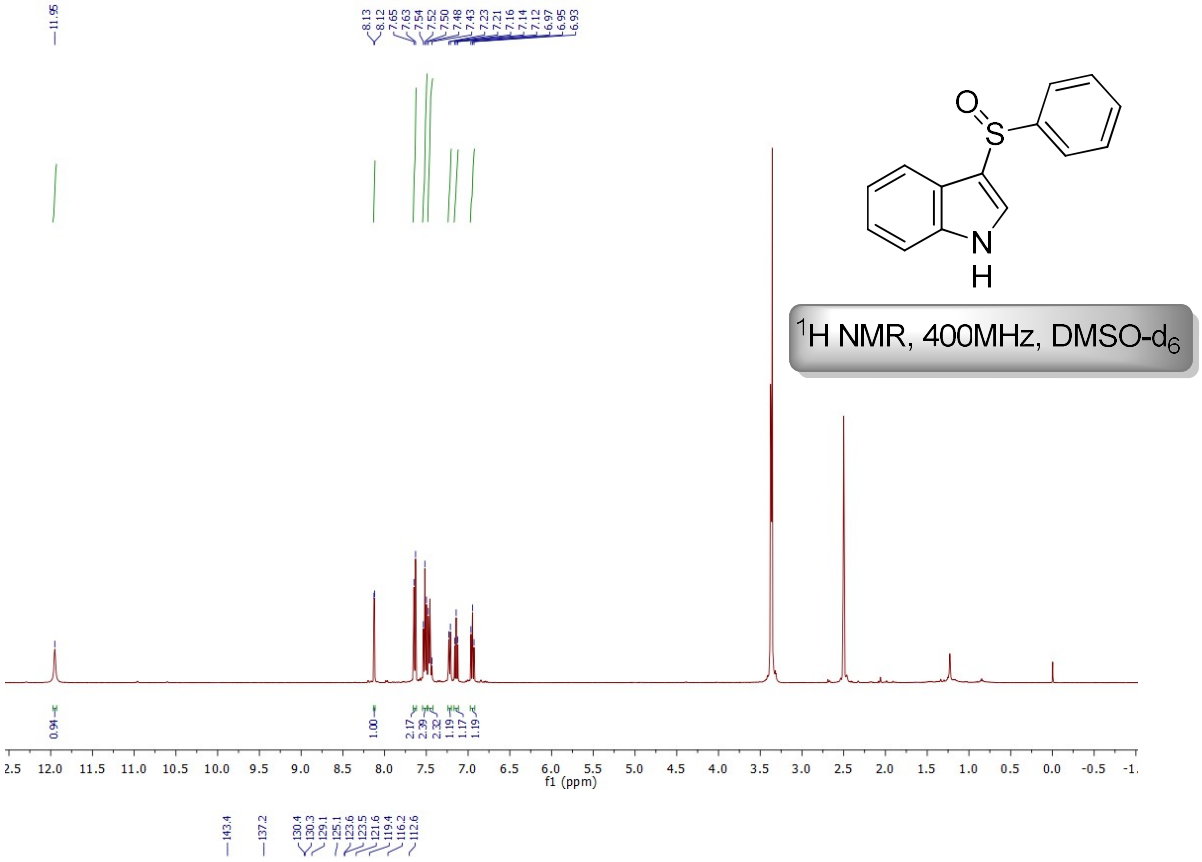


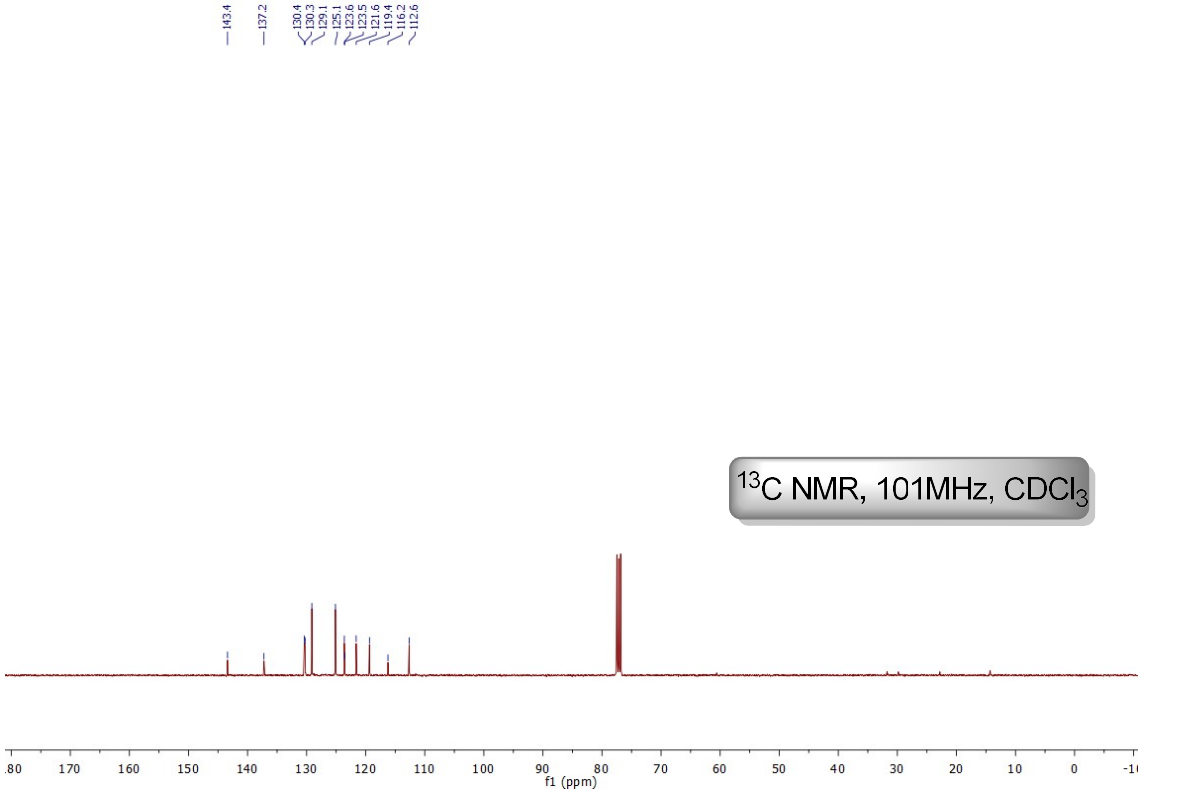
1,2,4-trimethoxy-5-(phenylsulfinyl)benzene (3x)



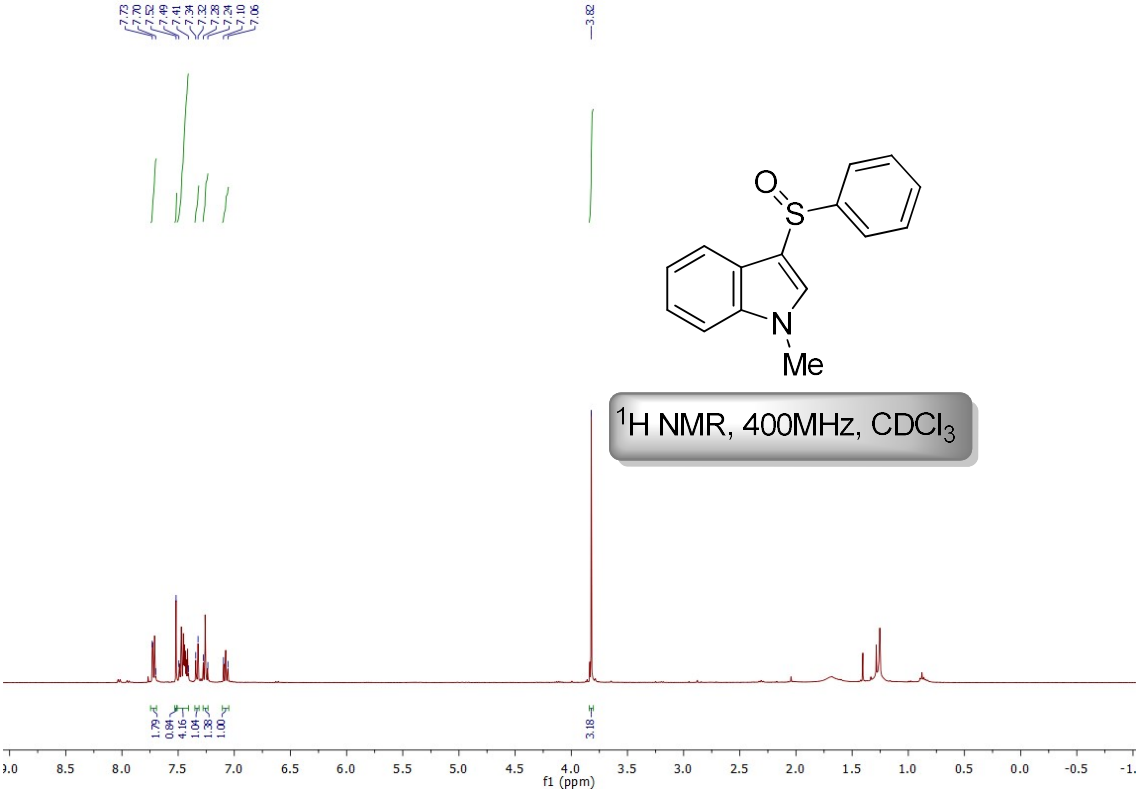


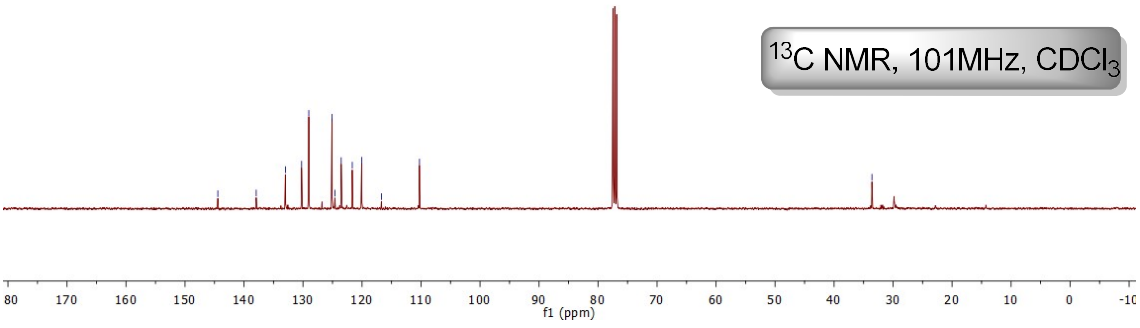
3-(phenylsulfinyl)-1*H*-indole (3y)



