

Supporting Information

Improved and Ligand-free Copper-Catalyzed Cyclization for an Efficient Synthesis of Benzimidazoles from *O*-Bromoarylamine and Nitriles

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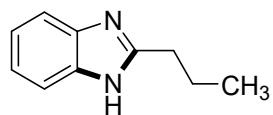
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Context

Analytical Data of Related Compounds

Benzimidazoles 2



$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.92 (brs, 1H), 7.56 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.35 – 7.16 (m, 2H), 2.93 (t, $J = 7.6$ Hz, 2H), 1.95 – 1.86 (m, 2H), 1.01 (t, $J = 7.4$ Hz, 3H)

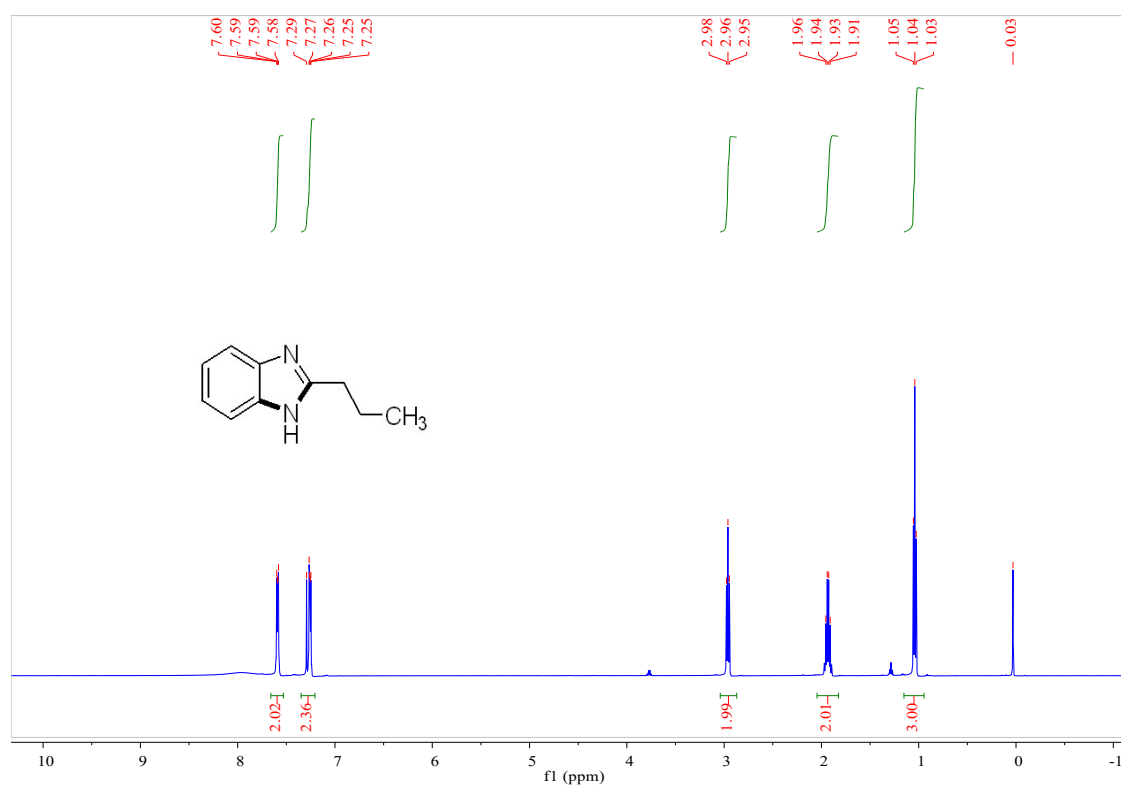


Figure S1 $^1\text{H NMR}$ of compound **2** in CDCl_3

^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 138.5, 122.1, 114.6, 31.2, 21.8, 13.8; HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2$ 161.1073, found 161.1071.

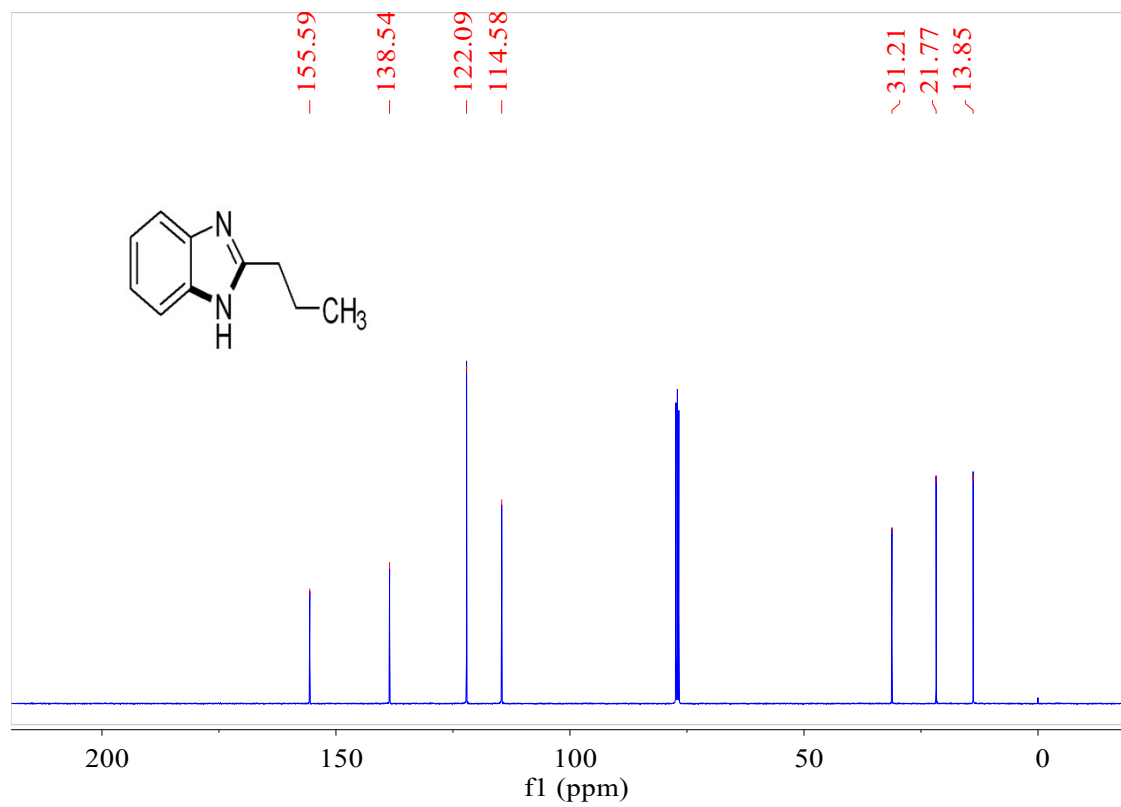
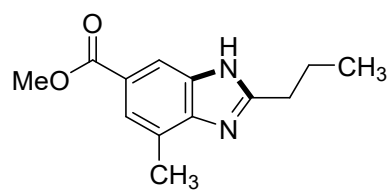


Figure S2 ^{13}C NMR of compound 2 in CDCl_3

Benzimidazoles 2a



^1H NMR (400 MHz, CDCl_3) δ 8.87 (brs, 1H), 8.11 (s, 1H), 7.77 (s, 1H), 3.91 (s, 3H), 2.93 (t, J = 7.6 Hz, 2H), 2.57 (s, 3H), 1.94 – 1.83 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H)

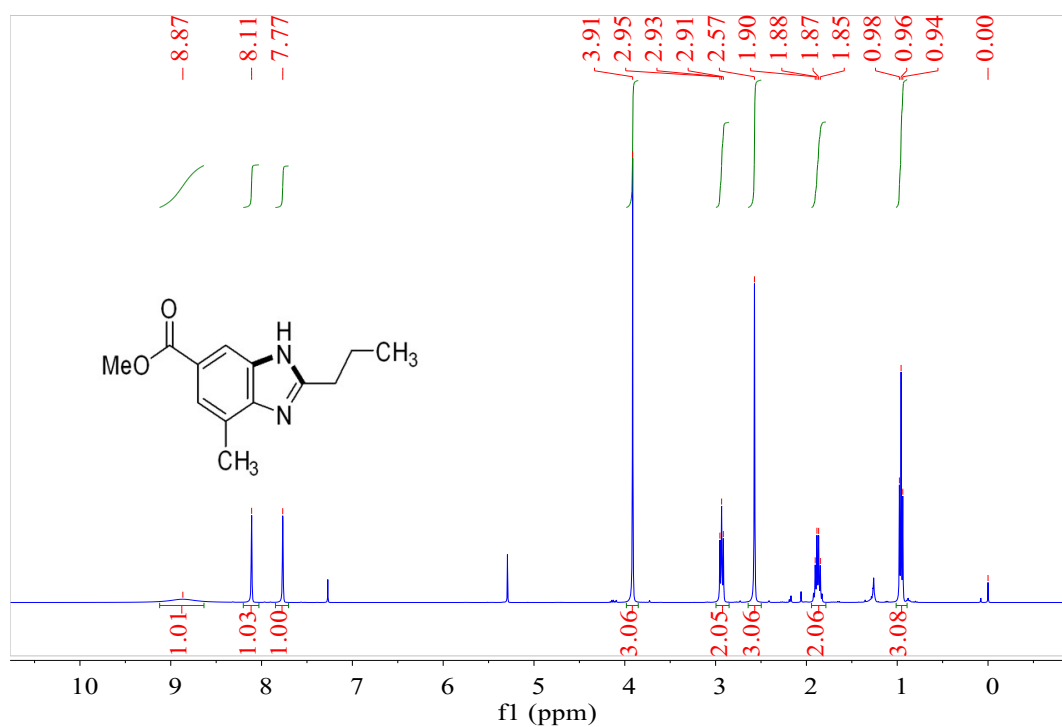


Figure S3 ^1H NMR of compound 2a in CDCl_3

^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 157.3, 141.8, 137.5, 124.6, 124.2, 124.1, 114.3, 52.1, 31.3, 21.8, 17.1, 13.8; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2$ 233.1285, found: 233.1281.

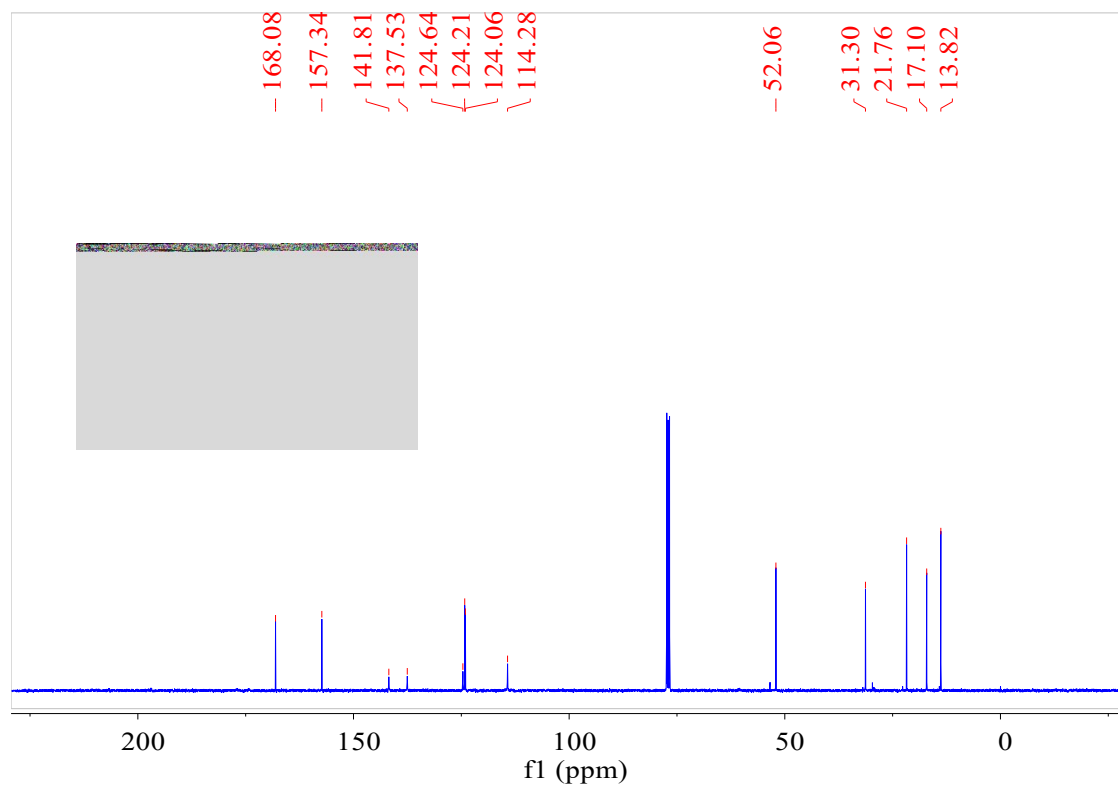
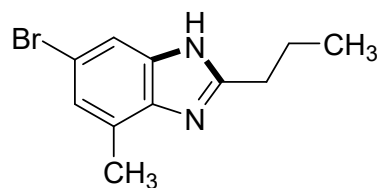


Figure S4 ^{13}C NMR of compound **2a** in CDCl_3

Benzimidazoles 2b



Two sets of ¹H NMR data representing two isomers (10:9) were observed as indicative of the presence of tautomerism; ¹H NMR (400 MHz, DMSO-*d*₆, major isomer) δ 12.30 (s, 1 H), 7.51 (s, 1 H), 7.08 (s, 1H), 2.77 (t, *J* = 7.1 Hz, 2H), 2.45 (s, 3 H), 1.78 (dt, *J* = 14.3, 7.2 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); HNMR (400 MHz, DMSO-*d*₆, minor isomer) δ 12.24 (s, 1 H), 7.40 (s, 1H), 7.08 (s, 1H), 2.77 (t, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.78 (dt, *J* = 14.3, 7.2 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H)

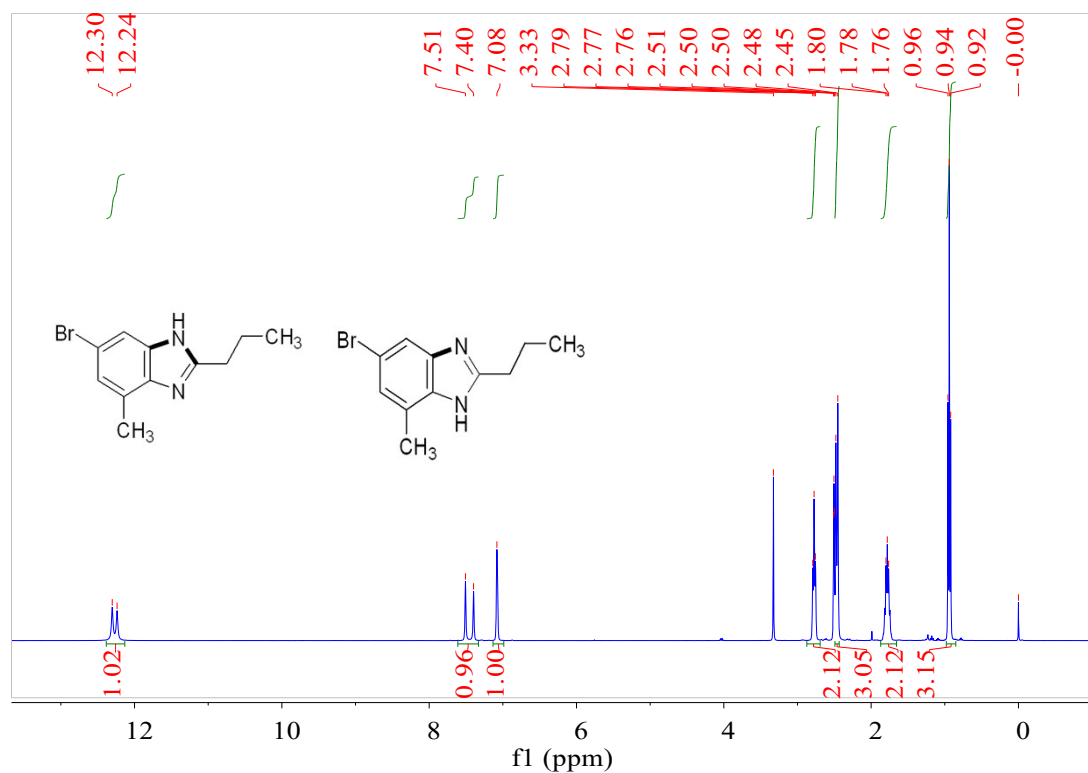


Figure S5 ¹H NMR of compound 2b in DMSO-*d*₆

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, minor isomer) δ 156.8, 155.6, 144.9, 142.3, 135.4, 133.6, 130.3, 124.9, 124.2, 123.2, 118.4, 113.8, 113.4, 111.3, 30.1, 30.9, 21.4, 17.1, 16.7, 14.1. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{BrN}_2$ 253.0335, found: 253.0332.

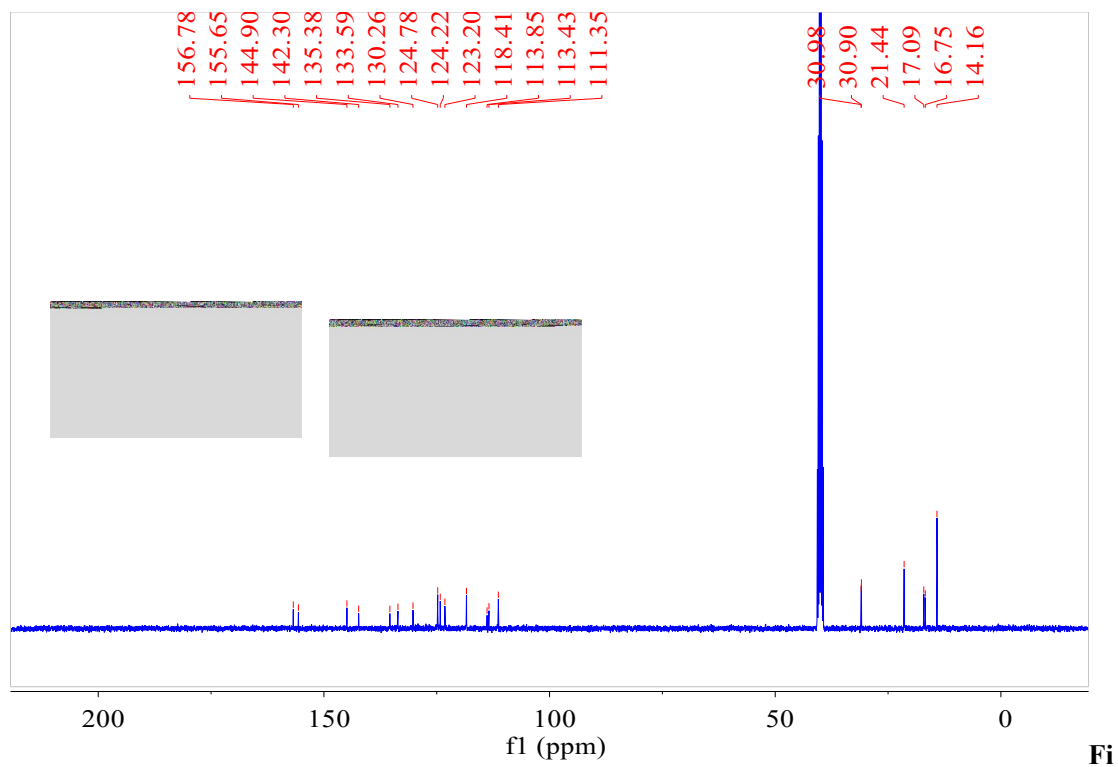
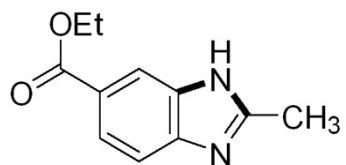


Figure S6 ^{13}C NMR of compound **2b** in $\text{DMSO-}d_6$

Benzimidazoles 2c



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.98 (dd, $J = 8.5, 1.4$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 2.70 (s, 3H), 1.43 (t, $J = 7.1$ Hz, 3H).

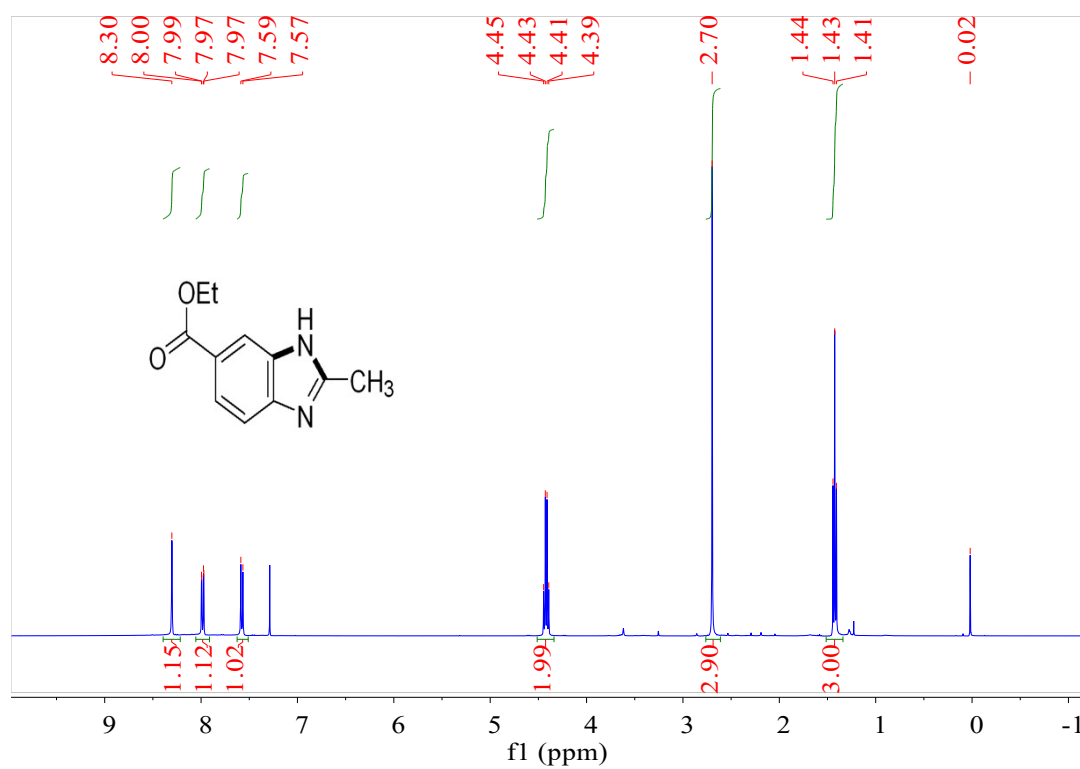


Figure S7 $^1\text{H NMR}$ of compound **2c** in CDCl_3

^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 153.7, 142.4, 138.1, 124.6, 123.9, 114.2, 60.1, 15.1, 14.3.

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$ 205.0972, found: 205.0969.

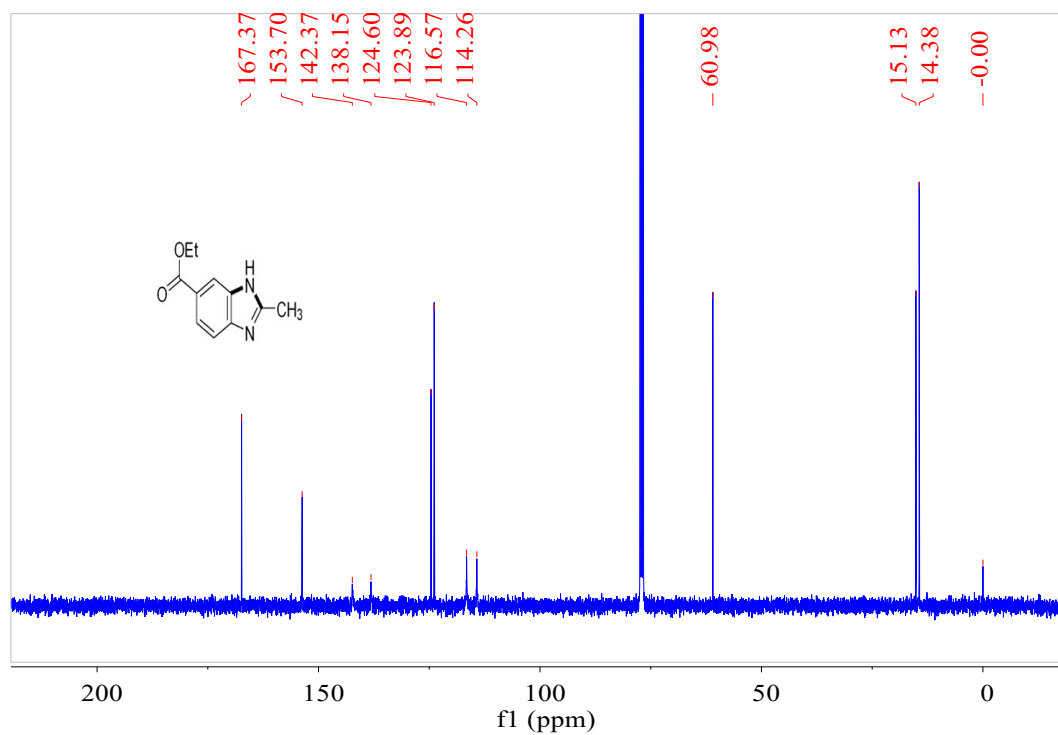
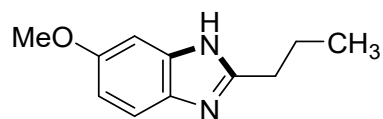


Figure S8 ^{13}C NMR of compound **2c** in CDCl_3

Benzimidazoles 2d



^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.7$ Hz, 1H), 6.97 (d, $J = 1.3$ Hz, 1H), 6.83 – 6.74 (m, 1H), 3.73 (s, 3H), 2.82 (t, $J = 7.5$ Hz, 2H), 1.86 – 1.72 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H)

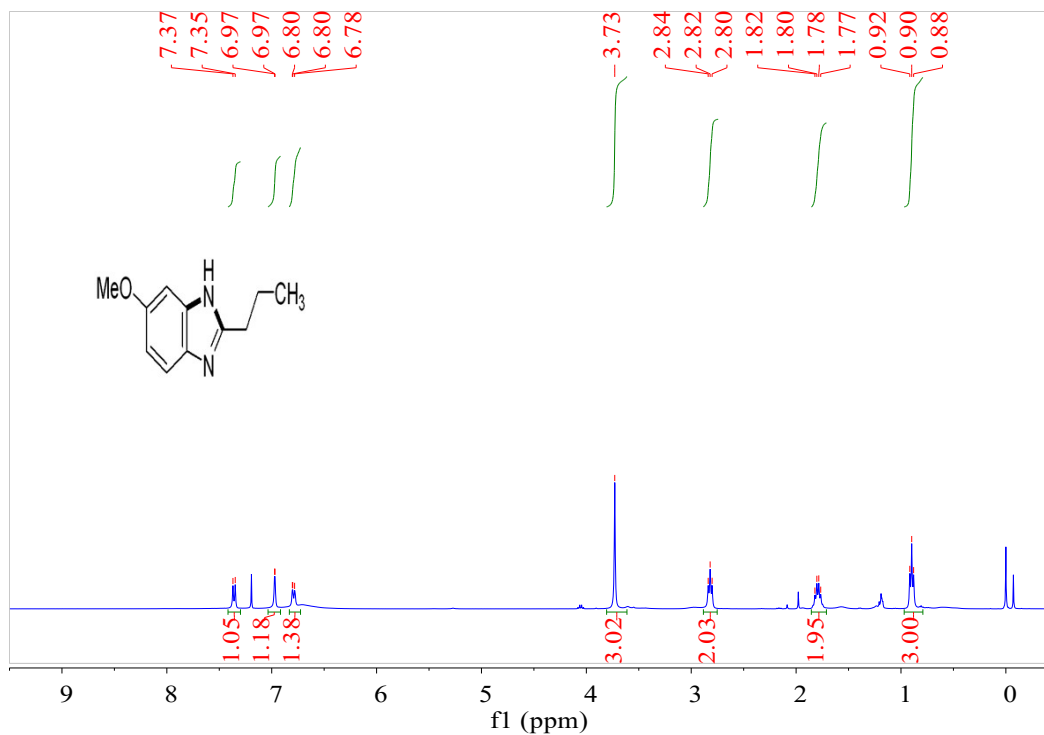


Figure S9 ^1H NMR of compound **2d** in CDCl_3

^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 154.5, 137.9, 132.4, 115.1, 111.8, 97.5, 55.8, 30.9, 21.6, 13.7;

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}$ 191.1179, found: 191.1177.

