Supporting Information
for

‘Sulfamic-acid-catalyzed conversion of 2-aminothiophenol and aromatic aldehydes to 2-arylbenzothiazoles’

Xiaofeng Yu, *[1] Renyuan Song,[1] Chunjie Shi[1] and Guangrong Wang[1]

[1]*School of Materials and Chemical Engineering, Bengbu University, Bengbu, Anhui 233030, P. R. China*

E-mail: feiyu@mail.ustc.edu.cn

Supporting Information

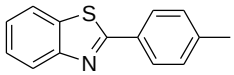
Table of contents

I. General Information

^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature on the spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The chemical-shifts scale is based on internal TMS.

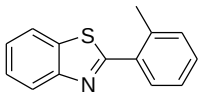
II. Characterization Data of the Products

2-*p*-Tolyl-benzothiazole (a)[1-3]



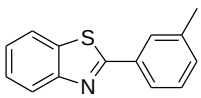
White solid; 98.3% yield; mp 88–90°C. IR (KBr): 3075, 2940, 1440, 1400, 752, 451 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.0 Hz, 1 H), 8.00 (d, *J* = 7.9 Hz, 2 H), 7.90(d, *J* = 8.0 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.40 (t, *J* = 8.2 Hz, 1 H), 7.32(t, *J* = 8.5 Hz, 2 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 155.2, 143.1, 136.3, 132.0, 131.1, 128.5, 127.2, 126.0, 124.1, 122.2, 22.5. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{14}H_{11}NS$: 225.06; found: 225.07.

2-*o*-Tolyl-benzothiazole (b)[1-3]



White solid; 90.1% yield; mp 63–65°C. IR (KBr): 3050, 2945, 1455, 1412, 756, 723 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.12 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.1 Hz, 1H), 7.41–7.29 (m, 4H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.9, 154.1, 137.2, 134.6, 132.9, 130.9, 129.5, 129.0, 126.5, 125.3, 123.9, 122.4, 22.6. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{14}H_{11}NS$: 225.06; found: 225.09.

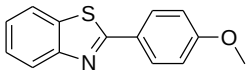
2-*m*-Tolyl-benzothiazole (c)[1-3]



White solid; 92.5% yield; mp 65–66°C. IR (KBr): 3077, 2940, 1458, 1421, 758, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.09 (d, *J* = 8.1 Hz, 1H), 7.93 (s, 1H), 7.89–7.85 (m, 2H), 7.51–7.50 (t, *J* = 8.1 Hz, 1H), 7.39 (m, 2H), 7.31 (m, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.5, 154.1, 139.1, 135.2, 133.4, 131.5, 128.7, 127.8, 126.5, 125.3, 125.1, 123.4, 121.8, 21.5. HRMS (EI): *m*/*z* $[M]^+$calcd for

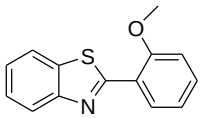
$C_{14}H_{11}NS$: 225.06; found: 225.08.

2-(4-Methoxyphenyl)benzothiazole (d)[2, 4]



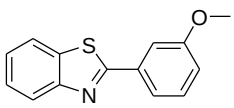
White solid; 91.2% yield; mp 120–122°C. IR (KBr): 3061, 2982, 1603 1489, 756, 735. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10–8.06 (m, 3H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 8.3 Hz, 1H), 7.03–6.99 (m, 2H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 161.7, 155.1, 135.2, 130.1, 126.5, 126.4, 124.5, 122.6, 121.4, 114.3, 55.1. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{11}NOS$: 241.06; found: 241.05.

2-(2-Methoxyphenyl) benzothiazole (e)[1]



White solid; 87.2% yield; mp 109–110°C. IR (KBr): 3058, 2845, 1628, 1523, 1365, 758, 728 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 8.0 Hz, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.93 (t, *J* = 8.0 Hz, 1 H), 7.44-7.49 (m, 2 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1 H), 6.96 (d, *J* = 7.9 Hz, 1 H), 4.06 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 158.1, 157.8, 140.0, 138.0, 127.2, 125.3, 123.8, 121.5, 119.2, 109.9, 106.1, 104.6, 59.9. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{14}H_{11}NOS$: 241.06; found: 241.07.

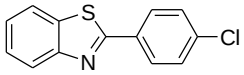
2-(3-Methoxyphenyl) benzothiazole (f)[1, 4]



White solid; 88.5% yield; mp 83–85°C. IR (KBr): 3062, 2855, 1629, 1521, 1345, 750, 712 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.1, 1 H), 7.90 (d, *J* = 8.0 Hz,

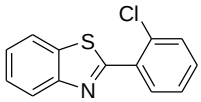
1 H), 7.43 (m, *J* = 7.9, Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.19 (t, *J* = 7.9 Hz, 1 H), 6.97-6.95 (m, 2 H), 6.95 (d, *J* = 7.9 Hz, 1 H), 3.56 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.1, 160.2, 154.3, 135.5, 135.1, 130.4, 126.5, 125.4, 123.6, 121.9, 120.6, 117.6, 112.4, 55.8. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{14}H_{11}NOS$: 241.06; found: 241.04.

2-(4-Chlorophenyl)benzothiazole (g)[2, 5]



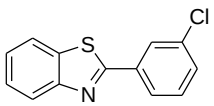
Yellow solid; 97.9% yield; mp 116–118°C. IR (KBr): 3058, 2930, 1570, 1448, 1326, 760, 755. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08-8.02 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.53-7.46 (m, 3H), 7.40 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.1, 141.2, 136.1, 135.0, 129.8, 128.9, 128.2, 126.1, 121.0, 120.5. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_8ClNS$: 245.01; found: 245.02.

2-(2-Chlorophenyl)benzothiazole (h)[2, 5]



Yellow solid; 92.8% yield; mp 85–87°C. IR (KBr): 3078, 1430, 1312, 1226, 762, 730. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.21–8.19 (m, 1H), 8.15 (d, *J* = 8.0, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.56–7.54 (m, 2H), 7.46–7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 152.7, 136.3, 132.9, 132.5, 131.9, 131.2, 130.9, 127.3, 126.5, 125.7, 123.6, 121.5. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_8ClNS$: 245.01; found: 245.03.

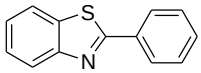
2-(3-Chlorophenyl)benzothiazole (i)[2, 5]



Yellow solid; 94.3% yield; mp 98–100°C. IR (KBr): 3090, 1436, 1323, 1235, 756,

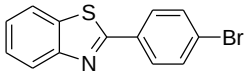
735. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09-8.05 (m, 2H), 7.90-7.86(m, 2H), 7.50-7.48 (m, 1H), 7.43-7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 155.0, 136.0, 135.5, 135.2, 131.8, 131.2, 128.5, 127.6, 126.6, 125.9, 123.8, 121.9. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_8ClNS$: 245.01; found: 245.01.

2-phenylbenzothiazole (j)[2, 5]



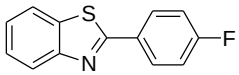
White solid (yield: 97.5%); mp 112-114ºC. IR (KBr): 3060, 2953, 1572, 1451, 1330, 758, 745. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12-8.07 (m, 3H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.51-7.49 (m, 3H), 7.36(t, *J* = 8.0 Hz, 1H), 7.28(t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 155.0, 134.8, 133.9, 131.6, 129.8, 128.0, 127.0, 125.3, 123.6, 121.9. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_{10}NS$: 211.05; found: 211.09.

2-(4-Bromophenyl)benzothiazole (k)[2, 5]



Yellow solid (yield: 93.4%); mp 130-132ºC. IR (KBr): 3066, 1438, 1227, 744, 732. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 154.9, 136.8, 134.9, 131.8, 128.5, 126.6, 125.1, 122.9, 122.5. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_8BrNS$: 290.2; found: 290.1.

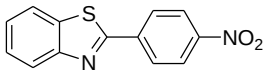
2-(4-Fluorophenyl)benzothiazole (l)[2, 5]



White solid (yield: 90.1%); mp 102-104ºC. IR (KBr): 3056, 1482, 1229, 758, 727. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09–8.04 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.47 (m, 1H), 7.35 (m, 1H), 7.21–7.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 165.5, 163.1, 153.9, 134.8, 129.9, 129.6, 129.4, 129.3, 126.3, 125.1, 123.3, 121.8, 116.3,

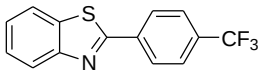
116.1. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_8FNS$: 229.3; found: 229.5.

2-(4-Nitrophenyl)benzothiazole (m)[2, 5]



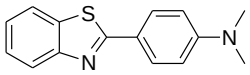
Yellow solid (yield: 40.5%); mp 130-132°C. IR (KBr): 3045, 1446, 1230, 746, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (d, *J* = 8.0 Hz, 2H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 154.3, 149.6, 139.1, 136.0, 127.1, 128.06, 127.1, 125.8, 122.6, 122.8. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{13}H_8N_2O_2S$: 256.3; found: 256.2.

2-[4-(Trifluoromethyl)phenyl]-benzothiazole (n)[2, 6]



White solid; 65.1% yield; mp 159–161°C. IR (KBr): 3045, 1638, 1456, 1432, 1078, 985, 789 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.0 Hz, 2 H), 8.11 (d, *J* = 8.0 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 154.1, 136.8, 135.2, 132.5 (q, *J* = 32.6 Hz), 127.8, 126.7, 126.5(q, J = 3.7 Hz), 126.02, 123.6 (q, J = 273.4 Hz), 121.7, 119.8. HRMS (EI): *m*/*z* $[M]^+$calcd for $C_{14}H_8F_3NS$: 279.03; found: 279.01.

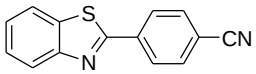
2-[4-(N, N-dimethyl)phenyl]-benzothiazole (o)[2, 5] .



White solid; 95.6% yield; mp 167–169°C. IR (KBr): 3080, 1445, 1287, 1232, 749, 735. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.95 (m, 3H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.43(t, *J* = 8.1 Hz, 1H), 7.30(t, *J* = 8.1 Hz, 1H), 6.76- 6.74 (d, *J* = 8.8 Hz, 2H), 3.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 158.6, 156.1, 138.4, 131.1, 128.3, 126.1,

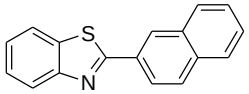
124.1, 120.9, 118.8, 111.0, 39.7. HRMS (EI): *m/z* $[M]^+$calcd for $C_{15}H_{11}N_2S$: 254.09; found: 254.10.

2-(4-Cyanophenyl)benzothiazole(p).



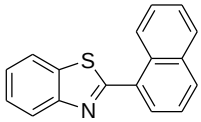
White solid; 90.2% yield; mp 168–170°C. IR (KBr): 3079, 1445, 1258, 1239, 755, 732. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22−8.20 (m, 2 H), 8.14 (d, J = 8.1 Hz, 1 H), 7.96 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2 H), 7.62−7.60 (m, 1 H), 7.53−7.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 154.8, 138.4, 136.5, 133.1, 128.1, 127.2, 126.3, 123.9, 121.9, 118.6, 114.3. HRMS (EI): *m/z* $[M]^+$calcd for $C_{14}H_{11}N_2S$: 236.3; found: 236.1.

2-(Naphthalen-3-yl)benzothiazole (q) [2, 5]



White solid; 96.2% yield; mp 127–129 °C. IR (KBr): 3056, 1503, 1432, 1365, 1225, 756, 724. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.98-7.93 (m, 4H), 7.56-7.54 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 155.1, 135.2, 134.2, 132.0, 129.7, 128.5, 127.7, 126.8, 125.9, 123.2, 122.8, 122.2, 121.5, 120.6, 119.8, 112.1. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{11}NS$: 261.06; found: 261.06.

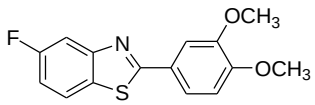
2-(Naphthalen-2-yl)benzothiazole (r) [1]



White solid; 97.1% yield; mp 125–127 °C. IR (KBr): 3066, 1538, 1445, 1348, 1200, 756, 735 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 8.0 Hz, 1 H), 8.18 (d, *J* = 8.0 Hz, 1 H), 7.97 (t, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 7.66 (t, *J* = 8.0 Hz, 1

H),7.62-7.60(m, 3 H), 7.43 (t, *J* = 7.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 152.9, 130.0, 132.9, 131.6, 130.3, 129.1, 127.6, 127.2, 126.6, 126.1, 125.8, 124.6, 124.1, 122.6, 122.3, 120.9. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{11}NS$: 261.06; found: 261.08.

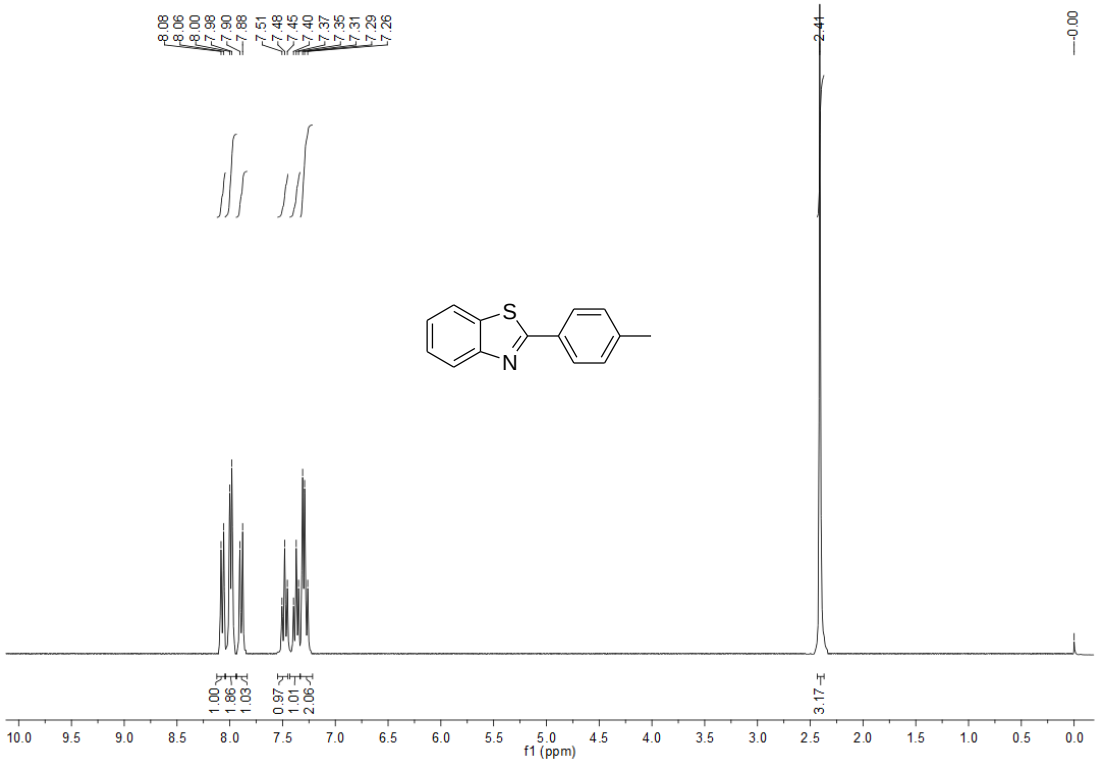
GW610 (5-Fluoro-2-(3,4-dimethoxyphenyl)benzothiazole)[7]

