Functionalization of activated methylene C–H bonds with nitroarenes and sulfur for synthesis of thioamides

Nhan T. Do,[‡] Khoa M. Tran,[‡] Hao T. Phan, Tuong A. To, Tung T. Nguyen,[*] Nam T. S. Phan[*]

Faculty of Chemical Engineering, HCMC University of Technology, VNU-HCM,

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

[*]Email: tungtn@hcmut.edu.vn, ptsnam@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681 Fx: (+84 8) 38637504

Supporting information

1. Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich, Acros and Merck, and were used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 160 ^{o}C for 1 min; heated them from 160 to 280 ^{o}C at 40 ^{o}C/min; held them at 280 ^{o}C for 6 min. Inlet and detector temperatures were set constant at 280 ^{o}C. The GC yield was calculated using diphenyl ether as the internal standard. GC-MS analyses were analyzed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and

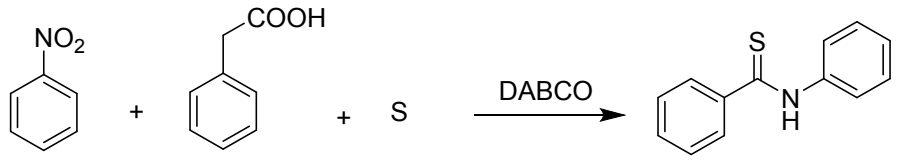
film thickness = 0.25 μm). The temperature program for GC-MS analysis held samples at 50 ^{o}C for 2 min; heated samples from 50 to 280^{o}C at 10 ^{o}C/min and held them at 280 ^{o}C for 10 min. Inlet temperature was set constant at 280 ^{o}C. MS spectra were compared with the spectra gathered in the NIST library. The ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference. HR-MS spectra were recorded by an Agilent HPLC 1200 Series coupled to Bruker micrOTOF-QII.

2. Optimization

2.1. General procedure 1a (for Table 1)

In a typical experiment, a vial equipped with a magnetic stir bar was charged with nitrobenzene (**1aa**, 61.5 mg, 0.5 mmol), phenylacetic acid (**2aa**, 102 mg, 0.75 mmol), sulfur (32 mg, 1 mmol) and DABCO (56 mg, 0.5 mmol). The vial was purged with argon for 2 min, placed on a pre-heated oil bath (120 ℃), and then stirred for 16 h. Upon the completion of the reaction, ethyl acetate (2 mL) was added to dilute the reaction mixture. The GC yield of product was monitored by withdrawing aliquots from the resulting mixture, quenching with brine (1 mL), extracting with ethyl acetate (3 x 1 mL), drying over anhydrous Na_2SO_4, and analyzing the sample by GC regarding diphenyl ether (0.5 mmol, 85 mg) as internal standard.

2.2. Results of optimization



1a **2a** **3aa**

Entry	Base	Base amount (equiv.)	**2a** amount (equiv.)	Sulfur amount (equiv.)	Temperature (^{o}C)	Yield[b] (%)
1	MeIM	1	1.5	2	120	24
2	MePy	1	1.5	2	120	trace
3	NMM	1	1.5	2	120	7
4	MPRZ	1	1.5	2	120	52
5	DABCO	1	1.5	2	120	94
6	MPPR	1	1.5	2	120	50
7	DIPEA	1	1.5	2	120	16
8	DBU	1	1.5	2	120	36
9	DMF	1	1.5	2	120	trace
10	NaOAc	1	1.5	2	120	trace
11	K_2CO_3	1	1.5	2	120	12
12	DABCO	0	1.5	2	120	trace
13	DABCO	0.25	1.5	2	120	10
14	DABCO	0.5	1.5	2	120	59

15	DABCO	0.75	1.5	2	120	89
16	DABCO	1	1.5	2	120	94
17	DABCO	1.5	1.5	2	120	95
18	DABCO	2	1.5	2	120	86
19	DABCO	1	0.5	2	120	69
20	DABCO	1	0.8	2	120	77
21	DABCO	1	1	2	120	79
22	DABCO	1	1.5	2	120	94
23	DABCO	1	2	2	120	90
24	DABCO	1	1.5	0	120	0
25	DABCO	1	1.5	1	120	60
26	DABCO	1	1.5	1.5	120	89
27	DABCO	1	1.5	2	120	94
28	DABCO	1	1.5	2.5	120	87
29	DABCO	1	1.5	2	80	23
30	DABCO	1	1.5	2	100	70
31	DABCO	1	1.5	2	120	94
32	DABCO	1	1.5	2	140	41

[a] Reaction conditions: nitrobenezene (0.5 mmol); solvent-free; under argon; 16 h. [b]GC yield. MeIM: 1-methylimidazole; MePy: 3-methylpyridine; NMM: *N*-methylmorpholine; MPRZ: *N*-methylpiperazine; DABCO: 1,4-diazabicyclo[2.2.2]octane; MPPR: *N*-methylpiperidine; DIPEA: *N*,*N'*-diisopropylethylamine; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; DMF: *N*,*N'*-dimethylformamide.

3. Synthesis of *N*-arylthioamides

3.1. General procedure 1b (for Schemes 2, 3 and 4)

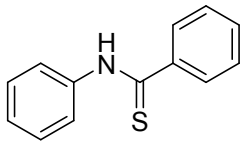
To isolate the thioamide products, the reactions were set up similarly to the above conditions. For a typical substrate, the crude reaction mixture was diluted with EtOAc (15 mL). The organic phase was washed with brine (3 x 5 mL) before dried over anhydrous Na_2SO_4, filtered, and concentrated using rotary evaporator. The resulting residue was purified by silica gel column chromatography using appropriate ratio of EtOAc/hexanes mixture.

3.2. General procedure 2 (for Table 2)

In a typical experiment, a vial equipped with a magnetic stir bar was charged with benzyl alcohols (0.5 mmol), nitrobenzene (123 mg, 1 mmol), sulfur (48 mg, 1.5 mmol) and DABCO (112 mg, 1 mmol). The vial was purged with argon for 5 min, placed on a pre-heated oil bath (120 °C), and then stirred for 16 h. Working up followed the general procedure for Table 1.

3.2. Characterization of products

***N*-phenylbenzothioamide (3aa, Scheme 2 and entry 1-Table 2)**



Nitrobenzene (0.5 mmol, 62 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 92 mg (86%) of a yellow solid was obtained. This compound is known.[1]

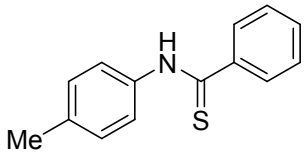
^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.75 (s, 1H), 7.83 (d, J = 7.7 Hz, 4H), 7.53 (t, J = 7.2 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.28 (t, J = 7.3 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 197.6, 142.8, 140.0, 130.7, 128.5, 128.0, 127.4, 126.2, 124.2.

At 1.5 mmol scale: Nitrobenzene (1.5 mmol, 185 mg), phenylacetic acid (2.25 mmol, 306 mg), sulfur (3 mmol, 69 mg), DABCO (1.5 mmol, 168 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 5:1), 230 mg (72%) of the thioamide was obtained. The purity of the product was confirmed by GC-MS.

For entry 1, Table 2: benzyl alcohol (0.5 mmol, 54 mg) was used. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 64 mg (60%) of the desired product was obtained.

_N_-(_p_-tolyl)benzothioamide (3ab, Scheme 2)



4-Nitrotoluene (0.5 mmol, 69 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 96 mg (84%) of a yellow solid was obtained. This compound is known.[1]

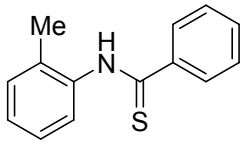
[1] Guntreddi T.; Vanjari R.; Singh K. N., *Org. Lett.* **2014,** *16*, 3624.

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.62 (s, 1H), 7.75 (d, J = 6.1 Hz, 2H), 7.63 (d, J = 6.7 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.17 (d, J = 6.6 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 197.2, 142.7, 137.6, 135.6, 130.7, 128.9, 128.0, 127.4, 124.1, 20.7.

At 1.5 mmol scale: 4-Nitrotoluene (1.5 mmol, 206 mg), phenylacetic acid (2.25 mmol, 306 mg), sulfur (3 mmol, 69 mg), DABCO (1.5 mmol, 168 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 232 mg (68%) of the thioamide was obtained. The purity of the product was confirmed by GC-MS.

_N_-(_o_-tolyl)benzothioamide (3ac, Scheme 2)



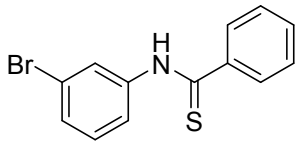
2-Nitrotoluene (0.5 mmol, 69 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 89 mg (78%) of a yellow solid was obtained. This compound is known.[2]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.53 (s, 1H), 7.91 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.22 (m, 3H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 199.0, 141.7, 139.3, 135.1, 131.4, 131.0, 128.6, 128.0, 128.0, 127.9, 126.9, 18.0.

_N_-(3-bromophenyl)benzothioamide (3ad, Scheme 2)

[2] Nahakpam L.; Chipem F. A. S.; Chingakham B. S.; Laitonjam W. S., *New J. Chem.* **2015**, *39*, 2240.

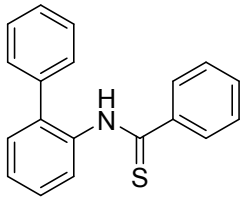


1-Bromo-3-nitrobenzene (0.5 mmol, 101 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 91 mg (62%) of a yellow solid was obtained. This compound is known.[3]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.83 (s, 1H), 8.18 (s, 1H), 7.83 (d, J = 6.7 Hz, 3H), 7.54 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.4 Hz, 3H), 7.41 (t, J = 8.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 198.2, 142.5, 141.5, 131.0, 130.5, 128.9, 128.1, 127.5, 126.5, 123.1, 120.9. One signal was not located.

***N*-([1,1'-Biphenyl]-2-yl)benzothioamide (3ae, Scheme 2)**



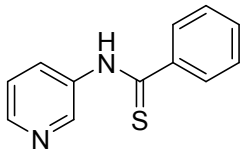
2-Nitrobiphenyl (0.5 mmol, 100 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 41 mg (28%) of a yellow solid was obtained. This compound is known.[4]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.54 (s, 1H), 7.67 (d, J = 7.9 Hz, 2H), 7.50 – 7.45 (m, 6H), 7.43 – 7.37 (m, 5H), 7.34 (d, J = 7.2 Hz, 1H).

[3] Inamoto K.; Hasegawa C.; Hiroya K.; Doi K., *Org. Lett.* **2008**, *10*, 5147.
[4] Inamoto K.; Nozawa K.; Kondo Y., *Synlett* **2012**, *23*, 1678.

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 199.1, 141.4, 138.8, 138.7, 137.5, 130.7, 130.3, 129.2, 128.5, 128.2, 128.04, 128.00, 127.9, 127.4, 127.2.

***N*-(pyridin-3-yl)benzothioamide (3af, Scheme 2)**

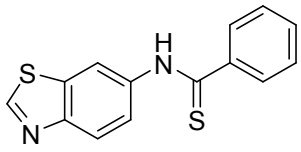


3-Nitropyridine (0.5 mmol, 62 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 73 mg (68%) of a yellow solid was obtained. This compound is known.[5]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.87 (s, 1H), 8.90 (d, J = 2.1 Hz, 1H), 8.50 – 8.45 (m, 1H), 8.28 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.52 – 7.47 (m, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 198.9, 146.9, 145.8, 142.1, 136.7, 131.7, 131.1, 128.1, 127.5, 123.3.

***N*-(Benzo[*d*]thiazol-6-yl)benzothioamide (3ag, Scheme 2)**



6-Nitrobenzothiazole (0.5 mmol, 90 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 2:3), 84 mg (62%) of a yellow solid was obtained.

[5] Pathare S. P.; Chaudhari P. S.; Akamanchi K. G., *Appl. Catal. A Gen.* **2012**, *425–426*, 125.

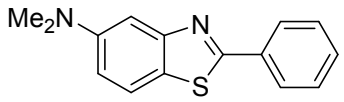
R_f = 0.43 (hexane/ethyl acetate 1:1)

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.97 (s, 1H), 9.41 (s, 1H), 8.72 (d, J = 1.6 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H), 7.90 – 7.83 (m, 3H), 7.55 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 198.2, 156.6, 151.1, 142.4, 137.6, 133.6, 130.9, 128.1, 127.5, 123.6, 122.7, 117.7.

HR-MS (ESI) calcd. for $C_{14}H_{10}N_2S_2$ $[M+H]^+$: 271.0364; found 271.0358.

***N*,*N*-Dimethyl-2-phenylbenzo[*d*]thiazol-5-amine (3ah, Scheme 3)**

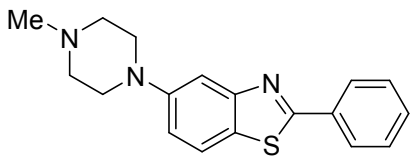


N,*N*-Dimethyl-3-nitroaniline (0.5 mmol, 83 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 69 mg (54%) of a yellow solid was obtained. This compound is known.[6]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 8.07 – 8.02 (m, 2H), 7.86 (d, J = 8.9 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.29 (d, J = 2.2 Hz, 1H), 7.00 (dd, J = 8.9, 2.3 Hz, 1H), 2.98 (s, 6H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 167.3, 155.4, 150.1, 133.3, 131.0, 129.3, 126.9, 122.0, 113.2, 104.9, 40.5.

5-(4-Methylpiperazin-1-yl)-2-phenylbenzo[*d*]thiazole (3ai, Scheme 3)



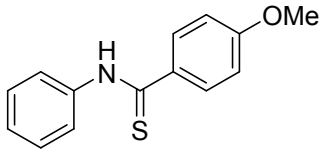
[6] Zhu X.; Yang Y.; Xiao G.; Song J.; Liang Y.; Deng G., *Chem. Commun.* **2017**, *53*, 11917.

1-Methyl-4-(3-nitrophenyl)piperazine (0.5 mmol, 118 mg), phenylacetic acid (0.75 mmol, 102 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 ^{o}C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 125 mg (81%) of a yellow solid was obtained.

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 8.06 – 8.04 (m, 2H), 7.90 (d, J = 9.0 Hz, 1H), 7.57 – 7.54 (m, 3H), 7.50 (d, J = 2.5 Hz, 1H), 7.20 (dd, J = 9.0, 2.5 Hz, 1H), 3.23 – 3.21 (m, 4H), 2.51 – 2.48 (m, 4H, overlapping with DMSO signal), 2.36 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 167.5, 155.1, 150.7, 133.2, 131.1, 129.3, 126.9, 124.6, 122.0, 116.3, 108.0, 54.5, 48.6, 45.7.

