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Supplementary Information

Cesium carbonate-promoted synthesis of aryl methyl sulfides using *S*-methylisothiourea sulfate under transition-metal-free conditions

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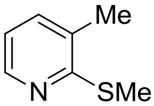
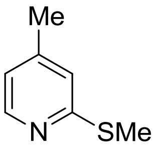
1. Characterization data for compounds 3~5

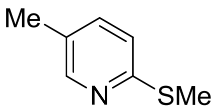
2-(Methylthio)pyridine (3a).[1]
Yield 99% (62 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.33 (d, J = 4.8 Hz, 1H), 7.38−7.32 (m, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.87−6.83 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.7, 149.2, 135.6, 121.2, 118.9, 13.0.



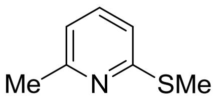
3-Methyl-2-(methylthio)pyridine (3b).[2]
Yield 90% (63 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.31 (dd, J_1 = 4.8 Hz, J_2 = 1.0 Hz, 1H), 7.30−7.27 (m, 1H), 6.92−6.88 (m, 1H), 2.58 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.5, 146.5, 135.9, 130.7, 118.7, 18.4, 12.8.



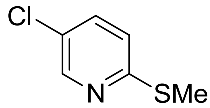
4-Methyl-2-(methylthio)pyridine (3c).[3]
Yield 85% (59 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (d, J = 5.1 Hz, 1H), 7.00 (s, 1H), 6.79 (d, J = 5.0 Hz, 1H), 2.55 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.6, 149.0, 146.9, 121.8, 120.5, 20.8, 13.2.



5-Methyl-2-(methylthio)pyridine (3d).[4]
Yield 80% (56 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 7.30 (dd, J_1 = 8.2 Hz, J_2 = 1.9 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 2.54 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.4, 149.5, 136.7, 128.4, 120.8, 17.7, 13.3.

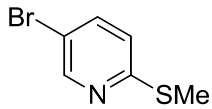


2-Methyl-6-(methylthio)pyridine (3e).[5]
Yield 90% (63 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 2.53 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.0, 158.1, 136.1, 118.4, 117.7, 24.3, 13.3.



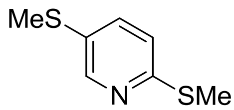
5-Chloro-2-(methylthio)pyridine (3f).[6]

Yield 86% (69 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.39 (s, 1H), 7.44 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 2.54 (S, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.1, 148.0, 135.5, 127.4, 122.0, 13.4.



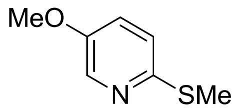
5-Bromo-2-(methylthio)pyridine (3g).[6]

Yield 84% (86 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.47 (d, J = 2.1 Hz, 1H), 7.57−7.52 (m, 1H), 7.07−7.03 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.5, 150.0, 138.0, 122.4, 115.5, 13.3; ESI-MS: *m/z* 203.76 $[M+H]^+$.



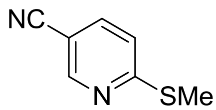
2,5-Bis(methylthio)pyridine (3h).[7]

Yield 80% (69 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.25 (s, 1H), 7.30 (dd, J_1 = 8.3 Hz, J_2 = 2.2 Hz, 1H), 6.97 (d, J = 8.3 Hz 1H), 2.43(s, 3H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.8, 148.2, 135.5, 129.7, 121.1, 16.7, 13.1; ESI-MS: *m/z* 171.80 $[M+H]^+$.



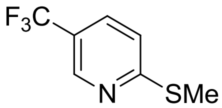
5-Methoxy-2-(methylthio)pyridine (3i, new compound)

Yield 92% (71 mg); yellow oil; IR (KBr) ν 3441, 2965, 1732, 1670, 1594, 1413, 1232, 1019, 764, 487cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 7.10 (s, 2H), 3.81 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.1, 150.4, 136.2, 122.3, 121.8, 55.6, 13.8; HRMS (ESI): *m/z* calcd for C_7H_9NOS: 156.0478, found: 156.0484 $[M+H]^+$.



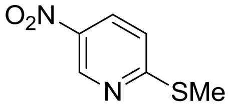
6-(Methylthio)nicotinonitrile (3j).[8]

Yield 98% (74 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.67 (d, J = 1.4 Hz, 1H), 7.66 (dd, J_1 = 8.5 Hz, J_2 = 2.2 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.0, 152.2, 137.5, 121.3, 117.1, 104.4, 13.2.



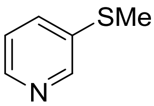
2-(Methylthio)-5-(trifluoromethyl)pyridine (3k).[9]

Yield 98% (95 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.68 (s, 1H), 7.65 (dd, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 2.59 (s, 3H); 13C NMR (75 MHz, CDCl3) δ: 164.9, 146.2 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 132.3 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 269.8 Hz), 121.9 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 121.0, 13.1.



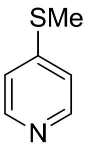
2-(Methylthio)-5-nitropyridine (3l).[10]

Yield 88% (75 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.25 (d, J = 2.2 Hz, 1H), 8.23 (dd, J_1 = 8.9 Hz, J_2 = 2.7 Hz, 1H), 7.30 (dd, J_1 = 8.9 Hz, J_2 = 0.5 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.4, 145.0, 141.0, 130.1, 121.0, 13.5.



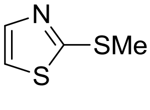
3-(Methylthio)pyridine (3m). [11]

Yield 80% (50 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.52 (s, 1H), 8.38 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.23−7.19 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.9, 146.2, 135.5, 134.3, 123.5, 15.8.



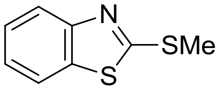
4-(Methylthio)pyridine (3n).[12]

Yield 96% (60 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.32 (s, 2H), 7.01 (d, J = 3.6 Hz, 2H), 2.39, (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.1, 148.9, 119.8, 13.5.

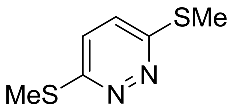


2-(methylthio)thiazole (3o).[13]

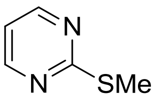
Yield 97% (64 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64 (d, J = 3.2 Hz, 1H), 7.20 (d, J = 3.3 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 142.5, 118.1, 16.5.



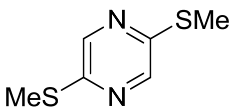
2-(Methylthio)benzo[d]thiazole (3p).[14]
Yield 95% (86 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.85 (d, J = 7.8 Hz, 1H), 7.70 (dd, J_1 = 7.9 Hz, J_2 = 0.5 Hz, 1H), 7.40−7.35 (m, 1H), 7.27−7.21 (m, 1H), 2.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.9, 153.1, 134.9, 125.9, 123.9, 121.2, 120.8, 15.7; ESI-MS: m/z 181.82 $[M+H]^+$.



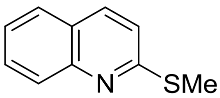
3,6-Bis(methylthio)pyridazine (3q).[15]
Yield 97% (84 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.09 (s, 2H), 2.69 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.9, 125.0, 13.2; ESI-MS: m/z 172.70 $[M+H]^+$.



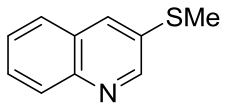
2-(Methylthio)pyrimidine (3r).[14]
Yield 99% (62 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.44 (d, J = 4.8 Hz, 2H), 6.88 (t, J = 4.8 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.7, 156.9, 116.1, 13.9.



2,5-Bis(methylthio)pyrazine (3s).[16]
Yield 97% (84 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.30 (s, 2H), 2.55 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.6, 142.3, 13.2; ESI-MS: m/z 172.70 $[M+H]^+$.

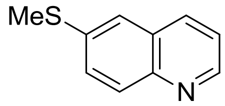


2-(Methylthio)quinoline (3t).[17]
Yield 92% (81 mg); white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.65−7.57 (m, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 8.6 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.8, 148.3, 135.0, 129.5, 127.9, 127.5, 125.8, 125.0, 120.5, 12.8; ESI-MS: m/z 175.85 $[M+H]^+$.



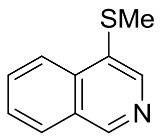
3-(Methylthio)quinoline (3u).[1]

Yield 95% (93 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.84 (J = 2.2 Hz, 1H), 7.70−7.59 (m, 2H), 7.52−7.47 (m, 1H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.7, 145.7, 132.6, 131.1, 129.1, 128.5, 128.2, 127.1, 126.5, 15.6; ESI-MS: m/z 175.83 $[M+H]^+$.



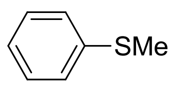
6-(Methylthio)quinoline (3v).[1]

Yield 88% (77 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.77~8.76 (m, 1H), 7.95 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.52 (dd, J_1 = 8.9 Hz, J_2 = 2.1 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.27−7.23 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.9, 145.9, 137.0, 134.2, 129.1, 128.4, 128.3, 121.9, 121.1, 15.1; ESI-MS: m/z 175.86 $[M+H]^+$.



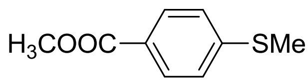
4-(Methylthio)isoquinoline (3w).[18]

Yield 95% (83 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.03 (s, 1H), 8.39 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.9, 140.3, 134.0, 130.2, 130.1, 127.7, 127.3, 123.1, 15.9; ESI-MS: m/z 175.92 $[M+H]^+$.



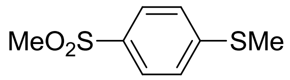
Methyl(phenyl)sulfane (4a).[11]

Yield 82% (51 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28−7.25 (m, 5H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.4, 128.8, 126.6, 125.0, 15.8.

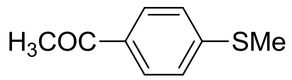


Methyl 4-(methylthio)benzoate (4b).[19]

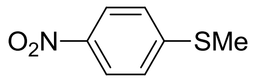
Yield 93% (91 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.8, 145.4, 129.8, 126.2, 124.9, 51.9, 14.8.



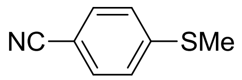
Methyl(4-(methylsulfonyl)phenyl)sulfane (4c).[20]
Yield 97% (98 mg); white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 3.04 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.1, 136.1, 127.5, 125.4, 44.6, 14.7.



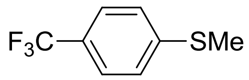
1-(4-(Methylthio)phenyl)ethanone (4d).[21]
Yield 96% (80 mg); white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 2.56 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.1, 145.8, 133.4, 128.6, 124.9, 26.3, 14.7.



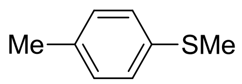
Methyl(4-nitrophenyl)sulfane (4e).[1]
Yield 96% (81 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.9 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.8, 144.6, 124.9, 123.8, 14.7.



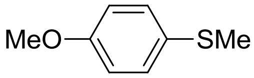
4-(Methylthio)benzonitrile (4f).[1]
Yield 92% (69 mg); white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.9, 131.9, 125.2, 118.7, 107.3, 14.4.



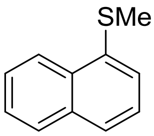
Methyl(4-(trifluoromethyl)phenyl)sulfane (4g).[1]
Yield 97% (93 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.0, 127.1 (q, $^2J_{C-F}$ = 32.5 Hz), 124.3 (q, $^1J_{C-F}$ = 269.7 Hz), 125.9, 125.6 (q, $^3J_{C-F}$ = 3.7 Hz), 15.1.



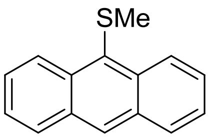
Methyl(p-tolyl)sulfane (4h).[1]
Yield 83% (57 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 135.0, 134.7, 129.6, 127.3, 20.9, 16.5.



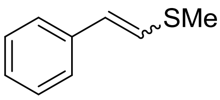
(4-Methoxyphenyl)(methyl)sulfane (4i).[1]
Yield 20% (15 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.2, 130.2, 128.7, 114.6, 55.3, 18.0.



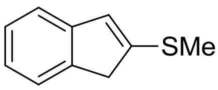
Methyl(naphthalen-1-yl)sulfane (4j).[1]
Yield 80% (70 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.27 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.52−7.42 (m, 2H), 7.38−7.30 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 135.7, 133.5, 131.6, 128.4, 126.1, 126.0, 125.7, 125.6, 124.2, 123.5, 16.1; ESI-MS: m/z 175.85 $[M+H]^+$.



Anthracen-9-yl(methyl)sulfane (4k).[22]
Yield 92% (103 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.92 (dd, J_1 = 8.8 Hz, J_2 = 0.7 Hz, 2H), 8.39 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.59−7.53 (m, 2H), 7.47−7.42 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 133.9, 131.8, 131.0, 129.0, 128.7, 126.8, 126.6, 125.3, 20.0.

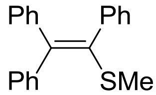


Methyl(styryl)sulfane (4l).[23]
Yield 95% (71 mg); yellow oil; *Z/E* =1:5; *Trans:* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.26 (d, J = 4.3 Hz, 4H), 7.18−7.13 (m, 1H), 6.76 (d, J = 15.4 Hz, 1H), 6.27 (d, J = 15.4 Hz, 1H), 2.32 (s, 3H); *Cis*: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.5 Hz, 3H), 6.40 (d, J = 10.8 Hz, 1H), 6.16 (d, J = 10.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.0, 136.8, 128.9, 128.5, 128.1, 126.5, 125.7, 125.2, 125.1, 124.5, 18.7, 14.6.

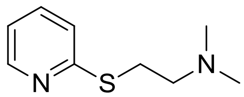


(1*H*-Inden-2-yl)(methyl)sulfane (4m).[24]

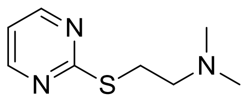
Yield 95% (77 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 6.7 Hz, 1H), 7.27−7.16 (m, 2H), 7.07−6.99 (m, 1H), 6.36 (s, 1H), 3.43 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.2, 145.0, 142.0, 126.4, 123.2, 123.0, 122.8, 118.8, 41.6, 15.3.



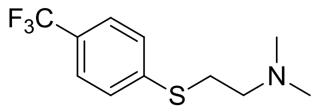
Methyl(1,2,2-triphenylvinyl)sulfane (4n).[25]
Yield 90% (136 mg); white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39−7.15 (m, 10H), 7.00−6.90 (m, 5H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.5, 142.5, 140.9, 138.7, 137.0, 130.7, 130.4, 129.8, 128.2, 128.0, 127.5, 127.1, 126.9, 126.1, 16.1.



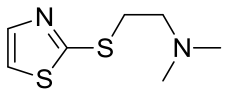
N,N-dimethyl-2-(pyridin-2-ylthio)ethanamine (5a).[26]
Yield 80% (73 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93−7.85 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.66−7.61 (m, 1H), 7.44−7.39 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 3.49(t, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.9, 148.3, 135.2, 129.5, 128.0, 127.6, 126.0, 125.2, 121.1, 58.7, 45.3, 27.2; ESI-MS: *m/z* 183.07 $[M+H]^+$.



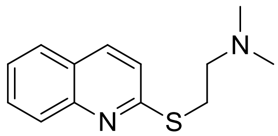
N,N-dimethyl-2-(pyrimidin-2-ylthio)ethanamine (5b).[27]
Yield 90% (82 mg); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 4.8 Hz, 2H), 6.96 (t, *J* = 4.8 Hz, 1H), 3.28 (t, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.3, 157.1, 116.3, 58.4, 45.1, 28.4; ESI-MS: *m/z* 184.08 $[M+H]^+$.



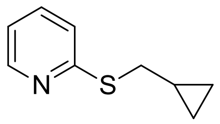
***N,N*-Dimethyl-2-((4-(trifluoromethyl)phenyl)thio)ethanamine (5c, new compound)**
Yield 88% (110 mg); yellow oil; IR (KBr) ν 3440, 2923, 1733, 1631, 1594, 1400, 1275, 1175, 1025, 747 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.3, 127.2, 125.6 (q, $^3J_{C-F}$ = 3.6 Hz), 124.1 (q, $^1J_{C-F}$ = 270.0 Hz), 58.1, 45.3, 30.5; HRMS (ESI): *m/z* calcd for $C_{11}H_{14}F_3NS$: 250.0872, found: 250.0874 $[M+H]^+$.



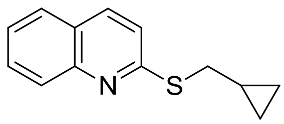
N,N-dimethyl-2-(thiazol-2-ylthio)ethanamine (5d, new compound)
Yield 85% (80 mg); yellow oil; IR (KBr) ν 3433, 3193, 2924, 2852, 1631, 1597, 1399, 1036, 750, 488 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 3.3 Hz, 1H), 7.20 (d, *J* = 3.4 Hz, 1H), 3.36 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 142.5, 118.6, 58.1, 45.1, 32.2; HRMS (ESI): *m/z* calcd for $C_7H_{12}N_2S_2$: 189.0515, found: 189.0521 $[M+H]^+$.



***N,N*-Dimethyl-2-(quinolin-2-ylthio)ethanamine (5e, new compound)**
Yield 92% (107 mg); yellow oil; IR (KBr) ν 3434, 3086, 2923, 1720, 1677, 1597, 1474, 1398, 1278, 749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93−7.85 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.66−7.61 (m, 1H), 7.44−7.39 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 3.49 (t, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.9, 148.3, 135.2, 129.5, 128.0, 127.6, 126.0, 125.2, 121.1, 58.7, 45.3, 27.2; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}N_2S$: 233.1107, found: 233.1111 $[M+H]^+$.



2-((Cyclopropylmethyl)thio)pyridine (5f, new compound)
Yield 81% (67 mg); yellow oil; IR (KBr) ν 3423, 2975, 2924, 1632, 1413, 1048, 756, 723, 490, 424 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.41 (dd, J_1 = 4.9 Hz, J_2 = 0.8 Hz, 1H), 7.49−7.43 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.98−6.94 (m, 1H), 3.13 (d, *J* = 7.1 Hz, 2H), 1.19−1.10 (m, 1H), 0.60−0.57 (m, 2H), 0.33−0.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.6, 149.3, 135.8, 122.2, 119.2, 35.8, 10.6, 5.7. HRMS (ESI): *m/z* calcd for $C_9H_{11}NS$: 166.0685, found: 166.0687 $[M+H]^+$.



2-((Cyclopropylmethyl)thio)quinoline (5g, new compound)
Yield 95% (102 mg); yellow oil; IR (KBr) ν 3442, 3077, 2922, 1631, 1593, 1418, 1088, 814, 747, 601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.69−7.59 (m, 2H), 7.42−7.36 (m, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 3.30 (d, *J* = 7.2 Hz, 2H), 1.29−1.19 (m , 1H), 0.63−0.57 (m , 2H), 0.40−0.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.6, 148.2, 135.1, 129.5, 127.5, 125.8, 125.0, 120.9, 35.4, 10.7, 5.7; ESI-MS: *m/z* 215.92 $[M+H]^+$.

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2. ^{1}H and ^{13}C NMR spectra of compounds 3~5

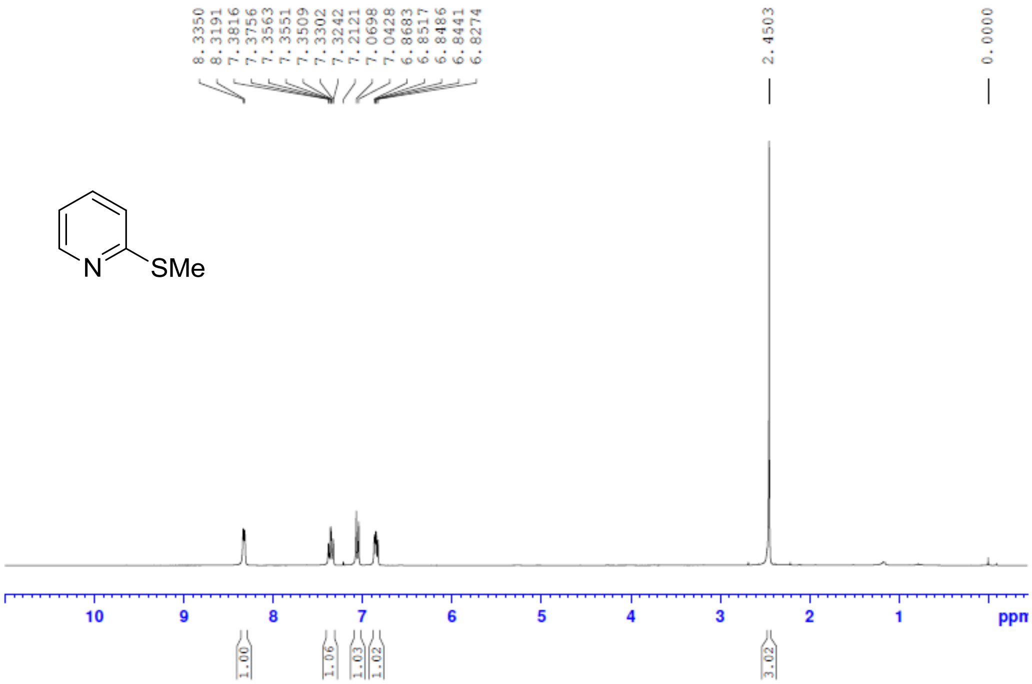

Figure 1 ^{1}H NMR spectrum of compound **3a** (300 MHz, $CDCl_3$)

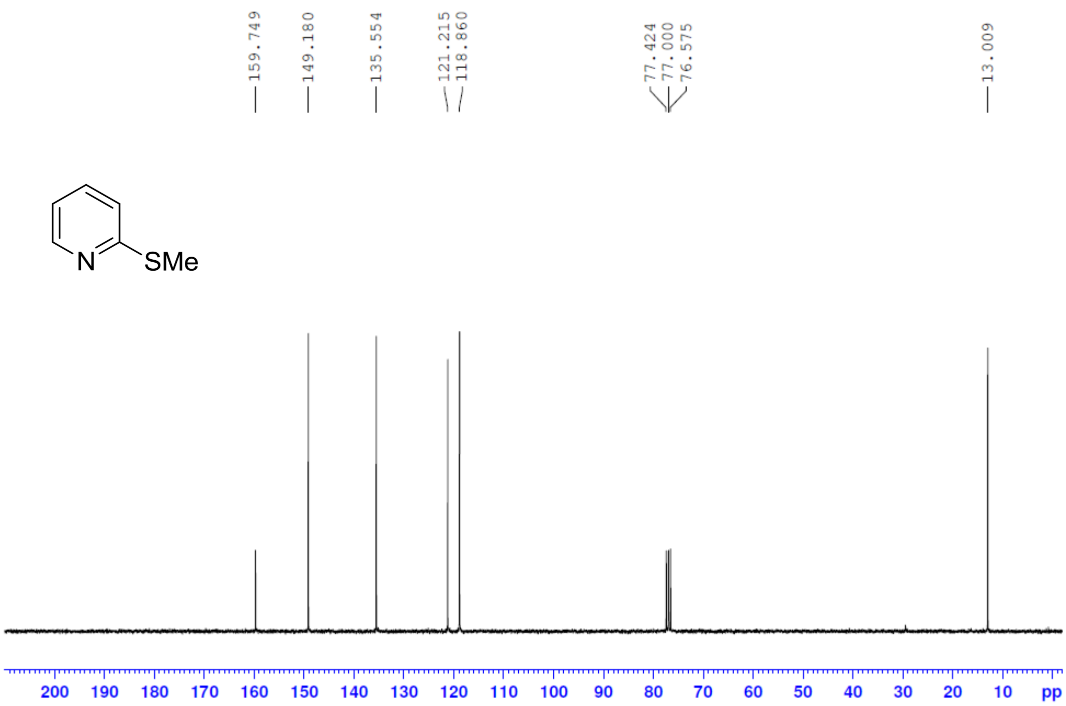

Figure 2 ^{13}C NMR spectrum of compound **3a** (75 MHz, $CDCl_3$)

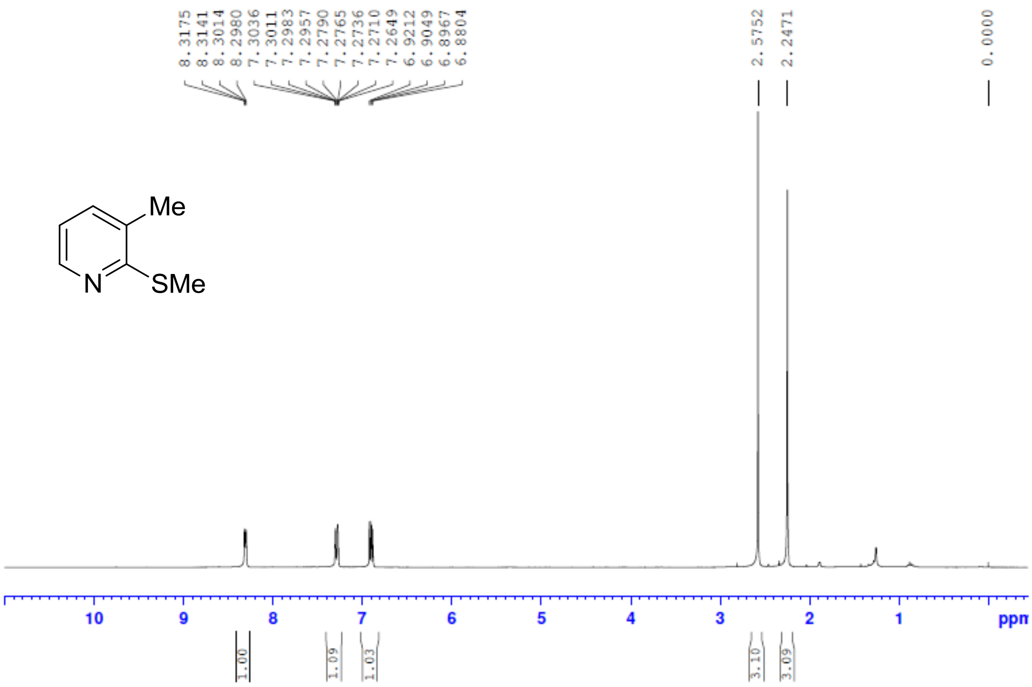

Figure 3 ^{1}H NMR spectrum of compound **3b** (300 MHz, $CDCl_3$)

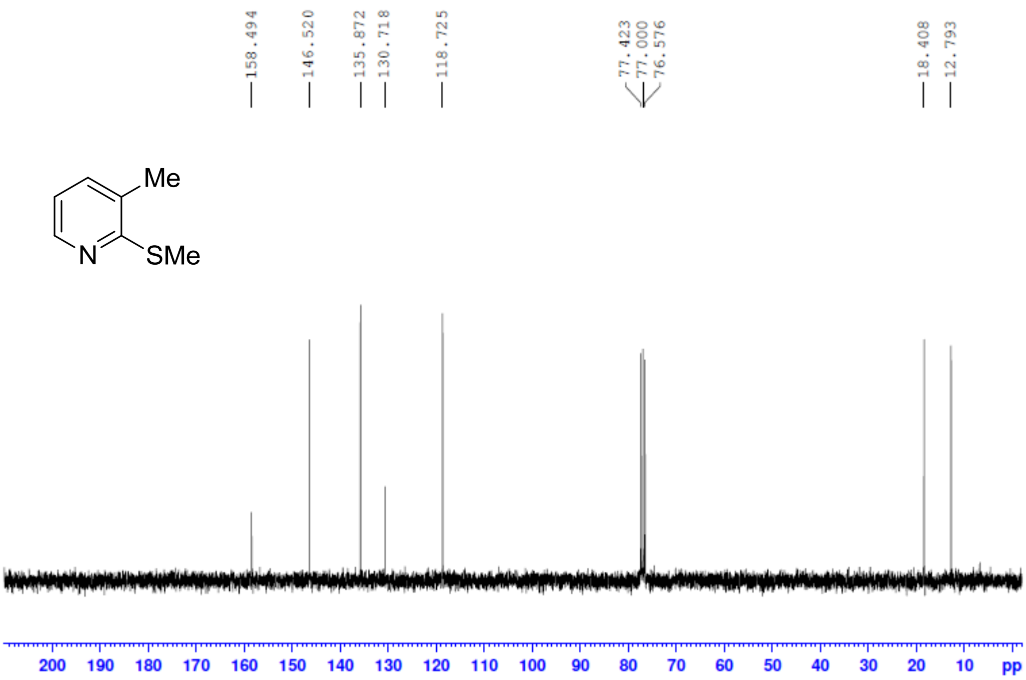

Figure 4 ^{13}C NMR spectrum of compound **3b** (75 MHz, $CDCl_3$)

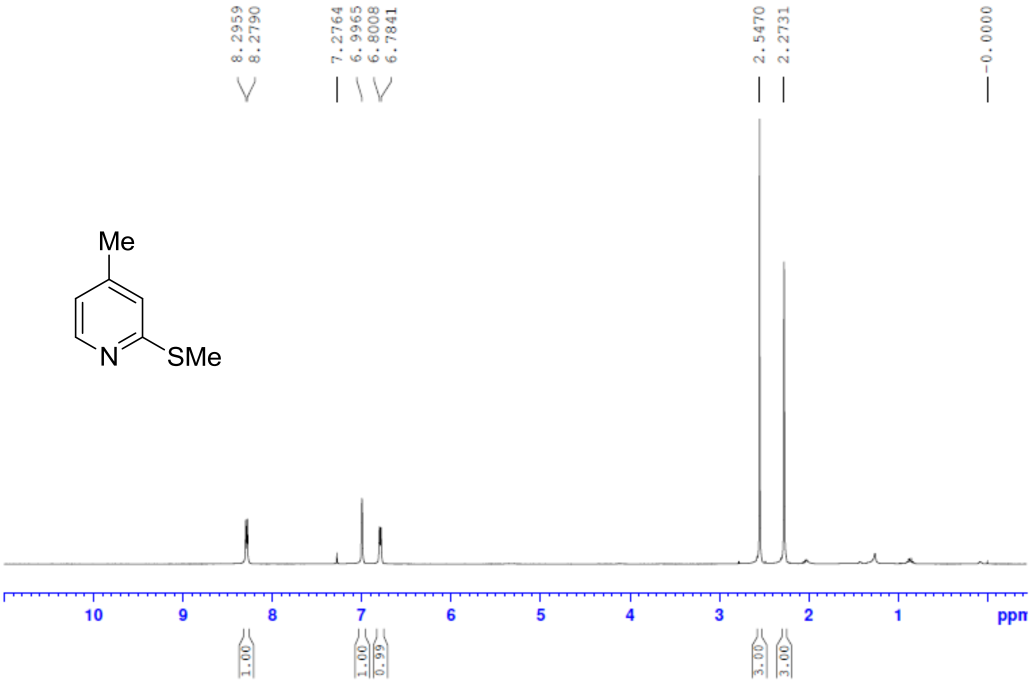

Figure 5 ^{1}H NMR spectrum of compound **3c** (300 MHz, $CDCl_3$)