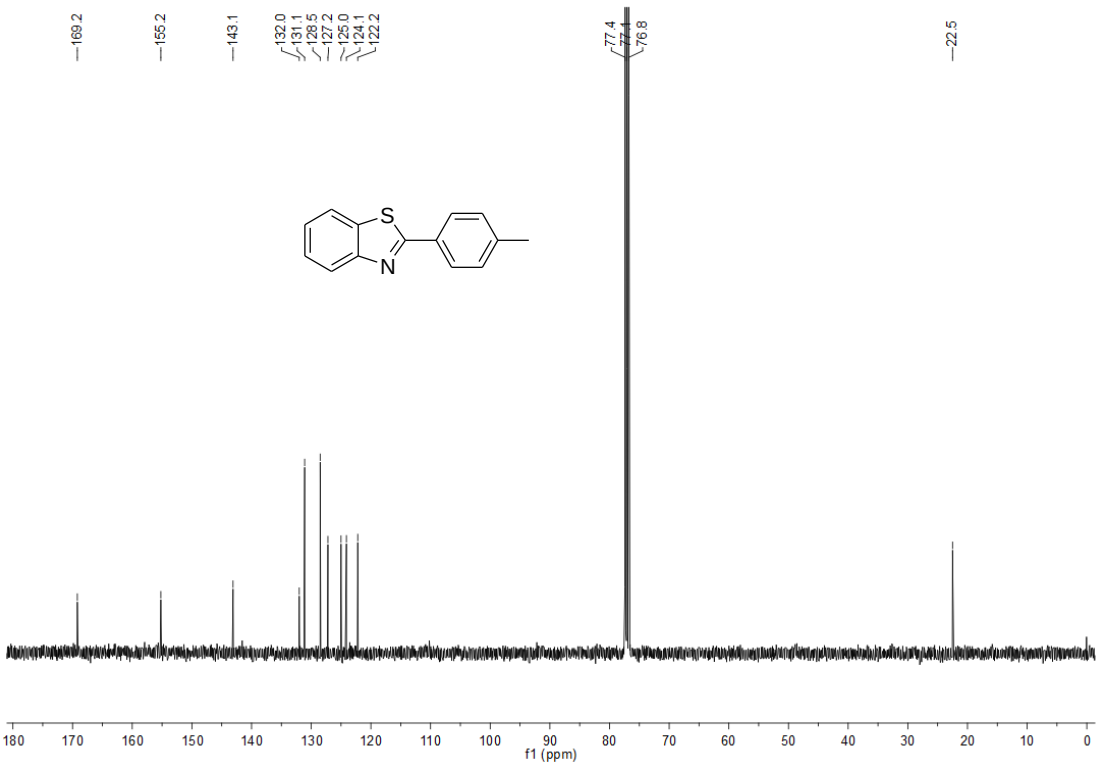


Yellow solid; 71.9% yield; mp 102–104 °C. IR (KBr): 3065, 2988, 1596, 1448, 1226, 856 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.8 Hz, 1H), 7.88 (s, 1H), 7.63(m, 2H,), 7.35 (t, *J* = 9.0 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 160.4, 151.8, 150.6, 149.3, 135.7, 126.3, 123.4, 121.0, 114.6, 111.0, 109.6, 107.6, 56.0, 55.8. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{12}FNO_2S$: 289.3; found: 289.2.

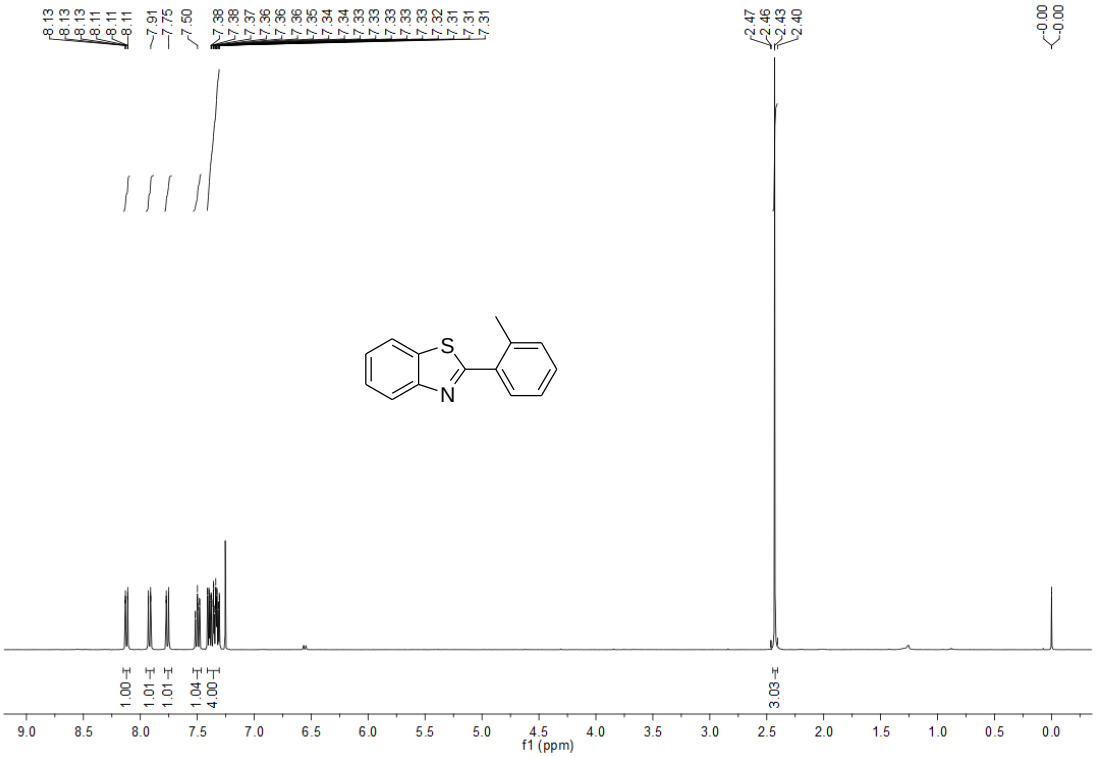
III. NMR Spectra

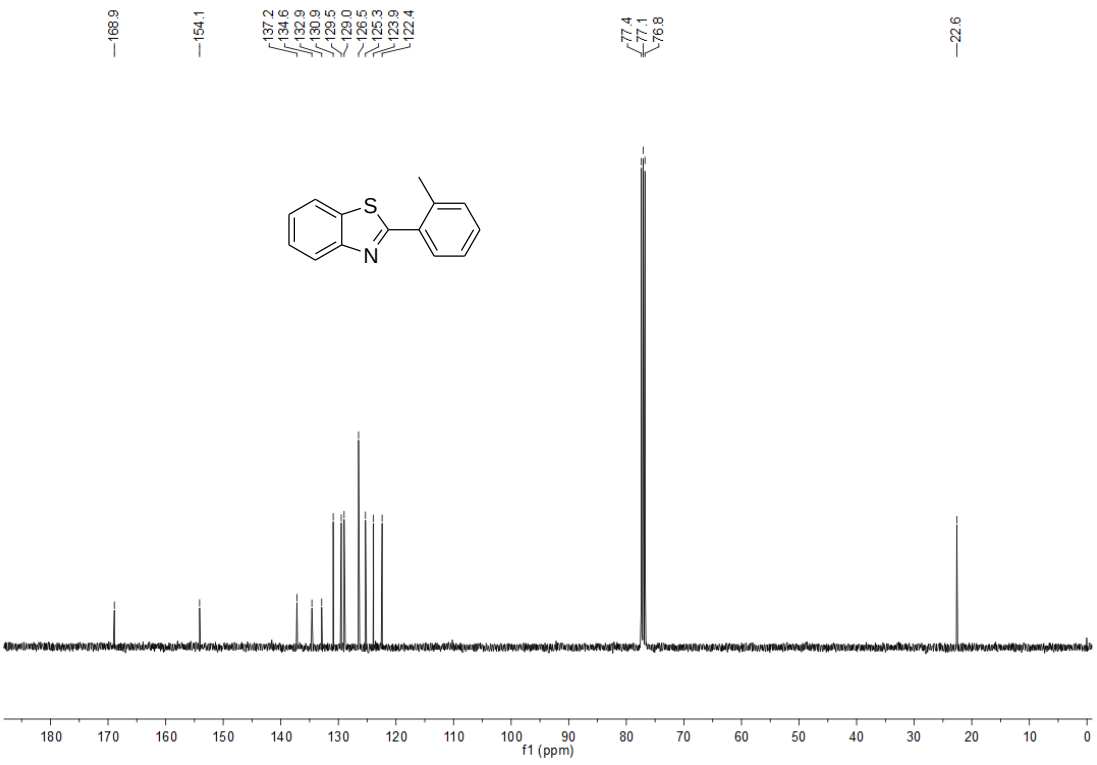
^{1}H NMR and ^{13}C NMR Spectra of 2-*p*-Tolyl-benzothiazole (a)



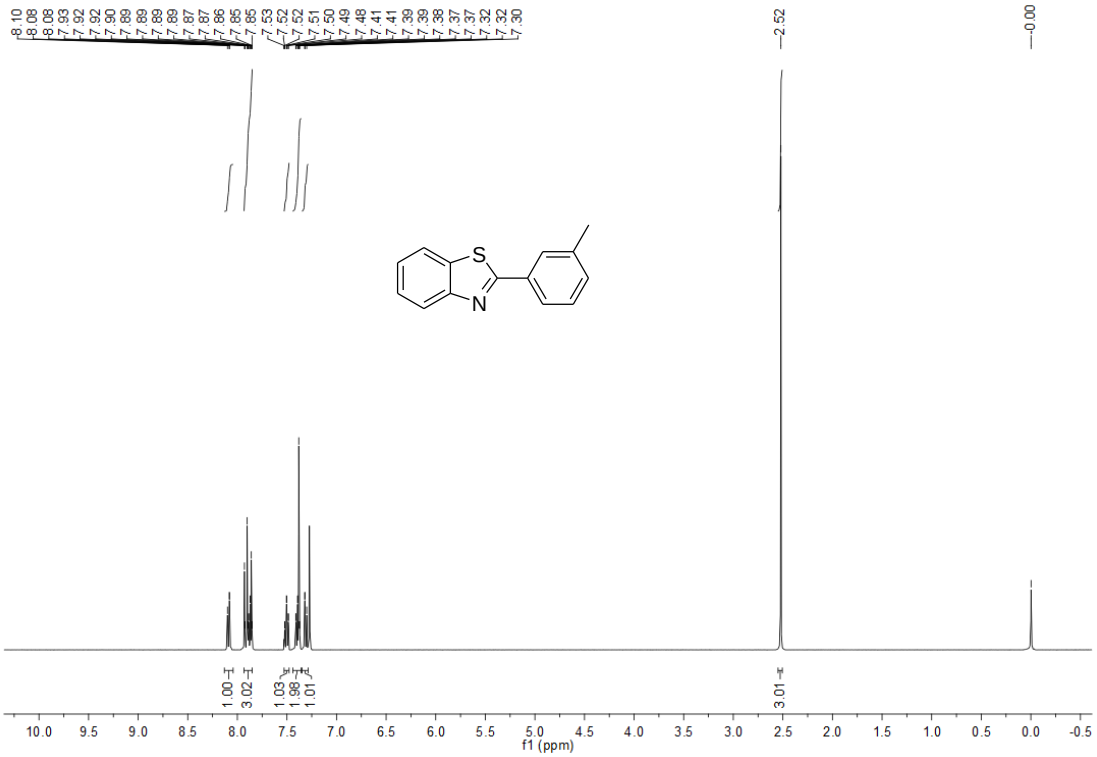


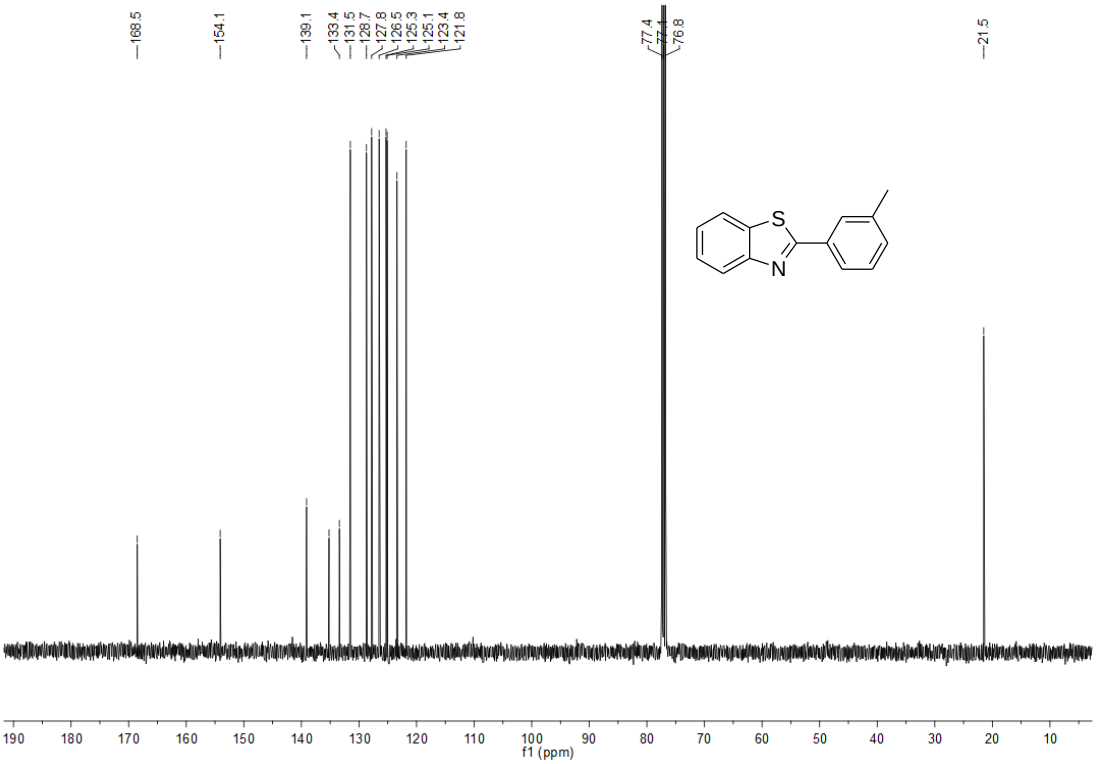
^{1}H NMR and ^{13}C NMR Spectra of 2-*o*-Tolyl-benzothiazole (b)[1-3]