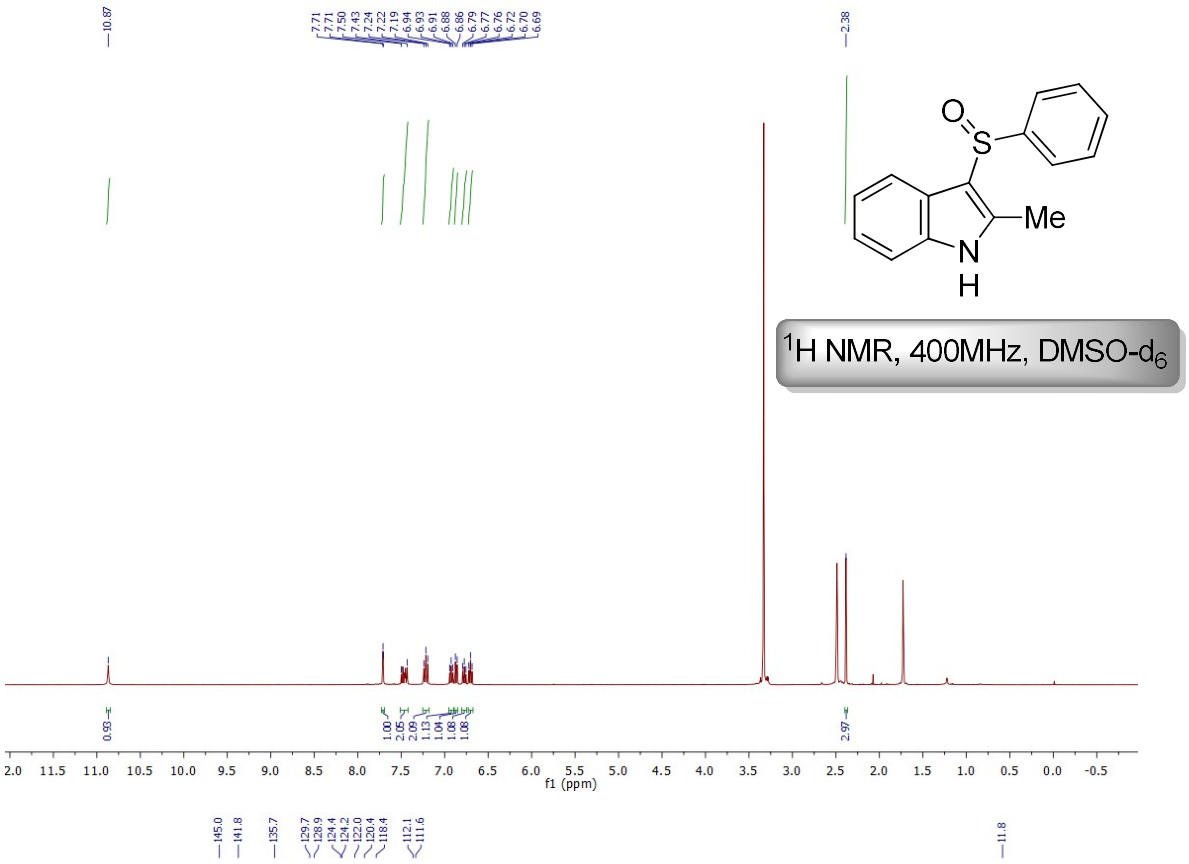


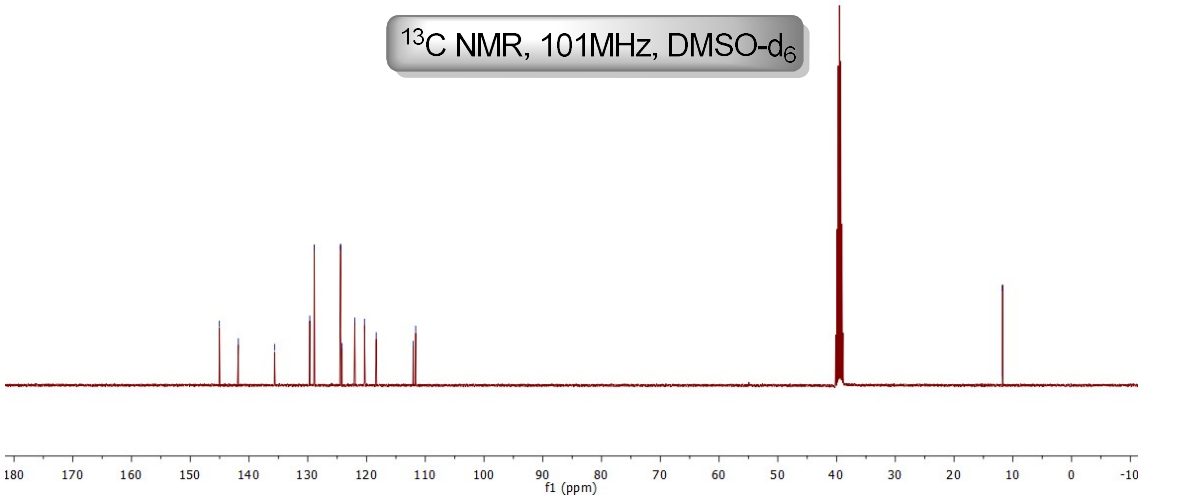
1-methyl-3-(phenylsulfinyl)-1*H*-indole (3z)



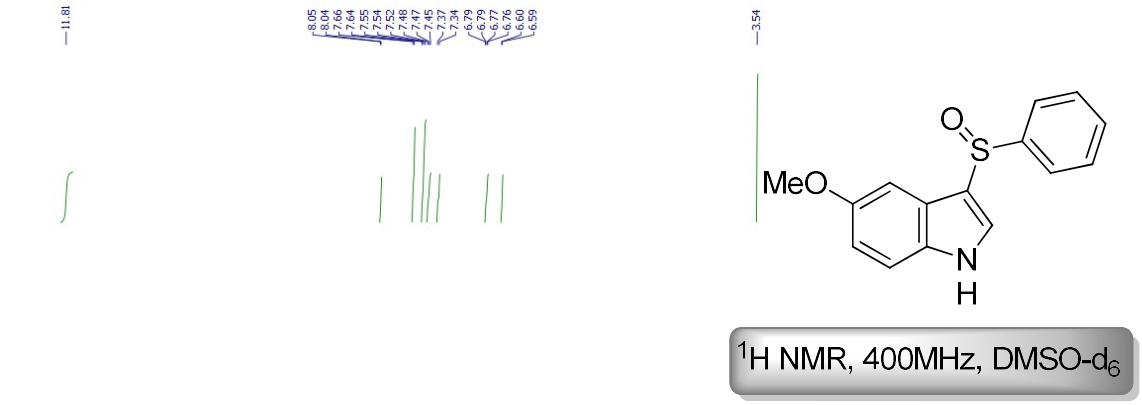


2-methyl-3-(phenylsulfinyl)-1*H*-indole (3aa)

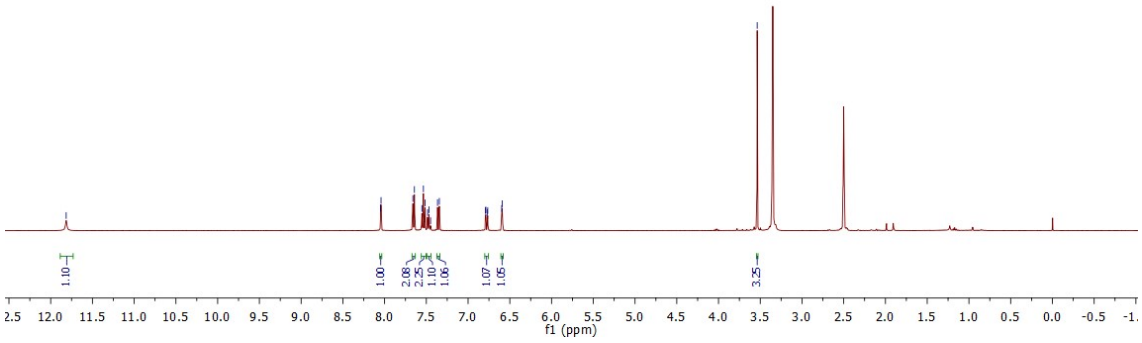


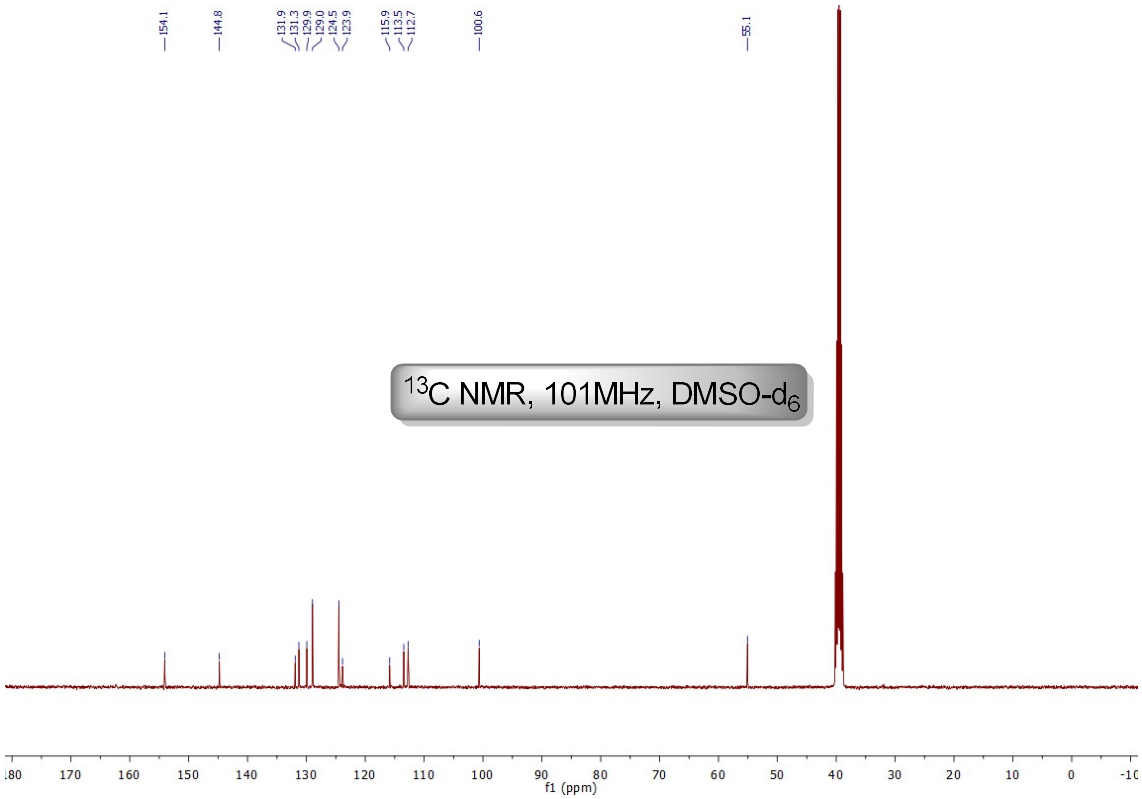


5-methoxy-3-(phenylsulfinyl)-1*H*-indole (3ab)



