Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

Copper-catalyzed reductive deamination of sulfoximines to sulfoxides

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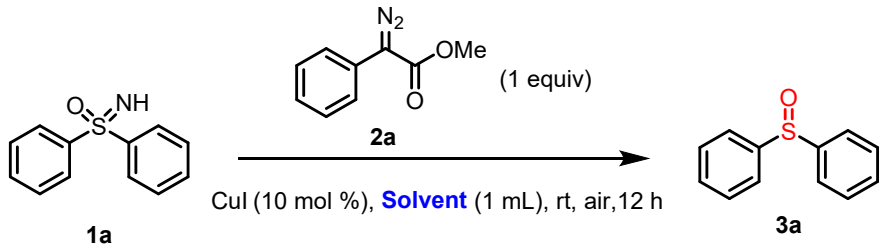
1. General Information

All the solvents were obtained from commercial supplier and used without further purification. The other commercial chemicals were used without further purification. All reactions were performed under an inert atmosphere of nitrogen in flame-dried glassware, unless otherwise stated. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate. Preparative TLC was performed on 1.0 mm silica gel. ^{1}H NMR spectra were recorded on a Bruker Avance III instrument (500 MHz). ^{13}C NMR spectra were recorded on a Bruker Avance III instrument (126 MHz) and were fully decoupled by broad band proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 mass spectrometer using ESI-TOF (electrospray ionization time-of-flight). NMR spectra were recorded in $CDCl_3$. Crystal structure and data were recorded on an Agilent Gemini E diffractometer. 1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, q = quartet, m = multiplet, etc.

2. Optimization of the Reaction Conditions

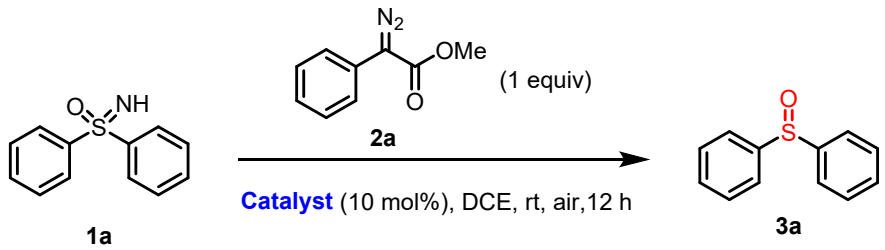
2.1 Table S1. Solvent screening[a]



Entry	Solvent	Yield (%)[b]
1	DCM	26
2	TCM	29
3	DCE	37
4	1,4-Dioxane	18
5	TBME	21
6	Toluene	20
7	EA	22
8	MeCN	20
9	DMF	trace
10	HFIP	trace
11	1,4-dioxane	26
12	1,4-dioxane	29
13	1,4-dioxane	37

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.2 mmol), CuI (10 mol%), in solvent (1 mL), at room temperature under air atmosphere for 12 h. [b] Isolated yield. DCM = Dichloromethane, TCM = Trichloromethane, DCE = 1,2-Dichloroethane.

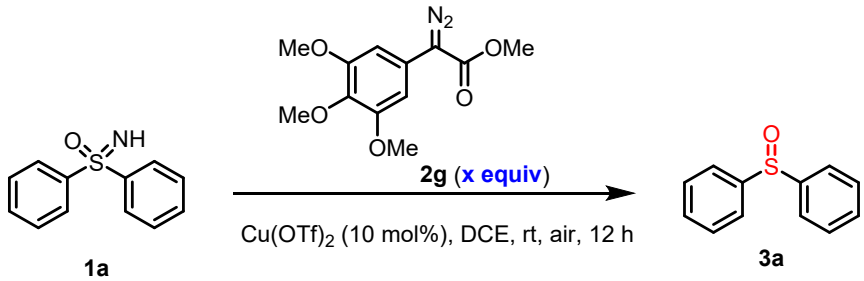
2.2 Table S2. Catalyst screening[a]



Entry	Catalyst	Yield (%)[b]
1	CuI	37
2	CuSCN	41
3	CuO	trace
4	$Cu(OAc)_2$	trace
5	$Cu(OTf)_2$	47
6	$CuBr_2$	26
7	CuOAc	trace
8	Cu_2O	15
9	CuCl2	trace

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.2 mmol), catalyst (10 mol%), in DCE (1 mL) at room temperature under air atmosphere for 12 h. [b] Isolated yield.

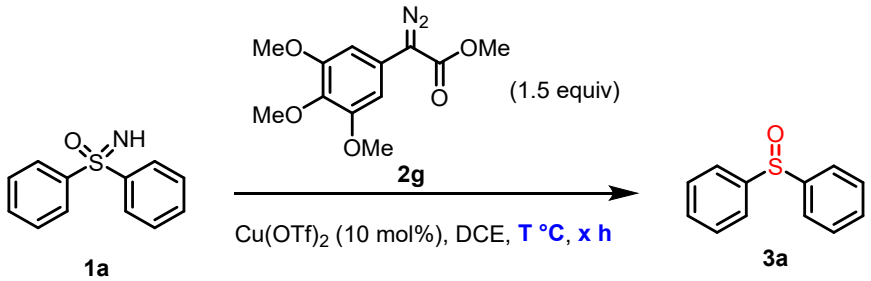
2.3 Table S3. The equivalent of diazo compounds screening[a]



Entry	2g (equiv)	Yield (%)[b]
1	0.75	58
2	1.0	79
3	1.25	85
4	1.5	91
5	1.75	89
6	2	88

[a] Reaction conditions: 1a (0.2 mmol), 2g, $Cu(OTf)_2$ (10 mol%), in DCE (1 mL) at room temperature under air atmosphere for 12 h. [b] Isolated yield.

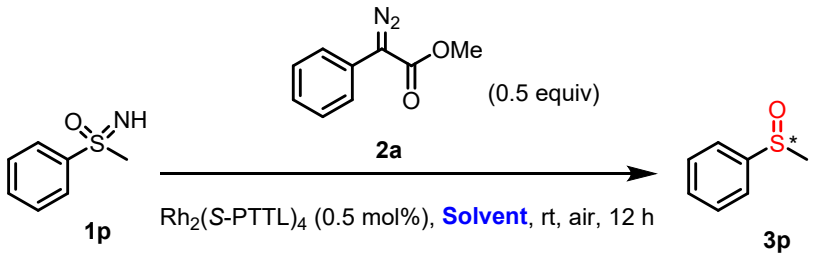
2.4 Table S4. The equivalent of diazo compounds screening[a]



Entry	Temp (°C)	Time (h)	Yield (%)[b]
1	0	12	37
2	room temperature	12	91
3	40	12	90
4	room temperature	6	47
5	room temperature	24	92

[a] Reaction conditions: 1a (0.2 mmol), 2g (0.3 mmol), $Cu(OTf)_2$ (10 mol%), in DCE (1 mL) under T °C for x h. [b] Isolated yield.

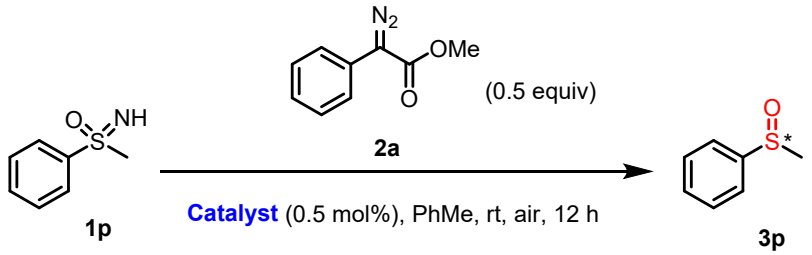
2.5 Table S5. The equivalent of diazo compounds screening[a]



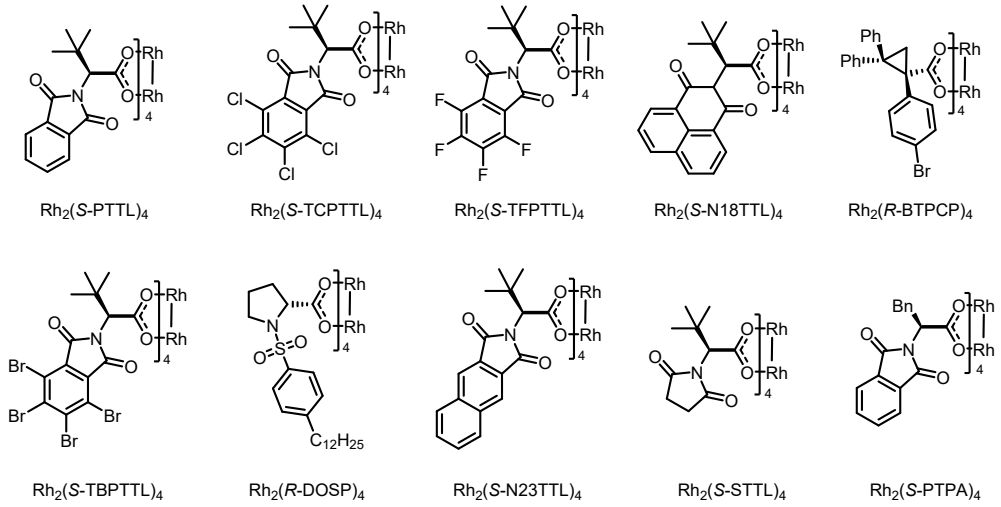
Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	DCM	27	22
2	TCM	24	20
3	DCE	28	22
4	1,4-Dioxane	trace	-
5	TBME	25	27
6	PhMe	32	36
7	EA	25	34
8	MeCN	30	12
9	DMF	trace	-
10	HFIP	trace	-

[a] Reaction conditions: 1p (0.1 mmol), 2a (0.05 mmol), Rh_2(*S*-PTTL)$_4$ (0.5 mol%), in solvent (0.6 mL) at room temperature under air atmosphere for 12 h. [b] Isolated yield. [c] The ee values were determined by high performance liquid chromatography (HPLC) analysis (Chiralpak AS-H column).

2.6 Table S6. The equivalent of diazo compounds screening[a]

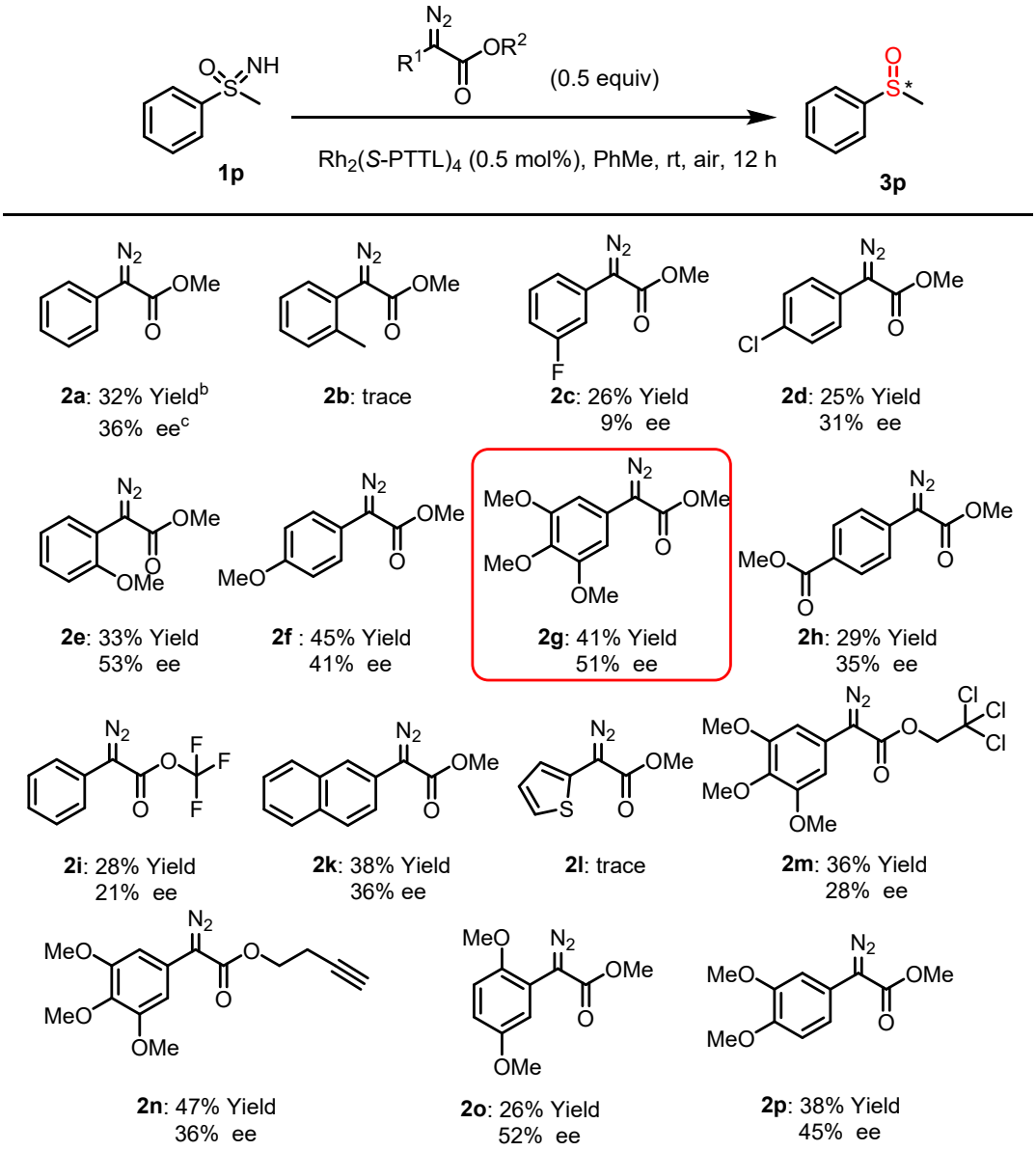


Entry	Catalyst	Yield (%)[b]	ee (%)[c]
1	Rh_2(S-PTTL)$_4$	32	36
2	Rh_2(S-TCPTTL)$_4$	trace	-
3	Rh_2(S-TFPTTL)$_4$	trace	-
4	Rh_2(S-N18TTL)$_4$	34	18
5	Rh_2(R-BTPCP)$_4$	trace	-
6	Rh_2(S-TBPTTL)$_4$	trace	-
7	Rh_2(R-DOSP)$_4$	35	4
8	Rh_2(S-N23TTL)$_4$	33	13
9	Rh_2(S-STTL)$_4$	25	15
10	Rh_2(S-PTPA)$_4$	36	15



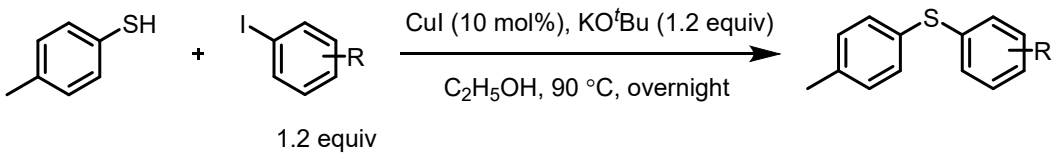
[a] Reaction conditions: 1p (0.1 mmol), 2a (0.05 mmol), catalyst (0.5 mol%), in PhMe (0.6 mL) at room temperature under air atmosphere for 12 h. [b] Isolated yield. [c] The ee values were determined by high performance liquid chromatography (HPLC) analysis (Chiralpak AS-H column).

2.7 Table S7. Diazos screening[a]

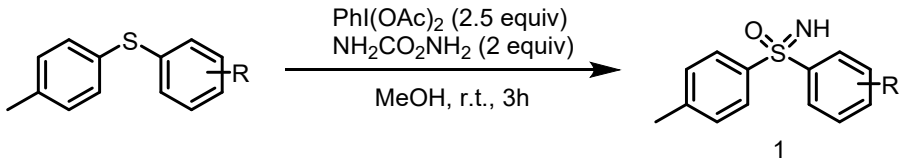


[a] Reaction conditions: **1p** (0.1 mmol), diazo compounds (0.05 mmol), Rh_2(*S*-PTTL)$_4$ (0.5 mol%), in PhMe (0.6 mL) at room temperature under air atmosphere for 12 h. [b] Isolated yield. [c] The ee values were determined by high performance liquid chromatography (HPLC) analysis (Chiralpak AS-H column).

3. Procedure for the Synthesis of Sulfoximines [1]

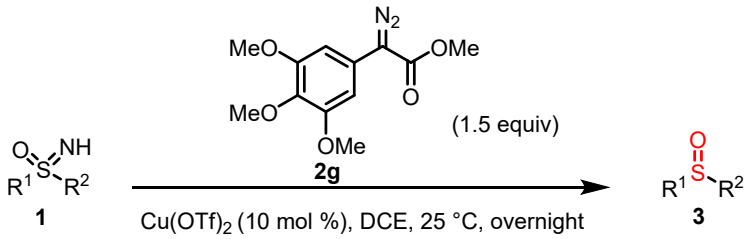


The aryl halides (2 mmol, 1 equiv), *p*-thiocresol (2.4 mmol, 1.2 equiv), cuprous iodide (0.2 mmol, 10 mol%), KO^{t}Bu (2.4 mmol, 1.2 equiv), and ethanol (10 mL) were added to a 50 mL reaction tube. After stirring overnight at 90 °C oil bath, The reaction was allowed to cool to room temperature. Subsequently, ethyl acetate (70 mL) was added and the reaction mixture was washed with water (2 × 50 mL). The organic layer was dried over anhydrous sodium sulphate, filtered and concentrated in vacuo. Purification of the crude mixture by flash column chromatography (100% petroleum ether) afforded a sulfide compound.



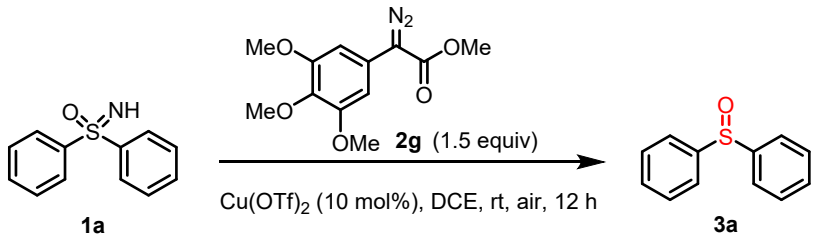
The sulfide (1 mmol), (diacetoxyiodo)benzene (2.5 mmol, 2.5 equiv) and ammonium carbamate (2 mmol，2 equiv) were added to a flask containing a stirrer bar. MeOH (1 mL, 0.5 M) was added and the reaction was stirred at 25 °C for 3 h. The solvent was removed under reduced pressure. Purification by flash chromatography (EA:PA=1:3) afforded the sulfoximine products.

4. Procedure for the Synthesis of sulfoxides



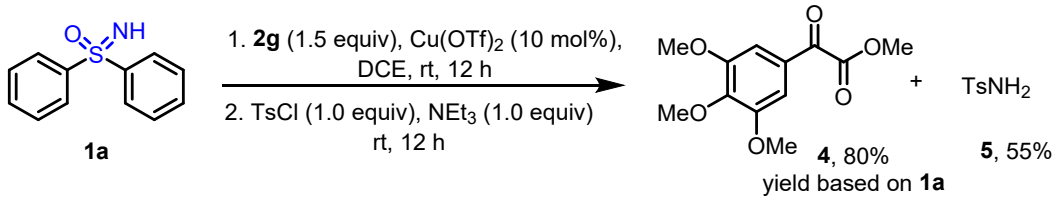
NH-Sulfoximines 1 (0.2 mmol, 1 equiv), α-diazo-3,4,5-trimethoxyphenyl acetic methyl ester 2g (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (0.02 mmol, 10 mol%), and 1 mL of 1,2-dichloroethane were added. The reaction was allowed to stir at room temperature under air atmosphere for 12 hours. The solvent was removed under reduced pressure. Purification by PTLC (EA:PA=1:4) afforded the sulfoxide products.

5. Procedure for the Gram-Scale Synthesis of 3a



In a 200 mL round-bottom flask, *S,S*-diphenylsulfonyl imine **1a** (6 mmol, 1 equiv), α-diazo-3,4,5-trimethoxyphenyl acetic methyl ester **2g** (9 mmol, 1.5 equiv), copper triflate (0.6 mmol, 10 mol%), and 1,2-dichloroethane (60 mL) were sequentially added. The reaction mixture was stirred at room temperature under air atmosphere for 12 hours under TLC monitoring. Upon completion of the reaction, ethyl acetate (70 mL) was added and the reaction mixture was washed with water (2 × 50 mL). The organic layer was dried over anhydrous sodium sulphate, filtered and concentrated in vacuo, followed by purification by column chromatography on silica gel plates (eluting with ethyl acetate/petroleum ether = 1:4) to yield Sulfinyldibenzene 3a (924.3 mg, 76%).

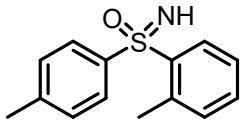
6. Procedure for the Mechanistic Studies[2]



In a 25 mL round-bottom flask, *S,S*-diphenylsulfonyl imine **1a** (108.5 mg, 0.5 mmol, 1 equiv), α-diazo-3,4,5-trimethoxyphenyl acetic methyl ester **2g** (199.5 mg, 0.75 mmol, 1.5 equiv), copper triflate (18.05 mg, 0.05 mmol, 10 mol%), and 1,2-dichloroethane (3 mL) were sequentially added. The flask was sealed with a septum, and the reaction mixture was stirred at room temperature for 12 hours under TLC monitoring. Triethylamine (0.7 mL, 0.5 mmol, 1 equiv) and *p*-toluenesulfonyl chloride (95.3 mg, 0.5 mmol, 1 equiv) dissolved in 1,2-dichloroethane (0.5 mL) were subsequently added to the reaction mixture using a syringe. The reaction was allowed to continue at room temperature for another 12 hours with TLC monitoring. Upon completion of the reaction, the reaction mixture was evaporated under reduced pressure, followed by purification by column chromatography (eluting with EA/PE = 1:5) to yield 3,4,5-trimethoxybenzoyl acetic methyl ester **4** and *p*-toluenesulfonamide **5**.

7. Compound Characterizations

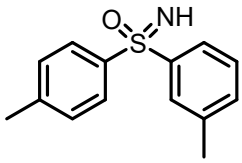
Imino(*o*-tolyl)(*p*-tolyl)-λ^6-sulfanone (1c)



1c

o-Tolyl(p-tolyl)sulfane (85.7 mg, 0.4mmol) as starting material. White solid, (83.3 mg, 85%). mp = 102-104 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.45 (td, J = 7.4, 1.5 Hz, 1H), 7.38 (td, J = 7.7, 1.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H), 3.07 (s, 1H), 2.48 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.28, 141.19, 139.29, 137.89, 132.80, 129.51, 129.21, 128.01, 126.34, 21.51, 20.59 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}NOS$ $[M+H]^+$, 246.0947; found: 246.0946.

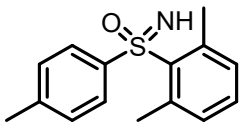
Imino(*m*-tolyl) (*p*-tolyl)-λ^6-sulfanone (1d)



1d

m-Tolyl(p-tolyl)sulfane (85.7 mg, 0.4mmol) as starting material. White solid, (90.6 mg, 92%). mp = 106-108 °C,^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 2H), 7.87–7.80 (m, 2H), 7.39–7.25 (m, 4H), 3.02 (s, 1H), 2.39 (d, J = 3.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.44, 143.37, 140.48, 139.30, 133.26, 129.78, 128.97, 128.07, 127.95, 124.92, 21.47, 21.37 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{16}NOS$ $[M+H]^+$, 246.0947; found: 246.0947.

(2,6-Dimethylphenyl) (imino)(*p*-tolyl)-λ^6-sulfanone (1f)

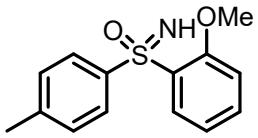


1f

(2,6-Dimethylphenyl)(*p*-tolyl)sulfane (85.7 mg, 0.4mmol) as starting material. Pale

yellow solid, (84.0 mg, 81%). mp = 102-104 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 2H), 7.31–7.24 (m, 3H), 7.11 (d, J = 7.5 Hz, 2H), 3.39–3.07 (m, 1H), 2.62 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.88, 141.26, 140.11, 139.50, 131.74, 131.72, 129.32, 126.71, 23.21, 21.50 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{18}NOS$ $[M+H]^+$, 260.1104; found: 260.1102.

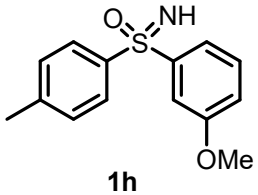
Imino(2-methoxyphenyl) (*p*-tolyl)-λ^6-sulfanone (1g)



1g

(2-Methoxyphenyl)(*p*-tolyl)sulfane (92.1 mg, 0.4mmol) as starting material. White solid, (80.6 mg, 78%). mp = 141-143 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.55–7.44 (m, 1H), 7.28 (d, J = 8.3 Hz, 2H), 7.09–7.01 (m, 1H), 6.91 (d, J = 8.3 Hz, 1H), 3.78 (s, 3H), 3.24 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.65, 143.20, 139.36, 134.43, 131.49, 129.18, 129.06, 128.74, 120.38, 112.54, 55.84, 21.54 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{16}NO_2S$ $[M+H]^+$, 262.0896; found: 262.0896.

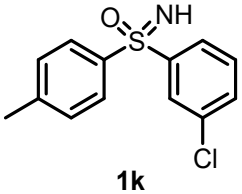
Imino(3-methoxyphenyl) (*p*-tolyl)-λ^6-sulfanone (1h)



1h

(3-Methoxyphenyl)(*p*-tolyl)sulfane (92.1 mg, 0.4mmol) as starting material. White solid, (83.8 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 7.8 Hz, 1H), 7.55 (s, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H), 2.89 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.91, 145.01, 143.47, 140.19, 130.13, 129.79, 127.95, 120.02, 118.77, 112.41, 55.65, 21.47 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{16}NO_2S$ $[M+H]^+$, 262.0896; found: 262.0896.

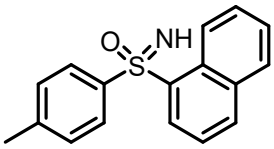
(3-Chlorophenyl) (imino)(*p*-tolyl)-λ^6-sulfanone (1k)



1k

(3-Chlorophenyl)(*p*-tolyl)sulfane (93.9 mg, 0.4mmol) as starting material. White solid, (84.9 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.92 (dd, J = 8.0, 4.5 Hz, 3H), 7.50–7.44 (m, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 3.11 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.66, 143.91, 139.63, 135.18, 132.54, 130.37, 129.7, 128.08, 127.85, 125.91, 21.51 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{13}H_{13}ClNOS$ $[M+H]^+$, 266.0401; found: 266.0401.

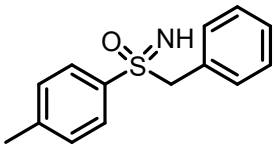
Imino(naphthalen-1-yl) (*p*-tolyl)-λ^6-sulfanone (1n)



1n

Naphthalen-1-yl(*p*-tolyl)sulfane (100.1 mg, 0.4mmol) as starting material. White solid, (91.4 mg, 81%). mp = 156-158 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, J = 8.6 Hz, 1H), 8.56 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.59–7.47 (m, 3H), 7.22 (d, J = 8.1 Hz, 2H), 3.36 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.31, 139.55, 138.51, 134.47, 134.43, 129.64, 129.50, 128.95, 128.65, 127.88, 127.71, 126.63, 125.00, 124.37, 21.46 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{17}H_{16}NOS$ $[M+H]^+$, 282.0947; found: 282.0947.

Benzyl(imino) (*p*-tolyl)-λ^6-sulfanone (1t)

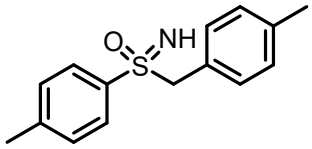


1t

Benzyl(*p*-tolyl)sulfane (85.7 mg, 0.4mmol) as starting material. White solid, (74.3

mg, 76%). mp = 143-145 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 2H), 7.33–7.27 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 4.37 (d, J = 13.4 Hz, 1H), 4.28 (d, J = 13.3 Hz, 1H), 2.75 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.00, 137.36, 131.06, 129.51, 128.88, 128.72, 128.47, 64.66, 21.56 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{16}NOS$ $[M+H]^+$, 246.0947; found: 246.0947

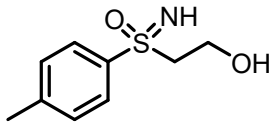
Imino(4-methylbenzyl) (*p*-tolyl)-λ^6-sulfanone (1u)



1u

(4-Methylbenzyl)(*p*-tolyl)sulfane (91.2 mg, 0.4mmol) as starting material. White solid, (79.2 mg, 77%); mp = 108-110 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 4.36 (d, J = 13.4 Hz, 1H), 4.27 (d, J = 13.4 Hz, 1H), 2.77 (s, 1H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.93, 138.68, 137.51, 130.92, 129.51, 129.49, 129.22, 128.88, 125.54, 64.36, 21.57, 21.26 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{18}NOS$ $[M+H]^+$, 260.1104; found: 260.1104.

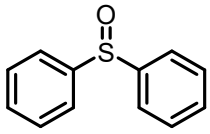
(2-Hydroxyethyl) (imino)(*p*-tolyl)-λ^6-sulfanone (1w)



1w

(4-Methylbenzyl)(*p*-tolyl)sulfane (67.3 mg, 0.4mmol) as starting material. Yellow oil, (60.6 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 4.76 (s, 1H), 4.04 (ddd, J = 12.9, 6.5, 3.4 Hz, 1H), 3.83 (ddd, J = 12.8, 7.2, 3.3 Hz, 1H), 3.36–3.25 (m, 2H), 2.89 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.64, 138.65, 130.06, 128.40, 58.26, 56.48, 21.58 cm^{-1}.

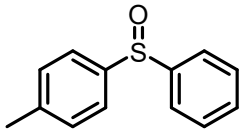
Sulfinyldibenzene (3a)



3a

White solid, (36.7 mg, 91%). mp = 70- 71 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.62 (m, 4H), 7.48–7.41 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.58, 131.07, 129.34, 124.79 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{12}H_{10}OSNa$ $[M + Na]^+$, 225.0345; found: 225.0345.

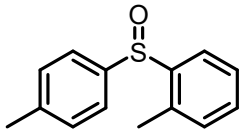
1-Methyl-4-(phenylsulfinyl)benzene (3b)



3b

Yellow solid, (37.9 mg, 88%). mp = 59-61 °C, ^{1}H NMR (500 MHz, $CDCl_3$) 7.65–7.61 (m, 2H), 7.55–7.51 (m, 2H), 7.47–7.42 (m, 3H), 7.26 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.76, 142.42, 141.67, 130.89, 130.04, 129.27, 125.01, 124.70, 21.43 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{13}H_{13}OS$ $[M+H]^+$, 217.0682; found: 217.0682.

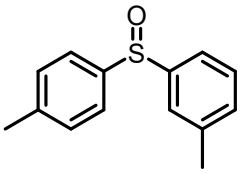
1-Methyl-2-(*p*-tolylsulfinyl)benzene (3c)



3c

White solid, (39.6 mg, 87%). mp = 90-92 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.8, 1.4 Hz, 1H), 7.53–7.45 (m, 2H), 7.41 (td, J = 7.7, 1.3 Hz, 1H), 7.35 (td, J = 7.5, 1.5 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.4 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.99, 141.73, 141.32, 135.56, 130.90, 130.83, 130.01, 127.08, 126.15, 124.48, 21.43, 18.58 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{15}OS$ $[M+H]^+$, 231.0838; found: 231.0838.

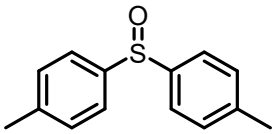
1-Methyl-3-(*p*-tolylsulfinyl)benzene (3d)



3d

Yellow oil, (37.5 mg, 82%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.46 (d, J = 1.7 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.5 Hz, 1H), 2.37 (d, J = 2.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.54, 142.51, 141.55, 139.50, 131.76, 130.01, 129.05, 124.98, 124.90, 121.90, 21.45, 21.43 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{15}OS$ $[M+H]^+$, 231.0838; found: 231.0838.

