Supporting information

Synthesis of benzoxazoles, benzimidazoles, and benzothiazoles using Brønsted acidic ionic liquid gel as an efficient heterogeneous catalyst under solvent-free condition.

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Section S1. Preparation and characterization of BAIL gel

All commercially available reagent-grade chemicals were purchased from chemical suppliers and used as received without further purification unless otherwise noted.

Preparation of 1-(4-sulfonic acid)butyl-3-methylimidazolium hydrogen sulfate ionic liquid (BAIL)

1-Methylimidazolium (123 mg, 1.5 mmol) and 1,4-butane sultone (0.204 mg, 1.5 mmol) were added into a glass-tube with Teflon cap. After 1 h of sonication, the reaction mixture was washed with diethyl ether (6 x 5 mL) and dried at 80 ^{o}C in 60 min. The obtained witterion (1.5 mmol, 327 mg) was then mixed with sulfuric acid (147 mg, 1.5 mmol). The resulting mixture was sonicated at room temperature for 2 h. The crude product was then washed with diethyl ether (10 x 3 mL) and dried under vacuum at 80 ^{o}C in 60 min. The BAIL was characterized by FT-IR, ^{1}H and ^{13}C NMR, HRMS (ESI).

1-(4-sulfonic acid)butyl-3-methylimidazolium hydrogen sulfate ionic liquid. FT-IR (KBr, cm^{-1}): 3410, 1639, 1457, 1171, 1042, 752; ^{1}H NMR (500 MHz, D_2O) δ 8.59 (s, 1H), 7.35 (t, J = 1.7 Hz, 1H), 7.29 (t, J = 1.7 Hz, 1H), 4.10 (t, J = 7.0 Hz, 2H), 3.75 (s, 3H), 2.83 (t, J = 8.0, 2H), 1.82 (m, 2H), 1.60 (m, 2H); ^{13}C NMR (125 MHz, D_2O) δ 135.9, 123.6, 122.1, 50.0, 48.9, 35.7, 28.1, 20.9; HRMS (ESI) m/z calcd for $[M]^+$ $C_8H_{15}N_2O_3S^+$ 219.0798, found 219.0783.

Preparation of BAIL gel

The BAIL (3.1635 g, 10 mmol), TEOS (3.125 g, 15 mmol) and ethanol (1.380 g, 30 mmol) were added to a 20 mL round-bottom flask and stirred for 10 min until the mixture became homogeneous. The mixture was left to stand and gelled in a week. The gel was then subjected to aging for 3 weeks. After that, the gel was transferred into a 100 mL round-bottom flask containing 50 mL of ethanol and heated to reflux for 2 h. The BAIL gel was washed with toluene (5 x 10 mL) and dried under vacuum for 3 h. It was finally characterized by FT-IR, TGA, ICP-OES, SEM, and EDS.

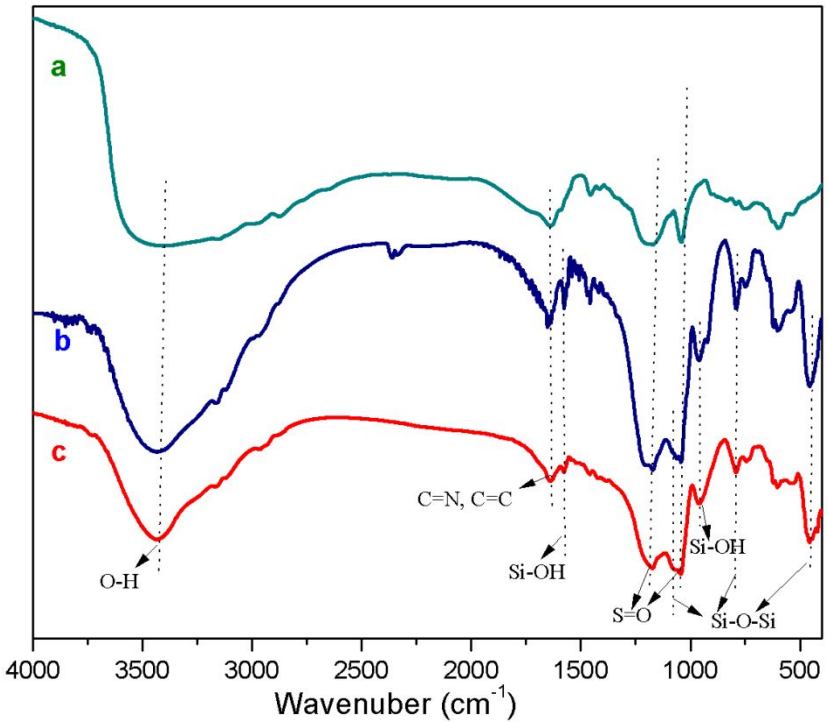


Figure S1. FT-IR spectra of BAIL (a), BAIL gel (b) and BAIL gel after the fifth recovery (c).

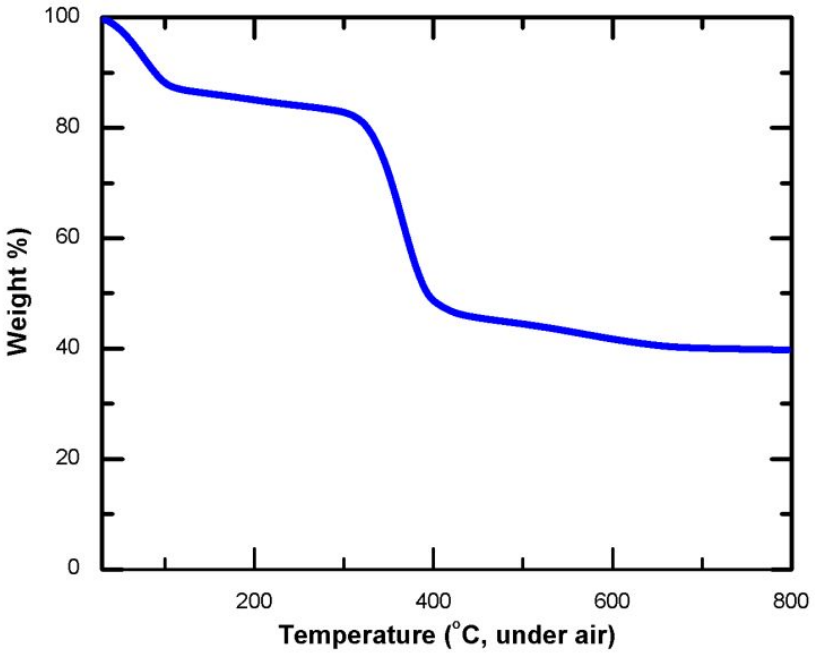


Figure S2. TG analysis of BAIL gel

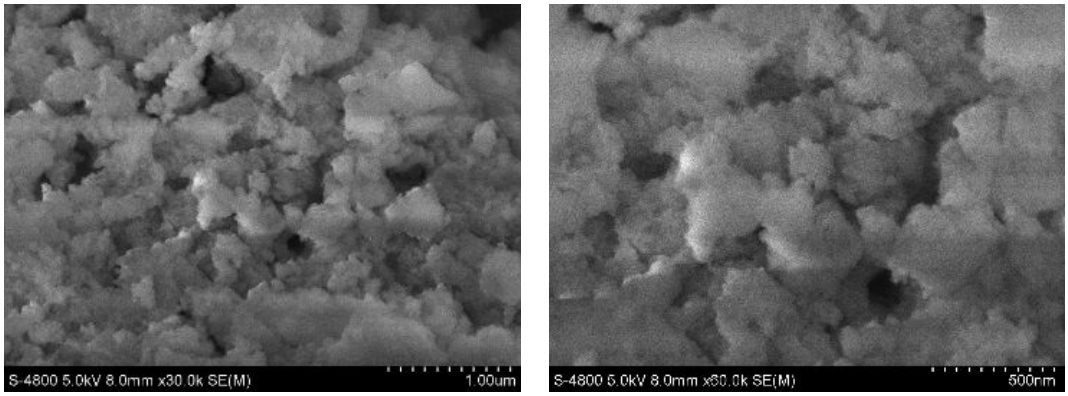


Figure S3. The SEM image of BAIL gel.

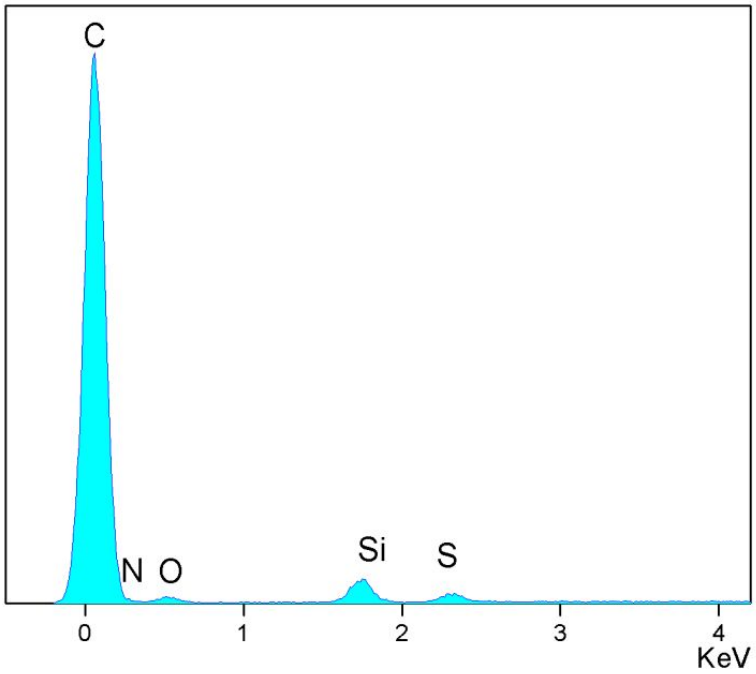
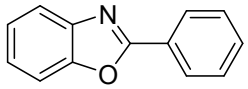


Figure S4. EDS spectrum of BAIL gel.

Section S2. Spectral data

2-Phenylbenzoxazole (1)[1,2]



Melting point: 102-103.5 °C

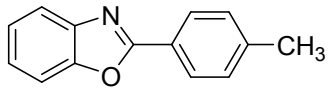
FT-IR (KBr, 4000-400 cm^{-1}) 3059, 2925, 2854, 1775, 1615, 1551, 1475, 1448, 1285, 1240.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31-8.22 (m, 2H), 7.82-7.75 (m, 1H), 7.61-7.56 (m, 1H), 7.55-7.50 (m, 3H), 7.40-7.33 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 150.9, 142.2, 131.7, 129.0, 127.8, 127.3, 125.3, 124.7, 120.1, 110.7.

GC-MS (EI, 70 eV) *m/z* 195 ($[M]^+$).

2-(*p*-Tolyl)benzoxazole (2)[1–3]



Melting point: 113-114.5 °C

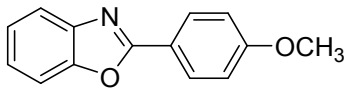
FT-IR (KBr, 4000-400 cm^{-1}) 3056, 2920, 2854, 1728, 1620, 1554, 1499, 1450, 1242.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.13 (m, 2H), 7.77-7.74 (m, 1H), 7.58-7.50 (m, 1H), 7.35-7.31 (m, 4H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 150.8, 142.3, 142.2, 129.8, 127.8, 125.1, 124.7, 124.5, 120.0, 110.6, 21.8.

GC-MS (EI, 70 eV) *m/z* 209 ($[M]^+$).

2-(4-Methoxyphenyl)benzoxazole (3)[2]



Melting point: 103-104.5 °C

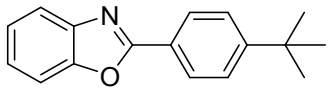
FT-IR (KBr, 4000-400 cm^{-1}) 3050, 2924, 2849, 1615, 1501, 1450, 1420, 1244.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23-8.17 (m, 2H), 7.75-7.73 (m, 1H), 7.56-7.54 (m, 1H), 7.35-7.29 (m, 2H), 7.05-7.01 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 162.6, 150.8, 142.1, 129.7, 124.8, 124.7, 119.7, 119.7, 114.6, 110.6, 55.6.

GC-MS (EI, 70 eV) *m/z* 225 ($[M]^+$).

2-(4-*tert*-Butylphenyl)benzoxazole (4)[2]



Melting point: 107-108 °C

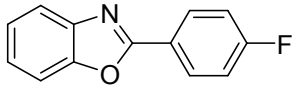
FT-IR (KBr, 4000-400 cm^{-1}) 3059, 2927, 1728, 1547, 1452, 1429, 1287, 1239.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.16 (m, 2H), 7.78-7.75 (m, 1H), 7.60-7.56 (m, 1H), 7.56-7.54 (m, 2H), 7.37-7.32 (m, 2H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 155.4, 150.8, 142.1, 127.7, 126.1, 125.1, 124.7, 124.4, 120.0, 110.7, 35.2, 31.3.

GC-MS (EI, 70 eV) *m/z* 251 ($[M]^+$).

2-(4-Fluorophenyl)benzoxazole (5)[2]



Melting point: 99-99.5 °C

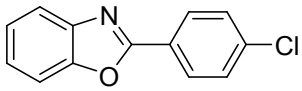
FT-IR (KBr, 4000-400 cm^{-1}) 3061, 2925, 1619, 1584, 1582, 1542, 1473, 1448, 1247, 1225.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-8.22 (m, 2H), 7.80-7.72 (m, 1H), 7.60-7.53 (m, 1H), 7.40-7.32 (m, 2H), 7.23-7.17 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0 (s), 164.0(s), 162.3 (s), 150.9 (s), 142.2 (s), 130.0 (d, J = 255.1 Hz), 130.0 (d, J = 8.8 Hz), 125.0 (d, J = 59.5 Hz), 123.67 (d, J = 3.2 Hz), 120.14 (s), 116.3 (d, J = 44.0 Hz), 110.7 (s).

GC-MS (EI, 70 eV) *m/z* 213 ($[M]^+$).

2-(4-Chlorophenyl)benzoxazole (6)[2]



Melting point: 148-150 °C

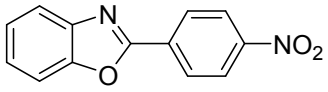
FT-IR (KBr, 4000-400 cm^{-1}) 3067, 2922, 1725, 1607, 1451, 1428, 1237.

^{1}H NMR (500 MHz, CD_3CO) δ 8.26-8.22 (m, 2H), 7.77-7.75 (m, 1H), 7.70-7.69 (m, 1H), 7.65-7.62 (m, 2H), 7.42 (pd, J = 7.5, 2.0 Hz, 2H).

^{13}C NMR (125 MHz, CD_3CO) δ 161.7, 150.8, 142.1, 137.2, 129.3, 129.0, 125.9, 125.6, 124.9, 120.0, 110.7.

GC-MS (EI, 70 eV) *m/z* 229.5 ($[M]^+$).

2-(4-Nitrophenyl)benzoxazole (7)[3]



Melting point: 156-157 ^oC

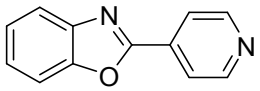
FT-IR (KBr, 4000-400 cm^{-1}) 2925, 2854, 1678, 1610, 1534, 1449, 1237.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.0, 1.0 Hz, 1H), 7.89 (dd, J = 8.0, 1.0 Hz, 1H), 7.83-7.80 (m, 1H), 7.74 (td, J = 8.0, 1.0 Hz, 1H), 7.69 (td, J = 8.0, 1.0 Hz, 1H), 7.59-7.57 (m, 1H), 7.42-7.37 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 151.2, 141.7, 132.4, 132.0, 131.6, 126.2, 125.1, 124.3, 121.7, 120.9, 111.1.

GC-MS (EI, 70 eV) *m/z* 240 ($[M]^+$).

2-(Pyridin-4-yl)benzoxazole (8)



Melting point: 102-104^oC

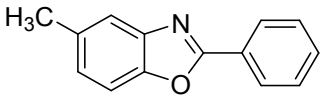
FT-IR (KBr, 4000-400 cm^{-1}) 3460, 2946, 1628, 878.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, J = 5.5 Hz, 2H), 8.09 (d, J = 6.0 Hz, 2H), 7.84-7.80 (m, 1H), 7.63 (m, 1H), 7.42 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 151.1, 150.9, 141.9, 134.6, 126.5, 125.3, 121.2, 120.9, 111.1.

GC-MS (EI, 70 eV) *m/z* 196 ($[M]^+$)

5-Methyl-2-phenylbenzoxazole (9)[2]



Melting point: 112-115 °C

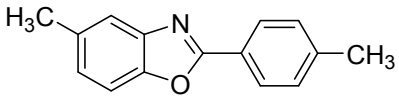
FT-IR (KBr, 4000-400 cm^{-1}) 2918, 1626, 1552, 1445, 1263.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.25-8.23 (m, 2H), 7.62-7.59 (m, 3H), 7.57-7.56 (m, 2H), 7.24 (d, J = 8.5, 1H), 2.47 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 149.2, 142.5, 134.5, 131.5, 129.0, 127.7, 127.5, 126.4, 120.1, 110.1, 21.6.

GC-MS (EI, 70 eV) *m/z* 209 ($[M]^+$).

5-Methyl-2-(*p*-tolyl)benzoxazole (10)[4]



Melting point: 138-139 °C.

