Heterocyclization by Catalytic Carbonickelation of Alkynes: a Domino Sequence Involving Vinylnickels

Muriel Durandetti,* Lucie Hardou, Marie Clément, Jacques Maddaluno*

Laboratoire des Fonctions Azotées & Oxygénées Complexes de l'IRCOF, CNRS UMR 6014 & FR3038, Université de Rouen et INSA de Rouen, 76821 – Mont St Aignan Cedex (France).

muriel.durandetti@univ-rouen.fr; jmaddalu@crihan.fr

Supporting Information

General Information. GC analysis was carried out using a 24-m HP-methyl silicon capillary column. Mass spectra were recorded with a quadrupolar MS instrument coupled to a gas chromatograph. Elemental analyses were performed by the Laboratoire de Microanalyse Organique (C.N.R.S., IRCOF, Rouen). Column chromatographies were performed on standard silica gel (230-400 mesh) or basic alumina. ^{1}H NMR spectra were recorded in $CDCl_3$ or C_6D_6 at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz; chemical shift (δ) are given in parts per million (ppm) and the coupling constants (*J*) in hertz.

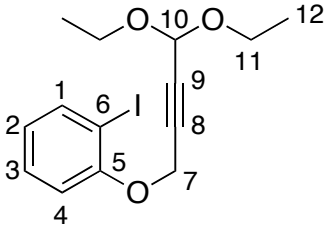
DMF was stored under argon. THF was distilled from sodium/benzophenone. The catalyst precursor $NiBr_2$bipy was prepared separately according to the literature.[1]

General procedure for the Mitsunobu reaction (Syntheses of compounds 1a-d). To a solution of 25 mmol of iodophenol (5.5 g), 25 mmol of triphenylphosphine (6.6 g) and 27 mmol of 2-butyn-1-ol (2.1 mL) in 100 mL of distilled THF at 0°C under argon was added dropwise 25 mmol of DIAD (5 mL). The solution was warmed to room temperature, stirred for 30 minutes and wash by adding NaOH 0.5M (100 mL). The mixture was diluted by Et_2O (100mL) and wash again by NaOH 0.5 M (100 mL) and then water (100 mL). The combined organic layers were dried over $MgSO_4$, and concentrated. Pentane (100 mL) was added to the residue to precipitate triphenylphosphine oxide. After filtration the oil thus obtained was purified by column chromatography eluted with 95/5 pentane/diethylether to give 6.20 g of desired compound **1b** (22.8 mmol, 91%). The same procedure was employed for compounds **1a** (83%), **1c** (85%) and **1d** (74%).

[1] (a) Uchino, M.; Asagi, K.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1975**, *84*, 93-103; (b) Dunach, E.; Périchon, J. *J. Organomet. Chem.* **1988**, *352*, 239-246.

General Procedure for the intramolecular carbonickelation of alkynes (Scheme 1). 1 mmol of aryl halides **1a-d** was added in a stirred flask under argon at room temperature with 5 mL of DMF. Then 0.11 g of Mn (2 mmol) was introduced, follow up by 0.374 g of $NiBr_2$bipy (1 mmol) and finally 20 μL of CF_3CO_2H to activate manganese metal. The reaction was conducted at room temperature. The reaction was monitored by GC and stopped after aryl halide was consumed (*ca*. 30 min). The mixture was then hydrolyzed with water (10 mL) and diluted with diethyl ether (10 mL). The crude mixture was filtered through celite. The aqueous layer was extracted with diethyl ether (2x10 mL), the combined organic layers were washed with water to ensure complete removal of DMF and saturated NaCl solution, dried over $MgSO_4$ and the solvent was evaporated. The oil thus obtained was purified by column chromatography eluted with 95/5 pentane/diethylether to give desired compounds.

General Procedure for the domino cyclisation-condensation of iodoaryl (Table 1 and Table 2). 1 mmol of aryl iodides **1a-d** and 1.3 to 1.8 mmol of electrophile were added in a stirred flask under argon at 50°C with 5 mL of DMF. Then 0.11 g of Mn (2 mmol) was introduced, follow up by 0.0374 g of $NiBr_2$bipy (0.1 mmol) and finally 20 μL of CF_3CO_2H to activate manganese metal. The reaction was conducted at 50°C and was monitored by GC-analysis and quenched after the aryl halide was consumed (*ca.* 2h). The mixture was then hydrolyzed with water (10 mL) and diluted with ethyl acetate (10 mL). The crude mixture was filtered through celite. The aqueous layer was extracted with ethyl acetate (2x10 mL), the combined organic layers were washed with water to ensure complete removal of DMF and saturated NaCl solution, dried over $MgSO_4$ and the solvent was evaporated. The product was isolated by column chromatography eluted with 95/5 pentane/ethyl acetate to give desired compounds.



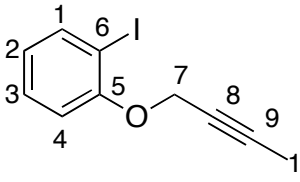
1-(4,4-diethoxybut-2-ynyloxy)-2-iodobenzene 1a

<u>*NMR* ^1H</u> : 1.13 (t, *J*=7.2Hz, $6H^{12}$) ; 3.47 (dq, *J*=9.4Hz *J*=7.2Hz, $2H^{11}$) ; 3.61 (dq, *J*=9.4Hz *J*=7.2Hz, $2H^{11}$) ; 4.74 (s, $2H^7$) ; 5.21 (s, $1H^{10}$) ; 6.67 (t, *J*=7.5Hz, $1H^2$) ; 6.91 (d, *J*=8.3Hz, $1H^4$) ; 7.22 (t, *J*=8.3Hz, $1H^3$) ; 7.70 (d, *J*=7.5Hz, $1H^1$).

NMR ^{13}C : 15.0 ($2C^{12}$) ; 56.9 (C^{7}); 61.0 ($2C^{11}$) ; 79.7 (C^{6}); 83.1 (C^{9}); 86.6 (C^{8}); 91.1 (C^{10}); 113.4 (C^{4}); 115.1 (C^{2}); 129.3 (C^{3}); 139.6 (C^{1}); 156.2 (C^{5}).

MS : 360 (M^{+}), 160, 141, 131, 85 (base).

IR (cm^{-1}) : 2975, 2358, 1472, 1142, 1052.



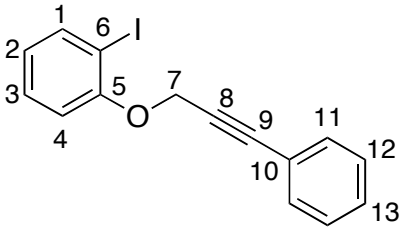
1-(but-2-ynyloxy)-2-iodobenzene 1b

NMR ^{1}H : 1.86 (t, *J*=2.0Hz, $3H^{10}$) ; 4.72 (q, *J*=2.0Hz, $2H^{7}$) ; 6.74 (td, *J*=7.5Hz *J*=1.2Hz, $1H^{2}$) ; 6.99 (dd, *J*=8.0Hz *J*=1.2Hz, $1H^{4}$) ; 7.31 (td, *J*=8.0Hz *J*=1.2Hz, $1H^{3}$) ; 7.78 (dd, *J*=7.5Hz *J*=1.2Hz, $1H^{1}$).

NMR ^{13}C : 4.2 (C^{10}); 57.9 (C^{7}); 74.0 (C^{8}); 84.7 (C^{9}); 86.9 (C^{6}); 113.3 (C^{4}); 123.4 (C^{2}); 129.7 (C^{3}); 140.0 (C^{1}); 156.9 (C^{5}).

MS : 272 (M^{+}), 220 (base), 145, 117, 53.

Anal. Calcd for $C_{10}H_{9}IO$: C, 44.14; H, 3.33. Found: C, 44.38; H, 3.46.

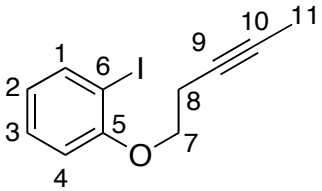


1-iodo-2-(3-phenylprop-2-ynyloxy)benzene 1c

NMR ^{1}H : 4.99 (s, $2H^{7}$) ; 6.76 (td, *J*=7.5Hz *J*=1.1Hz, $1H^{2}$) ; 7.10 (dd, *J*=8.3Hz *J*=1.1Hz, $1H^{4}$) ; 7.30-7.34 (m, $4H^{3,12,13}$) ; 7.44 (dd, *J*=7.2Hz *J*=2.6Hz, $2H^{11}$) ; 7.81 (dd, *J*=7.5Hz *J*=1.1Hz, $1H^{1}$).

NMR ^{13}C : 58.2 (C^{7}); 83.8 (C^{6}); 87.1 (C^{9}); 88.1 (C^{8}); 113.7 (C^{4}); 122.5 (C^{10}); 123.7 (C^{2}); 128.7 ($2C^{12}$) ; 129.2 (C^{13}); 129.8 (C^{3}); 132.2 ($2C^{11}$) ; 140.1 (C^{1}); 156.9 (C^{5}).

Anal. Calcd for $C_{15}H_{11}IO$: C, 53.92; H, 3.32. Found: C, 53.98; H, 3.31.



1-iodo-2-(pent-3-ynyloxy)benzene 1d

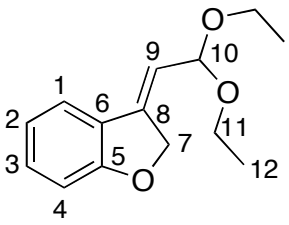
NMR ^{1}H : 1.80 (t, *J*=2.3Hz, $3H^{11}$) ; 2.64-2.72 (m, $2H^{8}$) ; 4.09 (t, *J*=7.5Hz, $2H^{7}$) ; 6.71 (td, *J*=7.5Hz *J*=1.5Hz, $1H^{2}$) ; 6.82 (dd, *J*=7.9Hz *J*=1.5Hz, $1H^{4}$) ; 7.28 (td, *J*=7.5Hz *J*=1.5Hz, $1H^{3}$) ; 7.77 (dd, *J*=7.9Hz *J*=1.5Hz, $1H^{1}$).

NMR ^{13}C : 3.7 (C^{11}); 19.8 (C^{8}); 68.0 (C^{7}); 74.8 (C^{10}); 77.7 (C^{9}); 86.9 (C^{6}); 112.7 (C^{4}); 123.0 (C^{2}); 129.6 (C^{3}); 139.7 (C^{1}); 157.3 (C^{5}).

MS : 286 (M^{+}), 220, 159 (M-I, base), 144, 131, 106, 92, 65.

IR (cm^{-1}) : 2976, 2870, 2242, 1383, 1113, 910, 741.

Anal. Calcd for $C_{11}H_{11}IO$: C, 46.18; H, 3.88. Found: C, 46.65; H, 3.76.



(*Z*)-3-(2,2-diethoxyethylidene)-2,3-dihydrobenzofuran 2a

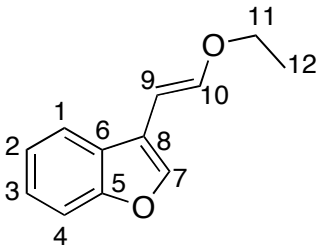
NMR ^{1}H : ($CDCl_3$) 1.25 (t, *J*=7.2Hz, $6H^{12}$) ; 3.55 (dq, *J*=9.3Hz *J*=7.2Hz, $2H^{11}$) ; 3.69 (dq, *J*=9.3Hz *J*=7.2Hz, $2H^{11}$) ; 5.20 (bs, $3H^{7,10}$) ; 5.82-5.86 (m, $1H^{9}$) ; 6.85 (t, *J*=8.1Hz, $1H^{2}$) ; 6.91 (d, *J*=7.8Hz, $1H^{4}$) ; 7.21 (t, *J*=8.1Hz, $1H^{3}$) ; 7.38 (d, *J*=7.5Hz, $1H^{1}$).

(C_6D_6) 1.05 (t, *J*=7.2Hz, $6H^{12}$) ; 3.29 (dq, *J*=9.3Hz *J*=7.2Hz, $2H^{11}$) ; 3.47 (dq, *J*=9.3Hz *J*=7.2Hz, $2H^{11}$) ; 5.01 (bs, $1H^{10}$) ; 5.12 (bs, $2H^{7}$) ; 5.79-5.83 (m, $1H^{9}$) ; 6.70 (td, *J*=7.5Hz *J*=1.0Hz, $1H^{2}$) ; 6.86 (d, *J*=8.5Hz, $1H^{4}$) ; 6.97 (t, *J*=8.5Hz, $1H^{3}$) ; 7.09 (d, *J*=8.0Hz, $1H^{1}$).

NMR ^{13}C : (C_6D_6) 16.1 ($2C^{12}$); 60.6 ($2C^{11}$); 74.8 (C^{7}); 100.1 (C^{10}); 111.5 (C^{4}); 114.6 (C^{9}); 121.5 (C^{2}); 121.8 (C^{6}); 126.6 (C^{1}); 131.5 (C^{3}); 140.8 (C^{8}); 164.5 (C^{5}).

NMR 2D NOESY : (C_6D_6) correlation between 5.79-5.83 (m, $1H^{9}$) and 7.09 (d, *J*=8.0Hz, $1H^{1}$) ; and between 1.05 (t, *J*=7.2Hz, $6H^{12}$) and 5.12 (bs, $2H^{7}$).

MS : 234 (M^{+}), 207, 188, 160, 131 (base), 102, 73.



3-(2-ethoxyvinyl)benzofuran 3

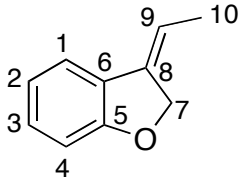
NMR ^{1}H : *E isomer* : 1.38 (t, *J*=7.1Hz, $3H^{12}$) ; 3.92 (q, *J*=7.1Hz, $2H^{11}$) ; 5.84 (d, *J*=13.1Hz, $1H^{9}$) ; 7.05 (d, *J*=13.1Hz, $1H^{10}$) ; 7.20-7.32 (m, $2H^{2,3}$) ; 7.45 (dd, *J*=7.2Hz *J*=1.4Hz, 1H) ; 7.50 (s, $1H^{7}$) ; 7.63 (dd, *J*=6,5Hz *J*=1.3Hz, 1H).

Z isomer : 1.35 (t, *J*=7.2Hz, $3H^{12}$) ; 4.04 (q, *J*=7.2Hz, $2H^{11}$) ; 5.41 (d, *J*=6.4Hz, $1H^{9}$) ; 6.37 (d, *J*=6.4Hz, $1H^{10}$) ; 7.20-7.32 (m, $2H^{2,3}$) ; 7.45 (dd, *J*=7.2Hz *J*=1.4Hz, 1H) ; 7.61 (dd, *J*=7,7Hz *J*=1.8Hz, 1H) ; 8.03 (s, $1H^{7}$).

<u>*NMR* ^{13}C</u> : *E isomer* : 15.2 (C^{12}); 65.8 (C^{11}); 95.5 (C^{9}); 112.0 (C^{4}); 117.3 (C^{8}); 120.8 (C^{1}); 123.0 (C^{2}); 124.8 (C^{3}); 126.8 (C^{6}); 140.7 (C^{7}); 148.5 (C^{10}); 156.0 (C^{5}).

Z isomer : 15.6 (C^{12}); 69.0 (C^{11}); 93.8 (C^{9}); 111.4 (C^{4}); 115.4 (C^{8}); 119.5 (C^{1}); 122.4 (C^{2}); 124.2 (C^{3}); 127.2 (C^{6}); 143.6 (C^{7}); 146.8 (C^{10}); 154.6 (C^{5}).

<u>*MS*</u> : 189 (M+1, base), 161.



(*Z*)-3-ethylidene-2,3-dihydrobenzofuran 2b

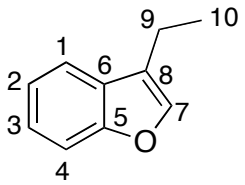
<u>*NMR* ^{1}H</u> : 1.74 (dt, *J*=7.1Hz *J*=1.9Hz, $3H^{10}$) ; 5.10 (bs, $2H^{7}$) ; 5.86 (qt, *J*=7.1Hz *J*=3.6Hz, $1H^{9}$) ; 6.84 (dd, *J*=7.3Hz *J*=1.0Hz, $1H^{4}$) ; 6.86 (td, *J*=7.6Hz *J*=1.0Hz, $1H^{2}$) ; 7.13 (td, *J*=7.5Hz *J*=1.2Hz, $1H^{3}$) ; 7.34 (dd, *J*=7.5Hz *J*=1.2Hz, $1H^{1}$).

<u>*NMR* ^{13}C</u> : 15.3 (C^{10}); 73.9 (C^{7}); 110.6 (C^{4}); 111.8 (C^{9}); 120.4 (C^{2}); 120.9 (C^{1}); 126.6 (C^{6}); 129.5 (C^{3}); 136.7 (C^{8}); 163.4 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 1.74 (dt, *J*=7.1Hz *J*=1.9Hz, $3H^{10}$) and 5.10 (s, $2H^{7}$).

<u>*MS*</u> : 146 (M^{+}), 131 (base), 115, 103, 77.

<u>Anal. Calcd</u> for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.77; H, 6.64.

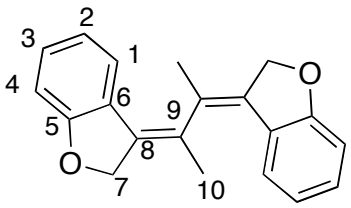


3-ethylbenzofuran 4b

<u>*NMR* ^{1}H</u> : 1.33 (t, *J*=7.6Hz, $3H^{10}$) ; 2.70 (q, *J*=7.6Hz, $2H^{9}$) ; 7.21 (t, *J*=8.3Hz, $1H^{2}$) ; 7.31 (t, *J*=8.3Hz, $1H^{3}$) ; 7.40 (s, $1H^{7}$) ; 7.45 (d, *J*=7.5Hz, $1H^{4}$) ; 7.56 (d, *J*=7.8Hz, $1H^{1}$).

<u>*NMR* ^{13}C</u> : 13.9 (C^{10}); 17.4 (C^{9}); 110.4 (C^{4}); 120.0 (C^{8}); 121.3 (C^{1}); 122.7 (C^{2}); 124.4 (C^{3}); 129.3 (C^{6}); 141.0 (C^{7}); 155.8 (C^{5}).

<u>*MS*</u> : 146 (M^{+}), 131 (base), 115, 103, 77.



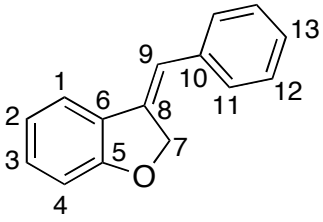
(3*E*,3'*E*)-3,3'-(butane-2,3-diylidene)bis(2,3-dihydrobenzofuran) 5

<u>*NMR* ^{1}H</u> : 1.89 (s, 6H^{10}) ; 5.17 (d, *J*=14.3Hz, 2H^{7}) ; 5.24 (d, *J*=14.3Hz, 2H^{7}) ; 6.74 (t, *J*=7.5Hz, 2H^{2}) ; 6.82 (d, *J*=8.3Hz, 2H^{4}) ; 7.08 (t, *J*=7.9Hz, 2H^{3}) ; 7.24 (d, *J*=7.2Hz, 2H^{1}).

<u>*NMR* ^{13}C</u> : 19.3 (C^{10}); 74.5 (C^{7}); 110.4 (C^{4}); 121.3 (C^{2}); 123.4 (C$_{q}$); 125.4 (C$_{q}$); 126.8 (C^{1}); 129.4 (C^{3}); 131.0 (C^{8}); 164.3 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 1.89 (s, 6H^{10}) and 5.17 (d, *J*=14.3Hz, 2H^{7}) 5.24 (d, *J*=14.3Hz, 2H^{7}).

<u>*MS*</u> : 290 (M^{+}, base), 275 (M-CH$_3$), 260, 182, 172, 145.



3-benzylidene-2,3-dihydrobenzofuran 2c

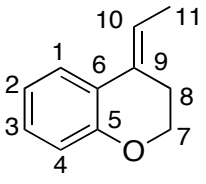
<u>*NMR* ^{1}H</u> : *Z isomer* : 5.44 (d, *J*=3Hz, 2H^{7}) ; 6.86 (t, *J*=3Hz, 1H^{9}) ; 6.93 (d, *J*=7.9Hz, 1H^{4}) ; 6.97 (t, *J*=6.4Hz, 1H^{2}) ; 7.21-7.28 (m, 4H^{11,12}) ; 7.42 (t, *J*=7.9Hz, 2H^{3,13}) ; 7.54 (d, *J*=7.5Hz, 1H^{1}).

E isomer : 5.24 (d, *J*=2.6Hz, 2H^{7}) ; 6.50 (t, *J*=2.5Hz, 1H^{9}) ; 6.68 (t, *J*=7.8Hz, 1H^{2}) ; 6.86 (d, *J*=7.8Hz, 1H^{4}) ; 7.16 (t, *J*=7.8Hz, 1H^{3}) ; 7.20-7.45 (m, 6H^{1,11,12,13}).

<u>*NMR* ^{13}C</u> : *Z isomer* : 75.1 (C^{7}); 110.9 (C^{4}); 117.1 (C^{2}); 120.7 (C^{6}); 121.4 (C^{9}); 124.3 (C^{1}); 127.1 (C^{3}); 128.4 (2C^{11}) ; 129.2 (2C^{12}) ; 130.6 (C^{13}); 137.1 (C^{10}); 137.4 (C^{8}); 163.0 (C^{5}).

E isomer : 76.5 (C^{7}); 111.1 (C^{4}); 118.5 (C^{2}); 120.6 (C^{6}); 121.7 (C^{9}); 127.2 (C^{1}); 128.4 (2C^{11}) ; 128.9 (C^{3}); 129.1 (C^{13}); 129.9 (2C^{12}) ; 131.1 (C^{10}); 137.1 (C^{8}); 156.3 (C^{5}).

<u>*MS*</u> : 208 (M^{+}, base), 207, 178, 131 (M-C$_6$H$_5$).



(*E*)-4-ethylidenechroman 2d

<u>*NMR* ^{1}H</u> : 1.77 (d, *J*=7.0Hz, 3H^{11}) ; 2.64 (t, *J*=7.0Hz, 2H^{8}) ; 4.10 (t, *J*=7.0Hz, 2H^{7}) ; 6.11 (q, *J*=7.0Hz, 1H^{10}) ; 6.84 (d, *J*=7.2Hz, 1H^{4}) ; 6.87 (t, *J*=8.3Hz, 1H^{2}) ; 7.08 (t, *J*=7.2Hz, 1H^{3}) ; 7.50 (d, *J*=8.3Hz, 1H^{1}).

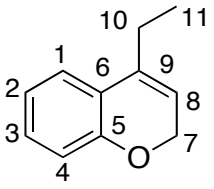
NMR ^{13}C : 13.4 (C^{11}); 25.7 (C^{8}); 66.3 (C^{7}); 116.8 (C^{10}); 117.5 (C^{4}); 120.9 (C^{2}); 123,2 (C^{9}); 123.6 (C^{1}); 128.2 (C^{3}); 128.9 (C^{6}); 154.1 (C^{5}).

NMR 2D NOESY : correlation between 1.77 (d, *J*=7.0Hz, $3H^{11}$) and 2.64 (t, *J*=7.0Hz, $2H^{8}$).

MS : 160 (M^{+}, base), 145 (M-CH_3), 131, 117, 102, 91, 77, 63, 51.

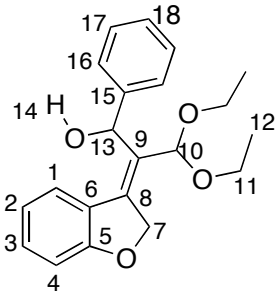
IR (cm^{-1}) : 2922, 1599, 1482, 1244, 1038.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.35; H, 7.63.



4-ethyl-2H-chromene 4d (obtained after acidic work-up in 65%)

NMR ^{1}H : 2.04 (t, *J*=7.5Hz, $3H^{11}$) ; 2.54 (q, *J*=7.5Hz, $2H^{10}$) ; 5.19 (d, *J*=5.6Hz, $2H^{7}$) ; 5.62 (t, *J*=7.0Hz, $1H^{8}$) ; 6.80-6.91 (m, $2H_{ar}$) ; 7.20-7.28 (m, $2H_{ar}$).



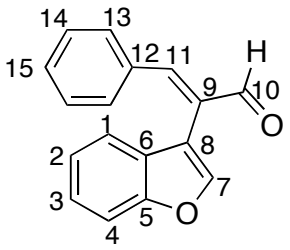
(*Z*)-2-(benzofuran-3(2*H*)-ylidene)-3,3-diethoxy-1-phenylpropan-1-ol 6a

NMR ^{1}H : 1.05 (t, *J*=7.1Hz, $3H^{12}$) ; 1.12 (t, *J*=7.1Hz, $3H^{12}$) ; 1.25 (bs, $1H^{14}$) ; 3.30 (dq, *J*=9.0Hz *J*=7.1Hz, $2H^{11}$) ; 3.54 (dq, *J*=9.0Hz *J*=7.1Hz, $2H^{11}$) ; 4.96 (s, $1H^{10}$) ; 5.25 (d, *J*=15.9Hz, $1H^{7}$) ; 5.34 (d, *J*=15.9Hz, $1H^{7}$) ; 6.34 (d, *J*=6.6Hz, $1H^{13}$) ; 6.86 (td, *J*=7.5Hz *J*=1.1Hz, $1H^{2}$) ; 6.92 (d, *J*=8.1Hz, $1H^{4}$) ; 7.22-7.27 (m, $2H^{3,18}$) ; 7.33 (t, *J*=7.3Hz, $2H^{17}$) ; 7.46 (d, *J*=7.3Hz, $2H^{16}$) ; 7.55 (d, *J*=7.8Hz, $1H^{1}$).

NMR ^{13}C : 15.1 ($2C^{12}$) ; 61.8 (C^{11}); 62.9 (C^{11}); 70.9 (C^{13}); 74.4 (C^{7}); 101.8 (C^{10}); 110.9 (C^{4}); 121.0 (C^{2}); 124.4 (C^{6}); 125.4 (C^{1}); 125.5 (C^{18}); 127.1 (C_{ar}); 128.4 (C_{ar}); 128.8 (C_{ar}); 129.1 (C_{ar}); 129.9 (C_{ar}); 131.1 (C^{9}); 134.6 (C^{8}); 142.4 (C^{15}); 164.7 (C^{5}).

MS : 248, 219 (base), 191, 165, 142, 114, 78.

IR (cm^{-1}) : 3451, 2975, 2925, 2874, 2359, 1603, 1475, 1466, 1449, 1228, 1103, 1060, 747.



