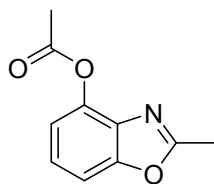


Synthesis of 2-Methylbenzoxazoles Directly from N-phenylacetamides Catalyzed by Palladium Acetate Biying Wang, Chengfei Jiang, Jiasheng Qian, Shuwei Zhang*, Xiaodong Jia, Yu Yuan*

The ¹H NMR and ¹³C NMR spectra of the productsS2-S24

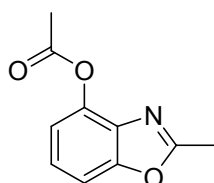
Date of compounds

1) 2-methylbenzo[d]oxazol-4-yl acetate (2a)



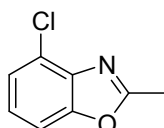
Yield: 68%. White solid; Mp: 68 - 71 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 8.2 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.04 (d, J = 8.0 Hz, 1H), 2.62 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.92, 164.23, 152.36, 141.08, 134.16, 125.67, 124.59, 108.16, 20.93, 14.54; IR (KBr): ν = 2925, 2855, 1769, 1620, 1493, 1438, 1373, 1253, 1193, 1044, 866, 803, 743, 582 cm^{-1} ; HRMS: Calculated for $\text{C}_{10}\text{H}_9\text{NO}_3$: 192.0660, found: 192.0653.

2) 2-methylbenzo[d]oxazol-4-yl acetate (2a)



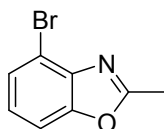
Yield: 68%. White solid; Mp: 68 - 71 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 8.2 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.04 (d, J = 8.0 Hz, 1H), 2.62 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.92, 164.23, 152.36, 141.08, 134.16, 125.67, 124.59, 108.16, 20.93, 14.54; IR (KBr): ν = 2925, 2855, 1769, 1620, 1493, 1438, 1373, 1253, 1193, 1044, 866, 803, 743, 582 cm^{-1} ; HRMS: Calculated for $\text{C}_{10}\text{H}_9\text{NO}_3$: 192.0660, found: 192.0653.

3) 4-chloro-2-methylbenzo[d]oxazole (2b)



Yield: 81%. White solid; Mp: 52 – 55 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.63, 151.47, 139.20, 124.95, 124.31, 123.87, 108.86, 14.56; IR (KBr): ν = 3079, 2926, 2855, 1677, 1611, 1471, 1425, 1254, 1159, 1092, 1031, 946, 866, 800, 146, 520 cm^{-1} ; HRMS: Calculated for $\text{C}_8\text{H}_6\text{BrNO}$: 211.9711, found: 211.9705.

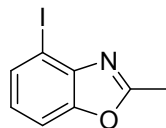
4) 4-bromo-2-methylbenzo[d]oxazole (2c)



Yield: 71%. White solid; Mp: 74 – 77°C; ^1H NMR (600 MHz, CDCl_3) δ 7.46 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR

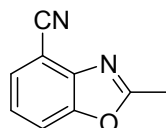
(150 MHz, CDCl₃) δ 164.49, 151.08, 140.95, 127.48, 125.68, 111.96, 109.43, 14.45; IR (KBr): ν = 3556, 3069, 2922, 2852, 1605, 1560, 1422, 1248, 1127, 1038, 916, 860, 790 cm⁻¹; HRMS: Calculated for C₈H₆BrNO: 211.9711, found: 211.9705.

5) 4-iodo-2-methylbenzo[d]oxazole (2d)



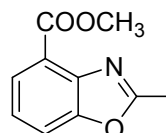
Yield: 42%. White solid; Mp: 71 – 74 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 2.67 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.98, 148.46, 143.30, 132.32, 124.98, 109.22, 83.24, 13.59; IR (KBr): ν = 3357, 3190, 3064, 2921, 2854, 1599, 1417, 1332, 1254, 1028, 904, 799, 697, 505 cm⁻¹; HRMS: Calculated for C₈H₆INO: 259.9572, found: 259.9574.

6) 2-methylbenzo[d]oxazole-4-carbonitrile (2e)



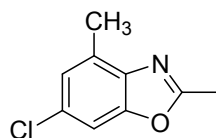
Yield: 74%. White solid; Mp: 110 - 113 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 2.66 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 164.28, 153.03, 149.37, 134.74, 126.98, 126.38, 126.21, 120.22, 22.27; IR (KBr): ν = 3172, 3040, 2914, 2019, 1684, 1619, 1462, 1259, 1026, 885, 780, 667, 595 cm⁻¹; HRMS: Calculated for C₉H₆N₂O: 159.0558, found: 159.0560.

7) methyl 2-methylbenzo[d]oxazole-4-carboxylate (2f)



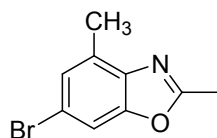
Yield: 89%. White solid; Mp: 80 - 83 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 4.00 (s, 3H), 2.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.89, 165.72, 151.49, 140.94, 126.60, 123.87, 121.52, 114.56, 52.48, 14.77; IR (KBr): ν = 3360, 2933, 2852, 1719, 1573, 1430, 1294, 1144, 1023, 926, 865, 807, 758 cm⁻¹; HRMS: Calculated for C₁₀H₉NO₃: 192.0660, found: 192.0652.

8) 6-chloro-2,4-dimethylbenzo[d]oxazole (2i)



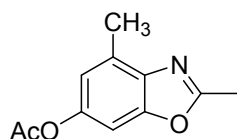
Yield: 80%. White solid; Mp: 82 - 85 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (s, 1H), 7.09 (s, 1H), 2.62 (s, 3H), 2.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.55, 150.71, 139.41, 130.67, 129.64, 125.19, 108.19, 16.27, 14.44; IR (KBr): ν = 3426, 2926, 2858, 1732, 1617, 1459, 1254, 1160, 925, 823 cm⁻¹; HRMS: Calculated for C₉H₈ClNO: 182.0373, found: 182.0365.

9) 6-bromo-2,4-dimethylbenzo[d]oxazole (2j)



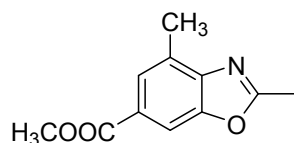
Yield: 84%. White solid; Mp: 101 - 104 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.44 (s, 1H), 7.23 (s, 1H), 2.61 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (150MHz, CDCl_3) δ 163.48, 151.04, 139.92, 131.21, 127.96, 117.03, 111.10, 16.24, 14.46; IR (KBr): ν = 3359, 3177, 3101, 3038, 2921, 2853, 1695, 1610, 1451, 1391, 1256, 1202, 1050, 921, 803, 684, 591 cm^{-1} ; HRMS: Calculated for $\text{C}_9\text{H}_8\text{BrNO}$: 225.9868, found: 225.9857.

10) methyl 2,6-dimethylbenzo[d]oxazole-4-carboxylate (2k)



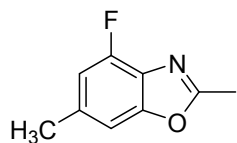
Yield: 81%. White solid; Mp: 101 - 104 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (s, 1H), 7.45 (s, 1H), 4.00 (s, 3H), 2.67 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.88, 165.24, 151.85, 138.78, 134.33, 127.55, 120.78, 114.85, 52.45, 21.41, 14.70; IR (KBr): ν = 3424, 2928, 1765, 1624, 1434, 1374, 1208, 1118, 1064, 1020, 903, 600 cm^{-1} ; HRMS: Calculated for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: 206.0817, found: 206.0790.

11) methyl 2,4-dimethylbenzo[d]oxazole-6-carboxylate (2l)



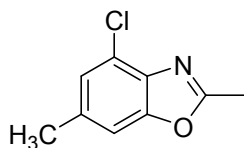
Yield: 90%. White solid; Mp: 105 - 108 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1H), 7.82 (s, 1H), 3.92 (s, 3H), 2.65 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.90, 165.78, 150.27, 144.55, 129.48, 126.34, 126.17, 109.32, 52.21, 16.37, 14.68; IR (KBr): ν = 3712, 3434, 2934, 1712, 1625, 1449, 1050, 889, 796, 731, 659, 540 cm^{-1} ; HRMS: Calculated for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: 206.0817, found: 206.0790.

12) 4-fluoro-2,6-dimethylbenzo[d]oxazole (2m)



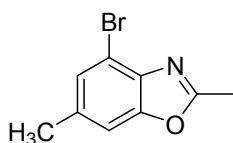
Yield: 52%. White solid; Mp: 55 - 58°C; ^1H NMR (600 MHz, CDCl_3) δ 7.07 (s, 1H), 6.84 (d, J = 10.6 Hz, 1H), 2.62 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 163.42, 153.53, 151.01, 135.79, 127.73, 111.56, 106.53, 21.68, 14.39; IR (KBr): ν = 3364, 2924, 2826, 1624, 1424, 1259, 1089, 1027, 805, 697, 503 cm^{-1} ; HRMS: Calculated for $\text{C}_9\text{H}_8\text{FNO}$: 166.0668, found: 166.0665.

13) 4-chloro-2,6-dimethylbenzo[d]oxazole (2n)



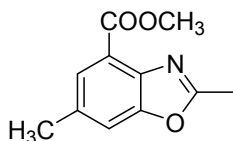
Yield: 77%. White solid; Mp: 72 - 75°C; ^1H NMR (600 MHz, CDCl_3) δ 7.09 (s, 1H), 7.05 (s, 1H), 2.56 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 163.03, 150.73, 136.05, 134.71, 124.33, 122.14, 108.16, 20.47, 13.45; IR (KBr): ν = 3492, 2924, 2858, 1696, 1613, 1468, 1256, 1188, 1099, 1025, 923, 811, 698, 594, 467 cm^{-1} ; HRMS: Calculated for $\text{C}_9\text{H}_8\text{ClNO}$: 182.0373, found: 182.0372.

14) 4-bromo-2,6-dimethylbenzo[d]oxazole (2o)



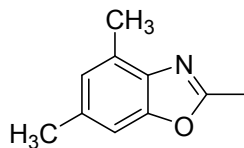
Yield: 76%. White solid; Mp: 96 - 99 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (s, 1H), 7.20 (s, 1H), 2.63 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.90, 151.11, 138.71, 136.12, 128.23, 111.14, 109.72, 21.38, 14.49; IR (KBr): ν = 3430, 2926, 2858, 1748, 1611, 1458, 1249, 1117, 834 cm^{-1} ; HRMS: Calculated for $\text{C}_9\text{H}_8\text{BrNO}$: 225.9868, found: 225.9850.

15) 2,4-dimethylbenzo[d]oxazol-6-yl acetate (2n)



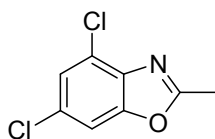
Yield: 93%. White solid; Mp: 119 - 122 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (s, 1H), 6.82 (s, 1H), 2.61 (s, 3H), 2.55 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.66, 163.64, 150.38, 147.27, 138.48, 130.15, 118.53, 101.73, 21.03, 16.42, 14.45; IR (KBr): ν = 2932, 2580, 1714, 1523, 1439, 1323, 1245, 1197, 1036, 859, 789, 594 cm^{-1} ; HRMS: Calculated for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: 206.0817, found: 206.0790.

16) 2,4,6-trimethylbenzo[d]oxazole (2o)



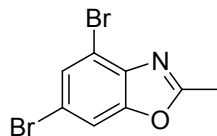
Yield: 62%. White solid; Mp: 66- 69°C; ^1H NMR (400 MHz, CDCl_3) δ 7.09 (s, 1H), 6.92 (s, 1H), 2.61 (s, 3H), 2.54 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.42, 150.95, 138.36, 134.29, 128.90, 125.94, 107.72, 21.59, 16.38, 14.50; IR (KBr): ν = 3721, 3362, 2923, 2855, 1644, 1458, 1261, 1093, 1029, 805, 695 cm^{-1} ; HRMS: Calculated for $\text{C}_{10}\text{H}_{11}\text{NO}$: 162.0919, found: 162.0915.

17) 4,6-dichloro-2-methylbenzo[d]oxazole (o)



Yield: 58%. White solid; Mp: 62- 65°C; ^1H NMR (600 MHz, CDCl_3) δ 7.40 (s, 1H), 7.33 (s, 1H), 2.66 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 165.26, 151.33, 138.20, 130.33, 124.83, 124.31, 109.73, 14.52; IR (KBr): ν = 3360, 2924, 2856, 1624, 1424, 1259, 1089, 1027, 805, 697, 503 cm^{-1} ; HRMS: Calculated for $\text{C}_8\text{H}_5\text{Cl}_2\text{NO}$: 201.9826, found: 201.9815.

