Supporting Information

Iron-catalyzed synthesis of arylsulfinates through radical coupling reaction

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1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Column chromatography was performed with silica gel (200–300 mesh). Liquid chromatography area percentage yields of products in Table 1 and **2p** in Table 2 were relative to internal standard, 1-(phenylsulfonyl)piperidine. The measurements were recorded on a SHIMADZU LC-15C high performance liquid chromatography instrument.

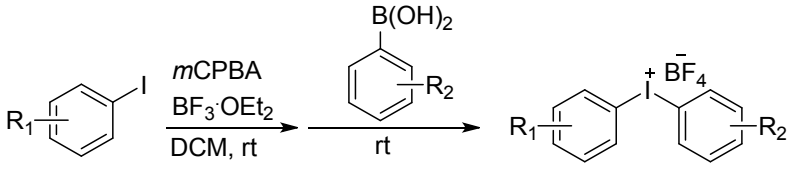
High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. Spectra were reported relative to Me_4Si (δ 0.0 ppm), $CDCl_3$ (δ 7.26 ppm), and DMSO-d_6 (δ 2.50 ppm). ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.0 ppm) and DMSO-d_6 (δ 39.5 ppm). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Known products were characterized by comparison of ^{1}H and ^{13}C NMR spectroscopic data with those available in the literature. Melting points were determined on a melting point apparatus and were uncorrected.

2. Synthesis of diaryliodonium salts

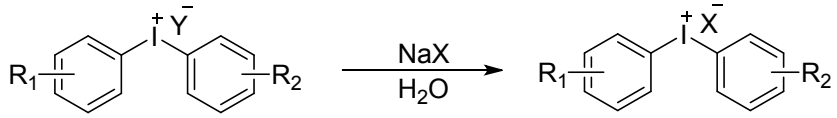
Diaryliodonium salts were synthesized according to the reported methods.

Method **A**[1]

Method **B**[2]



Method **C**[3]



Method D[4]

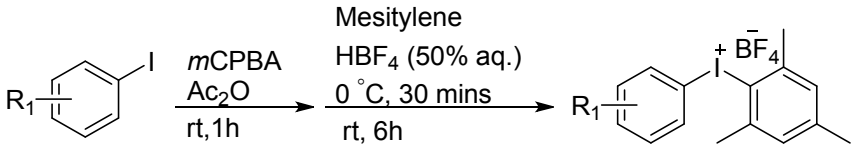
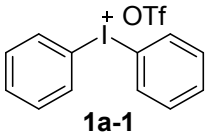
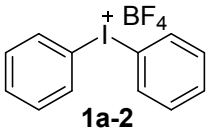
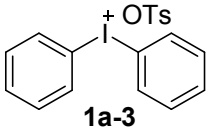
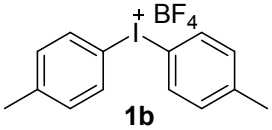
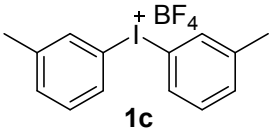
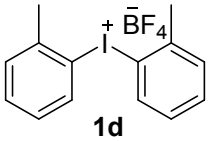
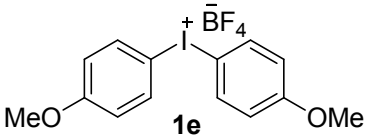
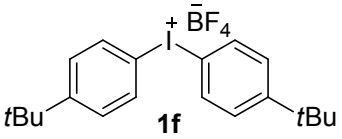
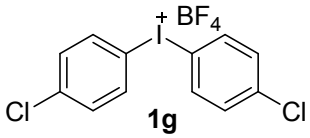
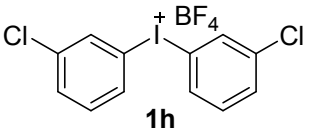
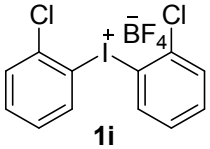
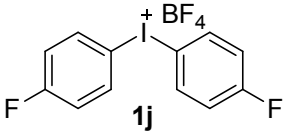
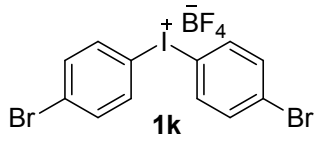
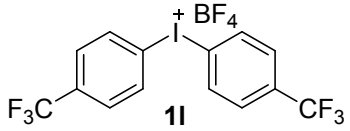
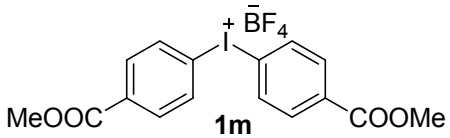
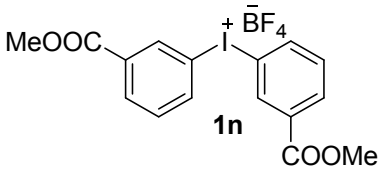
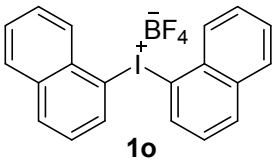
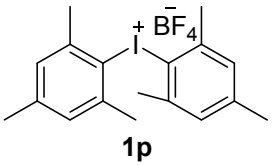
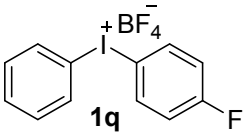
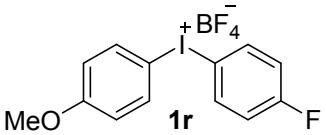
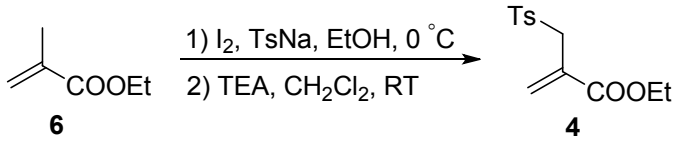


Table 1. Methods for the synthesis of diaryliodonium salts **1**

Diaryliodonium salts	Method	Diaryliodonium salts	Method
 **1a-1**	A	 **1a-2**	B
 **1a-3**	C	 **1b**	B
 **1c**	B	 **1d**	B
 **1e**	B	 **1f**	B
 **1g**	B	 **1h**	B
 **1i**	B	 **1j**	B

 **1k**	B	 **1l**	B
 **1m**	B	 **1n**	B
 **1o**	B	 **1p**	D
 **1q**	B	 **1r**	B

3. Synthesis of allylsulfone **4**. [5]



6 **4**

Iodine (7 mmol) and sodium benzenesulfinate (12 mmol) were added into ethanol containing ethyl methacrylate (8 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 5 h, then allowed to warm to room temperature. Dichloromethane (20 mL) was added and the dark brown reaction mixture was washed with water (2 × 20 mL), and the water solution was back-extracted with dichloromethane (2 × 10 mL). The combined organic layer was washed with saturated sodium hydrogen carbonate solution (30 mL) and sodium dithionite (5% solution, 2 × 30 mL). The resulting yellow solution was dried over Na_2SO_4 and concentrated to yield crude adduct as a dark oil.

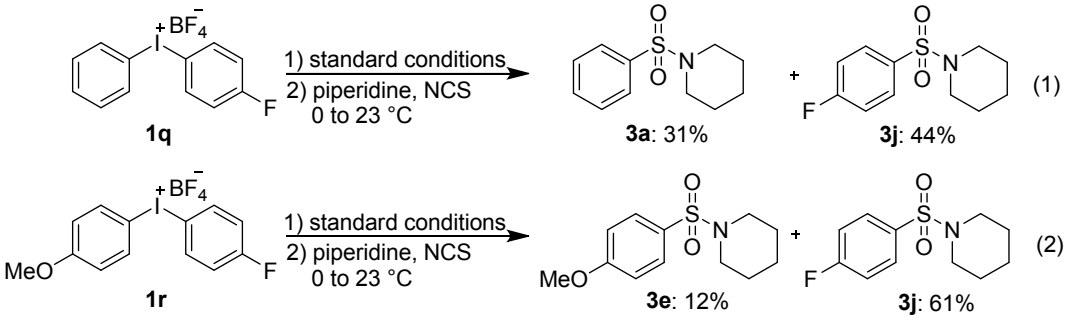
The crude adduct was diluted with dichloromethane (35 mL). Triethylamine (17

mmol) was added dropwise by a syringe over 10 min. The resulting mixture was stirred for 9 h at room temperature. The reaction mixture was concentrated by rotary evaporation. The crude product was separated by column chromatography on silica gel to afford pure allylsulfone 4 in 80% yield.

4. General procedure for the one-pot synthesis of sulfonamides.

A mixture of diaryliodonium tetrafluoroborate (0.3 mmol), rongalite (0.45 mmol), $FeCl_3$ (30 mol%) in DMF/MeCN (0.5 mL /0.5 mL) were stirred at room temperature for 20 minutes in a tube under air atmosphere. Then the suspension was dissolved in DMF (10 mL). Piperidine (0.6 mmol) and triethylamine (0.1 mmol) were then added, followed by dropwise addition of *N*-chlorosuccinimide (0.6 mmol) at 0 °C in 30 minutes. The reaction mixture was warmed to room temperature and stirred for 2 hours before water (8 mL) was added. The aqueous solution was extracted with dichloromethane (3 × 10 mL), and the combined extracts were dried with anhydrous Na_2SO_4. After removal of the solvent, the crude product was separated by column chromatography on silica gel to afford the pure sulfonamide product.

5. Investigation on the chemoselectivity of the reaction

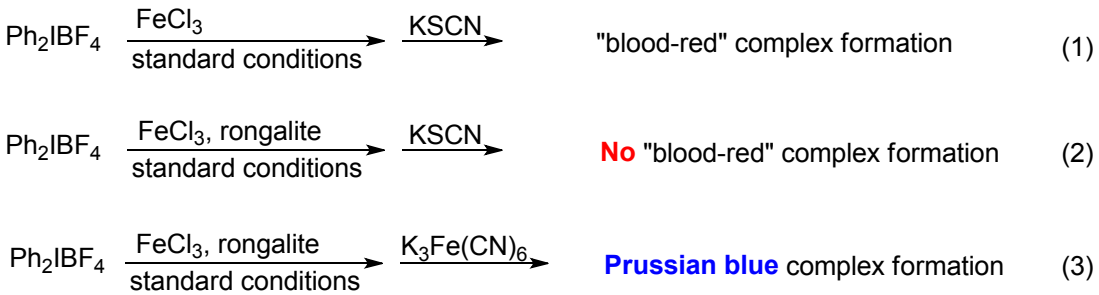


The reaction of diaryliodonium salts **1q** and **1r** with rongalite were conducted under standard conditions. The products were separated following the general procedure. **3a** and **3j** were obtained in 31% (21 mg) and 44% yields (32 mg), respectively (equation

1). **3e** and **3j** were obtained in 12% (9 mg) and 61% yields (44 mg), respectively (equation 2).

6. Controlled experiments for mechanism investigation.

(1) Determination of Fe^{2+} in the reaction system.[6]

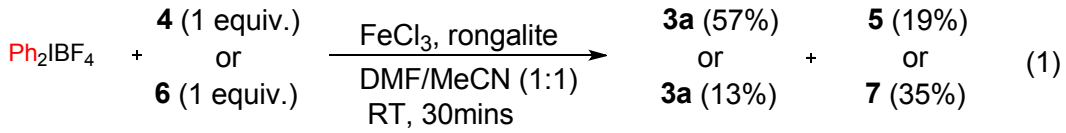


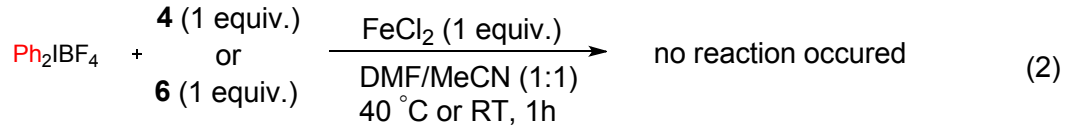
The mixture of diphenyliodonium salt (0.3 mmol) and $FeCl_3$ (15 mg, 0.09 mmol) was dissolved in DMF/MeCN (0.5ml/0.5ml) and stirred for 20 minutes. Potassium thiocyanate (aq., 2 mL, 1 mmol/mL) was then added, and "blood-red" complex was formed immediately which indicated the existence of Fe^{3+} cation and that Fe^{3+} cation could not be reduced without rongalite (equation 1).

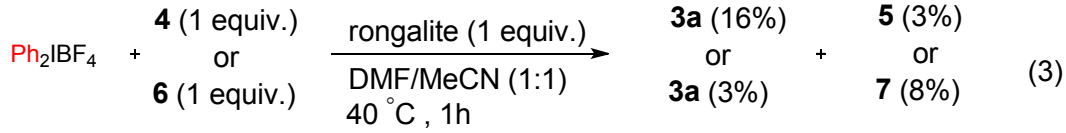
Following the general procedure, the mixture of diphenyliodonium salt (0.3 mmol), rongalite (0.45 mmol) and $FeCl_3$ (30 mol%) was dissolved in DMF/MeCN (0.5ml/0.5ml) and stirred for 20 minutes. Potassium thiocyanate (aq., 2 mL, 1 mmol/mL) was added, and the reaction mixture remained colourless. No "blood-red" complex formation indicated the absence of Fe^{3+} cation in the system after the reaction was complete (equation 2).

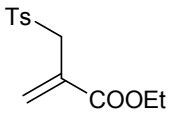
Following the general procedure, the mixture of diphenyliodonium salt (0.3 mmol), rongalite (0.45 mmol) and $FeCl_3$ (30 mol%) was dissolved in DMF/MeCN (0.5ml/0.5ml) and stirred for 20 minutes. K_3FeCN_6 (aq., 2 mL, 1 mmol/mL) was added and Prussian blue was noticed which indicated that Fe^{3+} cation was reduced to Fe^{2+} cation by rongalite (equation 3).

(2) Phenyl radical trapping reaction.









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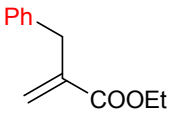

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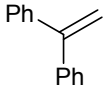
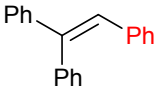


6



7

Allylsulfone **4** (0.3 mmol) was added to the mixture of diphenyliodonium salt (0.3 mmol), rongalite (0.45 mmol) and $FeCl_3$ (30 mol%) in DMF/CH_3CN (0.5 ml/0.5 ml) (equation 1).

The mixture was stirred at room temperature for 20 minutes in a tube under air atmosphere. After evaporation of the solvents, dichloromethane (20 mL) was added. The mixture was stirred vigorously, filtered and washed with dichloromethane twice (2 × 20 mL). The filtered residue was collected. The combined organic solution was dried and concentrated in vacuum. The crude product was separated by flash chromatography on a silica gel column to afford pure **5** in 19% yield (11 mg).

The collected filtered residue was dissolved in DMF (10 mL). Piperidine (0.6 mmol) and triethylamine (0.1 mmol) were then added. *N*-Chlorosuccinimide (0.6 mmol) was added dropwise at 0 °C in 30 minutes. The reaction mixture was warmed to room temperature and stirred for 2 hours. Then water (8 mL) was added. The aqueous solution was extracted with dichloromethane (3 × 10 mL), and the combined extract

was dried with anhydrous Na_2SO_4. The solvent was removed and the crude product was separated by column chromatography on silica gel to afford **3a** in 57% yield (38 mg).

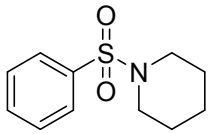
The reaction of diphenyliodonium salt with **6** was similarly performed to afford **7** in 35% yield (27 mg) and **3a** in 13% (9 mg) (equation 1).

Allylsulfone **4** (0.3 mmol) was added to the mixture of diphenyliodonium salt (0.3 mmol), $FeCl_2$ (0.3mmol) in DMF/CH_3CN (0.5 ml/0.5 ml) (equation 2). The mixture was stirred at room temperature or 40 ^oC for 1 hour. No **5** was detected.
The reaction of diphenyliodonium salt with **6** was similarly performed. No **7** was detected (equation 2).