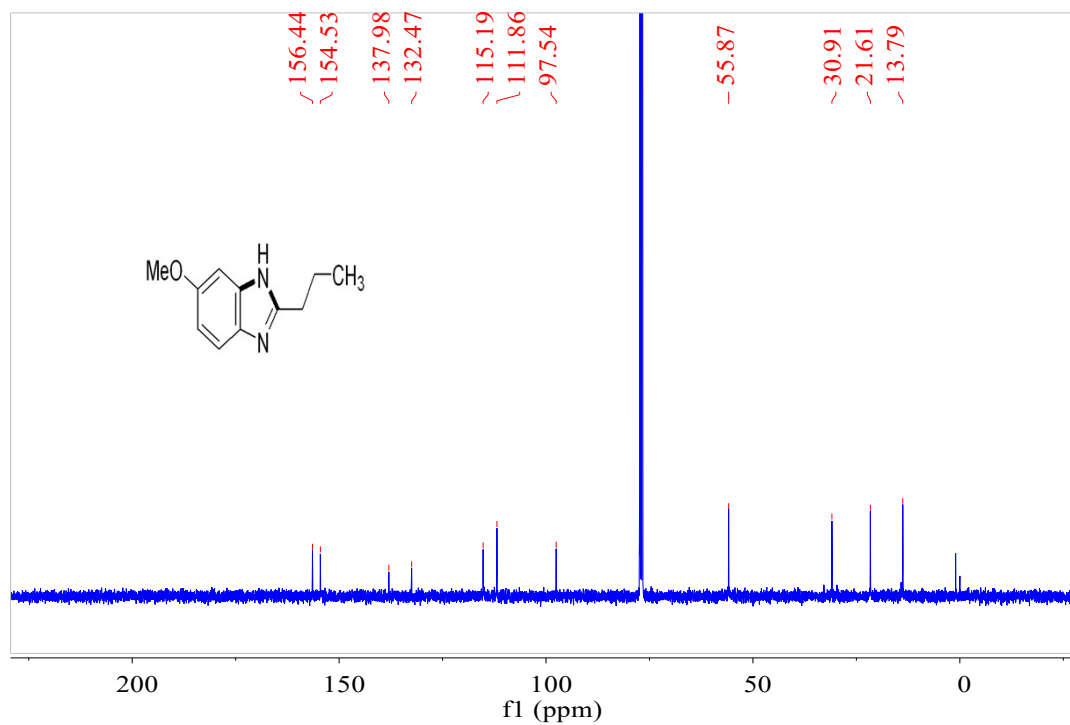
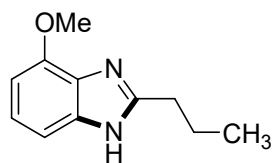


Figure S10 ^{13}C NMR of compound **2d** in CDCl_3

Benzimidazoles 2e



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 – 7.07 (m, 2H), 6.67 (dd, $J = 7.5, 1.2$ Hz, 1H), 3.94 (s, 3H), 2.90 (t, $J = 7.4$ Hz, 2H), 2.03 – 1.76 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H);

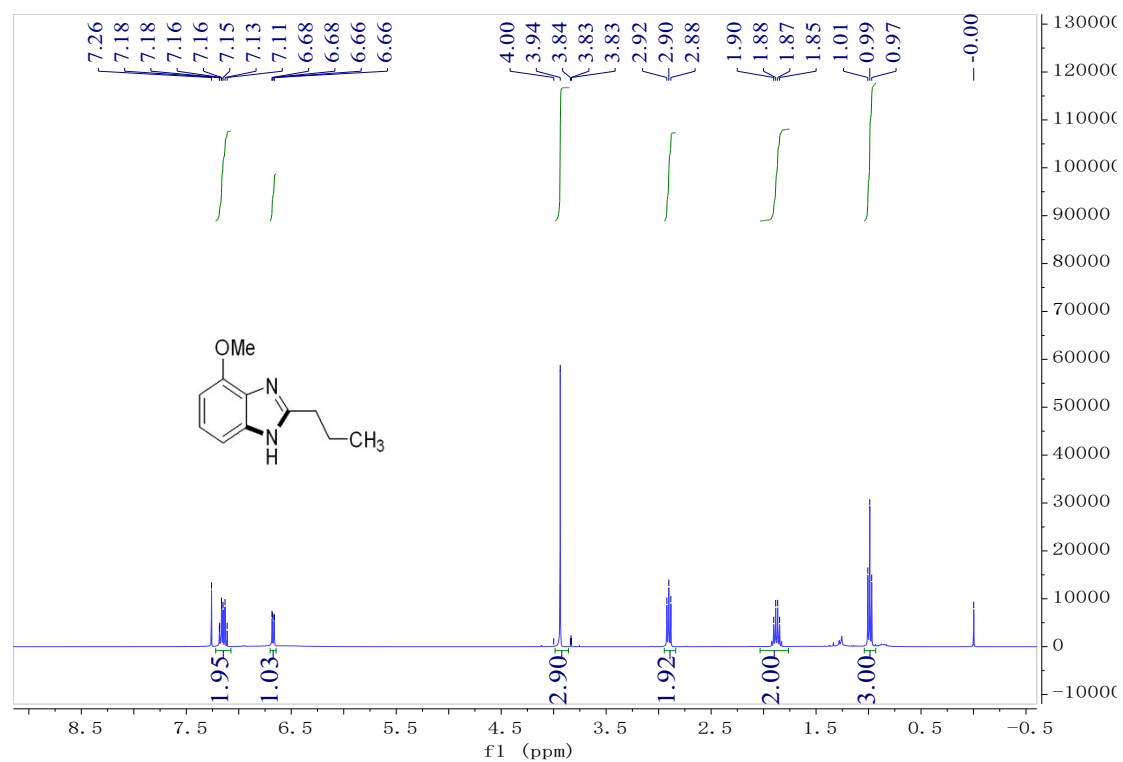


Figure S11 $^1\text{H NMR}$ of compound **2e** in CDCl_3

^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 148.3, 139.7, 128.6, 122.6, 107.4, 102.6, 55.5, 31.1, 21.7, 13.8; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}$ 191.1179, found: 191.1176.

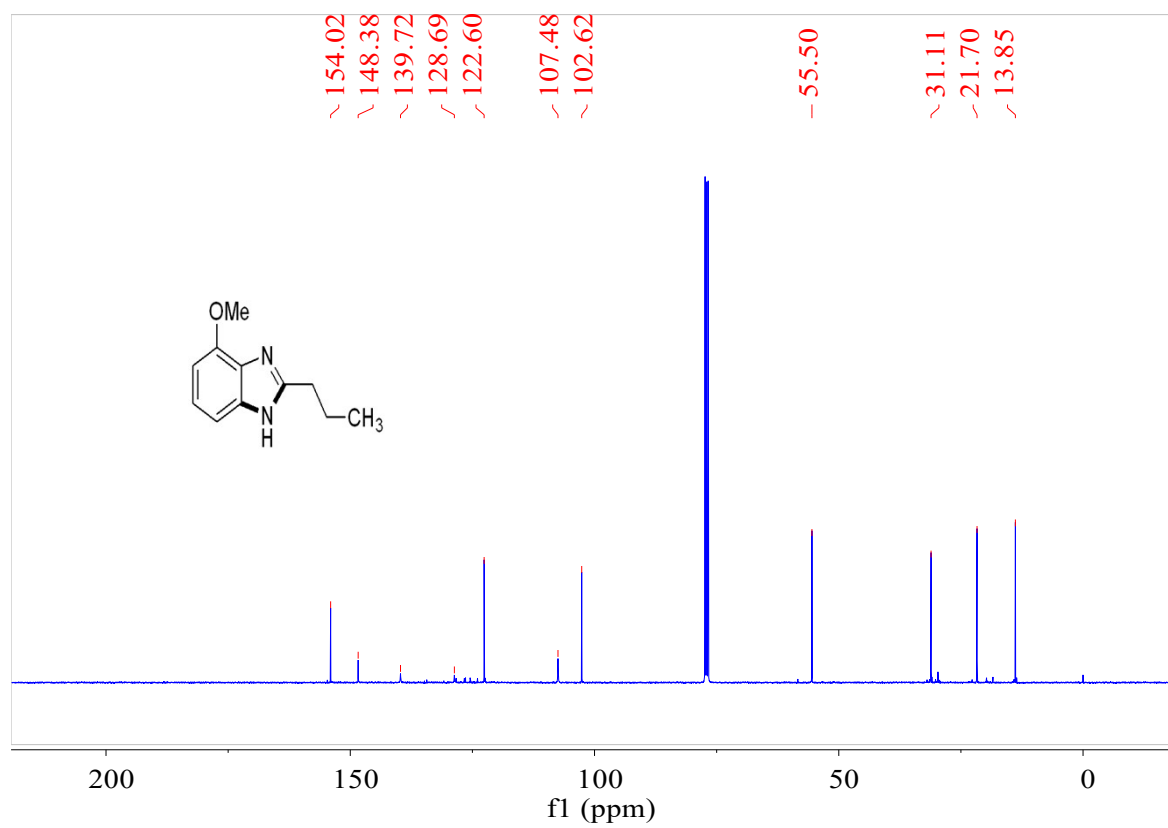
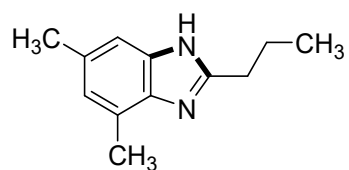


Figure S12 ^{13}C NMR of compound **2e** in CDCl_3

Benzimidazoles 2f



^1H NMR (400 MHz, CD_3OD) δ 7.34 (s, 1H), 7.20 (s, 1H), 3.16 – 3.12 (m, 2 H), 2.59 (s, 3H), 2.49 (s, 3H), 2.07 – 1.86 (m, 2H), 1.07 (t, $J = 7.4$ Hz, 3H)

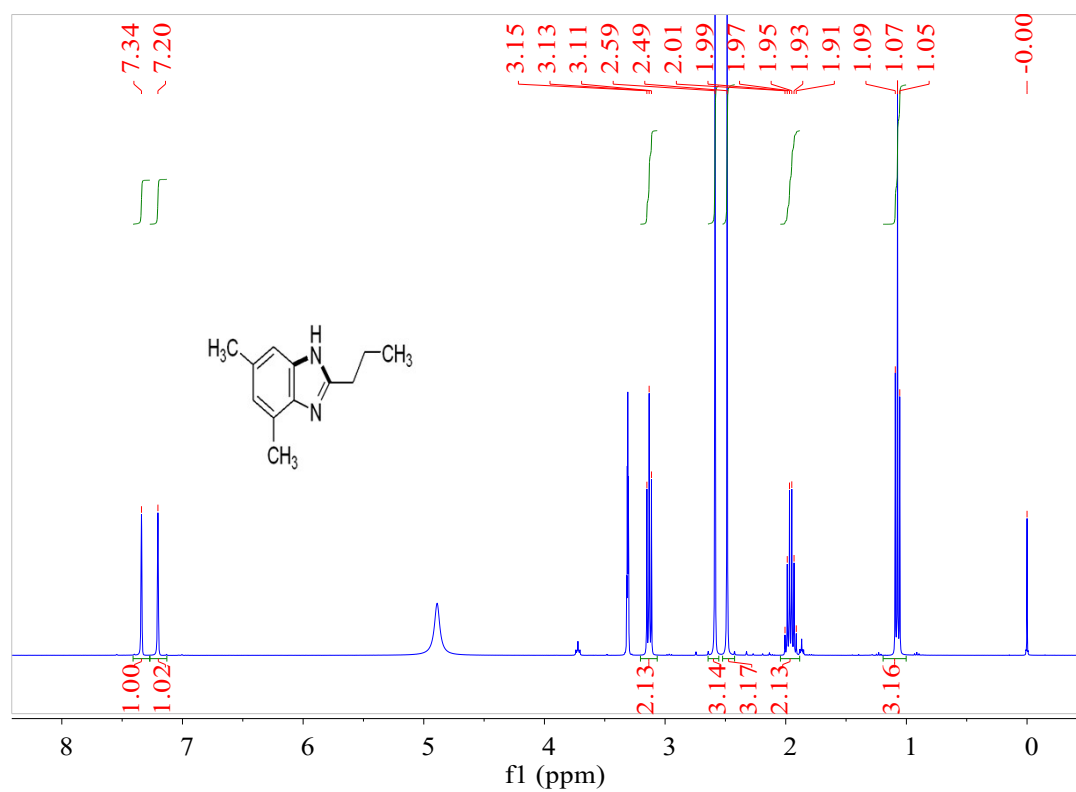


Figure S13 ^1H NMR of compound 2f in CD_3OD

^{13}C NMR (100 MHz, CD_3OD) δ 153.3, 136.7, 131.0, 128.6, 127.9, 123.6, 110.1, 27.8, 20.6, 20.1, 15.1, 12.3; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{N}_2$ 189.1386, found: 189.1383

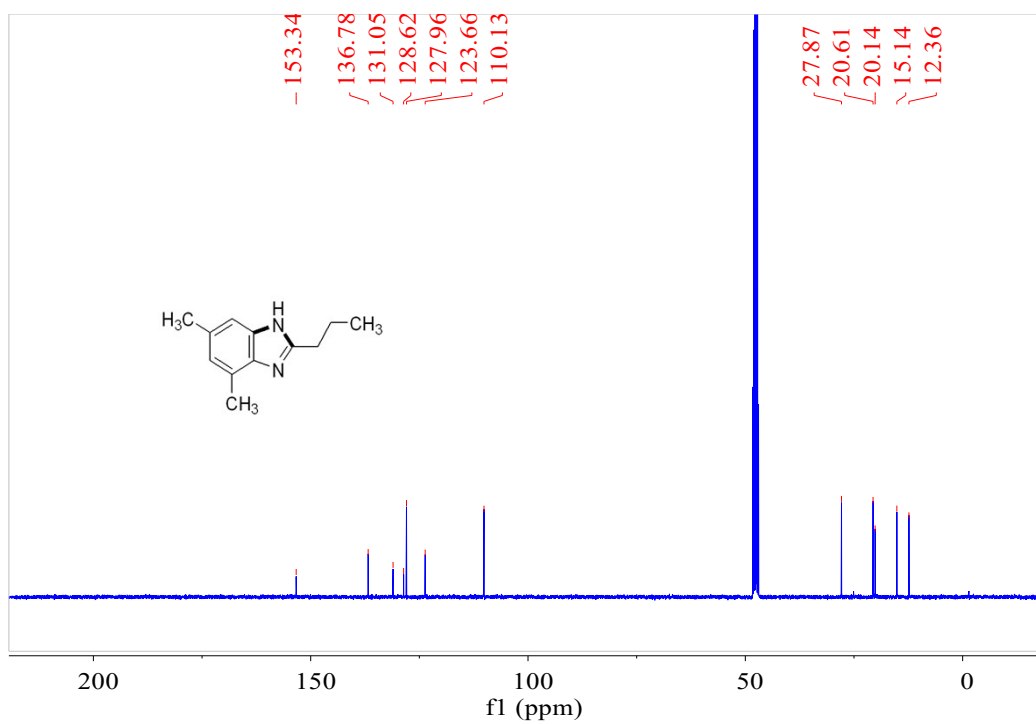
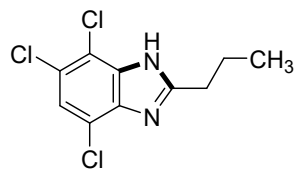


Figure S14 ^{13}C NMR of compound **2f** in CD_3OD

Benzimidazoles 2g



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 13.12 (s, 1H), 7.52 (s, 1H), 2.84 (t, $J = 7.5$ Hz, 2H), 1.87 – 1.75 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H)

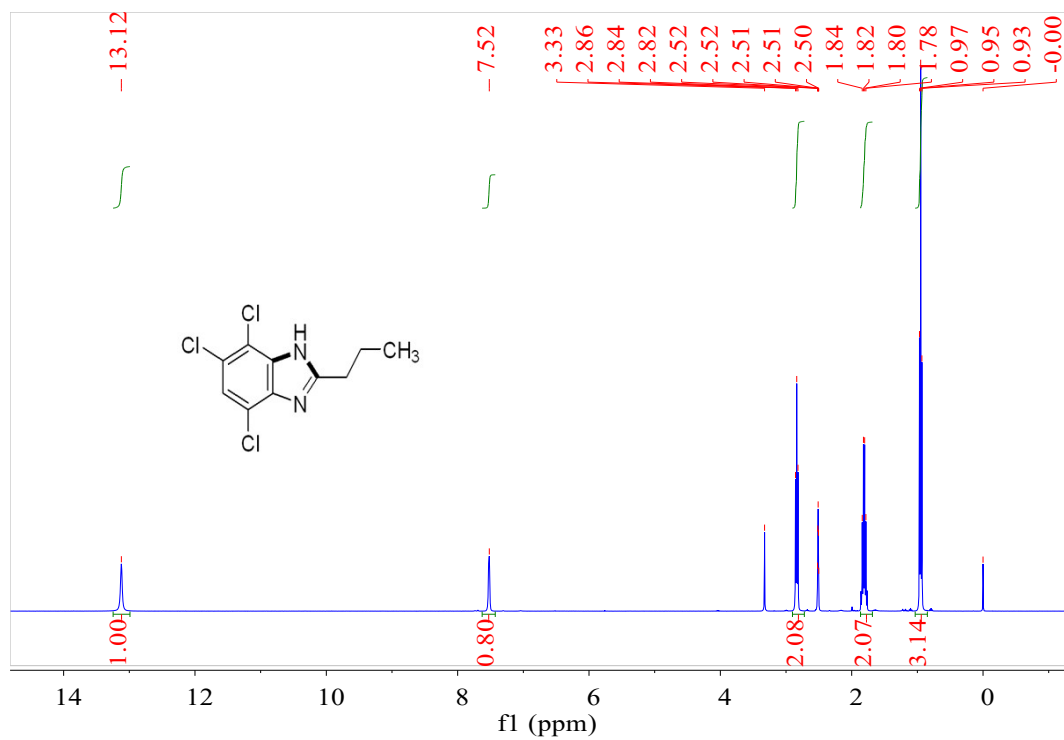


Figure S15 $^1\text{H NMR}$ of compound **2g** in $\text{DMSO-}d_6$

^{13}C NMR (100 MHz, CD_3OD) δ 159.6, 132.6, 131.2, 130.7, 128.1, 119.3, 117.7, 29.65, 22.6, 13.9;

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{N}_2$ 262.9904, found: 262.9898.

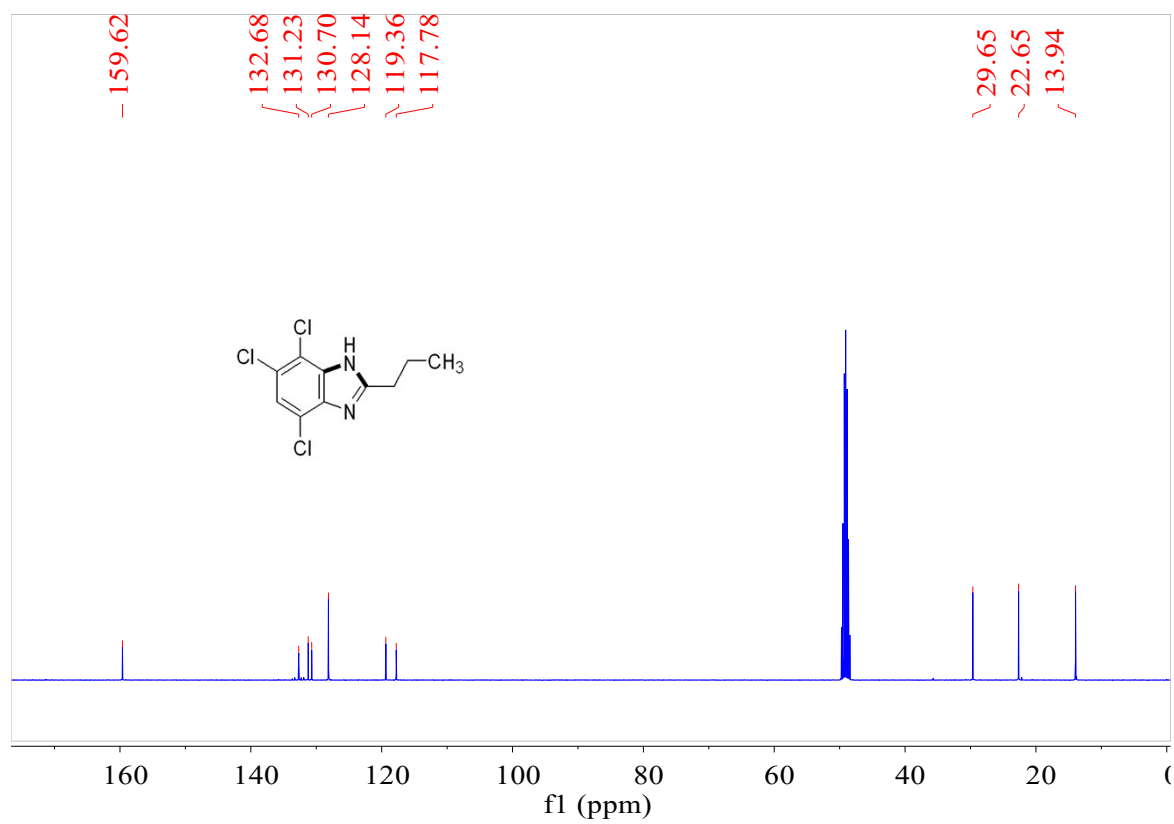
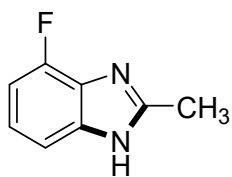


Figure S16 ^{13}C NMR of compound **2g** in CD_3OD

Benzimidazoles 2h



Two sets of ^1H NMR data representing two isomers (3:1) were observed as indicative of the presence of tautomerism; ^1H NMR (400 MHz, $\text{DMSO-}d_6$, major isomer) δ 12.47 (s, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.13 – 7.03 (m, 1H), 6.99 – 6.84 (m, 1H), 2.49 (s, 3H). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, minor isomer) δ 12.71 (s, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.13 – 7.03 (m, 1H), 7.01 – 6.89 (m, 1H), 2.49 (s, 3H).

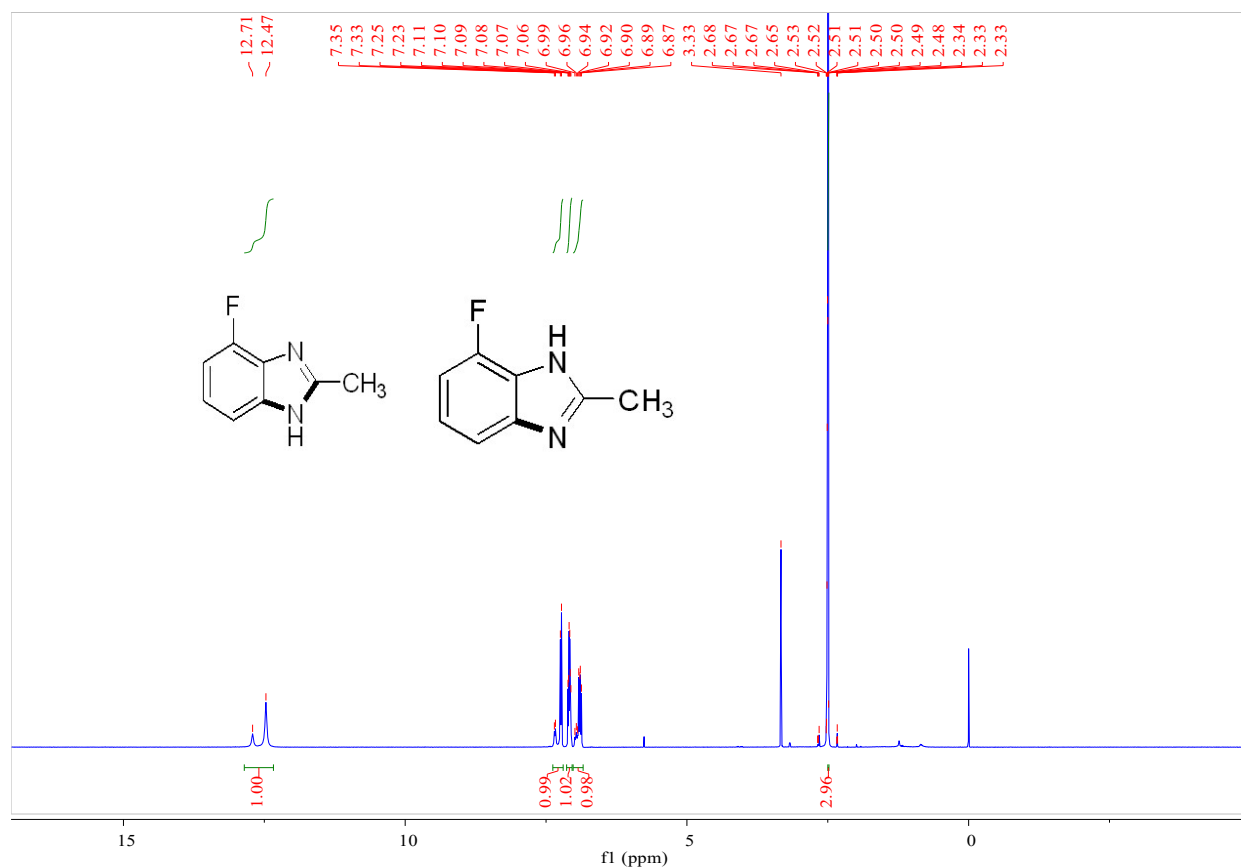


Figure S17 ^1H NMR of compound **2h** in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 154.2, 152.3, 151.7, 138.1, 138.0, 132.0, 122.3, 122.2, 107.5, 106.80, 106.6, 15.0; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_8\text{H}_8\text{FN}_2$ 151.0666, found: 151.0662.