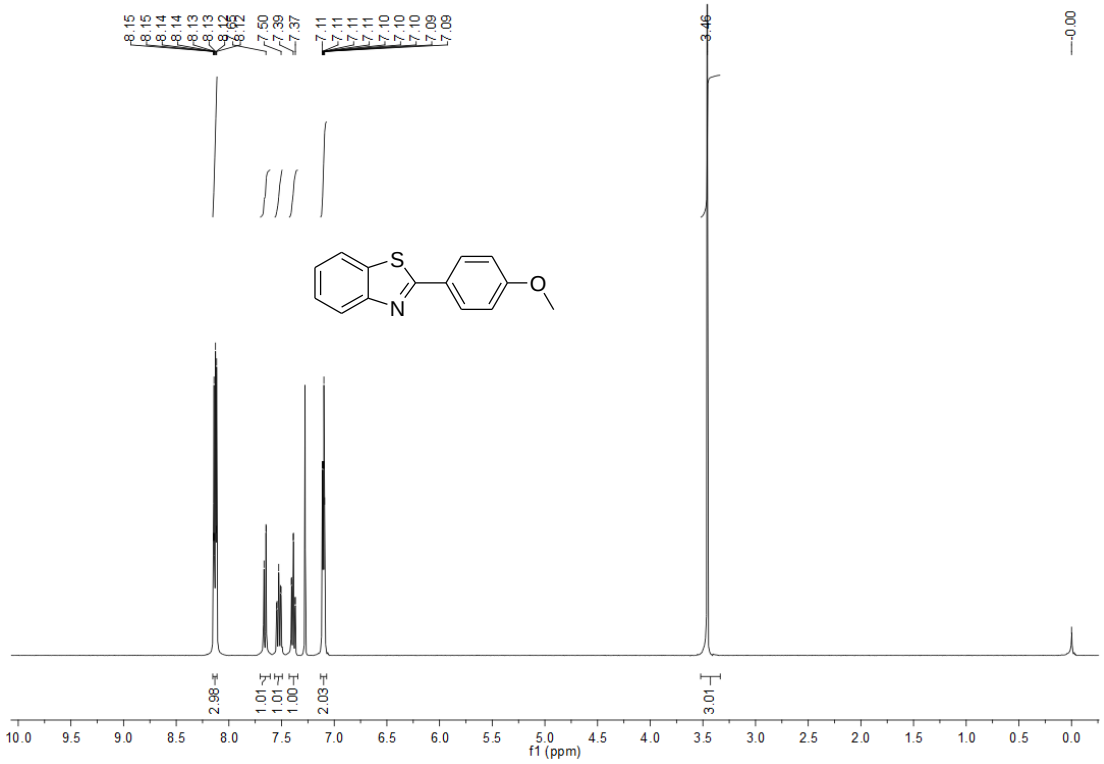


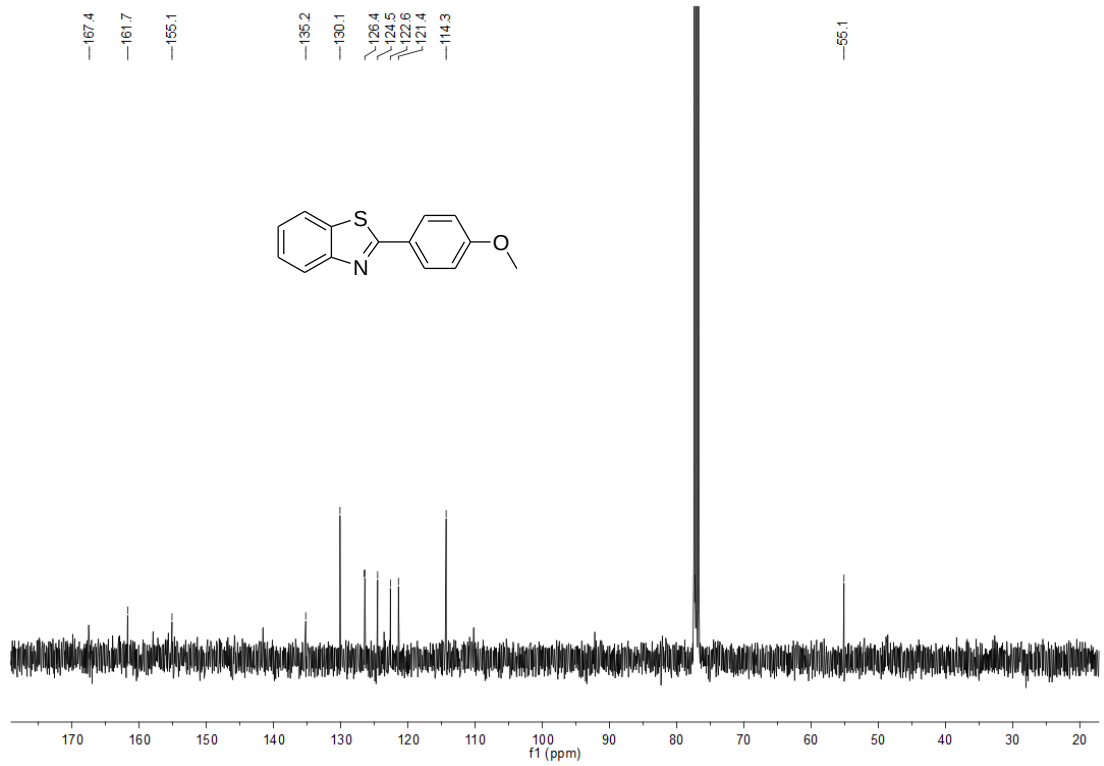
^{1}H NMR and ^{13}C NMR Spectra of 2-*m*-Tolyl-benzothiazole (c)[1-3]



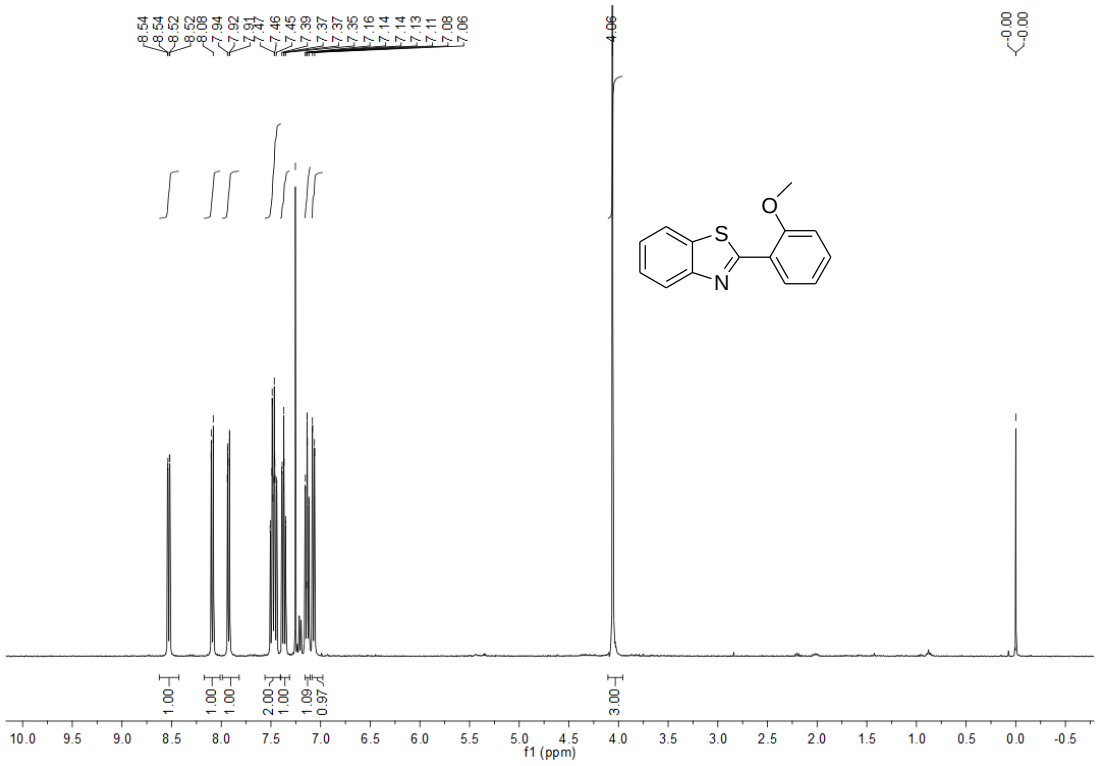


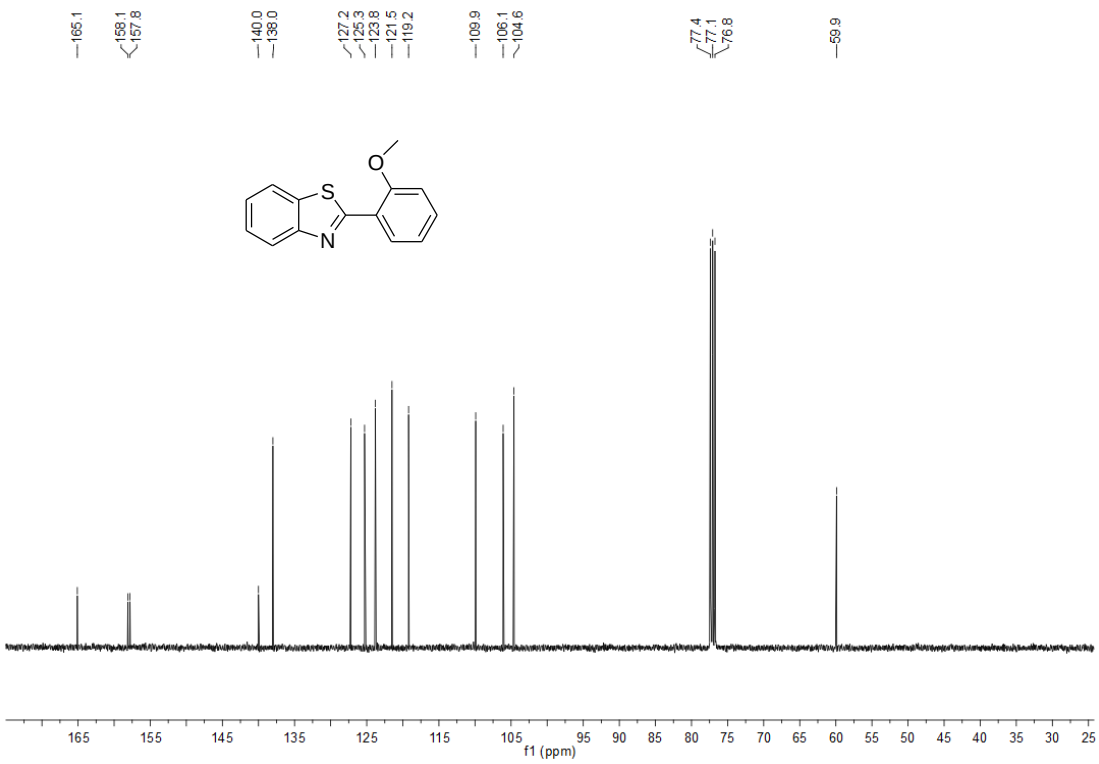
^{1}H NMR and ^{13}C NMR Spectra of 2-(4-Methoxyphenyl)benzothiazole (d)[2, 4]



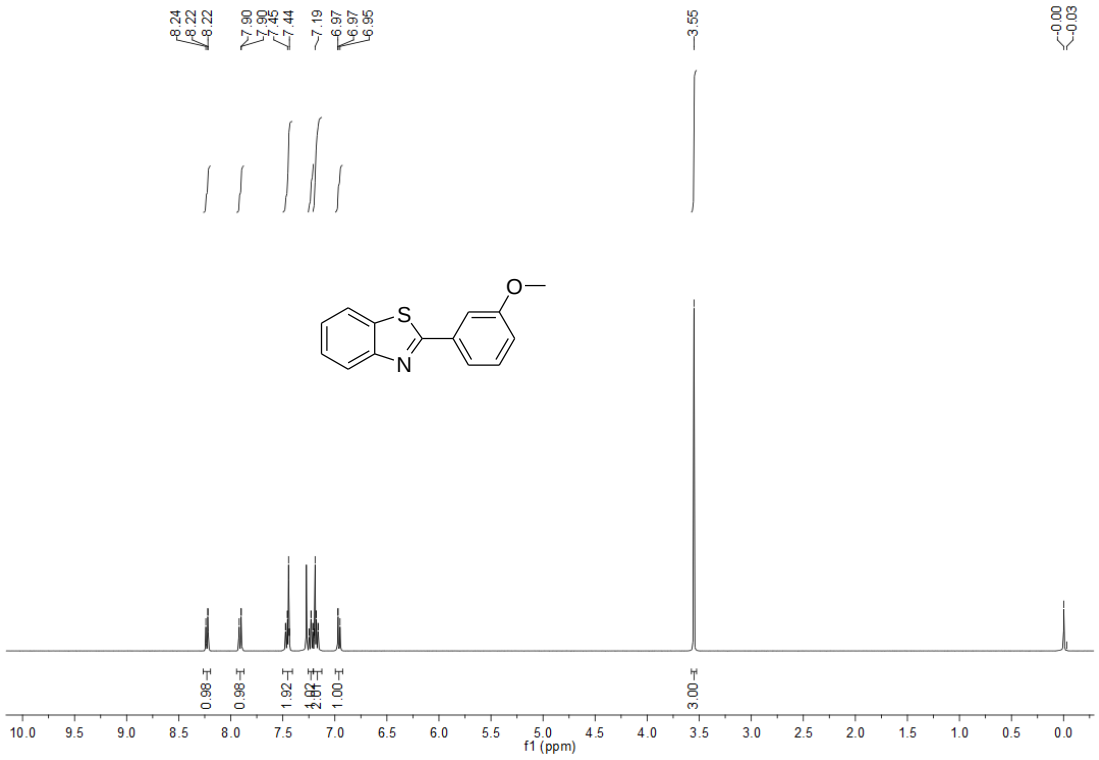


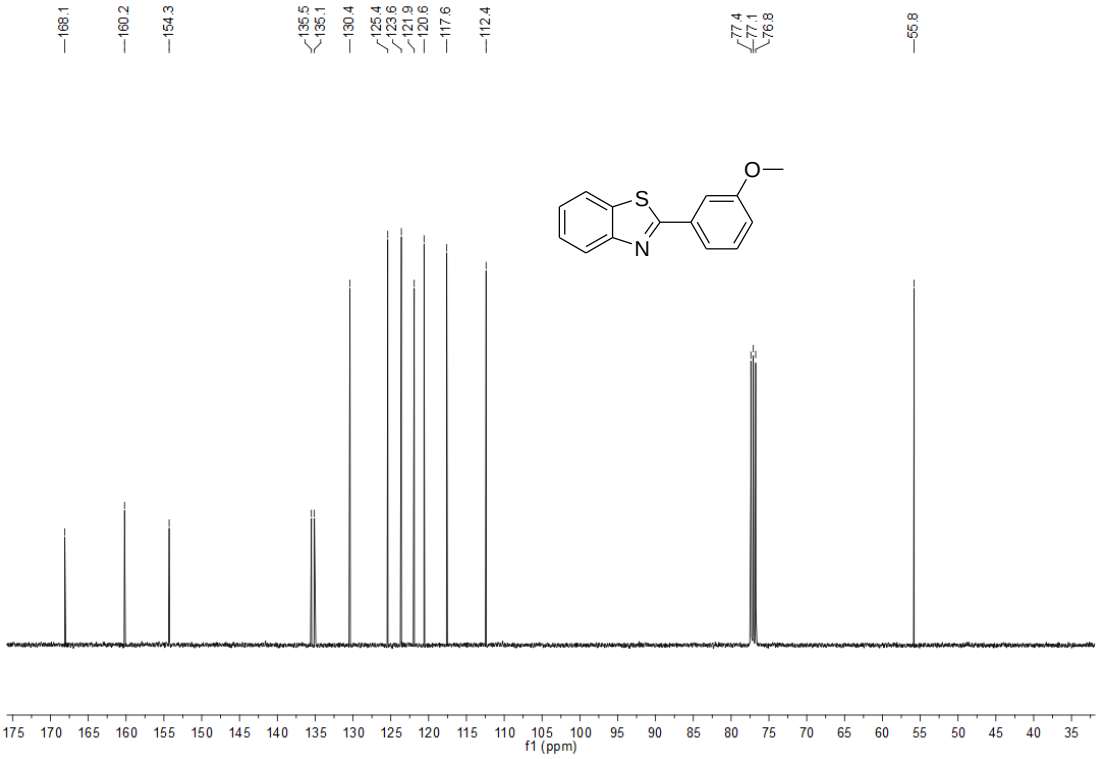
^{1}H NMR and ^{13}C NMR Spectra of 2-(2-Methoxyphenyl) benzothiazole (e)[1]



