

An Efficient Synthesis of Carbazoles from PtCl₂-Catalyzed Cyclization of 1-(Indol-2-yl)-2,3-allenols

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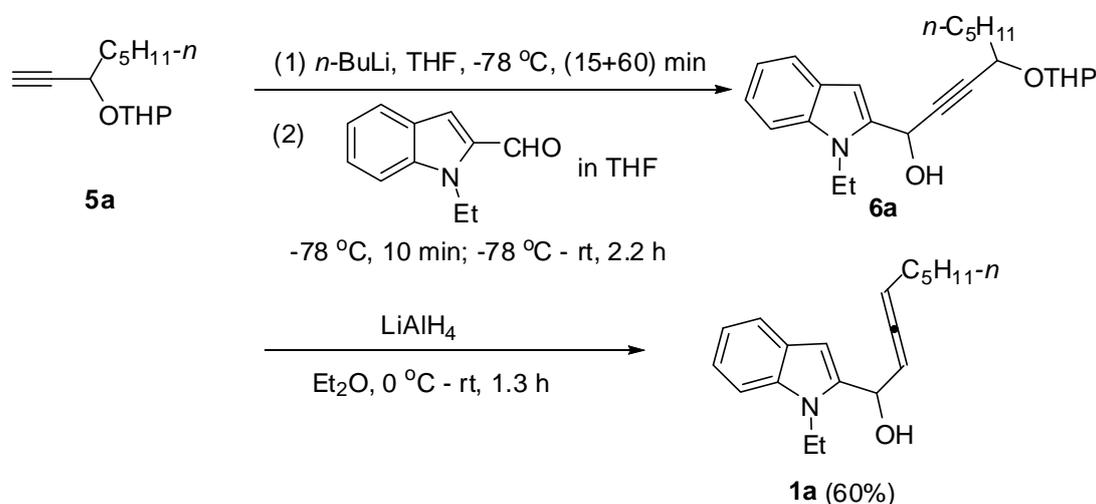
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Supporting Information

Experimental details and analytical data for all the products listed in the text	S2
¹ H and ¹³ C NMR spectra of all compounds	S34

1. Synthesis of Allenic Alcohols 1a-1f

(1) 1-(1-Ethyl-1*H*-indol-2-yl)nona-2,3-dien-1-ol (1a)^[1]



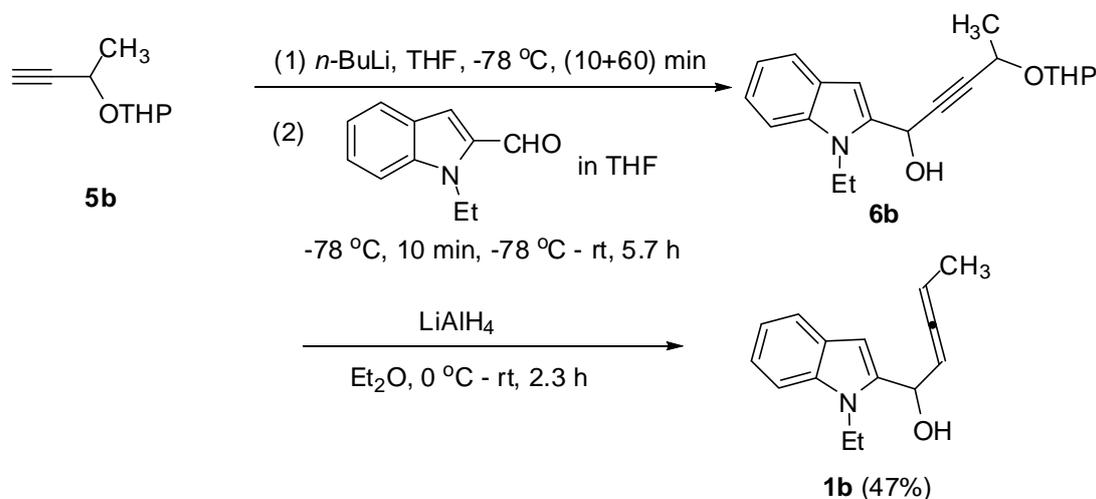
Typical procedure: To a solution of **5a**^[2] (2.5010 g, 12 mmol) in THF (25 mL) was slowly added dropwise *n*-butyl lithium (5.8 mL, 2.5 M in hexane, 14.5 mmol) at $-78\text{ }^\circ\text{C}$ with stirring under a nitrogen atmosphere within 15 min. After being stirred for 1 h at $-78\text{ }^\circ\text{C}$, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (2.4801 g, 14.3 mmol) in anhydrous THF (5 mL) was added dropwise at this temperature within 10 min. Then the mixture was allowed to warm up to room temperature, quenched with the addition of saturated aqueous NH_4Cl (20 mL), and extracted with diethyl ether (25 mL \times 3). The ether layer was dried over anhydrous Na_2SO_4 , filtrated, and concentrated in vacuo. The product **6a** was then used without further purification.

To an ice-cold suspension of LiAlH_4 (0.5101 g, 13.4 mmol) in dry Et_2O (15 mL) under N_2 was added dropwise a solution of **6a** prepared in the previous step in Et_2O (5 mL) within 10 min. Then the mixture was allowed to warm up to room temperature. After being stirred at rt for 1.1 h, the resulting mixture was quenched with a saturated aqueous solution of NH_4Cl . The aqueous layer was extracted with diethyl ether (15

mL×3). The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1~15/1) afforded **1a** (2.0376 g, combined yield from **5a** to **1a** is 60%): a pall yellow solid, m.p. 45-46 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.21 (td, *J* = 7.8 and 1.2 Hz, 1H), 7.14-7.04 (m, 1H), 6.52-6.45 (m, 1H), 5.67-5.56 (m, 1H), 5.52-5.36 (m, 2H), 4.45-4.17 (m, 2H), 2.16-1.95 (m, 3H), 1.50-1.36 (m, 5H), 1.35-1.20 (m, 4H), 0.96-0.75 (m, 3H); IR (neat) ν (cm⁻¹) 3383, 3056, 2957, 2929, 2856, 1963, 1611, 1534, 1461, 1412, 1379, 1347, 1316, 1265, 1220, 1170, 1122, 1053, 1014; MS (70 ev, EI) *m/z* (%) 283 (M⁺, 2.04), 265 (M⁺-H₂O, 69.04), 208 (100); Elemental analysis calcd (%) for C₁₉H₂₅NO: C, 80.52; H, 8.89; N, 4.94; Found: C, 80.69, H, 8.79; N, 5.02.

The following compounds **1b-1f** were prepared according to this procedure.

(2) 1-(1-Ethyl-1*H*-indol-2-yl)penta-2,3-dien-1-ol (**1b**)^[1]

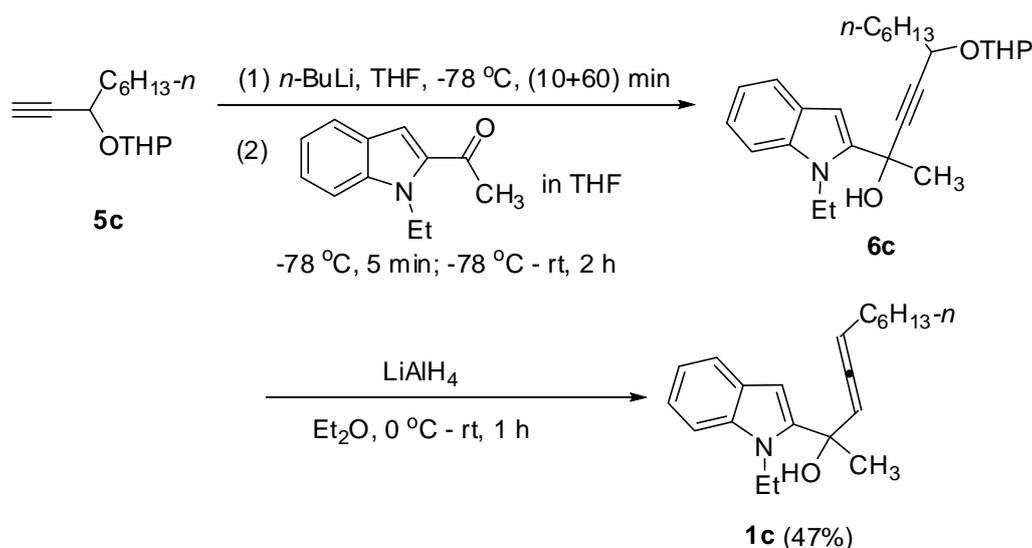


The reaction of **5b**^[2] (3.0912 g, 20 mmol), *n*-BuLi (8.0 mL, 2.5 M in hexane, 20

mmol), and 1-ethyl-1*H*-indole-2-carbaldehyde (3.5014 g, 20 mmol) in THF (40 mL) afforded **6b**, which was then used without further purification.

The reaction of **6b** (5.8120 g, 18 mmol) and LiAlH₄ (0.7612 g, 20 mmol) in Et₂O (30 mL) afforded **1b** (2.1416 g, combined yield from **5b** to **1b** is 47%) (petroleum ether/ethyl acetate = 15/1~5/1): a pall yellow solid, m.p. 70-71 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.65-7.55 (m, 1H), 7.33 (dd, *J* = 8.1 and 0.6 Hz, 1H), 7.26-7.16 (m, 1H), 7.14-7.04 (m, 1H), 6.53-6.47 (m, 1H), 5.65-5.52 (m, 1H), 5.50-5.34 (m, 2H), 4.45-4.17 (m, 2H), 2.15-2.05 (m, 1H), 1.82-1.67 (m, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); IR (neat) ν (cm⁻¹) 3379, 3057, 2976, 2926, 1969, 1611, 1534, 1460, 1408, 1371, 1347, 1316, 1269, 1220, 1165, 1126, 1078, 1049, 1013; MS (70 ev, EI) *m/z* (%) 228 (M⁺+1, 8.08), 227 (M⁺, 48.42), 194 (100); Elemental analysis calcd (%) for C₁₅H₁₇NO: C, 79.26; H, 7.54; N, 6.16; Found: C, 79.31, H, 7.46; N, 5.91.

(3) 2-(1-Ethyl-1*H*-indol-2-yl)undeca-3,4-dien-2-ol (**1c**)^[1]

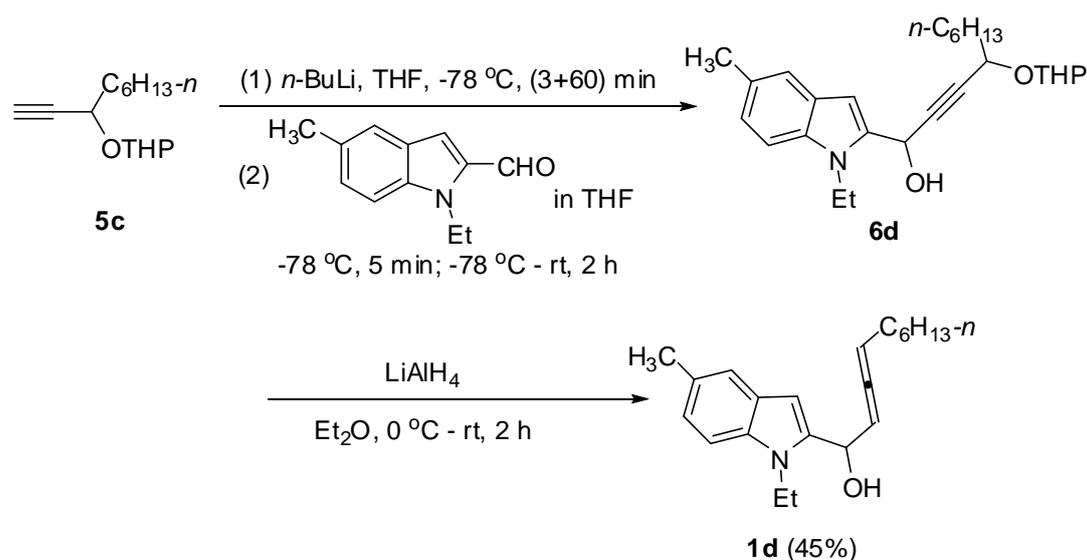


The reaction of **5c**^[2] (0.9130 g, 4.0 mmol), *n*-BuLi (1.8 mL, 2.5 M in hexane, 4.5

mmol), and 1-(1-ethyl-1*H*-indol-2-yl)ethanone (0.7495 g, 4.0 mmol) in THF (20 mL) afforded **6c**, which was then used without further purification.

The reaction of **6c** (1.0197 g, 2.5 mmol) and LiAlH₄ (0.1000 g, 2.6 mmol) in Et₂O (20 mL) afforded **1c** (0.5802 g, combined yield from **5c** to **1c** is 47%) (petroleum ether/ethyl acetate = 10/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.36-7.27 (m, 1H), 7.24-7.14 (m, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.46-6.36 (m, 1H), 5.63-5.52 (m, 1H), 5.50-5.36 (m, 1H), 4.60-4.31 (m, 2H), 2.20 (s, 1H), 2.10-1.98 (m, 2H), 1.88-1.78 (m, 3H), 1.47-1.35 (m, 3H), 1.34-1.15 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H); IR (neat) ν (cm⁻¹) 3431, 2956, 2928, 2855, 1964, 1611, 1533, 1462, 1397, 1368, 1345, 1313, 1274, 1228, 1172, 1151, 1088, 1014; MS (70 ev, EI) *m/z* (%) 312 (M⁺+1, 8.25), 311 (M⁺, 37.99), 146 (100); Elemental analysis calcd (%) for C₂₁H₂₉NO: C, 80.98; H, 9.38; N, 4.50; Found: C, 81.01, H, 9.31; N, 4.64.

(4) 1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)deca-2,3-dien-1-ol (1d)^[1]

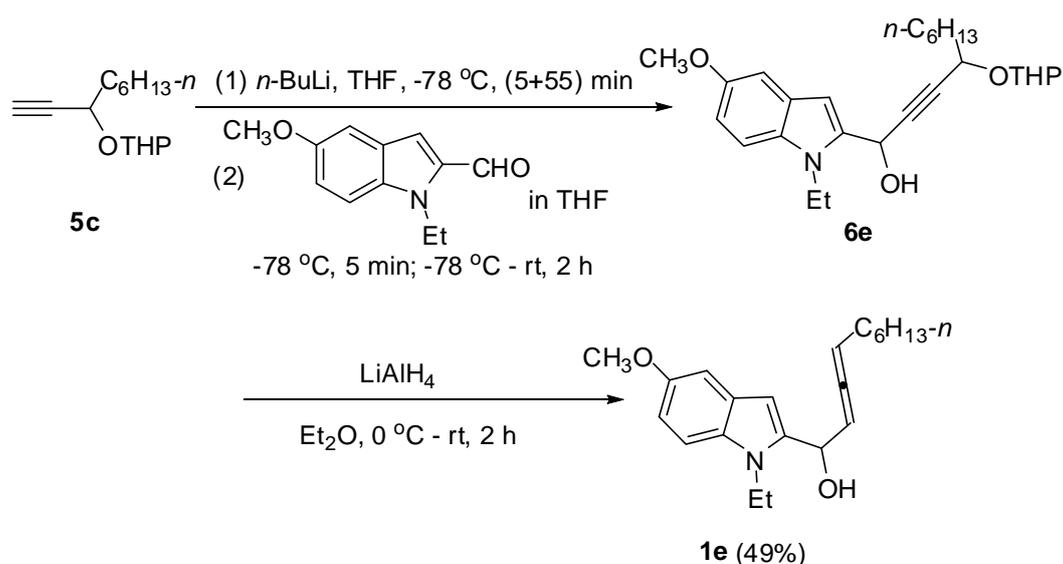


The reaction of **5c**^[2] (1.3450 g, 6 mmol), *n*-BuLi (2.4 mL, 2.5 M in hexane, 6

mmol), and 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (1.1301 g, 6 mmol) in THF (20 mL) afforded **6d**, which was then used without further purification.

The reaction of **6d** (1.8000 g, 4.4 mmol) and LiAlH₄ (0.2301 g, 6.1 mmol) in Et₂O (20 mL) afforded **1d** (0.8485 g, combined yield from **5c** to **1d** is 45%) (petroleum ether/ethyl acetate = 10/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.33 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 8.1 Hz and *J* = 1.2 Hz, 1H), 6.44-6.36 (m, 1H), 5.67-5.55 (m, 1H), 5.51-5.33 (m, 2H), 4.40-4.15 (m, 2H), 2.43 (s, 3H), 2.15-1.98 (m, 3H), 1.50-1.20 (m, 11H), 0.95-0.80 (m, 3H); IR (neat) ν (cm⁻¹); 3356, 2955, 2927, 2856, 1965, 1543, 1484, 1458, 1378, 1347, 1299, 1222, 1181, 1159, 1113, 1043; MS (70 ev, EI) *m/z* (%) 312 (M⁺+1, 21.01), 311 (M⁺, 89.70), 212 (M⁺-C₇H₁₅, 100); Elemental analysis calcd (%) for C₂₁H₂₉NO: C, 80.98; H, 9.38; N, 4.50; Found: C, 80.97; H, 9.36; N, 4.59.

(5) 1-(1-Ethyl-5-methoxy-1*H*-indol-2-yl)deca-2,3-dien-1-ol (**1e**)^[1]

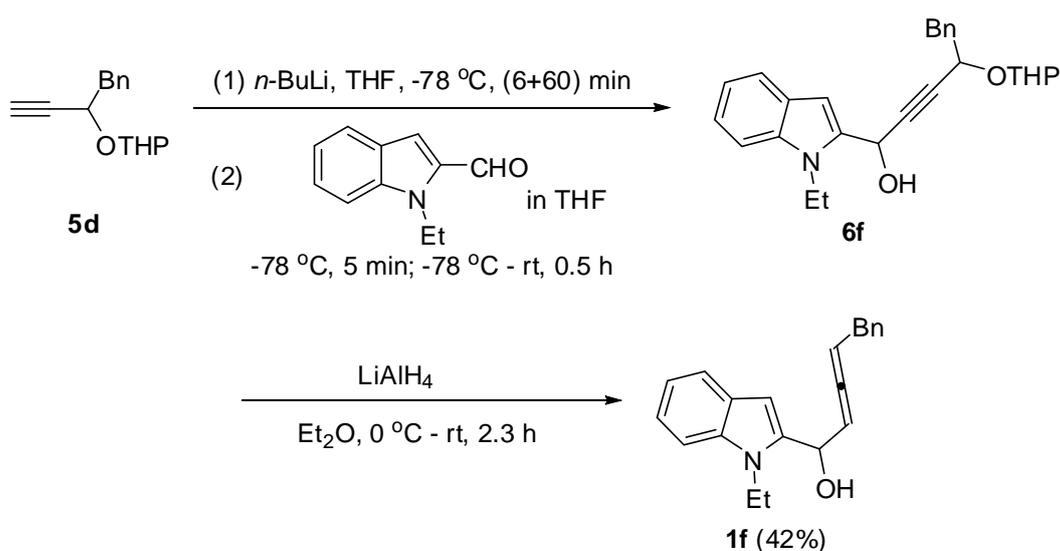


The reaction of **5c**^[2] (1.3501 g, 6 mmol), *n*-BuLi (2.5 mL, 2.5 M in hexane, 6.3

mmol), and 1-ethyl-5-methoxy-1*H*-indole-2-carbaldehyde (0.6501 g, 3.2 mmol) in THF (20 mL) afforded **6e**, which was then used without further purification.

The reaction of **6e** (0.8030 g, 1.9 mmol) and LiAlH₄ (0.1190 g, 3 mmol) in Et₂O (15 mL) afforded **1e** (0.5140 g, combined yield from **5c** to **1e** is 49%) (petroleum ether/ethyl acetate = 8/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.23 (d, *J* = 9.0 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.7 Hz and *J* = 2.7 Hz, 1H), 6.45-6.38 (m, 1H), 5.68-5.57 (m, 1H), 5.53-5.34 (m, 2H), 4.40-4.15 (m, 2H), 3.85 (s, 3H), 2.16-2.00 (m, 3H), 1.50-1.20 (m, 11H), 0.95-0.80 (m, 3H); IR (neat) ν (cm⁻¹): 3415, 2949, 2928, 2855, 1964, 1621, 1576, 1534, 1483, 1452, 1379, 1350, 1297, 1208, 1175, 1151, 1107, 1035; MS (70 ev, EI) *m/z* (%) 328 (M⁺+1, 23.75), 327 (M⁺, 100); Elemental analysis calcd (%) for C₂₁H₂₉NO₂: C, 77.02; H, 8.93; N, 4.28; Found: C, 77.11, H, 8.92; N, 4.32.

(6) 1-(1-Ethyl-1*H*-indol-2-yl)-5-phenylpenta-2,3-dien-1-ol (**1f**)^[1]



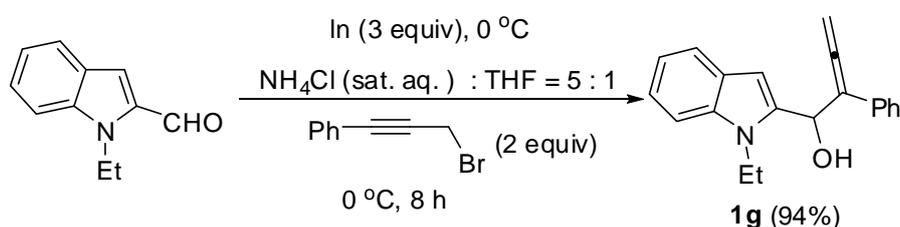
The reaction of **5d**^[2] (2.3001 g, 10 mmol), *n*-BuLi (4 mL, 2.5 M in hexane, 10

mmol), and 1-ethyl-1*H*-indole-2-carbaldehyde (1.7010 g, 9.8 mmol) in THF (40 mL) afforded **6f** (3.8701 g), which was then used without further purification.

The reaction of **6f** (3.8701 g, 10 mmol) and LiAlH₄ (0.3891 g, 10 mmol) in Et₂O (40 mL) afforded **1f** (1.2601 g, combined yield from **5d** to **1f** is 42%) (petroleum ether/ethyl acetate = 5/1): a pall yellow solid, m.p. 52-53 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.65-7.54 (m, 1H), 7.40-7.05 (m, 8H), [6.45 (s, 0.66H), 6.30 (s, 0.34 H)], 5.74-5.55 (m, 2H), 5.46-5.32 (m, 1H), 4.40-4.14 (m, 2H), 3.50-3.32 (m, 2H), 2.12-1.80 (m, 1H), 1.46-1.31 (m, 3H); IR (neat) ν (cm⁻¹) 3387, 3058, 3027, 2976, 2931, 1965, 1602, 1537, 1494, 1460, 1413, 1379, 1347, 1316, 1263, 1221, 1165, 1127, 1077, 1014; MS (70 ev, EI) *m/z* (%) 304 (M⁺+1, 18.67), 303 (M⁺, 80.19), 286 (M⁺-OH, 79.63), 118 (100); Elemental analysis calcd (%) for C₂₁H₂₁NO: C, 83.13; H, 6.98; N, 4.62; Found: C, 83.11, H, 6.93; N, 4.70.

2. Synthesis of Allenic Alcohols 1g-1m

(1) 1-(1-Ethyl-1*H*-indol-2-yl)-2-phenylbuta-2,3-dien-1-ol (**1g**)^[3]

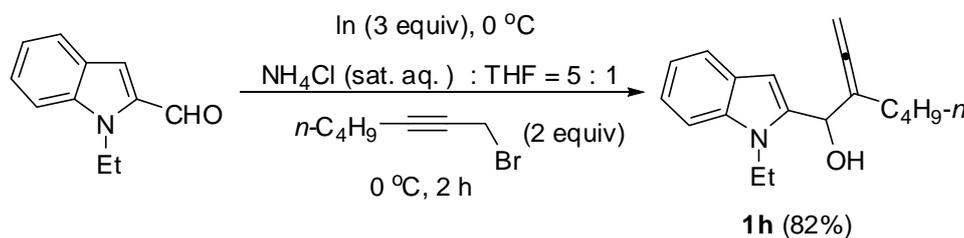


Typical Procedure: To a mixture of 1-ethyl-1*H*-indole-2-carbaldehyde (1.7211 g, 9.9 mmol) and indium powder (3.524 g, 31 mmol) in saturated aqueous NH₄Cl (50 mL) and THF (5 mL) was added dropwise a solution of 3-phenyl-2-propynyl bromide (3.901 g, 20 mmol) in THF (5 mL) with vigorous stirring at 0 °C. After 8 h the

reaction was complete as monitored by TLC, the mixture was quenched with 30 mL of H₂O, extracted with diethyl ether (30 mL×3), and dried over anhydrous Na₂SO₄. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1) afforded **1g** (2.7038 g, 94%): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.36-7.10 (m, 7H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.41 (s, 1H), 5.80-5.68 (m, 1H), 5.38 (dd, *J* = 12.0 and 3.0 Hz, 1H), 5.31 (dd, *J* = 12.0 and 3.0 Hz, 1H), 4.42-4.18 (m, 2H), 2.48 (d, *J* = 7.8 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 207.2, 139.2, 137.0, 133.9, 128.4, 127.13, 127.09, 126.4, 121.8, 121.0, 119.3, 109.3, 109.0, 101.6, 82.7, 65.0, 38.3, 15.4; IR (neat) ν (cm⁻¹) 3396, 3056, 2977, 2933, 1941, 1598, 1541, 1494, 1460, 1413, 1380, 1347, 1316, 1221, 1164, 1125, 1047; MS (70 ev, EI) *m/z* (%) 290 (M⁺+1, 27.69), 289 (M⁺, 100); HRMS Calcd (%) for C₂₀H₁₉NO (M⁺): 289.1467, Found: 289.1465.

The following compounds **1h-1m** were prepared according to this procedure.

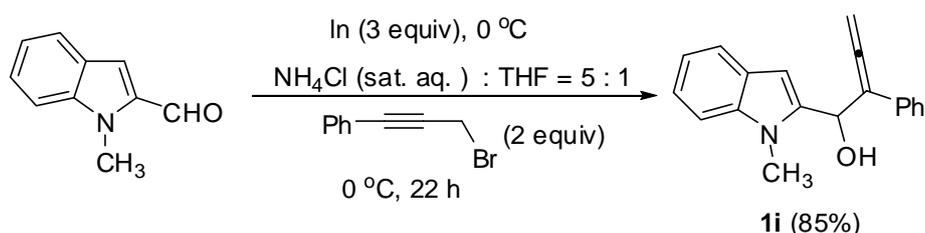
(2) **1-(1-Ethyl-1*H*-indol-2-yl)-2-butylbuta-2,3-dien-1-ol (1h)** ^[3]



The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (1.570 g, 9.1 mmol), indium powder (3.4501 g, 30 mmol), and hept-2-ynyl bromide (3.5111 g, 20 mmol) in THF (10 mL) and saturated aqueous NH₄Cl solution (50 mL) at 0 °C for 2 h afforded **1h** (2.0018 g, 82%) (petroleum ether/ethyl acetate = 10/1): oil; ¹H NMR (300 MHz,

CDCl₃) δ 7.62-7.54 (m, 1H), 7.32 (dd, *J* = 8.1 Hz and 0.8 Hz, 1H), 7.25-7.15 (m, 1H), 7.14-7.04 (m, 1H), 6.44 (s, 1H), 5.27 (t, *J* = 2.7 Hz, 1H), 5.12-4.96 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.25 (bs, 1H), 2.05-1.75 (m, 2H), 1.50-1.20 (m, 7H), 0.86 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.1, 138.8, 137.1, 127.3, 121.7, 120.8, 119.3, 109.3, 106.9, 101.0, 80.5, 67.5, 38.4, 29.7, 28.3, 22.3, 15.1, 13.9; IR (neat) ν (cm⁻¹) 3419, 3054, 2957, 2930, 2871, 1956, 1682, 1613, 1534, 1462, 1414, 1379, 1346, 1316, 1221, 1164, 1138, 1125, 1080, 1015; MS (70 ev, EI) *m/z* (%) 269 (M⁺, 3.38), 253 (100); HRMS Calcd for C₁₈H₂₃NO (M⁺): 269.1780, Found: 269.1781.