Allylsulfone **4** (0.3 mmol) was added to the mixture of diphenyliodonium salt (0.3 mmol), rongalite (0.45 mmol) in DMF/CH_3CN (0.5 ml/0.5 ml) (equation 3).
The mixture was stirred at room temperature for 20 minutes in a tube under air atmosphere. After evaporation of the solvents, dichloromethane (20 mL) was added. The mixture was stirred vigorously, filtered and washed with dichloromethane twice (2 × 20 mL). The filtered residue was collected. The combined organic solution was dried and concentrated in vacuum. The crude product was separated by flash chromatography on a silica gel column to afford pure **5** in 3% yield (2 mg).
The collected filtered residue was dissolved in DMF (10 mL). Piperidine (0.6 mmol) and triethylamine (0.1 mmol) were then added. *N*-Chlorosuccinimide (0.6 mmol) was added dropwise at 0 ^oC in 30 minutes. The reaction mixture was warmed to room temperature and stirred for 2 hours. Then water (8 mL) was added. The aqueous solution was extracted with dichloromethane (3 × 10 mL), and the combined extract was dried with anhydrous Na_2SO_4. The solvent was removed and the crude product was separated by column chromatography on silica gel to afford **3a** in 16% yield (11 mg).
The reaction of diphenyliodonium salt with **6** was similarly performed to afford **7** in 8% yield (6 mg) and **3a** in 3% yield (2 mg) (equation 3).

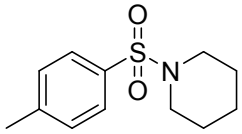
8. The spectra data of products

(1) 1-(Phenylsulfonyl)piperidine **3a**[7]



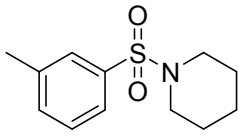
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded **3a** as a white solid (89% yeild); m.p. = 91–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 2H), 7.61–7.51 (m, 3H), 2.99 (t, *J* = 5.2 Hz, 4H), 1.67–1.61 (m, 4H), 1.43–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 132.5, 128.9, 127.7, 46.9, 25.2, 23.5. HRMS (ESI): m/z calcd for $C_{11}H_{16}NO_2S$ $[M+H]^+$: 226.0902, found: 226.0895.

(2) 1-Tosylpiperidine **3b**[7]



Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded **3b** as a white solid (87% yield); m.p. = 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 5.6 Hz, 4H), 2.43 (s, 3H), 1.65–1.59 (m, 4H), 1.44–1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 133.3, 129.5, 127.7, 46.9, 25.2, 23.5, 21.5. HRMS (ESI): m/z calcd for $C_{12}H_{18}NO_2S$ $[M+H]^+$: 240.1058, found: 240.1066.

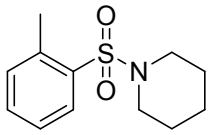
(3) 1-(*m*-Tolylsulfonyl)piperidine **3c**



Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded **3c** as a white solid (86% yield); m.p. = 62–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 6.4 Hz, 2H), 7.43–7.39 (m, 2H), 2.98 (t, *J* = 5.2 Hz, 4H), 2.44 (s, 3H), 1.67–1.62 (m, 4H), 1.45–1.40 (m, 2H); ^{13}C NMR (100 MHz,

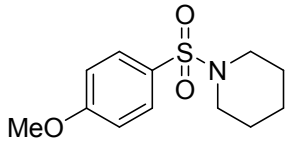
$CDCl_3$): δ = 139.1, 136.2, 133.4, 128.8, 128.0, 124.8, 47.0, 25.2, 23.5, 21.4. HRMS (ESI): m/z calcd for $C_{12}H_{18}NO_2S$ $[M+H]^+$: 240.1058, found: 240.1061.

(4) 1-(*o*-Tolylsulfonyl)piperidine **3d**



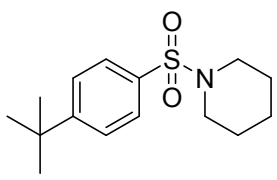
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded **3d** as colorless oil (71% yield); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.89 (m, 1H), 7.47–7.42 (m, 1H), 7.33–7.29 (m, 2H), 3.15 (t, *J* = 5.2 Hz, 4H), 2.64 (s, 3H), 1.64–1.59 (m, 4H), 1.54–1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 136.3, 132.7, 132.6, 130.2, 125.9, 46.0, 25.4, 23.8, 20.7. HRMS (ESI): m/z calcd for $C_{12}H_{18}NO_2S$ $[M+H]^+$: 240.1058, found: 240.1053.

(5) 1-((4-Methoxyphenyl)sulfonyl)piperidine **3e**



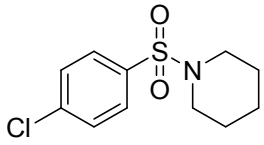
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3e** as a white solid (86% yield); m.p. = 66–68 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.96 (t, *J* = 5.2 Hz, 4H), 1.67–1.61 (m, 4H), 1.43–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 129.8, 128.0, 114.1, 55.6, 46.9, 25.2, 23.5. HRMS (ESI): m/z calcd for $C_{12}H_{18}NO_3S$ $[M+H]^+$: 256.1007, found: 240.1016.

(6) 1-((4-(*tert*-Butyl)phenyl)sulfonyl)piperidine **3f**



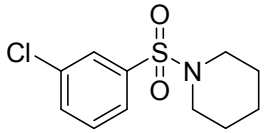
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded **3f** as a white solid (87% yield); m.p. = 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.99 (t, *J* = 5.2 Hz, 4H), 1.66–1.62 (m, 4H), 1.44–1.42 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 133.3, 127.6, 125.9, 46.9, 35.1, 31.1, 25.2, 23.5. HRMS (ESI): m/z calcd for $C_{15}H_{24}NO_2S$ $[M+H]^+$: 282.1528, found: 282.1521.

(7) 1-((4-Chlorophenyl)sulfonyl)piperidine **3g**



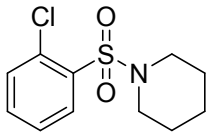
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3g** as a white solid (84% yield); m.p. = 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 2.99 (t, *J* = 5.6 Hz, 4H), 1.68–1.62 (m, 4H), 1.46–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =139.1, 135.0, 129.3, 129.1, 46.9, 25.1, 23.5. HRMS (ESI): m/z calcd for $C_{11}H_{15}ClNO_2S$ $[M+H]^+$: 260.0512, found: 260.0511.

(8) 1-((3-Chlorophenyl)sulfonyl)piperidine **3h**



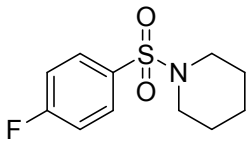
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3h** as a white solid (76% yield); m.p. = 74–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (t, *J* = 1.8 Hz, 2H), 7.64 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.56 (dq, *J* = 8.0, 0.8 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 3.01 (t, *J* = 5.6 Hz, 4H), 1.69–1.63 (m, 4H), 1.47–1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 135.3, 132.7, 130.3, 127.6, 125.7, 46.9, 25.2, 23.4. HRMS (ESI): m/z calcd for $C_{11}H_{15}ClNO_2S$ $[M+H]^+$: 260.0512, found: 260.0518.

(9) 1-((2-Chlorophenyl)sulfonyl)piperidine **3i**



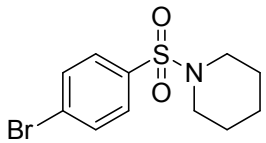
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3i** as colourless oil (61% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47 (td, *J* = 8.0, 1.6 Hz, 1H), 7.38 (td, *J* = 8.0, 1.2 Hz, 1H), 3.26 (t, *J* = 5.2 Hz, 4H), 1.65–1.60 (m, 4H), 1.56–1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 133.4, 132.3, 132.1, 132.1, 126.8, 46.5, 25.6, 23.8. HRMS (ESI): m/z calcd for $C_{11}H_{15}ClNO_2S$ $[M+H]^+$: 260.0512, found: 260.0505.

(10) 1-((4-Fluorophenyl)sulfonyl)piperidine **3j**



Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3j** as a white solid (79% yield); m.p. = 76–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.75 (m, 2H), 7.23–7.19 (m, 2H), 2.99 (t, *J* = 5.6 Hz, 4H), 1.68–1.62 (m, 4H), 1.46–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1 (d, $J_{C\text{-}F}$ = 260 Hz), 132.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.3 (d, $J_{C\text{-}F}$ = 9.1 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22.3 Hz), 46.9, 25.1, 23.5. HRMS (ESI): m/z calcd for $C_{11}H_{15}FNO_2S$ $[M+H]^+$: 244.0808, found: 244.0803.

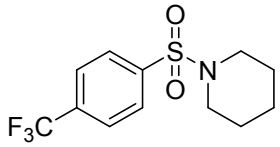
(11) 1-((4-Bromophenyl)sulfonyl)piperidine **3k**[7]



Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3k** as a white solid (62% yield); m.p. = 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 2.99 (t, *J* = 5.2

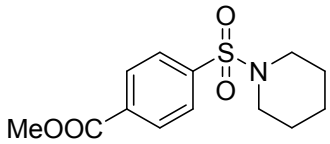
Hz, 4H), 1.67–1.62 (m, 4H), 1.46–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.5, 132.3, 129.2, 127.6, 46.9, 25.1, 23.5. HRMS (ESI): m/z calcd for $C_{11}H_{15}BrNO_2S$ $[M+H]^+$: 304.0007, found: 304.0000.

(12) 1-((4-(Trifluoromethyl)phenyl)sulfonyl)piperidine **3l**



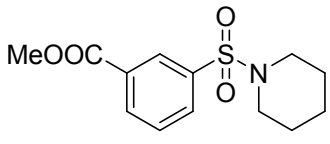
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3l** as a white solid (85% yield); m.p. = 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 3.03 (t, J = 5.2 Hz, 4H), 1.69–1.63 (m, 4H), 1.48–1.44(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 134.3 (q, $J_{C\text{-}F}$ = 32.8 Hz), 128.1, 126.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.3 (q, $J_{C\text{-}F}$ = 271 Hz), 46.9, 25.2, 23.4. HRMS (ESI): m/z calcd for $C_{12}H_{15}F_3NO_2S$ $[M+H]^+$: 294.0776, found: 294.0766.

(13) Methyl 4-(piperidin-1-ylsulfonyl)benzoate **3m**



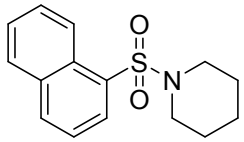
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3m** as a white solid (81% yield); m.p. = 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 3.97 (s, 3H), 3.01 (t, J = 5.6 Hz, 4H), 1.67–1.62 (m, 4H), 1.44–1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 140.5, 133.8, 130.2, 127.6, 52.7, 46.9, 25.1, 23.5. HRMS (ESI): m/z calcd for $C_{13}H_{18}NO_4S$ $[M+H]^+$: 284.0957, found: 284.0950.

(14) Methyl 3-(piperidin-1-ylsulfonyl)benzoate **3n**



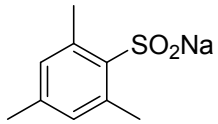
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **3n** as a white solid (84% yield); m.p. = 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 3.01 (s, *J* = 5.2 Hz, 4H), 1.67–1.63 (m, 4H), 1.44–1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 137.2, 133.5, 131.7, 131.3, 129.2, 128.6, 52.6, 47.0, 25.1, 23.5. HRMS (ESI): m/z calcd for $C_{13}H_{18}NO_4S$ $[M+H]^+$: 284.0957, found: 284.0964.

(15) 1-(Naphthalen-1-ylsulfonyl)piperidine **3o**



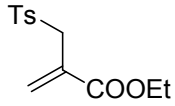
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 7/1, v/v) afforded **3o** as a white solid (82% yield); m.p. = 67–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 8.8 Hz, 1H), 8.21 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.65–7.52 (m, 3H), 3.17 (s, 4H), 1.61–1.55 (m, 4H), 1.46–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 134.2, 133.3, 130.4, 129.0, 128.8, 127.9, 126.8, 125.4, 124.1, 46.4, 25.4, 23.7. HRMS (ESI): m/z calcd for $C_{15}H_{18}NO_2S$ $[M+H]^+$: 276.1058, found: 276.1049.

(16) Sodium 2,4,6-trimethylbenzenesulfinate **2p**



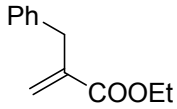
Liquid chromatography area percentage yield of **2p** was relative to internal standard. The characterization of products was performed on UPLC/Q-TOF-MS, (ESI): m/z calcd for $C_9H_{11}O_2S$ $[M-Na]^-$: 183.0480, found: 183.0485. **2p** was further identified by comparing its HPLC performance with that of an authentic sample prepared following literature.[8]

(17) Ethyl 2-(tosylmethyl)acrylate **4**[9]



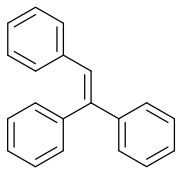
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 0.8 Hz, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 4.14 (d, *J* = 0.4 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 144.9, 135.5, 133.2, 129.7, 129.3, 128.8, 61.5, 57.6, 21.6, 14.0. HRMS (ESI): m/z calcd for $C_{13}H_{16}O_4S$ $[M+H]^+$: 269.0848, found: 269.0841.

(18) Ethyl 2-benzylacrylate **5**[9]



Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.12 (m, 5H), 6.16 (s, 1H), 5.37 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.56 (s, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 139.4, 137.8, 128.0, 127.4, 125.3, 124.9, 59.7, 37.1, 13.1. HRMS (ESI): m/z calcd for $C_{14}H_{12}O_2$ $[M+H]^+$: 191.1072, found: 191.1077.

(19) Triphenylethylene **7**[10]



Colourless oil; ^{1}H NMR (400 MHz, CDCl3): δ = 7.33–7.27 (m, 8H), 7.22–7.19 (m, 2H), 7.16–7.08 (m, 3H), 7.04–7.02 (m, 2H), 6.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl3): δ = 143.5, 142.6, 140.4, 137.4, 130.4, 129.6, 128.7, 128.2, 128.2, 128.0, 127.6, 127.5, 127.4, 126.8. MS (EI) m/z (%) 256 (M^+, 100).

