Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Metal-organic framework mediated expeditious synthesis of benzimidazole and benzothiazole derivatives through oxidative cyclization pathway

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[#]Equally Contributed

FESEM and EDX images

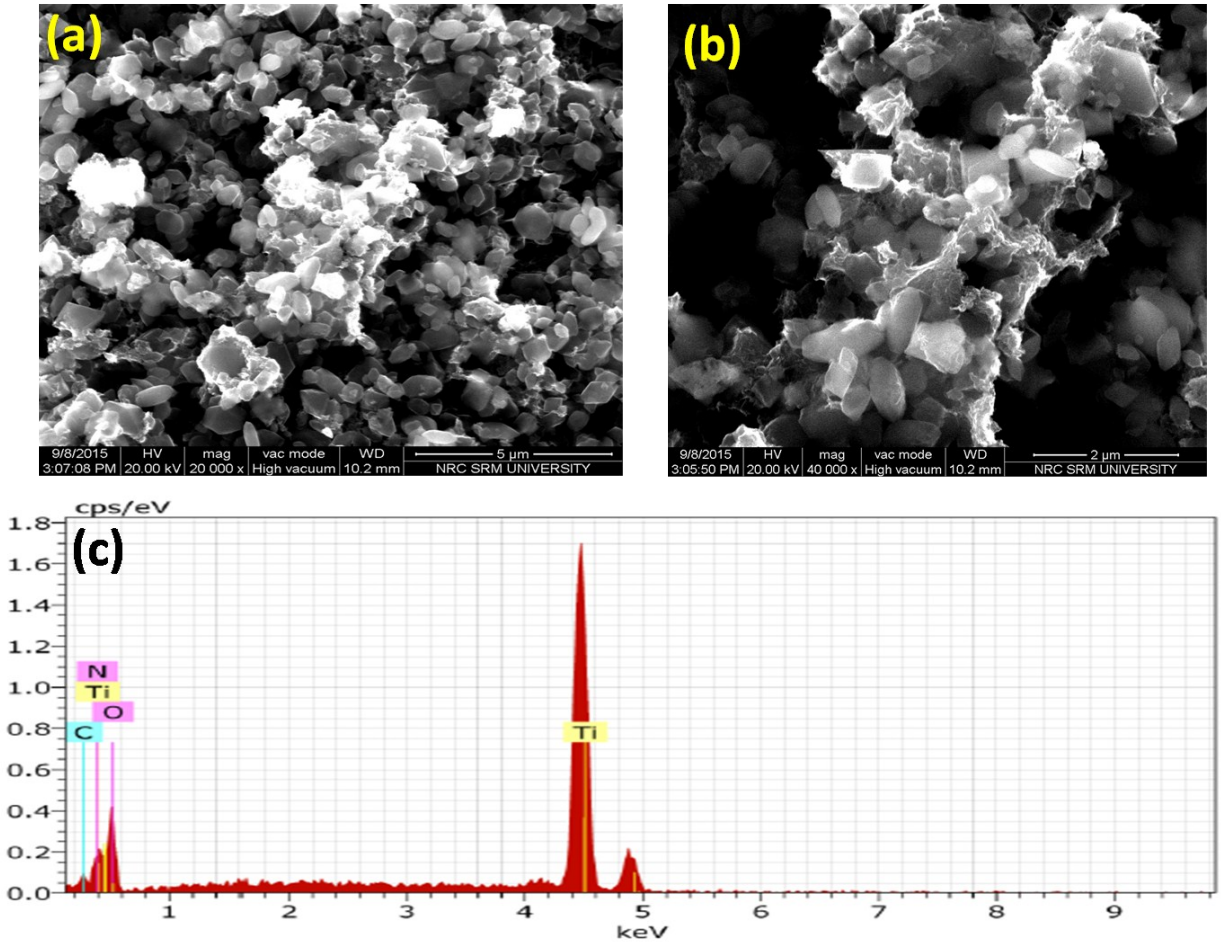


Fig. S1. (a, b) FESEM images and (c) EDX analysis of synthesized NH_2-MIL-125(Ti) MOF

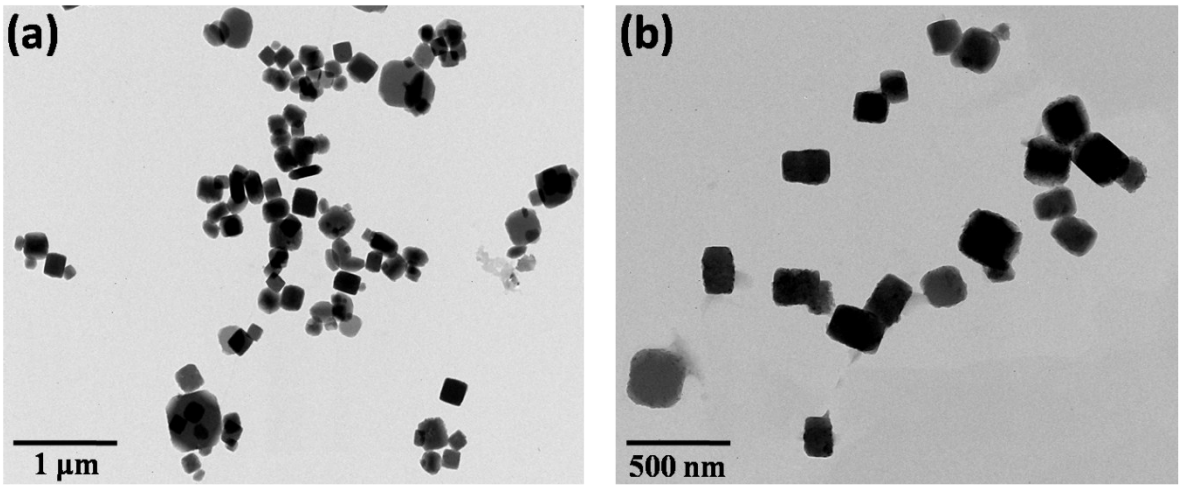


Fig. S2. (a, b) TEM images of synthesized NH_2-MIL-125(Ti) MOF

XRD and FTIR images

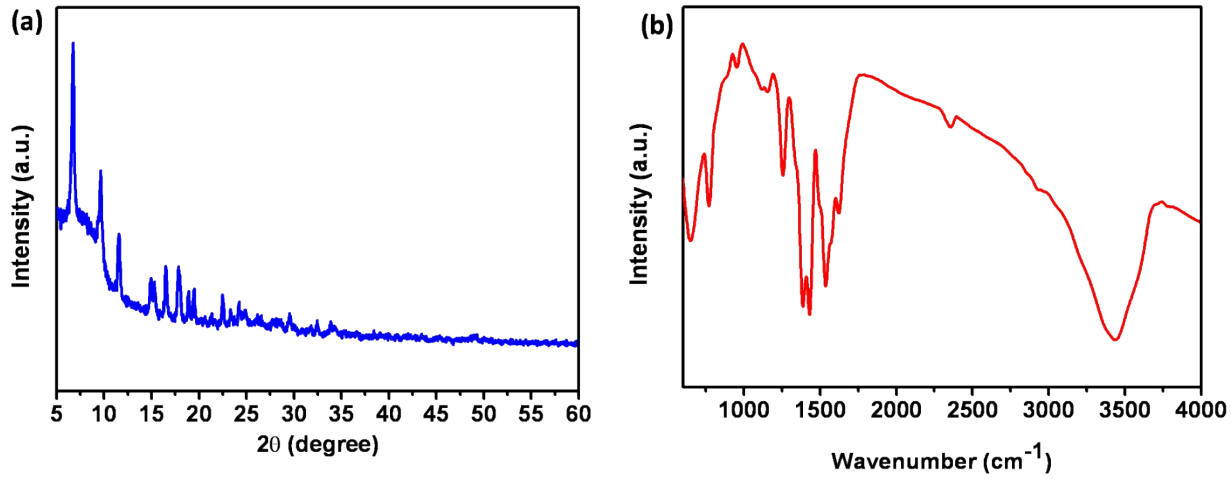


Fig. S3. (a) X-ray diffraction pattern and (b) FTIR studies of synthesized NH_2-MIL-125(Ti) MOF

UV-vis DRS and BET images

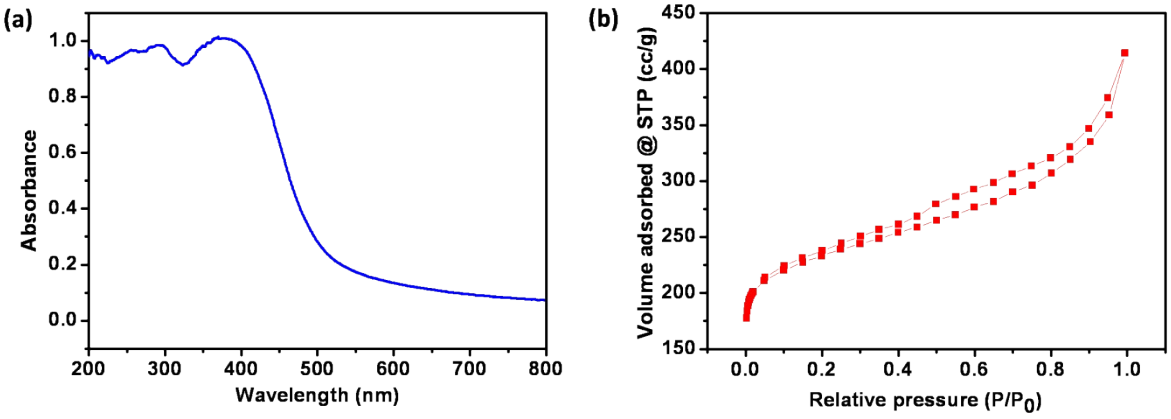


Fig. S4. (a) UV-vis DRS spectra and (b) BET analysis of NH_2-MIL-125(Ti) MOF

Name of samples	S_{BET} (m^2 g^{-1})	Pore volume (cc/g)
NH_2-MIL-125(Ti)	710	0.649

Recyclability and FT-IR images

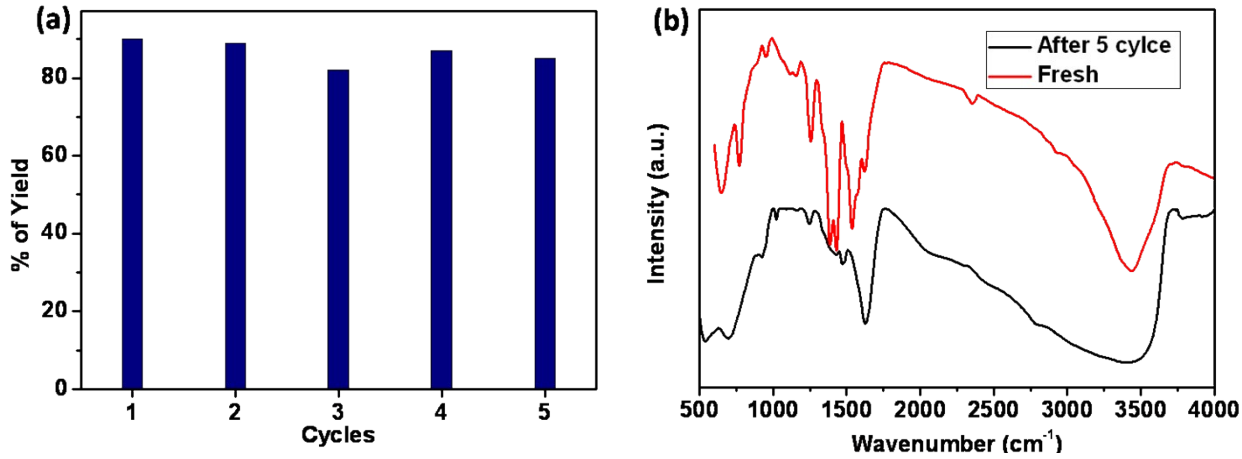


Fig S5. (a) Recyclability study of NH_2-MIL-125(Ti) MOF for synthesis of benimidazole (b) FT-IR spectra of NH_2-MIL-125(Ti) MOF before and after 5threcycle.

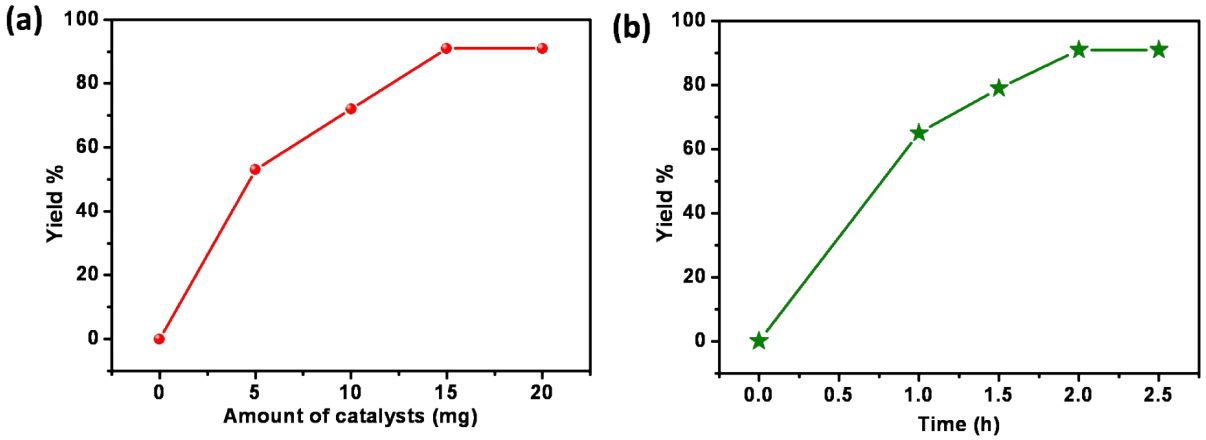
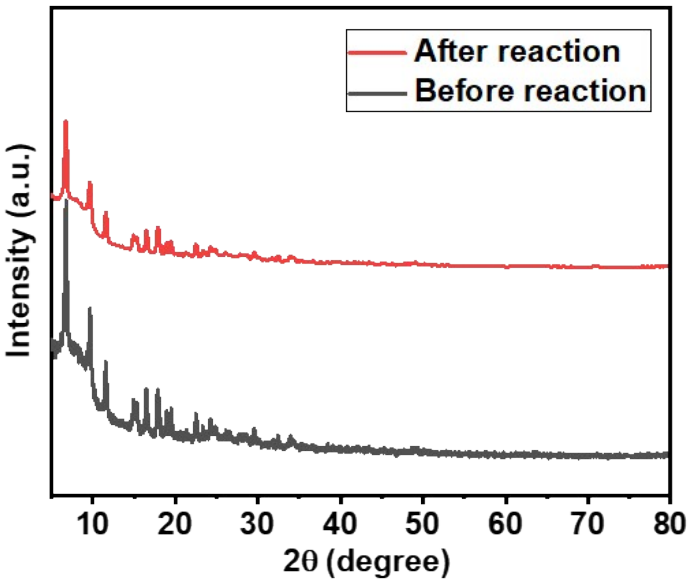
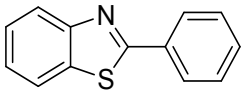


Fig S6. (a) Effect of different amount of catalyst and (b) reaction time on synthesis of benzimidazole


After reaction
Before reaction
Intensity (a.u.)
10
20
30
40
50
60
70
80
2θ (degree)

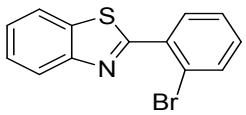
Spectral data of products.

1a. 2-phenylbenzo[d]thiazole



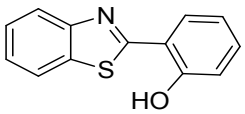
White crystals; IR (ATR cm^{-1}): 3066, 1556, 1474, 1316, 1074, 960, 756; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.08 (m, 3H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.47 (m, 4H), 7.41 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.10, 154.17, 135.09, 133.65, 131.00, 129.05, 127.59, 126.35, 125.22, 123.27, 121.65.

2a. 2-(2-bromophenyl)benzo[d]thiazole



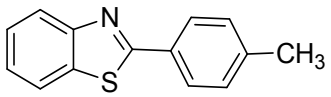
Yellow solid; IR (ATR cm^{-1}): 2923, 1589, 959, 752; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.47 (m, 4H), 7.39 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.04, 153.07, 134.00, 132.55, 129.93, 127.98, 126.51, 125.27, 124.15, 122.18, 120.57.

3a. 2-(benzo[d]thiazole-2-yl)phenol



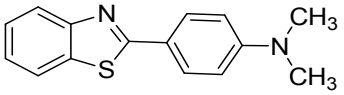
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.41 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.28, 156.86, 150.73, 131.67, 131.50, 127.33, 125.60, 124.45, 121.08, 120.42, 118.44, 116.78, 115.69.

4a. 2-(p-tolyl)benzo[d]thiazole



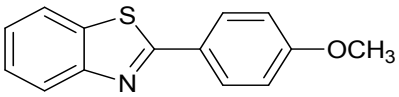
White solid; IR (ATR cm^{-1}): 2919, 1603, 1482, 1310, 959, 817; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.28, 154.17, 141.46, 134.95, 130.96, 129.74, 127.50, 126.26, 125.02, 123.06, 121.59, 22.72.

5a. 4-(benzo[d]thiazol-2-yl)-N,N-dimethylaniline



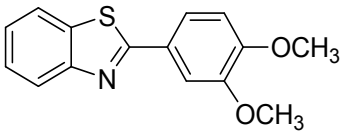
White solid; IR (ATR cm^{-1}): 2927, 1610, 1524, 1203, 1067, 810, 738; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.95 (m, 3H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 6.74 (d, *J* = 9.0 Hz, 2H), 3.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.86, 154.34, 152.20, 134.51, 128.90, 126.02, 124.22, 122.26, 121.37, 111.71, 40.21.

6a. 2-(4-methoxyphenyl)benzo[d]thiazol



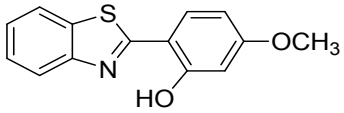
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 3H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.92, 161.94, 154.15, 134.87, 129.14, 126.24, 124.91, 124.82, 122.84, 121.54, 121.18, 114.39, 56.07.

7a. 2-(3,4-dimethoxyphenyl)benzo[d]thiazol



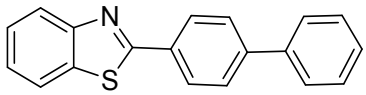
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.61 (d, *J* = 10.4 Hz, 1H), 7.48 (t, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.03 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.91, 161.93, 154.22, 134.86, 129.13, 126.44, 126.23, 124.82, 122.83, 121.54, 114.39, 55.50, 55.48.

8a. 2-(benzo[d]thiazol-2-yl)-5-methoxyphenol



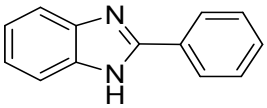
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.65 (s, 1H), 7.80 (dd, *J* = 34.9, 8.1 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.1 Hz, 1H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.44 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.22, 162.38, 158.91, 150.79, 131.11, 128.56, 125.49, 123.96, 120.62, 120.34, 109.34, 106.62, 100.27, 54.43.

9a. 2-([1,1'-biphenyl]-4-yl)benzo[d]thiazole



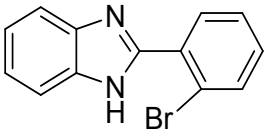
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 37.7, 8.2 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 34.3, 7.9 Hz, 3H), 7.58 (dd, *J* = 10.2, 7.9 Hz, 2H), 7.52 – 7.33 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.75, 154.22, 143.75, 140.08, 135.08, 132.51, 128.97, 128.02, 127.99, 127.68, 127.15, 126.40, 125.23, 123.22, 121.66.