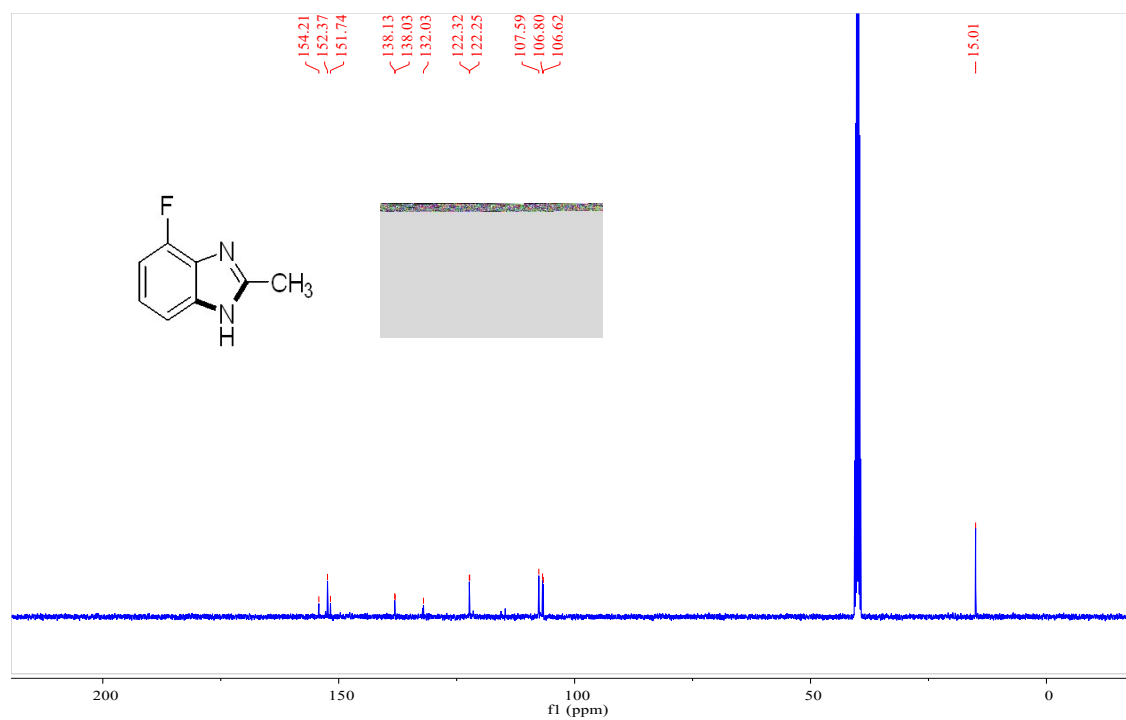


Figure S18 ^{13}C NMR of compound **2h** in $\text{DMSO}-d_6$

^{19}F NMR (377 MHz, DMSO) δ -135.23.

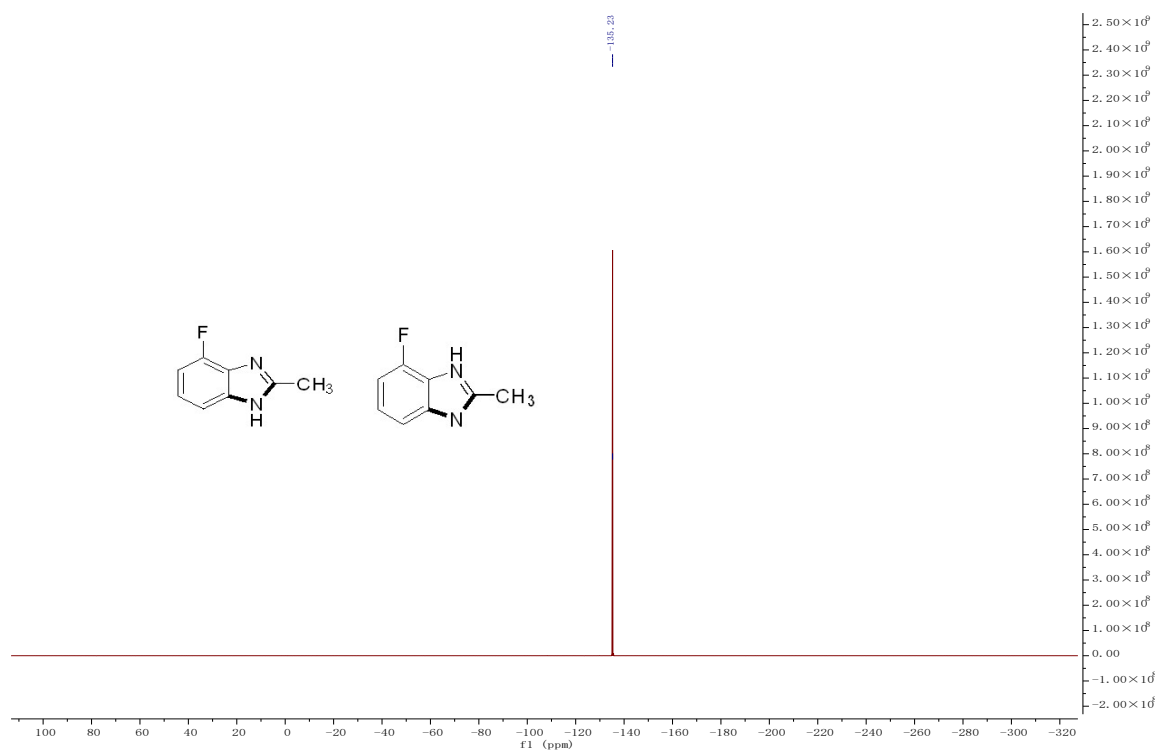
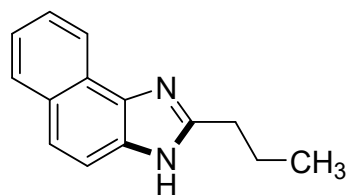


Figure S19 ^{19}F NMR of compound **2h** in $\text{DMSO-}d_6$

Benzimidazoles 2i



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.36 – 8.28 (m, 1H), 8.09 – 8.01 (m, 1H), 7.97 – 7.89 (m, 1H), 7.78 – 7.67 (m, 2H), 7.67 – 7.60 (m, 1H), 3.22 (t, $J = 7.7$ Hz, 2H), 2.08 – 1.95 (m, 2H), 1.11 (t, $J = 7.3$ Hz, 3H).

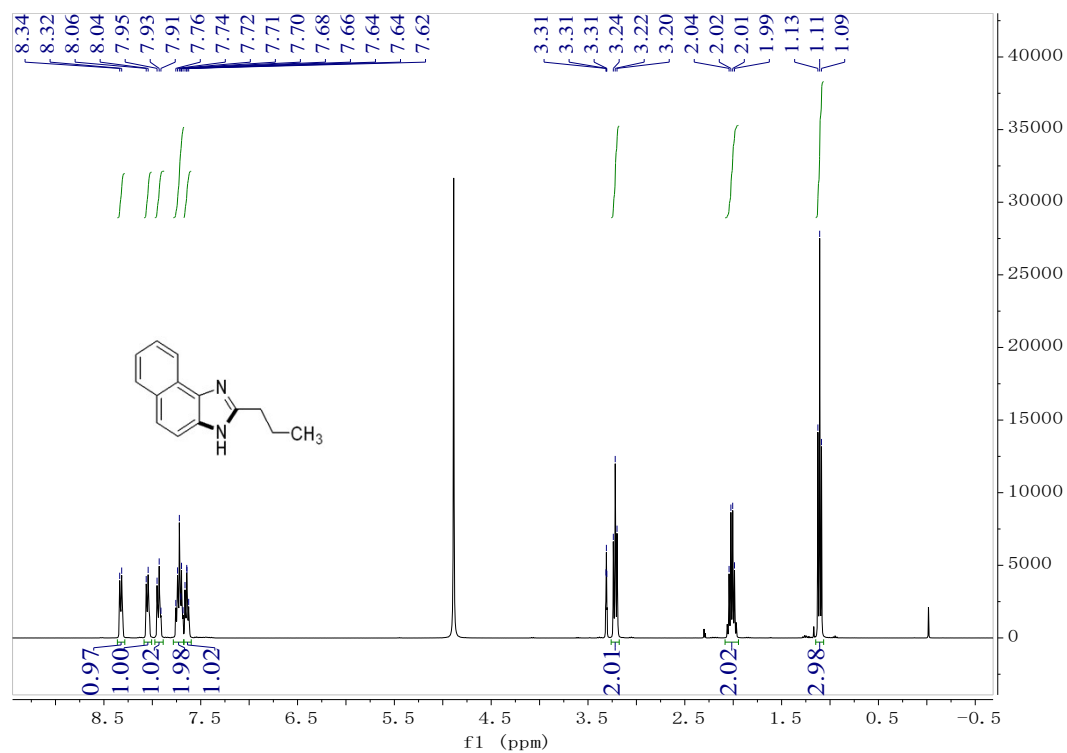


Figure S20 $^1\text{H NMR}$ of compound **2i** in CD_3OD

^{13}C NMR (100 MHz, CD_3OD) δ 153.0, 132.6, 132.6, 130.3, 129.3, 129.2, 128.6, 127.9, 122.1, 121.9, 113.1, 29.2, 22.1, 13.8; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2$ 211.1230, found: 211.1226.

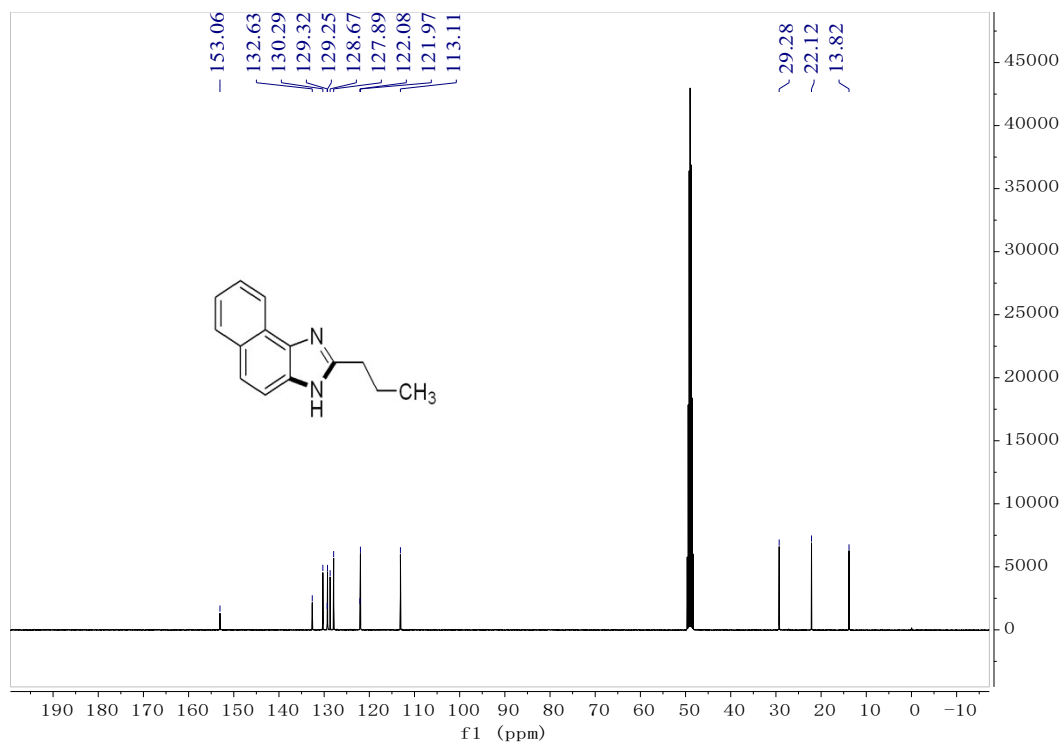
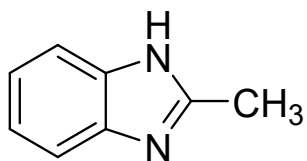


Figure S21 ^{13}C NMR of compound **2i** in CD_3OD

Benzimidazoles 2j



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 12.15 (s, 1H), 7.43 (d, $J = 3.2$ Hz, 2H), 7.09 (dd, $J = 5.9, 3.1$ Hz, 2H), 2.56 – 2.21 (m, 3H).

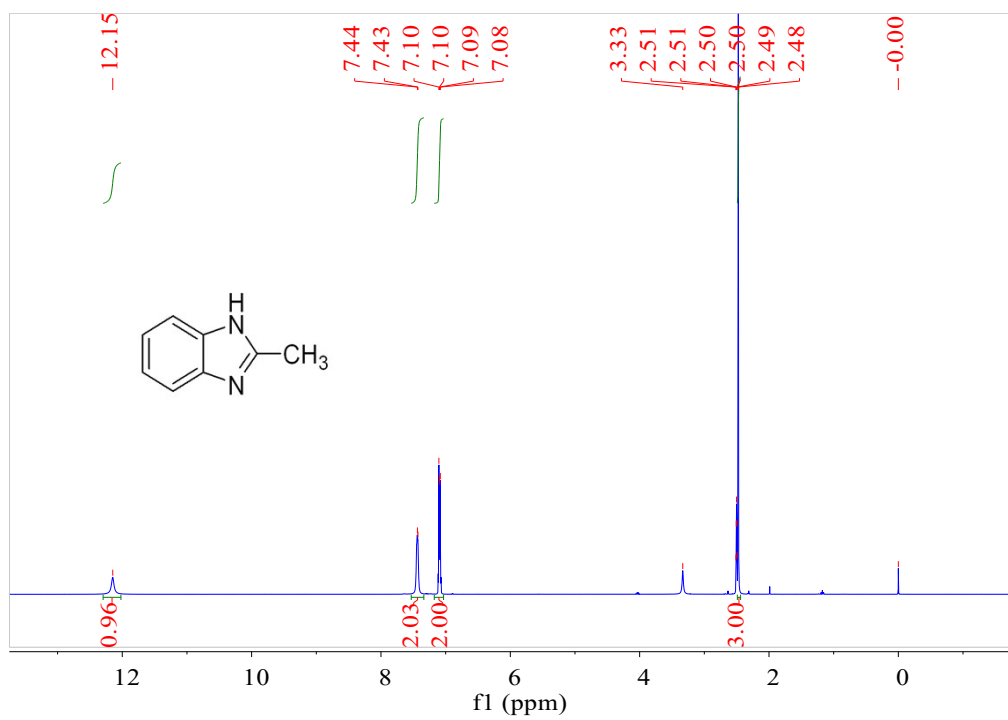


Figure S22 $^1\text{H NMR}$ of compound 2j in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 151.6, 121.4, 40.6, 40.4, 15.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_8\text{H}_9\text{N}_2$ 133.0760

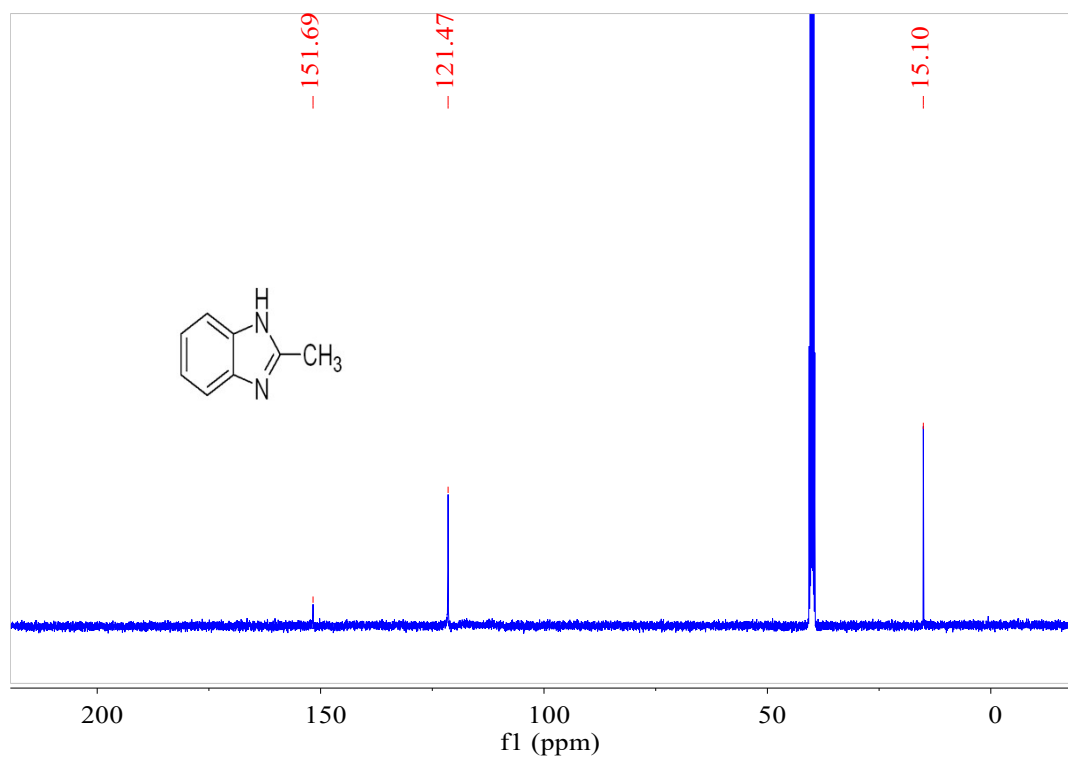
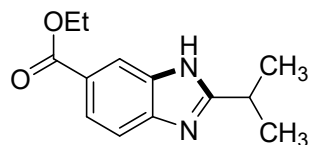


Figure S23 ^{13}C NMR of compound **2j** in $\text{DMSO-}d_6$

Benzimidazoles 2k



^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 0.7$ Hz, 1H), 8.26 (dd, $J = 8.6, 1.4$ Hz, 1H), 7.86 (d, $J = 8.6$ Hz, 1H), 4.46 (q, $J = 7.1$ Hz, 2H), 3.59 (dt, $J = 14.0, 7.0$ Hz, 1H), 1.60 (d, $J = 7.0$ Hz, 6H), 1.45 (t, $J = 7.1$ Hz, 3H)

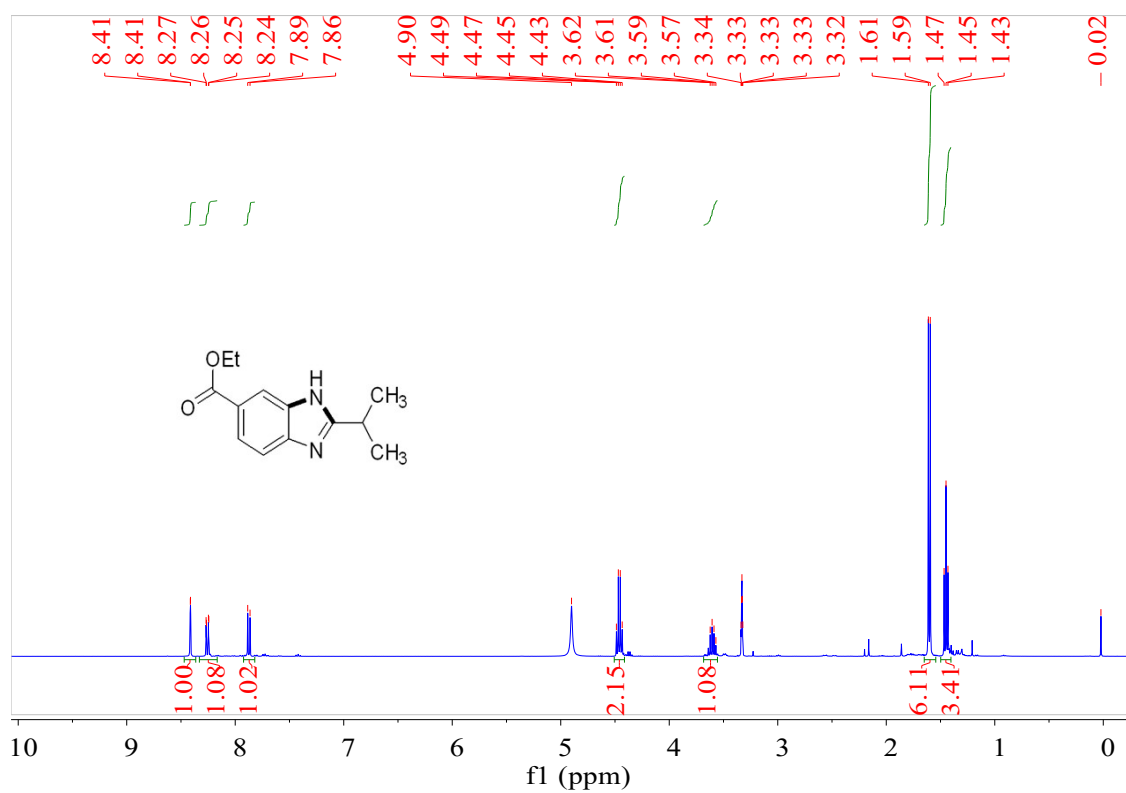


Figure S24 ^1H NMR of compound **2k** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) δ 166.8, 162.5, 135.2, 132.1, 129.9, 128.2, 116.5, 114.8, 62.8, 29.1, 20.3, 14.6; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2$ 233.1285, found: 233.1282.

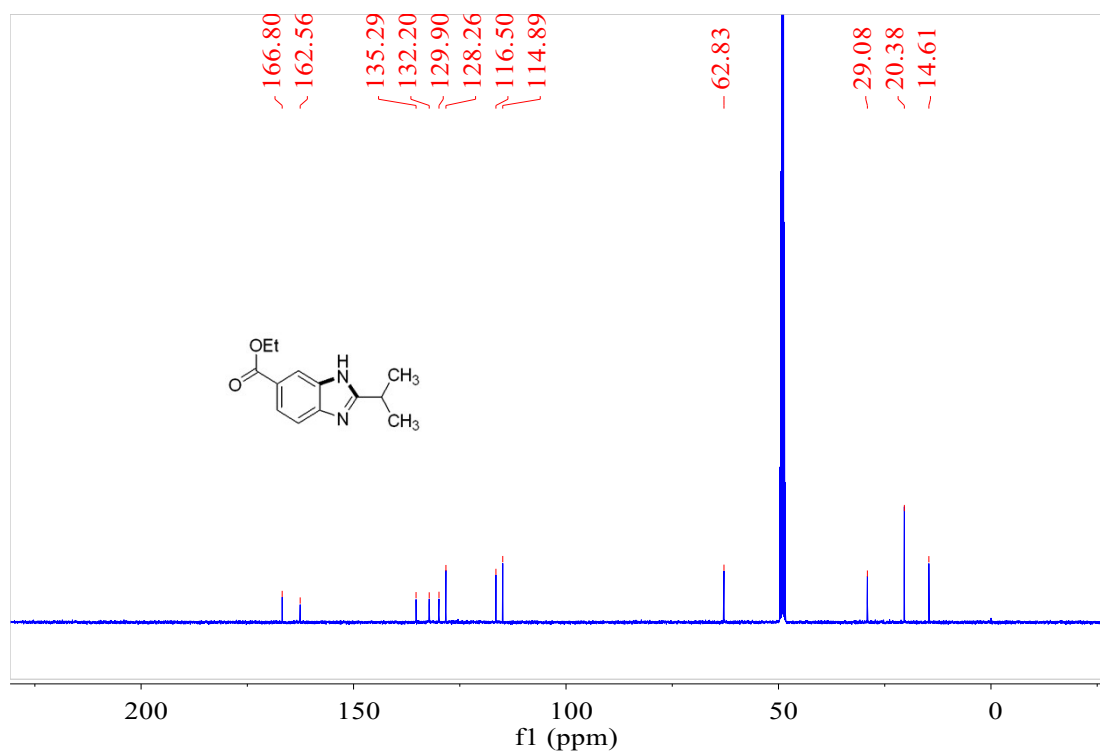
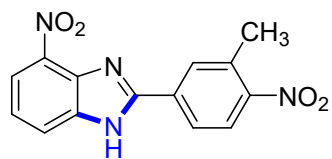


Figure S25 ^{13}C NMR of compound **2k** in CD_3OD

Benzimidazoles 2l



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 9.76 – 9.38 (s, 1H), 8.03 – 7.94 (m, 2H), 7.71 – 7.67 (m, 1H), 7.53 – 7.51 (s, 1H), 7.31 – 7.24 (m, 1H), 7.03 – 6.97 (dd, $J = 8.1, 1.0$ Hz, 1H), 2.24 – 1.93 (s, 3H).