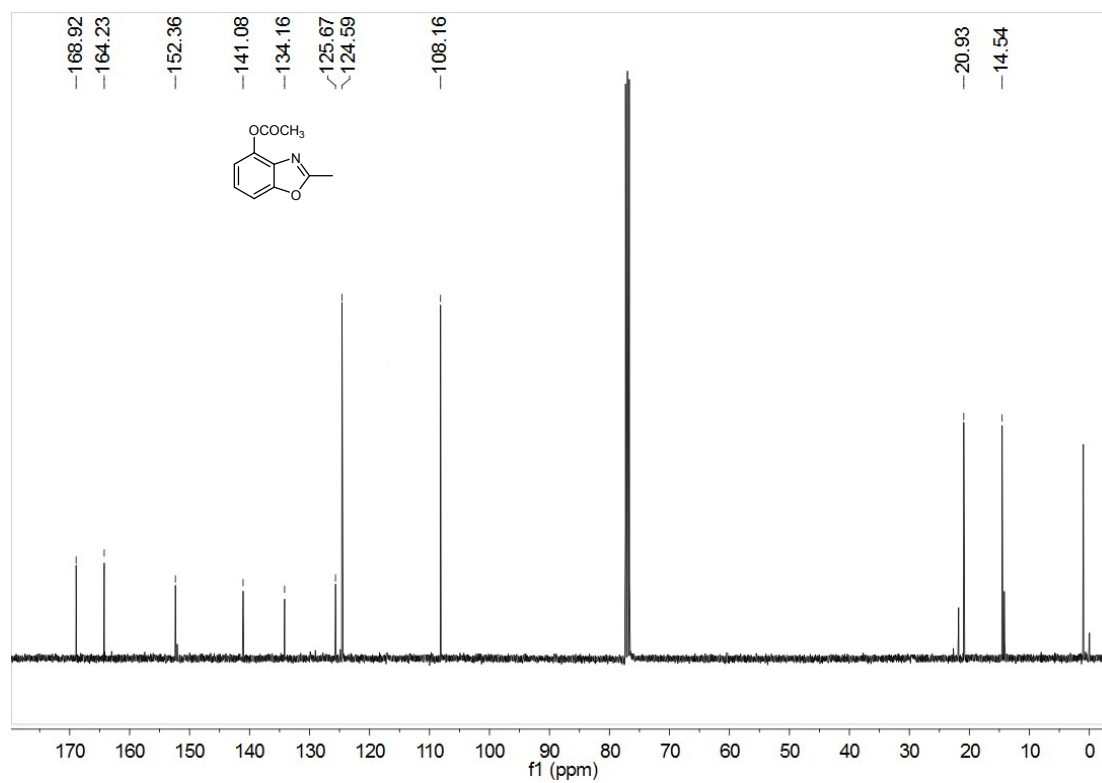
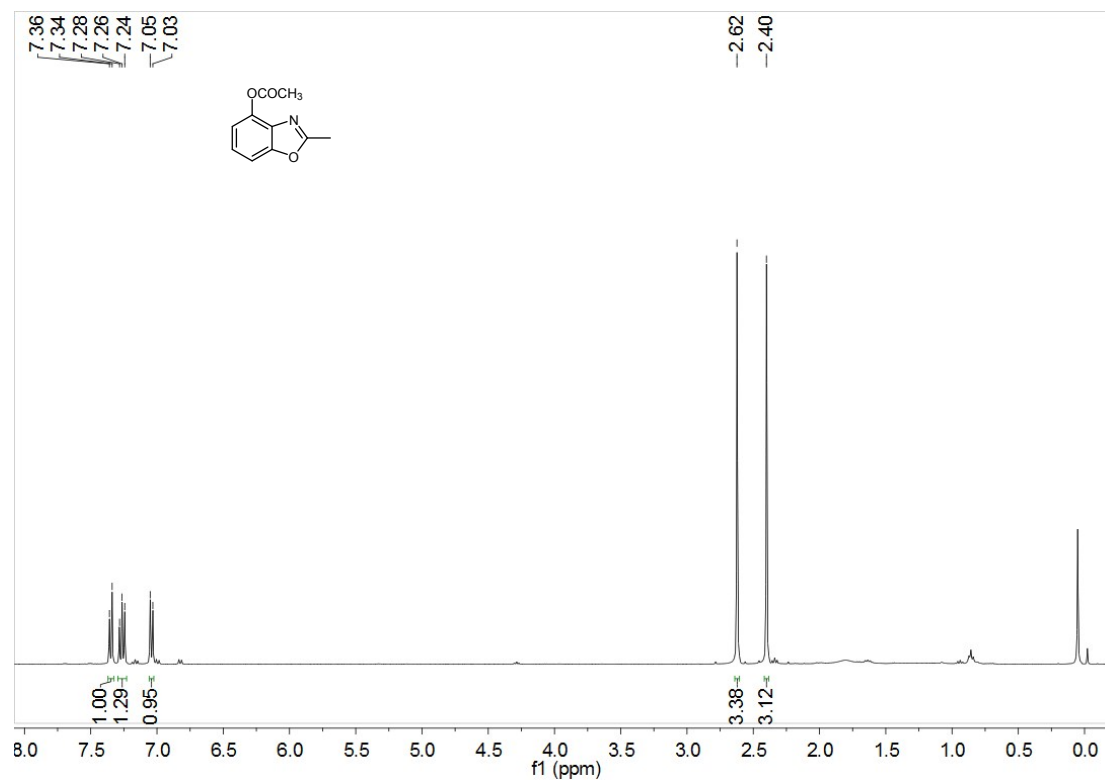
18) 4,6-dibromo-2-methylbenzo[d]oxazole



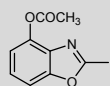
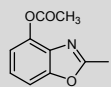
Yield: 41%. White solid; Mp: 148 - 151 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.59 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.26, 151.33, 138.20, 130.33, 124.83, 124.31, 109.73, 14.52; IR (KBr): ν = 3717, 3424, 3087, 2926, 2858, 1725, 1608, 1448, 1388, 1258, 1158, 1051, 939, 848, 745 cm^{-1} ; HRMS: Calculated for $\text{C}_8\text{H}_5\text{Br}_2\text{NO}$: 289.8816, found: 289.8798.

¹H NMR and ¹³C NMR spectrum of

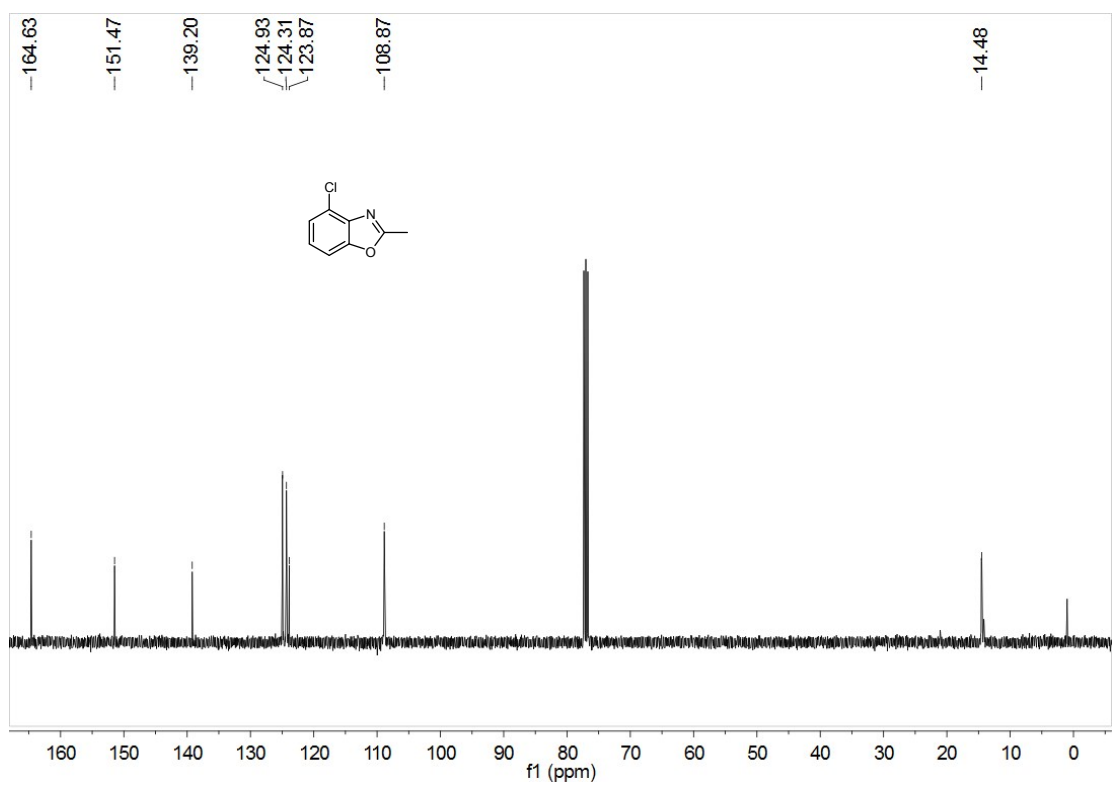
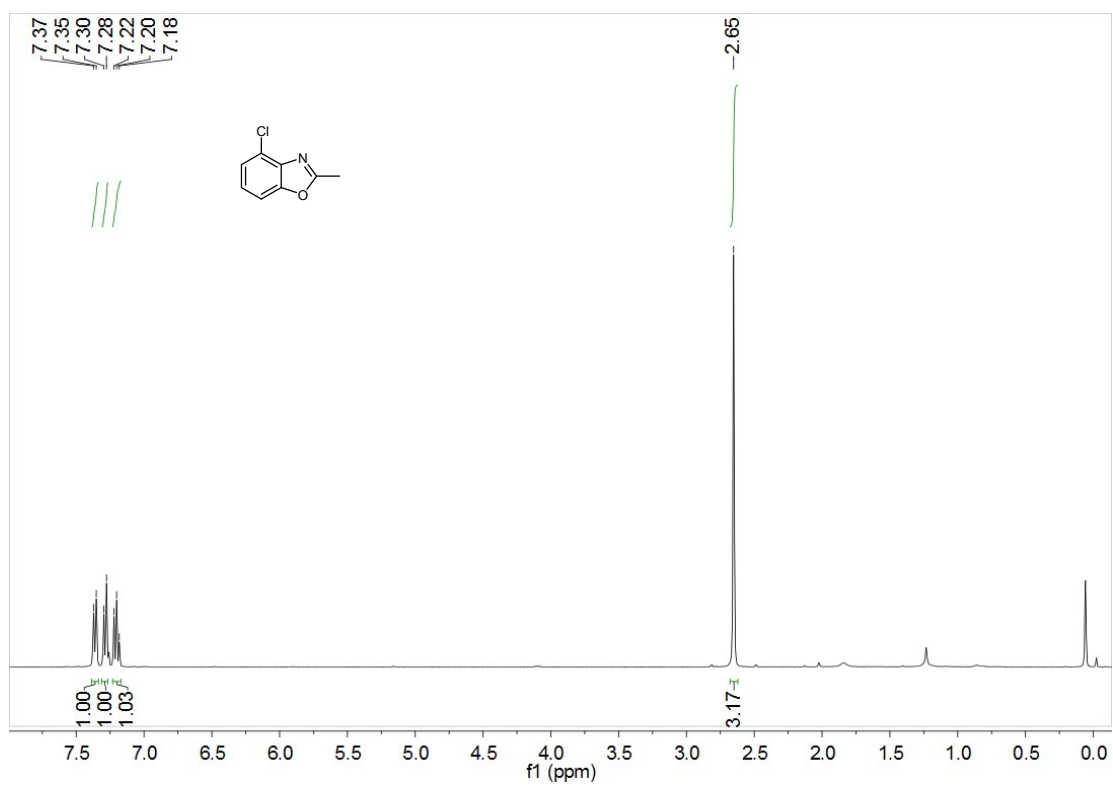
1) 2-methylbenzo[d]oxazol-4-yl acetate (2a)



