Supplementary Information (SI) for New Journal of Chemistry.

SUPPORTING INFORMATION

Visible Light Assisted Oxidations of Organic Compounds by Iridium(III)dipyrrinato Complexes

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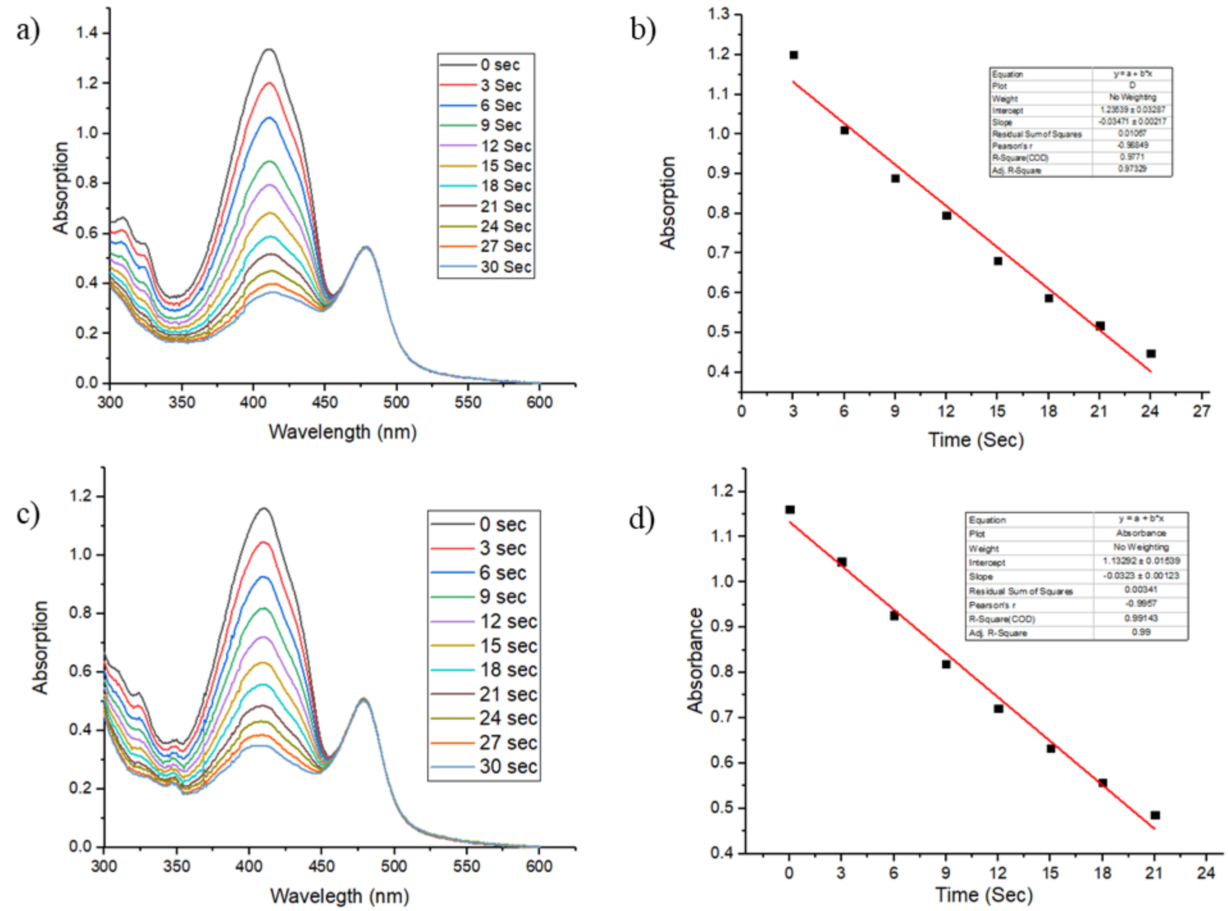
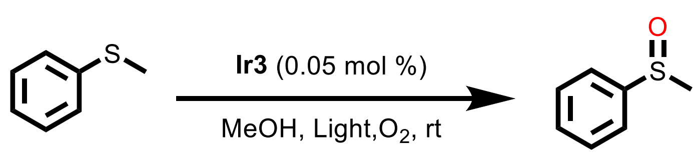


Figure S1: Singlet oxygen generation experiment absorbance spectra of: (a) **Ir1** and (c) **Ir2** complex upon irradiation of light (λ = 300–600 nm); rate of decrease of absorbance of DPBF at 411 nm by: (b) **Ir1** and (d) **Ir2** complex.

Table S1. Light optimization experiments[a]



1a 2a

Entry	Light	Catalyst	% Yield[b]
1	Blue	**Ir 3**	16
2	Green	**Ir 3**	93
3	Red	**Ir 3**	26
4	White	**Ir 3**	98
5	Sunlight	**Ir 3**	96

[a]Reaction condition**:** Methylphenyl sulfide (1 mmol), **Ir3** (0.05 mol %), solvent MeOH 4mL, irradiation with light (24 W) for under O_2 at rt. [b]Yield was calculated by ^{1}H-NMR using 1,3,5 trimethylbenzene (1 mmol) as an internal standard.

Characterization data of substrates

N-benzyliden-1-phenylmethanimine (2a): R_f = 0.59 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.39 (s, 1H), 7.79-7.77 (m, 2H), 7.43-7.41 (m, 3H), 7.33-7.32 (m, 4H), 7.27-7.24 (m, 1H), 4.82 (s, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 162.0, 139.2, 136.1, 130.7, 128.5, 128.4, 128.2, 127.9, 126.9, 65.0.

N-(4-methoxybenzylidene)-4-methoxybenzylamine (2b): R_f = 0.32 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.28 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 9 Hz 2H), 6.91 (d, *J* = 9 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.72 (s, 2H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 161.7, 161.1, 158.6, 131.5, 129.8, 129.2, 129.0, 114.0, 113.9, 64.3, 55.4, 55.3.

N-(2-methylbenzyl)-1-(o-tolyl)methanimine (2c): R_f = 0.50 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.67 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.31-7.25 (m, 2H), 7.24-7.23 (m, 1H), 7.22-7.14 (m, 4H), 4.82 (s, 2H), 2.50 (s, 3H), 2.39 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 160.5, 137.7, 137.6, 136.1, 134.2, 130.8, 130.2, 130.1, 128.3, 127.6, 127.0, 126.2, 126.0, 63.3, 19.4, 19.3.

N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (2d): R_f = 0.32 (hexane: EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.34 (s, 1H), 7.78-7.76 (m, 2H), 7.31-7.28 (m, 2H), 7.12-7.08(m, 2H), 7.05-7.01 (m, 2H), 4.77 (s, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 165.4, 163.2 (*J* = 58 Hz), 160.9 (*J* = 19 Hz), 134.7, 132.1, 130.2 (*J* = 8 Hz), 129.5 (*J* = 7 Hz), 115.7 (*J* = 21 Hz), 115.3 (*J* = 21 Hz), 64.1; ^{19}F (470 MHz, Chloroform-d) δ_F (in ppm): -108, -115.

N-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (2e): R_f = 0.32 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.72 (s, 1H), 8.03 (t, *J* = 7.5 Hz, 1H), 7.42-7.36 (m, 2H), 7.28-7.23 (m, 1H), 7.18-7.04 (m, 4H), 4.88 (s, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 162.5(d, *J* = 191.2 Hz), 160.5(d, *J* = 185.0 Hz), 156.1(d, *J* = 5 Hz), 132.4 (d, *J* = 8.7 Hz), 130.1 (d, *J* = 3.7 Hz), 128.8 (d, *J* = 7.5 Hz), 127.8 (d, *J* = 2.5 Hz), 126.1 (d, *J* = 15 Hz), 124.4 (d, *J* = 2.5 Hz), 124.1 (d, *J* = 2.5 Hz), 123.7 (d, *J* = 8.7 Hz), 115.7 (d, *J* = 21.2 Hz), 115.2 (d, *J* = 21.2 Hz), 58.5 (d, *J* = 2.5 Hz); ^{19}F (470 MHz, Chloroform-d) δ_F (in ppm): -118, -121.

N-(4-(Trifluoromethyl)benzylidene)-4-benzylamine (2f): R_f = 0.49 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.4 (s, 1H), 7.91 (d, *J* = 8 Hz, 2H), 7.69 (d, *J* = 8 Hz, 2H), 7.61 (d, *J* = 8 Hz, 2H), 7.47 (d, *J* = 8 Hz, 2H), 4.90 (s, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 161.1, 142.9, 138.9, 132.6 (q, *J* = 31 Hz),129.4 (q, *J* = 32 Hz), 128.5, 128.1, 125.6 (q, *J* = 7 Hz), 125.4 (q, *J* = 7 Hz), 124.2 (q, *J* = 270 Hz), 123.8 (q, *J* = 270 Hz); ^{19}F (470 MHz, Chloroform-d) δ_F (in ppm): -62.4, -62.8.

N-(4-bromobenzyl)-1-(4-Bromophenyl)methanimine (2g): R_f = 0.53 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.31 (s, 1H), 7.64 (d, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 7 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 4.74 (s, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 161.0, 138.1, 134.8, 131.9, 131.6, 129.7, 129.6, 125.4, 120.9, 64.2.

N-(2-bromobenzyl)-1-(2-bromophenyl)methanimine (2h): R_f = 0.52 (hexane:EtOAc, 9:1); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.81 (s, 1H), 8.10 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.58 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 8 Hz, 1H), 7.37-7.27 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.93 (s, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 162.0, 138.4, 134.5, 133.0, 132.6, 132.0, 129.8, 128.9, 128.6, 127.6, 127.5, 125.2, 123.6, 64.4.

N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (2i): R_f = 0.54 (hexane: EtOAc, 9:1); ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ_H (in ppm): 8.51 (s, 1H), 7.80 (d, *J* = 8.5 Hz 2H), 7.53 (d, *J* = 8.5 Hz 2H), 7.40 (d, *J* = 6.5 Hz, 2H), 7.36 (d, *J* = 9 Hz 2H), 4.76 (s, 2H); ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ_C (in ppm): 161.5, 139.0, 135.9, 135.2, 131.8, 130.1, 130.1, 129.3, 128.8, 63.3.

3,4-dihydroisoquinoline (2j): R_f = 0.32 (EtOAc); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.33 (s, 1H), 7.36-7.33 (m, 1H), 7.31-7.25 (m, 2H), 7.15 (d, *J* = 7 Hz, 1H), 3.78-3.75 (m, 2H), 2.74 (t, *J* = 8 Hz, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 160.3, 136.3, 131.0, 128.5, 127.4, 127.2, 127.0, 47.3, 25.0.

(methylsulfinyl)benzene (4a): R_f = 0.63 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.57-7.55 (m, 2H), 7.45-7.40 (m, 3H), 2.63 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 145.6, 131.0, 129.3, 123.5, 43.9.

1-methyl-4-(methylsulfinyl)benzene (4b): R_f = 0.58 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.50 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.67 (s, 3H), 2.37 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 142.4, 141.5, 130.0, 123.5, 43.9, 21.4.

1-methoxy-4-(methylsulfinyl)benzene (4c): R_f = 0.80 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.58 (d, *J* = 9 Hz, 2H), 7.01 (d, *J* = 9 Hz, 2H), 3.84 (s, 3H), 2.68 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 161.9, 136.5, 125.4, 114.8, 55.5, 43.9.

1-fluoro-4-(methylsulfinyl)benzene (4d): R_f = 0.47 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d): δ_H (in ppm) 7.58-7.55 (m, 2H), 7.13 (t, *J* = 8.5 Hz , 2H), 2.63 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 164.2 (*J* = 250), 141.0 (*J* = 2.5), 125.8 (*J* = 7.5), 116.6 (*J* = 22.5), 44.0 ; ^{19}F (470 MHz, Chloroform-d) δ_F (in ppm): -108.

1-chloro-4-(methylsulfinyl)benzene (4e): R_f = 0.61 (hexane:EtOAc:MeOH, 6.5:3:0.5)**;** ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.57 (d, J = 8.5 Hz , 2H), 7.49 (d, J = 8.5 Hz , 2H), 2.70 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 144.2, 137.2, 129.6, 124.9, 44.0.

1-bromo-4-(methylsulfinyl)benzene (4f): R_f = 0.62 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.63 (d, J = 10 Hz , 2H), 7.49 (d, J = 5 Hz , 2H), 2.68 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 144.7, 132.6, 125.5, 125.1, 43.9.

1-bromo-3-(methylsulfinyl)benzene (4g): R_f = 0.35 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.79 (t, J = 2 Hz, 1H), 7.62-7.60 (m, 1H), 7.54-7.52 (m, 1H), 7.39 (t, J = 8 Hz, 1H), 2.73 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 148.0, 134.1, 130.8, 126.4, 123.6, 122.0, 44.0.

1-bromo-2-(methylsulfinyl)benzene (4h): R_f = 0.49 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.94 (dd, J = 8 Hz, J = 1.5 Hz, 2H), 7.60-7.55 (m, 2H), 7.38 (td, J = 8 Hz, J = 1 Hz, 1H) 2.82 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 145.2, 132.8, 132.2, 128.7, 125.6, 118.3, 41.8.

1-bromo-3-(ethylsulfinyl)benzene (4i): R_f = 0.46 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.74 (s, 1H), 7.60-7.58 (m, 1H), 7.48-7.47 (d, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 1H), 2.94-2.87 (m, 1H), 2.77-2.70 (m, 1H), 1.18 (t, J = 7.5 Hz, 3H) ; ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 145.6, 134.0, 130.6, 127.0, 123.4, 122.7, 50.3, 5.8.

1-(methylsulfinyl)-4-nitrobenzene (4j): R_f = 0.58 (EtOAc); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 8.37 (d, J = 9 Hz , 2H), 7.82 (d, J = 9 Hz , 2H), 2.78 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 153.2, 149.5, 124.6, 124.4, 43.8.

4-(methylsulfinyl)benzonitrile (4k): R_f = 0.55 (EtOAc); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.80 (d, J = 8.5 Hz , 2H), 7.74 (d, J = 8.5 Hz , 2H), 2.73 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 151.4, 133.0, 124.3, 117.4, 114.7 43.7.

4-(methylsulfinyl)phenol (4l): R_f = 0.44 (EtOAc); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.48 (d, J = 8.5 Hz , 2H), 6.95 (d, J = 8.5 Hz , 2H), 2.74 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 160.5, 133.3, 126.1, 116.8, 43.0.

Tetrahydro-4H-thiopyran-4-one 1-oxide (4m): R_f = 0.54 (EtOAc); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 9.67 (s, 1H), 7.86 (d, J = 7.5 Hz, 2H), 3.37-3.30 (m, 4H), 2.90-2.87 (m, 2H), 2.56-2.52 (m, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 204.7, 47.2, 32.2.

2-(tert-butylsulfinyl)-2-methylpropane (4n): R_f = 0.38 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 1.32 (s, 18H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 57.2, 25.5.

1-(butylsulfinyl)butane (4o): R_f = 0.71 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 2.68-2.55 (m, 4H), 1.71-1.64 (m, 4H), 1.48-1.35 (m, 4H), 0.90 (t, J = 7 Hz, 6H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 51.9, 24.5, 22.0, 13.6.

Sulfinyldibenzene (4p): R_f = 0.79 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 7.66-7.64 (m, 4H), 7.48-7.43 (m, 6H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 145.6, 131.0, 129.3, 124.8.

10H-phenothiazine 5-oxide (4q): R_f = 0.19 (hexane:EtOAc:MeOH, 6.5:3:0.5); ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 9.67 (s, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.15-7.11 (m, 2H), 7.07-7.04 (m, 2H), 6.59-6.58 (m, 2H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 136.5, 132.2, 131.0, 121.1, 119.8, 116.7.

4-methoxyphenol (6a): ^{1}H-NMR (500 MHz, Chloroform-d) δ_H (in ppm): 6.79-6.77 (m, 4H), 3.76 (s, 3H); ^{13}C-NMR (125 MHz, Chloroform-d) δ_C (in ppm): 153.7, 149.5, 116.0, 114.8, 55.8.

4-methylphenol (6b): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 9.11 (s, 1H), 6.96(d, *J* = 6.5 Hz, 2H), 6.68 (s, 2H), 2.18 (s, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 155.5, 130.1, 127.6, 115.4, 20.5.

3-methylphenol (6c): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 9.21 (s, 1H), 7.03 (t, *J* = 8 Hz, 1H), 6.58-6.53 (m, 3H), 2.21 (s, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 157.7, 139.1, 129.5, 120.0, 116.3, 112.7, 21.5.

2-methylphenol (6d): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 9.21 (s, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.97 (m, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.69 (m, *J* = 7 Hz, 1H), 2.10 (s, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 155.8, 130.9, 127.0, 124.1, 119.2, 115.0, 16.42.

3,4-dimethoxyphenol (6e): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 8.98 (s, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 3 Hz, 1H), 6.24 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 3.69 (s, 3H), 3.64 (s,3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 152.3, 150.1, 142.1, 114.0, 106.0, 101.2, 56.8, 55.7.

phenol (6f): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 9.37 (s, 1H), 7.18-7.15 (m, 2H), 6.79-6.77 (m, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 157.7, 129.8, 119.2, 115.7.

4-hydroxybenzonitrile (6g): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 10.62 (s, 1H), 7.65 (d, *J* = 9 Hz, 2H), 6.91 (d, *J* = 9 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 162.0, 134.7, 120.0, 116.8, 111.4.

4-nitrophenol (6h): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 11.05 (s, 1H), 8.12 (d, *J* = 9 Hz, 2H), 6.94 (d, *J* = 9 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 164.3, 140.0, 126.6, 116.2.

3-(trifluoromethyl)phenol (6i): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 10.12 (s, 1H), 7.40 (t, *J* = 8 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 11.5 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 196.4, 162.4, 131.1, 129.0, 115.6, 26.7. ^{19}F-NMR (470 MHz, DMSO-d_6) δ_C (in ppm): 61.2.

4-chlorophenol (6j): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 9.68 (s, 1H), 7.20-7.18 (m, 2H), 6.77-6.76 (d, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 156.7, 129.5, 122.7, 117.3.

4-bromophenol (6k): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 9.70 (s, 1H), 7.32 (d, *J* = 9 Hz, 2H), 6.73 (d, *J* = 9 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 157.2, 132.4, 118.0, 110.3.

1-(4-hydroxyphenyl)ethan-1-one (6l): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 10.36 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 9 Hz, 2H), 2.47 (s, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 196.4, 162.4, 131.1, 129.0, 115.6, 26.7.

4-hydroxybenzoic acid (6m): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 12.40 (s, 1H), 10.24 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 167.6, 162.0, 131.9, 121.8, 115.5.

ethyl 4-hydroxybenzoate (6n): ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H (in ppm): 10.32 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 9 Hz, 2H), 4.27 (q, *J* = 14.5 Hz, 2H) 1.30 (t, *J* = 7.5 Hz 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C (in ppm): 166.0, 162.3, 131.8, 120.9, 115.77, 60.5, 14.7.

4-hydroxybenzaldehyde (6o): ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ_H (in ppm): 10.61 (s, 1H), 9.79 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ_C (in ppm): 191.4, 163.7, 132.5, 128.8, 116.3.

naphthalen-2-ol (6p): ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ_H (in ppm): 9.72 (s, 1H), 7.75 (t, *J* = 6.5 Hz, 2H), 7.68 (d, *J* = 8 Hz, 1H), 7.38 (t, *J* = 7 Hz, 1H), 7.25 (t, *J* = 7 Hz, 1H), 7.10-7.06 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ_C (in ppm): 155.7, 135.0, 129.7, 128.1, 127.9, 126.5, 126.4, 123.0, 119.0, 109.0.

naphthalen-1-ol (6q): ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ_H (in ppm): 10.11 (s, 1H), 8.13 (d, *J* = 8 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.48-7.41 (m, 2H), 7.34-7.28 (m, 2H), 6.88-6.86 (m, 1H); ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ_C (in ppm): 153.6, 134.8, 127.8, 126.8, 126.5, 124.9, 122.4, 118.7, 108.4.