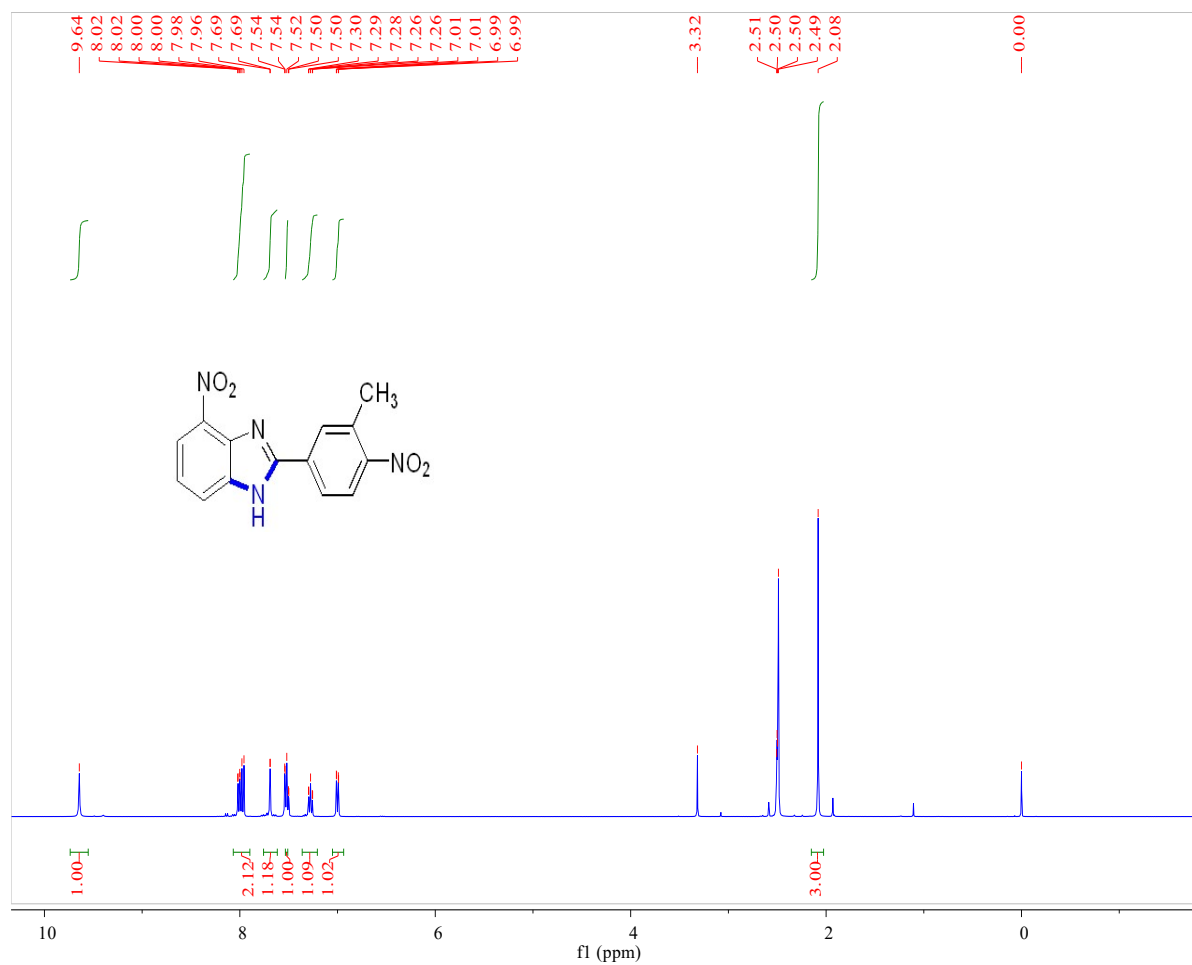


Figure S26 $^1\text{H NMR}$ of compound **2l** in $\text{DMSO-}d_6$

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 167.9, 152.8, 150.4, 142.1, 135., 134.5, 134.4, 133.4, 133.4, 128.1, 127.1, 125.8, 125.2, 125.1, 19.7; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_4$ 299.0775, found: 299.0772.

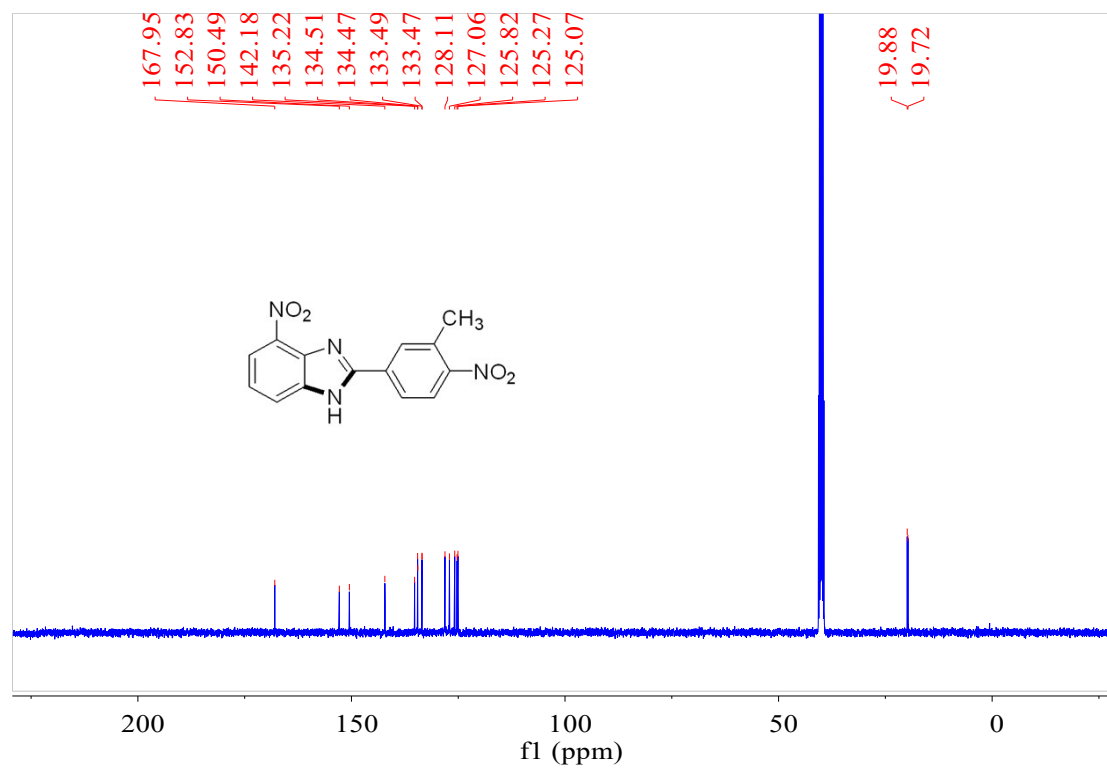
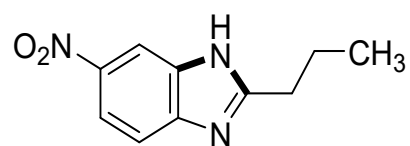


Figure S27 ^{13}C NMR of compound **2I** in $\text{DMSO-}d_6$

Benzimidazoles **2m**



^1H NMR (400 MHz, CD_3OD) δ 8.66 (d, $J = 1.9$ Hz, 1H), 8.46 (dd, $J = 9.0, 2.1$ Hz, 1H), 7.97 (d, $J = 9.0$ Hz, 1H), 3.28 – 3.20 (m, 2H), 2.07 – 1.95 (m, 2H), 1.12 (t, $J = 7.4$ Hz, 3H).

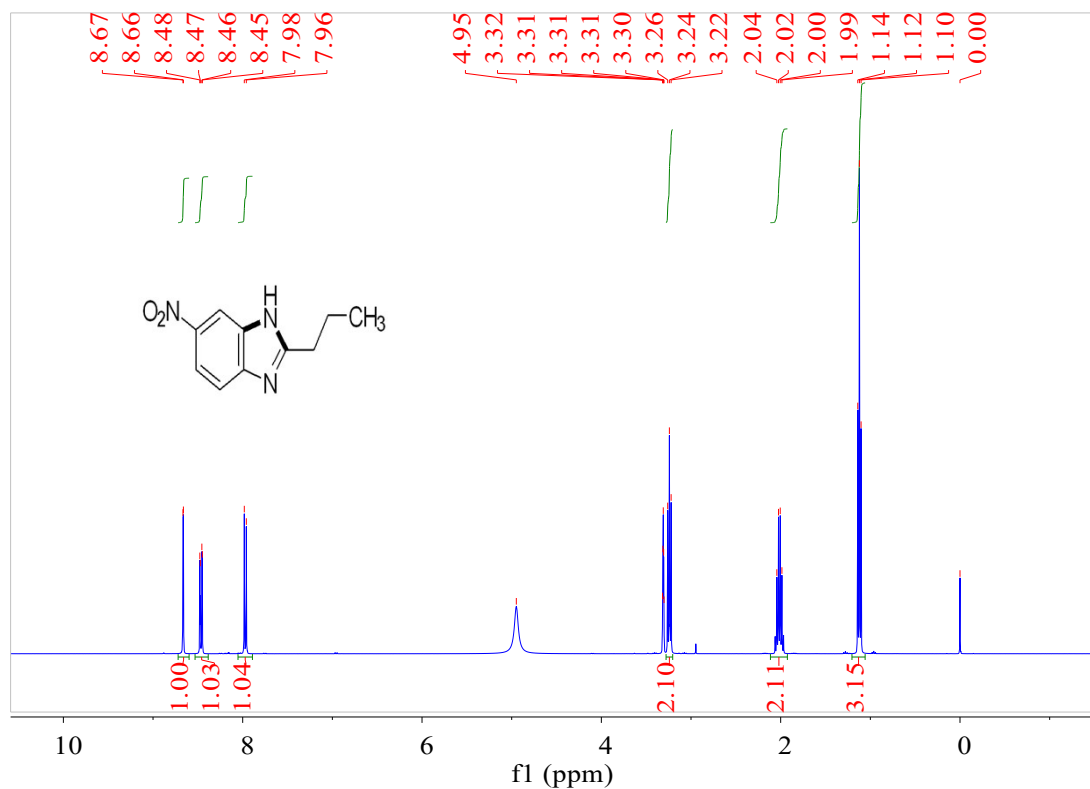


Figure S28 ^1H NMR of compound **2m** in CD_3OD

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) δ 158.8, 145.8, 134.8, 130.7, 121.1, 114.3, 110.1, 28.3, 20.1, 12.3; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_2$ 206.0924, found: 206.0921.

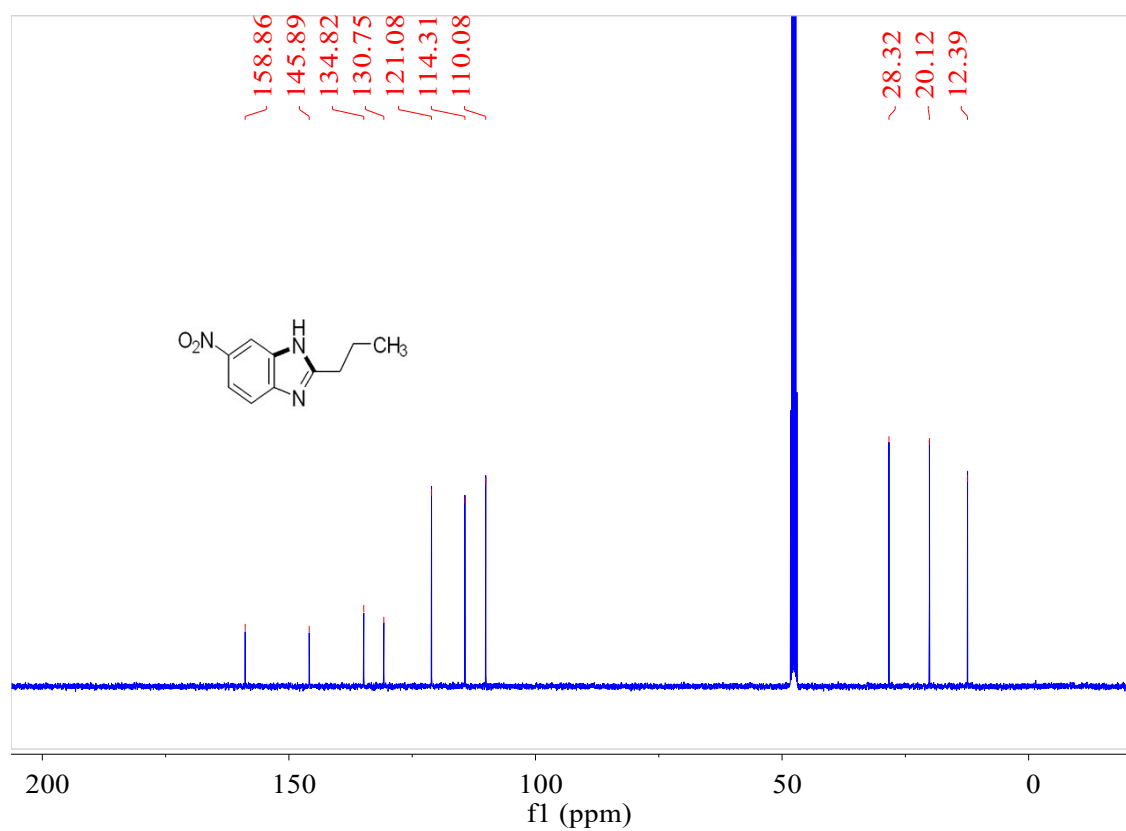
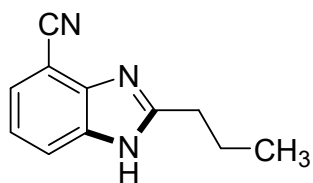


Figure S29 ^{13}C NMR of compound **2m** in CD_3OD

Benzimidazoles 2n



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.12 (d, $J = 8.3$ Hz, 1H), 8.02 (d, $J = 7.7$ Hz, 1H), 7.75 (t, $J = 8.0$ Hz, 1H), 3.24 (t, $J = 7.7$ Hz, 2H), 2.12 – 1.93 (m, 2H), 1.13 (t, $J = 7.4$ Hz, 3H).

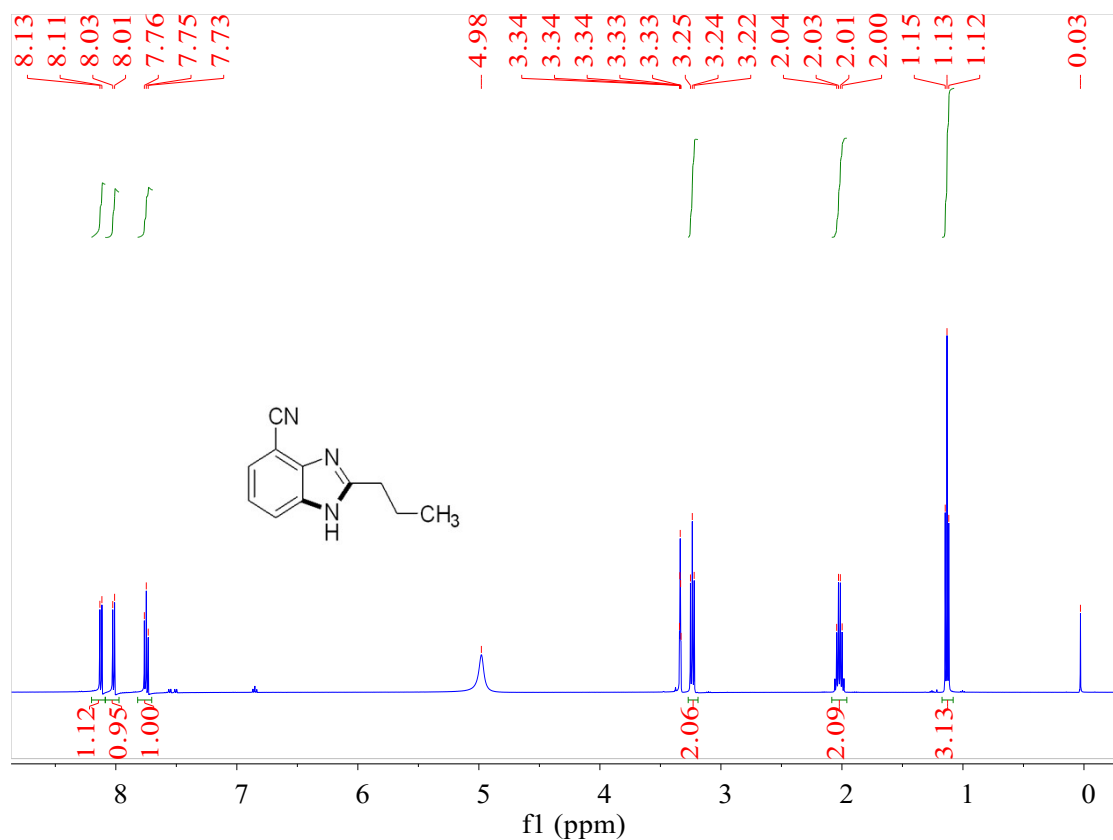


Figure S30 $^1\text{H NMR}$ of compound **2n** in CD_3OD

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) δ 157.0, 131.8, 131.6, 130.5, 126.1, 118.7, 113.9, 97.9, 28.1, 20.4, 12.4; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{12}\text{N}_3$ 186.1026, found: 186.1024.

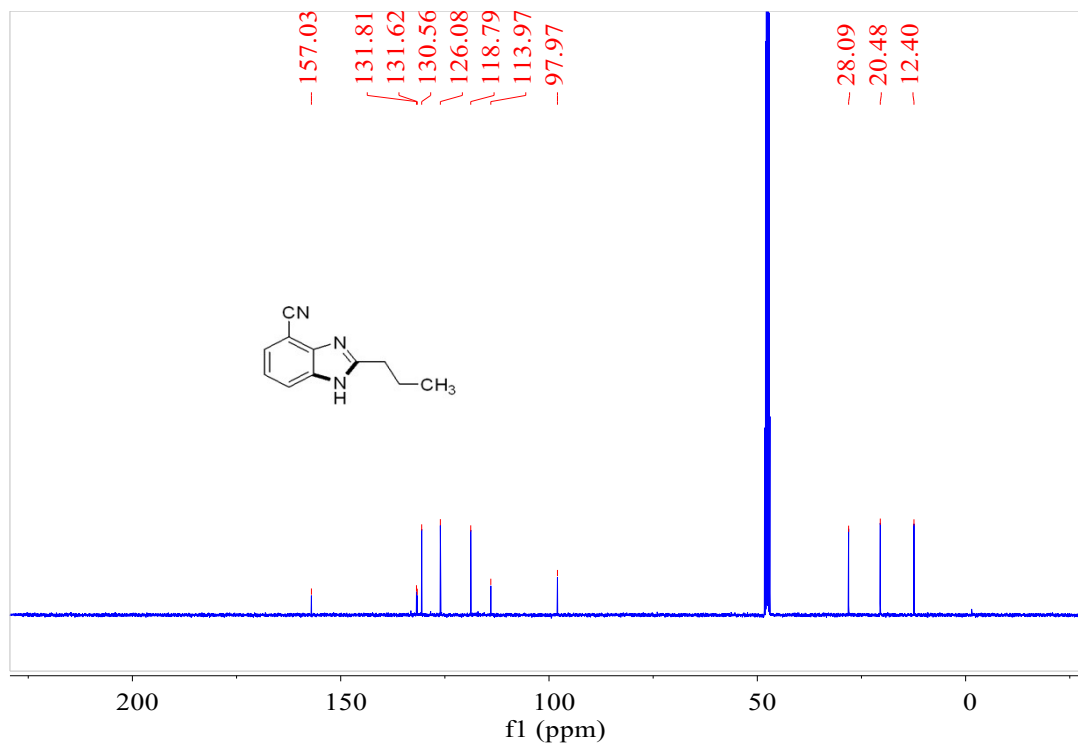
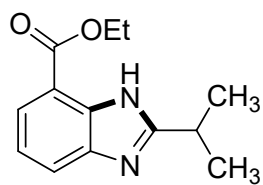


Figure S31 ^{13}C NMR of compound **2n** in CD_3OD

Benzimidazoles 2o



2o ^1H NMR (400 MHz, CD_3OD) δ 8.22 (d, $J = 7.7$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 7.76 – 7.68 (m, 1H), 4.57 (q, $J = 7.1$ Hz, 1H), 3.72 (dd, $J = 14.0, 7.0$ Hz, 1H), 1.59 (d, $J = 7.0$ Hz, 1H), 1.48 (t, $J = 7.1$ Hz, 1H)

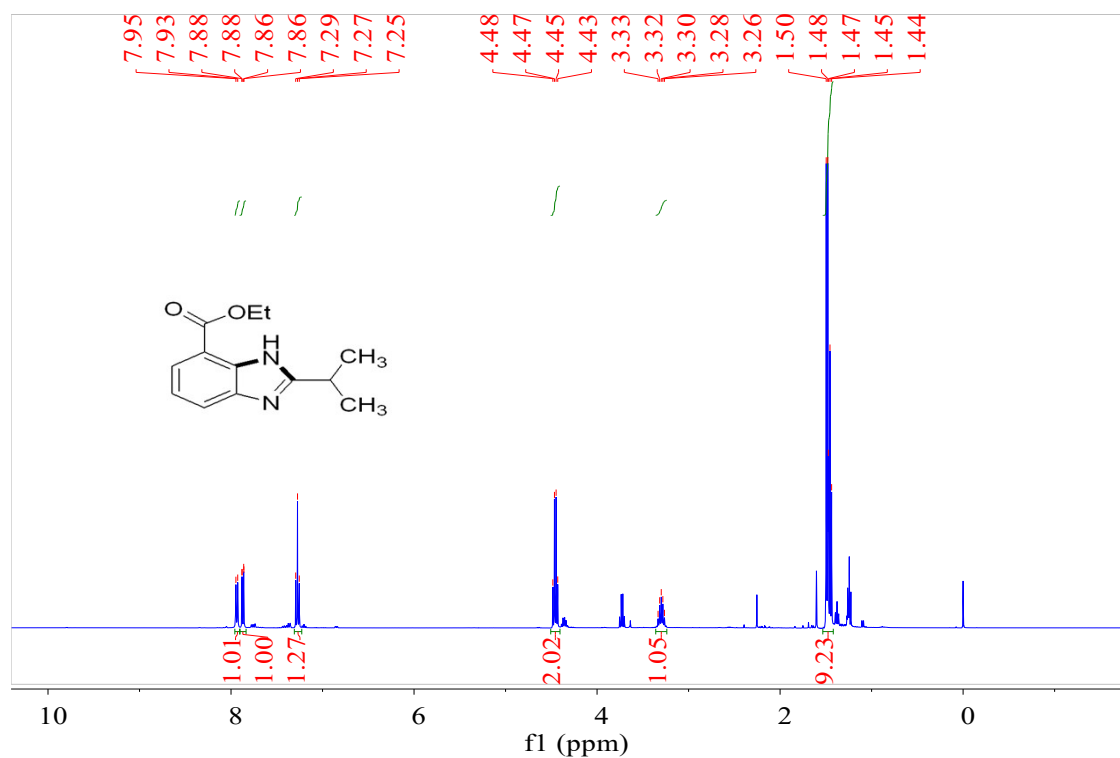


Figure S32 ^1H NMR of compound **2o** in CD_3OD

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) δ 165.8, 162.5, 134.8, 131.8, 128.3, 126.4, 120.4, 117.9, 62.9, 28.8, 21.0, 14.7; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2$ 233.1285, found: 233.1283.

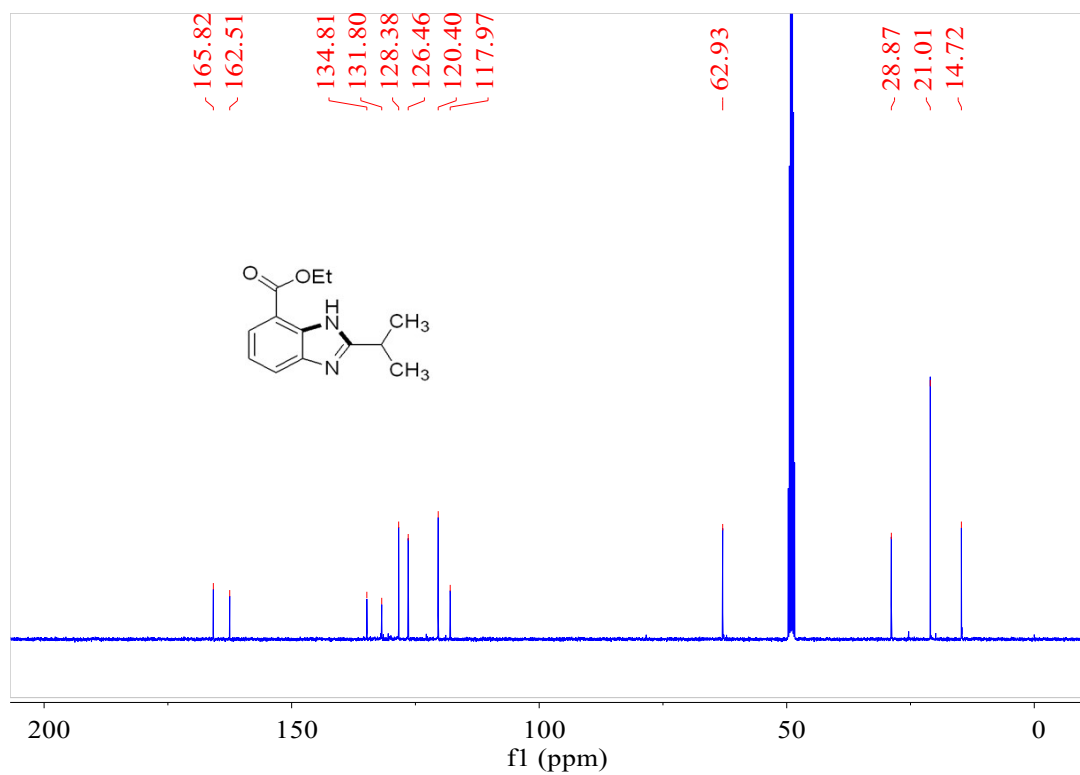
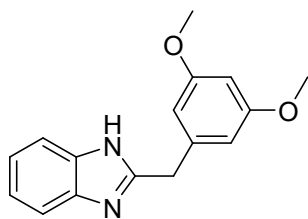


Figure S33 ^{13}C NMR of compound **2o** in CD_3OD

Benzimidazoles 2p



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (s, 2H), 7.21 (dd, $J = 6.0, 3.2$ Hz, 2H), 6.44 (d, $J = 2.1$ Hz, 2H), 6.37 (d, $J = 2.1$ Hz, 1H), 4.21 (s, 6H), 3.73 (s, 3H).