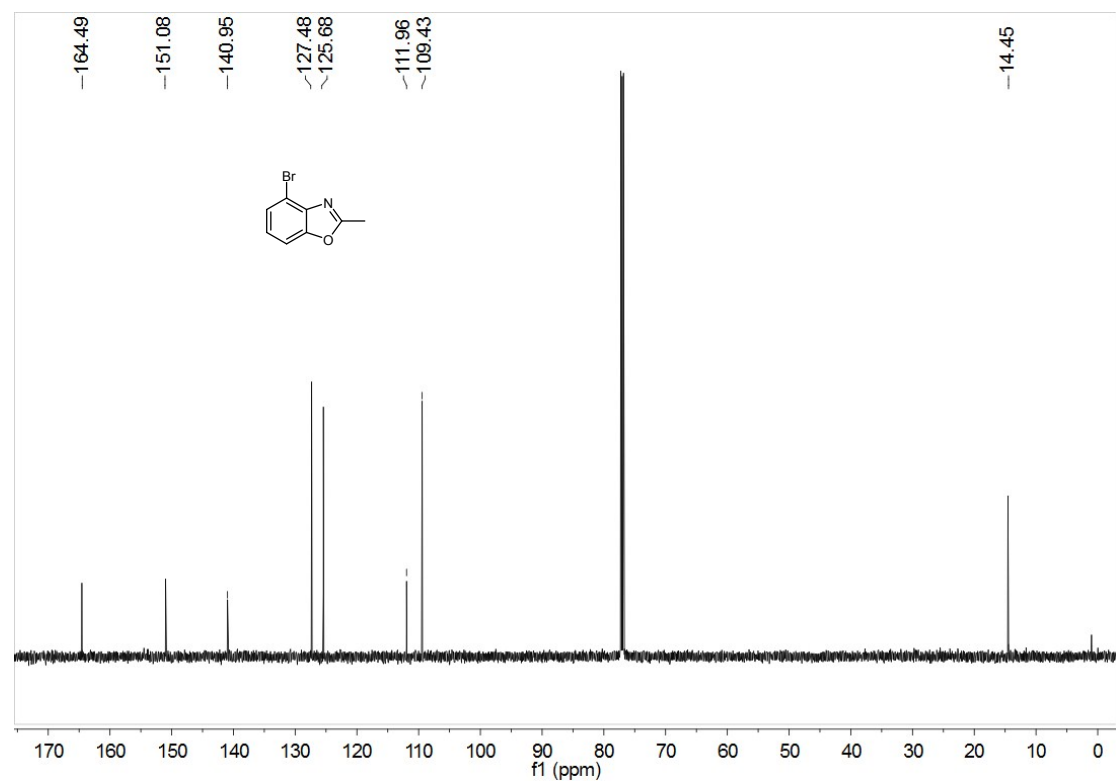
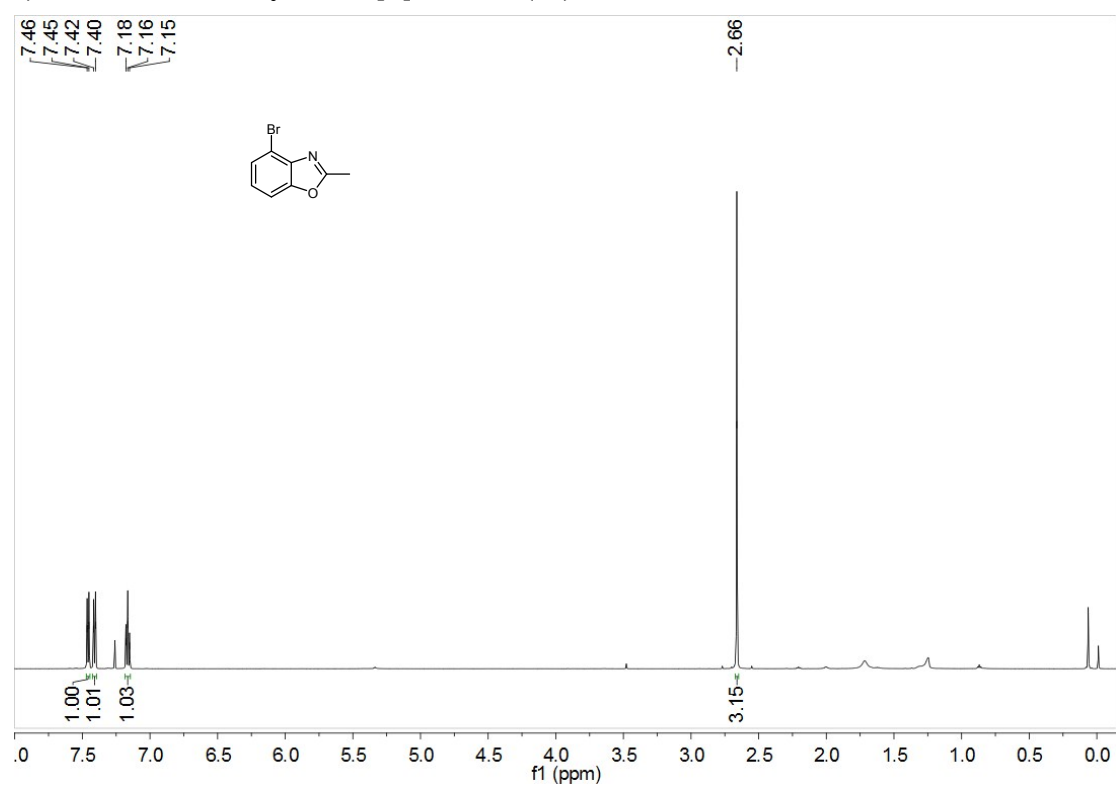
2) 2-methylbenzo[d]oxazol-4-yl acetate (2a)



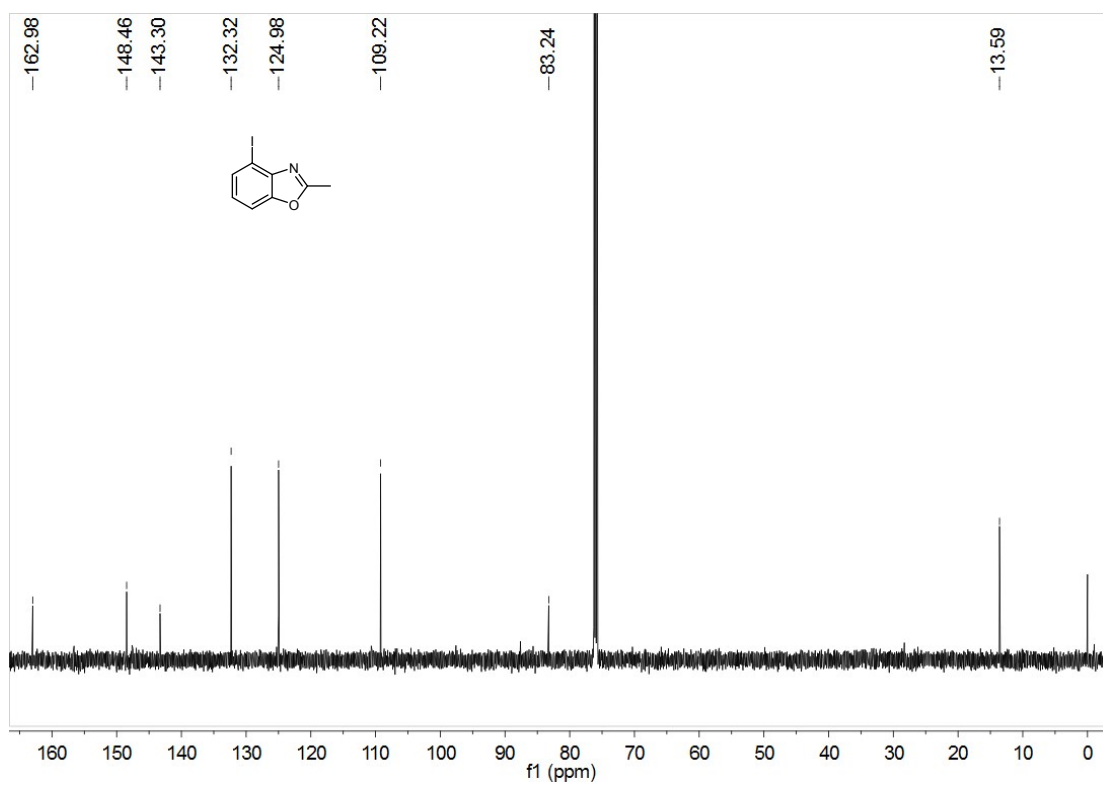
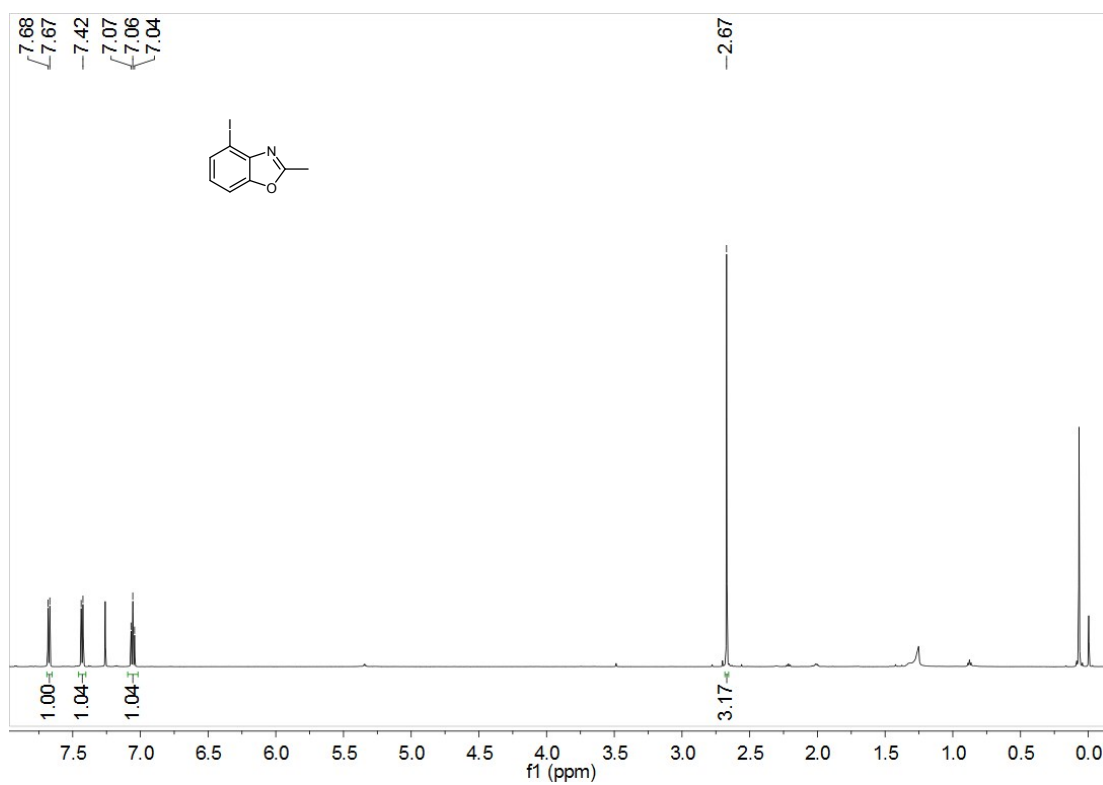
3) 4-chloro-2-methylbenzo[d]oxazole (2b)