(*E*)-2-(benzofuran-3-yl)-3-phenylacrylaldehyde 7a

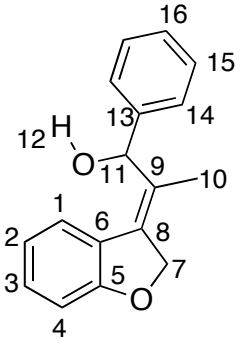
<u>*NMR* ^{1}H</u> : 6.83 (d, *J*=7.9Hz, 1H^{4}) ; 7.00 (t, *J*=8.3Hz, 1H^{2}) ; 7.18-7.28 (m, 4H^{3,14,15}) ; 7.35 (d, *J*=7.2Hz, 2H^{13}) ; 7.50 (d, *J*=8.3Hz, 1H^{1}) ; 7.57 (s, 1H^{11}) ; 7.83 (s, 1H^{7}) ; 9.80 (s, 1H^{10}).

<u>*NMR* ^{13}C</u> : 112.1 (C^{1}); 112.6 (C^{8}); 121.7 (C^{4}); 123.0 (C^{2}); 124.9 (C^{15}); 125.7 (C^{6}); 129.0 (2C^{14}) ; 130.9 (C^{3}); 131.0 (2C^{13}) ; 131.9 (C^{12}); 134.5 (C^{9}); 145.6 (C^{7}); 151.5 (C^{11}); 155.6 (C^{5}); 193.5 (C^{10}).

<u>*NMR 2D NOESY*</u> : correlation between 7.57 (s, 1H^{11}) and 9.80 (s, 1H^{10}).

<u>*MS*</u> : 248 (M^{+}), 219 (base), 191, 189, 165.

<u>Anal. Calcd</u> for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.54; H, 4.89.



(*E*)-2-(benzofuran-3(2H)-ylidene)-1-phenylpropan-1-ol 6b

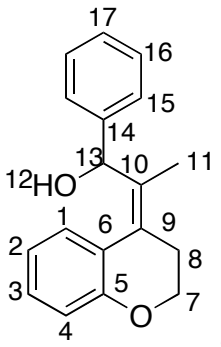
<u>*NMR* ^{1}H</u> : 1.61 (s, 3H^{10}) ; 2.00 (s, 1H^{12}) ; 5.10 (bs, 2H^{7}) ; 6.37 (s, 1H^{11}) ; 6.88 (t, *J*=7.9Hz, 1H^{2}) ; 6.89 (d, *J*=8.0Hz, 1H^{4}) ; 7.19 (t, *J*=7.9Hz, 1H^{3}) ; 7.29 (d, *J*=7.1Hz, 1H^{16}) ; 7.35 (t, *J*=7.9Hz, 2H^{15}) ; 7.45 (d, *J*=7.9Hz, 2H^{14}) ; 7.58 (d, *J*=7.9Hz, 1H^{1}).

<u>*NMR* ^{13}C</u> : 15.0 (C^{10}); 71.6 (C^{11}); 75.0 (C^{7}); 111.1 (C^{4}); 121.2 (C^{2}); 124.5 (C^{1}); 125.0 (C^{6}); 126.0 (2C^{14}) ; 127.8 (C^{16}); 128.5 (C^{9}); 128.8 (2C^{15}) ; 130.0 (C^{3}); 133.2 (C^{8}); 141.8 (C^{13}); 165.0 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 1.61 (s, 3H^{10}) and 5.12 (bs, 2H^{7}).

<u>*MS*</u> : 234 (M-H_2O), 219 (base), 218, 191, 189.

<u>Anal. Calcd</u> for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.89; H, 6.35.



(*Z*)-2-(chroman-4-ylidene)-1-phenylpropan-1-ol 6d

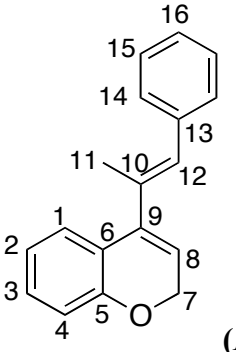
<u>*NMR ^{1}H*</u> : 1.68 (s, 3H^{11}) ; 2.05 (s, 1H^{12}) ; 2.69 (m, 2H^{8}) ; 4.35 (m, 2H^{7}) ; 6.16 (s, 1H^{13}) ; 6.80 (td, *J*=7.8Hz *J*=1.2Hz, 1H^{2}) ; 6.86 (dd, *J*=8.0Hz *J*=1.2Hz, 1H^{4}) ; 7,17 (td, *J*=8.0Hz *J*=1.5Hz, 1H^{3}) ; 7.28 (m, 3H$_{ar}$) ; 7.38 (m, 3H$_{ar}$).

<u>*NMR ^{13}C*</u> : 13.8 (C^{11}); 28.0 (C^{8}); 67.7 (C^{7}); 72.9 (C^{13}); 116.9 (C^{4}); 119.9 (C^{2}); 123.0 (C^{14}); 126.2 (2C^{15}) ; 127.3 (C^{17}); 128.5 (2C^{16}) ; 128.7 (C^{1}); 129.2 (C^{3}); 130.1 (C^{6}); 130.3 (C^{10}); 142.6 (C^{9}); 154.9 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 1.68 (s, 3H^{11}) and 2.69 (m, 2H^{8}).

<u>*MS*</u> : 248 (M-H_2O), 233 (base), 215, 205, 171, 131, 91, 77.

<u>*IR (cm^{-1})*</u> : 3418, 2976, 2869, 2359, 1486,1449, 1119.



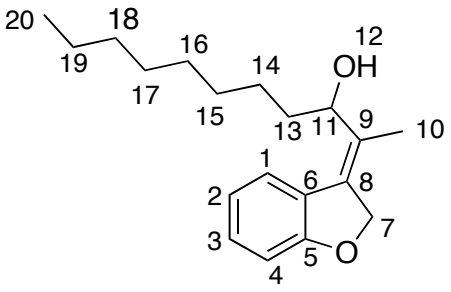
(*E*)-4-(1-phenylprop-1-en-2-yl)-2H-chromene 7d

<u>*NMR ^{1}H :*</u> 2.07 (d, *J*=1.5Hz, 3H^{11}) ; 4.74 (d, *J*=4.0Hz, 2H^{7}) ; 5.75 (t, *J*=4.0Hz, 1H^{8}) ; 6.56 (q, *J*=1.5Hz, 1H^{12}) ; 6.87 (t, *J*=7.8Hz, 2H^{2,4}) ; 7.12 (t, *J*=7.2Hz, 2H^{15}) ; 7.21-7.26 (m, 1H^{16}) ; 7.35 (d, *J*=4.5Hz, 4H^{1,3,14}).

<u>*NMR ^{13}C*</u> : 17.3 (C^{11}); 64.1 (C^{7}); 115.3 (C^{4}); 117.0 (C^{8}); 120.2 (C^{6}); 121.9 (C^{2}); 124.5 (C^{12}); 125.6 (C^{16}); 127.2 (2C^{14}) ; 128.0 (2C^{15}); 128.4 (C^{3}); 128.6 (C^{1}); 134.6 (C^{13}); 136.5 (C^{9}); 139.5 (C^{10}); 153.8 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 5.75 (t, *J*=4Hz, 1H^{8}) and 6.57 (q, *J*=1Hz, 1H^{12}).

<u>*MS :*</u> 248 (M^{+}, base), 233.



(*E*)-2-(benzofuran-3(2*H*)-ylidene)undecan-3-ol 8b

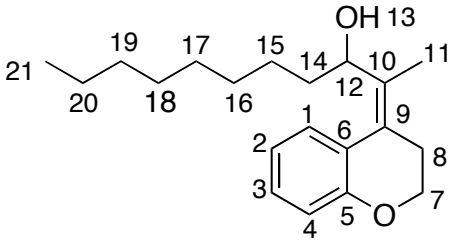
<u>*NMR ^{1}H :*</u> 0.85-0.90 (m, $3H^{20}$) ; 1.26 (m, $14H^{13-19}$) ; 1.69 (t, *J*=1.9Hz, $3H^{10}$) ; 2.04 (s, $1H^{12}$) ; 5.01 (s, $2H^{7}$) ; 5.10 (t, *J*=7.7Hz, $1H^{11}$) ; 6.85 (d, *J*=7.9Hz, $1H^{4}$) ; 6.87 (t, *J*=7.6Hz, $1H^{2}$) ; 7.14 (t, *J*=7.6Hz, $1H^{3}$) ; 7.44 (d, *J*=7.9Hz, $1H^{1}$).

<u>*NMR ^{13}C*</u> : 14.1 (C^{20}); 14.2 (C^{10}); 22.8 (C^{19}); 25.9 (C^{18}); 29.4 (C^{17}); 29.6 (C^{16}); 29.8 (C^{15}); 32.0 (C^{14}); 34.9 (C^{13}); 70.4 (C^{11}); 74.6 (C^{7}); 110.6 (C^{4}); 120.7 (C^{2}); 124.5 (C^{1}); 124.8 (C^{6}); 129.2 (C^{3}); 129.8 (C^{9}); 131.0 (C^{8}); 164.5 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 1.69 (t, *J*=1.9Hz, $3H^{10}$) and 5.01 (s, $2H^{7}$).

<u>*MS*</u> : 287 (M-H), 270 (M-H_2O, base), 171, 158, 145, 128, 115.

<u>*IR (cm^{-1})*</u> : 3379, 2924, 1466, 1226, 745.



(*Z*)-2-(chroman-4-ylidene)undecan-3-ol 8d

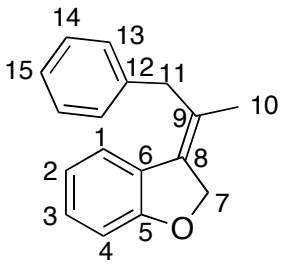
<u>*NMR ^{1}H*</u> : 0.87 (t, *J*=7.2Hz, $3H^{21}$) ; 1.26 (m, $14H^{14-20}$) ; 1.48 (d, *J*=3.6Hz, $1H^{13}$) ; 1.82 (s, $3H^{11}$) ; 2.61 (dd, *J*=5.7Hz *J* = 5.4Hz, $2H^{8}$) ; 4.23 (dt, *J*=10.8Hz *J*=5.7Hz, $1H^{7}$) ; 4.33 (dt, *J*=10.8Hz *J*=5.4Hz, $1H^{7}$) ; 4.93 (m, $1H^{12}$) ; 6.82 (d, *J*=8.1Hz, $1H^{4}$) ; 6.85 (td, *J*=7.5Hz *J*=1.2Hz, $1H^{2}$) ; 7.13 (t, *J*=7.2Hz, $1H^{3}$) ; 7.19 (dd, *J*=7.8Hz *J*=1.5Hz, $1H^{1}$).

<u>*NMR ^{13}C*</u> : 12.5 (C^{11}); 14.1 (C^{21}); 22.7 (C^{20}); 26.0 (C^{19}); 27.9 (C^{18}); 29.4 (C^{17}); 29.6 ; 29.8 ; 31.9 (C^{15}); 35.3 (C^{14}); 67.7 (C^{7}); 71.4 (C^{12}); 116.6 (C^{4}); 119.5 (C^{2}); 123.1 (C^{3}); 128.5 (C^{6}); 128.7 (C^{1}); 129.1 (C^{10}); 131.5 (C^{9}); 154.6 (C^{5}).

<u>*NMR 2D NOESY*</u> : correlation between 1.82 (s, $3H^{11}$) and 2.61 (dd, *J*=5.7Hz *J* = 5.4Hz, $2H^{8}$).

<u>*MS*</u> : 302 (M^{+}), 189, 133 (base).

<u>*IR (cm^{-1})*</u> : 3393, 2977, 2873, 2242, 1110, 909, 739.



3-(1-phenylpropan-2-ylidene)-2,3-dihydrobenzofuran 9b

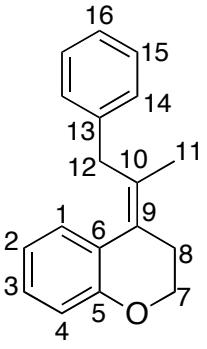
<u>NMR ^{1}H</u> : *E isomer* : 1.66 (t, *J*=1.6Hz, $3H^{10}$) ; 3.80 (s, $2H^{11}$) ; 5.11 (s, $2H^{7}$) ; 6.80-6.86 (m, $2H^{2,4}$); 7.08-7.30 (m, $6H^{3,13-15}$) ; 7.49 (d, *J*=7.9Hz, $1H^{1}$).

Z isomer : 1.42 (s, $3H^{10}$) ; 3.36 (s, $2H^{11}$) ; 5.02 (s, $2H^{7}$) ; 6.80-6.86 (m, $2H^{2,4}$) ; 7.08-7.30 (m, $6H^{3,13-15}$) ; 7.49 (d, *J*=7.9Hz, $1H^{1}$).

<u>NMR ^{13}C</u> : *E isomer* : 21.1 (C^{10}); 40.1 (C^{11}); 74.8 (C^{7}); 110.3 (C^{3}); 120.7 (C^{4}); 123.4 (C^{1}); 126.0 (C^{6}); 126.4 (C^{2}); 128.5 (2C) ; 128.7 (2C) ; 128.9 (C^{15}); 138.9 (C^{12}); 139.6 (C^{9}); 139.7 (C^{8}); 164.4 (C^{5}).

<u>NMR 2D NOESY</u> : *E isomer* : correlation between 1.66 (t, *J*=1.6Hz, $3H^{10}$) and 5.11 (s, $2H^{7}$).

<u>MS</u> : 236 (M^{+}), 221 (M-CH_3), 145 (base), 118, 115, 91.



4-(1-phenylpropan-2-ylidene)chroman 9d

<u>NMR ^{1}H</u> : *Z isomer* : 1.79 (s, $3H^{11}$) ; 2.72 (t, *J*=5.9Hz, 2H8) ; 3.84 (s, $2H^{12}$) ; 4.34 (t, *J*=5.9Hz, $2H^{7}$) ; 6.75 (td, *J*=7.5Hz *J*=1.2Hz, $1H^{2}$) ; 6.83 (m, $2H^{3,4}$) ; 7.26 (m, $6H_{ar}$).

E isomer : 1.59 (s, $3H^{11}$) ; 2.59 (m, $2H^{8}$) ; 3.60 (s, $2H^{12}$) ; 4.01 (m, $2H^{7}$) ; 6.83 (m, $3H^{2-4}$) ; 7.26 (m, $6H_{ar}$).

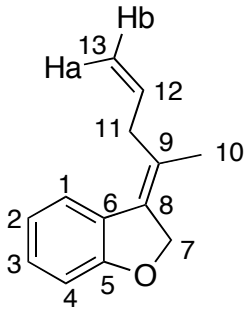
<u>NMR ^{13}C</u> : *Z isomer* : 19.4 (C^{11}); 27.9 (C^{8}); 41.3 (C^{12}); 67.9 (C^{7}); 111.6 (C^{3}); 116.8 (C^{4}); 119.7 (C^{1}); 123.8 (C^{6}); 126.1 (C^{2}); 127.5 (C^{16}); 128.65 (2C) ; 128.67 (2C) ; 129.1 (C^{13}); 130.5 (C^{10}); 140.3 (C^{9}); 154.7 (C^{5}).

E isomer : 19.9 (C^{11}); 21.1 (C^{8}); 40.7 (C^{12}); 66.8 (C^{7}); 111.4 (C^{3}); 116.6 (C^{4}); 119.3 (C^{1}); 123.7 (C^{6}); 125.8 (C^{2}); 128.3 (C^{16}); 128.65 (2C) ; 128.67 (2C) ; 129.1 (C^{13}); 130.2 (C^{10}); 141.2 (C^{9}); 156.4 (C^{5}).

NMR 2D NOESY : *Z isomer* : correlation between 1.79 (s, $3H^{11}$) and 2.73 (t, *J*=5.9Hz, $2H^{8}$).

MS : 250 (M^+, base), 235 , 207 , 157 , 91 , 77.

IR (cm^{-1}) : 2977, 2242, 1383, 1112, 909.



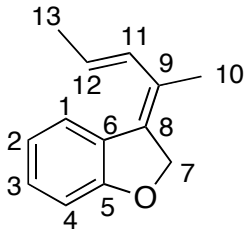
(*E*)-3-(pent-4-en-2-ylidene)-2,3-dihydrobenzofuran 10b

NMR ^1H : 1.74 (t, *J*=1.9Hz, $3H^{10}$) ; 3.18 (d, *J*=6.0Hz, $2H^{11}$) ; 5.08-5.11 (m, $3H^{7,13b}$) ; 5.15 (dd, *J*=7.4Hz *J*=1.9Hz, $1H^{13a}$) ; 5.73-5.95 (m, $1H^{12}$) ; 6.83-6.90 (m, $2H^{2,4}$) ; 7.15 (td, *J*=7.9Hz *J*=1.1Hz, $1H^{3}$) ; 7.44 (d, *J*=7.5Hz, $1H^{1}$).

NMR ^{13}C : 21.4 (C^{10}); 39.0 (C^{11}); 75.0 (C^{7}); 110.5 (C^{4}); 116.3 (C^{13}); 120.9 (C^{2}); 124.0 (C^{1}); 124.4 (C^{9}); 128.9 (C^{6}); 129.4 (C^{3}); 130.4 (C^{8}); 134.5 (C^{12}); 164.5 (C^{5}).

NMR 2D NOESY : correlation between 1.74 (t, *J*=1.9Hz, $3H^{10}$) and 5.08-5.11 (m, $2H^{7}$).

MS : 186 (M^+), 171 (M-CH_3), 145 (M-C_3H_5, base), 128, 118, 91.

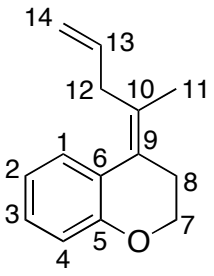


(*E*)-3-((*E*)-pent-3-en-2-ylidene)-2,3-dihydrobenzofuran 10bconj

NMR ^1H : 1.81 (t, *J*=1.5Hz, $3H^{10}$) ; 1.91 (dd, *J*=6.8Hz *J*=1.1Hz, $3H^{13}$) ; 5.06-5.11 (m, $2H^{7}$) ; 5.81-5.95 (m, $1H^{12}$) ; 6.82-6.89 (m, $3H^{2,4,11}$) ; 7.12 (td, *J*=7.9Hz *J*=1.1Hz, $1H^{3}$) ; 7.62 (d, *J*=7.5Hz, $1H^{1}$).

NMR 2D NOESY : correlation between 1.81 (t, *J*=1.5Hz, $3H^{10}$) and 5.06-5.11 (m, $2H^{7}$) and between 1.91 (dd, *J*=6.8Hz *J*=1.1Hz, $3H^{13}$) and 6.82-6.89 (m, H^{11}).

MS : 186 (M^+), 173, 171 (M-CH_3), 145 (M-C_3H_5, base), 118, 91, 77.



(*Z*)-4-(pent-4-en-2-ylidene)chroman 10d

<u>NMR ^{1}H</u> : *Z isomer* : 1.84 (s, 3H^{11}) ; 2.66 (t, *J*=5.7Hz, 2H^{8}) ; 3.15 (d, *J*=5.7Hz, 2H^{12}) ; 4.29 (t, *J*=5.7Hz, 2H^{7}) ; 5.12-5.22 (m, 2H^{14}) ; 5.96-6.05 (m, 1H^{13}) ; 6.81-6.86 (m, 2H^{2,4}) ; 7.13 (t, *J*=8.1Hz, 1H^{3}) ; 7.26 (dd, *J*=8.1Hz *J*=1.5Hz, 1H^{1}).

E isomer : 1.81 (s, 3H^{11}) ; 2.66 (t, *J*=5.7Hz, 2H^{8}) ; 2.94 (d, *J*=6.0Hz, 2H^{12}) ; 4.29 (t, *J*=5.7Hz, 2H^{7}) ; 5.02-5.08 (m, 2H^{14}) ; 5.71-5.80 (m, 1H^{13}) ; 6.81-6.86 (m, 2H^{2,4}) ; 7.13 (t, *J*=8.1Hz, 1H^{3}) ; 7.26 (dd, *J*=8.1Hz *J*=1.5Hz, 1H^{1}).

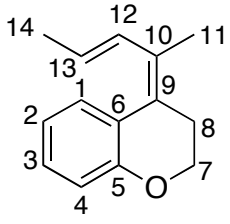
<u>NMR ^{13}C</u> : *Z isomer* : 19.3 (C^{11}); 27.9 (C^{8}); 40.0 (C^{12}); 67.8 (C^{7}); 116.2 (C^{14}); 116.6 (C^{4}); 119.5 (C^{2}); 123.6 (C^{6}); 126.6 (C^{10}); 127.8 (C^{9}); 128.3 (C^{3}); 128.5 (C^{1}); 136.6 (C^{13}); 154.5 (C^{5}).

E isomer : 19.3 (C^{11}); 27.4 (C^{8}); 39.4 (C^{12}); 68.0 (C^{7}); 115.4 (C^{14}); 116.6 (C^{4}); 119.2 (C^{2}); 123.6 (C^{6}); 126.1 (C^{10}); 127.4 (C^{9}); 128.6 (C^{3}); 128.7 (C^{1}); 135.1 (C^{13}); 154.5 (C^{5}).

<u>NMR 2D NOESY</u> : *Z isomer* : correlation between 1.84 (s, 3H^{11}) and 2.66 (t, *J*=5.7Hz, 2H^{8}) and between 3.15 (d, *J*=5.7Hz, 2H^{12}) and 7.26 (dd, *J*=8.1Hz *J*=1.5Hz, 1H^{1}).

<u>MS</u> : 200 (M^{+}, base), 185, 171, 157, 131, 91, 77.

<u>IR *(cm^{-1})*</u> : 2976, 2873, 2243, 1449, 1111, 909.

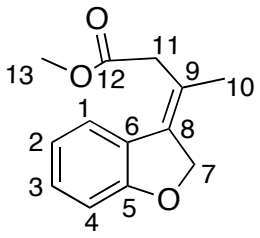


(*Z*)-4-((*E*)-pent-3-en-2-ylidene)chroman 10dconj

<u>NMR ^{1}H</u> : 1.81 (d, *J*=6.8Hz, 3H^{14}) ; 1.84 (s, 3H^{11}) ; 2.66 (t, *J*=5.7Hz, 2H^{8}) ; 4.21 (t, *J*=5.7Hz, 2H^{7}) ; 6.15 (q, *J*=7.8Hz, 1H^{13}) ; 6.73 (t, *J*=8.4Hz, 1H^{12}) ; 6.81-6.86 (m, 1H^{2}) ; 7.13 (t, *J*=8.1Hz, 1H^{3}) ; 7.53 (dd, *J*=8.1Hz *J*=1.5Hz, 1H^{1}) ; 7.76 (d, *J*=8.1Hz, 1H^{4}).

<u>NMR ^{13}C</u> : 13.4 (C^{11}); 21.0 (C^{14}); 25.7 (C^{8}); 66.3 (C^{7}); 116.8 (C^{12}); 117.5 (C^{4}); 120.9 (C^{2}); 123.2 (C^{6}); 123.9 (C^{13}); 128.2 (C^{10}); 128.9 (C^{9}); 129.6 (C^{3}); 139.7 (C^{1}); 154.2 (C^{5}).

<u>NMR 2D NOESY</u> : correlation between 1.84 (s, 3H^{11}) and 2.66 (t, *J*=5.7Hz, 2H^{8}) and between 6.15 (q, *J*=7.8Hz, 1H^{13}) and 7.53 (dd, *J*=8.1Hz *J*=1.5Hz, 1H^{1}).



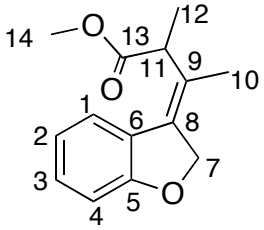
(*E*)-methyl 3-(benzofuran-3(2*H*)-ylidene)butanoate 11

<u>*NMR* ^{1}H</u> : 1.87 (t, *J*=1.9Hz, $3H^{10}$) ; 3.48 (s, $2H^{11}$) ; 3.75 (s, $3H^{13}$) ; 5.11 (bs, $2H^{7}$) ; 6.85 (d, *J*=7.9Hz, $1H^{4}$) ; 6.90 (t, *J*=7.4Hz, $1H^{2}$) ; 7.18 (t, *J*=7.4Hz, $1H^{3}$) ; 7.55 (d, *J*=7.5Hz, $1H^{1}$).

<u>*NMR* ^{13}C</u> : 22.0 (C^{10}); 39.6 (C^{11}); 52.4 (C^{13}); 74.7 (C^{7}); 110.5 (C^{4}); 118.4 (C^{9}); 120.8 (C^{2}); 123.8 (C^{3}); 125.4 (C^{6}); 129.4 (C^{1}); 133.8 (C^{8}); 164.5 (C^{5}); 170.5 (C^{12}).

<u>*NMR 2D NOESY*</u> : correlation between 1,87 (t, *J*=1.9Hz, $3H^{10}$) and 5.11 (bs, $2H^{7}$).

<u>*MS :*</u> 218 (M^{+}), 159 (M-CO_2Me), 145 (base), 131, 115, 91.



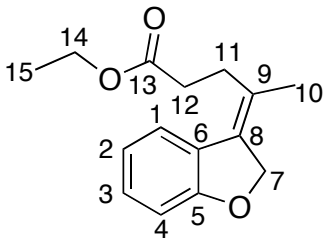
(*E*)-methyl 3-(benzofuran-3(2*H*)-ylidene)-2-methylbutanoate 12

<u>*NMR* ^{1}H *:*</u> 1.35 (d, *J*=7.2Hz, $3H^{12}$) ; 1.67 (t, *J*=1.7Hz, $3H^{10}$) ; 3.70 (s, $3H^{14}$) ; 4.18 (q, *J*=7.2Hz, $1H^{11}$) ; 5.00 (d, *J*=14Hz, $1H^{7}$) ; 5.10 (d, *J*=14Hz, $1H^{7}$) ; 6.86 (d, *J*=7.9Hz, $1H^{4}$) ; 6.89 (t, *J*=7.5Hz, $1H^{2}$) ; 7.15 (t, *J*=7.7Hz, $1H^{3}$) ; 7.56 (d, *J*=7.9Hz, $1H^{1}$).

<u>*NMR* ^{13}C</u> : 15.2 (C^{10}); 16.7 (C^{12}); 42.3 (C^{11}); 52.4 (C^{14}); 75.1 (C^{7}); 110.8 (C^{4}); 121.0 (C^{2}); 124.1 (C^{3}); 124.6 (C_q); 125.2 (C_q); 129.6 (C^{1}); 132.3 (C^{8}); 164.9 (C^{5}); 174.8 (C^{13}).

<u>*NMR 2D NOESY*</u> : correlation between 1.67 (t, *J*=1.7Hz, $3H^{10}$) and 5.00 (d, *J*=14Hz, $1H^{7}$) 5.10 (d, *J*=14Hz, $1H^{7}$).