10a. 2-Phenylbenzimidazole



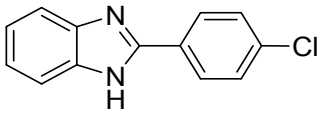
Yellow solid; IR (ATR cm^{-1}): 2926, 1442, 1274, 1110, 977, 741; ^{1}H NMR (500 MHz, DMSO) δ 8.20 (d, *J* = 8.3 Hz, 2H), 7.72 – 7.42 (m, 5H), 7.21 (d, *J* = 3.8 Hz, 2H); ^{13}C NMR (126 MHz, DMSO) δ 151.69, 144.23, 135.49, 133.28, 130.64, 130.31, 129.42, 126.90, 122.17, 119.41, 111.74. MS (ESI): *m/z* 195 $[M+H]^{+}$

11a. 2-(2-bromophenyl)-1H-benzo[d]imidazole



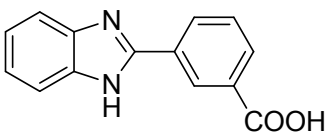
Brown solid; ^{1}H NMR (500 MHz, DMSO) δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.49 (m, 4H), 7.22 (dd, *J* = 5.8, 3.0 Hz, 2H); ^{13}C NMR (126 MHz, DMSO) δ 151.70, 133.28, 130.65, 130.30, 129.74, 129.42, 129.02, 126.91, 122.70, 119.75, 111.57.

12a. 2-(4-chlorophenyl)-1H-benzo[d]imidazole



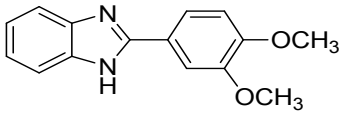
White solid; ^{1}H NMR (500 MHz, DMSO) δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.66 (dd, *J* = 17.6, 8.0 Hz, 3H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.22 (dt, *J* = 14.9, 7.2 Hz, 2H); ^{13}C NMR (126 MHz, DMSO) δ 150.62, 144.07, 135.41, 135.02, 129.57, 129.39, 128.61, 123.34, 122.40, 119.37, 111.92.

13a. 3-(1H-benzo[d]imidazol-2yl)benzoicacid



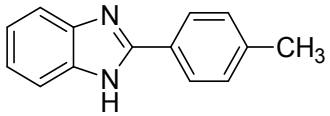
Brown solid; ^{1}H NMR (500 MHz, DMSO) δ 13.10 (s, 1H), 8.79 (s, 1H), 8.42 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.65 (dd, *J* = 40.6, 32.9 Hz, 3H), 7.22 (d, *J* = 3.1 Hz, 2H); ^{13}C NMR (126 MHz, DMSO) δ 167.43, 150.82, 132.07, 130.98, 130.91, 129.82, 127.66.

14a. 2-(3,4-dimethoxyphenyl)-1H-benzo(d)imidazole



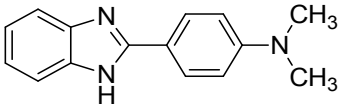
Yellow solid; IR (ATR cm^{-1}): 2948, 1610, 1427, 1264, 836, 731; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.66 (d, *J* = 9.7 Hz, 1H), 7.60 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.22 (dd, *J* = 6.4, 3.5 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.31, 150.76, 149.36, 142.57, 139.06, 128.89, 123.26, 122.81, 122.51, 121.87, 119.56, 118.11, 114.85, 111.20, 109.77, 55.93, 55.58.

15a. 2-(p-tolyl)-1H-benzo[d]imidazole



White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.54 (s, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 6.0, 3.1 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 151.84, 140.02, 129.98, 129.80, 129.57, 127.92, 126.85, 21.44. MS (ESI): *m/z* 209 $[M+H]^+$

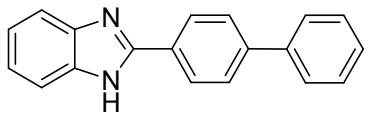
16a. 4-(1H-benzo[d]imidazole-2yl)-N,N-dimethylaniline



Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.33 – 7.13 (m, 3H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 25.7, 8.8 Hz, 2H), 3.01 (s, 3H),

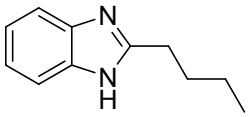
2.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.99, 151.26, 150.01, 136.33, 130.33, 126.95, 124.30, 122.20, 119.22, 112.82, 111.83, 110.41, 40.54, 40.20.

17a. 2-([1,1'-biphenl]-4-yl)-1H-benzo[d]imidazole



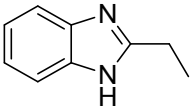
Yellow solid; IR (ATR cm^{-1}): 3056, 1428, 1231, 966, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.3 Hz, 2H), 7.69 (dd, *J* = 44.1, 7.5 Hz, 6H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.28 (m, 2H); ^{13}C NMR (126 MHz, DMSO) δ 151.40, 144.40, 141.77, 139.73, 135.53, 129.62, 129.51, 128.38, 127.62, 127.48, 127.17, 123.06, 122.21, 119.34, 111.81. MS (ESI): *m/z* 271 $[M+H]^+$

18a. 2-butyl-1H-benzo[d]imidazole



White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.21 (dd, *J* = 6.0, 3.2 Hz, 2H), 3.01 – 2.85 (m, 2H), 1.84 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.48 – 1.31 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.31, 138.38, 122.19, 114.59, 30.33, 29.02, 22.43, 13.73.

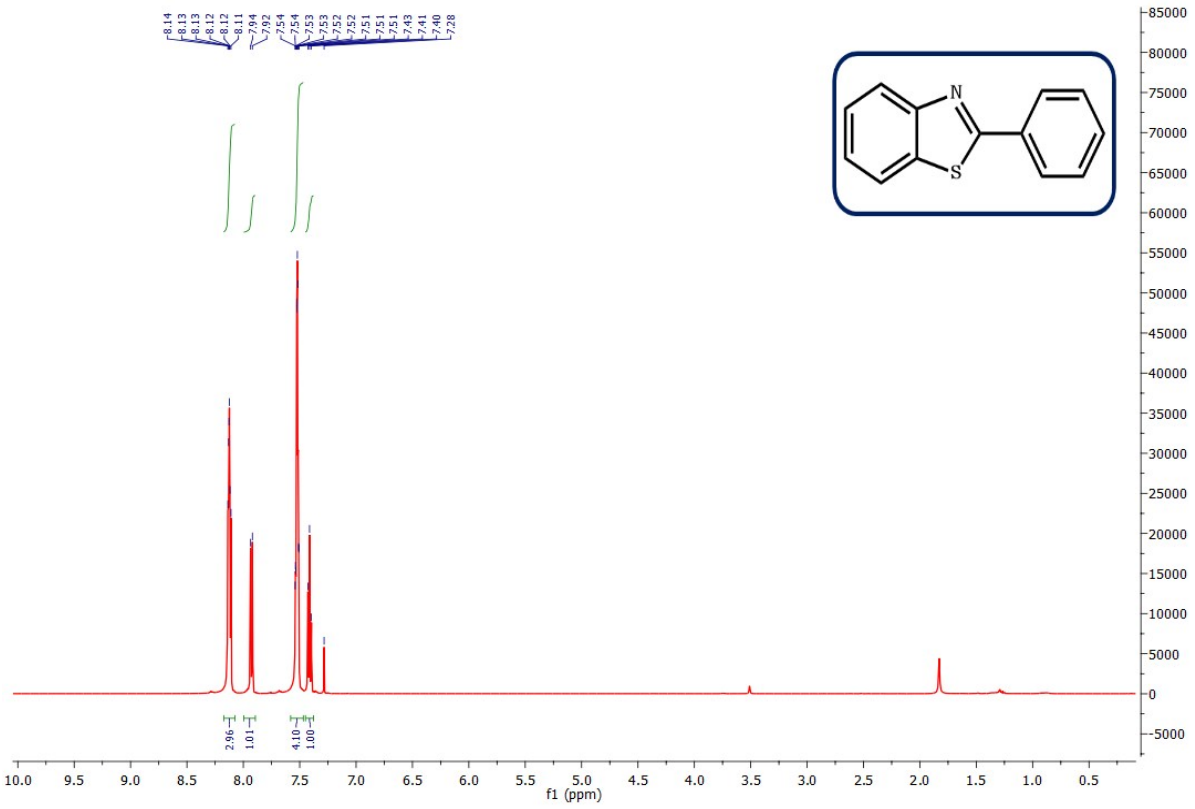
19a. 2-ethyl-1H-benzo[d]imidazole

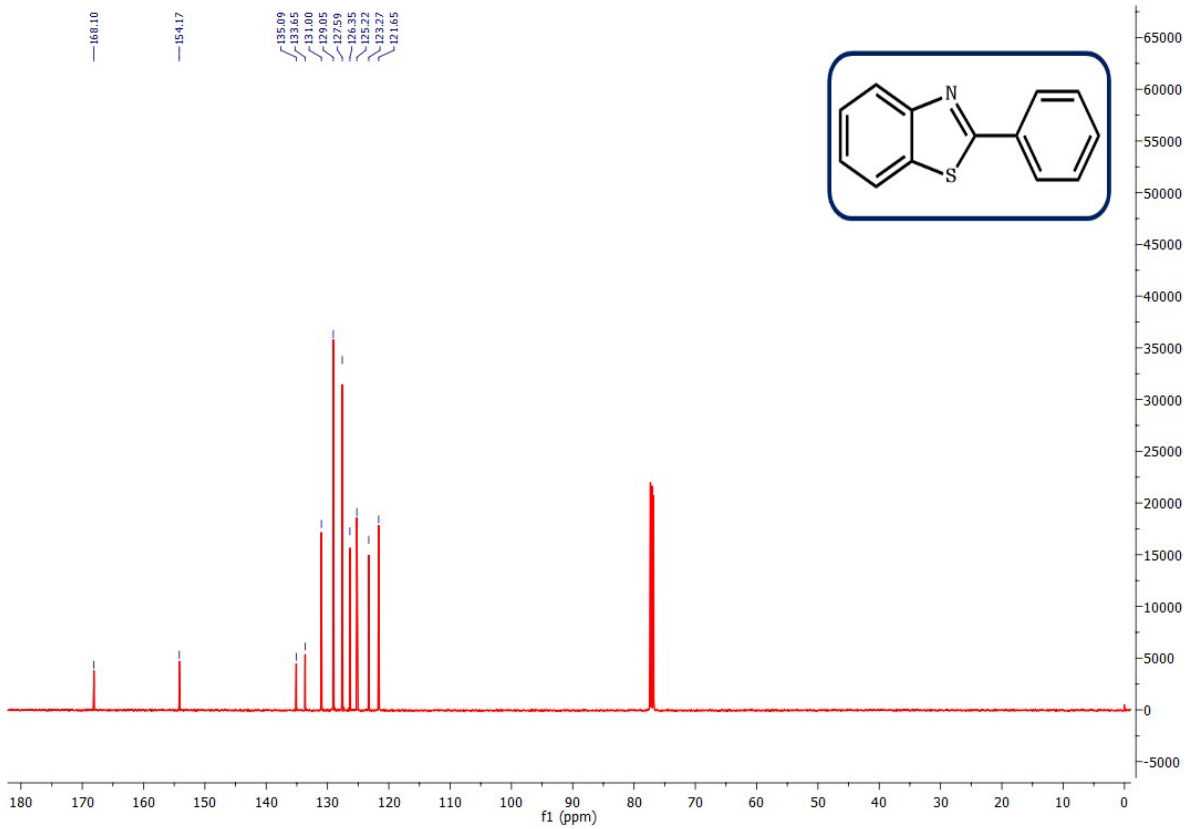


Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.21 (dd, *J* = 6.1, 3.1 Hz, 2H), 3.00 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.79, 138.43, 122.16, 114.57, 22.56, 12.56.

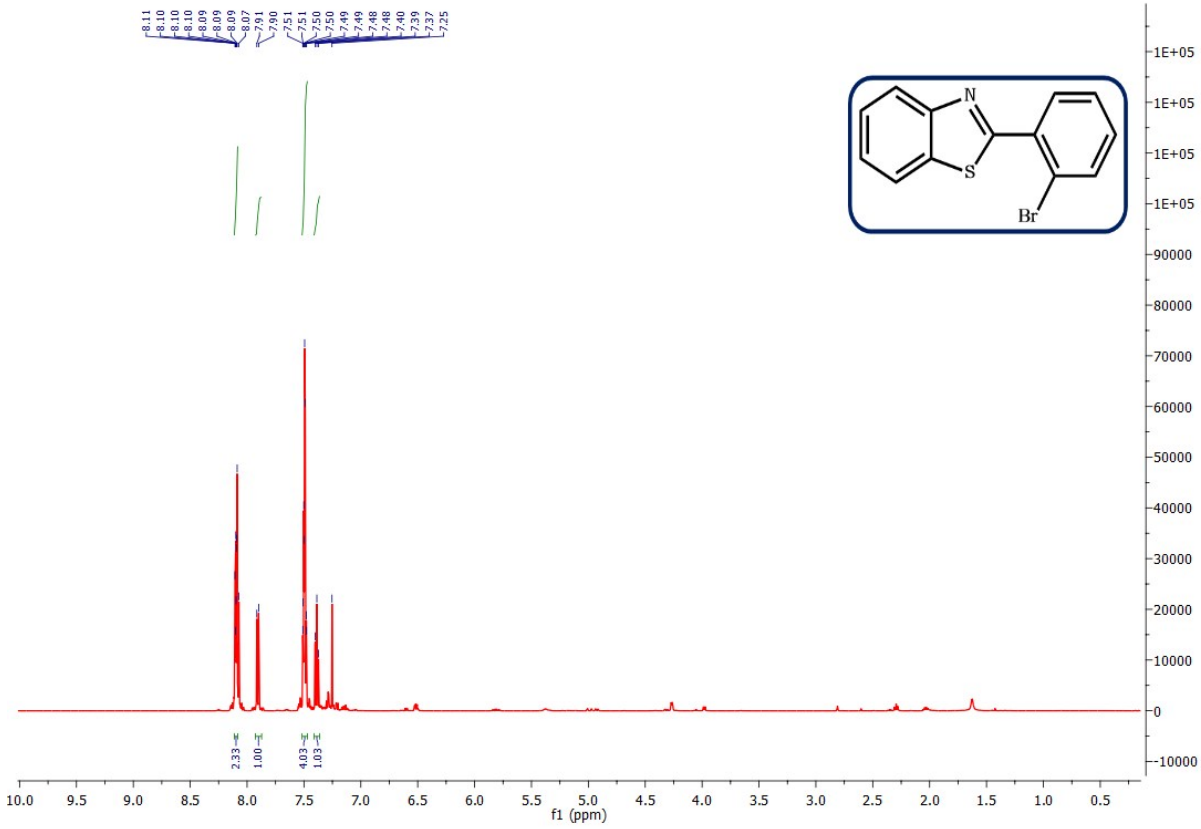
^{1}H, ^{13}C NMR Spectral analysis of products.