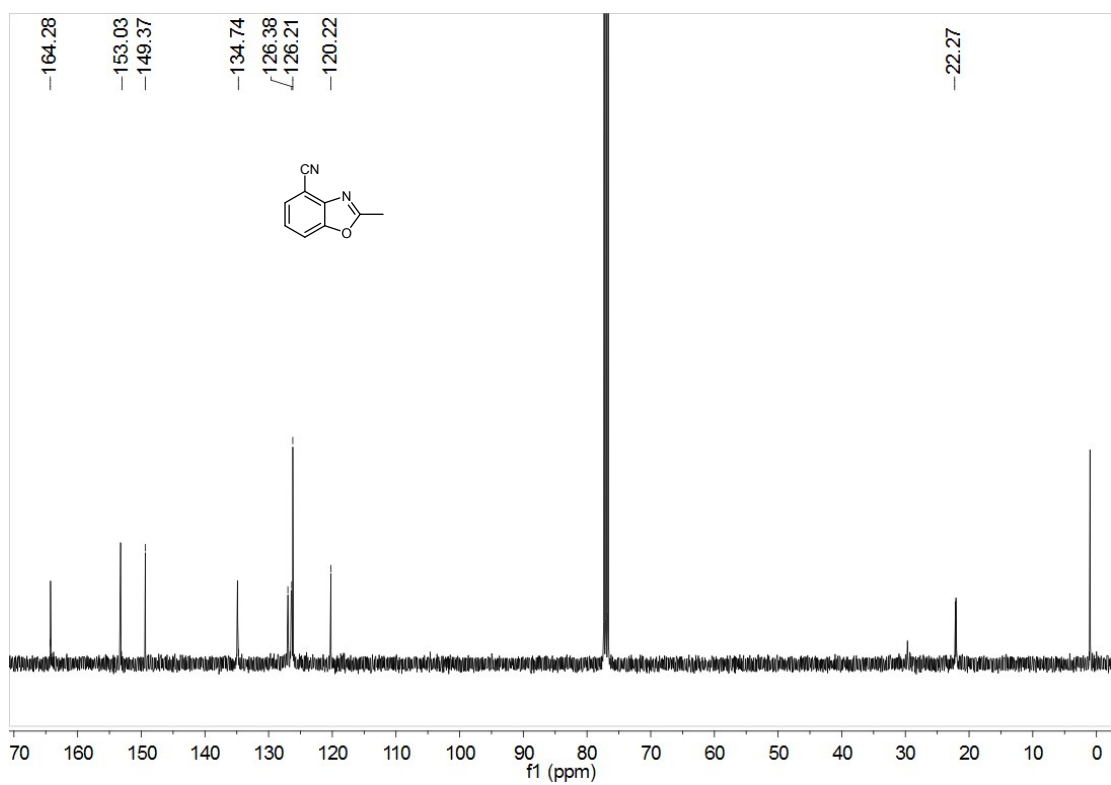
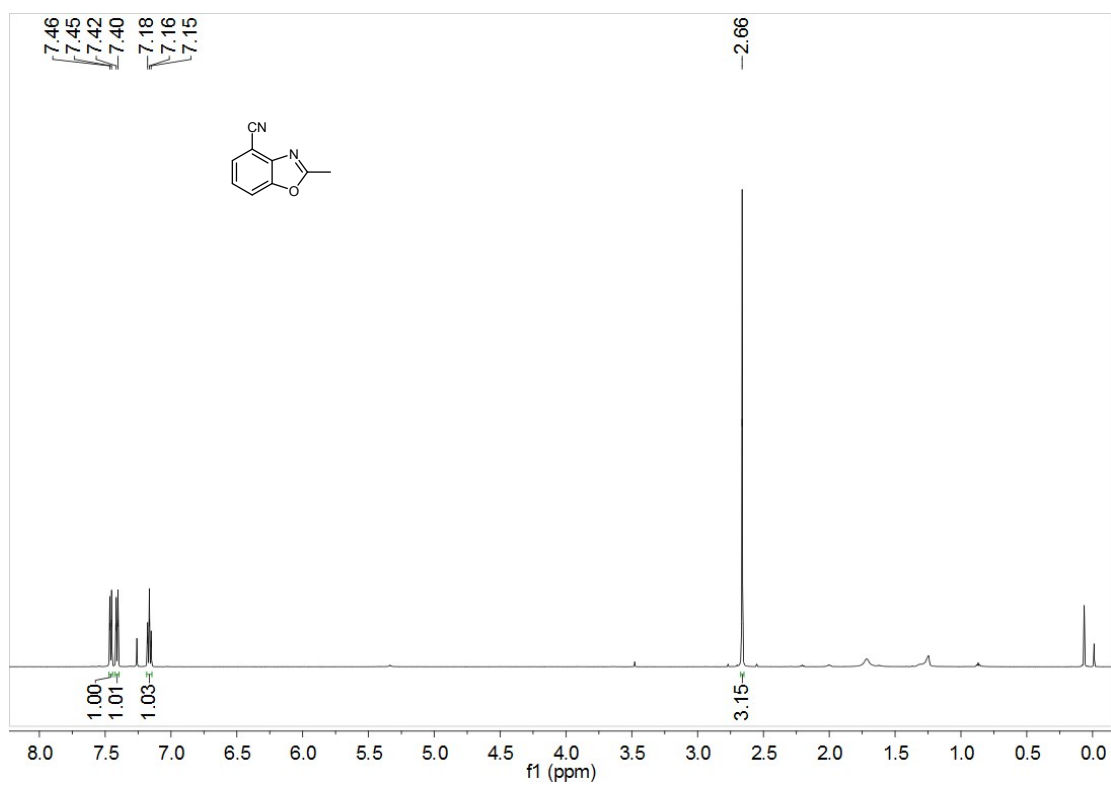
4) 4-bromo-2-methylbenzo[d]oxazole (2c)



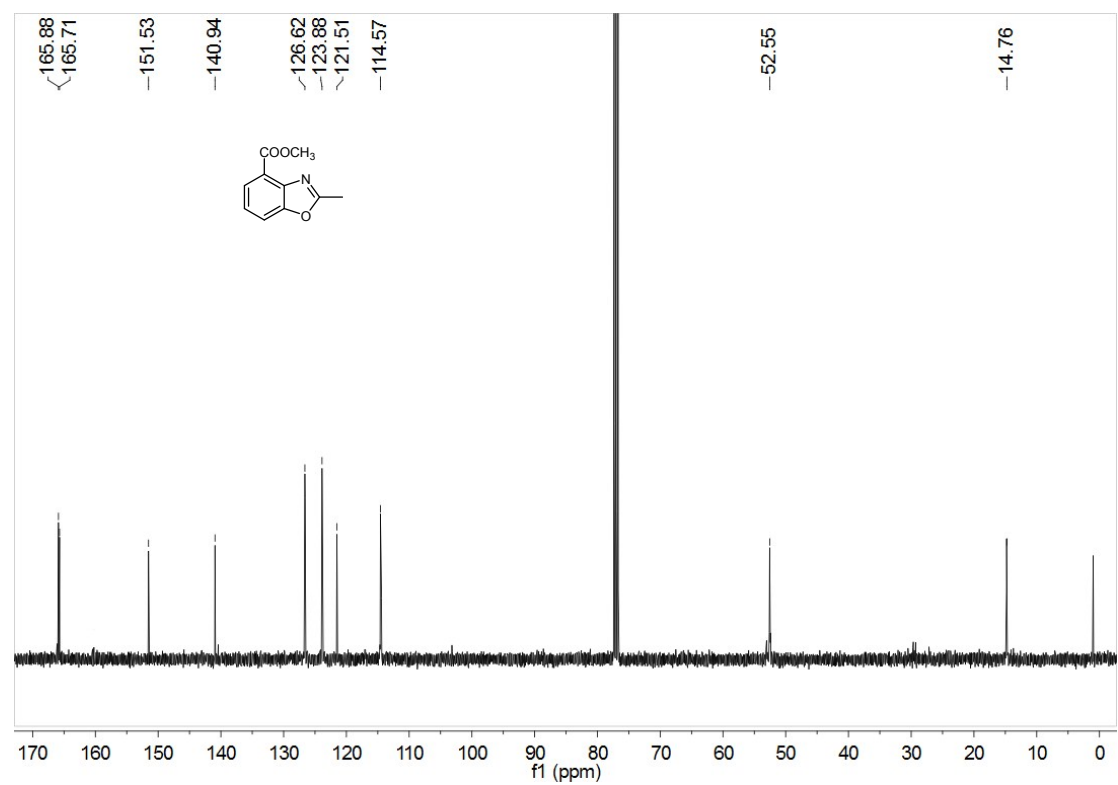
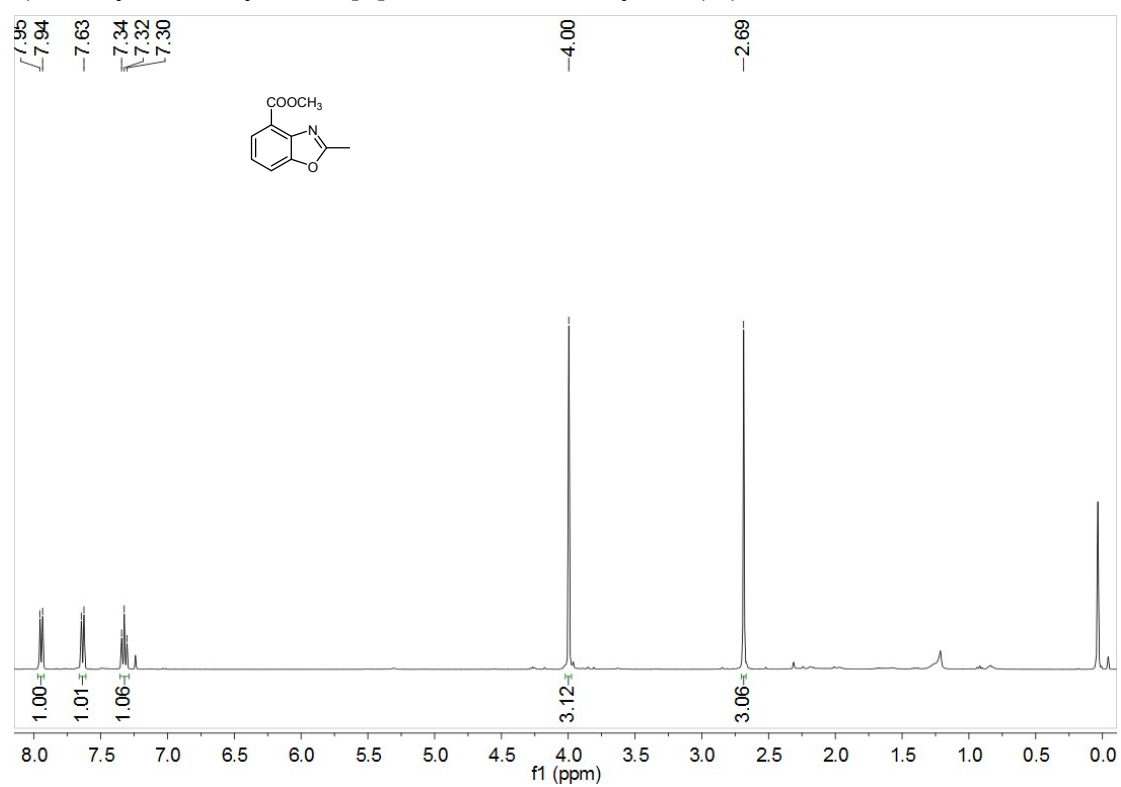
5) 4-iodo-2-methylbenzo[d]oxazole (2d)