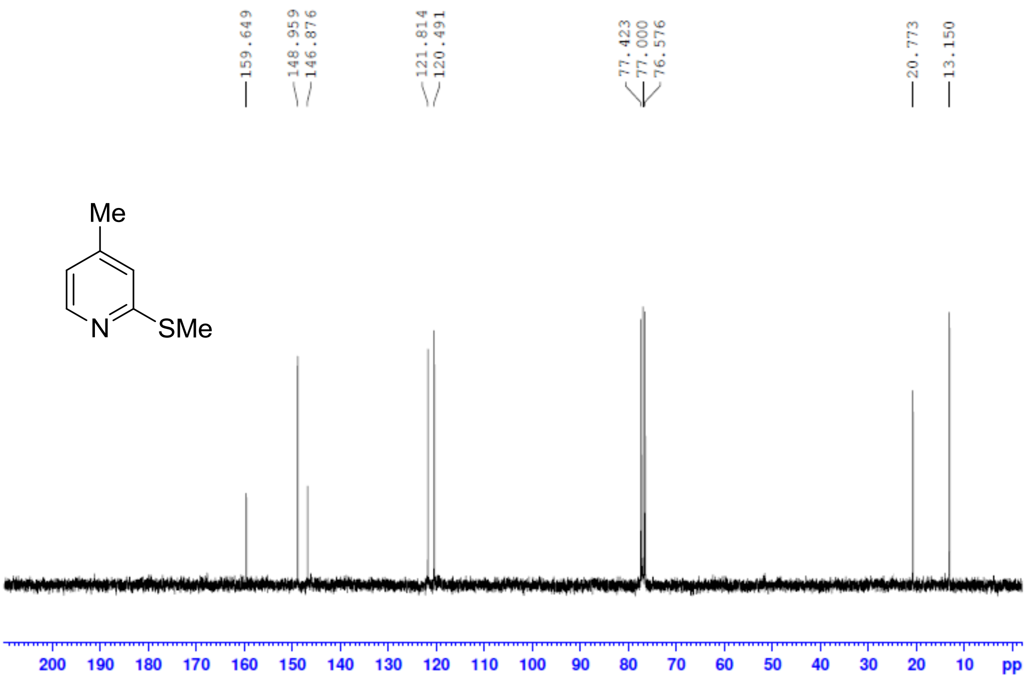

Figure 6 ^{13}C NMR spectrum of compound **3c** (75 MHz, $CDCl_3$)

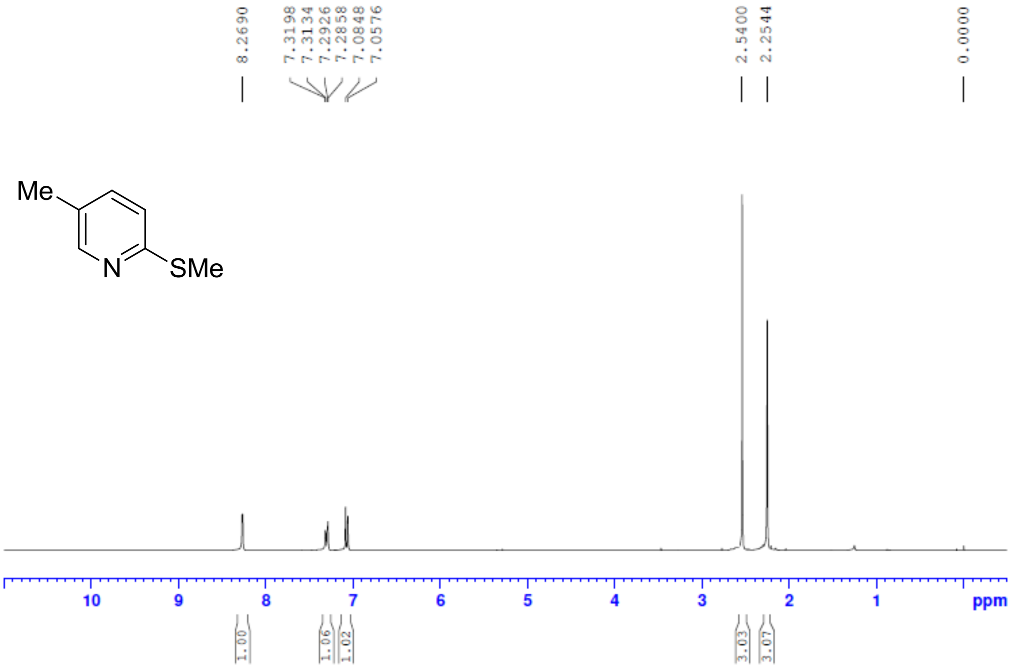

Figure 7 ^{1}H NMR spectrum of compound **3d** (300 MHz, $CDCl_3$)

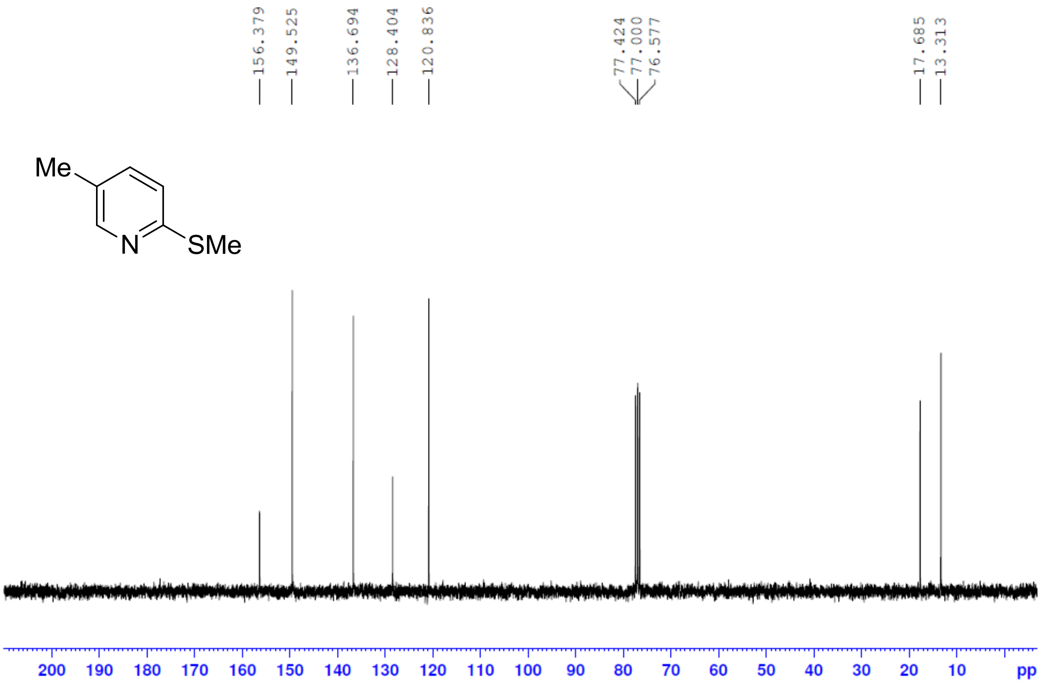

Figure 8 ^{13}C NMR spectrum of compound **3d** (75 MHz, $CDCl_3$)

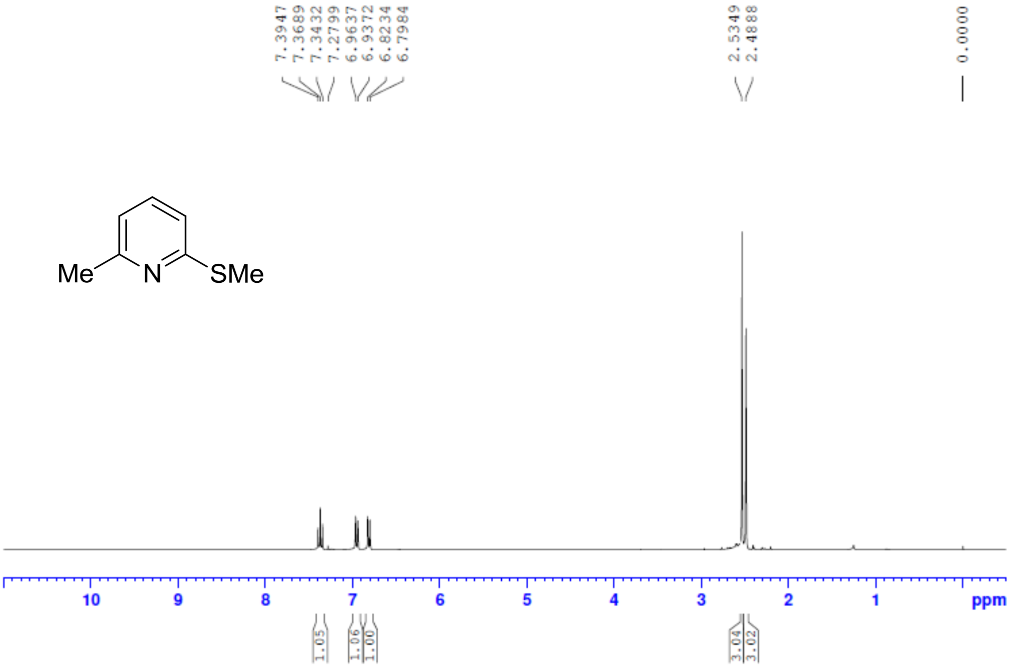

Figure 9 ^{1}H NMR spectrum of compound **3e** (300 MHz, $CDCl_3$)

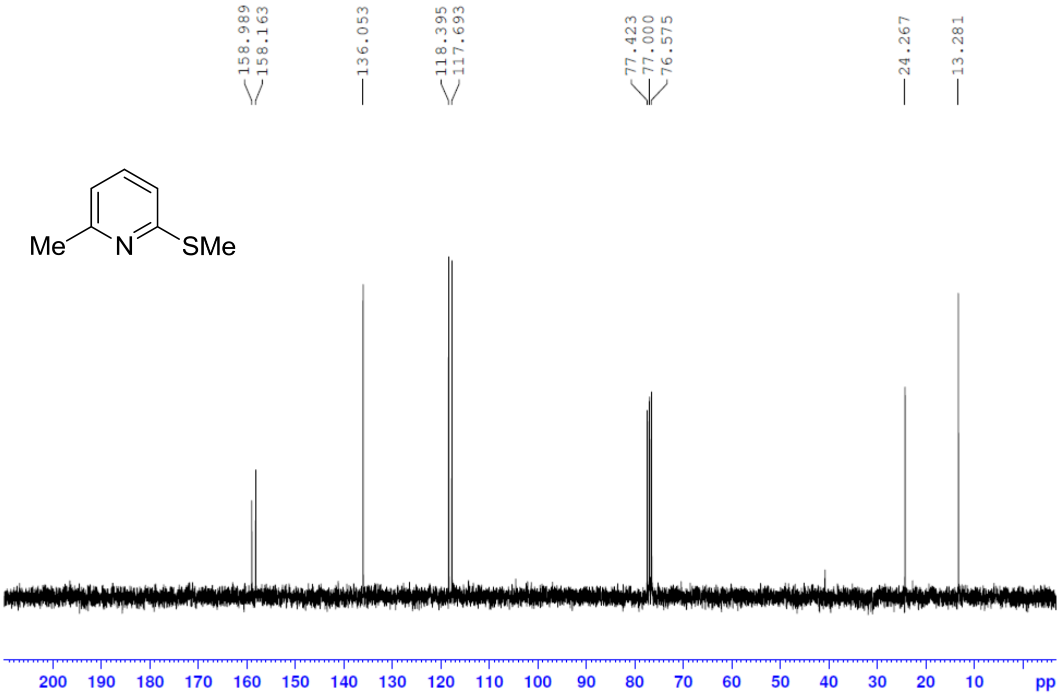

Figure 10 ^{13}C NMR spectrum of compound **3e** (75 MHz, $CDCl_3$)

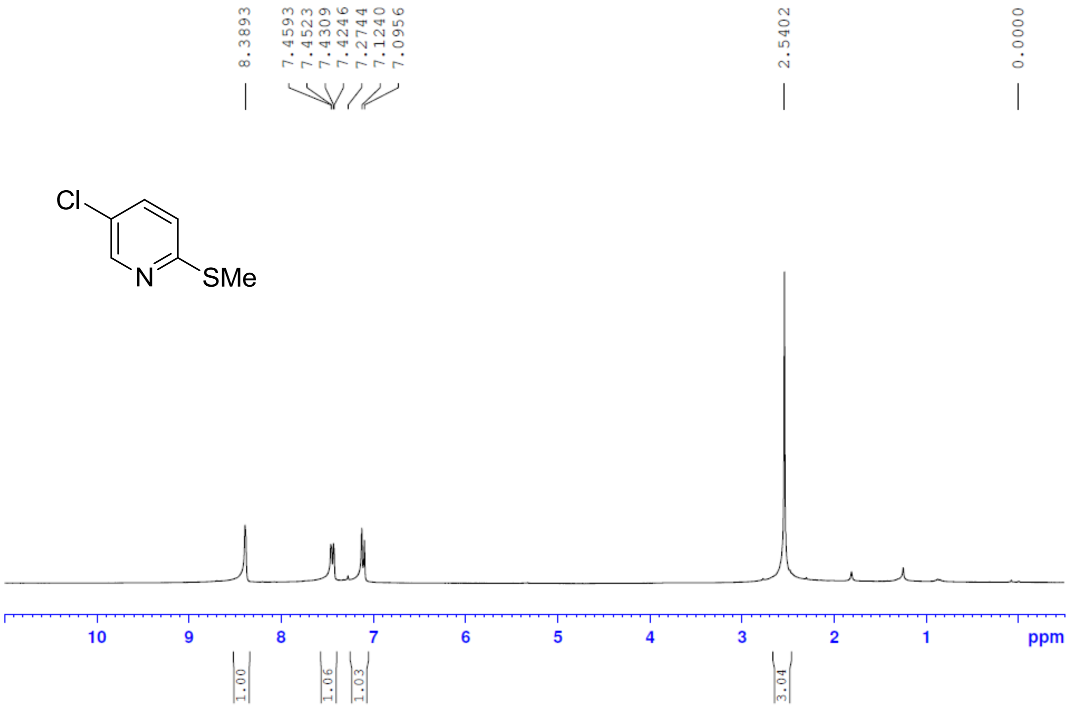

Figure 11 ^{1}H NMR spectrum of compound **3f** (300 MHz, $CDCl_3$)

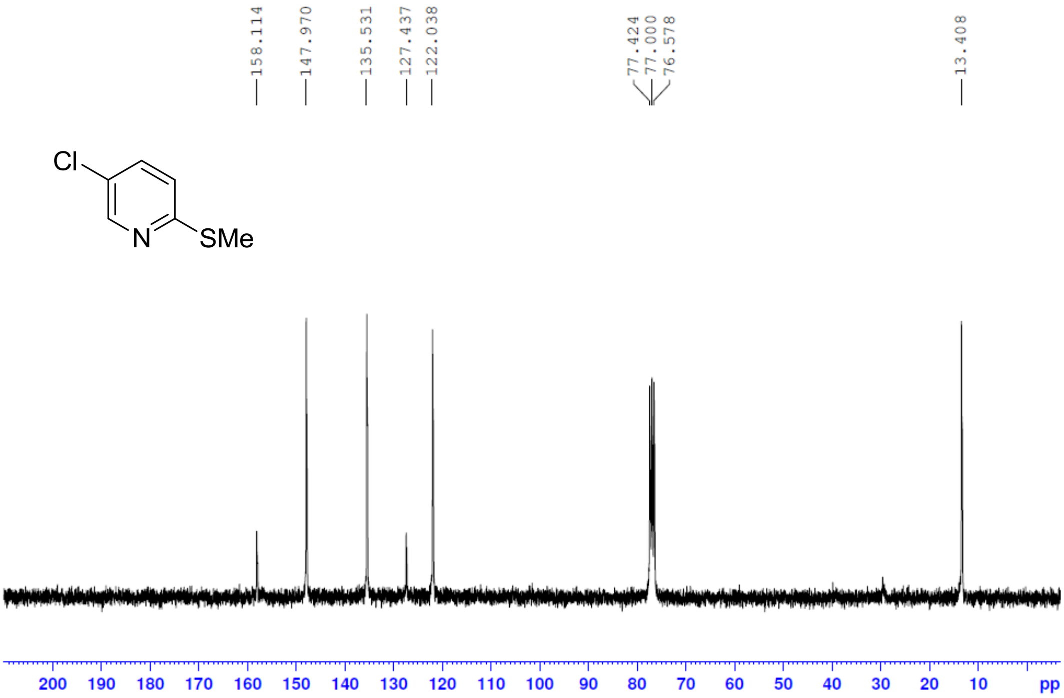

Figure 12 ^{13}C NMR spectrum of compound **3f** (75 MHz, $CDCl_3$)

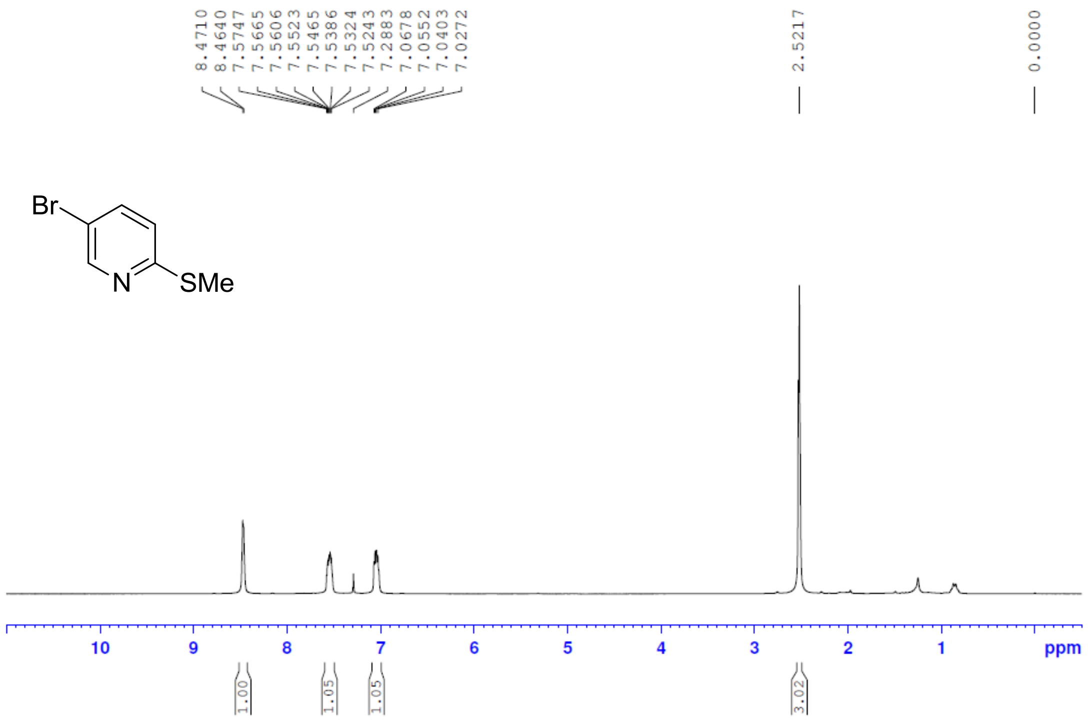

Figure 13 ^{1}H NMR spectrum of compound **3g** (300 MHz, $CDCl_3$)

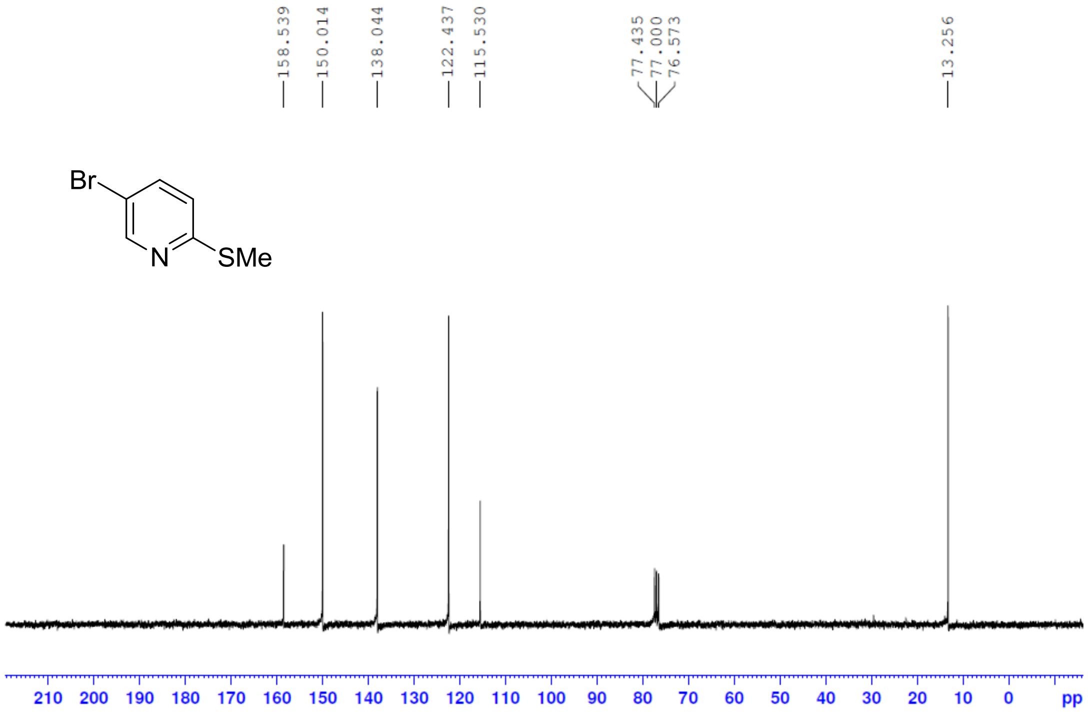

Figure 14 ^{13}C NMR spectrum of compound **3g** (75 MHz, $CDCl_3$)

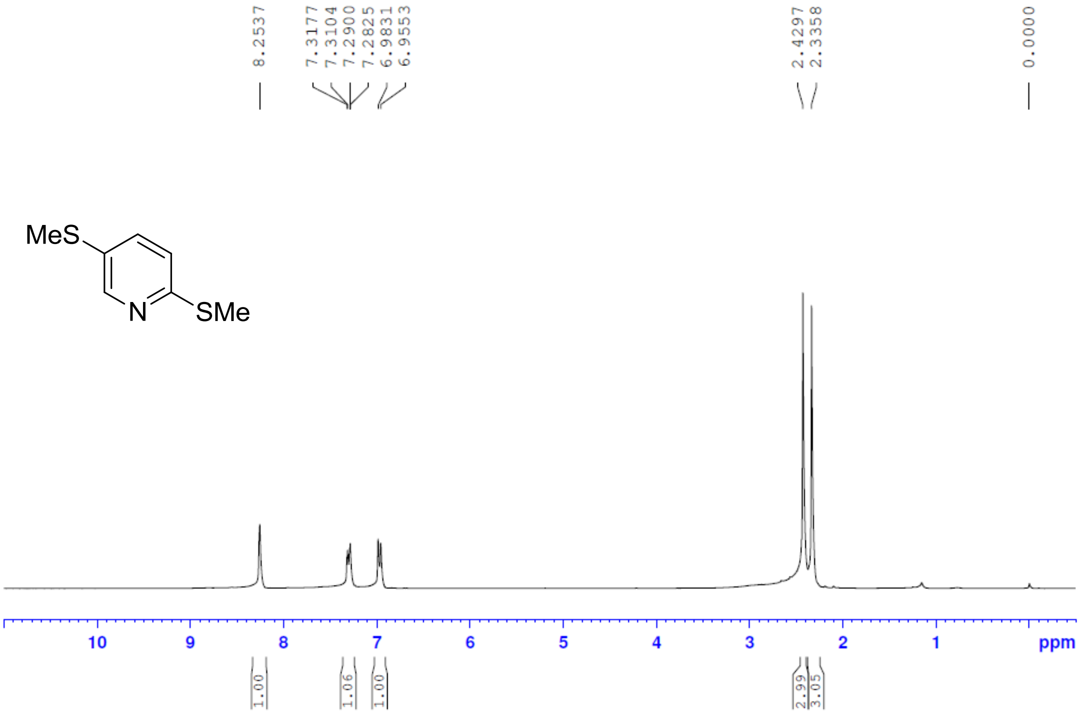

Figure 15 ^{1}H NMR spectrum of compound **3h** (300 MHz, $CDCl_3$)

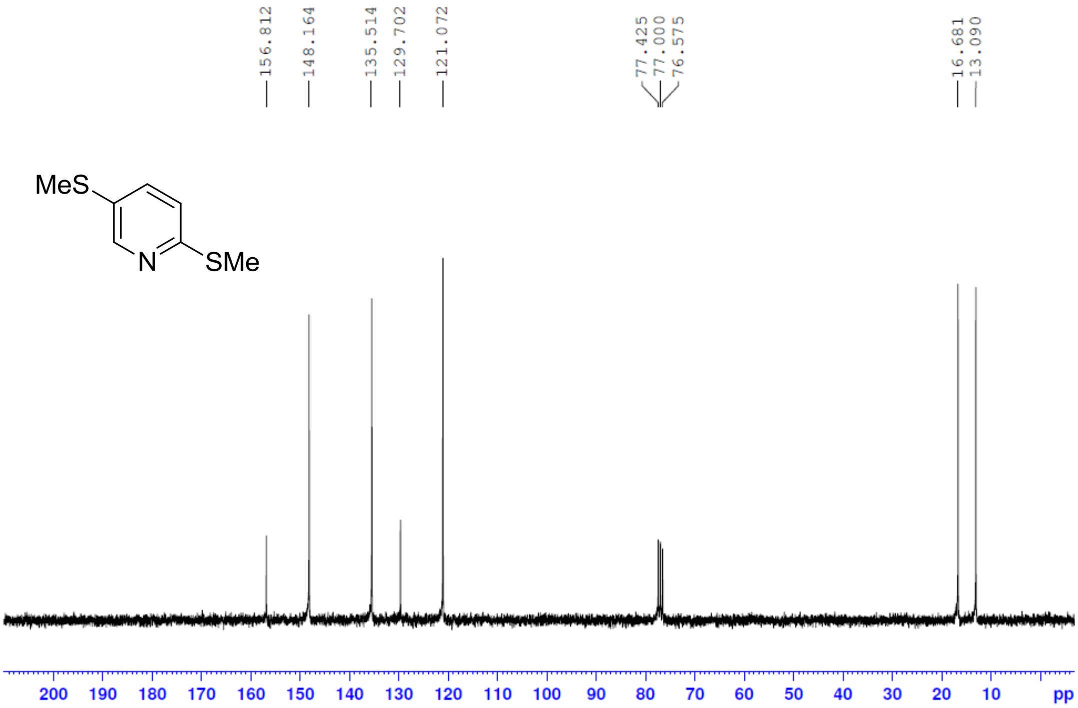

Figure 16 ^{13}C NMR spectrum of compound **3h** (75 MHz, $CDCl_3$)

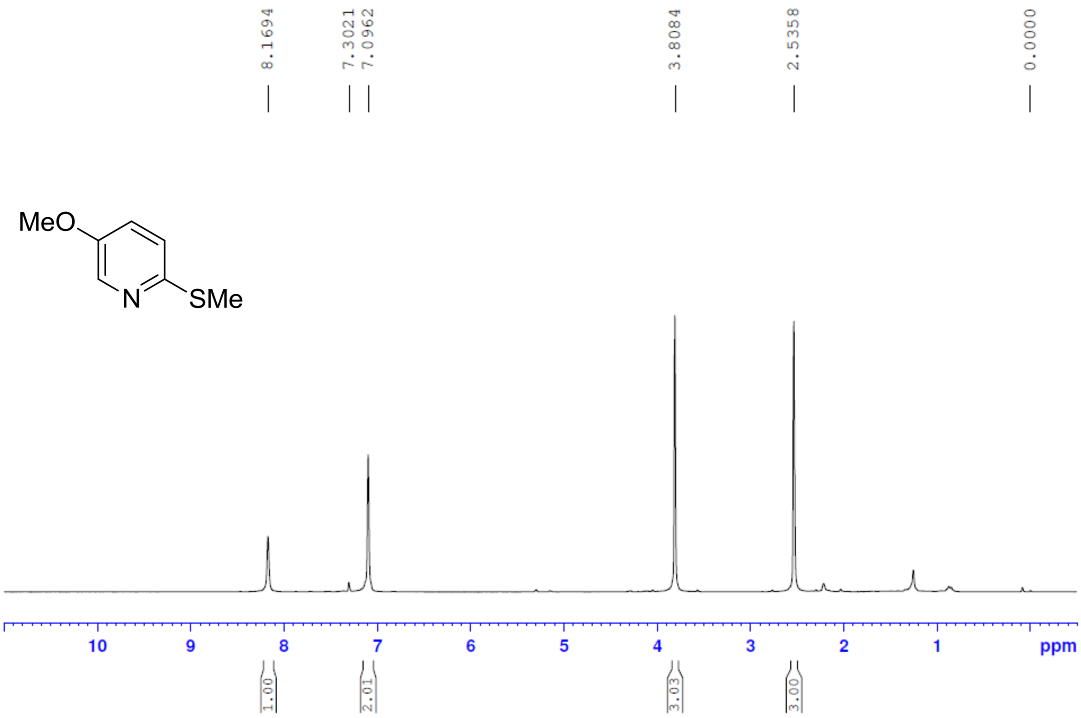

Figure 17 ^{1}H NMR spectrum of compound **3i** (300 MHz, $CDCl_3$)