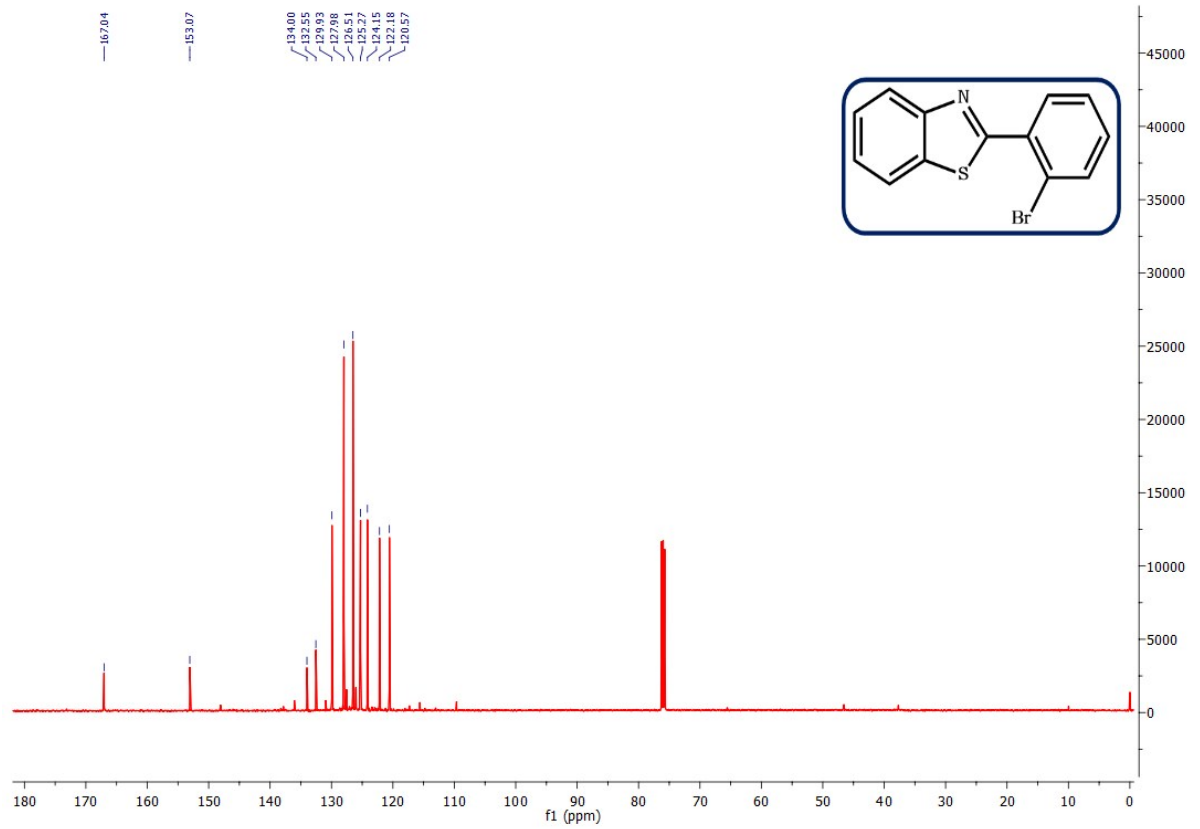
1a. 2-phenylbenzo[d]thiazole



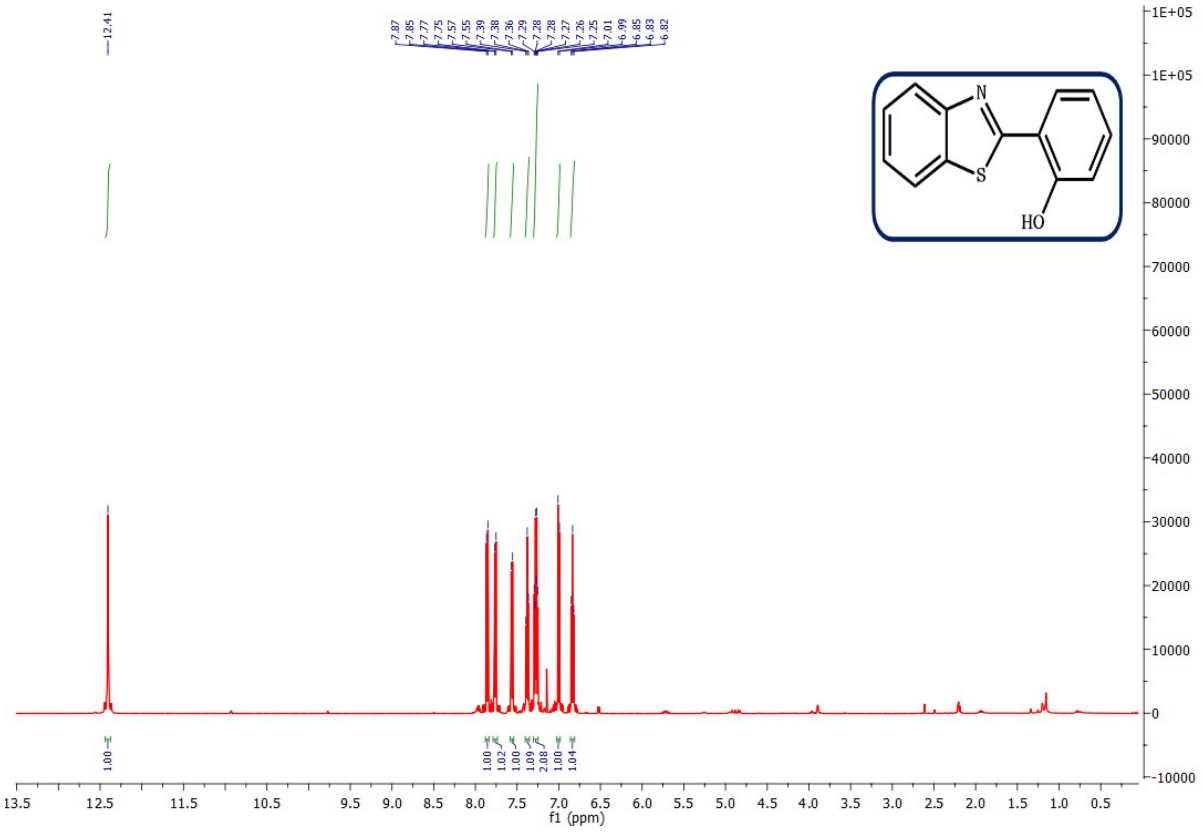


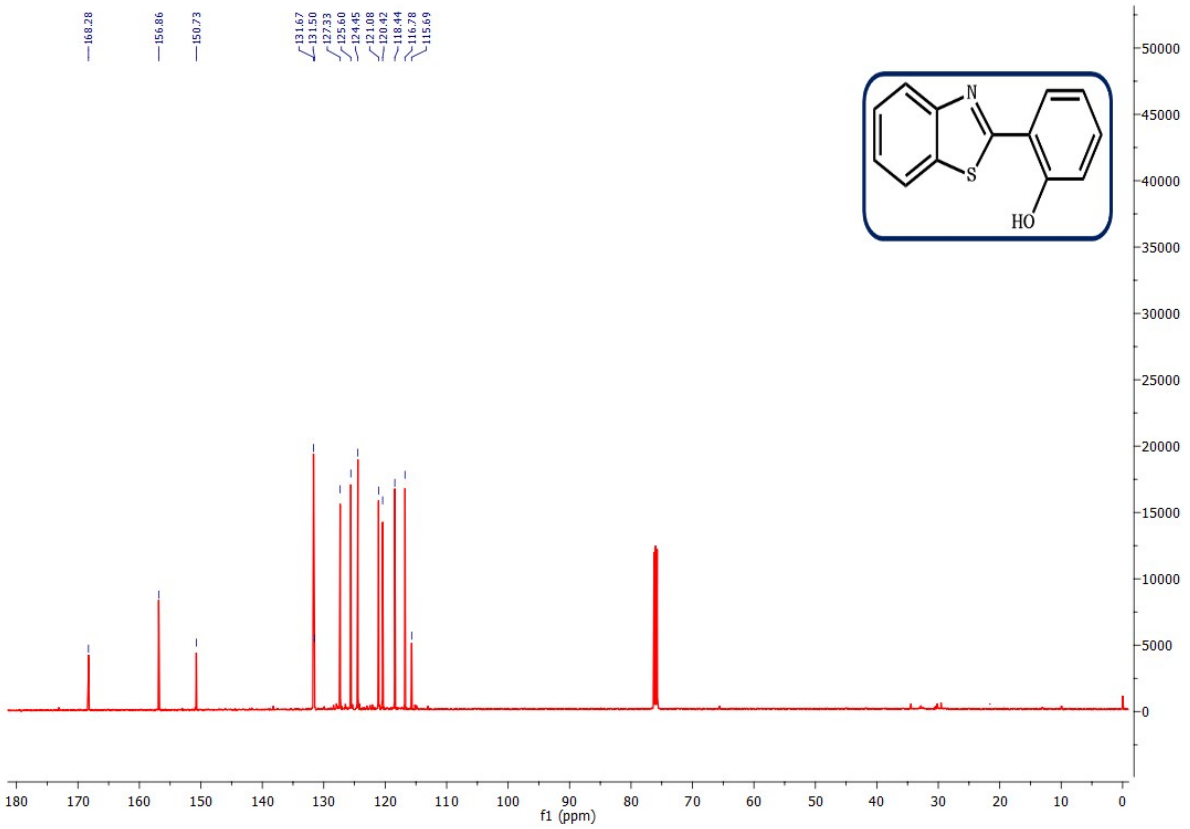
2a. 2-(2-bromophenyl)benzo[d]thiazole



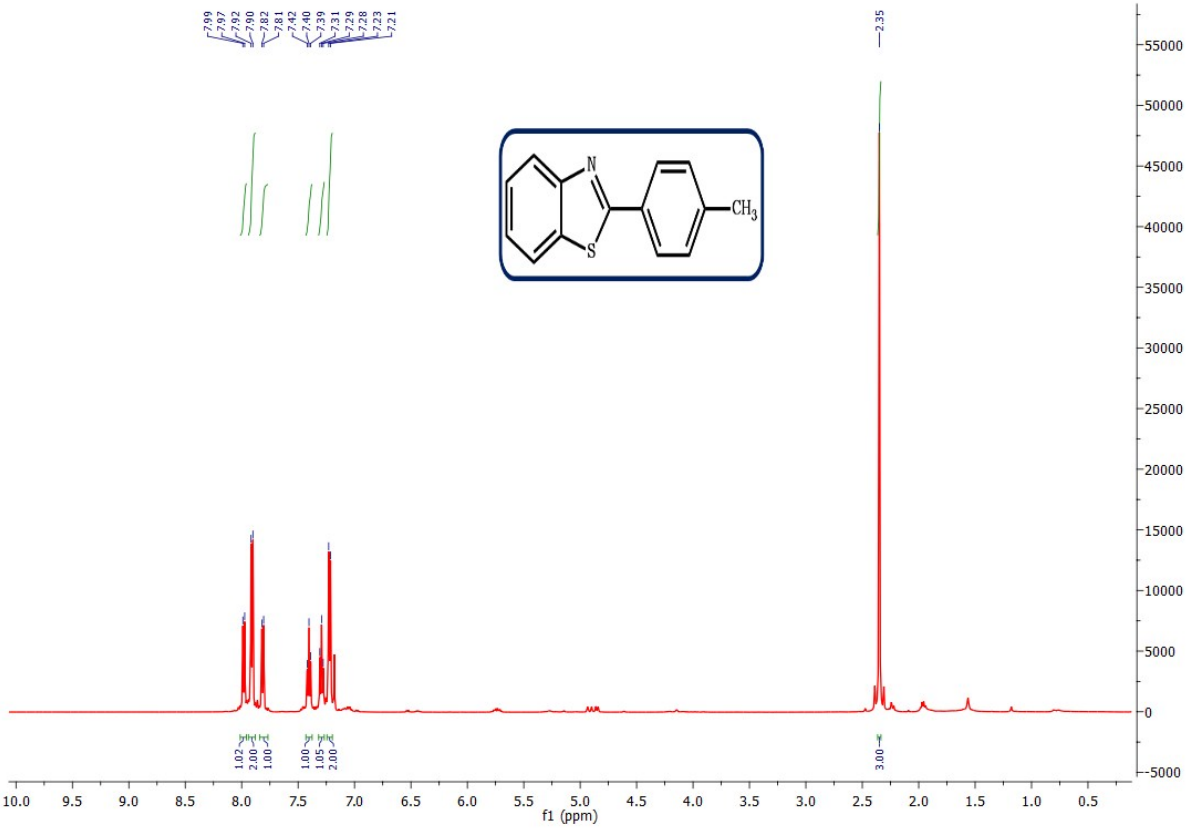


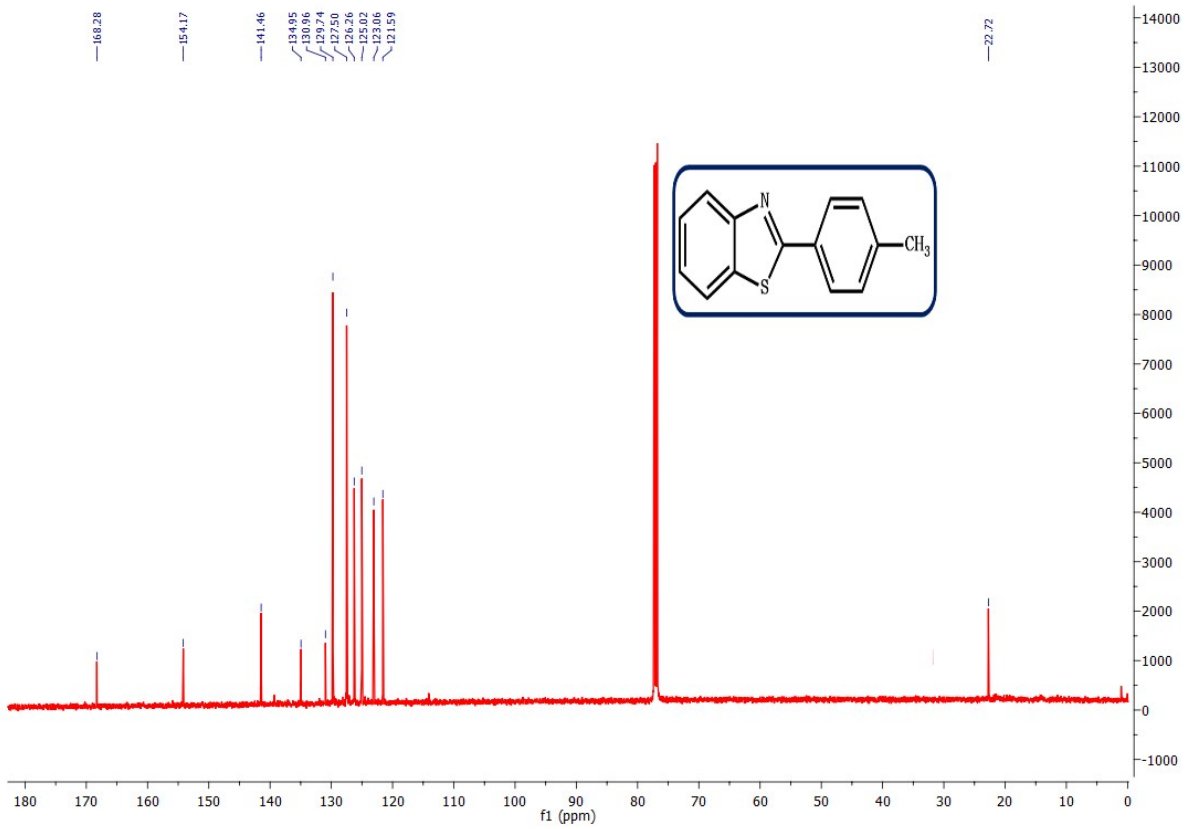
3a.2-(benzo[d]thiazole-2-yl)phenol



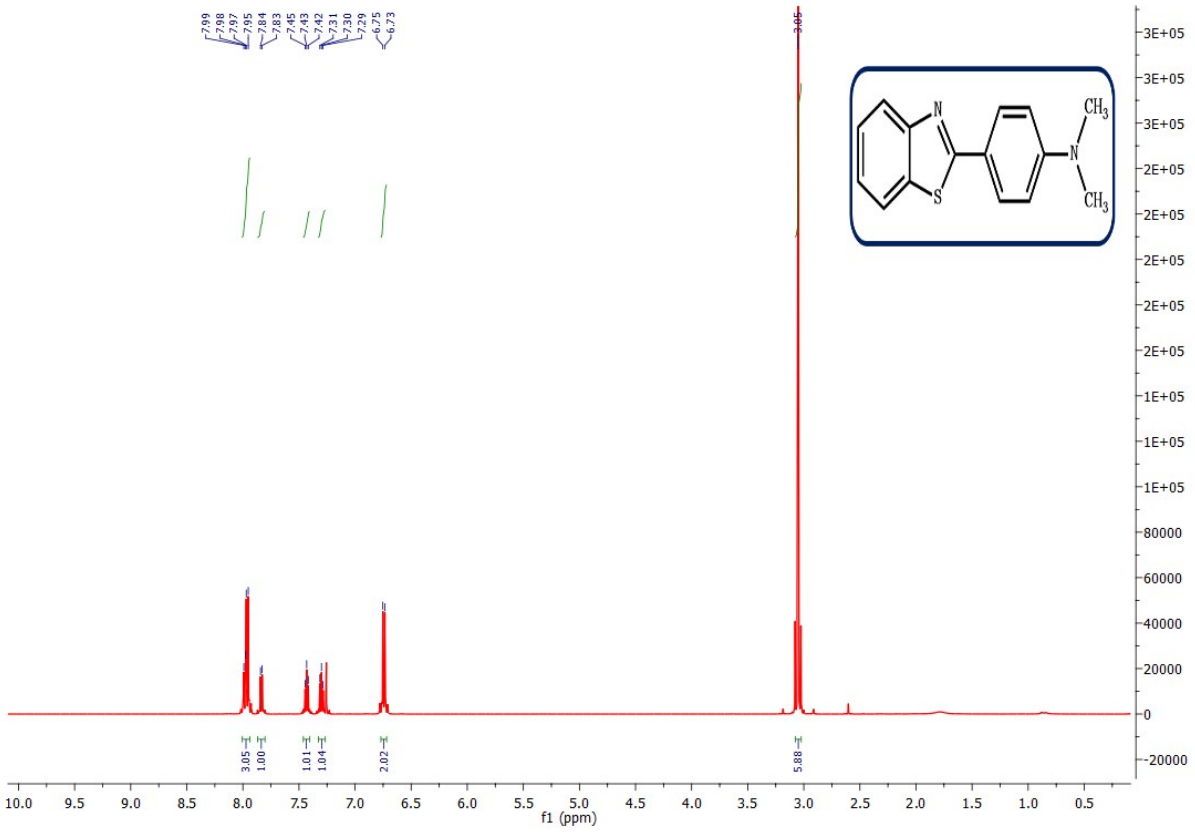


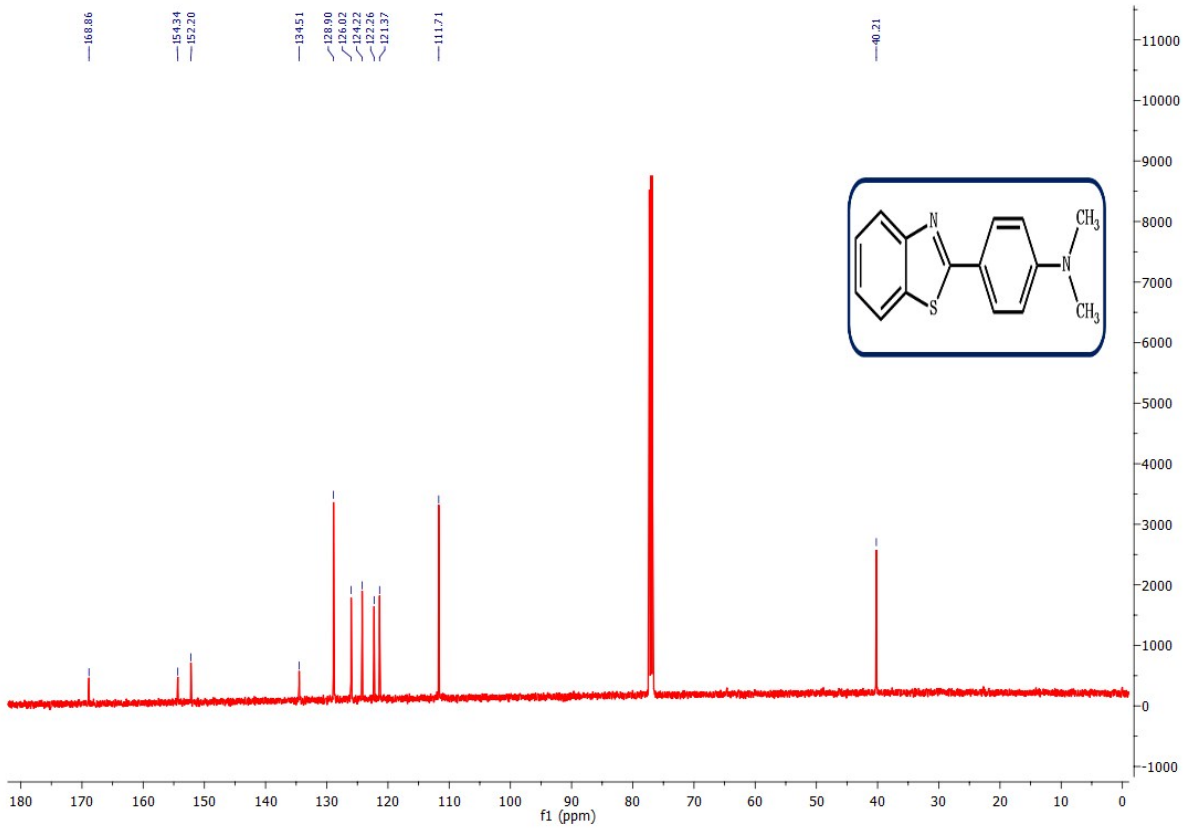