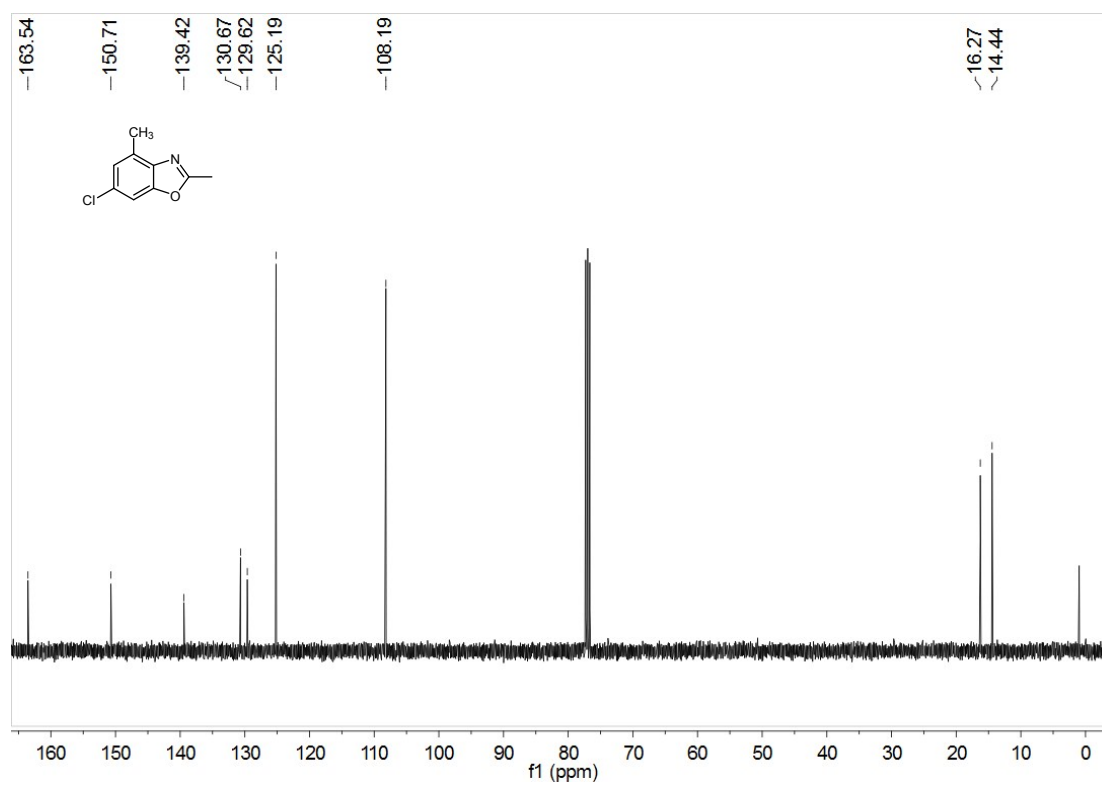
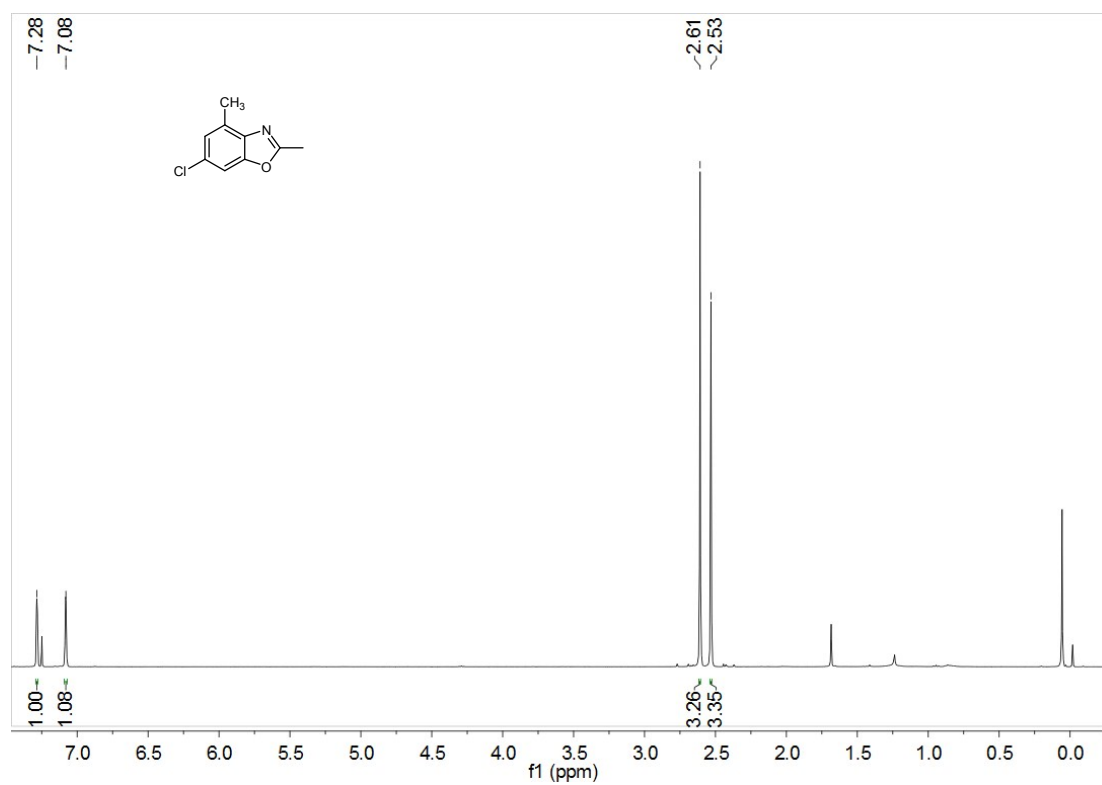
6) 2-methylbenzo[d]oxazole-4-carbonitrile (2e)



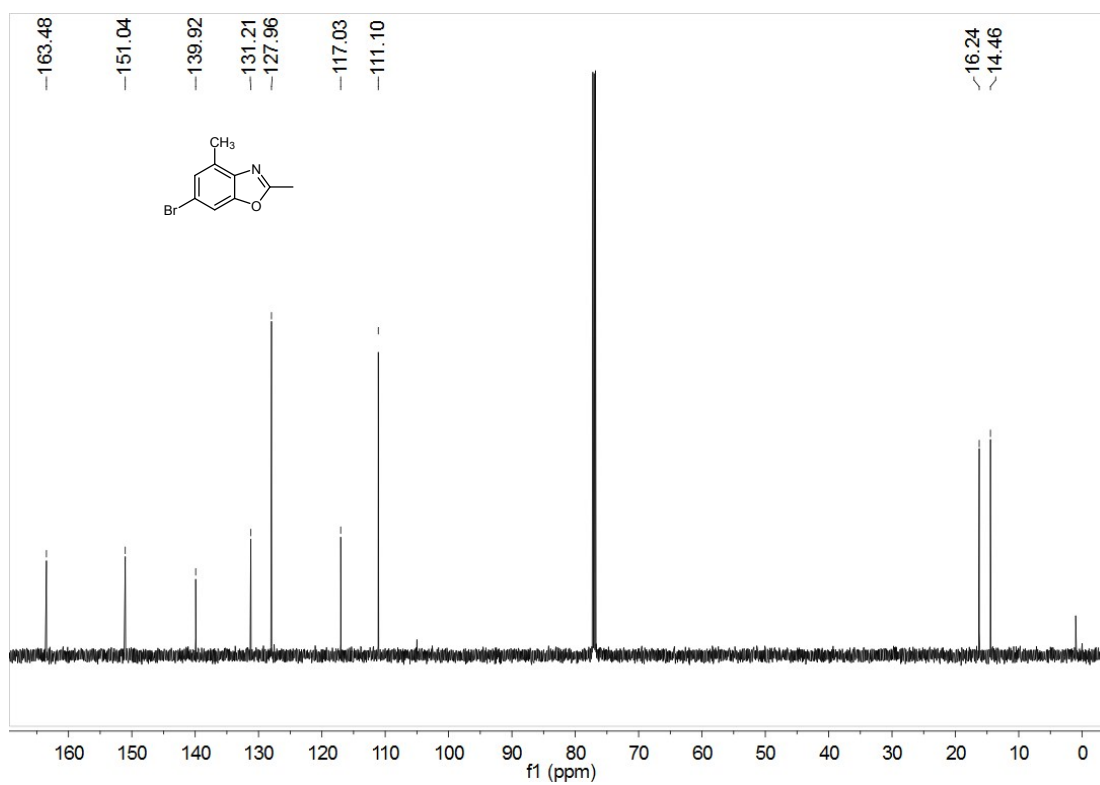
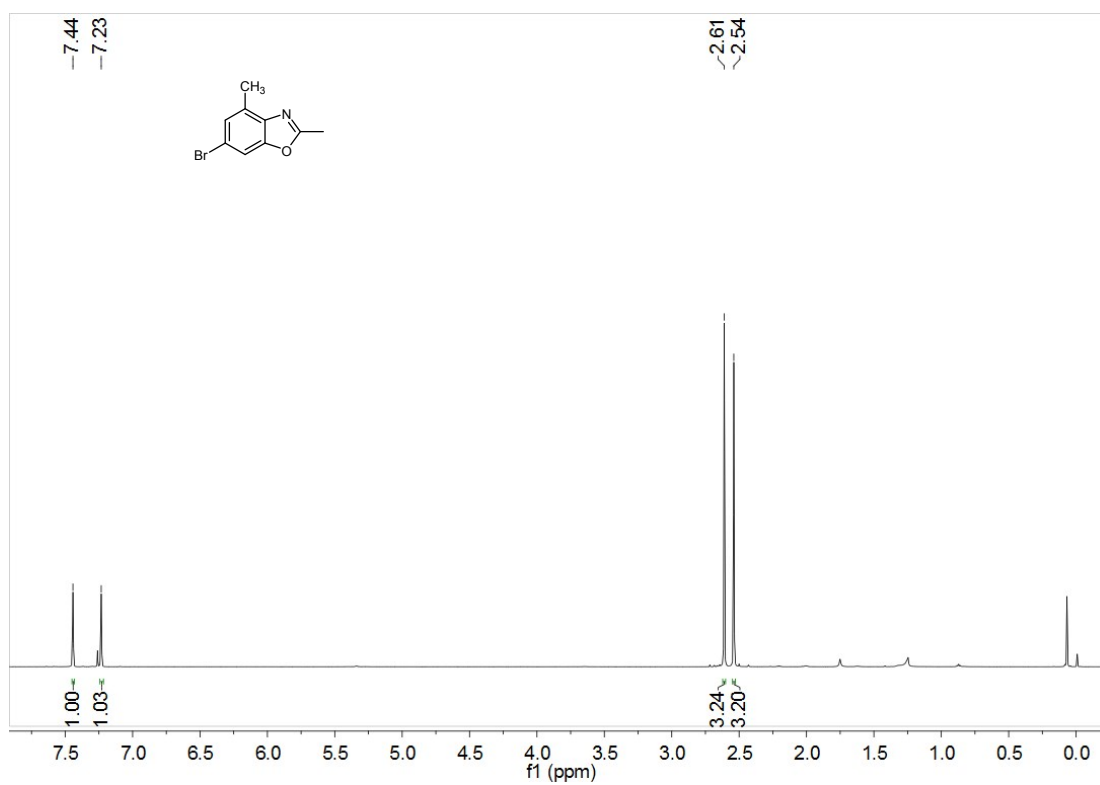
7) methyl 2-methylbenzo[d]oxazole-4-carboxylate (2f)



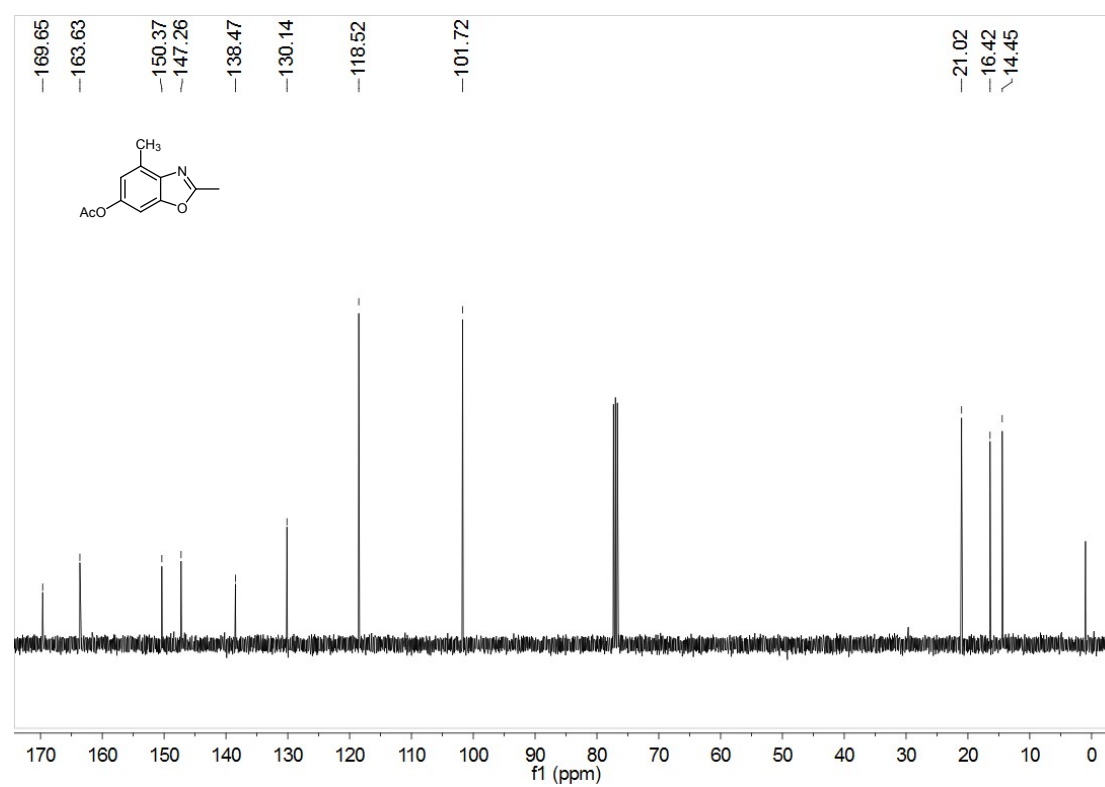
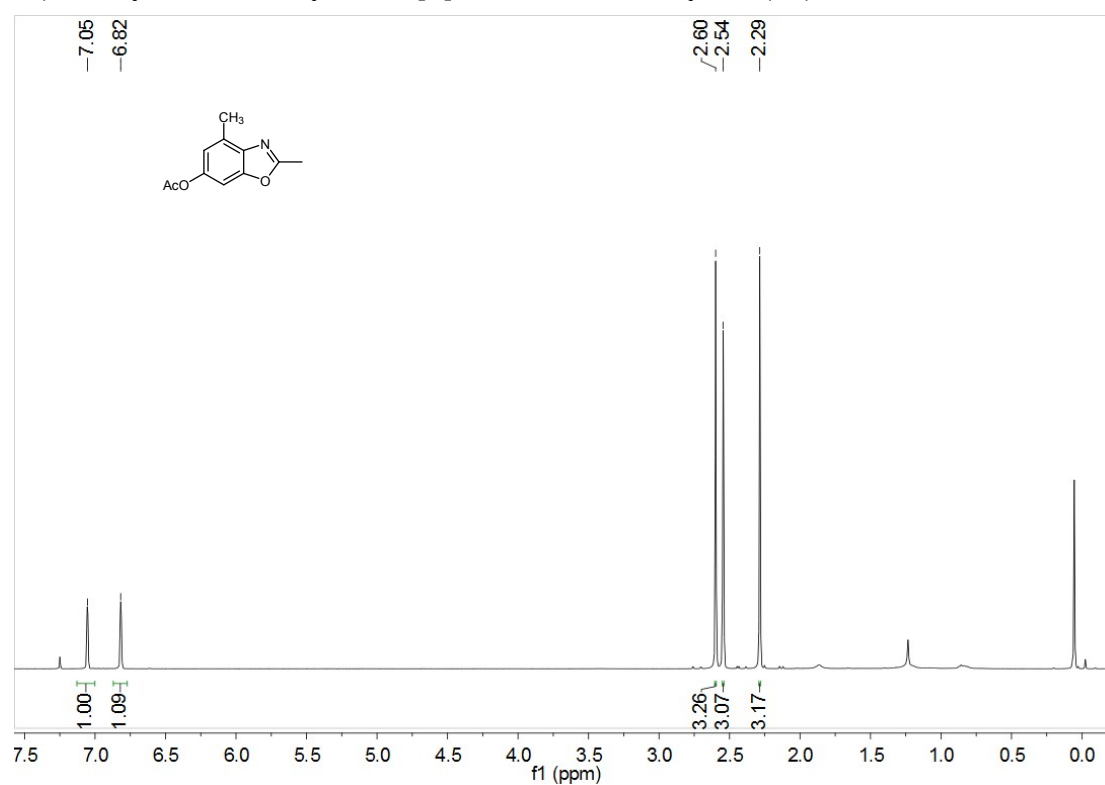
8) 6-chloro-2,4-dimethylbenzo[d]oxazole (2i)