9. References

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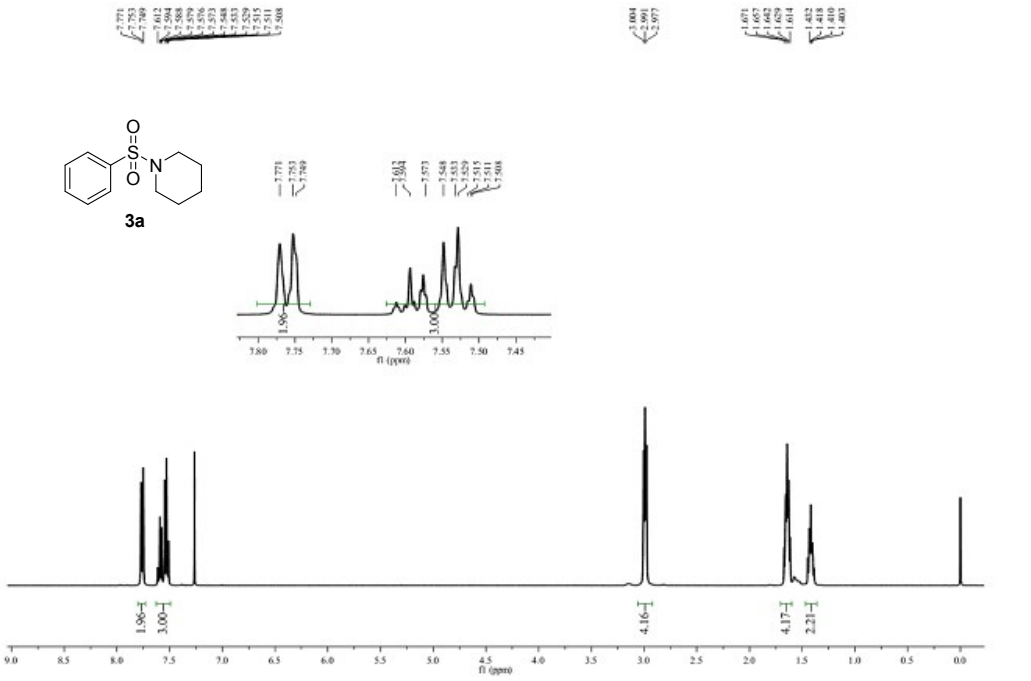
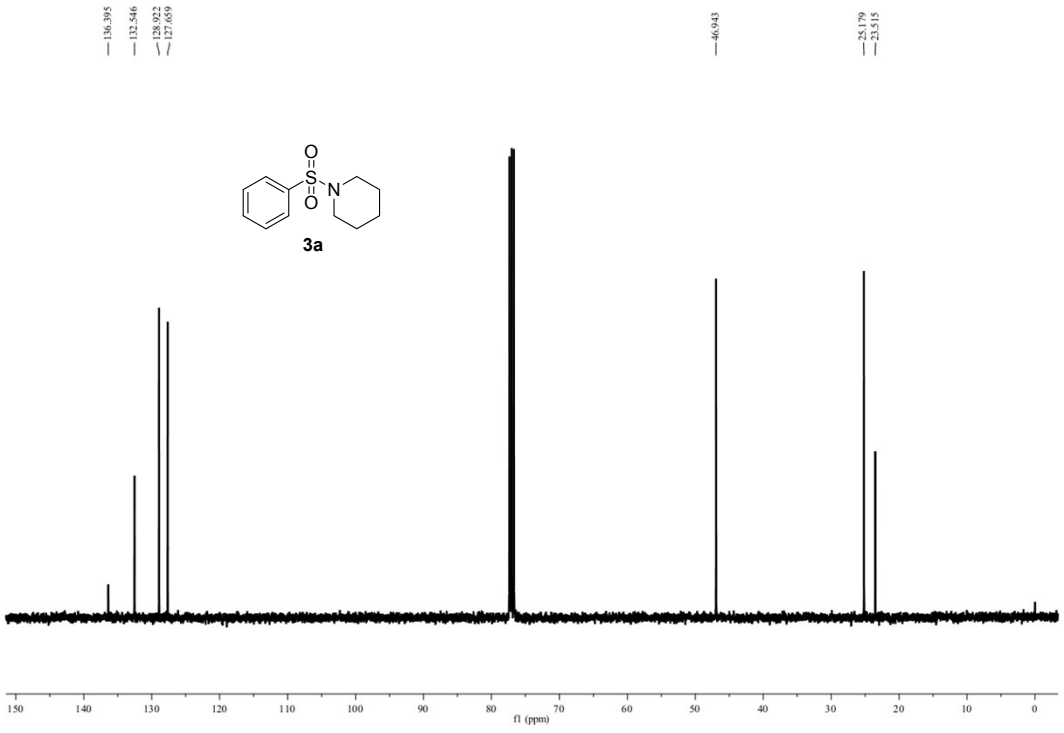
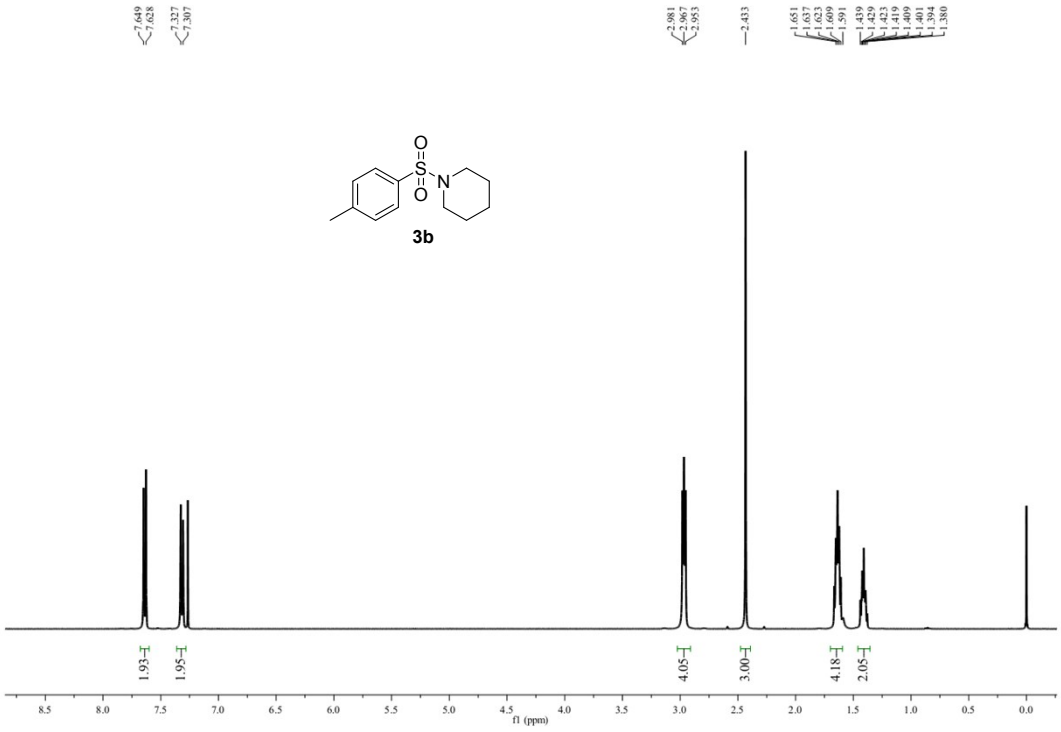
^{1}H and ^{13}C NMR spectra



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7.628
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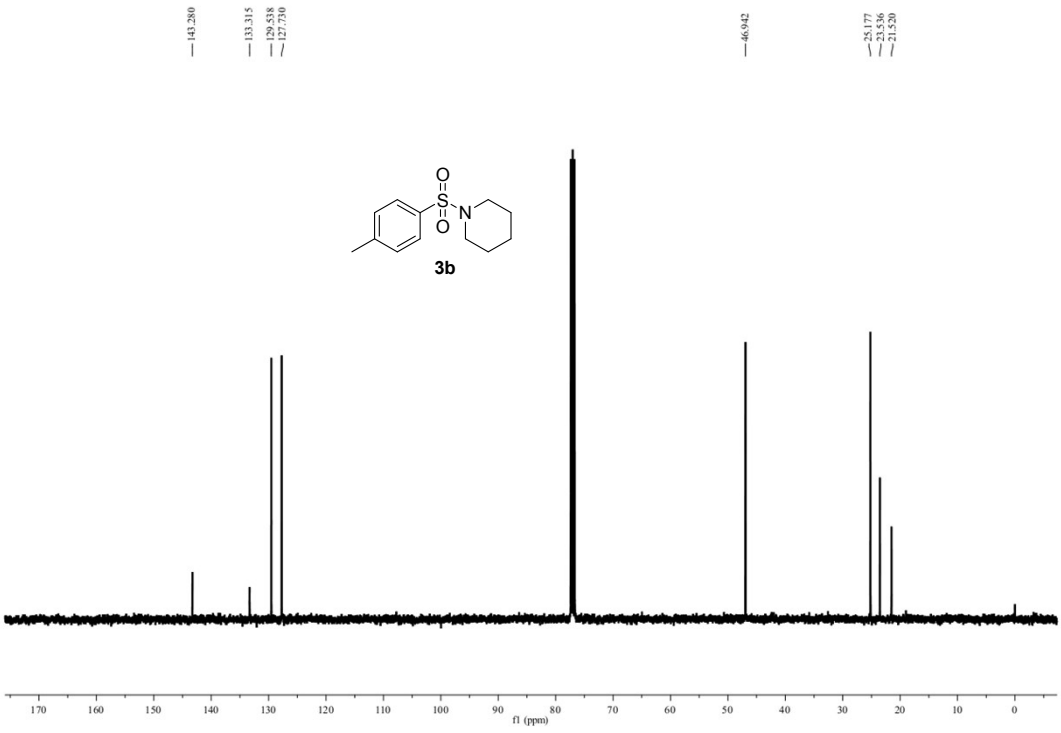
2.967
2.953
2.433
1.651
1.637
1.623
1.609
1.591
1.439
1.429
1.423
1.419
1.409
1.401
1.394
1.380
3b
1.93
1.95
4.05
3.00
4.18
2.05
f1 (ppm)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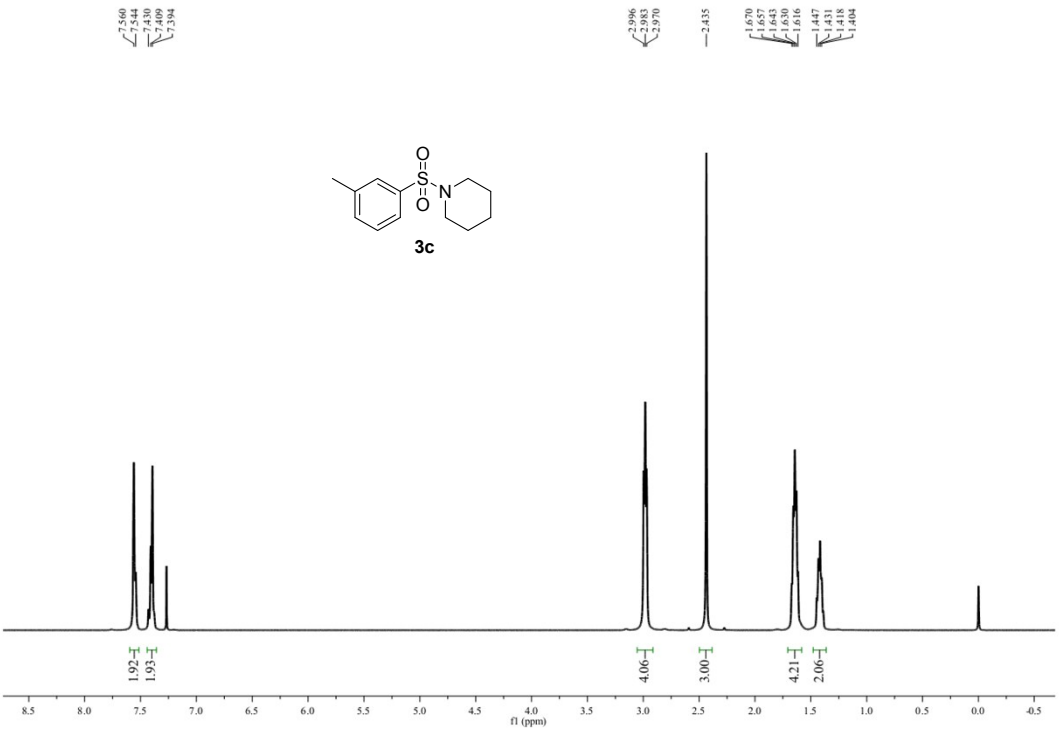
21.520
3b
f1 (ppm)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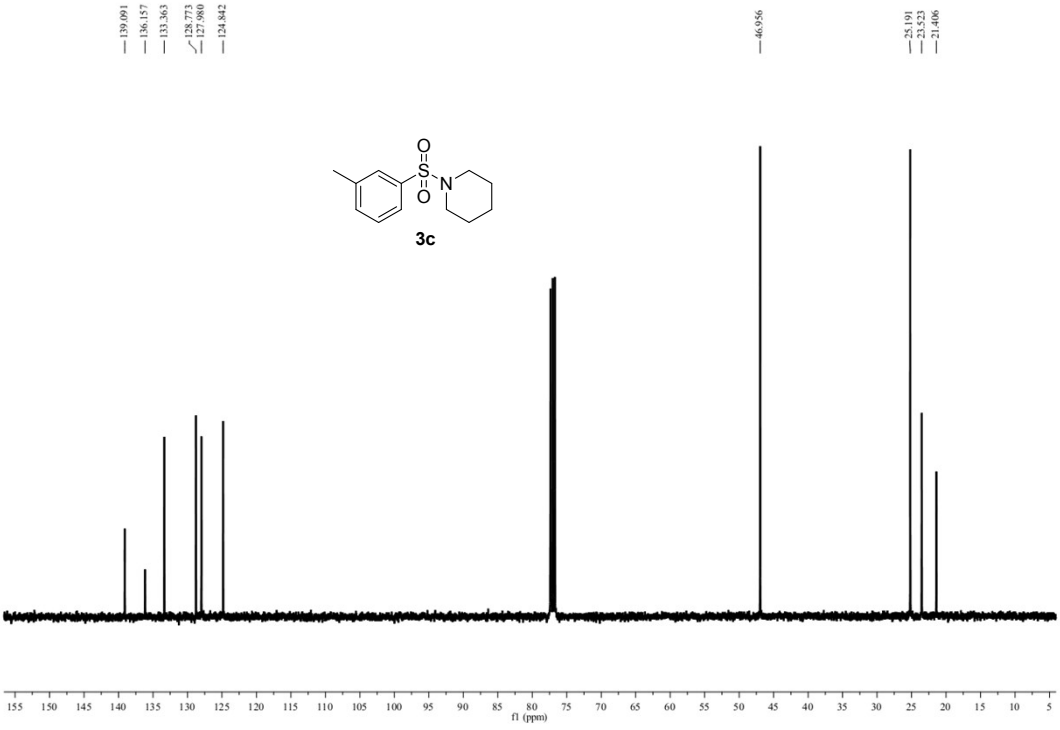
f1 (ppm)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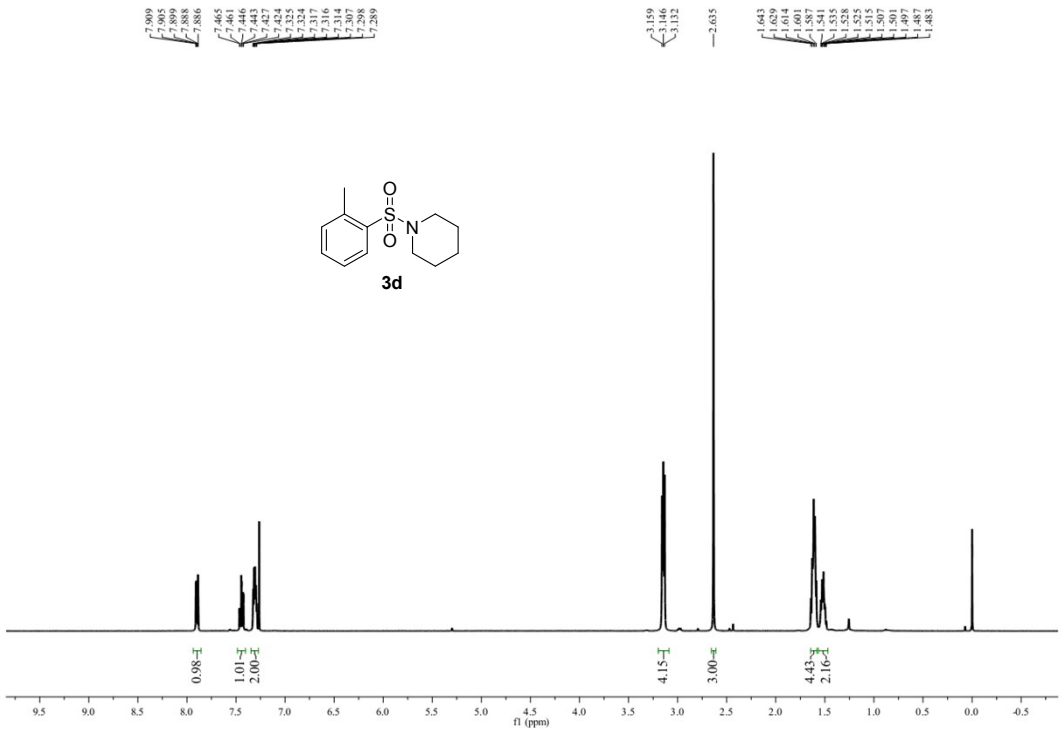
3c
f1 (ppm)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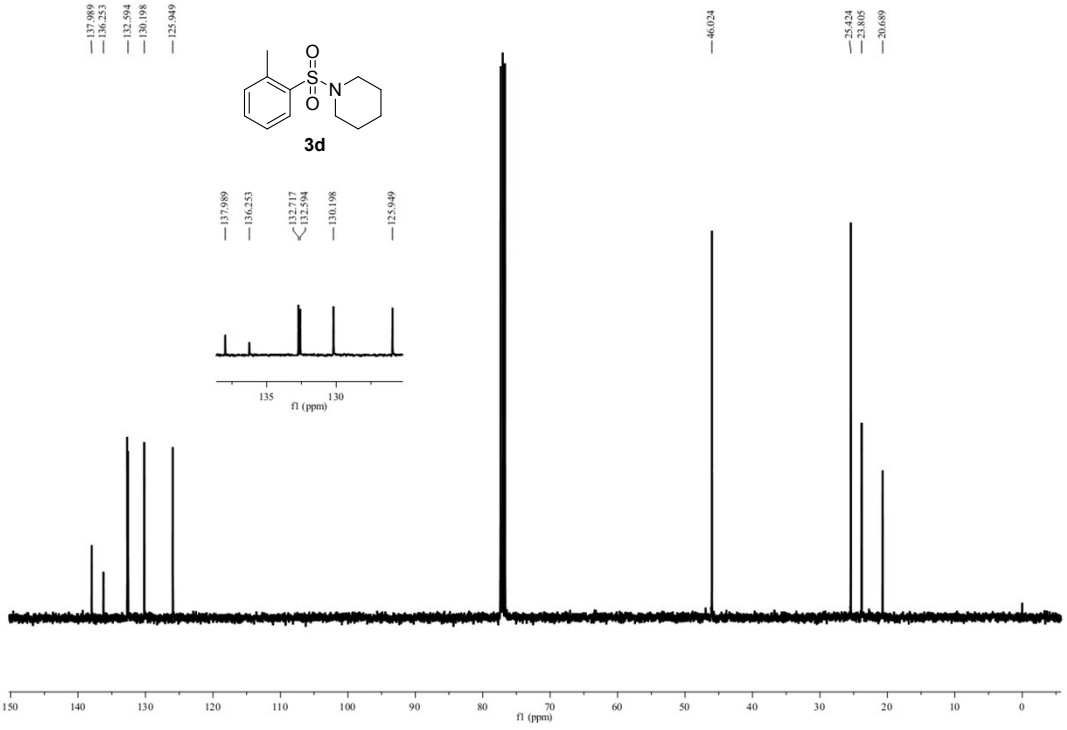
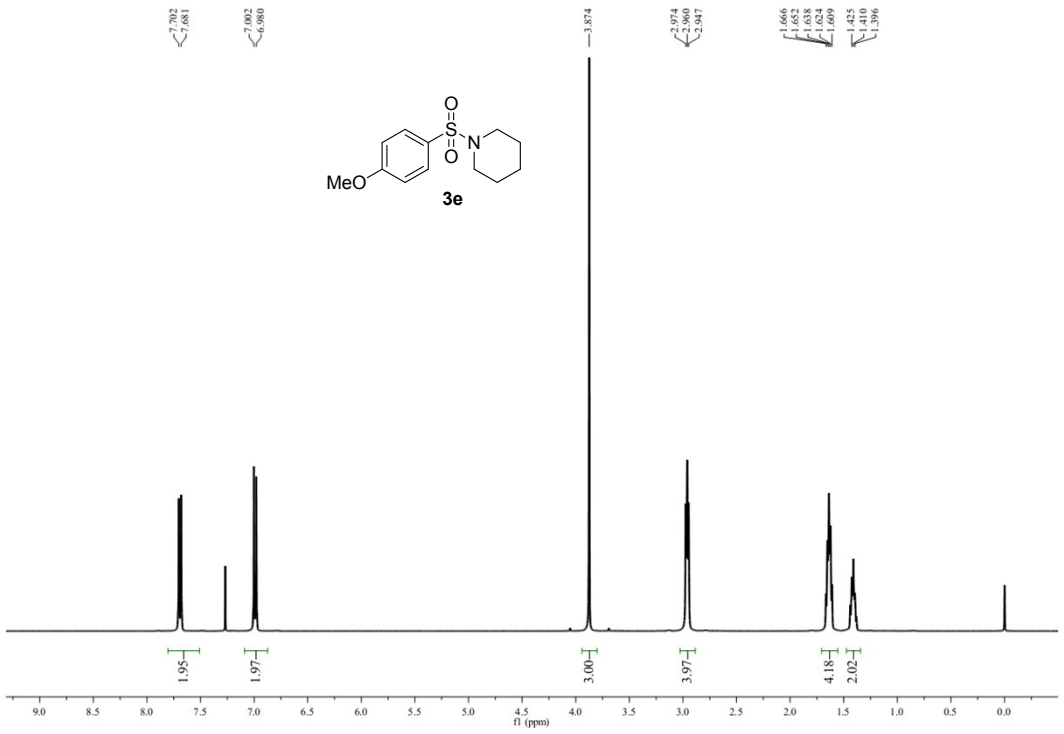
7.905
7.899
7.888
7.886
7.465
7.461
7.446
7.443
7.427
7.424
7.325
7.324
7.317
7.316
7.314
7.307
7.298
7.289
3.159
3.146
3.132
2.635
1.643
1.629
1.614
1.601
1.587
1.541
1.535
1.528
1.515
1.507
1.501
1.497
1.487
1.483
3d
0.98
1.01
2.00
4.15
3.00
4.43
2.16
f1 (ppm)


