Supplementary Material (ESI) for Dalton Transactions

Supporting information

Tao Wang[1], and Junliang Zhang*[1,2]

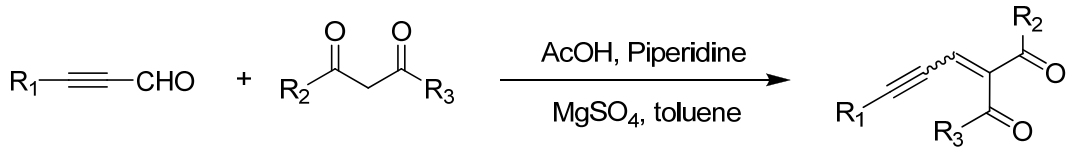
[1]Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062 and [2]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

Fax:(+86)-021-6223-5039; e-mail : jlzhang@chem.ecnu.edu.cn

General Information

All reactions were carried out without special operation and commercial available reagents were used directly. ^{1}H and ^{13}C NMR spectra were measured at 300 and 75 MHz in $CDCl_3$. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened).

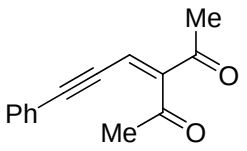
General procedure for synthesis of substrates



1

Typical procedure for synthesis of substrates 1: To a solution of the aldehyde[1] (12 mmol) in 40 mL of toluene, AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and 2,4-dione (10 mmol) were added, and the resulting mixture was stirred at 30 ^oC until the reaction was completed (monitored by TLC). Then the reaction mixture was added water (30 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under vaccuo. The crude residue was purified by flash chromatography on silica gel (hexanes : EtOAc = 10 : 1) to give the desired products.

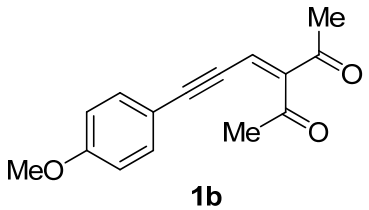
1. 3-(3-phenylprop-2-ynylidene)pentane-2,4-dione (**1a**).



1a

The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and pentane-2,4-dione (1.00 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 6 h to afford 1.72 g of **1a** (81% yield) as a yellow solid (Rf: 0.43, hexane / EtOAc = 5:1). m.p. 58 – 60 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, 2 H, *J* = 7.8 Hz); 7.44 - 7.35 (m, 3 H); 6.94 (s, 1 H); 2.57 (s, 3 H); 2.37 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 200.84, 195.54, 149.38, 132.09, 130.13, 128.61, 122.25, 121.59, 107.03, 85.26, 31.02, 27.42 ppm, MS (EI, 70 ev) m/z (%): 212 (M^+, 89.79), 155 (100). Anal calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70; found: C, 79.06; H, 5.70.

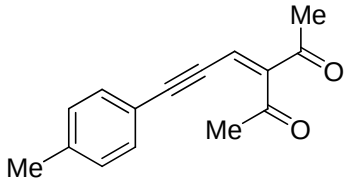
2. 3-(3-(4-methoxyphenyl)prop-2-ynylidene)pentane-2,4-dione (**1b**).



1b

The reaction of 3-(4-methoxyphenyl)propiolaldehyde (1.92 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and pentane-2,4-dione (1.00 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 6 h to afford 1.32 g of **1b** (51% yield) as a yellow solid (Rf: 0.30, hexane / EtOAc = 5:1). m.p. 59 – 61 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, 2 H, *J* = 8.4 Hz); 6.96 (s, 1 H); 6.88 (d, 2 H, *J* = 8.4 Hz); 3.83 (s, 3 H); 2.36 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 201.21, 195.67, 161.20, 148.21, 133.98, 123.10, 114.33, 113.61, 85.09, 55.40, 31.07, 27.48 ppm, MS (EI, 70 ev) m/z (%): 242 (M^+, 100). HRMS calcd for $C_{15}H_{14}O_3$: 242.0943, found: 242.0942.

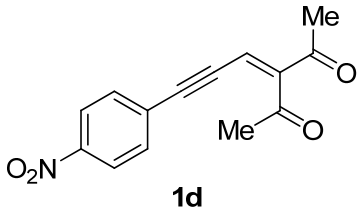
3. 3-(3-p-tolylprop-2-ynylidene)pentane-2,4-dione (**1c**).



1c

The reaction of 3-P-tolylpropiolaldehyde (1.73 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and pentane-2,4-dione (1.00 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 6 h to afford 1.28 g of **1c** (53% yield) as a yellow solid (Rf: 0.47, hexane / EtOAc = 5:1). m.p. 62 – 64 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37 (d, 2 H, *J* = 7.5 Hz); 7.17 (d, 2 H, *J* = 7.5 Hz); 6.95 (s, 1 H); 2.56 (s, 3 H); 2.38 (s, 3 H); 2.36 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 200.94, 195.62, 148.83, 140.79, 132.07, 129.39, 122.69, 118.51, 107.82, 85.07, 31.05, 27.45, 21.67 ppm, MS (EI, 70 ev) m/z (%): 226 (M^+, 100). Anal calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; found: C, 79.39; H, 6.25.

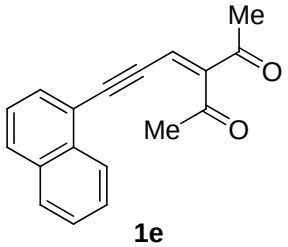
4. 3-(3-(4-nitrophenyl)prop-2-ynylidene)pentane-2,4-dione (**1d**).



1d

The reaction of 3-(4-nitrophenyl)propiolaldehyde (2.10 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and pentane-2,4-dione (1.00 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 8 h to afford 300 mg of **1d** (11% yield) as a yellow solid (Rf: 0.20, hexane / EtOAc = 5:1). m.p. 87 – 89 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, 2 H, *J* = 8.1 Hz); 7.63 (d, 2 H, *J* = 8.1 Hz); 6.88 (s, 1 H); 2.54 (s, 3 H); 2.39 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 200.41, 195.25, 151.05, 148.00, 132.82, 128.09, 123.79, 120.49, 102.89, 88.84, 30.97, 27.29 ppm, MS (EI, 70 ev) m/z (%): 257 (M^+, 100). HRMS calcd for $C_{14}H_{11}NO_4$: 257.0688, found: 257.0688.

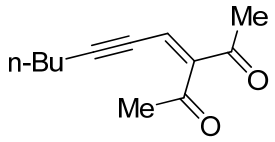
5. 3-(3-(naphthalen-1-yl)prop-2-ynylidene)pentane-2,4-dione (**1e**).



1e

The reaction of 3-(naphthalen-1-yl)propiolaldehyde (2.16 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and pentane-2,4-dione (1.00 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 10 h to afford 2.00 g of **1e** (72% yield) as a yellow solid (Rf: 0.37, hexane / EtOAc = 5:1). m.p. 63 – 65 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, 1 H, *J* = 8.4 Hz); 7.92 - 7.85 (m, 2 H); 7.72 (d, 1 H, *J* = 7.2 Hz); 7.63 (t, 1 H, *J* = 7.5 Hz); 7.55 (t, 1 H, *J* = 7.5 Hz); 7.46 (t, 1 H, *J* = 7.5 Hz); 7.06 (s, 1 H); 2.60 (s, 3 H); 2.41 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 201.00, 195.62, 149.21, 133.09, 133.03, 131.95, 130.86, 128.42, 127.53, 126.80, 125.67, 125.15, 122.32, 119.17, 105.43, 89.78, 31.08, 27.18 ppm, MS (EI, 70 ev) m/z (%): 262 (M^+, 58.39), 261 (100). HRMS calcd for $C_{18}H_{14}O_2$: 262.0994, found: 262.0995.

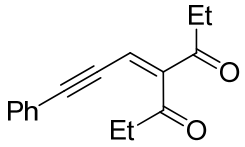
6. 3-(hept-2-ynylidene)pentane-2,4-dione (**1f**).



1f

The reaction of hept-2-ynal (1.32 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and pentane-2,4-dione (1.00 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 2 h to afford 1.29 g of **1f** (65% yield) as a yellow oil (Rf: 0.57, hexane / EtOAc = 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.65 (s, 1 H); 2.42 (s, 3 H); 2.40 (t, 2 H, J = 7.5 Hz); 2.26 (s, 3 H); 1.55 - 1.46 (m, 2 H); 1.43 - 1.31(m, 2 H); 0.87 (t, 3 H, *J* = 7.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 201.15, 195.63, 149.45, 123.06, 110.26, 76.74, 30.75, 29.99, 27.03, 21.82, 19.76, 13.33 ppm, MS (EI, 70 ev) m/z (%): 192 (M^+, 1.67), 135 (100). HRMS calcd for $C_{12}H_{16}O_2$: 192.1150, found: 192.1149.

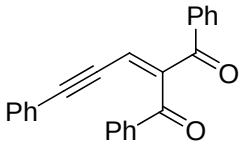
7. 4-(3-phenylprop-2-ynylidene)heptane-3,5-dione (**1g**).



1g

The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and heptane-3,5-dione (1.28 g, 10 mmol) in toluene (40 mL) at 30 ^oC for 6 h to afford 1.72 g of **1g** (67% yield) as a yellow oil (Rf: 0.60, hexane / EtOAc = 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, 2 H, *J* = 7.8 Hz); 7.43 - 7.32 (m, 3 H); 6.88 (s, 1 H); 2.87 (q, 2 H, *J* = 7.2 Hz); 2.66 (q, 2 H, *J* = 7.2 Hz); 1.20 (t, 3 H, *J* = 7.2 Hz); 1.12 (t, 3 H, *J* = 7.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 204.77, 198.10, 149.82, 132.01, 129.92, 128.57, 121.68, 120.24, 105.43, 85.05, 36.75, 32.67, 7.89, 7.61 ppm, MS (EI, 70 ev) m/z (%): 240 (M^+, 38.57), 155 (100). HRMS calcd for $C_{16}H_{16}O_2$: 240.1150, found: 240.1149.

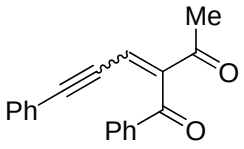
8. 1,3-diphenyl-2-(3-phenylprop-2-ynylidene)propane-1,3-dione (**1h**).



1h

The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and 1,3-diphenylpropane-1,3-dione (2.24 g, 10 mmol) in toluene (40 mL) at 60 ^oC for 10 h to afford 1.69 g of **1h** (48% yield) as a yellow solid (Rf: 0.50, hexane / EtOAc = 5:1). m.p. 95 – 97 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, 2 H, *J* = 7.8 Hz); 7.84 (d, 2 H, *J* = 7.8 Hz); 7.63 - 7.43 (m, 6 H); 7.34 - 7.21 (m, 3 H); 7.08 (d, 2 H, *J* = 7.8 Hz); 6.99 (s, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.06, 192.84, 147.73, 136.73, 136.32, 133.71, 132.91, 131.94, 129.71, 129.60, 129.23, 128.71, 128.54, 128.26, 124.32, 121.51, 106.46, 85.29 ppm, MS (EI, 70 ev) m/z (%): 336 (M^+, 34.84), 105 (100). HRMS calcd for $C_{24}H_{16}O_2$: 336.1150, found: 336.1151.

9. 1-phenyl-2-(3-phenylprop-2-ynylidene)butane-1,3-dione (**1i**).



1i

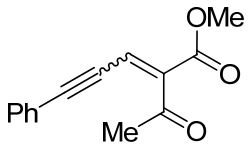
The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and 1-phenylbutane-1,3-dione (1.62 g, 10 mmol) in toluene (40 mL) at 60 ^oC for 6 h to afford 173 mg of (***E***)-**1i** (6% yield) as a yellow oil (Rf: 0.53, hexane / EtOAc = 5:1) and 1.53 g of (***Z***)-**1i** (55% yield) as a yellow solid (Rf: 0.43, hexane / EtOAc = 5:1). The stereochemistry was determinated by NOESY spectra.

(***Z***)-**1i**: m.p. 82-84 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, 2 H, *J* = 7.2 Hz); 7.60 (t, 1 H, *J* = 7.5 Hz); 7.49 (t, 2 H, *J* = 7.2 Hz); 7.29 - 7.14 (m, 4 H); 6.99 (d, 2 H, *J* = 7.2 Hz); 2.35 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 195.08, 194.11, 147.72, 136.02, 133.91, 131.83, 129.68, 129.39, 128.72, 128.19, 122.27, 121.33, 106.34, 85.33, 27.36 ppm, MS (EI, 70 ev) m/z (%): 274 (M^+, 70.26), 105 (100). HRMS calcd

for $C_{19}H_{14}O_2$: 274.0994, found: 274.0993.

(***E***)-**1i**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, 2 H, *J* = 7.2 Hz); 7.59 (t, 1 H, *J* = 7.2 Hz); 7.54 - 7.36 (m, 8 H); 6.68 (s, 1 H); 2.60(s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 198.12, 194.20, 148.46, 136.71, 133.28, 132.12, 130.04, 129.34, 128.63, 128.58, 123.17, 121.76, 106.51, 85.68, 30.64 ppm, MS (EI, 70 ev) m/z (%): 274 (M^+, 70.26), 105 (100). HRMS calcd for $C_{19}H_{14}O_2$: 274.0994, found: 274.0993.

10. methyl 2-acetyl-5-phenylpent-2-en-4-ynoate (**1j**).



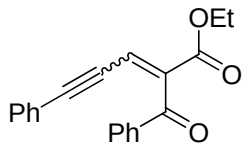
1j

The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and methyl 3-oxobutanoate (1.16 g, 10 mmol) in toluene (40 mL) at 30 ^{o}C for 3 h to afford 1.66 g of **1j** (68% yield, *E* / *Z* = 1.2 / 1) as a yellow oil [Rf: (*E*)-1j, 0.53; (*Z*)-1j, 0.47, hexane / EtOAc = 5:1]. The stereochemistry was determinated by NOESY spectra.

Major (***E***): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, 2 H, *J* = 7.8 Hz); 7.46 - 7.31(m, 3 H); 7.04 (s, 1 H); 3.82 (s, 3 H); 2.52 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 198.43, 164.30, 141.81, 132.18, 129.94, 128.49, 123.41, 121.63, 105.42, 85.01, 52.50, 30.46 ppm, MS (EI, 70 ev) m/z (%): 228 (M^+, 100), HRMS calcd for $C_{14}H_{12}O_3$: 228.0786, found: 228.0785.

Minor (***Z***): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, 2 H, *J* = 7.8 Hz); 7.45 - 7.30 (m, 3 H); 7.01 (s, 1 H); 3.90 (s, 3 H); 2.38 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.73, 165.61, 141.01, 132.16, 129.94, 128.45, 124.88, 121.70, 106.60, 85.37, 52.16, 27.48 ppm, MS (EI, 70 ev) m/z (%): 228 (M^+, 100), HRMS calcd for $C_{14}H_{12}O_3$: 228.0786, found: 228.0785.

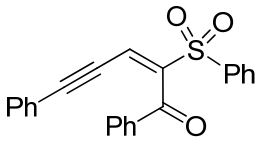
11. ethyl 2-benzoyl-5-phenylpent-2-en-4-ynoate (**1k**).



1k

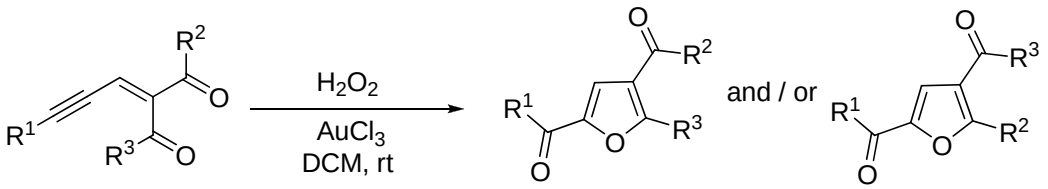
The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and ethyl 3-oxo-3-phenylpropanoate (1.92 g, 10 mmol) in toluene (40 mL) at 60 ^oC for 7 h to afford 1.27 g of **1k** (40% yield, major / minor = 5 / 1) as mixtured yellow oil (Rf: 0.57, hexane / EtOAc = 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = [7.98 (d, 1.66 H, *J* = 7.8 Hz), 7.81 (d, 0.34 H, *J* = 7.8 Hz)]; 7.63 - 7.43 (m, 4 H); 7.39 - 7.18 (m, 3 H); 7.09 (s, 1 H); [7.07 (s, 0.83 H), 6.82 (s, 0.17 H)]; 4.24 (q, 2 H, *J* = 7.2 Hz); 1.21 (t, 3 H, *J* = 7.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = (192.71, 192.00), (164.22, 163.87), (141.08, 141.02), (136.83, 135.98), (133.72, 133.06), (132.71, 131.90), (129.81, 129.59), 129.34, (128.91, 128.63), (128.45, 128.20), 125.55, (121.97, 121.45), (106.07, 104.70), (85.45, 84.76), (61.64, 61.32), (13.92, 13.89) ppm, MS (EI, 70 ev) m/z (%): 304 (M^+, 25.26), 105 (100). HRMS calcd for $C_{20}H_{16}O_3$: 304.1099, found: 304.1098.

12. 1,5-diphenyl-2-(phenylsulfonyl)pent-2-en-4-yn-1-one (**1l**).



1l

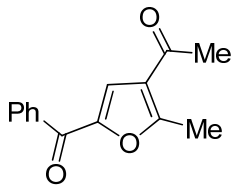
The reaction of 3-phenylpropiolaldehyde (1.56 g, 12 mmol), AcOH (360 mg, 6 mmol), piperidine (86 mg, 1 mmol), $MgSO_4$ (240 mg, 2 mmol) and 1-phenyl-2-(phenylsulfonyl)ethanone (2.60 g, 10 mmol) in toluene (40 mL) at 60 ^oC for 6 h to afford 3.12 g of **1l** (80% yield) as a yellow oil (as a single isomer of (*E*)-isomer; Rf: 0.33, hexane / EtOAc = 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, 4 H, *J* = 7.2 Hz); 7.62 - 742 (m, 7 H); 7.26 (t, 1 H, *J* = 7.2 Hz); 7.16 (t, 2 H, *J* = 7.5 Hz); 6.89 (d, 2 H, *J* = 8.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 189.68, 148.46, 139.40, 135.68, 134.12, 133.74, 131.76, 130.02, 129.60, 128.95, 128.55, 128.43, 128.14, 124.03, 120.50, 107.59, 83.07 ppm, MS (EI, 70 ev) m/z (%): 372 (M^+, 14.43), 105 (100). HRMS calcd for $C_{23}H_{16}O_3S$: 372.0820, found: 372.0821.



1 **2** **2'**

Typical procedure for synthesis of 2-acylfurans : To a solution of **1** (0.5 mmol) and $AuCl_3$(0.025 mmol, 7.6 mg) in DCM (5 mL), H_2O_2 (30%, 1.5 mmol, 170 mg) was added. The resulting solution was stirred at rt until the reaction was completed (monitored by TLC). After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes : AcOEt = 10 : 1) to give the desired product **2.**

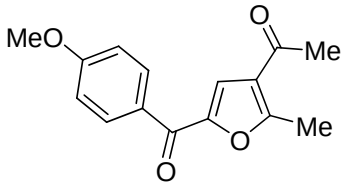
13. 1-(5-benzoyl-2-methylfuran-3-yl)ethanone (**2a**).



2a

The reaction of **1a** (106 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 2 h to afford **2a** (99.9 mg) in 88% yield as a white solid (Rf: 0.42, hexane / EtOAc = 3:1). m.p. 126-128 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, 2 H, *J* = 7.5 Hz); 7.55 (t, 1 H, *J* = 7.5 Hz); 7.44 (t, 2 H, *J* = 7.5 Hz); 7.37 (s, 1 H); 2.70 (s, 3 H); 2.43 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.01, 181.85, 162.87, 149.21, 136.61, 132.60, 128.87, 128.35, 123.02, 120.55, 28.86, 14.72 ppm, MS (EI, 70 ev) m/z (%): 228 (M^+, 70.01), 213 (100). HRMS calcd for $C_{14}H_{12}O_3$: 228.0786, found: 228.0785.

14. 1-(5-(4-methoxybenzoyl)-2-methylfuran-3-yl)ethanone (**2b**).

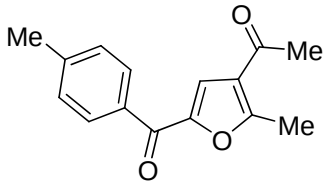


2b

The reaction of **1b** (121 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and

$AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 17 h to afford **2b** (95 mg) in 74% yield as a yellow solid (Rf: 0.30, hexane / EtOAc = 3:1). m.p. 139-140 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, 2 H, *J* = 8.4 Hz); 7.38 (s, 1 H); 6.98 (d, 2 H, *J* = 8.4 Hz); 3.88 (s, 3 H); 2.72 (s, 3 H); 2.45 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.34, 180.66, 163.46, 162.46, 149.84, 131.54, 129.39, 123.07, 119.71, 113.82, 55.47, 29.04, 14.90 ppm, MS (EI, 70 ev) m/z (%): 258 (M^+, 79.40), 135 (100). HRMS calcd for $C_{15}H_{14}O_4$: 258.0892, found: 258.0891.

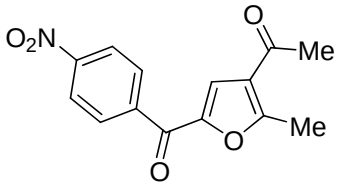
15. 1-(2-methyl-5-(4-methylbenzoyl)furan-3-yl)ethanone (**2c**).



2c

The reaction of **1c** (113 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 11 h to afford **2c** (102 mg) in 84% yield as a yellow solid (Rf: 0.45, hexane / EtOAc = 3:1). m.p. 132-133 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, 2 H, *J* = 7.8 Hz); 7.37 (s, 1 H); 7.30 (d, 2 H, *J* = 7.8 Hz); 2.72 (s, 3 H); 2.45 (s, 3 H); 2.43 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.19, 181.72, 162.73, 149.60, 143.61, 134.11, 129.20, 129.16, 123.08, 120.18, 28.96, 21.56, 14.83 ppm, MS (EI, 70 ev) m/z (%): 242 (M^+, 68.18), 227 (100). HRMS calcd for $C_{15}H_{14}O_3$: 242.0943, found: 242.0943.

16. 1-(2-methyl-5-(4-nitrobenzoyl)furan-3-yl)ethanone (**2d**).

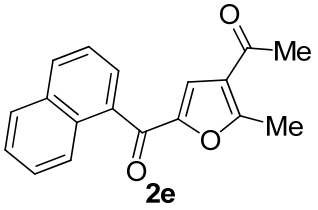


2d

The reaction of **1d** (103 mg, 0.4 mmol), H_2O_2 (30%) (136 mg, 1.2 mmol) and $AuCl_3$ (0.020 mmol, 6.1 mg) in DCM (4 mL) was carried out at rt for 11 h to afford **2d** (89 mg) in 82% yield as a yellow solid (Rf: 0.30, hexane / EtOAc = 3:1). m.p. 199-200 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.36 (d, 2 H, *J* = 7.8 Hz); 8.10 (d, 2 H, *J* = 7.8 Hz); 7.47 (s, 1 H); 2.75 (s, 3 H); 2.48 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$):

δ = 192.89, 180.01, 163.92, 150.06, 149.04, 141.73, 130.10, 123.74, 123.60, 121.52, 29.06, 15.04 ppm, MS (EI, 70 ev) m/z (%): 273 (M^+, 56.59), 258 (100). HRMS calcd for $C_{14}H_{11}NO_5$: 273.0637, found: 273.0638.

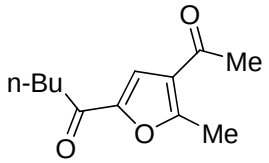
17. 1-(5-(1-naphthoyl)-2-methylfuran-3-yl)ethanone (**2e**).



2e

The reaction of **1e** (131 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 14.5 h to afford **2e** (89 mg) in 64% yield as a yellow solid (Rf: 0.39, hexane / EtOAc = 3:1). m.p. 122-123 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (t, 1 H, *J* = 5.7 Hz); 8.02 (d, 1 H, *J* = 8.1 Hz); 7.94-7.86 (m, 1 H); 7.54 (d, 1 H, *J* = 6.9 Hz); 7.53 (t, 3 H, *J* = 7.5 Hz); 7.19 (s, 1 H); 2.74 (s, 3 H); 2.38 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.08, 183.75, 163.83, 150.31, 134.64, 133.72, 131.94, 130.54, 128.38, 127.54, 127.36, 126.65, 125.09, 124.20, 123.30, 121.62, 28.95, 14.96 ppm, MS (EI, 70 ev) m/z (%): 278 (M^+, 100). HRMS calcd for $C_{18}H_{14}O_3$: 278.0943, found: 278.0943.

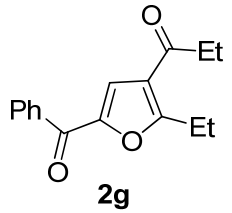
18. 1-(4-acetyl-5-methylfuran-2-yl)pentan-1-one (**2f**).



2f

The reaction of **1f** (96 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 8 h to afford **2f** (66 mg) in 64% yield as a yellow oil (Rf: 0.52, hexane / EtOAc = 3:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33 (s, 1 H), 2.74 (t, 2 H, *J* = 7.5 Hz); 2.62 (s, 3 H); 2.40 (s, 3 H); 1.69 - 1.59 (m, 2 H); 1.40 - 1.28 (m, 2 H); 0.89 (t, 3 H, *J* = 7.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.20, 189.20, 161.99, 150.02, 123.01, 116.85, 37.96, 28.88, 26.24, 22.26, 14.68, 13.70 ppm, MS (EI, 70 ev) m/z (%): 208 (M^+, 8.07), 166 (100). HRMS calcd for $C_{12}H_{16}O_3$: 208.1099, found: 208.1099.

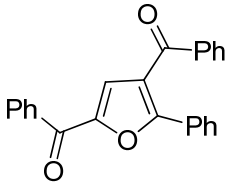
19. 1-(5-benzoyl-2-ethylfuran-3-yl)propan-1-one (**2g**).



2g

The reaction of **1g** (120 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 3.5 h to afford **2g** (107 mg) in 83% yield as a yellow oil (Rf: 0.64, hexane / EtOAc = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, 2 H, *J* = 7.2 Hz); 7.56 (t, 1 H, *J* = 7.2 Hz); 7.46 (t, 2 H, *J* = 7.2 Hz); 7.39 (s, 1 H); 3.10 (q, 2 H, *J* = 7.5 Hz); 2.76 (q, 2 H, *J* = 7.5 Hz); 1.29 (t, 3 H, *J* = 7.5 Hz); 1.13 (t, 3 H, *J* = 7.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.03, 181.91, 167.58, 149.49, 136.84, 132.60, 129.01, 128.39, 121.72, 120.15, 34.28, 22.01, 11.55, 7.52 ppm, MS (EI, 70 ev) m/z (%): 256 (M^+, 39.92), 227 (100). HRMS calcd for $C_{16}H_{16}O_3$: 256.1099, found: 256.1100.

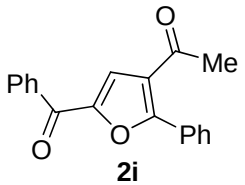
20. (5-phenylfuran-2,4-diyl)bis(phenylmethanone) (**2h**).



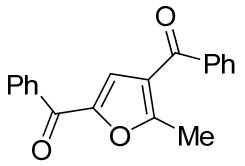
2h

The reaction of **1h** (168 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 10 h to afford **2h** (154 mg) in 87% yield as white solid (Rf: 0.61, hexane / EtOAc = 3:1). m.p. 131-132 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, 2 H, *J* = 7.5 Hz); 7.84 (m, 4 H); 7.65 - 7.35 (m, 10 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 190.71, 182.08, 158.82, 149.91, 137.18, 136.89, 133.42, 132.85, 130.37, 129.69, 129.24, 128.55, 128.45, 128.09, 123.09, 122.54 ppm, MS (EI, 70 ev) m/z (%): 352 (M^+, 89.27), 105 (100). HRMS calcd for $C_{24}H_{16}O_3$: 352.1099, found: 352.1100.

21. 1-(5-benzoyl-2-phenylfuran-3-yl)ethanone (**2i**) and (5-methylfuran-2,4-diyl)bis -(phenylmethanone) (**2i'**).



2i



2i'

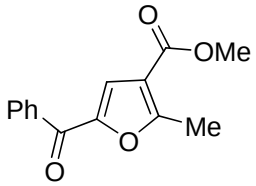
The reaction of **(*Z*)-1i** (137 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 12 h to afford **2i** (129 mg) in 89% yield as a yellow solid (Rf: 0.48, hexane / EtOAc = 3:1).

The reaction of **(*E*)-1i** (137 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 12 h to afford **2i** (34 mg) in 23% yield as a yellow solid and **2i'** (82 mg) in 57% yield as a yellow oil (Rf: 0.61, hexane / EtOAc = 3:1).

2i: m.p. 117-118 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 - 7.99 (m, 4 H); 7.65 - 7.48 (m, 7 H); 2.48 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.11, 182.05, 159.69, 150.07, 136.78, 132.91, 130.91, 129.24, 129.06, 128.75, 128.58, 128.45, 123.82, 121.90, 29.77 ppm, MS (EI, 70 ev) m/z (%): 290 (M^+, 75.50), 275 (100). HRMS calcd for $C_{19}H_{14}O_3$: 290.0943, found: 290.0943.

2i': ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.92 (d, 2 H, *J* = 7.2 Hz); 7.78 (d, 2 H, *J* = 7.2 Hz); 7.56 (t, 2 H, *J* = 7.2 Hz); 7.47 (t, 4 H, *J* = 7.2 Hz); 7.34 (s, 1 H); 2.66 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 190.03, 182.01, 163.73, 149.35, 138.05, 136.78, 132.69, 129.03, 128.86, 128.51, 128.44, 122.36, 121.71, 14.62 ppm, MS (EI, 70 ev) m/z (%): 290 (M^+, 35.91), 105 (100). HRMS calcd for $C_{19}H_{14}O_3$: 290.0943, found: 290.0942.

22. methyl 5-benzoyl-2-methylfuran-3-carboxylate (**2j**).



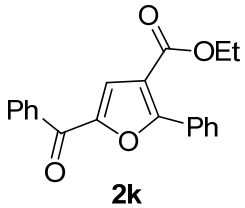
2j

The reaction of **(*E*)-1j** (114 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 36 h to afford **2j** (98 mg) in 79% yield as a yellow oil (Rf: 0.61, hexane / EtOAc = 3:1); ^{1}H NMR (300

MHz, $CDCl_3$): δ = 7.78 (d, 2 H, *J* = 7.5 Hz); 7.49 - 7.33 (m, 3 H); 3.72 (s, 3 H); 2.59 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 181.65, 163.58, 162.88, 149.14, 136.58, 132.44, 128.74, 128.22, 121.09, 115.42, 51.39, 13.98 ppm, MS (EI, 70 ev) m/z (%): 244 (M^+, 100). HRMS calcd for $C_{14}H_{12}O_4$: 244.0736, found: 244.0733.

The title compand could be also afforded from the (***Z***)-**1j** in 66% yield.

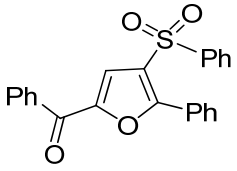
23. ethyl 5-benzoyl-2-phenylfuran-3-carboxylate (**2k**).



2k

The reaction of **1k** (152 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 16 h to afford **2k** (117 mg) in 73% yield as a white solid (Rf: 0.70, hexane / EtOAc = 3:1). m.p. 91-92 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.16 - 8.08 (m, 2 H); 8.01 (d, 2 H, *J* = 7.8 Hz); 7.63 (t, 3 H, *J* = 7.2 Hz); 7.56 - 7.48 (m, 5 H); 4.34 (q, 2 H, *J* = 7.2 Hz); 1.35 (t, 3 H, *J* = 7.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 182.12, 162.57, 160.67, 149.76, 136.97, 132.84, 130.69, 129.24, 129.10, 128.58, 128.29, 123.01, 115.87, 61.08, 14.18 ppm, MS (EI, 70 ev) m/z (%): 320 (M^+, 100). Anal calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03; found: C, 75.00; H, 5.01.

24. phenyl(5-phenyl-4-(phenylsulfonyl)furan-2-yl)methanone (**2l**).

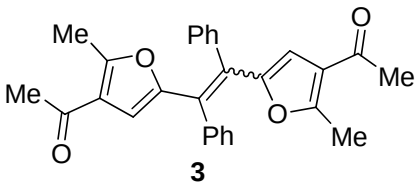


2l

The reaction of **1l** (186 mg, 0.5 mmol), H_2O_2 (30%) (170 mg, 1.5 mmol) and $AuCl_3$ (0.025 mmol, 7.6 mg) in DCM (5 mL) was carried out at rt for 16 h to afford **2l** (153 mg) in 79% yield as a colorless oil (Rf: 0.45, hexane / EtOAc = 3:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 - 7.95 (m, 4 H); 7.79 (d, 2 H, *J* =7.5 Hz); 7.65 - 7.55 (m, 2 H); 7.58 - 7.36 (m, 8 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 181.45, 157.88, 149.36, 140.75, 136.18, 133.58, 133.10, 131.18, 129.06, 129.01, 128.57, 128.42, 127.03,

127.00, 126.06, 121.54 ppm, MS (EI, 70 ev) m/z (%): 388 (M^+, 55.20), 105 (100). HRMS calcd for $C_{23}H_{16}O_4S$: 388.0769, found: 388.0770.

25. 1,1'-(5,5'-(1,2-diphenylethene-1,2-diyl)bis(2-methylfuran-5,3-diyl))diethanone (**3**).



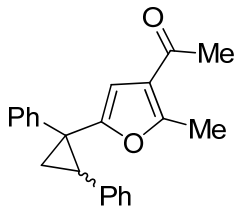
3

The solution of **1a** (0.5 mmol, 106 mg), Ph_3PAuCl (0.025 mmol, 12.4 mg) and AgOTf (0.025 mmol, 6.4 mg) was stirred in DCM (5 mL) at rt for 2 h to afford **3** in 93% yield (*E* / *Z* = 1.5 / 1) as yellow solid.

(***E***)-isomer (Rf: 0.52, hexane / EtOAc = 3:1): mp. 176-177 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37 - 7.30 (m, 10 H); 5.91 (s, 2 H); 2.20 (s, 12 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.95, 157.86, 152.43, 139.95, 130.04, 128.40, 128.07, 127.63, 122.53, 112.81, 28.89, 14.08 ppm, MS (EI, 70 ev) m/z (%): 424 (M^+, 13.64), 43 (100). HRMS calcd for $C_{28}H_{24}O_4$: 424.1675, found: 424.1675.