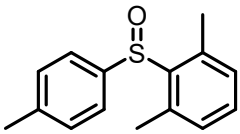
4,4'-Sulfinylbis(methylbenzene) (3e)



3e

Yellow solid, (42.4 mg, 92%). mp = 97-99 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.49 (m, 4H), 7.26–7.23 (m, 4H), 2.36 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.65, 141.44, 129.97, 124.87, 21.41 cm^{-1}; HRMS (ESI) m/z: calcd for C14H15OS $[M+H]^+$, 231.0838; found: 231.0838.

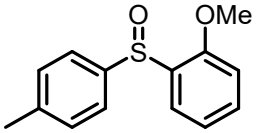
1,3-Dimethyl-2-(*p*-tolylsulfinyl)benzene (3f)



3f

White solid, (40.6 mg, 83%). mp = 95-97 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.28–7.21 (m, 4H), 7.05 (d, J = 7.6 Hz, 2H), 2.47 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.78, 139.95, 139.86, 139.70, 131.64, 130.01, 129.62, 124.52, 21.27, 19.46 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{17}OS$ $[M+H]^+$, 244.0995; found: 244.0995.

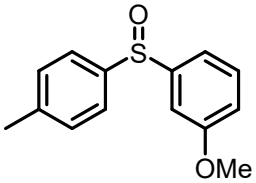
Methoxy-2-(*p*-tolylsulfinyl)benzene (3g)



3g

Pale yellow solid, (43.5 mg, 88%). mp = 104-106 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.7, 1.7 Hz, 1H), 7.61–7.56 (m, 2H), 7.38 (ddd, J = 8.7, 7.5, 1.7 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.17–7.11 (m, 1H), 6.83 (d, J = 8.1 Hz, 1H), 3.77 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.58, 142.32, 141.28, 133.25, 132.04, 129.65, 125.38, 124.52, 121.55, 111.00, 55.66, 21.43 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{15}O_2S$ $[M+H]^+$, 247.0787; found: 247.0787.

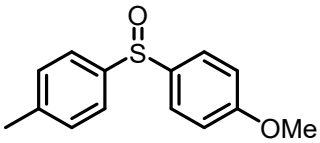
1-Methoxy-3-(*p*-tolylsulfinyl)benzene (3h)



3h

Yellow oil, (40.2 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.48 (m, 2H), 7.34–7.27 (m, 1H), 7.26–7.19 (m, 3H), 7.15–7.09 (m, 1H), 6.91 (d, J = 8.2 Hz, 1H), 3.78 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.30, 147.12, 142.45, 141.67, 130.20, 130.02, 124.94, 117.14, 116.82, 108.98, 55.52, 21.40 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{15}O_2S$ $[M+H]^+$, 247.0787; found: 247.0786.

1-Methoxy-4-(*p*-tolylsulfinyl)benzene (3i)

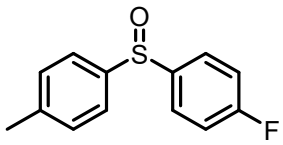


3i

Yellow oil, (44.7 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.9 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 2.36 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.90, 142.62, 141.27, 136.96,

129.92, 127.10, 124.75, 114.77, 55.50, 21.39 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{14}H_{15}O_2S$ $[M+H]^+$, 247.0787; found: 247.0787.

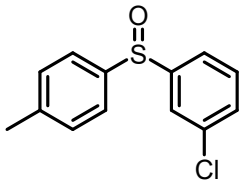
Fluoro-4-(*p*-tolylsulfinyl)benzene (3j)



3j

Yellow oil, (42.5 mg, 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.63–7.57 (m, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 8.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.16 (d, J = 251.5 Hz), 142.24, 141.84, 141.42 (d, J = 3.2 Hz), 130.12, 127.06 (d, J = 8.8 Hz), 124.80, 116.55 (d, J = 22.6 Hz), 21.40 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{13}H_{12}FOS$ $[M+H]^+$, 235.0587; found: 235.0587.

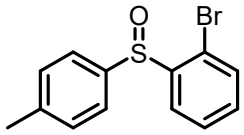
1-Chloro-3-(*p*-tolylsulfinyl)benzene (3k)



3k

White solid, (42.8 mg, 86%). mp = 88-90 °C, ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.50–7.46 (m, 1H), 7.39–7.36 (m, 2H), 7.27 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.93, 142.18, 141.90, 135.51, 130.97, 130.46, 130.24, 125.00, 124.44, 122.64, 21.45 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{13}H_{12}ClOS$ $[M+H]^+$, 251.0292; found: 251.0290.

Bromo-2-(*p*-tolylsulfinyl)benzene (3l).

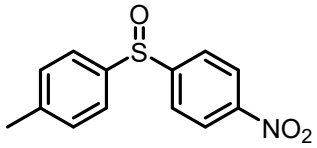


3l

White solid, (49.7 mg, 85%). mp = 100-102 °C, ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.8, 1.7 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.54 (td, J = 7.6, 1.2 Hz, 1H), 7.49 (dd, J = 7.9, 1.1 Hz, 1H), 7.30 (td, J = 7.7, 1.7 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 2.33

(s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.00, 142.16, 141.22, 133.12, 132.20, 129.98, 128.52, 126.42, 126.20, 119.93, 21.51 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{13}H_{12}BrOS$ $[M+H]^+$, 294.9787; found: 294.9781

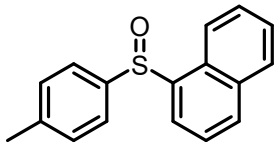
1-Methyl-4-((4-nitrophenyl)sulfinyl)benzene (3m)



3m

White solid, (46.3 mg, 89%). mp = 127-129 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.9 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.24, 149.17, 142.89, 141.26, 130.51, 125.26, 125.17, 124.38, 21.50 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{13}H_{11}NO_3S$ $[M+H]^+$, 262.0532; found: 262.0532.

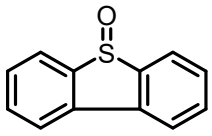
1-(*p*-Tolylsulfinyl)naphthalene (3n)



3n

White solid, (47.9 mg, 90%). MP = 113-115 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 1H), 8.16 (dt, J = 6.2, 3.5 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.89 (dt, J = 6.3, 3.5 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.52 (dt, J = 6.4, 3.5 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.85, 141.64, 140.54, 133.73, 131.62, 130.01, 129.23, 128.89, 127.23, 126.64, 125.64, 125.52, 123.86, 122.52, 21.39 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{17}H_{15}OS^+$: 267.0838; found: 267.0838.

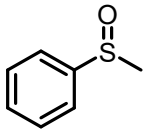
Dibenzo[*b*,*d*]thiophene 5-oxide (3o)



3o

White solid, (31.8 mg, 80%). mp = 178-180 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.98, 137.10, 132.61, 129.58, 127.56, 121.95 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{17}OS$ $[M+H]^+$, 201.0369; found: 201.0367.

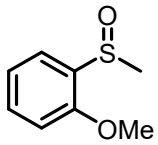
(Methylsulfinyl)benzene (3p)



3p

Colorless oil, (34.5 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65–7.61 (m, 2H), 7.53–7.45 (m, 3H), 2.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.45, 130.84, 129.16, 123.28, 43.76 cm^{-1}; HRMS (ESI) m/z: calcd for C_7H_9OS $[M+H]^+$, 141.0369; found: 141.0367.

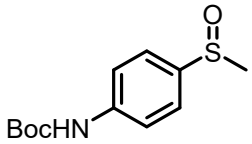
1-Methyl-4-(phenylsulfinyl)benzene (3q)



3q

Yellow oil, (25.9 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.6, 1.8 Hz, 1H), 7.45 (td, J = 7.8, 1.7 Hz, 1H), 7.18 (td, J = 7.6, 0.9 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 3.88 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.79, 133.04, 131.96, 124.63, 121.71, 110.56, 55.71, 41.20 cm^{-1}; HRMS (ESI) m/z: calcd for $C_8H_{11}O_2S$ $[M+H]^+$, 171.0474; found: 171.0471.

1-Methyl-4-(phenylsulfinyl)benzene (3r)

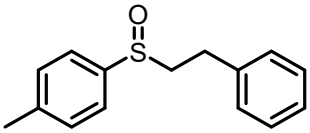


3r

White solid, (33.3 mg, 66%). mp = 174-176 °C , ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.60–7.52 (m, 4H), 6.74 (s, 1H), 2.70 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.37, 141.25, 138.94, 124.75, 118.82, 81.27, 44.05, 28.29 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{12}H_{18}NO_3S$ $[M+H]^+$, 256.1002; found: 256.0998.

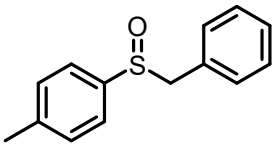
1-Methyl-4-(phenethylsulfinyl)benzene (3s)



3s

Colorless oil, (38.8 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.33–7.28 (m, 2H), 7.24 (t, J = 7.3 Hz, 1H), 7.20 (d, J = 7.0 Hz, 2H), 3.13–3.01 (m, 3H), 2.95–2.87 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.52, 140.34, 138.85, 129.98, 128.73, 128.54, 126.66, 124.08, 58.35, 28.22, 21.44 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{17}OS$ $[M+H]^+$, 245.0995; found: 245.0995.

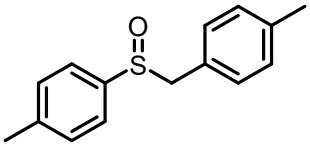
1-(Benzylsulfinyl)-4-methylbenzene (3t)



3t

White solid, (34.5 mg, 74%). mp = 146-148 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.26 (m, 5H), 7.25 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 7.3 Hz, 2H), 4.11 (d, J = 12.6 Hz, 1H), 3.99 (d, J = 12.5 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.64, 139.57, 130.37, 129.57, 129.34, 128.45, 128.19, 124.48, 63.72, 21.46 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{17}OS$ $[M+H]^+$, 231.0838; found: 231.0839.

1-Methyl-4-((4-methylbenzyl)sulfinyl)benzene (3u)

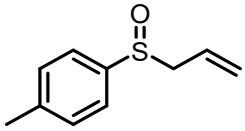


3u

White solid, (28.5 mg, 58%). mp = 141-143 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29

(d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 4.05 (d, J = 12.6 Hz, 1H), 3.93 (d, J = 12.6 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.55, 139.75, 138.05, 130.26, 129.56, 129.19, 126.24, 124.51, 63.54, 21.48, 21.22 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{15}H_{17}OS$ $[M+H]^+$, 245.0995; found: 245.0995.

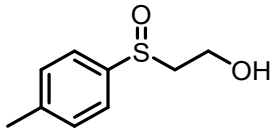
1-(Allylsulfinyl)-4-methylbenzene (3v)



3v

Colorless oil, (24.1 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.70–5.57 (m, 1H), 5.32 (d, J = 10.1 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 3.52 (qd, J = 12.8, 7.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.59, 139.66, 129.77, 125.41, 124.39, 123.78, 60.95, 21.46 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{10}H_{13}OS$ $[M+H]^+$, 181.0682; found: 181.0681.

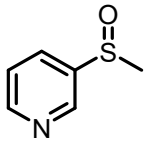
2-(*p*-Tolylsulfinyl)ethan-1-ol (3w)



3w

White solid, (25.5 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.16 (ddd, J = 12.1, 8.7, 3.1 Hz, 1H), 4.00 (dt, J = 12.2, 4.7 Hz, 1H), 3.68 (s, 1H), 3.13 (ddd, J = 13.1, 8.7, 3.9 Hz, 1H), 2.87 (ddd, J = 13.6, 5.5, 3.1 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.81, 139.65, 130.14, 124.03, 58.29, 57.11, 21.45 cm^{-1}.

3-(Methylsulfinyl)pyridine (3x)

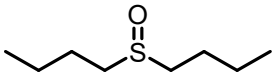


3x

Colorless liquid (28.2 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 4.6 Hz,

1H), 7.94 (d, J = 7.9 Hz, 1H), 7.88 (td, J = 7.7, 1.7 Hz, 1H), 7.32 (ddd, J = 7.5, 4.7, 1.3 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.80, 149.53, 138.13, 124.62, 119.19, 41.25 cm^{-1}; HRMS (ESI) m/z: calcd for C_6H_8NOS $[M+H]^+$, 142.0321; found: 142.0322.

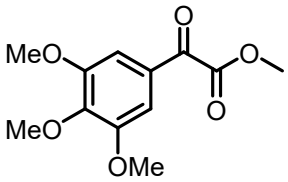
1-(Butylsulfinyl)butane (3y)



3y

Colorless liquid, (23.2 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74–2.57 (m, 4H), 1.76–1.66 (m, 4H), 1.52–1.36 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 51.87, 24.58, 22.03, 13.66 cm^{-1}; HRMS (ESI) m/z: calcd for $C_8H_{19}OS$ $[M+H]^+$, 163.1151; found: 163.1151.

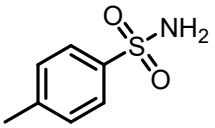
Methyl 2-oxo-2-(3,4,5-trimethoxyphenyl)acetate (4)



4

White solid, (101.7mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 2H), 4.00 (s, 3H), 3.97 (s, 3H), 3.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.55, 163.93, 153.21, 144.42, 127.32, 107.52, 61.09, 56.35, 52.86 cm^{-1}.

4-Methylbenzenesulfonamide (5)



5

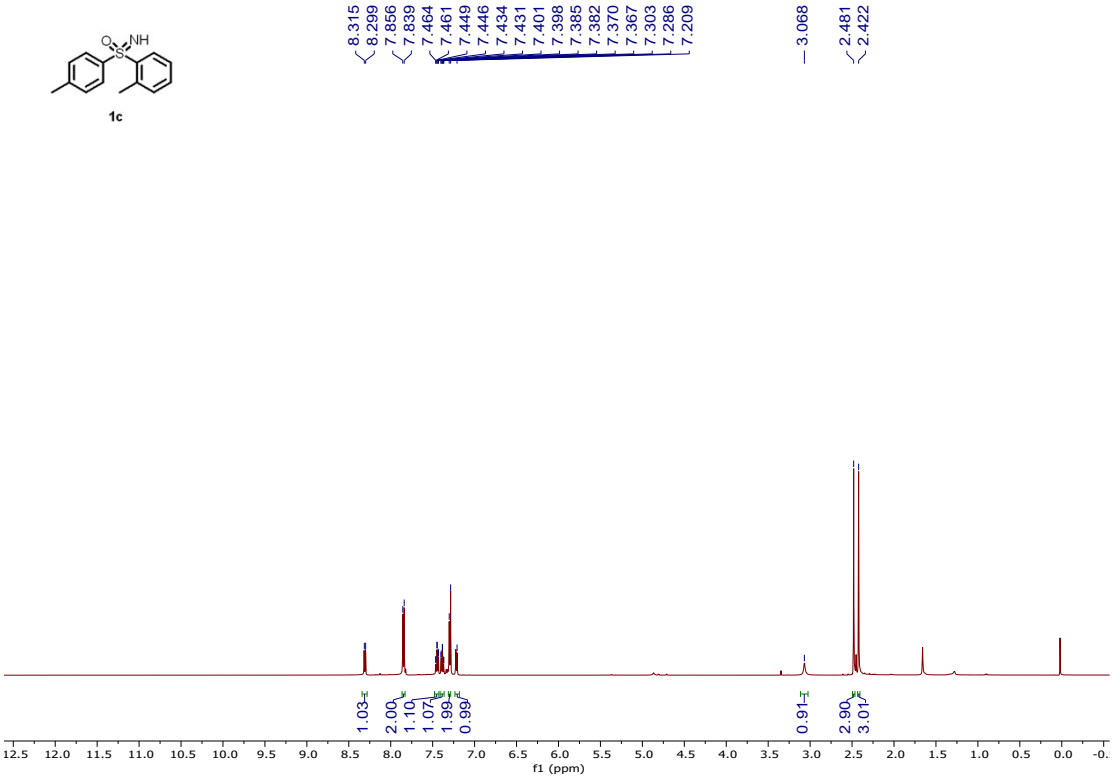
White solid, (47.0 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.03 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.62, 139.06, 129.73, 126.44, 21.56. cm^{-1}

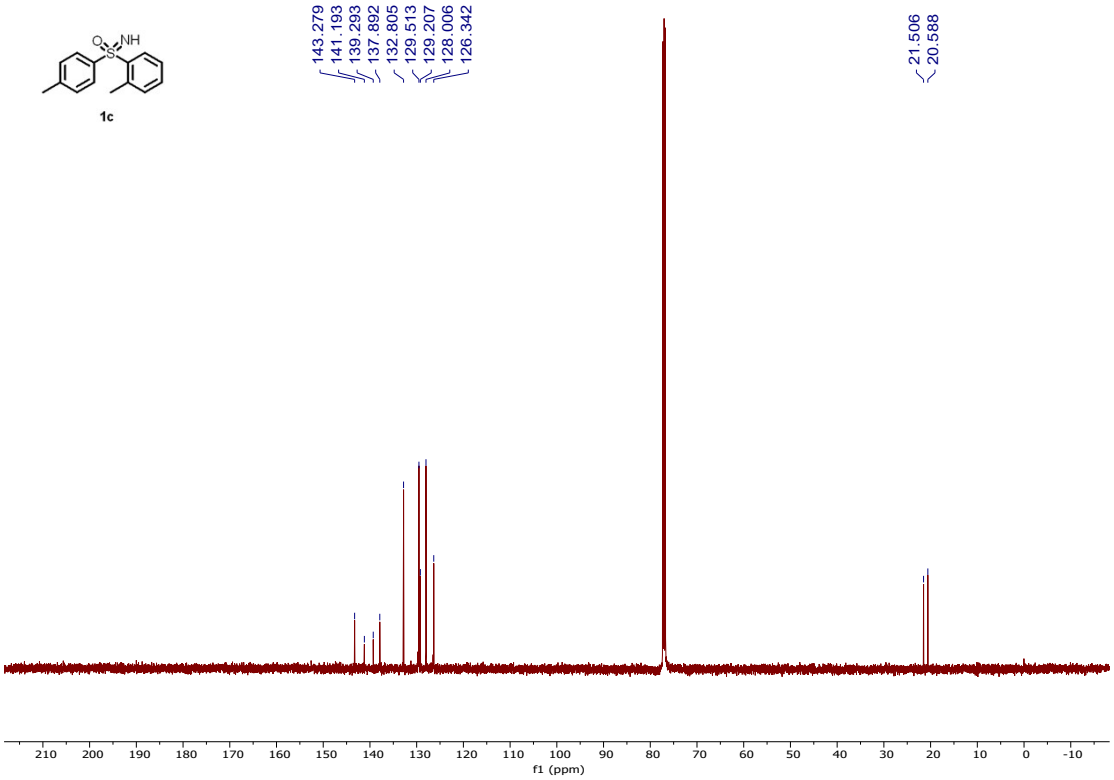
7. References

[1] (a) A. V. Dubey, S. B. Gharat and A. Vijay Kumar, *ChemistrySelect*, 2017, **2**, 4852-4856; (b) A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi, *Chem. Commun.*, 2017, **53**, 348-351.

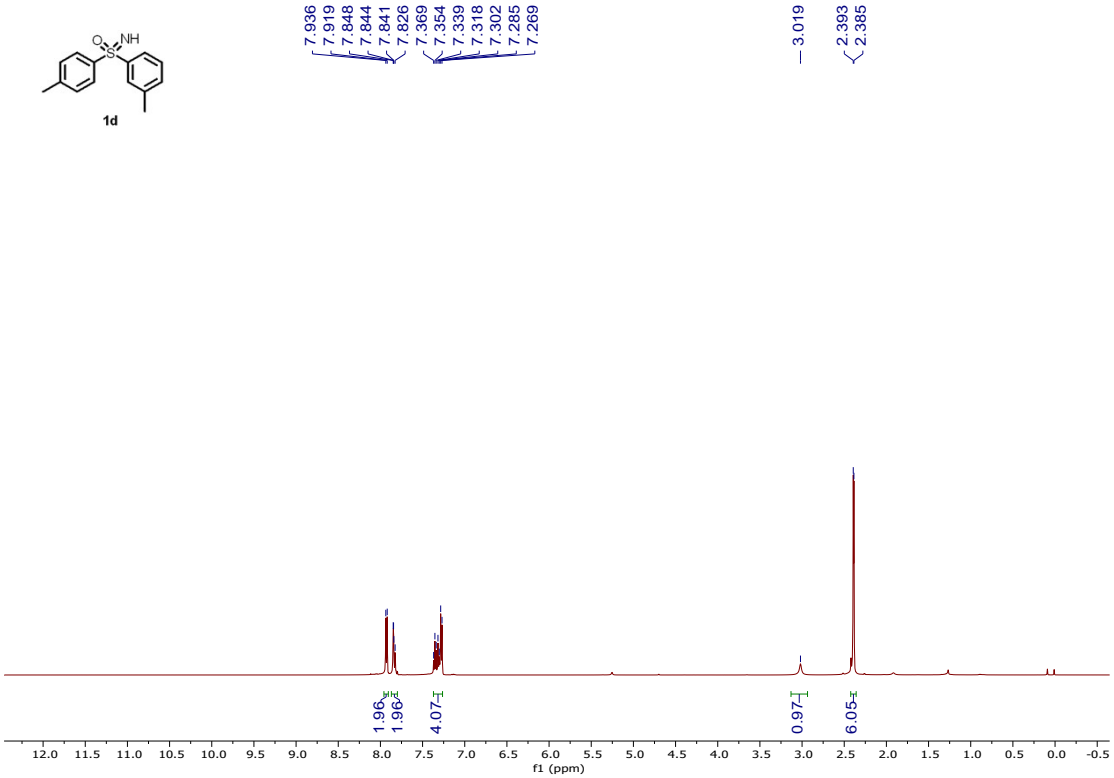
[2] F. W. Patureau, J. Groß, J. M. Ernsting, C. van Wüllen and J. N. H. Reek, *Eur. J. Inorg. Chem.*, 2018, **2018**, 3761-3769.

8. ^{1}H and ^{13}C NMR Spectra





1d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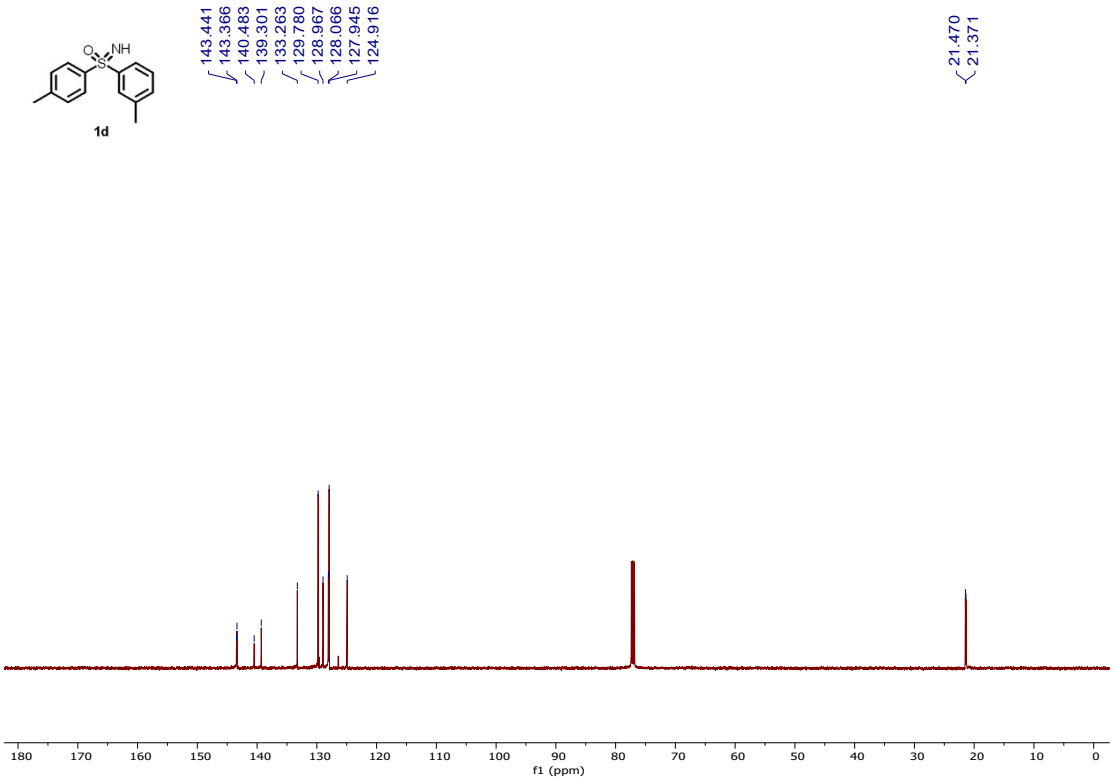
7.848
7.844
7.841
7.826
7.369
7.354
7.339
7.318
7.302
7.285
7.269
3.019
2.393
2.385
1.96
1.96
4.07
0.97
6.05
f1 (ppm)

