Electronic supplementary information

Copper-promoted S-arylation reactions with triarylbismuths for the synthesis of diaryl sulfides

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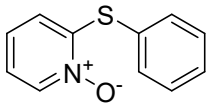
Characterization data of compound 3, 6 and 7

2-(Phenylthio)pyridine 1-oxide (**3a**)[1]

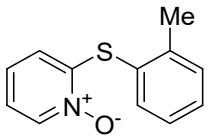


White solid, m.p.: 109-110℃, 58.6 mg, yield: 96% (Table 2) and 60.4 mg, yield: 99% (for Ar_3Sb, Table 2); 57.9 mg, 95% (Table 4) and 58.6 mg, 96% (for Ar_3Sb, Table 4).

^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 6.8 Hz, 1H), 7.63 (dd, J = 6.8, 1.8 Hz, 2H), 7.53-7.48 (m, 3H), 7.06-6.99 (m, 2H), 6.52 (dd, *J* = 7.9, 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.41, 138.50, 136.26, 130.56, 130.40, 128.63, 126.02, 122.21, 120.77.

2-(O -tolylthio)pyridine 1-oxide (**3b**)



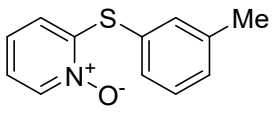
Yellow oil, 59.3 mg, yield: 91% (Table 2) and 56.1 mg, 86% (Table 4).

^1H NMR (400 MHz, $CDCl_3$): δ 8.29-8.27 (m, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.48-7.40 (m, 2H), 7.31 (td, *J* = 7.6, 2.0 Hz, 1H), 7.11-7.06 (m, 2H), 6.41 (dd, *J* = 7.5, 2.5 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.26, 152.51, 143.11, 138.28, 136.87, 131.23, 130.76, 127.46, 127.14, 125.94, 121.29, 120.46, 20.22.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{12}H_{12}NOS^+$ 218.0634, found 218.0634.

2-(M-tolylthio)pyridine 1-oxide (**3c**)



Yellow oil, 60.6 mg, yield: 93% (Table 2); 61.9 mg, 95% (for Ar_3Sb, Table 2); 64.5 mg, 99% (Table 4), and 45.6 mg, 70% (for Ar_3Sb, Table 4).

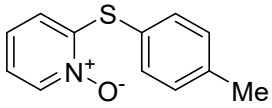
^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.42 (d, *J* = 10.8 Hz, 2H), 7.38 (t, *J* = 7.4

Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 5.1 Hz, 2H), 6.57-6.54 (m, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.64, 140.45, 138.59, 136.70, 133.21, 131.36, 130.20, 128.23, 126.12, 122.18, 120.59, 21.41.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{12}H_{12}NOS^+$ 218.0634, found 218.0634.

2-(P-tolylthio)pyridine 1-oxide (**3d**)[1]

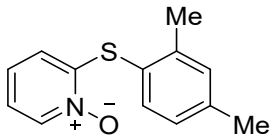


White solid, m.p.: 144-145 ℃, 60.6 mg, yield: 93% (Table 2) and 63.9 mg, 98% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 5.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.03-6.97 (m, 2H), 6.53 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.73, 140.95, 138.51, 136.17, 131.18, 125.82, 125.05, 122.14, 120.59, 21.52.

2-((2,4-Dimethylphenyl)thio)pyridine 1-oxide (**3e**)



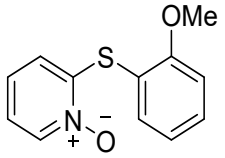
Yellow oil, 62.5 mg, yield: 90% (Table 2) and 62.5 mg, 90% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 6.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.02-6.94 (m, 2H), 6.37 (dd, *J* = 8.0, 2.1 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.36, 143.28, 141.37, 138.64, 137.16, 132.37, 128.58, 125.86, 124.08, 121.59, 120.48, 21.34, 20.49.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{13}H_{14}NOS^+$ 232.0790, found 232.0790

2-((2-Methoxyphenyl)thio)pyridine 1-oxide (**3f**)[1]

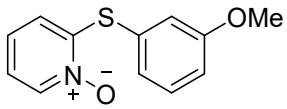


Red solid, m.p.: 111-113 ℃, 60.2 mg, yield: 86% (Table 2) and 64.4 mg, 92% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 6.1 Hz, 1H), 7.54 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.47 (td, *J* = 7.9, 1.7 Hz, 1H), 7.01-6.93 (m, 4H), 6.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.31, 152.74, 138.41, 137.82, 132.68, 125.72, 121.93, 121.77, 120.44, 116.00, 111.91, 55.92.

2-((3-Methoxyphenyl)thio)pyridine 1-oxide (**3g**)



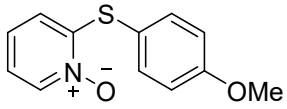
White solid, m.p.: 107-109℃, 69.3 mg, yield: 99% (Table 2) and 66.5 mg, 95% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 6.3, 1.5 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 2.1 Hz, 1H), 7.06-6.97 (m, 3H), 6.58 (dd, *J* = 8.0, 2.1 Hz, 1H), 3.82 (s, 3H).

13C NMR (101 MHz, $CDCl_3$): δ 160.78, 154.27, 138.44, 131.19, 129.63, 128.26, 125.93, 122.30, 121.00, 120.78, 116.58, 55.60.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{12}H_{12}NO_2S^+$ 234.0583, found 234.0582.

2-((4-Methoxyphenyl)thio)pyridine 1-oxide (**3h**)[1]

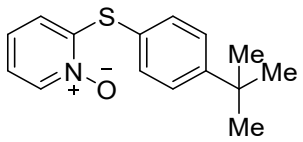


White solid, m.p.: 193-194 ℃, 63 mg, yield: 90% (Table 2) and 64.4 mg, 92% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.05-6.97 (m, 4H), 6.52 (dd, *J* = 8.0, 2.1 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.53, 155.03, 138.52, 137.84, 125.84, 122.10, 120.58, 118.91, 115.97, 55.62.

2-((4-(Tert-butyl)phenyl)thio)pyridine 1-oxide (**3i**)



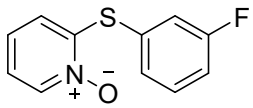
Yellow oil, 65.4 mg, yield: 84% (Table 2) and 41.2 mg, 53% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 6.1 Hz, 1H), 7.49 (q, *J* = 8.4 Hz, 4H), 7.04-6.95 (m, 2H), 6.54 (d, *J* = 9.5 Hz, 1H), 1.33 (s, 9H).

13C NMR (101 MHz, $CDCl_3$): δ 154.53, 153.96, 138.41, 135.82, 127.40, 125.87, 124.90, 122.15, 120.57, 34.96, 31.25.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{15}H_{18}NOS^+$ 260.1104, found 260.1103.

2-((3-Fluorophenyl)thio)pyridine 1-oxide (**3j**)



White solid, m.p.: 107-108 ℃, 63.7 mg, yield: 96% (Table 2), 55.7 mg, 84% (Table 8) and 50.4 mg, 76% (for Ar_3Sb, Table 4)

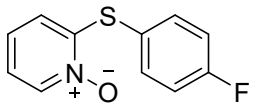
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 5.2 Hz, 1H), 7.51-7.45 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (dt, *J* = 8.3, 2.0 Hz, 1H), 7.22 (td, *J* = 8.3, 1.6 Hz, 1H), 7.08-7.01 (m, 2H), 6.58-6.55 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.20 (d, *J* = 251.3 Hz), 153.57, 138.57, 131.91 (d, *J* = 3.3 Hz), 131.76 (d, *J* = 8.2 Hz), 130.71 (d, *J* = 7.5 Hz), 126.08, 122.93 (d, *J* = 21.6 Hz), 122.09, 121.09, 117.84 (d, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -109.85.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{11}H_9FNOS^+$ 222.0383, found 222.0381.

2-((4-Fluorophenyl)thio)pyridine 1-oxide (**3k**)[1]



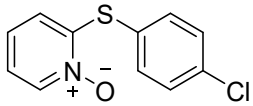
White solid, m.p.: 145-146 °C, 65.7 mg, yield: 99% (Table 2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (dd, *J* = 6.1, 1.5 Hz, 1H), 7.63-7.60 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 7.08-7.00 (m, 2H), 6.50 (dd, *J* = 8.0, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.26 (d, *J* = 252.0 Hz), 154.15, 138.55, 138.42 (d, *J* = 8.7 Hz), 125.91, 124.05 (d, *J* = 3.6 Hz), 122.01, 120.94, 117.74 (d, *J* = 22.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.23.

2-((4-Chlorophenyl)thio)pyridine 1-oxide (**3l**)[1]

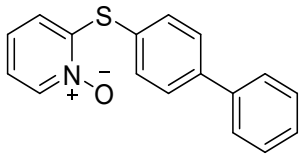


White solid, m.p.: 174-175 °C, 65.6 mg, yield: 92% (Table 2); 66.3 mg, 93% (for Ar_3Sb, Table 2); 50.6 mg, 71% (Table 4) and 64.2 mg, 90% (for Ar_3Sb, Table 4)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 5.6 Hz, 1H), 7.58-7.54 (m, 2H), 7.49-7.46 (m, 2H), 7.07-7.01 (m, 2H), 6.54-6.52 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.72, 138.58, 137.50, 137.16, 130.69, 127.28, 125.91, 122.06, 121.03.

2-([1,1'-Biphenyl]-4-ylthio)pyridine 1-oxide (**3m**)[1]

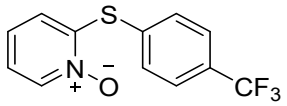


White solid, m.p.: 193-194 °C, 57 mg, yield: 68% (Table 2) and 74.6 mg, 89% (Table 4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 6.2 Hz, 1H), 7.74-7.69 (m, 4H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.10-7.01 (m, 2H), 6.65 (dd, *J* = 8.0, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.40, 143.51, 139.80, 138.58, 136.62, 129.16, 129.02, 128.30, 127.37, 127.30, 126.04, 122.31, 120.82.

2-((4-(Trifluoromethyl)phenyl)thio)pyridine 1-oxide (**3n**)[1]



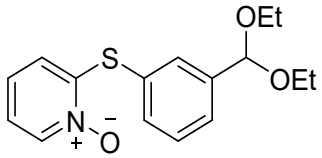
White solid, m.p.: 145-146 ℃, 61 mg, yield: 75% (Table 2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.79-7.74 (m, 4H), 7.08-7.07 (m, 2H), 6.58 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 150.55, 138.22, 136.17, 134.12 (d, *J* = 1.3 Hz), 130.43 (d, *J* = 32.2 Hz), 127.11 (q, *J* = 3.7 Hz), 126.04, 125.27, 122.56, 122.44 (d, *J* = 13.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.97.

2-((3-(Diethoxymethyl)phenyl)thio)pyridine 1-oxide (**3o**)[2]

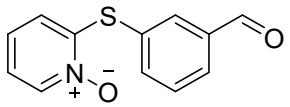


Green solid, easily decomposed, 88 mg, yield: 96% (Table 2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 5.6 Hz, 1H), 7.73 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.04-6.98 (m, 2H), 6.51 (dd, *J* = 7.5, 2.5 Hz, 1H), 5.52 (s, 1H), 3.66 – 3.47 (m, 4H), 1.22 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.22, 141.76, 138.44, 135.98, 134.37, 130.22, 128.90, 128.56, 125.85, 122.20, 120.76, 100.75, 61.44, 15.27.

2-((3-Formylphenyl)thio)pyridine 1-oxide (**3p**)



White solid, m.p.: 124-126 ℃, 52.7 mg, yield: 76% (Table 2).

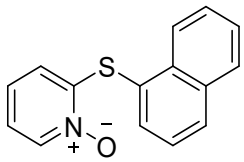
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.25 (t, *J* = 4.0 Hz, 1H), 8.12 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 4.4 Hz, 2H), 6.52 (t, *J* = 5.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.94, 153.28, 141.74, 138.68, 138.19, 137.14,

131.32, 131.12, 130.60, 126.20, 122.14, 121.29.

HRMS (APCI) m/z: $[M+H]^+$ Clacd for $C_{12}H_{10}NO_2S^+$ 232.0427, found 232.0425.

2-(Naphthalen-1-ylthio)pyridine 1-oxide (**3q**)[1]

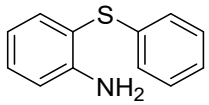


Brown solid, m.p.: 126-127 ℃, 69.9 mg, yield: 92% (Table 2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (t, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.57-7.49 (m, 3H), 6.97-6.93 (m, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.17 (dd, *J* = 8.0, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.17, 138.53, 136.38, 134.47, 131.86, 128.94, 127.98, 127.04, 126.25, 125.83, 125.57, 125.43, 122.40, 120.66.

2-(Phenylthio)aniline (**6a**)[2]

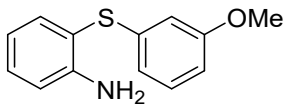


Green oil, 39.8 mg, yield: 66% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.17-7.11 (m, 3H), 7.04-6.99 (m, 3H), 6.71-6.65 (m, 2H), 4.14 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.82, 137.56, 136.90, 131.23, 129.10, 126.58, 125.53, 118.90, 115.52, 114.53.

2-((3-Methoxyphenyl)thio)aniline (**6b**)[3]

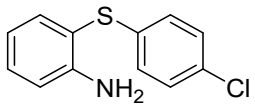


Black oil, 50 mg, yield: 72% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.21 (td, *J* = 8.0, 1.2 Hz, 1H), 7.11 (t, *J* = 8.2 Hz, 1H), 6.76-6.72 (m, 2H), 6.66-6.63 (m, 3H), 4.14 (s, 2H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.12, 148.93, 138.35, 137.59, 131.31, 129.90, 128.84, 127.23, 118.81, 115.48, 114.17, 112.11, 111.06, 55.24.

2-((4-Chlorophenyl)thio)aniline (**6c**)[3]

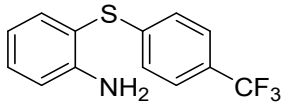


Red oil, 50.9 mg, yield: 72% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.23 (td, *J* = 7.7, 1.5 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.78-6.73 (m, 2H), 4.12 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.81, 137.52, 135.54, 131.52, 131.34, 129.17, 127.79, 118.99, 115.59, 114.00.

2-((4-(Trifluoromethyl)phenyl)thio)aniline (**6d**)[4]



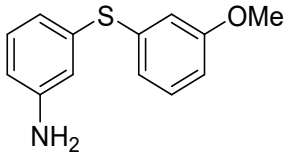
Yellow solid, m.p.: 69-70 ℃, 54.1 mg, yield: 67% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.44 (m, 3H), 7.32-7.28 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.84-6.78 (m, 2H), 4.28 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.18, 142.41, 137.87, 132.00, 127.41 (m), 125.88 (q, *J* = 3 Hz), 122.95, 119.10, 115.64, 112.49.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.34.

3-((3-Methoxyphenyl)thio)aniline (**6e**)[5]



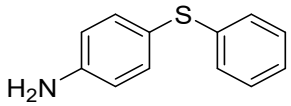
Red oil, 50.7 mg, yield: 73% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.91 (s, 1H), 6.80-6.76 (m, 2H), 6.68 (s, 1H), 6.57 (dd, *J* = 8.0,

1.8 Hz, 1H), 3.77 (s, 3H), 3.56 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.07, 147.18, 137.25, 136.13, 130.06, 129.98, 123.21, 121.49, 117.57, 116.11, 114.22, 112.87, 55.38.

4-(Phenylthio)aniline (**6f**)[6]

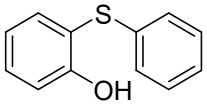


White solid, m.p.:95-97 ℃, 45.9 mg, yield: 76% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.14-7.09 (m, 3H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.68, 139.67, 136.12, 128.95, 127.54, 125.44, 121.08, 116.19.

2-(Phenylthio)phenol (**7a**)[7]

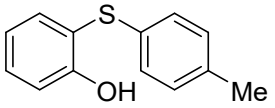


Colorless oil, 60.1 mg, yield: 99% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.27 (td, *J* = 7.8, 1.7 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 3H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.43 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.37, 137.03, 135.96, 132.39, 129.31, 126.95, 126.23, 121.39, 116.39, 115.67.

2-(P-tolylthio)phenol (**7b**)[8]



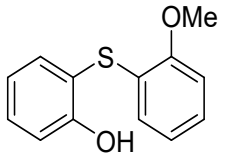
Colorless oil, 53.9 mg, yield: 83% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.09-7.04 (m, 5H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.58 (s, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.18, 136.75, 136.38, 132.24, 132.11, 130.10,

127.58, 121.29, 117.30, 115.58, 21.04.

2-((2-Methoxyphenyl)thio)phenol (**7c**)[9]

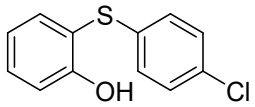


Colorless oil, 52.3 mg, yield: 75% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.95-6.82 (m, 5H), 3.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.78, 156.68, 137.14, 132.10, 129.69, 128.21, 123.90, 121.66, 121.18, 116.73, 115.58, 110.83, 56.01.

2-((4-Chlorophenyl)thio)phenol (**7d**)[8]

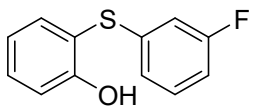


Colorless oil, 60.4 mg, yield: 85% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 (td, *J* = 7.8, 1.7 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.48 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.28, 136.93, 134.56, 132.66, 132.23, 129.41, 128.21, 121.56, 116.0, 115.86.

2-((3-Fluorophenyl)thio)phenol (**7e**)



Colorless oil, 50.2 mg, yield: 76% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.20 (q, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.89-6.83 (m, 2H), 6.74 (d, *J* = 9.2 Hz, 1H), 6.46 (s, 1H).

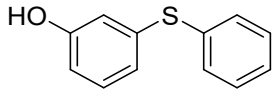
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.26 (d, *J* = 248.7 Hz), 157.44, 138.53 (d, *J* = 7.6

Hz), 137.17, 132.91, 130.57 (d, J = 8.5 Hz), 121.62, 115.94, 115.31, 122.22 (d, J = 3.0 Hz), 113.61 (d, J = 24.3 Hz), 113.17 (d, J = 21.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.45.

HRMS (ESI) m/z: $[M+H]^+$ Clacd for $C_{12}H_{10}FOS^+$ 219.0279, found 219.0285

3-(Phenylthio)phenol (**7f**)[10]

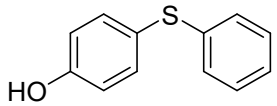


Red oil, 44.9 mg, yield: 74% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.1 Hz, 2H), 7.33-7.24 (m, 3H), 7.14 (t, J = 7.9 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.73 (s, 1H), 6.67 (dd, J = 8.1, 2.1 Hz, 1H), 5.15 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.07, 137.88, 134.85, 131.98, 130.31, 129.40, 127.61, 122.78, 117.00, 114.08.

4-(Phenylthio)phenol (**7g**)[11]



Yellow oil, 49.2 mg, yield: 81% (Table 5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.5 Hz, 2H), 7.18-7.11 (m, 3H), 6.81 (d, J = 8.4 Hz, 2H), 5.69 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.91, 138.41, 135.59, 129.08, 128.44, 126.00, 124.65, 116.63.

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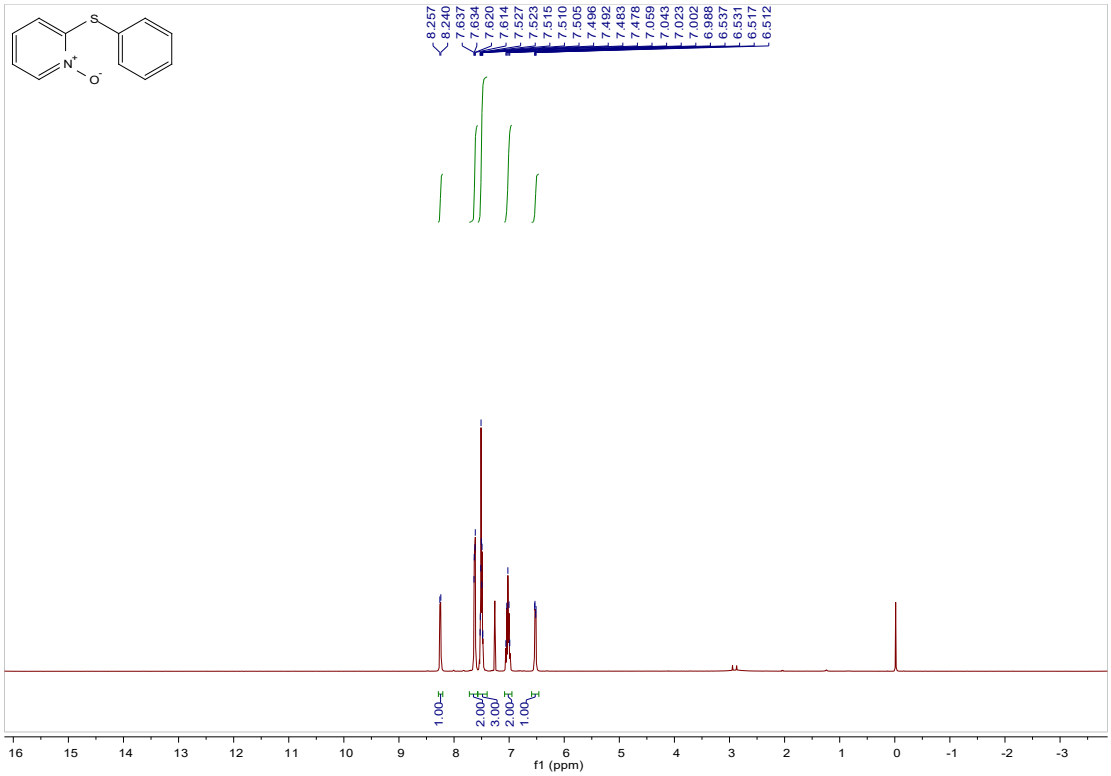
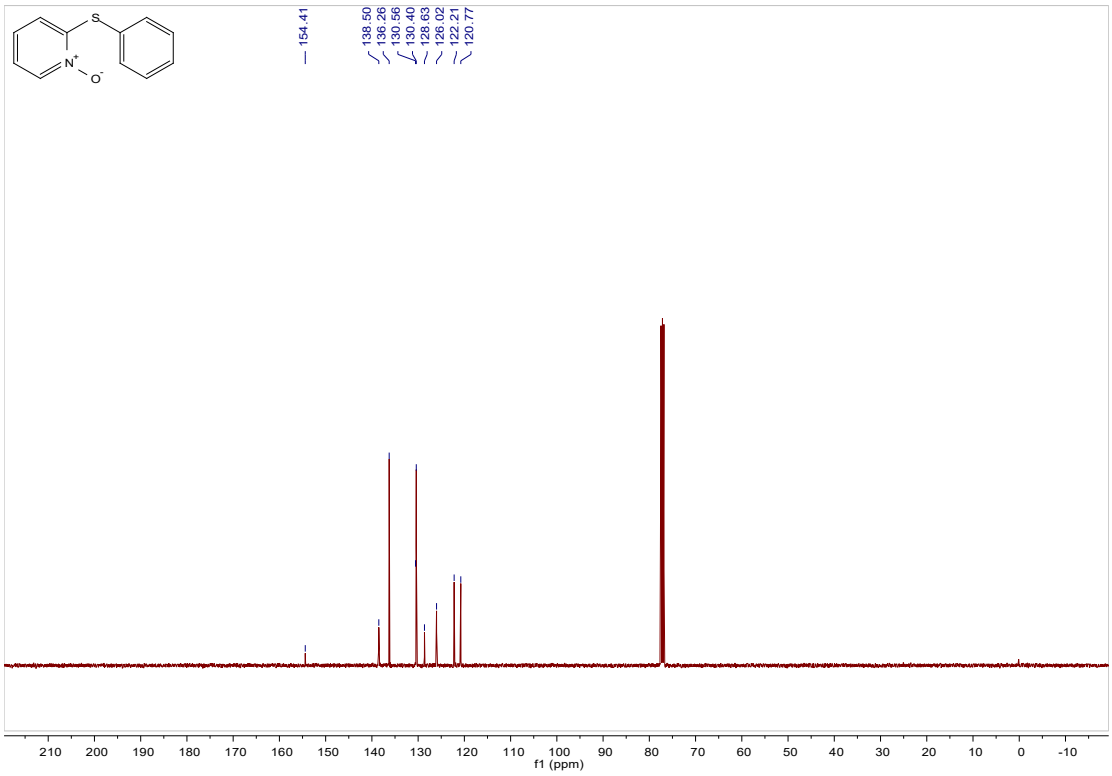
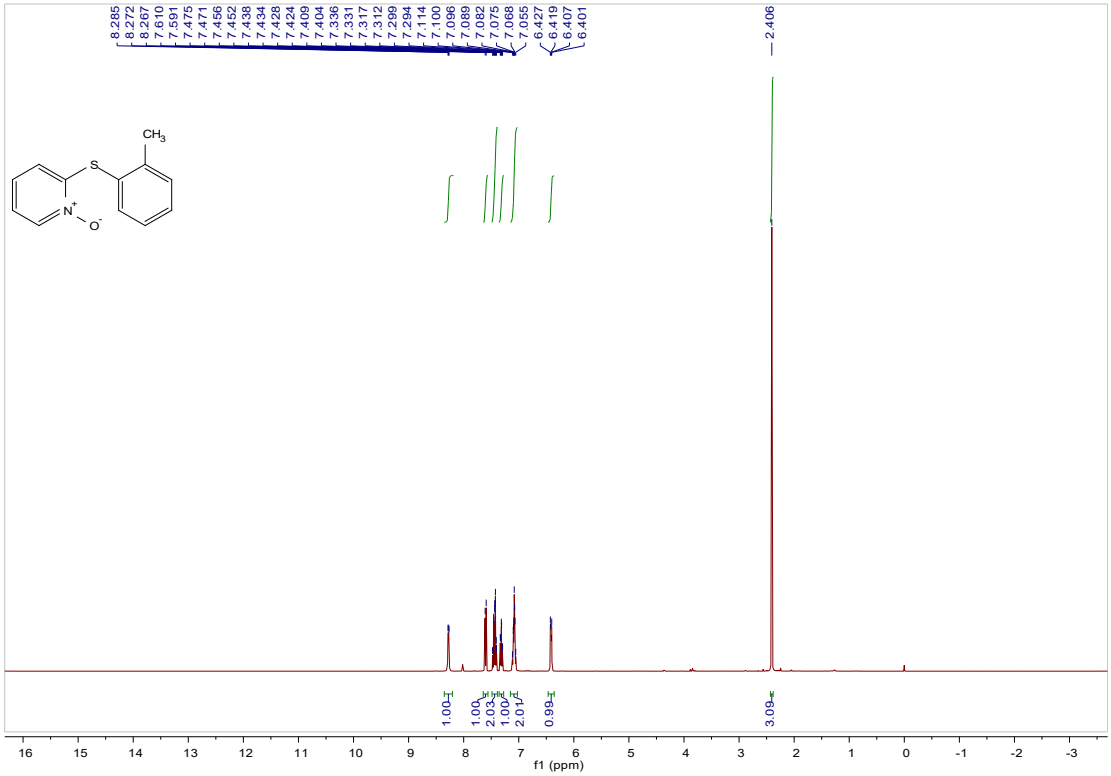
Copies of ^{1}NMR, ^{13}CNMR and ^{19}F NMR spectra

