Electronic Supplementary Material (ESI) for ChemComm.

Metal-free C–H thioarylation of arenes using sulfoxides: A direct, general diaryl sulfide synthesis

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General experimental:

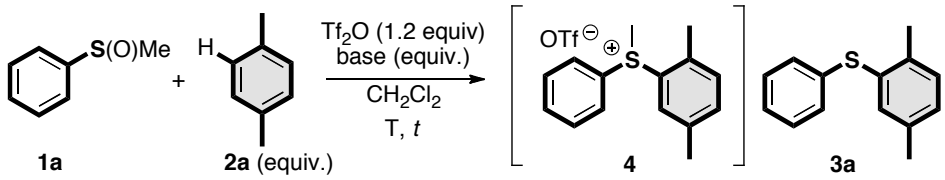
All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. THF was distilled from sodium/benzophenone and CH_2Cl_2 was distilled from CaH_2. All other solvents and reagents were purchased from commercial sources and used as supplied. ^{1}H NMR spectra were recorded on a 400 or 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a 100 or 125 MHz spectrometer. All chemical shift values are reported in ppm, with coupling constants in Hz. Mass spectra were obtained using positive or negative electrospray (ESI), atmospheric pressure chemical ionization (APCI), gas chromatography-mass spectrometry methodology and photoionization (PI). Infra-red spectra were recorded as evaporated films or neat using FT/IR spectrometers. Melting points were measured on solids as obtained after chromatography

Column chromatography was carried out using 35 – 70 μ, 60Å silica gel. Routine TLC analysis was carried out on silica gel 60 F254 coated aluminium sheets of 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp and developed by dipping in aqueous potassium permanganate solution.

Details for the preparation of compounds **1b-h** can be found in: Eberhart, A. J.; Procter, D. J. *Angew. Chem. Int. Ed.* **2013**, *52,* 4008-4011; Eberhart, A. J.; Shrives, H. J.; Álvarez, E.; Carrër, A.; Zhang, Y.; Procter, D. J. *Chem. Eur. J.* **2015**, *21*, 7428-7434; Eberhart, A. J.; Imbriglio, J. E.; Procter, D. J. *Org. Lett.* **2011**, *13*, 5882-5885.

For the preparation of compound **1i**-**1k, see;** J. A. Fernández-Salas, A. J. Eberhart, D. J. Procter, *J. Am. Chem. Soc.* **2016**, *138*, 790-793.

Optimization of the metal-free C-H thioarylation of arenes:



1a **2a** (equiv.) **4** **3a**

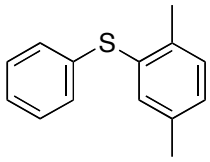
	2a (equiv.)	**Base (equiv.)**	**T (º C)**	**t (h)**	**Yield.[a] (%)**
1	10	-	–30→rt	16	94 (83) (**4**)
2	10	2,6-Lutidine (3)	–30→rt→65	16	78 (73) (**3a**)
3	2	2,6-Lutidine (2.5)	–30→rt→65	16	59 (**3a**)
4	2	Pyridine (2.5)	–30→rt→65	16	84 (**3a**)
5	2	Et_2NH (2.5)	–30→rt→65	16	65 (**3a**)
6	2	DBU (2.5)	–30→rt→65	16	95 (**3a**)
7	1.5	DBU (2.1)	–30→rt→65	4	94 (**3a**)
8	1.5	DBU (2.1)	–30→rt	16	95 (**3a**)
9	1.5	DBU (2.1)	–30→rt	6	95 (90) (**3a**)

[a] Yield determined by ^{1}H NMR. Isolated yield in brackets

General procedure A. Metal-free C-H thioarylation of arenes.

The corresponding sulfoxide (**1**) (0.15 mmol) was dissolved in CH_2Cl_2 (0.75 mL, 0.2 M) in an oven-dried tube flushed with N_2. Tf_2O or TFAA (0.165 mmol, 1.1 equiv.) was then added at –30 ºC, followed by addition of the corresponding arene coupling partner (**2**) (1-1.5 equiv.) at the same temperature. After 15 min at –30 ºC, the reaction was stirred at room temperature for 1.5 h. DBU (0.315 mmol, 2.1 equiv.) was then added, and the reaction mixture was stirred at room temperature for 4 h. The solution was quenched with H_2O (3 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane (indicated if different eluent was used).

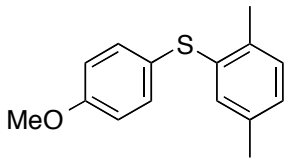
(2,5-Dimethylphenyl)(phenyl)sulfide (3a).[1]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3a** (29.3 mg, 91%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (3H, s, CH_3), 2.25 (3H, s, CH_3), 6.95-6.97 (1H, m, Ar-H), 7.05-7.10 (5H, m, Ar-H), 7.15-7.19 (2H, m, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.3 (CH_3), 21.0 (CH_3), 126.2 (Ar-CH), 129.2 (Ar-CH), 129.3 (Ar-CH), 130.7 (Ar-CH), 133.0 (Ar-C), 134.4 (Ar-CH), 136.6 (Ar-C), 136.9 (Ar-C), 137.5 (Ar-C).

(2,5-Dimethylphenyl)(4-methoxyphenyl)sulfide (3b).[2]

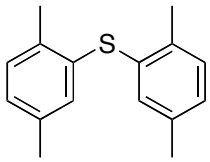


Following general procedure A, **1b** (25.5 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3b** (31.2 mg, 85%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (3H, s, CH_3), 2.33 (3H, s, CH_3), 3.80 (3H, s, CH_3), 6.85-6.89 (3H, m, Ar-H), 6.92 (1H, d, *J* = 7.6, Ar-H), 7.07 (1H, d, *J* = 7.6, Ar-H), 7.28-7.31 (2H,

m, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.1 (CH_3), 21.1 (CH_3), 55.5 (CH_3), 115.1 (Ar-CH), 125.2 (Ar-C), 127.5 (Ar-CH), 130.3 (Ar-CH), 130.5 (Ar-CH), 134.2 (Ar-CH), 134.6 (Ar-C), 136.3 (Ar-C), 136.4 (Ar-C), 159.5 (Ar-C).

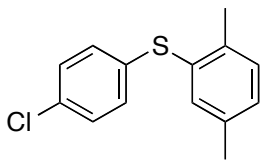
Bis(2,5-dimethylphenyl)sulfide (3c).[3]



Following general procedure A, **1c** (25 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3c** (33 mg, 91%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (6H, s, CH_3), 2.33 (6H, s, CH_3), 6.88 (2H, br s, Ar-H), 6.97 (2H, d, *J* = 7.7, Ar-H), 7.11 (2H, d, *J* = 7.7, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.1 (CH_3), 21.1 (CH_3), 128.1 (Ar-CH), 130.5 (Ar-CH), 131.8 (Ar-CH), 134.1 (Ar-C), 135.9 (Ar-C), 136.4 (Ar-C).

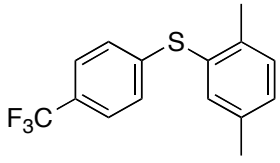
(4-Chlorophenyl)(2,5-dimethylphenyl)sulfide (3d).



Following general procedure A, **1d** (26 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3d** (31.5 mg, 85%) as a yellow oil.

ν_{max} (neat)/cm^{-1} 2919, 1475, 1091, 1010, 810, 741, 566. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 7.08-7.12 (3H, m, Ar-H), 7.18-7.22 (2H, m, Ar-H), 7.22-7.27 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.3 (CH_3), 21.0 (CH_3), 129.4 (Ar-CH), 129.6 (Ar-CH), 130.2 (Ar-CH), 130.9 (Ar-CH), 132.0 (Ar-C), 132.4 (Ar-C), 134.6 (Ar-CH), 135.7 (Ar-C), 136.8 (Ar-C), 137.7 (Ar-C). **MS** (GC/MS): *m/z* 248 (100); **HRMS** (EI): Calcd. for $C_{15}H_{13}F_3S$ (M^+), 248.0421; found 248.0433.

(2,5-Dimethylphenyl)(4-(trifluoromethyl)phenyl)sulfide (3e).

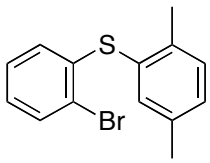


Following general procedure A, **1e** (31 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol)

and DBU (50 μL, 0.315 mmol), gave **3e** (35.5 mg, 84%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 2922, 1604, 1489, 1162, 1092, 1089, 1062, 1012, 825, 813. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.31 (6H, s, CH_3), 7.09 (2H, d, *J* = 8.8, Ar-H), 7.14 (1H, d, *J* = 7.9, Ar-H), 7.21 (1H, d, *J* = 7.9, Ar-H), 7.32 (1H, br s, Ar-H), 7.43 (2H, d, *J* = 8.8, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.4 (CH_3), 21.0 (CH_3), 124.4 (q, *J* = 271, CF_3), 125.9 (Ar-CH), 126.8 (Ar-CH), 127.4 (q, *J* = 33, Ar-C), 130.1 (Ar-C), 130.8 (Ar-CH), 131.1 (Ar-CH), 136.6 (Ar-CH), 137.1 (Ar-C), 139.2 (Ar-C), 143.5 (Ar-C). **^{19}F NMR** (470.6 MHz, $CDCl_3$) δ -62.31. **MS** (GC/MS): *m/z* 282 (M^+, 100); **MS** (GC/MS): *m/z* 282 (100); **HRMS** (APCI): Calcd. for $C_{15}H_{13}F_3S$ ($M+H^+$), 282.0685; found 282.0683.

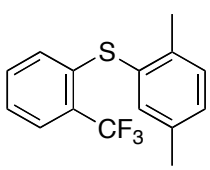
(2-Bromophenyl)(2,5-dimethylphenyl)sulfide (3f).



Following general procedure A, **1f** (33 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3f** (41.7 mg, 95%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 2918, 1487, 144.8, 1426, 1103, 1019, 812, 710, 650. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.30 (3H, s, CH_3), 2.31 (3H, s, CH_3), 6.59 (1H, dd, *J* = 7.9, 1.6, Ar-H), 6.96 (1H, td, *J* = 7.6, 1.6, Ar-H), 7.07 (1H, td, *J* = 7.6, 1.4, Ar-H), 7.14 (1H, d, *J* = 7.9, Ar-H), 7.21 (1H, d, *J* = 7.9, Ar-H), 7.30 (1H, br s, Ar-H), 7.52 (1H, dd, *J* = 7.9, 1.5, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) 20.3 (CH_3), 21.0 (CH_3), 121.7 (Ar-C), 126.5 (Ar-CH), 127.7 (Ar-CH), 127.9 (Ar-CH), 130.6 (Ar-CH), 130.8 (Ar-CH), 131.1 (Ar-C), 133.0 (Ar-CH), 136.6 (Ar-CH), 137.1 (Ar-C), 139.3 (Ar-C). **MS** (APCI): *m/z* 292 (12), 294 (9); **HRMS** (APCI): Calcd. for $C_{14}H_{14}BrS$ ($M+H^+$), 292.9994; found 292.9983.

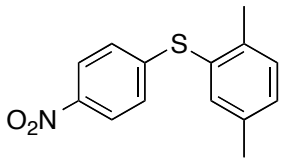
(2,5-Dimethylphenyl)(2-(trifluoromethyl)phenyl)sulfide (3g).



Following general procedure A, **1g** (31 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3g** (37.3 mg, 88%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 2922, 1593, 1442, 1309, 1256, 1170, 1112, 1031, 813, 760, 646. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.27 (3H, s, CH_3), 2.30 (3H, s, CH_3), 6.84 (1H, d, *J* = 7.8, Ar-H), 7.10-7.13 (1H, m, Ar-H), 7.16-7.20 (2H, m, Ar-H), 7.23-7.30 (2H, m, Ar-H), 7.64 (1H, d, *J* = 7.8, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.3 (CH_3), 21.0 (CH_3), 124.1 (q, *J* = 271, CF_3), 125.3 (Ar-CH), 126.8 (Ar-CH), 127.4 (q, *J* = 33, Ar-C), 129.4 (Ar-CH), 130.5 (Ar-CH), 130.1 (Ar-C), 131.1 (Ar-CH), 132.1 (Ar-CH), 136.6 (Ar-CH), 136.9 (Ar-C), 137.9 (Ar-C), 139.1 (Ar-C). **^{19}F NMR** (376.8 MHz, $CDCl_3$) δ -61.58. **MS** (GC/MS): *m/z* 282 (M^+, 100); **HRMS** (ESI): Calcd. for $C_{15}H_{14}F_3S$ ($M+H^+$), 283.0763; found 283.0760.

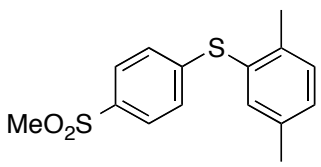
(2,5-Dimethylphenyl)(4-nitrophenyl)sulfide (3h).



Following general procedure A, **1h** (28 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3h** (37.5 mg, 96%) as a yellow oil. Column chromatography eluent: *n*-hexane/Et_2O (50/1)

ν_{max} (neat)/cm^{-1} 2918, 1579, 1510, 1331, 1085, 851, 839, 740, 681. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.34 (3H, s, CH_3), 2.37 (3H, s, CH_3), 7.04 (2H, d, *J* = 9.0, Ar-H), 7.19 (1H, d, *J* = 7.6, Ar-H), 7.25 (1H, d, *J* = 7.6, Ar-H), 7.40 (1H, br s, Ar-H), 8.07 (2H, d, *J* = 9.0, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.3 (CH_3), 21.0 (CH_3), 124.3 (Ar-CH), 125.9 (Ar-CH), 128.7 (Ar-C), 131.3 (Ar-CH), 131.5 (Ar-CH), 137.2 (Ar-CH), 137.5 (Ar-C), 139.7 (Ar-C), 145.2 (Ar-C), 148.8 (Ar-C). **MS** (APCI): *m/z* 260 ($M+H^+$, 74); **HRMS** (ESI): Calcd. for $C_{14}H_{14}O_2NS$ ($M+H^+$), 260.0740; found 260.0730.

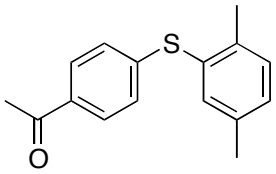
(2,5-Dimethylphenyl)(4-(methylsulfonyl)phenyl)sulfide (3i).



Following general procedure A, **1i** (33 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3i** (38 mg, 86%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (2/1)

m.p.: 86-87 ºC. ν_{max} (neat)/cm^{-1} 3017, 2922, 1577, 1488, 1308, 1150, 1094, 1078, 955, 820, 771. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.34 (3H, s, CH_3), 2.36 (3H, s, CH_3), 3.04 (3H, s, CH_3), 7.12-7.16 (2H, m, Ar-H), 7.20-7.23 (1H, m, Ar-H), 7.26-7.29 (1H, m, Ar-H), 7.39 (1H, br s, Ar-H), 7.74-7.77 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.4 (CH_3), 21.0 (CH_3), 44.8 (CH_3), 126.4 (Ar-CH), 128.0 (Ar-CH), 128.9 (Ar-C), 131.3 (Ar-CH), 131.4 (Ar-CH), 136.8 (Ar-C), 137.1 (Ar-CH), 137.4 (Ar-C), 139.6 (Ar-C), 147.2 (Ar-C). **MS** (ESI): *m/z* 293 (M+H$^+$, 42), 310 (M+NH$_4^+$, 85); **HRMS** (ESI): Calcd. for $C_{15}H_{16}O_2NaS_2$ (M+Na), 315.0484; found 315.0476.

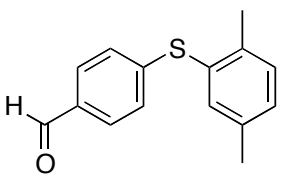
1-{4-[(2,5-Dimethylphenyl)thio]phenyl}ethanone (3j).



Following general procedure A, **1j** (28 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3j** (29 mg, 75%) as a yellow oil. Column chromatography eluent: *n*-hexane/Et_2O (20/1)

ν_{max} (neat)/cm^{-1} 2919, 1677, 1586, 1487, 1397, 1355, 1260, 1092, 954, 814, 589. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.29 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.52 (3H, s, CH_3), 7.04 (2H, d, *J* = 8.1, Ar-H), 7.14 (1H, d, *J* = 7.6, Ar-H), 7.21 (1H, d, *J* = 7.6, Ar-H), 7.33 (1H, br s, Ar-H), 7.77 (2H, d, *J* = 8.1, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.4 (CH_3), 21.0 (CH_3), 26.6 (CH_3), 126.3 (Ar-CH), 129.1 (Ar-CH), 129.8 (Ar-C), 130.8 (Ar-CH), 131.1 (Ar-CH), 134.2 (Ar-C), 136.7 (Ar-CH), 137.1 (Ar-C), 139.3 (Ar-C), 145.5 (Ar-C), 197.4 (C=O). **MS** (APCI): *m/z* 257 (M+H$^+$, 100); **HRMS** (APCI): Calcd. for $C_{16}H_{17}OS$ (M+H$^+$), 257.0995; found 257.0985.

4-[(2,5-Dimethylphenyl)thio]benzaldehyde (3k).

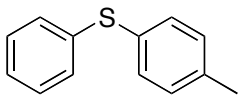


Following general procedure A, **1k** (26 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3k** (22 mg, 60%) as a

colorless oil.

ν_{max} (neat)/cm^{-1} 2919, 2827, 2730, 1694, 1588, 1561, 1487, 1210, 1167, 1084, 834, 812. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.30 (3H, s, CH_3), 2.32 (3H, s, CH_3) 7.09 (2H, d, *J* = 8.1, Ar-H), 7.17 (1H, d, *J* = 7.4, Ar-H), 7.22 (1H, d, *J* = 7.4, Ar-H), 7.36 (1H, br s, Ar-H), 7.68 (2H, d, *J* = 8.1, Ar-H), 9.88 (1H, CHO). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.4 (CH_3), 21.0 (CH_3), 126.3 (Ar-CH), 129.4 (Ar-C), 130.4 (Ar-CH), 131.1 (Ar-CH), 131.3 (Ar-CH), 133.6 (Ar-C), 137.1 (Ar-CH), 137.2 (Ar-C), 139.6 (Ar-C), 147.7 (Ar-C), 191.4 (C=O). **MS** (APCI): *m*/*z* 243 ($M+H^+$, 12); **HRMS** (APCI): Calcd. for $C_{15}H_{15}OS$ ($M+H^+$), 243.0838; found 243.0831.

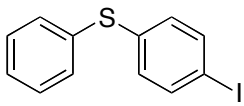
(2,4-Dimethylphenyl)(phenyl)sulfide (3l).[4]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and toluene (**2b**) (24 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3l** (26 mg, 85%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s, CH_3), 7.16-7.19 (2H, m, Ar-H), 7.21-7.25 (1H, m, Ar-H), 7.28-7.31 (4H, m, Ar-H), 7.32-7.35 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 126.6 (Ar-CH), 129.3 (Ar-CH), 129.9 (Ar-CH), 130.3 (Ar-CH), 131.5 (Ar-C), 132.5 (Ar-CH), 137.3 (Ar-C), 137.8 (Ar-C).

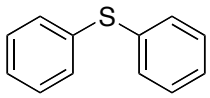
(4-Iodophenyl)(phenyl)sulfide (3m).[5]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and iodobenzene (**2c**) (25 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3m** (43 mg, 91%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-7.02 (2H, m, Ar-H), 7.26-7.37 (5H, m, Ar-H), 7.56-7.59 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 92.1 (Ar-C), 127.8 (Ar-CH), 129.6 (Ar-CH), 132.0 (Ar-CH), 132.2 (Ar-CH), 134.7 (Ar-C), 136.8 (Ar-C), 138.4 (Ar-CH).

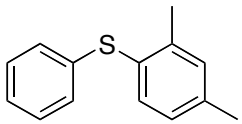
Diphenyl sulfide (3n).[4]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and benzene (**2d**) (21 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3n** (14 mg, 50%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.33 (10H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 127.2 (Ar-CH), 129.4 (Ar-CH), 131.2 (Ar-CH), 135.9 (Ar-C).

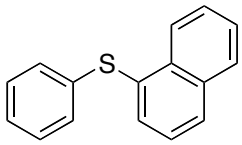
(2,4-Dimethylphenyl)(phenyl)sulfide (3o).[6]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and *m*-xylene (**2e**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3o** (31.5 mg, 98%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (3H, s, CH_3), 2.35 (3H, s, CH_3), 6.99 (1H, d, J = 7.9, Ar-H), 7.09-7.17 (4H, m, Ar-H), 7.21-7.26 (2H, m, Ar-H), 7.30 (1H, d, J = 7.6, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.6 (CH_3), 21.2 (CH_3), 125.7 (Ar-CH), 127.6 (Ar-CH), 128.3 (Ar-CH), 129.0 (Ar-CH), 129.3 (Ar-C), 131.6 (Ar-CH), 134.5 (Ar-CH), 137.4 (Ar-C), 138.6 (Ar-C), 140.9 (Ar-C).

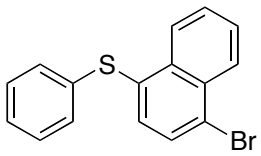
Naphthalen-1-yl(phenyl)sulfide (3p).[4]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and naphthalene (**2e**) (29 mg, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3p** (33 mg, 91%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03-7.15 (5H, m, Ar-H), 7.31-7.37 (1H, m, Ar-H), 7.40-7.44 (2H, m, Ar-H), 7.58 (1H, dd, J = 7.2, 1.2, Ar-H), 7.75-7.81 (2H, m, Ar-H), 8.27-8.32 (1H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 125.8 (Ar-CH), 126.0 (Ar-CH), 126.3 (Ar-CH), 126.6 (Ar-CH), 127.1 (Ar-CH), 128.8 (Ar-CH), 129.1 (Ar-CH), 129.3 (Ar-CH), 129.4 (Ar-CH), 131.4 (Ar-C), 132.7 (Ar-CH), 133.8 (Ar-C), 134.4 (Ar-C), 137.1 (Ar-C).

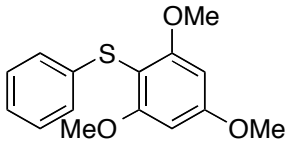
(4-Bromonaphthalen-1-yl)(phenyl)sulfide (3q).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and 1-bromonaphthalene (**2g**) (31 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3q** (44.5 mg, 93%) as a yellow oil.

ν_{max} (neat)/cm^{-1} 3069, 1575, 1476, 1366, 1251, 1185, 975. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.30 (5H, m, Ar-H), 7.48 (1H, d, *J* = 7.8, Ar-H), 7.58-7.63 (1H, m, Ar-H), 7.64-7.69 (1H, m, Ar-H), 7.76 (1H, d, *J* = 7.8, Ar-H), 8.33 (1H, dd, *J* = 8.4, 1.4, Ar-H), 8.44 (1H, dd, *J* = 8.4, 1.4, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 124.1 (Ar-C), 126.3 (Ar-CH), 126.8 (Ar-CH), 127.9 (Ar-CH), 128.0 (Ar-CH), 128.1 (Ar-CH), 129.4 (Ar-CH), 129.7 (Ar-CH), 130.1 (Ar-CH), 132.2 (Ar-C), 132.3 (Ar-CH), 132.8 (Ar-C), 134.6 (Ar-C), 136.2 (Ar-C). **MS** (GC/MS): *m/z* 314 (100), 316 (99); **HRMS** (APCI): Calcd. for $C_{16}H_{11}BrS$ (M^+), 313.9759; found 313.9759.

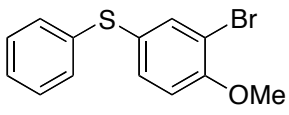
Phenyl(2,4,6-trimethoxyphenyl)sulfide (3r).[7]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and 1,3,5-trimethoxybenzene (**2h**) (38 mg, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3r** (38 mg, 99%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (5/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (6H, s, CH_3), 3.85 (3H, s, CH_3), 6.19 (2H, s, Ar-H), 6.99-7.03 (3H, m, Ar-H), 7.10-7.16 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 55.6 (CH_3), 56.5 (CH_3), 91.4 (Ar-CH), 98.9 (Ar-C), 124.5 (Ar-CH), 125.8 (Ar-CH), 128.7 (Ar-CH), 138.9 (Ar-C), 162.7 (Ar-C), 163.1 (Ar-C).

(3-Bromo-4-methoxyphenyl)(phenyl)sulfide (3s).[8]

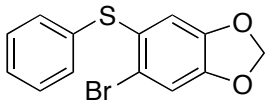


Following general procedure A, **1a** (21 mg, 0.15 mmol) and 2-bromoanisole (**2i**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165

mmol) and DBU (50 μL, 0.315 mmol), gave **3s** (43.5 mg, 98%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s, CH_3), 6.85 (1H, d, *J* = 8.6, Ar-H), 7.16-7.21 (3H, m, Ar-H), 7.23-7.27 (2H, m, Ar-H), 7.35 (1H, dd, *J* = 8.6, 2.2 Ar-H), 7.35 (1H, d, *J* = 2.2 Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 56.7 (CH_3), 112.5 (Ar-C), 112.7 (Ar-CH), 126.7 (Ar-CH), 126.8 (Ar-C), 129.3 (Ar-CH), 133.8 (Ar-CH), 137.5 (Ar-C), 137.8 (Ar-CH), 156.2 (Ar-C).

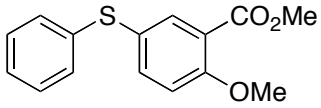
5-Bromo-6-(phenylthio)benzo[*d*][1,3]dioxole (3t).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and 1-bromo-3,4-(methylenedioxy)benzene (**2j**) (27 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3t** (44 mg, 94%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 2895, 1499, 1464, 1229, 1034, 935, 854, 737, 688. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.95 (2H, s, Ar-H), 6.68 (1H, s, Ar-H), 7.07 (1H, s, Ar-H), 7.24-7.28 (1H, m, Ar-H), 7.28-7.33 (4H, m, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 102.3 (CH_2), 112.6 (Ar-CH), 113.4 (Ar-CH), 117.3 (Ar-C), 127.6 (Ar-CH), 128.9 (Ar-CH), 129.6 (Ar-C), 131.2 (Ar-CH), 135.2 (Ar-C), 148.1 (Ar-C), 148.2 (Ar-C). **MS** (APCI): *m/z* 310 ($M+H^+$, 18); **HRMS** (APCI): Calcd. for $C_{13}H_9O_2BrS$ (M^+), 307.9501; found 307.9490.

Methyl 2-methoxy-5-(phenylthio)benzoate (3u).

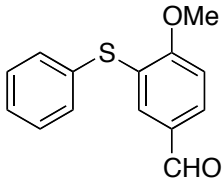


Following general procedure A, **1a** (21 mg, 0.15 mmol) and methyl 2-methoxybenzoate (**2k**) (33 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3u** (37 mg, 97%) as a colorless oil. Column chromatography eluent: *n*-hexane/Et_2O (5/1)

ν_{max} (neat)/cm^{-1} 2948, 2841, 1729, 1592, 1486, 1433, 1299, 1237, 1080, 1022, 735. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.89 (3H, s, CH_3), 3.94 (3H, s, CH_3), 6.99 (1H, d, *J* = 8.7, Ar-H), 7.17-7.23 (3H, m, Ar-H), 7.25-7.30 (2H, m, Ar-H), 7.57 (1H, dd, *J* = 8.7, 2.4 Ar-H), 7.94 (1H, d, *J* = 2.4 Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 52.3 (CH_3), 56.4 (CH_3), 113.3 (Ar-CH), 121.3

(Ar-C), 125.0 (Ar-C), 126.5 (Ar-CH), 129.0 (Ar-CH), 129.3 (Ar-CH), 136.9 (Ar-CH), 137.7 (Ar-C), 138.8 (Ar-CH), 159.3 (Ar-C), 166.0 (C=O). **MS** (ESI): *m/z* 275 ($M+H^+$, 100), 297 ($M+Na^+$, 77); **HRMS** (ESI): Calcd. for $C_{15}H_{14}O_3NaS$ ($M+Na^+$), 297.0556; found 297.0550.

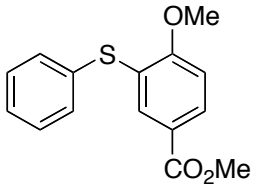
4-Methoxy-3-(phenylthio)benzaldehyde (3v).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and *p*-anisaldehyde (**2l**) (27 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3v** (31 mg, 85%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (5/1)

m.p.: 98-99 ºC. ν_{max} (neat)/cm^{-1} 2940, 2839, 1692, 1586, 1569, 1487, 1251, 1197, 813, 750. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.95 (3H, s, CH_3), 6.97 (1H, d, *J* = 8.5, Ar-H), 7.32-7.38 (3H, m, Ar-H), 7.40-7.43 (2H, m, Ar-H), 7.45 (1H, d, *J* = 2.1 Ar-H), 7.71 (1H, dd, *J* = 8.5, 2.1 Ar-H), 9.72 (1H, s, CHO). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 56.5 (CH_3), 110.6 (Ar-CH), 127.5 (Ar-C), 128.5 (Ar-CH), 129.8 (Ar-CH), 130.4 (Ar-CH), 130.5 (Ar-C), 131.2 (Ar-CH), 132.3 (Ar-C), 133.2 (Ar-CH), 161.3 (Ar-C), 190.5 (C=O). **MS** (APCI): *m/z* 245 ($M+H^+$, 100); **HRMS** (APCI): Calcd. for $C_{14}H_{13}O_2S$ ($M+H^+$), 245.0631; found 245.0624.

Methyl 4-methoxy-3-(phenylthio)benzoate (3w).