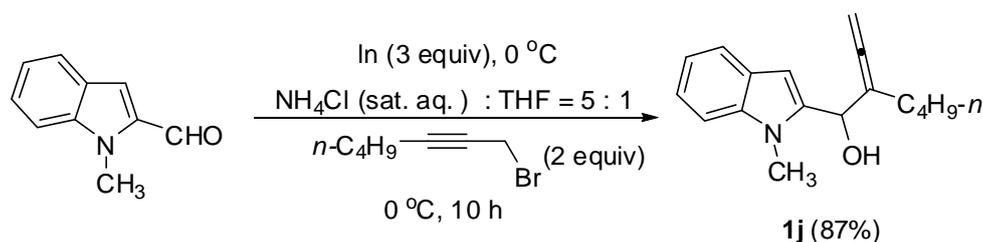
(3) 1-(1-Methyl-1*H*-indol-2-yl)-2-phenylbuta-2,3-dien-1-ol (1i**)**^[3]



The reaction of 1-methyl-1*H*-indole-2-carbaldehyde (1.5901 g, 10 mmol), indium powder (3.431 g, 30 mmol), and 3-phenyl-2-propynyl bromide (3.8902 g, 20 mmol) in THF (10 mL) and saturated aqueous NH₄Cl solution (50 mL) at 0 °C for 22 h afforded **1i** (2.3392 g, 85%) (petroleum ether/ethyl acetate = 10/1): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.38-7.13 (m, 7H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.44 (s, 1H), 5.85-5.75 (m, 1H), 5.38 (dd, *J* = 12.3 and 2.6 Hz, 1H), 5.31 (dd, *J* = 12.3 and 2.6 Hz, 1H), 3.82 (s, 3H), 2.38 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 207.4, 139.8, 138.2, 133.9, 128.5, 127.2, 126.9, 126.5, 121.9, 120.9, 119.4, 109.1, 108.9, 101.5, 82.5, 65.4, 30.1; IR (neat) ν (cm⁻¹) 3390, 3055, 2937, 1940, 1612,

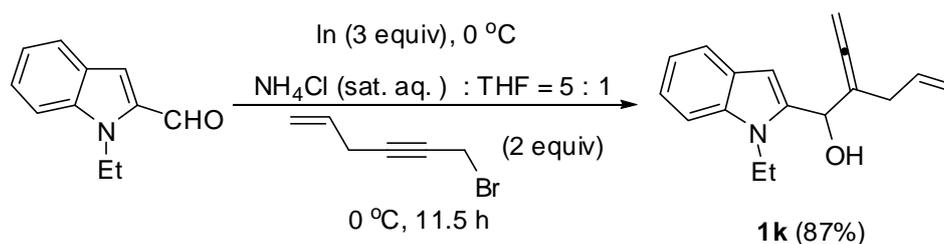
1597, 1539, 1494, 1469, 1451, 1402, 1343, 1317, 1267, 1234, 1166, 1136, 1101, 1045, 1011; MS (70 ev, EI) m/z (%) 276 ($M^{+}+1$, 4.02), 275 (M^{+} , 18.20), 257 ($M^{+}-H_2O$, 31.78), 160 ($M^{+}-C_9H_7$, 100); HRMS Calcd (%) for $C_{19}H_{17}NO$ (M^{+}): 275.1310, Found: 275.1310.

(4) 1-(1-Methyl-1*H*-indol-2-yl)-2-butylbuta-2,3-dien-1-ol (1j)^[3]



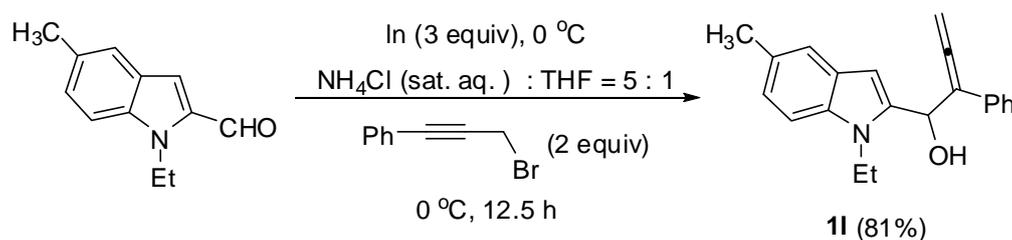
The reaction of 1-methyl-1*H*-indole-2-carbaldehyde (1.5910 g, 10 mmol), indium powder (3.430 g, 30 mmol), and hept-2-ynyl bromide (3.5101 g, 20 mmol) in THF (10 mL) and saturated aqueous NH_4Cl solution (50 mL) at 0 °C for 10 h afforded **1j** (2.2264 g, 87%) (petroleum ether/ethyl acetate = 10/1): oil; 1H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.1$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.21 (td, $J = 7.2$ Hz and 0.9 Hz, 1H), 7.14-7.04 (m, 1H), 6.44 (s, 1H), 5.26 (t, $J = 3.0$ Hz, 1H), 5.10-4.90 (m, 2H), 3.73 (s, 3H), 2.31 (bs, 1H), 2.05-1.75 (m, 2H), 1.50-1.20 (m, 4H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.2, 139.3, 138.2, 127.0, 121.7, 120.7, 119.4, 109.0, 106.6, 101.1, 80.4, 67.7, 30.1, 29.6, 28.3, 22.3, 13.9; IR (neat) ν (cm^{-1}) 3396, 3054, 2956, 2929, 2871, 1956, 1612, 1539, 1468, 1434, 1340, 1317, 1234, 1165, 1135, 1101, 1011; MS (70 ev, EI) m/z (%) 256 ($M^{+}+1$, 12.42), 255 (M^{+} , 46.40), 238 ($M^{+}-OH$, 100); HRMS Calcd (%) for $C_{17}H_{21}NO$ (M^{+}): 255.1623, Found: 255.1621.

(5) 1-(1-Ethyl-1*H*-indol-2-yl)-2-allylbuta-2,3-dien-1-ol (1k**)**^[3]



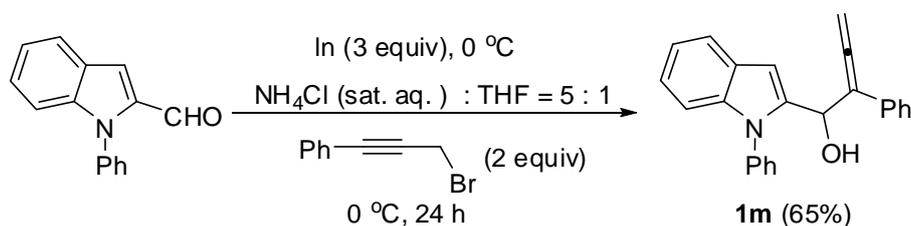
The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (0.3471 g, 2 mmol), indium powder (0.6900 g, 6.1 mmol), and hex-5-en-2-ynyl bromide (0.6375 g, 4 mmol) in THF (2 mL) and saturated aqueous NH₄Cl solution (10 mL) at 0 °C for 11.5 h afforded **1k** (0.4416 g, 87%) (petroleum ether/ethyl acetate = 20/1~10/1): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.58 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.27-7.15 (m, 1H), 7.14-7.04 (m, 1H), 6.45 (s, 1H), 5.90-5.70 (m, 1H), 5.35-5.25 (m, 1H), 5.12-4.95 (m, 4H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.90-2.73 (m, 1H), 2.72-2.54 (m, 1H), 2.29 (d, *J* = 5.1 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.5, 138.4, 137.1, 134.9, 127.2, 121.7, 120.8, 119.4, 116.6, 109.3, 105.0, 101.1, 80.3, 67.0, 38.4, 33.7, 15.1; IR (neat) ν (cm⁻¹) 3406, 3056, 2978, 2932, 1957, 1641, 1611, 1540, 1460, 1413, 1380, 1346, 1316, 1267, 1222, 1164, 1125, 1079, 1015; MS (70 ev, EI) *m/z* (%) 254 (M⁺+1, 8.92), 253 (M⁺, 51.15), 238 (M⁺-CH₃, 71.96), 236 (M⁺-OH, 79.65), 118 (100); HRMS Calcd for C₁₇H₁₉NO (M⁺): 253.1467, Found: 253.1471.

(6) 1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-2-phenylbuta-2,3-dien-1-ol (1l**)**^[3]



The reaction of 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (1.101 g, 6 mmol), indium powder (2.4000 g, 21 mmol), and 3-phenyl-2-propynyl bromide (2.251 g, 12 mmol) in THF (4 mL) and saturated aqueous NH₄Cl solution (20 mL) at 0 °C for 12.5 h afforded **1l** (1.4417 g, 81%) (petroleum ether/ethyl acetate = 10/1): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.12 (m, 7H), 7.04 (dd, *J* = 8.4 Hz and 1.5 Hz, 1H), 6.36 (s, 1H), 5.85-5.75 (m, 1H), 5.44 (dd, *J* = 12.0 and 2.7 Hz, 1H), 5.37 (dd, *J* = 12.0 and 2.7 Hz, 1H), 4.49-4.20 (m, 2H), 2.41 (s, 3H), 2.26 (bs, 1H), 1.44 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 207.2, 139.2, 135.4, 133.9, 128.5, 128.4, 127.4, 127.1, 126.4, 123.4, 120.6, 109.1, 109.0, 101.1, 82.6, 65.0, 38.3, 21.3, 15.4; IR (neat) ν (cm⁻¹) 3411, 3017, 2976, 2933, 1941, 1666, 1597, 1540, 1494, 1483, 1451, 1413, 1379, 1338, 1299, 1267, 1223, 1181, 1158, 1123, 1077, 1044, 1001; MS (70 ev, EI) *m/z* (%) 304 (M⁺+1, 21.48), 303 (M⁺, 100); HRMS Calcd for C₂₁H₂₁NO (M⁺): 303.1623, Found: 303.1636.

(7) 2-Phenyl-1-(1-phenyl-1*H*-indol-2-yl)buta-2,3-dien-1-ol (1m**)**^[3]

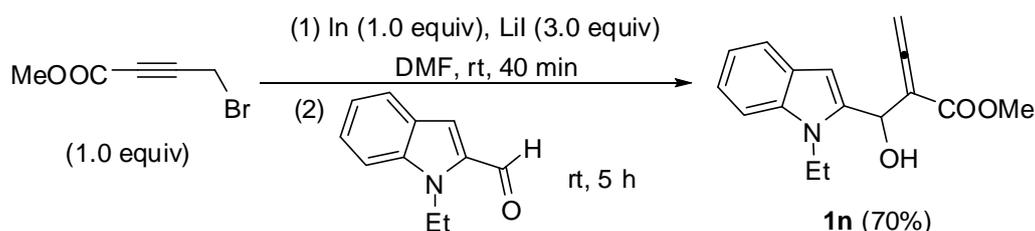


The reaction of 1-phenyl-1*H*-indole-2-carbaldehyde (1.1210 g, 5 mmol), indium powder (1.7150 g, 15 mmol), and 3-phenyl-2-propynyl bromide (2.0240 g, 10 mmol) in THF (3 mL) and saturated aqueous NH₄Cl solution (15 mL) at 0 °C for 24 h afforded **1m** (1.1080 g, 65%) (petroleum ether/ethyl acetate = 20/1): oil; ¹H NMR

(300 MHz, CDCl₃) δ 7.65-7.35 (m, 6H), 7.25-7.02 (m, 8H), 6.68 (s, 1H), 5.70-5.50 (m, 1H), 5.35-5.15 (m, 2H), 2.35 (d, $J = 7.8$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 207.1, 140.8, 138.7, 137.4, 133.7, 129.5, 128.3, 128.2, 127.2, 127.0, 126.4, 122.3, 120.8, 120.2, 110.5, 109.1, 102.4, 82.4, 64.7; IR (neat) ν (cm⁻¹) 3388, 3056, 2925, 1941, 1596, 1545, 1497, 1475, 1454, 1393, 1346, 1317, 1216, 1134, 1073, 1050, 1016; MS (70 ev, EI) m/z (%) 338 (M⁺+1, 2.66), 337 (M⁺, 10.27), 319 (M⁺-H₂O, 18.08), 222 (M⁺-C₉H₇, 100); HRMS Calcd for C₂₄H₁₉NO (M⁺): 337.1467, Found: 337.1465.

3. Synthesis of Allenic Alcohols 1n-1r

(1) Methyl 2-((1-ethyl-1*H*-indol-2-yl)(hydroxy)methyl)buta-2,3-dienoate^[4] (**1n**)



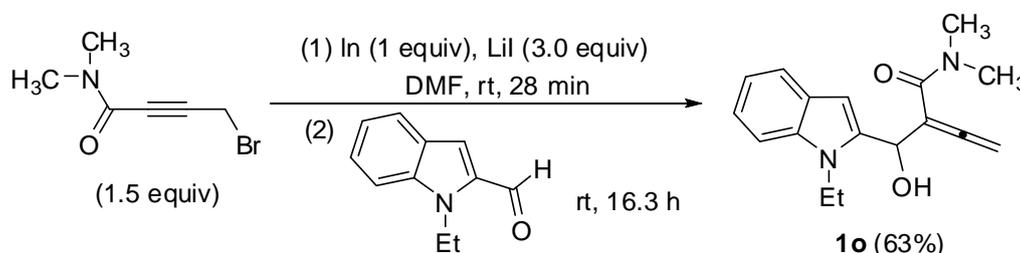
Typical Procedure: To a dry Schlenk tube were added sequentially indium powder (120.1 mg, 1.1 mmol), LiI (402.0 mg, 3.0 mmol), and methyl 4-bromobut-2-ynoate (181.5 mg, 1.0 mmol) in DMF (4 mL) with vigorous stirring at room temperature under a nitrogen atmosphere. After being stirred for 40 min, 1-ethyl-1*H*-indole-2-carbaldehyde (181.5 mg, 1.0 mmol) was added. After 5 h (monitored by TLC), the reaction mixture was quenched with saturated NaHCO₃ (20 mL), extracted with diethyl ether (20 mL×3), washed with water, and dried over anhydrous Na₂SO₄. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~1/1) afforded **1n** (198.1 mg, 70%): oil; ¹H NMR

(300 MHz, CDCl₃) δ 7.57 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.41 (s, 1H), 5.80-5.68 (m, 1H), 5.40-5.25 (m, 2H), 4.38-4.13 (m, 2H), 3.74 (s, 3H), 3.27 (d, J = 8.1 Hz, 1H), 1.39 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 212.4, 166.4, 138.8, 136.8, 127.0, 121.7, 120.8, 119.3, 109.3, 102.5, 100.3, 82.2, 64.6, 52.4, 38.3, 15.1; IR (neat), ν (cm⁻¹) 3492, 3059, 2983, 2952, 2901, 2845, 1965, 1714, 1611, 1538, 1461, 1436, 1381, 1347, 1260, 1221, 1165, 1127, 1105, 1080, 1029; MS (70 ev, EI) m/z (%) 271 (M⁺, 4.06), 253 (M⁺, 100); HRMS Calcd for C₁₆H₁₇NO₃ (M⁺): 271.1208, Found: 271.1203.

The following compounds **1o-1r** were prepared according to this procedure.

(2) *N,N*-Dimethyl 2-((1-ethyl-1*H*-indol-2-yl)(hydroxy)methyl)buta-2,3-dienamide

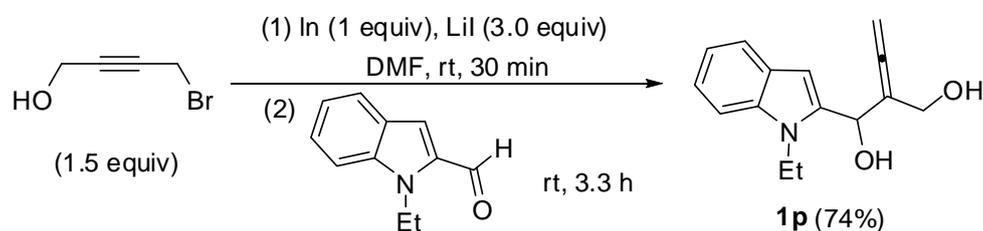
(1o)^[4]



The reaction of indium powder (231.0 mg, 2.0 mmol), LiI (810.5 mg, 6.0 mmol), *N,N*-dimethyl 4-bromobut-2-ynamide (610.2 mg, 3.2 mmol), and 1-ethyl-1*H*-indole-2-carbaldehyde (343.5 mg, 2.0 mmol) in DMF (8 mL) at rt under a nitrogen atmosphere for 16.3 h afforded **1o** (357.4 mg, 63%) (petroleum ether/ethyl acetate = 2/1): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.39 (s, 1H), 5.78 (s, 1H), 5.19-4.81 (m, 3H), 4.43-4.10 (m, 2H), 3.12 (s, 3H), 2.99 (s, 3H), 1.41 (t, J = 7.1

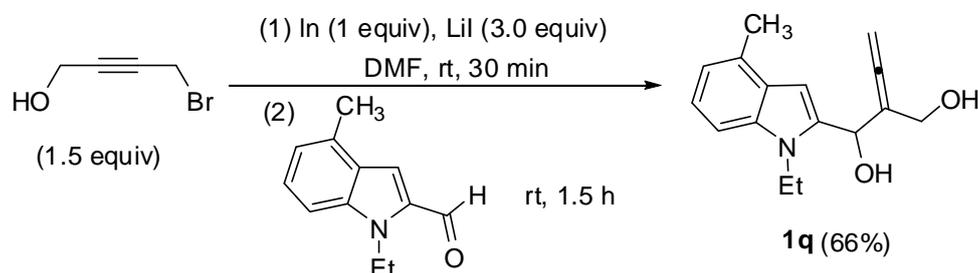
Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.5, 166.8, 139.1, 136.6, 127.3, 121.3, 120.6, 119.1, 109.1, 100.8, 99.5, 80.1, 67.5, 38.9, 38.3, 35.5, 15.1; IR (neat) ν (cm^{-1}) 3373, 3055, 2979, 2933, 1951, 1615, 1481, 1461, 1397, 1347, 1316, 1261, 1223, 1188, 1128, 1080, 1055, 1015; MS (70 ev, EI) m/z (%) 285 ($\text{M}^+ + 1$, 19.54), 284 (M^+ , 100); HRMS Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$ (M^+): 284.1525, Found: 284.1524.

(3) 1-(1-Ethyl-1*H*-indol-2-yl)-2-(hydroxymethyl)buta-2,3-dienol (1p**)** ^[4]



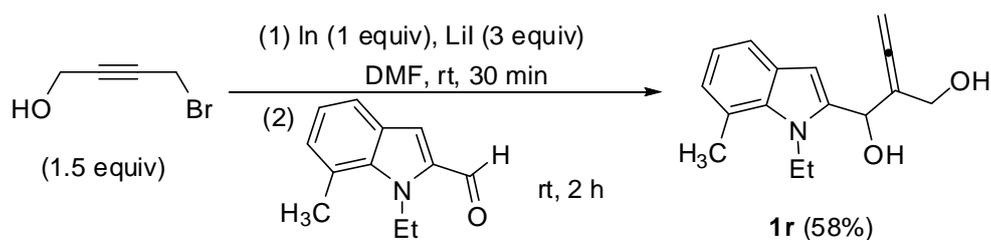
The reaction of indium powder (229.1 mg, 2.0 mmol), LiI (812.5 mg, 6.1 mmol), 4-bromobut-2-yn-1-ol (450.1 mg, 3.0 mmol), and 1-ethyl-1*H*-indole-2-carbaldehyde (350.1 mg, 2.0 mmol) in DMF (8 mL) at rt under a nitrogen atmosphere for 3.3 h afforded **1p** (364.5 mg, 74%) (petroleum ether/ethyl acetate = 3/1~1/1): oil; ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, $J = 8.1$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 1H), 7.18-7.06 (m, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.37 (s, 1H), 5.42 (s, 1H), 4.90 (d, $J = 1.8$ Hz, 2H), 4.20-3.90 (m, 4H), 3.40-3.16 (m, 1H), 2.70-2.40 (m, 1H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.0, 138.8, 137.0, 127.2, 121.7, 120.8, 119.5, 109.3, 105.4, 100.5, 79.6, 66.9, 61.5, 38.4, 15.0; IR (neat) ν (cm^{-1}) 3358, 3055, 2979, 2934, 2873, 1957, 1610, 1540, 1460, 1414, 1381, 1346, 1316, 1223, 1164, 1125, 1079, 1013; MS (70 ev, EI) m/z (%) 244 ($\text{M}^+ + 1$, 11.29), 243 (M^+ , 67.06), 226 ($\text{M}^+ - \text{OH}$, 100); HRMS Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$ (M^+): 243.1259, Found: 243.1260.

(4) 1-(1-Ethyl-4-methyl-1*H*-indol-2-yl)-2-(hydroxymethyl)buta-2,3-dienol (1q)^[4]



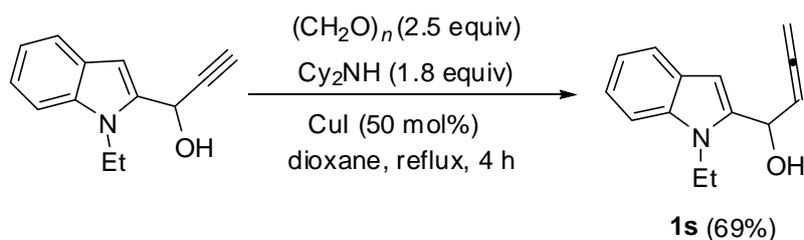
The reaction of indium powder (230.1 mg, 2.0 mmol), LiI (805.2 mg, 6.0 mmol), 4-bromobut-2-yn-1-ol (450.2 mg, 3.0 mmol), and 1-ethyl-4-methyl-1*H*-indole-2-carbaldehyde (382.5 mg, 2.0 mmol) in DMF (8 mL) at rt under a nitrogen atmosphere for 1.5 h afforded **1q** (347.3 mg, 66%) (petroleum ether/ethyl acetate = 5/1~1/1): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.24-7.10 (m, 2H), 6.94 (d, *J* = 6.0 Hz, 1H), 6.54 (s, 1H), 5.62-5.50 (m, 1H), 5.05 (d, *J* = 2.1 Hz, 2H), 4.32-4.05 (m, 4H), 3.35-3.45 (m, 1H), 2.75-2.60 (m, 1H), 2.57 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.9, 138.1, 136.6, 130.3, 127.1, 121.9, 119.7, 107.0, 105.4, 98.9, 79.5, 66.9, 61.5, 38.5, 18.6, 15.0; IR (neat) ν (cm⁻¹) 3384, 3045, 2968, 2932, 2872, 1957, 1583, 1549, 1489, 1458, 1414, 1380, 1315, 1234, 1122, 1076, 1013; MS (70 ev, EI) *m/z* (%) 258 (M⁺+1, 18.48), 257 (M⁺, 100); HRMS Calcd for C₁₆H₁₉NO₂ (M⁺): 257.1416, Found: 257.1416.

(5) 1-(1-Ethyl-7-methyl-1*H*-indol-2-yl)-2-(hydroxymethyl)buta-2,3-dienol (1r)^[4]



The reaction of indium powder (1.1592 g, 10 mmol), LiI (4.0102 g, 30 mmol), 4-bromobut-2-yn-1-ol (2.3520 g, 15 mmol), and 1-ethyl-7-methyl-1*H*-indole-2-carbaldehyde (1.8901 g, 10 mmol) in DMF (30 mL) at rt under a nitrogen atmosphere for 2 h afforded **1r** (1.5097 g, 58%) (petroleum ether/ethyl acetate = 5/1~1/1): oil; ¹H NMR (300 MHz, CDCl₃) δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.10-6.95 (m, 2H), 6.55 (s, 1H), 5.54 (s, 1H), 5.06 (d, *J* = 1.8 Hz, 2H), 4.50-4.31 (m, 2H), 4.26 (d, *J* = 12.2 Hz, 1H), 4.11 (d, *J* = 12.2 Hz, 1H), 3.79 (d, *J* = 5.4 Hz, 1H), 3.16 (bs, 1H), 2.78 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 205.0, 139.2, 135.8, 128.2, 125.1, 120.6, 119.5, 118.9, 105.5, 101.6, 79.6, 66.5, 61.4, 39.7, 19.9, 17.4; IR (neat) ν (cm⁻¹) 3384, 3045, 2968, 2932, 2872, 1957, 1583, 1549, 1489, 1458, 1414, 1380, 1315, 1234, 1122, 1076, 1013; MS (70 ev, EI) *m/z* (%) 258 (M⁺+1, 11.92), 257 (M⁺, 68.15), 240 (100); HRMS Calcd for C₁₆H₁₉NO₂ (M⁺): 257.1416, Found: 257.1418.

4. Synthesis of 1-(1-Ethyl-1*H*-indol-2-yl)buta-2,3-dien-1-ol (**1s**)^[5]

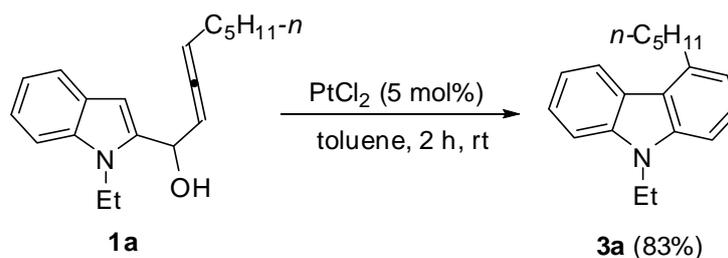


To a three-necked flask equipped with a reflux condenser were added

paraformaldehyde (0.7601 g, 25 mmol), CuI (0.9673 g, 5 mmol), dioxane (50 mL), 1-(1-ethyl-1*H*-indol-2-yl)-prop-2-yn-1-ol (1.9992 g, 10 mmol), and dicyclohexylamine (3.2957 g, 18 mmol) sequentially. The resulting mixture was gently refluxed with stirring. After 4 h as monitored by TLC, the resulting mixture was then cooled to room temperature and filtered. The filtrate was diluted with 30 mL of ether. The resulting mixture was then acidified with 1 N hydrochloric acid to pH 1-2. The organic layer was washed with water to neutral and dried over anhydrous Na₂SO₄. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1~5/1) afforded the terminal allene **1s** (1.4657 g, 69%): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 (td, *J* = 7.8 and 0.9 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 5.66 (q, *J* = 6.3 Hz, 1H), 5.52-5.40 (m, 1H), 5.06-4.98 (m, 2H), 4.43-4.17 (m, 2H), 2.07 (d, *J* = 5.7 Hz, 1H), 1.41 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 207.3, 139.7, 137.0, 127.2, 121.9, 121.0, 119.5, 109.4, 100.1, 93.4, 79.0, 65.0, 38.5, 15.3; IR (neat) ν (cm⁻¹) 3384, 3051, 2977, 2931, 1956, 1543, 1460, 1414, 1380, 1346, 1315, 1220, 1165, 1131, 1107, 1033; MS (70 ev, EI) *m/z* (%) 214 (M⁺+1, 13.02), 213 (M⁺, 84.97), 118 (100); HRMS Calcd for C₁₄H₁₅NO (M⁺): 213.1154, Found: 213.1157.

5. Synthesis of Carbazoles 3a-3s

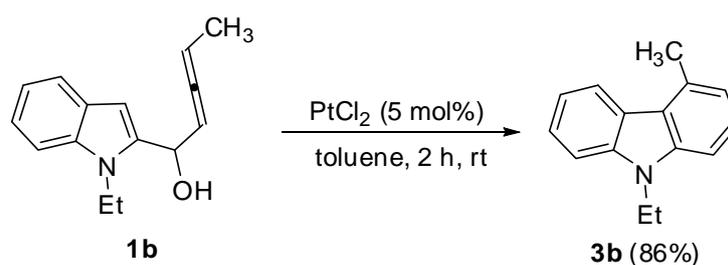
(1) 9-Ethyl-4-pentyl-9*H*-carbazole (3a)



Typical Procedure: To a dry Schlenk tube were added sequentially PtCl_2 (2.9 mg, 0.011 mmol), **1a** (57.0 mg, 0.20 mmol), and toluene (1 mL) under N_2 . After continuous stirring for 2 h at rt, the reaction was complete as monitored by TLC. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) afforded **3a** (44.4 mg, 83%): liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.52-7.34 (m, 3H), 7.32-7.20 (m, 2H), 7.02 (d, $J = 7.2$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 3.22 (t, $J = 7.8$ Hz, 2H), 1.92-1.78 (m, 2H), 1.58-1.33 (m, 7H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.2, 139.8, 138.6, 125.4, 124.9, 122.9, 122.7, 120.7, 119.5, 118.7, 108.2, 106.0, 37.4, 34.5, 32.1, 29.4, 22.7, 14.1, 13.7; IR (neat) ν (cm^{-1}) 3049, 2955, 2930, 2860, 1618, 1594, 1581, 1498, 1469, 1435, 1381, 1329, 1297, 1245, 1216, 1151, 1110, 1079, 1027; MS (70 eV, EI) m/z (%) 266 ($\text{M}^+ + 1$, 21.45), 265 (M^+ , 100); HRMS Calcd for $\text{C}_{19}\text{H}_{23}\text{N}$ (M^+): 265.1830, Found: 265.1829.

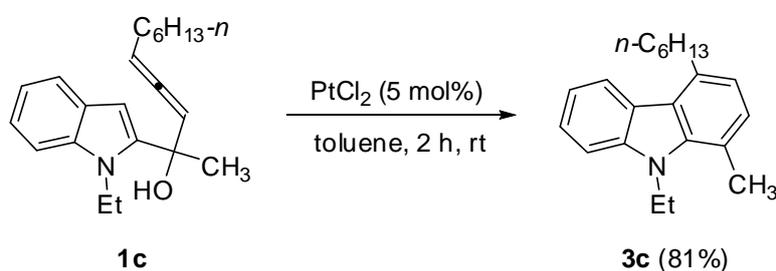
The following compounds **3b-3s** were prepared according to this procedure.