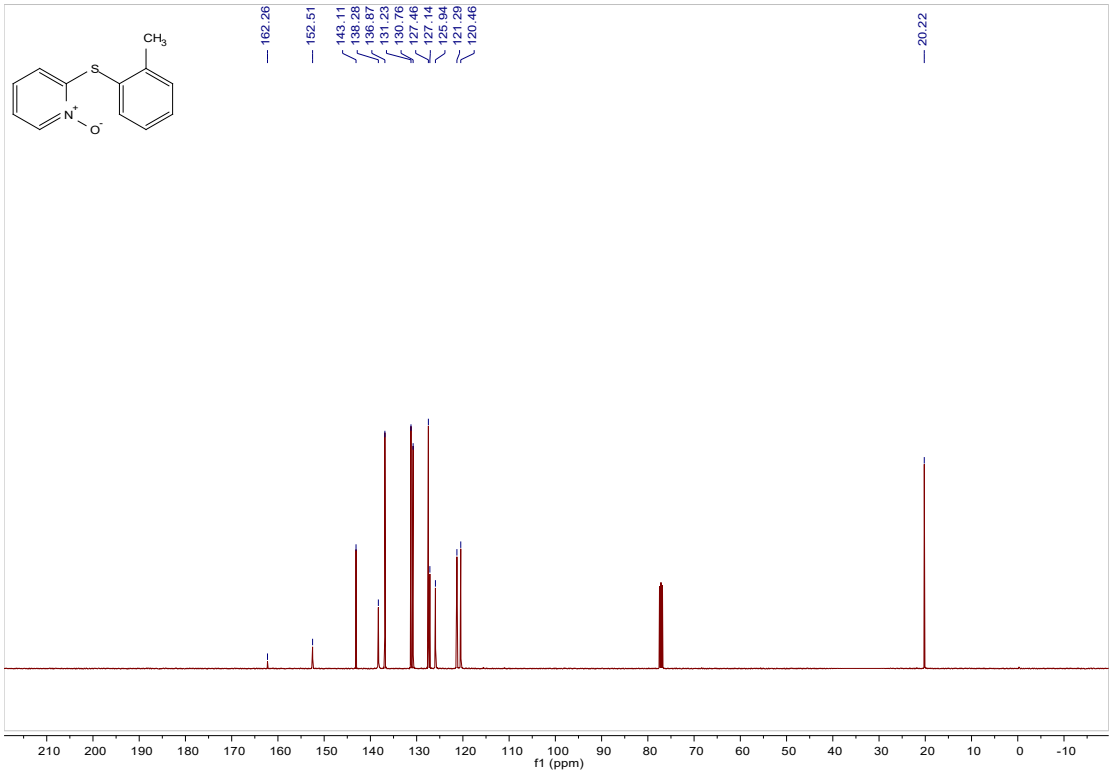
2-(Phenylthio)pyridine 1-oxide (**3a**)



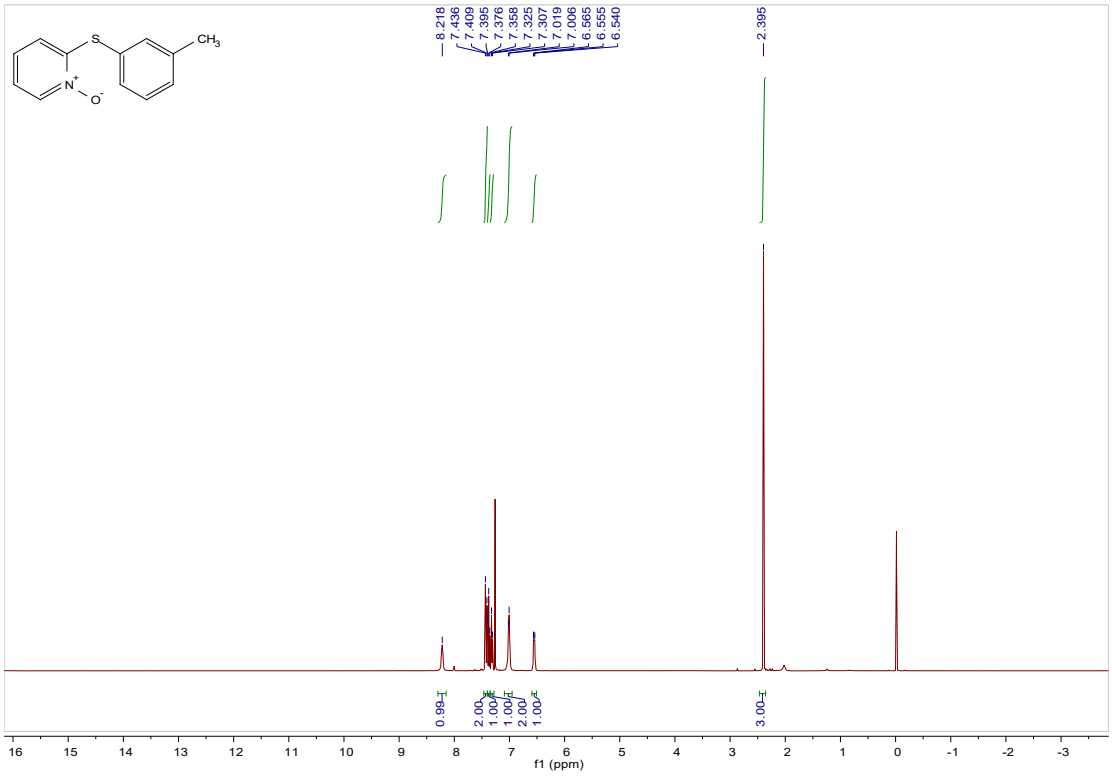


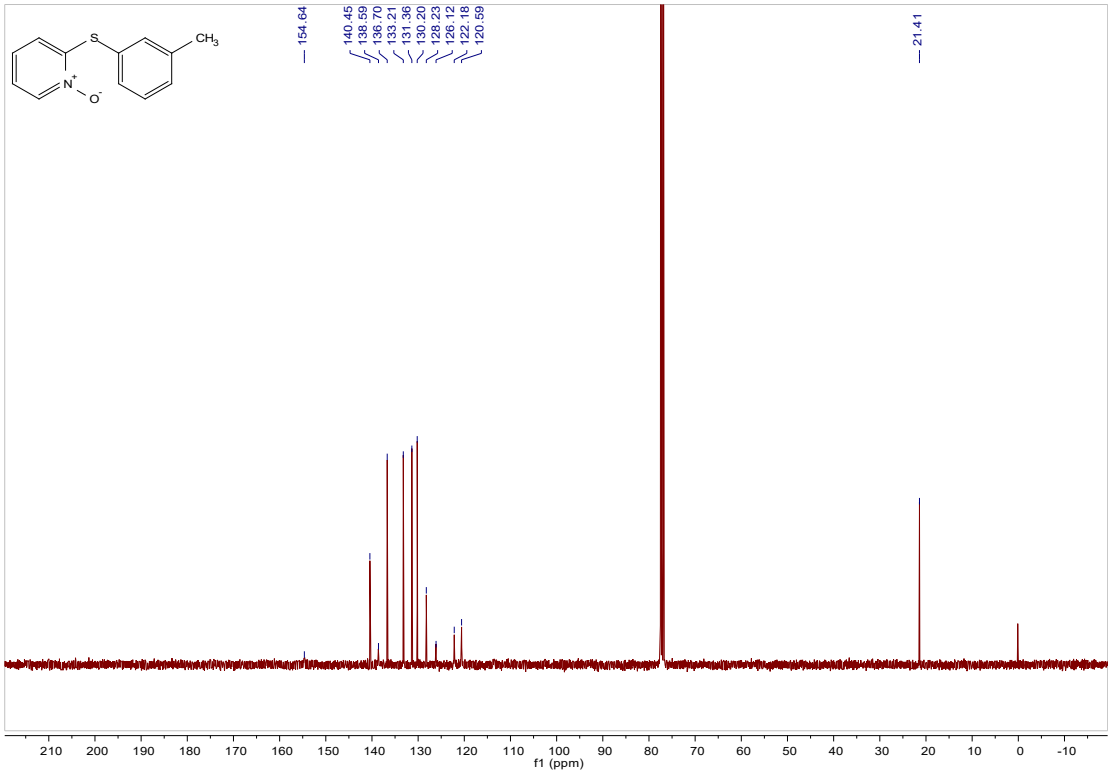
2-(O -tolylthio)pyridine 1-oxide (**3b**)



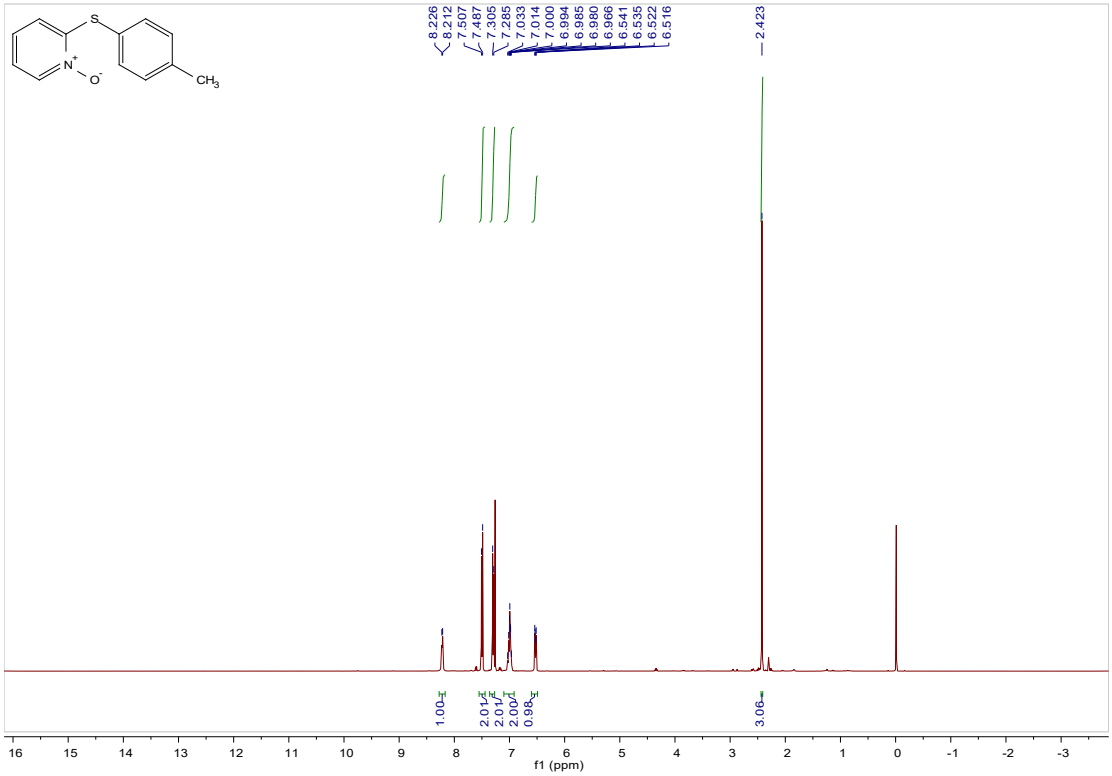


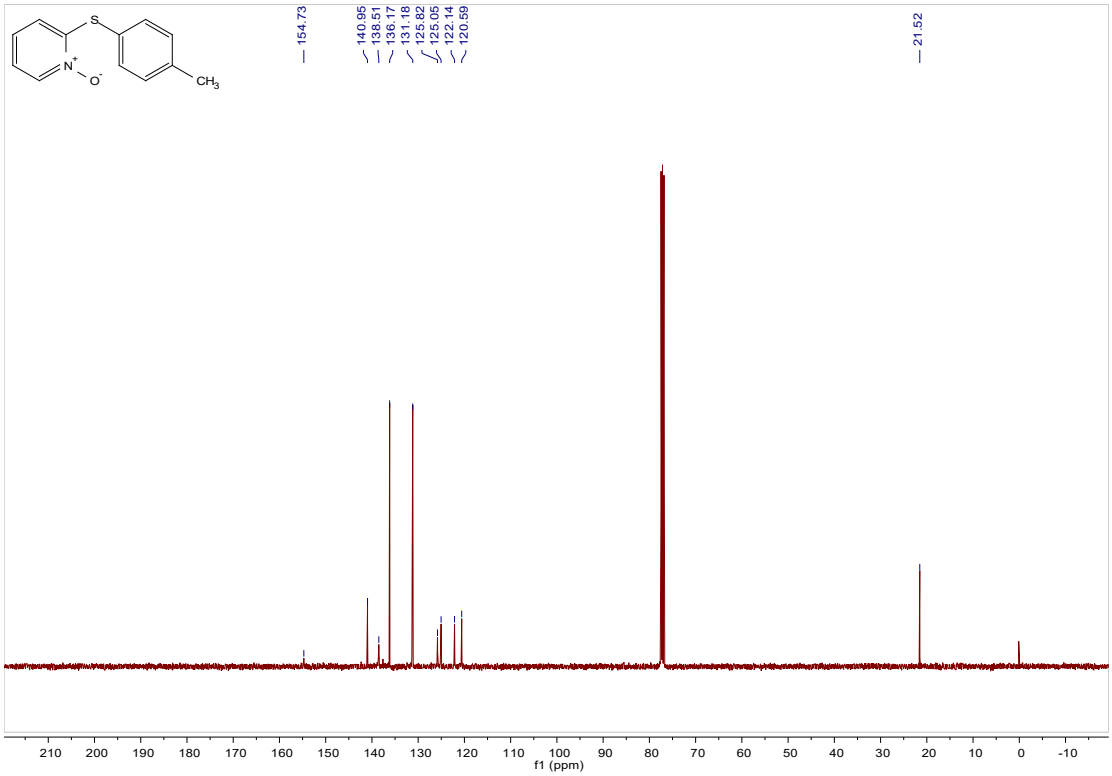
2-(M -tolylthio)pyridine 1-oxide (**3c**)



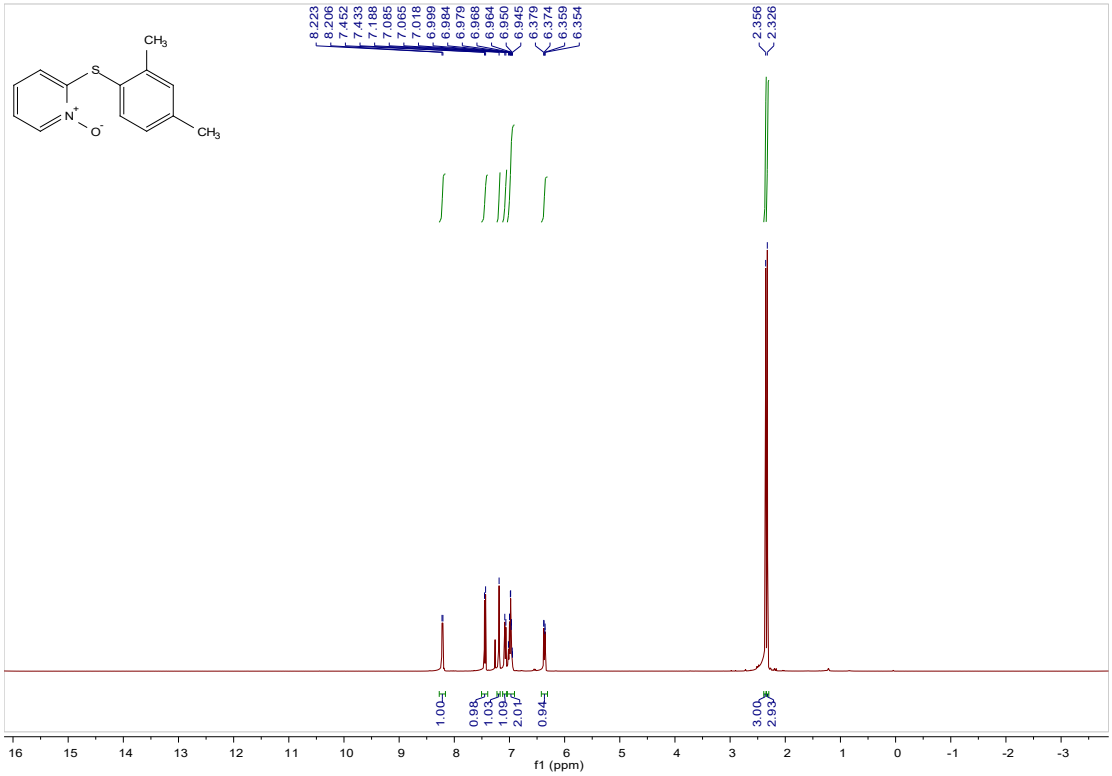


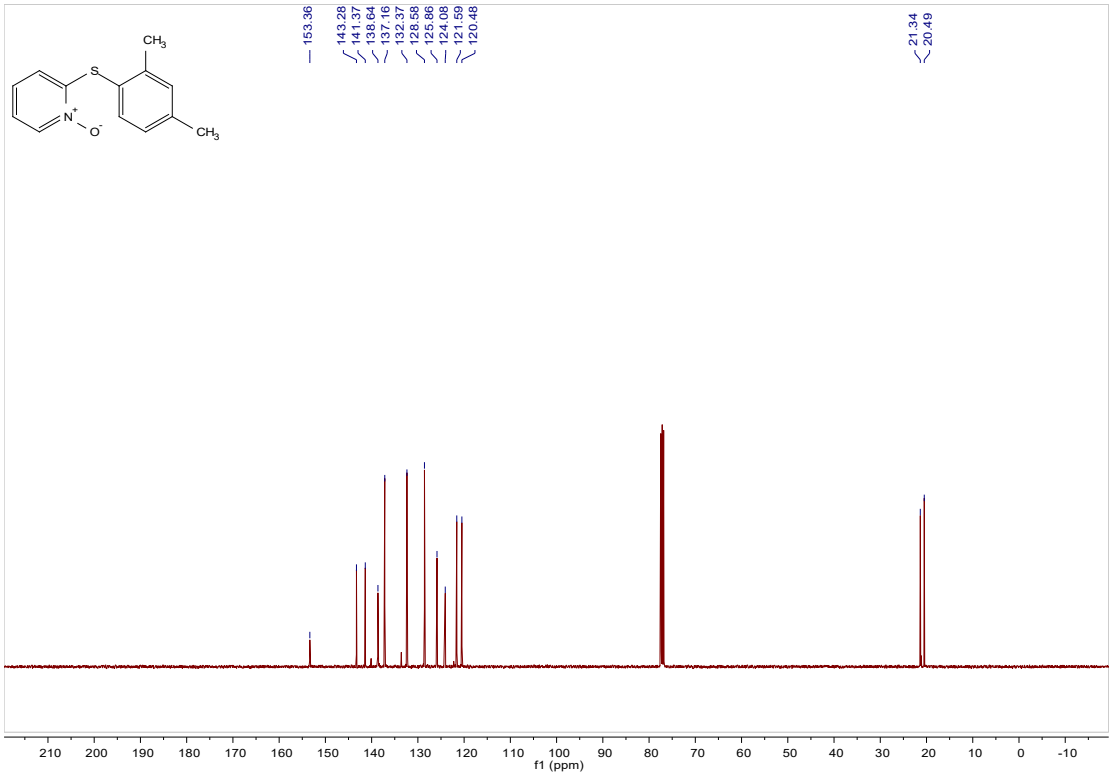
2-(P-tolylthio)pyridine 1-oxide (**3d**)