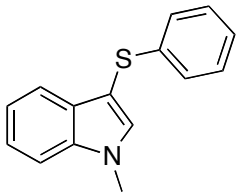


Following general procedure A, **1a** (21 mg, 0.15 mmol) and methyl 4-methoxybenzoate (**2m**) (33 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3w** (40 mg, 90%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (5/1)

m.p.: 59-60 ºC. ν_{max} (neat)/cm^{-1} 2948, 2845, 1714, 1591, 1433, 1289, 1252, 1115, 1021, 765. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.80 (3H, s, CH_3), 3.90 (3H, s, CH_3), 6.90 (1H, d, *J* = 8.6, Ar-H), 7.25-7.35 (5H, m, Ar-H), 7.76 (1H, d, *J* = 2.2 Ar-H), 7.92 (1H, dd, *J* = 8.6, 2.4 Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 52.2 (CH_3), 56.4 (CH_3), 110.3 (Ar-CH), 123.4 (Ar-C), 125.1 (Ar-C), 127.7 (Ar-CH), 129.5 (Ar-CH), 130.6 (Ar-CH), 131.9 (Ar-CH), 133.0 (Ar-CH), 133.7

(Ar-C), 160.9 (Ar-C), 166.5 (C=O). **MS** (APCI): *m/z* 275 ($M+H^+$, 100); **HRMS** (APCI): Calcd. for $C_{15}H_{15}O_3S$ ($M+H^+$), 275.0736; found 275.0728.

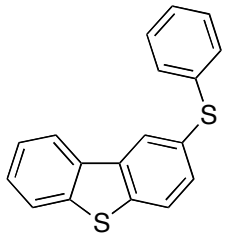
1-Methyl-3-(phenylthio)-1*H*-indole (3x).[9]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and 1-metylindole (**2n**) (19 μL, 0.15 mmol), using TFAA (25 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3x** (35 mg, 97%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (50/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (3H, s, CH_3), 7.01-7.05 (1H, m, Ar-H), 7.05-7.07 (2H, m, Ar-H), 7.11-7.18 (3H, m, Ar-H), 7.27-7.31 (1H, m, Ar-H), 7.32 (1H, s, Ar-H), 7.38 (1H, dt, *J* = 8.2, 0.6, Ar-H), 7.61 (1H, dt, *J* = 8.2, 0.6, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 33.5 (Ar-CH_3), 100.7 (Ar-C), 109.7 (Ar-CH), 119.9 (Ar-CH), 120.7 (Ar-CH), 122.8 (Ar-CH), 124.8 (Ar-CH), 125.9 (Ar-CH), 128.8 (Ar-CH), 130.0 (Ar-C), 135.3 (Ar-CH), 137.7 (Ar-C), 139.9 (Ar-C).

2-(Phenylthio)dibenzo[*b*,*d*]thiophene (3y).

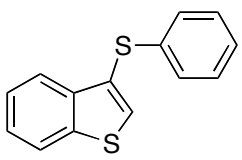


Following general procedure A, **1a** (21 mg, 0.15 mmol) and dibenzothiophene (**2o**) (41 mg, 0.15 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3y** (39 mg, 88%) as a white solid.

m.p.: 100-101 ºC. ν_{max} (neat)/cm^{-1} 3055, 1580, 1476, 1424, 1226, 1077, 1023, 806, 760, 729, 688. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.25 (1H, m, Ar-H), 7.27-7.35 (4H, m, Ar-H), 7.44-7.52 (3H, m, Ar-H), 7.81 (1H, d, *J* = 8.4, Ar-H), 7.84-7.88 (1H, m, Ar-H), 8.07-8.10 (1H, m, Ar-H), 8.28 (1H, d, *J* = 1.6, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 122.0 (Ar-CH), 123.1 (Ar-CH), 123.8 (Ar-CH), 124.8 (Ar-CH), 125.8 (Ar-CH), 126.8 (Ar-CH), 127.4 (Ar-CH), 129.4 (Ar-CH), 130.0 (Ar-CH), 130.9 (Ar-C), 131.1 (Ar-CH), 135.0 (Ar-C), 136.8 (Ar-C),

137.3 (Ar-C), 139.2 (Ar-C), 140.0 (Ar-C). **MS** (APCI): *m/z* 293 ($M+H^+$, 10), 310 ($M+NH_4^+$, 13); **HRMS** (APCI): Calcd. for $C_{18}H_{13}S_2$ ($M+H^+$), 293.0453; found 293.0450.

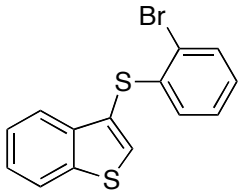
3-(Phenylthio)benzo[*b*]thiophene (3z).[10]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and benzo[b]thiophene (**2p**) (22 mg, 0.165 mmol), using Tf_2O (32 μL, 0.165 mmol). After Tf_2O addition at –30 ºC, the reaction mixture was stirred at –20 ºC for 3 h. DBU (50 μL, 0.315 mmol) was then added at –20 ºC, and the mixture was allowed to warm to RT for 2 h. **3z** (30 mg, 82%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.21 (5H, m, Ar-H), 7.34-7.39 (2H, m, Ar-H), 7.70 (1H, s, Ar-H), 7.77-7.80 (1H, m, Ar-H), 7.86-7.89 (1H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 123.1 (Ar-CH), 123.3 (Ar-CH), 124.2 (Ar-C), 125.0 (Ar-CH), 125.2 (Ar-CH), 126.1 (Ar-CH), 127.8 (Ar-CH), 129.2 (Ar-CH), 132.2 (Ar-CH), 136.8 (Ar-C), 139.1 (Ar-C), 140.2 (Ar-C).

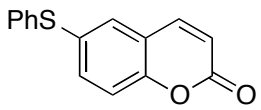
3-[(2-Bromophenyl)thio]benzo[*b*]thiophene (3aa).[10]



Following general procedure A, **1f** (33 mg, 0.15 mmol) and benzo[b]thiophene (**2q**) (22 mg, 0.165 mmol), using Tf_2O (32 μL, 0.165 mmol). After Tf_2O addition at –30 ºC, the reaction mixture was stirred at –20 ºC for 3h. DBU (50 μL, 0.315 mmol) was then added at –20 ºC, and the mixture was allowed to warm to RT for 2 h. **3aa** (29 mg, 60%) was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52-6.55 (1H, m, Ar-H), 6.92-6.99 (2H, m, Ar-H), 7.35-7.42 (2H, m, Ar-H), 7.50-7.54 (1H, m, Ar-H), 7.74-7.77 (1H, m, Ar-H), 7.83 (1H, s, Ar-H), 7.89-7.92 (1H, m, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 120.7 (Ar-C), 122.9 (Ar-C), 123.2 (Ar-CH), 123.3 (Ar-CH), 125.3 (Ar-CH), 125.4 (Ar-CH), 126.6 (Ar-CH), 127.5 (Ar-CH), 127.9 (Ar-CH), 133.0 (Ar-CH), 134.5 (Ar-CH), 138.7 (Ar-C), 139.0 (Ar-C), 140.4 (Ar-C).

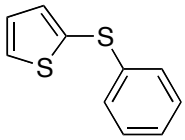
6-(Phenylthio)-2*H*-chromen-2-one (3ab).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and coumarin (**2r**) (33 mg, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3ab** (17 mg, 45%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (4/1)

m.p.: 108-109 ºC. ν_{max} (neat)/cm^{-1} 3057, 1727, 1597, 1476, 1257, 1179, 1110, 895, 821, 741, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.36 (1H, d, *J* = 9.6, CH), 7.18-7.21 (1H, m, Ar-H), 7.21-7.28 (5H, m, Ar-H), 7.39 (1H, d, *J* = 2.1, Ar-H), 7.42 (1H, dd, *J* = 8.6, 2.1, Ar-H), 7.54 (1H, d, *J* = 9.6, CH). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 117.5 (Ar-CH), 118.1 (Ar-CH), 119.7 (Ar-C), 127.8 (Ar-CH), 129.7 (Ar-CH), 130.3 (Ar-CH), 131.3 (Ar-CH), 132.3 (Ar-C), 134.9 (Ar-CH), 135.4 (Ar-C), 142.9 (Ar-CH), 153.4 (Ar-C), 160.5 (C=O). **MS** (ESI): *m/z* 255 ($M+H^+$, 65); **HRMS** (ESI): Calcd. for $C_{15}H_{11}O_2S$ ($M+H^+$), 255.0474; found 255.0464.

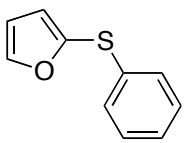
2-(Phenylthio)thiophene (3ac).[11]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and thiophene (**2s**) (14 μL, 0.165 mmol), using Tf_2O (32 μL, 0.165 mmol). After Tf_2O addition at –30 ºC, the reaction mixture was stirred at –20 ºC for 3 h. DBU (50 μL, 0.315 mmol) was then added at –20 ºC, and the mixture was allowed to warm to RT for 2 h. **3ac** (27 mg, 92%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (1H, dd, *J* = 5.4, 3.6, Ar-H), 7.04-7.09 (3H, m, Ar-H), 7.10-7.15 (2H, m, Ar-H), 7.17 (1H, dd, *J* = 3.6, 1.0 Ar-H), 7.35 (1H, dd, *J* = 5.4, 1.4, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) 126.3 (Ar-CH), 127.3 (Ar-CH), 128.1 (Ar-CH), 129.2 (Ar-CH), 133.1 (Ar-C), 131.5 (Ar-CH), 136.3 (Ar-CH), 138.8 (Ar-C).

2-(Phenylthio)furan (3ad).[11]

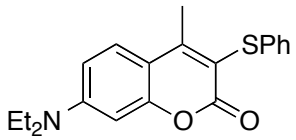


Following general procedure A, **1a** (21 mg, 0.15 mmol) and furan (**2t**) (13 μL, 0.165 mmol), using Tf_2O (32 μL, 0.165 mmol. After Tf_2O addition at –

30 ºC, the reaction mixture was stirred at –20 ºC for 3 h. DBU (50 μL, 0.315 mmol) was then added at –20 ºC, and the mixture was allowed to warm to RT for 2 h. **3ad** (21 mg, 80%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (1H, dd, *J* = 3.3, 2.0, Ar-H), 6.78 (1H, dd, *J* = 3.3, 0.9, Ar-H), 7.17-7.22 (3H, m, Ar-H), 7.26-7.30 (2H, m, Ar-H), 7.61 (1H, dd, *J* = 2.0, 0.9, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 112.1 (Ar-CH), 119.7 (Ar-CH), 126.5 (Ar-CH), 127.7 (Ar-CH), 129.3 (Ar-CH), 136.5 (Ar-C), 143.3 (Ar-C), 146.7 (Ar-CH).

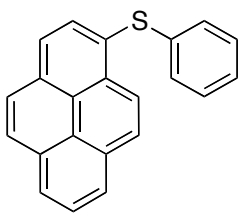
7-(Diethylamino)-4-methyl-3-(phenylthio)-2*H*-chromen-2-one (3ae).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and (**2u**) (52 mg, 0.225 mmol), using TFAA (25 μL, 0.165 mmol). After Tf_2O addition at – 30 ºC, the mixture was allowed to warm to RT for 2.5 h. Addition of DBU (50 μL, 0.315 mmol) then gave **3ae** (36 mg, 70%) as a yellow solid. Column chromatography eluent: *n*-hexane/AcOEt (4/1)

m.p.: 110-111 ºC. ν_{max} (neat)/cm^{-1} 2971, 2928, 1712, 1609, 1567, 1509, 1409, 1351, 1263, 1143, 1068, 738. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.20 (6H, t, *J* = 7.0, CH_3), 2.62 (3H, s, CH_3), 3.41 (4H, q, *J* = 7.0, CH_2), 6.48 (1H, d, *J* = 2.6, Ar-H), 6.60 (1H, dd, *J* = 9.1, 2.6, Ar-H), 7.06-7.11 (1H, m, Ar-H), 7.17-7.21 (4H, m, Ar-H), 7.45 (1H, d, *J* = 9.1, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 12.7 (CH_3), 17.7 (CH_3), 45.1 (CH_2), 97.5 (Ar-CH), 109.0 (Ar-CH), 109.5 (Ar-C), 111.8 (Ar-C), 125.8 (Ar-CH), 127.2 (Ar-CH), 127.2 (Ar-CH), 129.2 (Ar-CH), 136.9 (Ar-C), 151.3 (Ar-C), 155.9 (Ar-C), 159.3 (Ar-C), 161.7 (C=O). **MS** (ESI): *m/z* 340 (M+H$^+$, 100); **HRMS** (ESI): Calcd. for $C_{20}H_{22}O_2NS$ (M+H$^+$), 340.1366; found 340.1357.

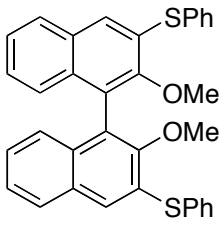
Phenyl(pyren-1-yl)sulfide (3af).[12]



Following general procedure A, **1a** (21 mg, 0.15 mmol) and (**2v**) (33 mg, 0.165 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3af** (46 mg, 98%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.27 (5H, m, Ar-H), 8.04-8.25 (8H, m, Ar-H), 8.70 (1H, d, *J* = 9.3, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 124.6 (Ar-C), 125.1 (Ar-CH), 125.4 (Ar-CH), 125.6 (Ar-C), 125.8 (Ar-CH), 125.8 (Ar-CH), 126.2 (Ar-CH), 126.5 (Ar-CH), 127.4 (Ar-CH), 128.2 (Ar-C), 128.4 (Ar-CH), 128.8 (Ar-CH), 129.3 (Ar-CH), 131.2 (Ar-C), 131.4 (Ar-C), 131.9 (Ar-C), 132.6 (Ar-C), 132.7 (Ar-CH), 138.0 (Ar-C).

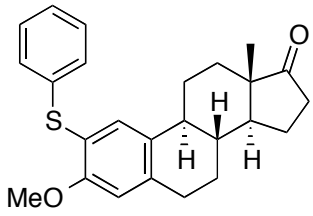
(±)-[2,2'-Dimethoxy-(1,1'-binaphthalene)-3,3'-diyl]bis(phenylsulfide) (3ag).



Following general procedure A, **1a** (44 mg, 0.31 mmol) and (**2w**) (47 mg, 0.15 mmol), using Tf_2O (60 μL, 0.31 mmol) and DBU (100 μL, 0.61 mmol), gave **3ag** (69 mg, 86%) as a white solid.

m.p.: 67-68 ºC. ν_{max} (neat)/cm^{-1} 3056, 3002, 2935, 2836, 1612, 1579, 1488, 1475, 1335, 1264, 1078, 1061, 740, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.80 (6H, s, CH_3), 7.05-7.08 (2H, m, Ar-H), 7.29-7.21 (2H, m, Ar-H), 7.23-7.25 (2H, m, Ar-H), 7.27-7.31 (4H, m, Ar-H), 7.34-7.37 (4H, m, Ar-H), 7.47 (2H, d, *J* = 9.0, Ar-H), 7.90 (2H, d, *J* = 9.0, Ar-H), 7.91-7.92 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 56.8 (CH_3), 114.6 (Ar-CH), 119.3 (Ar-C), 126.3 (Ar-CH), 126.7 (Ar-CH), 129.1 (Ar-CH), 129.2 (Ar-CH), 129.6 (Ar-C), 129.7 (Ar-C), 129.8 (Ar-CH), 130.4 (Ar-CH), 130.8 (Ar-CH), 133.0 (Ar-C), 136.5 (Ar-C), 155.4 (Ar-C). **HRMS** (APCI): Calcd. for $C_{34}H_{27}O_2S_2$ ($M+H^+$), 531.14437; found 531.1443.

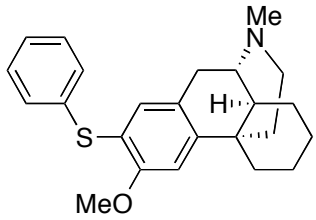
(8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-2-(phenylthio)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (3ah).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and OMe-estrone (**2x**) (47 mg, 0.165 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3ah** (50 mg, 84%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (3/1)

m.p.: 69-70 ºC. ν_{max} (neat)/cm^{-1} 2929, 2858, 1735, 1582, 1486, 1251, 1059, 750. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.90 (3H, s, CH_3), 1.41-1.68 (6H, m), 1.89-1.95 (1H, m), 2.02-2.29 (5H, m), 2.55 (1H, dd, *J* = 18.5, 8.9), 2.90-2.98 (2H, m), 3.83 (3H, s, OCH_3), 6.68 (1H, s, Ar-H), 7.18-7.22 (1H, m, Ar-H), 7.23-7.30 (5H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.0 (CH_3), 21.8 (CH_2), 26.0 (CH_2), 26.7 (CH_2), 29.9 (CH_2), 31.7 (CH_2), 36.0 (CH_2), 38.4 (CH), 44.0 (CH), 48.2 (C), 50.5 (CH), 56.2 (OCH_3), 111.8 (Ar-CH), 119.3 (Ar-C), 126.3 (Ar-CH), 129.1 (Ar-CH), 129.4 (Ar-CH), 131.6 (Ar-CH), 132.9 (Ar-C), 136.6 (Ar-C), 138.4 (Ar-C), 156.7 (Ar-C), 220.9 (C=O). **MS** (ESI): *m/z* 393 (M+H$^+$, 61), 393 (M+NH_4^+, 21), 807 (2M+Na, 10); **HRMS** (ESI): Calcd. for $C_{25}H_{29}O_2S$ (M+H$^+$), 393.1883; found 393.1879.

(4b*S*,8a*S*)-3-Methoxy-11-methyl-2-(phenylthio)-6,7,8,8a,9,10-hexahydro-5*H*-9,4b-(epiminoethano)phenanthrene (3ai).



Following general procedure A, **1a** (21 mg, 0.15 mmol) and dextromethorphan (**2y**) (41 mg, 0.15 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3ai** (40 mg, 70%) as a white solid. Column chromatography eluent: 2% MeOH in CH_2Cl_2.

m.p.: 75-76 ºC. ν_{max} (neat)/cm^{-1} 2932, 2857, 1596, 1488, 1281, 1237, 1160, 1027, 750, 637. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.00-1.12 (1H, m), 1.21-1.31 (1H, m), 1.35-1.54 (4H, m), 1.55-1.70 (2H, m), 2.00-2.10 (1H, m), 2.12-2.18 (1H, m), 2.33-2.41 (1H, m), 2.50-2.61 (1H, m), 2.78 (3H, s, NCH_3), 2.81 (1H, d, *J* = 19.4), 2.94 (1H, dd, *J* = 19.4, 6.2), 3.03-3.09 (1H, m), 3.35-3.40 (1H, m), 3.84 (3H, s, OCH_3), 6.70 (1H, s, Ar-H), 6.74 (1H, s, Ar-H), 7.30-7.42 (5H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.8 (CH_2), 24.2 (CH_2), 25.8 (CH_2), 26.0 (CH_2), 35.6 (CH_2), 36.2 (C), 39.0 (CH_2), 41.6 (CH), 42.0 (CH_3), 48.4 (CH_2), 56.3 (OCH_3), 60.6 (CH), 107.7 (Ar-CH), 124.6 (Ar-C), 126.0 (Ar-C), 128.1 (Ar-CH), 129.4 (Ar-CH), 126.6 (Ar-CH), 132.9 (Ar-CH), 133.1 (Ar-C), 137.4 (Ar-C), 156.7 (Ar-C). **MS** (ESI): *m/z* 380 (M+H$^+$, 100); **HRMS** (ESI): Calcd. for $C_{24}H_{30}ONS$ (M+H$^+$), 380.2043; found 380.2026.

Iterative C-H thiolation:

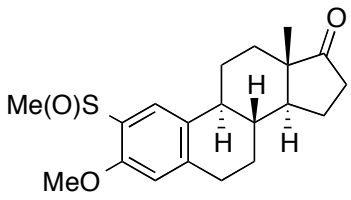
General procedure B. Metal-free C-H thiomethylation of arenes.

Tf_2O (1.1 equiv.) was added to a solution of DMSO (1.1 equiv.) and the corresponding arene (1 equiv.) in CH_2Cl_2 (0.2 M) in an oven-dried tube flushed with N_2 at –30 ºC. After 15 min at –30 ºC, the reaction was stirred at room temperature for 1.5 h. Et_2NH (4.1 equiv.) was then added, and the reaction mixture was stirred at room temperature for 6 h. The solution was quenched with H_2O (3 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane.

General procedure C. Sulfide *m*-CPBA oxidation.

To a solution of the in CH_2Cl_2 (0.2 M) at 0 °C, was added *m*-CPBA (1.05 mmol) in portions. The resulting mixture was stirred at 0 °C for 1 h. The reaction was then quenched with saturated $NaHCO_3$ solution (5 mL) and the layers separated. The aqueous layer was washed with CH_2Cl_2 (3 × 5 mL) and the combined organic layers dried with $MgSO_4$ and the solvent removed *in vacuo*.

(8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-2-(methylsulfinyl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (1ah).



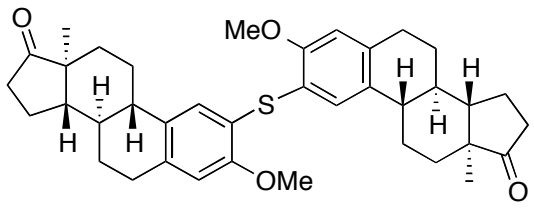
Following general procedure B, DMSO (30 μL, 0.396 mmol) and OMe-estrone (**2ah**) (100 mg, 0.36 mmol), using Tf_2O (72 μL, 0.396 mmol, 1.1 equiv.) and Et_2NH (0.150 mL, 1.48 mmol, 4.1 equiv.), gave the corresponding methyl sulfide derivative as a colorless oil (104 mg, 88%). Column chromatography eluent: *n*-Hexane/Et_2O (4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, s, CH_3), 1.38-1.68 (7H, m), 1.92-1.96 (1H, m), 1.97-2.06 (2H, m), 2.09-2.16 (1H, m), 2.22-2.28 (1H, m), 2.34 (3H, s, CH_3), 2.45-2.54 (1H, m), 2.84-2.90 (2H, m), 3.85 (3H, s, OCH_3), 6.56 (1H, s, Ar-H), 7.13 (1H, s, Ar-H).

Following general procedure C, methyl sulfide derivative (0.1 g, 0.3 mmol) and *m*-CPBA (0.31 mmol), gave sulfoxide **1ah** (1:1 mixture of diasteoisomers) as a white solid (93 mg, 90%). Column chromatography eluent: *n*-Hexane/AcOEt (1:1).

m.p.: 214-215 ºC. ν_{max} (neat)/cm^{-1} 2930, 1734, 1599, 1485, 1247, 1033, 748. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.84 (3H, s, CH_3), 0.85 (3H, s, CH_3), 1.37-1.62 (6H, m), 1.87-2.13 (4H, m), 2.19-2.27 (1H, m), 2.39-2.53 (2H, m), 2.67 (3H, s, $S(O)CH_3$), 2.69 (3H, s, $S(O)CH_3$), 2.86-2.92 (2H, m), 3.85 (3H, s, OCH_3), 6.57 (1H, s, Ar-H), 7.64 (1H, s, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.0 (CH_3), 14.1 (CH_3), 21.8 (CH_2), 26.1 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 26.5 (CH_2), 30.0 (CH_2), 30.1 (CH_2), 31.6 (CH_2), 36.0 (CH_2), 38.4 (CH), 38.5 (CH), 41.6 (CH), 44.3 (CH), 44.4 (CH), 48.2 (C), 50.5 (CH), 50.6 (CH), 55.9 (OCH_3), 111.3 (Ar-CH), 111.3 (Ar-CH), 121.8 (Ar-C), 121.9 (Ar-CH), 130.2 (Ar-C), 130.3 (Ar-C), 133.7 (Ar-C), 141.1 (Ar-C), 141.1 (Ar-C), 152.9 (Ar-C), 220.8 (C=O). **MS** (ESI): *m*/*z* 347 ($M+H^+$, 100), 693 ($2M+H^+$, 90); **HRMS** (ESI): Calcd. for $C_{20}H_{27}O_3S$ ($M+H^+$), 347.1675; found 347.1667.

(8*R*,8'*R*,9*S*,9'*S*,13*S*,13'*S*,14*S*,14'*S*)-2,2'-Thiobis(3-methoxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one) (3aj).

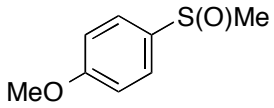


Following general procedure A, **1ah** (15 mg, 0.044 mmol) and OMe-estrone (**2ah**) (13 mg, 0.044 mmol), using Tf_2O (9 μL, 0.05 mmol) and DBU (15 μL, 0.09 mmol), gave **3aj** (15 mg, 58%) as a white solid. Column chromatography eluent: *n*-hexane/Et_2O (2/1)

m.p.: 245-246 ºC. ν_{max} (neat)/cm^{-1} 2929, 2856, 1735, 1595, 1486, 1250, 1055, 751. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.85 (6H, s, CH_3), 1.34-1.65 (12H, m), 1.78-1.85 (2H, m), 1.94-2.21 (10H, m), 2.47 (2H, dd, *J* = 18.5, 8.9), 2.86-2.91 (4H, m), 3.81 (6H, s, OCH_3), 6.61 (2H, s,

Ar-H), 6.96 (2H, s, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 21.8 (CH_2), 26.1 (CH_2), 26.7 (CH_2), 29.8 (CH_2), 31.8 (CH_2), 36.0 (CH_2), 38.5 (CH), 44.1 (CH), 48.1 (C), 50.5 (CH), 56.1 (OCH_3), 111.4 (Ar-CH), 120.0 (Ar-C), 129.3 (Ar-CH), 132.7 (Ar-C), 136.9 (Ar-C), 156.7 (Ar-C), 221.0 (C=O). **MS** (ESI): *m/z* 599 ($M+H^+$, 10), 616 ($M+NH_4^+$, 12); **HRMS** (ESI): Calcd. for $C_{38}H_{46}O_4SNa$ (M+Na), 621.3009; found 621.2995.

1-Methoxy-4-(methylsulfinyl)benzene (1b).[13]



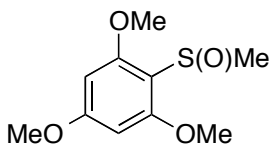
Following general procedure B, DMSO (78 μL, 1.1 mmol) and anisole (110 μL, 1 mmol), using Tf_2O (186 μL, 1.1 mmol) and Et_2NH (430 μL, 4.1 mmol), gave (4-methoxyphenyl)(methyl)sulfide (123 mg, 82%) as a colorless oil. Column chromatography eluent: *n*-Hexane.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (3H, s, CH_3), 3.76 (3H, s, CH_3), 6.79-6.84 (2H, m, Ar-H), 7.22-7.26 (2H, m, Ar-H).

Following general procedure C, (4-methoxyphenyl)(methyl)sulfane (123 mg, 0.8 mmol) and *m*-CPBA (0.85 mmol), gave **1b** (125 mg, 92%). Column chromatography eluent: *n*-Hexane/AcOEt (1:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74 (3H, s, CH_3), 3.84 (3H, s, OCH_3), 7.02-7.05 (2H, m, Ar-H), 7.55-7.61 (2H, m, Ar-H).

1,3,5-Trimethoxy-2-(methylsulfinyl)benzene (1l).



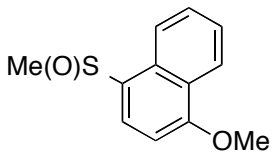
Following general procedure B, DMSO (0.110 mL, 1.5 mmol) and 1,3,5-trimethoxybenzene (250 mg, 1.5 mmol), using Tf_2O (1.65 mmol, 1.1 equiv.) and Et_2NH (0.64 mL, 0.615 mmol, 4.1 equiv.), gave methyl(2,4,6-trimethoxyphenyl)sulfide (253 mg, 79%) as a colorless oil. Column chromatography eluent: *n*-Hexane.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (3H, s, CH_3), 3.81 (3H, s, OCH_3), 3.87 (6H, s, OCH_3), 6.13 (2H, s, Ar-H).

Following general procedure C, methyl(2,4,6-trimethoxyphenyl)sulfide (0.1 g, 0.46 mmol) and *m*-CPBA (0.46 mmol), give sulfoxide **1l** as a white solid (96 mg, 91%). Column chromatography eluent: *n*-Hexane/AcOEt (1:2).

m.p.: 118-120 ºC. ν_{max} (neat)/cm^{-1} 2967, 1656, 1581, 1456, 1410, 1228, 1124, 1085, 1029. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.00 (3H, s, CH_3), 3.80 (3H, s, CH_3), 3.84 (6H, s, CH_3), 6.08 (2H, s, Ar-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 38.0 (CH_3), 55.7 (OCH_3), 56.3 (OCH_3), 91.4 (Ar-CH), 111.7 (Ar-C), 161.3 (Ar-C), 164.7 (Ar-C). **MS** (ESI): *m/z* 231 (M+H$^+$, 85), 253 (M+Na, 80), 483 (2M+Na, 95); **HRMS** (APCI): Calcd. for $C_{10}H_{15}O_4S$ (M+H$^+$), 231.0686; found 231.0676.

1-Methoxy-4-(methylsulfinyl)naphthalene (1m).



Following general procedure B, DMSO (78 μL, 1.1 mmol) and 1-methoxynaphthalene (158 mg, 1 mmol), using Tf_2O (186 μL, 1.1 mmol) and Et_2NH (430 μL, 4.1 mmol), gave (4-methoxynaphthalen-1-yl)(methyl)sulfide (194 mg, 95%) as colorless oil. Column chromatography eluent: *n*-Hexane/Et_2O (10:1).