4-Methoxy-*N*-phenylbenzothioamide (3ba, Scheme 4 and entry 4-Table 2)



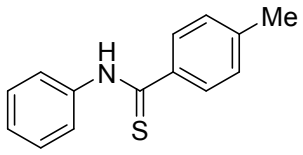
Nitrobenzene (0.5 mmol, 62 mg), 4-methoxyphenylacetic acid (0.75 mmol, 125 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 ^{o}C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 97 mg (80%) of a yellow solid was obtained. This compound is known.[1]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.59 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.0 Hz, 1H), 7.06 (d, J = 8.3 Hz, 2H), 3.88 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 196.7, 161.8, 140.4, 134.8, 129.7, 128.6, 126.3, 124.7, 113.4, 55.7.

For entry 4, Table 2: 4-methoxybenzyl alcohol (0.5 mmol, 69 mg) was used. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 63 mg (52%) of the desired product was obtained.

4-Methyl-*N*-phenylbenzothioamide (3ca, Scheme 4 and entry 2-Table 2)



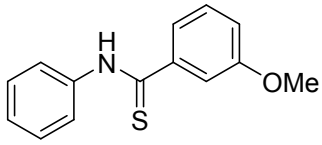
Nitrobenzene (0.5 mmol, 62 mg), *p*-tolylacetic acid (0.75 mmol, 113 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 61 mg (54%) of a yellow solid was obtained. This compound is known.[7]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.63 (s, 1H), 7.82 – 7.74 (m, 4H), 7.43 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 197.4, 140.9, 140.1, 139.8, 128.5, 128.4, 127.5, 126.2, 124.3, 20.9.

For entry 4, Table 2: 4-methylbenzyl alcohol (0.5 mmol, 61 mg) was used. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 48 mg (42%) of the desired product was obtained.

3-Methoxy-*N*-phenylbenzothioamide (3da, Scheme 4)



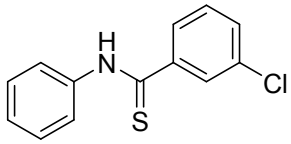
[7] Zhang P.; Chen W.; Liu M.; Wu H., *J. Org. Chem.* **2018**, *83*, 14269.

Nitrobenzene (0.5 mmol, 62 mg), 3-methoxyphenylacetic acid (0.75 mmol, 125 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 91 mg (75%) of an orange solid was obtained. This compound is known.[3]

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.71 (s, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.46 – 7.36 (m, 5H), 7.28 (t, J = 7.4 Hz, 1H), 7.10 (dd, J = 7.9, 1.3 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 197.2, 158.7, 143.9, 140.0, 129.1, 128.4, 126.3, 124.2, 119.8, 116.5, 112.7, 55.3.

3-Chloro-*N*-phenylbenzothioamide (3ea, Scheme 4)



Nitrobenzene (0.5 mmol, 62 mg), 3-chlorophenylacetic acid (0.75 mmol, 128 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 90 mg (73%) of a yellow solid was obtained.

R_f = 0.32 (hexanes/ethyl acetate 7:1).

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.88 (s, 1H), 7.86 – 7.76 (m, 4H), 7.60 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H).

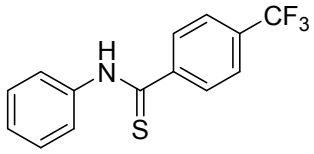
^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 195.5, 144.4, 139.8, 132.7, 130.4, 130.0, 128.6, 127.0, 126.5, 126.3, 124.1.

HR-MS (ESI) calcd. for $C_{13}H_{10}{}^{35}ClNS$ $[M+H]^+$: 248.0295; found 248.0301.

At 3 mmol scale: Nitrobenzene (3 mmol, 369 mg), 3-chlorophenylacetic acid (4.5 mmol, 613 mg), sulfur (6 mmol, 192 mg), DABCO (3 mmol, 337 mg) under Ar at 120 °C for 16

h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 482 mg (65%) of the thioamide was obtained. The purity of the product was confirmed by GC-MS.

***N*-phenyl-4-(trifluoromethyl)benzothioamide (3fa, Scheme 4)**



Nitrobenzene (0.5 mmol, 62 mg), (α,α,α-trifluoro-*p*-tolyl)acetic acid (0.75 mmol, 153 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 79 mg (56%) of a yellow solid was obtained.

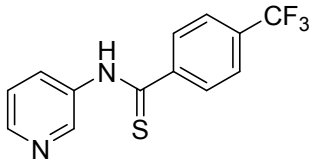
R_f = 0.32 (hexanes/ethyl acetate 7:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.30 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 196.7, 146.3, 138.7, 132.8 (q, *J* = 33.8 Hz, two signals of the quartet could not be located), 129.2, 127.5, 127.4, 127.1, 123.8 (q, *J* = 271.3 Hz, two signal of the quartet could not be located), 123.6. One carbon signal could not be located.

HR-MS (ESI) calcd. for $C_{14}H_{10}F_3NS$ $[M+H]^+$: 282.0559; found 220.0564.

***N*-(pyridin-3-yl)-4-(trifluoromethyl)benzothioamide (3ff, Scheme 4)**



3-Nitropyridine (0.5 mmol, 62 mg), (α,α,α-trifluoro-*p*-tolyl)acetic acid (0.75 mmol, 153 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16

h. After column chromatography (hexanes/ethyl acetate 10:1 to 1:1), 87 mg (62%) of a yellow solid was obtained.

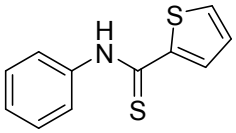
R_f = 0.29 (hexanes/ethyl acetate 1:1).

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 12.12 (s, 1H), 8.92 (d, J = 2.4 Hz, 1H), 8.49 (dd, J = 4.7, 1.3 Hz, 1H), 8.33 – 8.28 (m, 1H), 8.02 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 8.2, 4.7 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 197.3, 147.2, 145.7, 145.6, 136.4, 131.5, 130.6 (q, $J_{C\text{-}F}$ = 32 Hz), 128.2, 125.1 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.9 (q, $J_{C\text{-}F}$ = 270.8 Hz, two signals of the quartet could be located), 123.4.

HR-MS (ESI) calcd. for $C_{13}H_9F_3N_2S$ $[M+H]^+$: 283.0511; found 283.0517.

***N*-phenylthiophene-2-carbothioamide (3ga, Scheme 4)**



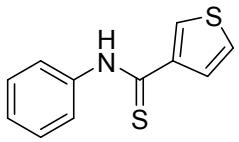
Nitrobenzene (0.5 mmol, 62 mg), 2-thiopheneacetic acid (0.75 mmol, 107 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 58 mg (53%) of a brown solid was obtained. This compound is known.[8]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.97 (s, 1H), 7.67 (d, J = 5.3 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.42 (dd, J = 10.1, 5.3 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 188.0, 148.0, 138.7, 133.1, 129.2, 128.1, 127.2, 124.7, 124.4.

[8] Pace V.; Castoldi L.; Monticelli S.; Safranek S.; Roller A.; Langer T.; Holzer W., *Chem. Eur. J.* **2015**, *21*, 18966.

***N*-phenylthiophene-3-carbothioamide (3ha, Scheme 4)**



Nitrobenzene (0.5 mmol, 62 mg), 3-thiopheneacetic acid (0.75 mmol, 107 mg), sulfur (1 mmol, 32 mg), and DABCO (0.5 mmol, 56 mg) under Ar at 120 °C for 16 h. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 57 mg (52%) of a red solid was obtained.

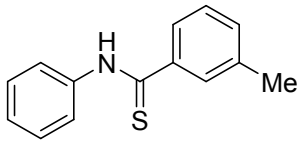
R_f = 0.18 (hexanes/ethyl acetate 7:1).

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.47 (s, 1H), 8.23 (d, J = 1.5 Hz, 1H), 7.72 (d, J = 7.9 Hz, 2H), 7.69 (d, J = 4.9 Hz, 1H), 7.60 (dd, J = 4.9, 3.0 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 190.3, 144.4, 140.1, 128.9, 128.7, 128.0, 126.8, 126.7, 125.4.

HR-MS (ESI) calcd. for $C_{11}H_9NS_2$ $[M+H]^+$: 220.0249; found 220.0254.

3-Methyl-*N*-phenylbenzothioamide (entry 3, Table 2)



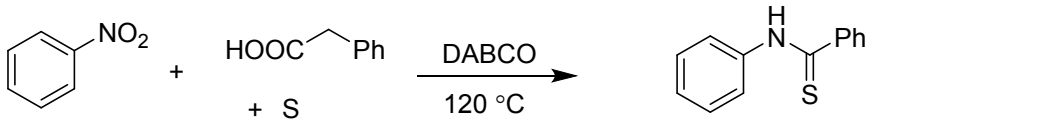
3-Methylbenzyl alcohol (0.5 mmol, 61 mg), nitrobenzene (123 mg, 1 mmol), sulfur (48 mg, 1.5 mmol) and DABCO (112 mg, 1 mmol) were used. After column chromatography (hexanes/ethyl acetate 20:1 to 7:1), 53 mg (47%) of the desired product was obtained.

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 11.72 (s, 1H), 7.84 (d, J = 7.9 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.45 (t, J = 7.7 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.29 (t, J = 7.3 Hz, 1H), 2.40 (s, 3H).

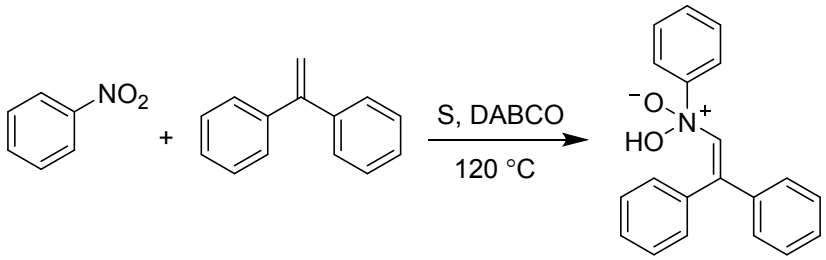
^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 198.3, 143.2, 140.5, 137.8, 131.8, 128.9, 128.42, 128.37, 126.7, 125.2, 124.7, 21.4.

4. Control experiments

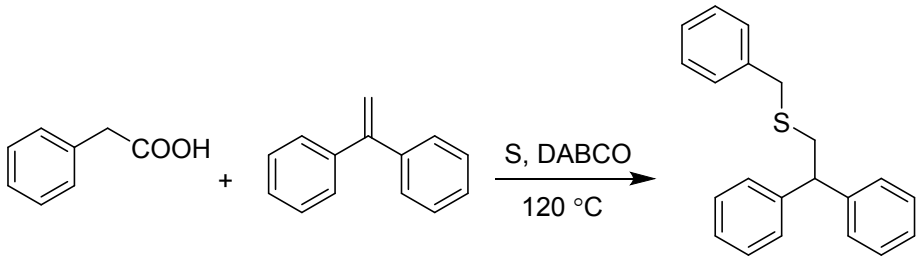
4.1. Reactions with radical quenchers



with TEMPO (50 mol%): 15% yield
with diphenylethylene (50 mol%): 35% yield

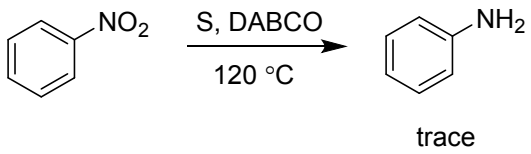


detected by GC-MS



detected by GC-MS

4.2. Reduction of nitrobenzene



4.3. Reaction of nitrosoarene and thioaldehyde

4-Methyl nitrosobenzene was synthesized by following the known procedure.[9] A 0.5 mmol (61 mg) of the compound was then added to a vial which contained a fresh, recrystallized thioaldehyde (which was also synthesized based on the known procedure[10]) (0.75 mmol, 92 mg), sulfur (1 mmol, 32 g), and DABCO (0.5 mmol, 56 mg). The vial was then purged with Argon for 5 min, capped, and heated at 120 ℃ for 6h. Upon completion, using the General Procedure 1 for work up. The GC yield was determined as 40% yield.

5. Copies of NMR spectra

[9] N. Yasukawa, M. Kuwata, T. Imai, Y. Monguchi, H. Sajiki, Y. Sawama, *Green Chem.* **2018,** *20*, 4409.
[10] D. Bansal, S. Pandey, G. Hundal, R. Gupta, *New J. Chem.* **2015**, *39*, 9772.