NMR Spectra of substrates

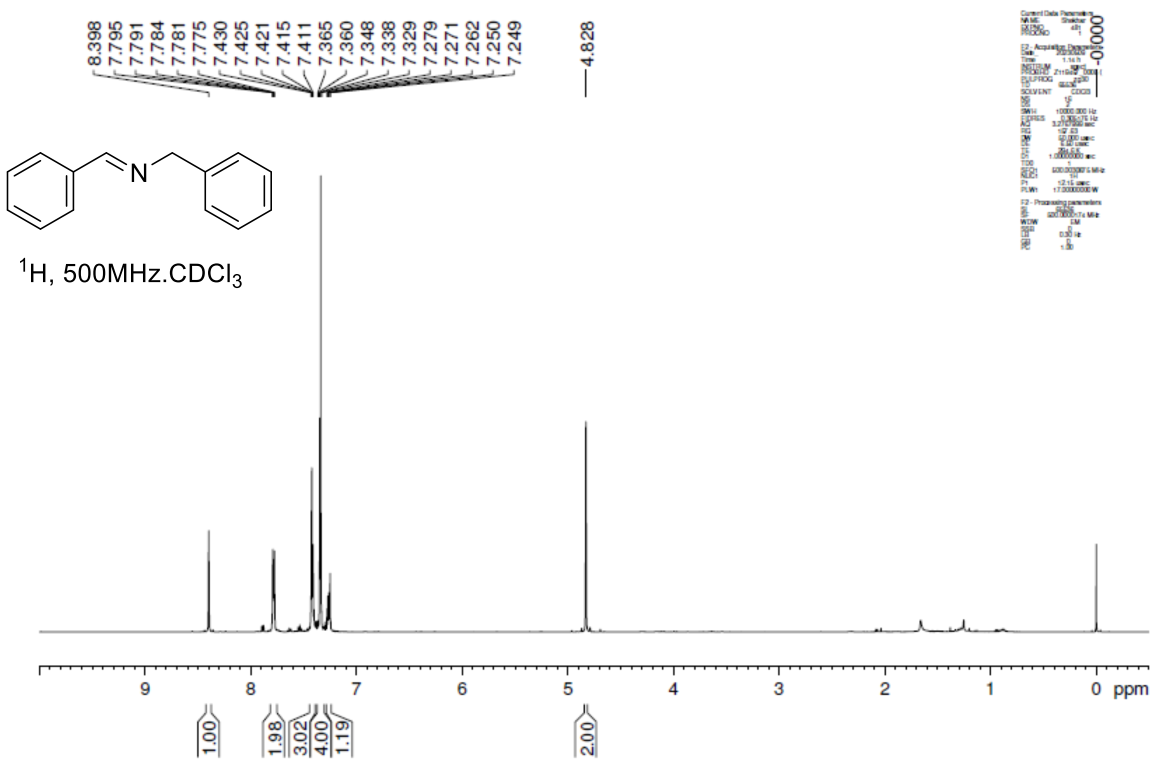


Figure S2. ^{1}H NMR spectrum of **2a** in $CDCl_3$

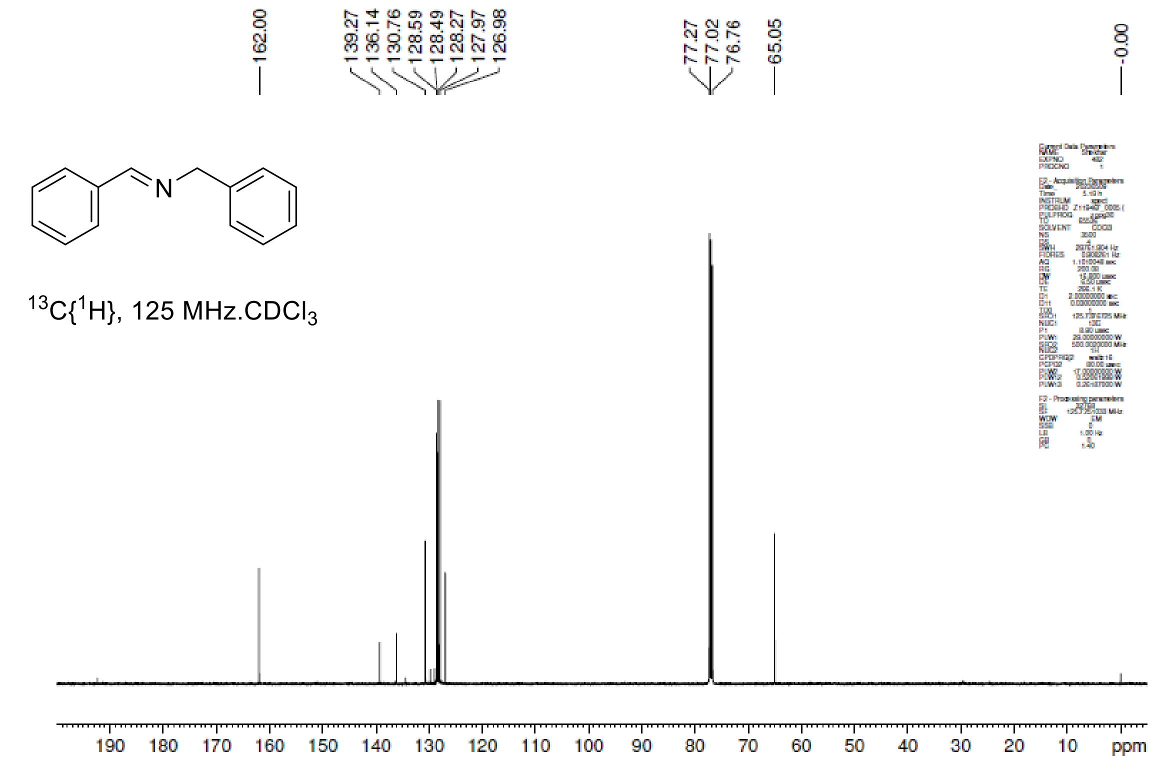


Figure S3. ^{13}C NMR spectrum of **2a** in $CDCl_3$

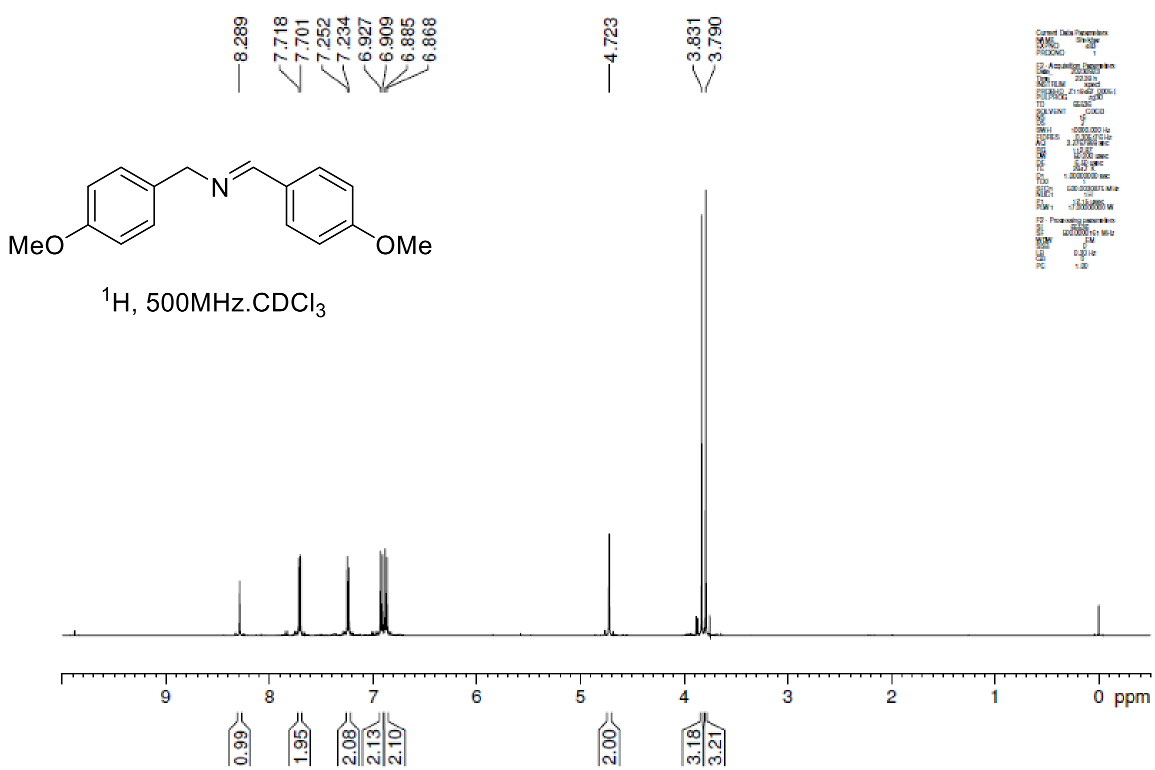


Figure S4. ^{1}H NMR spectrum of **2b** in $CDCl_3$

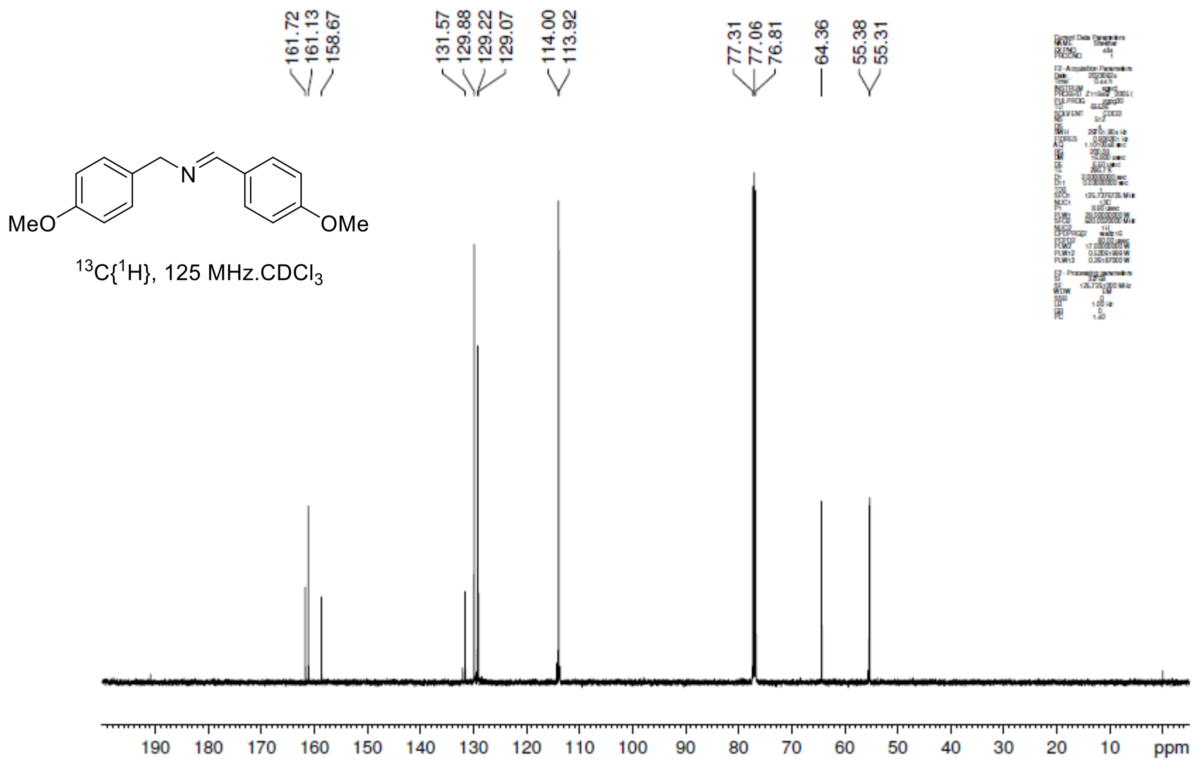


Figure S5. ^{13}C NMR spectrum of **2b** in $CDCl_3$

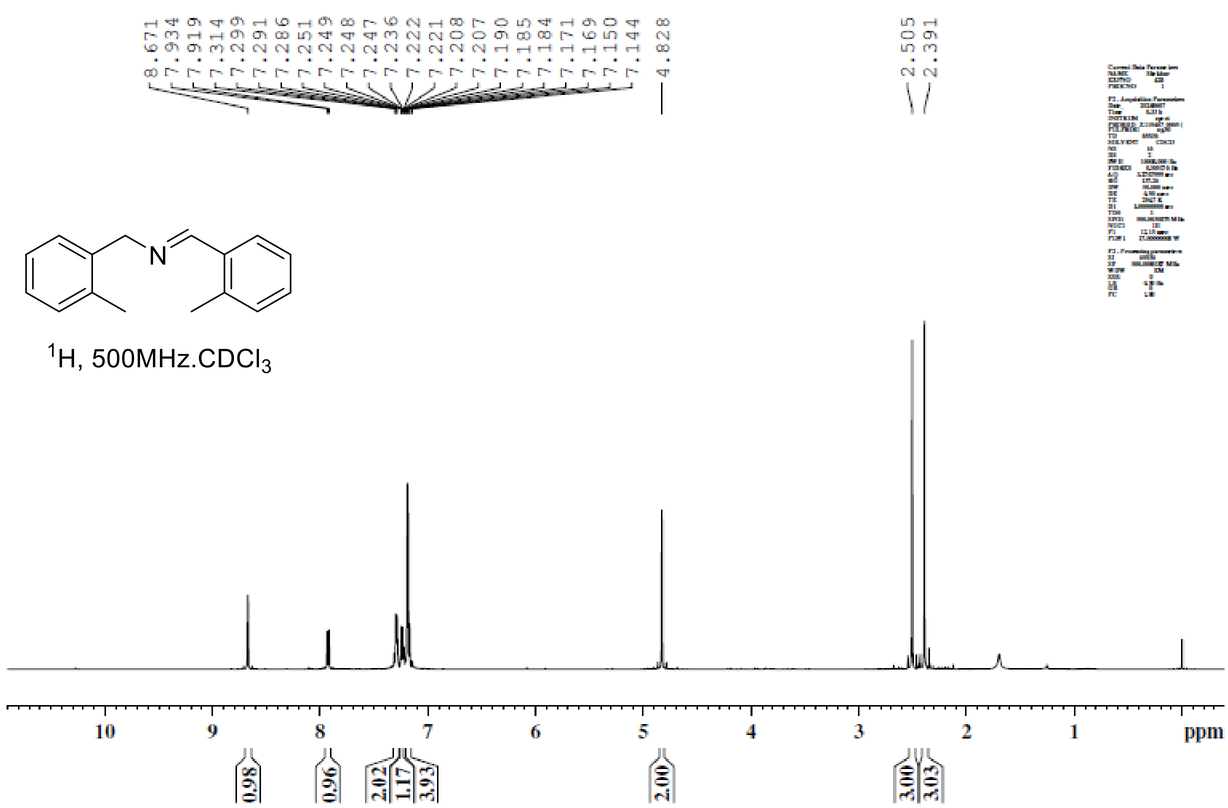


Figure S6. ^1H NMR spectrum of **2c** in $CDCl_3$

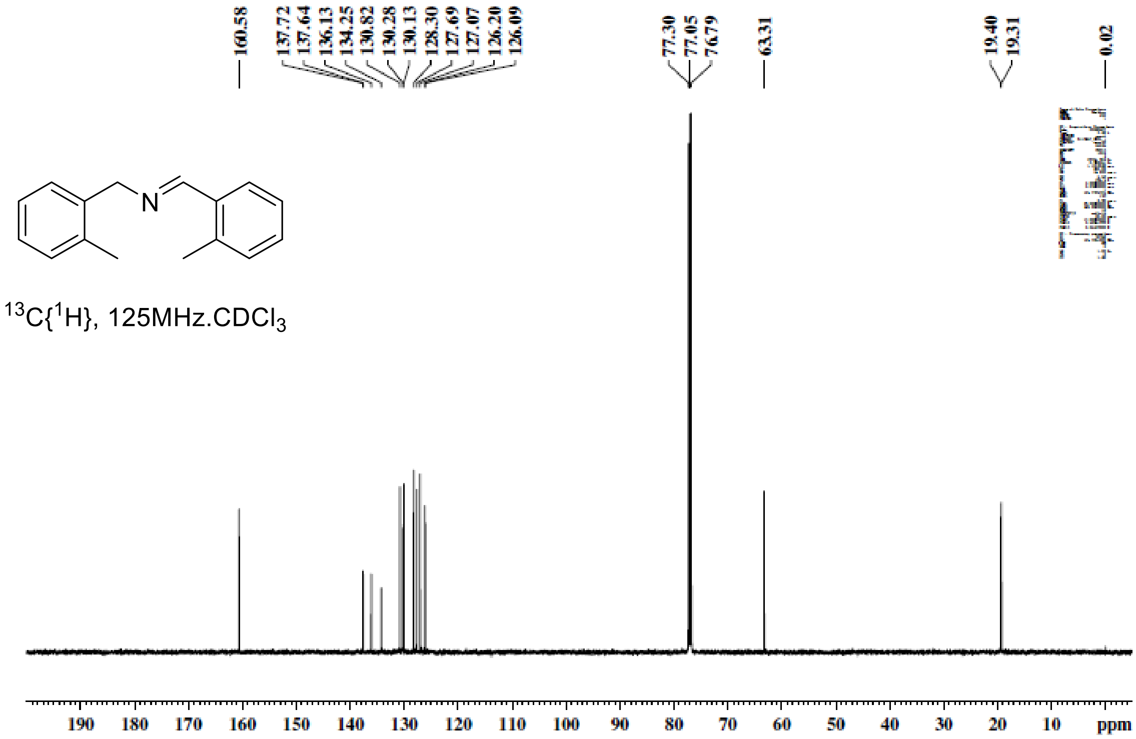


Figure S7. ^{13}C NMR spectrum of **2c** in $CDCl_3$

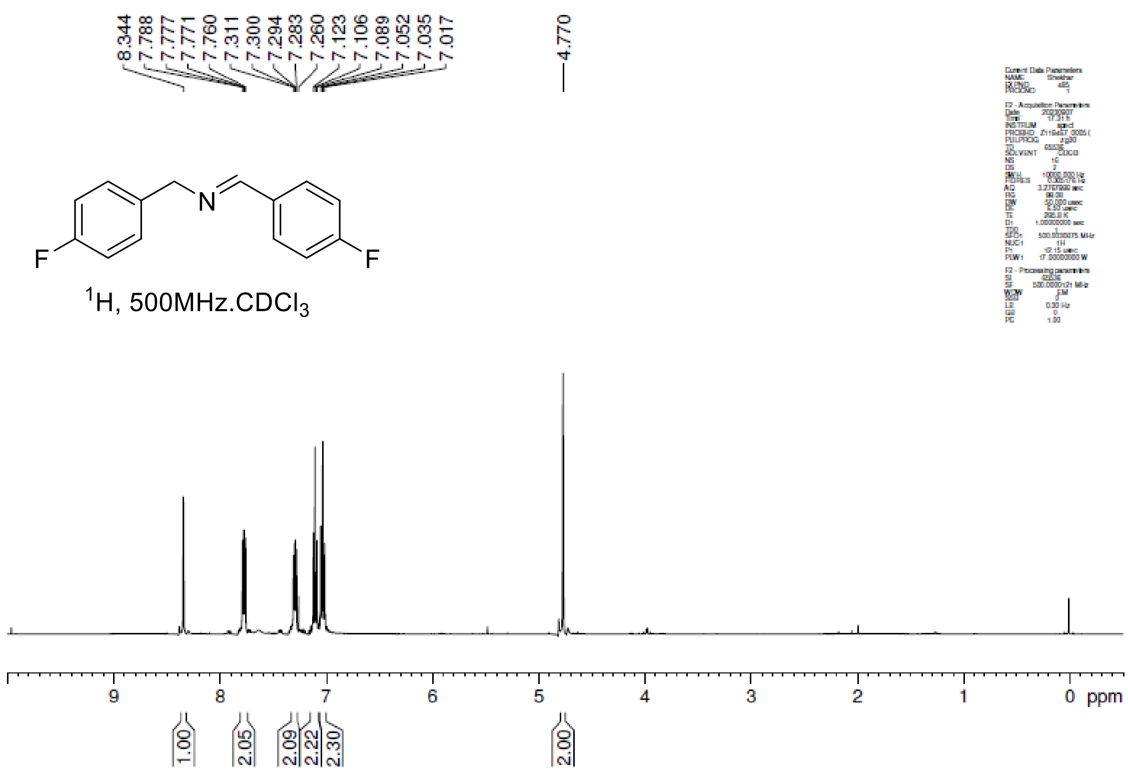


Figure S8. ^{1}H NMR spectrum of **2d** in $CDCl_3$

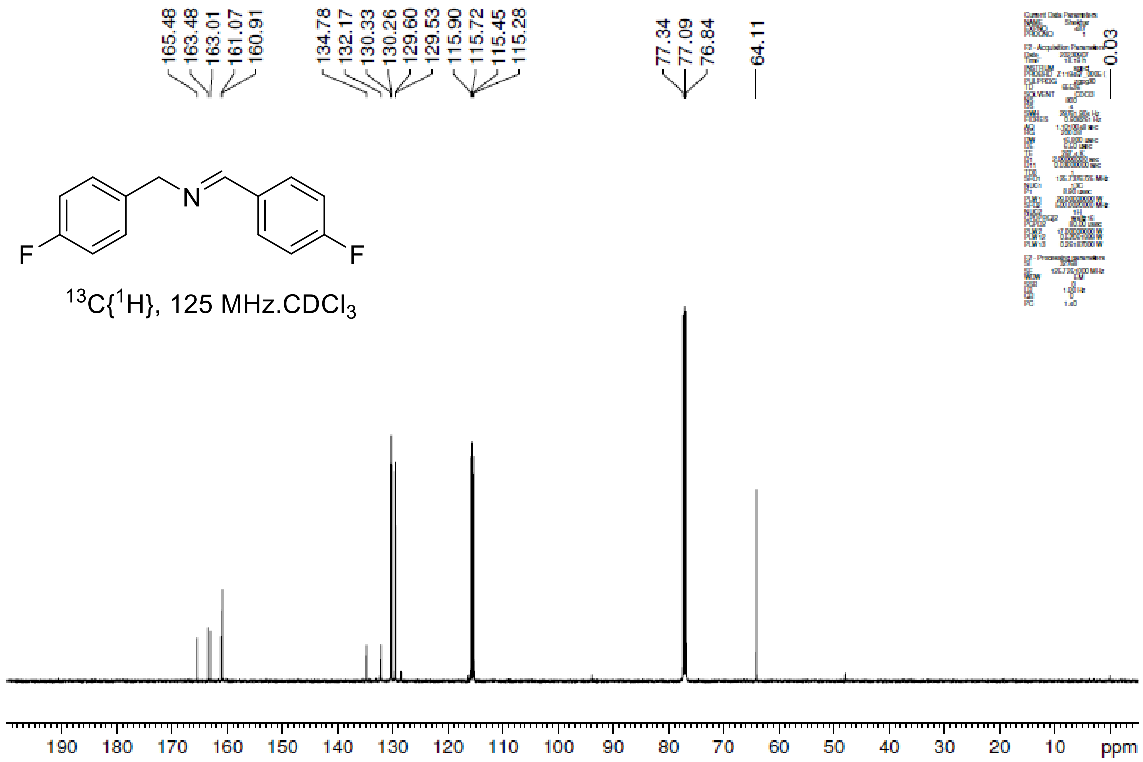


Figure S9. ^{13}C NMR spectrum of **2d** in $CDCl_3$

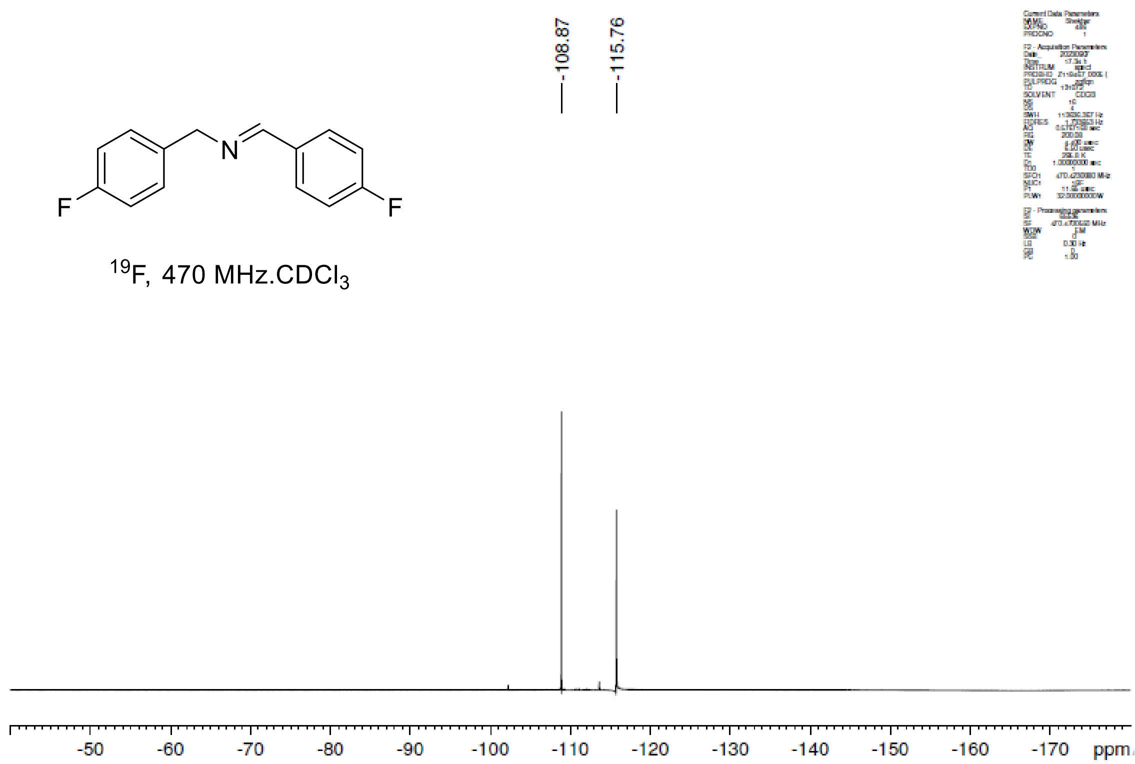


Figure S10. ^{19}F NMR spectrum of **2d** in $CDCl_3$

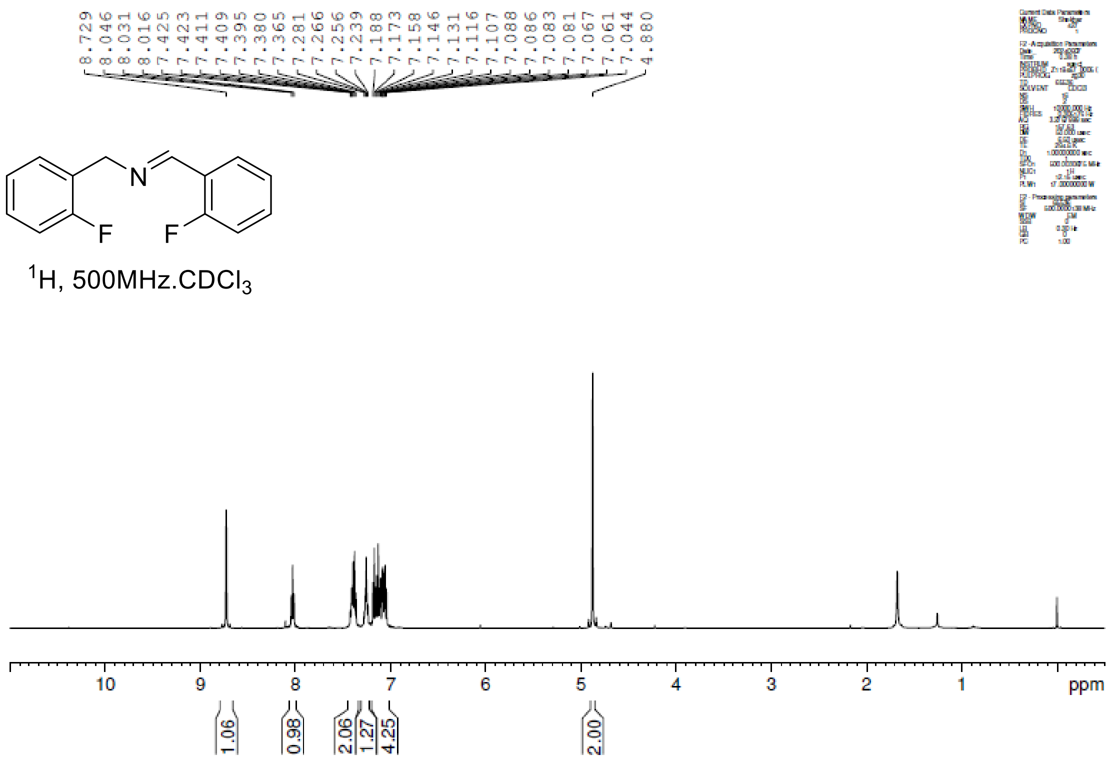


Figure S11. ^{1}H NMR spectrum of **2e** in $CDCl_3$

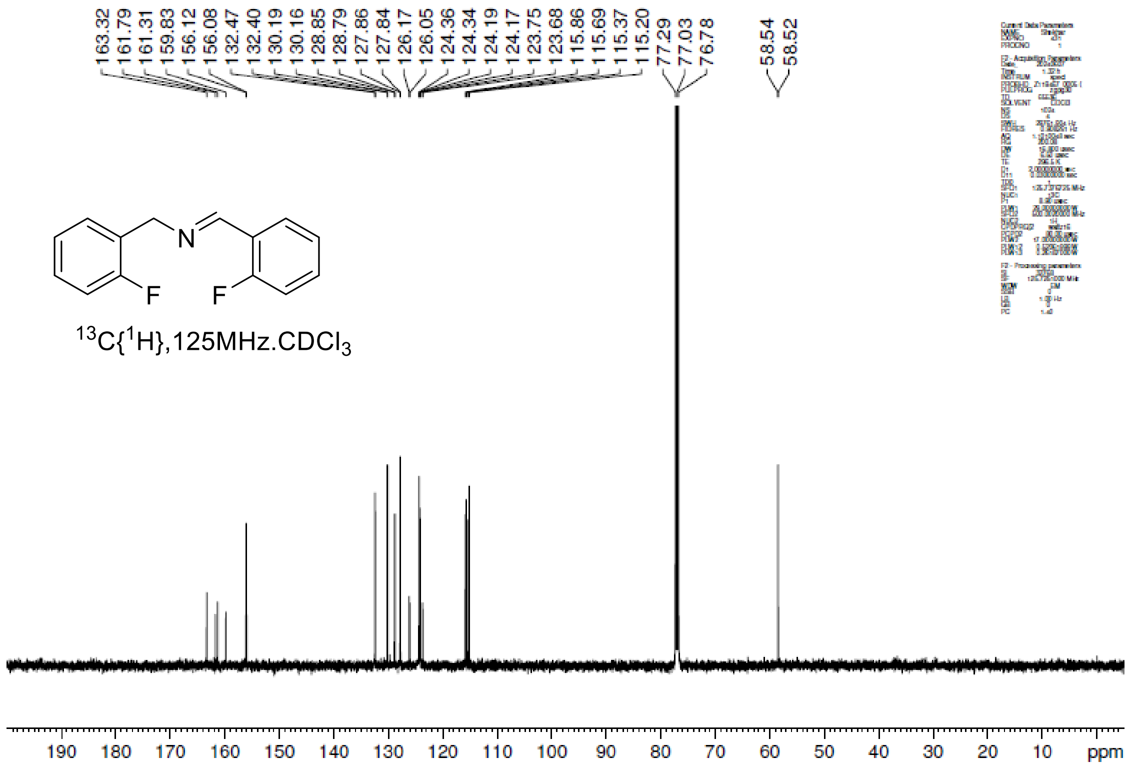


Figure S12. ^{13}C NMR spectrum of **2e** in $CDCl_3$

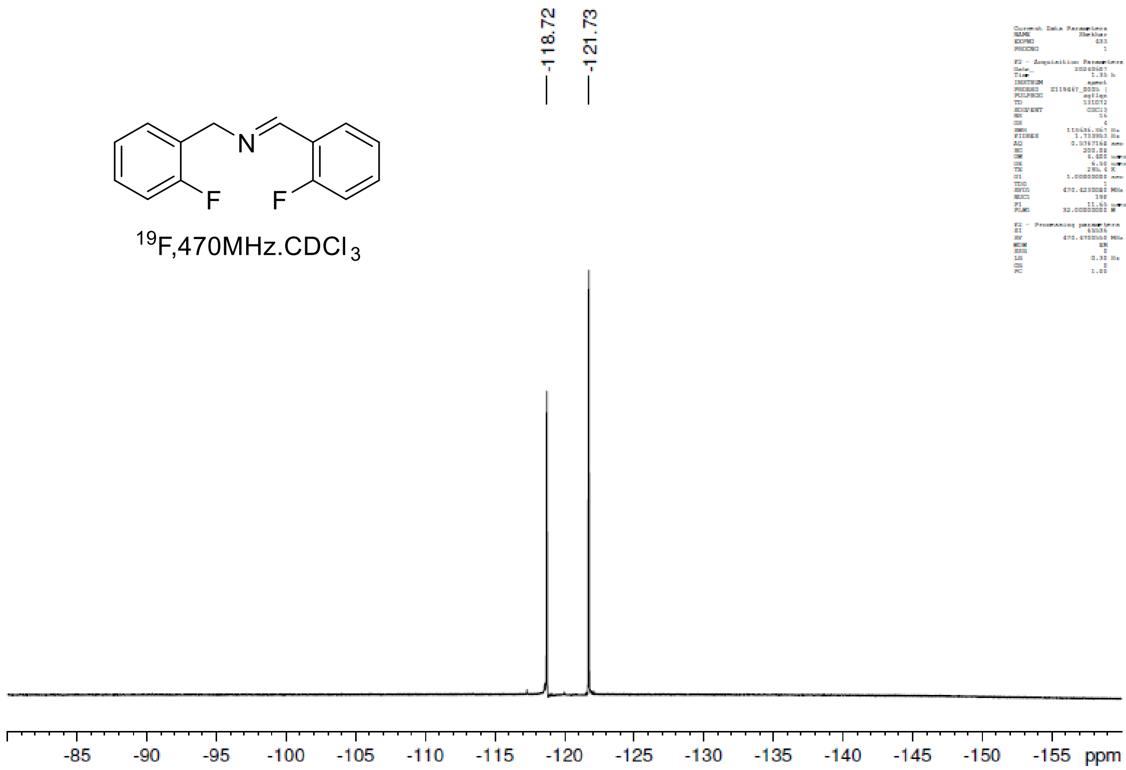


Figure S13. ^{19}F NMR spectrum of **2e** in $CDCl_3$

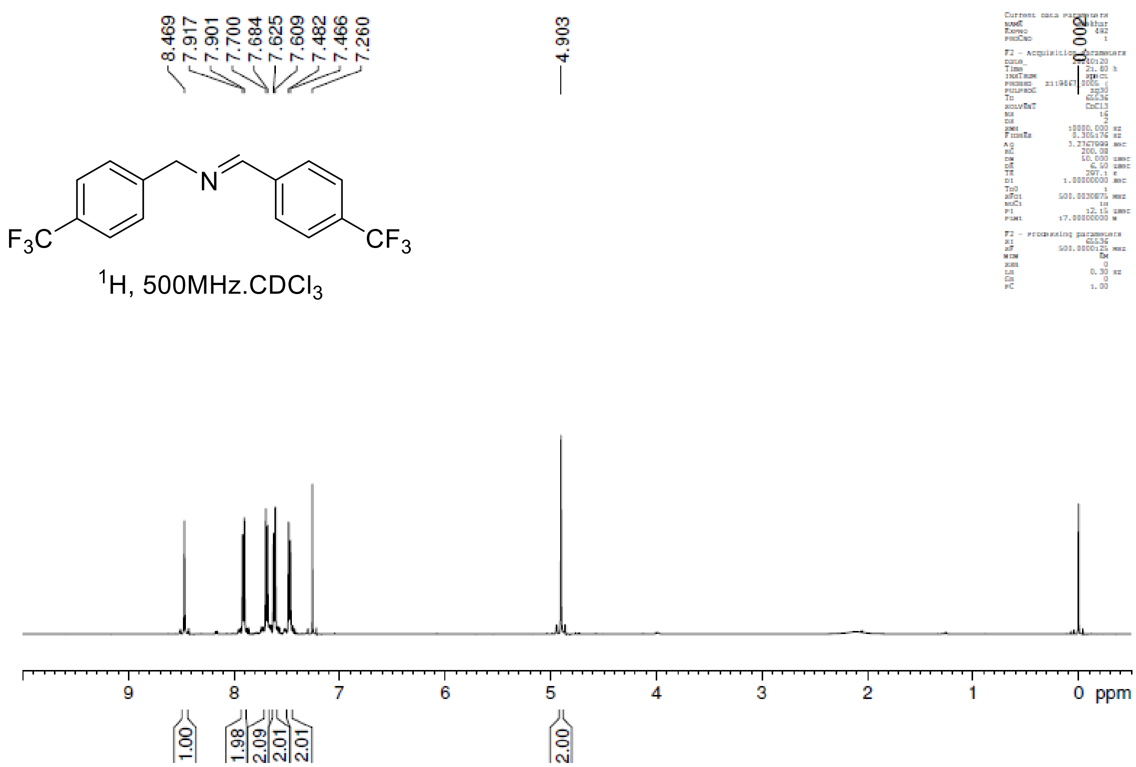


Figure S14. ^{1}H NMR spectrum of **2f** in $CDCl_3$

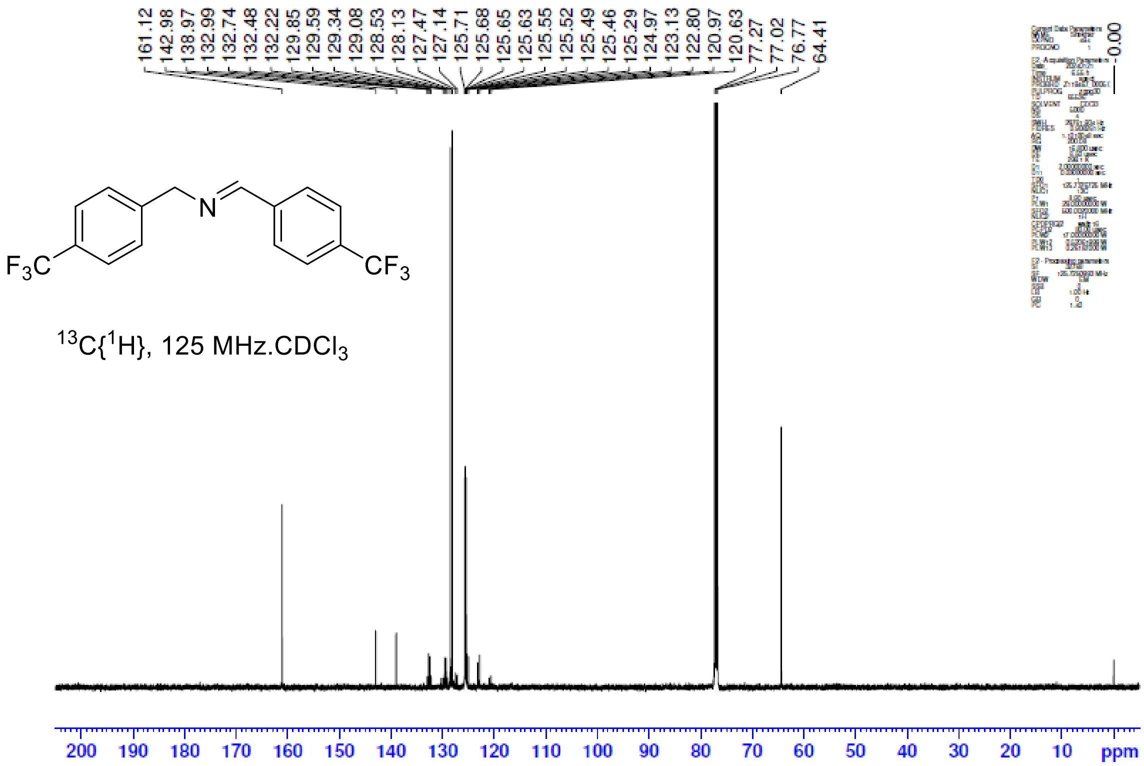


Figure S15. ^{13}C NMR spectrum of **2f** in $CDCl_3$

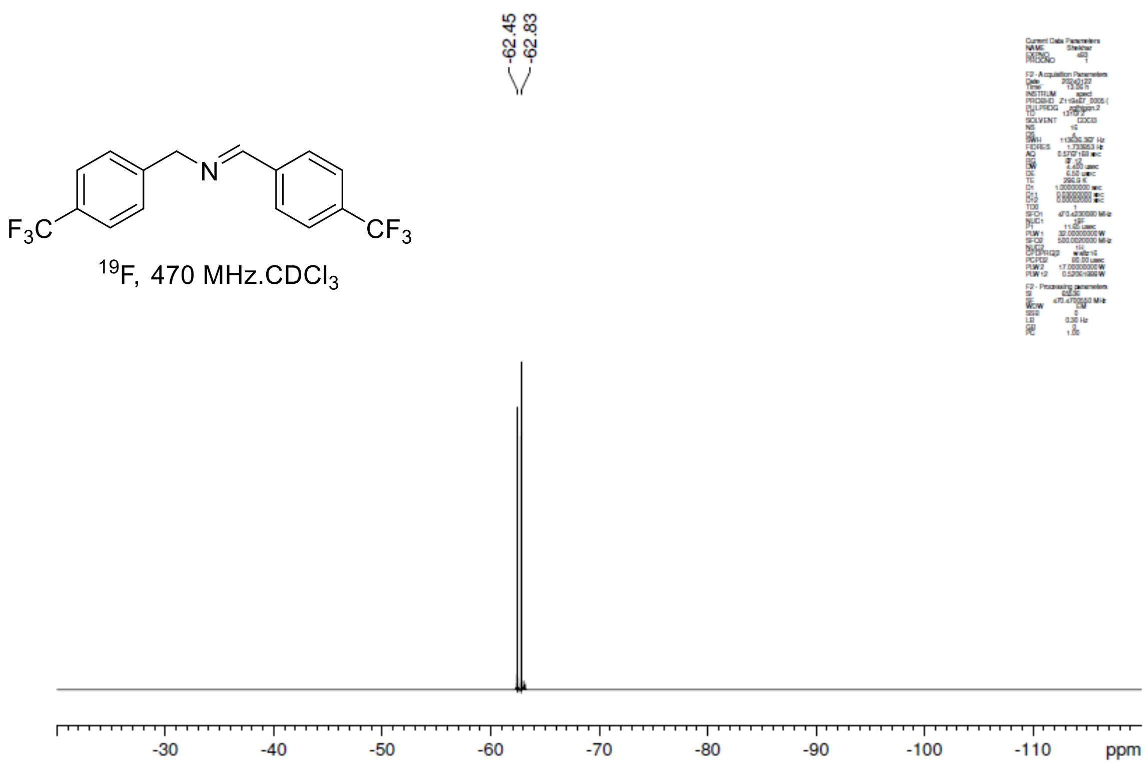


Figure S16. ^{19}F NMR spectrum of **2f** in $CDCl_3$

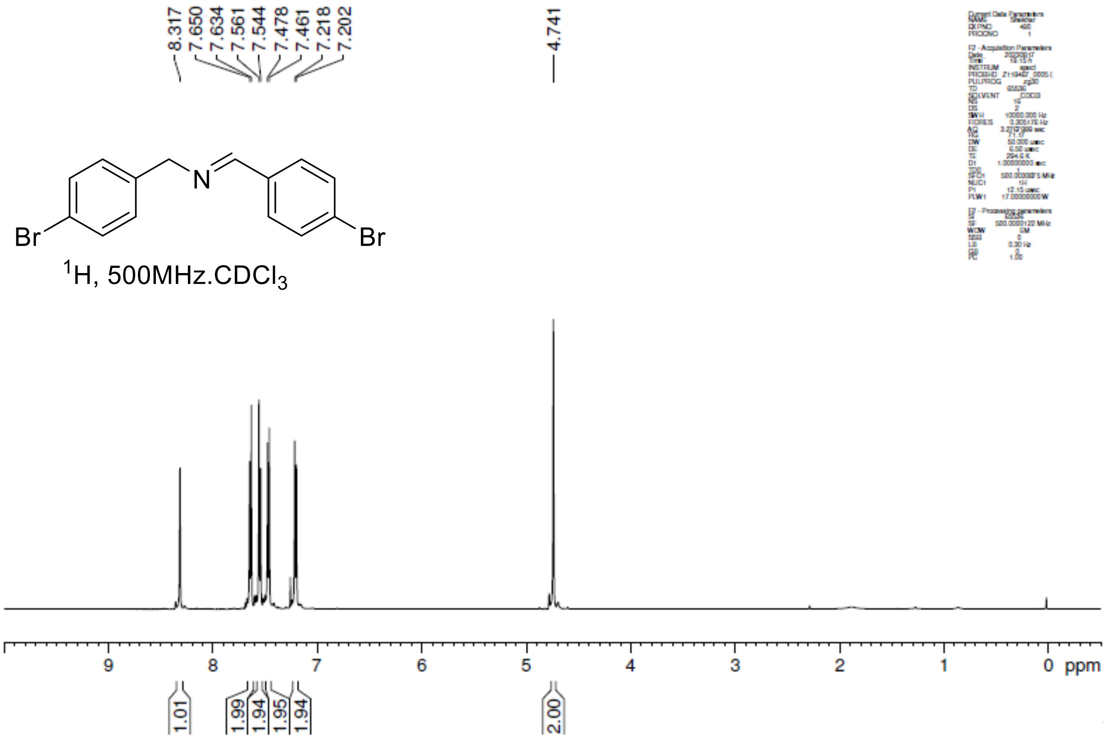


Figure S17. ^{1}H NMR spectrum of **2g** in $CDCl_3$

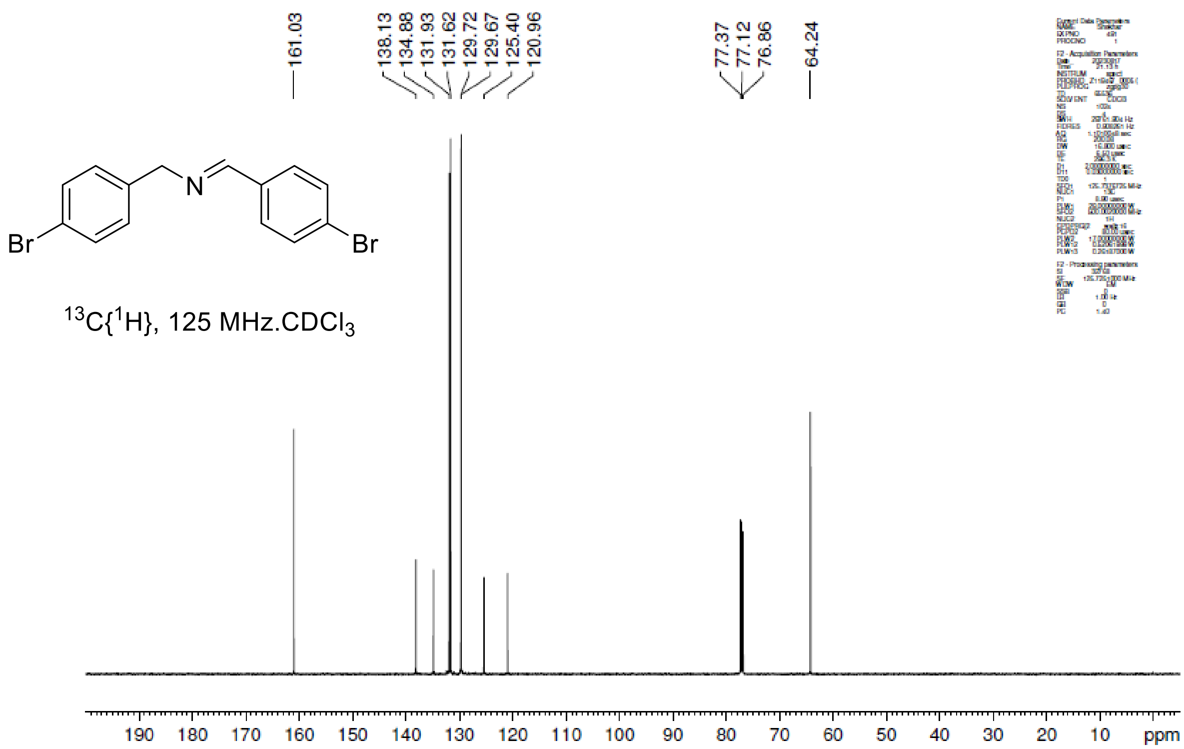