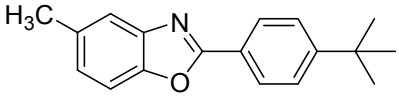
FT-IR (KBr, 4000-400 cm^{-1}) 3304, 2921, 2856, 1616, 1555, 1499, 1332, 1262.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.11 (d, J = 8.0 Hz, 2H), 7.53-7.51 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.22-7.19 (m, 1H), 2.46 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ 163.2, 149.2, 142.7, 142.3, 134.5, 129.9, 127.5, 126.3, 124.8, 119.9, 110.1, 20.9, 20.8.

GC-MS (EI, 70 eV) *m/z* 223 ($[M]^+$).

5-Methyl-2-(4-*tert*-butylphenyl)benzoxazole (11)[5]



Melting point: 137-140 °C

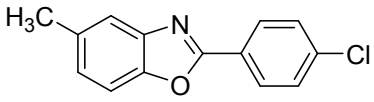
FT-IR (KBr, 4000-400 cm^{-1}) 3107, 2963, 2930, 2871, 1729, 1621, 1532, 1460, 1269.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.56 (d, J = 2.0 Hz, 1H), 8.34 (dd, J = 9.0, 2.0 Hz, 1H), 8.20 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 9.0 Hz, 2H), 2.81 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (125 MHz, acetone-d_6) δ 162.9, 155.0, 149.0, 142.5, 134.3, 127.2, 126.1, 126.0, 124.6, 119.7, 109.9, 34.7, 30.5, 20.5.

GC-MS (EI, 70 eV) *m/z* 265 ([M]$^+$).

5-Methyl-2-(4-chlorophenyl)benzoxazole (12)[4]



Melting point: 150-151^{o}C

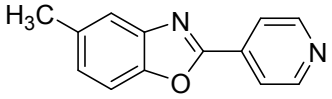
FT-IR (KBr, 4000-400 cm^{-1}) 3102, 2930, 2875, 1759, 1635, 1530, 1462, 1272.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.18 (d, J = 8.5 Hz, 2H), 7.55 (s, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 2.49 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ 162.3, 149.2, 142.4, 137.7, 134.7, 129.3, 128.9, 126.6, 126.0, 120.1, 110.1, 21.6.

GC-MS (EI, 70 eV) *m/z* 243.5 ([M]$^+$).

5-Methyl-2-(pyridin-4-yl)benzoxazole (13)



Melting point: 129-130 ^{o}C.

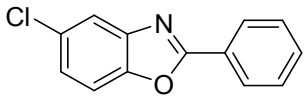
FT-IR (KBr, 4000-400 cm^{-1}) 3406, 2921, 1612, 1537, 1414, 1344, 1068, 808.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.80 (d, J = 4.5 Hz, 2H), 8.07 (d, J = 5.0 Hz, 2H), 7.59 (s, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) 160.8, 150.7, 149.3, 142.1, 135.2, 134.8, 127.7, 121.1, 120.6, 110.4, 21.6.

GC-MS (EI, 70 eV) *m/z* 210 ([M]$^+$)

5-Chloro-2-phenylbenzoxazole (14)[6]



Melting point: 102-104 °C.

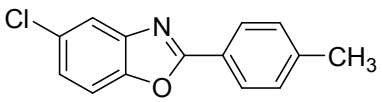
FT-IR (KBr, 4000-400 cm^{-1}) 3061, 1612, 1551, 1443, 1333, 1265.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.23 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 1.5 Hz, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.64-7.59 (m, 3H), 7.42 (dd, J = 9.0, 1.5 Hz, 1H).

^{13}C NMR (125MHz, acetone-d_6) δ 165.3, 150.6, 144.5, 133.1, 130.7, 130.2, 128.6, 127.7, 126.4, 120.7, 112.9.

GC-MS (EI, 70 eV) *m/z* 229.5 ($[M]^+$).

5-Chloro-2-(*p*-tolyl)benzoxazole (15)[7]



Melting point: 148-150 °C

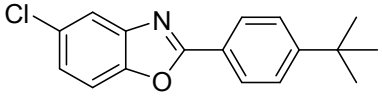
FT-IR (KBr, 4000-400 cm^{-1}) 2953, 1610, 1551, 1479, 1448, 1258.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.13 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 2.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.40-7.33 (m, 4H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ 165.6, 150.5, 144.6, 143.8, 130.8, 130.6, 128.6, 126.2, 125.0, 120.5, 112.8, 21.7.

GC-MS (EI, 70 eV) *m/z* 243.5 ($[M]^+$).

5-Chloro-2-(4-*tert*-butylphenyl)benzoxazole (16)[8]



Melting point: 137-138 °C

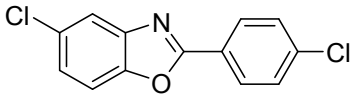
FT-IR (KBr, 4000-400 cm^{-1}): 2957, 2902, 2866, 1611, 1552, 1493, 1457, 1262.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.17 (d, J = 8.5 Hz, 2H), 7.76 (s, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.41 (dd, J = 8.5, 2.0 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, acetone-d_6) δ 165.5, 156.7, 150.6, 144.6, 130.6, 128.6, 127.2, 126.2, 125.0, 120.5, 112.8, 35.9, 31.5.

GC-MS (EI, 70 eV) *m/z* 285.5 ([M]$^+$).

5-Chloro-2-(4-chlorophenyl)benzoxazole (17)[7]



Melting point: 195-197^{o}C

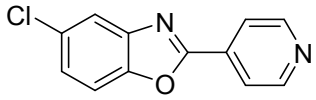
FT-IR (KBr, 4000-400 cm^{-1}) 2913, 1727, 1550, 1448, 1245.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.28-8.23 (m, 2H), 7.81 (d, J = 1.5 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.69-7.65 (m, 2H), 7.46 (dd, J = 8.5, 2.0 Hz, 1H).

^{13}C NMR (125 MHz, acetone-d_6) δ 149.6, 143.4, 137.7, 129.8, 129.4, 129.2, 125.7, 125.5, 119.7, 111.9.

GC-MS (EI, 70 eV) *m/z* 285.5 ([M]$^+$).

5-Chloro-2-(pyridin-4-yl)benzoxazole (18)



Melting point: 152-153 ^{o}C.

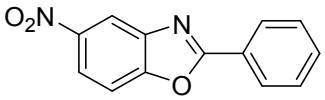
FT-IR (KBr, 4000-400 cm^{-1}) 3431, 2922, 1612, 1568, 1539, 1449, 1057, 874.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.83 (d, J = 5.5 Hz, 2H), 8.07 (dd, J = 4.5, 1.5 Hz, 2H), 7.80 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.40 (dd, J = 8.5, 2.0 Hz, 1H).

^{13}C NMR (125 MHz, acetone-d_6) δ 162.0, 150.8, 149.6, 143.0, 134.2, 130.9, 126.9, 121.3, 120.8, 111.9.

GC-MS (EI, 70 eV) *m/z* 230 ([M]$^+$)

5-Nitro-2-phenylbenzoxazole (19)[7]



Melting point: 166-169 °C.

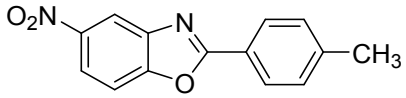
FT-IR (KBr, 4000-400 cm^{-1}): 3105, 2925, 2853, 1709, 1604, 1526, 1463, 1348, 1286.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.68 (d, J = 2.5 Hz, 1H), 8.35 (dd, J = 9.0, 2.0 Hz, 1H), 8.26-8.24 (m, 2H), 8.06 (d, J = 9.0 Hz, 1H), 7.71-7.65 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 154.0, 145.1, 141.9, 132.9, 129.5, 127.8, 125.5, 121.5, 121.4, 115.8, 115.7, 111.8.

GC-MS (EI, 70 eV) *m/z* 240 ($[M]^+$).

5-Nitro-2-(*p*-tolyl)benzoxazole (20)[9]



Melting point: 125-126 °C.

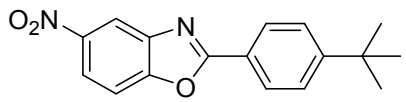
FT-IR (KBr, 4000-400 cm^{-1}) 2923, 2850, 1695, 1628, 1515, 1416, 1328, 1250.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.31-8.27 (m, 2H), 7.57-7.55 (m, 2H), 7.40-7.35 (m, 2H), 7.24 (d, J = 9.0 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ 166.7, 164.7, 150.0, 143.3, 135.5, 130.8, 130.7, 127.3, 124.8, 120.7, 117.2, 117.0, 110.9, 21.4.

GC-MS (EI, 70 eV) *m/z* 254 ($[M]^+$).

5-Nitro-2-(4-*tert*-butylphenyl)benzoxazole (21)[10]



Melting point: 136-137 °C.

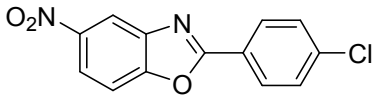
FT-IR (KBr, 4000-400 cm^{-1}) 3106, 2964, 2869, 1724, 1619, 1531, 1496, 1462, 1343, 1267.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.18-8.16 (m, 2H), 7.66-7.63 (m, 2H), 7.56-7.54 (m, 2H), 7.23-7.21 (m, 1H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, acetone-d_6) δ 166.9, 157.3, 155.3, 146.4, 143.6, 132.1, 129.7, 128.7, 127.2, 124.2, 122.0, 116.4, 112.1, 35.8, 31.4.

GC-MS (EI, 70 eV) *m/z* 296 ([M]$^+$).

5-Nitro-2-(4-chlorophenyl)benzoxazole (22)[7]



Melting point: 215-217 ^{o}C.

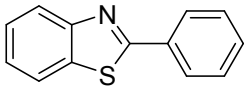
FT-IR (KBr, 4000-400 cm^{-1}) 3105, 2924, 2854, 1615, 1528, 1481, 1346, 1257, 1088.

^{1}H NMR (500 MHz, acetone-d_6) δ 8.63 (d, J = 2.0 Hz, 1H), 8.39 (dd, J = 9.0, 2.0 Hz, 1H), 8.32-8.29 (m, 2H), 7.98 (d, J = 9.0 Hz, 1H), 7.71-7.70 (m, 2H).

^{13}C NMR (125 MHz, acetone-d_6) δ 155.4, 130.5, 130.4, 130.3, 129.7, 125.9, 122.4, 116.7, 112.4.

GC-MS (EI, 70 eV) *m/z* 274.5 ([M]$^+$).

2-Phenylbenzothiazole (23)[11]



Melting point: 111-113 ^{o}C

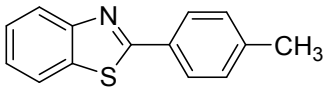
FT-IR (KBr, 4000-400 cm^{-1}) 3063, 1631, 1476, 1452, 1311, 1223.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.08 (m, 3H), 7.91 (d, J = 8.0 Hz, 1H), 7.51-7.48 (m, 4H), 7.41-7.37 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 154.3, 135.2, 133.8, 131.1, 129.2, 127.7, 126.5, 125.3, 123.4, 121.8.

GC-MS (EI, 70 eV) *m/z* 211 ([M]$^+$).

2-(*p*-Tolyl)benzothiazole (24)[11]



Melting point: 85-86 ^{o}C

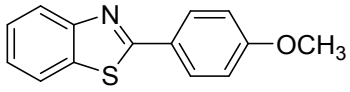
FT-IR (KBr, 4000-400 cm^{-1}) 2920, 2855, 1605, 1477, 1308, 1216.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0, 0.5 Hz, 1H), 7.50 (td, J = 7.0, 1.0, 1H), 7.36 (td, J = 7.0, 1.0, 1H), 7.29 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 154.3, 141.5, 135.1, 131.1, 129.8, 127.6, 126.4, 125.1, 123.2, 121.7, 21.6.

GC-MS (EI, 70 eV) *m/z* 225 ($[M]^+$).

2-(4-Methoxyphenyl)benzothiazole (25)[11]



Melting point: 121-122 °C

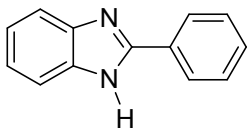
FT-IR (KBr, 4000-400 cm^{-1}) 2917, 1599, 1478, 1518, 1479, 1308, 1256.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.02 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.47 (td, J = 8.0, 1.0 Hz, 1H), 7.35 (td, J = 8.0, 1.0 Hz, 1H), 7.02-6.99 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 162.1, 154.3, 135.0, 129.3, 126.6, 126.4, 125.0, 123.0, 121.7, 114.5, 55.6.

GC-MS (EI, 70 eV) *m/z* 241 ($[M]^+$).

2-Phenylbenzimidazole (26)[12]



Melting point: 293-294 °C

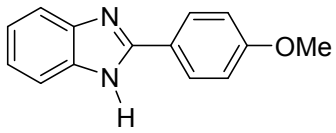
FT-IR (KBr, 4000-400 cm^{-1}) 3411, 1540, 1450, 1408, 967, 774.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 (d, J = 7.5 Hz, H), 7.60 (s, 1H), 7.57-7.55 (m, 2H), 7.51-7.48 (m, 1H), 7.22-7.19 (m, 2H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 151.2, 130.2, 129.8, 128.9, 126.4, 122.1.

GC-MS (EI, 70 eV) *m/z* 195 ($[M]^+$).

2-(4-Methoxyphenyl)benzimidazole (27)[12]



Melting point: 204 °C

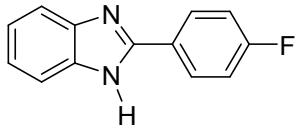
FT-IR (KBr, 4000-400 cm^{-1}): 3395, 3055, 1452, 1406, 1274, 741.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.49 (s, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.88 (d, J = 9Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.47-7.41 (m, 2H), 7.17 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H) ppm.

^{13}C NMR (125 MHz, DMSO-d_6): δ 166.4, 163.2, 144.3, 143.7, 132.4, 132.1, 131.6, 125.1, 124.7, 124.5, 120.1, 115.0, 114.4, 55.7 ppm.

GC-MS (EI, 70 eV) *m/z* 225 ($[M]^+$).

2-(4-Fluorophenyl)benzimidazole (28)[12]



Melting point: 253-254 °C

FT-IR (KBr, 4000-400 cm^{-1}) 3429, 3060, 1604, 1440, 964, 743.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.23-8.21 (m, 2H), 7.59-7.58 (m, 2H), 7.42-7.38 (m, 2H), 7.22-7.18 (m, 2H) ppm.

^{13}C NMR (125 MHz, DMSO-d_6) δ 163.0 (d, J = 245.0 Hz), 150.4, 131.3, 128.7 (d, J = 8.75 Hz), 126.8, 122.1, 116.0, 115.9 ppm.

GC-MS (EI, 70 eV) *m/z* 213 ($[M]^+$).

Section S3. ^{1}H, ^{13}C NMR spectroscopy

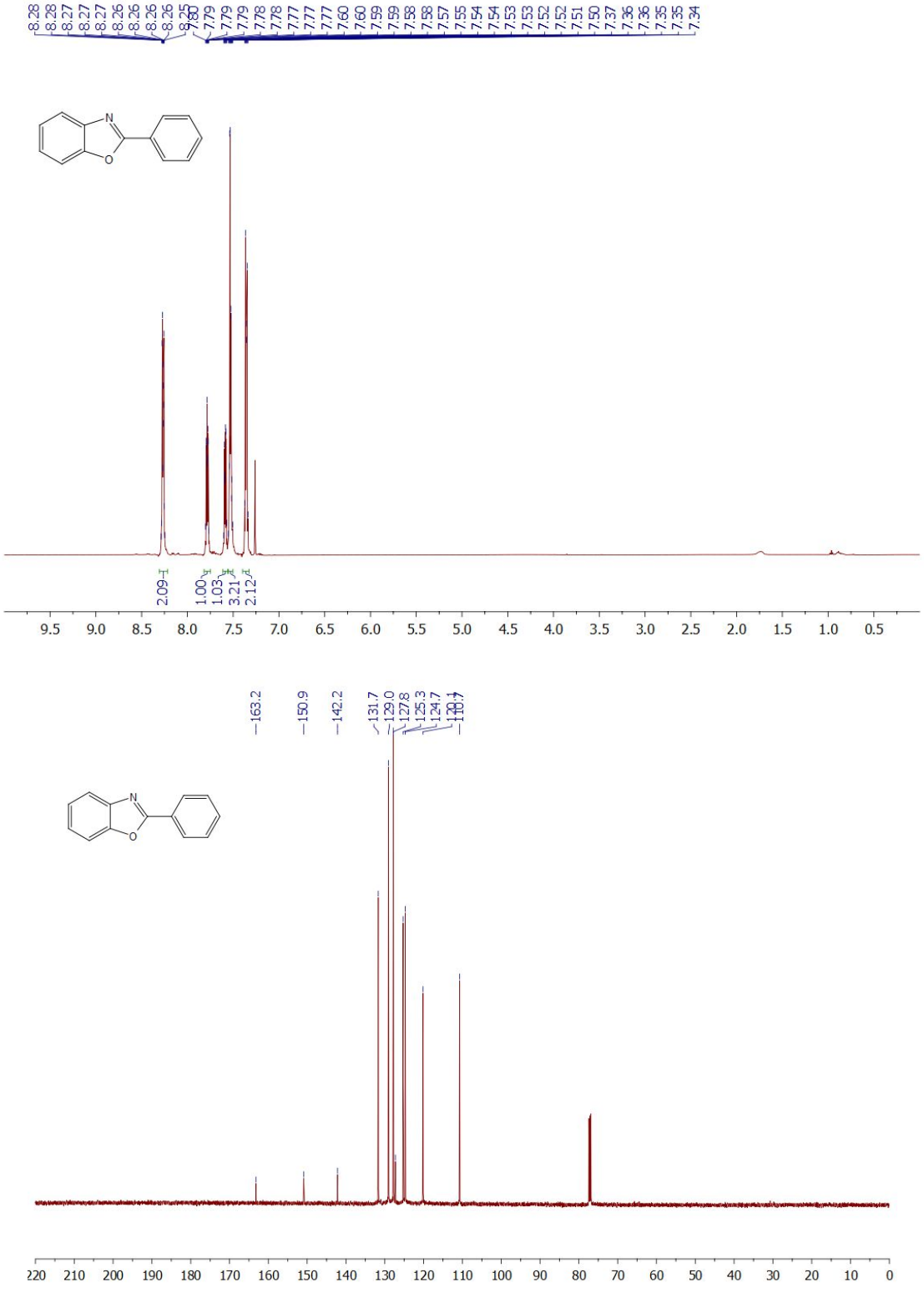


Figure S5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenylbenzoxazole (1).