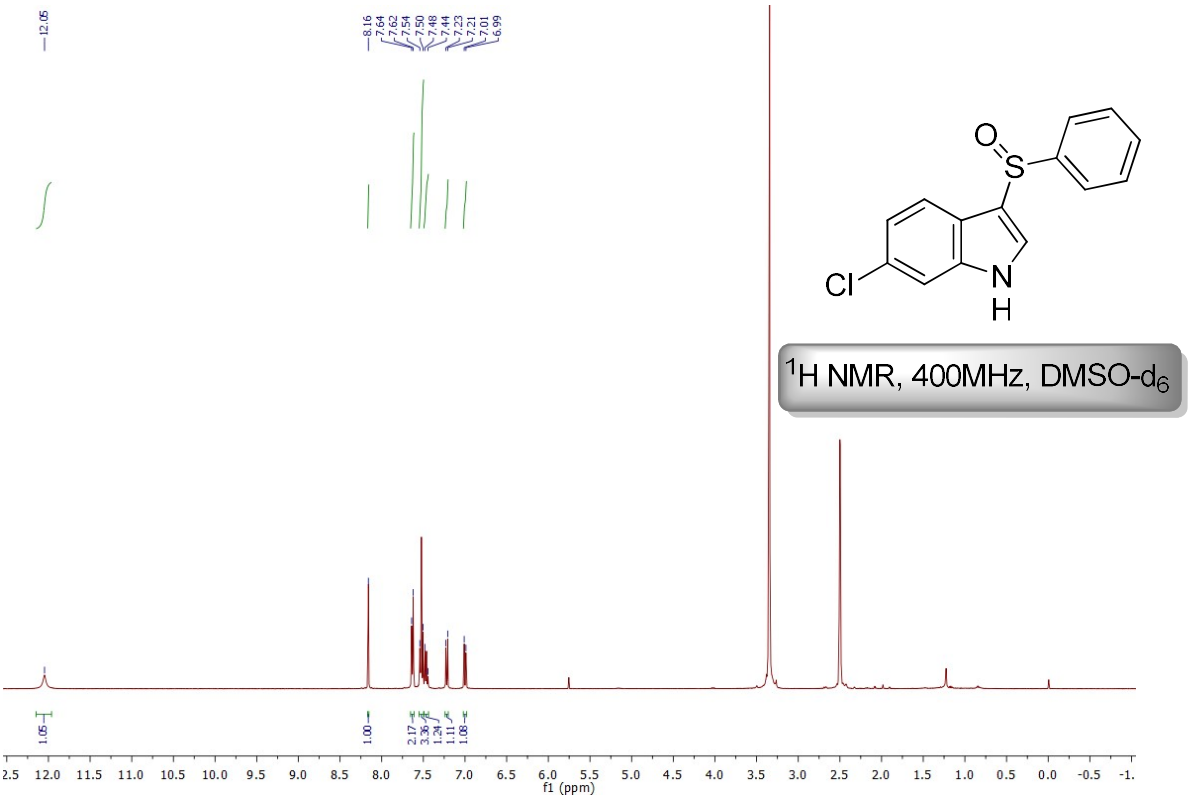
^{1}H NMR, 400MHz, DMSO-d$_6$

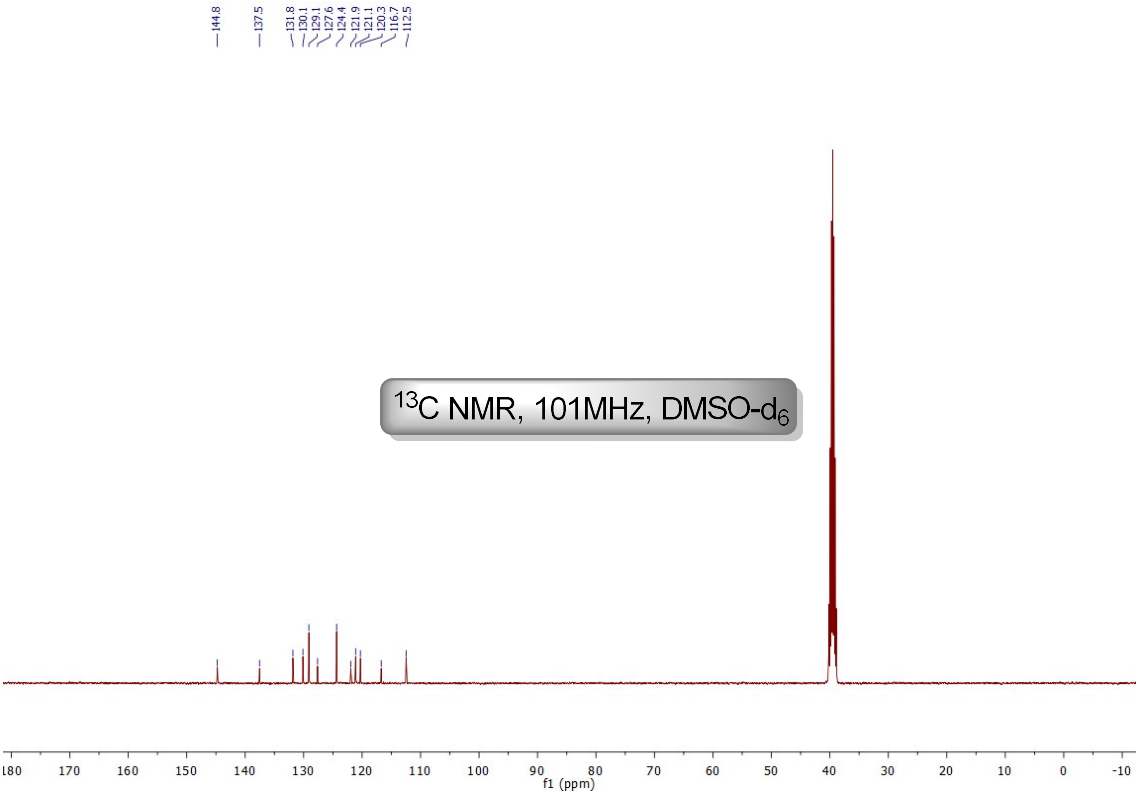




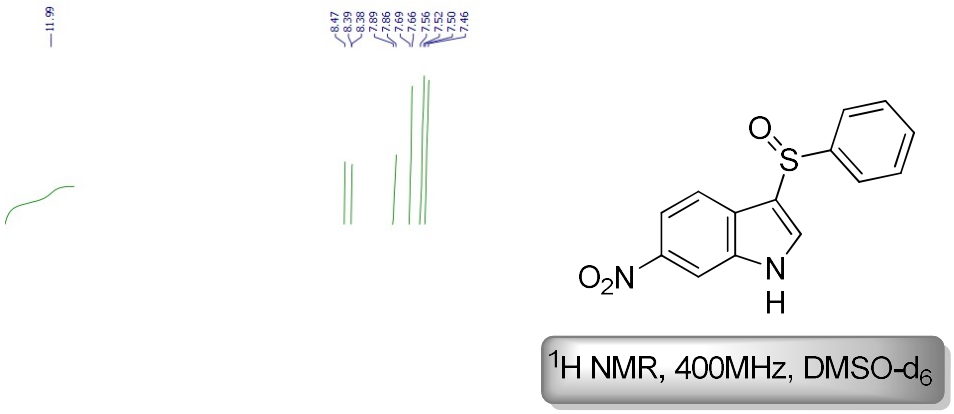
^{13}C NMR, 101MHz, DMSO-d$_6$

6-chloro-3-(phenylsulfinyl)-1*H*-indole (3ac)

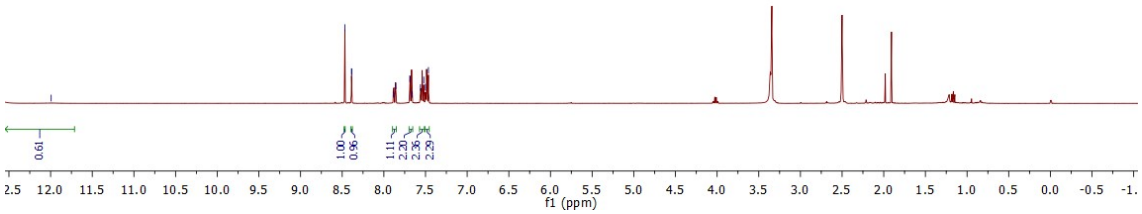


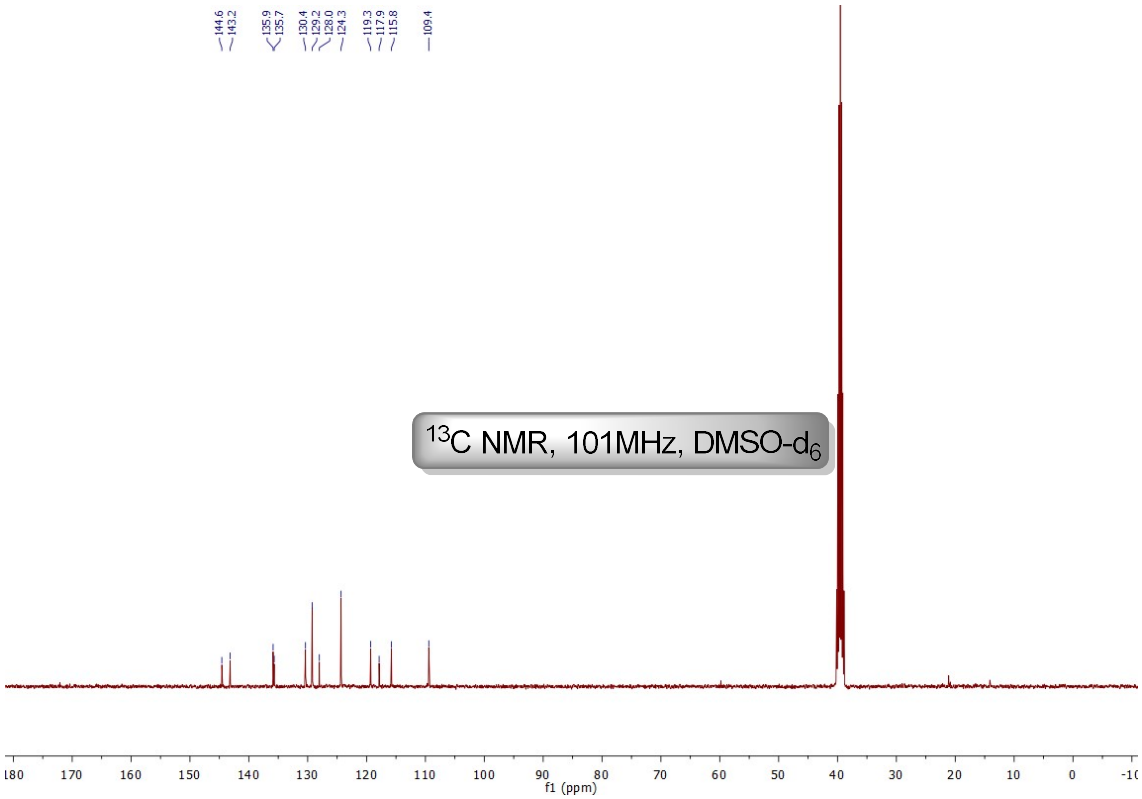


6-nitro-3-(phenylsulfinyl)-1*H*-indole (3ad)