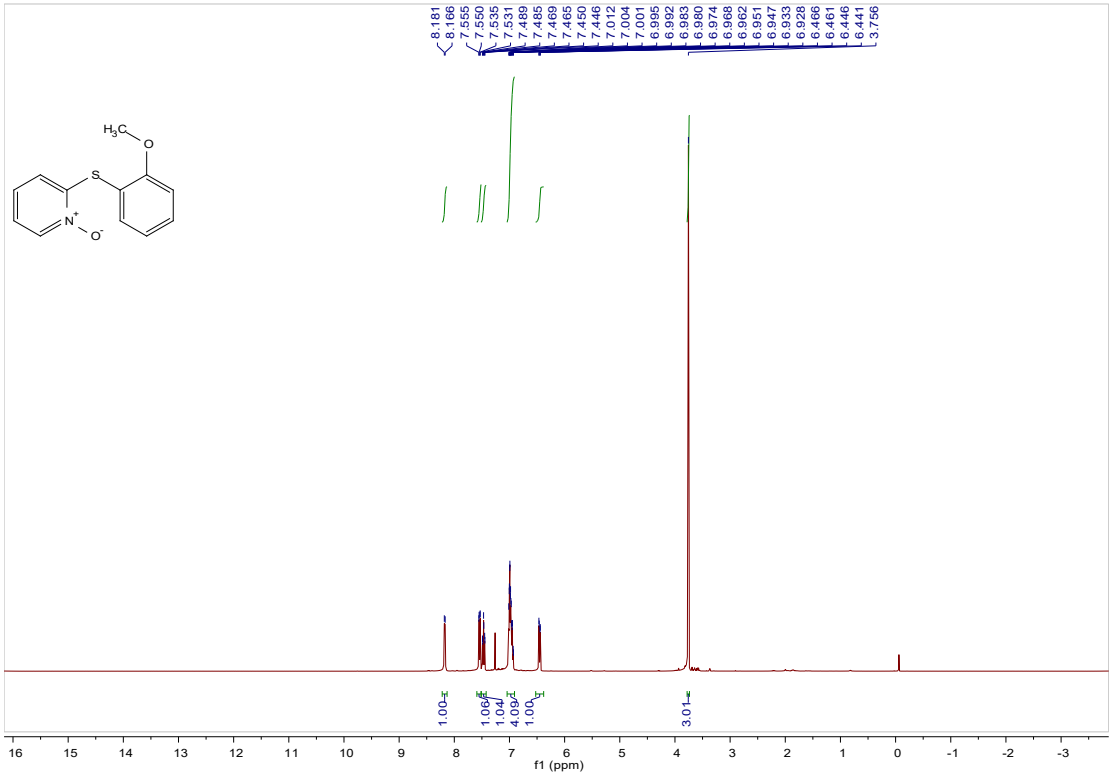


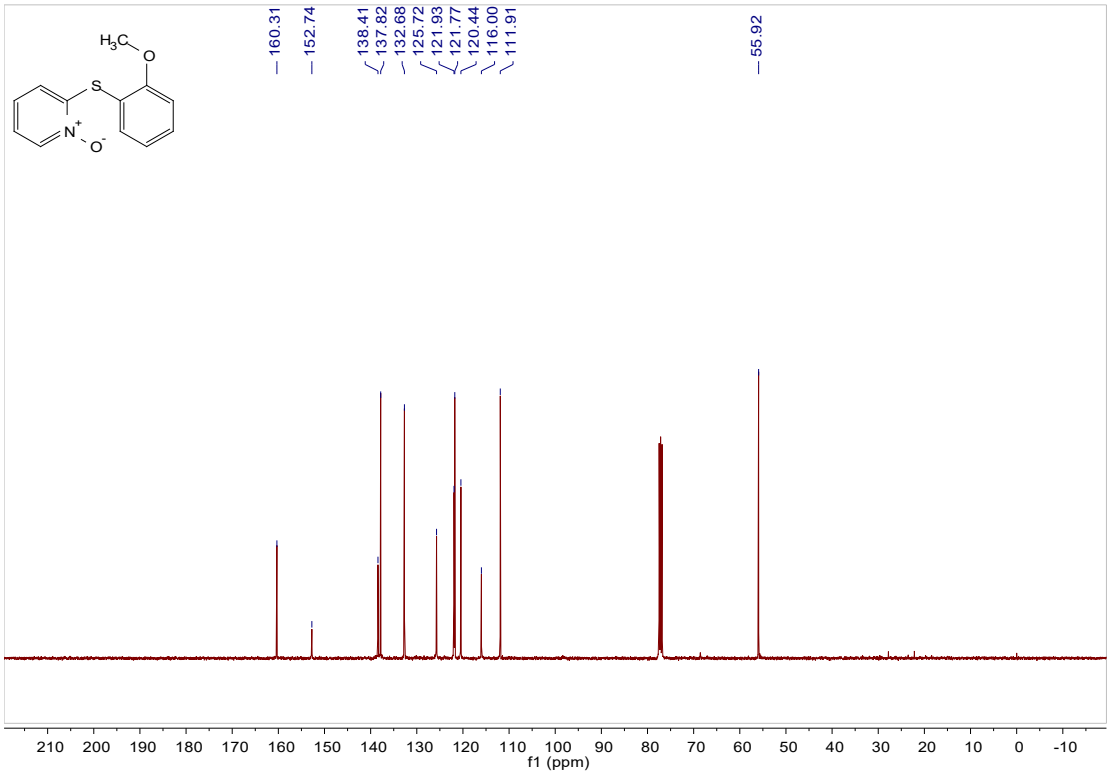
2-((2,4-Dimethylphenyl)thio)pyridine 1-oxide (**3e**)



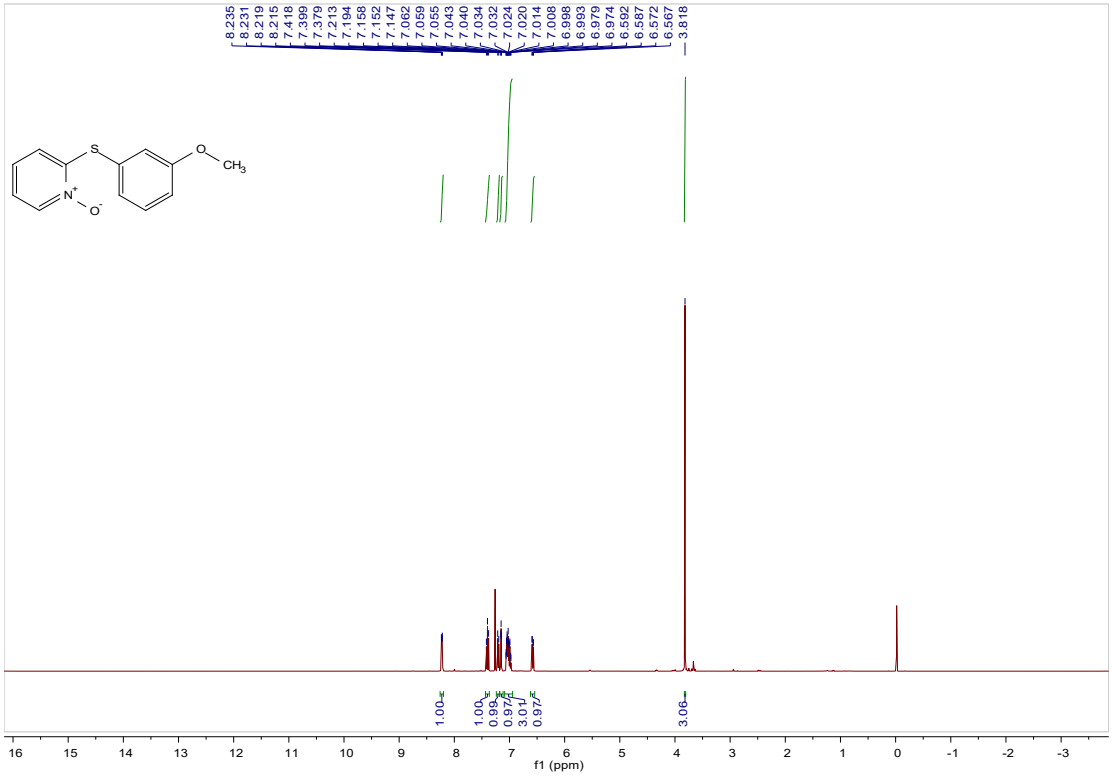


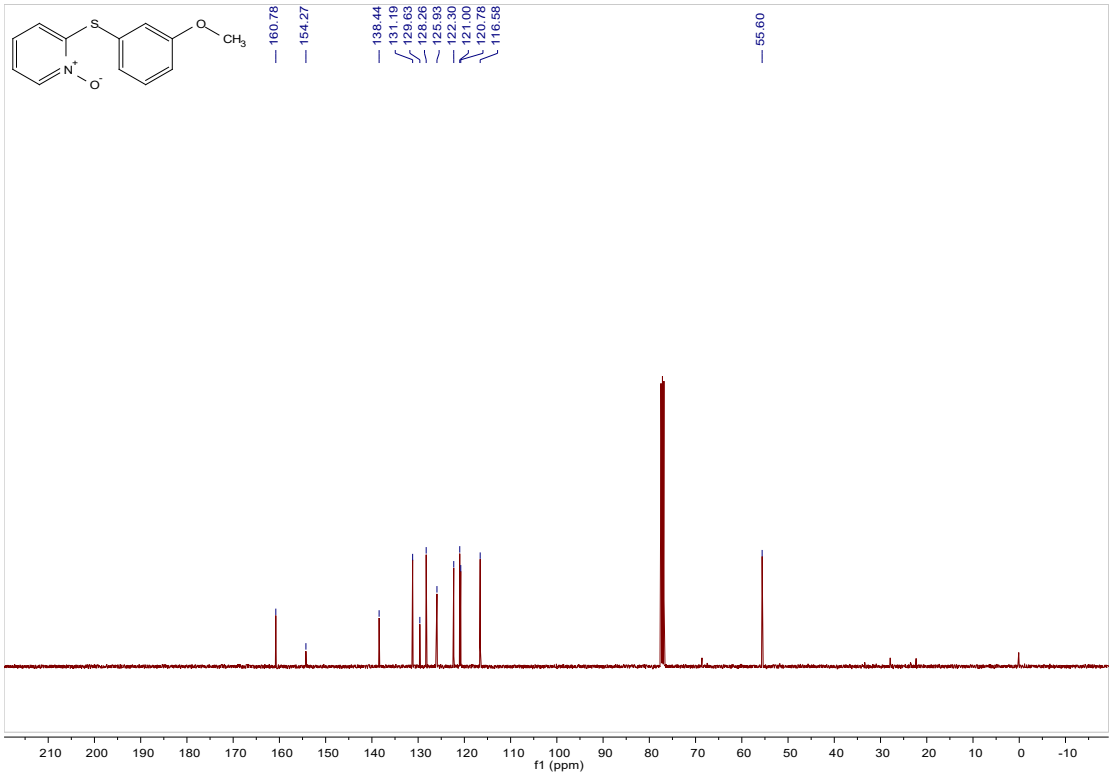
2-((2-Methoxyphenyl)thio)pyridine 1-oxide (**3f**)



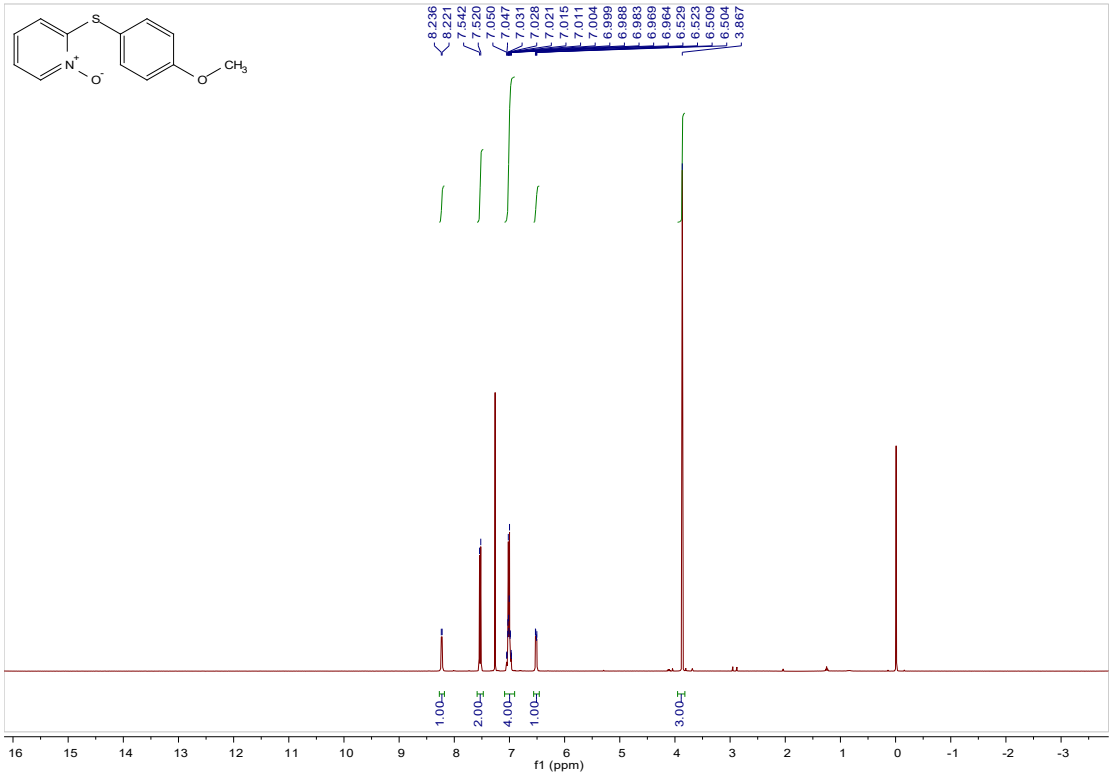


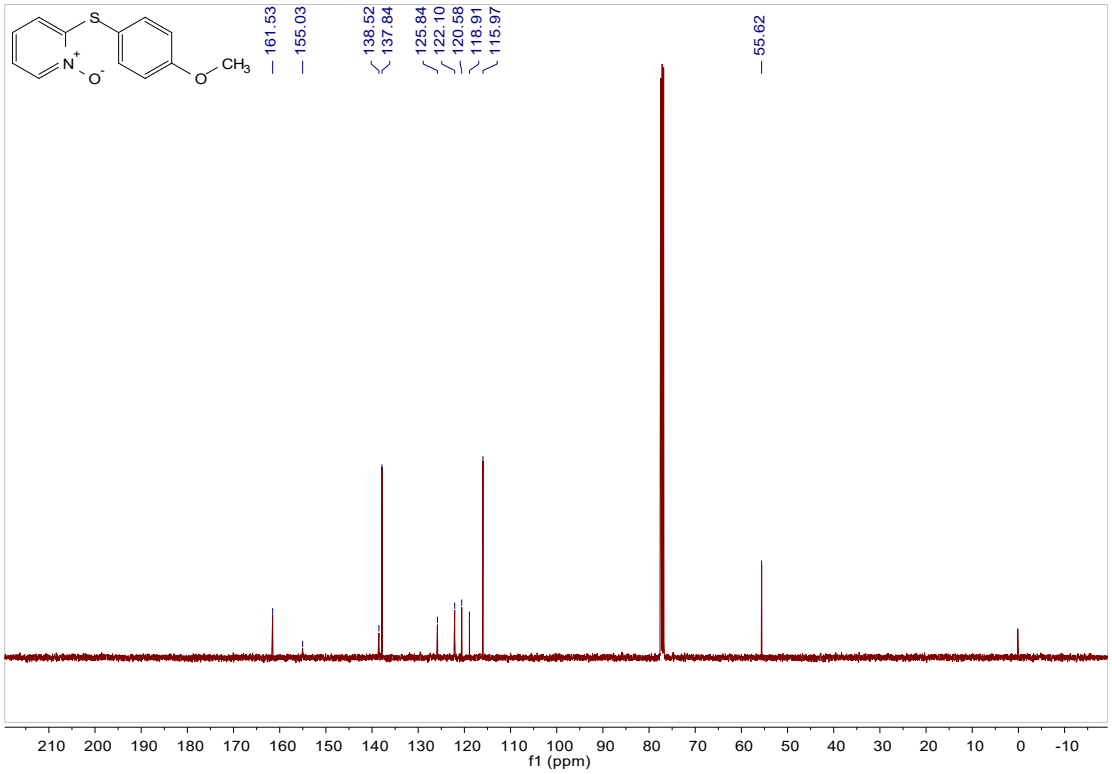
2-((3-Methoxyphenyl)thio)pyridine 1-oxide (**3g**)



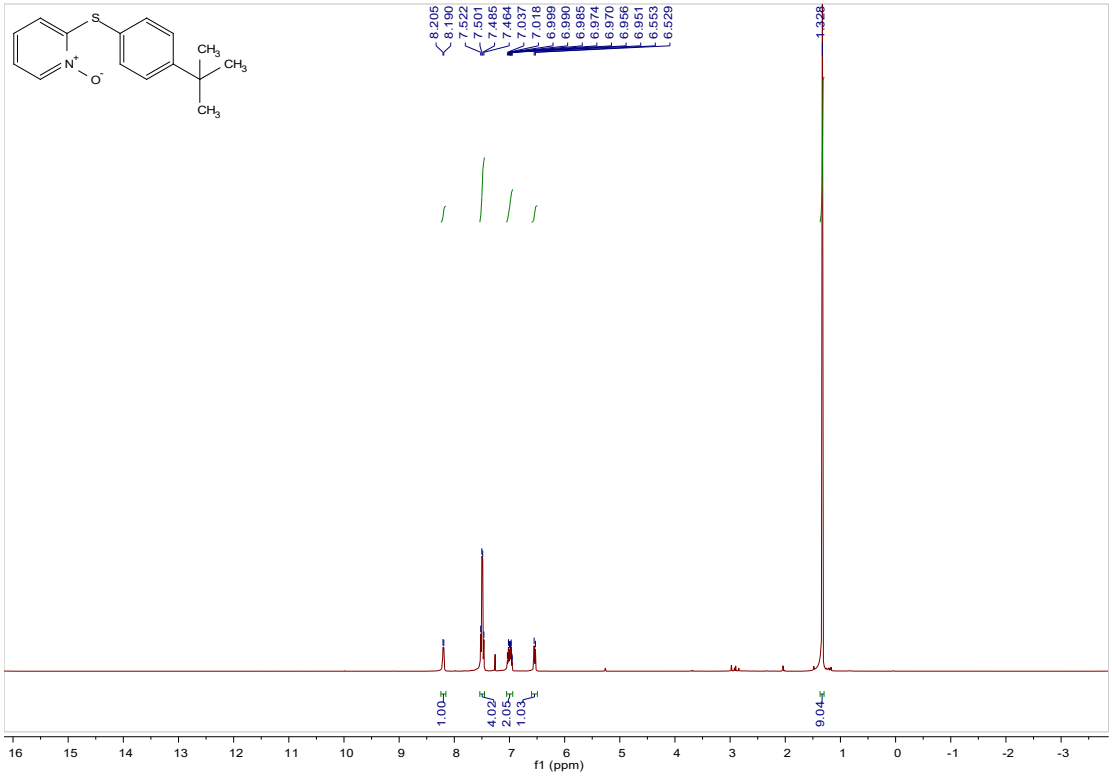


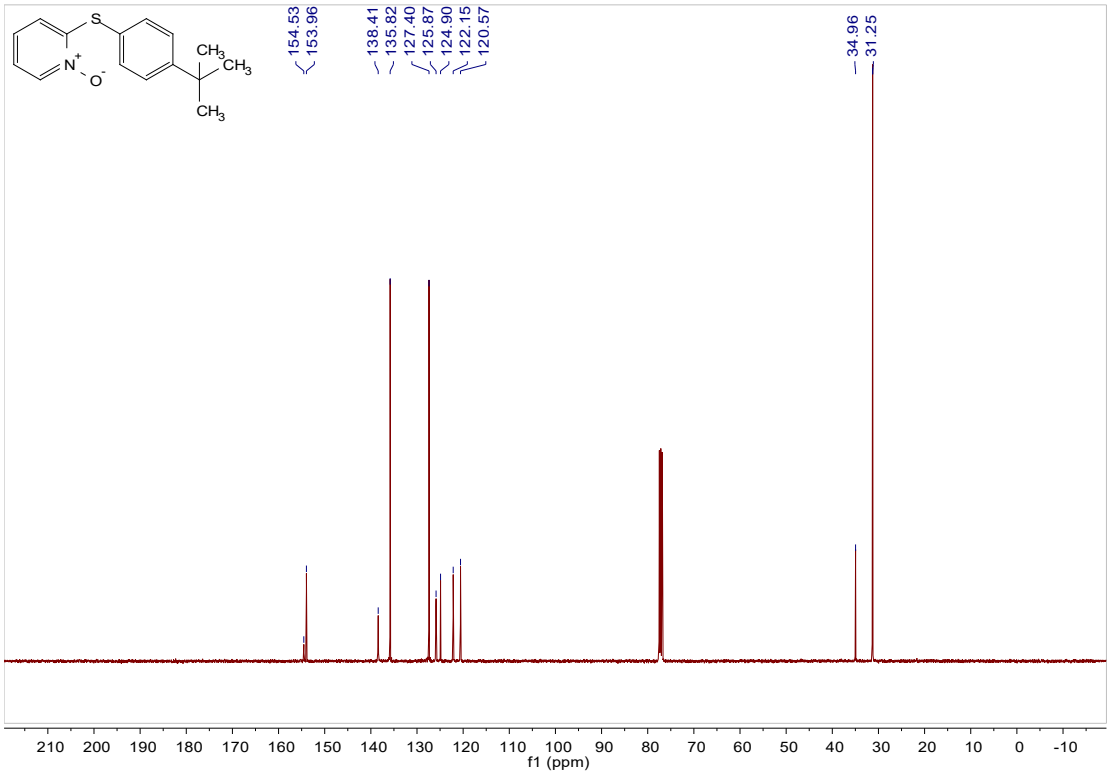
2-((4-Methoxyphenyl)thio)pyridine 1-oxide (**3h**)



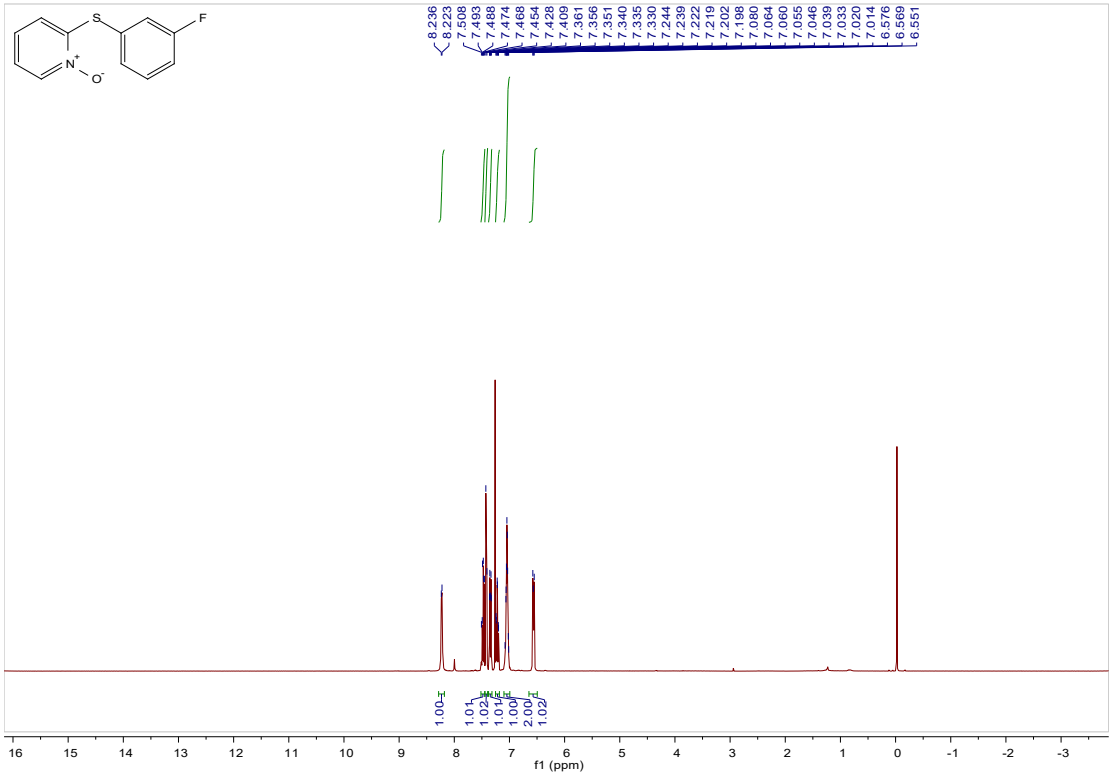


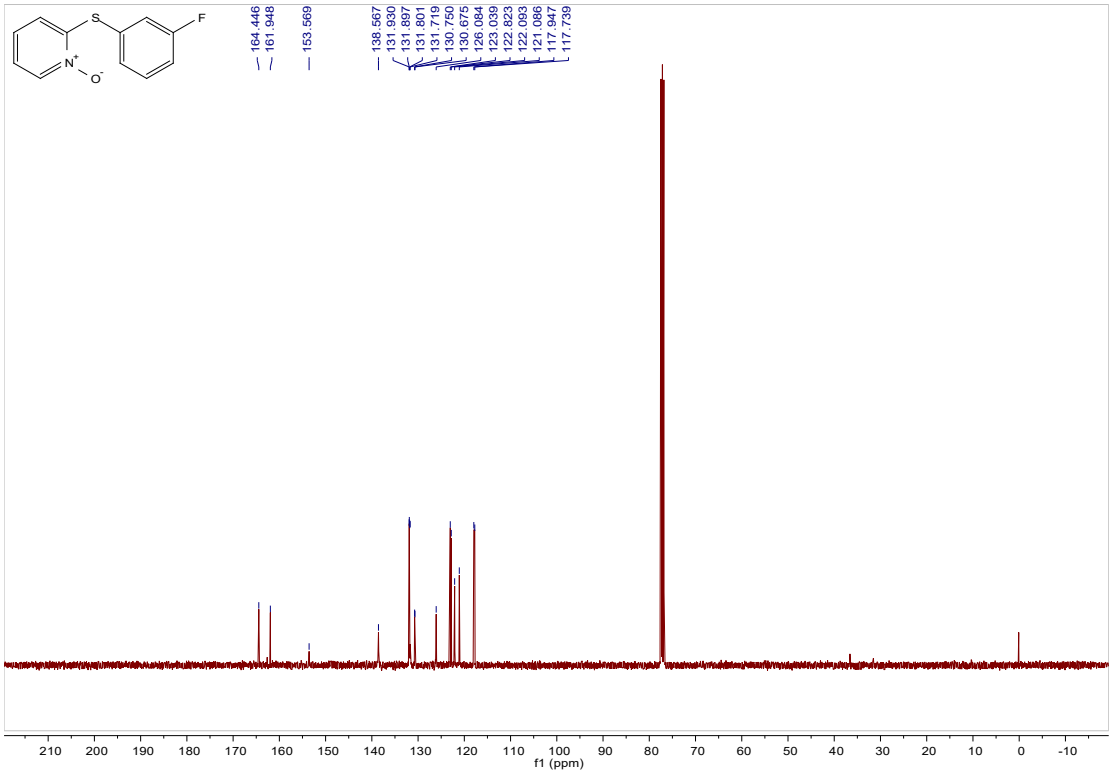
2-((4-(Tert-butyl)phenyl)thio)pyridine 1-oxide (**3i**)