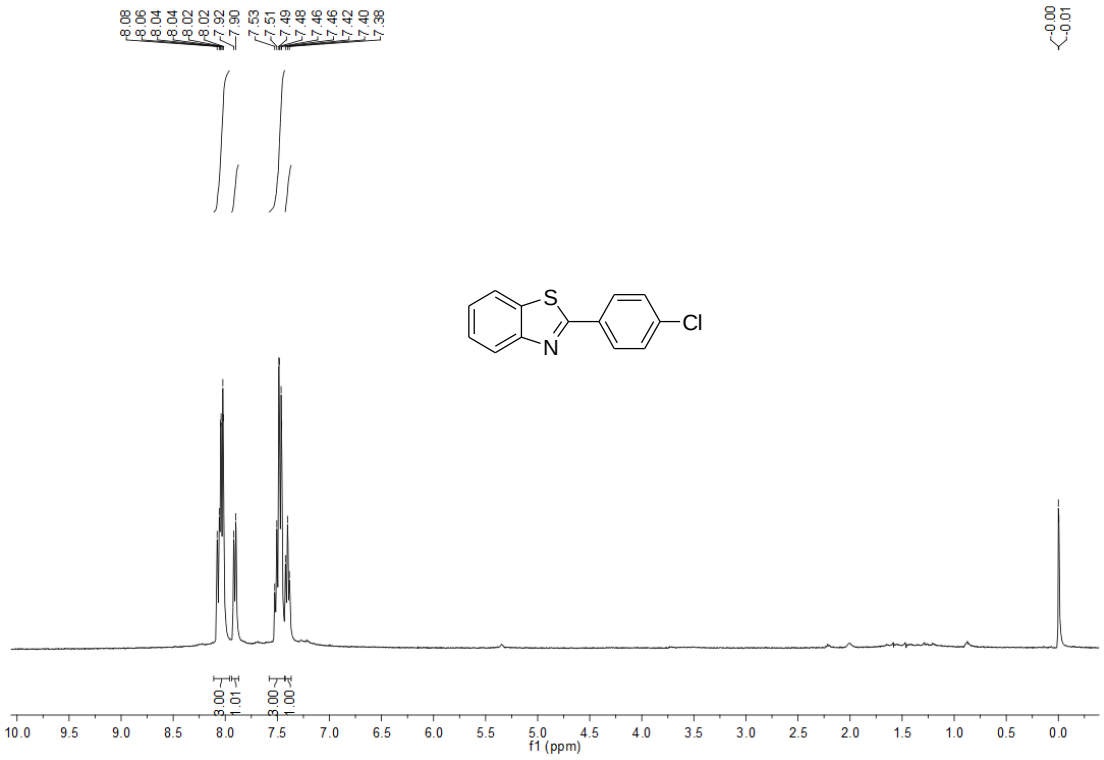


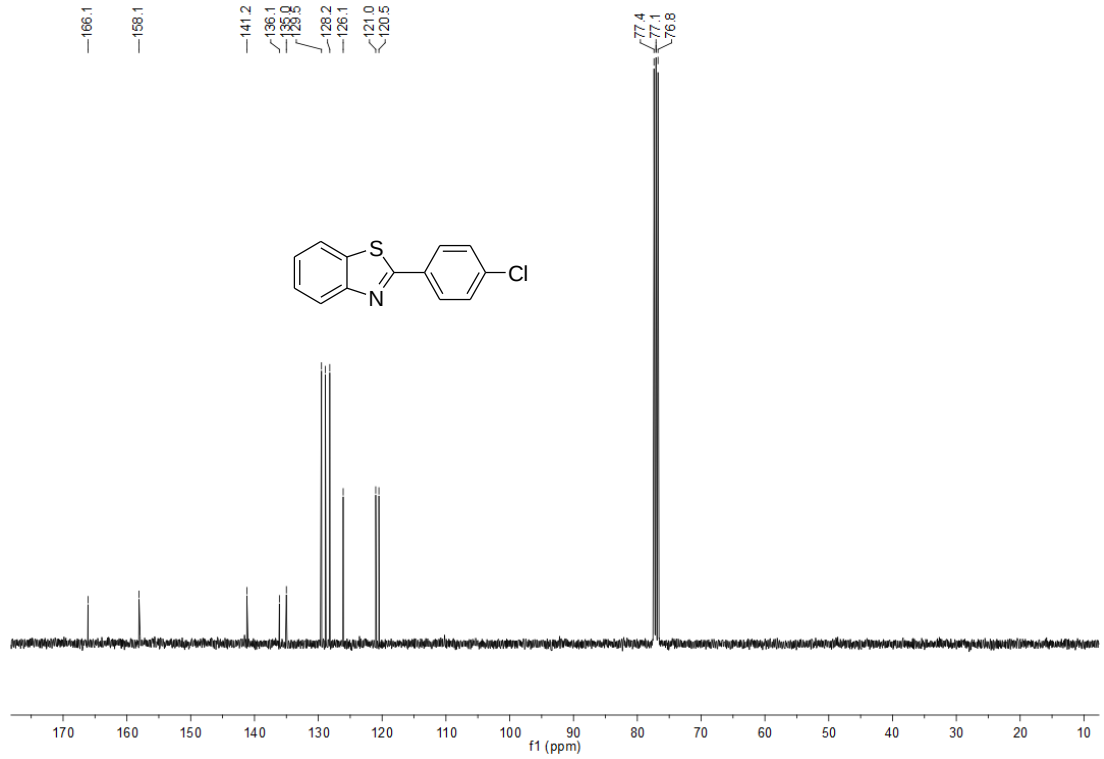
^{1}H NMR and ^{13}C NMR Spectra of 2-(3-Methoxyphenyl) benzothiazole (f)[1, 4]



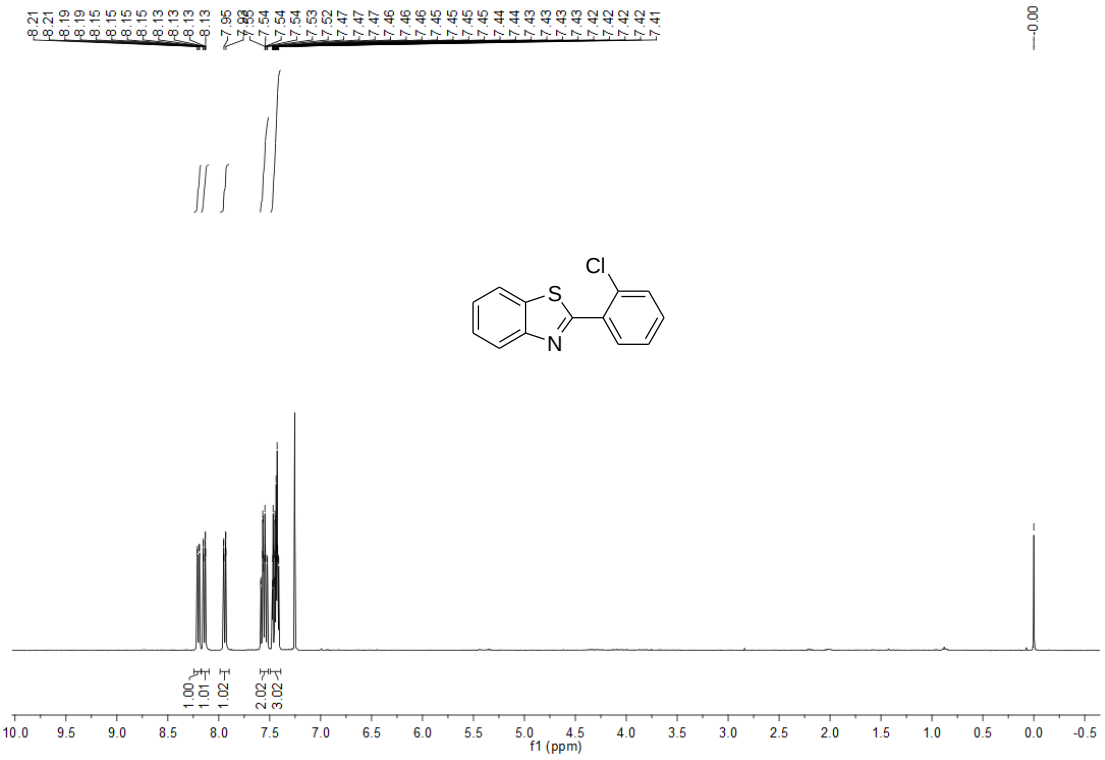


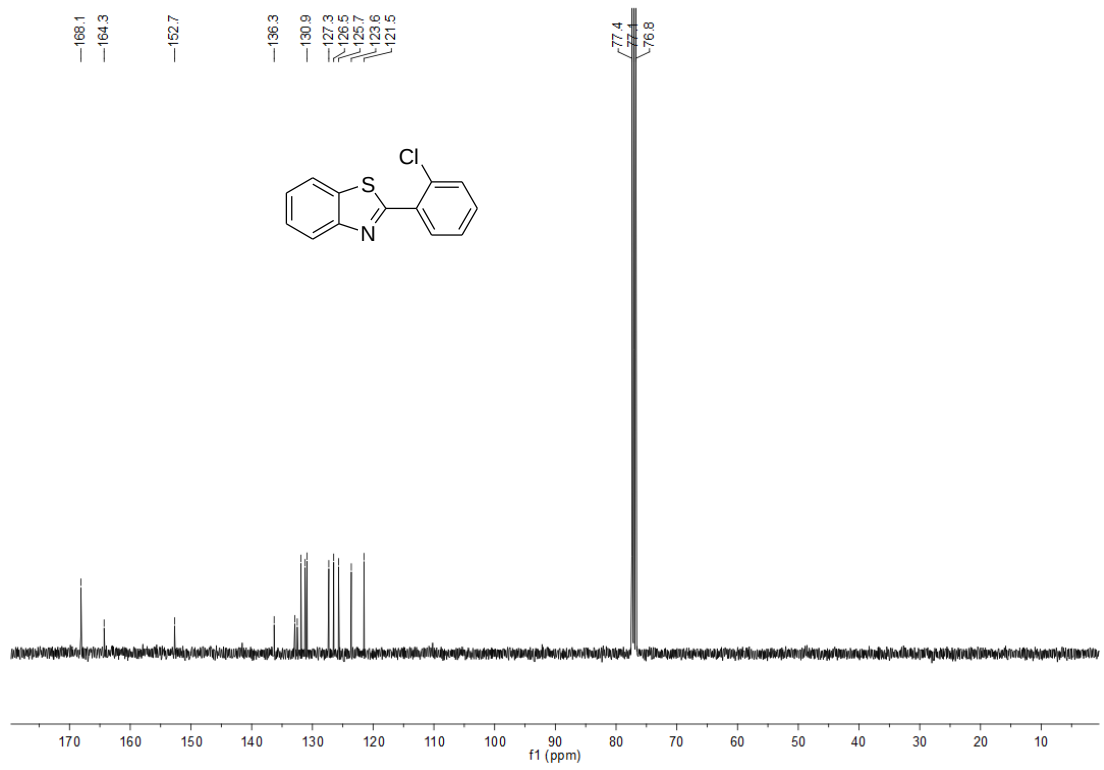
^{1}H NMR and ^{13}C NMR Spectra of 2-(4-Chlorophenyl)benzothiazole (g)[2, 5]