(***Z***)-isomer (Rf: 0.39, hexane / EtOAc = 3:1): mp. 149-150 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.14 (s, 10 H); 6.29 (s, 2 H); 2.48 (s, 6 H); 2.34 (s, 6 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.15, 157.76, 153.24, 139.62, 131.35, 129.36, 127.84, 127.51, 122.72, 112.47, 29.11, 14.37 ppm, MS (EI, 70 ev) m/z (%): 424 (M^+, 100). HRMS calcd for $C_{28}H_{24}O_4$: 424.1675, found: 424.1675.

26. 1-(5-(1,2-diphenylcyclopropyl)-2-methylfuran-3-yl)ethanone (**4**).



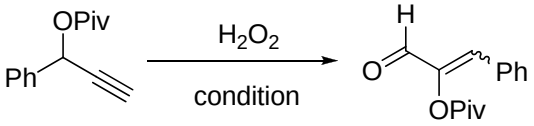
4

To the solution of **1a** (0.5 mmol, 106 mg) and styrene (5 mmol, 521 mg) in DCM (10 mL), $AuCl_3$ (0.025 mmol, 7.6 mg) was added. The resulting solution was stirred at rt for 12 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes : Et_2O = 10 : 1) to give the desired product **4** (90 mg) in 56% yield as a yellow oil (fraction 1 / fraction 2 = 1 / 1.2).

First fraction (Rf: 0.67, hexane / EtOAc = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 - 7.10 (m, 5 H); 7.06 (d, 3 H, *J* = 6.9 Hz); 6.81 (d, 2 H, J = 7.8 Hz); 5.90 (s, 1 H); 2.94 (t, 1 H, *J* = 7.5 Hz); 2.57 (s, 3 H), 2.29 (s, 3 H); 2.01- 1.91 (m, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.25, 156.82, 156.58, 137.41, 136.82, 131.37, 128.03, 127.73, 127.64, 127.00, 125.79, 122.25, 105.75, 33.51, 31.24, 29.05, 19.00, 14.42 ppm, MS (EI, 70 ev) m/z (%): 316 (M^+, 100). HRMS calcd for $C_{22}H_{20}O_2$: 316.1463, found: 316.1462.

Second fraction (Rf: 0.64, hexane / EtOAc = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 - 7.22 (m, 4 H); 7.15 (t, 1 H, *J* = 7.5 Hz); 7.10 - 7.02 (m, 5 H); 5.94 (s, 1 H); 2.75 (t, 1 H, *J* = 7.5 Hz); 2.21 (s, 3 H); 2.12 (s, 3 H); 1.96 (t, 1 H, *J* = 6.6 Hz); 1.67 (q, 1 H, *J* = 5.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.03, 157.25, 152.65, 143.12, 137.44, 128.46, 128.27, 128.00, 127.72, 126.68, 126.24, 121.55, 109.00, 32.26, 31.99, 28.88, 18.92, 14.07 ppm, MS (EI, 70 ev) m/z (%): 316 (M^+, 88.85), 43 (100). HRMS calcd for $C_{22}H_{20}O_2$: 316.1463, found: 316.1464.

27. 3-oxo-1-phenylprop-1-en-2-yl pivalate (**6**).



5 **6**

Typical Procedure forsynthesis of 6 and 6': To a solution of **5**[2] (0.5 mmol, 108 mg) and catalyst (0.025 mmol) in DCM (5 mL), H_2O_2 (30%, 1.5 mmol, 170 mg) was added. The resulting solution was stirred at rt until the reaction was completed (monitored by TLC). After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes : AcOEt = 10 : 1) to give the desired product **6** as colorless oil. [3]

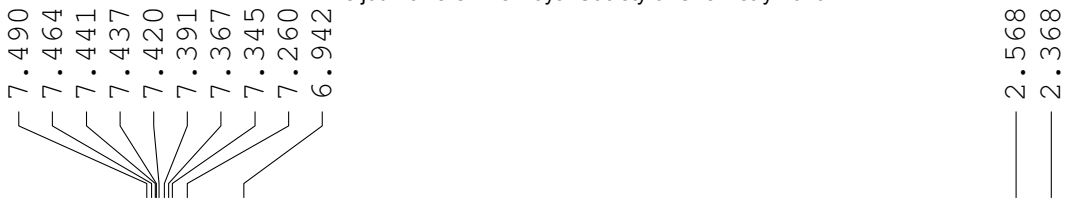
(***Z***)-isomer (Rf: 0.22, hexane / EtOAc = 10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.40 (s, 1 H), 7.66 - 7.64 (m, 2 H), 7.43-7.41 (m, 3 H), 7.01 (s, 1 H), 1.41 (s, 9 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ = 185.46, 175.26, 146.38, 136.39, 131.73, 130.68, 130.30, 128.79, 39.06, 27.10 ppm.

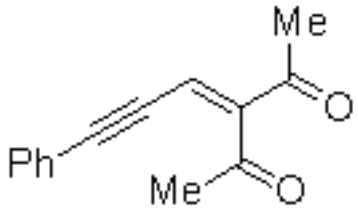
(***E***)-isomer (Rf: 0.36, hexane / EtOAc = 10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ =

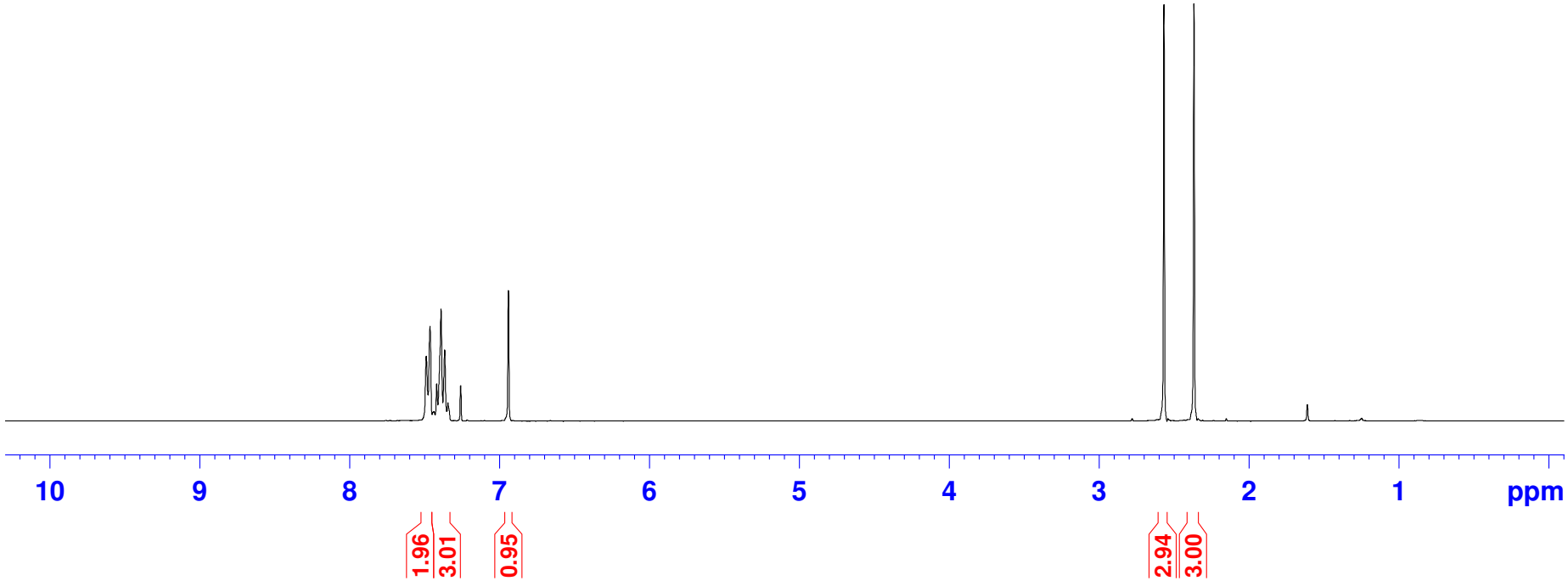
9.69 (s, 1 H), 7.45-7.39 (m, 6 H), 1.36 (s, 9 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ = 183.96, 176.52, 146.54, 136.57, 131.12, 129.96, 129.74, 128.77, 38.95, 27.15 ppm.

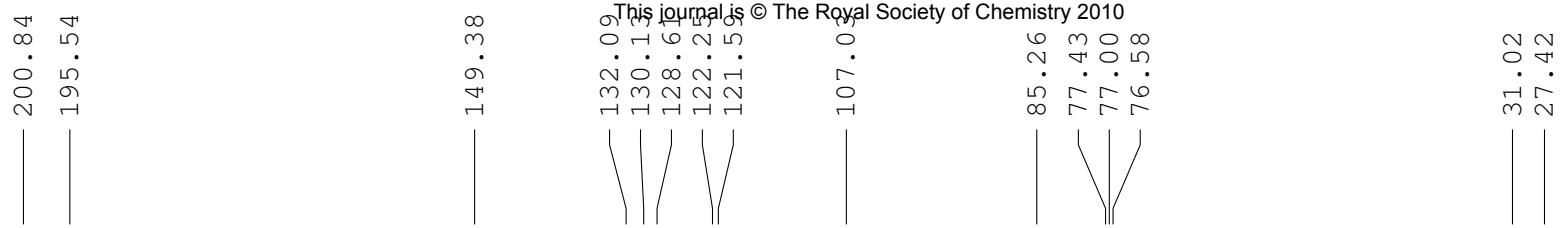
Reference:

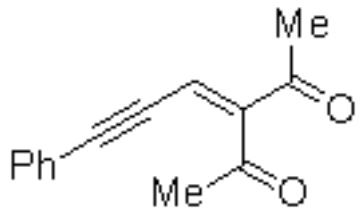
1. For synthesis of 3-phenylpropiolaldehyde, see: D. W. Knight, H. C. Rost, C. M. Sharland and J. Singkhonrat, *Tetrahedron Lett*., 2007, **48**, 7906–7910.
2. For synthesis of **5**, see: A. K. Chakraborti, L. Sharma and R. Gulhane, *Tetrahedron*, 2003, **59**, 7661.
3. For the judgement of Z/E isomer of **6**, see: C. A. Witham, P. Mauleon, N. D. Shapiro, B. D. Sherry and F. D. Toste, *J. Am. Chem. Soc*., 2007, **129**, 5838.