Figure S18. ^{13}C NMR spectrum of **2g** in $CDCl_3$

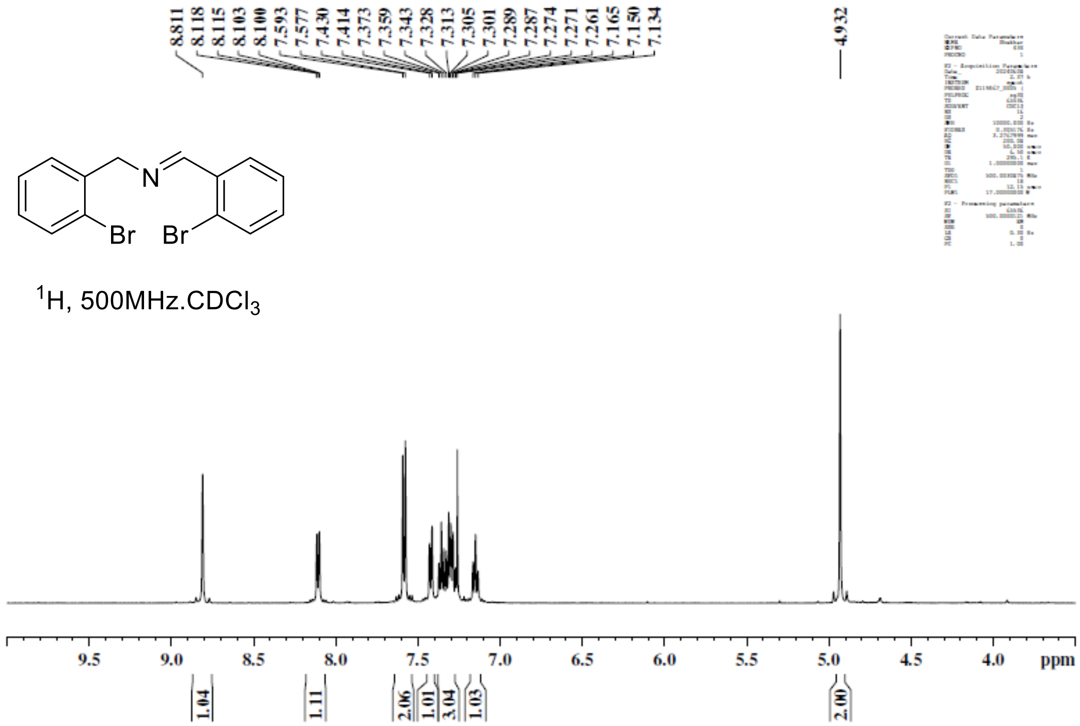


Figure S19. ^{1}H NMR spectrum of **2h** in $CDCl_3$

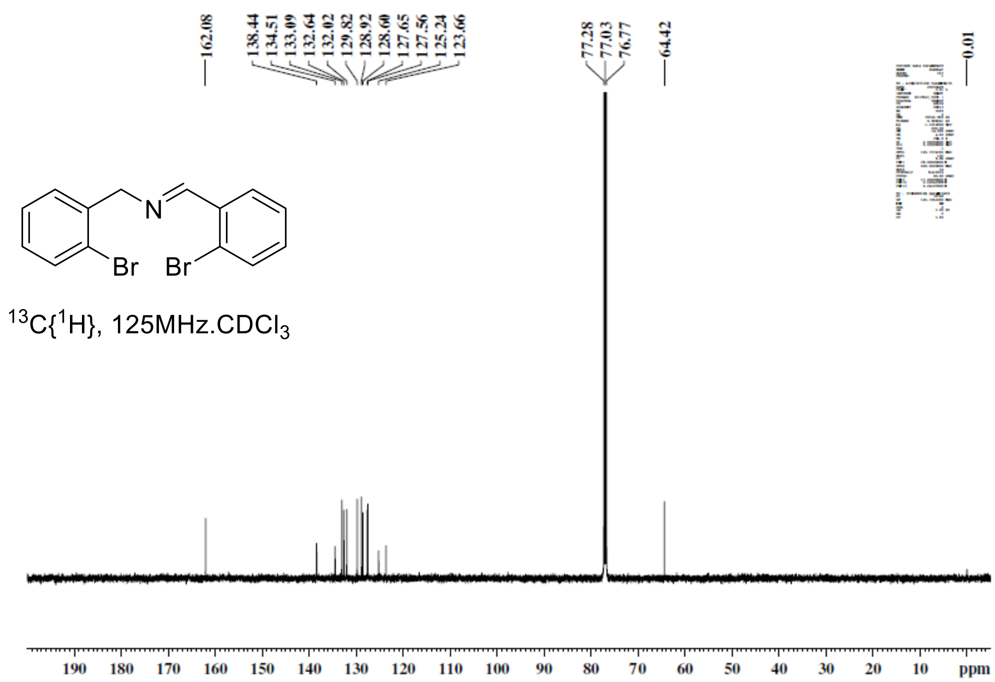


Figure S20. ^{13}C NMR spectrum of **2h** in $CDCl_3$

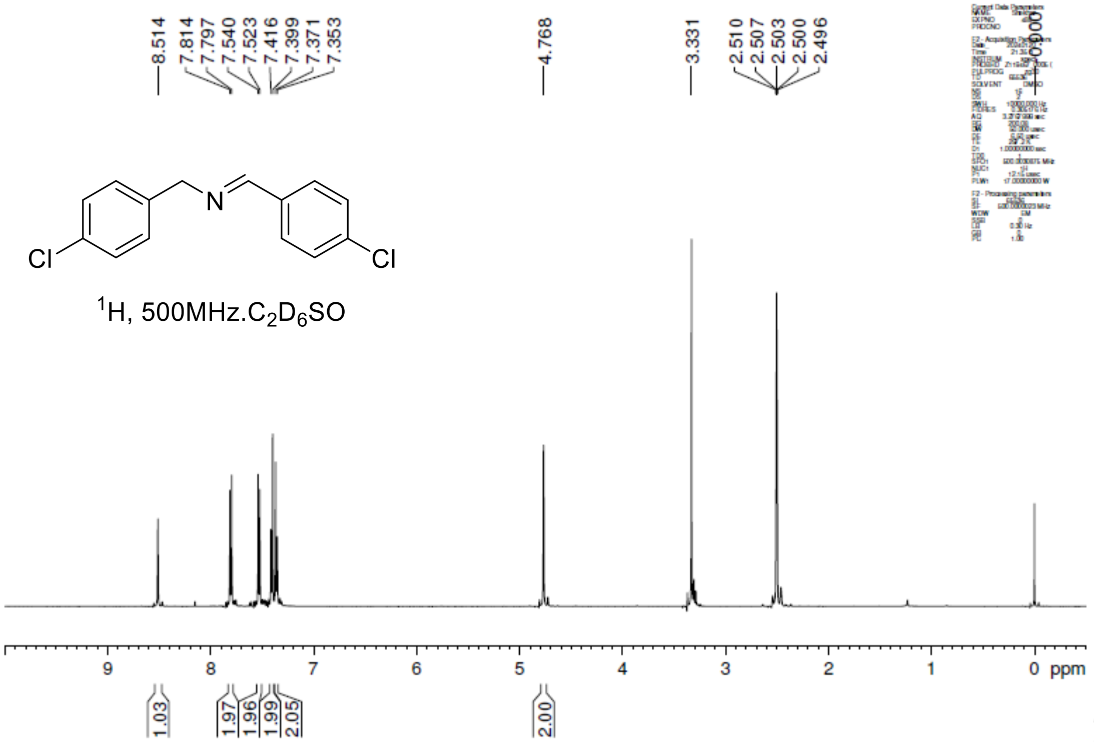


Figure S21. ^{1}H NMR spectrum of **2i** in C_2D_6SO

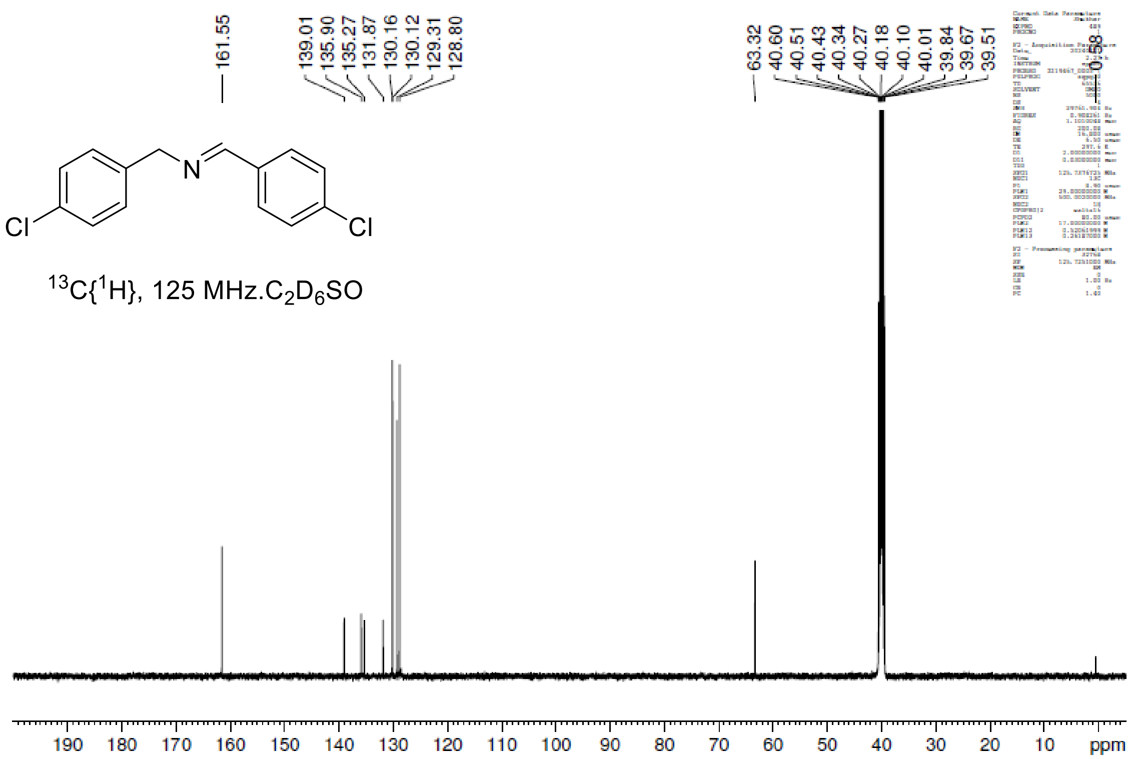


Figure S22. ^{13}C NMR spectrum of **2i** in C_2D_6SO

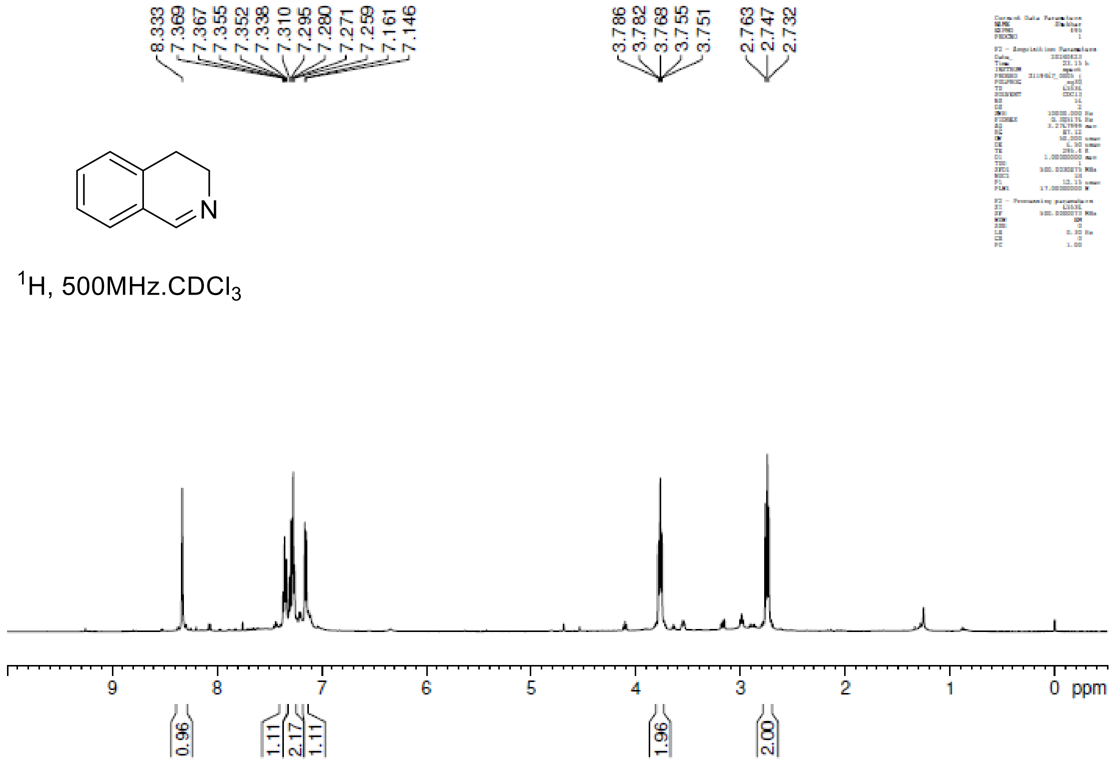


Figure S23. ^{1}H NMR spectrum of **2j** in $CDCl_3$

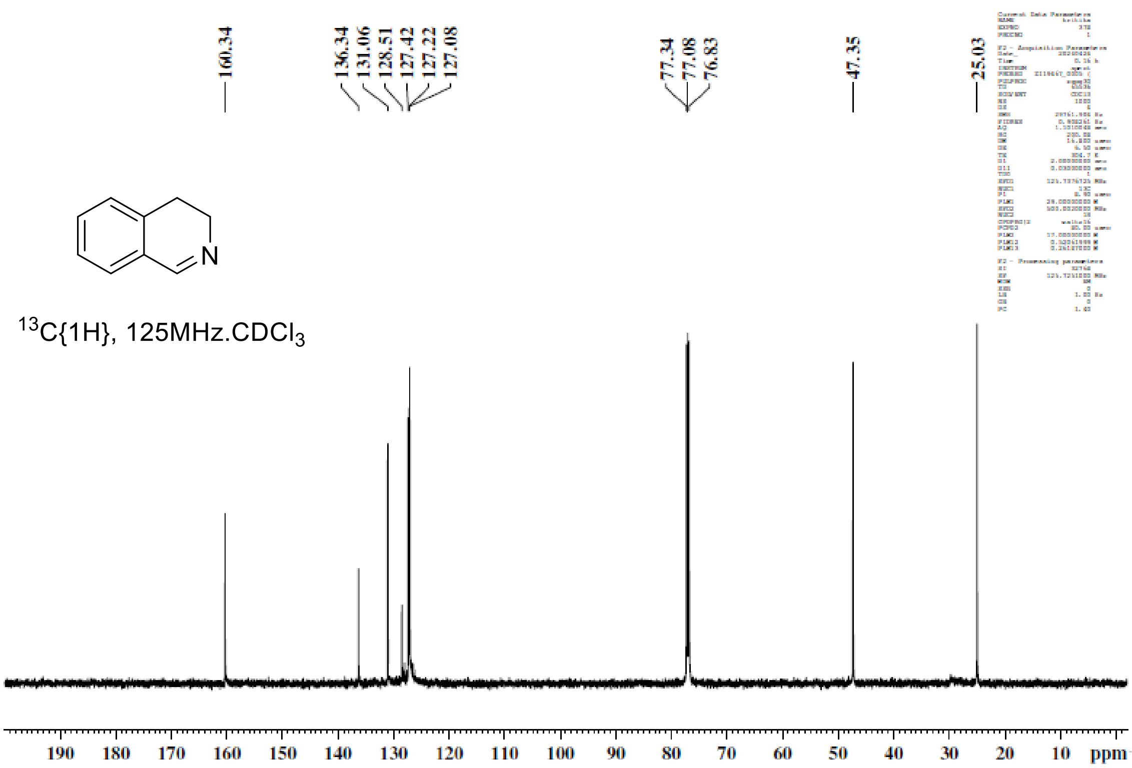


Figure S24. ^{13}C NMR spectrum of **2j** in $CDCl_3$

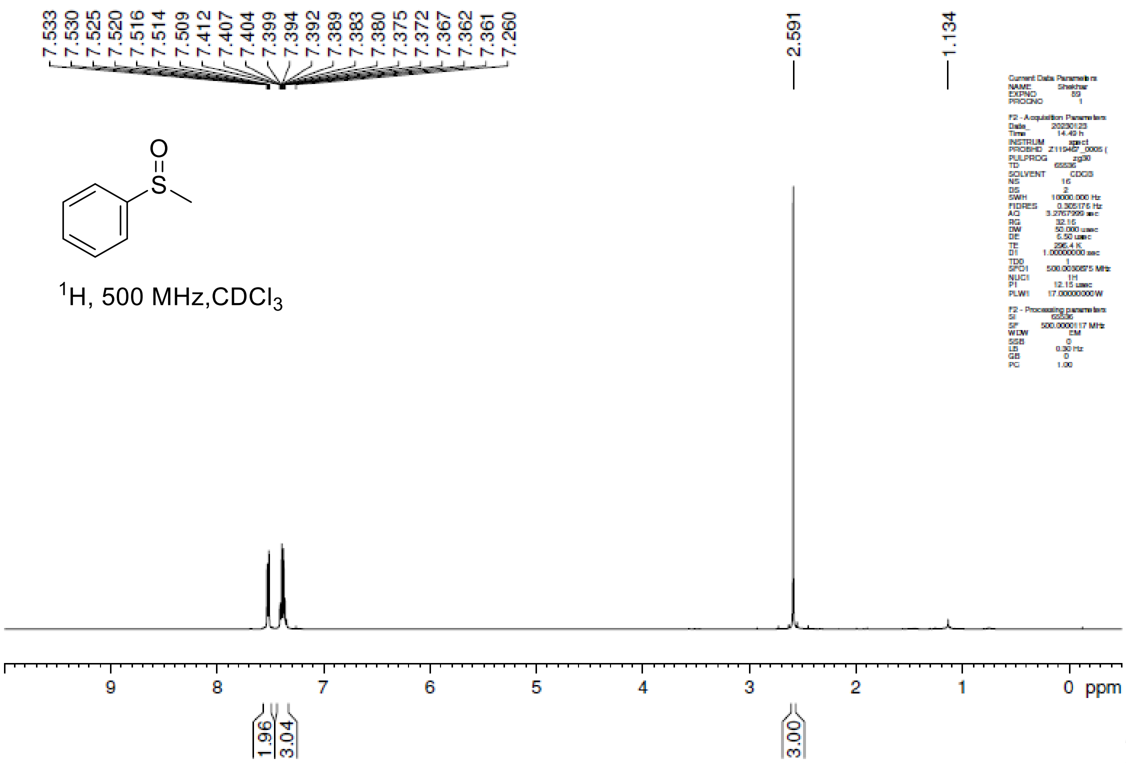


Figure S25. ^{1}H NMR spectrum of **4a** in $CDCl_3$

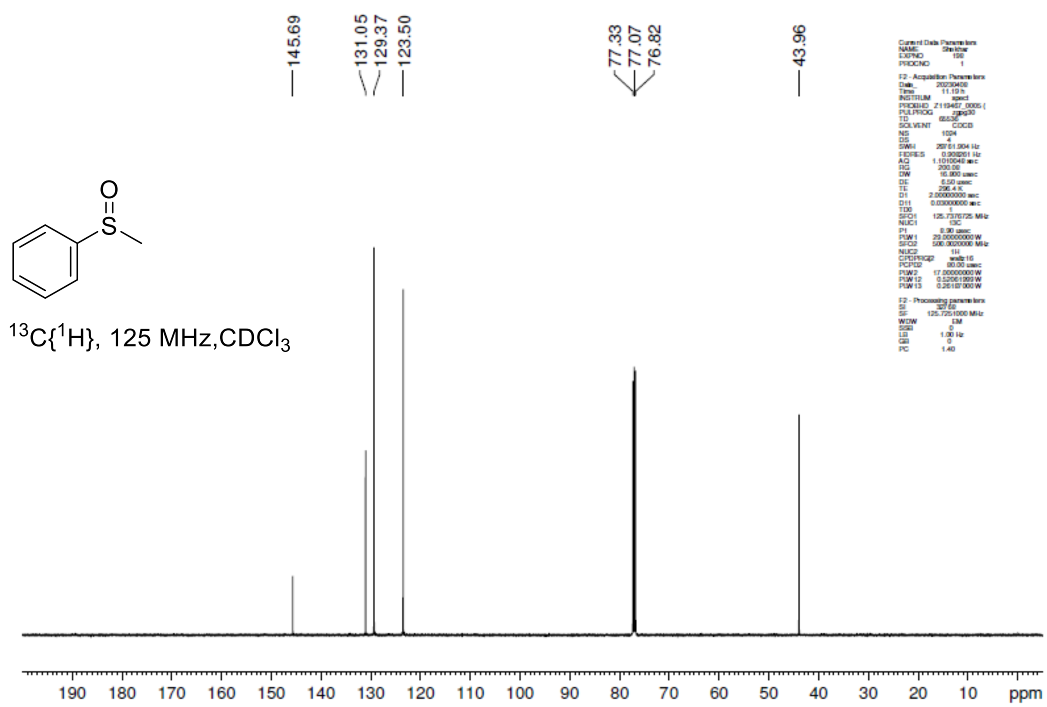


Figure S26. ^{13}C NMR spectrum of **4a** in $CDCl_3$

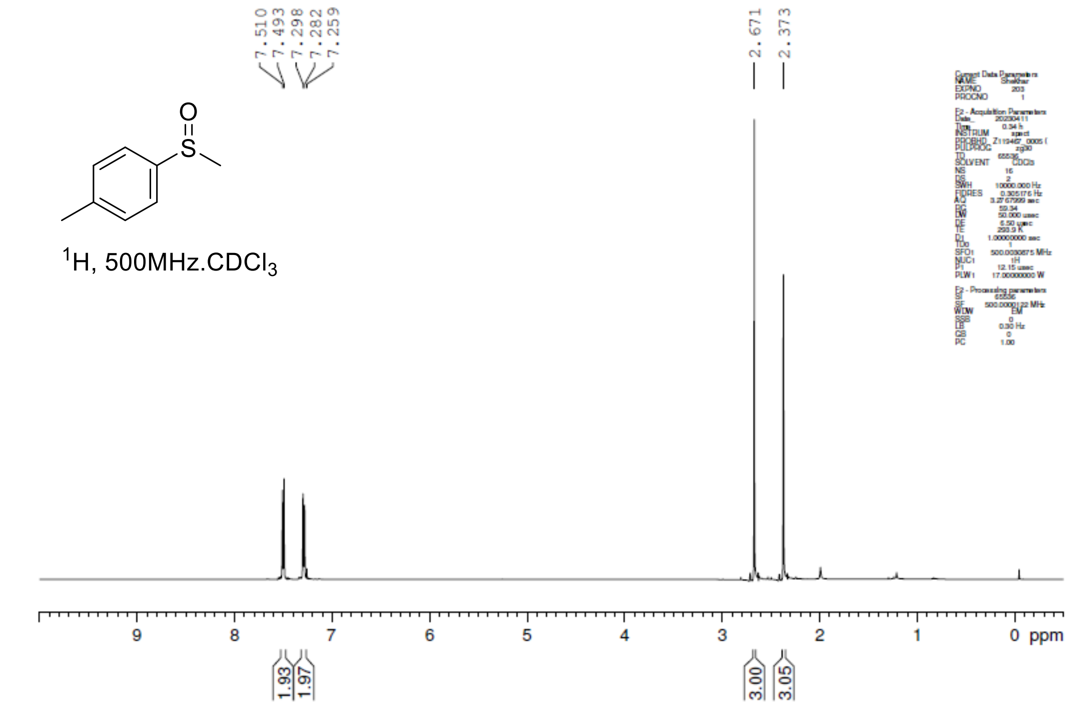


Figure S27. ^{1}H NMR spectrum of **4b** in $CDCl_3$

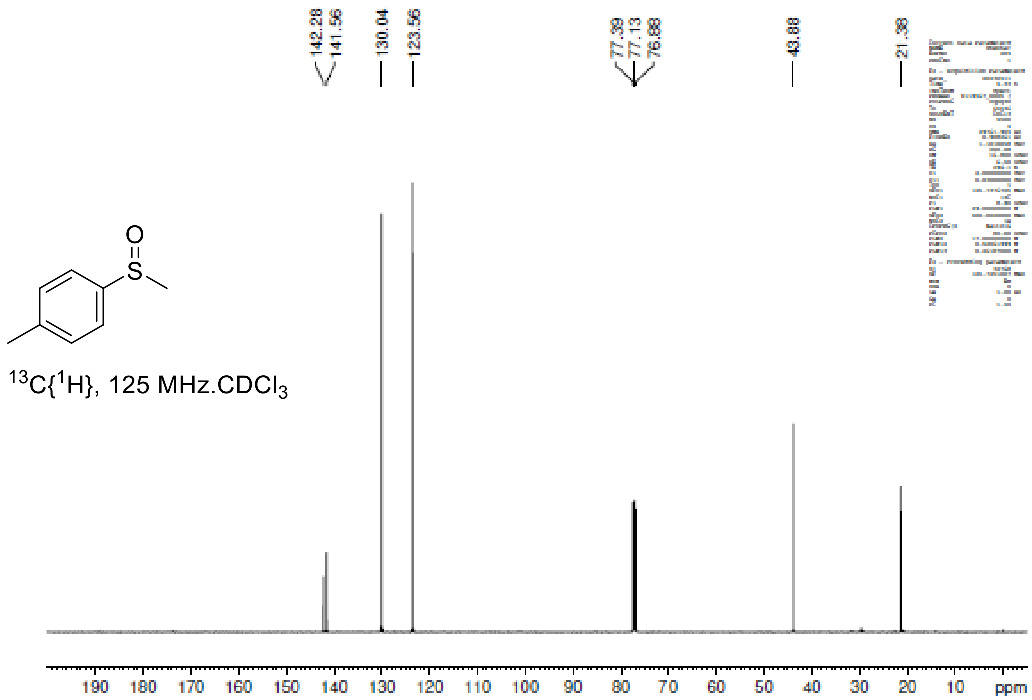


Figure S28. ^{13}C NMR spectrum of **4b** in $CDCl_3$

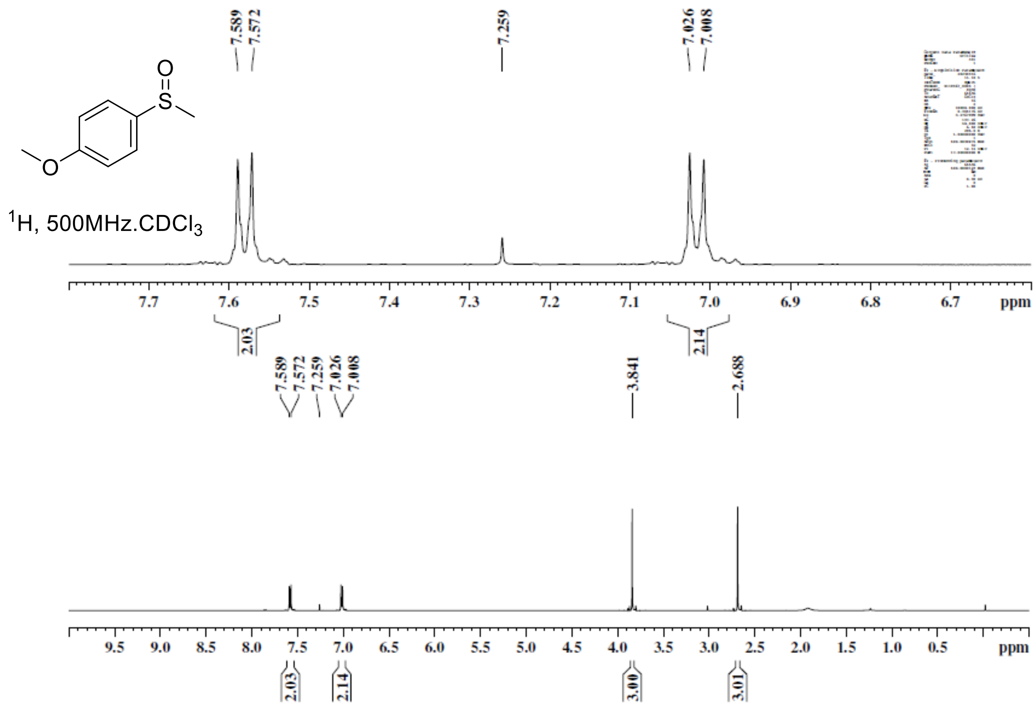


Figure S29. ^{1}H NMR spectrum of **4c** in $CDCl_3$

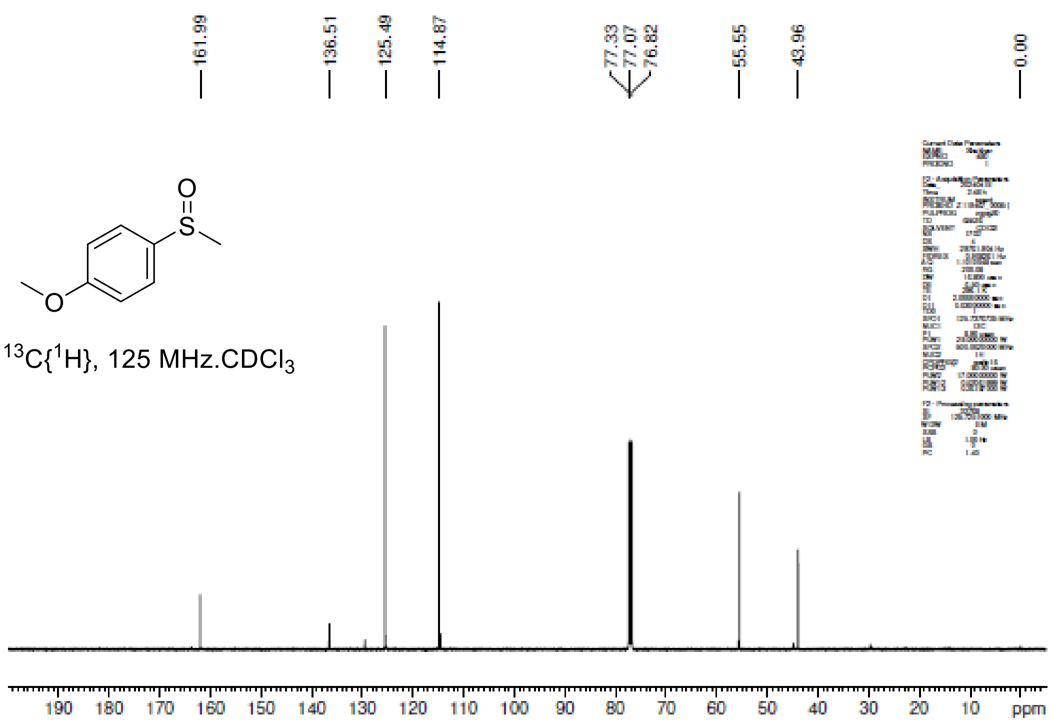


Figure S30. ^{13}C NMR spectrum of **4c** in $CDCl_3$

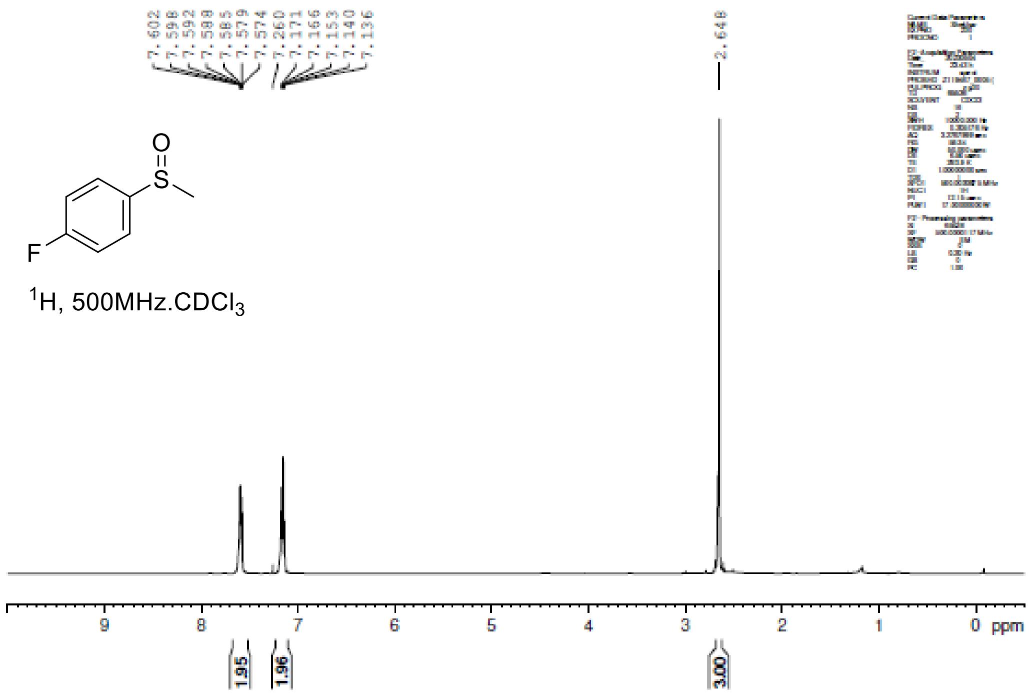


Figure S31. ^{1}H NMR spectrum of **4d** in $CDCl_3$

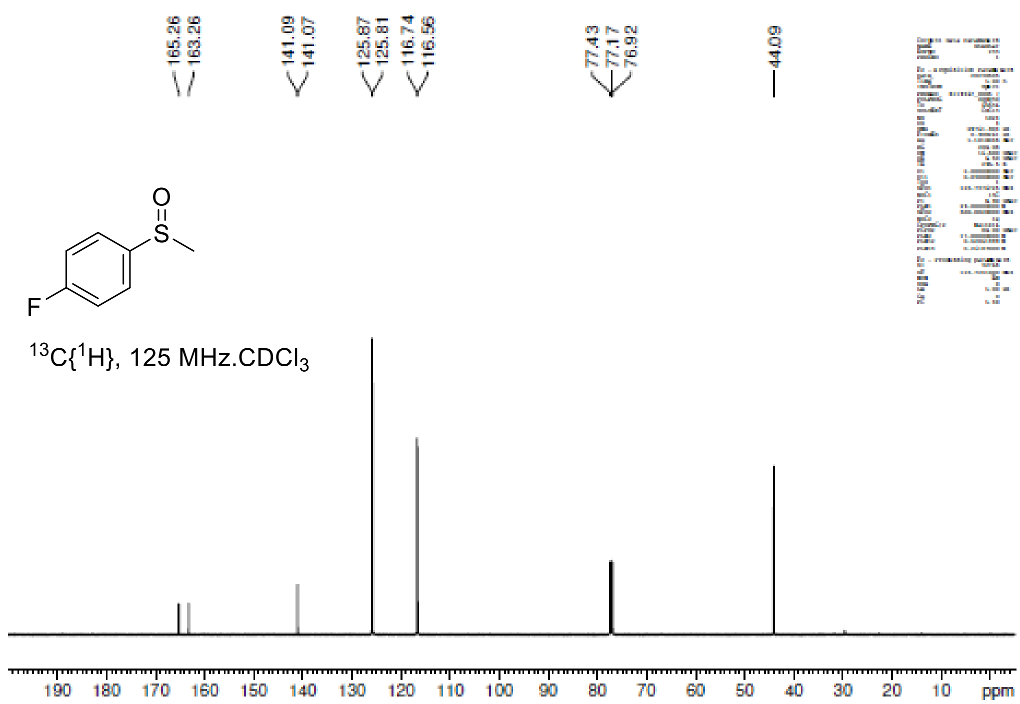


Figure S32. ^{13}C NMR spectrum of **4d** in $CDCl_3$

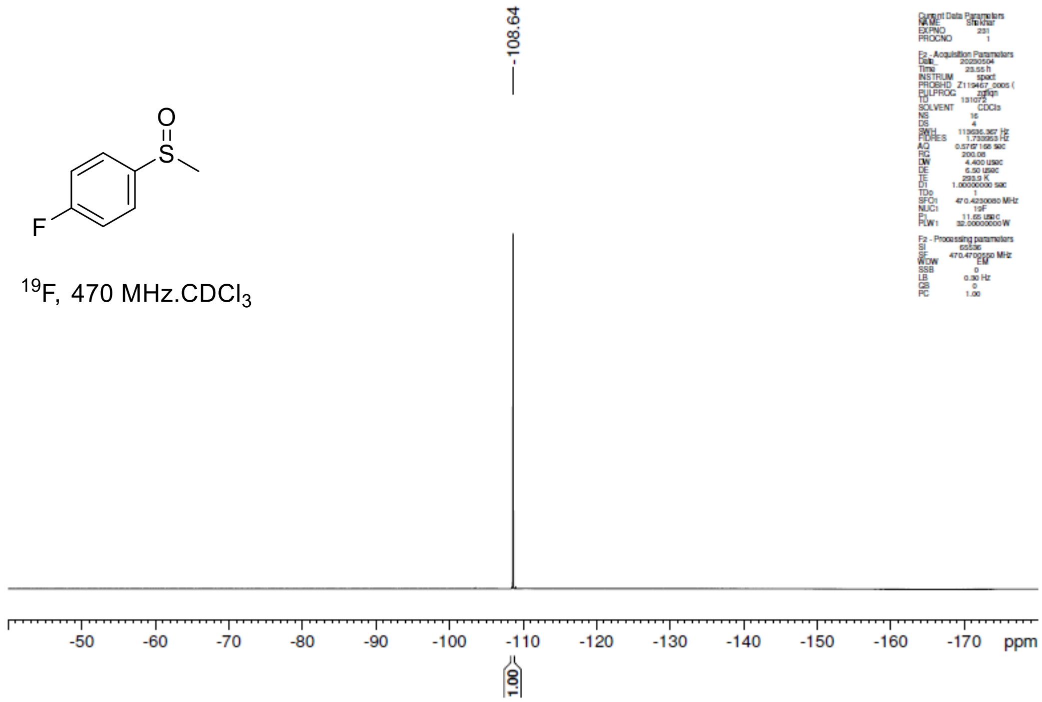


Figure S33. ^{19}F NMR spectrum of **4d** in $CDCl_3$

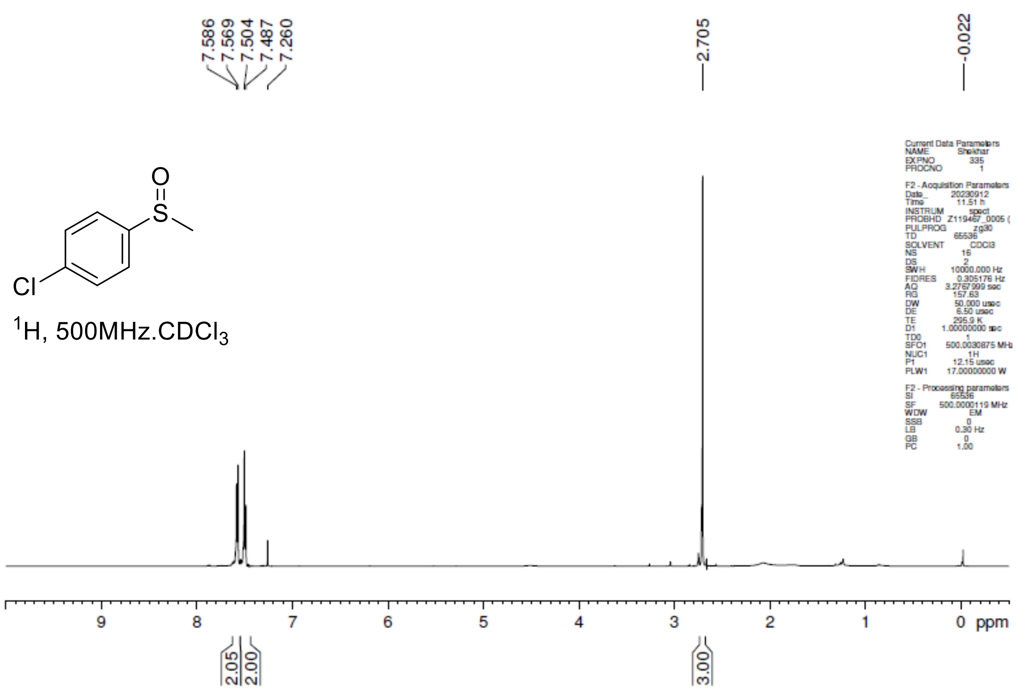


Figure S34. ^{1}H NMR spectrum of **4e** in $CDCl_3$