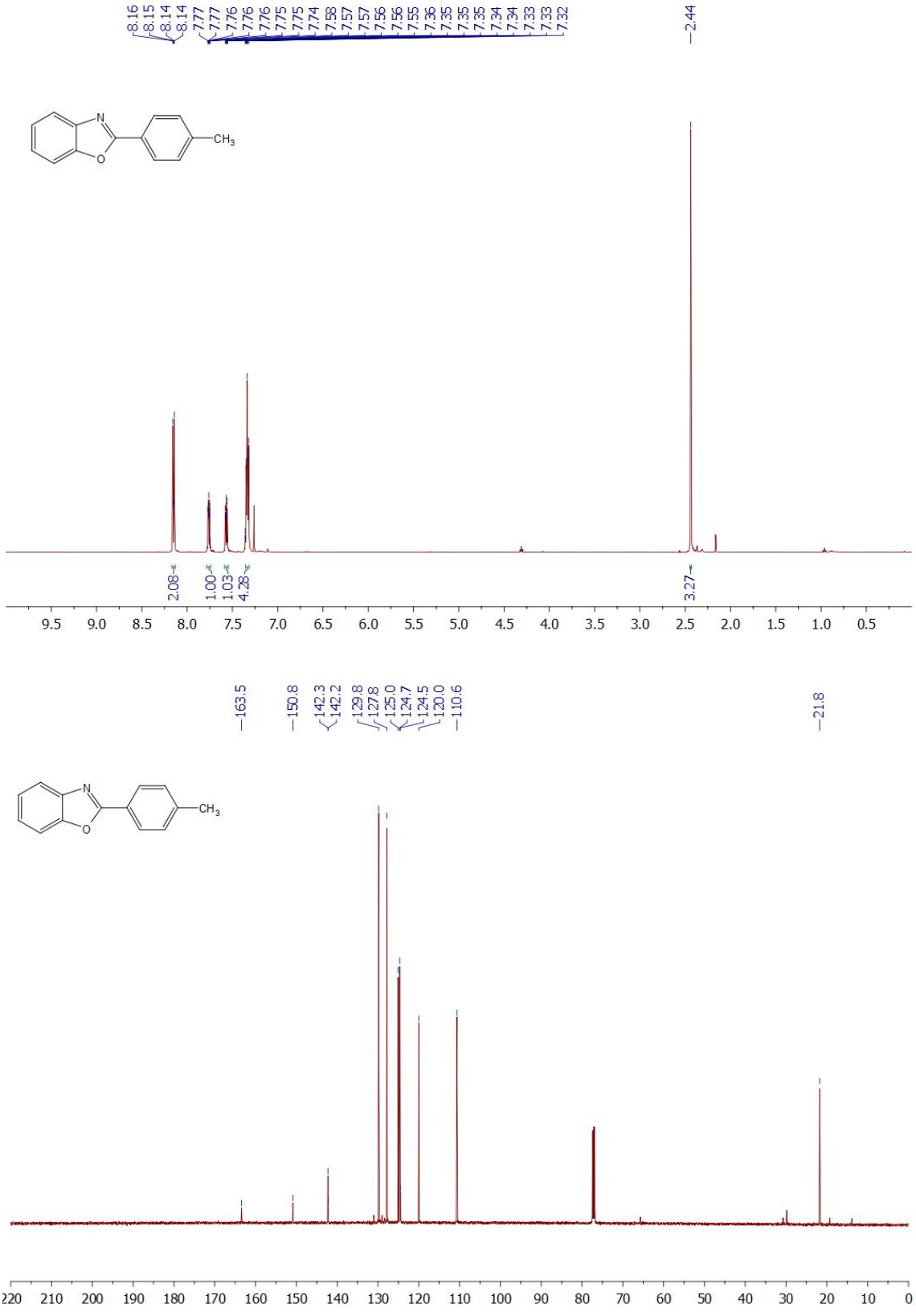


Figure S6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(*p*-tolyl)benzoxazole (2).

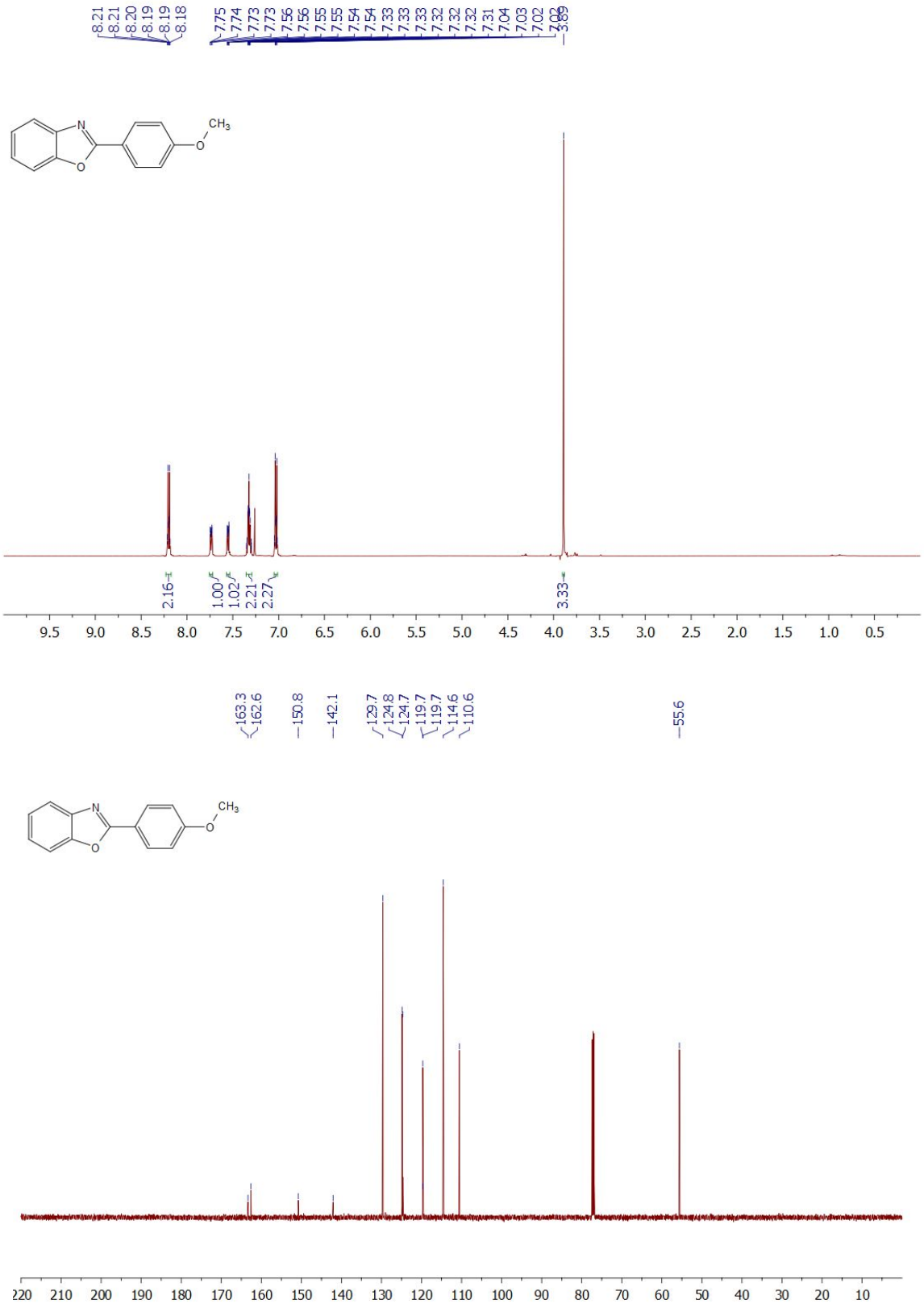


Figure S7. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-methoxyphenyl)benzoxazole (3).

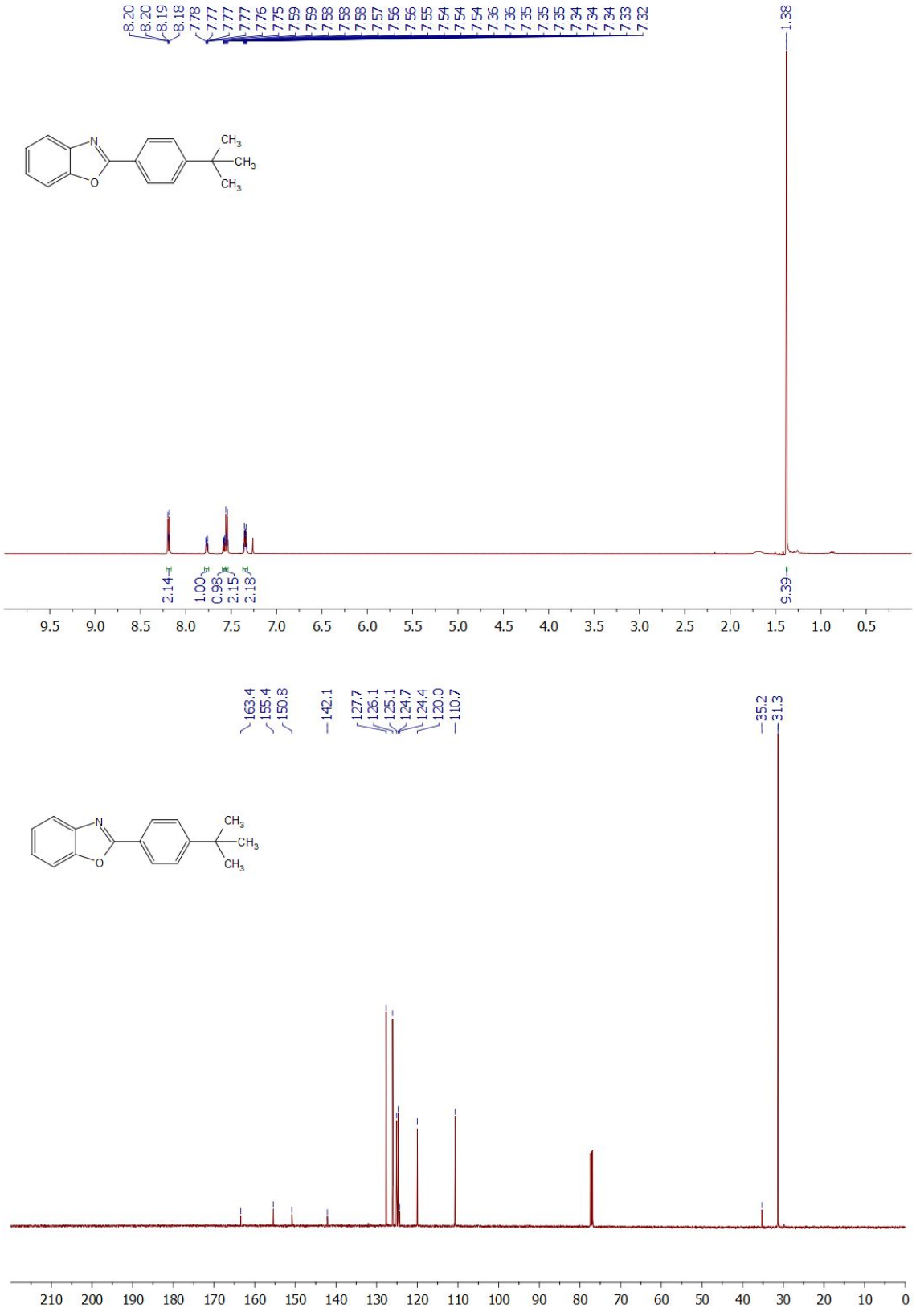


Figure S8. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-*tert*-butylphenyl)benzoxazole (4).

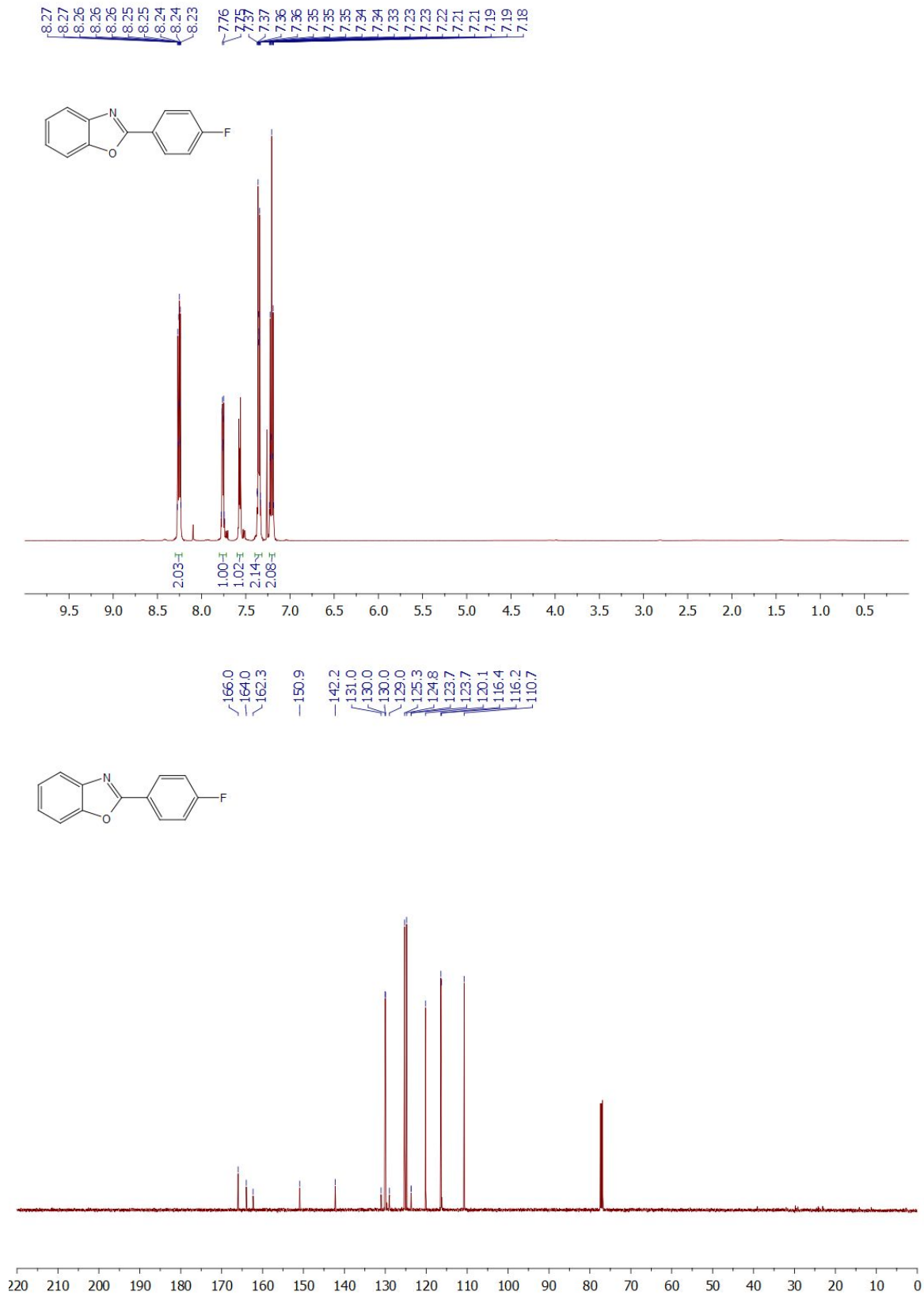


Figure S9. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-fluorophenyl)benzoxazole (5).