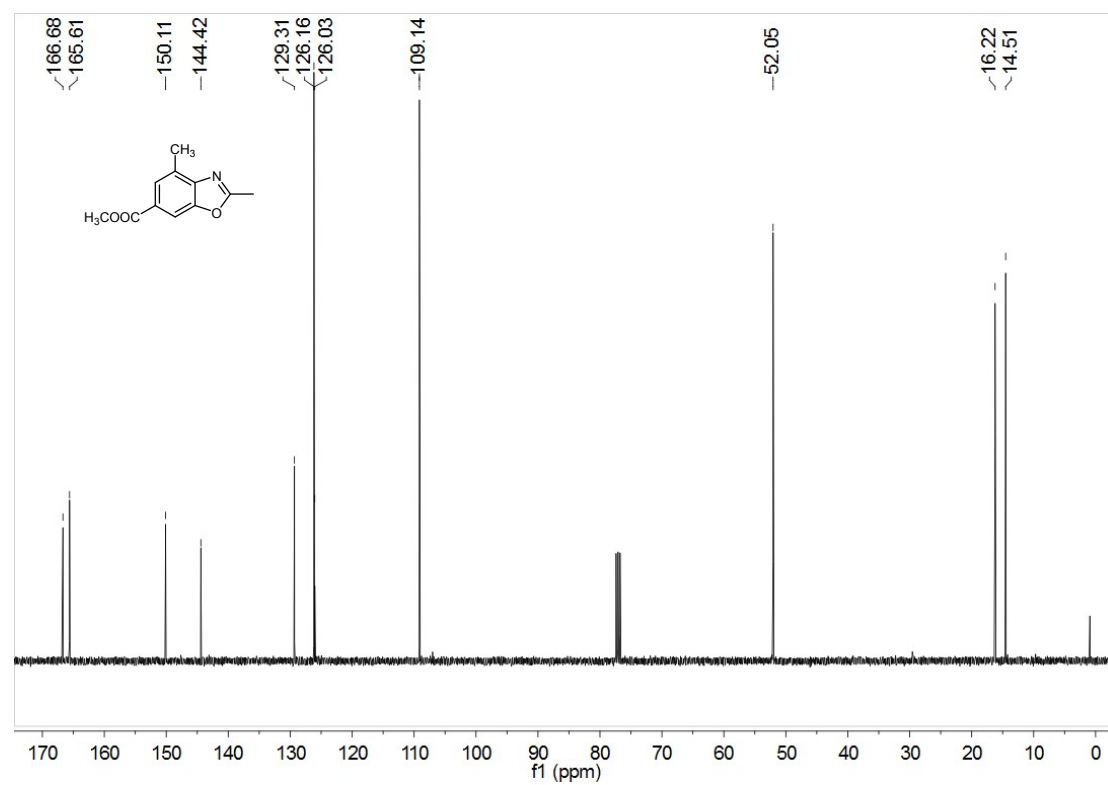
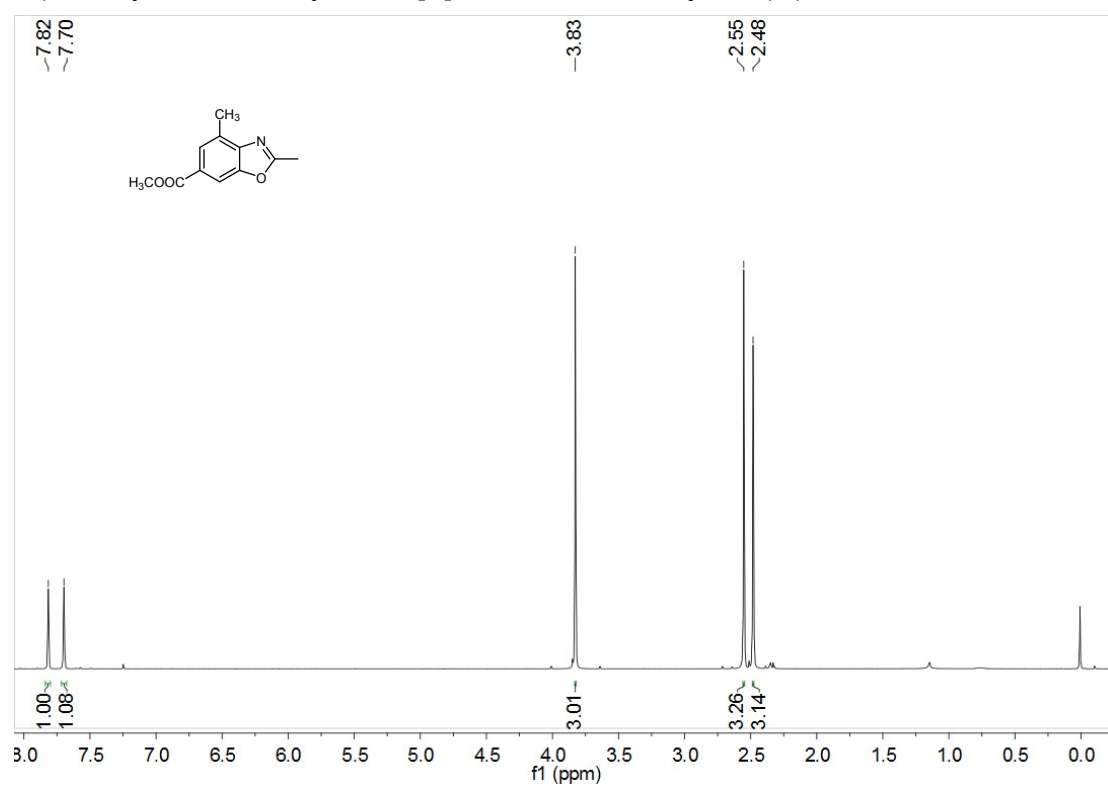
9) 6-bromo-2,4-dimethylbenzo[d]oxazole (2j)



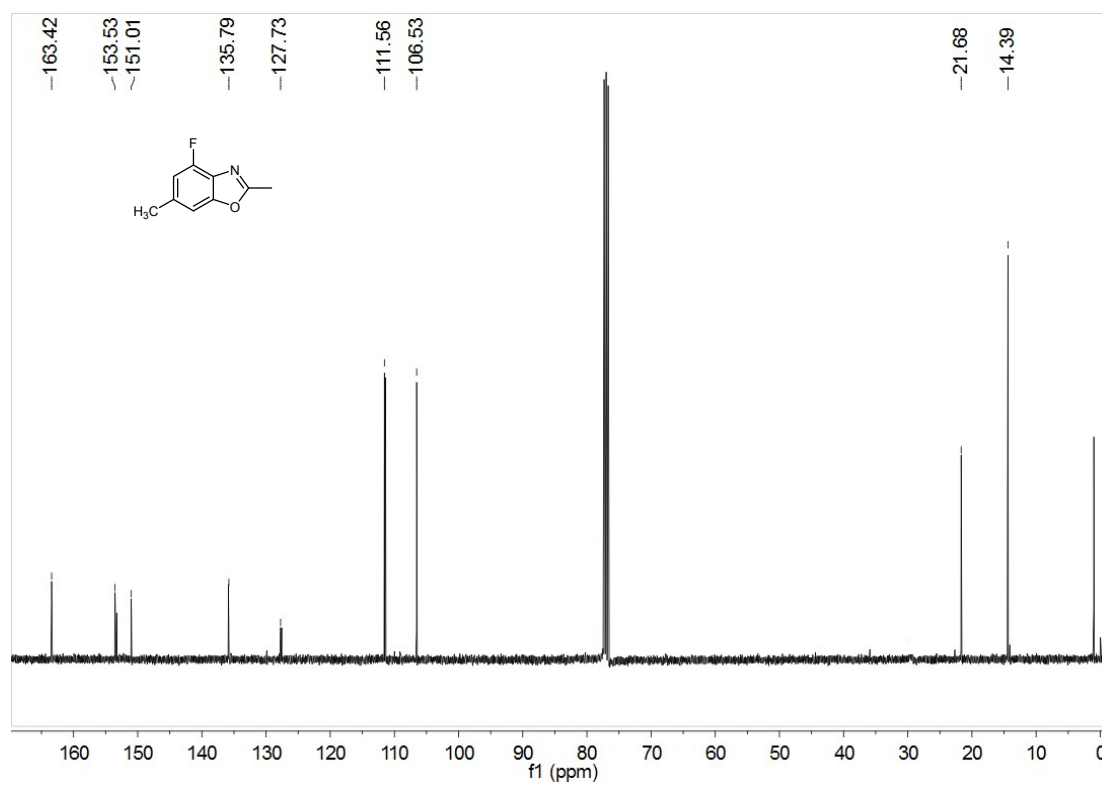
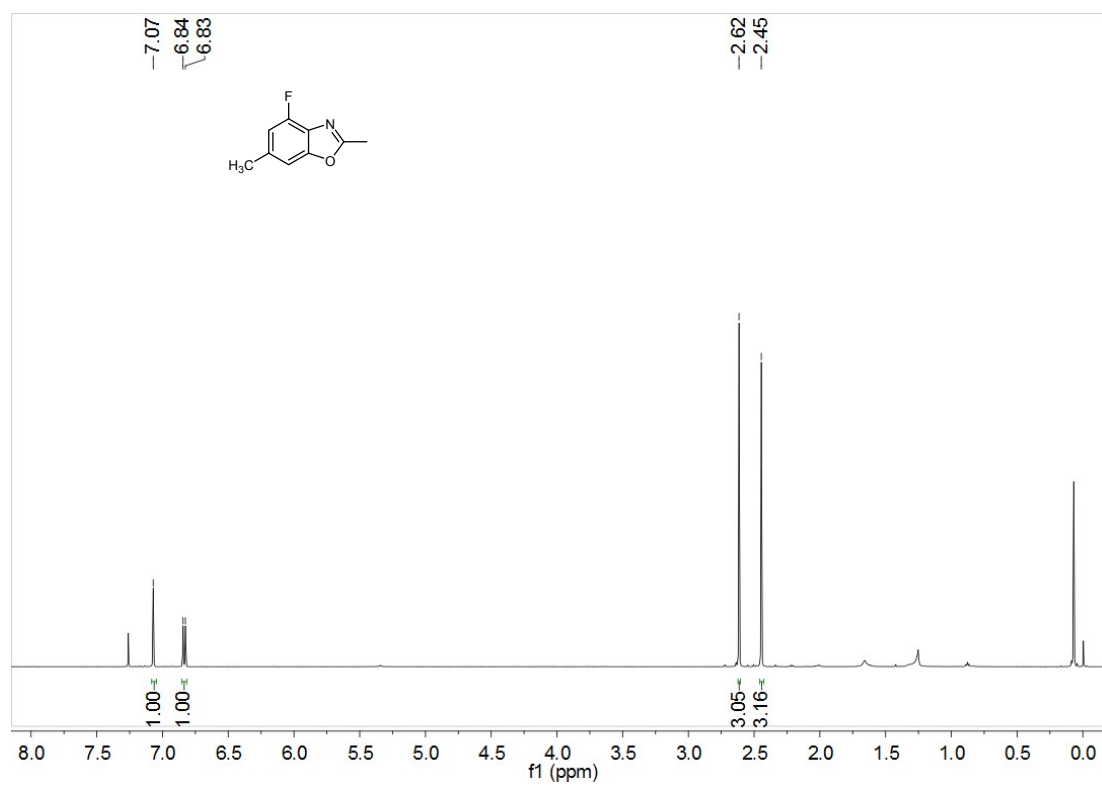
10) methyl 2,6-dimethylbenzo[d]oxazole-4-carboxylate (2k)