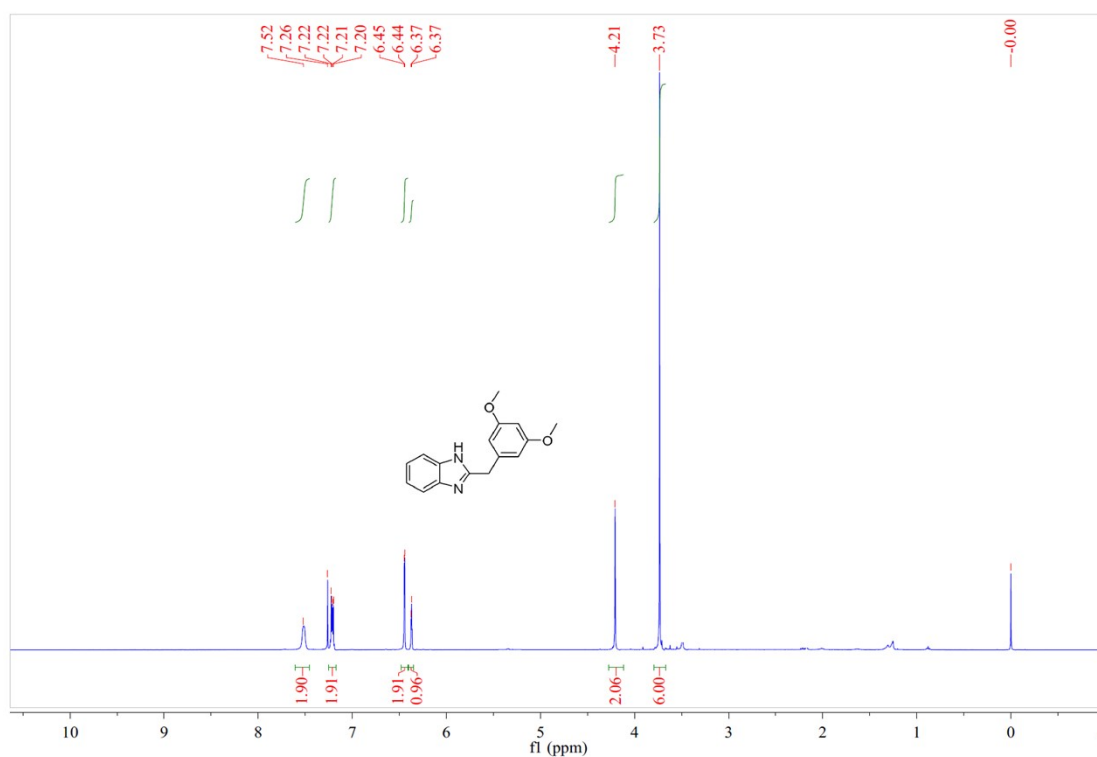


Figure S34 $^1\text{H NMR}$ of compound **2p** in CDCl_3

^{13}C NMR (101 MHz, CDCl_3) δ 161.3, 153.0, 138.3, 122.4, 107.1, 99.2, 55.3, 36.2; HRMS (ESI):
 m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2$ 269.1285

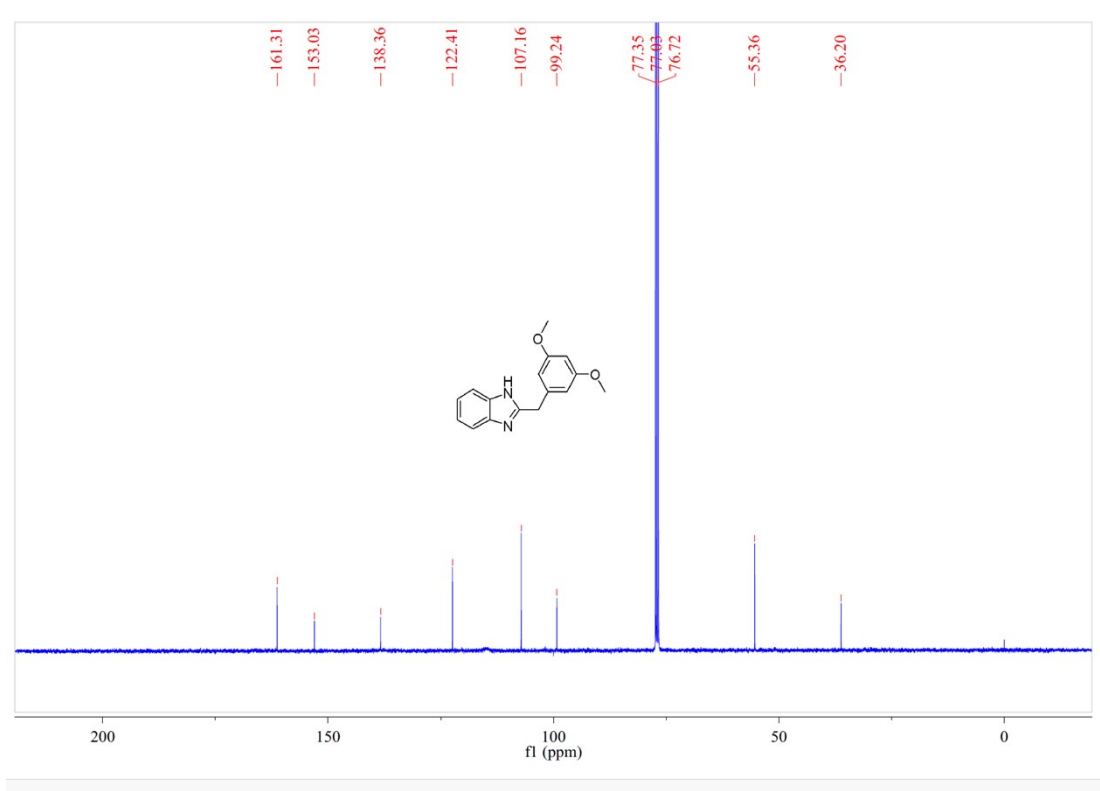
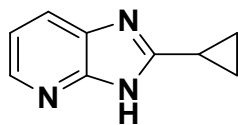


Figure S35 ^{13}C NMR of compound **2p** in CDCl_3

Benzimidazoles 2q



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.24 (d, $J = 4.4$ Hz, 1H), 7.83 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.21 (dd, $J = 8.0, 4.9$ Hz, 1H), 2.19 (s, 0H), 1.43 – 1.03 (m, 4H).

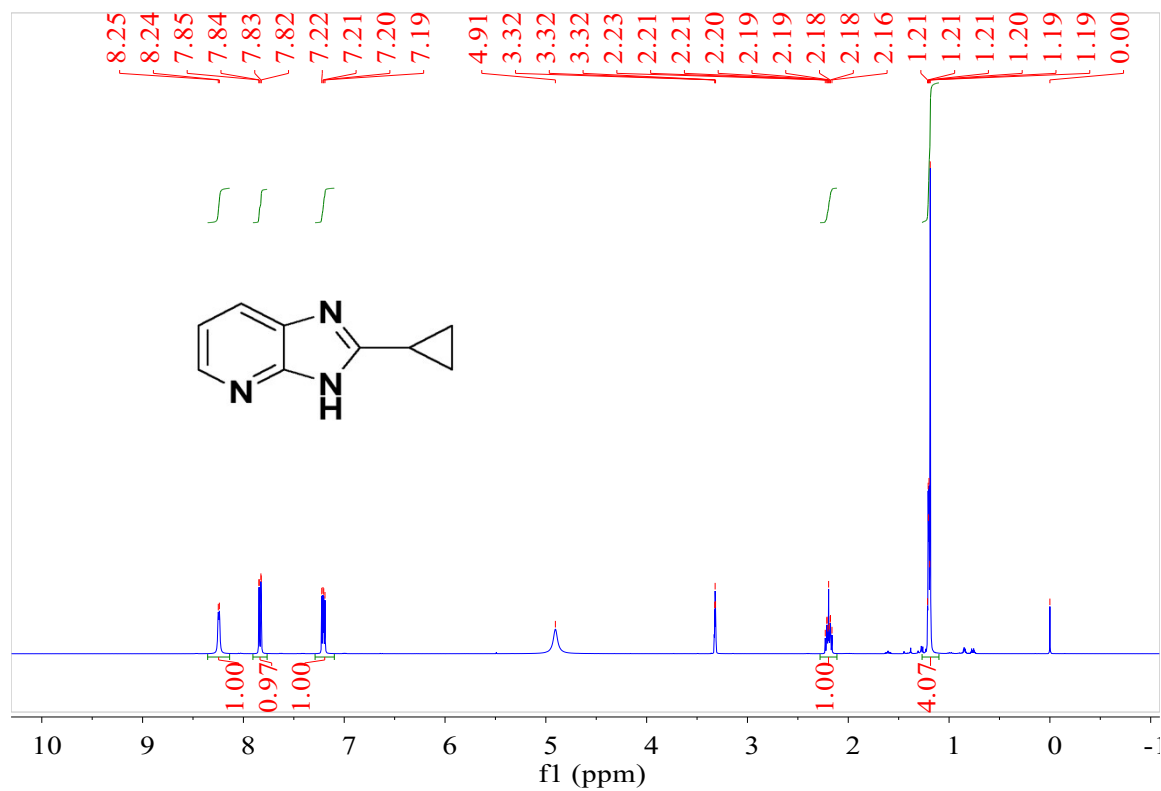


Figure S36 $^1\text{H NMR}$ of compound 2q in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 160.4, 151.6, 142.4, 130.7, 121.8, 117.5, 9.2, 8.4; HRMS (ESI):

m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{10}\text{N}_3$ 160.0869

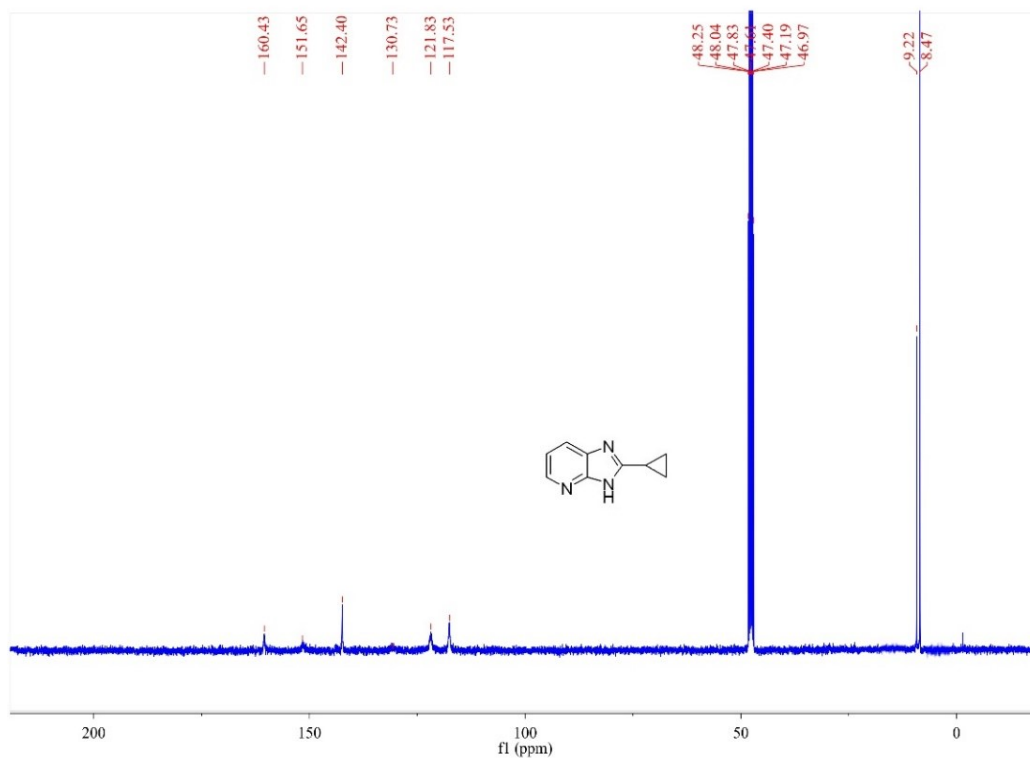
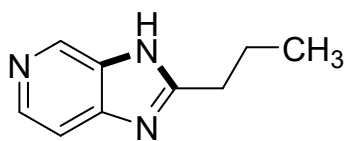


Figure S37 ^1H NMR of compound **2q** in CD_3OD

Benzimidazoles 2r



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.62 (dd, $J = 5.2, 1.2$ Hz, 1H), 8.33 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.66 (dd, $J = 8.2, 5.2$ Hz, 1H), 3.16 (t, $J = 7.6$ Hz, 2H), 1.98 (q, $J = 7.5$ Hz, 2H), 1.09 (t, $J = 7.4$ Hz, 3H).

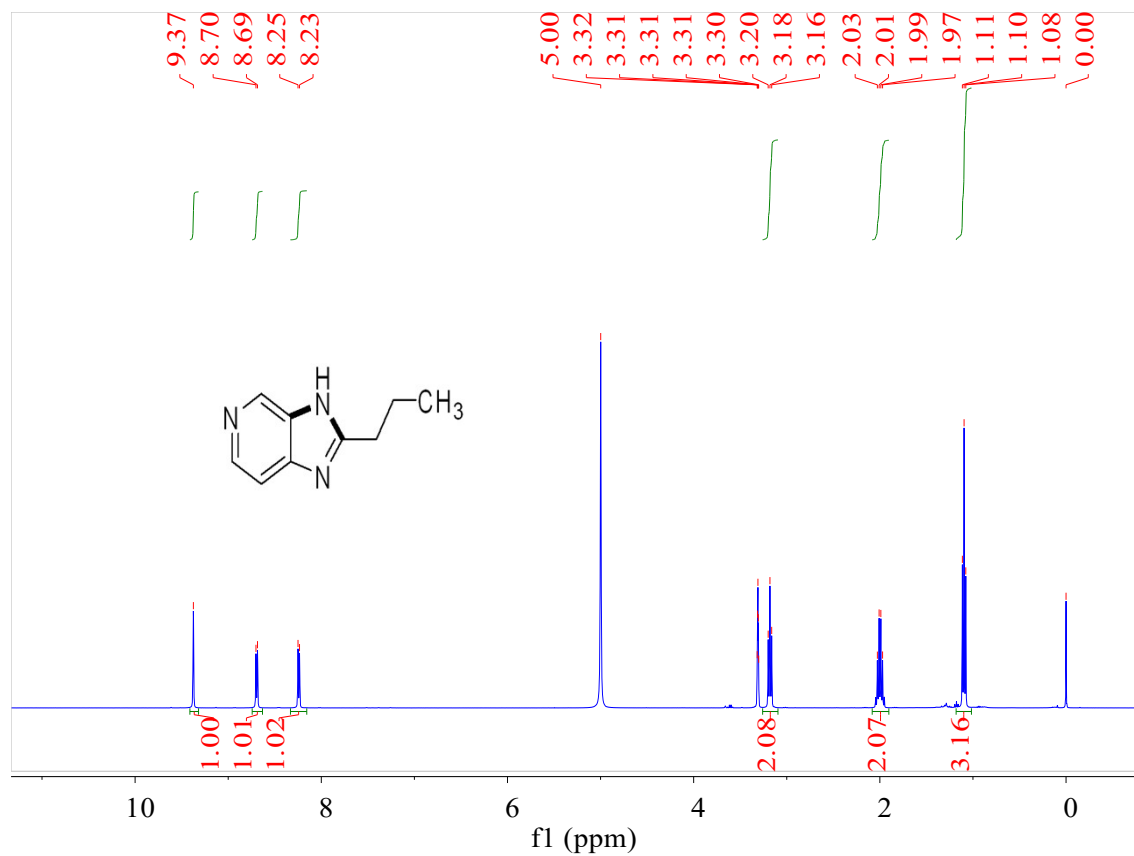


Figure S38 $^1\text{H NMR}$ of compound 2r in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 164.7, 145.0, 135.1, 134.6, 131.5, 111.2, 29.8, 20.4, 12.5; HRMS

(ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{N}_3$ 162.1026.

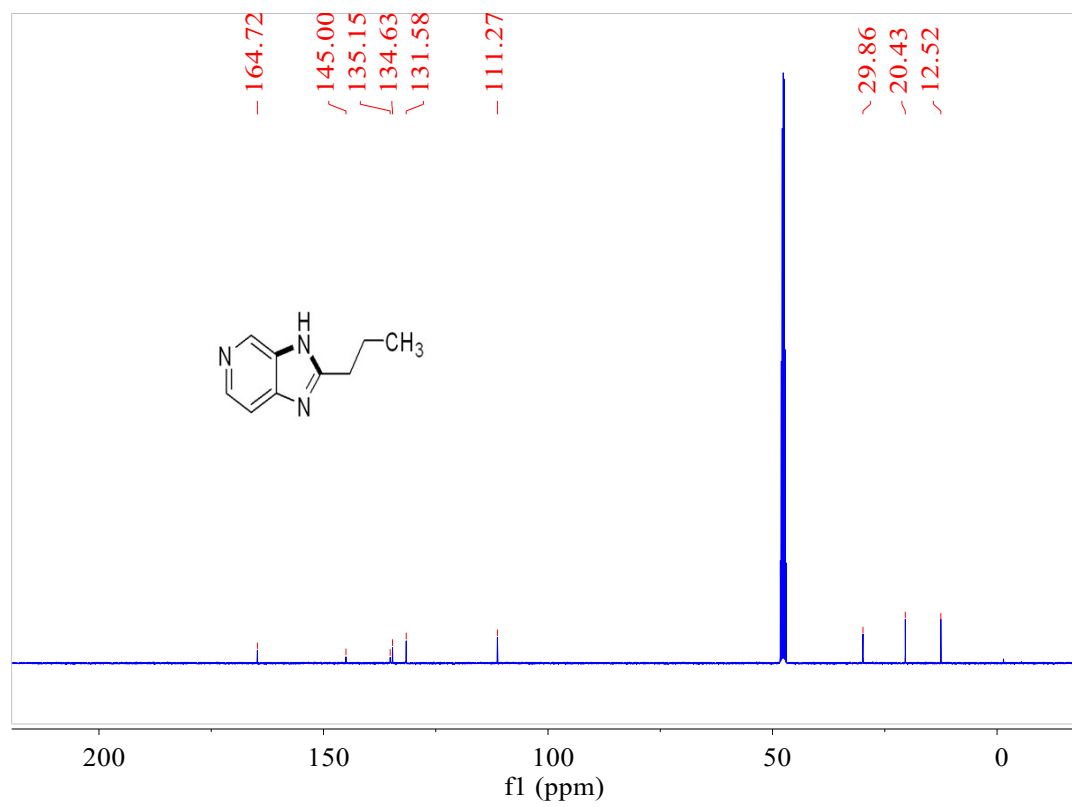
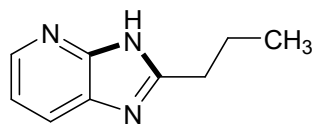


Figure S39 ^{13}C NMR of compound **2r** in CD_3OD

Benzimidazoles 2s



^1H NMR (400 MHz, CD_3OD) δ 8.62 (dd, $J = 5.2, 1.2$ Hz, 1H), 8.33 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.66 (dd, $J = 8.2, 5.2$ Hz, 1H), 3.16 (t, $J = 7.6$ Hz, 2H), 1.98 (q, $J = 7.5$ Hz, 2H), 1.09 (t, $J = 7.4$ Hz, 3H).

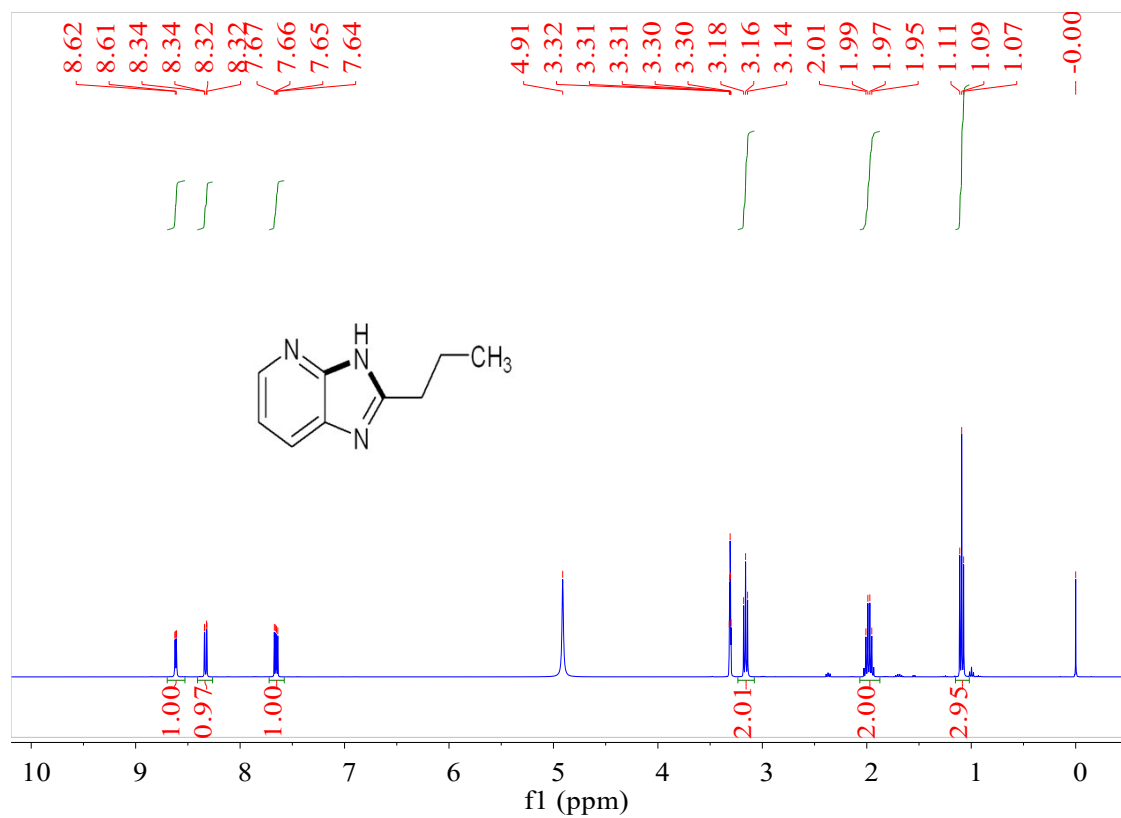


Figure S40 ^1H NMR of compound 2s in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 160.5, 147.0, 144.8, 127.5, 125.6, 121.8, 30.4, 21.7, 13.8; HRMS

(ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{11}\text{N}_3$ 235.1077, found: 162.1023.

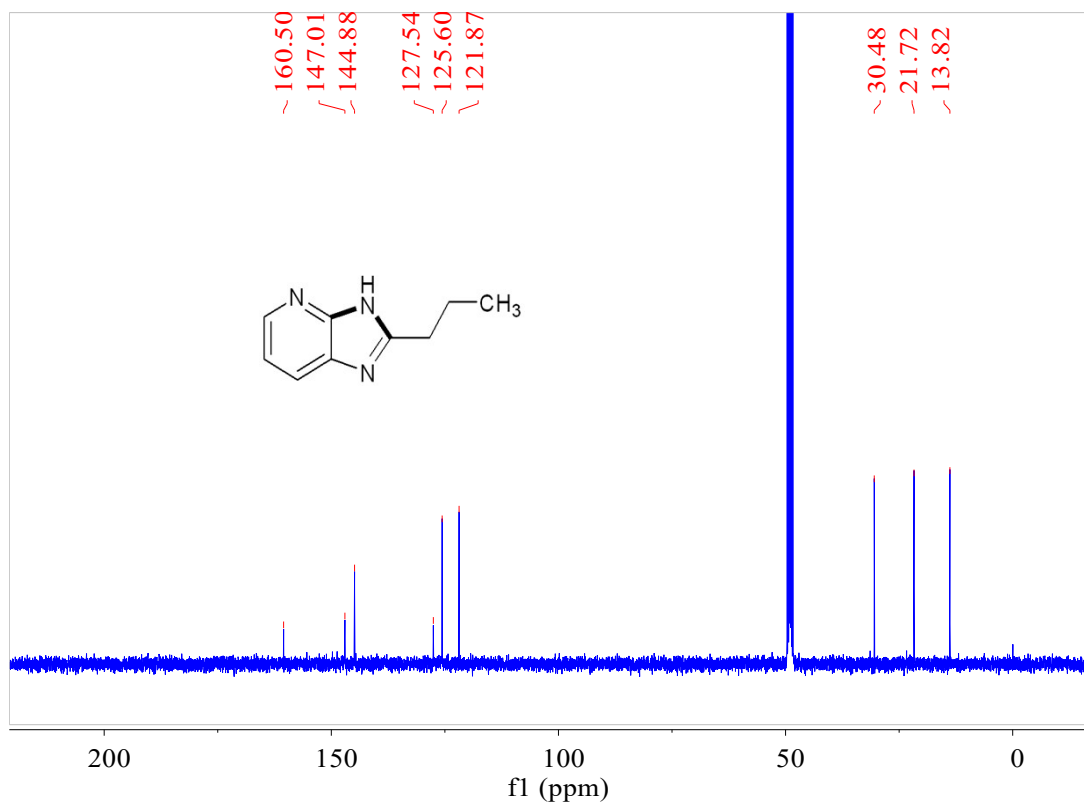
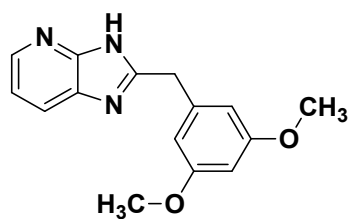


Figure S41 ^{13}C NMR of compound **2s** in CD_3OD

Benzimidazoles 2t



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.30 (s, 1H), 7.91 (s, 1H), 7.25 (dd, $J = 7.9, 4.9$ Hz, 1H), 6.51 (d, $J = 1.7$ Hz, 2H), 6.37 (s, 1H), 4.86 (s, 3H), 4.19 (s, 2H), 3.74 (s, 6H), 3.31 (s, 3H).

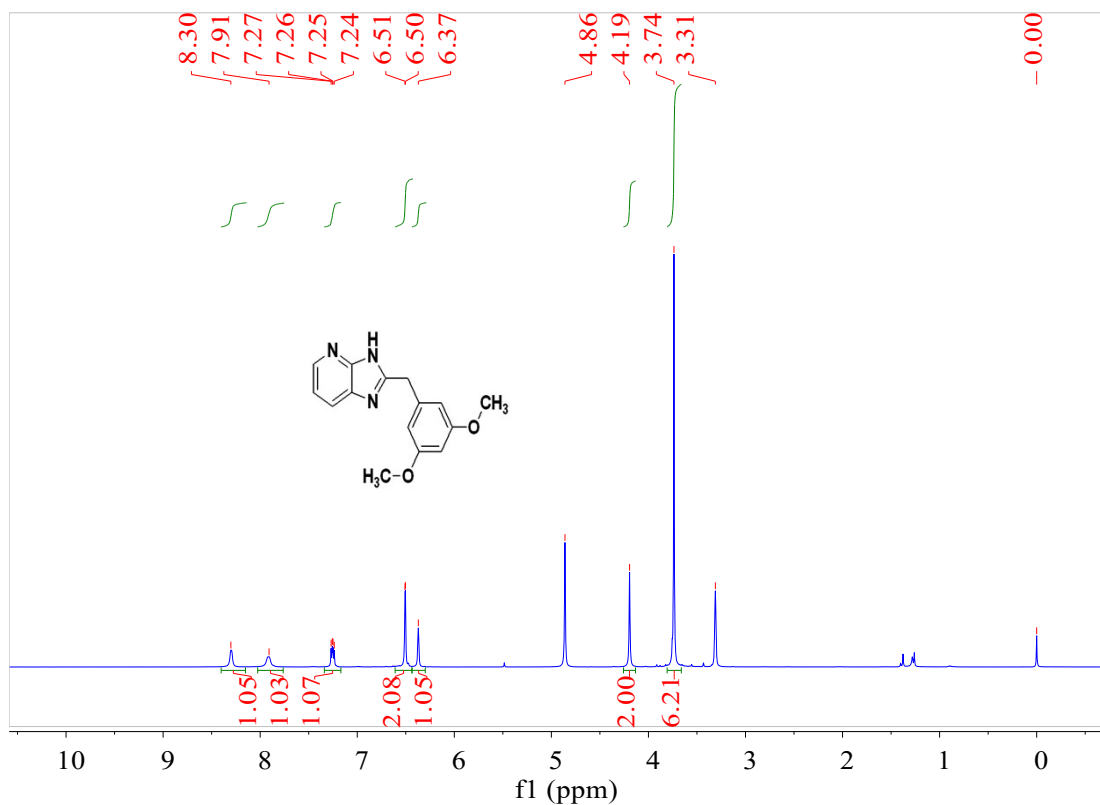


Figure S42 $^1\text{H NMR}$ of compound **2t** in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 162.7, 144.5, 139.6, 119.4, 107.9, 100.0, 55.7, 36.6. HRMS (ESI):
 m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2$ 270.1237.

