Sulfoxide-TFAA and Nucleophile Combination as New Reagent for Aliphatic C-H Functionalization at Indole 2α-position

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I. General

All melting points were measured on a Yanagimoto micro melting point apparatus, and are uncorrected. IR spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-AL300 (300 MHz) or a JEOL JMN-AL400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. J-Values are given in Hertz. Mass spectra were recorded on a JEOL JMS 700 instrument with a direct inlet system. Elemental analyses were obtained using a Yanaco MT-6 elemental analyzer. Column chromatography was carried out on a silica gel [Kanto Chemical Co. Inc. (Silica Gel 60N, Spherical, neutral 40-100 μm) or Merck Ltd. (Silica Gel 60, 230-400 mesh)]. PTLC was performed Merck silica gel plates ($60F_{254}$, 1 mm).

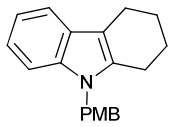
The following compounds have been prepared previously and characterized: **5f**,[1] **5g**,[1] **5j**,[2] **6b**[3] and **6u**[4].

II. Experimental Procedures and Characterization Data

General procedure for synthesis of **6**

Under nitrogen atmosphere, to a suspension of NaH in dry DMF was added starting material at 0 °C. After being stirred for time-1, tetrabutylammonium iodide and 4-methoxybenzyl chloride were added to the above reaction mixture, and stirred at room temperature for time-2. After the neutralization with saturated aqueous NH_4Cl, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was chromatographed on a column with *n*-hexane/AcOEt as an eluent to provide **6**.

9-(4-Methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**6d**)



6d

NaH (0.36 g, 60%, 9.0 mmol); DMF (30 mL); 1,2,3,4-Tetrahydrocarbazole (1.0 g, 5.8 mmol); Time-1 = 20 min; Tetrabutylammonium iodide (41 mg, 0.58 mmol); 4-Methoxybenzyl chloride (0.95 mL, 7.0 mmol); Time-2 = 2.5 h; **6d** (4.6 g, 90%).

Colorless oil.

IR ($CHCl_3$): 3007, 2934, 1512, 1466, 1246, 1223 cm^{-1}.

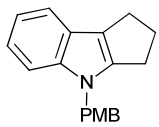
^1H NMR (400 MHz, $CDCl_3$): δ 1.82-1.94 (4H, m), 2.63 (2H, t, *J* = 6.0 Hz), 2.75 (2H, t, *J* = 6.0 Hz), 3.74 (3H, s), 5.17 (2H, s), 6.78 (2H, d, *J* = 8.6 Hz), 6.93 (2H, d, *J* = 8.6 Hz), 7.04-7.12 (2H, m), 7.22 (1H, m), 7.49 (1H, dd, *J* = 7.1, 2.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 22.3, 23.3, 23.4, 45.7, 55.2, 108.9, 109.7, 113.9, 117.6, 118.6, 120.5, 127.2, 127.3, 130.2, 135.3, 136.3, 158.5.

MS (EI): *m/z* (%) 291 (M^+, 58), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{20}H_{21}NO$: 291.1623; Found: 291.1623.

4-(4-Methoxybenzyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**6e**)



6e

NaH (0.39 g, 60%, 9.6 mmol); DMF (32 mL); 1,2,3,4-Tetrahydrocyclopenta[*b*]indole (1.0 g, 6.4 mmol). Time-1 = 15 min; Tetrabutylammonium iodide (45 mg, 0.64 mmol): 4-Methoxybenzyl chloride (1.0 mL, 7.7 mmol); Time-2 = 15 min; **6e** (1.5 g, 84%).

White powder.

Mp: 62-64 °C.

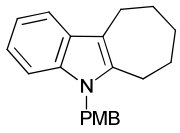
IR ($CHCl_3$): 3007, 2955, 2936, 1512, 1458, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 2.49 (2H, quint, *J* = 6.6 Hz), 2.73 (2H, t, *J* = 6.6 Hz), 2.85 (2H, t, *J* = 6.6 Hz), 3.72 (3H, s), 5.12 (2H, s), 6.66-6.83 (2H, m), 6.91-7.03 (2H, m), 7.03-7.12 (2H, m), 7.19 (1H, m), 7.42 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 25.3, 28.5, 47.8, 55.2, 109.7, 113.9, 118.0, 118.4, 118.9, 119.9, 124.4, 127.8, 129.9, 140.9, 145.9, 158.7.

Anal Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05; Found: C, 82.17; H, 7.04; N, 5.03.

5-(4-Methoxybenzyl)-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (**6f**)



6f

NaH (0.34 g, 60%, 8.6 mmol); DMF (28 mL); 5,6,7,8,9,10-Hexahydrocyclohepta[*b*]indole (1.1 g, 5.7 mmol); Time-1 = 10 min; Tetrabutylammonium iodide (42 mg, 0.57 mmol); 4-Methoxybenzyl chloride (0.80 mL, 5.7 mmol); Time-2 = 15 min; **6f** (1.4 g, 80%).

White needles.

Mp: 70-72 °C.

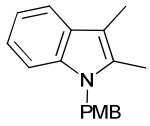
IR ($CHCl_3$): 3007, 2924, 1512, 1466, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (2H, quint, *J* = 5.4 Hz), 1.74 (2H, quint, *J* = 5.4 Hz), 1.83 (2H, quint, *J* = 5.4 Hz), 2.71 (2H, t, *J* = 5.6 Hz), 2.84 (2H, t, *J* = 5.6 Hz), 3.63 (3H, s), 5.13 (2H, s), 6.66-6.76 (2H, m), 6.76-6.86 (2H, m), 7.05 (2H, dd, *J* = 6.0, 3.2 Hz), 7.15 (1H, dt, *J* = 3.2, 6.0 Hz), 7.49 (1H, dt, *J* = 3.2, 6.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 26.5, 27.2, 28.5, 31.7, 45.7, 55.1, 108.9, 113.8, 113.9, 117.4, 118.6, 120.3, 126.8, 127.8, 130.3, 135.5, 138.6, 158.4.

Anal Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59; Found: C, 82.58; H, 7.74; N, 4.56.

1-(4-Methoxybenzyl)-2,3-dimethyl-1*H*-indole (**6g**)



6g

NaH (0.62 g, 60%, 15 mmol); DMF (50 mL); 2,3-Dimethylindole (1.5 g, 10 mmol); Time-1 = 10 min; Tetrabutylammonium iodide (0.37 g, 1.0 mmol); 4-Methoxybenzyl chloride (1.7 mL, 12 mmol); Time-2 = 10 min; **6g** (1.2 g, 44%).

Yellowish oil.

IR ($CHCl_3$): 3007, 2916, 1612, 1512, 1468, 1246, 1175 cm^{-1}.

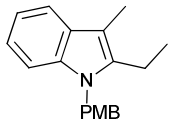
^1H NMR (300 MHz, $CDCl_3$): δ 2.260 (3H, s), 2.264 (3H, s), 3.71 (3H, s), 5.19 (2H, s), 6.64-6.80 (2H, m), 6.80-6.97 (2H, m), 7.02-7.13 (2H, m), 7.19 (1H, m), 7.51 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 9.0, 10.3, 46.0, 55.2, 106.8, 108.7, 114.0, 117.8, 118.6, 120.6, 127.0, 128.5, 130.2, 132.2, 136.2, 158.5.

MS (EI): *m/z* (%) 265 (M^+, 48), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{18}H_{19}NO$: 265.1467; Found: 265.1464.

2-Ethyl-1-(4-methoxybenzyl)-3-methyl-1*H*-indole (**6t**)



6t

NaH (0.72 g, 60%, 18 mmol); DMF (60 mL); 2-Ethyl-3-methyl-1*H*-indole (1.9 g, 12 mmol); Time-1 = 10 min; Tetrabutylammonium iodide (0.44 g, 1.2 mmol); 4-Methoxybenzyl chloride (1.9 mL, 14 mmol); Time-2 = 5 min; **6t** (2.5 g, 76%).

Colorless oil.

IR (CHCl3): 3005, 2968, 2934, 1512, 1468, 1246 cm^{-1}.

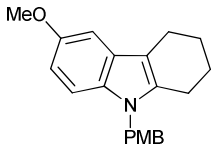
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (3H, t, *J* = 7.5 Hz), 2.29 (3H, s), 2.72 (2H, q, *J* = 7.5 Hz), 3.73 (3H, s), 5.25 (2H, s), 6.63-6.80 (2H, m), 6.80-6.96 (2H, m), 7.00-7.20 (3H, m), 7.50 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 8.7, 14.5, 17.8, 45.9, 55.2, 106.3, 109.1, 114.0, 118.0, 118.8, 120.8, 127.1, 128.7, 130.5, 136.3, 138.3, 158.7.

MS (EI): *m/z* (%) 279 (M^+, 45), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{19}H_{21}NO$: 279.1623; Found: 279.1621.

6-Methoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**6r**)



6r

NaH (0.24 g, 60%, 4.8 mmol); DMF (20 mL); 6-Methoxy-1,2,3,4-tetrahydro-*9H*-carbazole (0.80 g, 4.0 mmol); Time-1 = 15 min; Tetrabutylammonium iodide (0.15 g, 0.40 mmol); 4-Methoxybenzyl chloride (0.65 mL, 4.8 mmol); Time-2 = 5 min; **6r** (1.2 g, 90%).

Colorless oil.

IR (CHCl3): 3005, 2936, 1512, 1481, 1207 cm^{-1}.

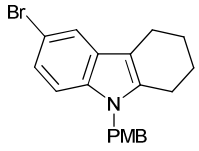
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74-2.02 (4H, m), 2.62 (2H, t, *J* = 5.9 Hz), 2.71 (2H, t, *J* = 5.9 Hz), 3.74 (3H, s), 3.84 (3H, s), 5.13 (2H, s), 6.73 (1H, dd, *J* = 8.8, 2.4 Hz), 6.74-6.84 (2H, m), 6.84-6.94 (2H, m), 6.96 (2H, d, *J* = 2.4 Hz), 7.08 (1H, d, *J* = 8.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 22.3, 23.2, 45.8, 55.2, 56.0, 100.2, 109.4, 109.6, 110.2, 114.0, 127.3, 127.7, 129.4, 130.4, 131.7, 136.3, 153.7, 158.7.

MS (EI): *m/z* (%) 321 (M^+, 83), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{21}H_{23}NO_2$: 321.1729; Found: 321.1730.

6-Bromo-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**6s**)



6s

NaH (0.32 g, 60%, 8.1 mmol); DMF (27 mL); 6-Bromo-1,2,3,4-tetrahydro-9*H*-carbazole (2.0 g, 5.4 mmol); Time-1 = 30 min; Tetrabutylammonium iodide (0.20 mg, 0.54 mmol); 4-Methoxybenzyl chloride (0.86 mL, 6.5 mmol); Time-2 = 65 min; **6s** (2.5 g, 92%).

Yellowish oil.

IR ($CHCl_3$): 3009, 2938, 2839, 1512, 1466, 1246, 1207 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.69-2.08 (4H, m), 2.62 (2H, t, J = 4.8 Hz), 2.69 (2H, t, J = 4.8 Hz), 3.75 (3H, s), 5.14 (2H, s), 6.70-6.84 (2H, m), 6.84-6.89 (2H, m), 7.05 (1H, d, J = 6.6 Hz), 7.15 (1H, dd, J = 6.6, 1.4 Hz), 7.59 (1H, d, J = 1.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 22.3, 23.16, 23.21, 45.9, 55.3, 109.5, 110.3, 112.0, 114.0, 120.3, 123.2, 127.2, 129.0, 129.6, 135.0, 136.8, 158.6.

MS (EI): *m/z* (%) 371 ([M^++2], 30), 369 (M^+, 30), 121 (100).

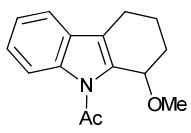
HRMS (EI): *m/z* Calcd for $C_{20}H_{20}BrNO$: 369.0728; Found: 369.0732.

General procedure for substitution reaction induced by acyloxythinoium species generated from sulfoxide (1.0 equiv.)/TFAA (1.0 equiv.)

Under argon atmosphere, to a solution of **6** and sulfoxide (1.0 equiv.) in CH_2Cl_2 (0.20 M) was added TFAA (1.0 equiv.). After being stirred for 10 or 90 min at -40 °C or r.t., MeOH (10.0 equiv.) was added to the above reaction mixture, and the reaction mixture was stirred for 10 min at same temperature. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$, then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with *n*-hexane/AcOEt as an eluent to give **7** and **8**.

For Table 1

9-Acetyl-1-methoxy-1,2,3,4-tetrahydro-9*H*-carbazole (**7a**)



7a

Entry 1: **6a** (0.10 g, 0.47 mmol); Diphenyl sulfoxide (95 mg, 0.47 mmol); CH_2Cl_2 (2.3 mL); TFAA (65 μL, 0.47 mmol); 90 min; MeOH (0.19 mL, 4.7 mmol); **7a** (10 mg, 9 %). (Recovery of **6a**, 87 mg, 87%)

Colorless oil.

IR ($CHCl_3$): 3007, 2943, 2824, 1730, 1456, 1443, 1375, 1364 cm^{-1}.

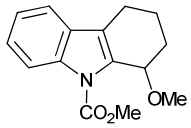
^1H NMR (300 MHz, $CDCl_3$): δ 1.71 (1H, tt, *J* = 13.2, 3.3 Hz), 1.80-2.20 (2H, m), 2.32 (1H, m), 2.57 (1H, ddd, *J* = 16.8, 10.8, 6.2 Hz), 2.83 (1H, m), 2.77 (3H, s), 3.46 (3H, s), 4.87 (1H, t, *J* = 3.3 Hz), 7.24 (1H, t, *J* = 7.5 Hz), 7.32 (1H, t, *J* = 7.5 Hz), 7.46 (1H, d, *J* = 7.5 Hz), 8.03 (1H, d, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 17.1, 21.1, 26.9, 53.4, 56.6, 70.9, 115.8, 118.6, 120.6, 122.7, 124.9, 129.0, 133.8, 136.2, 152.1.

MS (EI): *m/z* (%) 243 (M^+, 1), 211 (43), 170 (12), 169 (70), 168 (100), 167 (47).

HRMS (EI): *m/z* Calcd for $C_{15}H_{17}NO_3$: 243.1259; Found: 243.1263.

9-Methoxycarbonyl-1-methoxy-1,2,3,4-tetrahydro-9*H*-carbazole (**7b**)



7b

Entry 2: **6b** (97 mg, 0.42 mmol); Diphenyl sulfoxide (86 mg, 0.42 mmol); CH_2Cl_2 (2.1 mL); TFAA (59 μL, 0.42 mmol); 90 min; MeOH (0.17 mL, 4.2 mmol); **7b** (22 mg, 20 %). (Recovery of **6b**, 69 mg, 71%)

Yellowish oil.

IR ($CHCl_3$): 3007, 2943, 1695, 1371, 1308 cm^{-1}.

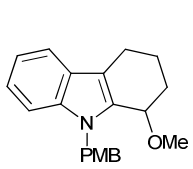
^1H NMR (300 MHz, $CDCl_3$): δ 1.72 (1H, tt, *J* = 13.9, 3.3 Hz), 1.78-2.20 (2H, m), 2.32 (1H, ddt, *J* = 13.9, 4.8, 3.3 Hz), 2.57 (1H, ddd, *J* = 17.4, 12.1, 6.0 Hz), 2.81 (1H, ddd, *J* = 17.4, 5.3, 1.6 Hz), 3.48 (3H, s), 4.05 (3H, s), 4.90 (1H, t, *J* = 3.3 Hz), 7.24 (1H, dt, *J* = 1.0, 7.2 Hz), 7.30 (1H, ddd, *J* = 8.4, 7.2, 1.3 Hz), 7.46 (1H, ddd, *J* = 7.2, 1.3, 0.8 Hz), 8.03 (1H, dt, *J* = 8.4, 0.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 21.4, 26.5, 26.9, 60.0, 71.2, 115.6, 118.8, 121.4, 122.8, 125.1, 129.2, 133.8, 136.3, 169.6.

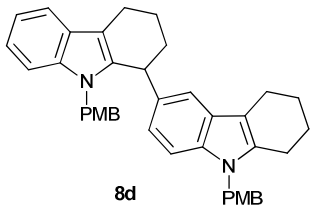
MS (EI): *m/z* (%) 259 (M^+, 2), 228 (23), 227 (100), 266 (15), 194 (16), 168 (37), 167 (56), 106 (27).

HRMS (EI): *m/z* Calcd for $C_{15}H_{17}NO_2$: 259.1208; Found: 259.1212.

1-Methoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7d**) and Dimer **8d**



7d



8d

Entry 4: **6d** (0.12 g, 0.42 mmol); Diphenyl sulfoxide (85 mg, 0.42 mmol); CH_2Cl_2 (2.1 mL); TFAA (58 μL, 0.42 mmo); 10 min; MeOH (0.17 mL, 4.2 mmol); **7d** (44 mg, 32 %); **8d** (40 mg, 33 %).

7d: Colorless oil.

IR ($CHCl_3$): 3007, 2940, 1512, 1464, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.70-1.82 (2H, m), 1.95 (1H, m), 2.17 (1H, m), 2.61 (1H, ddd, *J* = 15.6, 10.1, 5.1 Hz), 2.84 (1H, dt, *J* = 3.8, 15.6 Hz), 3.33 (3H, s), 3.65 (3H, s), 4.34 (1H, t, *J* = 3.8 Hz), 5.24 (2H, s), 6.66-6.80 (2H, m), 6.89-7.00 (2H, m), 7.01-7.11 (2H, m), 7.17 (1H, d, *J* = 8.0 Hz), 7.51 (1H, d, *J* = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 21.3, 27.2, 46.2, 55.0, 55.6, 70.7, 109.4, 112.7, 113.7, 118.61, 118.62, 121.8, 126.4, 127.3, 130.3, 133.6, 136.9, 158.3.

MS (EI): *m/z* (%) 321 (M^+, 3), 290 (10), 289 (42), 287 (13), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{21}H_{23}NO_2$: 321.1729; Found: 321.1730.

8d: Yellowish amorphous.

IR ($CHCl_3$): 3003, 2936, 2837, 1512, 1462, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.12-1.34 (2H, m), 1.48 (1H, m), 1.70-1.97 (5H, m), 2.10 (1H, m), 2.45-2.77 (5H, m), 3.70 (3H, s), 3.72 (3H, s), 4.50 (1H, d, *J* = 16.1 Hz), 4.63 (1H, d, *J* = 16.1 Hz), 4.75 (1H, t, *J* = 3.8 Hz), 4.96 (1H, d, *J* = 16.1 Hz), 5.10 (1H, d, *J* = 16.1 Hz), 6.39 (1H, d, *J* = 7.8 Hz), 6.66 (1H, d, *J* = 7.8 Hz), 6.68-6.72 (2H, m), 6.72-6.82 (2H, m), 6.82-6.93 (2H, m), 6.94 (1H, t, *J* = 7.8 Hz), 7.10-7.25 (2H, m), 7.25-7.32 (2H, m), 7.35 (1H, d, *J* = 7.8 Hz), 7.39 (1H, d, *J* = 7.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 21.3, 22.3, 22.5, 23.3, 23.4, 33.5, 45.9, 46.7, 51.5, 55.3, 93.0, 105.6, 107.9, 109.4, 113.8, 113.9, 117.30, 117.33, 118.1, 122.6, 125.2, 127.1, 127.75, 127.83, 130.1, 130.4, 135.2, 136.3, 136.9, 137.7, 147.0, 150.1, 158.4, 158.48, 158.49.

MS (EI): *m/z* (%) 580 (M^+, 42), 461 (13), 460 (37), 289 (23), 121 (100).

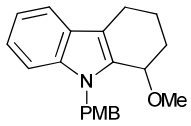
HRMS (EI): *m/z* Calcd for $C_{40}H_{40}N_2O_2$: 580.3090; Found: 580.3089.

General procedure for substitution reaction induced by acyloxythionium species generated from sulfoxide (3.0 equiv.)/TFAA (3.0 equiv.).

Under argon atmosphere, to a solution of **6** and sulfoxide (3.0 equiv.) in CH_2Cl_2 (0.20 M) was added TFAA (3.0 equiv.). After being stirred at -40 °C for 10 min, MeOH (10.0 equiv.) was added to the above reaction mixture, and the mixture was stirred at same temperature for 10 min. The resulting mixture was neutralized with saturated aqueous $NaHCO_3$, then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with *n*-hexane/AcOEt as an eluent to give **7**.

For Table 3

1-Methoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7d**)

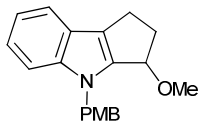


7d

Entry 3: **6d** (0.11 g, 0.39 mmol); Di(*p*-tolyl) sulfoxide (0.27 g, 1.2 mmol); CH_2Cl_2 (2.0 mL); TFAA (0.16 mL, 1.2 mmol); MeOH (0.16 mL, 3.9 mmol); **7d** (0.12 g, 93%).

For Table 4

3-Methoxy-4-(4-methoxybenzyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**7e**)



7e

Entry 1: **6e** (65 mg, 0.23 mmol); Di(*p*-tolyl) sulfoxide (0.16 g, 0.70 mmol); CH_2Cl_2 (1.2 mL); TFAA (98 μL, 0.70 mmol); MeOH (95 μL, 2.3 mmol); **7e** (52 mg, 72%).

Purplish oil.

IR ($CHCl_3$): 3007, 2936, 1512, 1462, 1246 cm^{-1}.

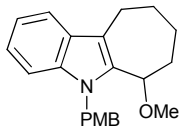
^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (1H, m), 2.63-2.85 (2H, m), 2.99 (1H, m), 3.23 (3H, s), 3.71 (3H, s), 4.93 (1H, t, J = 3.9 Hz), 5.17 (1H, d, J = 15.6 Hz), 5,27 (1H, d, J = 15.6 Hz), 6.70-6.85 (2H, m), 7.00-7.17 (4H, m), 7.22 (1H, d, J = 7.6 Hz), 7.49 (1H, d, J = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 35.1, 47.4, 54.5, 55.2, 110.2, 113.8, 113.9, 119.0, 119.5, 121.3, 121.5, 123.7, 128.0, 130.0, 141.7, 143.0, 158.6.

MS (EI): *m/z* (%) 307 (M^+, 3), 276 (11), 275(50), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{20}H_{21}NO_2$: 307.1572; Found: 307.1575.

6-Methoxy-5-(4-methoxybenzyl)-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (**7f**)



7f

Entry 2: **6f** (74 mg, 0.24 mmol); Di (*p*-tolyl) sulfoxide (0.17 mg, 0.72 mmol); CH_2Cl_2 (1.2 mL); TFAA (0.10 mL, 0.72 mmol); MeOH (98 μL, 2.4 mmol); **7f** (46 mg, 57%).

Colorless oil.

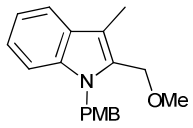
IR ($CHCl_3$): 3005, 2930, 1512, 1466, 1248 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.56-1.80 (3H, m), 1.98-2.10 (2H, m), 2.28 (1H, m), 2.81-3.02 (2H, m), 3.22 (3H, s), 3.74 (3H, s), 4.55 (1H, dd, *J* = 6.0, 2.1 Hz), 5.30 (1H, d, *J* = 17.0 Hz), 5.37 (1H, d, *J* = 17.0 Hz), 6.66-6.84 (2H, m), 6.84-7.00 (2H, m), 7.08 (1H, dt, *J* = 1.3. 7.0 Hz), 7.14 (1H, dt, *J* = 1.3, 7.0 Hz), 7.22 (1H, d, *J* = 7.0 Hz), 7.56 (1H, d, *J* = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 23.4, 23.6, 28.3, 29.8, 46.1, 55.3, 55.8, 73.5, 109.4, 113.9, 116.2, 118.6, 118.9, 121.6, 127.0, 127.4, 130.3, 136.0, 136.2, 158.5.

HRMS (FAB): *m/z* Calcd for $C_{22}H_{25}NO_2$: 335.1885; Found: 335.1885.

1-(4-Methoxybenzyl)-2-(methoxymethyl)-3-methyl-1*H*-indole (**7g**)



7g

Entry 3: **6g** (0.11 g, 0.41 mmol); Di(*p*-tolyl) sulfoxide (0.28 g, 1.2 mmol); CH_2Cl_2 (2.1 mL); TFAA (0.17 mL, 1.2 mmol); MeOH (0.17 mL, 4.1 mmol); **7g** (35 mg, 29%). (Recovery of **6g** 13 mg, 12%)

Yellowish oil.

IR ($CHCl_3$): 3007, 2930, 1512, 1466, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (3H, s), 3.28 (3H, s), 3.72 (3H, s), 4.52 (2H, s), 5.34 (2H, s), 6.60-6.84 (2H, m), 6.84-7.00 (2H, m), 7.09 (1H, dt, *J* = 1.0, 7.8 Hz), 7.15 (1H, dt, *J* = 1.0, 7.8 Hz), 7.23 (1H, m), 7.57 (1H, m).

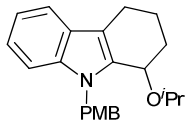
^{13}C NMR (100 MHz, $CDCl_3$): δ 8.8, 46.3, 55.2, 57.1, 63.6, 109.5, 111.2, 114.0, 118.8, 118.9, 122.3, 127.3, 128.0, 130.5, 131.3, 137.0, 158.7.

MS (EI): *m/z* (%) 295 (M^+, 50), 264 (11), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{19}H_{21}NO_2$: 295.1572; Found: 295.1569.

For Table 5

1-Isopropoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7h**)



7h

Entry 1: **6d** (0.12 g, 0.40 mmol); Di(*p*-tolyl) sulfoxide (0.27 g, 1.2mmol); CH_2Cl_2 (2.0 mL); TFAA (0.17 mL, 1.2 mmol); ^{i}PrOH (0.30 mL, 4.0 mmol); **7h** (67 mg, 51 %).

Colorless oil.

IR ($CHCl_3$): 3005, 2970, 2936, 1612, 1512, 1464, 1246 cm^{-1}.

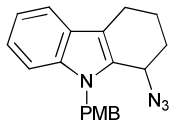
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (3H, d, *J* = 6.2 Hz), 1.18 (3H, d, *J* = 6.2 Hz), 1.64-1.92 (2H, m), 1.93-2.32 (2H, m), 2.64 (1H, ddd, *J* = 15.7, 10.2, 5.5 Hz), 2.88 (1H, ddd, *J* = 15.7, 5.3, 3.1 Hz), 3.71 (3H, s), 3.81 (1H, sept, *J* = 6.2 Hz), 4.59 (1H, t, *J* = 3.3 Hz), 5.29 (1H, d, *J* = 16.7 Hz), 5.36 (1H, d, *J* = 16.7 Hz), 6.65-6.86 (2H, m), 6.86-7.00 (2H, m), 7.00-7.18 (3H, m), 7.51 (1H, dt, *J* = 8.0, 0.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5, 21.2, 21.7, 24.1, 28.6, 45.7, 55.1, 66.5, 68.7, 109.5, 112.9, 113.9, 118.70, 118.74, 121.9, 16.7, 127.2, 130.5, 134.1, 137.1, 158.5.

MS (EI): *m/z* (%) 349 (M^+, 5), 290 (13), 289 (48), 121(100).

HRMS (EI): *m/z* Calcd for $C_{23}H_{27}NO_2$: 349.2042; Found: 349.2040.

1-Azido-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7k**)



7k

Entry 4: **6d** (0.13 g, 0.45 mmol); Di(*p*-tolyl) sulfoxide (0.31 g, 1.4 mmol); CH_2Cl_2 (2.2 mL); TFAA (0.19 mL, 1.4 mmol); Trimethylsilyl azide (0.60 mL, 4.5 mmol); **7k** (0.14 mg, 93%).

Yellowish oil.

IR ($CHCl_3$): 3007, 2940, 2097, 1512, 1464, 1246 cm^{-1}.

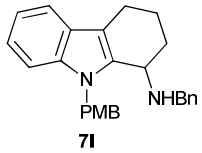
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87-2.13 (3H, m), 2.15 (1H, m), 2.68 (1H, m), 2.92 (1H, m), 3.73 (3H, s), 4.43 (1H, t, *J* = 3.1 Hz), 5.27 (1H, d, *J* = 16.8 Hz), 5.37 (1H, d, *J* = 16.8 Hz), 6.72-6.82 (2H, m), 6.82-7.00 (2H, m), 7.06-7.26 (3H, m), 7.55 (1H, d, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 19.2, 20.9, 30.4, 46.2, 53.1, 55.2, 109.7, 113.9, 114.1, 119.0, 119.3, 122.6, 126.3, 127.3, 129.8, 130.8, 137.3, 158.8.

MS (EI): *m/z* (%) 332 (M^+, 1), 290 (14), 289 (47), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{20}H_{20}N_4O$: 332.1637; Found: 332.1641.

N-Benzylamino-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7l**)



7l

Entry 5: **6d** (83 mg, 0.29 mmol); Di(*p*-tolyl) sulfoxide (0.12 g, 0.86 mmol); CH_2Cl_2 (1.4 mL); TFAA (0.12 mL, 0.86 mmol); Benzyl amine (0.31 mL, 2.9 mmol); **7l** (85 mg, 75%).

Colorless oil.

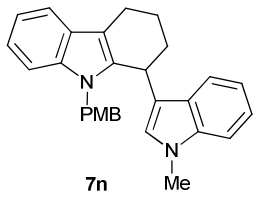
IR ($CHCl_3$): 3007, 2936, 2839, 1612, 1512, 1464, 1454, 1246, 1223, 1175 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.65-2.05 (3H, m), 2.23 (1H, m), 2.64 (1H, dt, *J* = 15.4, 8.0 Hz), 2.85 (1H, dt, *J* = 15.4, 3.8 Hz), 3.72 (3H, s), 3.73 (1H, d, *J* = 13.0 Hz), 3.86 (1H, t, *J* = 3.5 Hz), 3.93 (1H, d, *J* = 13.0 Hz), 5.44 (1H, d, *J* = 16.5 Hz), 5.22 (1H, d, *J* = 16.5 Hz), 6.62-6.79 (2H, m), 6.79-6.90 (2H, m), 7.05 (1H, dt, *J* = 1.3, 6.9 Hz), 7.11 (1H, dt, *J* = 1.3, 6.9Hz), 7.15-7.34 (6H, m), 7.51 (1H, dt, *J* = 7.9, 0.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.4, 21.2, 27.1, 45.7, 48.8, 50.9, 55.2, 109.4, 111.5, 113.9, 118.4, 118.7, 121.5, 126.76, 126.84, 127.3, 128.2, 130.8, 136.2, 137.0, 140.5, 158.5.

HRMS (FAB): *m/z* Calcd for $C_{27}H_{29}N_2O$ $[M+H]^+$: 397.2280; Found: 397.2273.

9-(4-Methoxybenzyl)-1-(1-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7n**)



7n

Entry 7: **6d** (50 mg, 0.17 mmol); Di(*p*-tolyl) sulfoxide (0.12 g, 0.51 mmol); CH_2Cl_2 (0.90 mL); TFAA (72 µL, 0.51 mmol); *N*-Methylindole (0.22 mL, 1.7 mmol); **7n** (71 mg, 99%).

Yellowish amorphous.

IR ($CHCl_3$): 3007, 2936, 1512, 1466, 1246 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.73-1.88 (2H, m), 2.03-2.20 (2H, m), 2.75 (1H, dt, *J* = 15.0, 7.7 Hz), 2.92 (1H, dt, *J* = 15.0, 4.1 Hz), 3.58 (3H, s), 3.72 (3H, s), 4.40 (1H, t, *J* = 4.1 Hz), 4.87 (1H, d, *J* = 16.5 Hz), 4.99 (1H, d, *J* = 16.5 Hz), 6.35 (1H, s), 6.58-6.70 (2H, m), 6.70-6.78 (2H, m), 7.06-7.17 (3H, m), 7.18-7.30 (3H, m), 7.52-7.63 (2H, m).

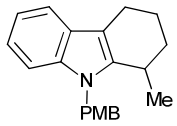
^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 21.3, 29.8, 31.2, 32.5, 45.9, 55.1, 109.1, 109.2, 110.6, 113.5, 117.0, 117.9, 118.56, 118.63, 118.7, 120.8, 121.3, 126.5, 127.15, 127.16, 127.9, 130.4, 136.7, 136.9, 137.0, 158.2.

MS (EI): *m/z* (%) 420 (M^+, 100), 299 (13), 289 (39), 288 (29), 271 (18), 258 (16), 255 (11), 251 (16), 250 (13), 121 (68).

HRMS (EI): *m/z* Calcd for $C_{29}H_{28}N_2O$: 420.2202; Found: 420.2204.

For Table 6

9-(4-Methoxybenzyl)-1-methyl-1,2,3,4-tetrahydro-9*H*-carbazole (**7o**)



7o

Entry 1: **6d** (0.12 g, 0.41 mmol); Di(*p*-tolyl) sulfoxide (0.29 g, 1.2 mmol); TFAA (0.18 mL, 1.2 mmol); CH_2Cl_2 (2.1 mL); Methyl magnesium iodide (0.93 M solution in Et_2O, 4.4 mL, 4.1 mmol); **7o** (56 mg, 44 %).

White crystals.

Mp: 106-108 °C.

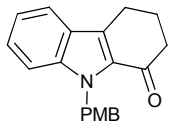
IR (CHCl3): 3005, 2963, 2934, 1512, 1466, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.20 (3H, d, *J* = 7.1 Hz), 1.76 (1H, m), 1.82-2.00 (3H, m), 2.66 (1H, m), 2.84 (1H, m), 2.99 (1H, m), 3.73 (3H, s), 5.18 (1H, d, *J* = 16.6 Hz), 5.28 (1H, d, *J* = 16.6 Hz), 6.70-6.82 (2H, m), 6.82-6.98 (2H, m), 7.03-7.13 (3H, m), 7.49 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 18.8, 21.0, 21.4, 26.5, 31.5, 45.9, 55.2, 109.0, 109.3, 113.9, 117.8, 118.7, 120.8, 126.9, 127.3, 130.2, 136.6, 139.8, 158.4.

Anal Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59; Found: C, 82.72; H, 7.75; N, 4.52.

9-(4-Methoxybenzyl)-1-oxo-1,2,3,4-tetrahydro-9*H*-carbazole (**11**)



11

Entry 2: **6d** (0.13 g, 0.43 mmol); Di(*p*-tolyl) sulfoxide (0.30 g, 1.3 mmol); TFAA (0.18 mL, 1.3 mmol); CH_2Cl_2 (2.1 mL); Methyl magnesium chloride (3.0 M solution in THF, 1.4 mL, 4.3 mmol); **11** (49 mg, 37%).

Yellowish oil.

IR ($CHCl_3$): 3009, 2934, 1653, 1512, 1462, 1246 cm^{-1}.

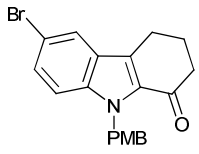
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (2H, quint, *J* = 6.3 Hz), 2.65 (2H, t, *J* = 6.3 Hz), 3.04 (2H, t, *J* = 6.3 Hz), 3.74 (3H, s), 5.75 (2H, s), 6.70-6.88 (2H, m), 7.04-7.13 (2H, m), 7.16 (1H, m), 7.34-7.38 (2H, m), 7.67 (1H, d, *J* = 8.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 24.9, 29.8, 40.1, 47.4, 55.3, 110.9, 113.8, 120.1, 121.3, 124.9, 126.7, 128.0, 129.8, 130.5, 139.2, 158.5, 191.7.

MS (EI): *m/z* (%) 305 (M^+, 49), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{20}H_{19}NO_2$: 305.1416; Found: 305.1420.

6-Bromo-9-(4-methoxybenzyl)-1-oxo-1,2,3,4-tetrahydro-9*H*-carbazole (**12**)



12

Entry 3: **6d** (0.16 g, 0.56 mmol); Di(*p*-tolyl) sulfoxide (0.39 g, 1.7 mmol); TFAA (0.23 mL, 1.7 mmol); CH_2Cl_2 (2.8 mL); Methyl magnesium bromide (1.06 M solution in THF, 5.2 mL, 5.6 mmol); **12** (0.10 g, 47 %).

Yellowish amorphous.

IR ($CHCl_3$): 3011, 2949, 2936, 1659, 1512, 1464, 1275, 1246 cm^{-1}.