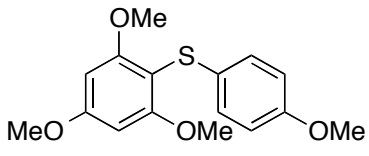
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s, CH_3), 3.98 (3H, s, CH_3), 6.76 (1H, *J* = 8.4, Ar-H), 7.48-7.53 (2H, m, Ar-H), 7.55-7.60 (1H, m, Ar-H), 8.28 (1H, *J* = 8.4, Ar-H), 8.35 (1H, *J* = 8.4, Ar-H).

Following general procedure C, (4-Methoxynaphthalen-1-yl)(methyl)sulfide (194 mg, 0.95 mmol) and *m*-CPBA (1 mmol), gave sulfoxide **1m** (198 mg, 95%). Column chromatography eluent: *n*-Hexane/AcOEt (1:1).

m.p.: 105-106 ºC. ν_{max} (neat)/cm^{-1} 2937, 2841, 1572, 1507, 1459, 1420, 1379, 1242, 1087, 1051, 993, 761. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.79 (3H, s, CH_3), 4.04 (3H, s, OCH_3), 6.96 (1H, *J* = 8.2, Ar-H), 7.51-7.60 (2H, m, Ar-H), 7.89-7.93 (1H, m, Ar-H), 8.05 (1H, *J* = 8.2, Ar-H), 8.32-8.35 (1H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 43.2 (CH_3), 56.0 (OCH_3), 103.9 (Ar-CH), 121.4 (Ar-CH), 123.6 (Ar-CH), 123.7 (Ar-CH), 125.8 (Ar-C), 126.2 (Ar-CH), 127.9

(Ar-CH), 129.8 (Ar-C), 132.3 (Ar-C), 158.2 (Ar-C). **MS** (ESI): *m/z* 221 ($M+H^+$, 62), 463 (2M+Na, 53); **HRMS** (ESI): Calcd. for $C_{12}H_{13}O_2S$ ($M+H^+$), 221.0631; found 221.0624.

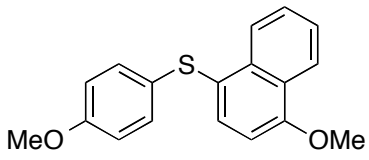
(4-Methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfide (3ak).[14]



Following general procedure A, **1l** (35 mg, 0.15 mmol) and anisole (**2z**) (25 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3ak** (38 mg, 83%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (3H, s, CH_3), 3.80 (6H, s, CH_3), 3.83 (3H, s, CH_3), 6.17 (2H, s, Ar-H), 6.69-6.73 (2H, m, Ar-H), 7.03-7.06 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 55.5 (OCH_3), 55.6 (OCH_3), 56.5 (OCH_3), 91.4 (Ar-CH), 100.8 (Ar-C), 114.5 (Ar-CH), 128.8 (Ar-CH), 129.4 (Ar-C), 157.7 (Ar-C), 162.5 (Ar-C), 163.8 (Ar-C).

(4-Methoxynaphthalen-1-yl)(4-methoxyphenyl)sulfide (3al).

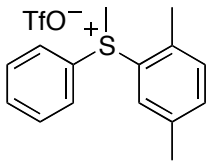


Following general procedure A, **1m** (33 mg, 0.15 mmol) and anisole (**2z**) (25 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol) and DBU (50 μL, 0.315 mmol), gave **3al** (42.5 mg, 95%) as colorless oil.

ν_{max} (neat)/cm^{-1} 2935, 1834, 1586, 1492, 1456, 1317, 1263, 1237, 1986, 1027, 906, 816, 762, 729. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.72 (3H, s, OCH_3), 4.00 (3H, s, OCH_3), 6.69-6.79 (3H, m, Ar-H), 7.11 (2H, d, *J* = 7.9, Ar-H), 7.45-7.54 (2H, m, Ar-H), 7.64 (1H, d, *J* = 7.8, Ar-H), 8.29 (1H, d, *J* = 7.8, Ar-H), 8.34 (1H, d, *J* = 7.8, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 55.5 (CH_3), 55.8 (CH_3), 104.1 (Ar-CH), 114.8 (Ar-CH), 122.6 (Ar-C), 122.7 (Ar-CH), 125.8 (Ar-CH), 125.9 (Ar-CH), 126.6 (Ar-C), 127.6 (Ar-CH), 128.7 (Ar-C), 130.3 (Ar-CH), 133.9 (Ar-CH), 134.7 (Ar-C), 156.6 (Ar-C), 158.3 (Ar-C). **HRMS** (APCI): Calcd. for $C_{18}H_{17}O_2S$ ($M+H^+$), 297.0934; found 297.0944.

Isolation of a sulfonium salt intermediate:

(2,5-Dimethylphenyl)(methyl)(phenyl)sulfonium (4).

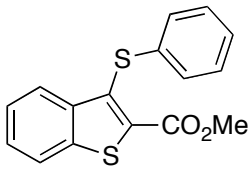


Following general procedure A without the addition of base, **1a** (21 mg, 0.15 mmol) and *p*-xylene (**2a**) (28 μL, 0.225 mmol), using Tf_2O (32 μL, 0.165 mmol), gave **3a** (47 mg, 83%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s, CH_3), 2.49 (3H, s, CH_3), 3.66 (3H, s, CH_3), 7.28 (1H, d, *J* = 7.8, Ar-H), 7.40 (1H, d, *J* = 7.8, Ar-H), 7.59-7.68 (3H, m, Ar-H), 7.73 (1H, br s, Ar-H), 7.78-7.84 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.4 (CH_3), 21.1 (CH_3), 28.1 (CH_3), 120.9 (q, *J* = 318, CF_3), 123.4 (Ar-C), 126.1 (Ar-C), 128.5 (Ar-CH), 130.0 (Ar-CH), 131.6 (Ar-CH), 132.6 (Ar-CH), 134.4 (Ar-CH), 135.6 (Ar-CH), 137.5 (Ar-C), 140.4 (Ar-C). **^{19}F NMR** (376.8 MHz, $CDCl_3$) δ -78.3.

Manipulation of products:

Methyl 3-(phenylthio)benzo[*b*]thiophene-2-carboxylate (5).[15]



To a solution of the sulfide **3z** (37 mg, 0.15 mmol) in THF (1 mL) at –78 ºC, *n*-BuLi (0.16 mmol, 1.6 M solution in hexane) was added dropwise. After 1.5 h at the same temperature, the mixture was added to a solution of methyl chloroformate (1.2 mmol) in THF (0.5 mL). The mixture was then stirred for 3 h at –78 ºC. The solution was quenched with saturated NH_4Cl solution (3 mL) and the aqueous layer was extracted with EtOAc (3 × 3 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane:Et_2O (10:1), to give product **5** (33 mg, 78%) as a yellow oil.

ν_{max} (neat)/cm^{-1} 3057, 2949, 1723, 1699, 1581, 1490, 1434, 1283, 1221, 1092, 1057, 730, 688. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.91 (3H, s, CH_3), 7.09-7.13 (1H, m, Ar-H), 7.14-7.19 (4H, m, Ar-H), 7.29-7.34 (1H, m, Ar-H), 7.42-7.48 (1H, m, Ar-H), 7.80-7.86 (2H, m, Ar-H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 52.8 (OCH_3), 122.6 (Ar-CH), 125.4 (Ar-CH), 125.7 (Ar-CH),

126.3 (Ar-CH), 127.7 (Ar-CH), 128.4 (Ar-CH), 129.2 (Ar-CH), 131.4 (Ar-C), 134.6 (Ar-C), 136.5 (Ar-C), 140.1 (Ar-C), 140.2 (Ar-C), 162.4 (C=O). **MS** (ESI): *m/z* 301 ($M+H^+$, 36), 323 ($M+Na^+$, 85); **HRMS** (ESI): Calcd. for $C_{16}H_{12}O_2NaS_2$ ($M+Na^+$), 323.0161; found 323.0171.

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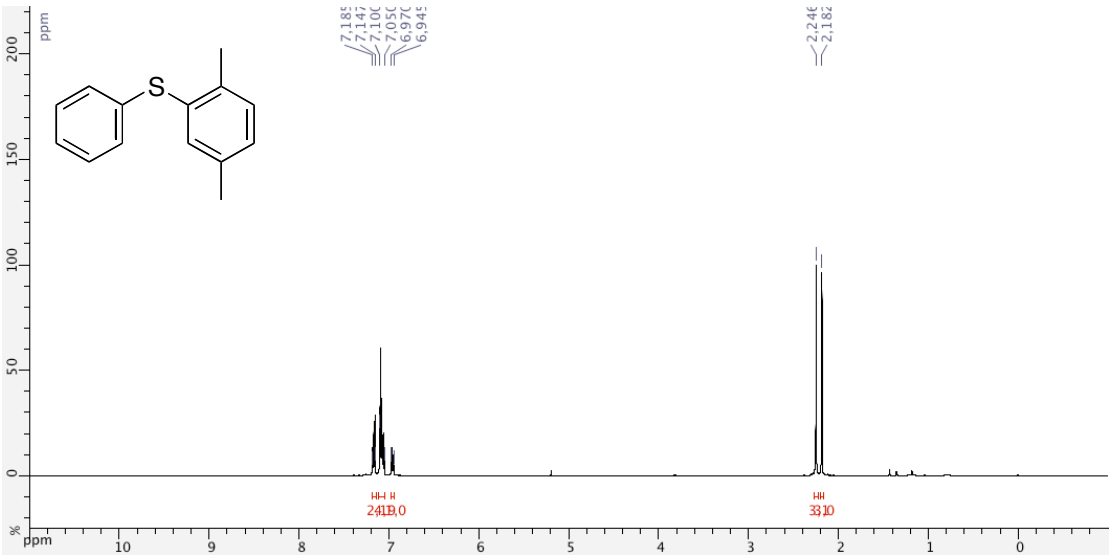
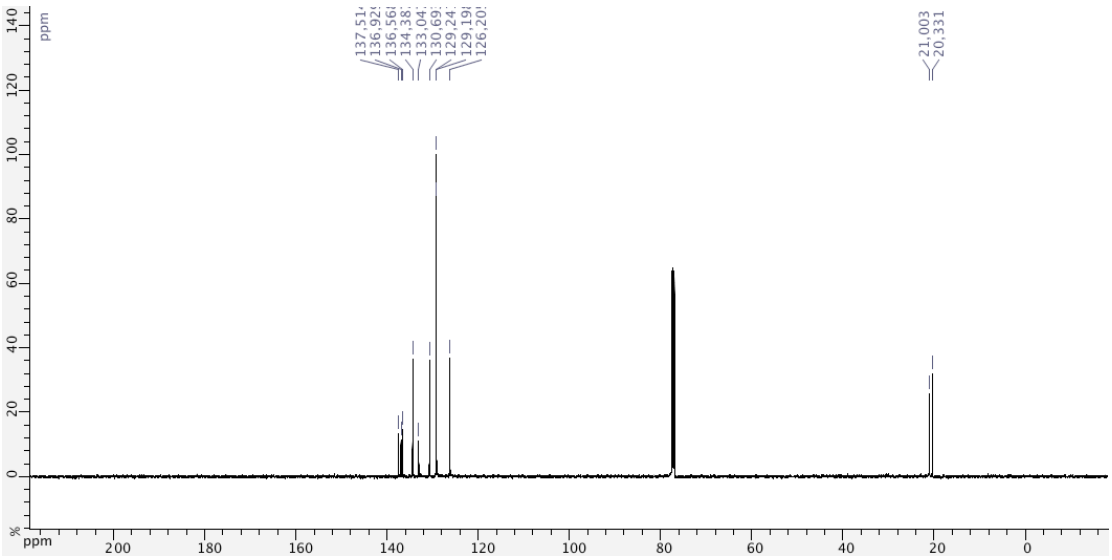
1H and 13C NMR spectra:
Compound **3a:**