1d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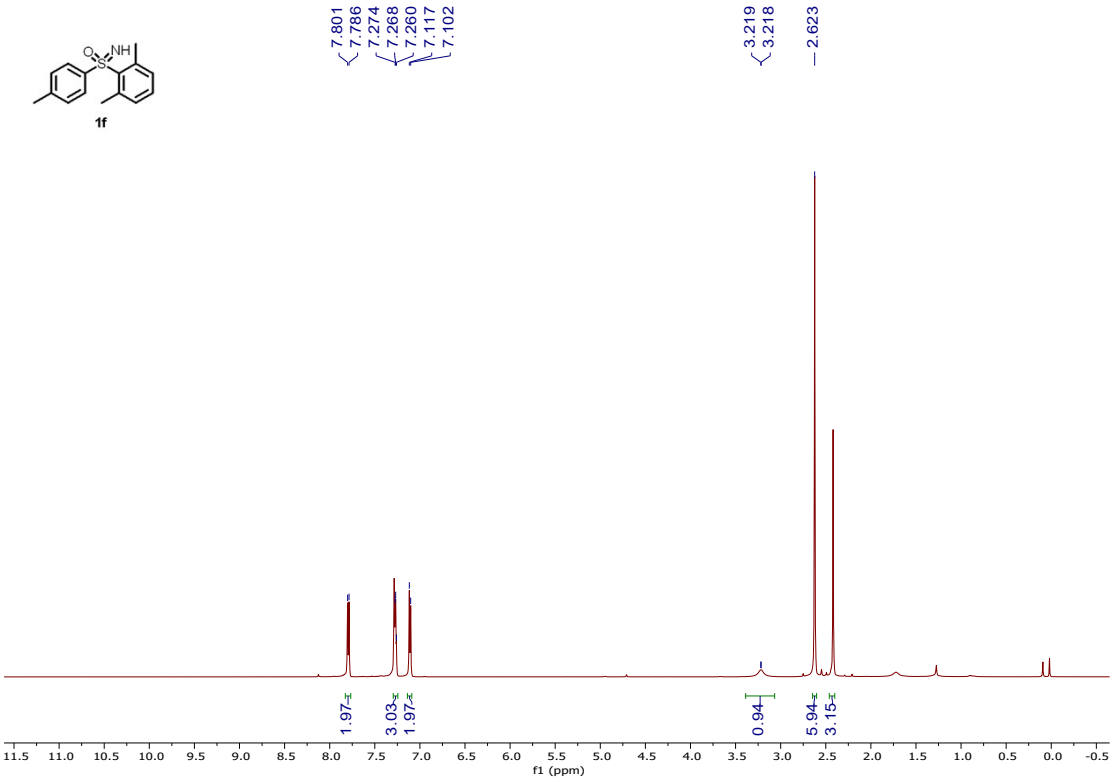
143.366
140.483
139.301
133.263
129.780
128.967
128.066
127.945
124.916
21.470
21.371
f1 (ppm)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7.786
7.274
7.268
7.260
7.117
7.102
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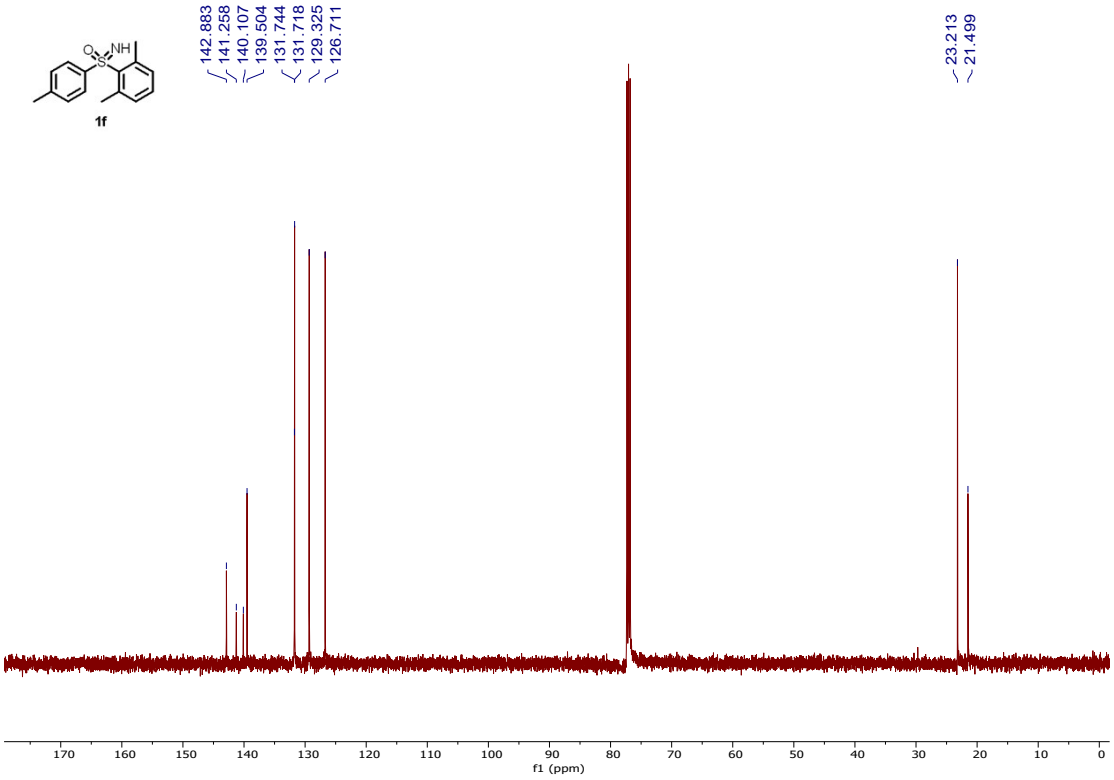
3.218
2.623
1.97
3.03
1.97
0.94
5.94
3.15
f1 (ppm)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131.718
129.325
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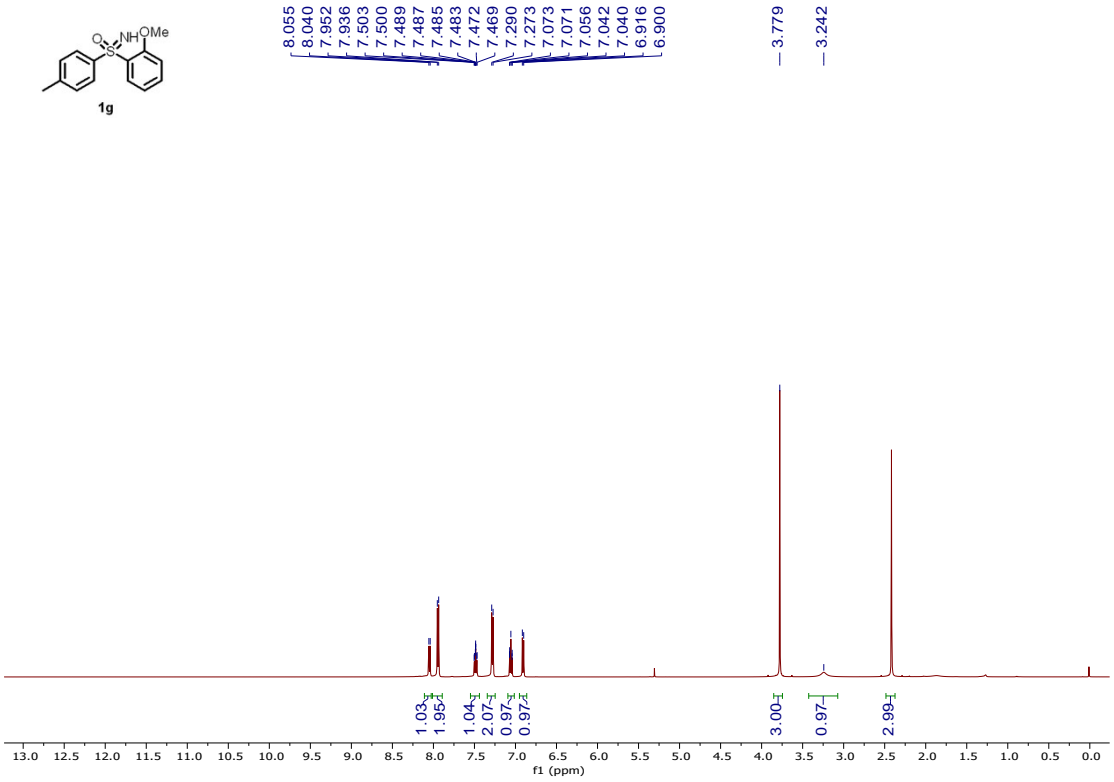
23.213
21.499
f1 (ppm)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8.040
7.952
7.936
7.503
7.500
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7.487
7.485
7.483
7.472
7.469
7.290
7.273
7.073
7.071
7.056
7.042
7.040
6.916
6.900
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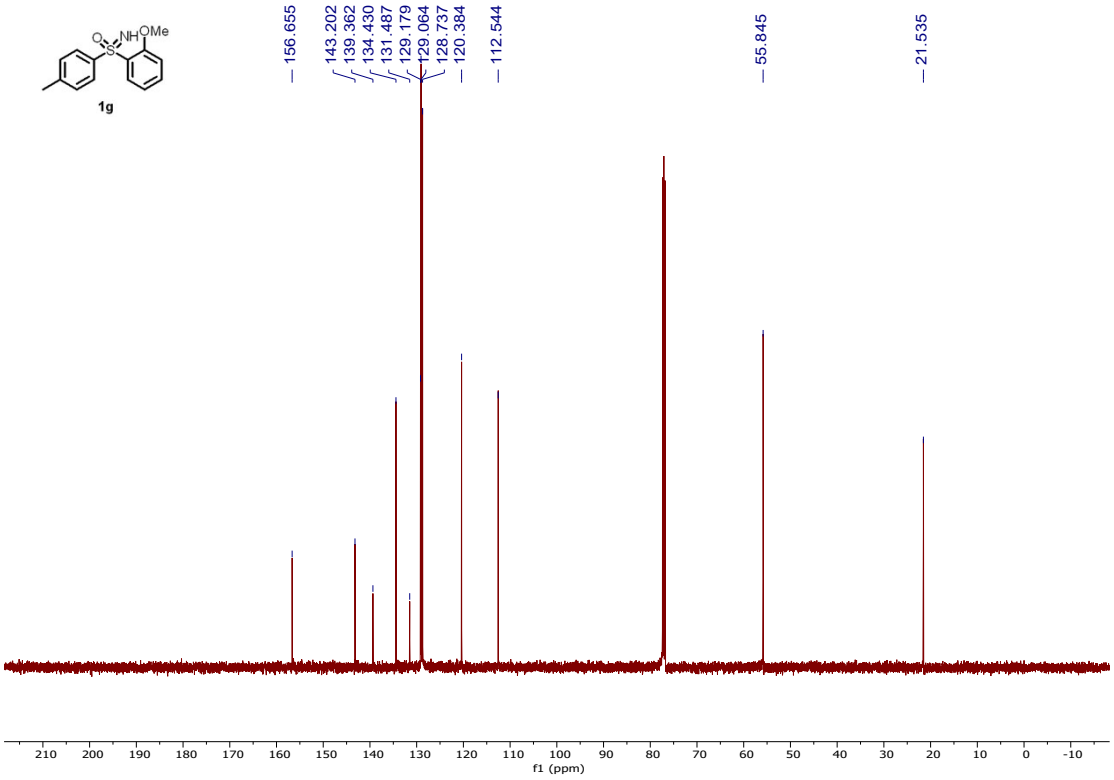
3.242
1.03
1.95
1.04
2.07
0.97
0.97
3.00
0.97
2.99
f1 (ppm)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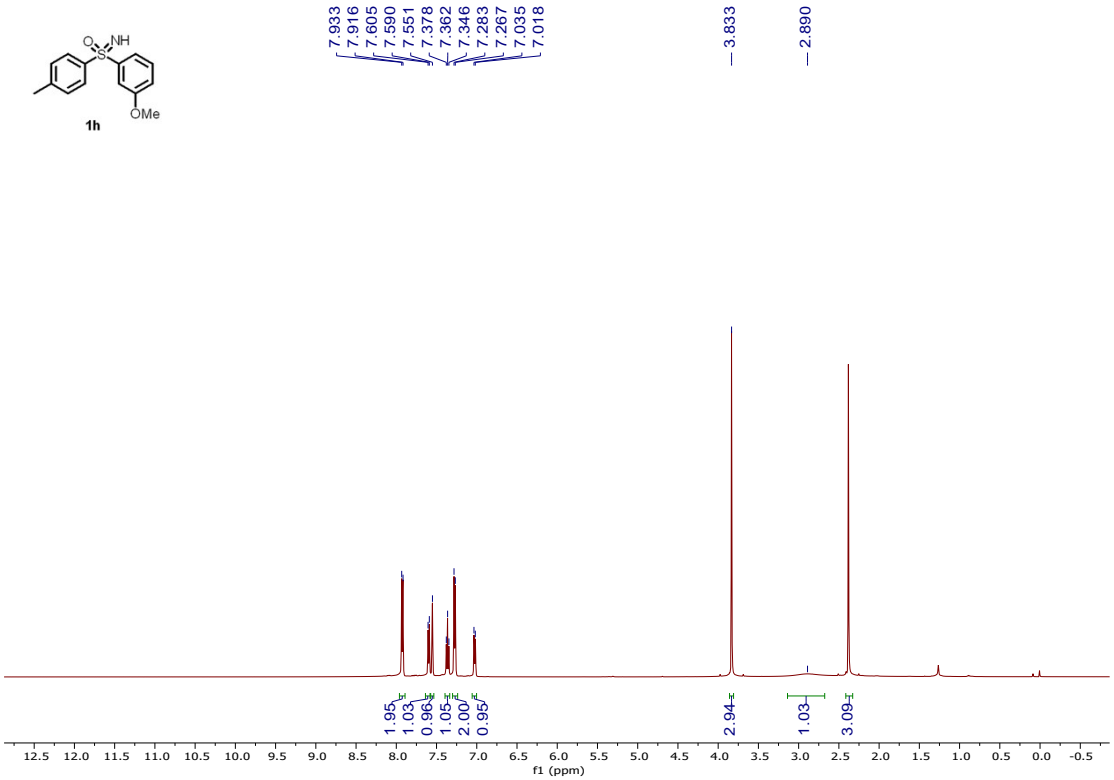
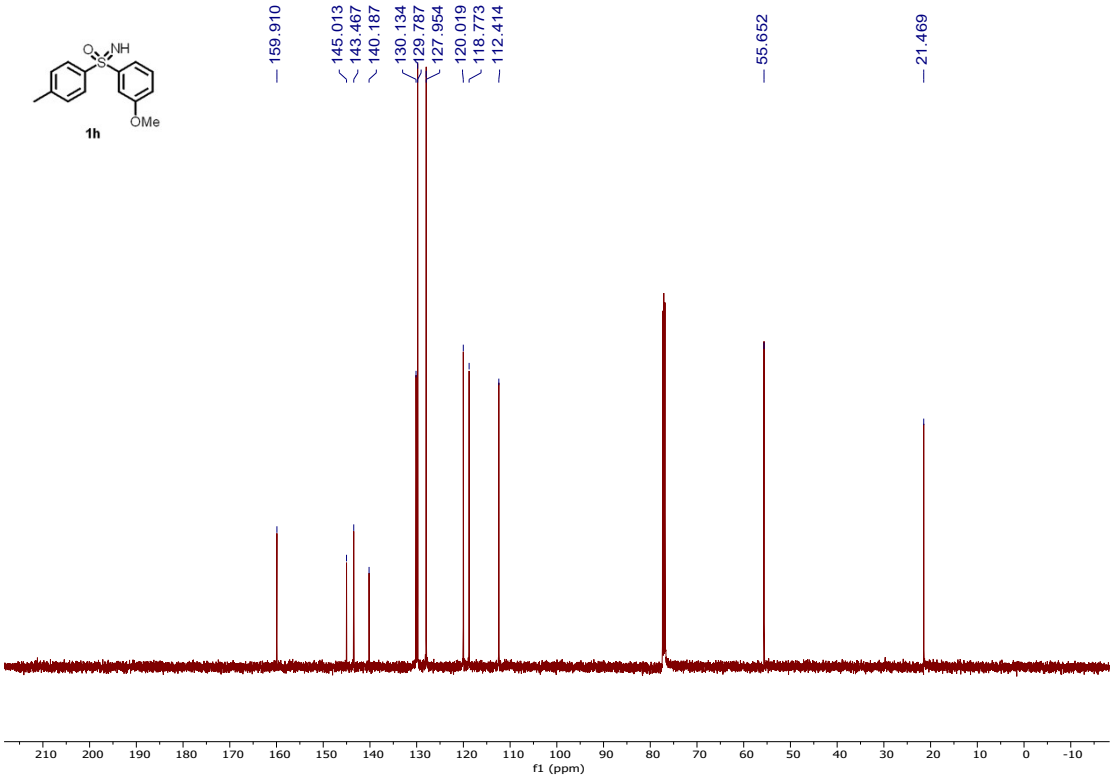
21.535
f1 (ppm)


7.933
7.916
7.605
7.590
7.551
7.378
7.362
7.346
7.283
7.267
7.035
7.018
3.833
2.890
1.95
1.03
0.96
1.05
2.00
0.95
2.94
1.03
3.09
f1 (ppm)


159.910
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140.187
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129.787
127.954
120.019
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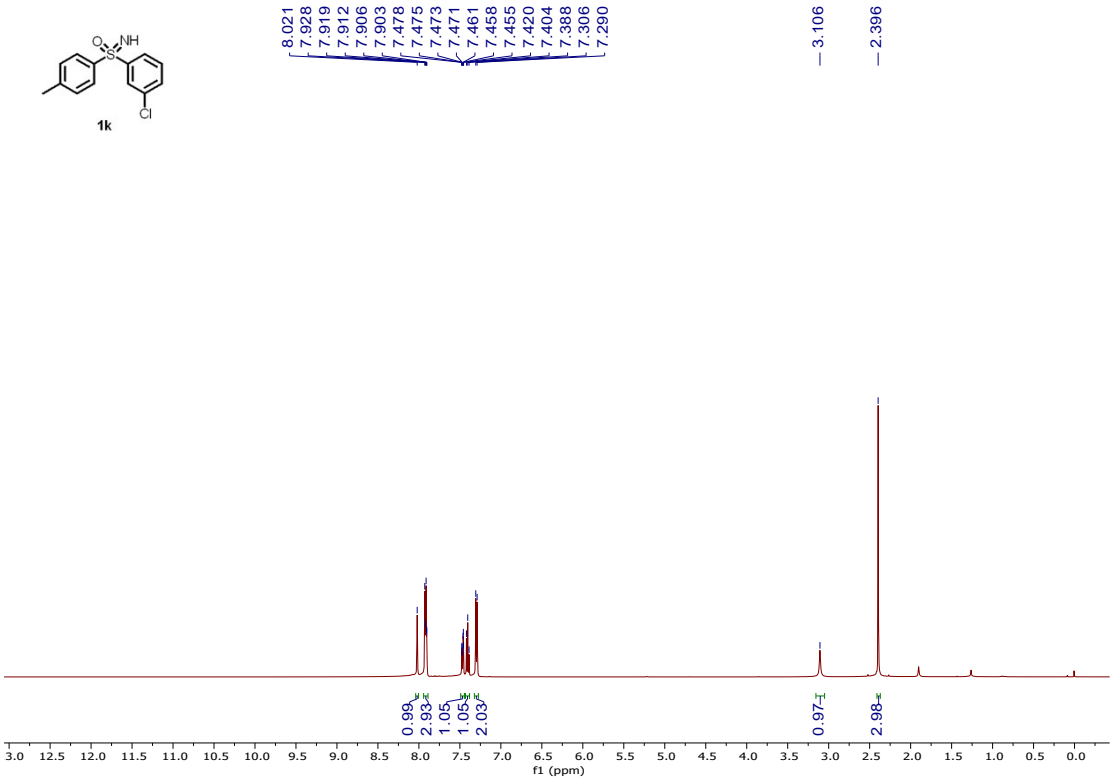
55.652
21.469
f1 (ppm)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7.912
7.906
7.903
7.478
7.475
7.473
7.471
7.461
7.458
7.455
7.420
7.404
7.388
7.306
7.290
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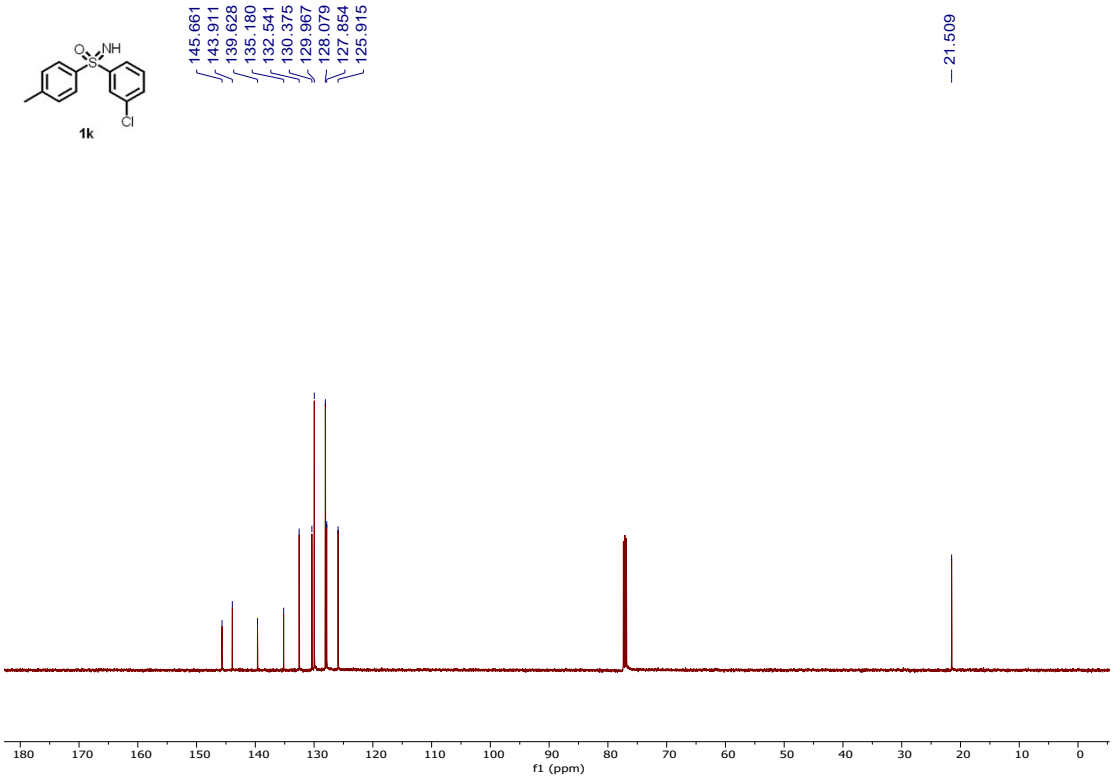
2.396
0.99
2.93
1.05
1.05
2.03
0.97
2.98
f1 (ppm)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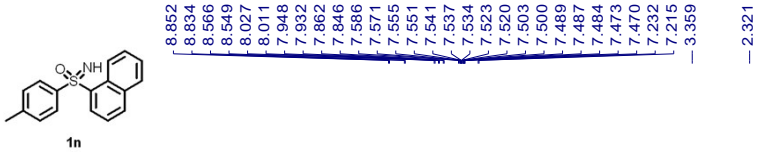
21.509
f1 (ppm)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8.566
8.549
8.027
8.011
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7.932
7.862
7.846
7.586
7.571
7.555
7.551
7.541
7.537
7.534
7.523
7.520
7.503
7.500
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7.484
7.473
7.470
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3.359
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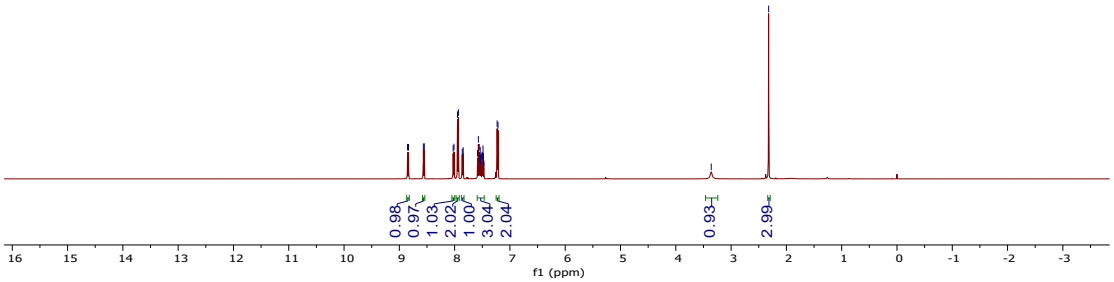
O
S
NH
1n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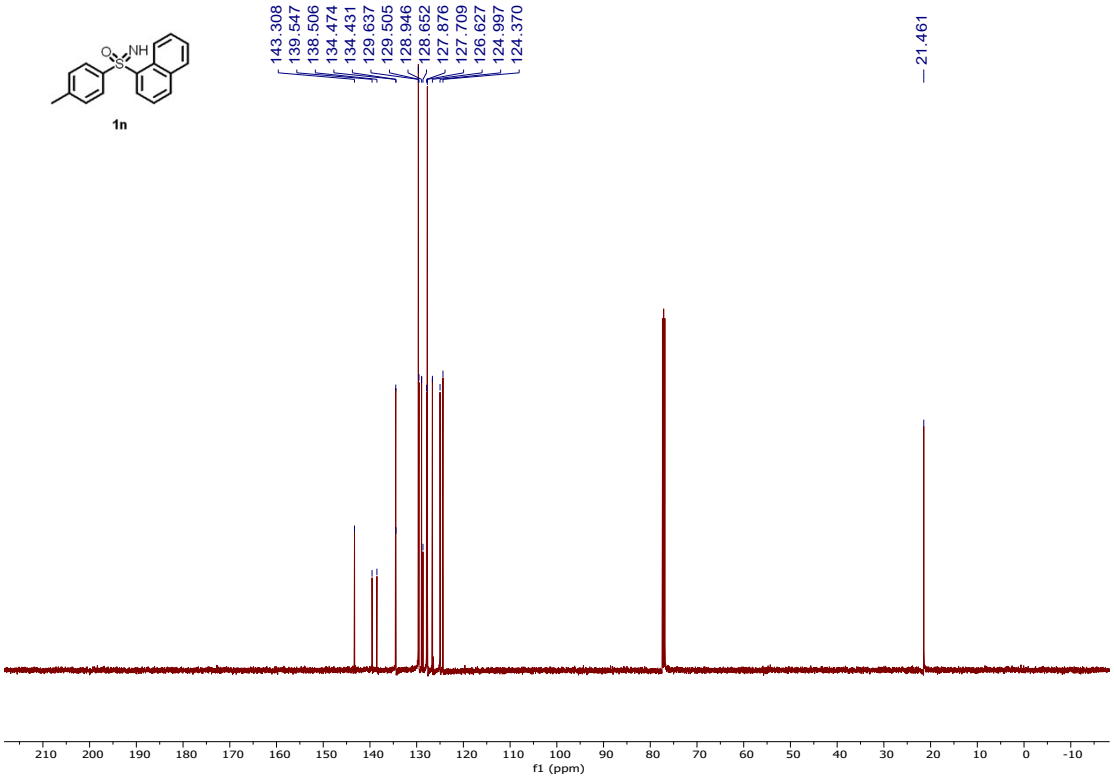
0.97
1.03
2.02
1.00
3.04
2.04
0.93
2.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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O
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NH
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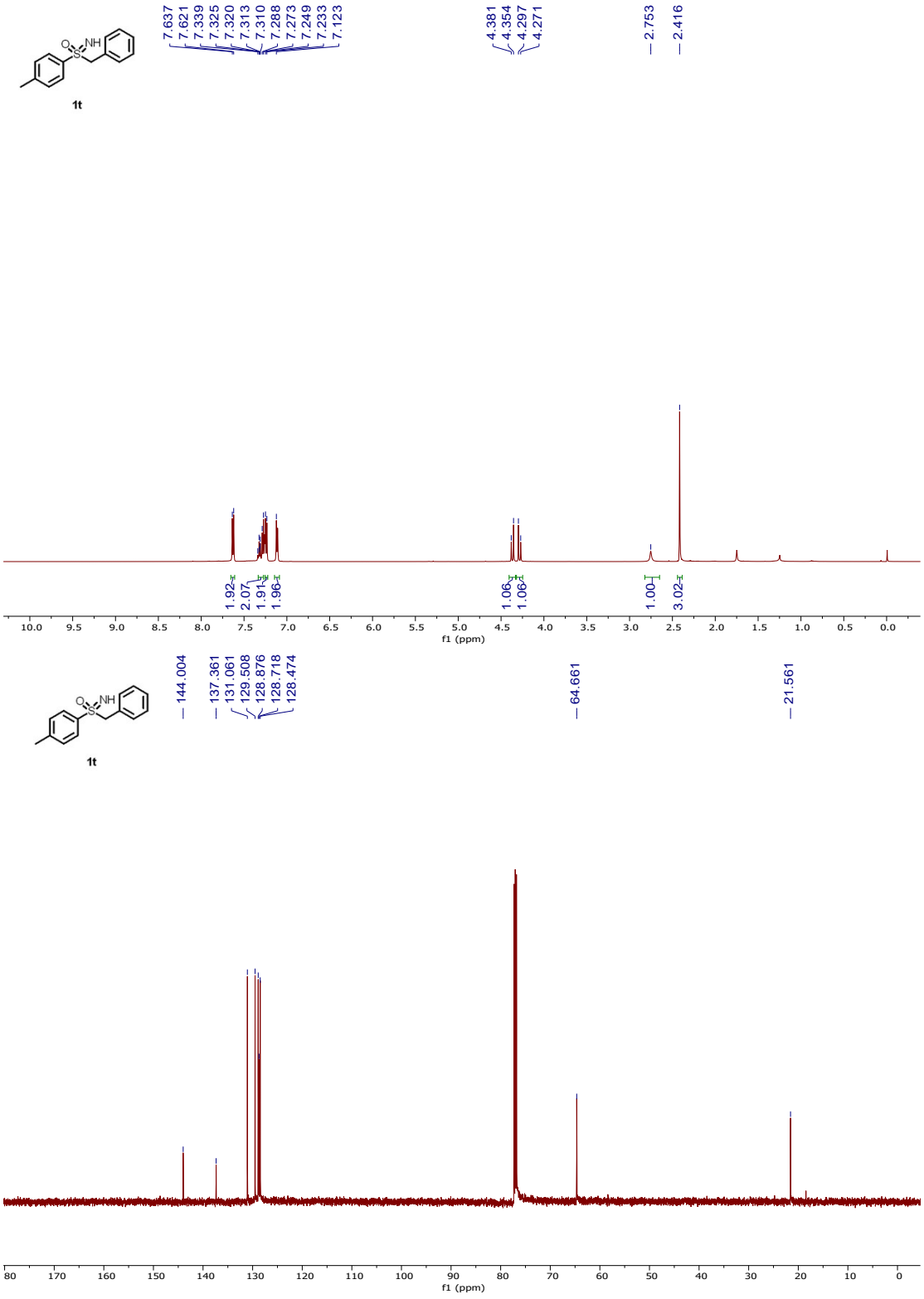
f1 (ppm)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7.310
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7.249
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4.271
2.753
2.416
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2.07
1.91
1.96
1.06
1.06
1.00
3.02
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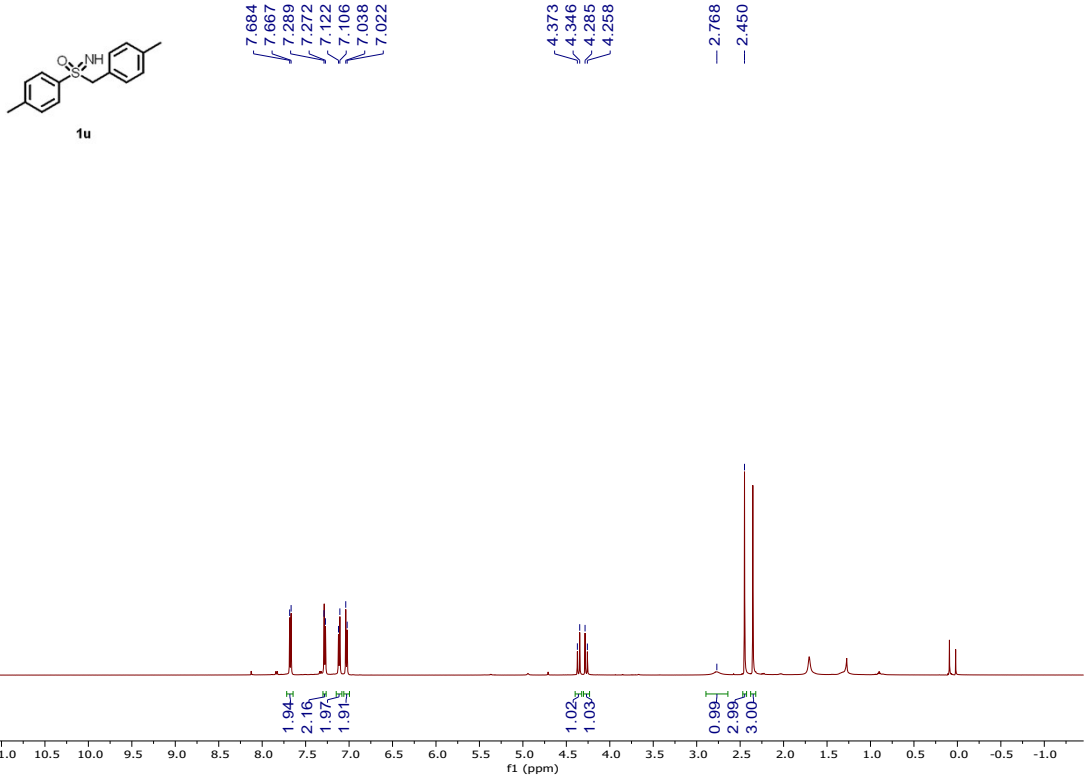
f1 (ppm)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2.16
1.97
1.91
1.02
1.03
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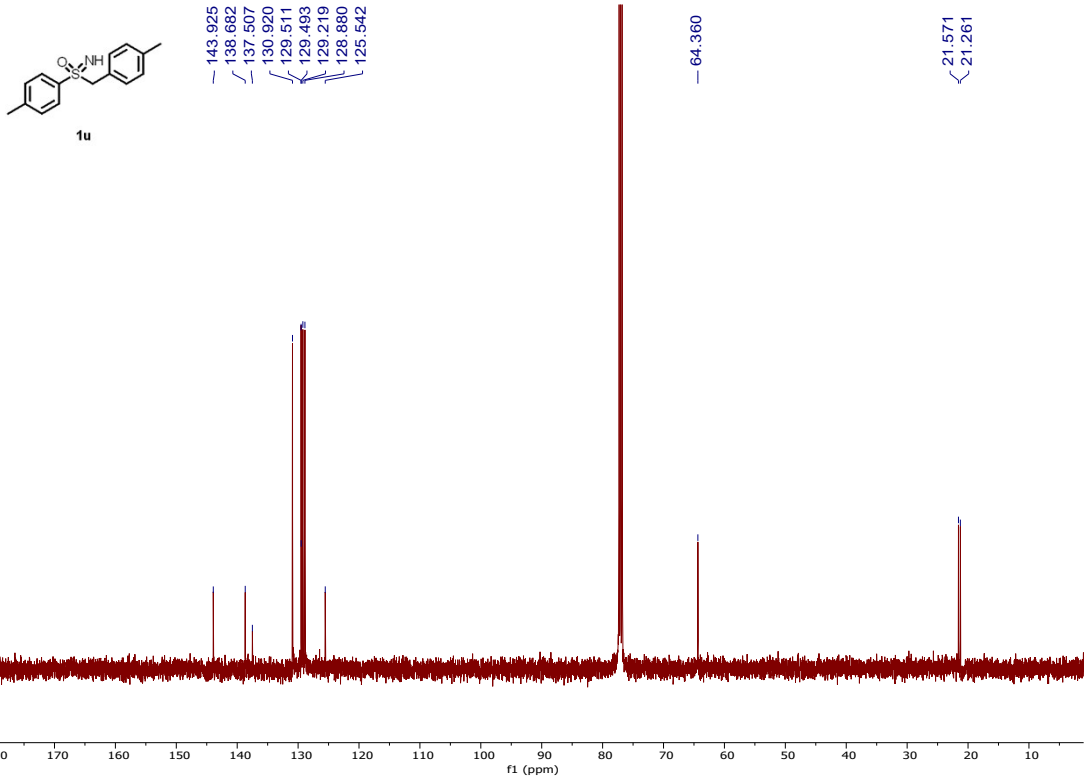
2.99
3.00
f1 (ppm)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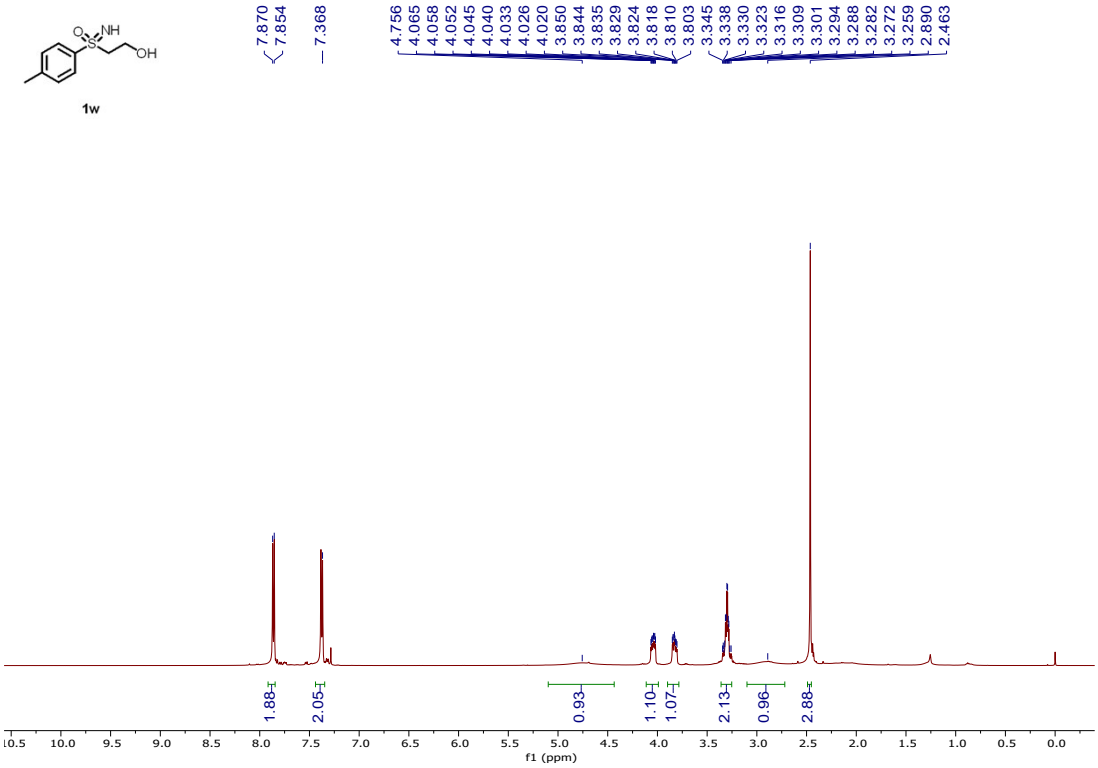
1w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3.824
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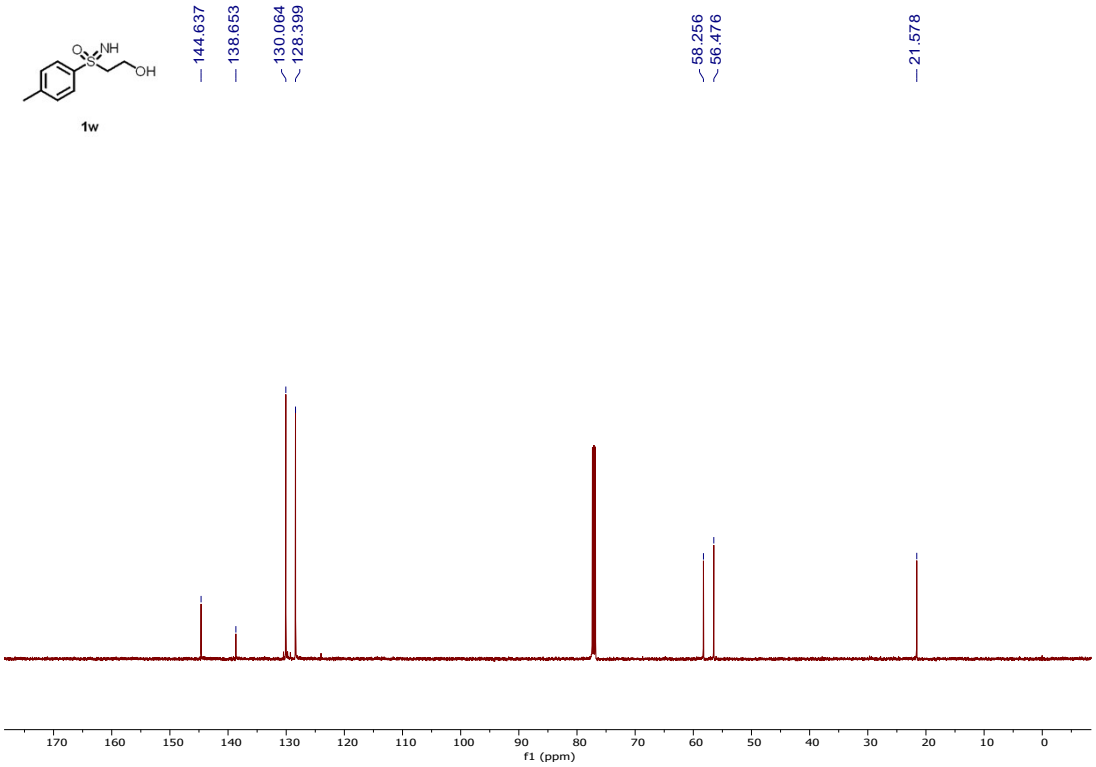
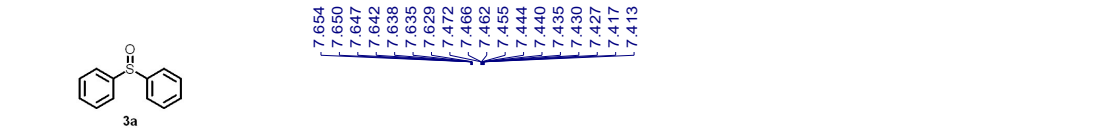
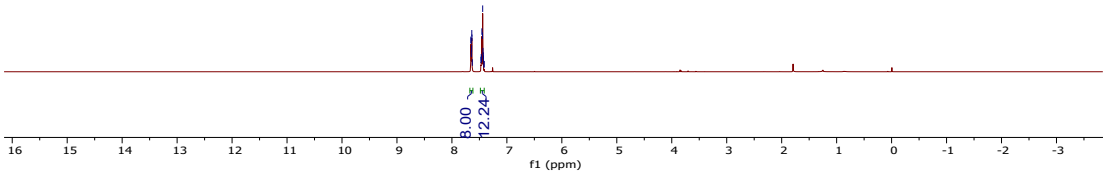
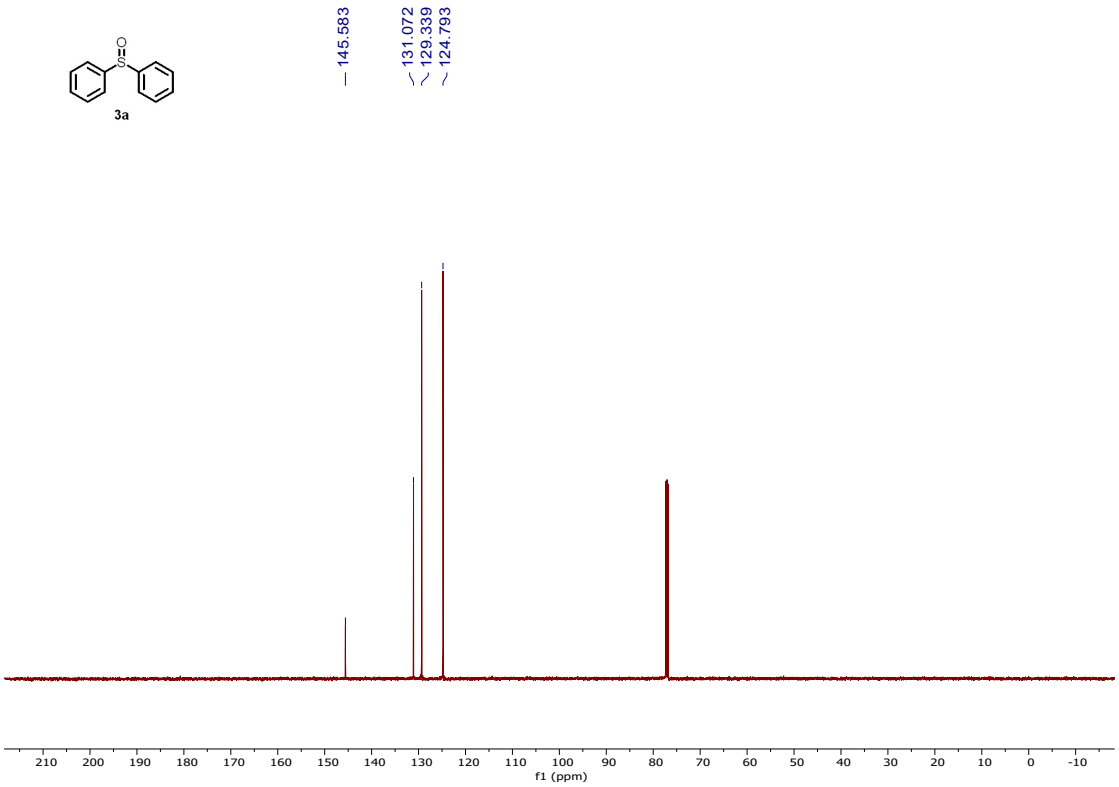
3.803
3.345
3.338
3.330
3.323
3.316
3.309
3.301
3.294
3.288
3.282
3.272
3.259
2.890
2.463
1.88
2.05
0.93
1.10
1.07
2.13
0.96
2.88
f1 (ppm)