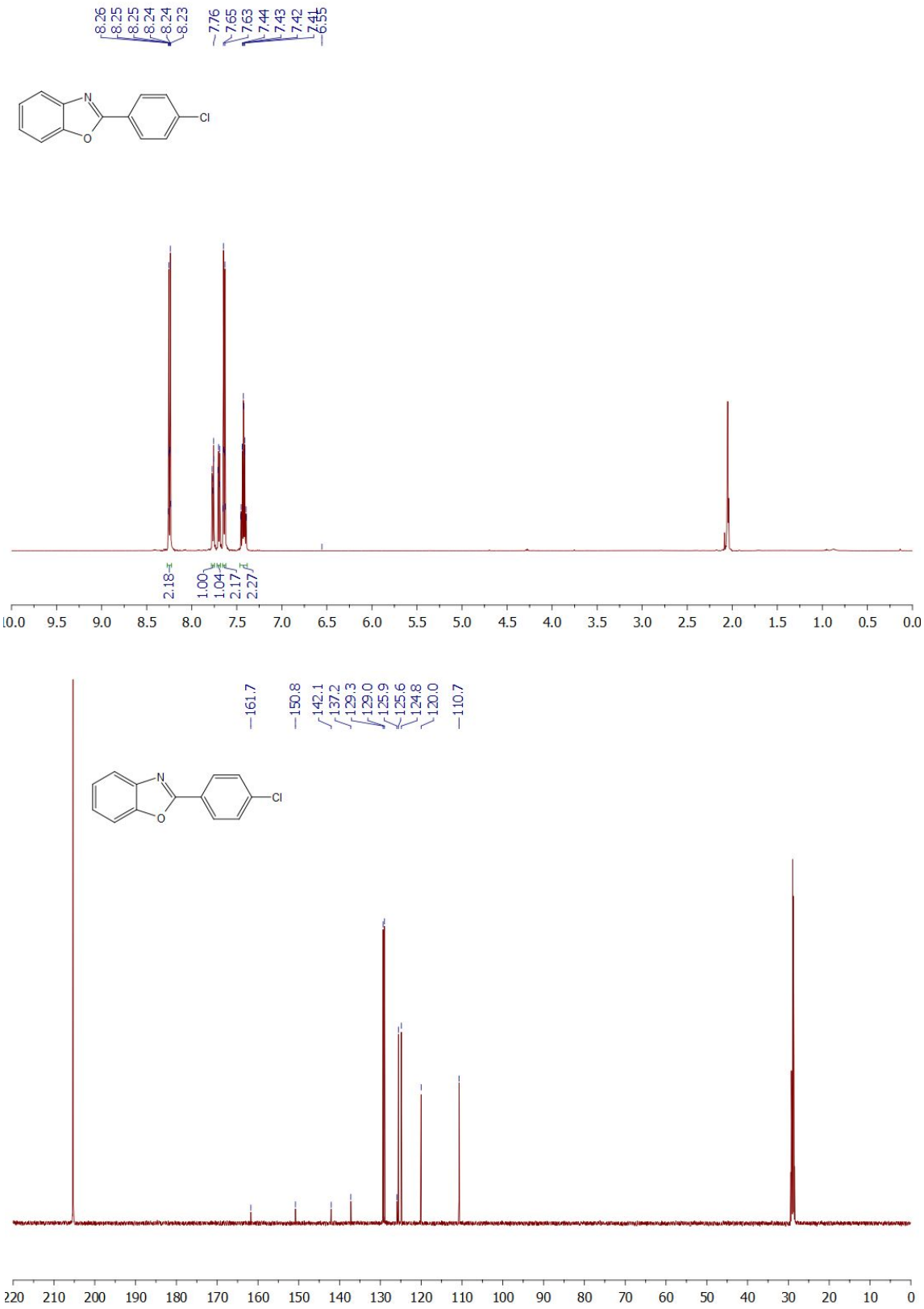


Figure S10. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-chlorophenyl)benzoxazole (6).

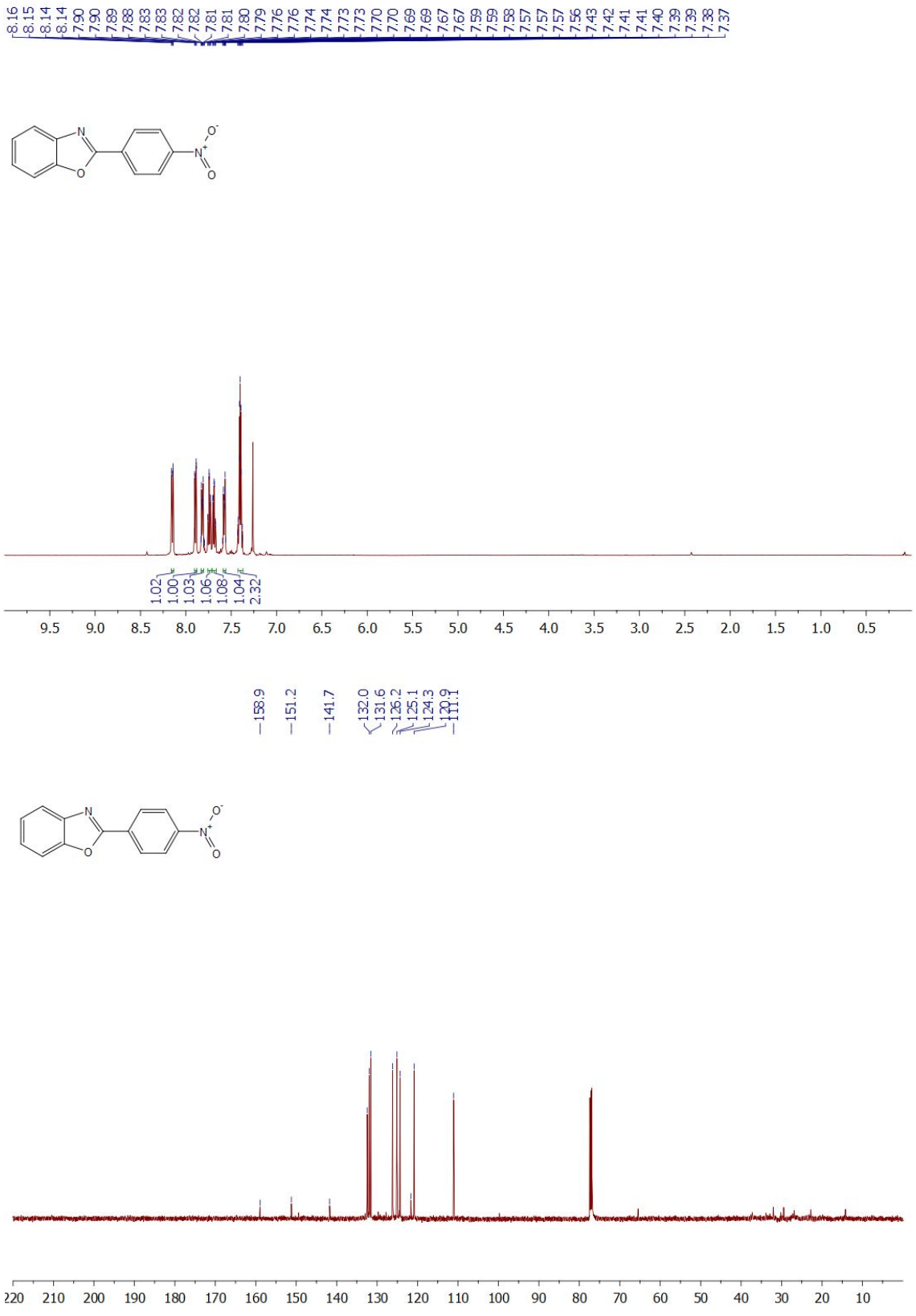


Figure S11. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-nitrophenyl)benzoxazole (7).

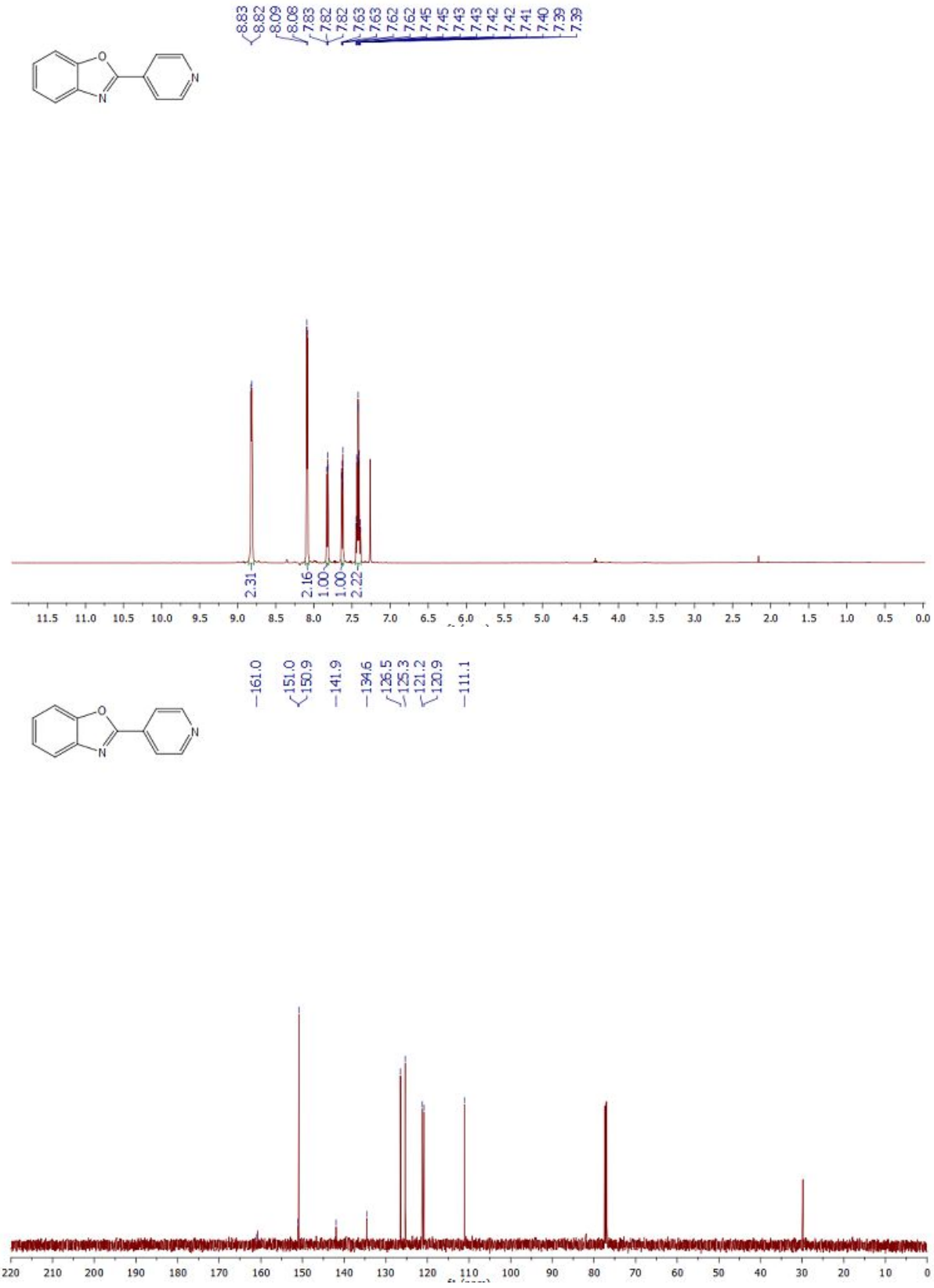


Figure S12. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(pyridin-4-yl)benzoxazole (8).

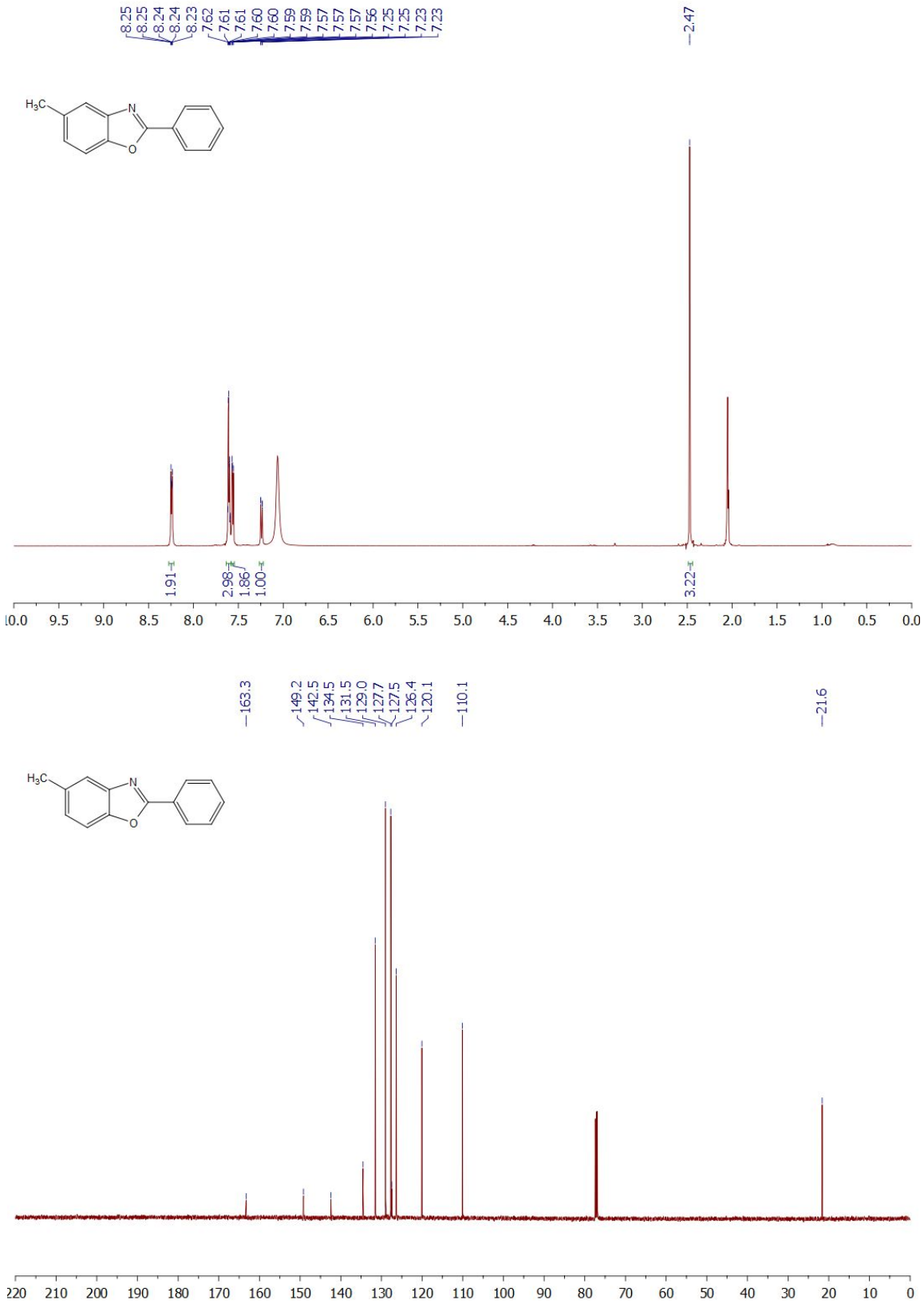


Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-2-phenylbenzoxazole (9).

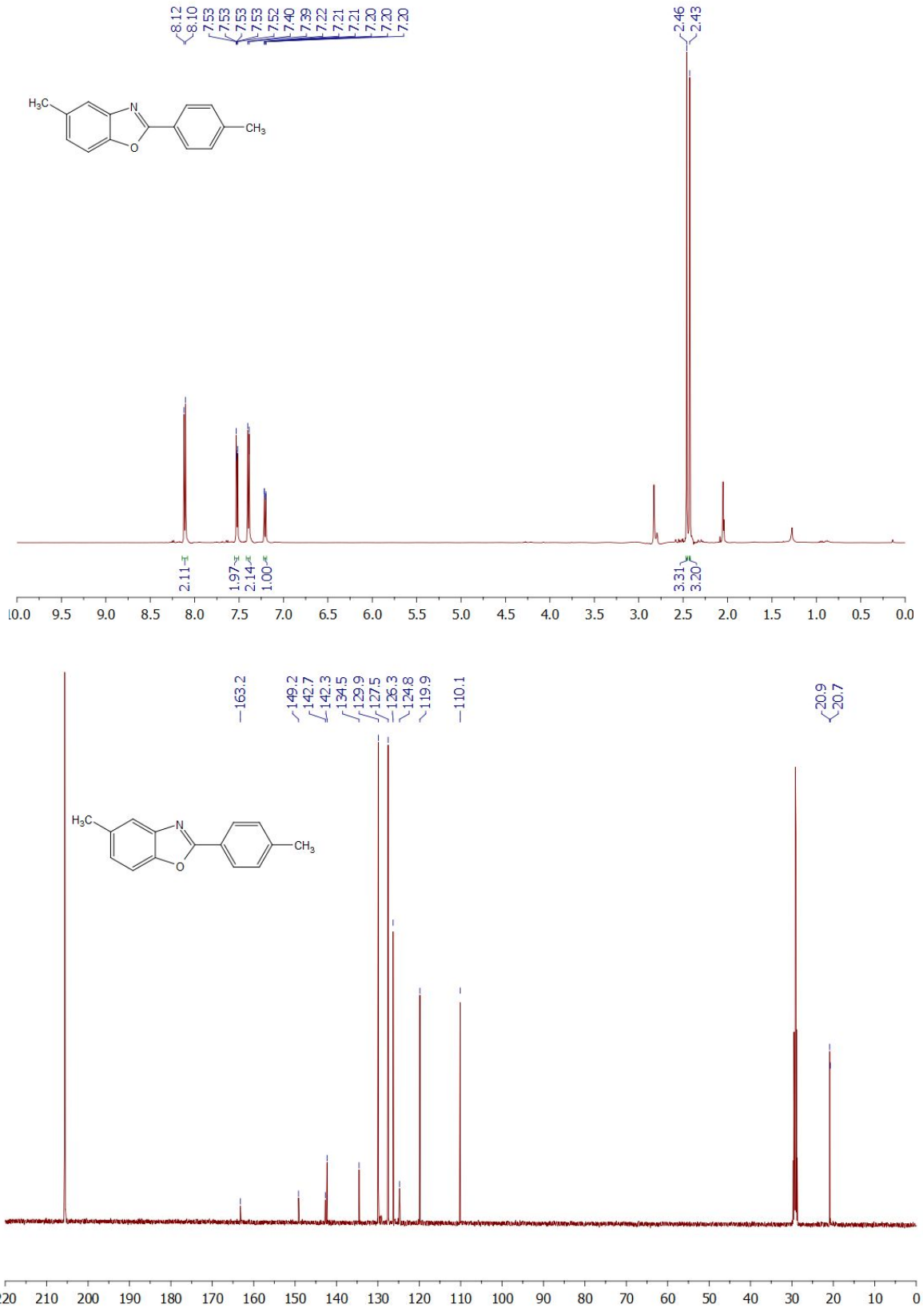


Figure S14. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-2-(*p*-tolyl)benzoxazole (10).