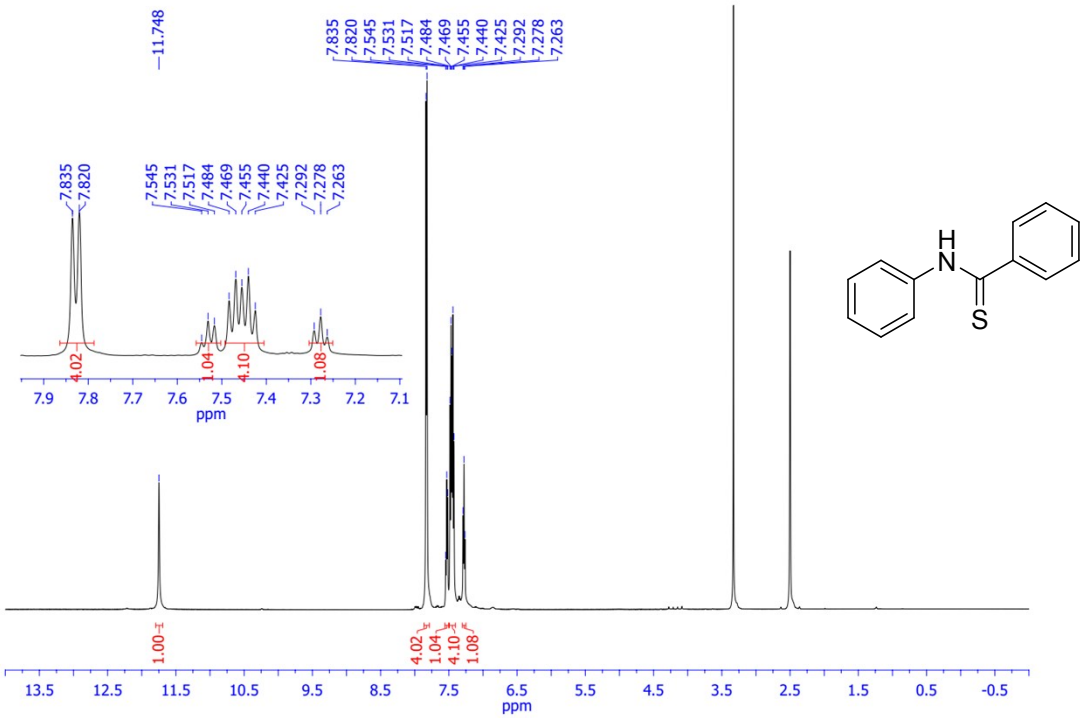


Fig. S1. ^{1}H NMR spectrum of **3aa.**

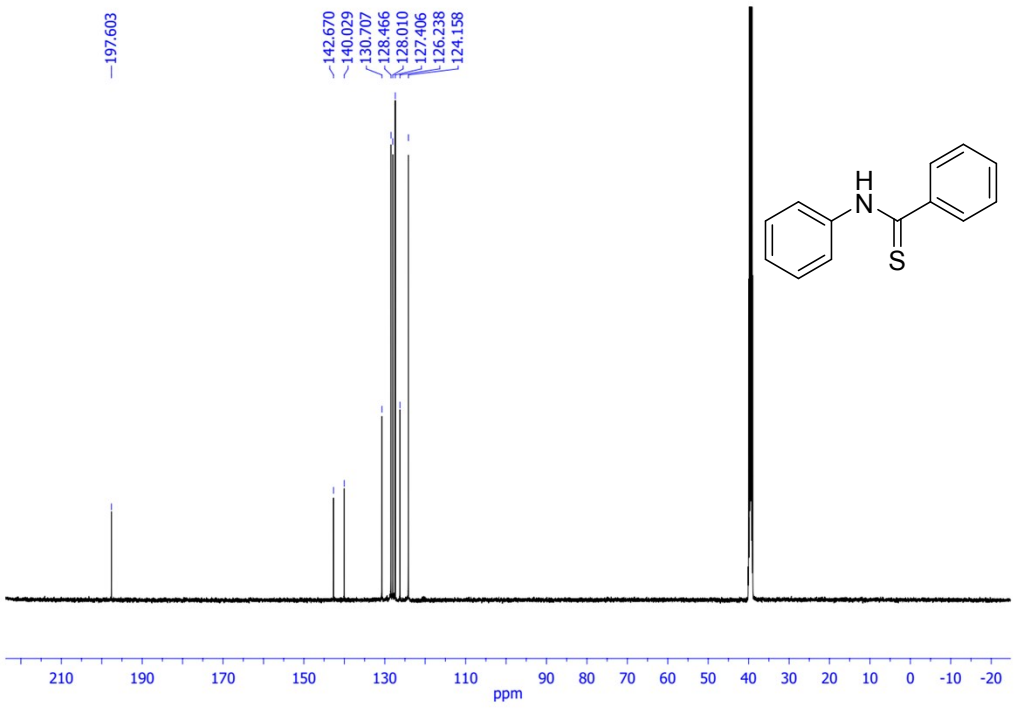


Fig. S2. ^{13}C NMR spectrum of **3aa.**

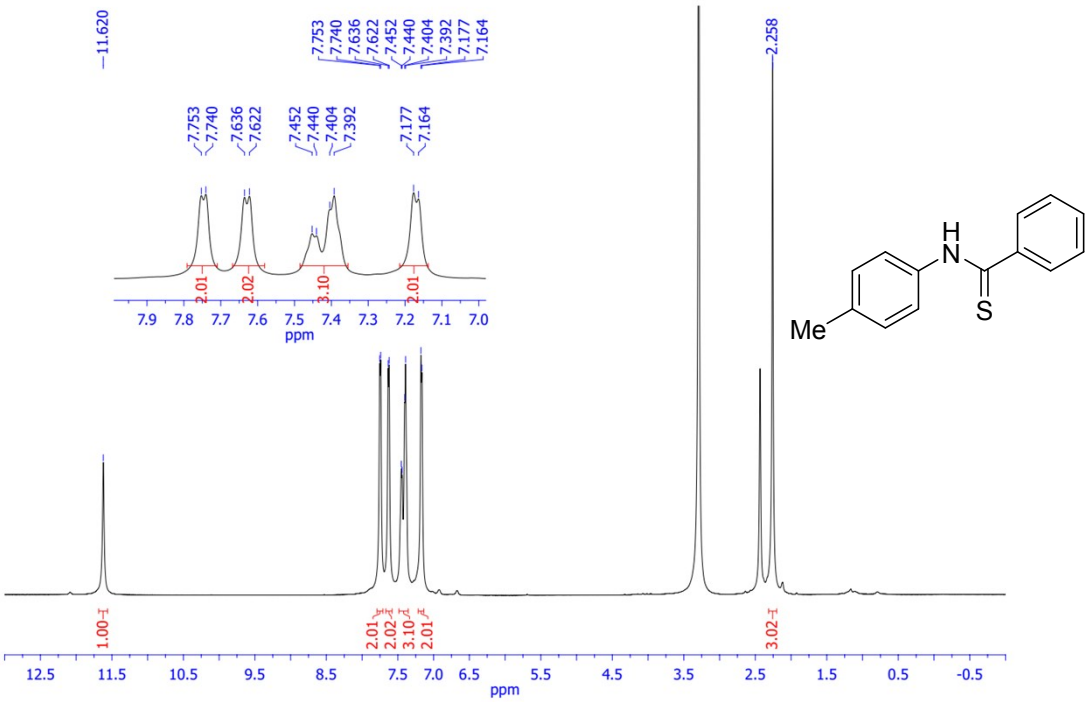


Fig. S3. ^{1}H NMR spectrum of **3ab.**

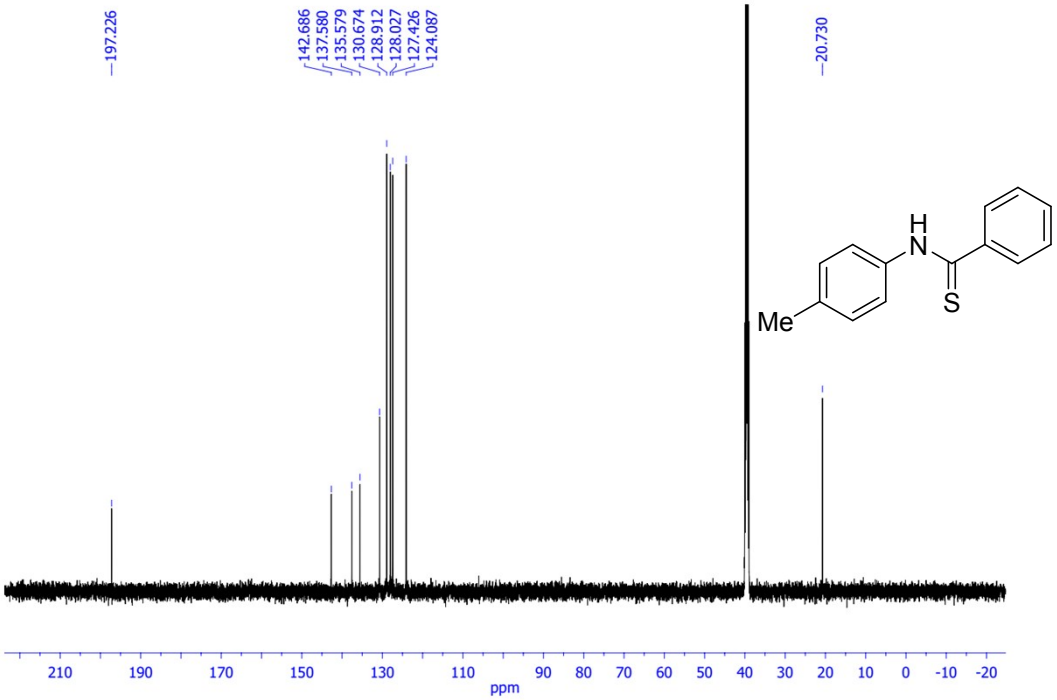


Fig. S4. ^{13}C NMR spectrum of **3ab.**

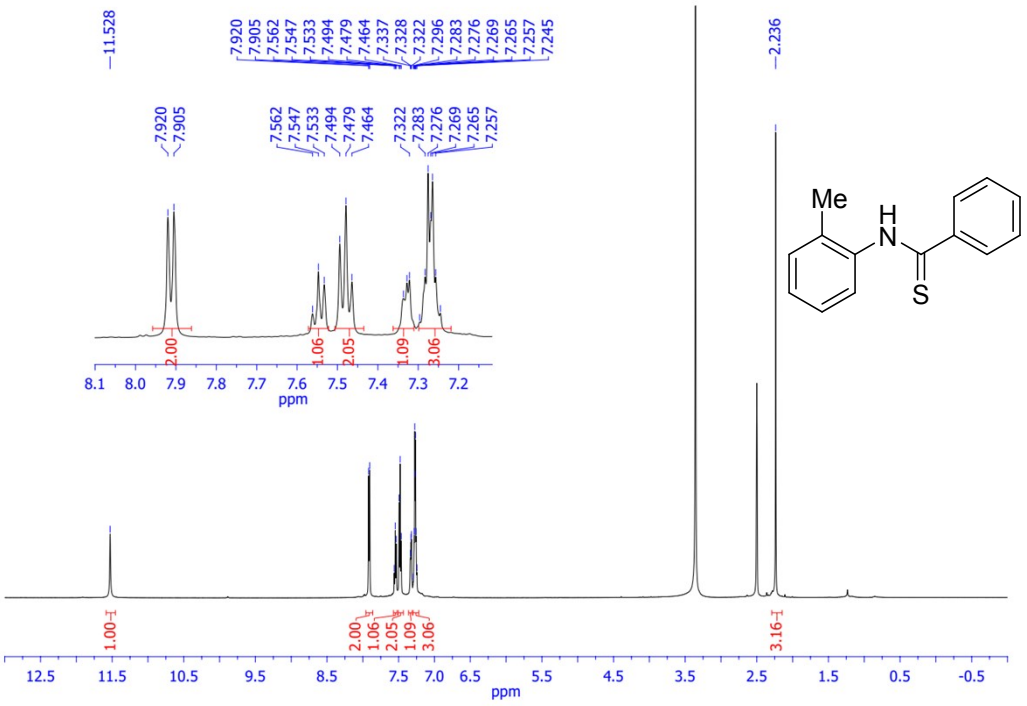


Fig. S5. ^{1}H NMR spectrum of **3ac.**

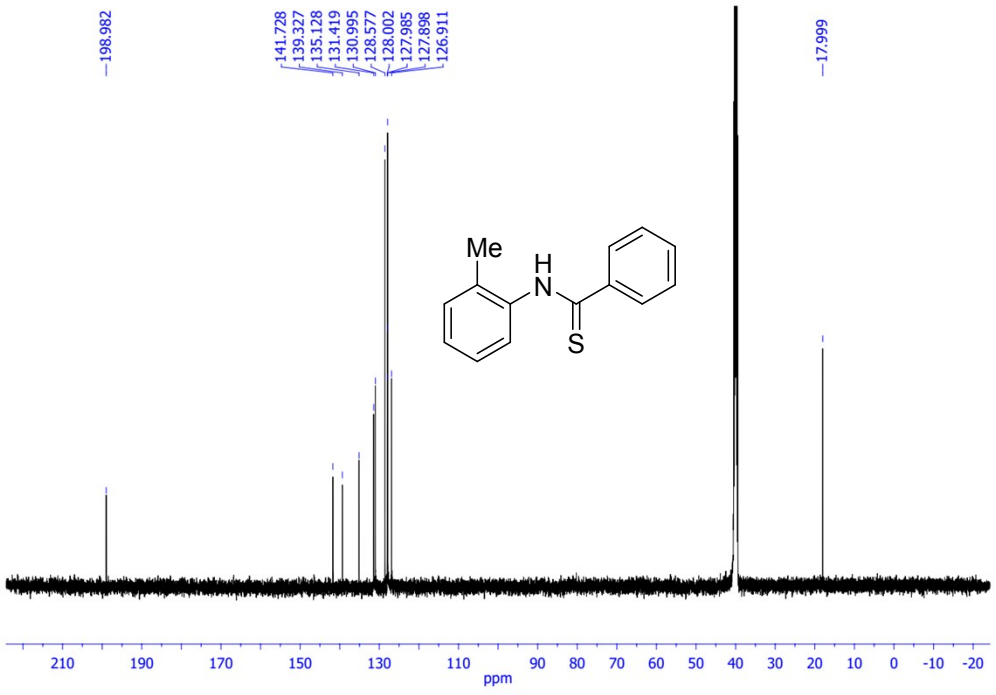


Fig. S6. ^{13}C NMR spectrum of **3ac.**

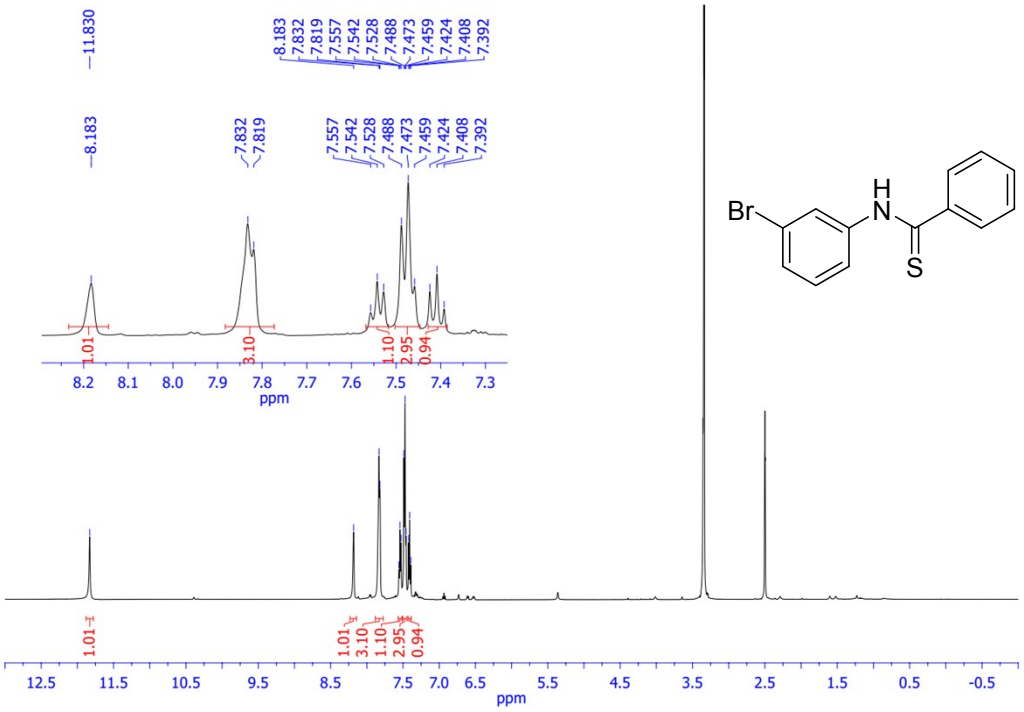


Fig. S7. ^{1}H NMR spectrum of **3ad**.