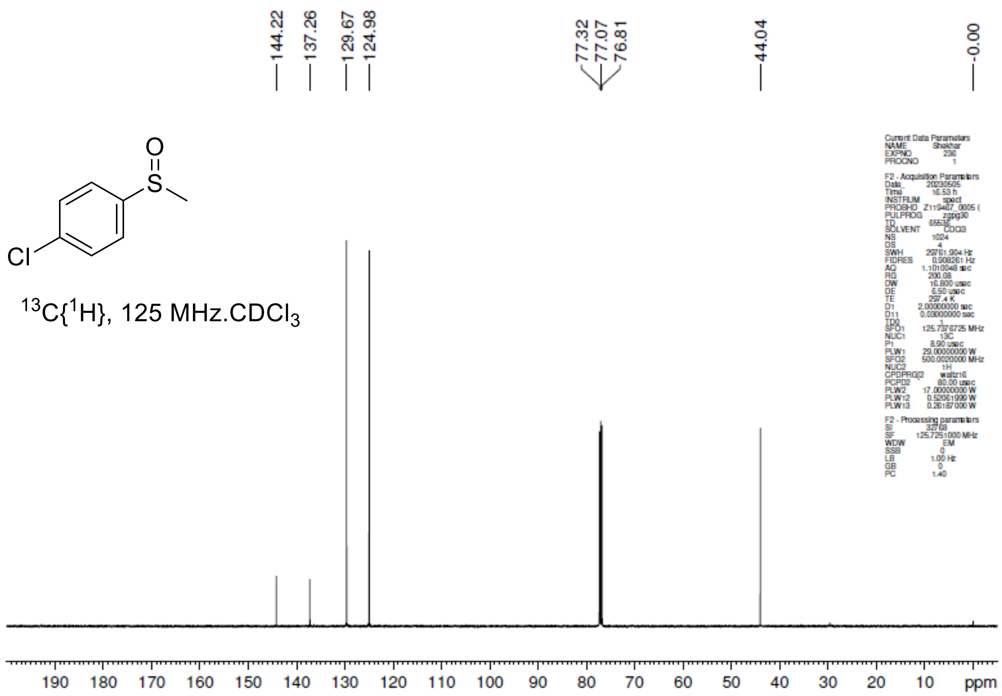


Figure S35. ^{13}C NMR spectrum of **4e** in $CDCl_3$

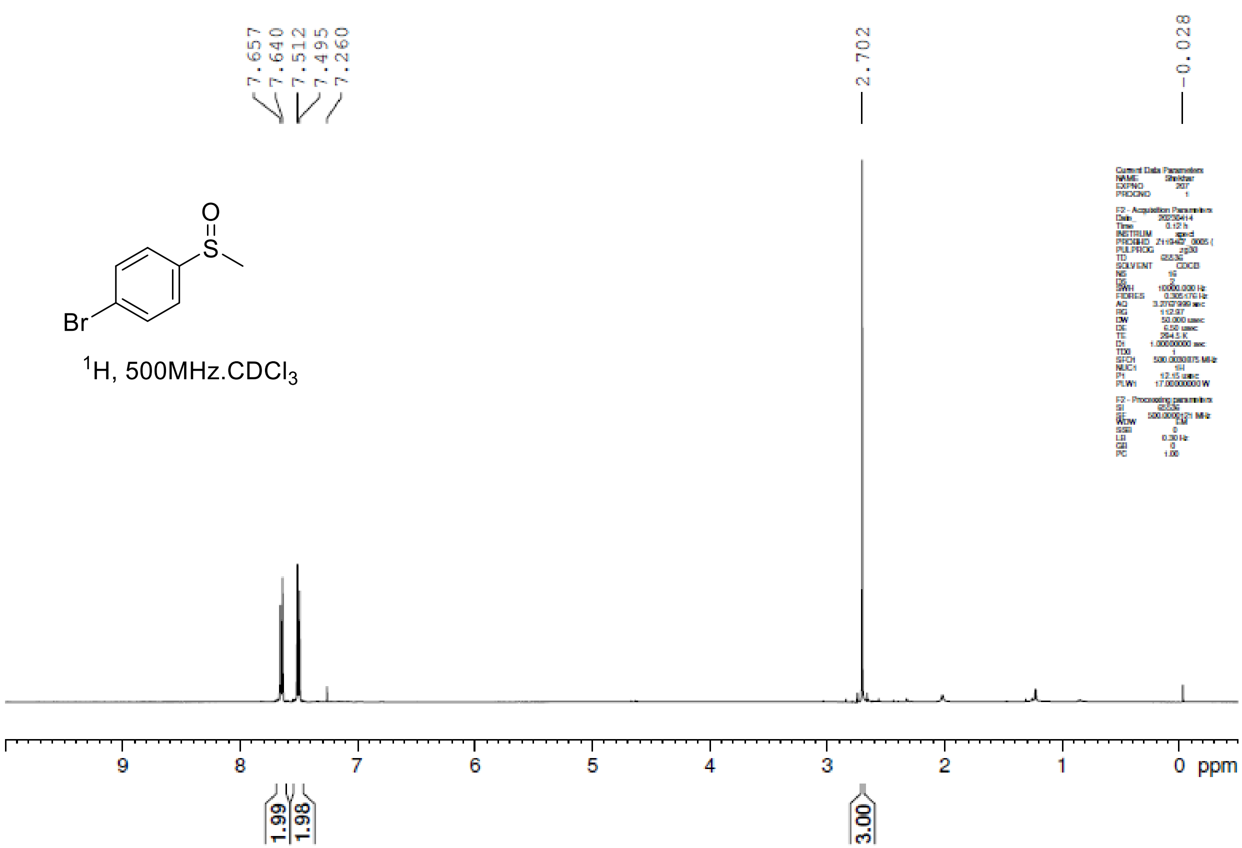


Figure S36. ^1H NMR spectrum of **4f** in $CDCl_3$

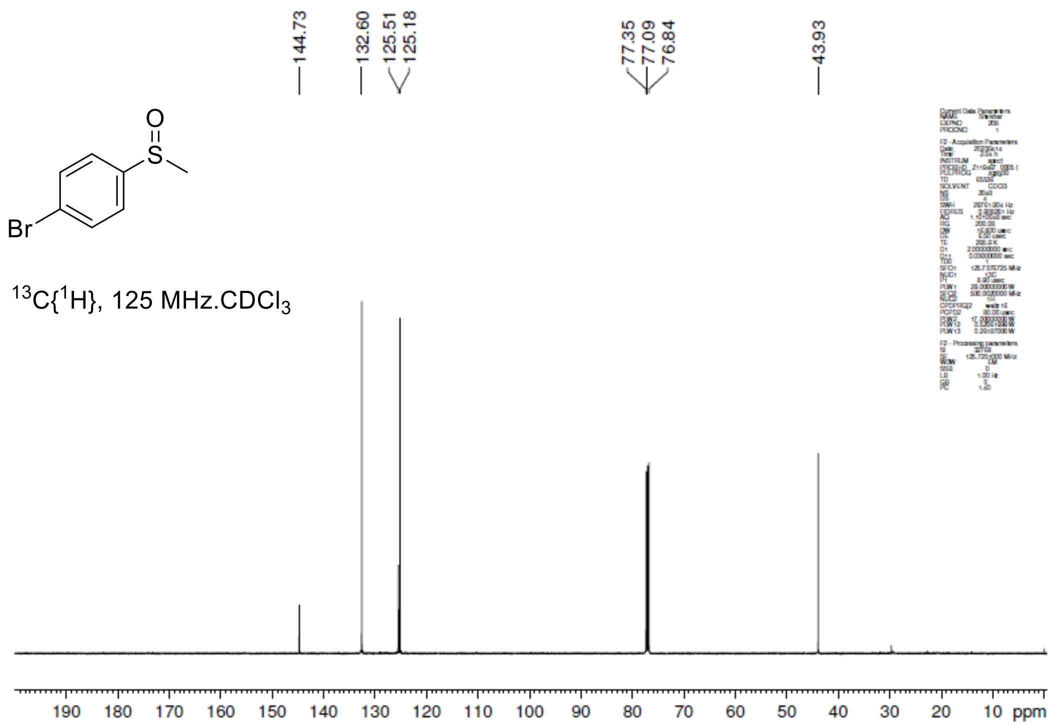


Figure S37. ^{13}C NMR spectrum of **4f** in $CDCl_3$

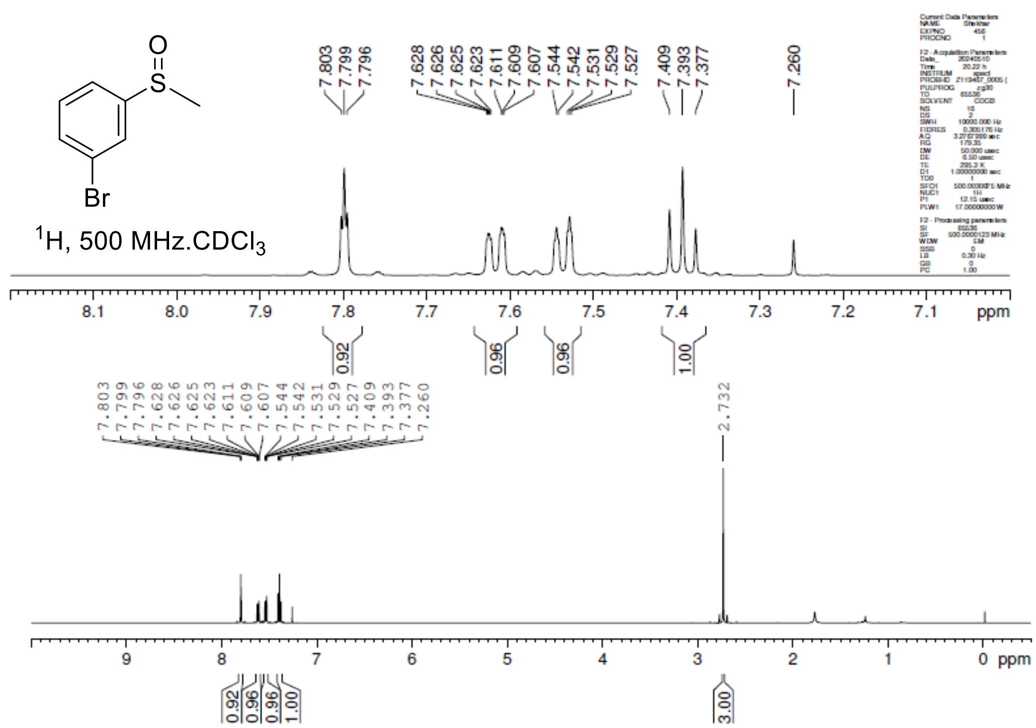


Figure S38. ^{1}H NMR spectrum of **4g** in $CDCl_3$

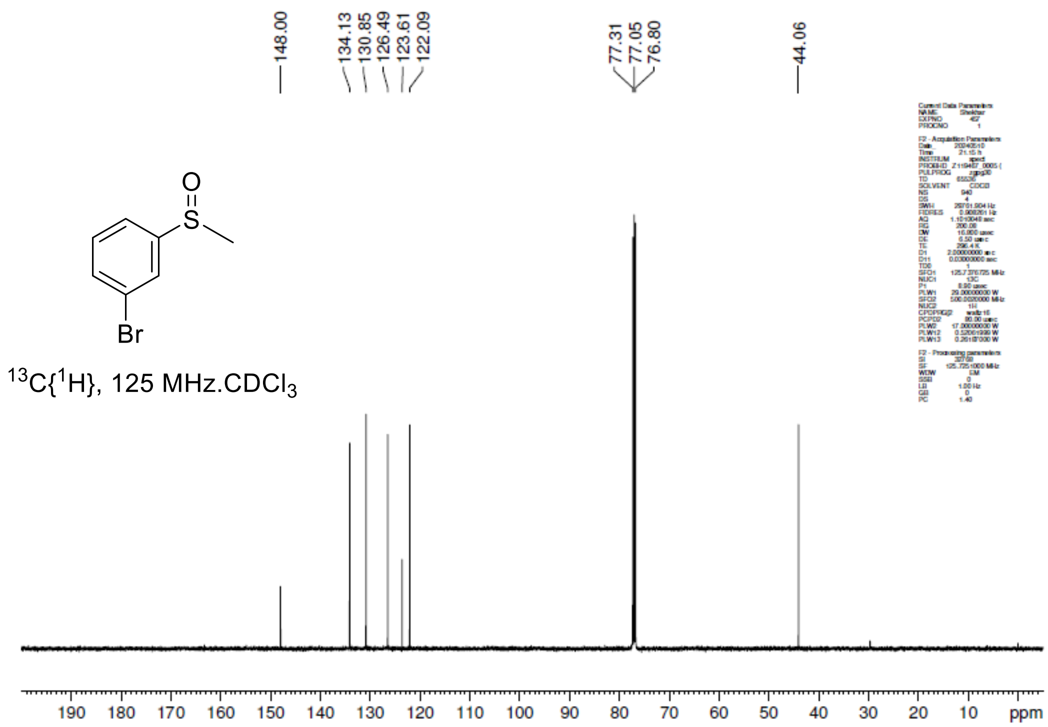


Figure S39. ^{13}C NMR spectrum of **4g** in $CDCl_3$

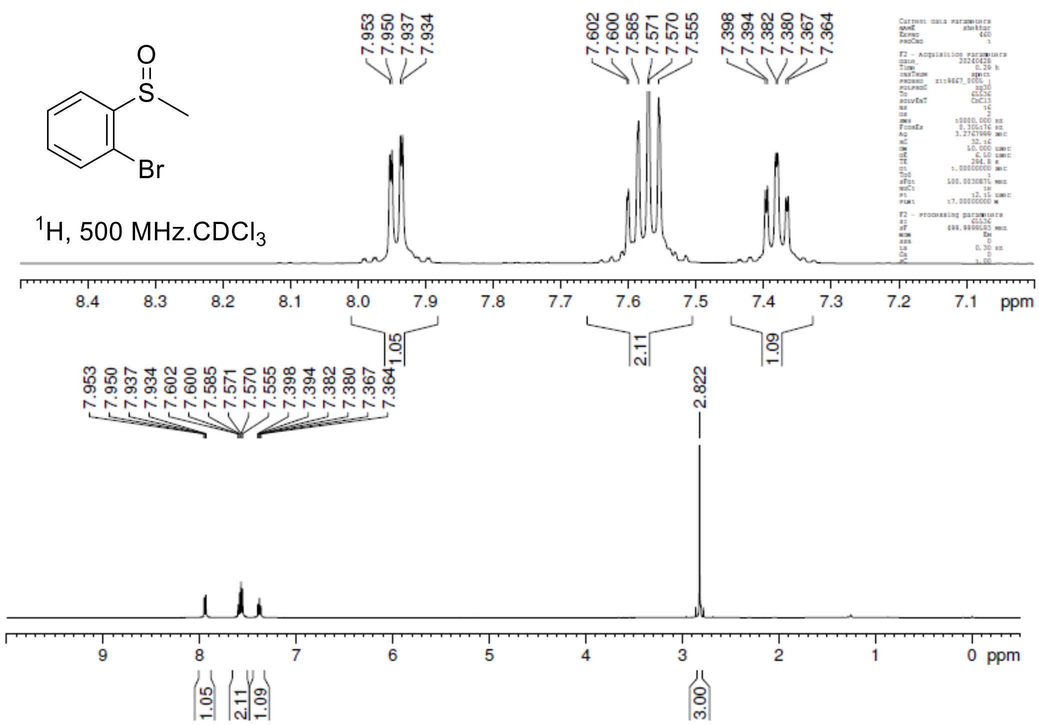


Figure S40. ^{1}H NMR spectrum of **4h** in $CDCl_3$

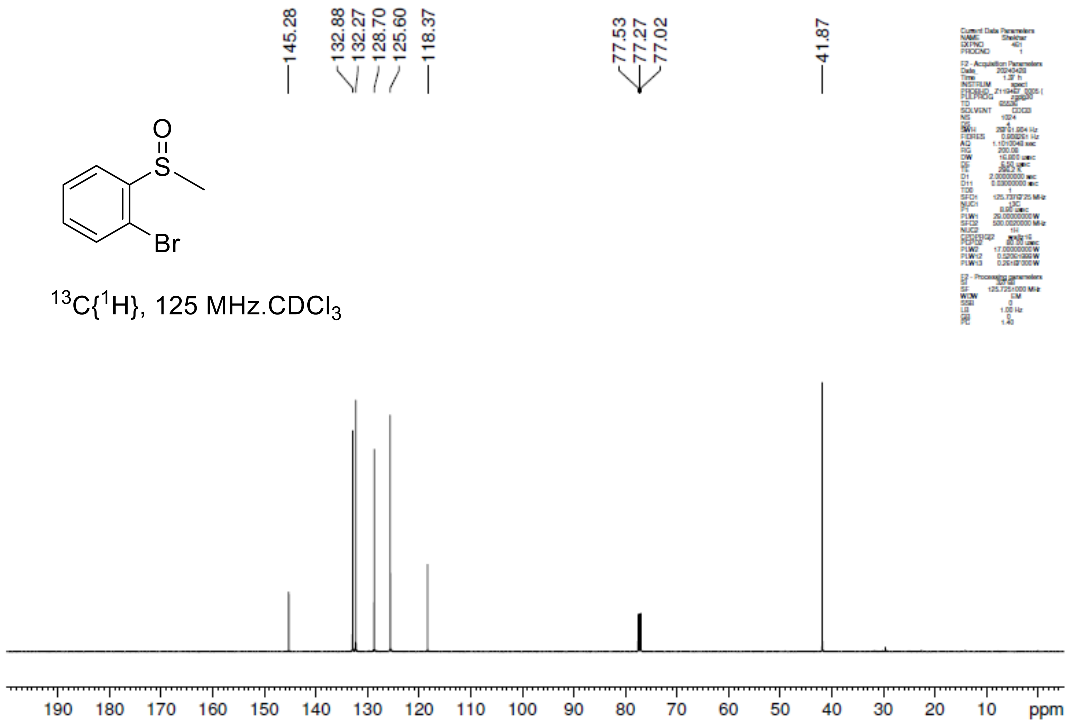


Figure S41. ^{13}C NMR spectrum of **4h** in $CDCl_3$

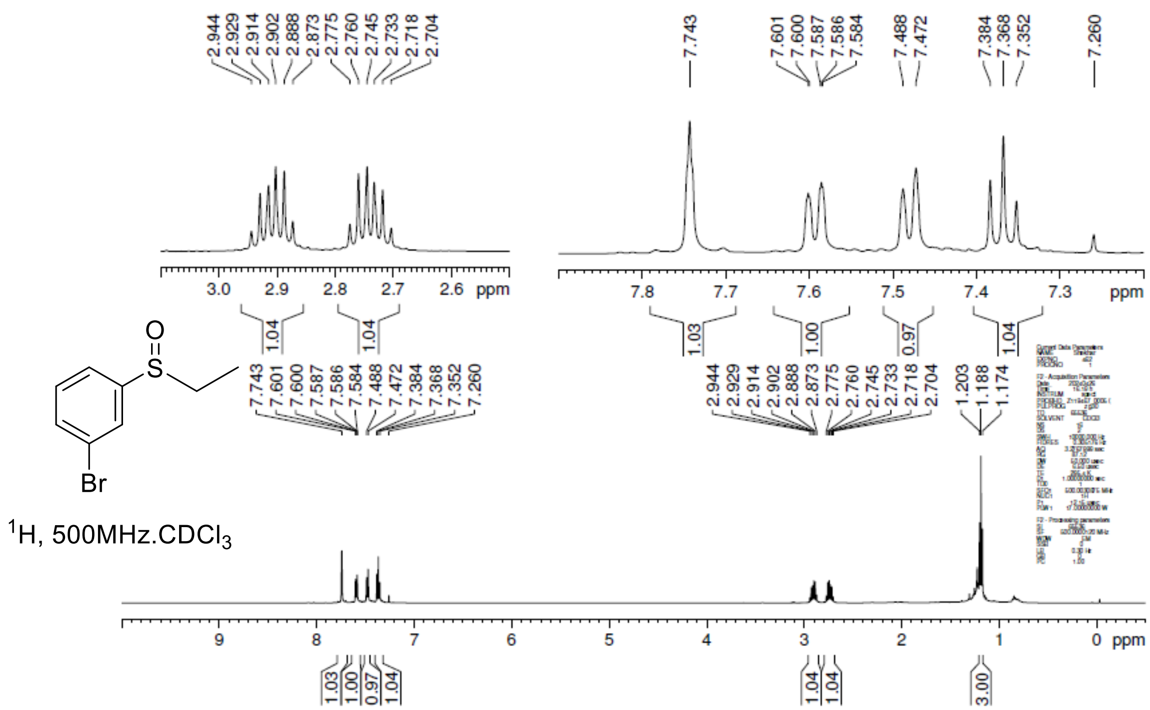


Figure S42. ^{1}H NMR spectrum of **4i** in $CDCl_3$

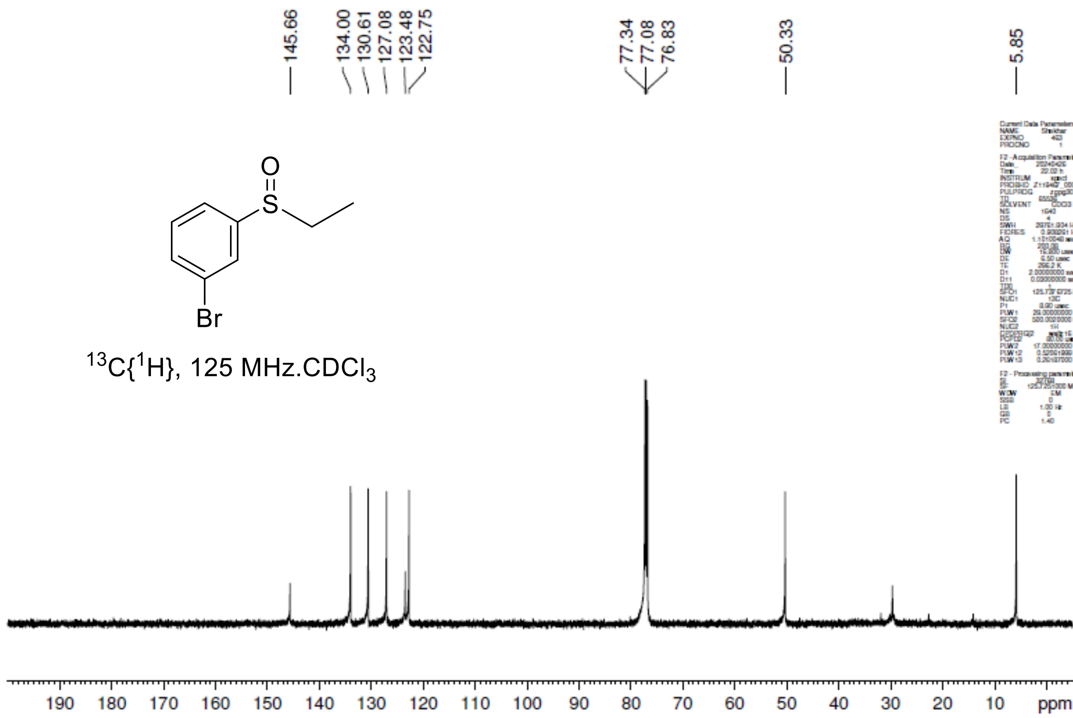


Figure S43. ^{13}C NMR spectrum of **4i** in $CDCl_3$

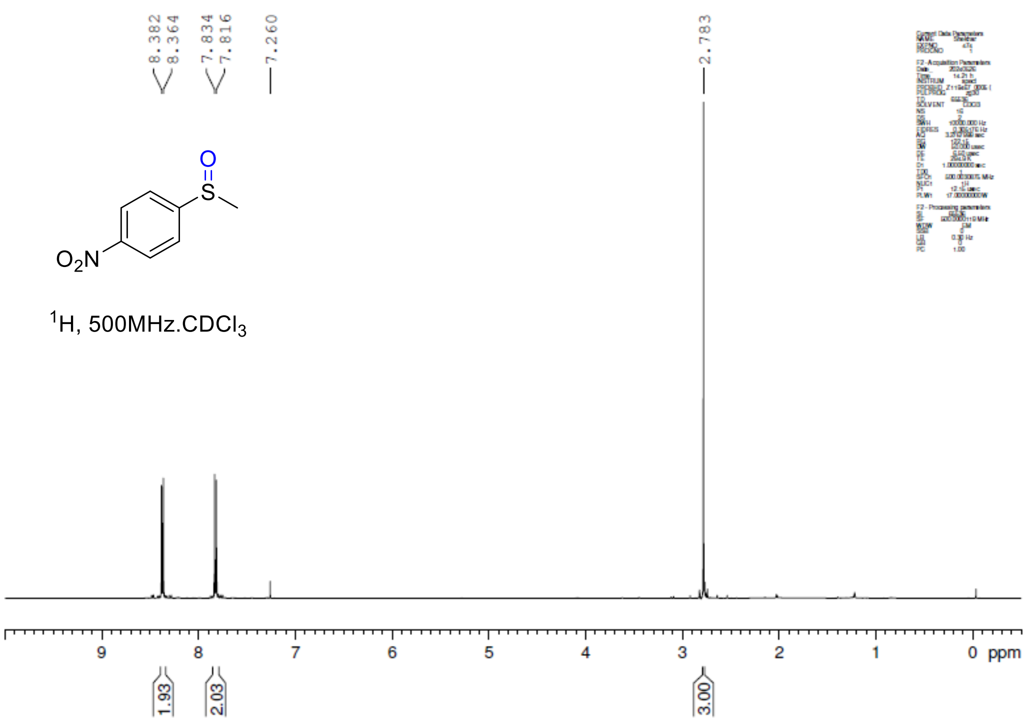


Figure S44. ^{1}H NMR spectrum of **4j** in $CDCl_3$

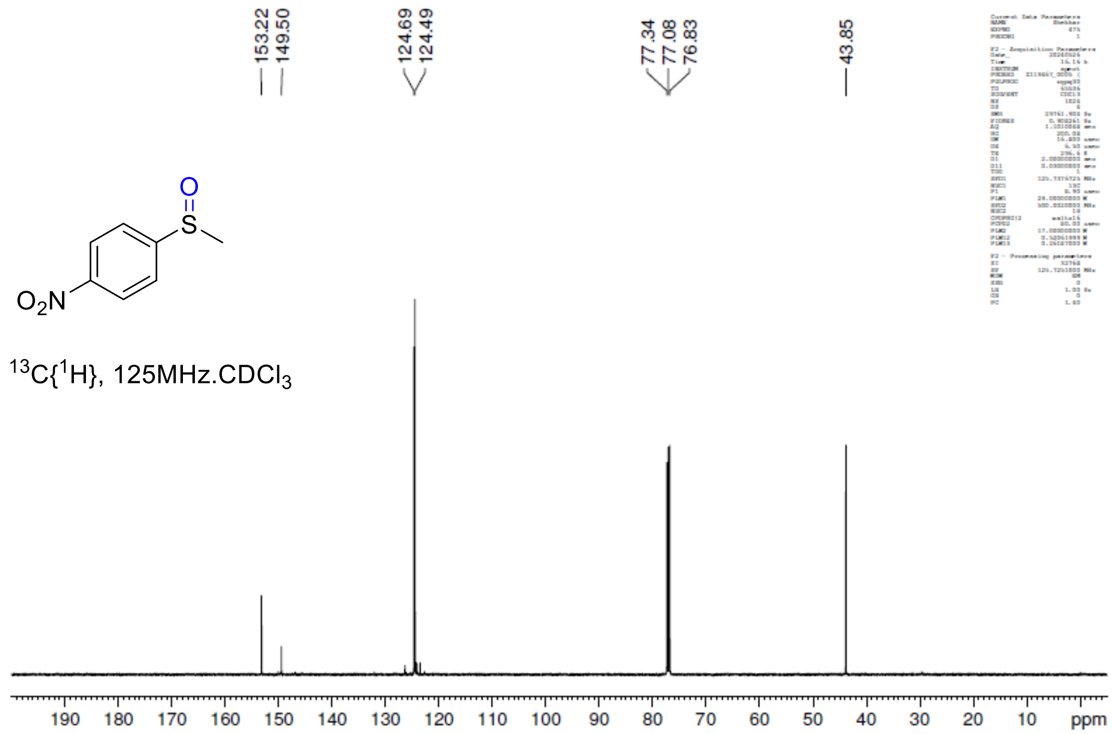


Figure S45. ^{13}C NMR spectrum of **4j** in $CDCl_3$

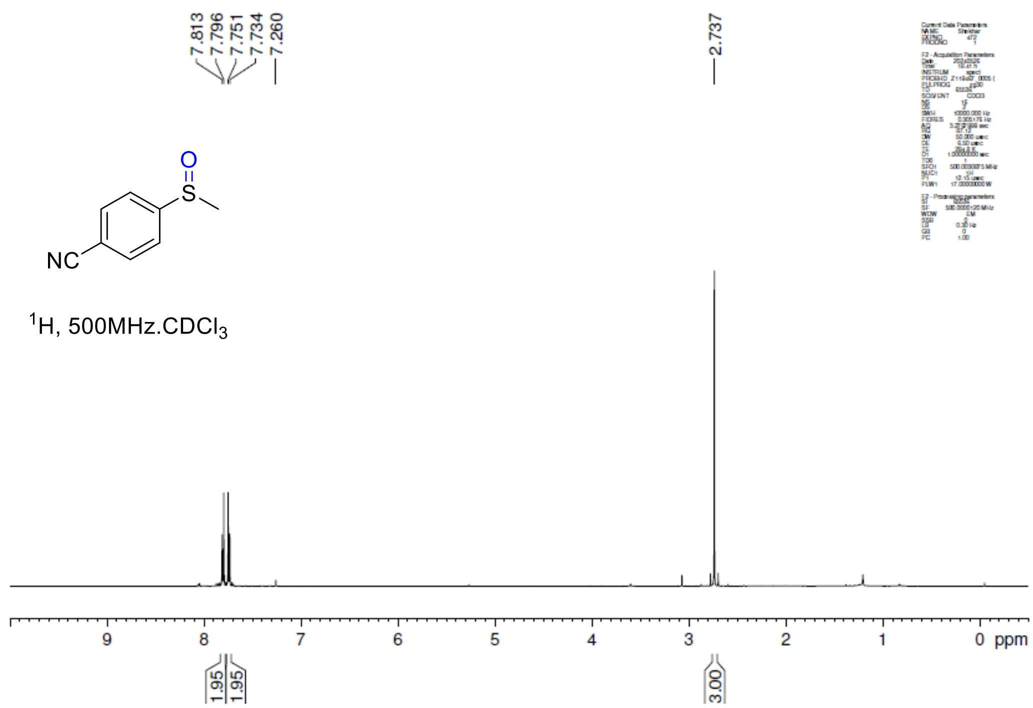


Figure S46. ^1H NMR spectrum of **4k** in $CDCl_3$

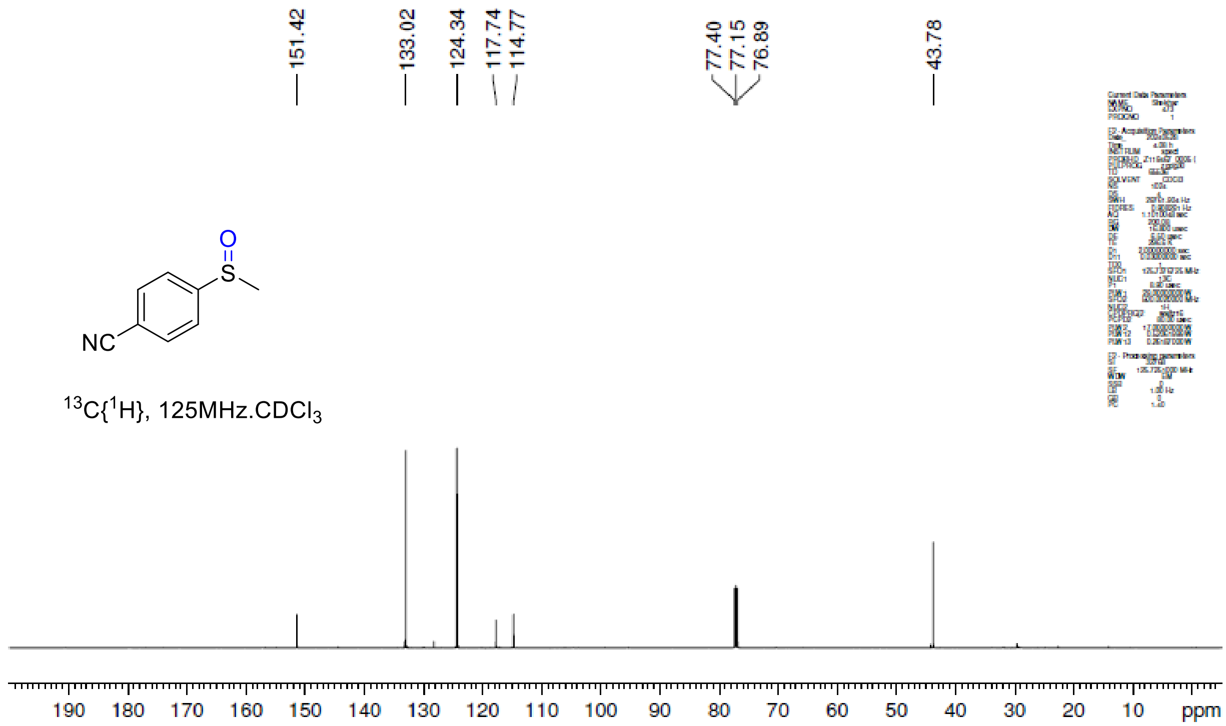


Figure S47. ^{13}C NMR spectrum of **4k** in $CDCl_3$

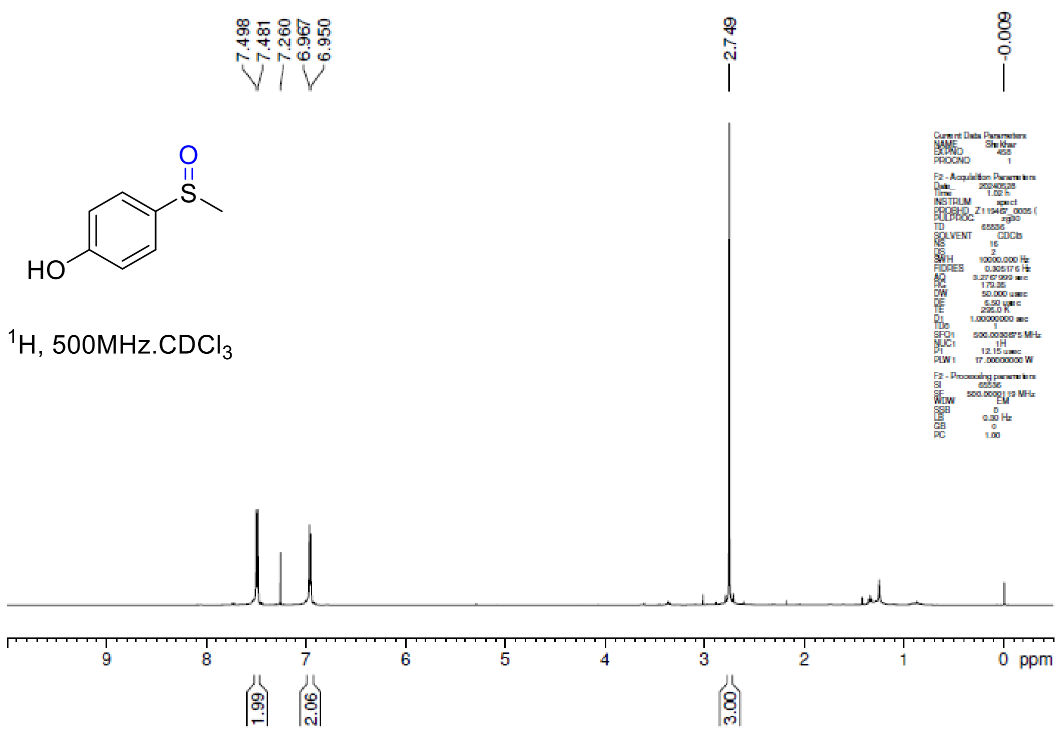


Figure S48. ^{1}H NMR spectrum of **4l** in $CDCl_3$

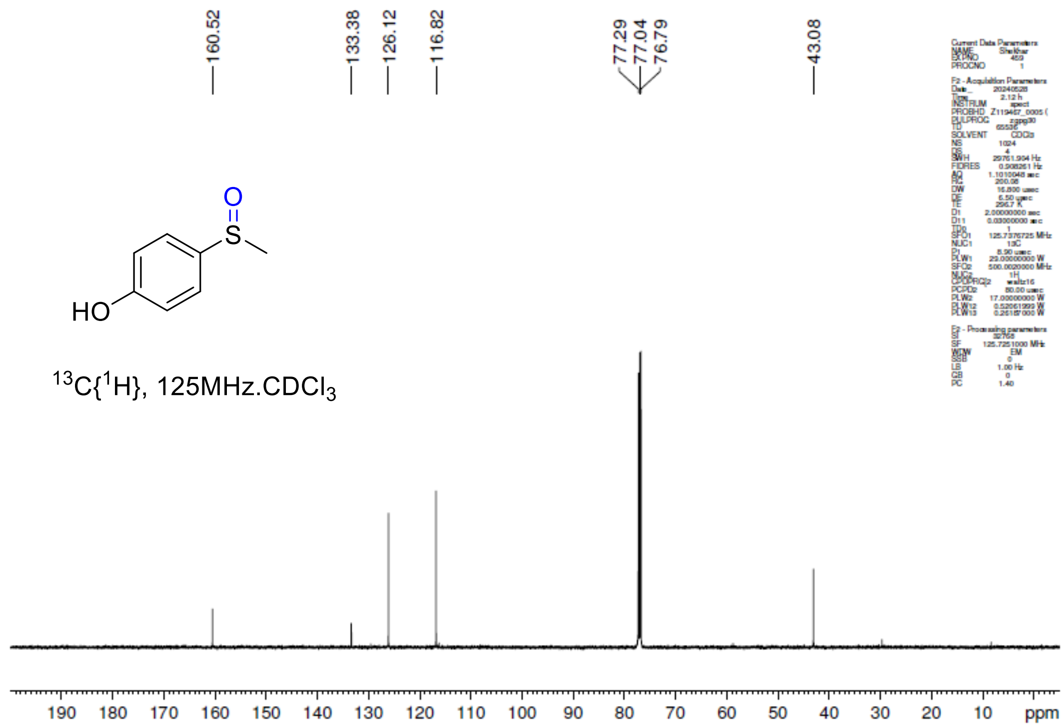


Figure S49. ^{13}C NMR spectrum of **4l** in $CDCl_3$

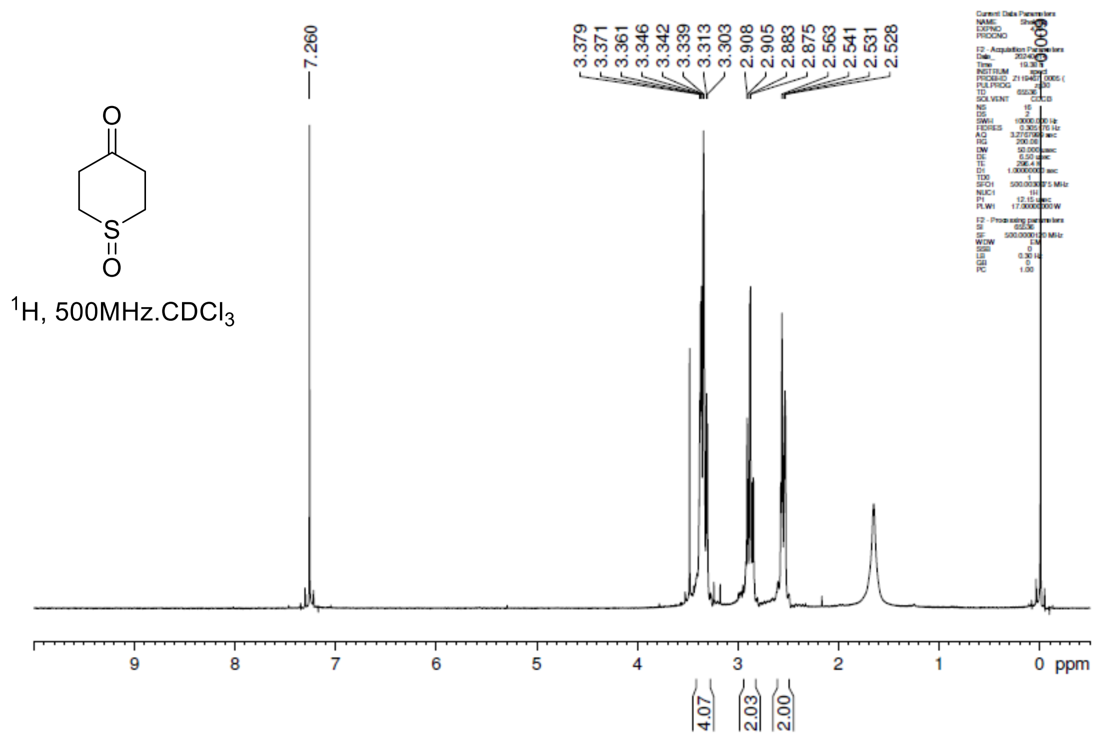


Figure S50. ^1H NMR spectrum of **4m** in $CDCl_3$

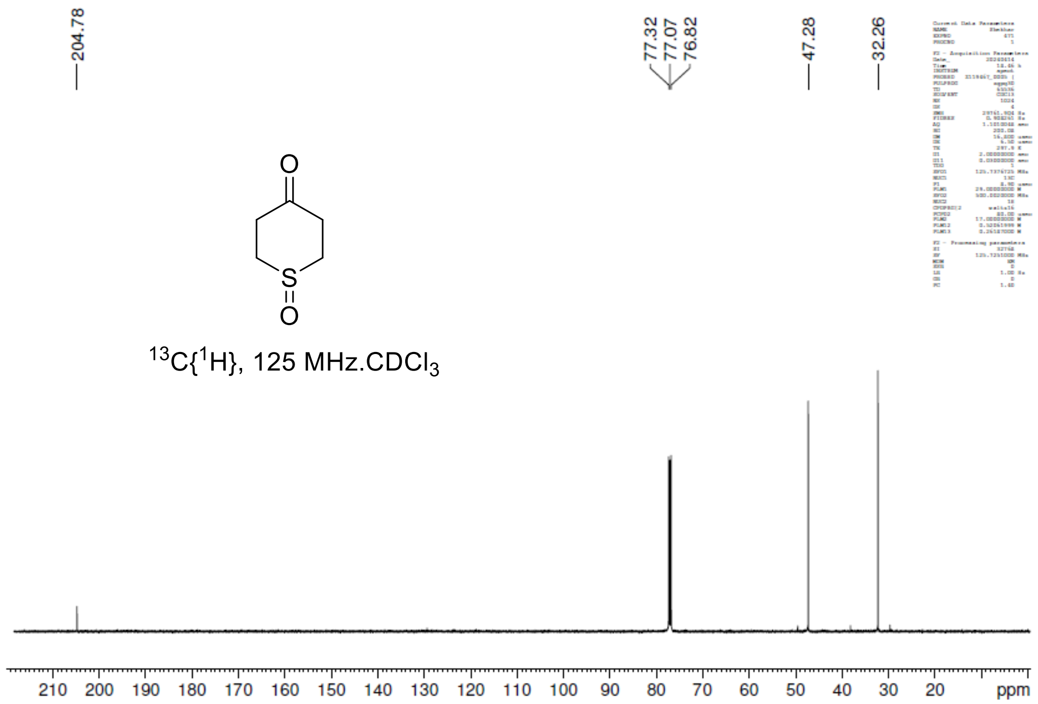


Figure S51. ^{13}C NMR spectrum of **4m** in $CDCl_3$