137.989
136.253
132.594
130.198
125.949
46.024
25.424
23.805
20.689
3d
137.989
136.253
132.717
132.594
130.198
125.949
135
130
f1 (ppm)
f1 (ppm)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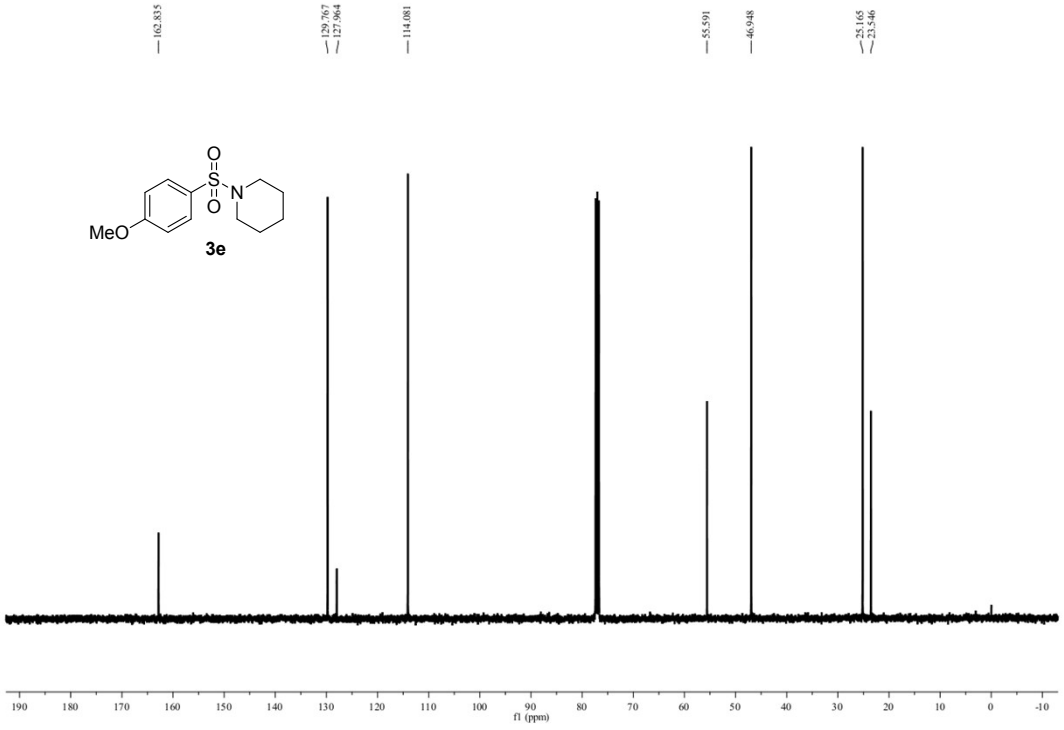
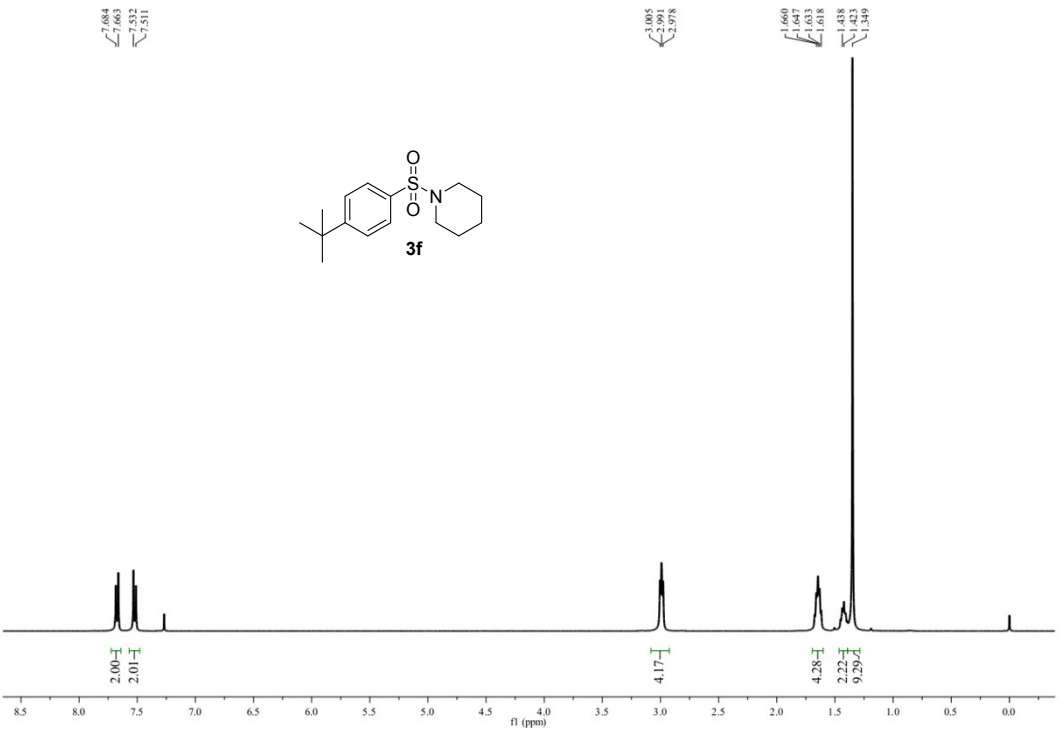
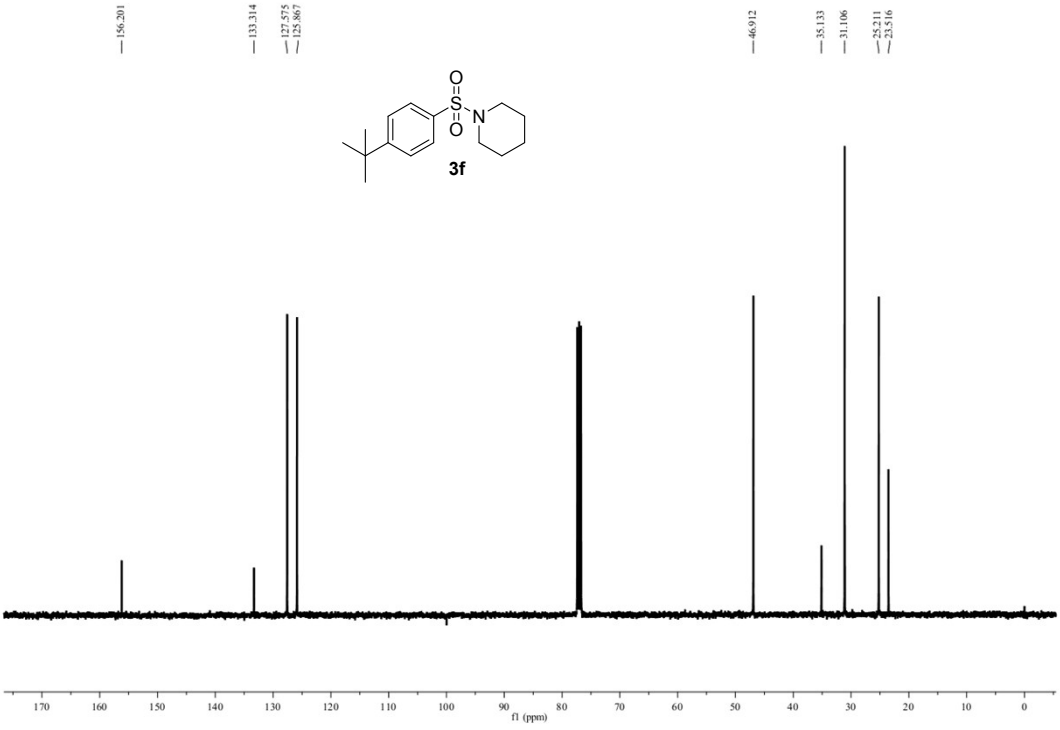
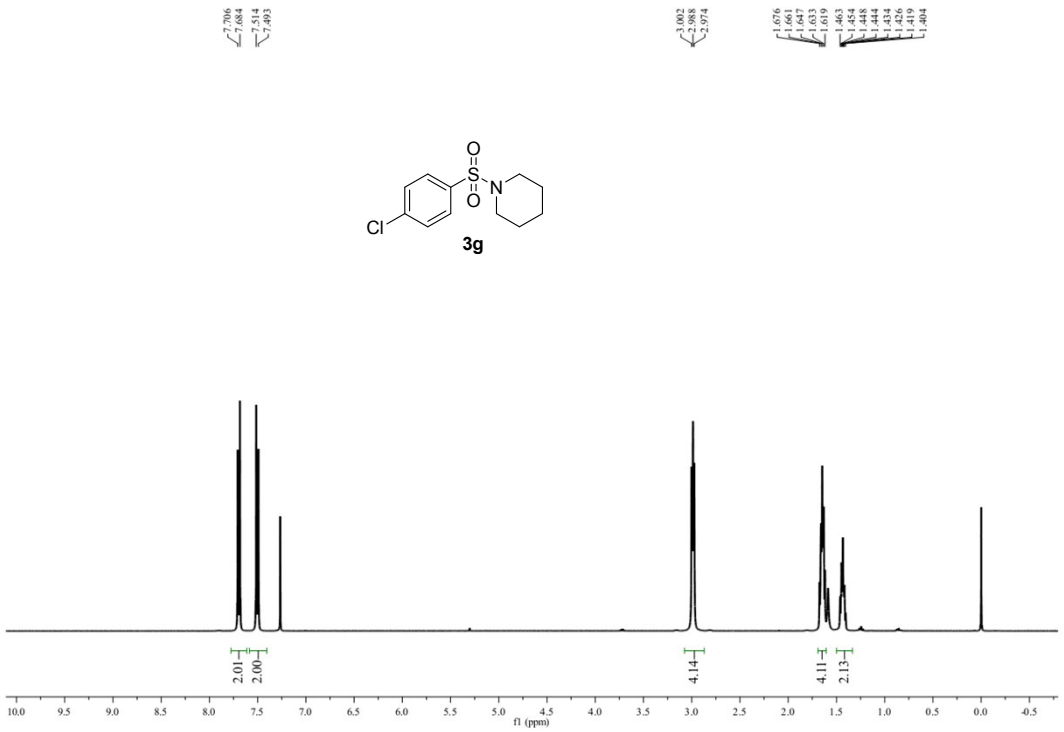
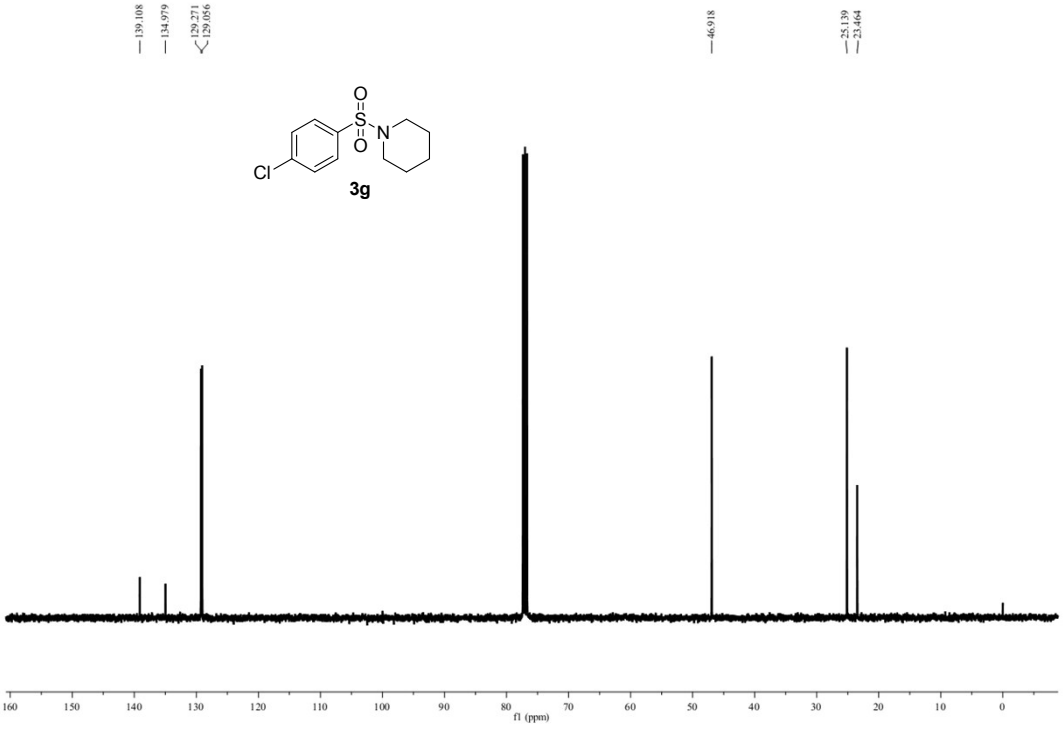
7.681
7.002
6.980
3.874
2.974
2.960
2.947
1.666
1.652
1.638
1.624
1.609
1.425
1.410
1.396
MeO
3e
1.95
1.97
3.00
3.97
4.18
2.02
f1 (ppm)