<u>*MS :*</u> 232 (M^{+}), 173 (M-CO_2Me), 158, 145 (base), 91.



ethyl 4-(benzofuran-3(2*H*)-ylidene)pentanoate 13

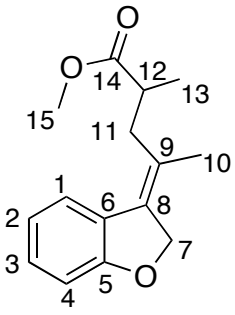
<u>*NMR* ^{1}H</u> : *E isomer* : 1.27 (t, *J*=7.2Hz, $3H^{15}$) ; 1.75 (t, *J*=1.9Hz, $3H^{10}$) ; 2.51 (t, *J*=6.8Hz, $2H^{11}$) ; 2.76 (t, *J*=6.8Hz, $2H^{12}$) ; 4.15 (q, *J*=7.2Hz, $2H^{14}$) ; 5.03 (bs, $2H^{7}$) ; 6.84 (d, *J*=7.9Hz, $1H^{4}$) ; 6.89 (td, *J*=7.9Hz *J*=1.1Hz, $1H^{2}$) ; 7.13 (td, *J*=7.5Hz *J*=1.1Hz, $1H^{3}$) ; 7.50 (d, *J*=7.2Hz, $1H^{1}$).

Z isomer : 1.27 (t, *J*=7.2Hz, 3H[15]) ; 2.03 (t, *J*=2.6Hz, 3H[10]) ; 2.35 (t, *J*=6.8Hz, 2H[11]) ; 2.51 (t, *J*=6.8Hz, 2H[12]) ; 4.15 (q, *J*=7.2Hz, 2H[14]) ; 5.14 (s, 2H[7]) ; 6.84 (d, *J*=7.9Hz, 1H[4]) ; 6.89 (td, *J*=7.9Hz *J*=1.1Hz, 1H[2]) ; 7.13 (td, *J*=7.5Hz *J*=1.1Hz, 1H[3]) ; 7.50 (d, *J*=7.2Hz, 1H[1]).

<u>*NMR* ^{13}C</u> : *E isomer* : 14.4 (C[15]); 21.1 (C[10]); 30.0 (C[11]); 32.4 (C[12]); 60.7 (C[14]); 74.7 (C[7]); 110.3 (C[4]); 120.8 (C[2]); 123.7 (C[6]); 125.5 (C[1]); 125.7 (C[9]); 128.8 (C[3]); 130.6 (C[8]); 164.3 (C[5]); 173.3 (C[13]).

<u>*NMR 2D NOESY*</u> : *E isomer* : correlation between 1.74 (t, *J*=1.9Hz, 3H[10]) and 5.03 (bs, 2H[7]).

<u>*MS*</u> : 246 (M^+), 201 (M-OEt), 173 (M-CO_2Et), 159, 158 (base), 145, 131, 115, 91, 77.



methyl 4-(benzofuran-3(2*H*)-ylidene)-2-methylpentanoate 14

<u>*NMR* ^{1}H</u> : *E isomer* : 1.18 (d, *J*=6.8Hz, 3H[13]) ; 1.72 (t, *J*=1.9Hz, 3H[10]) ; 2.60-2.66 (m, 1H[12]) ; 2.73-2.81 (m, 2H[11]) ; 3.66 (s, 3H[15]) ; 5.04 (bs, 2H[7]) ; 6.84 (d, *J*=7.9Hz, 1H[4]) ; 6.88 (t, *J*=7.5Hz, 1H[2]) ; 7.13 (t, *J*=7.5Hz, 1H[3]) ; 7.53 (d, *J*=7.5Hz, 1H[1]).

Z isomer : 1.22 (d, *J*=6.8Hz, 3H[13]) ; 2.02 (t, *J*=2.3Hz, 3H[10]) ; 2.08-2.15 (m, 1H[12]) ; 2.37-2.48 (m, 1H[11]) ; 2.71-2.84 (m, 1H[11]) ; 3.66 (s, 3H[15]) ; 5.12 (s, 2H[7]) ; 6.84 (d, *J*=7.9Hz, 1H[4]) ; 6.88 (t, *J*=7.5Hz, 1H[2]) ; 7.13 (t, *J*=7.5Hz, 1H[3]) ; 7.48 (d, *J*=7.2Hz, 1H[1]).

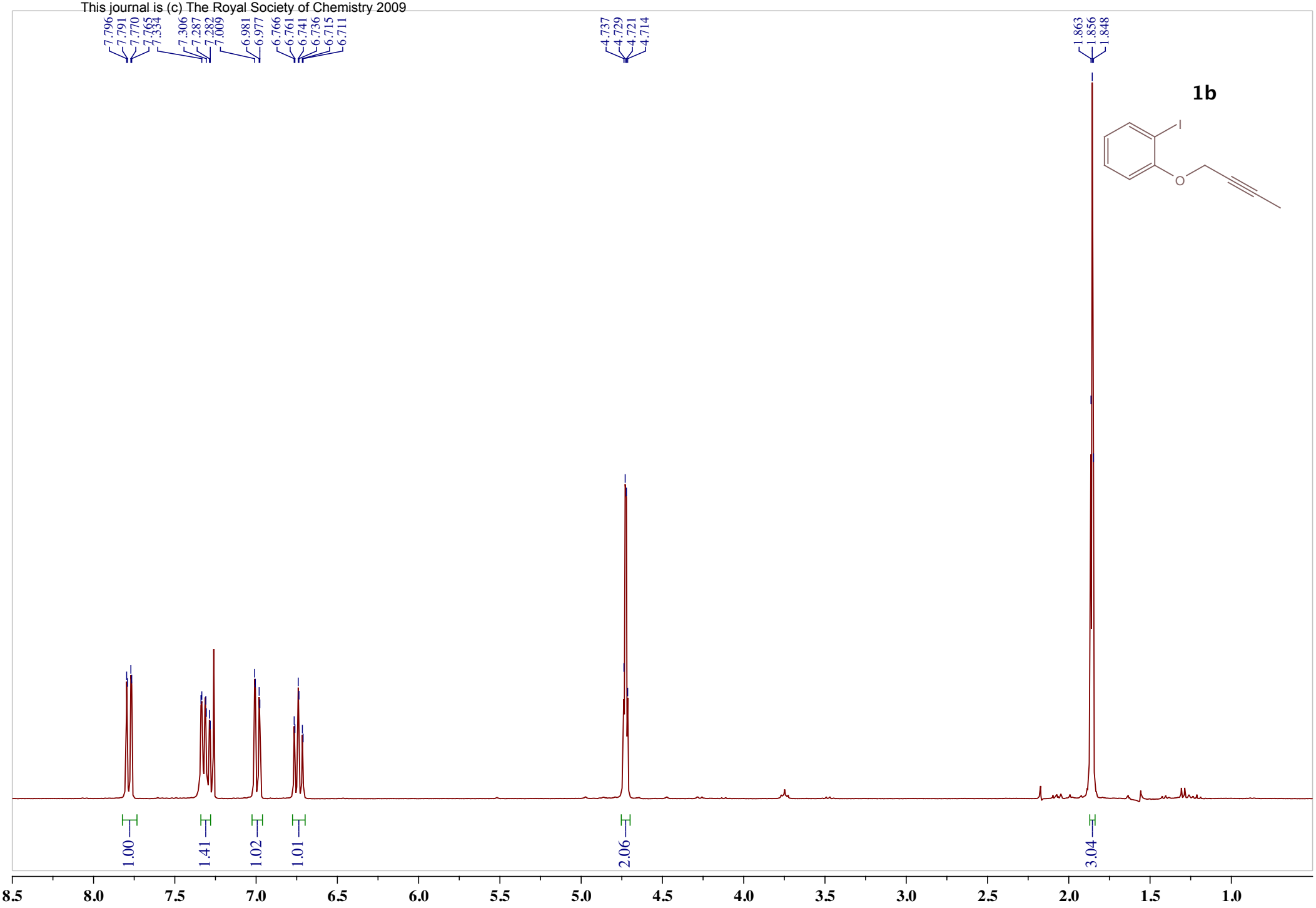
<u>*NMR* ^{13}C</u> : *E isomer* : 16.8 (C[13]); 21.5 (C[10]); 38.2 (C[11]); 38.3 (C[12]); 51.9 (C[15]); 74.8 (C[7]); 110.4 (C[4]); 120.5 (C[2]); 123.9 (C[6]); 124.5 (C[1]); 124.8 (C[9]); 128.8 (C[3]); 131.6 (C[8]); 164.4 (C[5]); 176.8 (C[14]).

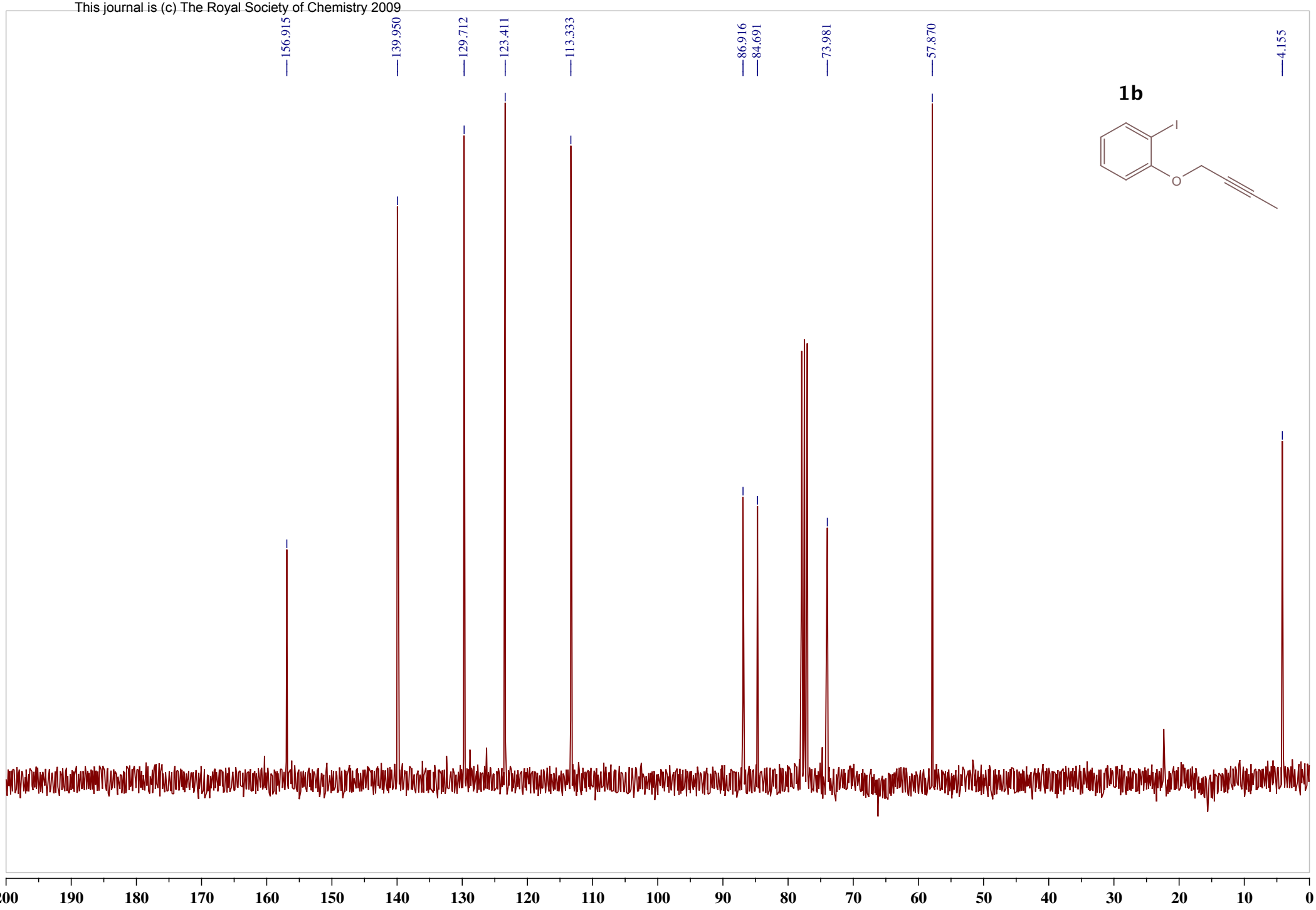
Z isomer : 17.0 (C[13]); 18.7 (C[10]); 38.0 (C[11]); 41.6 (C[12]); 51.9 (C[15]); 74.5 (C[7]); 110.1 (C[4]); 120.7 (C[2]); 124.4 (C[6]); 125.4 (C[1]); 126.5 (C[9]); 128.9 (C[3]); 130.7 (C[8]); 164.3 (C[5]); 176.8 (C[14]).

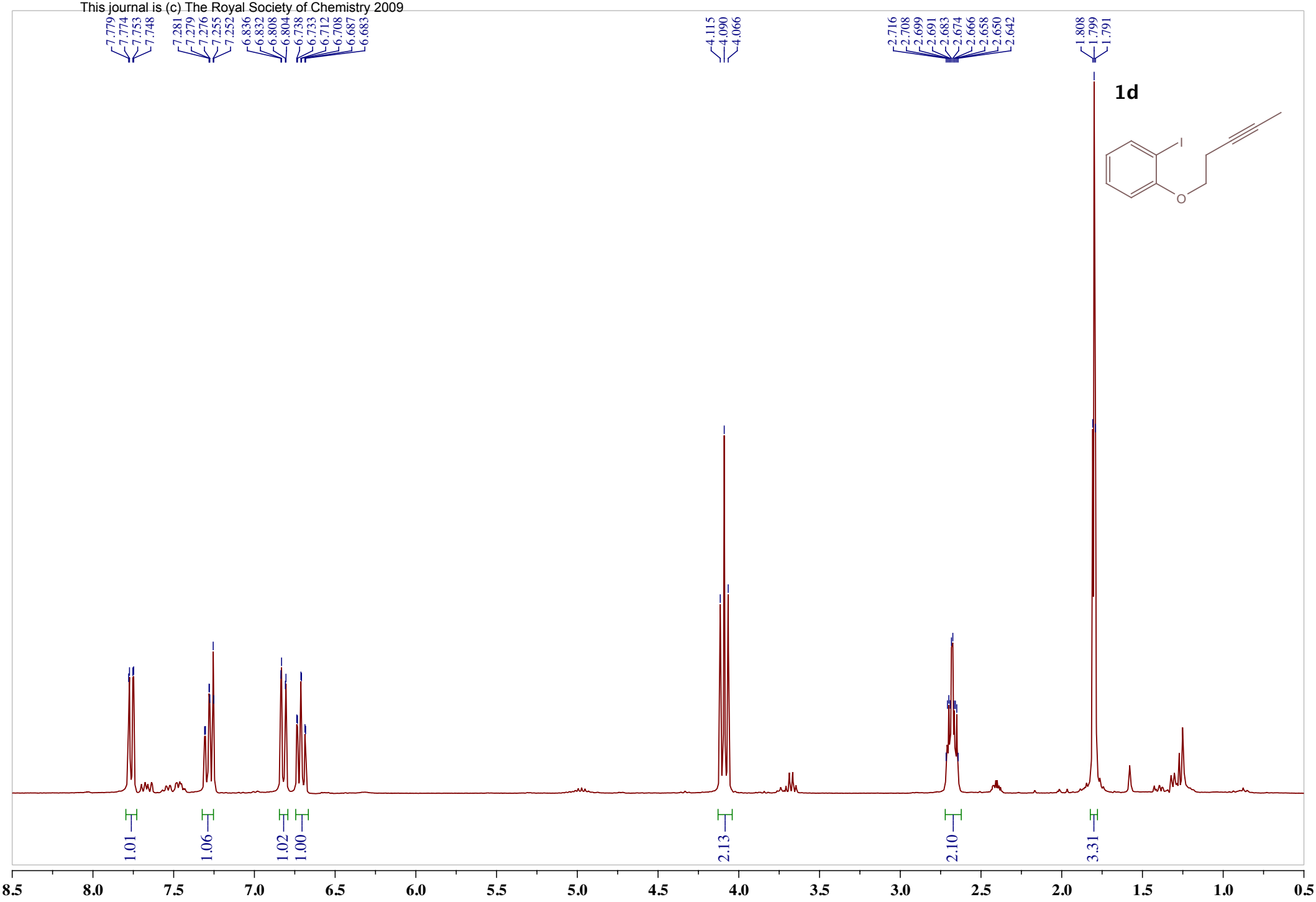
<u>*NMR 2D NOESY*</u> : *E isomer* : correlation between 1.72 (t, *J*=1.9Hz, 3H[10]) and 5.04 (bs, 2H[7]) and between 3.66 (s, 3H[15]) and 7.53 (d, *J*=7.5Hz, 1H[1]).

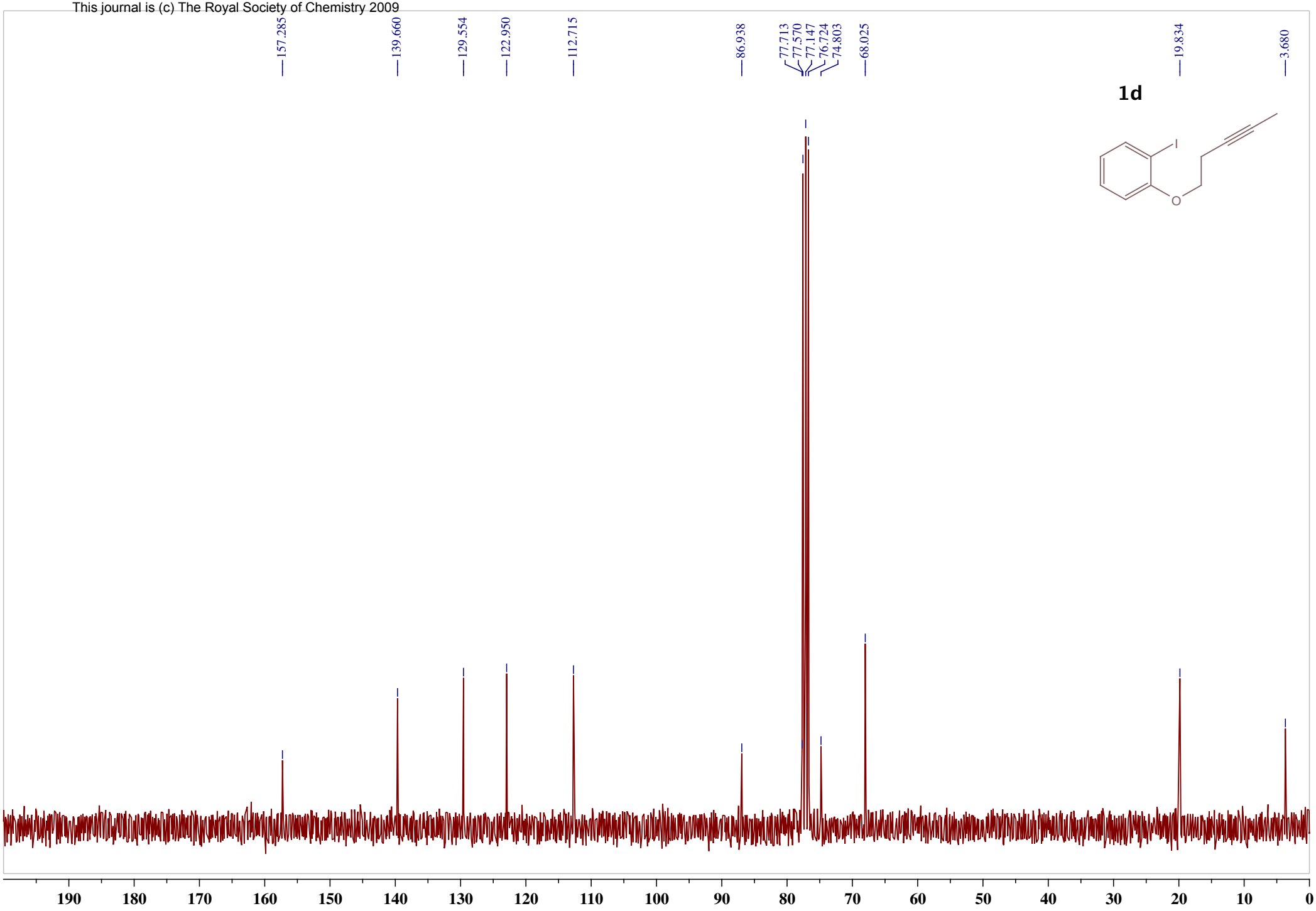
Z isomer : correlation between 2.02 (t, *J*=2.3Hz, 3H[10]) and 7.48 (d, *J*=7.2Hz, 1H[1]) and between 1.22 (d, *J*=6.8Hz, 3H[13]) and 5.12 (s, 2H[7]).

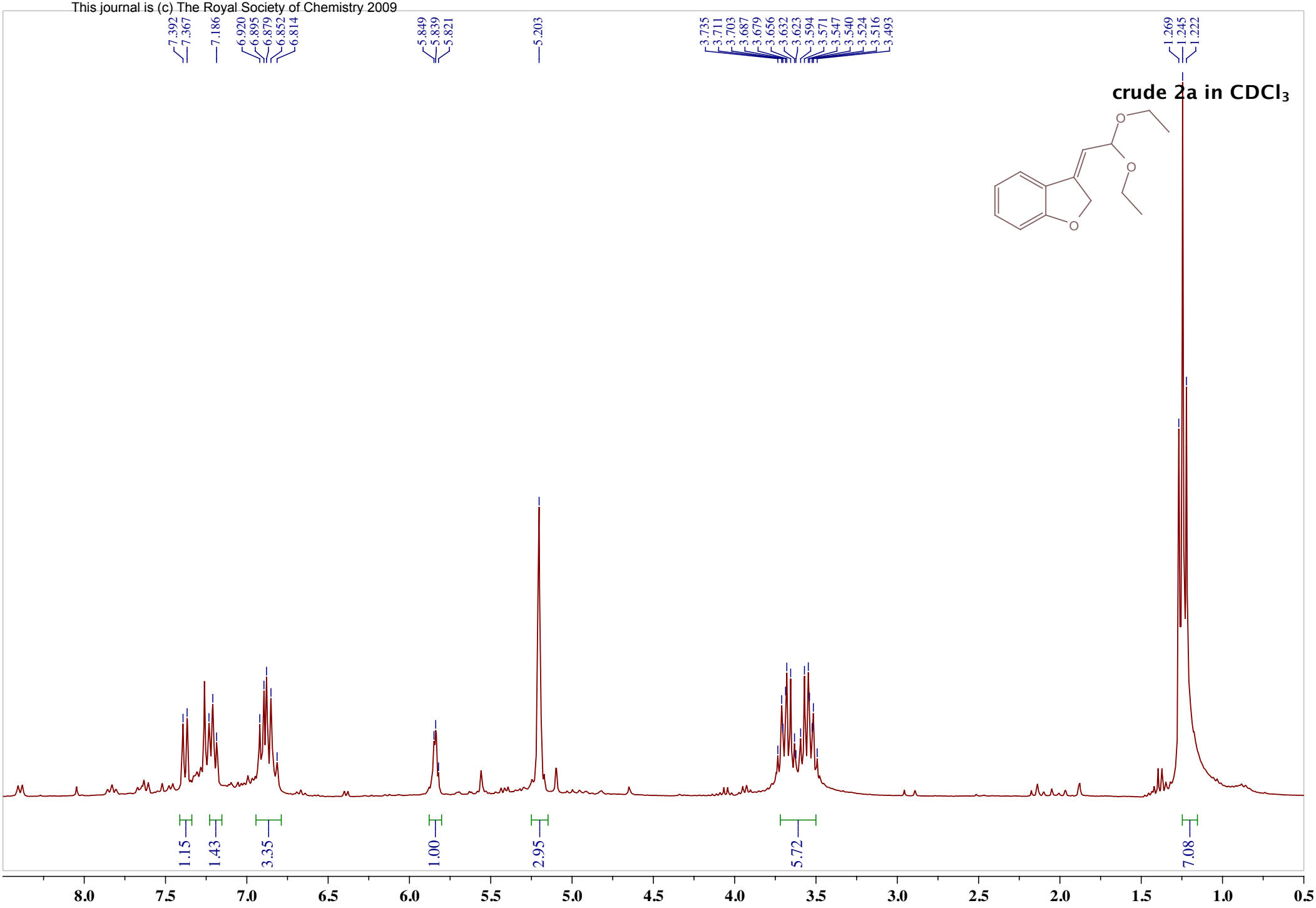
<u>*MS*</u> : 246 (M^+), 159 (base), 145, 131, 115, 88.