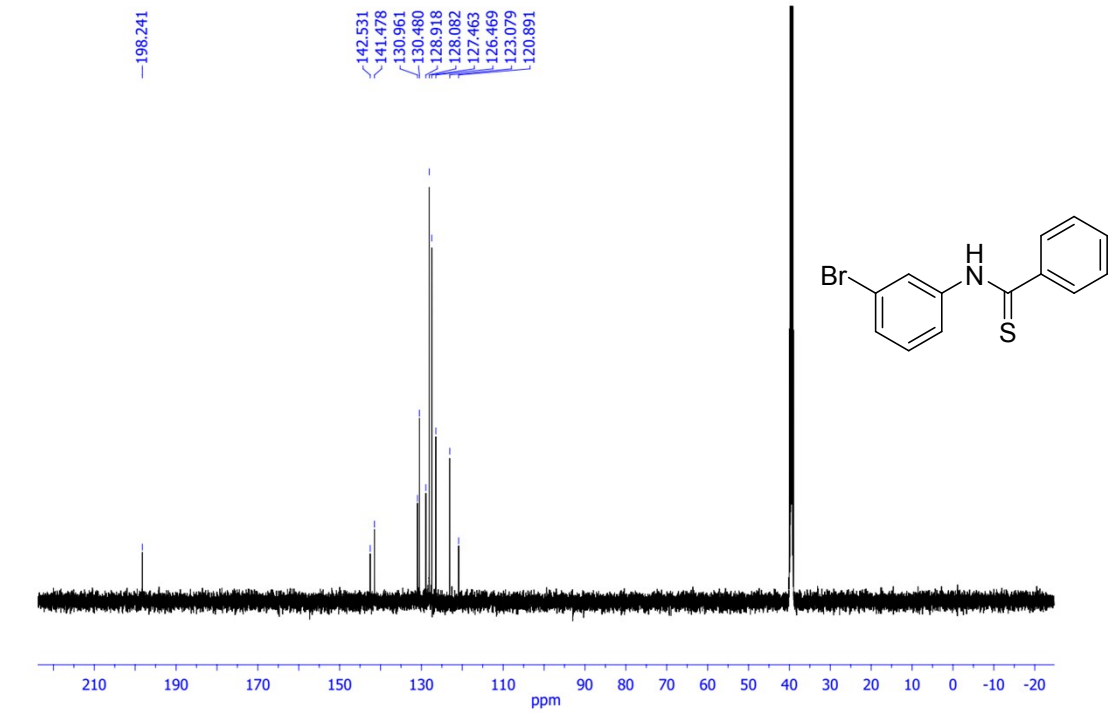


Fig. S8. ^{13}C NMR spectrum of **3ad**.

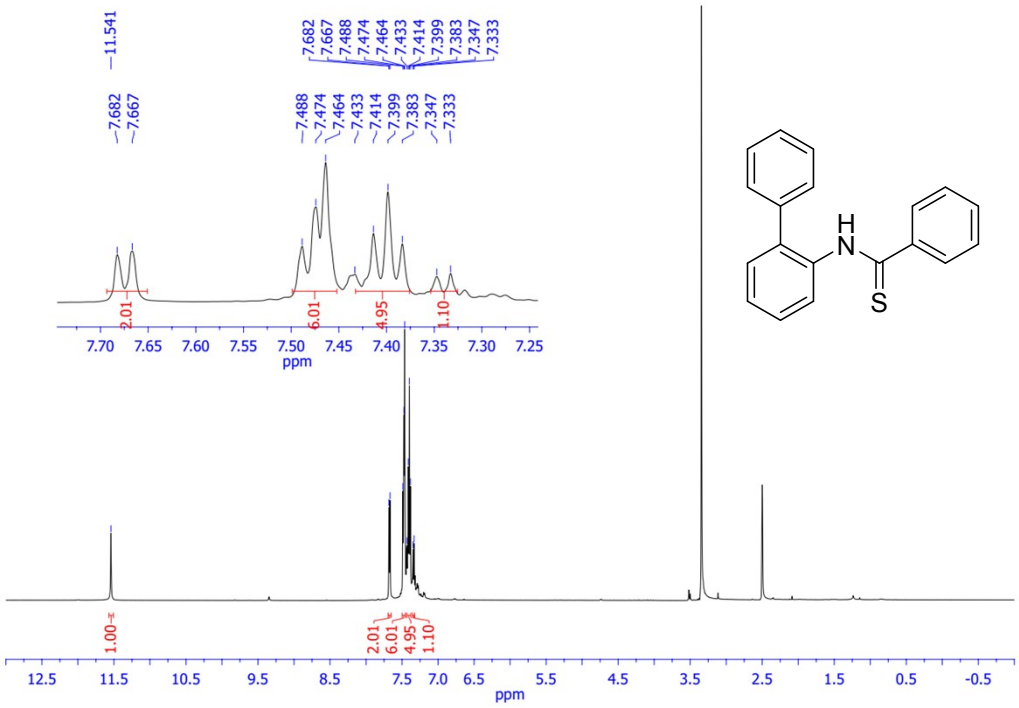


Fig. S9. ^{1}H NMR spectrum of **3ae**.

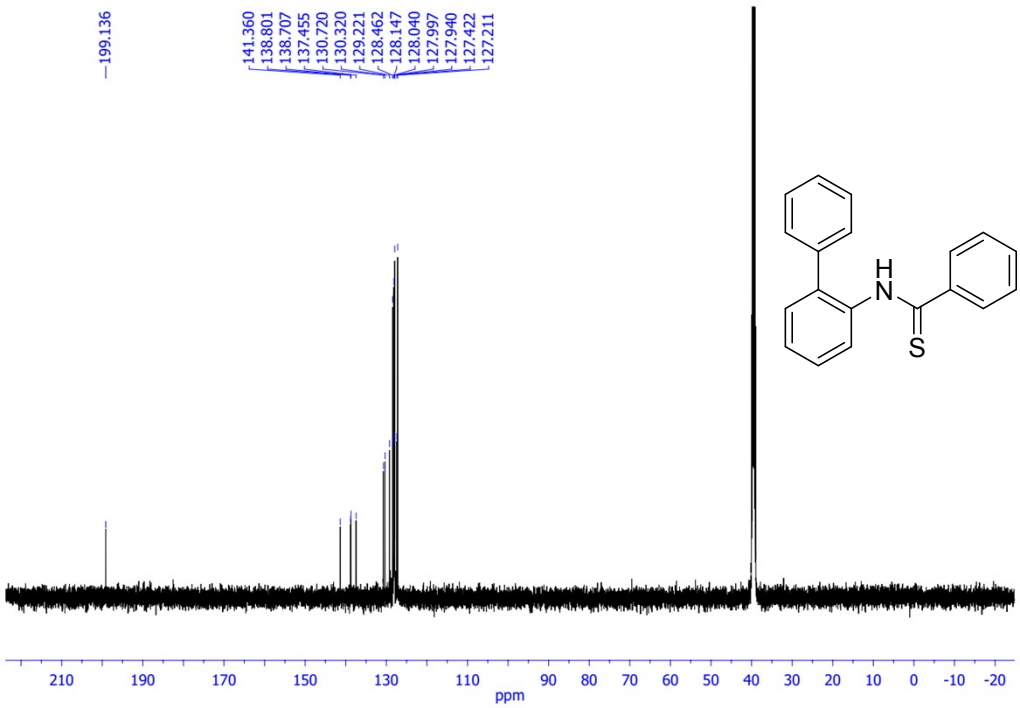


Fig. S10. ^{13}C NMR spectrum of **3ae**.