500 MHz, $CDCl_3$

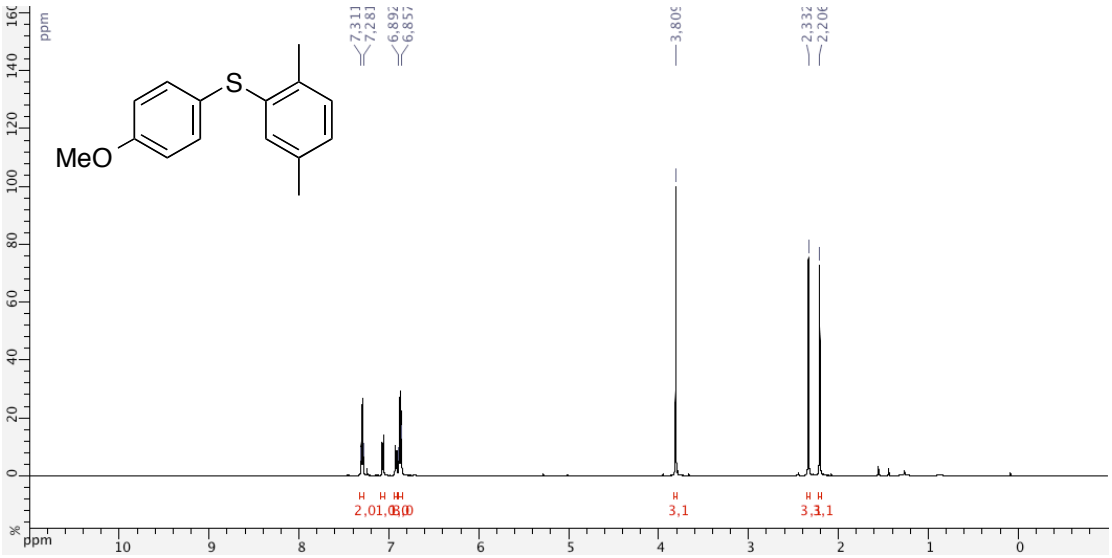


125 MHz, $CDCl_3$

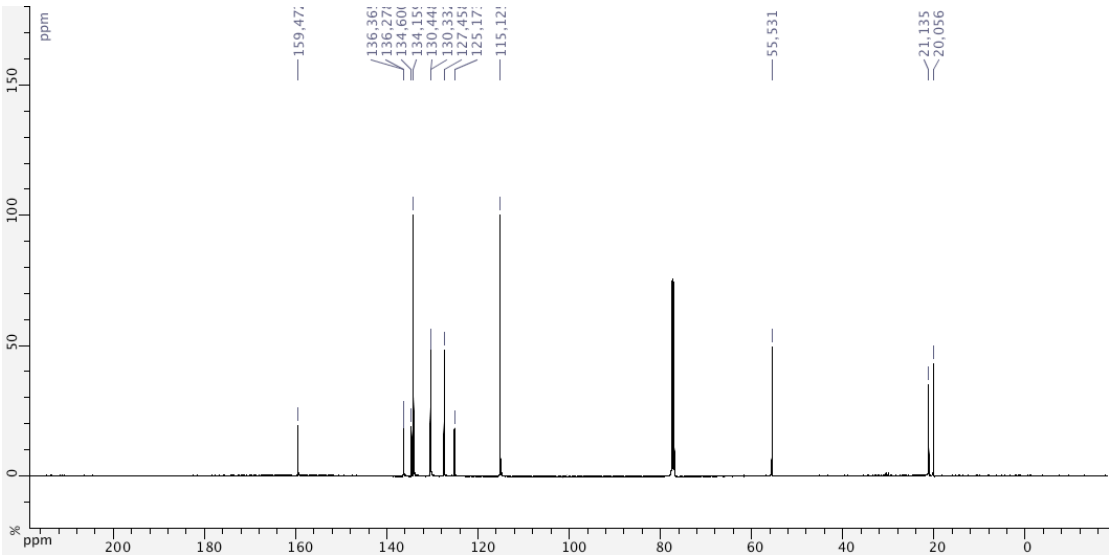


Compound **3b:**

500 MHz, $CDCl_3$

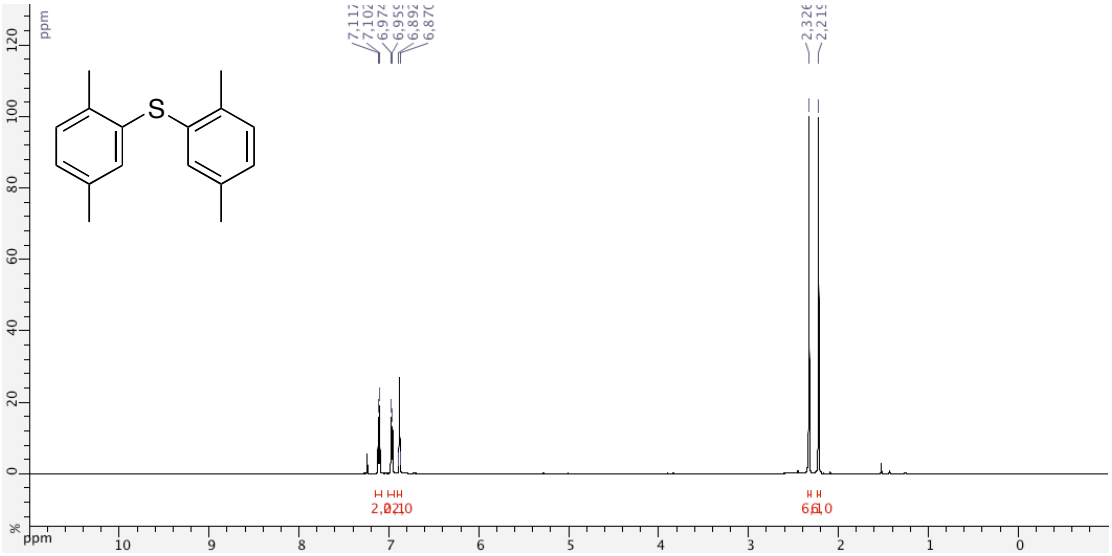


125 MHz, $CDCl_3$

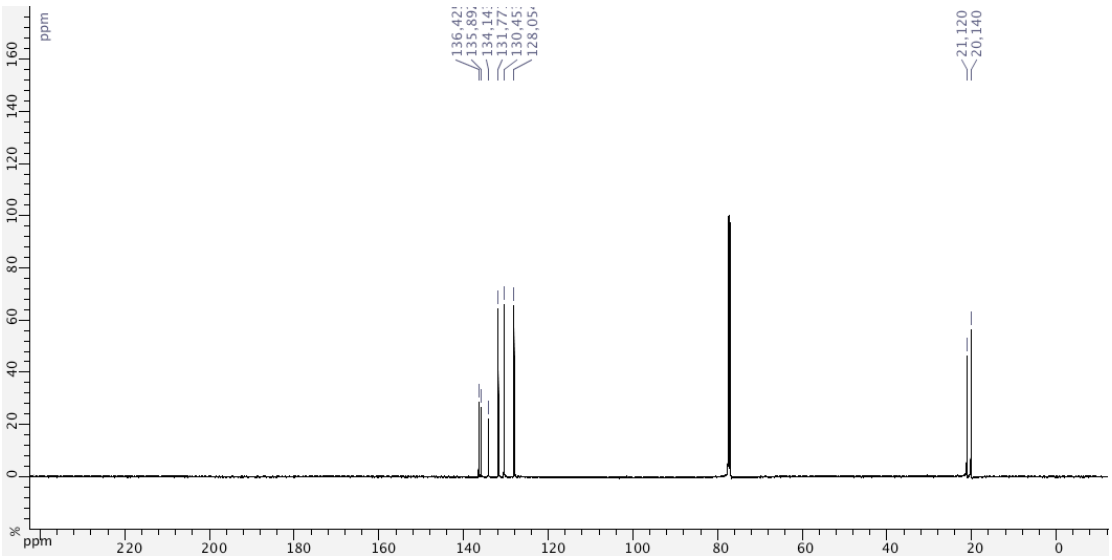


Compound **3c:**

500 MHz, $CDCl_3$

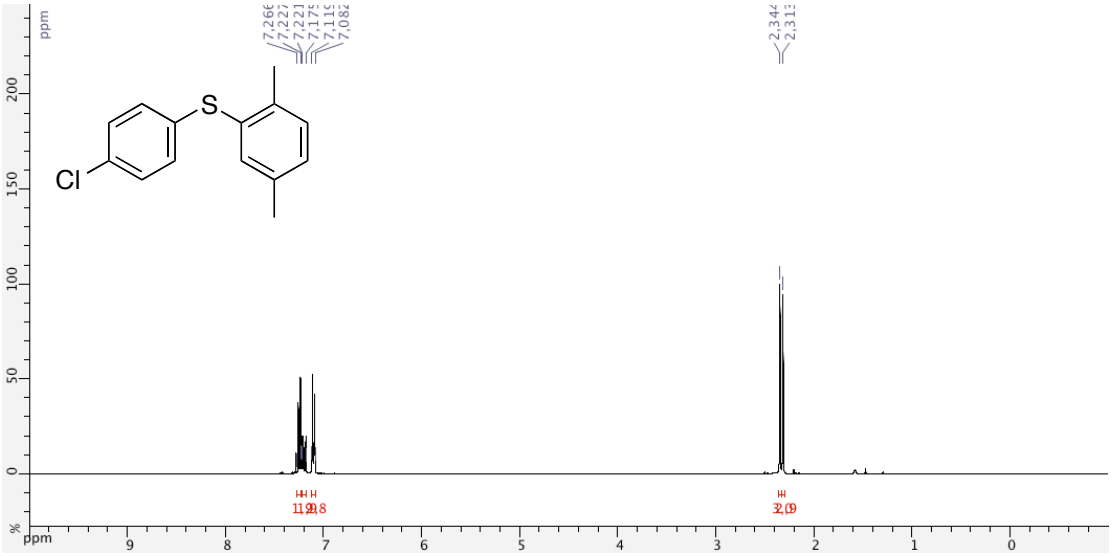


125 MHz, $CDCl_3$

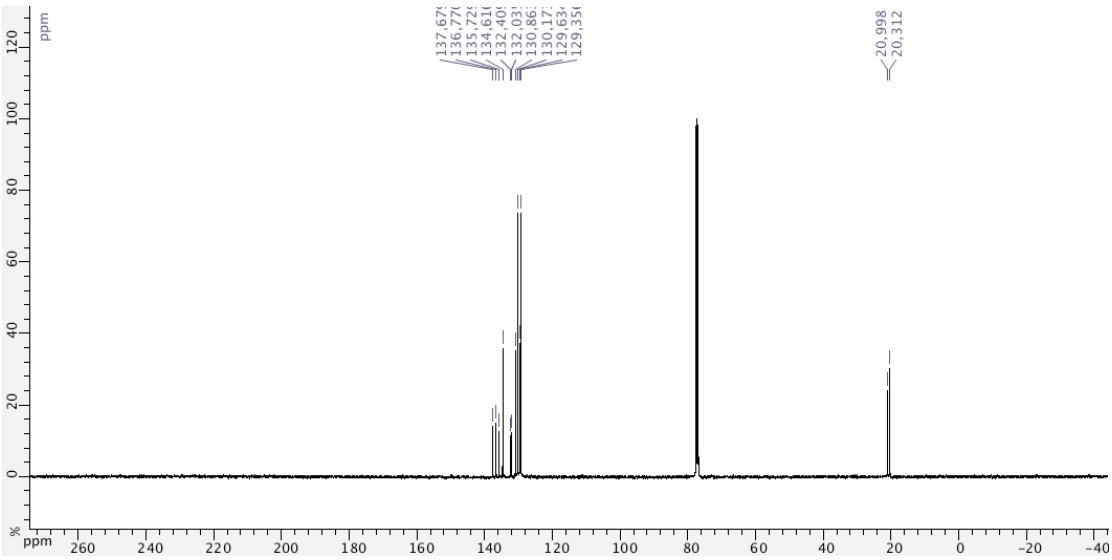


Compound **3d:**

400 MHz, $CDCl_3$

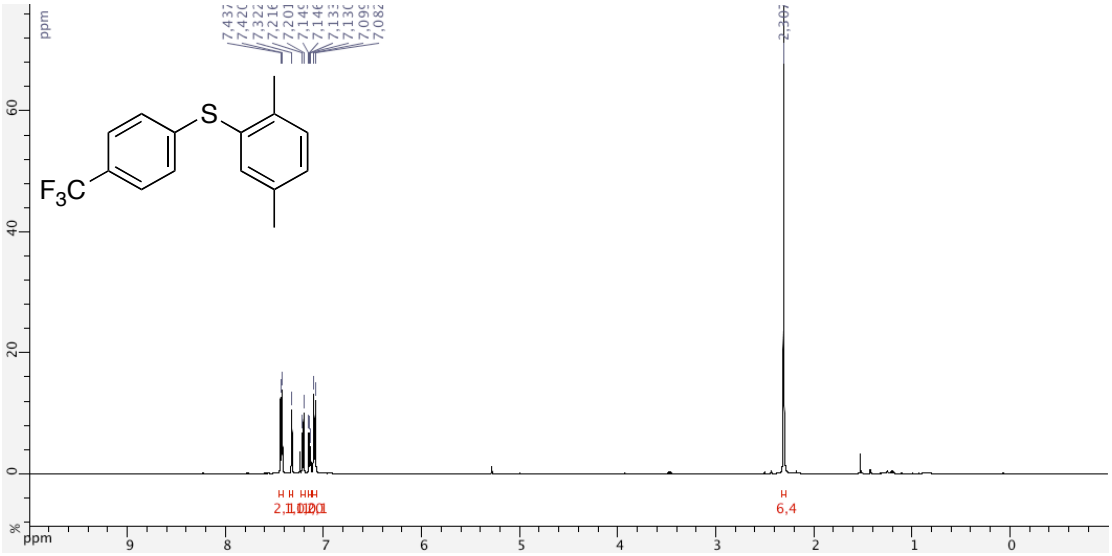


100 MHz, $CDCl_3$

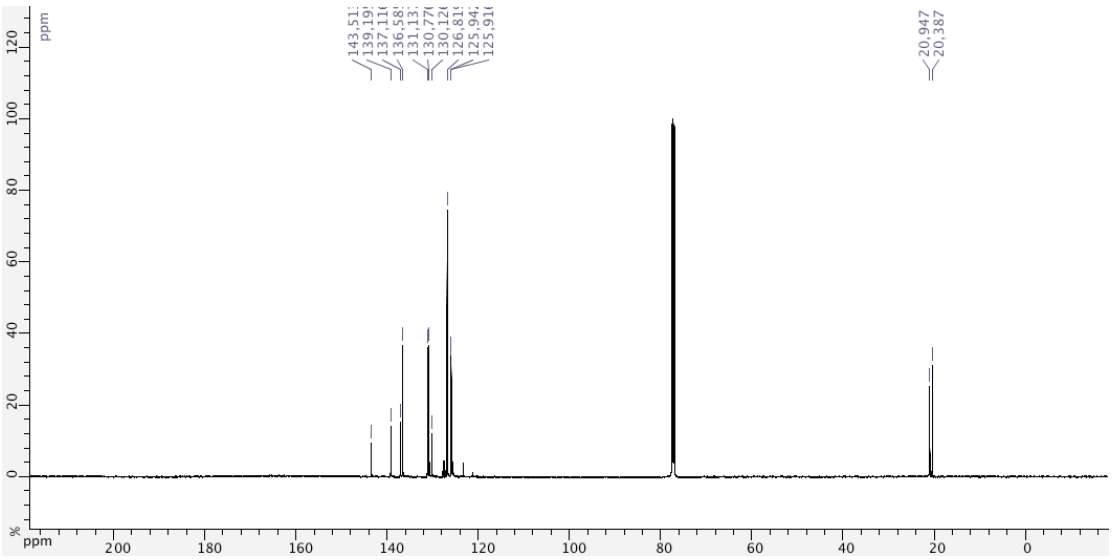


Compound **3e:**

500 MHz, $CDCl_3$

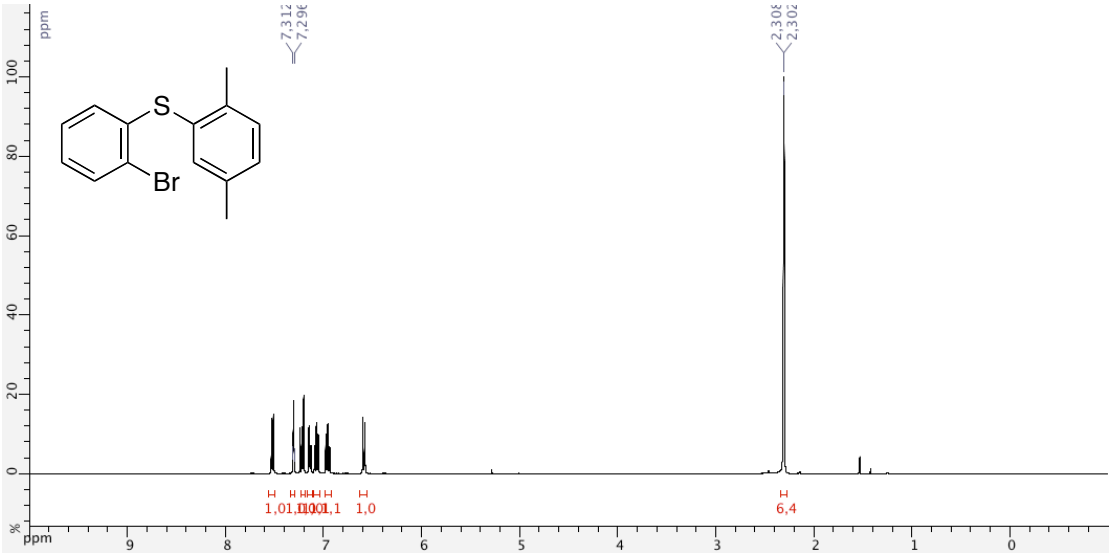


125 MHz, $CDCl_3$

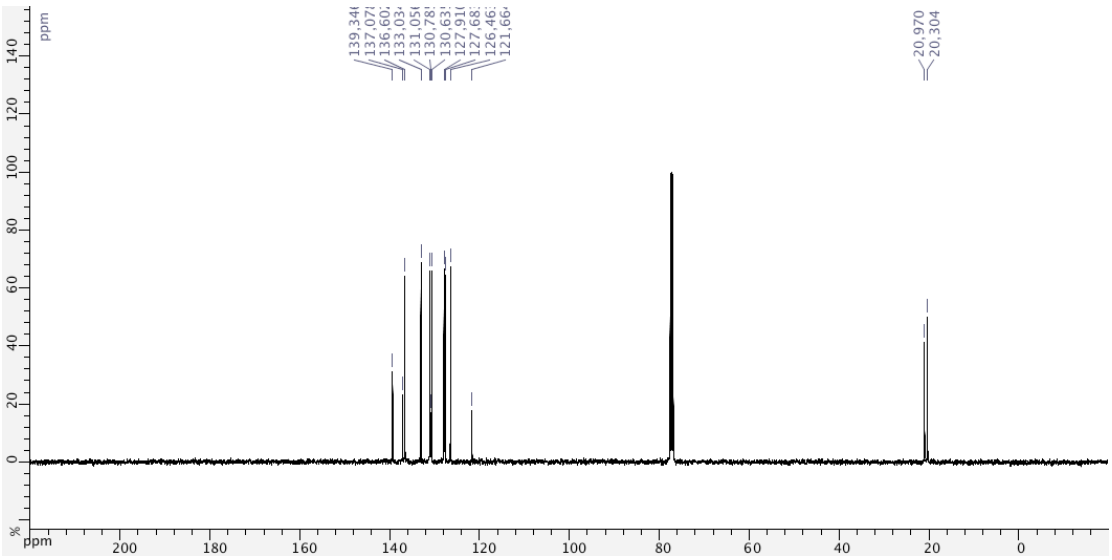


Compound **3f:**

400 MHz, $CDCl_3$

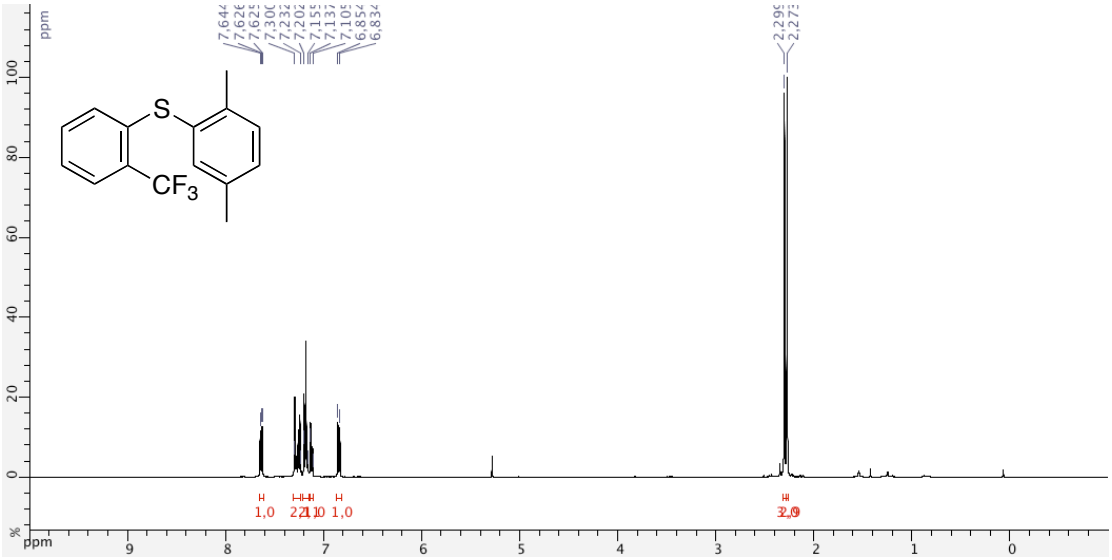


100 MHz, $CDCl_3$

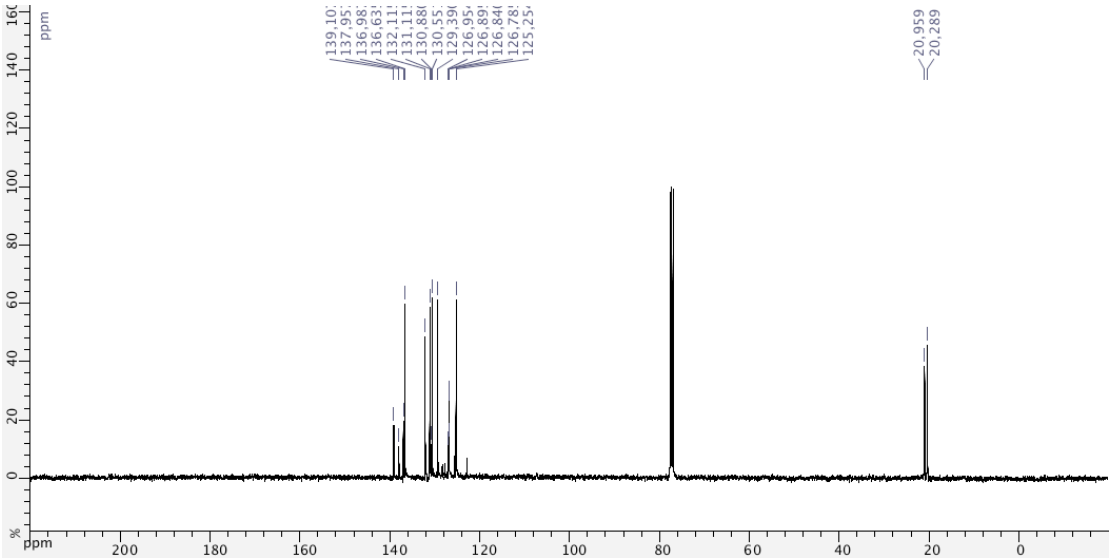


Compound **3g:**

400 MHz, $CDCl_3$

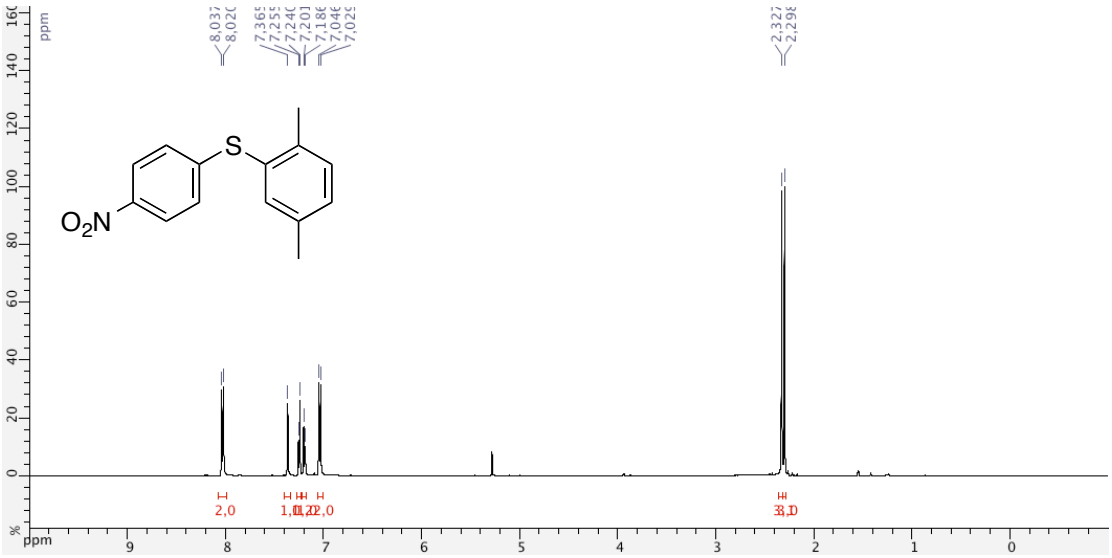


100 MHz, $CDCl_3$

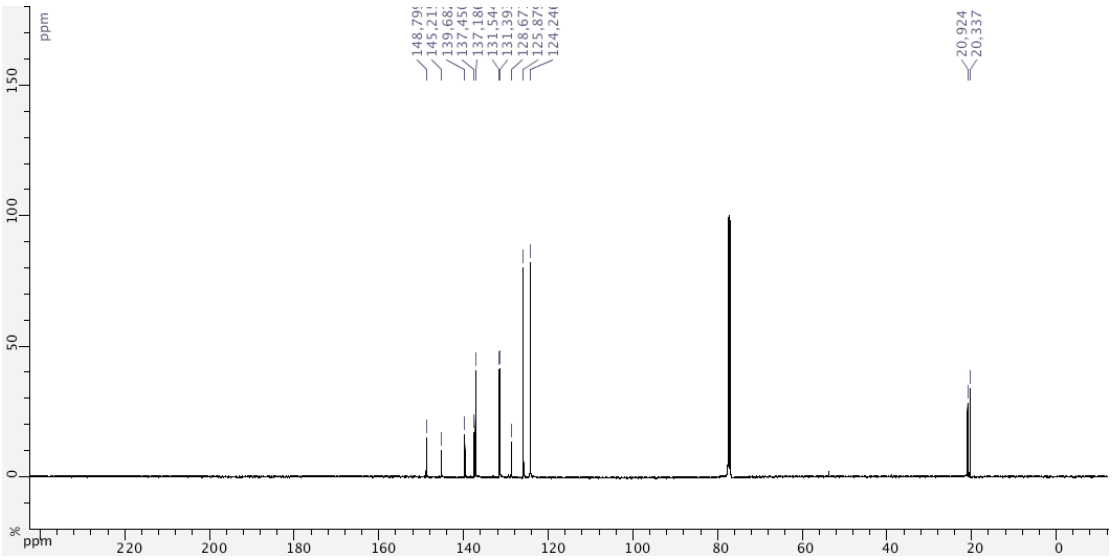


Compound **3h:**

500 MHz, $CDCl_3$

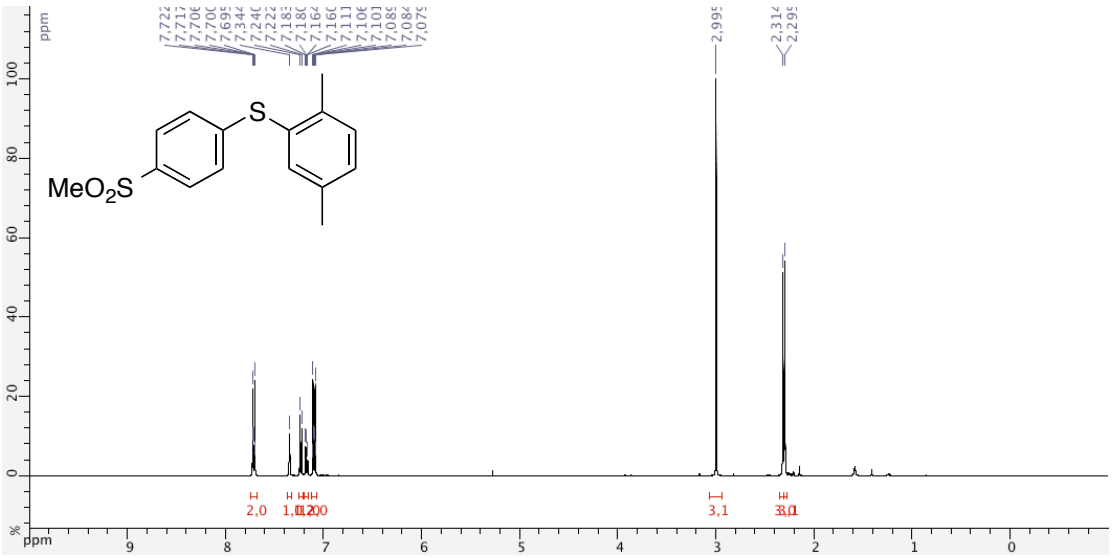


125 MHz, $CDCl_3$

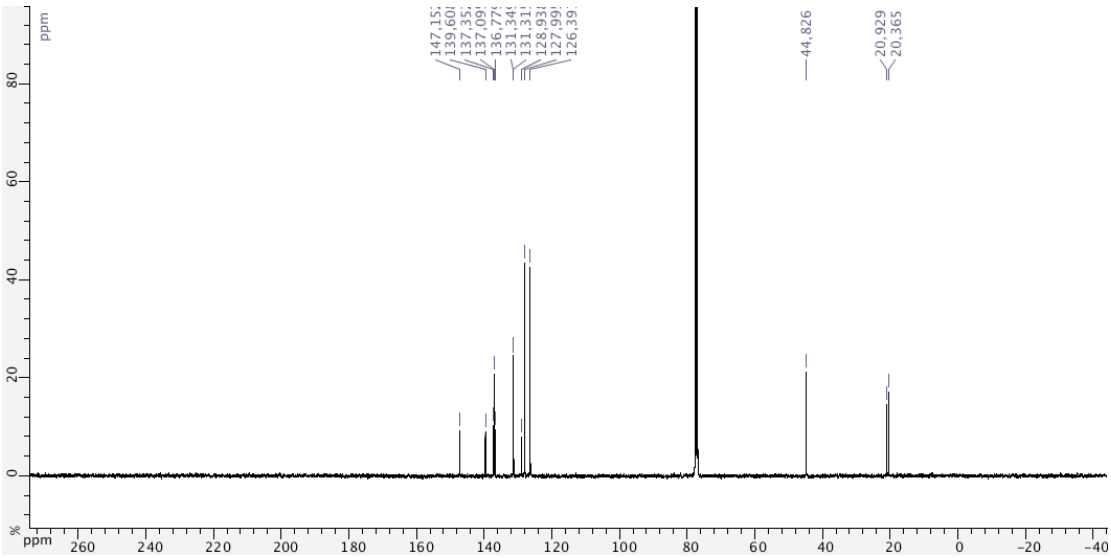


Compound **3i:**

400 MHz, $CDCl_3$

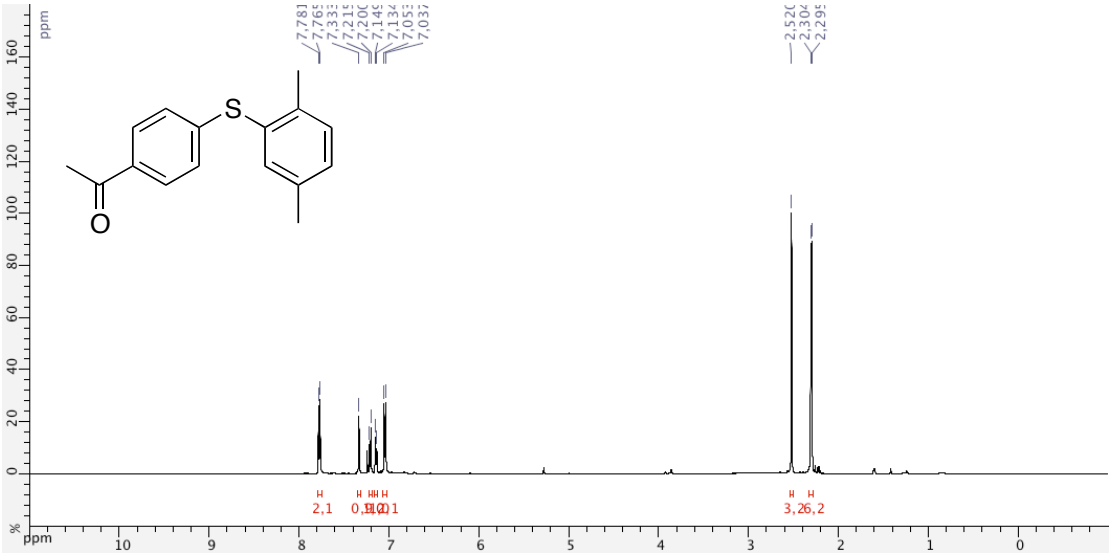


100 MHz, $CDCl_3$

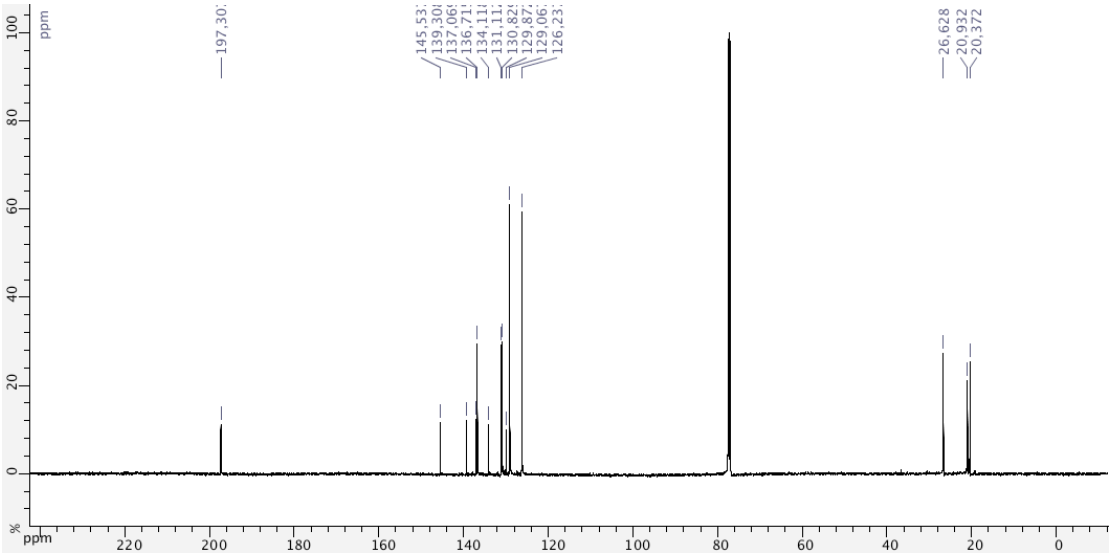


Compound **3j:**

500 MHz, $CDCl_3$



125 MHz, $CDCl_3$



Compound **3k:**

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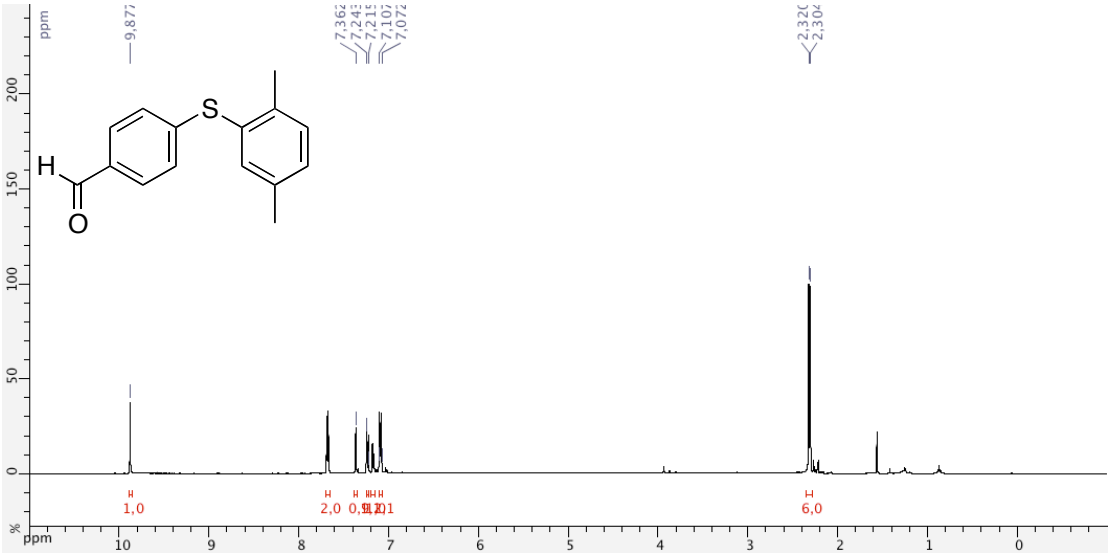
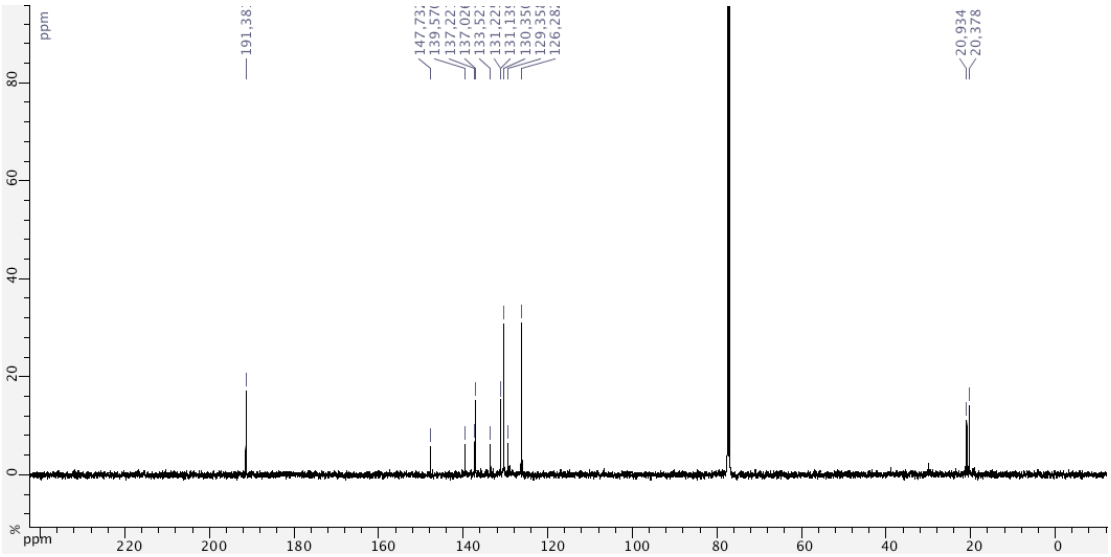
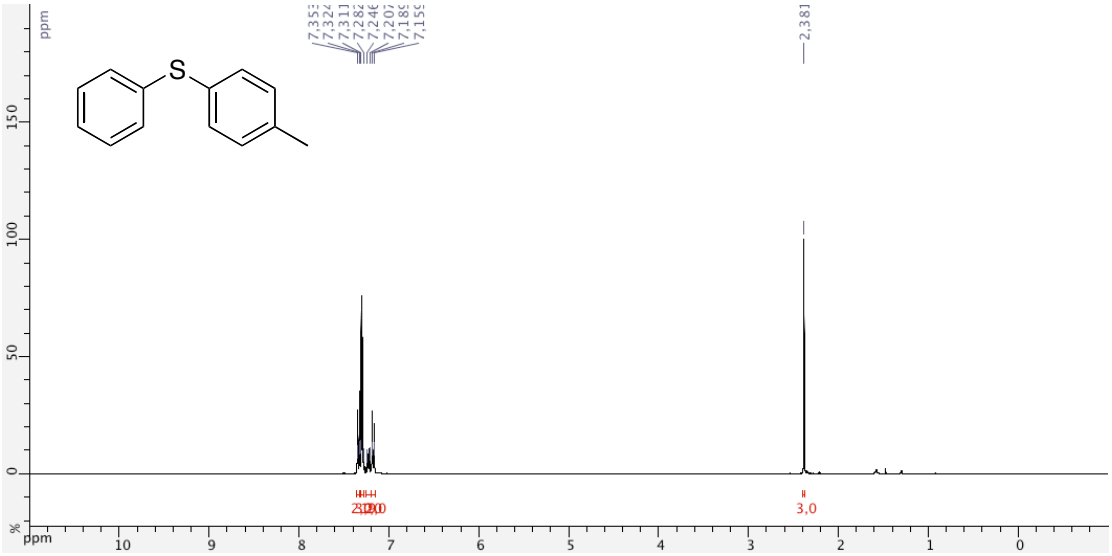