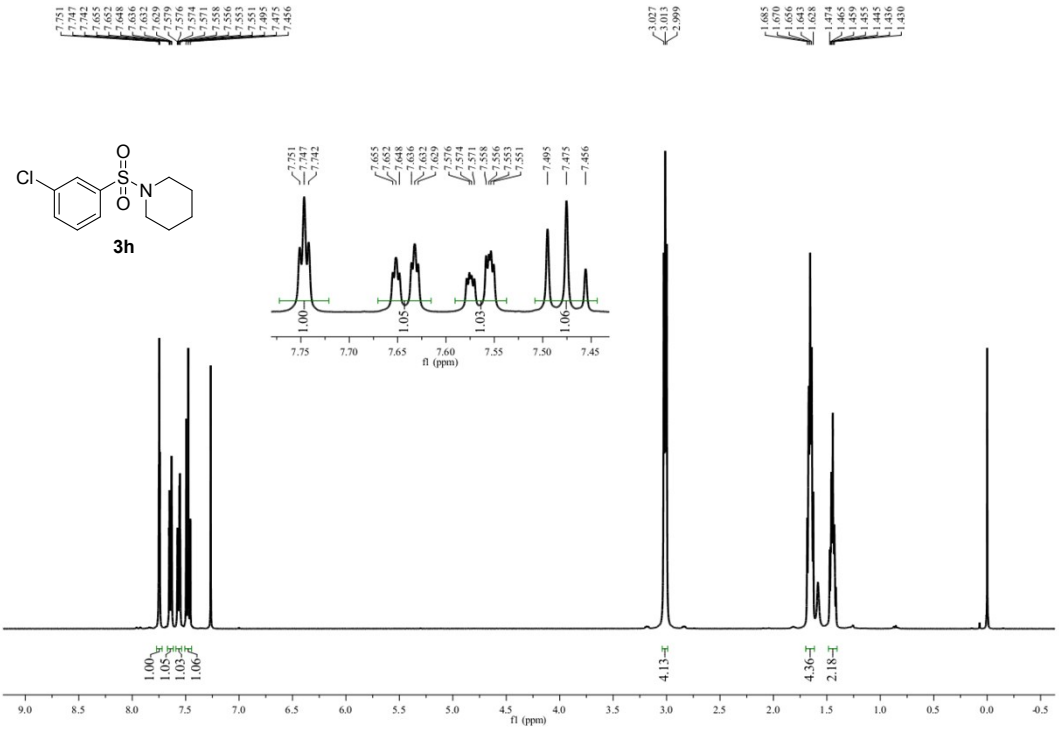

162.835
129.767
127.964
114.081
55.591
46.948
25.165
23.546
MeO
3e
f1 (ppm)

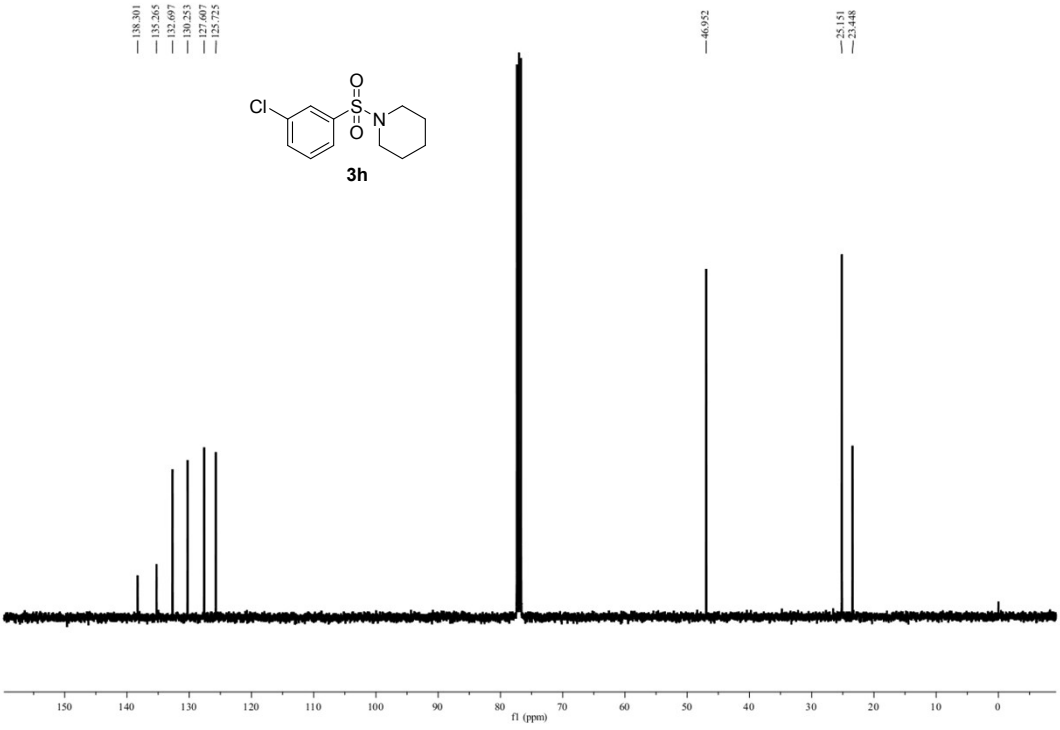

7.684
7.663
7.532
7.511
3.005
2.991
2.978
1.660
1.647
1.633
1.618
1.438
1.423
1.349
3f
2.00
2.01
4.17
4.28
2.22
9.29
f1 (ppm)

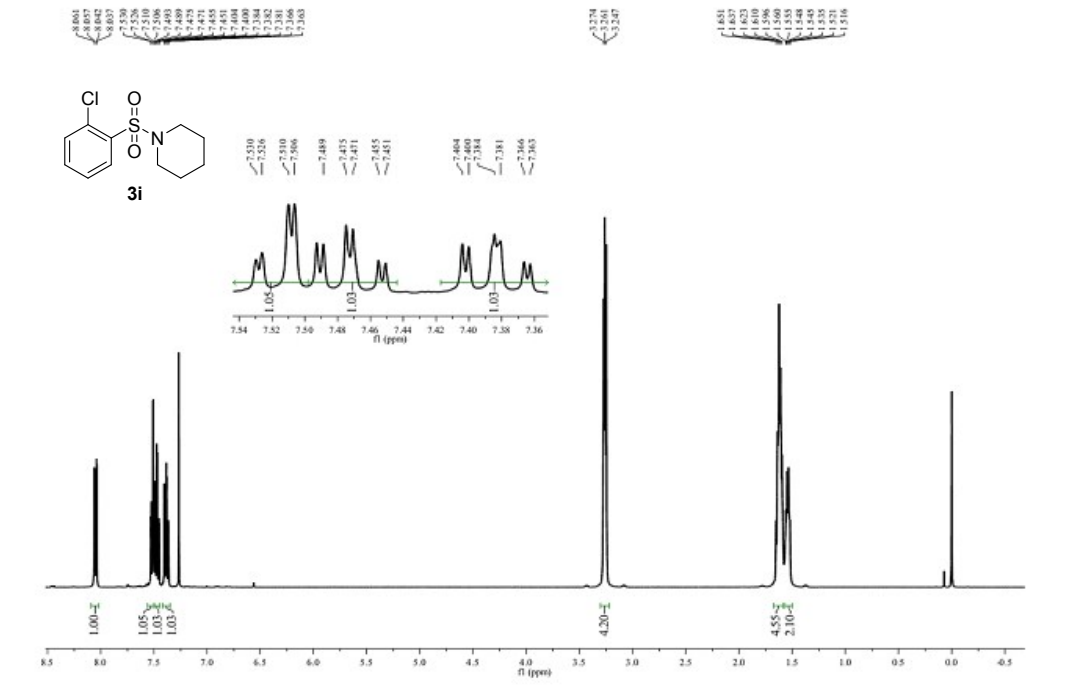

156.201
133.314
127.575
125.867
46.912
35.133
31.106
25.211
23.516
3f
f1 (ppm)

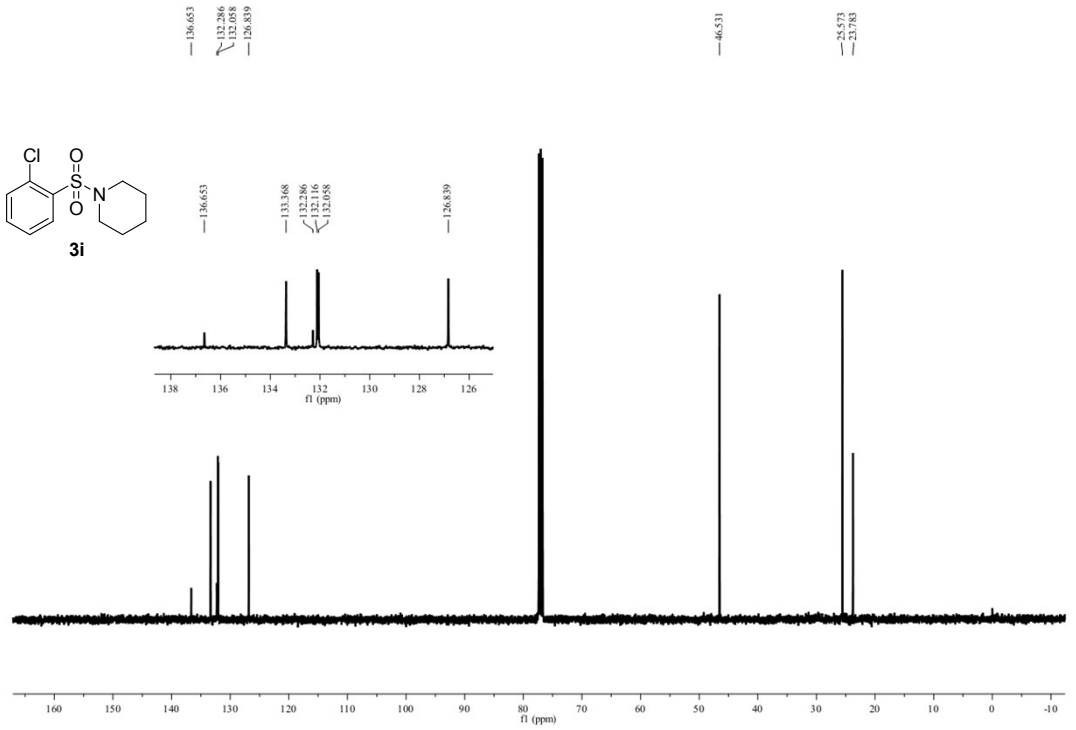

7.706
7.684
7.514
7.493
3.002
2.988
2.974
1.676
1.661
1.647
1.633
1.619
1.463
1.454
1.448
1.444
1.434
1.426
1.419
1.404
Cl
3g
2.01
2.00
4.14
4.11
2.13
f1 (ppm)

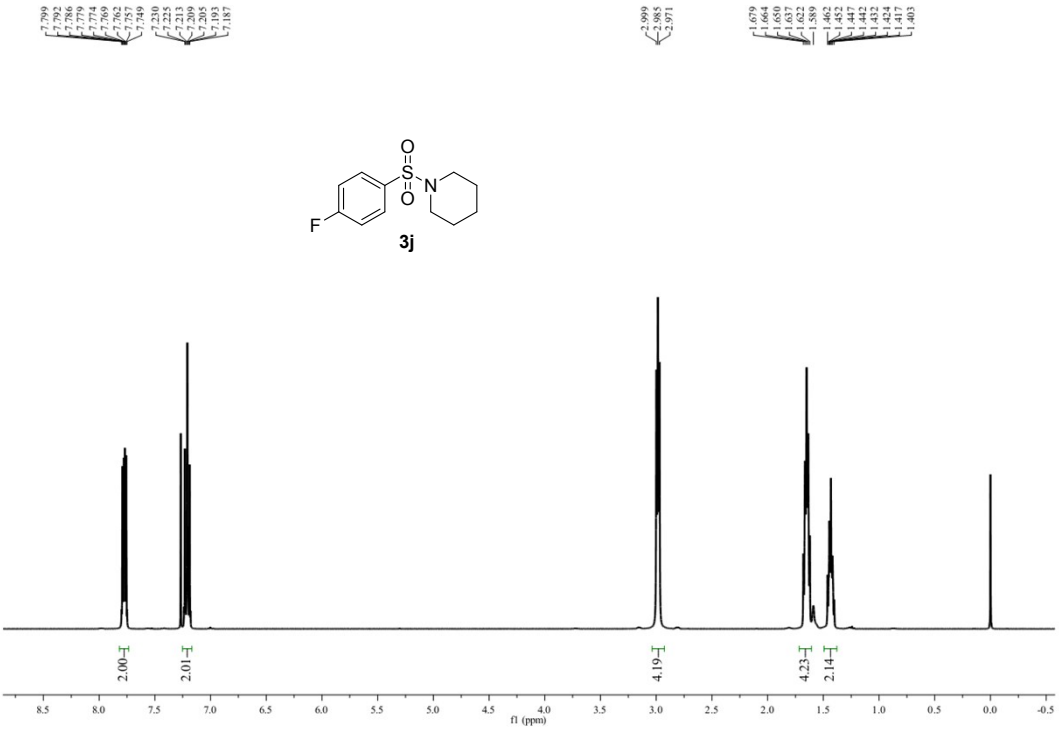

139.108
134.979
129.271
129.056
46.918
25.139
23.464
Cl
3g
f1 (ppm)