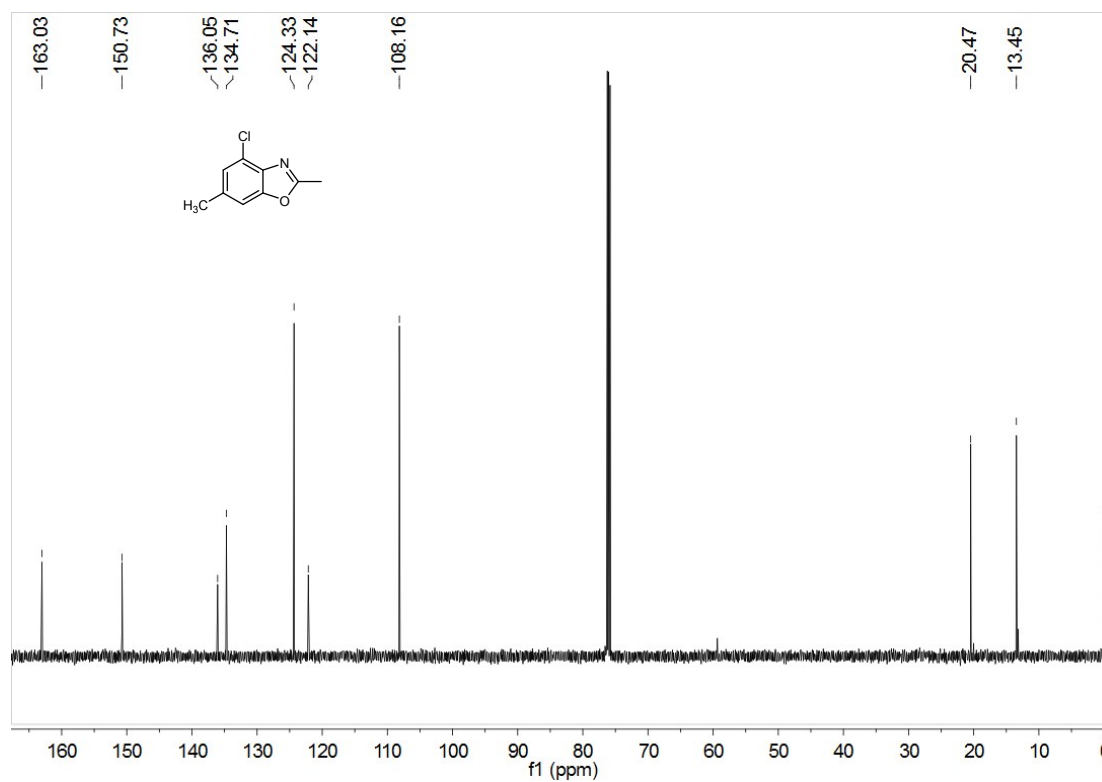
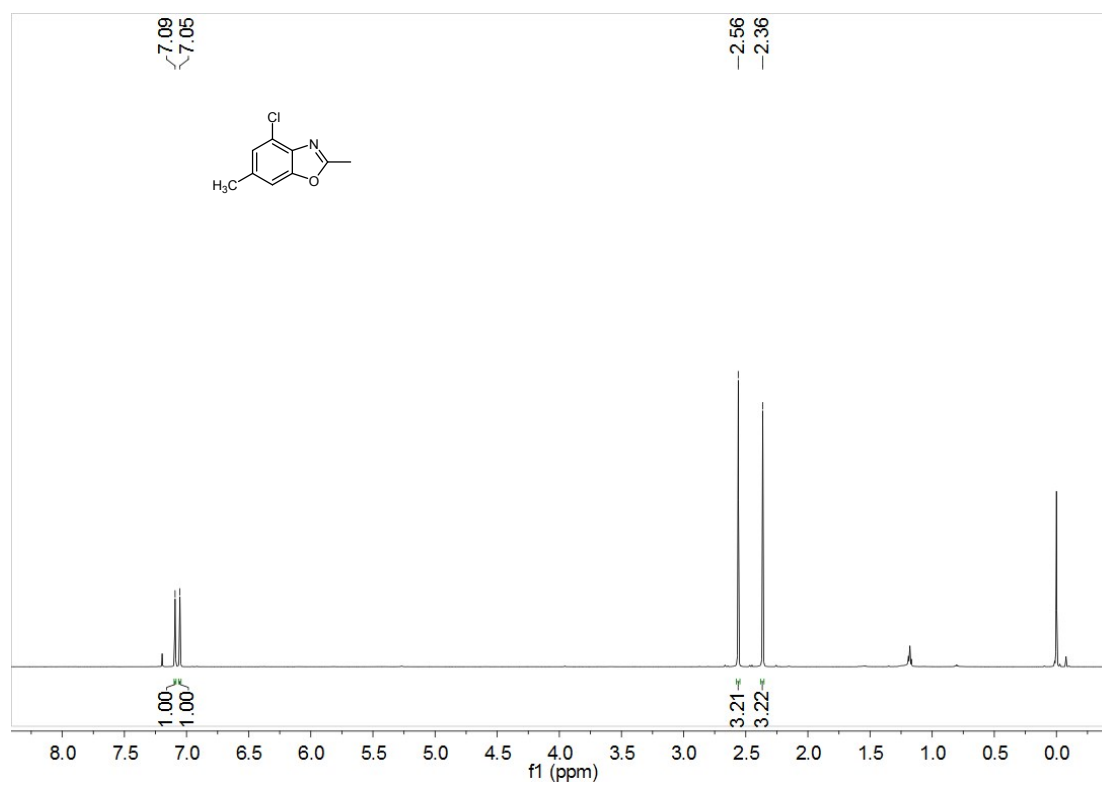
11) methyl 2,4-dimethylbenzo[d]oxazole-6-carboxylate (2l)



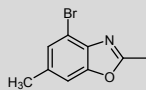
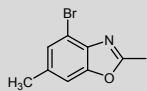
12) 4-fluoro-2,6-dimethylbenzo[d]oxazole (2m)



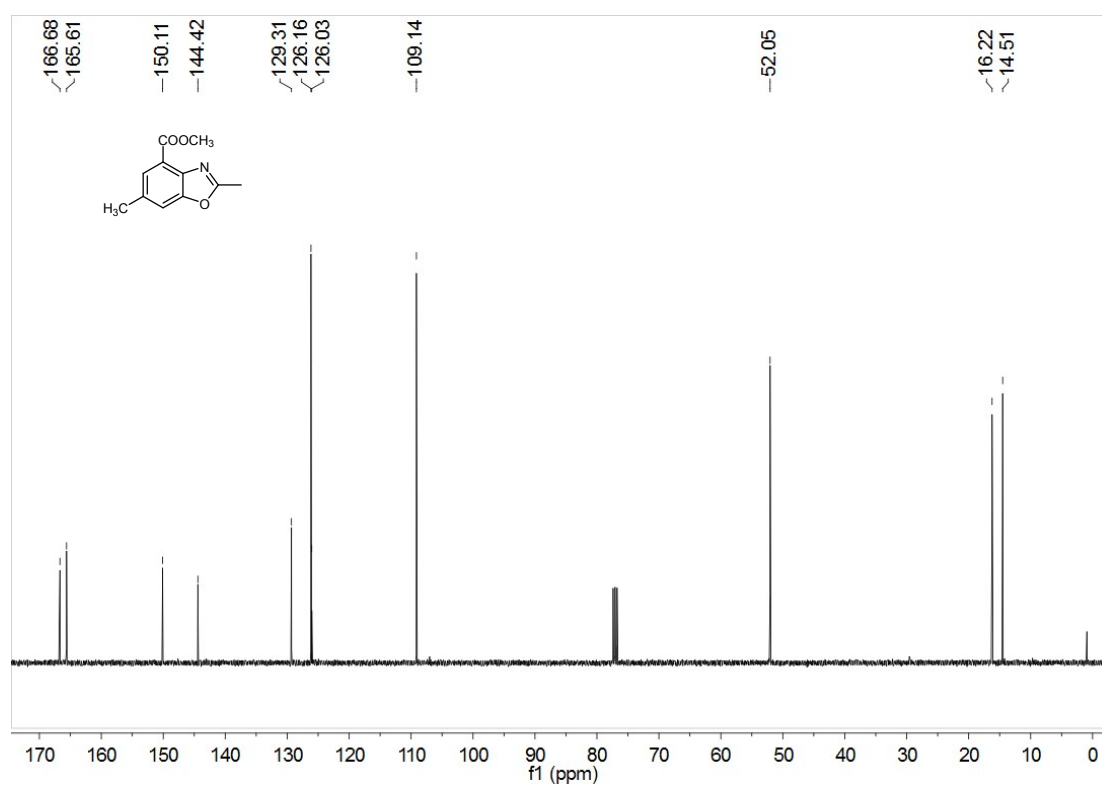
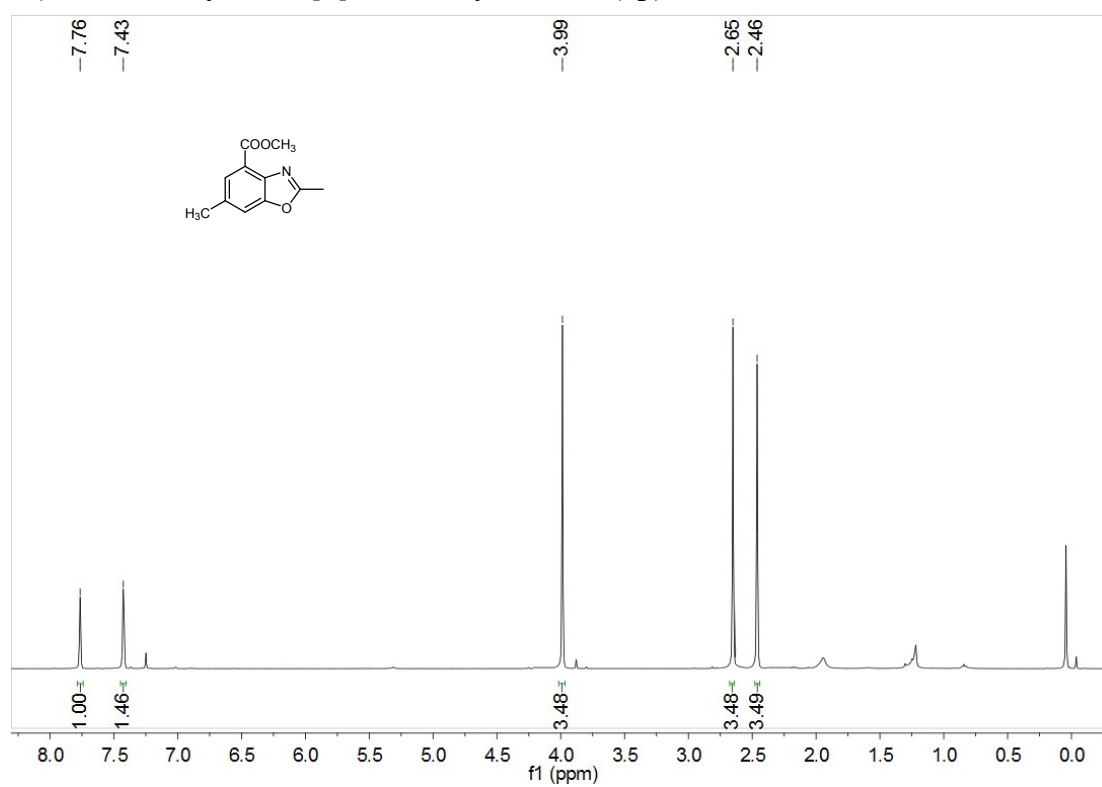
13) 4-chloro-2,6-dimethylbenzo[d]oxazole (2n)