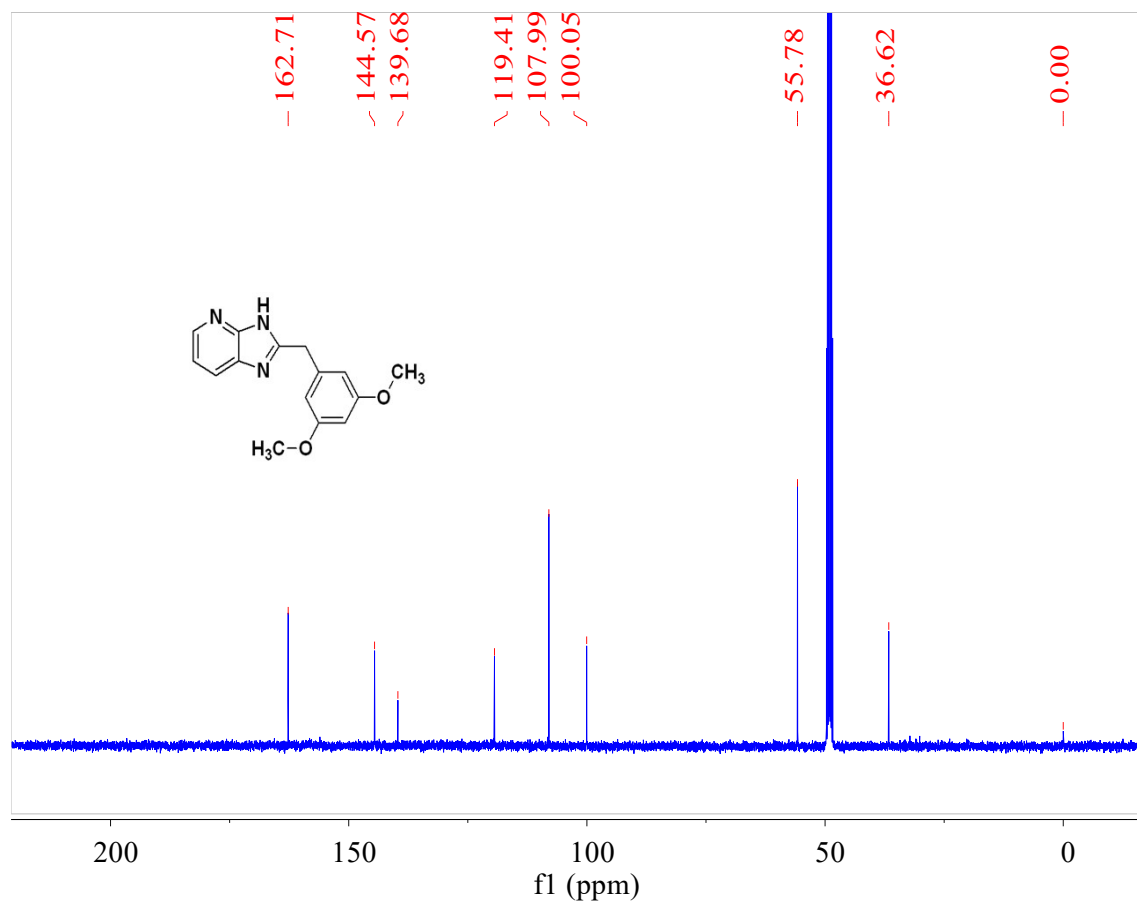
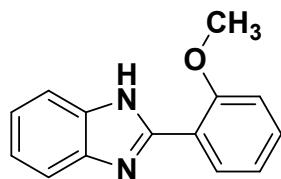


Figure S43 ^{13}C NMR of compound **2t** in CD_3OD

Benzimidazoles 2u



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.24 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.64 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.47 (ddd, $J = 8.7, 7.5, 1.7$ Hz, 1H), 7.24 (dd, $J = 6.1, 3.2$ Hz, 2H), 7.19 (d, $J = 8.3$ Hz, 1H), 7.15 – 7.08 (m, 1H), 4.05 (s, 3H).

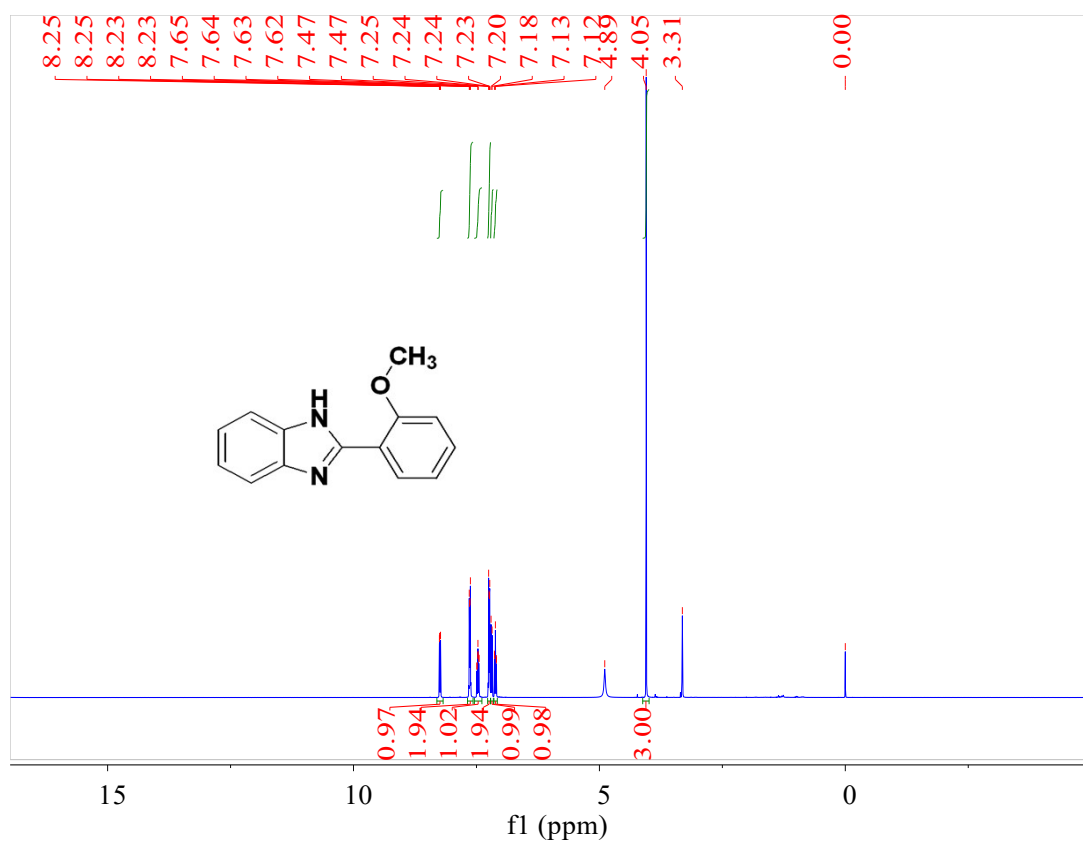


Figure S44 $^1\text{H NMR}$ of compound 2u in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 157.3, 149.6, 138.1, 131.4, 129.5, 122.2, 120.7, 117.5, 114.4, 111.4, 54.8. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}$ 225.1022

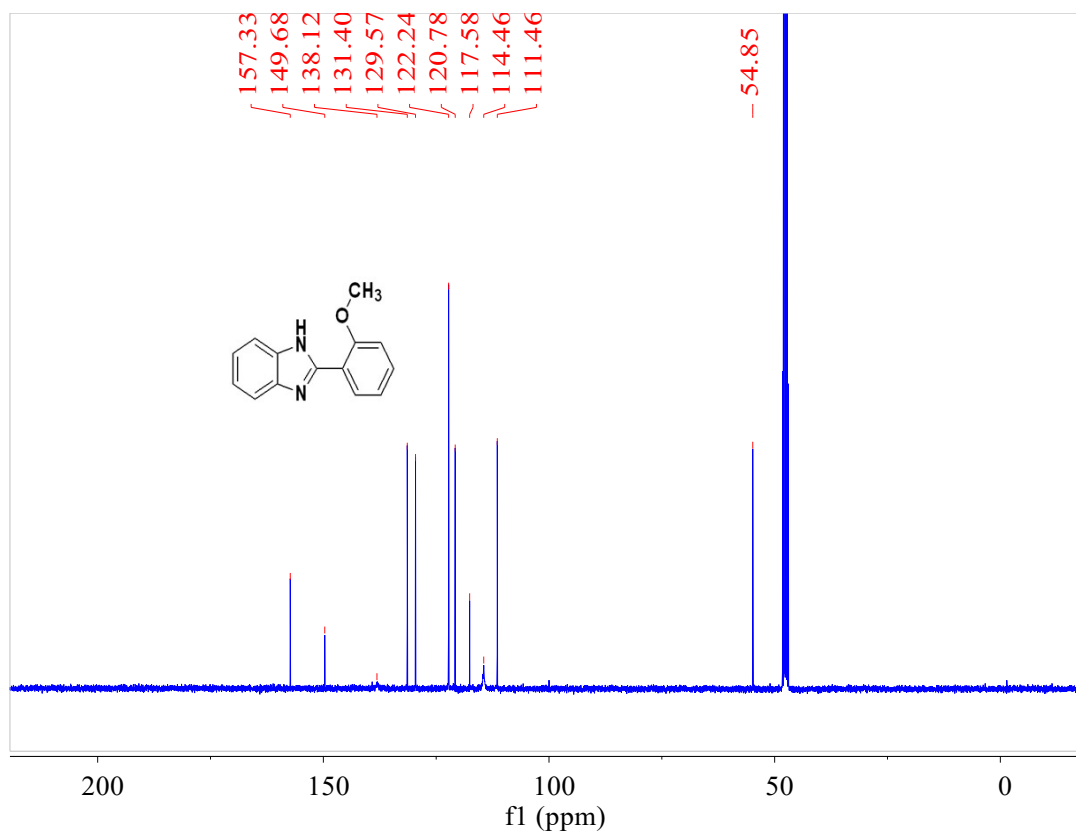
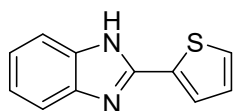


Figure S45 ^{13}C NMR of compound **2u** in CD_3OD

Benzimidazoles 2v



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.20 (dd, $J = 3.9, 1.1$ Hz, 1H), 8.11 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.78 (dt, $J = 6.8, 3.4$ Hz, 2H), 7.60 (dt, $J = 6.2, 3.4$ Hz, 2H), 7.43 (dd, $J = 4.9, 3.9$ Hz, 1H).

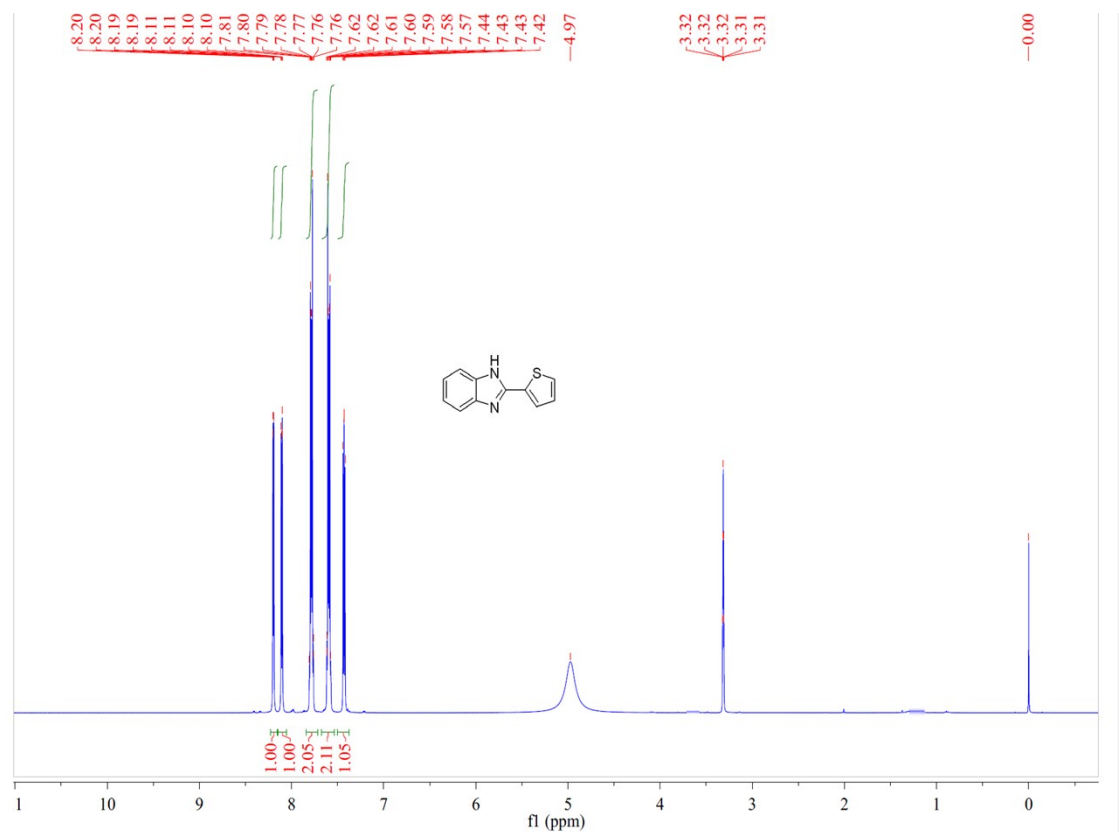


Figure S46 $^1\text{H NMR}$ of compound 2v in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 145.8, 135.5, 134.5, 132.7, 130.6, 127.8, 124.9, 114.7. HRMS

(ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{S}_2$ 201.0481

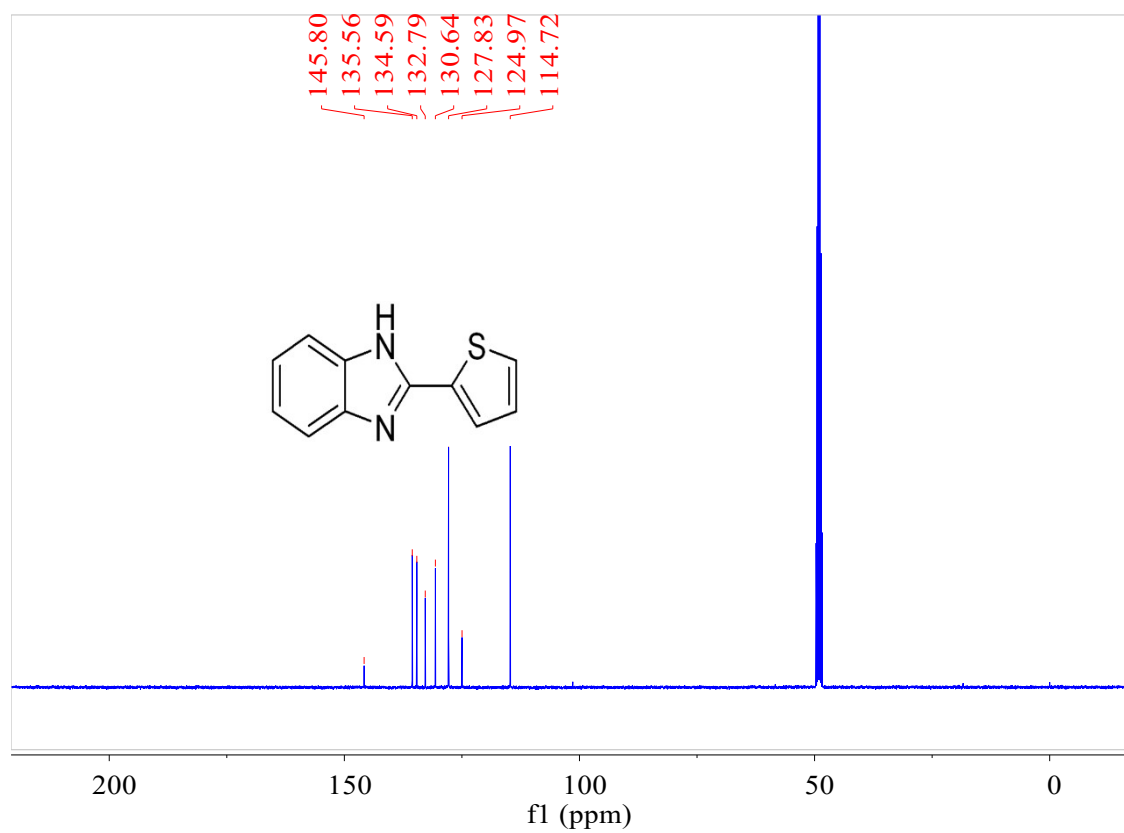
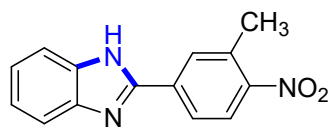


Figure S47 ^{13}C NMR of compound **2v** in Methano CD_3OD

Benzimidazoles 2w



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 13.33 (s, 1H), 8.31 (s, 1H), 8.25 – 8.16 (m, 2H), 7.66 (dd, $J = 5.9$, 3.2 Hz, 2H), 7.32 – 7.23 (m, 2H), 2.64 (s, 3H)

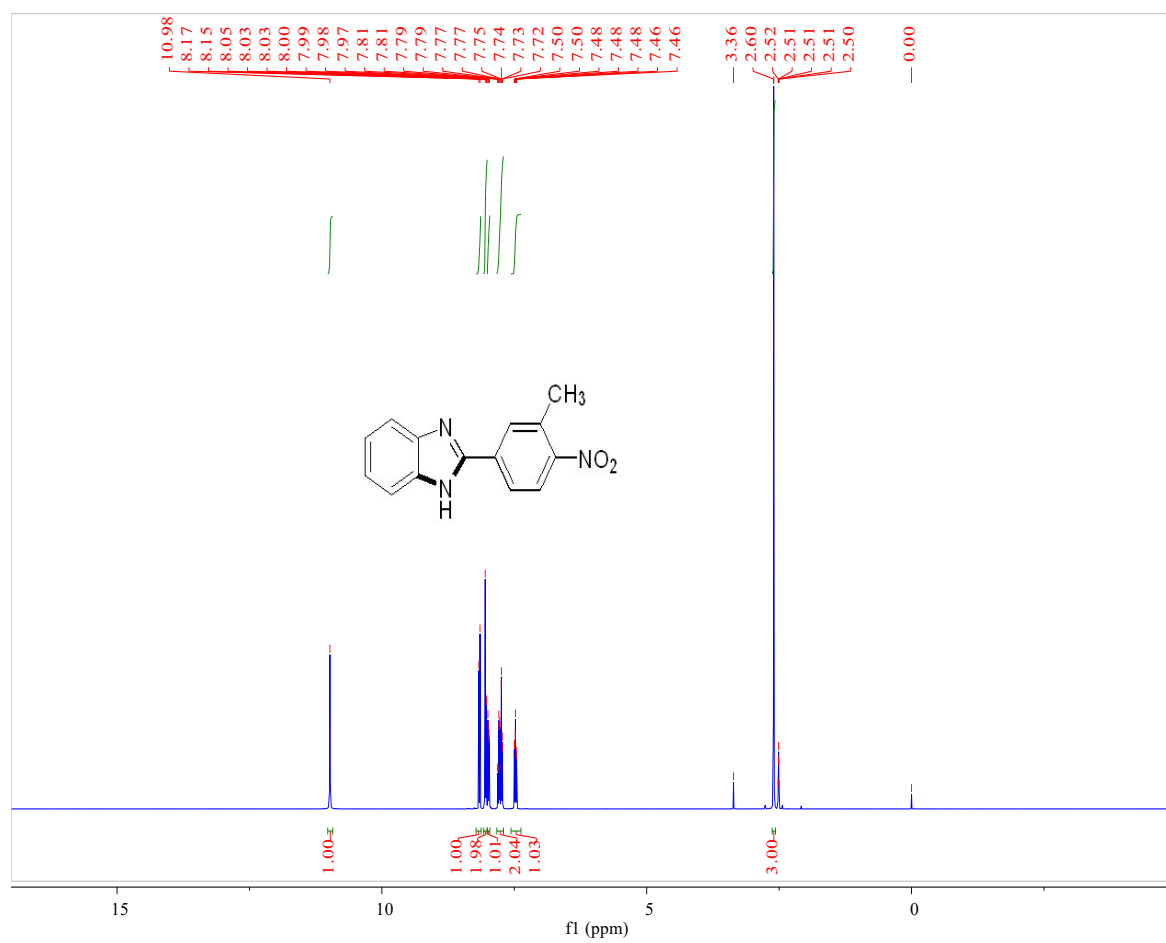


Figure S48 $^1\text{H NMR}$ of compound 2w in $\text{DMSO-}d_6$

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 149.4, 149.3, 139.9, 134.7, 134.1, 130.8, 130.7, 125.8, 125.3, 123.2, 115.9, 20.3; HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2$ 254.0924, found 254.0919.

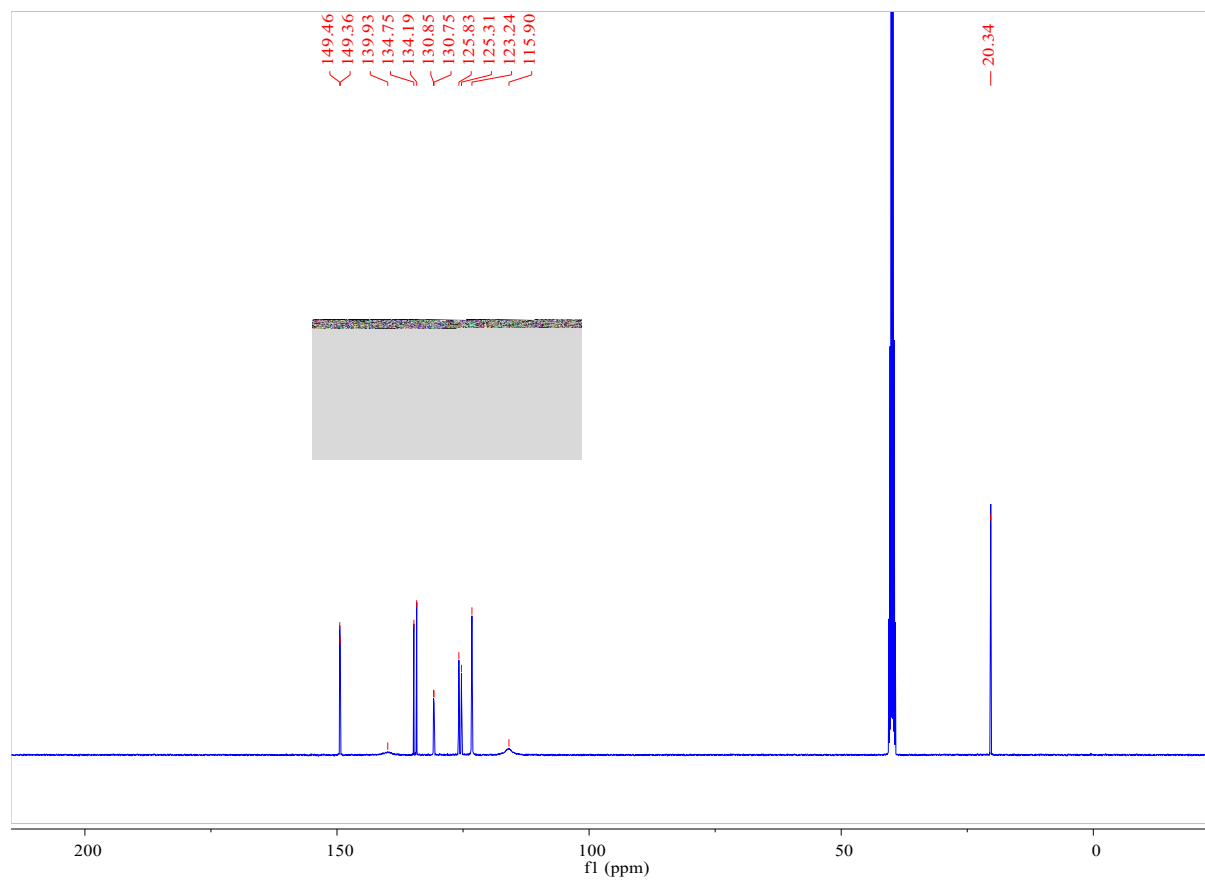
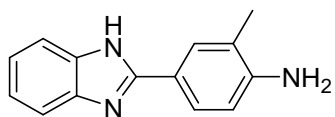


Figure S49 ^{13}C NMR of compound **2w** in $\text{DMSO-}d_6$

Benzimidazoles 2x



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 12.40 (s, 1H), 7.81 – 7.66 (m, 3H), 7.47 (s, 2H), 7.10 (dd, $J = 5.9$, 3.2 Hz, 2H), 6.69 (d, $J = 8.3$ Hz, 1H), 5.35 (s, 2H), 2.14 (s, 3H).