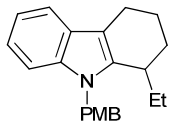
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (2H, quint, *J* = 6.2 Hz), 2.63 (2H, t, *J* = 6.2 Hz), 2.96 (2H, t, *J* = 6.2 Hz), 3.71 (3H, s), 5.70 (2H, s), 6.70-6.85 (2H, m), 6.98-7.12 (2H, m), 7.21 (1H, m), 7.38 (1H, dt, *J* = 8.8, 1.5 Hz), 7.78 (1H, brs).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 24.6, 40.0, 47.5, 55.2, 112.4, 113.2, 113.8, 123.6, 126.5, 127.9, 128.6, 129.4, 129.9, 130.4, 137.6, 158.6, 191.6.

MS (EI): *m/z* (%) 385 ([M^++2], 21), 383 (M^+, 21), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{20}H_{18}N_4O_2Br$: 383.0521; Found: 383.0522.

1-Ethyl-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7p**)



7p

Entry 6: **6d** (0.10 g, 0.35 mmol); Di(*p*-tolyl) sulfoxide (0.24 g, 1.1 mmol); CH_2Cl_2 (1.8 mL); TFAA (0.15 mL, 1.1 mmol); Diethyl zinc (1.0 M solution in *n*-hexane, 3.5 mL, 3.5 mmol); **7p** (85 mg, 76 %).

Colorless oil.

IR ($CHCl_3$): 3005, 2959, 2936, 1512, 1466, 1246, 1223 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (3H, t, *J* = 7.5 Hz), 1.30-1.70 (2H, m), 1.70-2.18 (4H, m), 2.66 (2H, dq, *J* = 15.4, 7.5 Hz), 2.81 (1H, dt, *J* = 15.4, 4.0 Hz), 3.72 (3H, s), 5.14 (1H, d, *J* = 16.7 Hz), 5.25 (1H, d, *J* = 16.7 Hz), 6.67-6.80 (2H, m), 6.80-6.96 (2H, m), 6.97-7.15 (3H, m), 7.48 (1H, dt, *J* = 8.9, 3.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 12.4, 18.6, 21.1, 26.1, 33.5, 45.9, 55.2, 109.4, 109.5, 114.0, 117.9, 118.8, 120.8, 127.1, 127.5, 130.3, 136.8, 139.6, 158.6.

MS (EI): *m/z* (%) 319 (M^+, 56), 290 (29), 121 (100).

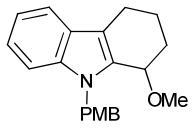
HRMS (EI): *m/z* Calcd for $C_{22}H_{25}NO$: 319.1936; Found: 319.1936.

General procedure for substitution reaction induced by acyloxythionium species generated from DMSO (1.0 equiv.)/TFAA (1.0 equiv.).

Under argon atmosphere, to a solution of **6** (1.0 equiv.) and DMSO (1.0 equiv.) in CH_2Cl_2 (0.20 M) was added TFAA (1.0 equiv.). After being stirred at -40 °C for 30 min, MeOH (5.0 equiv.) was added to the above reaction mixture and, the mixture was stirred at same temperature for 10 min. The resulting mixture was neutralized with saturated aqueous $NaHCO_3$, then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with *n*-hexane/AcOEt as an eluent to give **7**.

For Table 7

1-Methoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7d**)

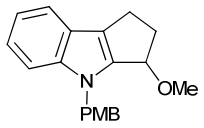


7d

Entry 5: **6d** (0.12 g, 0.40 mmol); DMSO (29 μL, 0.40 mmol); CH_2Cl_2 (2.0 mL); TFAA (56 μL, 0.40 mmol); MeOH (81 μL, 2.0 mmol); **7d** (0.12 g, 95%).

For Table 8

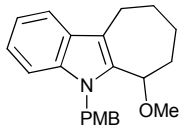
3-Methoxy-4-(4-methoxybenzyl)-1,2,3,4-tetrahydrocyclopenta[*b*]-indole (**7e**)



7e

Entry 1: **6e** (0.11 g, 0.39 mmol); DMSO (27 μL, 0.39 mmol); CH_2Cl_2 (1.9 mL); TFAA (54 μL, 0.39 mmol); MeOH (78 μL, 1.9 mmol); **7e** (0.11 g, 88%).

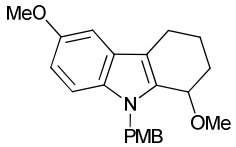
6-Methoxy-5-(4-methoxybenzyl)-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (**7f**)



7f

Entry 2: **6f** (0.12 g, 0.40 mmol); DMSO (28 μL, 0.40 mmol); CH_2Cl_2 (2.0 mL); TFAA (56 μL, 0.40 mmol); MeOH (81 μL, 2.0 mmol); **7f** (0.12 g, 90%).

1,6-Dimethoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7r**)



7r

Entry 3: **6r** (96 mg, 0.30 mmol); DMSO (21 μL, 0.30 mmol); CH_2Cl_2 (1.5 mL); TFAA (42 μL, 0.30 mmol); MeOH (61 μL, 1.5 mmol); **7r** (80 mg, 76 %).

Colorless oil.

IR ($CHCl_3$): 3005, 2940, 1512, 1483, 1246, 1207 cm^{-1}.

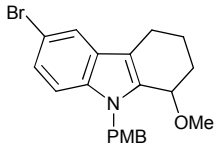
^1H NMR (300 MHz, $CDCl_3$): δ 1.65-2.10 (3H, m), 2.21 (1H, ddt, *J* = 13.7, 5.5, 2.8 Hz), 2.60 (1H, ddd, *J* = 15.5, 9.9, 5.5 Hz), 2.82 (1H, dt, *J* = 15.5, 5.5), 3.38 (3H, s), 3.74 (3H, s), 3.83 (3H, s), 4.37 (1H, t, *J* = 3.7 Hz), 5.25 (2H, s), 6.73-6.84 (2H, m), 6.79 (1H, d, *J* = 8.6 Hz), 6.94-7.03 (2H, m), 6.98 (1H, s), 7.07 (1H, d, *J* = 8.6 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 21.3, 27.2, 46.4, 55.2, 55.7, 55.9, 70.8, 100.8, 110.3, 112.0, 112.5, 113.9, 126.8, 127.5, 130.6, 132.5, 134.5, 153.6, 158.6.

MS (EI): *m/z* (%) 351 (M^+, 4), 321 (14), 320 (14), 319 (53), 317 (14), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{22}H_{25}NO_3$: 351.1834; Found: 351.1837.

6-Bromo-1-methoxy-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7s**)



7s

Entry 4: **6s** (0.13 g, 0.35 mmol); DMSO (25 μL, 0.35 mmol); CH_2Cl_2 (1.8 mL); TFAA (49 μL, 0.35 mmol); MeOH (71 μL, 1.8 mmol); **7s** (98 mg, 70%).

Colorless oil.

IR ($CHCl_3$): 3007, 2938, 1512, 1464, 1246 cm^{-1}.

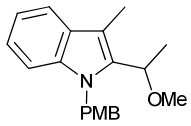
^1H NMR (300 MHz, $CDCl_3$): δ 1.66-2.04 (3H, m), 2.21 (1H, ddt, *J* = 13.5, 5.5, 2.9 Hz), 2.57 (1H, ddd, *J* = 15.2, 9.5, 5.5 Hz), 2.79 (1H, dt, *J* = 15.2, 5.5 Hz), 3.38 (3H, s), 3.73 (3H, s), 4.35 (1H, t, *J* = 3.5 Hz), 5.25 (2H, s), 6.72-6.87 (2H, m), 6.87-7.02 (2H, m), 7.04 (1H, d, *J* = 8.6 Hz), 7.18 (1H, dd, *J* = 8.6, 1.8 Hz), 7.64 (1H, d, *J* = 1.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.8, 21.1, 27.0, 46.4, 55.2, 55.8, 70.6, 111.1, 112.1, 112.6, 114.0, 121.5, 124.7, 127.5, 128.3, 130.0, 135.1, 135.8, 158.8.

MS (EI): *m/z* (%) 401 ([M^++2], 7), 399 (M^+, 7), 369 (20), 367 (21), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{21}H_{22}BrNO_2$: 399.0834; Found: 399.0831.

1-(4-Methoxybenzyl)-2-(1-methoxyethyl)-3-methyl-1*H*-indole (**7t**)



7t

Entry 5: **2t** (85 mg, 0.30 mmol); DMSO (22 μL, 0.30 mmol); CH_2Cl_2 (1.5 mL); TFAA (42 μL, 0.30 mmol); MeOH (62 μL, 1.5 mmol); **7t** (77 mg, 82%).

Colorless oil.

IR ($CHCl_3$): 3005, 2986, 2932, 1512, 1466, 1246 cm^{-1}.

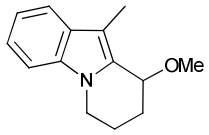
^1H NMR (300 MHz, $CDCl_3$): δ 1.43 (3H, d, *J* = 6.8 Hz), 2.36 (3H, s), 3.12 (3H, s), 3.74 (3H, s), 4.74 (1H, q, *J* = 6.8 Hz), 5.36 (1H, d, *J* = 17.0 Hz), 5.54 (1H, d, *J* = 17.0 Hz), 6.70-6.82 (2H, m), 6.82-6.98 (2H, m), 7.00-7.19 (3H, m), 7.57 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 8.7, 21.7, 46.7, 55.2, 56.3, 72.0, 109.3, 109.6, 113.9, 118.6, 119.0, 121.8, 127.1, 128.4, 130.5, 134.8, 137.2, 158.5.

MS (EI): *m/z* (%) 309 (M^+, 31), 277 (11), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{20}H_{23}NO_2$: 309.1729; Found: 309.1726.

9-Methoxy-10-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**7u**)



7u

Entry 6: **6u** (50 mg, 0.27 mmol); DMSO (19 μL, 0.27 mmol); CH_2Cl_2 (1.4 mL); TFAA (38 μL, 0.27 mmol); MeOH (55 μL, 1.4 mmol); **7u** (40 mg, 61%).

Colorless oil.

IR ($CHCl_3$): 3007, 2953, 2932, 2920, 1460, 1325, 1082 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.79 (1H, tt, *J* = 13.0, 3.3 Hz), 1.95 (1H, m), 2.18-2.60 (2H, m), 2.36 (3H, s), 3.37 (3H, s), 3.73 (1H, dt, *J* = 5.0, 11.5 Hz), 4.25 (1H, ddd, *J* = 11.5, 5.9, 2.6 Hz), 4.66 (1H, t, *J* = 3.3 Hz), 7.11 (1H, ddd, *J* = 8.0, 7.4, 1.1 Hz), 7.20 (1H, ddd, *J* = 8.0, 7.4, 1.3 Hz), 7.26 (1H, dt, *J* = 7.4, 1.1Hz), 7.65 (1H, ddd, *J* = 7.4, 1.3, 1.1 Hz).

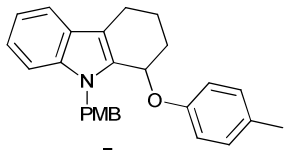
^{13}C NMR (75 MHz, $CDCl_3$): δ 8.8, 17.9, 27.0, 42.3, 55.8, 69.2, 109.1, 109.2, 118.8, 119.1, 121.6, 128.3, 131.3, 136.4.

MS (EI): *m/z* (%) 215 (M^+, 30), 185 (16), 184 (100), 183 (79), 182 (73), 180 (21), 169 (12), 168 (27), 167 (36).

HRMS (EI): *m/z* Calcd for $C_{14}H_{17}NO$: 215.1310; Found: 215.1311.

For Table 9

9-(4-Methoxybenzyl)-1-(4-methylphenyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7v**)



7v

Entry 1: **6d** (0.14 g, 0.47 mmol); DMSO (33 μL, 0.47 mmol); CH_2Cl_2 (2.3 mL); TFAA (65 μL, 0.47 mmol); *p*-cresol (0.25 g, 2.3 mmol); **7v** (0.13 g, 70%).

Colorless amorphous.

IR ($CHCl_3$): 3007, 2936, 1612, 1508, 1464, 1246, 1225 cm^{-1}.

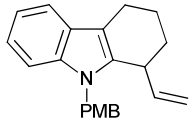
^1H NMR (300 MHz, $CDCl_3$): δ 1.74-1.94 (2H, m), 2.00 (1H, m), 2.29 (3H, s), 2.50-2.83 (2H, m), 2.95 (1H, ddd, *J* = 15.9, 4.7, 2.7 Hz), 3.73 (3H, s), 5.16 (1H, d, *J* = 16.5 Hz), 5.26 (1H, d, *J* = 16.5 Hz), 5.35 (1H, t, *J* = 2.9 Hz), 6.65-6.77 (2H, m), 6.77-6.85 (2H, m), 6.85-6.98 (2H, m), 7.00-7.10 (2H, m), 7.10-7.30 (3H, m), 7.57 (1H, d, *J* = 7.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7, 20.4, 21.1, 28.2, 46.2, 55.1, 67.4, 109.6, 113.9, 114.0, 115.7, 119.0, 122.4, 126.5, 127.3, 127.6, 130.0, 130.2, 130.3, 132.5, 137.3, 155.1, 158.7.

MS (EI): *m/z* (%) 397 (M^+, 1), 290 (16), 289 (55), 121 (100), 108 (10), 107 (11).

HRMS (EI): *m/z* Calcd for $C_{27}H_{27}NO_2$: 397.2042; Found: 397.2038.

9-(4-Methoxybenzyl)-1-vinyl-1,2,3,4-tetrahydro-9*H*-carbazole (**7q**)



7q

Entry 5: **6d** (0.11 g, 0.38 mmol); DMSO (27 μL, 0.38 mmol); CH_2Cl_2 (1.9 mL); TFAA (53 μL, 0.38 mmol); Vinyl magnesium bromide (1.0 M solution in THF, 1.9 mL, 1.9 mmol); **7q** (0.12 g, quant.).

Colorless oil.

IR ($CHCl_3$): 3007, 2936, 1512, 1466, 1246, 1223 cm^{-1}.

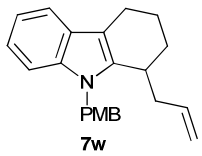
^1H NMR (300 MHz, $CDCl_3$): δ 1.72-2.10 (4H, m), 2.46-2.95 (2H, m), 3.45 (1H, m), 3.70 (3H, s), 4.87 (1H, dt, *J* = 17.2, 1.5 Hz), 5.07 (1H, ddd, *J* = 10.3, 1.5, 1.1 Hz), 5.13 (1H, d, *J* = 16.7 Hz), 5.22 (1H, d, *J* = 16.7 Hz), 5.95 (1H, ddd, *J* = 17.2, 10.3, 6.9 Hz), 6.65-6.80 (2H, m), 6.80-6.92 (2H, m), 6.98-7.28 (3H, m), 7.50 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.9, 21.1, 30.3, 36.7, 45.7, 55.1, 109.3, 110.7, 113.9, 115.9, 118.0, 118.7, 121.0, 127.1, 127.2, 130.5, 135.6, 136.9, 140.6, 158.6.

MS (EI): *m/z* (%) 317 (M^+, 14), 121 (100).

HRMS (EI): *m/z* Calcd for $C_{22}H_{23}NO$: 317.1780; Found: 317.1781.

1-Allyl-9-(4-methoxybenzyl)-1,2,3,4-tetrahydro-9*H*-carbazole (**7w**)



7w

Entry 6: **6d** (95 mg, 0.33 mmol); DMSO (23 μL, 0.33 mmol); CH_2Cl_2 (1.6 mL); TFAA (45 μL, 0.33 mmol); Allyl magnesium bromide (0.70 M solution in THF, 2.3 mL, 1.6 mmol); **7w** (0.11 g, quant.).

Colorless oil.

IR ($CHCl_3$): 3005, 2936, 1612, 1512, 1466, 1246 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.57-2.10 (4H, m), 2.10-2.50 (2H, m), 2.50-3.00 (3H, m), 3.73 (3H, s), 5.01 (2H, m), 5.19 (1H, d, *J* = 15.0 Hz), 5.28 (1H, d, *J* = 15.0 Hz), 5.80 (1H, m), 6.69-6.83 (2H, m), 6.83-6.98 (2H, m), 7.00-7.40 (3H, m), 7.53 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.2, 21.0, 26.5, 31.4, 38.4, 45.9, 55.2, 109.5, 109.9, 114.0, 116.4,

118.0, 118.9, 121.0, 127.1, 127.4, 130.2, 136.8, 136.9, 138.5, 158.7.

MS (EI): *m/z* (%) 331 (M^+, 30), 291 (29), 290 (100), 121 (78).

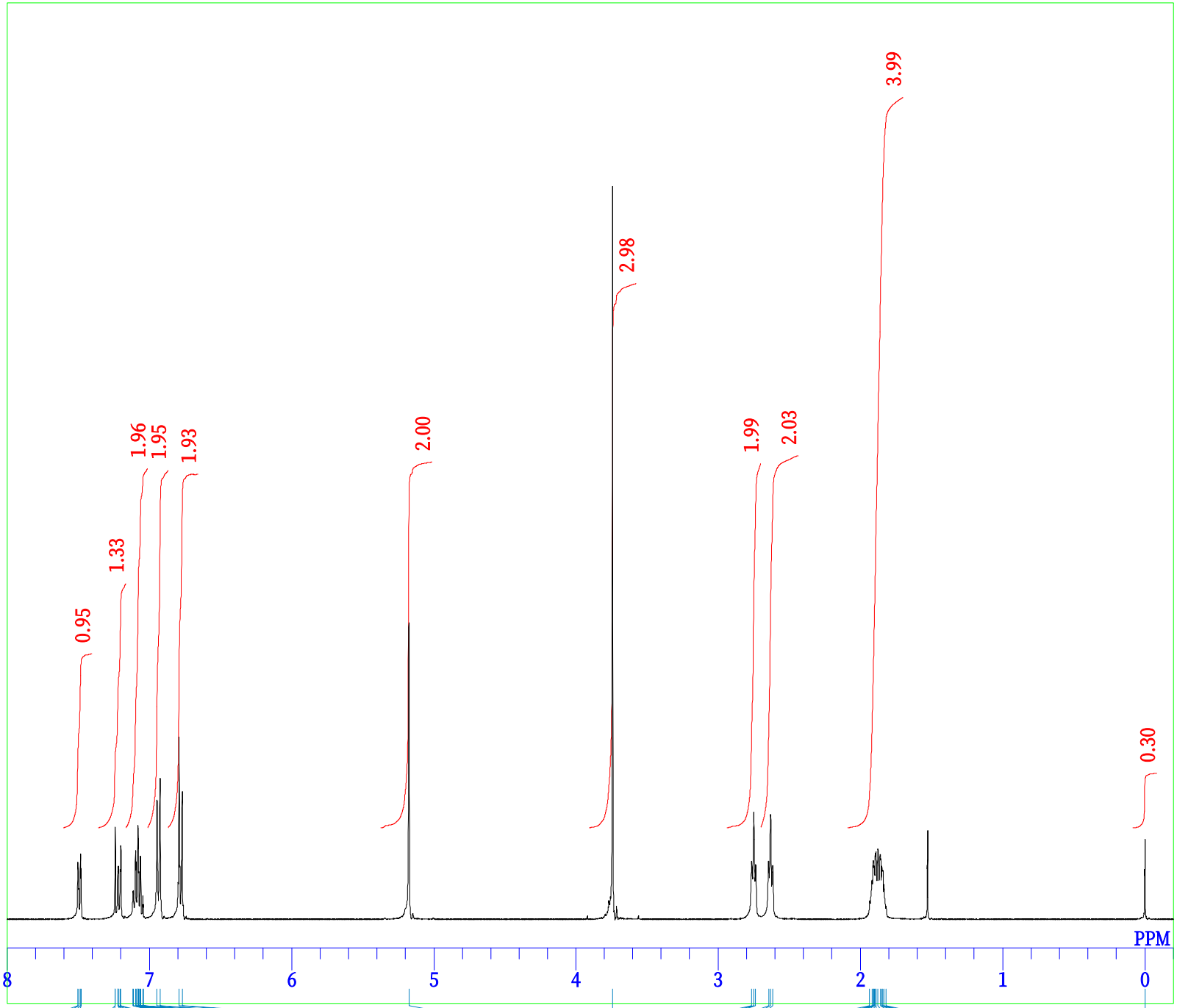
HRMS (EI): *m/z* Calcd for $C_{23}H_{25}NO$: 331.1936; Found: 331.1941.

1 G. A. Olah, E. R. Marienez, G.A. Suryaprakash, *Synlett*, 1999, 1397.

2 M. S. Yusubov, R. Y. Yusubova, T. V. Funk, K.-W. Chi, V. V. Zhdankin, *Synthesis*, 2009, 2505.

3 H. Takechi, M. Machida, Y. Kanaoka, *Chem. Pharm. Bull*., 1988, **36**, 3770.

4 D. R. Artis, I.-S. Cho, S. Jaime-Figueroa, J. M. Muchowski, *J. Org. Chem*., 1994, **59**, 2456.



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PD	2.9010 sec
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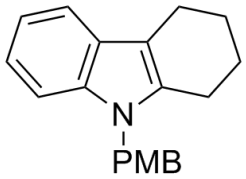
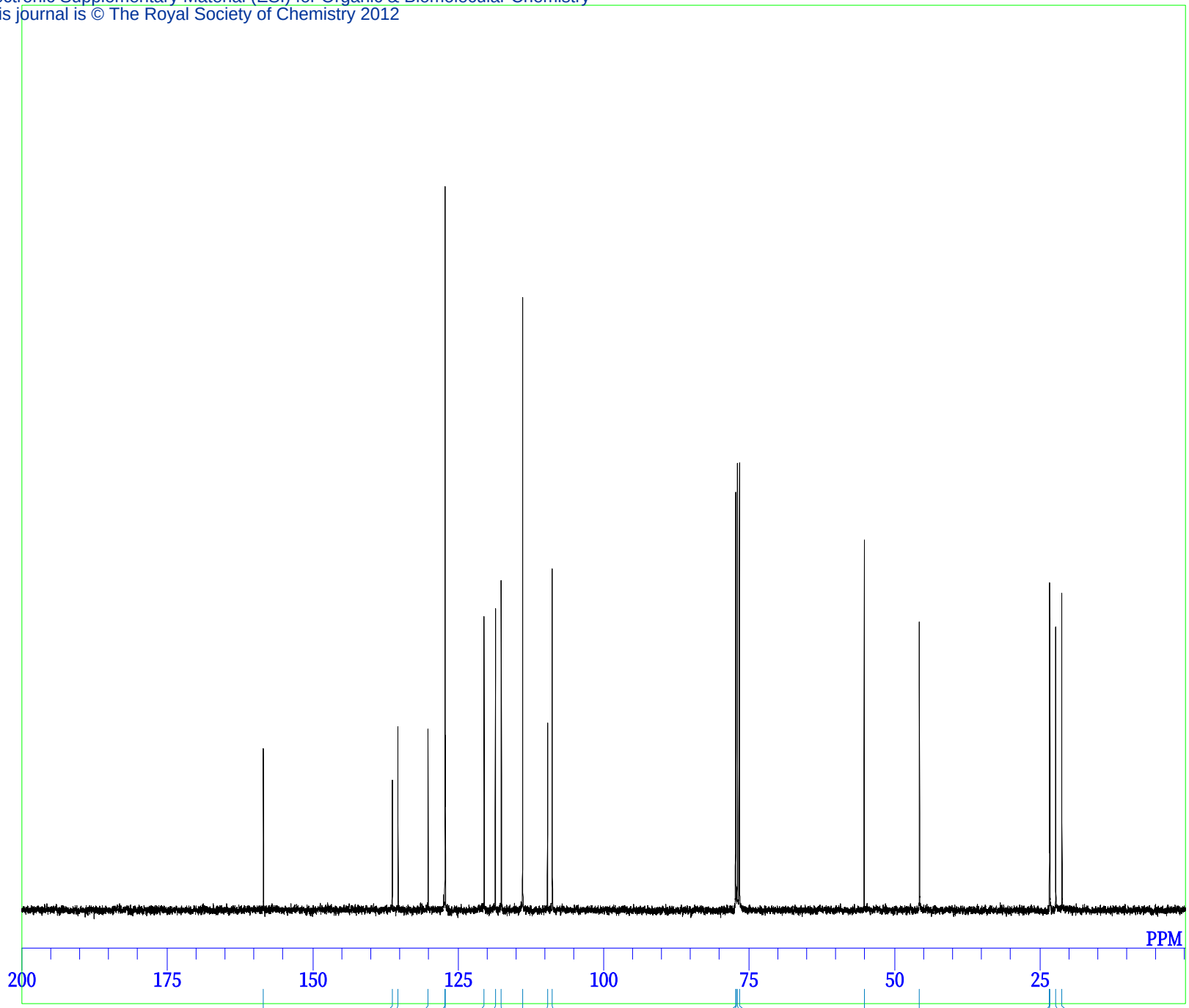
RGAIN	16





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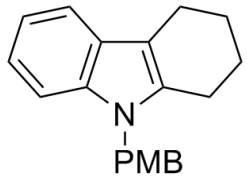

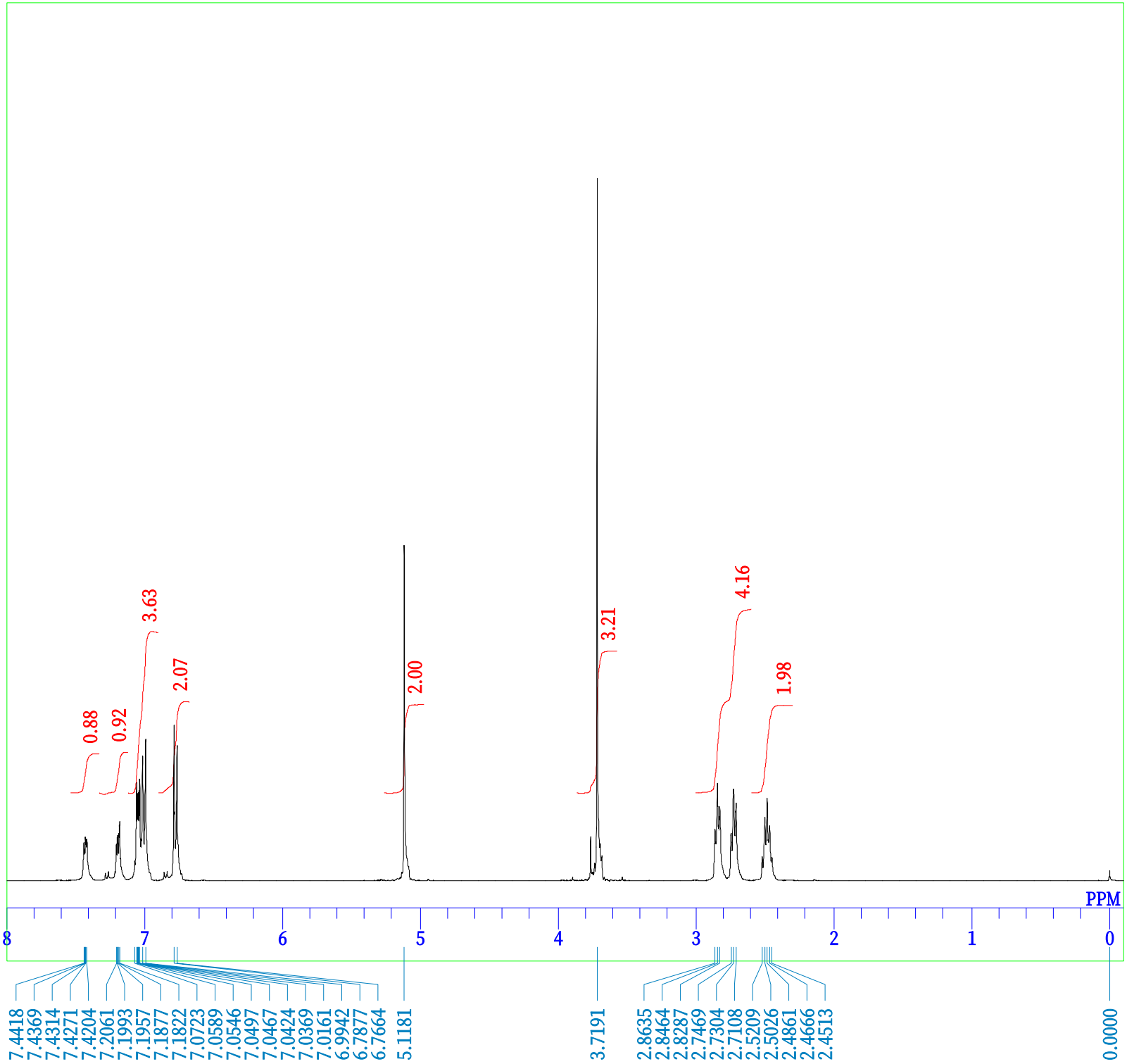

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OBFIN	10500.00 Hz
POINT	32768
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PD	2.9010 sec
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IRNUC	1H
CTEMP	26.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
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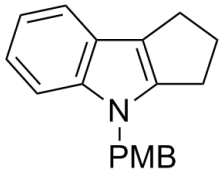
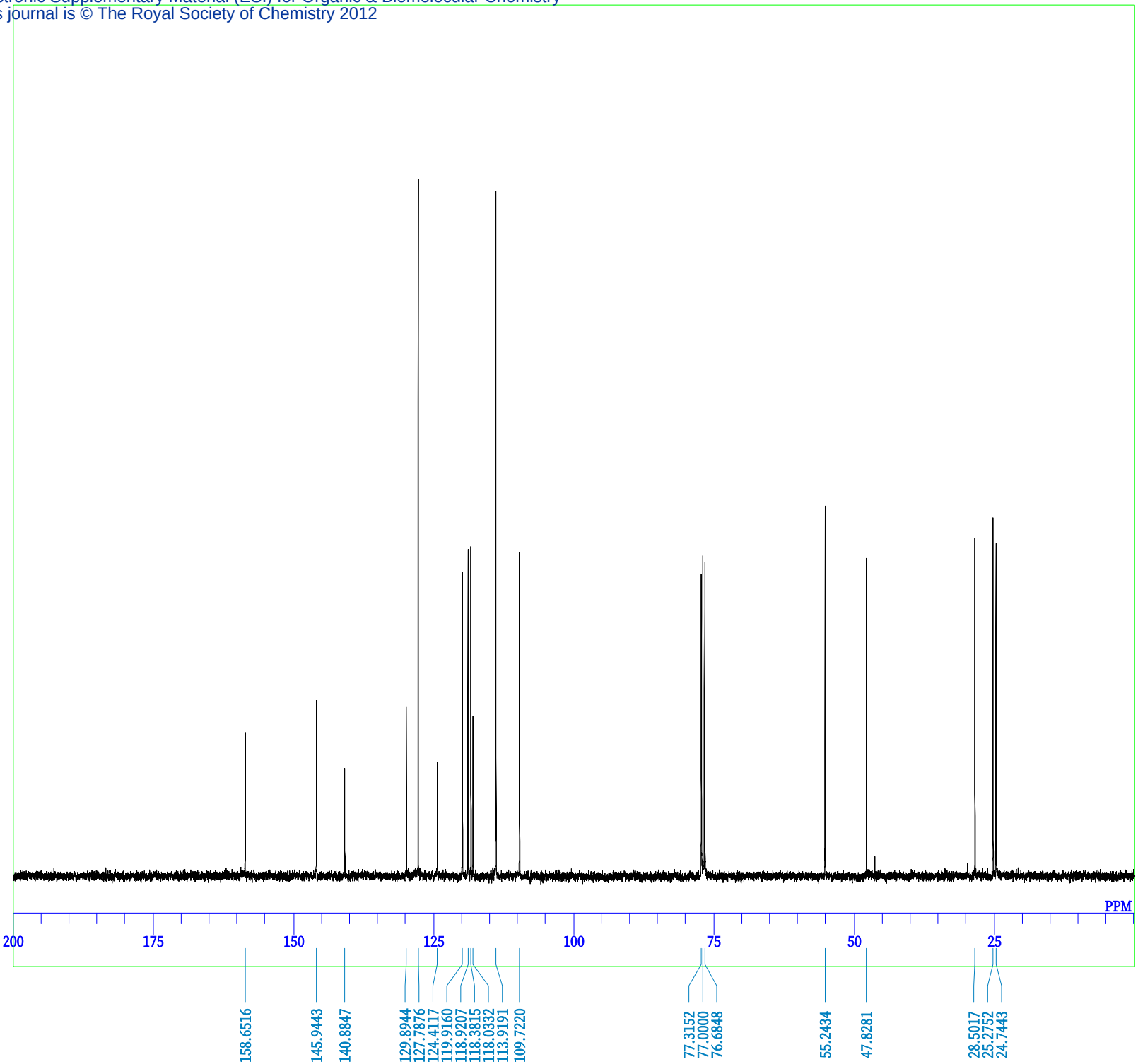
RGAIN	12





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OBFIN	10500.00 Hz
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PD	1.7940 sec
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SLVNT	CDCL3
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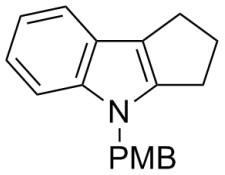
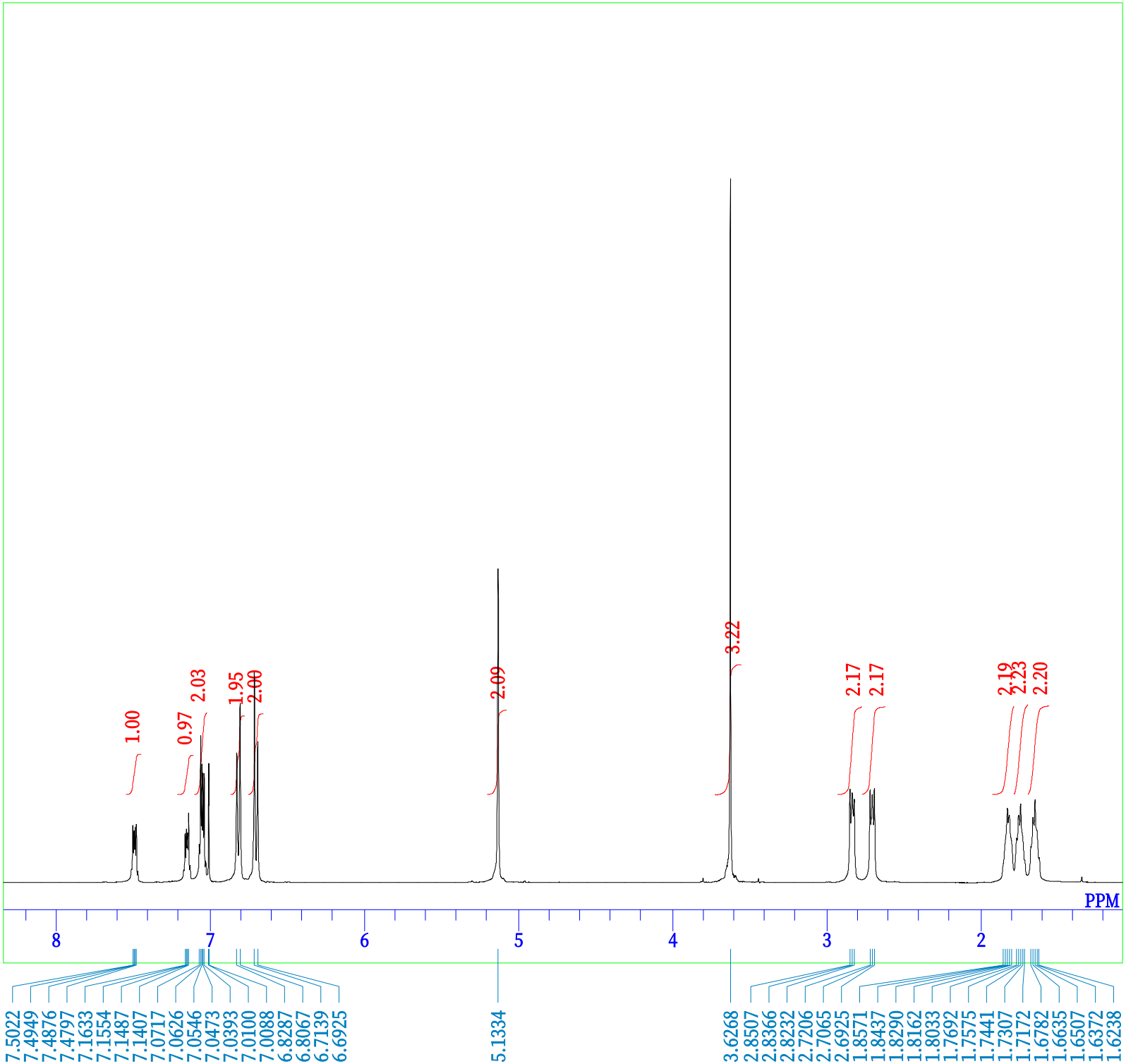
BF	1.20 Hz
RGAIN	24