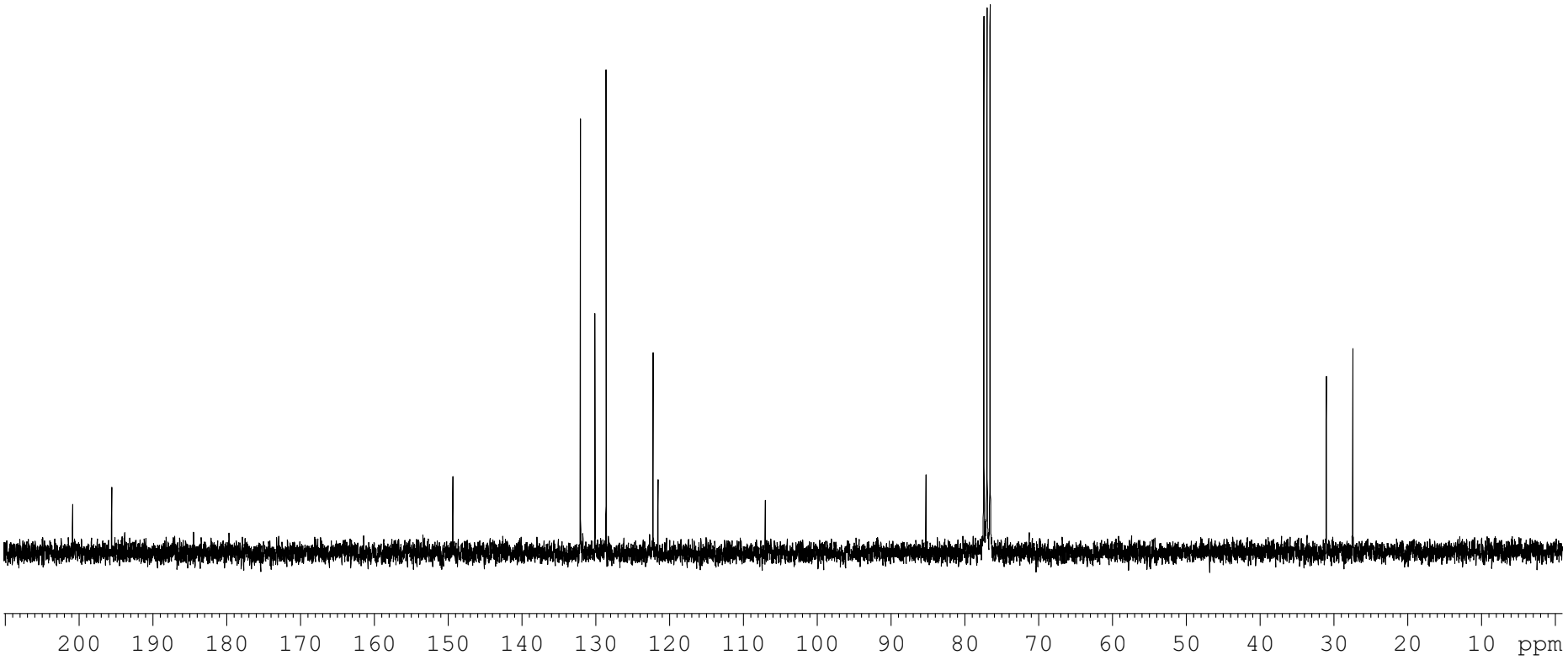


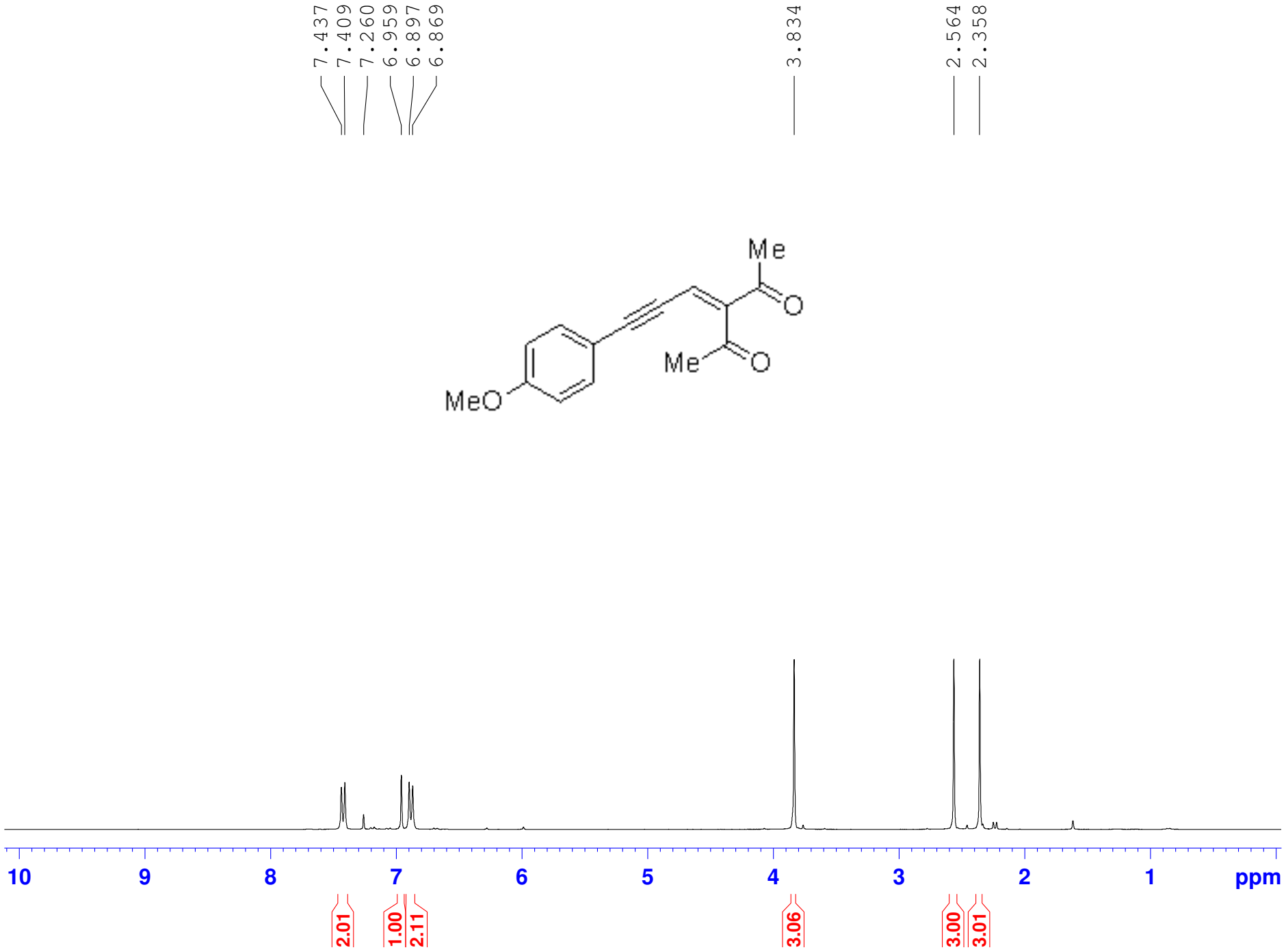


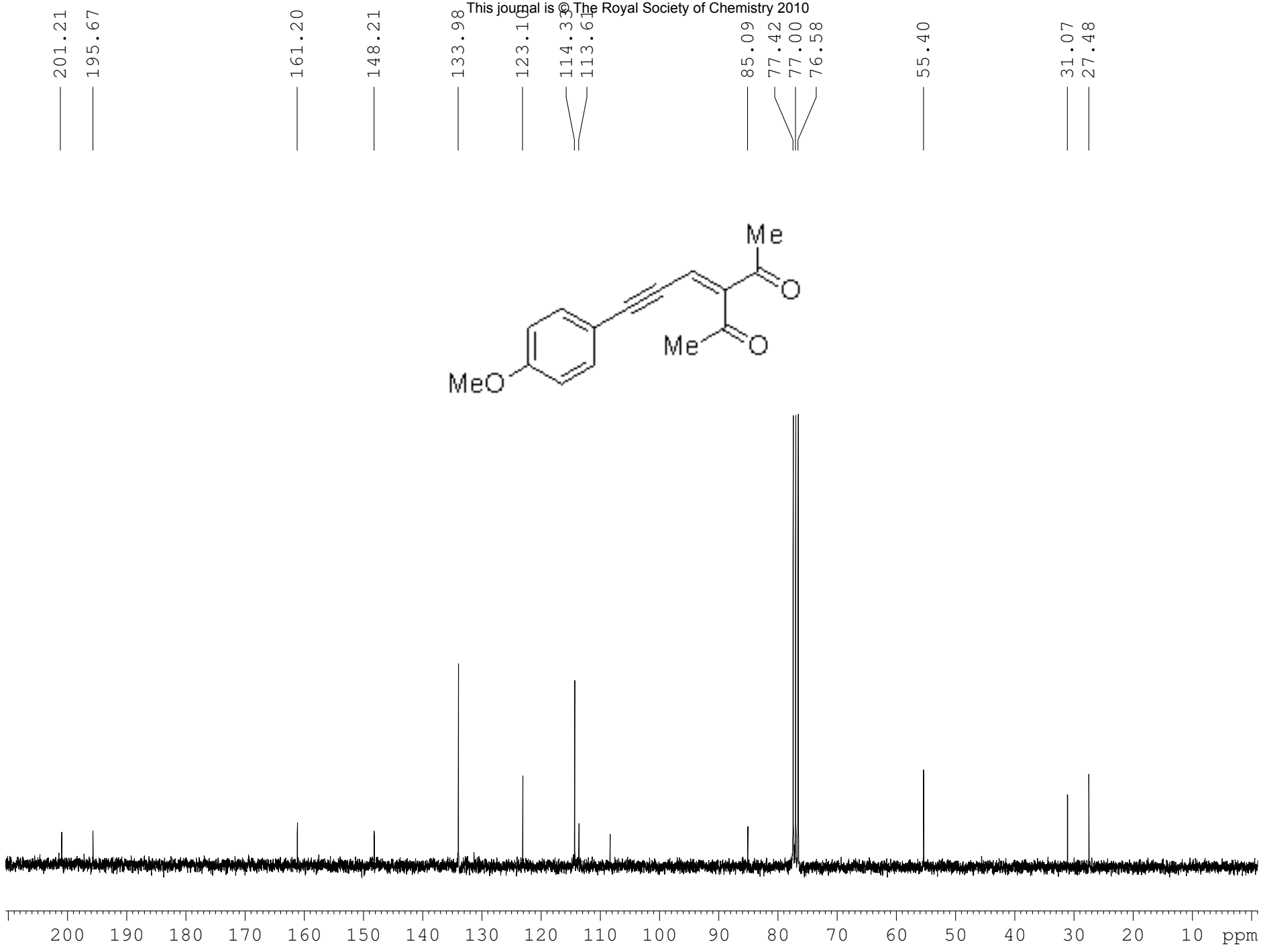


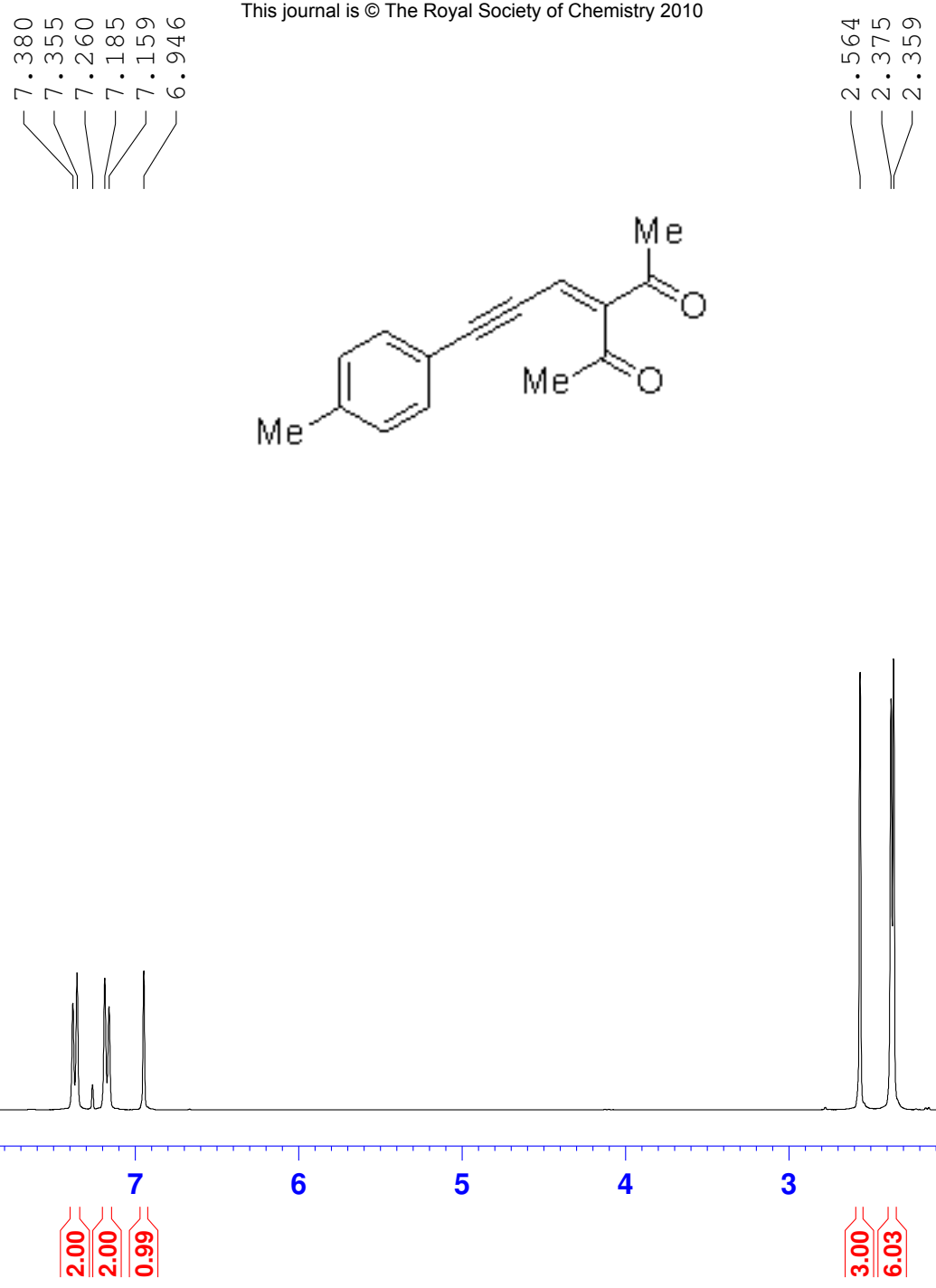


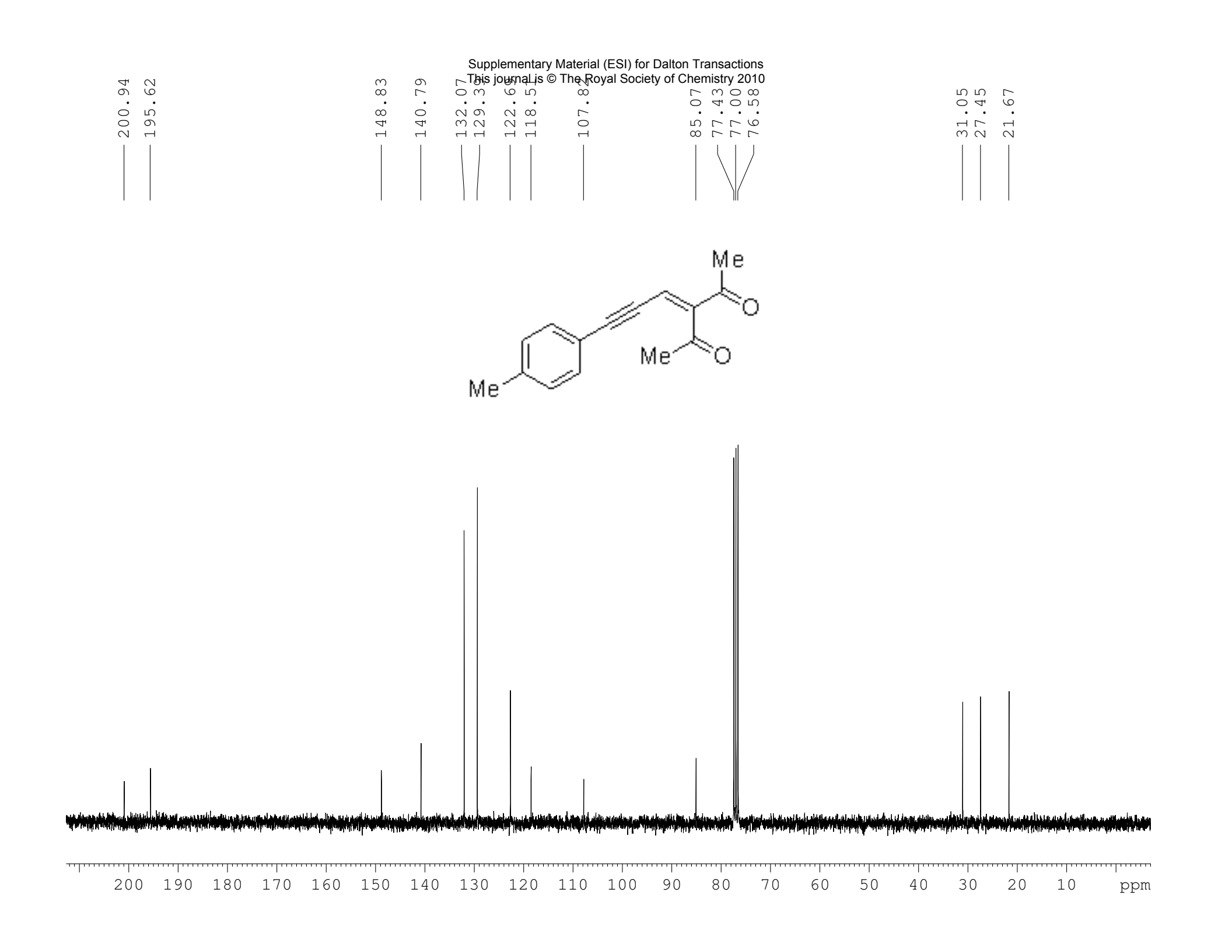


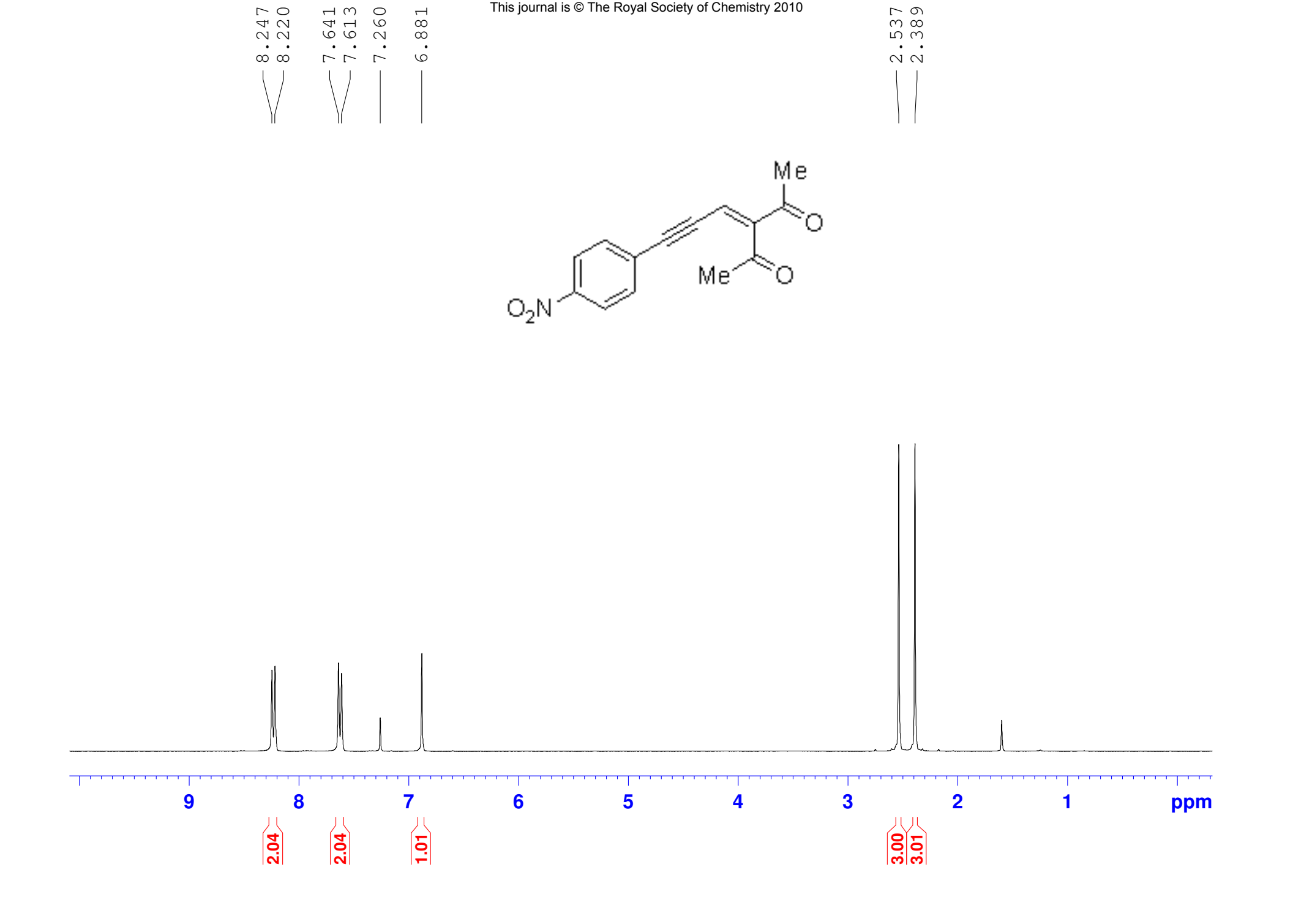


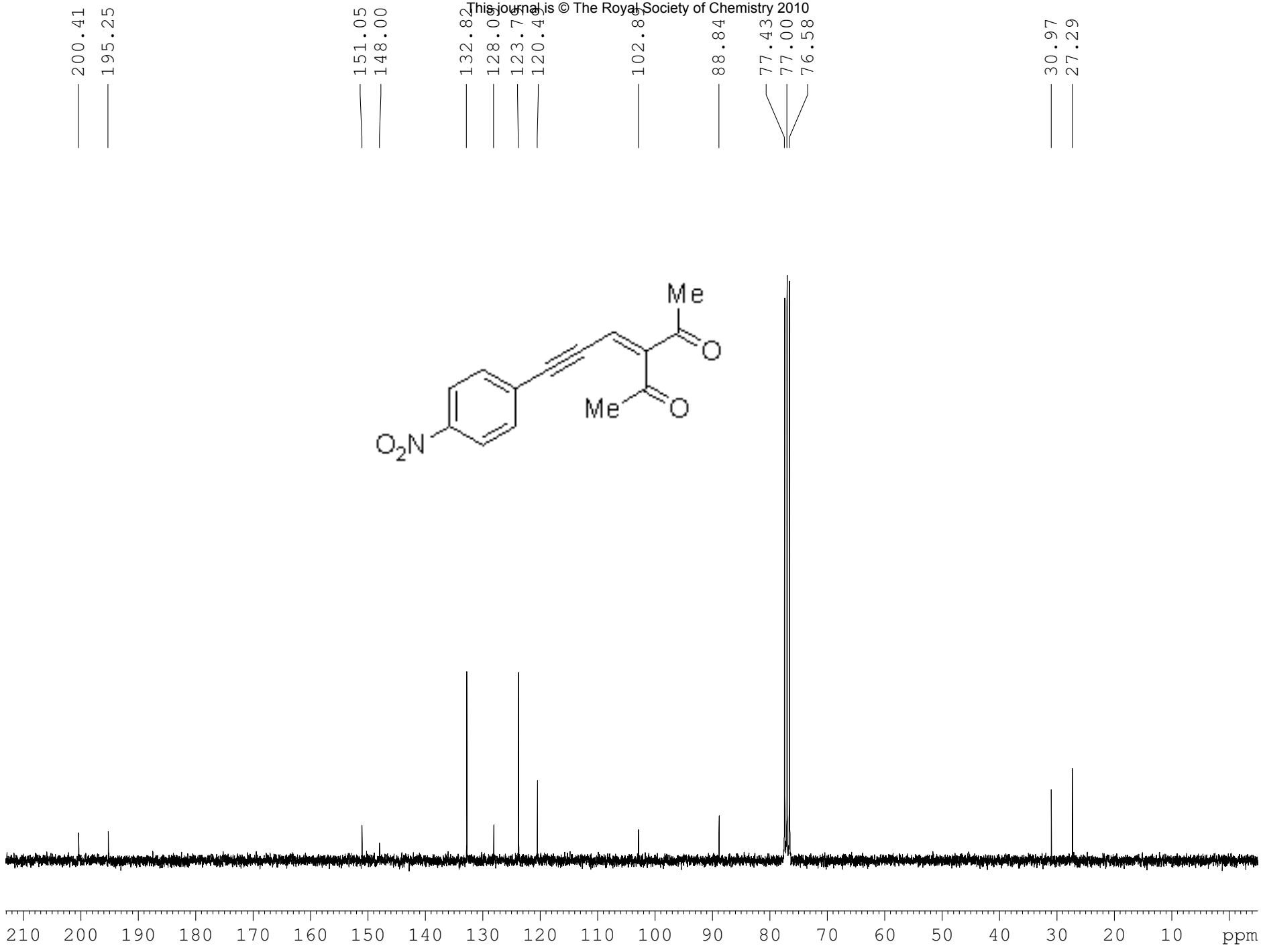


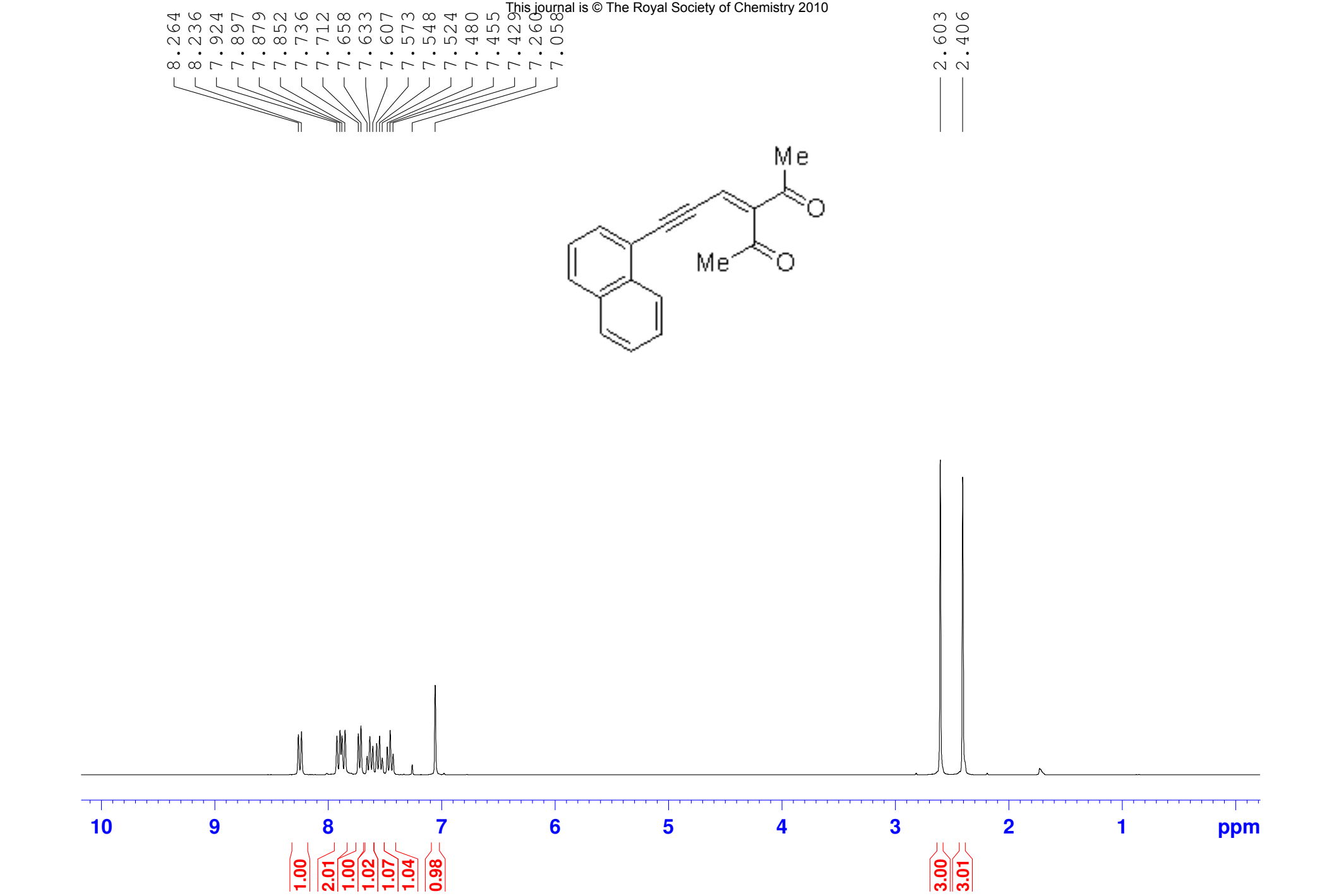


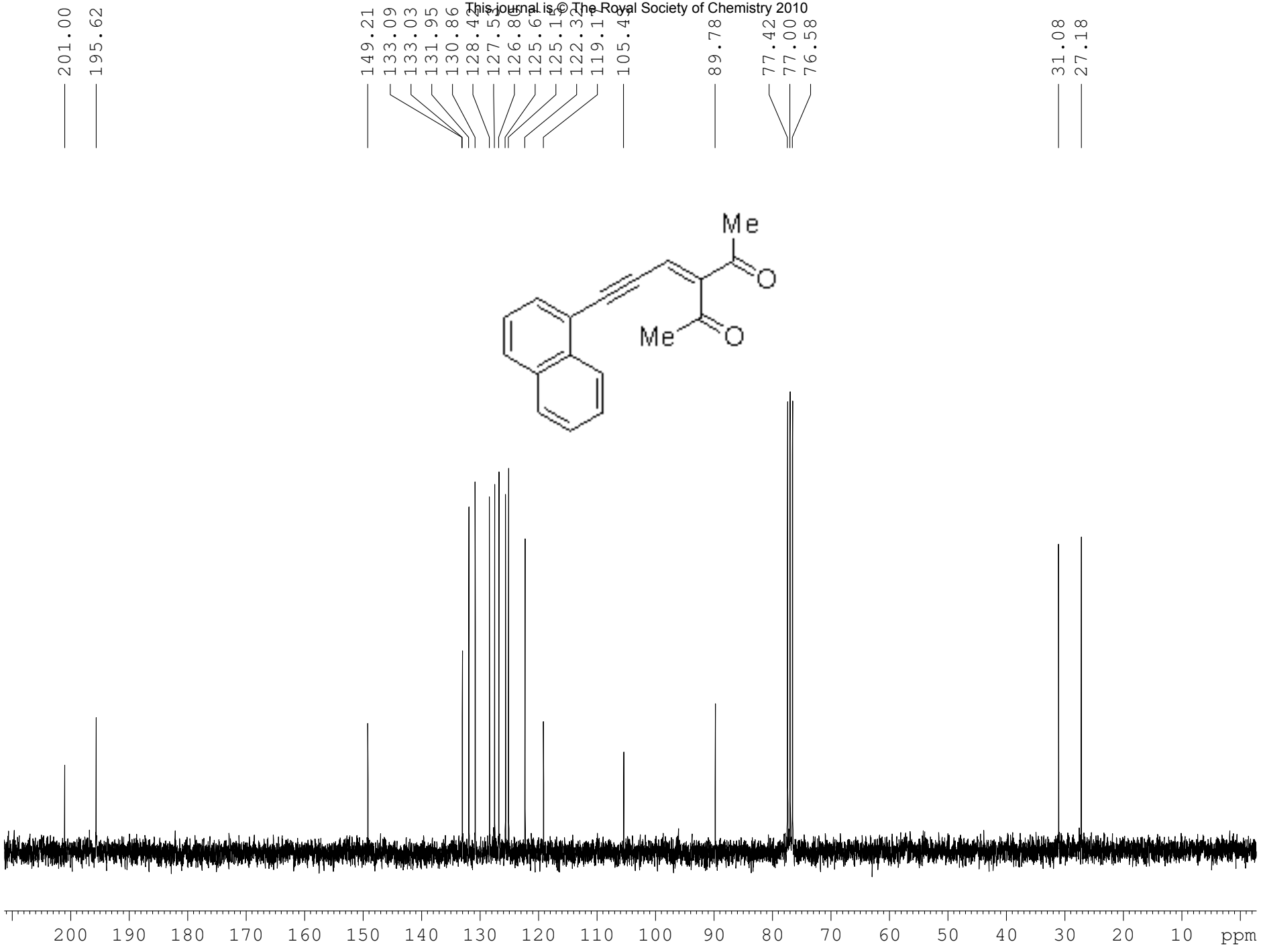


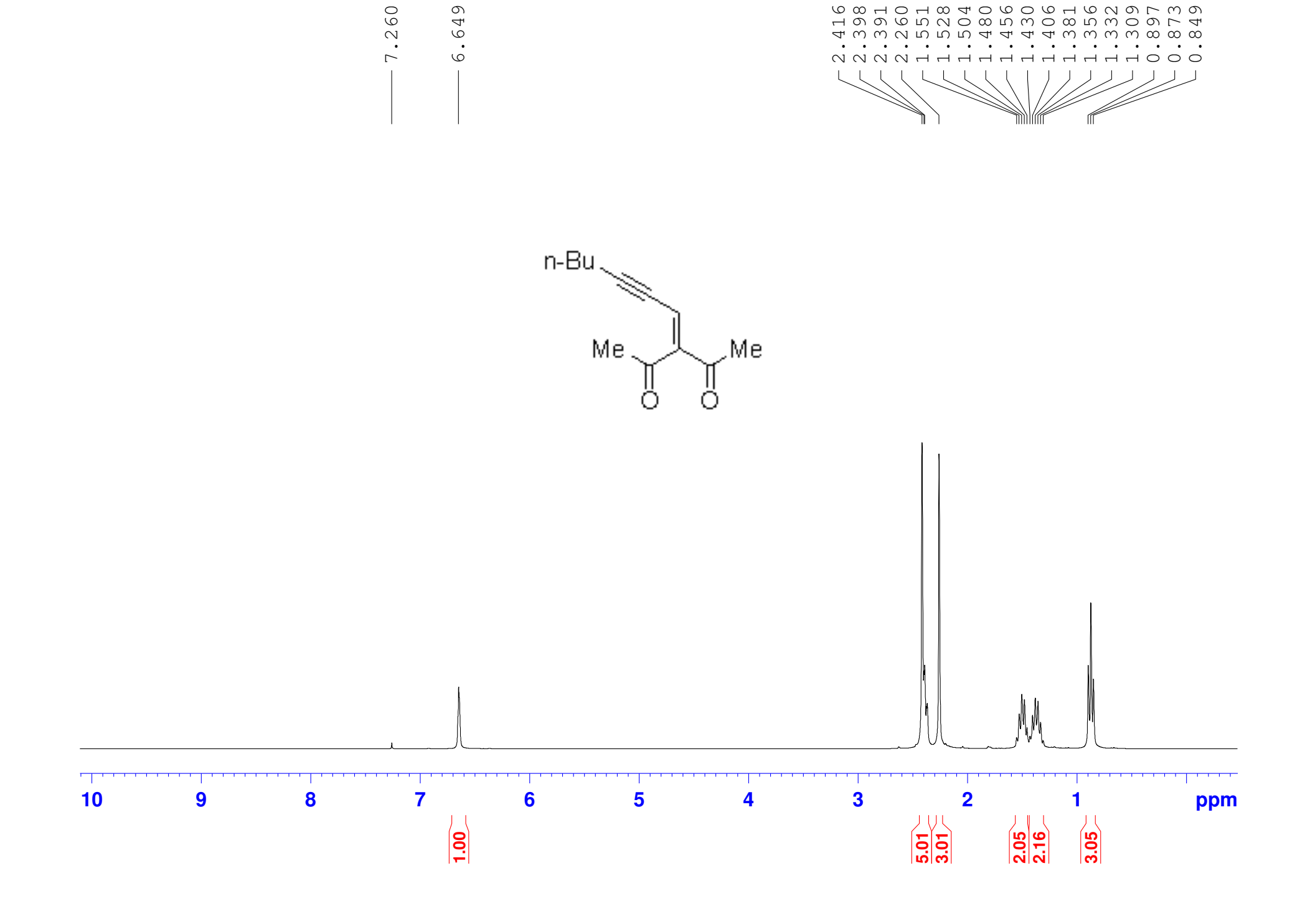


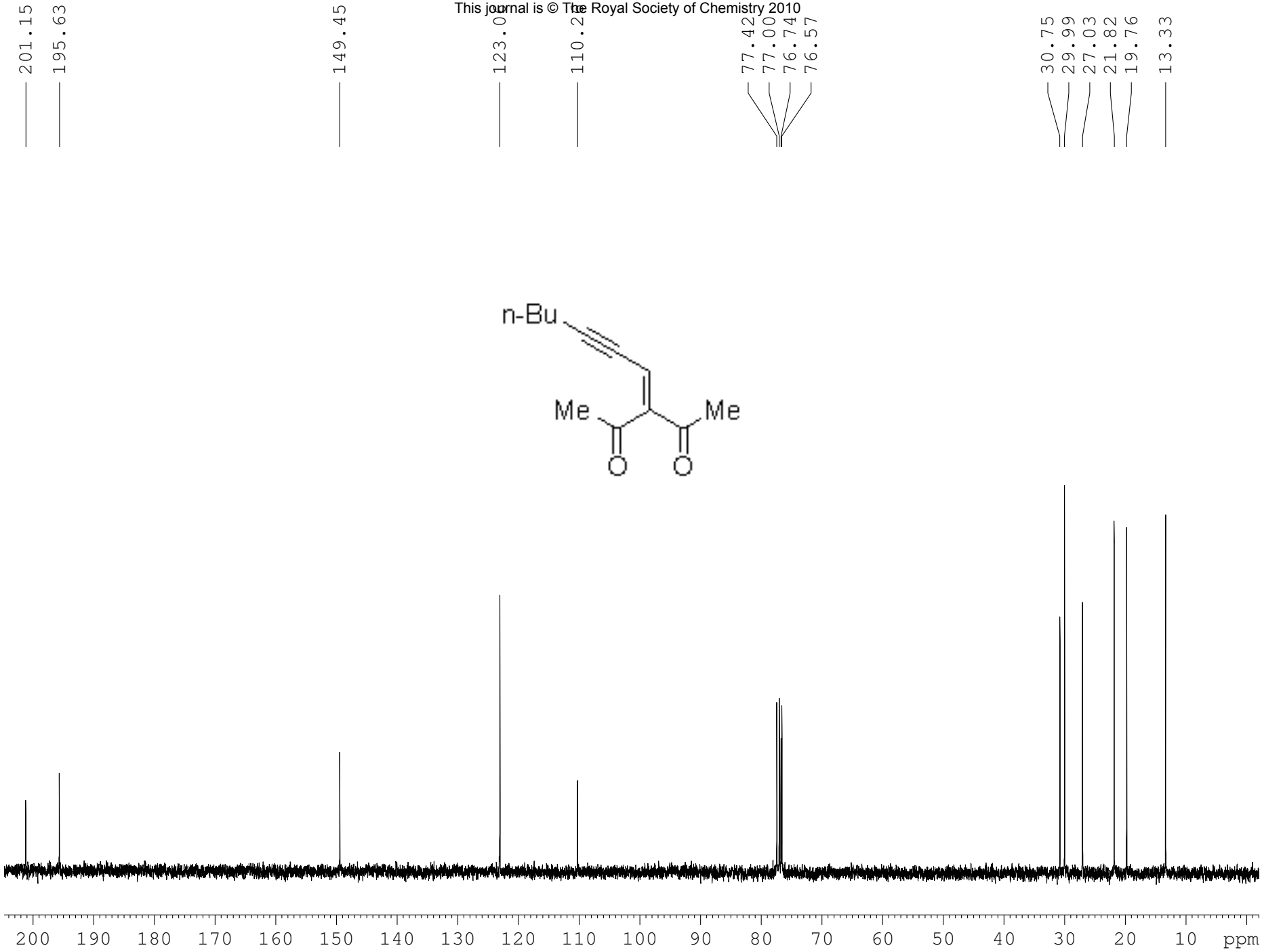


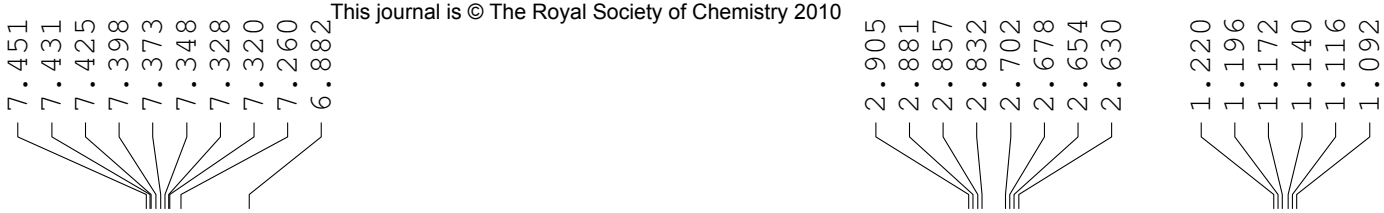


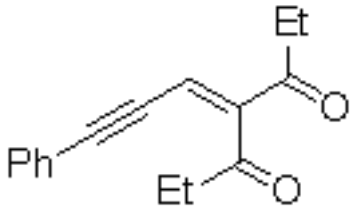


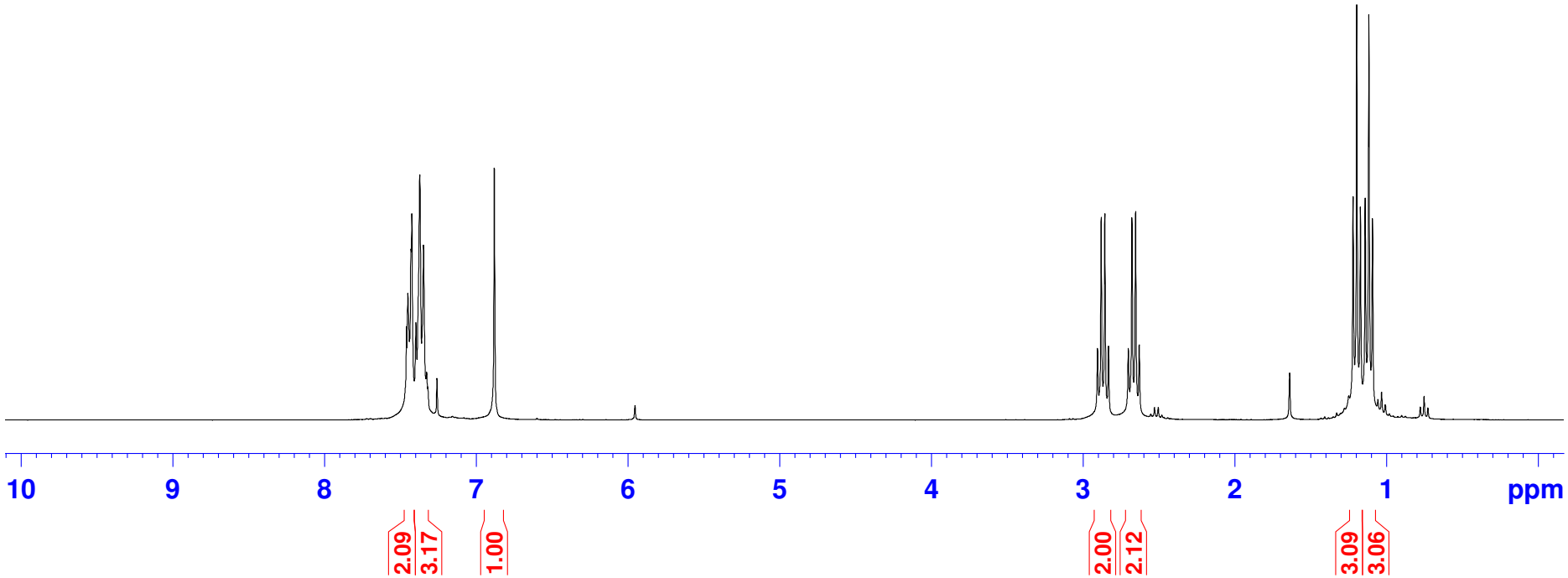


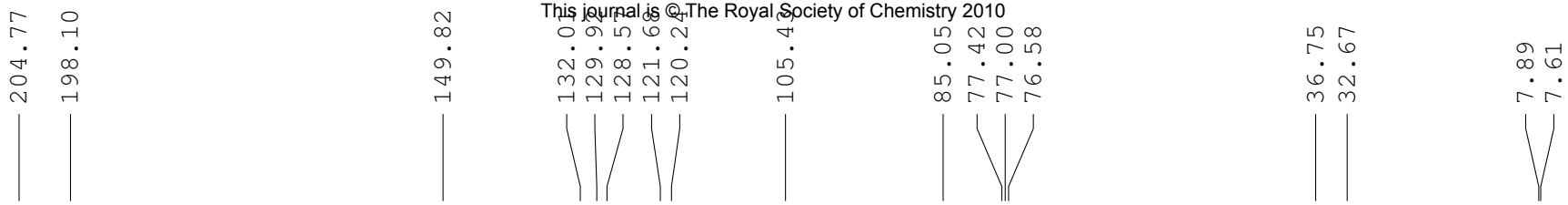


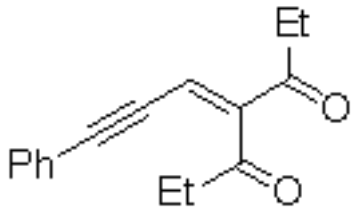


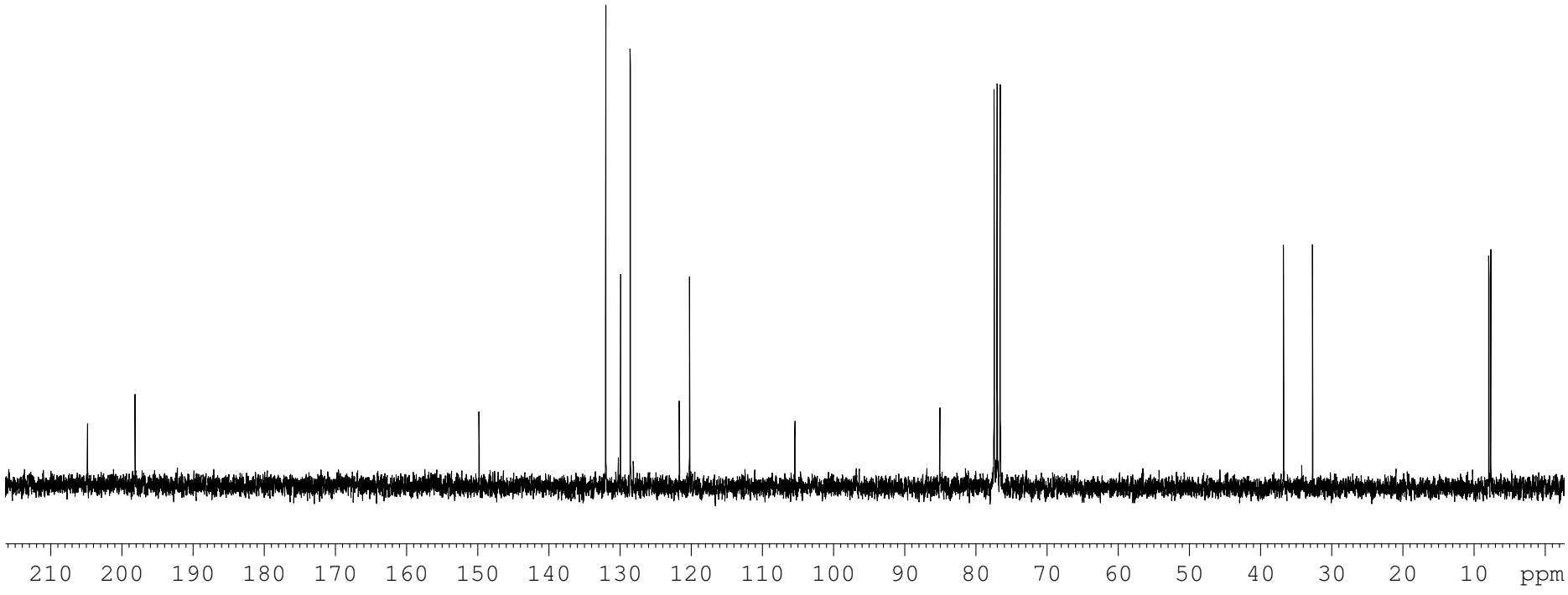


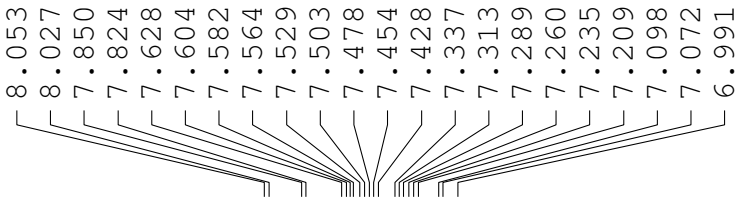


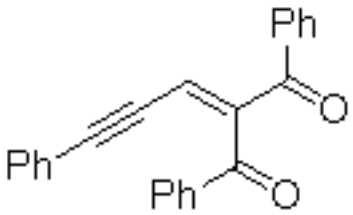


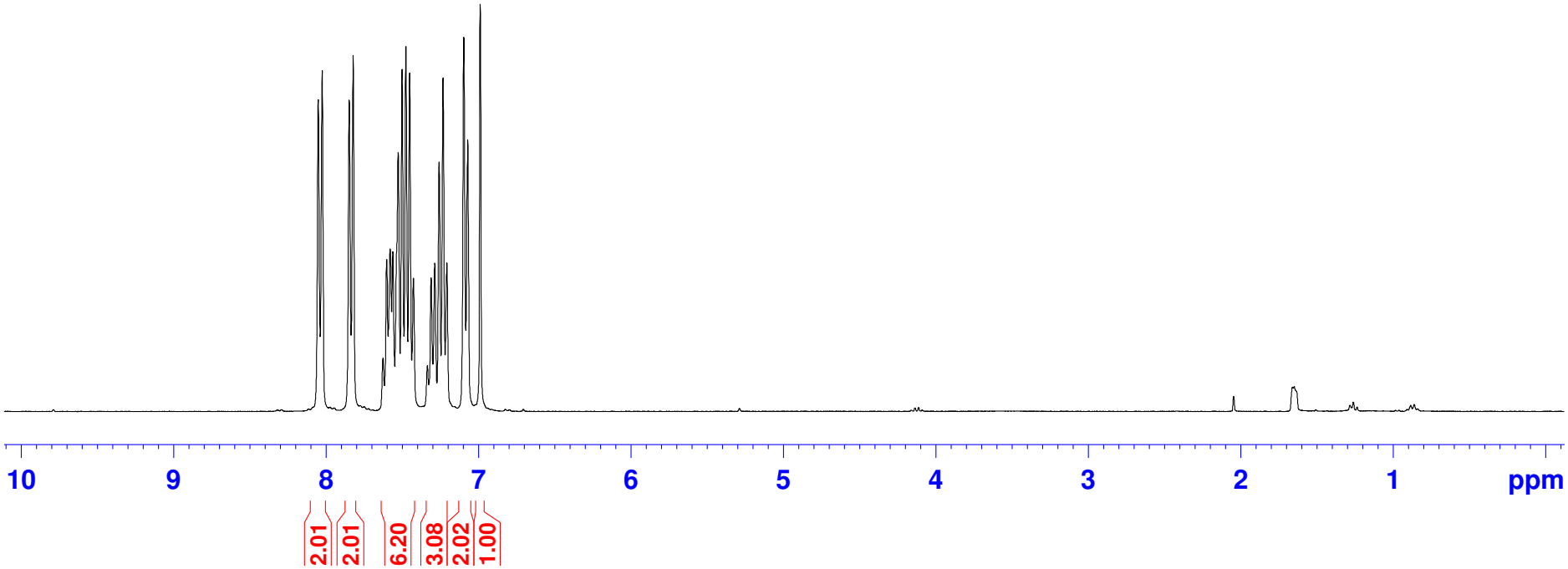












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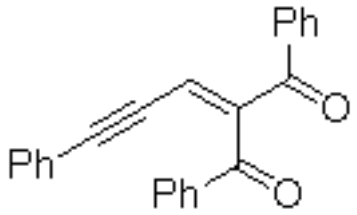