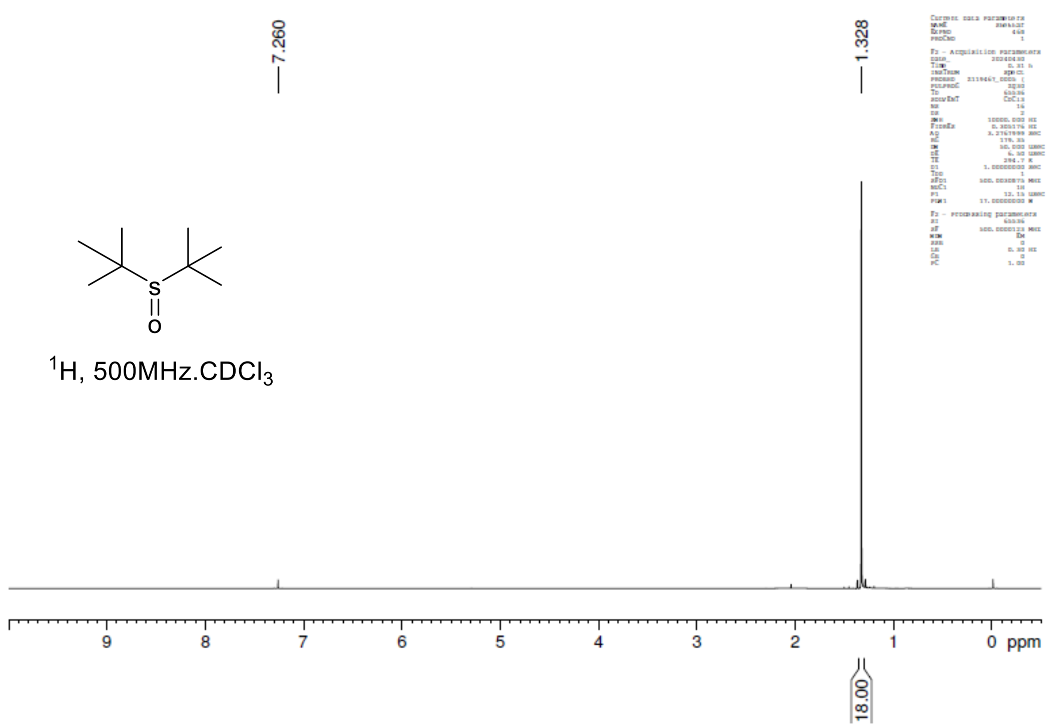


Figure S52. ^{1}H NMR spectrum of **4n** in $CDCl_3$

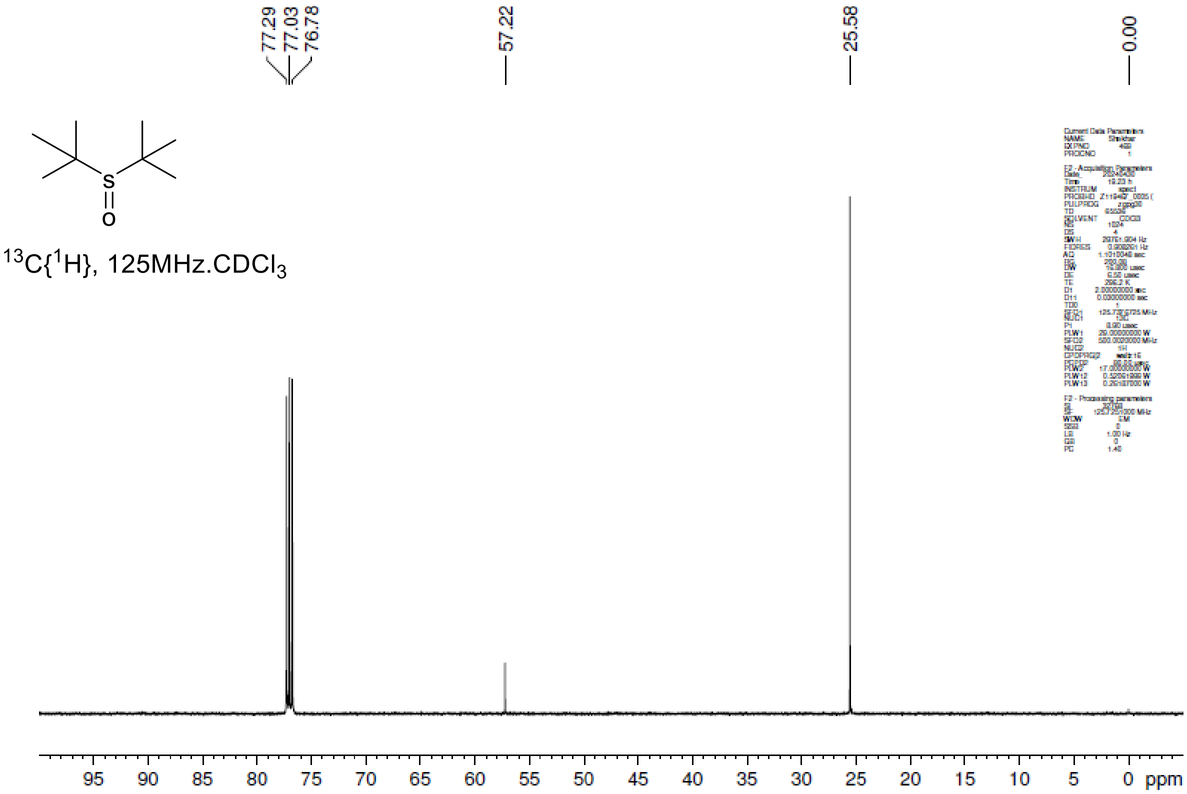


Figure S53. [13]C NMR spectrum of **4n** in $CDCl_3$

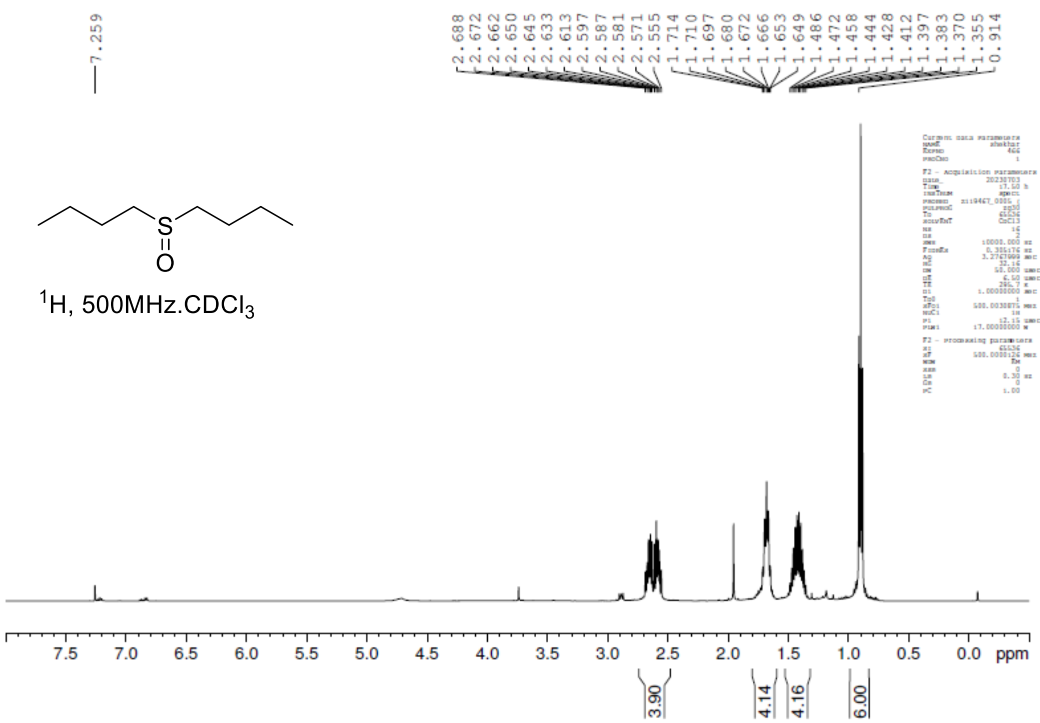


Figure S54. [1]H NMR spectrum of **4o** in $CDCl_3$

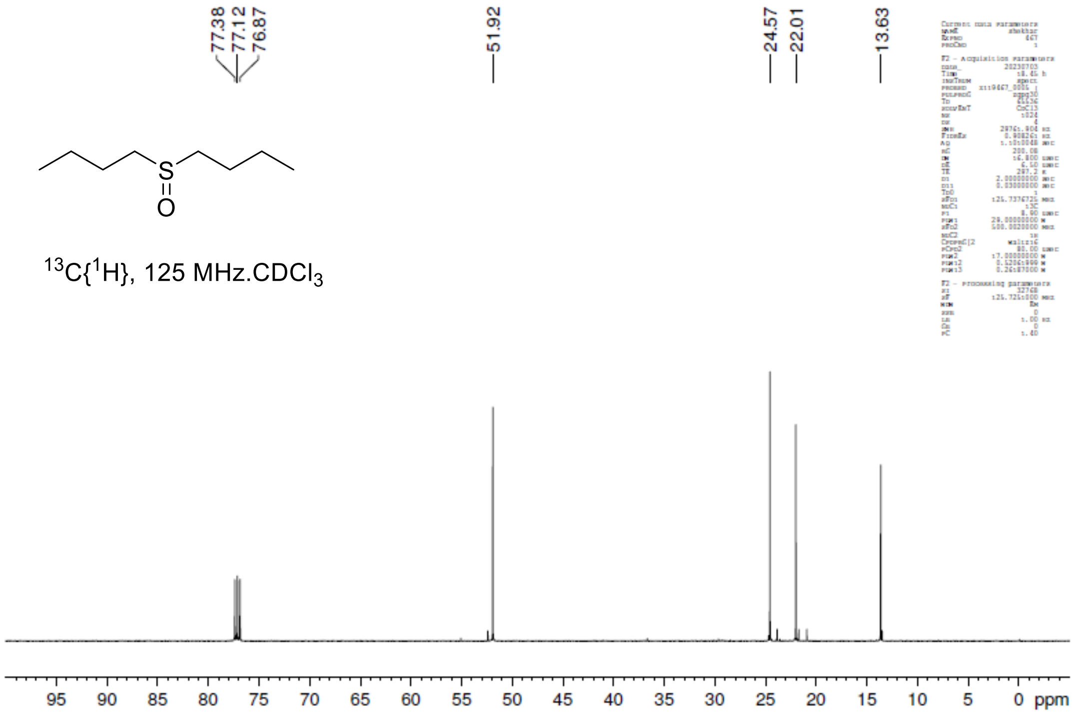


Figure S55. ^{13}C NMR spectrum of **4o** in $CDCl_3$

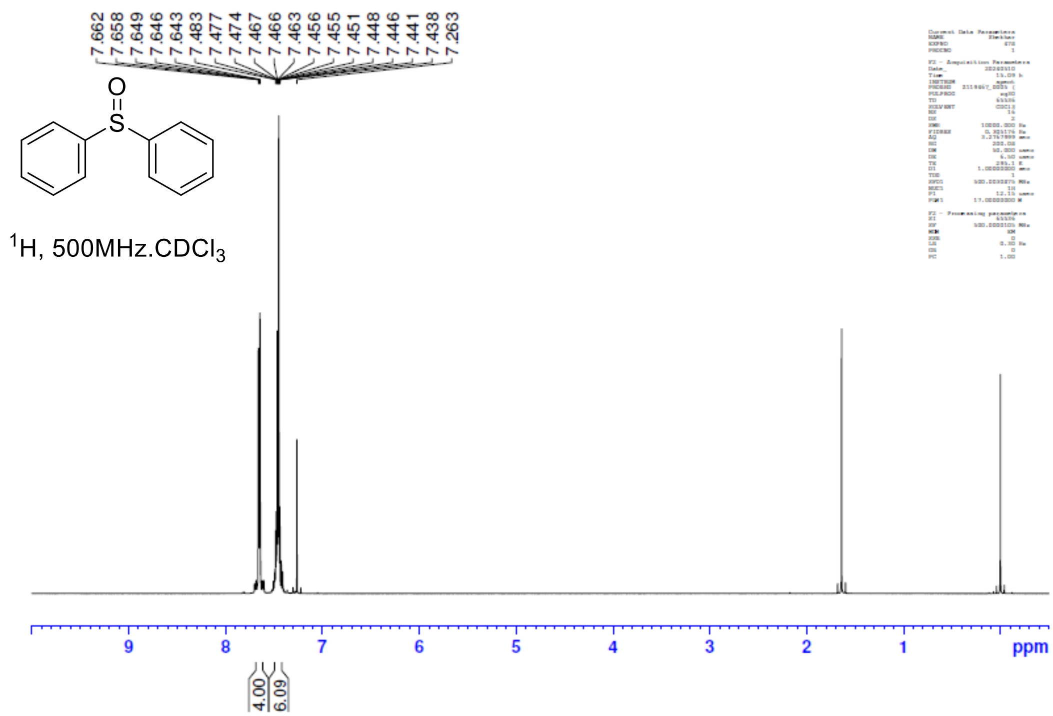


Figure S56. ^{1}H NMR spectrum of **4p** in $CDCl_3$

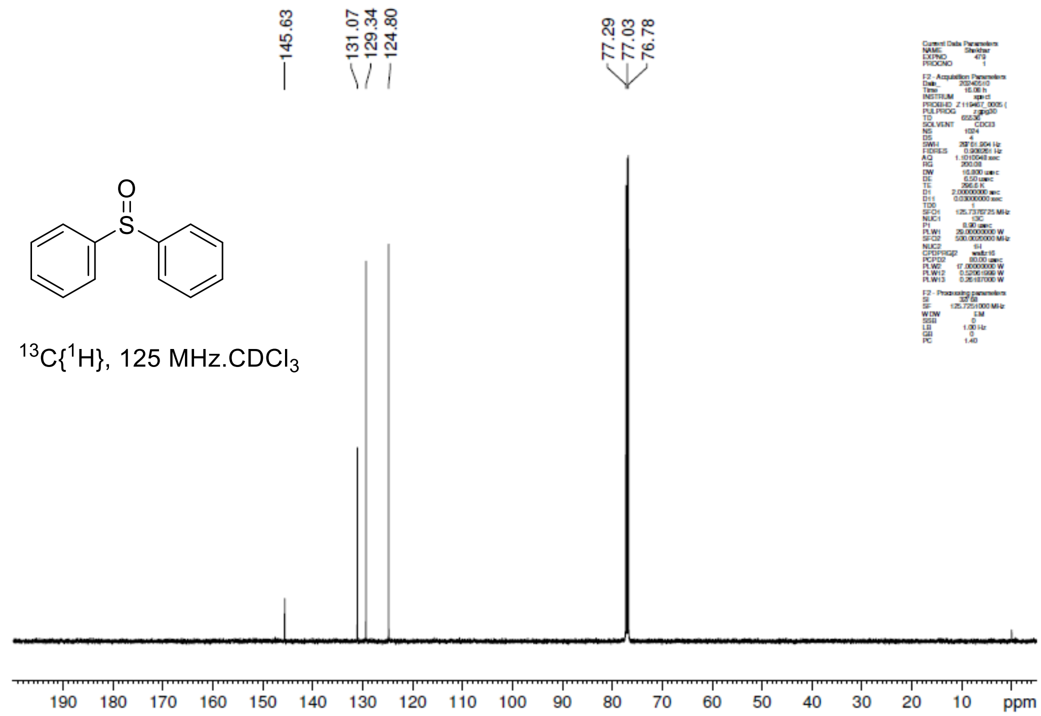


Figure S57. ^{13}C NMR spectrum of **4p** in $CDCl_3$

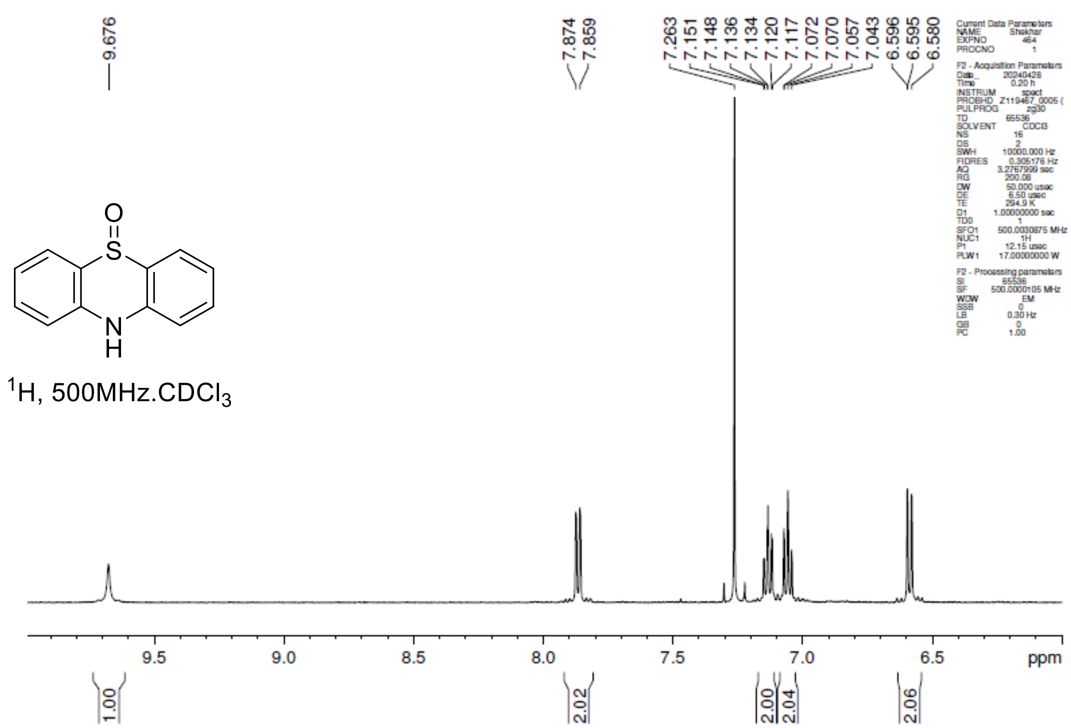


Figure S58. ^{1}H NMR spectrum of **4q** in $CDCl_3$

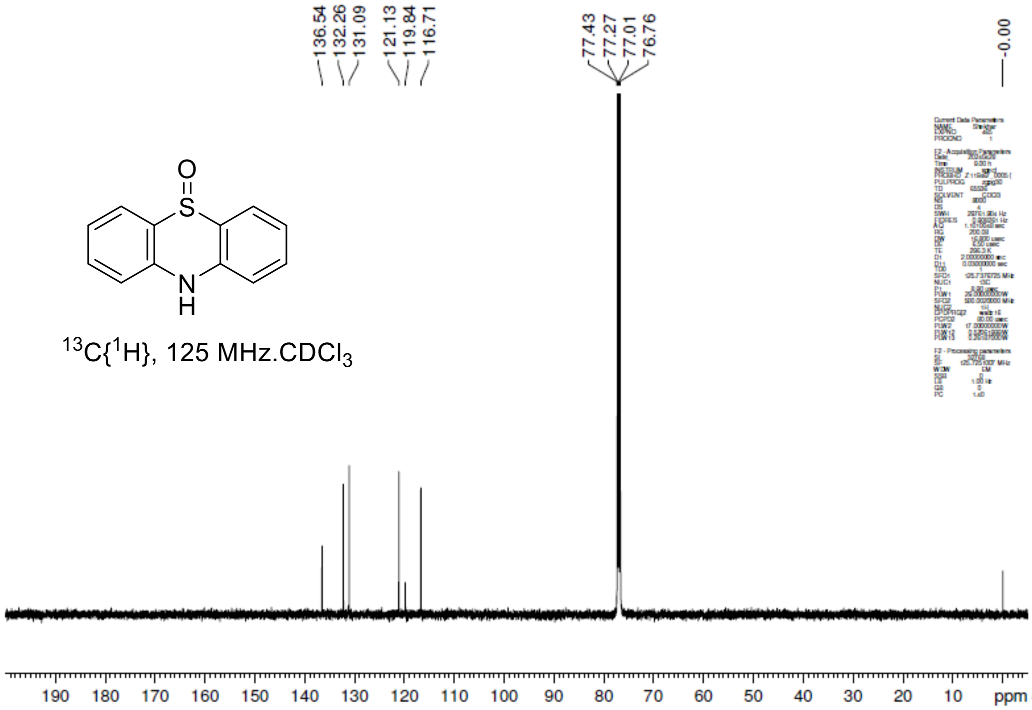


Figure S59. ^{13}C NMR spectrum of **4q** in $CDCl_3$

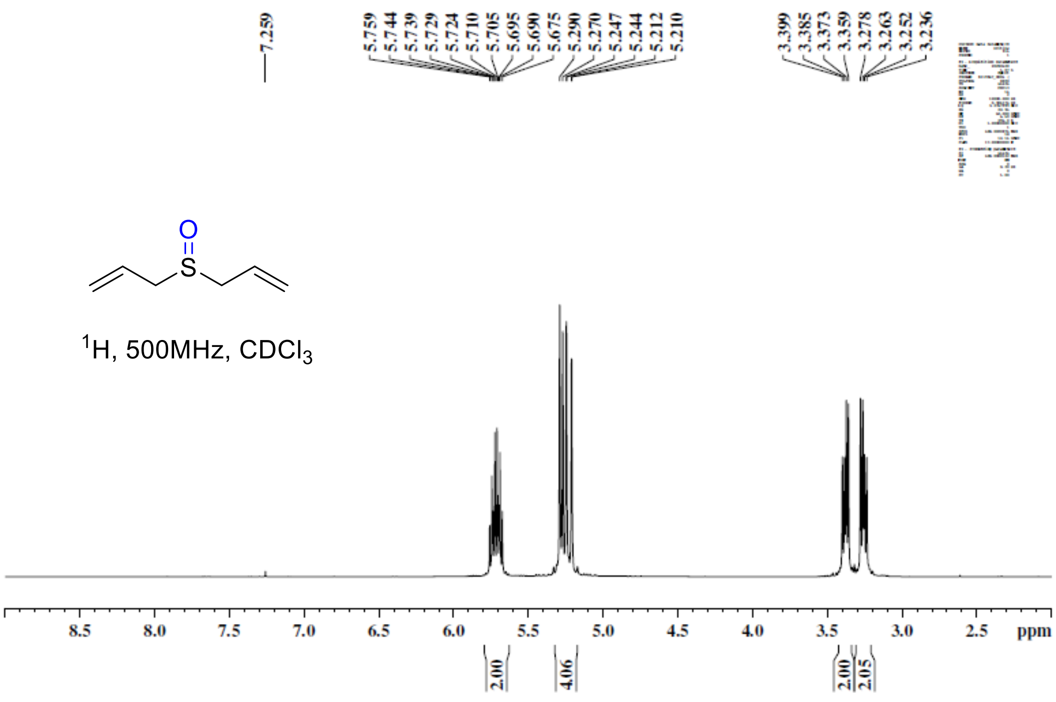


Figure S60. ^{1}H NMR spectrum of **4r** in $CDCl_3$

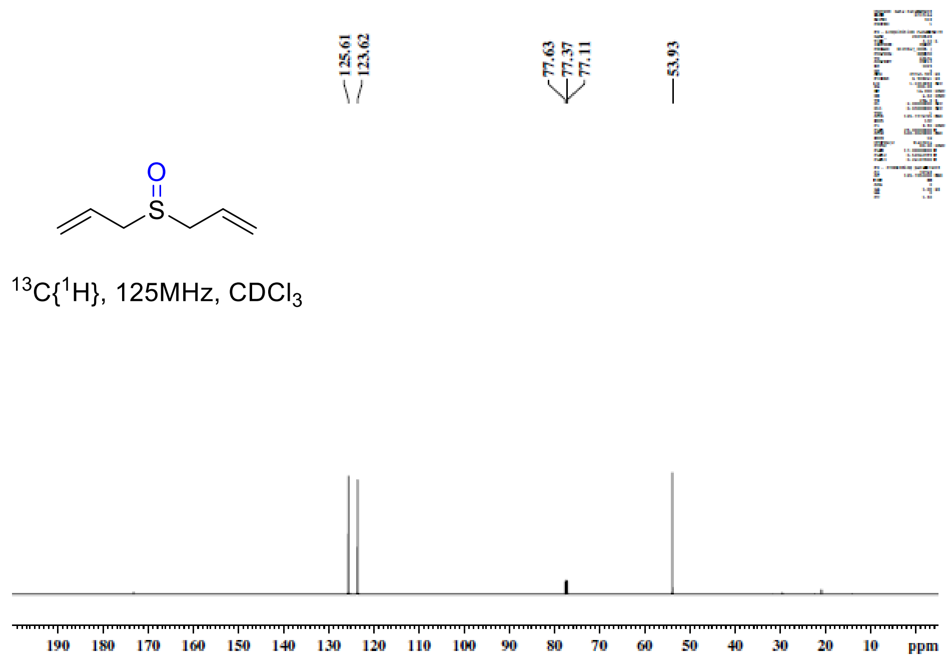


Figure S61. ^{13}C NMR spectrum of **4s** in $CDCl_3$

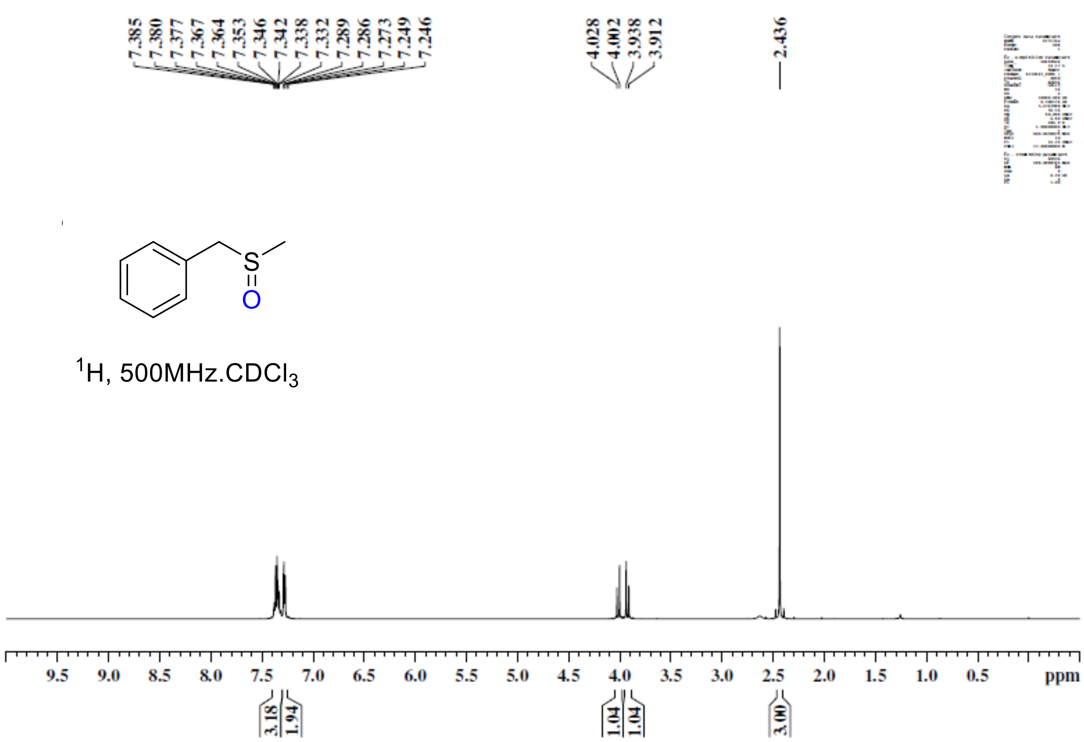


Figure S62. ^{1}H NMR spectrum of **4s** in $CDCl_3$

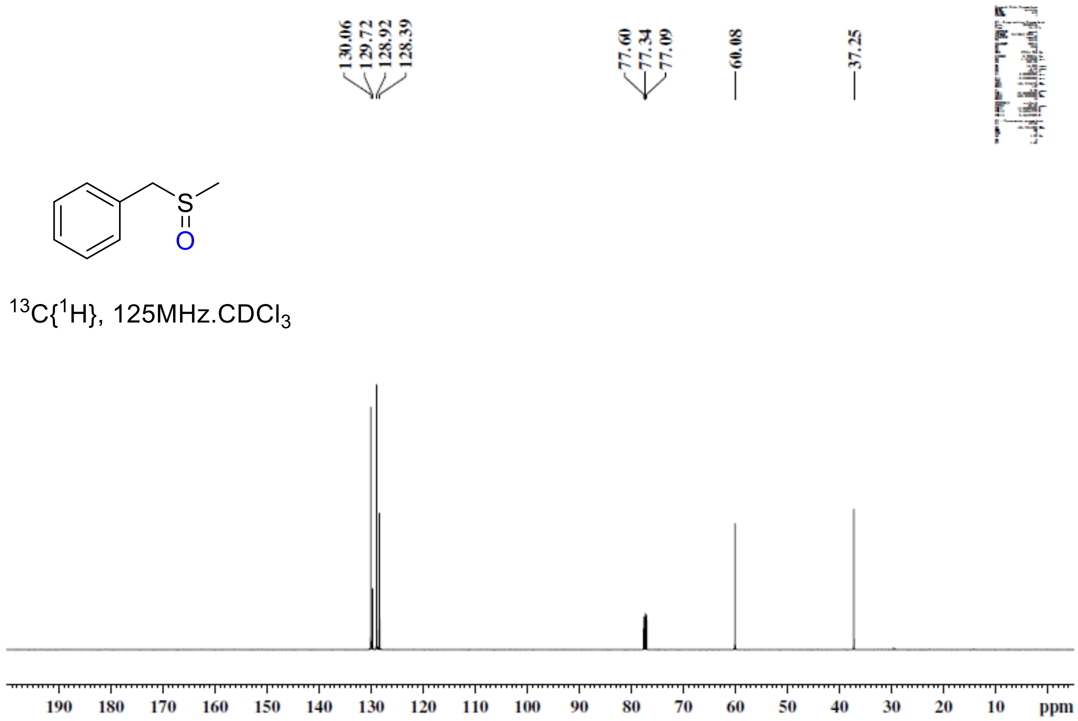


Figure S63. ^{13}C NMR spectrum of **4s** in $CDCl_3$

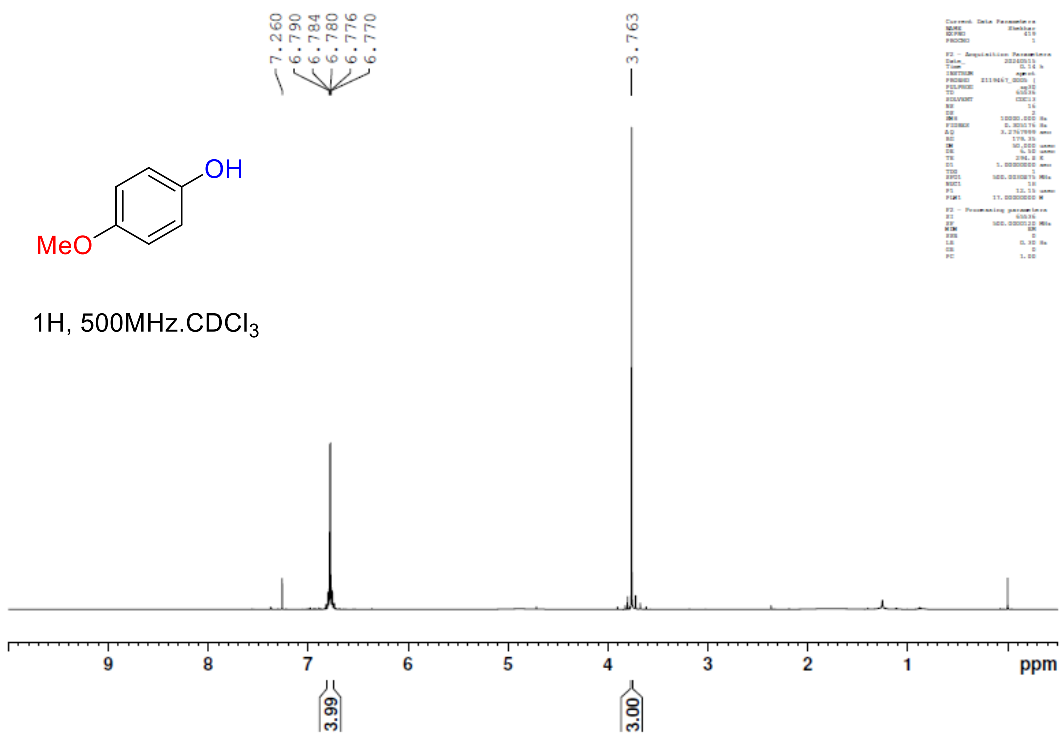


Figure S64. ^{1}H NMR spectrum of **6a** in $CDCl_3$

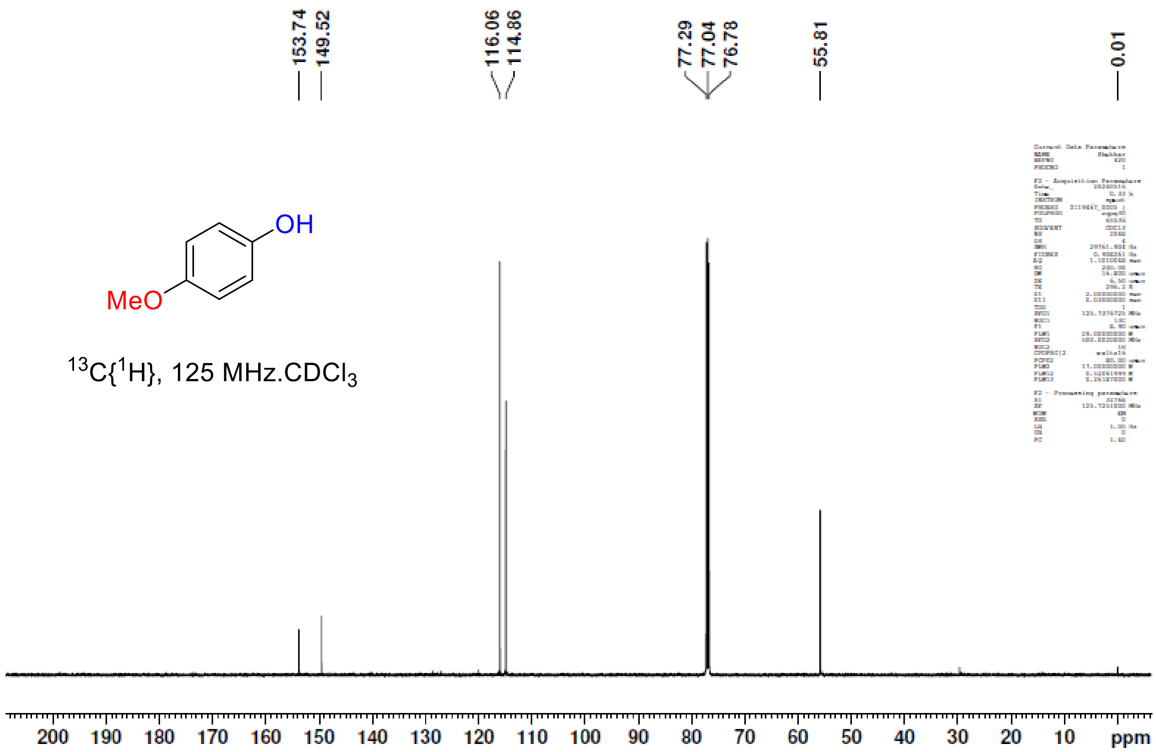


Figure S65. ^{13}C NMR spectrum of **6a** in $CDCl_3$

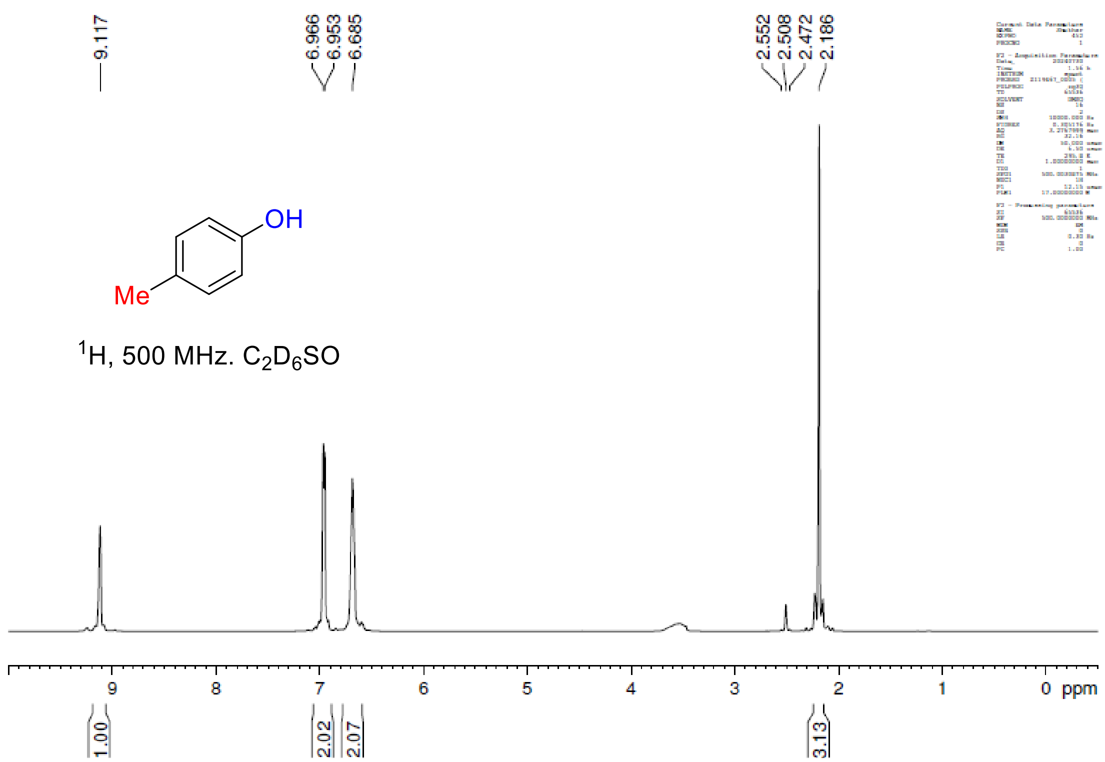


Figure S66. ^{1}H NMR spectrum of **6b** in C_2D_6SO

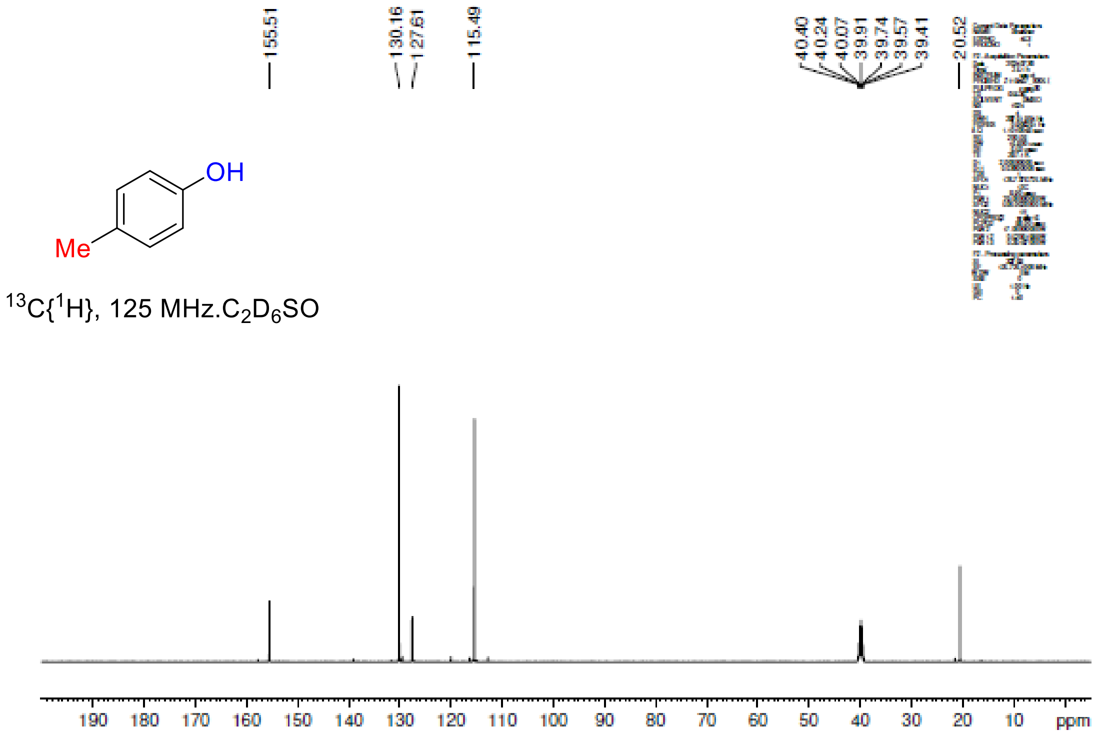


Figure S67. ^{13}C NMR spectrum of **6b** in C_2D_6SO

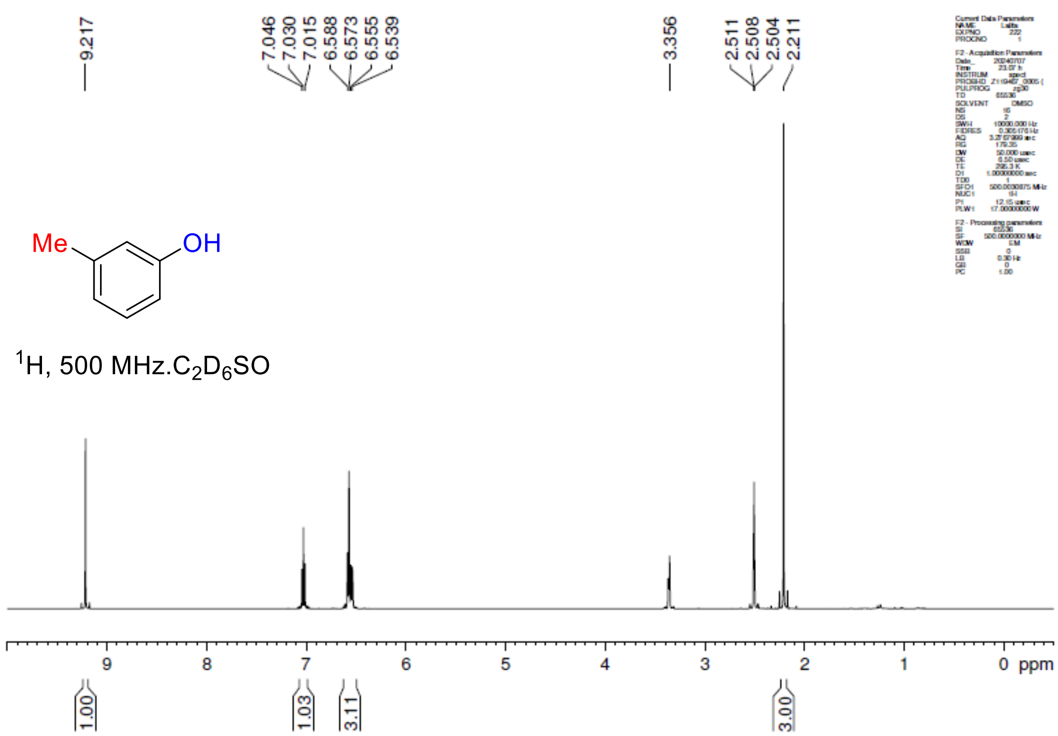


