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Synthesis of Benzimidazoles *via* Iridium-catalyzed Acceptorless Dehydrogenative Coupling

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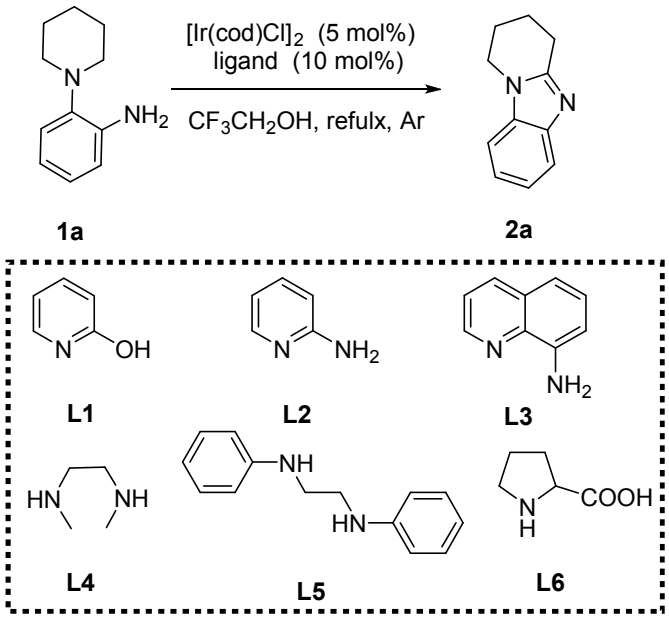
1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26, DMSO: δ 2.50). Chemical shifts of carbons are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0, DMSO: δ 39.5). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q) multiplet (m) and broad (br). Melting points were measured on a WRS-2A melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor 37 spectrophotometer. Data are represented as the frequency of absorption (cm^{-1}). All products were further characterized by HRMS (high resolution mass spectra) with the Shimadzu IT-TOF instrument. Anhydrous solvents were transferred by oven-dried syringes. $[Cp^*IrCl_2]_2$ and nitrogen ligands were purchased from Alfa-Aesar chemical company and used without further purification.

2. Screening of nitrogen ligands

Table S1: Screening of ligands.[a]

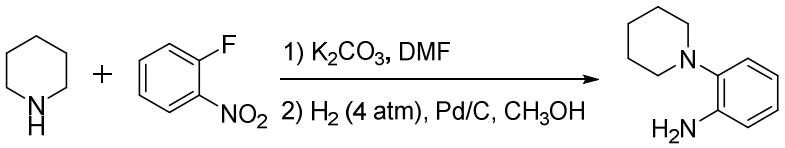


Entry	Ligand	Yield [%] [b]
1	**L1**	48
2	**L2**	52
3	**L3**	51
4	**L4**	6
5	**L5**	42
6	**L6**	20

[a] Conditions: **1a** (0.2 mmol), $[Ir(cod)Cl]_2$ (5 mol%), ligand (10 mol%), trifluoroethanol (2 mL), argon atmosphere, 80 °C, 72 h. [b] The yields were determined by ^1H NMR using dimethyl terephthalate as the internal standard.

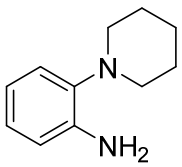
3. Preparation of the substrates

Typical procedure for the preparation of substrate:



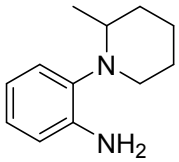
To a solution of K_2CO_3 (6.6 mmol) in DMF (8 mL), were added piperidine (6.6 mmol) and 2-fluoronitrobenzene (6 mmol). The reaction mixture was stirred at 120 °C for 12 h and then poured into water (100 mL). The mixture was extracted with ethyl acetate (25 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was dissolved in methanol (25 mL). Pd/C (10 %, 0.3 mmol) was added and the reaction mixture was hydrogenated (4 atm) at room temperature for 4 h. The mixture was filtered through a sintered glass funnel, and washed with methanol (5 mL). The filtrate was concentrated under vacuum. The residue was purified by flash column chromatography over silica gel to give **1a** as a white solid (0.97 g, 92% yield).

2-(piperidin-1-yl)aniline (1a)



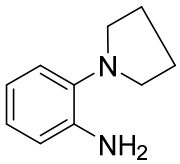
White solid, mp 44.8–46.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (dd, J = 8.2, 1.4 Hz, 1H), 6.93–6.87 (m, 1H), 6.75–6.70 (m, 2H), 3.96 (br, 2H), 2.83 (br, 4H), 1.73–1.66 (m, 4H), 1.57 (br, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 140.6, 124.1, 119.7, 118.4, 114.9, 52.6, 26.8, 24.3; **IR (KBr)** ν/cm^{-1}: 3431, 3340, 3065, 2932, 2842, 2793, 1606, 1499, 1453, 1437, 1274, 1231, 1206, 1139, 1110, 920, 744, 480; **HRMS** (ESI) calculated for $C_{11}H_{17}N_2$ $(M+H)^+$: 177.1386, found : 177.1386.

2-(2-methylpiperidin-1-yl)aniline (1b)



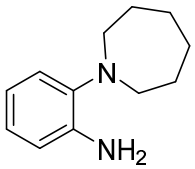
Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.95–6.90 (m, 1H), 6.74–6.68 (m, 2H), 4.15 (br, 2H), 2.96–2.88 (m, 2H), 2.51 (td, *J* = 11.4, 3.2 Hz, 1H), 1.81–1.75 (m, 2H), 1.71–1.58 (m, 2H), 1.48–1.32 (m, 2H), 0.84 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 138.5, 125.0, 122.8, 118.0, 114.9, 55.1, 35.1, 27.1, 24.5, 20.0; **IR (KBr)** *ν*/cm^{-1}: 3461, 3356, 3026, 2930, 2853, 2794, 1607, 1499, 1451, 1376, 1287, 1265, 1239, 1207, 1112, 745, 487; **HRMS** (ESI) calculated for $C_{12}H_{19}N_2$ $(M+H)^+$: 191.1543, found : 191.1552.

2-(pyrrolidin-1-yl)aniline (1c)



Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.91–6.85 (m, 1H), 6.76–6.69 (m, 2H), 3.84 (br, 2H), 3.08–3.01 (m, 4H), 1.95–1.88 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.2, 137.6, 123.3, 118.5, 118.4, 115.3, 50.7, 24.0; **IR (KBr)** *ν*/cm^{-1}: 3430, 3345, 3020, 2973, 2875, 2814, 1605, 1502, 1450, 1287, 1198, 1115, 962, 742, 473; **HRMS** (ESI) calculated for $C_{10}H_{15}N_2$ $(M+H)^+$: 163.1230, found : 163.1235.

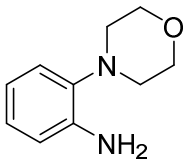
2-(azepan-1-yl)aniline (1d)



Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.91–6.86 (m, 1H), 6.75–6.67 (m, 2H), 4.02 (br, 2H), 3.06–3.00 (m, 4H), 1.79–1.71

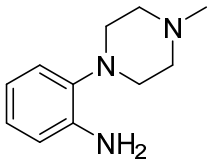
(m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 141.7, 124.1, 121.7, 118.5, 115.0, 55.8, 29.8, 26.9; **IR (KBr)** *ν*/cm^{-1}: 3440, 3345, 2921, 2854, 1606, 1498, 1454, 1265, 1176, 1153, 1016, 890, 740, 476; **HRMS** (ESI) calculated for $C_{12}H_{19}N_2$ $(M+H)^+$: 191.1543, found : 191.1551.

2-morpholinoaniline (1e)



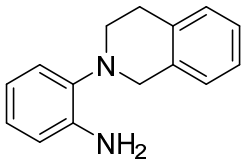
White solid, mp 98.0–100.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.95 (td, *J* = 7.6, 1.4 Hz, 1H), 6.78–6.71 (m, 2H), 3.98 (br, 2H), 3.87–3.81 (m, 4H), 2.94–2.89 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 138.9, 124.9, 119.8, 118.7, 115.2, 67.7, 51.5; **IR (KBr)** *ν*/cm^{-1}: 3411, 3327, 2974, 2857, 2834, 1619, 1589, 1505, 1445, 1372, 1299, 1275, 1255, 1221, 1202, 1111, 1068, 929, 757, 669; **HRMS** (ESI) calculated for $C_{10}H_{15}N_2O$ $(M+H)^+$: 179.1179, found : 179.1185.

2-(4-methylpiperazin-1-yl)aniline (1f)



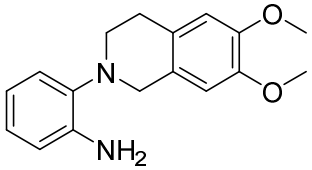
White solid, mp 87.3–89.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04–7.00 (m, 1H), 6.96–6.91 (m, 1H), 6.77–6.71 (m, 2H), 3.96 (br, 2H), 2.95 (t, *J* = 4.7 Hz, 4H), 2.58 (br, 4H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 139.2, 124.6, 119.9, 118.6, 115.1, 55.9, 51.0, 46.2; **IR (KBr)** *ν*/cm^{-1}: 3433, 3332, 2945, 2851, 1602, 1500, 1451, 1380, 1266, 1211, 745; **HRMS** (ESI) calculated for $C_{11}H_{18}N_3$ $(M+H)^+$: 192.1495, found : 192.1504.

2-(3,4-dihydroisoquinolin-2(1H)-yl)aniline (1g)



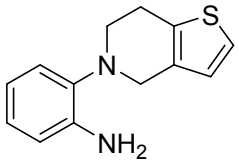
White solid, mp 110.5–112.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19–7.12 (m, 3H), 7.08–7.03 (m, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.79–6.72 (m, 2H), 4.08 (s, 2H), 4.00 (br, 2H), 3.23 (t, *J* = 5.8 Hz, 2H), 3.00 (t, *J* = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 139.2, 135.4, 134.3, 128.9, 126.4, 126.2, 125.7, 124.8, 120.1, 118.6, 115.1, 53.8, 49.3, 29.8; **IR (KBr)** *v*/cm^{-1}: 3692, 3428, 3340, 3018, 2898, 2807, 1606, 1500, 1454, 1380, 1288, 1267, 1206, 1145, 1035, 929, 743; **HRMS** (ESI) calculated for $C_{15}H_{17}N_2$ $(M+H)^+$: 225.1386, found: 225.1396.

2-(6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)aniline (1h)



White solid, mp 126.2–128.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.96 (td, *J* = 7.7, 1.4 Hz, 1H), 6.79–6.74 (m, 2H), 6.66 (s, 1H), 6.57 (s, 1H), 4.01 (br, 4H), 3.87 (s, 3H), 3.85 (s, 3H), 3.22 (t, *J* = 5.7 Hz, 2H), 2.92 (t, *J* = 5.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 147.3, 141.8, 139.3, 127.3, 126.2, 124.7, 120.2, 118.6, 115.1, 111.7, 109.3, 55.9, 53.4, 49.3, 29.4; **IR (KBr)** *v*/cm^{-1}: 3430, 3340, 2960, 2885, 2821, 1606, 1516, 1497, 1462, 1370, 1255, 1228, 1185, 1114, 1024, 857, 745; **HRMS** (ESI) calculated for $C_{17}H_{21}N_2O_2$ $(M+H)^+$: 285.1598, found : 285.1591.

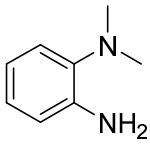
2-(6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)aniline (1i)



White solid, mp 103.9–106.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 5.1 Hz, 1H), 7.07–7.03 (m, 1H), 6.96 (td, *J* = 7.8, 1.3 Hz, 1H), 6.80–6.71 (m, 3H), 4.01 (br,

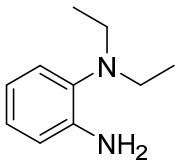
4H), 3.27 (t, *J* = 5.5 Hz, 2H), 2.97 (t, *J* = 5.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.9, 138.9, 134.4, 133.5, 125.1, 124.9, 122.7, 120.6, 118.6, 115.2, 51.0, 49.3, 26.2; **IR (KBr)** *v*/cm^{-1}: 3423, 3335, 3096, 2899, 2830, 1611, 1585, 1499, 1452, 1320, 1297, 1269, 1228, 1207, 1182, 1158, 1120, 996, 919, 739; **HRMS** (ESI) calculated for $C_{13}H_{15}N_2S$ $(M+H)^+$: 231.0950, found : 231.0942.

N^1,*N*^{1}-dimethylbenzene-1,2-diamine (1k)



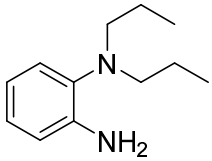
Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.90 (td, *J* = 7.6, 1.4 Hz, H), 6.75–6.68 (m, 2H), 3.94 (br, 2H), 2.65 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.4, 140.6, 124.1, 119.3, 118.4, 115.1, 43.6; **IR (KBr)** *v*/cm^{-1}: 3438, 3347, 3028, 2946, 2843, 2795, 1608, 1500, 1453, 1364, 1295, 1265, 1215, 1167, 1099, 939, 745, 698; **HRMS** (ESI) calculated for $C_8H_{13}N_2$ $(M+H)^+$: 137.1073, found : 137.1068.

N^1,*N*^{1}-diethylbenzene-1,2-diamine (1l)



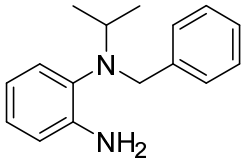
Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.96–6.89 (m, 1H), 6.77–6.68 (m, 2H), 4.07 (br, 2H), 2.94 (q, *J* = 7.1 Hz, 4H), 0.98 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.1, 137.1, 124.7, 122.9, 118.0, 115.0, 47.6, 12.6; **IR (KBr)** *v*/cm^{-1}: 3450, 3352, 3024, 2972, 2927, 2816, 1604, 1498, 1450, 1376, 1286, 1228, 1171, 1135, 1086, 742, 484; **HRMS** (ESI) calculated for $C_{10}H_{17}N_2$ $(M+H)^+$: 165.1386, found : 165.1378.

N^1,*N*^{1}-dipropylbenzene-1,2-diamine (1m)



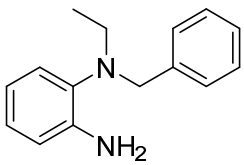
Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.92 (ddd, *J* = 7.8, 7.3, 1.5 Hz, 1H), 6.75–6.68 (m, 2H), 4.08 (br, 2H), 2.87–2.80 (m, 4H), 1.48–1.38 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 137.9, 124.7, 122.9, 118.1, 115.0, 56.1, 20.6, 11.7; **IR (KBr)** *v*/cm^{-1}: 3457, 3362, 3021, 2962, 2878, 2809, 1610, 1500, 1460, 1382, 1301, 1277, 1215, 1133, 1080, 752, 598; **HRMS** (ESI) calculated for $C_{12}H_{21}N_2$ $(M+H)^+$: 193.1699, found : 193.1690.

N^1-benzyl-*N*^{1}-isopropylbenzene-1,2-diamine (1o)



White solid, mp 67.0–69.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.15 (m, 4H), 7.13–7.09 (m, 1H), 7.08–7.04 (m, 1H), 6.87–6.82 (m, 1H), 6.65–6.60 (m, 2H), 4.13 (s, 2H), 3.98 (br, 2H), 3.29 (dq, *J* = 13.2, 6.6 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 139.9, 136.1, 128.3, 127.9, 126.5, 124.8, 124.6, 117.7, 115.2, 52.3, 51.2, 19.5; **IR (KBr)** *v*/cm^{-1}: 3372, 3274, 3033, 2966, 2863, 1607, 1497, 1461, 1385, 1364, 1265, 1230, 1146, 1077, 1041, 926, 868, 745, 711; **HRMS** (ESI) calculated for $C_{16}H_{21}N_2$ $(M+H)^+$: 241.1699, found : 241.1685.

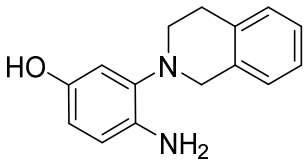
N^1-benzyl-*N*^{1}-ethylbenzene-1,2-diamine (1p)



Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5H), 7.02 (dd, *J*=7.8, 1.3 Hz, 1H), 6.93 (td, *J*=7.8, 1.4 Hz, 1H), 6.76–6.68 (m, 2H), 4.10 (br, 2H), 4.03 (s, 2H), 2.93 (q, *J*=7.1, 2H), 0.97 (t, *J*=7.1, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 139.0, 137.2, 128.7, 128.1, 126.9, 124.8, 122.9, 118.1, 115.1, 58.1, 46.1, 12.1; **IR (KBr)**

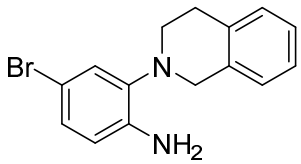
ν/cm^{-1}: 3443, 3351, 3027, 2969, 2929, 2821, 1606, 1498, 1453, 1368, 1290, 1204, 1157, 1108, 745, 698; **HRMS** (ESI) calculated for $C_{15}H_{19}N_2$ $(M+H)^+$: 227.1543, found : 227.1532.

4-amino-3-(3,4-dihydroisoquinolin-2(1H)-yl)phenol (3f)



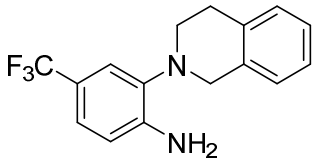
Light yellow solid, mp 186.8–190.3 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.41 (s, 1H), 7.17–7.09 (m, 4H), 6.54 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 2.6 Hz, 1H), 6.30 (dd, J = 8.4, 2.6 Hz, 1H), 4.16 (br, 2H), 3.98 (s, 2H), 3.09 (t, J = 5.8 Hz, 2H), 2.93 (t, J = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO) δ 149.1, 139.2, 135.3, 134.3, 134.2, 128.7, 126.4, 126.1, 125.6, 115.5, 110.4, 107.1, 52.9, 48.5, 29.1; **IR (KBr)** ν/cm^{-1}: 3366, 3292, 3021, 2889, 2819, 1608, 1558, 1515, 1470, 1454, 1382, 1327, 1235, 1171, 1132, 951, 756, 728; **HRMS** (ESI) calculated for $C_{15}H_{17}N_2O$ $(M+H)^+$: 241.1335, found : 241.1331.

4-bromo-2-(3,4-dihydroisoquinolin-2(1H)-yl)aniline (3g)



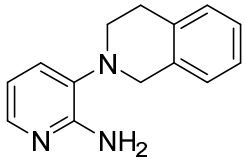
White solid, mp 76.8–79.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.13 (m, 4H), 7.10–7.02 (m, 2H), 6.63 (d, J = 8.4 Hz, 1H), 4.06 (s, 2H), 4.00 (br, 2H), 3.21 (t, J = 5.8 Hz, 2H), 3.01 (t, J = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.8, 140.5, 134.9, 134.0, 128.9, 127.4, 126.4, 126.3, 125.8, 123.4, 116.2, 109.8, 53.6, 49.2, 29.8; **IR (KBr)** ν/cm^{-1}: 3448, 3342, 3016, 2954, 2925, 2782, 1598, 1490, 1452, 1378, 1277, 1199, 1133, 929, 811, 746; **HRMS** (ESI) calculated for $C_{15}H_{16}BrN_2$ $(M+H)^+$: 303.0491, found :303.0478.

2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-(trifluoromethyl)aniline (3h)



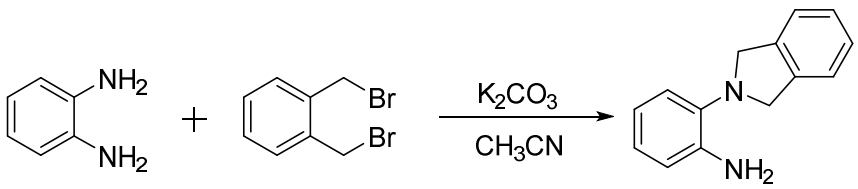
Light yellow solid, mp 97.0–99.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.27 (m, 1H), 7.23–7.15 (m, 4H), 7.10–7.06 (m, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.29 (br, 2H), 4.07 (s, 2H), 3.23 (t, *J* = 5.7 Hz, 2H), 3.04 (t, *J* = 5.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 138.7, 134.8, 134.0, 128.9, 126.5, 126.4, 125.8, 124.8 (q, $^1J_{CF3}$ = 269 Hz), 122.1 (q, $^3J_{CF3}$ = 4 Hz), 120.2 (q, $^2J_{CF3}$ = 32 Hz), 117.3 (q, $^3J_{CF3}$ = 4 Hz), 114.2, 53.6, 49.3, 29.9; **IR (KBr)** *ν*/cm^{-1}: 3452, 3349, 2935, 2850, 2785, 1617, 1581, 1517, 1435, 1331, 1300, 1282, 1200, 1145, 1100, 1068, 960, 817, 756; **HRMS** (ESI) calculated for $C_{16}H_{16}F_3N_2$ $(M+H)^+$: 293.1260, found : 293.1252.

3-(3,4-dihydroisoquinolin-2(1H)-yl)pyridin-2-amine (3i)



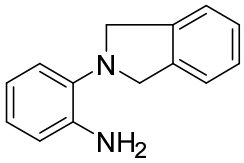
White solid, mp 130.7–132.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.21–7.14 (m, 3H), 7.10–7.06 (m, 1H), 6.67 (dd, *J* = 7.6, 5.0 Hz, 1H), 4.76 (br, 2H), 4.10 (s, 2H), 3.25 (t, *J* = 5.8 Hz, 2H), 3.00 (t, *J* = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 142.7, 134.7, 134.0, 133.9, 128.9, 126.6, 126.4, 126.3, 125.8, 114.1, 53.3, 48.7, 29.4; **IR (KBr)** *ν*/cm^{-1}: 3425, 3261, 3122, 2918, 2900, 1620, 1588, 1463, 1382, 1269, 1200, 1133, 1038, 928, 768, 742; **HRMS** (ESI) calculated for $C_{14}H_{16}N_3$ $(M+H)^+$: 226.1339, found : 226.1349.

Procedure for the preparation of substrate 1j:



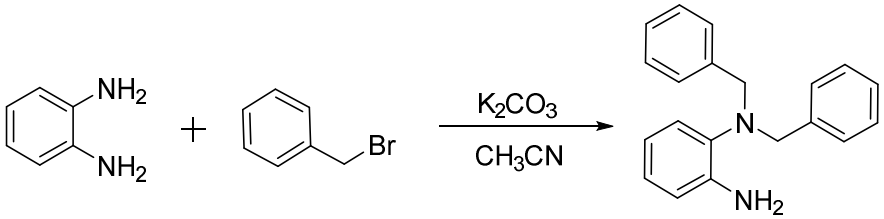
To a solution of K_2CO_3 (6.6 mmol) in acetonitrile (8 mL), were added 1,2-diaminobenzene (6.6 mmol) and 1,2-bis(bromomethyl)-benzen (6 mmol). The reaction mixture was stirred at 75 °C for 12 h. After completed, the reaction was cooled to room temperature, and then the mixture was filtered through a sintered glass funnel. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography over silica gel to give **1j** as a white solid (1.07 g, 85% yield).

2-(isoindolin-2-yl)aniline (1j)



White solid, mp 100.8–103.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 4H), 7.21–7.16 (m, 1H), 6.96–6.91 (m, 1H), 6.79–6.74 (m, 2H), 4.45 (s, 4H), 3.95 (br, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 139.8, 136.8, 126.8, 124.3, 122.3, 120.4, 118.7, 115.7, 56.4; **IR (KBr)** ν/cm^{-1}: 3414, 3329, 3027, 2940, 2802, 1616, 1500, 1457, 1353, 1280, 1266, 1244, 1166, 745, 689; **HRMS** (ESI) calculated for $C_{14}H_{15}N_2$ $(M+H)^+$: 211.1230, found : 211.1232.

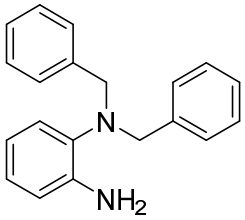
Procedure for the preparation of substrate 1n:



To a solution of K_2CO_3 (6.6 mmol) in acetonitrile (5 mL), were added 1,2-diaminobenzene (6 mmol) and benzyl bromide (6.6 mmol). The reaction mixture was stirred at room temperature for 2 h. Then the mixture was filtered through a sintered glass funnel. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography over silica gel to give **1n** as a light yellow

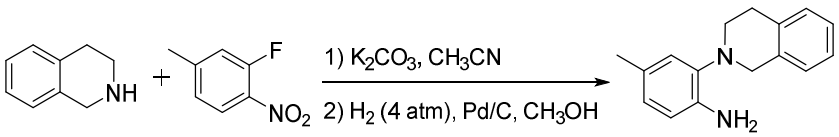
oil (0.33 g, 19% yield).

N^1,N^1-dibenzylbenzene-1,2-diamine (1n)



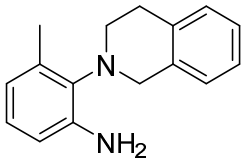
Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.19 (m, 10H), 6.93–6.85 (m, 2H), 6.72 (dd, J = 7.8, 1.4 Hz, 1H), 6.63 (td, J = 7.6, 1.4 Hz, 1H), 4.08 (br, 2H), 4.05 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 138.2, 137.1, 128.9, 128.1, 127.0, 124.9, 123.2, 118.1, 115.3, 56.2; **IR (KBr)** ν/cm^{-1}: 3445, 3352, 3062, 3028, 2927, 2842, 1726, 1606, 1498, 1452, 1374, 1277, 1190, 1120, 1070, 1029, 956, 740, 697, 499; **HRMS** (ESI) calculated for $C_{20}H_{21}N_2$ $(M+H)^+$: 289.1699, found : 289.1691.

Typical procedure for the preparation of substrate 3a-3d, 3f:



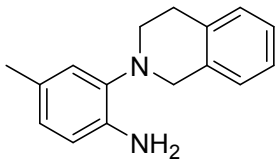
To a solution of K_2CO_3 (6.6 mmol) in acetonitrile (5 mL), were added 1,2,3,4-tetrahydroisoquinoline (6.6 mmol) and 2-fluoro-4-methyl-1-nitrobenzene (6 mmol). The reaction mixture was stirred at 75 °C for 12 h. After completed, the reaction was cooled to room temperature, and then the mixture was filtered through a sintered glass funnel. The filtrate was concentrated under vacuum and the residue was dissolved in methanol (25 mL). Pd/C (10 %, 0.3 mmol) was added and the reaction mixture was hydrogenated (4 atm) at room temperature for 4 h. The mixture was filtered through a sintered glass funnel, and washed with methanol (5 mL). The filtrate was concentrated under vacuum. The residue was purified by flash column chromatography over silica gel to give **3a** as a white solid (1.12 g, 78% yield).

2-(3,4-dihydroisoquinolin-2(1H)-yl)-3-methylaniline (3a)



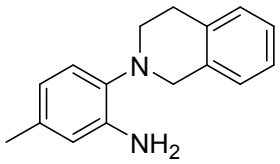
White solid, mp 109.2–112.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 3H), 7.07–7.02 (m, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.54–6.50 (m, 1H), 4.41 (d, *J* = 15.6 Hz, 1H), 4.17 (br, 2H), 4.05 (d, *J* = 15.6 Hz, 1H), 3.56 (td, *J* = 11.2, 3.4 Hz, 1H), 3.28–3.21 (m, 1H), 3.18–3.08 (m, 1H), 2.87–2.80 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 137.0, 135.8, 135.2, 134.9, 129.2, 126.4, 126.3, 125.9, 125.6, 121.1, 112.8, 50.9, 48.2, 31.5, 19.5; **IR (KBr)** *ν*/cm^{-1}: 3444, 3348, 3020, 2955, 2927, 2834, 2798, 1596, 1482, 1452, 1380, 1287, 1202, 1155, 933, 773, 749; **HRMS** (ESI) calculated for $C_{16}H_{19}N_2$ $(M+H)^+$: 239.1543, found : 239.1532.

2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-methylaniline (3b)



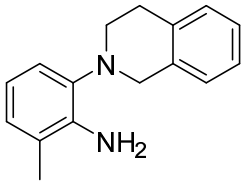
White solid, mp 79.2–81.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 3H), 7.07–7.03 (m, 1H), 6.87 (d, *J* = 1.5 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.06 (s, 2H), 3.84 (br, 2H), 3.20 (t, *J* = 5.8 Hz, 2H), 3.00 (t, *J* = 5.8 Hz, 2H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.3, 139.1, 135.5, 134.3, 128.8, 127.9, 126.4, 126.2, 125.6, 125.0, 120.7, 115.2, 53.8, 49.4, 30.0, 20.7; **IR (KBr)** *ν*/cm^{-1}: 3427, 3336, 3021, 2923, 2901, 2805, 2776, 2749, 1615, 1580, 1512, 1451, 1384, 1280, 1265, 1226, 1131, 1023, 930, 808, 755, 636; **HRMS** (ESI) calculated for $C_{16}H_{19}N_2$ $(M+H)^+$: 239.1543, found : 239.1536.

2-(3,4-dihydroisoquinolin-2(1H)-yl)-5-methylaniline (3c)



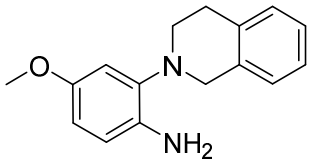
White solid, mp 127.3–129.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 3H), 7.06–7.02 (m, 1H), 6.96–6.92 (m, 1H), 6.58 – 6.54 (m, 2H), 4.04 (s, 2H), 3.95 (br, 2H), 3.18 (t, *J* = 5.7 Hz, 2H), 2.98 (t, *J* = 5.7 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.6, 136.9, 135.5, 134.4, 134.3, 128.8, 126.4, 126.2, 125.6, 120.0, 119.1, 115.9, 54.1, 49.5, 29.9, 21.0; **IR (KBr)** *v*/cm^{-1}: 3446, 3352, 3019, 2957, 2930, 2833, 2785, 1602, 1579, 1480, 1380, 1277, 1244, 1160, 930, 774; **HRMS** (ESI) calculated for $C_{16}H_{19}N_2$ $(M+H)^+$: 239.1543, found : 239.1534.