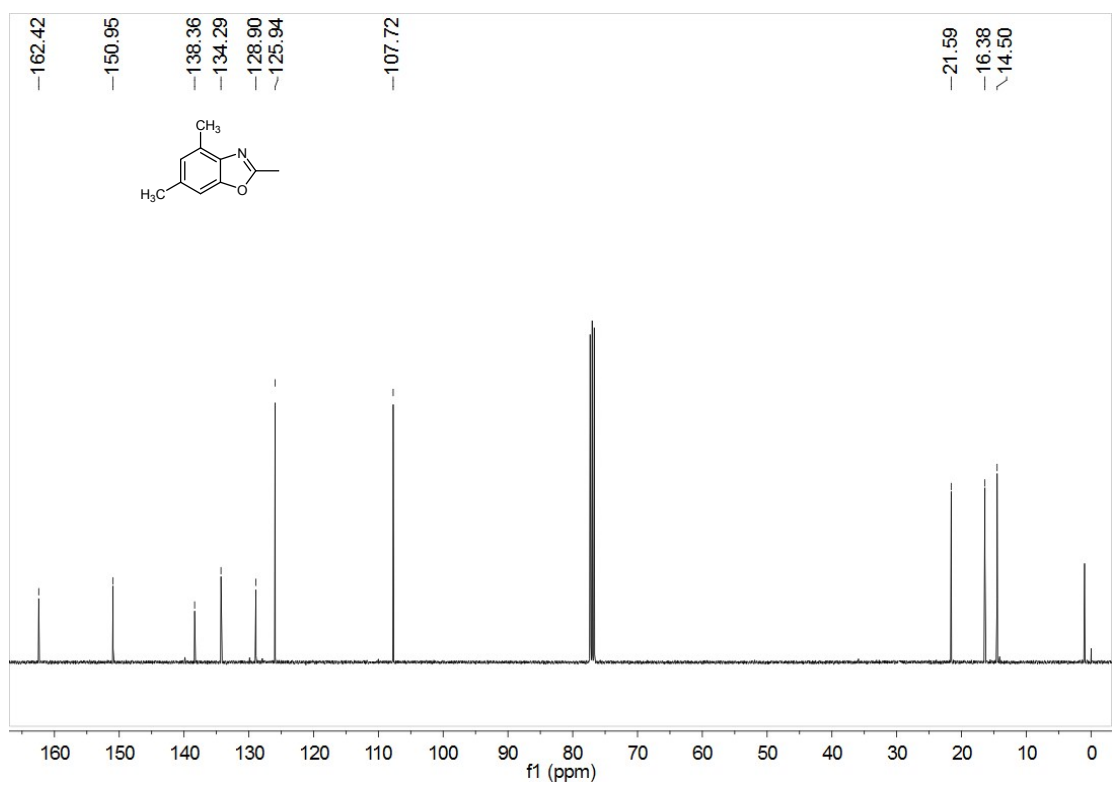
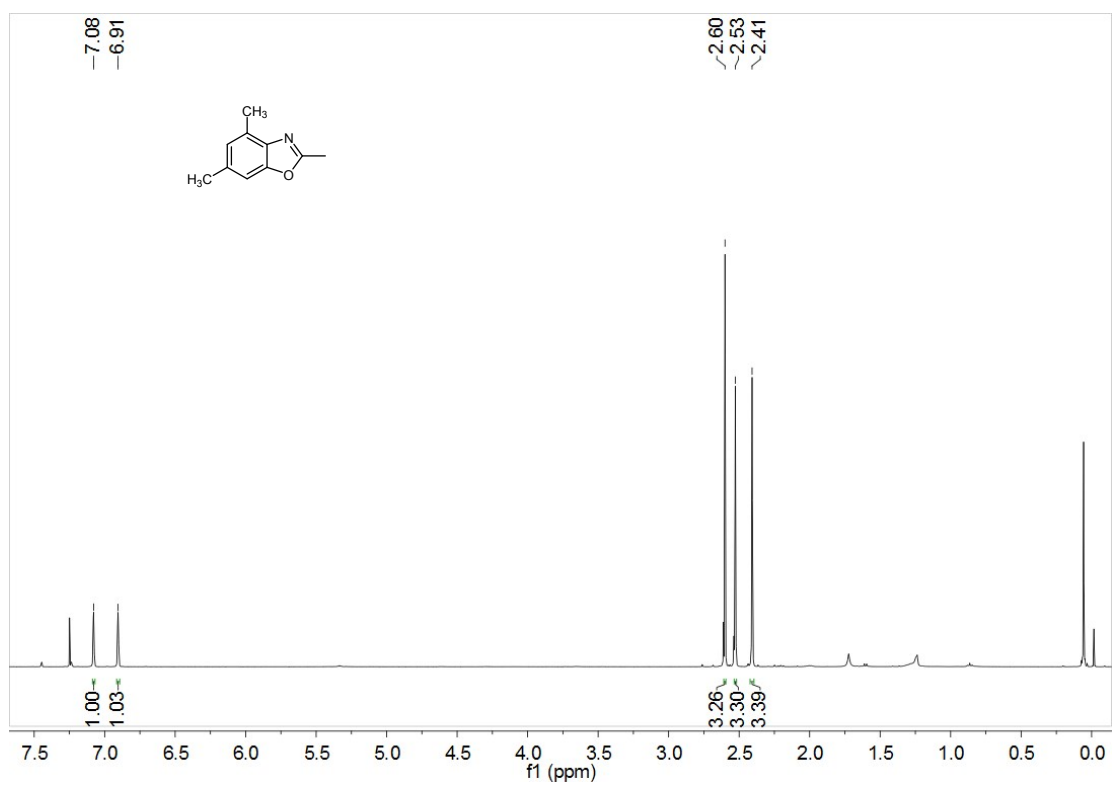
14) 4-bromo-2,6-dimethylbenzo[d]oxazole (2o)



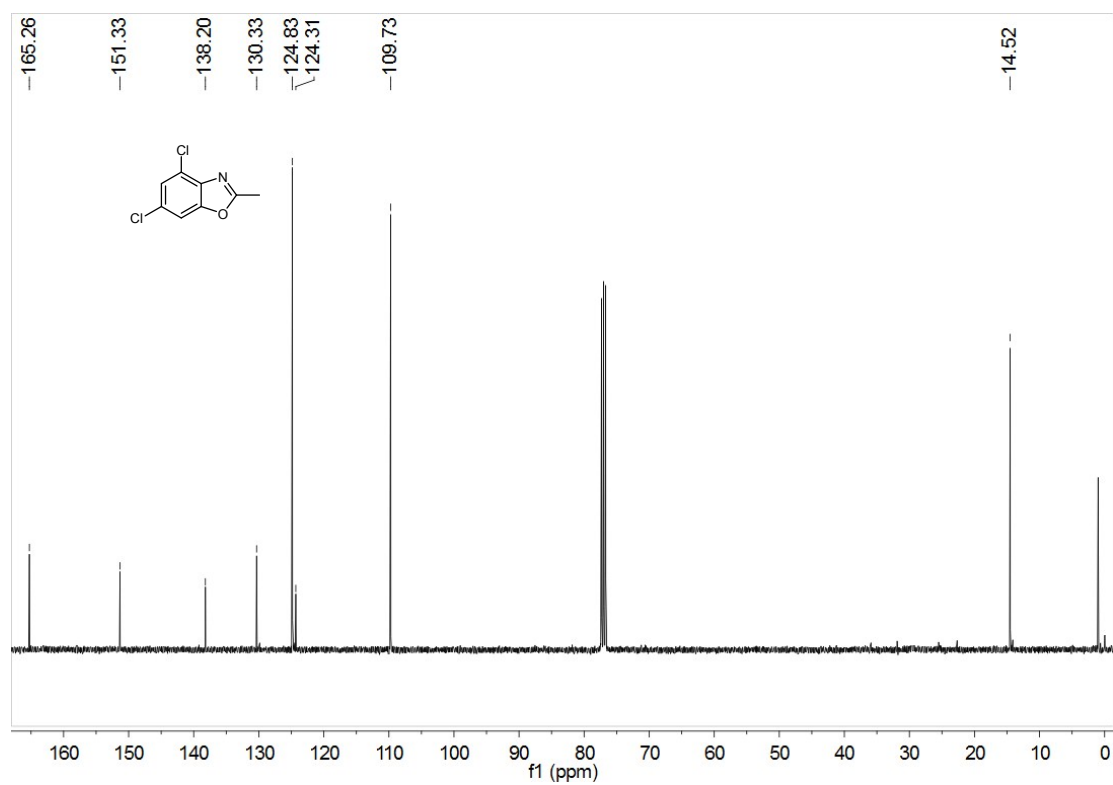
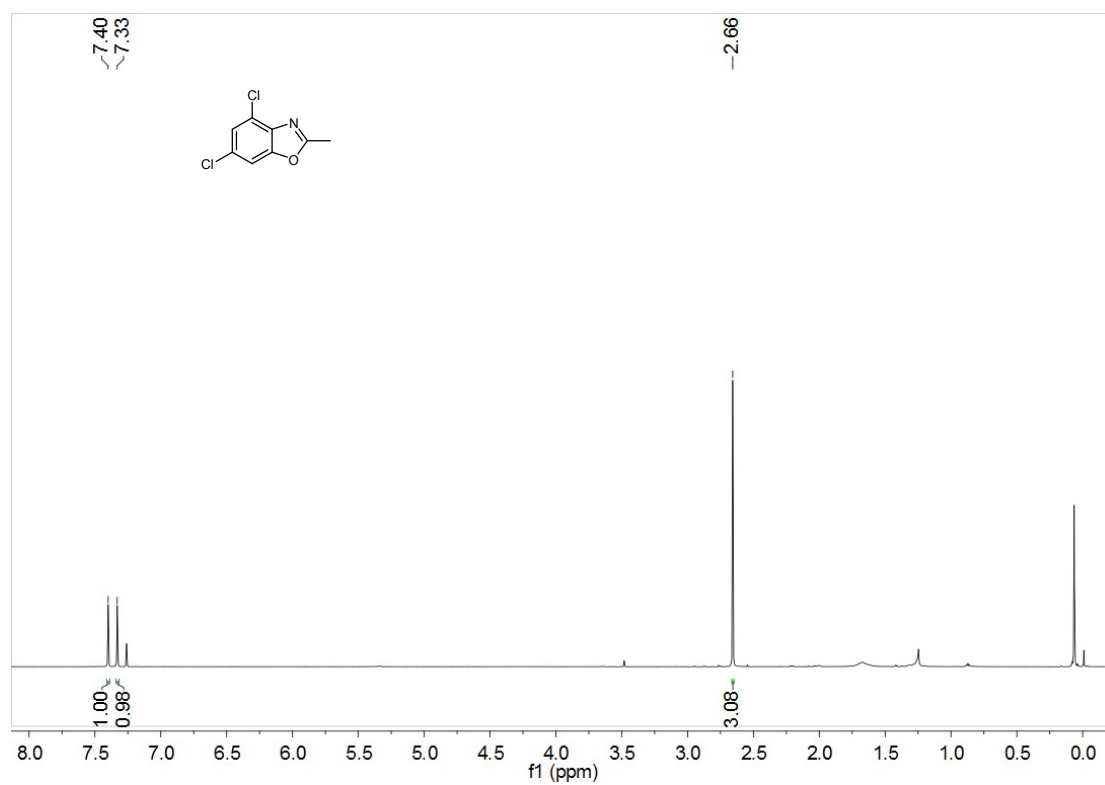
15) 2,4-dimethylbenzo[d]oxazol-6-yl acetate (2p)



16) 2,4,6-trimethylbenzo[d]oxazole (2q)



17) 4,6-dichloro-2-methylbenzo[d]oxazole (2r)



18) 4,6-dibromo-2-methylbenzo[d]oxazole (2s)