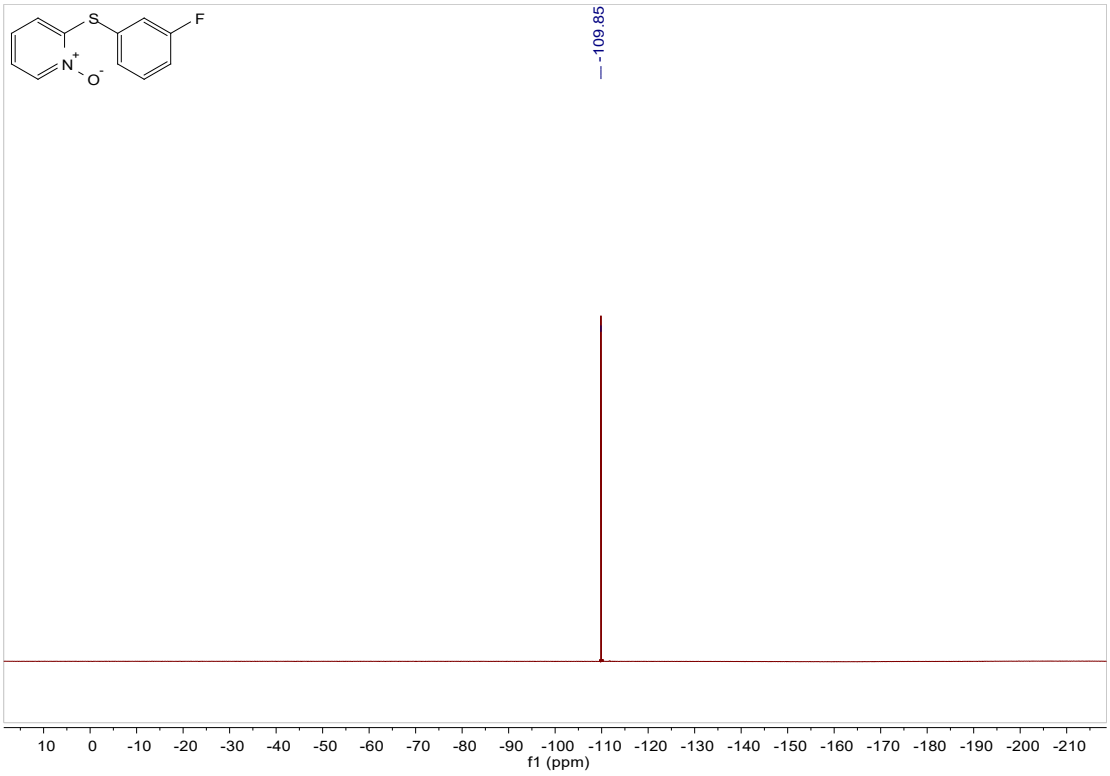




2-((3-Fluorophenyl)thio)pyridine 1-oxide (**3j**)



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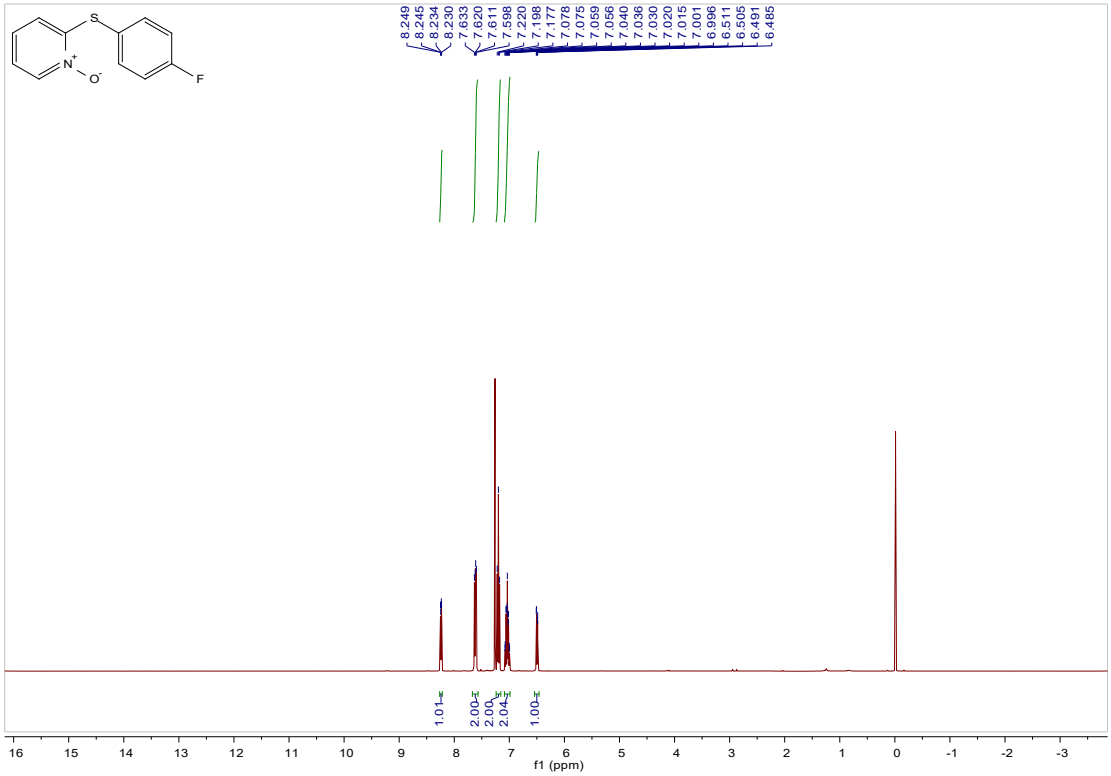
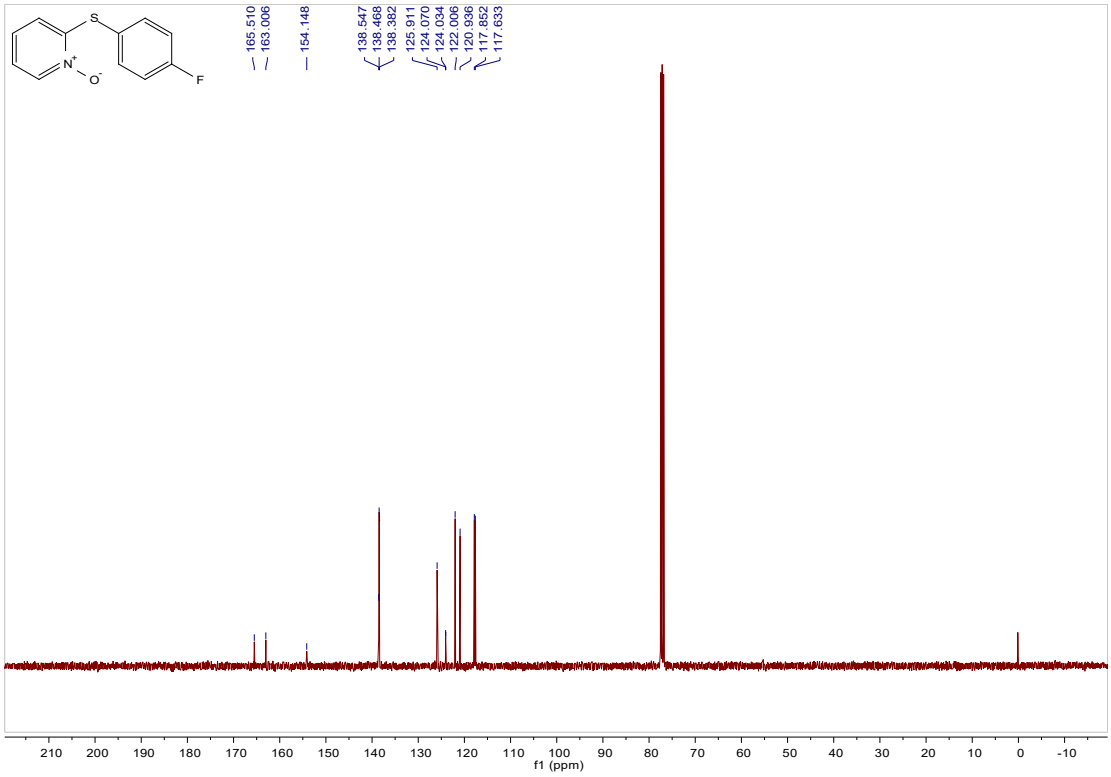
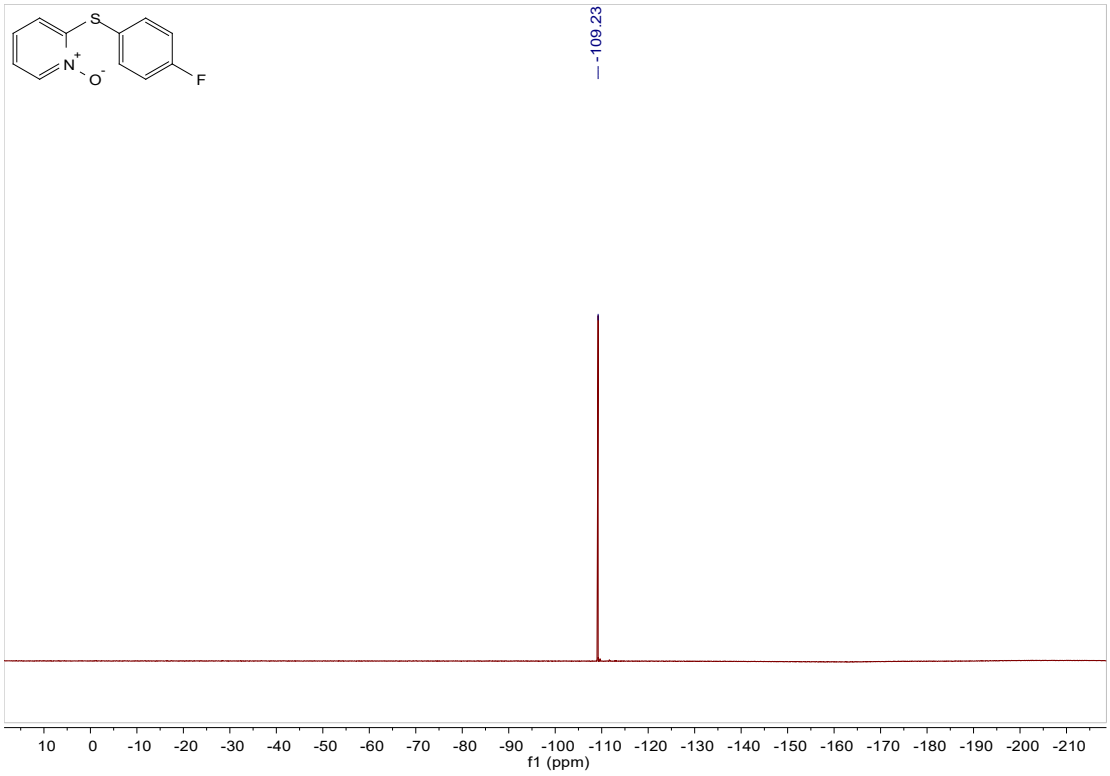
F
N+
O-
-109.85
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2-((4-Fluorophenyl)thio)pyridine 1-oxide (**3k**)



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N+
O-
F
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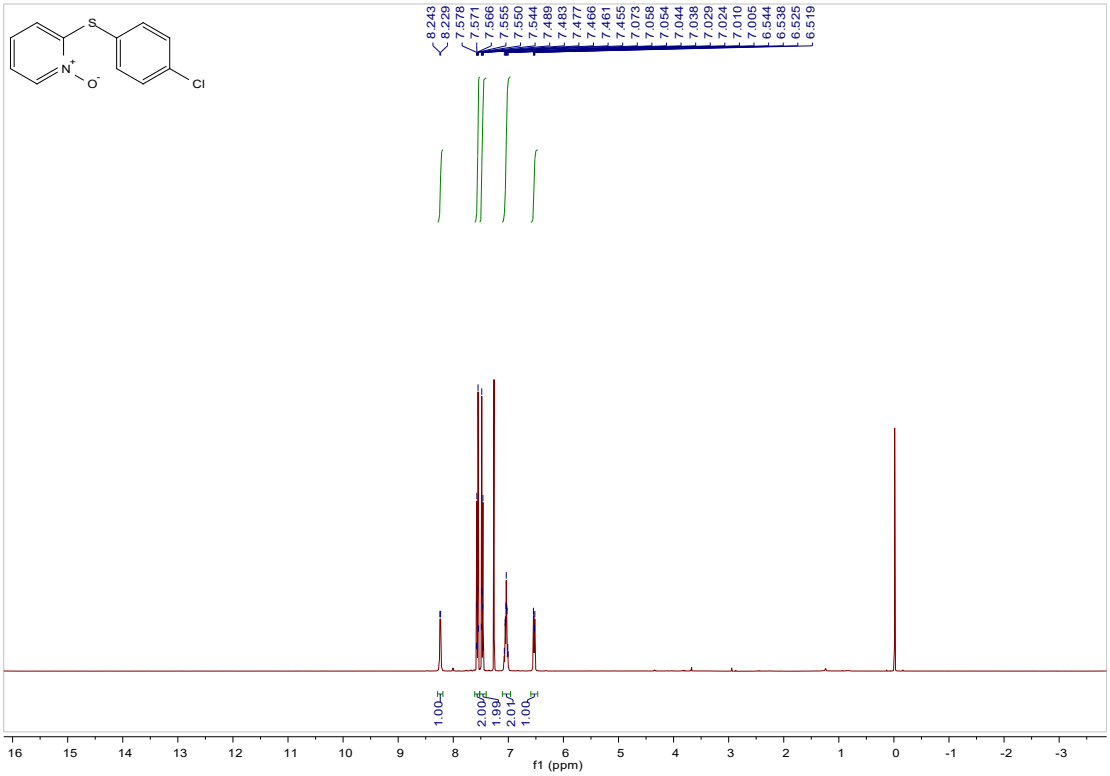
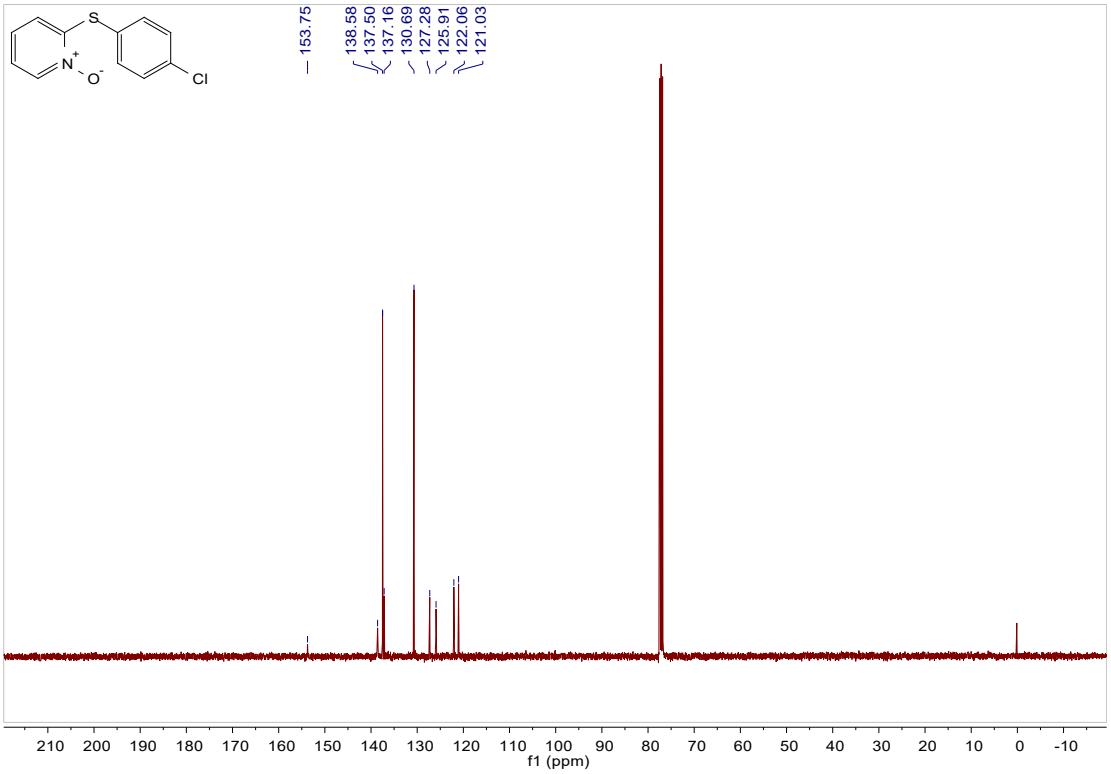
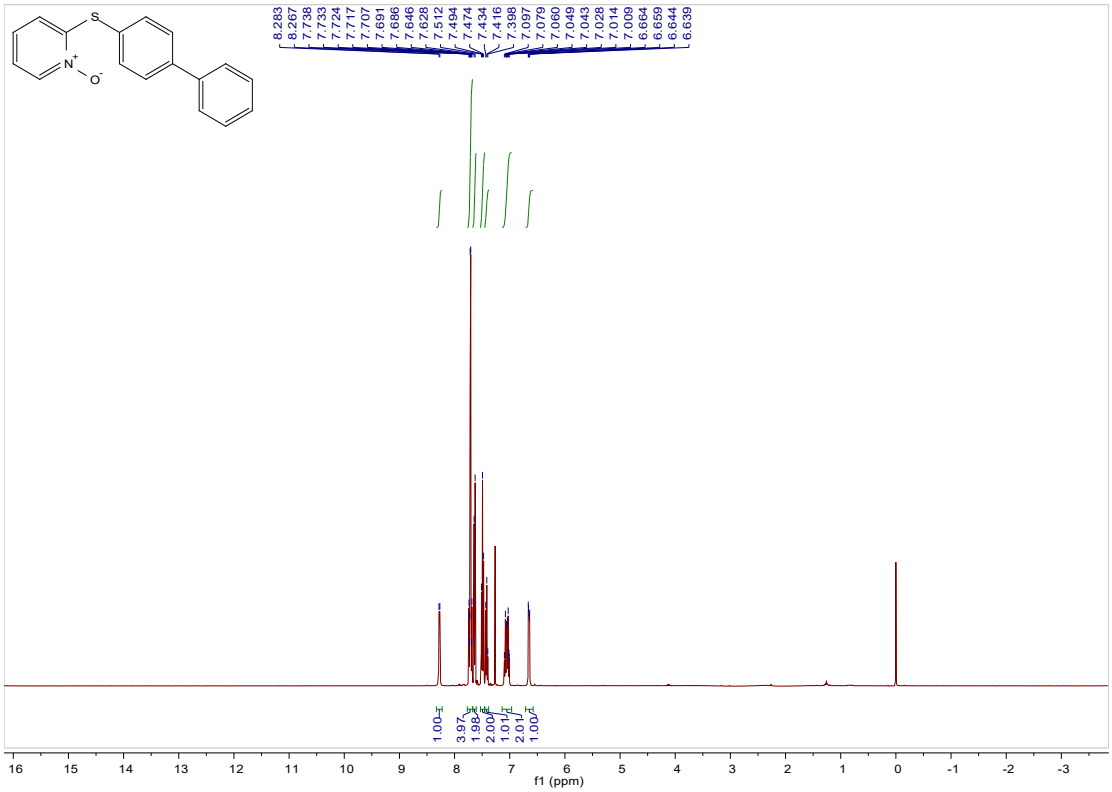
f1 (ppm)

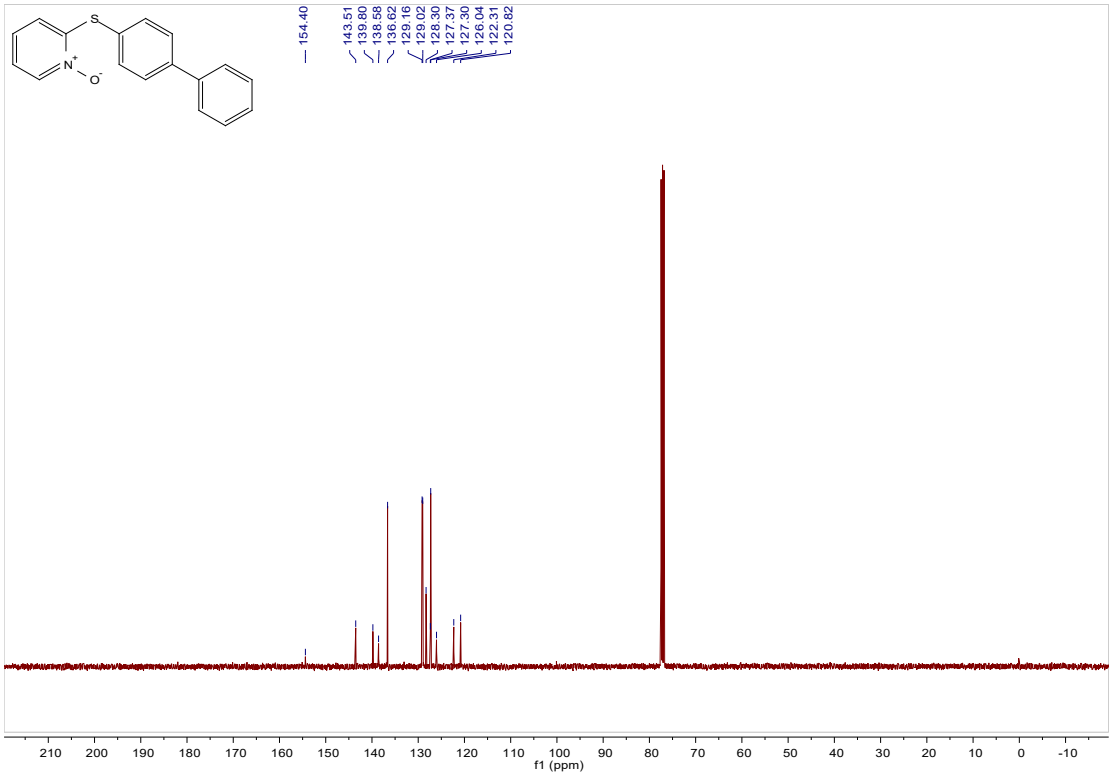
2-((4-Chlorophenyl)thio)pyridine 1-oxide (**3l**)