2-(3,4-dihydroisoquinolin-2(1H)-yl)-6-methylaniline (3d)



White solid, mp 107.6–109.4 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.18–7.10 (m, 4H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 4.51 (br, 2H), 3.97 (s, 2H), 3.08 (t, *J* = 5.2 Hz, 2H), 2.95 (t, *J* = 5.3 Hz, 2H), 2.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.1, 138.9, 135.5, 134.3, 128.9, 126.4, 126.2, 126.1, 125.7, 122.4, 117.9, 117.8, 54.1, 49.6, 30.0, 17.7; **IR (KBr)** *v*/cm^{-1}: 3458, 3360, 3019, 2958, 2927, 2896, 2820, 2782, 1607, 1574, 1481, 1380, 1347, 1310, 1275, 1230, 1168, 1108, 933, 777, 739; **HRMS** (ESI) calculated for $C_{16}H_{19}N_2$ $(M+H)^+$: 239.1543, found : 239.1534.

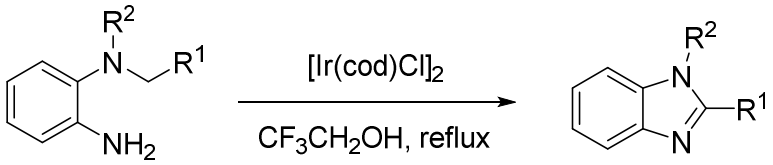
2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-methoxyaniline (3e)



White solid, mp 102.6–104.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 3H),

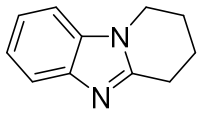
7.09–7.05 (m, 1H), 6.72–6.67 (m, 2H), 6.55 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.09 (s, 2H), 3.75 (s, 3H), 3.74 (br, 2H), 3.24 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 140.4, 135.3, 135.2, 134.2, 128.9, 126.4, 126.3, 125.7, 115.6, 108.9, 107.4, 55.8, 53.6, 49.2, 29.8; **IR (KBr)** *v*/cm^{-1}: 3423, 3336, 3014, 2983, 2919, 2821, 2780, 1589, 1511, 1450, 1378, 1319, 1236, 1193, 1166, 1024, 968, 927, 813, 754, 644, 480; **HRMS** (ESI) calculated for $C_{16}H_{19}N_2O$ $(M+H)^+$: 255.1492, found : 255.1486.

4. General procedure for the dehydrogenative coupling



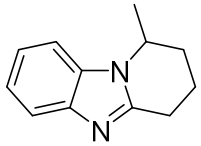
Under an argon atmosphere, a mixture of $[Ir(cod)Cl]_2$ (0.01 mmol), the substrate (0.2 mmol) in trifluoroethanol (2 mL) was stirred at 80 °C for the indicated time in the Table 1–2. The solvent was removed under vacuum. The residue was purified by flash column chromatography over silica gel to give the product.

1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2a)



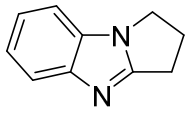
White solid, mp 62.4–64.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 1H), 7.31–7.27 (m, 1H), 7.25–7.19 (m, 2H), 4.08 (t, *J* = 6.1 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.17–2.10 (m, 2H), 2.06–1.99 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 142.8, 134.5, 122.0, 121.5, 118.8, 108.6, 42.3, 25.4, 22.6, 20.7; **IR (KBr)** *v*/cm^{-1}: 3043, 2944, 2891 1612, 1508, 1481, 1457, 1413, 1375, 1317, 1286, 1272, 1228, 1157, 1002, 769, 754, 680; **HRMS** (ESI) calculated for $C_{11}H_{13}N_2$ $(M+H)^+$: 173.1073, found : 173.1074.

1-methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2b)



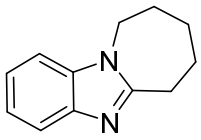
White solid, mp 96.7–99.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.66 (m, 1H), 7.35–7.32 (m, 1H), 7.25–7.18 (m, 2H), 4.64–4.56 (m, 1H), 3.19–3.11 (m, 1H), 3.04–2.94 (m, 1H), 2.25–2.04 (m, 2H), 2.00–1.92 (m, 2H), 1.52 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 143.1, 133.8, 121.8, 121.5, 119.0, 109.6, 48.3, 29.7, 25.5, 20.1, 16.8; **IR (KBr)** *v*/cm^{-1}: 3045, 2954, 1608, 1510, 1459, 1416, 1380, 1365, 1305, 1280, 1228, 1159, 755, 530, 431; **HRMS** (ESI) calculated for $C_{12}H_{15}N_2$ $(M+H)^+$: 187.1230, found : 187.1241.

2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (2c)



White solid, mp 105.4–108.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74–7.66 (m, 1H), 7.33–7.27 (m, 1H), 7.25–7.18 (m, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.77–2.68 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 148.8, 132.3, 121.7, 121.6, 119.5, 109.4, 42.7, 26.0, 23.4; **IR (KBr)** *v*/cm^{-1}: 3394, 3052, 2960, 2920, 2849, 1624, 1523, 1461, 1446, 1416, 1331, 1302, 1280, 1217, 1134, 1004, 936, 735; **HRMS** (ESI) calculated for $C_{10}H_{11}N_2$ $(M+H)^+$: 159.0917, found : 159.0910.

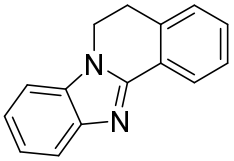
7,8,9,10-tetrahydro-6H-benzo[4,5]imidazo[1,2-a]azepine (2d)



White solid, mp 120.5–122.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 1H), 7.28–7.18 (m, 3H), 4.16–4.12 (m, 2H), 3.12–3.07 (m, 2H), 1.98–1.90 (m, 2H), 1.87–1.76 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 142.4, 135.7, 121.8, 121.4,

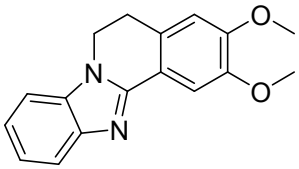
119.2, 108.6, 44.4, 30.8, 30.1, 28.7, 25.5; **IR (KBr)** ν/cm^{-1}: 3367, 3052, 2980, 2927, 2848, 1615, 1516, 1478, 1462, 1434, 1413, 1334, 1281, 1240, 1190, 1084, 1006, 885, 740; **HRMS** (ESI) calculated for $C_{12}H_{15}N_2$ $(M+H)^+$: 187.1230, found : 187.1240.

5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2g)



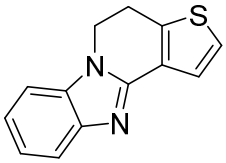
White solid, mp 145.1–147.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33–8.28 (m, 1H), 7.86–7.80 (m, 1H), 7.45–7.35 (m, 3H), 7.34–7.27 (m, 3H), 4.35 (t, J = 6.8 Hz, 2H), 3.30 (t, J = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 143.9, 134.6, 134.2, 130.1, 128.0, 127.6, 126.6, 125.6, 122.6, 122.4, 119.7, 109.0, 40.3, 28.2; **IR (KBr)** ν/cm^{-1}: 3682, 3014, 2962, 2892, 1615, 1527, 1482, 1448, 1408, 1325, 1233, 1171, 1003, 774, 735, 438; **HRMS** (ESI) calculated for $C_{15}H_{13}N_2$ $(M+H)^+$: 221.1073, found: 221.1069.

2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2h)



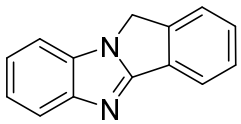
White solid, mp 151.1–153.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (ddd, J = 5.9, 3.1, 0.6 Hz, 1H), 7.78 (s, 1H), 7.35–7.31 (m, 1H), 7.29–7.24 (m, 2H), 6.79 (s, 1H), 4.30 (t, J = 6.9 Hz, 2H), 4.01 (s, 3H), 3.95 (s, 3H), 3.22 (t, J = 6.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 149.4, 148.6, 143.9, 134.7, 127.4, 122.3, 122.2, 119.3, 119.2, 110.7, 108.7, 108.0, 56.2, 56.0, 40.5, 27.8; **IR (KBr)** ν/cm^{-1}: 3442, 3047, 2967, 2843, 1620, 1585, 1531, 1486, 1456, 1410, 1243, 1215, 1163, 1064, 1024, 817, 765; **HRMS** (ESI) calculated for $C_{17}H_{17}N_2O_2$ $(M+H)^+$: 281.1285, found : 281.1275.

4,5-dihydrobenzo[4,5]imidazo[1,2-a]thieno[3,2-c]pyridine (2i)



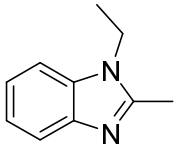
White solid, mp 187.8–189.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 1H), 7.68 (d, *J* = 5.2 Hz, 1H), 7.34–7.31 (m, 1H), 7.30–7.23 (m, 3H), 4.38 (t, *J* = 7.1 Hz, 2H), 3.39 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 143.8, 138.1, 134.4, 128.8, 124.5, 124.2, 122.6, 122.2, 119.7, 108.8, 41.0, 24.0; **IR (KBr)** *v*/cm^{-1}: 3102, 3044, 2890, 1616, 1565, 1469, 1446, 1425, 1315, 1278, 1153, 1076, 956, 919, 736, 707; **HRMS** (ESI) calculated for $C_{13}H_{11}N_2S$ $(M+H)^+$: 227.0637, found : 227.0632.

11H-benzo[4,5]imidazo[2,1-a]isoindole (2j)



Light brown solid, mp 210.7–213.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.8 Hz, 1H), 7.87–7.81 (m, 1H), 7.59–7.42 (m, 4H), 7.31–7.26 (m, 2H), 5.05 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 148.3, 143.4, 132.6, 129.4, 129.3, 128.7, 123.8, 122.6, 122.1, 122.0, 120.5, 109.3, 47.1; **IR (KBr)** *v*/cm^{-1}: 3050, 2922, 2850, 1620, 1587, 1540, 1472, 1453, 1377, 1329, 1316, 1234, 1158, 924, 739; **HRMS** (ESI) calculated for $C_{14}H_{11}N_2$ $(M+H)^+$: 207.0917, found : 207.0922.

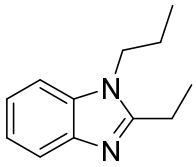
1-ethyl-2-methyl-1H-benzo[d]imidazole (2l)



White solid, mp 47.9–49.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 1H), 7.32–7.28 (m, 1H), 7.26–7.20 (m, 2H), 4.16 (q, *J* = 7.3 Hz, 2H), 2.61 (s, 3H), 1.41 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 142.6, 134.6, 121.9, 121.7, 119.0, 108.9, 38.5, 14.9, 13.7; **IR (KBr)** *v*/cm^{-1}: 3367, 3056, 2979, 2929, 1668, 1616,

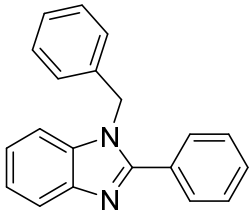
1511, 1461, 1400, 1348, 1328, 1274, 1234, 1166, 1131, 1081, 1008, 744, 661; **HRMS** (ESI) calculated for $C_{10}H_{13}N_2$ $(M+H)^+$: 161.1073, found : 161.1079.

2-ethyl-1-propyl-1H-benzo[d]imidazole (2m)



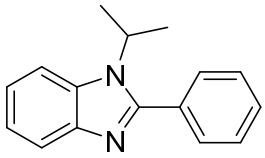
Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 1H), 7.32–7.28 (m, 1H), 7.25–7.19 (m, 2H), 4.07 (t, *J* = 7.4 Hz, 2H), 2.90 (q, *J* = 7.5 Hz, 2H), 1.89–1.79 (m, 2H), 1.48 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 142.6, 135.1, 121.8, 121.5, 119.1, 109.1, 45.0, 23.0, 20.7, 11.8, 11.3; **IR (KBr)** ν/cm^{-1}: 3461, 3050, 2924, 2850, 1645, 1561, 1528, 1465, 1411, 1380, 1168, 1107, 1090, 1054, 757, 653; **HRMS** (ESI) calculated for $C_{12}H_{17}N_2$ $(M+H)^+$: 189.1386, found :189.1392 .

1-benzyl-2-phenyl-1H-benzo[d]imidazole (2n)



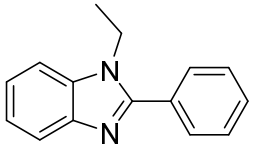
Light yellow solid, mp 137.5–139.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.71–7.67 (m, 2H), 7.49–7.42 (m, 3H), 7.36–7.28 (m, 4H), 7.24–7.18 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 5.45 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 143.1, 136.3, 136.0, 130.0, 129.8, 129.2, 129.0, 128.7, 127.7, 125.9, 122.9, 122.6, 119.9, 110.4, 48.3; **IR (KBr)** ν/cm^{-1}: 3430, 3058, 3027, 2942, 1602, 1467, 1446, 1390, 1361, 1328, 1278, 1249, 1160, 989, 775, 732, 698; **HRMS** (ESI) calculated for $C_{20}H_{17}N_2$ $(M+H)^+$: 285.1386, found : 285.1382.

1-isopropyl-2-phenyl-1H-benzo[d]imidazole (2o)



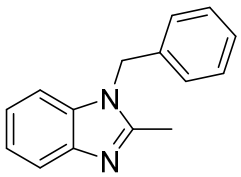
White solid, mp 147.3–148.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 1H), 7.67–7.61 (m, 3H), 7.54–7.50 (m, 3H), 7.31–7.26 (m, 2H), 4.83 (dt, *J* = 13.9, 6.9 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 143.8, 133.5, 131.1, 129.6, 129.5, 128.6, 122.2, 122.0, 120.3, 112.3, 48.8, 21.4; **IR (KBr)** *v*/cm^{-1}: 3396, 3063, 3032, 2979, 2935, 1601, 1523, 1453, 1377, 1283, 1159, 1134, 1017, 779, 751, 702; **HRMS** (ESI) calculated for $C_{16}H_{17}N_2$ $(M+H)^+$: 237.1386, found : 237.1377.

1-ethyl-2-phenyl-1H-benzo[d]imidazole (2pa)



White solid, mp 67.9–70.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 1H), 7.75–7.71 (m, 2H), 7.56–7.50 (m, 3H), 7.47–7.42 (m, 1H), 7.34–7.28 (m, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 143.2, 135.3, 130.5, 129.7, 129.2, 128.7, 122.6, 122.3, 119.9, 109.9, 39.6, 15.3; **IR (KBr)** *v*/cm^{-1}: 3057, 2990, 2942, 1610, 1523, 1467, 1443, 1391, 1349, 1329, 1153, 1130, 1074, 757, 699; **HRMS** (ESI) calculated for $C_{15}H_{15}N_2$ $(M+H)^+$: 223.1230, found : 223.1222.

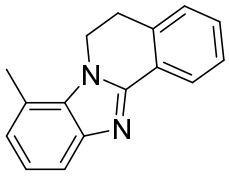
1-benzyl-2-methyl-1H-benzo[d]imidazole (2pb)



White solid, mp 102.9–104.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.71 (m, 1H), 7.33–7.26 (m, 3H), 7.25–7.17 (m, 3H), 7.07–7.03 (m, 2H), 5.32 (s, 2H), 2.57 (s, 3H);

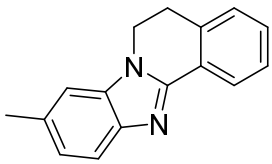
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 142.7, 135.8, 135.5, 129.0, 127.9, 126.2, 122.2, 122.0, 119.1, 109.3, 47.1, 14.0; **IR (KBr)** *v*/cm^{-1}: 3361, 3200, 3060, 3032, 2921, 2851, 1660, 1633, 1617, 1524, 1453, 1401, 1354, 1330, 1285, 1250, 1155, 1030, 1010, 743, 697; **HRMS** (ESI) calculated for $C_{15}H_{15}N_2$ $(M+H)^+$: 223.1230, found : 223.1225.

8-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4a)



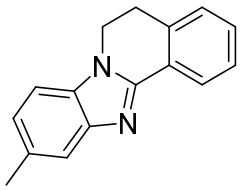
White solid, mp 146.6–149.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.43–7.35 (m, 2H), 7.31–7.28 (m, 1H), 7.15 (s, 1H), 7.10 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.29 (t, *J* = 6.8 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 142.0, 134.9, 134.1, 132.7, 129.9, 128.0, 127.7, 126.8, 125.5, 124.0, 119.2, 109.0, 40.3, 28.3, 21.8; **IR (KBr)** *v*/cm^{-1}: 3364, 3026, 2941, 2918, 2855, 1624, 1609, 1583, 1535, 1484, 1453, 1410, 1327, 1266, 1155, 1049, 803, 766, 734, 713; **HRMS** (ESI) calculated for $C_{16}H_{15}N_2$ $(M+H)^+$: 235.1230, found : 235.1222.

9-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4b)



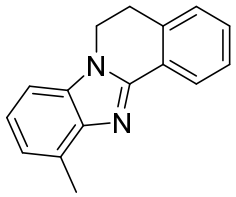
White solid, mp 98.2–100.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35–8.26 (m, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.45–7.35 (m, 2H), 7.33–7.27 (m, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 4.66 (t, *J* = 6.8 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.2, 144.0, 133.9, 133.4, 129.9, 127.7, 127.6, 126.8, 125.7, 125.2, 122.3, 120.8, 117.8, 42.9, 28.6, 18.9; **IR (KBr)** *v*/cm^{-1}: 3367, 3033, 2920, 1610, 1580, 1485, 1455, 1408, 1332, 1238, 1145, 1050, 799, 733, 715; **HRMS** (ESI) calculated for $C_{16}H_{15}N_2$ $(M+H)^+$: 235.1230, found : 235.1220.

10-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4c)



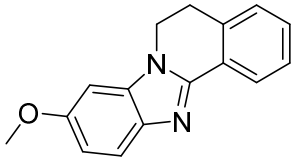
White solid, mp 174.5–176.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30–8.26 (m, 1H), 7.61 (s, 1H), 7.43–7.35 (m, 2H), 7.32–7.29 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.0 Hz, 1H), 4.30 (t, *J* = 6.9 Hz, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 144.2, 134.1, 132.7, 132.0, 129.9, 128.0, 127.6, 126.8, 125.5, 124.1, 119.5, 108.5, 40.3, 28.2, 21.6; **IR (KBr)** *v*/cm^{-1}: 3363, 3026, 2951, 2915, 2855, 1618, 1580, 1527, 1490, 1454, 1423, 1406, 1341, 1323, 1239, 1138, 881, 793, 764, 734, 708; **HRMS** (ESI) calculated for $C_{16}H_{15}N_2$ $(M+H)^+$: 235.1230, found : 235.1220.

11-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4d)



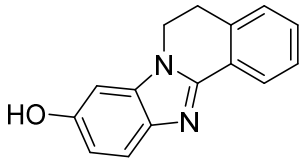
White solid, mp 132.5–134.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.42–7.35 (m, 2H), 7.31–7.27 (m, 1H), 7.19–7.16 (m, 2H), 7.09–7.05 (m, 1H), 4.29 (t, *J* = 6.8 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 143.3, 134.3, 134.1, 129.9, 129.8, 127.9, 127.6, 126.9, 125.8, 122.7, 122.5, 106.4, 40.5, 28.3, 16.8; **IR (KBr)** *v*/cm^{-1}: 3365, 3049, 3019, 2917, 1595, 1482, 1455, 1424, 1402, 1331, 1301, 1232, 1153, 1054, 775, 747, 720; **HRMS** (ESI) calculated for $C_{16}H_{15}N_2$ $(M+H)^+$: 235.1230, found : 235.1231.

9-methoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4e)



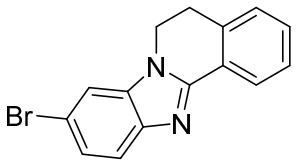
White solid, mp 153.0–155.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.43–7.34 (m, 2H), 7.32–7.28 (m, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.89 (s, 3H), 3.27 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 148.4, 138.4, 135.2, 133.8, 129.7, 128.0, 127.6, 126.8, 125.1, 120.1, 111.6, 92.7, 55.8, 40.3, 28.2; **IR (KBr)** *v*/cm^{-1}: 3429, 3001, 2967, 2838, 1620, 1585, 1531, 1486, 1456, 1410, 1361, 1243, 1215, 1163, 1064, 1024, 817, 765, 712; **HRMS** (ESI) calculated for $C_{16}H_{15}N_2O$ $(M+H)^+$: 251.1179, found: 251.1187.

5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-9-ol (4f)



White solid, mp 274.8–278.3 °C. **^{1}H NMR** (400 MHz, DMSO) δ 9.34 (s, 1H), 8.05–8.00 (m, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.43–7.36 (m, 3H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.2 Hz, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO) δ 153.9, 147.1, 137.0, 135.5, 134.6, 129.4, 128.4, 127.2, 126.6, 124.2, 119.3, 111.8, 95.1, 39.7, 27.4; **IR (KBr)** *v*/cm^{-1}: 3396, 3063, 2979, 2937, 1599, 1500, 1461, 1377, 1323, 1280, 1248, 1185, 1134, 1072, 1017, 779, 745, 702, 630; **HRMS** (ESI) calculated for $C_{15}H_{13}N_2O$ $(M+H)^+$: 237.1022, found : 237.1012.

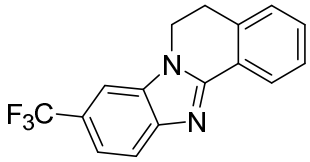
9-bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4g)



White solid, mp 180.4–183.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 5.4, 3.6

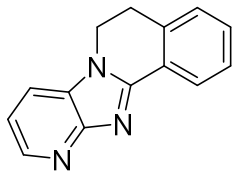
Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.45–7.40 (m, 2H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.36–7.31 (m, 1H), 4.31 (t, *J* = 6.8 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 142.9, 135.7, 134.2, 130.5, 128.1, 127.8, 126.3, 125.7, 120.9, 115.8, 112.2, 40.5, 28.1; **IR (KBr)** *v*/cm^{-1}: 3396, 3050, 2917, 2890, 1608, 1450, 1405, 1315, 1265, 1226, 1039, 835, 802, 769, 730, 700; **HRMS** (ESI) calculated for $C_{15}H_{12}BrN_2$ $(M+H)^+$: 299.0178, found : 299.0174.

9-(trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4h)



White solid, mp 184.7–187.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33–8.28 (m, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.66 (s, 1H), 7.53 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.48–7.42 (m, 2H), 7.37–7.33 (m, 1H), 4.39 (t, *J* = 6.9 Hz, 2H), 3.34 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 146.1, 134.5, 134.1, 130.9, 128.2, 127.9, 126.1, 126.0, 124.8 (q, $^{1}J_{CF3}$ = 270 Hz); 124.7 (q, $^{2}J_{CF3}$ = 32 Hz), 120.0, 119.4 (q, $^{3}J_{CF3}$ = 4 Hz), 106.8 (q, $^{3}J_{CF3}$ = 4 Hz), 40.7, 28.1; **IR (KBr)** *v*/cm^{-1}: 3359, 2920, 2850, 1626, 1580, 1533, 1483, 1456, 1337, 1303, 1274, 1162, 1109, 1047, 823, 774, 726; **HRMS** (ESI) calculated for $C_{16}H_{12}N_2F_3$ $(M+H)^+$: 289.0947, found : 289.0941.

5,6-dihydropyrido[2',3':4,5]imidazo[2,1-a]isoquinoline (4i)



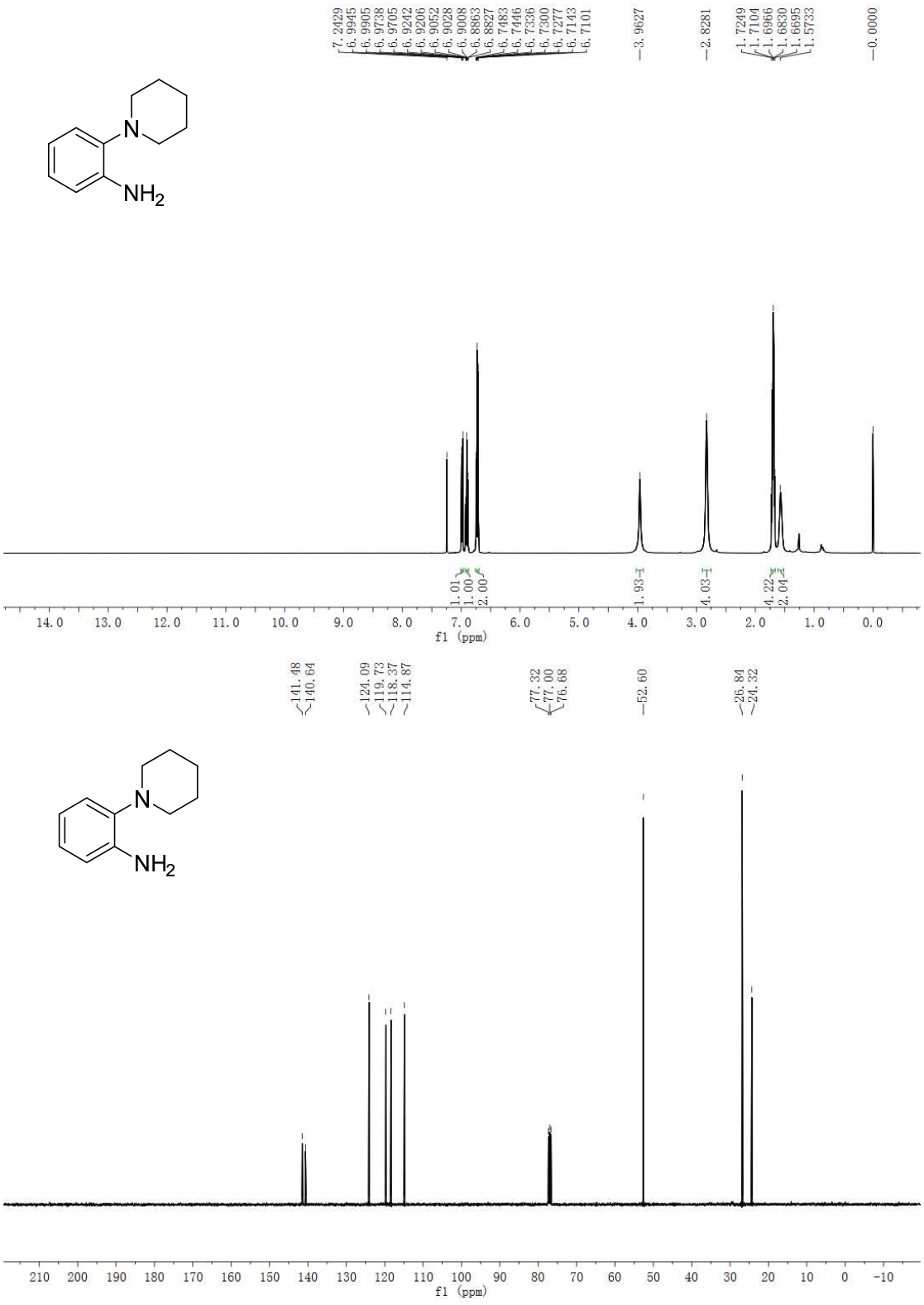
White solid, mp 143.3–146.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.41–8.36 (m, 1H), 7.65 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46–7.41 (m, 2H), 7.35–7.30 (m, 1H), 7.18 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.34 (t, *J* = 6.9 Hz, 2H), 3.32 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 151.1, 145.0, 134.2, 130.9, 128.1, 127.9, 127.1, 126.7, 126.0, 117.6, 116.7, 40.5, 27.9; **IR (KBr)** *v*/cm^{-1}: 3357, 3236,

3037, 2920, 1670, 1614, 1527, 1479, 1454, 1402, 1278, 1164, 1108, 771, 725, 696;

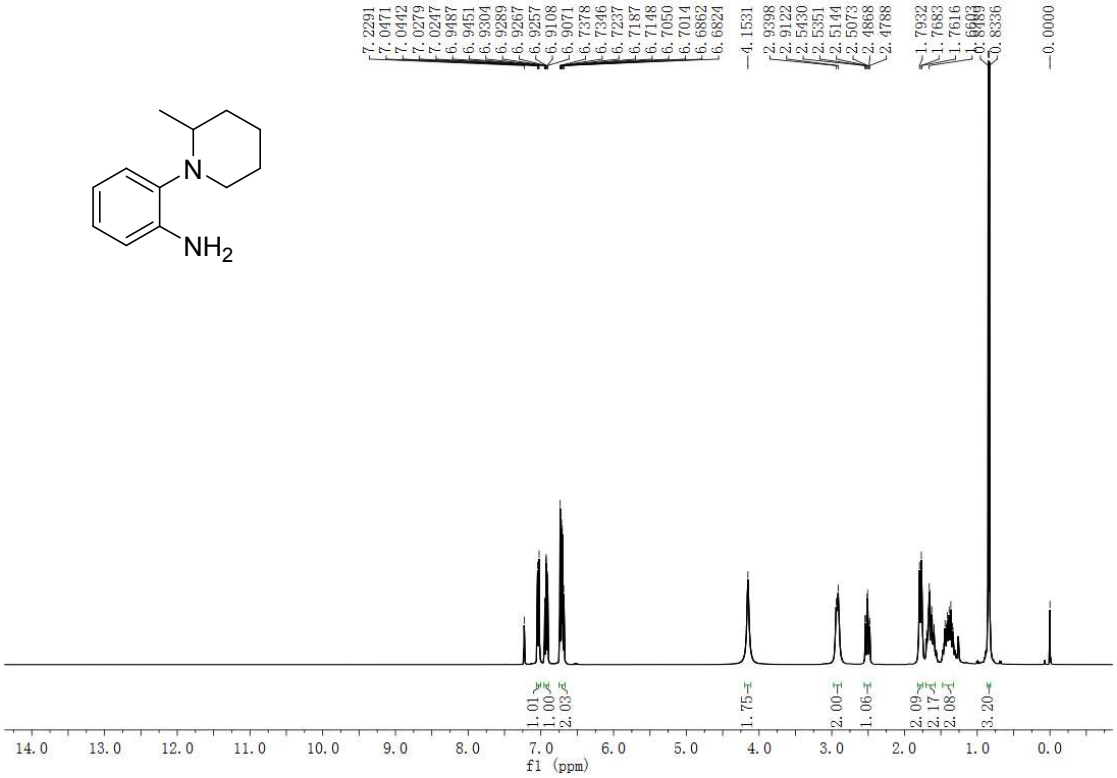
HRMS (ESI) calculated for $C_{14}H_{12}N_3$ $(M+H)^+$: 222.1026, found : 222.1021.