1w

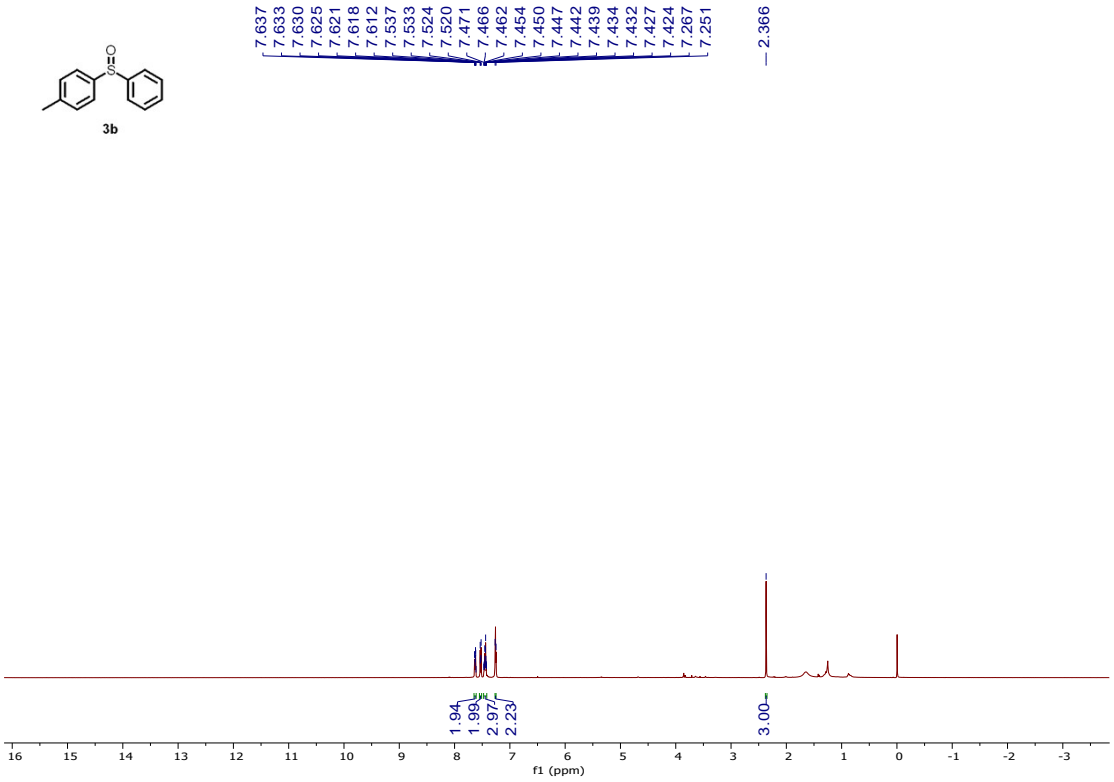

144.637
138.653
130.064
128.399
58.256
56.476
21.578
f1 (ppm)


7.654
7.650
7.647
7.642
7.638
7.635
7.629
7.472
7.466
7.462
7.455
7.444
7.440
7.435
7.430
7.427
7.417
7.413
3a

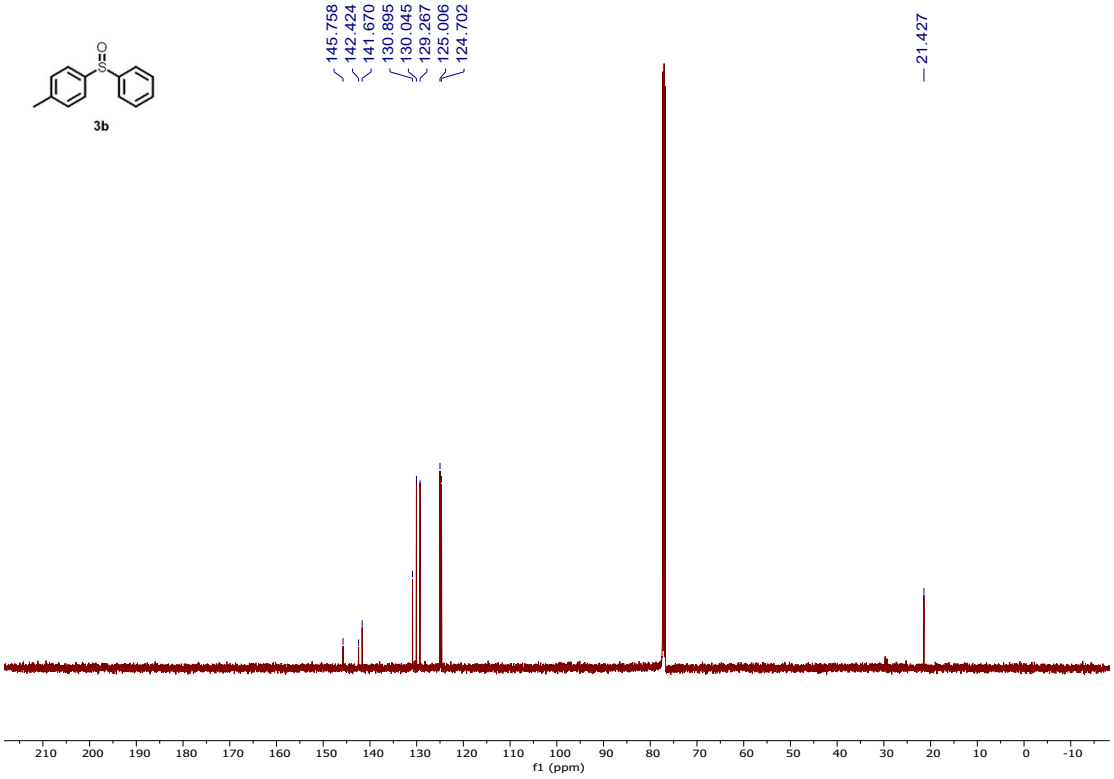

8.00
12.24
f1 (ppm)

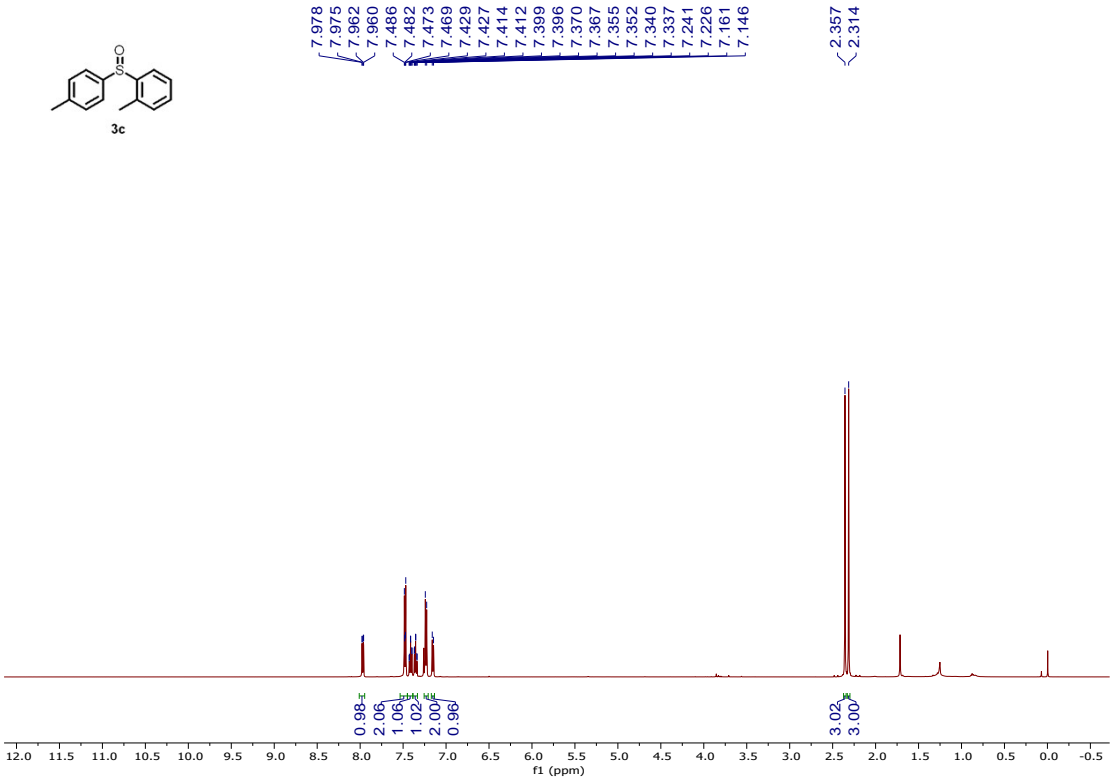

145.583
131.072
129.339
124.793
3a
f1 (ppm)

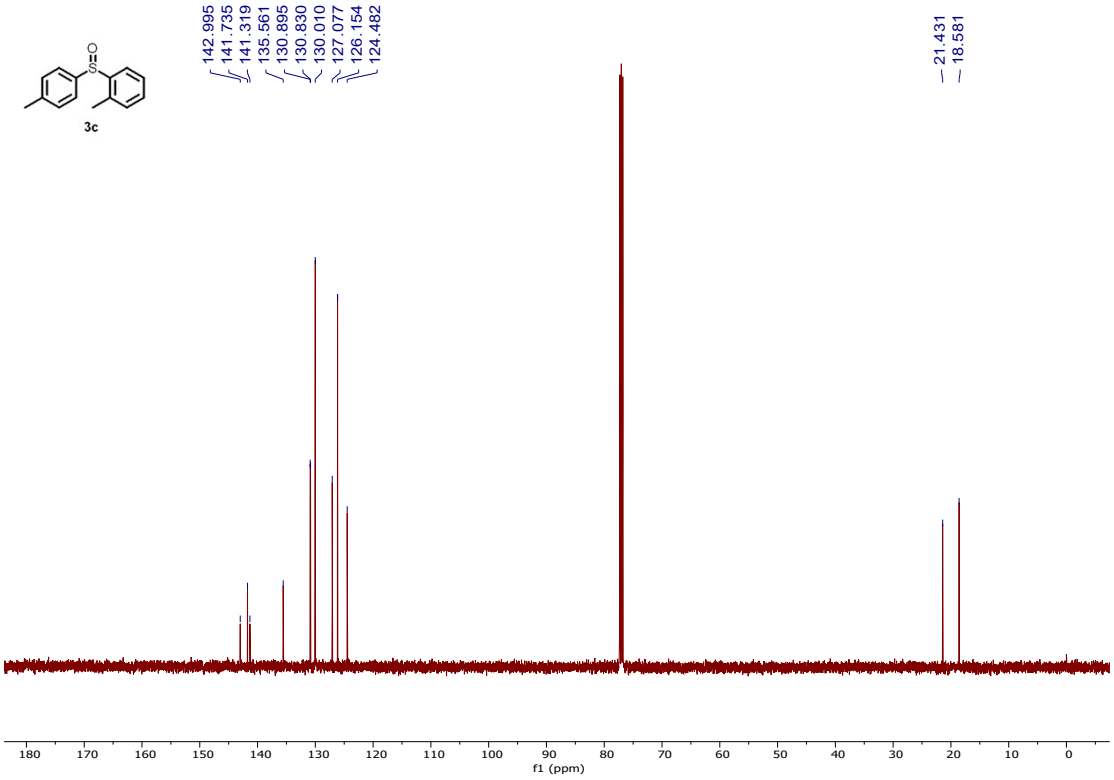
3b

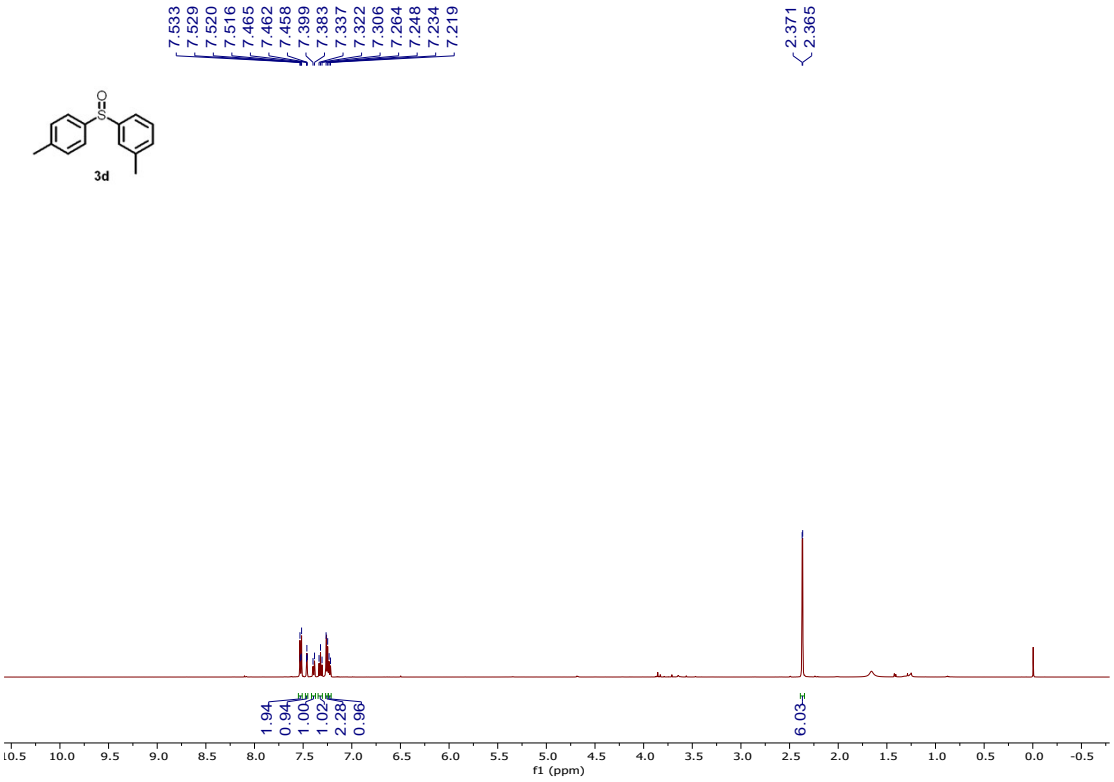

7.637
7.633
7.630
7.625
7.621
7.618
7.612
7.537
7.533
7.524
7.520
7.471
7.466
7.462
7.454
7.450
7.447
7.442
7.439
7.434
7.432
7.427
7.424
7.267
7.251
2.366
1.94
1.99
2.97
2.23
3.00
f1 (ppm)

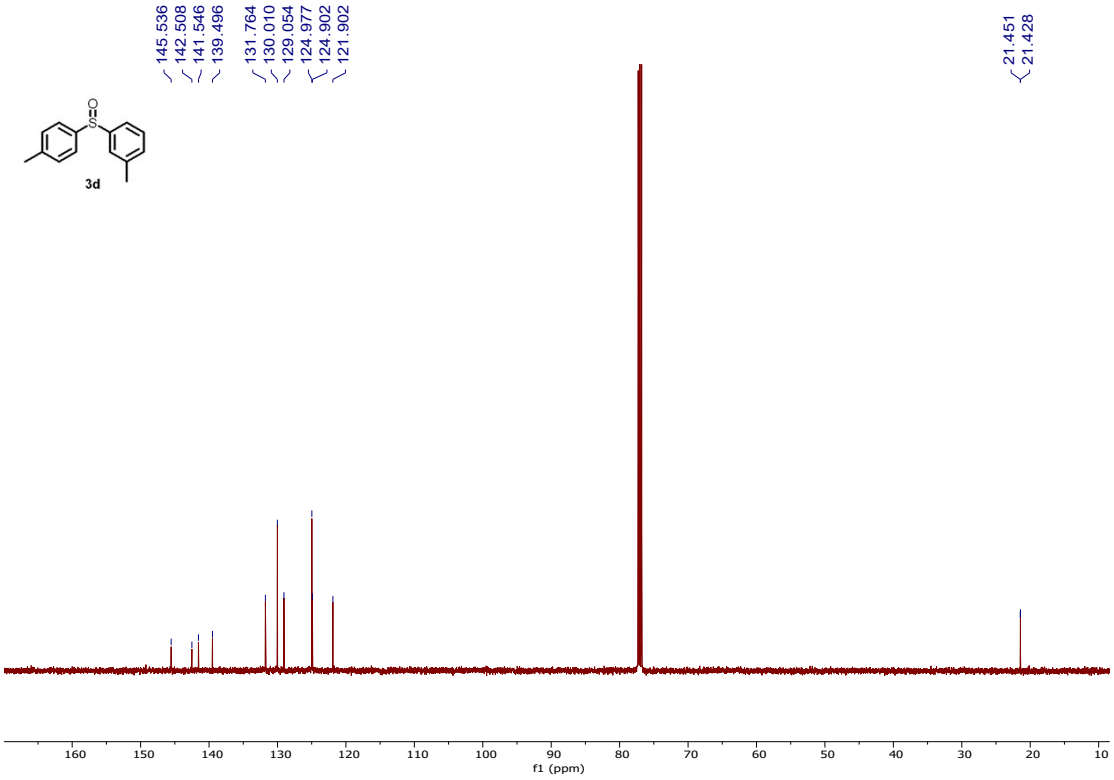
3b

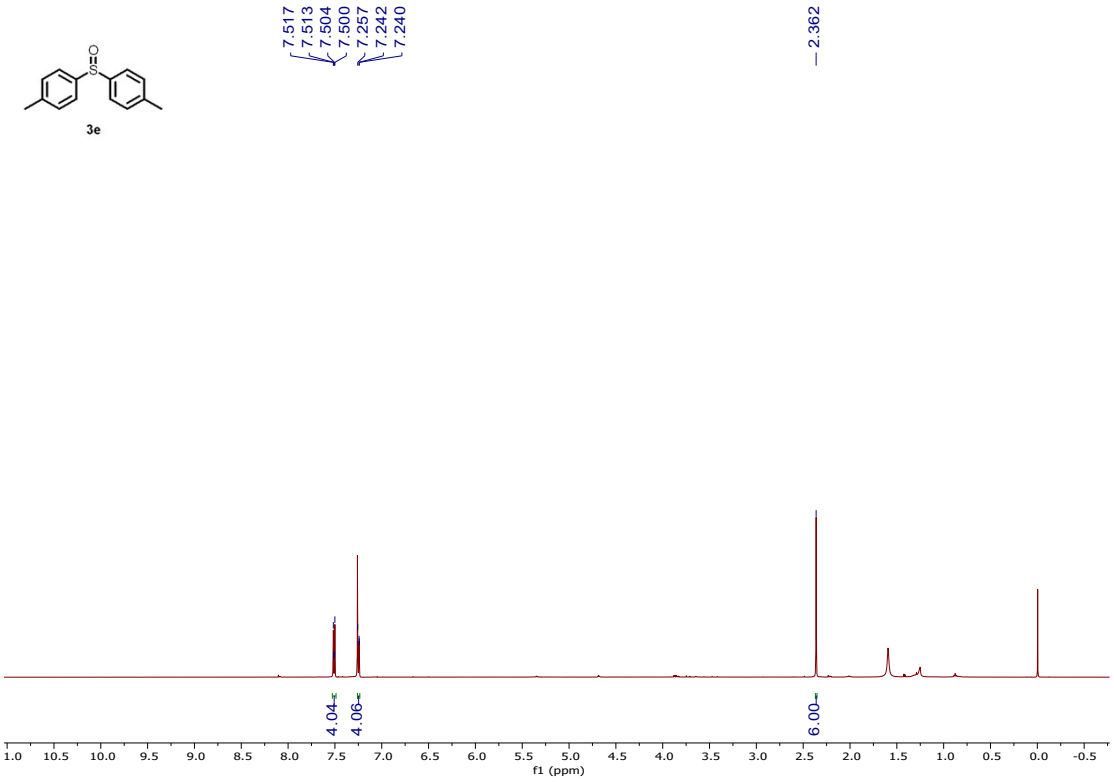

145.758
142.424
141.670
130.895
130.045
129.267
125.006
124.702
21.427
f1 (ppm)

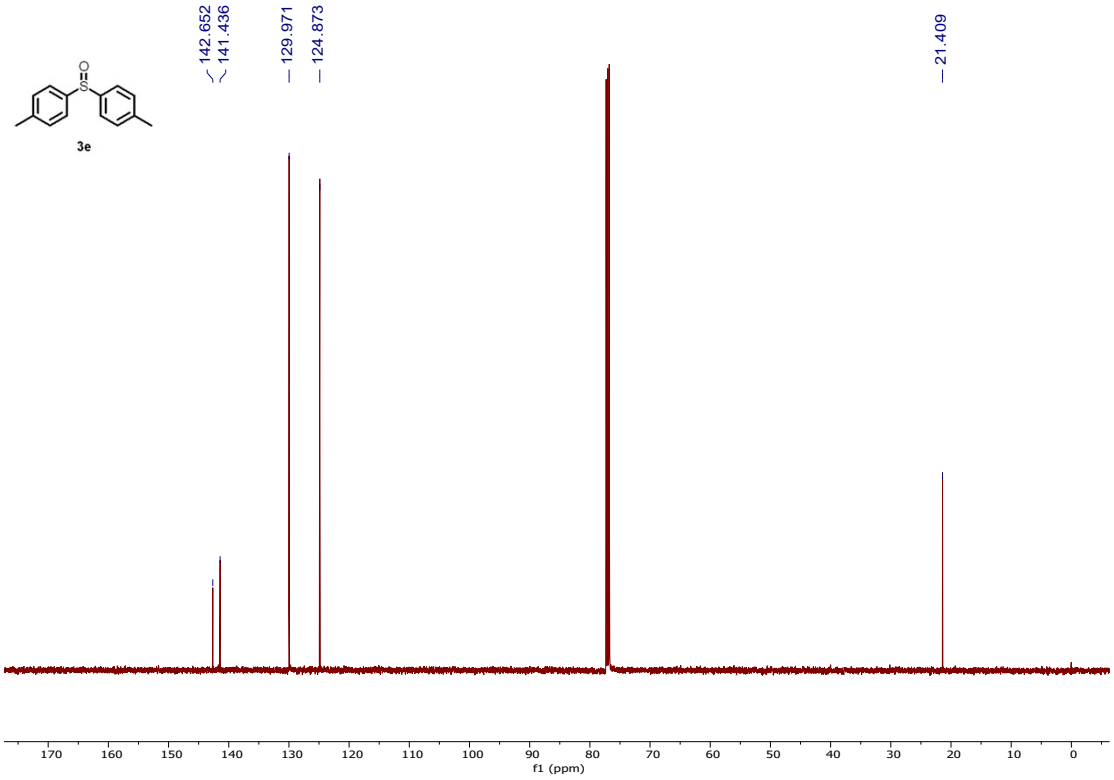

3c
7.978
7.975
7.962
7.960
7.486
7.482
7.473
7.469
7.429
7.427
7.414
7.412
7.399
7.396
7.370
7.367
7.355
7.352
7.340
7.337
7.241
7.226
7.161
7.146
2.357
2.314
0.98
2.06
1.06
1.02
2.00
0.96
3.02
3.00
f1 (ppm)