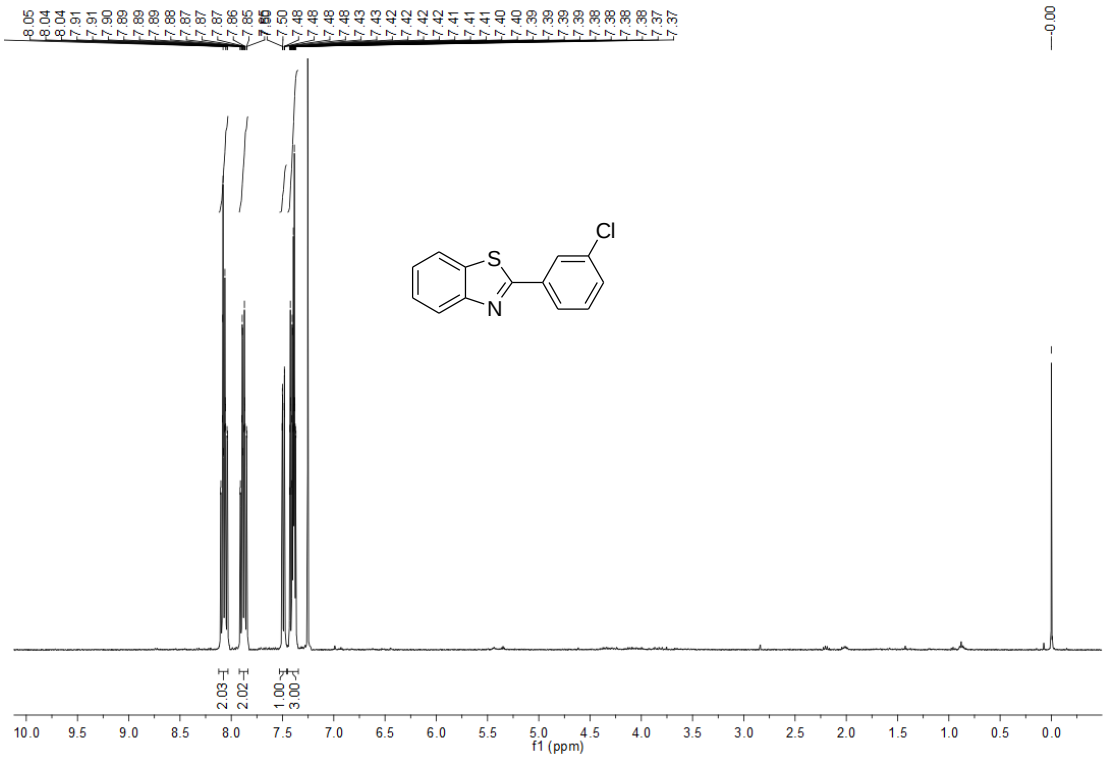


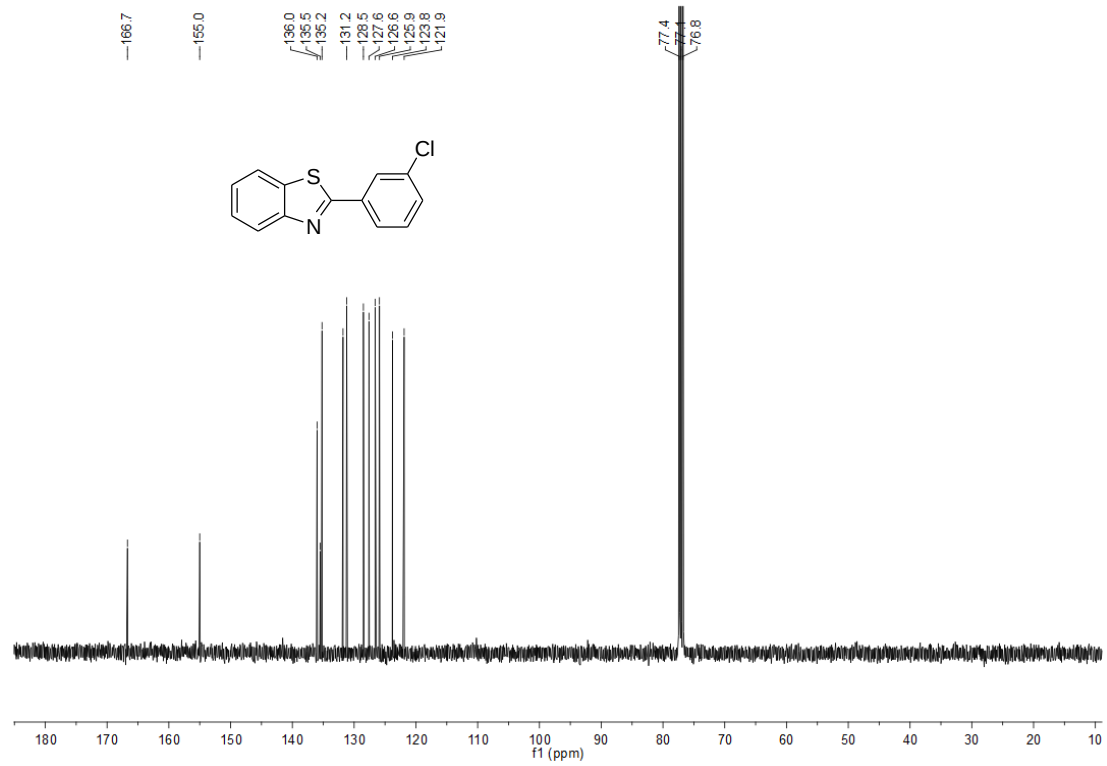
^{1}H NMR and ^{13}C NMR Spectra of 2-(2-Chlorophenyl)benzothiazole (h)[2, 5]



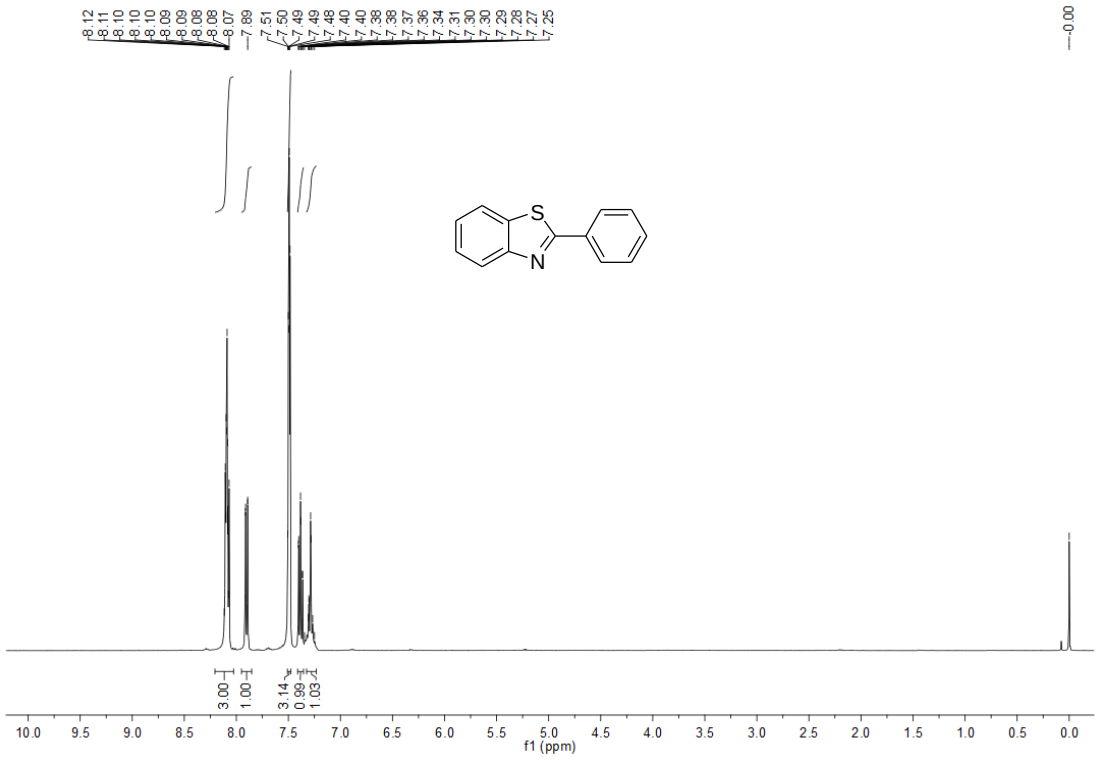


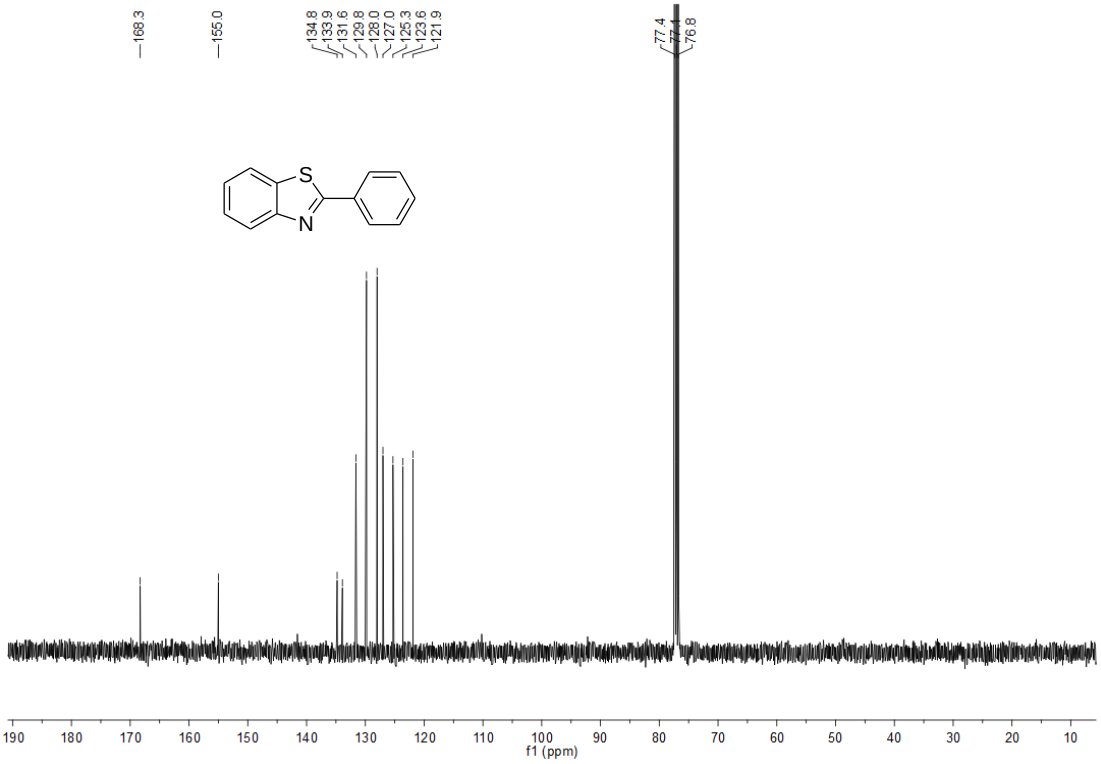
^{1}H NMR and ^{13}C NMR Spectra of 2-(3-Chlorophenyl)benzothiazole (i)[2, 5]



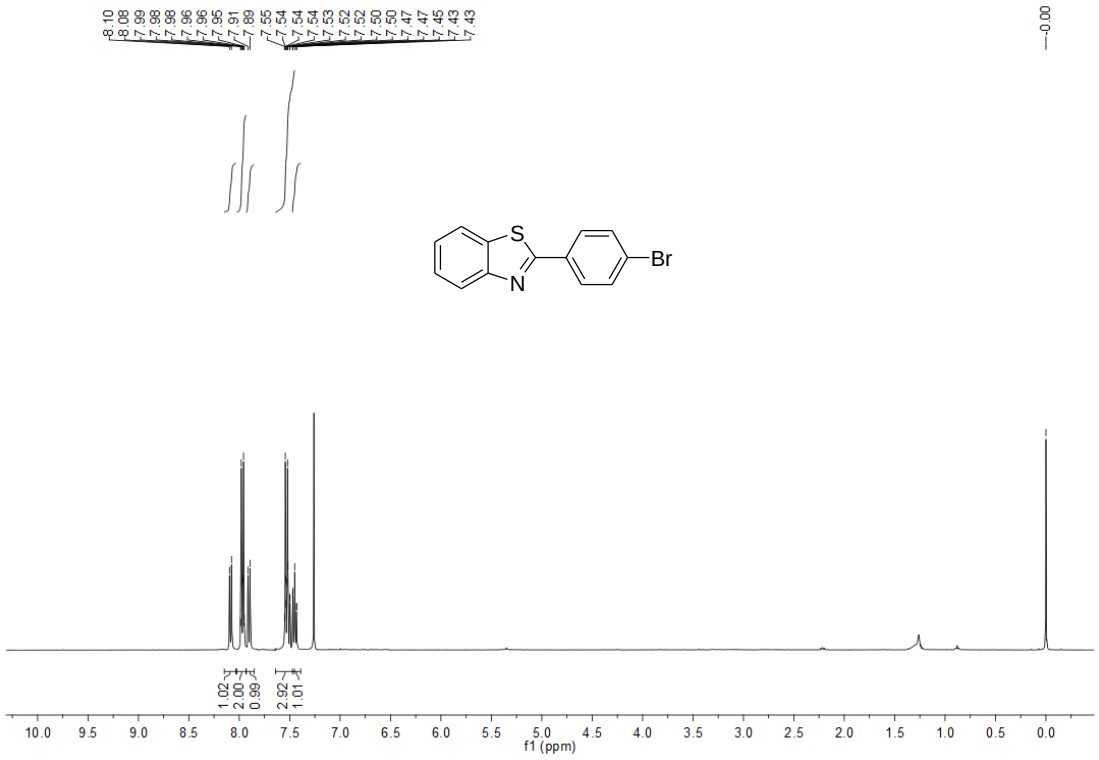


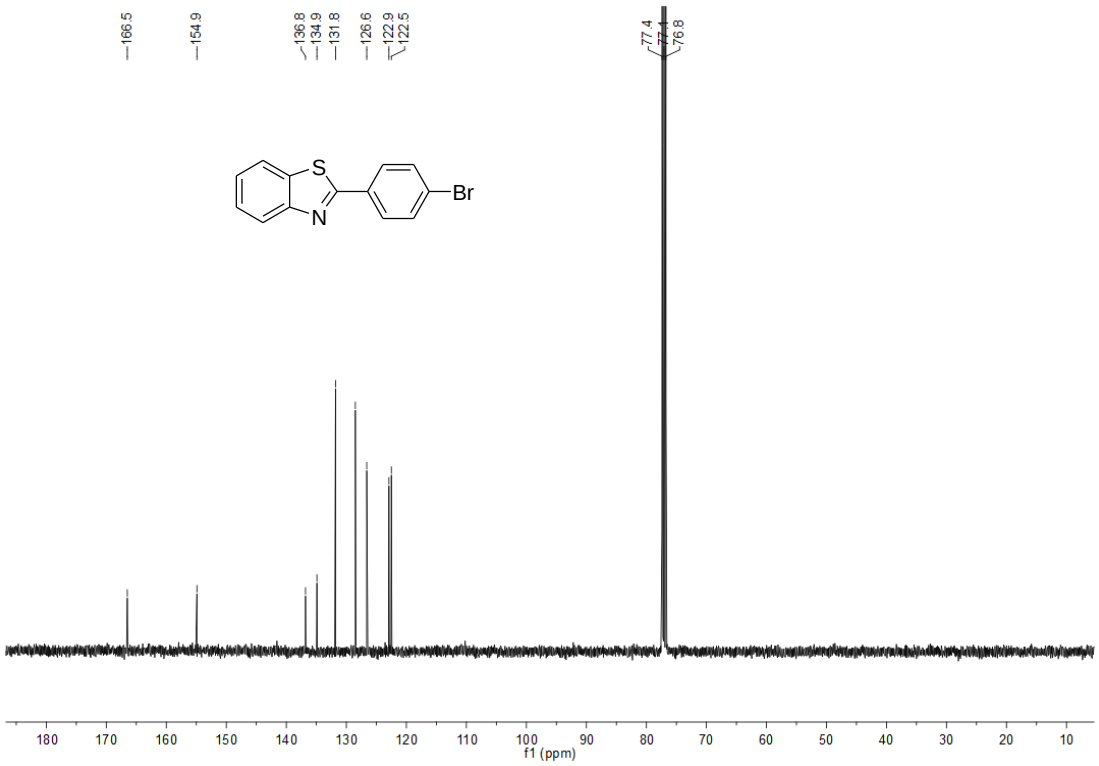
^{1}H NMR and ^{13}C NMR Spectra of 2-phenylbenzothiazole (j)[2, 5]