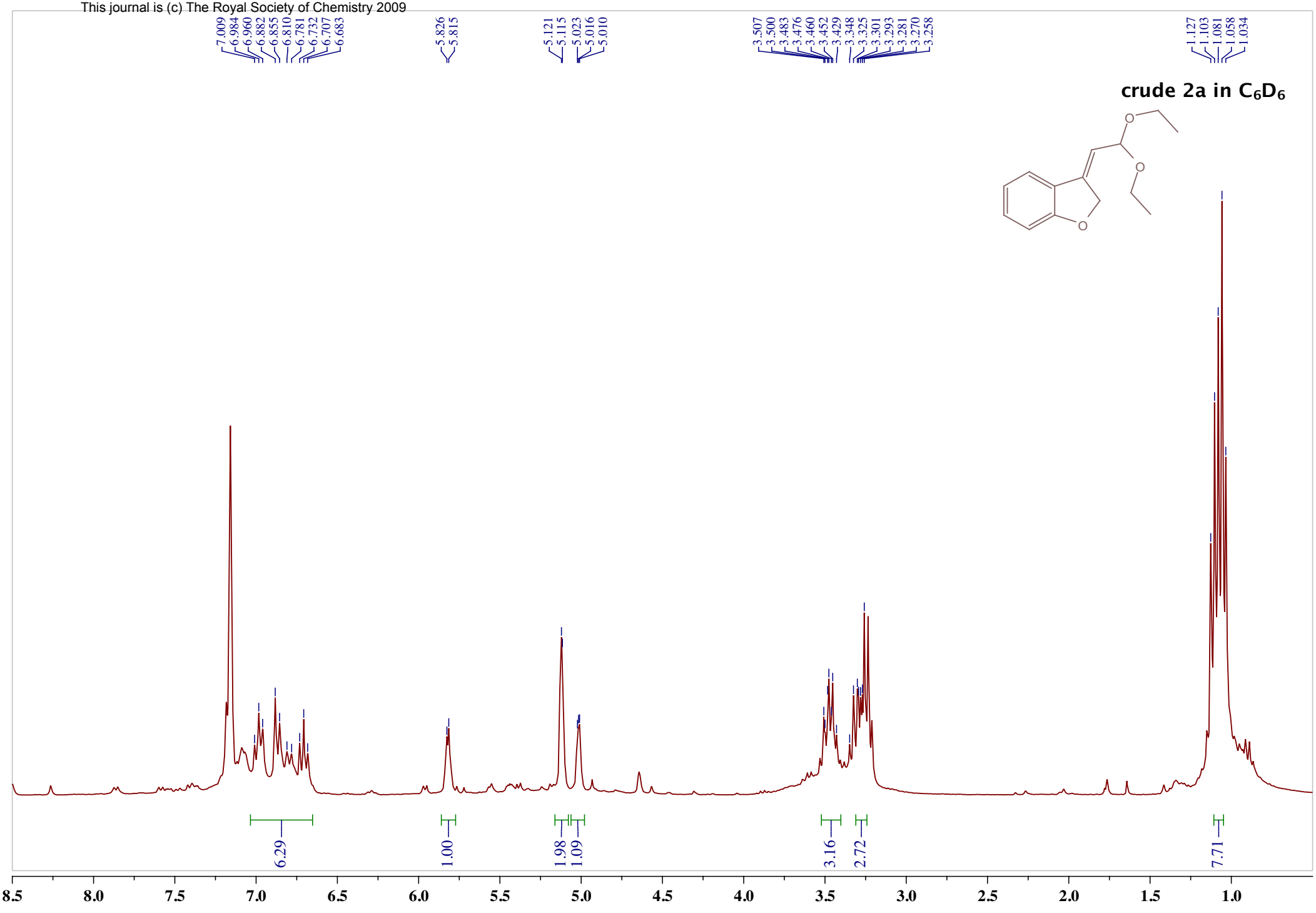


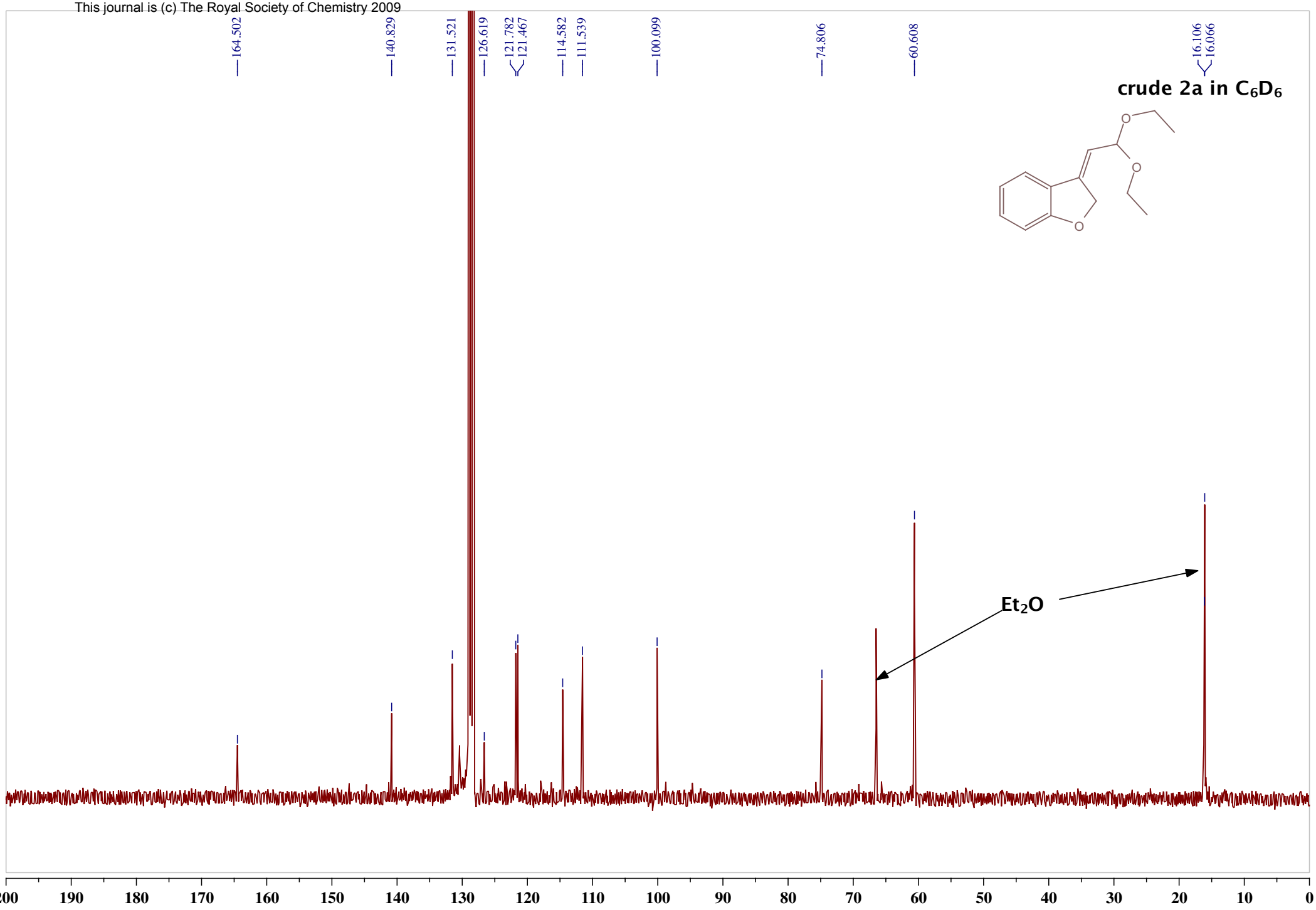


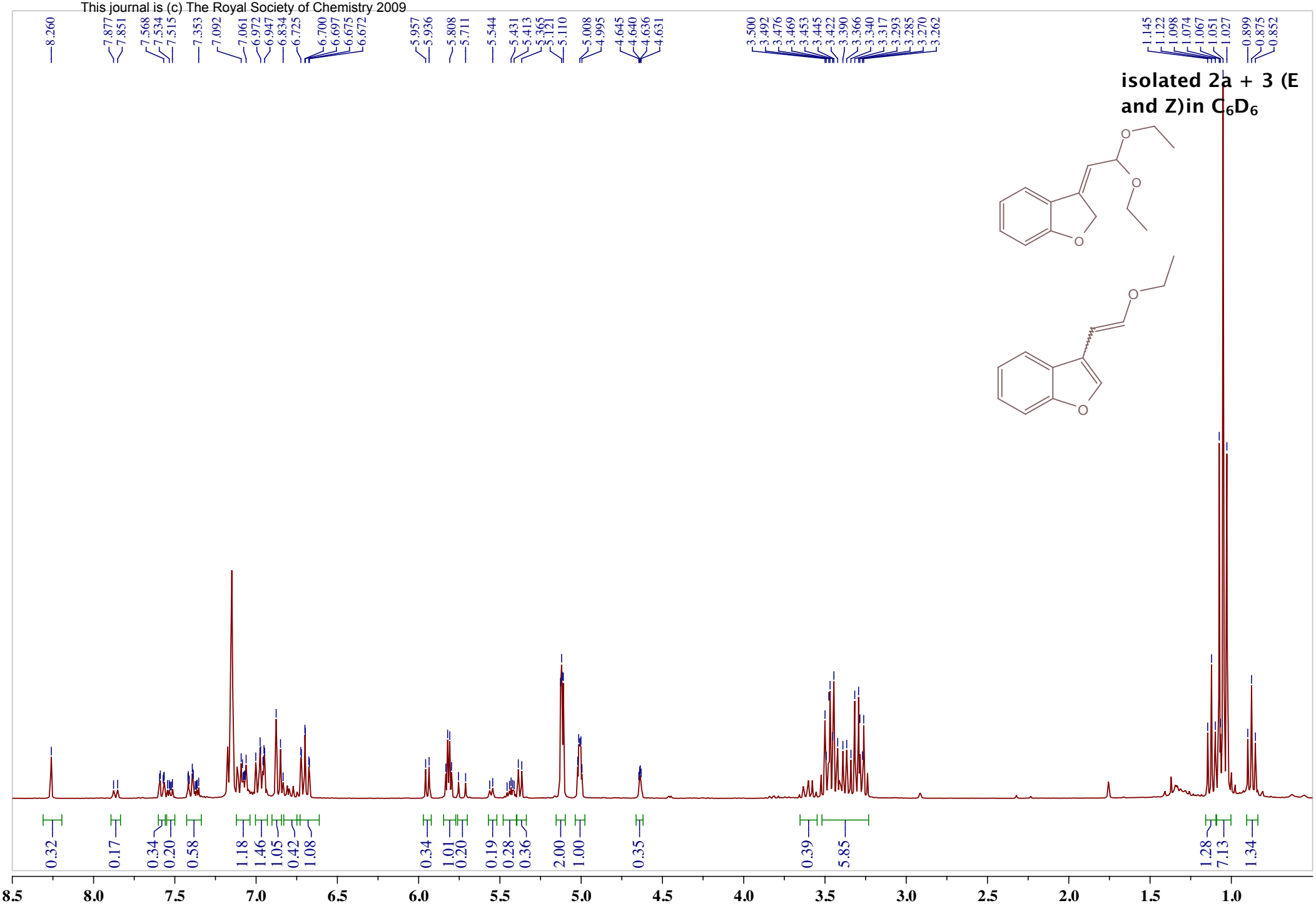








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5.110
5.008
4.995
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4.636
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3.390
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3.340
3.317
3.293
3.285
3.270
3.262
1.145
1.122
1.098
1.074
1.067
1.051
1.027
0.899
0.875
0.852
isolated 2a + 3 (E and Z)in C6D6
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0.17
0.34
0.20
0.58
1.18
1.46
1.05
0.42
1.08
0.34
1.01
0.20
0.19
0.28
0.36
2.00
1.00
0.35
0.39
5.85
1.28
7.13
1.34
8.5
8.0
7.5
7.0
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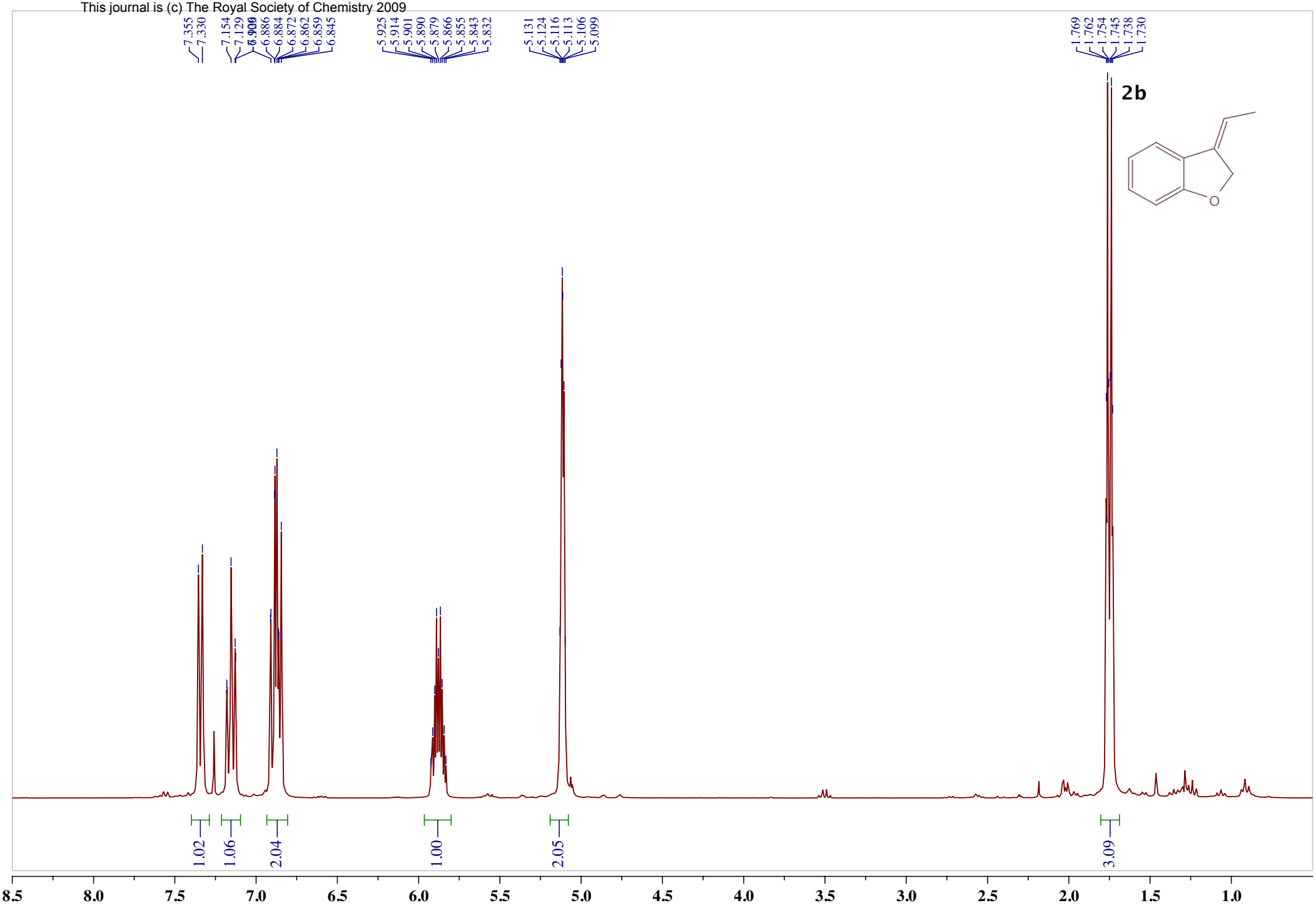

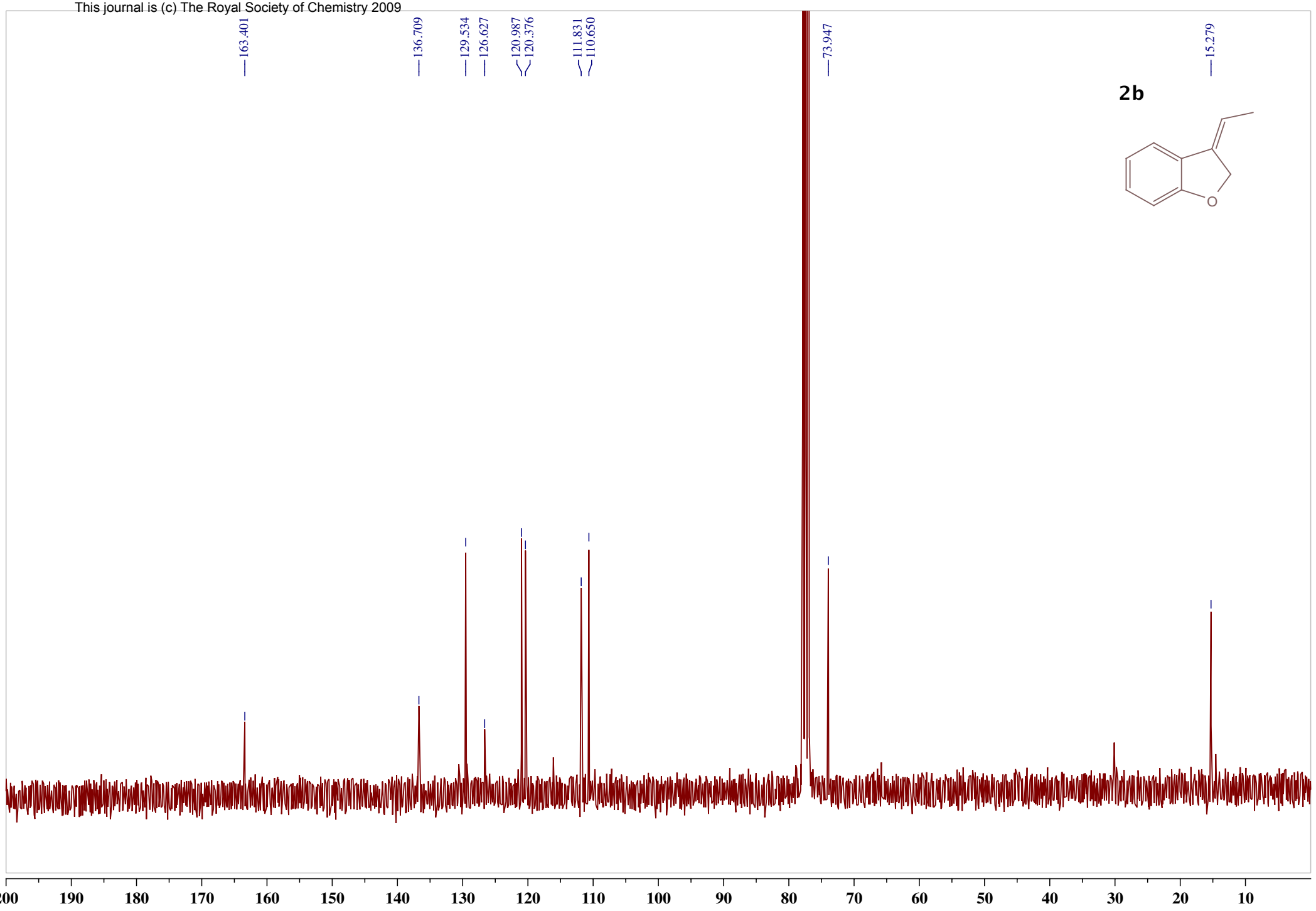

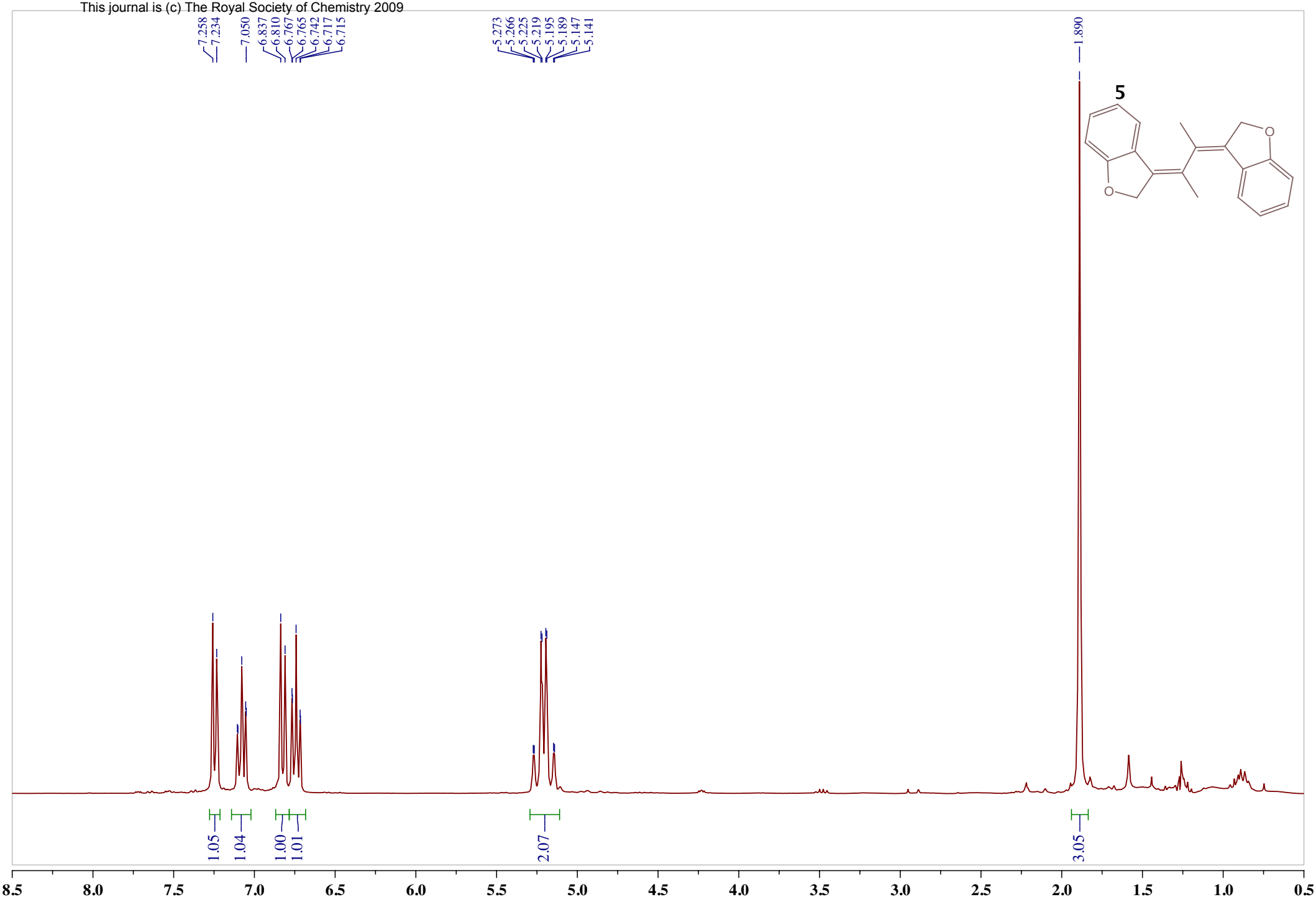

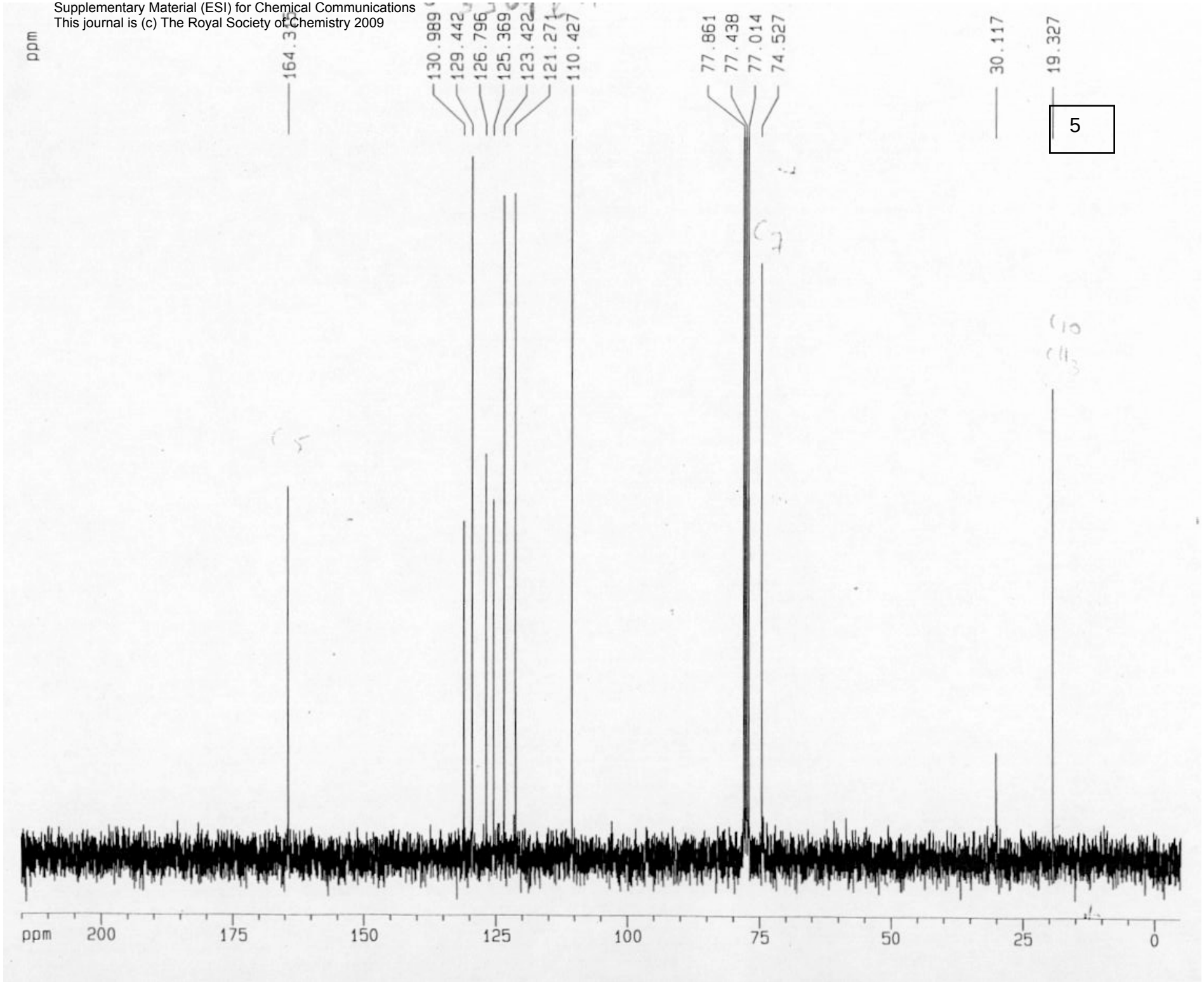
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19.327
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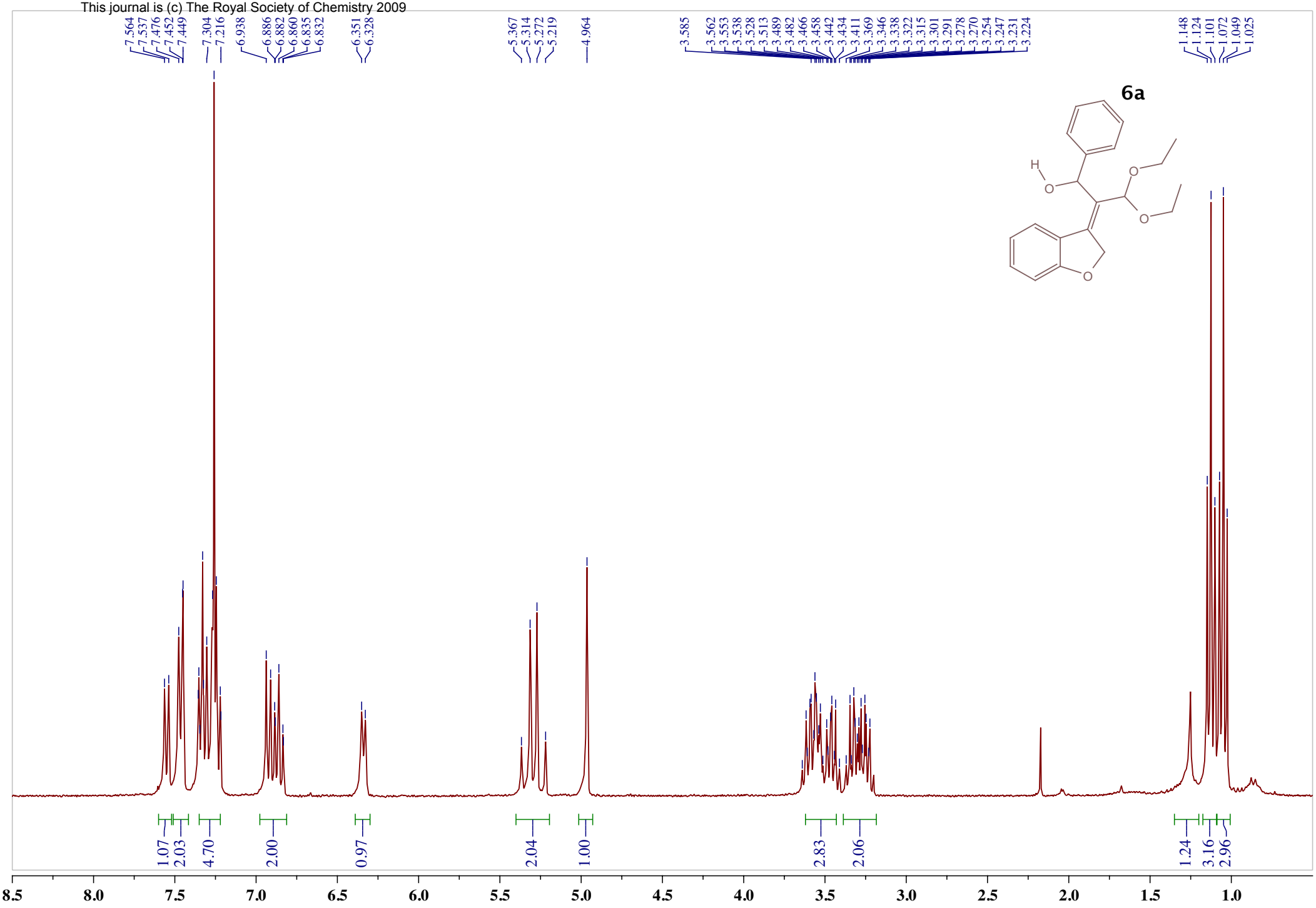