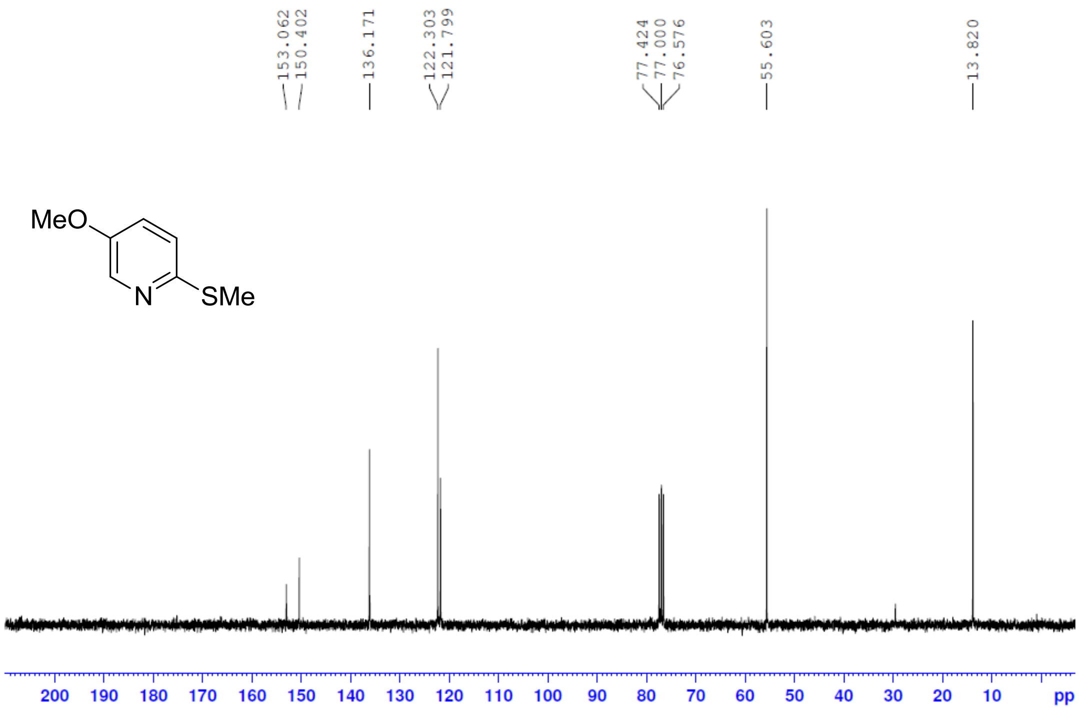

Figure 18 ^{13}C NMR spectrum of compound **3i** (75 MHz, $CDCl_3$)

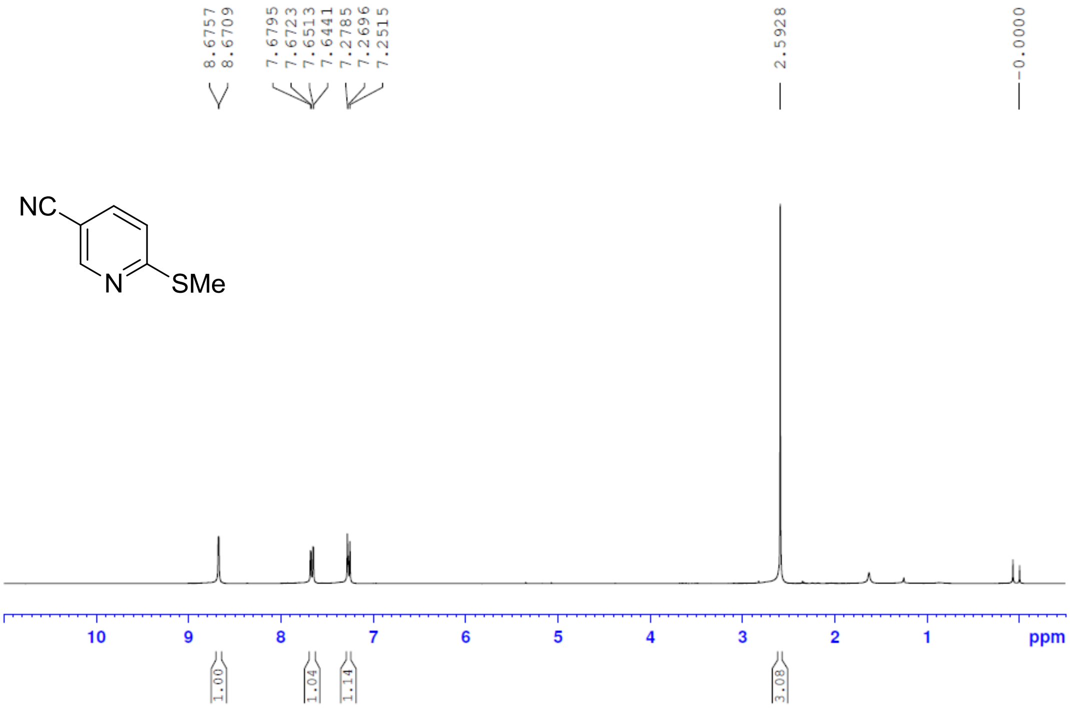

Figure 19 ^{1}H NMR spectrum of compound **3j** (300 MHz, $CDCl_3$)

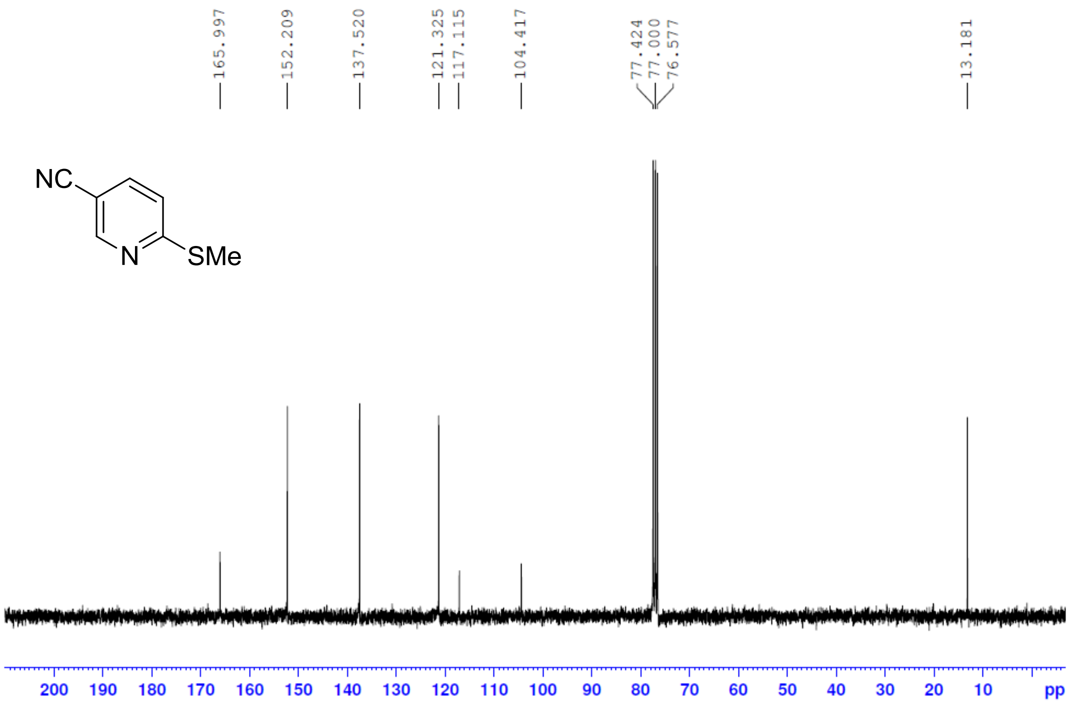

Figure 20 ^{13}C NMR spectrum of compound **3j** (75 MHz, $CDCl_3$)

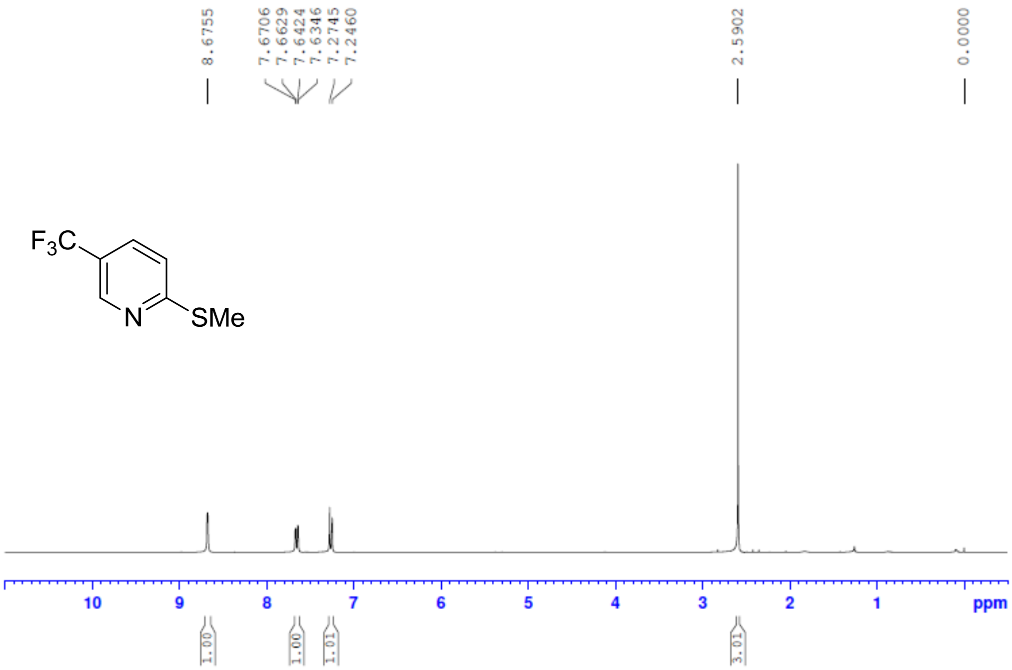

Figure 21 ^{1}H NMR spectrum of compound **3k** (300 MHz, $CDCl_3$)

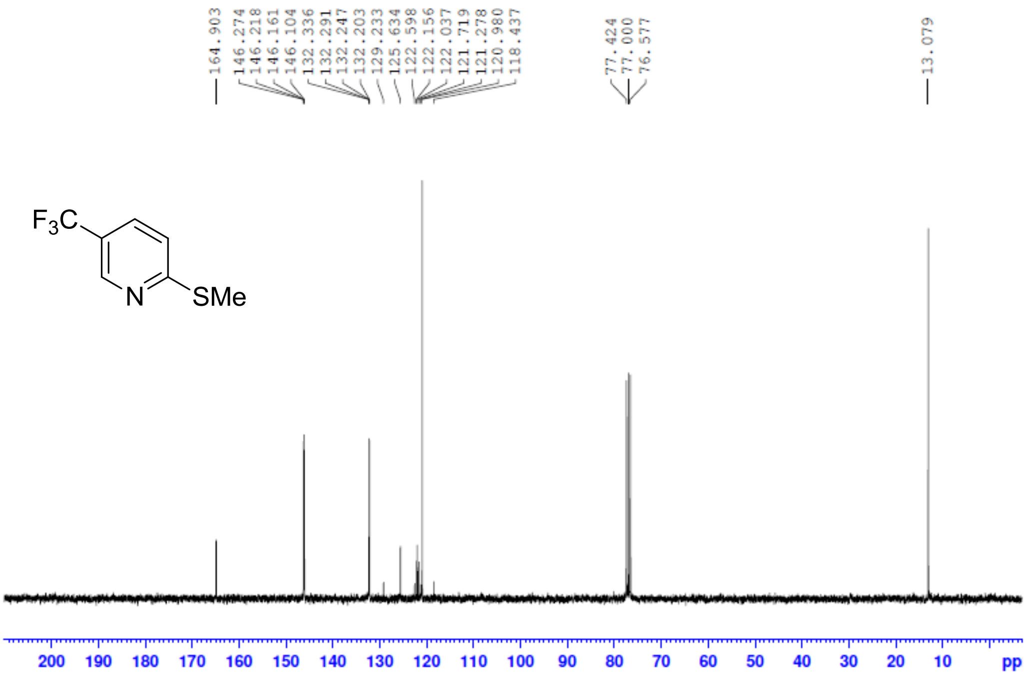

Figure 22 ^{13}C NMR spectrum of compound **3k** (75 MHz, $CDCl_3$)

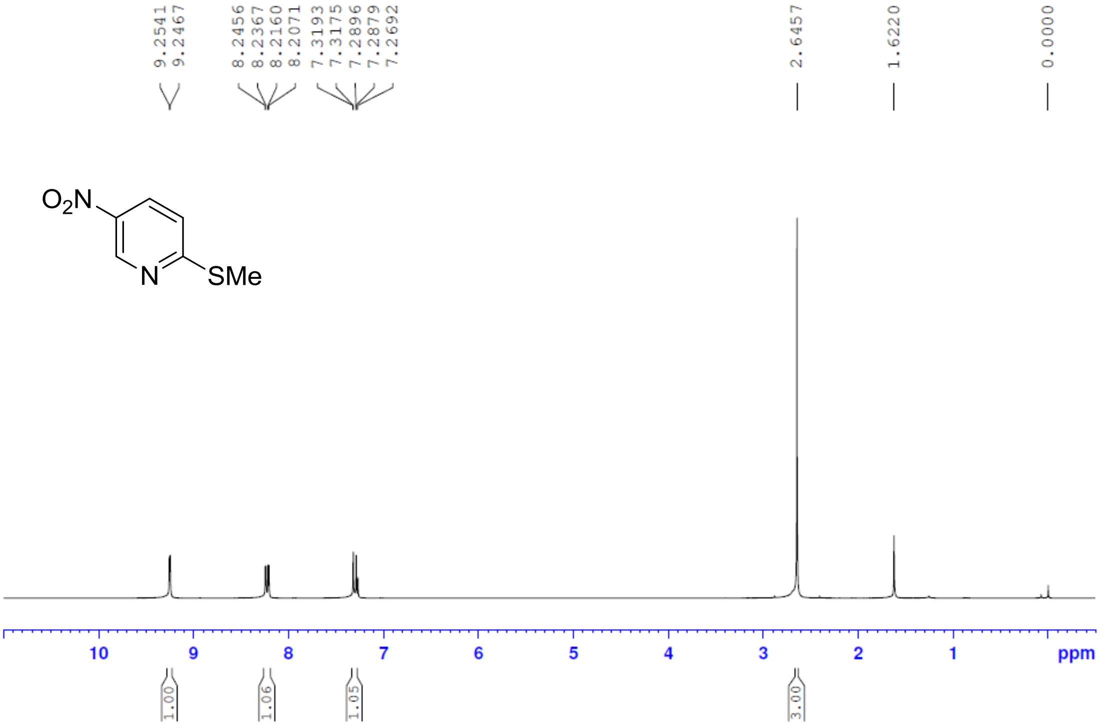

Figure 23 ^{1}H NMR spectrum of compound **3l** (300 MHz, $CDCl_3$)

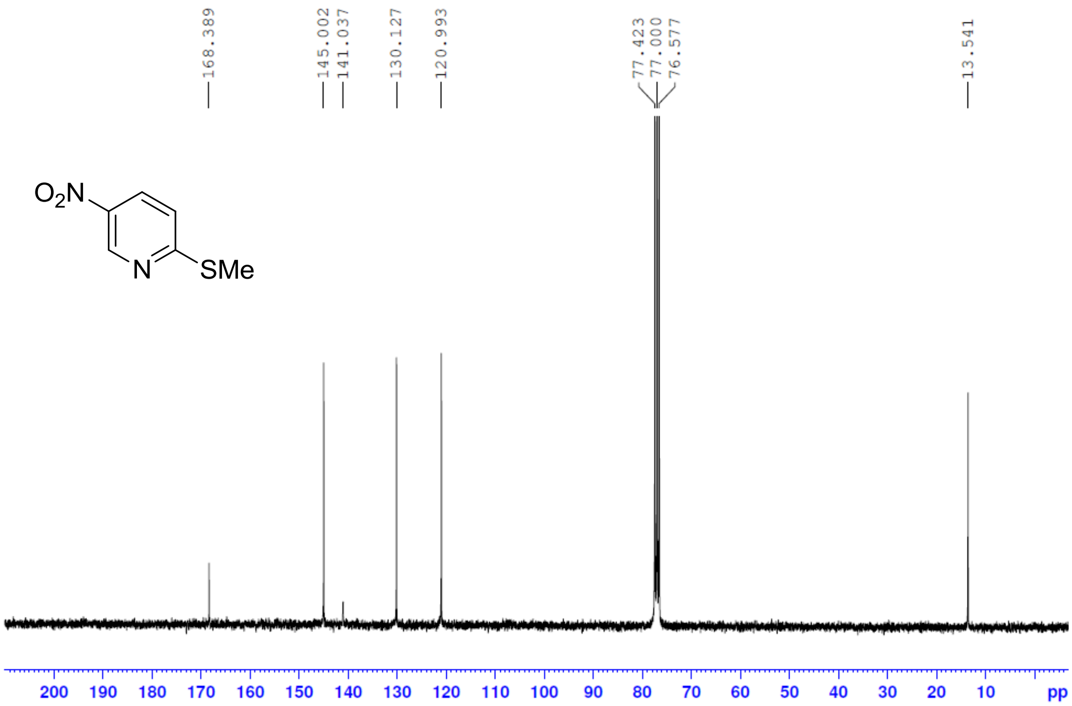

Figure 24 ^{13}C NMR spectrum of compound **3l** (75 MHz, $CDCl_3$)

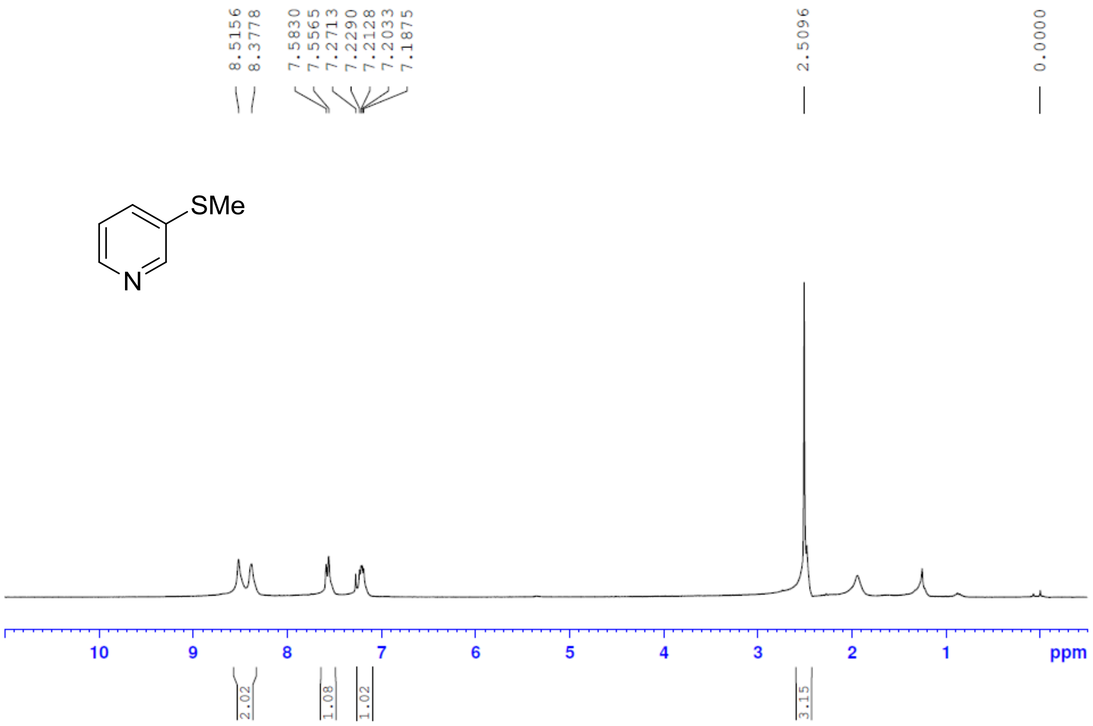

Figure 25 ^{1}H NMR spectrum of compound **3m** (300 MHz, $CDCl_3$)

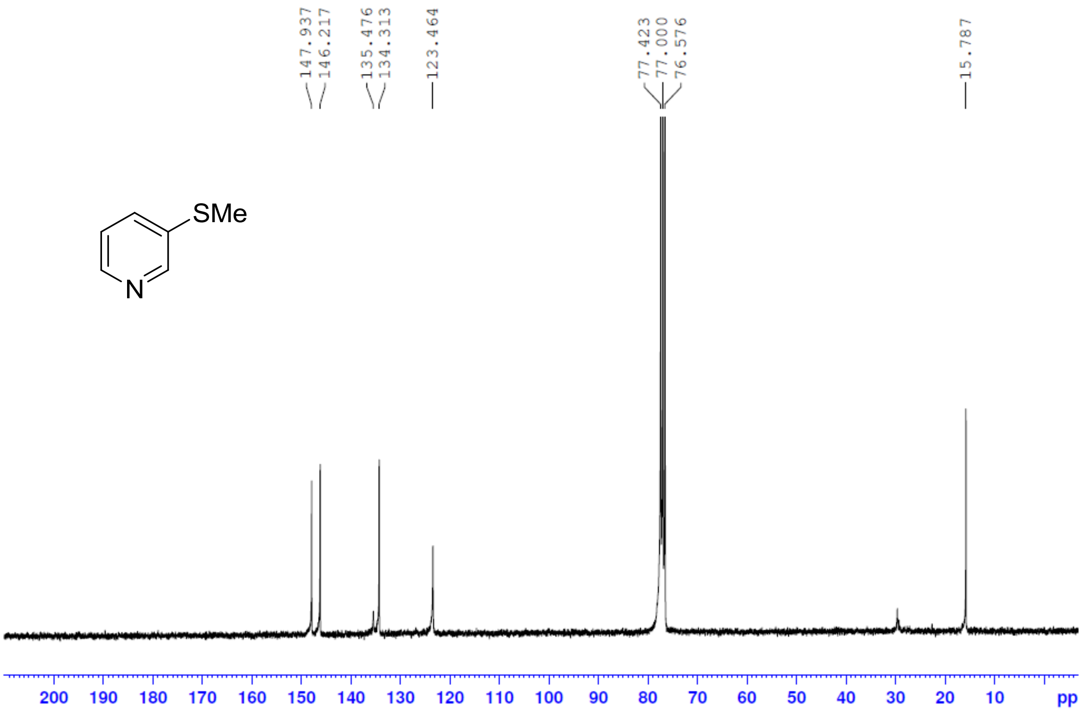

Figure 26 ^{13}C NMR spectrum of compound **3m** (75 MHz, $CDCl_3$)

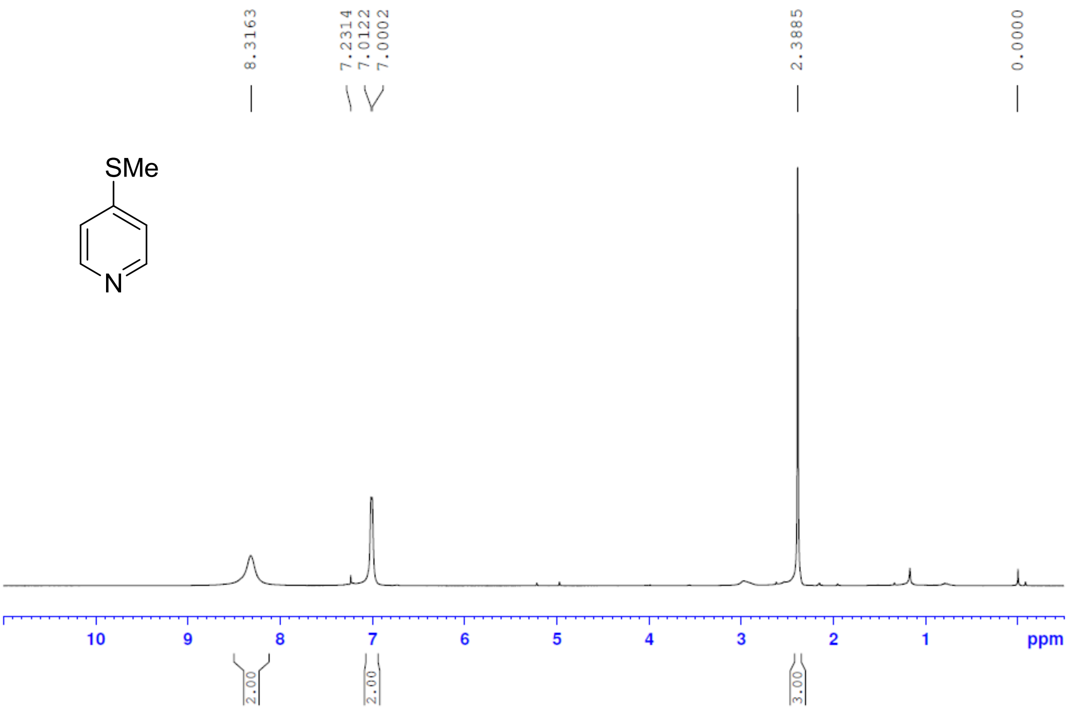

Figure 27 ^{1}H NMR spectrum of compound **3n** (300 MHz, $CDCl_3$)

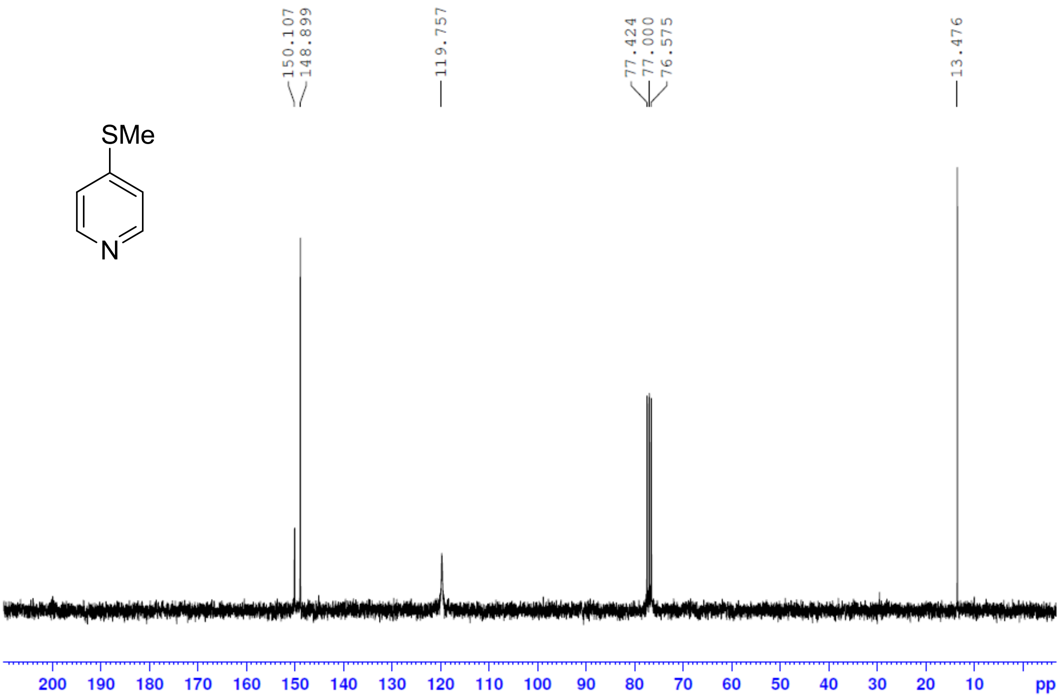

Figure 28 ^{13}C NMR spectrum of compound **3n** (75 MHz, $CDCl_3$)

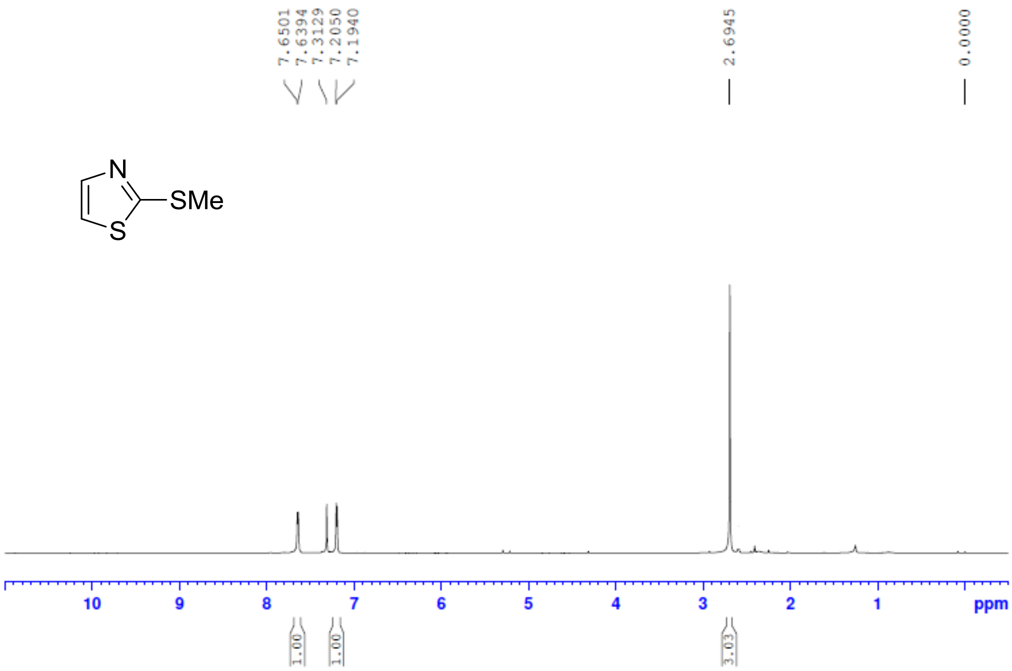

Figure 29 ^{1}H NMR spectrum of compound **3o** (300 MHz, $CDCl_3$)