4a. 2-(p-tolyl)benzo[d]thiazole



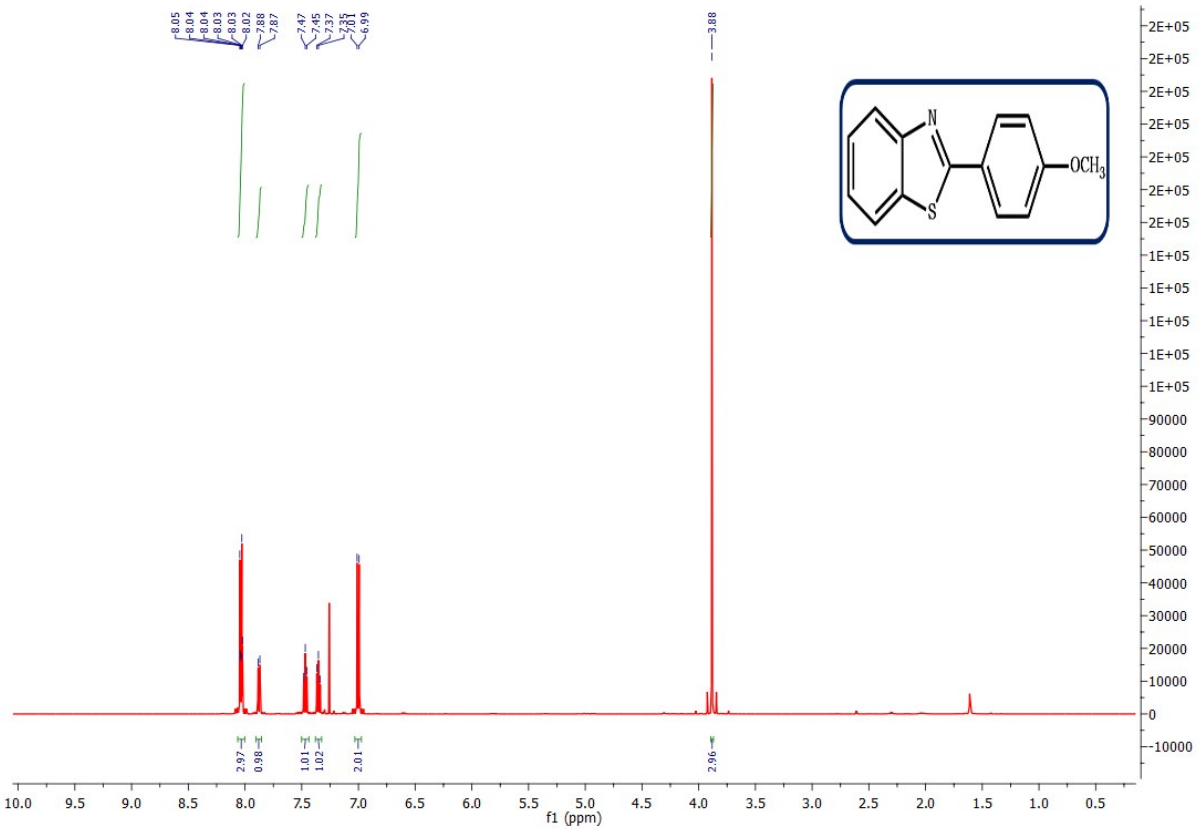


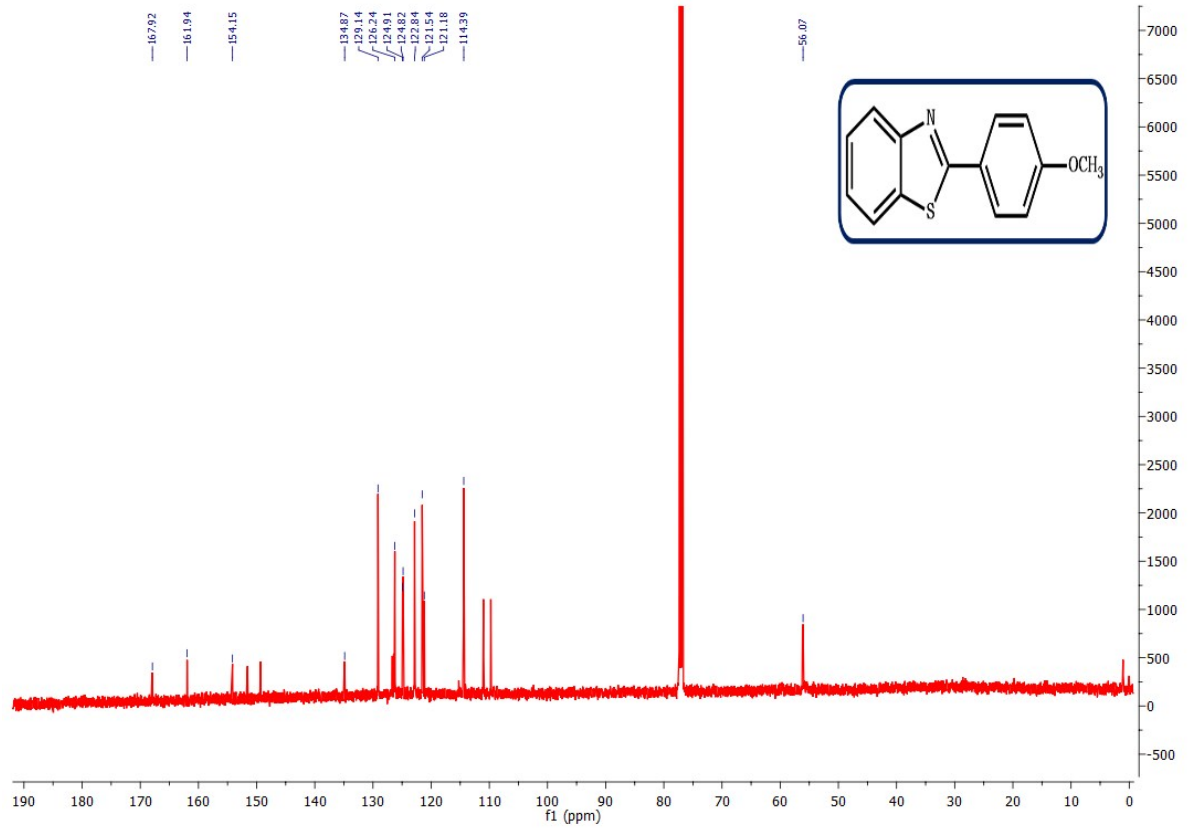
5a. 4-(benzo[d]thiazol-2-yl)-N,N-dimethylaniline



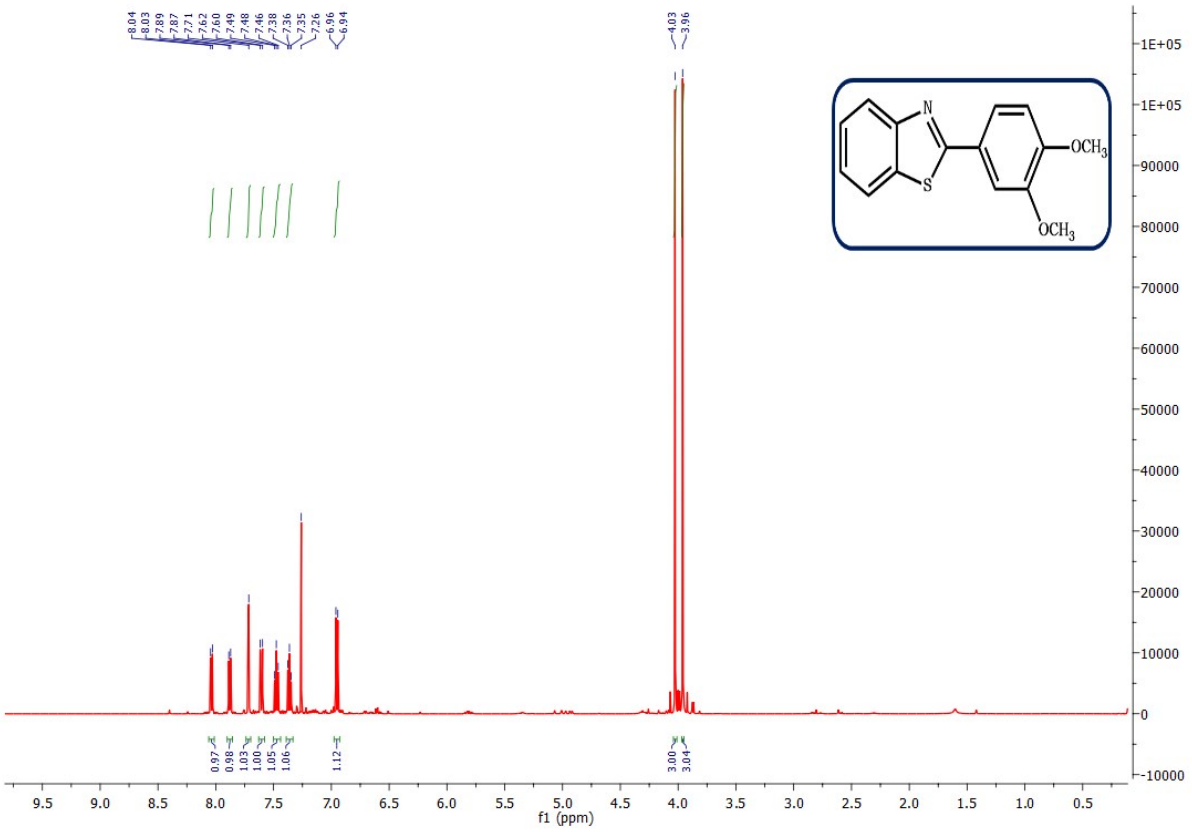


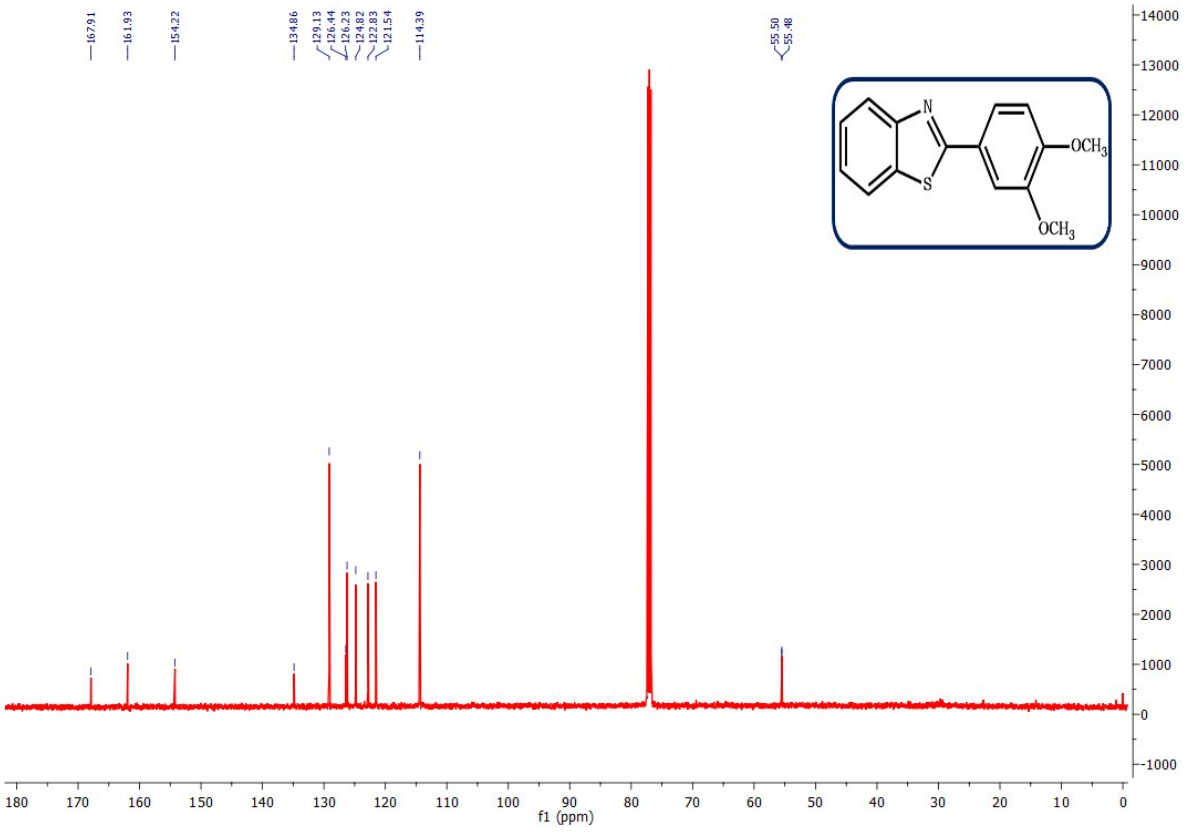
6a. 2-(4-methoxyphenyl)benzo[d]thiazol



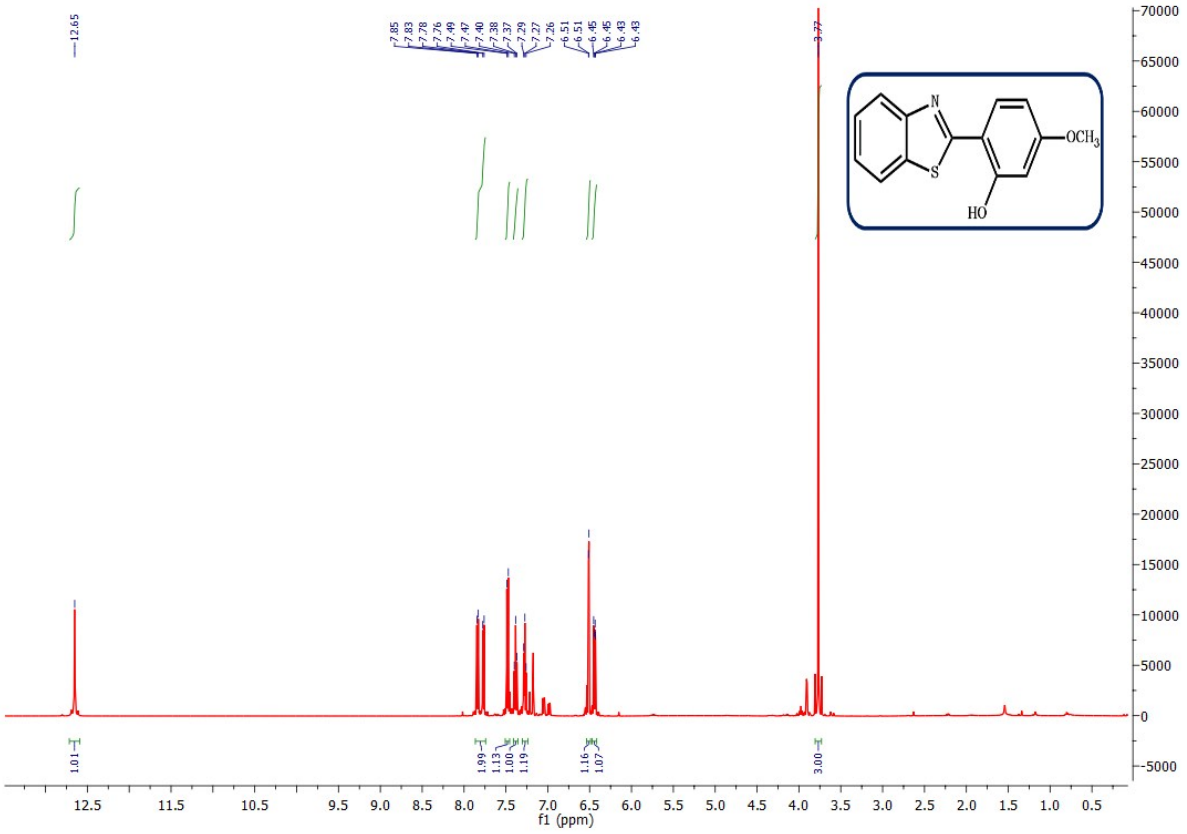


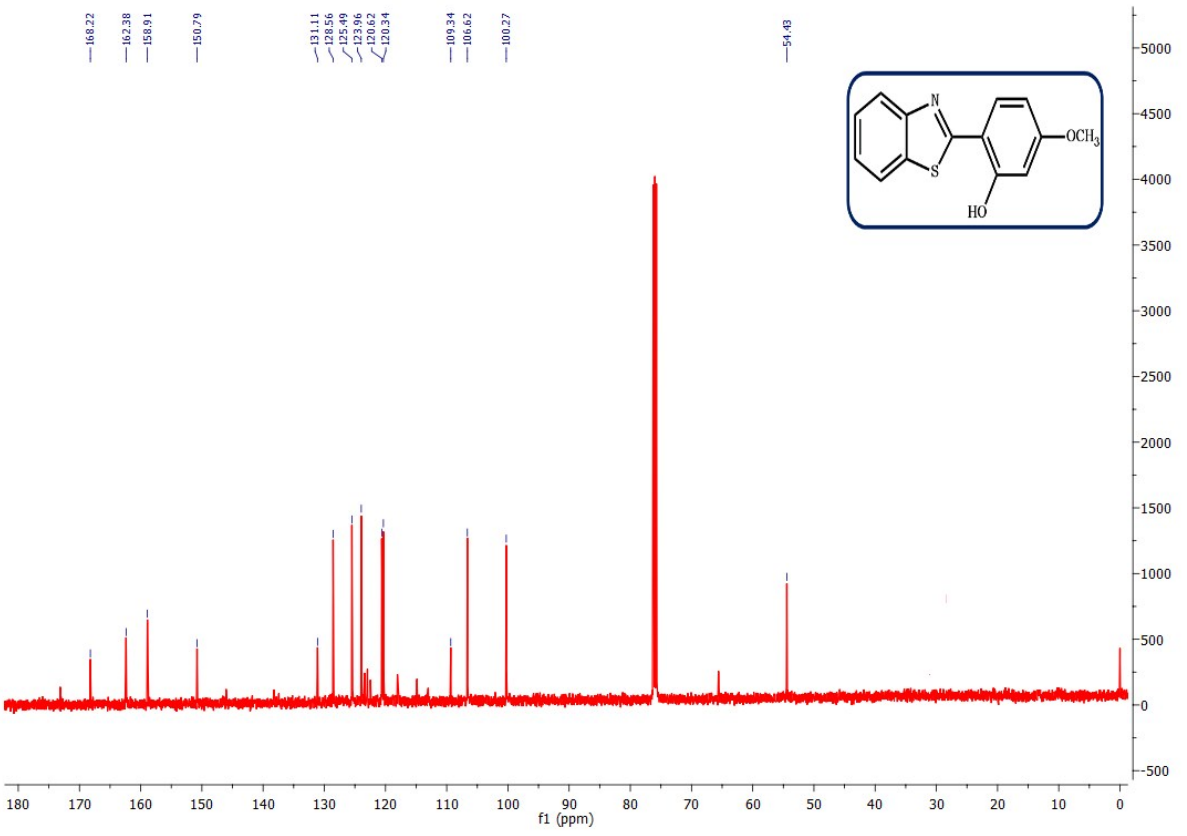
7a. 2-(3,4-dimethoxyphenyl)benzo[d]thiazole