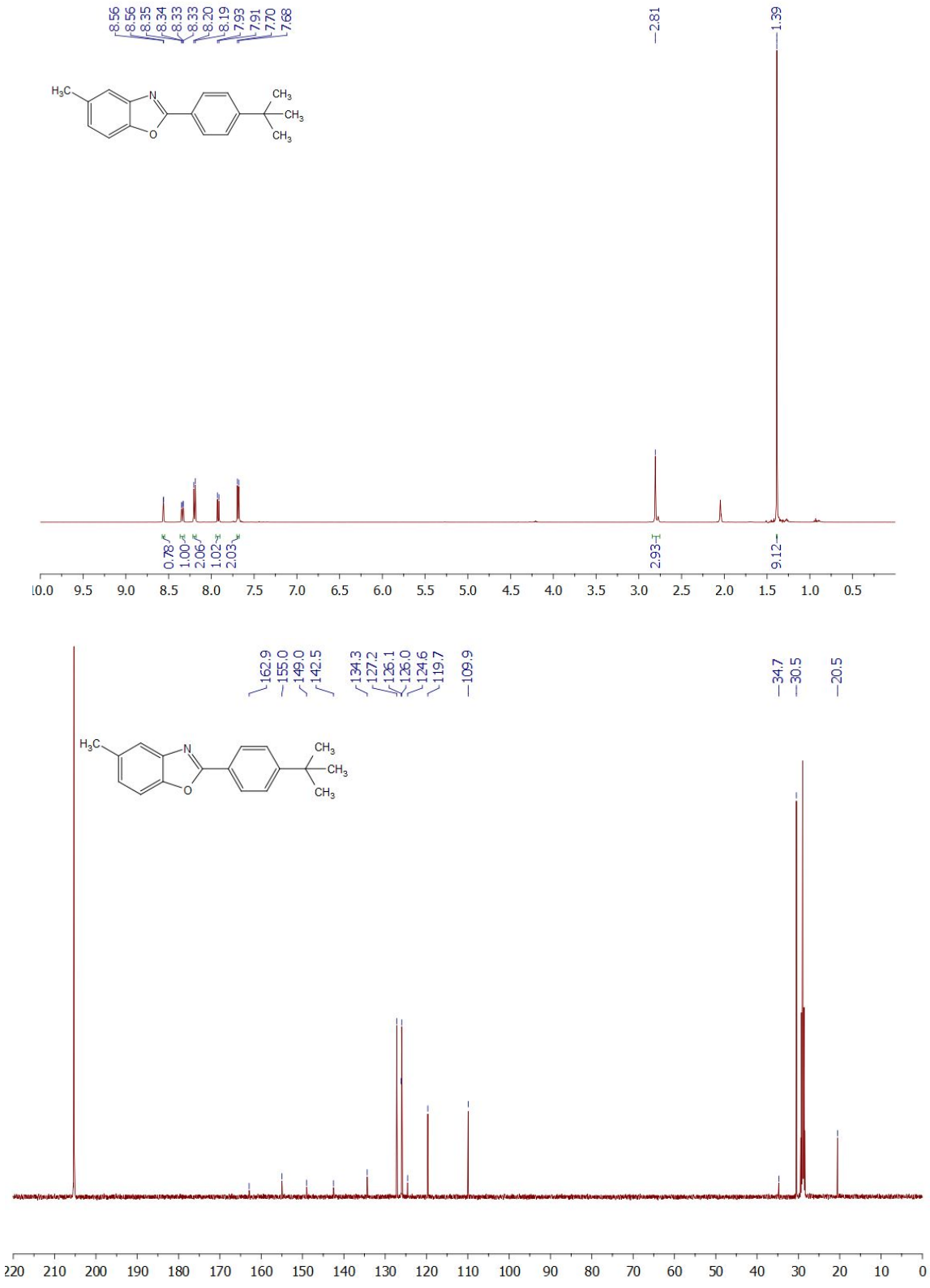


Figure S15. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-2-(4-*tert*-butylphenyl)benzoxazole (11).

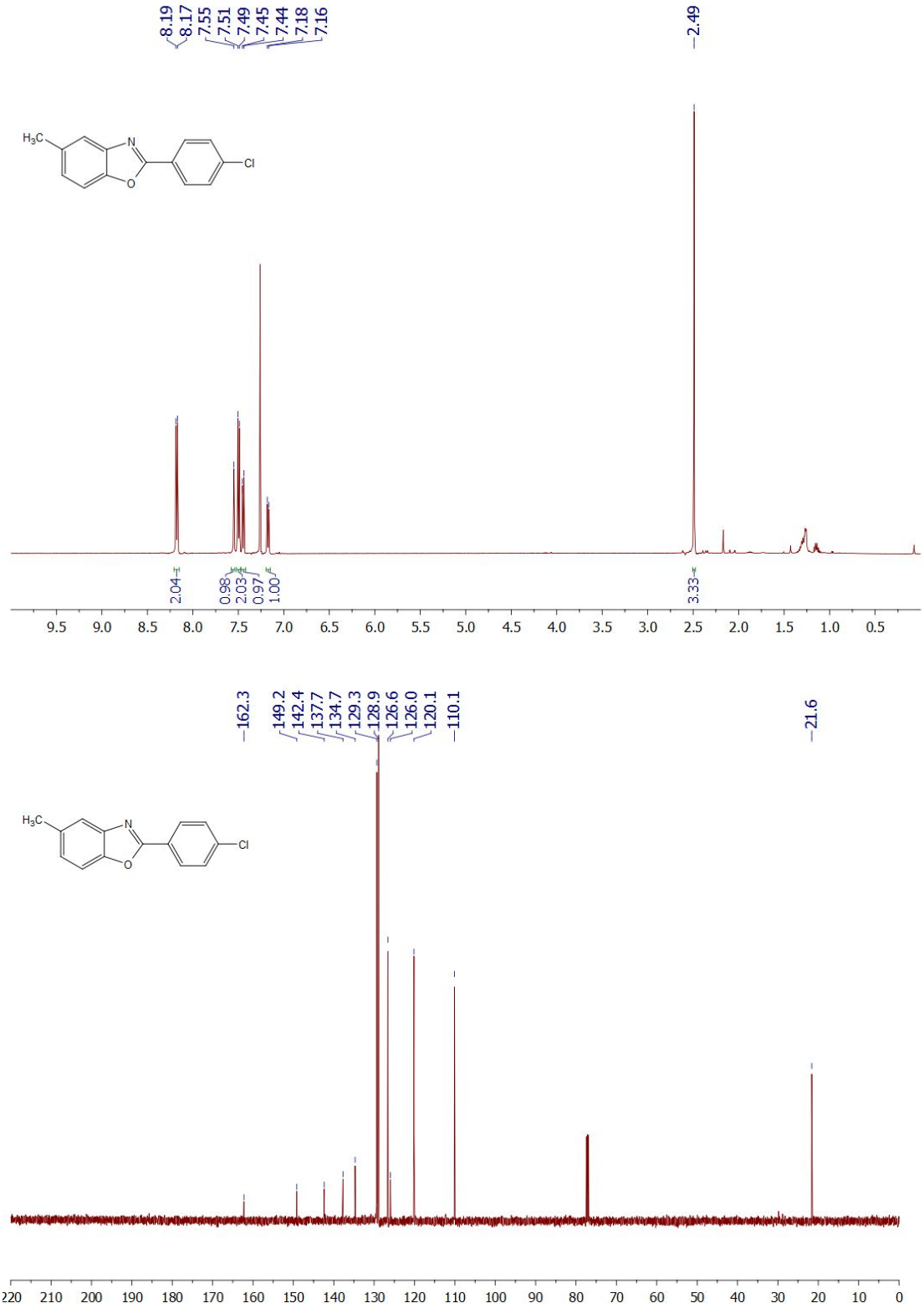


Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-2-(4-chlorophenyl)benzoxazole (12).

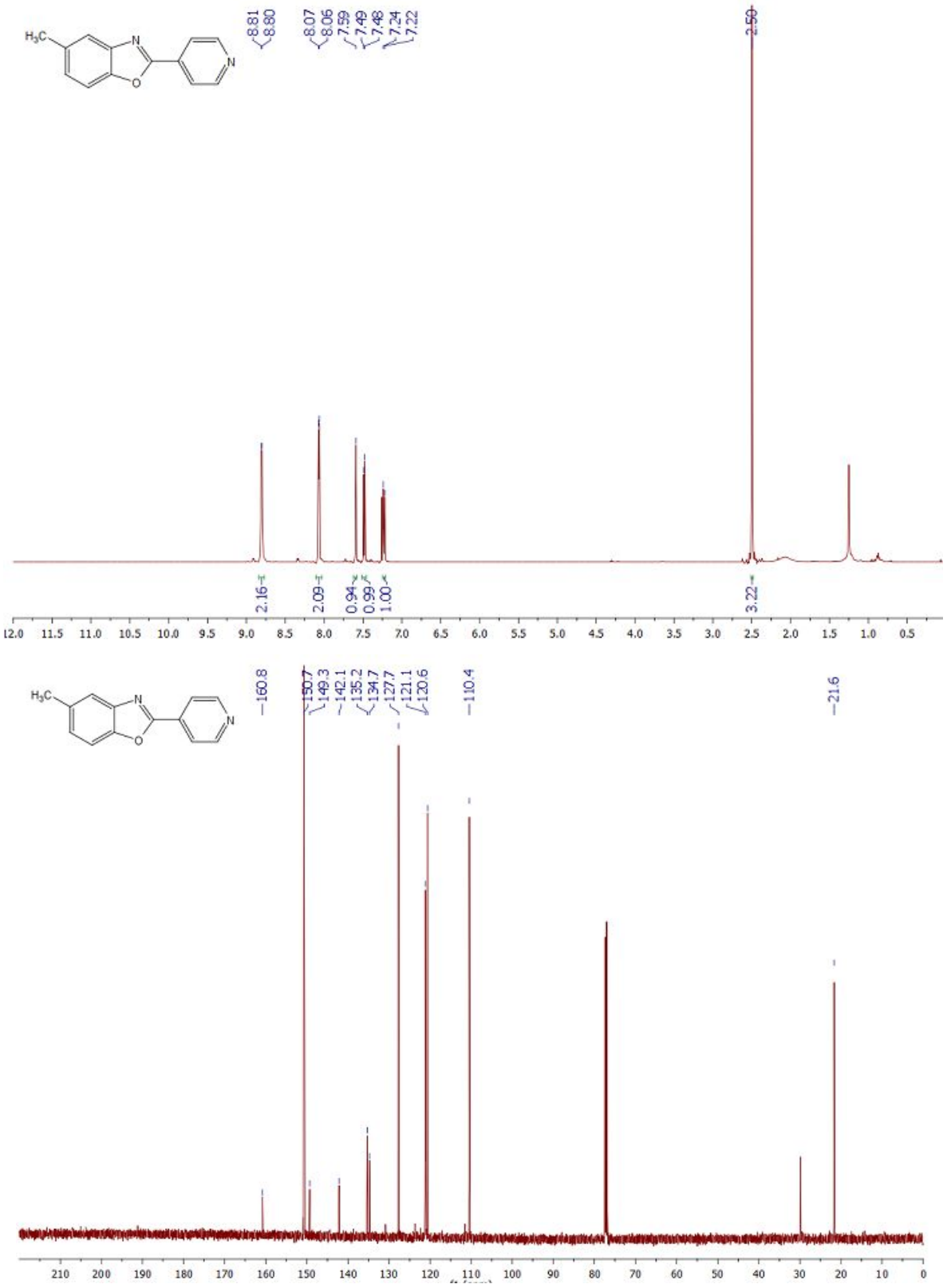


Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-2-(pyridin-4-yl)benzoxazole (13).

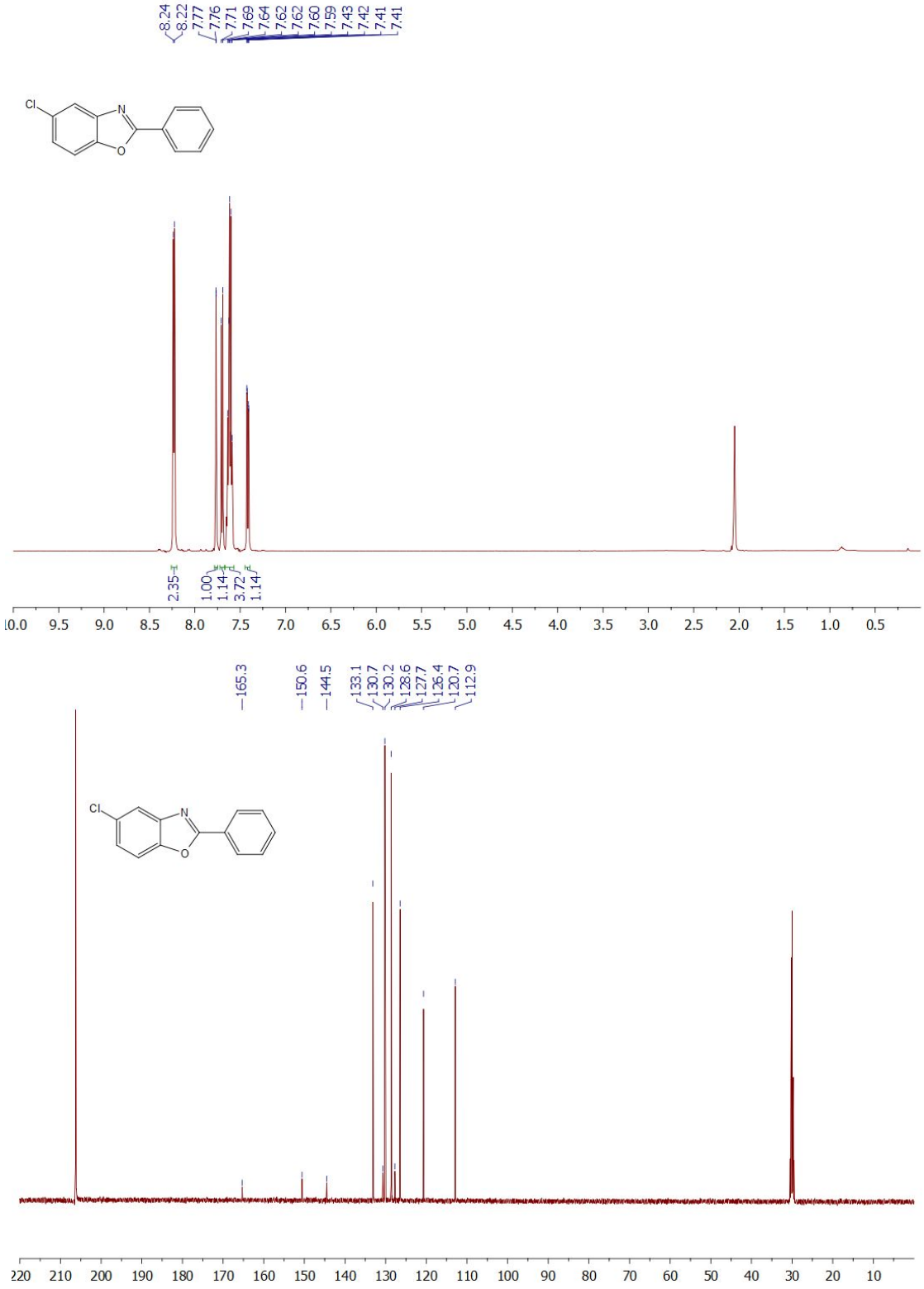


Figure S18. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-phenylbenzoxazole (14).