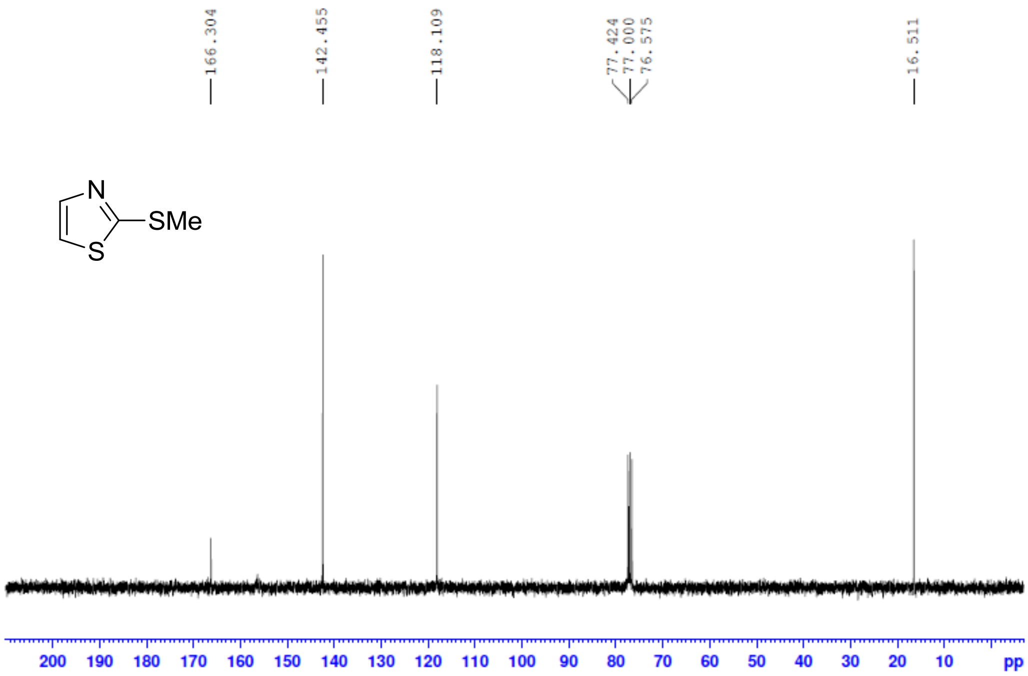

Figure 30 ^{13}C NMR spectrum of compound **3o** (75 MHz, $CDCl_3$)

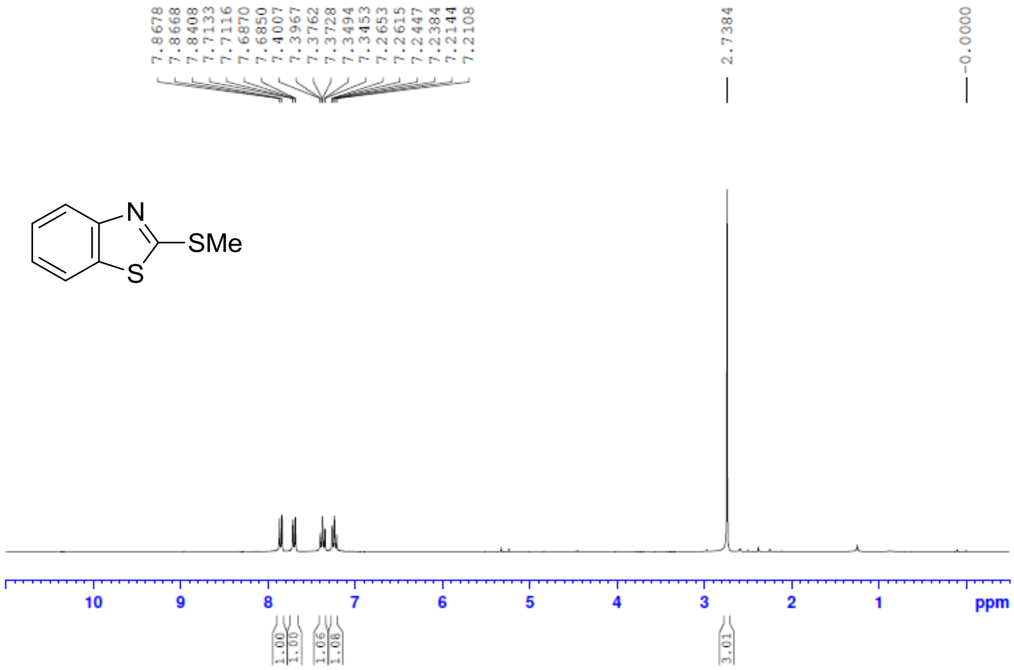

Figure 31 ^{1}H NMR spectrum of compound **3p** (300 MHz, $CDCl_3$)

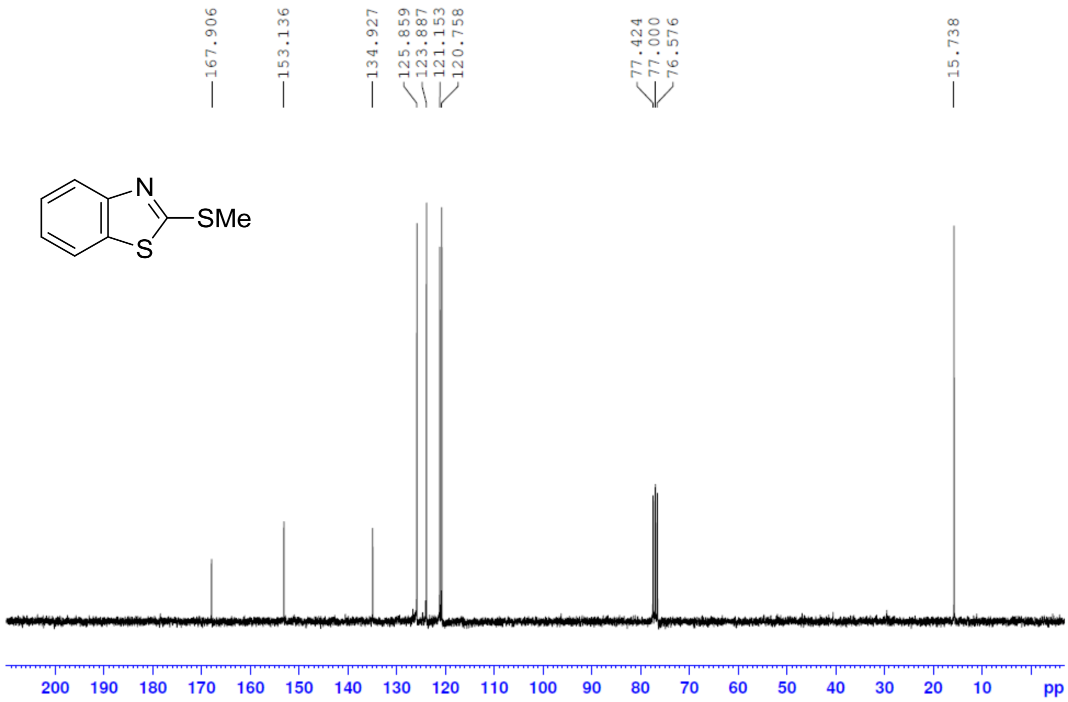

Figure 32 ^{13}C NMR spectrum of compound **3p** (75 MHz, $CDCl_3$)

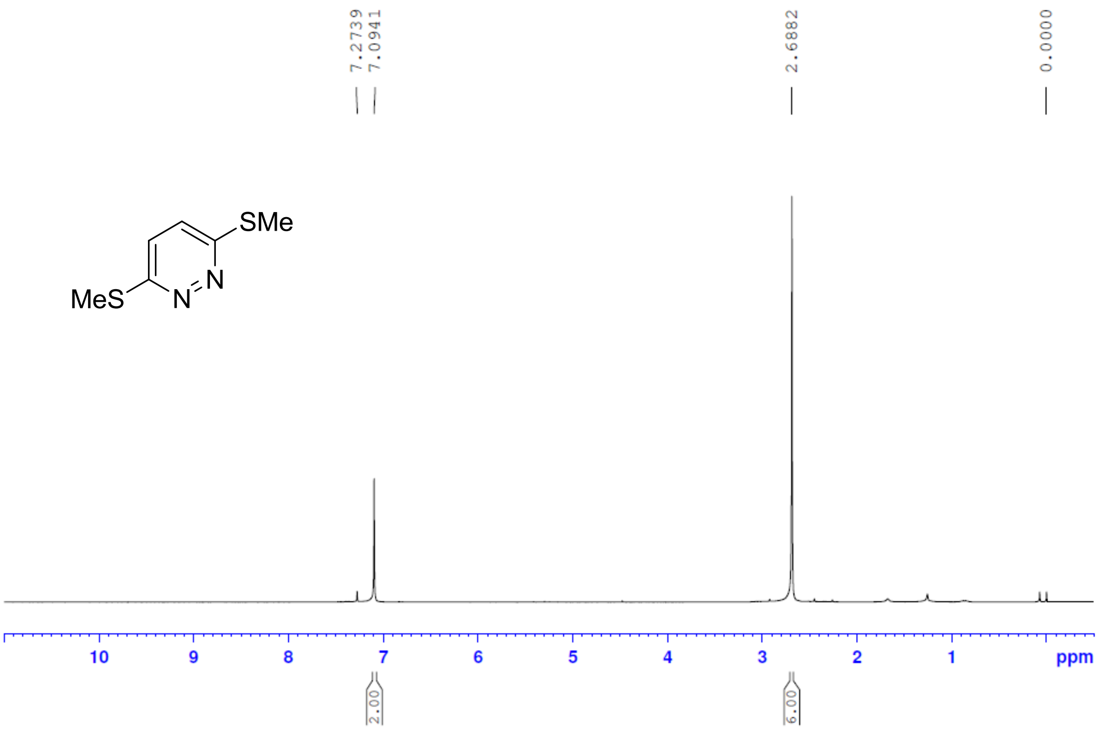

Figure 33 ^{1}H NMR spectrum of compound **3q** (300 MHz, $CDCl_3$)

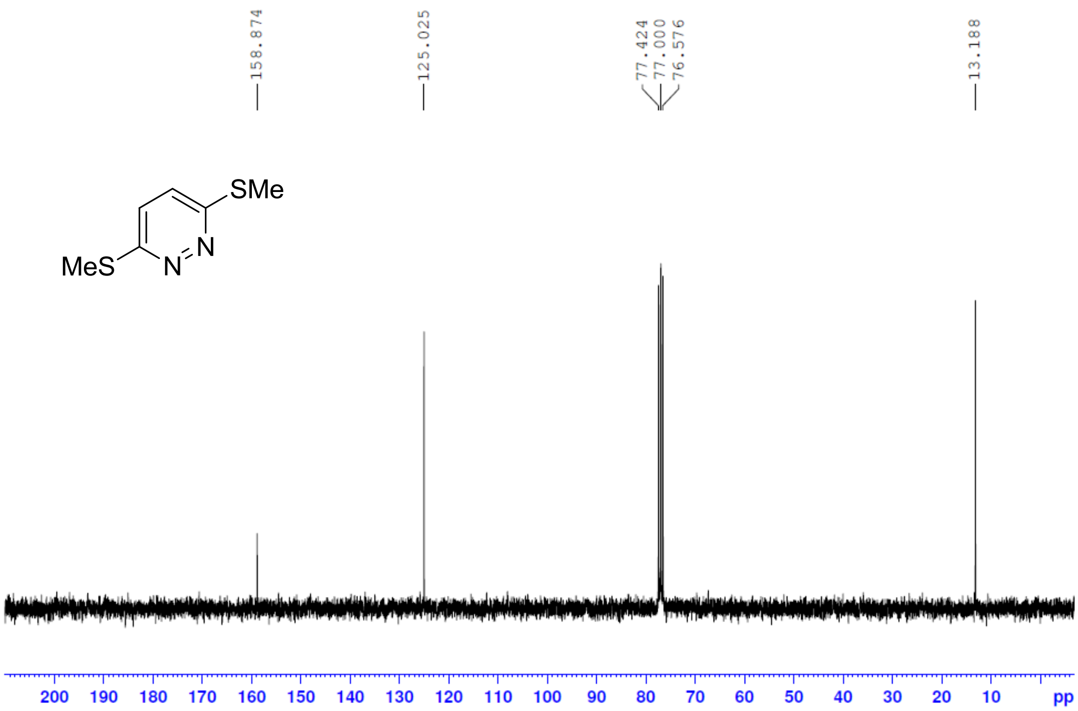

Figure 34 ^{13}C NMR spectrum of compound **3q** (75 MHz, $CDCl_3$)

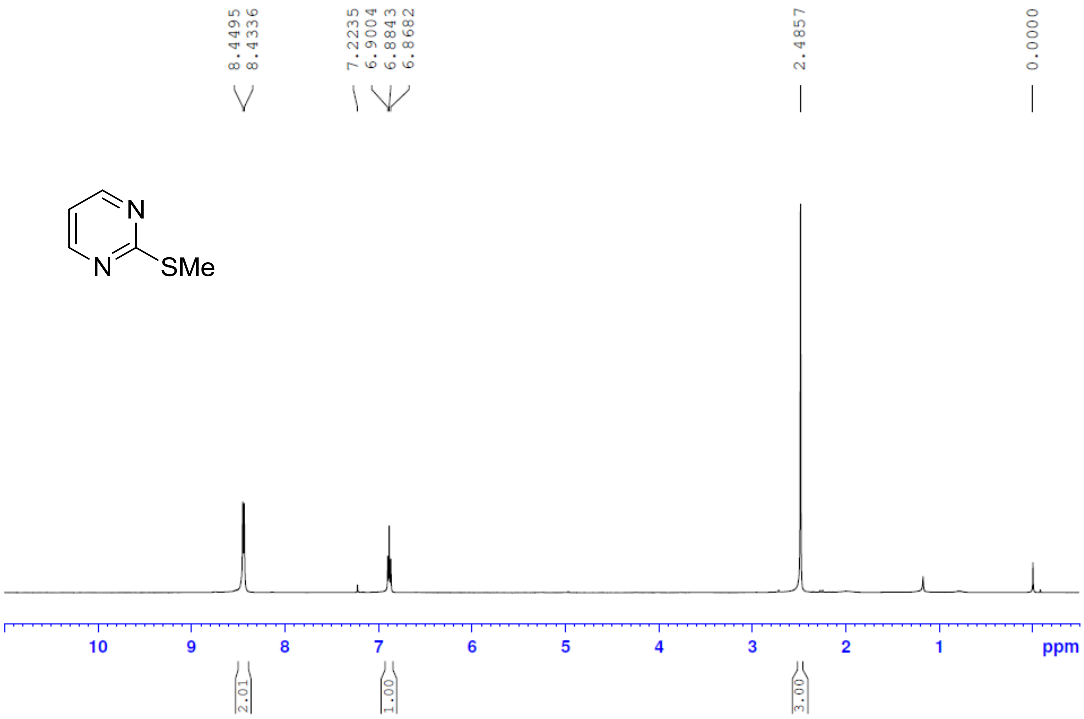

Figure 35 ^{1}H NMR spectrum of compound **3r** (300 MHz, $CDCl_3$)

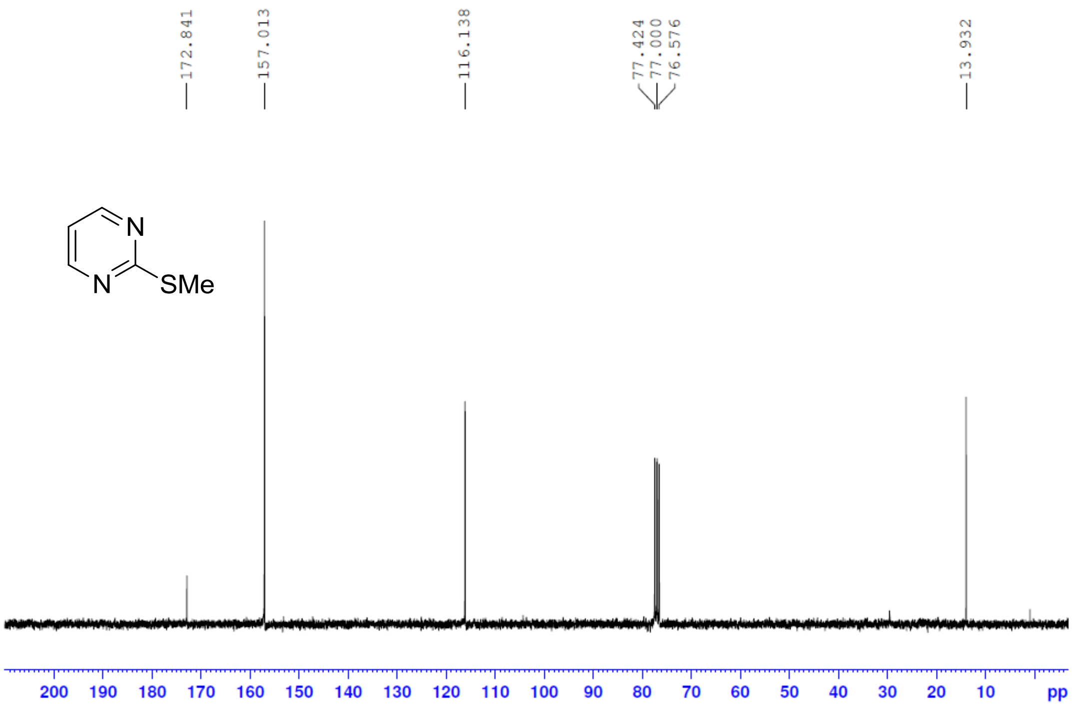

Figure 36 ^{13}C NMR spectrum of compound **3r** (75 MHz, $CDCl_3$)

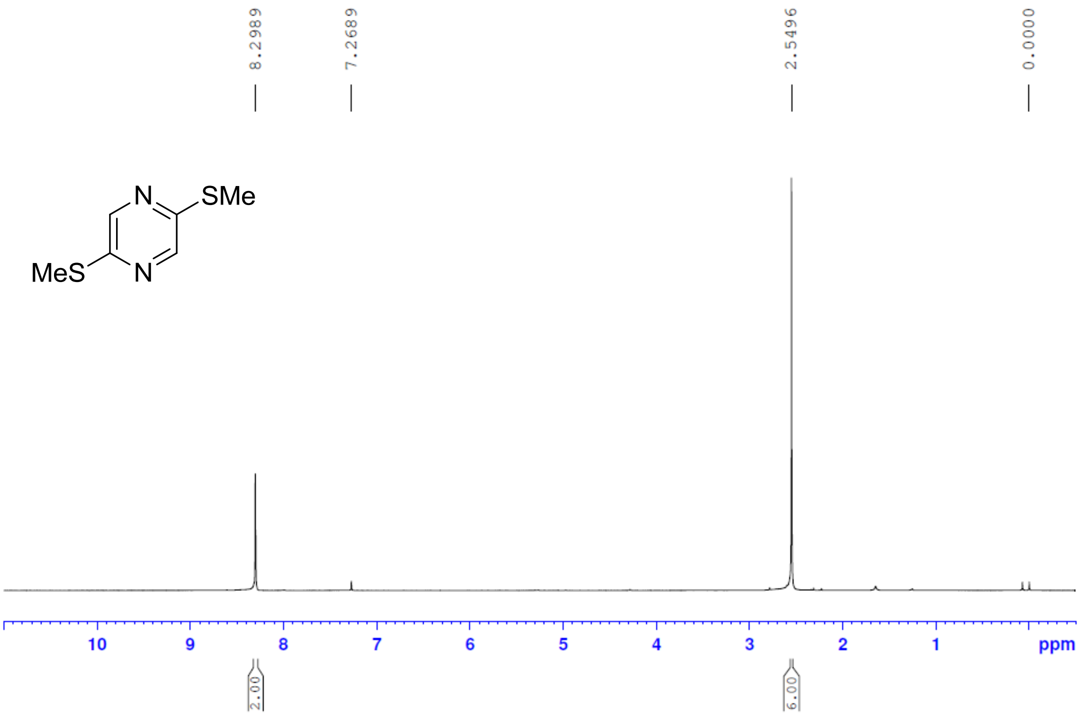

Figure 37 ^{1}H NMR spectrum of compound **3s** (300 MHz, $CDCl_3$)

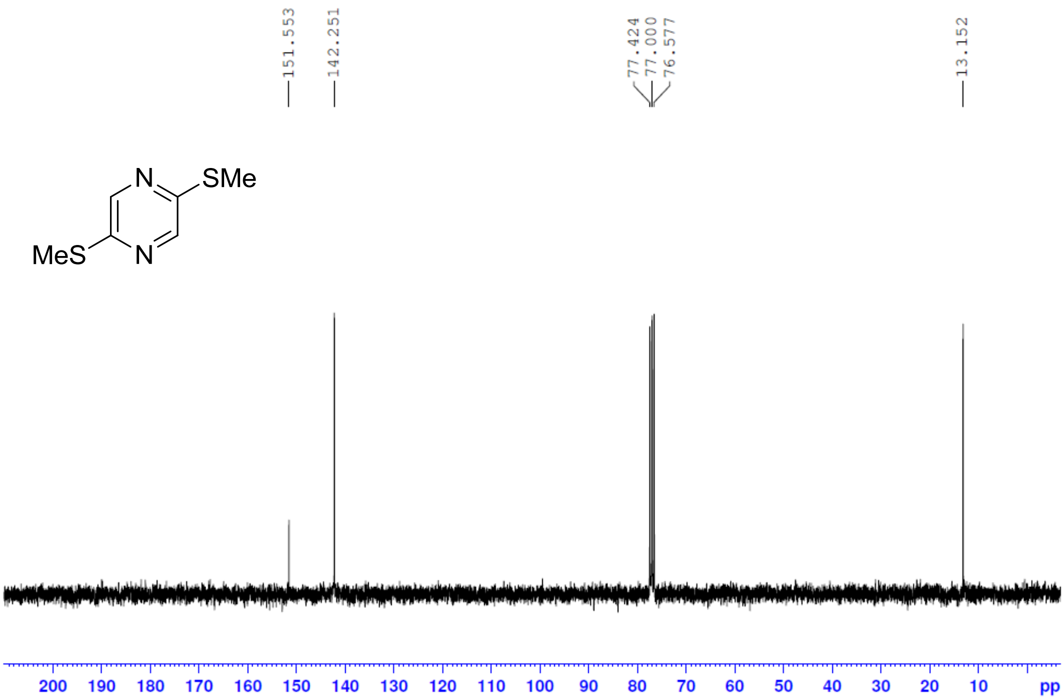

Figure 38 ^{13}C NMR spectrum of compound **3s** (75 MHz, $CDCl_3$)

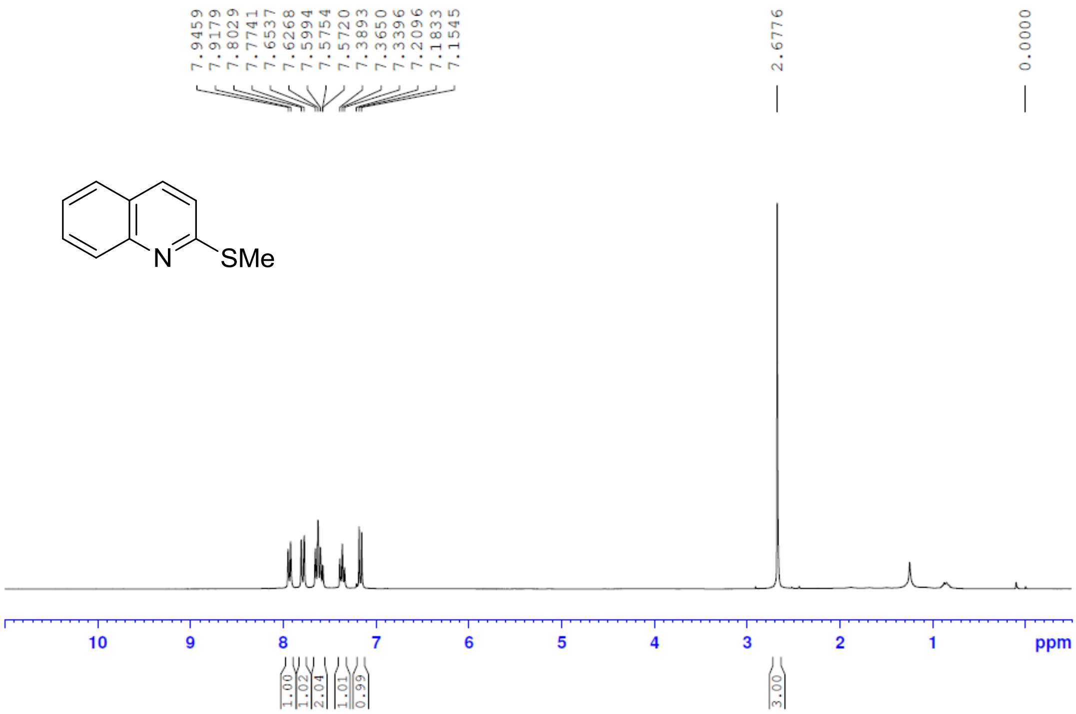

Figure 39 ^{1}H NMR spectrum of compound **3t** (300 MHz, $CDCl_3$)

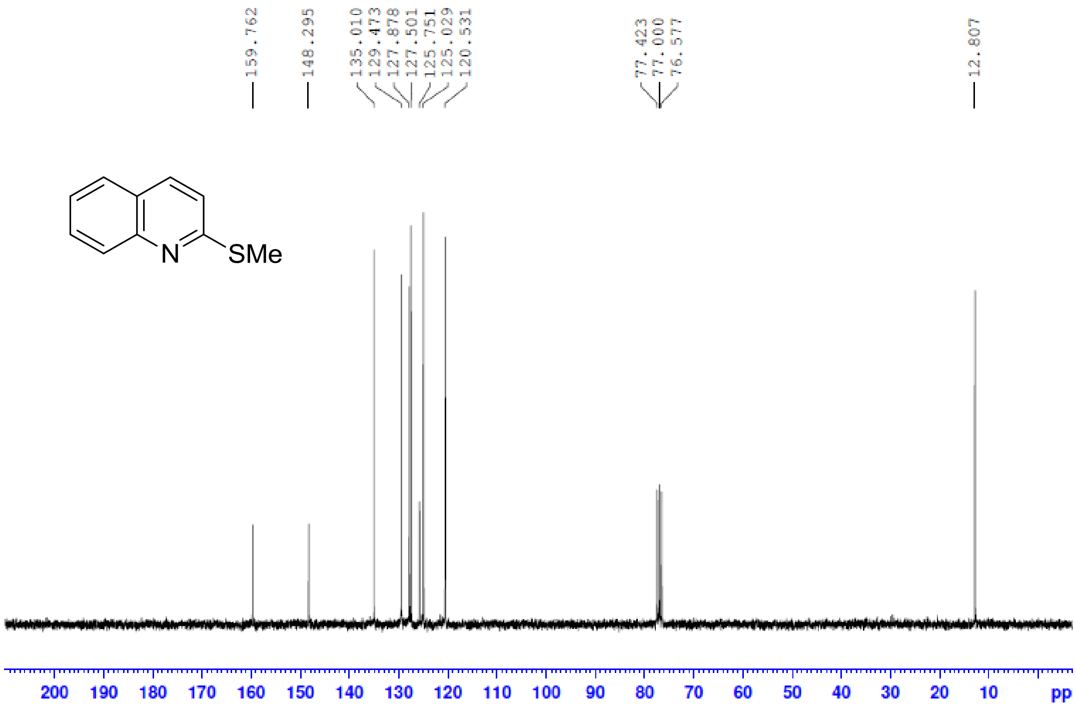

Figure 40 ^{13}C NMR spectrum of compound **3t** (75 MHz, $CDCl_3$)