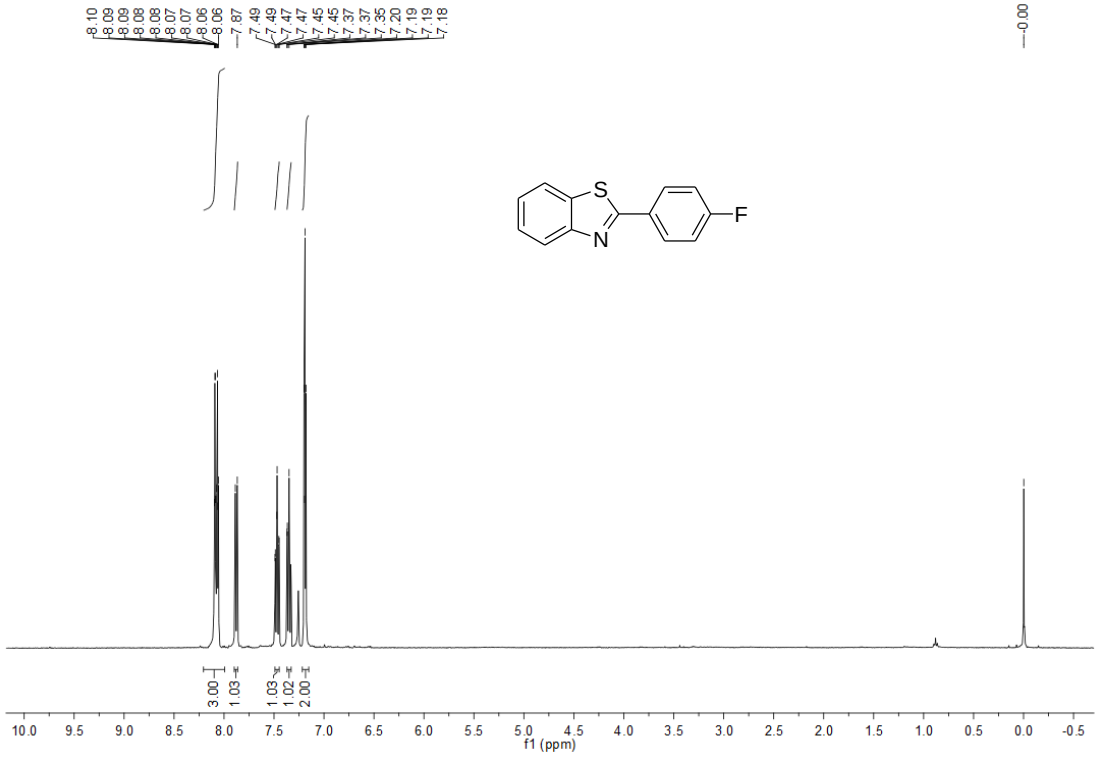


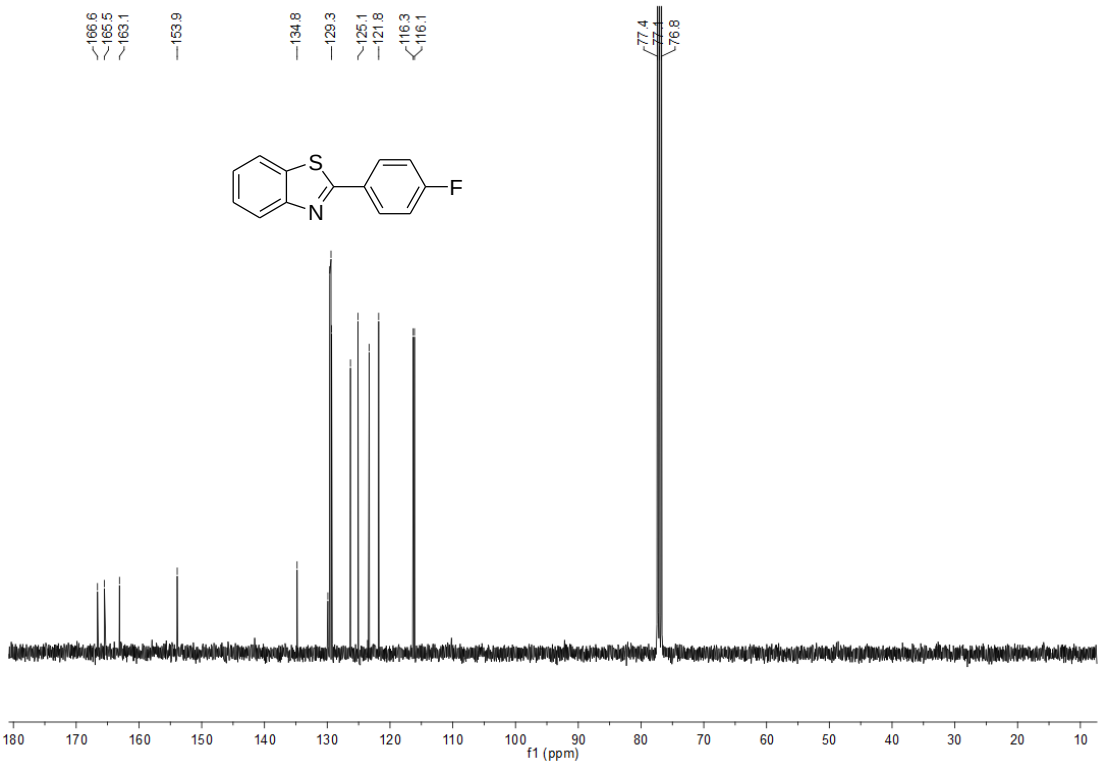
^{1}H NMR and ^{13}C NMR Spectra of 2-(4-Bromophenyl)benzothiazole (k)[2, 5]



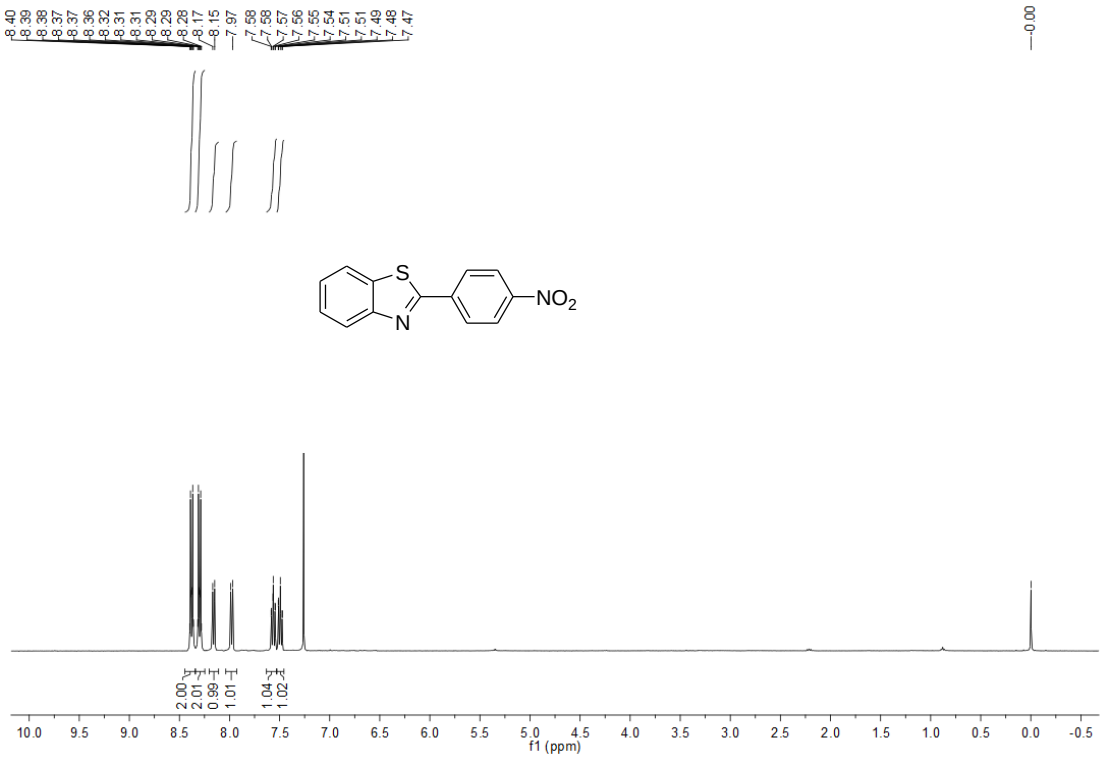


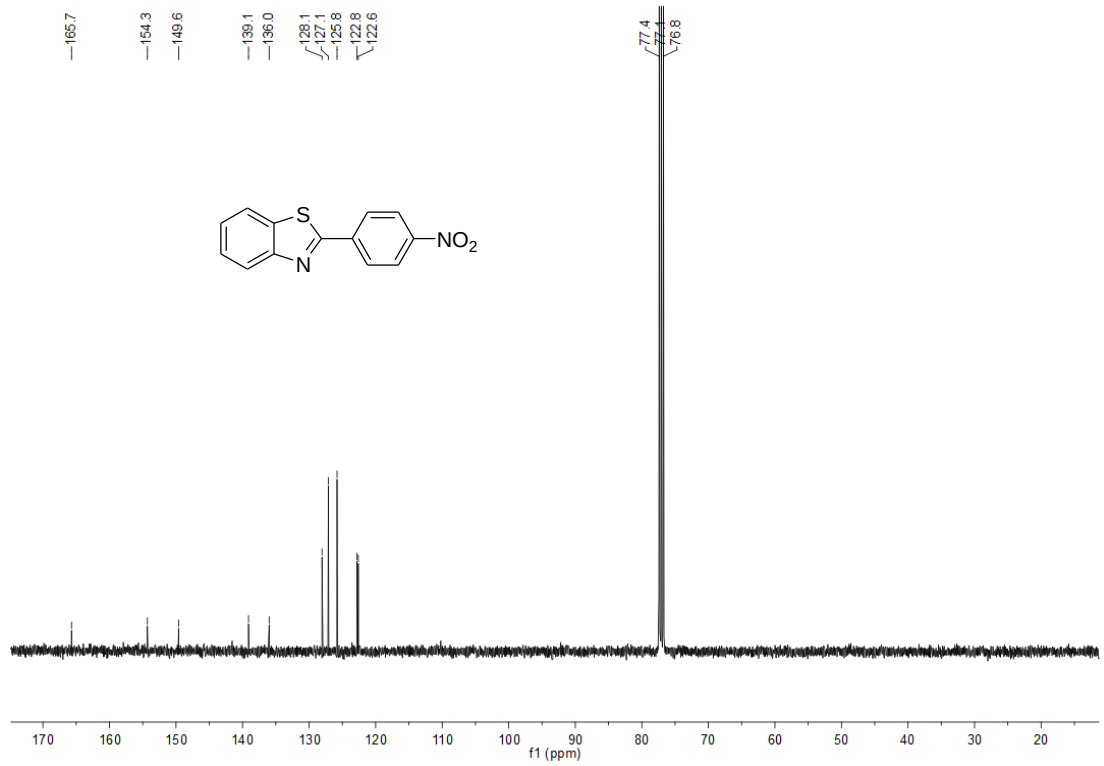
^{1}H NMR and ^{13}C NMR Spectra of 2-(4-Fluorophenyl)benzothiazole (l)[2, 5]



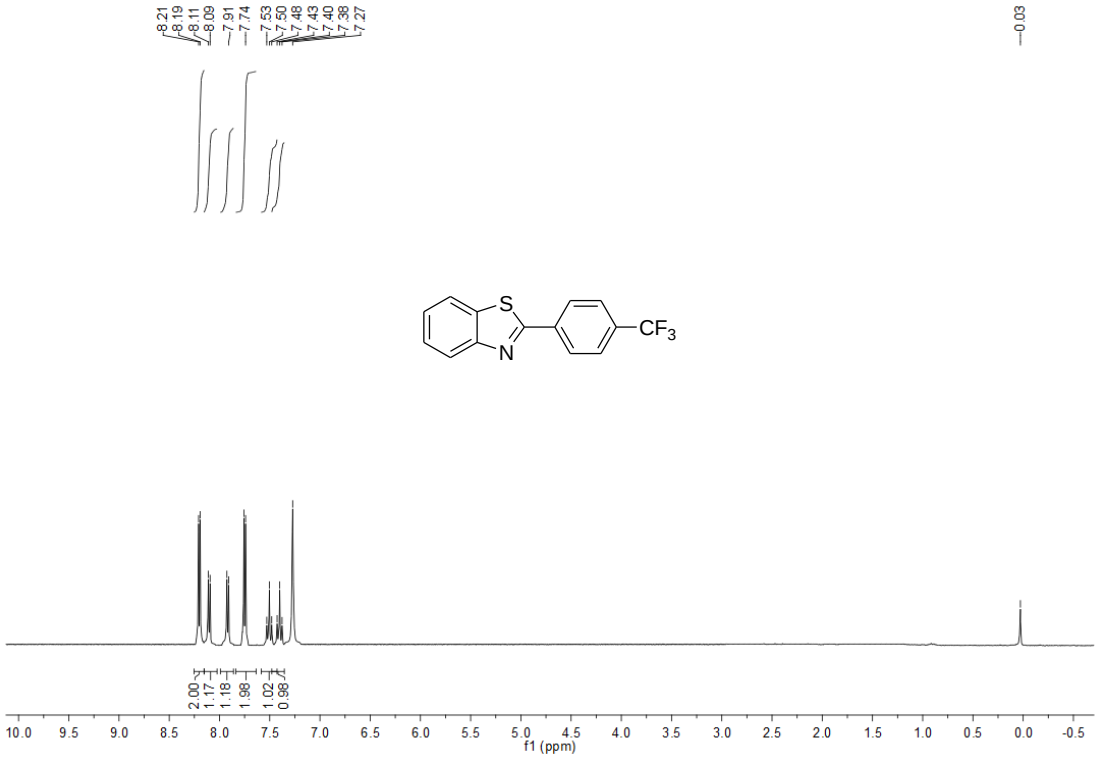


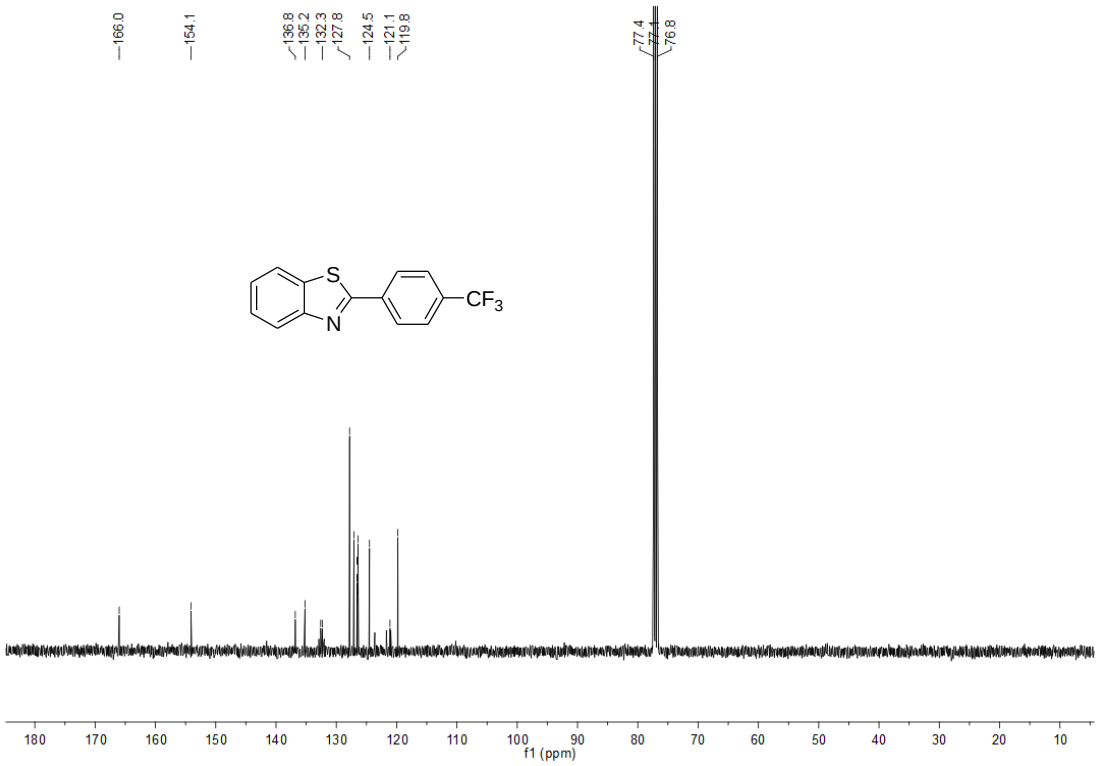
^{1}H NMR and ^{13}C NMR Spectra of 2-(4-Nitrophenyl)benzothiazole (m)[2, 5]