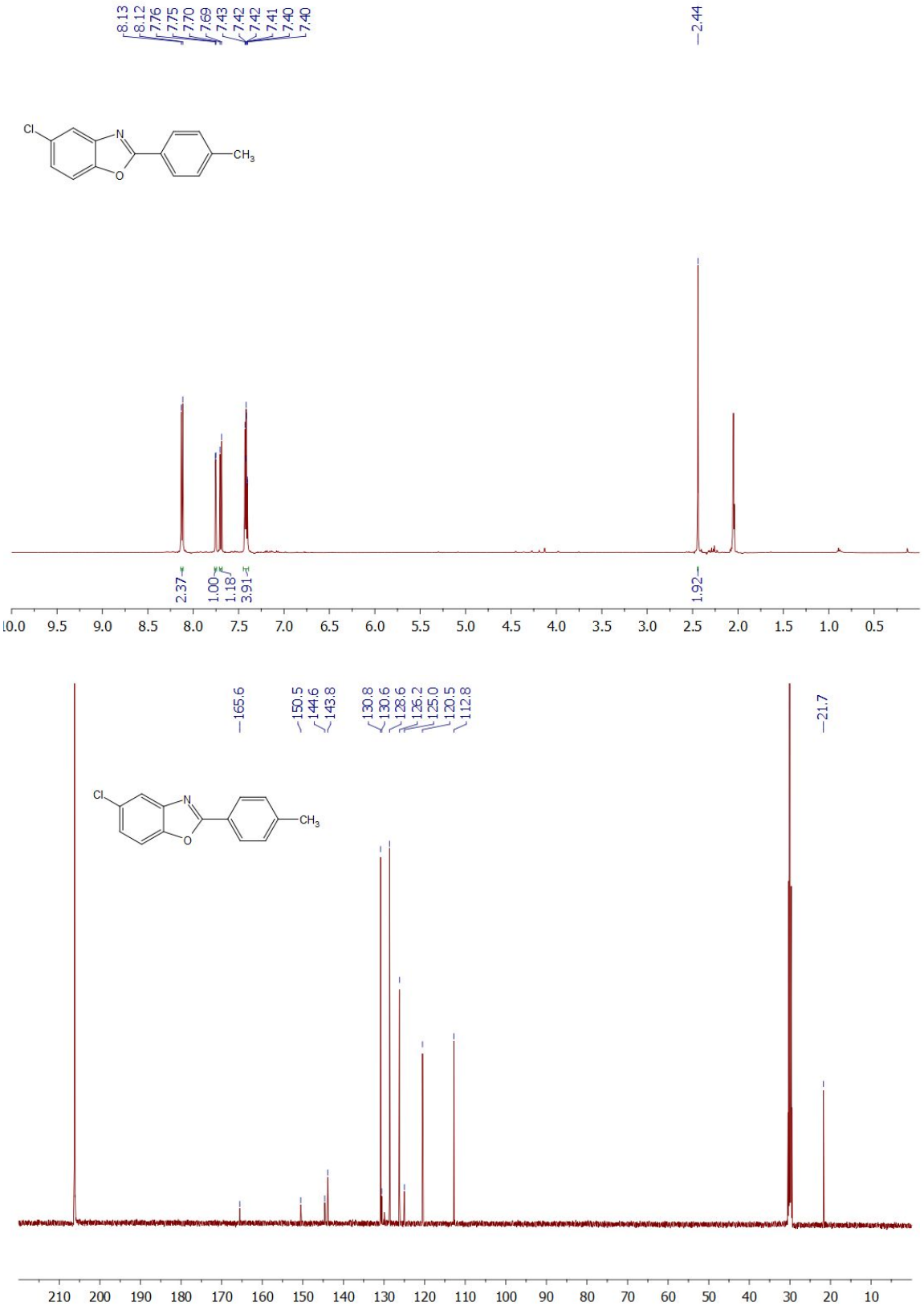


Figure S19. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-(*p*-tolyl)benzoxazole (15).

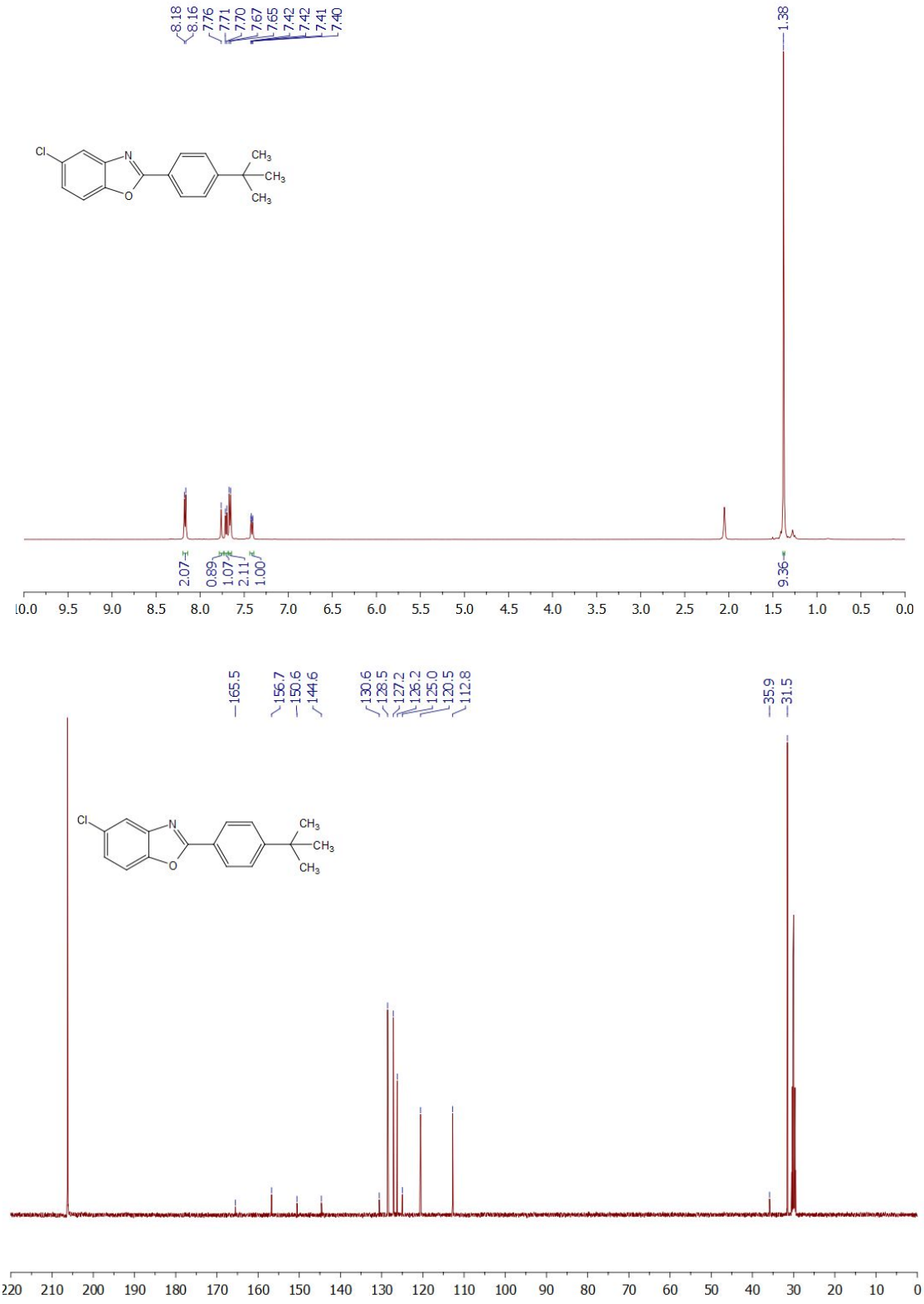


Figure S20. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-(4-*tert*-butylphenyl)benzoxazole (16).

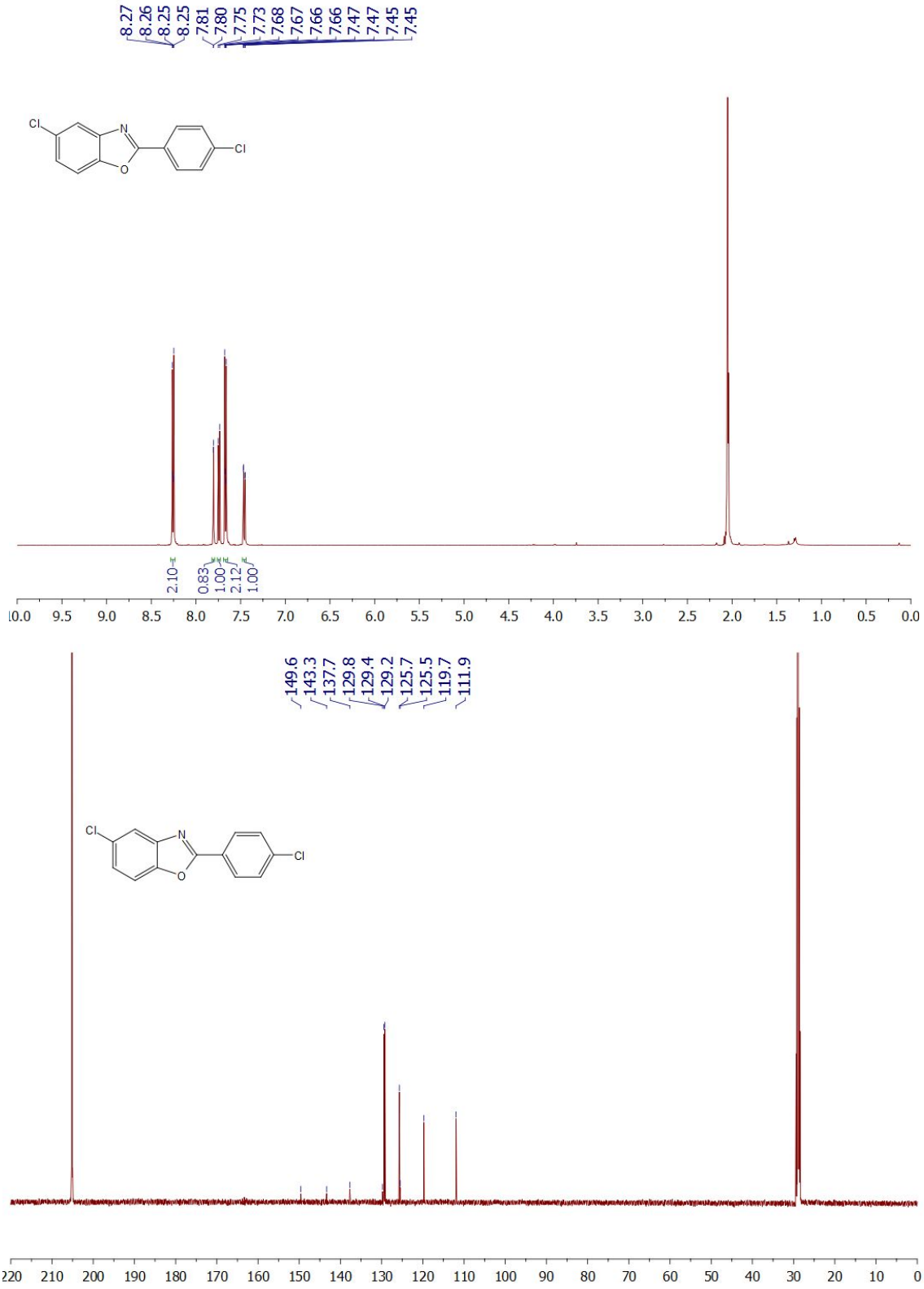


Figure S21. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-(4-chlorophenyl)benzoxazole (17).

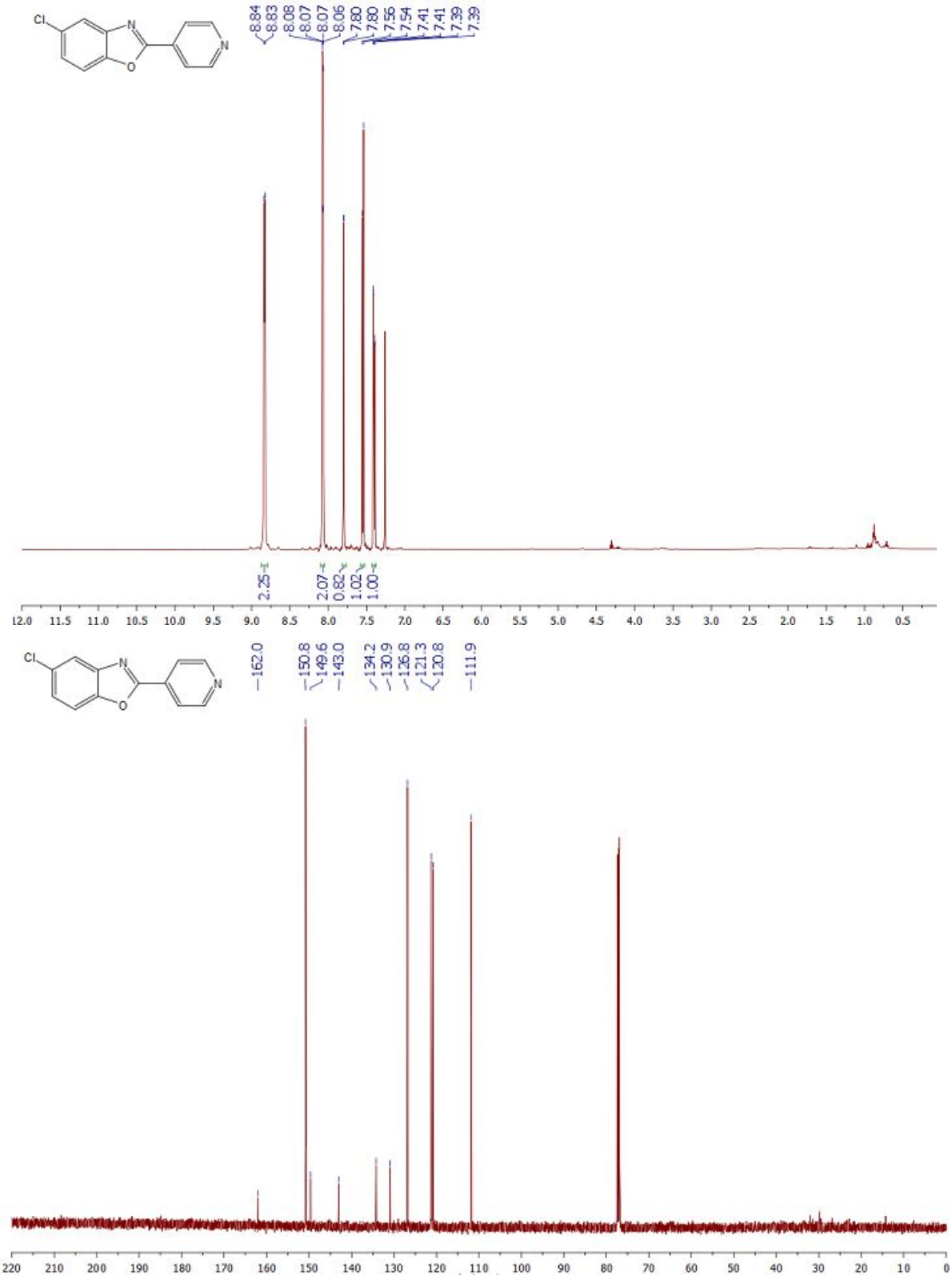


Figure S22. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-(pyridin-4-yl)benzoxazole (18).

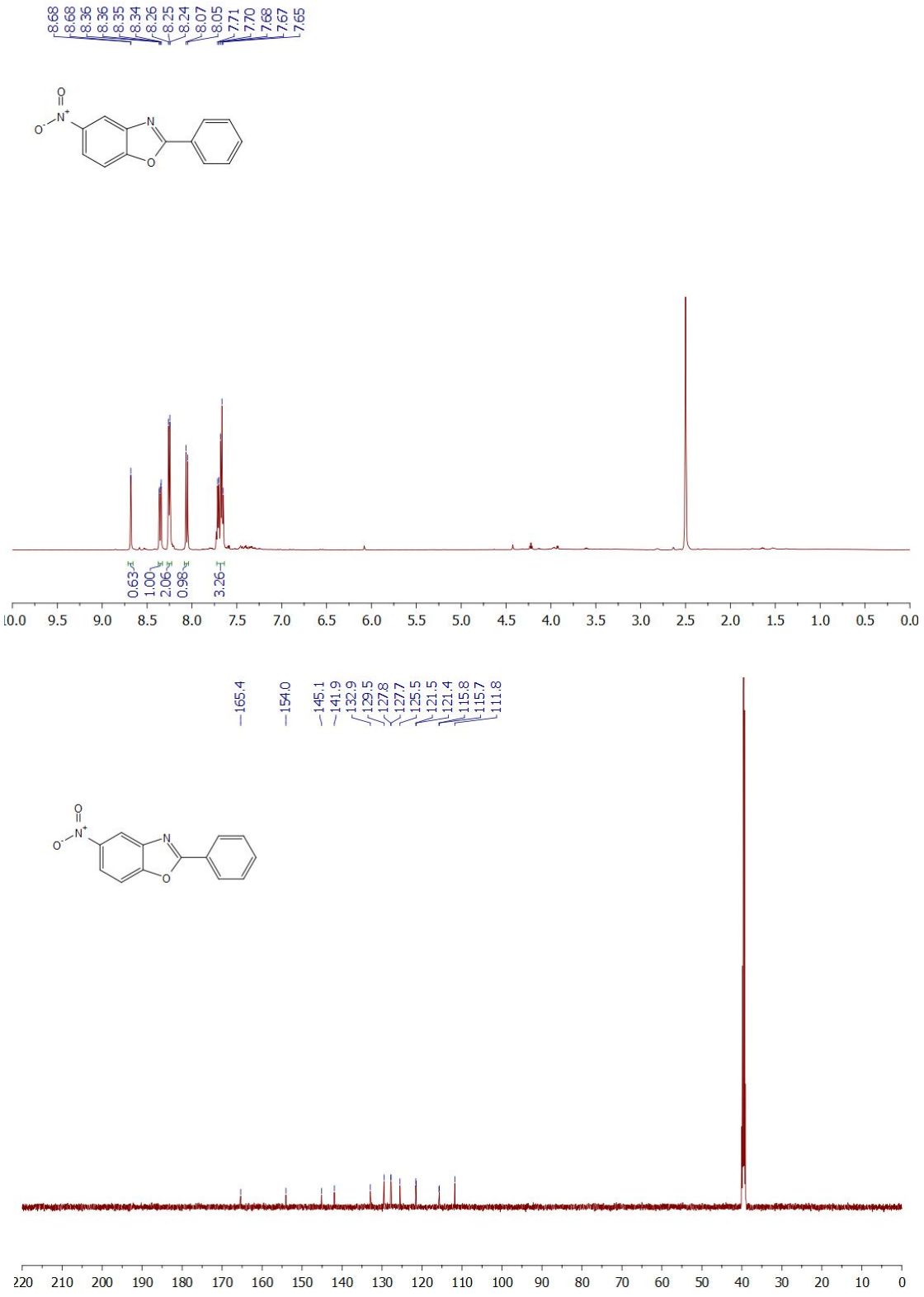


Figure S23. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-nitro-2-phenylbenzoxazole (19).