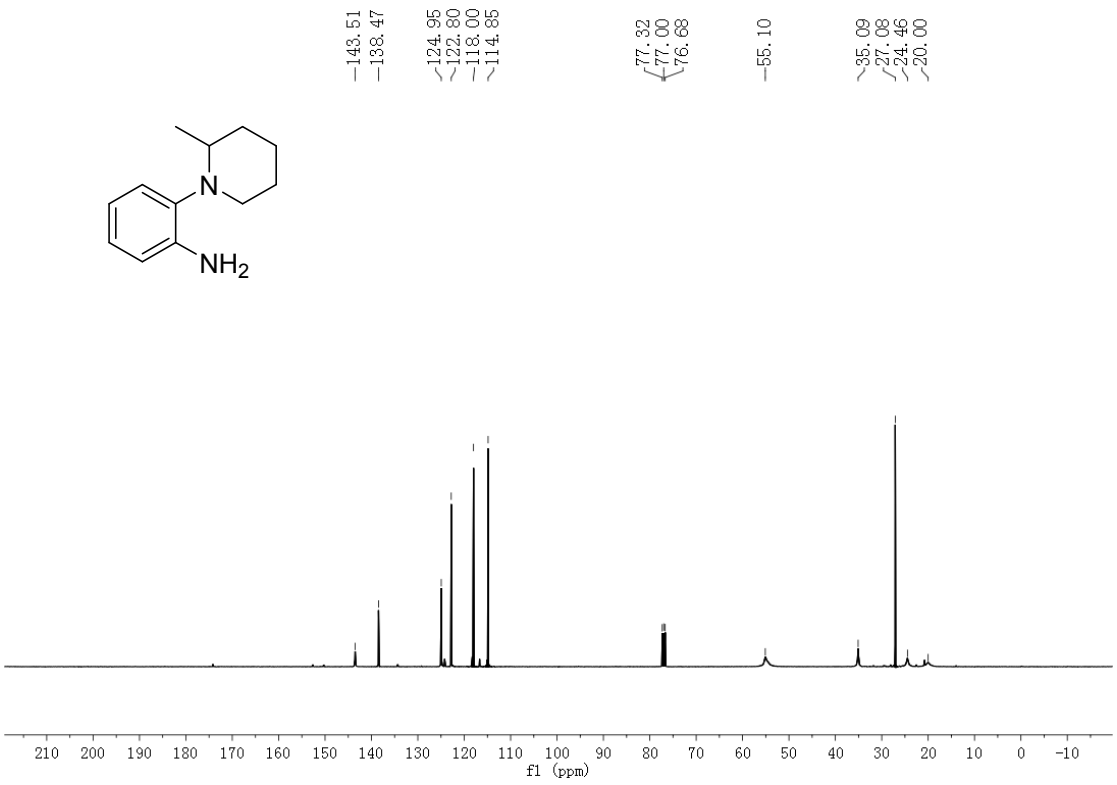
5. 1H and 13C NMR spectra of the substrates

2-(piperidin-1-yl)aniline (1a)

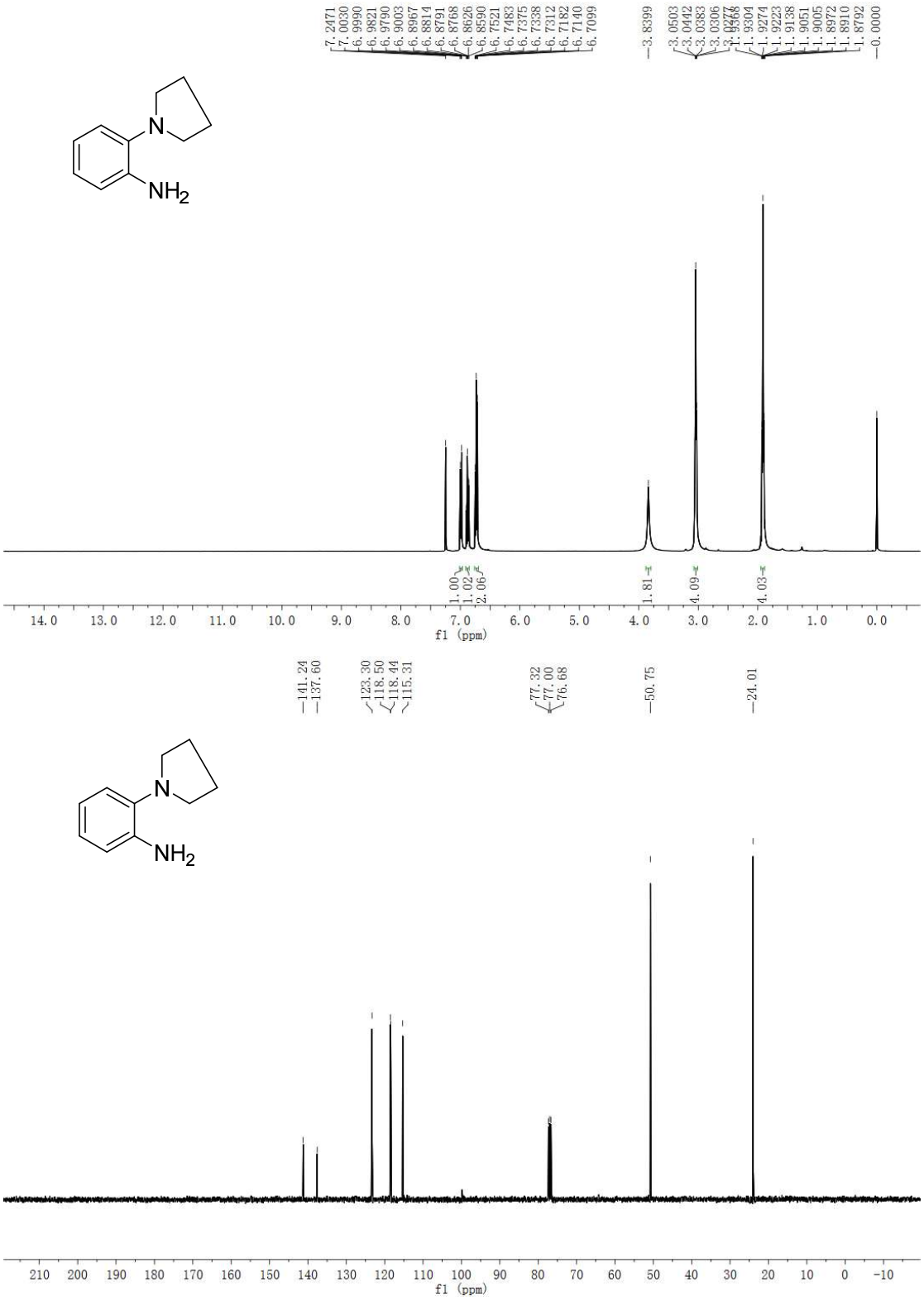


2-(2-methylpiperidin-1-yl)aniline (1b)

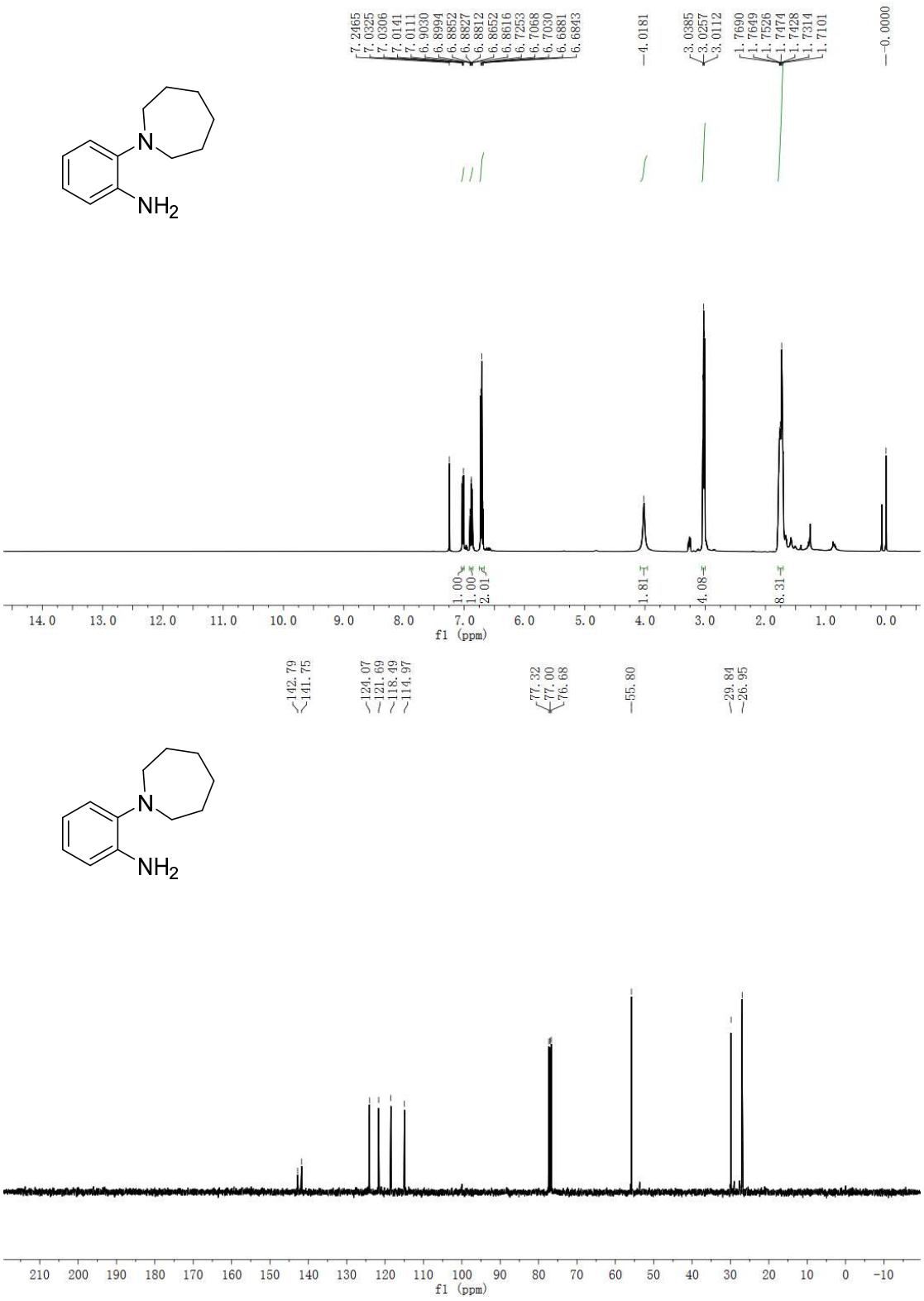




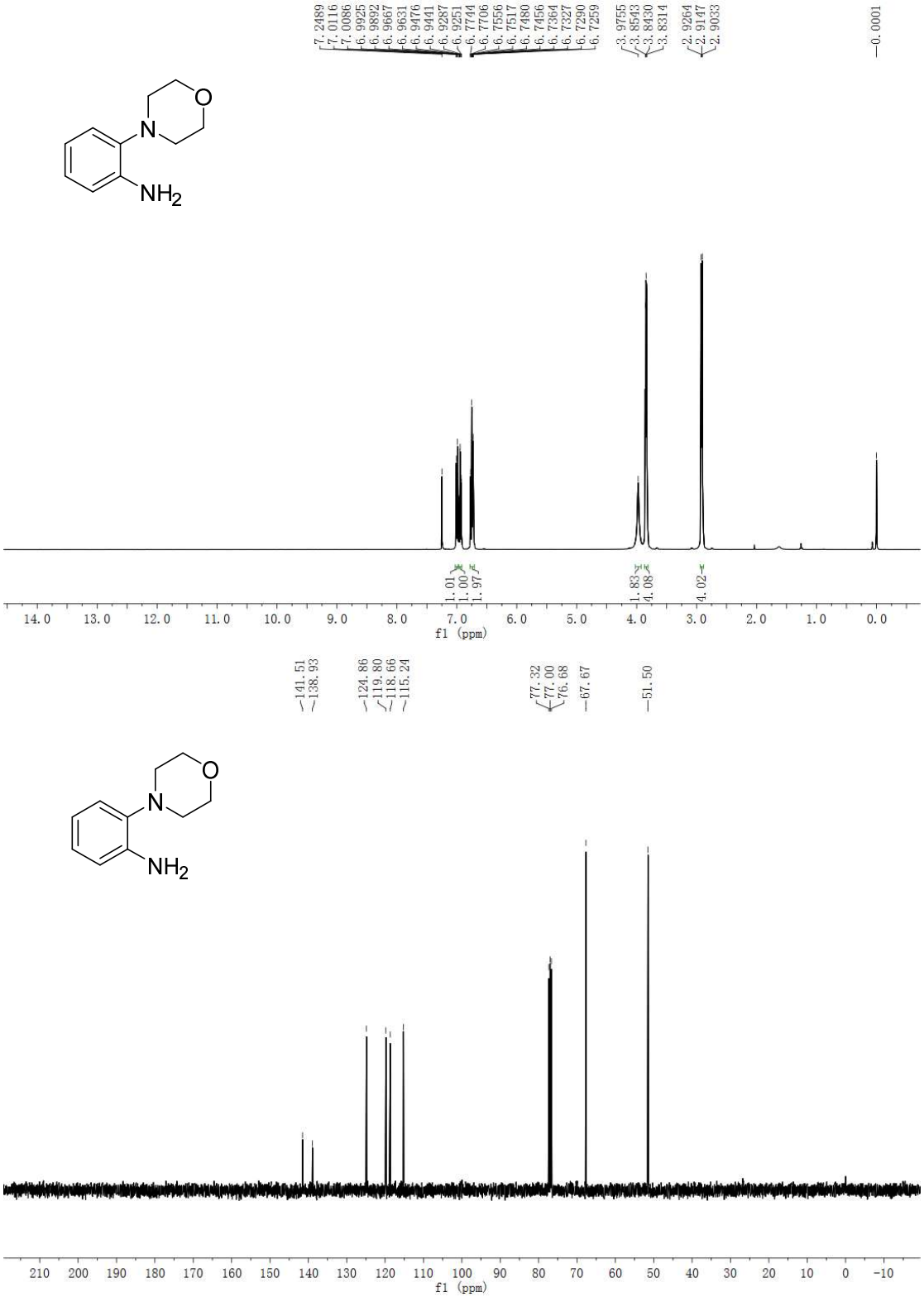
2-(pyrrolidin-1-yl)aniline (1c)



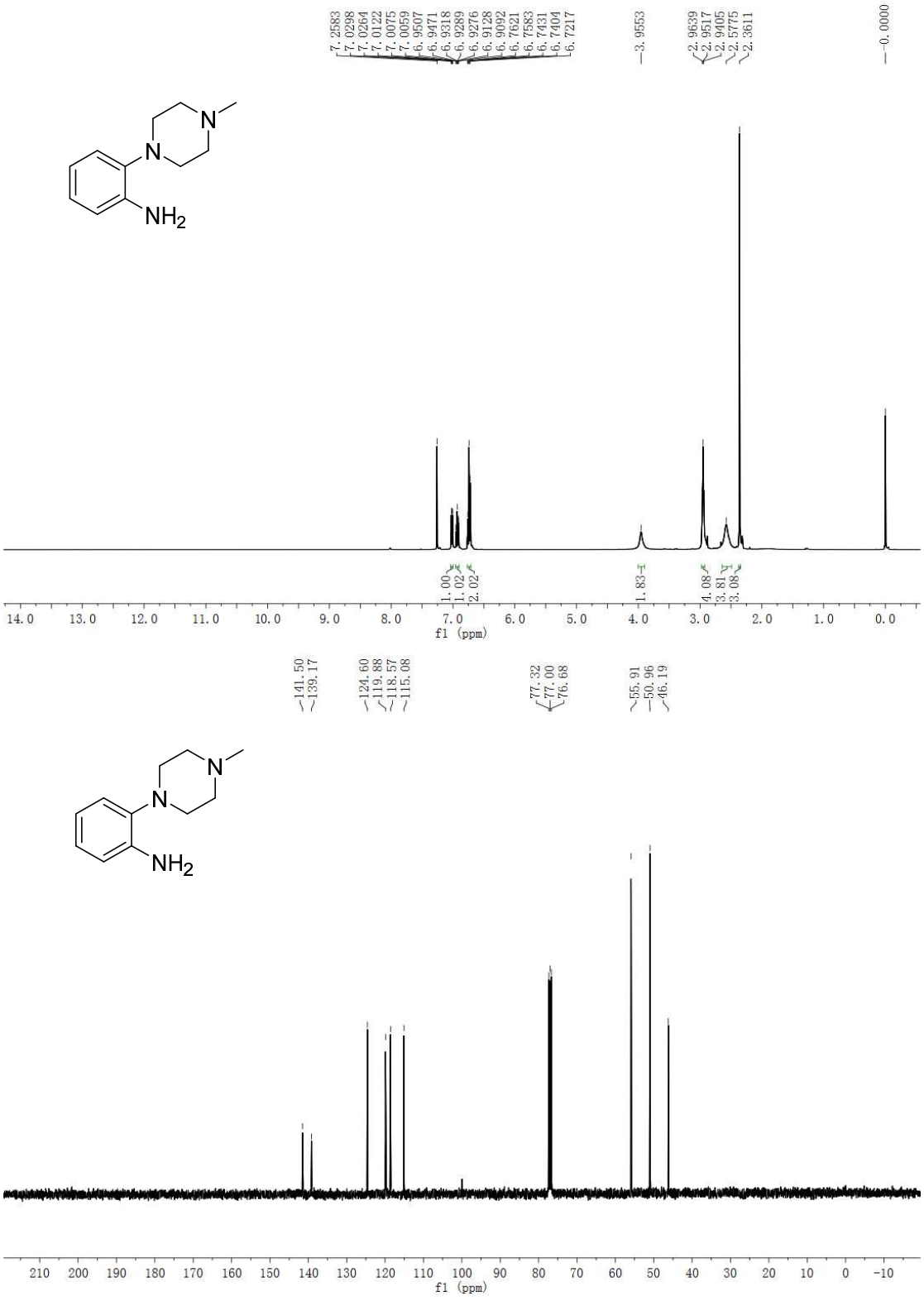
2-(azepan-1-yl)aniline (1d)



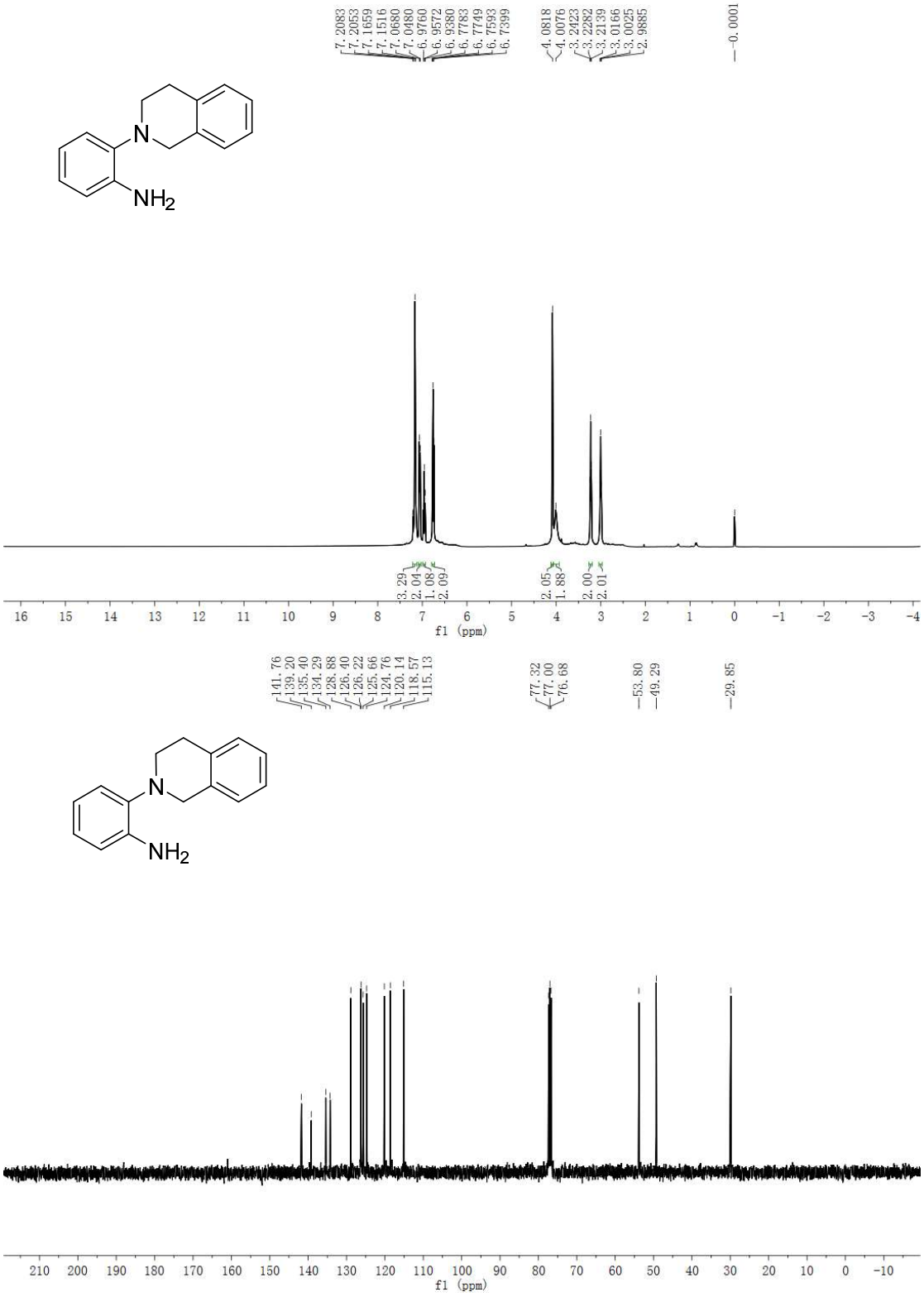
2-morpholinoaniline (1e)



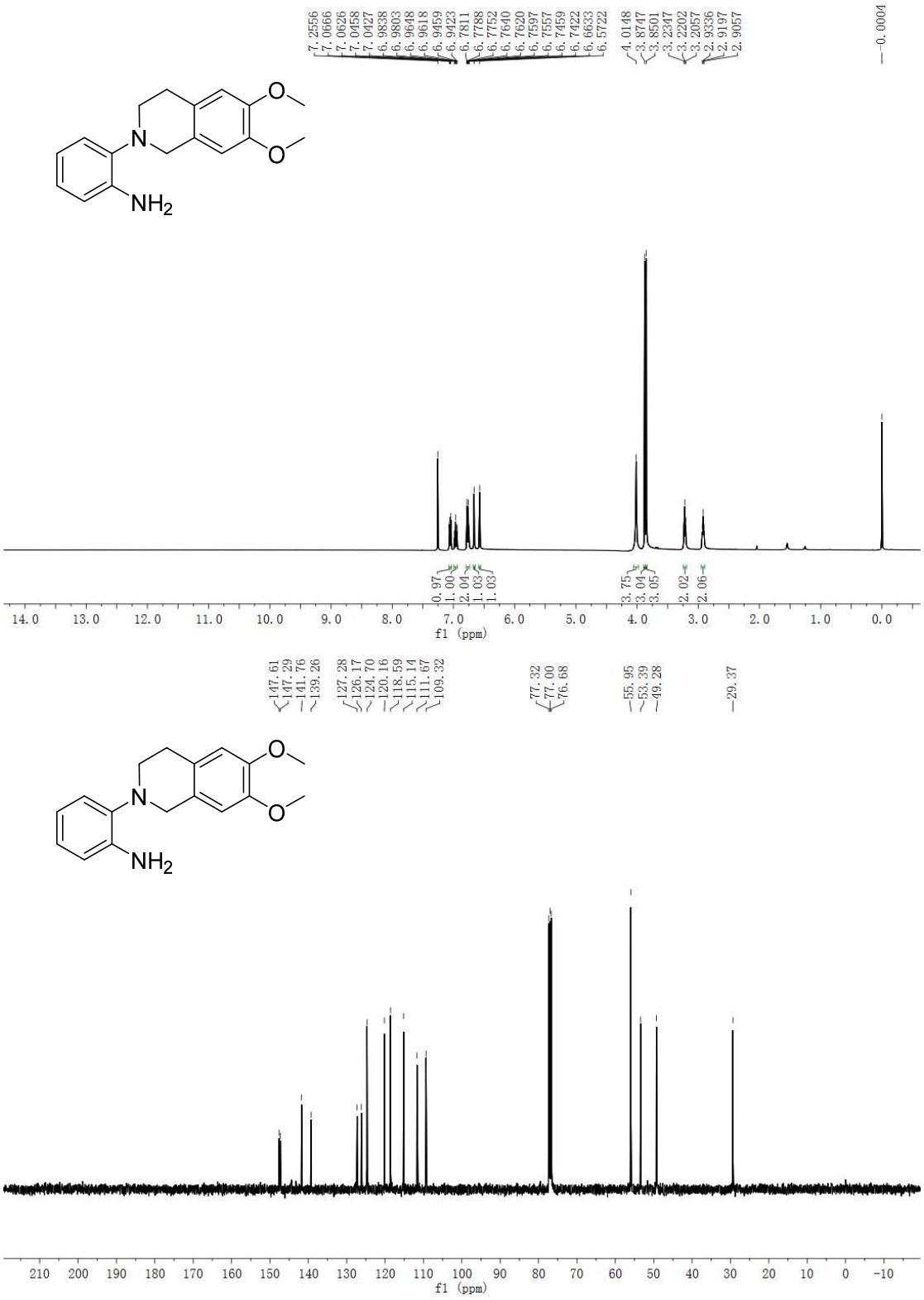
2-(4-methylpiperazin-1-yl)aniline (1f)



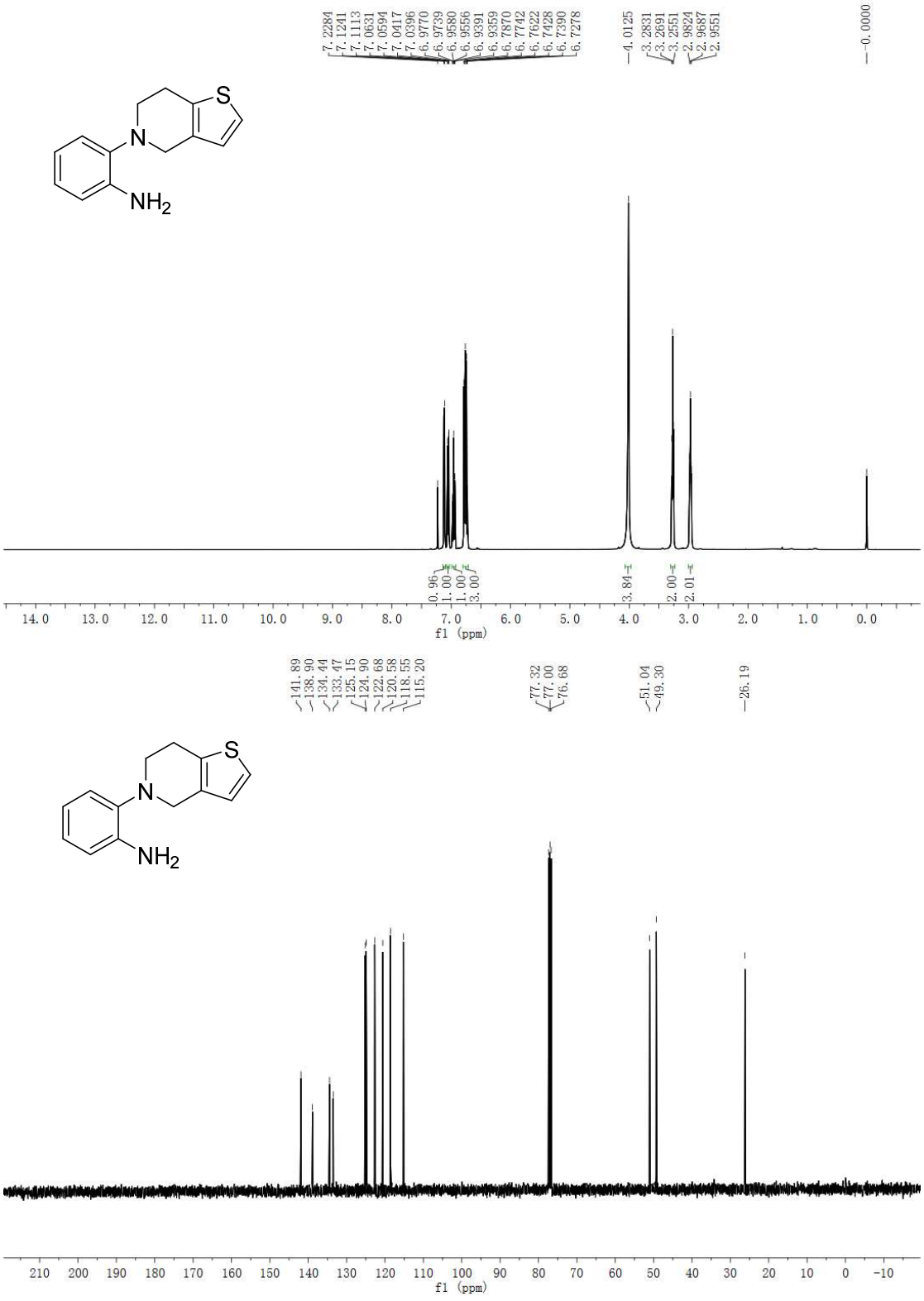
2-(3,4-dihydroisoquinolin-2(1H)-yl)aniline (1g)