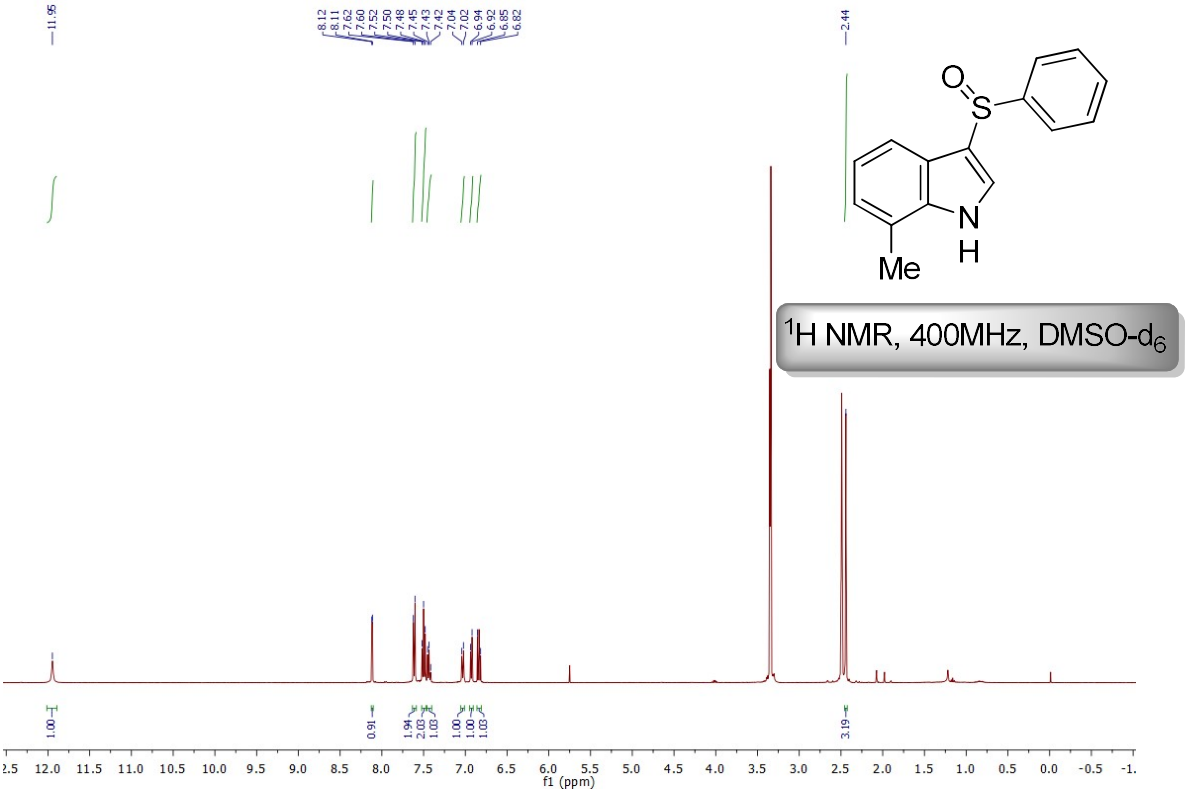
^{1}H NMR, 400MHz, DMSO-d_6

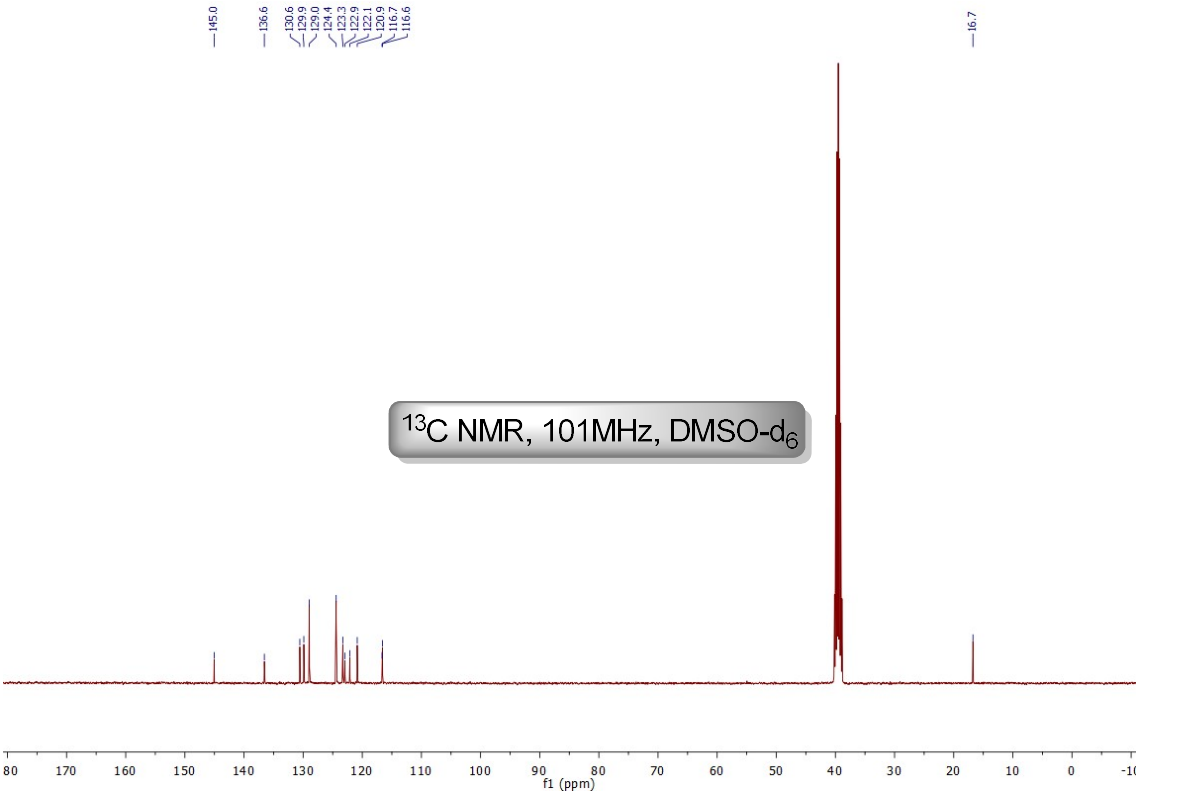




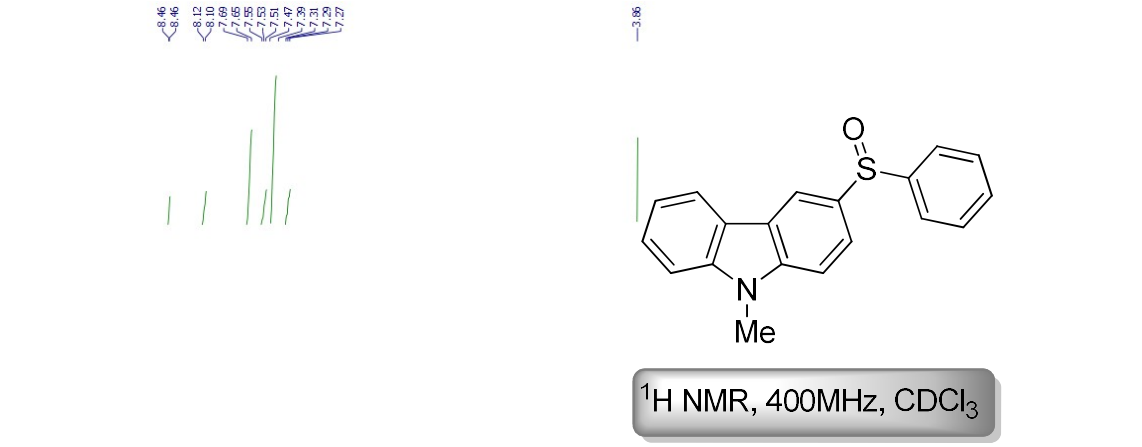
^{13}C NMR, 101MHz, DMSO-d_6

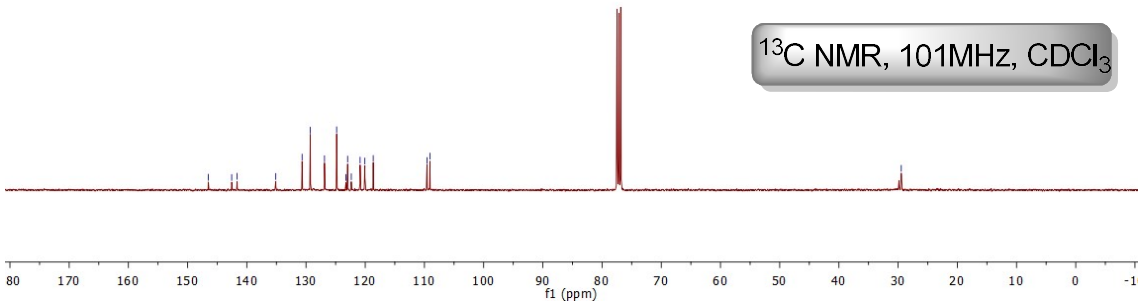
7-methyl-3-(phenylsulfinyl)-1*H*-indole (3ae)



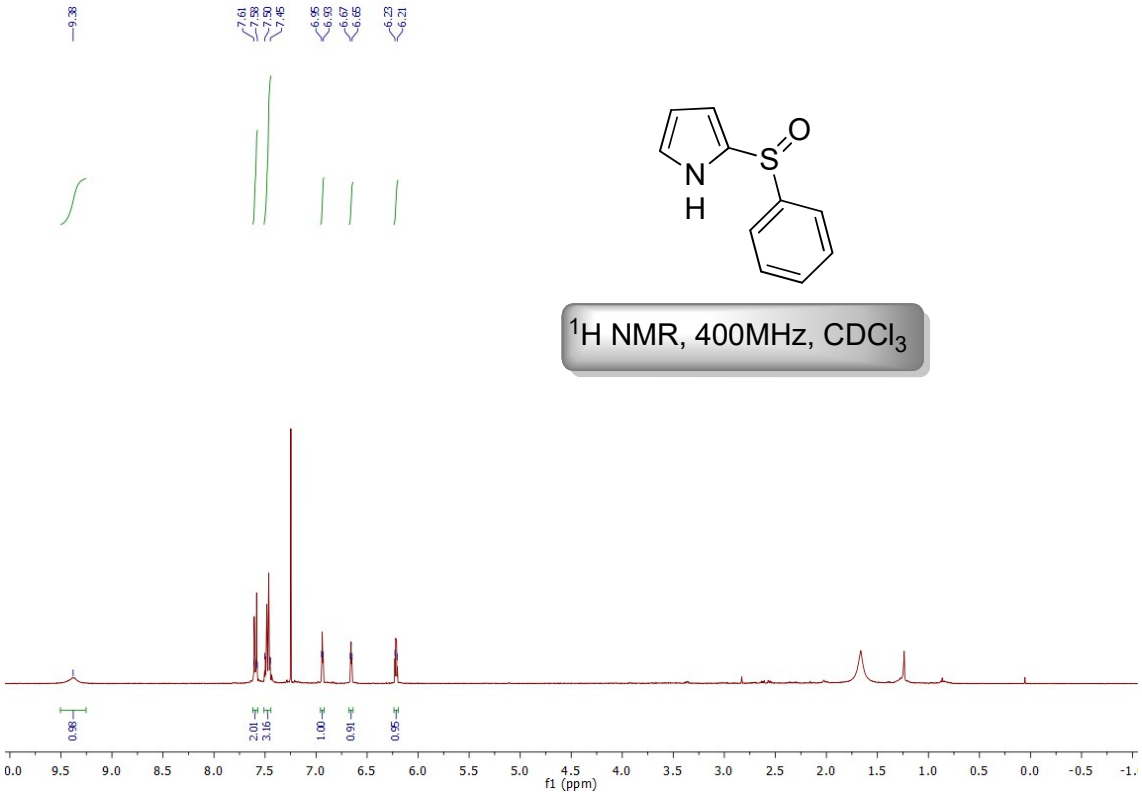


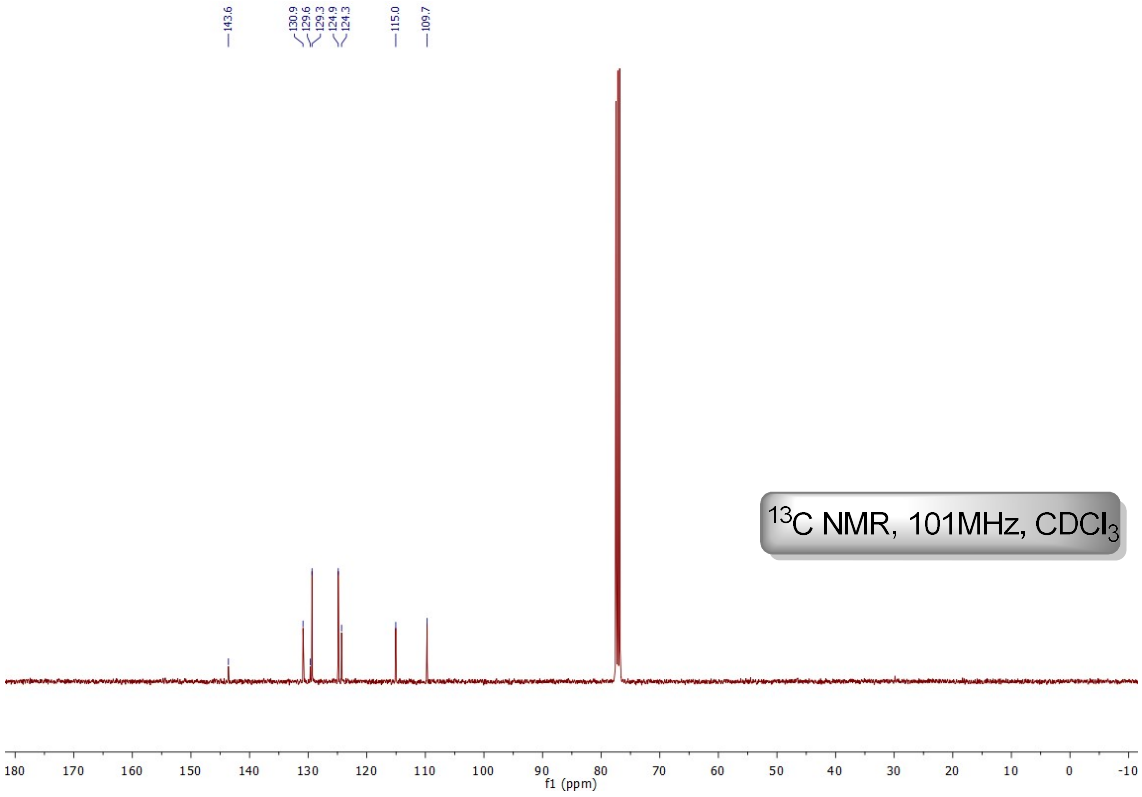
9-methyl-3-(phenylsulfinyl)-9*H*-carbazole (3af)