Figure S68. ^{1}H NMR spectrum of **6c** in C_2D_6SO

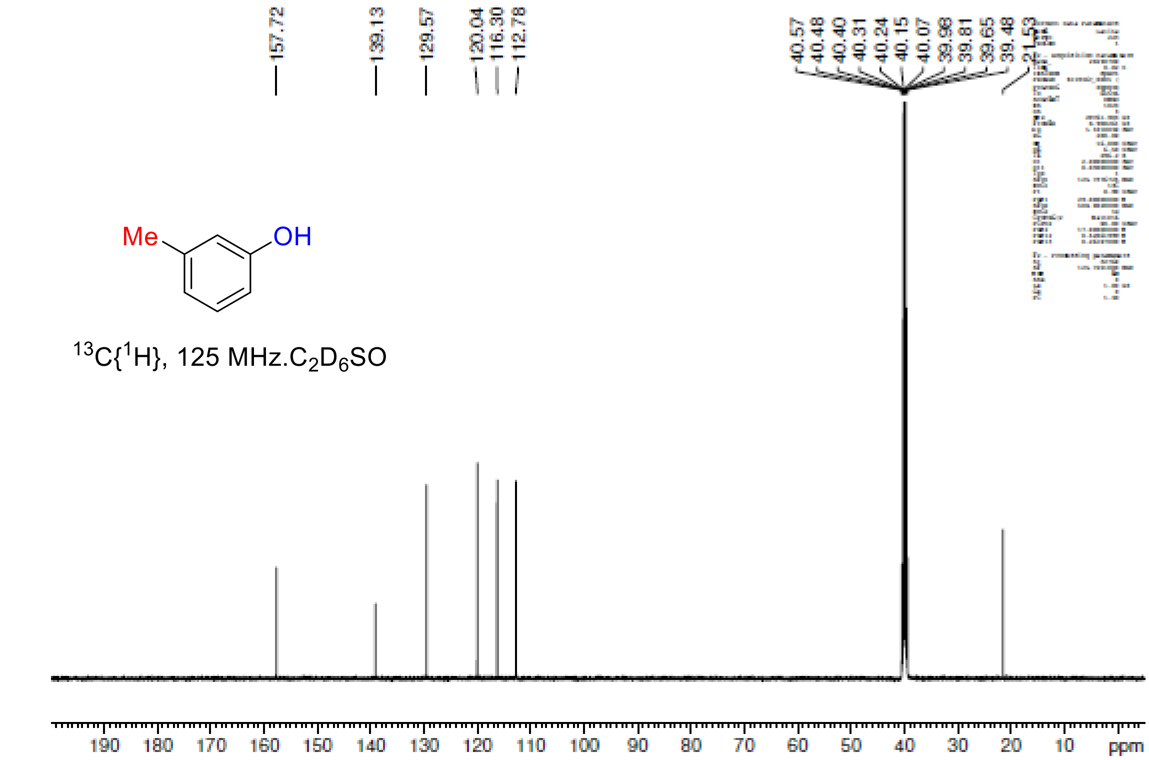


Figure S69. ^{13}C NMR spectrum of **6c** in C_2D_6SO

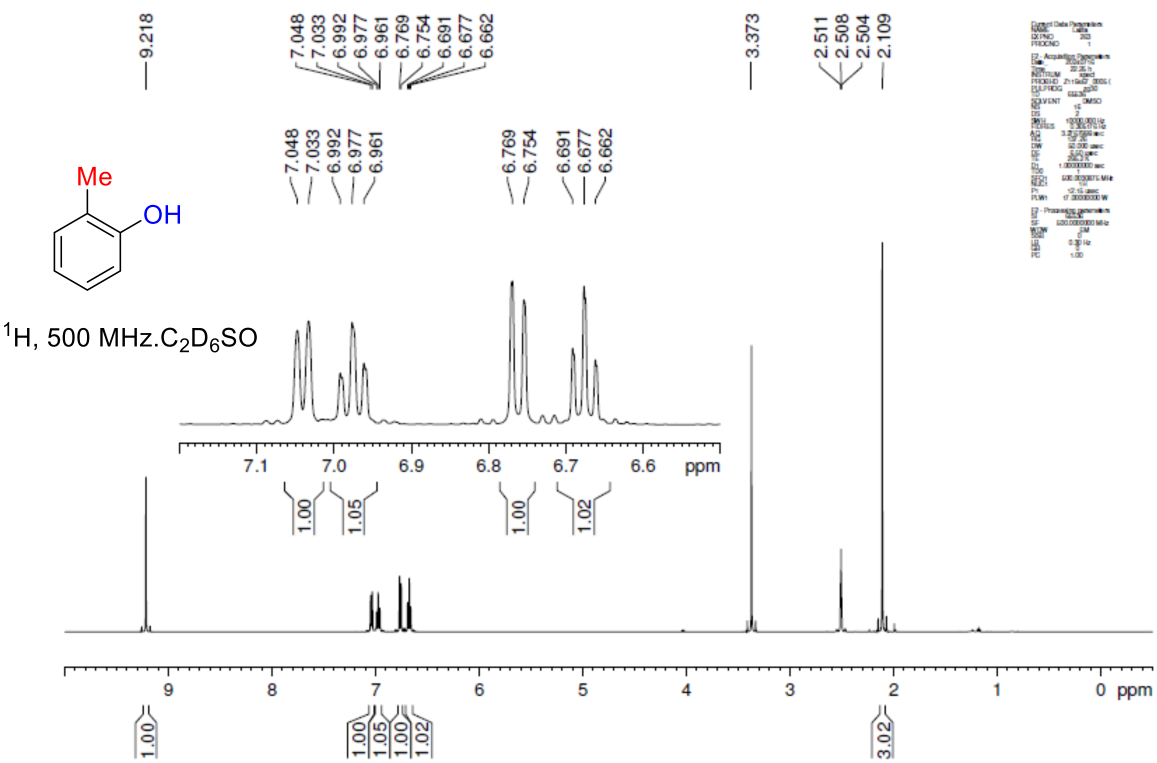


Figure S70. ^{1}H NMR spectrum of **6d** in C_2D_6SO

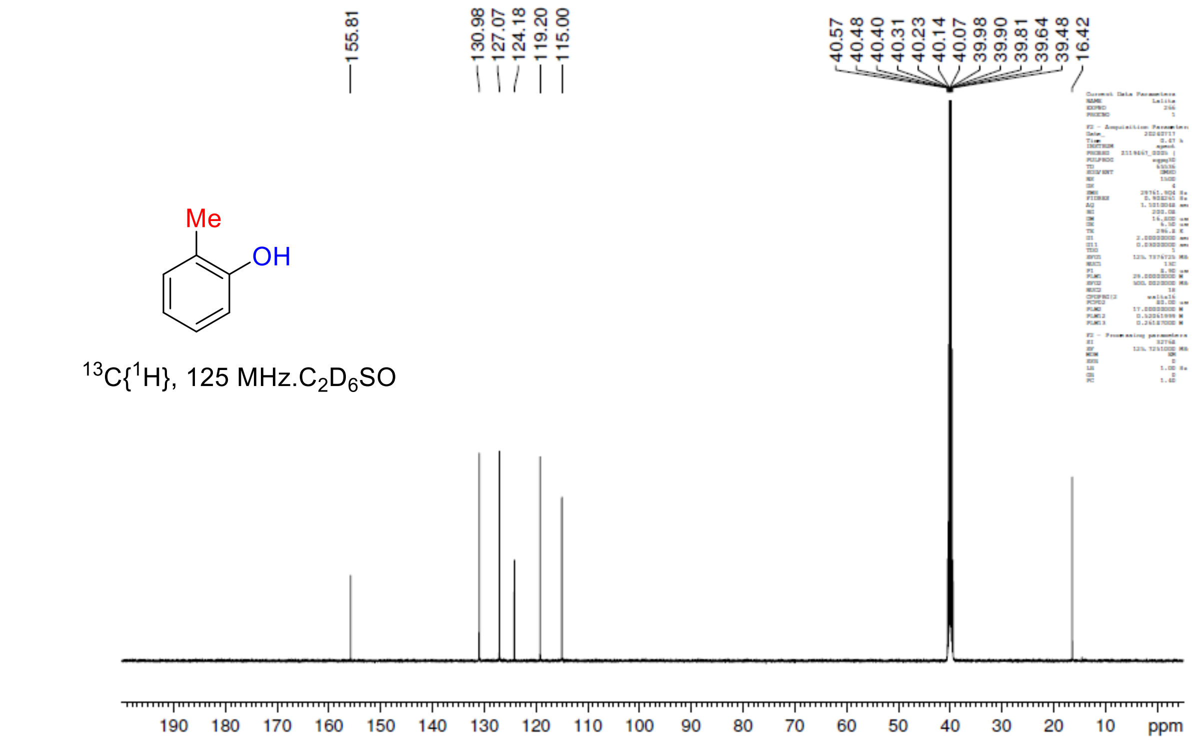


Figure S71. ^{13}C NMR spectrum of **6d** in C_2D_6SO

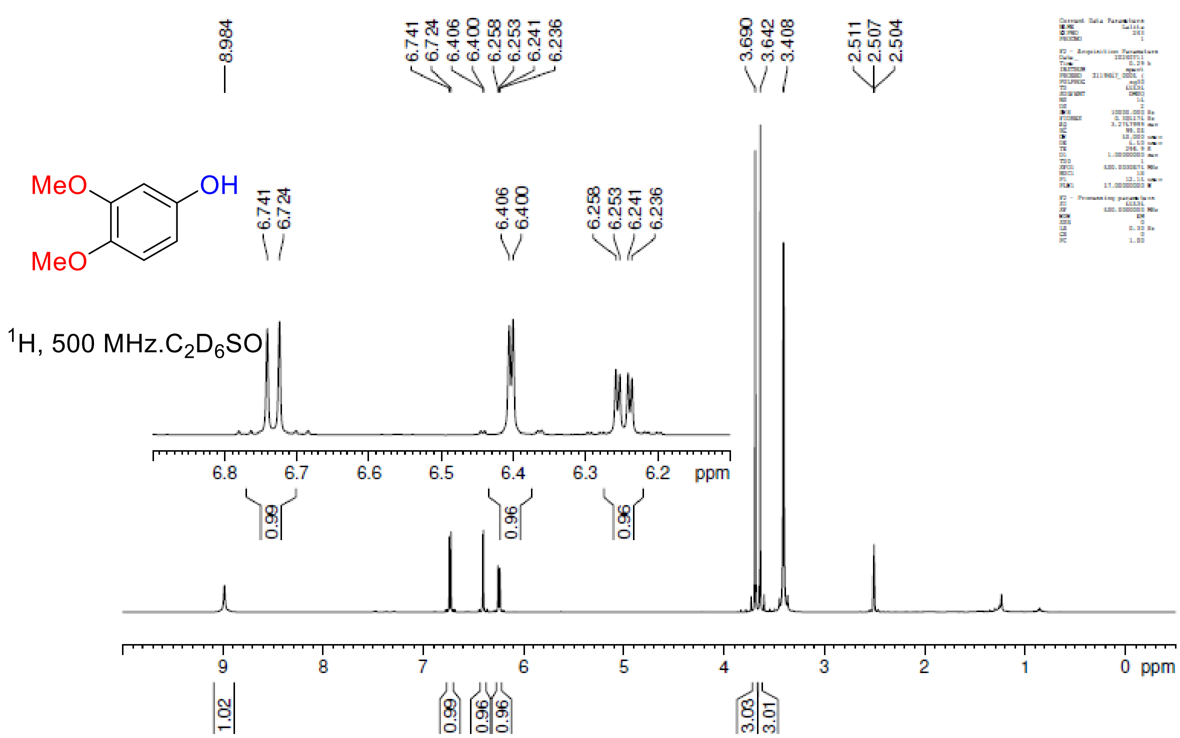


Figure S72. ^{1}H NMR spectrum of **6e** in C_2D_6SO

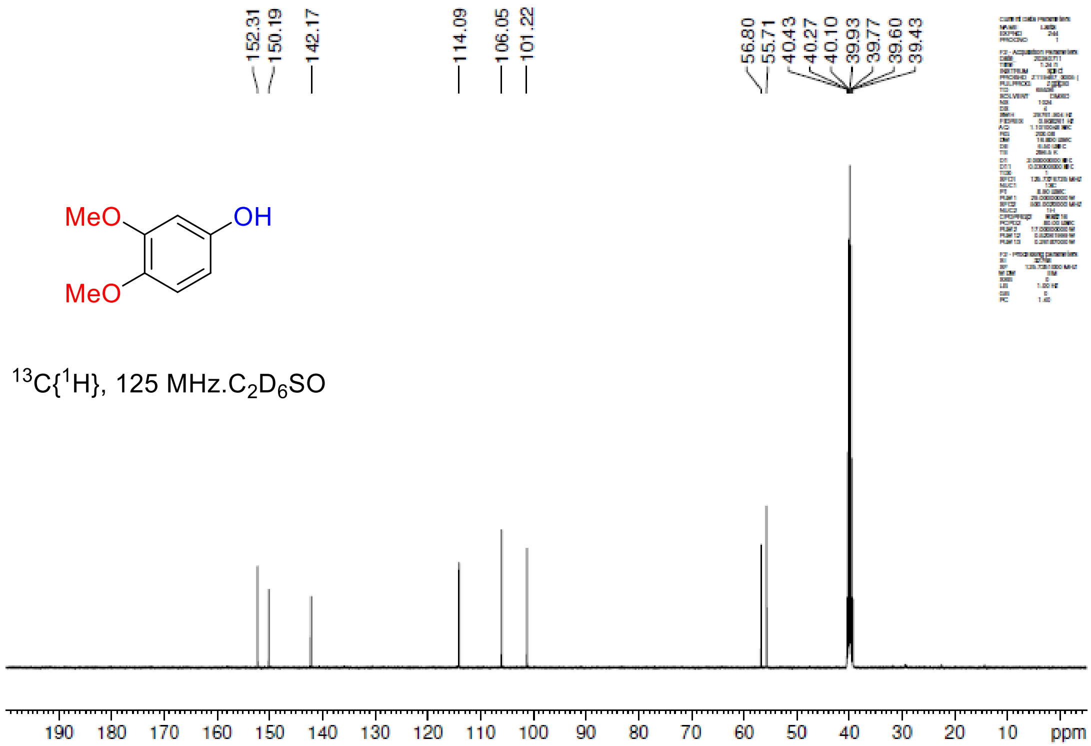


Figure S73. ^{13}C NMR spectrum of **6e** in C_2D_6SO

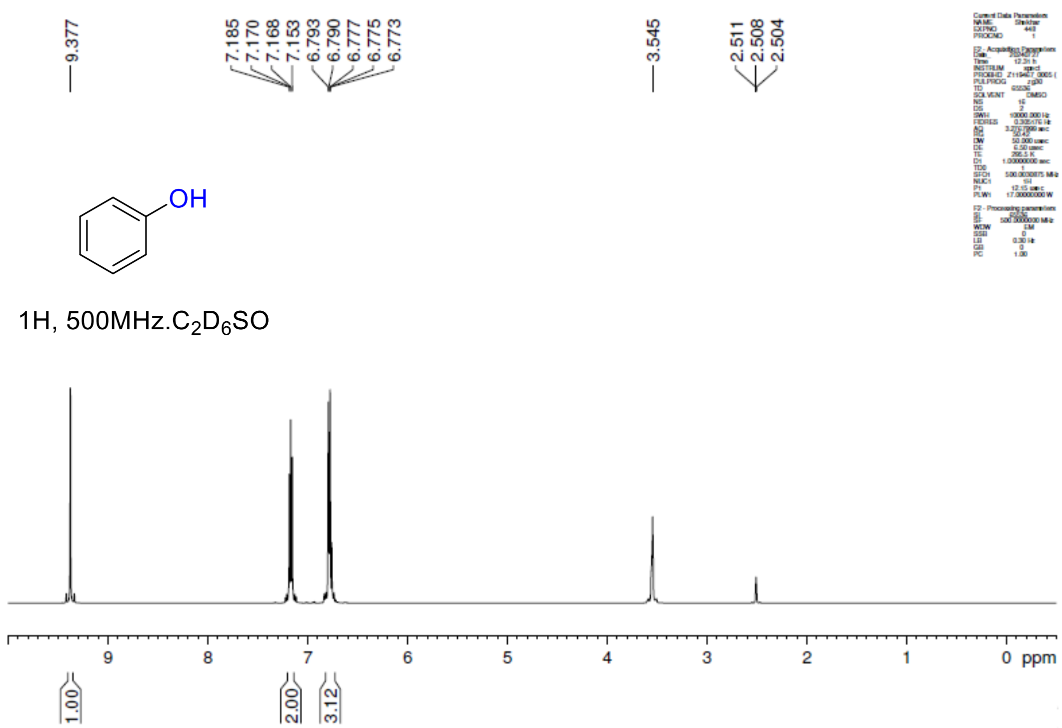


Figure S74. ^{1}H NMR spectrum of **6f** in C_2D_6SO

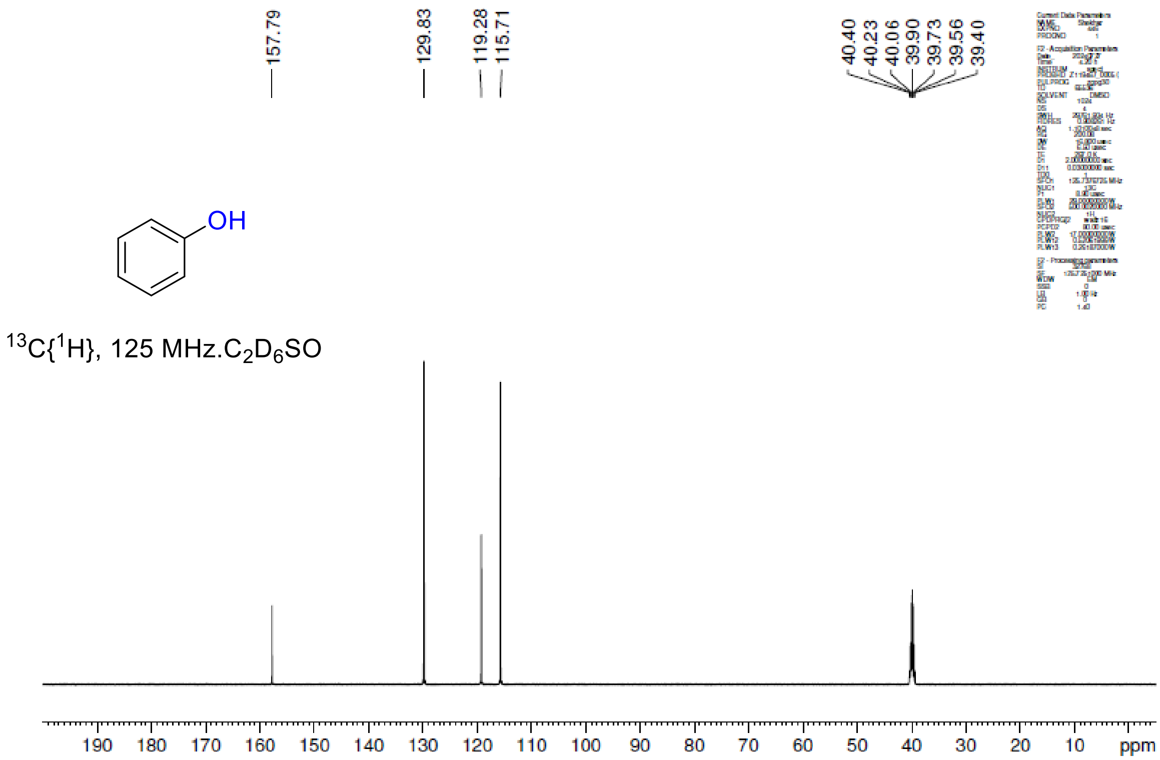


Figure S75. ^{13}C NMR spectrum of **6f** in C_2D_6SO

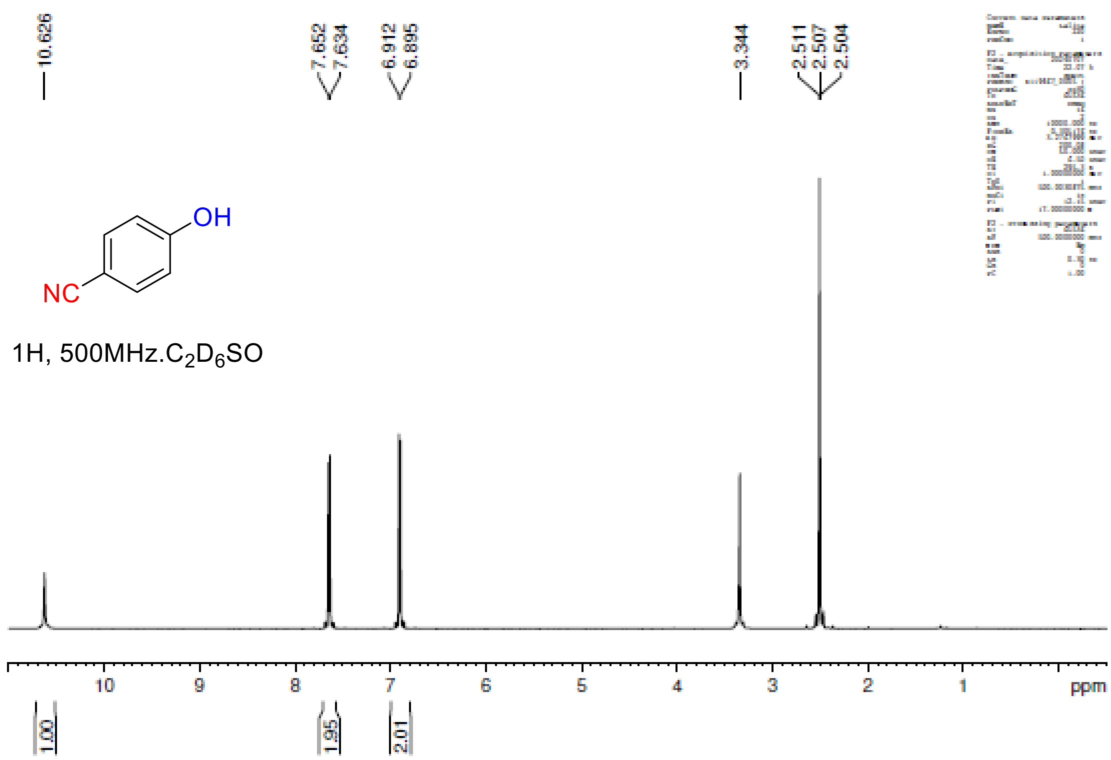


Figure S76. ^{1}H NMR spectrum of **6g** in C_2D_6SO

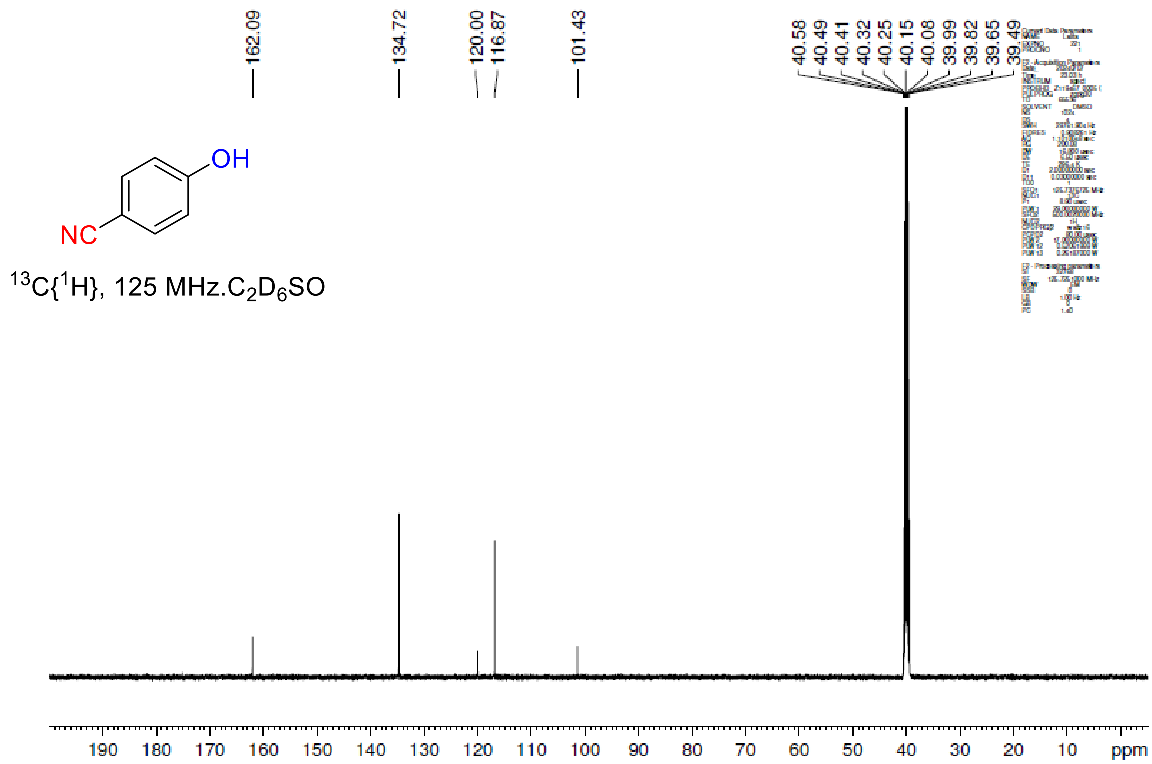


Figure S77. ^{13}C NMR spectrum of **6g** in C_2D_6SO

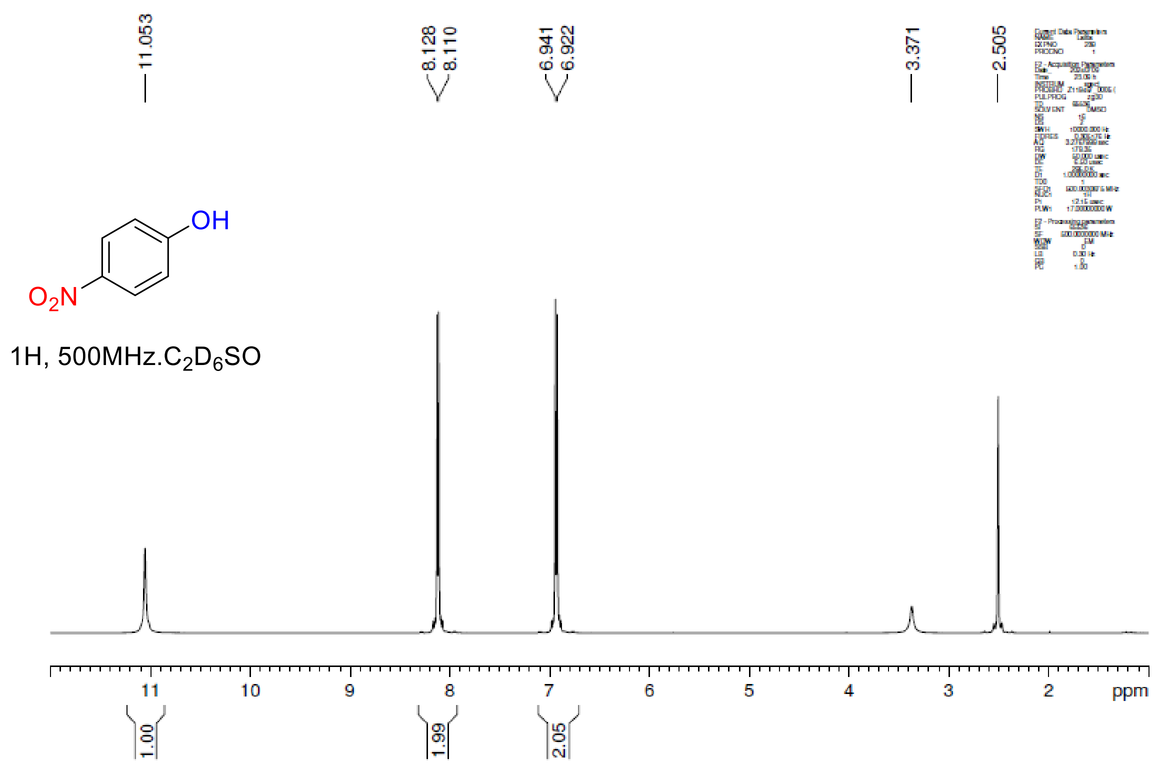


Figure S78. ^{1}H NMR spectrum of **6h** in C_2D_6SO

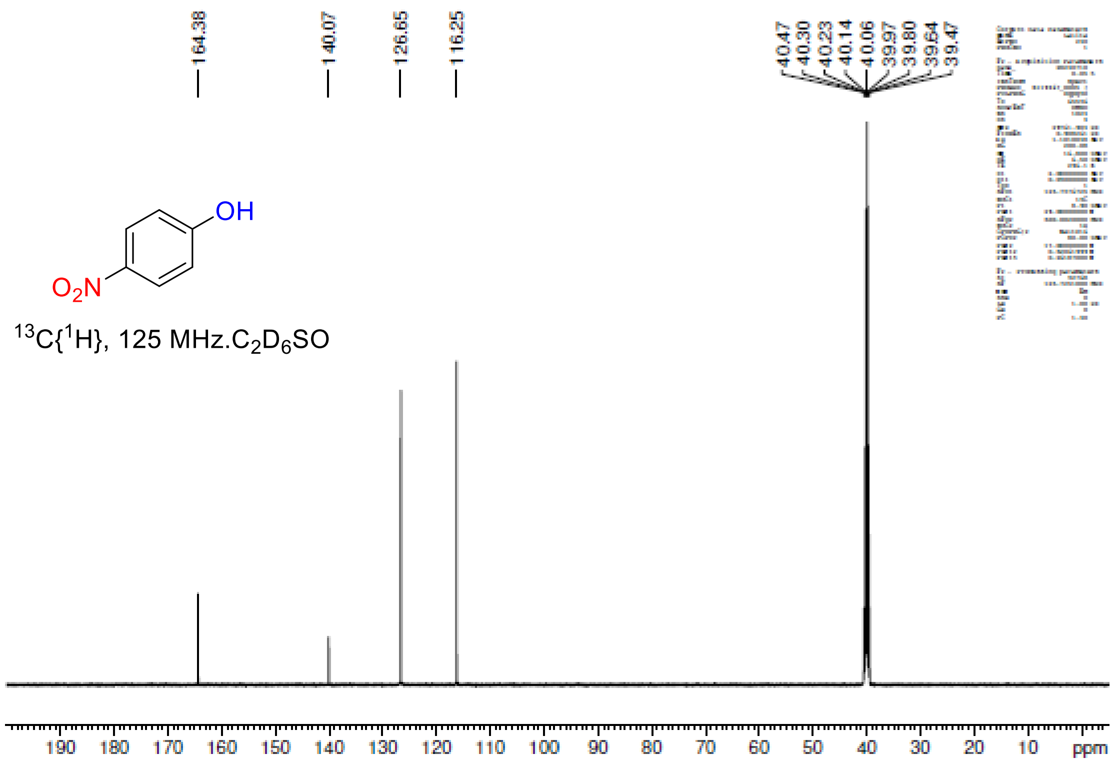


Figure S79. ^{13}C NMR spectrum of **6h** in C_2D_6SO

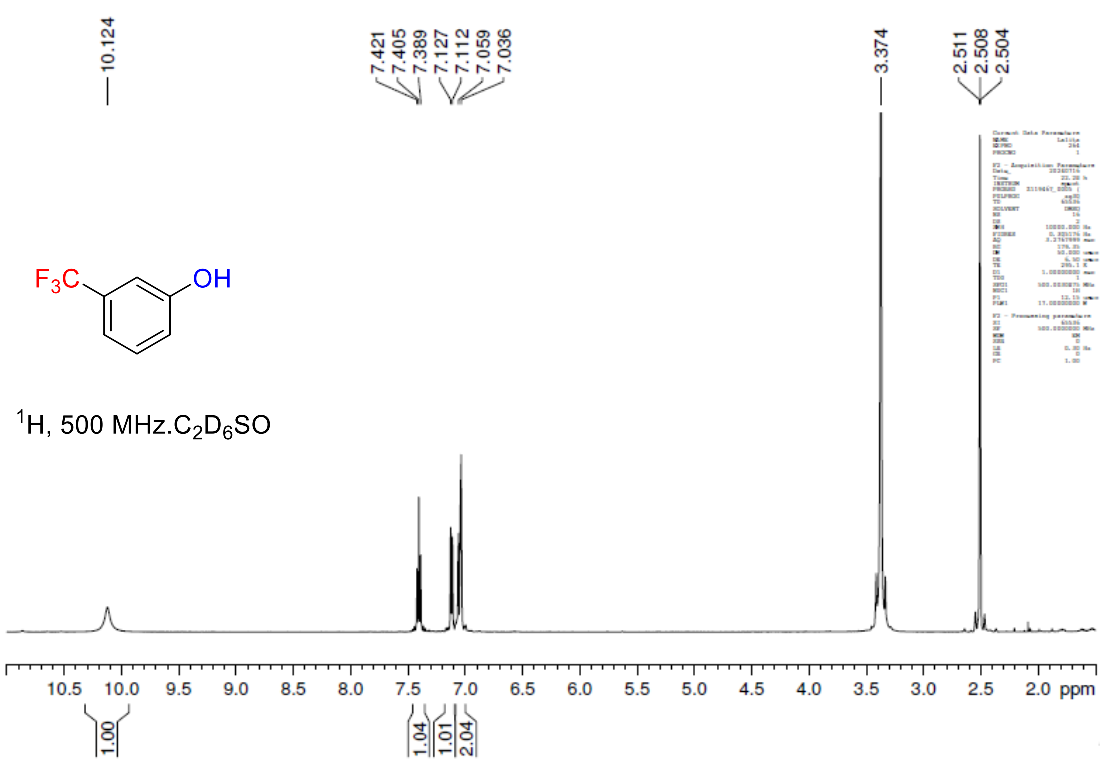


Figure S80. ^{1}H NMR spectrum of **6l** in C_2D_6SO

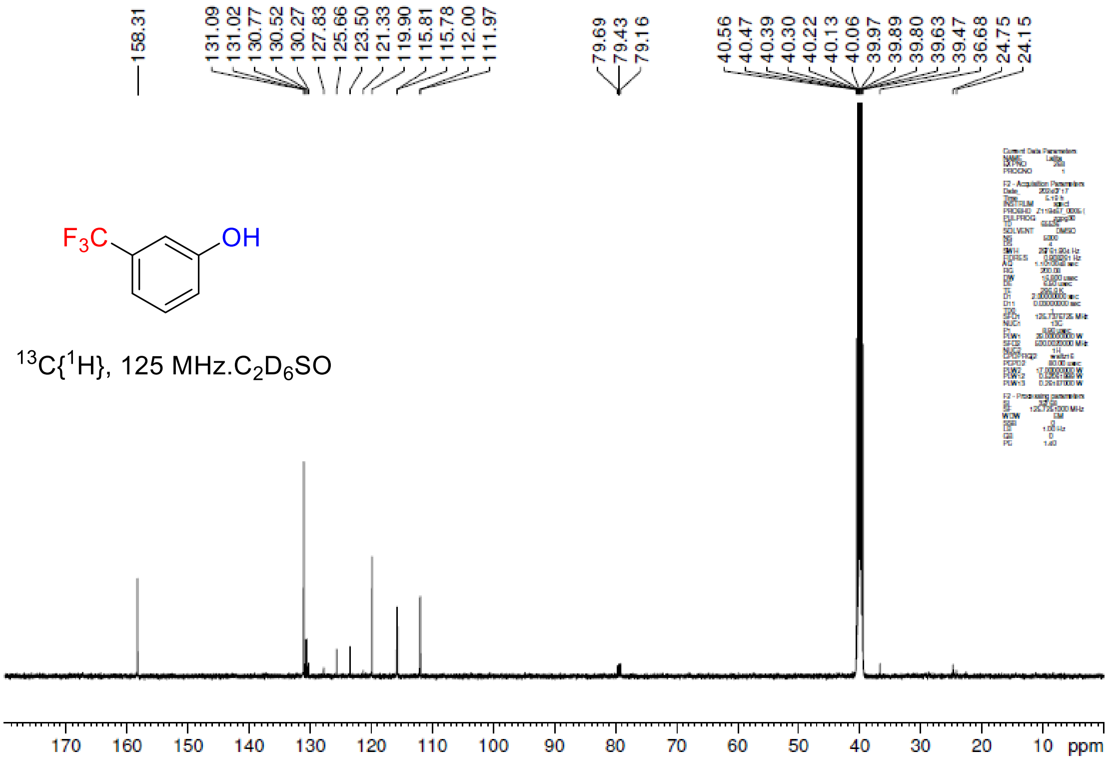


Figure S81. ^{13}C NMR spectrum of **6i** in C_2D_6SO

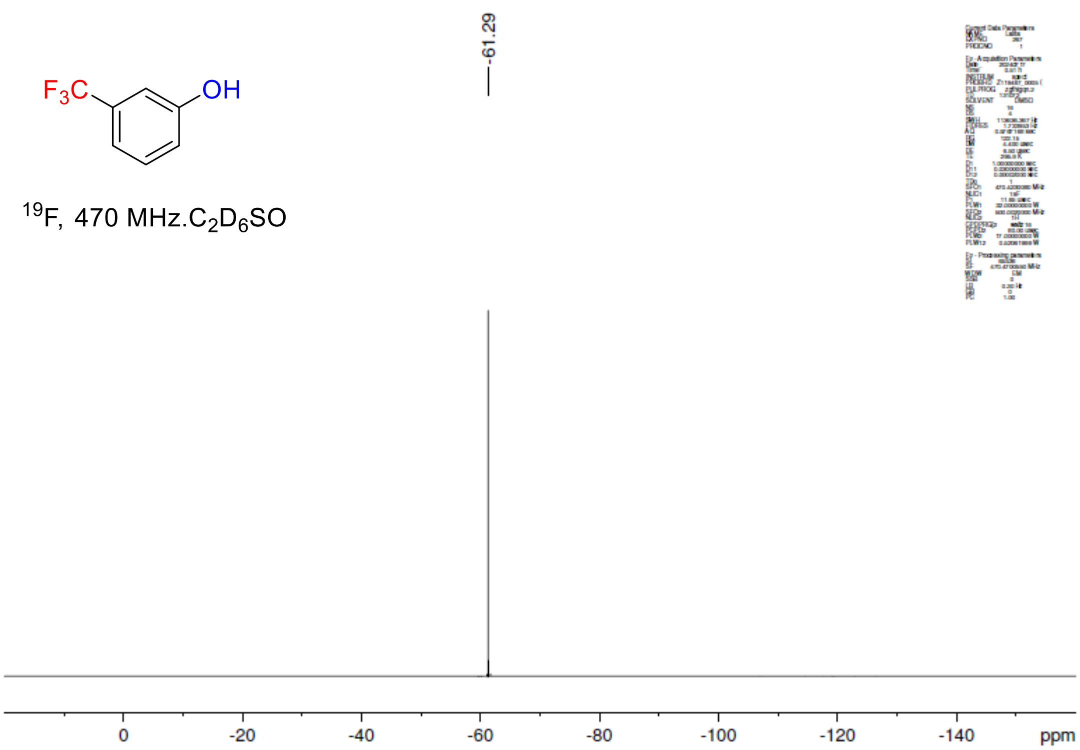


Figure S82. ^{19}F NMR spectrum of **6i** in C_2D_6SO

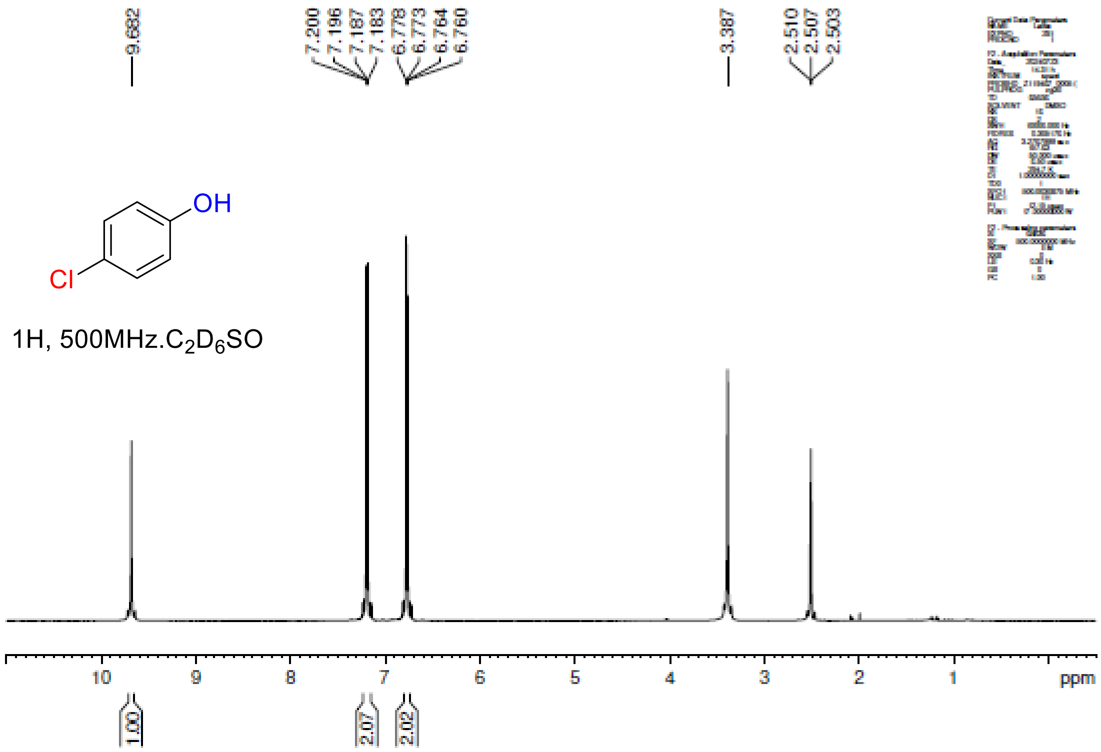


Figure S83. ^{1}H NMR spectrum of **6j** in C_2D_6SO

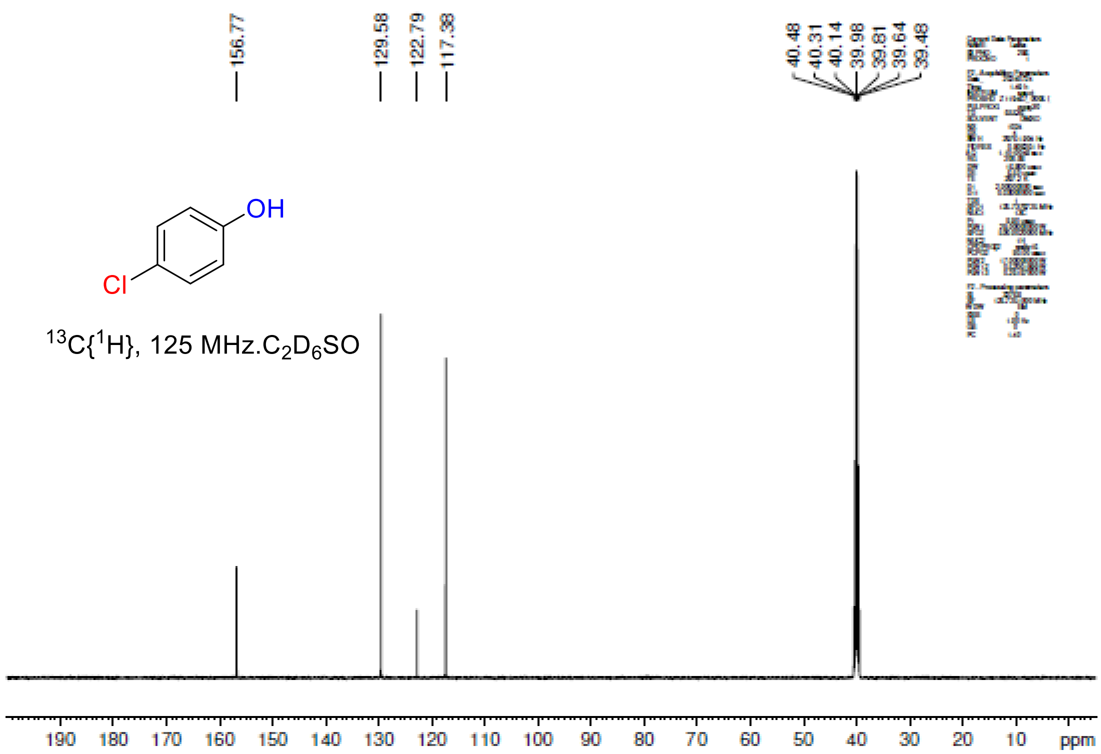


Figure S84. ^{13}C NMR spectrum of **6j** in C_2D_6SO

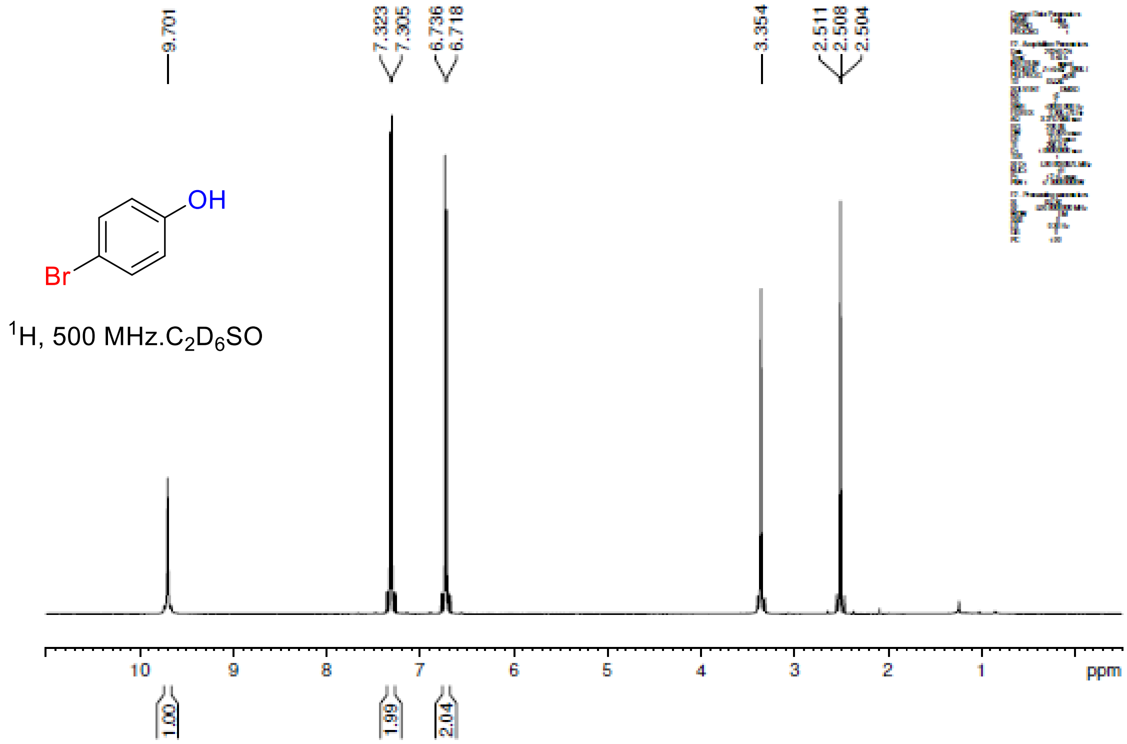