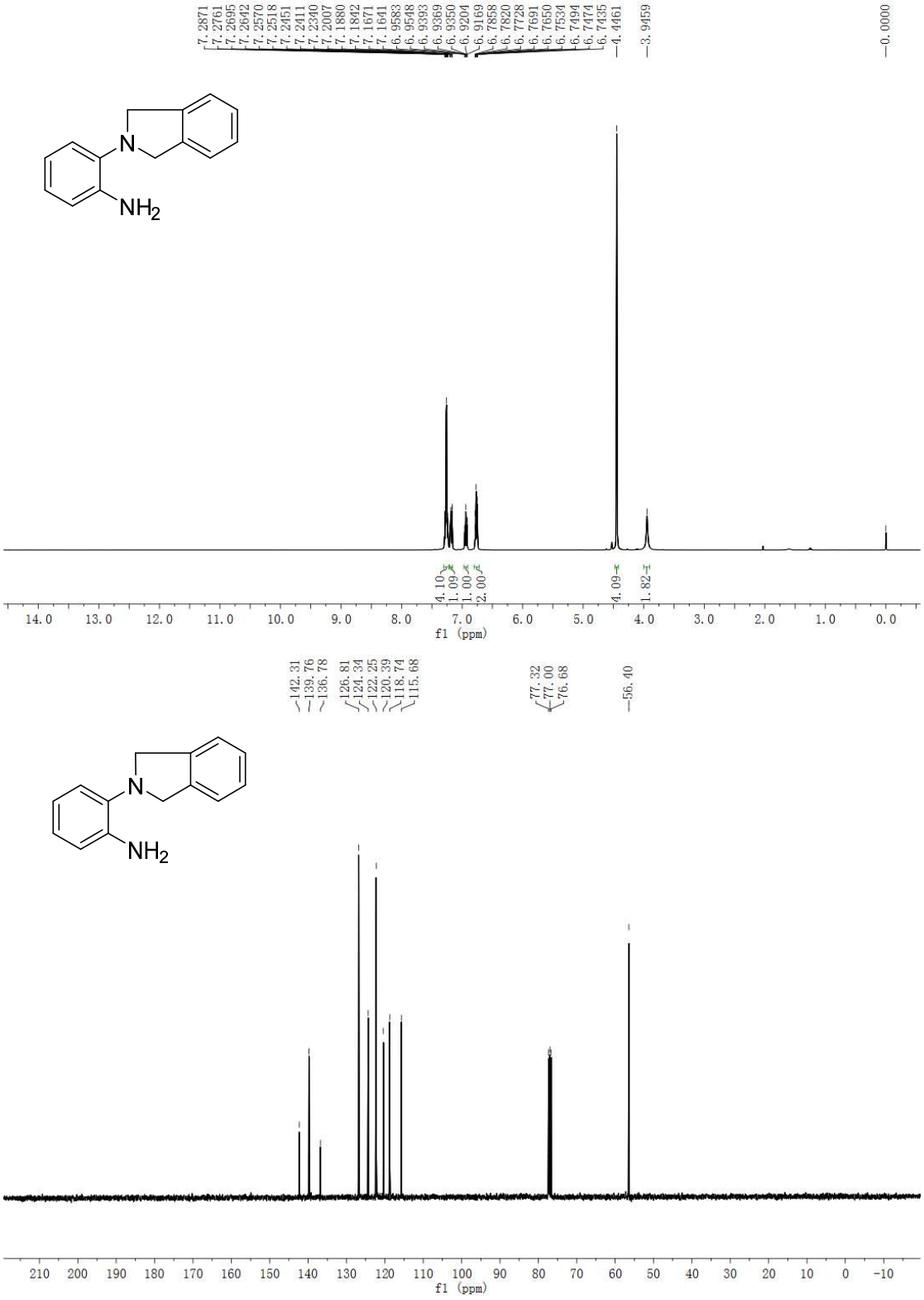
2-(6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)aniline (1h)



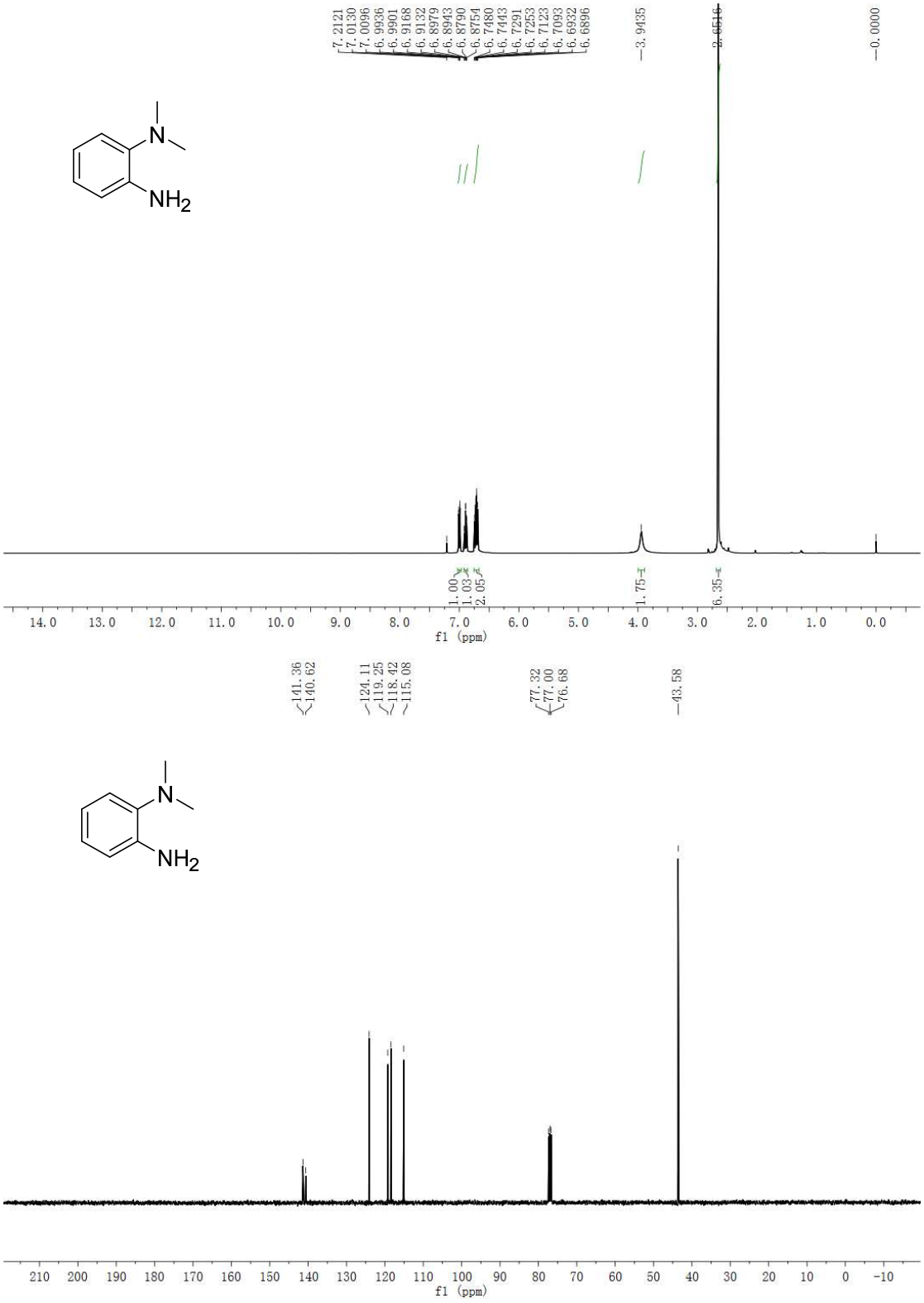
2-(6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)aniline (1i)



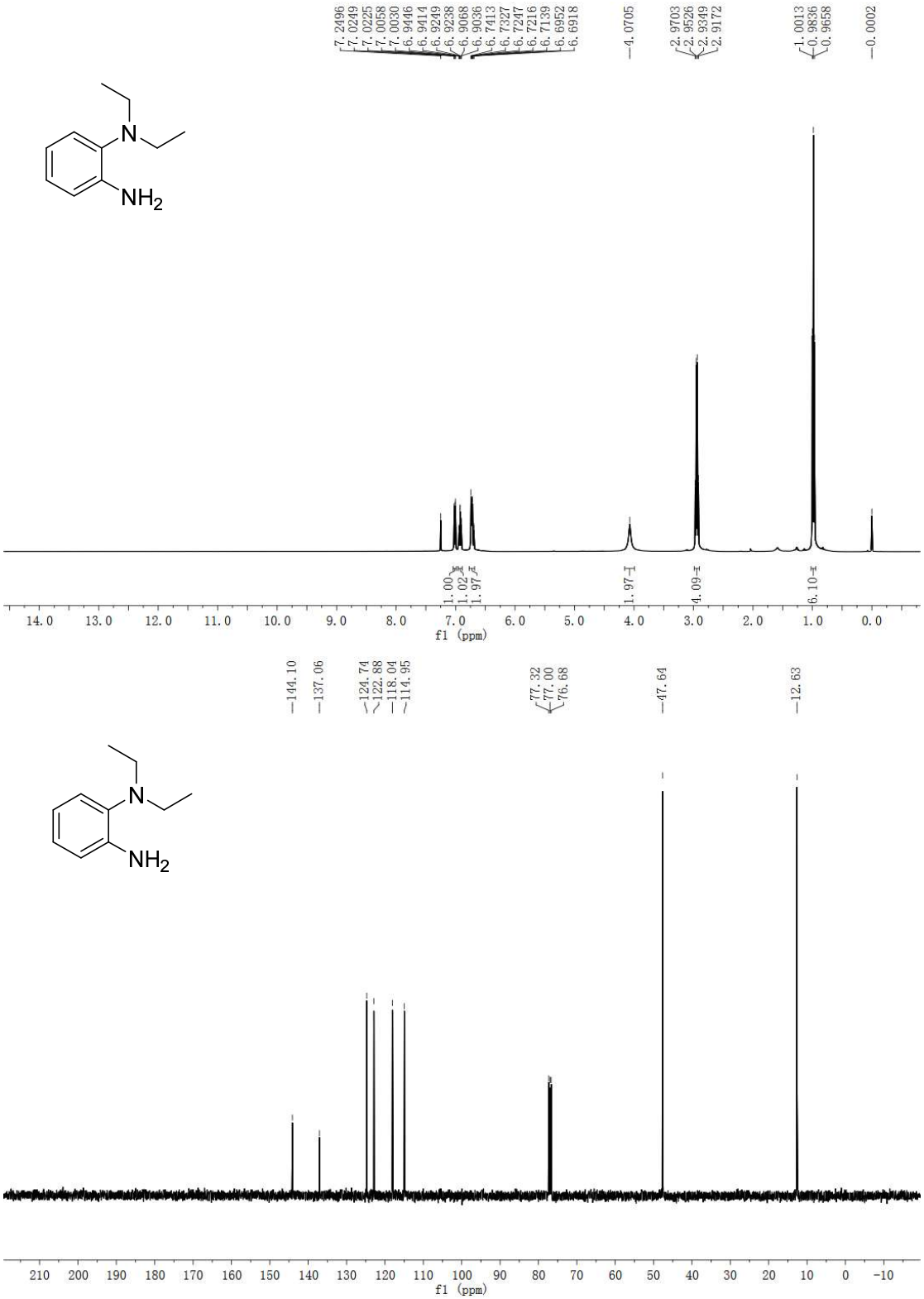
2-(isoindolin-2-yl)aniline (1j)



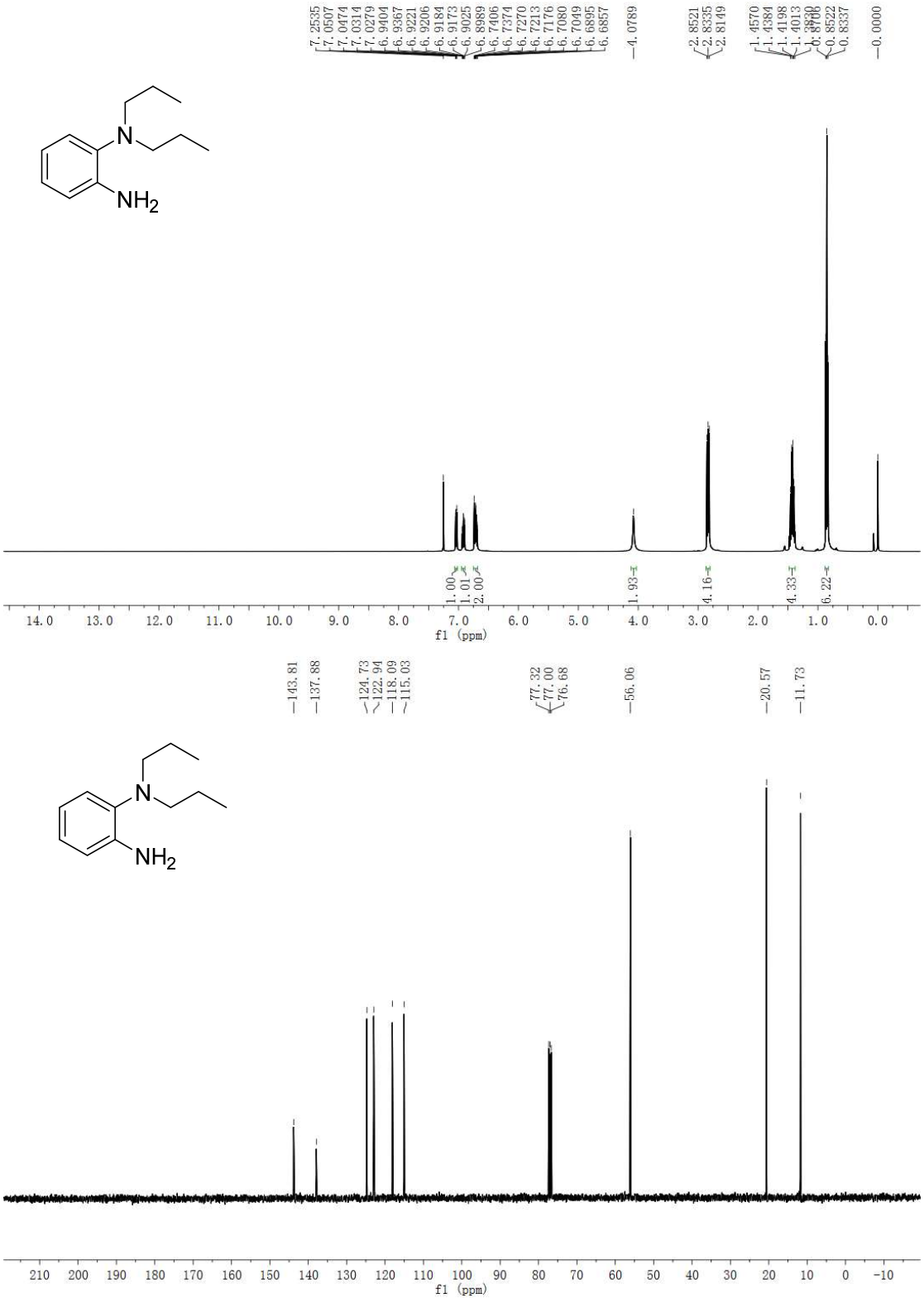
N^1,N^1-dimethylbenzene-1,2-diamine (1k)



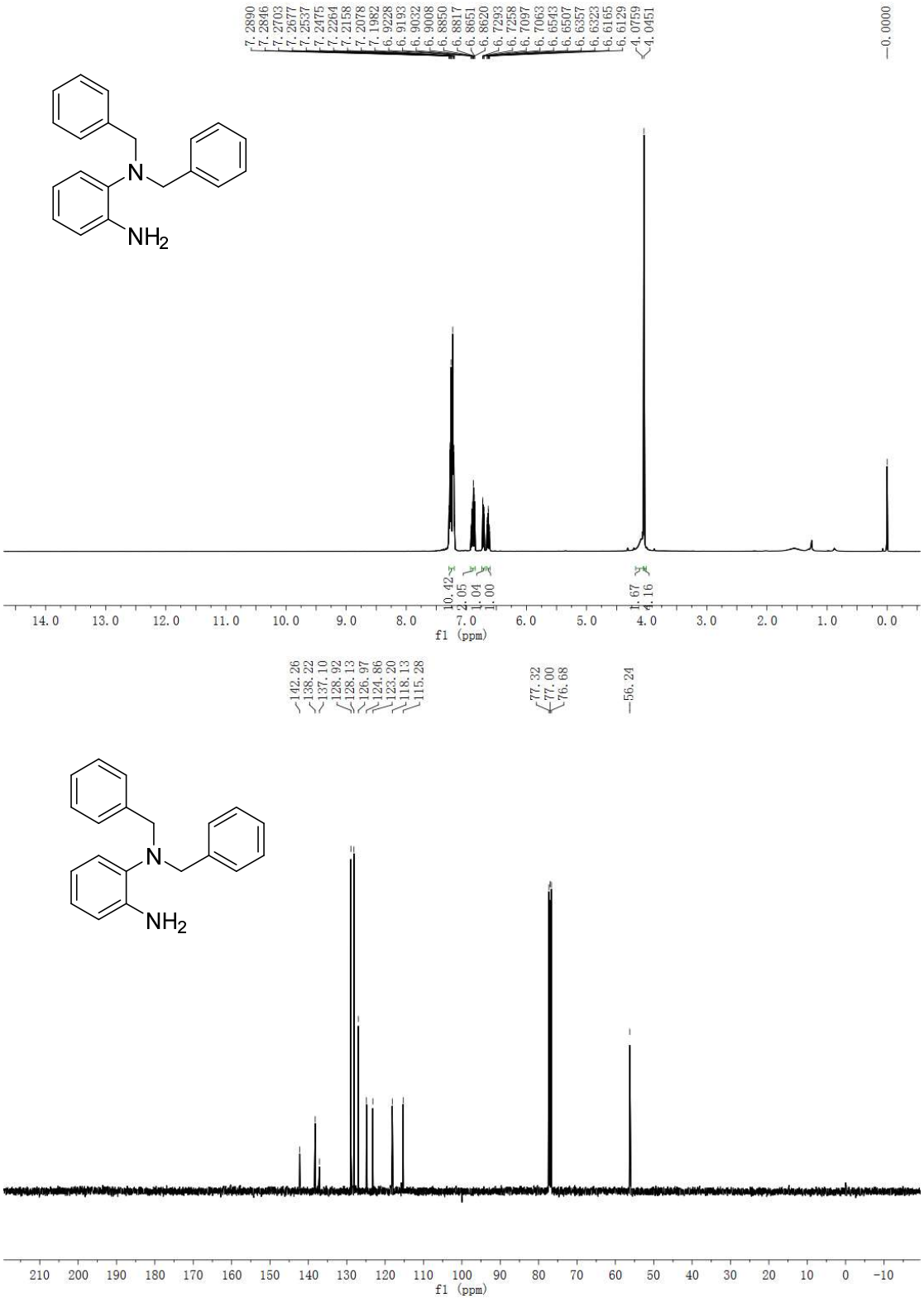
N^1,N^1-diethylbenzene-1,2-diamine (1l)



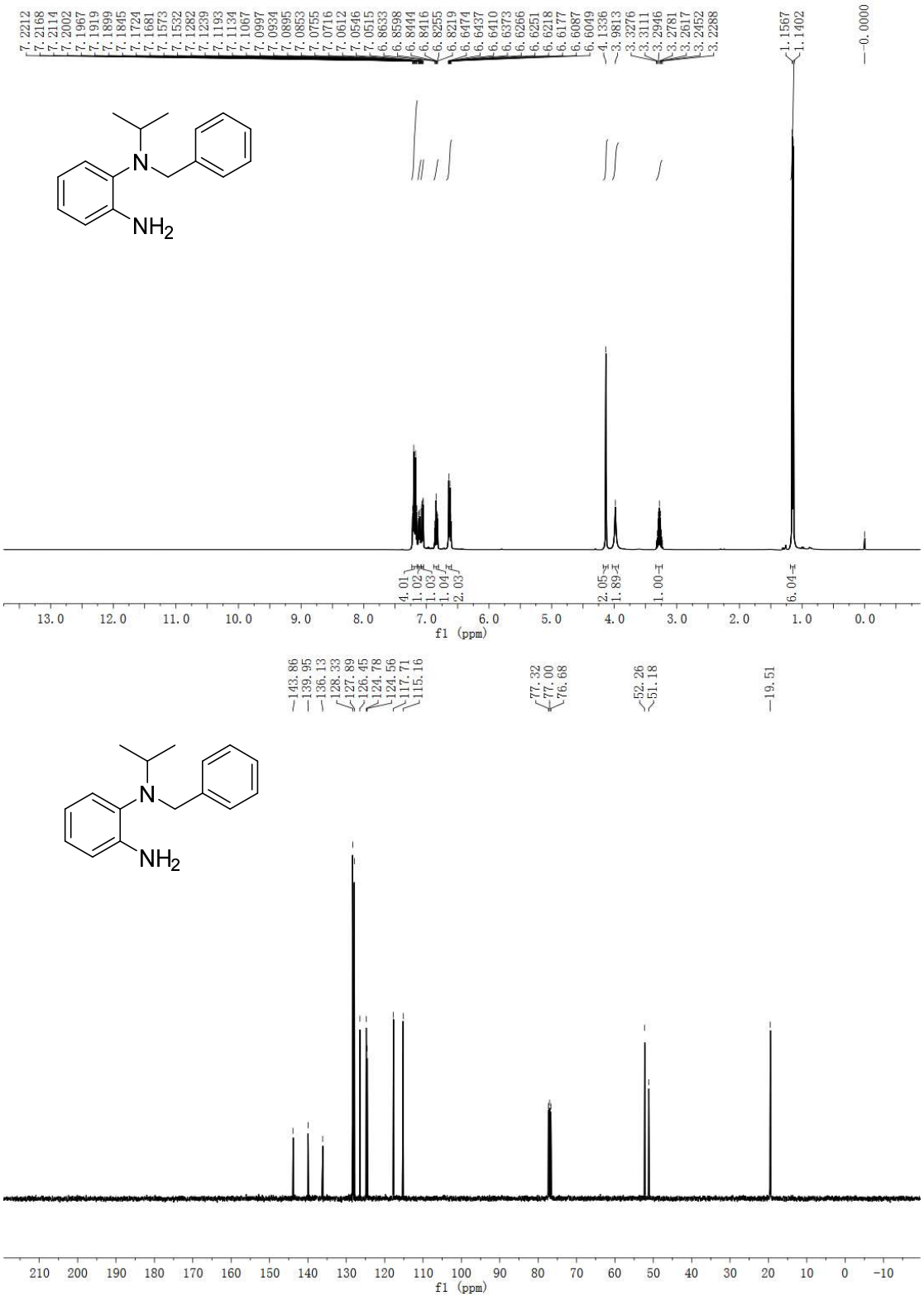
N^1,N^1-dipropylbenzene-1,2-diamine (1m)



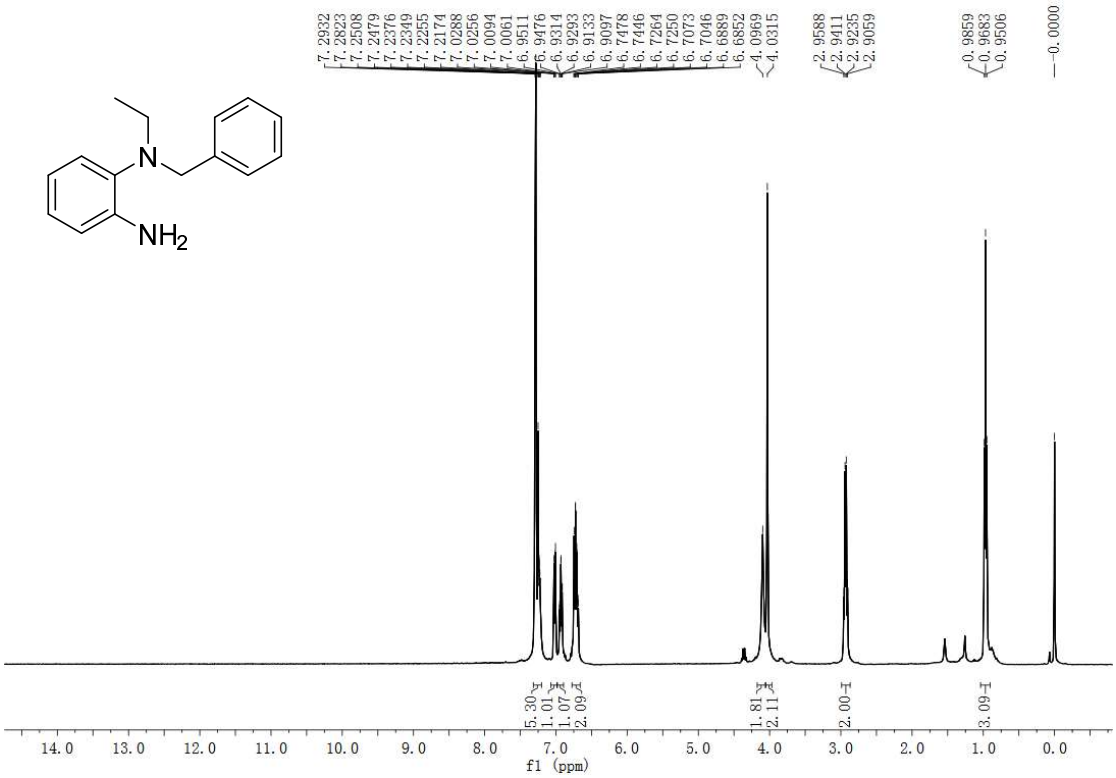
N^1,N^1-dibenzylbenzene-1,2-diamine (1n)

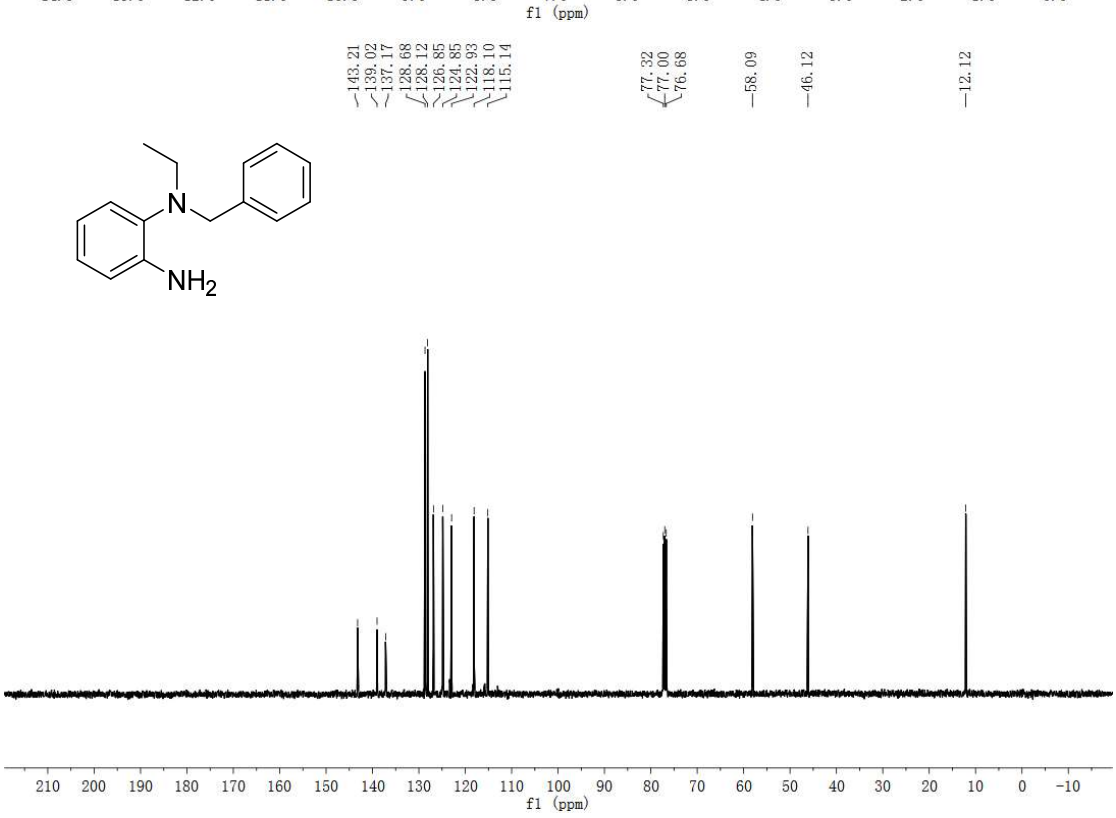


N^1-benzyl-N^1-isopropylbenzene-1,2-diamine (1o)

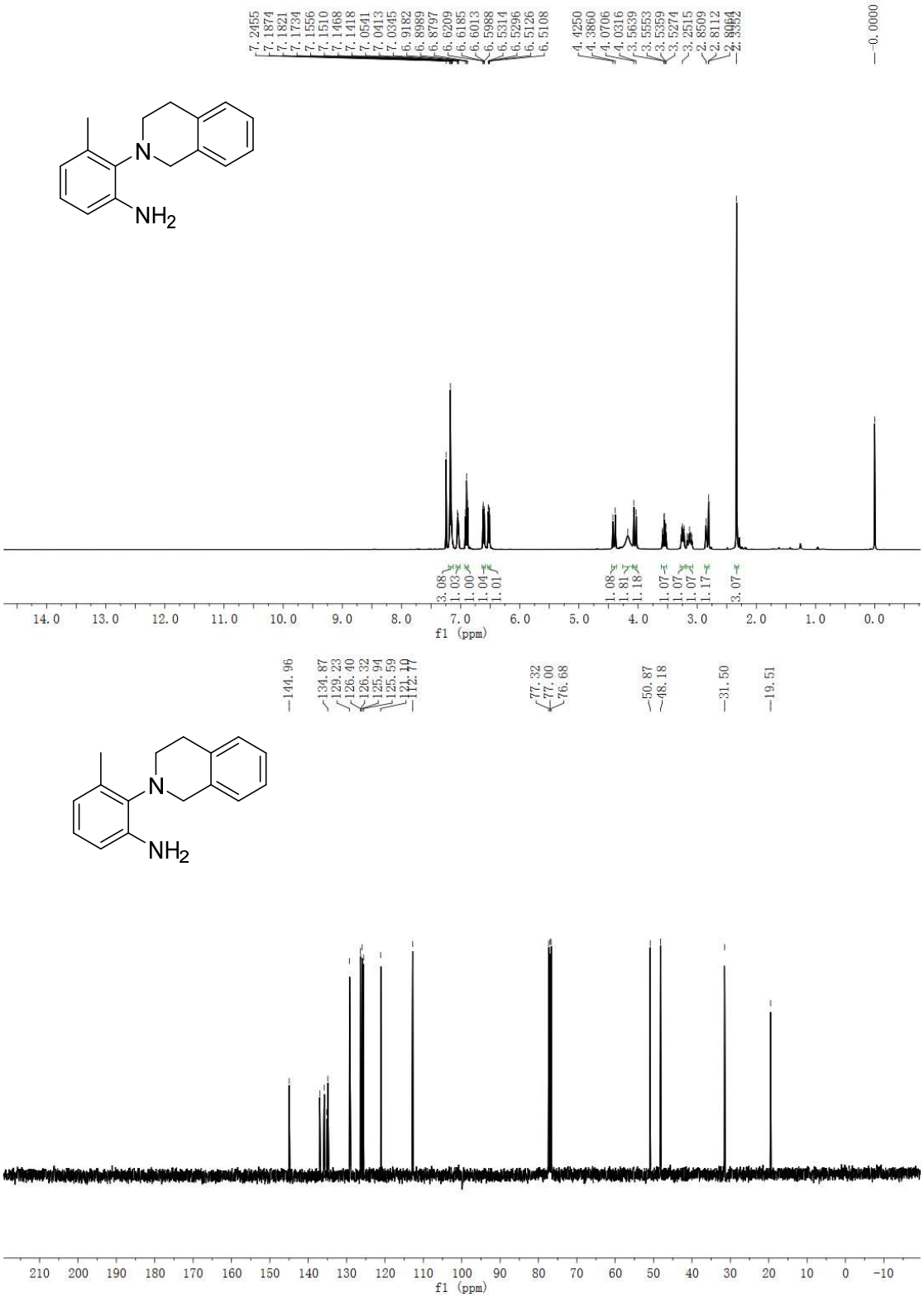


N^1-benzyl-N^1-ethylbenzene-1,2-diamine (1p)