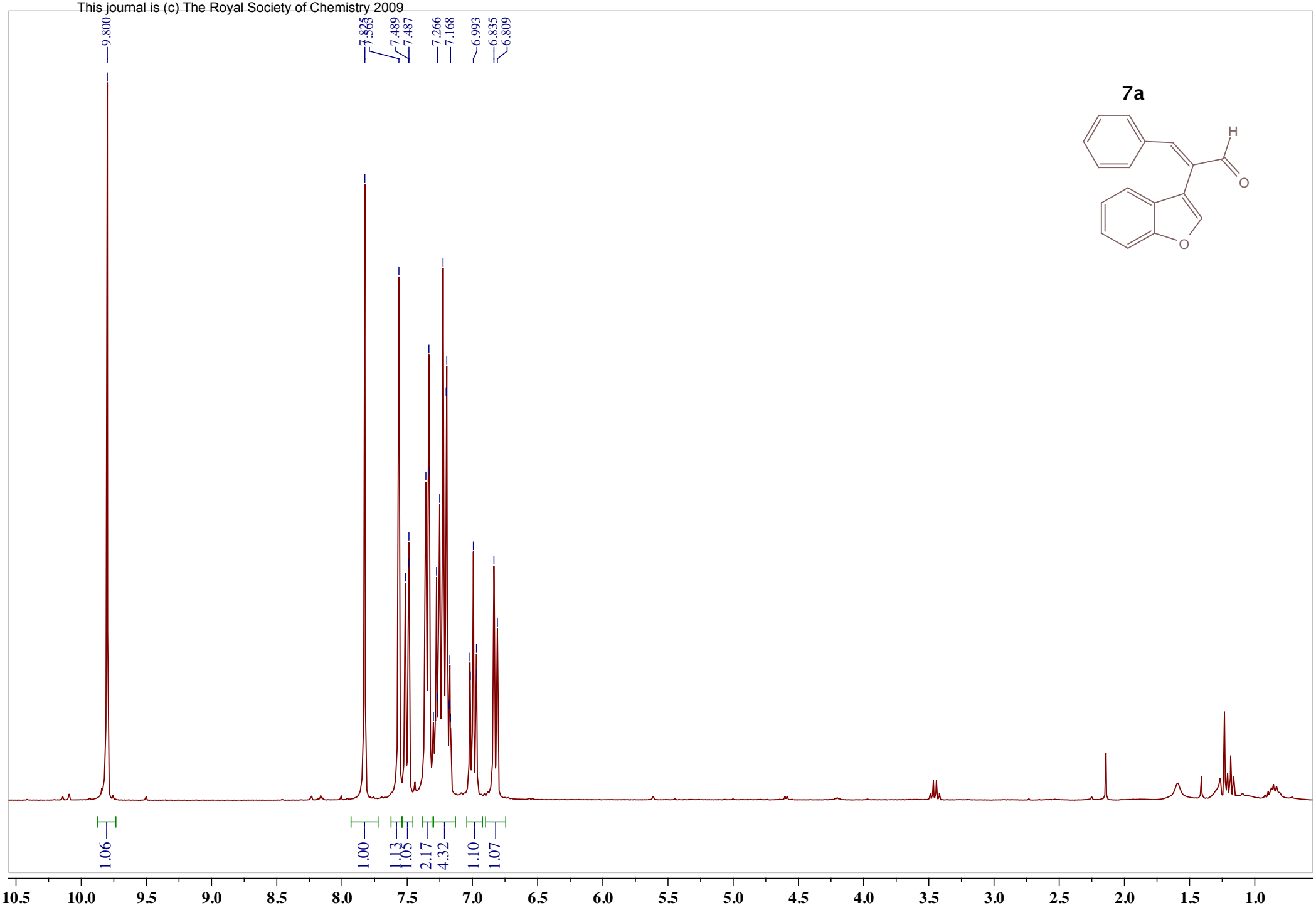

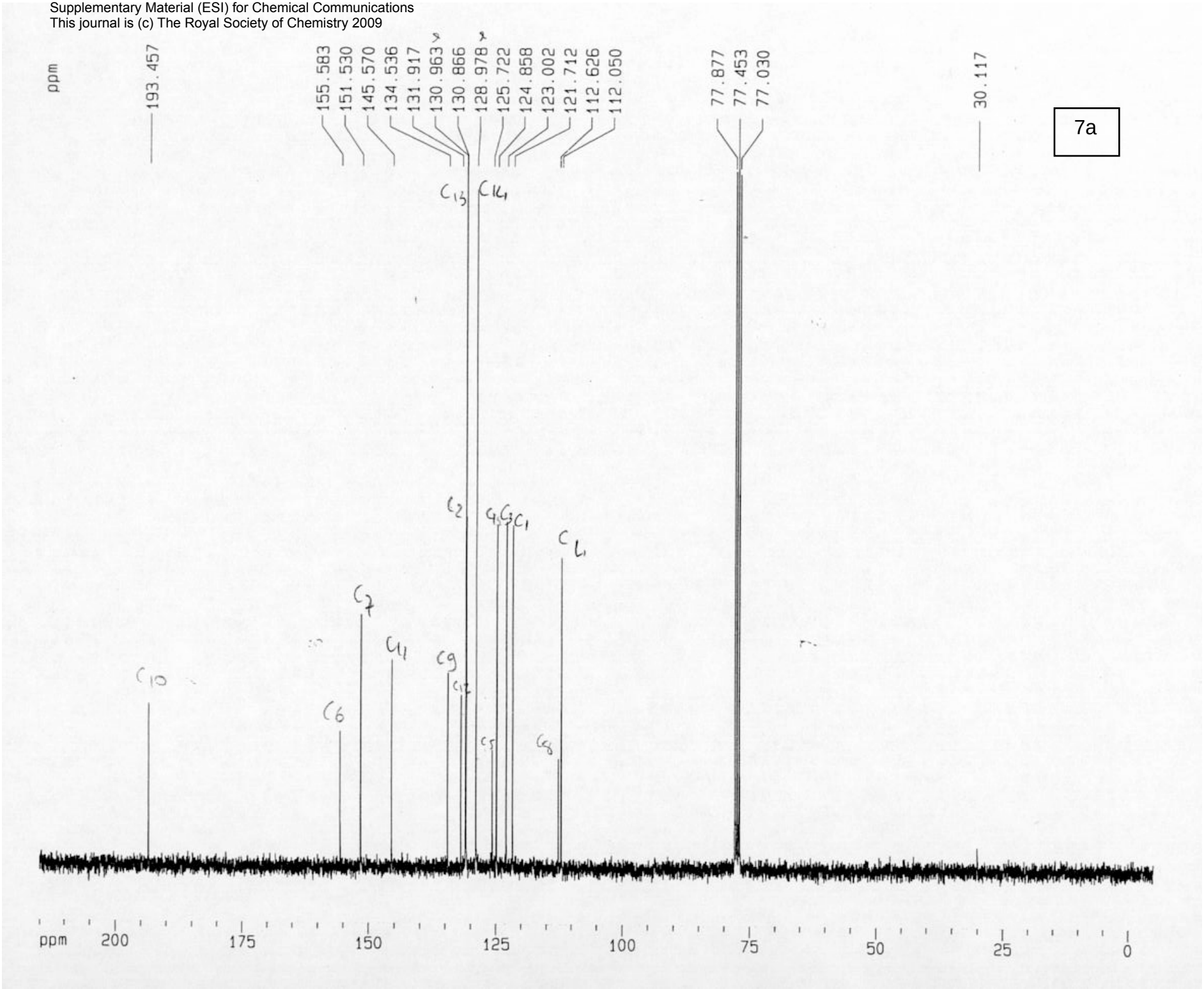
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30.117
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C13
C14
C2
C4
C3
C1
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C9
C10
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C5
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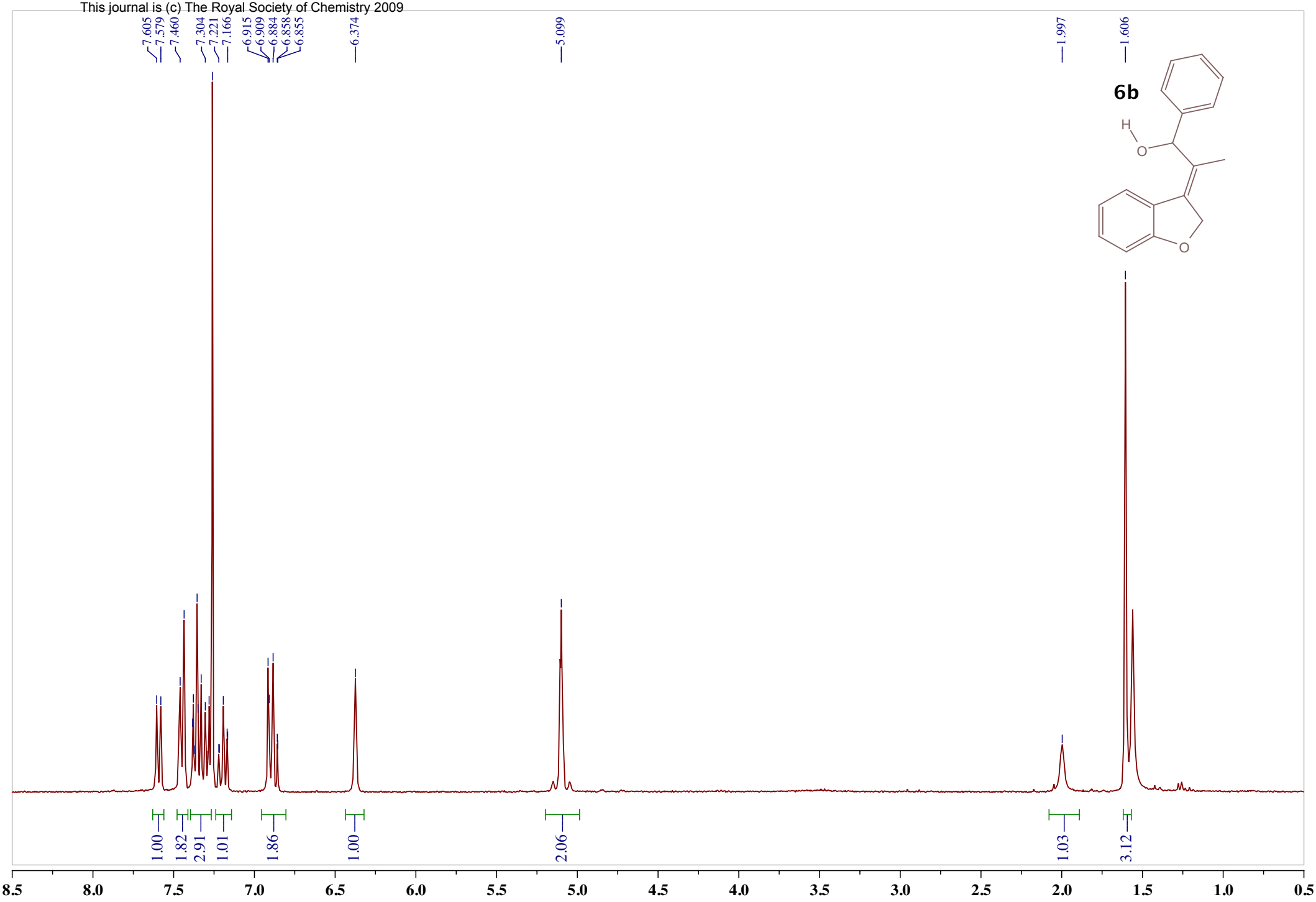

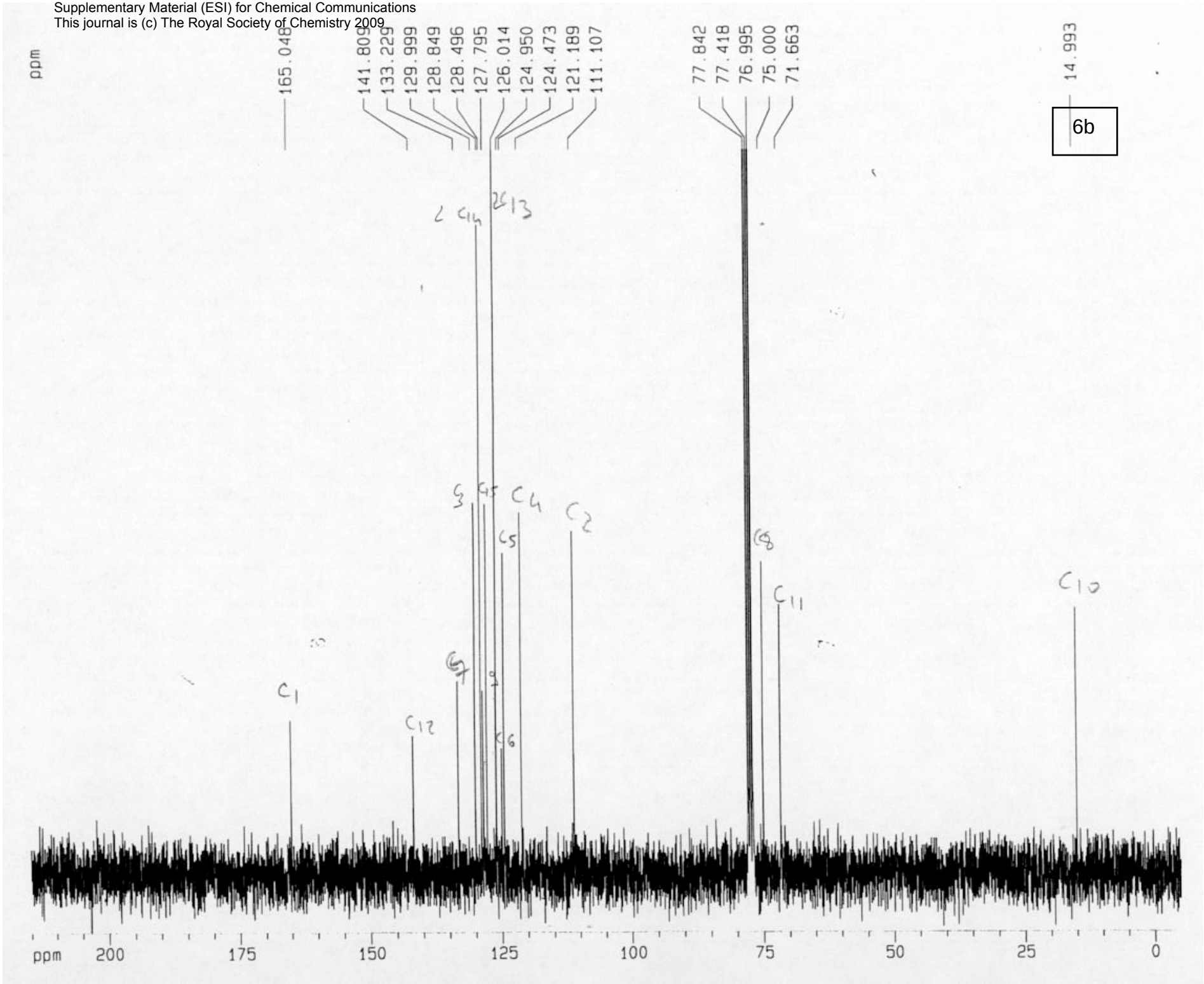
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77.418
76.995
75.000
71.663
14.993
6b
C14
C13
C3
C4
C2
C5
C8
C11
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C1
C12
C7
C9
C6
ppm
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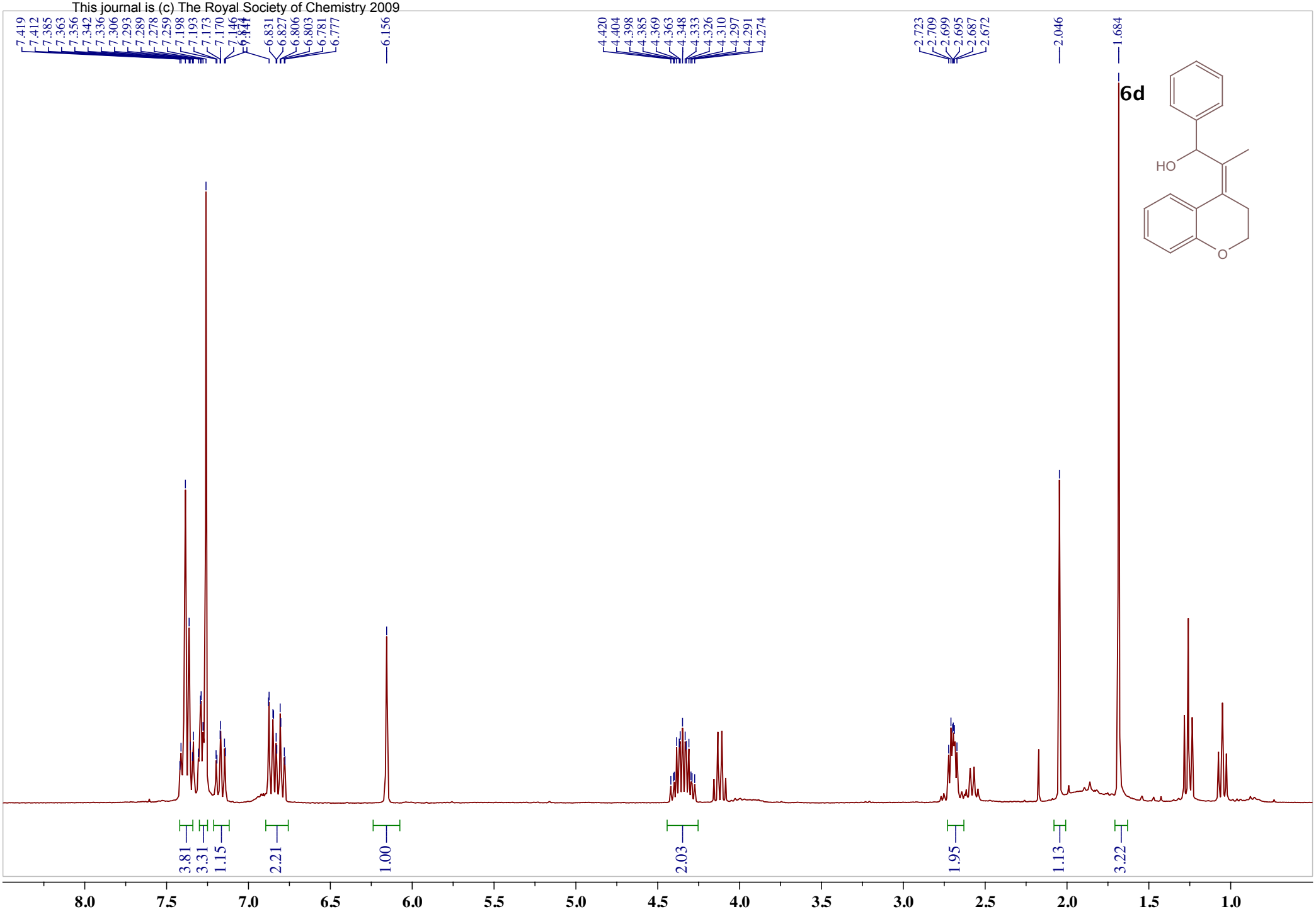