(2) 9-Ethyl-4-methyl-9H-carbazole (3b)



The reaction of PtCl₂ (5.3 mg, 0.02 mmol) and **1b** (90.9 mg, 0.40 mmol) in toluene (2 mL) at rt for 2 h afforded **3b** (71.9 mg, 86%) (petroleum ether/ethyl acetate = 50/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.51-7.32 (m, 3H), 7.30-7.18 (m, 2H), 7.00 (d, *J* = 6.9 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.89 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 139.9, 139.8, 133.5, 125.4, 124.9, 123.5, 122.7, 121.4, 120.3, 118.7, 108.1, 106.0, 37.4, 20.8, 13.7; IR (neat) ν (cm⁻¹) 3049, 2974, 2933, 1618, 1594, 1576, 1498, 1470, 1454, 1427, 1385, 1327, 1292, 1250, 1221, 1150, 1107, 1081, 1026, 1012; MS (70 ev, EI) *m/z* (%) 210 (M⁺+1, 9.17), 209 (M⁺, 53.14), 194 (M⁺-CH₃, 100); HRMS Calcd for C₁₅H₁₅N (M⁺): 209.1204, Found: 209.1205.

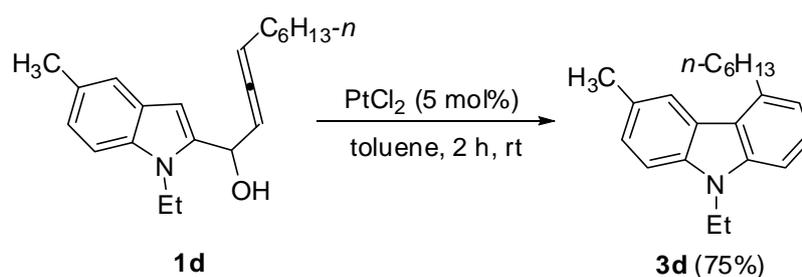
(3) 9-Ethyl-1-methyl-4-hexyl-9H-carbazole (3c)



The reaction of PtCl₂ (4.2 mg, 0.016 mmol) and **1c** (90.2 mg, 0.29 mmol) in toluene (1.5 mL) at rt for 2 h afforded **3c** (68.8 mg, 81%): liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.51-7.40 (m, 2H), 7.29-7.20 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 4.62 (q, *J* = 7.2 Hz, 2H), 3.19 (t, *J* = 7.8 Hz, 2H), 2.81 (s, 3H), 1.90-1.75 (m, 2H), 1.60-1.47 (m, 2H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.37-1.28 (m, 4H), 0.95-0.85 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.5, 138.9, 136.3, 128.7, 124.8, 123.1, 122.6, 121.4, 119.7, 118.8, 117.2, 108.4, 39.2, 34.3, 31.8, 29.61, 29.59, 22.7, 20.1, 15.5, 14.1; IR (neat) ν (cm⁻¹) 3048, 3013, 2955, 2928, 2857,

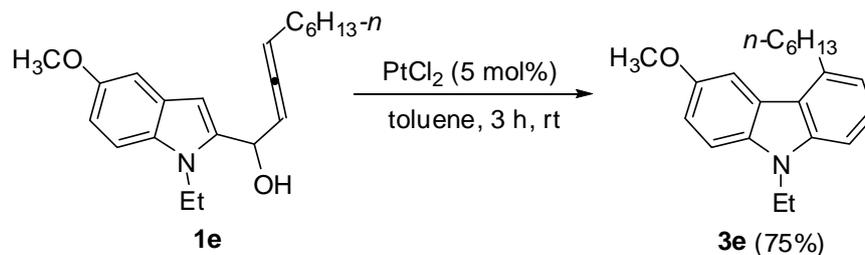
1611, 1577, 1512, 1463, 1394, 1378, 1350, 1323, 1252, 1230, 1161, 1148, 1118, 1082, 1029; MS (70 ev, EI) m/z (%) 294 ($M^{+}+1$, 36.81), 293 (M^{+} , 100); HRMS Calcd for $C_{21}H_{27}N$ (M^{+}): 293.2144, Found: 293.2135.

(4) 9-Ethyl-3-methyl-5-hexyl -9H-carbazole (3d)



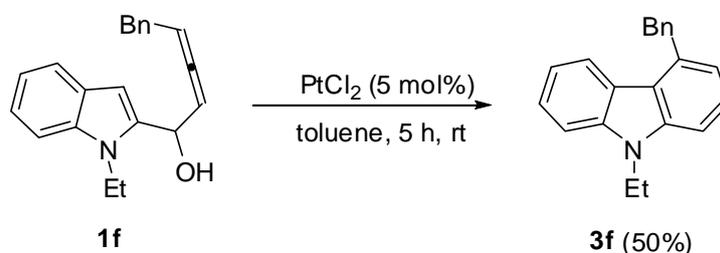
The reaction of PtCl_2 (4.0 mg, 0.015 mmol) and **1d** (92.0 mg, 0.30 mmol) in toluene (1.5 mL) at rt for 2 h afforded **3d** (65.1 mg, 75%): liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.92 (s, 1H), 7.41-7.17 (m, 4H), 6.98 (d, $J = 7.2$ Hz, 1H), 4.31 (q, $J = 7.2$ Hz, 2H), 3.21 (t, $J = 7.8$ Hz, 2H), 2.56 (s, 3H), 1.93-1.76 (m, 2H), 1.62-1.45 (m, 2H), 1.44-1.27 (m, 7H), 0.91 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.5, 138.6, 138.1, 127.8, 126.1, 125.2, 123.0, 122.8, 120.5, 119.2, 107.8, 105.9, 37.4, 34.5, 31.8, 29.7, 29.5, 22.7, 21.6, 14.1, 13.7; IR (neat) ν (cm^{-1}) 2955, 2928, 2858, 1615, 1597, 1579, 1499, 1476, 1379, 1331, 1309, 1248, 1150, 1116, 1080; MS (70 ev, EI) m/z (%) 294 ($M^{+}+1$, 22.27), 293 (M^{+} , 100); HRMS Calcd for $C_{21}H_{27}N$ (M^{+}): 293.2144, Found: 293.2131.

(5) 9-Ethyl-3-methoxy-5-hexyl -9H-carbazole (3e)



The reaction of PtCl_2 (4.1 mg, 0.015 mmol) and **1e** (92.5 mg, 0.28 mmol) in toluene (1.5 mL) at rt for 3 h afforded **3e** (65.3 mg, 75%) (petroleum ether/ethyl acetate = 50/1): liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 2.1$ Hz, 1H), 7.40-7.28 (m, 2H), 7.26-7.18 (m, 1H), 7.11 (dd, $J = 8.7$ and 2.4 Hz, 1H), 6.97 (d, $J = 7.2$ Hz, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 3.93 (s, 3H), 3.19 (t, $J = 7.8$ Hz, 2H), 1.92-1.78 (m, 2H), 1.61-1.46 (m, 2H), 1.45-1.27 (m, 7H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.3, 140.8, 138.5, 134.9, 125.4, 123.1, 120.5, 119.0, 113.4, 108.6, 106.4, 106.1, 56.1, 37.4, 34.5, 31.9, 29.9, 29.7, 22.7, 14.1, 13.7; IR (neat) ν (cm^{-1}) 3047, 2930, 2858, 1624, 1598, 1580, 1498, 1479, 1437, 1378, 1305, 1287, 1224, 1206, 1150, 1102, 1039; MS (70 ev, EI) m/z (%) 310 ($\text{M}^+ + 1$, 23.35), 309 (M^+ , 100); HRMS Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}$ (M^+): 309.2093, Found: 309.2101.

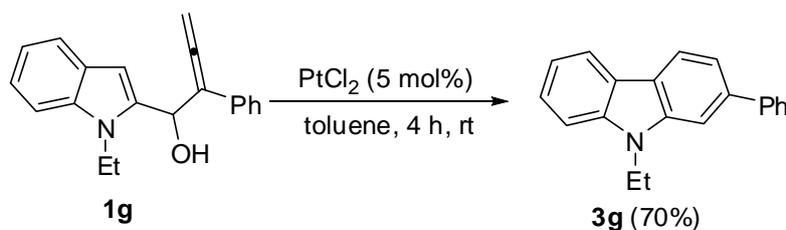
(6) 4-Benzyl-9-ethyl-9H-carbazole (3f)



The reaction of PtCl_2 (2.8 mg, 0.011 mmol) and **1f** (60.2 mg, 0.20 mmol) in toluene (1 mL) at rt for 5 h afforded **3f** (28.7 mg, 50%): liquid; ^1H NMR (300 MHz,

CDCl₃) δ 8.07 (d, J = 8.1 Hz, 1H), 7.48-7.12 (m, 10H), 6.91 (d, J = 7.5 Hz, 1H), 4.65 (s, 2H), 4.37 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.2, 139.9, 135.7, 128.9, 128.5, 126.0, 125.5, 125.1, 122.85, 122.79, 121.3, 120.5, 118.7, 108.2, 106.6, 39.9, 37.5, 13.7; IR (neat) ν (cm⁻¹) 3039, 2974, 2919, 1618, 1594, 1495, 1460, 1435, 1383, 1330, 1244, 1153, 1104, 1029; MS (70 ev, EI) m/z (%) 286 (M⁺+1, 19.99), 285 (M⁺, 90.76), 270 (M⁺-CH₃, 100); HRMS Calcd for C₂₁H₁₉N (M⁺): 285.1517, Found: 285.1517.

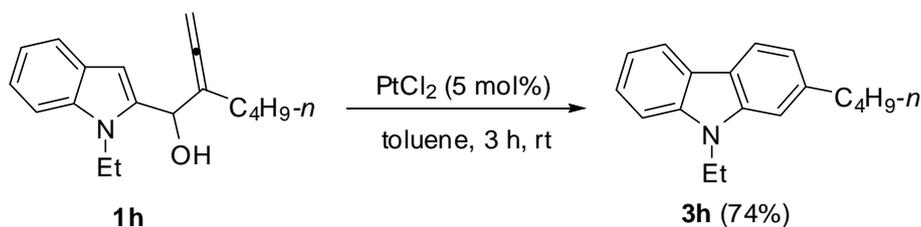
(7) 9-Ethyl-2-phenyl-9H-carbazole (3g)



The reaction of PtCl₂ (5.4 mg, 0.02 mmol) and **1g** (116.0 mg, 0.4 mmol) in toluene (2 mL) at rt for 4 h afforded **3g** (76.2 mg, 70%), which was stored in a refrigerator to produce the solid state product: a pall yellow solid, m.p. 118-119 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.18-8.08 (m, 2H), 7.78-7.70 (m, 2H), 7.58 (d, J = 1.2 Hz, 1H), 7.54-7.32 (m, 6H), 7.28-7.20 (m, 1H), 4.40 (q, J = 7.2 Hz, 2H), 1.45 (q, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 142.2, 140.4, 139.1, 128.8, 127.6, 127.0, 125.6, 122.7, 122.1, 120.6, 120.4, 118.9, 118.5, 108.4, 107.0, 37.5, 13.8; IR (neat) ν (cm⁻¹) 3057, 2975, 2931, 1627, 1599, 1564, 1488, 1470, 1457, 1436, 1380, 1328, 1255, 1232, 1156, 1125, 1087; MS (70 ev, EI) m/z (%) 272 (M⁺+1, 18.05), 271 (M⁺, 80.40), 256 (M⁺-CH₃, 100); HRMS Calcd for C₂₀H₁₇N (M⁺):

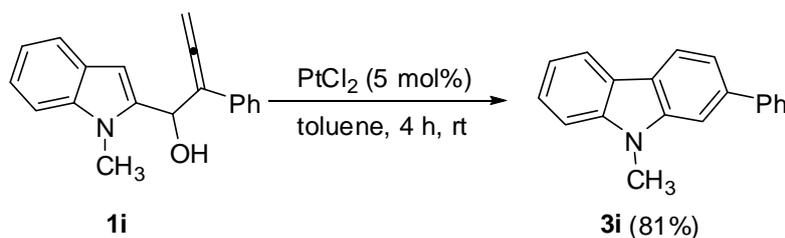
271.1361, Found: 271.1360.

(8) 2-Butyl-9-ethyl-9H-carbazole (3h)



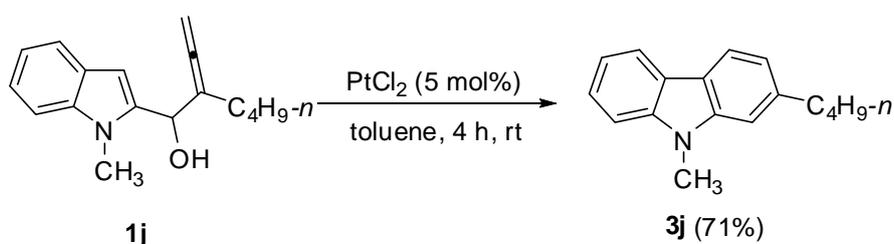
The reaction of PtCl_2 (5.4 mg, 0.02 mmol) and **1h** (100.1 mg, 0.37 mmol) in toluene (2 mL) at rt for 3 h afforded **3h** (69.1 mg, 74%) (petroleum ether/ethyl acetate = 50/1): liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.06 (dt, $J = 7.8$ and 0.9 Hz, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.48-7.36 (m, 2H), 7.25-7.17 (m, 2H), 7.07 (dd, $J = 7.8$ and 1.2 Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 2.83 (t, $J = 7.8$ Hz, 2H), 1.79-1.66 (m, 2H), 1.49-1.38 (m, 5H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.0, 140.3, 140.0, 125.0, 123.0, 120.8, 120.0, 119.7, 118.6, 108.2, 107.9, 37.4, 36.5, 34.3, 22.5, 14.0, 13.8; IR (neat) ν (cm^{-1}) 3051, 2955, 2929, 2857, 1685, 1629, 1602, 1577, 1498, 1458, 1377, 1326, 1234, 1180, 1155, 1133, 1120, 1102, 1086, 1058, 1020, 1000; MS (70 eV, EI) m/z (%) 251 (M^+ , 36.24), 194 ($\text{M}^+ - \text{C}_4\text{H}_9$, 100); HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{N}$ (M^+): 251.1674, Found: 251.1672.

(9) 9-Methyl-2-phenyl-9H-carbazole (3i)



The reaction of PtCl₂ (5.2 mg, 0.02 mmol) and **1i** (110.1 mg, 0.40 mmol) in toluene (2 mL) at rt for 4 h afforded **3i** (83.5 mg, 81%), which was stored in a refrigerator to produce the solid state product: a pall white solid, m.p. 139-140 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.12 (t, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.58 (s, 1H), 7.56-7.44 (m, 4H), 7.43-7.31 (m, 2H), 7.30-7.19 (m, 1H), 3.88 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 142.2, 141.44, 141.42, 139.1, 128.7, 127.5, 127.0, 125.6, 122.5, 122.0, 120.5, 120.3, 119.0, 118.5, 108.4, 107.0, 29.0; IR (KBr) ν (cm⁻¹) 3050, 2927, 1626, 1599, 1561, 1491, 1465, 1454, 1439, 1421, 1360, 1341, 1324, 1248, 1225, 1160, 1124, 1076, 1060, 1017; MS (70 ev, EI) *m/z* (%) 258 (M⁺+1, 20.65), 257 (M⁺, 100); HRMS Calcd for C₁₉H₁₅N (M⁺): 257.1204, Found: 257.1203.

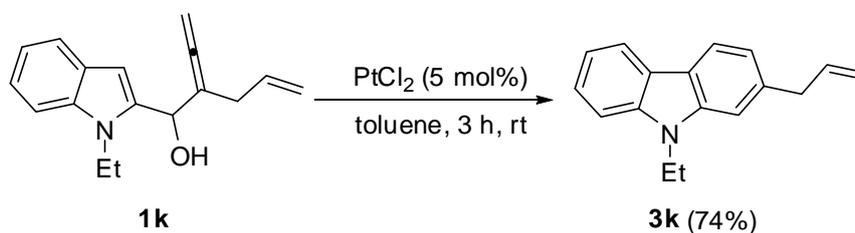
(10) 2-Butyl-9-methyl-9H-carbazole (**3j**)



The reaction of PtCl₂ (5.2 mg, 0.02 mmol) and **1j** (102.1 mg, 0.40 mmol) in toluene (2 mL) at rt for 4 h afforded **3j** (67.2 mg, 71%) (petroleum ether/ethyl acetate = 50/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.03 (dt, *J* = 7.8 and 0.9 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.48-7.38 (m, 1H), 7.37-7.30 (m, 1H), 7.24-7.15 (m, 2H), 7.05 (dd, *J* = 7.8 and 1.5 Hz, 1H), 3.78 (s, 3H), 2.81 (t, *J* = 7.8 Hz, 2H), 1.78-1.63 (m, 2H), 1.48-1.33 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 141.3,

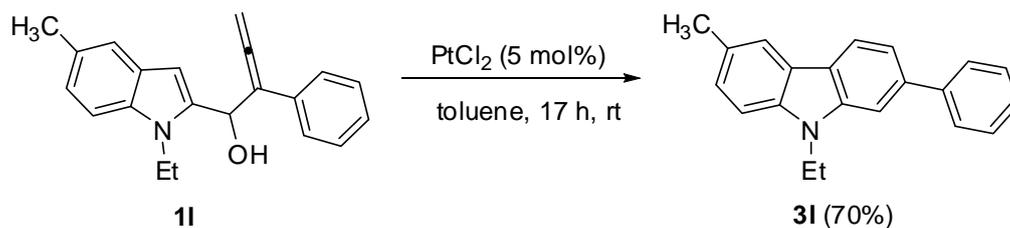
141.0, 125.0, 122.8, 120.6, 119.9, 119.7, 118.6, 108.2, 107.9, 36.5, 34.3, 28.9, 22.5, 14.0; IR (neat) ν (cm^{-1}) 3054, 3025, 2955, 2928, 2857, 1631, 1603, 1564, 1468, 1455, 1420, 1377, 1360, 1337, 1322, 1248, 1156, 1132, 1118, 1000; MS (70 eV, EI) m/z (%) 238 ($M^+ + 1$, 28.31), 237 (M^+ , 34.88), 44 (100); HRMS Calcd for $C_{17}H_{19}N$ (M^+): 237.1517, Found: 237.1516.

(11) 2-Allyl-9-ethyl-9H-carbazole (3k)



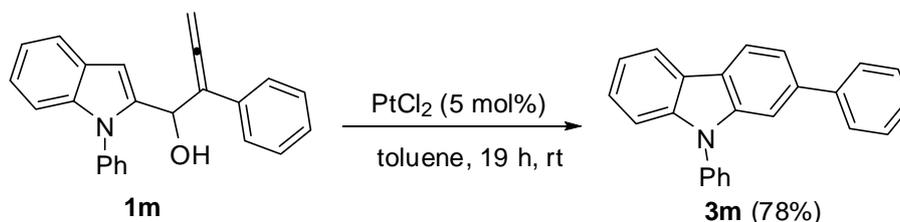
The reaction of PtCl_2 (5.3 mg, 0.02 mmol) and **1k** (100.2 mg, 0.39 mmol) in toluene (2 mL) at rt for 3 h afforded **3k** (69.2 mg, 74%) (petroleum ether/ethyl acetate = 80/1): liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.30-8.15 (m, 2H), 7.67-7.55 (m, 1H), 7.51 (d, $J = 8.1$ Hz, 1H), 7.45-7.35 (m, 2H), 7.30-7.21 (m, 1H), 6.39-7.21 (m, 1H), 5.43-5.25 (m, 2H), 4.43 (q, $J = 7.2$ Hz, 2H), 3.79 (d, $J = 6.3$ Hz, 2H), 1.54 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.2, 139.9, 137.9, 137.8, 125.1, 122.8, 121.1, 120.2, 120.1, 119.7, 118.6, 115.6, 108.3, 108.1, 40.9, 37.2, 13.7; IR (neat) ν (cm^{-1}) 3057, 2975, 2932, 2895, 1629, 1601, 1572, 1496, 1479, 1469, 1460, 1378, 1336, 1327, 1236, 1177, 1156, 1132, 1119, 1086, 1058, 1020, 1000; MS (70 eV, EI) m/z (%) 236 ($M^+ + 1$, 14.21), 235 (M^+ , 99.55), 234 ($M^+ - \text{H}$, 100); HRMS Calcd for $C_{17}H_{17}N$ (M^+): 235.1361, Found: 235.1360.

(12) 9-Ethyl-2-phenyl-6-methyl-9H-carbazole (3I)



The reaction of PtCl_2 (4.2 mg, 0.016 mmol) and **1I** (91.5 mg, 0.30 mmol) in toluene (1.5 mL) at rt for 17 h afforded **3I** (60.2 mg, 70%), which was stored in a refrigerator to produce the solid state product: a pall yellow solid, m.p. 107-108 °C ($\text{CH}_2\text{Cl}_2/n$ -hexane); ^1H NMR (300 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.93 (s, 1H), 7.80-7.70 (m, 2H), 7.58 (d, $J = 1.2$ Hz, 1H), 7.55-7.44 (m, 3H), 7.43-7.28 (m, 3H), 4.41 (q, $J = 7.2$ Hz, 2H), 2.57 (s, 3H), 1.46 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.3, 140.6, 138.9, 138.7, 128.7, 128.2, 127.6, 127.0, 126.9, 122.8, 122.0, 120.5, 120.4, 118.2, 108.1, 106.9, 37.5, 21.4, 13.8; IR (neat) ν (cm^{-1}) 3027, 2974, 2918, 1600, 1563, 1486, 1469, 1439, 1367, 1339, 1298, 1236, 1224, 1149, 1088; MS (70 ev, EI) m/z (%) 286 ($\text{M}^+ + 1$, 19.40), 285 (M^+ , 84.33), 270 ($\text{M}^+ - \text{CH}_3$, 100); HRMS Calcd for $\text{C}_{21}\text{H}_{19}\text{N}$ (M^+): 285.1517, Found: 285.1527.

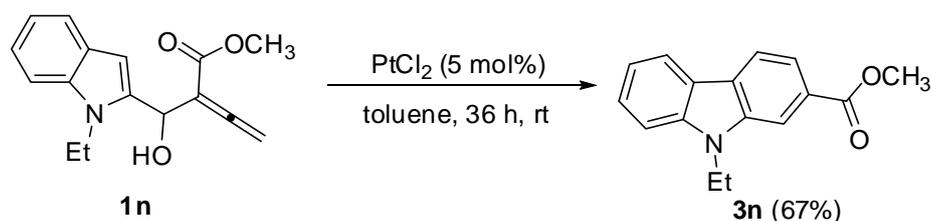
(13) 2,9-Diphenyl-9H-carbazole (3m)



The reaction of PtCl_2 (4.1 mg, 0.015 mmol) and **1m** (100.0 mg, 0.30 mmol) in toluene (1.5 mL) at rt for 19 h afforded **3m** (74.3 mg, 78%), which was stored in a

refrigerator to produce the solid state product: a pall yellow solid, m.p. 118-119 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.28-8.13 (m, 2H), 7.75-7.741 (m, 13H), 7.40-7.28 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 141.9, 141.39, 141.38, 139.4, 137.6, 129.9, 128.7, 127.5, 127.2, 127.0, 125.9, 123.1, 122.5, 120.5, 120.3, 120.0, 119.6, 109.8, 108.2; IR (neat) ν (cm⁻¹) 3059, 1626, 1598, 1558, 1501, 1484, 1457, 1428, 1364, 1339, 1319, 1236, 1218, 1127, 1073; MS (70 ev, EI) *m/z* (%) 320 (M⁺+1, 25.63), 319 (M⁺, 100); HRMS Calcd for C₂₄H₁₇N (M⁺): 319.1361, Found: 319.1374.

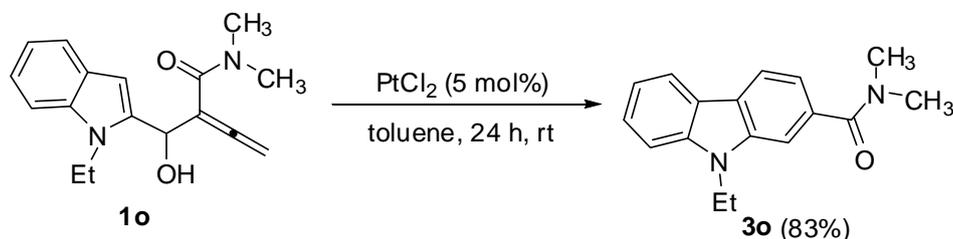
(14) Methyl 9-ethyl-9*H*-carbazole-2-carboxylate (**3n**)



The reaction of PtCl₂ (4.1 mg, 0.015 mmol) and **1n** (83.0 mg, 0.3 mmol) in toluene (1.5 mL) at rt for 36 h afforded **3n** (51.8 mg, 67%) (petroleum ether/ethyl acetate = 20/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.15-8.02 (m, 3H), 7.89 (dd, *J* = 8.1 and 1.2 Hz, 1H), 7.55-7.44 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.26-7.17 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.9, 141.1, 139.2, 126.94, 126.86, 126.5, 122.0, 121.1, 119.93, 119.90, 119.2, 110.2, 108.8, 52.1, 37.6, 13.9 ; IR (neat) ν (cm⁻¹) 3057, 2976, 2950, 1715, 1628, 1600, 1572, 1480, 1443, 1380, 1341, 1328, 1303, 1284, 1254, 1231, 1218, 1157, 1131, 1098, 1057; MS (70 ev, EI) *m/z* (%) 254 (M⁺+1, 11.02), 253 (M⁺, 62.47), 238

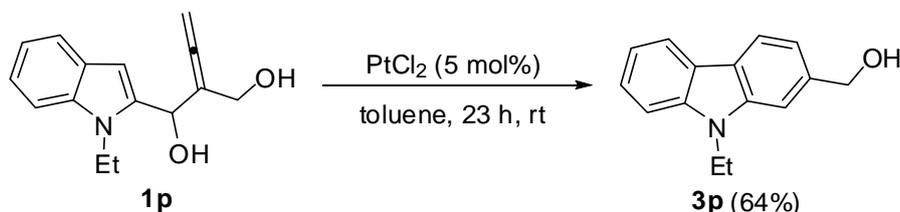
($M^+ - CH_3$, 100); HRMS Calcd for $C_{16}H_{15}NO_2$ (M^+): 253.1103, Found: 253.1095.

(15) *N,N*-Dimethyl 9-Ethyl-9*H*-carbazole-2-carboxamide (3o**)**



The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **1o** (92.1 mg, 0.3 mmol) in toluene (1.5 mL) at rt for 24 h afforded **3o** (71.6 mg, 83%) (petroleum ether/ethyl acetate = 3/1~1/1): liquid; 1H NMR (300 MHz, $CDCl_3$) δ 8.16-8.04 (m, 2H), 7.60-7.39 (m, 3H), 7.30-7.20 (m, 2H), 4.38 (q, $J = 7.2$ Hz, 2H), 3.17 (s, 3H), 3.06 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 140.5, 139.4, 133.3, 126.2, 123.8, 122.3, 120.7, 120.0, 119.1, 117.6, 108.6, 107.8, 39.9, 37.6, 35.5, 13.8; IR (neat) ν (cm^{-1}) 2973, 2931, 1631, 1566, 1483, 1477, 1444, 1391, 1327, 1260, 1234, 1196, 1157, 1077; MS (70 ev, EI) m/z (%) 267 ($M^+ + 1$, 10.46), 266 (M^+ , 55.07), 222 ($M^+ - C_2H_6N$, 100); HRMS Calcd for $C_{17}H_{18}N_2O$ (M^+): 266.1419, Found: 266.1418.