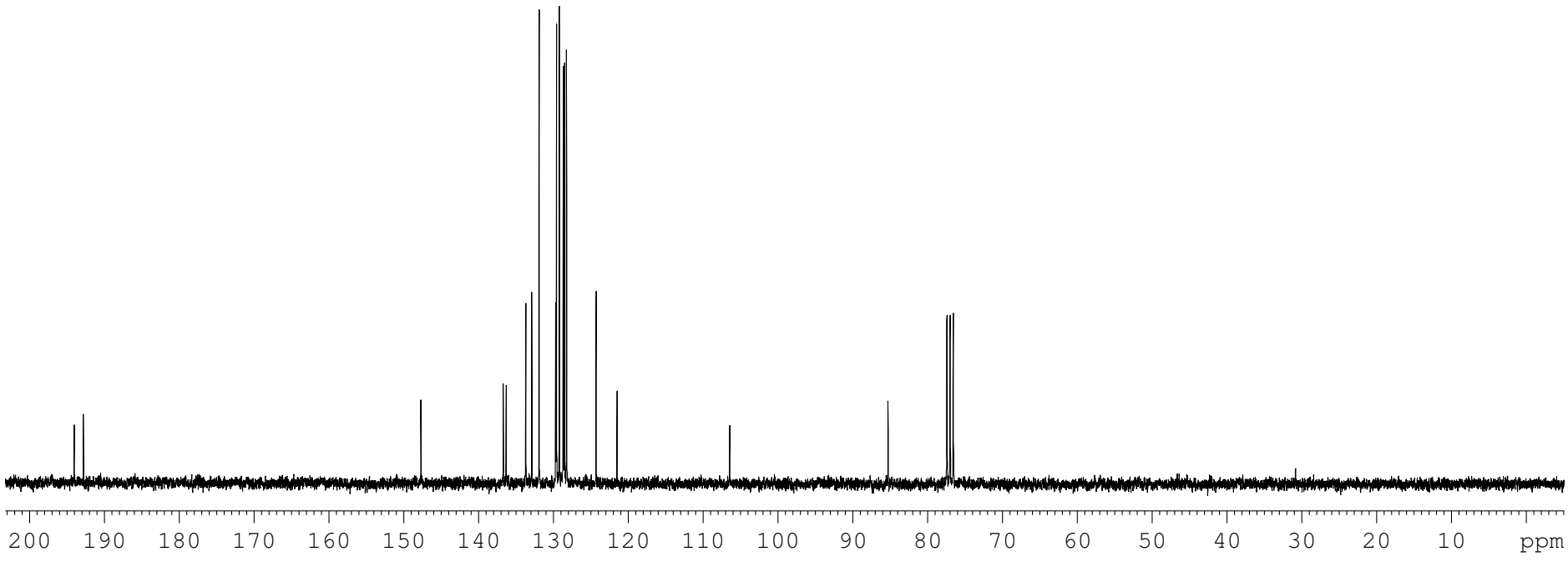

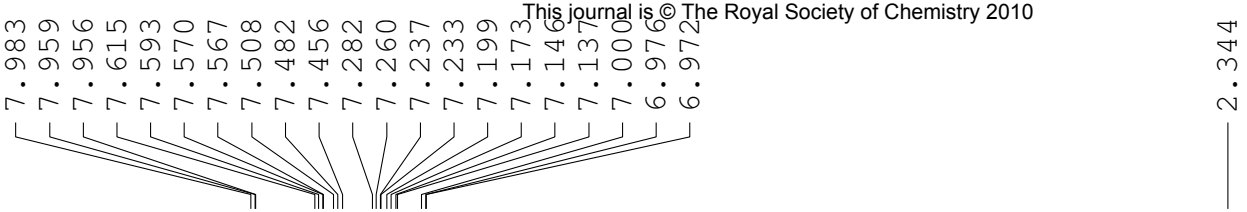

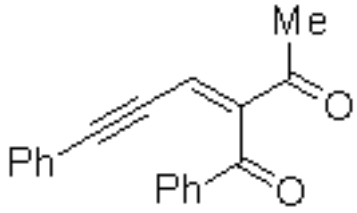

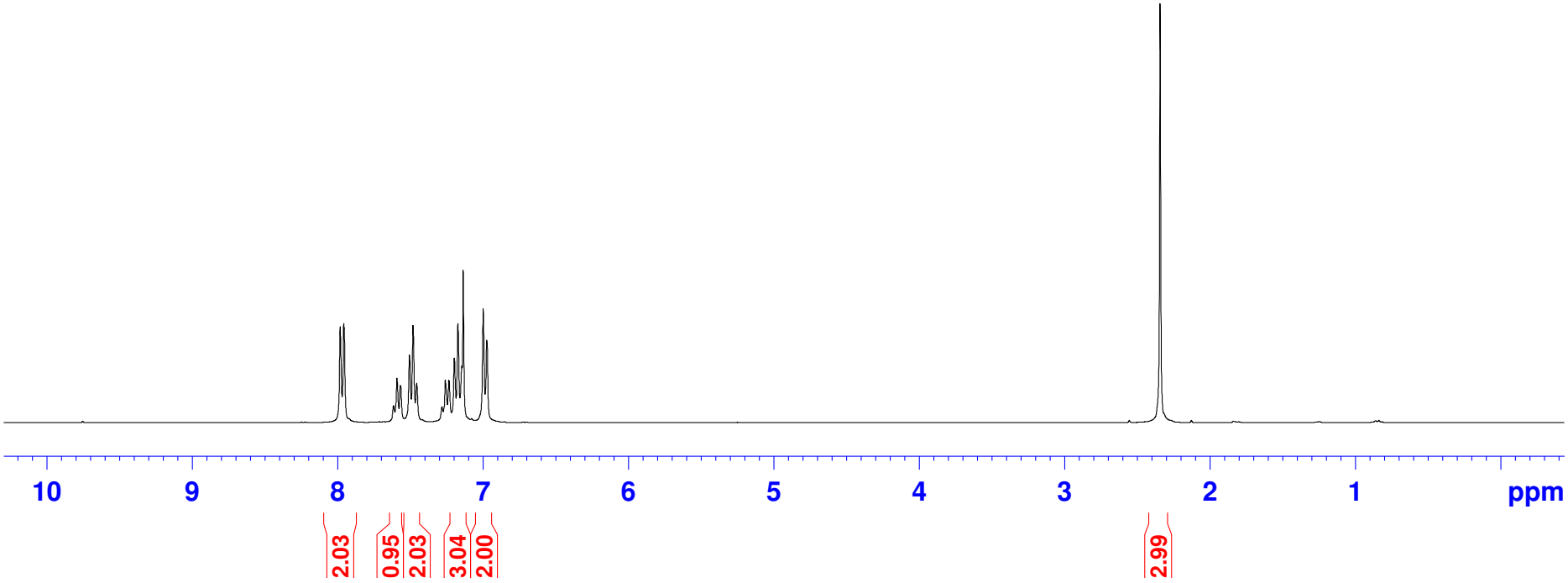

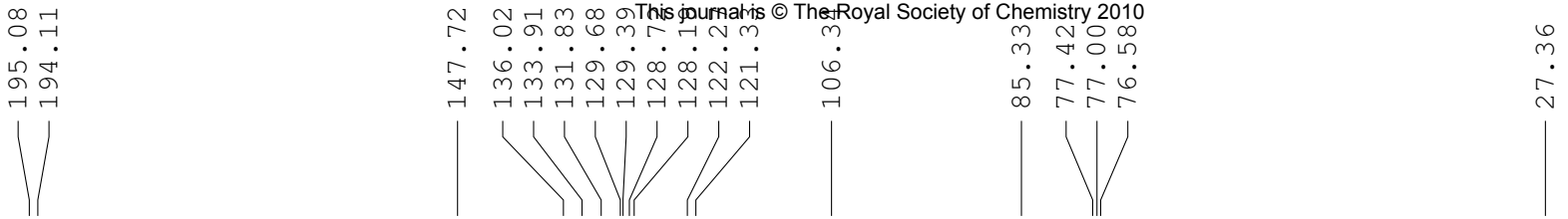

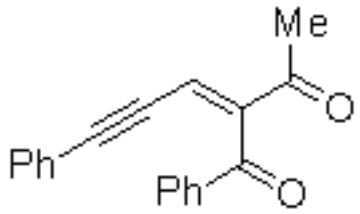

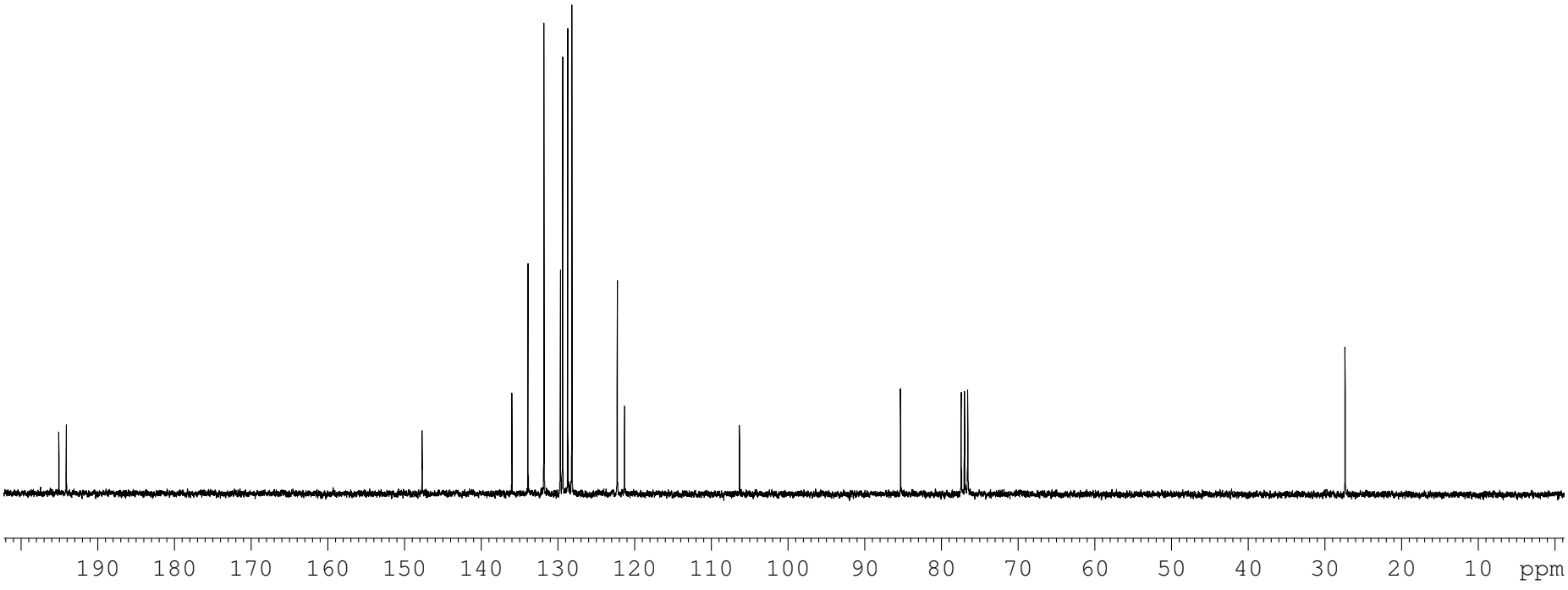

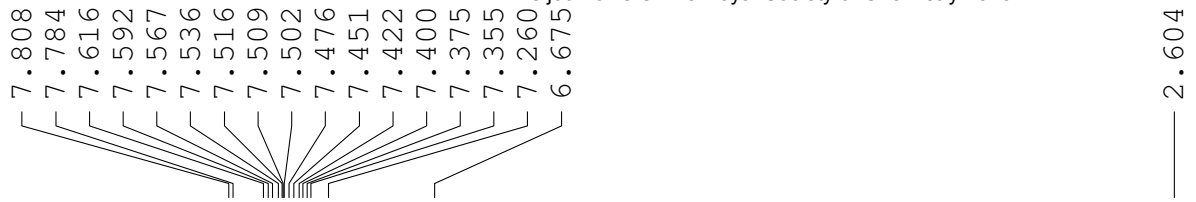

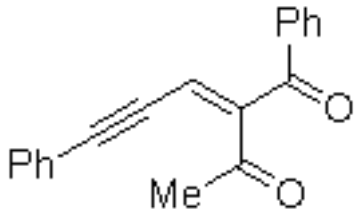

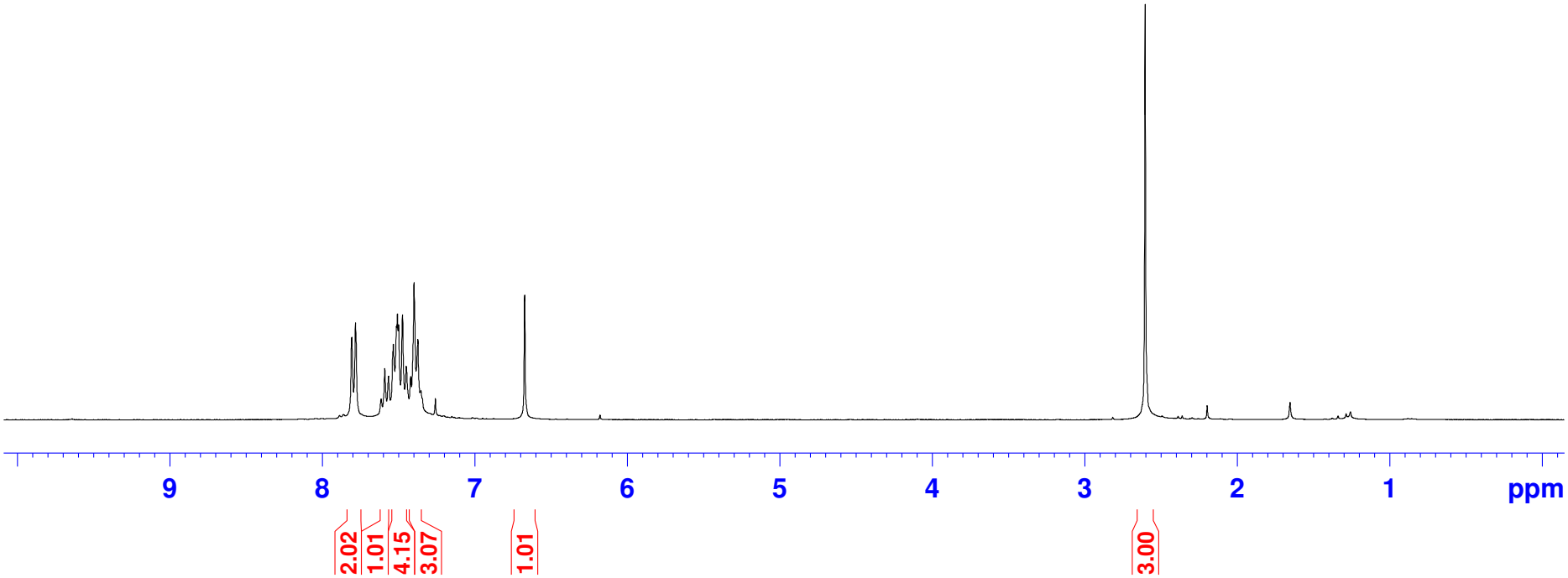

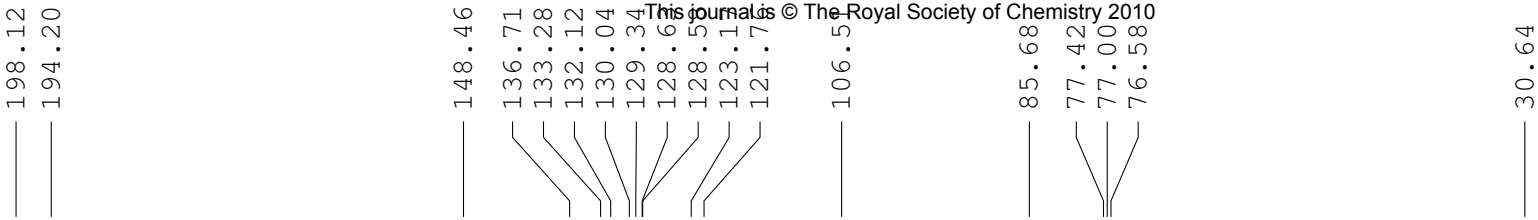

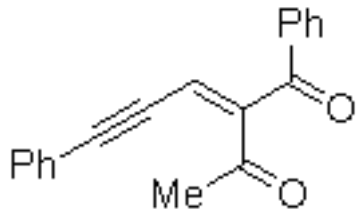

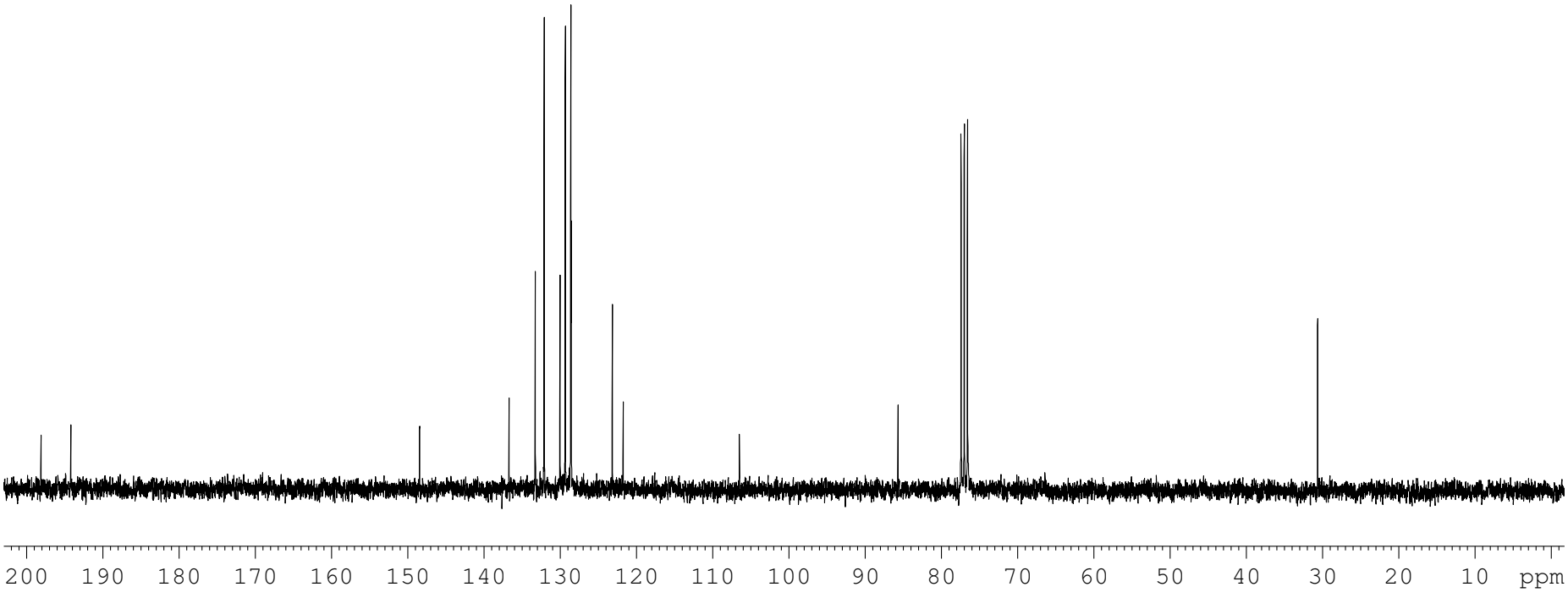

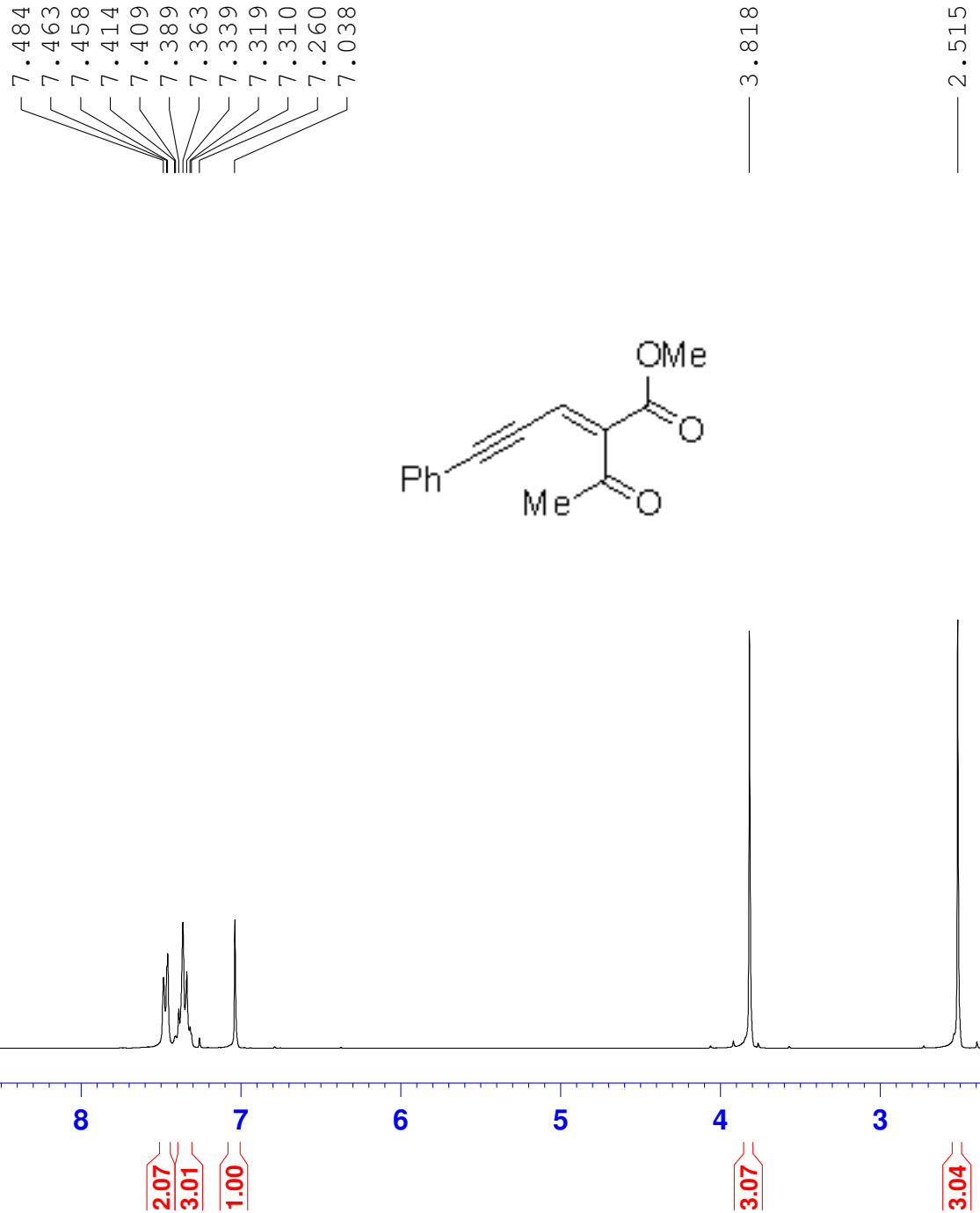

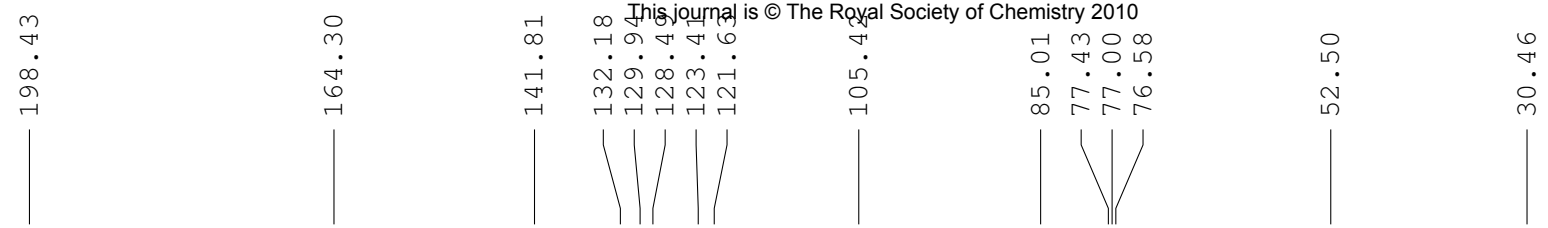

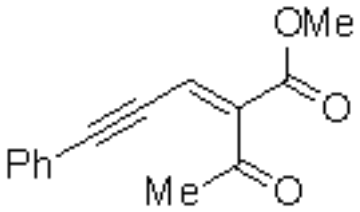

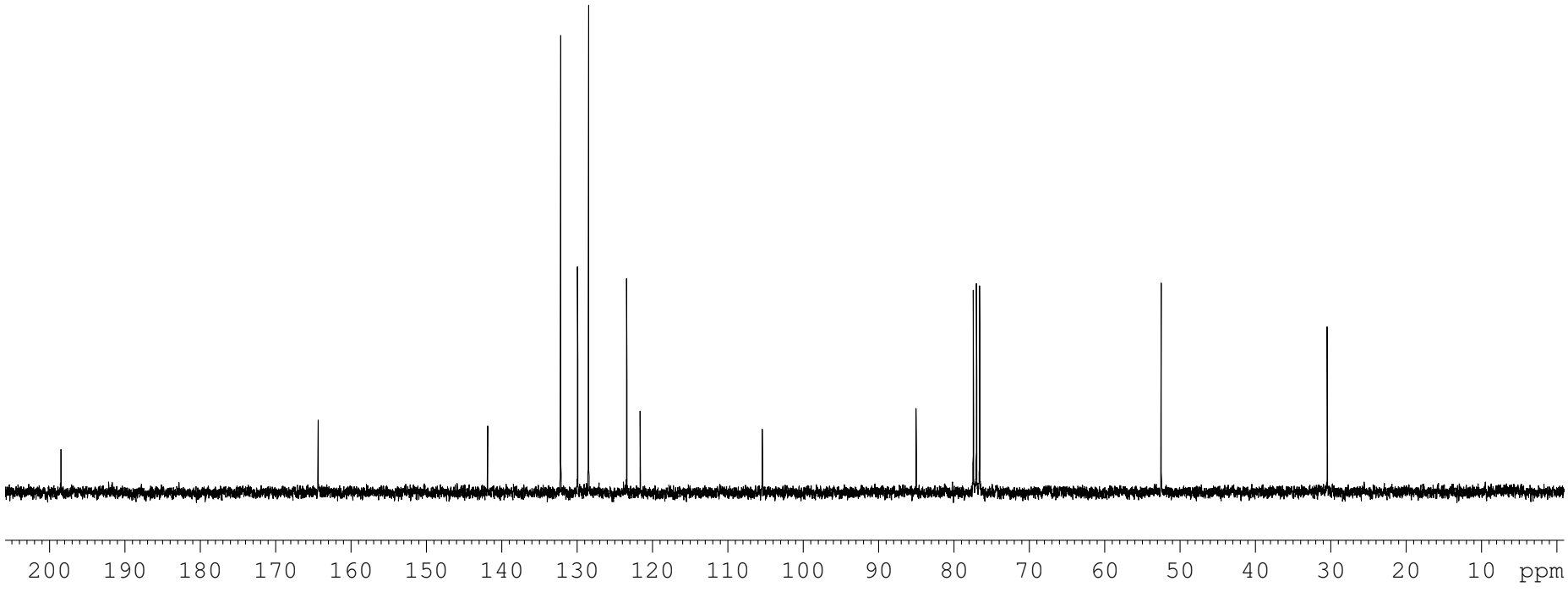

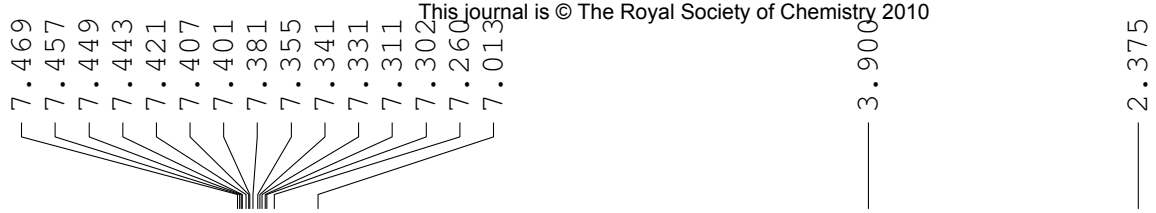

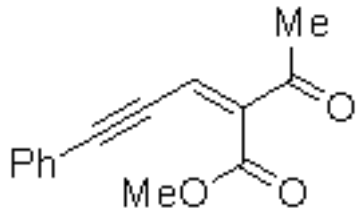

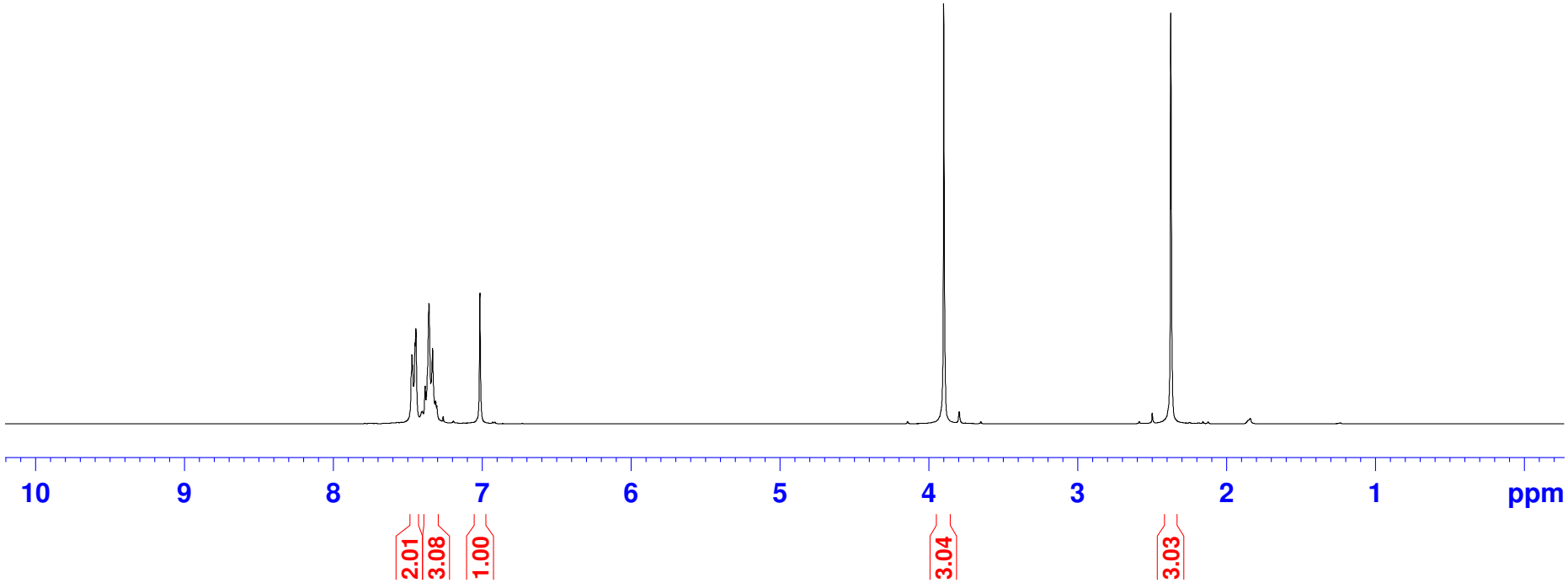

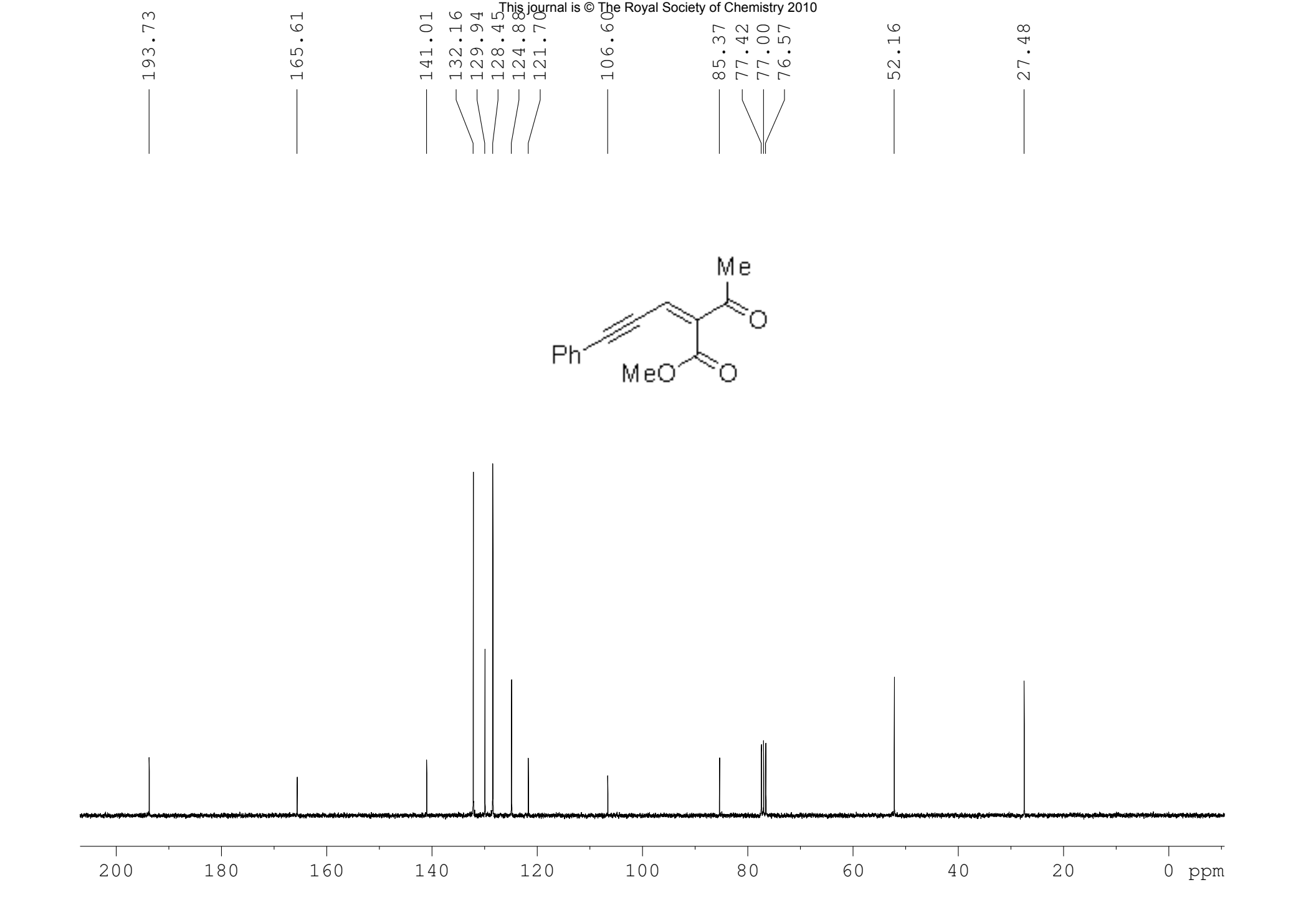

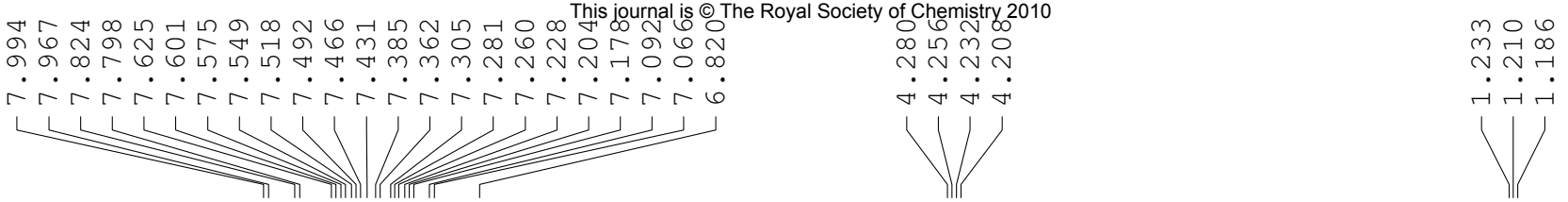

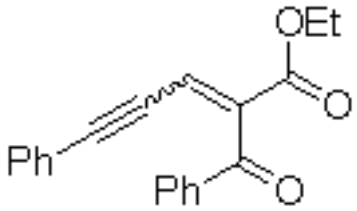

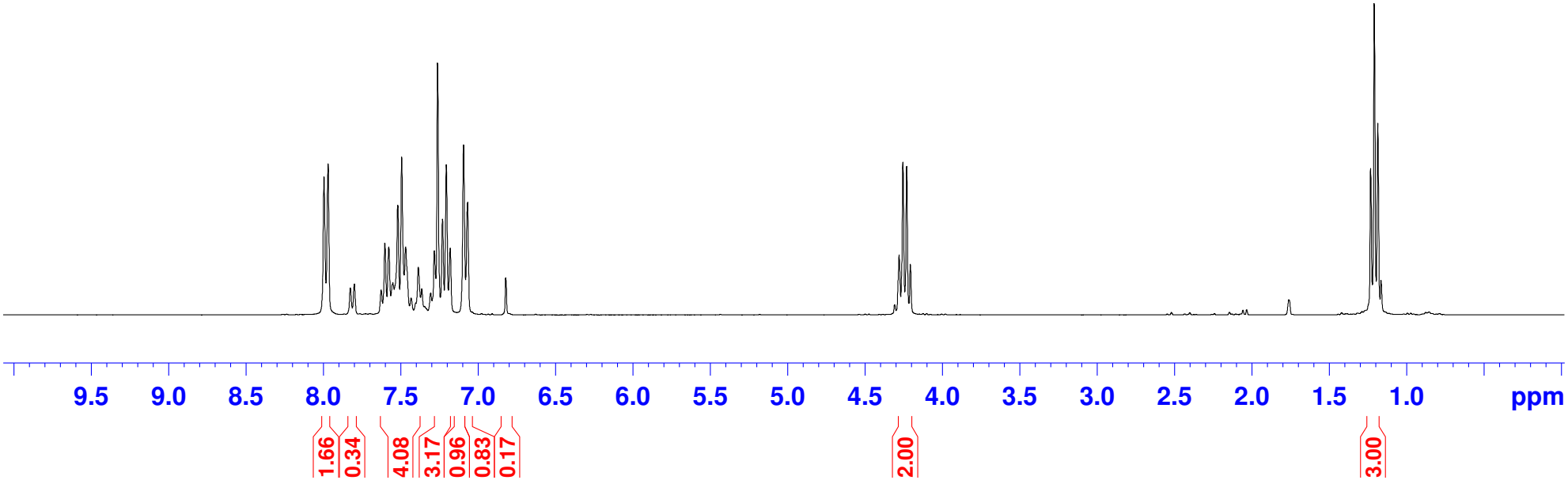

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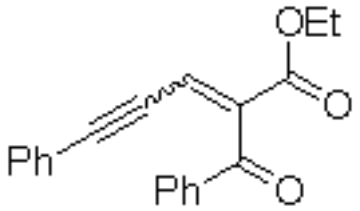