3h
f1 (ppm)


3h
f1 (ppm)


Cl
O
S
N
O
3i


Cl
O
S
N
O
3i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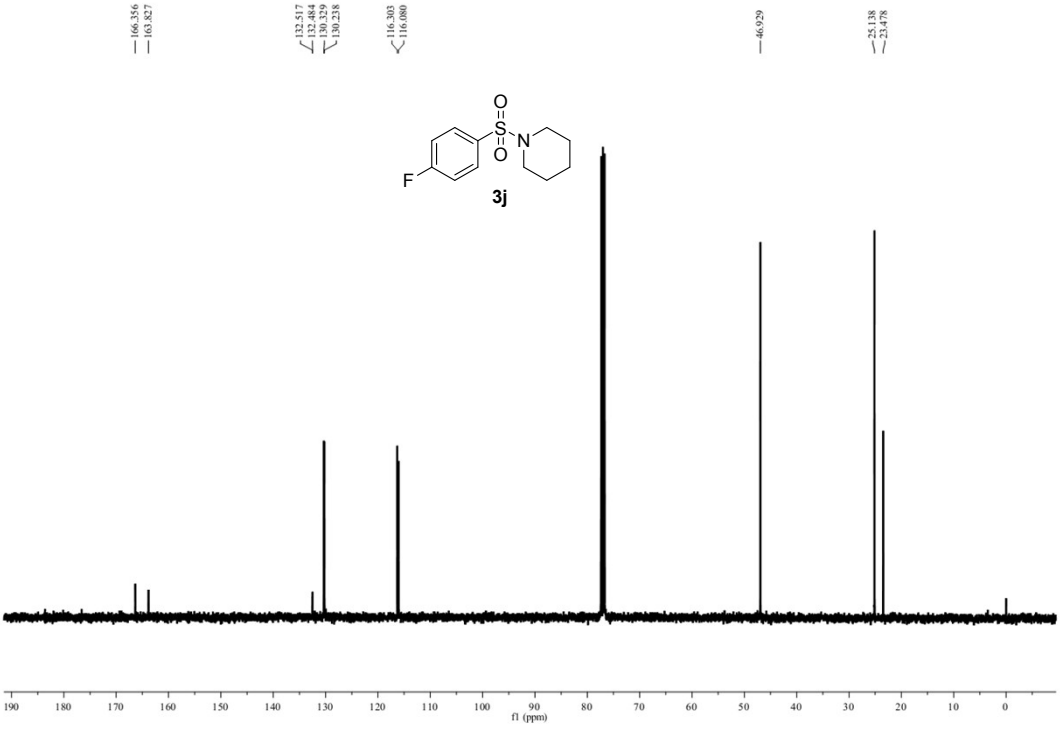
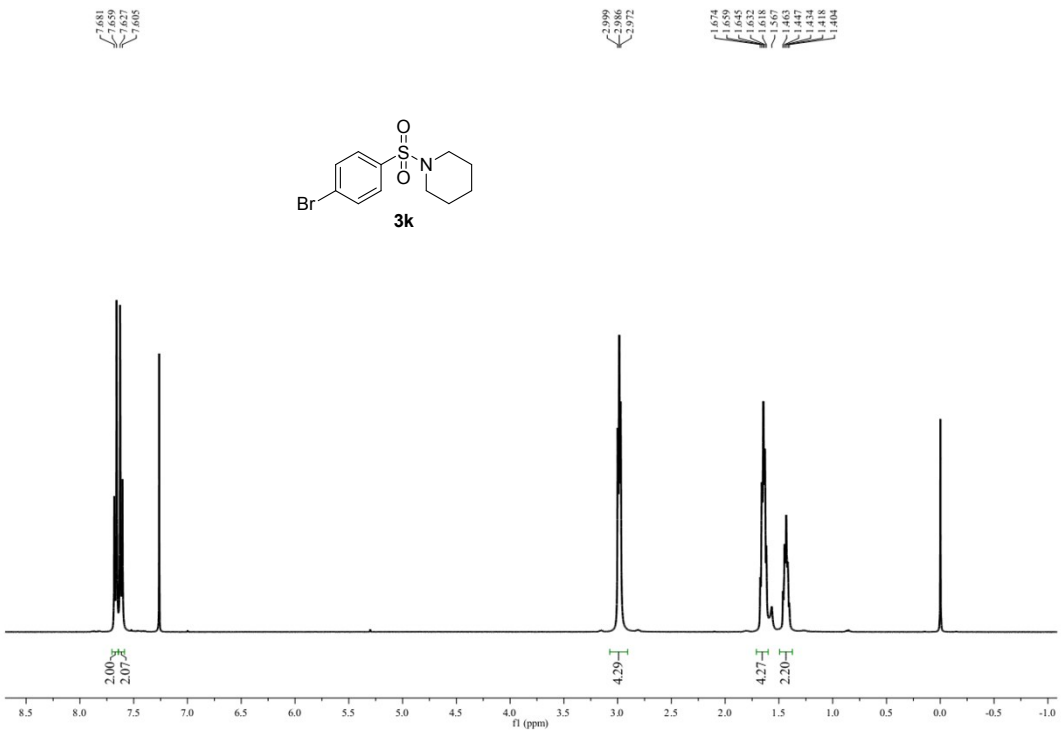
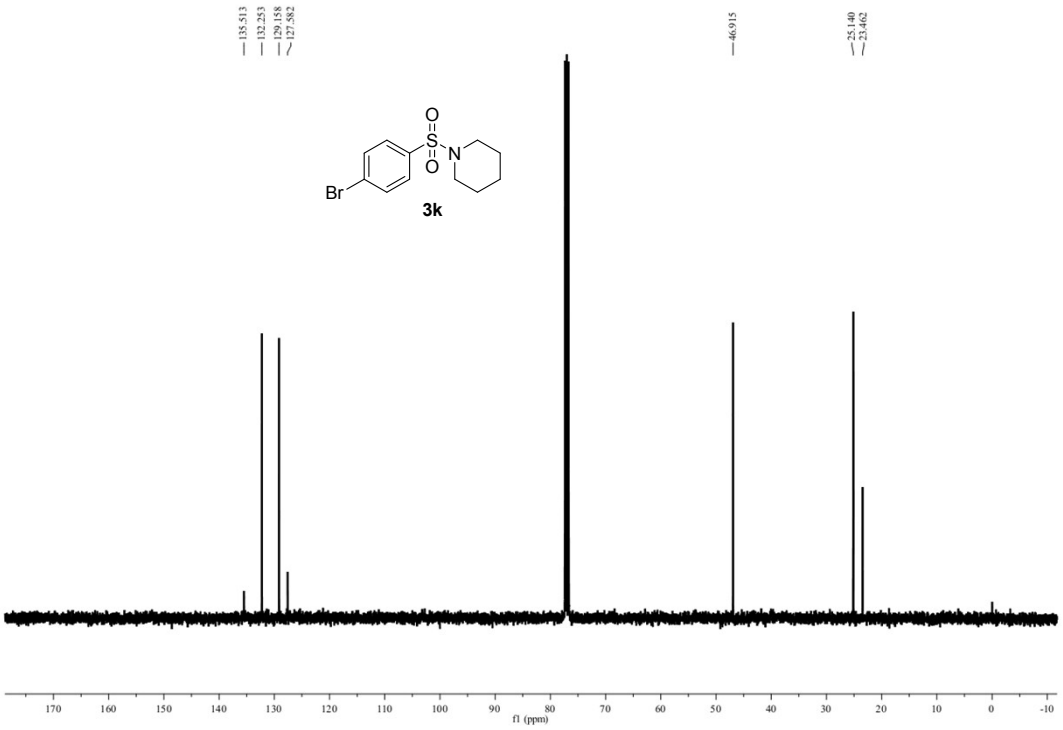
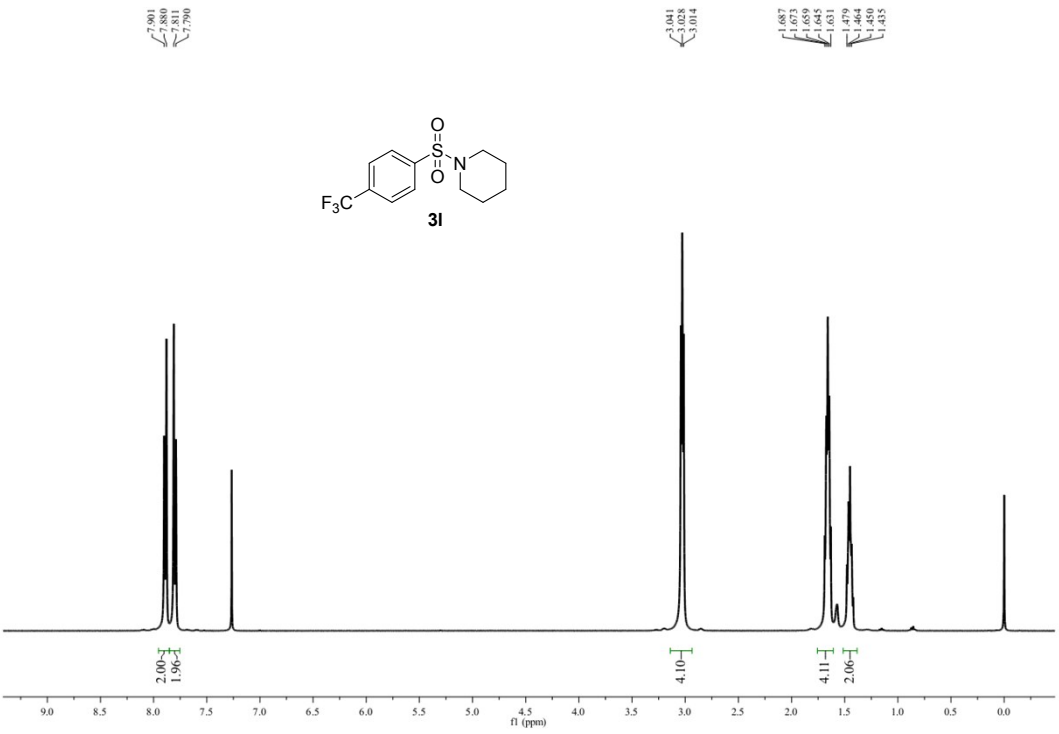
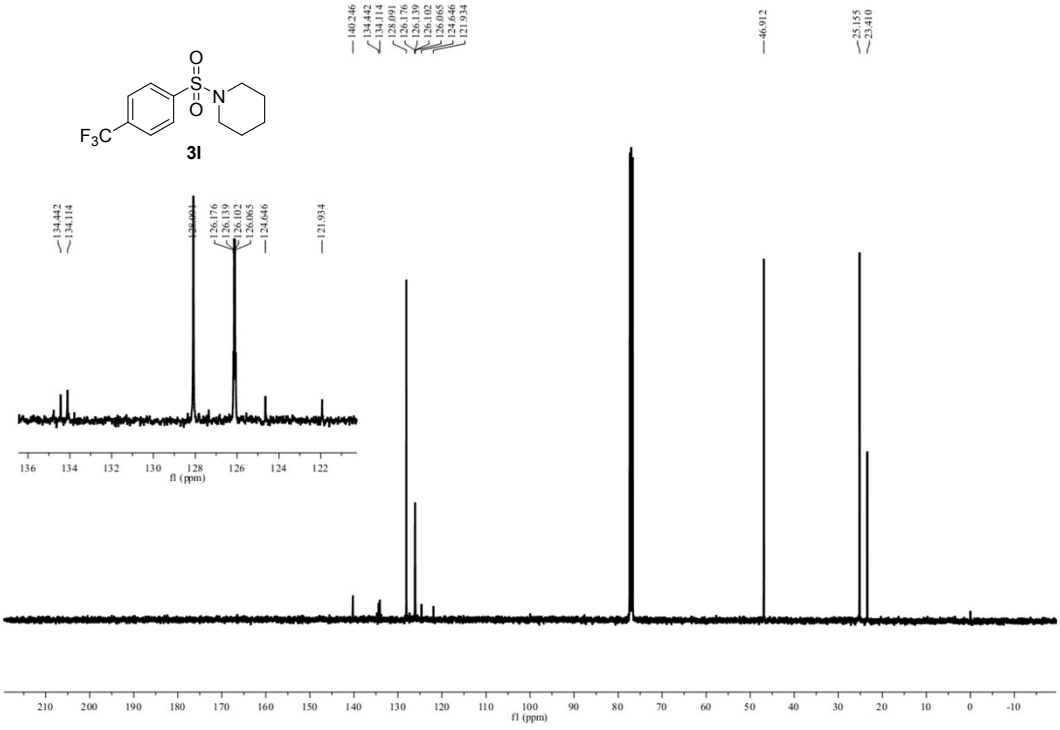
7.786
7.779
7.774
7.769
7.762
7.757
7.749
7.230
7.225
7.213
7.209
7.205
7.193
7.187
2.999
2.985
2.971
1.679
1.664
1.650
1.637
1.622
1.609
1.462
1.452
1.447
1.442
1.432
1.424
1.417
1.403
O
S
O
N
F
3j
2.00
2.01
4.19
4.23
2.14
f1 (ppm)

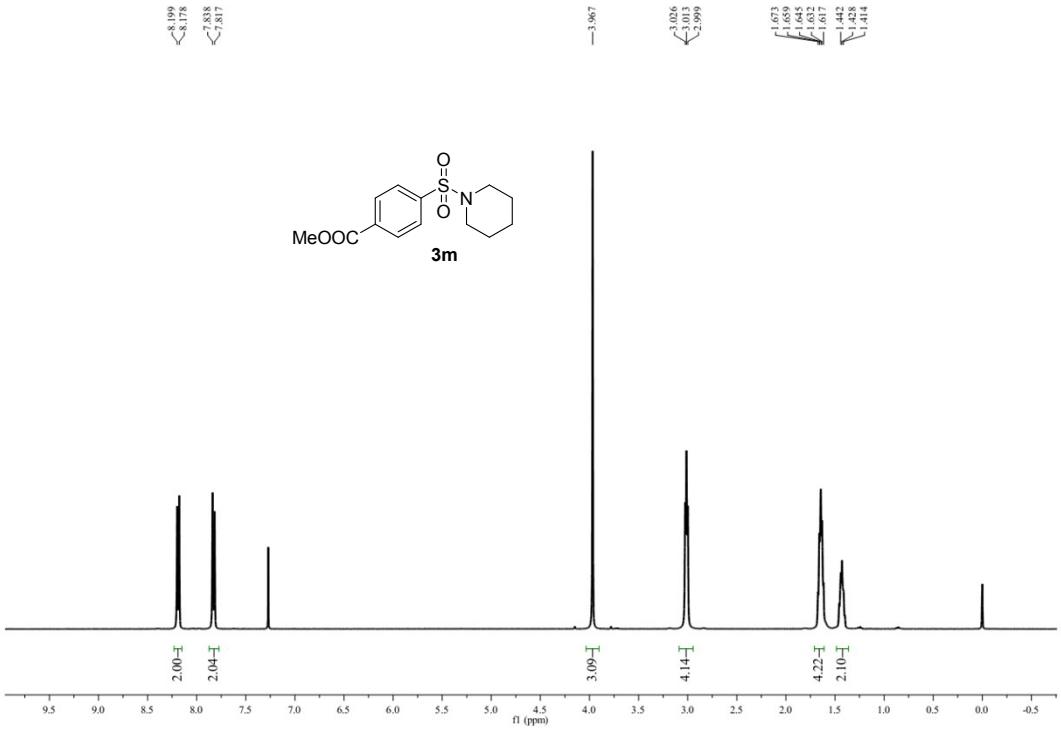

166.356
163.827
132.517
132.484
130.259
130.238
116.303
116.080
46.929
25.138
23.478
O
S
O
N
F
3j
f1 (ppm)