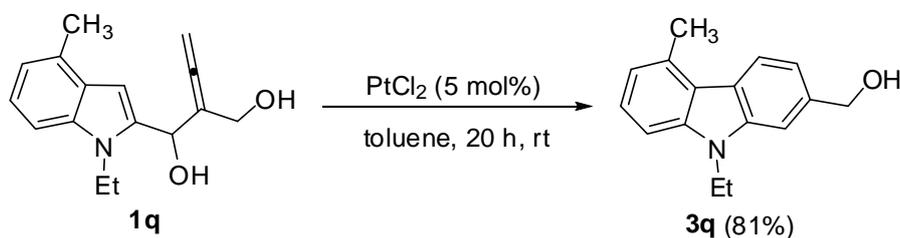
(16) (9-Ethyl-9*H*-carbazol-2-yl)methanol (3p**)**



The reaction of $PtCl_2$ (5.3 mg, 0.02 mmol) and **1p** (96.2 mg, 0.4 mmol) in toluene (2.0 mL) at rt for 23 h afforded **3p** (57.4 mg, 64%) (petroleum ether/ethyl

acetate = 10/1~3/1): liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.05 (d, $J = 7.8$ Hz, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.50-7.38 (m, 1H), 7.37-7.30 (m, 2H), 7.26-7.16 (m, 1H), 7.13 (d, $J = 8.1$ Hz, 1H), 4.81 (s, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.26 (bs, 1H), 1.35 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.1, 140.0, 138.6, 125.5, 122.6, 122.3, 120.33, 120.29, 118.7, 117.8, 108.4, 106.8, 65.9, 37.3, 13.7; IR (neat) ν (cm^{-1}) 3345, 3053, 2975, 2932, 2872, 1629, 1601, 1572, 1498, 1479, 1470, 1443, 1379, 1327, 1236, 1178, 1156, 1133, 1086, 1001; MS (70 eV, EI) m/z (%) 226 ($\text{M}^+ + 1$, 11.89), 225 (M^+ , 72.38), 210 ($\text{M}^+ - \text{CH}_3$, 100); HRMS Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$ (M^+): 225.1154, Found: 225.1156.

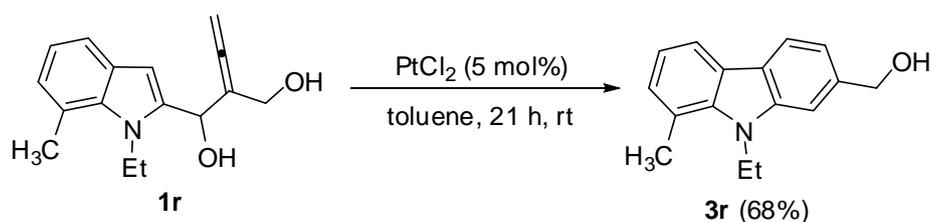
(17) (9-Ethyl-5-methyl-9H-carbazol-2-yl)methanol (3q)



The reaction of PtCl_2 (5.40 mg, 0.02 mmol) and **1q** (102.5 mg, 0.4 mmol) in toluene (2.0 mL) at rt for 20 h afforded **3q** (77.4 mg, 81%) (petroleum ether/ethyl acetate = 10/1~3/1): liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.18 (d, $J = 7.8$ Hz, 1H), 7.52-7.40 (m, 2H), 7.30 (d, $J = 8.1$ Hz, 1H), 7.23 (d, $J = 8.1$ Hz, 1H), 7.18-7.05 (m, 1H), 4.90 (s, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 2.94 (s, 4H), 1.43 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.1, 140.0, 137.9, 133.4, 125.3, 122.9, 122.6, 121.1, 120.4, 117.8, 106.5, 106.0, 65.9, 37.3, 20.8, 13.7; IR (neat) ν (cm^{-1}) 3334, 3049, 2974, 2933, 2872, 1624, 1597, 1489, 1469, 1447, 1379, 1322, 1274, 1253, 1222, 1187, 1165,

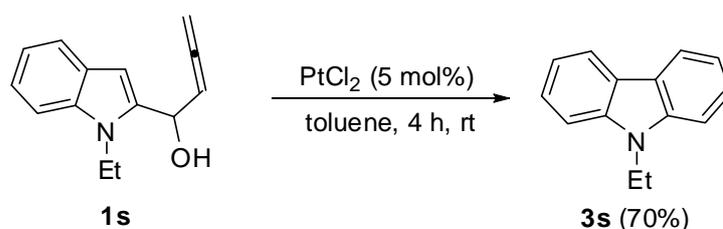
1152, 1138, 1105, 1080, 1012; MS (70 ev, EI) m/z (%) 240 (M^{+1} , 12.90), 239 (M^{+} , 73.21), 224 ($M^{+}-CH_3$, 100); HRMS Calcd for $C_{16}H_{17}NO$ (M^{+}): 239.1310, Found: 239.1315.

(18) (9-Ethyl-8-methyl-9H-carbazol-2-yl)methanol (3r)



The reaction of PtCl₂ (5.5 mg, 0.02 mmol) and **1r** (102.0 mg, 0.4 mmol) in toluene (2.0 mL) at rt for 21 h afforded **3r** (64.8 mg, 68%) (petroleum ether/ethyl acetate = 10/1~3/1): liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.40 (s, 2H), 7.25-7.10 (m, 3H), 4.87 (s, 1H), 4.52 (q, J = 7.0 Hz, 2H), 2.82 (s, 3H), 2.26 (bs, 1H), 1.41 (t, J = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.7, 138.8, 138.5, 128.8, 123.4, 122.6, 120.01, 119.95, 118.9, 118.1, 118.0, 107.0, 66.0, 39.2, 20.0, 15.6 ; IR (neat) ν (cm⁻¹) 3346, 3049, 2975, 2934, 2873, 1623, 1597, 1489, 1469, 1447, 1379, 1322, 1274, 1252, 1222, 1187, 1165, 1152, 1138, 1105, 1080, 1012; MS (70 ev, EI) m/z (%) 240 (M^{+1} , 12.25), 239 (M^{+} , 67.62), 224 ($M^{+}-CH_3$, 100); HRMS Calcd for $C_{16}H_{17}NO$ (M^{+}): 239.1310, Found: 239.1311.

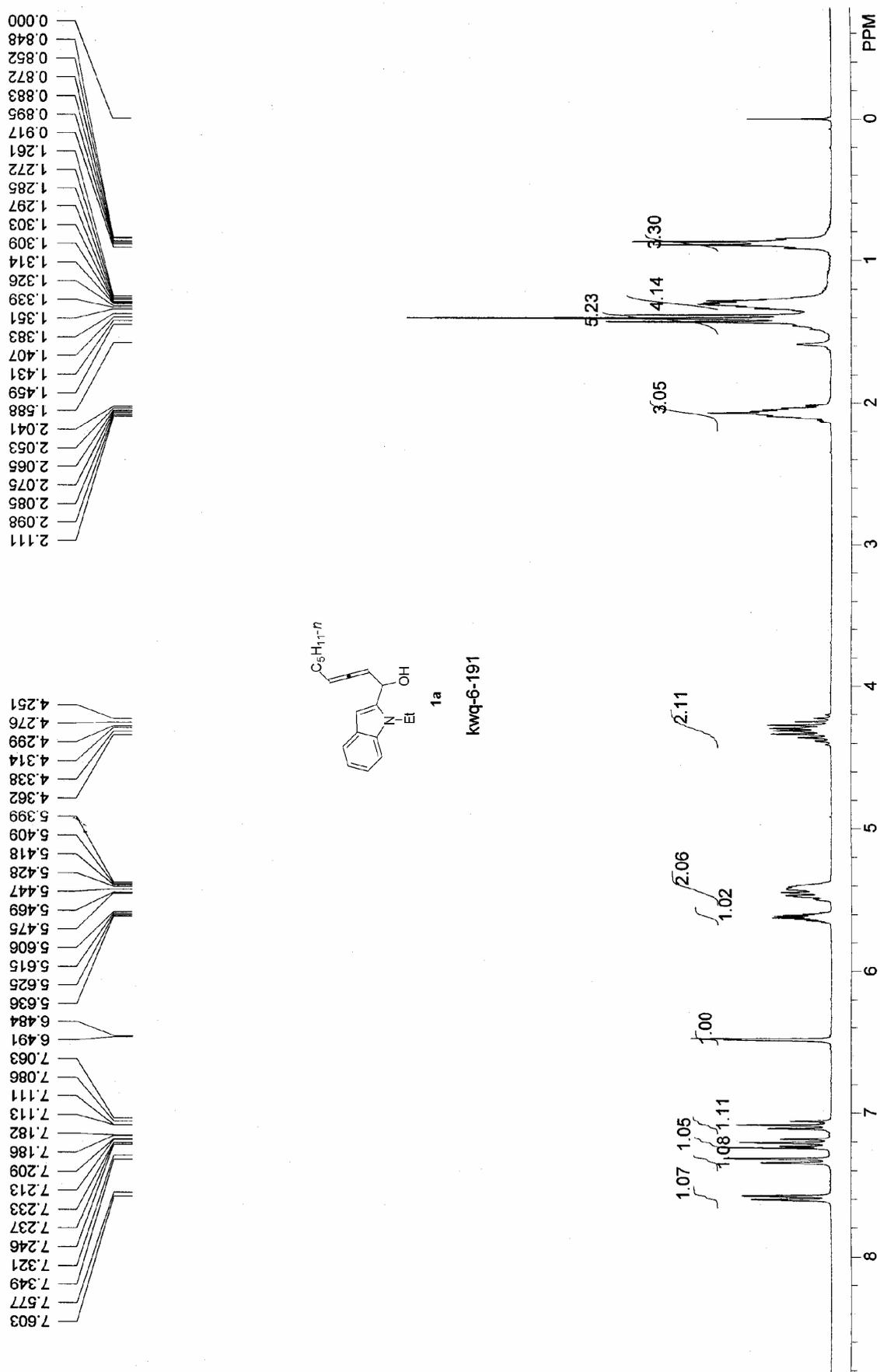
(19) 9-Ethyl-9H-carbazole (3s)

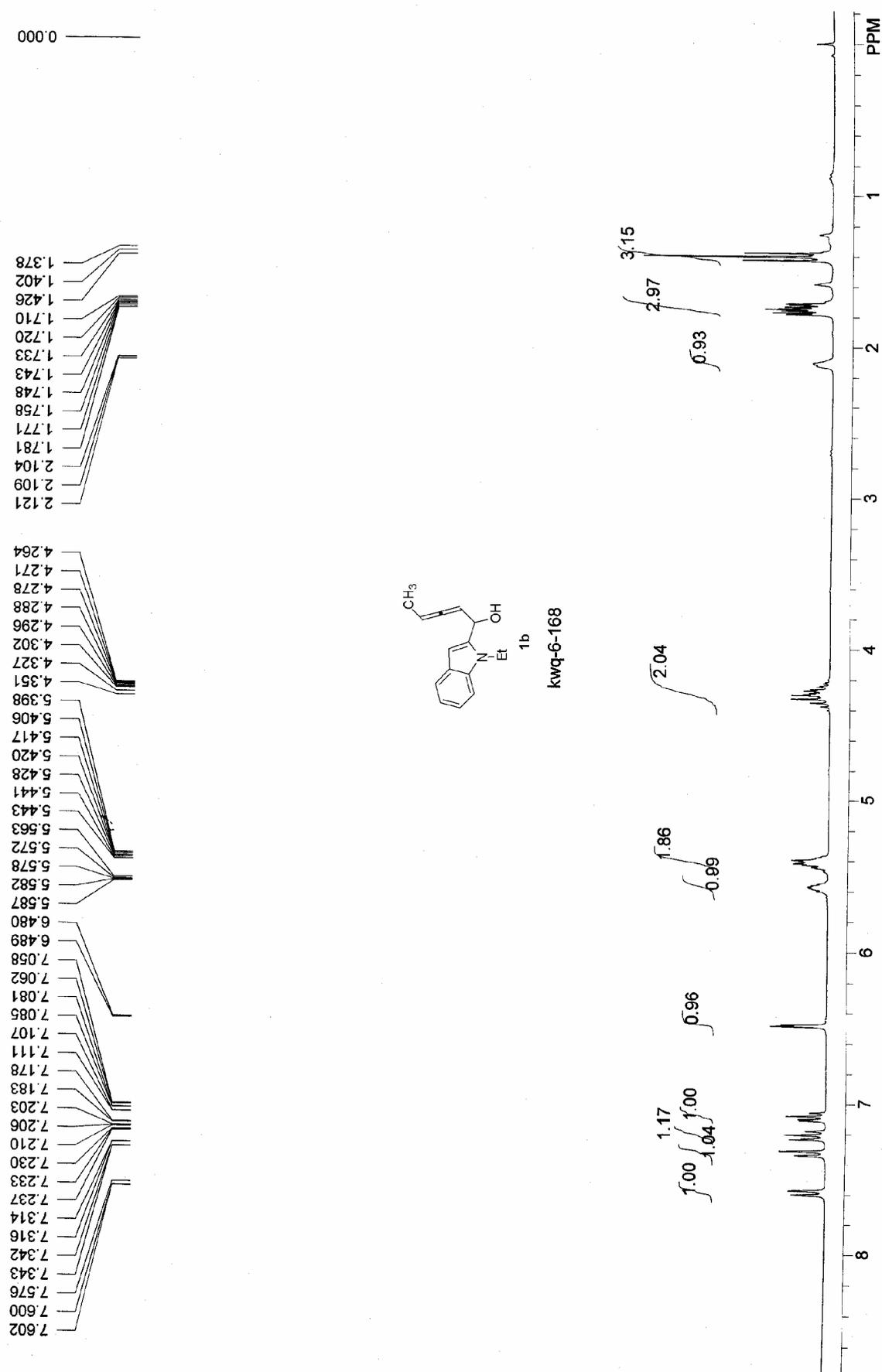


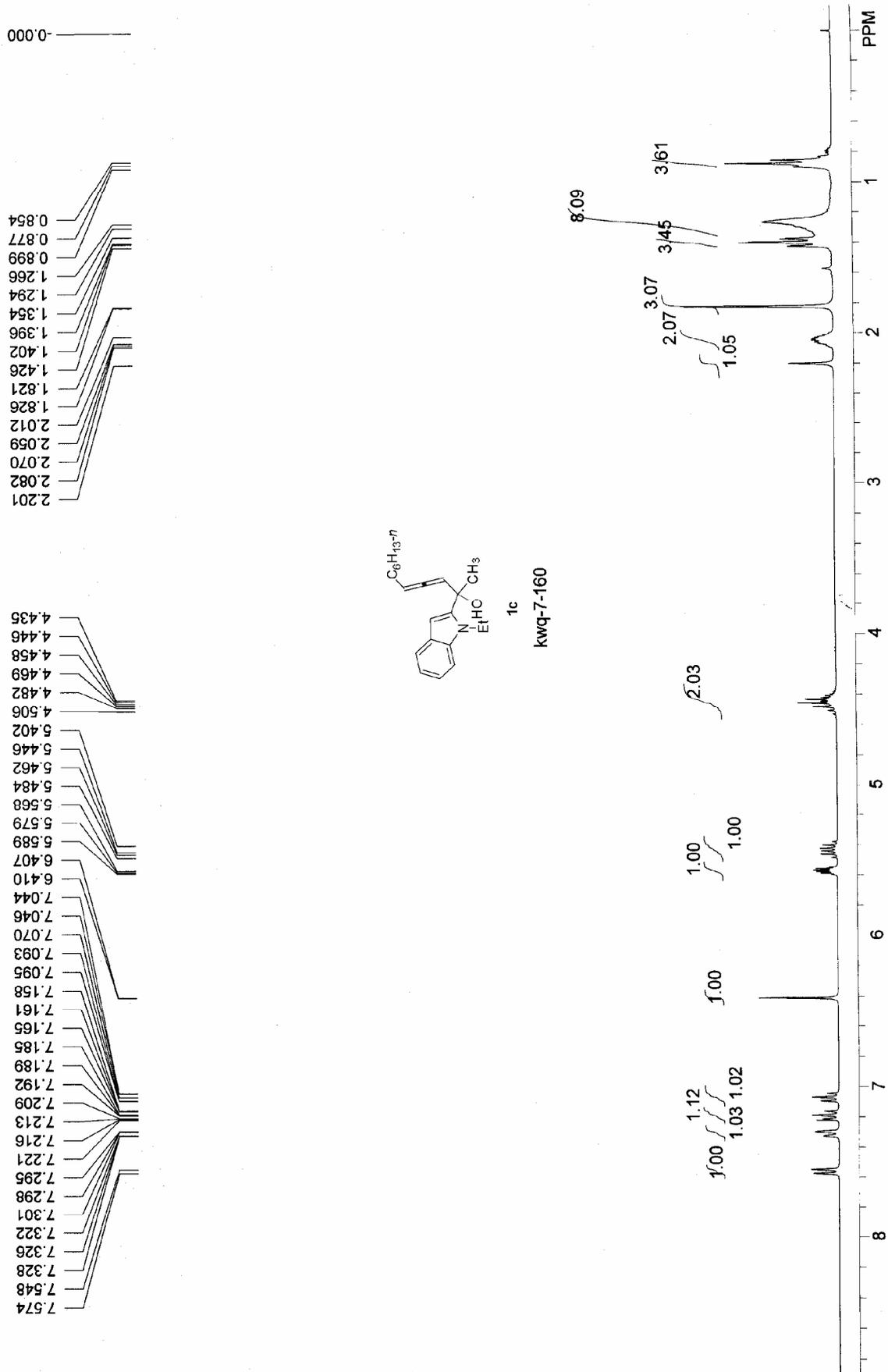
The reaction of PtCl_2 (5.3 mg, 0.02 mmol) and **1s** (85.7 mg, 0.40 mmol) in toluene (2 mL) at rt for 4 h afforded **3s** (55.1 mg, 70%) (petroleum ether/ethyl acetate = 80/1): liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.10 (d, $J = 7.8$ Hz, 2H), 7.52-7.36 (m, 4H), 7.23 (td, $J = 7.2$ and 1.0 Hz, 2H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.42 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.9, 125.6, 122.9, 120.4, 118.7, 108.4, 37.4, 13.8; IR (neat) ν (cm^{-1}) 3423, 3051, 2975, 2925, 2877, 1627, 1598, 1484, 1469, 1454, 1381, 1345, 1327, 1231, 1153, 1130, 1120, 1086, 1053; MS (70 eV, EI) m/z (%) 196 ($\text{M}^+ + 1$, 9.34), 195 (M^+ , 57.45), 180 ($\text{M}^+ - \text{CH}_3$, 100); HRMS Calcd for $\text{C}_{14}\text{H}_{13}\text{N}$ (M^+): 195.1048, Found: 195.1044.

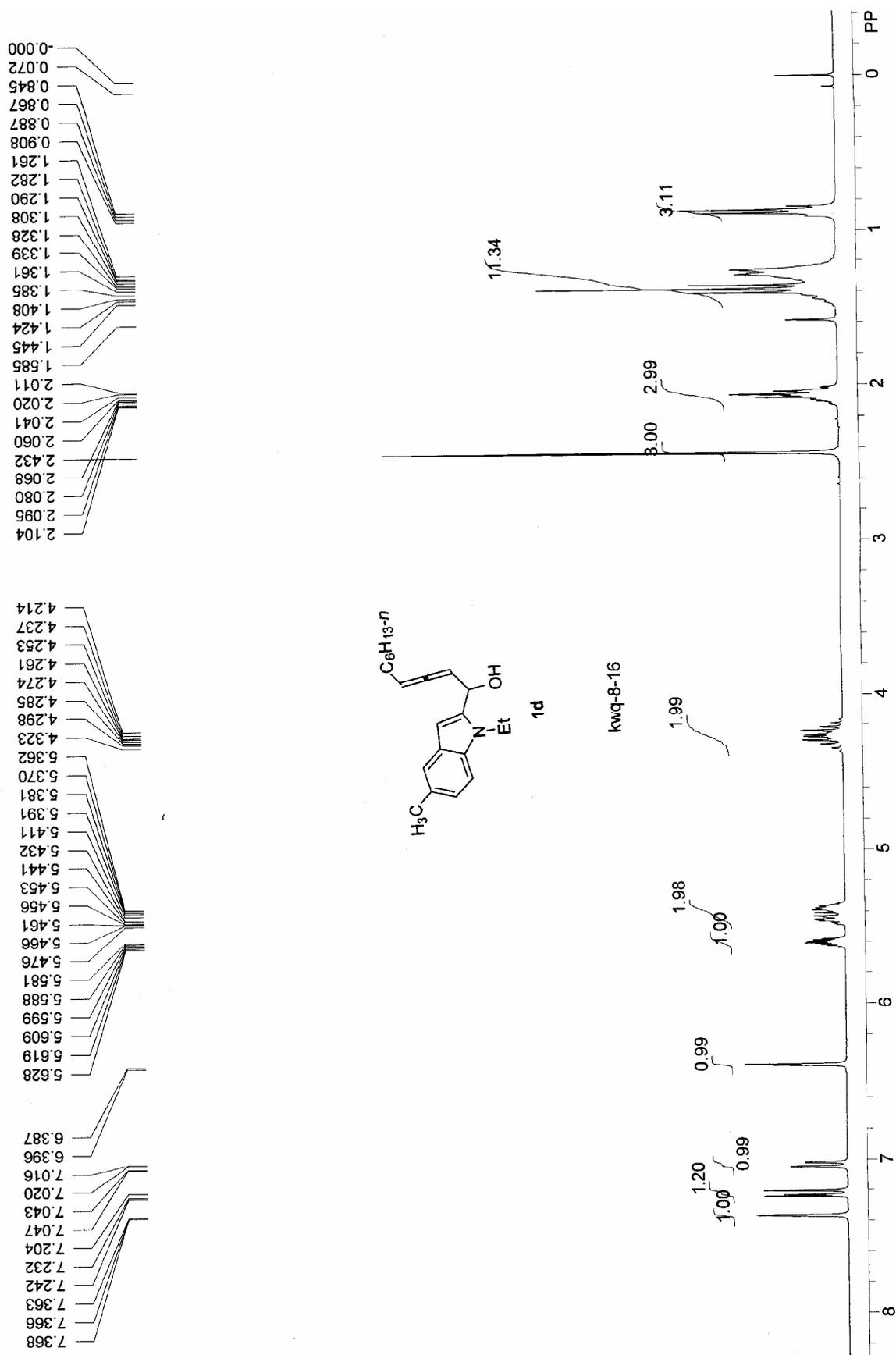
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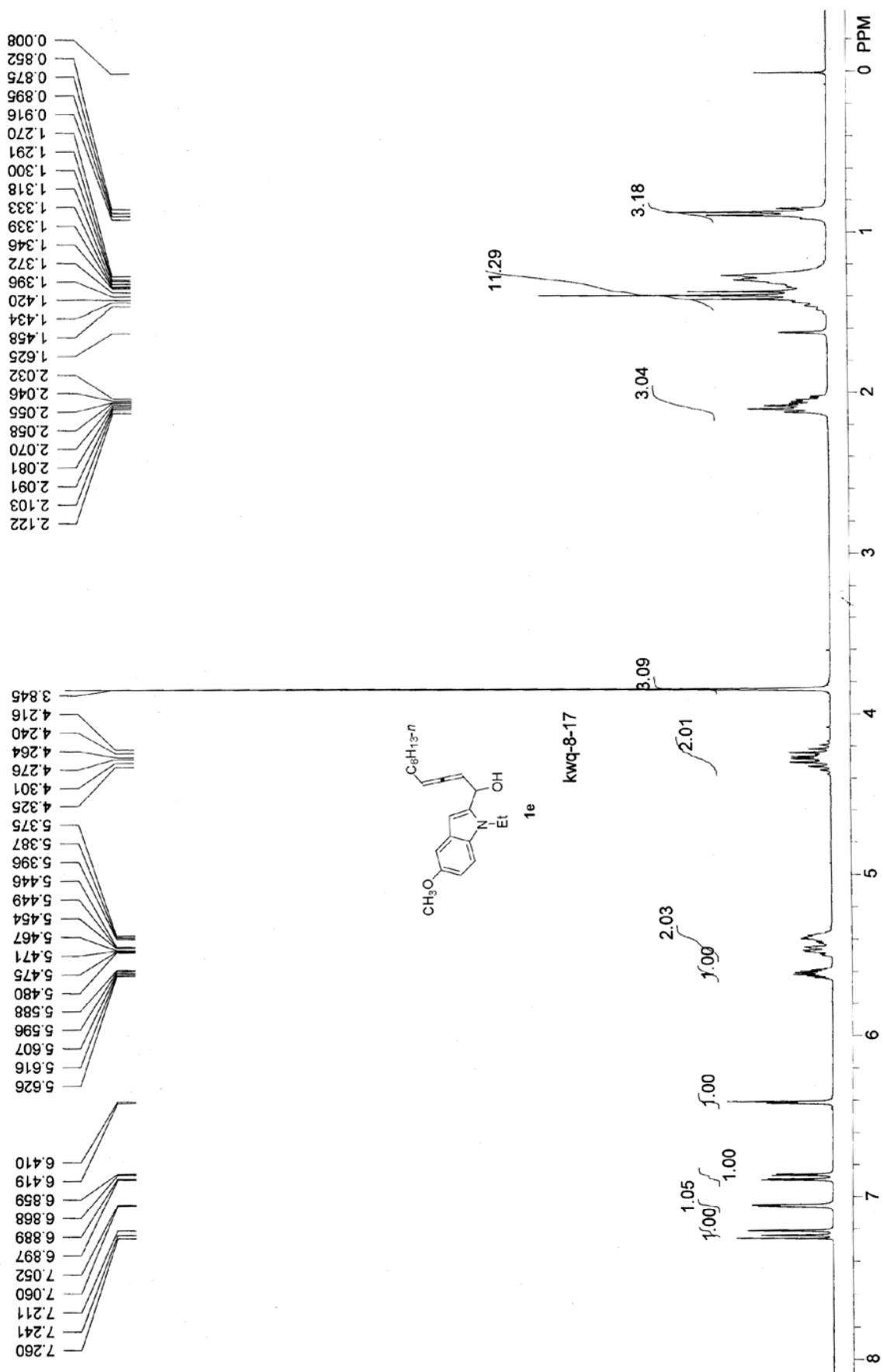
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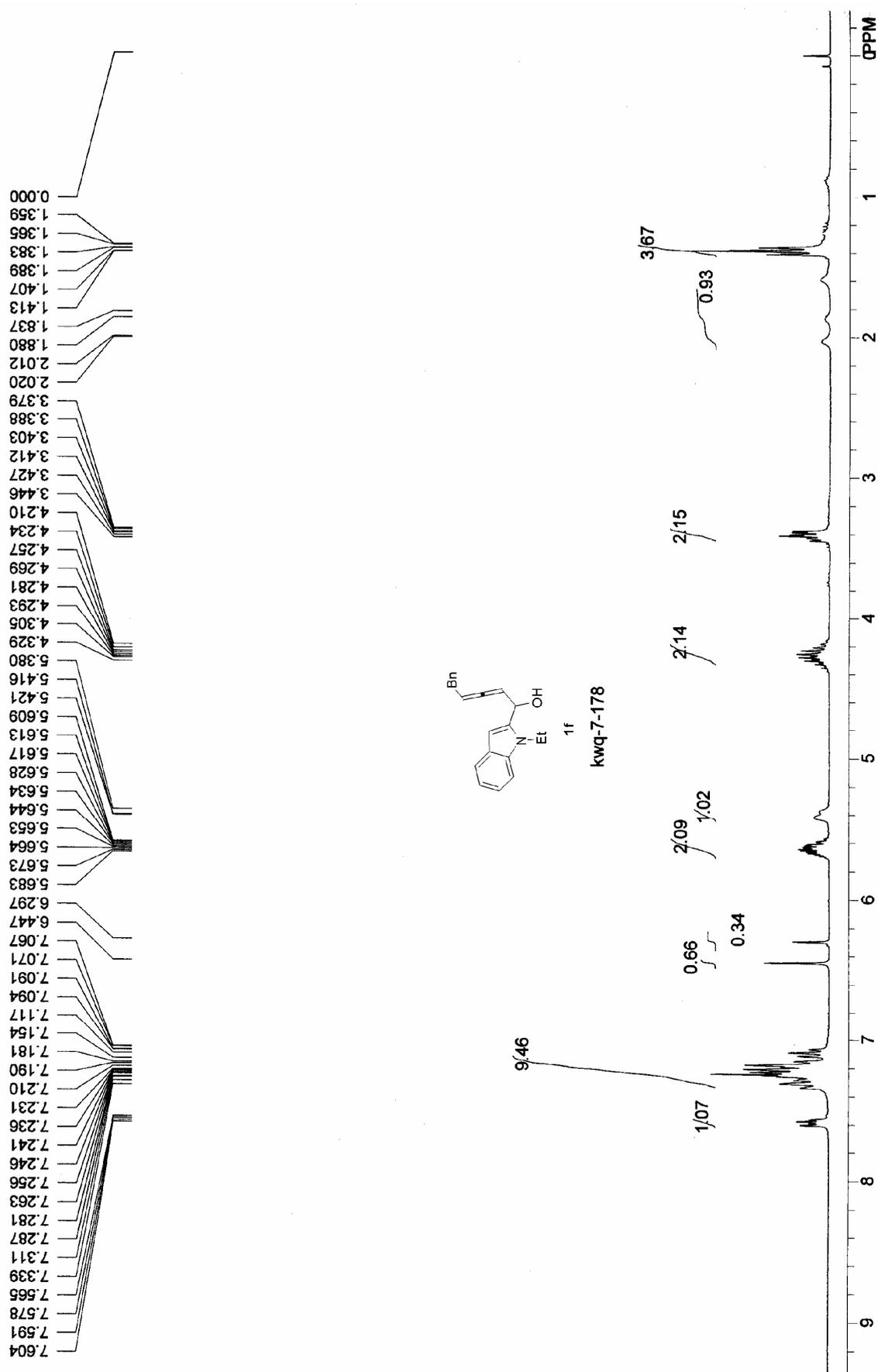