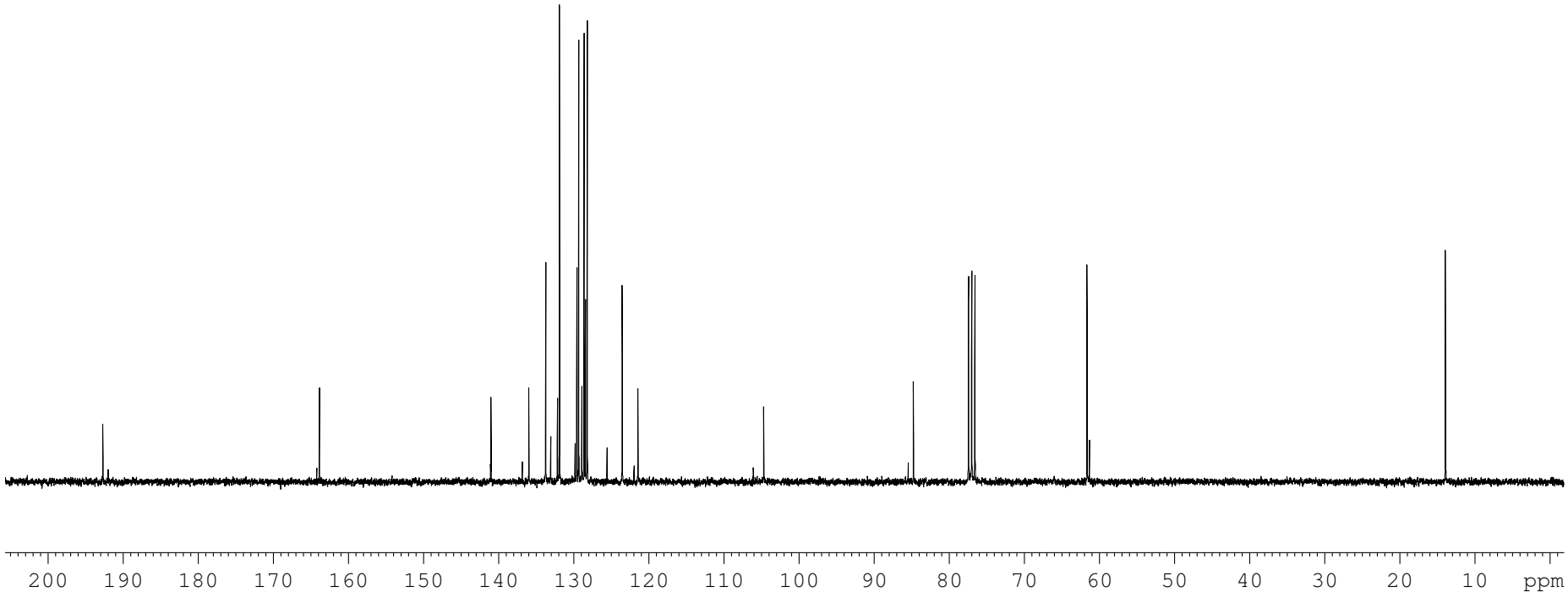

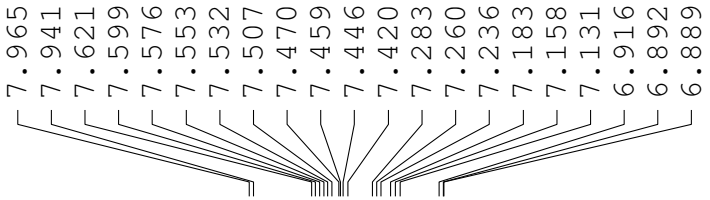

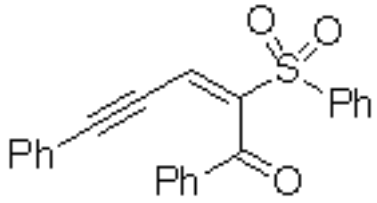

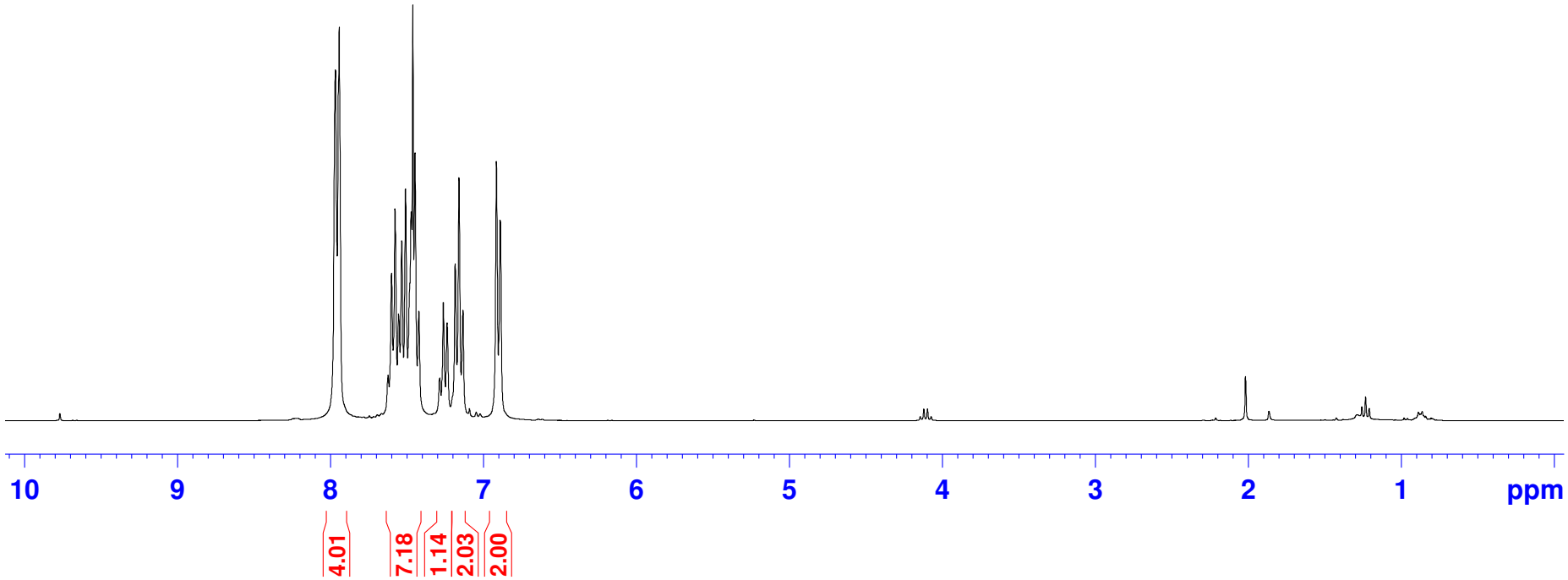

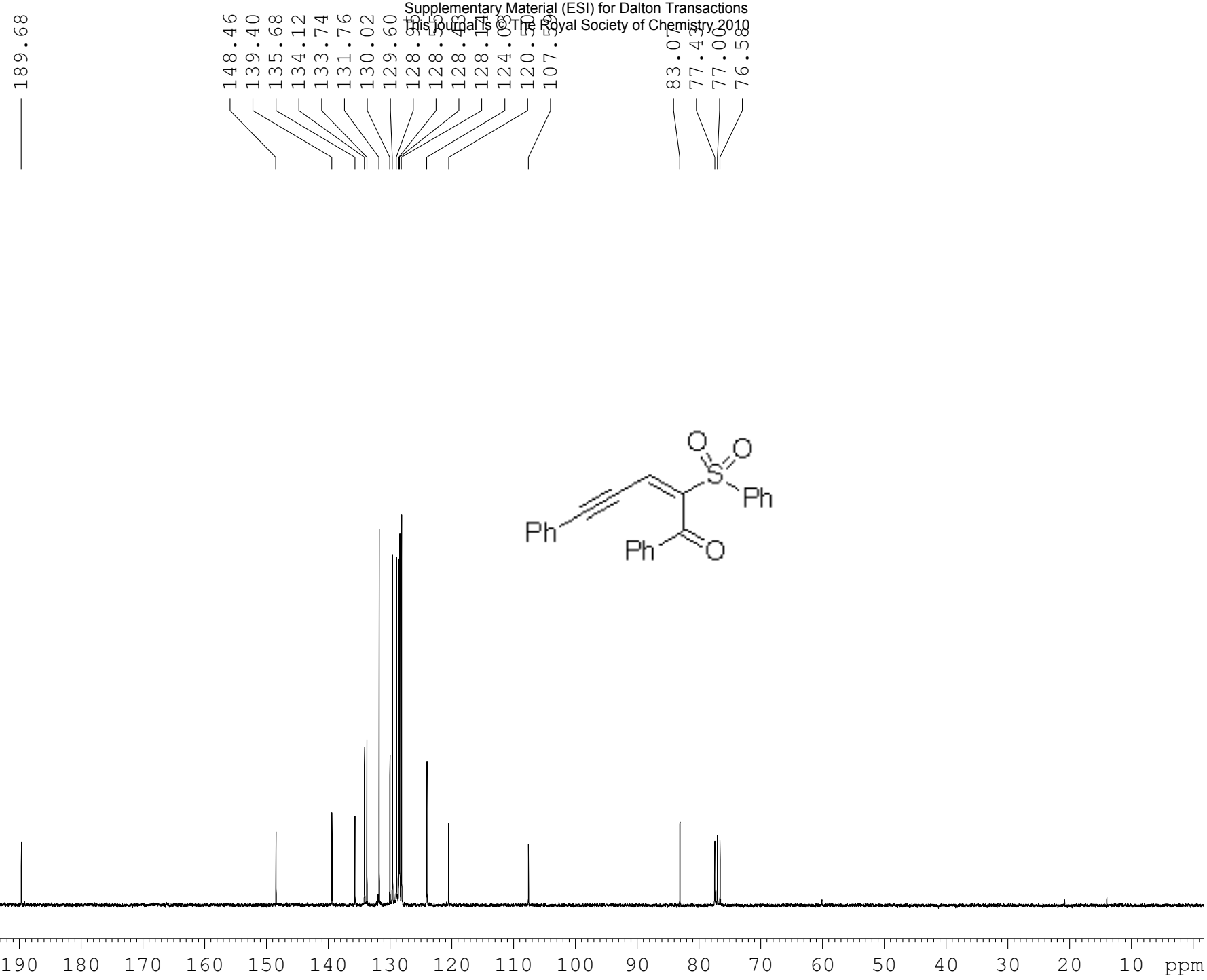

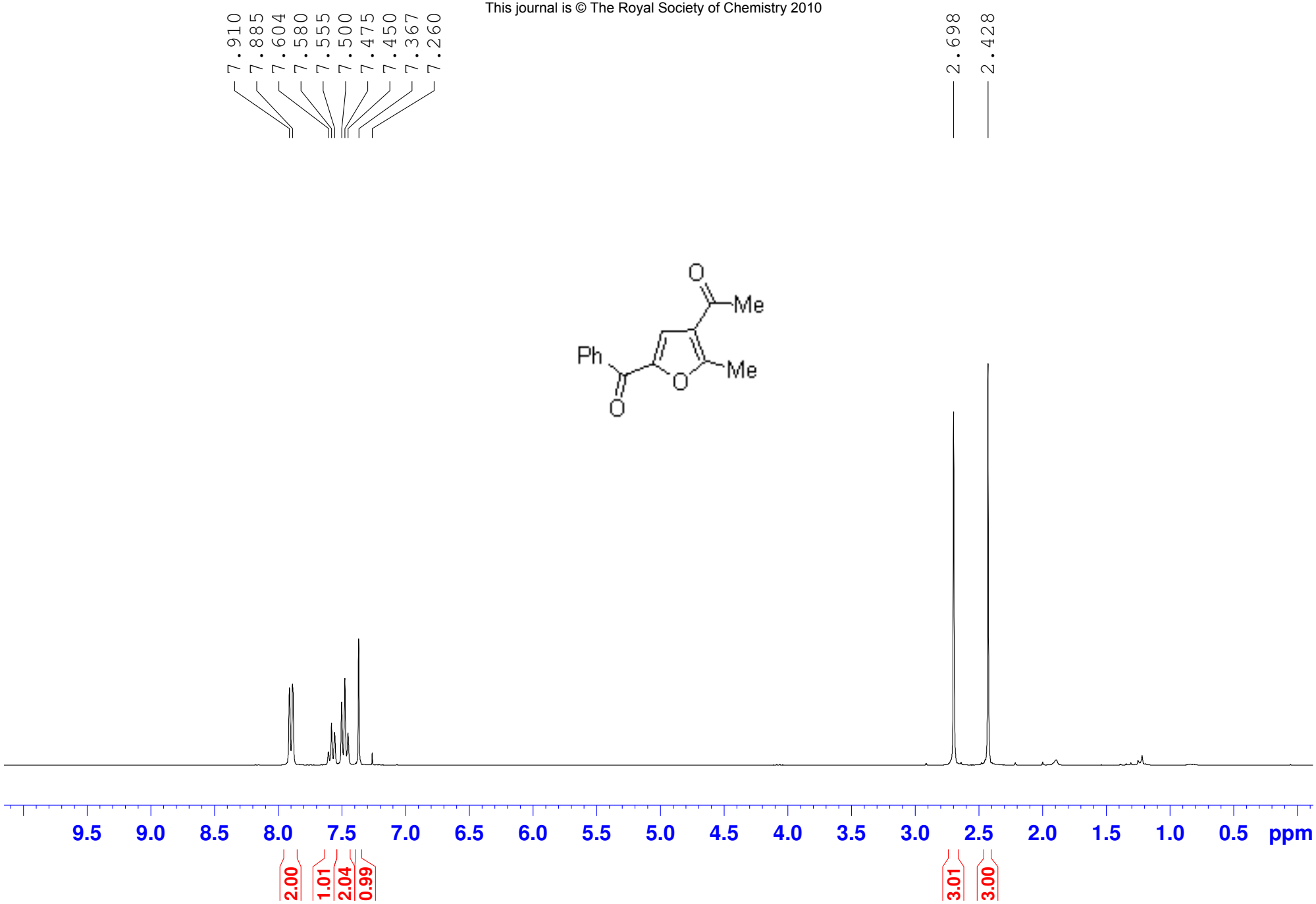

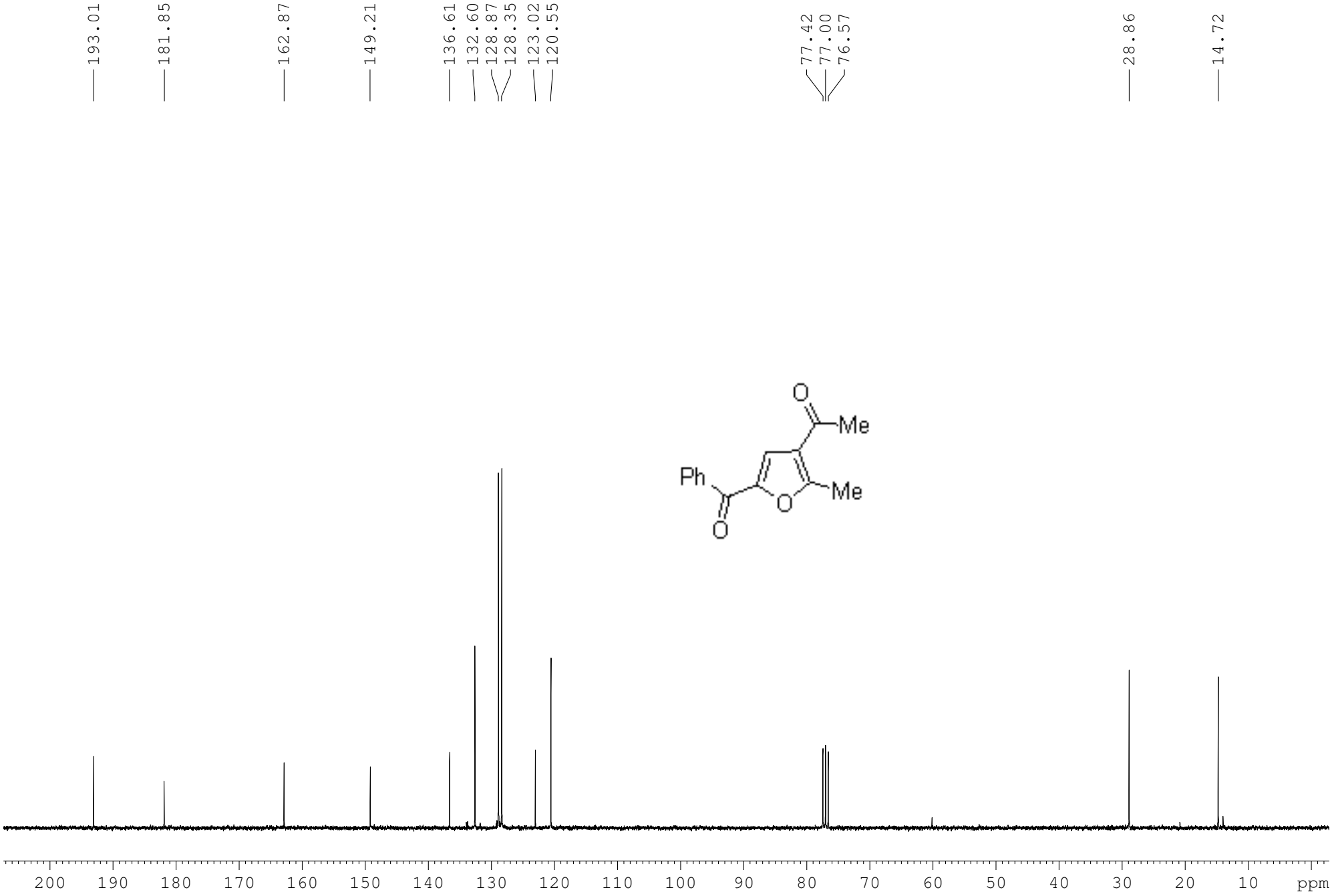

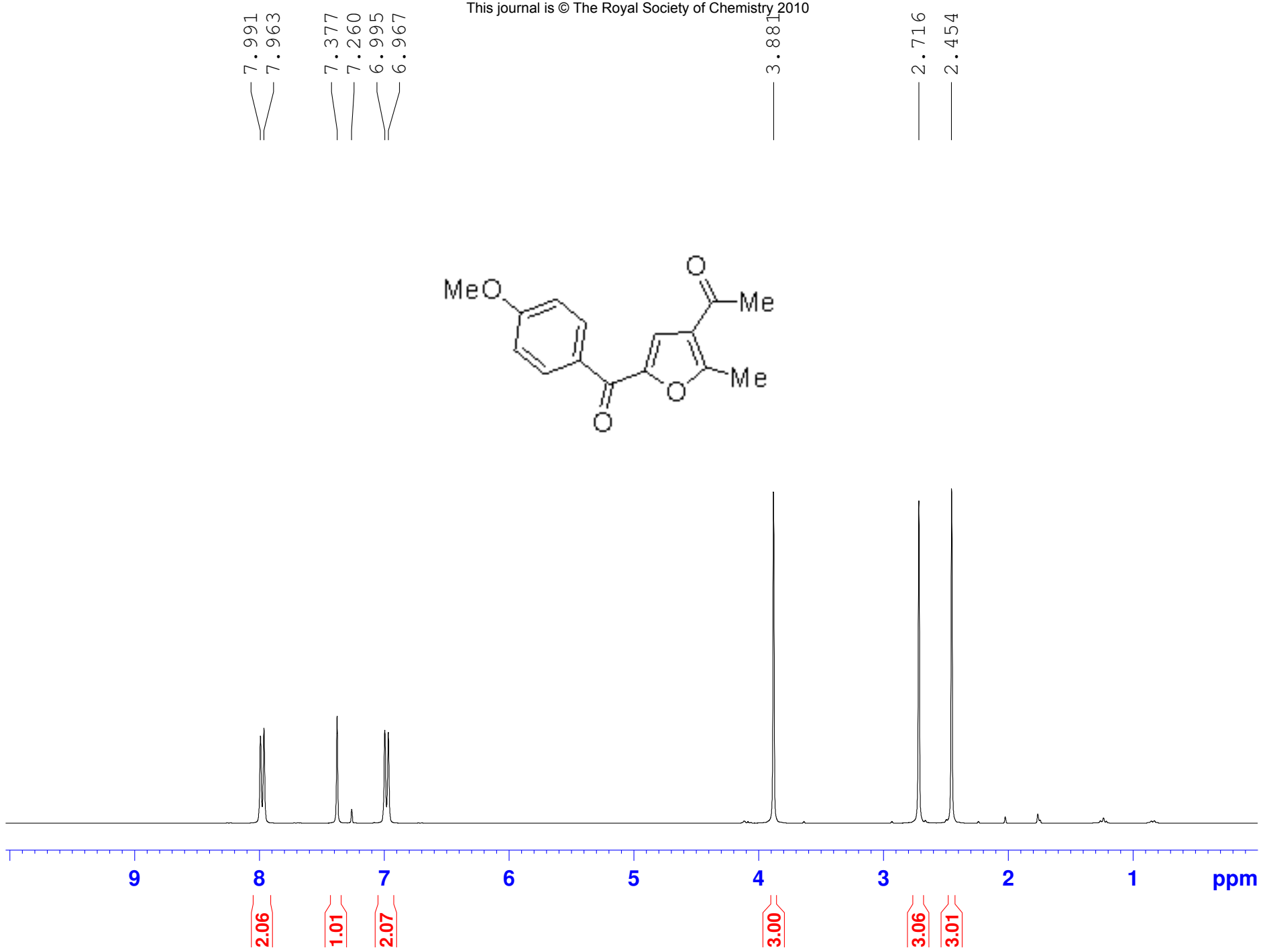

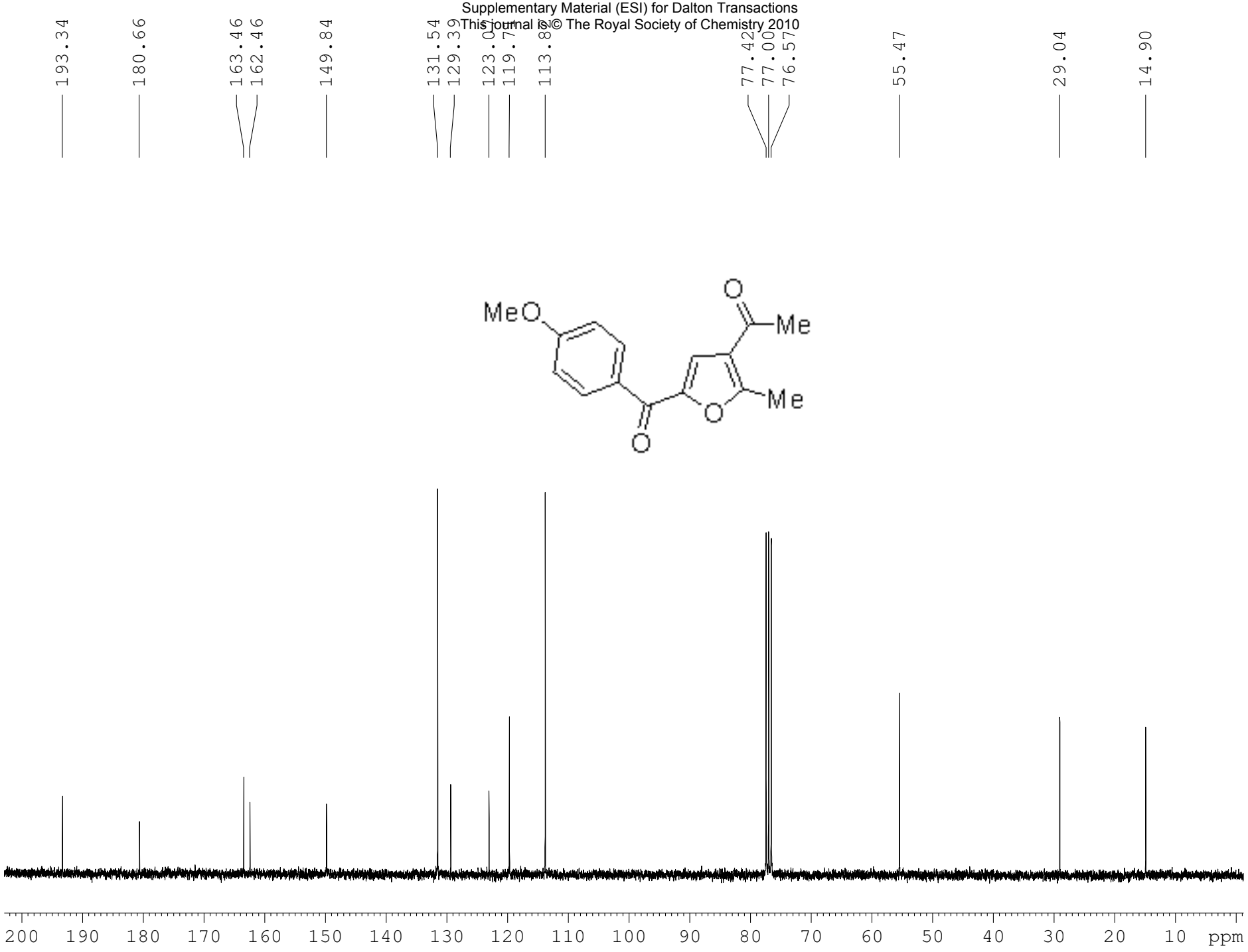

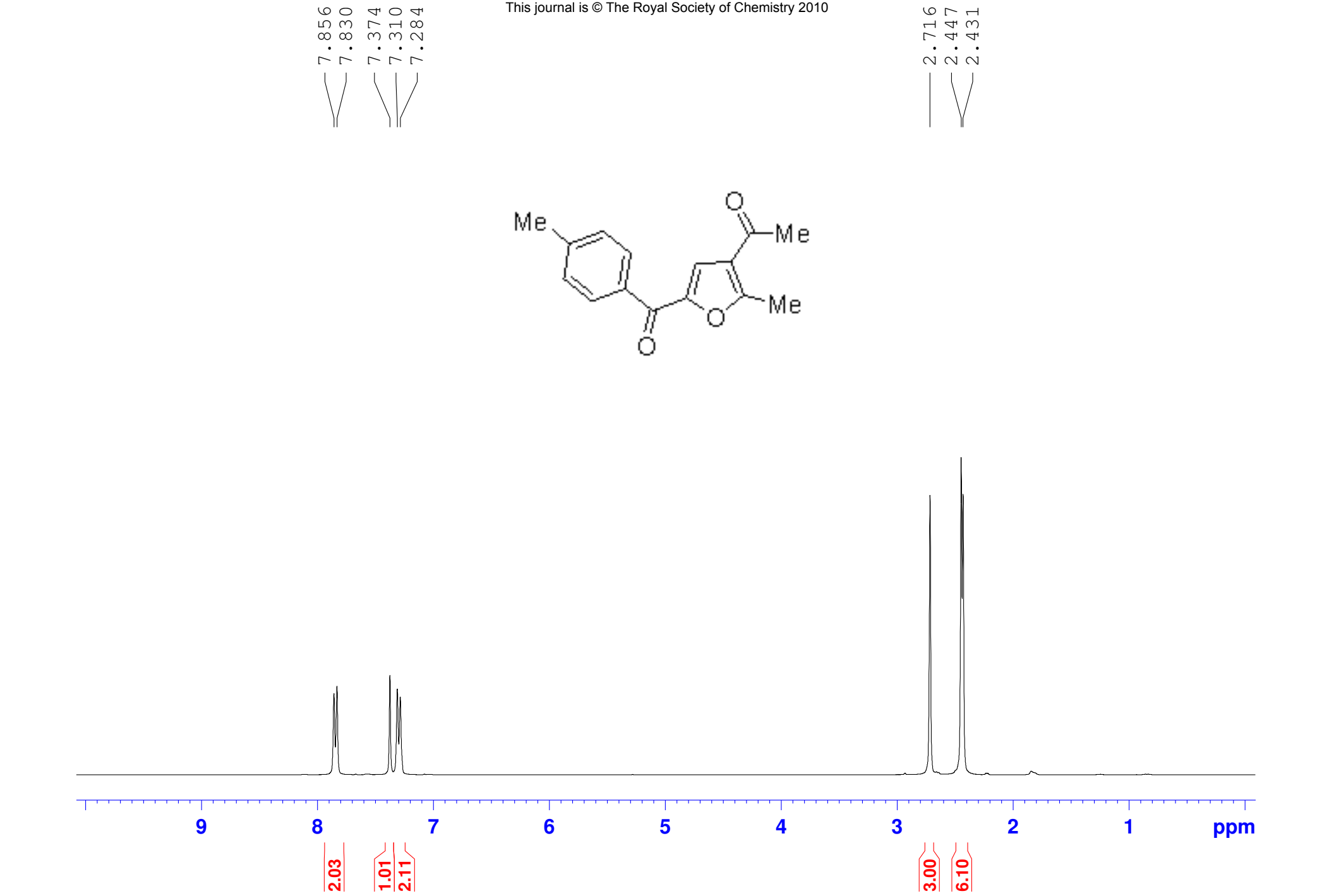

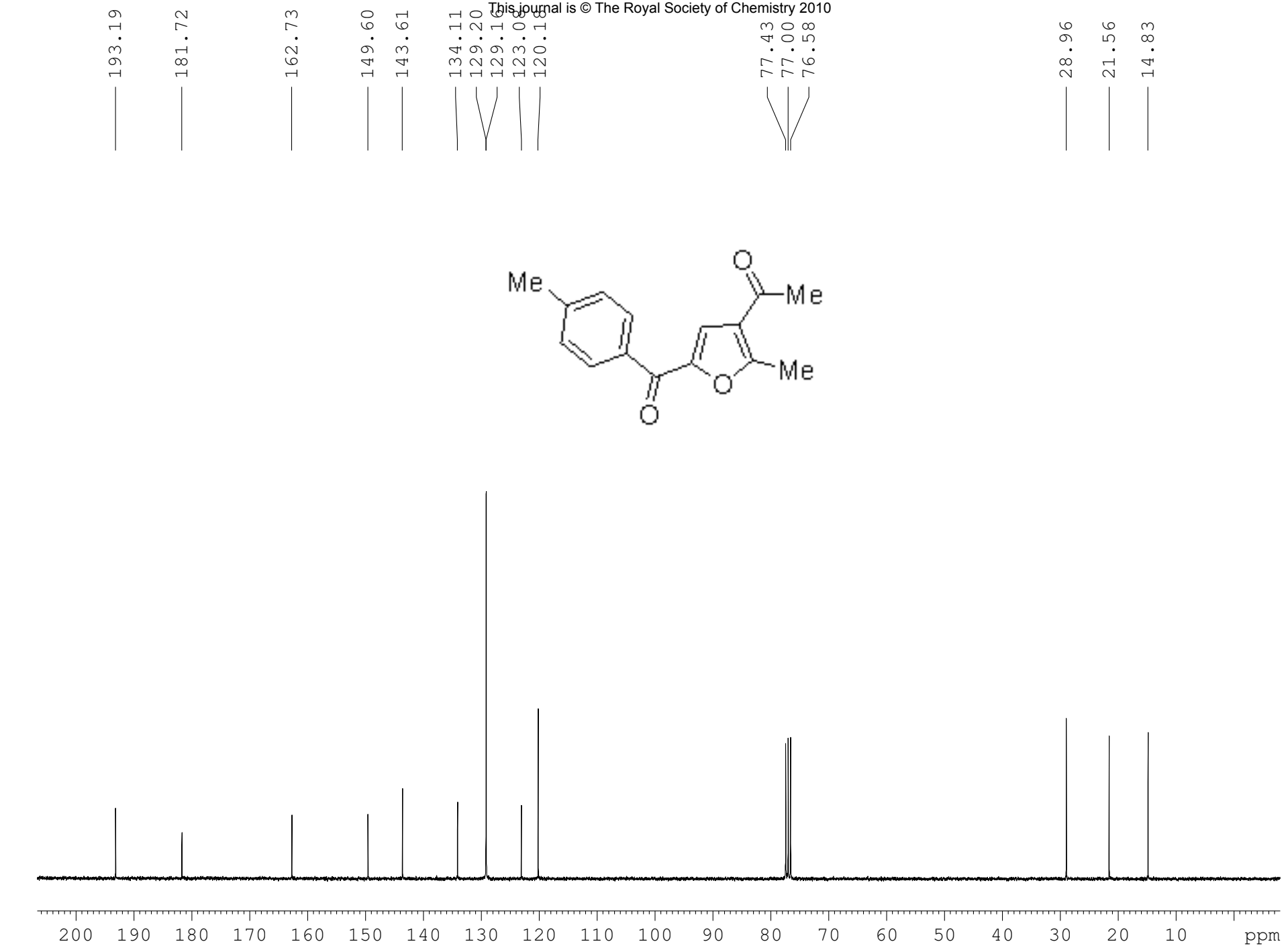

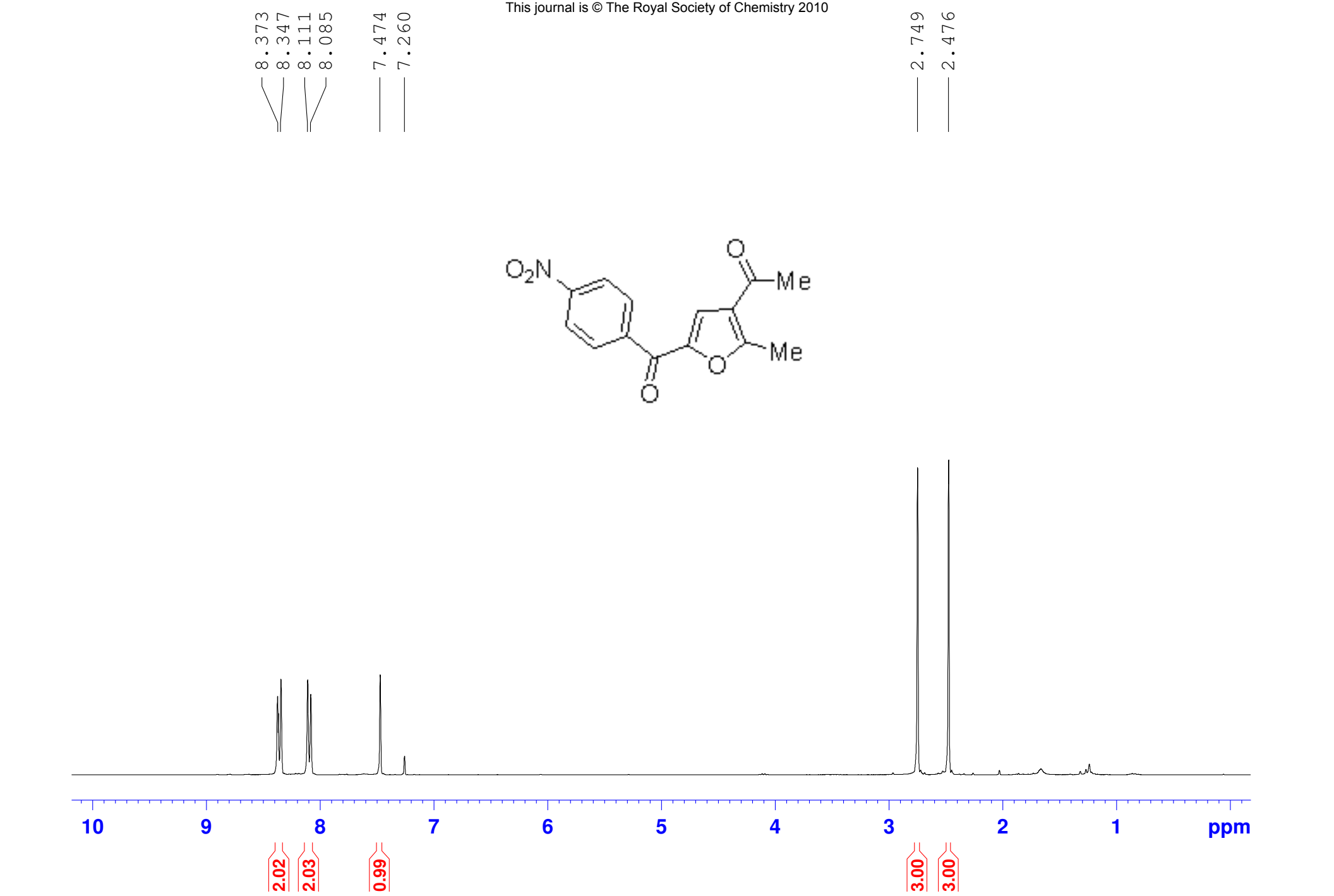

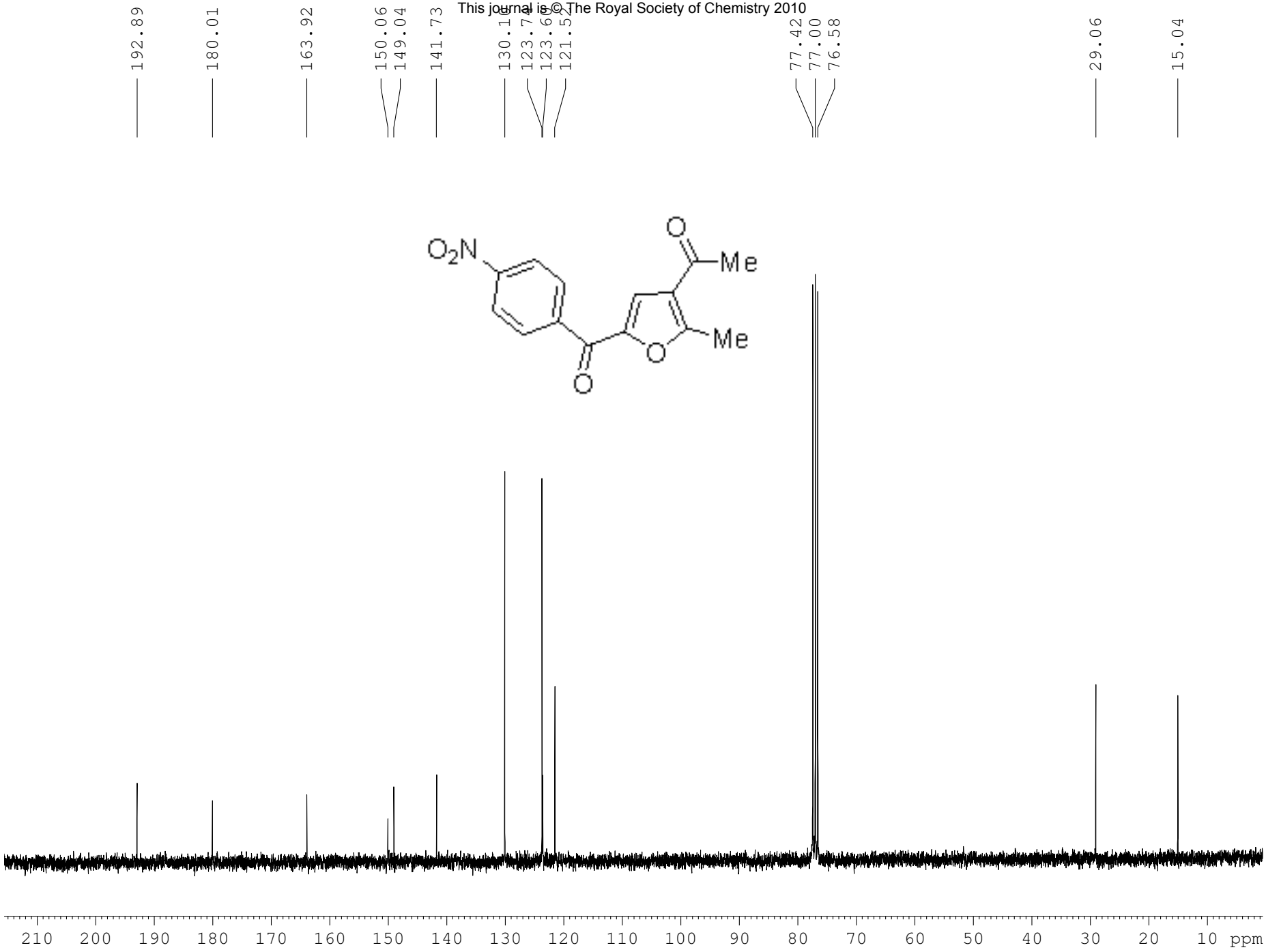

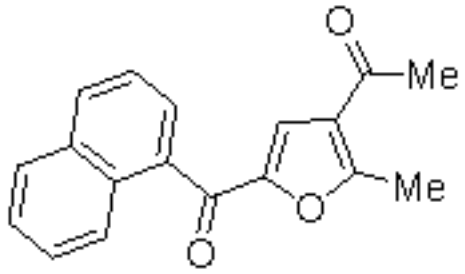

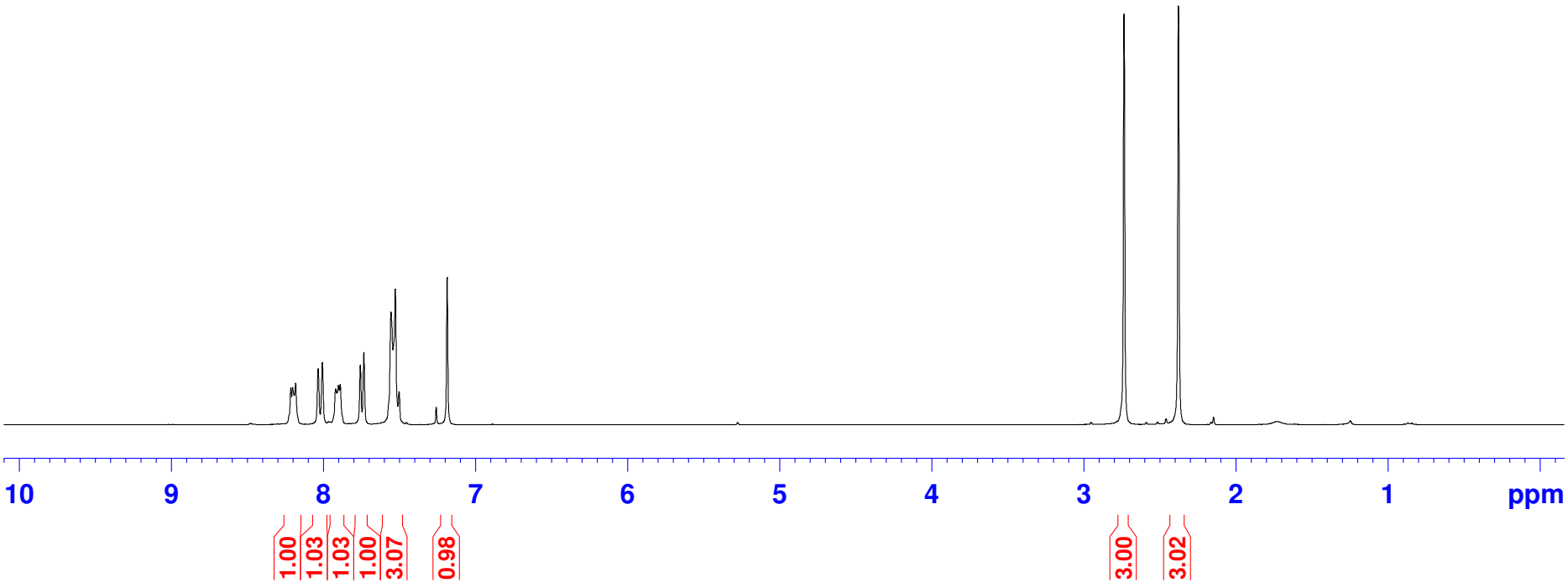

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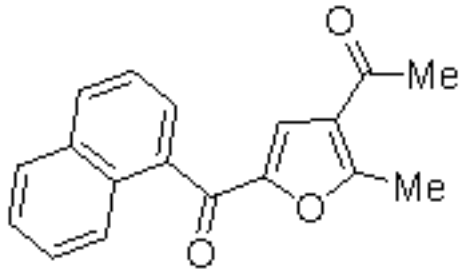

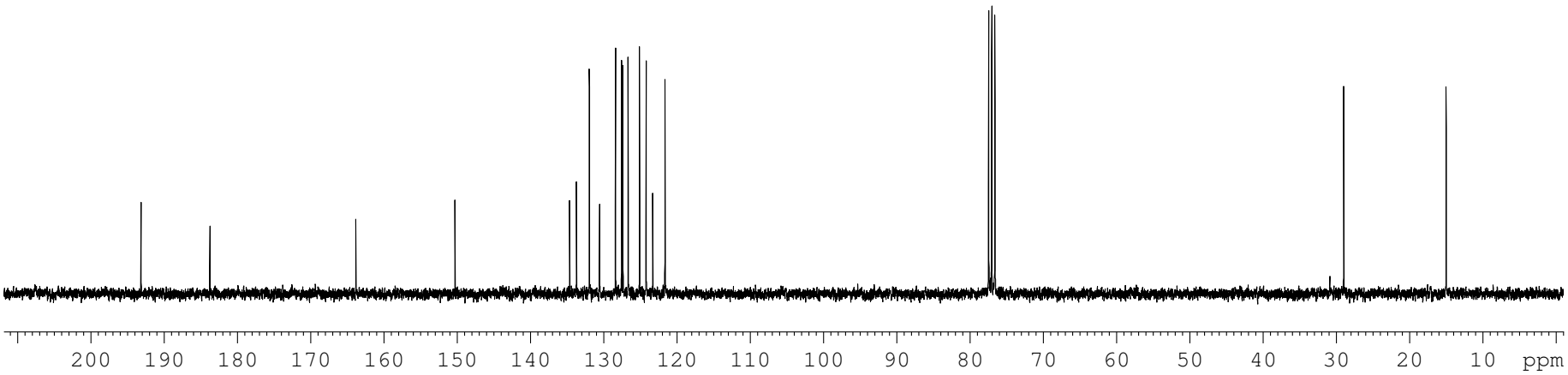

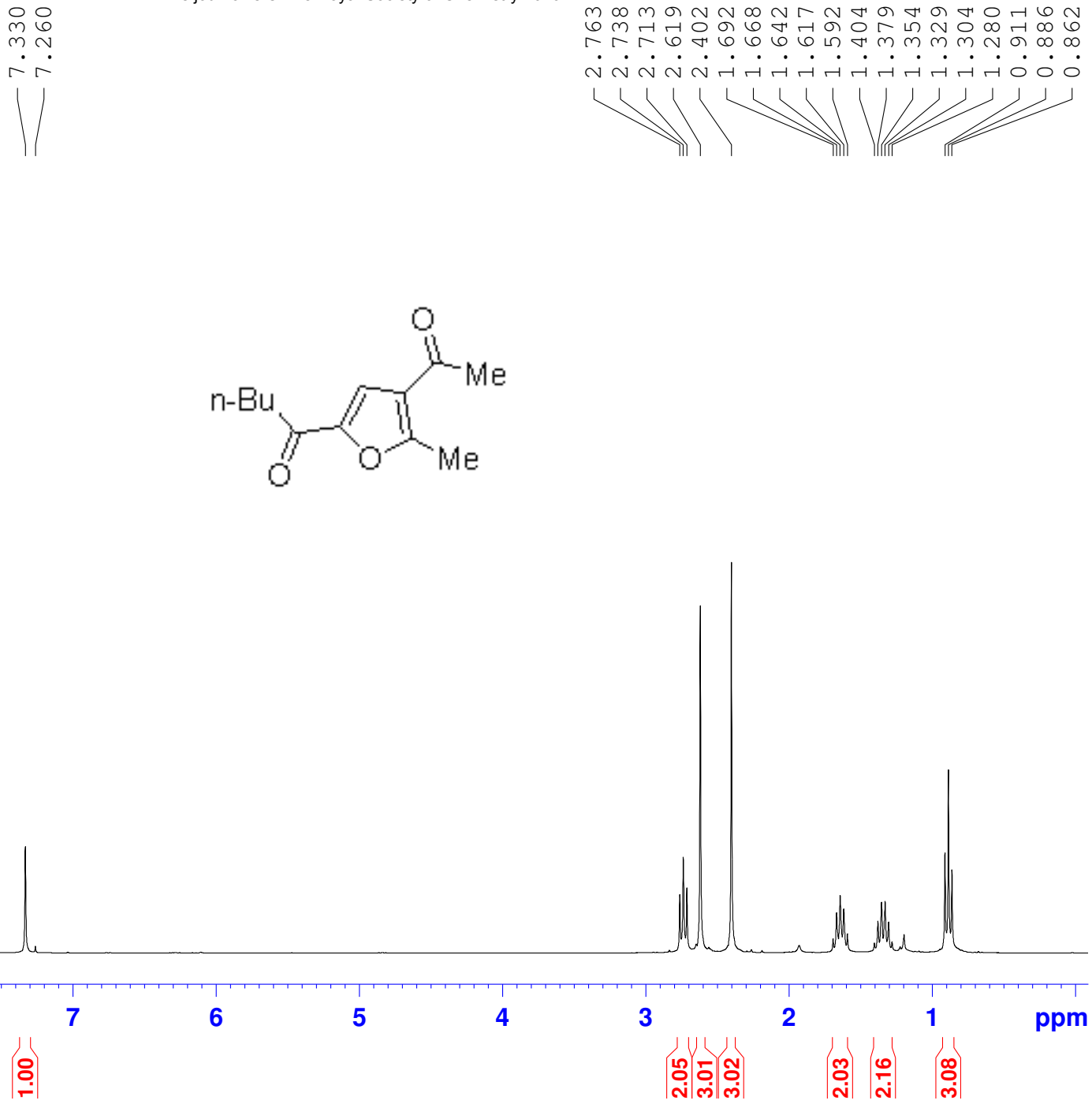
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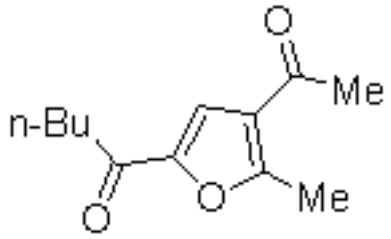