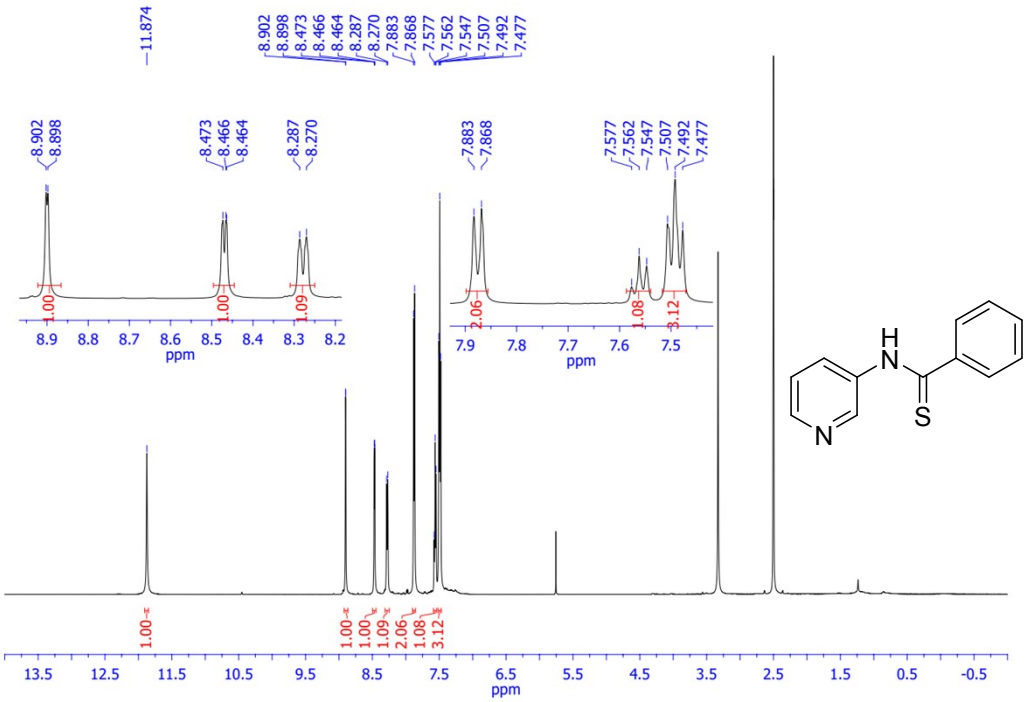


Fig. S11. ^{1}H NMR spectrum of **3af.**

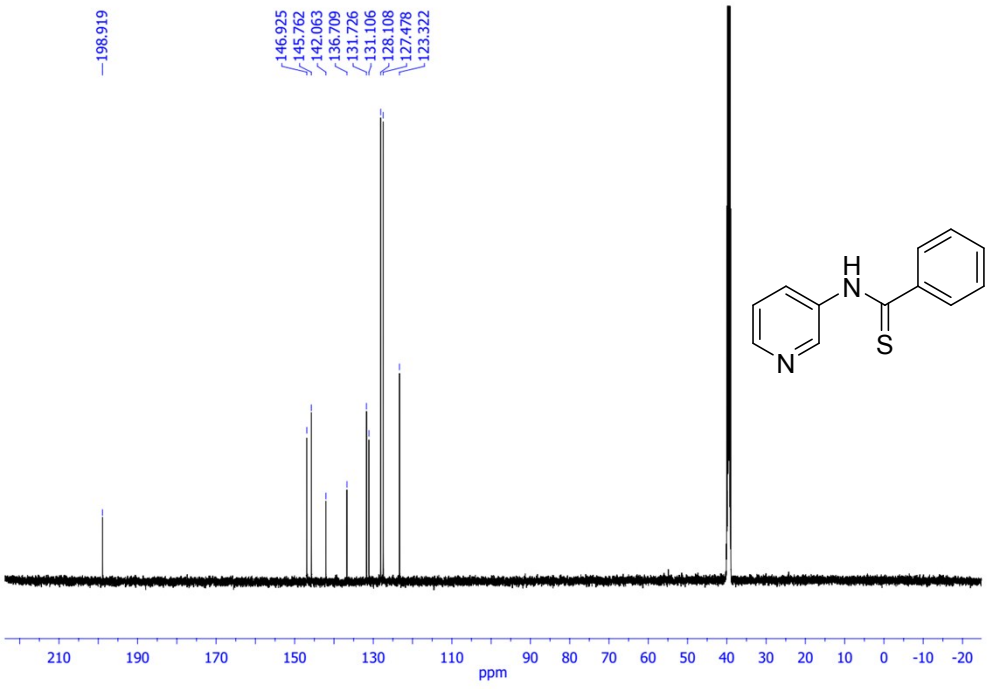


Fig. S12. ^{13}C NMR spectrum of **3af.**

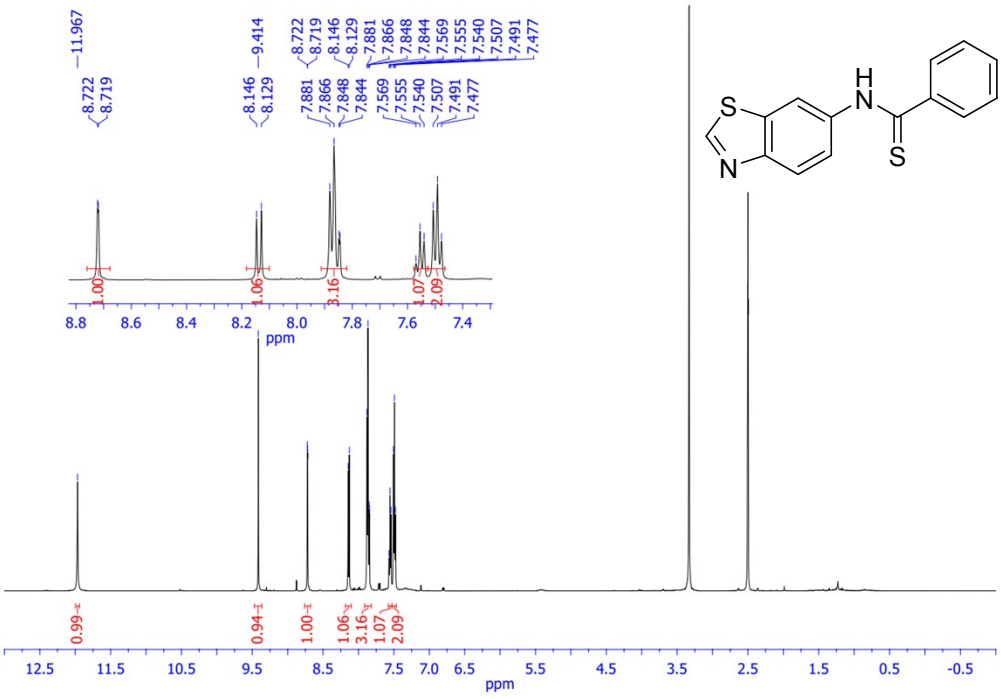


Fig. S13. [1]H NMR spectrum of **3ag.**

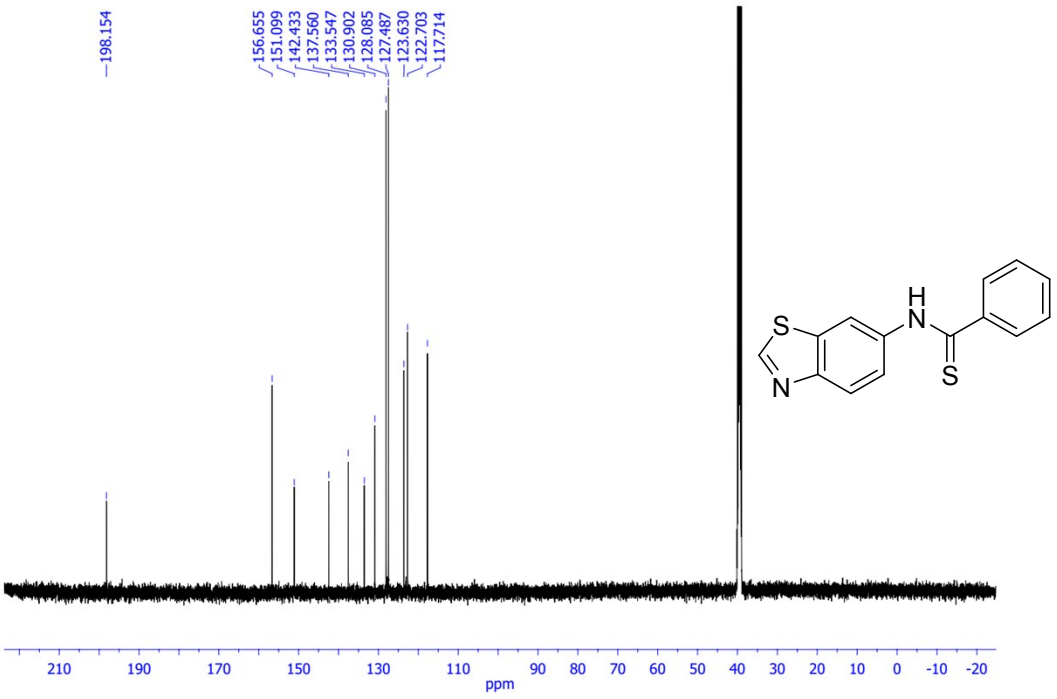


Fig. S14. [13]C NMR spectrum of **3da.**

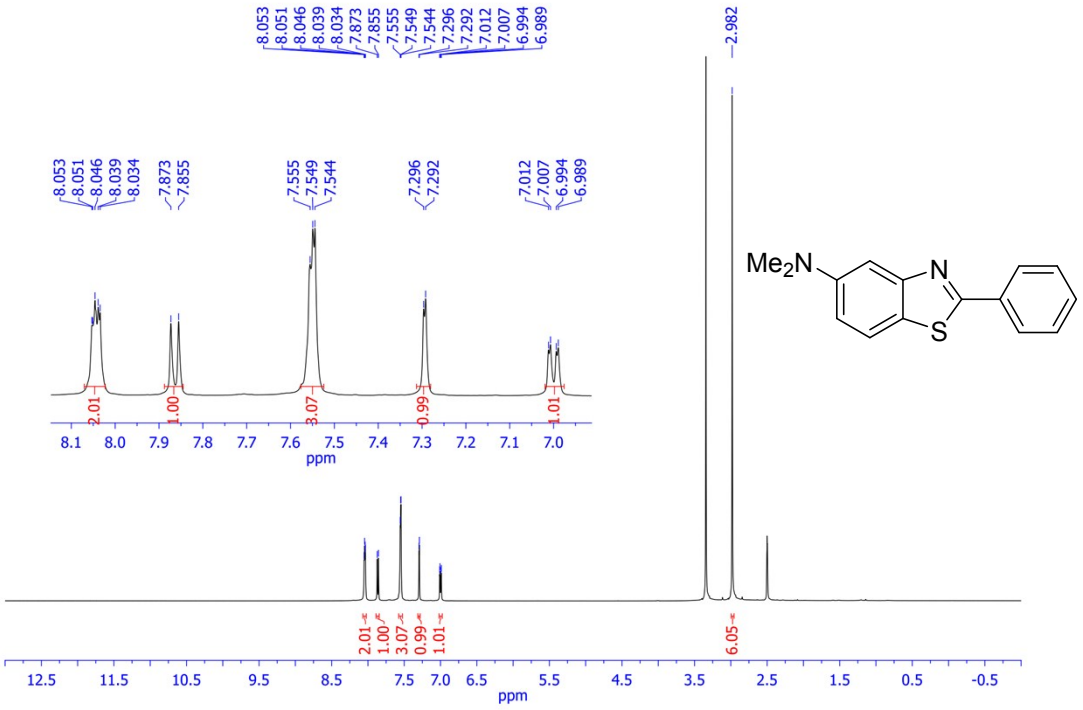


Fig. S15. [1]H NMR spectrum of **3ah**.

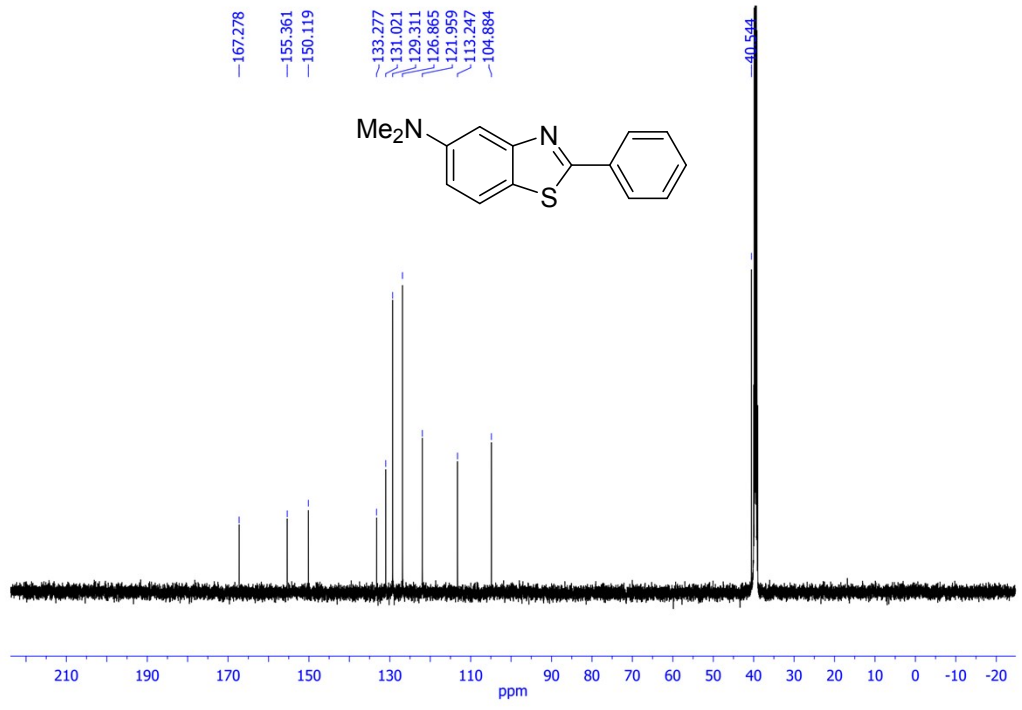


Fig. S16. [13]C NMR spectrum of **3ah**.

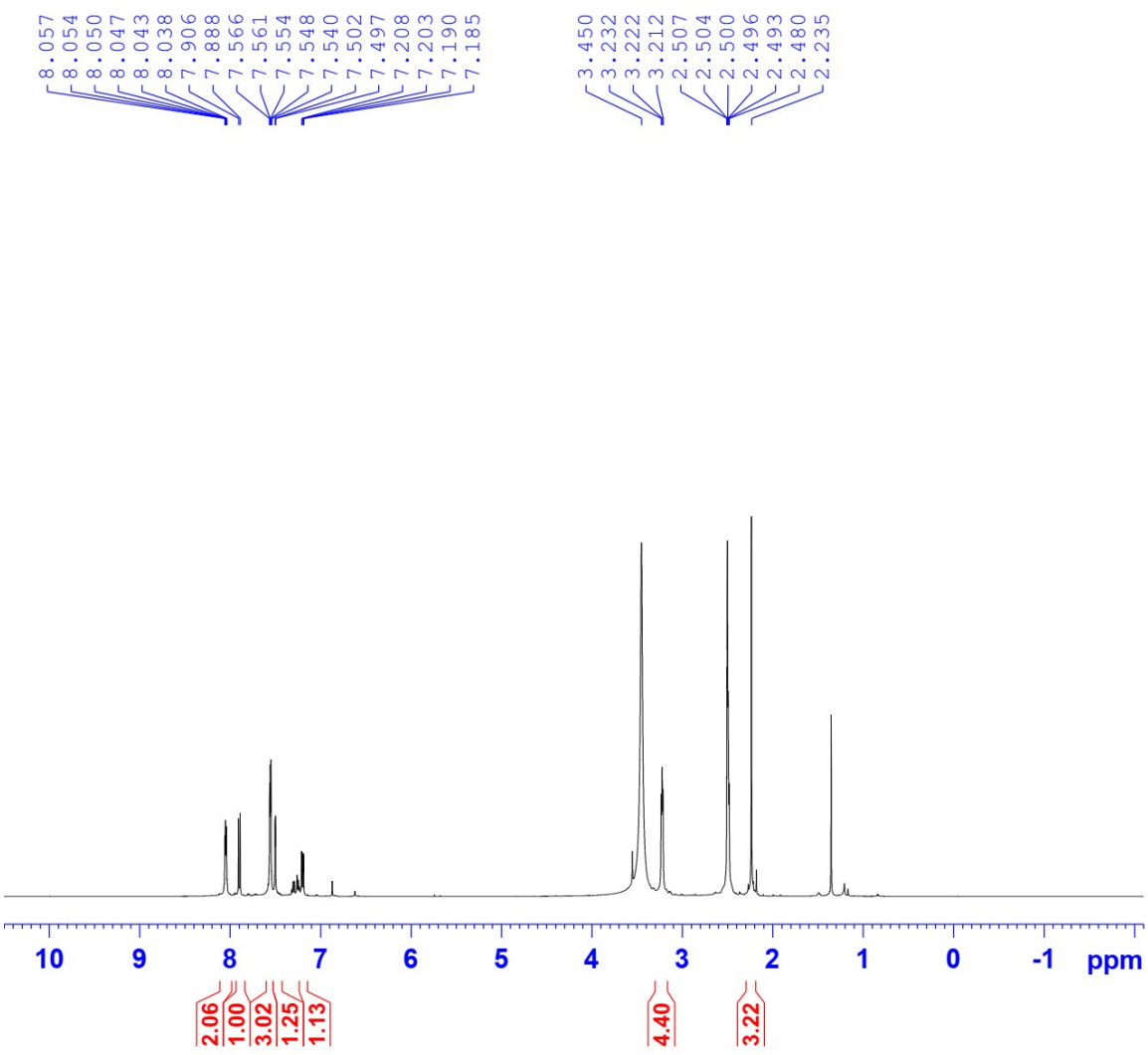


Fig. S17. ^{1}H NMR spectrum of **3ai**.

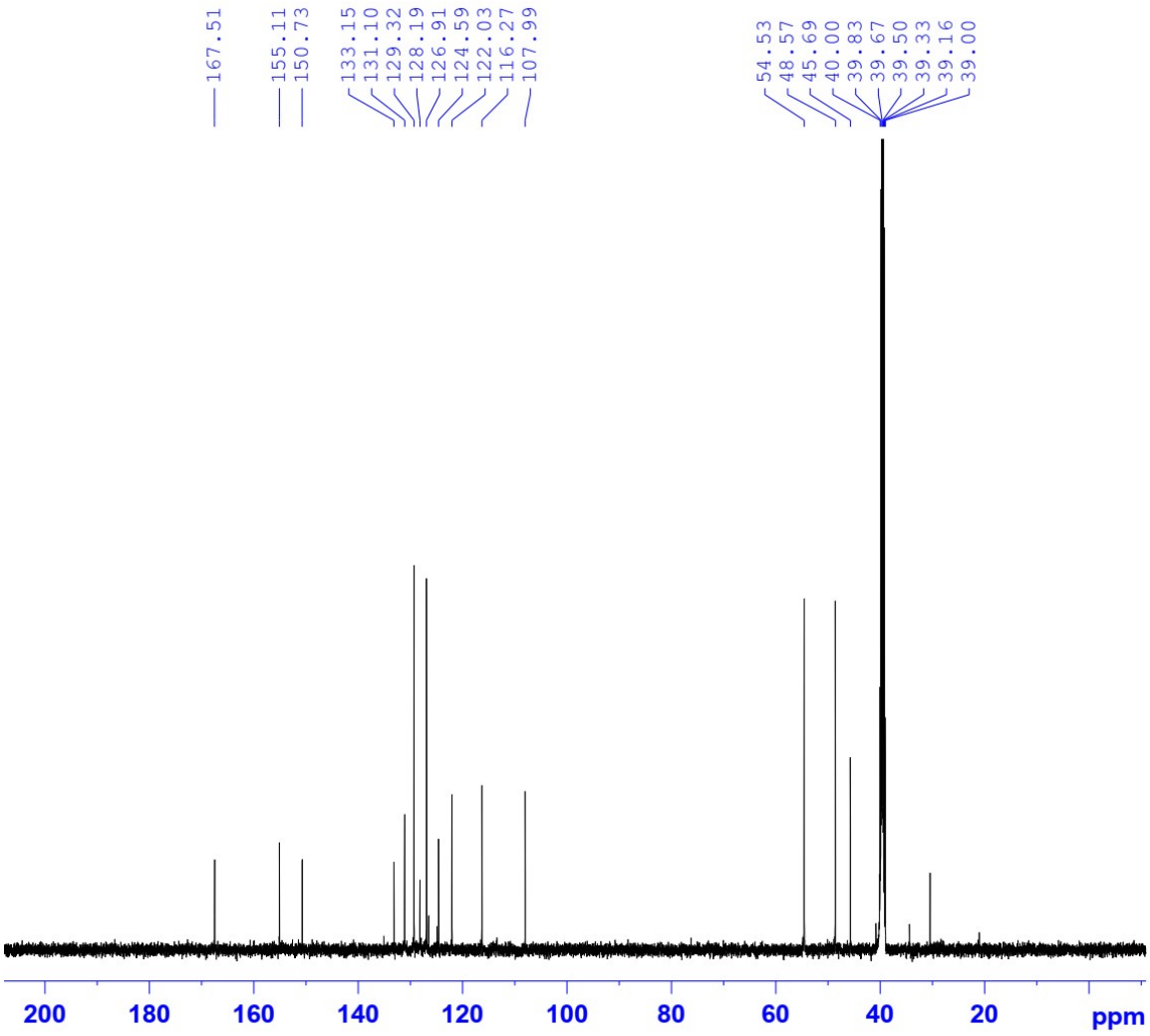


Fig. S18. ^{13}C NMR spectrum of **3ai**.