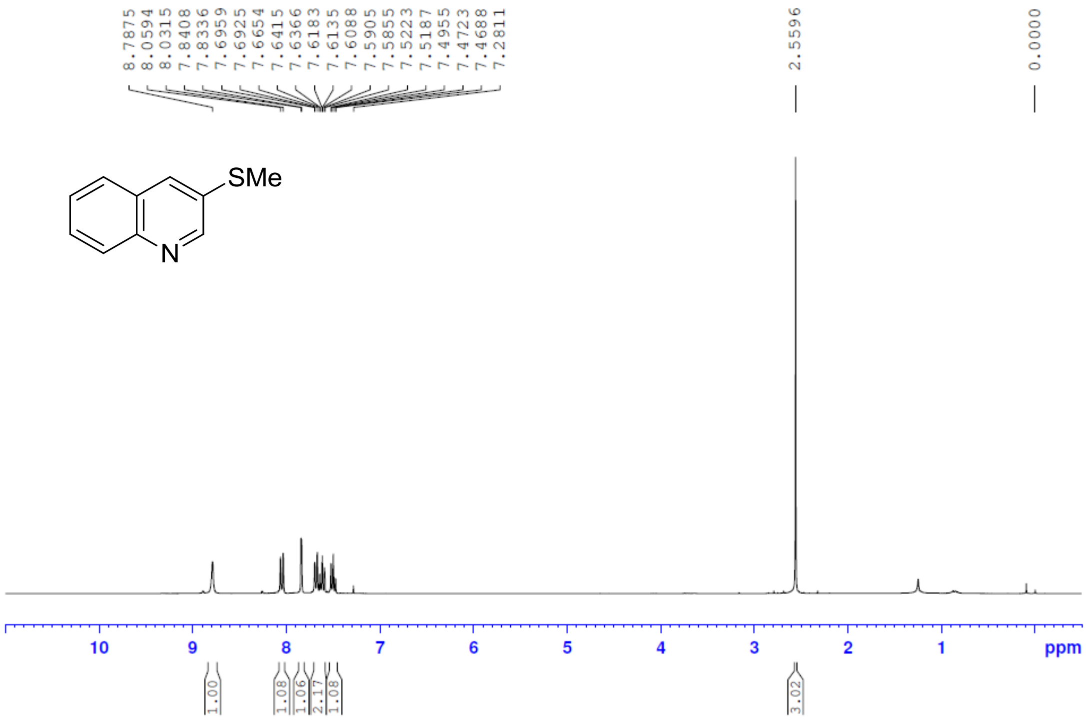

Figure 41 ^{1}H NMR spectrum of compound **3u** (300 MHz, $CDCl_3$)

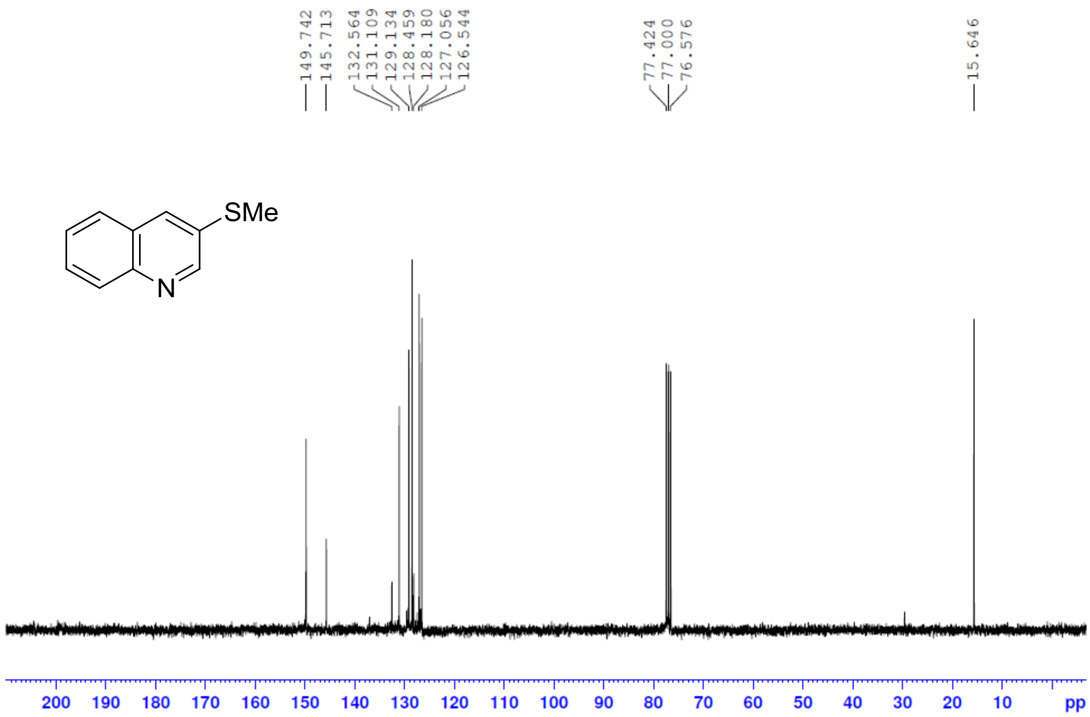

Figure 42 ^{13}C NMR spectrum of compound **3u** (75 MHz, $CDCl_3$)

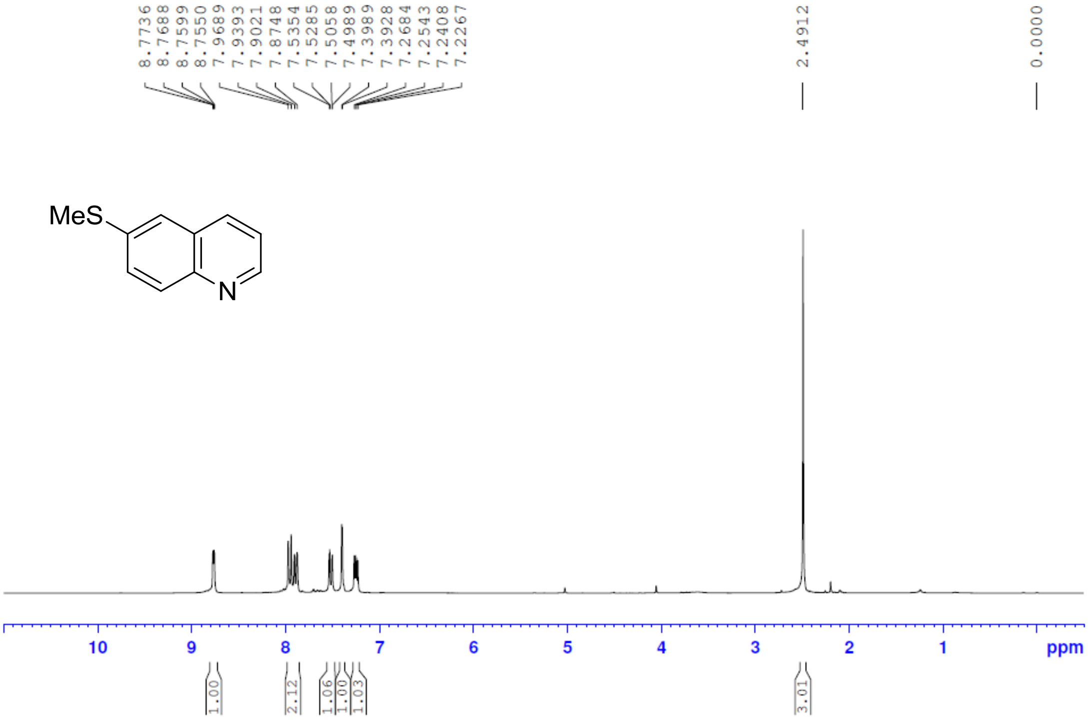

Figure 43 ^{1}H NMR spectrum of compound **3v** (300 MHz, $CDCl_3$)

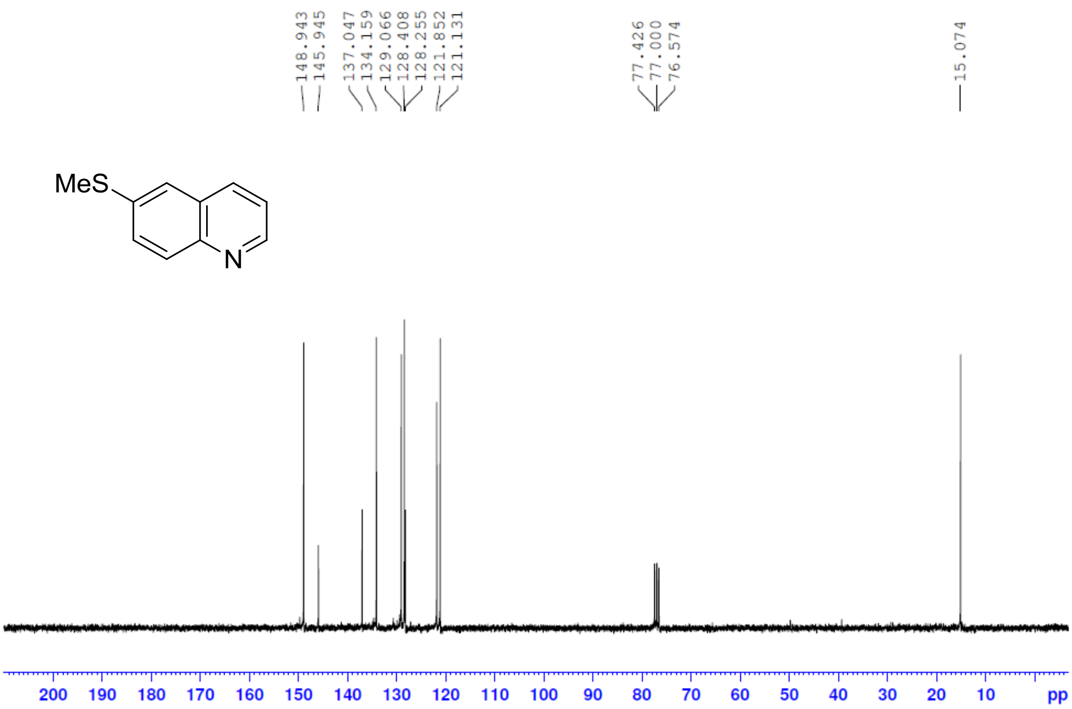

Figure 44 ^{13}C NMR spectrum of compound **3v** (75 MHz, $CDCl_3$)

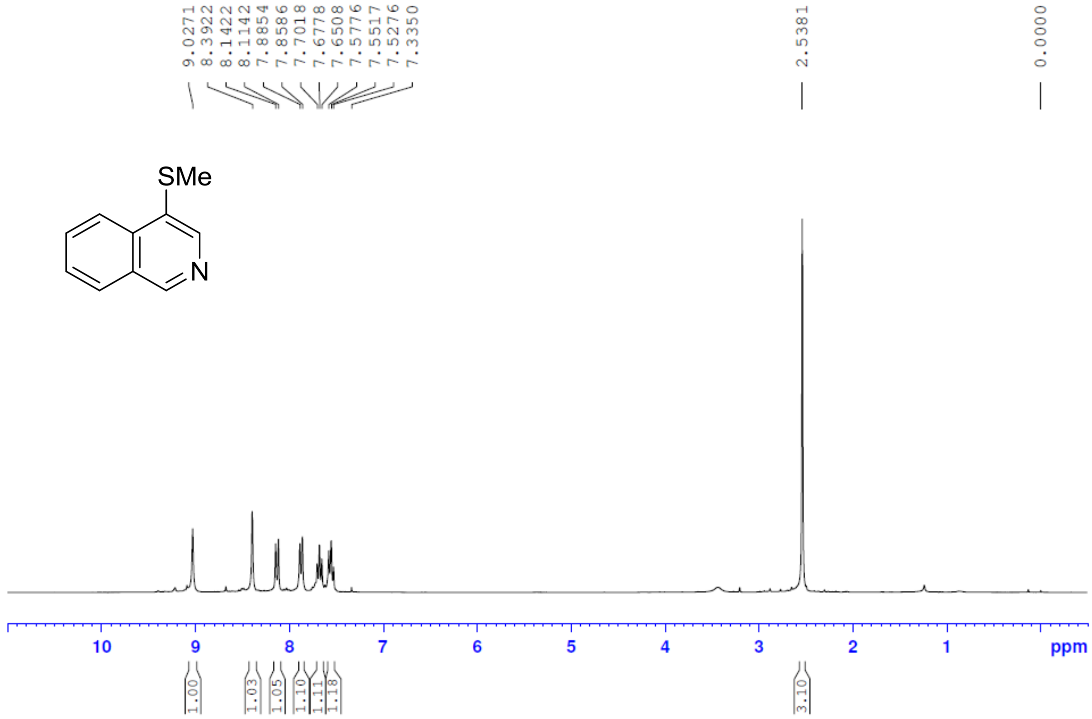

Figure 45 ^{1}H NMR spectrum of compound **3w** (300 MHz, $CDCl_3$)

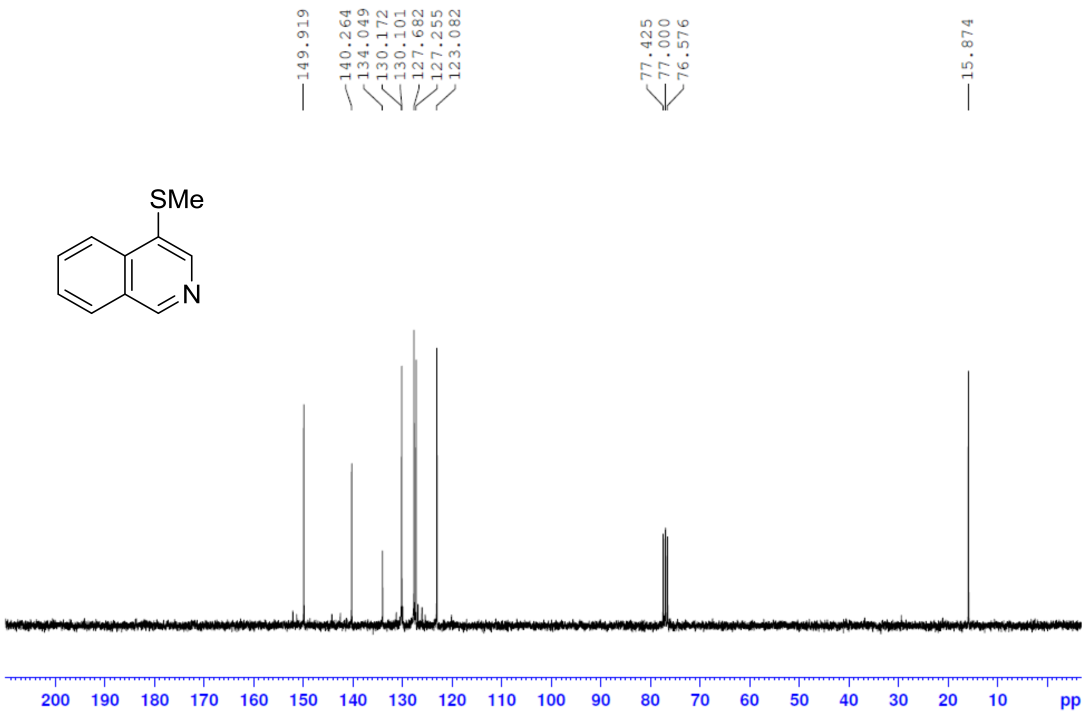

Figure 46 ^{13}C NMR spectrum of compound **3w** (75 MHz, $CDCl_3$)

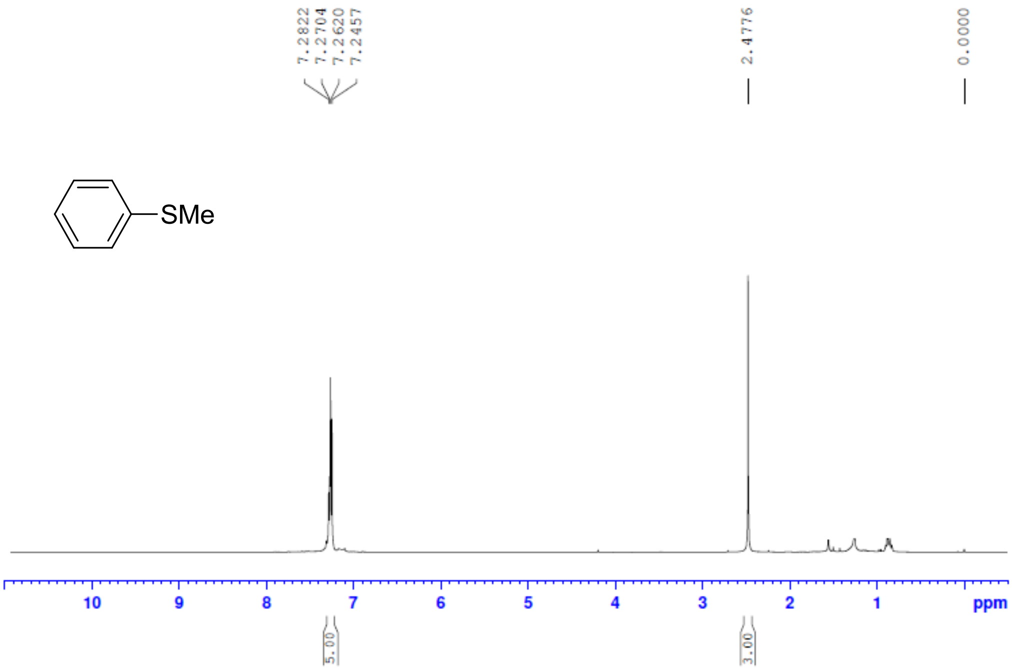

Figure 47 ^{1}H NMR spectrum of compound **4a** (300 MHz, $CDCl_3$)

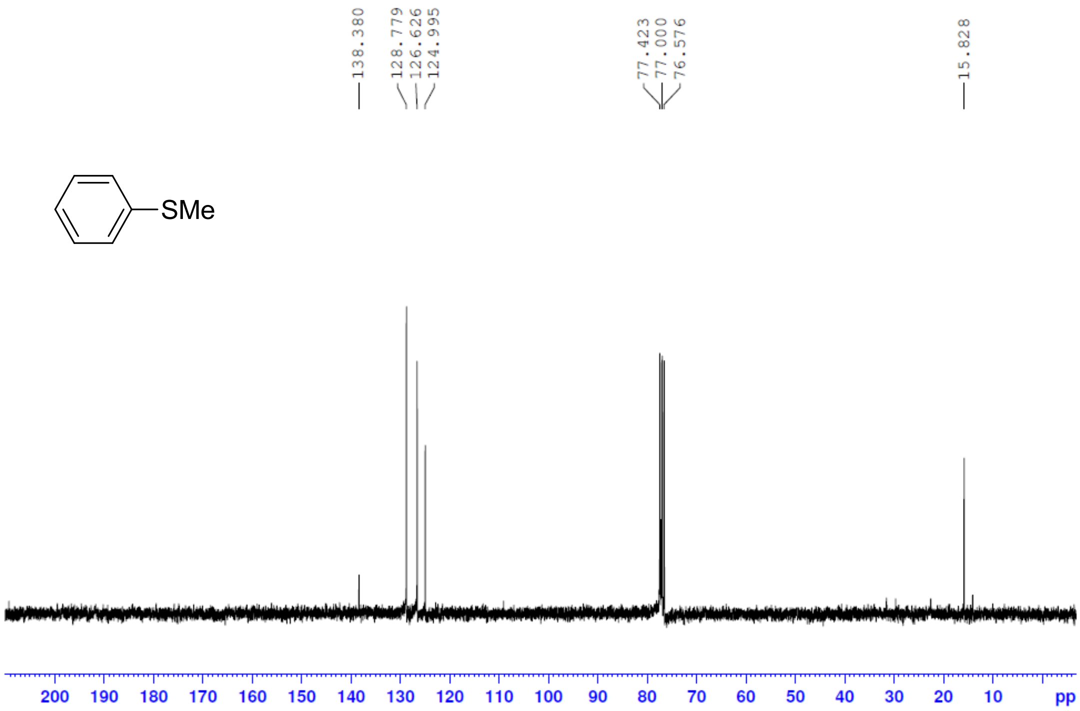

Figure 48 ^{13}C NMR spectrum of compound **4a** (75 MHz, $CDCl_3$)

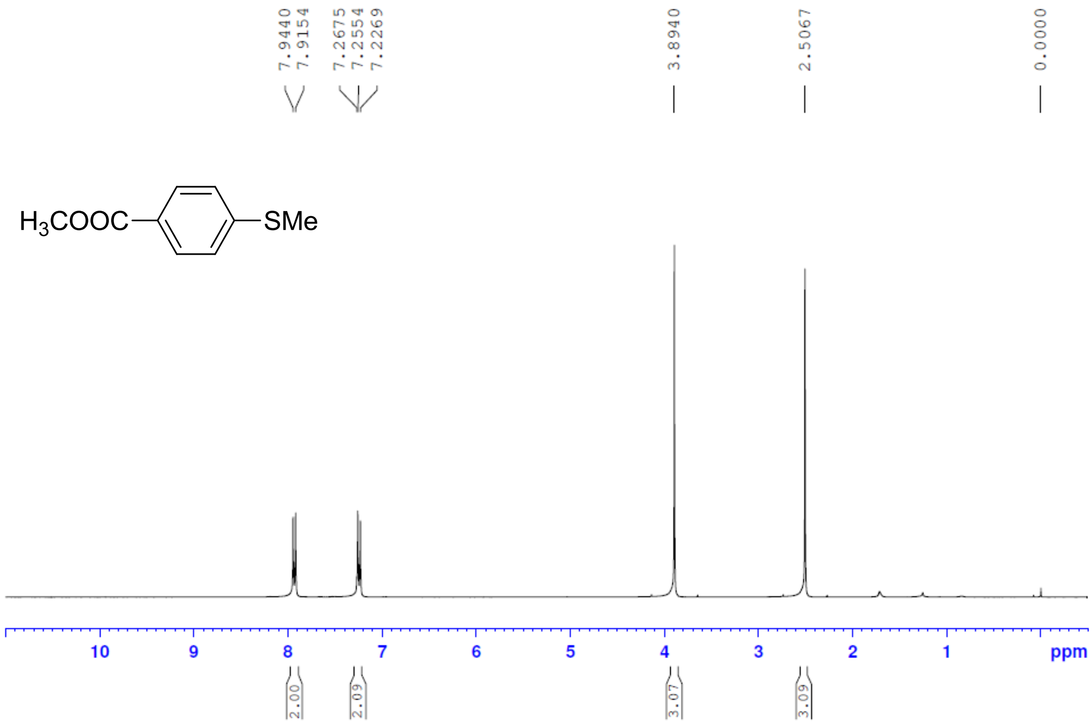

Figure 49 ^{1}H NMR spectrum of compound **4b** (300 MHz, $CDCl_3$)

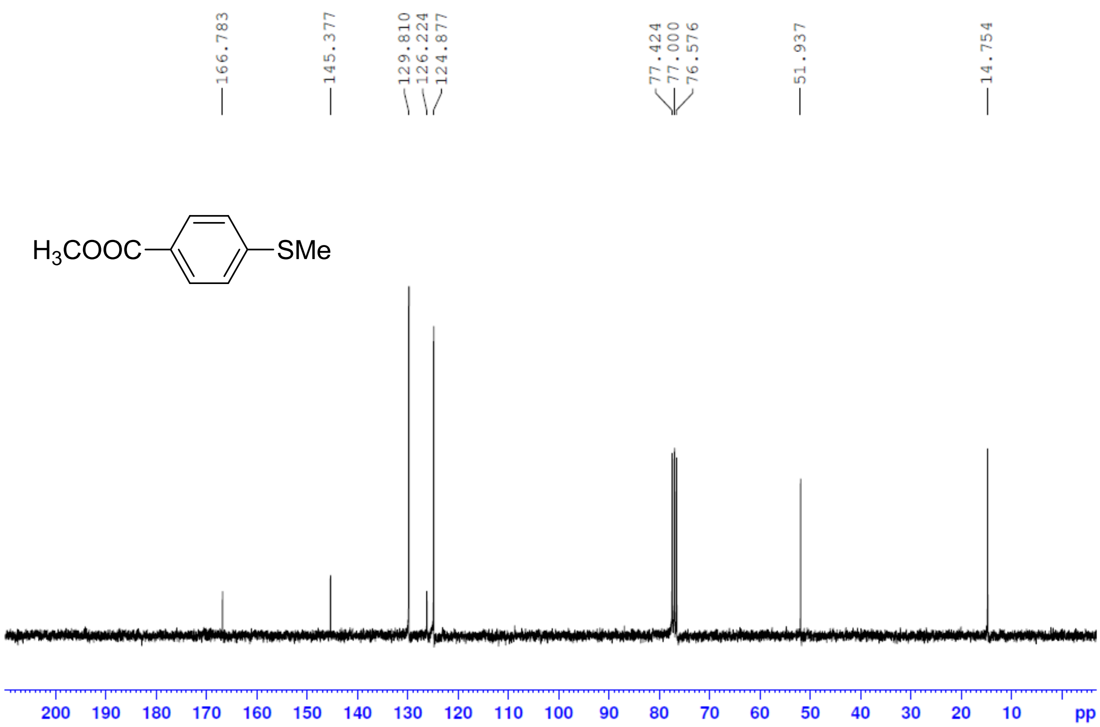

Figure 50 ^{13}C NMR spectrum of compound **4b** (75 MHz, $CDCl_3$)

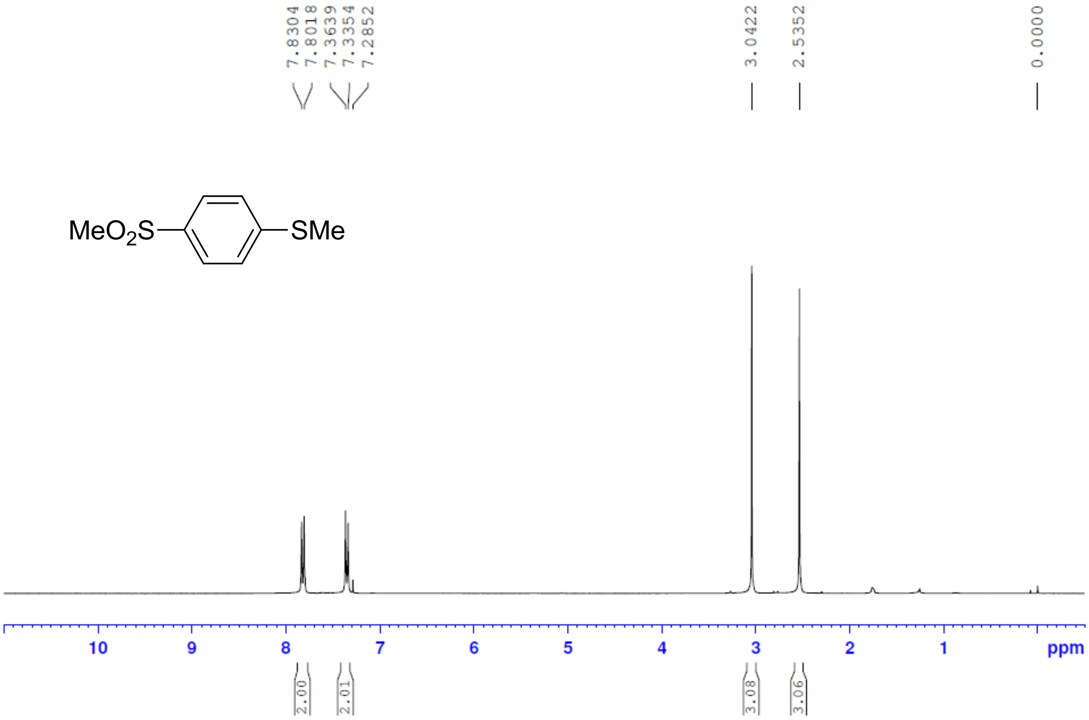

Figure 51 ^{1}H NMR spectrum of compound **4c** (300 MHz, $CDCl_3$)

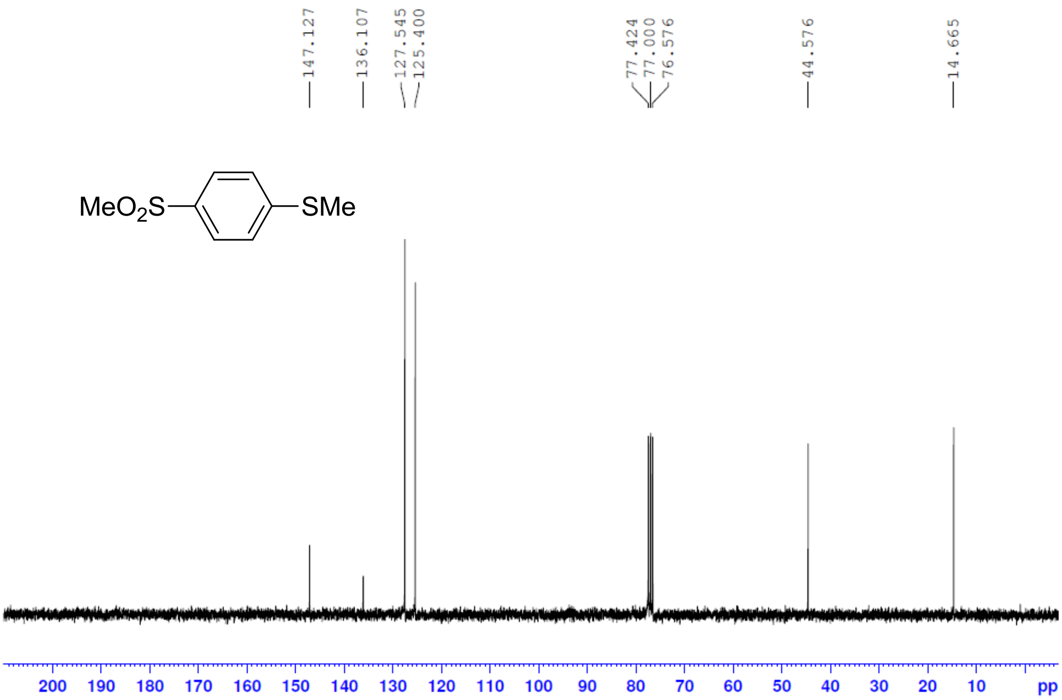

Figure 52 ^{13}C NMR spectrum of compound **4c** (75 MHz, $CDCl_3$)