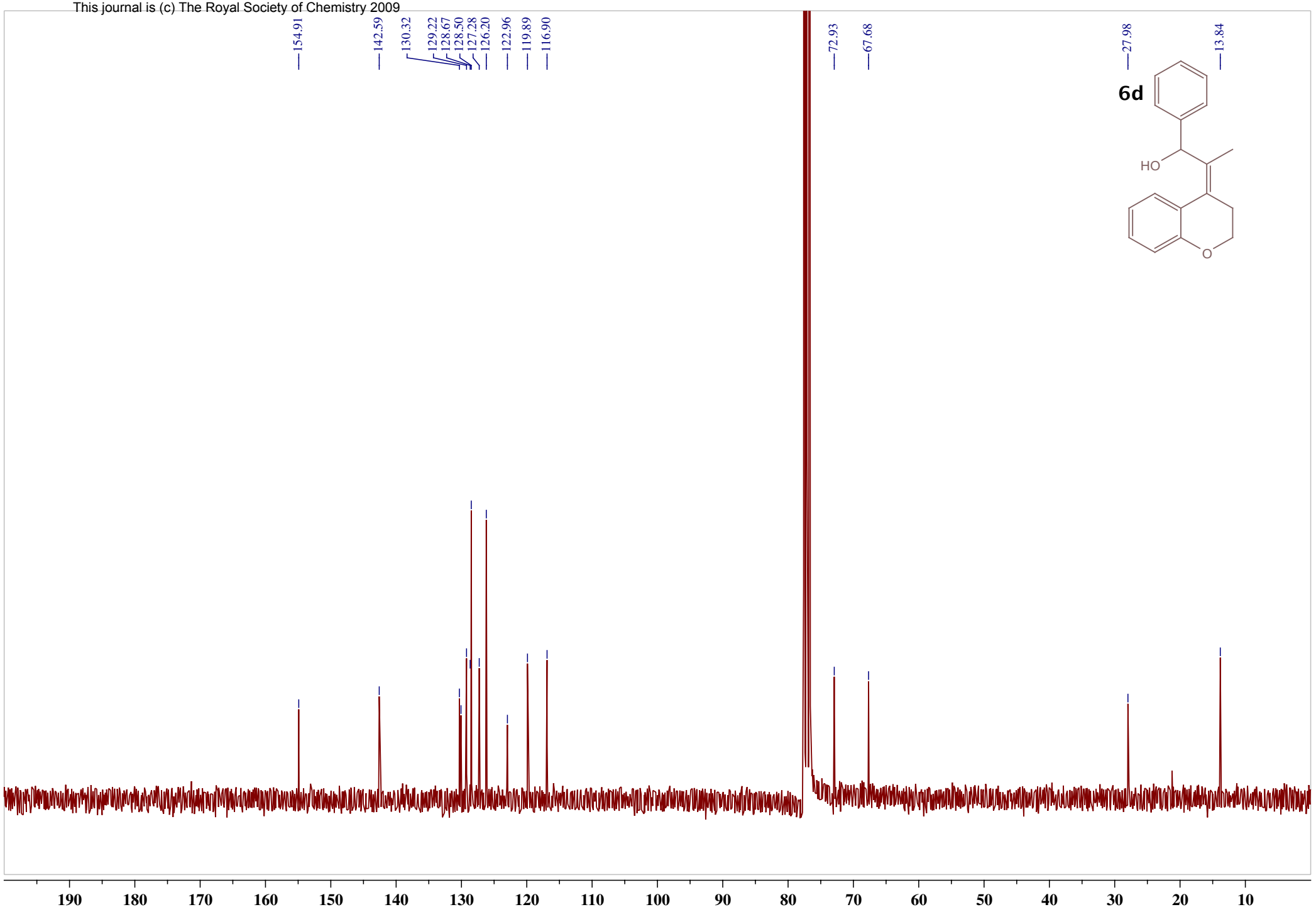

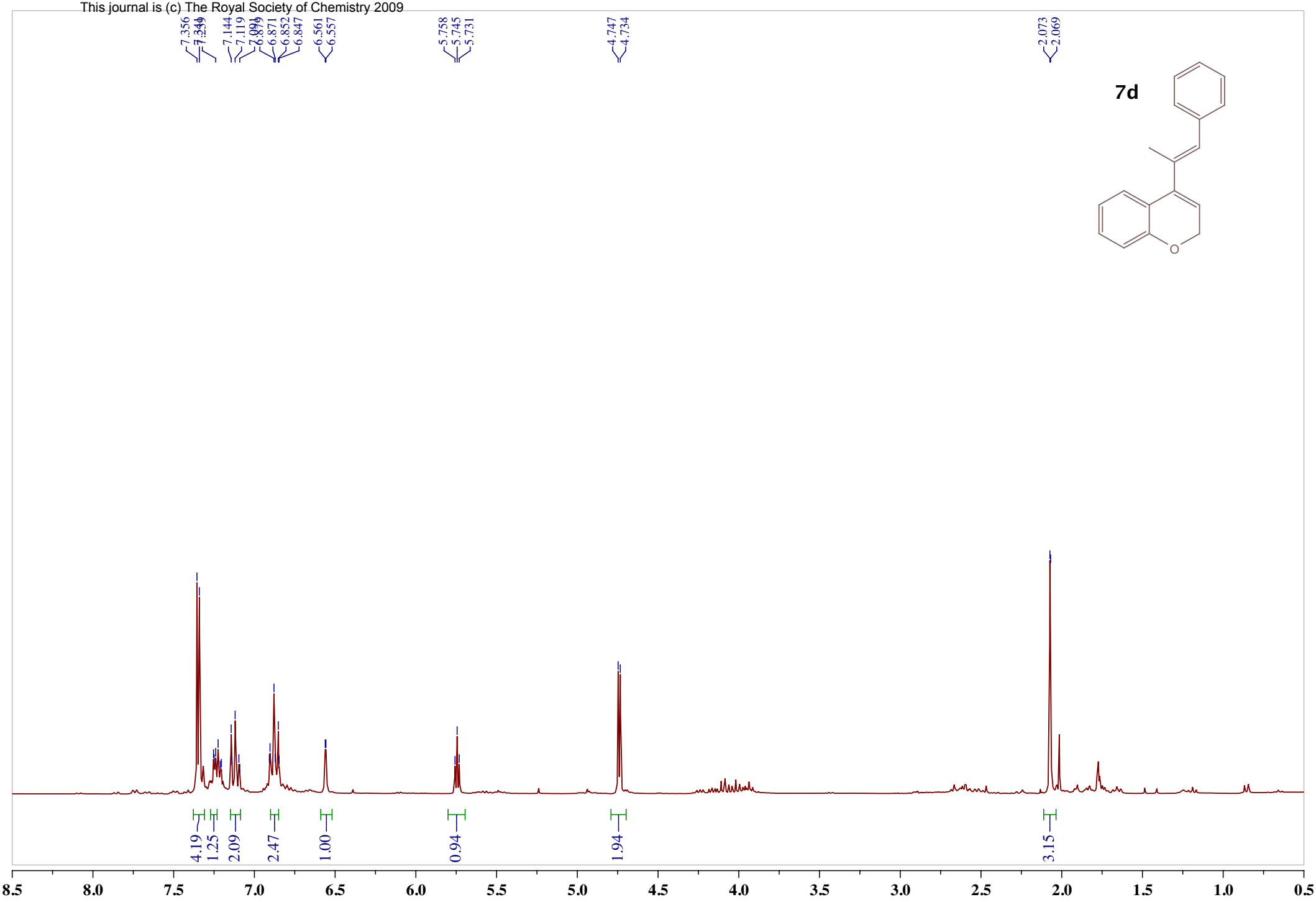

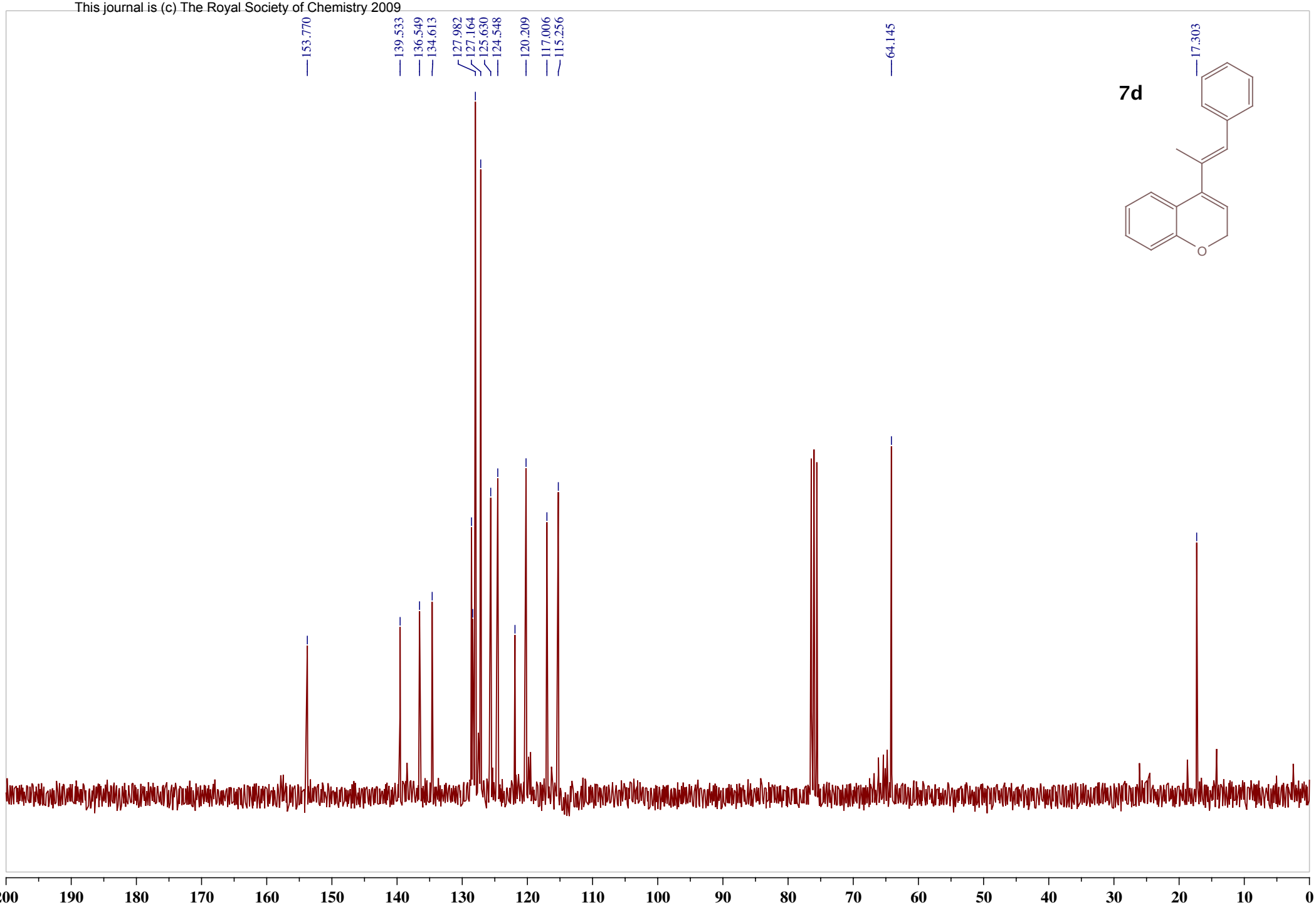

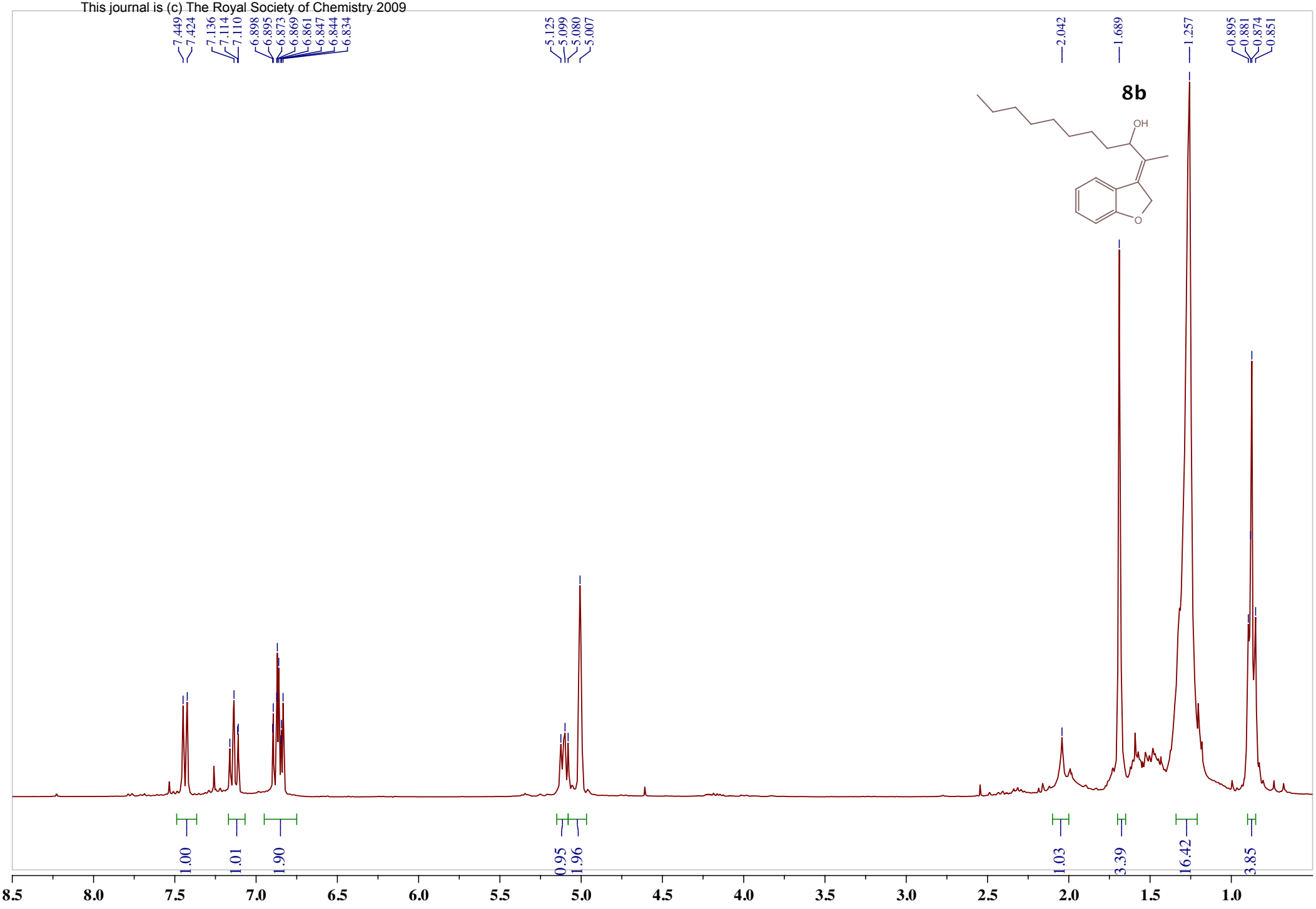

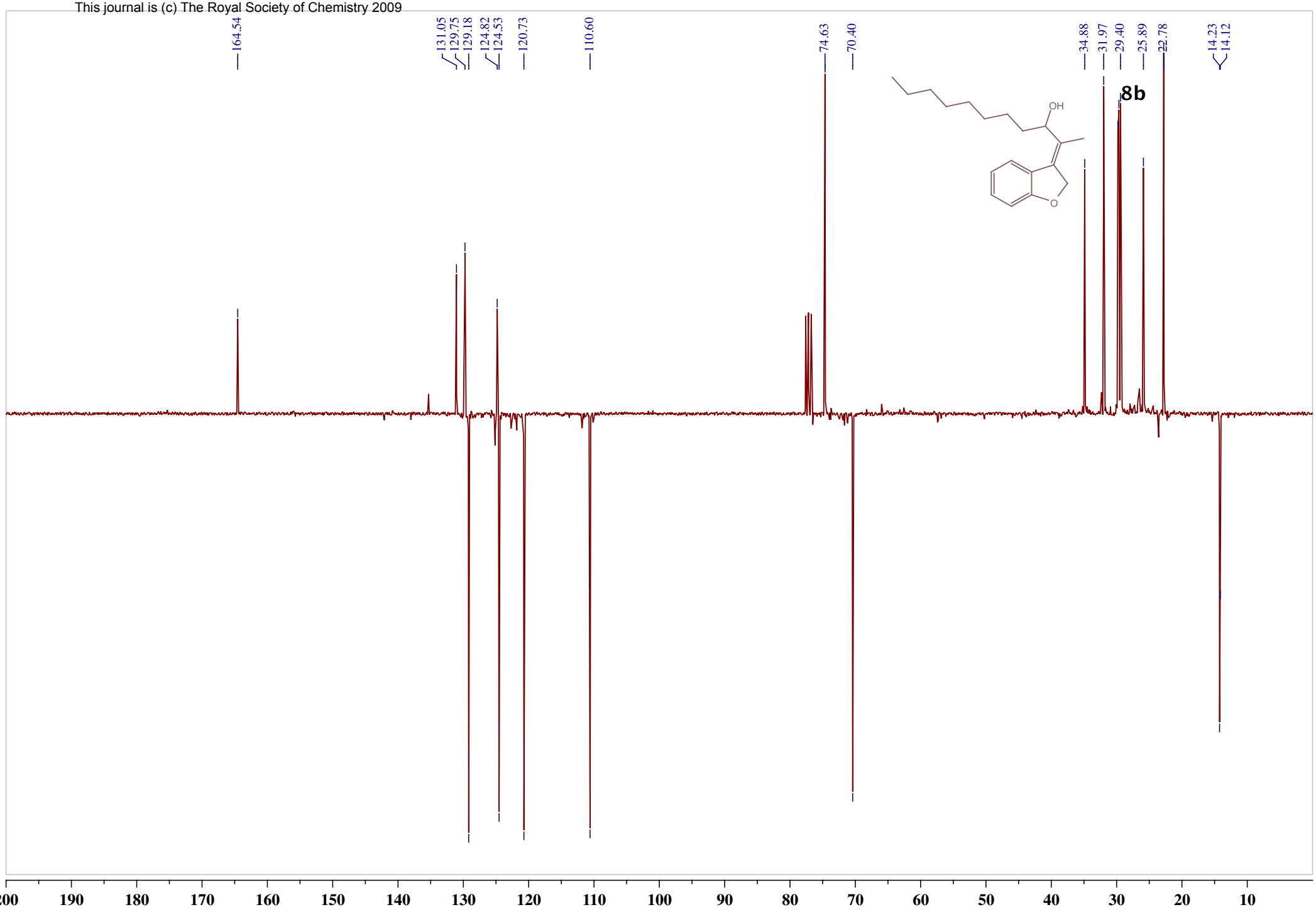

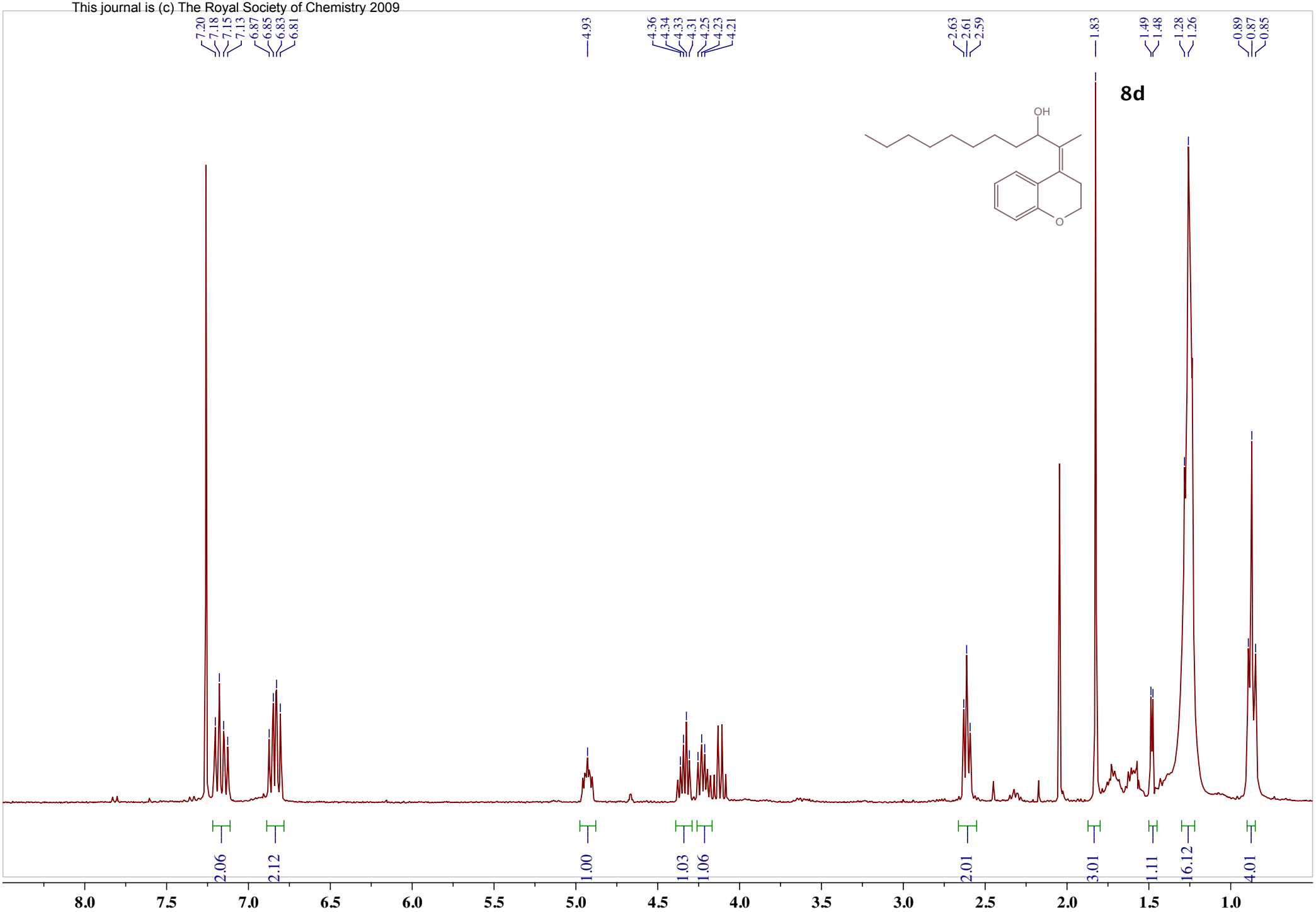

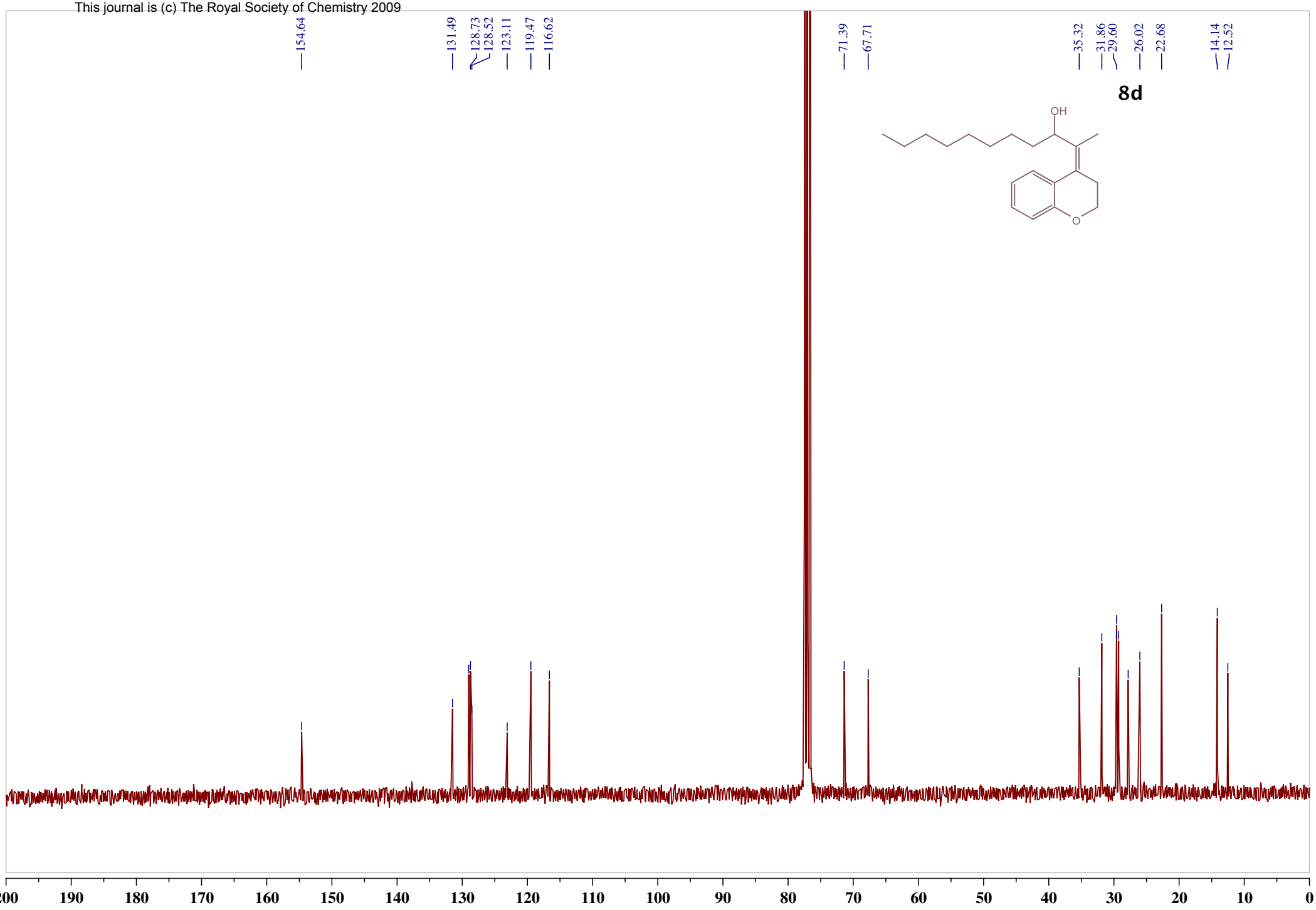
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71.39
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14.14
12.52
8d
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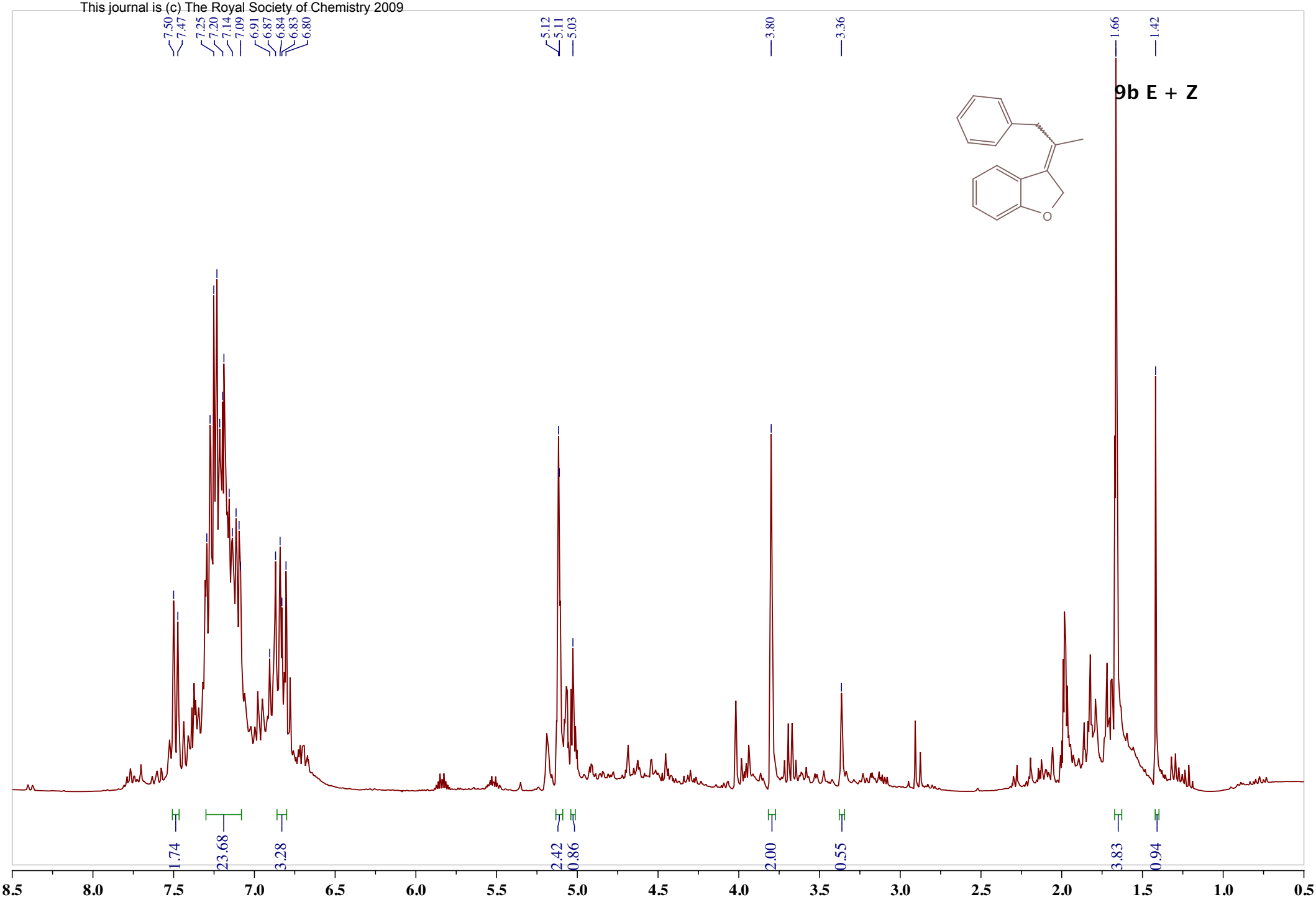