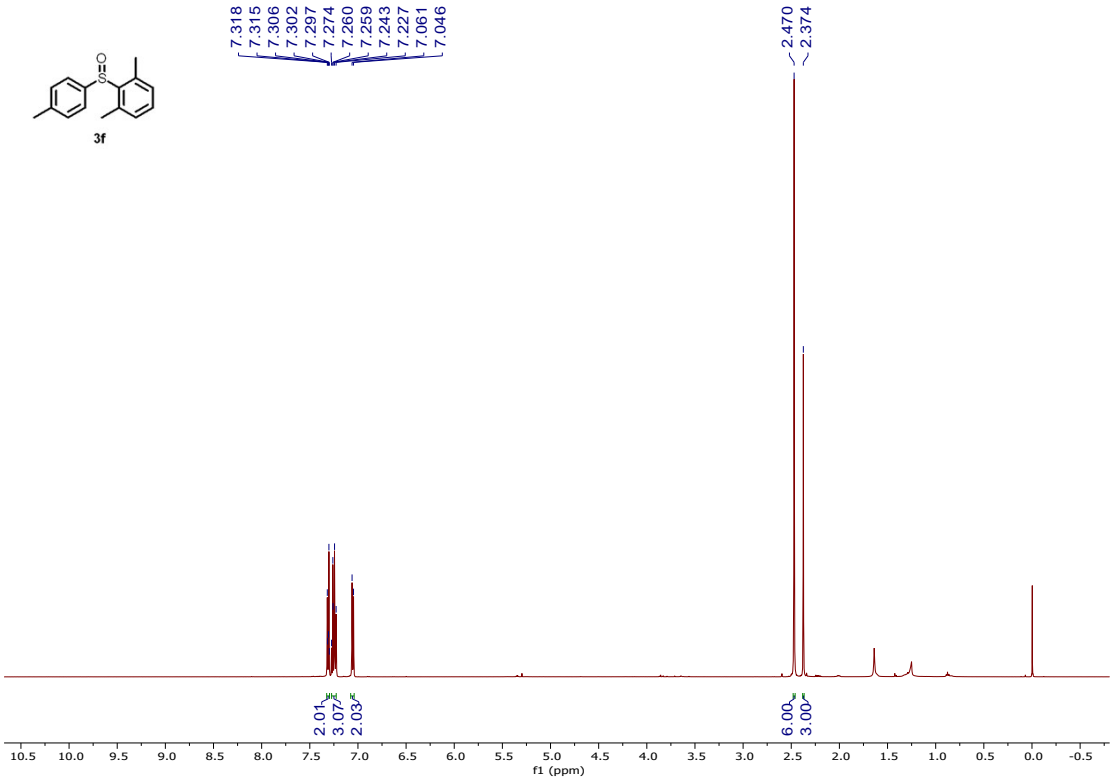

3c
142.995
141.735
141.319
135.561
130.895
130.830
130.010
127.077
126.154
124.482
21.431
18.581
f1 (ppm)

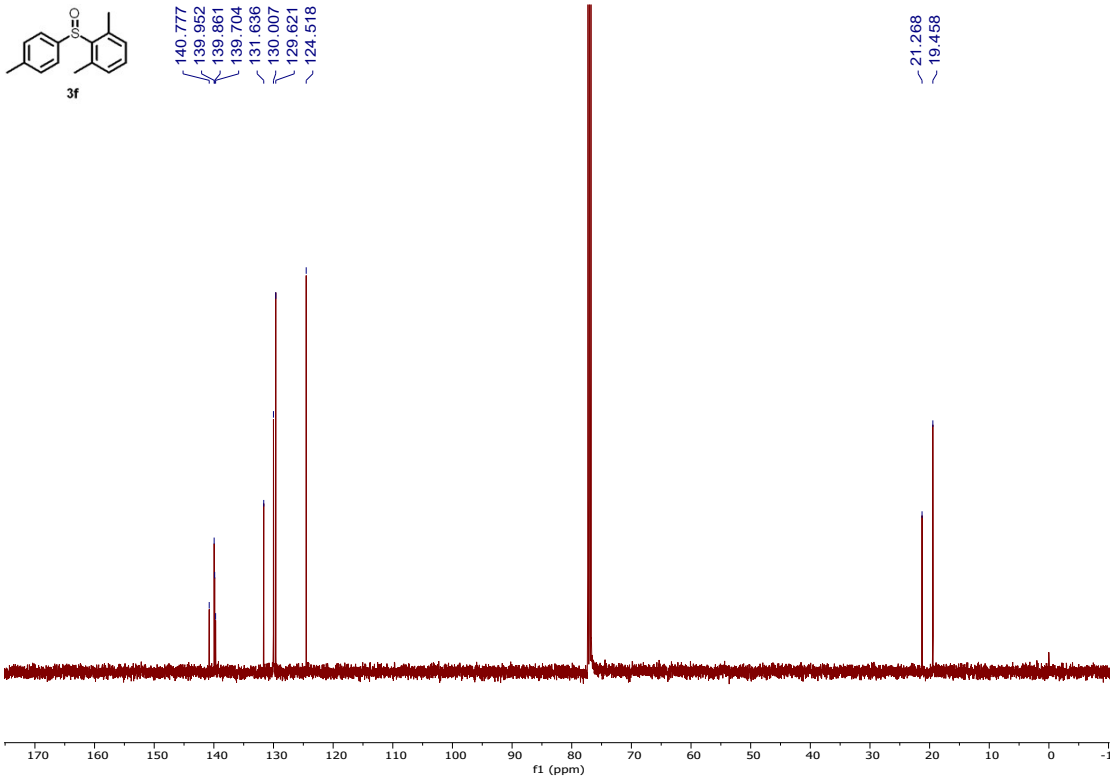

7.533
7.529
7.520
7.516
7.465
7.462
7.458
7.399
7.383
7.337
7.322
7.306
7.264
7.248
7.234
7.219
2.371
2.365
3d
1.94
0.94
1.00
1.02
2.28
0.96
6.03
f1 (ppm)

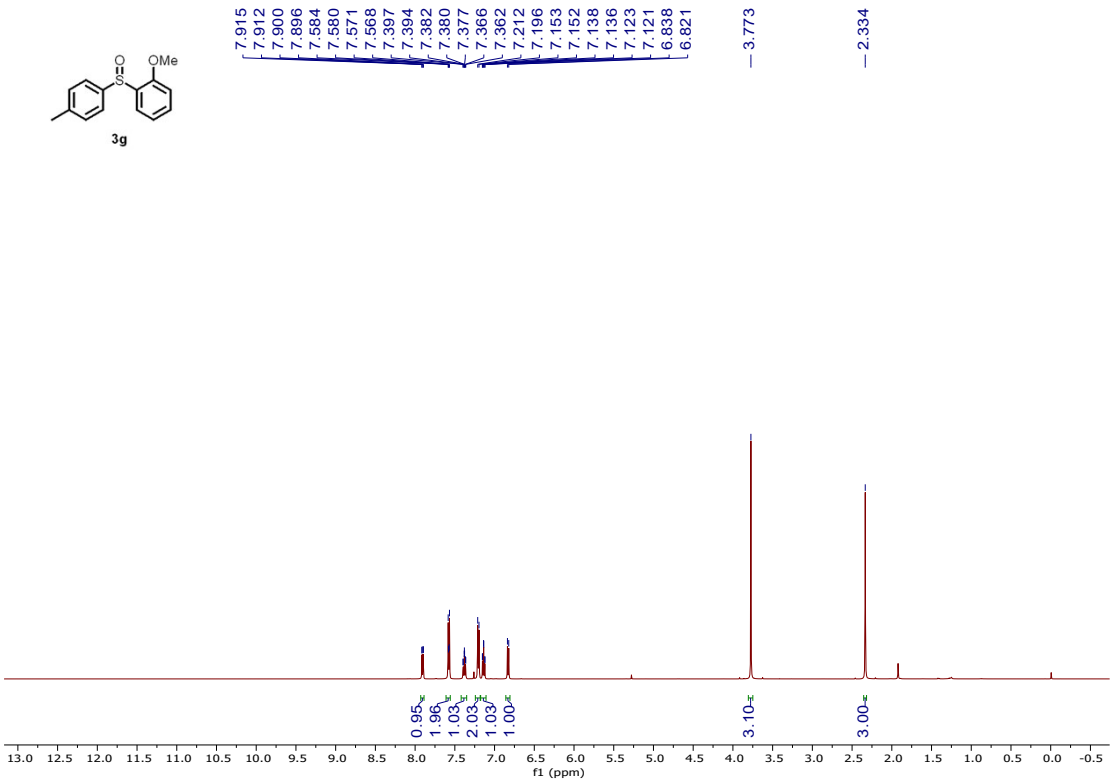

145.536
142.508
141.546
139.496
131.764
130.010
129.054
124.977
124.902
121.902
21.451
21.428
3d
f1 (ppm)

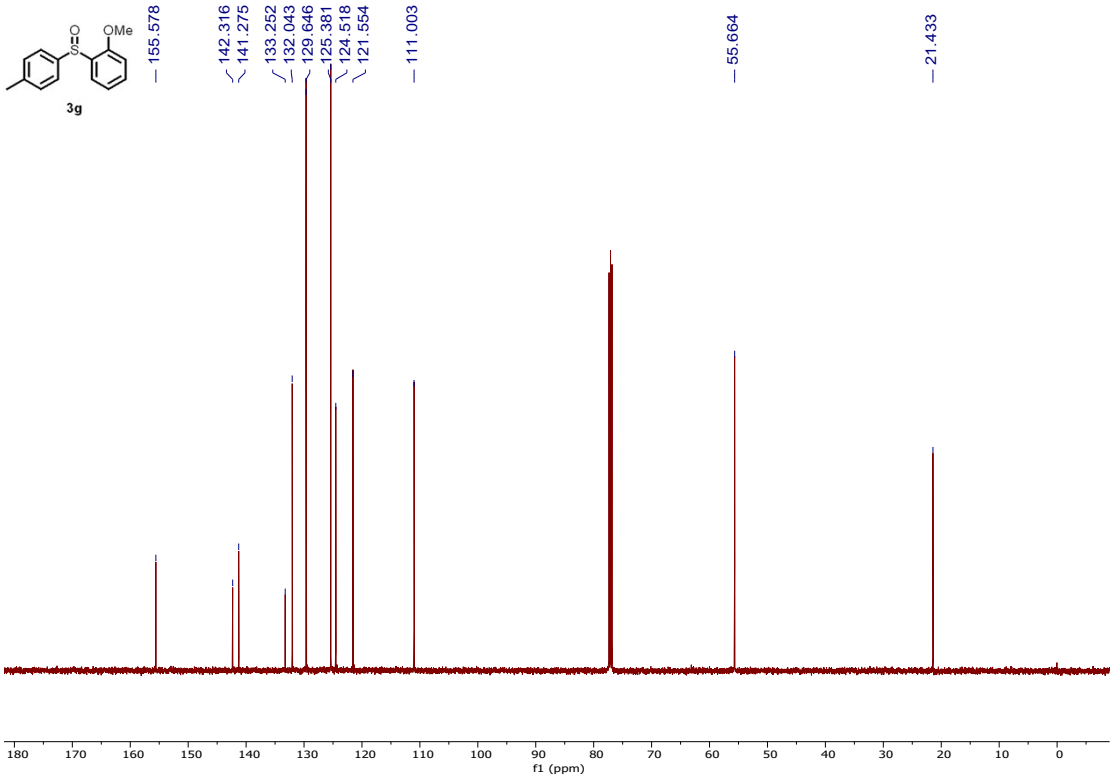

3e
7.517
7.513
7.504
7.500
7.257
7.242
7.240
2.362
4.04
4.06
6.00
f1 (ppm)

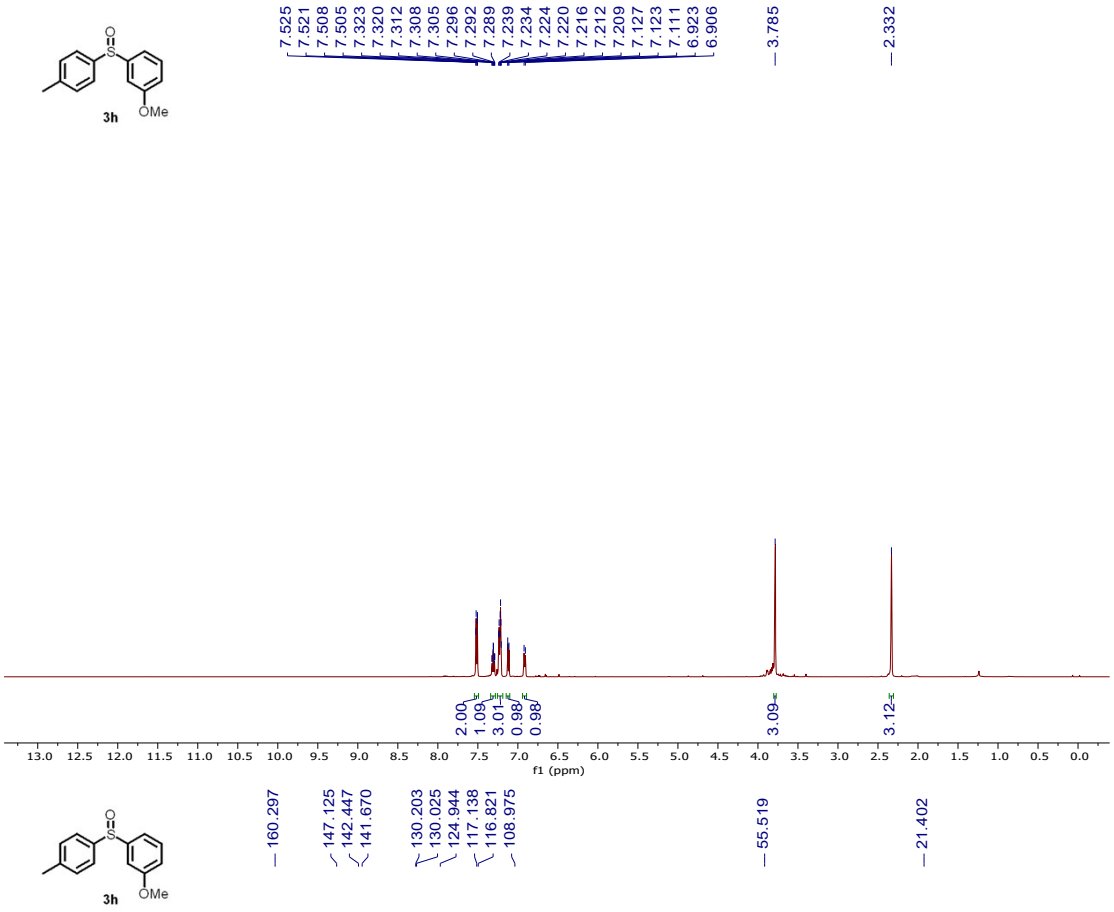

3e
142.652
141.436
129.971
124.873
21.409
f1 (ppm)

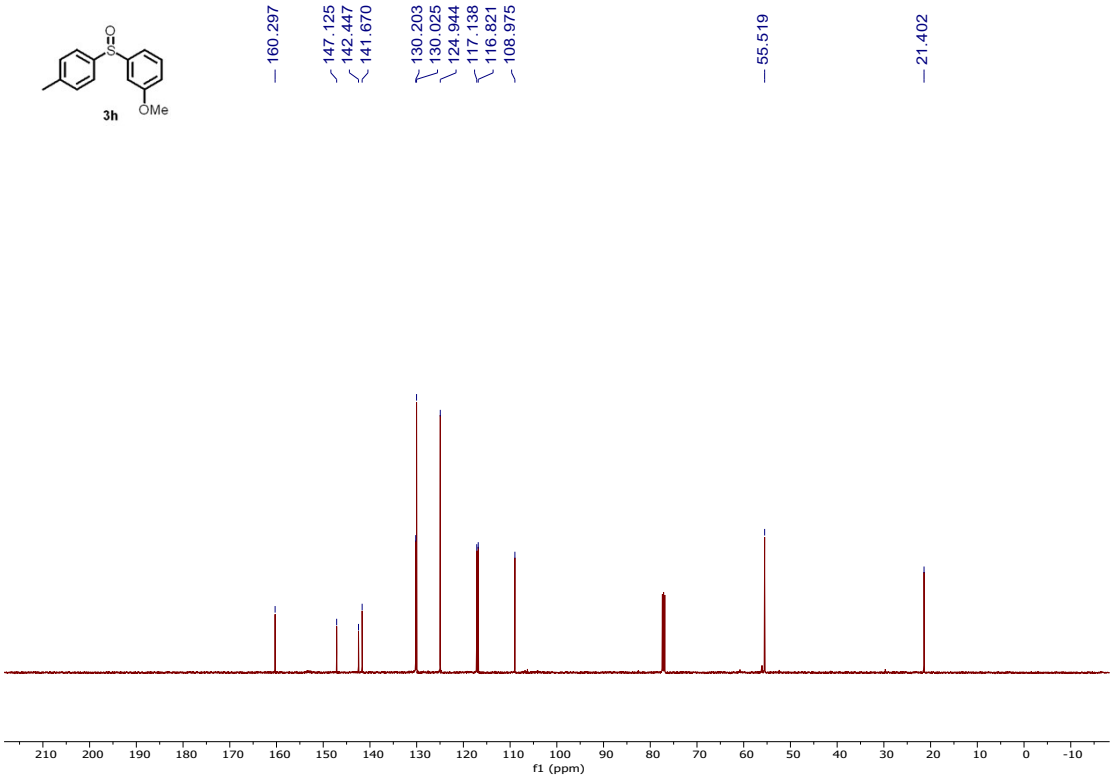

3f
7.318
7.315
7.306
7.302
7.297
7.274
7.260
7.259
7.243
7.227
7.061
7.046
2.470
2.374
2.01
3.07
2.03
6.00
3.00
f1 (ppm)

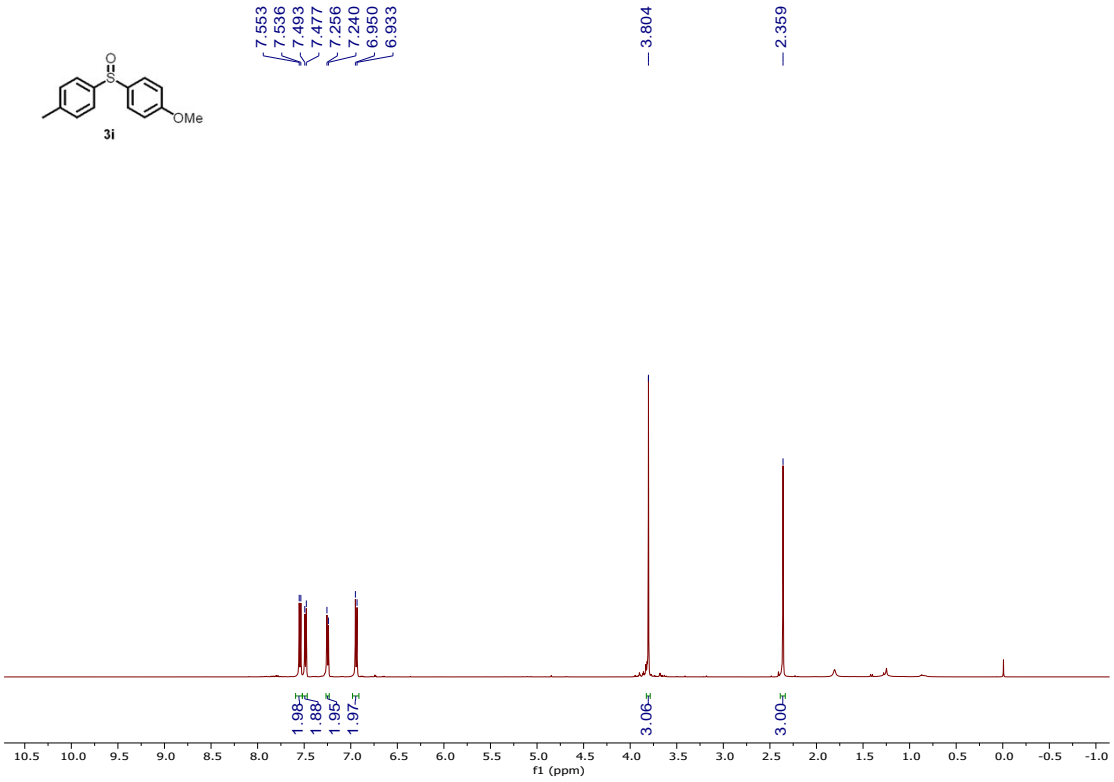

3f
140.777
139.952
139.861
139.704
131.636
130.007
129.621
124.518
21.268
19.458
f1 (ppm)

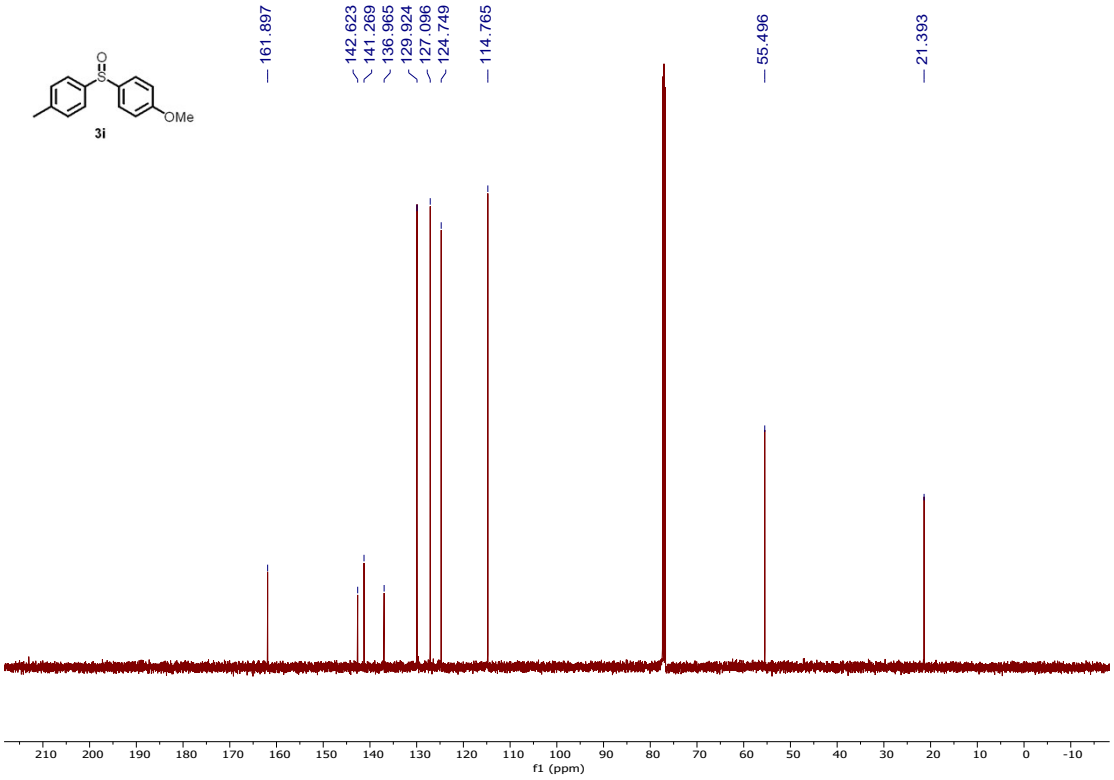

3g
7.915
7.912
7.900
7.896
7.584
7.580
7.571
7.568
7.397
7.394
7.382
7.380
7.377
7.366
7.362
7.212
7.196
7.153
7.152
7.138
7.136
7.123
7.121
6.838
6.821
3.773
2.334
0.95
1.96
1.03
2.03
1.03
1.00
3.10
3.00
f1 (ppm)

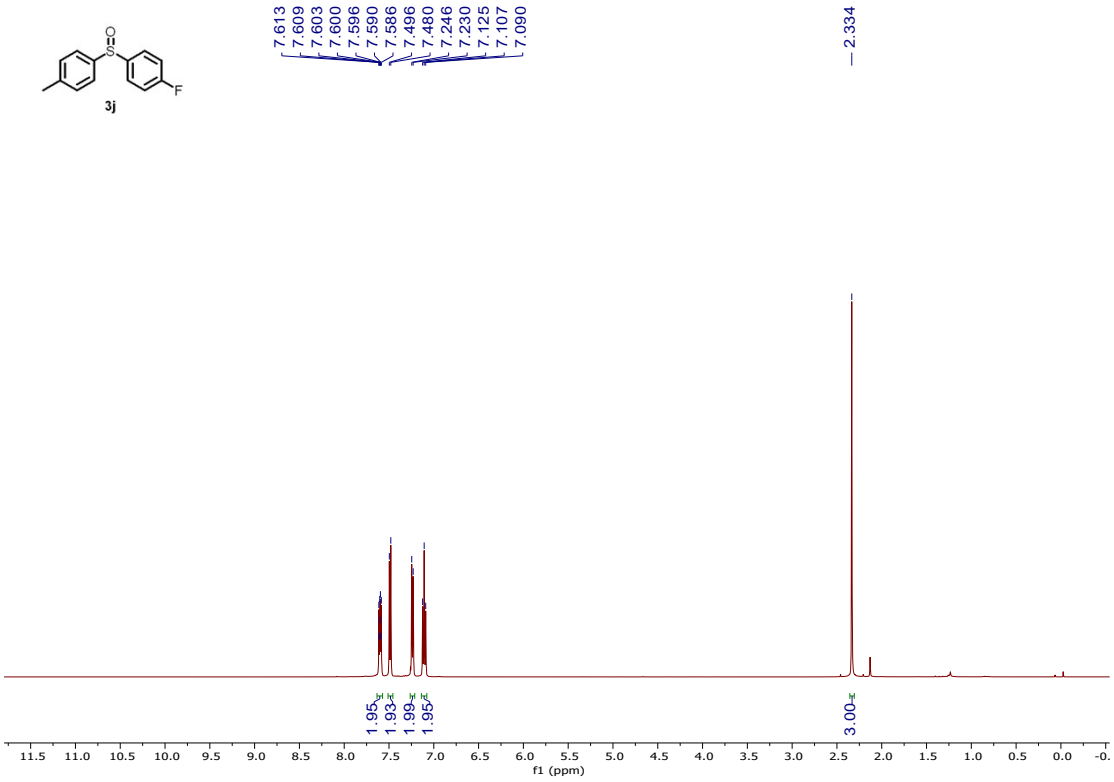

3g
155.578
142.316
141.275
133.252
132.043
129.646
125.381
124.518
121.554
111.003
55.664
21.433
f1 (ppm)

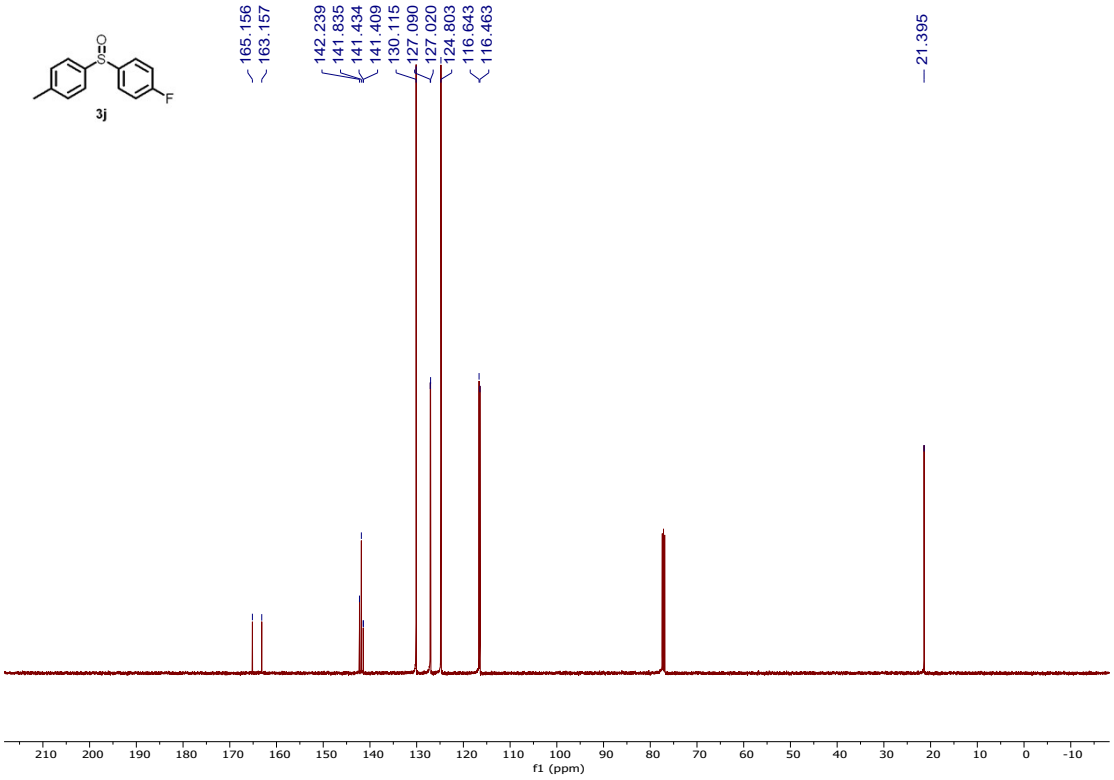

3h
OMe
7.525
7.521
7.508
7.505
7.323
7.320
7.312
7.308
7.305
7.296
7.292
7.289
7.239
7.234
7.224
7.220
7.216
7.212
7.209
7.127
7.123
7.111
6.923
6.906
3.785
2.332
2.00
1.09
3.01
0.98
0.98
3.09
3.12
f1 (ppm)

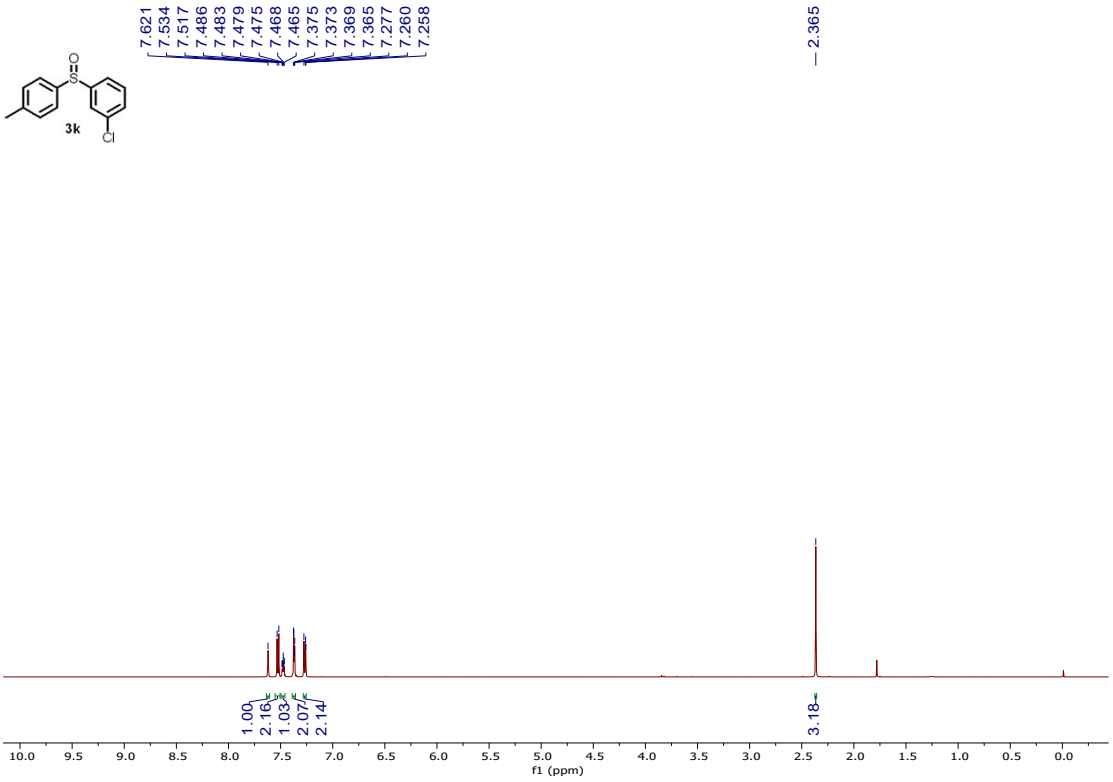

3h
OMe
160.297
147.125
142.447
141.670
130.203
130.025
124.944
117.138
116.821
108.975
55.519
21.402
f1 (ppm)


7.553
7.536
7.493
7.477
7.256
7.240
6.950
6.933
3.804
2.359
OMe
3i
1.98
1.88
1.95
1.97
3.06
3.00
f1 (ppm)