Figure S85. [1]H NMR spectrum of **6k** in C_2D_6SO

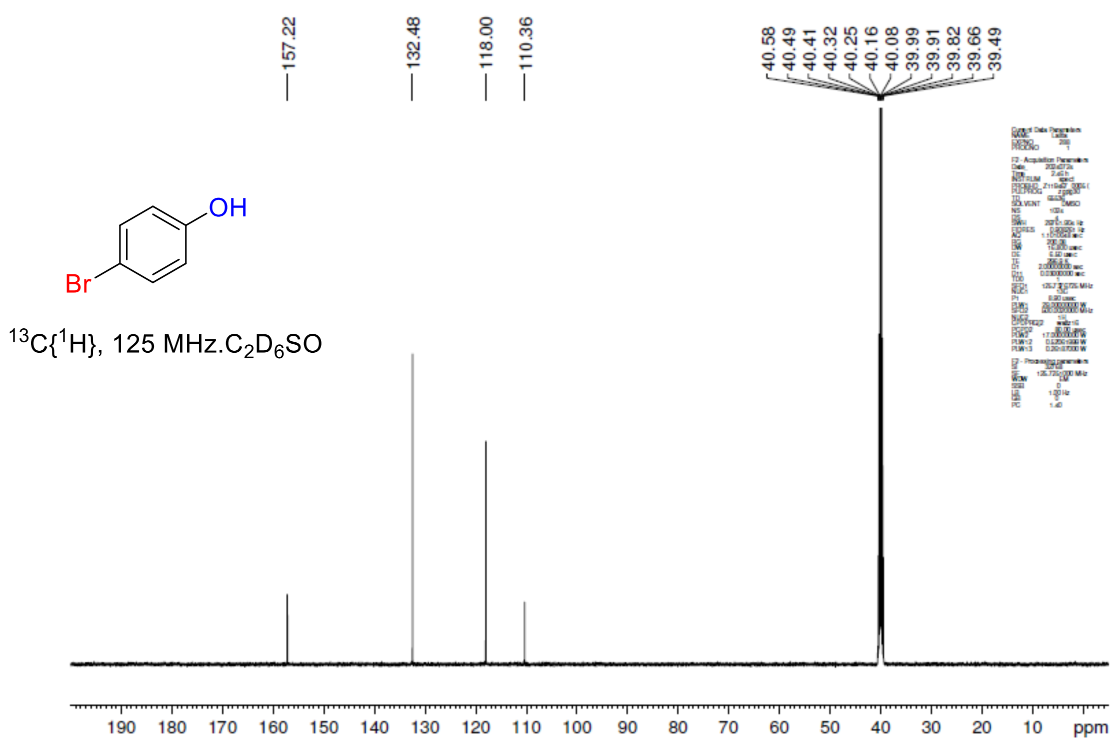


Figure S86. [13]C NMR spectrum of **6k** in C_2D_6SO

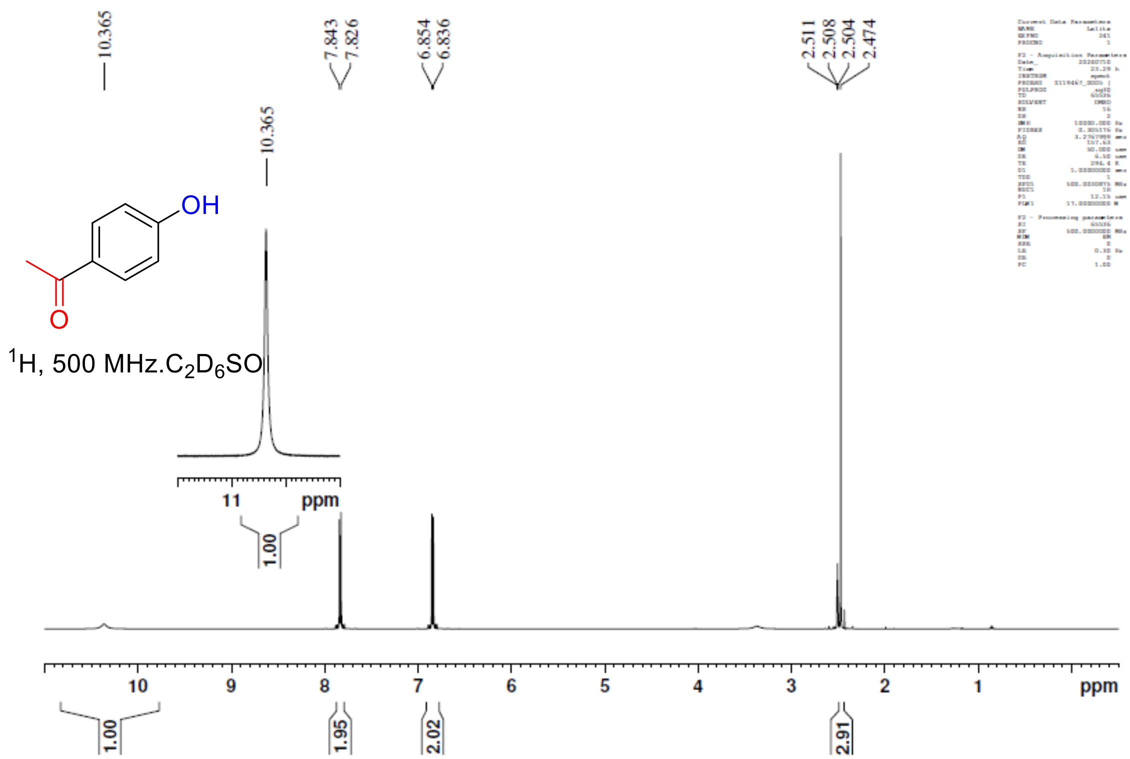


Figure S87. ^{1}H NMR spectrum of **6l** in C_2D_6SO

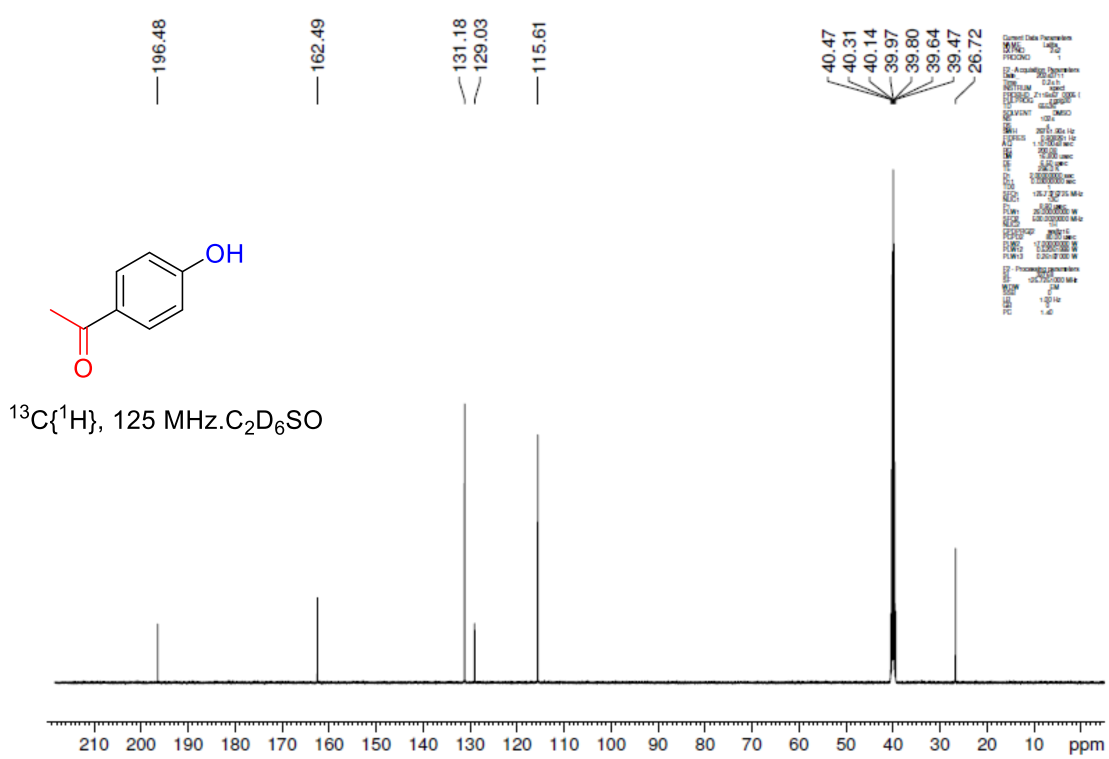


Figure S88. ^{13}C NMR spectrum of **6l** in C_2D_6SO

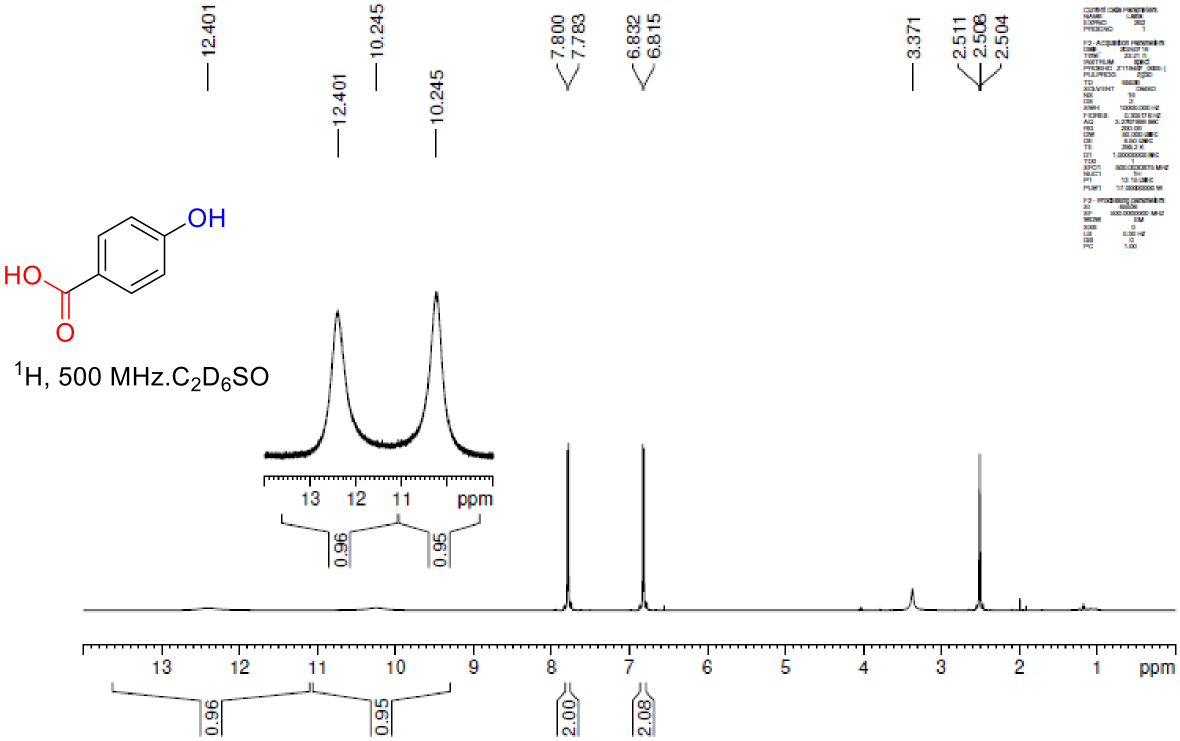


Figure S89. ^{1}H NMR spectrum of **6m** in C_2D_6SO

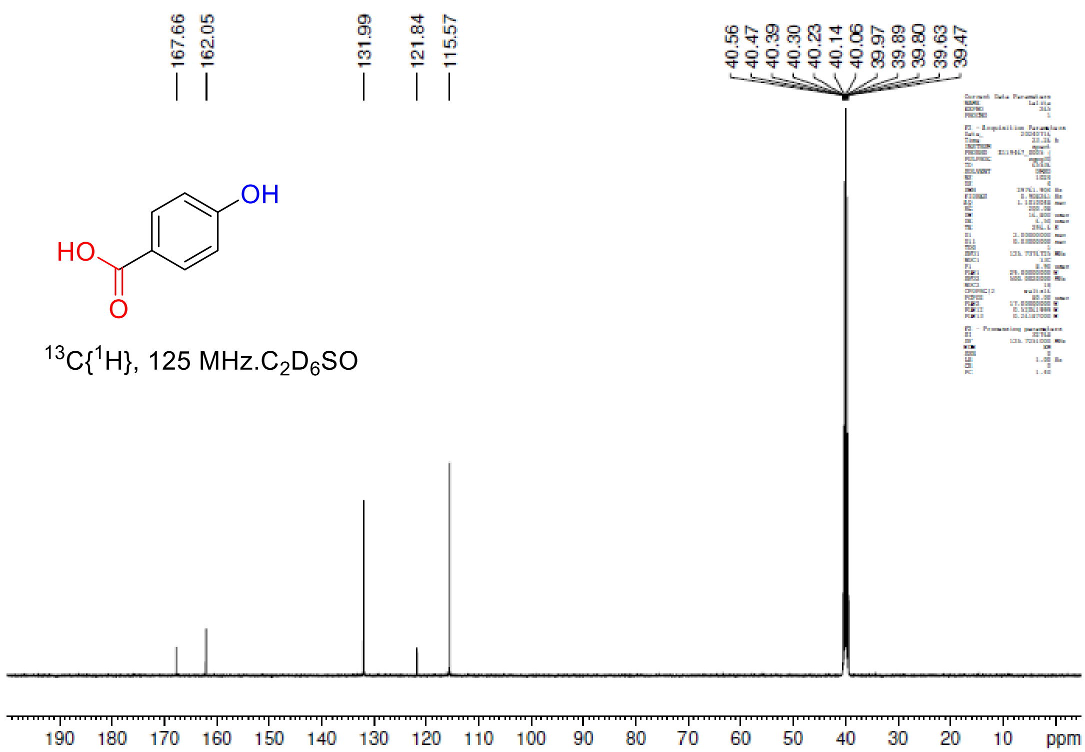


Figure S90. ^{13}C NMR spectrum of **6m** in C_2D_6SO

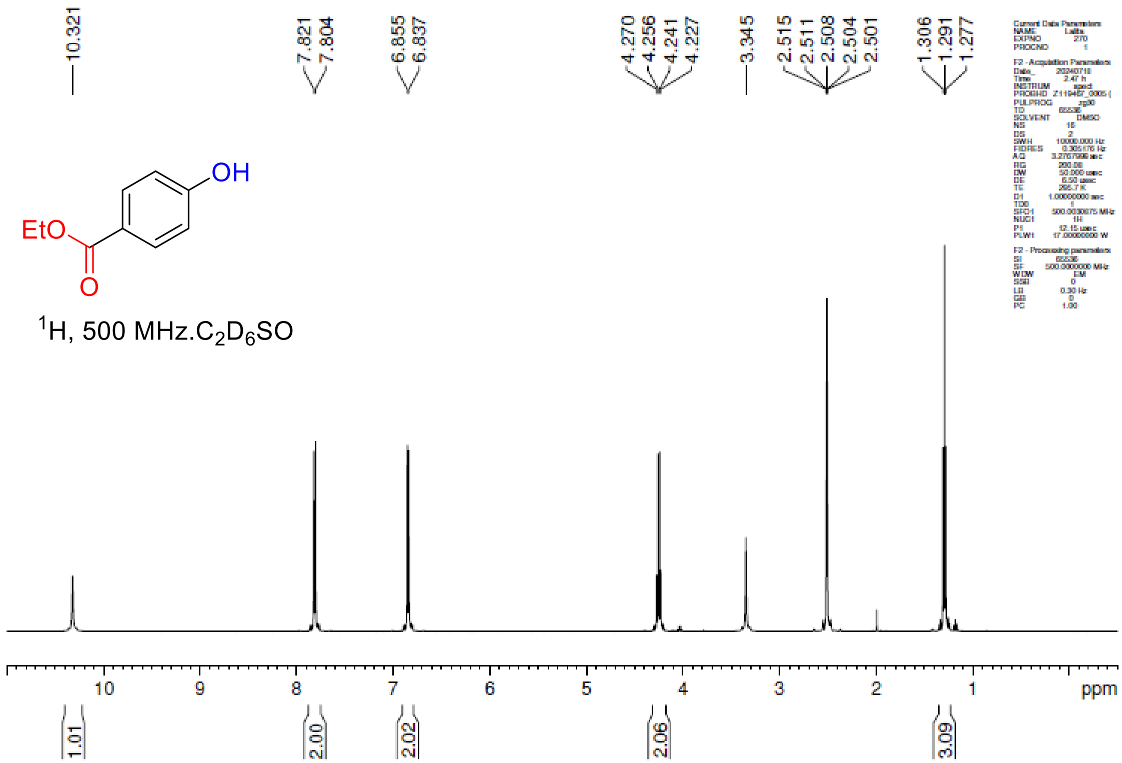


Figure S91. ^{1}H NMR spectrum of **6n** in C_2D_6SO

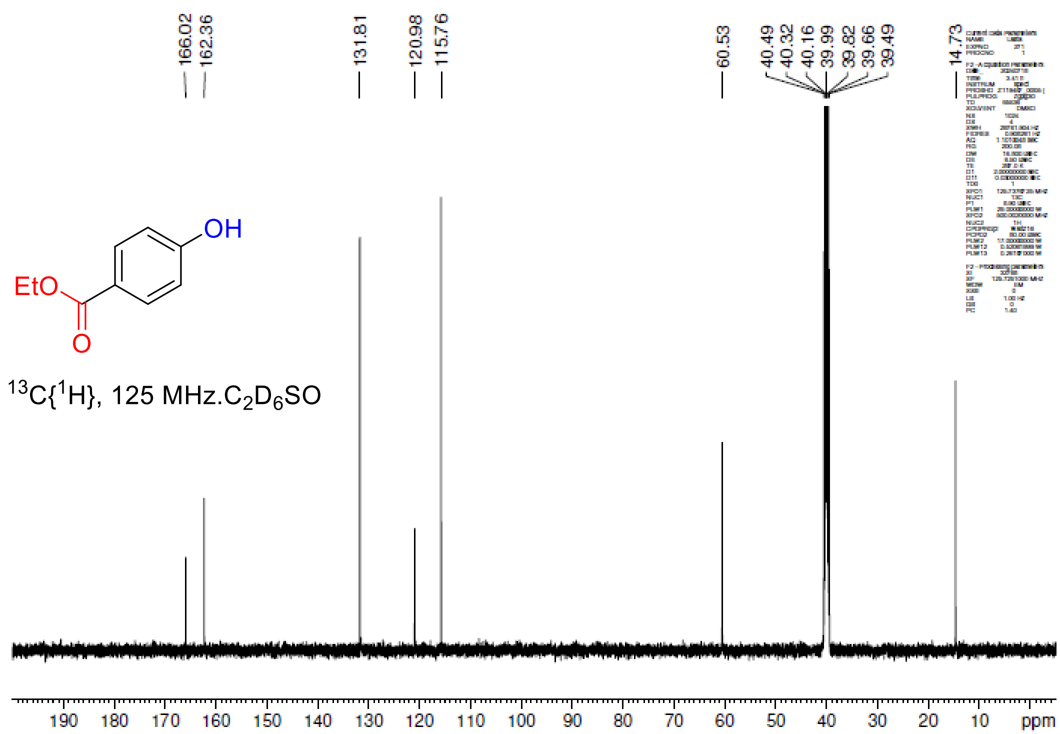


Figure S92. ^{13}C NMR spectrum of **6n** in C_2D_6SO

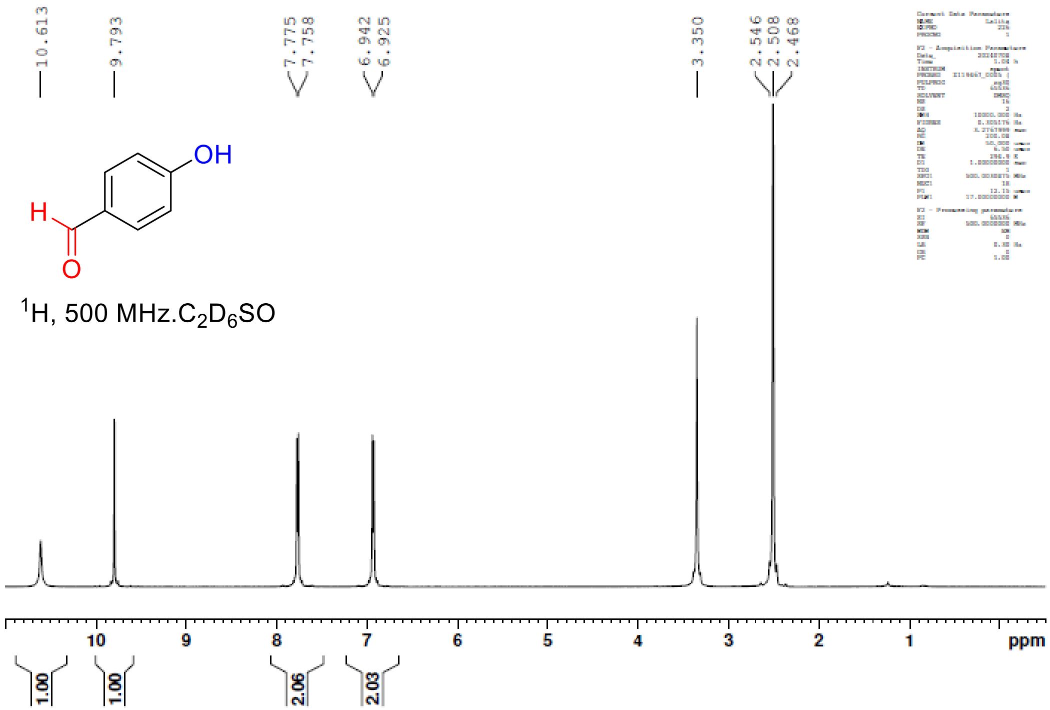


Figure S93. [1]H NMR spectrum of **6o** in C_2D_6SO

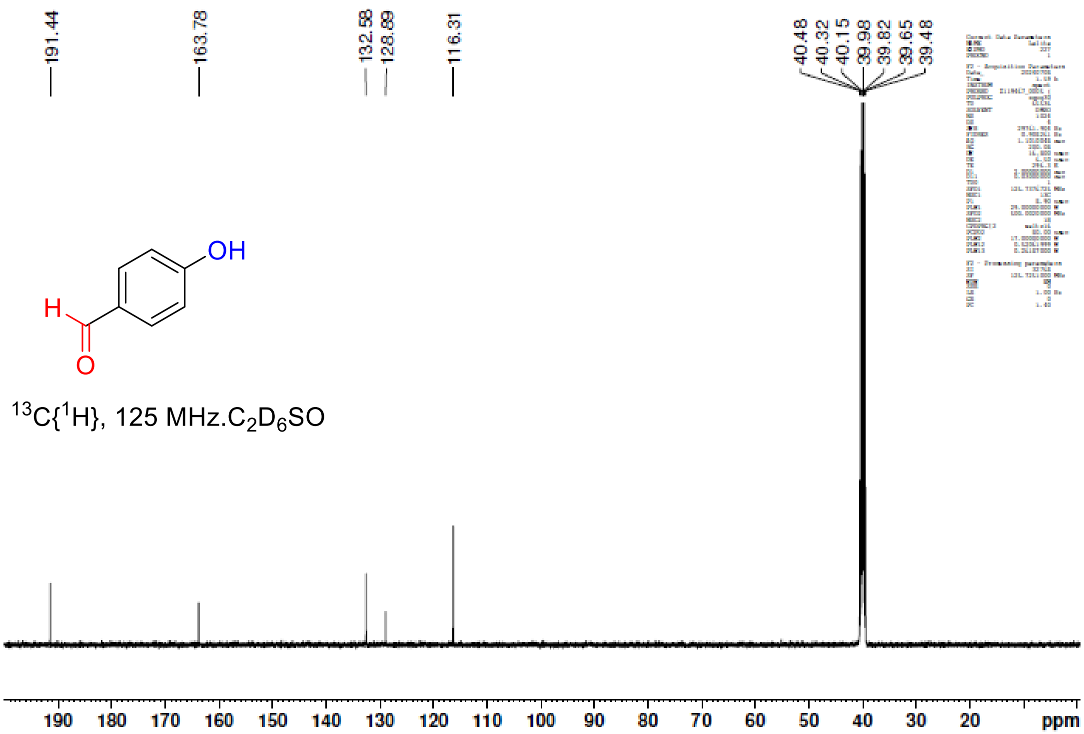


Figure S94. [13]C NMR spectrum of **6o** in C_2D_6SO

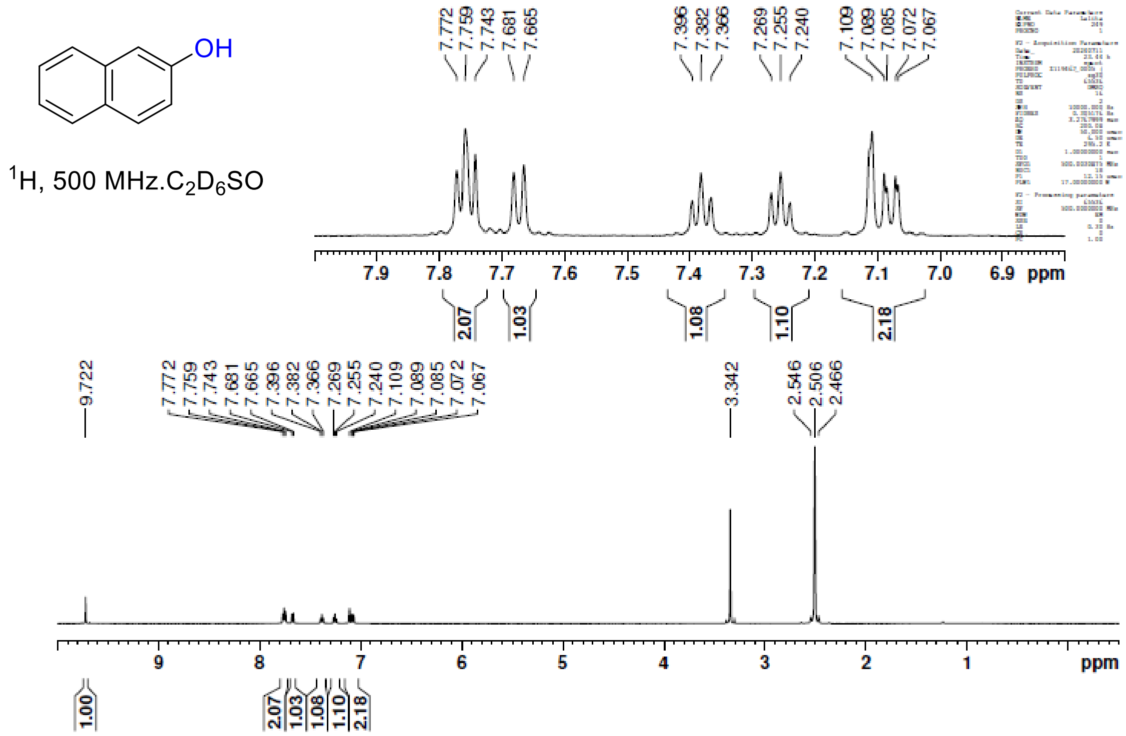


Figure S95. [1]H NMR spectrum of **6p** in C_2D_6SO

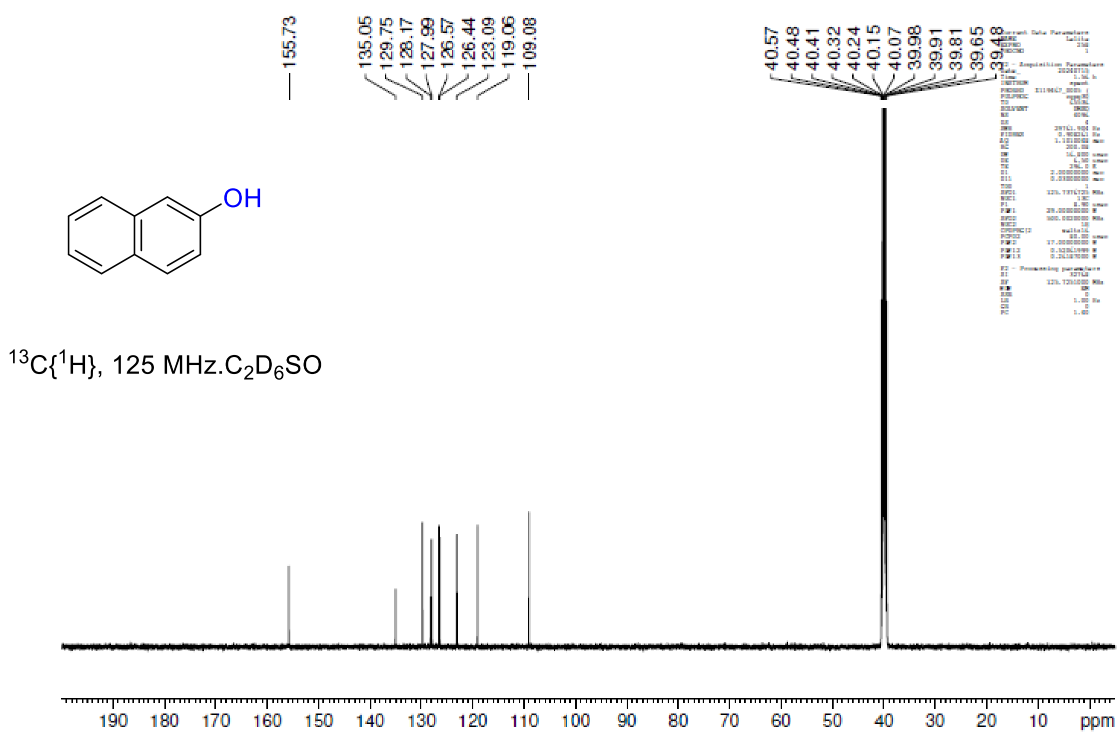


Figure S96. [13]C NMR spectrum of **6p** in C_2D_6SO

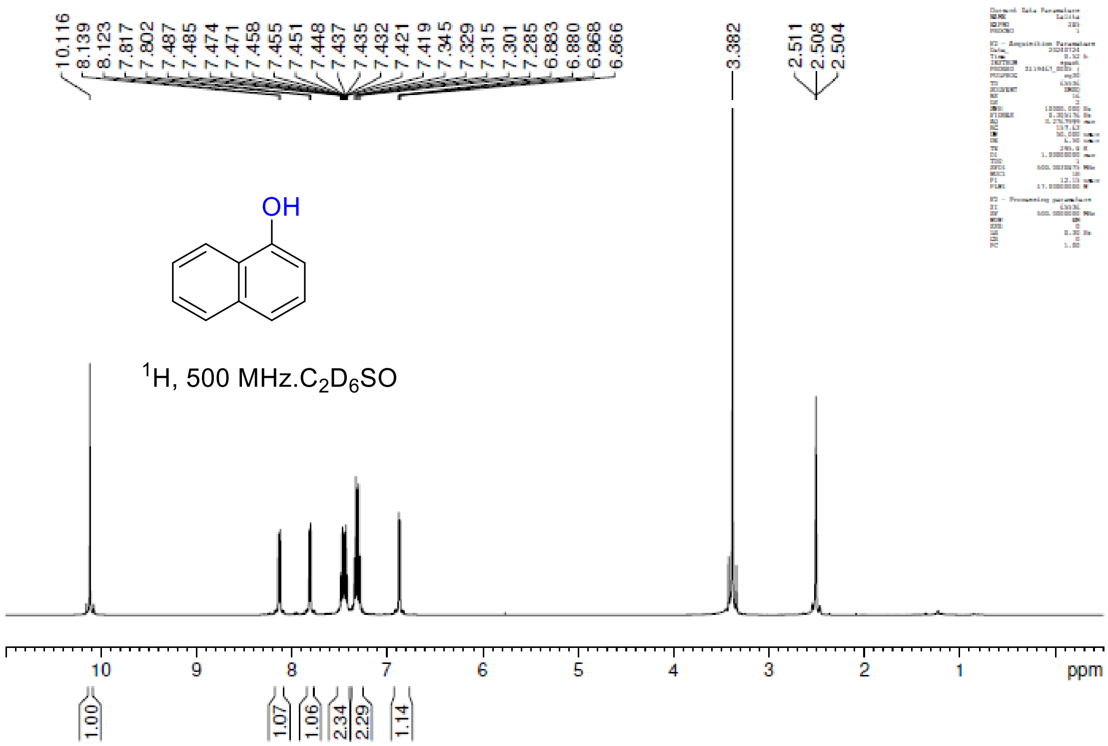


Figure S97. ^{1}H NMR spectrum of **6q** in C_2D_6SO

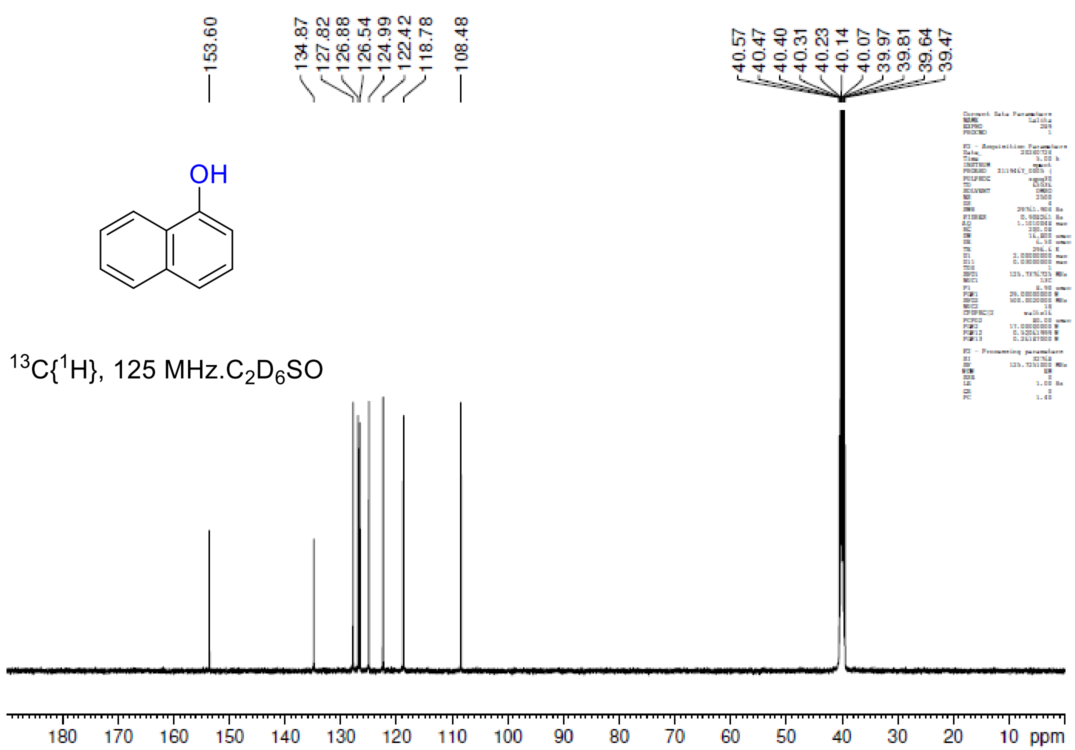


Figure S98. ^{13}C NMR spectrum of **6q** in C_2D_6SO

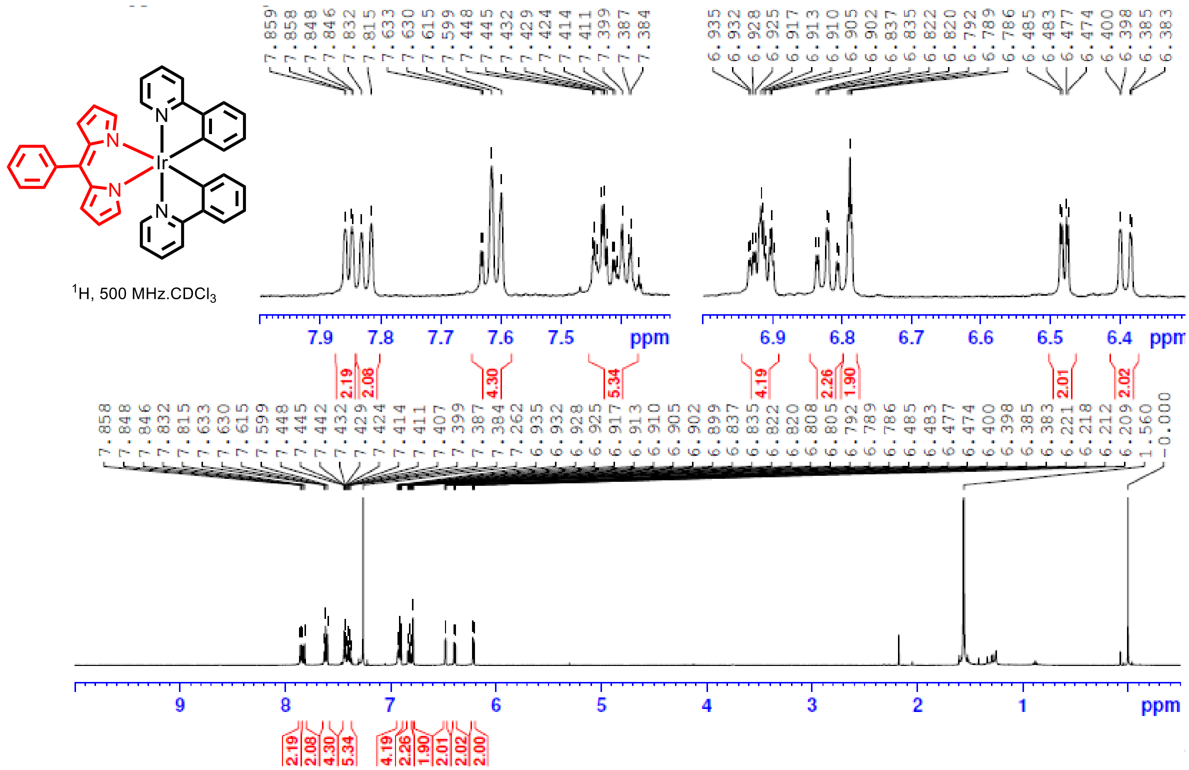


Figure S99. ^{1}H NMR spectrum of **Ir1** in $CDCl_3$

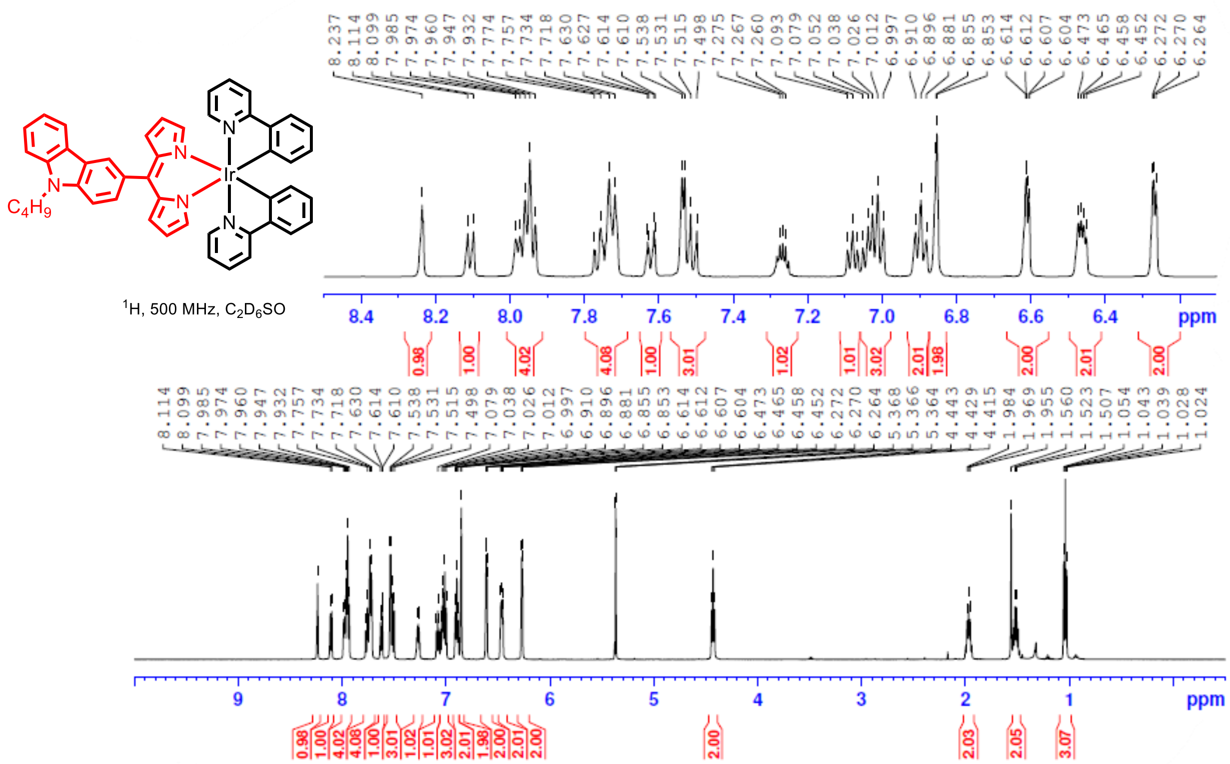


Figure S100. ^{1}H NMR spectrum of **Ir2** in C_2D_6SO

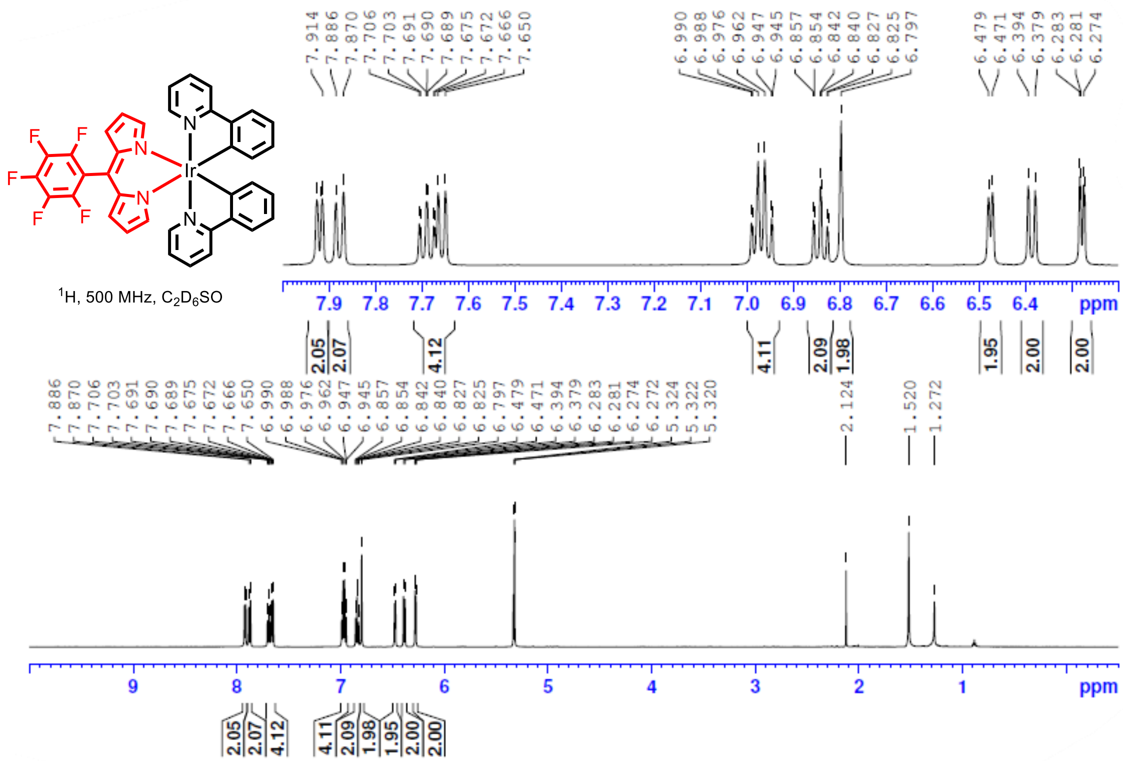


Figure S101. [1]H NMR spectrum of **Ir2** in C_2D_6SO