125 MHz, $CDCl_3$

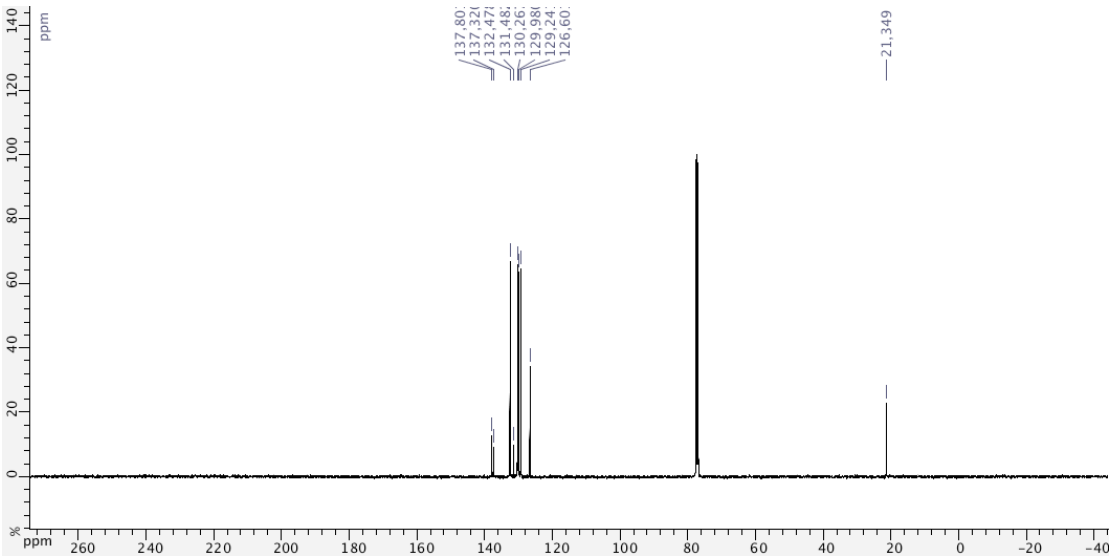


Compound **3l:**

400 MHz, $CDCl_3$

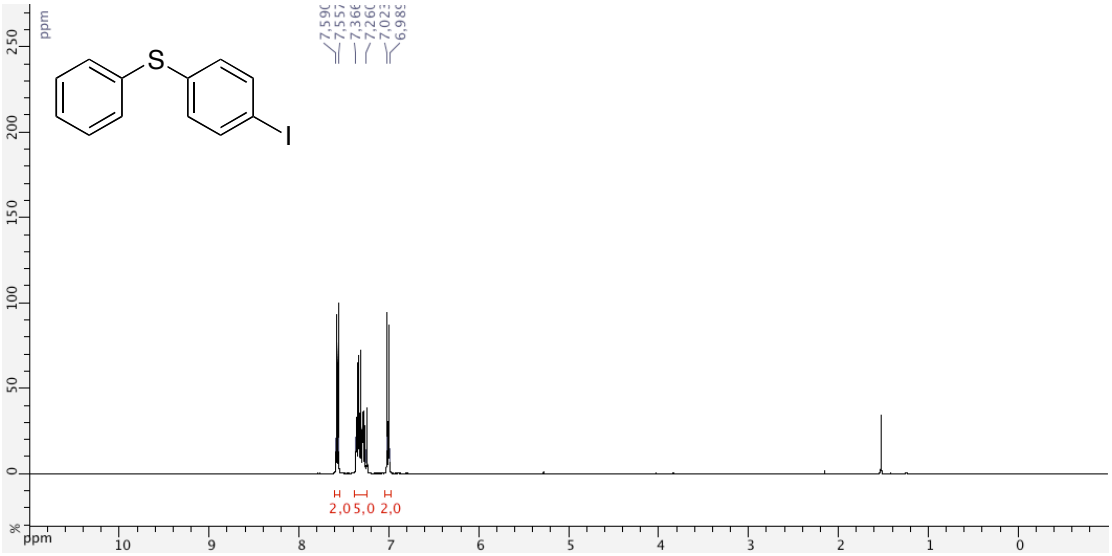


100 MHz, $CDCl_3$

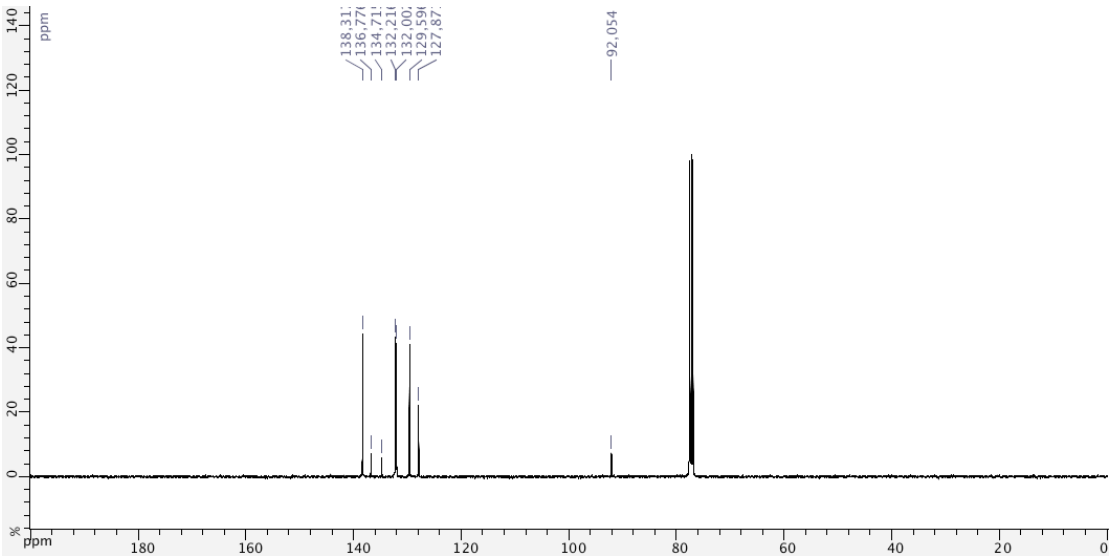


Compound **3m:**

400 MHz, $CDCl_3$

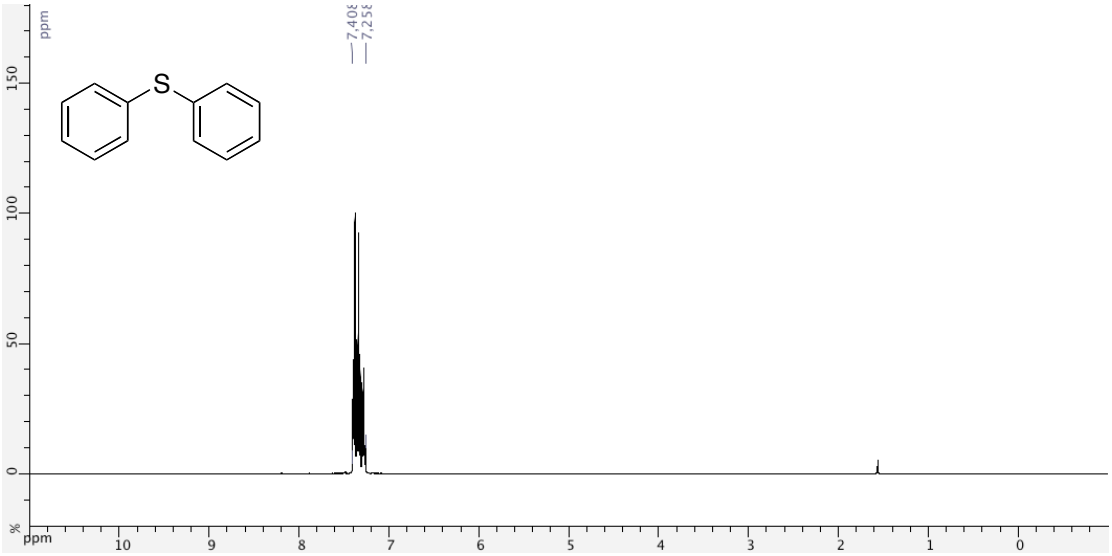


100 MHz, $CDCl_3$

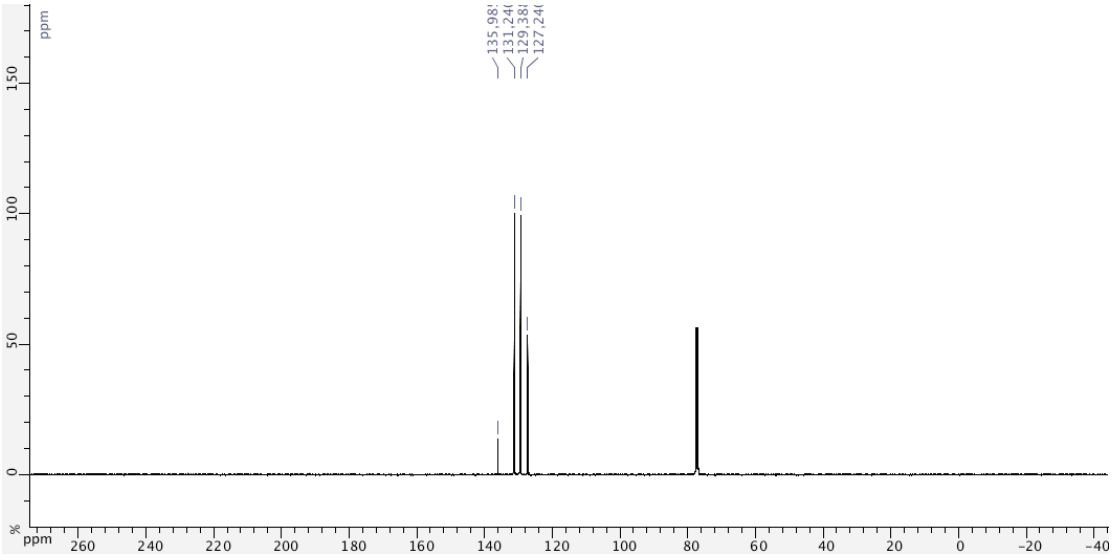


Compound **3n:**

400 MHz, $CDCl_3$

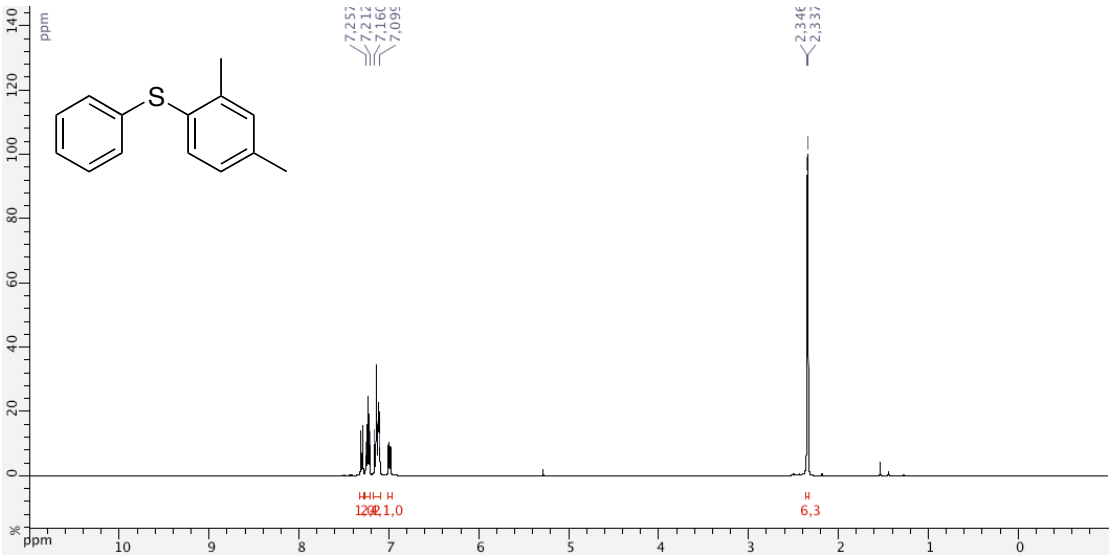


100 MHz, $CDCl_3$

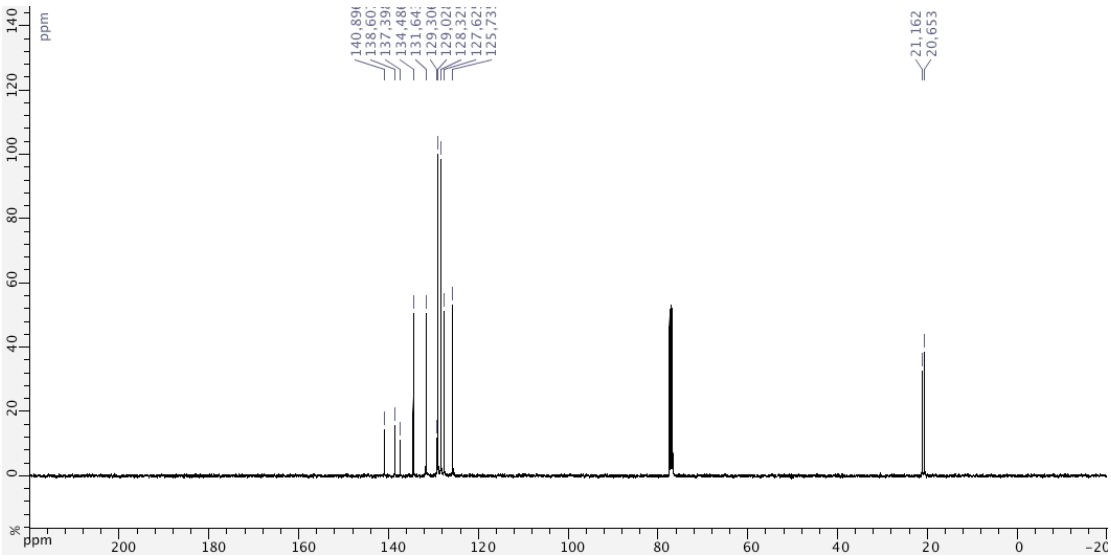


Compound **3o:**

400 MHz, $CDCl_3$

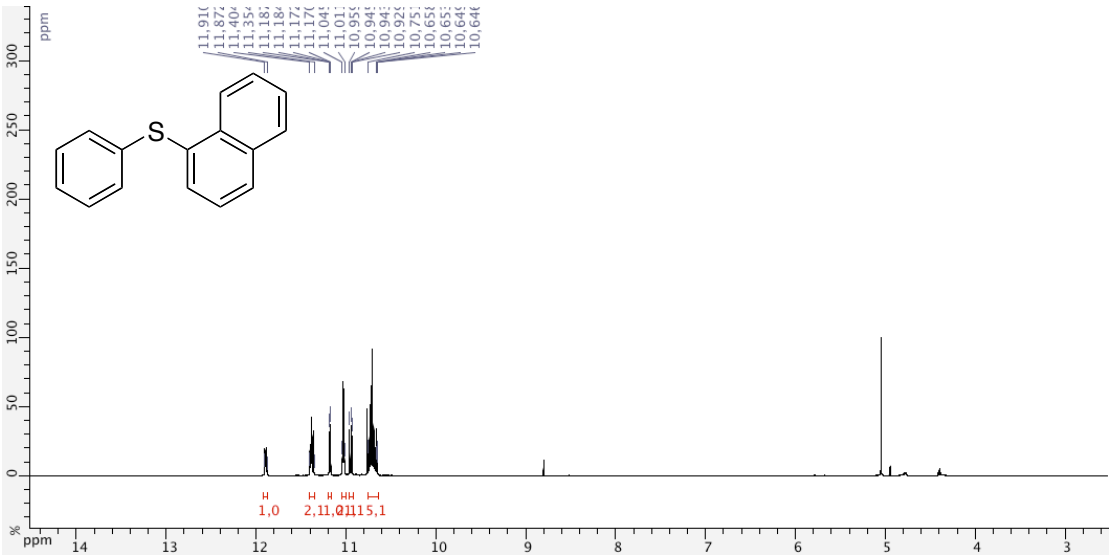


100 MHz, $CDCl_3$

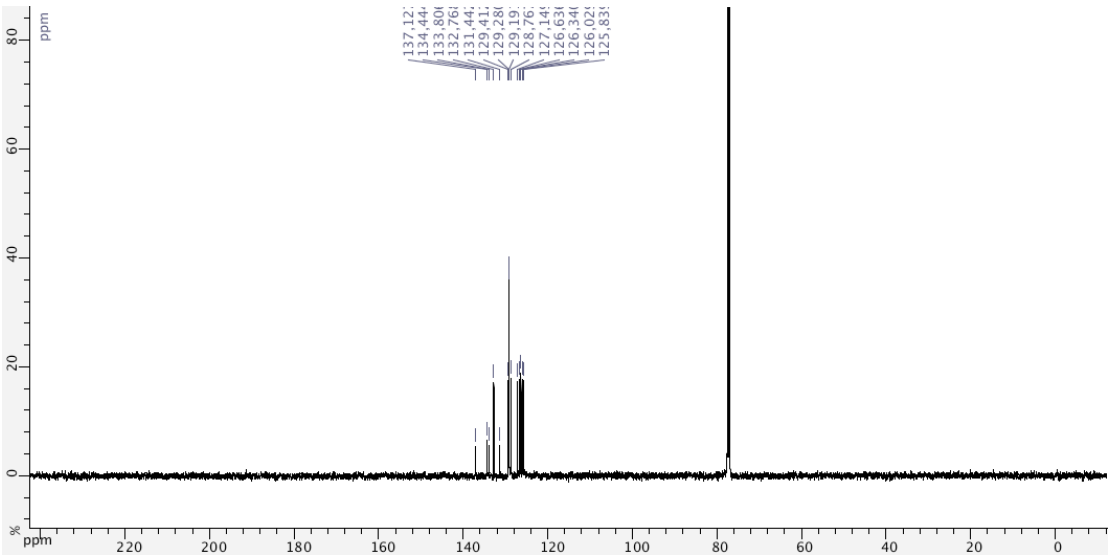


Compound **3p:**

500 MHz, $CDCl_3$

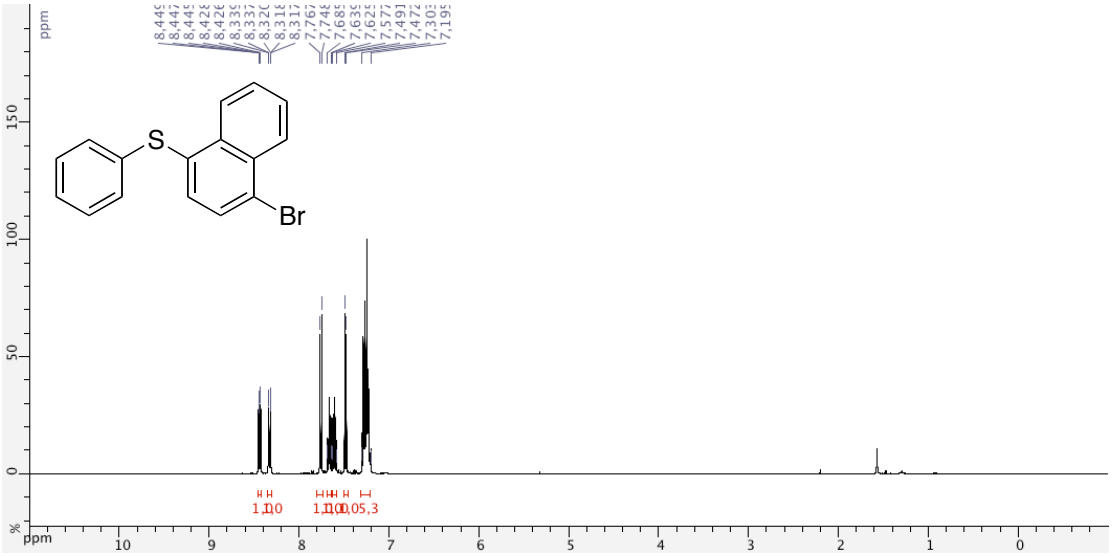


125 MHz, $CDCl_3$

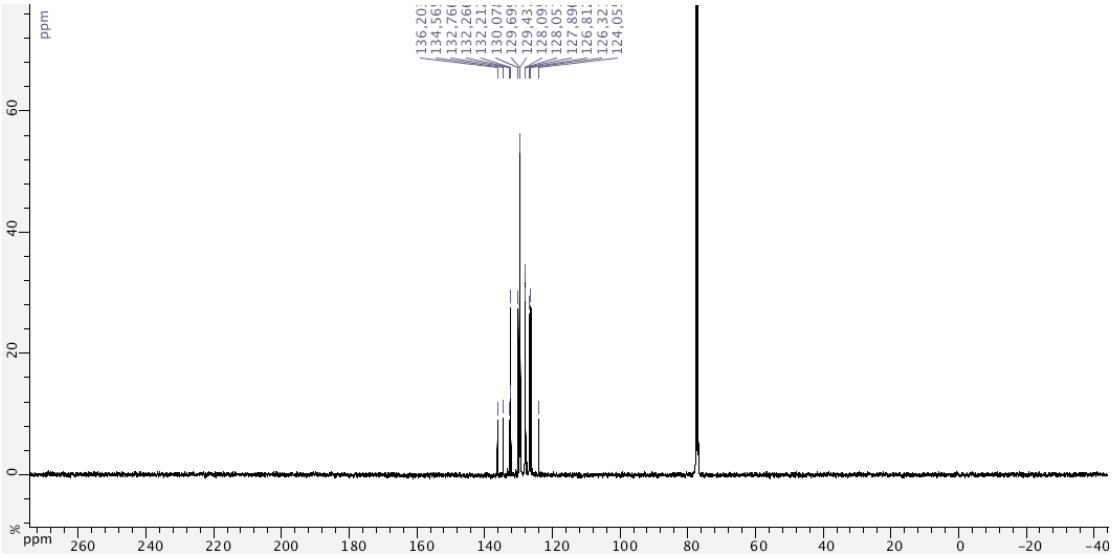


Compound **3q:**

400 MHz, $CDCl_3$

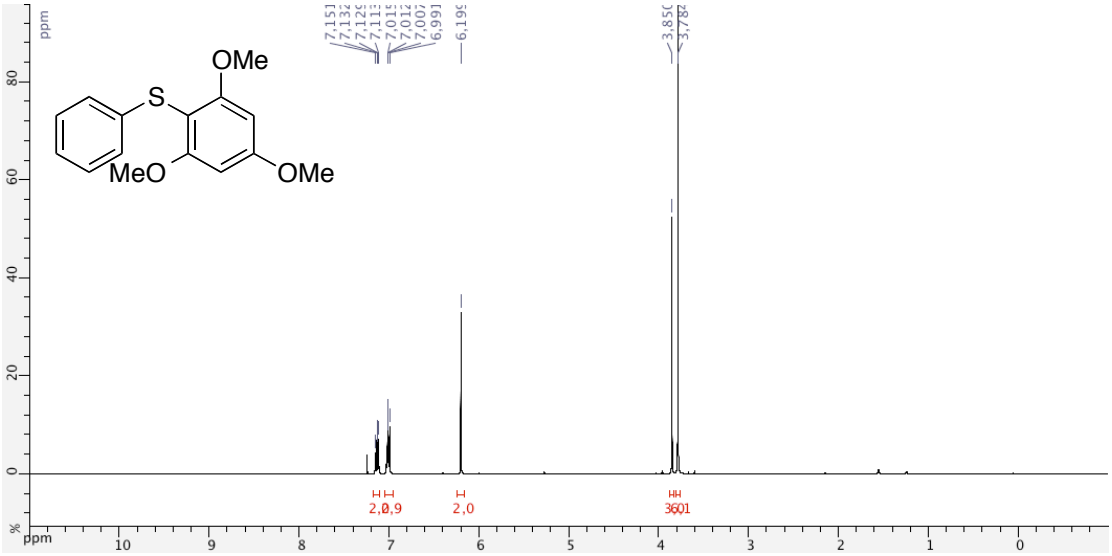


100 MHz, $CDCl_3$

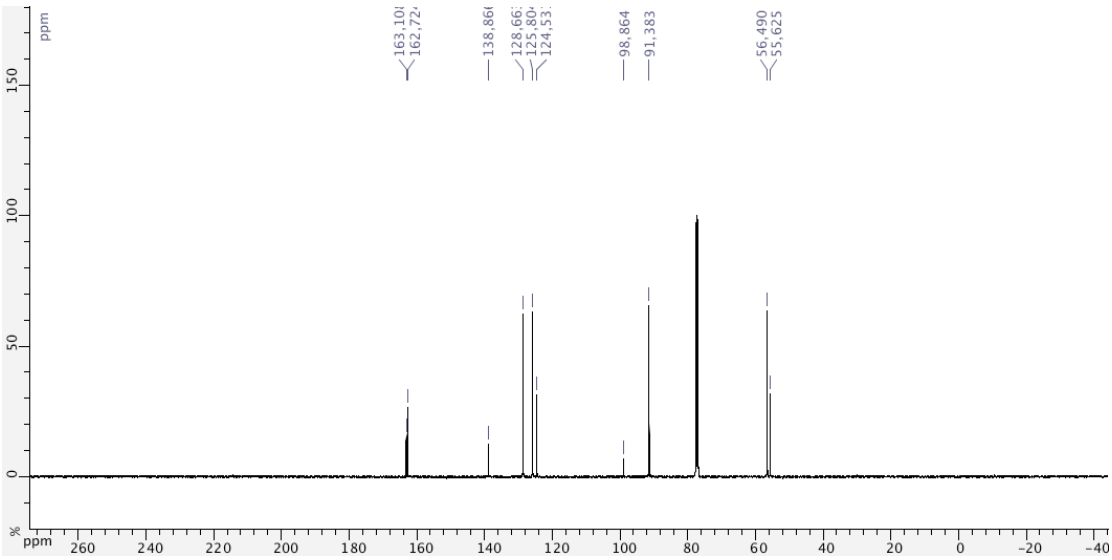


Compound **3r:**

400 MHz, $CDCl_3$

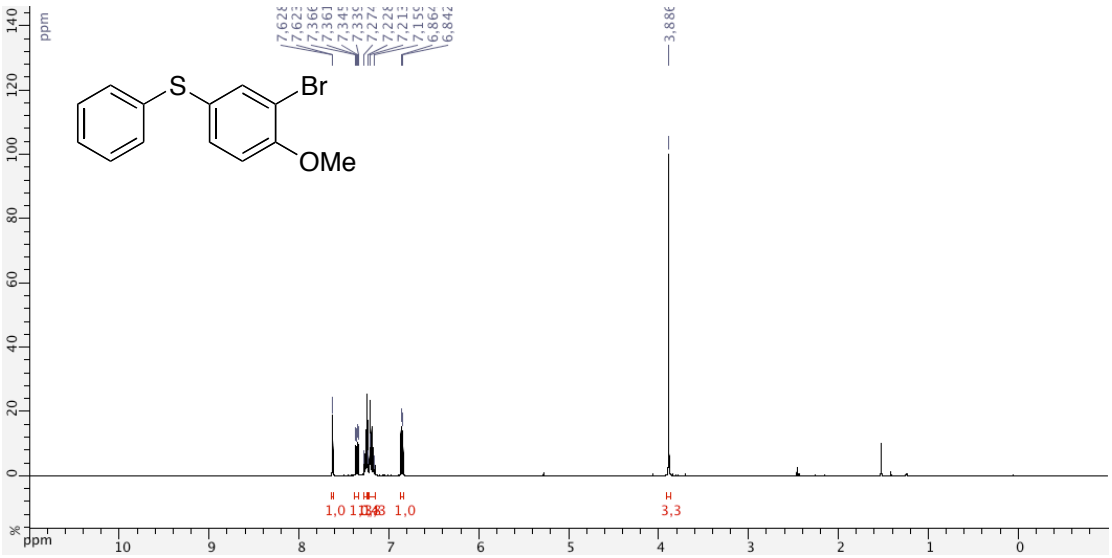


100 MHz, $CDCl_3$

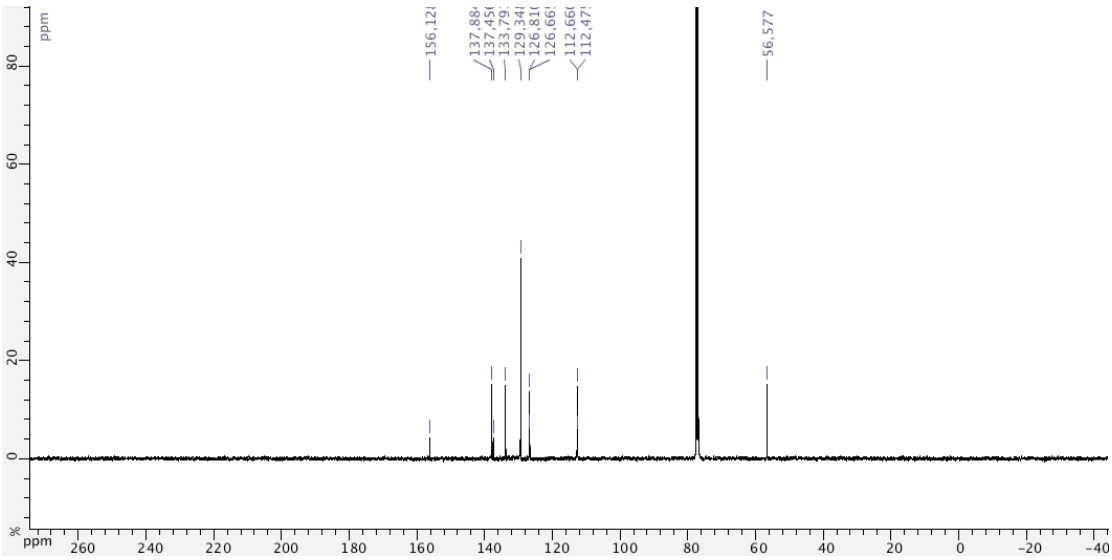


Compound **3s:**

400 MHz, $CDCl_3$

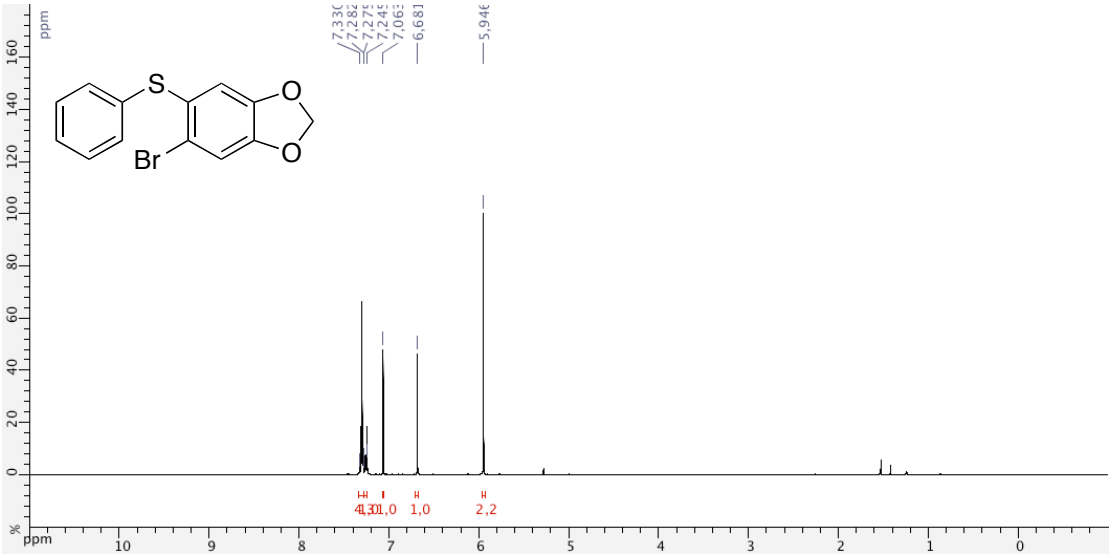