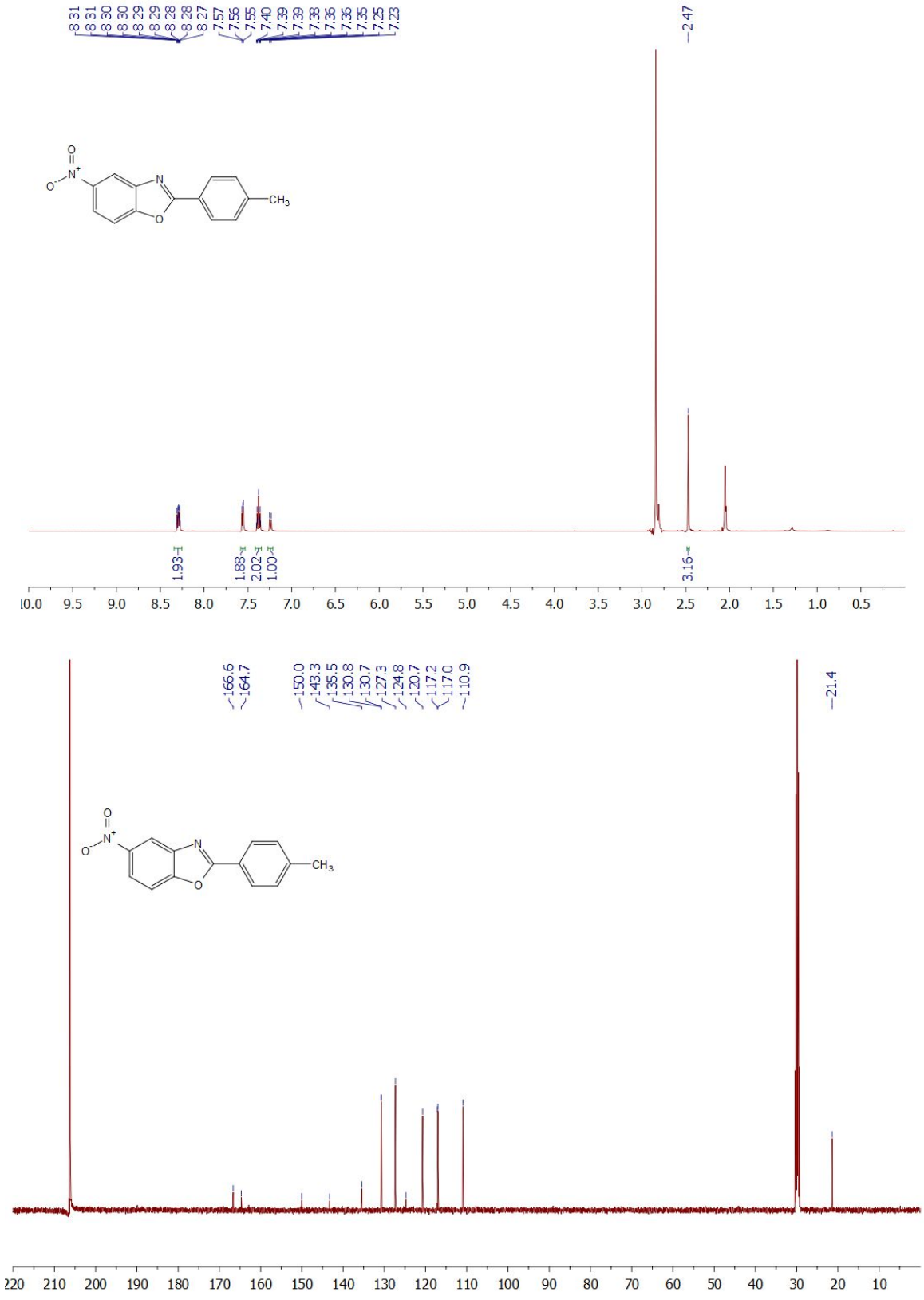


Figure S24. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-nitro-2-(*p*-tolyl)benzoxazole (20).

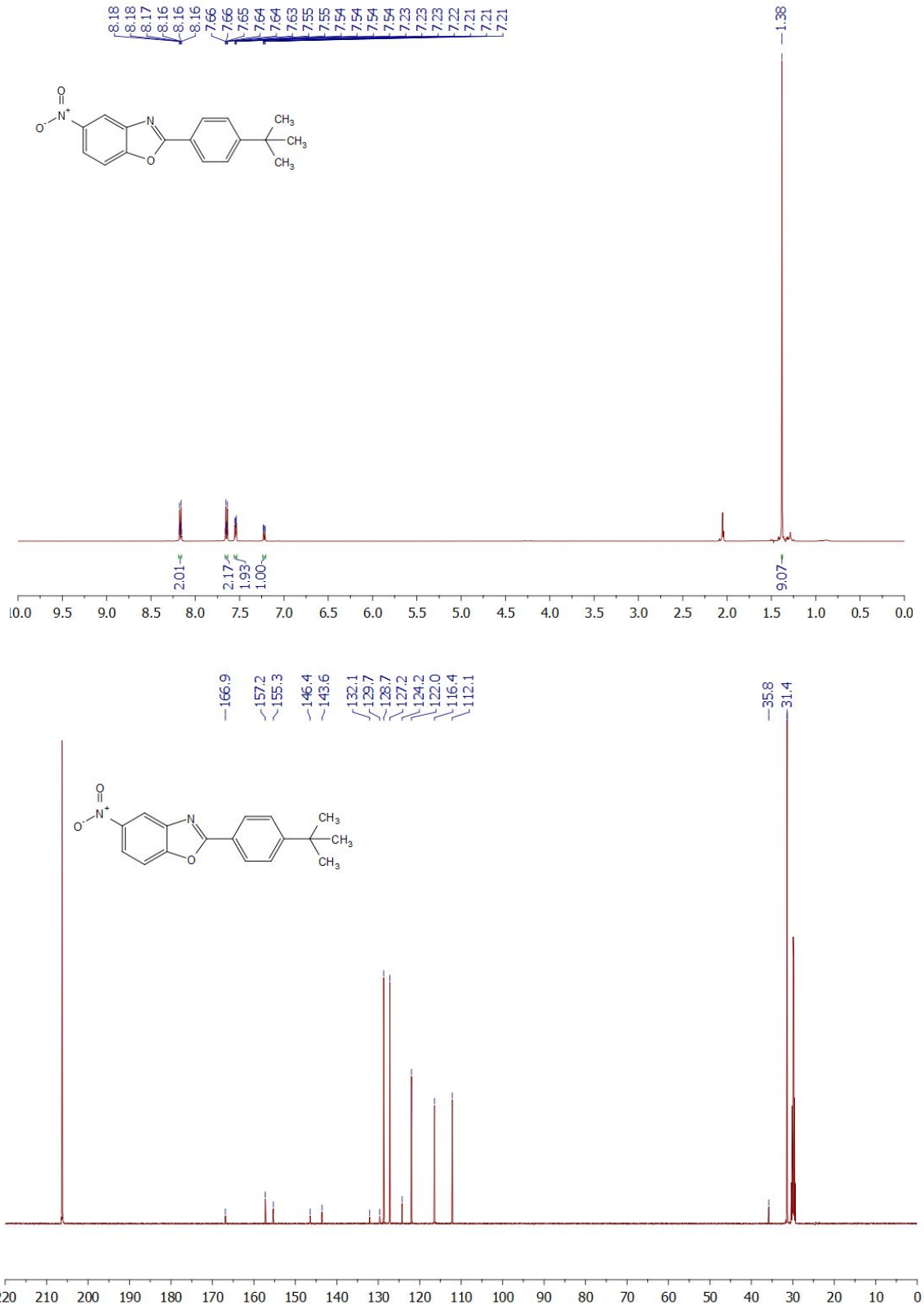


Figure S25. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-nitro-2-(4-*tert*-butylphenyl)benzoxazole (21).

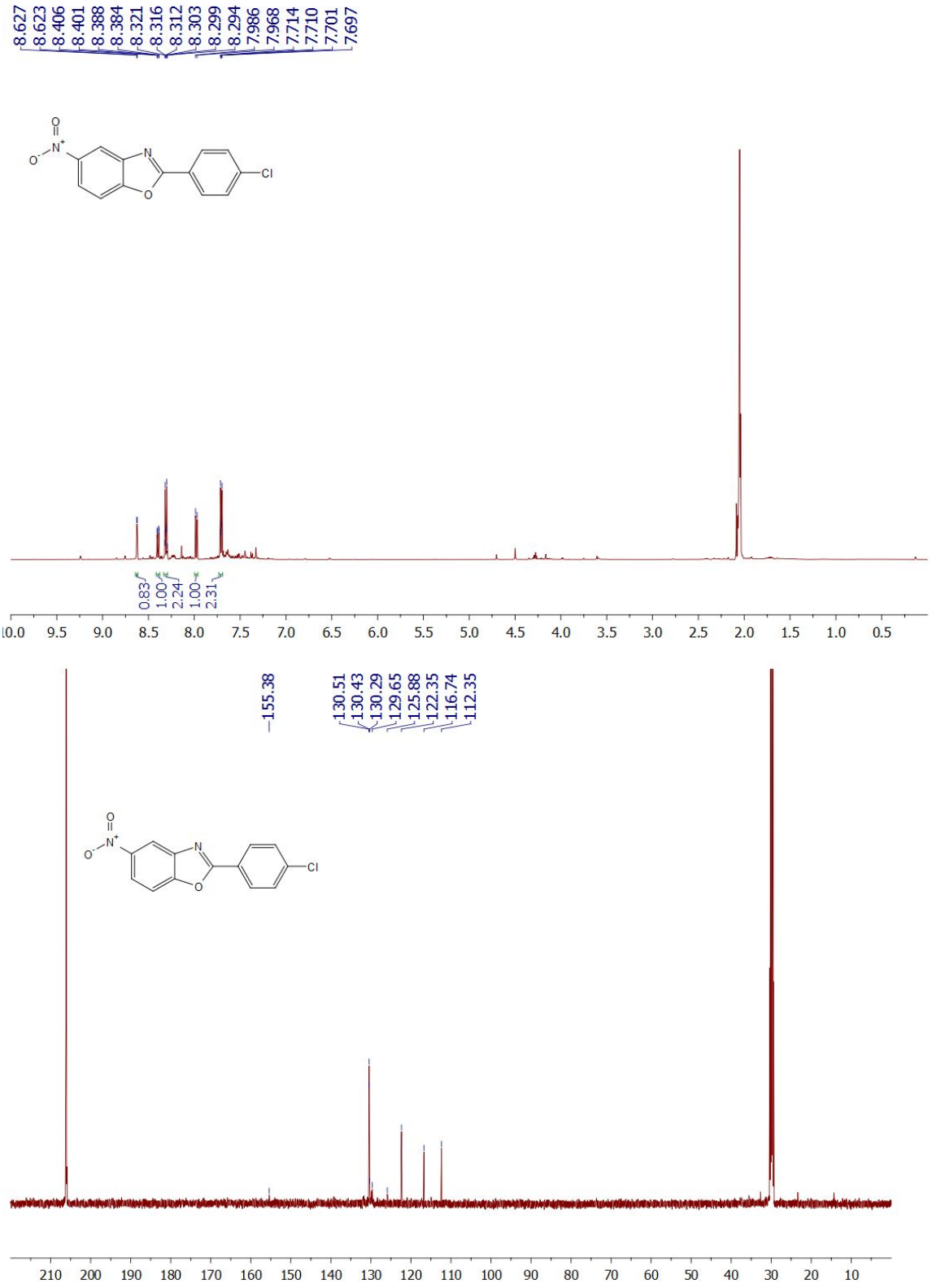


Figure S26. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-nitro-2-(4-chlorophenyl)benzoxazole (22).

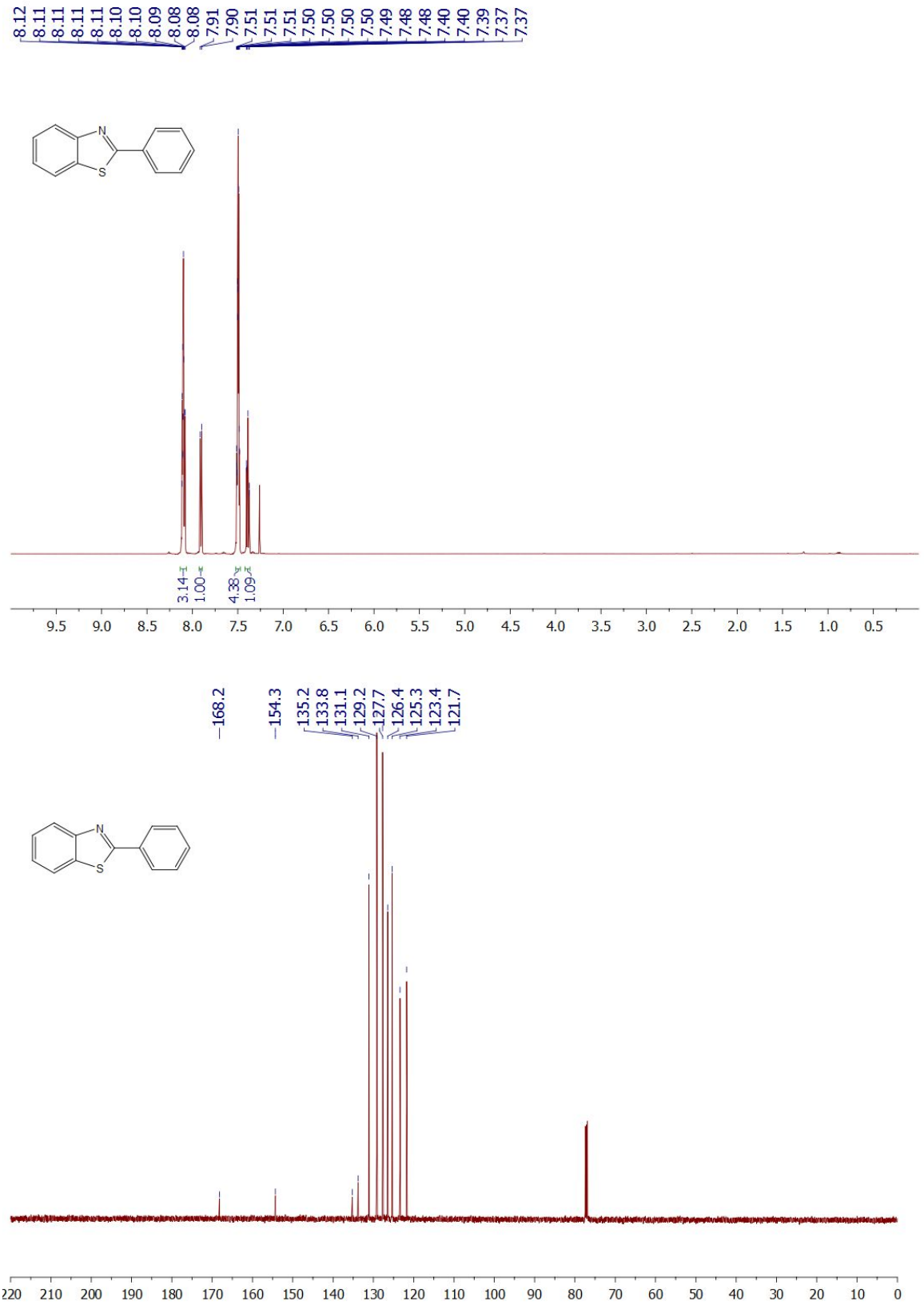


Figure S27. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenylbenzothiazole (23).