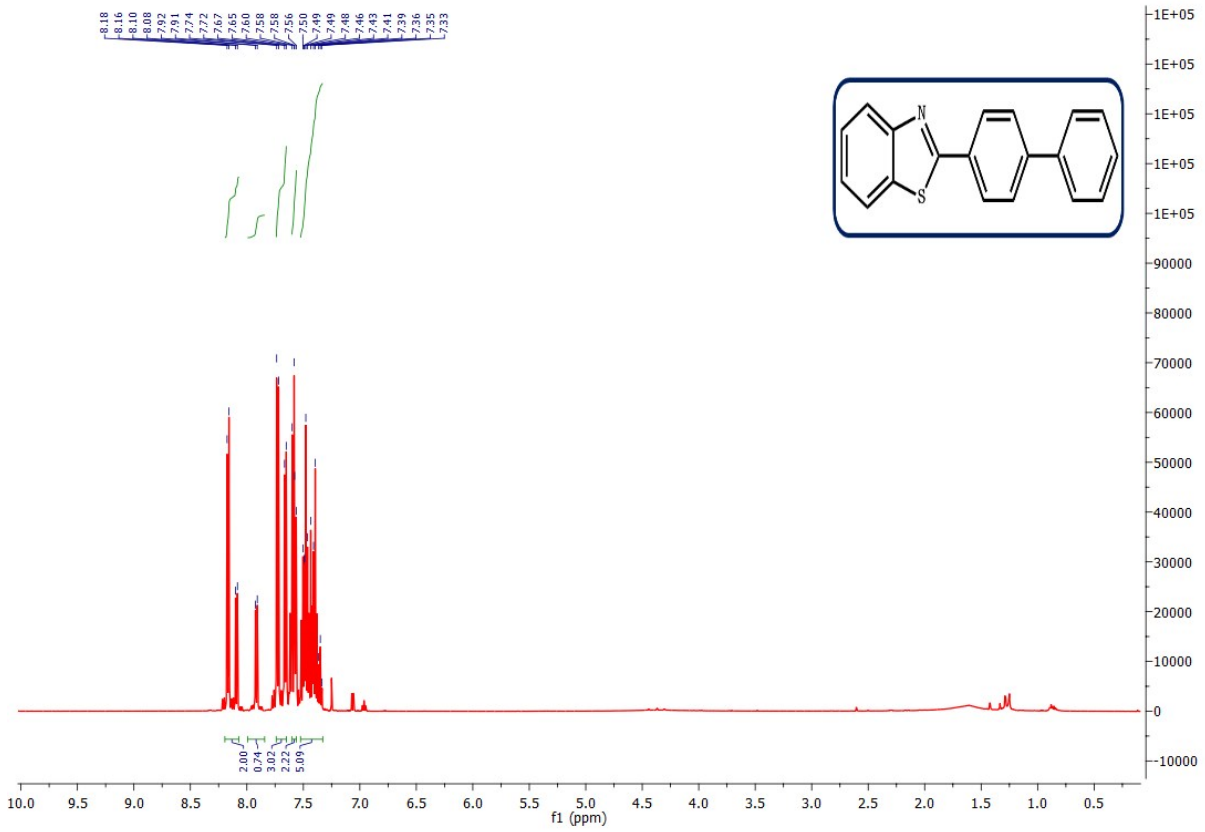


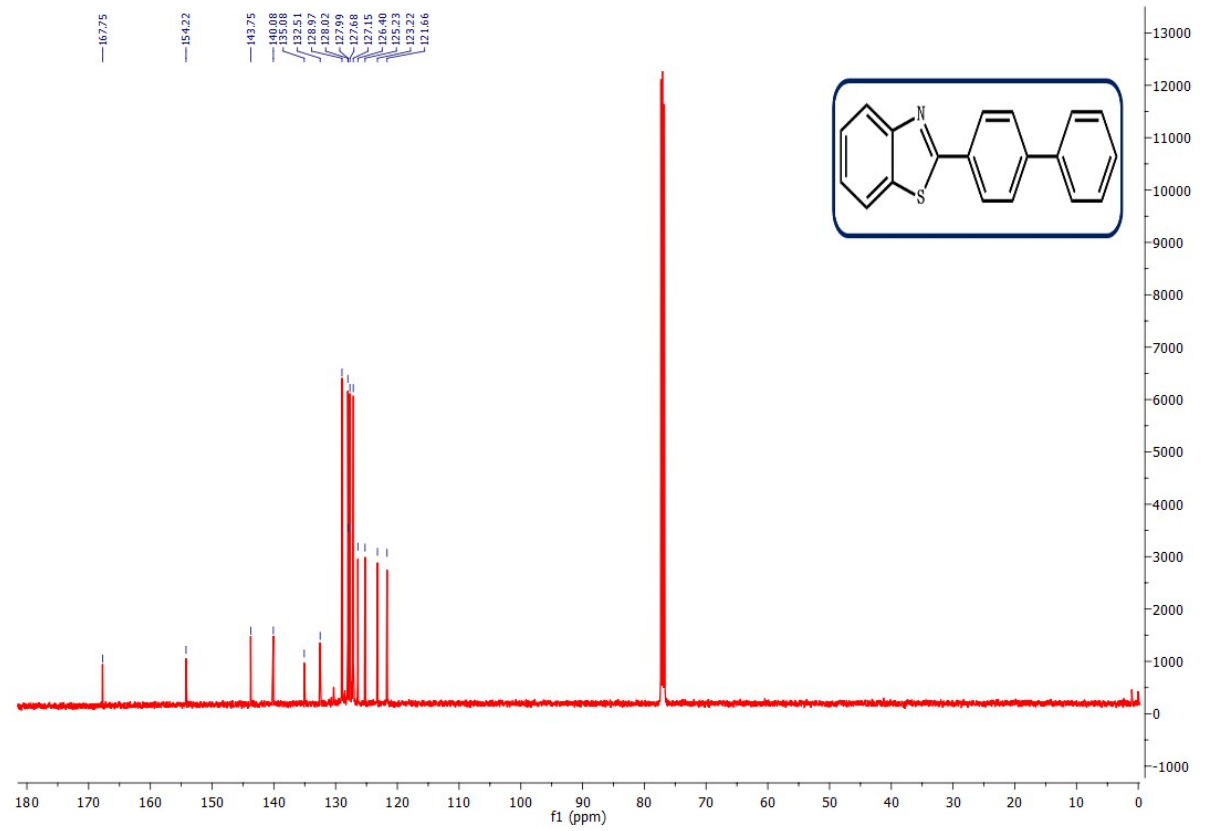
8a. 2-(benzo[d]thiazol-2-yl)-5-methoxyphenol



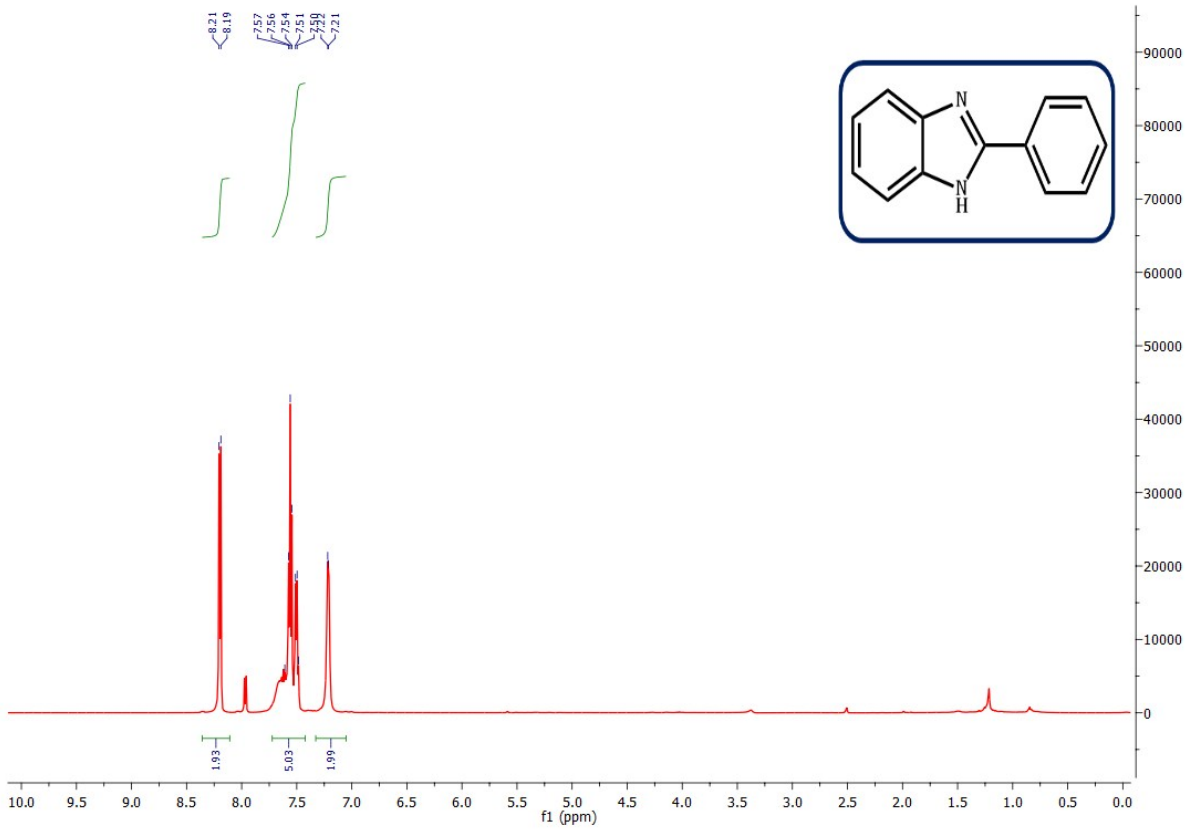


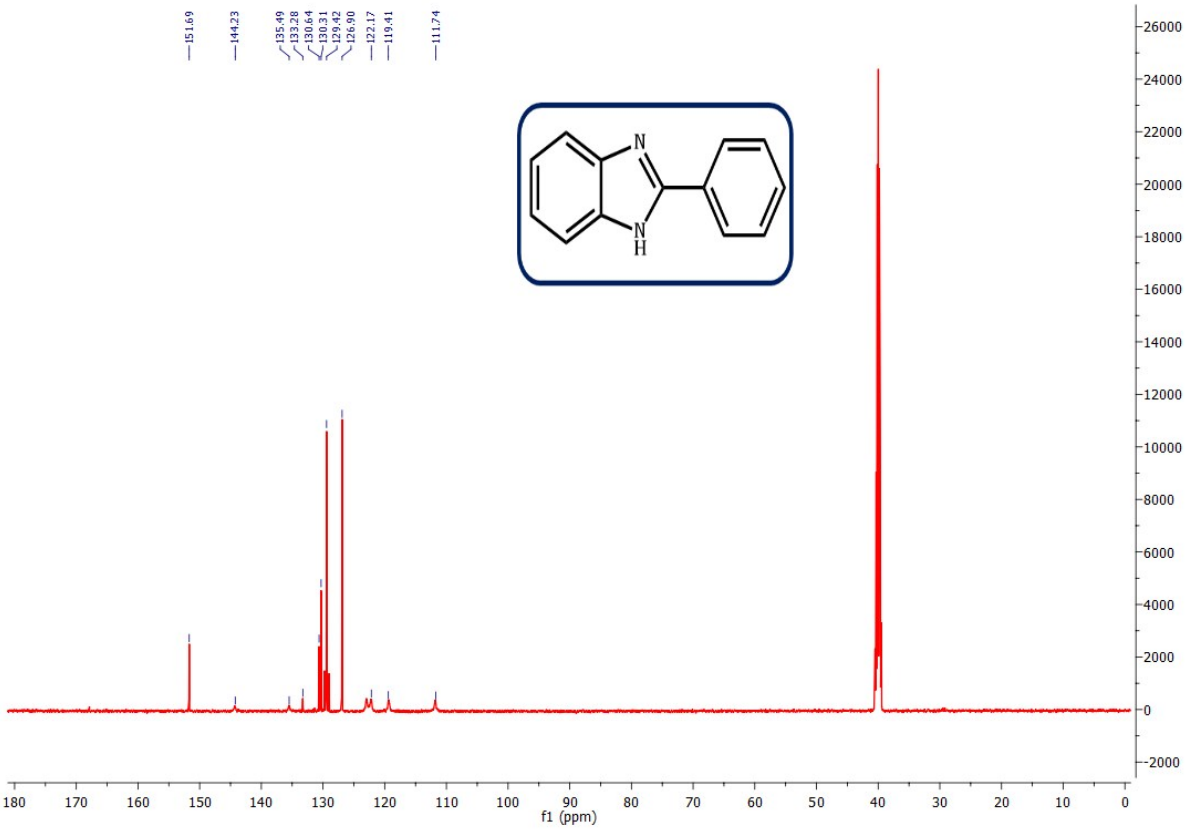
9a. 2-([1,1’-biphenyl]-4-yl)benzo[d]thiazole

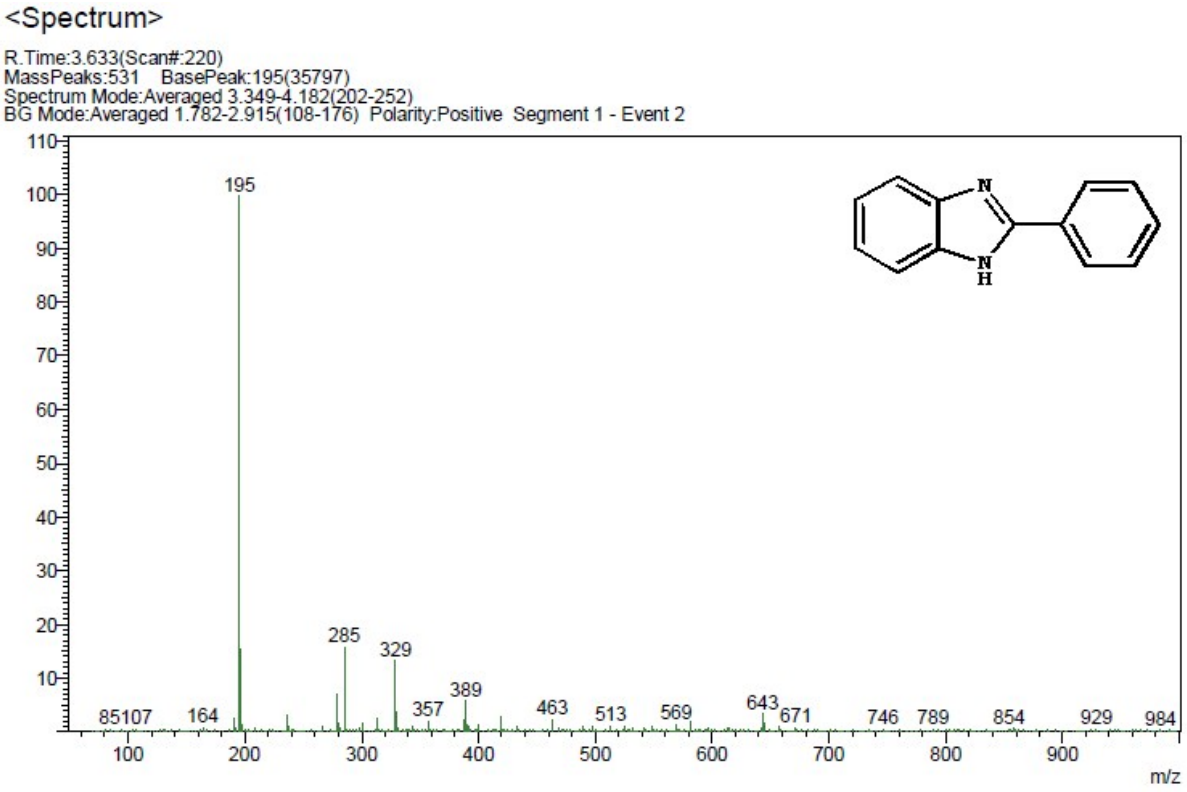




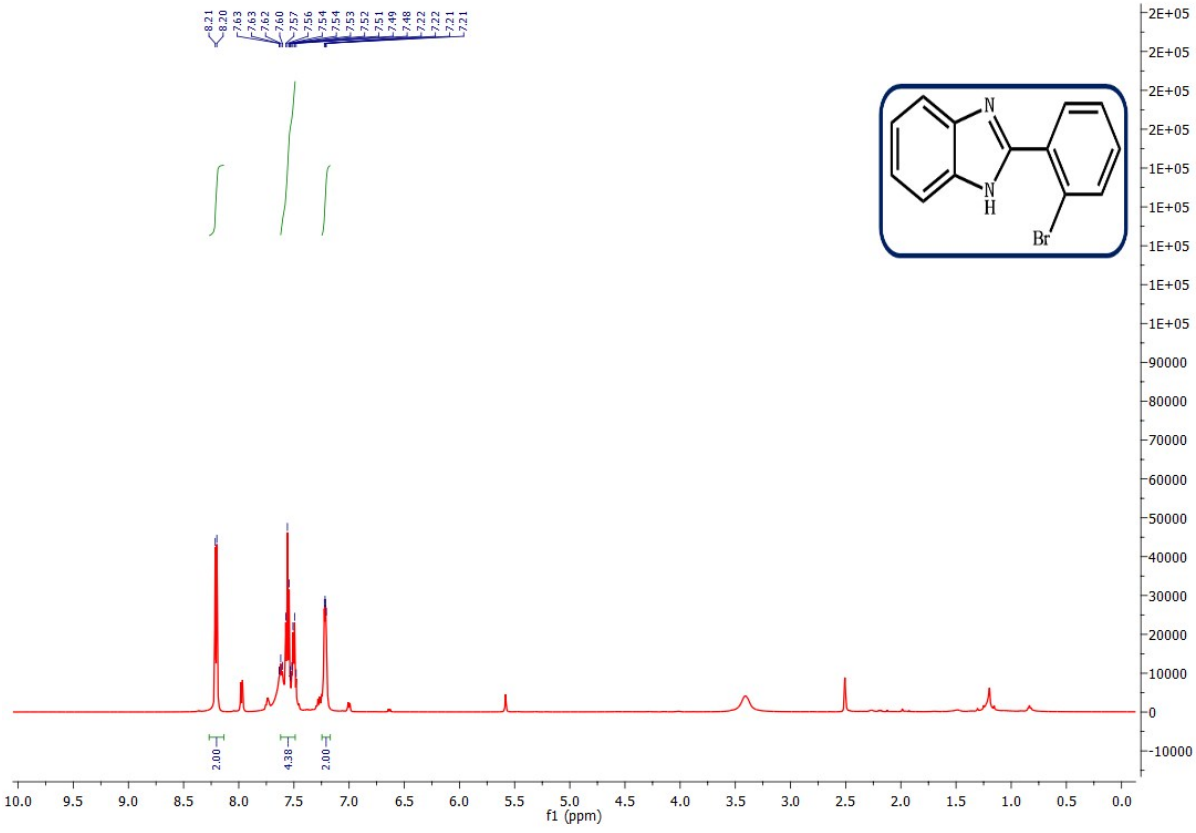
10a. 2-Phenylbenzimidazole

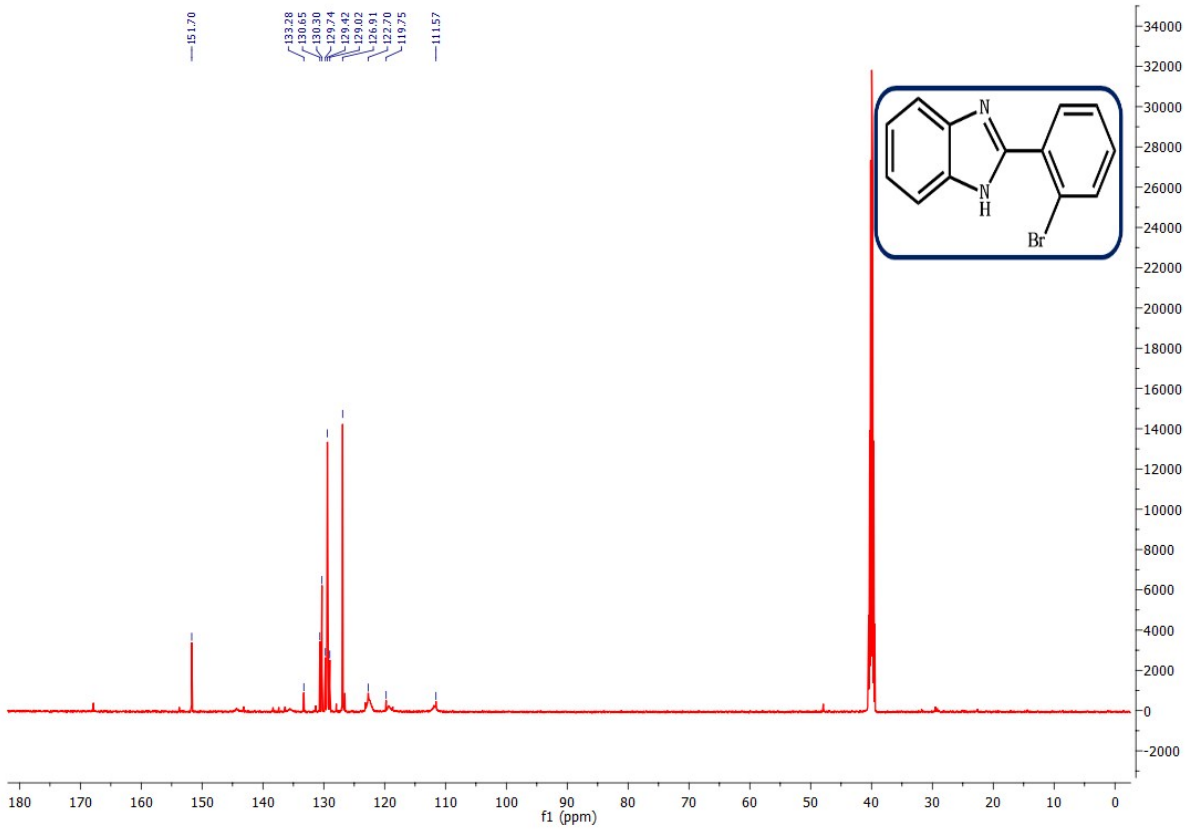

8.21
8.19
7.57
7.56
7.54
7.51
7.50
7.22
7.21
N
N
H
1.93
5.03
1.99
f1 (ppm)