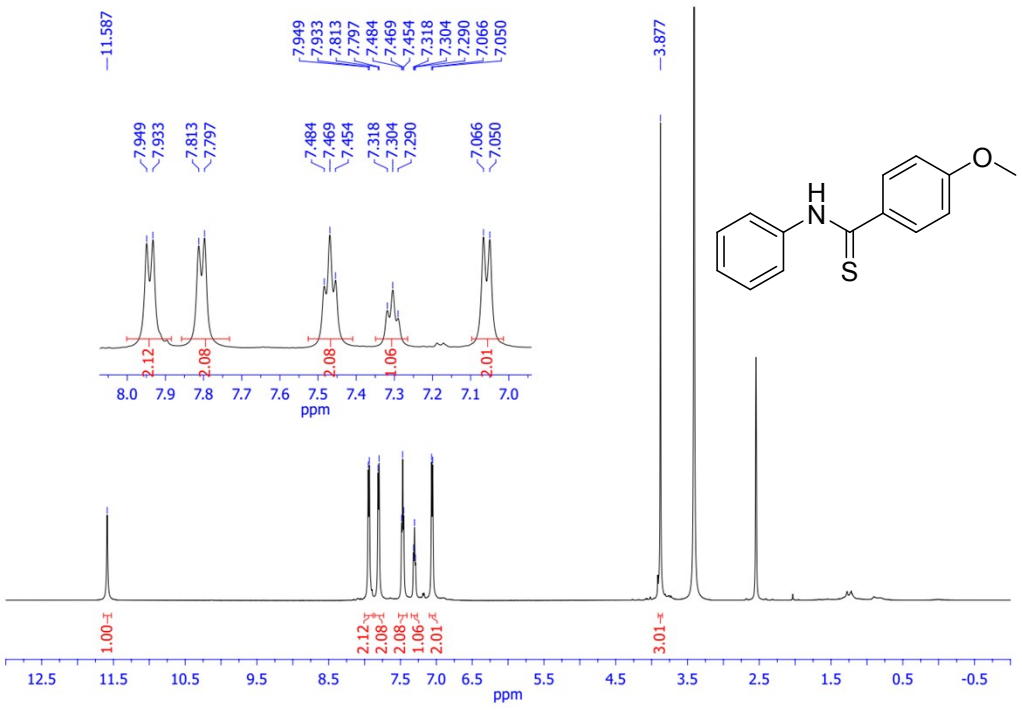


Fig. S19. ^{1}H NMR spectrum of **3ba.**

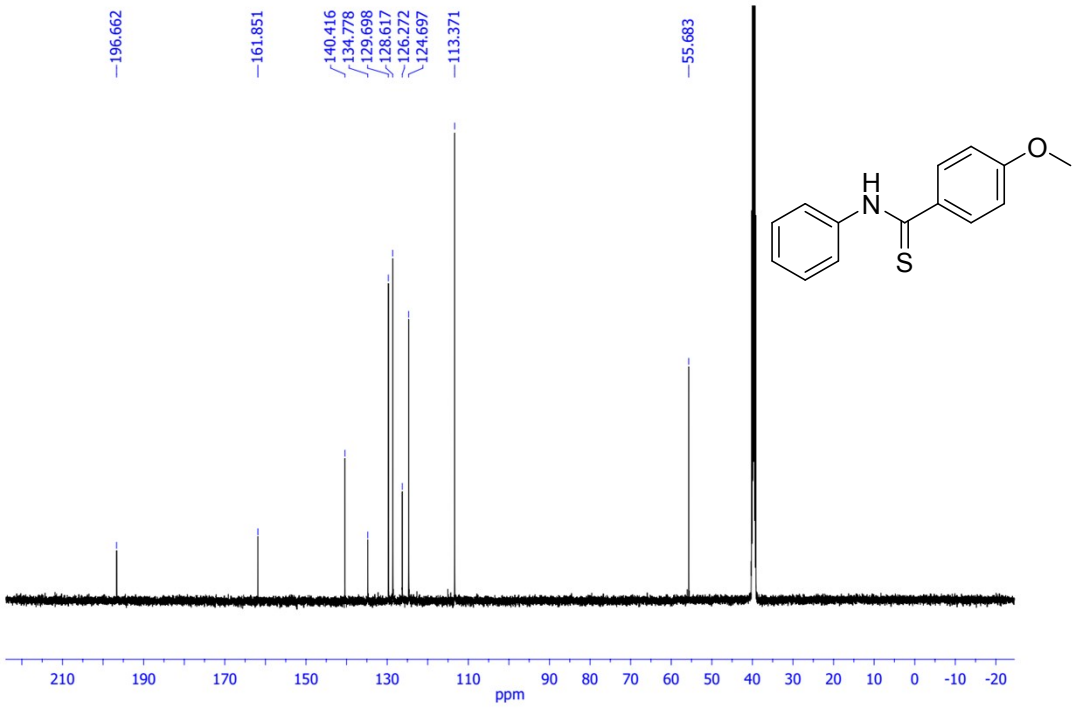


Fig. S20. ^{13}C NMR spectrum of **3ba.**

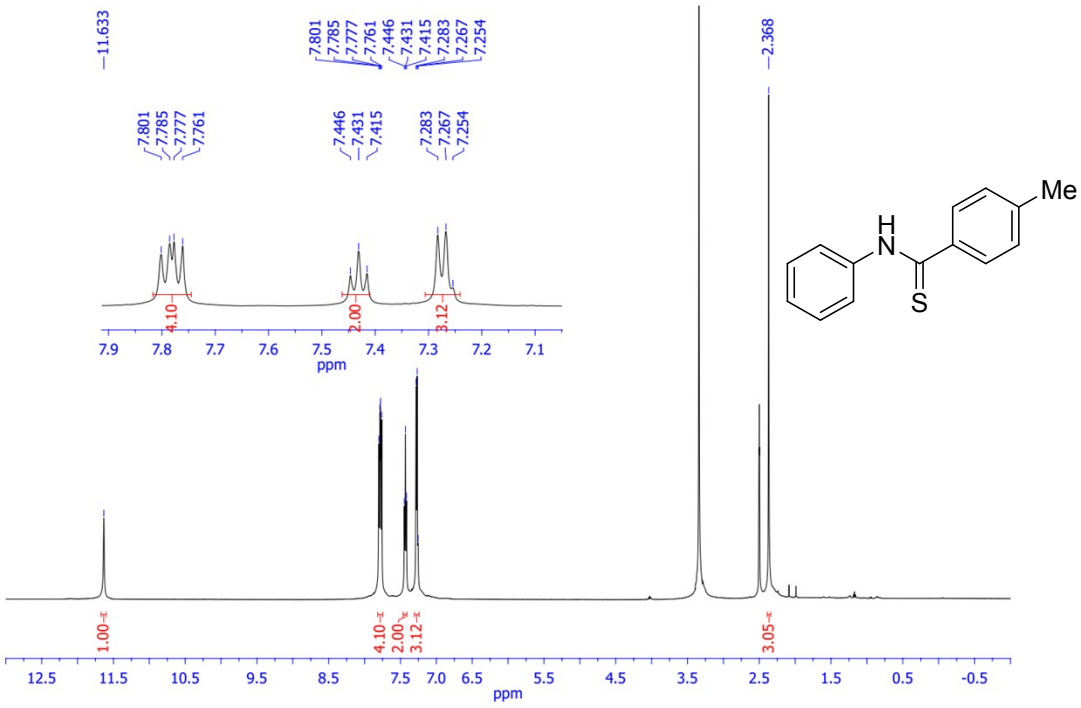


Fig. S21. ^{1}H NMR spectrum of **3ca**.

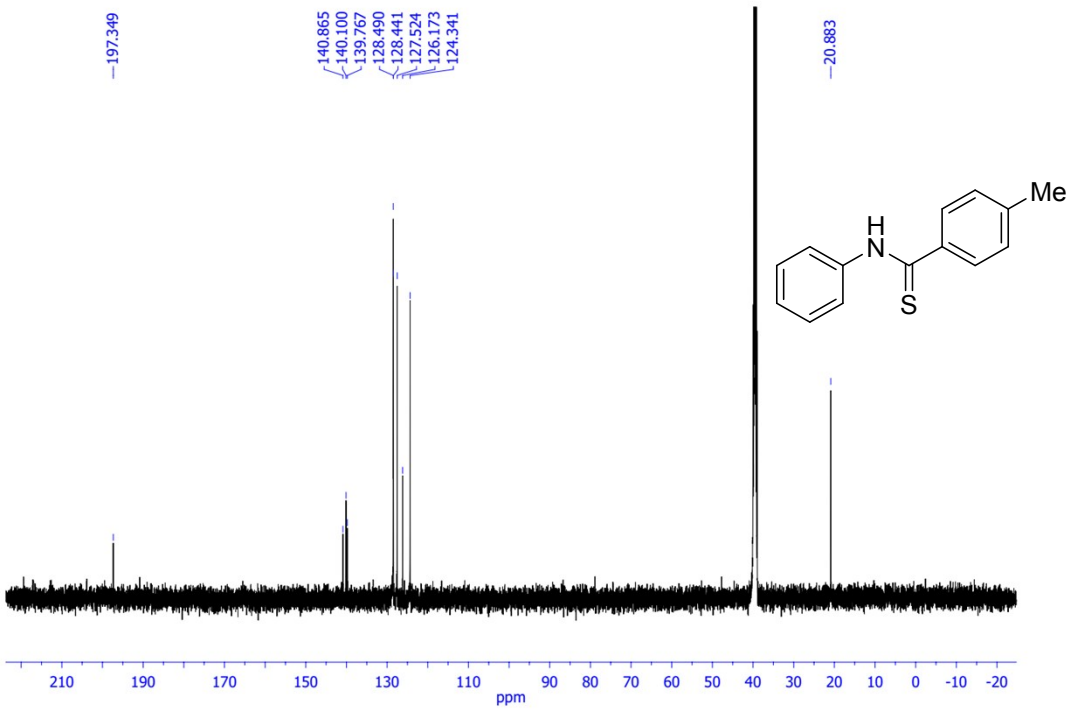


Fig. S22. ^{13}C NMR spectrum of **3ca**.

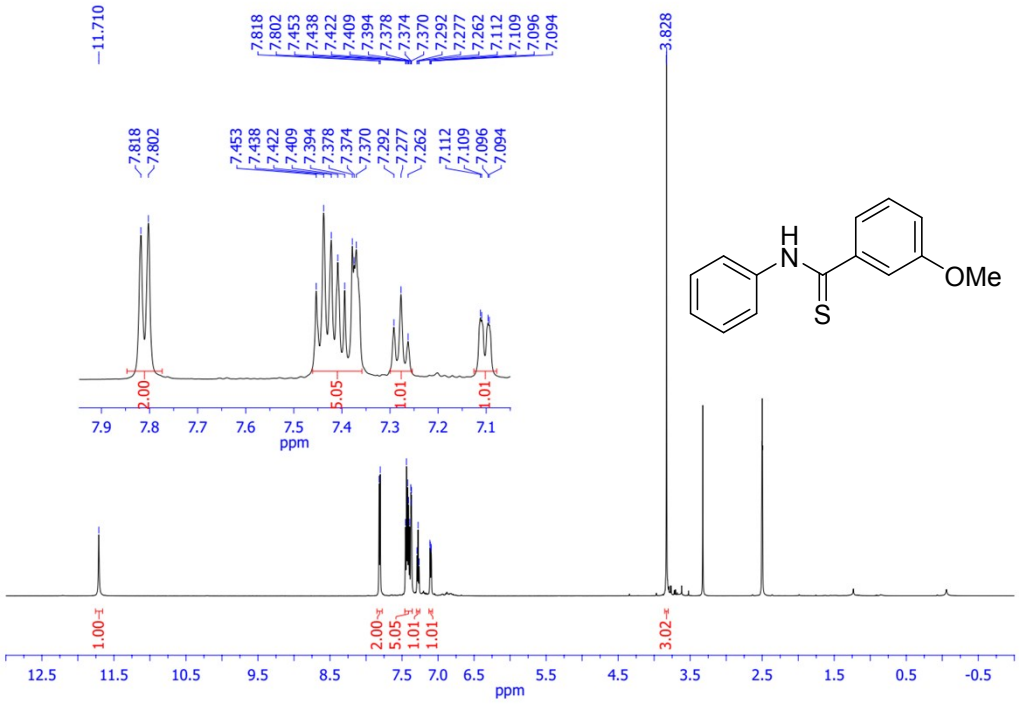


Fig. S23. [1]H NMR spectrum of **3da.**

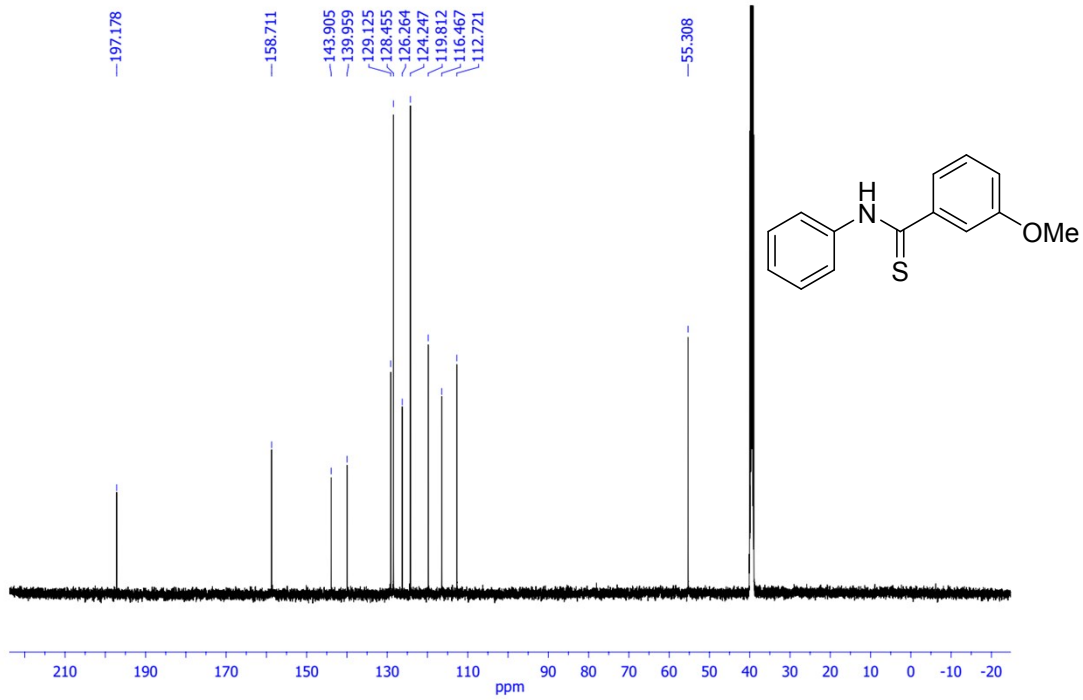


Fig. S24. [13]C NMR spectrum of **3da.**

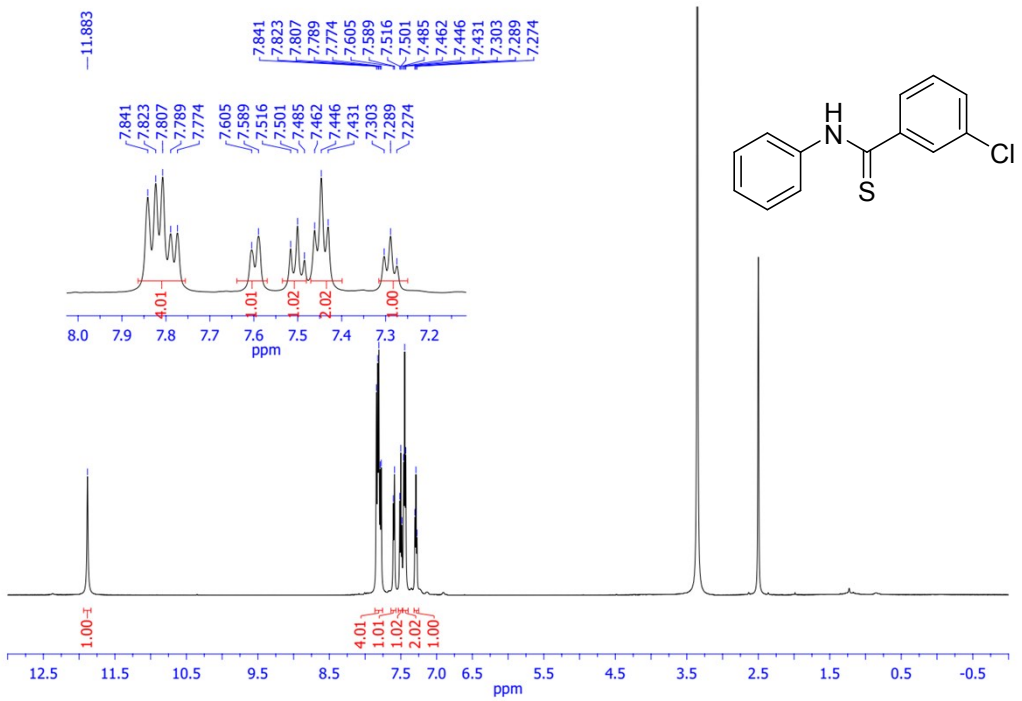


Fig. S25. ^{1}H NMR spectrum of **3ea**.