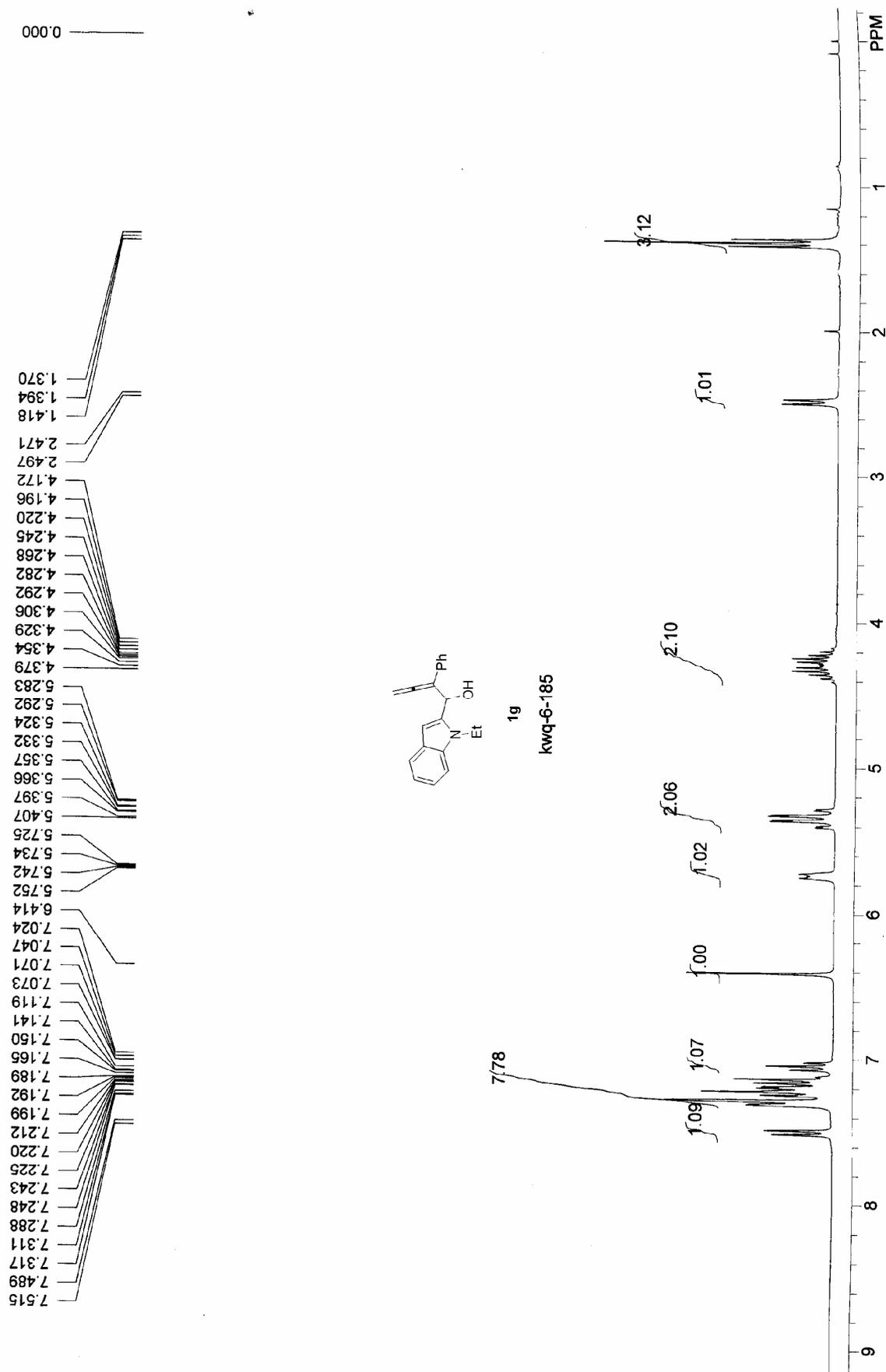


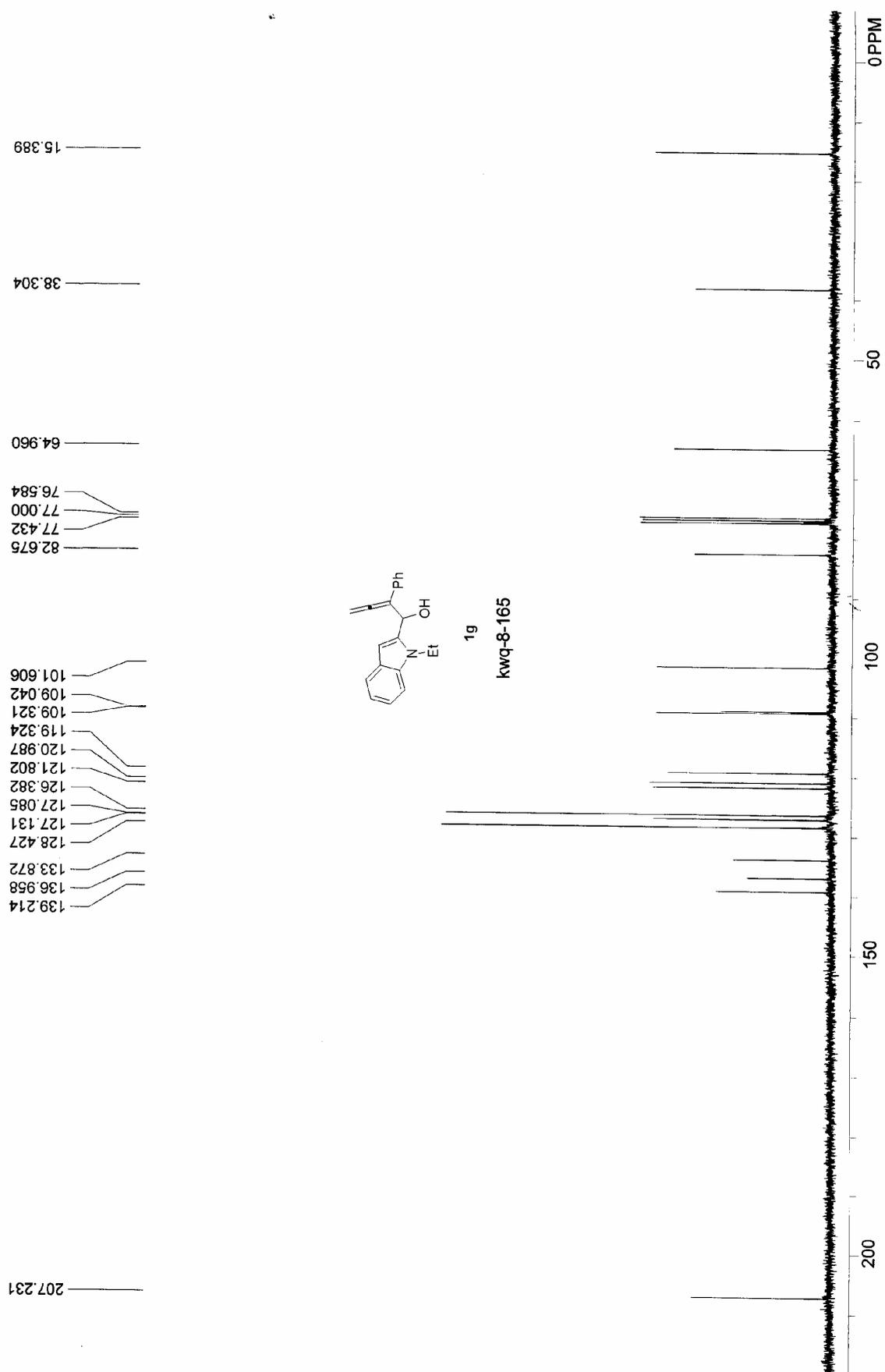


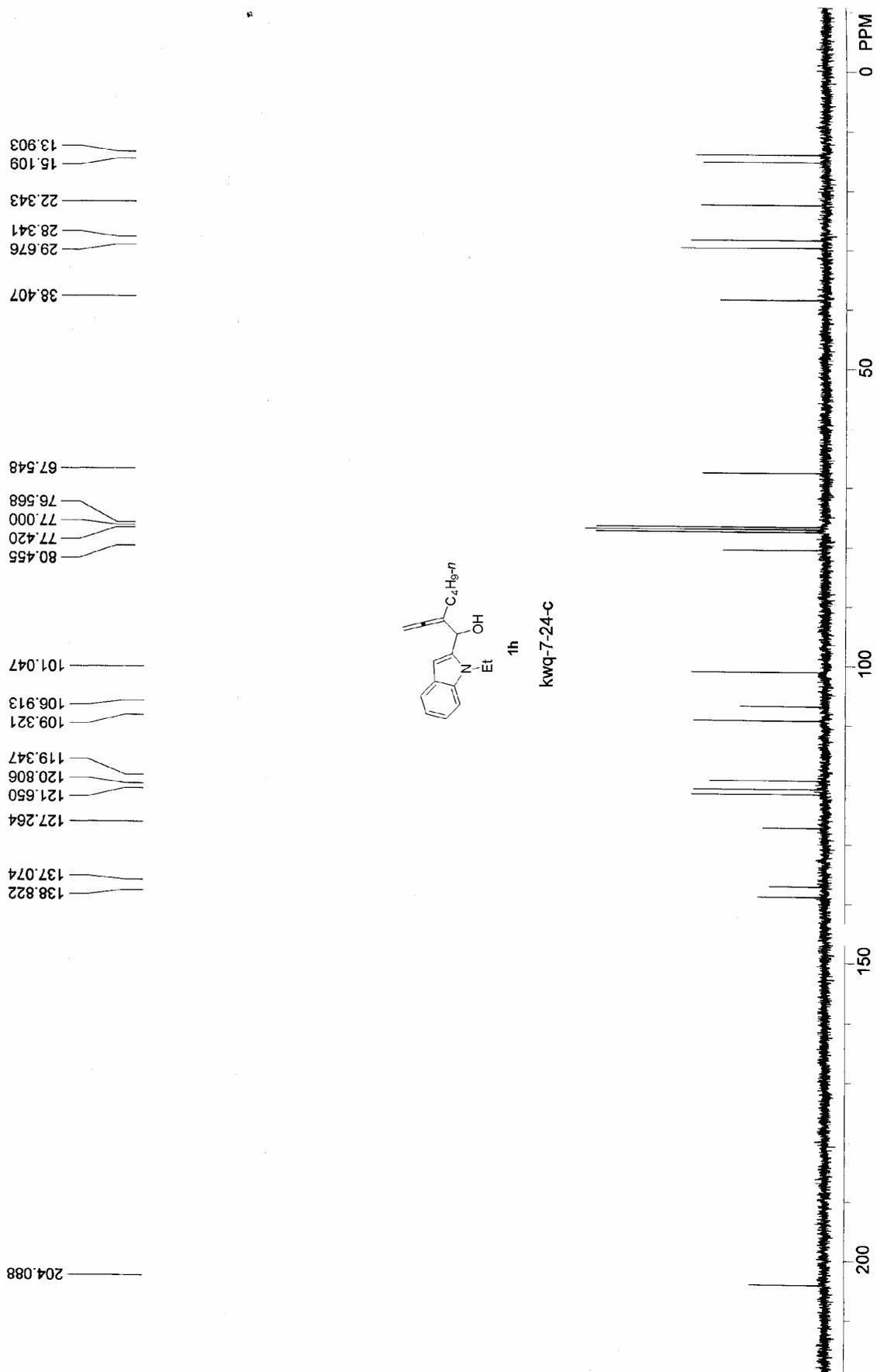


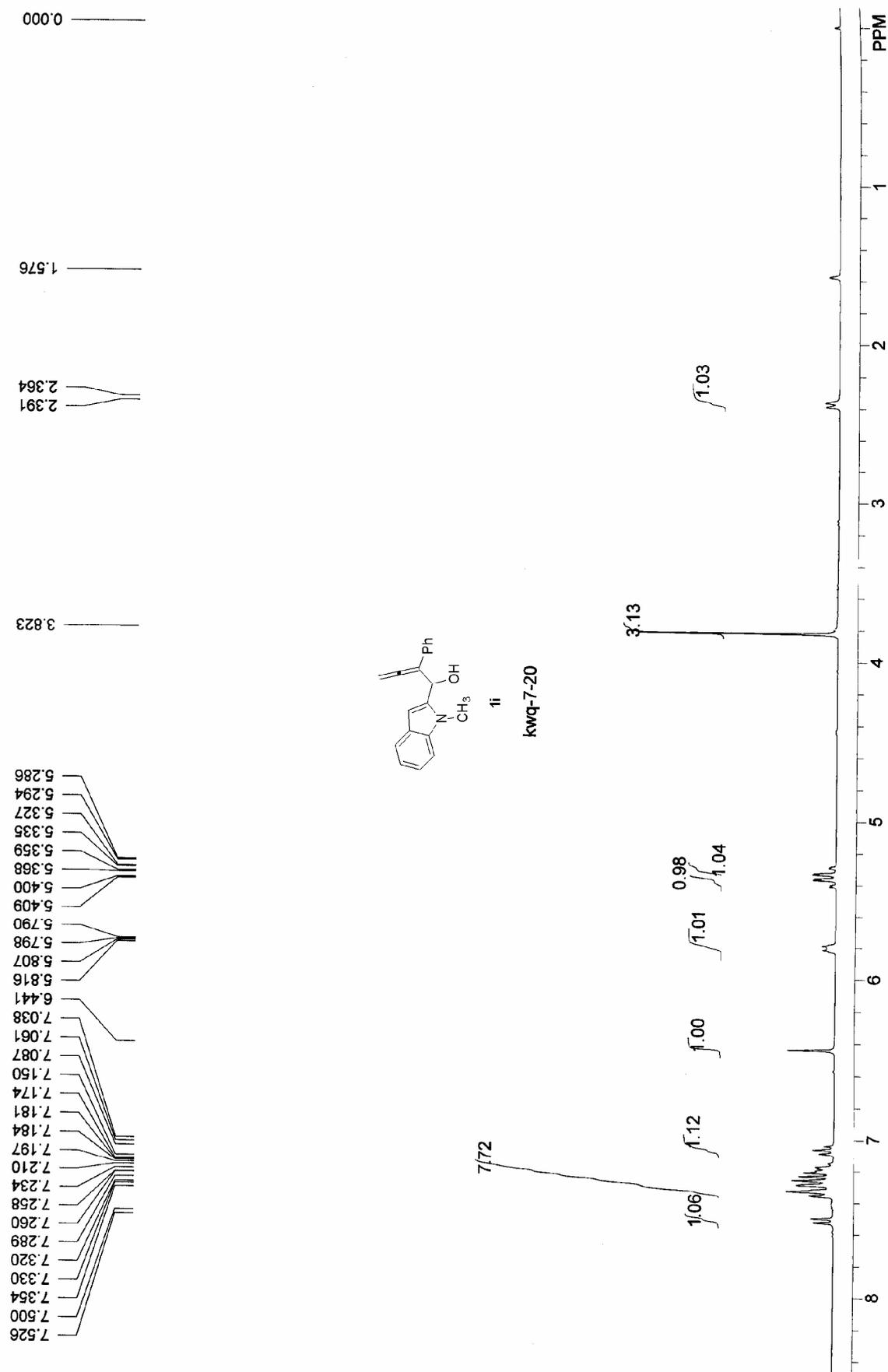


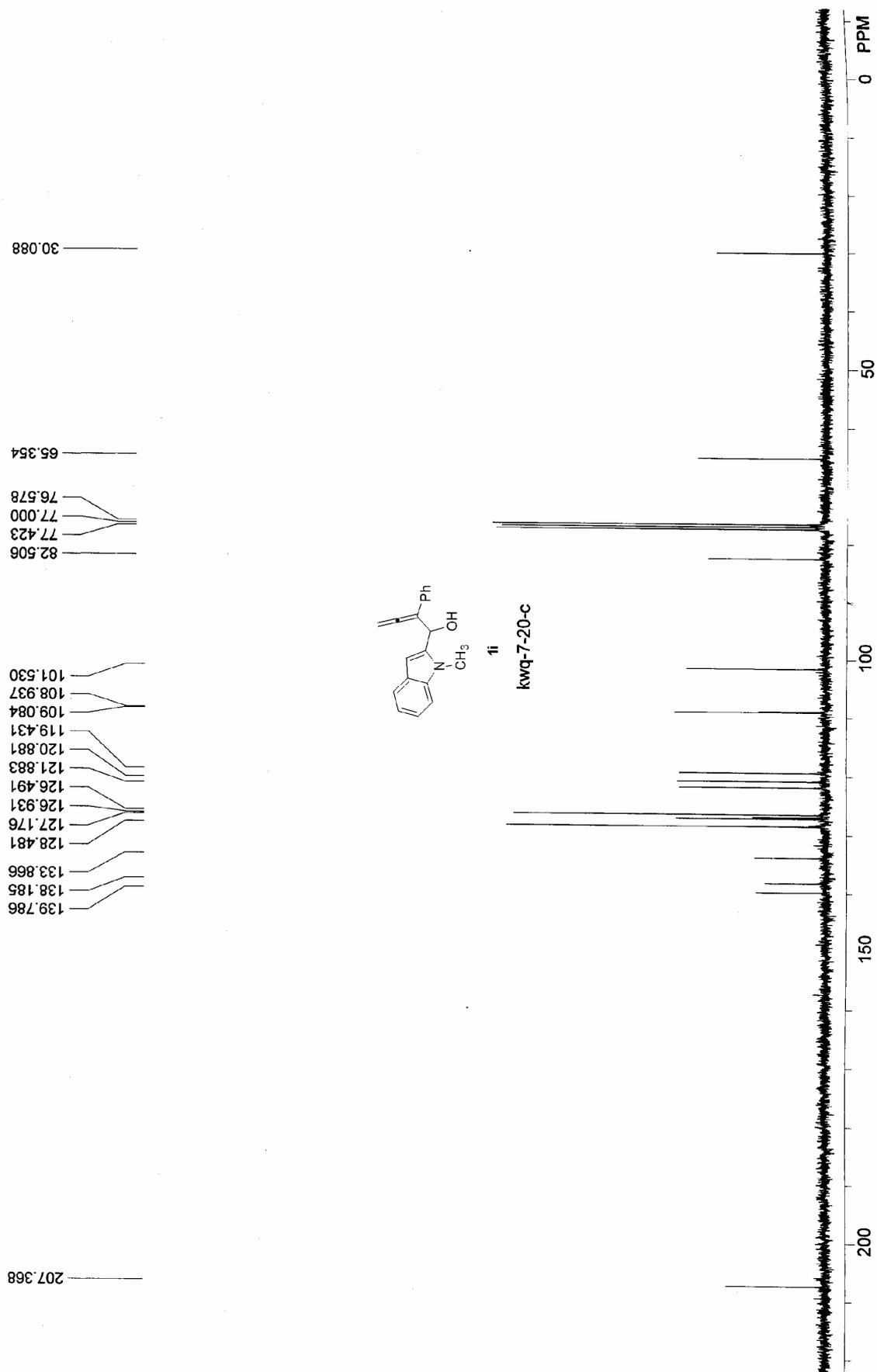


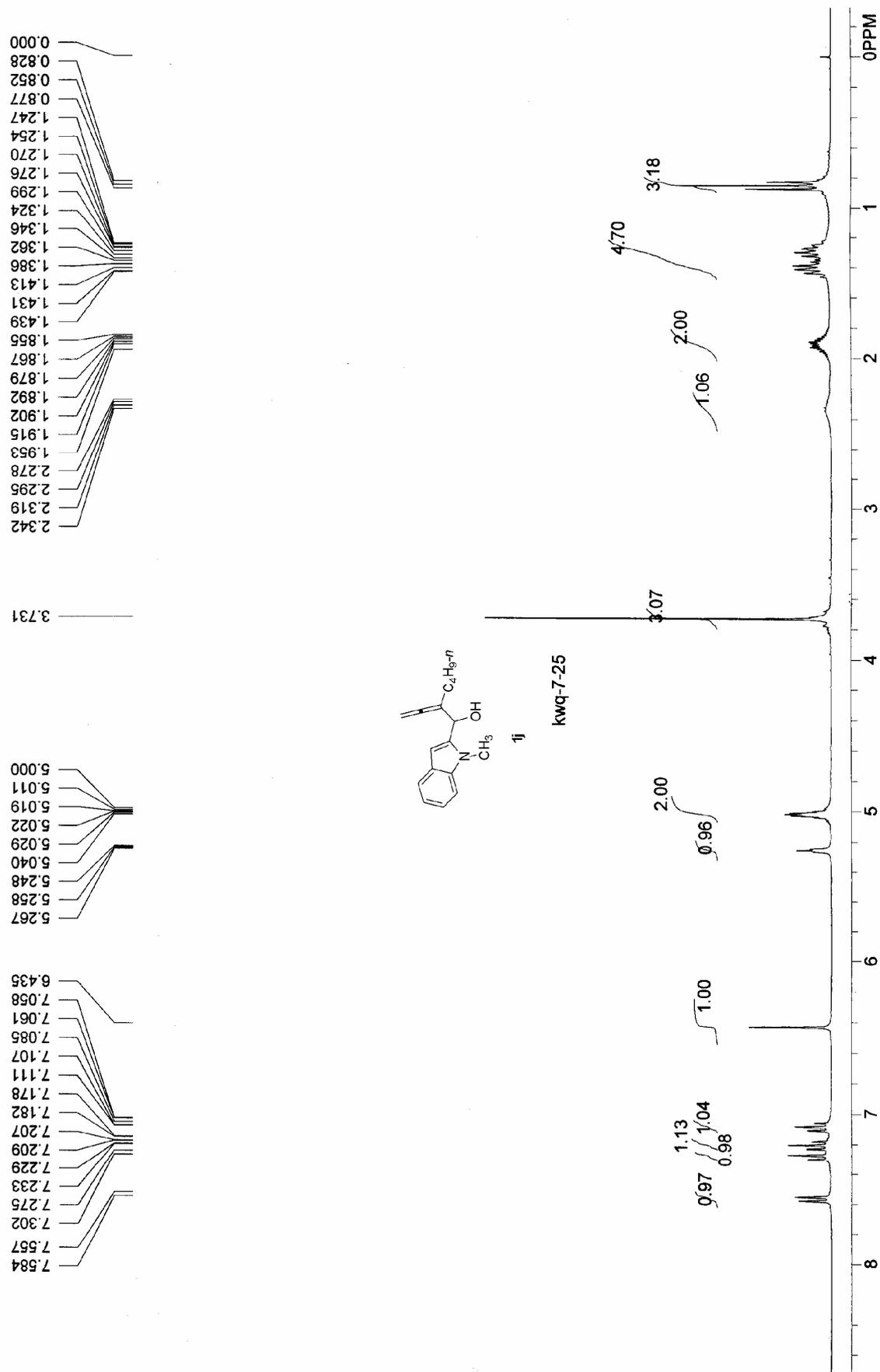


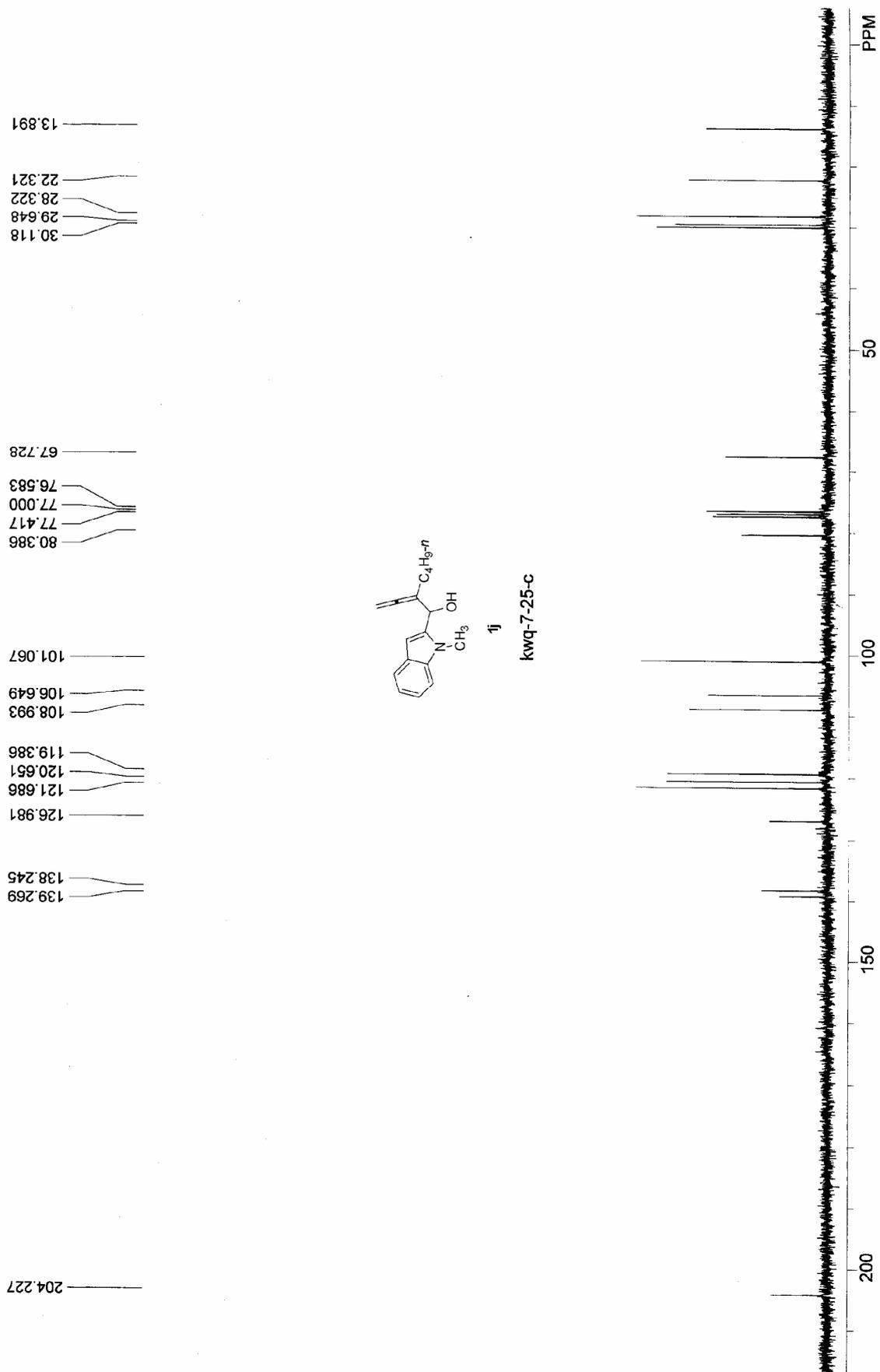


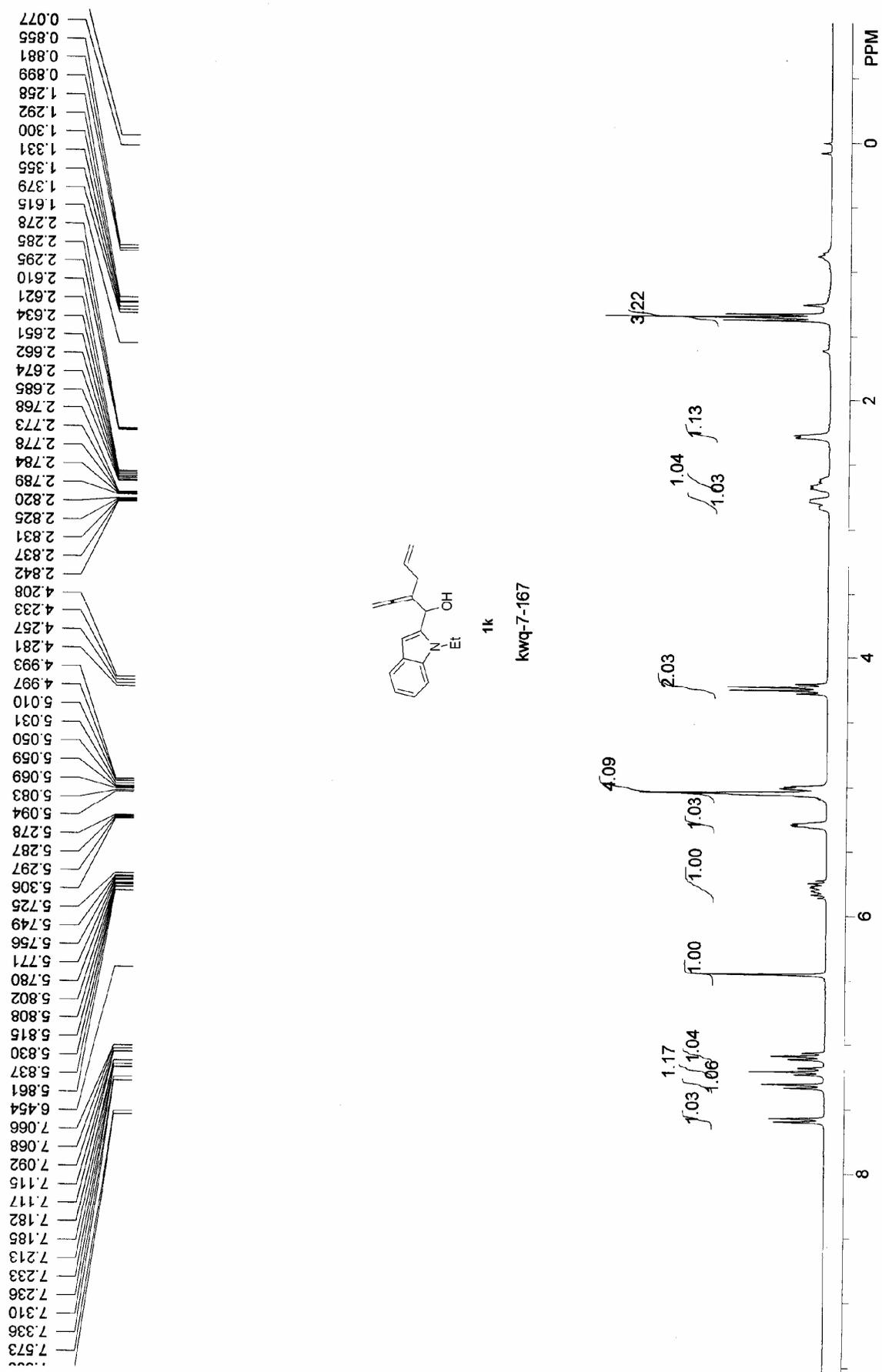


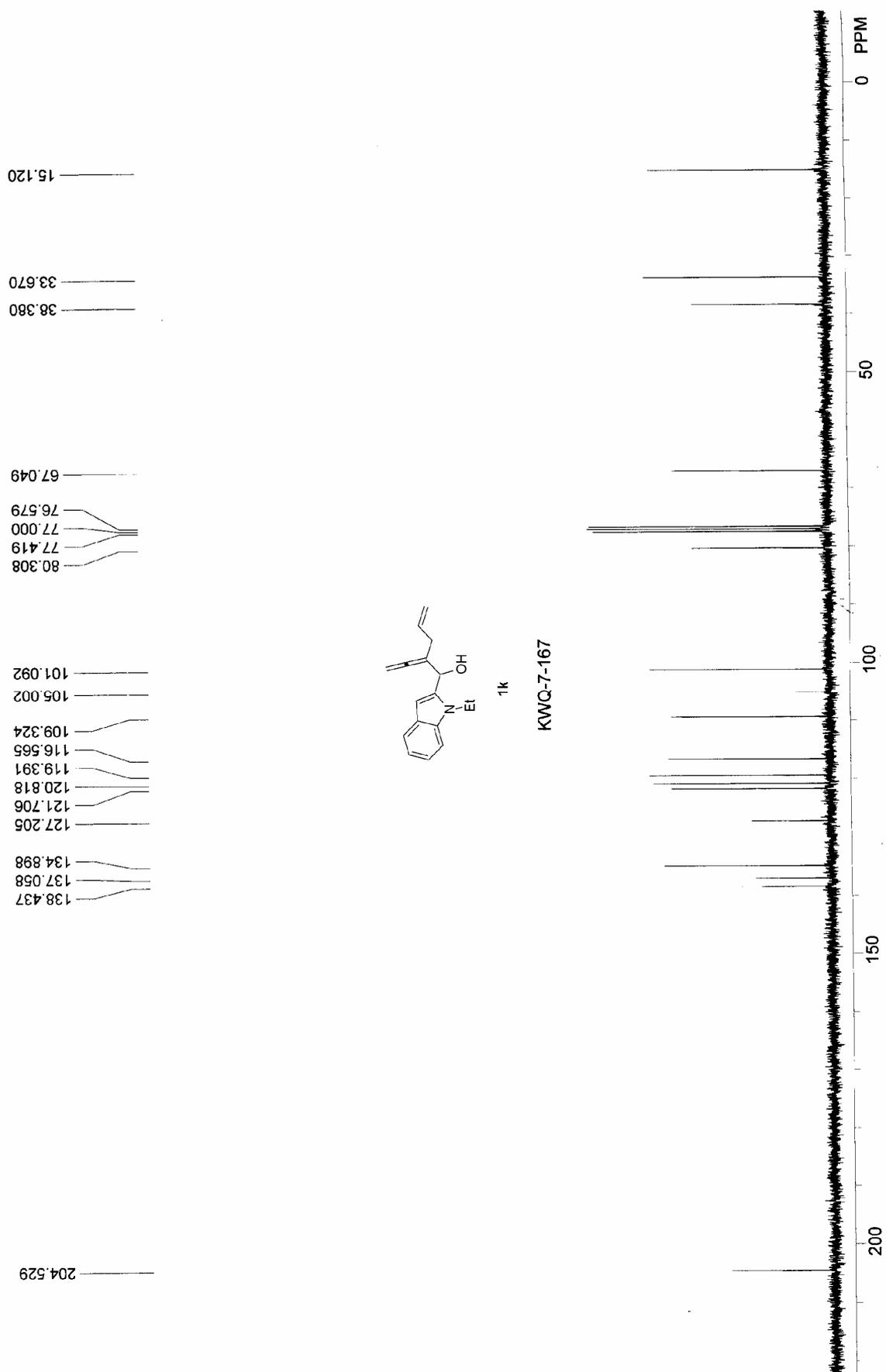