100 MHz, $CDCl_3$

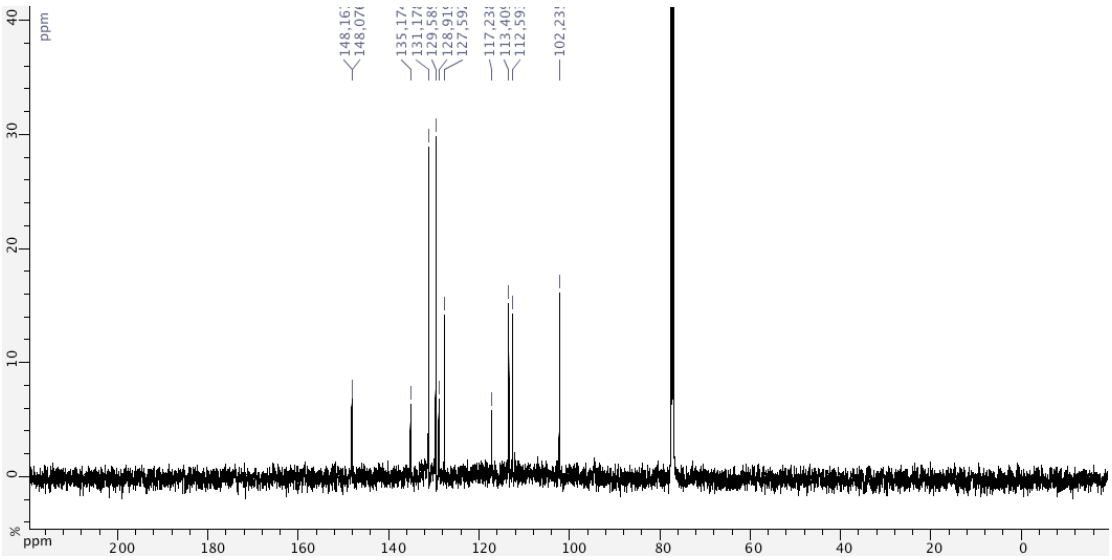


Compound **3t:**

500 MHz, $CDCl_3$

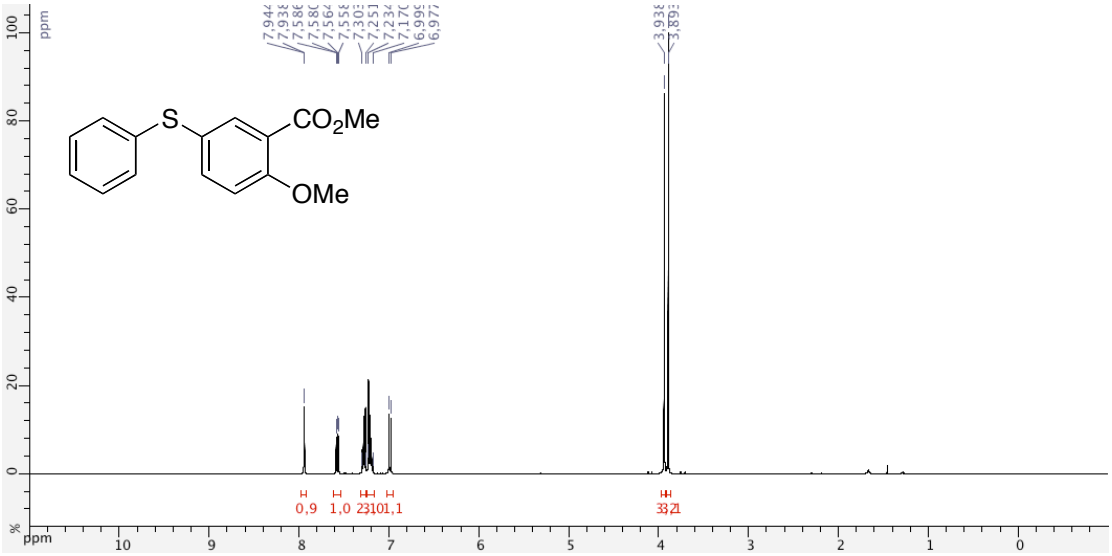


125 MHz, $CDCl_3$

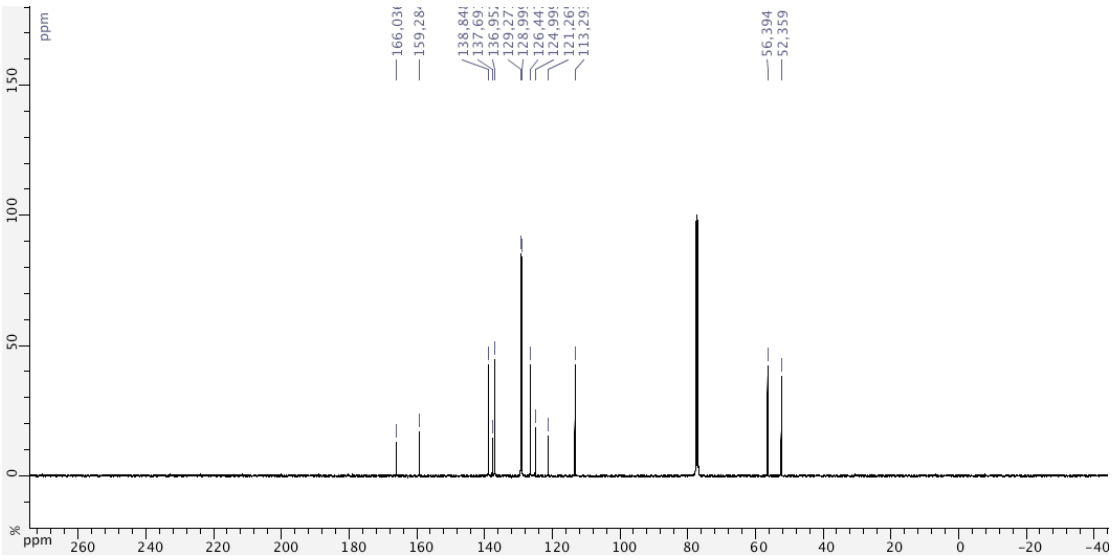


Compound **3u:**

400 MHz, $CDCl_3$

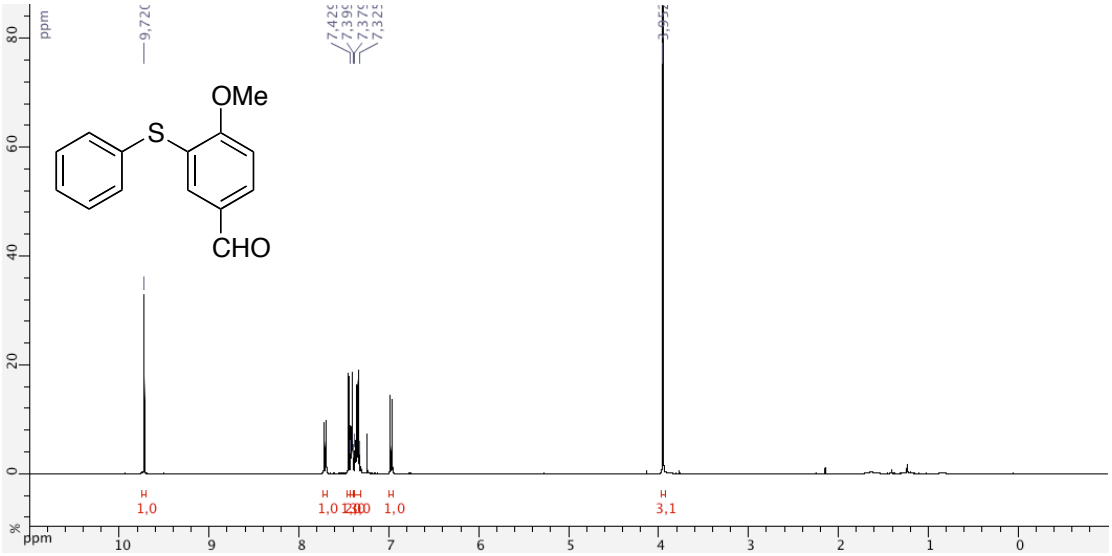


100 MHz, $CDCl_3$

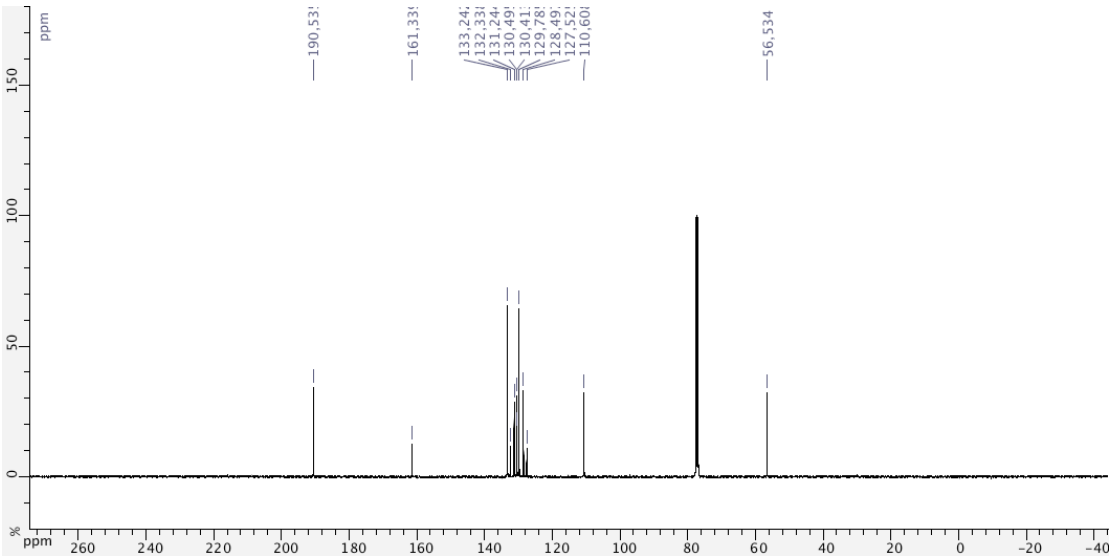


Compound **3v:**

400 MHz, $CDCl_3$

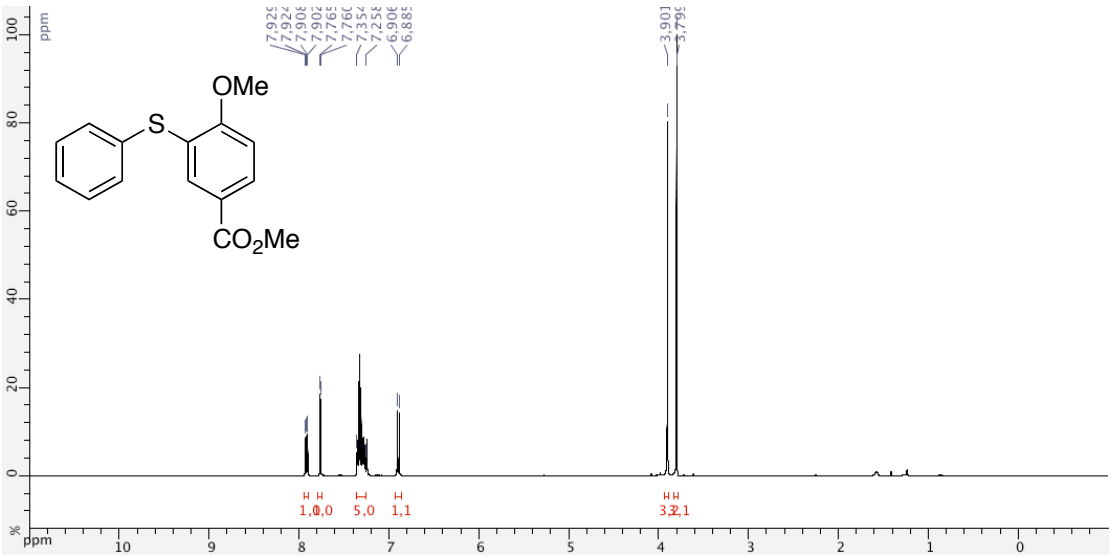


100 MHz, $CDCl_3$

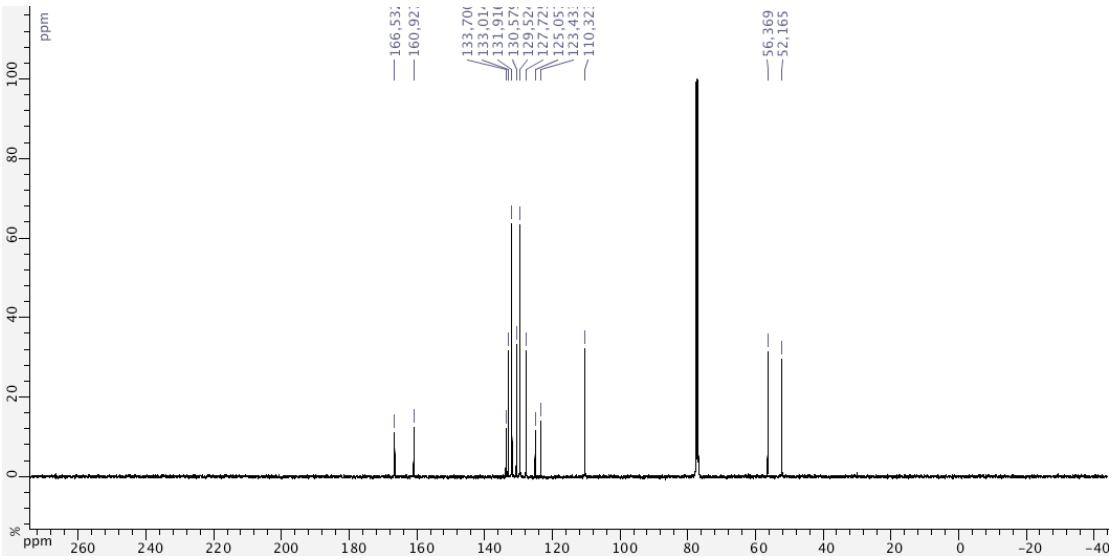


Compound **3w:**

400 MHz, $CDCl_3$

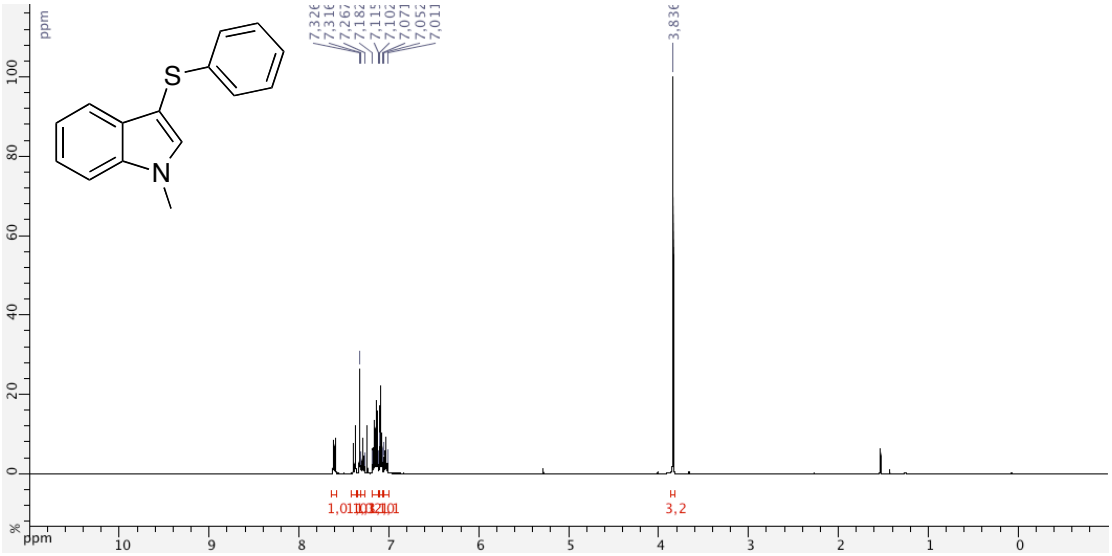


100 MHz, $CDCl_3$

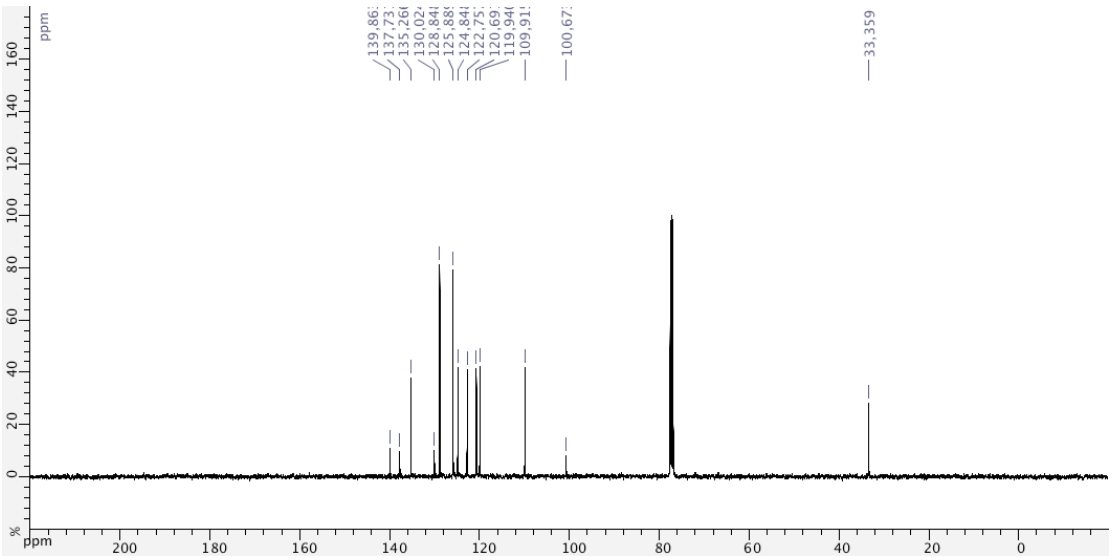


Compound **3x:**

400 MHz, $CDCl_3$

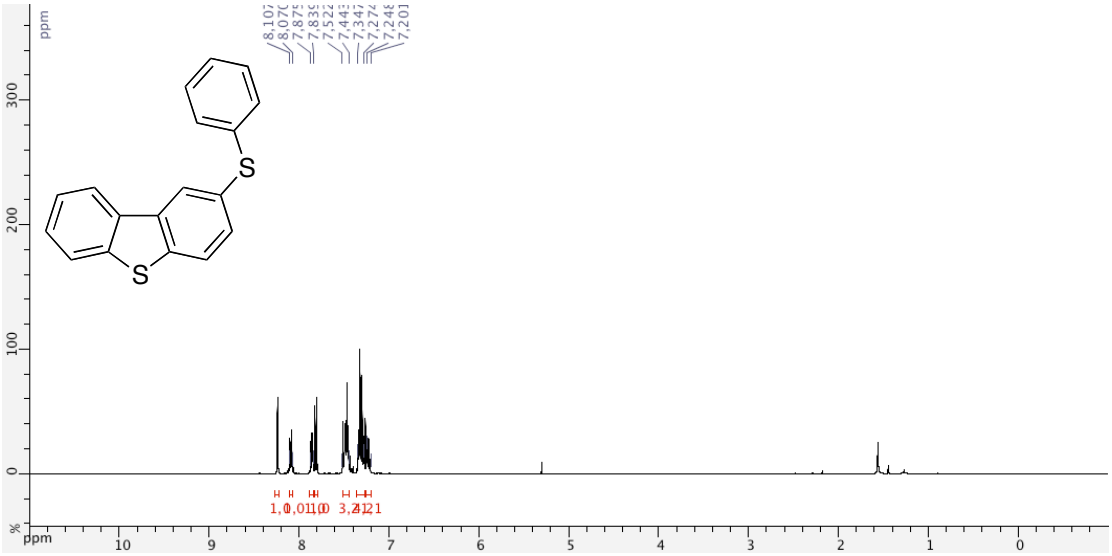


100 MHz, $CDCl_3$

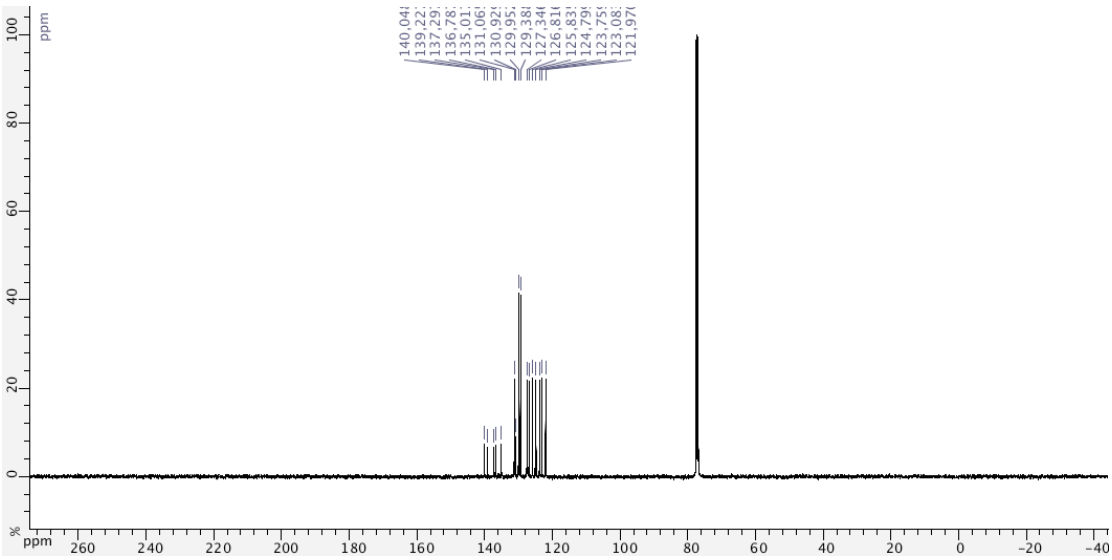


Compound **3y:**

400 MHz, $CDCl_3$

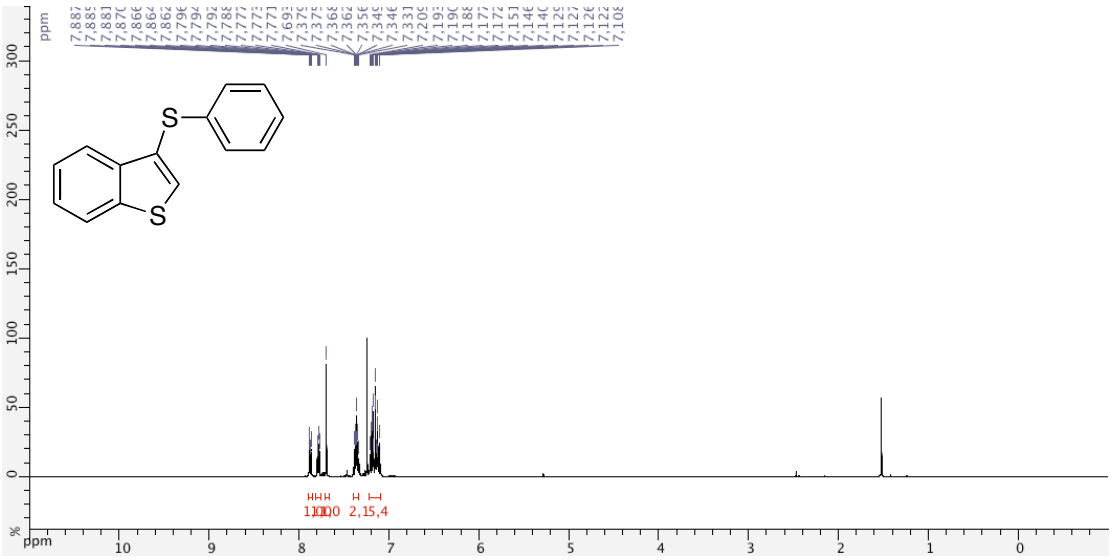


100 MHz, $CDCl_3$

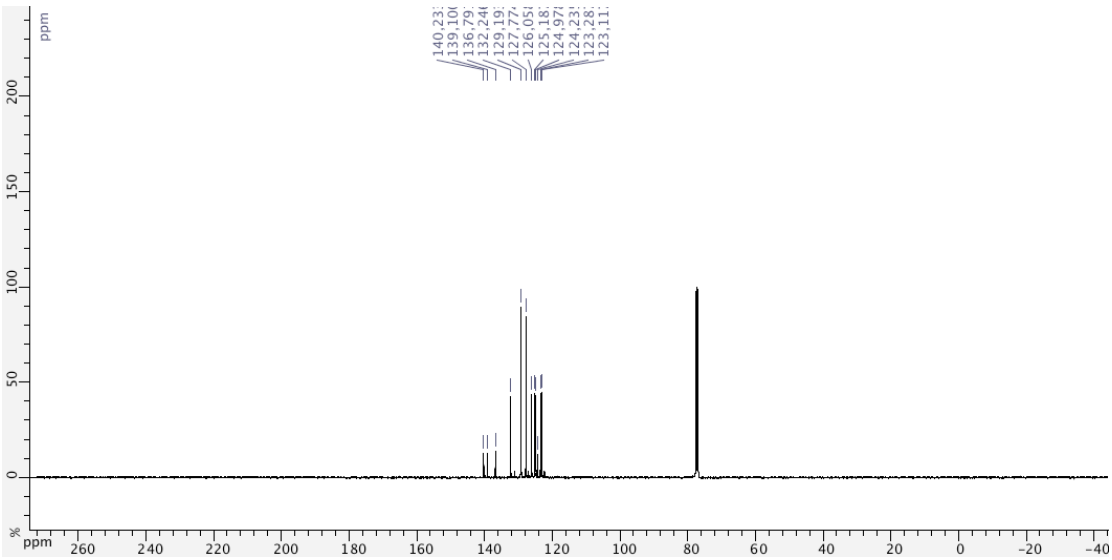


Compound **3z:**

400 MHz, $CDCl_3$

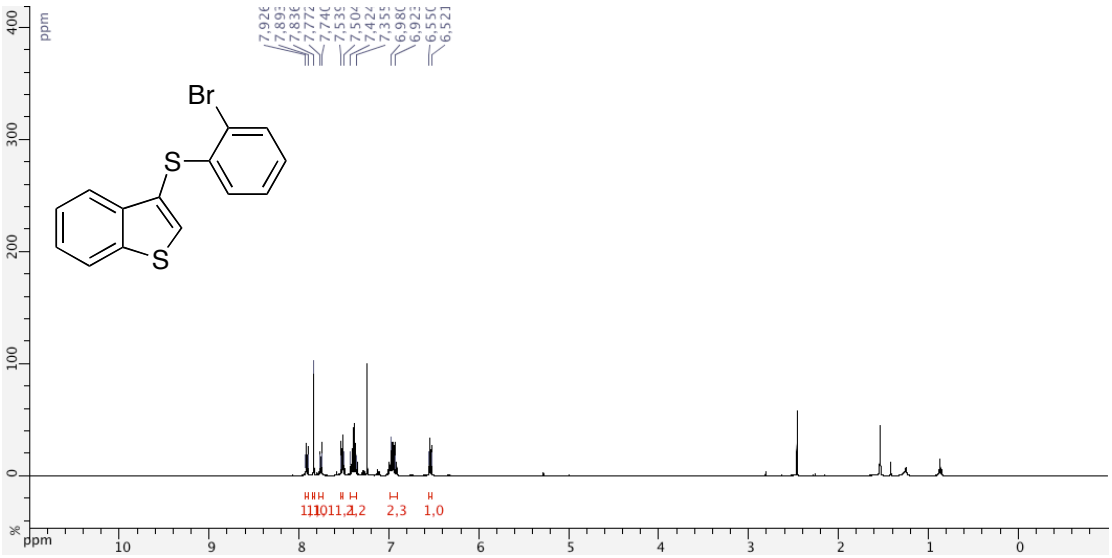


100 MHz, $CDCl_3$

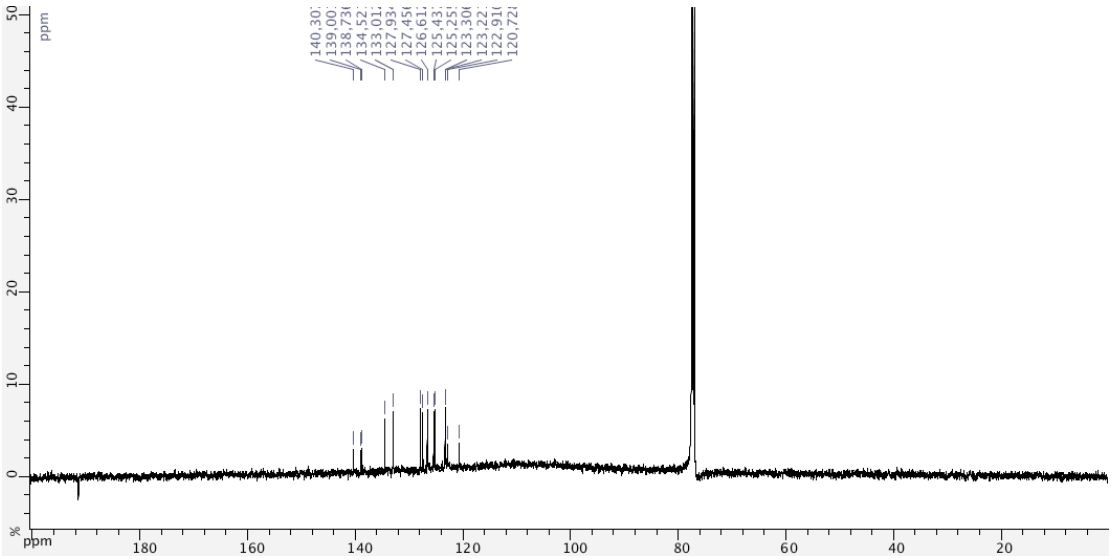


Compound **3aa:**

400 MHz, $CDCl_3$