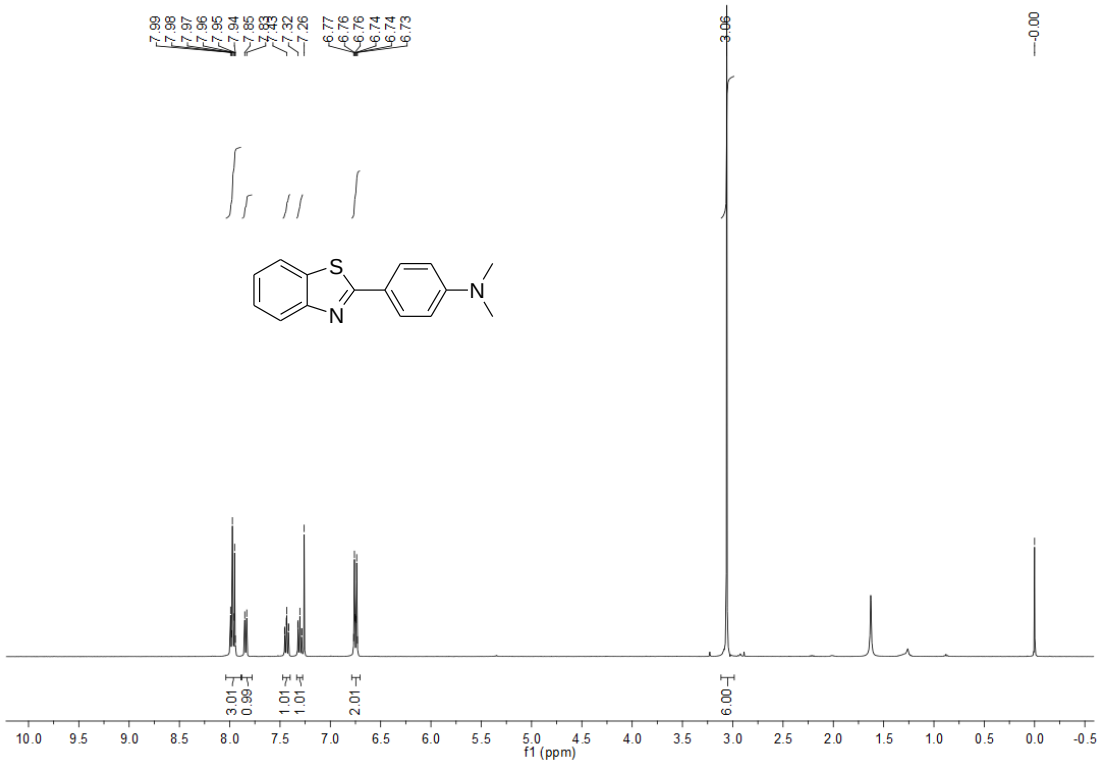


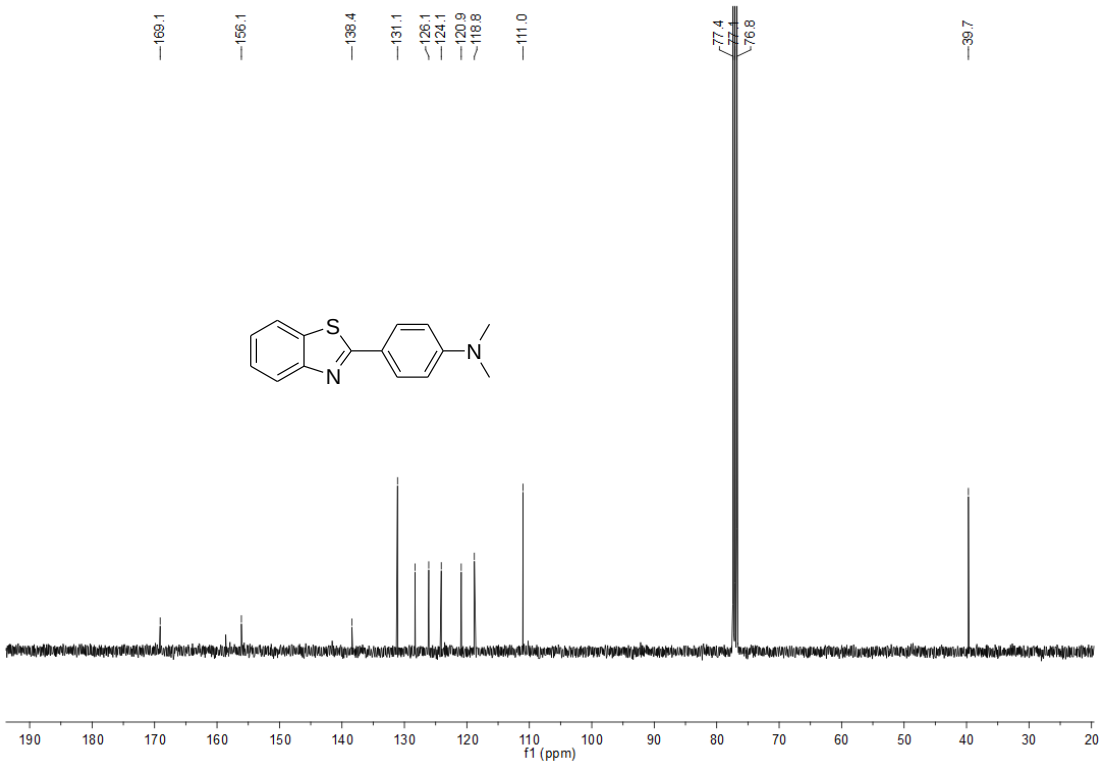
^{1}H NMR and ^{13}C NMR Spectra of 2-[4-(Trifluoromethyl)phenyl]-benzothiazole (n)[2, 6]



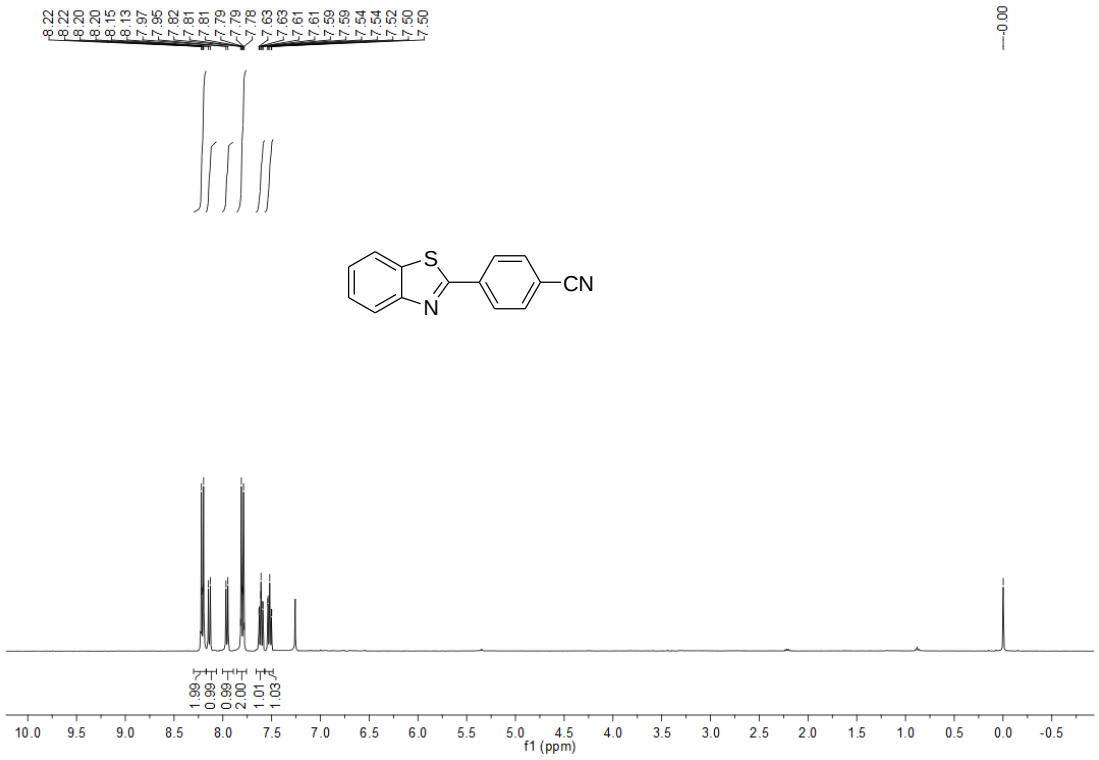


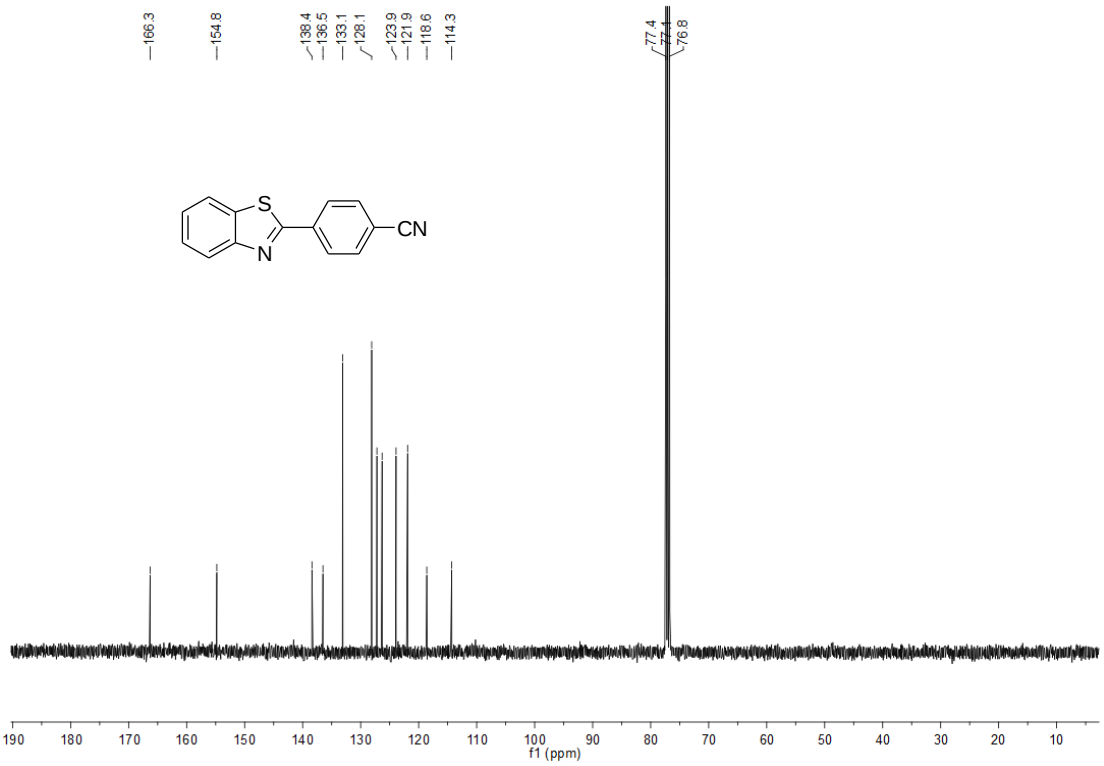
^{1}H NMR and ^{13}C NMR Spectra of 2-[4-(N, N-dimethyl)phenyl]-benzothiazole (o)[2, 5] .



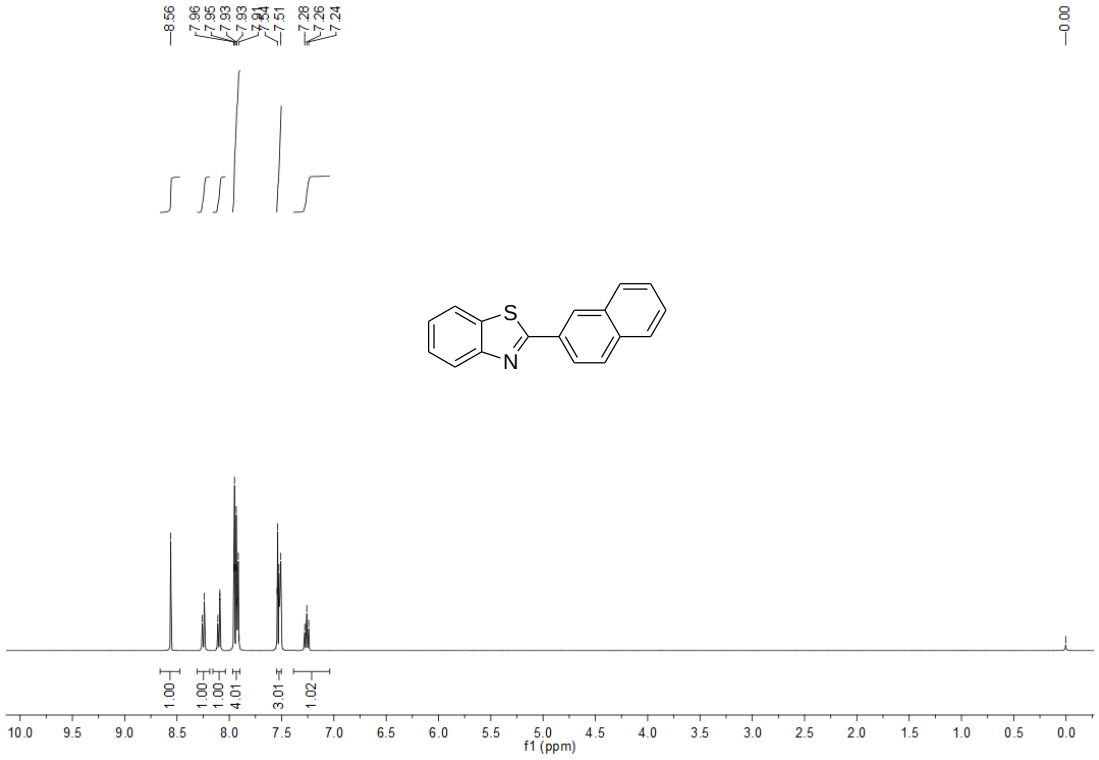


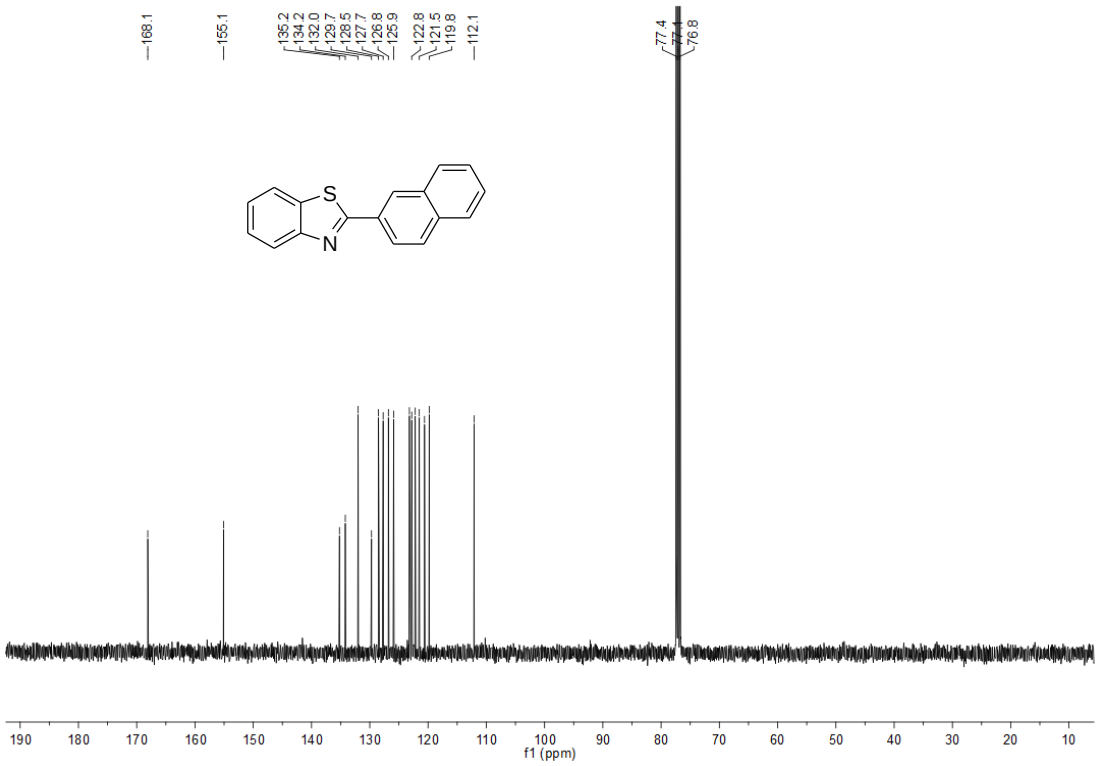
^{1}H NMR and ^{13}C NMR Spectra of 2-(4-Cyanophenyl)benzothiazole (p).