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EXMOD	NON
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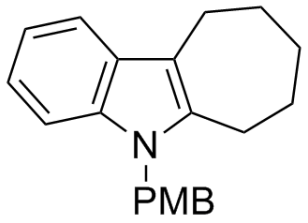
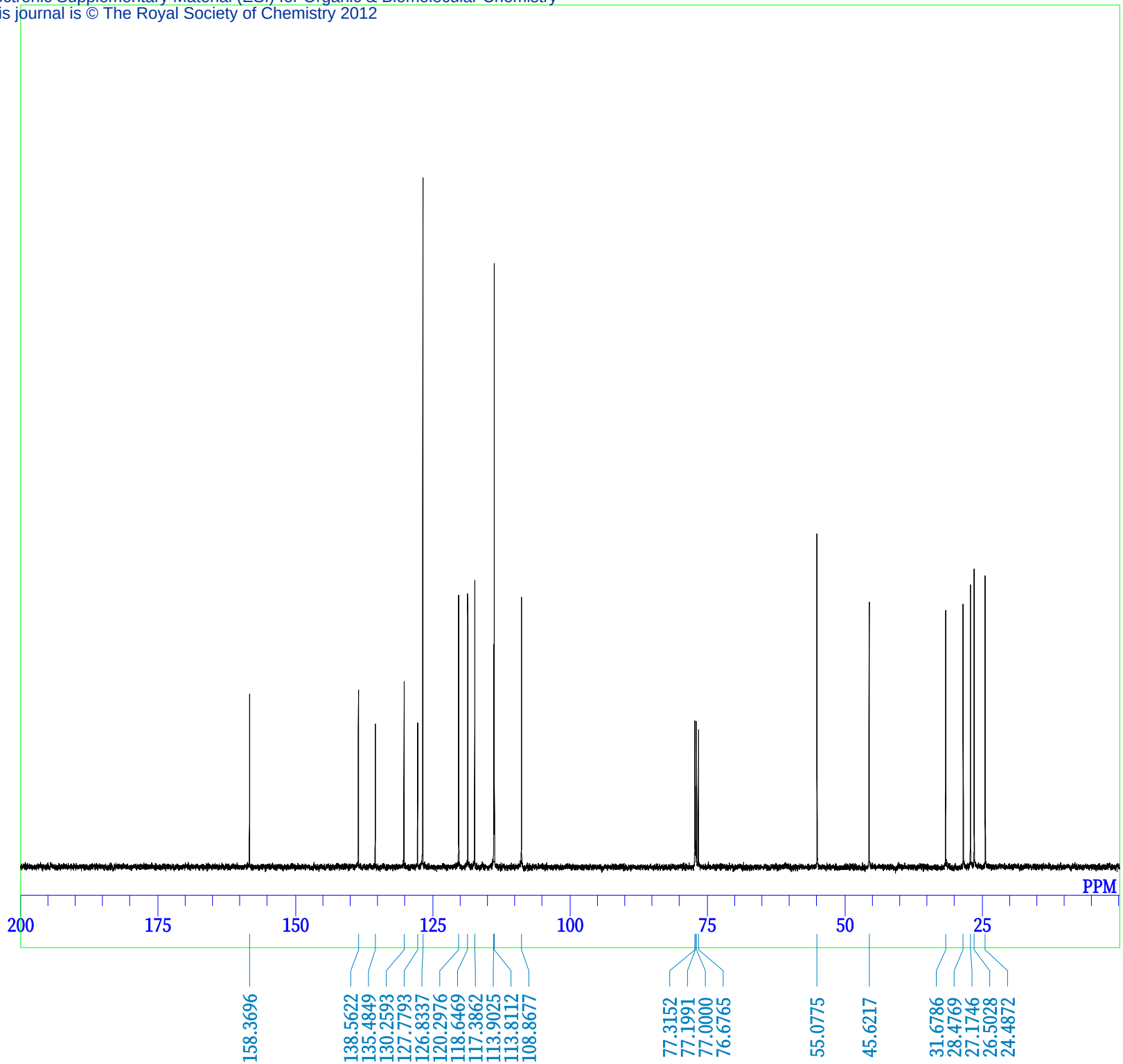
OBFIN	10500.00 Hz
POINT	32768
FREQU	8000.00 Hz
SCANS	4
ACQTM	4.0960 sec
PD	2.9010 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	7





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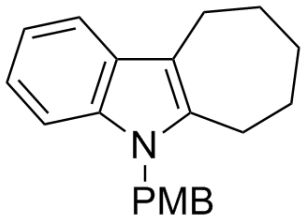
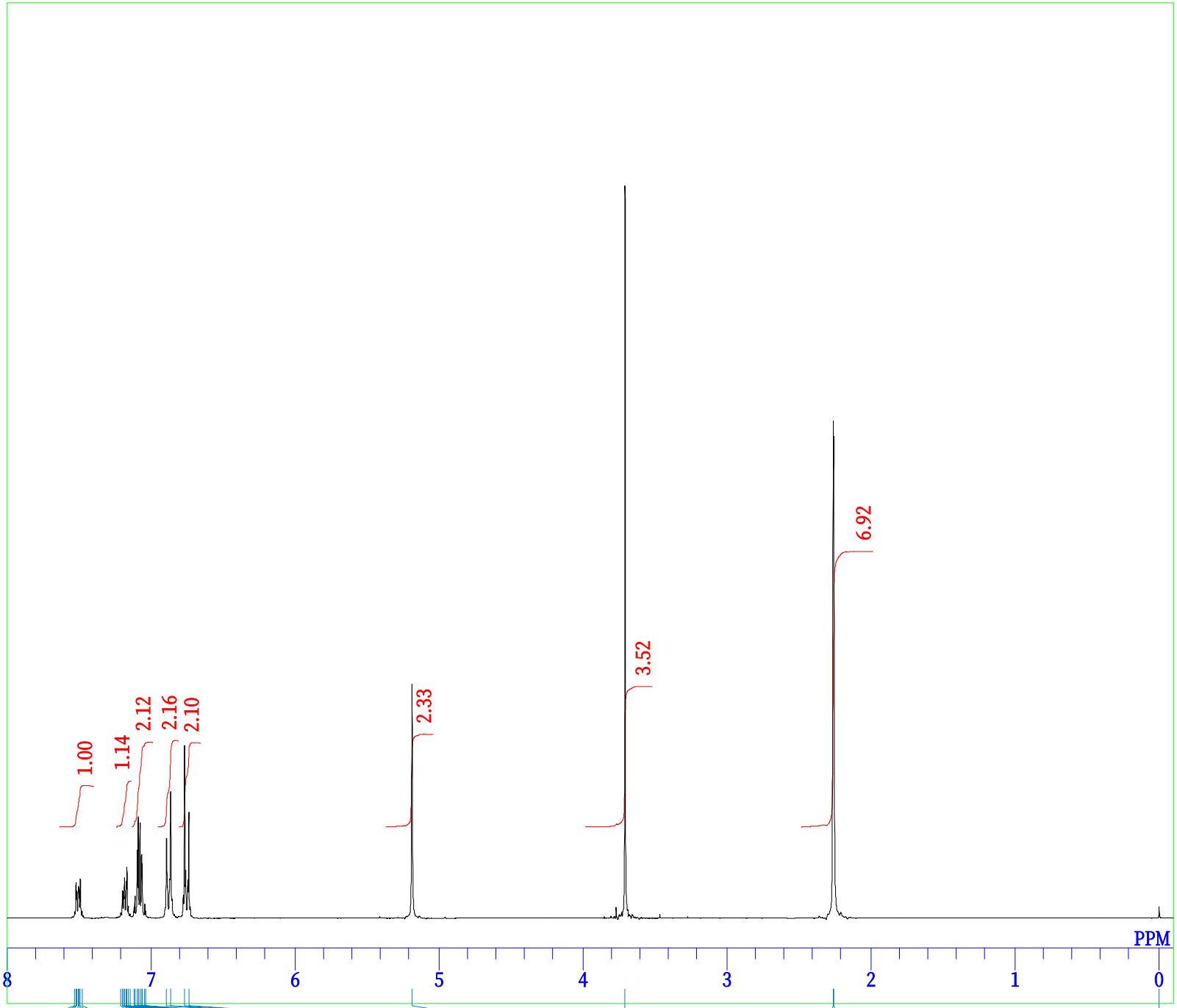
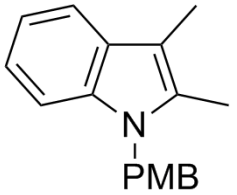
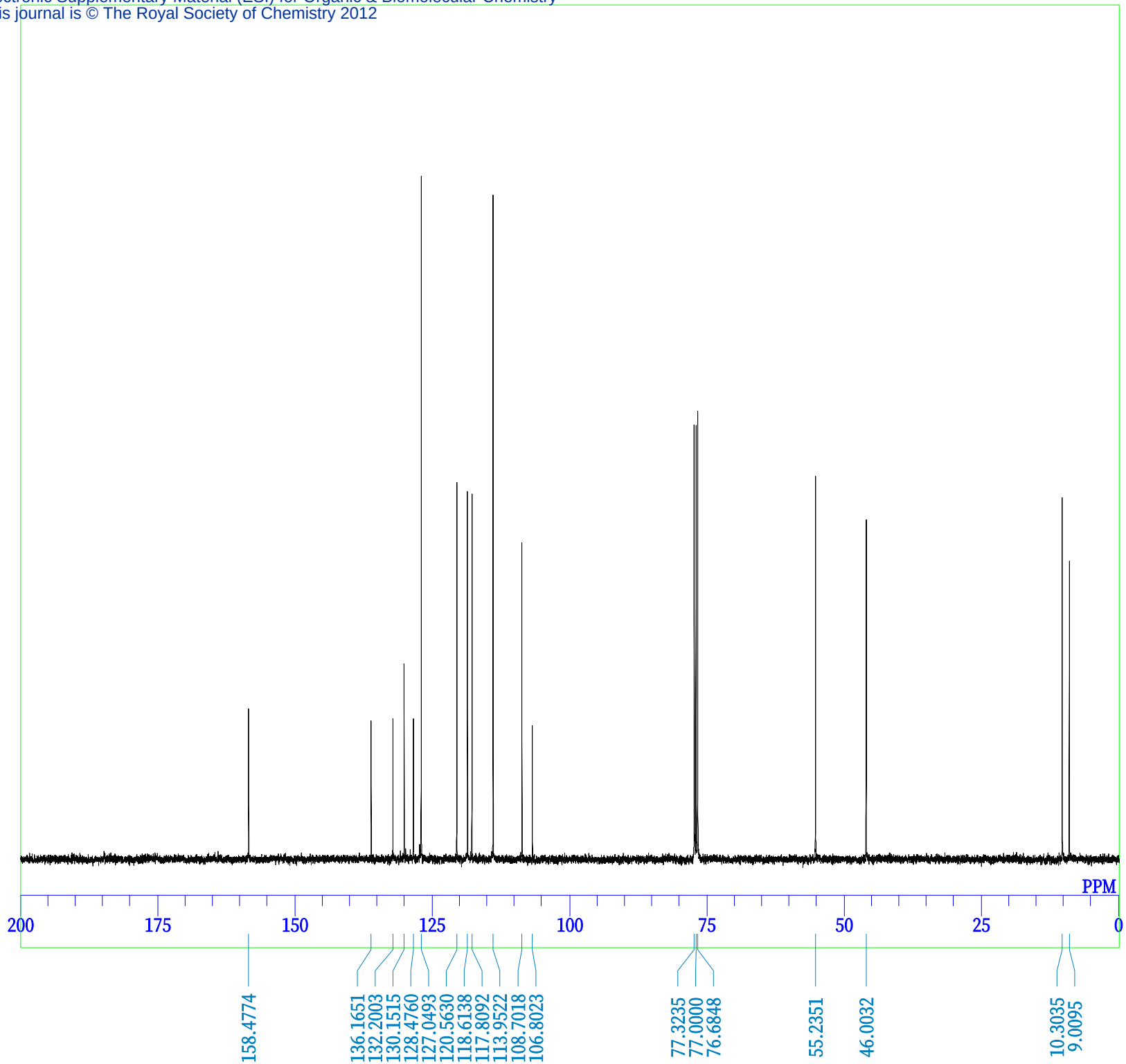
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	100
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



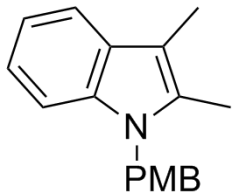


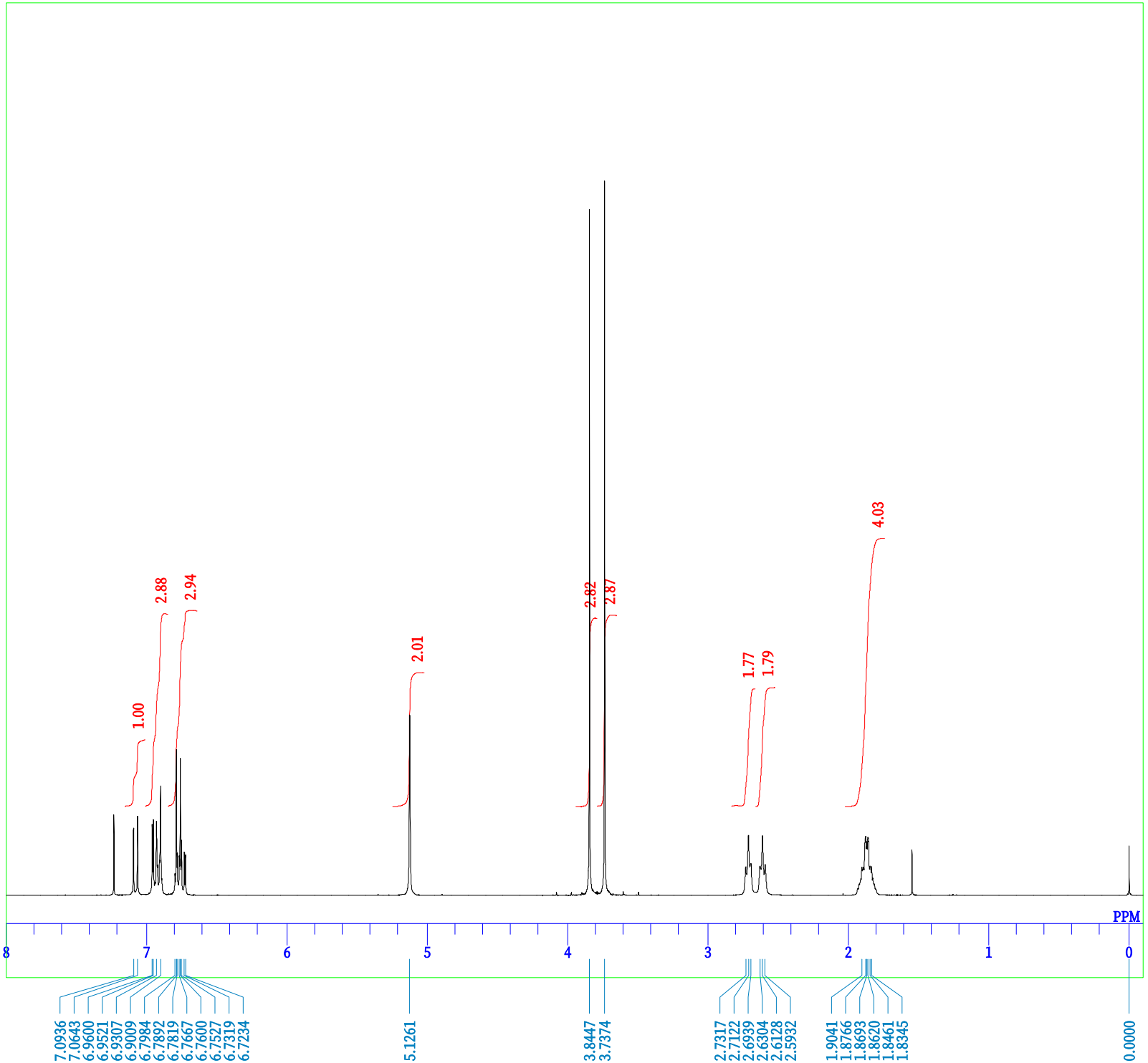
DFILE	2,3-DiMe-PMB 1H.als
COMNT	m083 diMe A.P. Fr.5-6
DATIM	Thu Jul 02 14:24:08 2009
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.30 usec
IRNUC	1H
CTEMP	27.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	10



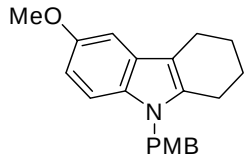


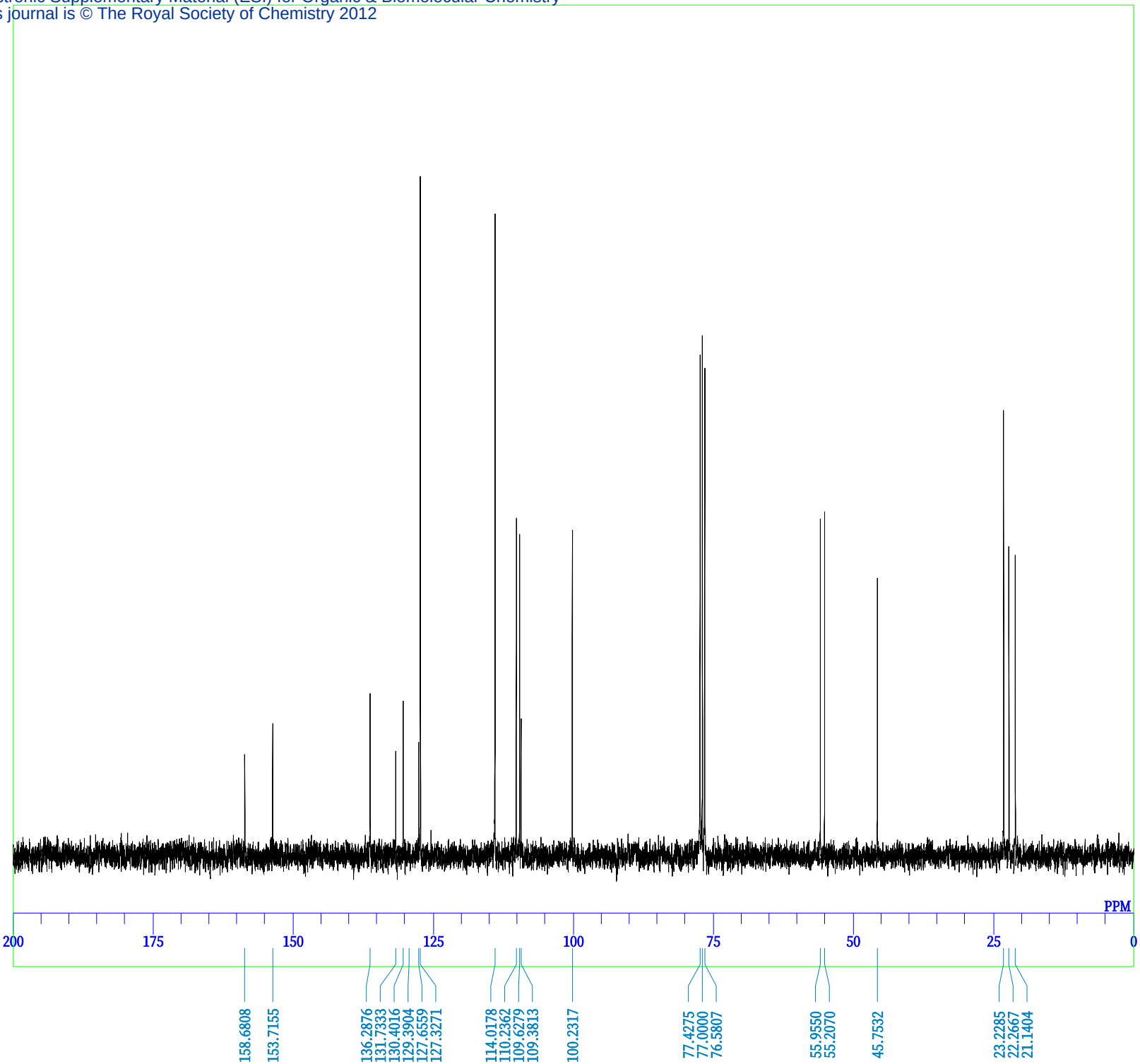
DFILE	2,3-DiMe-PMB 13C.als
COMNT	m083 Fr.5-6
DATIM	Thu Jul 02 19:20:40 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	500
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



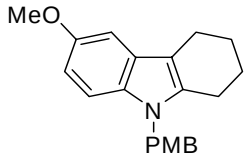


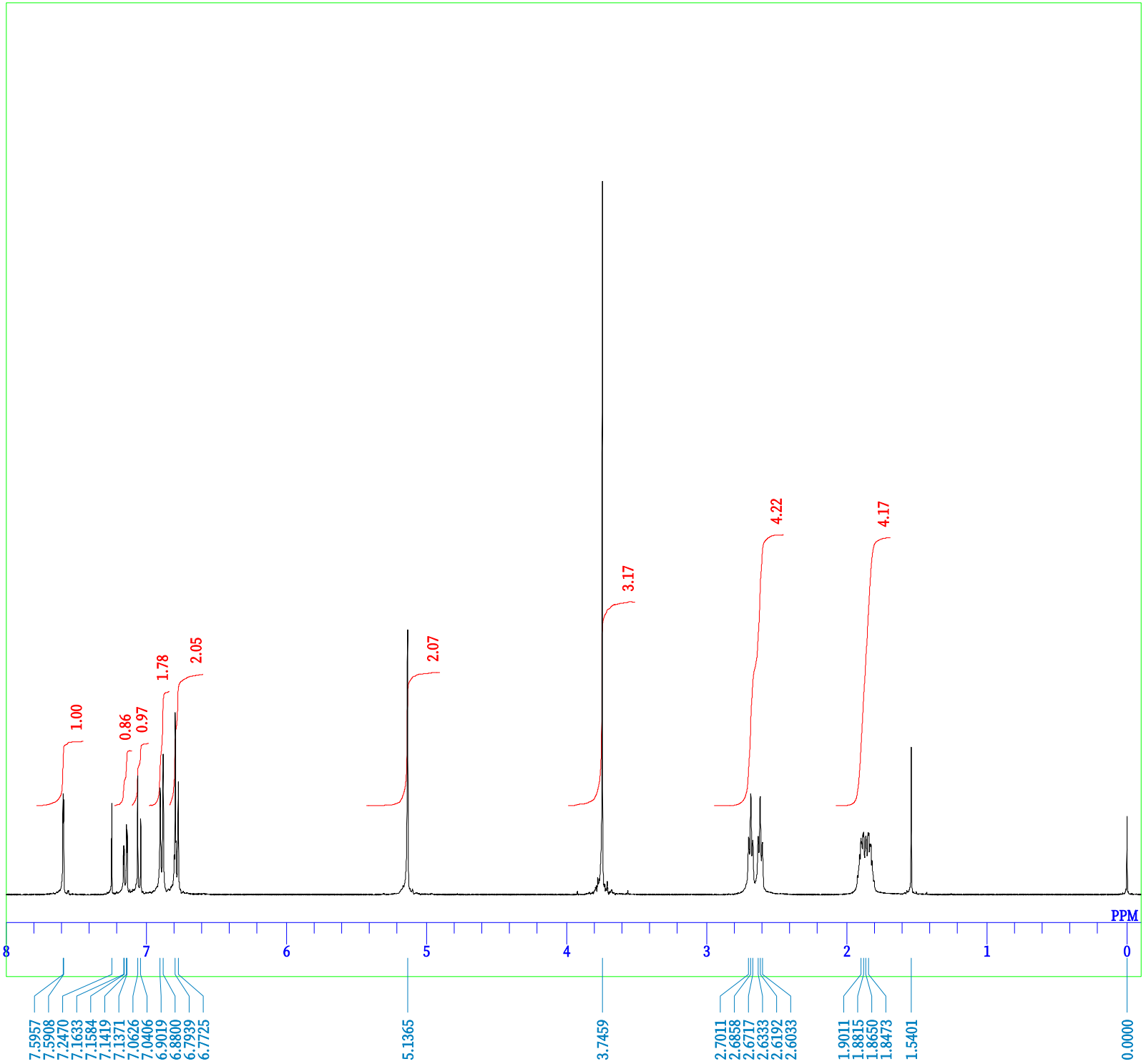
DFILE	MeO-6-PMB 1H.als
COMNT	MeO-6-PMB
DATIM	Wed Jan 26 09:10:52 2011
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.30 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	13

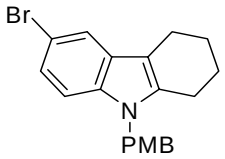


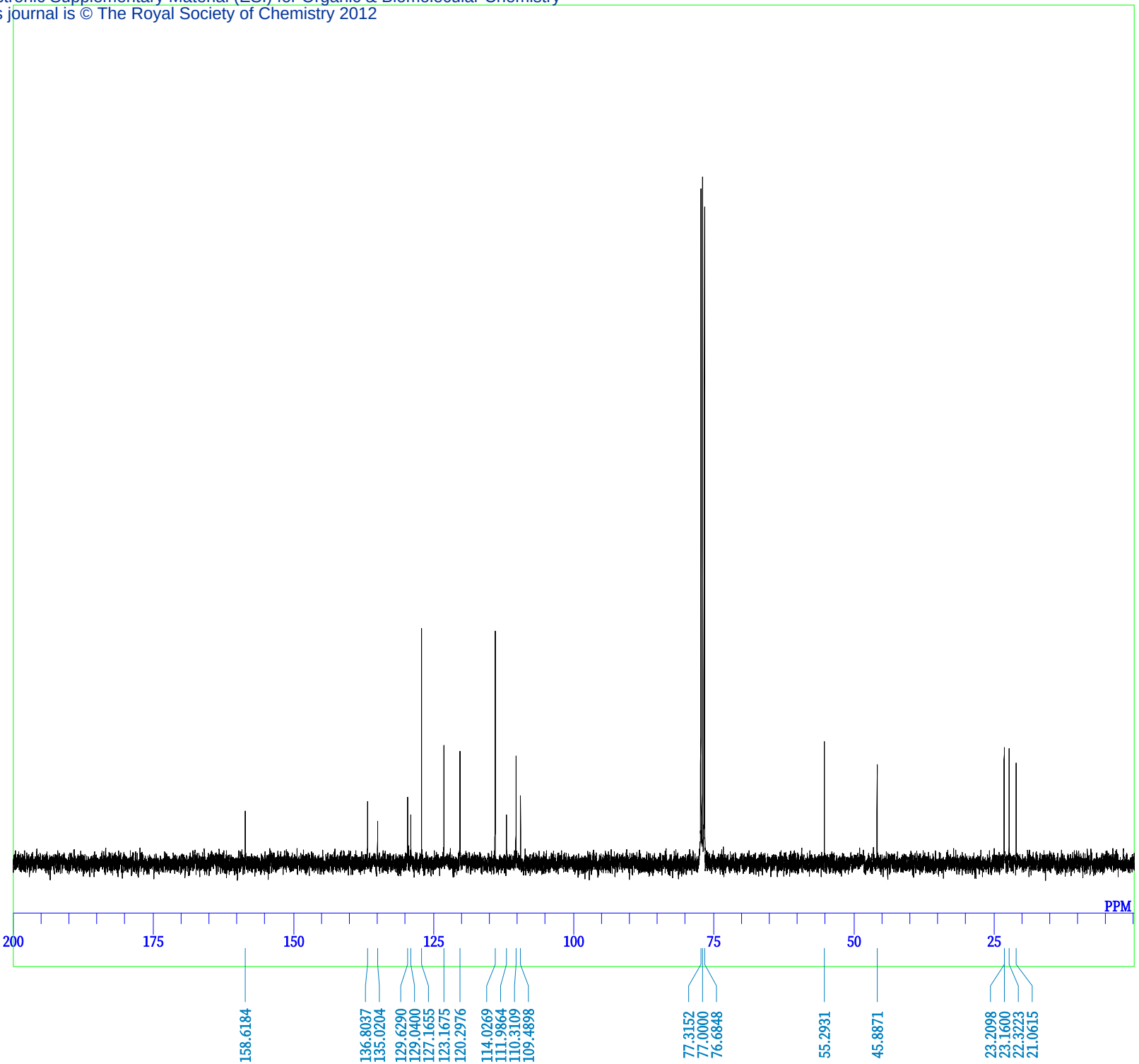


DFILE	MeO-6-PMB 13C.als
COMNT	MeO-6-PMB 13C
DATIM	Wed Jan 26 09:21:53 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	200
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	23

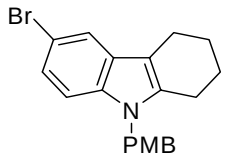


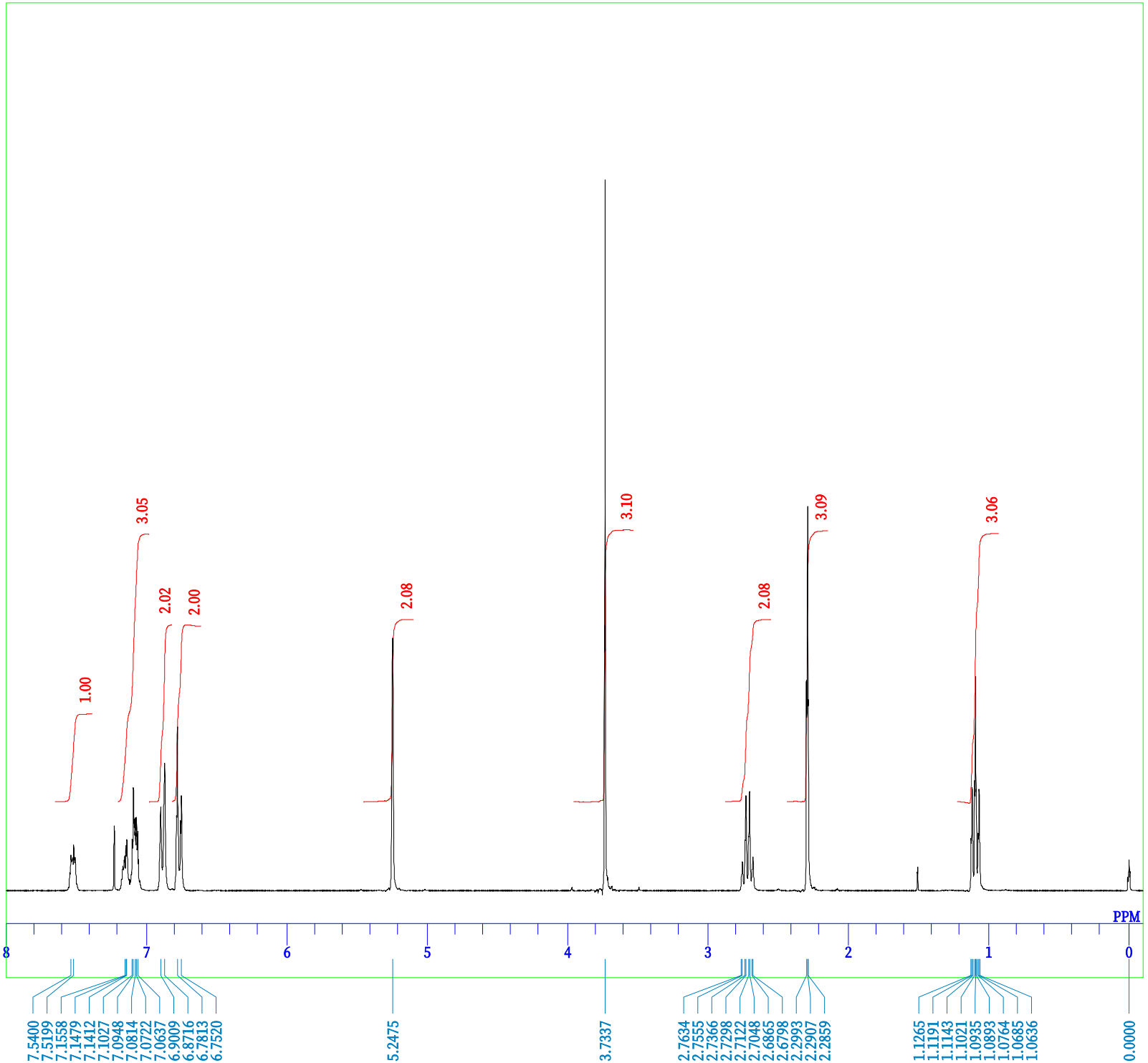


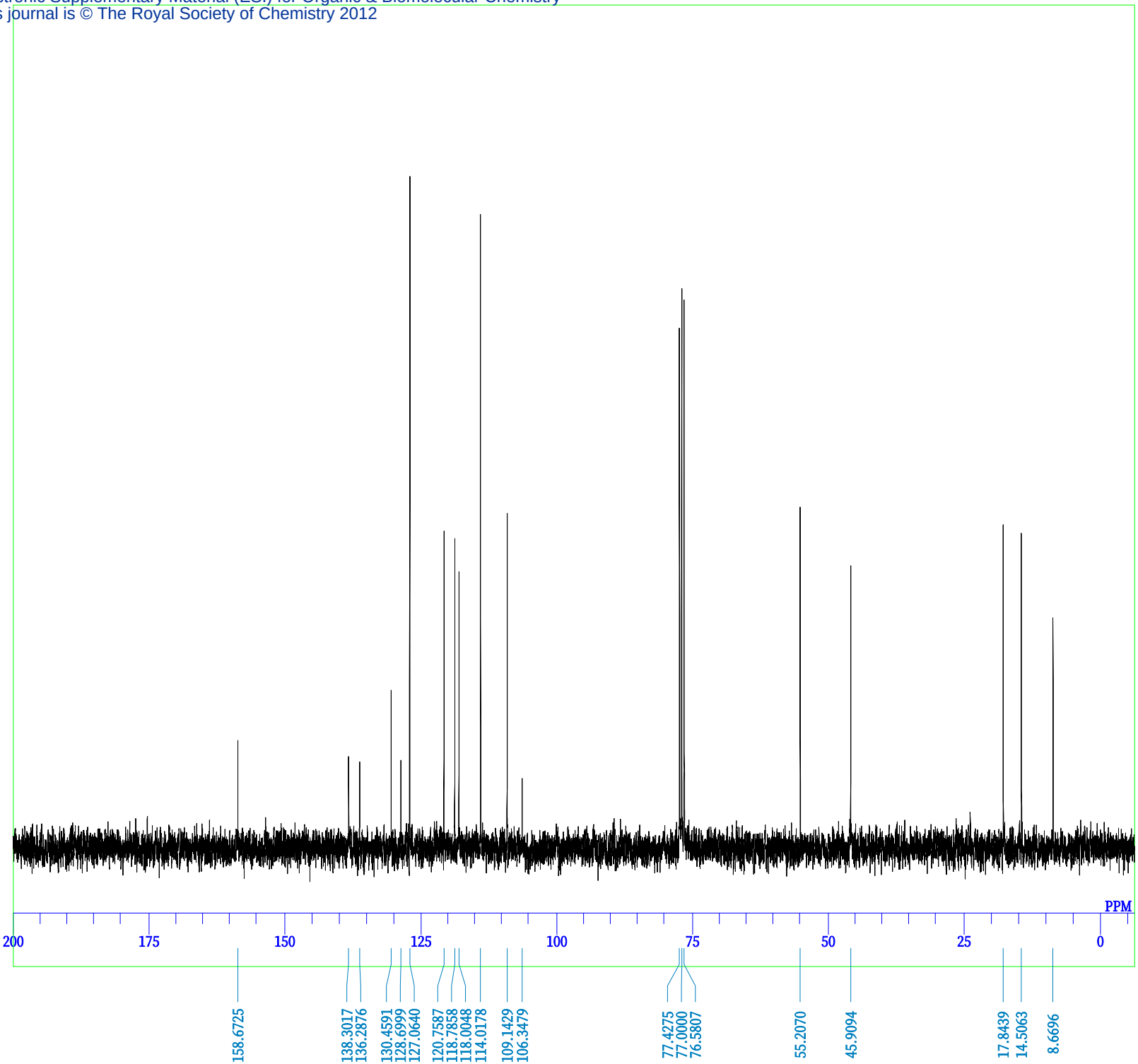




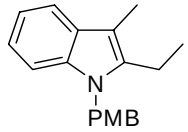
DFILE	Br-THC-PMB 13C FT.als
COMNT	Br-THC-PMB
DATIM	Sat Jun 26 13:47:38 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	200
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24