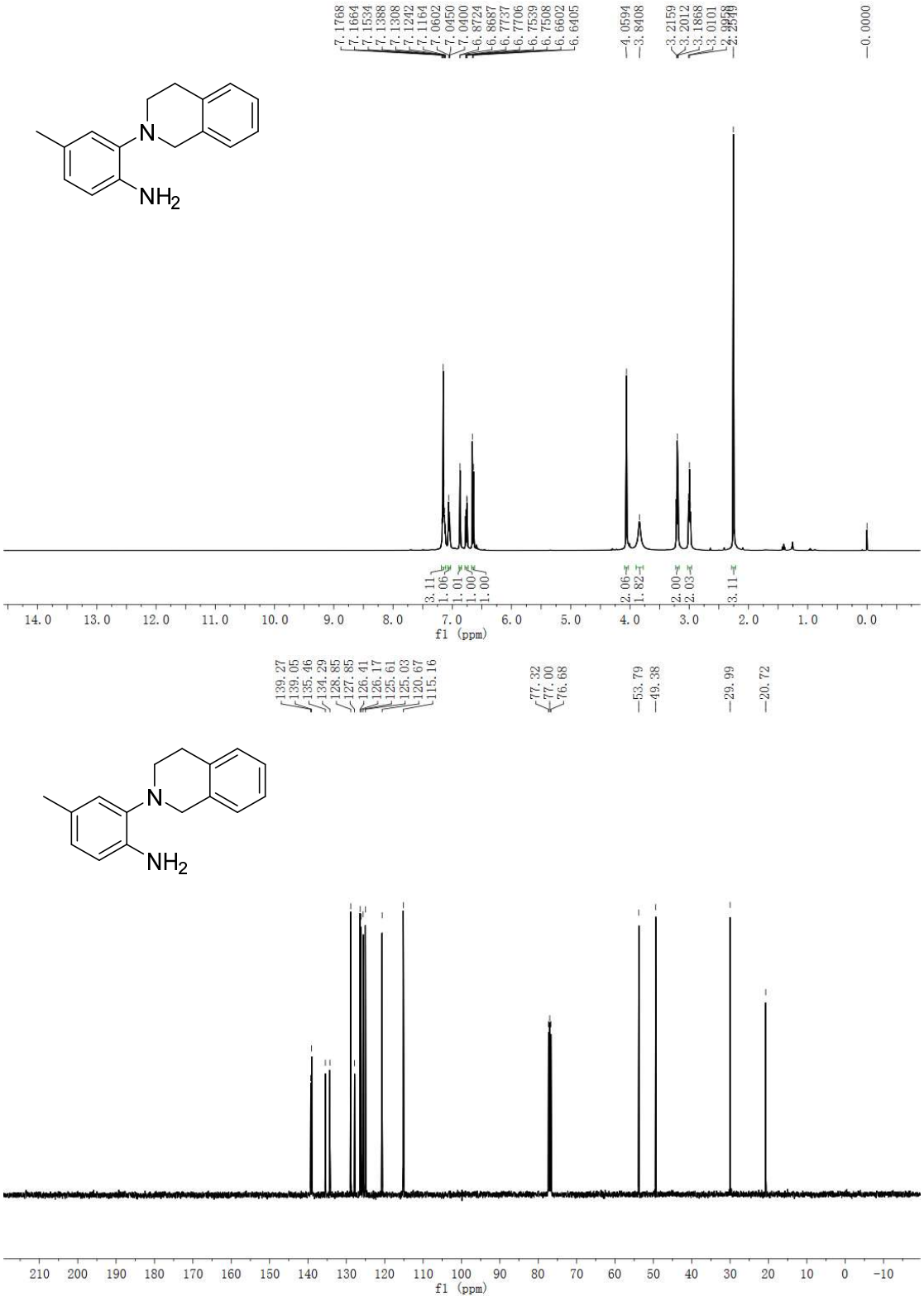




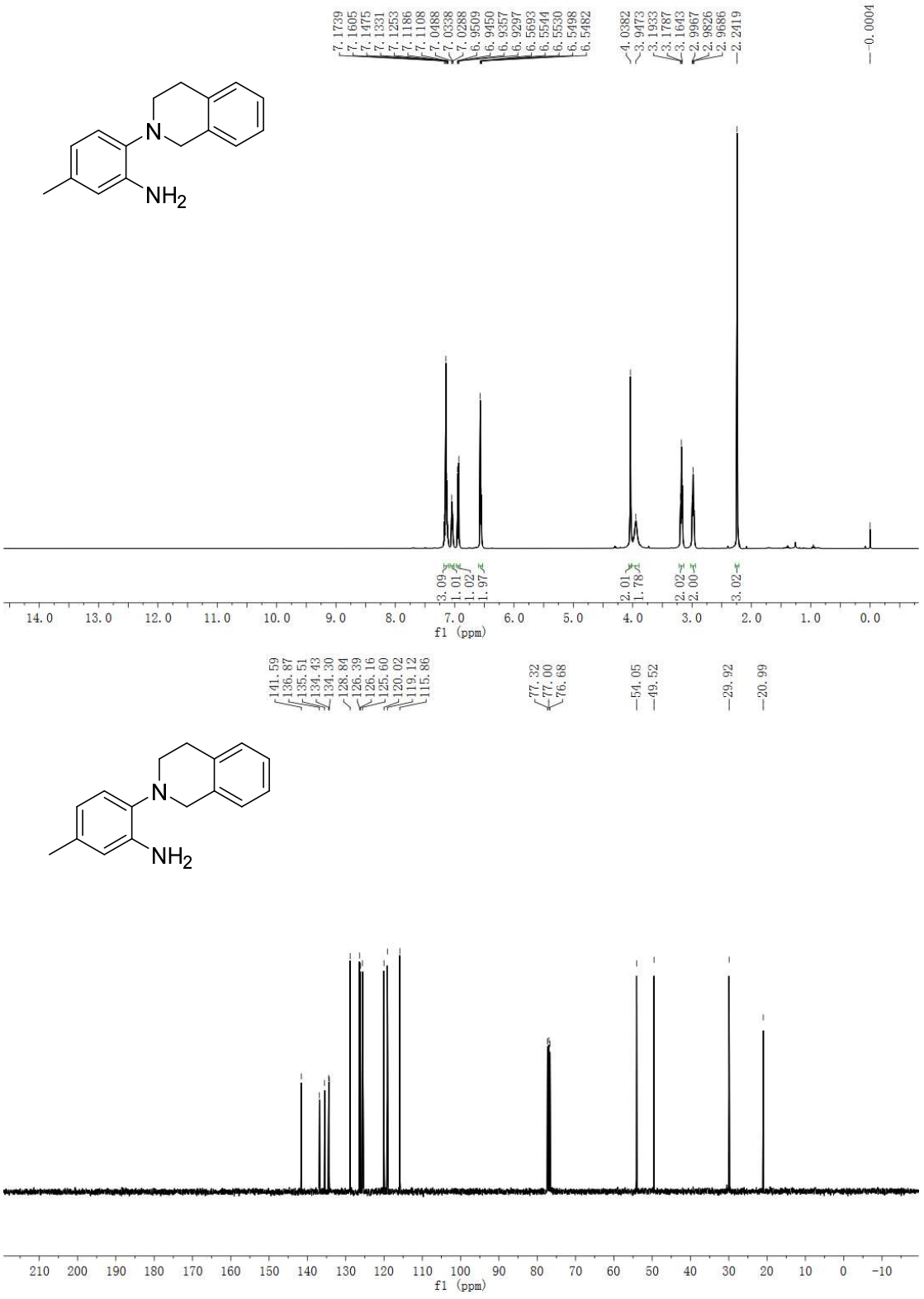
2-(3,4-dihydroisoquinolin-2(1H)-yl)-3-methylaniline (3a)



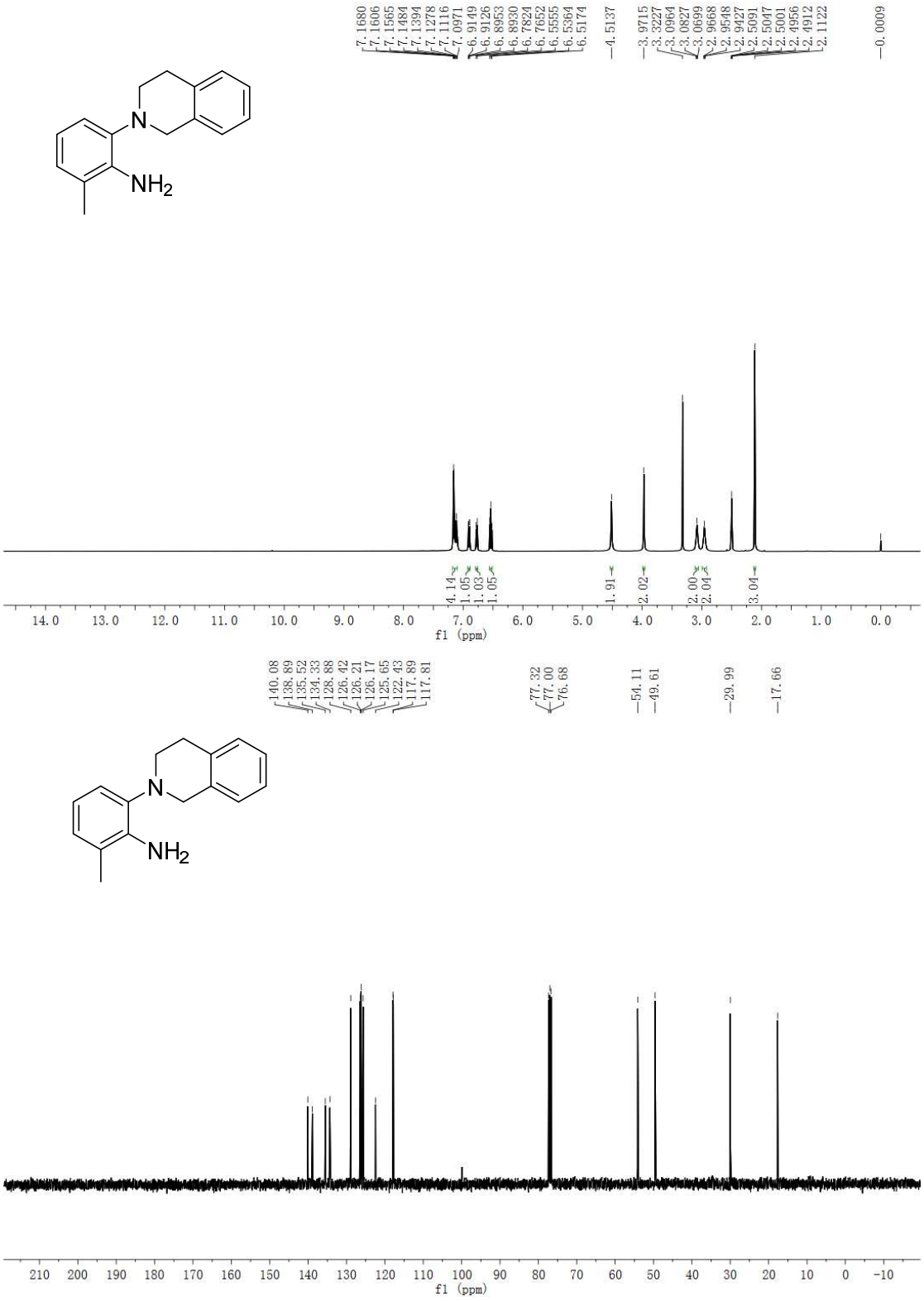
2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-methylaniline (3b)



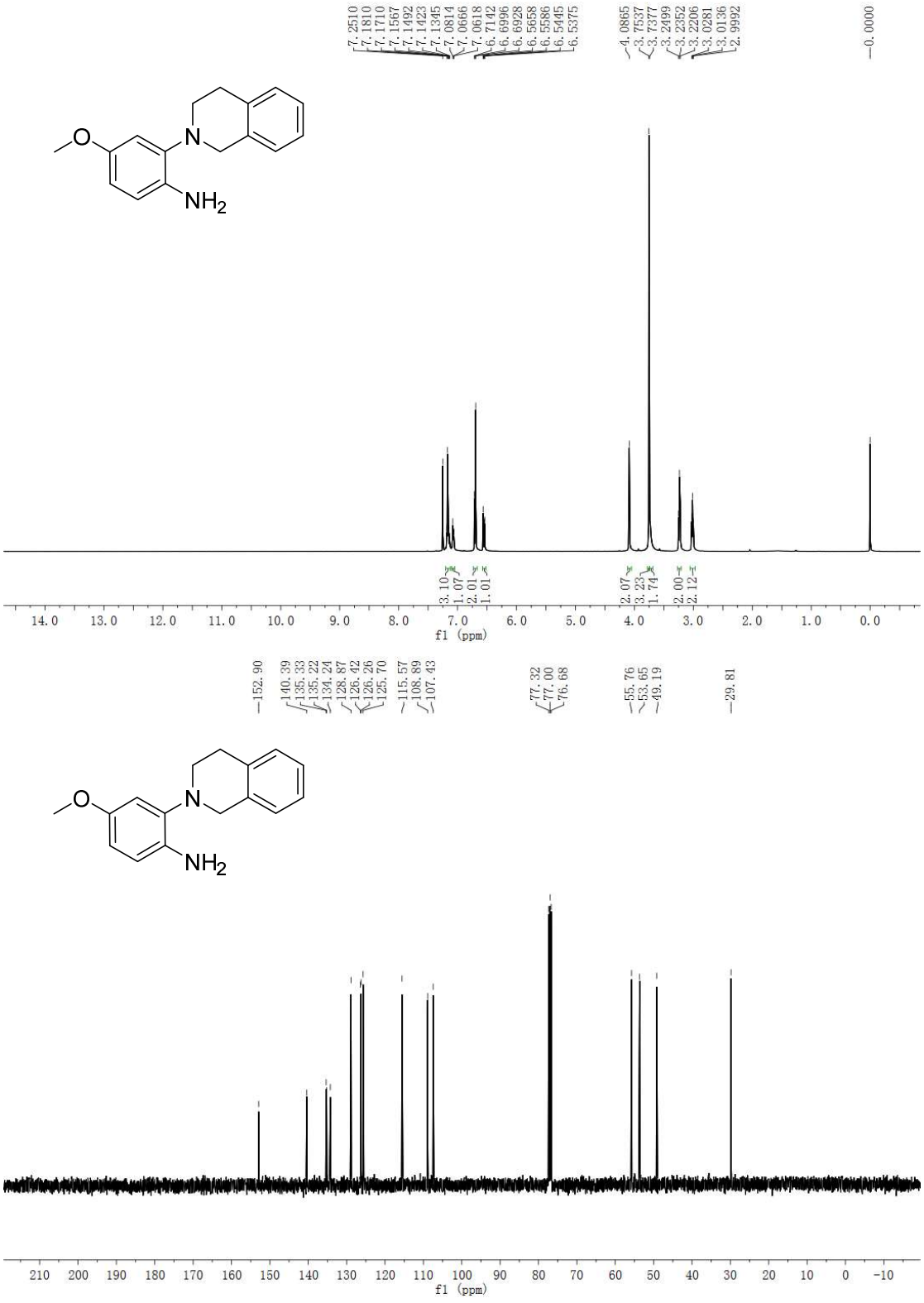
2-(3,4-dihydroisoquinolin-2(1H)-yl)-5-methylaniline (3c)



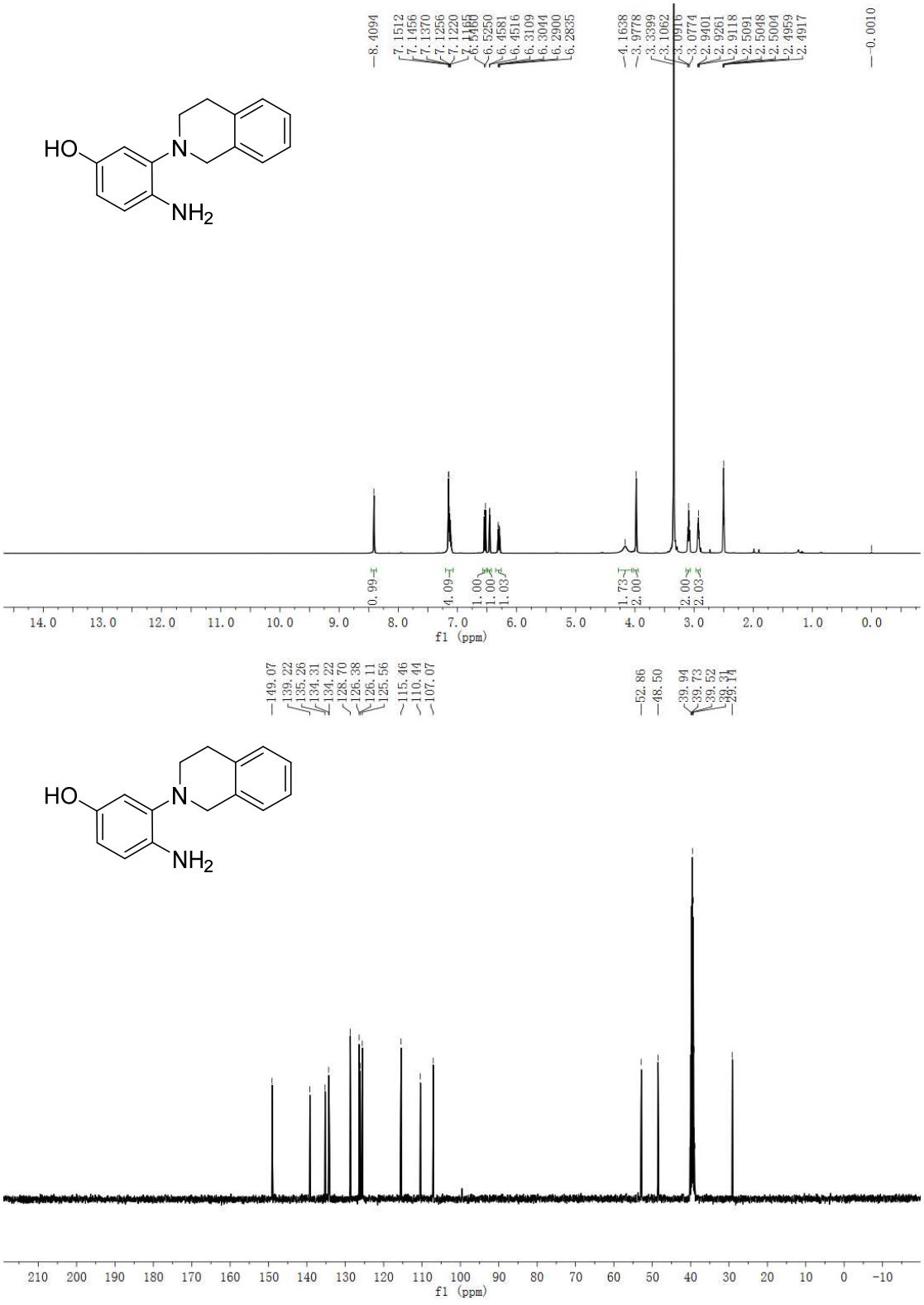
2-(3,4-dihydroisoquinolin-2(1H)-yl)-6-methylaniline (3d)



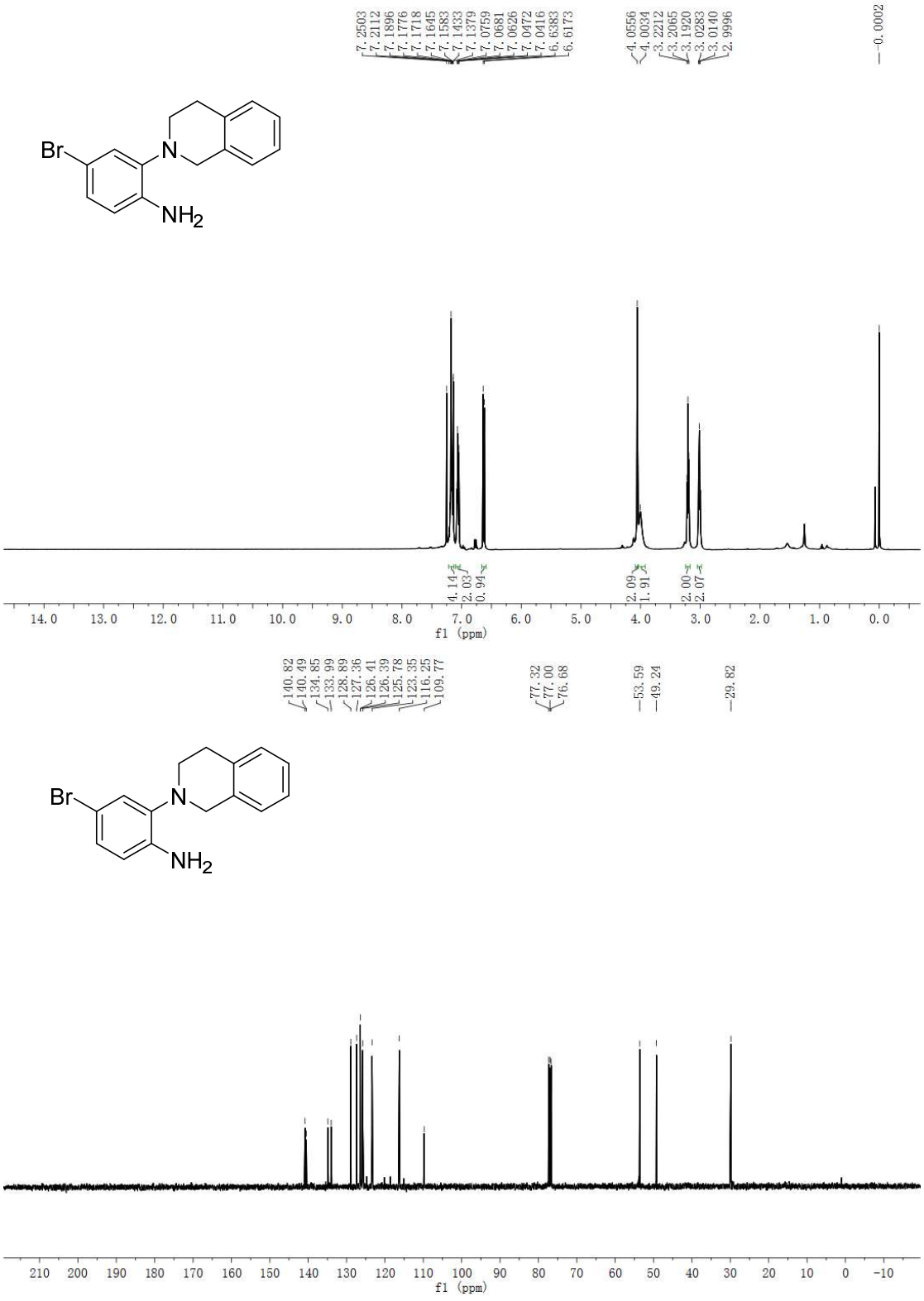
2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-methoxyaniline (3e)



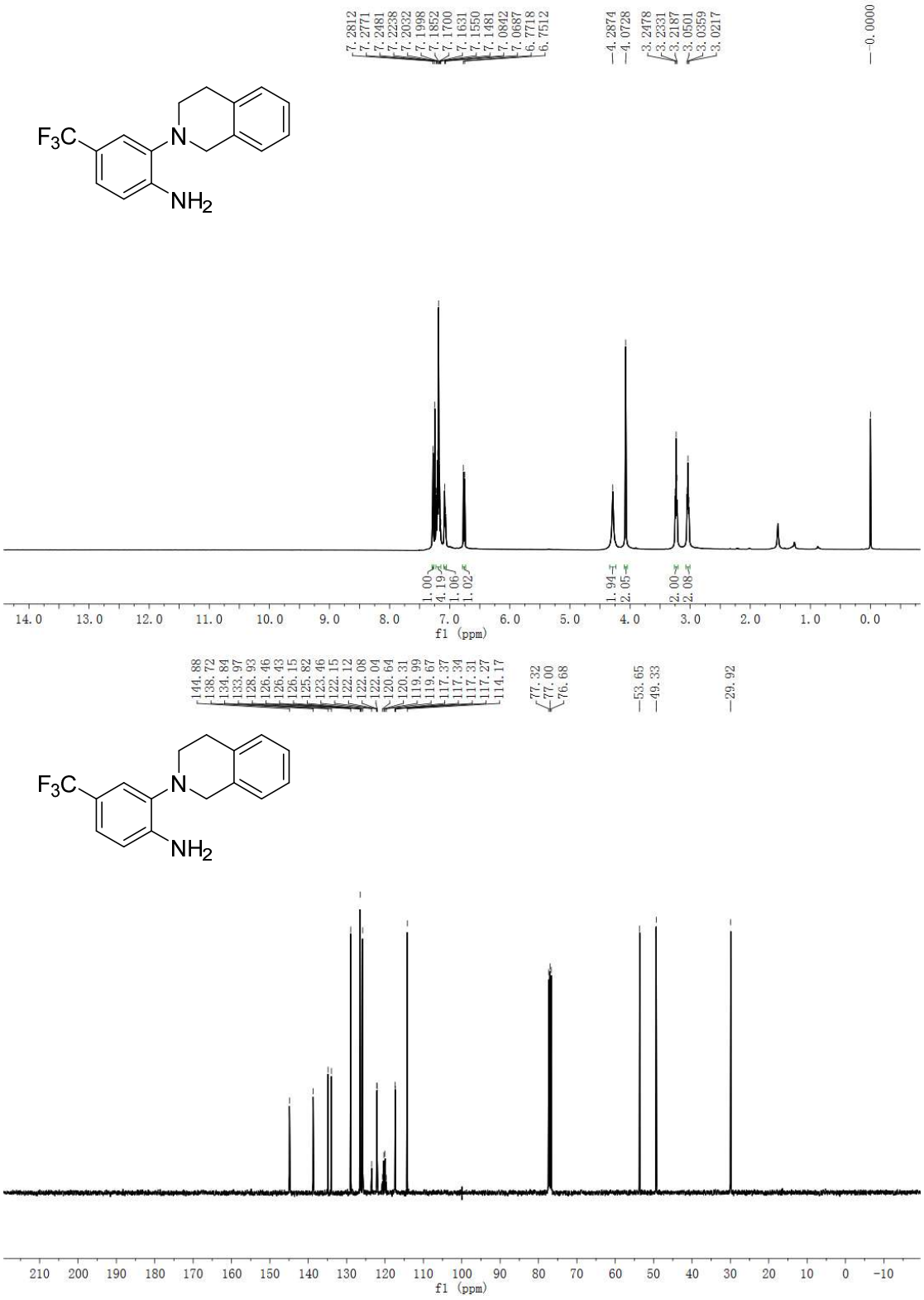
4-amino-3-(3,4-dihydroisoquinolin-2(1H)-yl)phenol (3f)



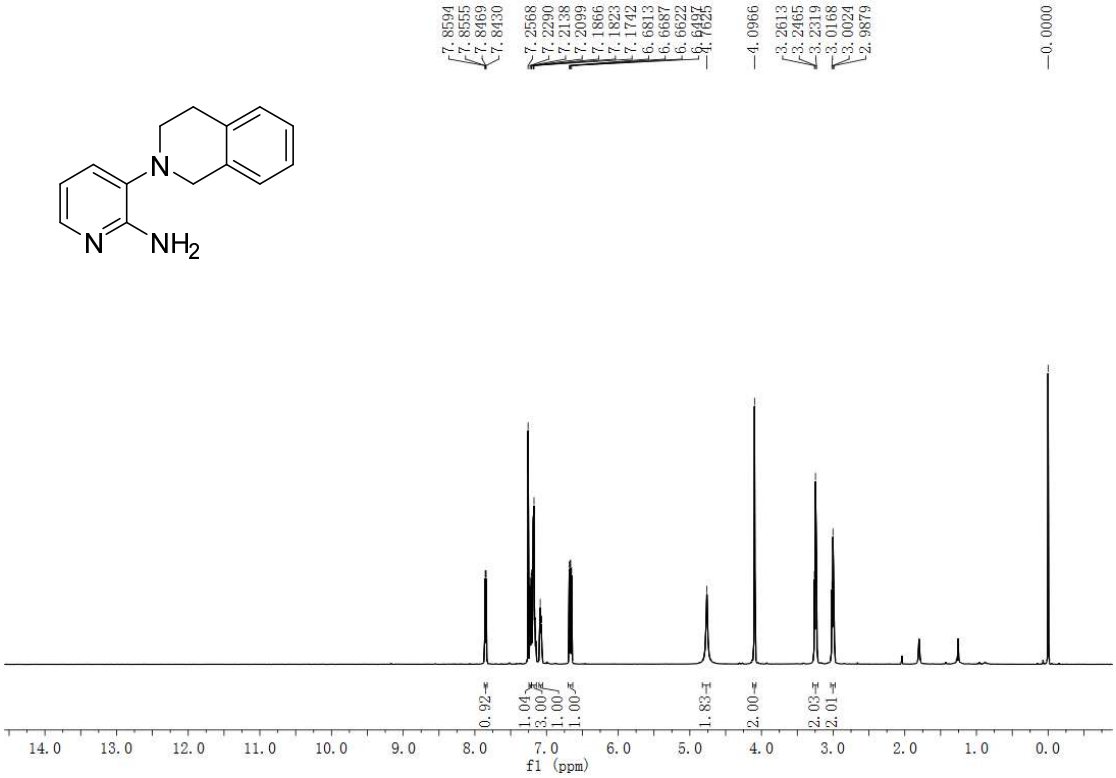
4-bromo-2-(3,4-dihydroisoquinolin-2(1H)-yl)aniline (3g)