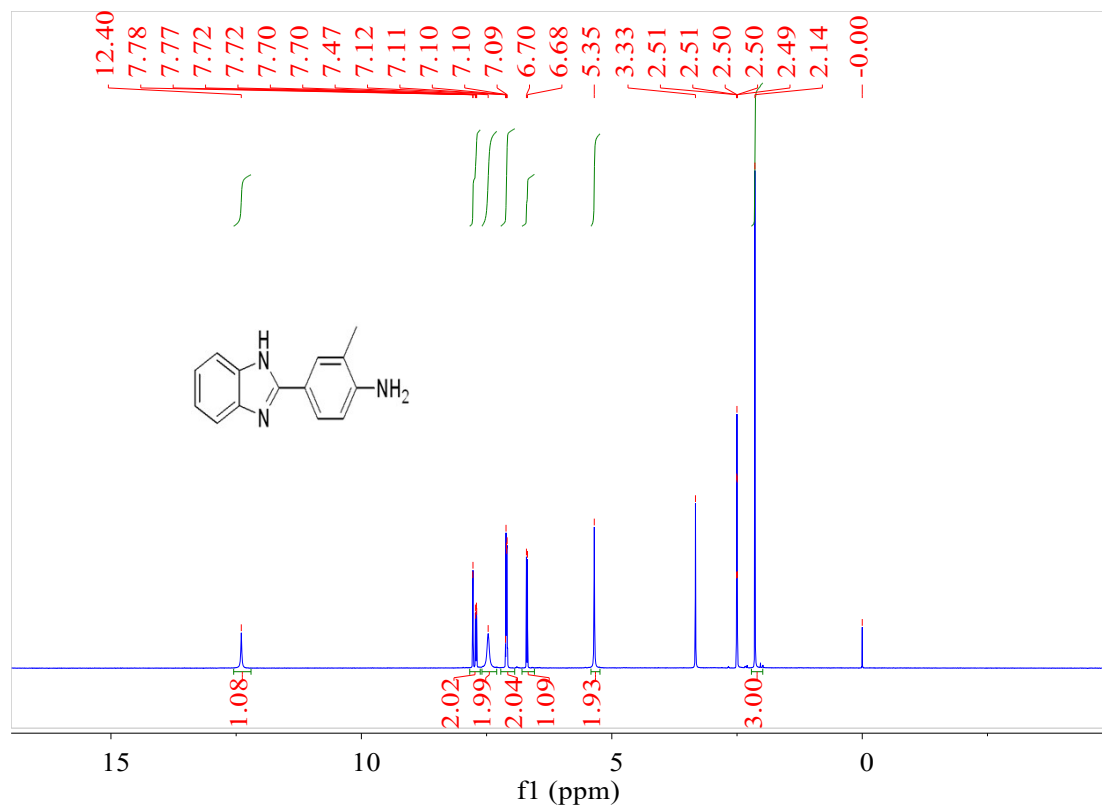


Figure S50 $^1\text{H NMR}$ of compound 2x in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 154.7, 148.7, 143.1, 137.1, 131.6, 128.3, 121.9, 121.9, 121.2, 118.77, 117.6, 113.8, 110.4, 32.2, 17.92. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{N}_3$ 224.1128

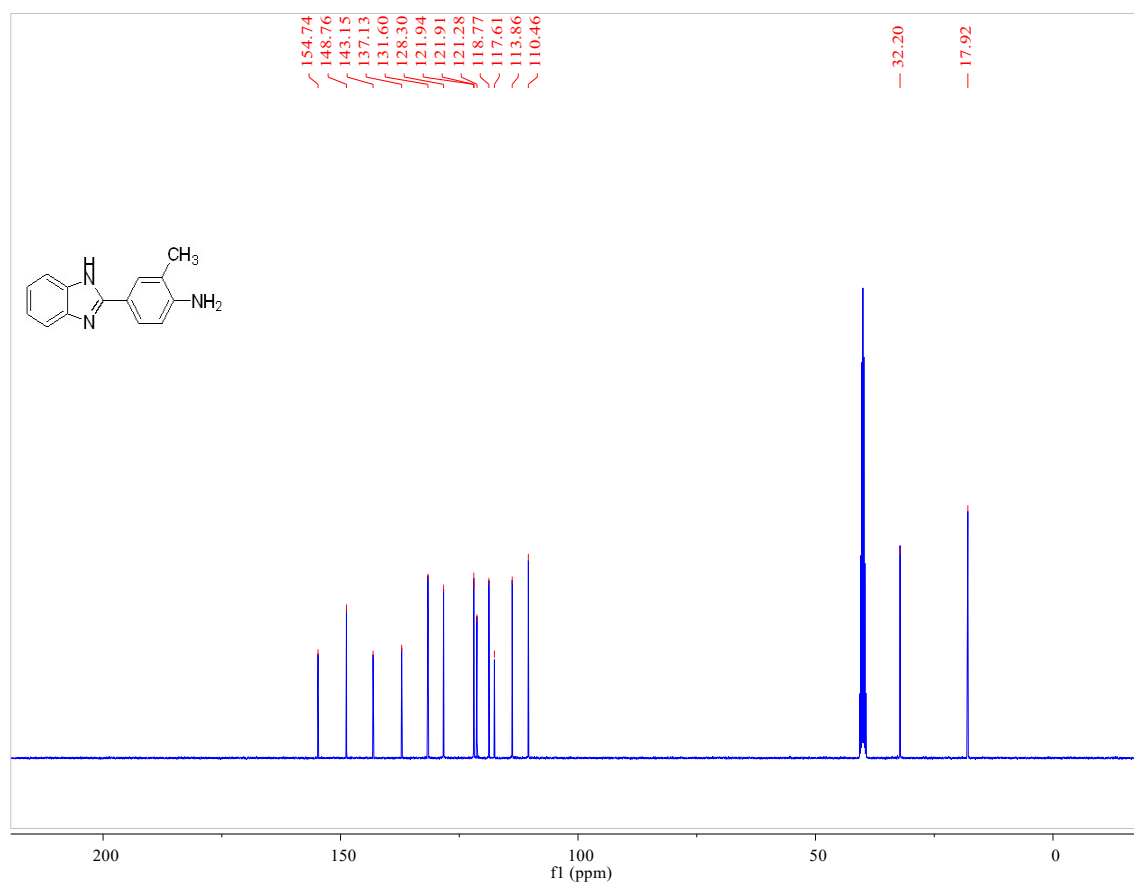
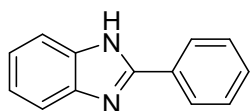


Figure S51 ^{13}C NMR of compound **2x** in $\text{DMSO-}d_6$

Benzimidazoles 2y



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 12.90 (s, 1H), 8.30 – 8.03 (m, 2H), 7.67 – 7.45 (m, 5H), 7.33 – 6.96 (m, 2H).

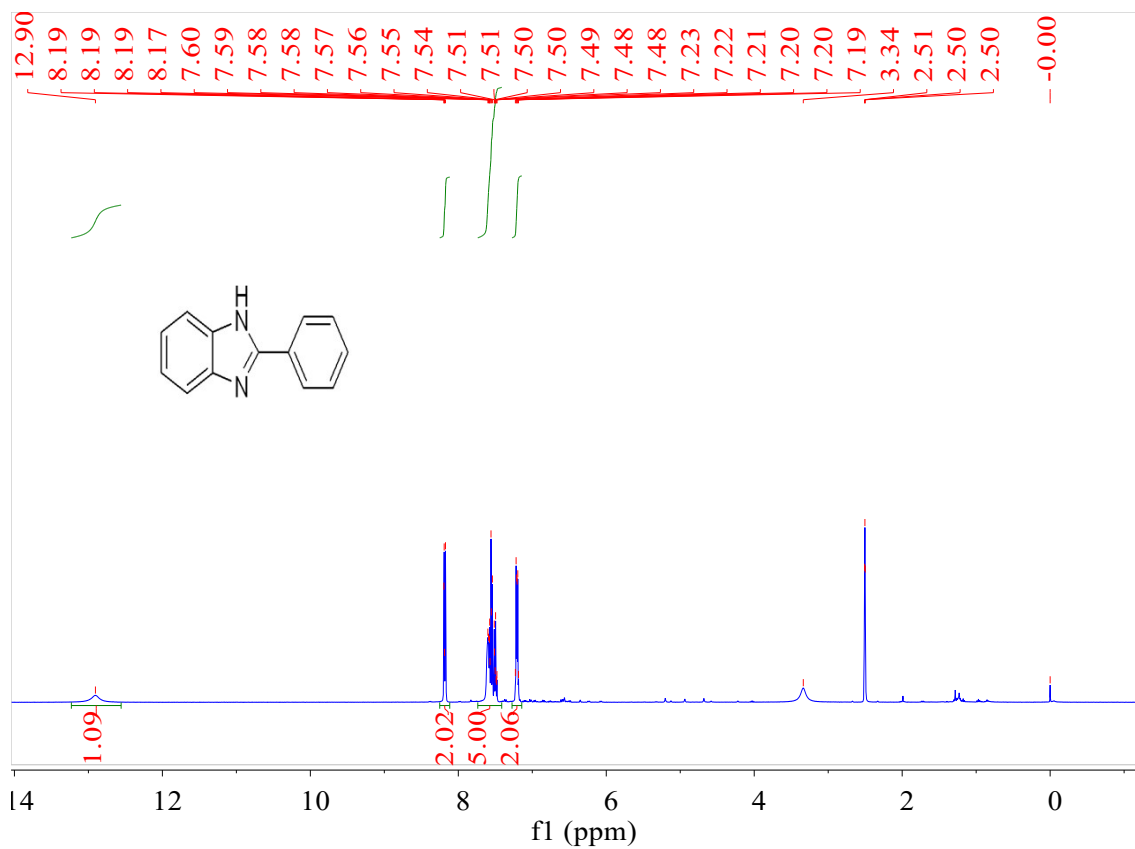


Figure S52 $^1\text{H NMR}$ of compound 2y in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 151.6, 130.6, 130.3, 129.4, 126.8, 122.5; HRMS (ESI): m/z [M + H] $^+$ calcd for $\text{C}_{13}\text{H}_{11}\text{N}_2$ 195.0917

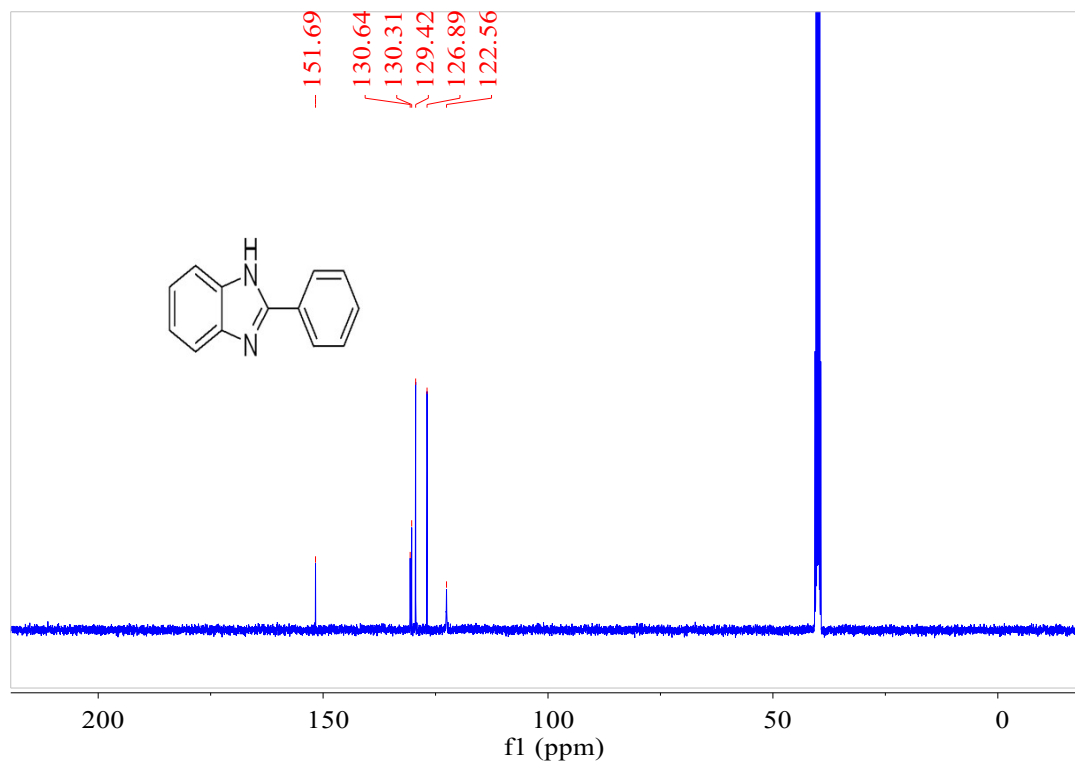
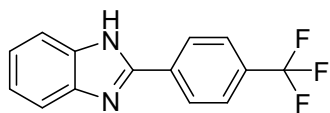


Figure S53 ^{13}C NMR of compound 2y in DMSO- d_6

Benzimidazoles 2z



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.36 (d, $J = 8.2$ Hz, 2H), 8.08 (d, $J = 8.3$ Hz, 2H), 7.90 (dd, $J = 6.2$, 3.2 Hz, 2H), 7.68 (dd, $J = 6.2$, 3.1 Hz, 2H).

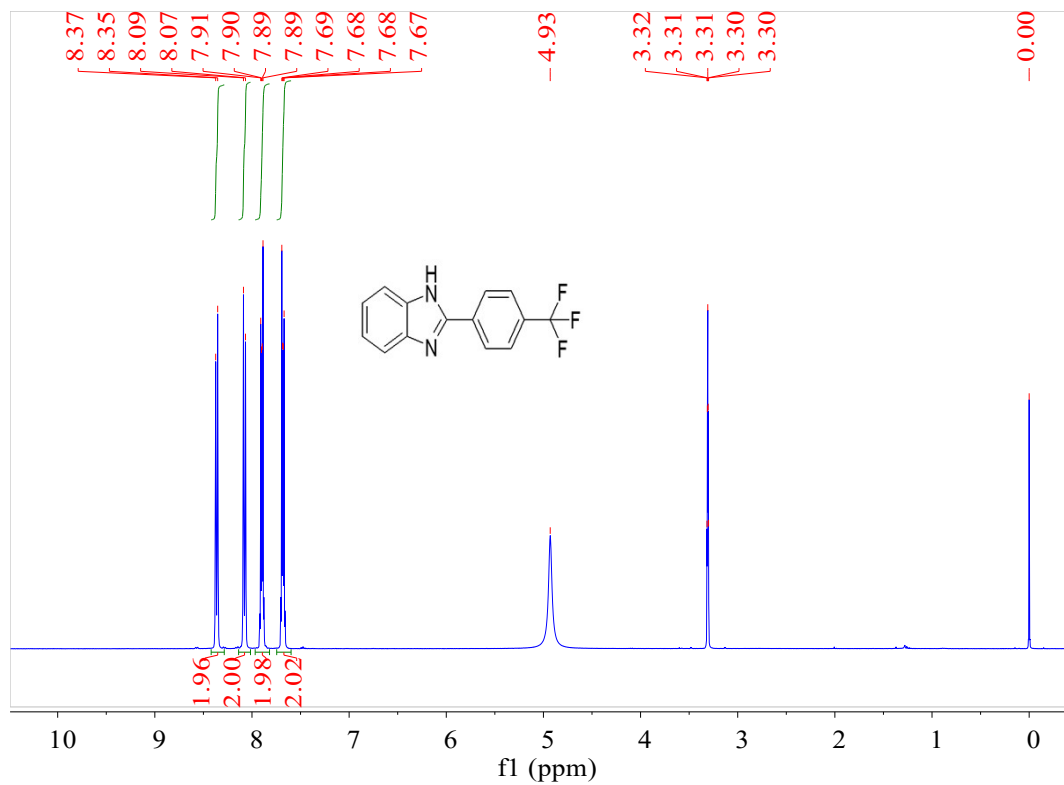


Figure S54 $^1\text{H NMR}$ of compound 2z in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 149.3, 135.9, 135.6, 133.2, 130.1, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 126.2, 123.5, 115.2, HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_2$ 263.0791

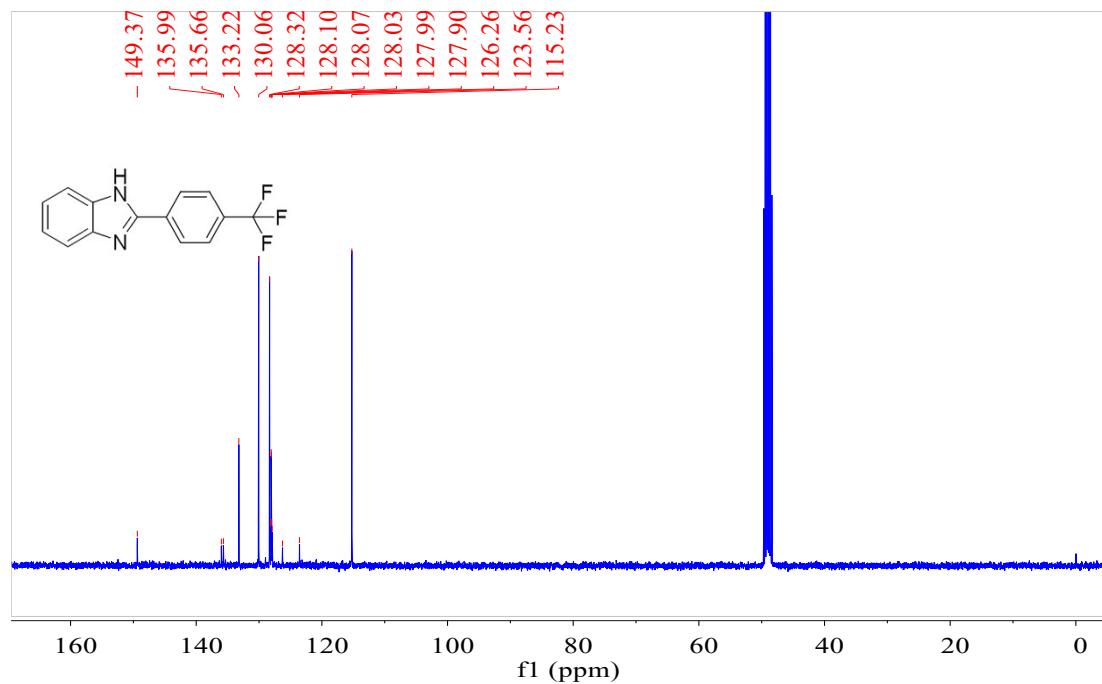


Figure S55 ^{13}C NMR of compound **2z** in CD_3OD

^{19}F NMR (377 MHz, CD_3OD) δ -62.90, -63.13, -63.61.

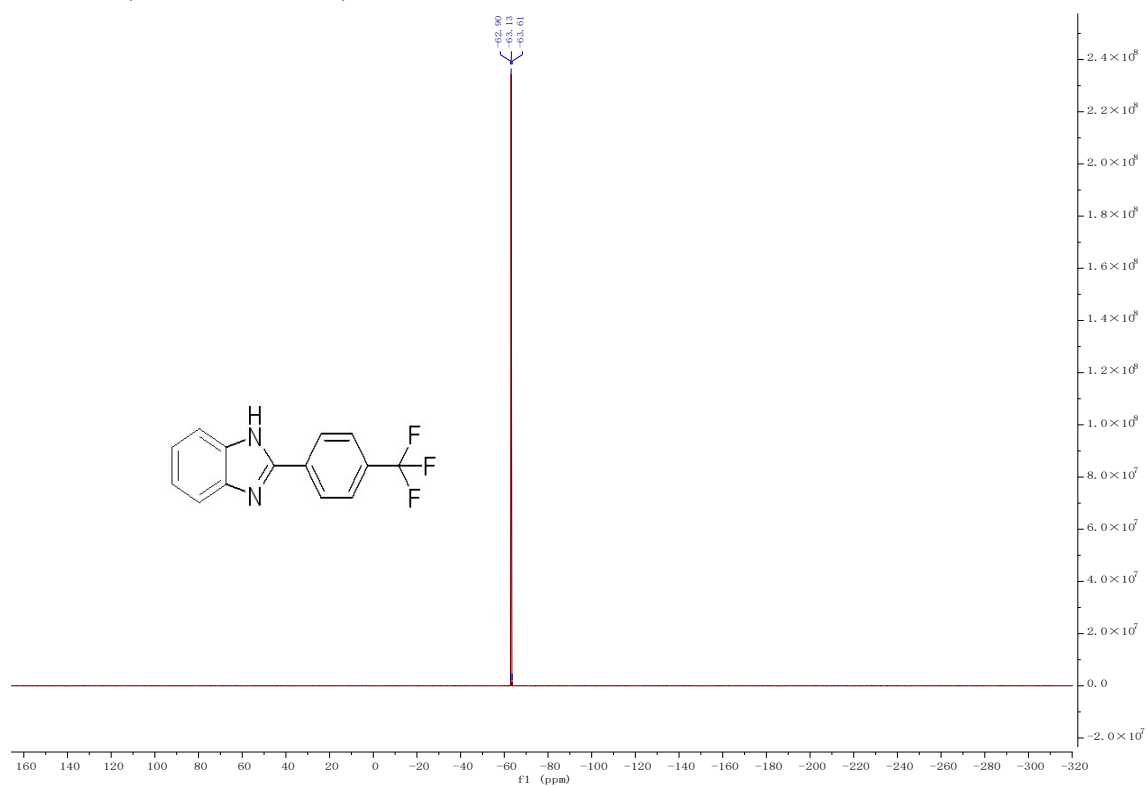
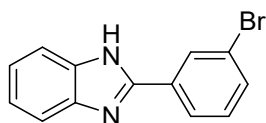


Figure S56 ^{19}F NMR of compound **2z** in CD_3OD

Benzimidazoles **2aa**



^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 13.33 – 12.82 (s, 1H), 8.42 – 8.33 (t, $J = 1.7$ Hz, 1H), 8.22 – 8.14 (dt, $J = 7.8, 1.1$ Hz, 1H), 7.74 – 7.68 (ddd, $J = 8.0, 1.9, 0.9$ Hz, 1H), 7.66 – 7.57 (s, 2H), 7.57 – 7.47 (t, $J = 7.9$ Hz, 1H), 7.30 – 7.15 (m, 2H).

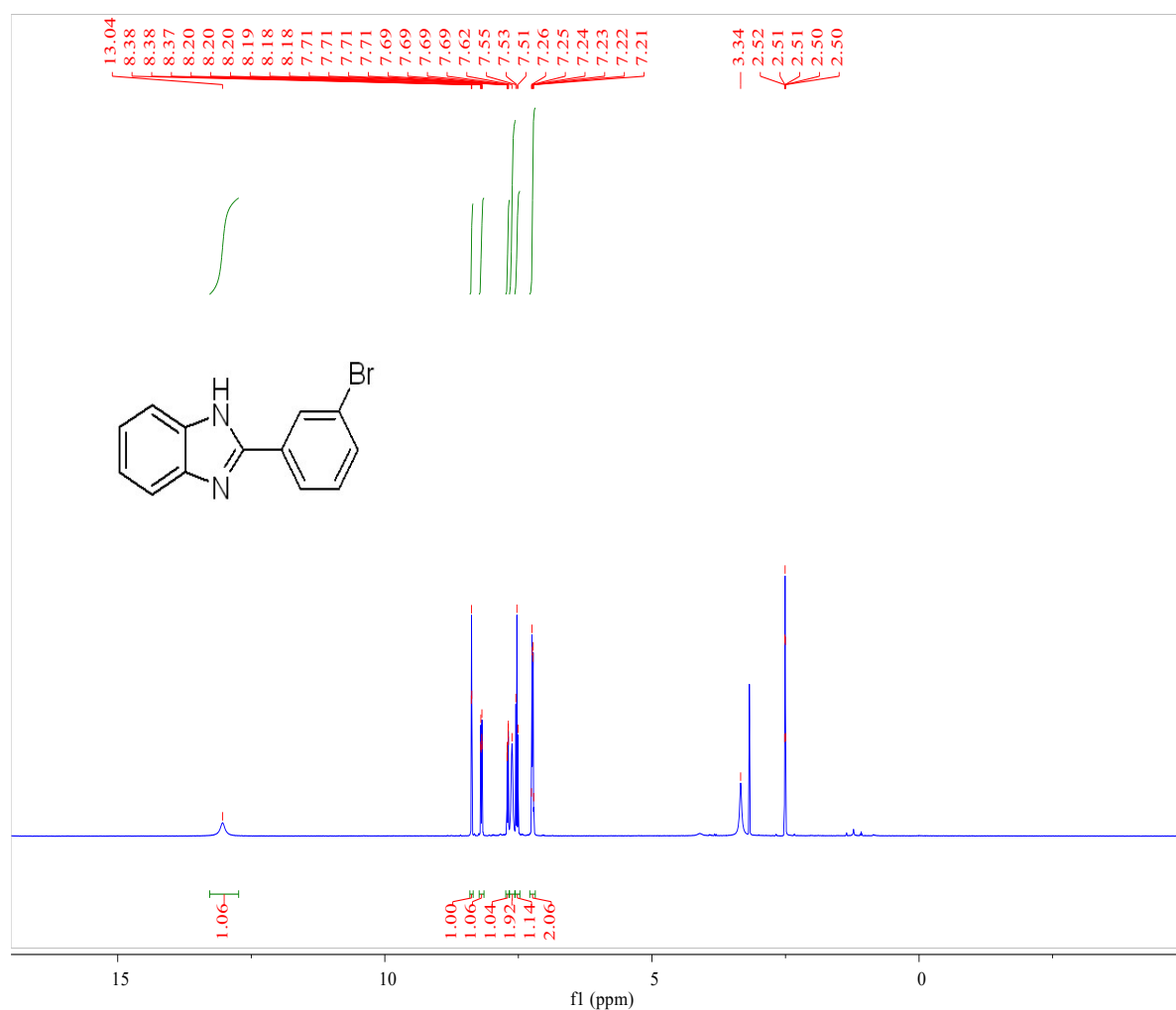


Figure S57 ^1H NMR of compound **2aa** in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 150.1, 132.9, 132.8, 131.6, 129.3, 125.8, 122.7, HRMS (ESI): m/z

$[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{BrN}_2$ 273.0022

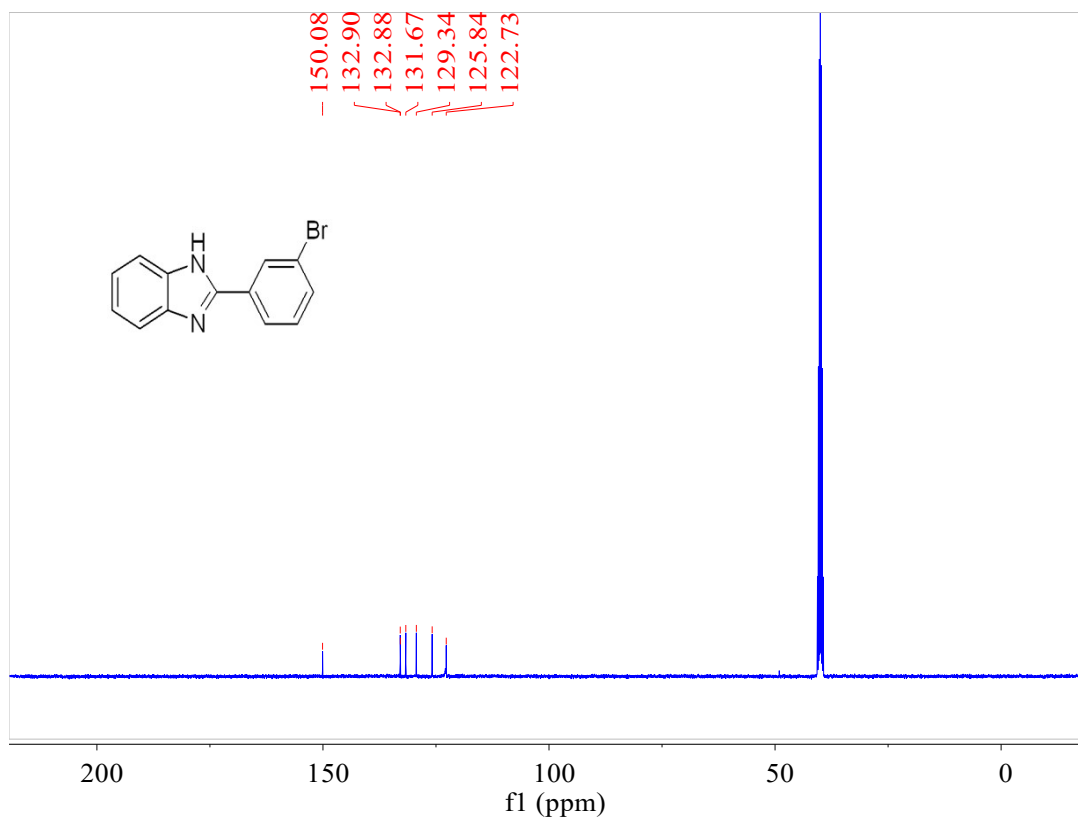
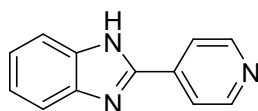


Figure S58 ^{13}C NMR of compound 2aa in $\text{DMSO-}d_6$

Benzimidazoles 2bb



$^1\text{H NMR}$ (400 MHz, CD_3OD) δ 8.69 (d, $J = 5.0$ Hz, 2H), 8.12 – 7.96 (m, 2H), 7.64 (dd, $J = 5.9, 3.2$ Hz, 2H), 7.40 – 7.22 (m, 2H).