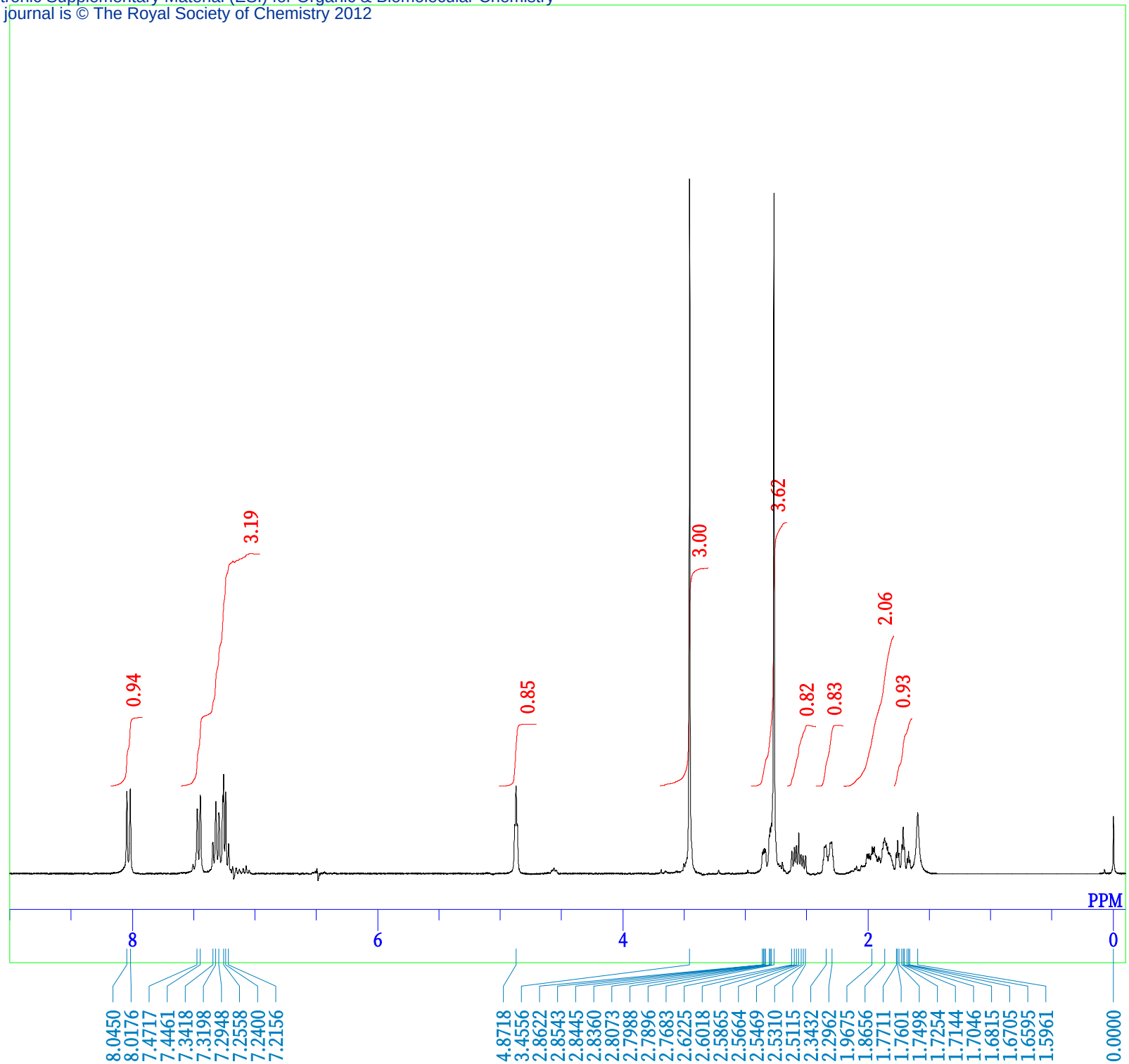




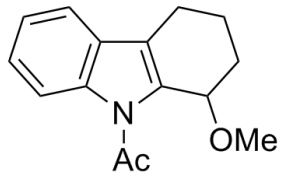


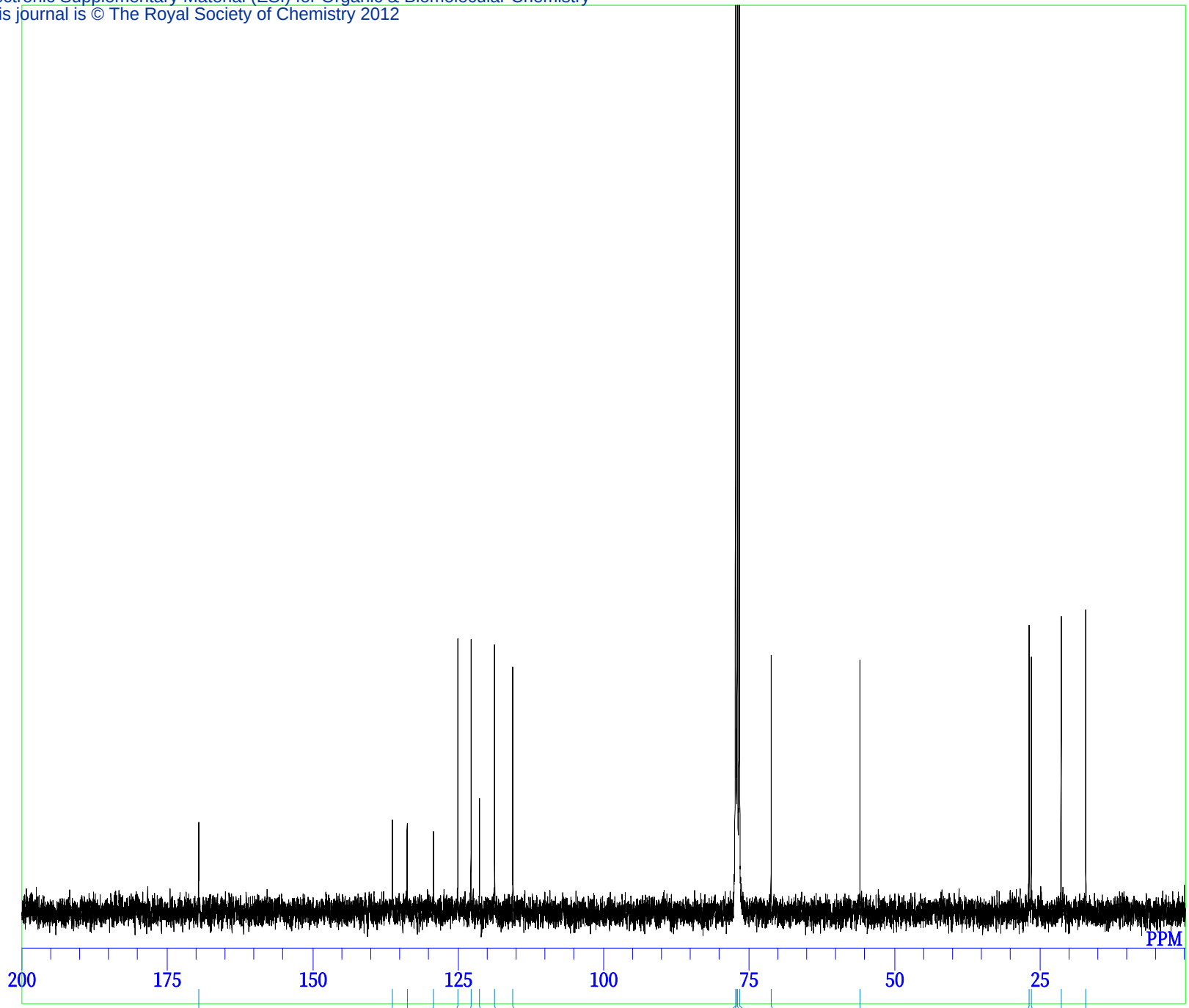
DFILE	m452 2E3M-PMB 13C.als
COMNT	m452 2E3M-PMB 13C
DATIM	Fri Jan 14 13:57:37 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	100
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	23



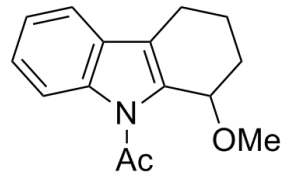


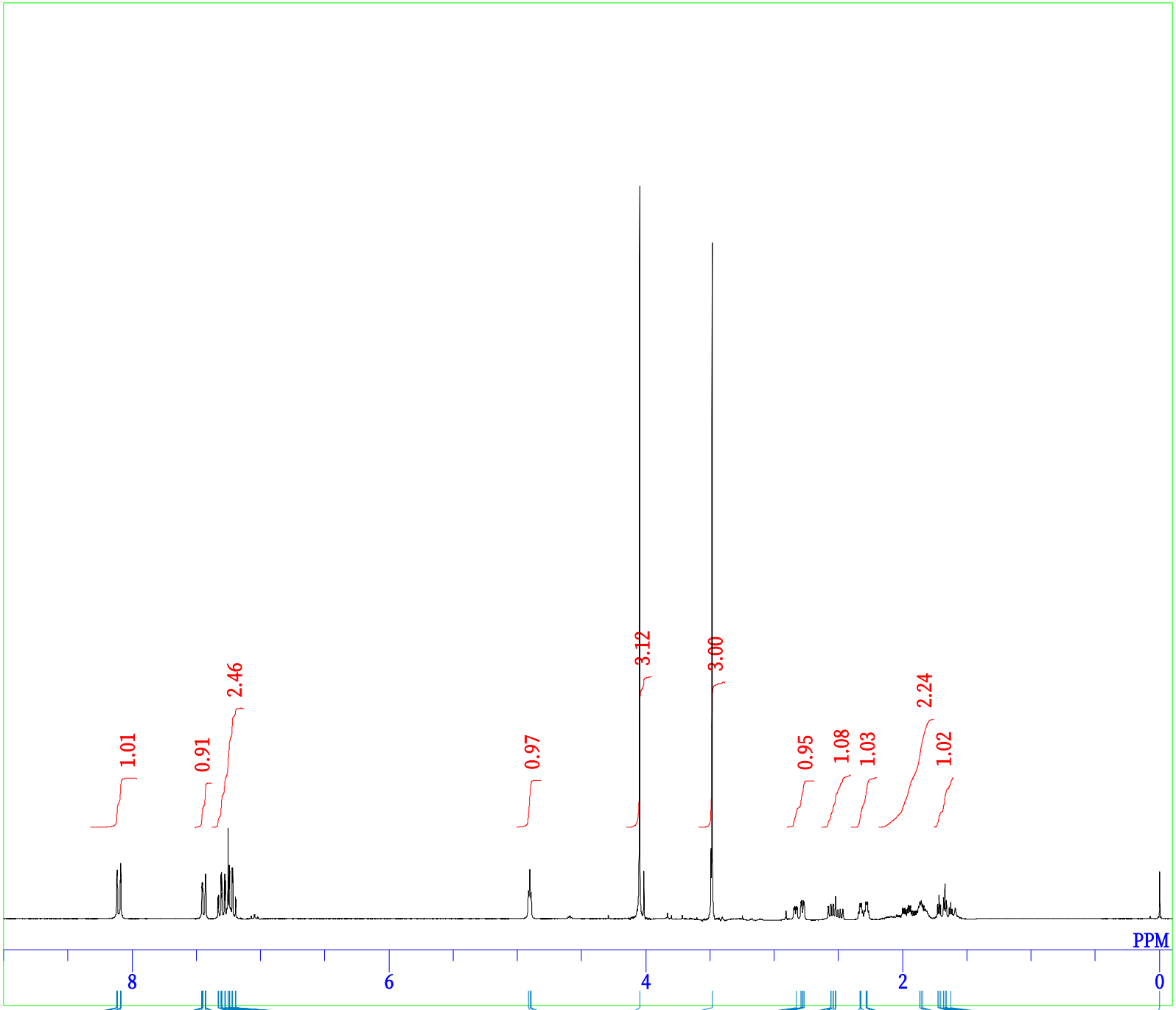
DFILE	6-Ac-OMe 1H.als
COMNT	m116 Fr.6-12
DATIM	Wed Aug 19 10:56:14 2009
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.30 usec
IRNUC	1H
CTEMP	27.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	16



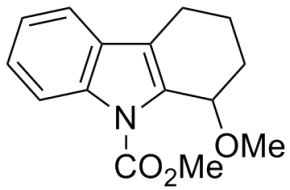


DFILE	6-Ac-OMe 13C.als
COMNT	m116 N-Ac -OMe
DATIM	Thu Aug 20 12:54:18 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	2100
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	26.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24

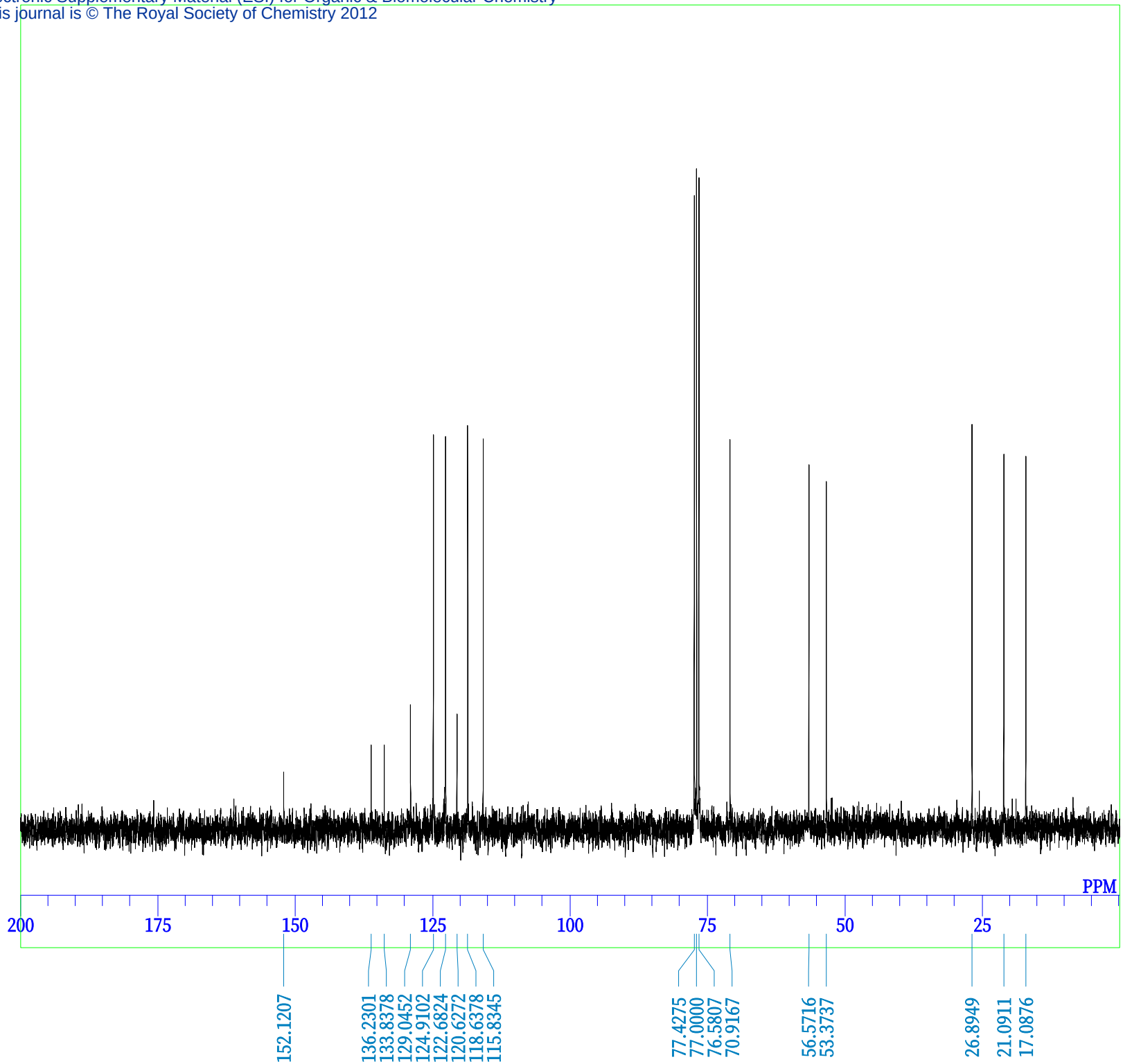




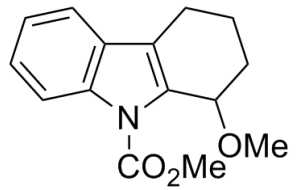
DFILE	6-CO2Me-OMe 1H.als
COMNT	CO2Me -OMe
DATIM	Wed Oct 06 13:04:41 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	26.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	13

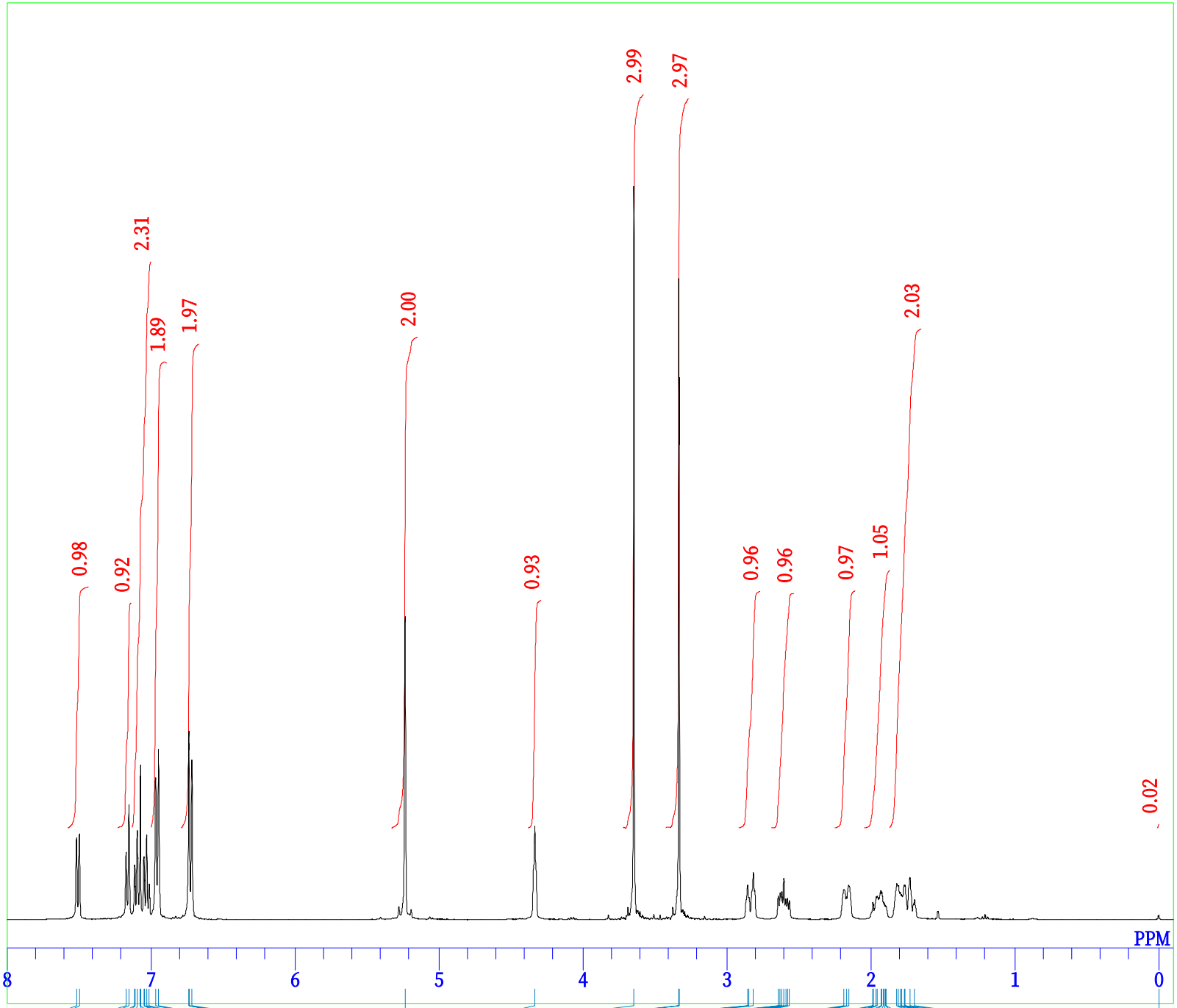


8.1188 8.1164 8.1133 8.0914 8.0889 8.0859 7.4565 7.4540 7.4522 7.4491 7.4308 7.4290 7.4266 7.4241 7.3308 7.3266 7.3070 7.3028 7.2985 7.2796 7.2747 7.2522 7.2448 7.2412 7.2198 7.2162 7.1954 7.1918 4.9132 4.9035 4.8937 4.0490 3.4849 2.8293 2.7921 2.7866 2.7744 2.7683 2.5609 2.5579 2.5432 2.5402 2.5231 2.5200 2.3334 2.3285 2.3231 2.2877 2.2822 2.2761 1.8687 1.8565 1.8443 1.7284 1.7174 1.7065 1.6827 1.6717 1.6607 1.6266 0.0000

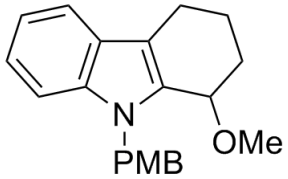


DFILE	6-CO2Me-OMe 13C.als
COMNT	CO2Me -OMe 13C
DATIM	Wed Oct 06 13:15:46 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	200
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	26.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	23

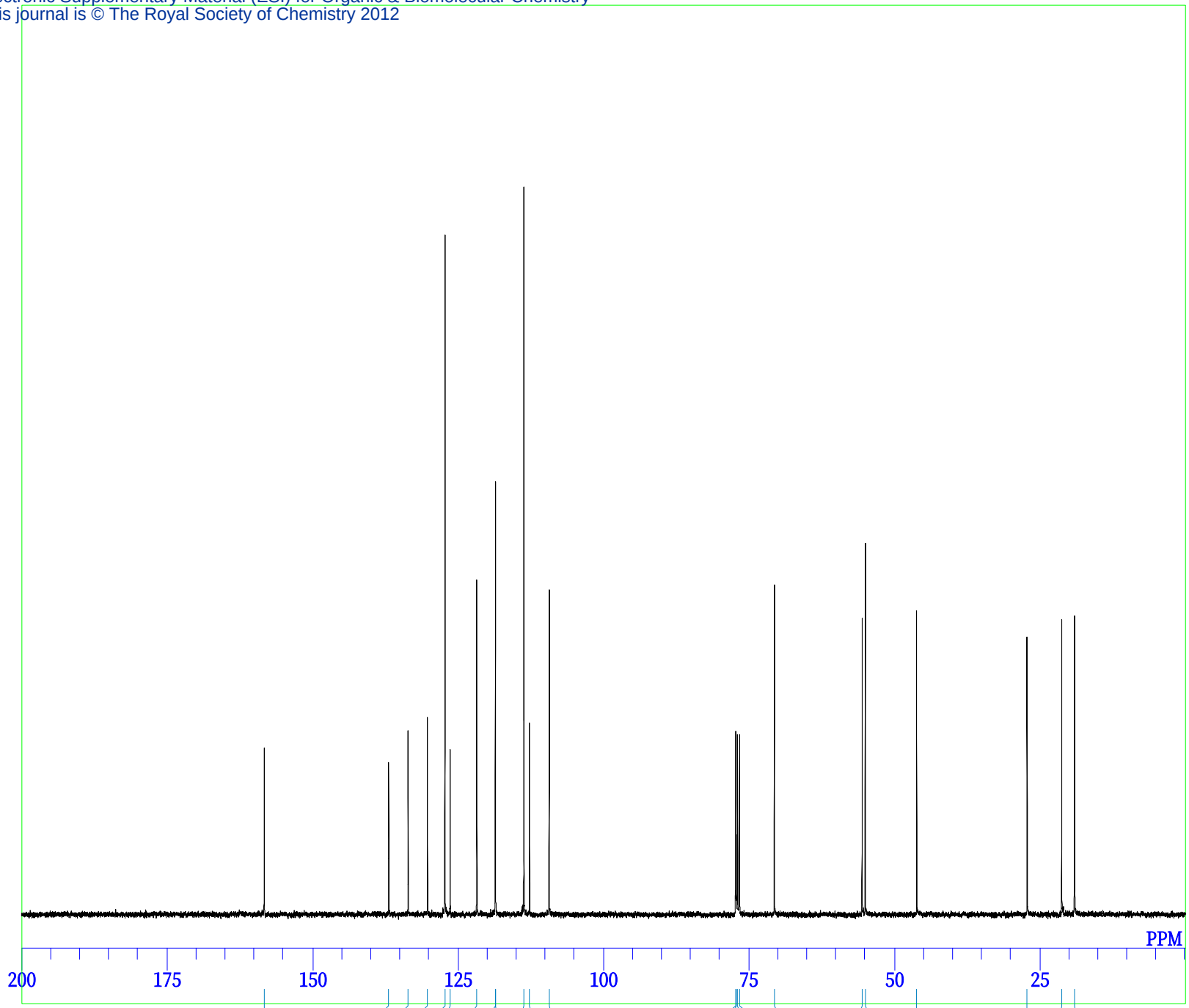




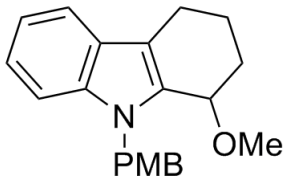
DFILE	6-PMB-OMe 1H FT.als
COMNT	6-PMB-OMe
DATIM	Tue Jun 22 11:04:23 2010
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	7993.60 Hz
SCANS	4
ACQTM	4.0993 sec
PD	2.9010 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	7

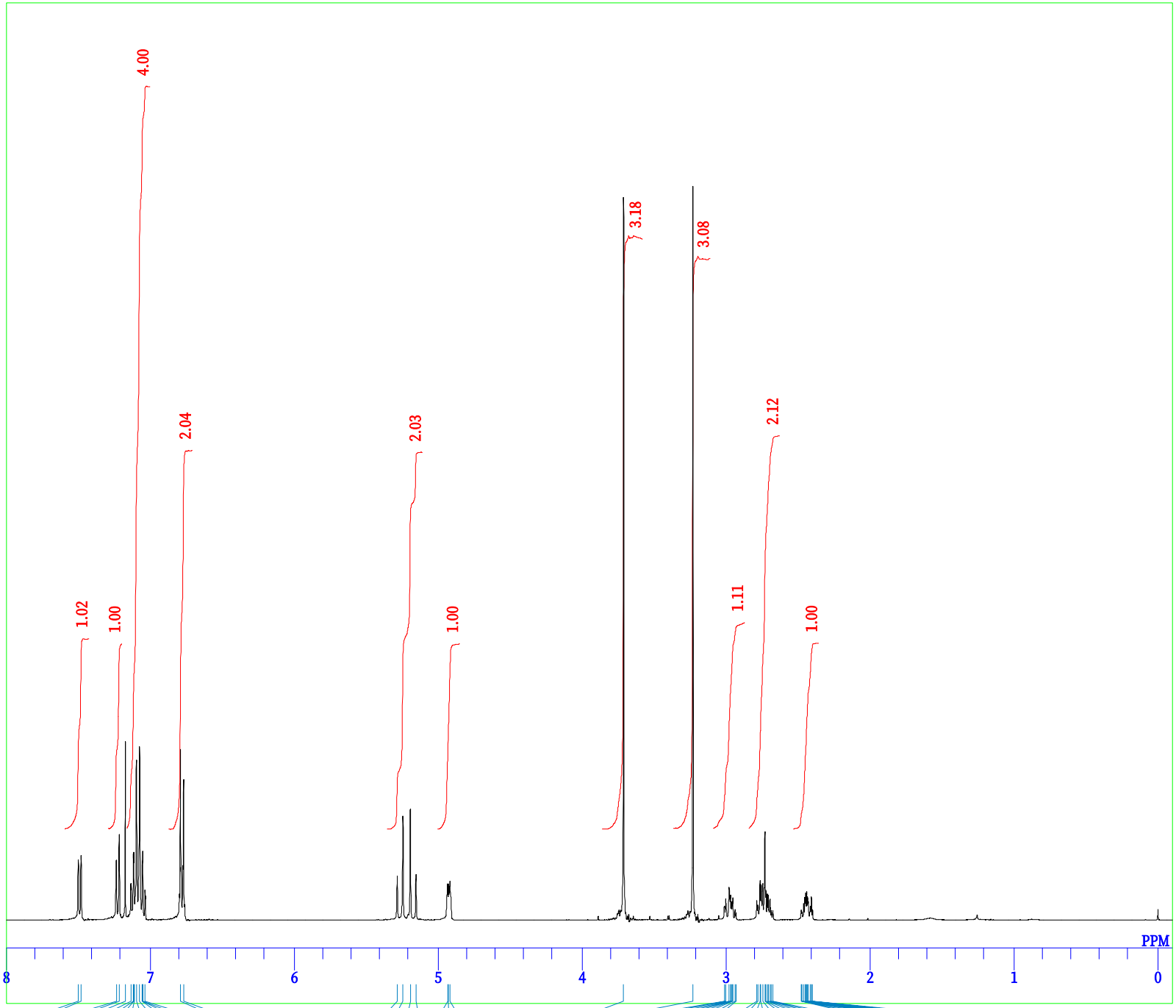


7.5188 7.4993 7.1753 7.1551 7.1149 7.1106 7.0966 7.0758 7.0740 7.0508 7.0459 7.0319 7.0142 6.9696 6.9495 6.7396 6.7366 6.7182 5.2373 4.3360 3.6484 3.3359 3.3323 2.8582 2.8484 2.8185 2.6458 2.6324 2.6208 2.6068 2.5933 2.5811 2.5677 2.1906 2.1717 2.1564 1.9880 1.9844 1.9648 1.9581 1.9331 1.9264 1.9142 1.9081 1.9014 1.8959 1.8220 1.8111 1.7976 1.7891 1.7708 1.7641 1.7317 1.6982 0.0000

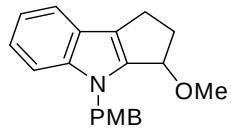


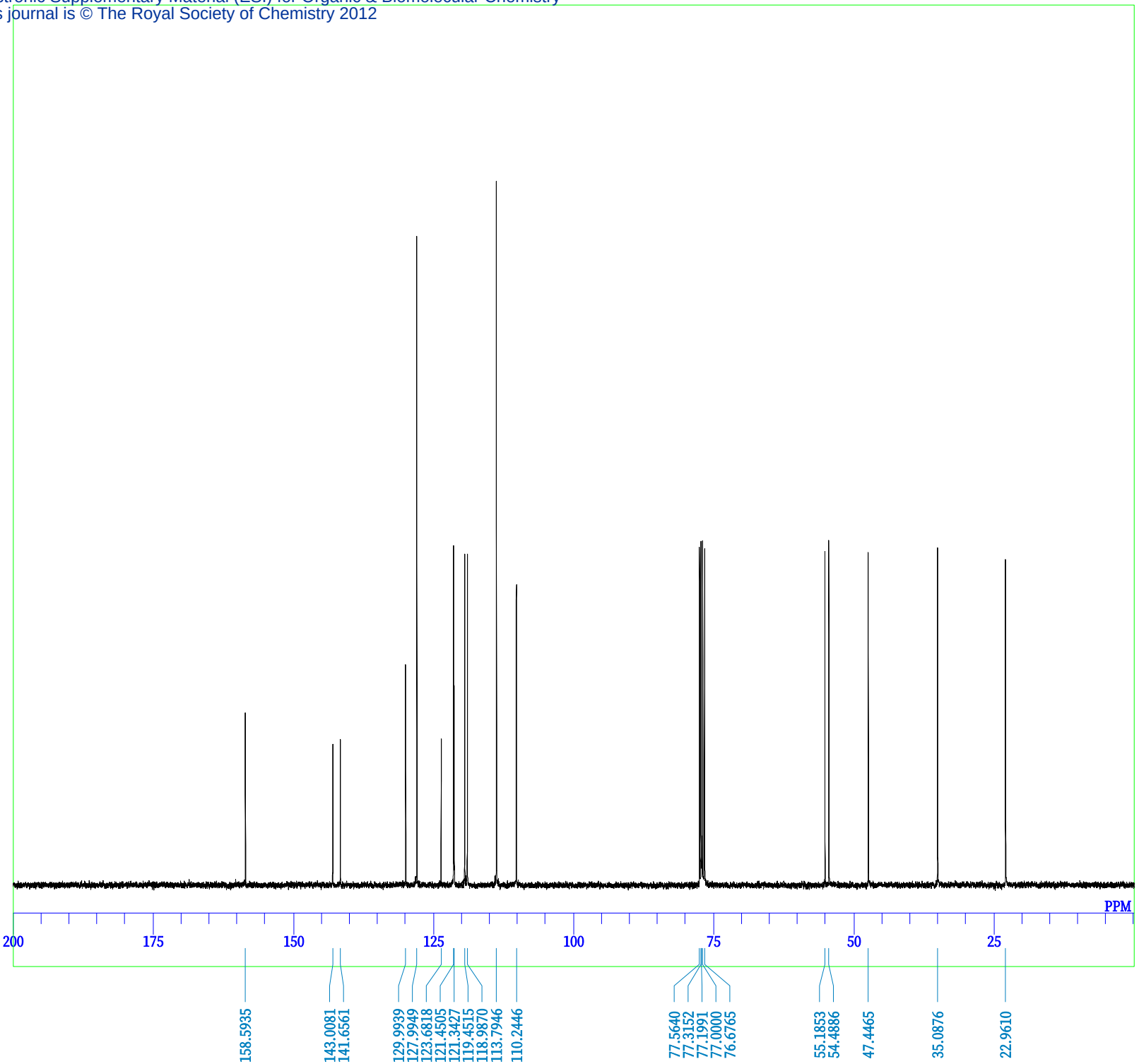
DFILE	3a C.als
COMNT	6-PMB-OMe
DATIM	Tue Jun 22 11:16:33 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	200
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



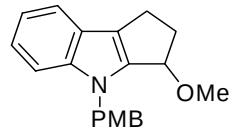


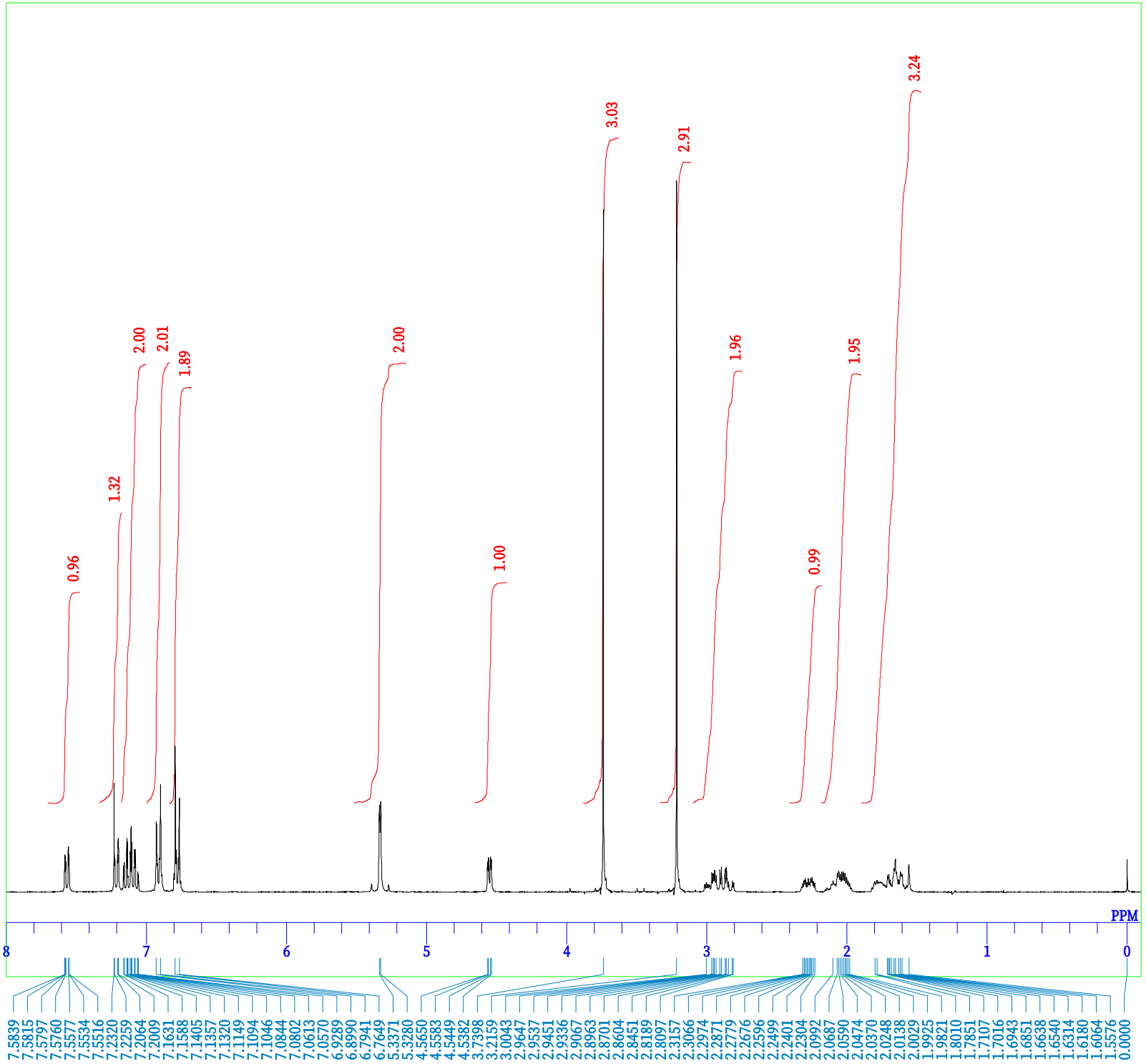
DFILE	Auto1NON_E1_FT.als
COMNT	m112 5-ring-OMe
DATIM	Sat Aug 22 09:11:42 2009
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	8000.00 Hz
SCANS	4
ACQTM	4.0960 sec
PD	2.9010 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	9