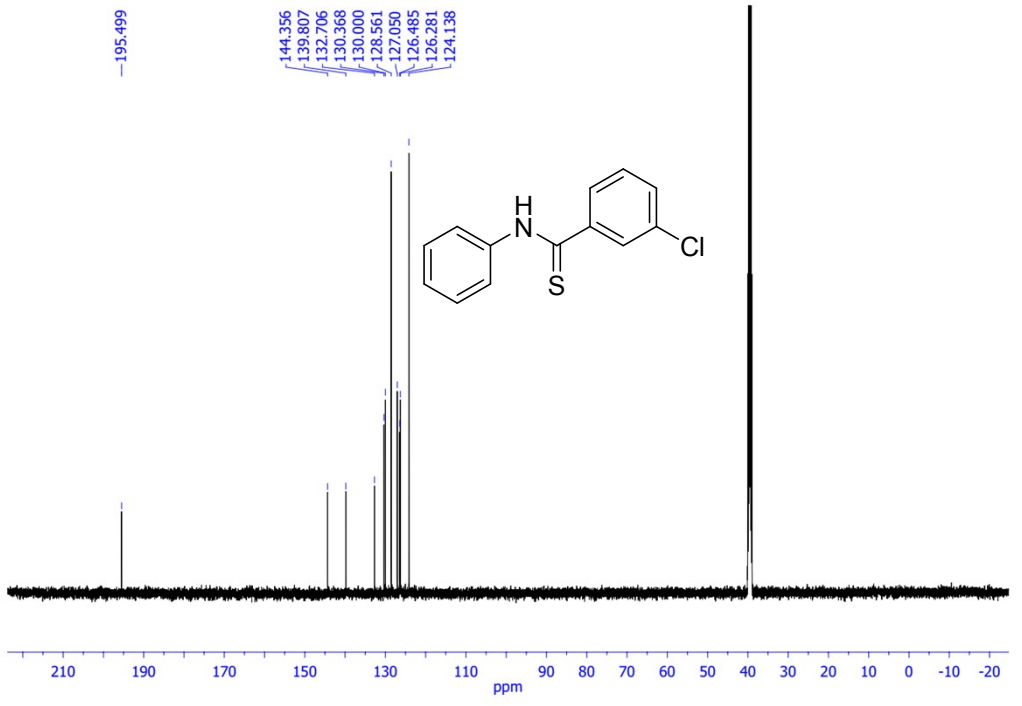


Fig. S26. ^{13}C NMR spectrum of **3ea**.

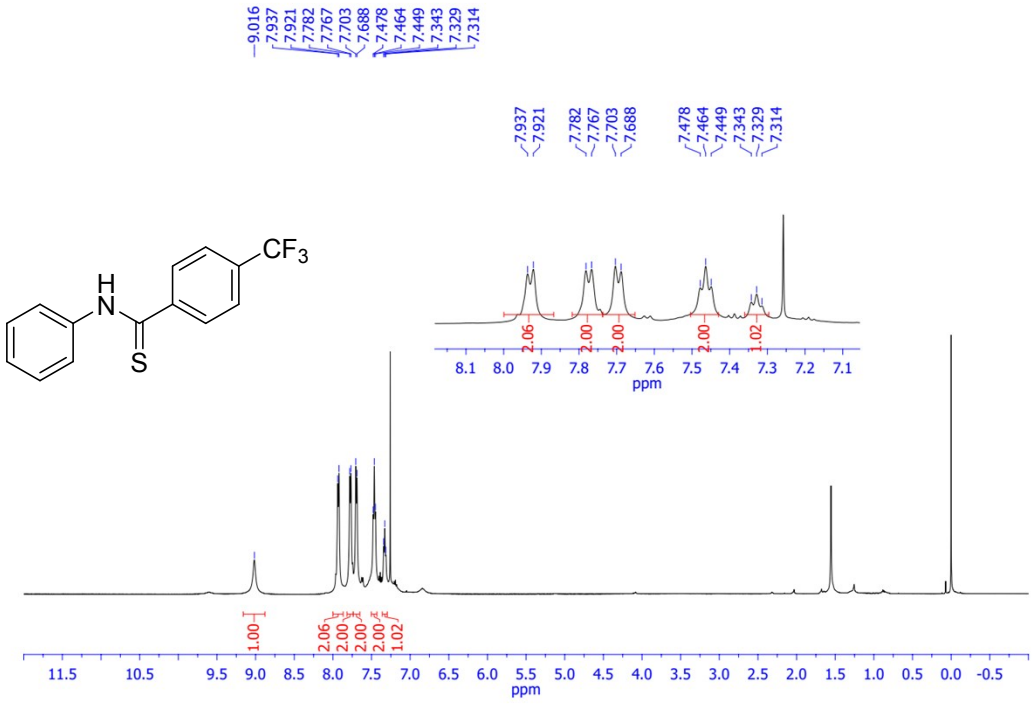


Fig. S27. ^{1}H NMR spectrum of **3fa**.

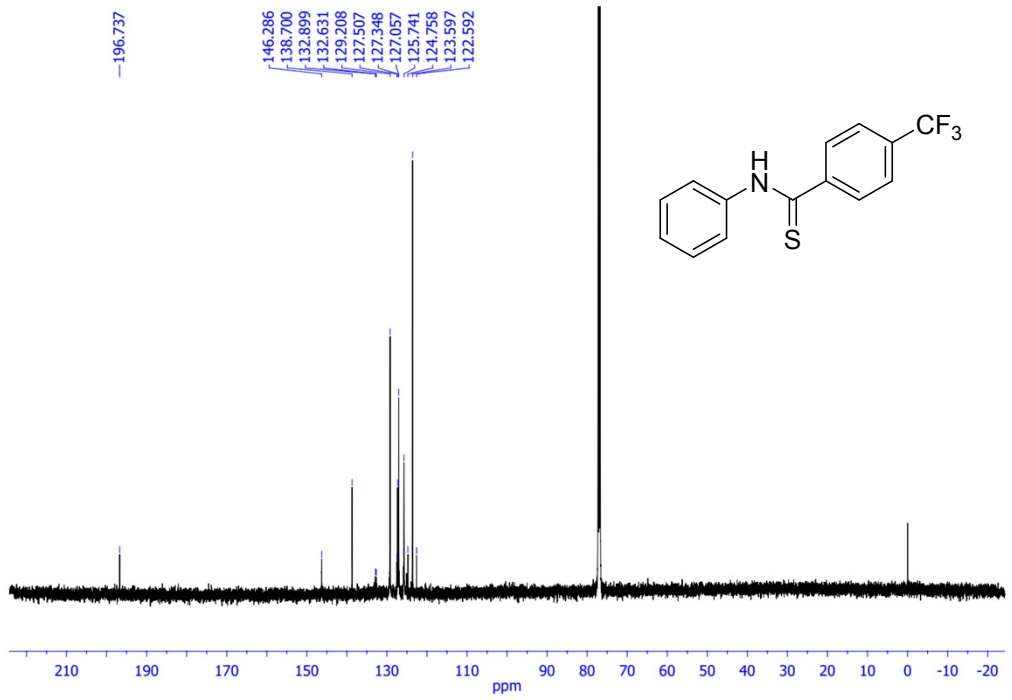


Fig. S28. ^{13}C NMR spectrum of **3fa**.

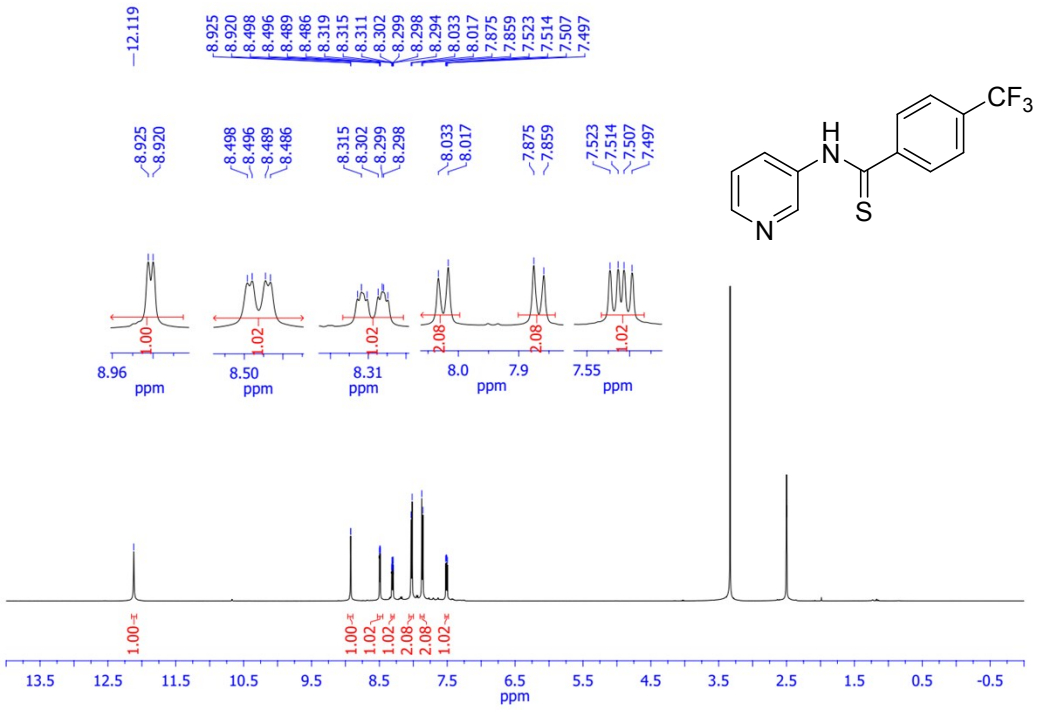


Fig. S27. ^{1}H NMR spectrum of **3ff**.

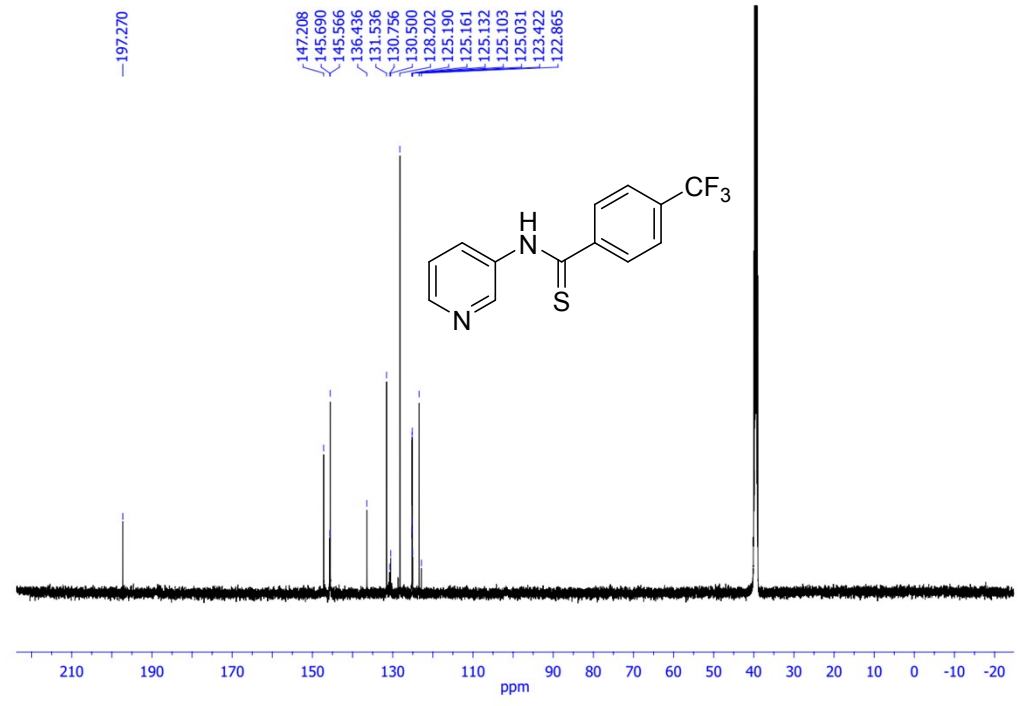


Fig. S29. ^{13}C NMR spectrum of **3ff**.