151.69
144.23
135.49
133.28
130.64
130.31
129.42
126.90
122.17
119.41
111.74
N
N
H
f1 (ppm)

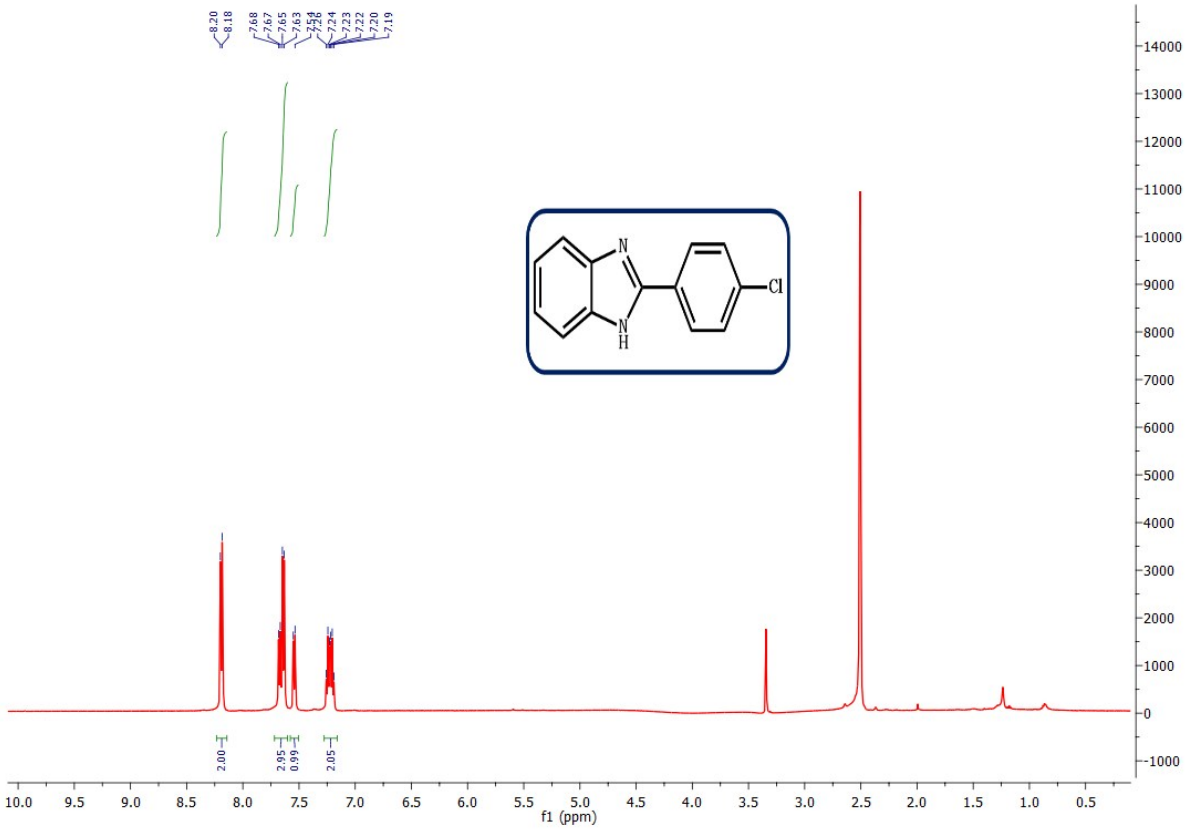


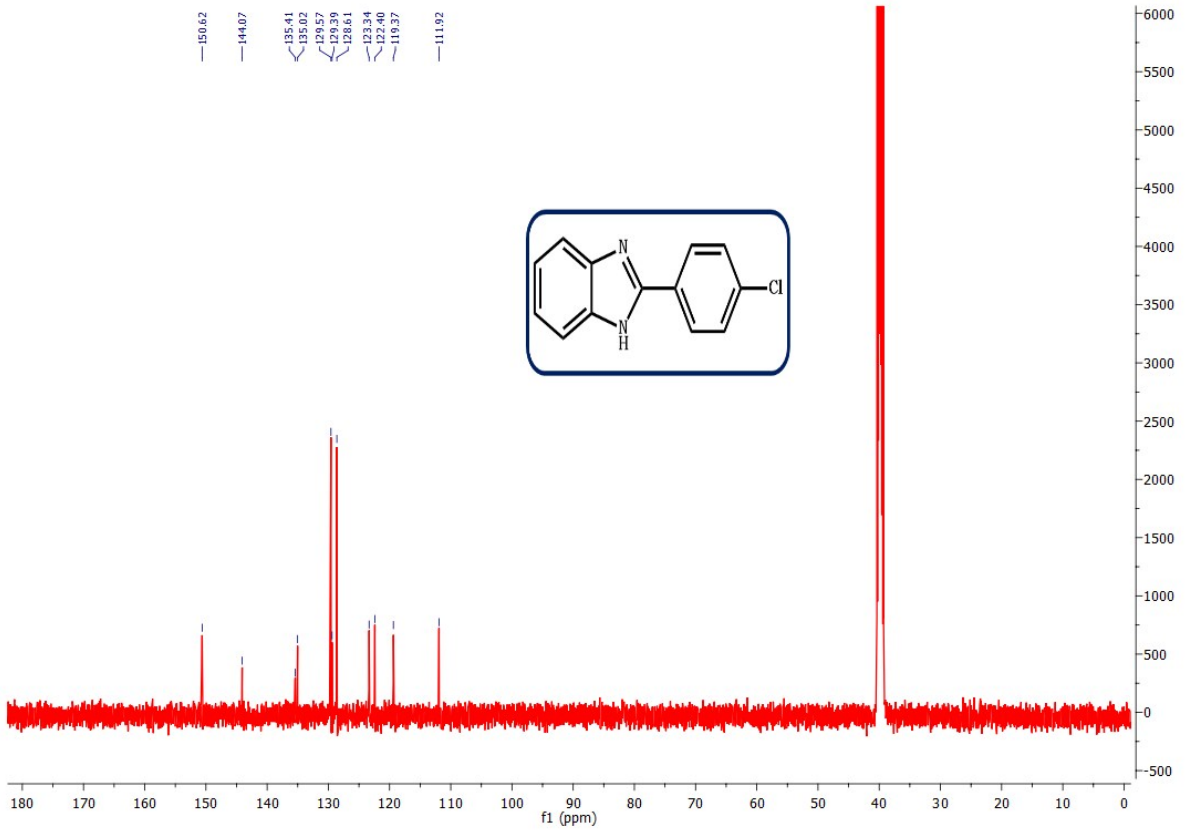
11a. 2-(2-bromophenyl)-1H-benzo[d]imidazole



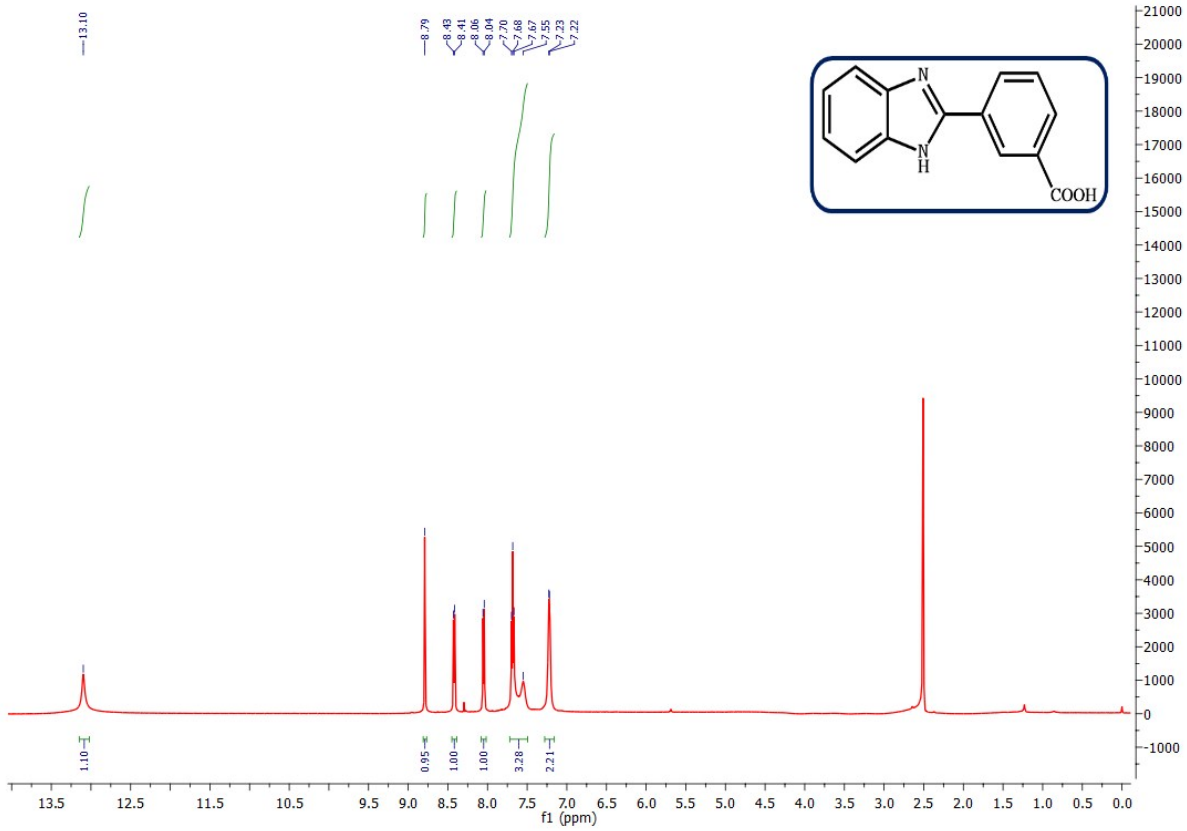


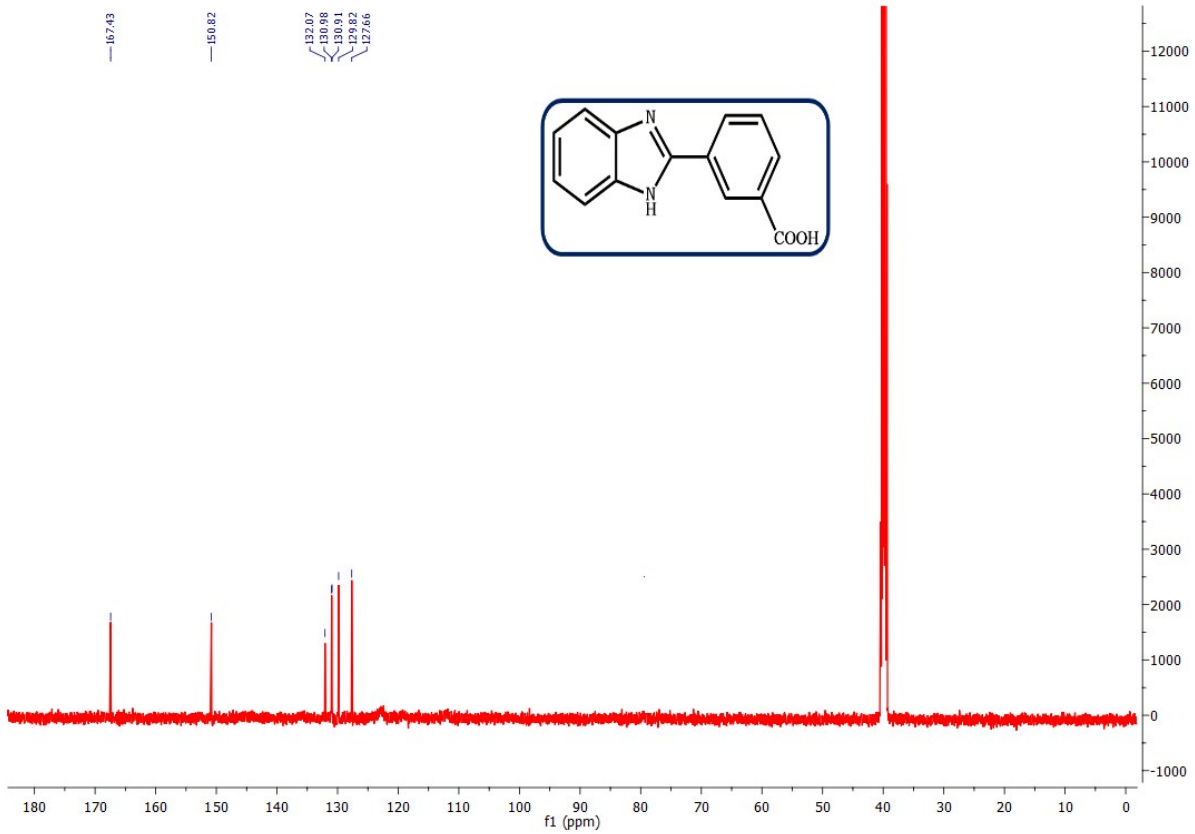
12a. 2-(4-chlorophenyl)-1H-benzo[d]imidazole



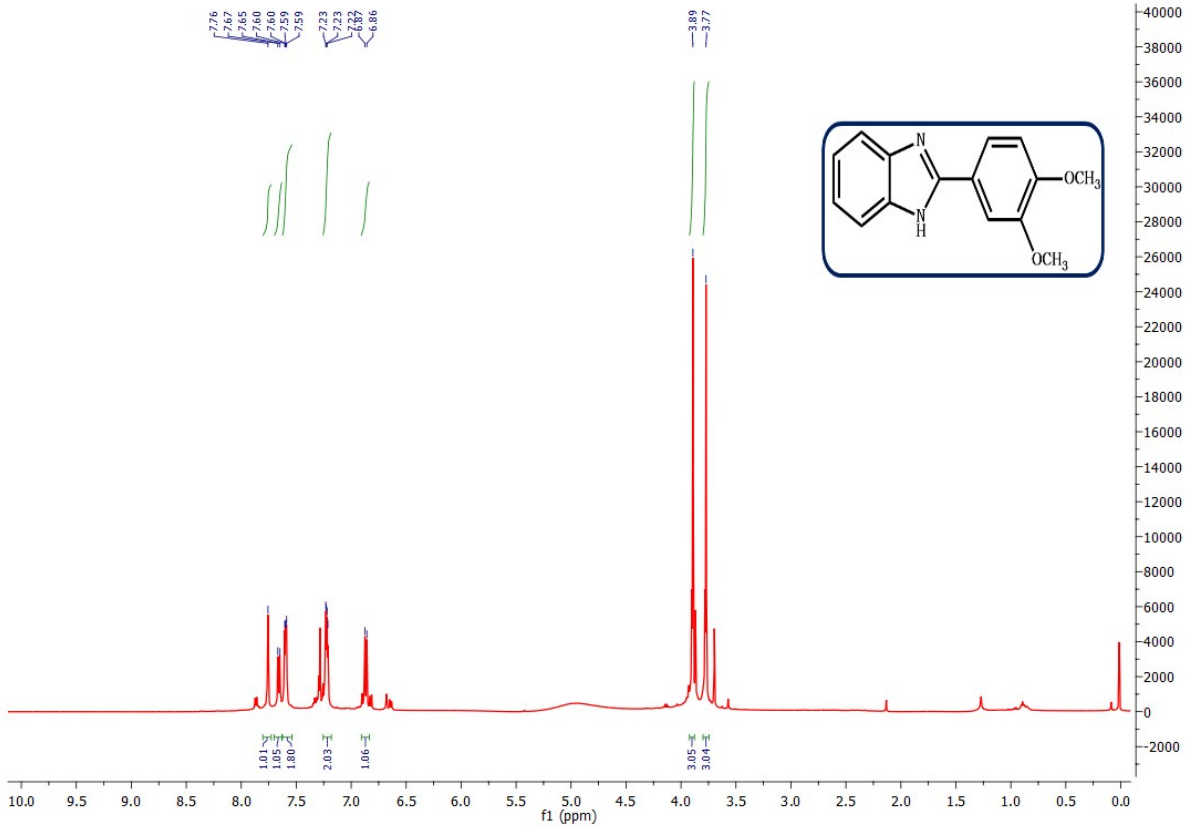


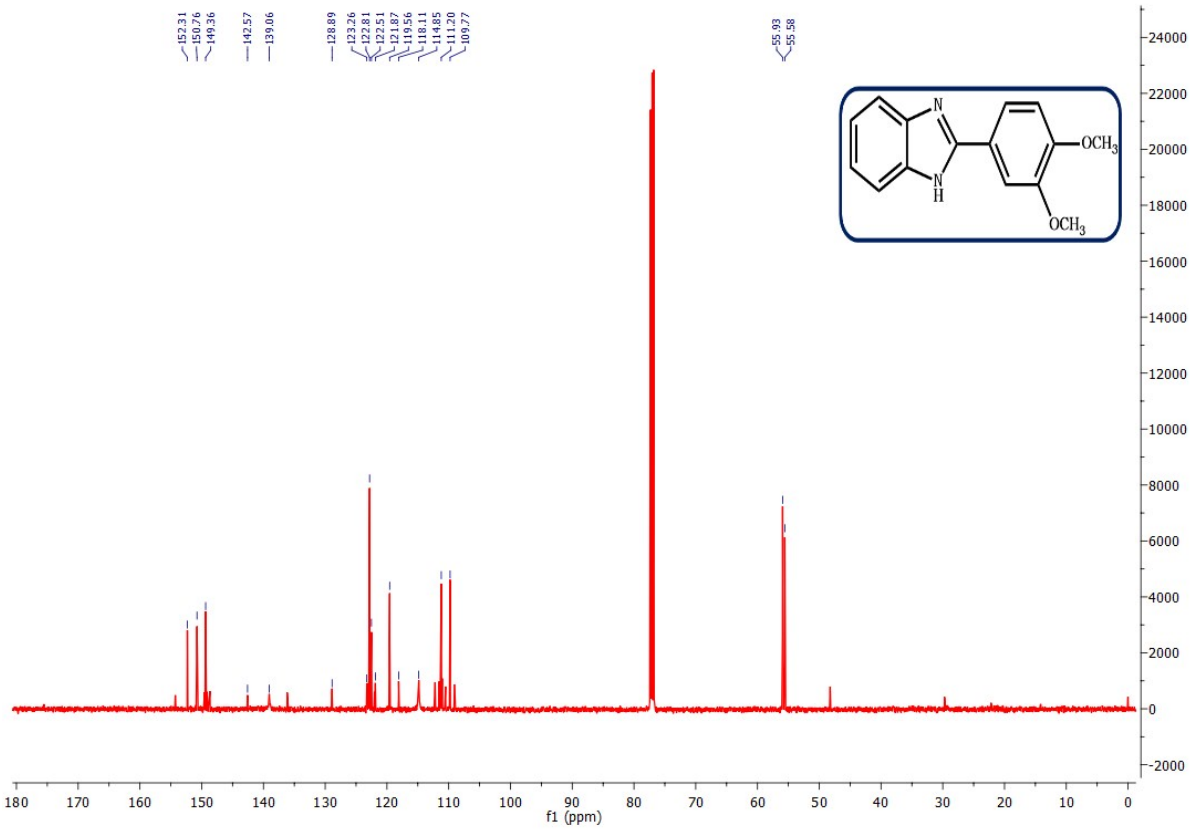
13a. 3-(1H-benzo[d]imidazol-2yl)benzoicacid