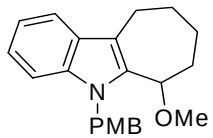


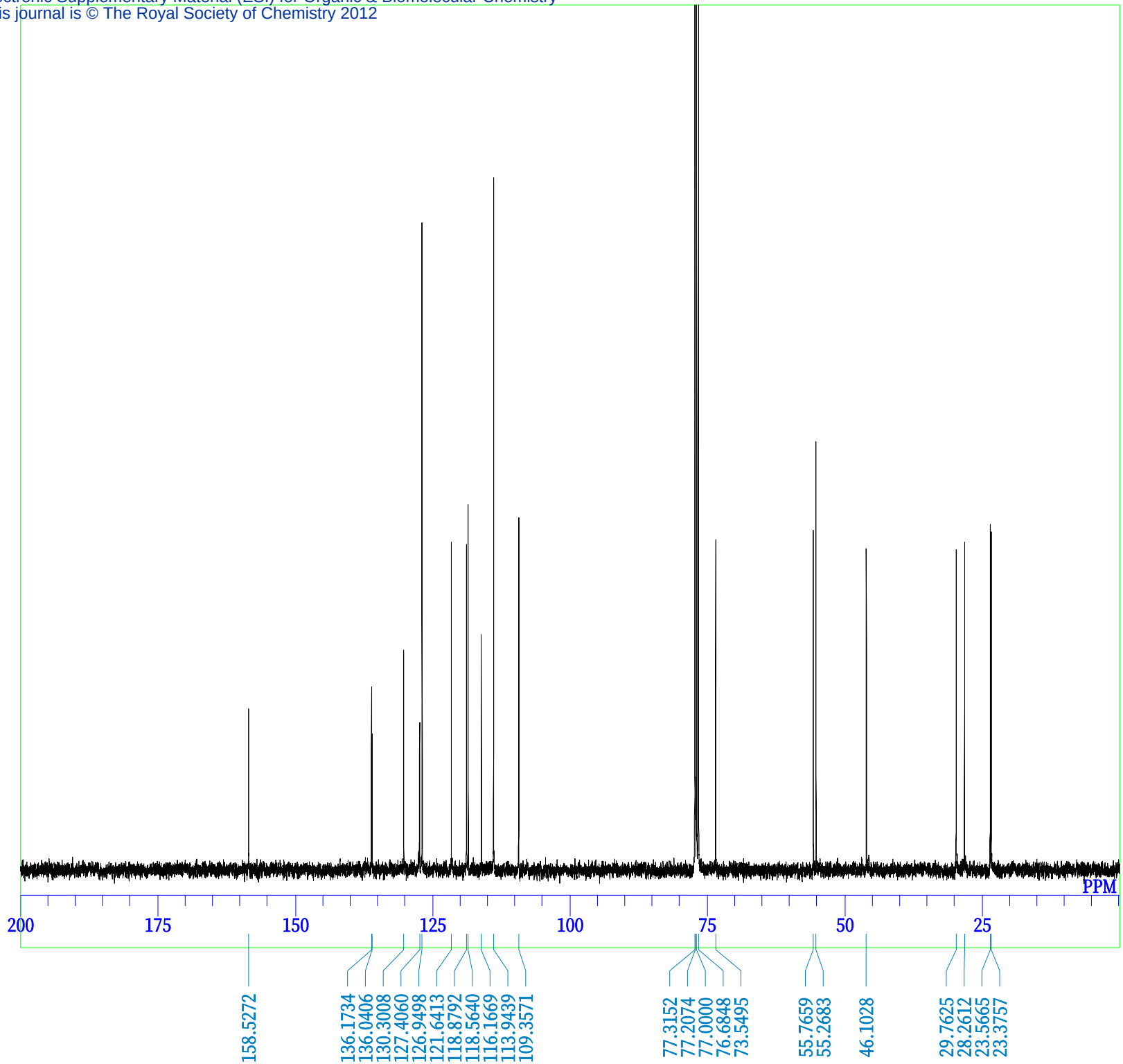
DFILE	Auto1BCM_E1_FT.als
COMNT	m112 Fr.8-20
DATIM	Sat Aug 01 11:27:30 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	600
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	26.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



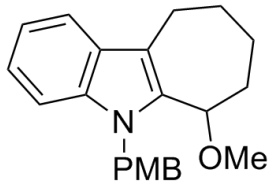


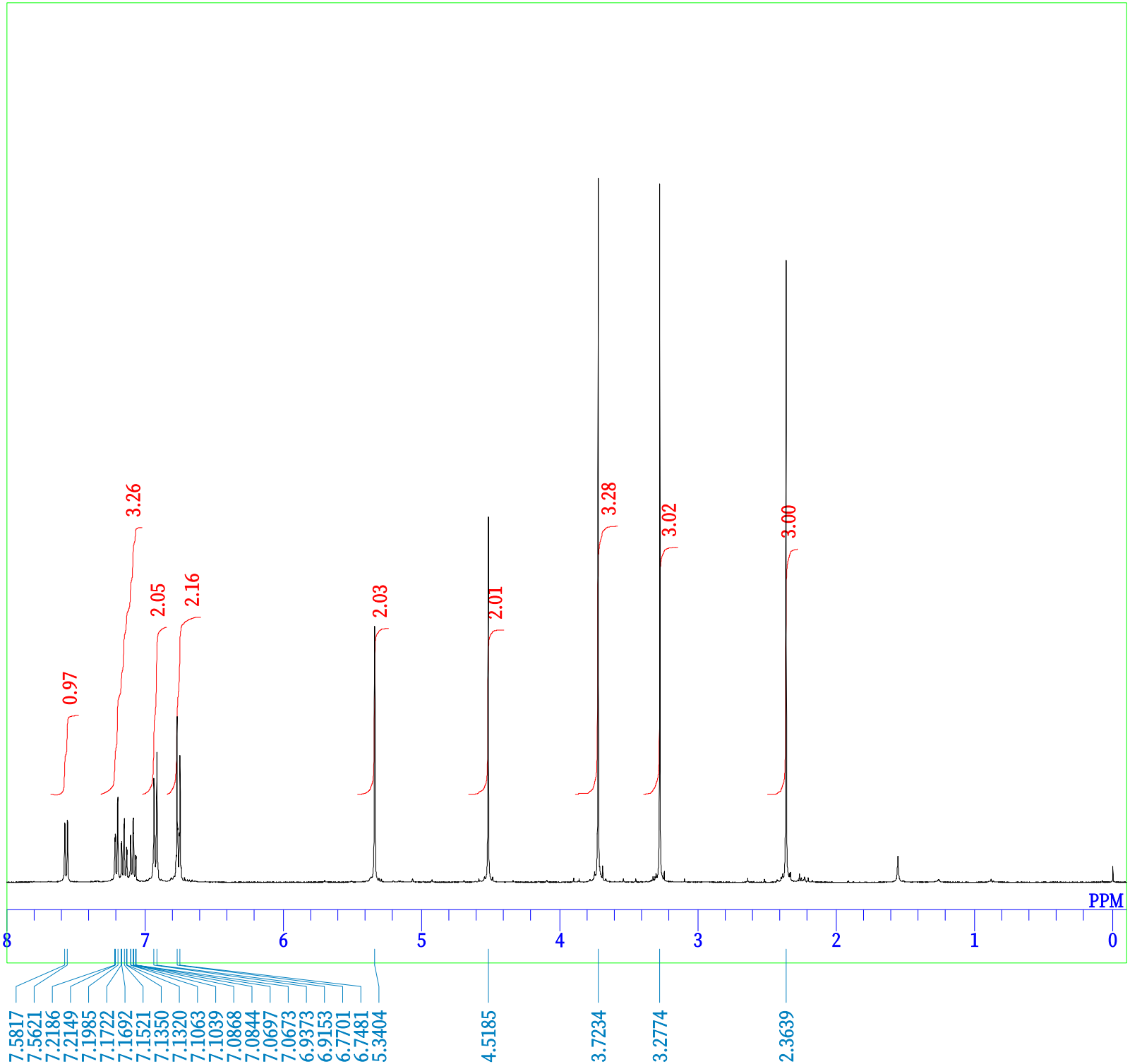
DFILE	7-PMB-OMe 1H FT.als
COMNT	7-PMB-OMe
DATIM	Wed Jul 14 11:09:35 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	27.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	12



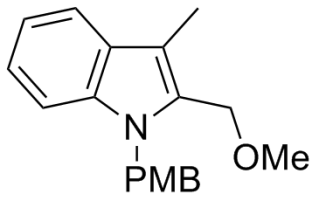


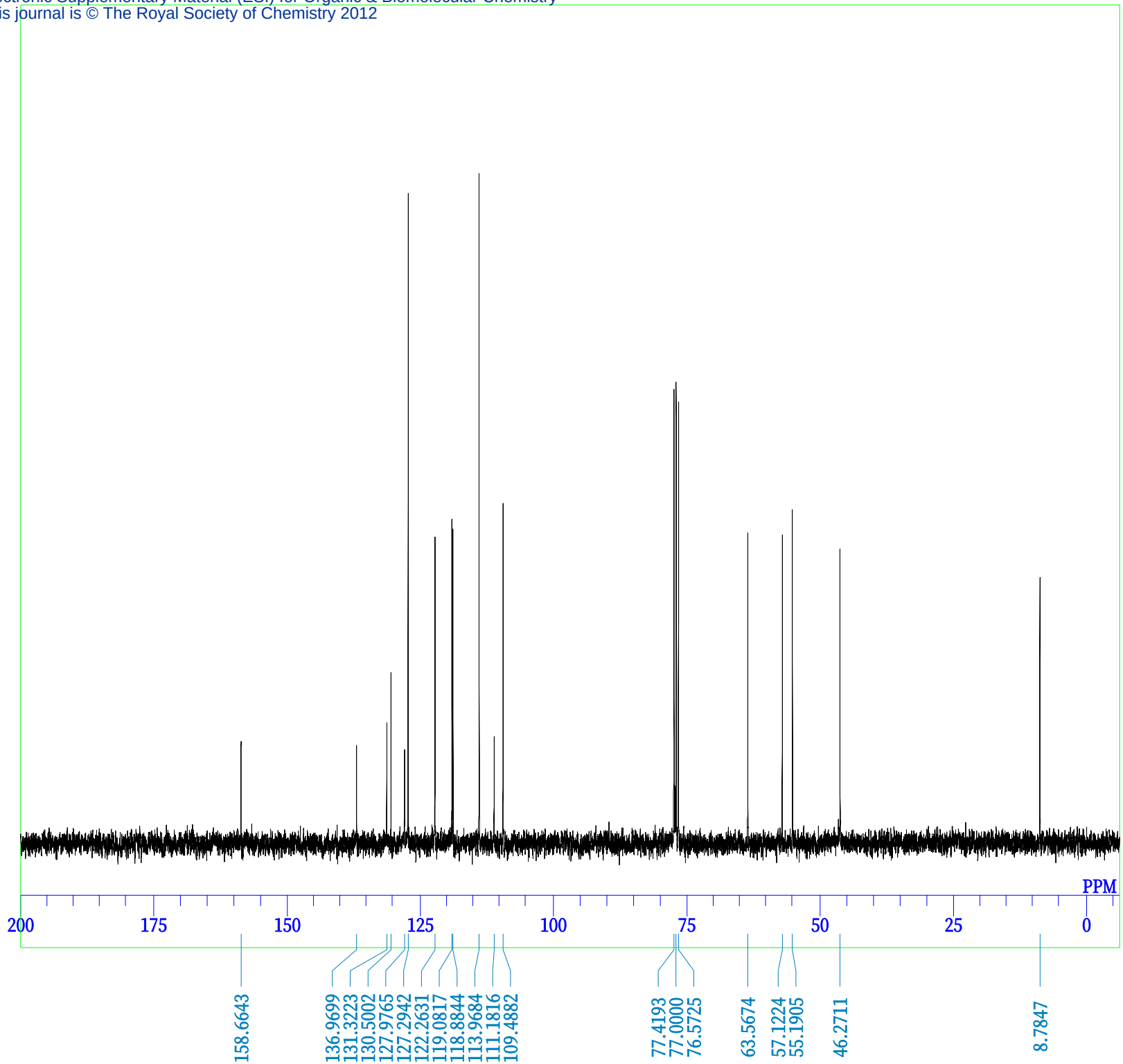
DFILE	7-PMB-OMe 13C.als
COMNT	m113 7ring -OMe
DATIM	Sat Aug 01 13:03:41 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	600
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	26.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



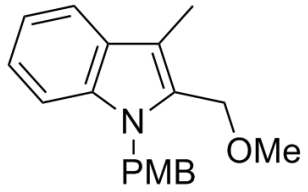


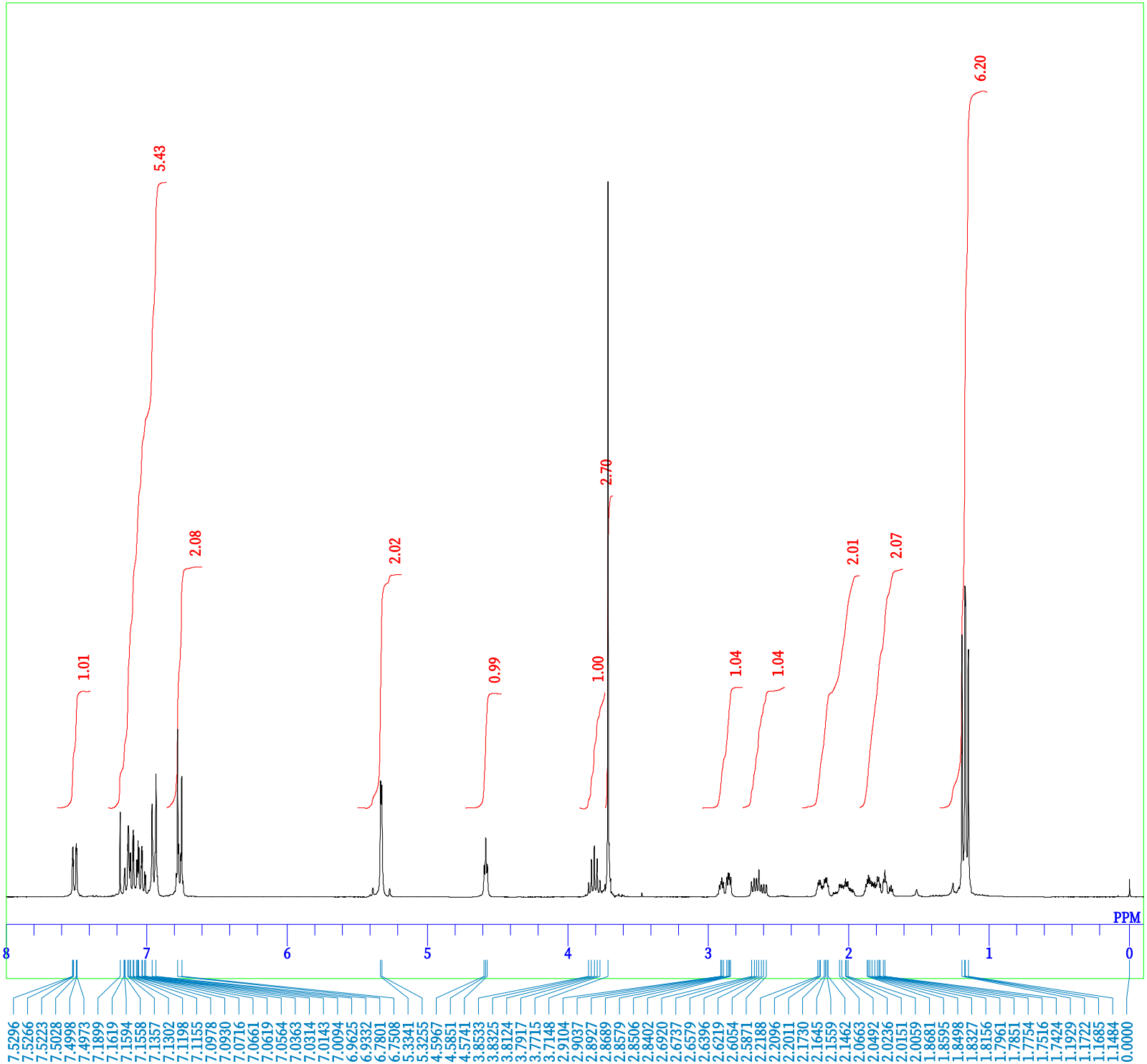
DFILE	DiMe-PMB-OMe 1H.als
COMNT	m083 2,3-diMe-PMB AP
DATIM	Fri Jul 24 16:38:19 2009
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	7993.60 Hz
SCANS	4
ACQTM	4.0993 sec
PD	2.9010 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	13



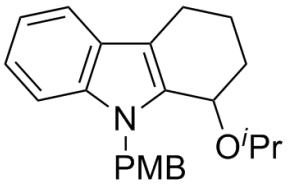


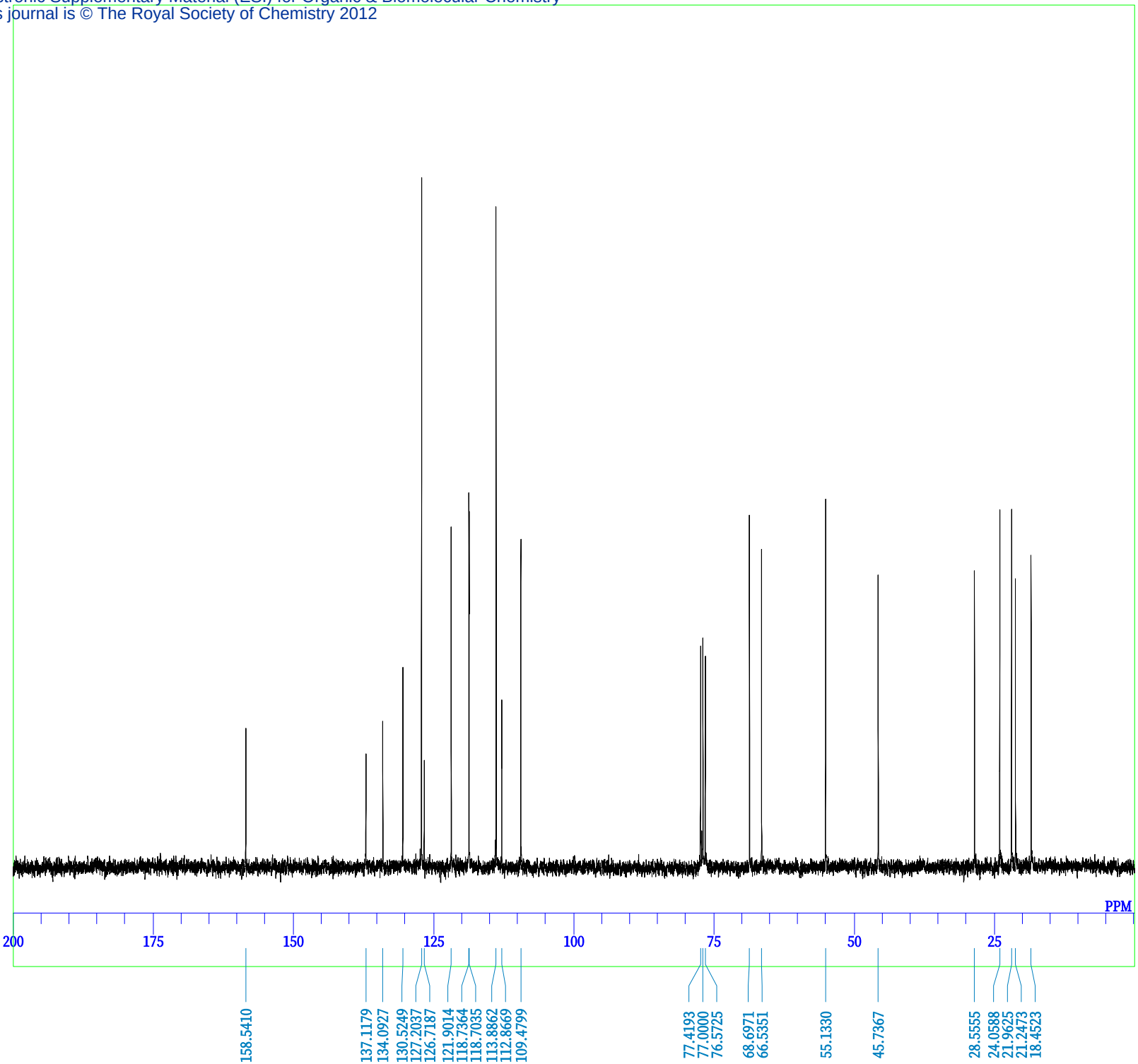
DFILE	DiMe-PMB-OMe 13C.als
COMNT	DiMe-PMB-OMe
DATIM	Fri Oct 08 15:17:02 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	200
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	26.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



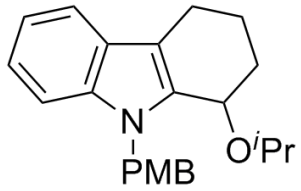


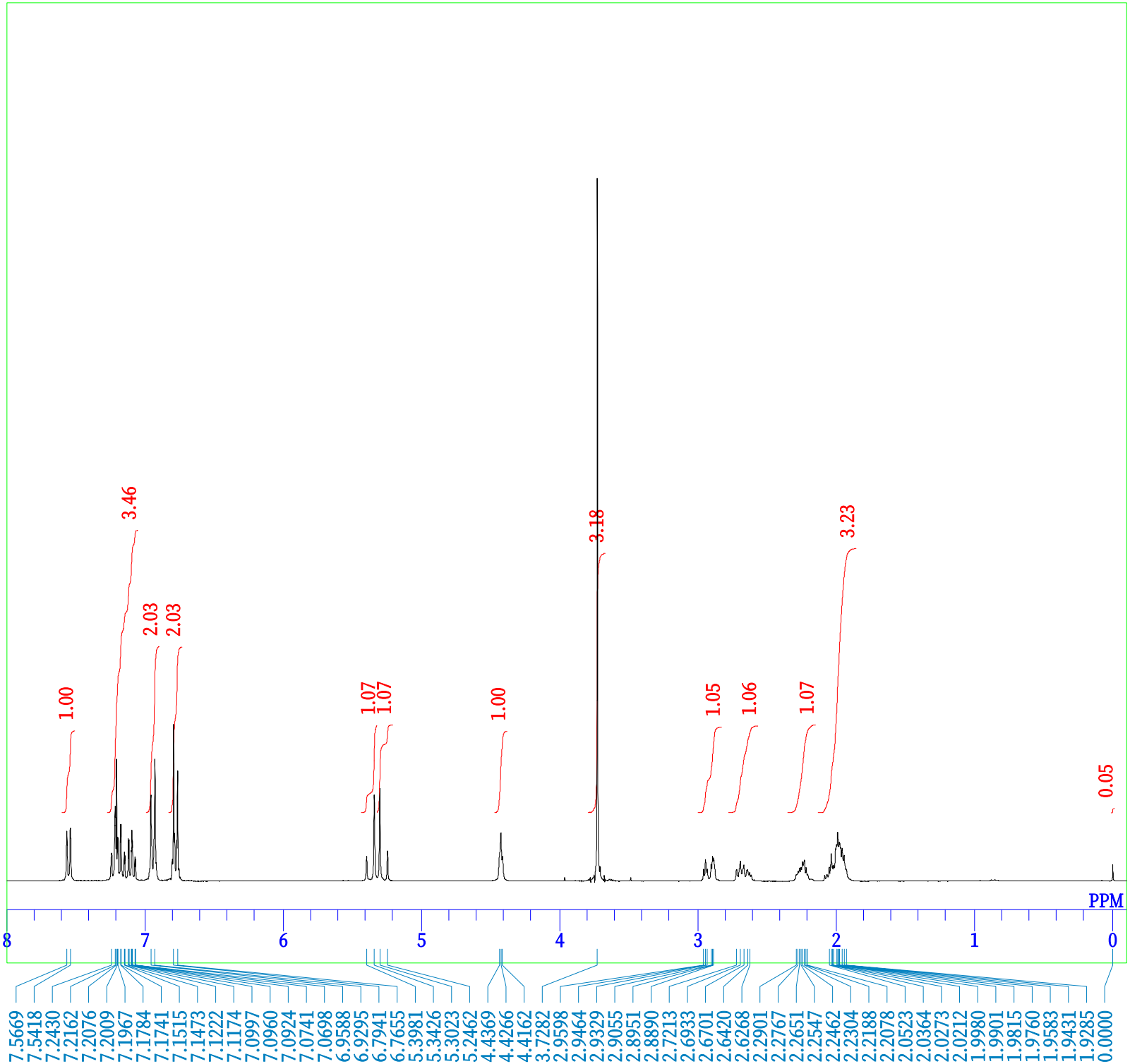
DFILE	6-PMB-OPr 1H.als
COMNT	iPrOH
DATIM	Fri Oct 01 18:05:40 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	16
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	9



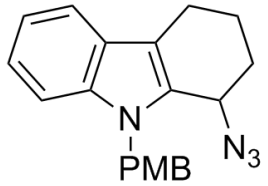


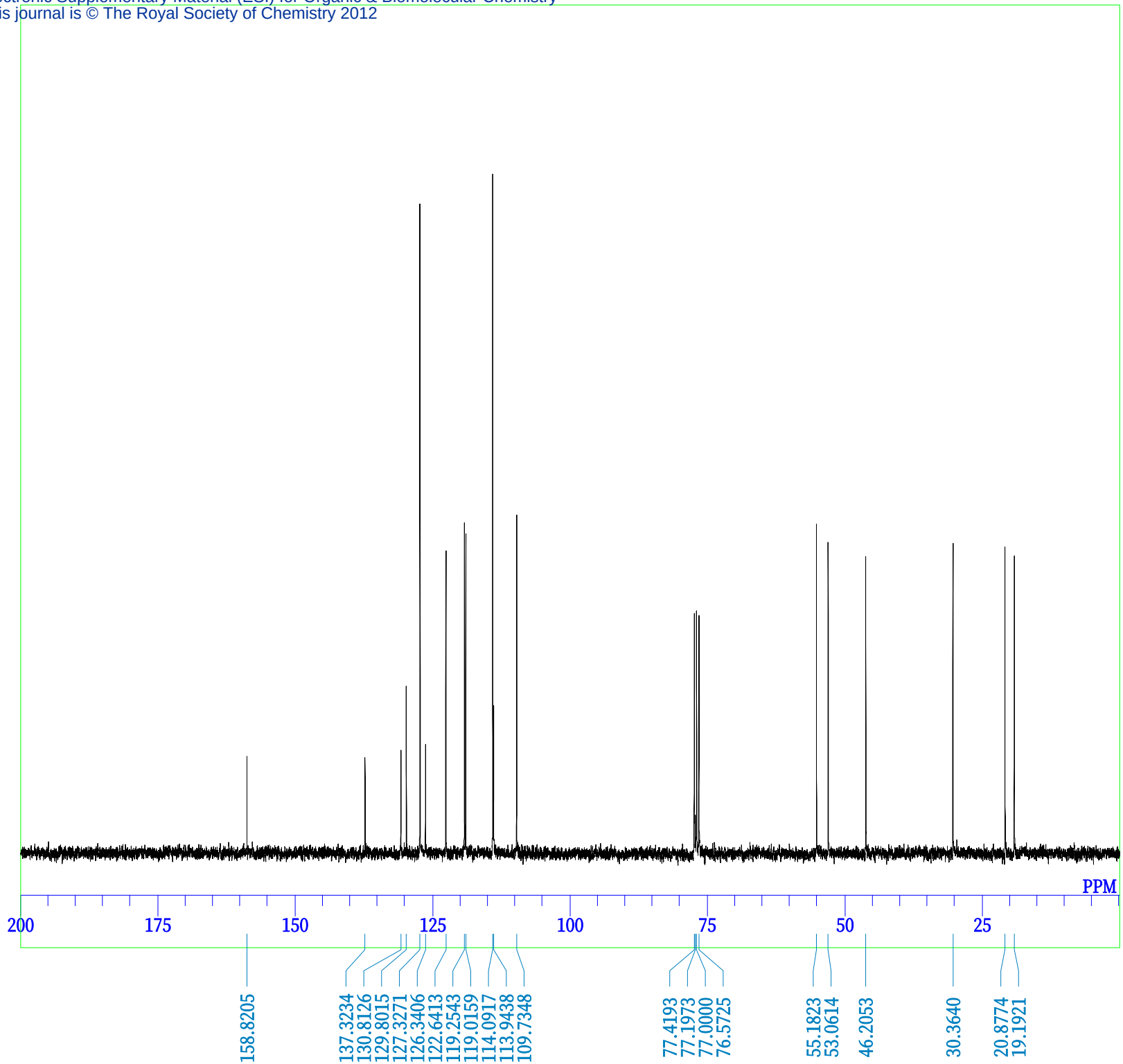
DFILE	6-PMB-OPr 13C.als
COMNT	iPrOH 13C
DATIM	Fri Oct 01 18:13:03 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	120
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	26.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	22



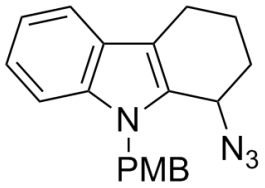


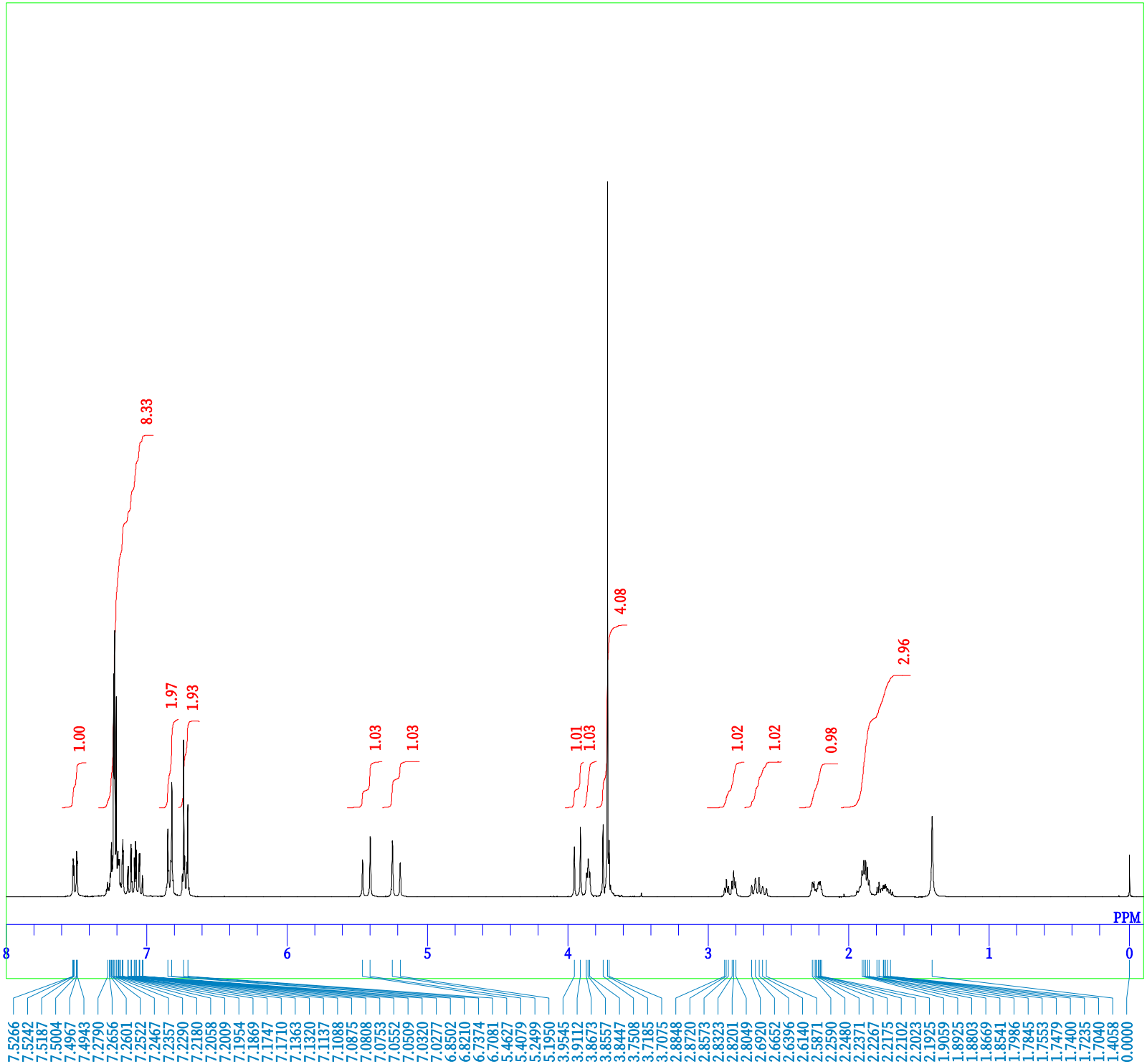
DFILE	6-PMB-N3 1H FT.als
COMNT	6-PMB-N3 1H
DATIM	Fri Jul 16 15:38:22 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	27.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	11



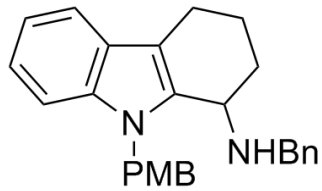


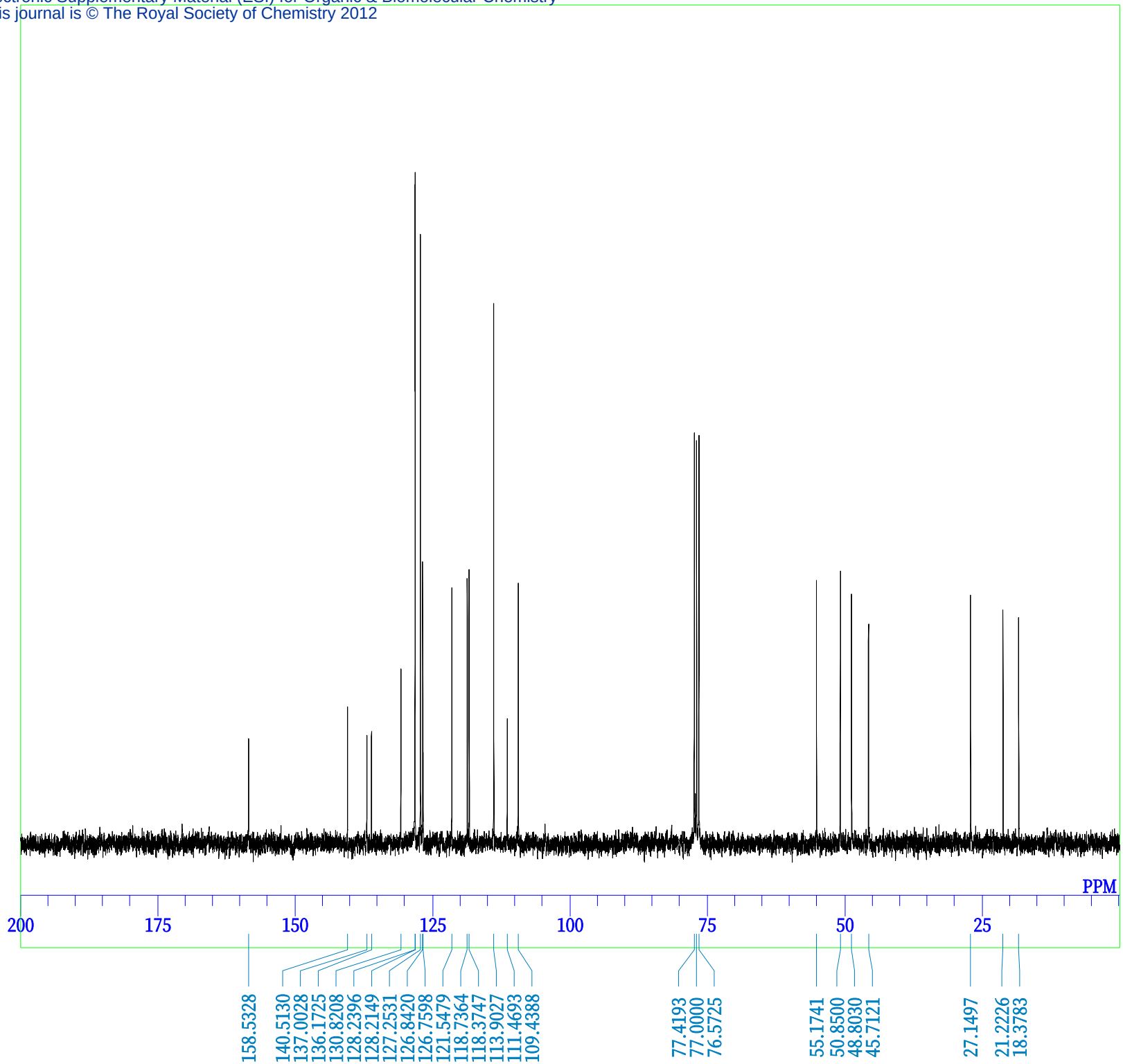
DFILE	6-PMB-N3 13C FT.als
COMNT	6-PMB-N3 13C
DATIM	Fri Jul 16 15:53:14 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	200
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	27.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