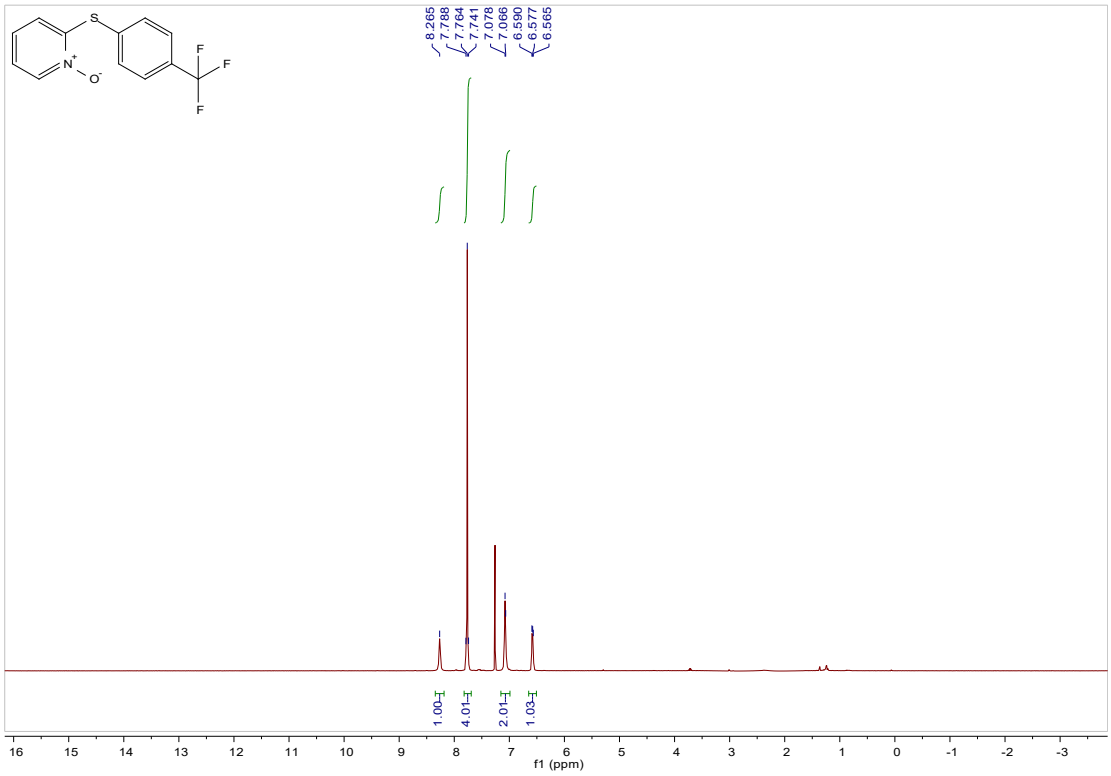


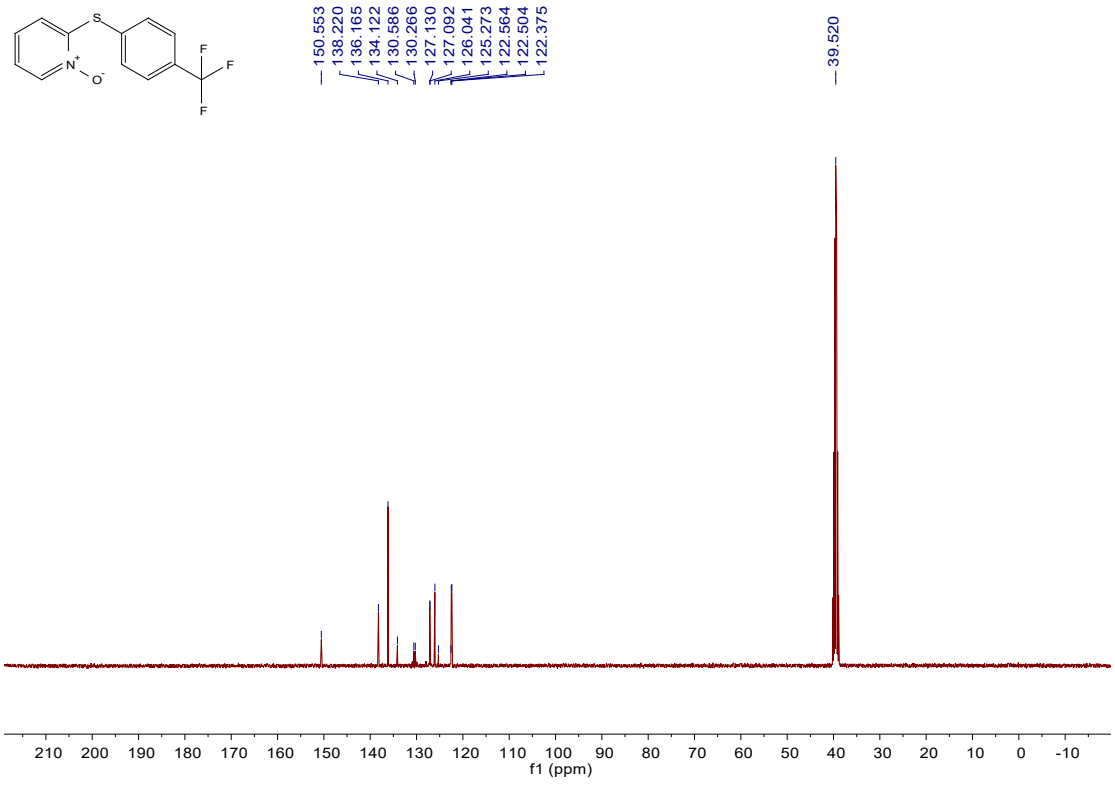
2-([1,1'-Biphenyl]-4-ylthio)pyridine 1-oxide (**3m**)

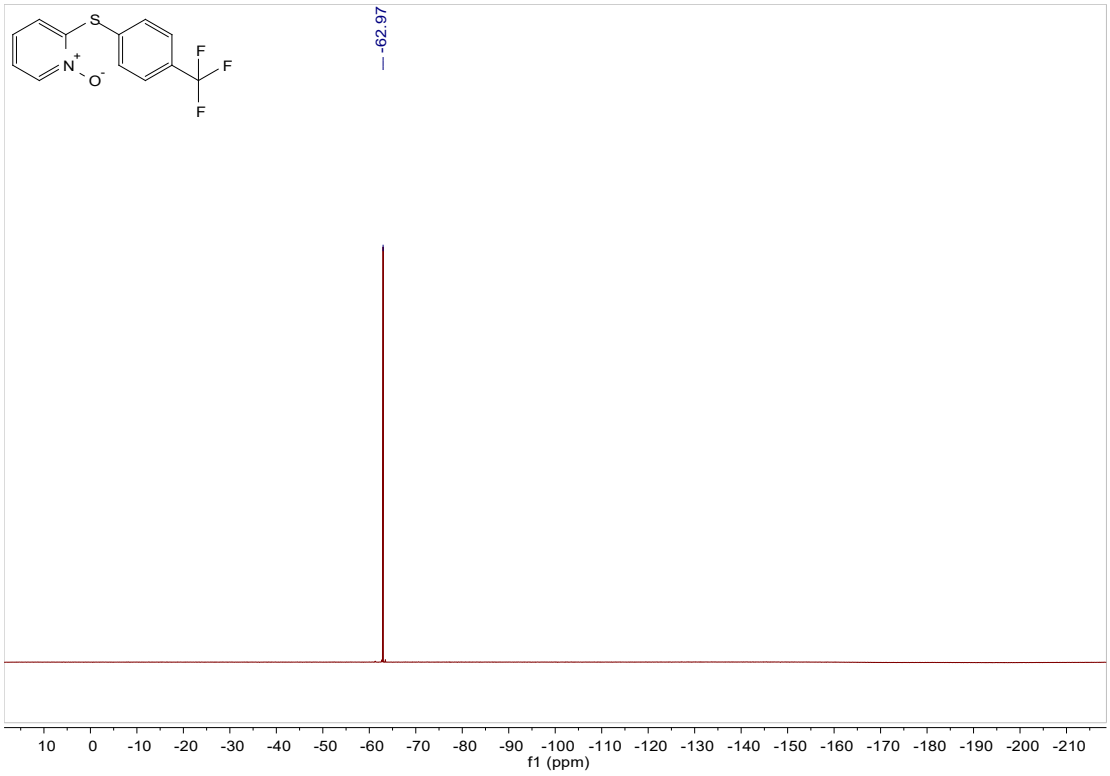




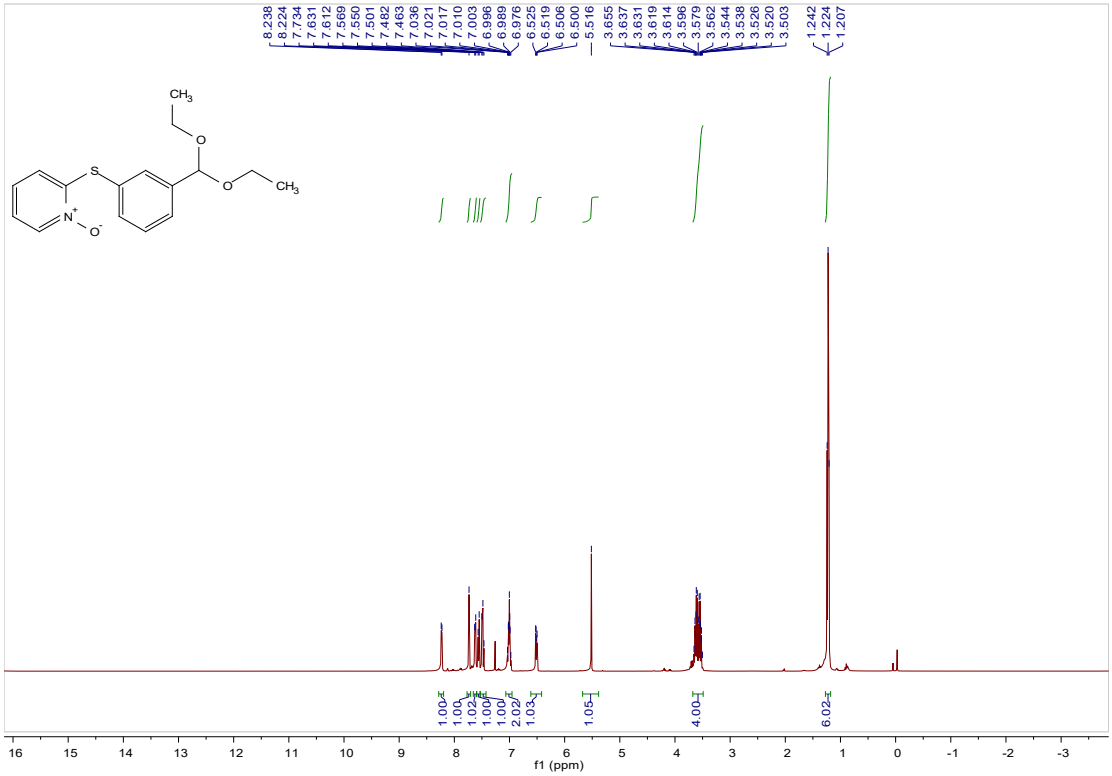
2-((4-(Trifluoromethyl)phenyl)thio)pyridine 1-oxide (**3n**)

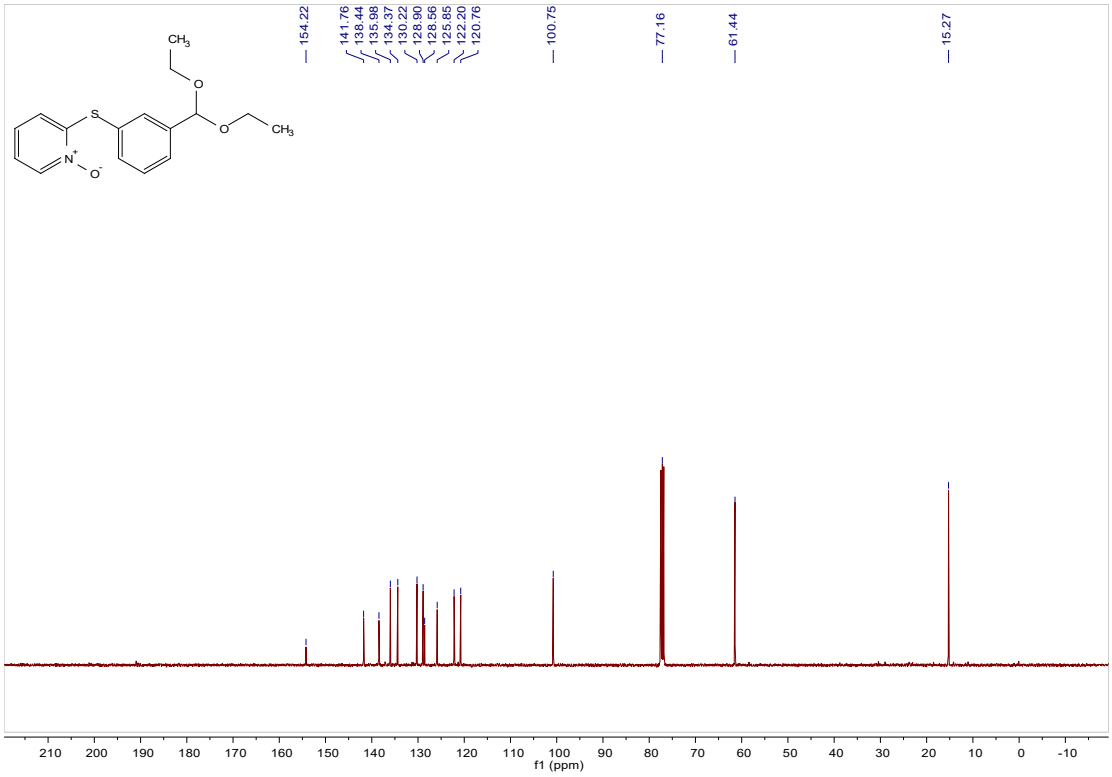




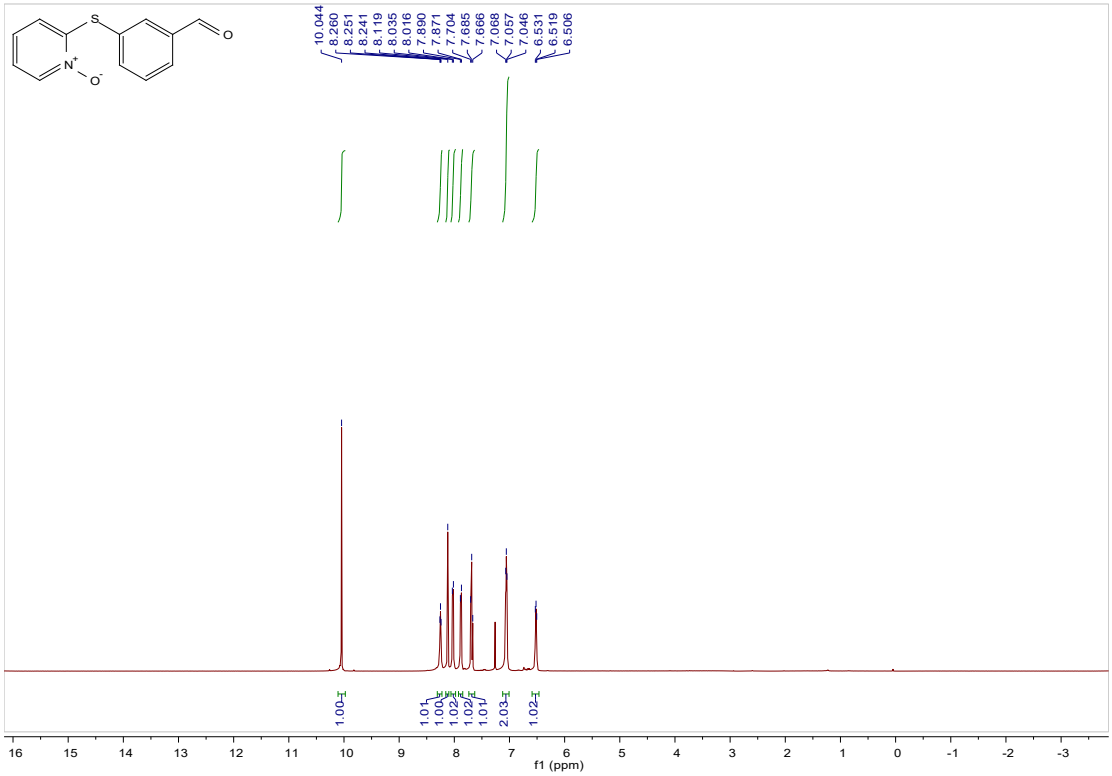

S
N+
O-
F
F
F
-62.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

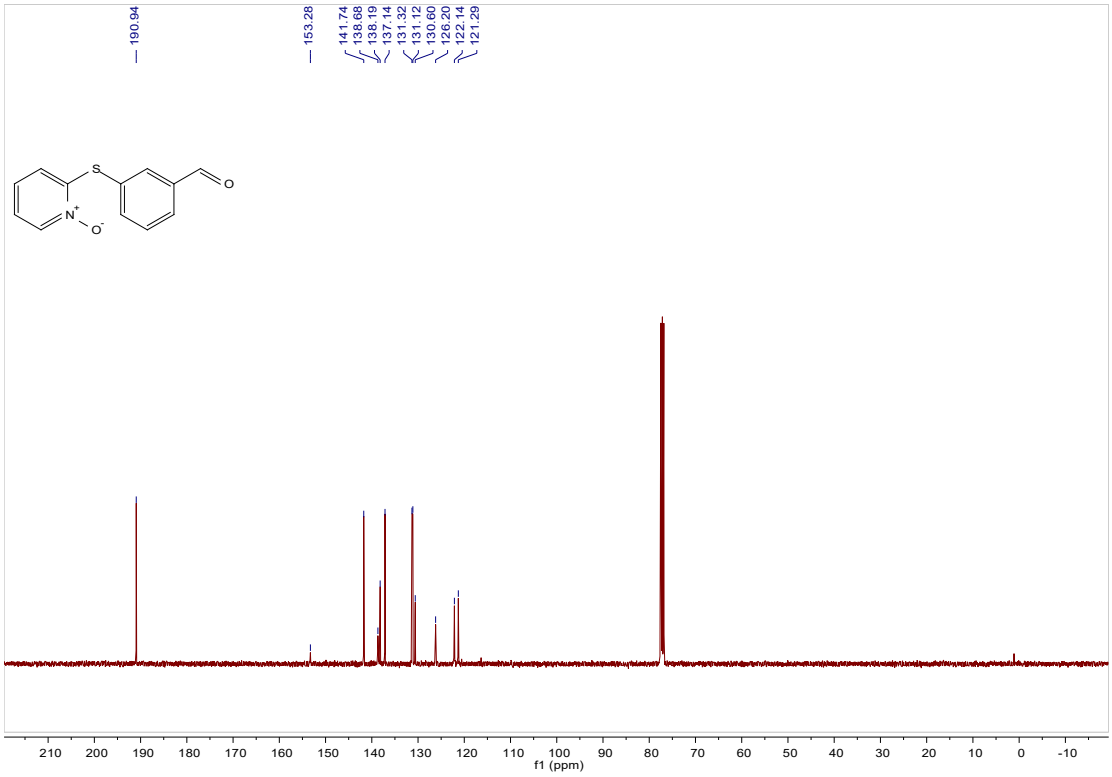
2-((3-(Diethoxymethyl)phenyl)thio)pyridine 1-oxide (**3o**)



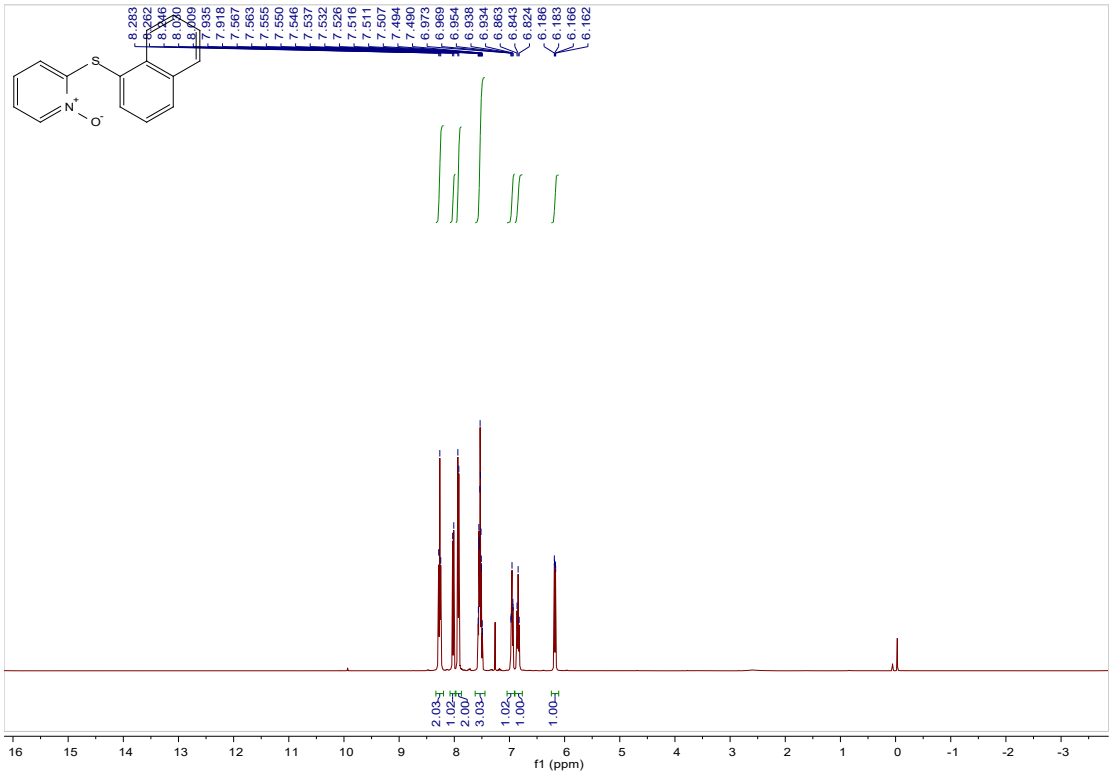


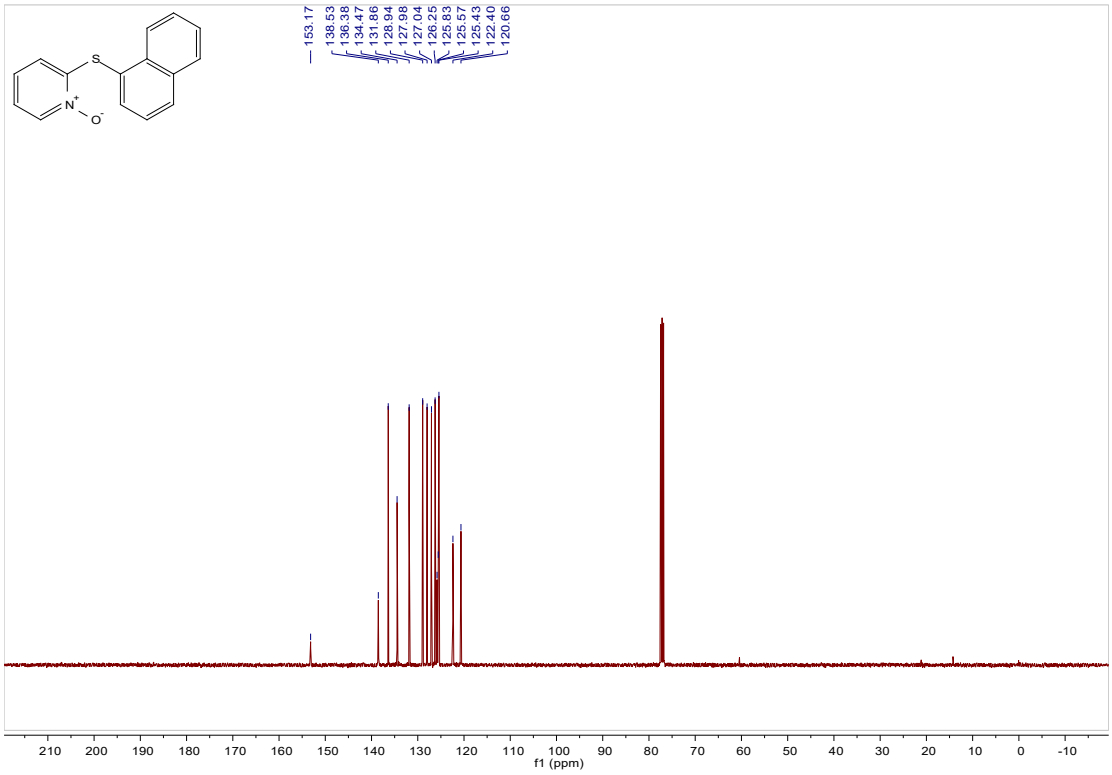
2-((3-Formylphenyl)thio)pyridine 1-oxide (**3p**)