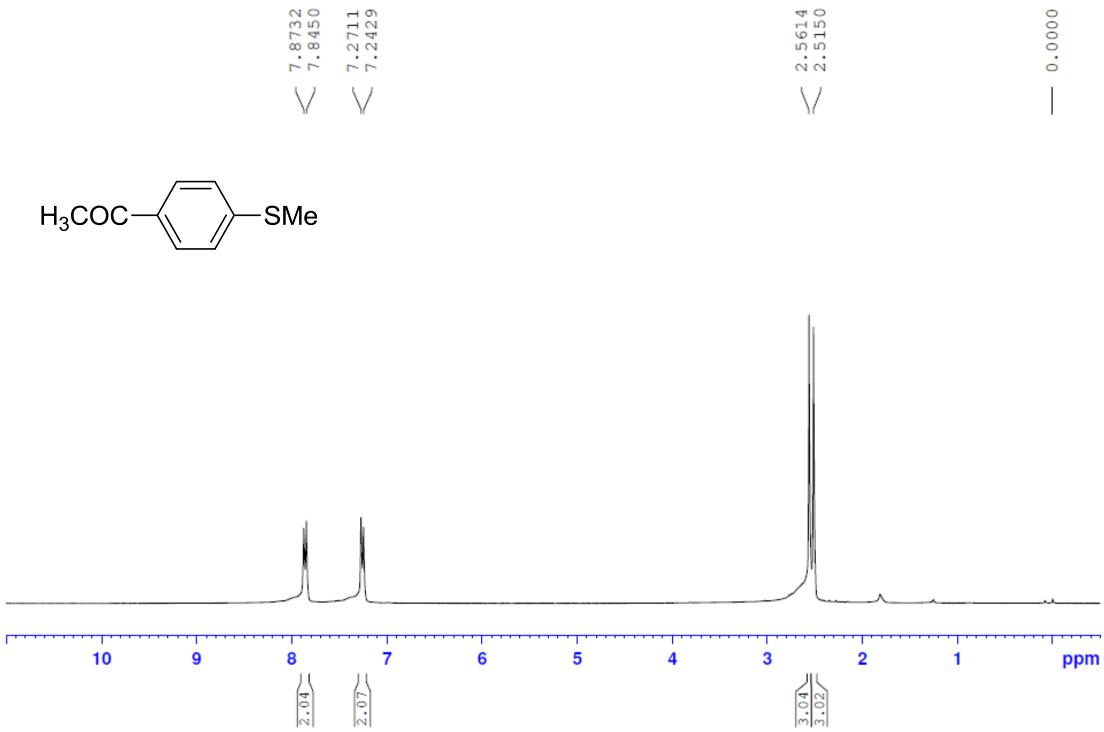

Figure 53 ^{1}H NMR spectrum of compound **4d** (300 MHz, $CDCl_3$)

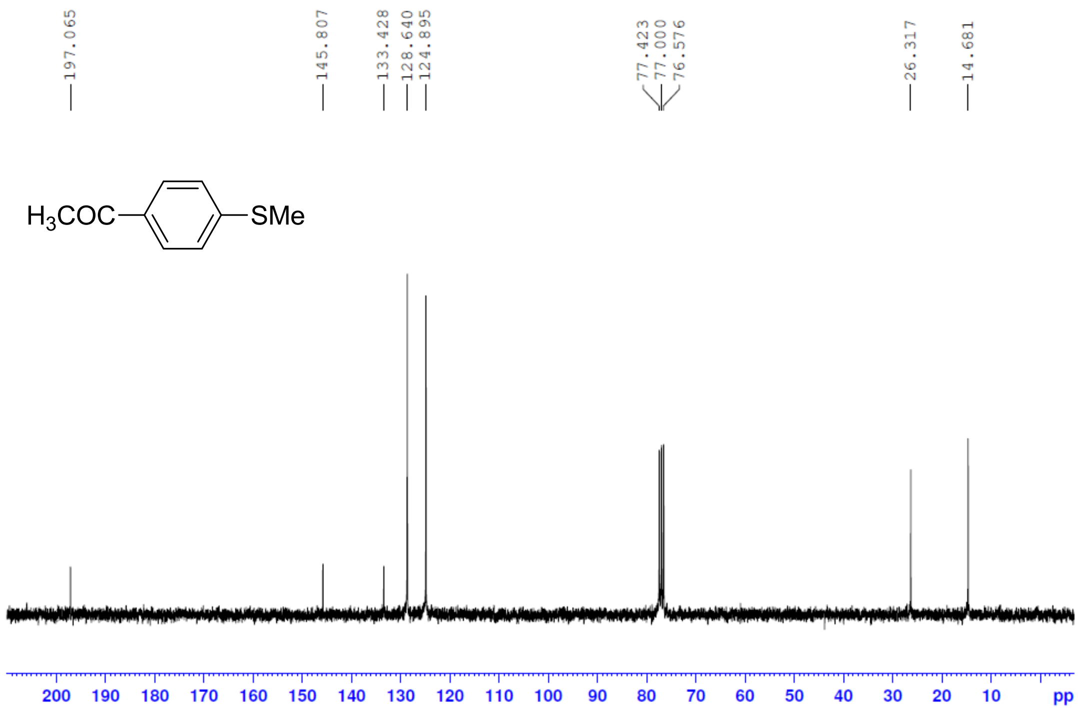

Figure 54 ^{13}C NMR spectrum of compound **4d** (75 MHz, $CDCl_3$)

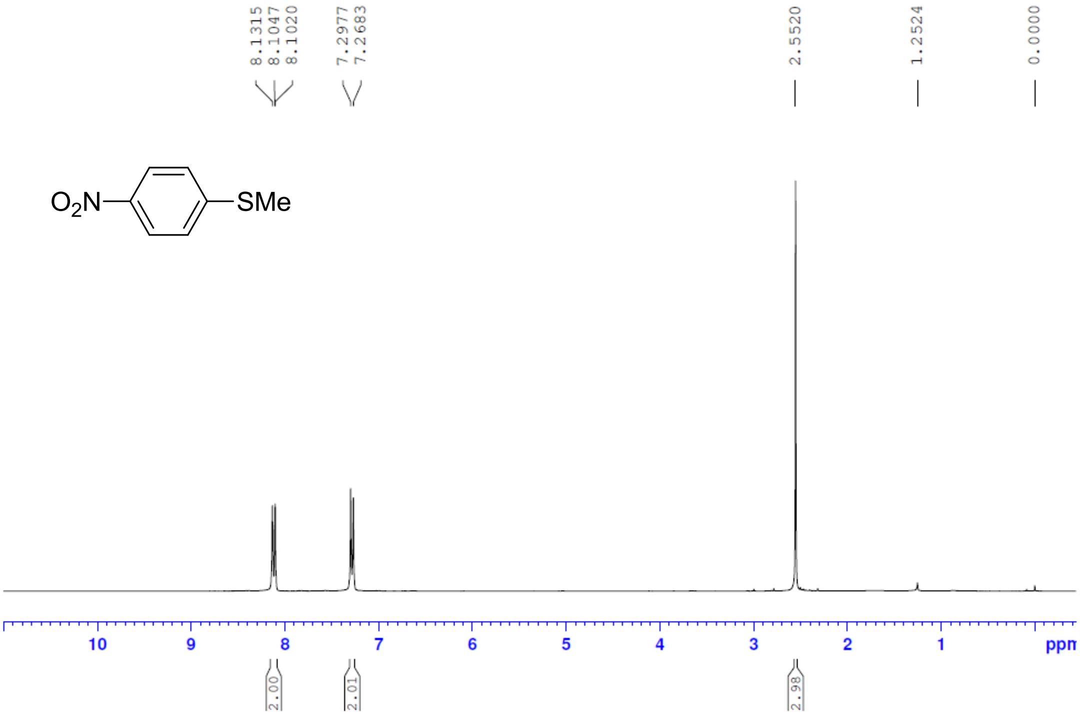

Figure 55 ^{1}H NMR spectrum of compound **4e** (300 MHz, $CDCl_3$)

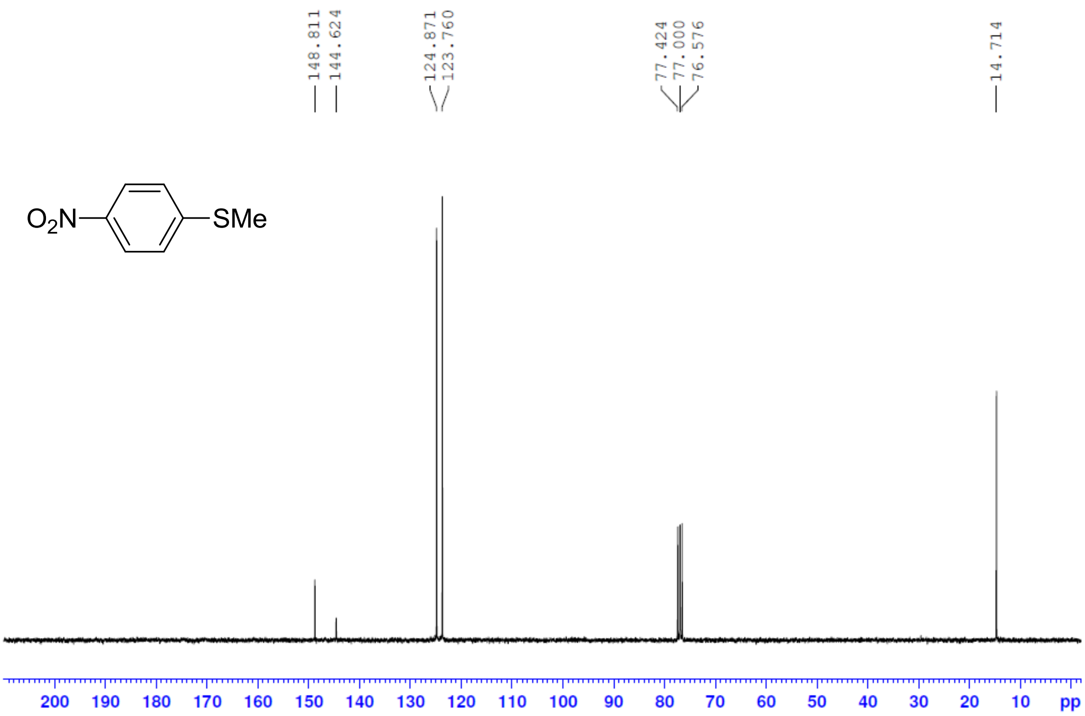

Figure 56 ^{13}C NMR spectrum of compound **4e** (75 MHz, $CDCl_3$)

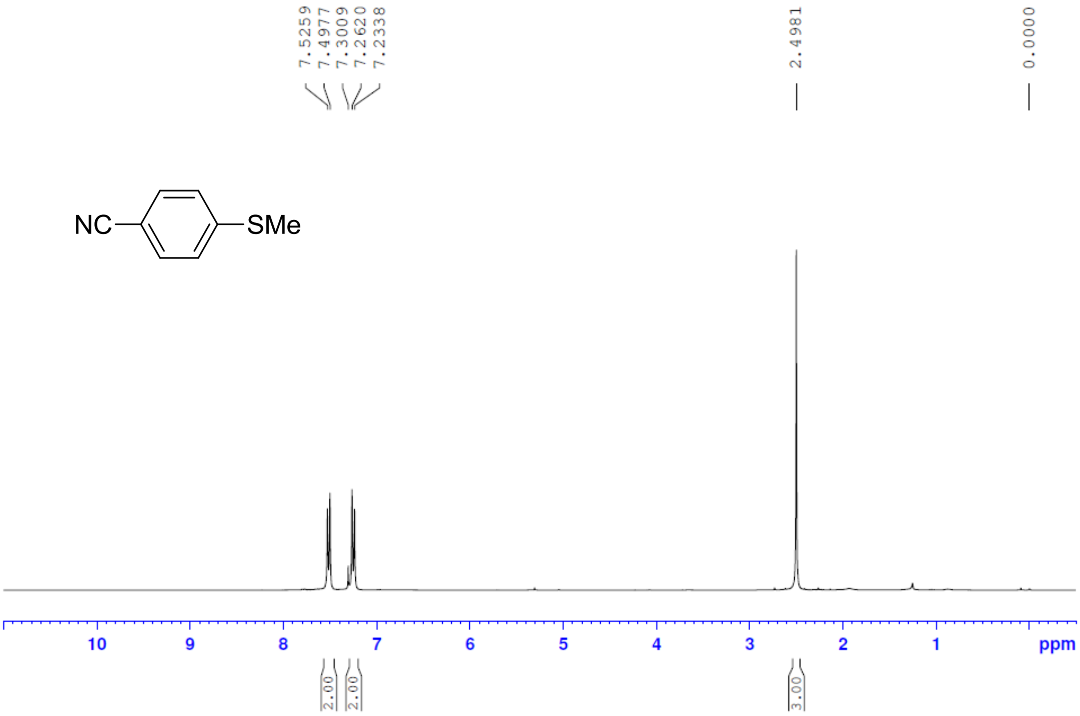

Figure 57 [1]H NMR spectrum of compound **4f** (300 MHz, $CDCl_3$)

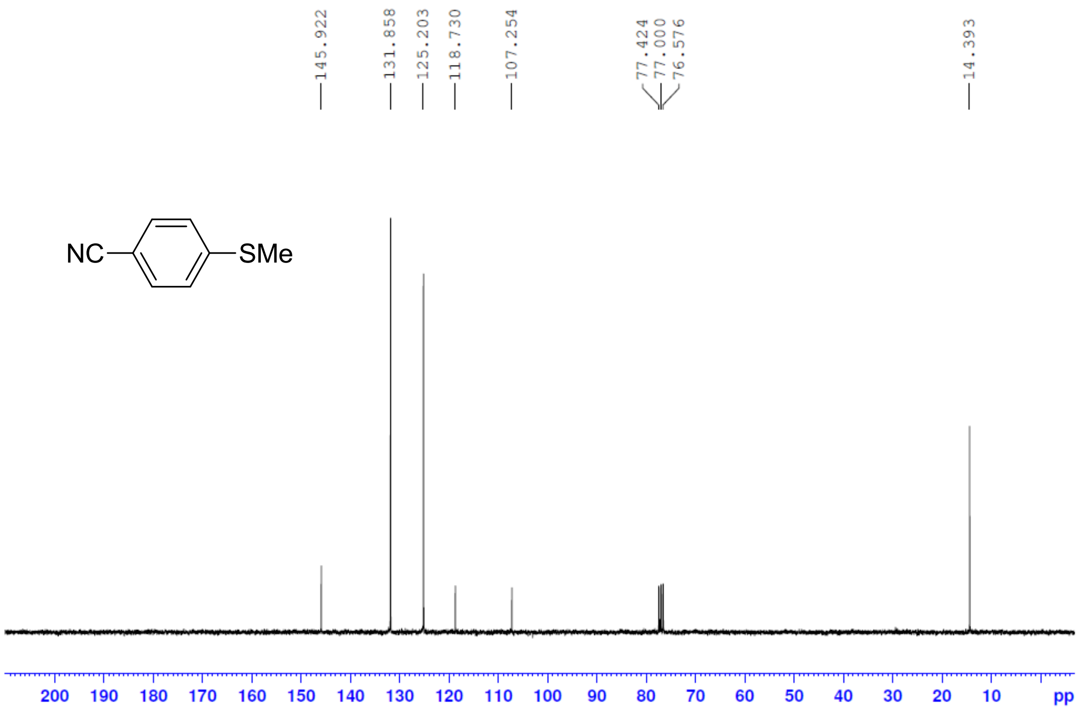

Figure 58 [13]C NMR spectrum of compound **4f** (75 MHz, $CDCl_3$)

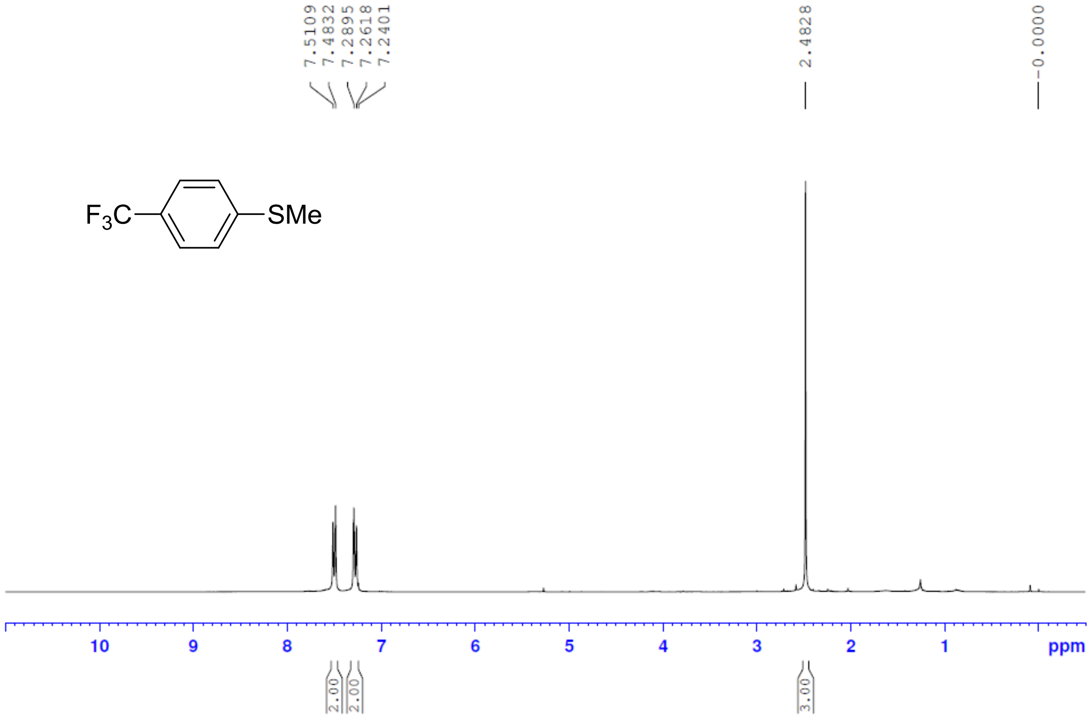

Figure 59 ^{1}H NMR spectrum of compound **4g** (300 MHz, $CDCl_3$)

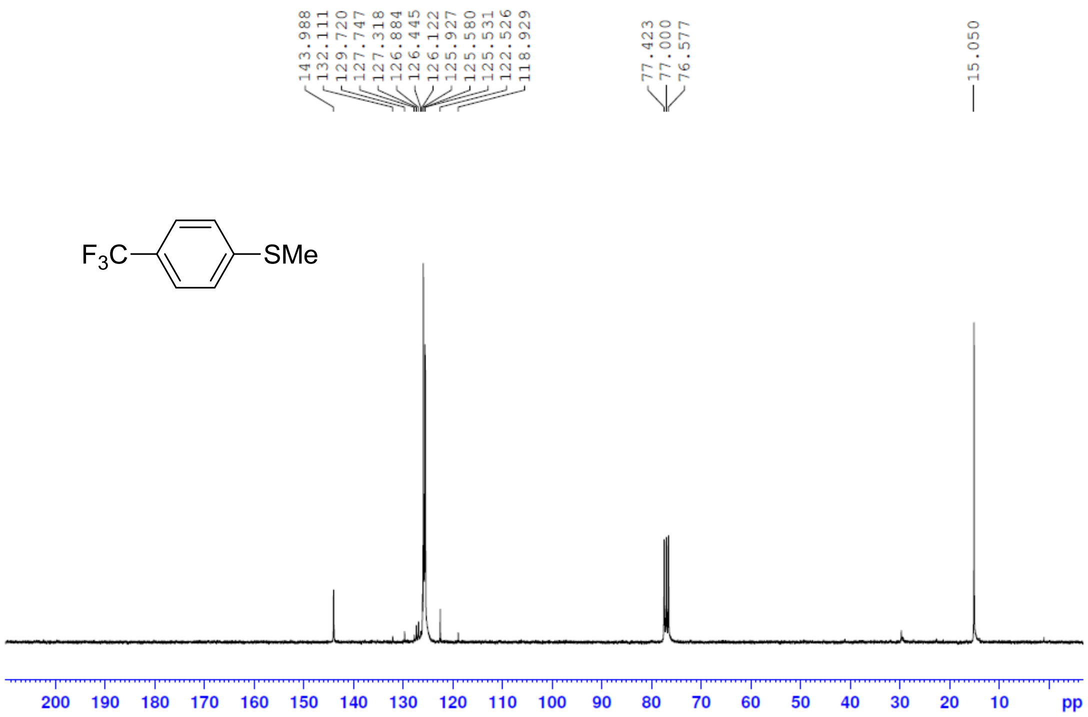

Figure 60 ^{13}C NMR spectrum of compound **4g** (75 MHz, $CDCl_3$)

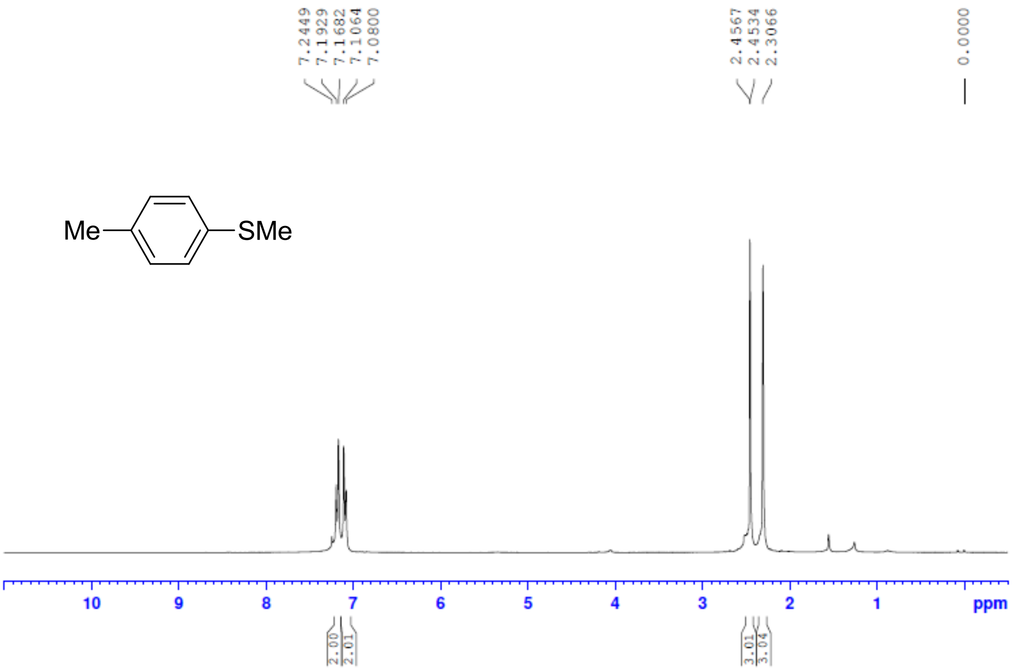

Figure 61 ^{1}H NMR spectrum of compound **4h** (300 MHz, $CDCl_3$)

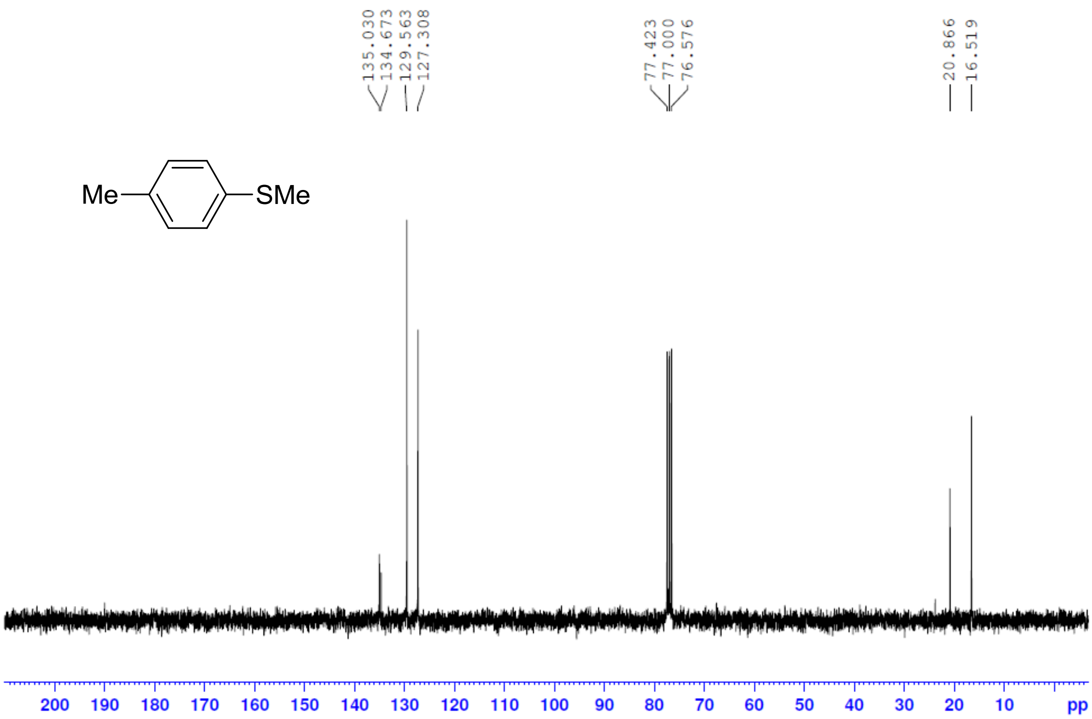

Figure 62 ^{13}C NMR spectrum of compound **4h** (75 MHz, $CDCl_3$)

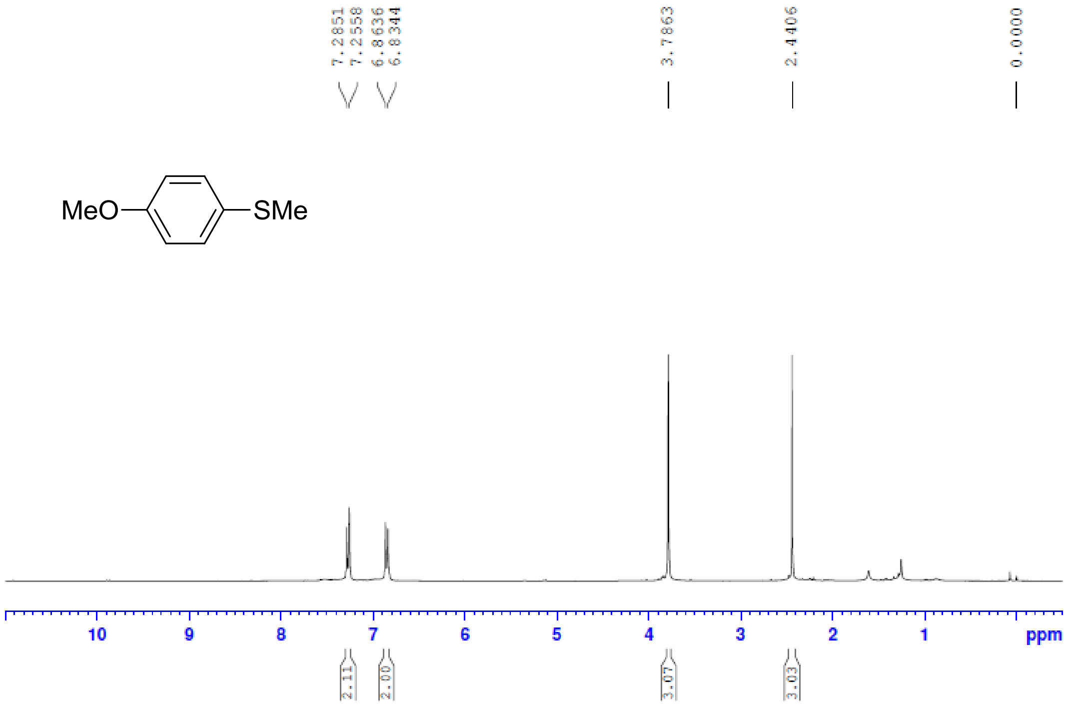

Figure 63 ^{1}H NMR spectrum of compound **4i** (300 MHz, $CDCl_3$)

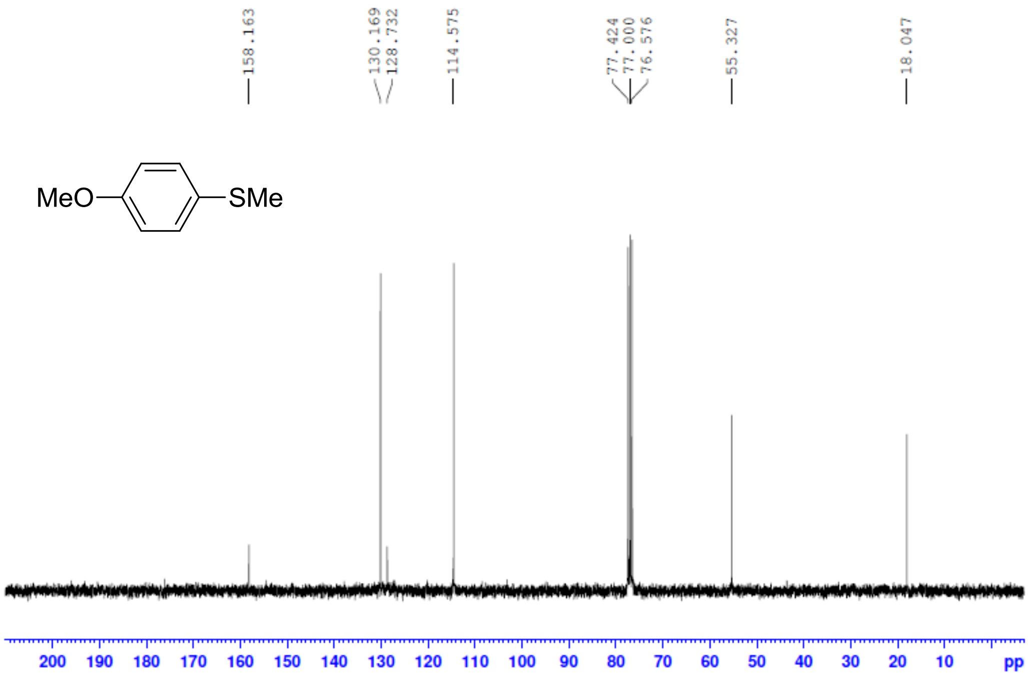

Figure 64 ^{13}C NMR spectrum of compound **4i** (75 MHz, $CDCl_3$)