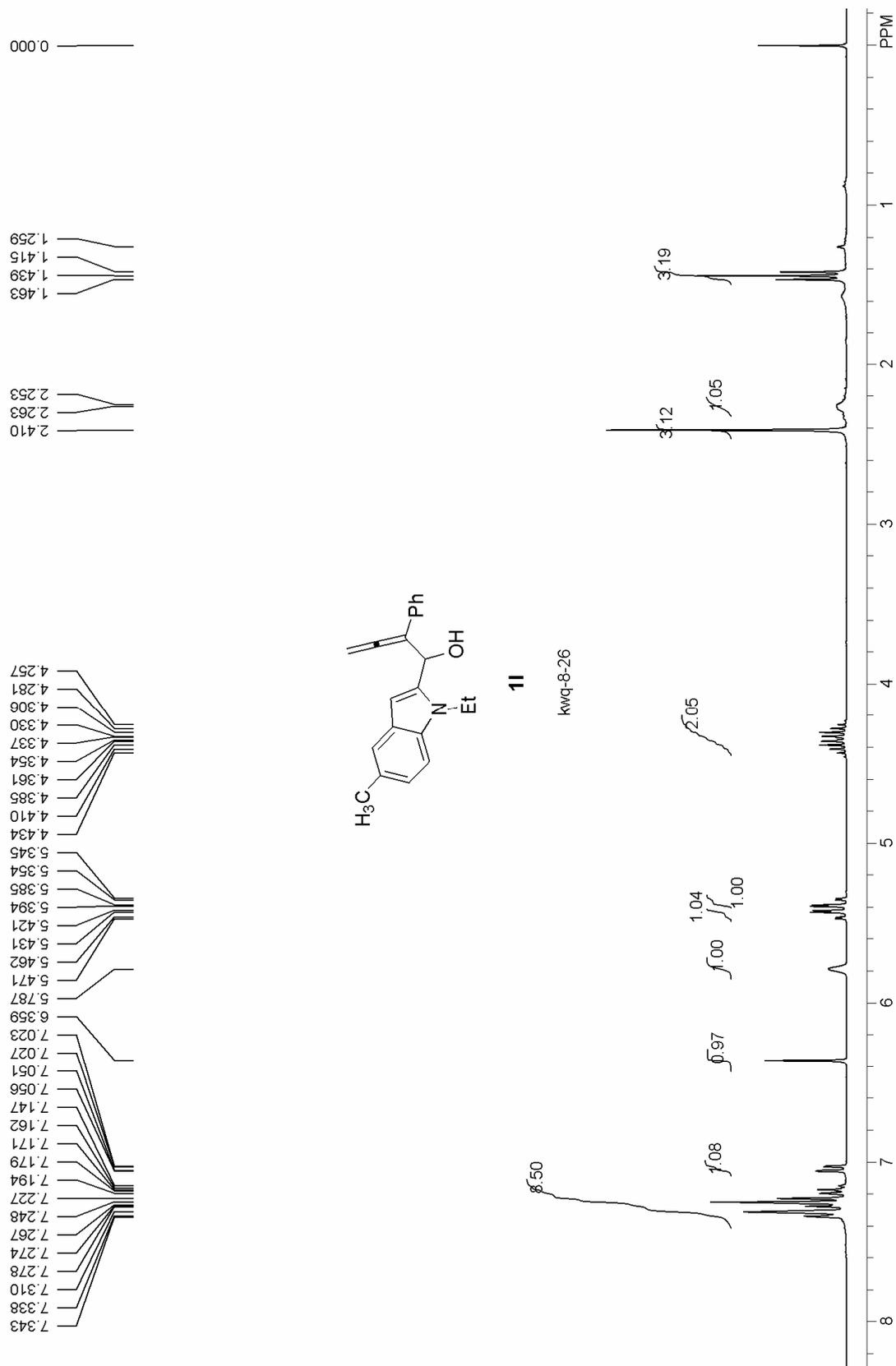


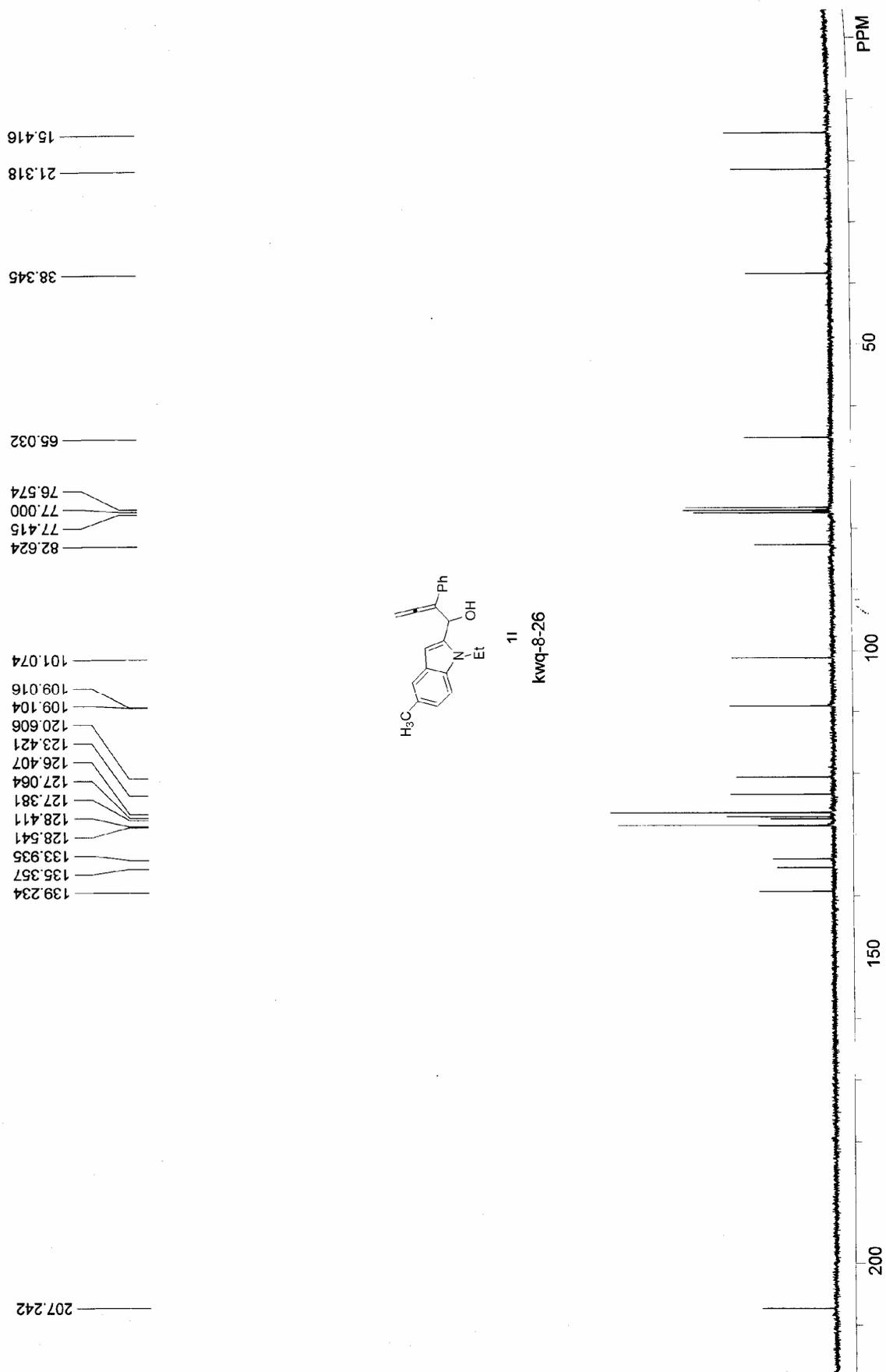


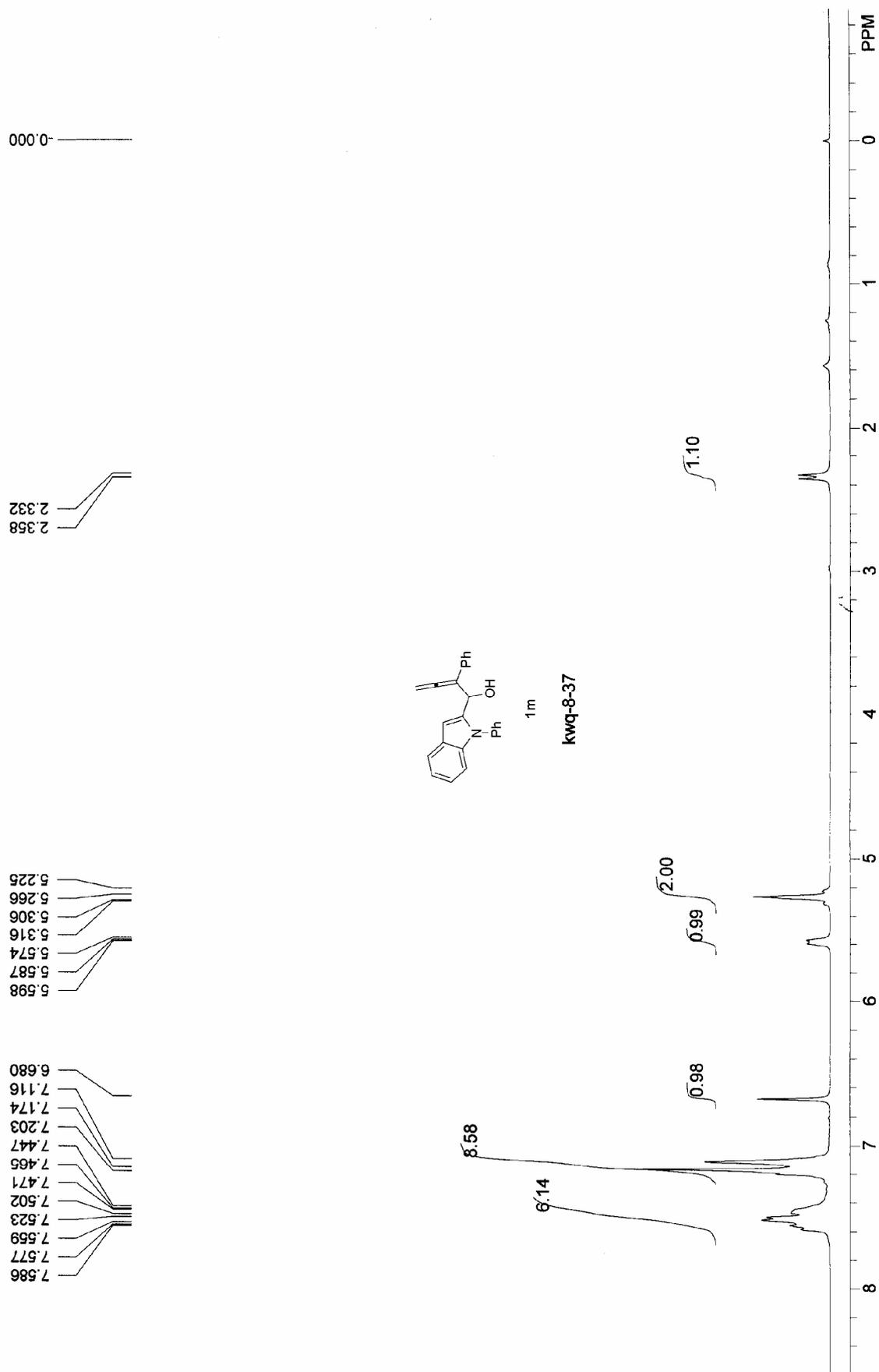


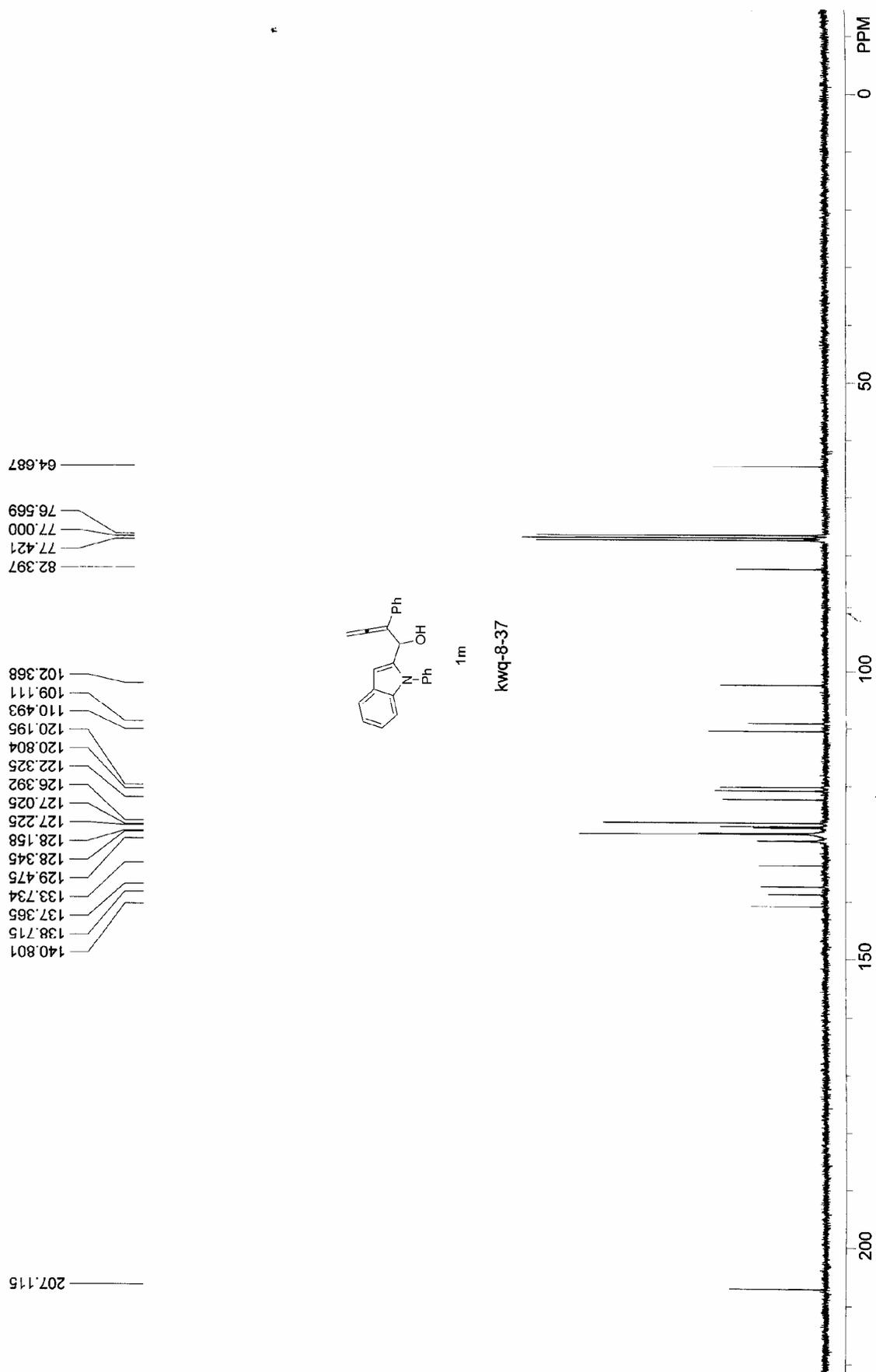


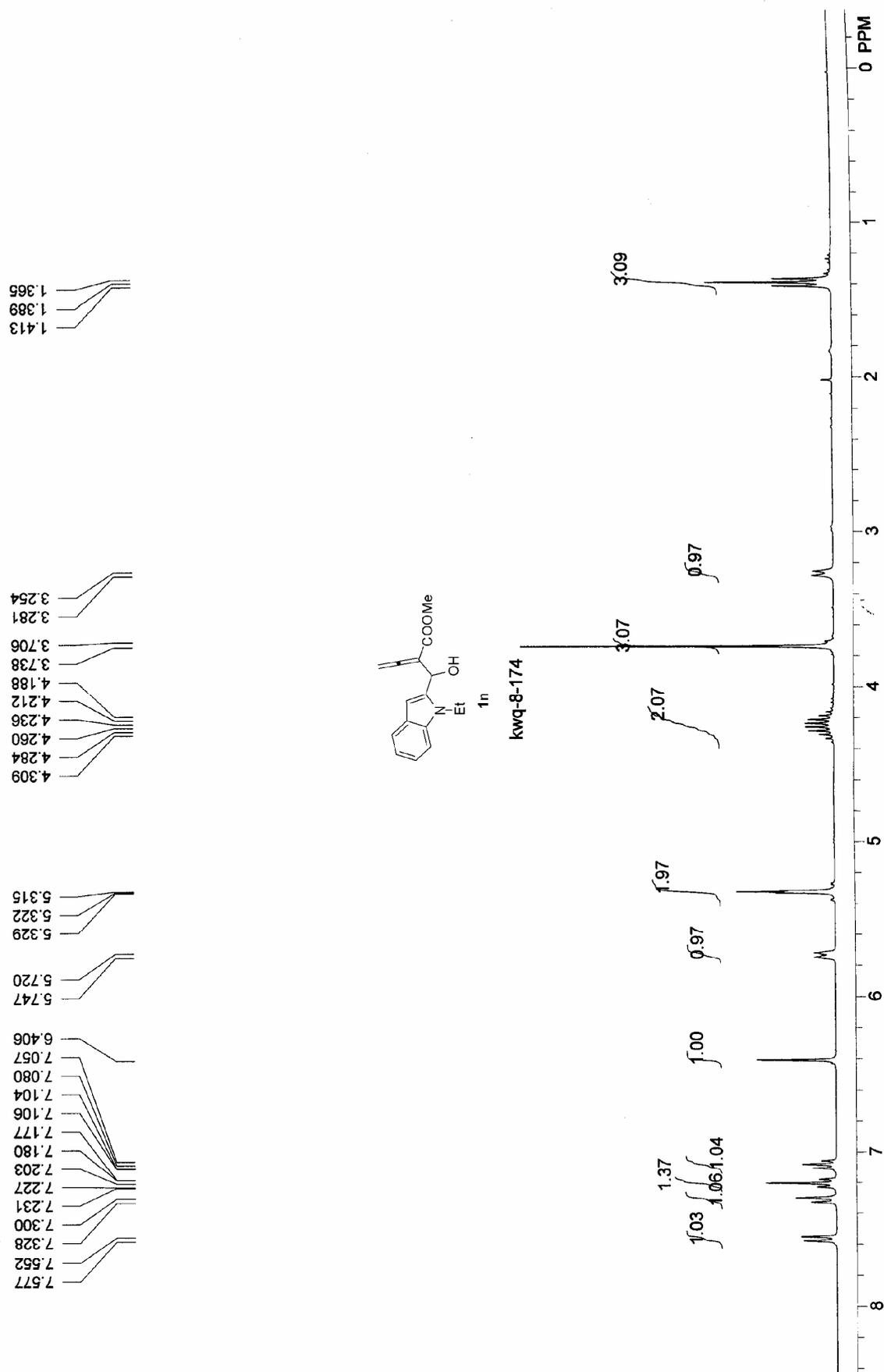


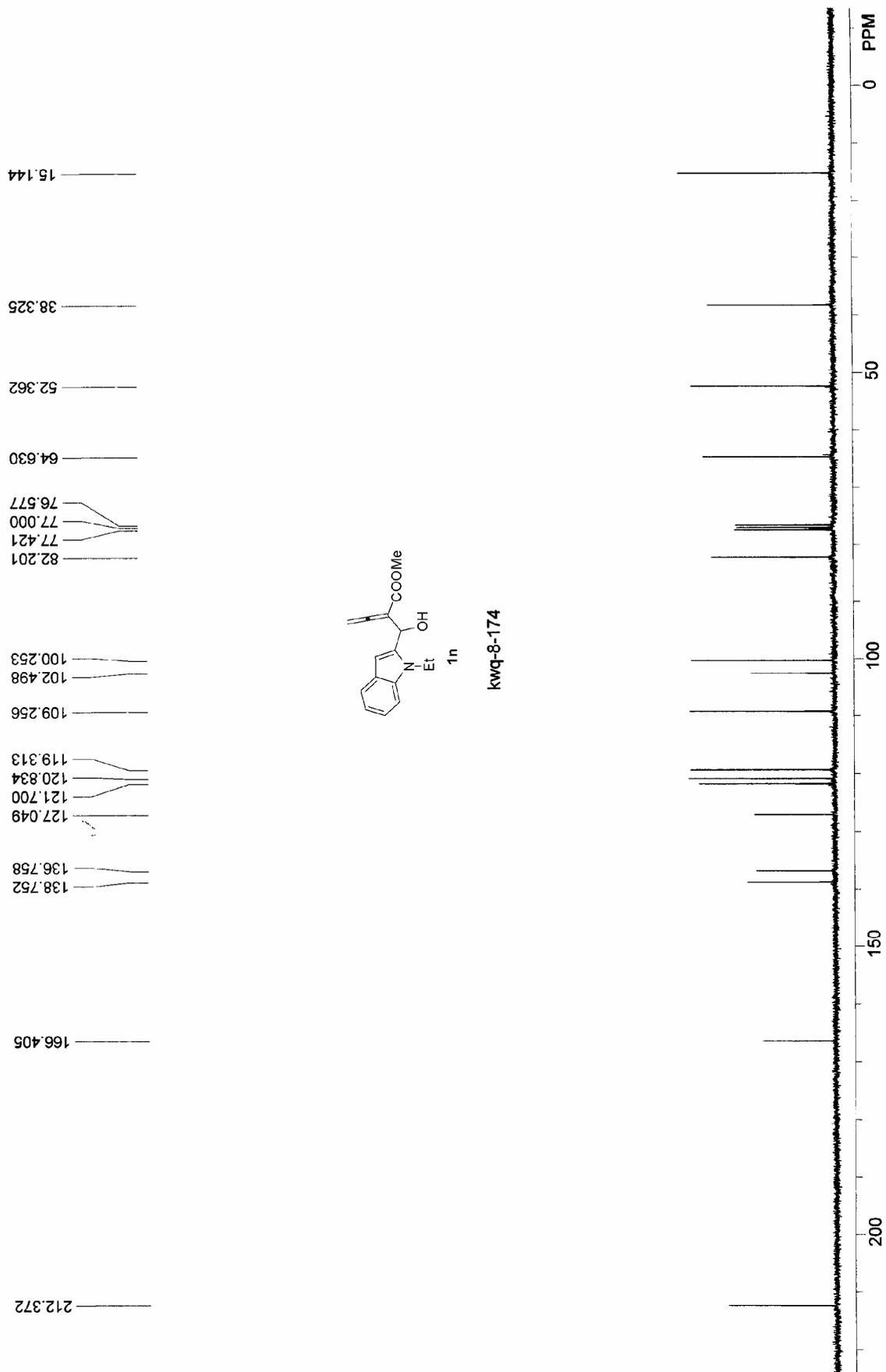


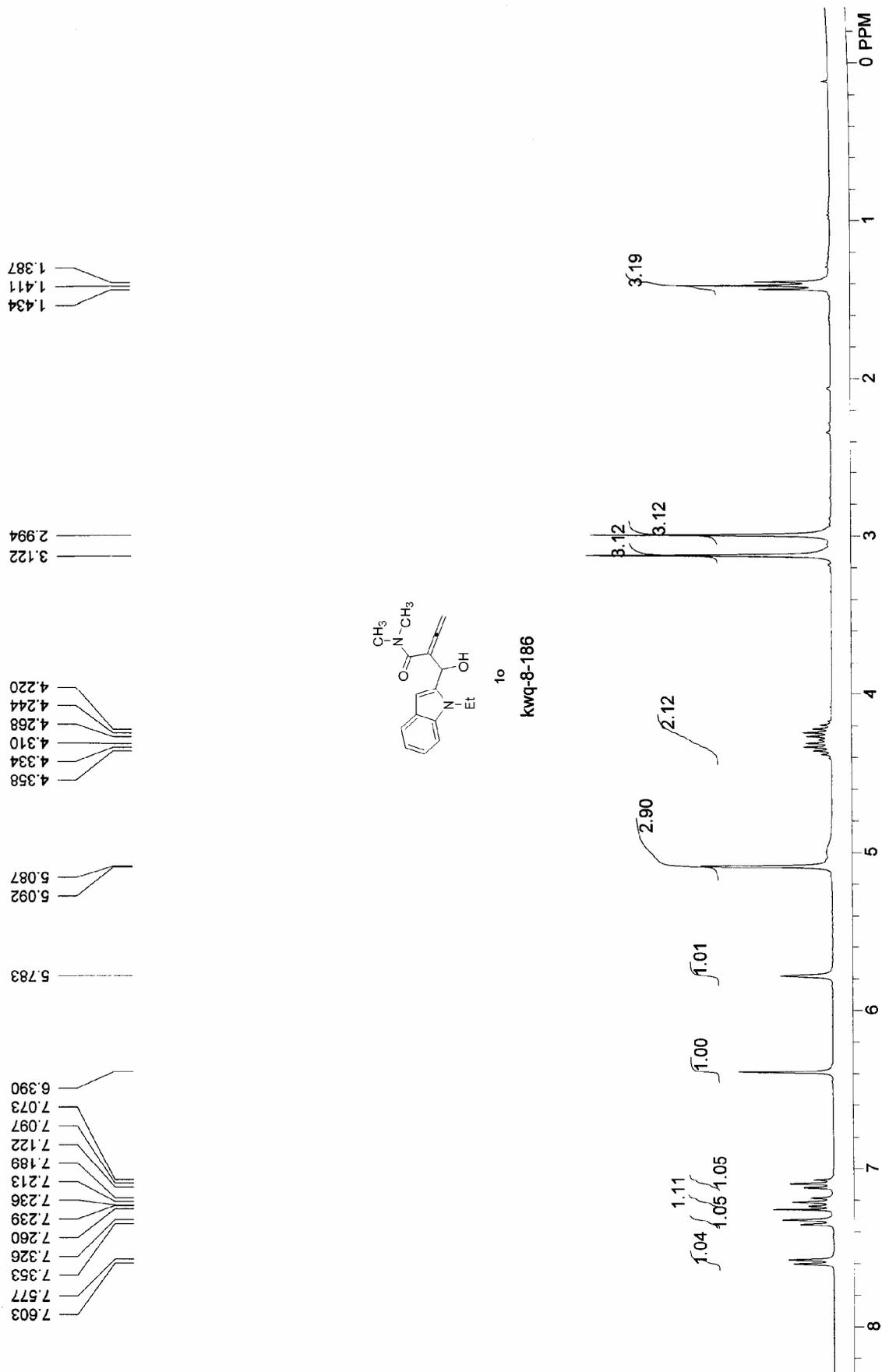


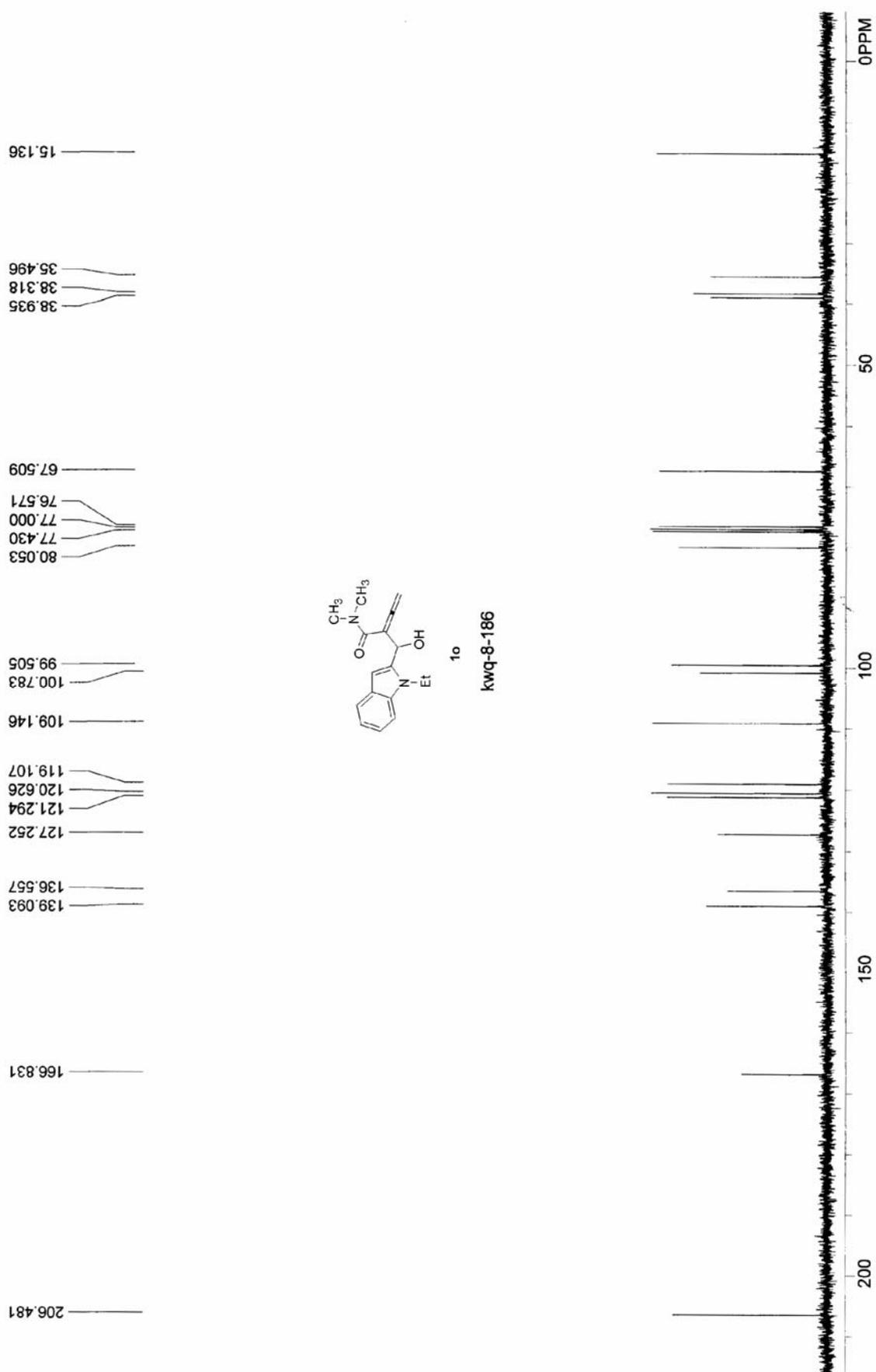


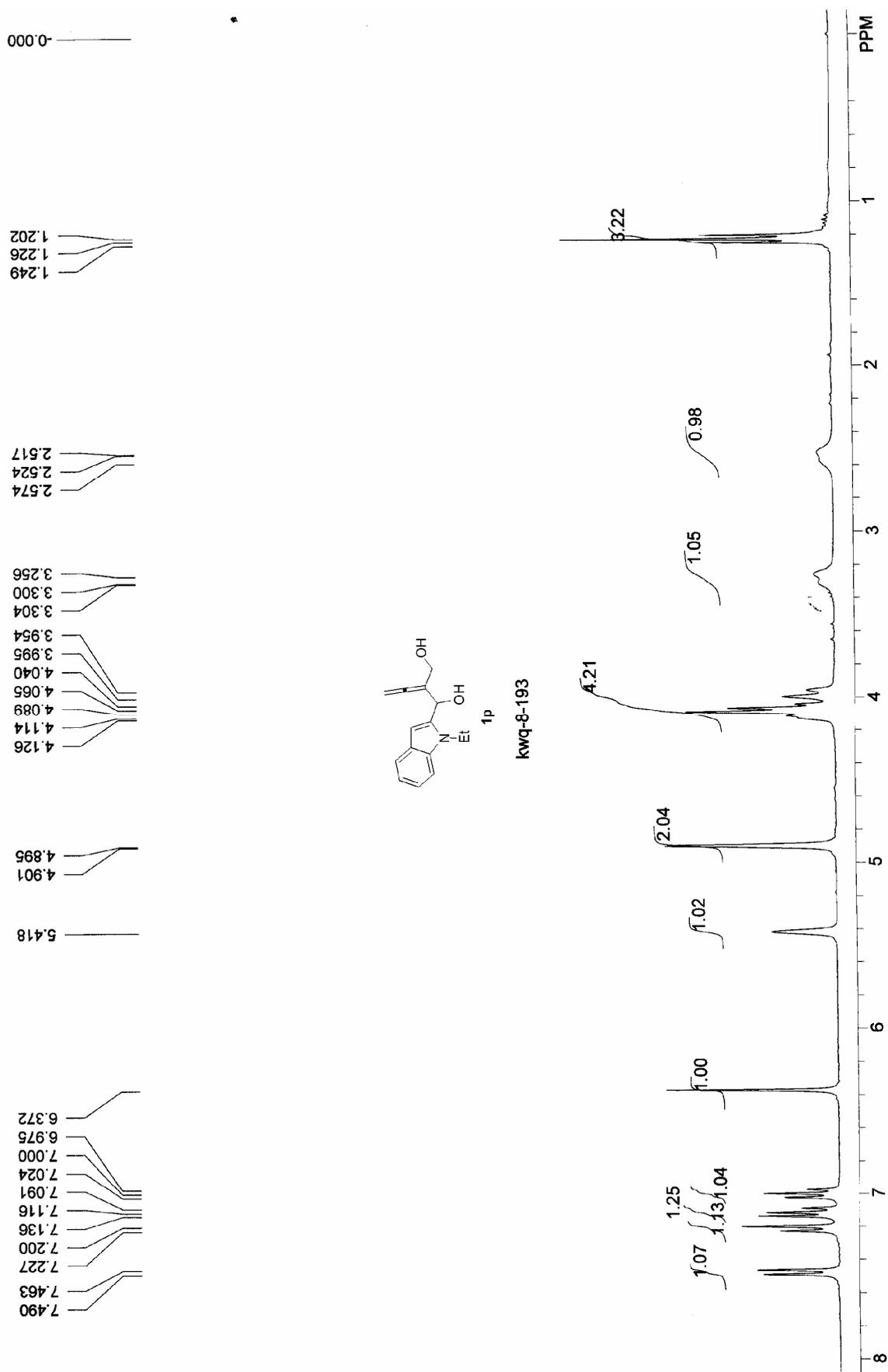