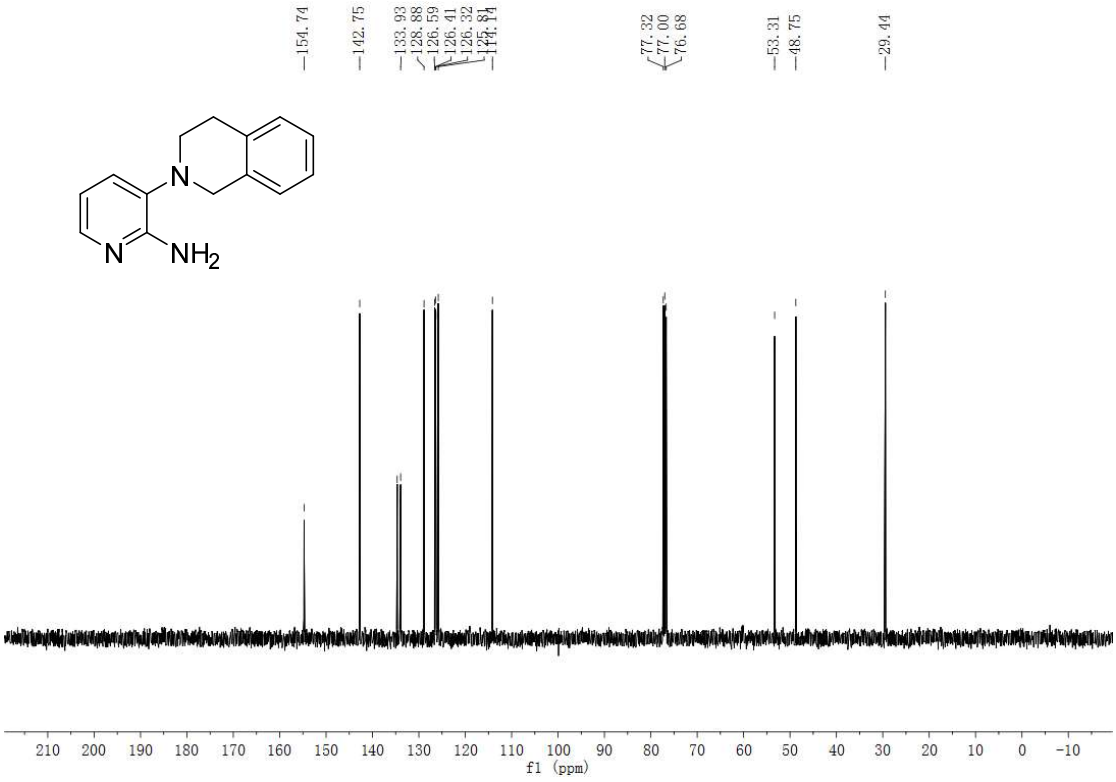


2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-(trifluoromethyl)aniline (3h)



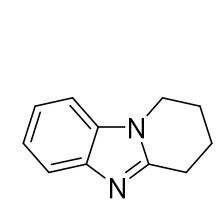
3-(3,4-dihydroisoquinolin-2(1H)-yl)pyridin-2-amine (3i)

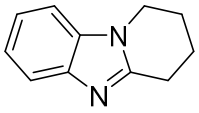




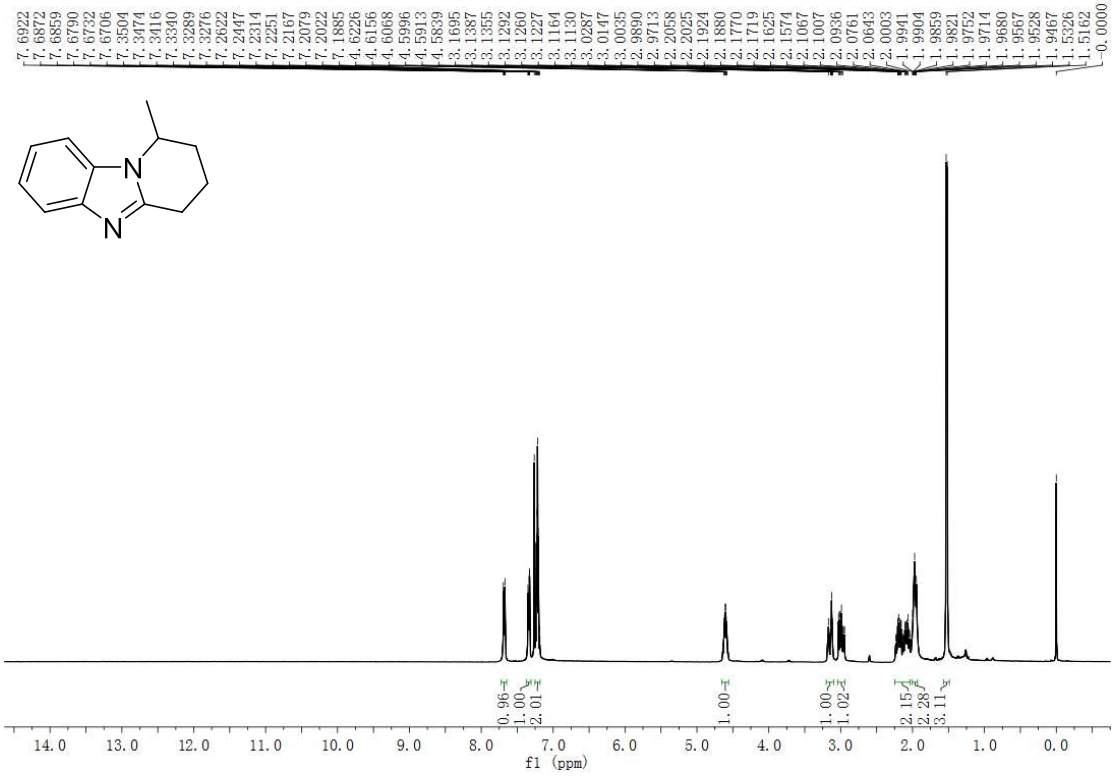
6. ^{1}H and ^{13}C NMR Spectra of the products

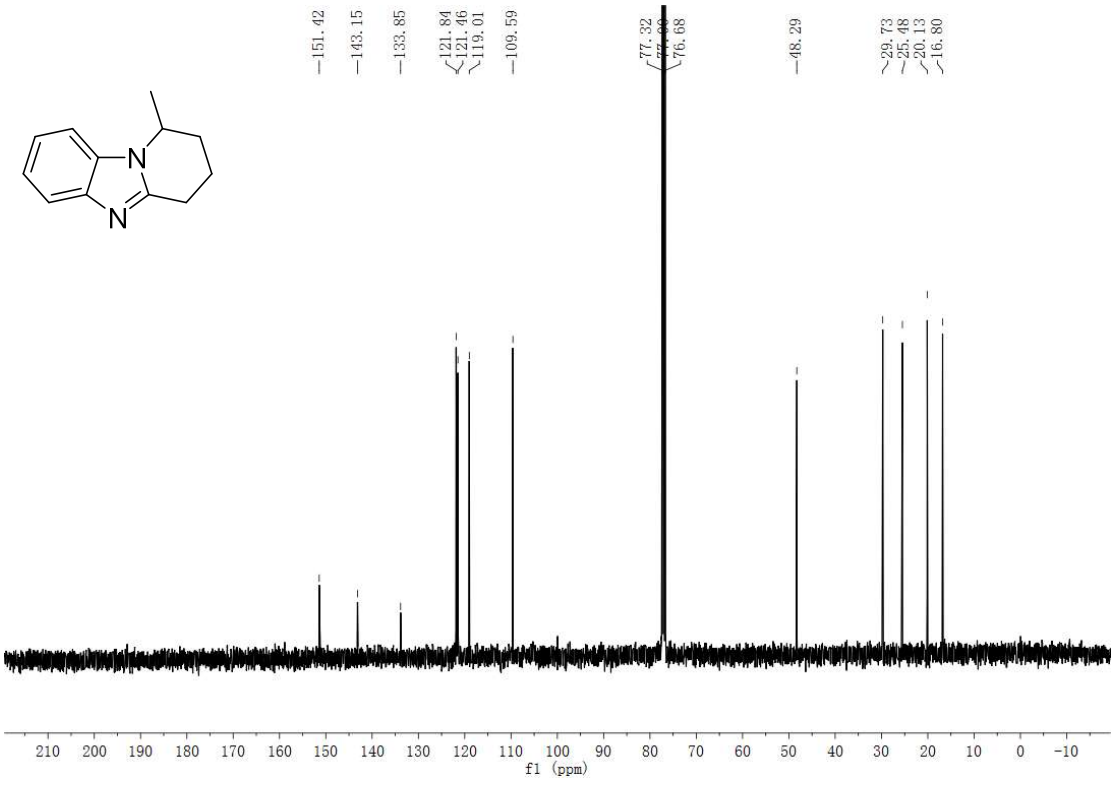
1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2a)



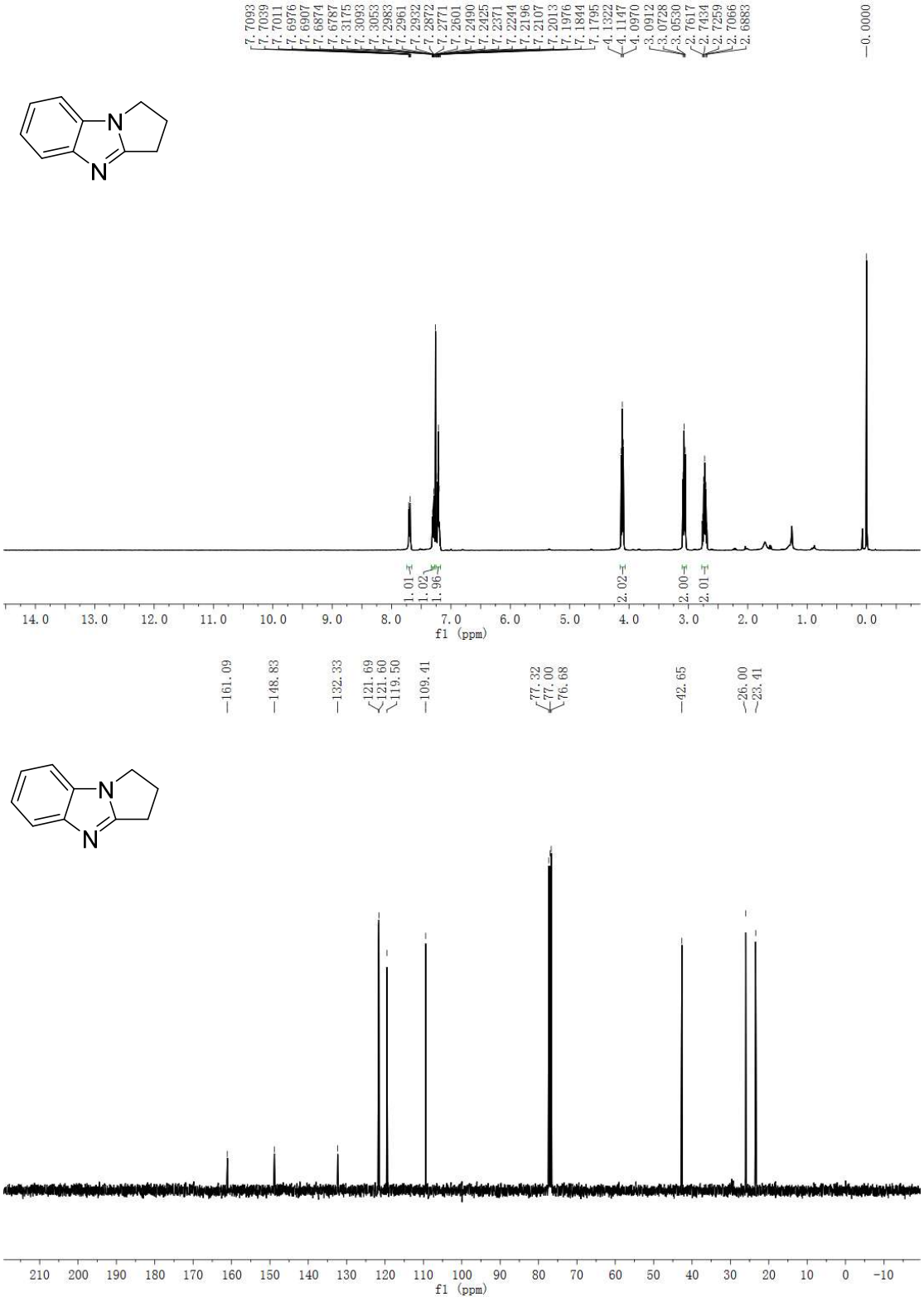


1-methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2b)

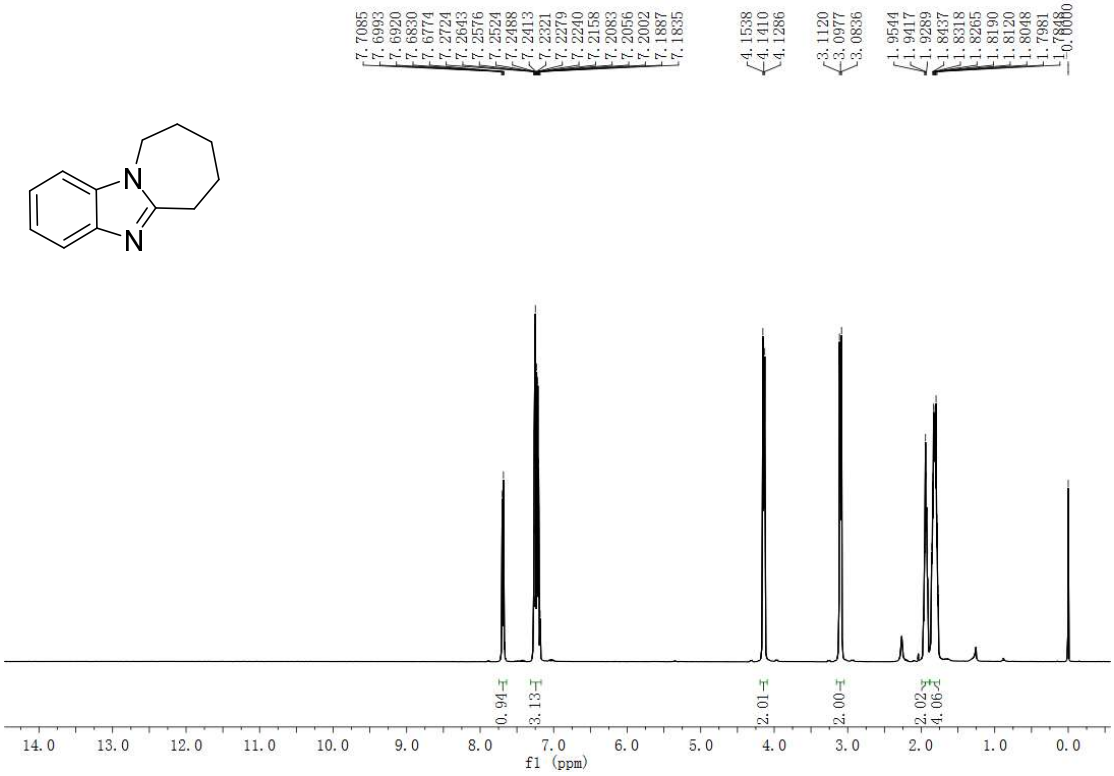


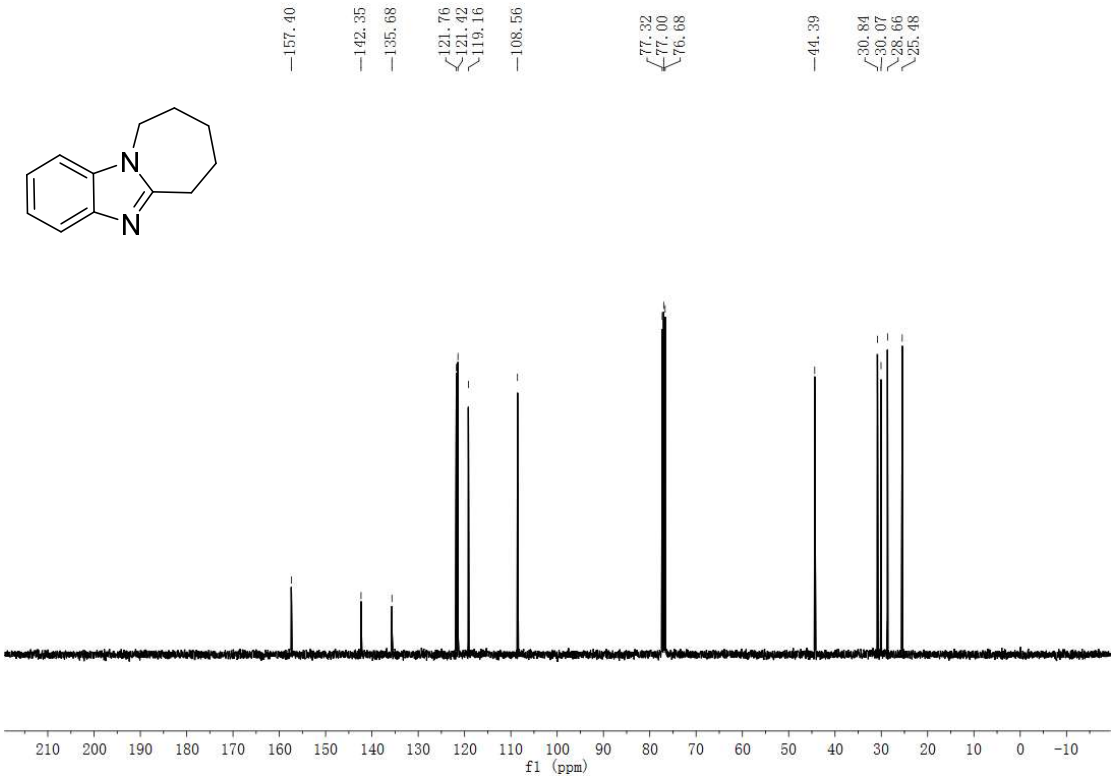


2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (2c)

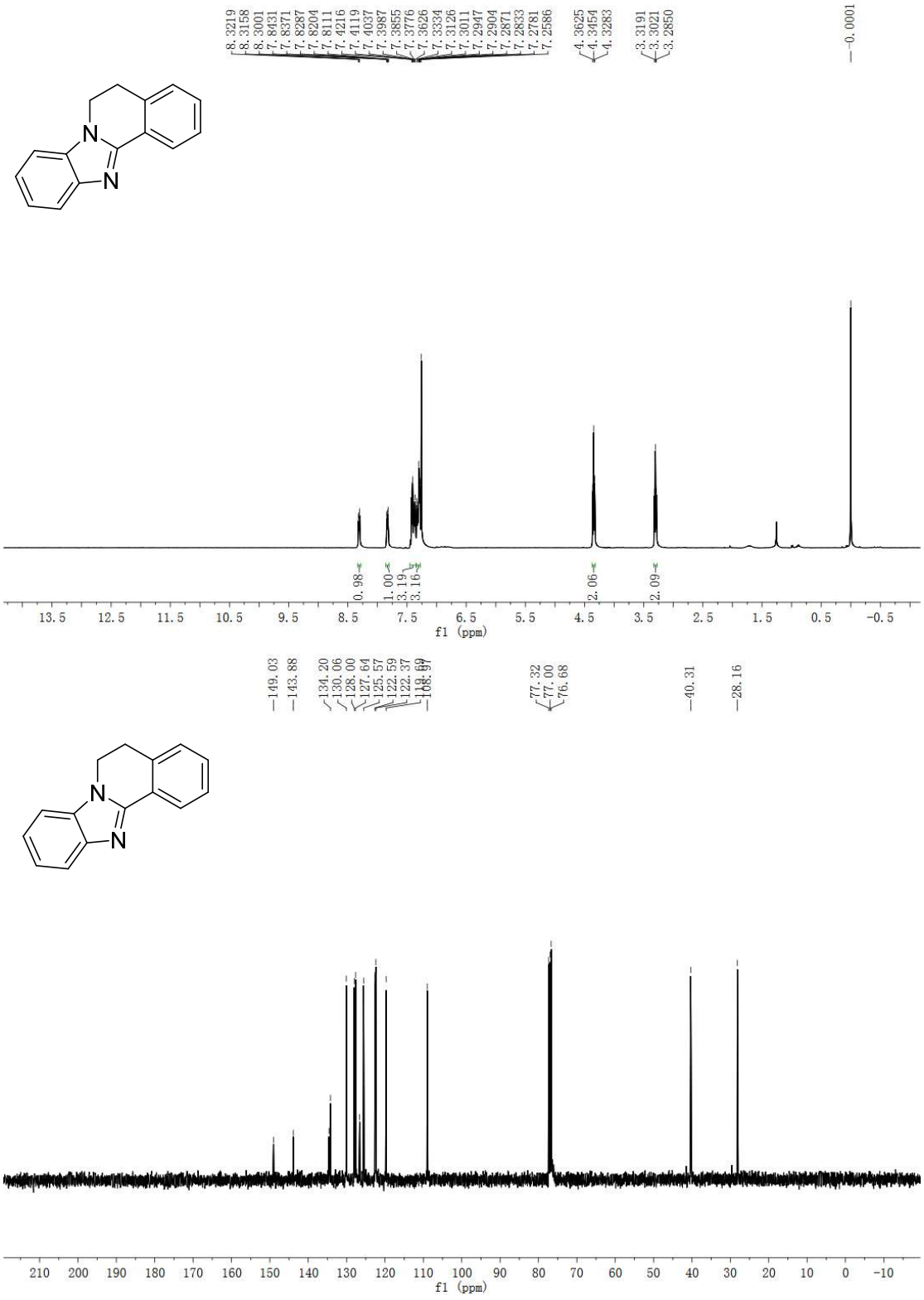


7,8,9,10-tetrahydro-6H-benzo[4,5]imidazo[1,2-a]azepine (2d)

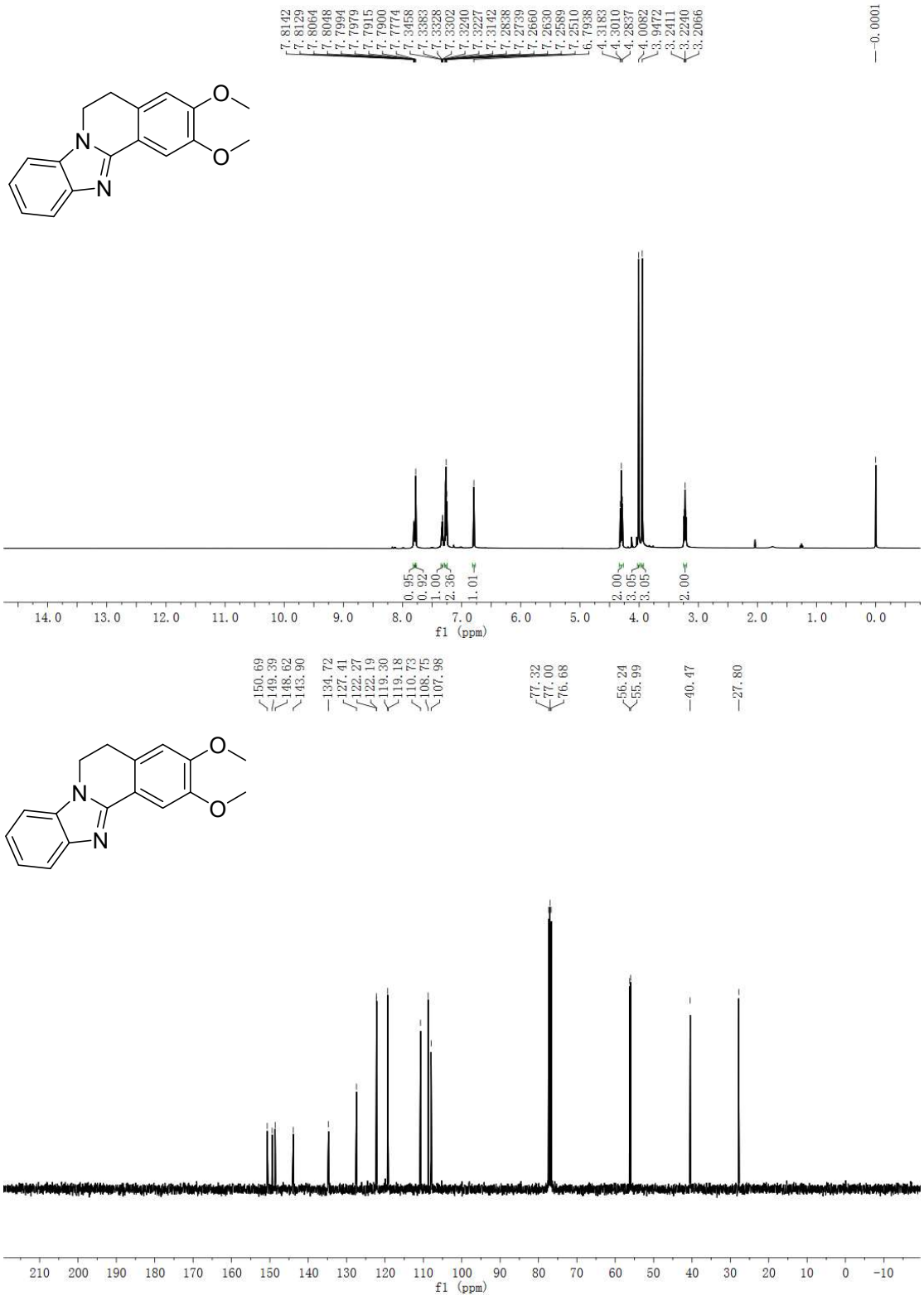




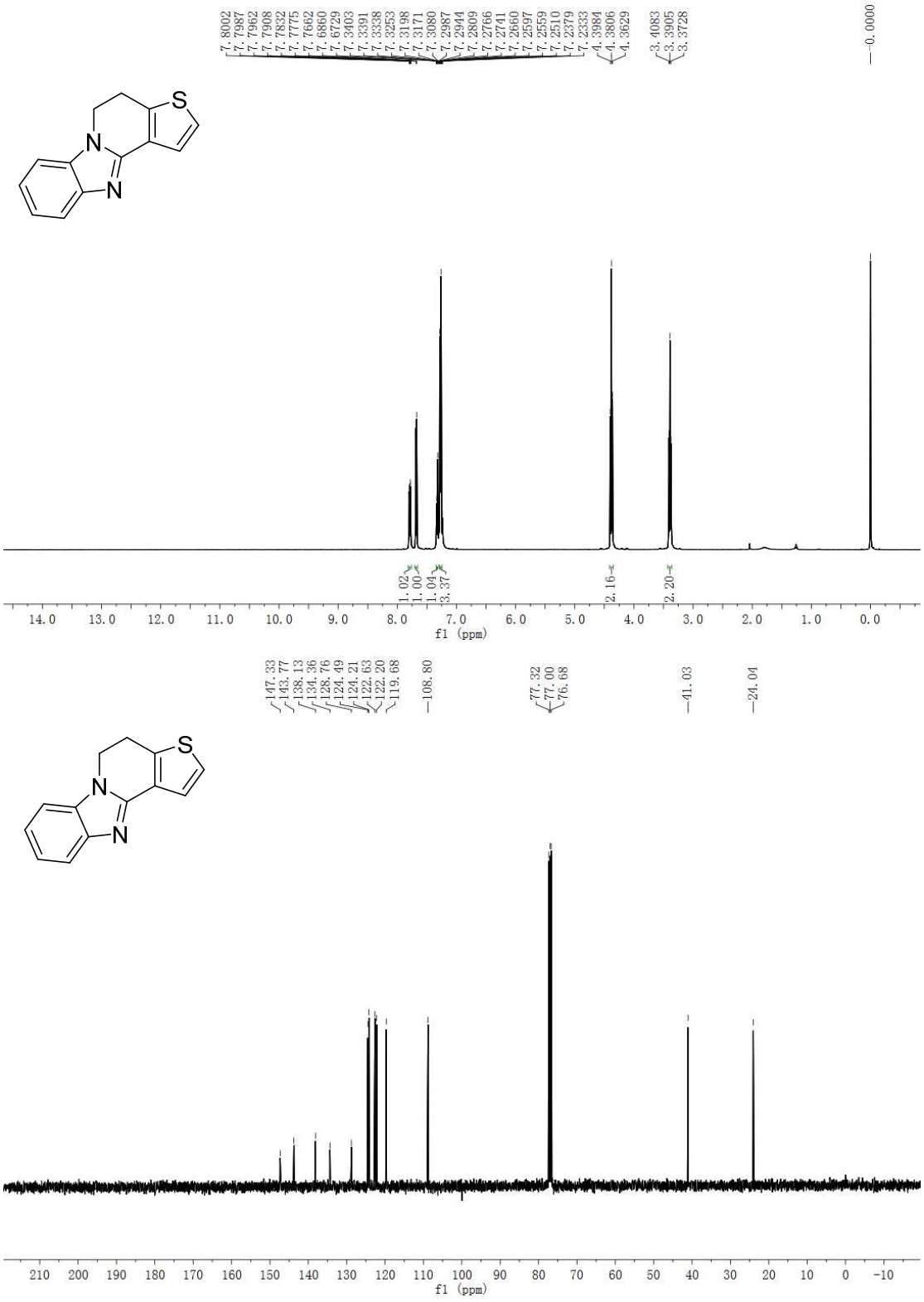
5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2g)