161.897
142.623
141.269
136.965
129.924
127.096
124.749
114.765
55.496
21.393
OMe
3i
f1 (ppm)


3j
7.613
7.609
7.603
7.600
7.596
7.590
7.586
7.496
7.480
7.246
7.230
7.125
7.107
7.090
2.334
1.95
1.93
1.99
1.95
3.00
f1 (ppm)


3j
165.156
163.157
142.239
141.835
141.434
141.409
130.115
127.090
127.020
124.803
116.643
116.463
21.395
f1 (ppm)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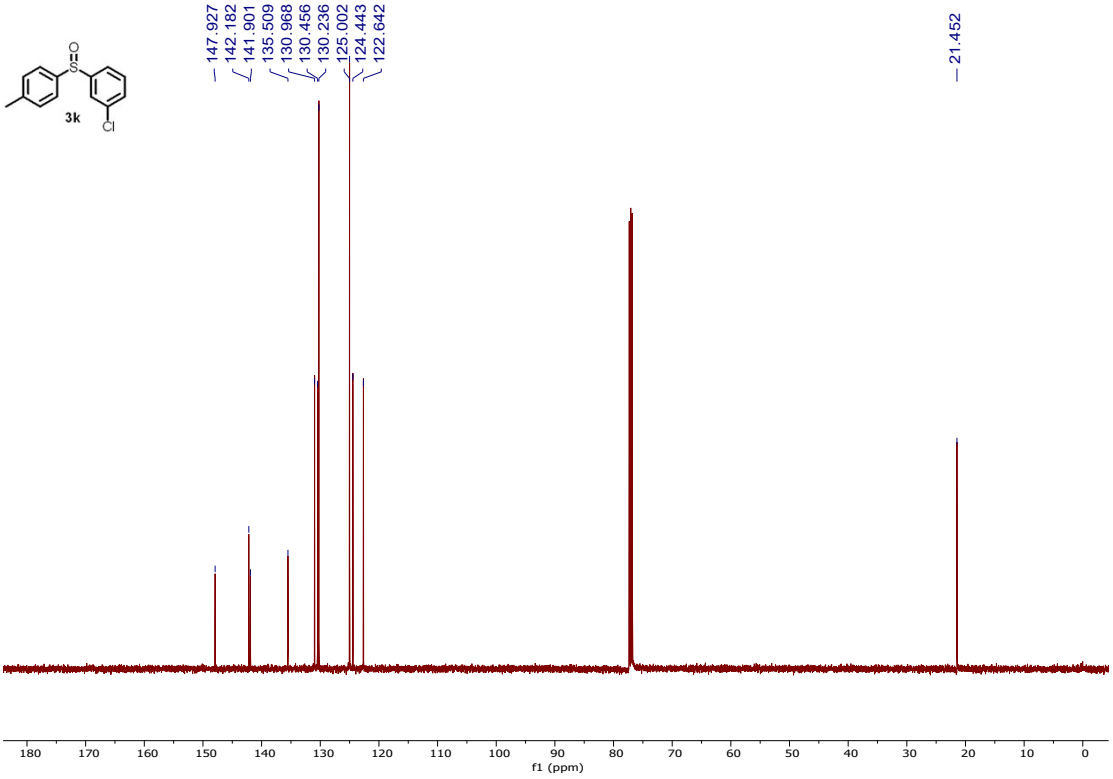
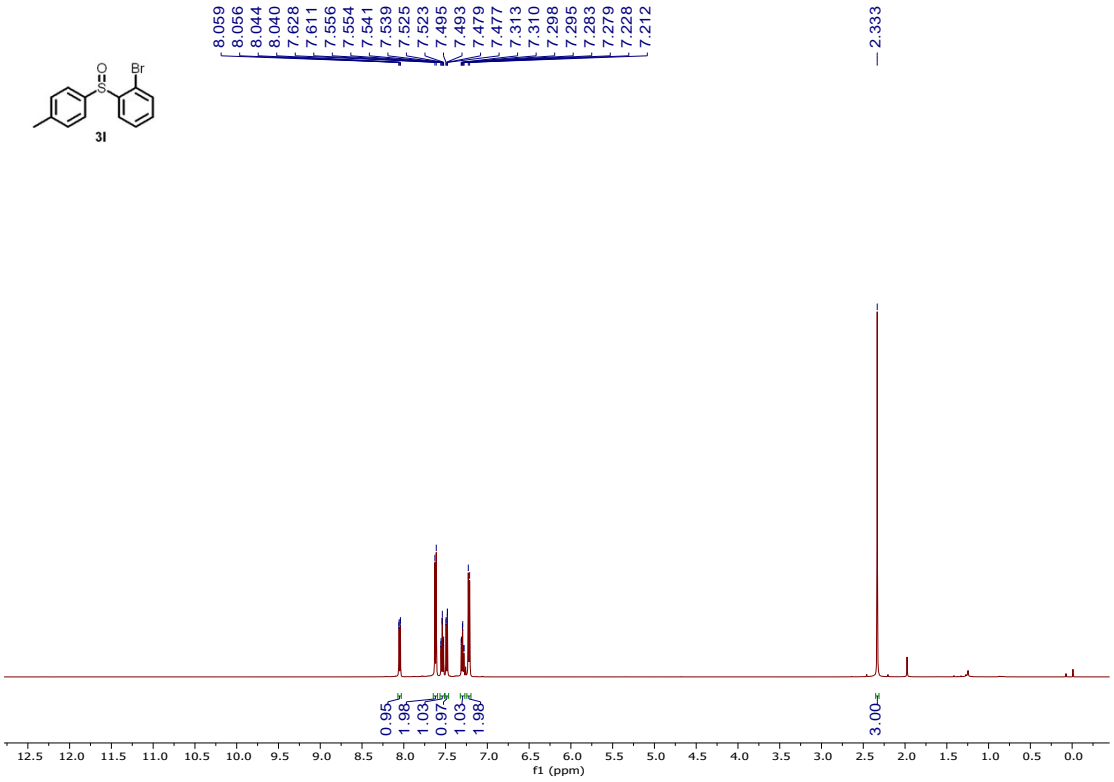
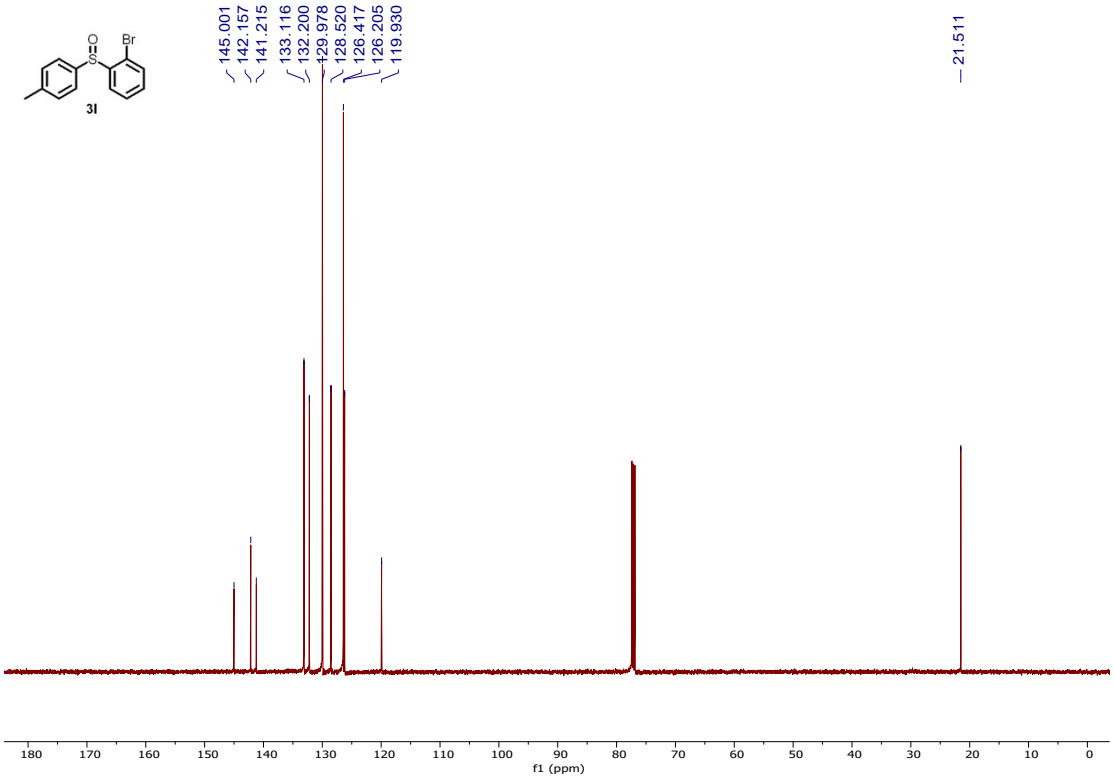
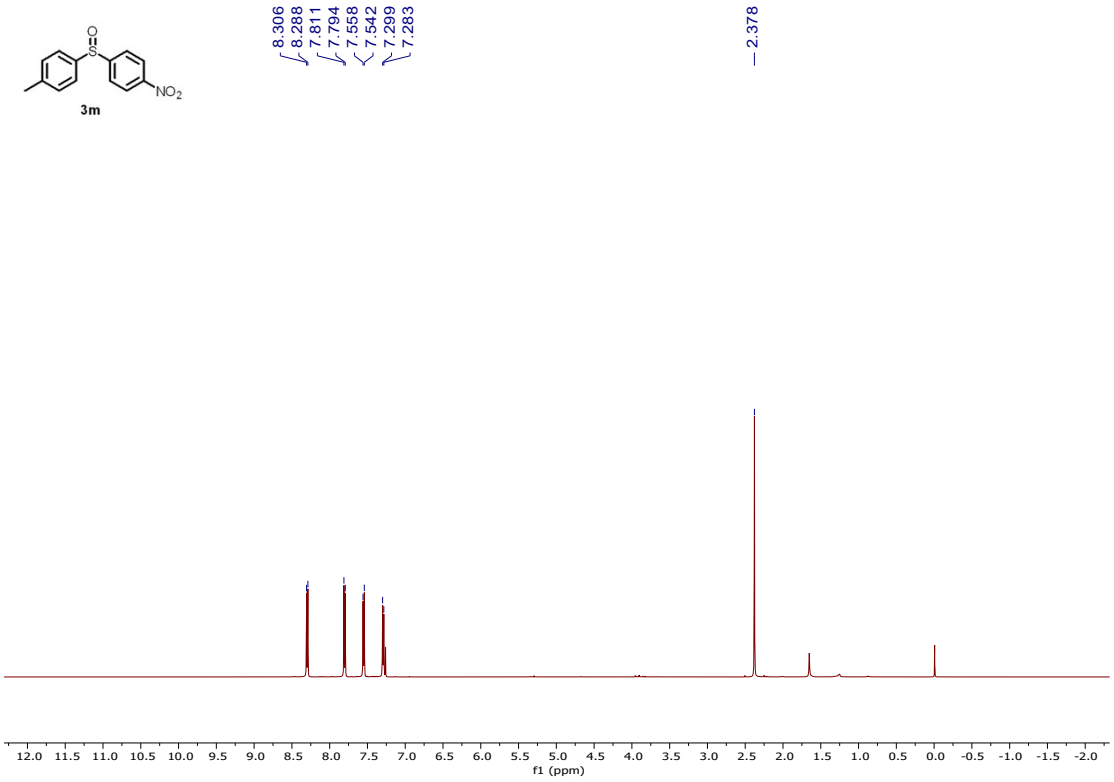
7.534
7.517
7.486
7.483
7.479
7.475
7.468
7.465
7.375
7.373
7.369
7.365
7.277
7.260
7.258
2.365
3k
1.00
2.16
1.03
2.07
2.14
3.18
f1 (ppm)


147.927
142.182
141.901
135.509
130.968
130.456
130.236
125.002
124.443
122.642
21.452
3k
f1 (ppm)


8.059
8.056
8.044
8.040
7.628
7.611
7.556
7.554
7.541
7.539
7.525
7.523
7.495
7.493
7.479
7.477
7.313
7.310
7.298
7.295
7.283
7.279
7.228
7.212
2.333
Br
O
S
3l
0.95
1.98
1.03
0.97
1.03
1.98
3.00
f1 (ppm)


145.001
142.157
141.215
133.116
132.200
129.978
128.520
126.417
126.205
119.930
21.511
Br
O
S
3l
f1 (ppm)


3m
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8.288
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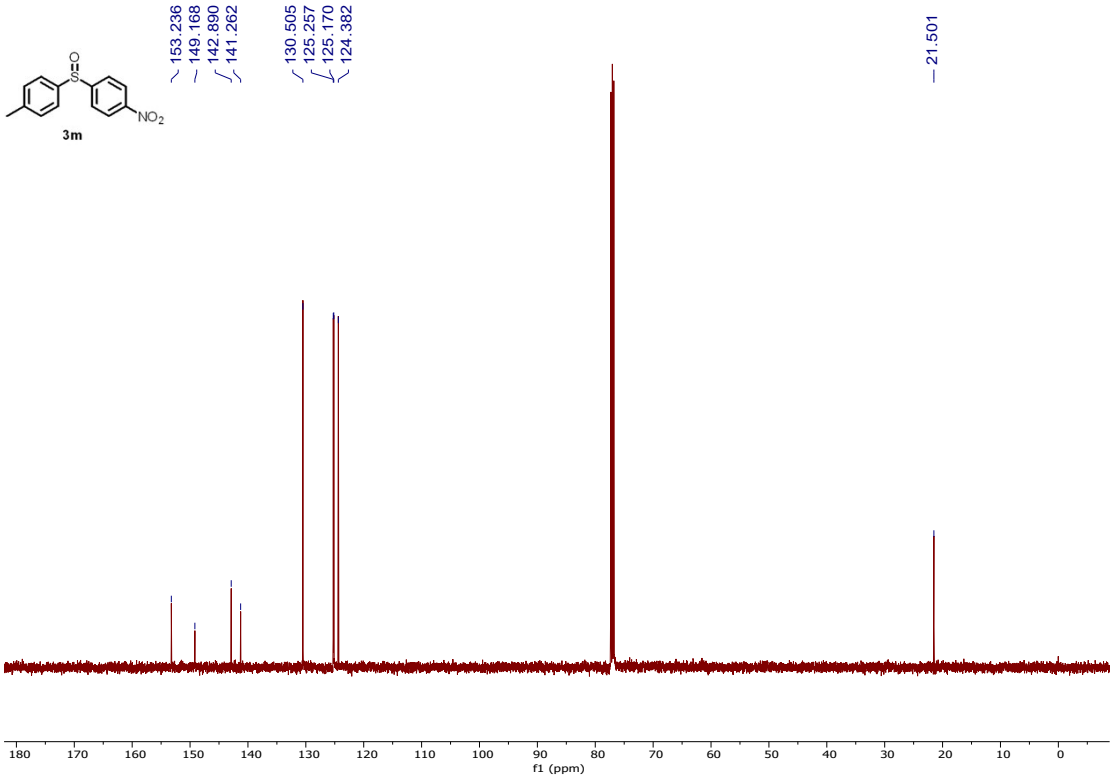
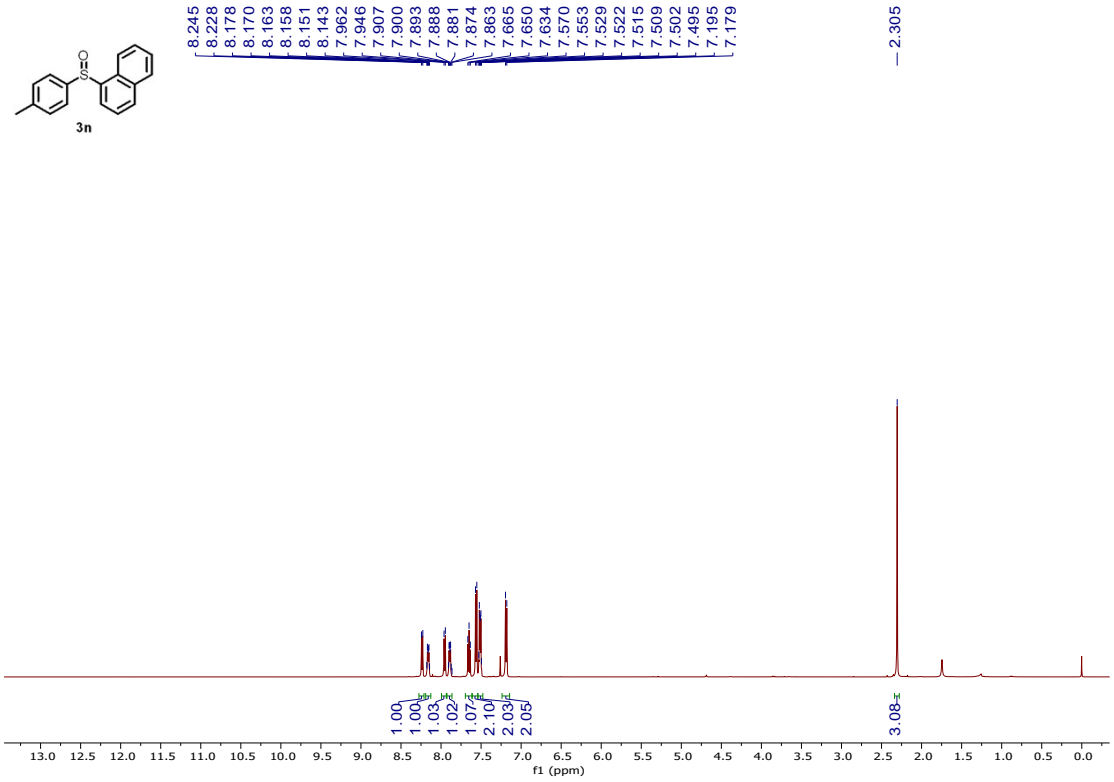
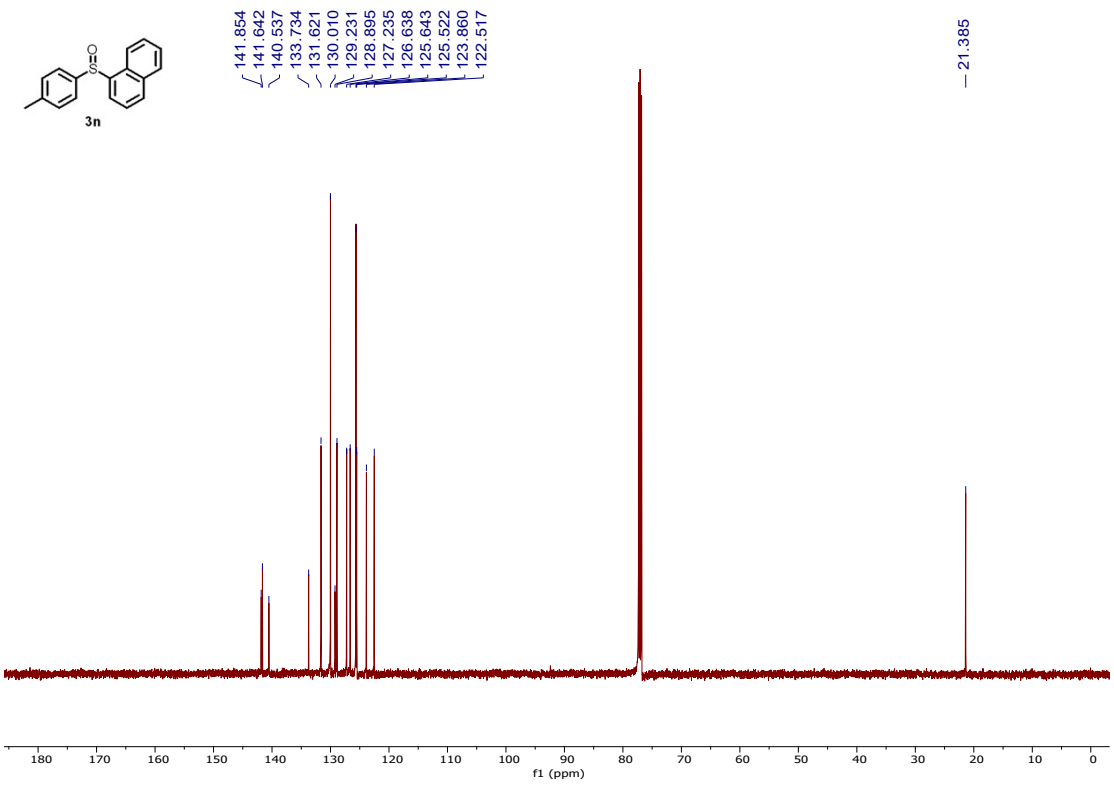
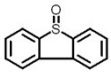
7.794
7.558
7.542
7.299
7.283
2.378
f1 (ppm)

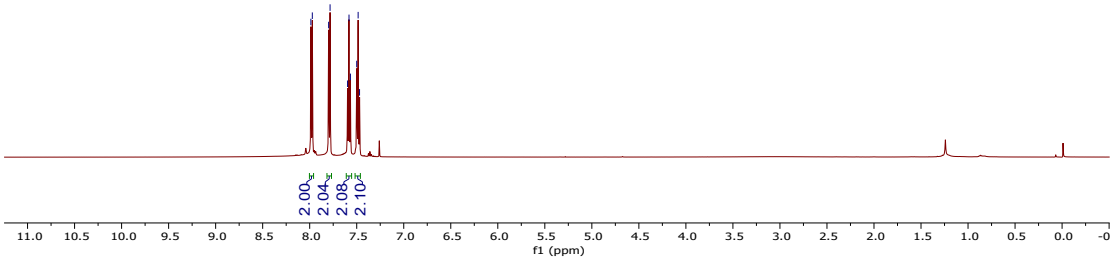

3m
153.236
149.168
142.890
141.262
130.505
125.257
125.170
124.382
21.501
f1 (ppm)

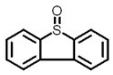

3n
8.245
8.228
8.178
8.170
8.163
8.158
8.151
8.143
7.962
7.946
7.907
7.900
7.893
7.888
7.881
7.874
7.863
7.665
7.650
7.634
7.570
7.553
7.529
7.522
7.515
7.509
7.502
7.495
7.195
7.179
2.305
1.00
1.00
1.03
1.02
1.07
2.10
2.03
2.05
3.08
f1 (ppm)


3n
141.854
141.642
140.537
133.734
131.621
130.010
129.231
128.895
127.235
126.638
125.643
125.522
123.860
122.517
21.385
f1 (ppm)

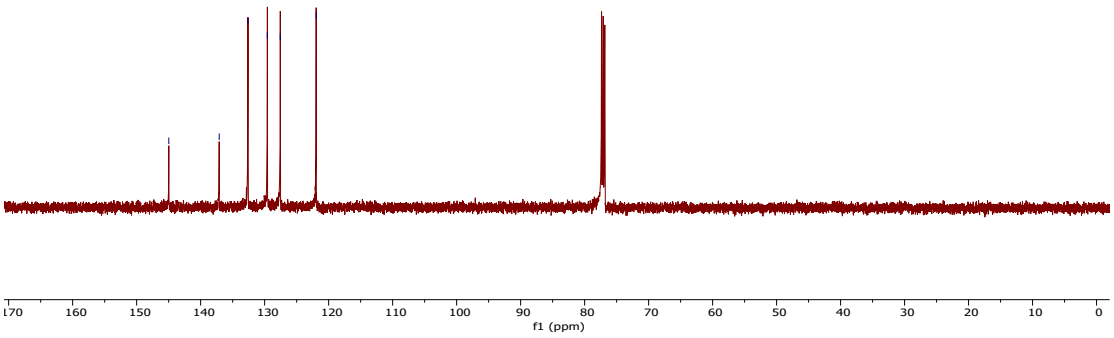


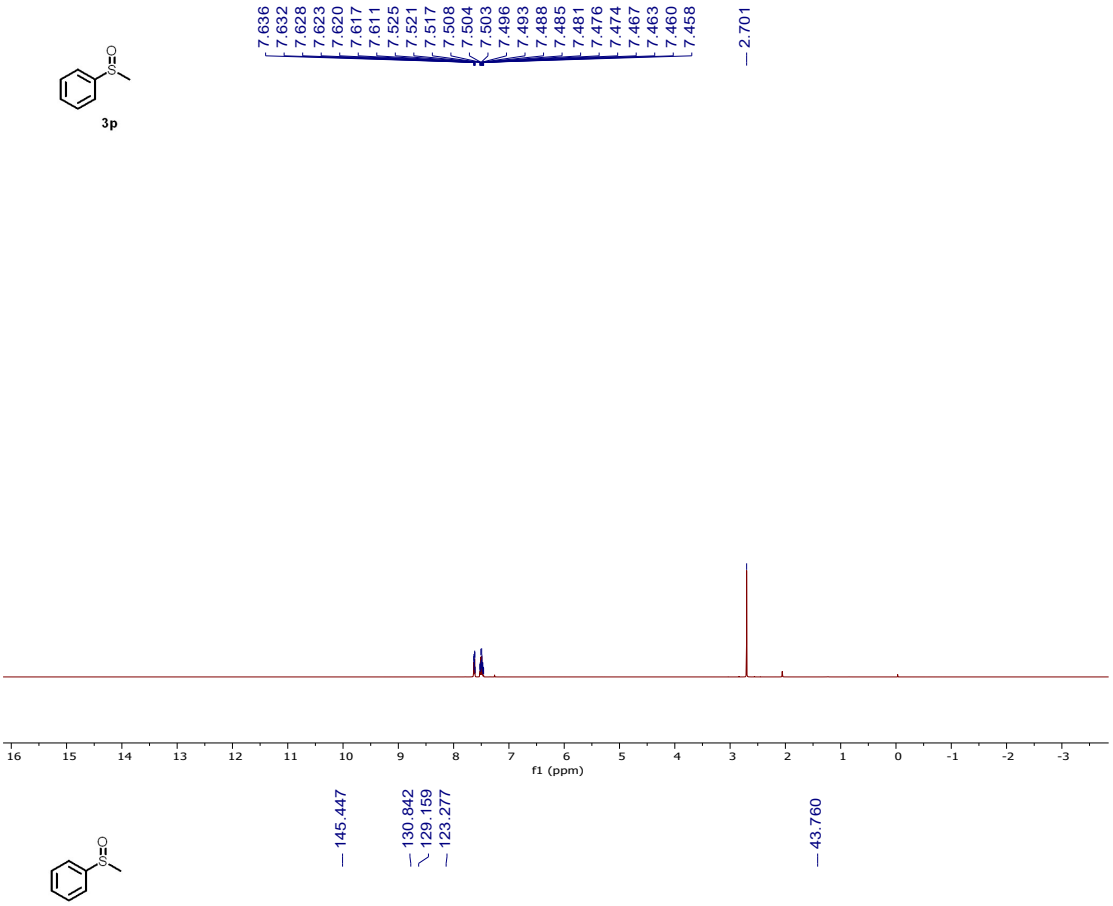
3o

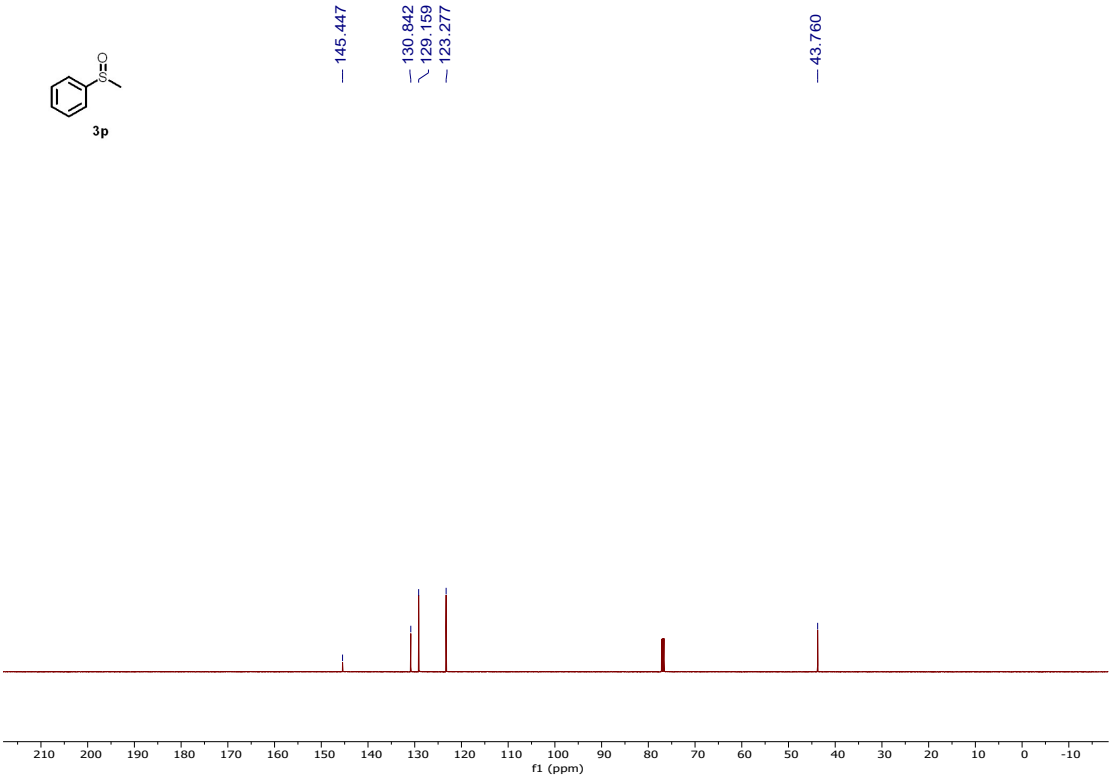

7.987
7.972
7.799
7.783
7.597
7.582
7.567
7.500
7.485
7.470
2.00
2.04
2.08
2.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