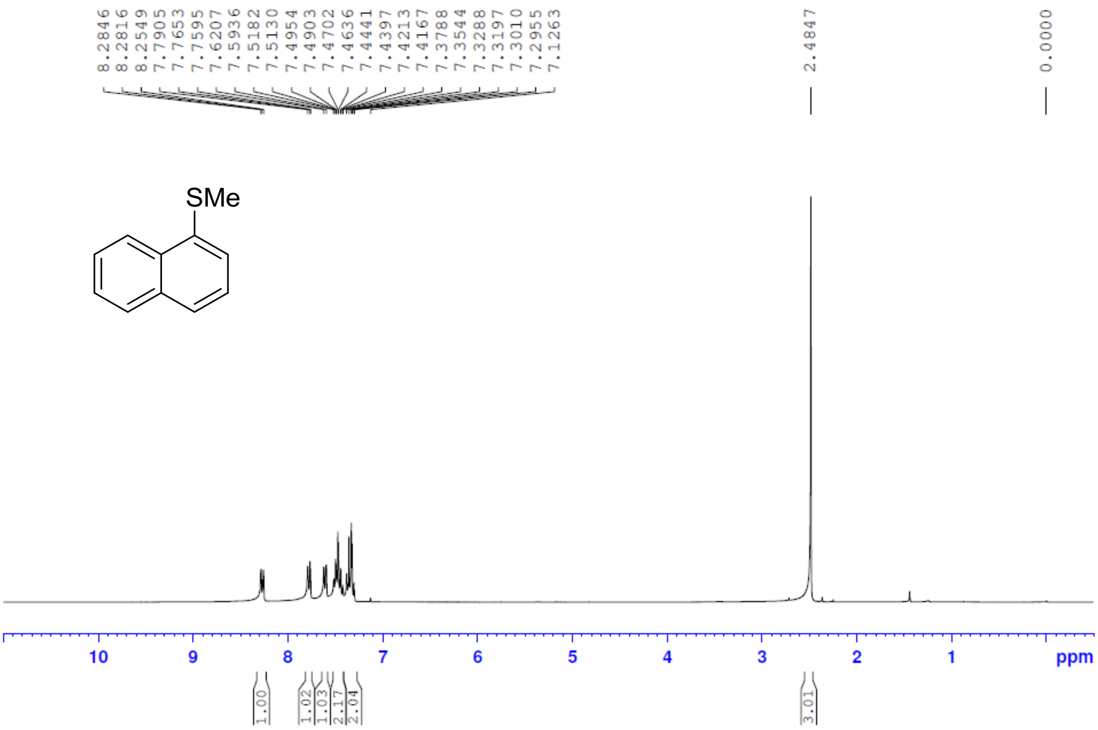

Figure 65 [1]H NMR spectrum of compound **4j** (300 MHz, $CDCl_3$)

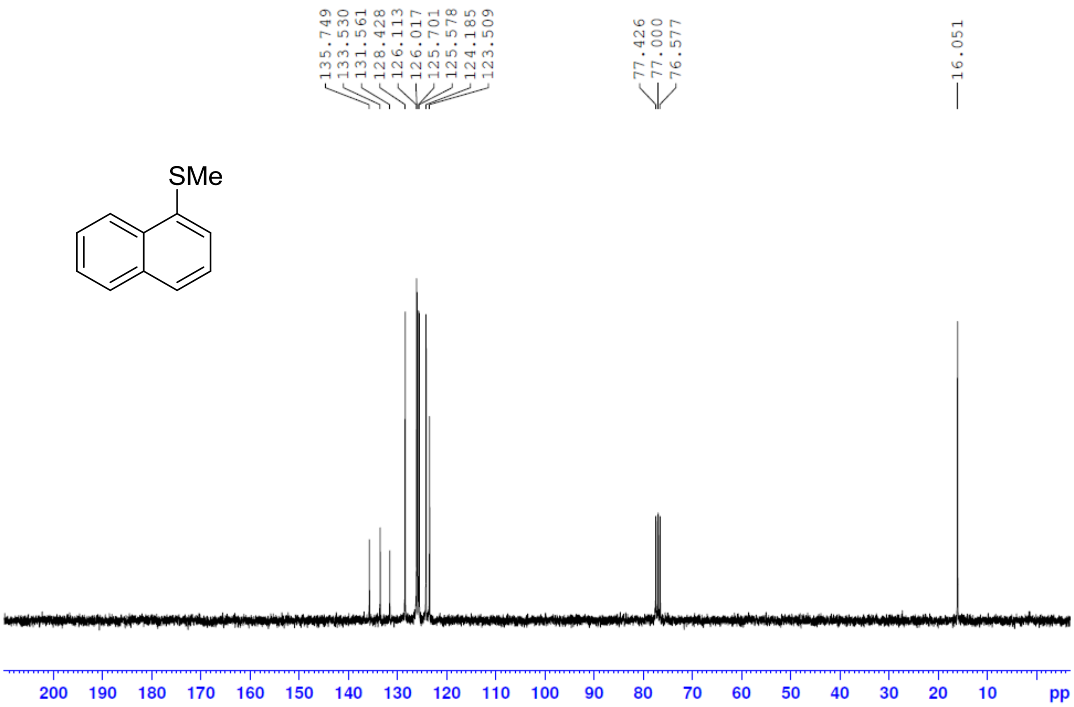

Figure 66 [13]C NMR spectrum of compound **4j** (75 MHz, $CDCl_3$)

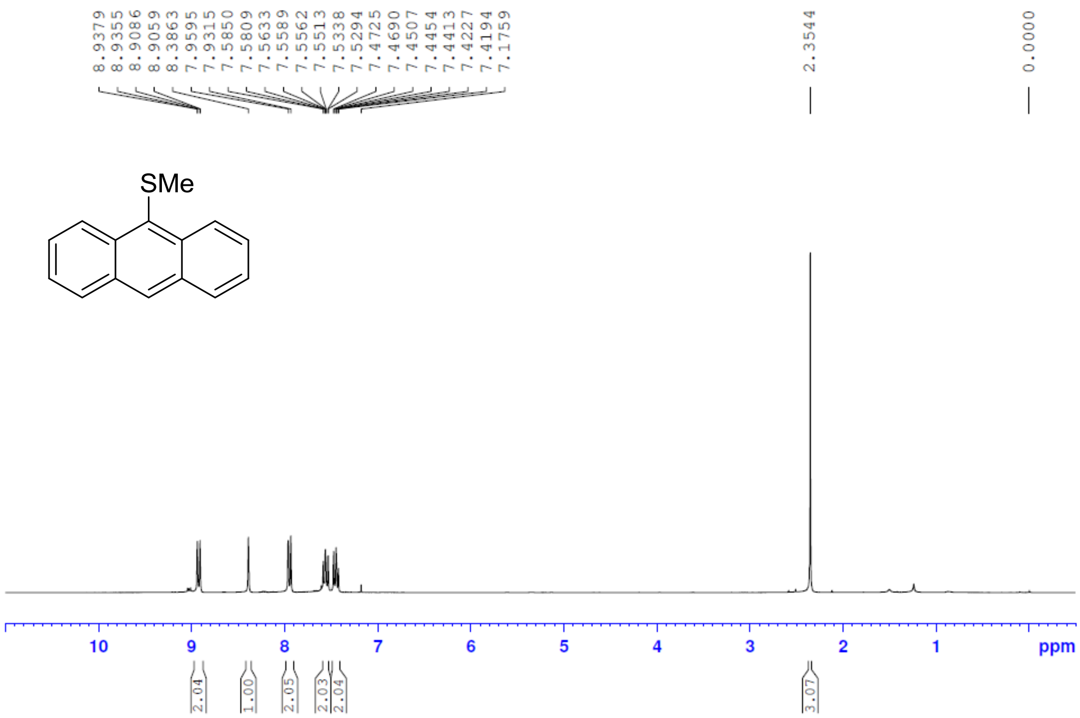

Figure 67 ^{1}H NMR spectrum of compound **4k** (300 MHz, $CDCl_3$)

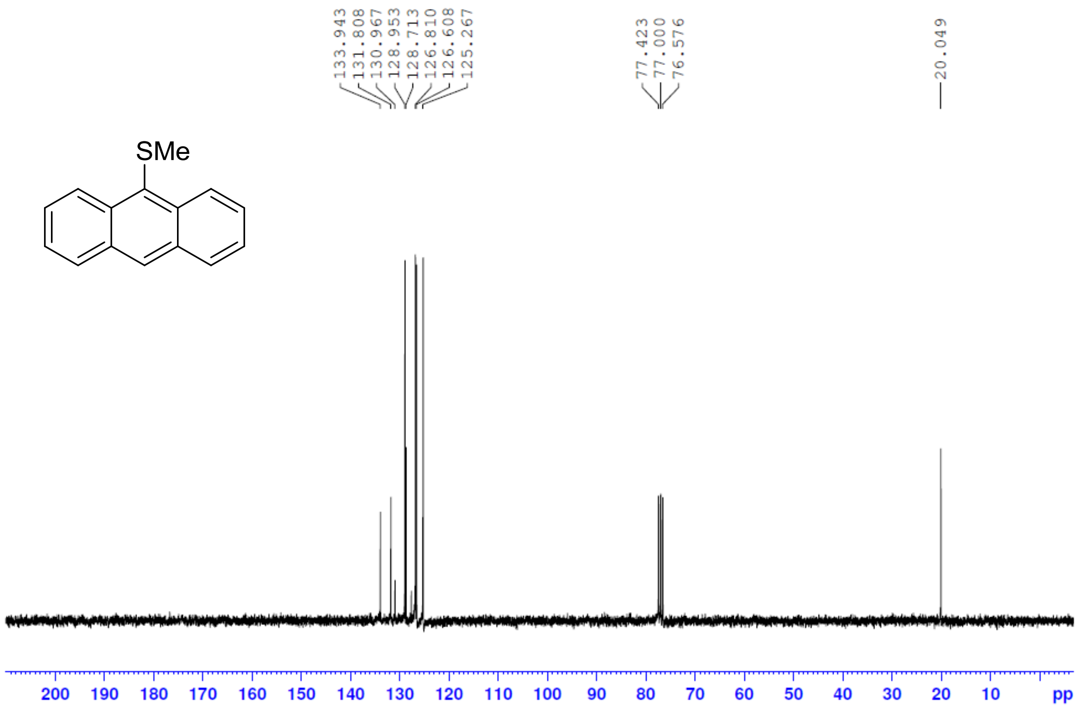

Figure 68 ^{13}C NMR spectrum of compound **4k** (75 MHz, $CDCl_3$)

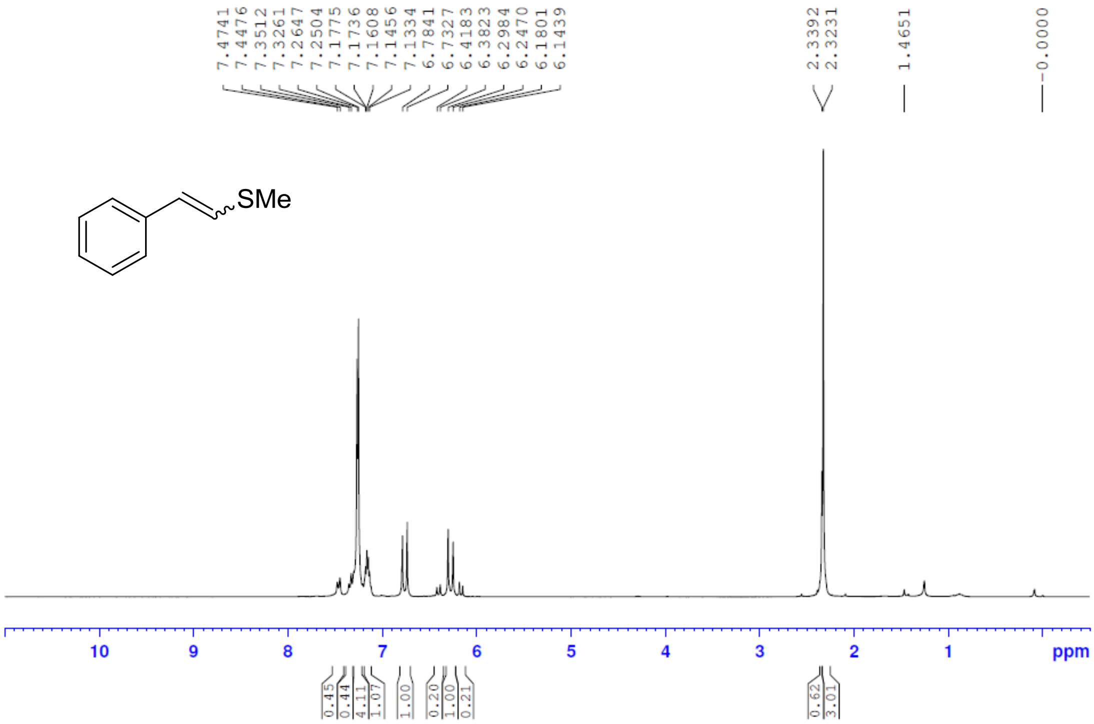

Figure 69 ^{1}H NMR spectrum of compound **4l** (300 MHz, $CDCl_3$)

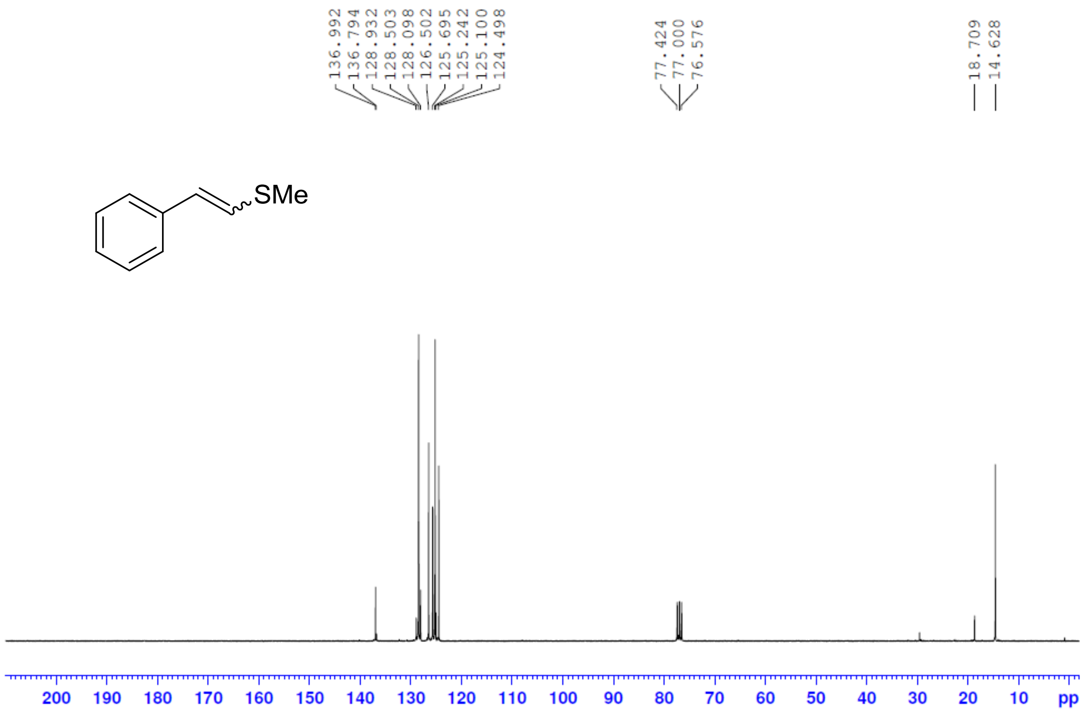

Figure 70 ^{13}C NMR spectrum of compound **4l** (75 MHz, $CDCl_3$)

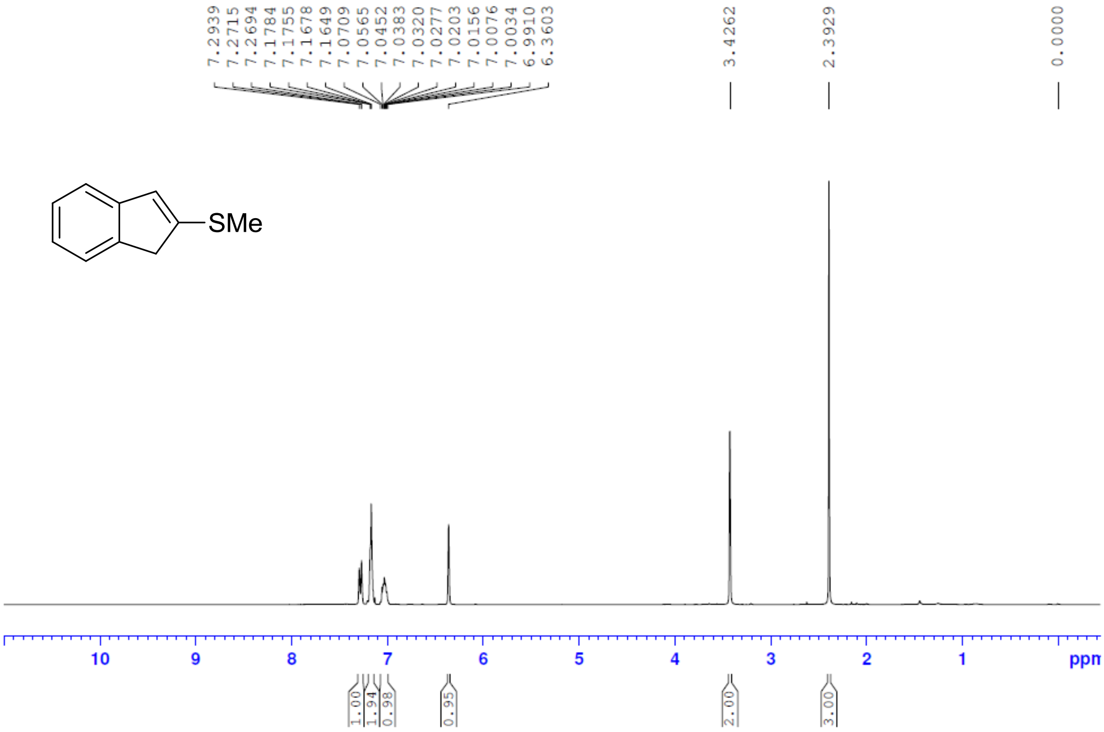

Figure 71 [1]H NMR spectrum of compound **4m** (300 MHz, $CDCl_3$)

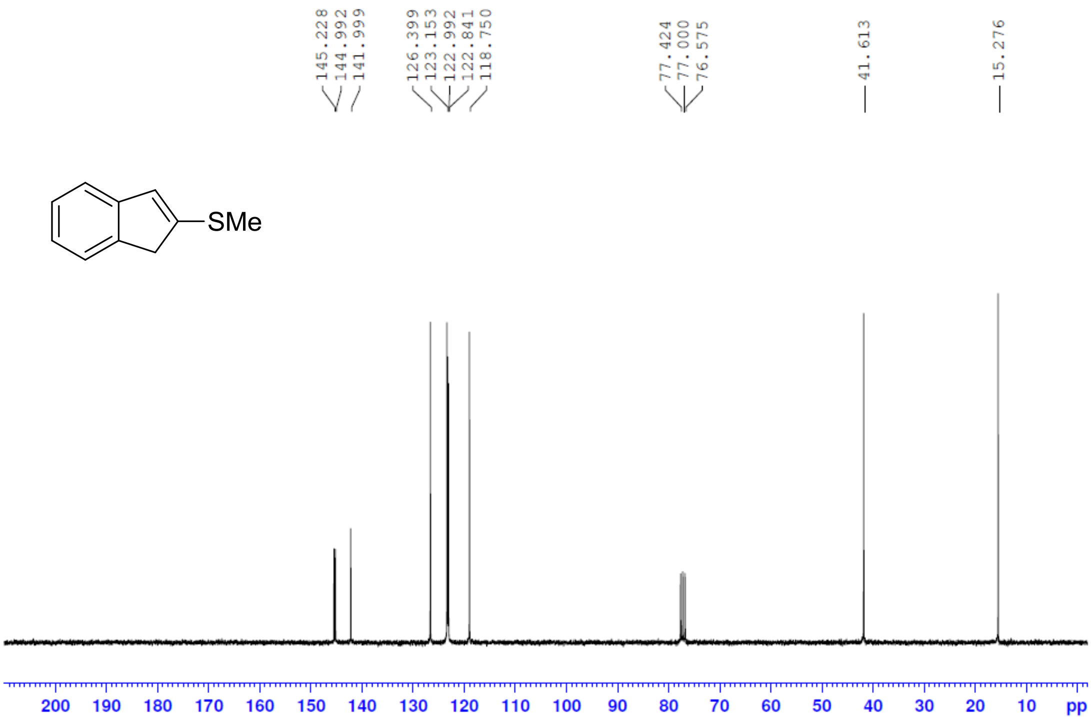

Figure 72 [13]C NMR spectrum of compound **4m** (75 MHz, $CDCl_3$)

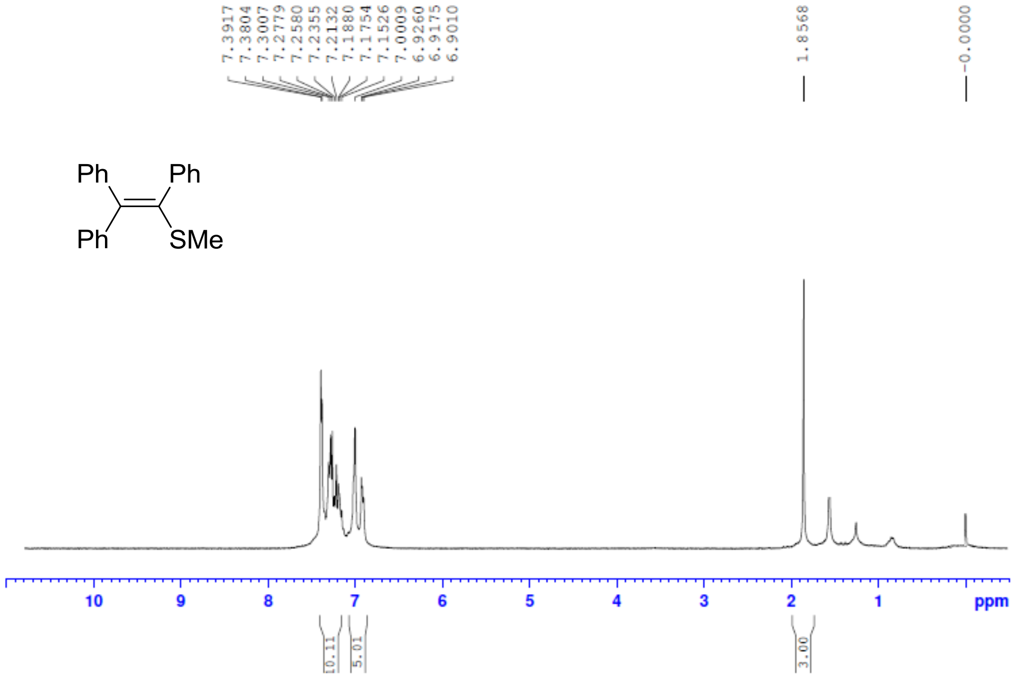

Figure 73 ^{1}H NMR spectrum of compound **4n** (300 MHz, $CDCl_3$)

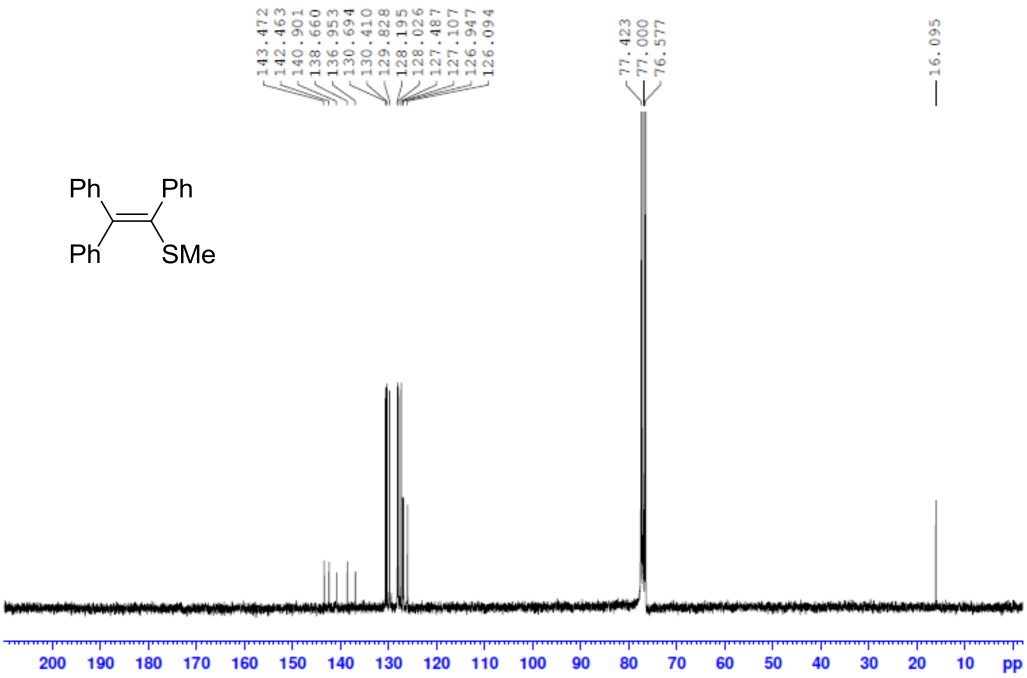

Figure 74 ^{13}C NMR spectrum of compound **4n** (75 MHz, $CDCl_3$)

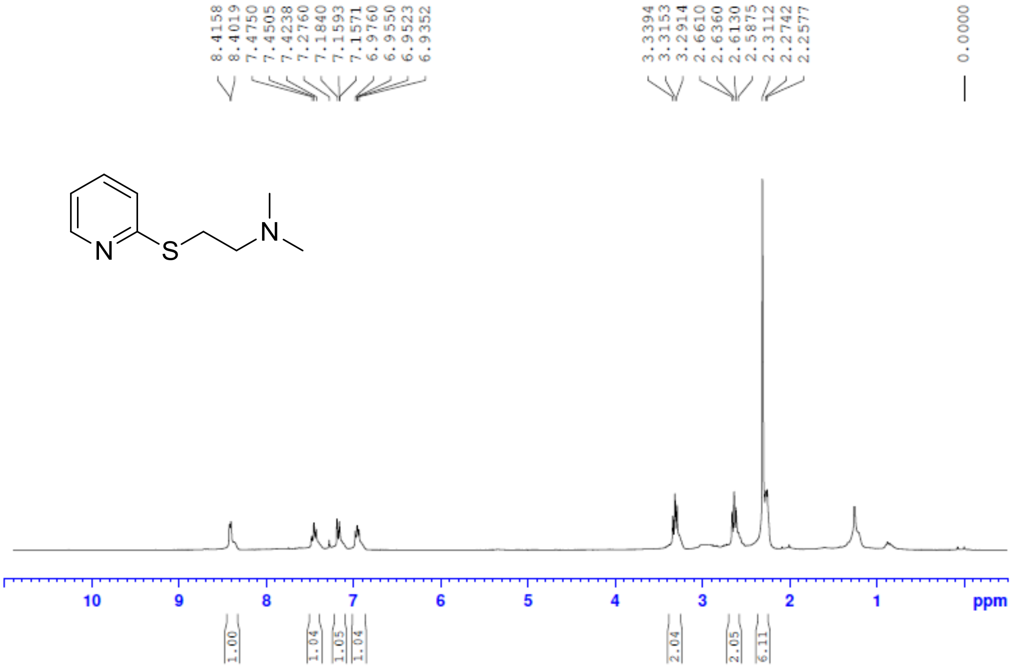

Figure 75 ^{1}H NMR spectrum of compound **5a** (300 MHz, $CDCl_3$)

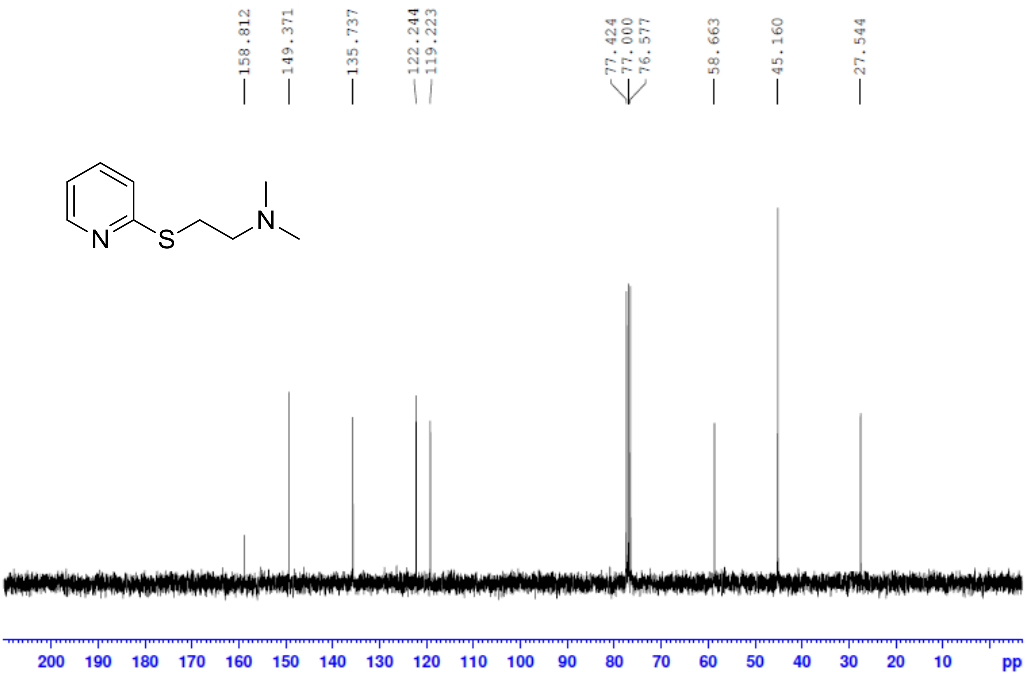

Figure 76 ^{13}C NMR spectrum of compound **5a** (75 MHz, $CDCl_3$)