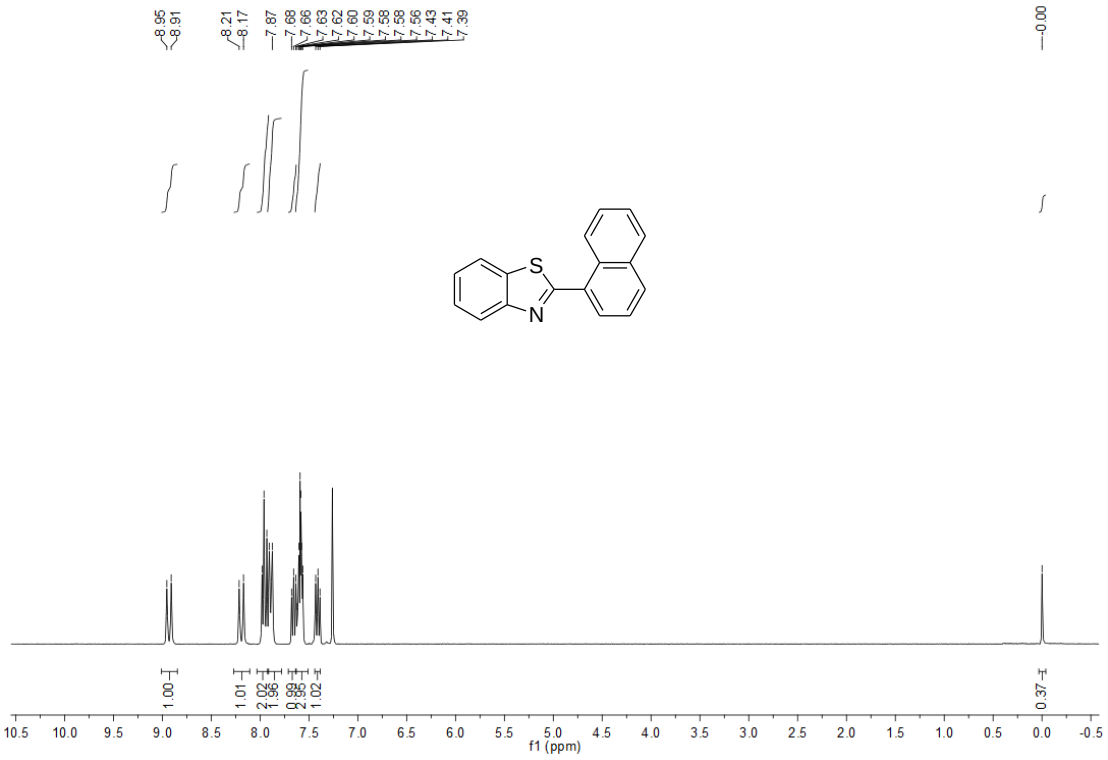


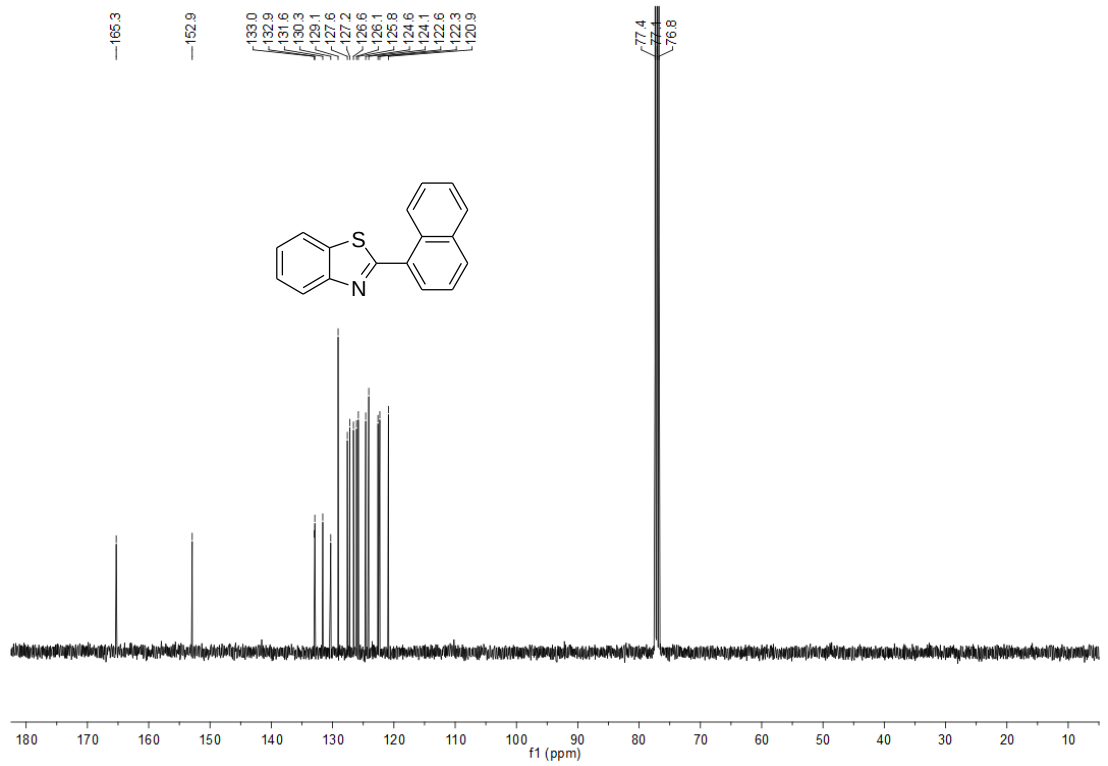
^{1}H NMR and ^{13}C NMR Spectra of 2-(Naphthalen-3-yl)benzothiazole (q) [2, 5]



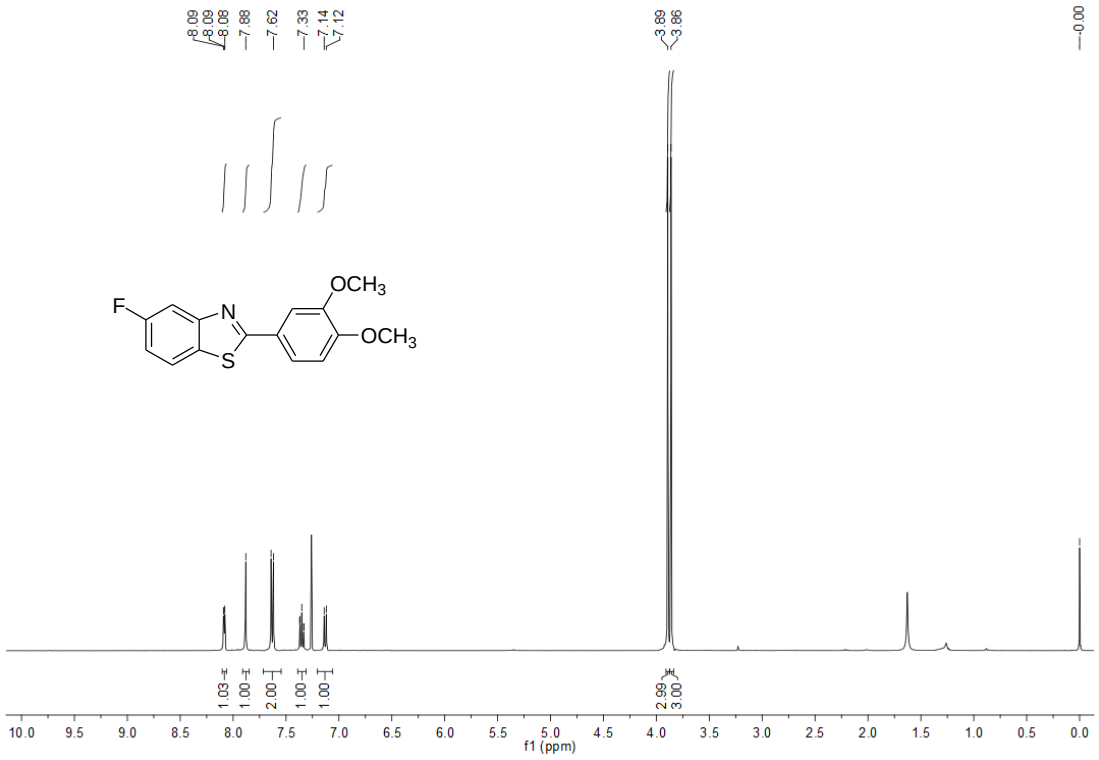


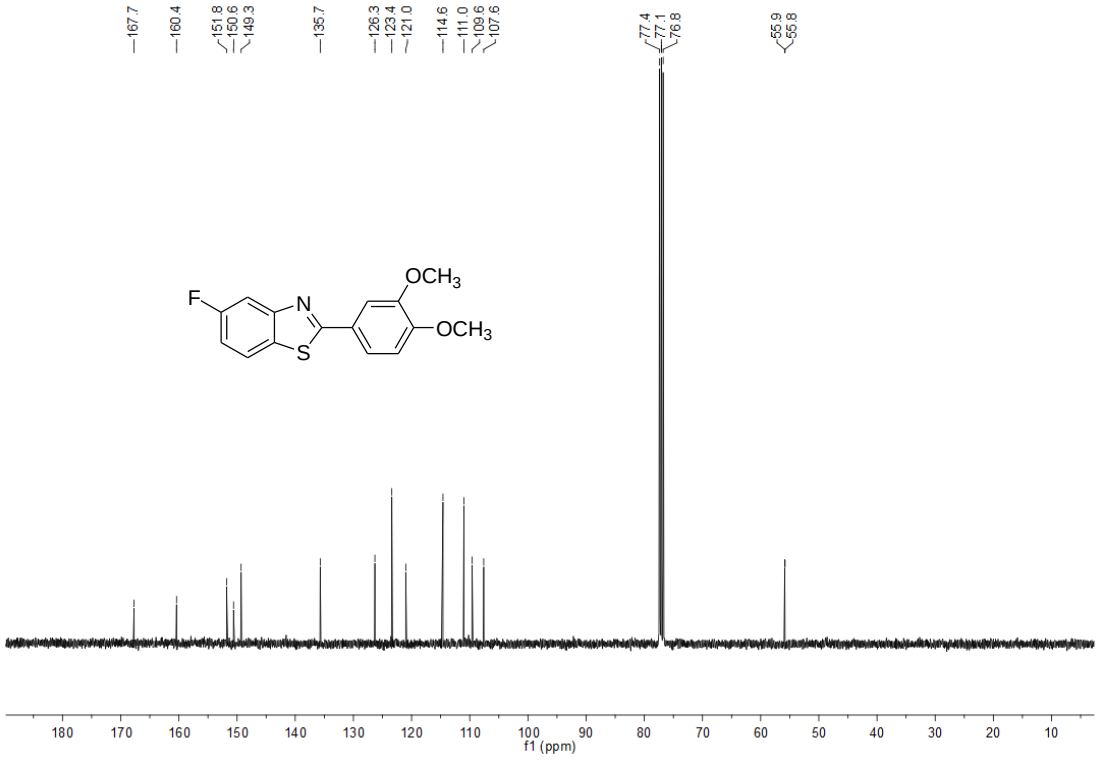
^{1}H NMR and ^{13}C NMR Spectra of 2-(Naphthalen-2-yl)benzothiazole (r) *1*





^{1}H NMR and ^{13}C NMR Spectra of 5-Fluoro-2-(3,4-dimethoxyphenyl)benzothiazole (s)[7]





IV. References

1. Ranu, B. C.; Jana, R.; Dey, S. S., An Efficient and Green Synthesis of 2-Arylbenzothiazoles in an Ionic Liquid, [pmIm]Br under Microwave Irradiation. *Chemistry Letters* **2004,** *33* (3), 274-275.

2. Sun, Y.; Jiang, H.; Wu, W.; Zeng, W.; Wu, X., Copper-Catalyzed Synthesis of Substituted Benzothiazoles via Condensation of 2-Aminobenzenethiols with Nitriles. *Organic Letters* **2013,** *15* (7), 1598-1601.

3. Deng, H.; Li, Z.; Ke, F.; Zhou, X., Cu-Catalyzed Three-Component Synthesis of Substituted Benzothiazoles in Water. *Chemistry – A European Journal* **2012,** *18* (16), 4840-4843.

4. Zhang, S.-L.; Hu, W.-Y.; Wang, P.-P., An Iron and Copper System Catalyzed C–H Arylation of Azoles with Arylboronic- Acids. *Synthesis* **2014,** *47* (01), 42-48.

5. Ranjit, S.; Liu, X., Direct Arylation of Benzothiazoles and Benzoxazoles with Aryl Boronic Acids. *Chemistry – A European Journal* **2011,** *17* (4), 1105-1108.

6. Fan, X.; Wang, Y.; He, Y.; Zhang, X.; Wang, J., Ru(III)-catalyzed oxidative reaction in ionic liquid: an efficient and practical route to 2-substituted benzothiazoles and their hybrids with pyrimidine nucleoside. *Tetrahedron Letters* **2010,** *51* (27), 3493-3496.

7. Mortimer, C. G.; Wells, G.; Crochard, J.-P.; Stone, E. L.; Bradshaw, T. D.; Stevens, M. F. G.; Westwell, A. D., Antitumor Benzothiazoles. 26. 2-(3,4-Dimethoxyphenyl)-5-fluorobenzothiazole (GW 610, NSC 721648), a Simple Fluorinated 2-Arylbenzothiazole, Shows Potent and Selective Inhibitory Activity against Lung, Colon, and Breast Cancer Cell Lines. *Journal of Medicinal Chemistry* **2006,** *49* (1), 179-185.