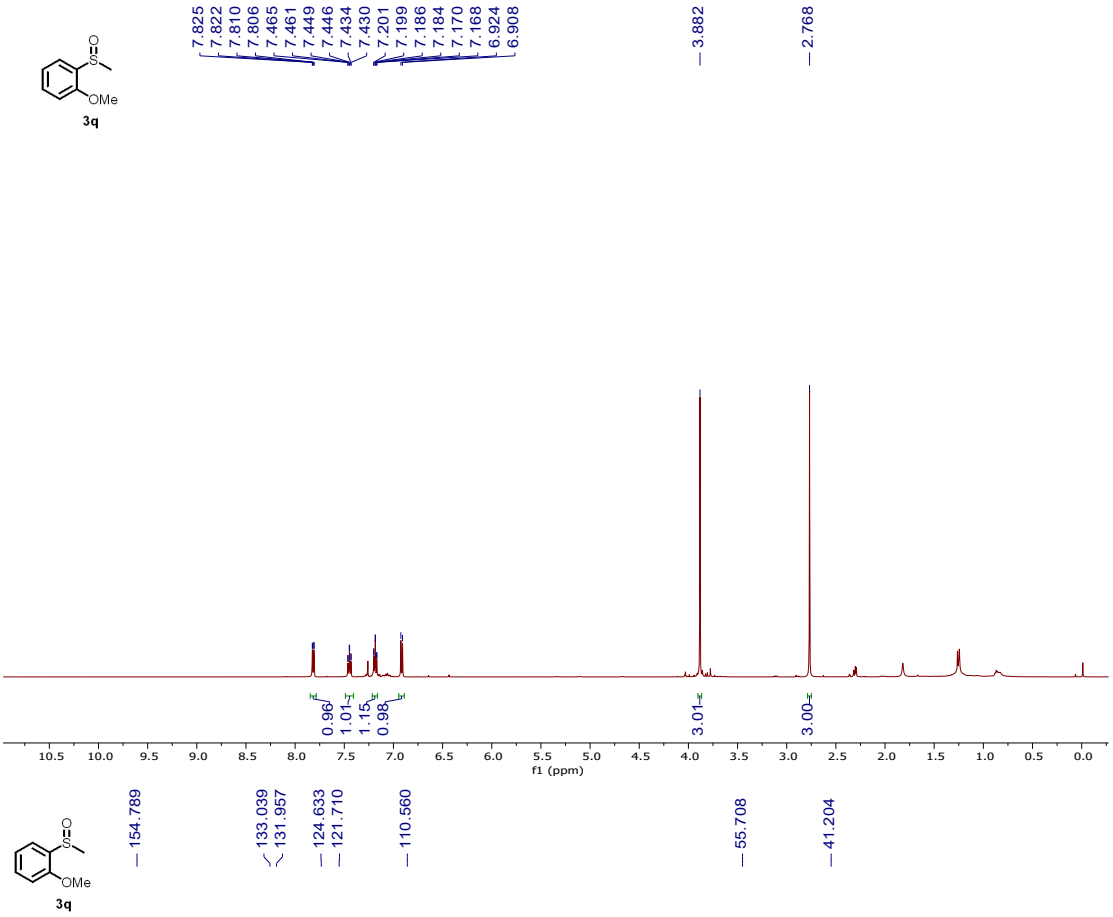


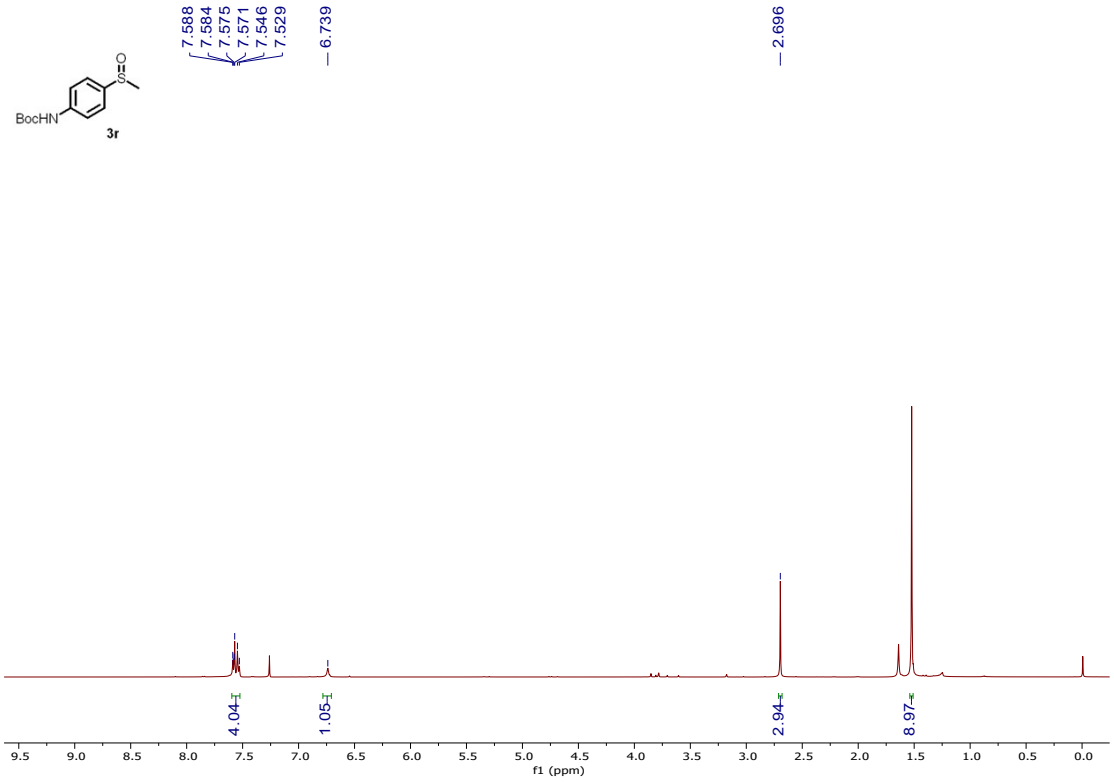
3o

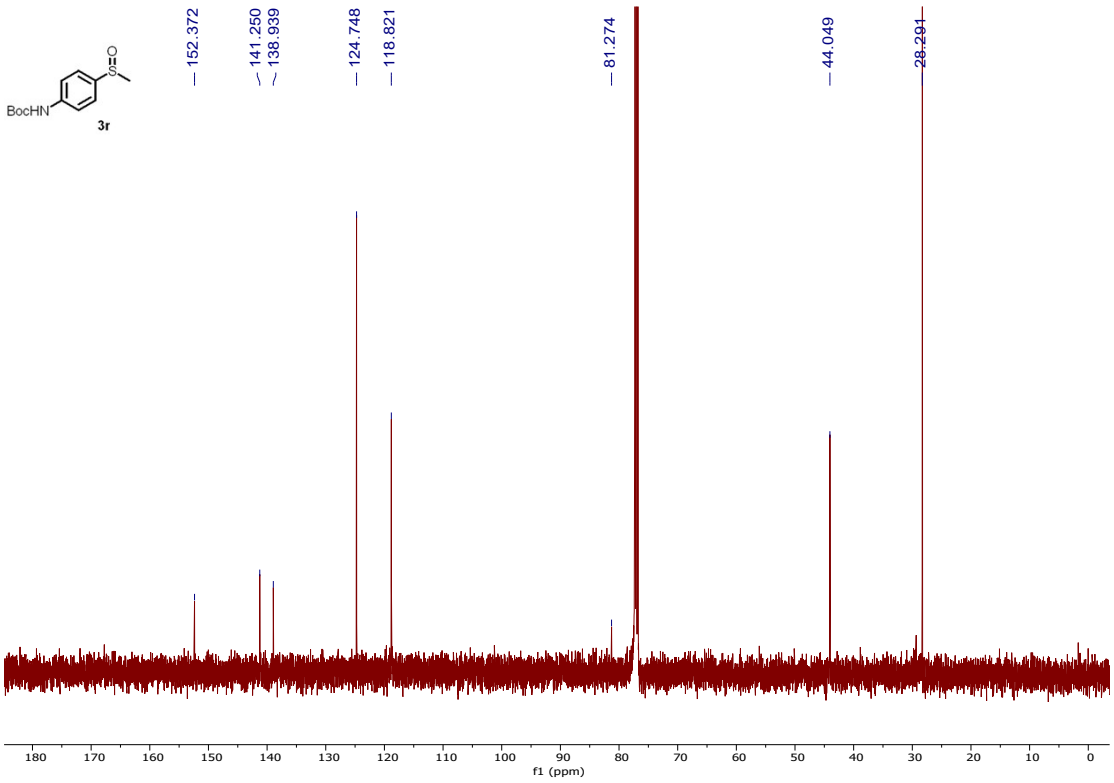

144.977
137.102
132.611
129.580
127.559
121.951
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.636
7.632
7.628
7.623
7.620
7.617
7.611
7.525
7.521
7.517
7.508
7.504
7.503
7.496
7.493
7.488
7.485
7.481
7.476
7.474
7.467
7.463
7.460
7.458
2.701
3p
f1 (ppm)

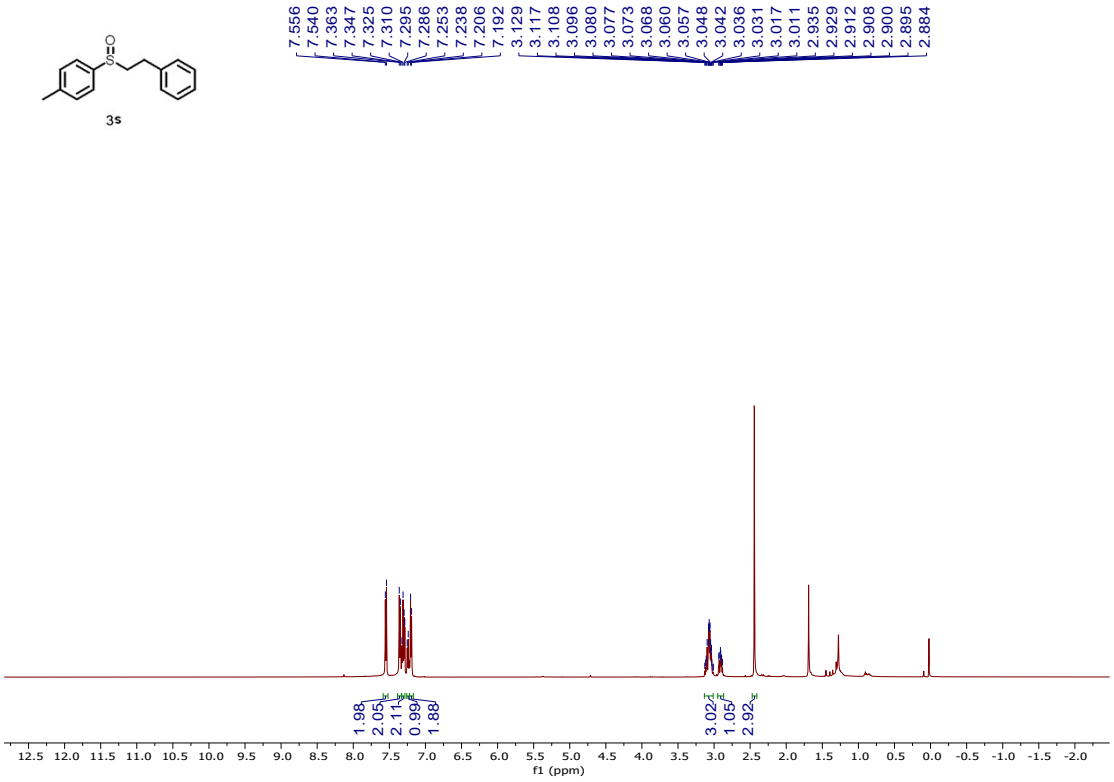

145.447
130.842
129.159
123.277
43.760
3p
f1 (ppm)


3q
7.825
7.822
7.810
7.806
7.465
7.461
7.449
7.446
7.434
7.430
7.201
7.199
7.186
7.184
7.170
7.168
6.924
6.908
3.882
2.768
0.96
1.01
1.15
0.98
3.01
3.00
f1 (ppm)
3q
154.789
133.039
131.957
124.633
121.710
110.560
55.708
41.204
f1 (ppm)

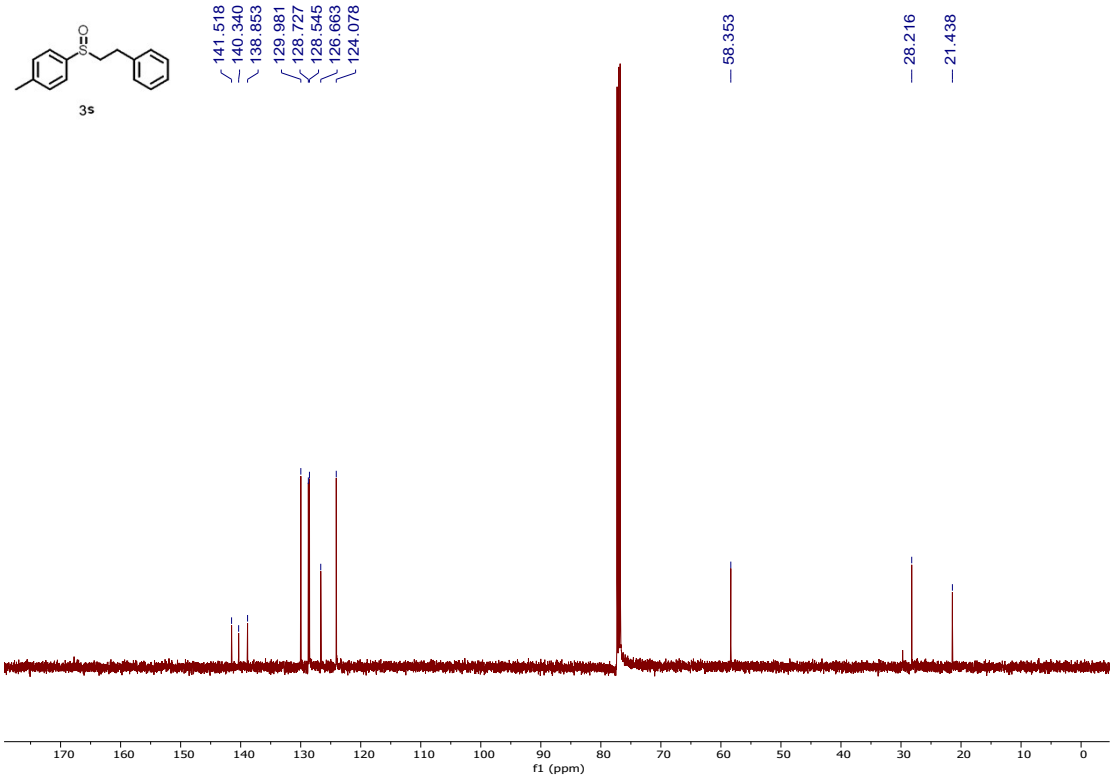

7.588
7.584
7.575
7.571
7.546
7.529
6.739
2.696
BocHN
3r
4.04
1.05
2.94
8.97
f1 (ppm)

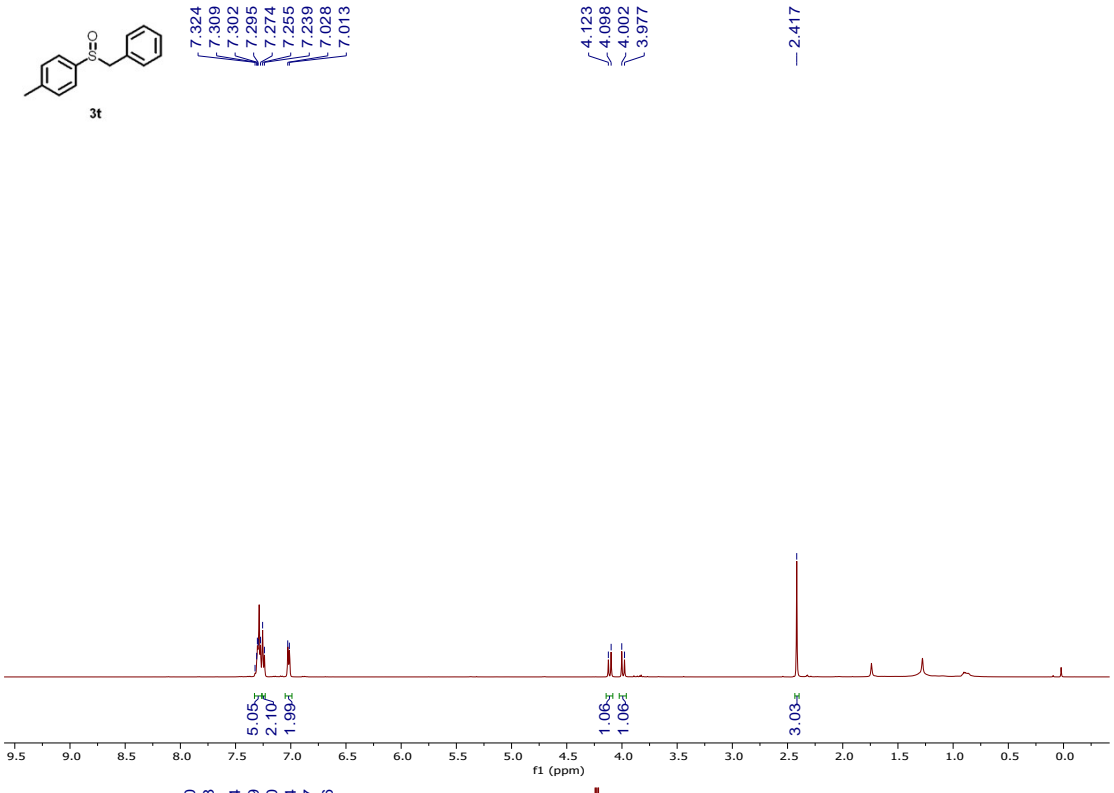

152.372
141.250
138.939
124.748
118.821
81.274
44.049
28.291
BocHN
3r
f1 (ppm)

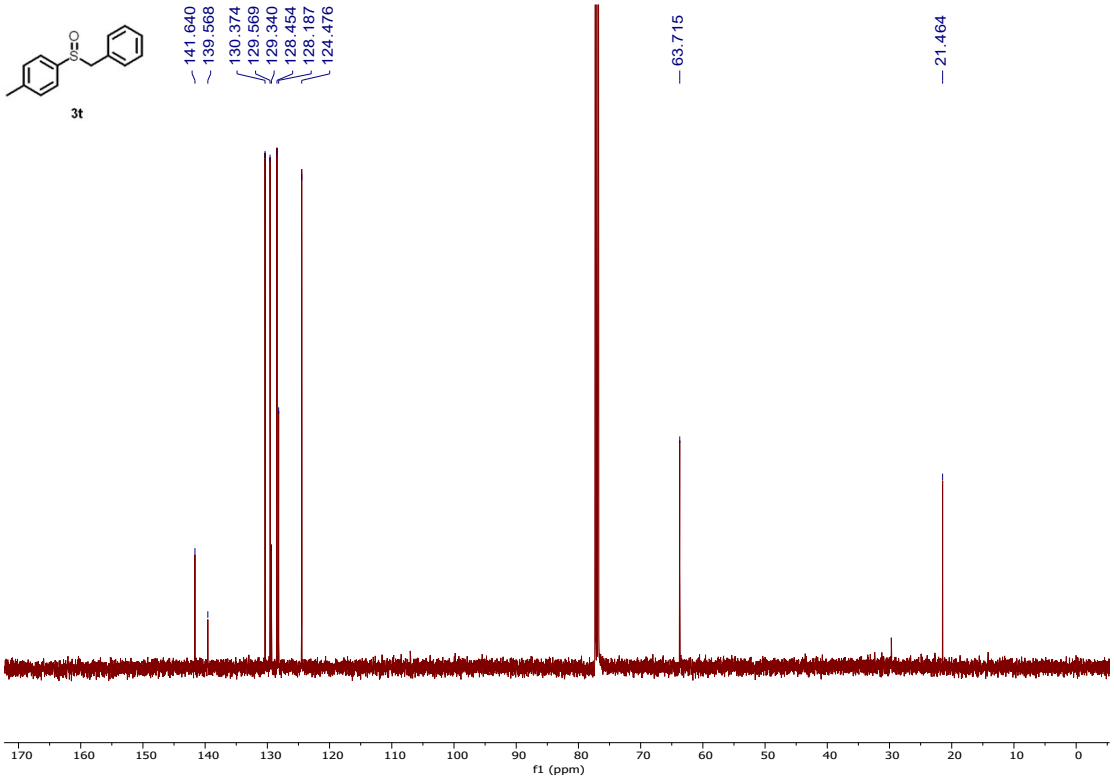
3s

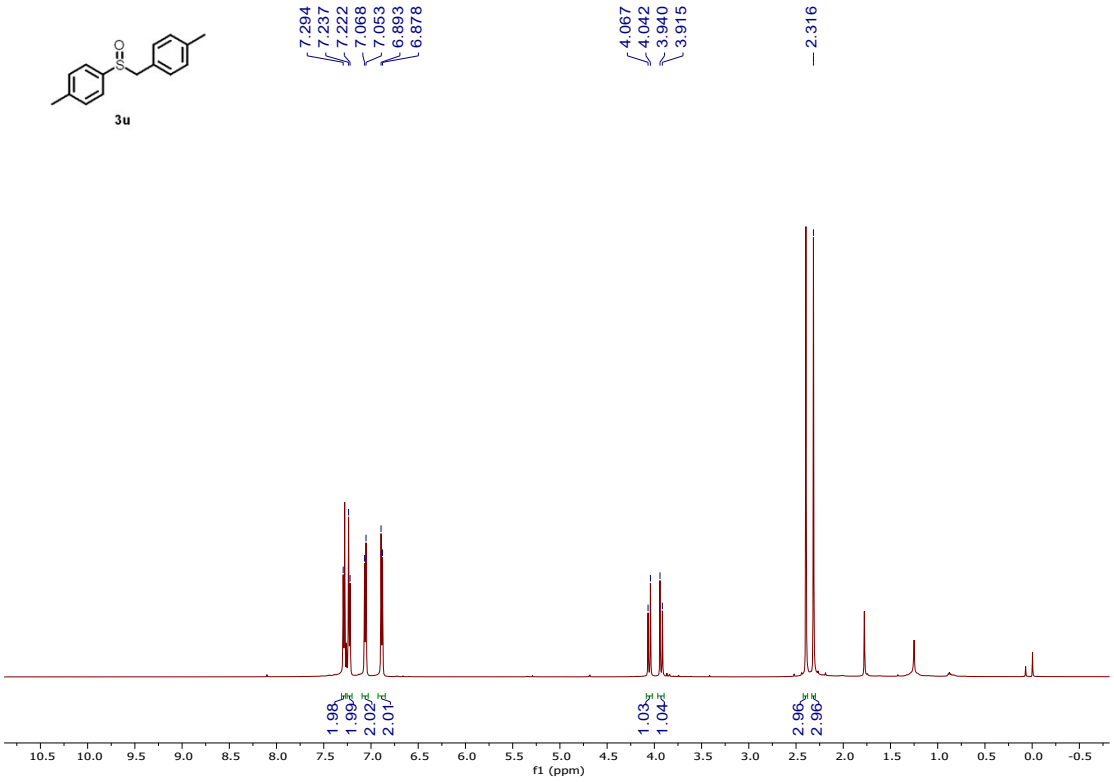

7.556
7.540
7.363
7.347
7.325
7.310
7.295
7.286
7.253
7.238
7.206
7.192
3.129
3.117
3.108
3.096
3.080
3.077
3.073
3.068
3.060
3.057
3.048
3.042
3.036
3.031
3.017
3.011
2.935
2.929
2.912
2.908
2.900
2.895
2.884
1.98
2.05
2.11
0.99
1.88
3.02
1.05
2.92
f1 (ppm)

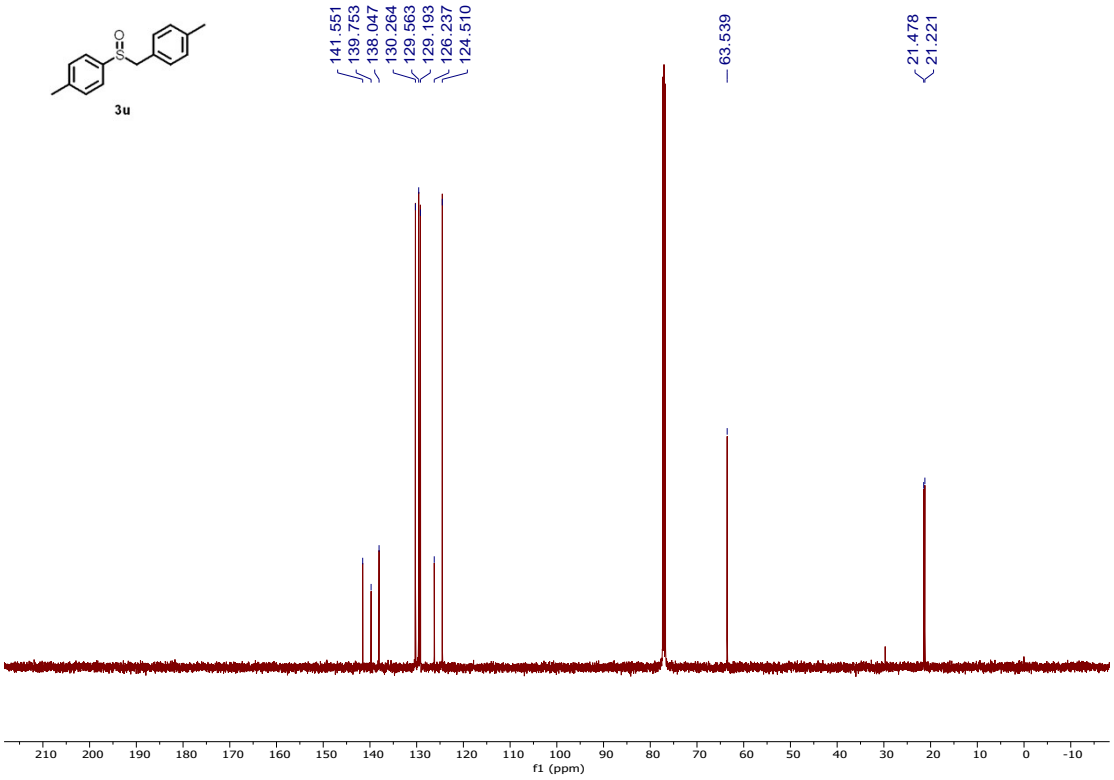
3s

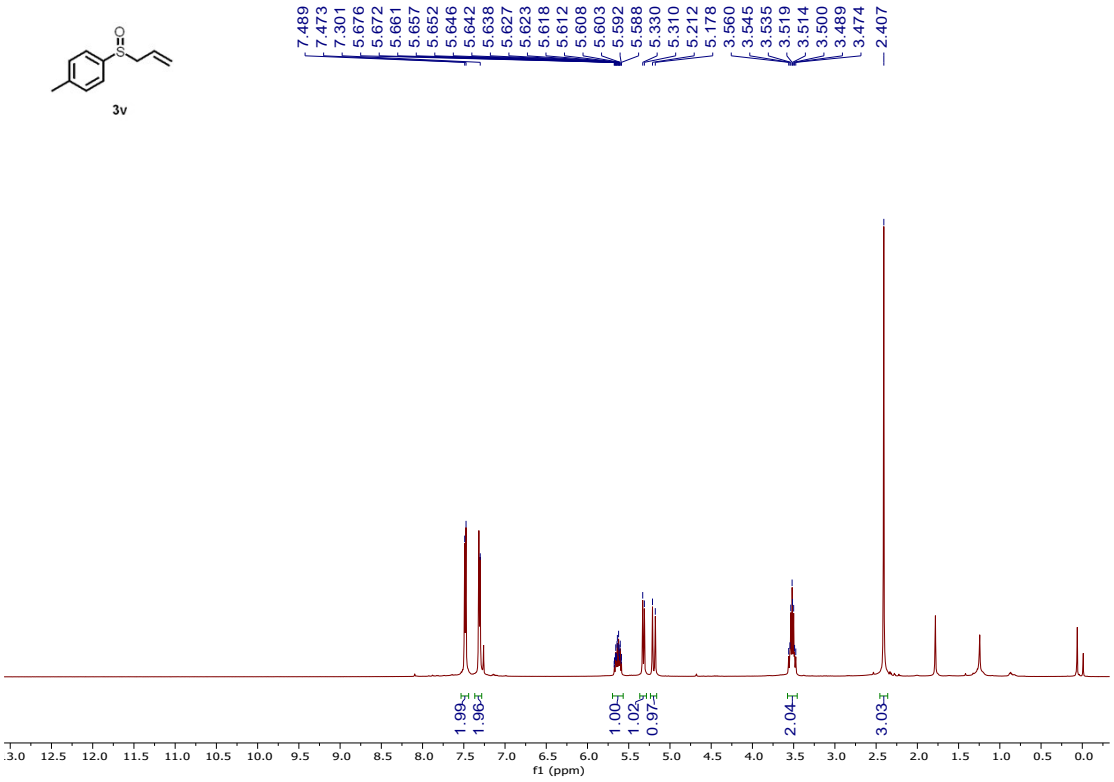

141.518
140.340
138.853
129.981
128.727
128.545
126.663
124.078
58.353
28.216
21.438
f1 (ppm)

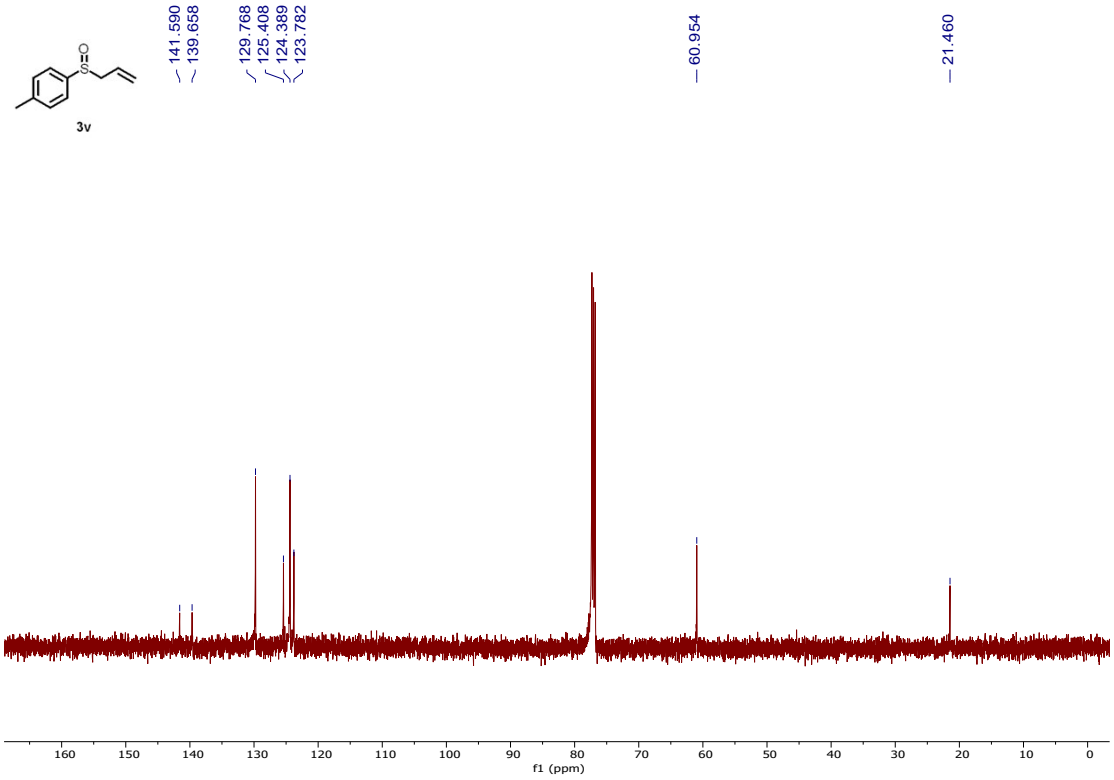

3t
7.324
7.309
7.302
7.295
7.274
7.255
7.239
7.028
7.013
4.123
4.098
4.002
3.977
2.417
5.05
2.10
1.99
1.06
1.06
3.03
f1 (ppm)


3t
141.640
139.568
130.374
129.569
129.340
128.454
128.187
124.476
63.715
21.464
f1 (ppm)

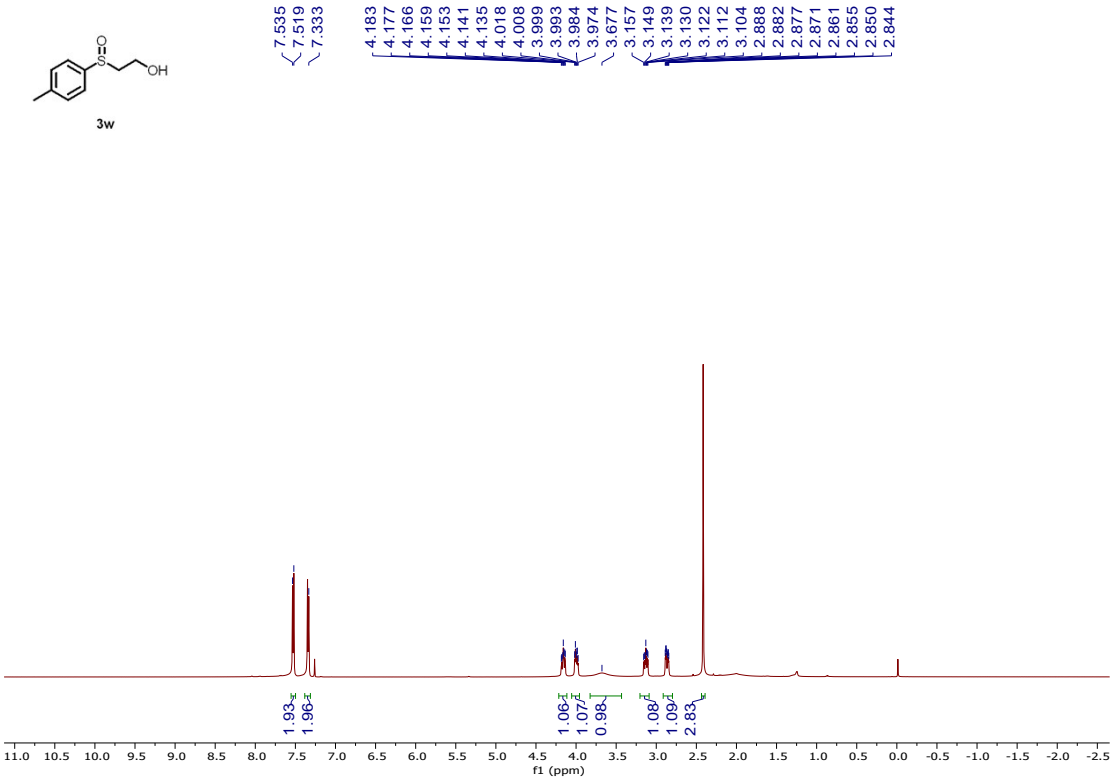

3u
7.294
7.237
7.222
7.068
7.053
6.893
6.878
4.067
4.042
3.940
3.915
2.316
1.98
1.99
2.02
2.01
1.03
1.04
2.96
2.96
f1 (ppm)