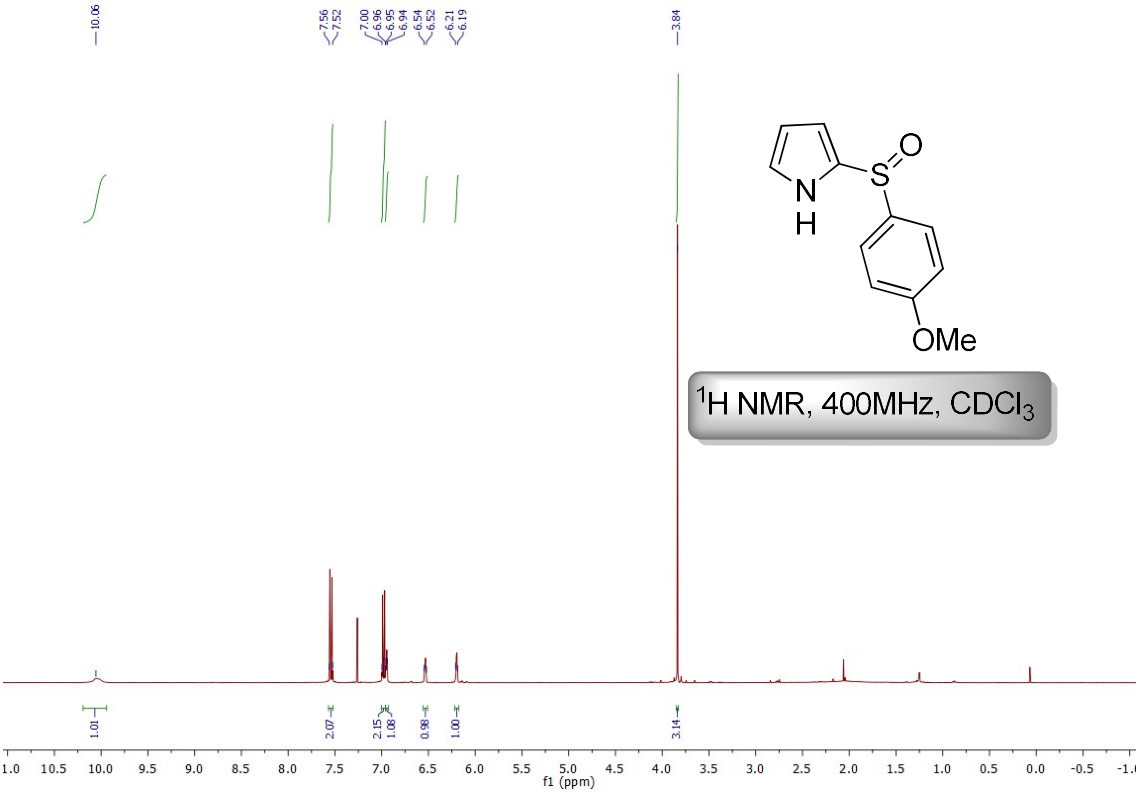


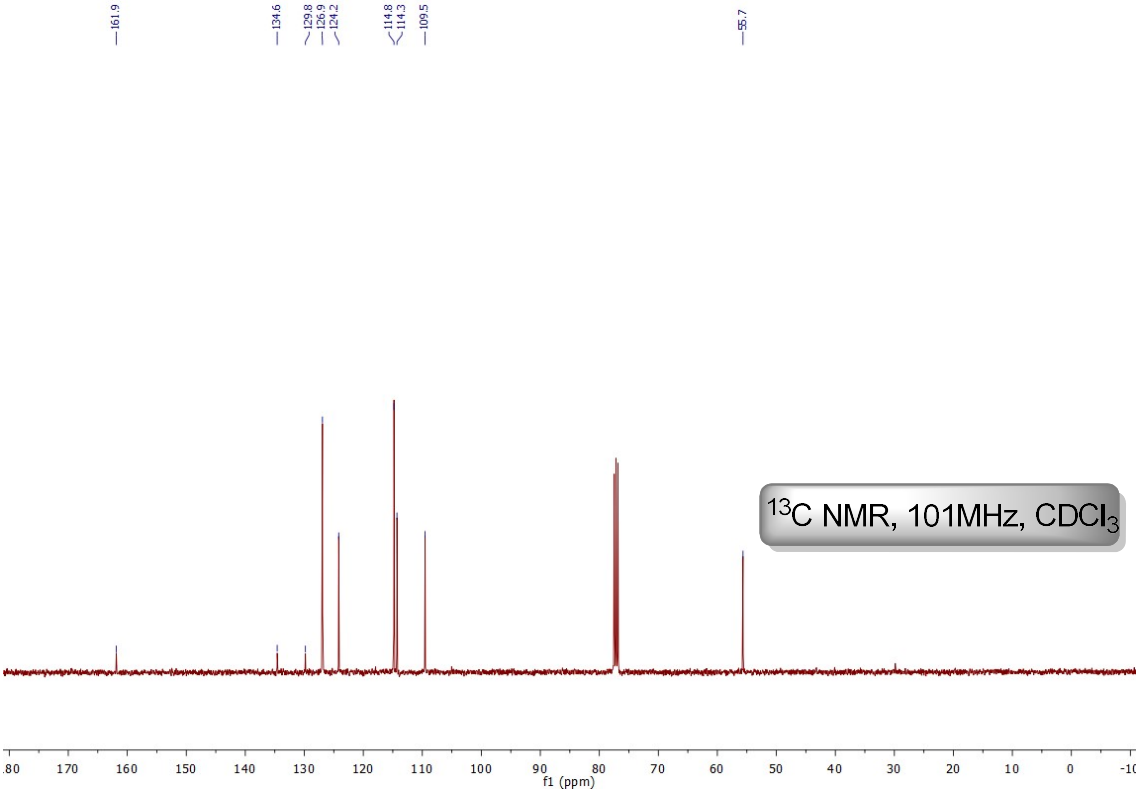
2-(phenylsulfinyl)-1*H*-pyrrole (3ag)



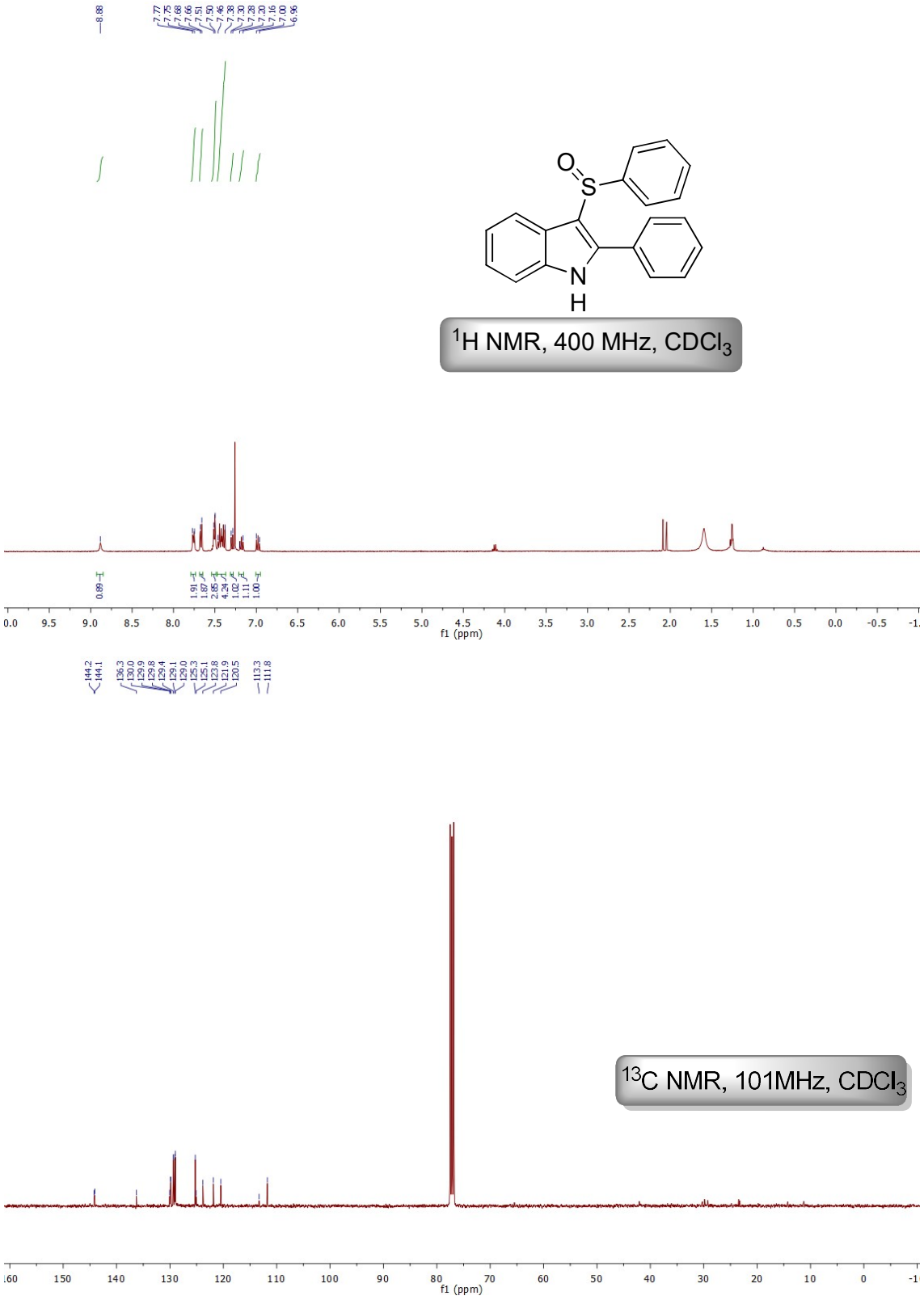


2-((4-methoxyphenyl)sulfinyl)-1*H*-pyrrole (3ah)

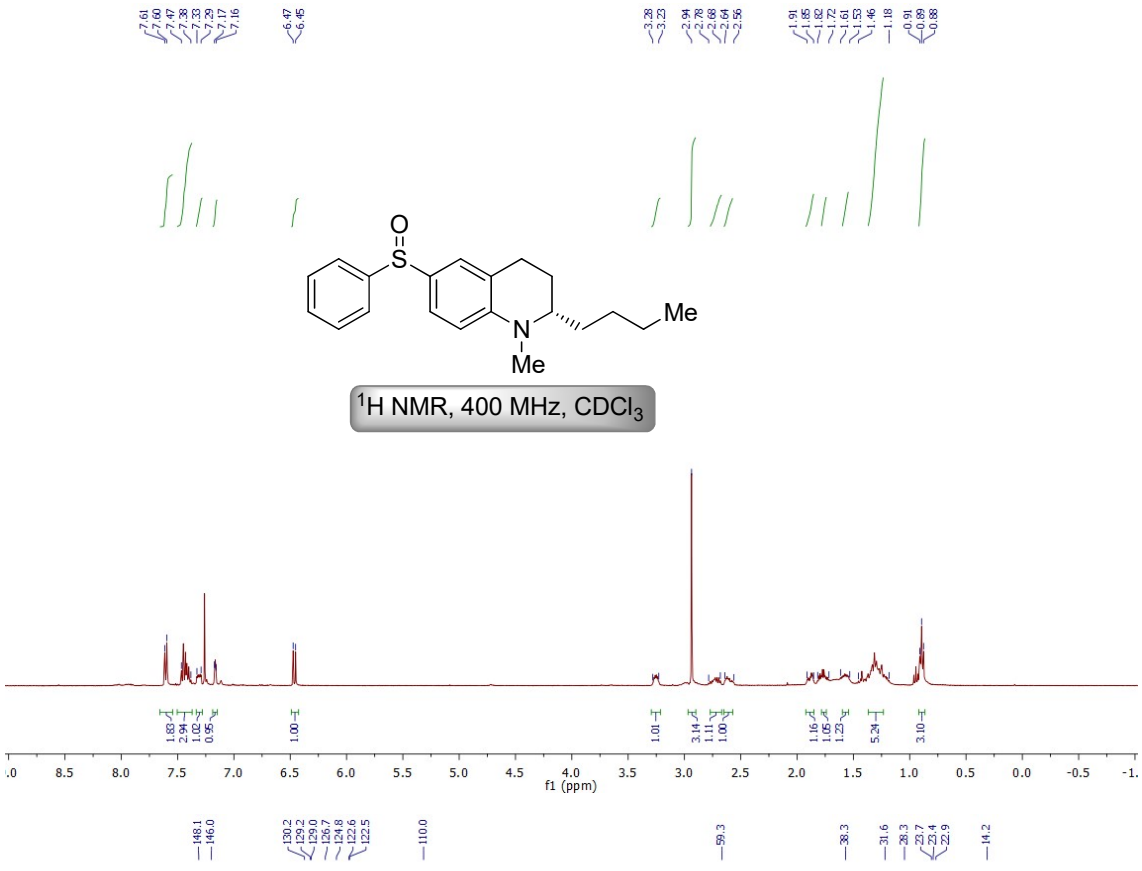




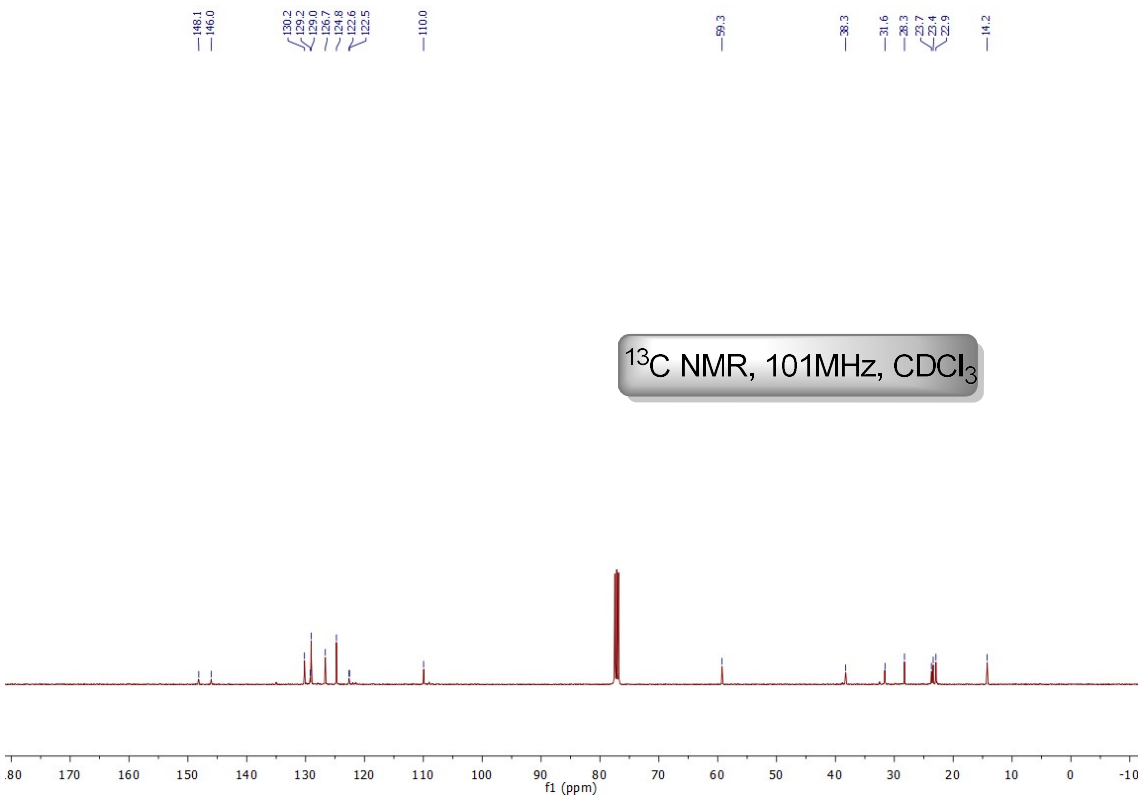
2-phenyl-3-(phenylsulfinyl)-1*H*-indole (3ai)