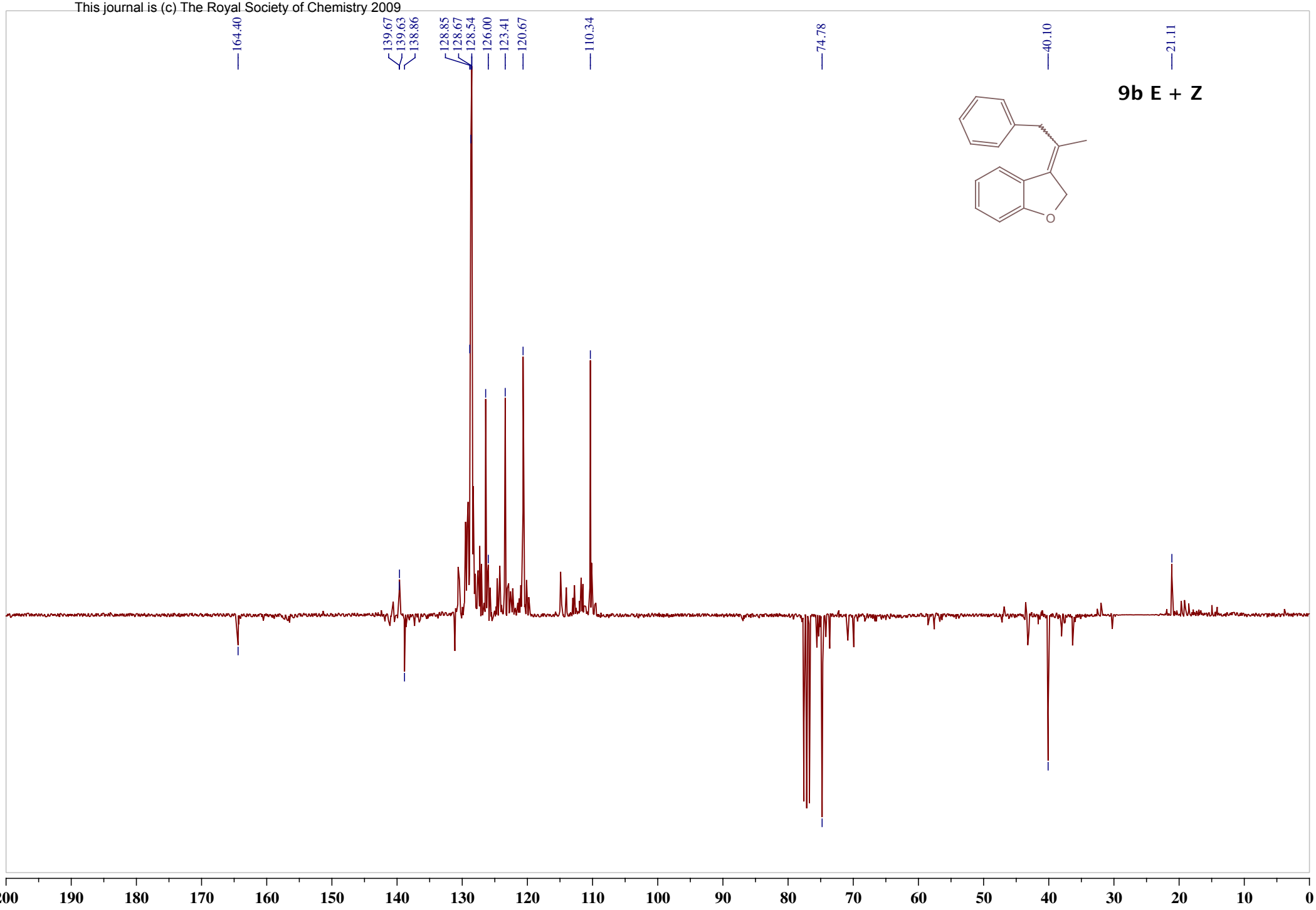

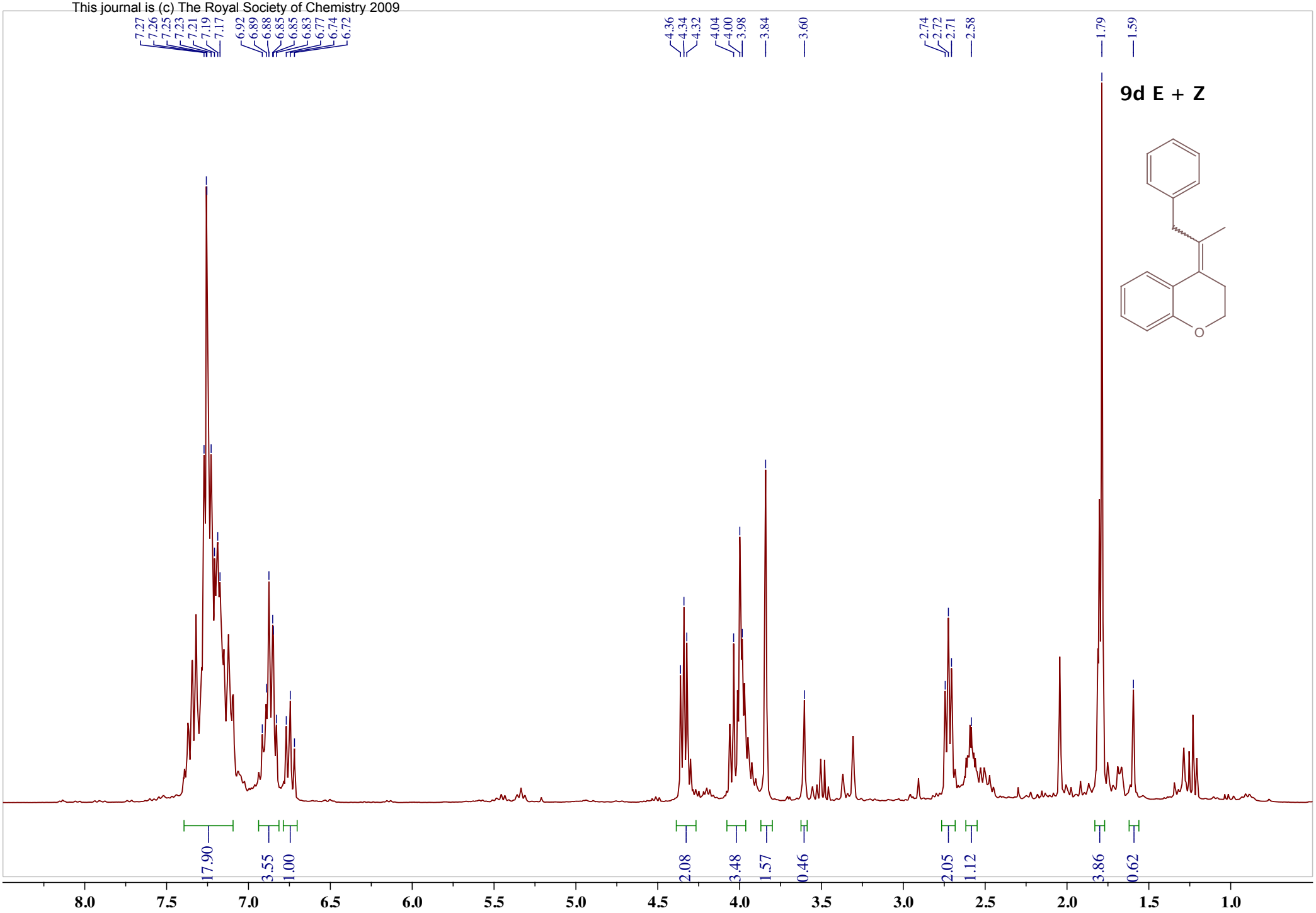

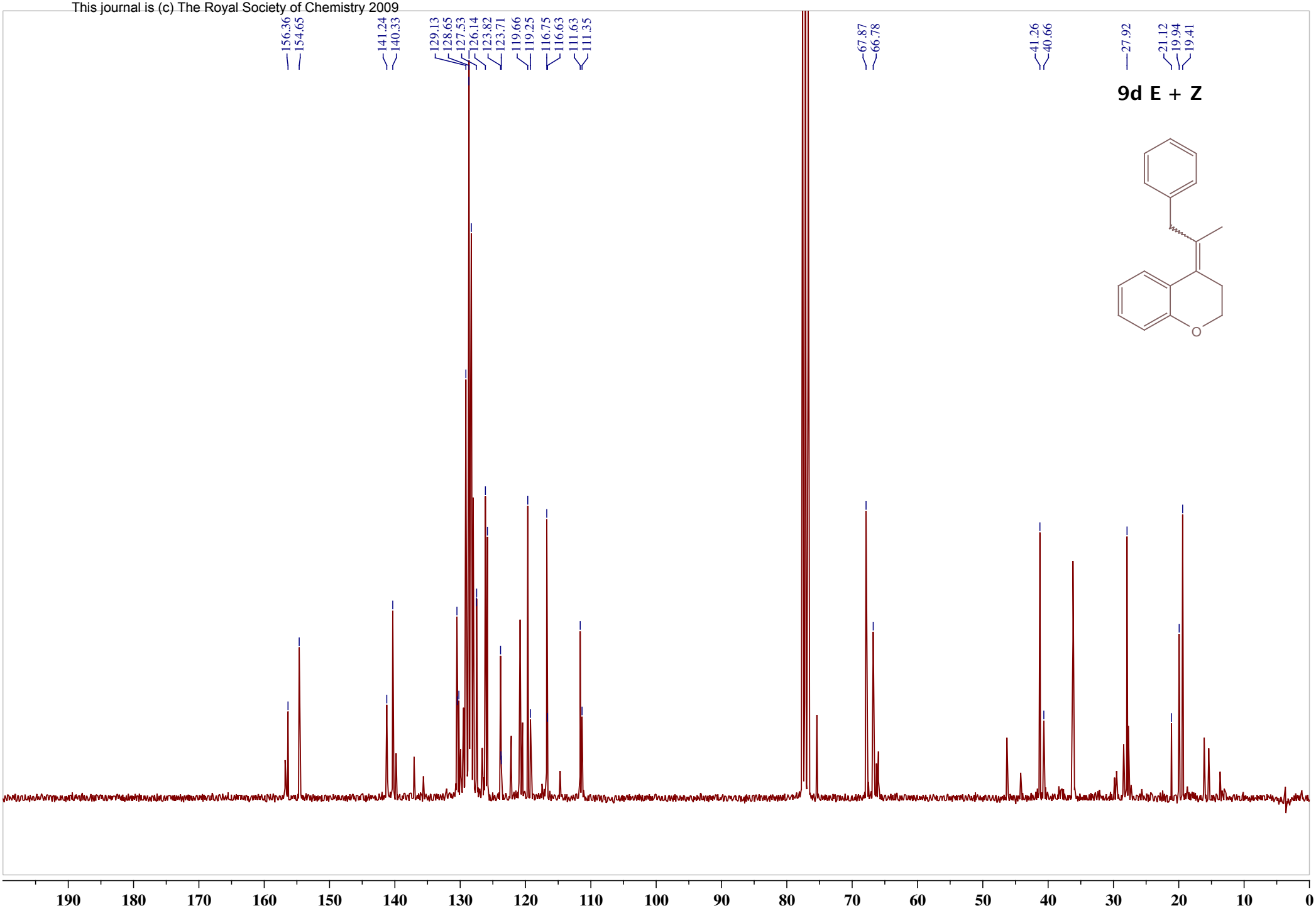

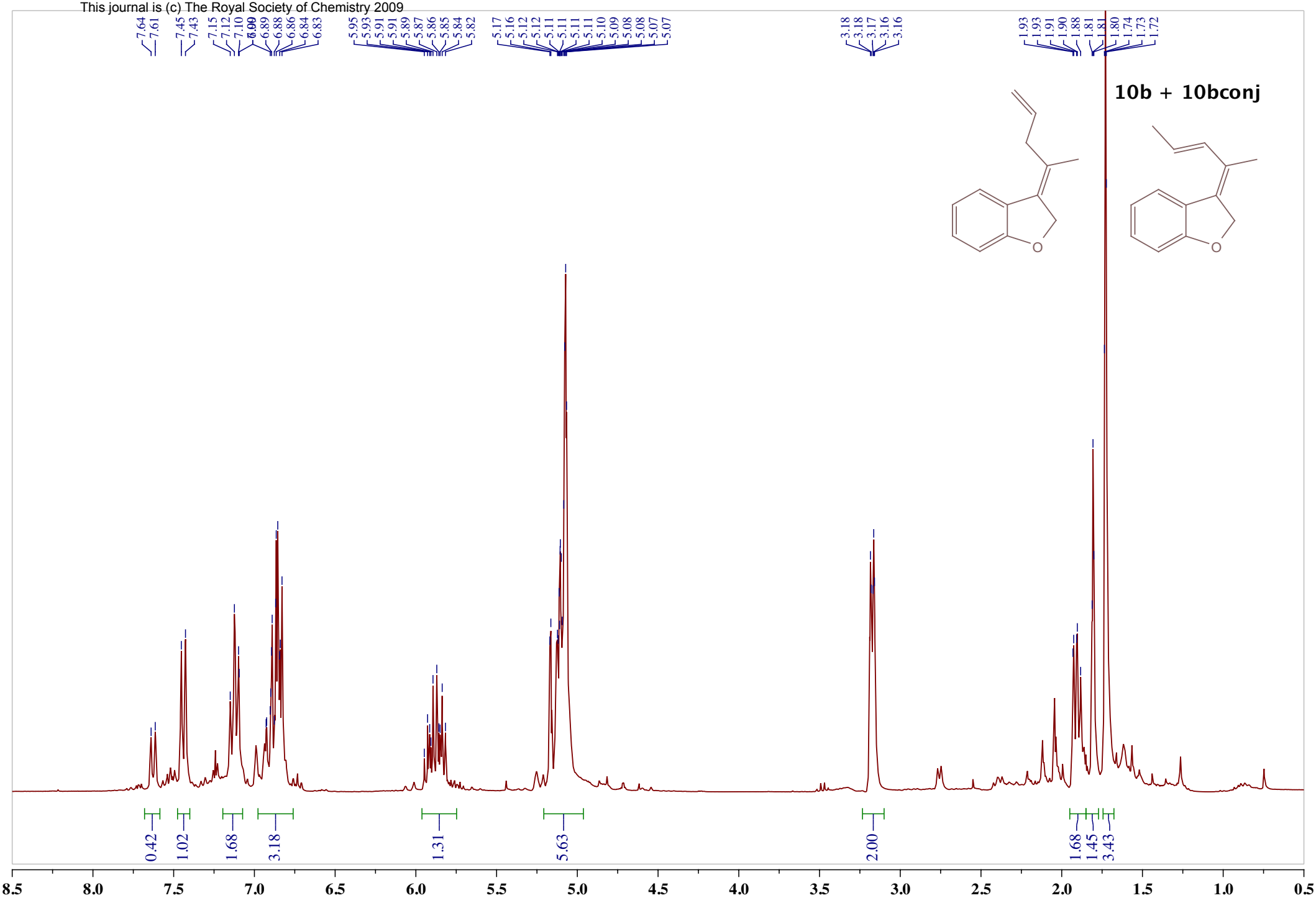

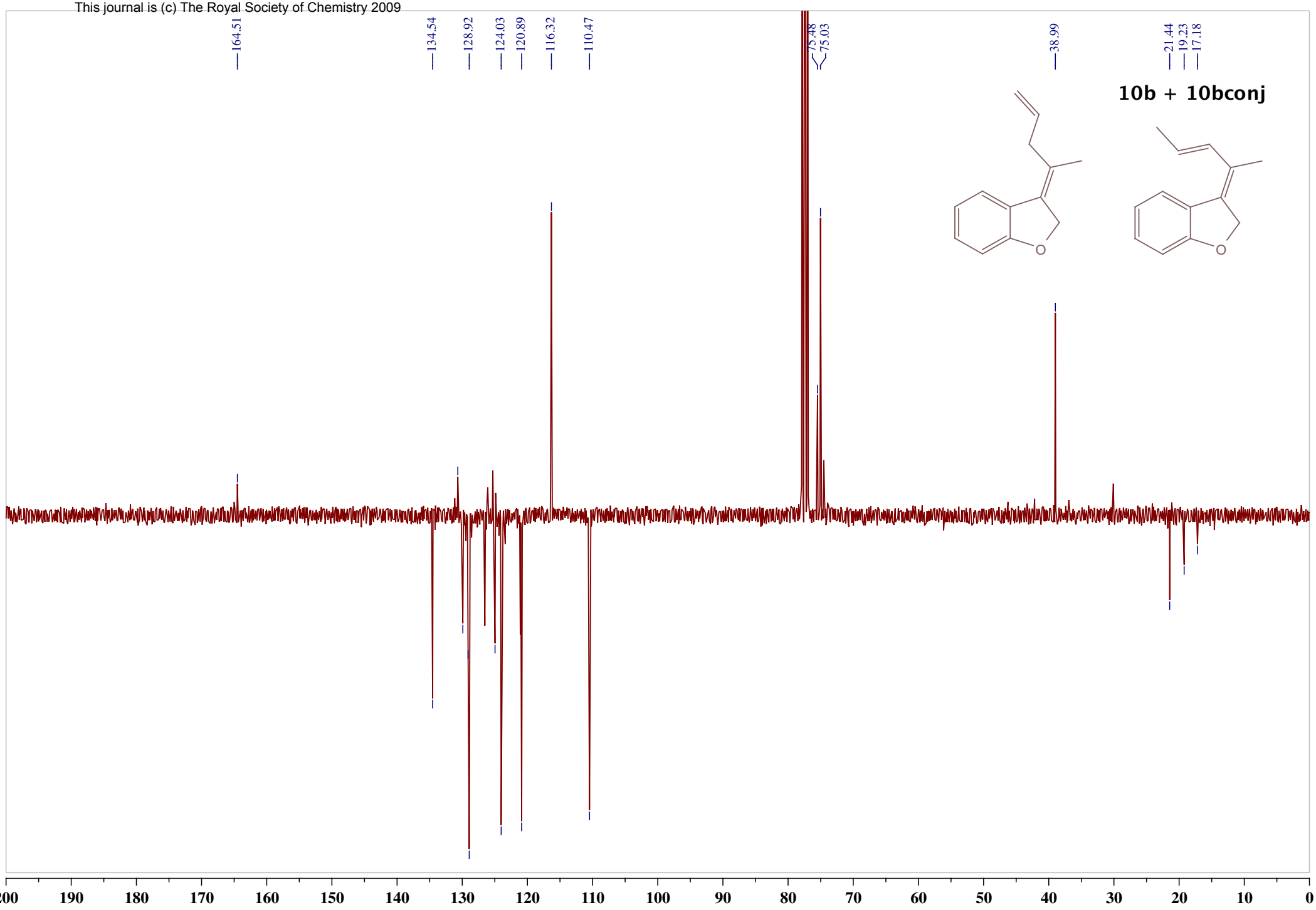
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120.89
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75.03
38.99
21.44
19.23
17.18
10b + 10bconj
O
O
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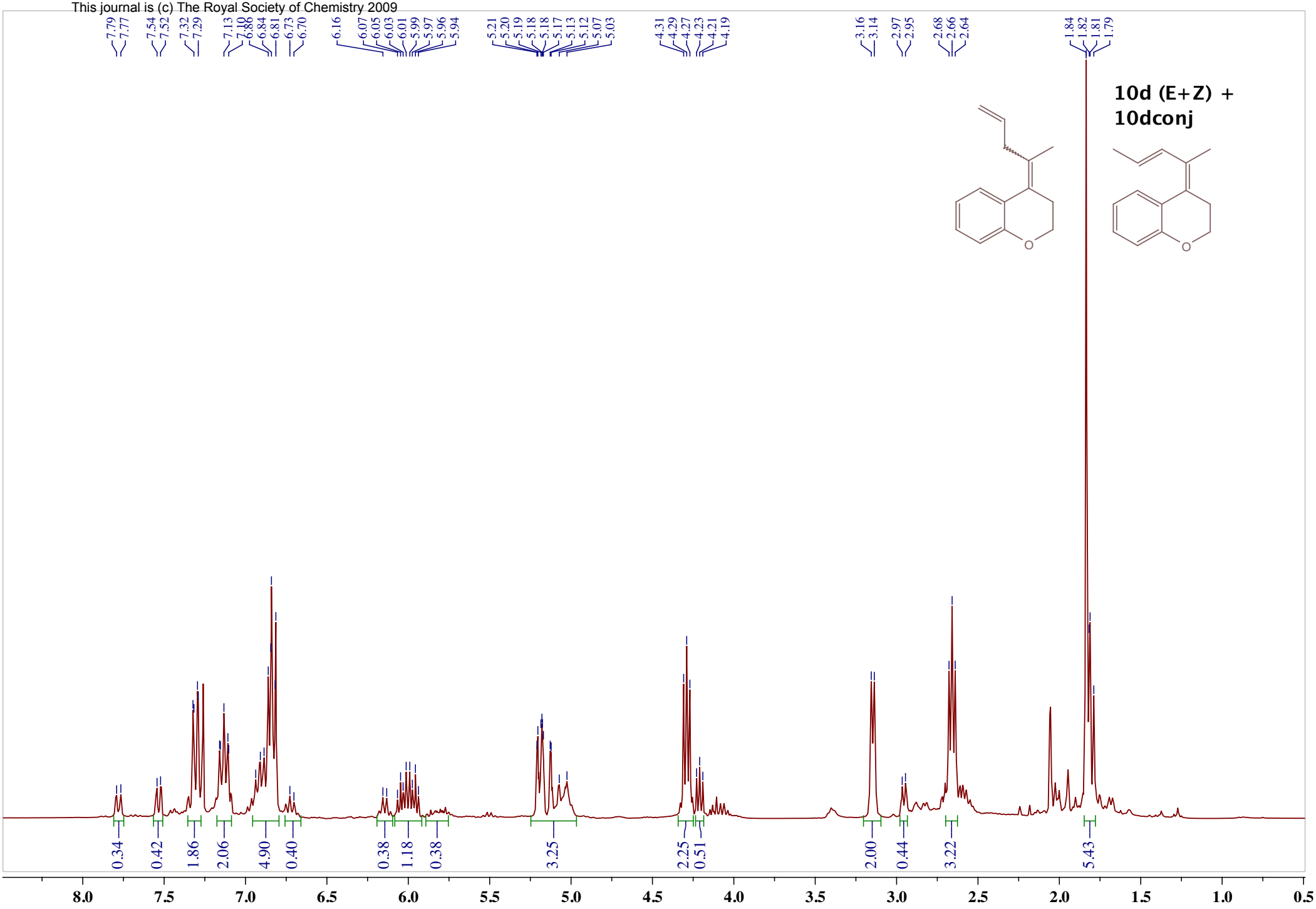

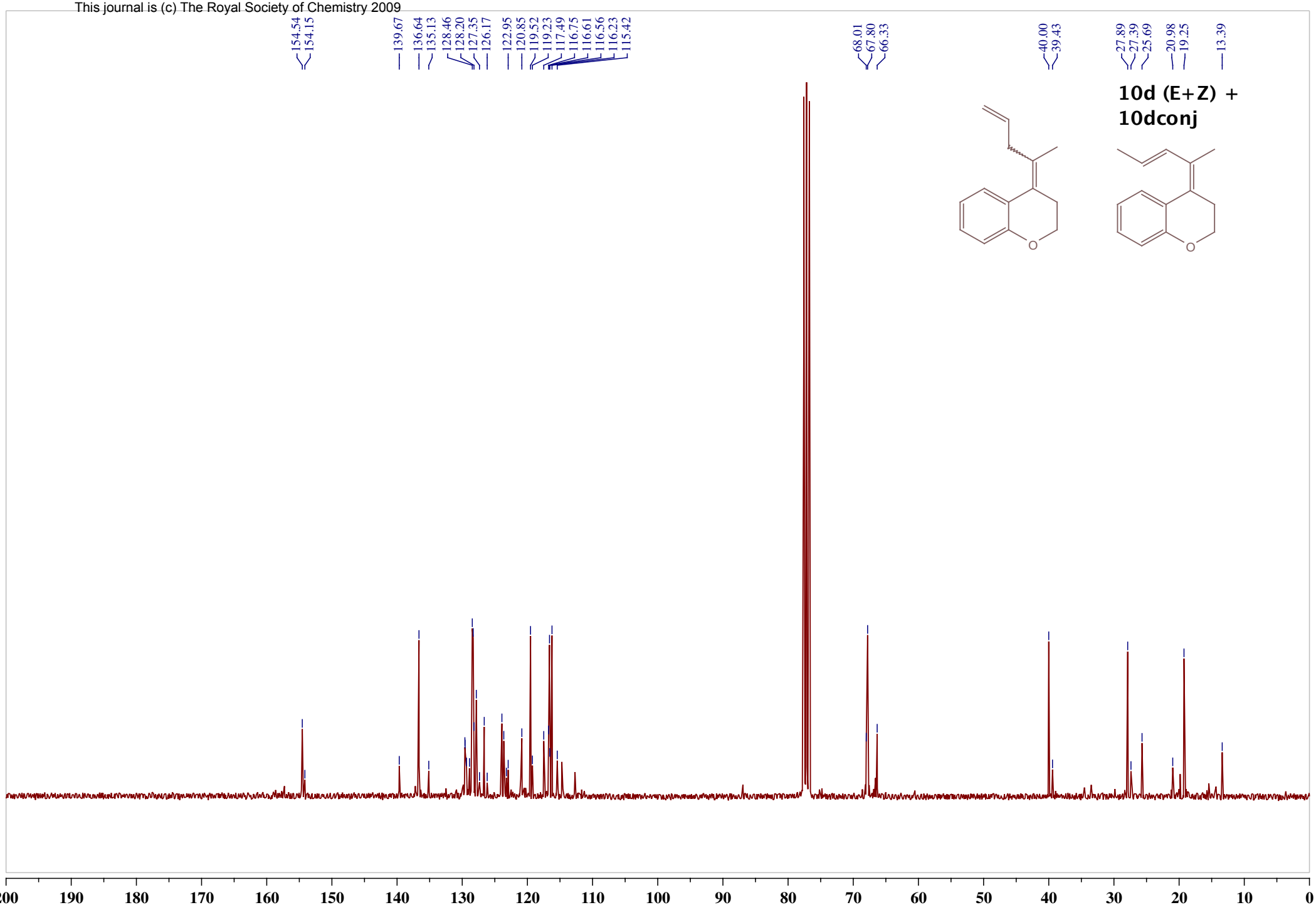
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67.80
66.33
40.00
39.43
27.89
27.39
25.69
20.98
19.25
13.39
10d (E+Z) +
10dconj
O
O
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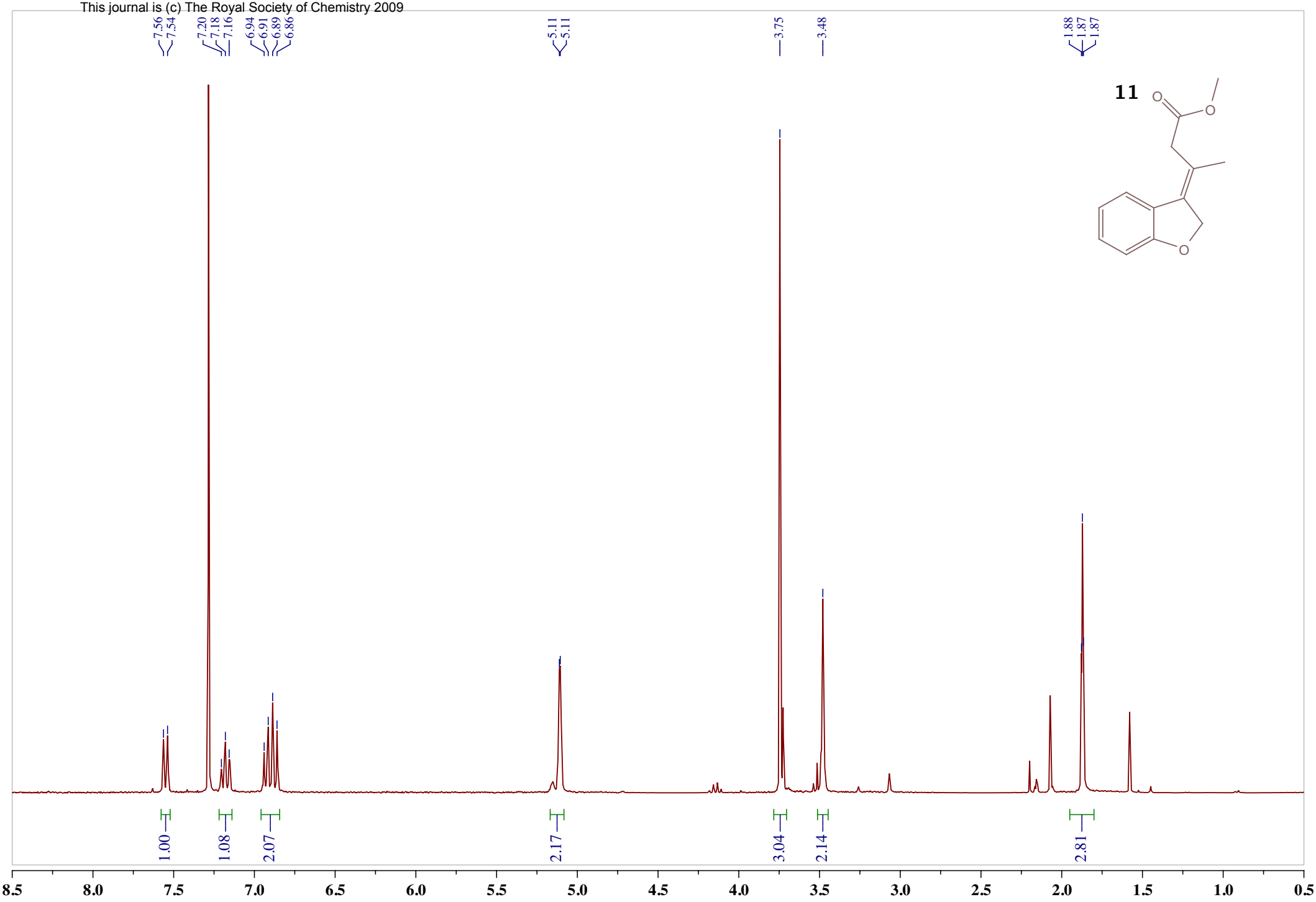