3u
141.551
139.753
138.047
130.264
129.563
129.193
126.237
124.510
63.539
21.478
21.221
f1 (ppm)

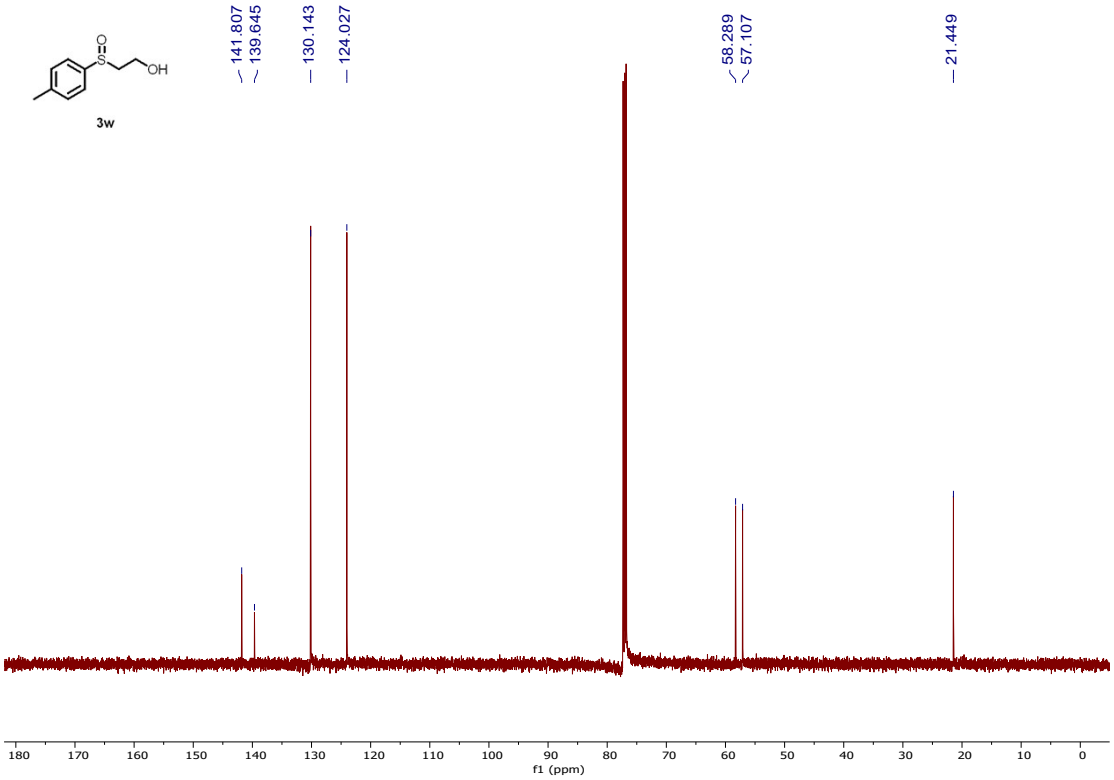

3v
7.489
7.473
7.301
5.676
5.672
5.661
5.657
5.652
5.646
5.642
5.638
5.627
5.623
5.618
5.612
5.608
5.603
5.592
5.588
5.330
5.310
5.212
5.178
3.560
3.545
3.535
3.519
3.514
3.500
3.489
3.474
2.407
1.99
1.96
1.00
1.02
0.97
2.04
3.03
f1 (ppm)

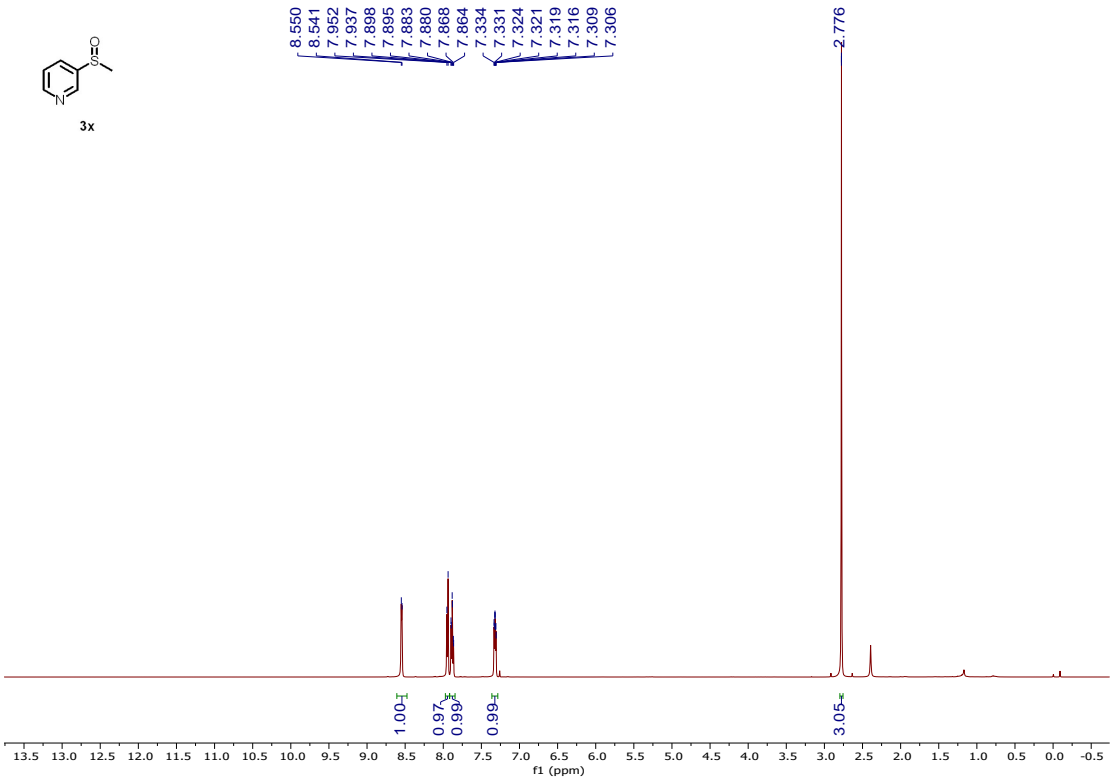

3v
141.590
139.658
129.768
125.408
124.389
123.782
60.954
21.460
f1 (ppm)

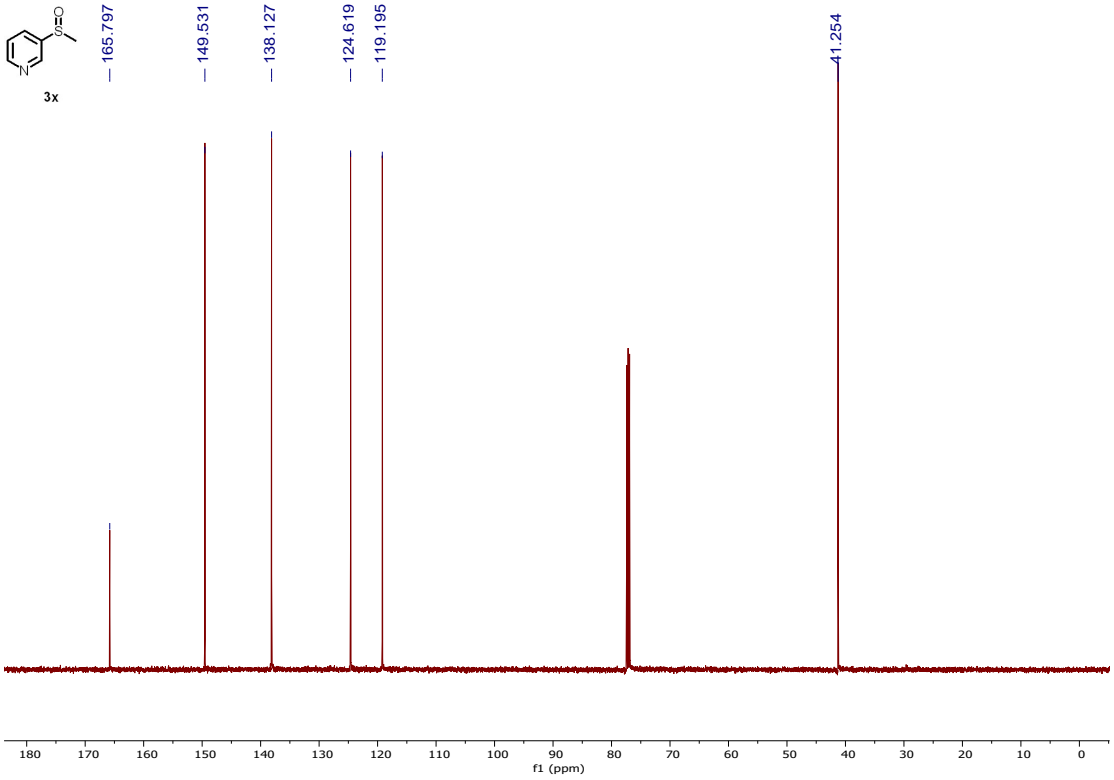
3w


7.535
7.519
7.333
4.183
4.177
4.166
4.159
4.153
4.141
4.135
4.018
4.008
3.999
3.993
3.984
3.974
3.677
3.157
3.149
3.139
3.130
3.122
3.112
3.104
2.888
2.882
2.877
2.871
2.861
2.855
2.850
2.844
1.93
1.96
1.06
1.07
0.98
1.08
1.09
2.83
f1 (ppm)

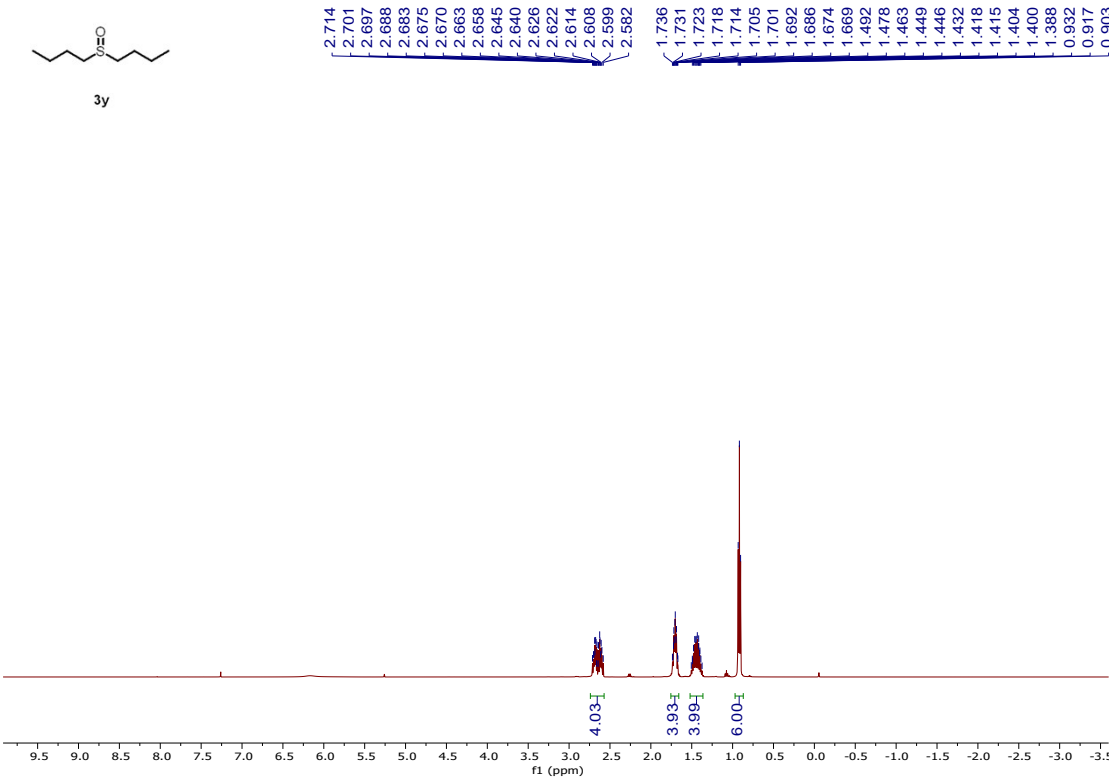
3w


141.807
139.645
130.143
124.027
58.289
57.107
21.449
f1 (ppm)

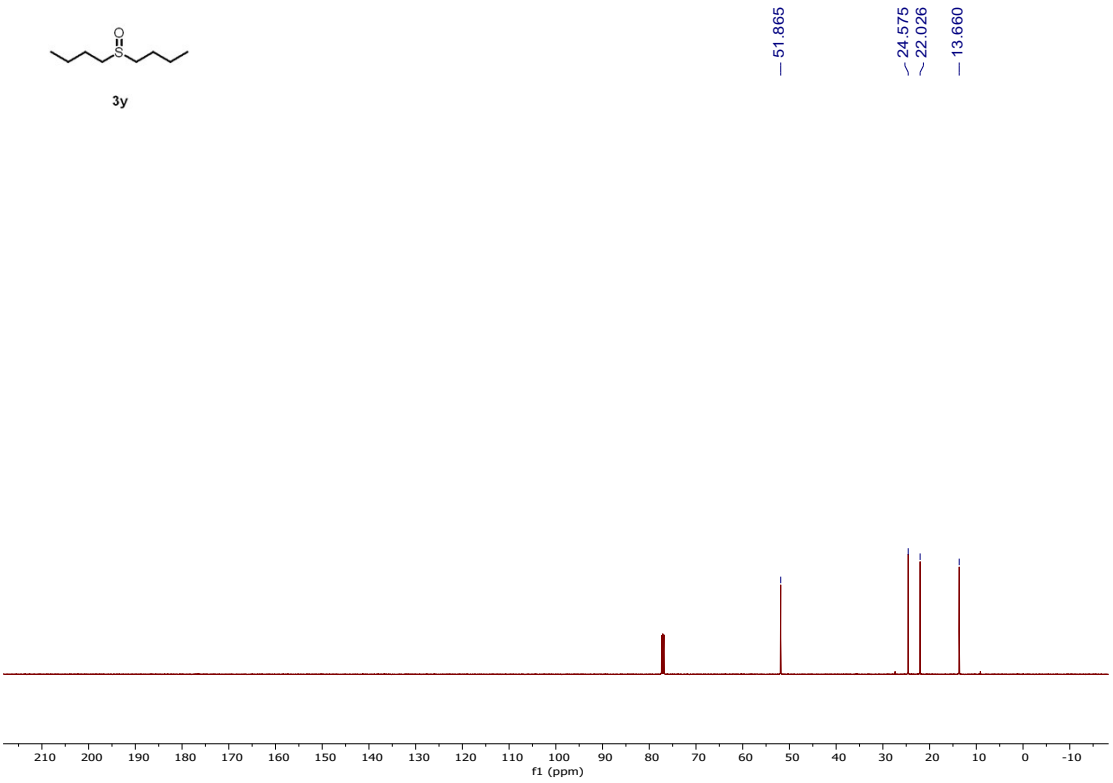

3x
8.550
8.541
7.952
7.937
7.898
7.895
7.883
7.880
7.868
7.864
7.334
7.331
7.324
7.321
7.319
7.316
7.309
7.306
2.776
1.00
0.97
0.99
0.99
3.05
f1 (ppm)

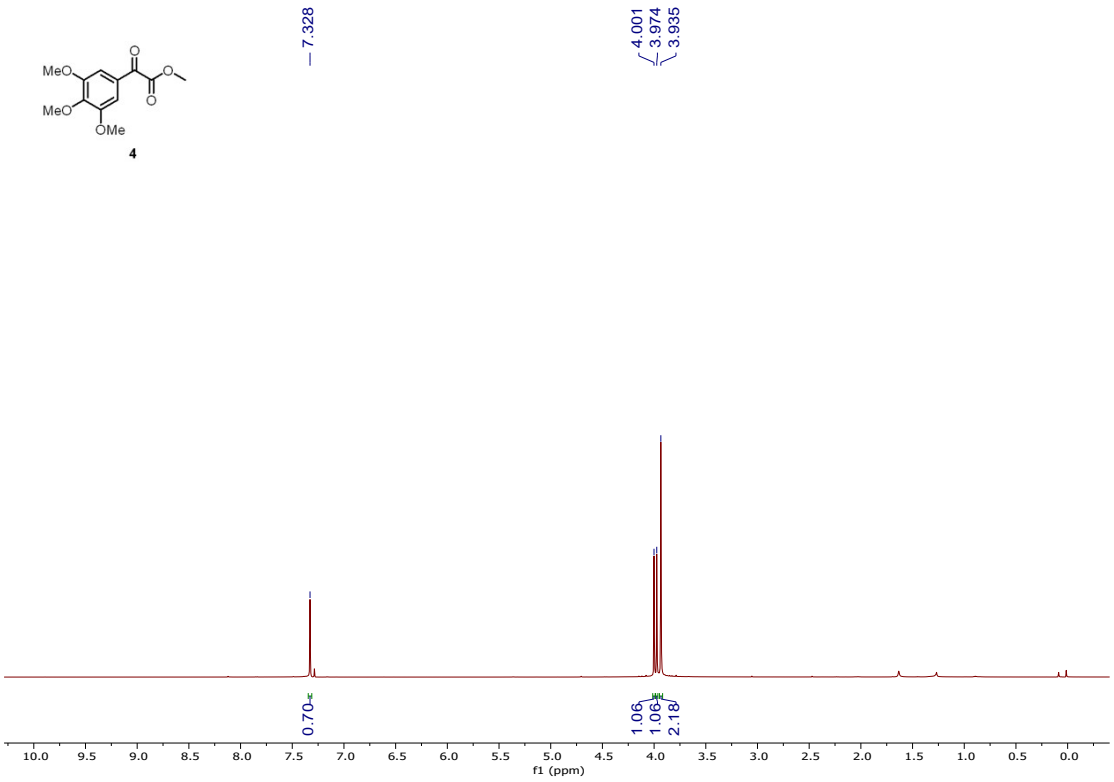

3x
165.797
149.531
138.127
124.619
119.195
41.254
f1 (ppm)

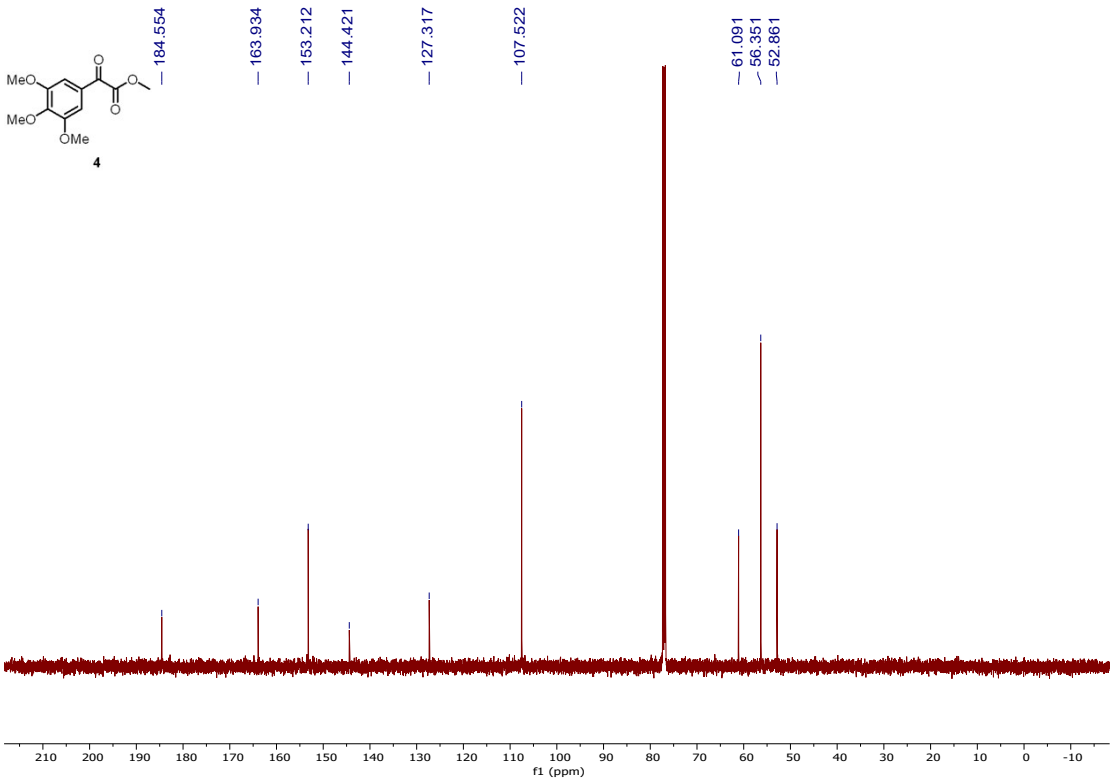
3y

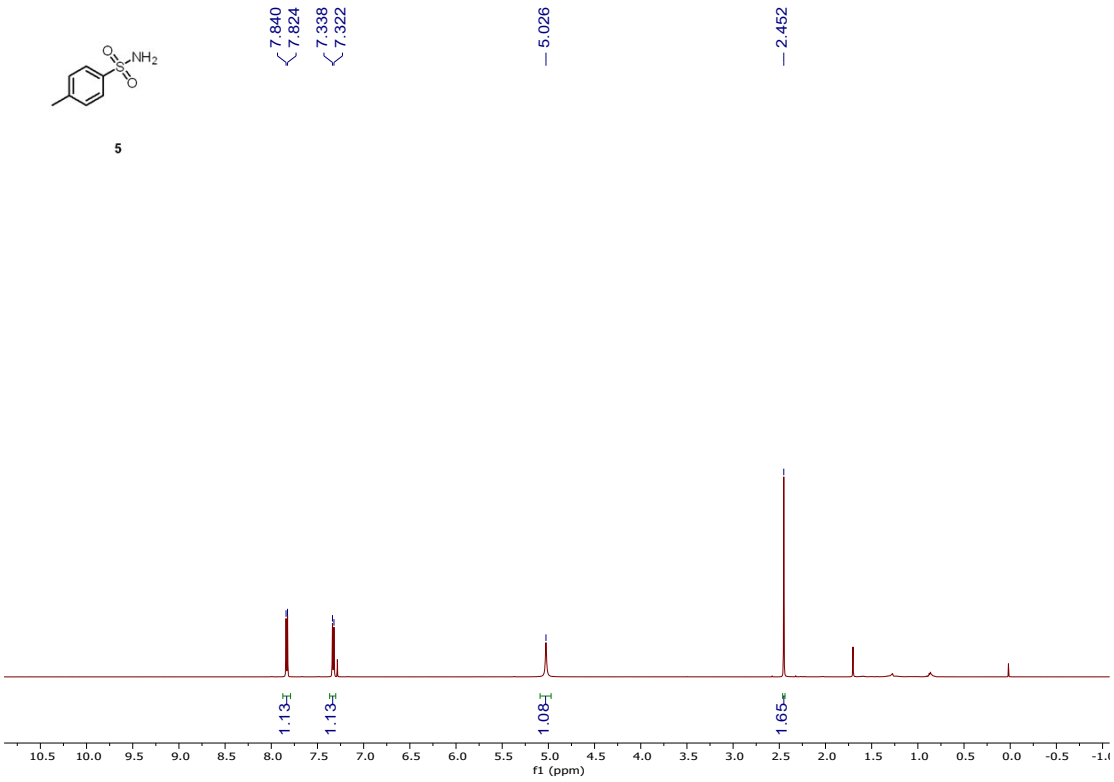

2.714
2.701
2.697
2.688
2.683
2.675
2.670
2.663
2.658
2.645
2.640
2.626
2.622
2.614
2.608
2.599
2.582
1.736
1.731
1.723
1.718
1.714
1.705
1.701
1.692
1.686
1.674
1.669
1.492
1.478
1.463
1.449
1.446
1.432
1.418
1.415
1.404
1.400
1.388
0.932
0.917
4.03
3.93
3.99
6.00
f1 (ppm)

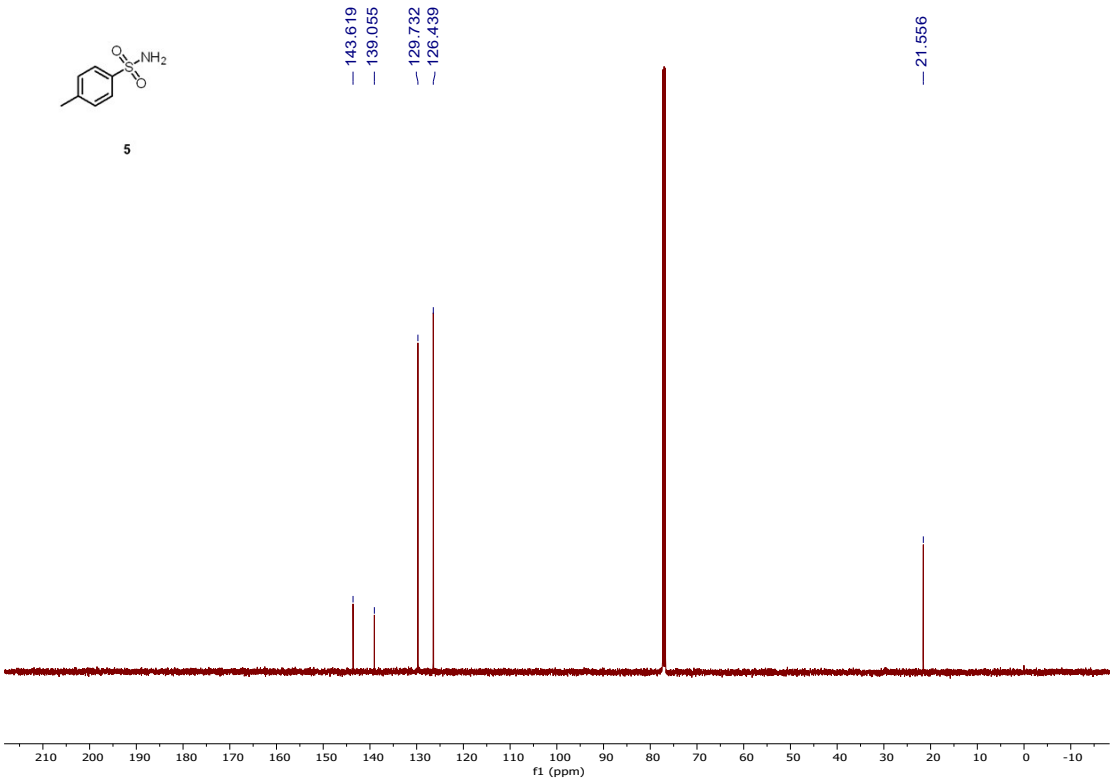
3y


51.865
24.575
22.026
13.660
f1 (ppm)


MeO
MeO
OMe
O
O
O
4
7.328
4.001
3.974
3.935
0.70
1.06
1.06
2.18
f1 (ppm)

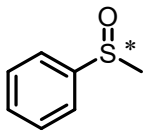

MeO
MeO
OMe
O
O
O
4
184.554
163.934
153.212
144.421
127.317
107.522
61.091
56.351
52.861
f1 (ppm)


7.840
7.824
7.338
7.322
5.026
2.452
5
1.13
1.13
1.08
1.65
f1 (ppm)


143.619
139.055
129.732
126.439
21.556
5
f1 (ppm)

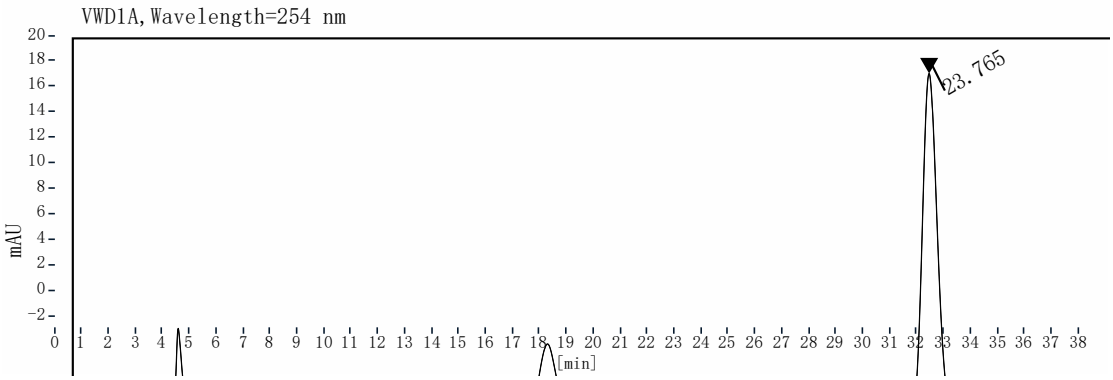
9. HPLC Data and Traces of 3p

DAICEL AS-H, hexane: *i*-PrOH= 80:20, flow rate: 1.0 mL/min, UV 254 nm, t_R =23.765 and 34.267 min).



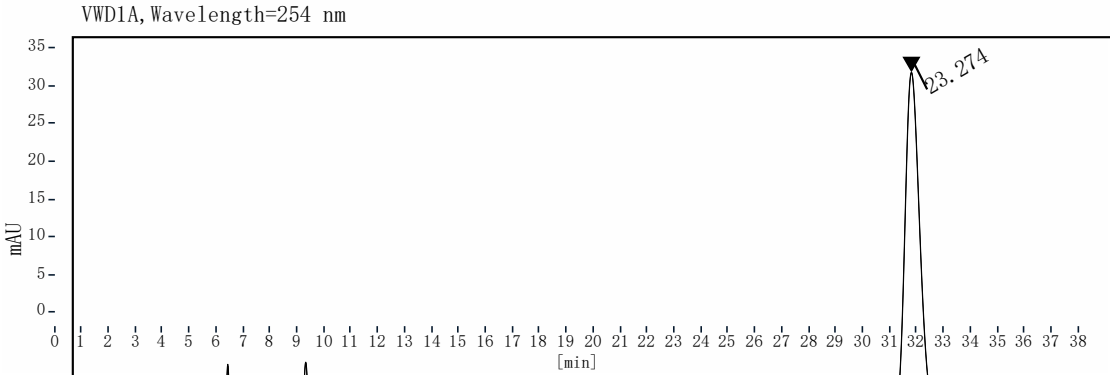
3p

Rac- 3p:



Peak	Ret Time	Width	Area	Height	Area %
1	23.765	1.25	577.96	20.25	50.07
2	34.267	2.45	576.43	13.53	49.93

Asy- 3p:



Peak	Ret Time	Width	Area	Height	Area %
1	23.274	1.95	998.85	34.61	75.28
2	33.424	3.22	328.08	7.85	24.72