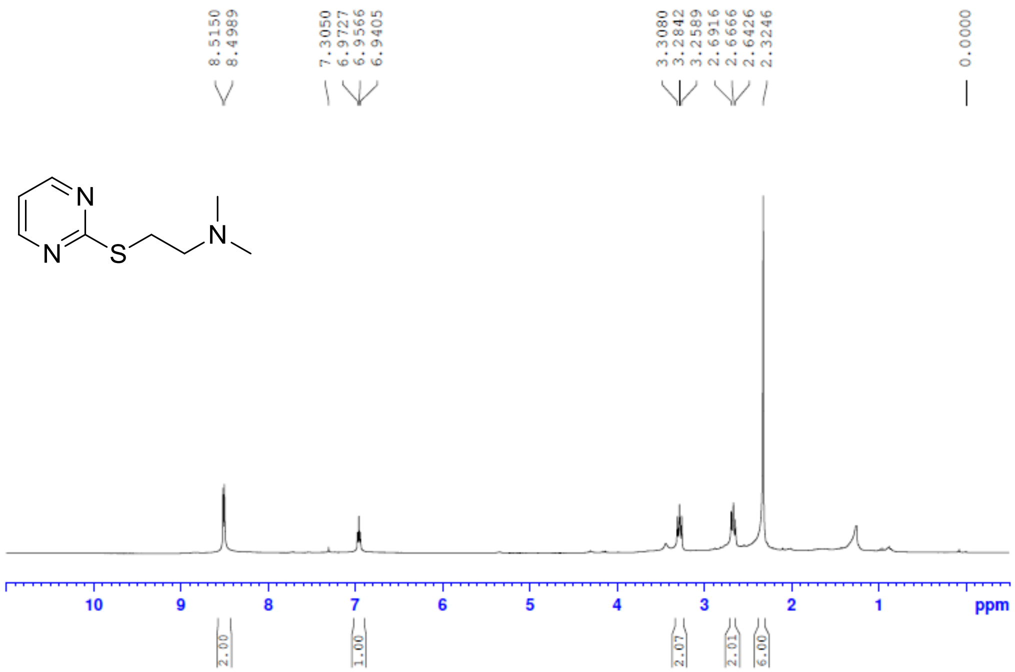

Figure 77 [1]H NMR spectrum of compound **5b** (300 MHz, $CDCl_3$)

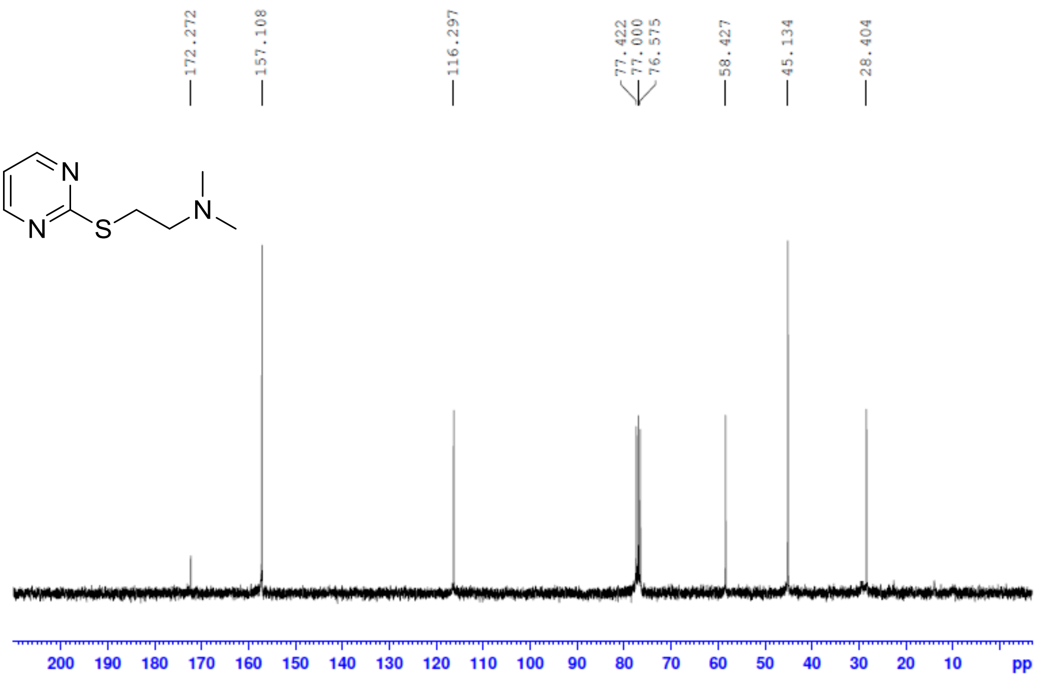

Figure 78 [13]C NMR spectrum of compound **5b** (75 MHz, $CDCl_3$)

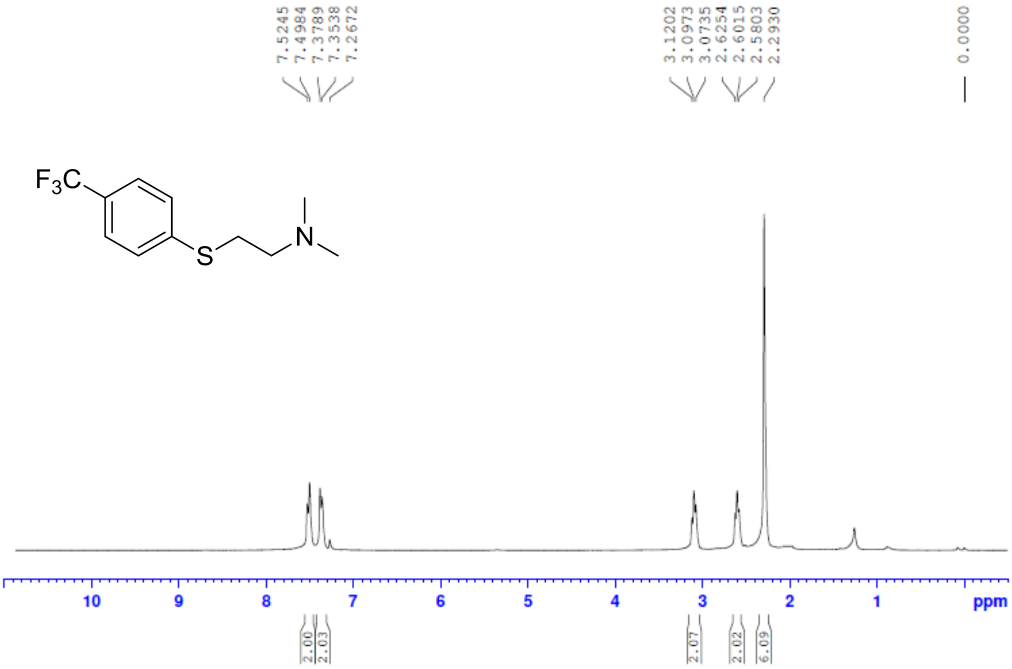

Figure 79 ^{1}H NMR spectrum of compound **5c** (300 MHz, $CDCl_3$)

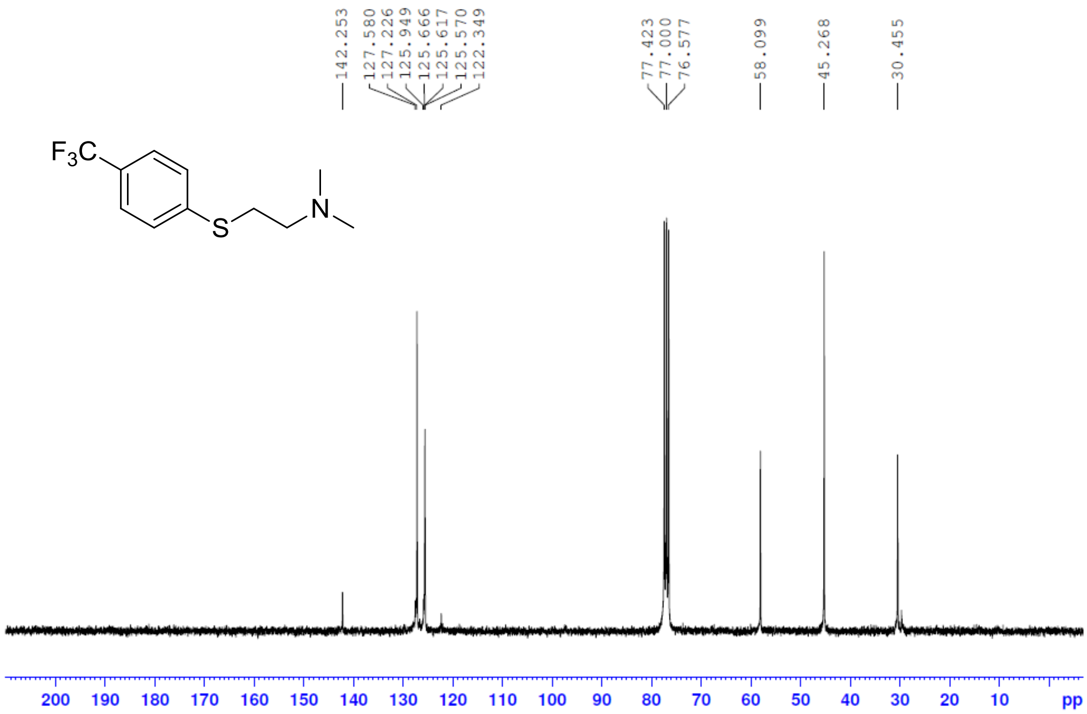

Figure 80 ^{13}C NMR spectrum of compound **5c** (75 MHz, $CDCl_3$)

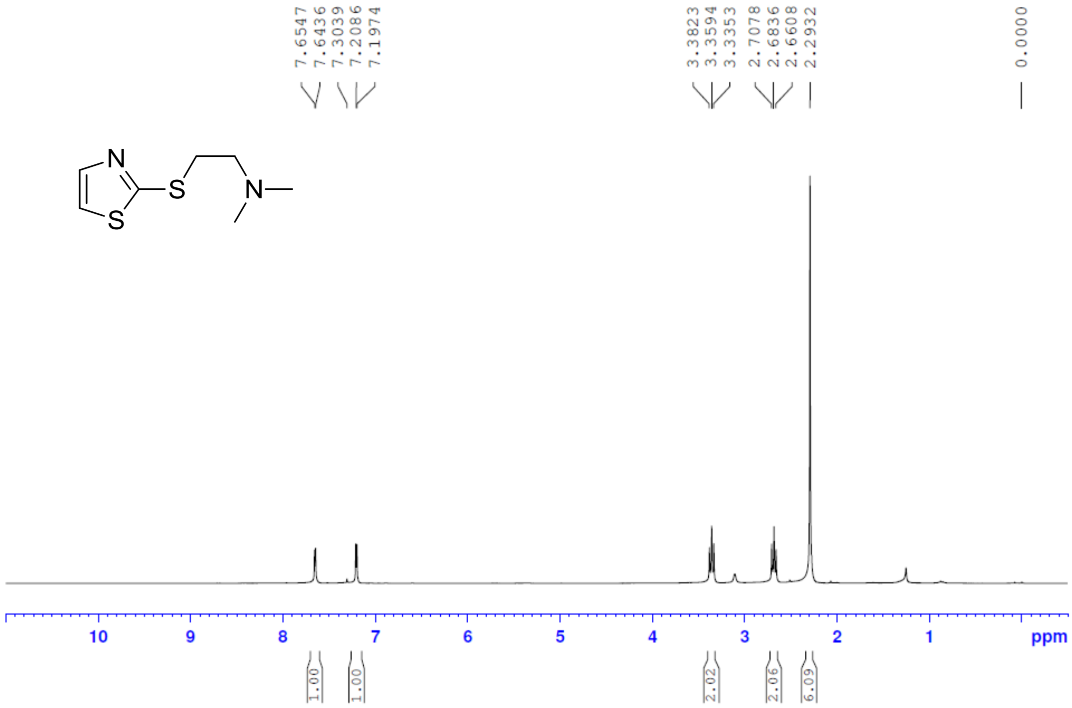

Figure 81 ^{1}H NMR spectrum of compound **5d** (300 MHz, $CDCl_3$)

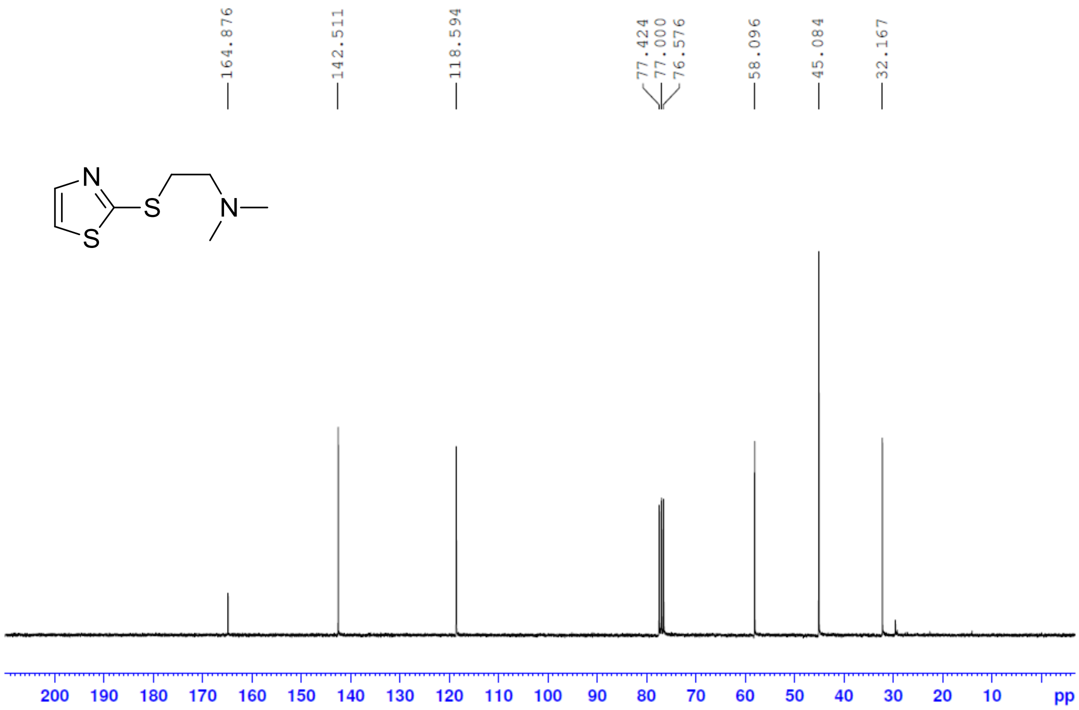

Figure 82 ^{13}C NMR spectrum of compound **5d** (75 MHz, $CDCl_3$)

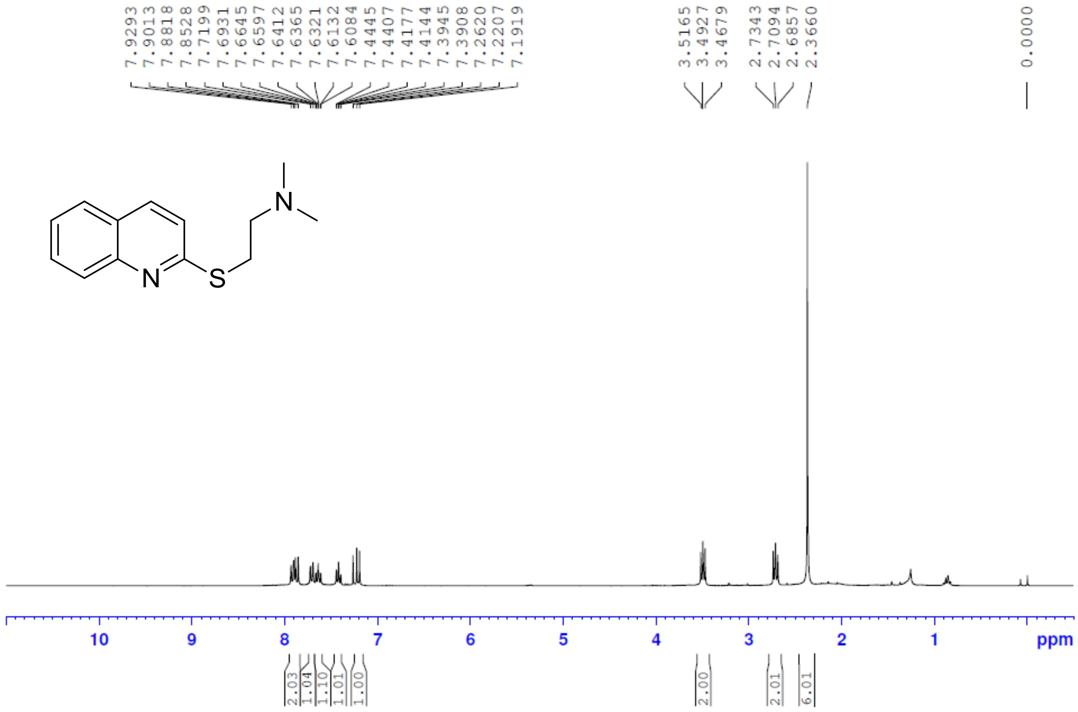

Figure 83 ^{1}H NMR spectrum of compound **5e** (300 MHz, $CDCl_3$)

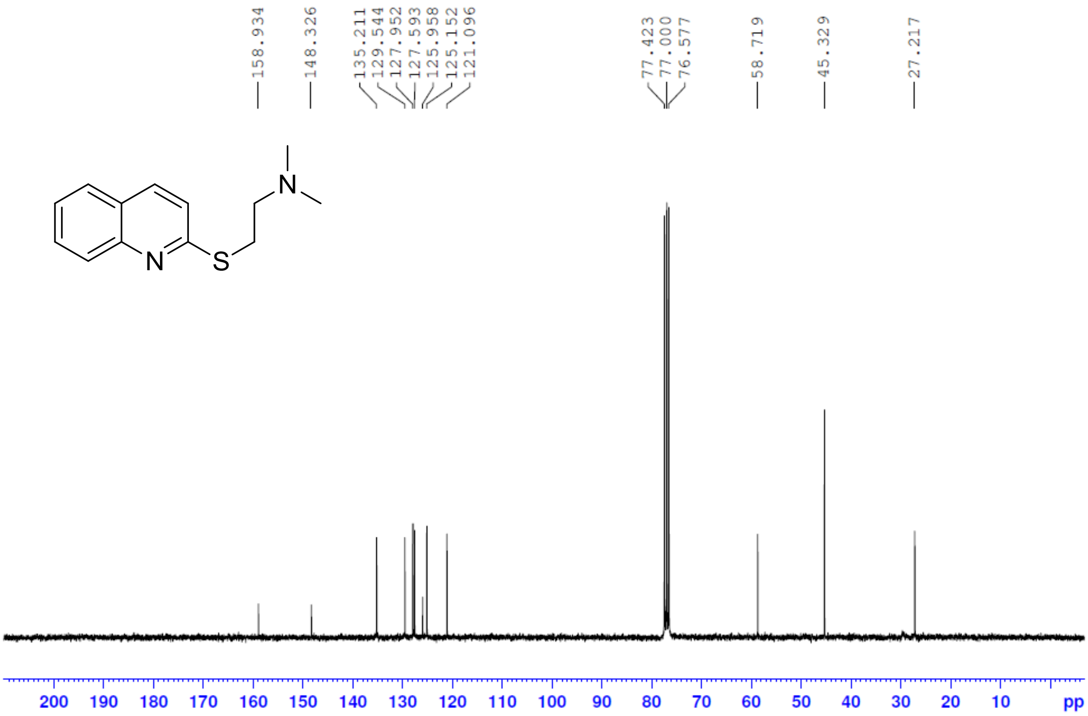

Figure 84 ^{13}C NMR spectrum of compound **5e** (75 MHz, $CDCl_3$)

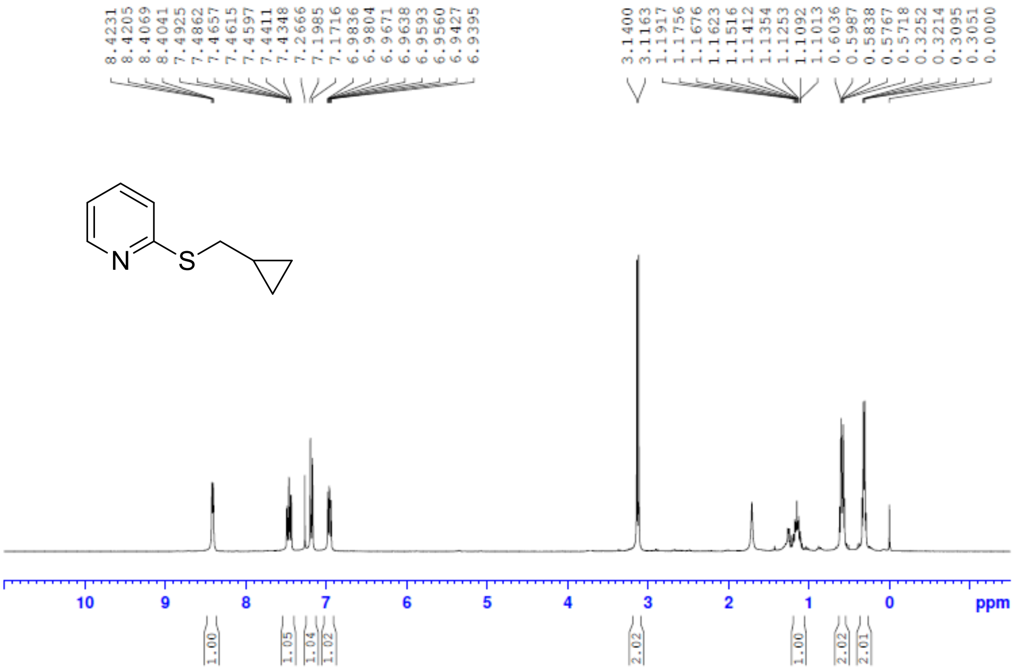

Figure 85 ^{1}H NMR spectrum of compound **5f** (300 MHz, $CDCl_3$)

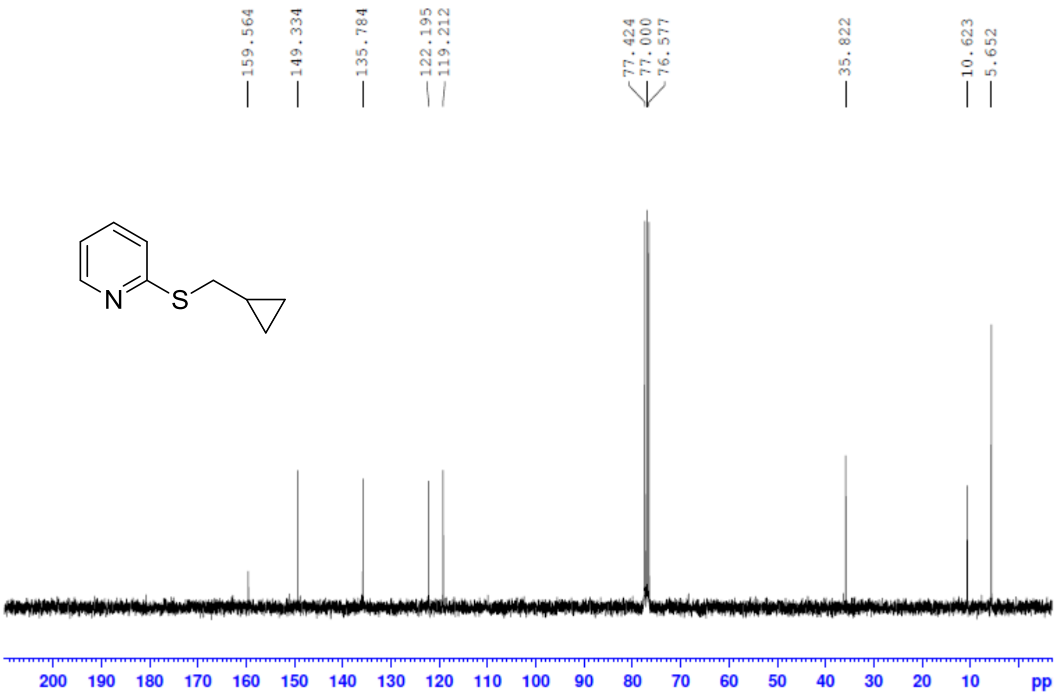

Figure 86 ^{13}C NMR spectrum of compound **5f** (75 MHz, $CDCl_3$)

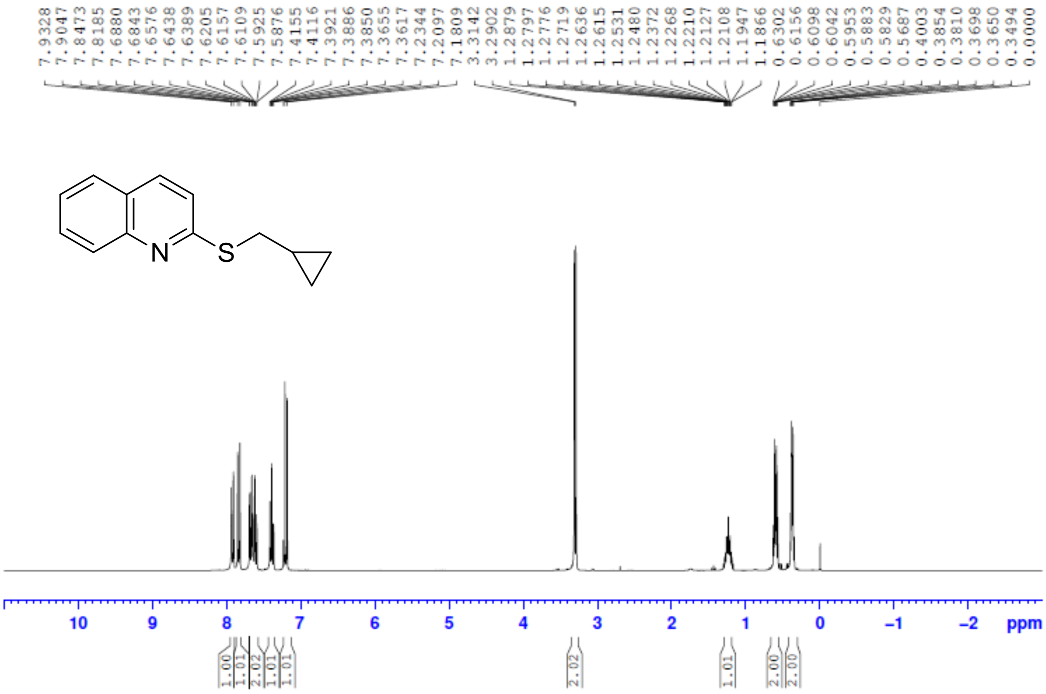

Figure 87 ^{1}H NMR spectrum of compound **5g** (300 MHz, $CDCl_3$)

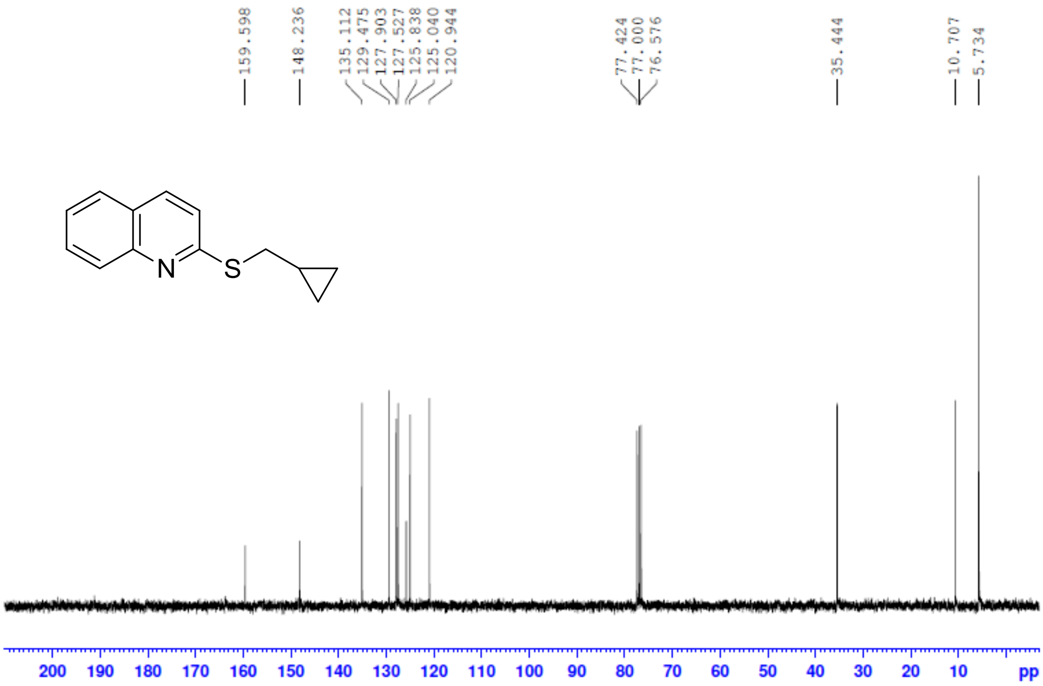

Figure 88 ^{13}C NMR spectrum of compound **5g** (75 MHz, $CDCl_3$)