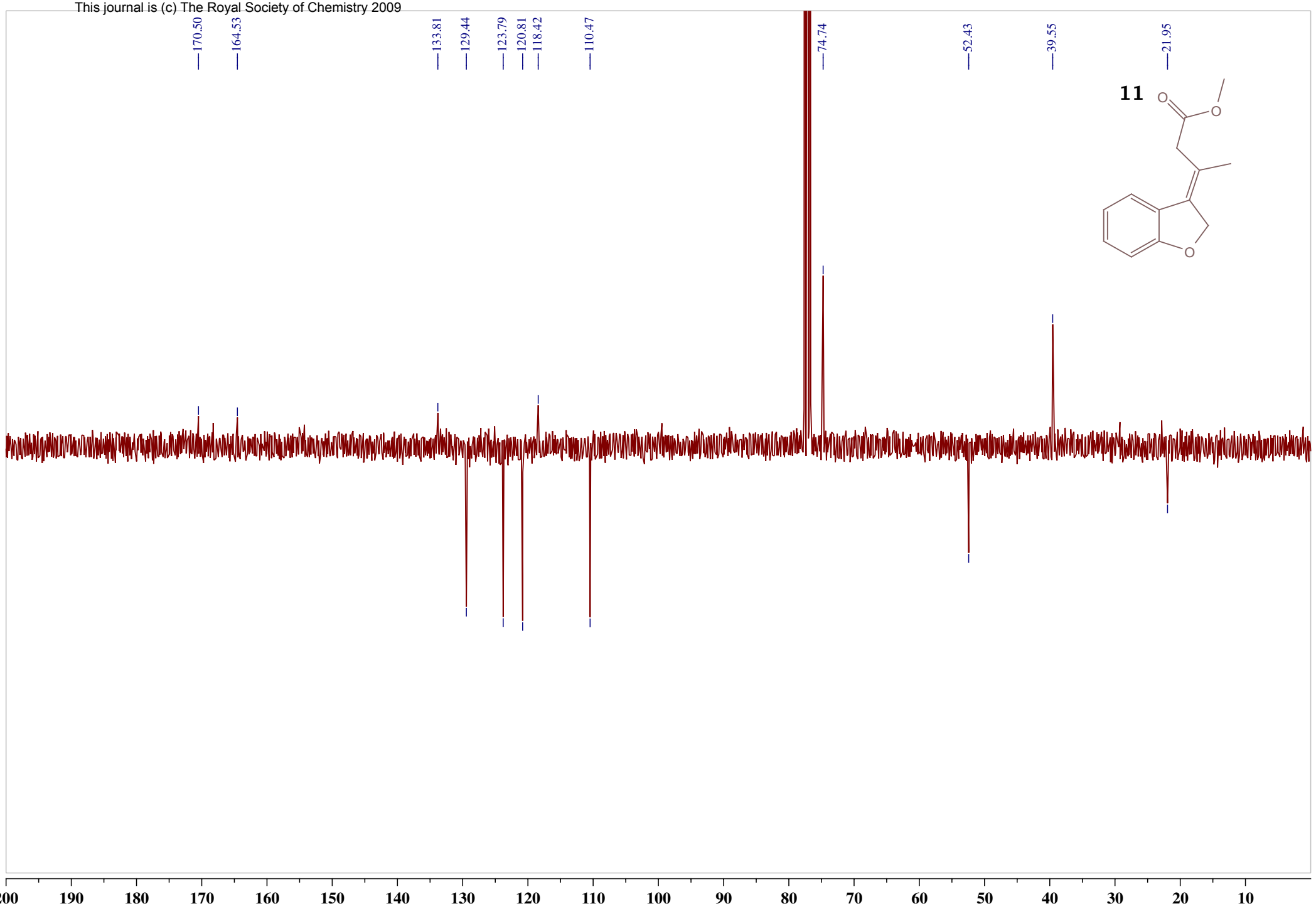

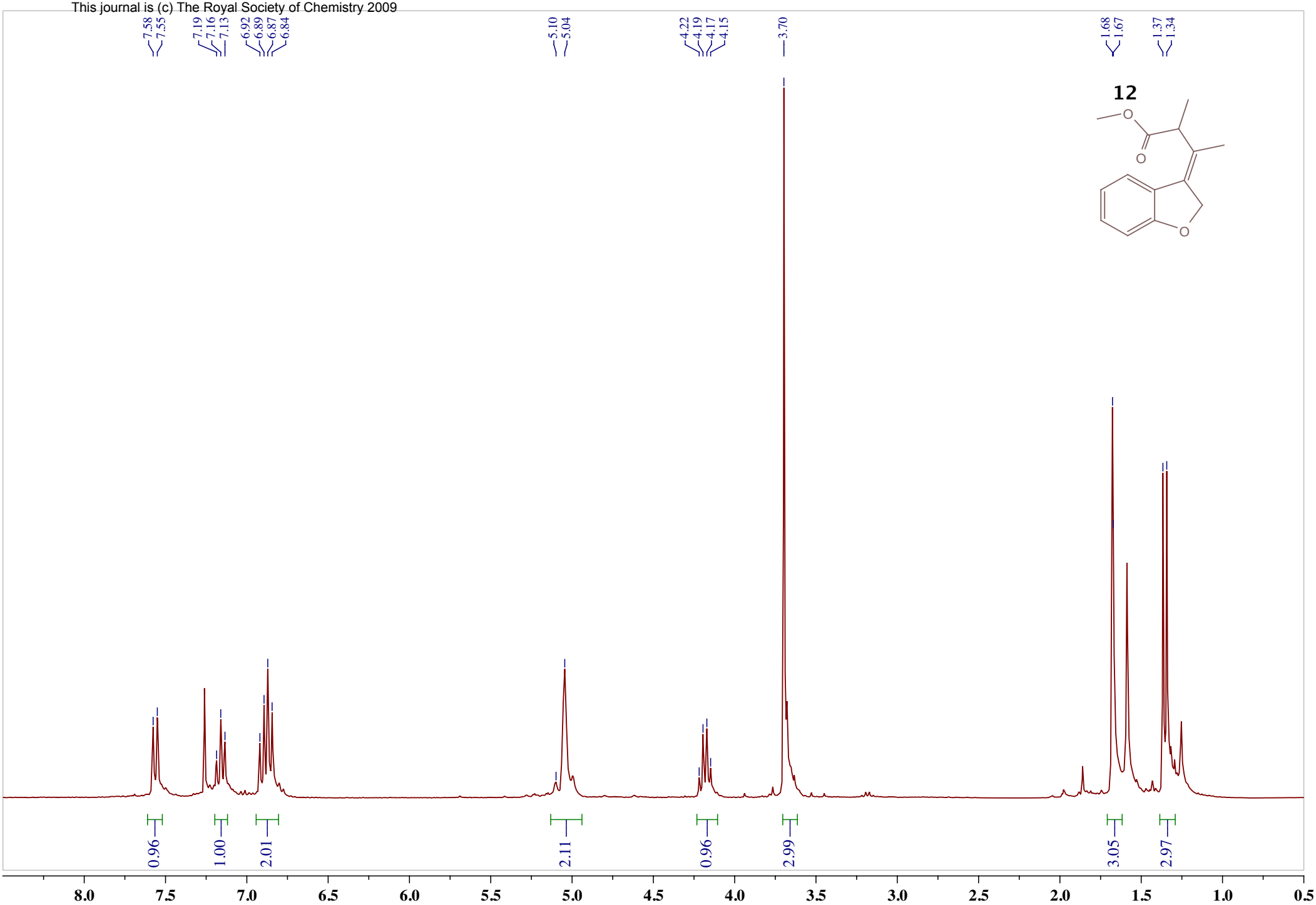

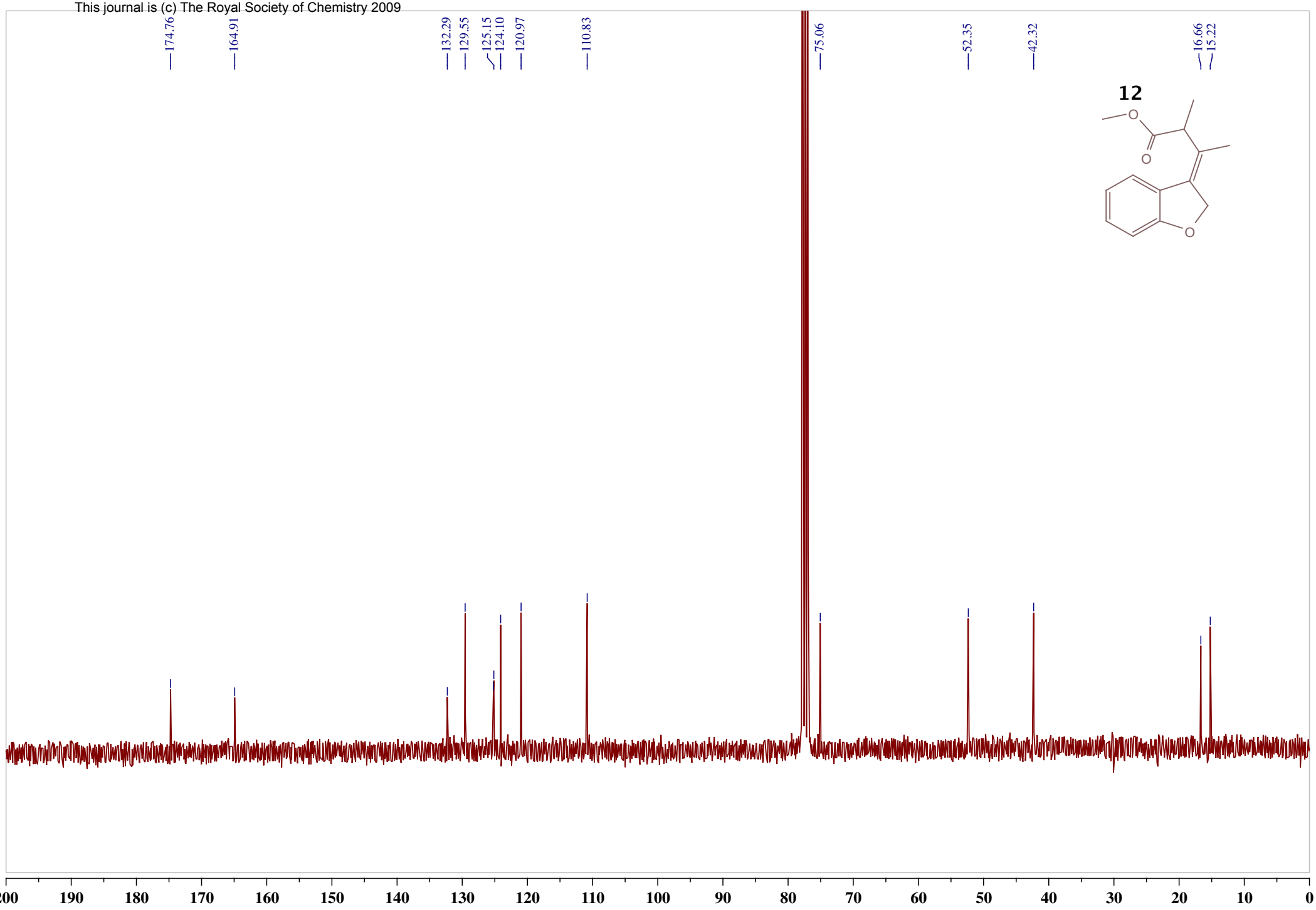

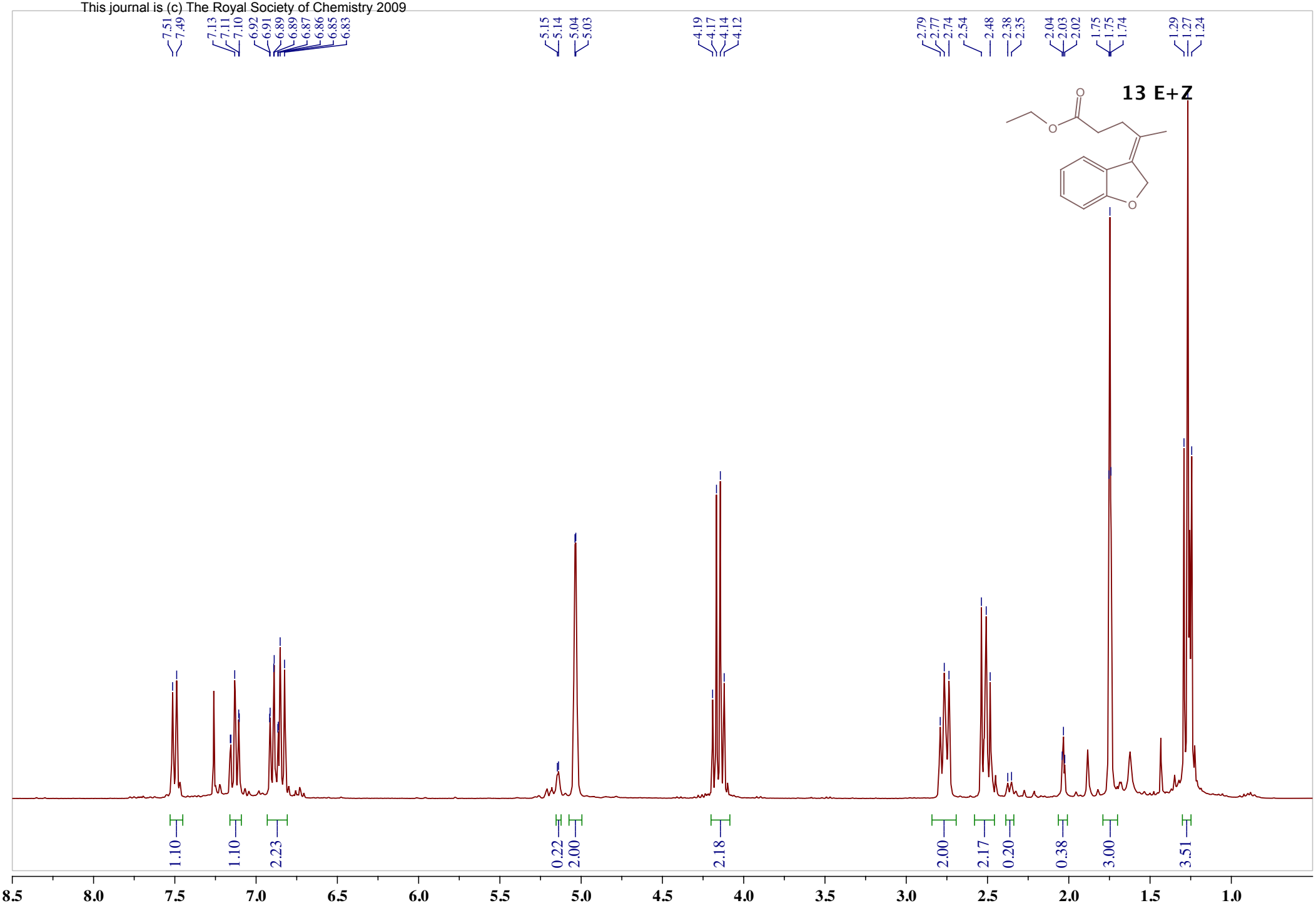

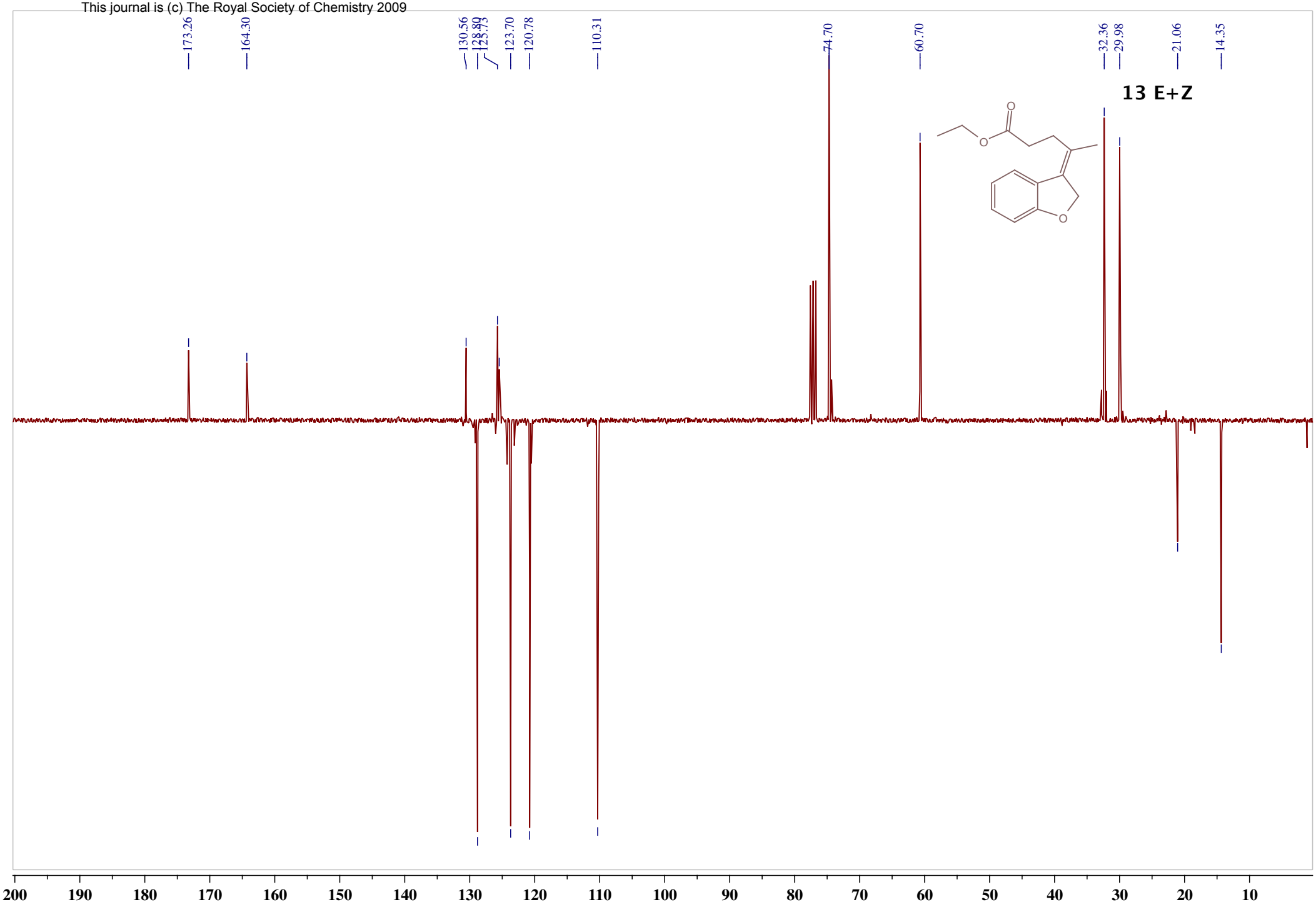

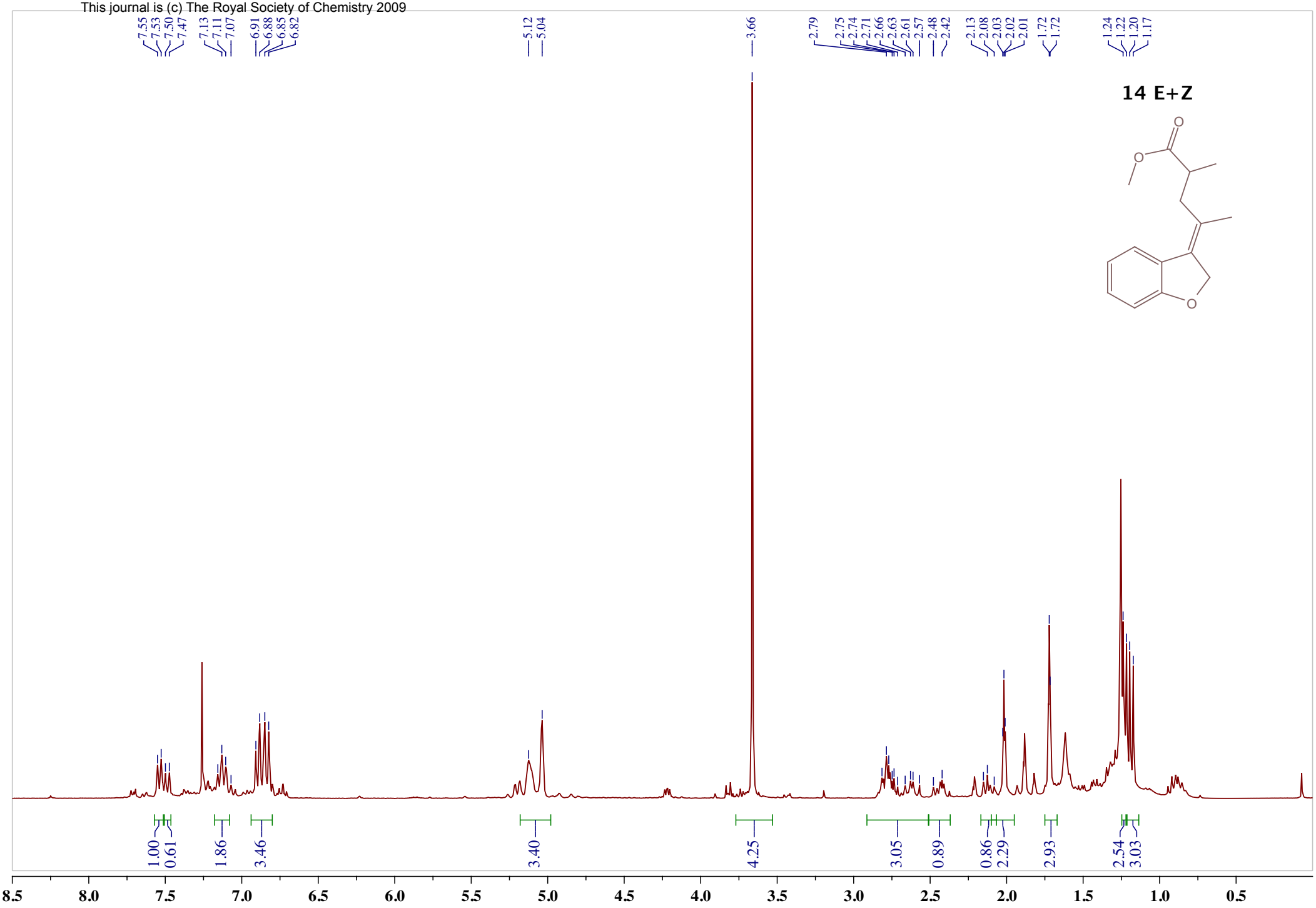

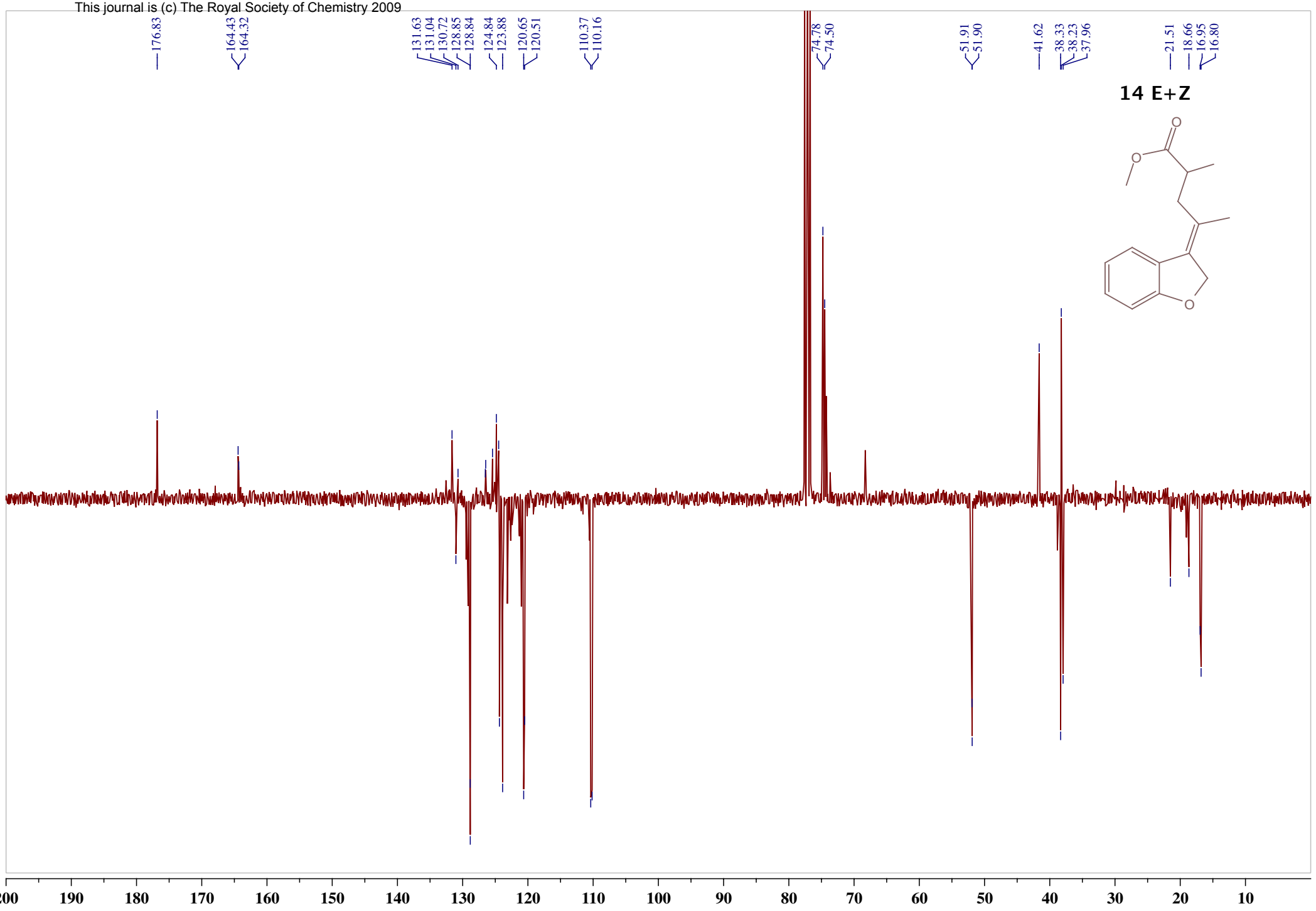
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74.78
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51.91
51.90
41.62
38.33
38.23
37.96
21.51
18.66
16.95
16.80
14 E+Z
O
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10