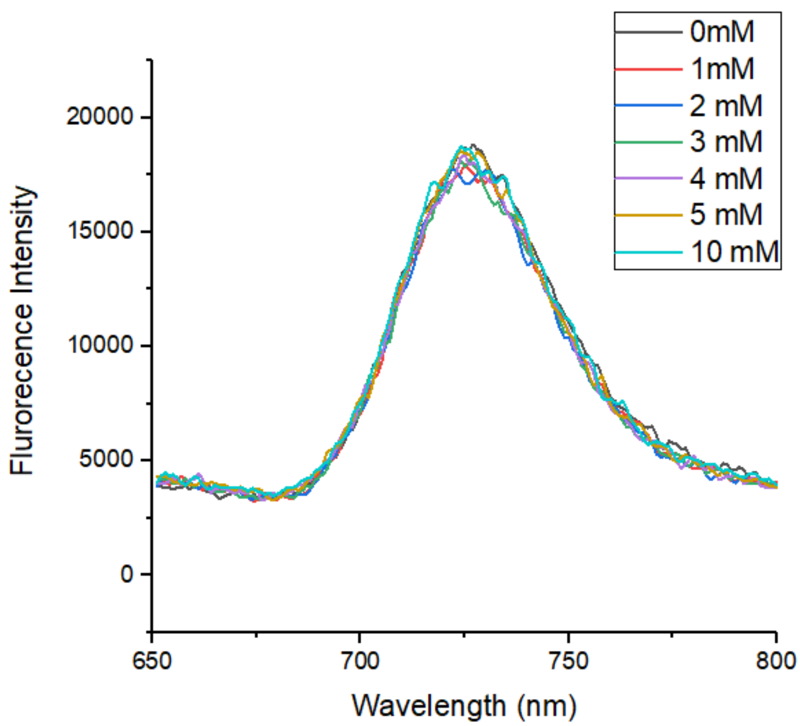


Figure S102. Fluorescence quenching experiment with Thioanisol

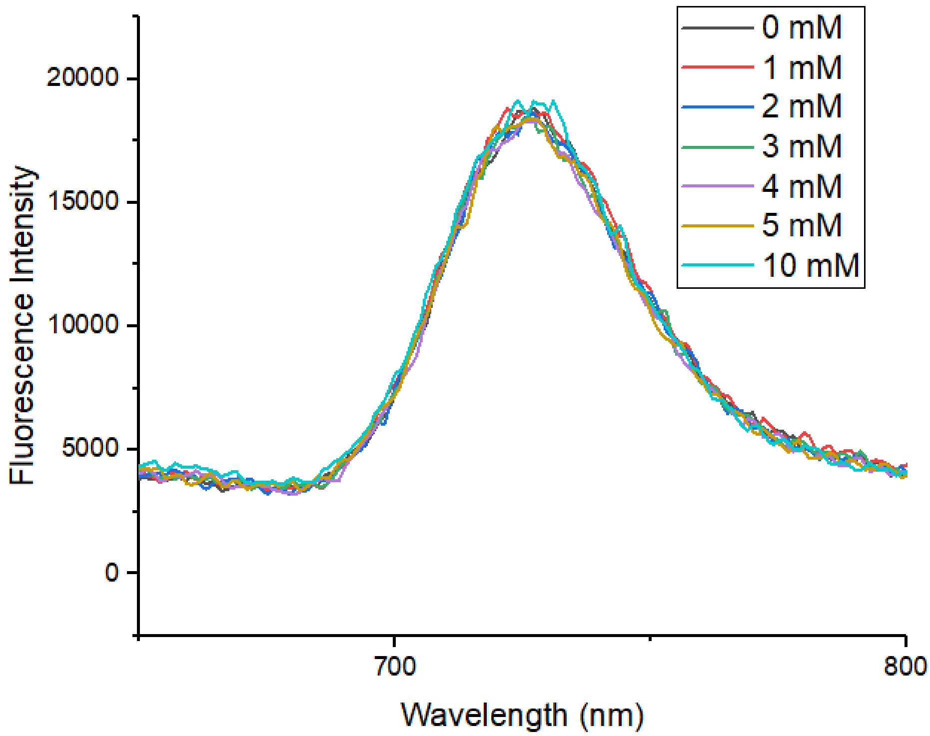


Figure S103. Fluorescence quenching experiment for Benzylamine

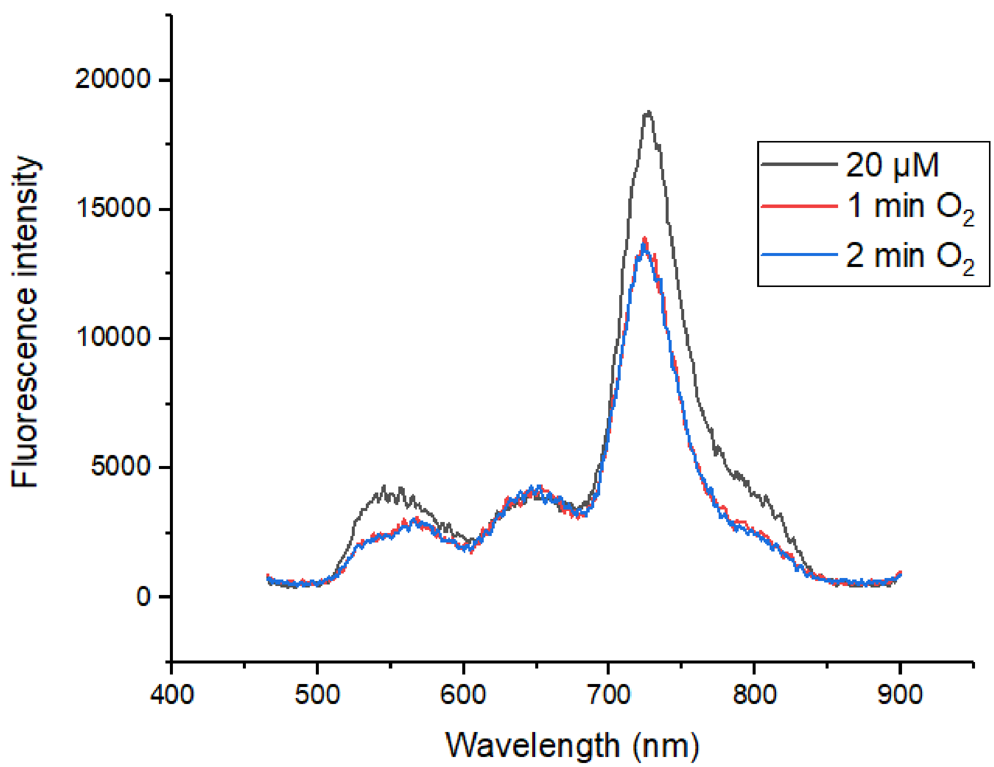


Figure S104. Fluorescence quenching experiment with O_2

Table S2: Comparison between various catalytic systems and the current catalyst.

Ref	Reaction	Catalyst	Catalytic loading	Time	Maximum Yield%
S1	Sulfoxidation	**P25 TiO_2** Et_3N	40 mg	10 h	77%
S2	Sulfoxidation	alizarin red S-sensitized TiO_2, TEMPO	9.6 mg	3 h	76%
S3	Sulfoxidation	**UNLPF-10**	0.1 mol%	8 h	99%
S4	oxidative benzylamine coupling	**4-NA-Cu2O - RDs**	3.0 mg	18 h	98%
S5	oxidative benzylamine coupling	Py-BSZ-COF	5mg	12 h	99 %
S6	Hydroxylation of aryl boronic acids	**Cu@C_3N_4-4** NaOH (1eq)	10 mg	6h	99 %
S7	Hydroxylation of aryl boronic acids	**NP-CTF**	25 mg	7-48h	99 %
This Work	Benzylamine coupling	**Ir3**	0.05 mol%, 0.4 mg	2 h	97%
	Sulfoxidation	**Ir3**	0.05 mol% 0.4 mg	2 h	98%
	Hydroxylation of aryl boronic acids	**Ir3**	0.05 mol% 0.4 mg	20 h	98%

S1 X. Lang, W. Hao, W. R. Leow, S. Li, J. Zhao and X. Chen, *Chem Sci*, 2015, **6**, 5000–5005.

S2 X. Lang, J. Zhao and X. Chen, *Angewandte Chemie*, 2016, **128**, 4775–4778.

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S5 S. Li, L. Li, Y. Li, L. Dai, C. Liu, Y. Liu, J. Li, J. Lv, P. Li and B. Wang, *ACS Catal*, 2020, **10**, 8717–8726.

S6 M. H. Muhammad, X.-L. Chen, Y. Liu, T. Shi, Y. Peng, L. Qu and B. Yu, *ACS Sustain Chem Eng*, 2020, **8**, 2682–2687.

S7 Y. Chen, H. Chen, J. Jiang and H. Ji, *Green Chemistry*, 2025, **27**, 1430–1439