(2-butyl-1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)(phenyl)methanone (3aj)

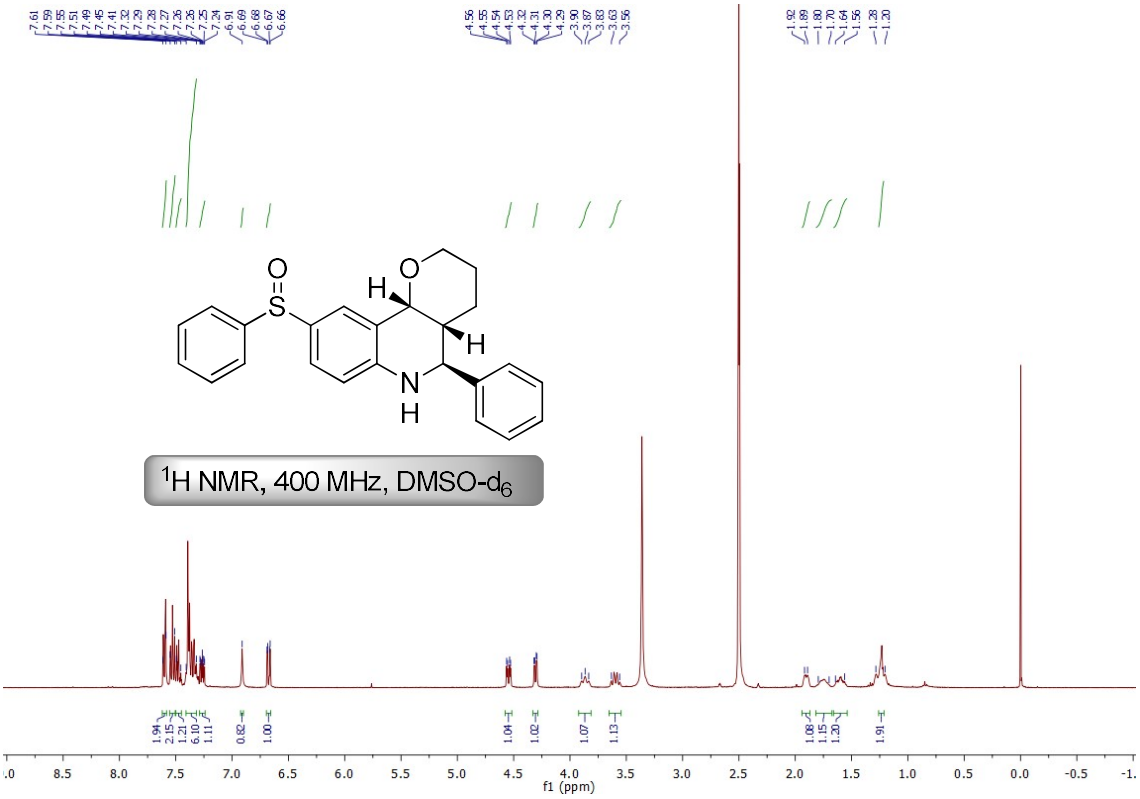


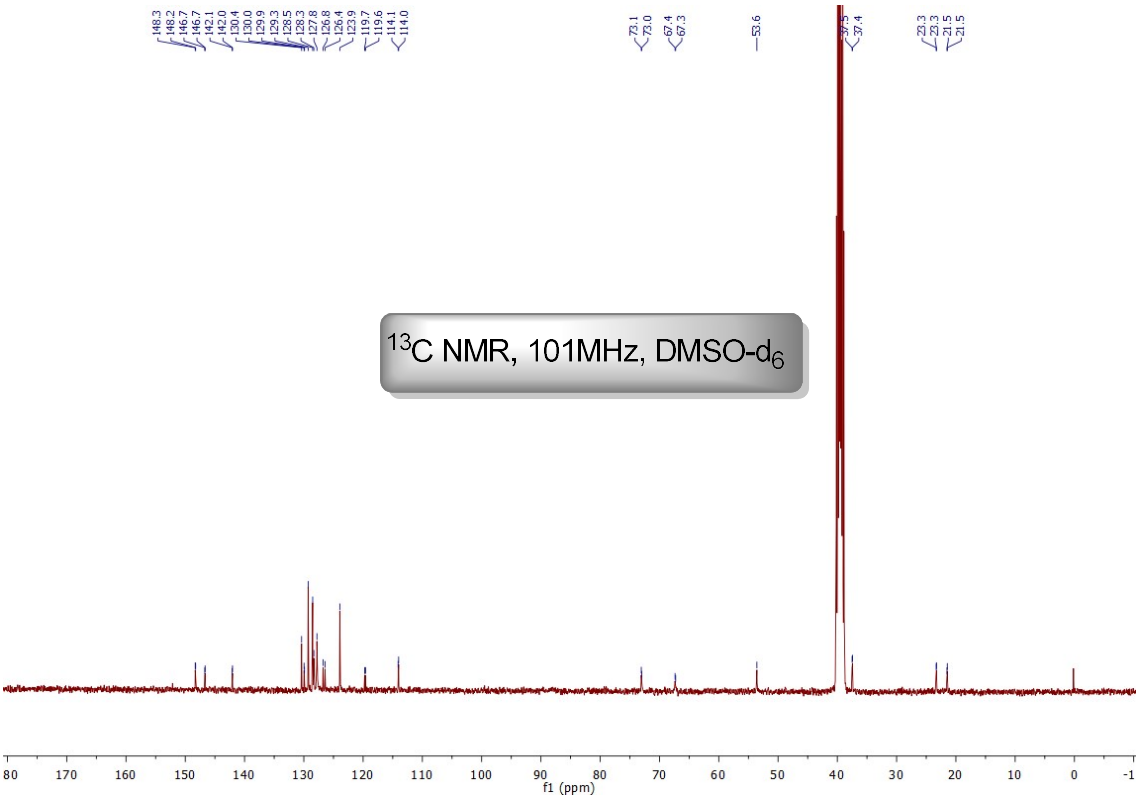
^{1}H NMR, 400 MHz, $CDCl_3$

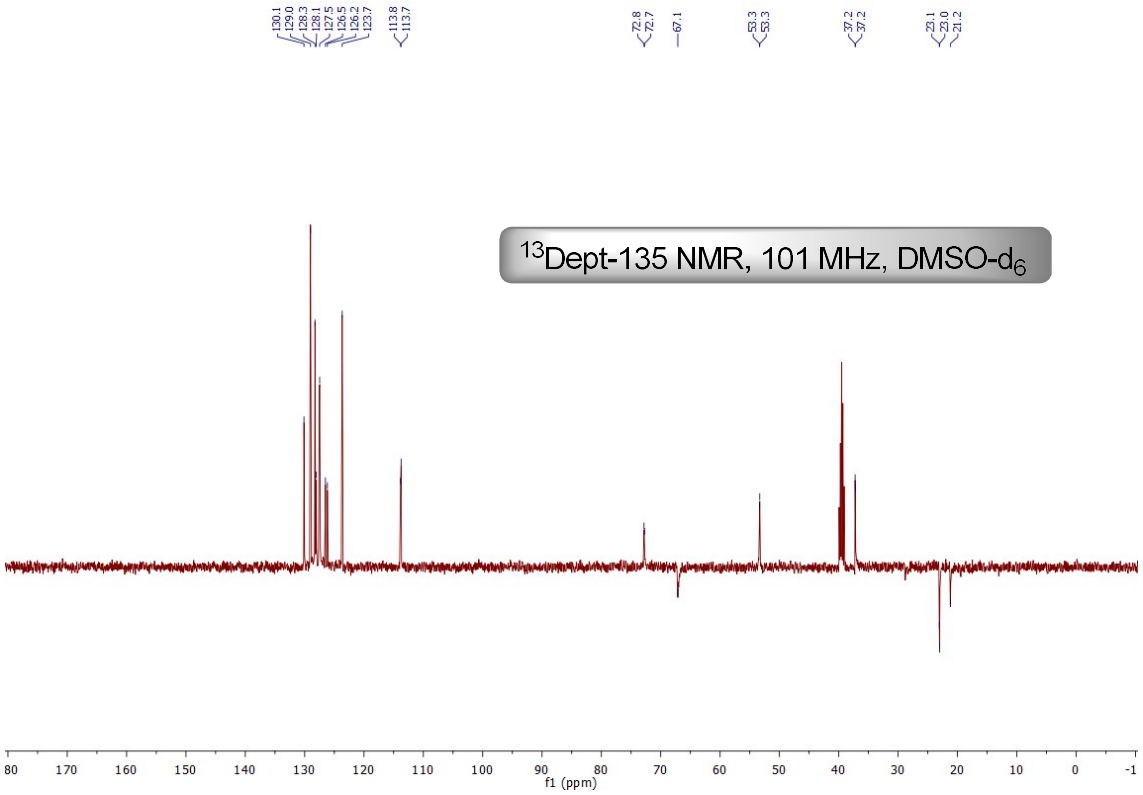


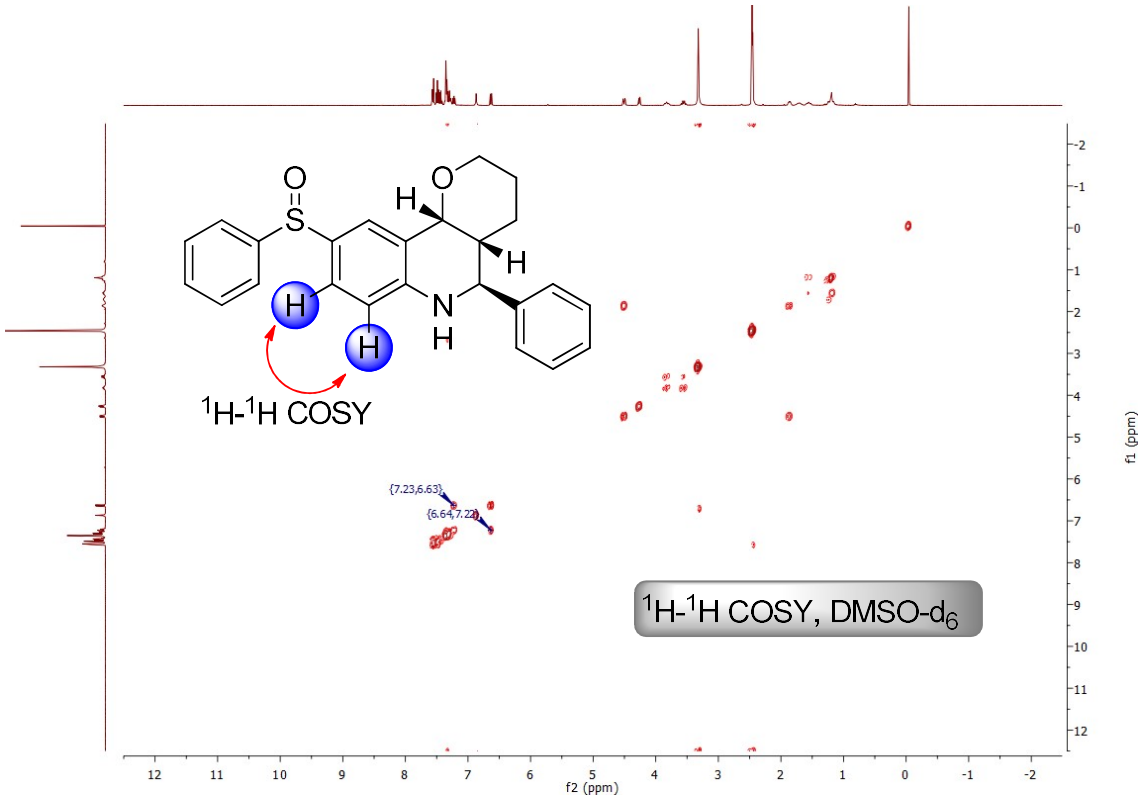
^{13}C NMR, 101MHz, $CDCl_3$

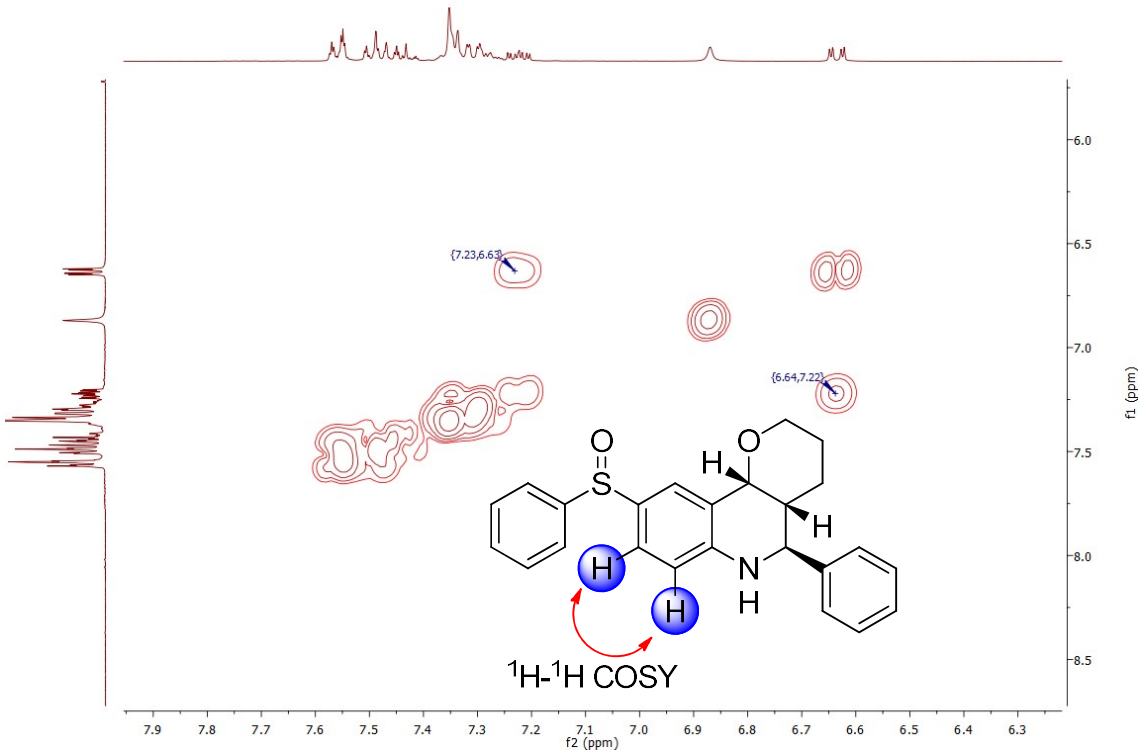