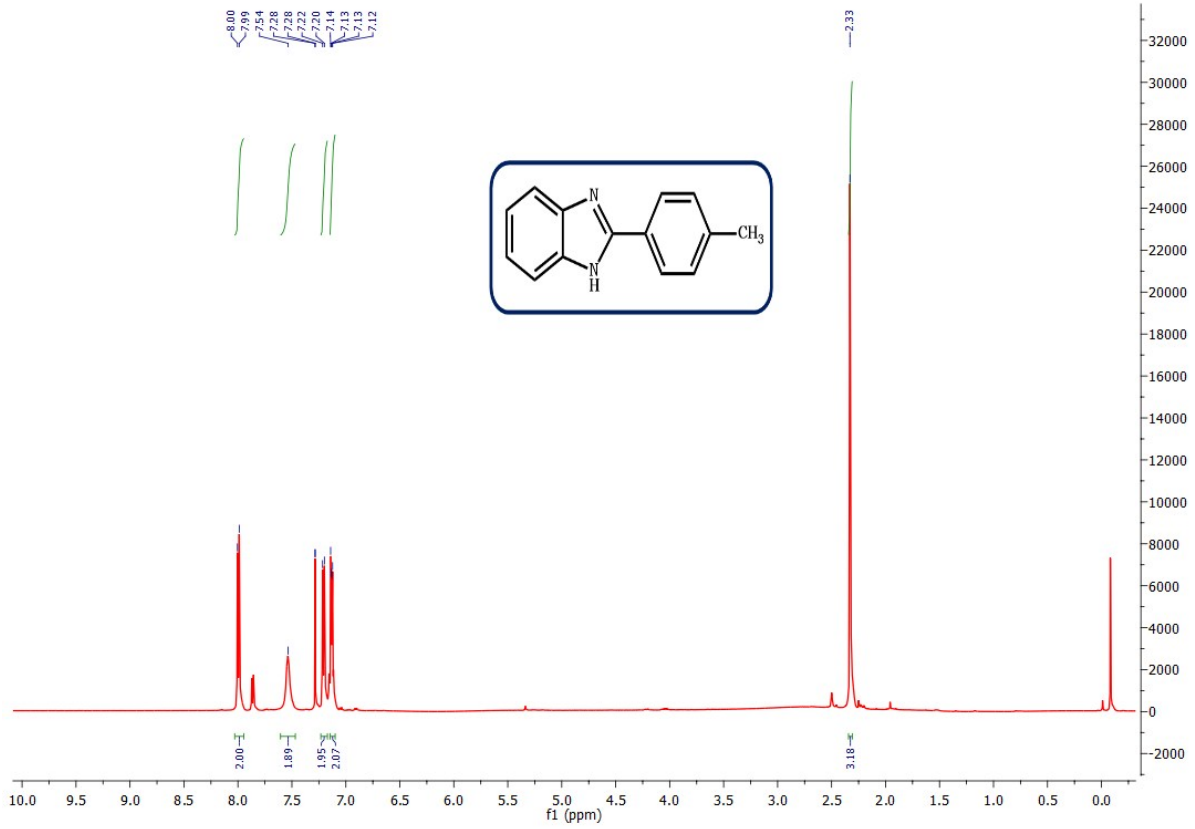


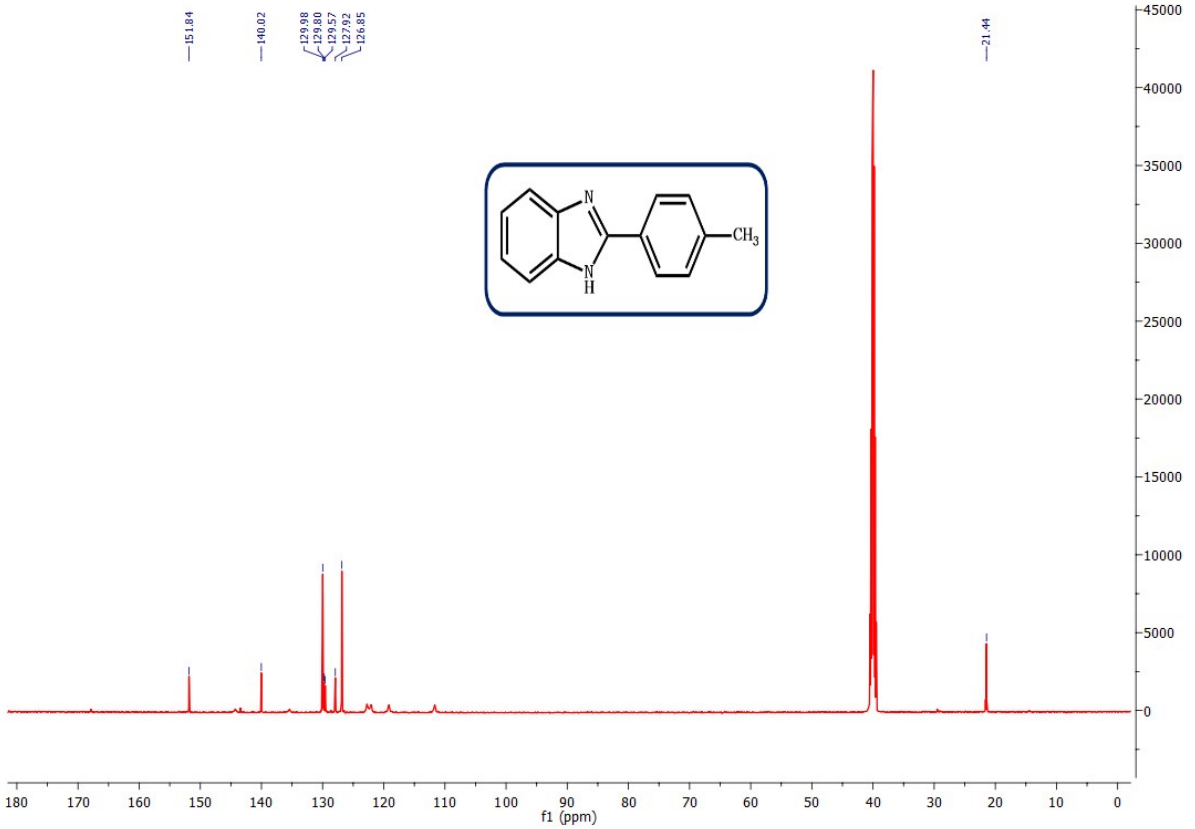
14a. 2-(3,4-dimethoxyphenyl)-1H-benzo(d)imidazole





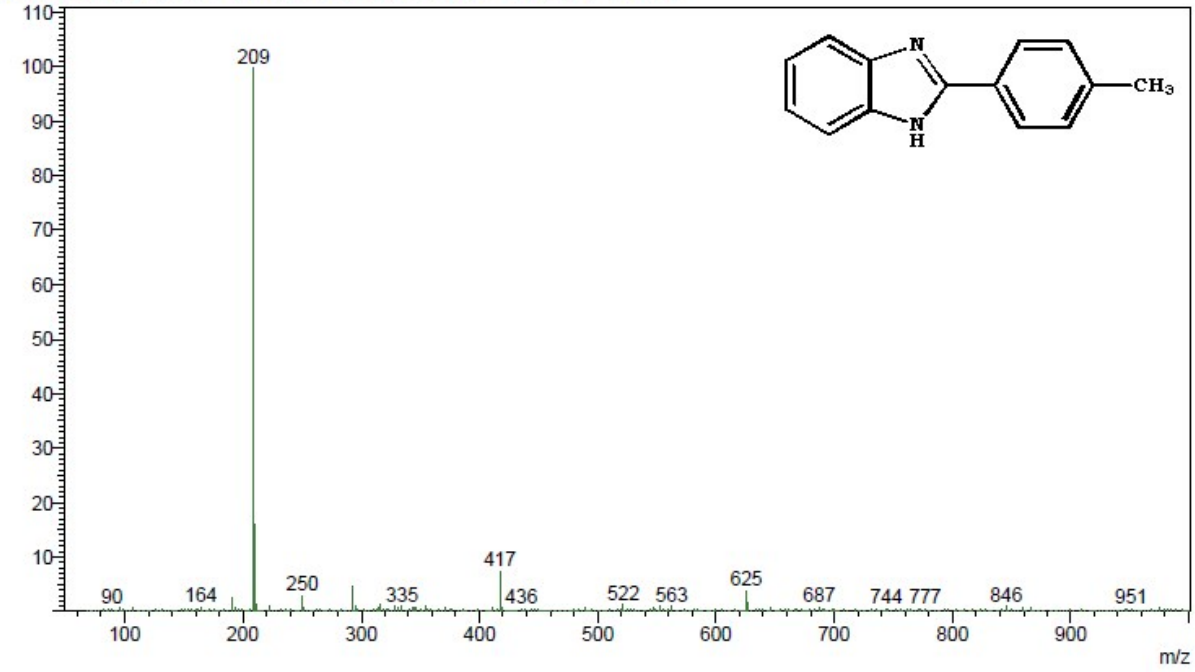
15a. 2-(p-tolyl)-1H-benzo[d]imidazole



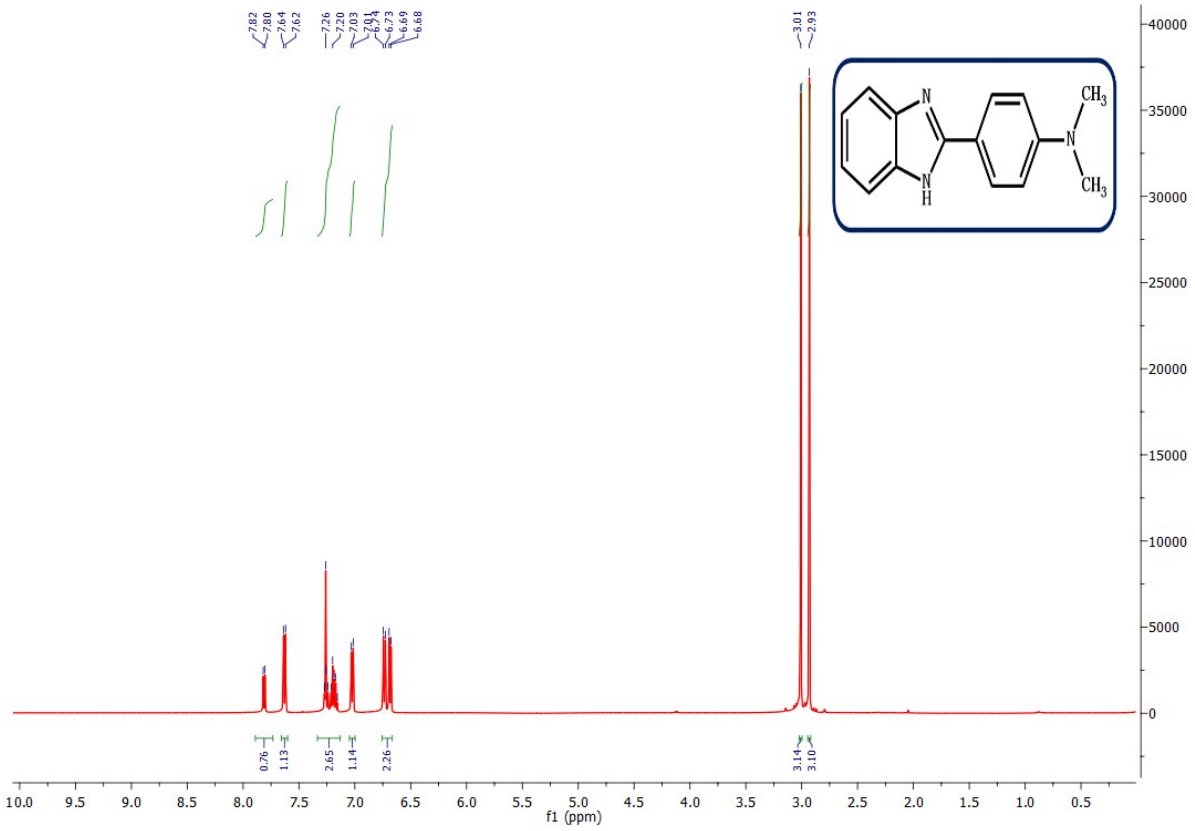


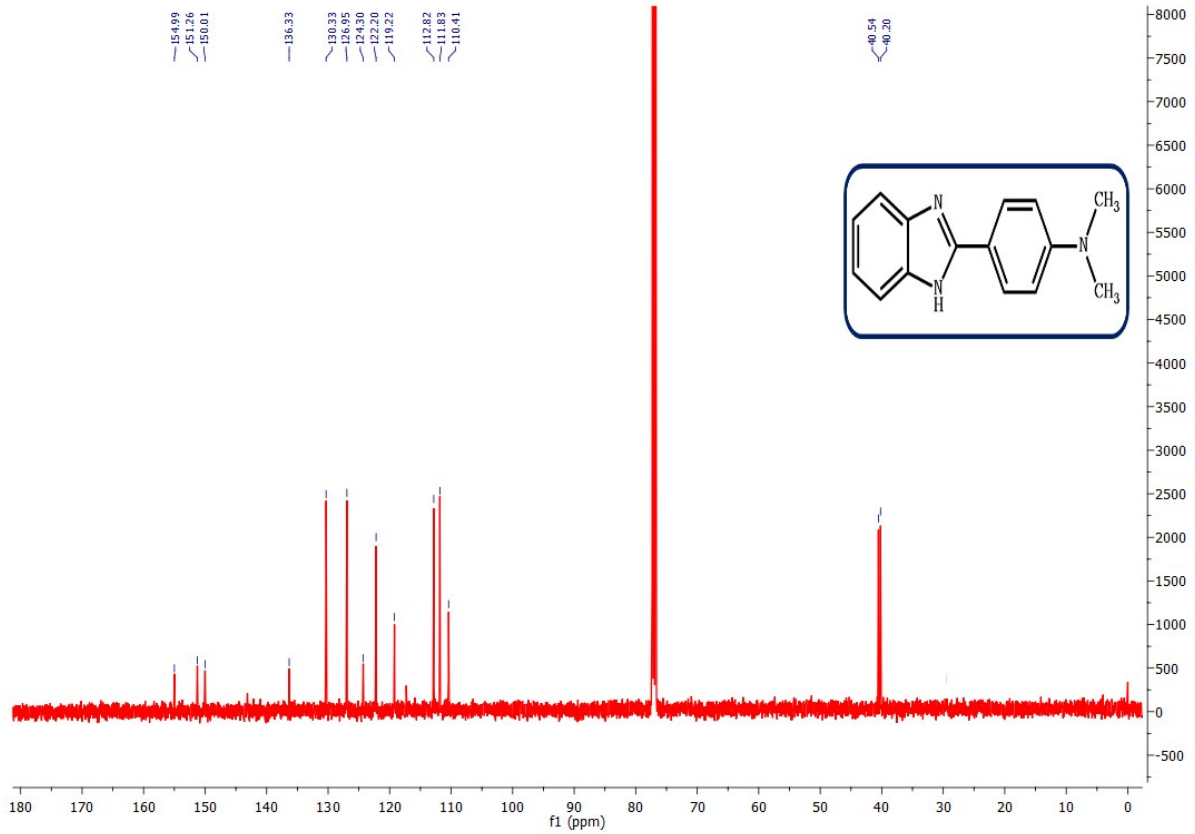
<Spectrum>

R.Time:2.633(Scan#:160)
MassPeaks:465 BasePeak:209(35629)
Spectrum Mode:Averaged 2.449-3.215(148-194)
BG Mode:Averaged 1.315-1.982(80-120) Polarity:Positive Segment 1 - Event 2