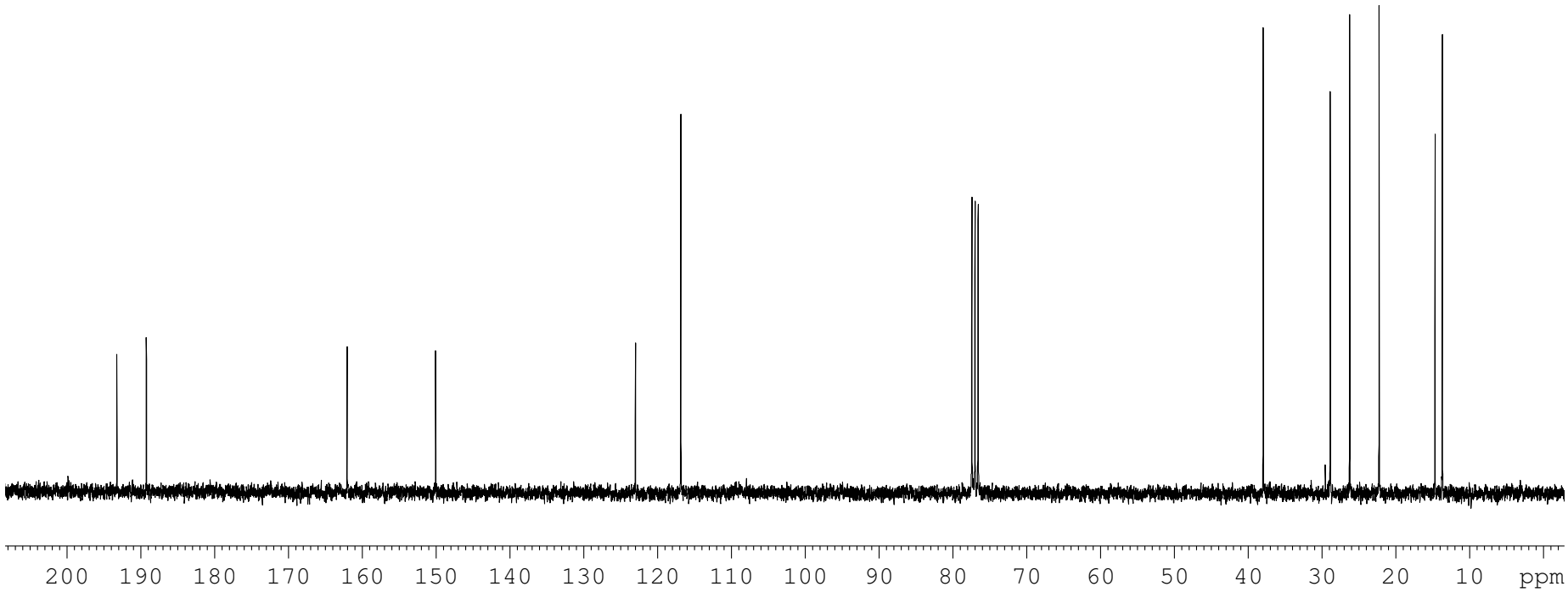

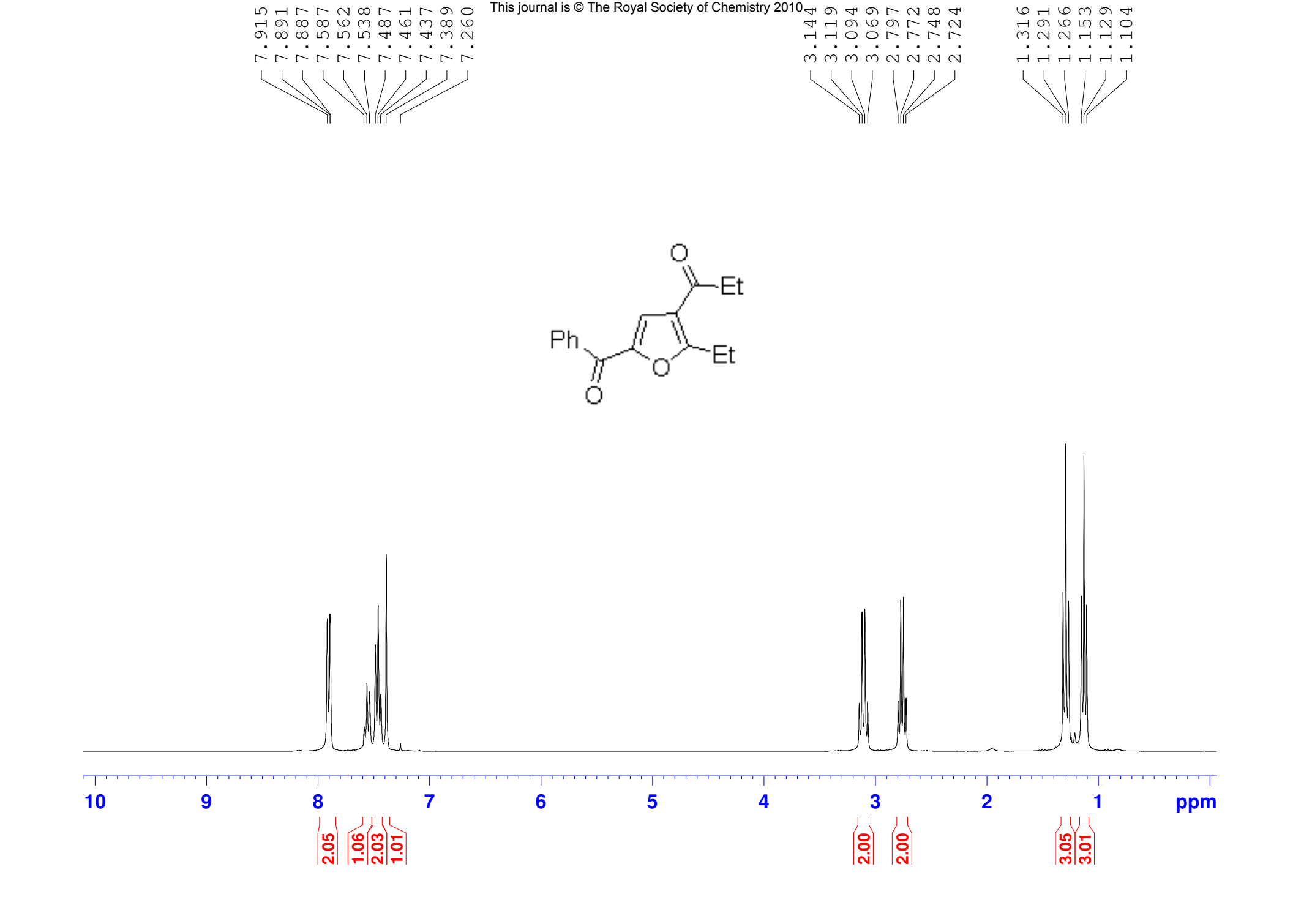

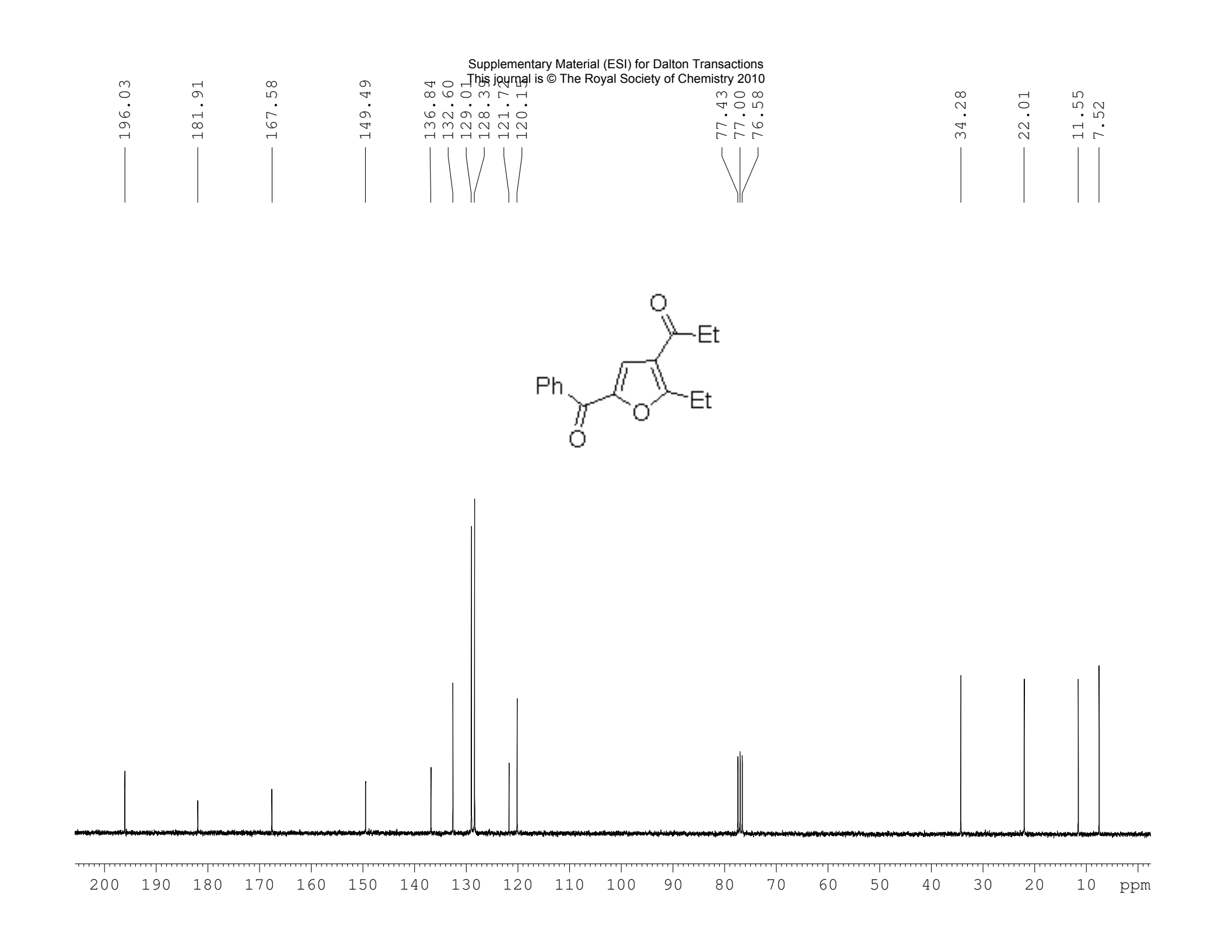

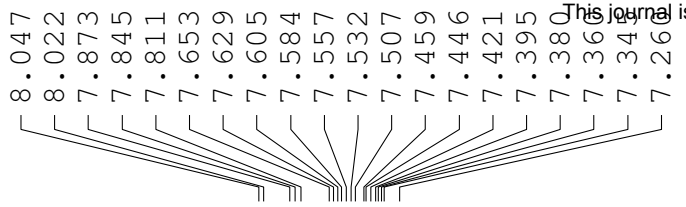

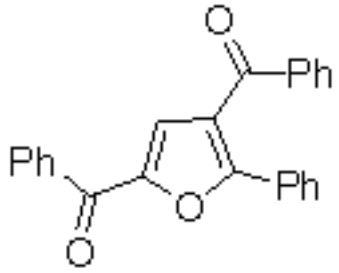

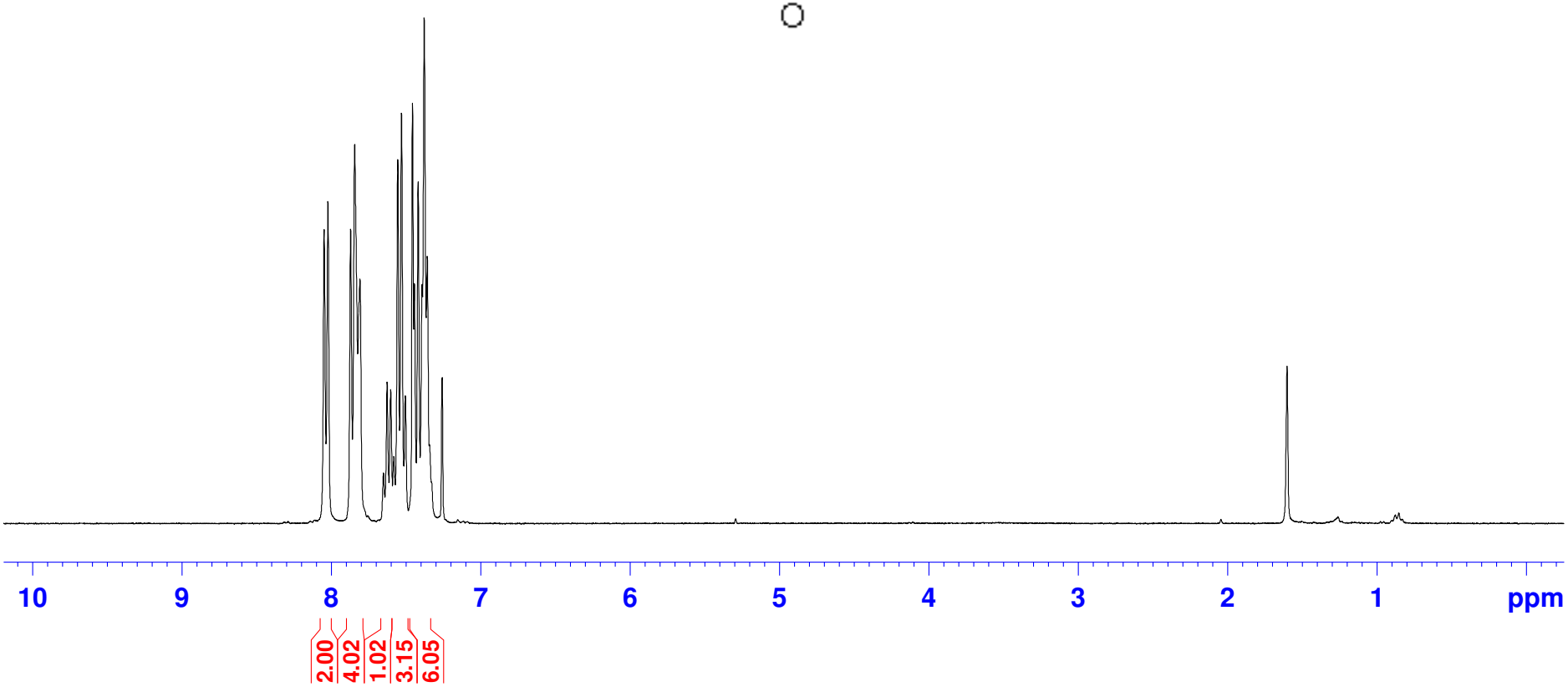

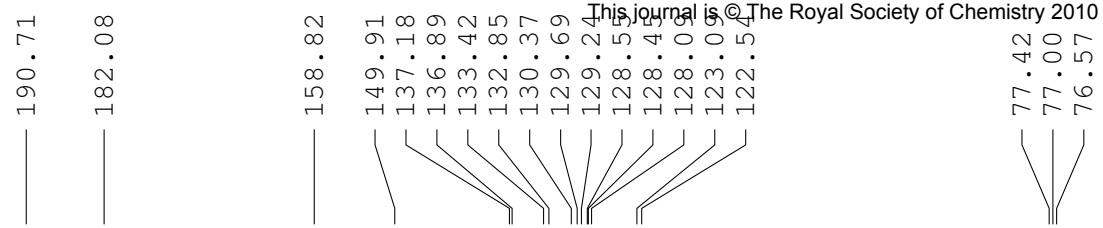

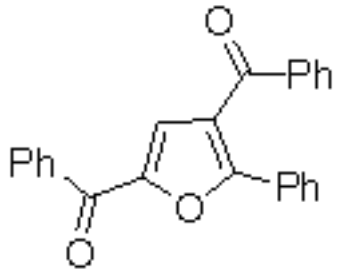

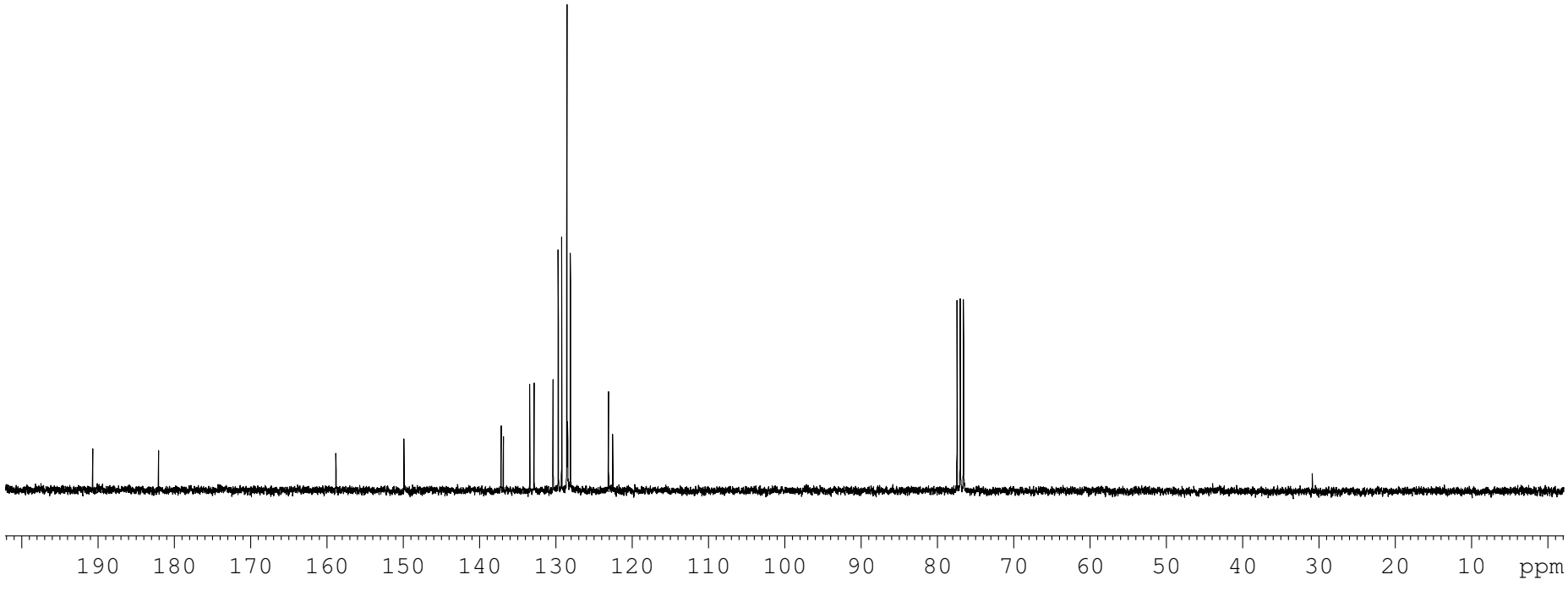

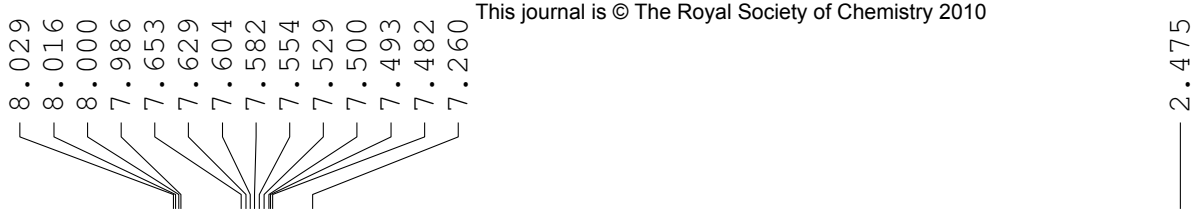

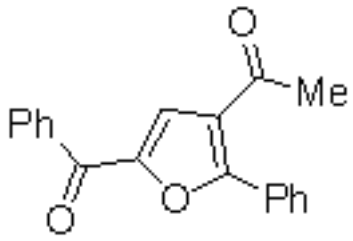

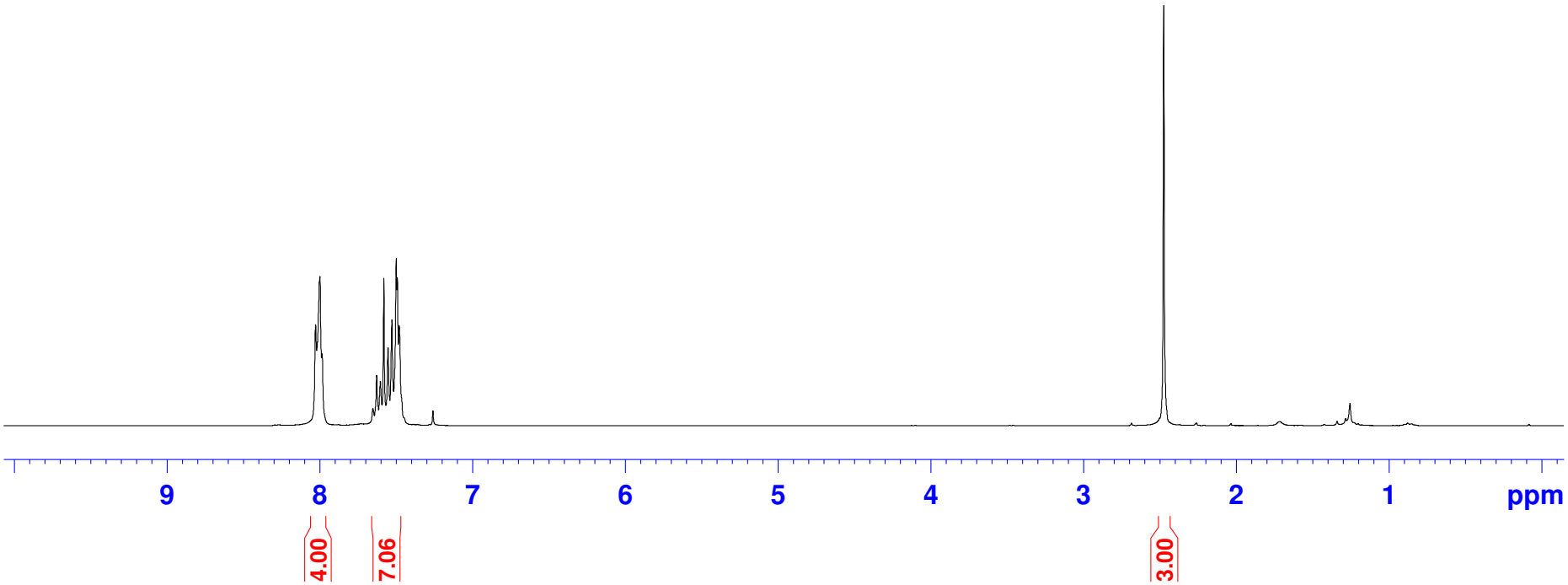

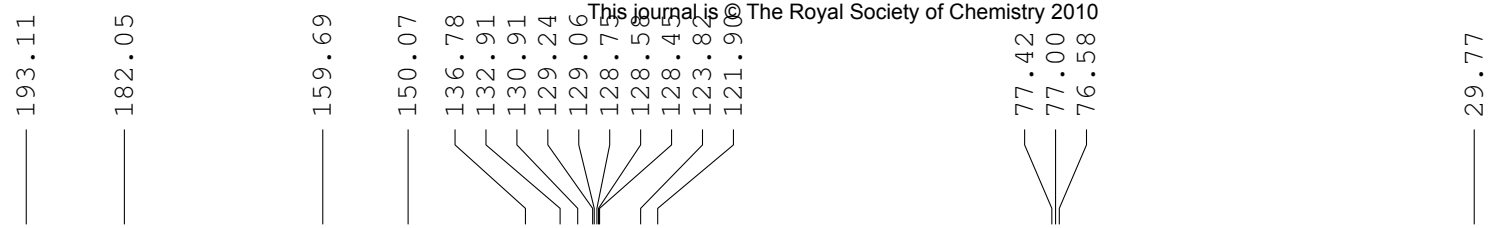

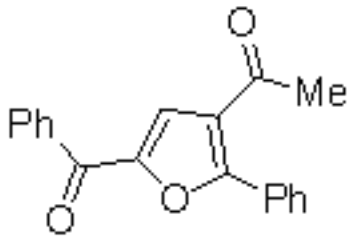

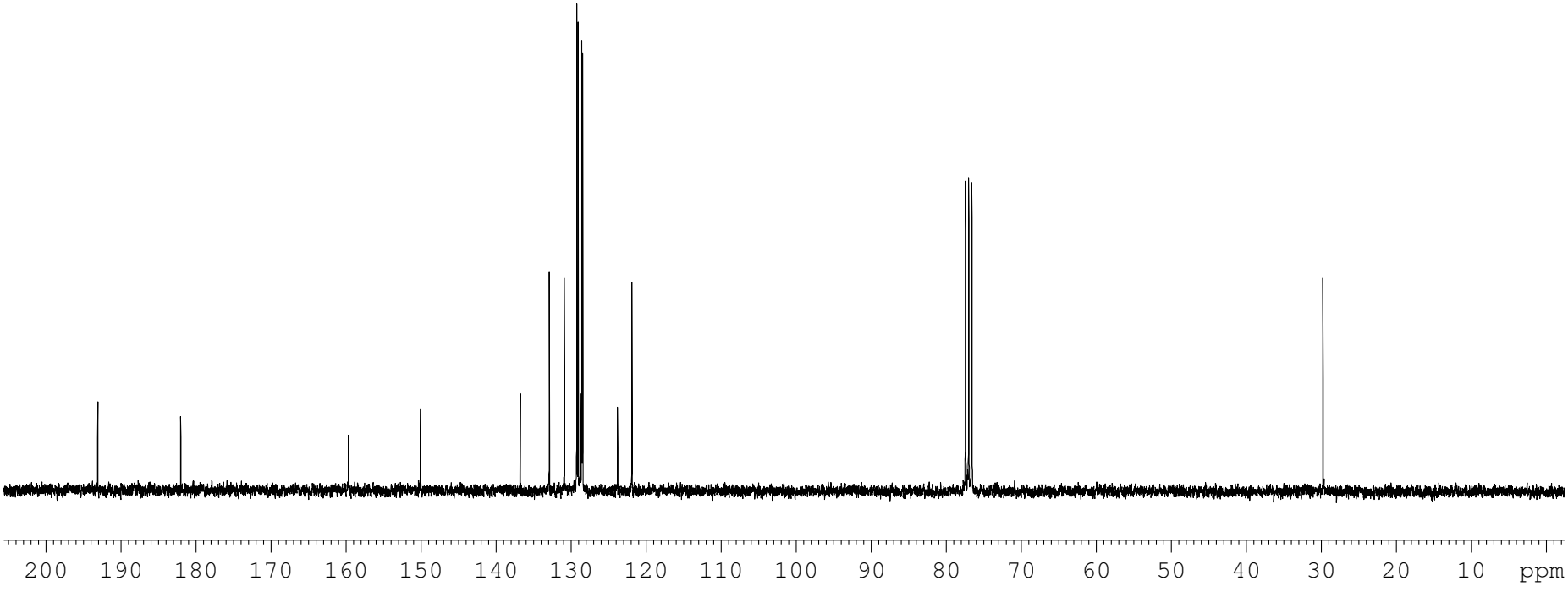

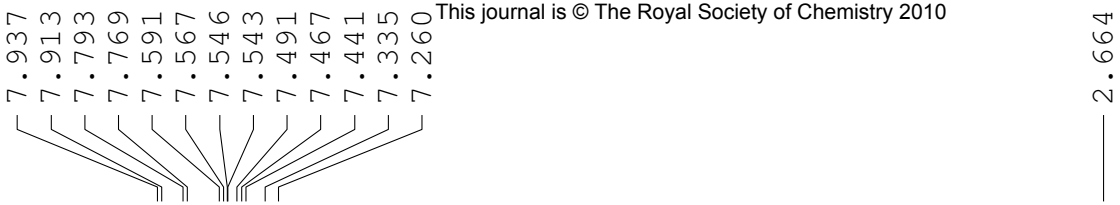

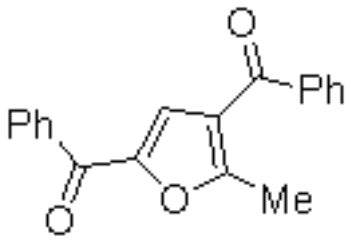

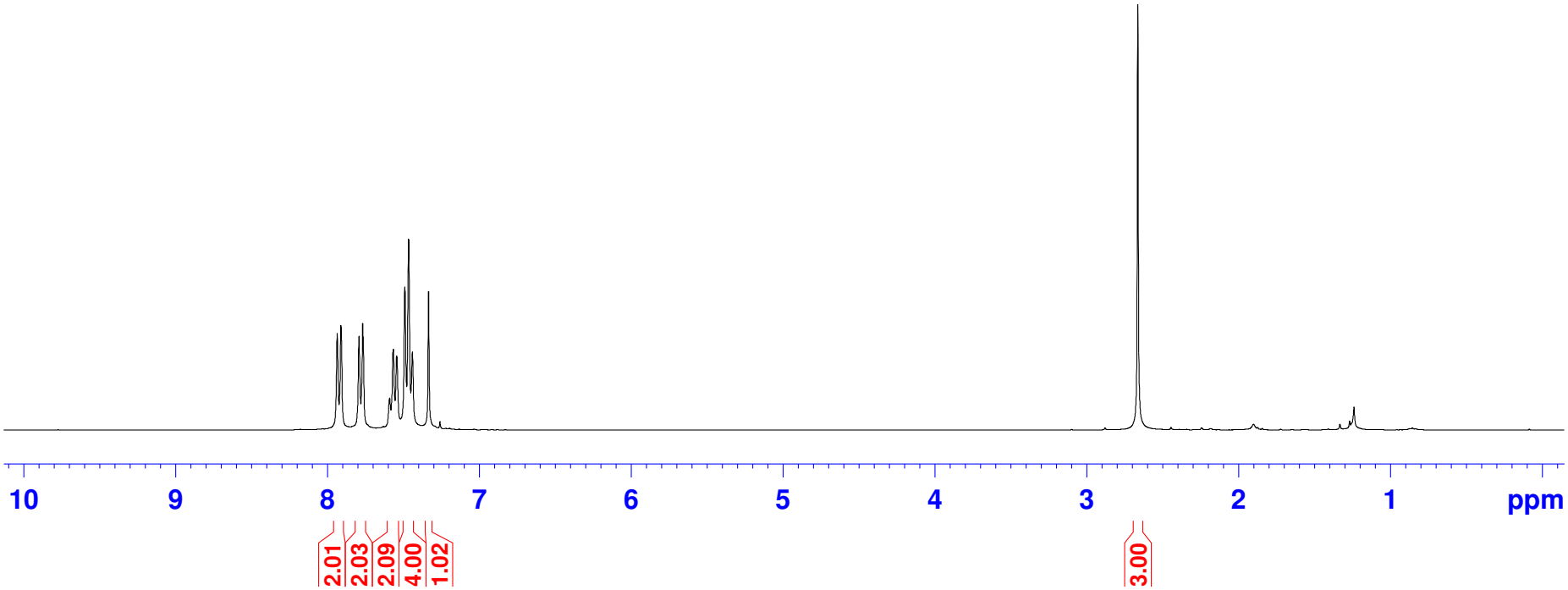