(4aR,5S,10bR)-5-phenyl-9-(phenylsulfinyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline (3ak)

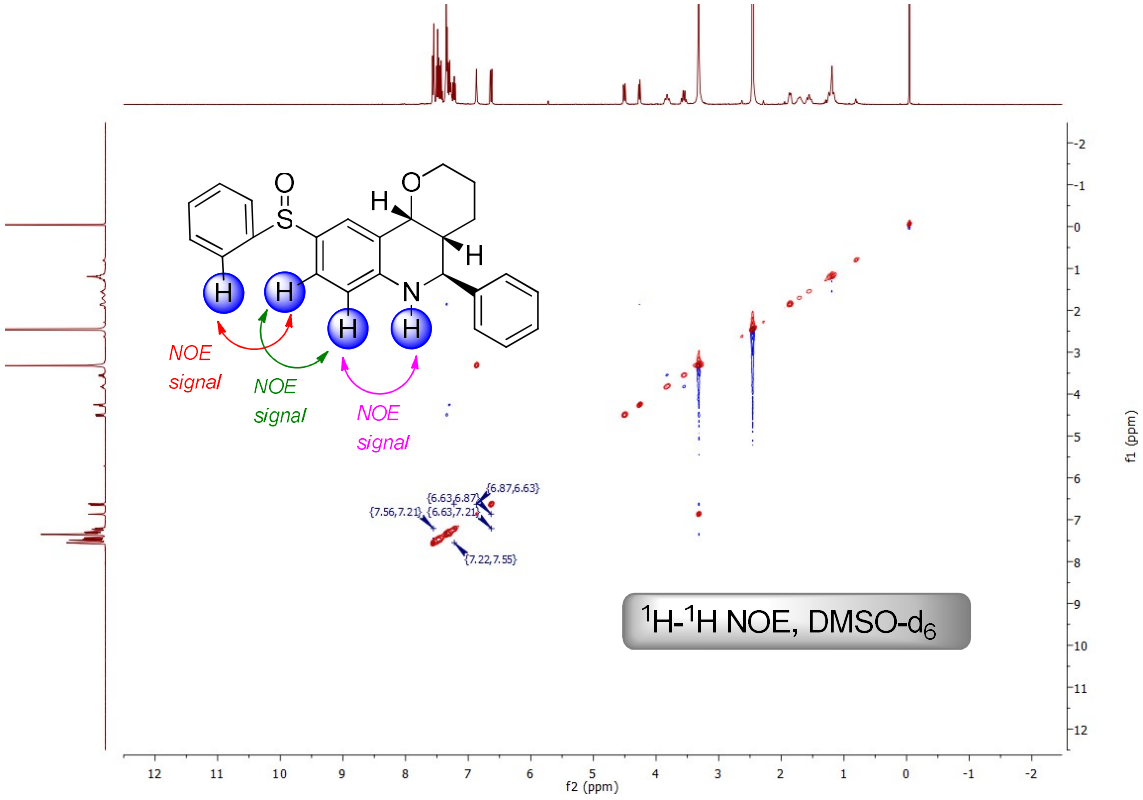


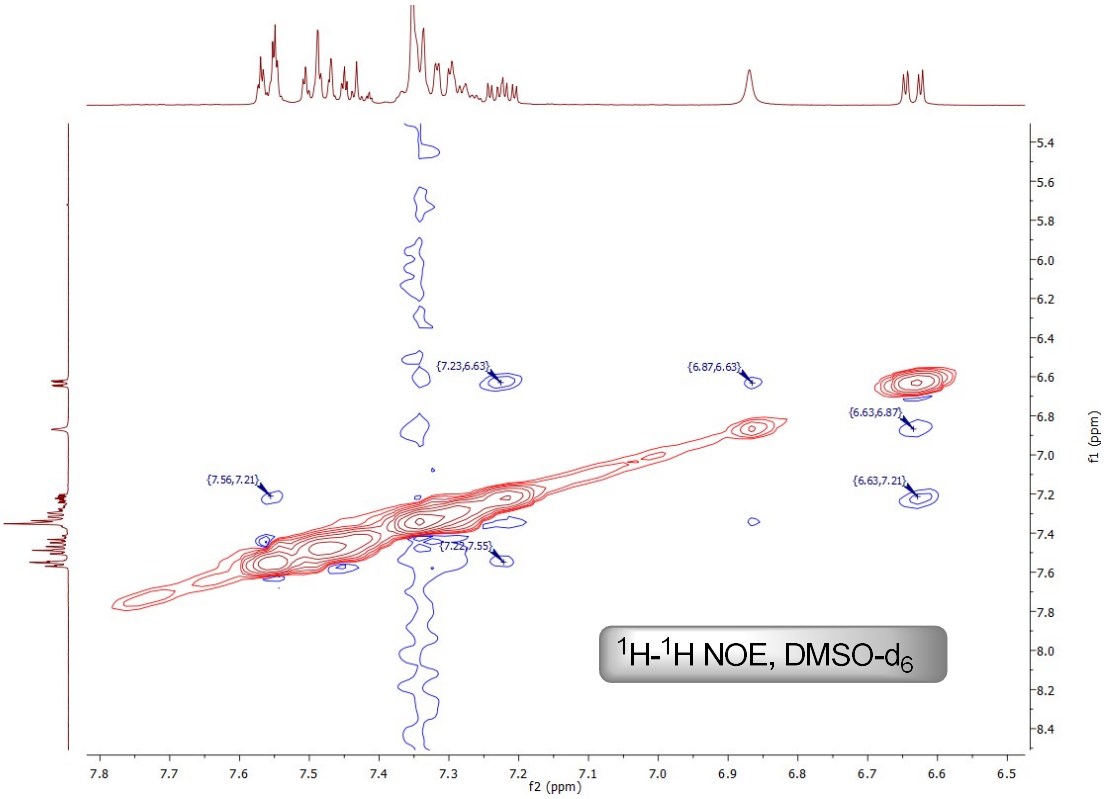


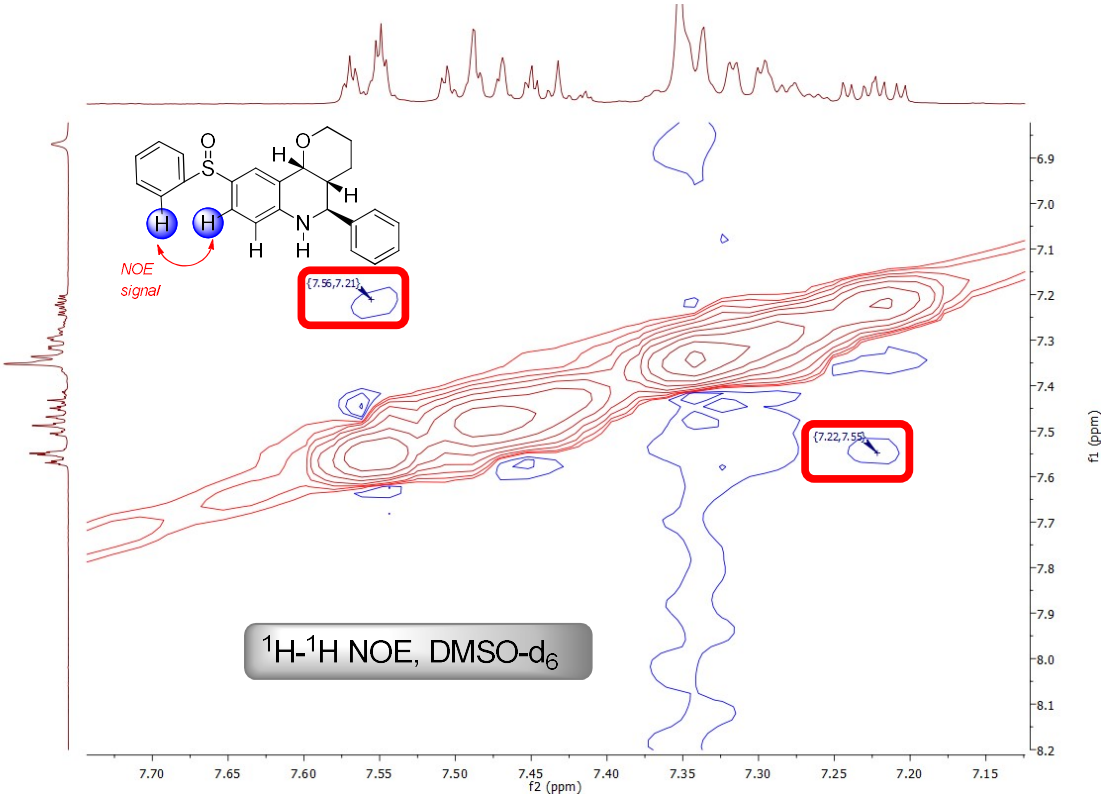

130.1
129.0
128.3
128.1
127.5
126.5
126.2
123.7
113.8
113.7
72.8
72.7
67.1
53.3
53.3
37.2
37.2
23.1
23.0
21.2
^{13}Dept-135 NMR, 101 MHz, DMSO-d$_6$
f1 (ppm)