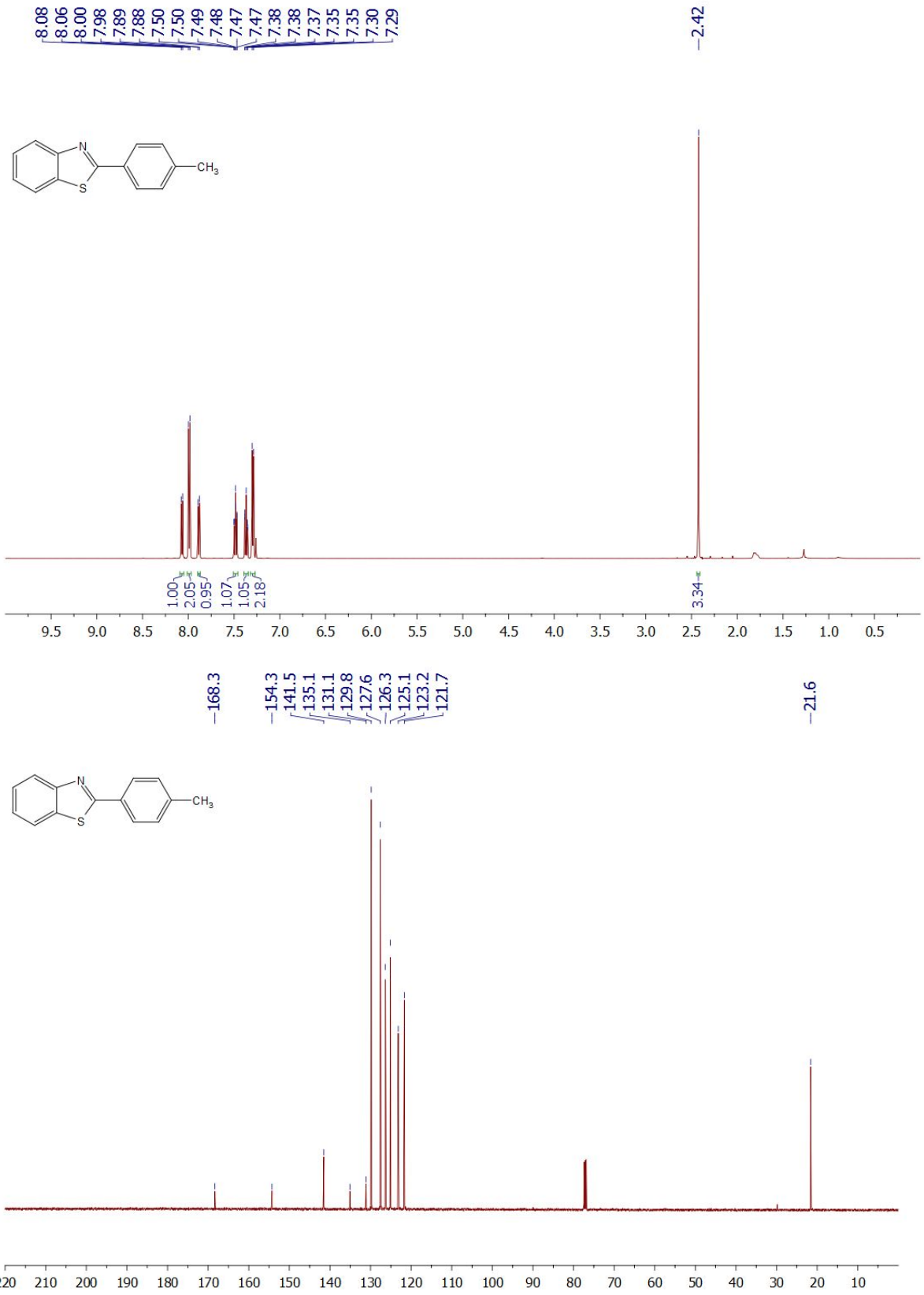


Figure S28. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(*p*-tolyl)benzothiazole (24).

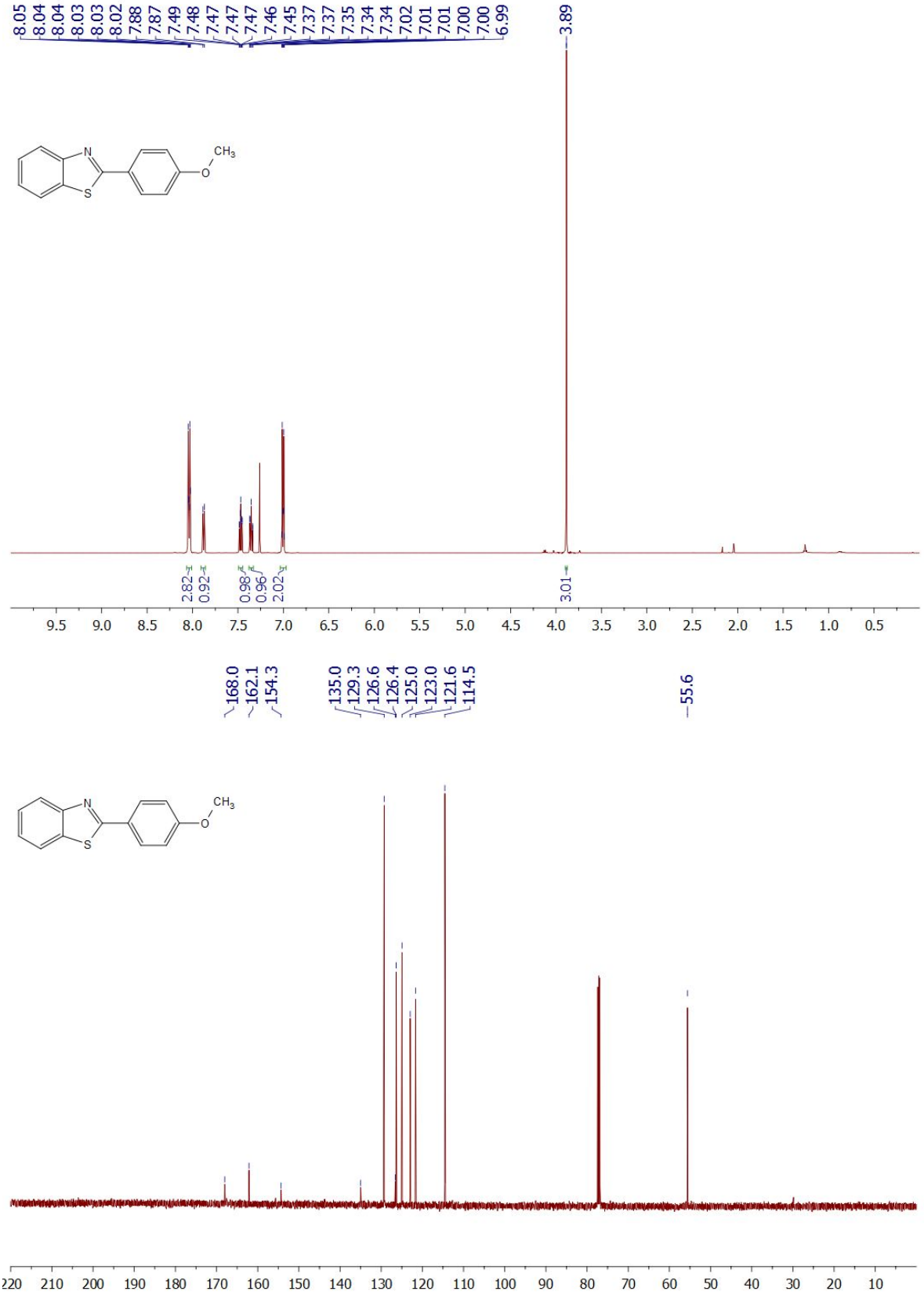


Figure S29. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-methoxyphenyl)benzothiazole (25).

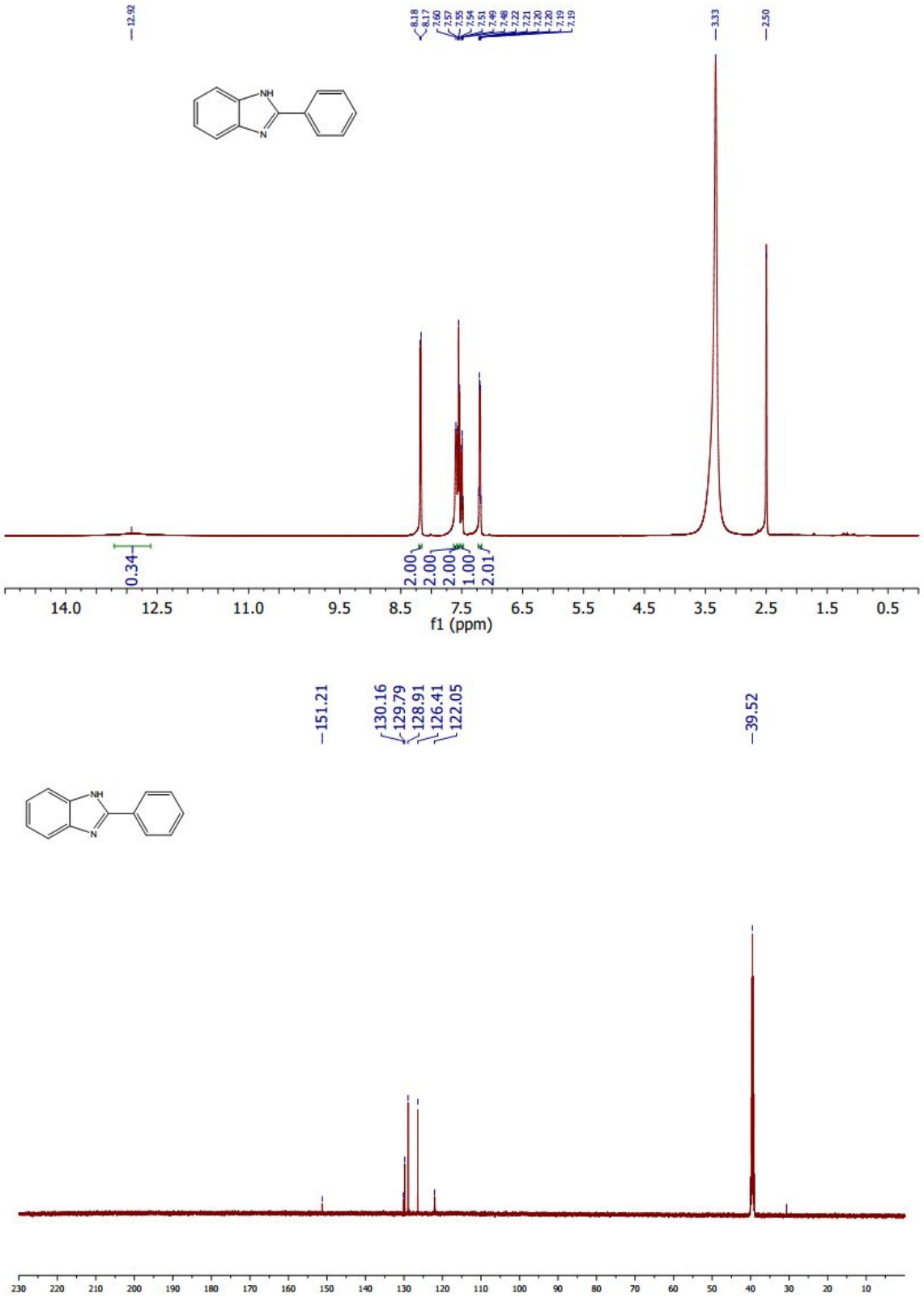


Figure S30. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenylbenzimidazole (26).

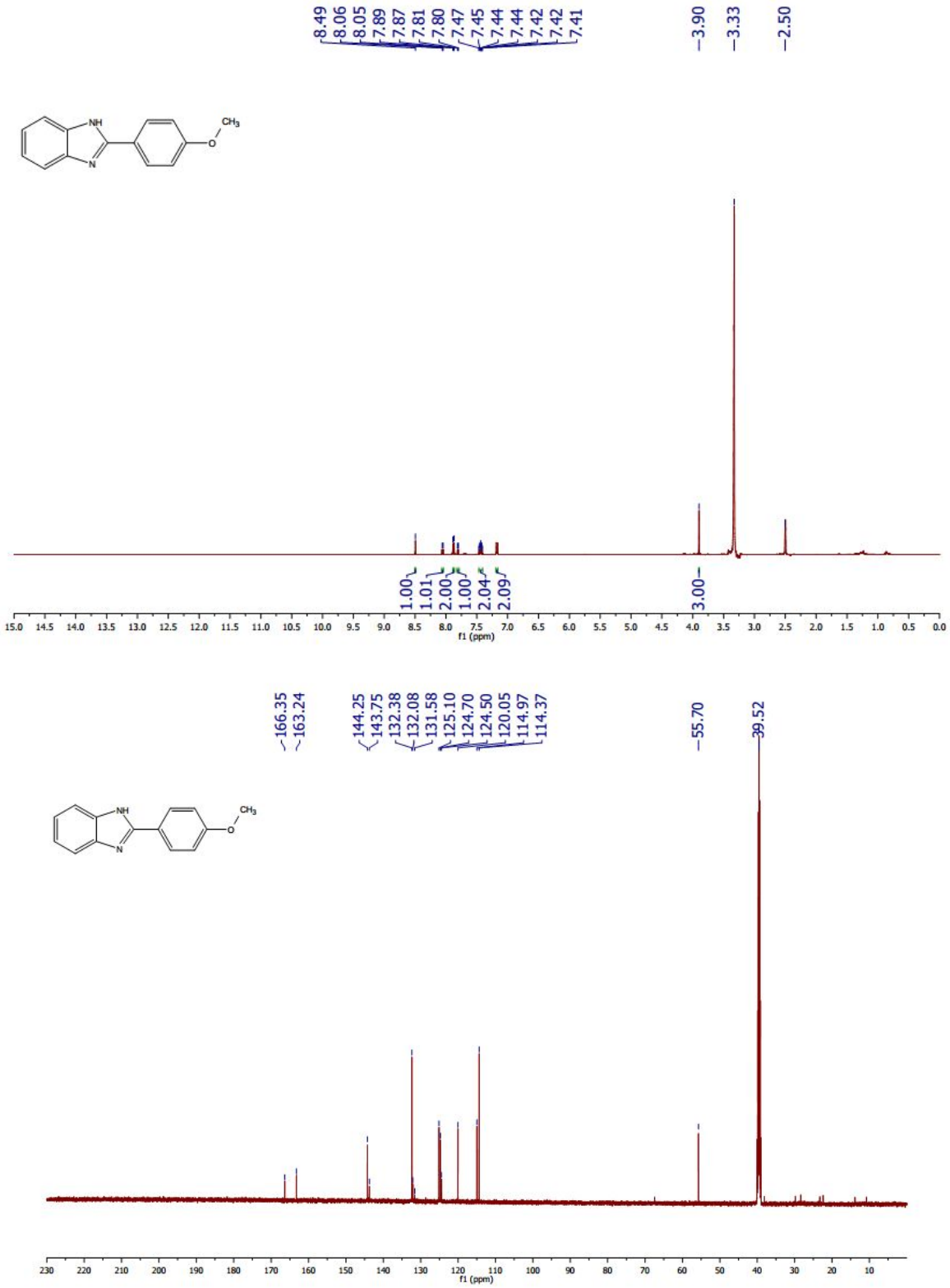


Figure S31. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-methoxyphenyl)benzimidazole (27).

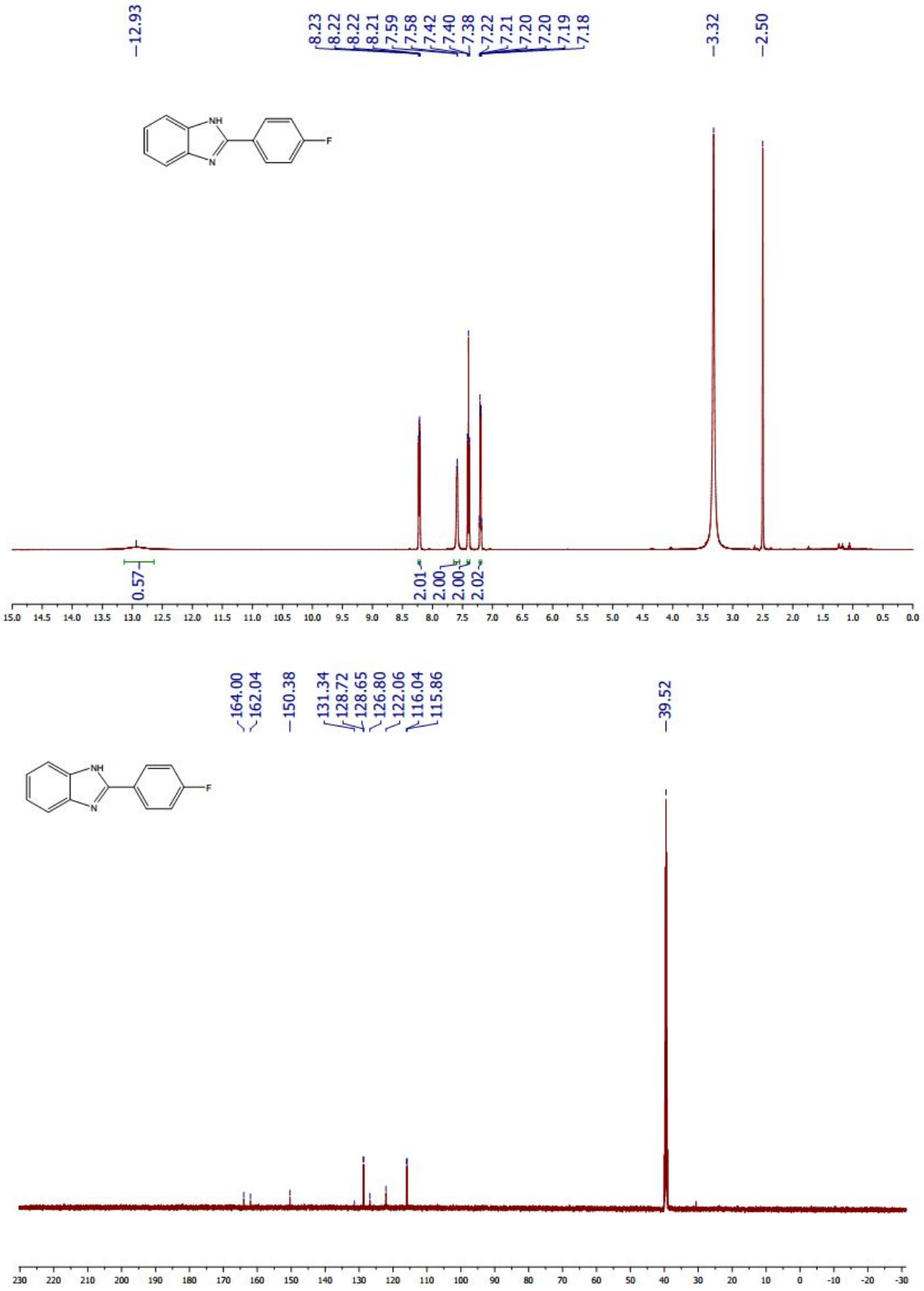


Figure S32. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-fluorophenyl)benzimidazole (28).

Section S3. References

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