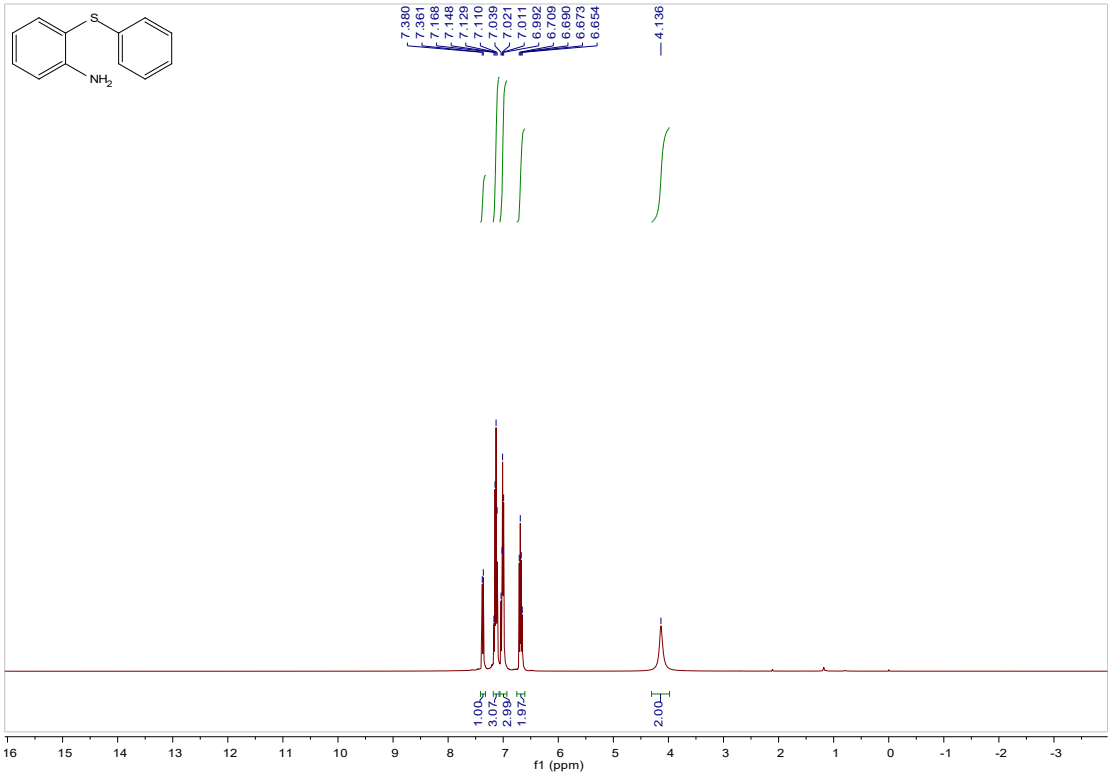


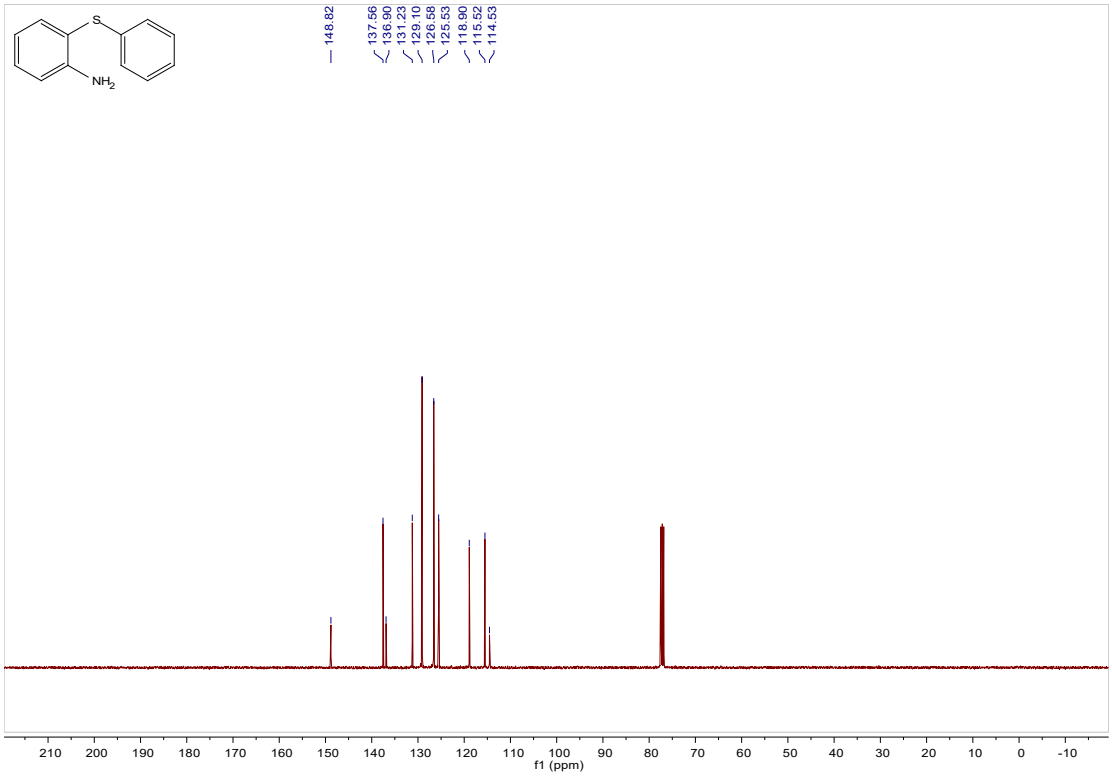
2-(Naphthalen-1-ylthio)pyridine 1-oxide (**3q**)



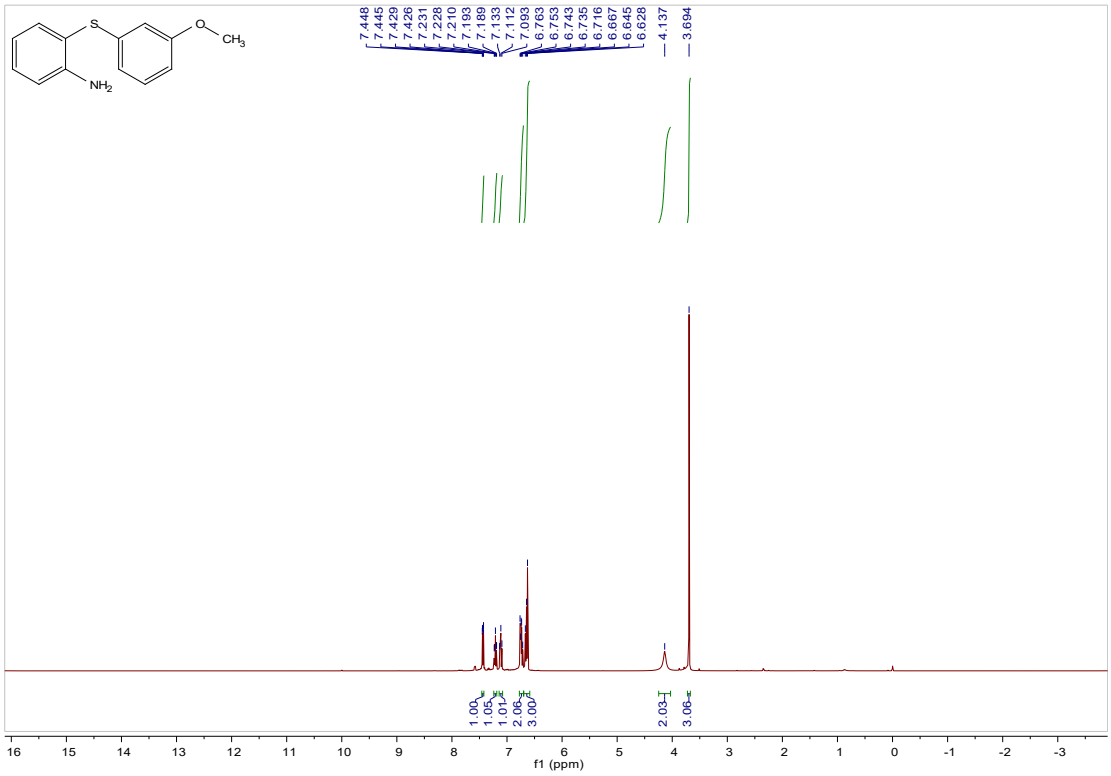


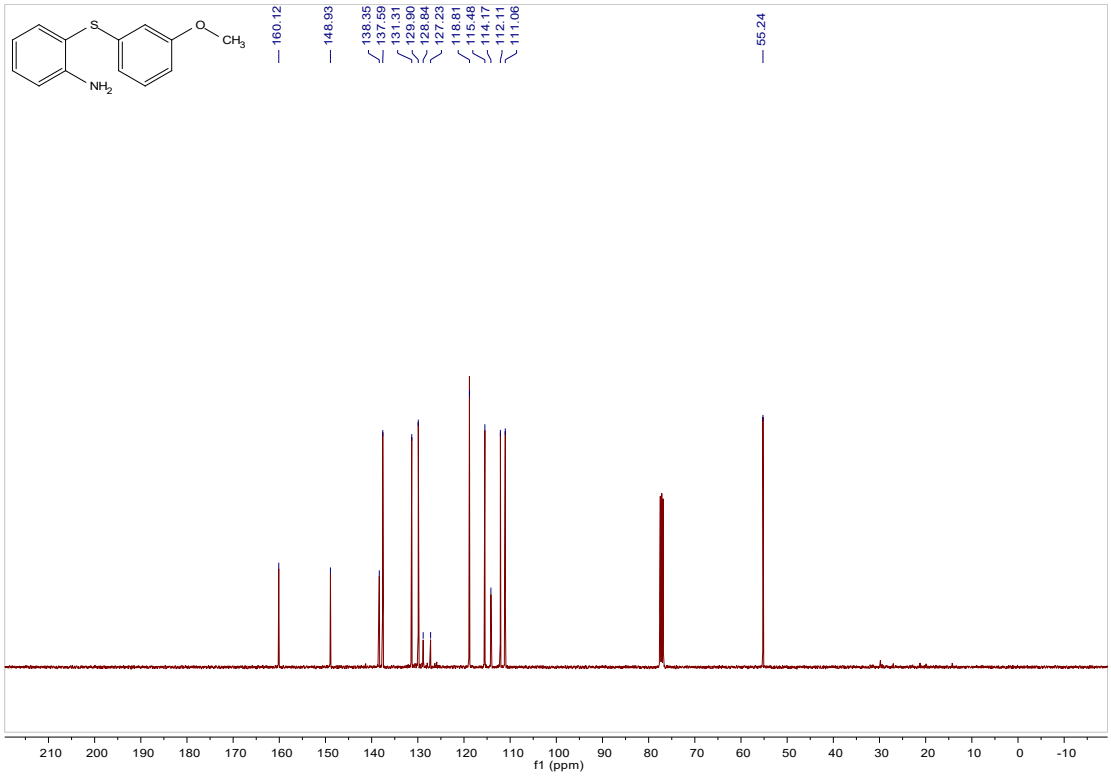
2-(Phenylthio)aniline (**6a**)



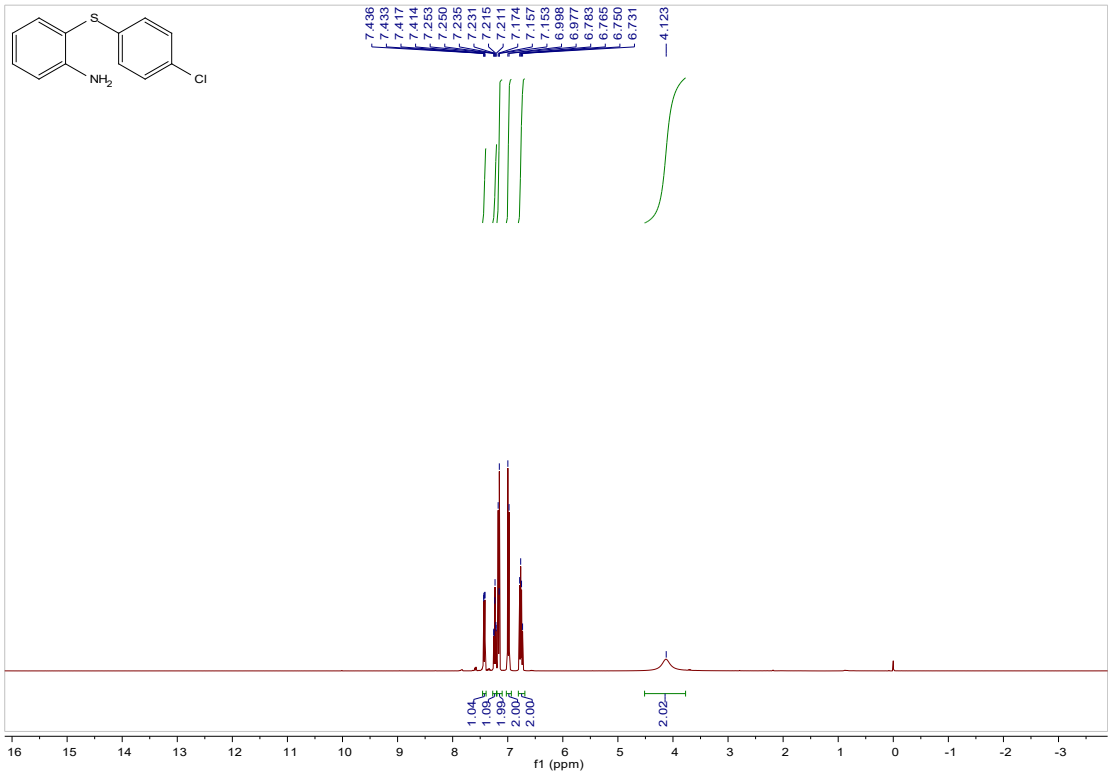


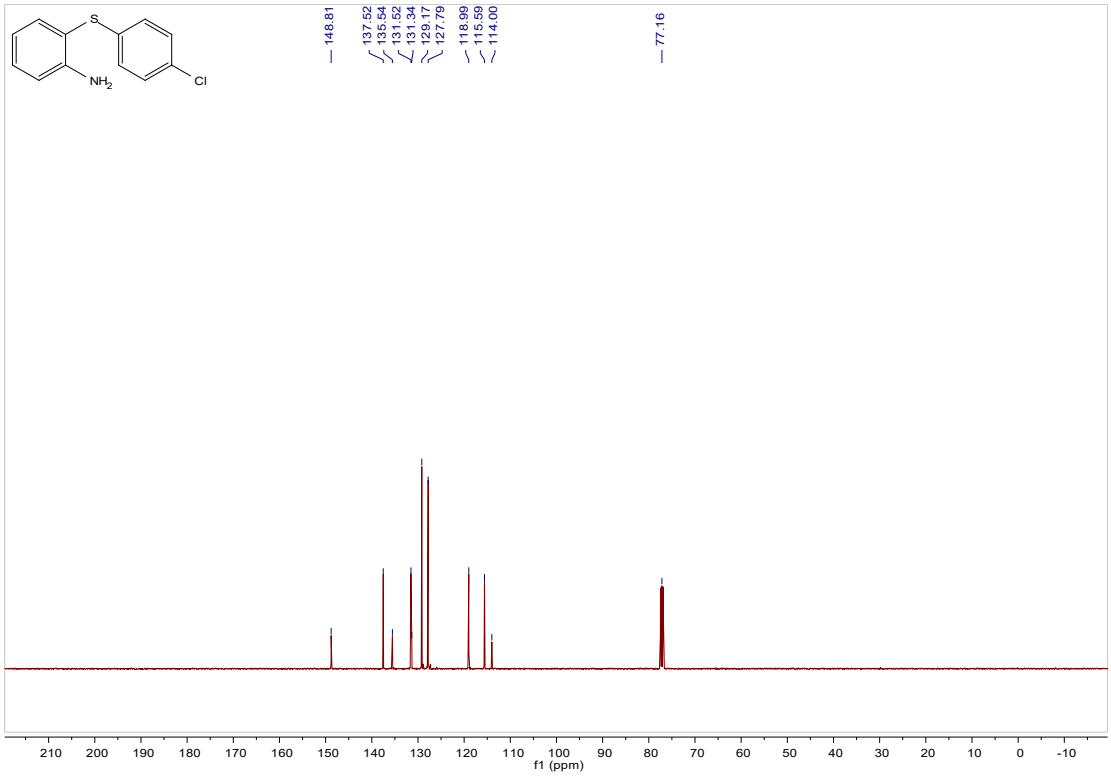
2-((3-Methoxyphenyl)thio)aniline (**6b**)



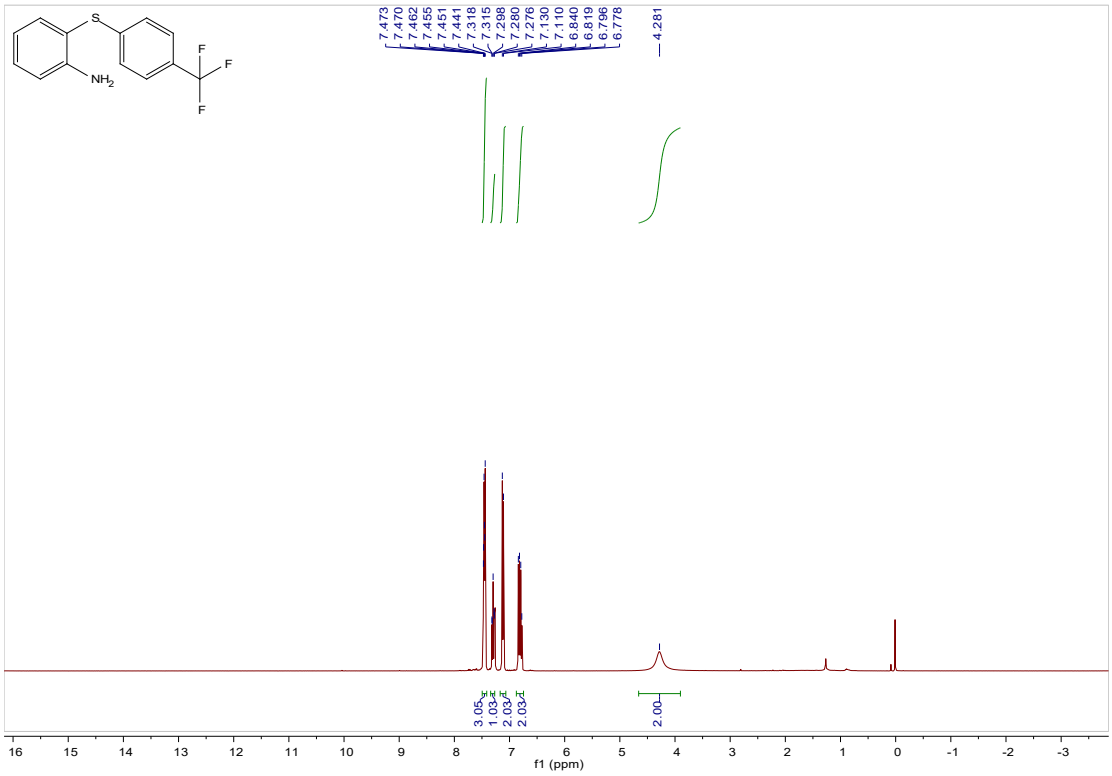


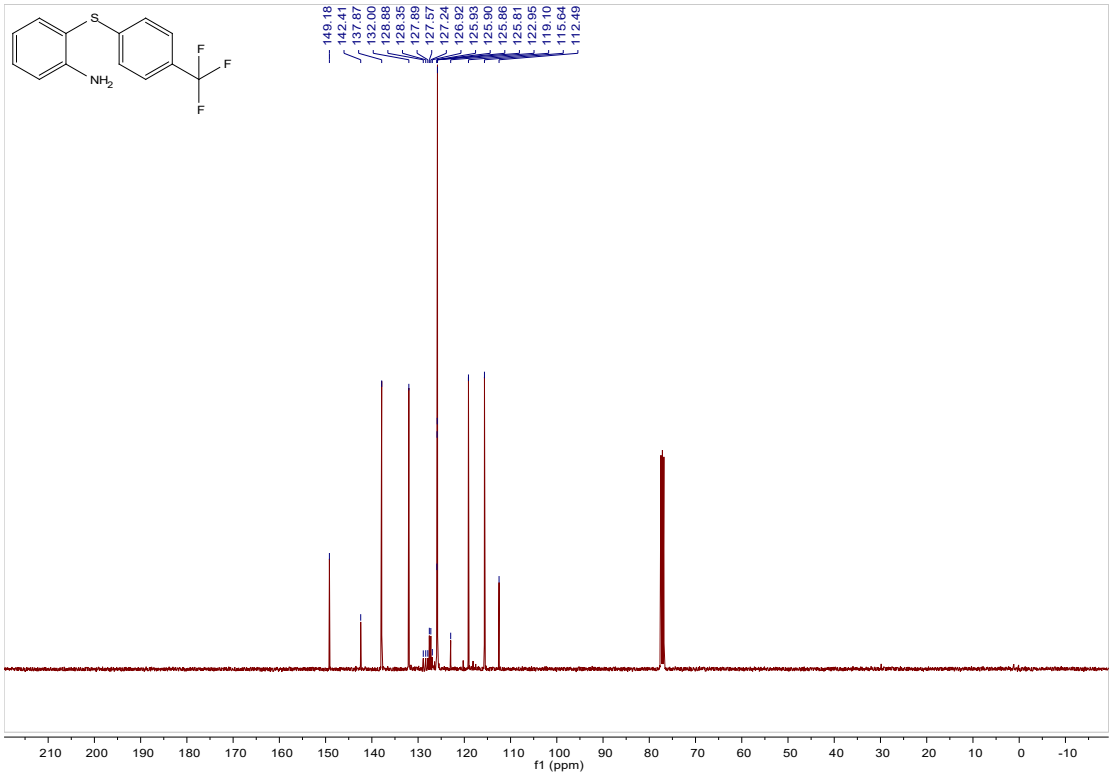
2-((4-Chlorophenyl)thio)aniline (**6c**)