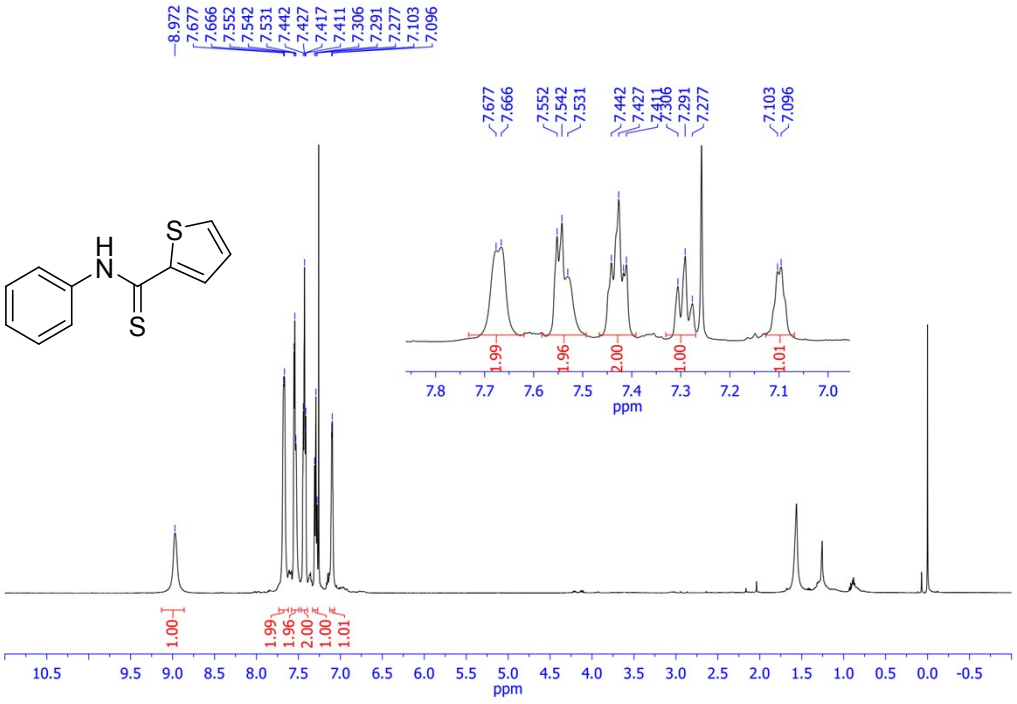


Fig. S30. [1]H NMR spectrum of **3ga.**

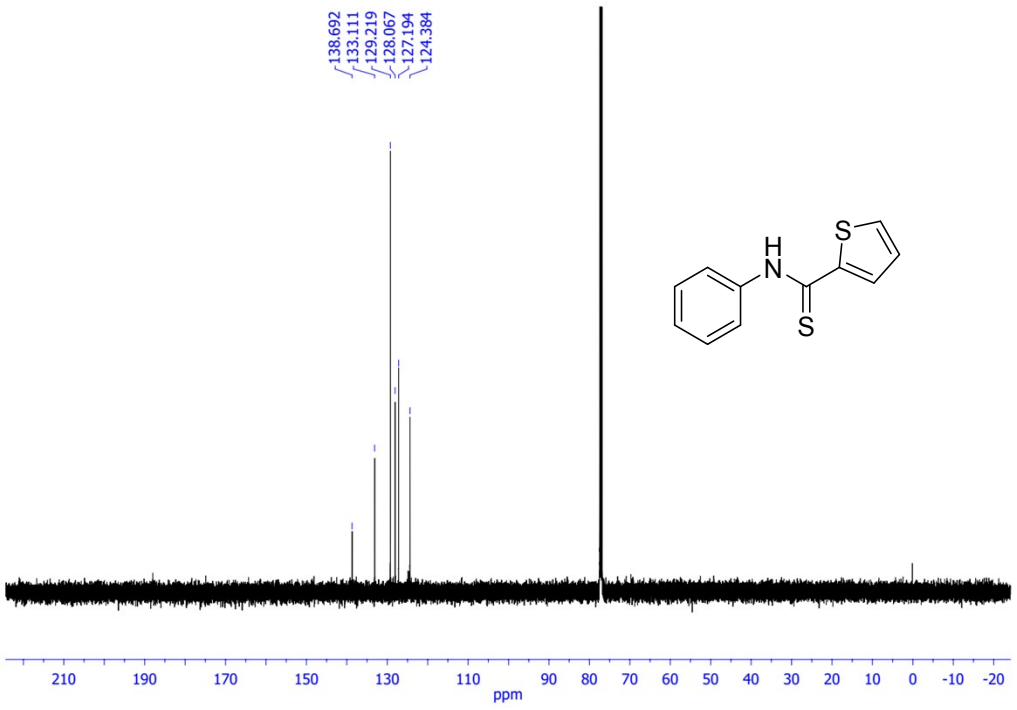


Fig. S31. [13]C NMR spectrum of **3ga.**

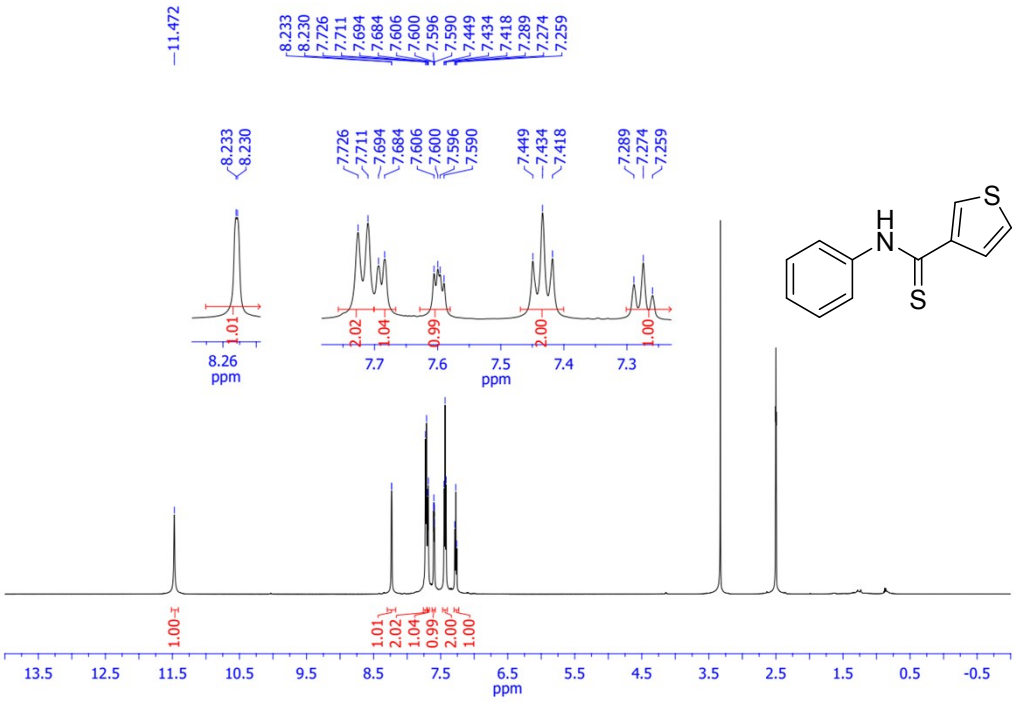


Fig. S32. [1]H NMR spectrum of **3ha.**

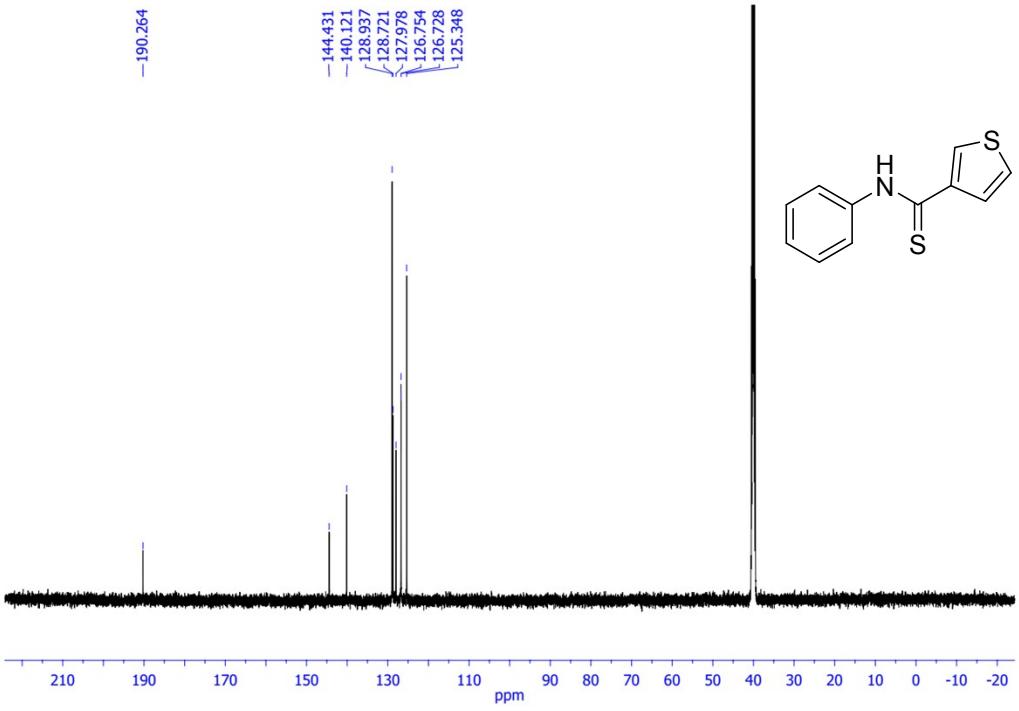


Fig. S33. [13]C NMR spectrum of **3ha.**

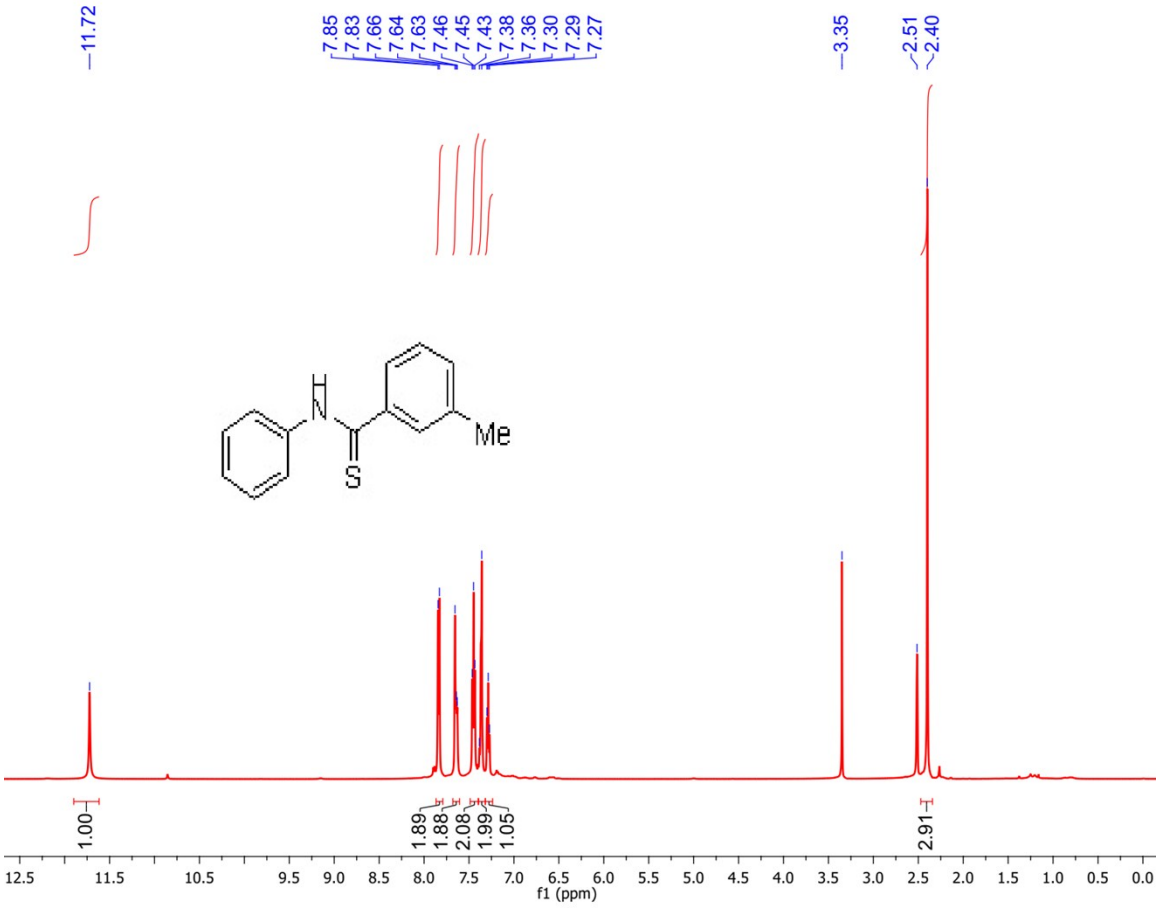


Fig. S34. ^{1}H NMR spectrum of **3ia.**

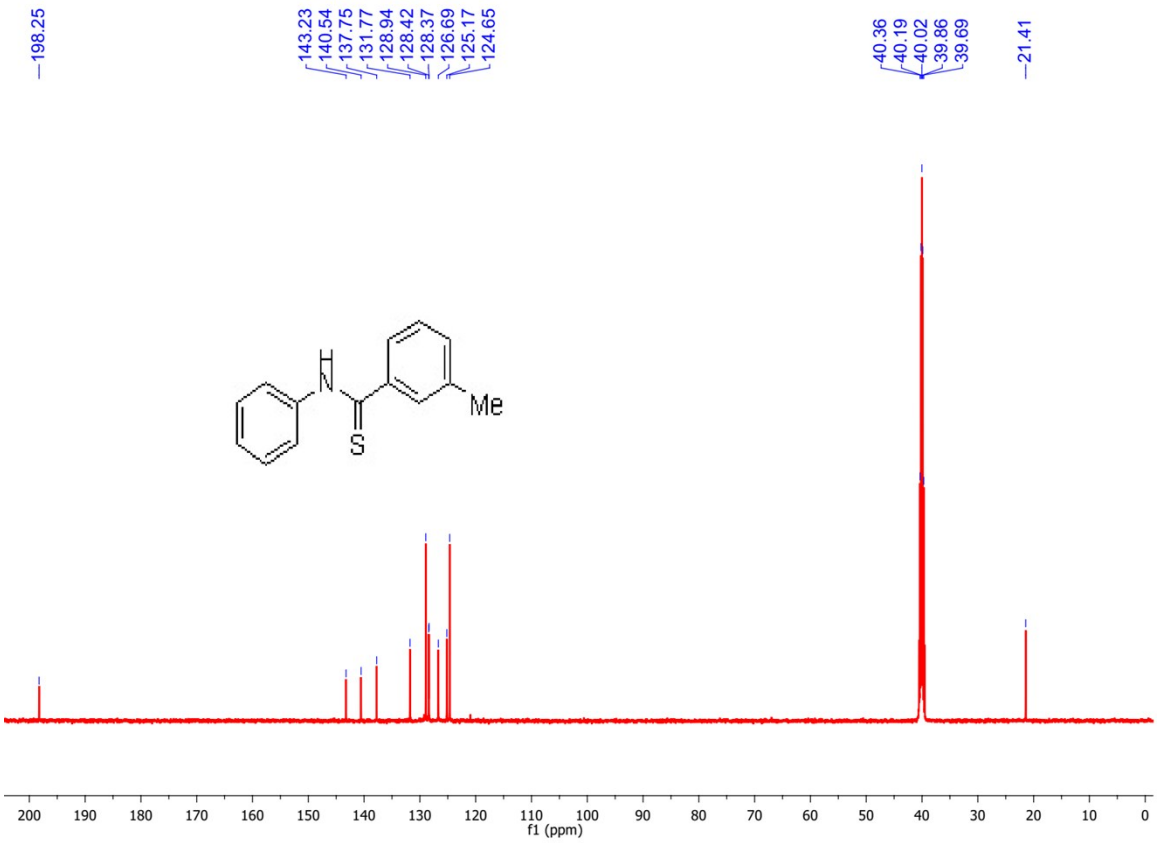


Fig. S35. ^{13}C NMR spectrum of **3ia.**