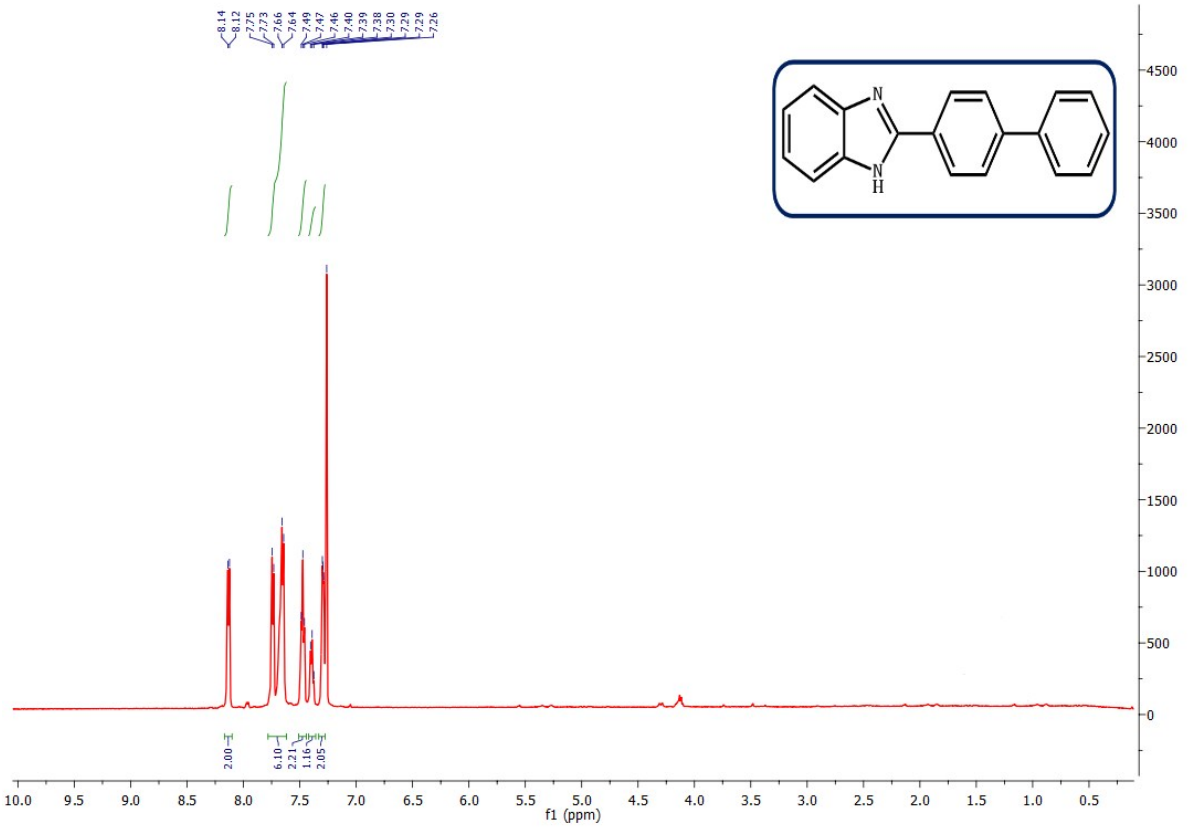


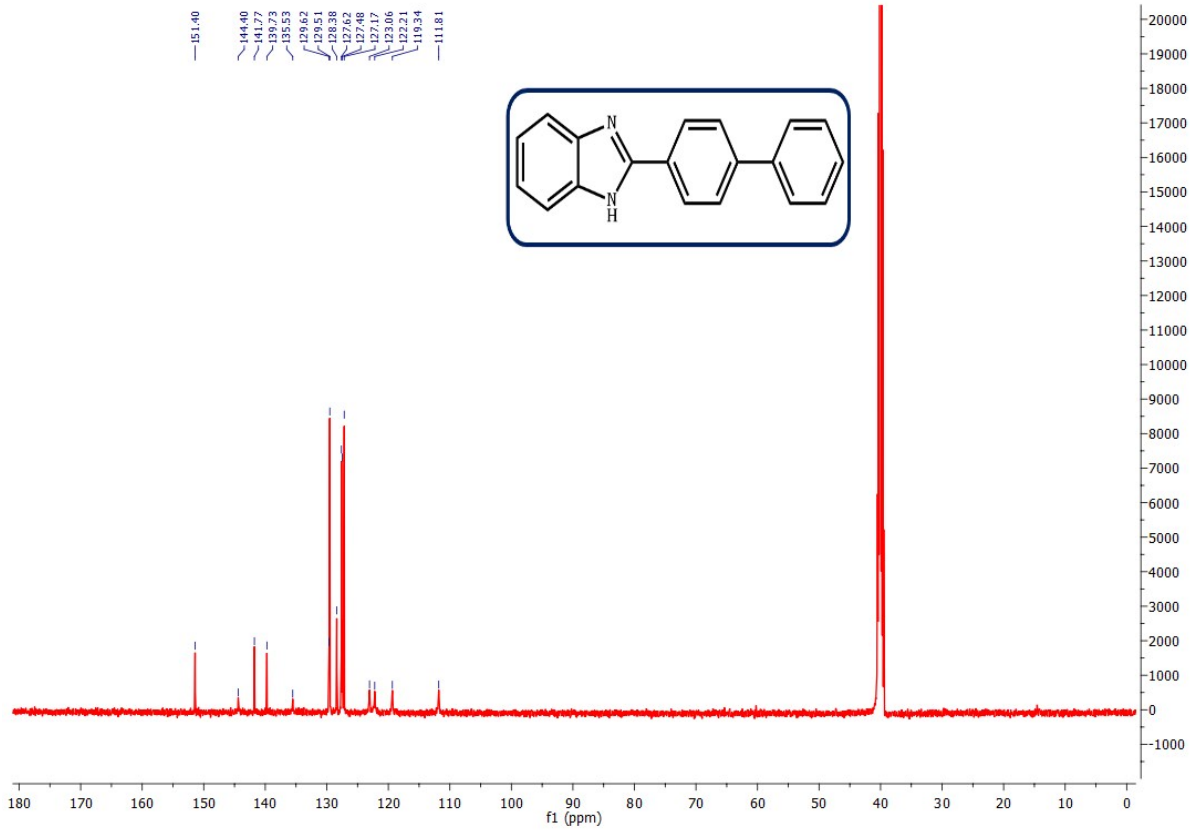
16a. 4-(1H-benzo[d]imidazole-2yl)-N,N-dimethylaniline





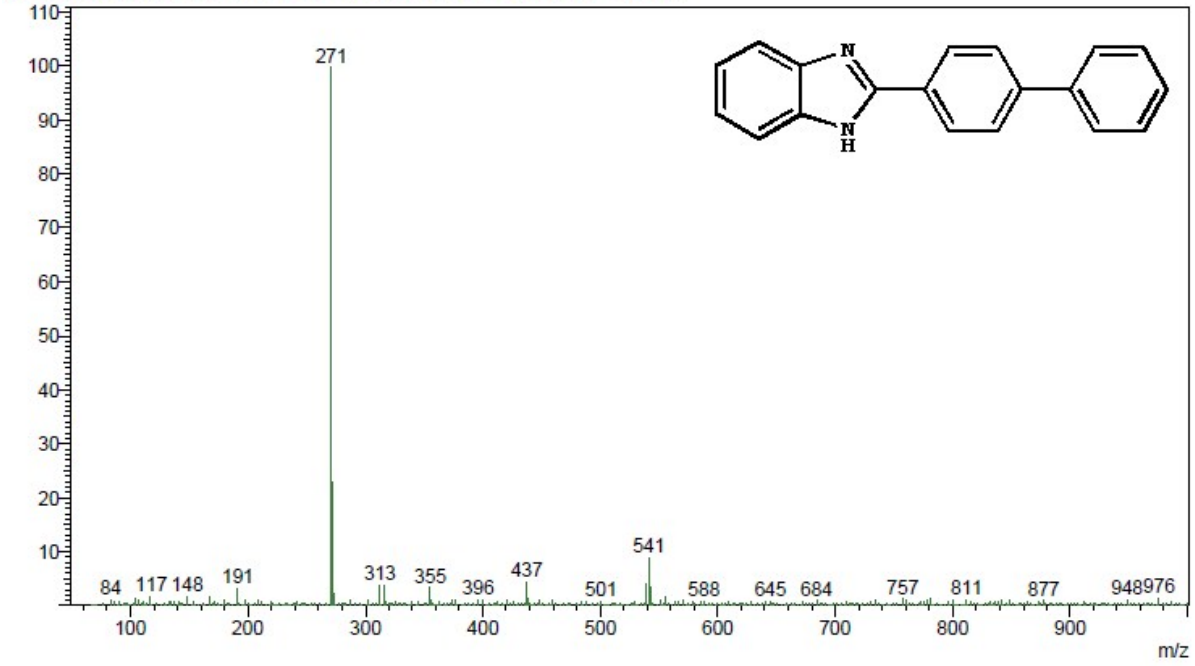
17a. 2-([1,1’-biphenl]-4-yl)-1H-benzo[d]imidazole



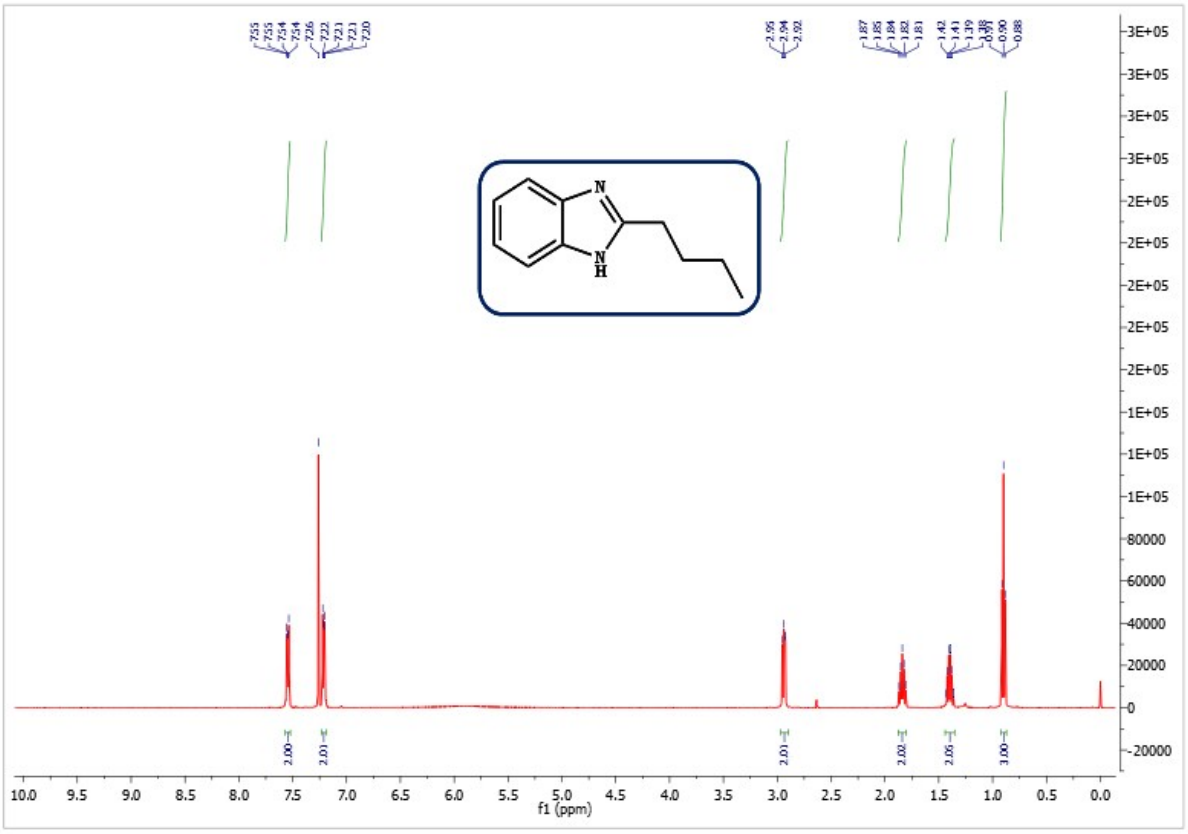


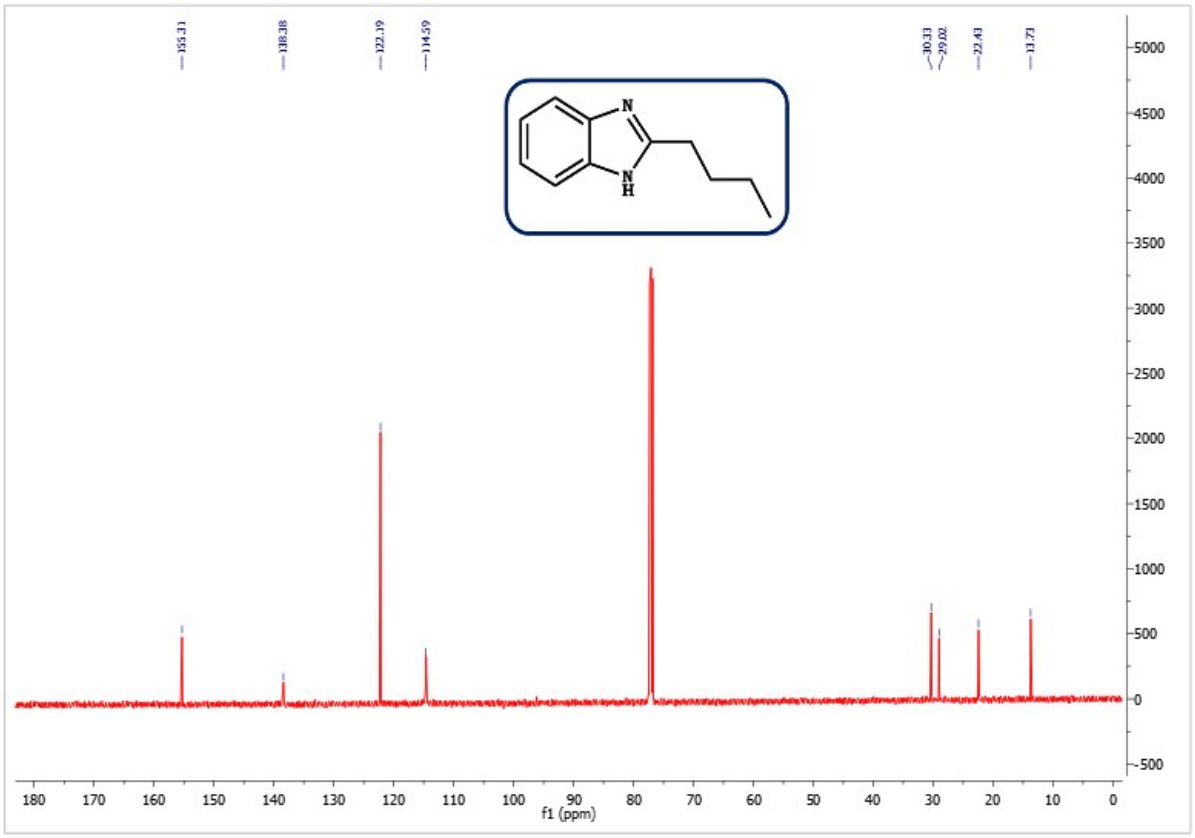
<Spectrum>

R.Time:2.900(Scan#:176)
MassPeaks:498 BasePeak:271(21273)
Spectrum Mode:Averaged 2.249-3.215(136-194)
BG Mode:Averaged 1.449-1.915(88-116) Polarity:Positive Segment 1 - Event 2

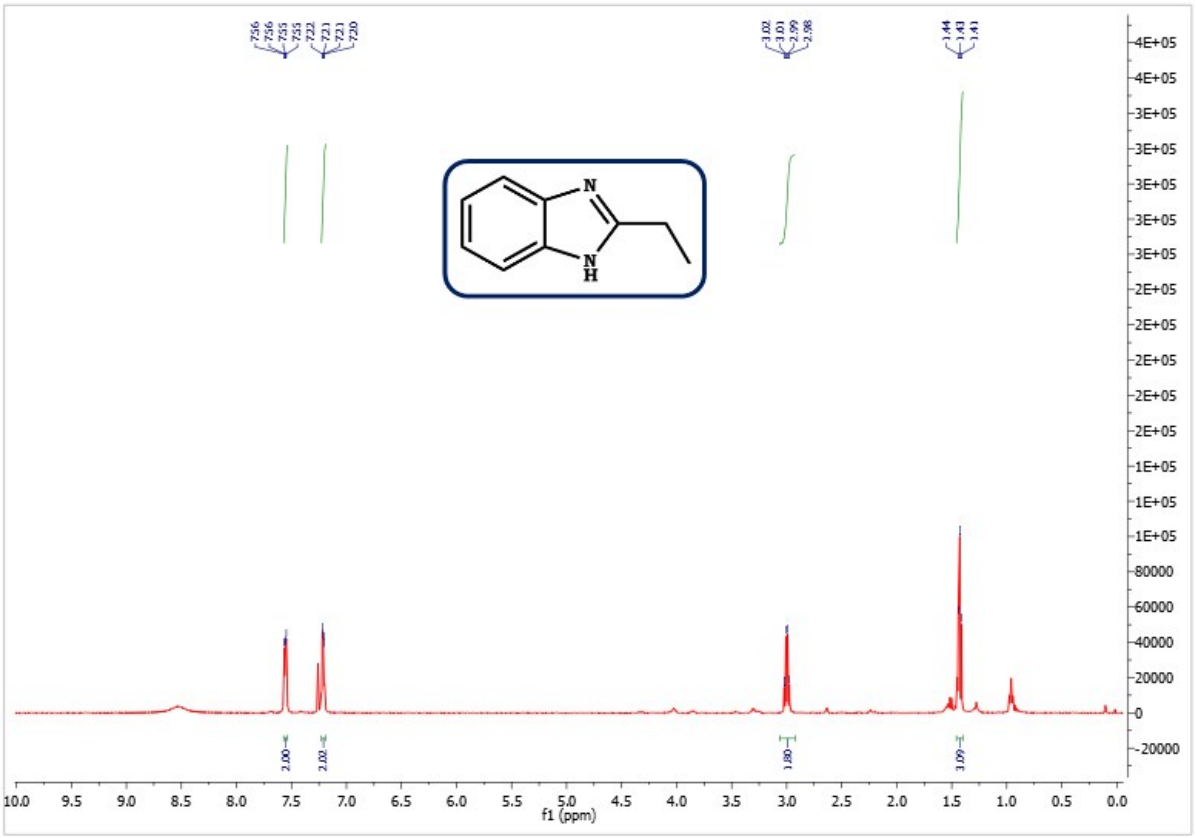


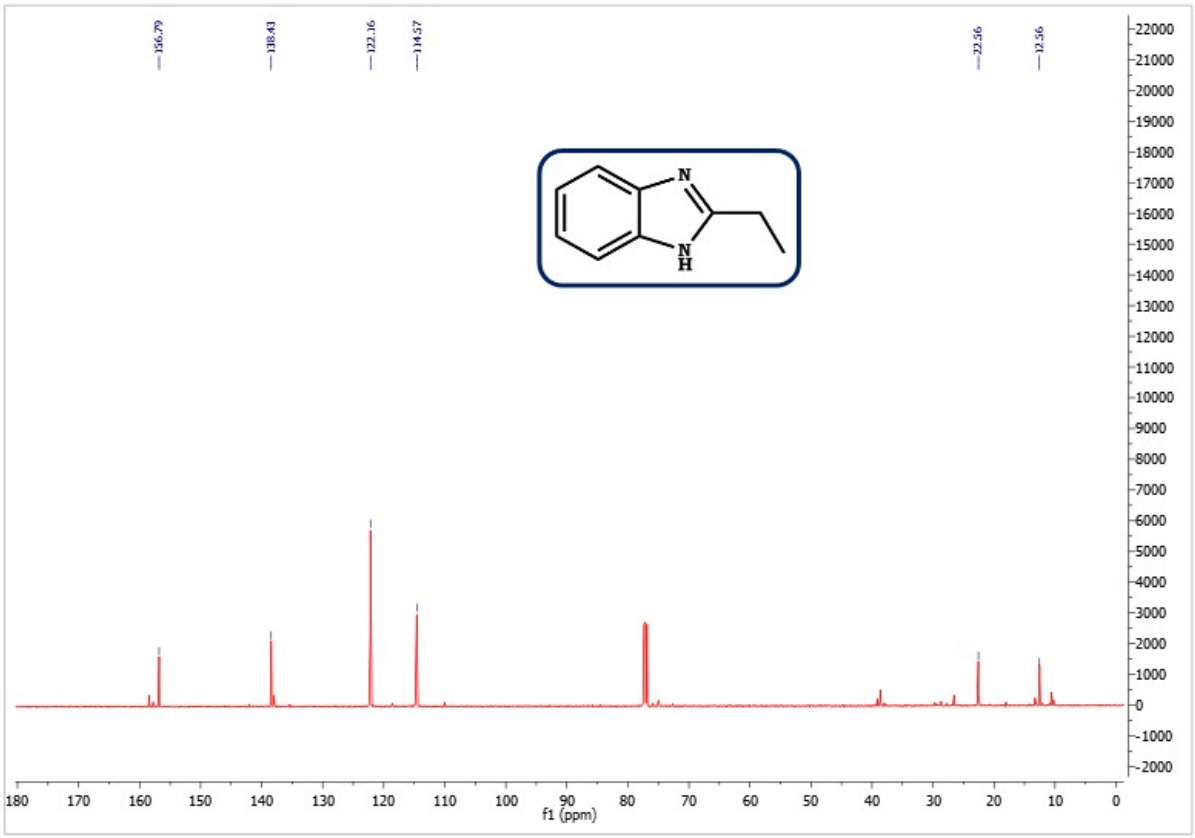
18a. 2-butyl-1H-benzo[d]imidazole





19a. 2-ethyl-1H-benzo[d]imidazole




156.79
138.43
122.16
114.57
23.56
12.56
N
N
H
f1 (ppm)