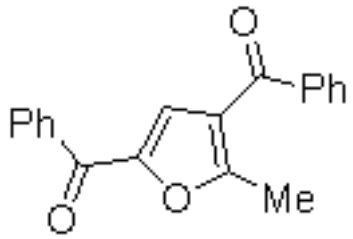

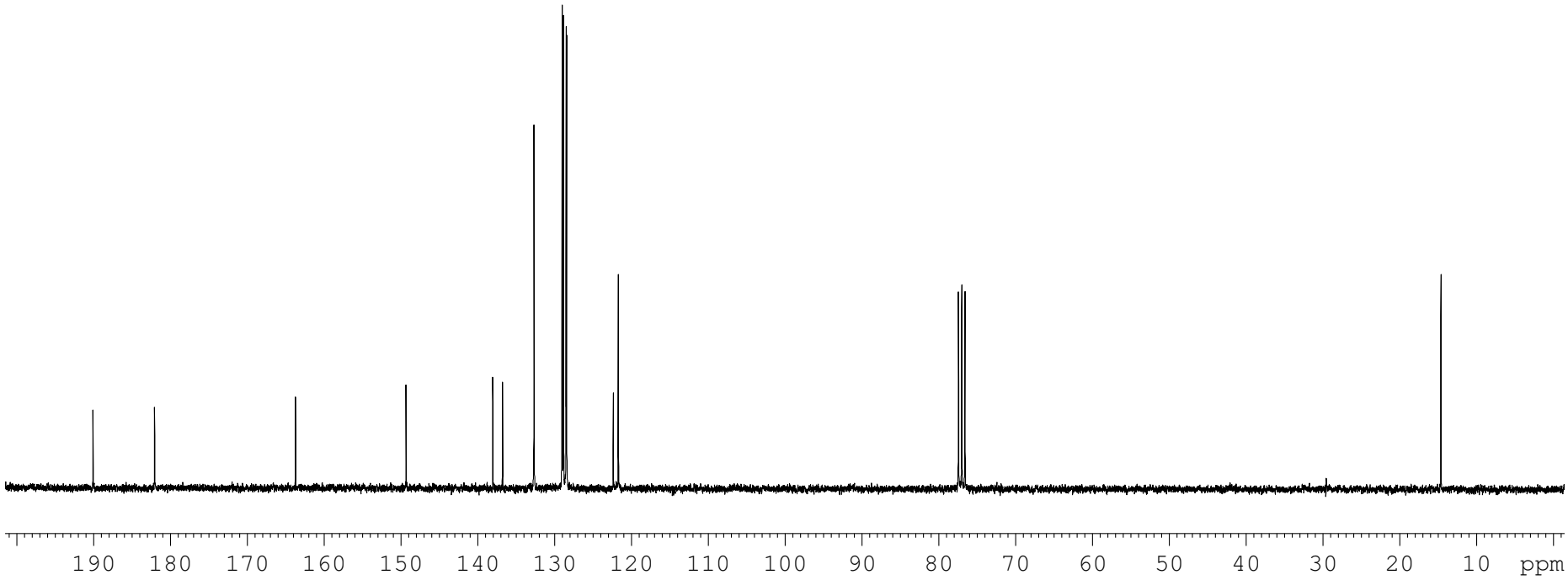

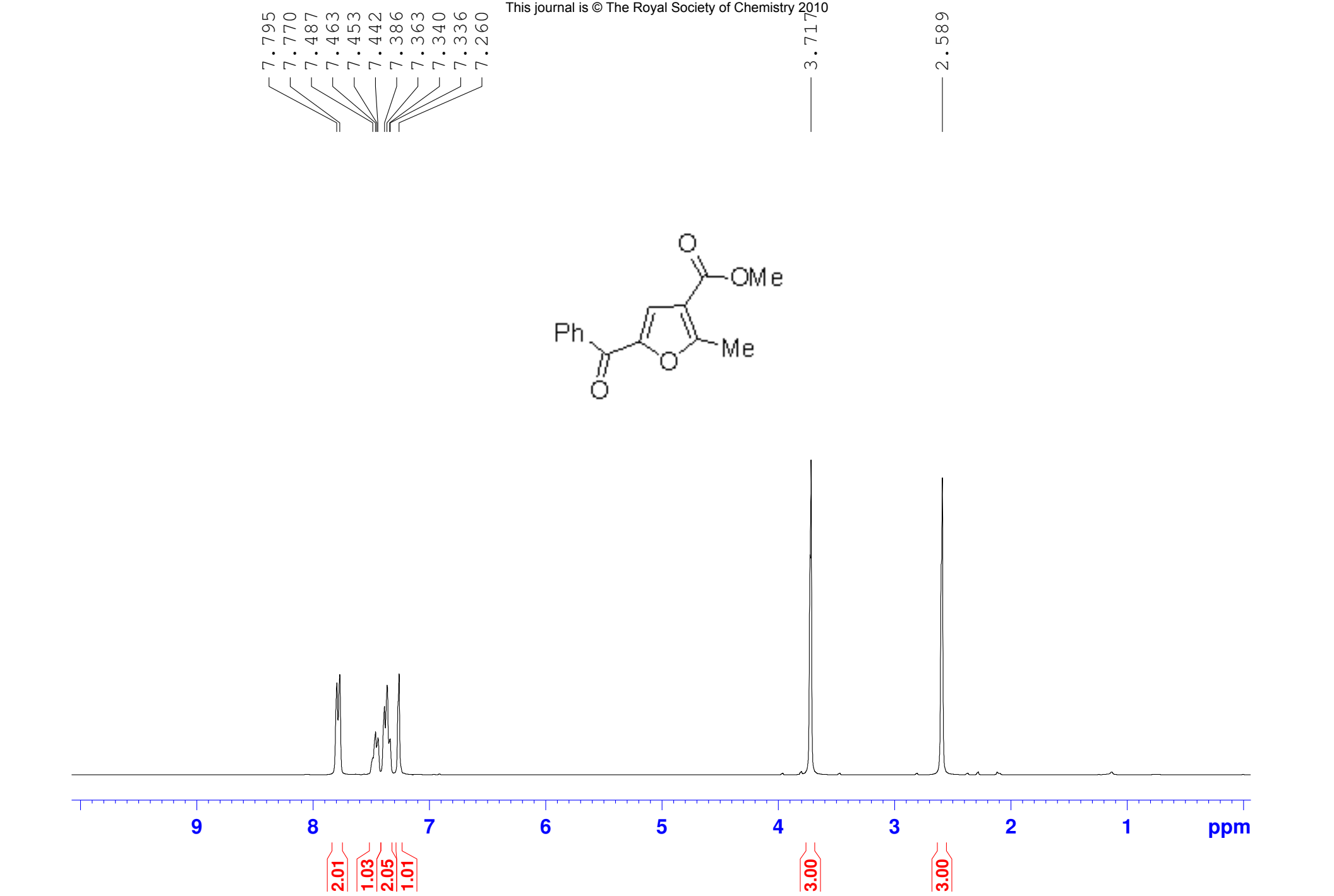

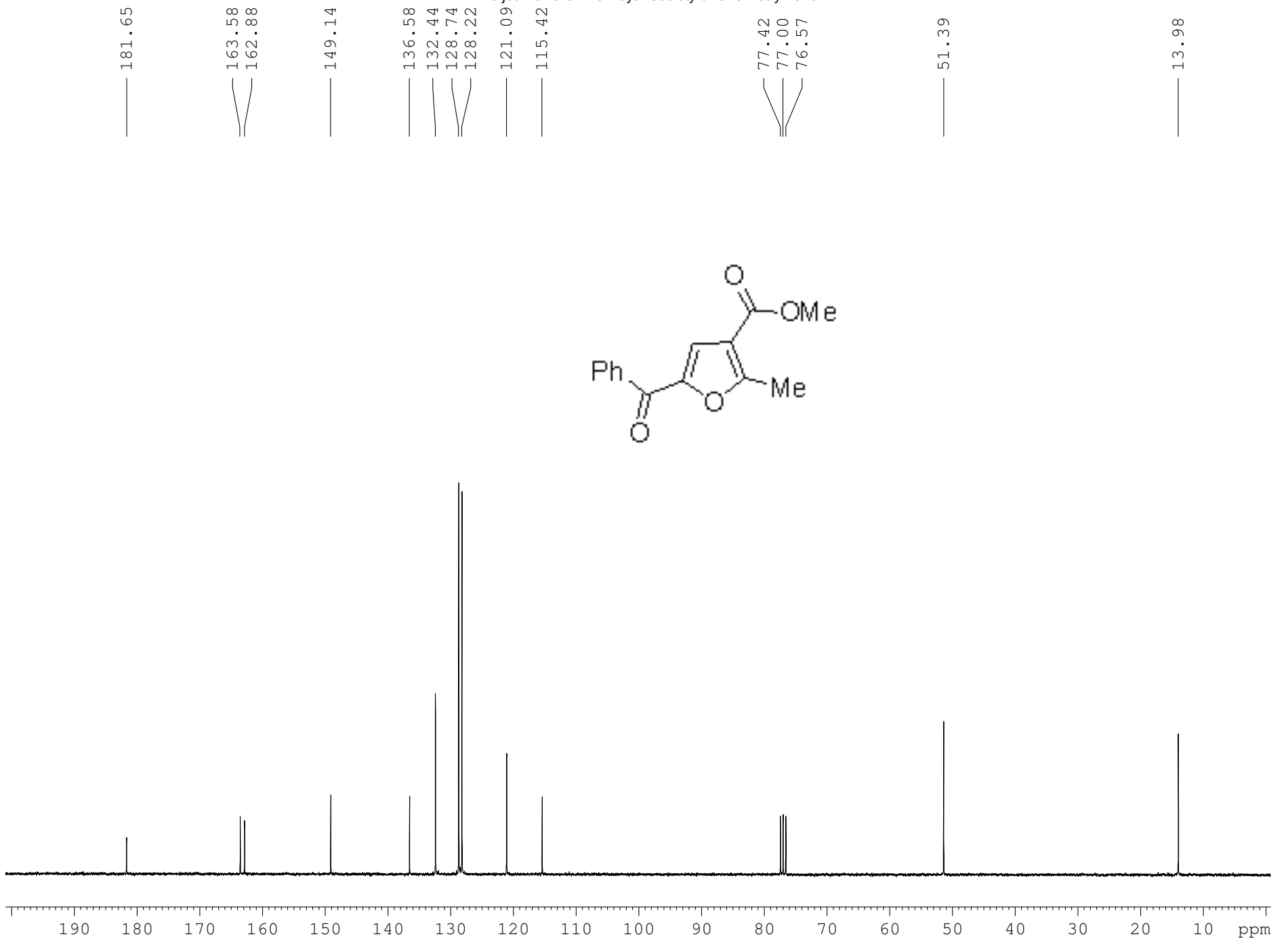

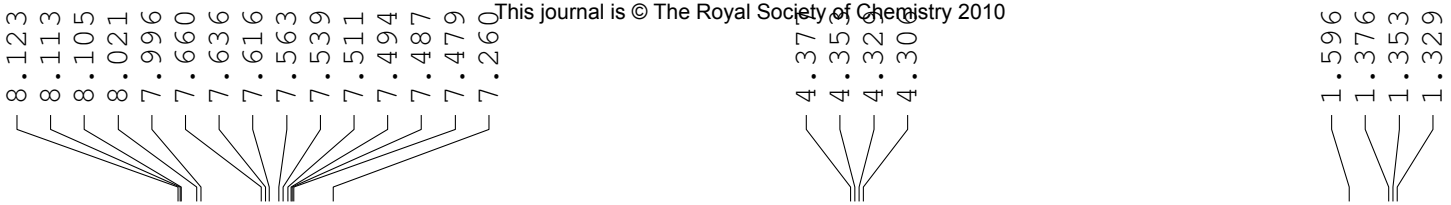

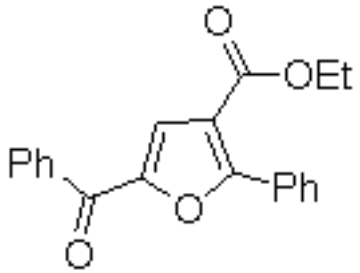

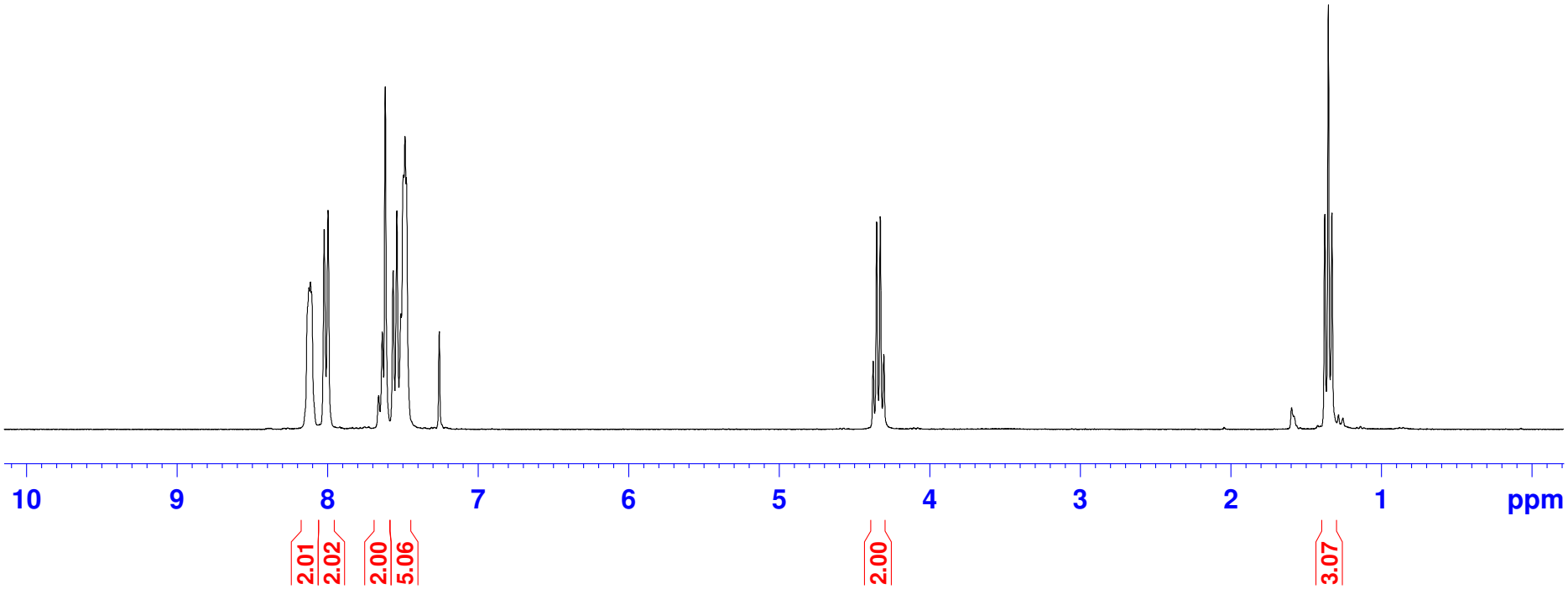

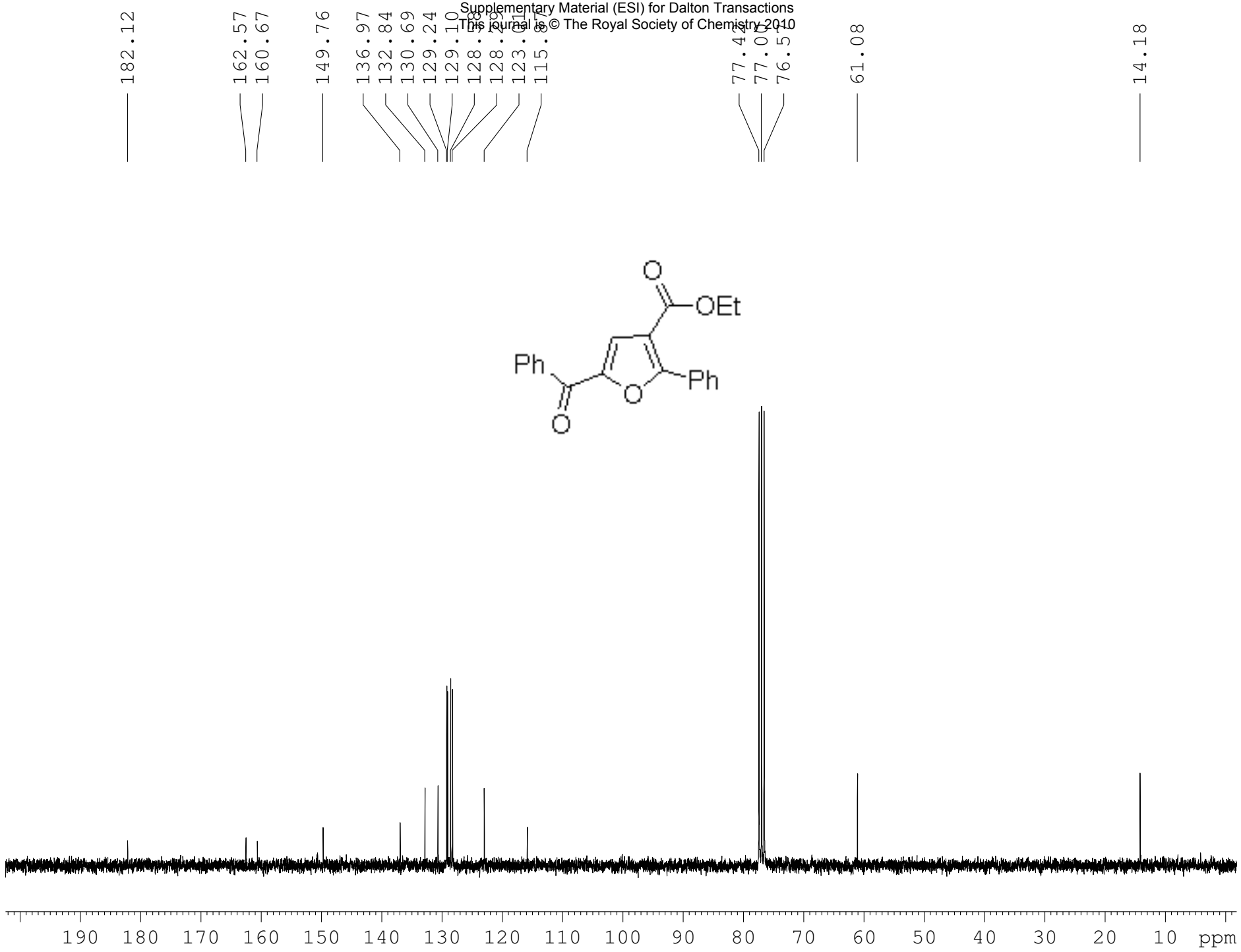

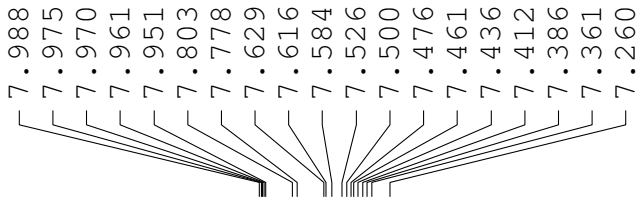

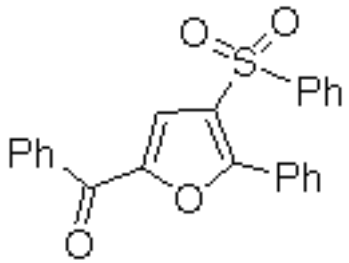

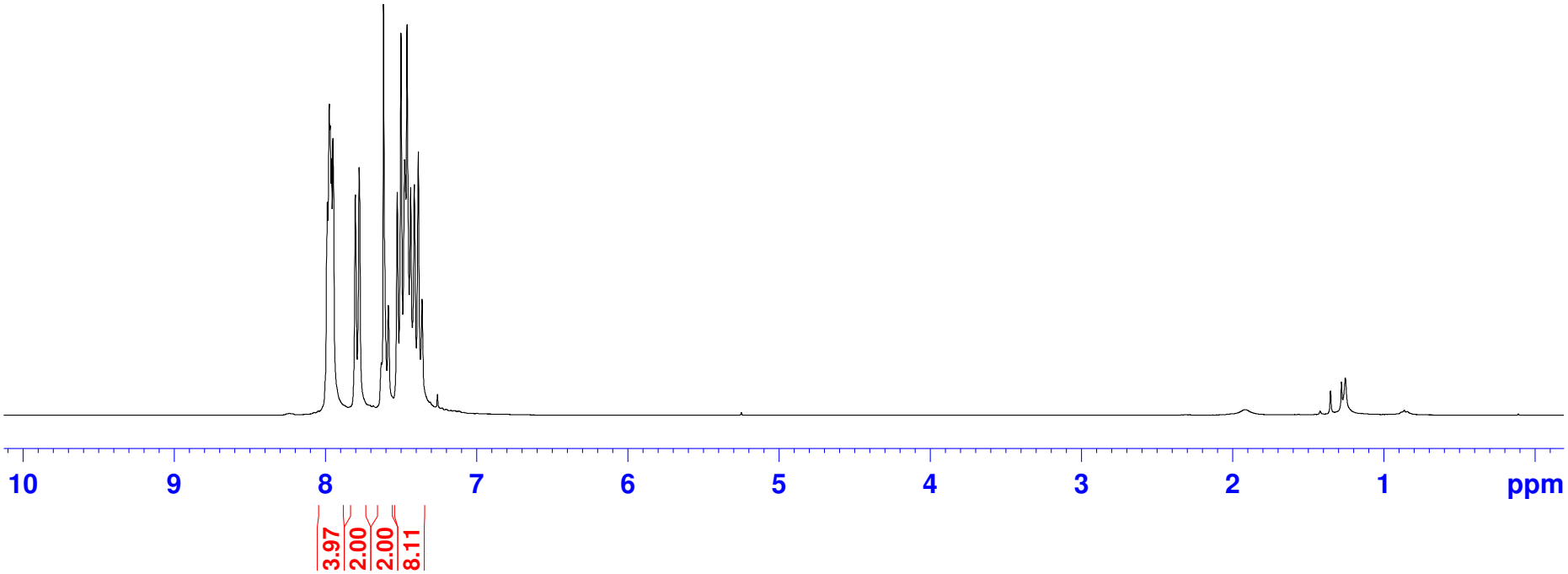

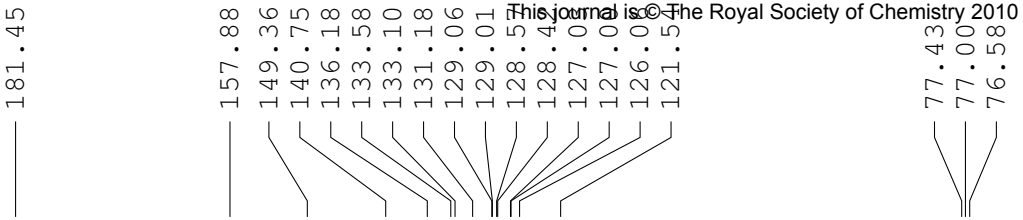

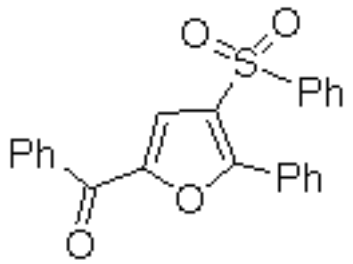

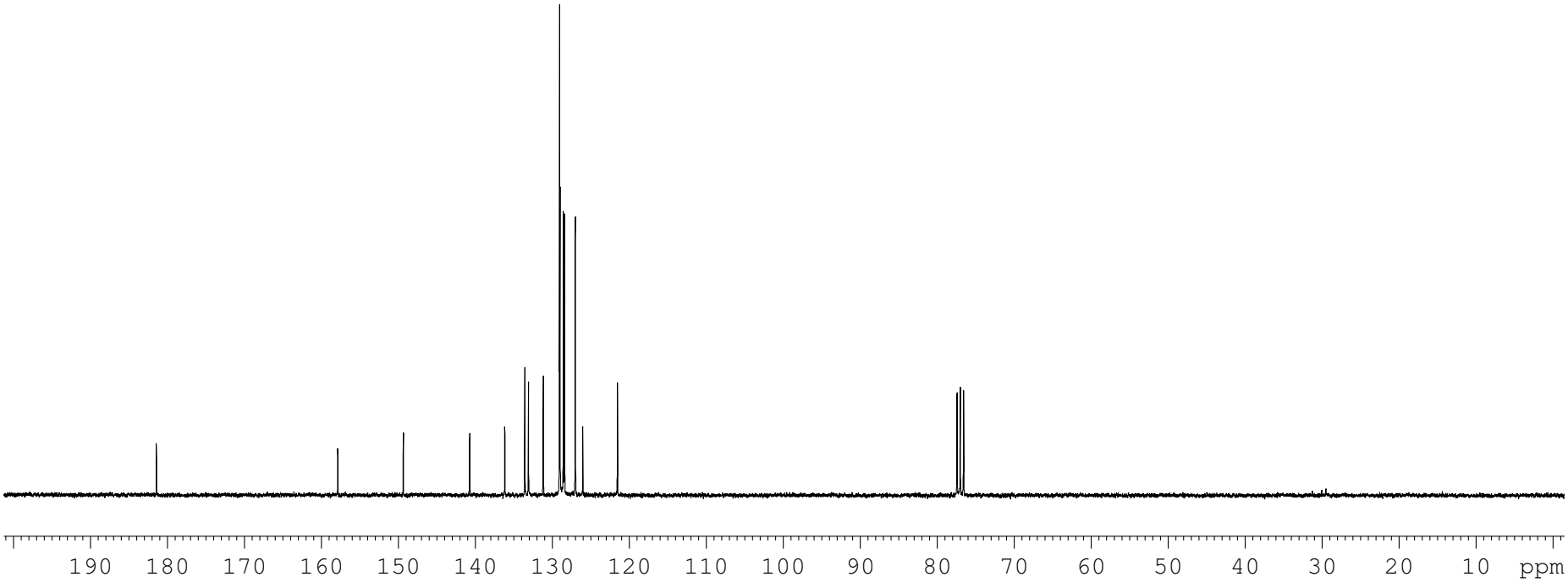

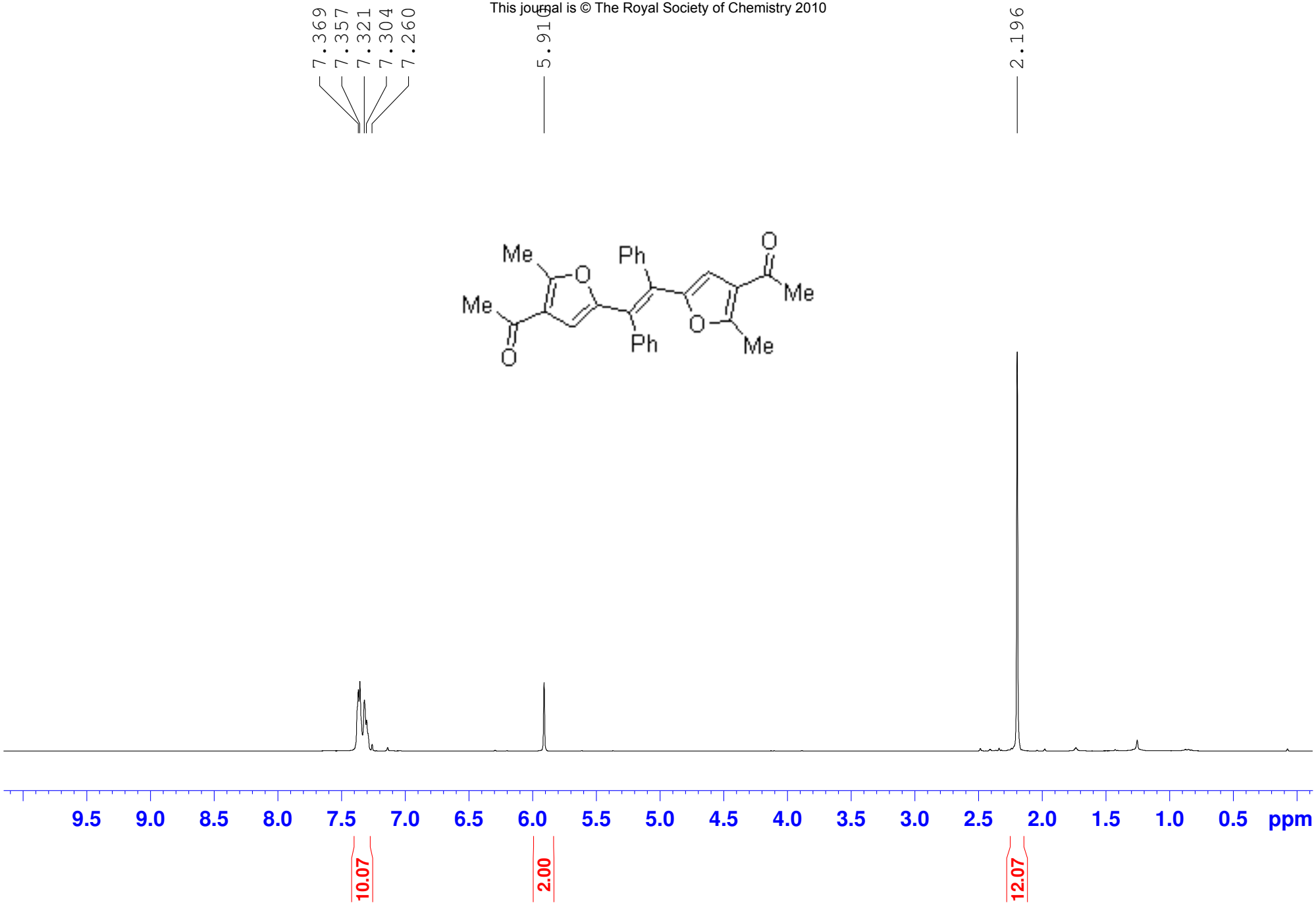

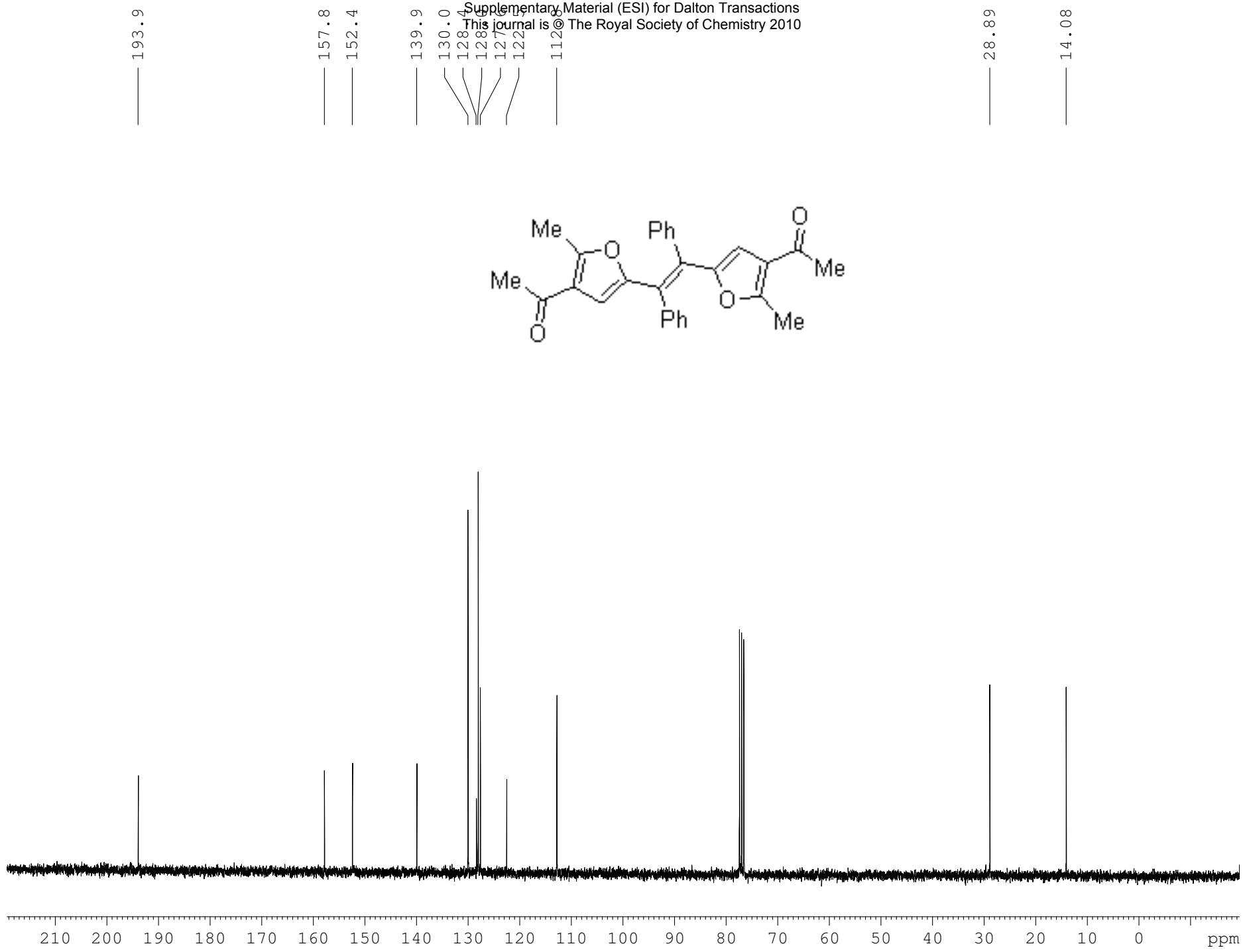

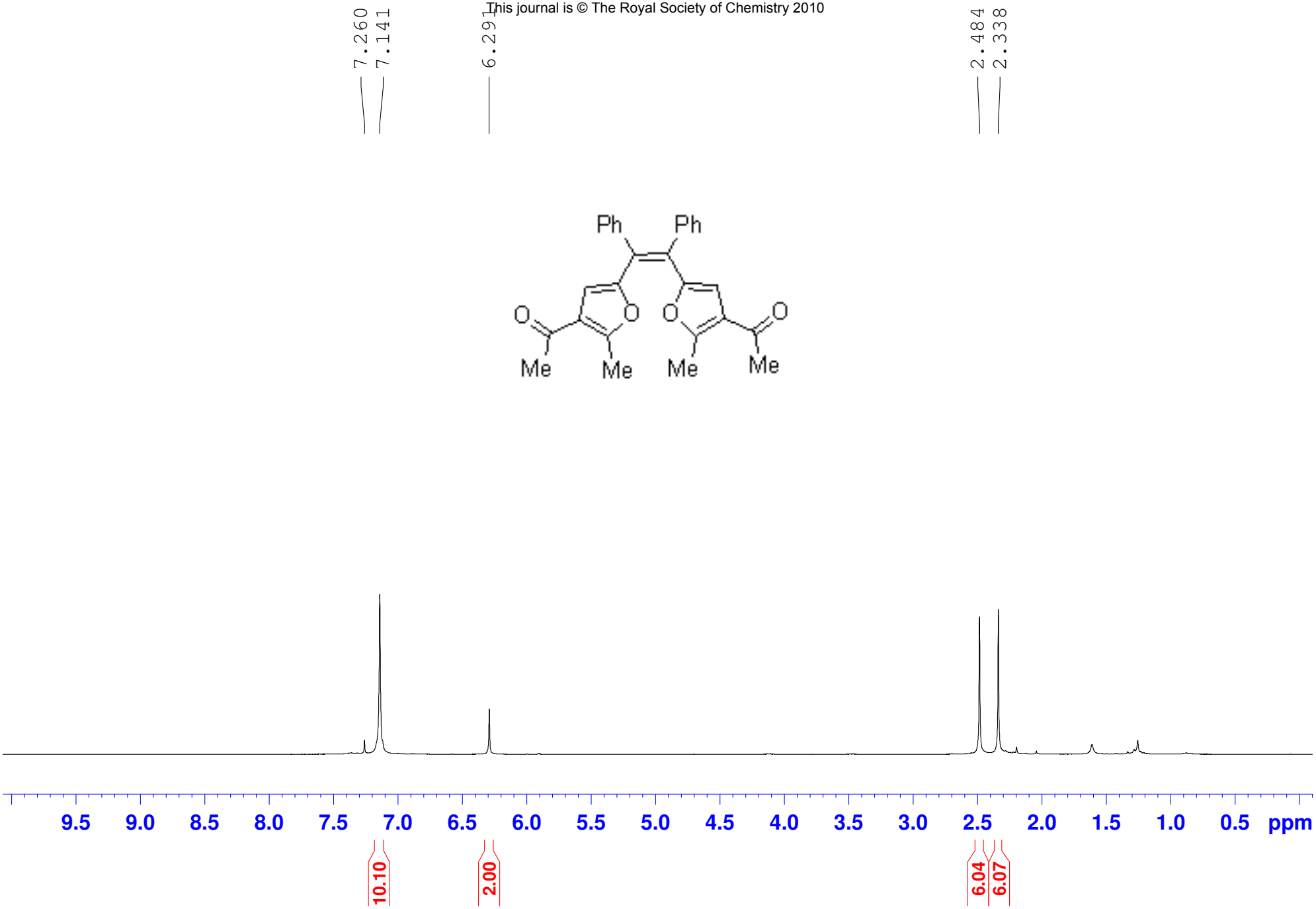