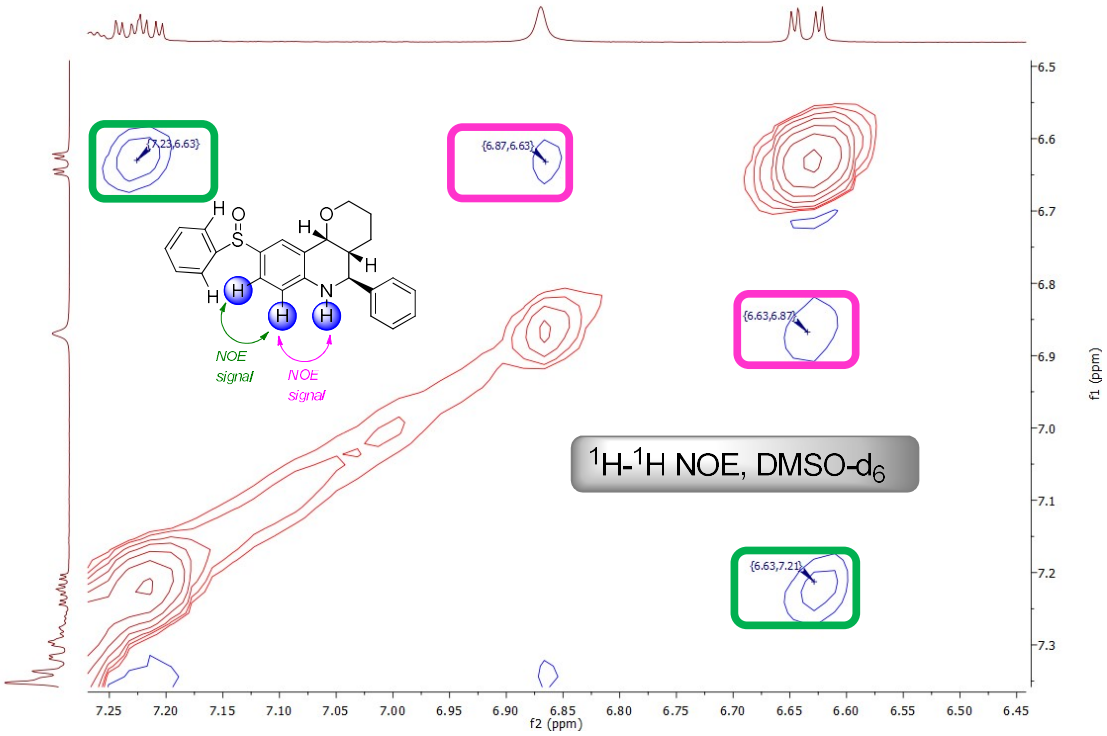

O
S
H
O
H
N
H
H
H
^{1}H-^{1}H COSY
{7.23,6.63}
{6.64,7.22}
^{1}H-^{1}H COSY, DMSO-d$_6$
f1 (ppm)
f2 (ppm)


{7.23,6.63}
{6.64,7.22}
O
S
O
H
H
H
H
N
H
^{1}H-^{1}H COSY
f2 (ppm)
f1 (ppm)

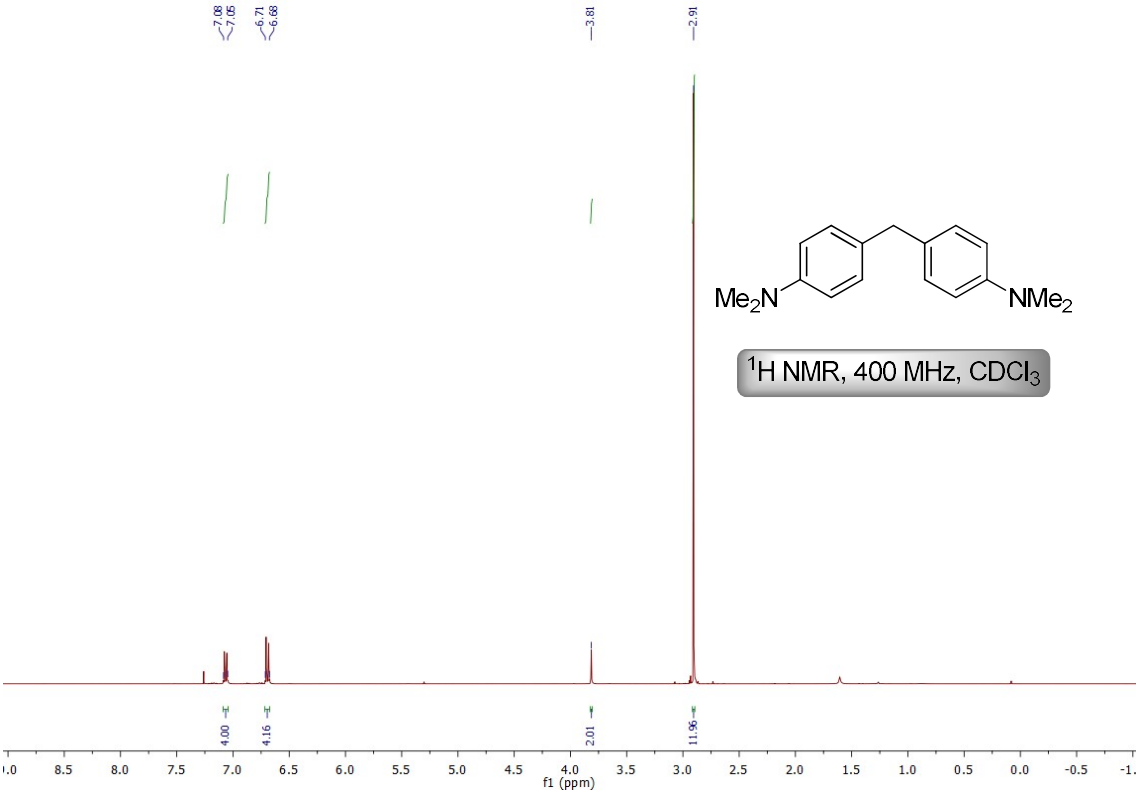

O
S
O
H
H
H
H
H
N
NOE signal
NOE signal
NOE signal
{6.63,6.87}
{6.87,6.63}
{7.56,7.21}
{6.63,7.21}
{7.22,7.55}
^{1}H-^{1}H NOE, DMSO-d$_6$
f2 (ppm)
f1 (ppm)

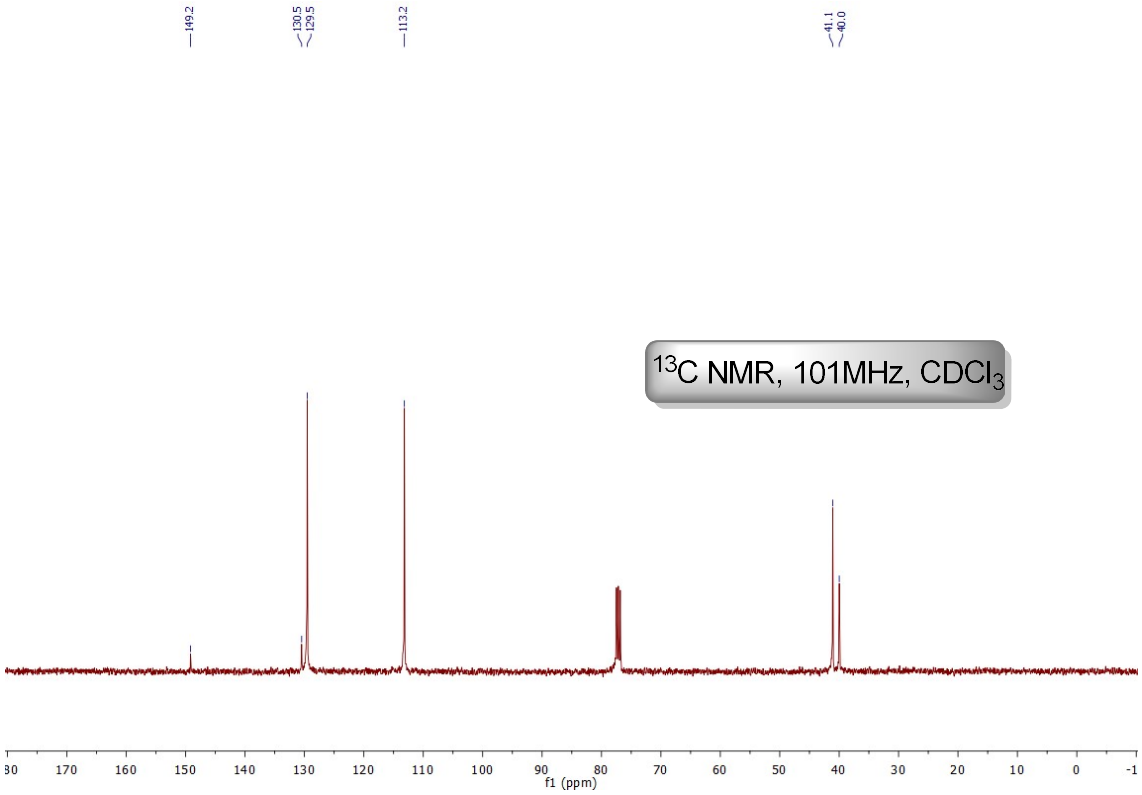

{7.23,6.63}
{6.87,6.63}
{6.63,6.87}
{7.56,7.21}
{6.63,7.21}
{7.25,7.55}
^{1}H-^{1}H NOE, DMSO-d$_6$
f2 (ppm)
f1 (ppm)

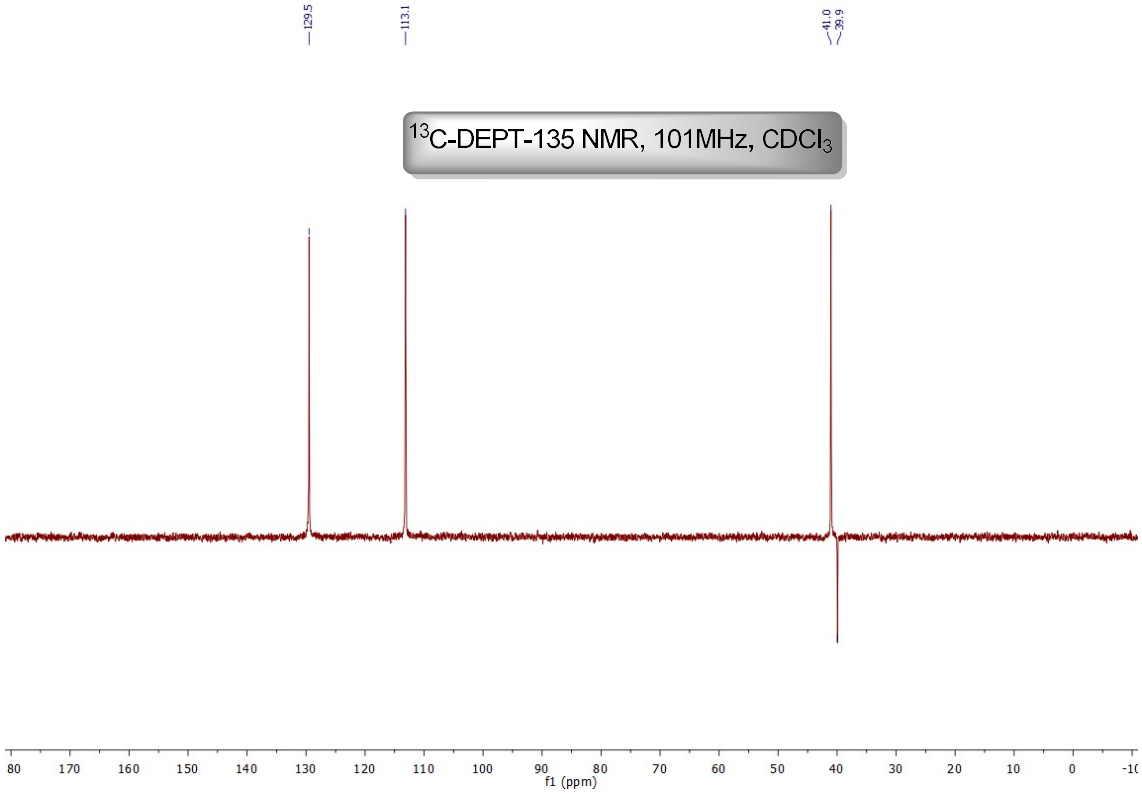

NOE
signal
{7.56,7.21}
{7.22,7.55}
^{1}H-^{1}H NOE, DMSO-d$_6$
f2 (ppm)
f1 (ppm)



4,4'-methylenebis(*N,N*-dimethylaniline) (4)




149.2
130.5
129.5
113.2
41.1
40.0
^{13}C NMR, 101MHz, CDCl$_3$
f1 (ppm)


129.5
113.1
41.0
39.9
^{13}C-DEPT-135 NMR, 101MHz, CDCl$_3$
f1 (ppm)