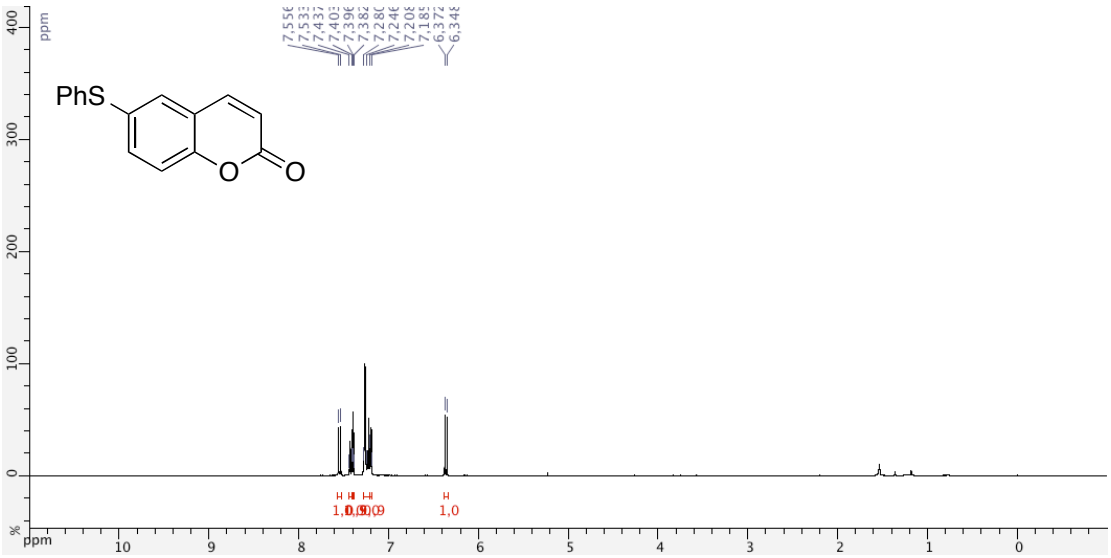


100 MHz, $CDCl_3$

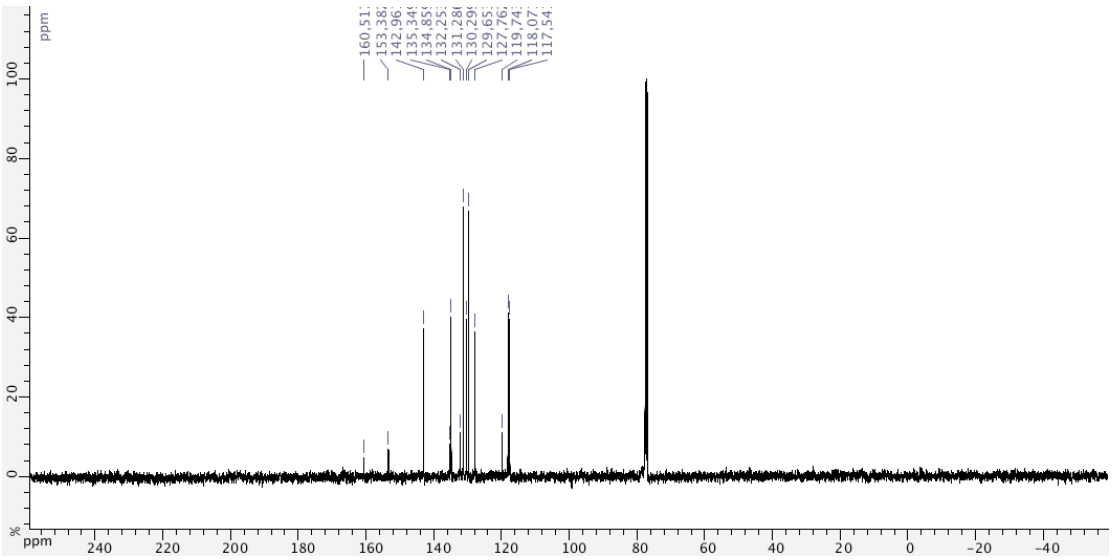


Compound **3ab:**

400 MHz, $CDCl_3$

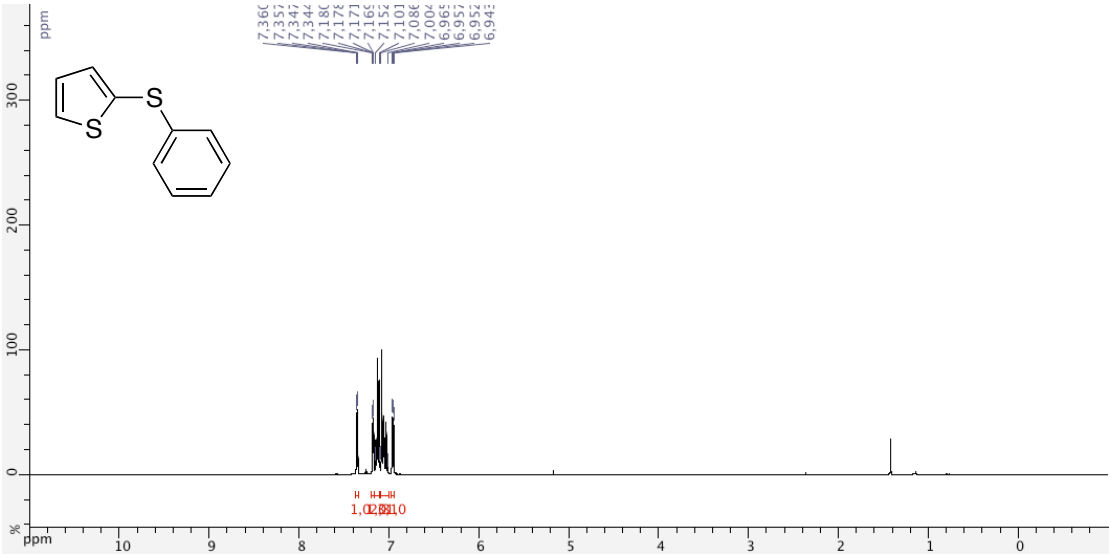


100 MHz, $CDCl_3$

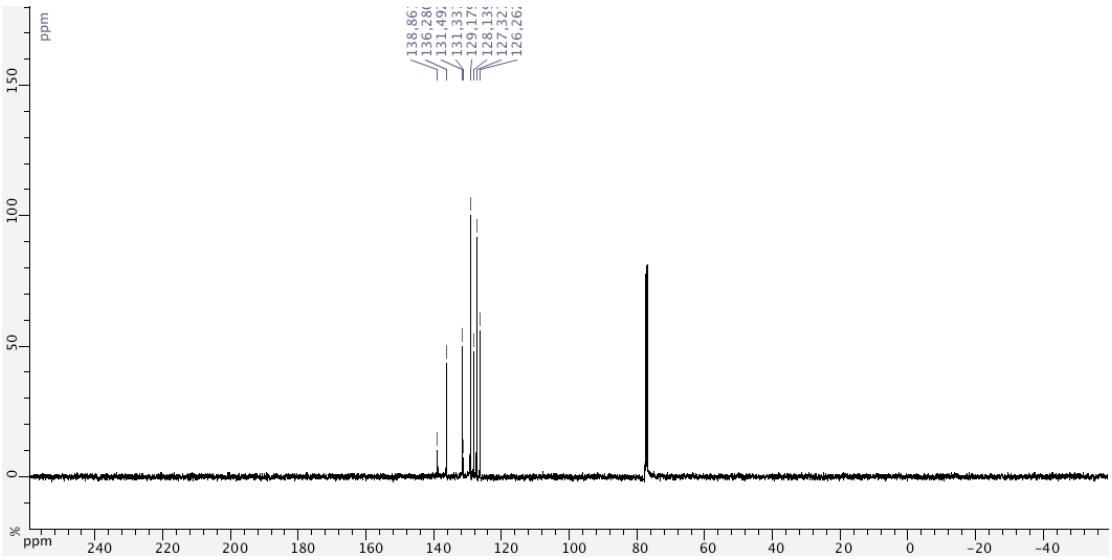


Compound **3ac:**

400 MHz, $CDCl_3$

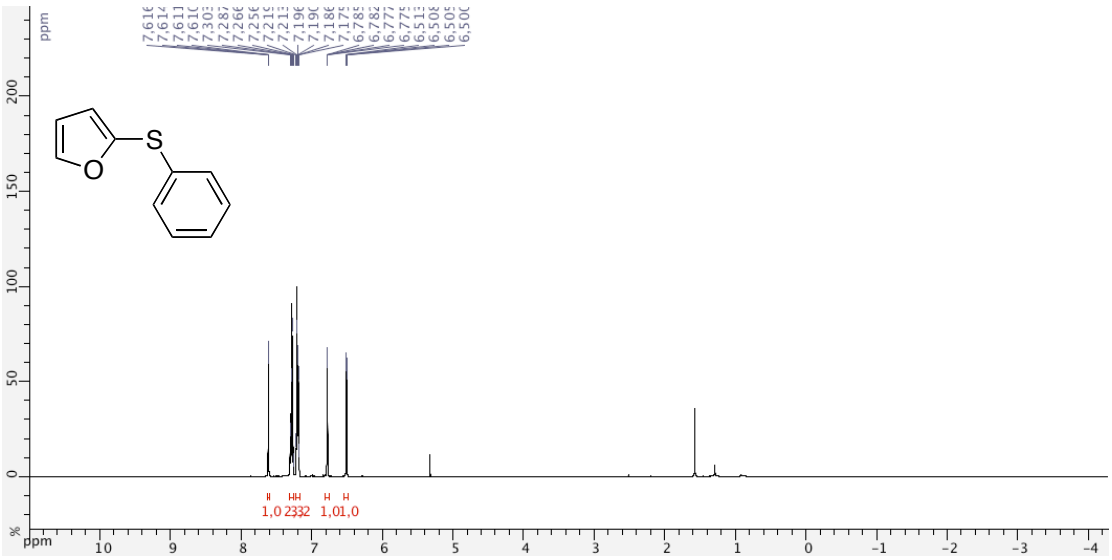


100 MHz, $CDCl_3$

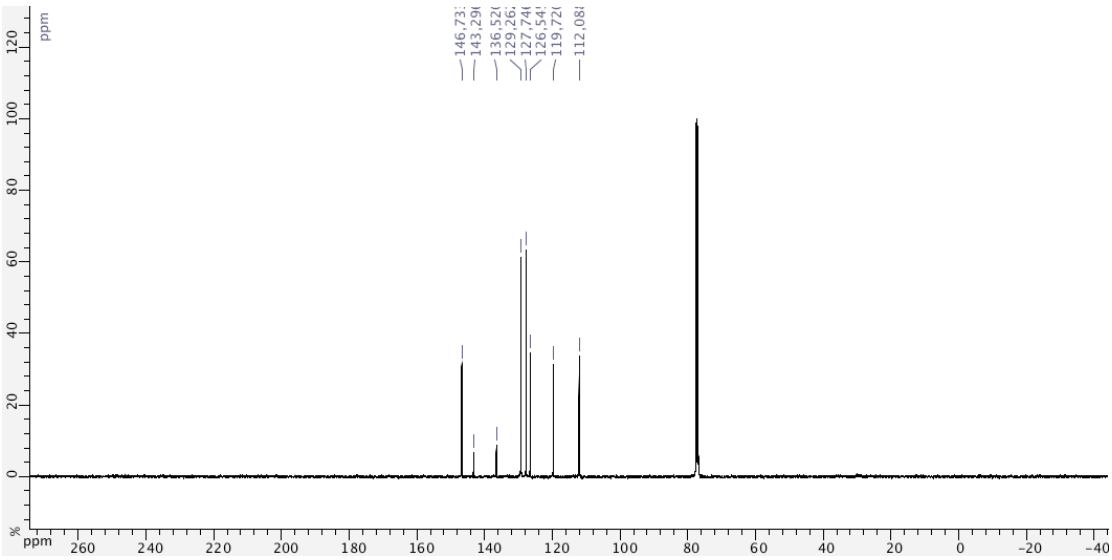


Compound **3ad:**

400 MHz, $CDCl_3$

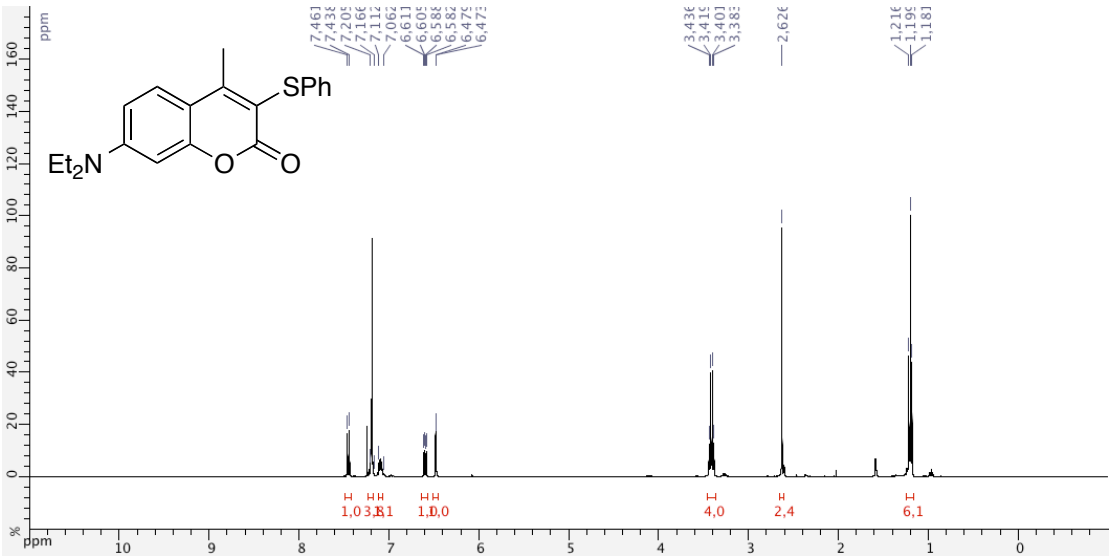


100 MHz, $CDCl_3$

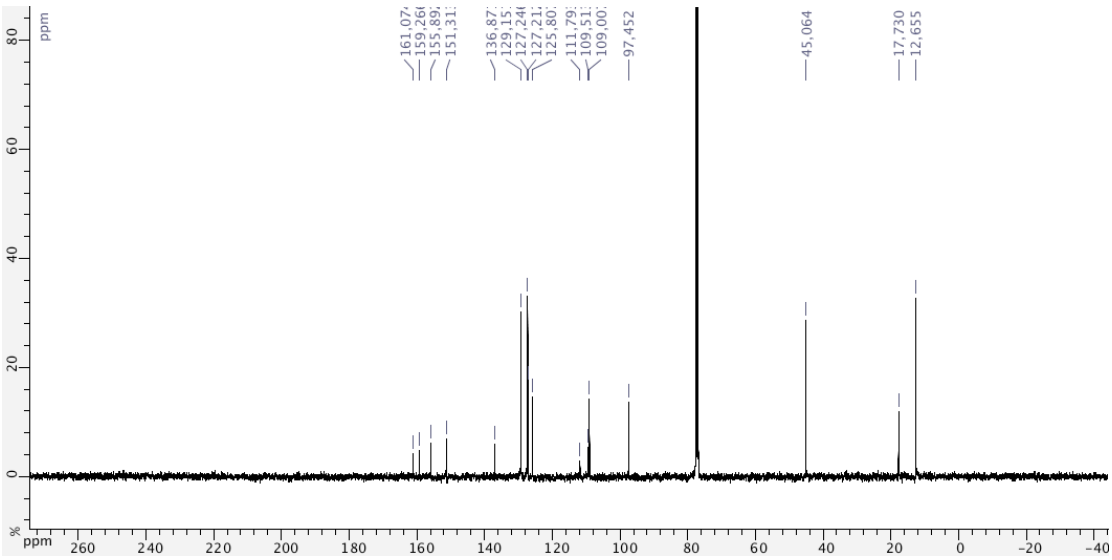


Compound **3ae:**

400 MHz, $CDCl_3$

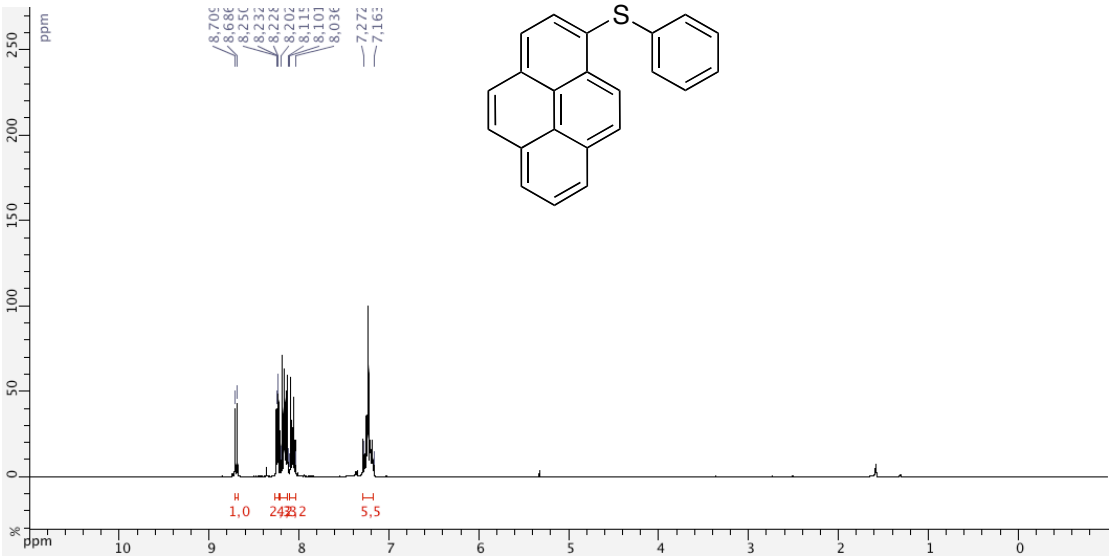


100 MHz, $CDCl_3$

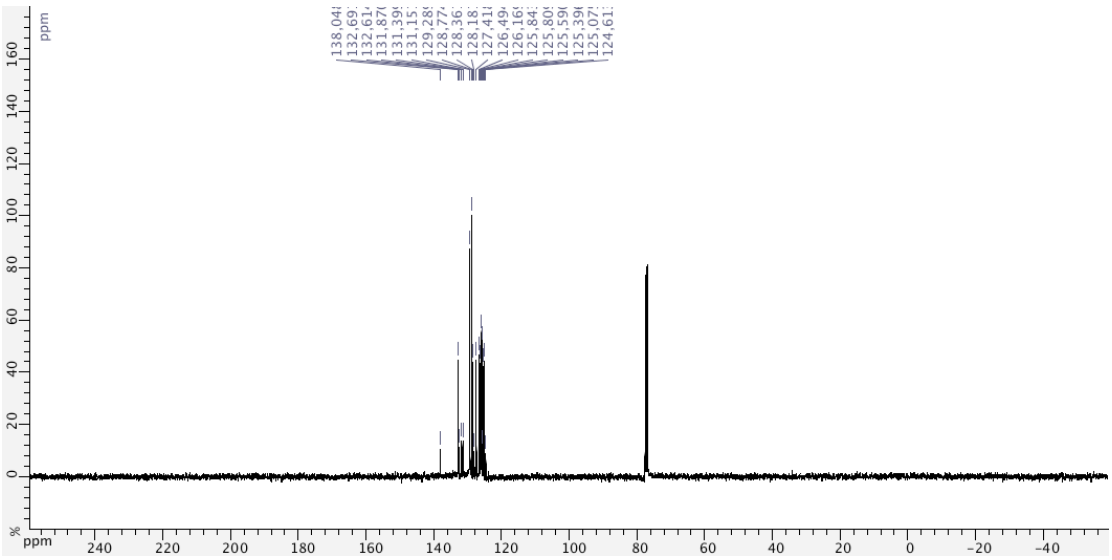


Compound **3af:**

400 MHz, $CDCl_3$

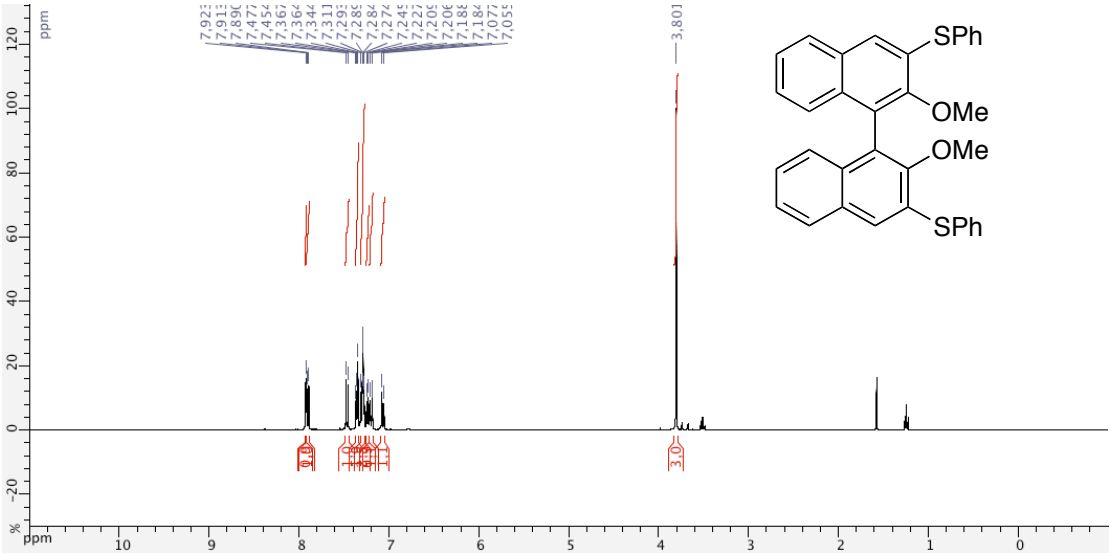


100 MHz, $CDCl_3$

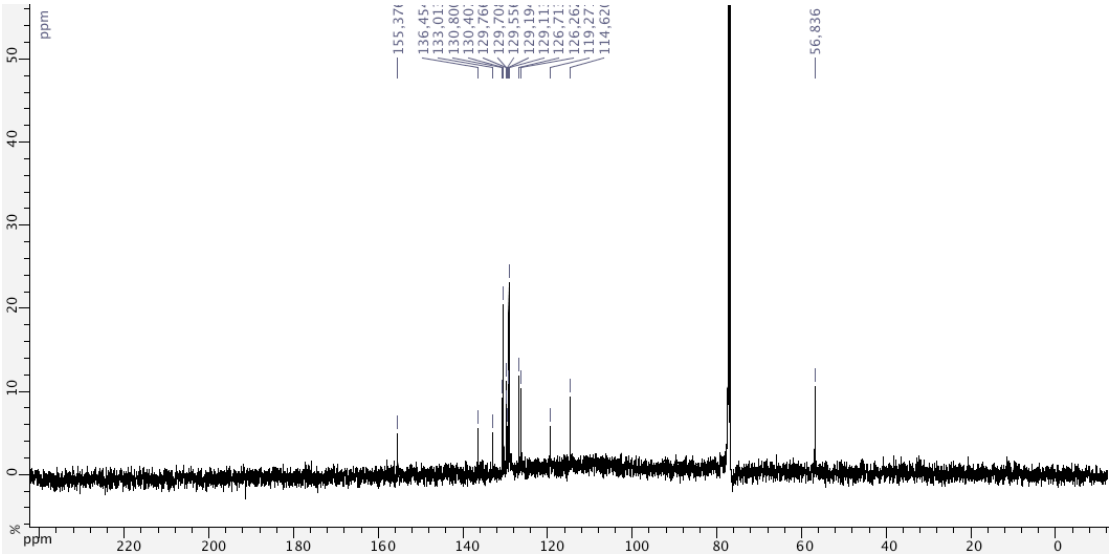


Compound **3ag:**

400 MHz, $CDCl_3$

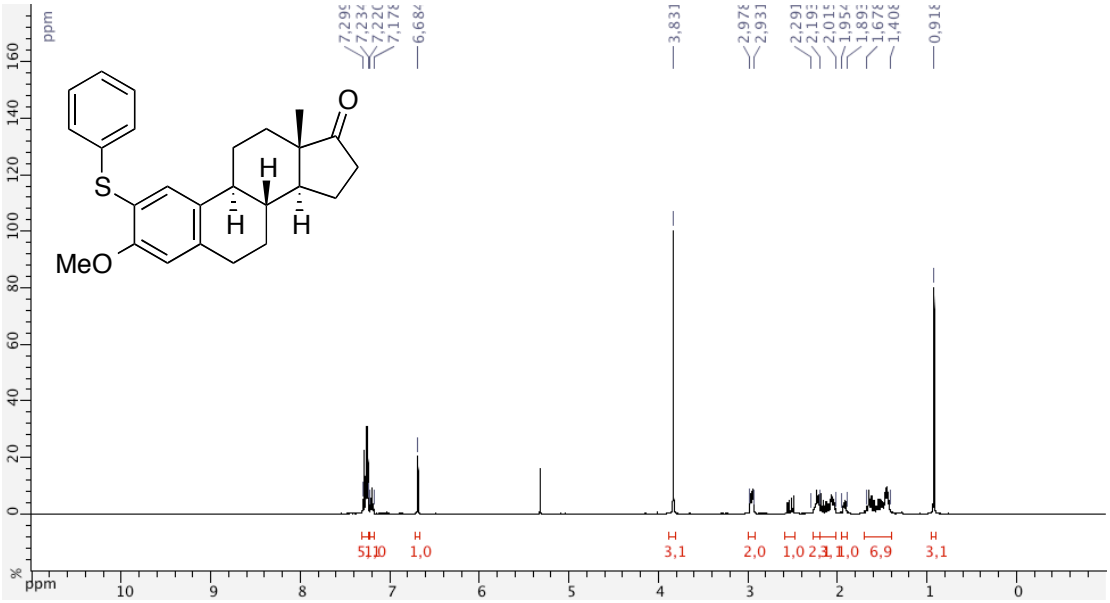


100 MHz, $CDCl_3$

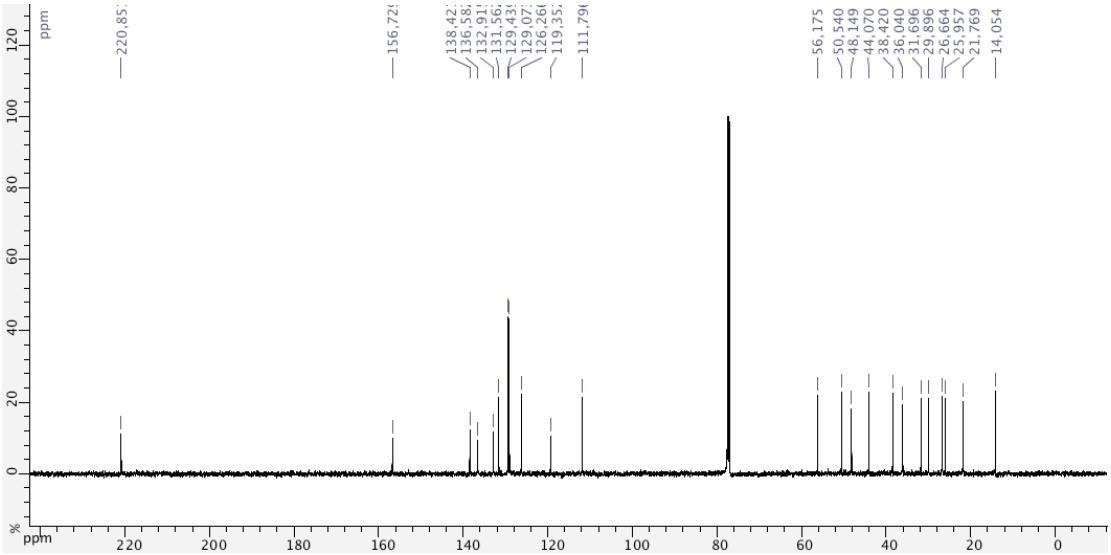


Compound **3ah:**

400 MHz, $CDCl_3$

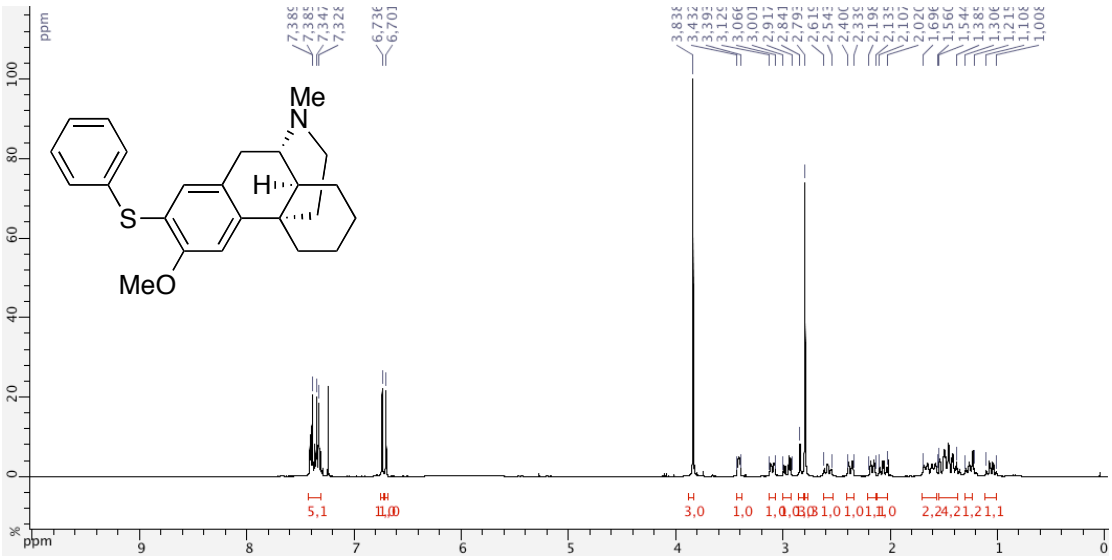


100 MHz, $CDCl_3$

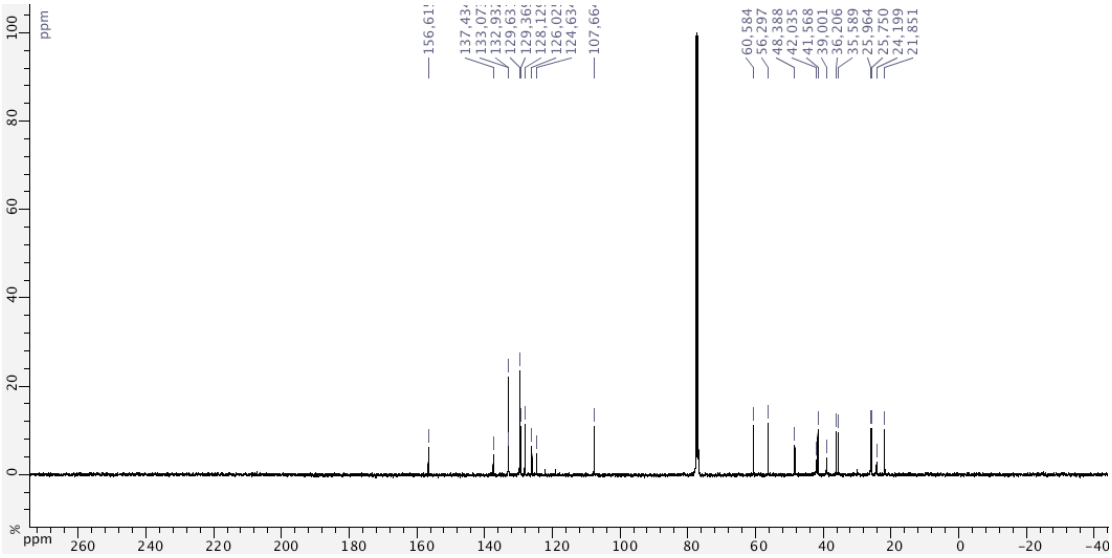


Compound **3ai:**

400 MHz, $CDCl_3$