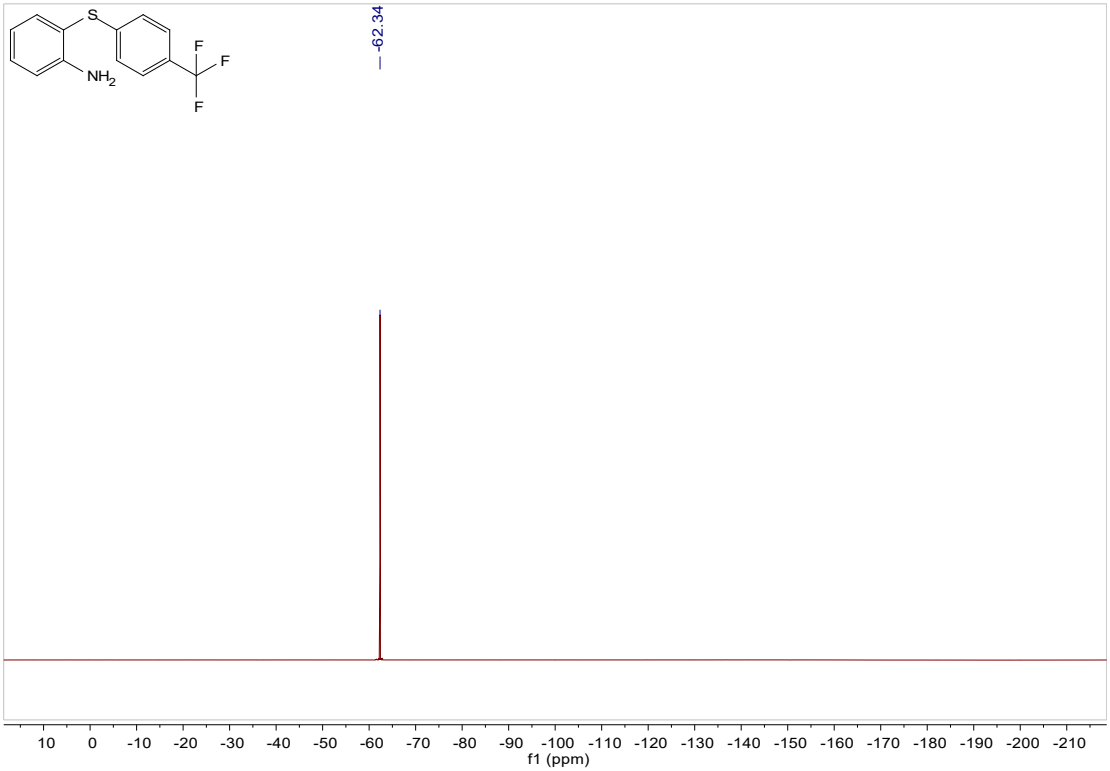




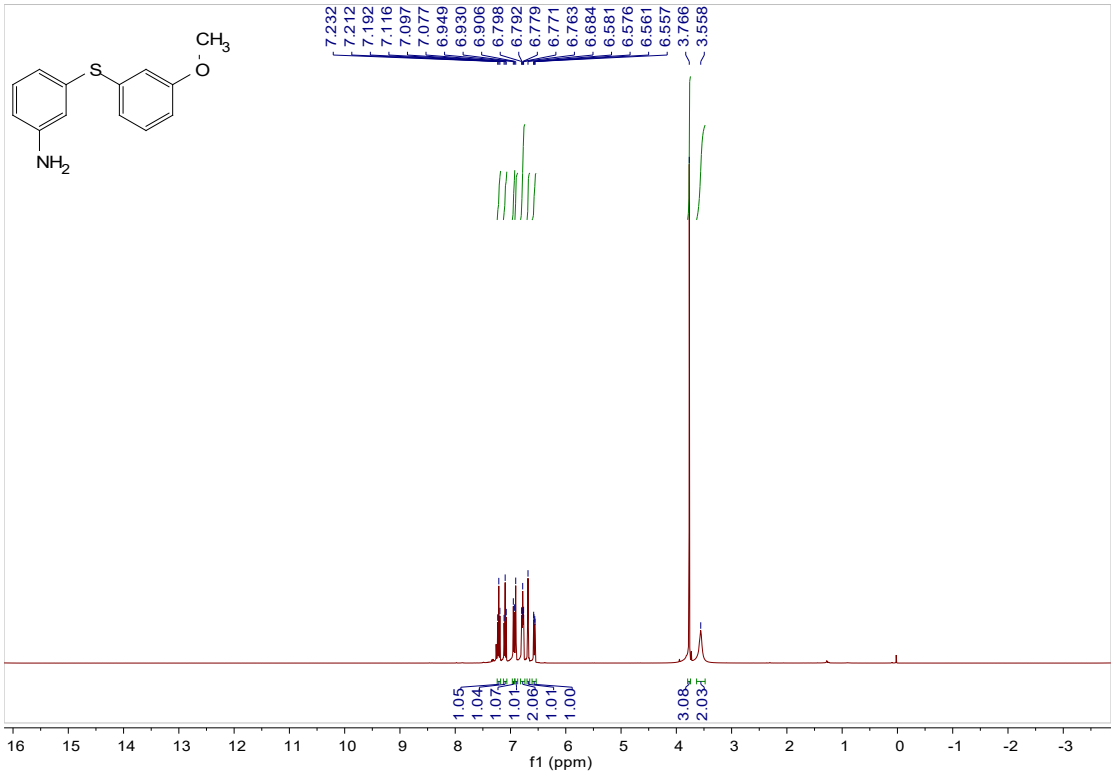
2-((4-(Trifluoromethyl)phenyl)thio)aniline (**6d**)

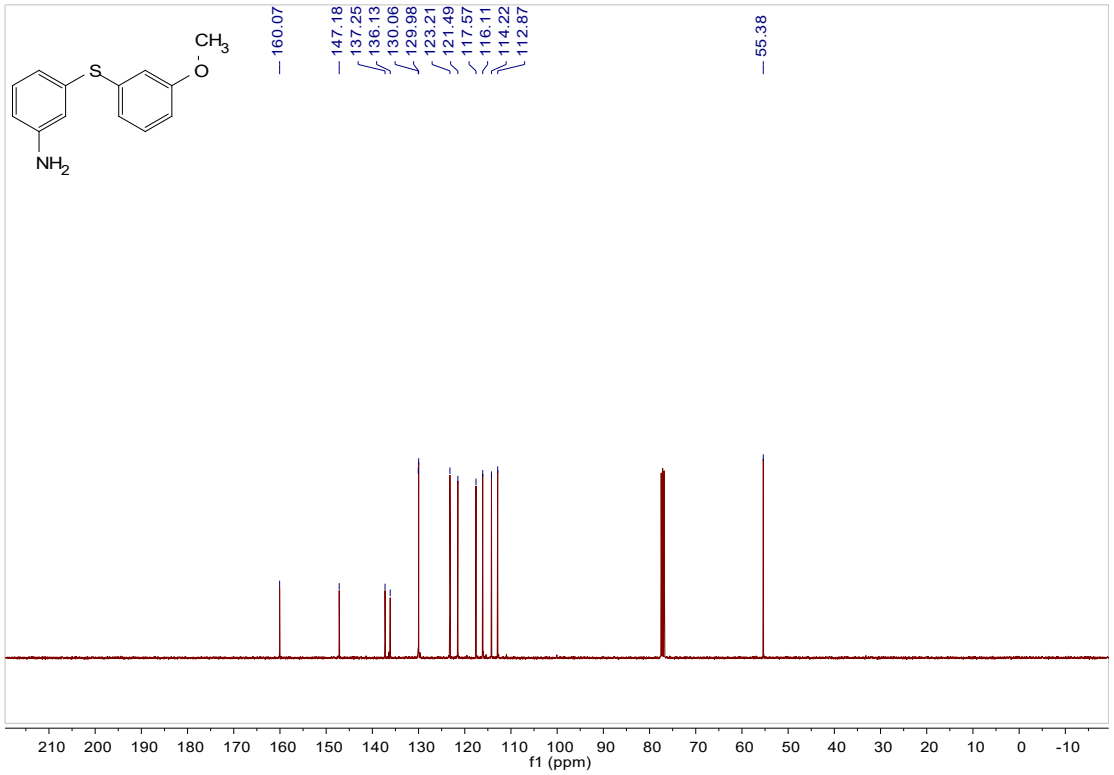




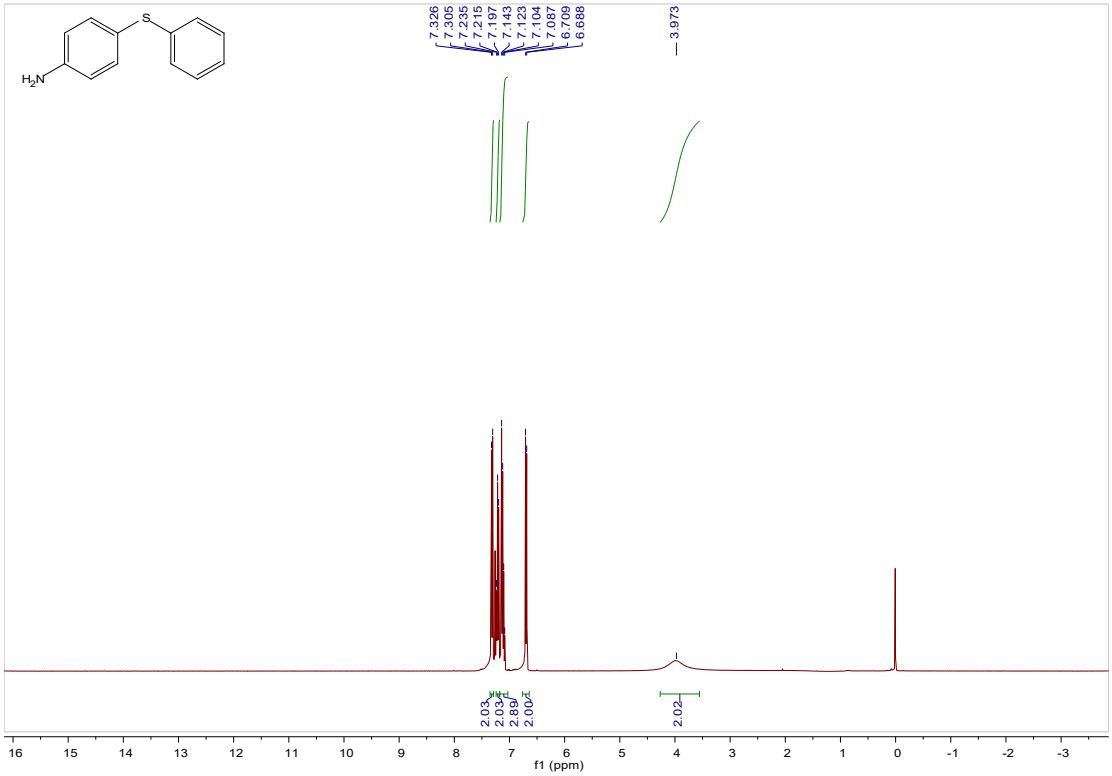

S
NH2
F
F
F
-62.34
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

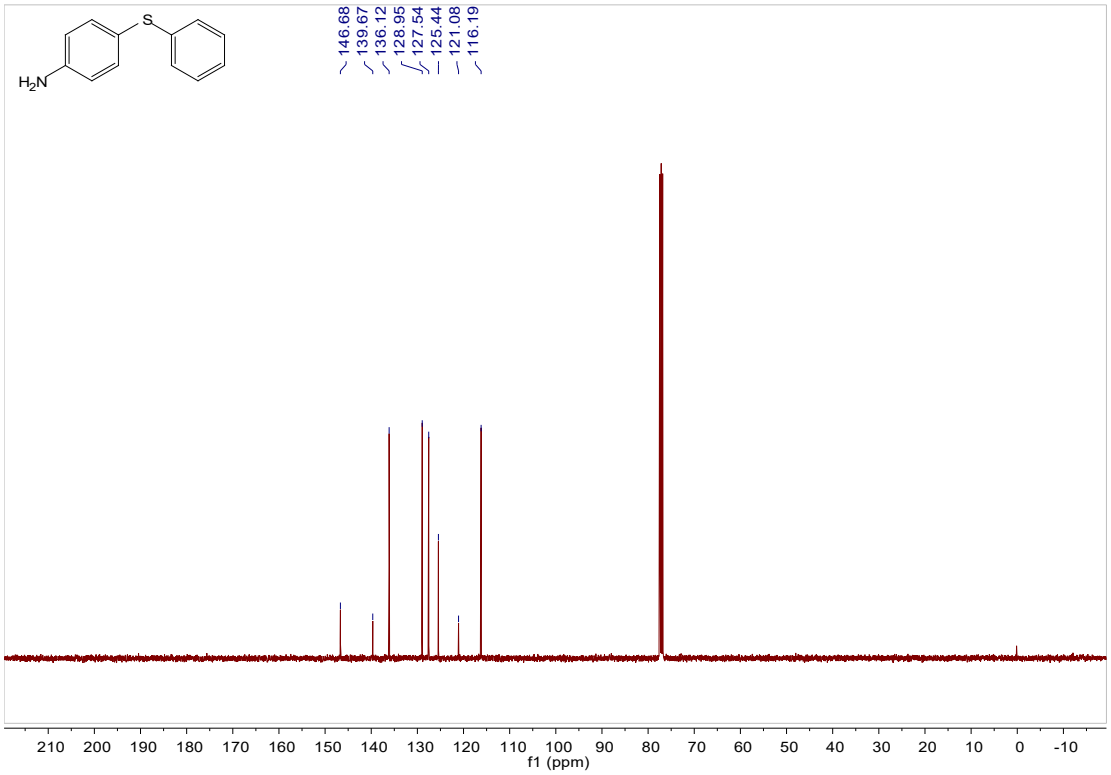
3-((3-Methoxyphenyl)thio)aniline (**6e**)



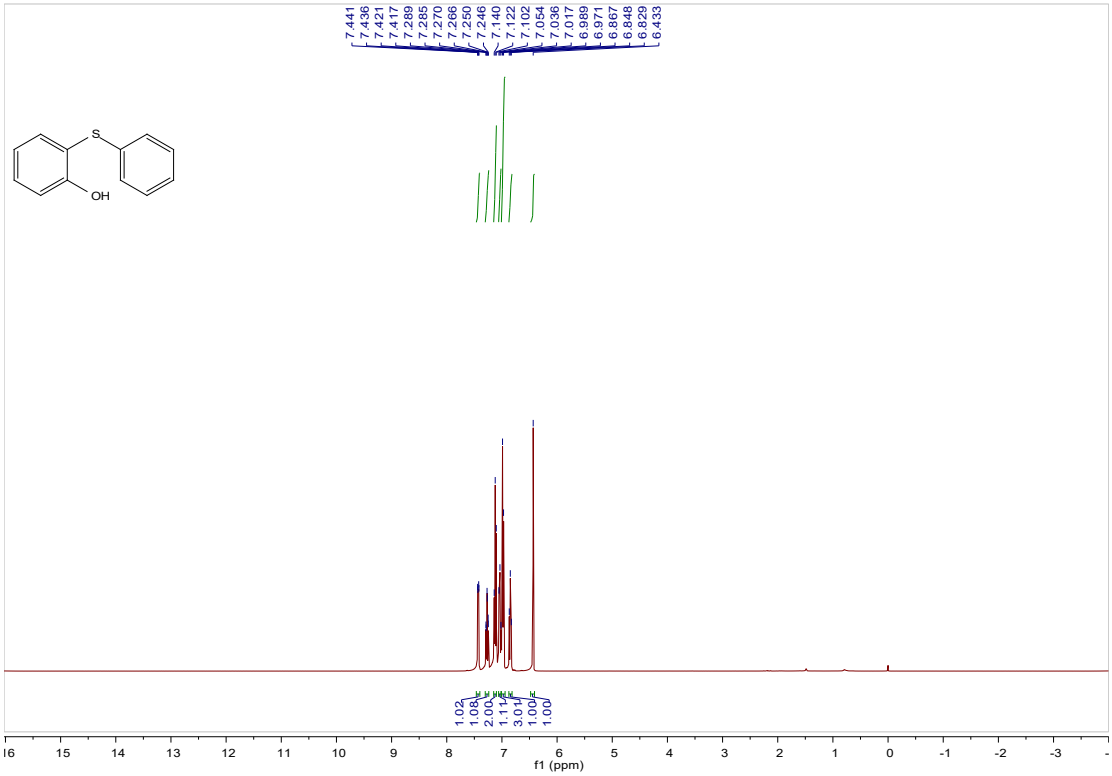


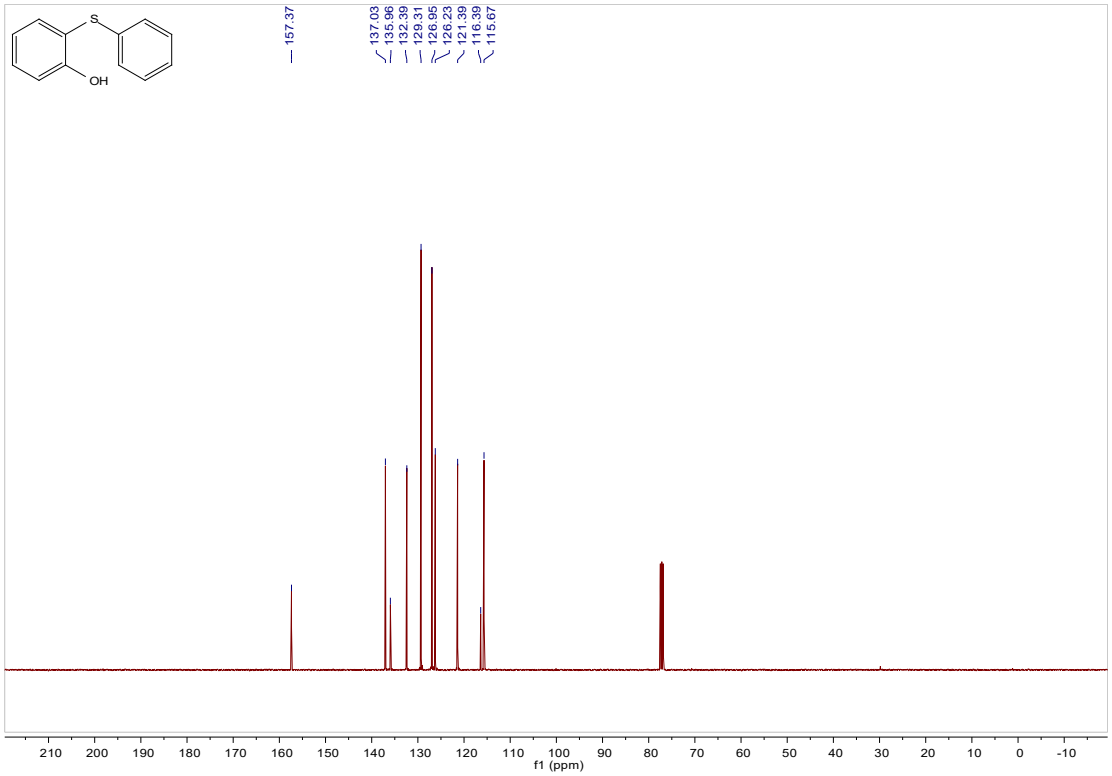
4-(Phenylthio)aniline (**6f**)



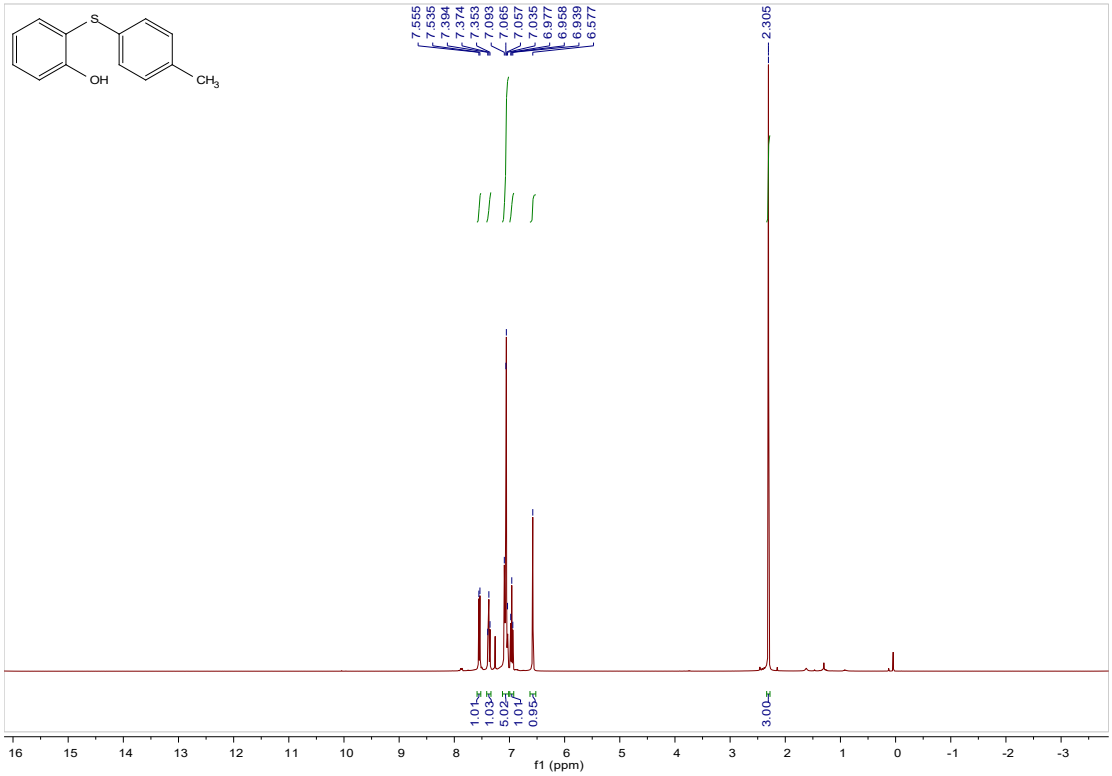


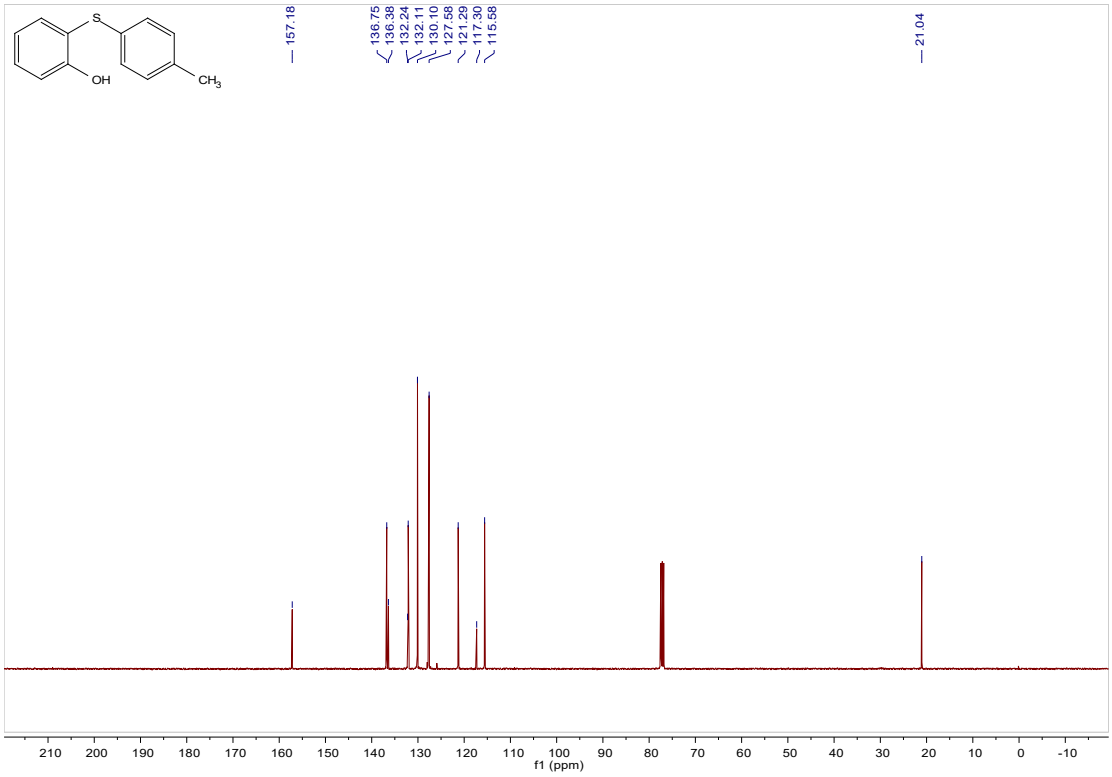
2-(Phenylthio)phenol (**7a**)