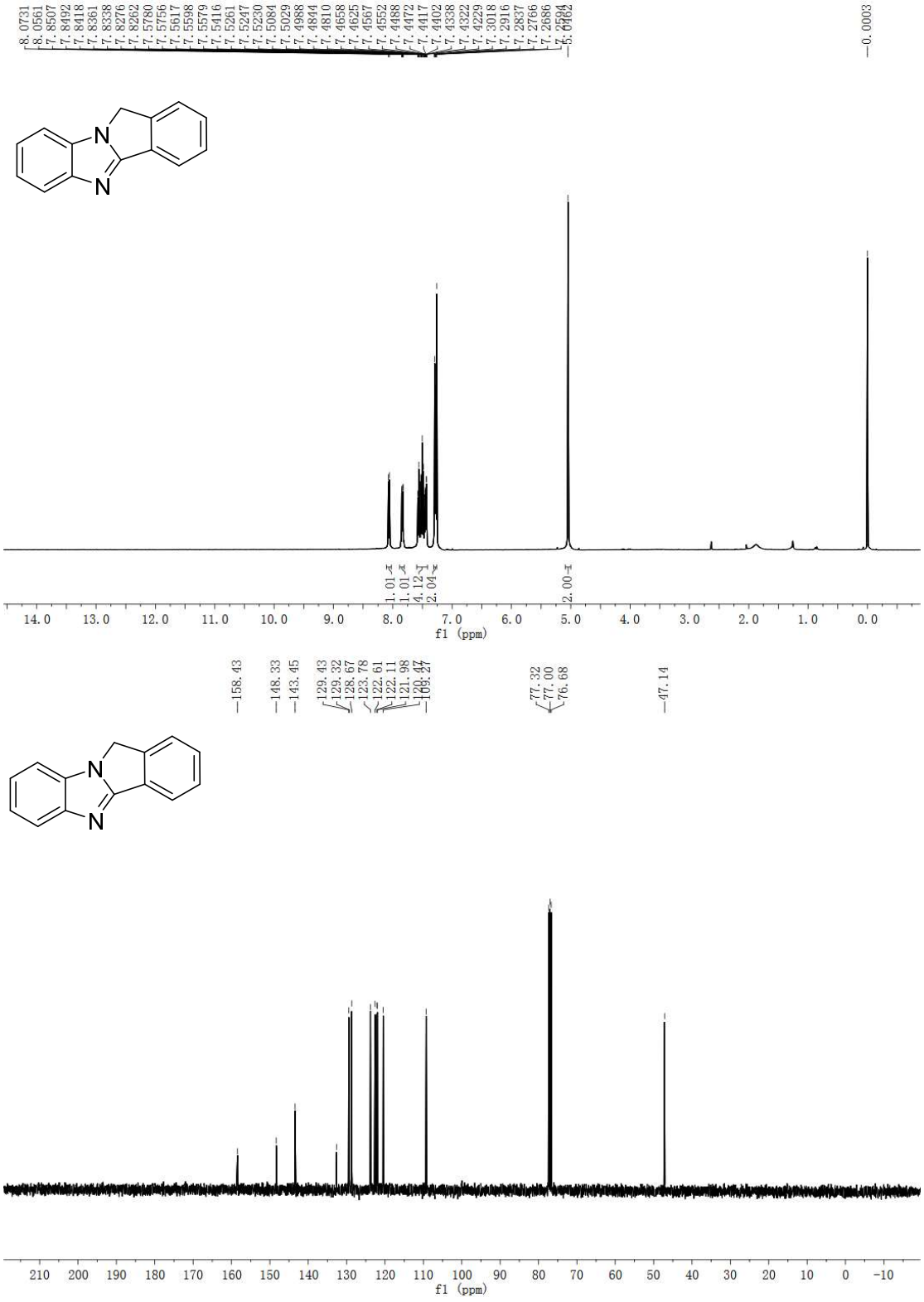
2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2h)



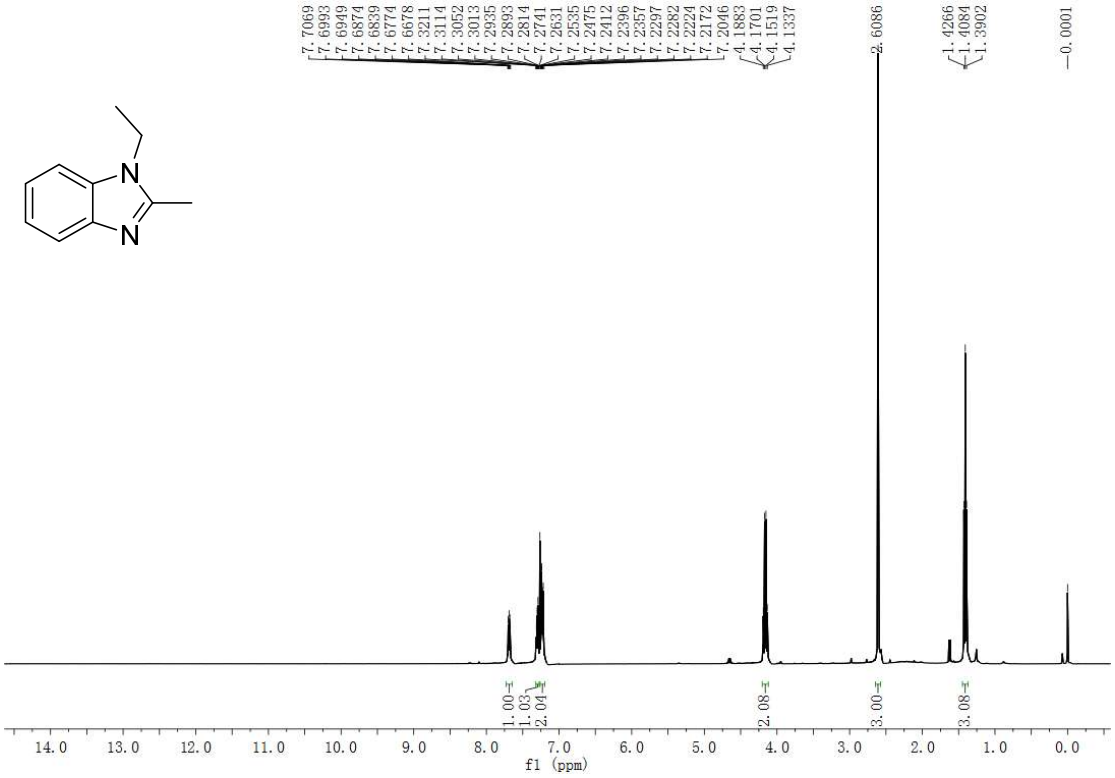
4,5-dihydrobenzo[4,5]imidazo[1,2-a]thieno[3,2-c]pyridine (2i)

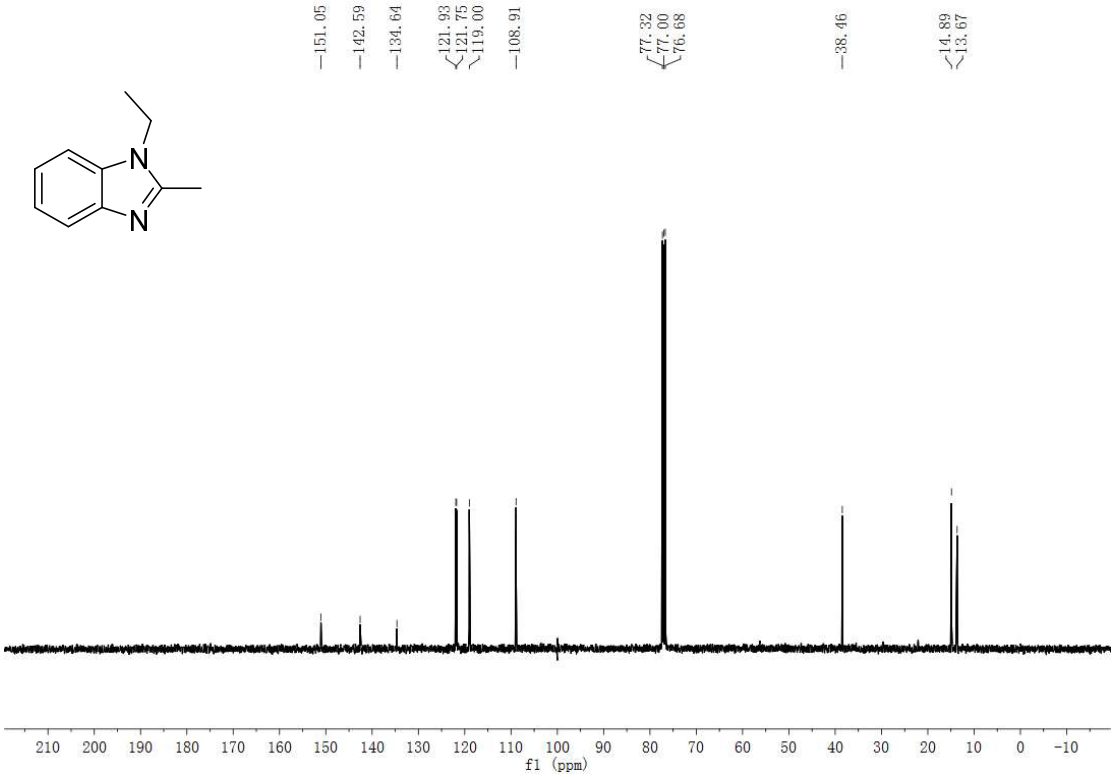


11H-benzo[4,5]imidazo[2,1-a]isoindole (2j)

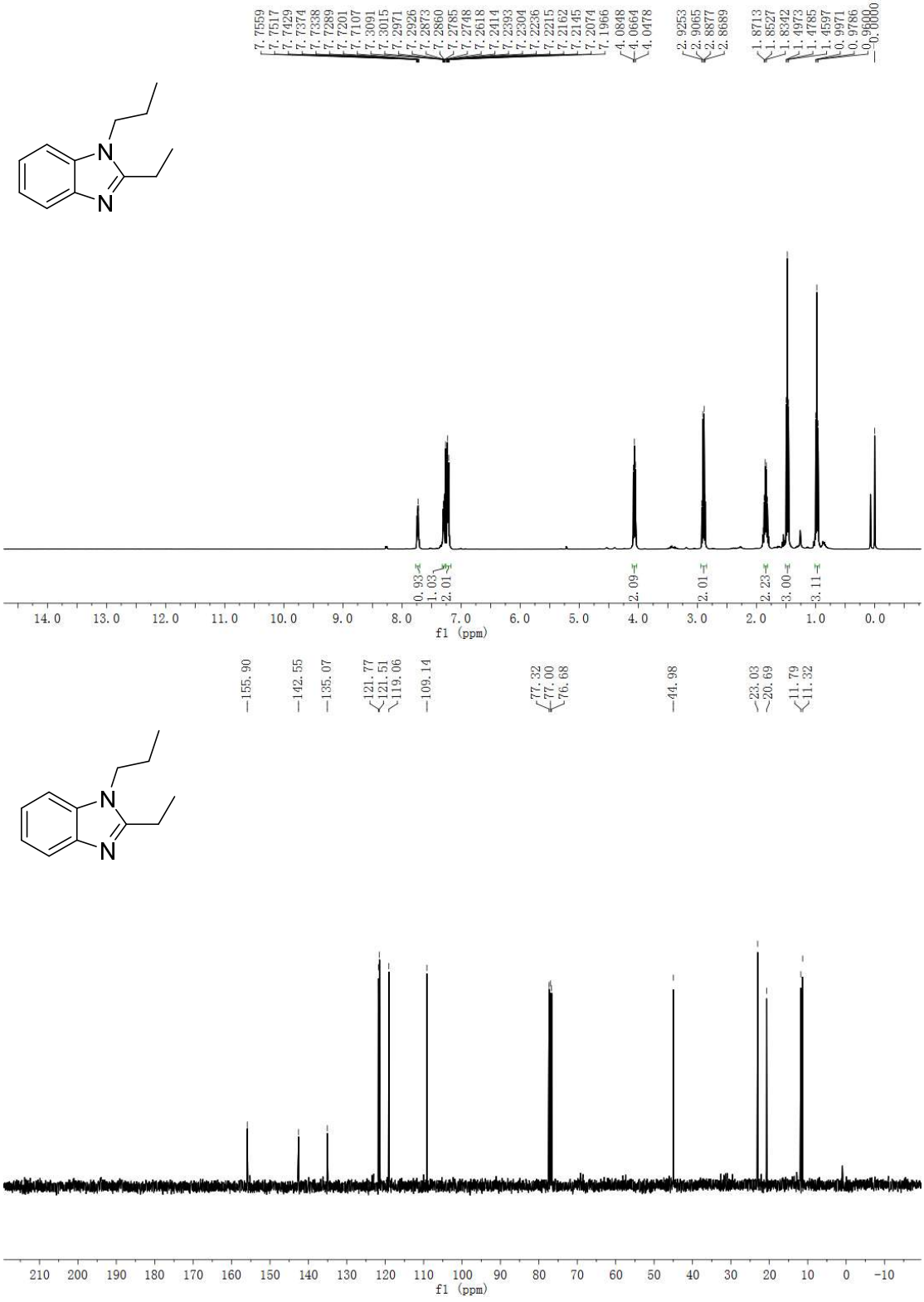


1-ethyl-2-methyl-1H-benzo[d]imidazole (2l)

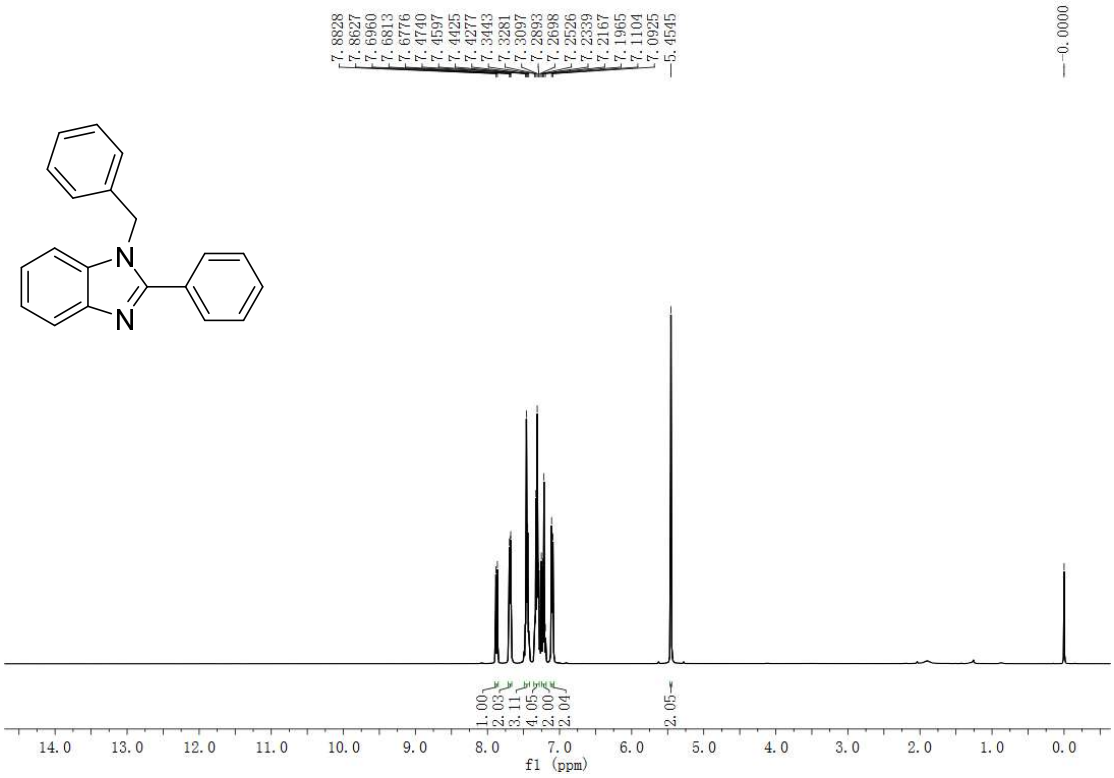


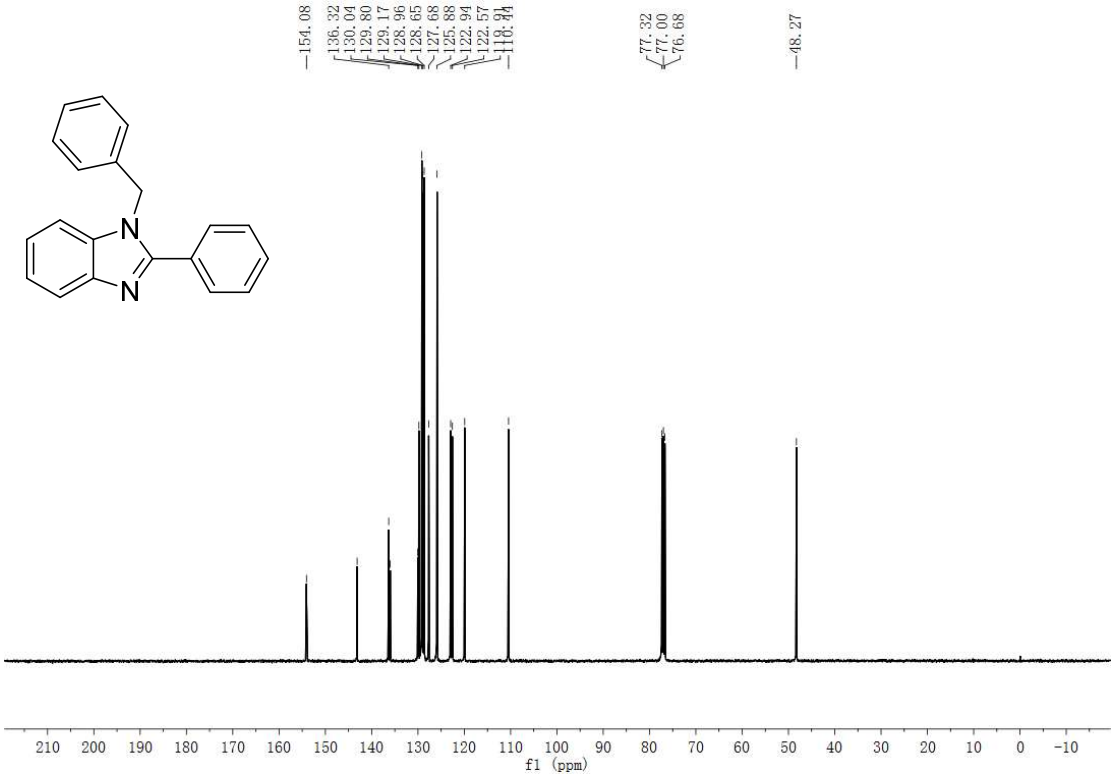


2-ethyl-1-propyl-1H-benzo[d]imidazole (2m)

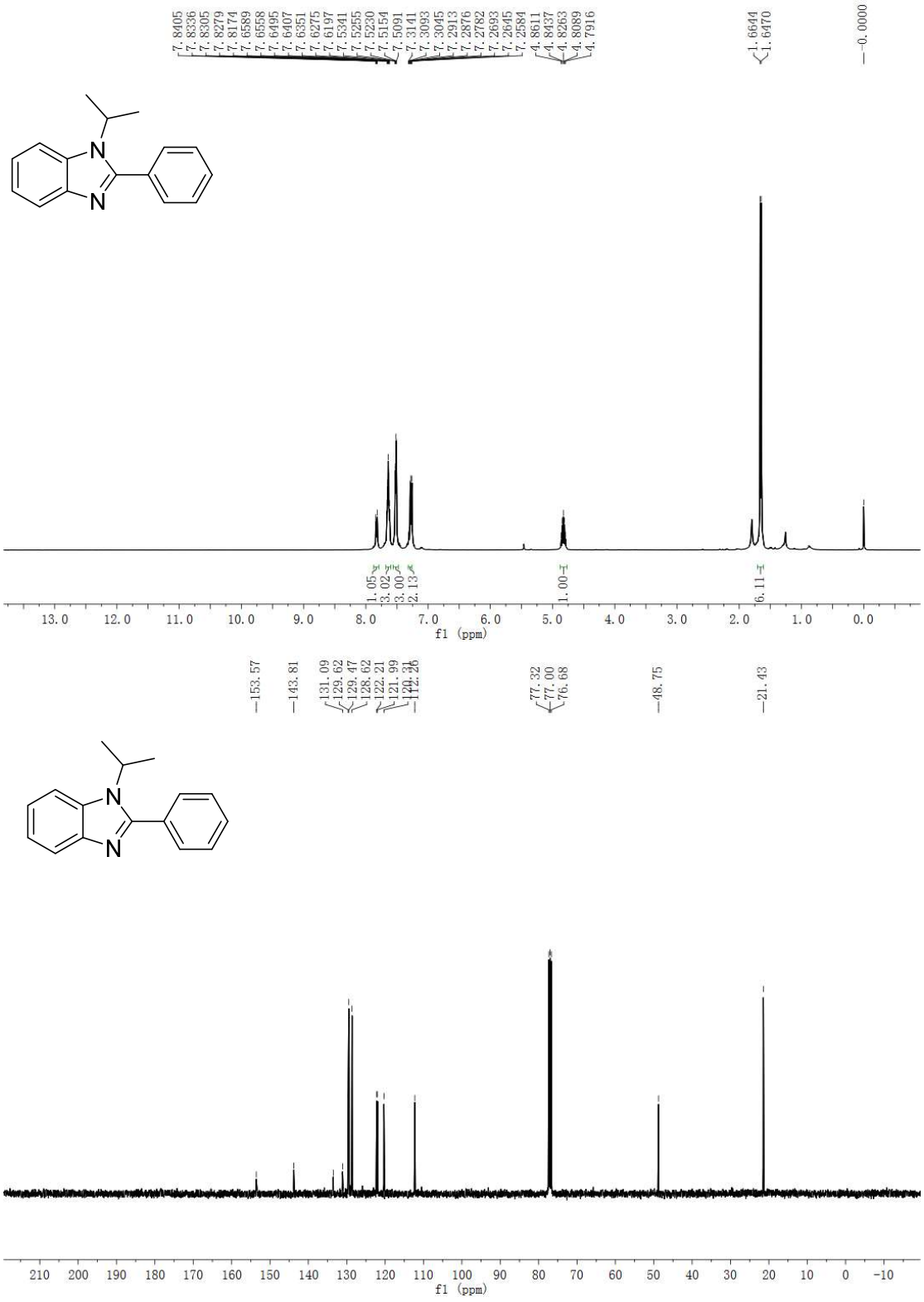


1-benzyl-2-phenyl-1H-benzo[d]imidazole (2n)

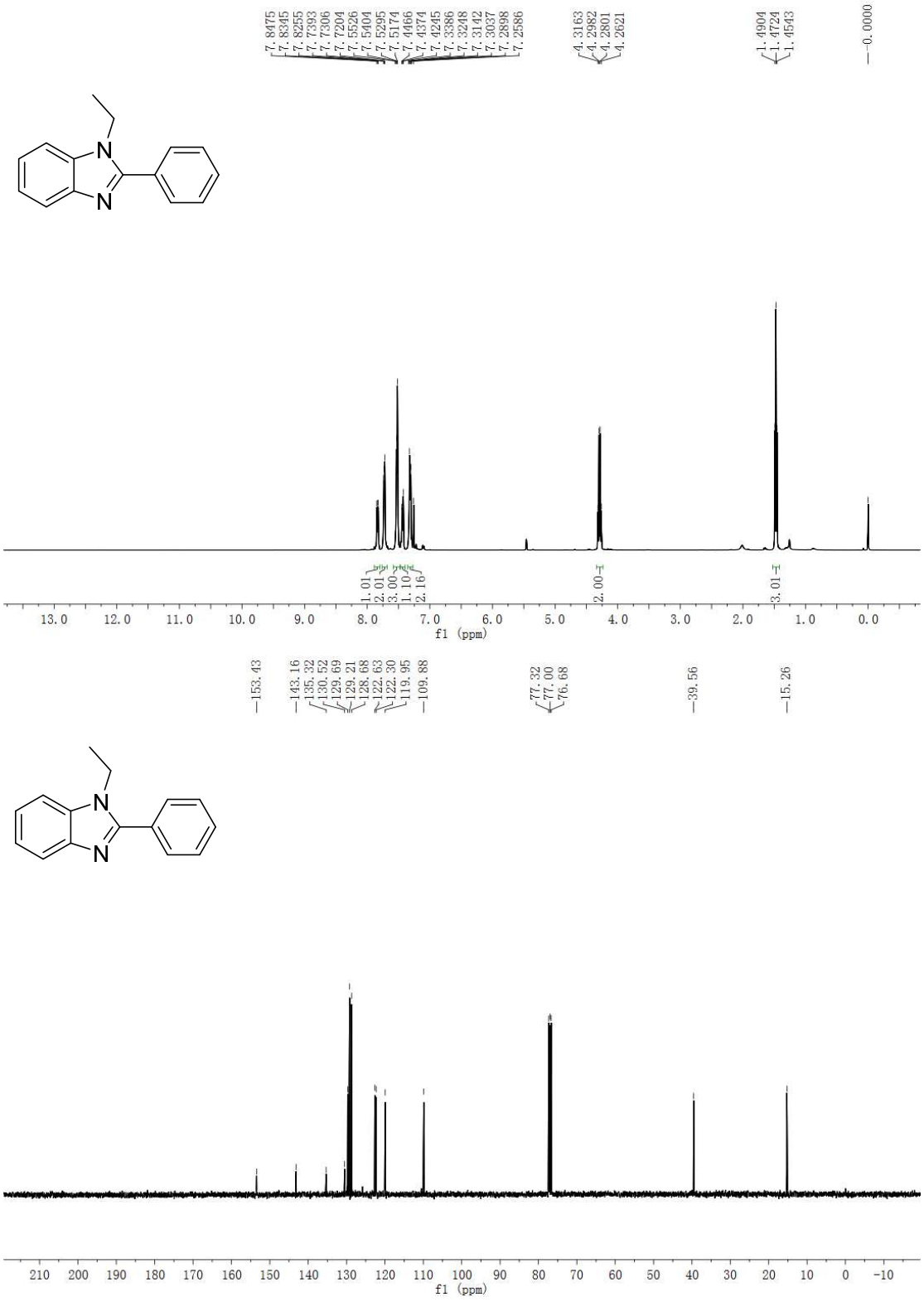




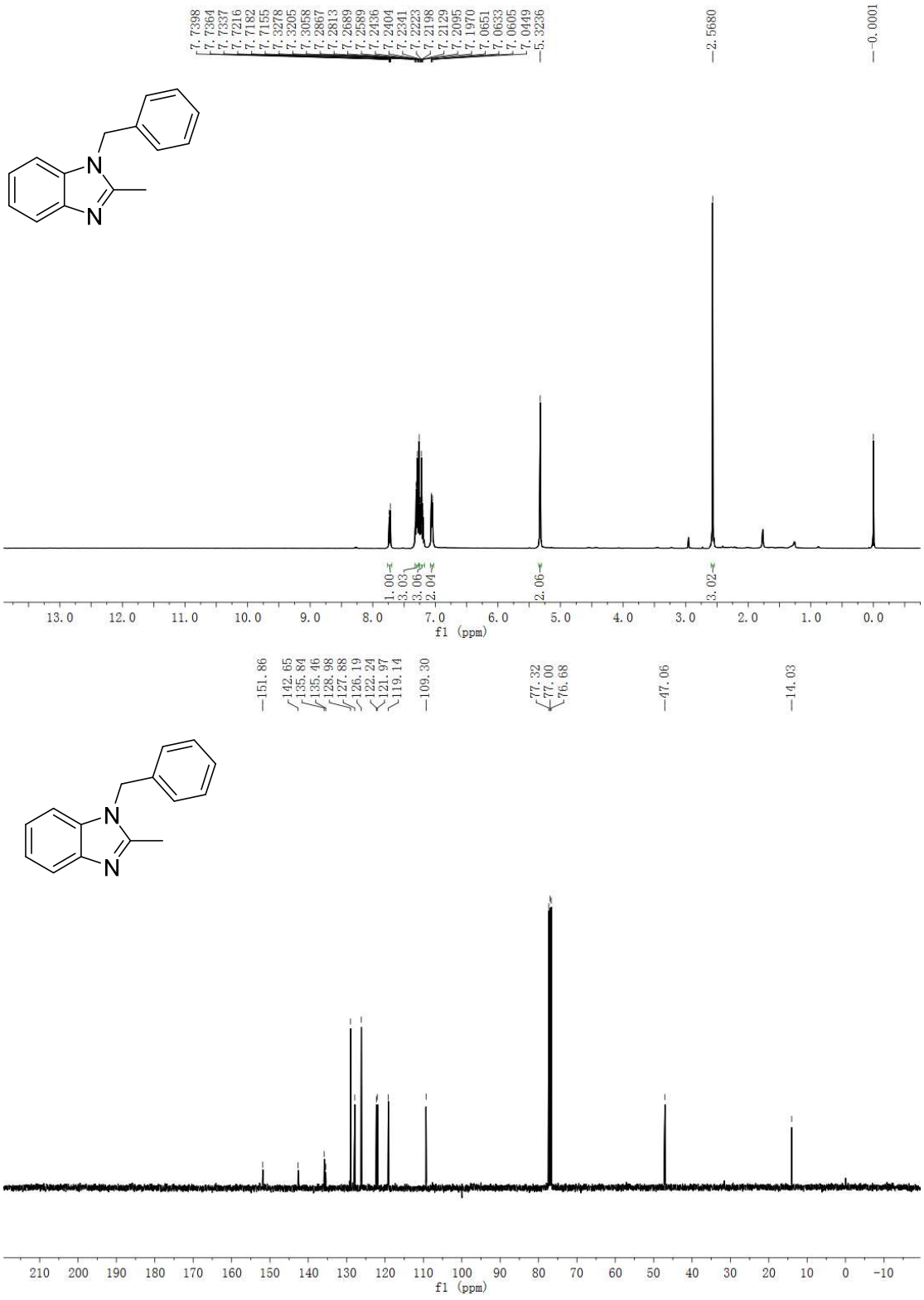
1-isopropyl-2-phenyl-1H-benzo[d]imidazole (2o)