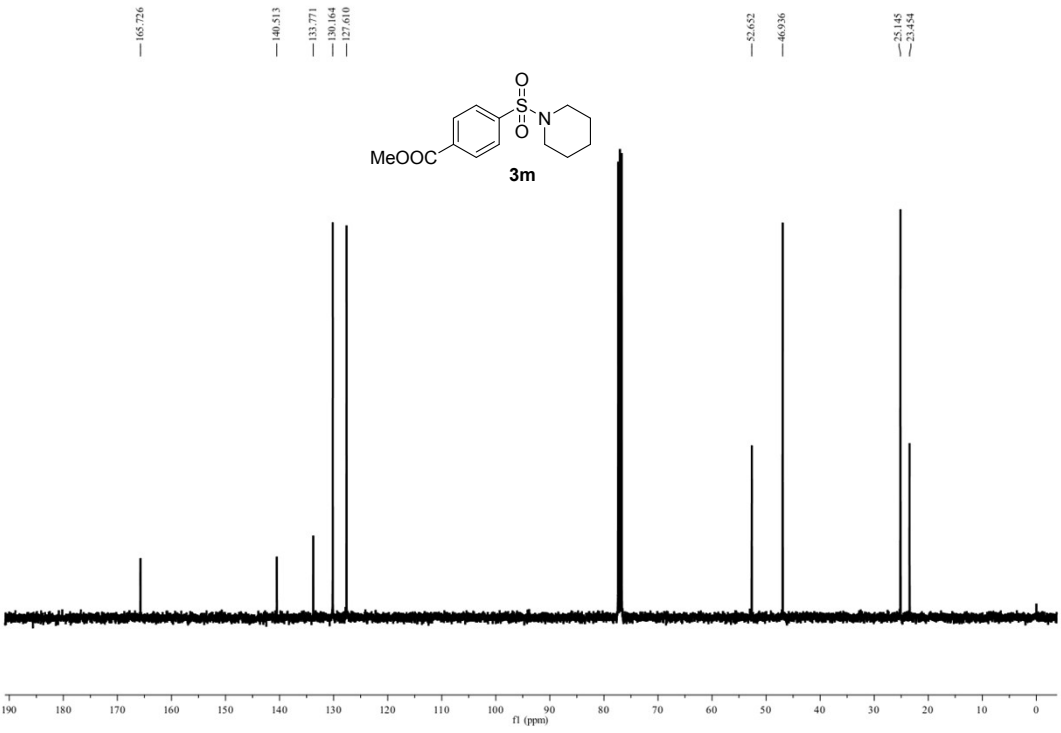

7.681
7.659
7.627
7.605
2.999
2.996
2.972
1.674
1.659
1.645
1.632
1.618
1.567
1.463
1.447
1.434
1.418
1.404
Br
3k
2.00
2.07
4.29
4.27
2.20
f1 (ppm)

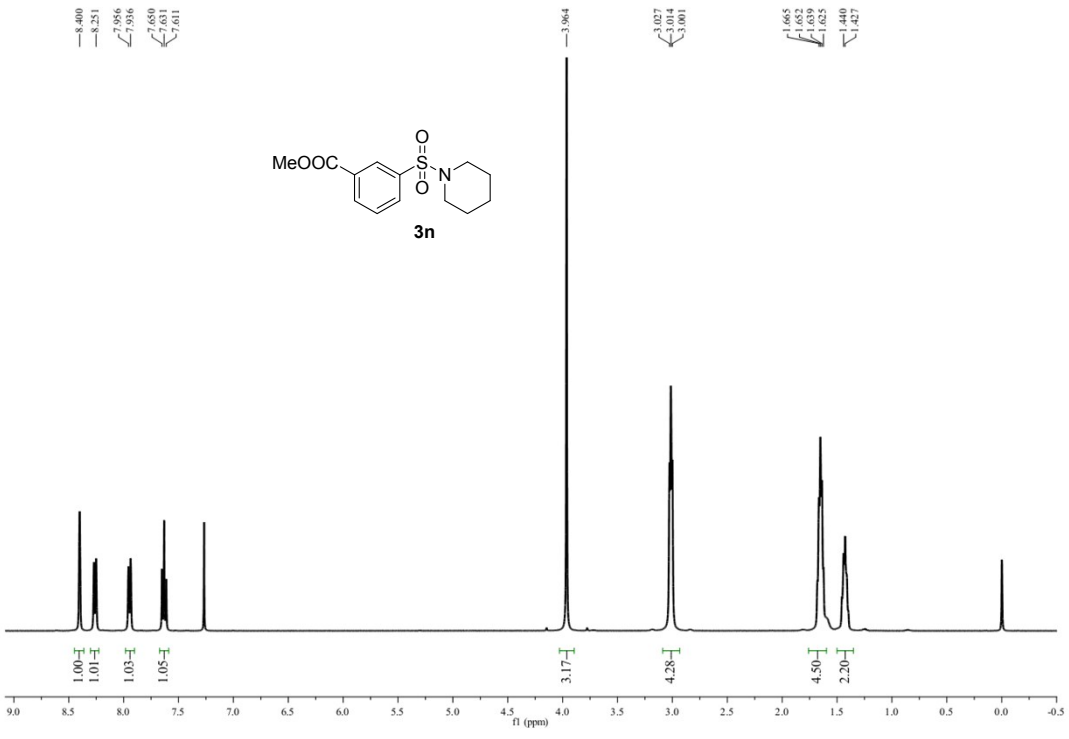

135.513
132.253
129.158
127.582
46.915
25.140
23.462
Br
3k
f1 (ppm)

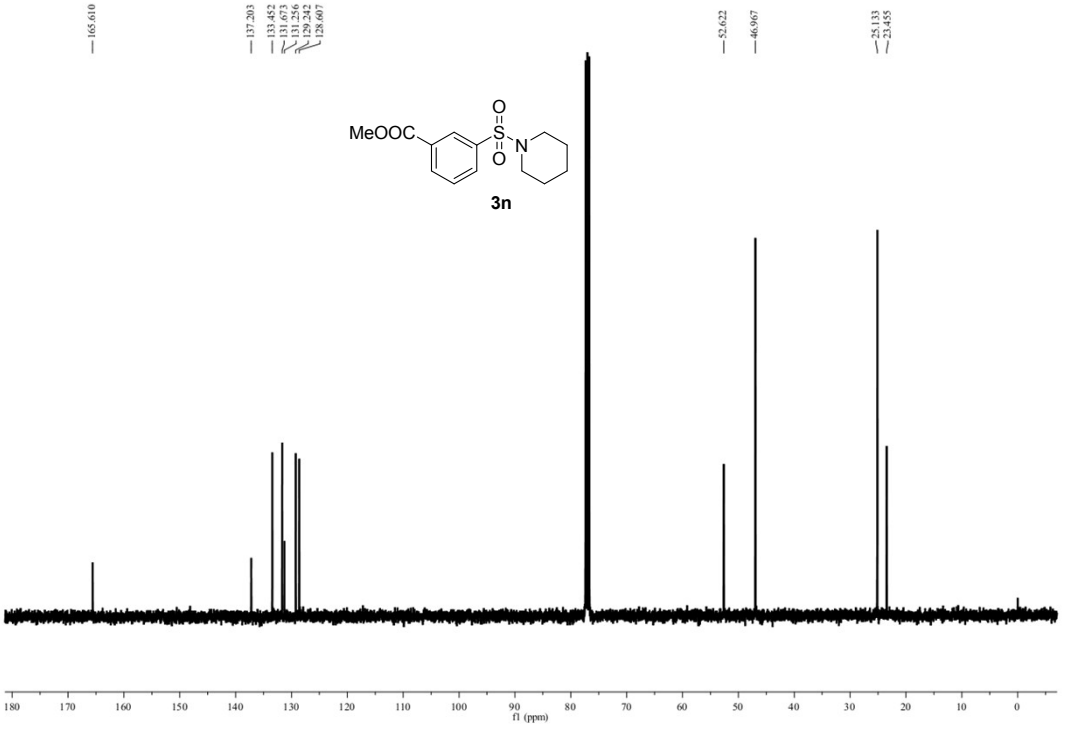

7.901
7.880
7.811
7.790
3.041
3.028
3.014
1.687
1.673
1.659
1.645
1.631
1.479
1.464
1.450
1.435
O
S
O
N
F3C
3l
2.00
1.96
4.10
4.11
2.06
f1 (ppm)


140.246
134.442
134.114
128.491
126.176
126.139
126.102
126.065
124.646
121.934
46.912
25.155
23.410
O
S
O
N
F3C
3l
134.442
134.114
128.491
126.176
126.139
126.102
126.065
124.646
121.934
f1 (ppm)
f1 (ppm)


8.199
8.178
7.838
7.817
3.967
3.026
3.013
2.999
1.673
1.659
1.645
1.632
1.617
1.442
1.428
1.414
MeOOC
3m
2.00
2.04
3.09
4.14
4.22
2.10
f1 (ppm)


165.726
140.513
133.771
130.164
127.610
52.652
46.936
25.145
23.454
MeOOC
3m
f1 (ppm)


8.400
8.251
7.956
7.936
7.650
7.631
7.611
3.964
3.027
3.014
3.001
1.665
1.652
1.639
1.625
1.440
1.427
MeOOC
O
S
O
N
3n
1.00
1.01
1.03
1.05
3.17
4.28
4.50
2.20
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
-0.5
f1 (ppm)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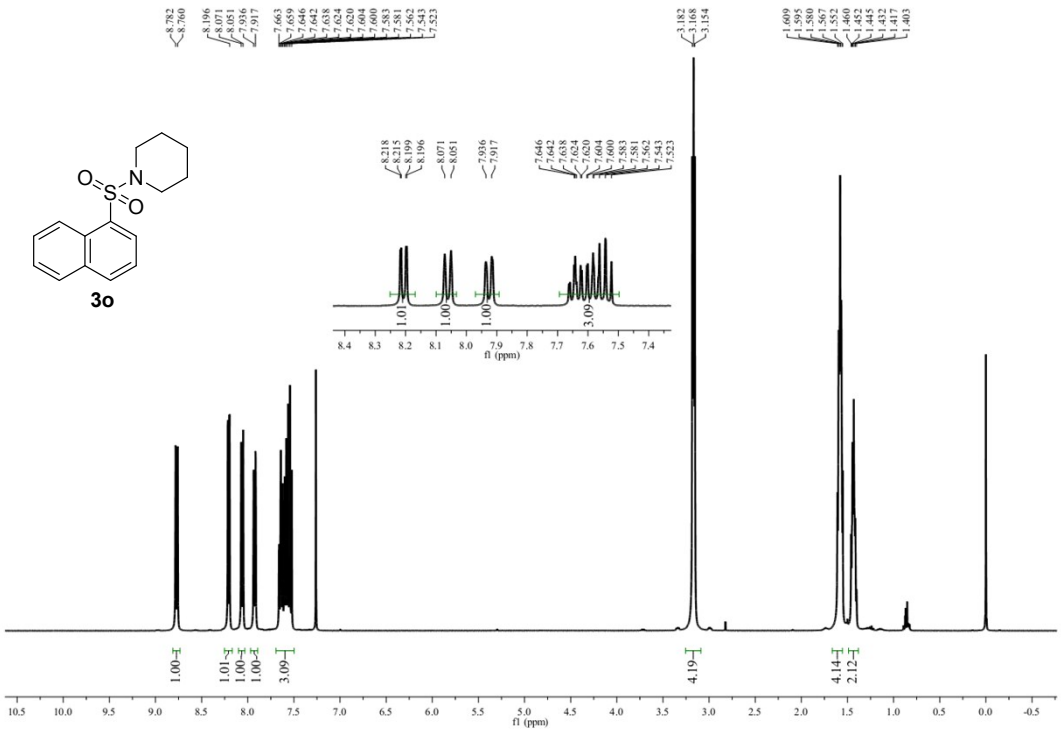
133.452
131.973
131.456
129.242
128.607
52.622
46.967
25.133
23.455
MeOOC
O
S
O
N
3n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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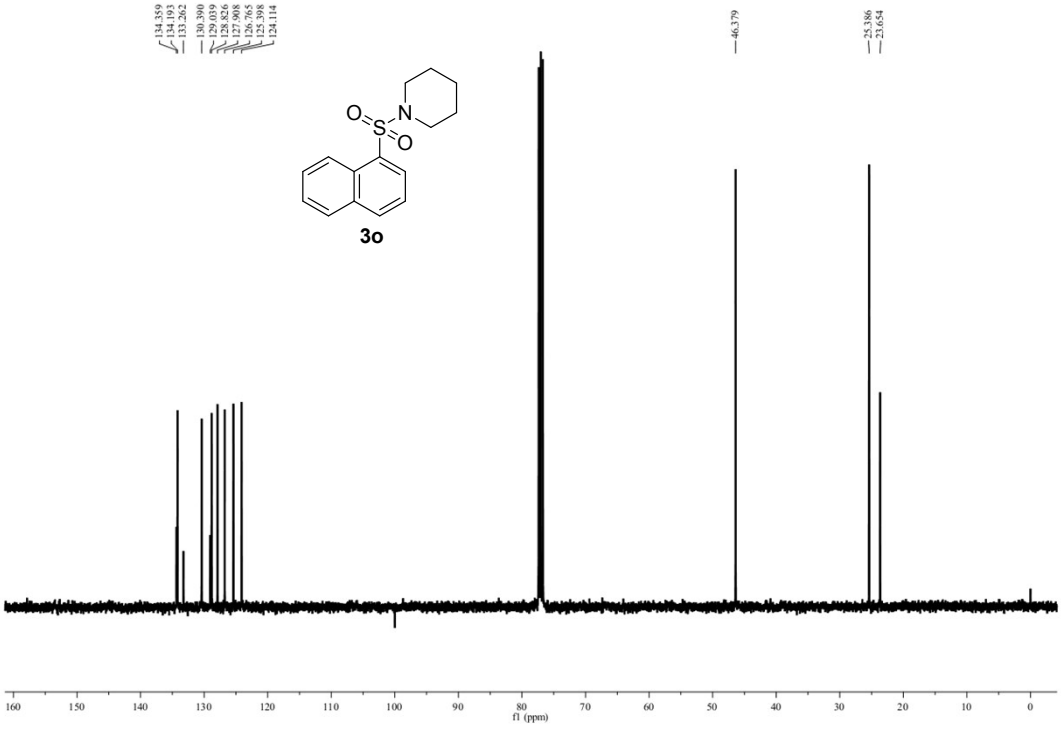
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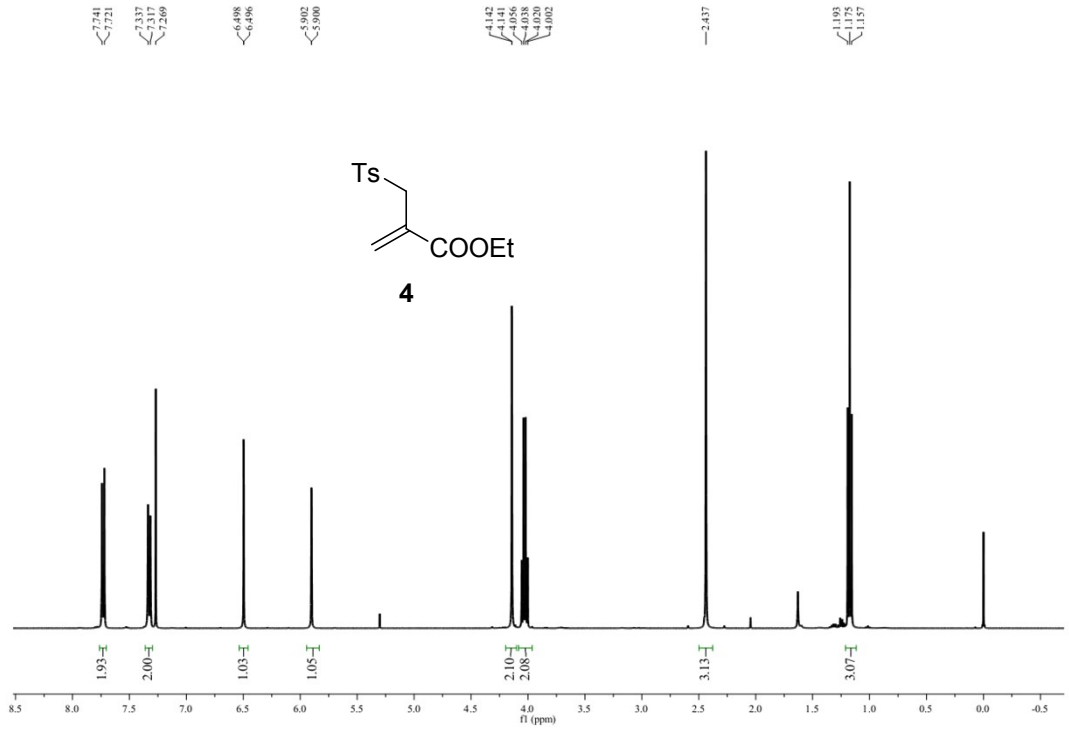
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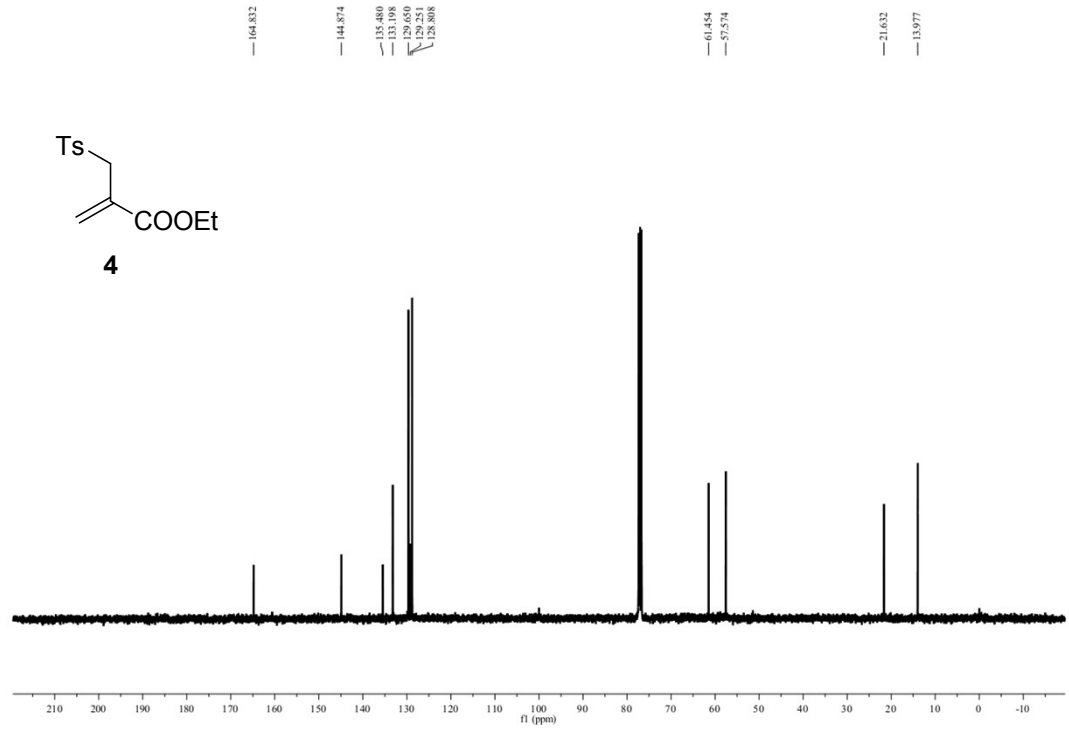
7.721
7.337
7.317
7.269
6.498
6.496
5.902
5.900
4.142
4.141
4.056
4.038
4.020
4.002
2.437
1.193
1.175
1.157
Ts
COOEt
4
1.93
2.00
1.03
1.05
2.10
2.08
3.13
3.07
f1 (ppm)