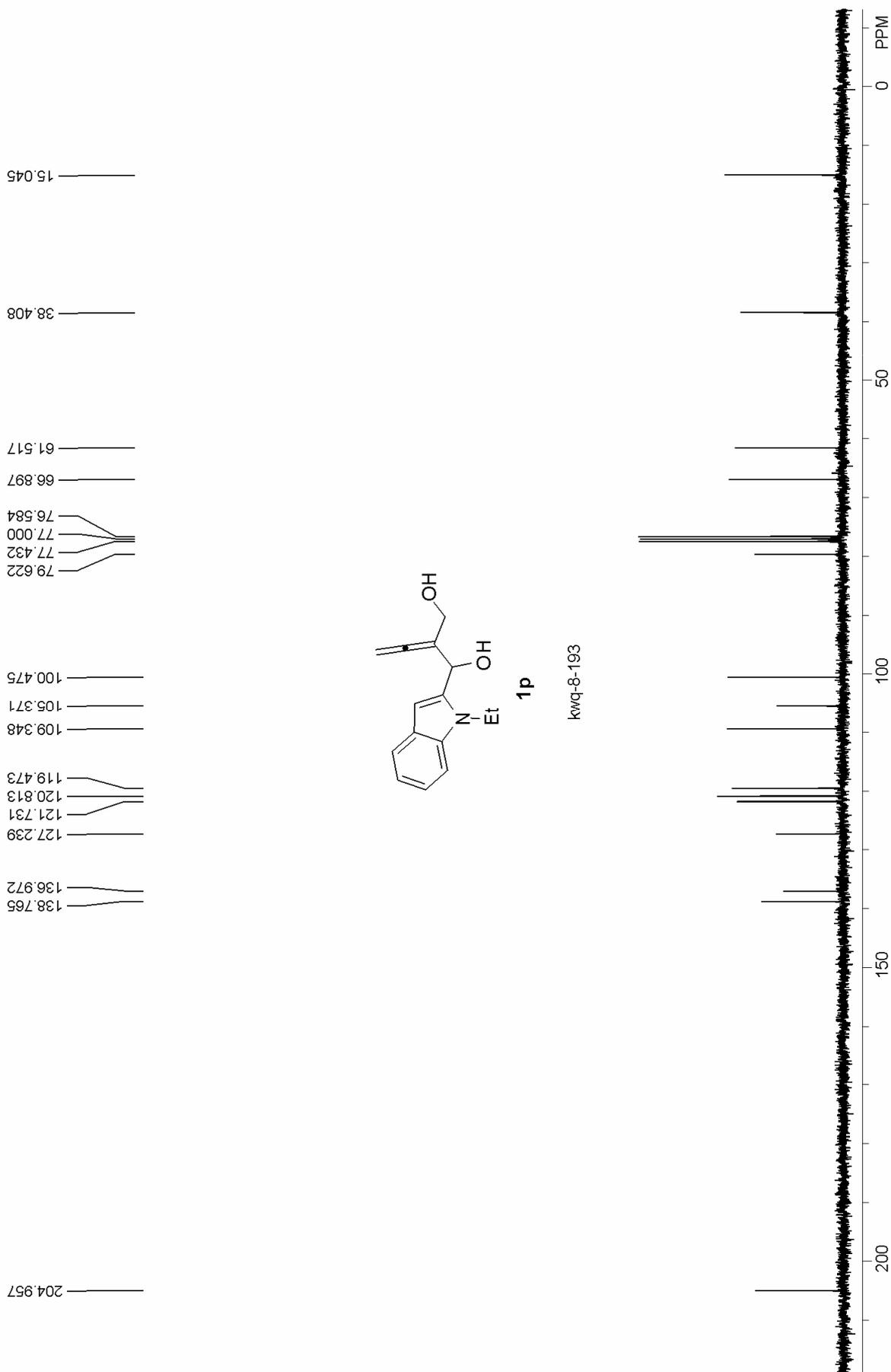


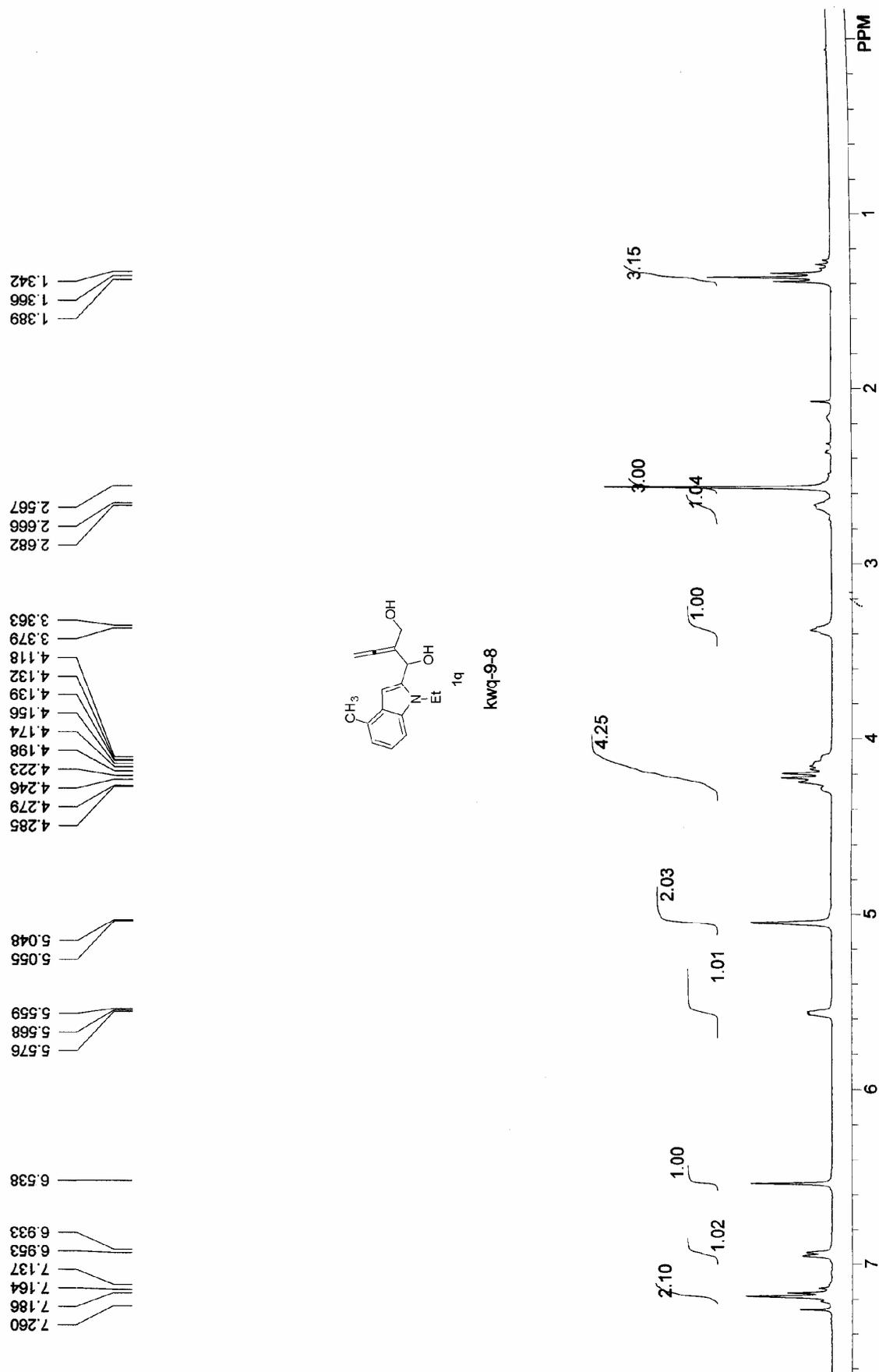


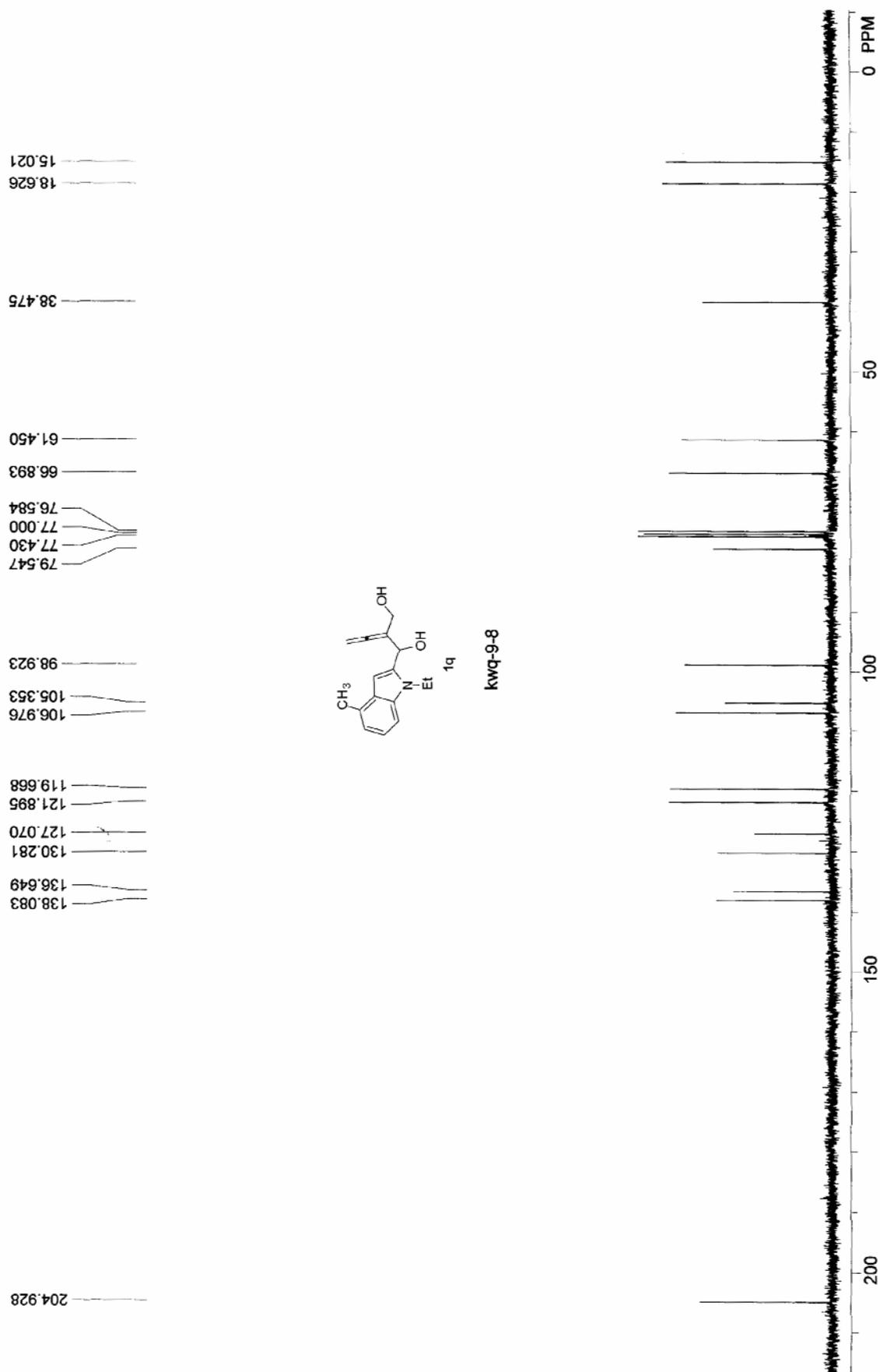


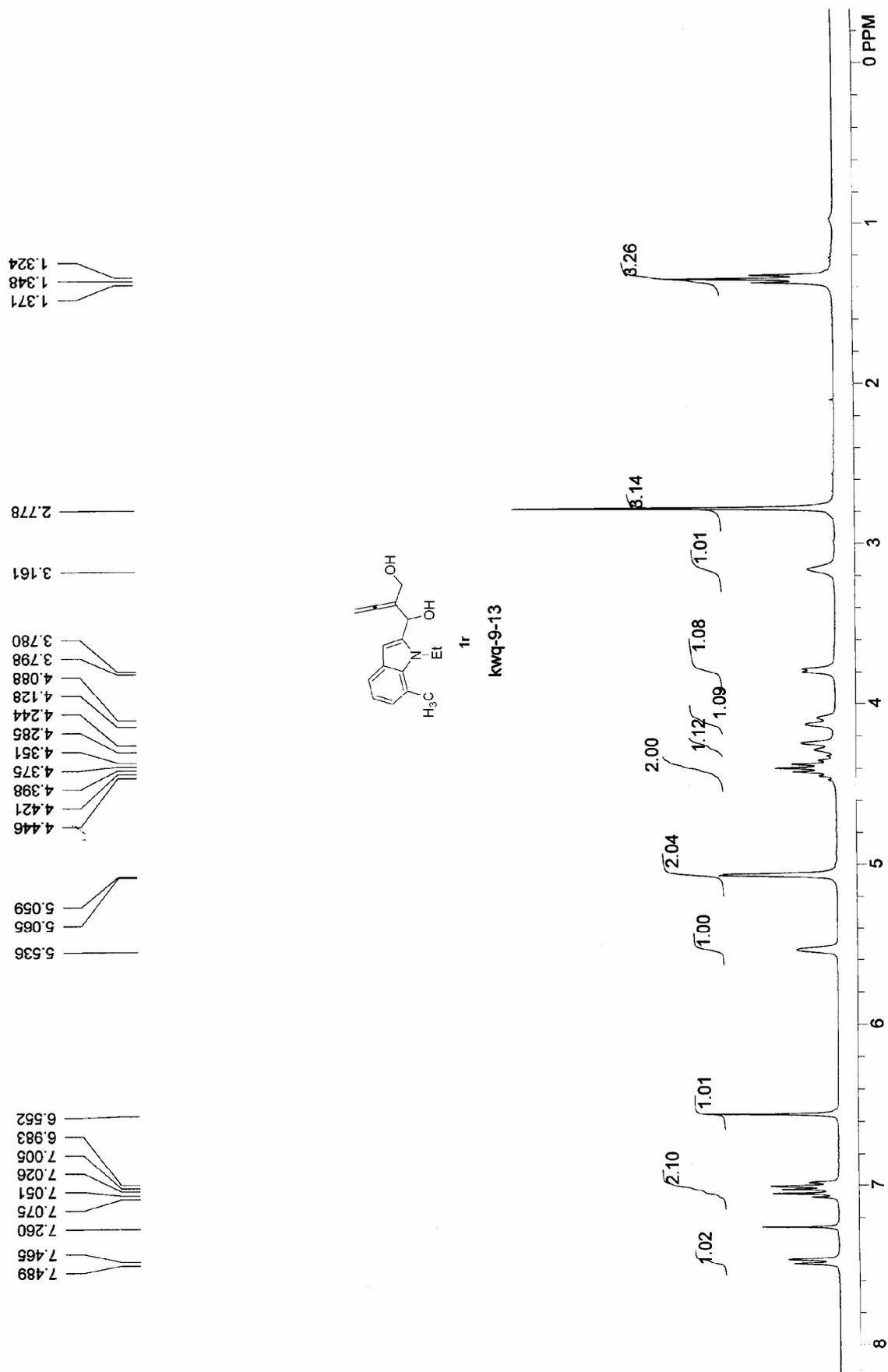


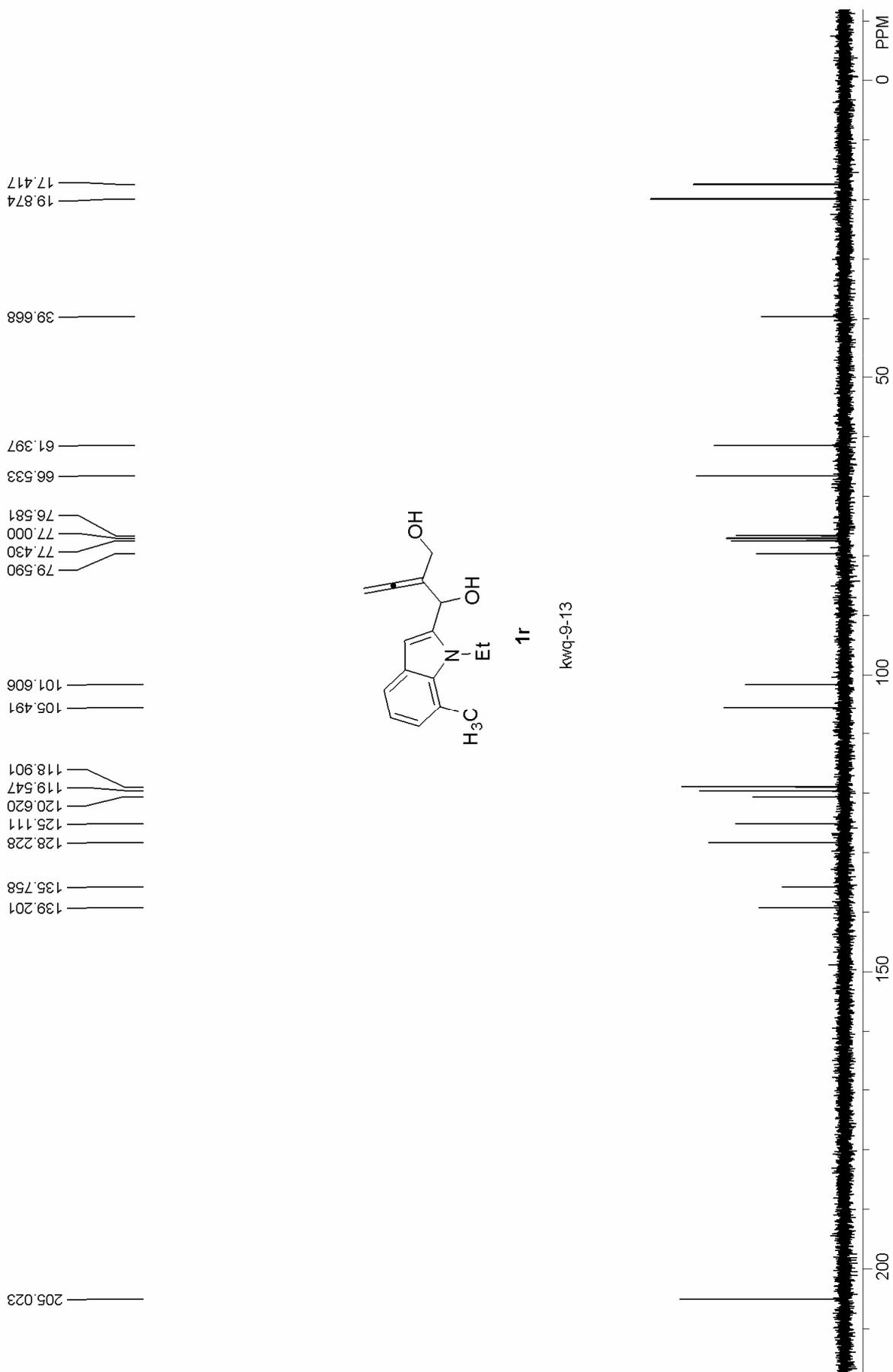




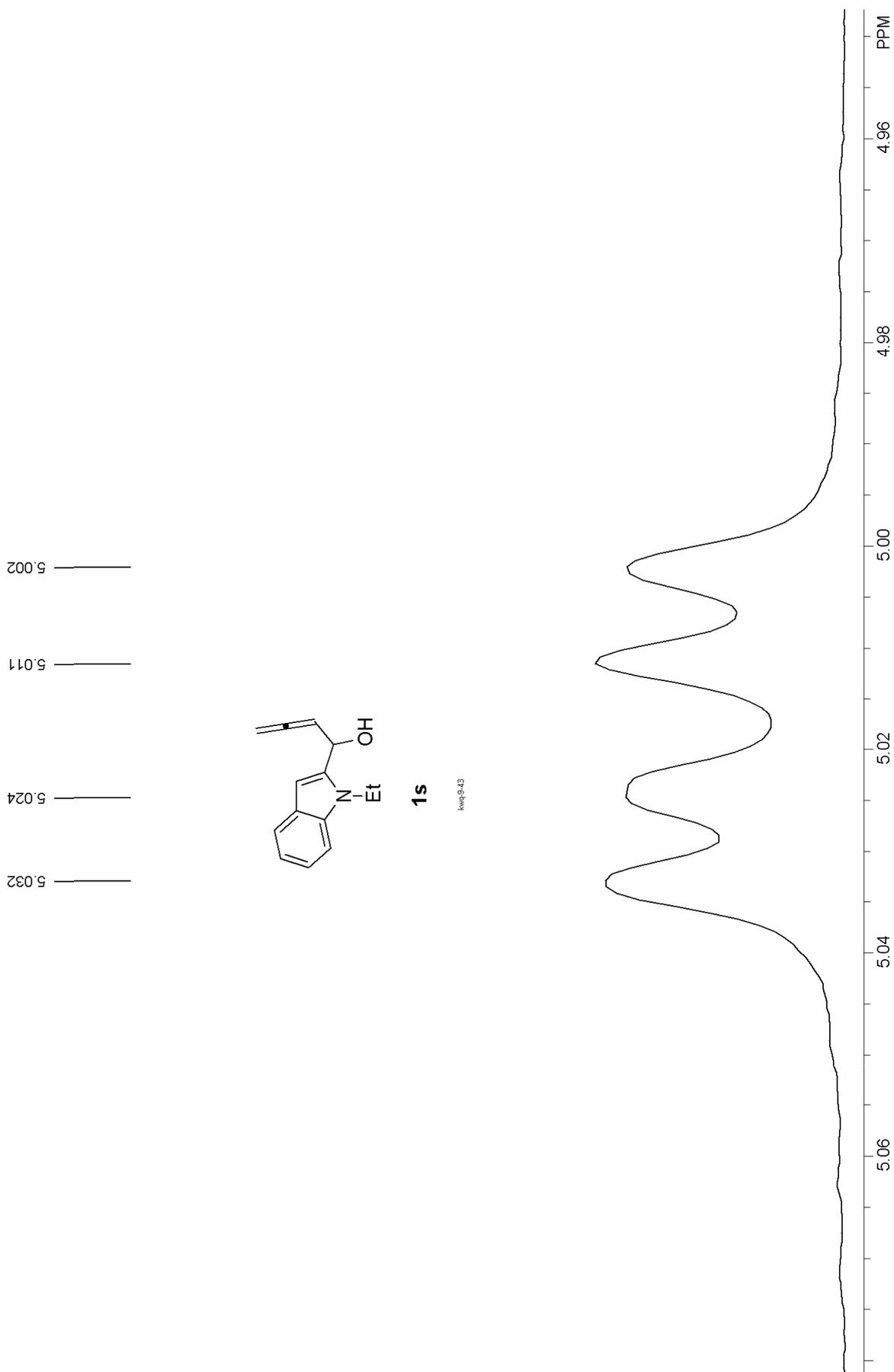


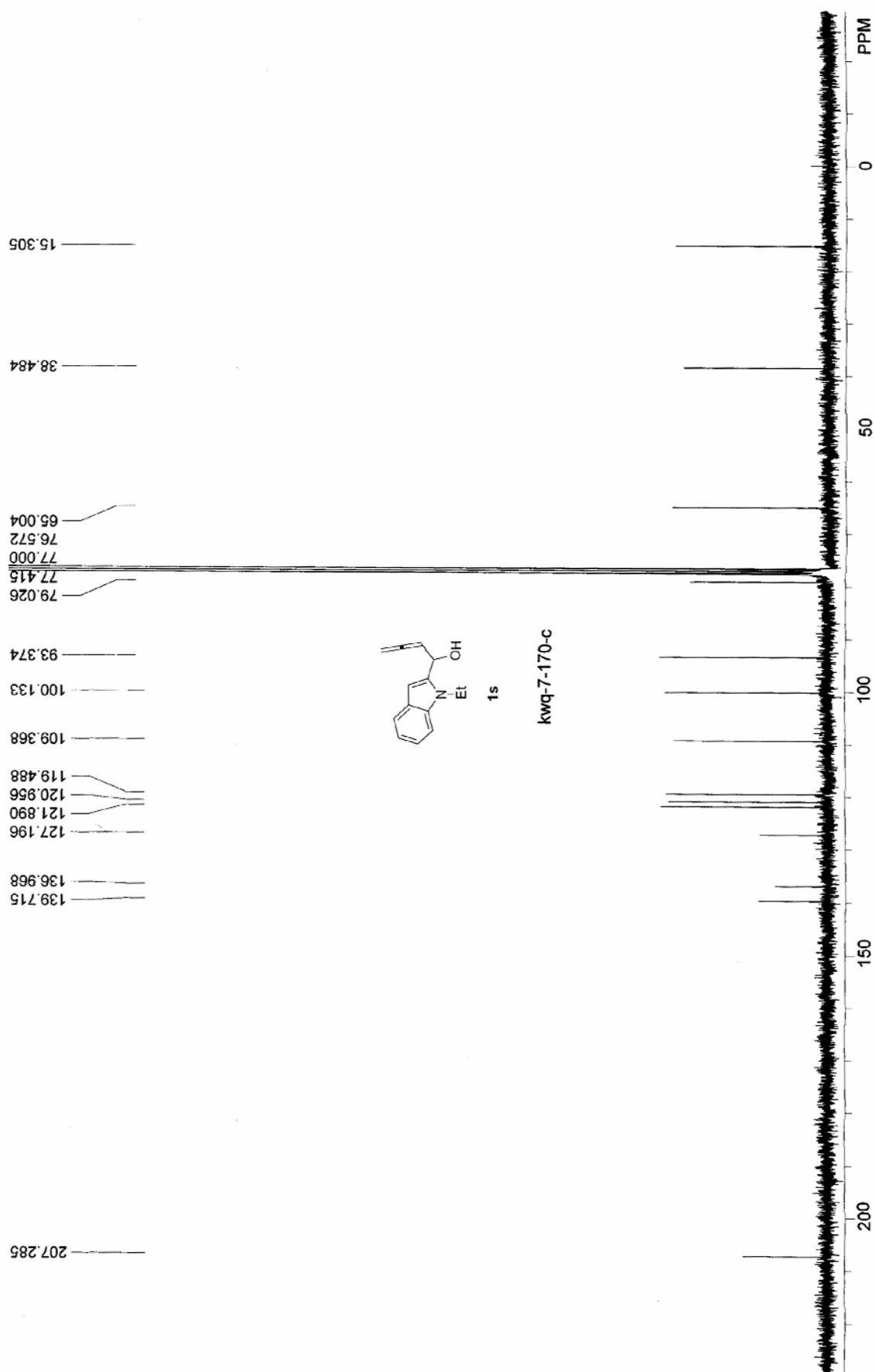


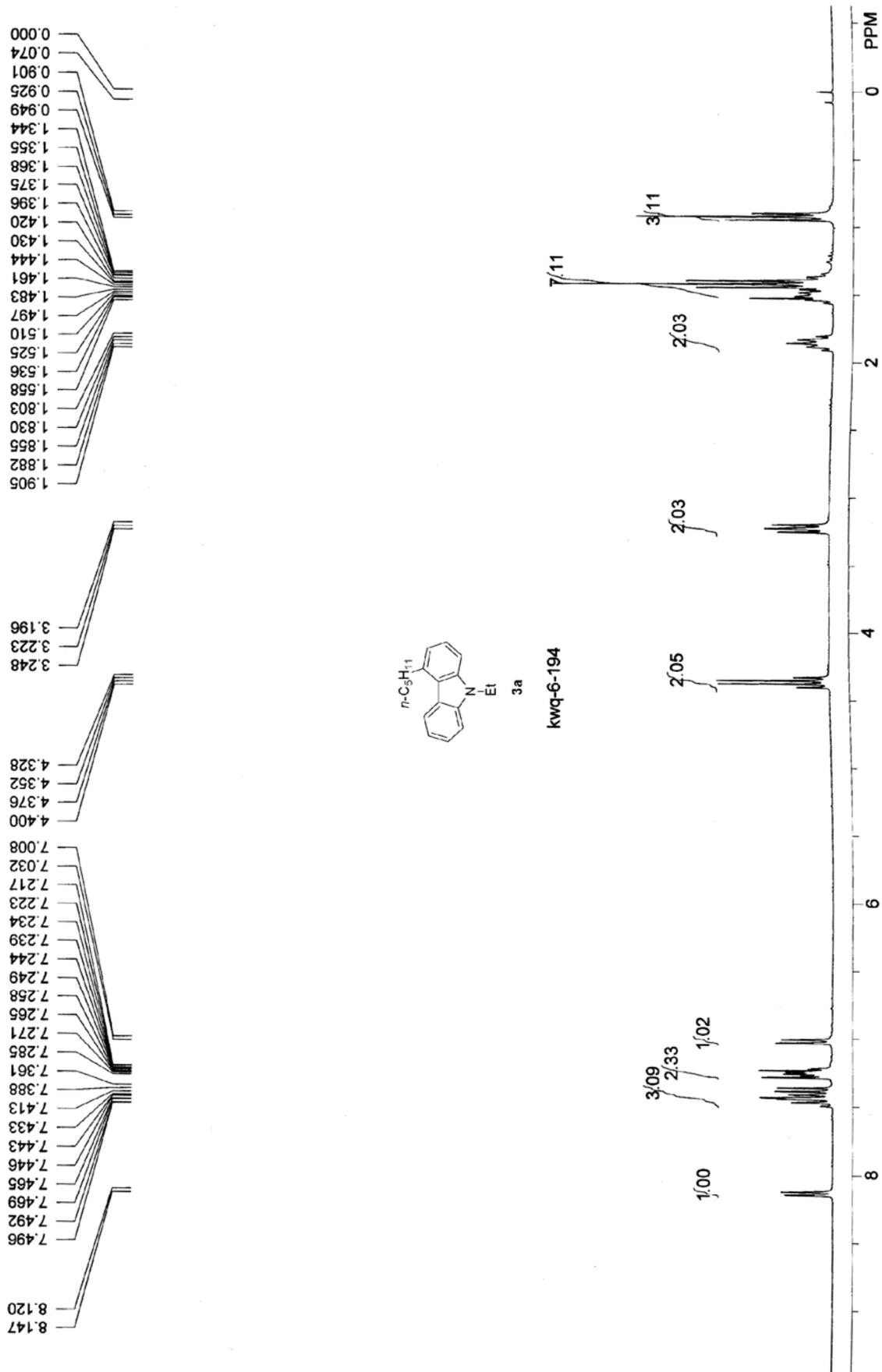