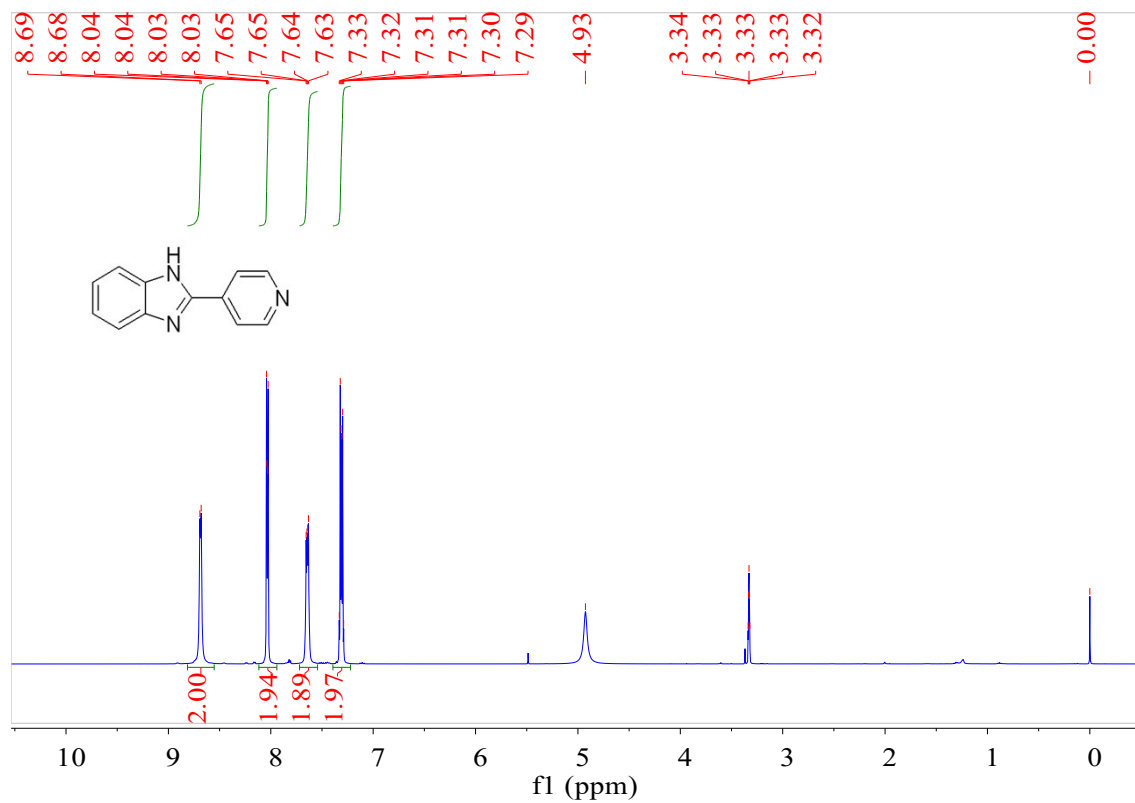


Figure S59 $^1\text{H NMR}$ of compound **2bb** in CD_3OD

^{13}C NMR (101 MHz, CD_3OD) δ 151.1, 150.0, 139.2, 124.8, 122.1, 116.6, 112.7, HRMS (ESI): m/z

$[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{10}\text{N}_3$ 196.0896

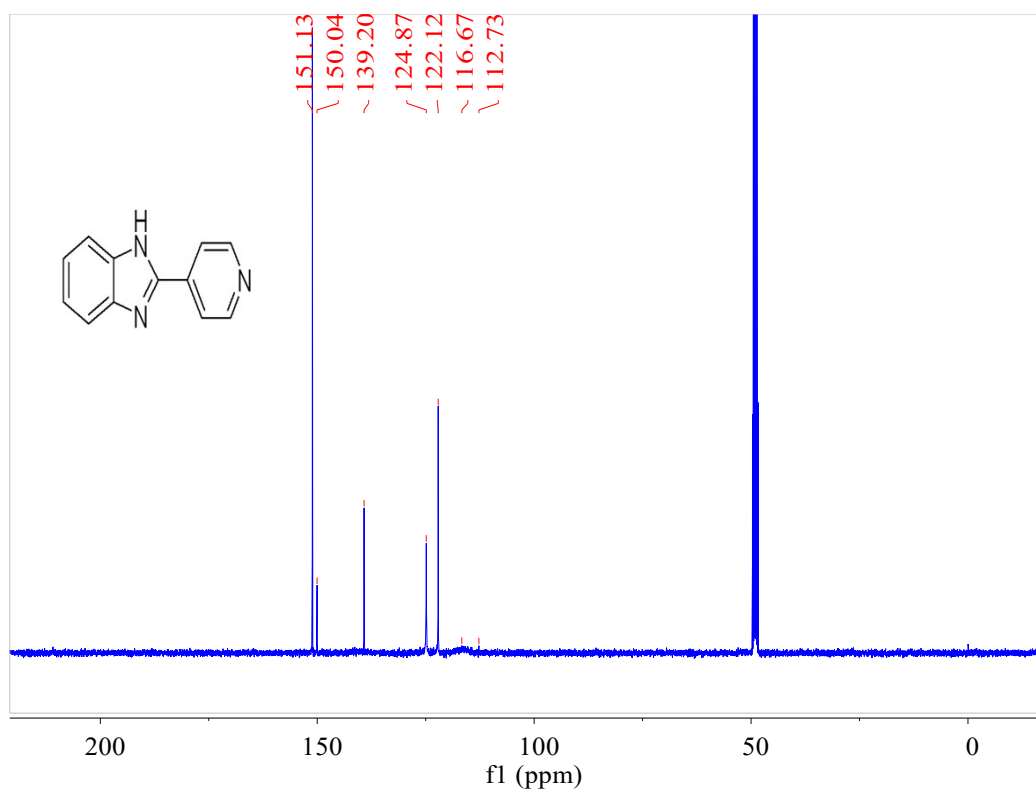
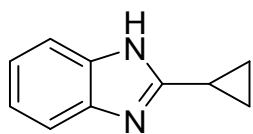


Figure S60 ^{13}C NMR of compound **2bb** in CD_3OD

Benzimidazoles 2cc



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.19 (dd, $J = 6.0, 3.2$ Hz, 2H), 2.16 – 1.99 (m, 1H), 1.35 – 1.19 (m, 2H), 1.18 – 0.97 (m, 2H).

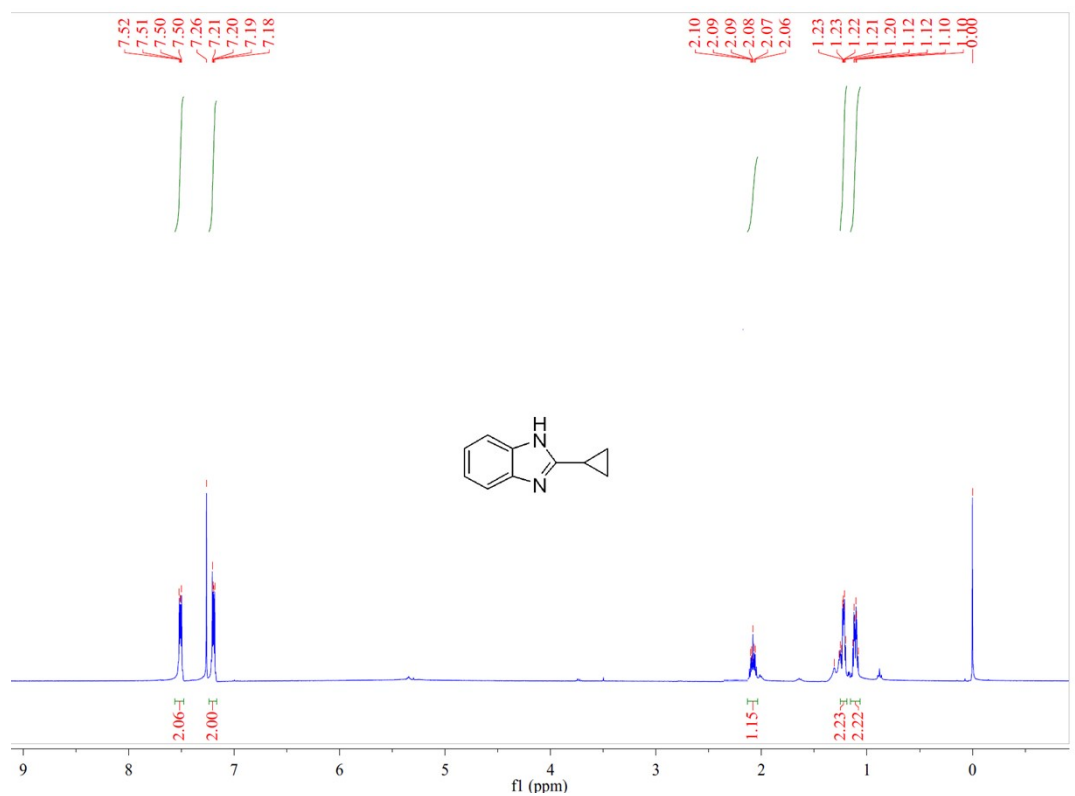


Figure S61 $^1\text{H NMR}$ of compound 2cc in CDCl_3

^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 135.5, 122.2, 114.3, 9.6, 8.8, -0.01. HRMS (ESI): m/z [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2$ 159.0917.

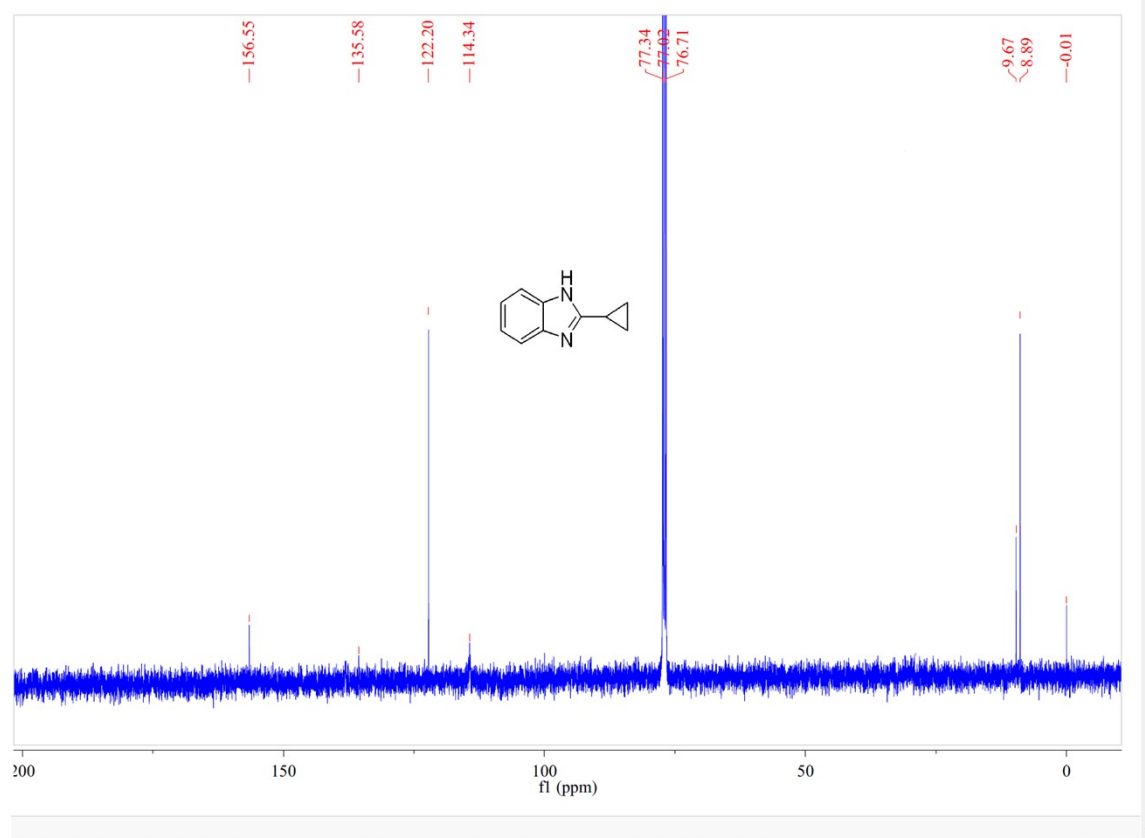
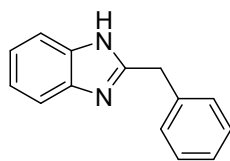


Figure S62 ^{13}C NMR of compound **2cc** in CDCl_3

Benzazol



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 15.53 (s, 1H), 7.77 (dt, $J = 6.7, 3.4$ Hz, 2H), 7.62 – 7.46 (m, 4H), 7.44– 6.86 (m, 3H), 4.57 (s, 2H).

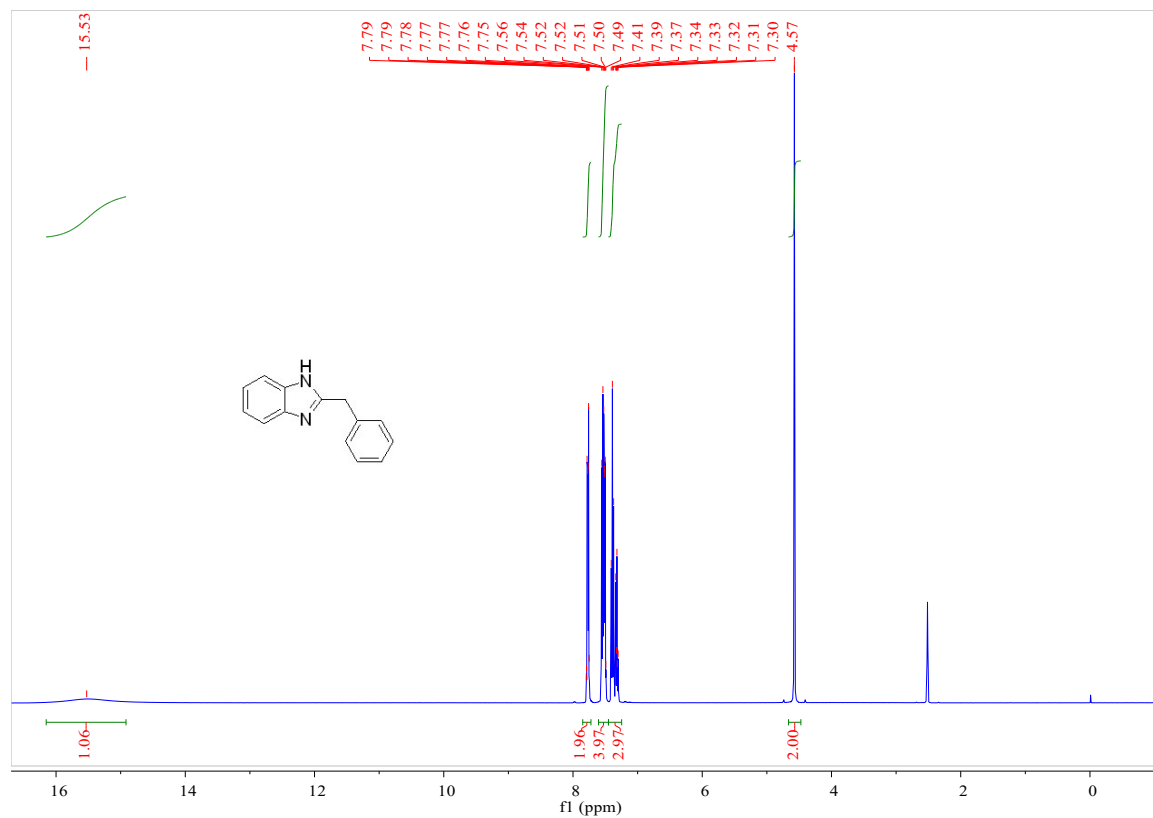


Figure S63 $^1\text{H NMR}$ of benzazol in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 152.5, 134.0, 130.7, 129.1, 128.9, 127.6, 125.5, 113.8, 31.8.

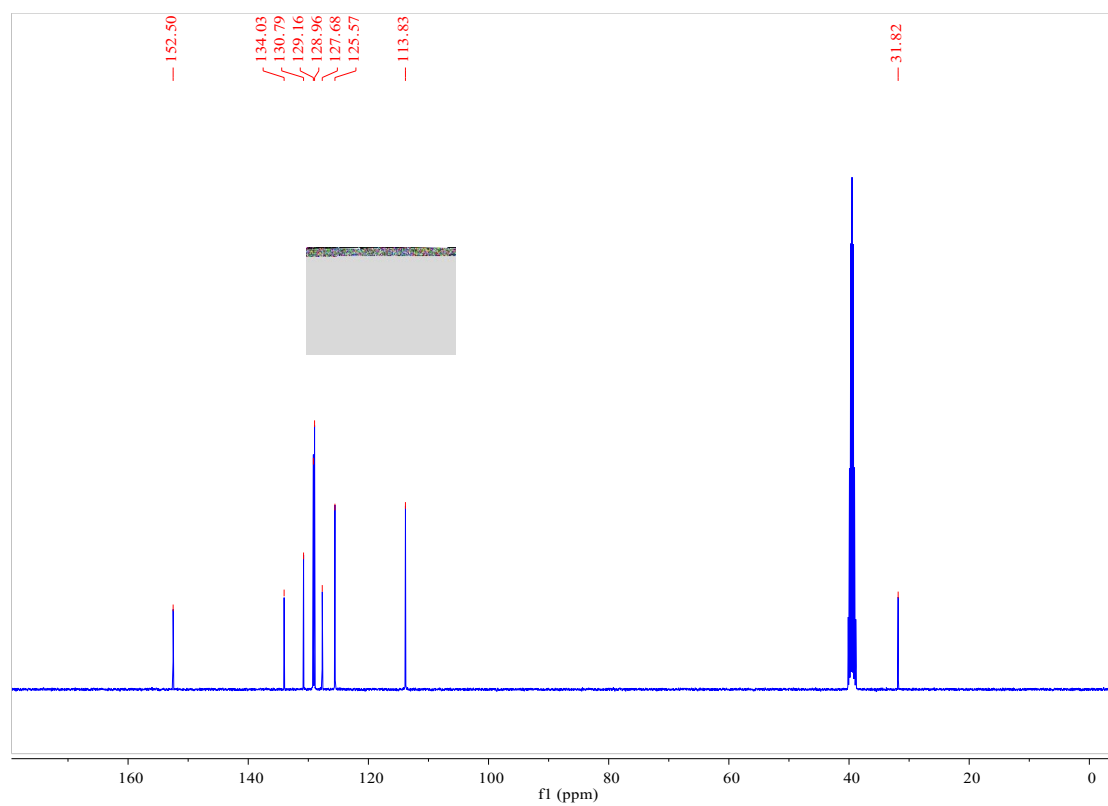
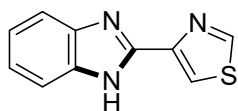


Figure S64 ^{13}C NMR of bendazol in $\text{DMSO-}d_6$

Thiabendazole



^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 13.00 (s, 1H), 9.34 (d, $J = 2.0$ Hz, 1H), 8.47 (d, $J = 1.9$ Hz, 1H), 7.61 (dd, $J = 55.4, 7.1$ Hz, 2H), 7.23 (dt, $J = 8.6, 4.9$ Hz, 2H).

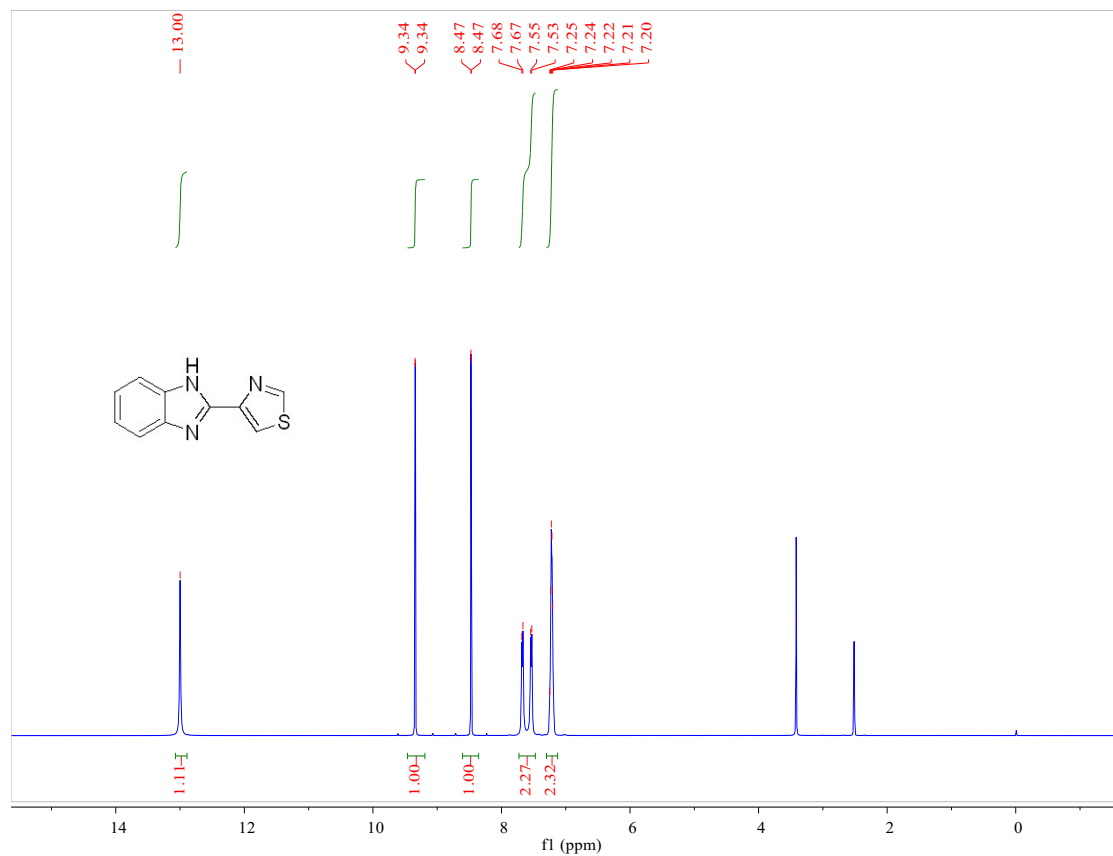


Figure S65 ^1H NMR of thiabendazole in $\text{DMSO-}d_6$

^{13}C NMR (101 MHz, DMSO) δ 155.5, 147.0, 146.9, 143.7, 134.3, 122.5, 121.7, 119.3, 118.7, 111.7.

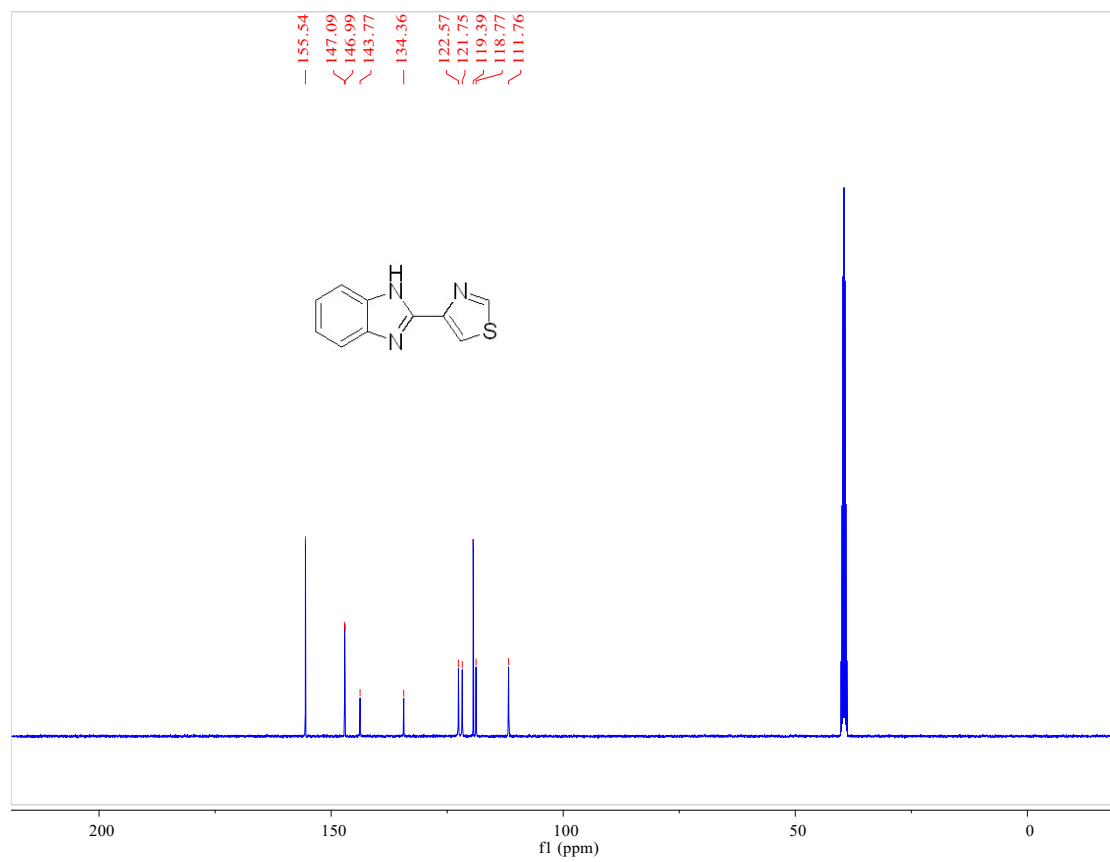


Figure S66 ^{13}C NMR of thiabendazole in $\text{DMSO-}d_6$