164.832
144.874
135.480
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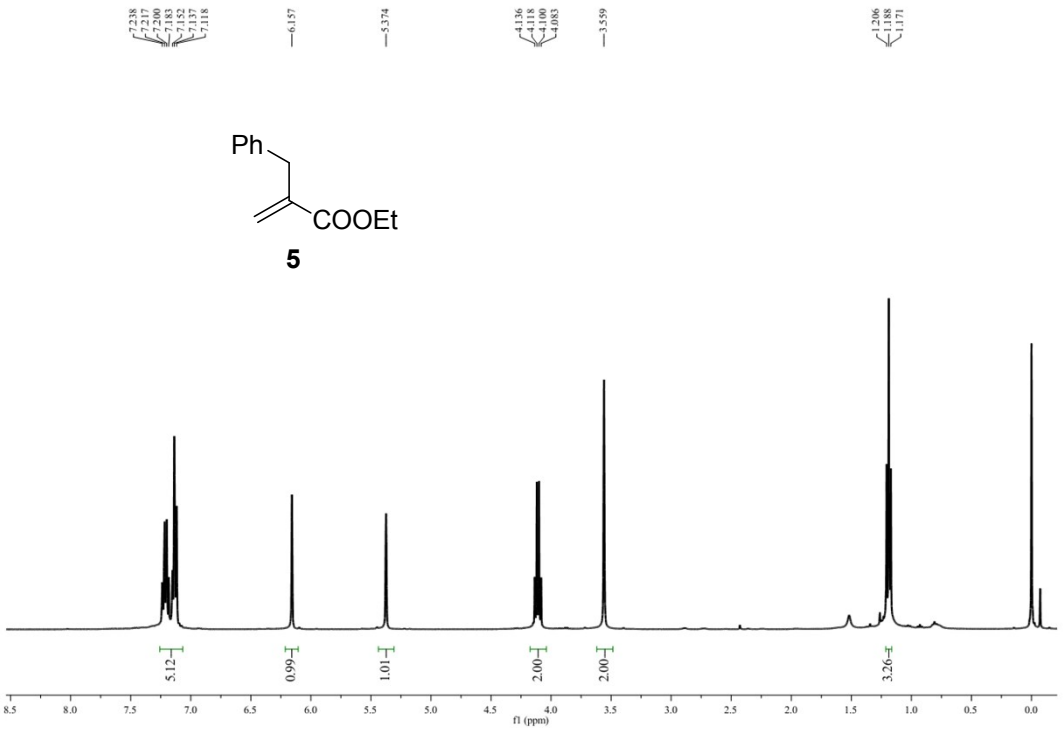
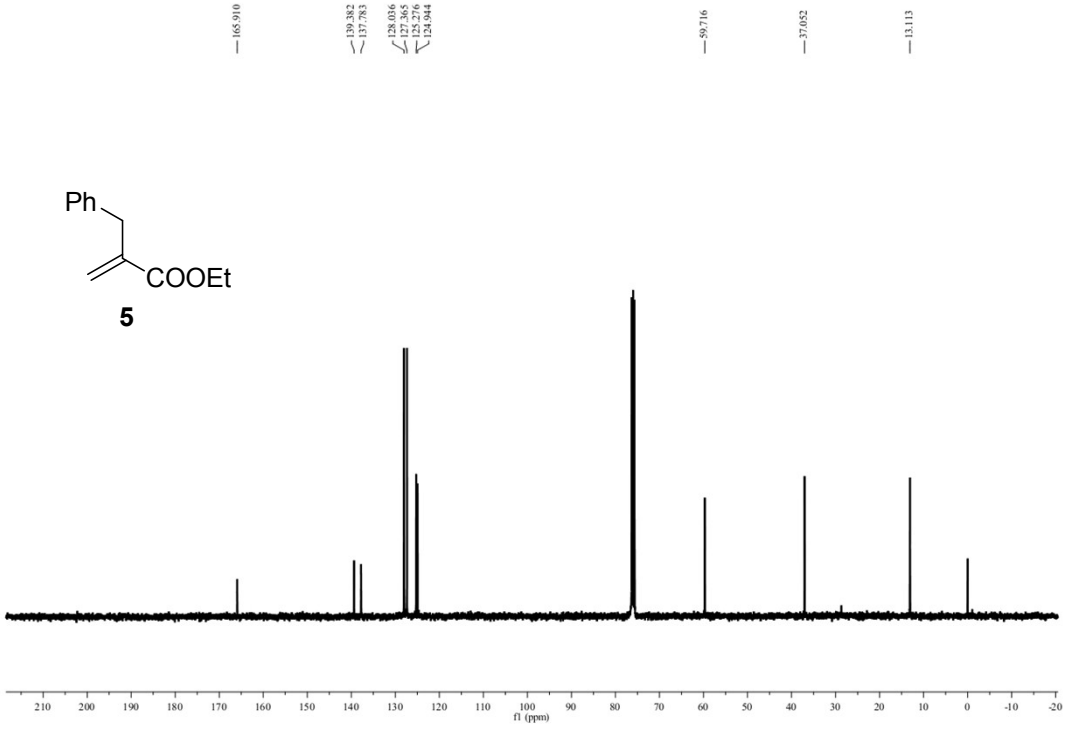
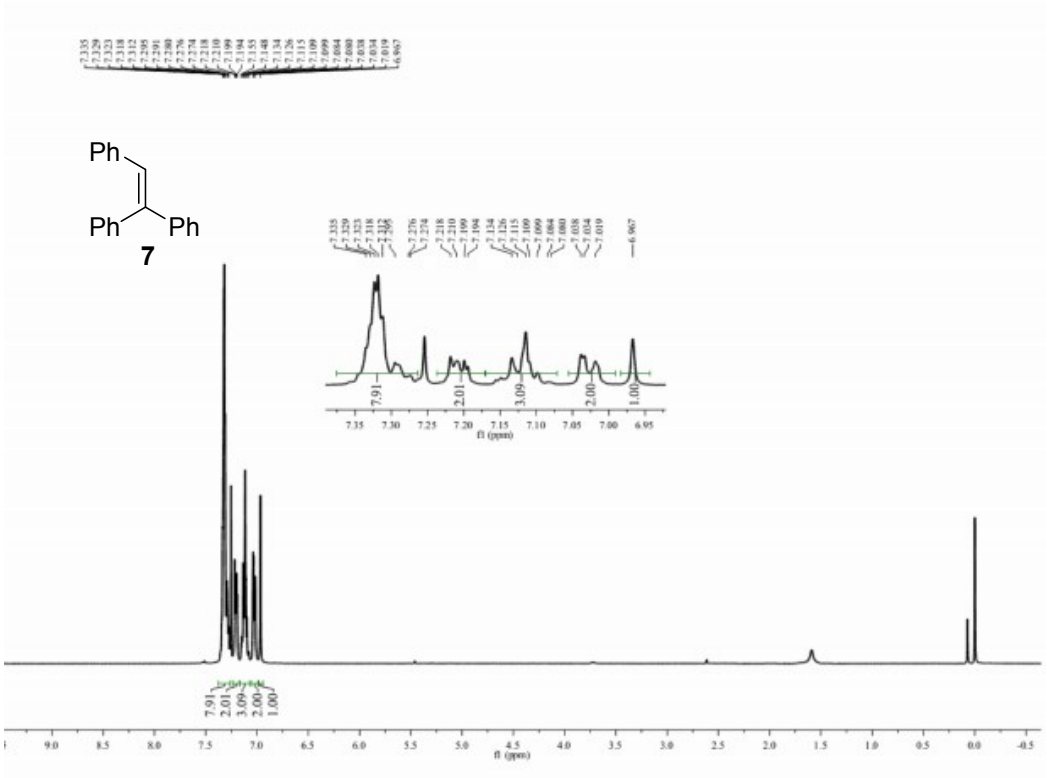
129.650
129.251
128.868
61.454
57.574
21.632
13.977
Ts
COOEt
4
f1 (ppm)


7.238
7.217
7.200
7.183
7.152
7.137
7.118
6.157
5.374
4.136
4.118
4.100
4.083
3.559
1.206
1.188
1.171
Ph
COOEt
5
5.12
0.99
1.01
2.00
2.00
3.26
f1 (ppm)


165.910
139.382
137.783
128.036
127.365
125.276
124.944
59.716
37.052
13.113
Ph
COOEt
5
f1 (ppm)


Ph
Ph
Ph
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7.91
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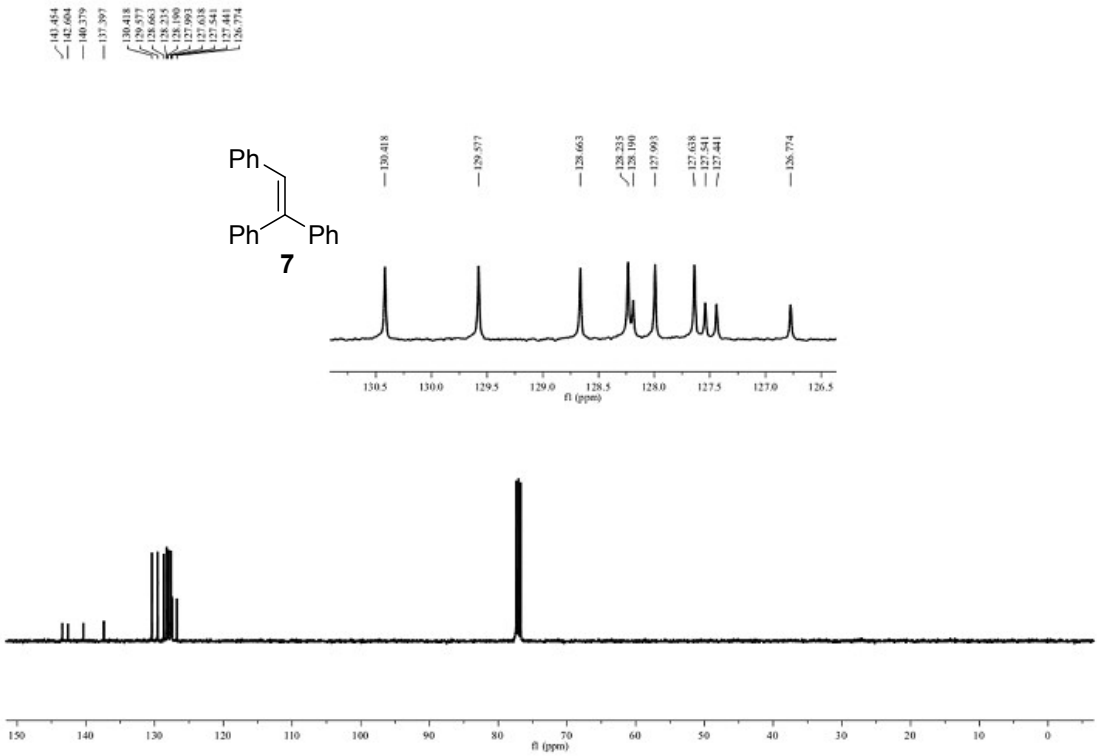
3.09
2.00
1.00
f1 (ppm)


Ph
Ph
Ph
7
130.418
129.577
128.663
128.235
128.190
127.993
127.638
127.541
127.441
126.774
f1 (ppm)