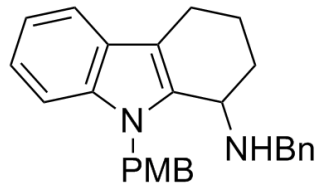


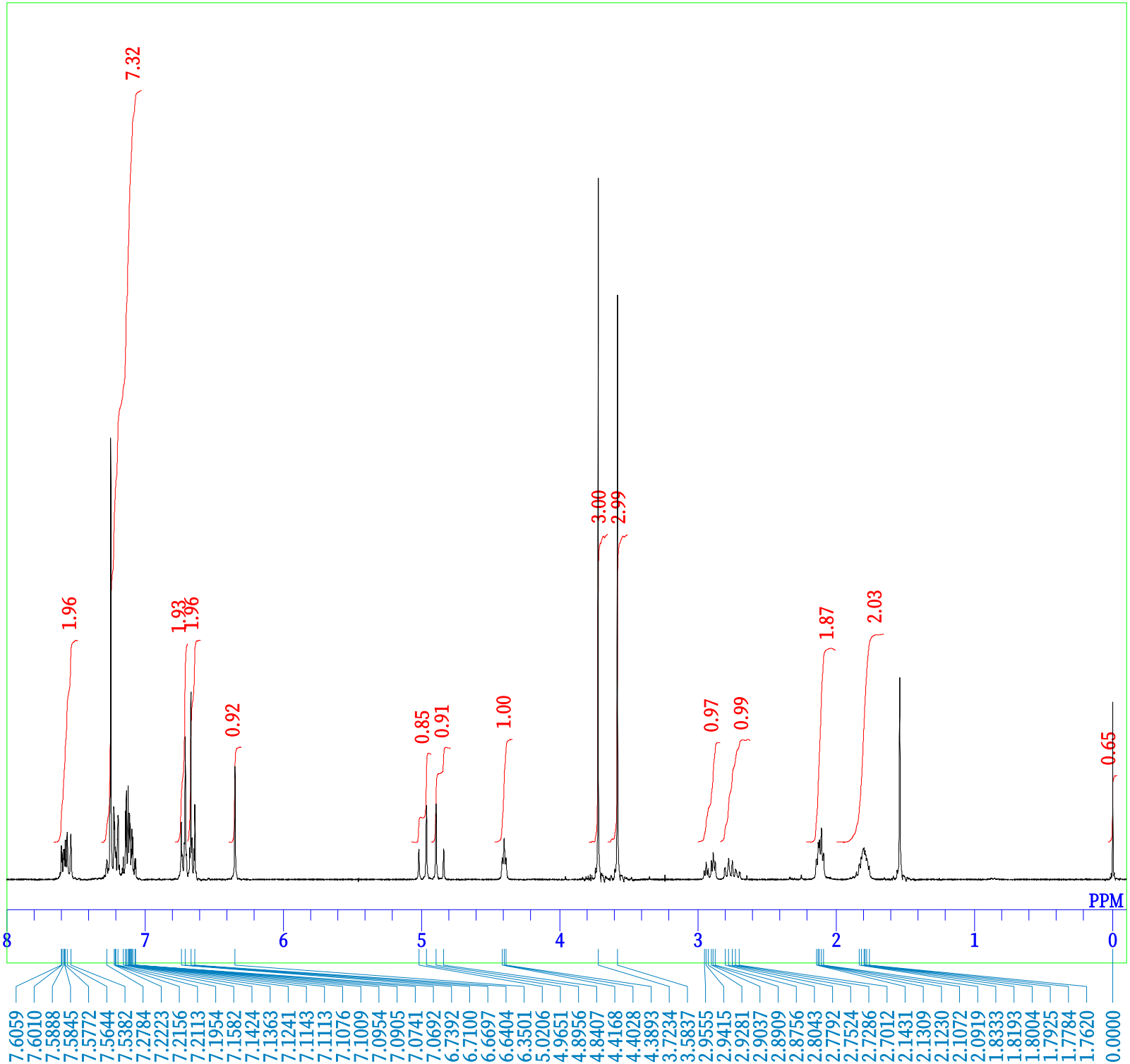
DFILE	6-PMB-NHBn 1H.als
COMNT	m347
DATIM	Wed Sep 29 16:04:18 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	16
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	26.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	12



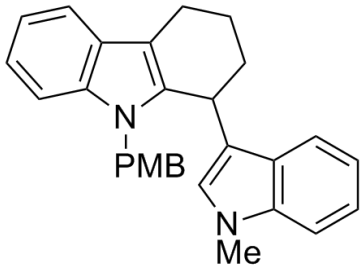


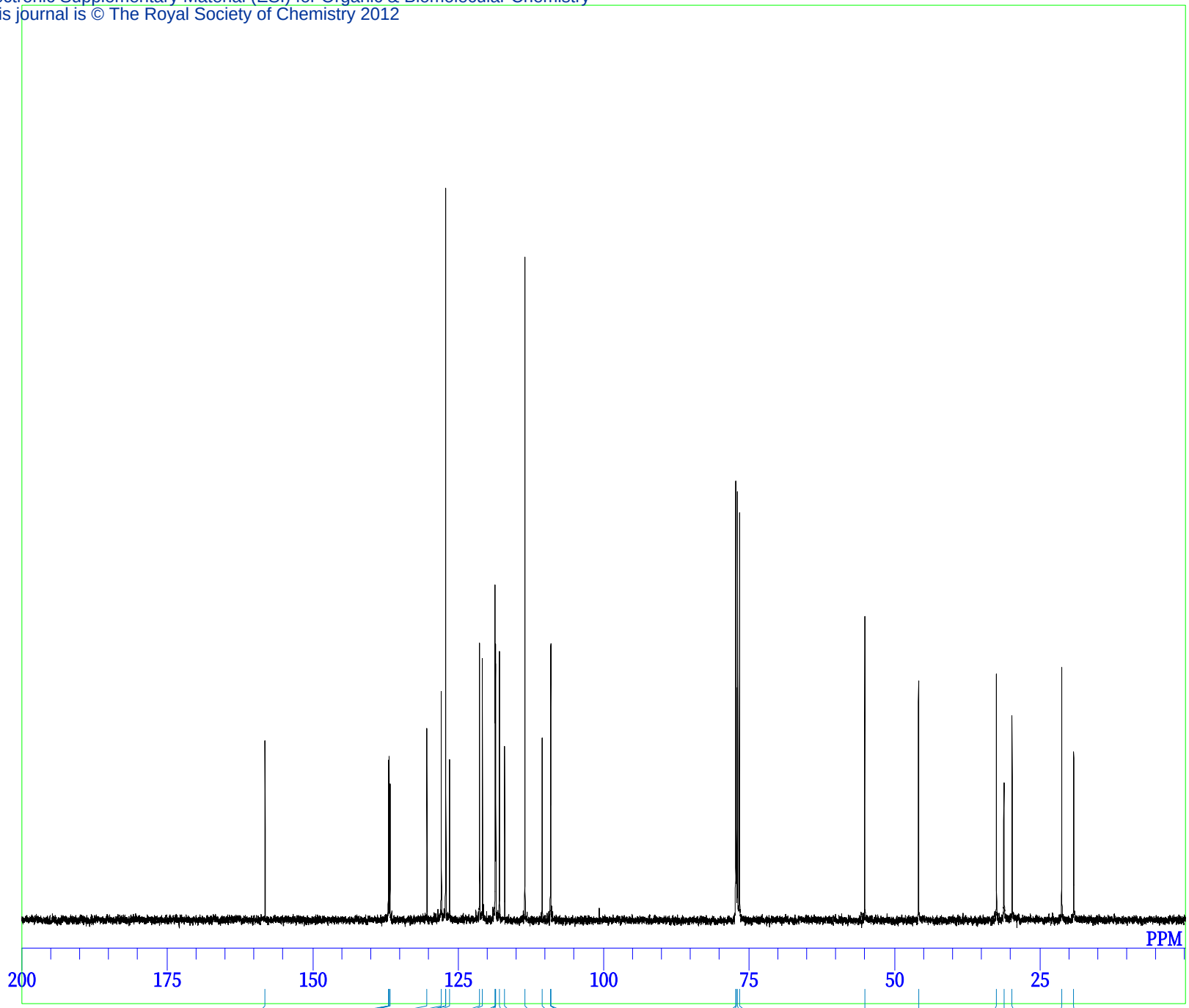
DFILE	6-PMB-NHBn 13C.als
COMNT	m347 13C
DATIM	Wed Sep 29 16:15:03 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	200
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	26.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	22



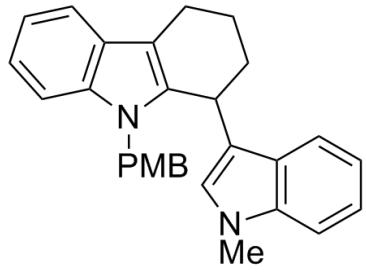


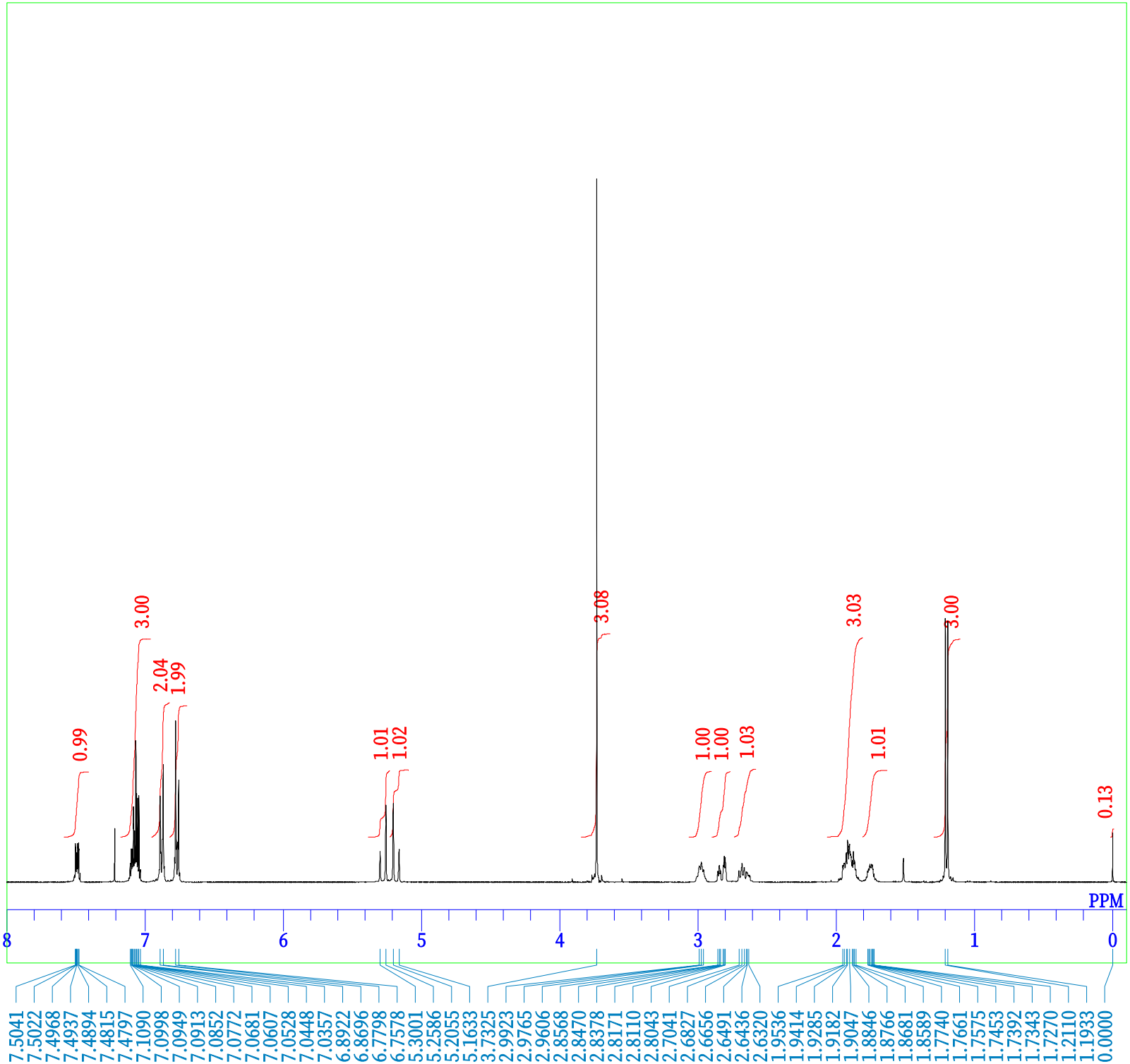
DFILE	3c H.als
COMNT	6-PMB-ind 1H
DATIM	Thu Jul 15 18:56:34 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	28.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	18



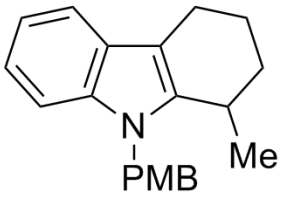


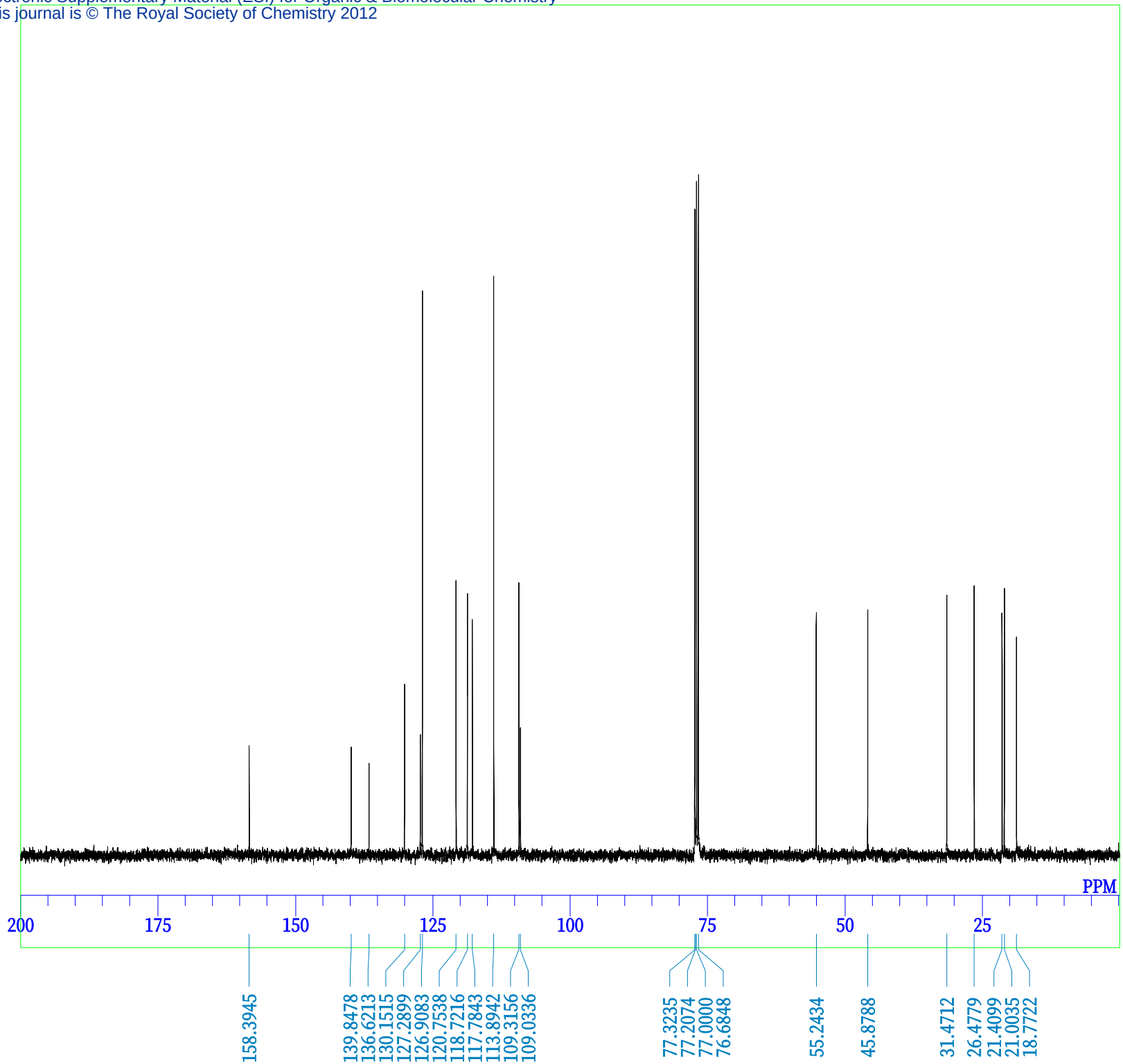
DFILE	Auto2BCM_E1_FT.als
COMNT	m153 N-Me indole
DATIM	Sat Oct 03 10:35:08 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	400
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	26.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



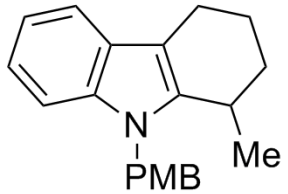


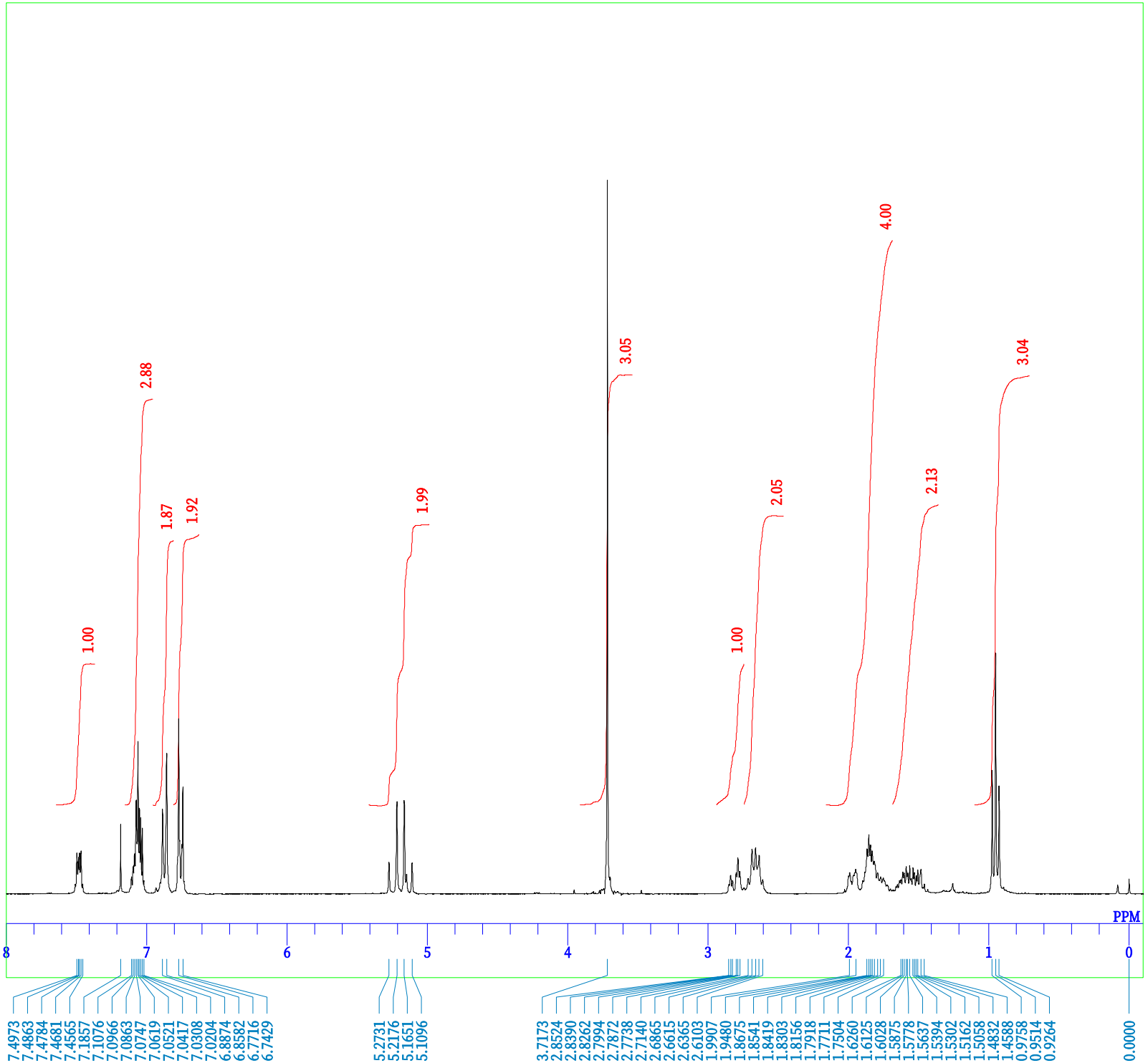
DFILE	3d H.als
COMNT	6-PMB-Me
DATIM	Fri Jun 11 11:42:22 2010
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	8000.00 Hz
SCANS	4
ACQTM	4.0960 sec
PD	2.9010 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	14



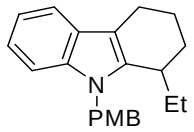


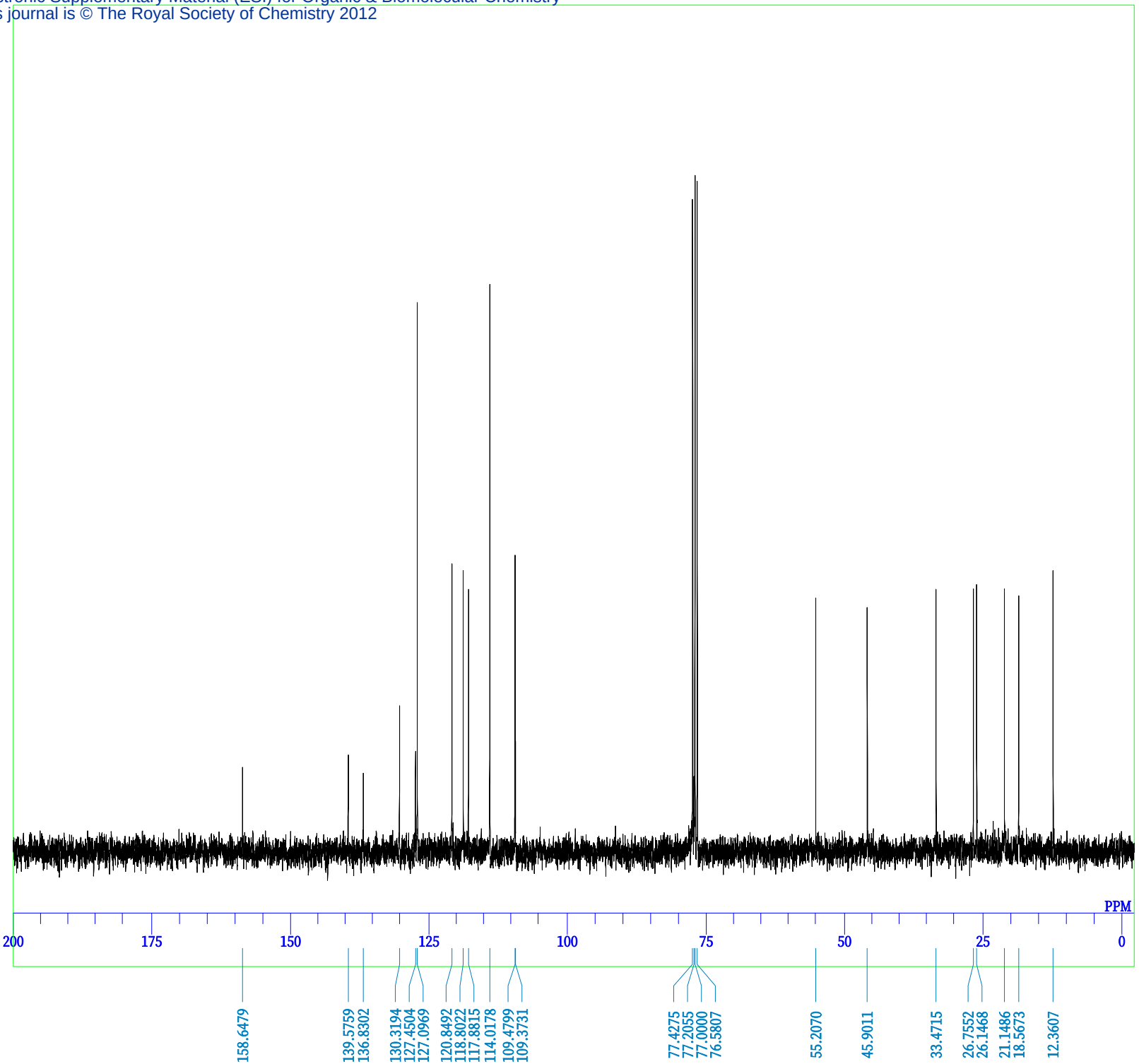
DFILE	3d C.als
COMNT	6-PMB-Me
DATIM	Fri Jun 11 12:07:44 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	500
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24

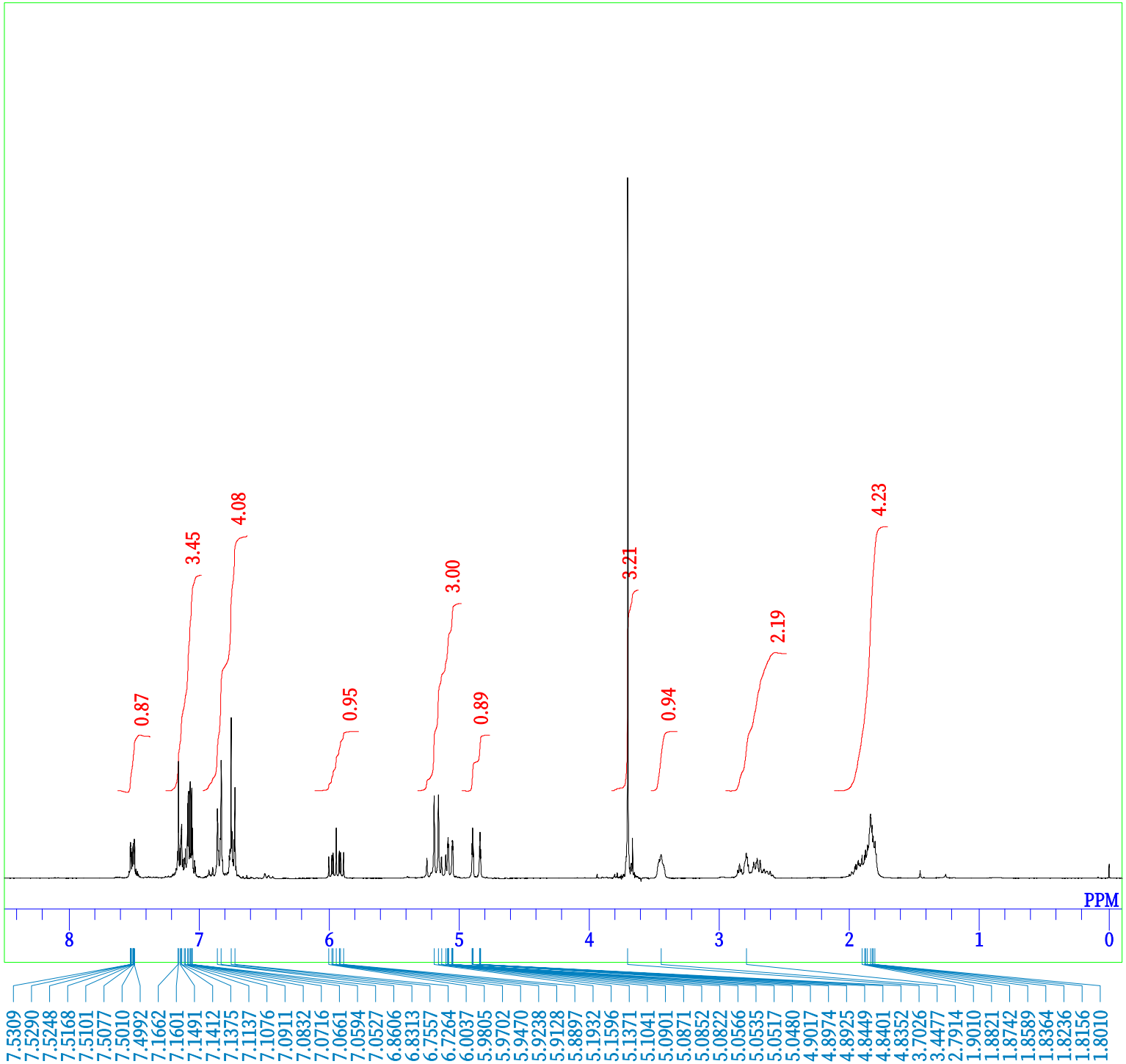




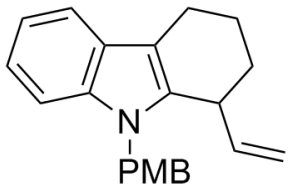
DFILE	m350 Et2Zn.als
COMNT	m350 Et2Zn
DATIM	Wed Sep 29 17:29:01 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	26.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	10

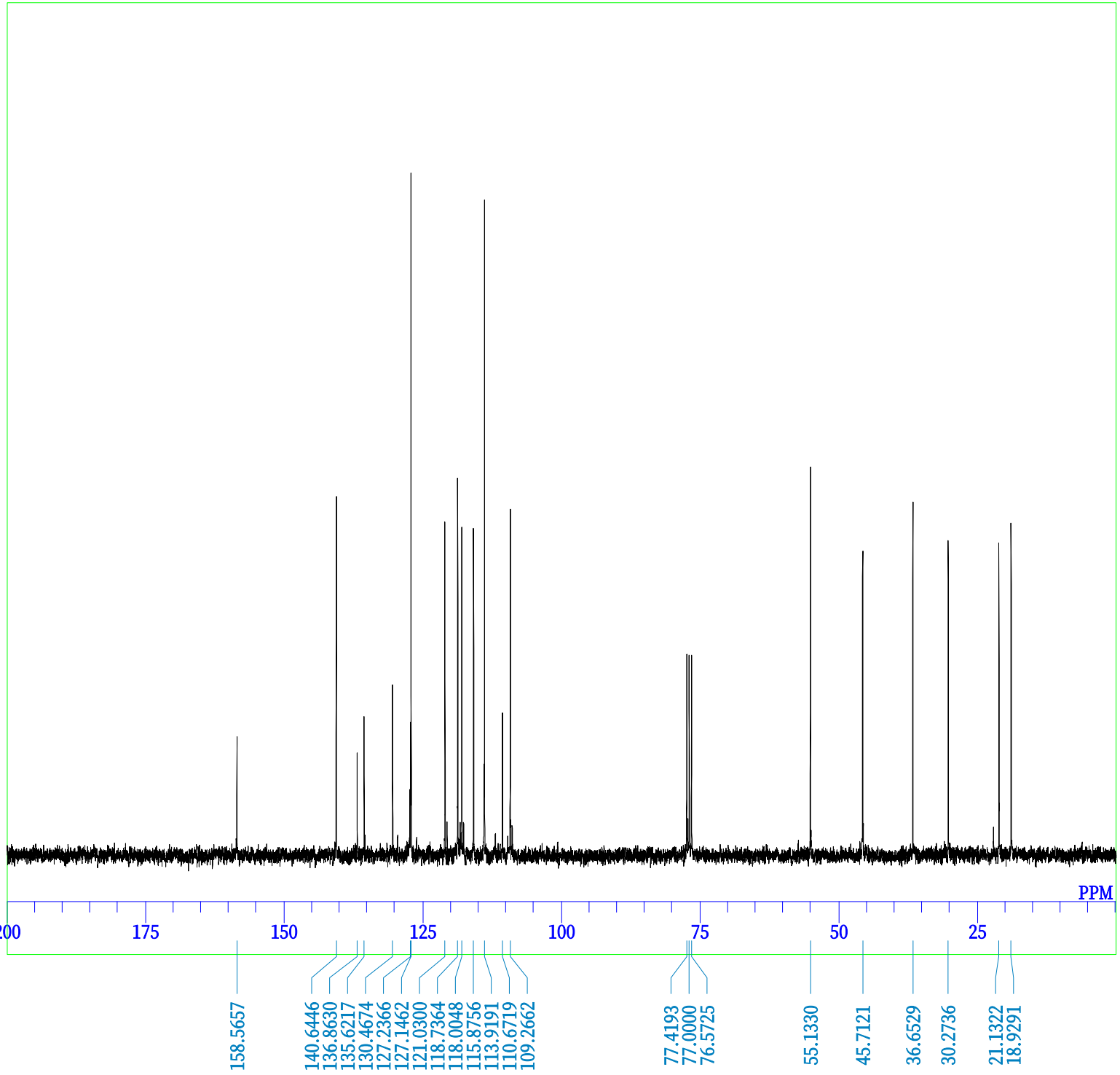




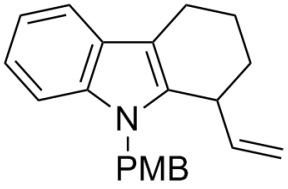


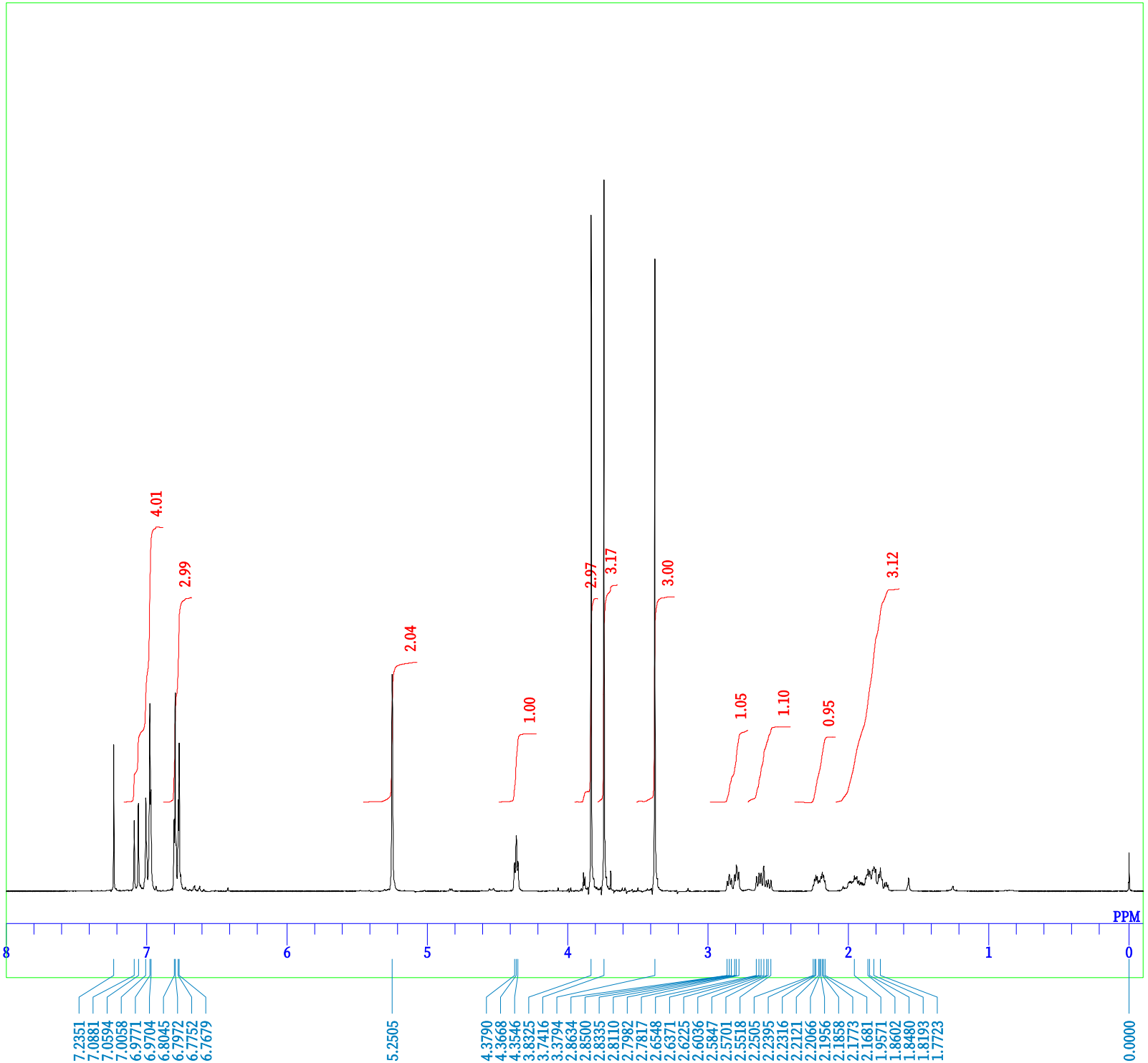
DFILE	6-PMB-Vinyl 1H FT.als
COMNT	6-PMB-Vinyl
DATIM	Fri Dec 24 15:42:55 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	4
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	10