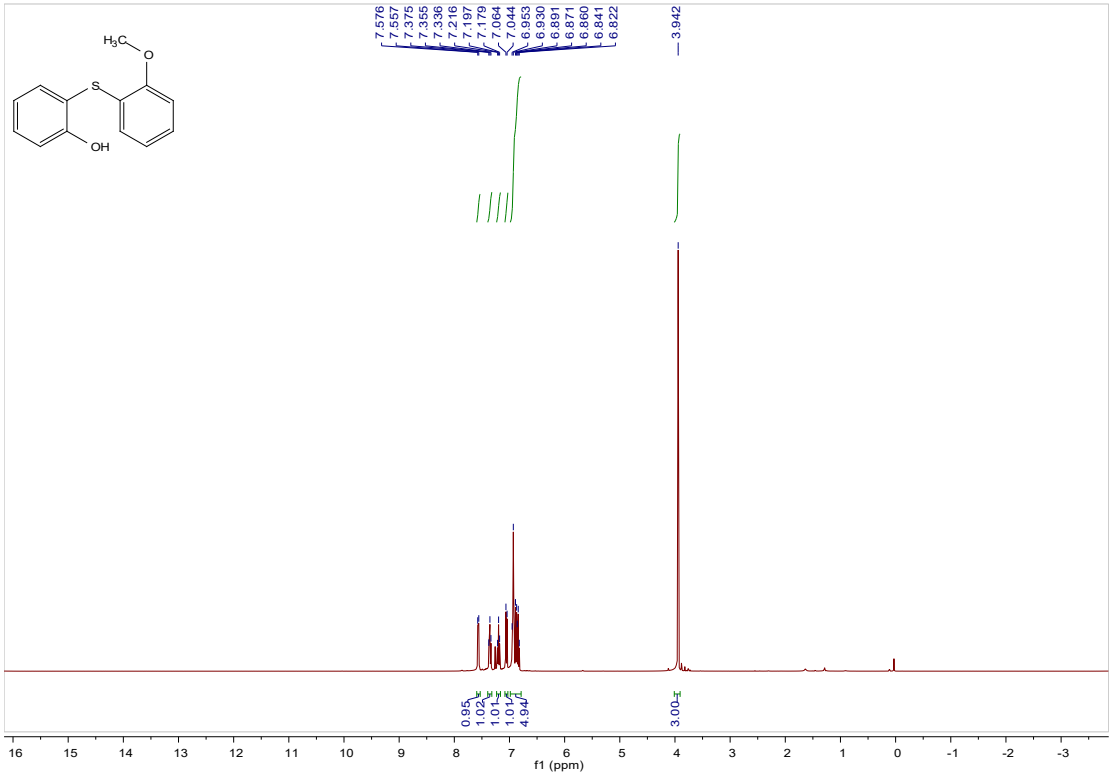


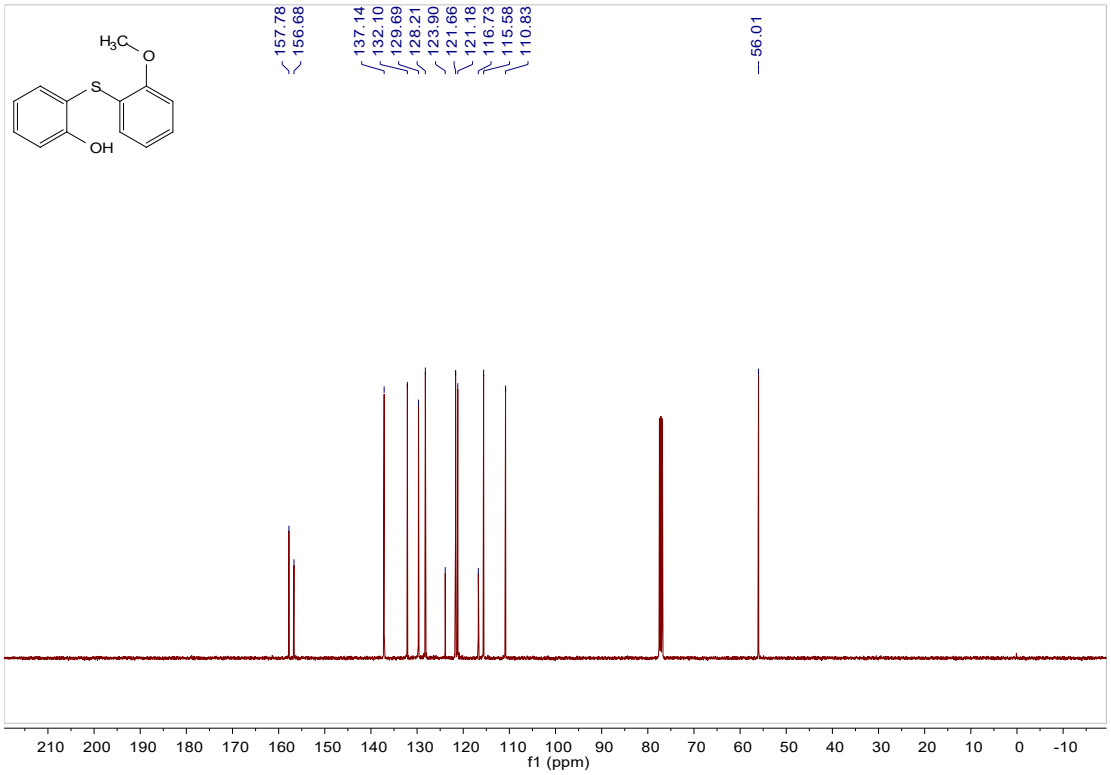
2-(P-tolylthio)phenol (**7b**)



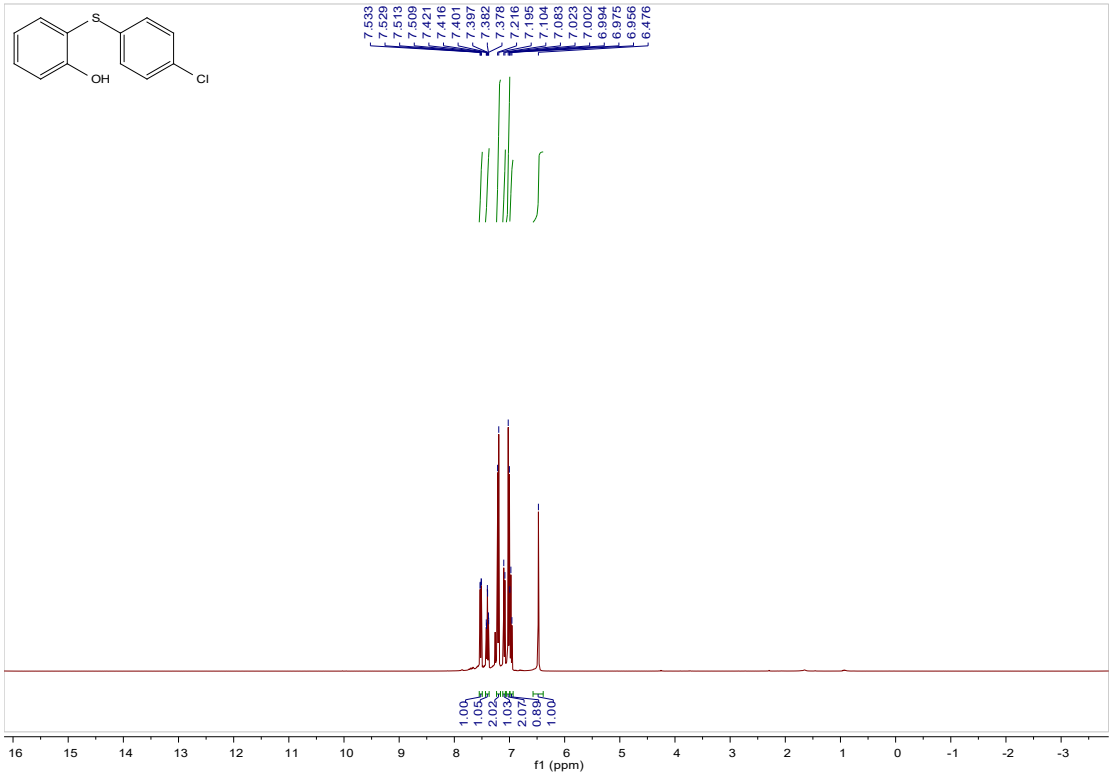


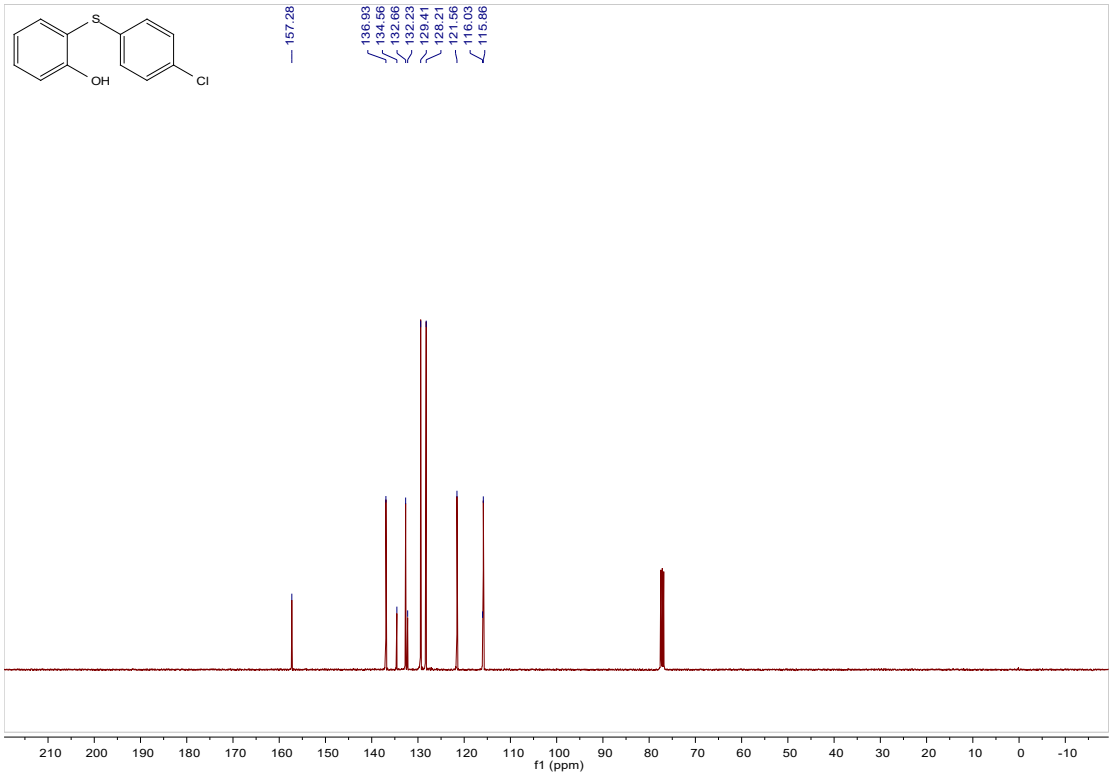
2-((2-Methoxyphenyl)thio)phenol (**7c**)



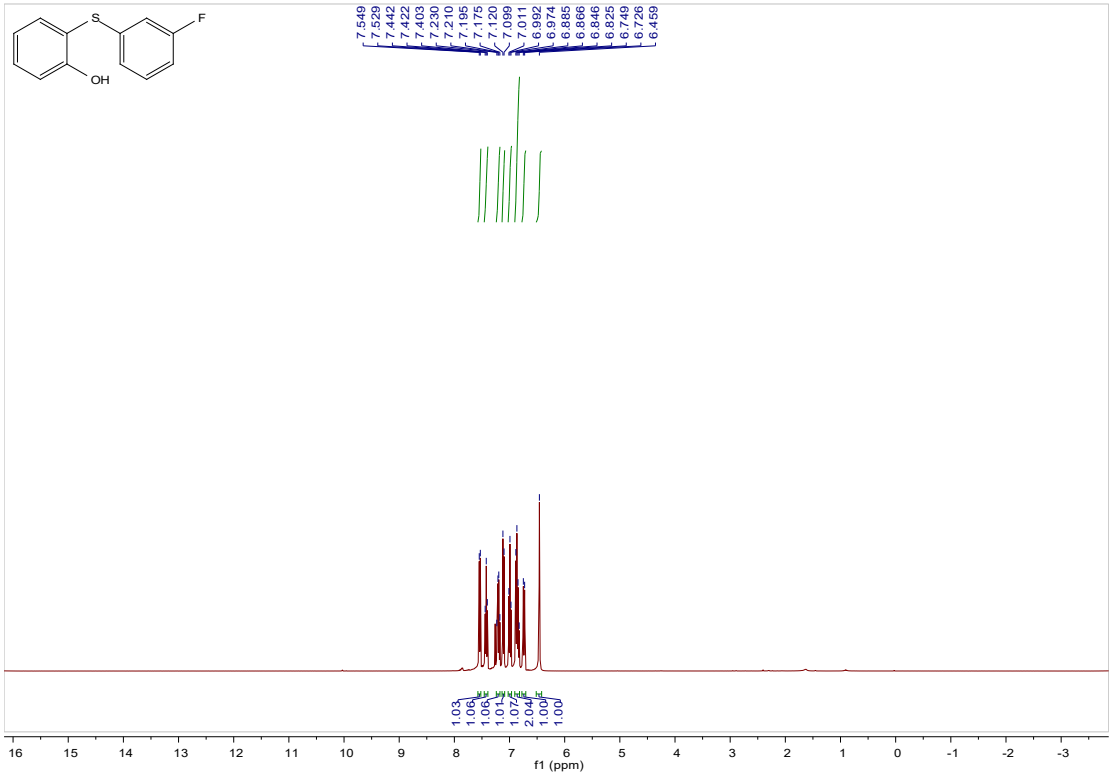


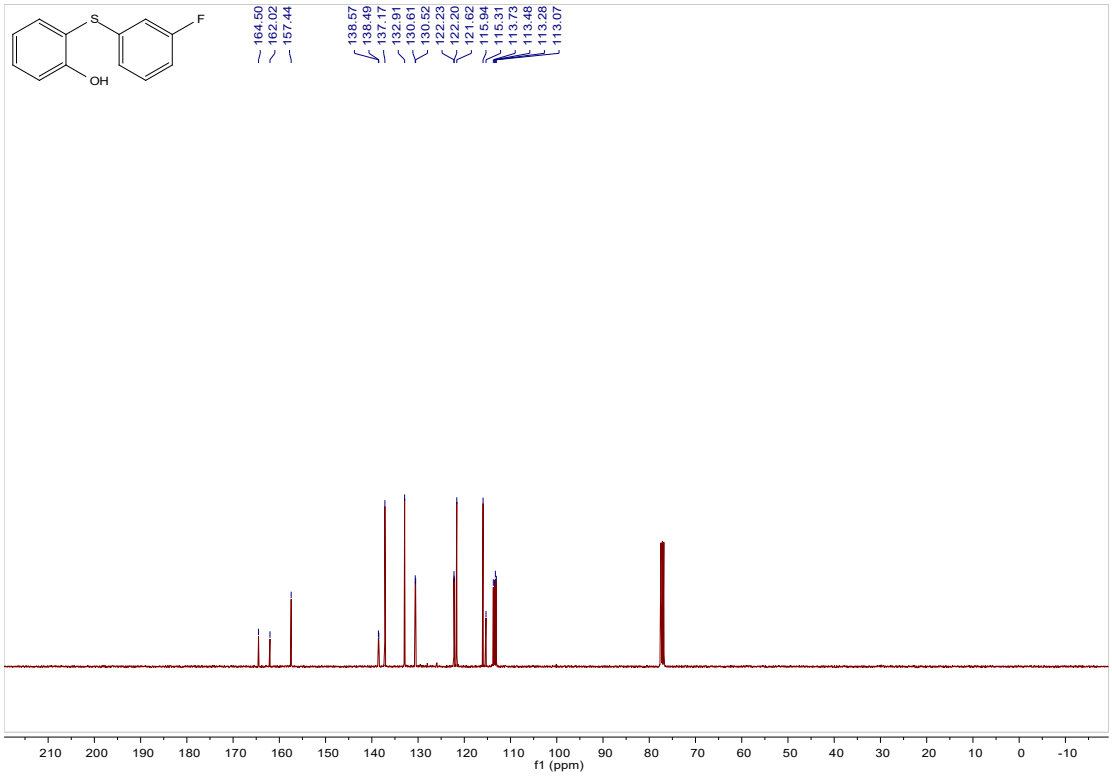
2-((4-Chlorophenyl)thio)phenol (**7d**)

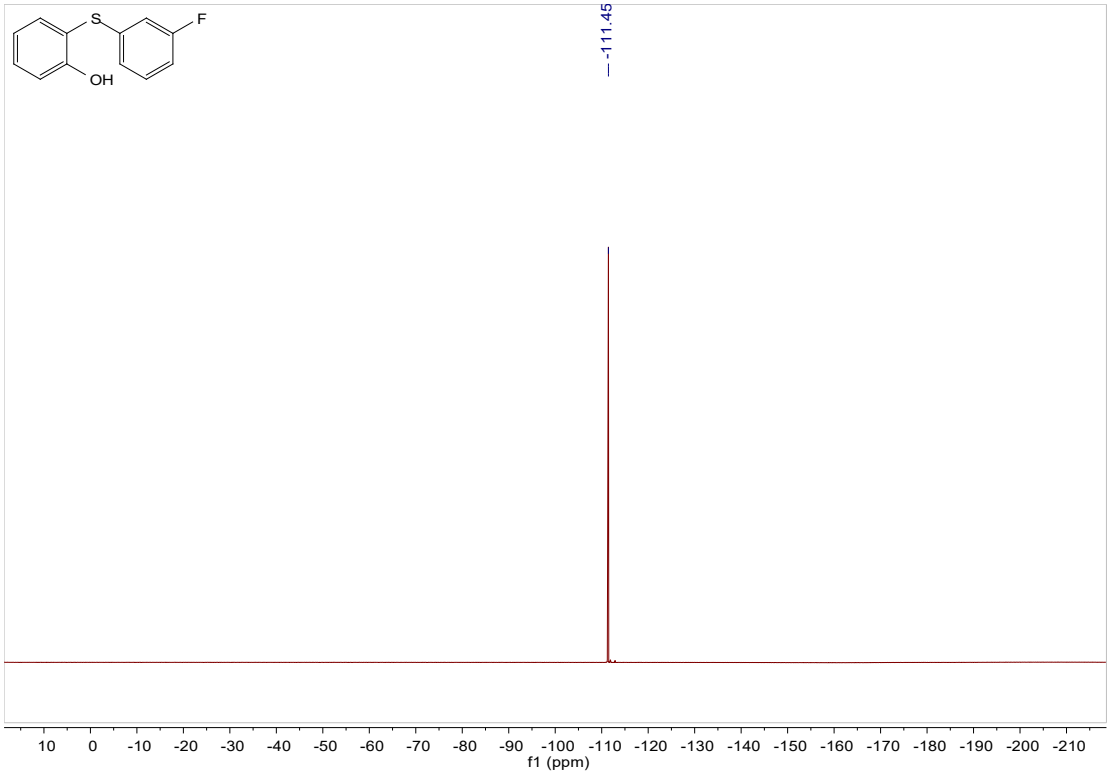




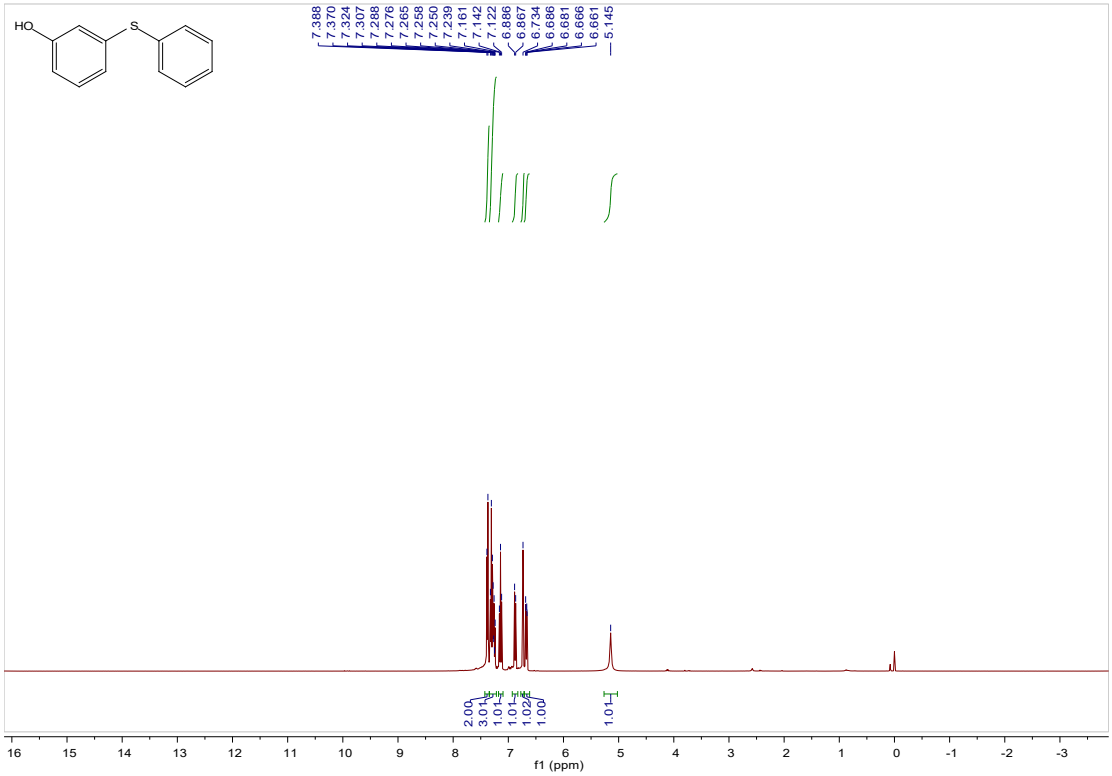
2-((3-Fluorophenyl)thio)phenol (**7e**)

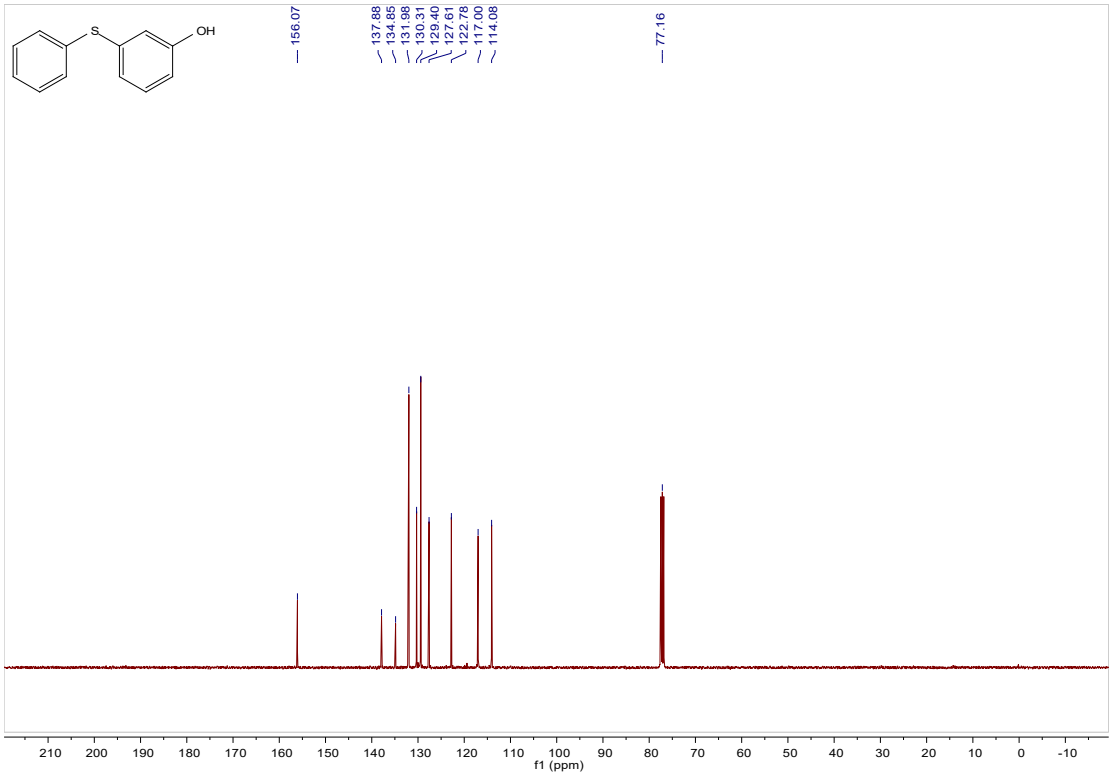





S
F
OH
-111.45
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3-(Phenylthio)phenol (**7f**)





4-(Phenylthio)phenol (**7g**)