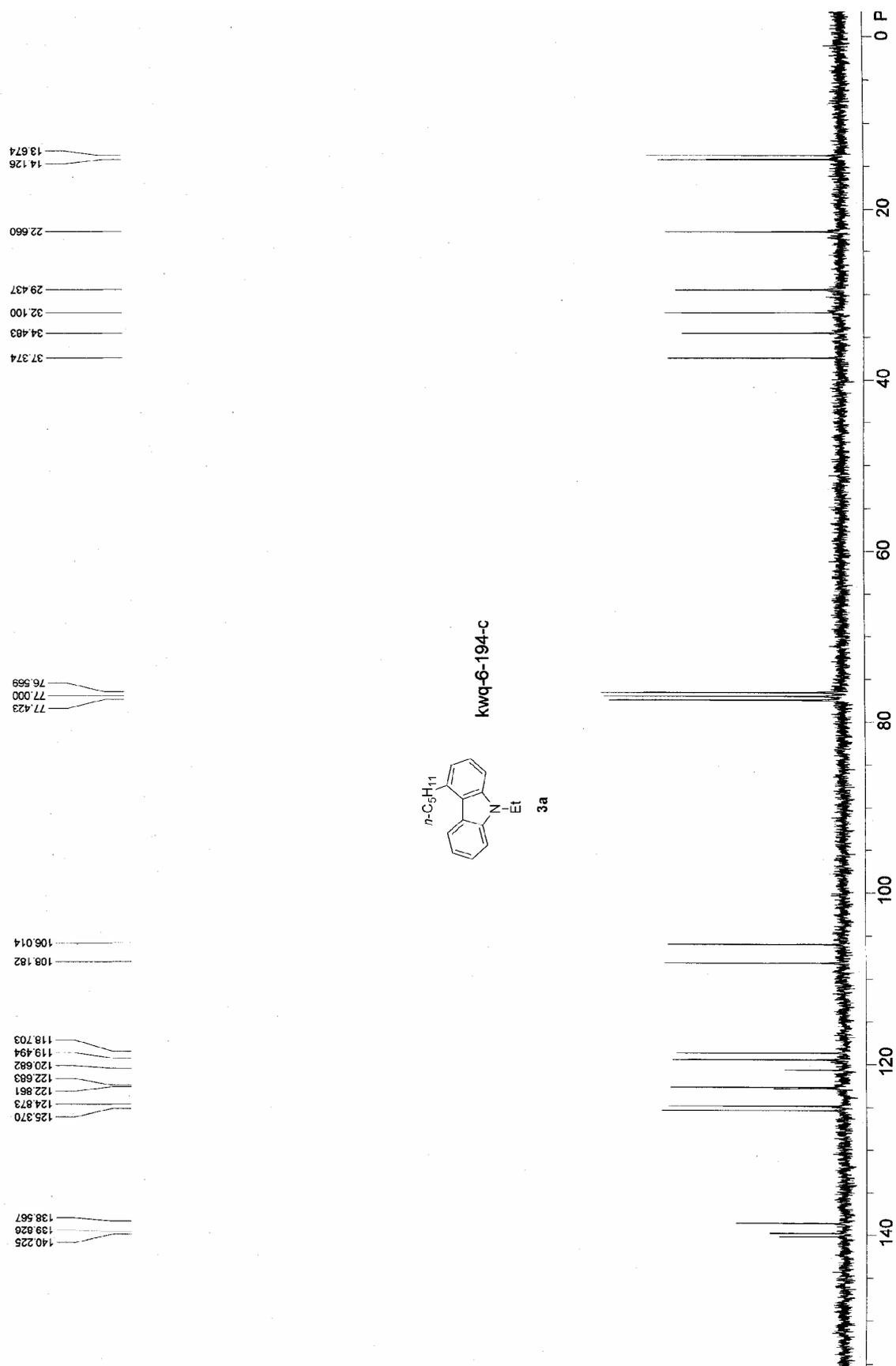


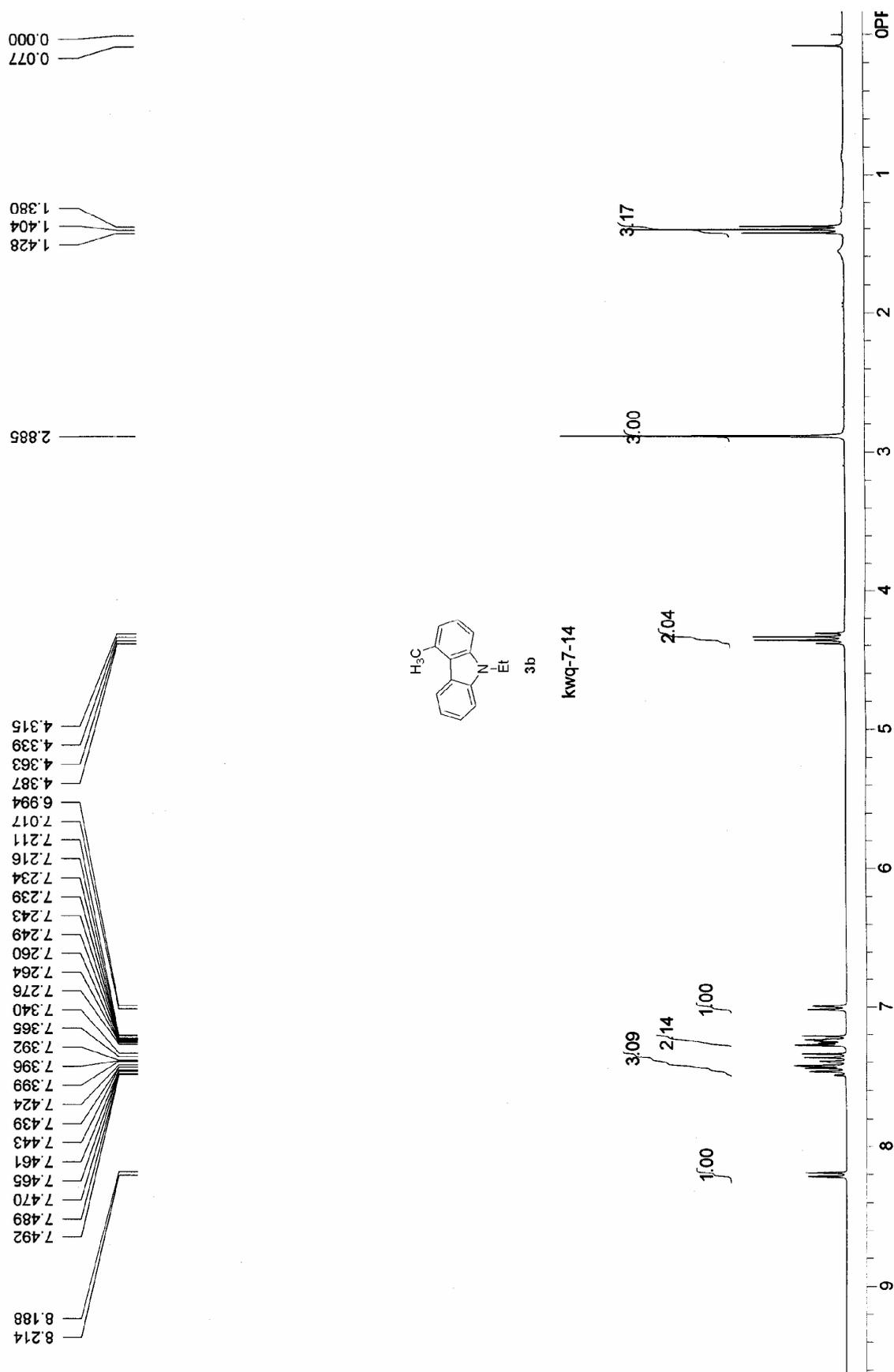


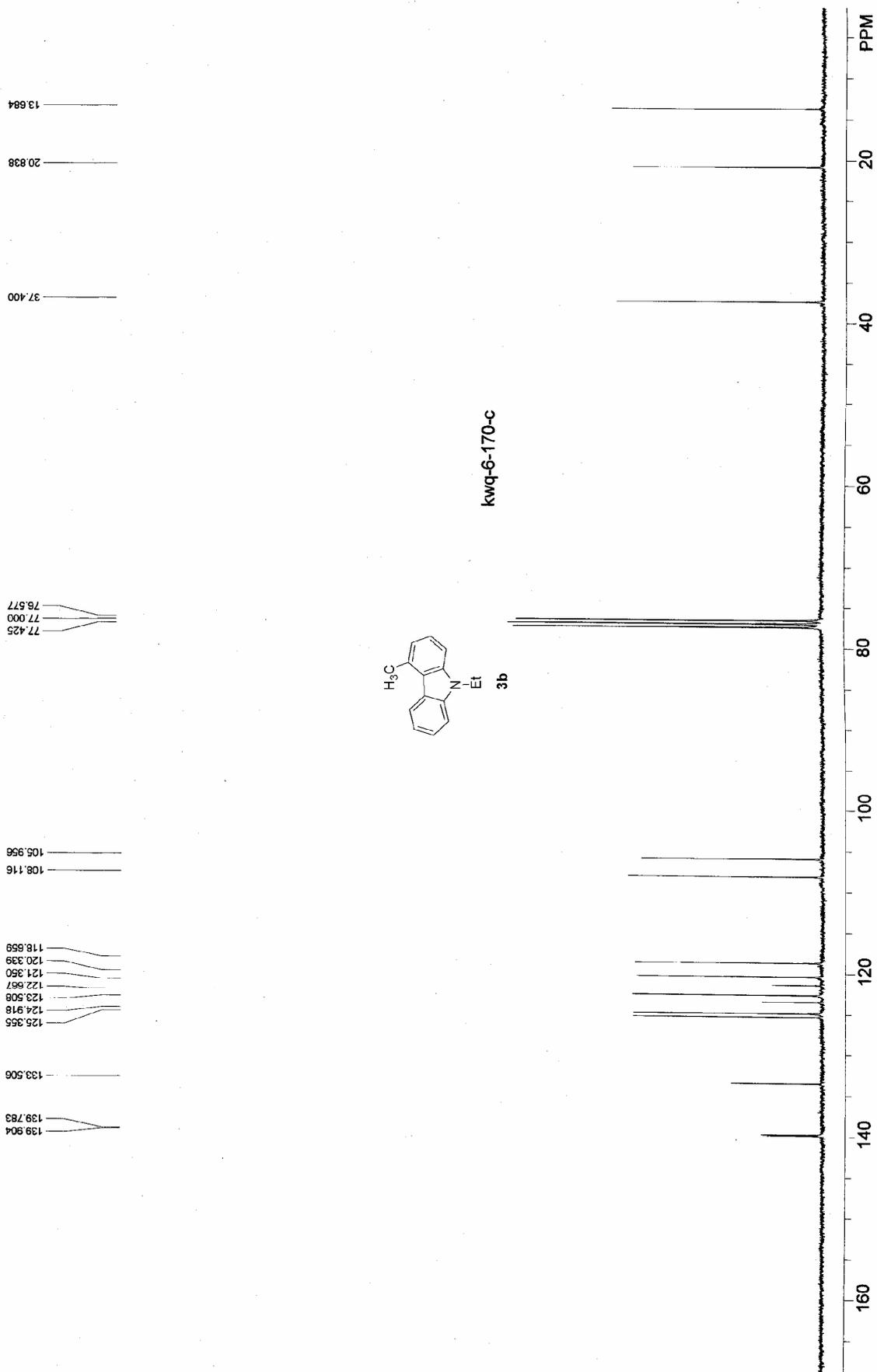


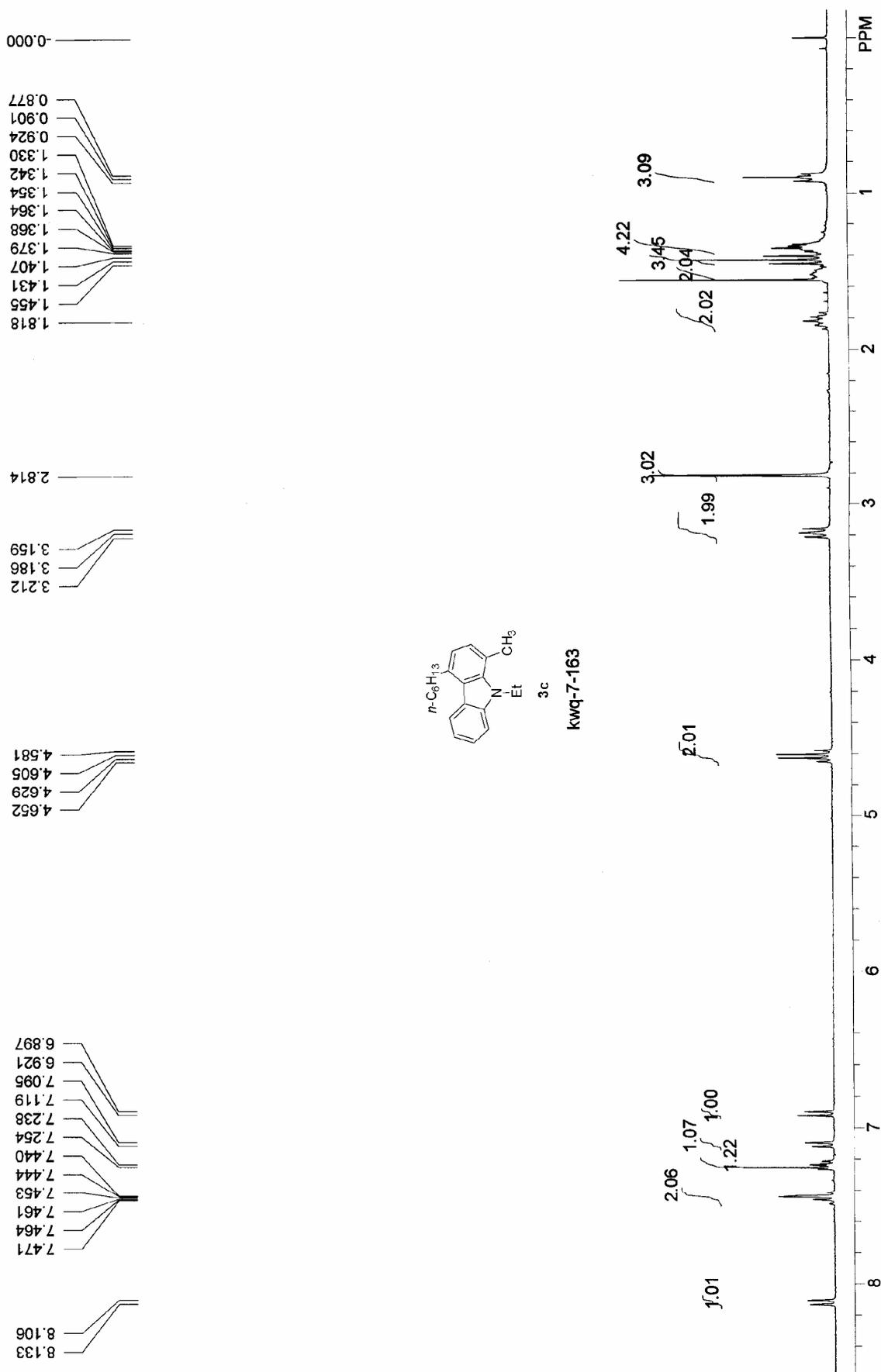


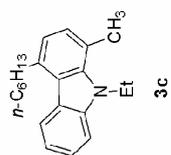
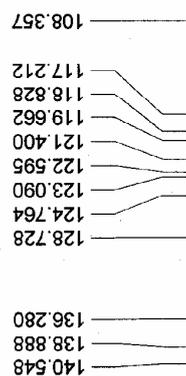
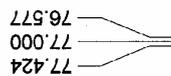
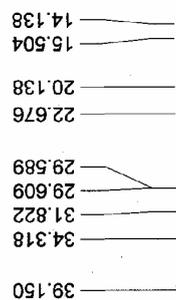












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