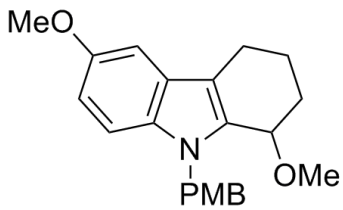


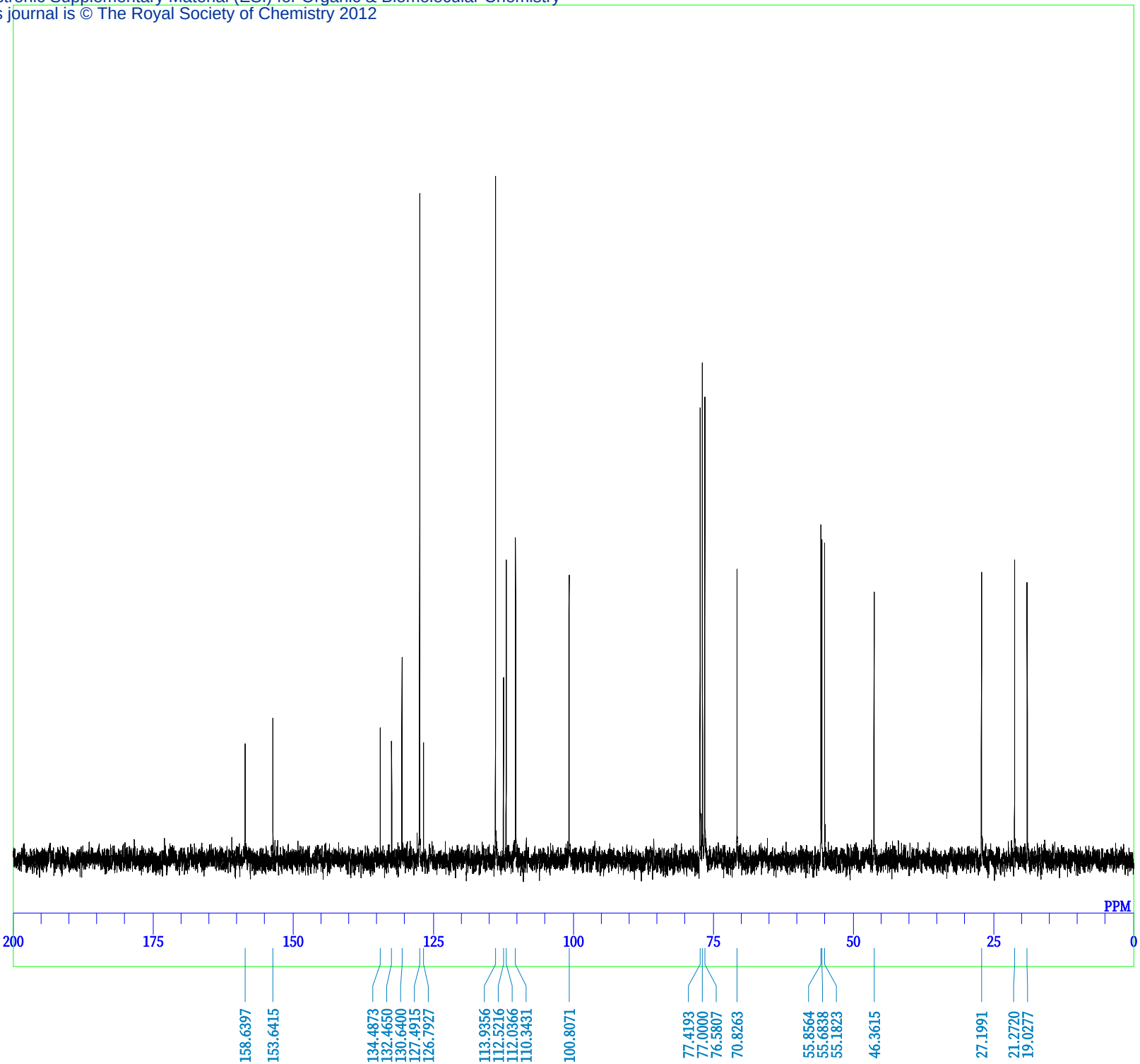
DFILE	6-PMB-Vinyl 13C FT.als
COMNT	6-PMB-Vinyl 13C
DATIM	Fri Dec 24 15:49:10 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	100
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	26.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



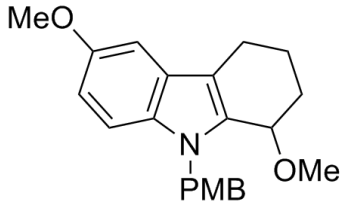


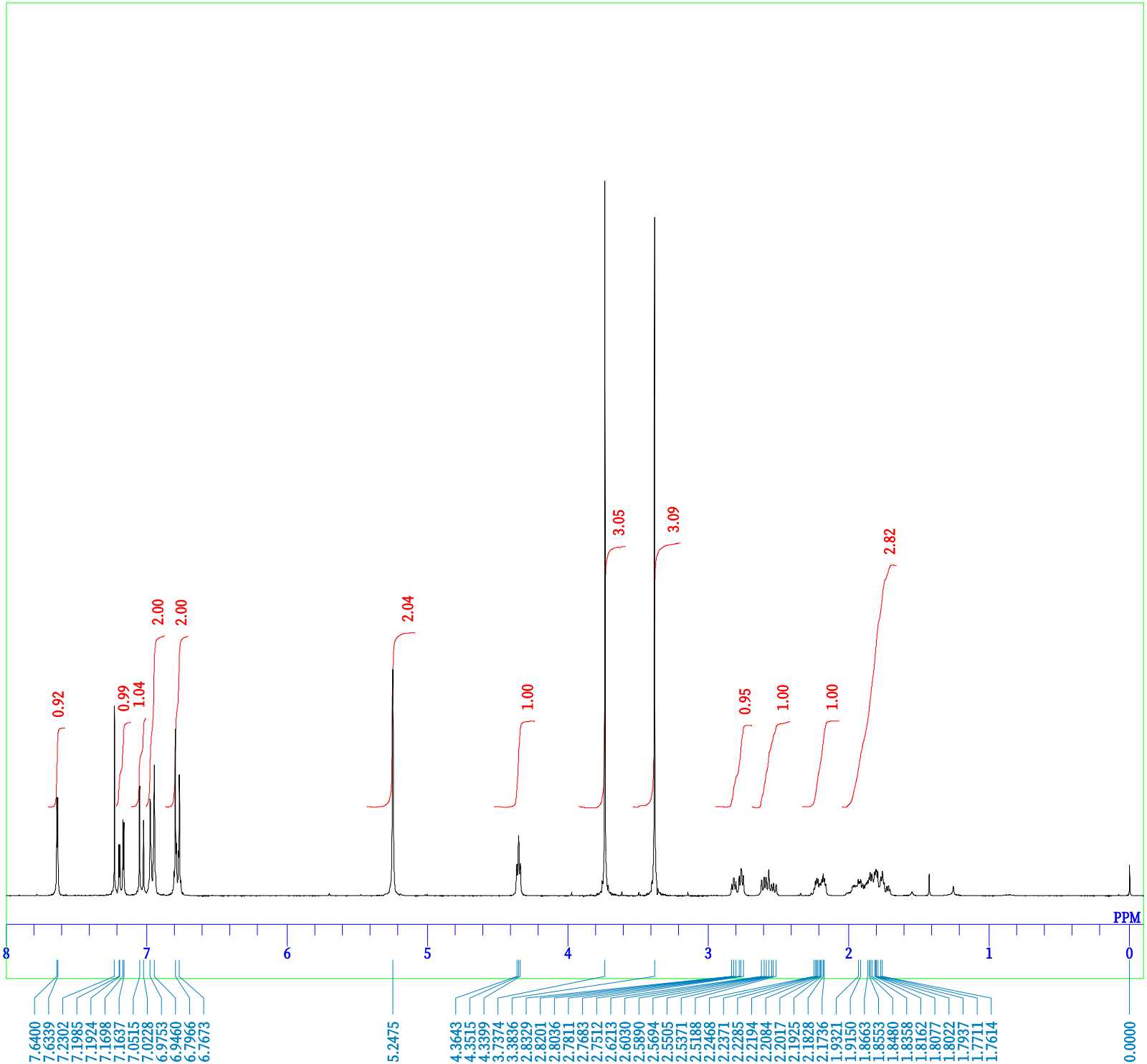
DFILE	MeO-6-PMB-OMe 1H.als
COMNT	MeO-6-PMB-OMe
DATIM	Mon Jan 24 16:01:20 2011
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	12



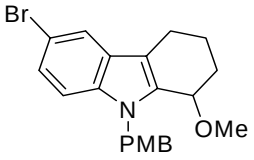


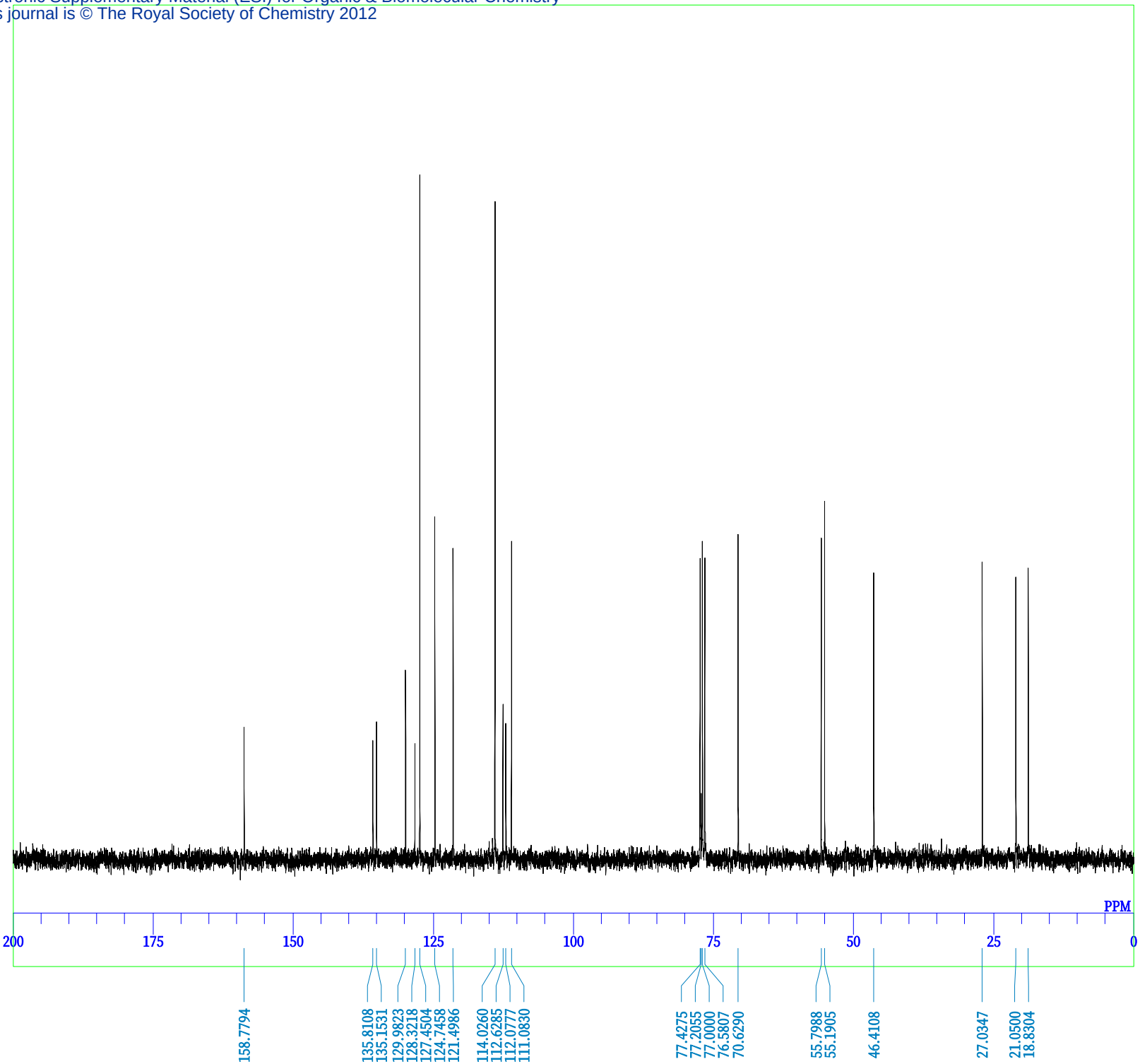
DFILE	m462 MeO-6-PMB-OMe 13C.als
COMNT	MeO-6-PMB-OMe 13C
DATIM	Mon Jan 24 16:09:45 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	148
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



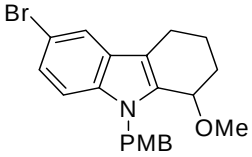


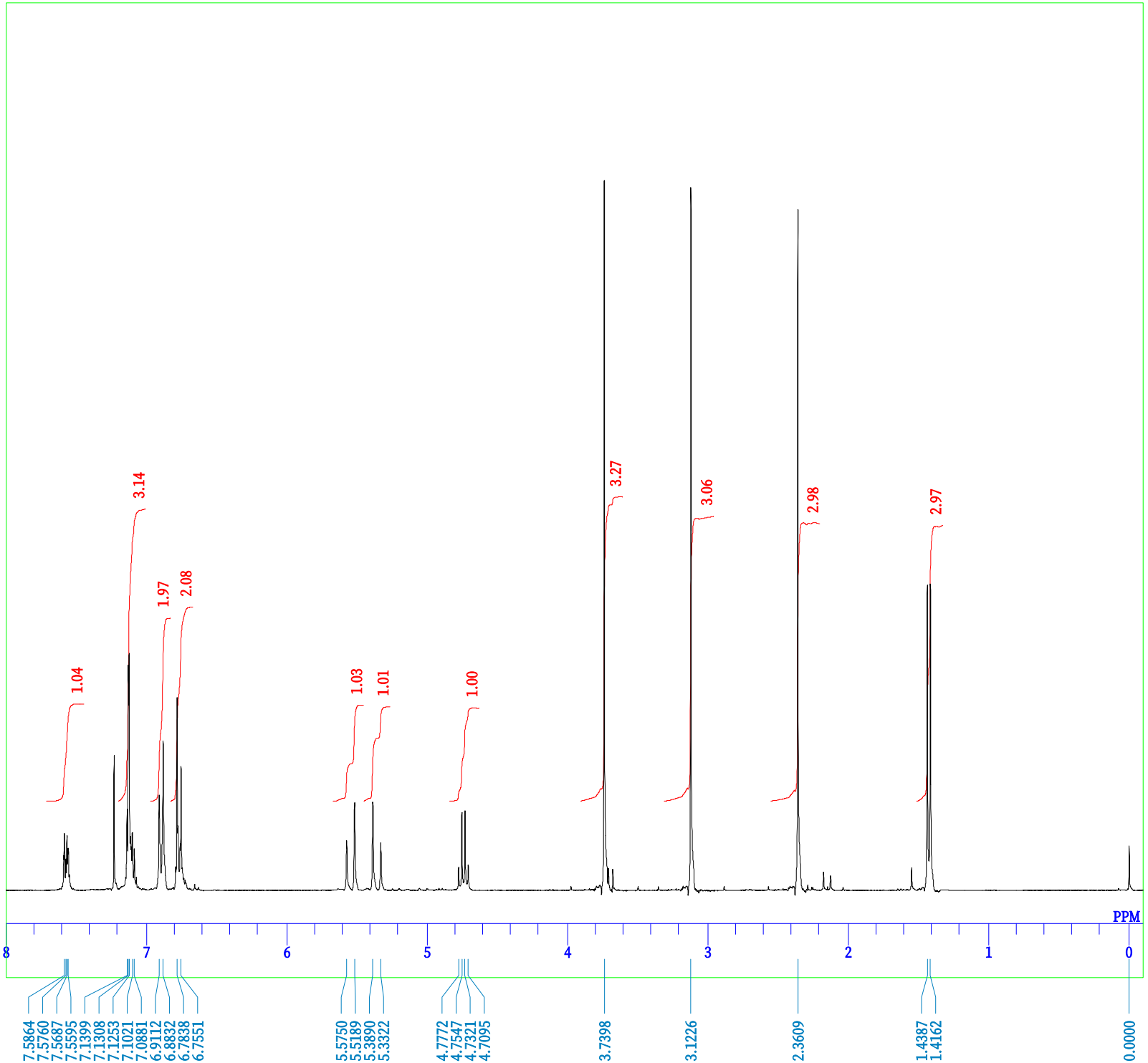
DFILE	Br-6-PMB-OMe 1H FT.als
COMNT	Br-6-PMB-OMe 1H
DATIM	Thu Jan 27 12:53:26 2011
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	26.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	12

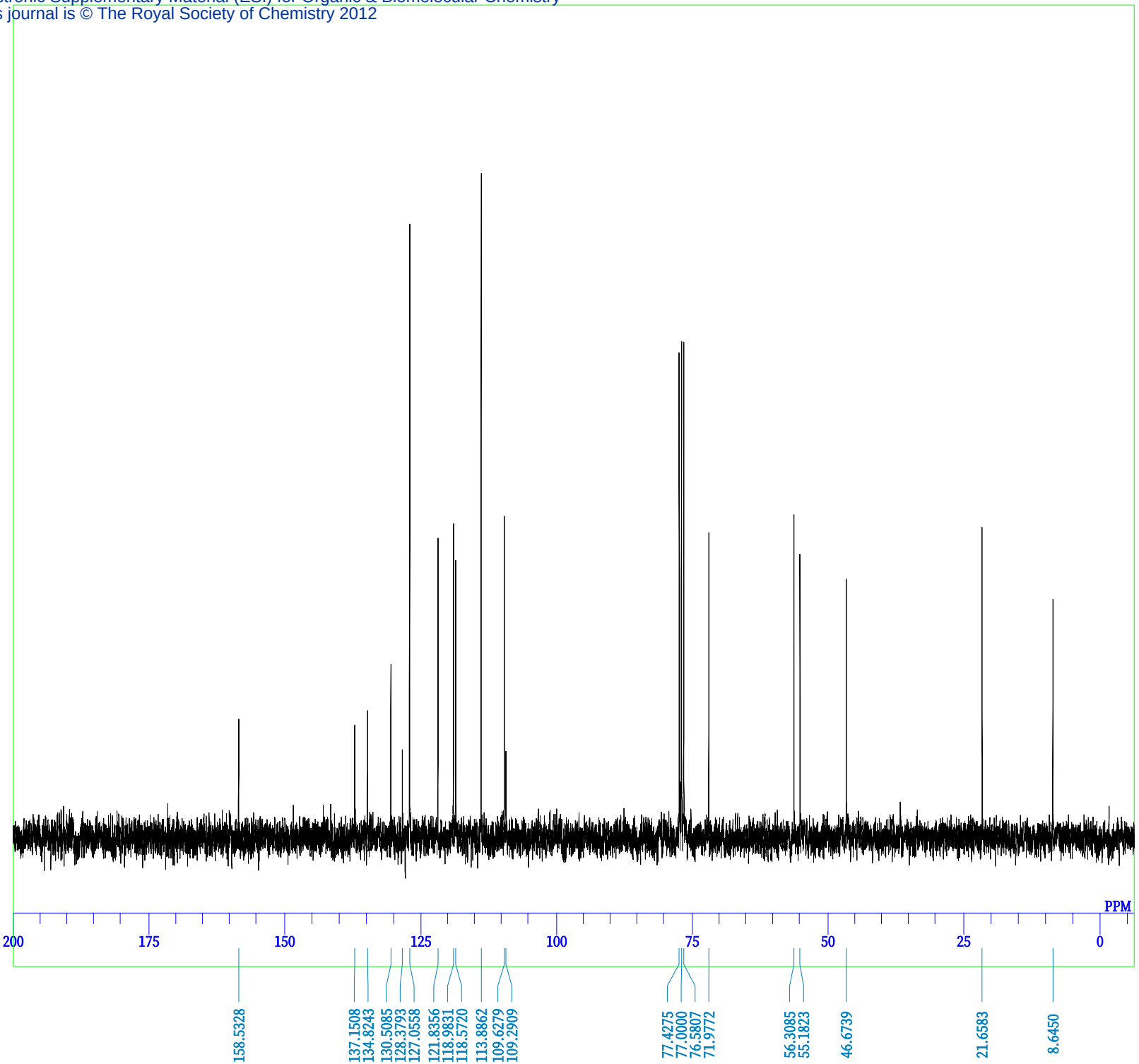




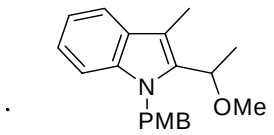
DFILE	Br-6-PMB-OMe 13C.als
COMNT	Br-6-PMB-OMe 13C
DATIM	Thu Jan 27 13:00:30 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	120
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	26.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24

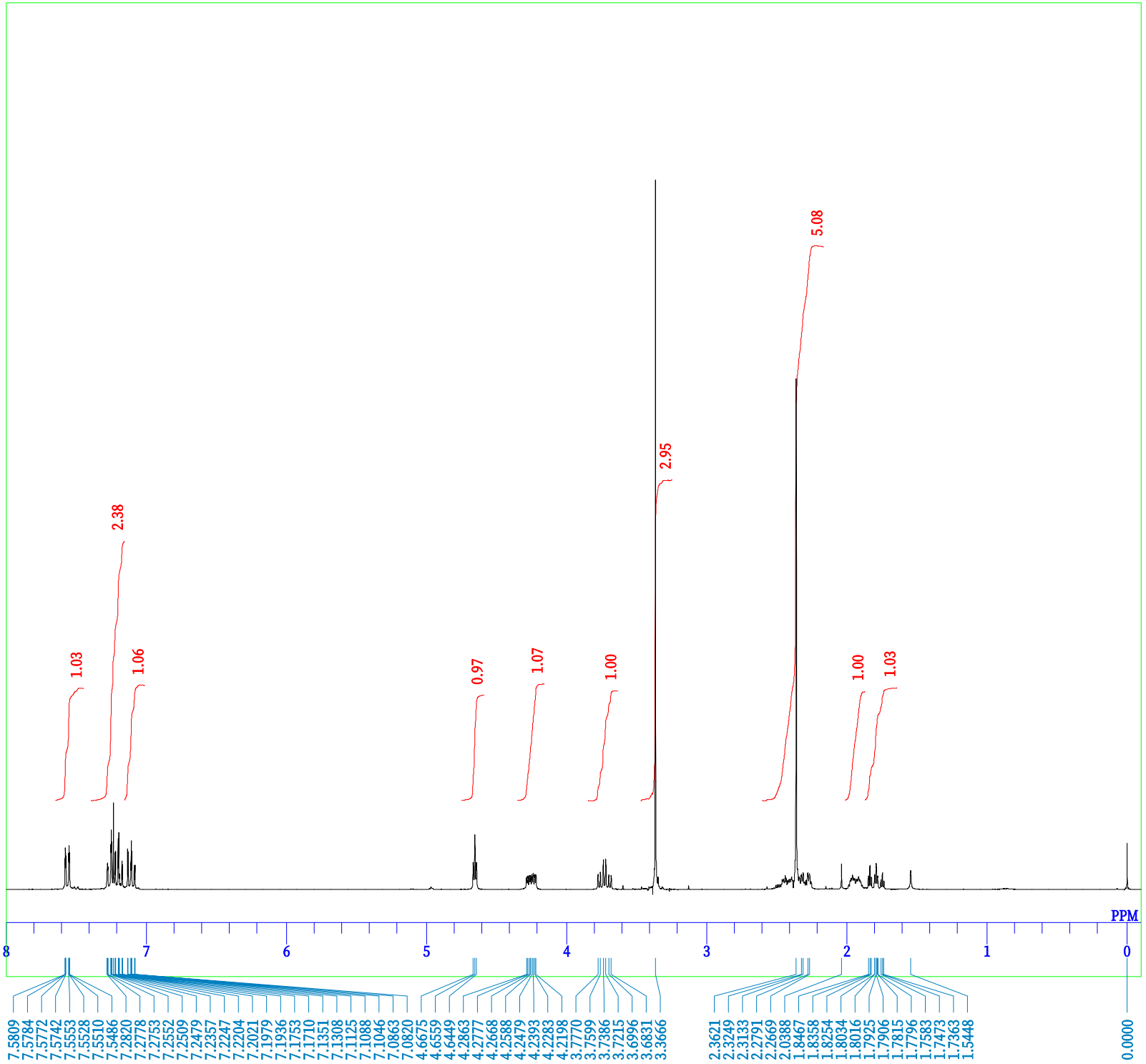


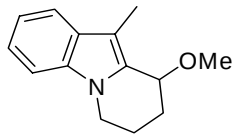


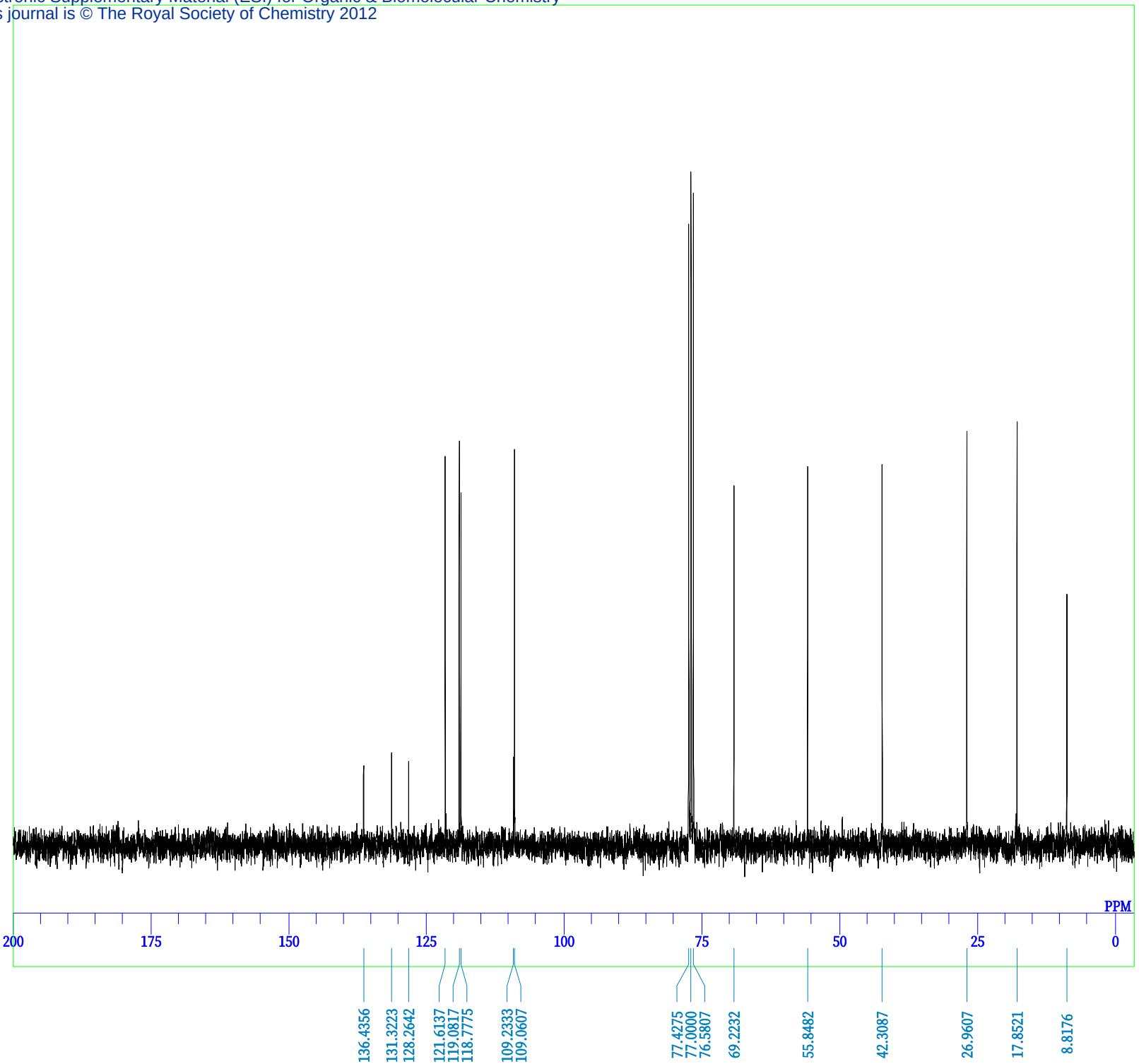


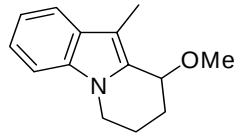
DFILE	m453 2E3M-PMB-OMe 13C.als
COMNT	m453 2E3M-PMB-OMe 13C
DATIM	Fri Jan 14 13:48:27 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	100
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	23