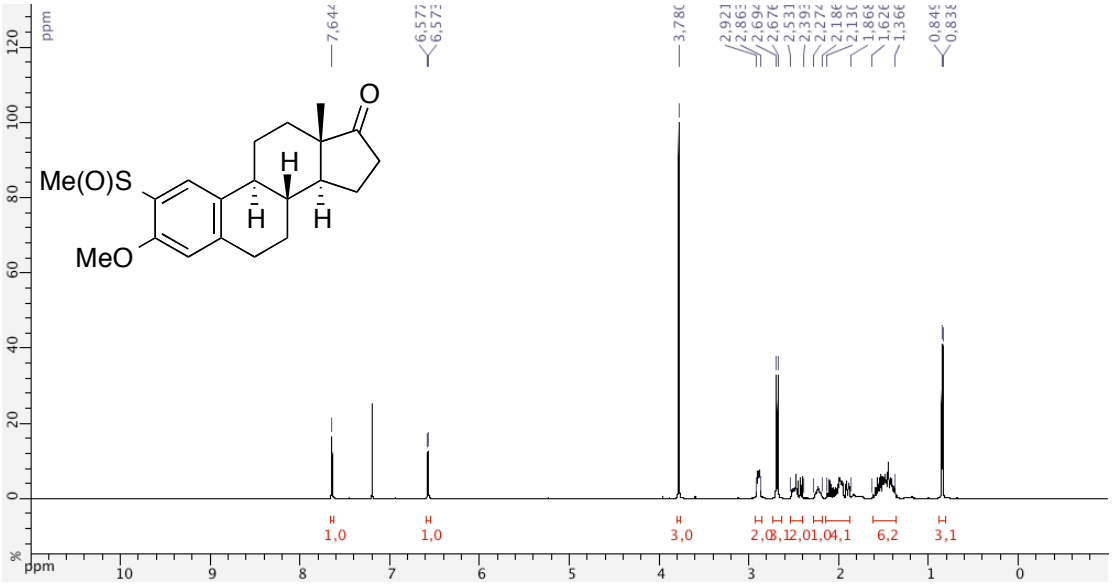


100 MHz, $CDCl_3$

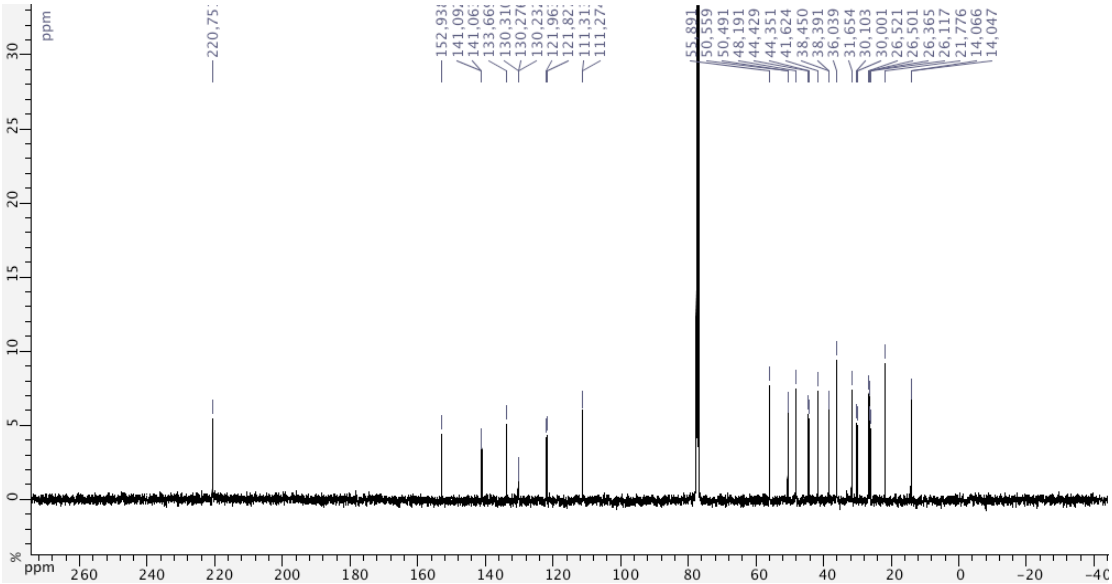


Compound **1ah:**

400 MHz, $CDCl_3$

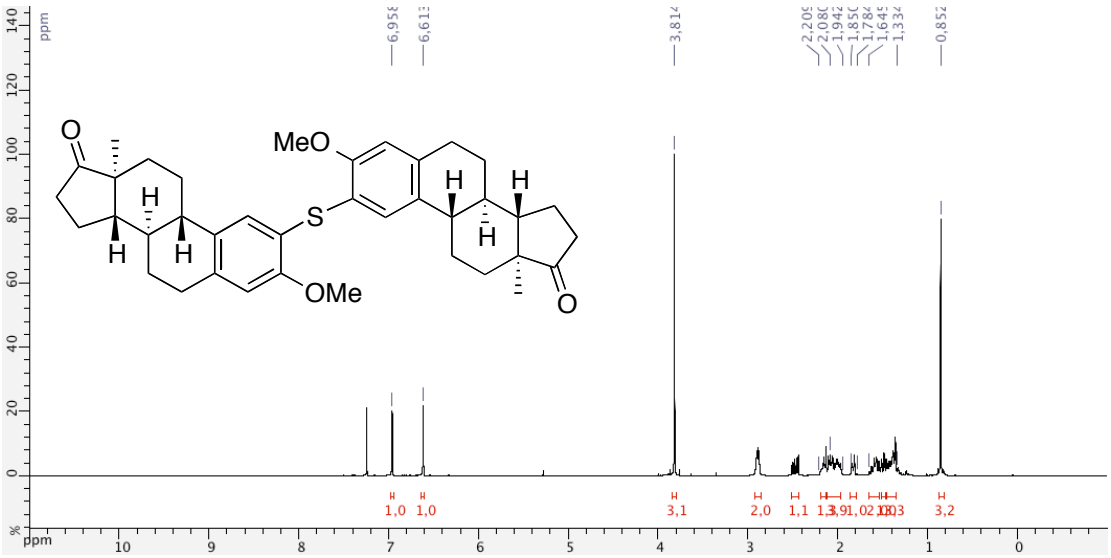


100 MHz, $CDCl_3$

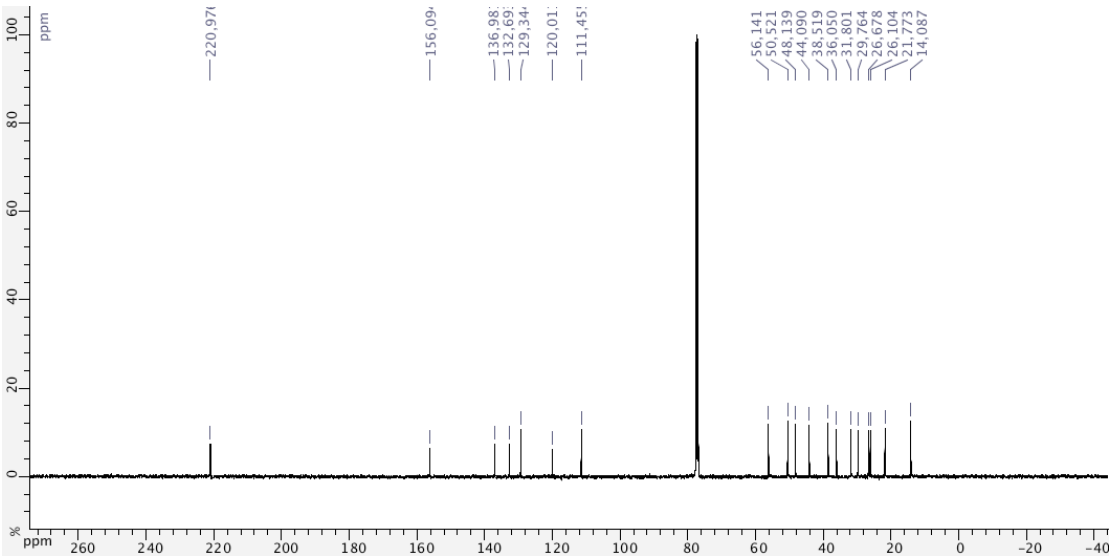


Compound **3aj:**

500 MHz, $CDCl_3$

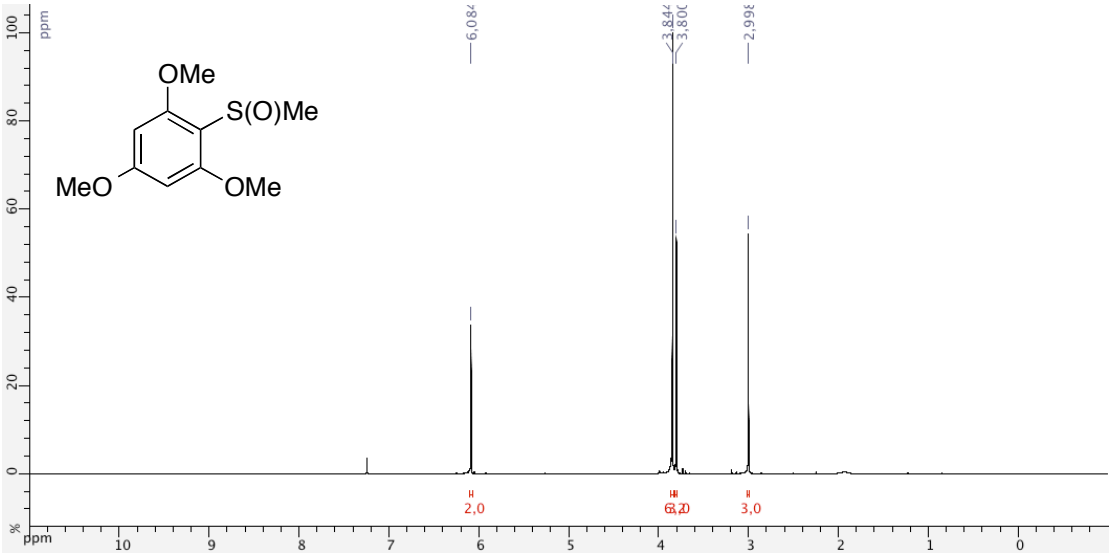


125 MHz, $CDCl_3$

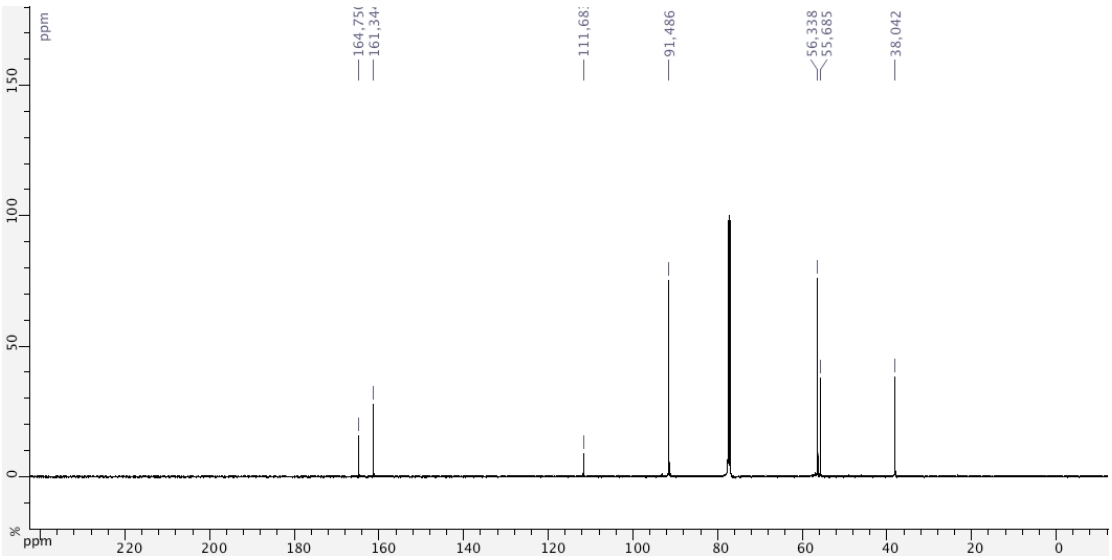


Compound **1l:**

500 MHz, $CDCl_3$

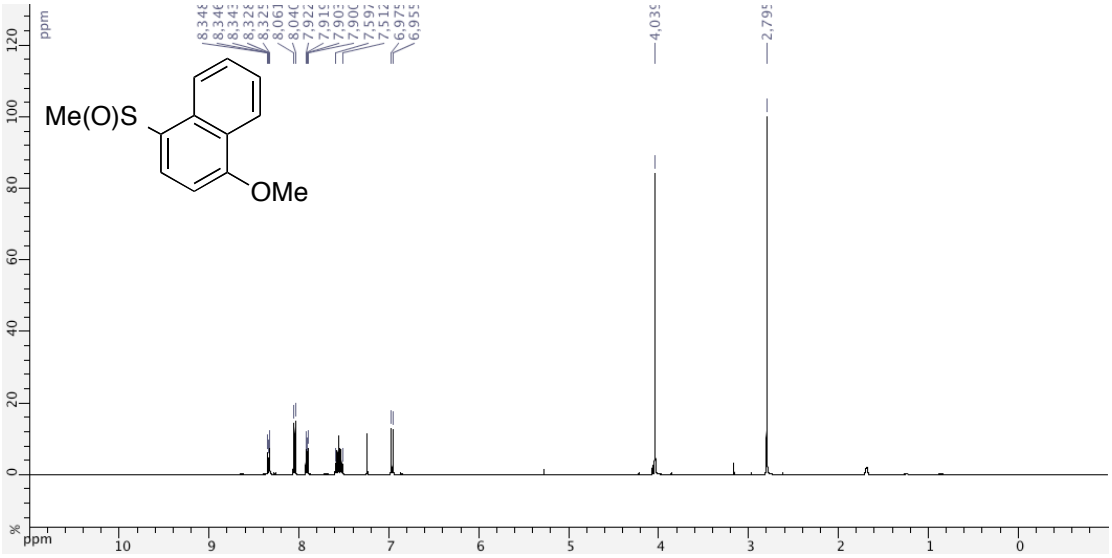


125 MHz, $CDCl_3$

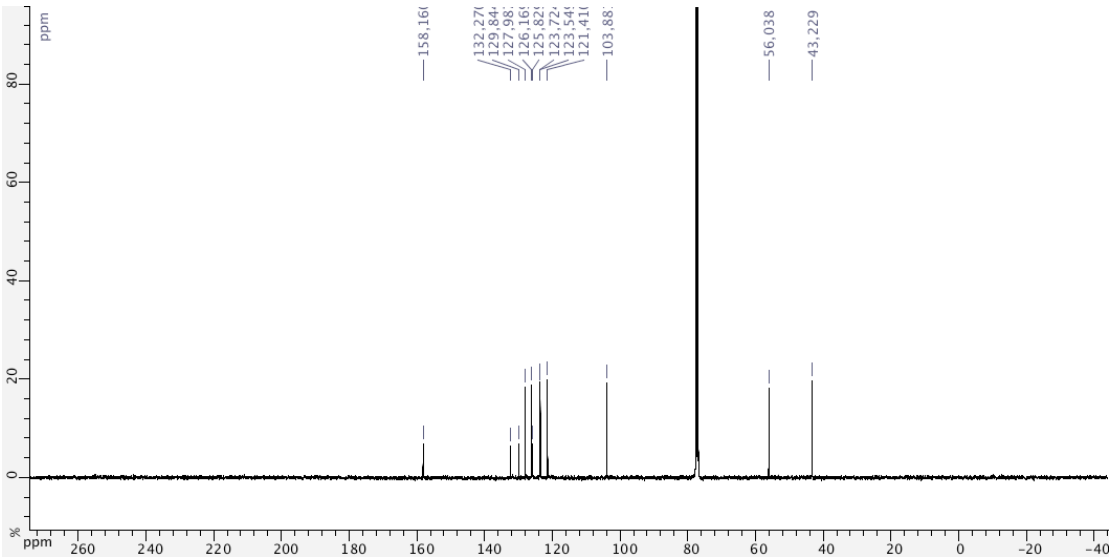


Compound **1m:**

500 MHz, $CDCl_3$

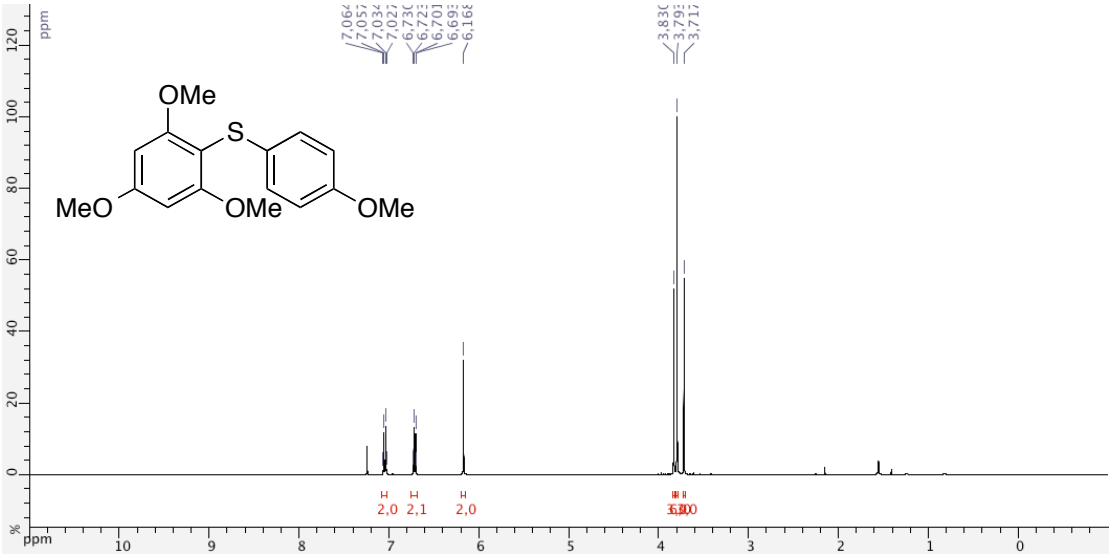


125 MHz, $CDCl_3$

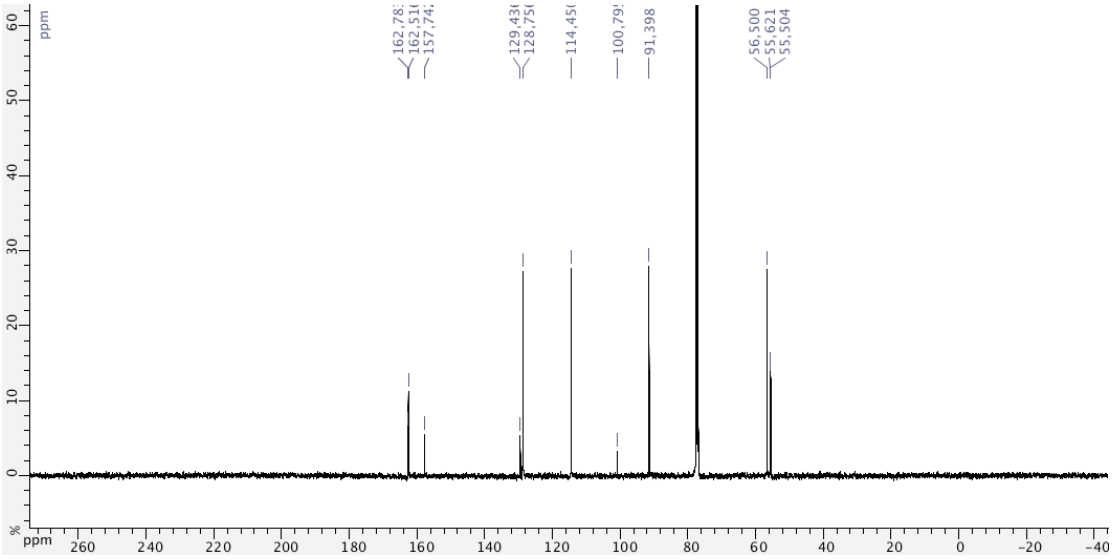


Compound **3ak:**

400 MHz, $CDCl_3$

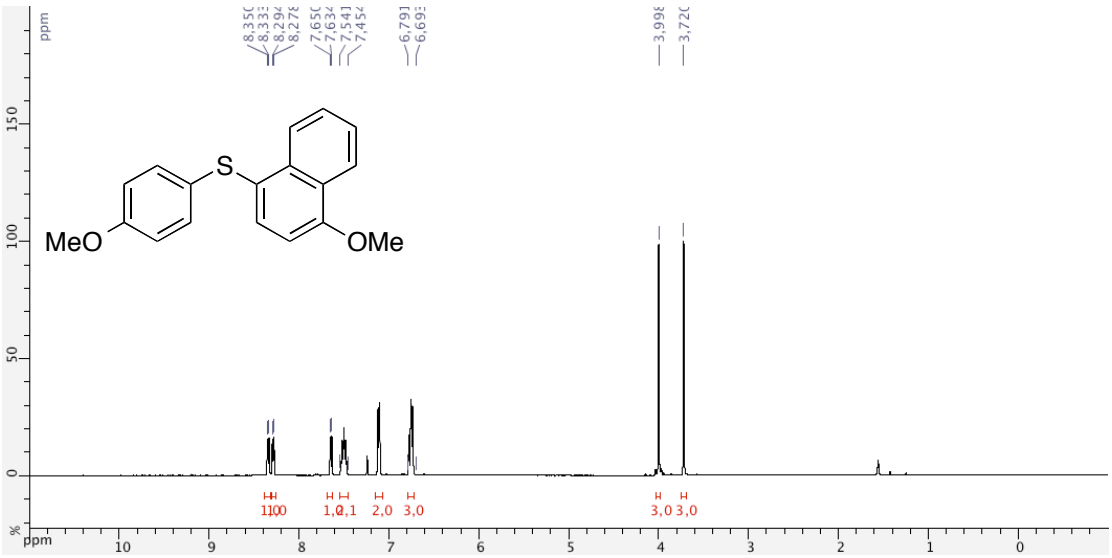


100 MHz, $CDCl_3$

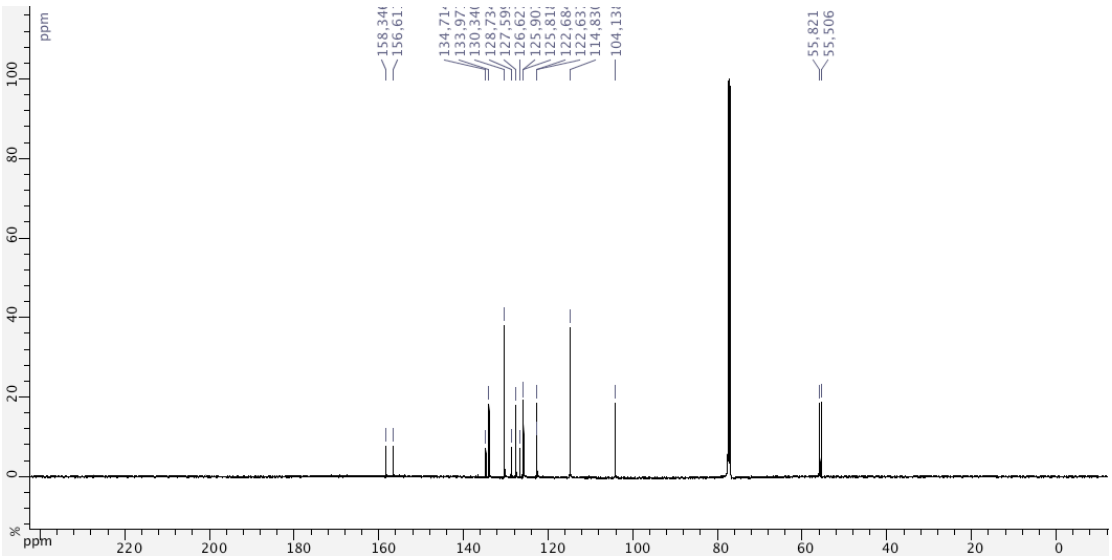


Compound **3al:**

400 MHz, $CDCl_3$

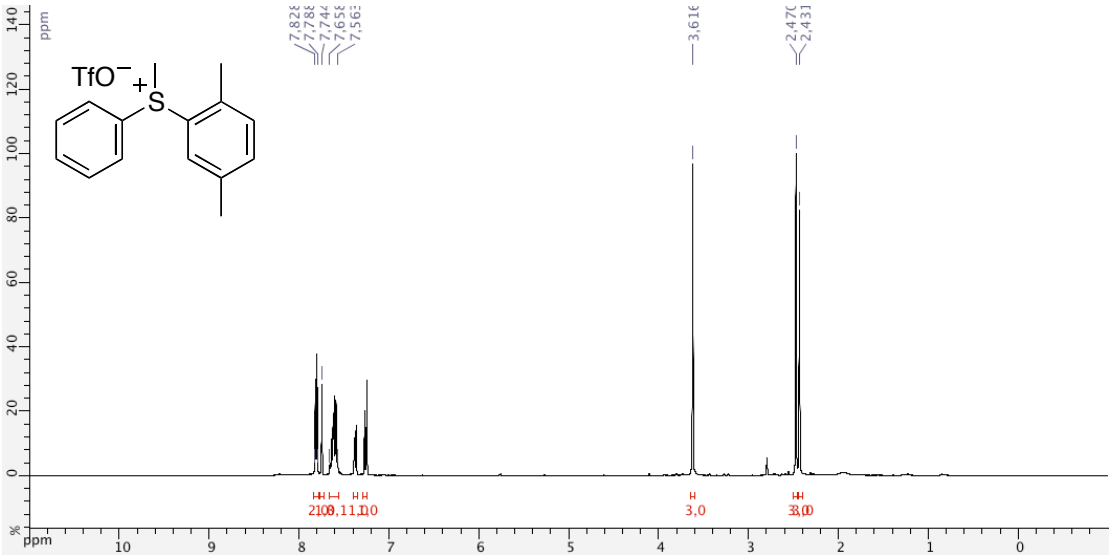


100 MHz, $CDCl_3$

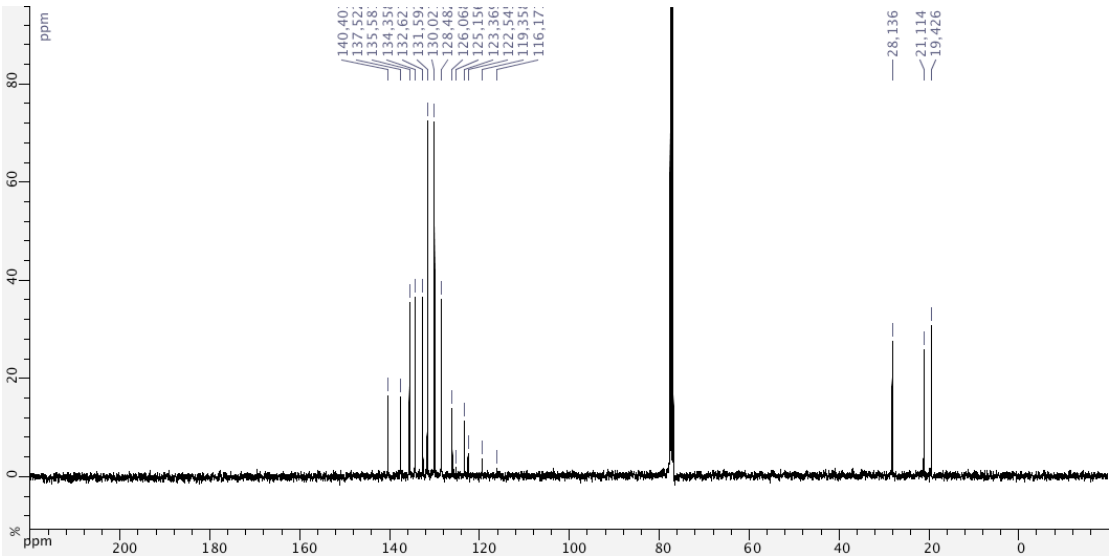


Compound **4:**

400 MHz, $CDCl_3$

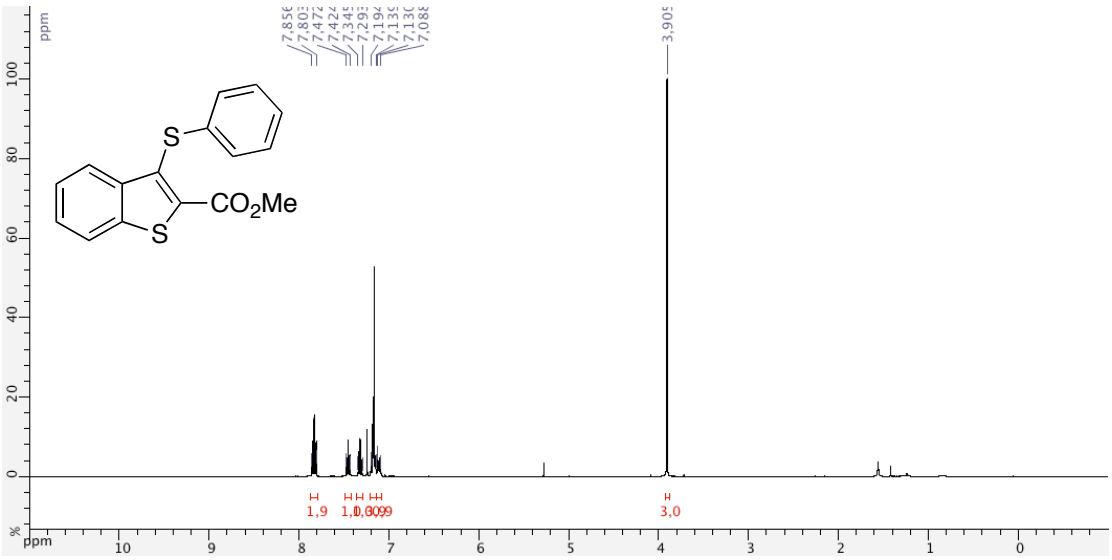


100 MHz, $CDCl_3$



Compound **5:**

400 MHz, $CDCl_3$



100 MHz, $CDCl_3$