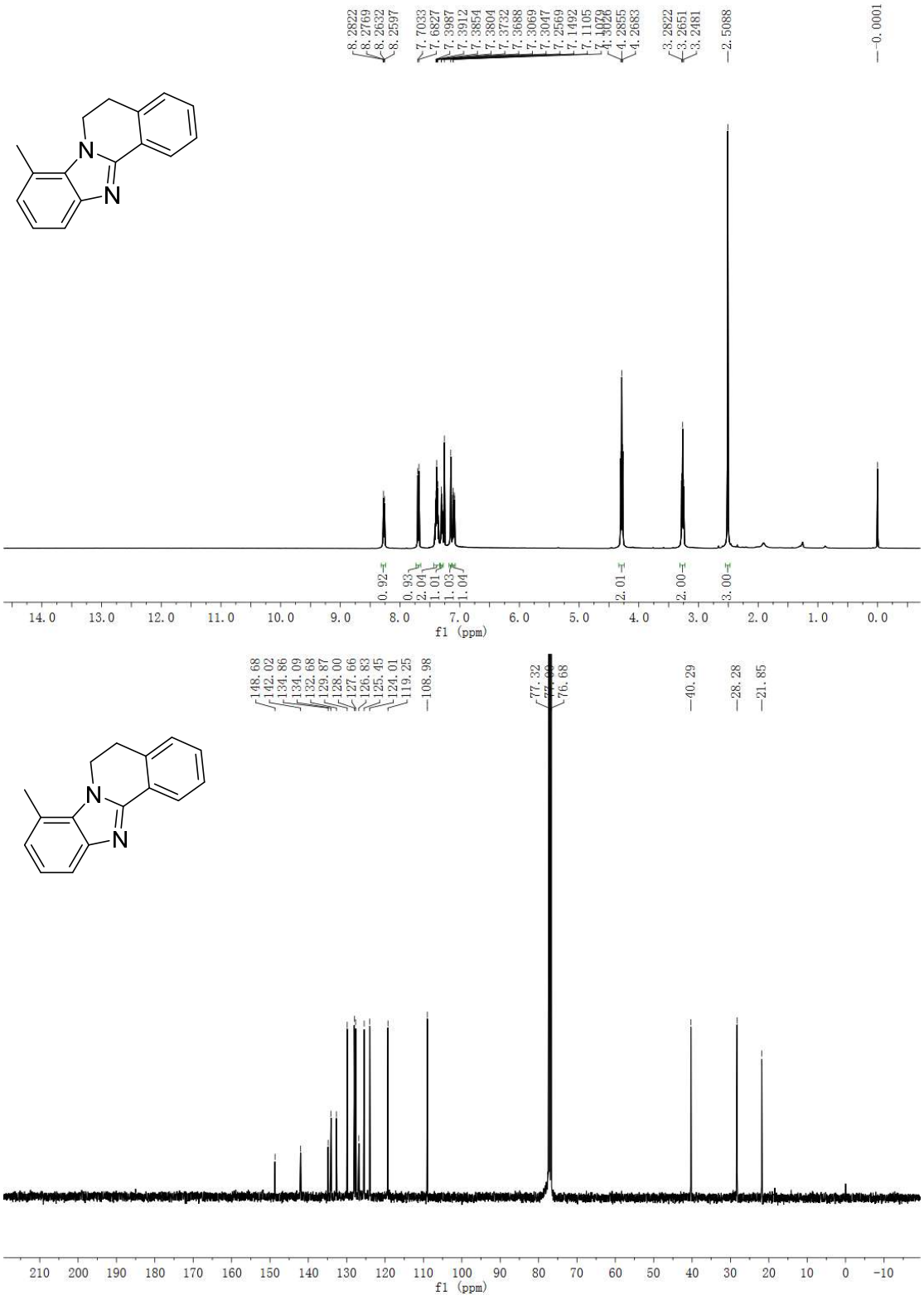
1-ethyl-2-phenyl-1H-benzo[d]imidazole (2pa)



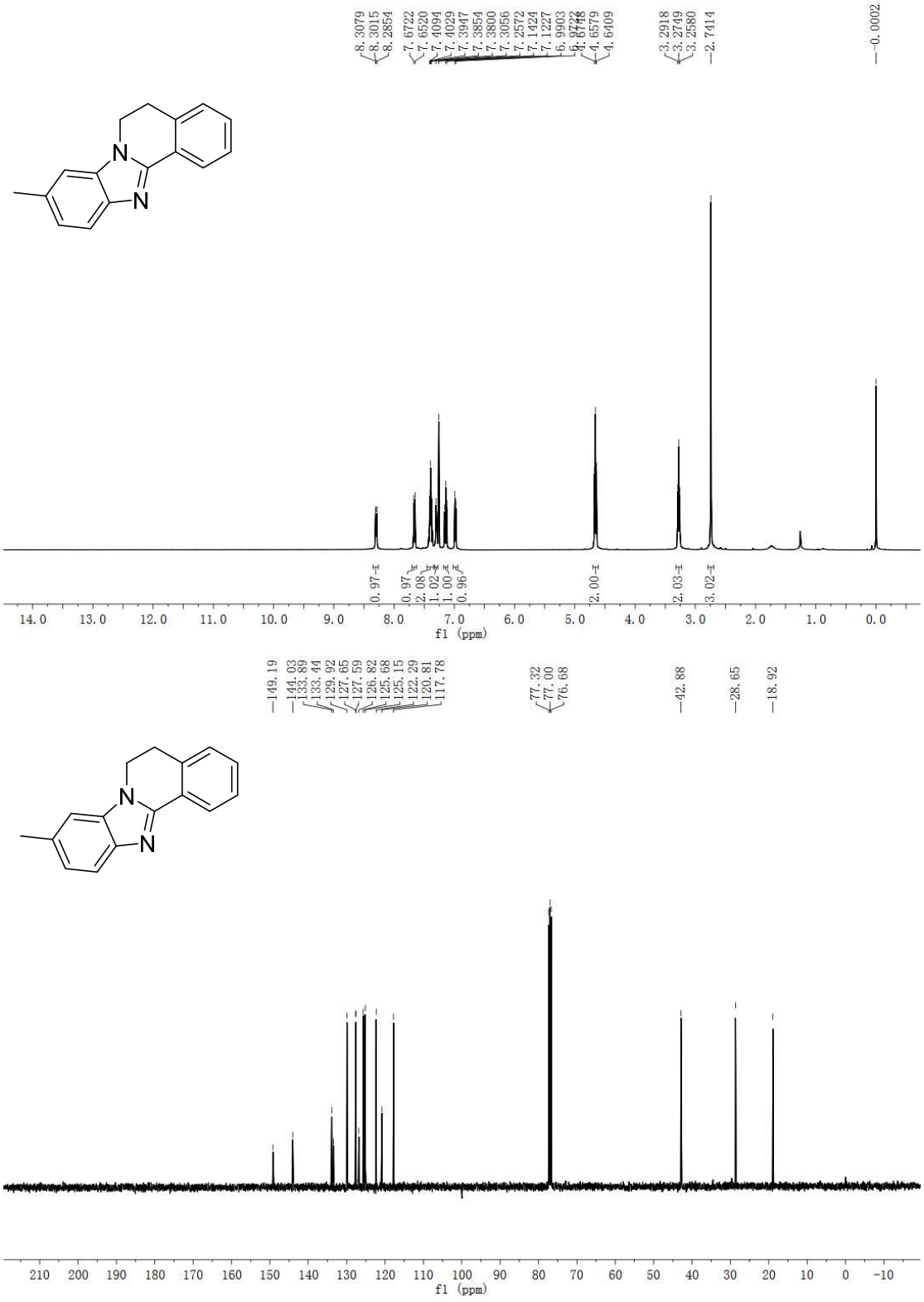
1-benzyl-2-methyl-1H-benzo[d]imidazole (2pb)



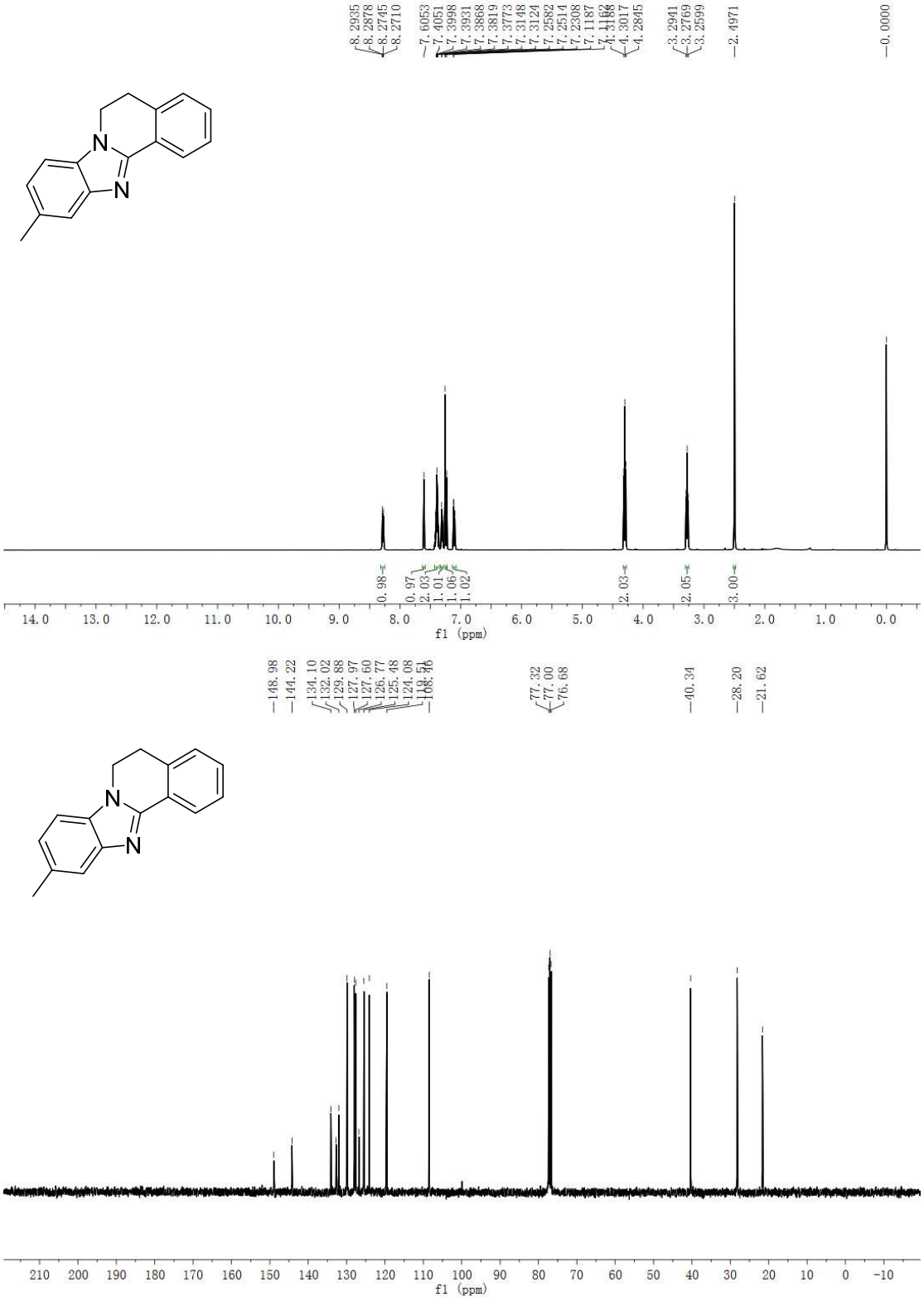
8-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4a)



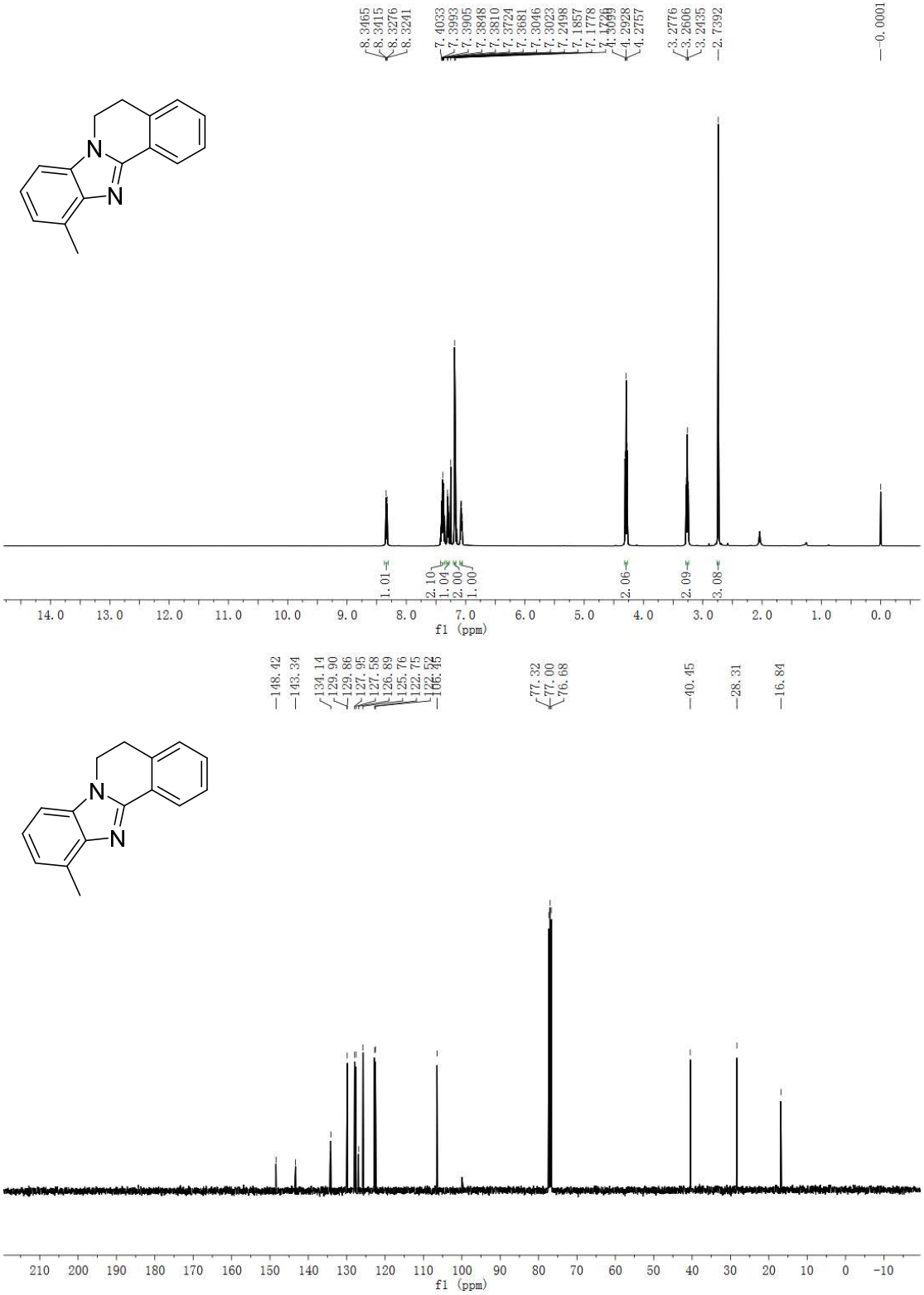
9-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4b)



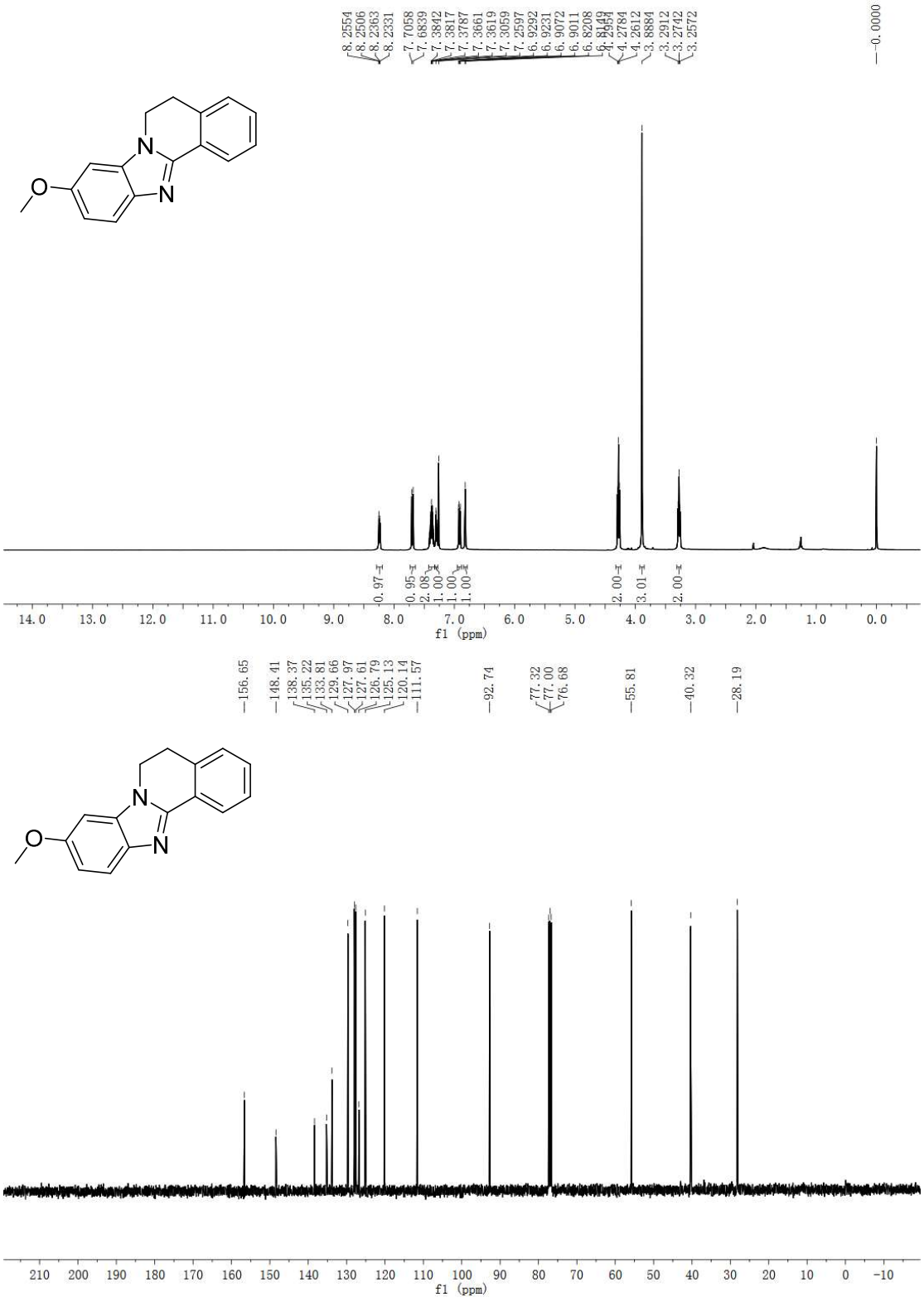
10-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4c)



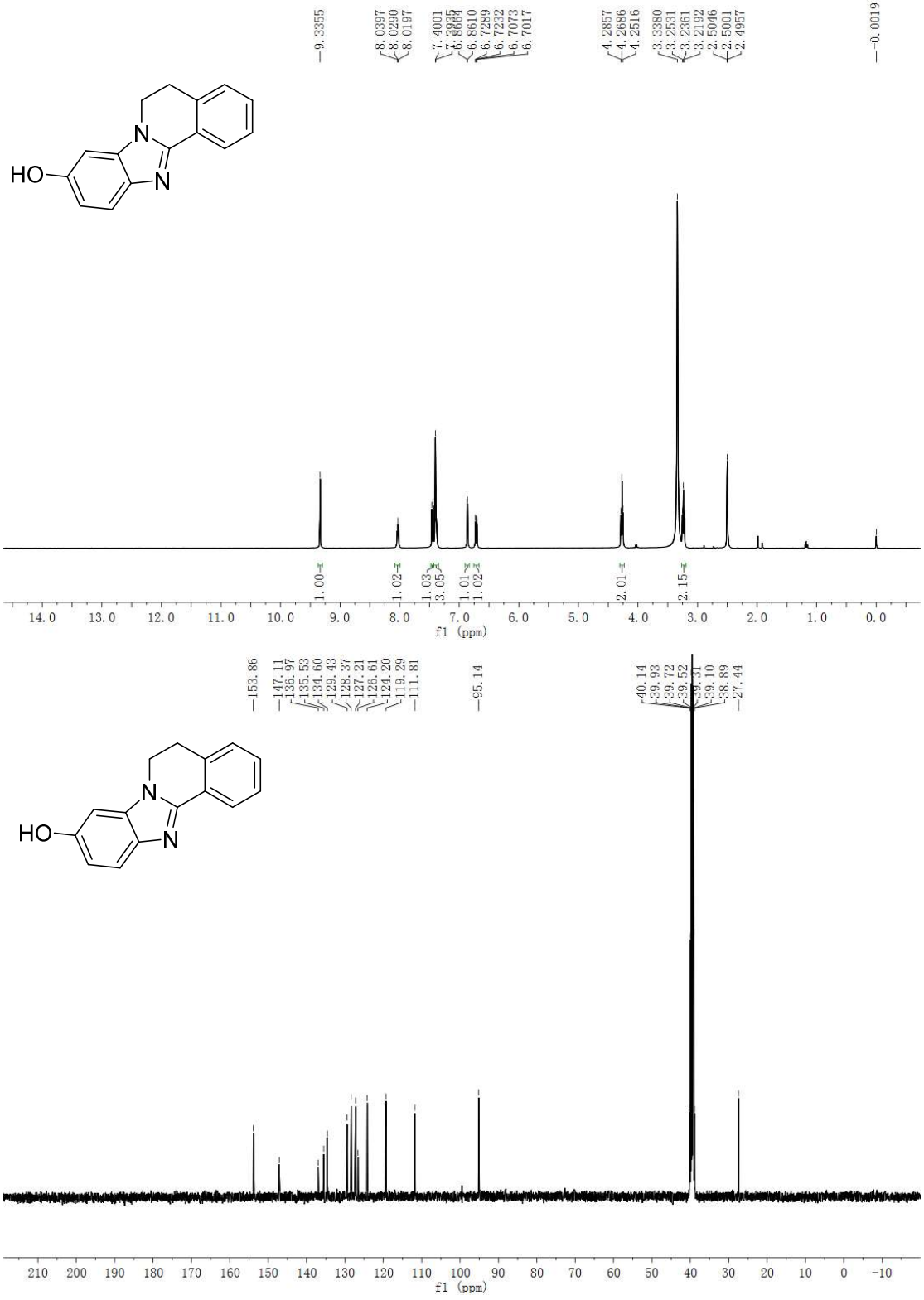
11-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4d)



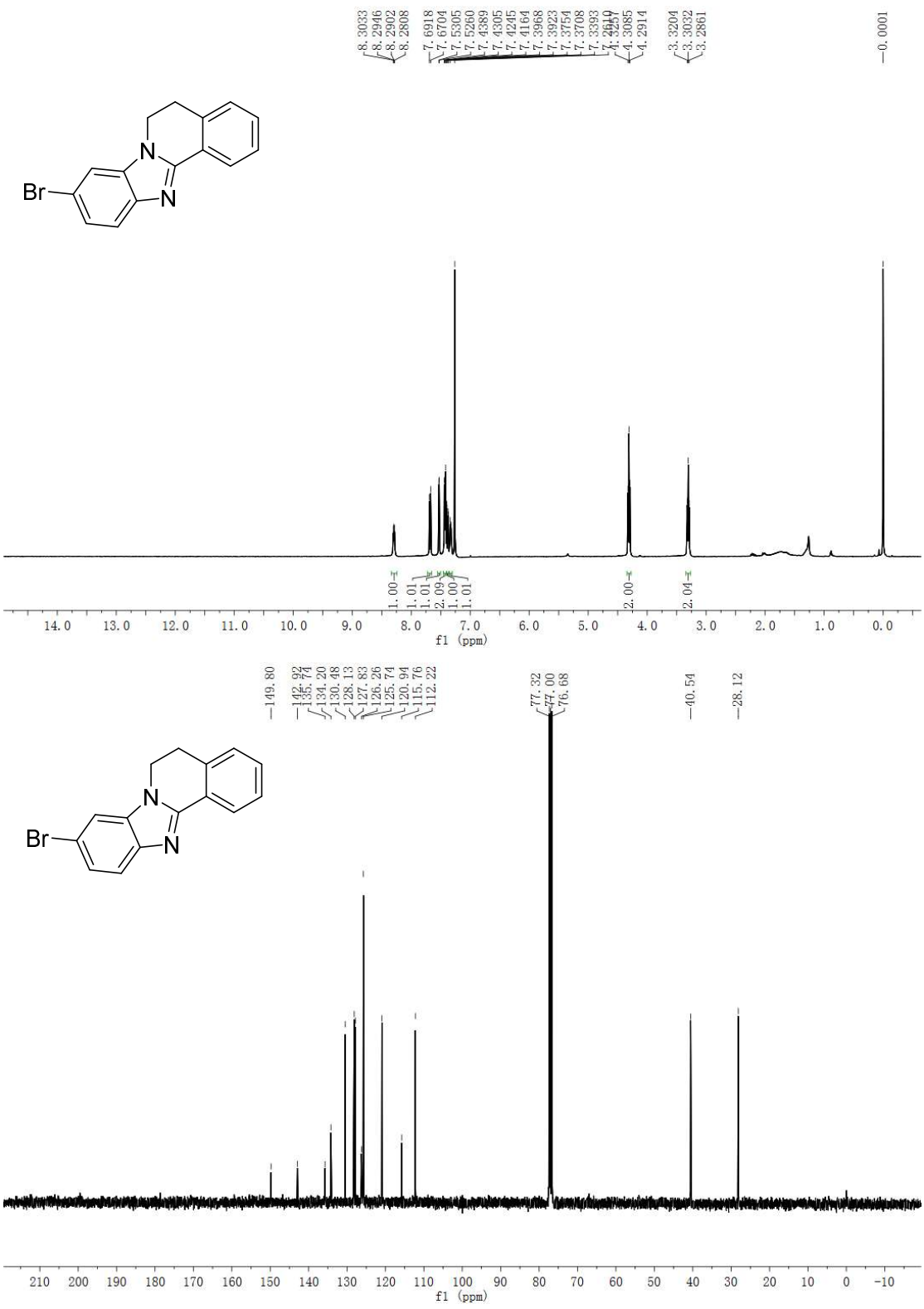
9-methoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4e)



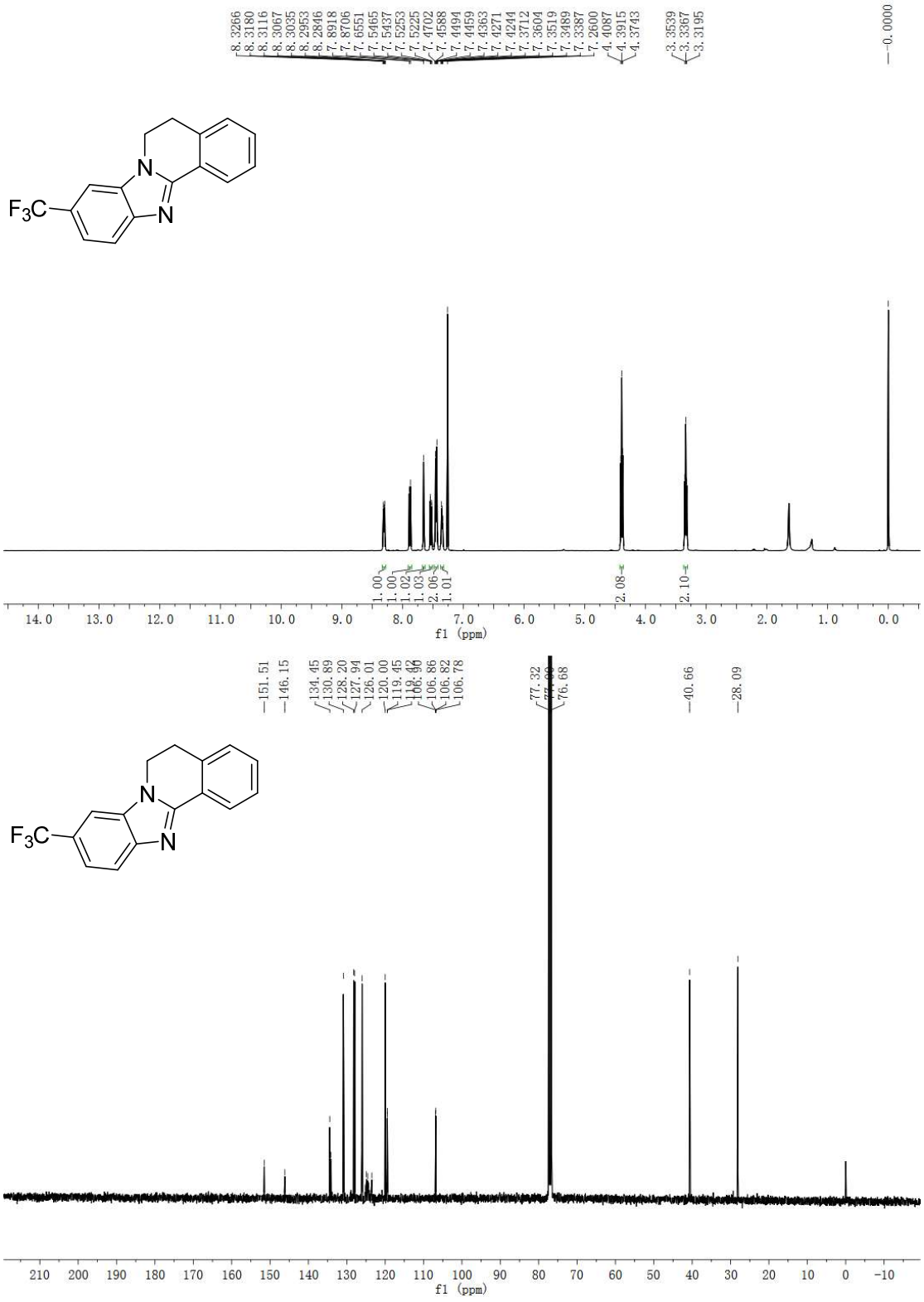
5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-9-ol (4f)



9-bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4g)



9-(trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (4h)



5,6-dihydropyrido[2',3':4,5]imidazo[2,1-a]isoquinoline (4i)