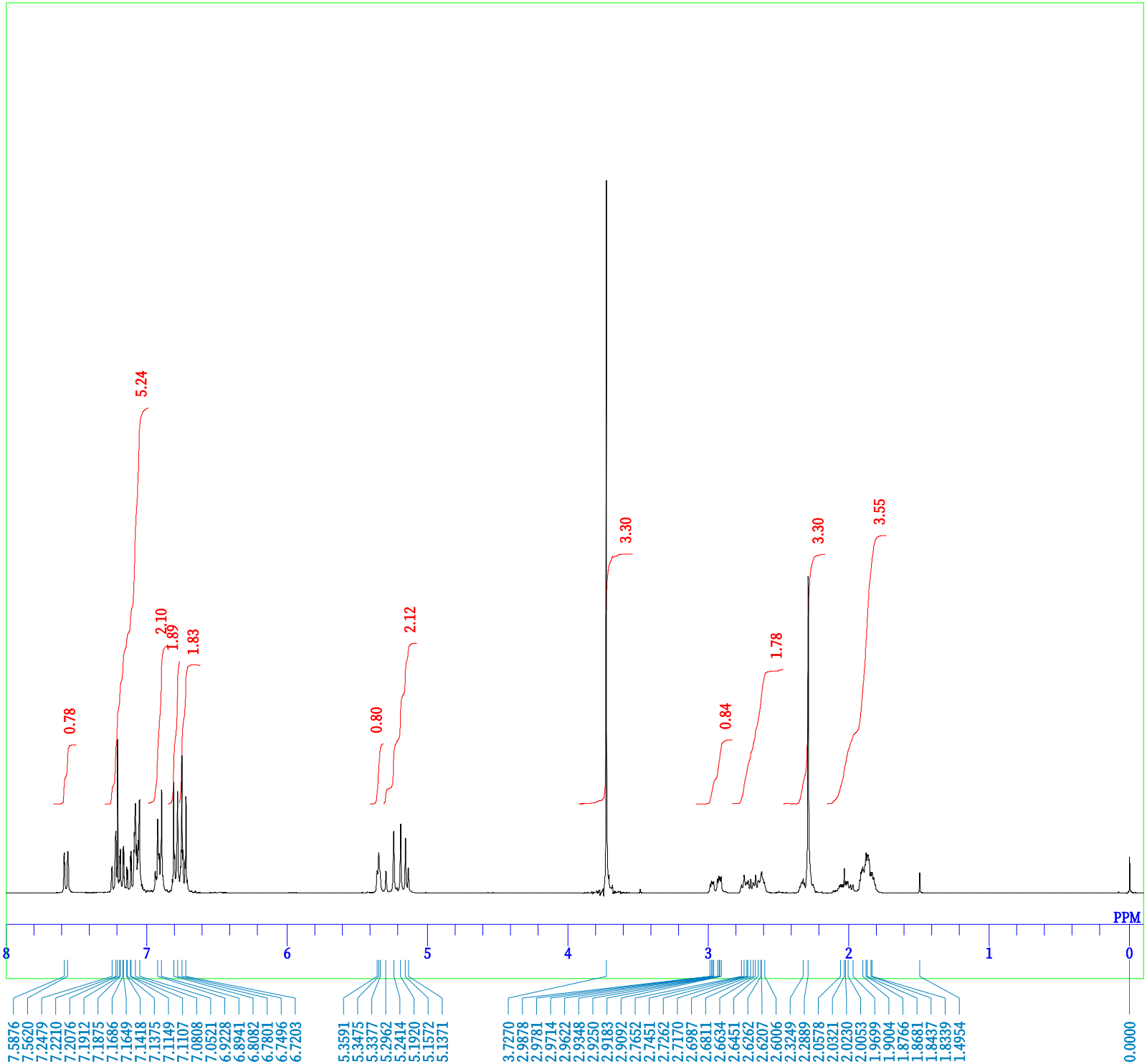


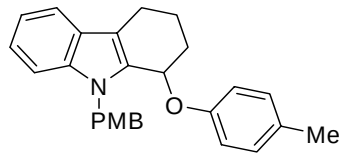


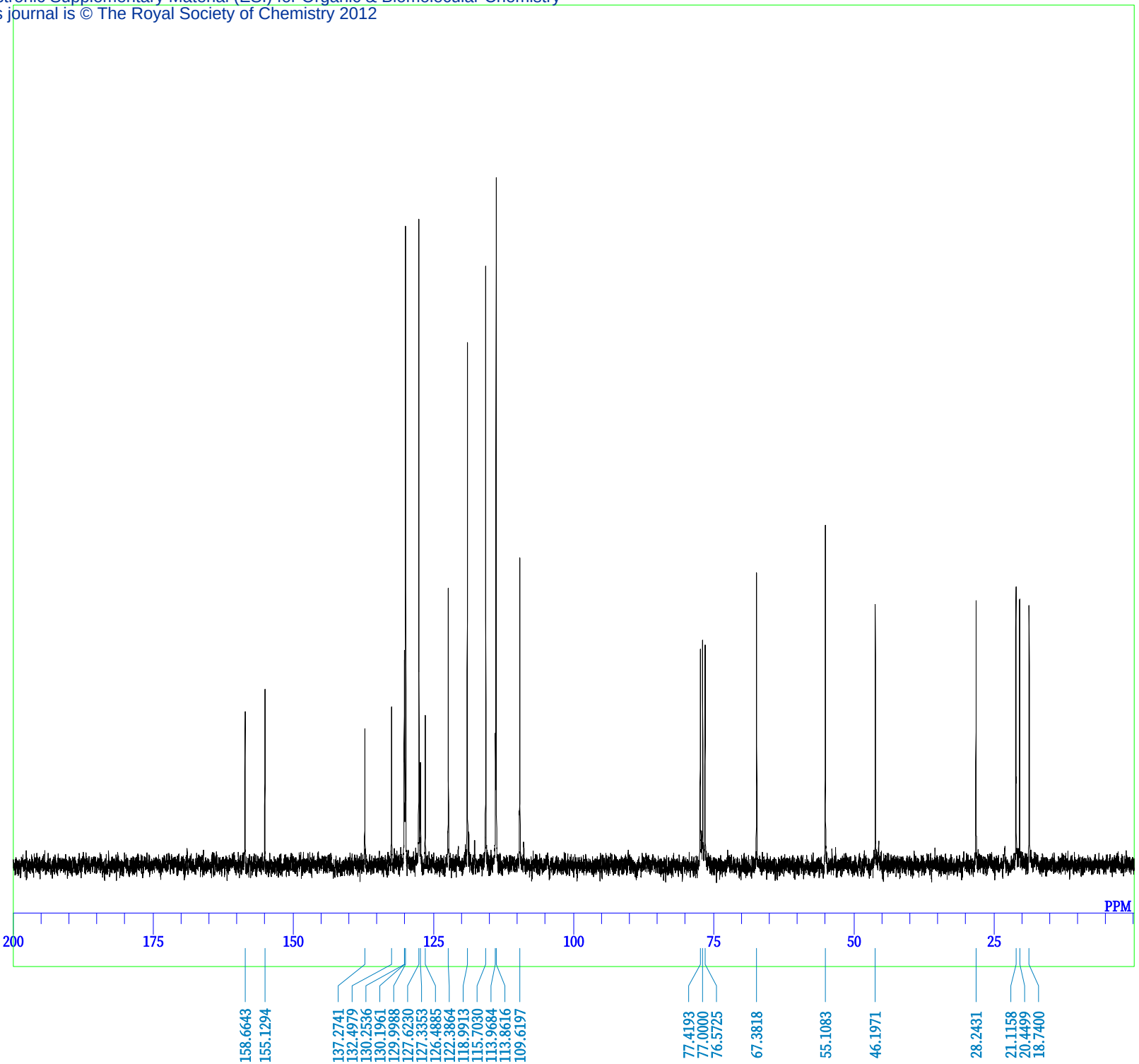




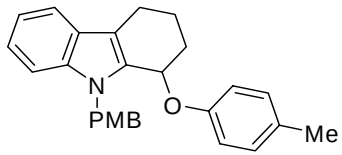


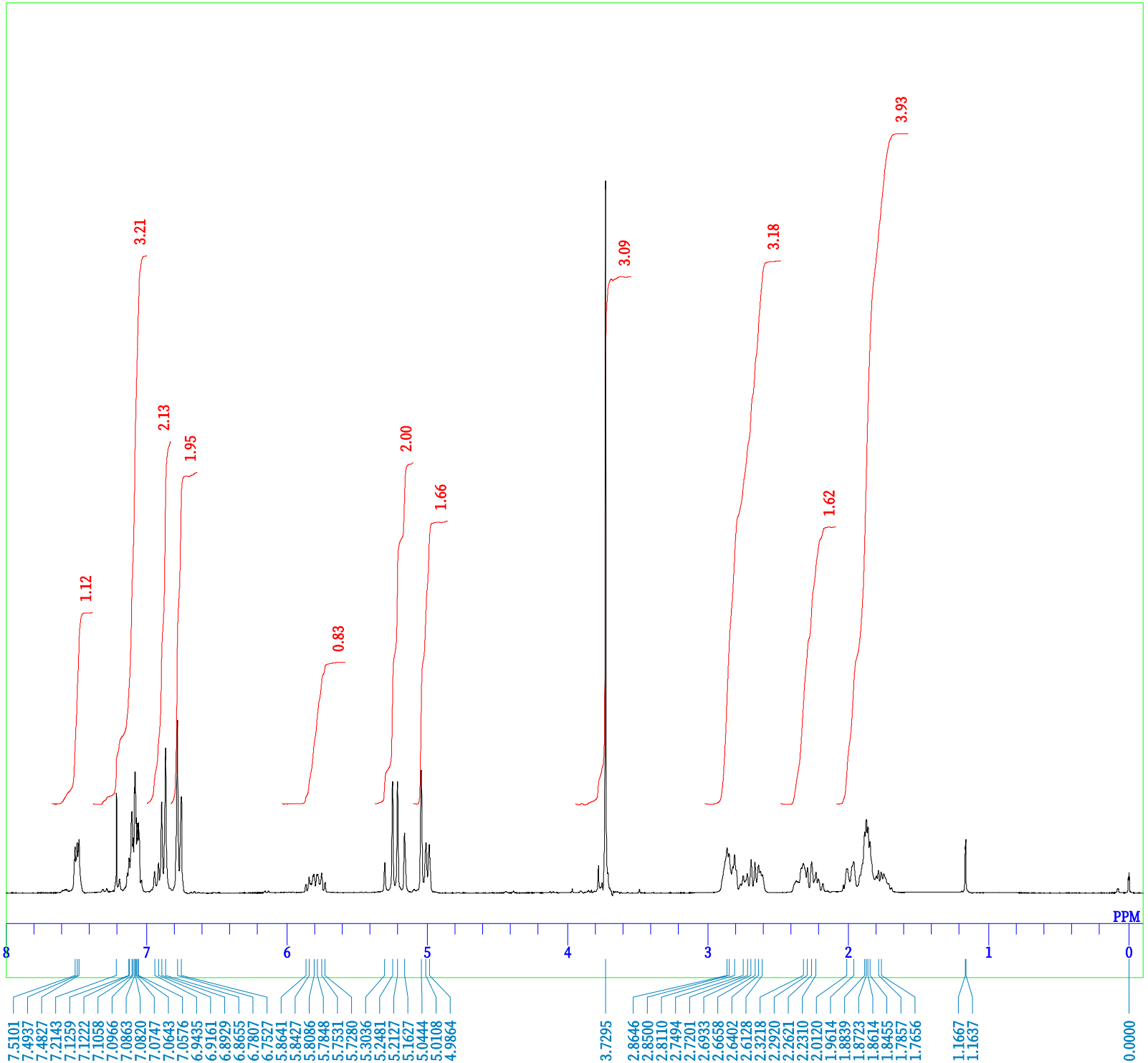




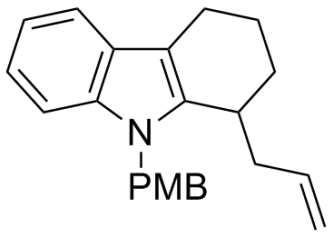


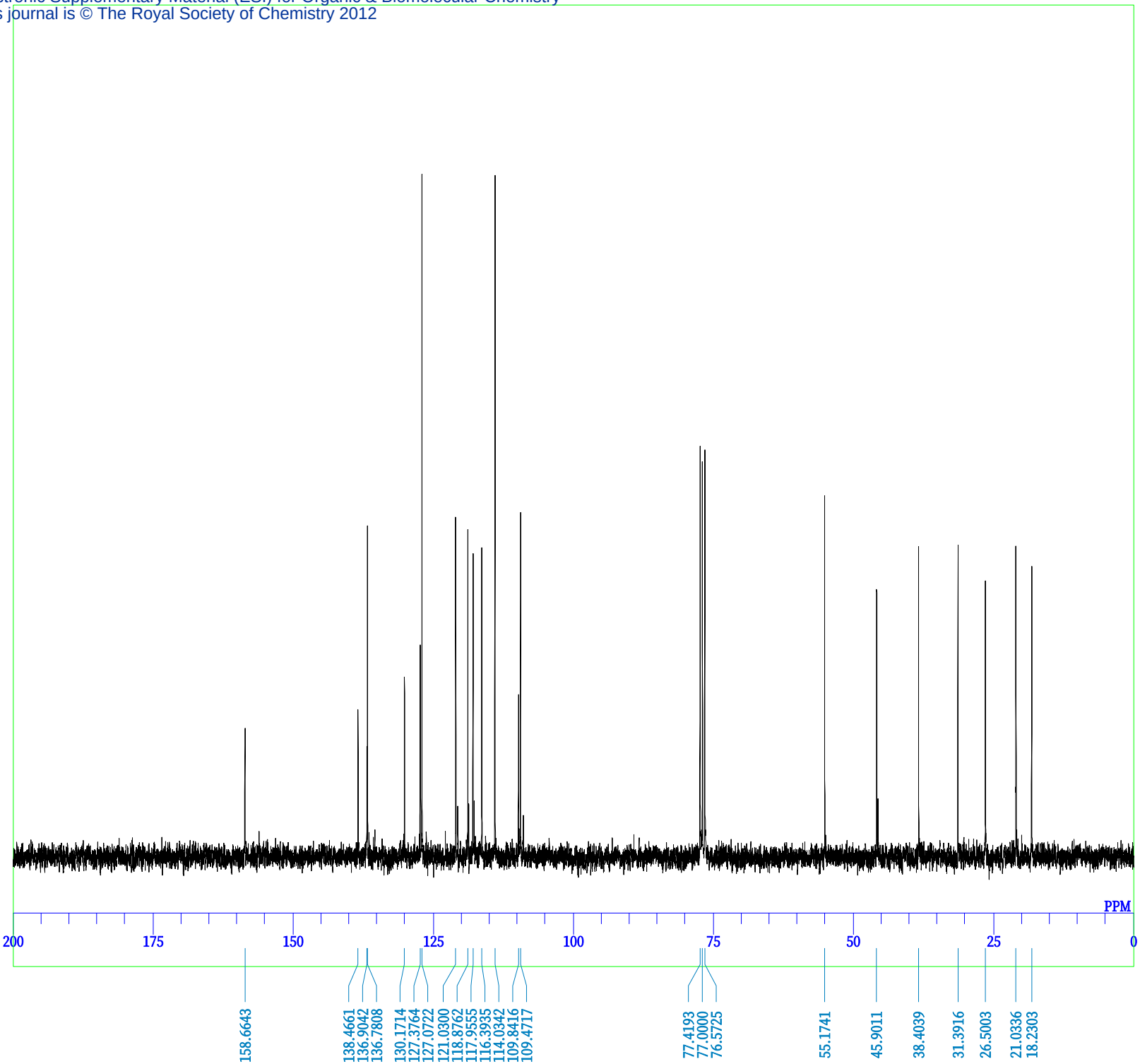
DFILE	6-PMB-OTol 13C.als
COMNT	6-PMB-OTol 13C
DATIM	Fri Jan 28 09:09:21 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	100
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	22



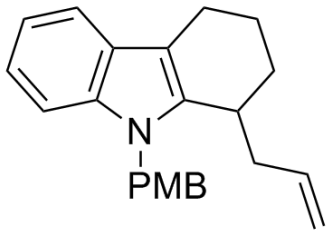


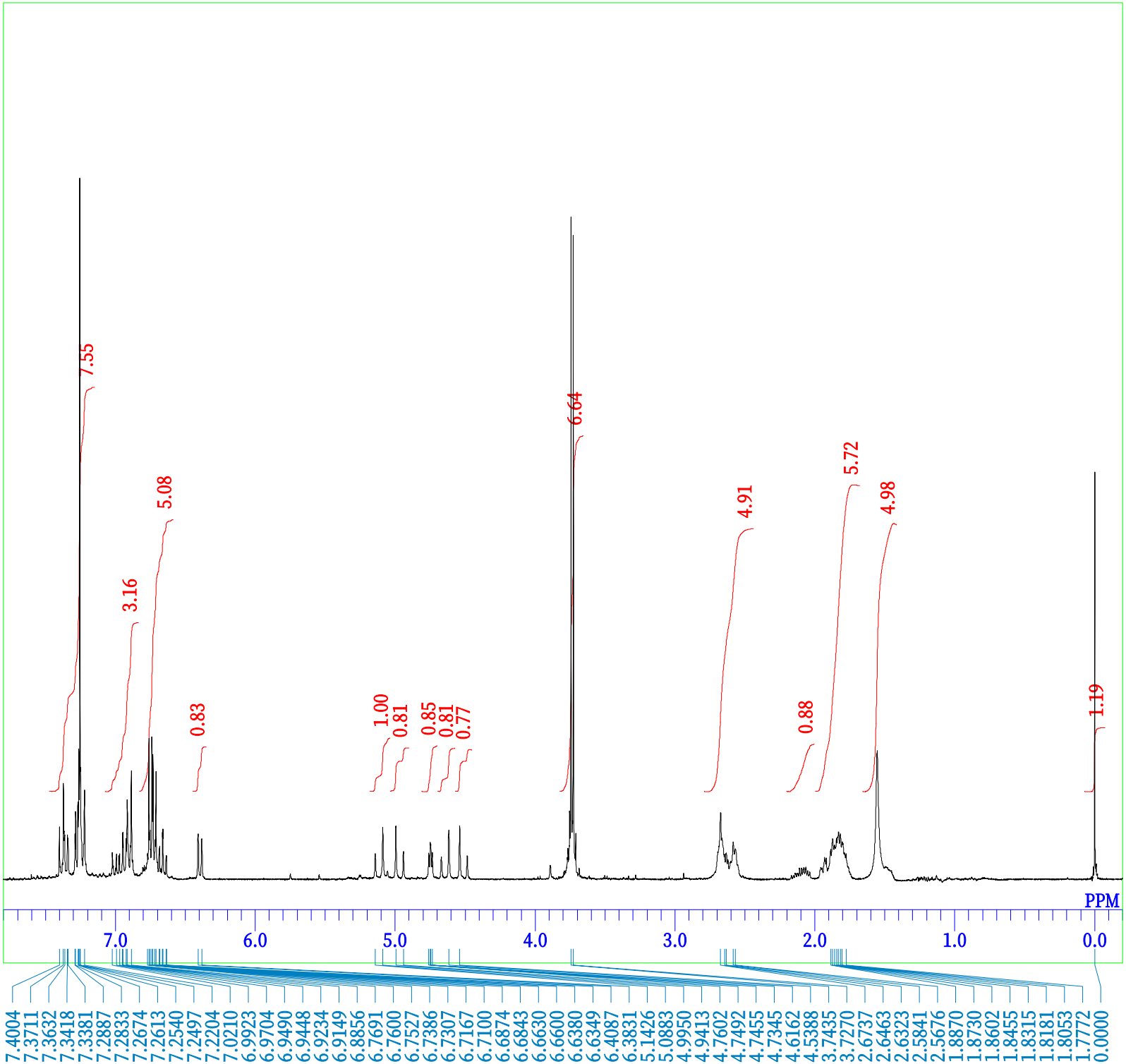
DFILE	6-PMB-Allyl 1H FT.als
COMNT	6-PMB-Allyl
DATIM	Fri Jan 21 14:43:10 2011
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	8
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	12



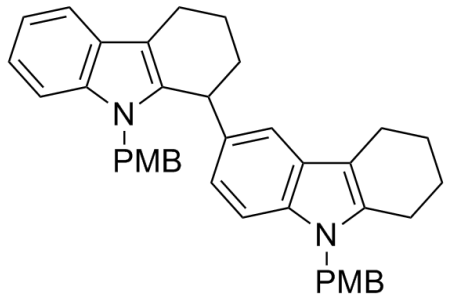


DFILE	6-PMB-Allyl 13C FT.als
COMNT	6-PMB-Allyl 13C
DATIM	Fri Jan 21 14:52:24 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	152
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.30 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24

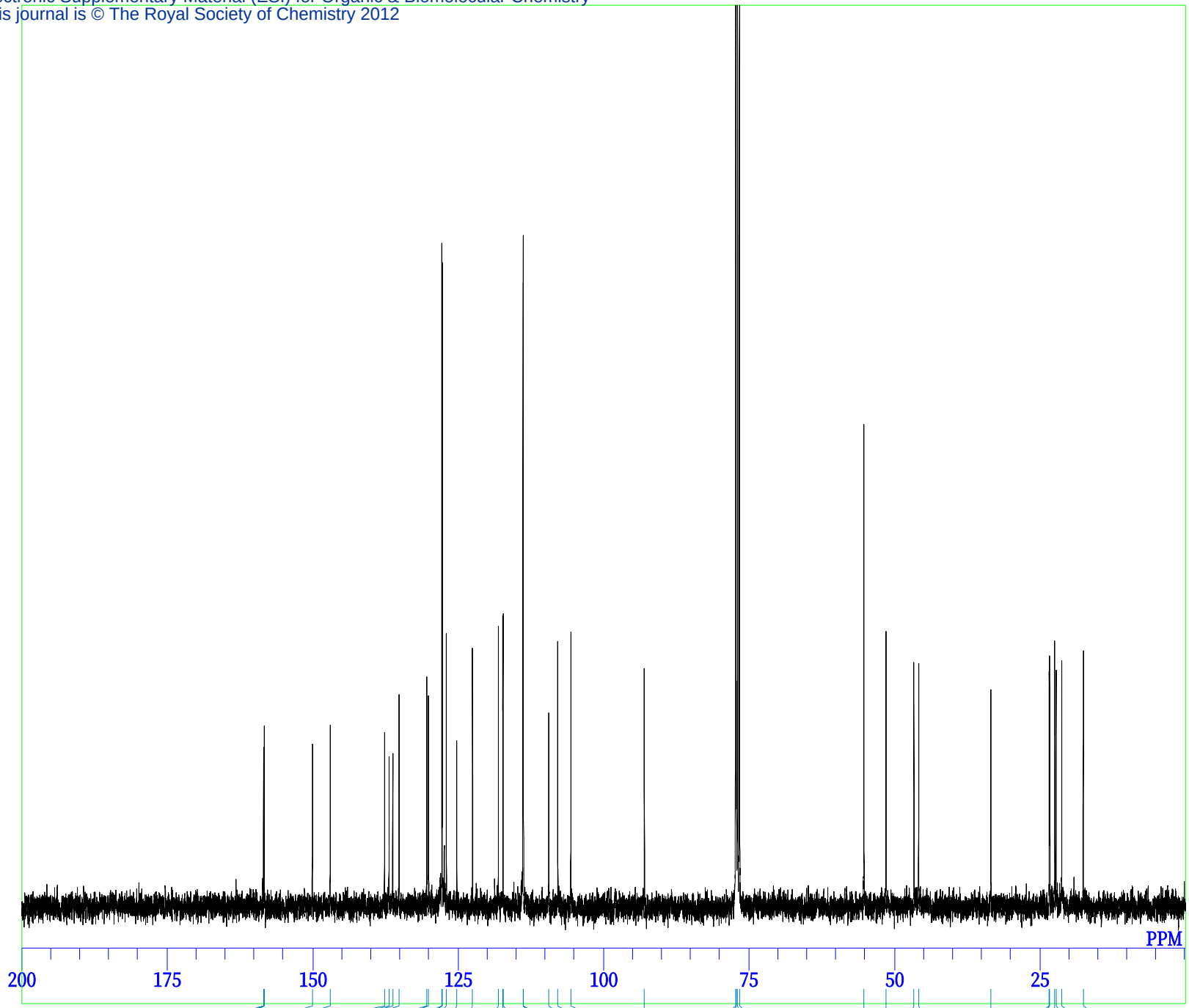




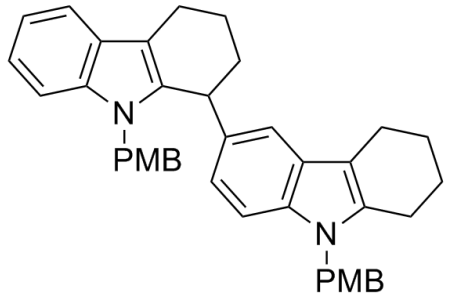
DFILE	4 H 2.als
COMNT	Dimer 1H
DATIM	Sat Jul 17 17:40:30 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	16
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	28.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	18

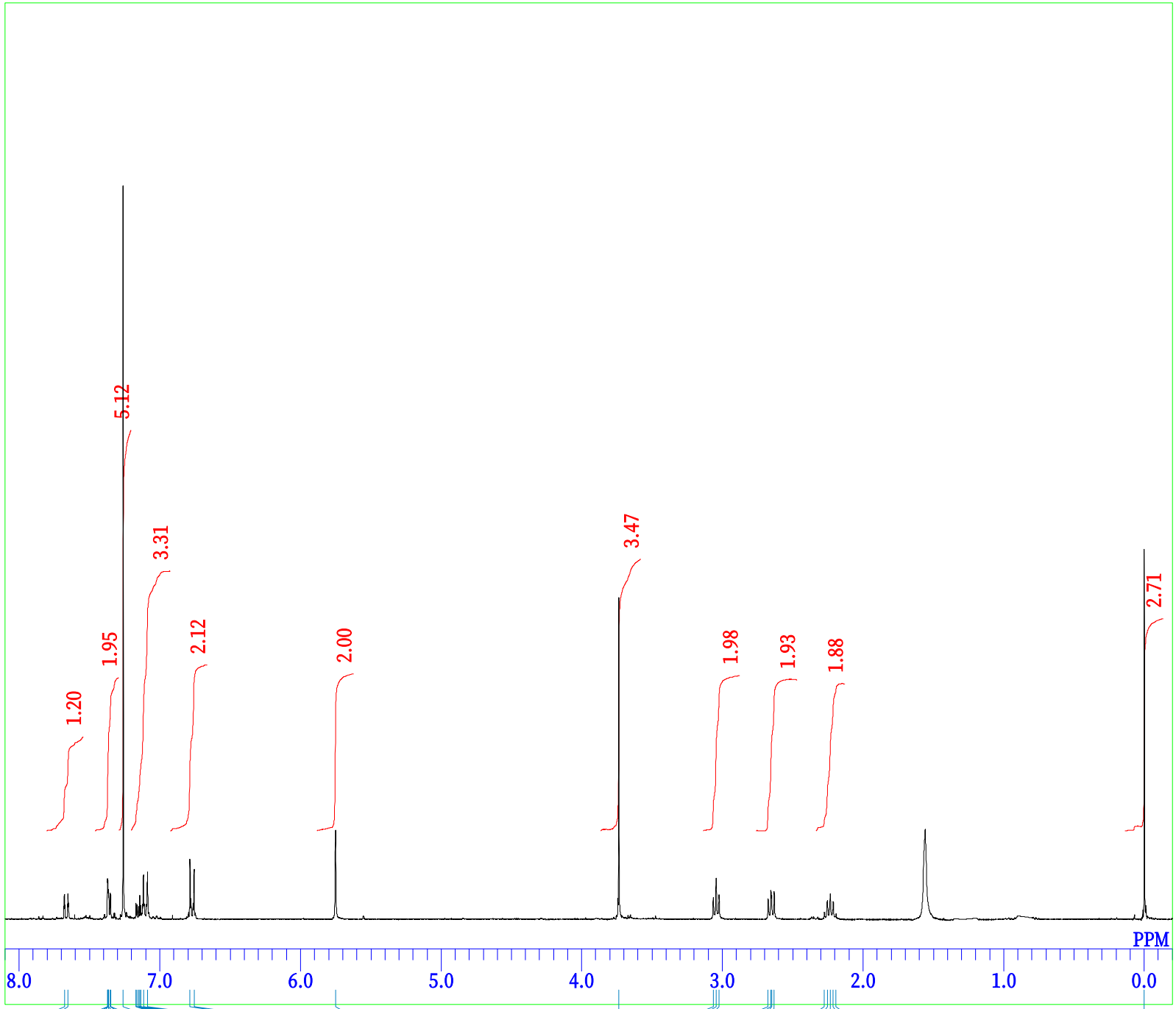


7.4004 7.3711 7.3632 7.3418 7.3381 7.2887 7.2833 7.2674 7.2613 7.2540 7.2497 7.2204 7.0210 6.9923 6.9704 6.9490 6.9448 6.9234 6.9149 6.8856 6.7691 6.7600 6.7527 6.7386 6.7307 6.7167 6.7100 6.6874 6.6843 6.6630 6.6600 6.6380 6.6349 6.4087 6.3831 5.1426 5.0883 4.9950 4.9413 4.7602 4.7492 4.7455 4.7345 4.6162 4.5388 3.7435 3.7270 2.6737 2.6463 2.6323 2.5841 2.5676 1.8870 1.8730 1.8602 1.8455 1.8315 1.8181 1.8053 1.7772 0.0000

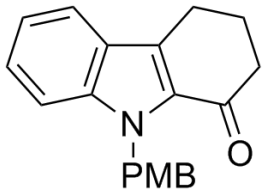


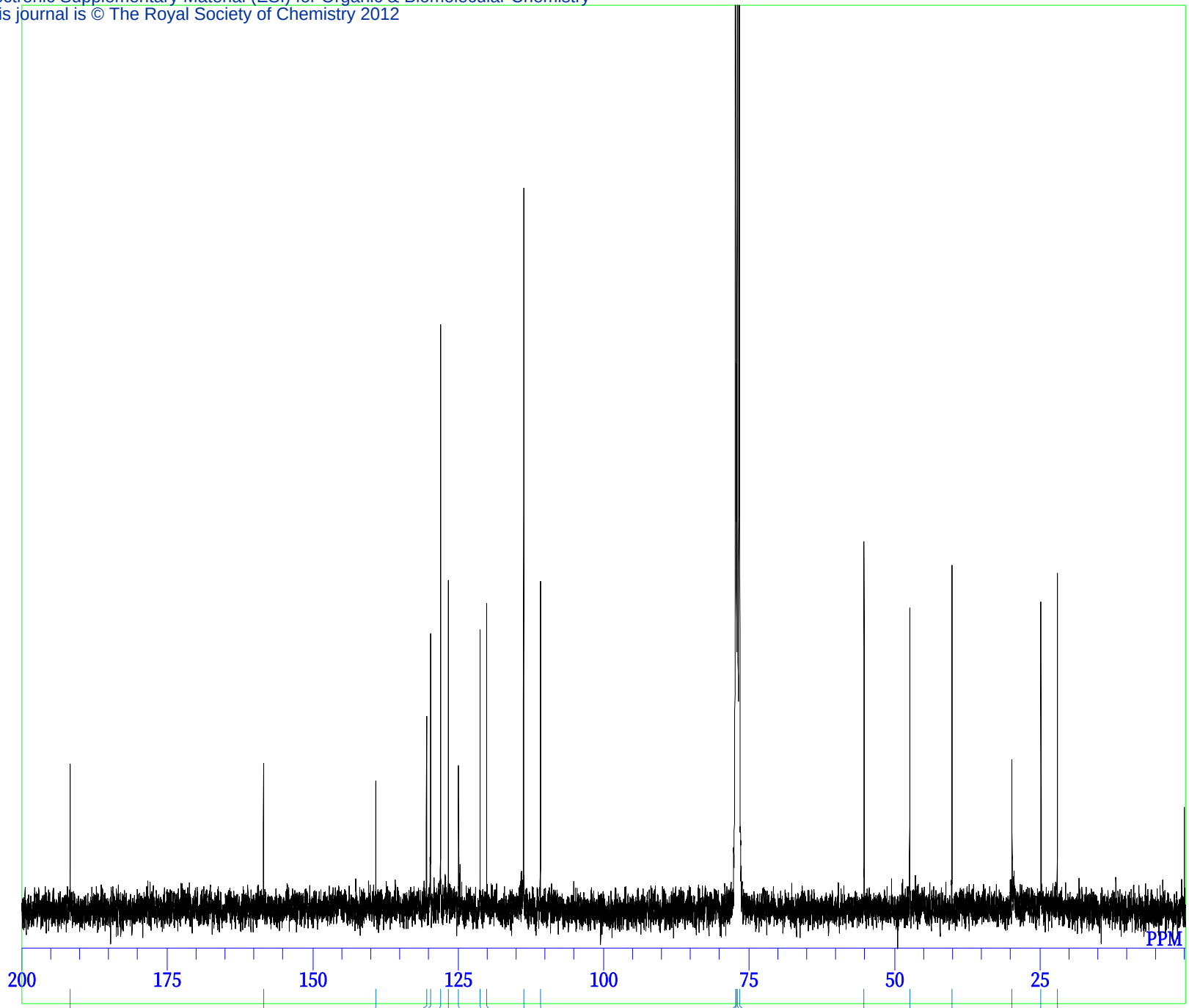
DFILE	4 C.als
COMNT	Abnormal Pummerer Dimer
DATIM	Thu Aug 27 09:49:00 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	800
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	26.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24



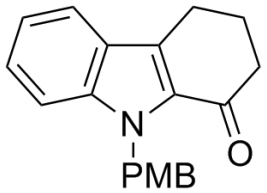


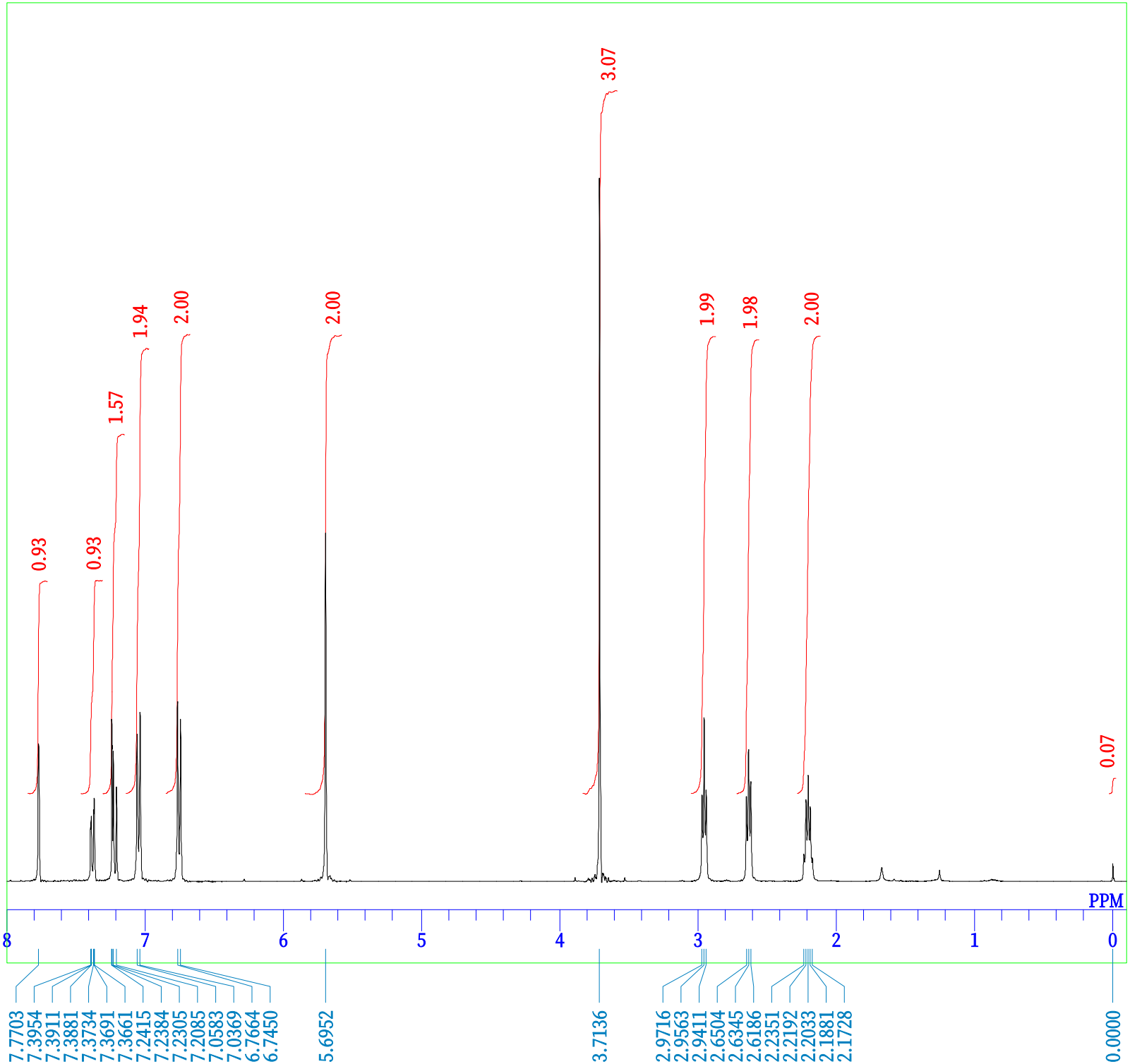
DFILE	8 H 2.als
COMNT	6-PMB-ketone
DATIM	Tue Jul 20 14:49:52 2010
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.00 Hz
POINT	32768
FREQU	6006.01 Hz
SCANS	32
ACQTM	5.4559 sec
PD	1.5440 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	26.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	21



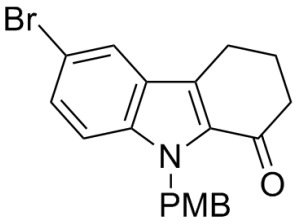


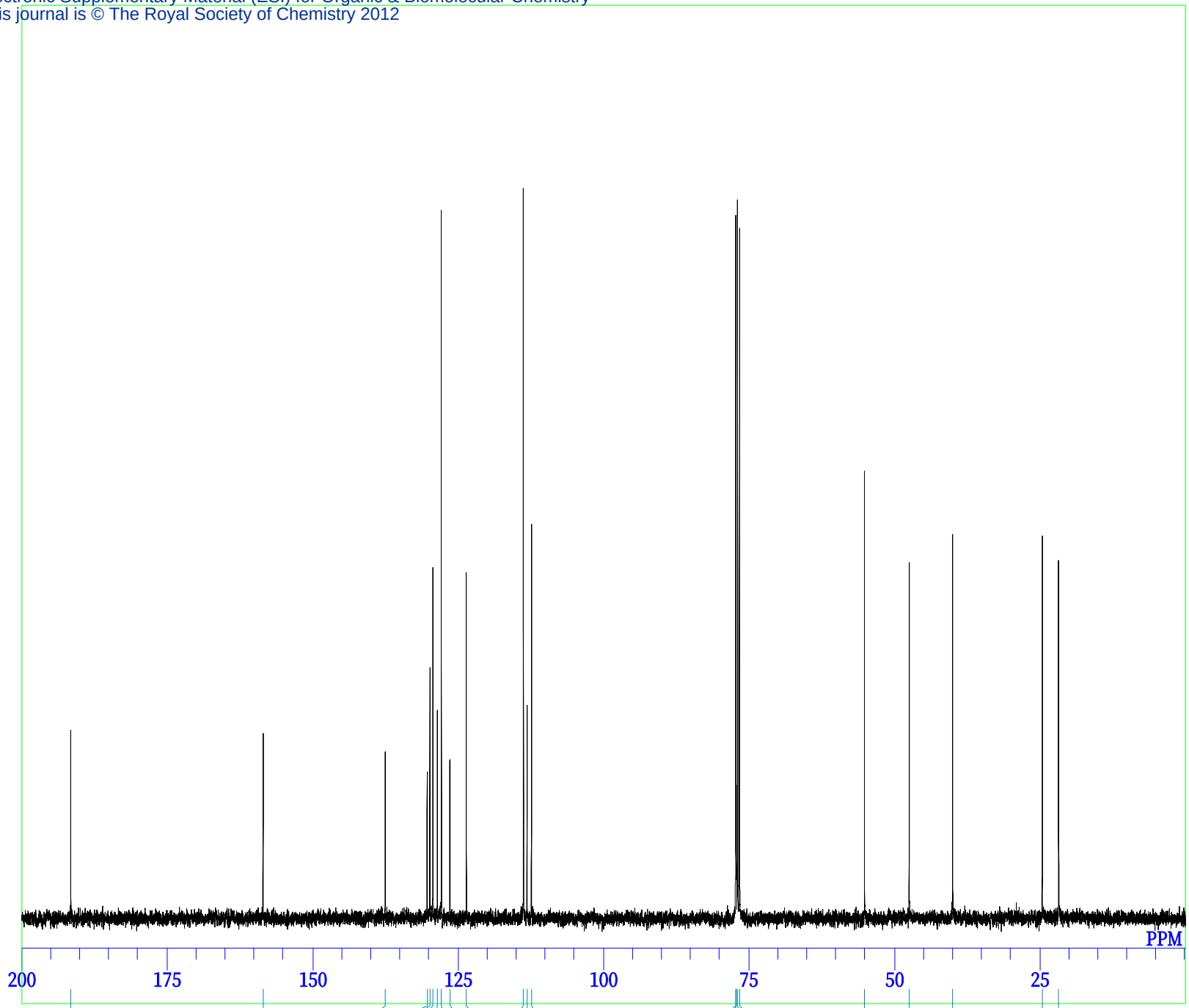
DFILE	Auto2BCM_E1_FT.als
COMNT	6-PMB-ketone
DATIM	Sat Jul 24 08:26:49 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	12800
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	25





DFILE	Auto1NON_E1_FT.als
COMNT	m130 main product
DATIM	Thu Sep 03 10:09:37 2009
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	8000.00 Hz
SCANS	4
ACQTM	4.0960 sec
PD	2.9010 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	25.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	12





DFILE	9 C.als
COMNT	m130 main product
DATIM	Thu Sep 03 10:24:00 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27322.40 Hz
SCANS	280
ACQTM	1.1993 sec
PD	1.7940 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	26.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24