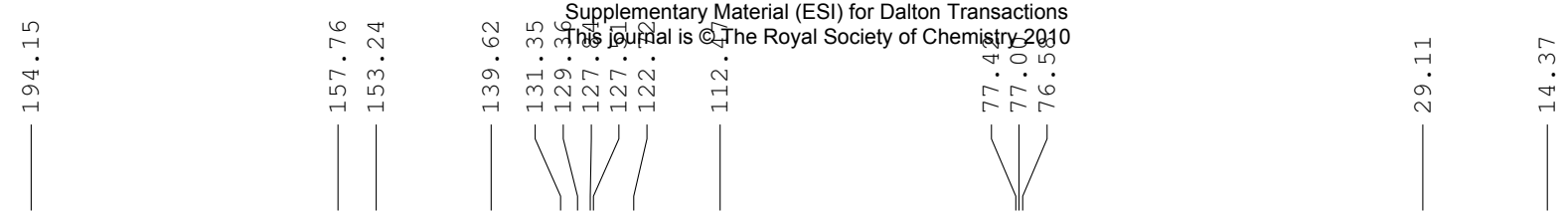

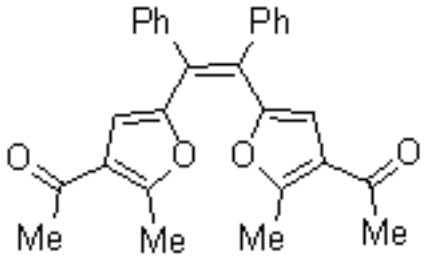

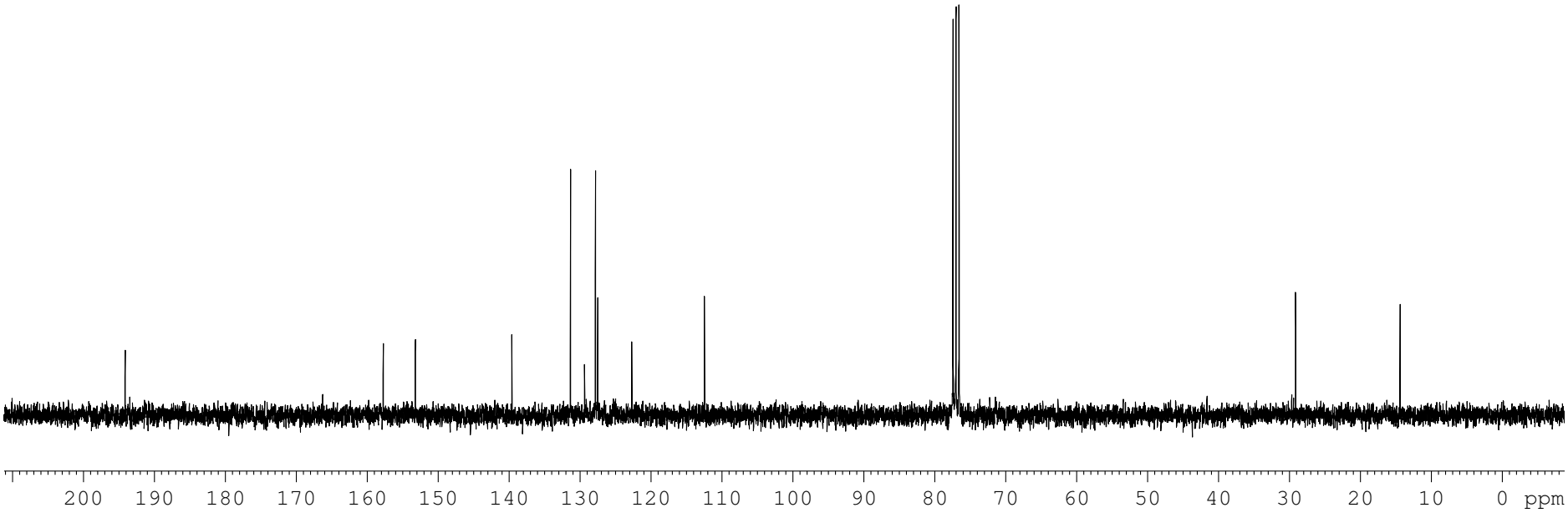

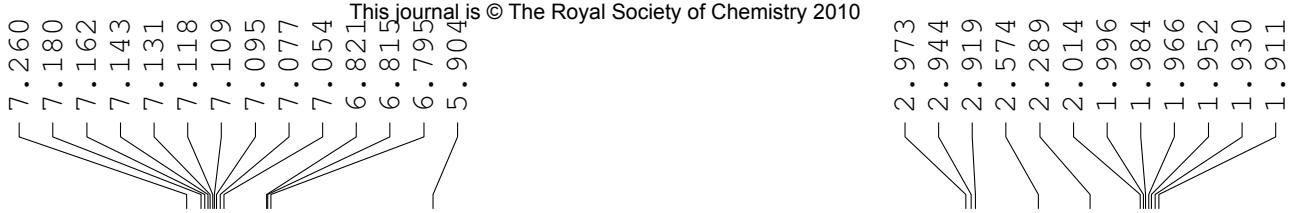

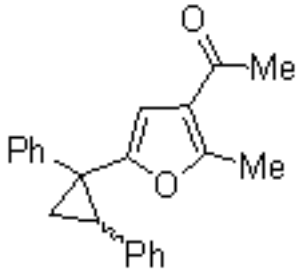

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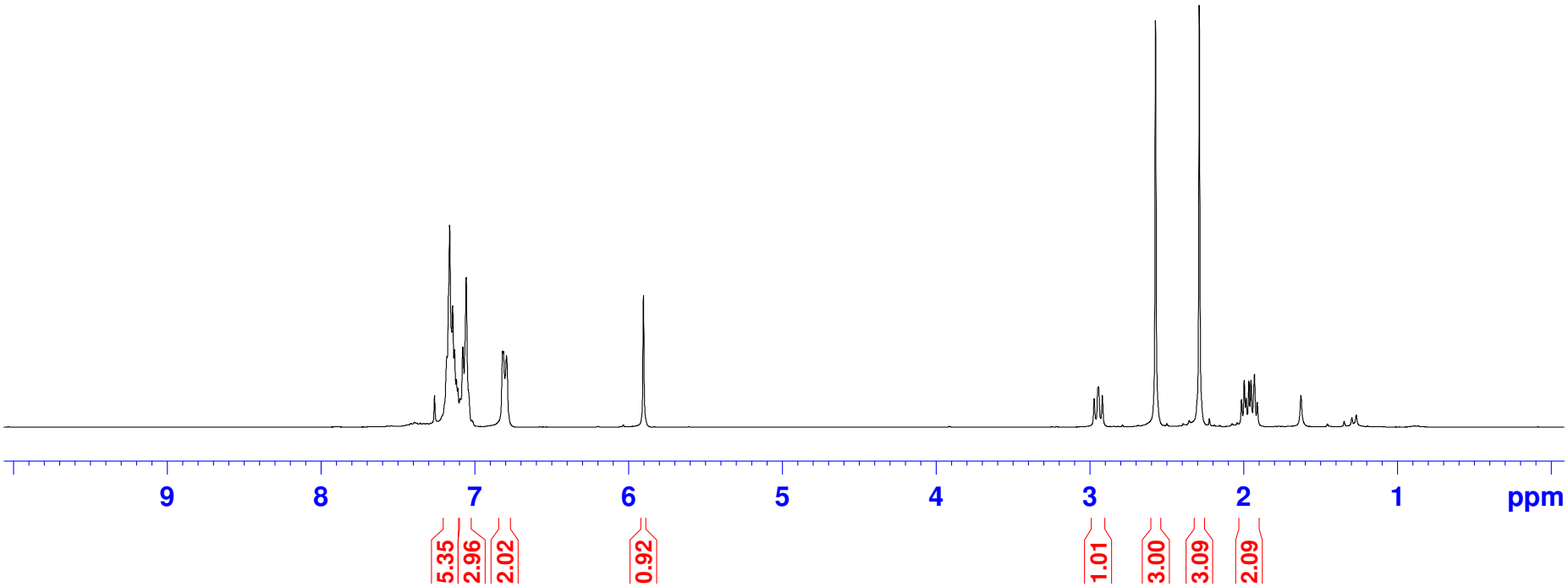

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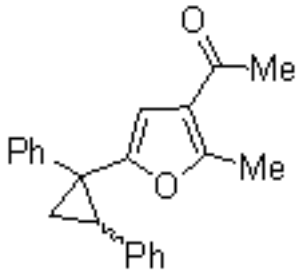

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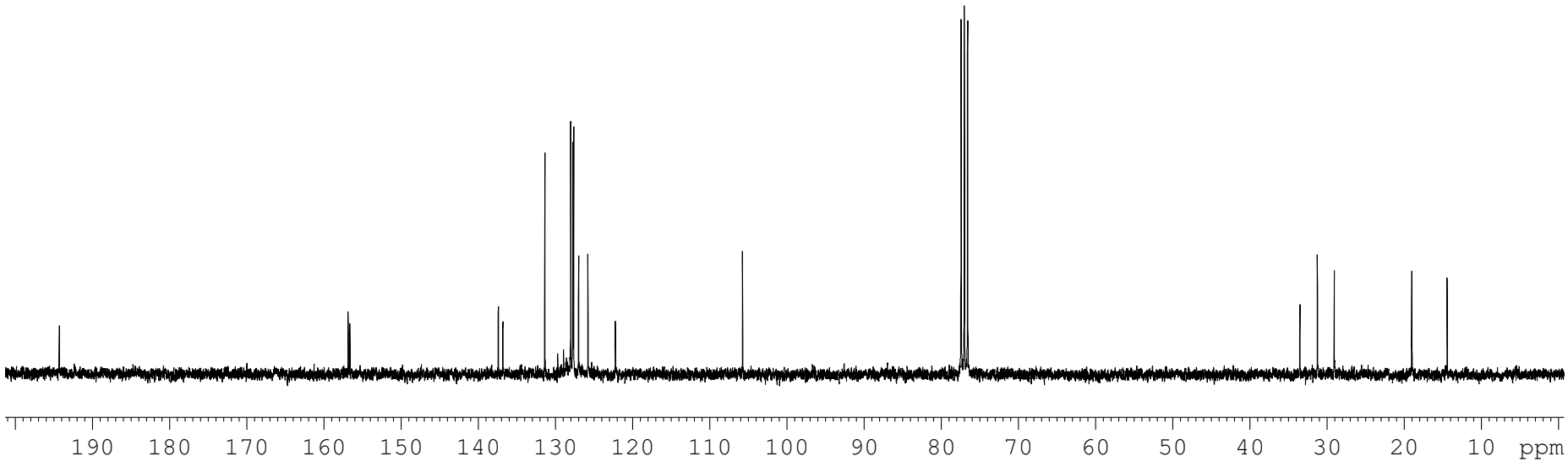

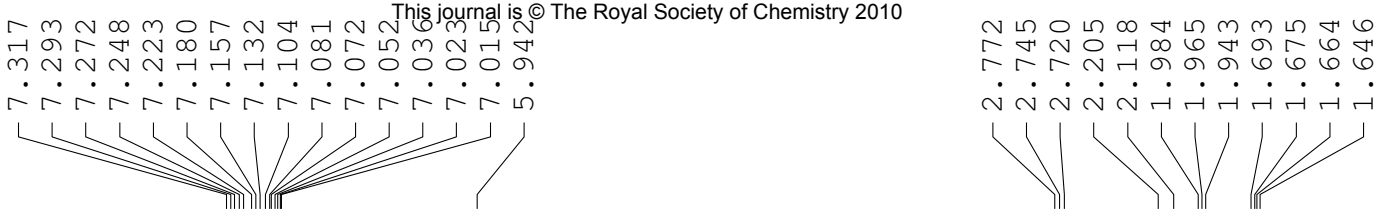

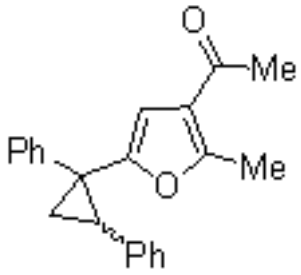

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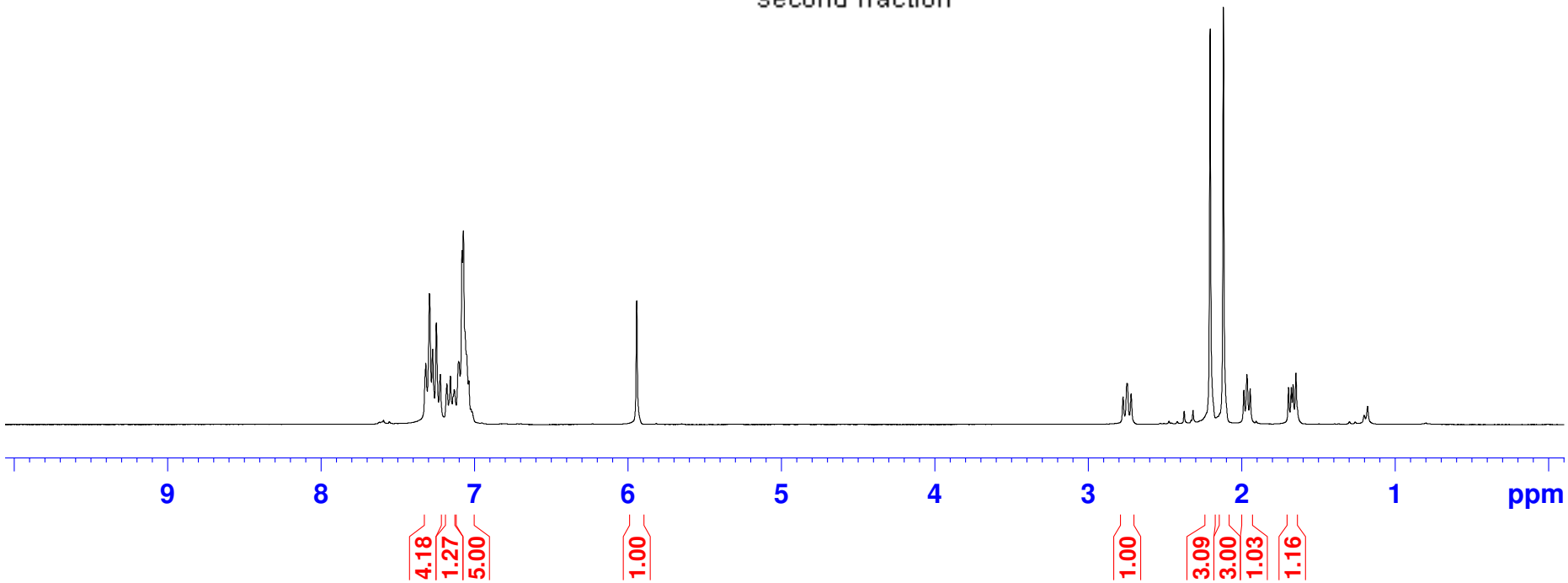

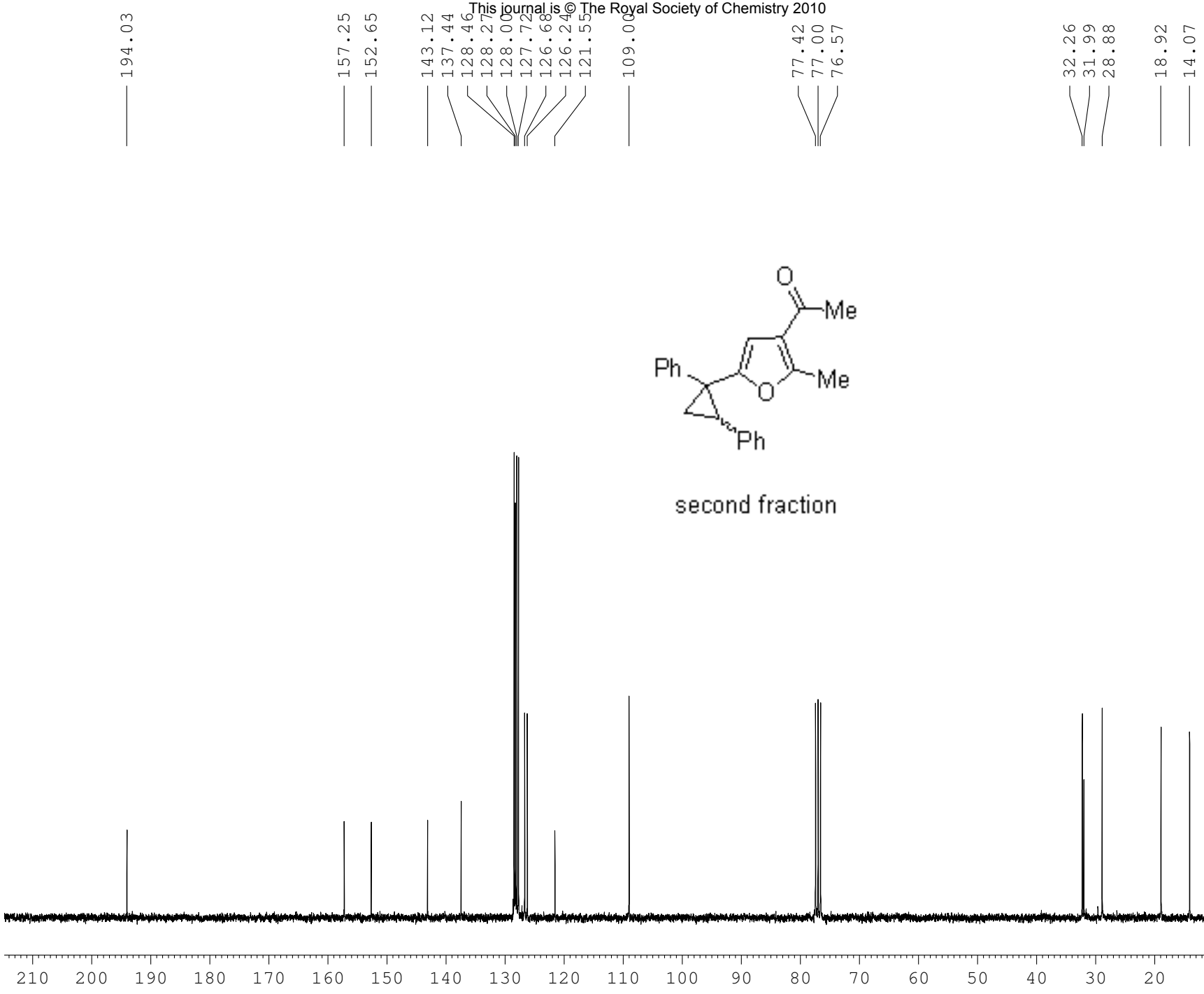

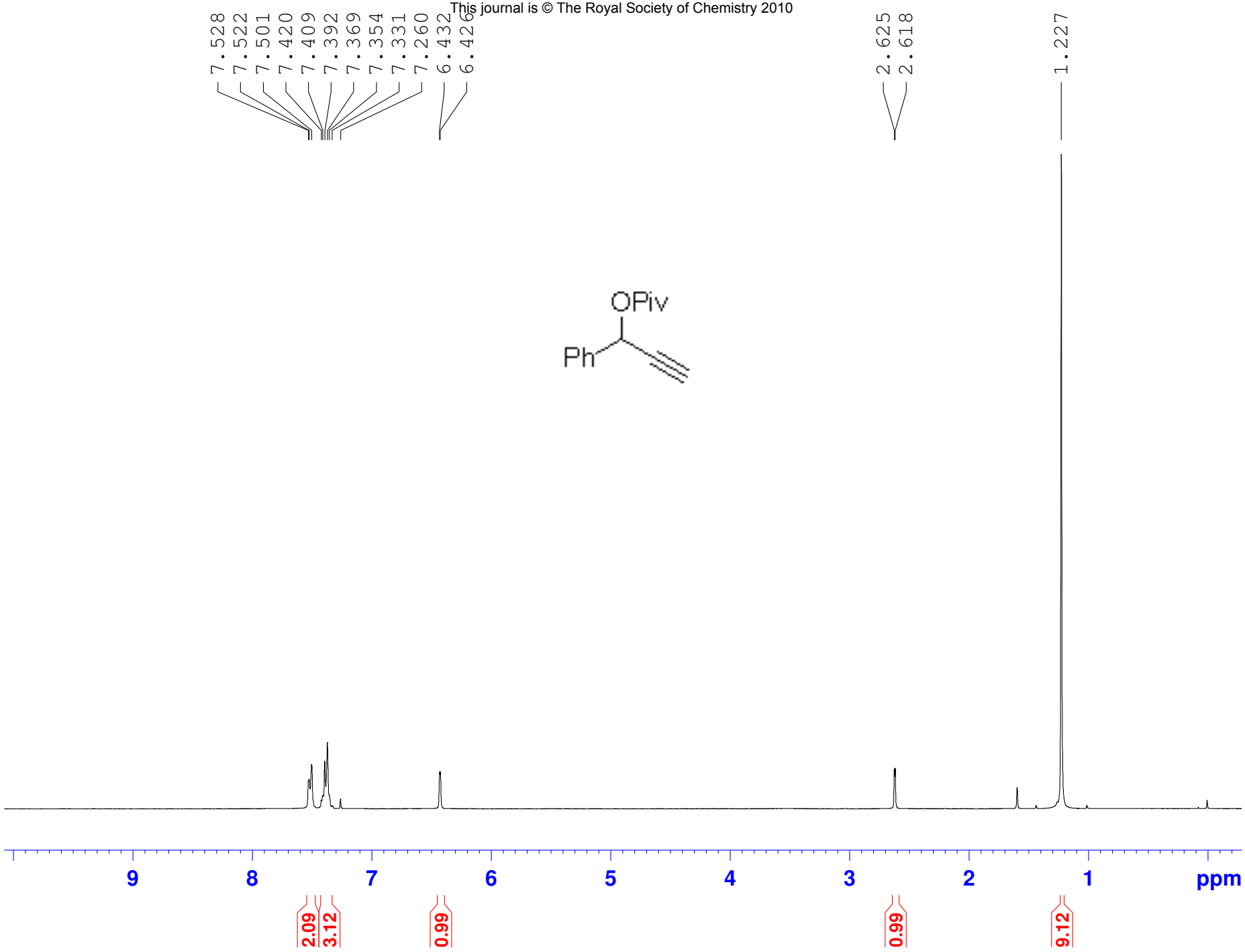

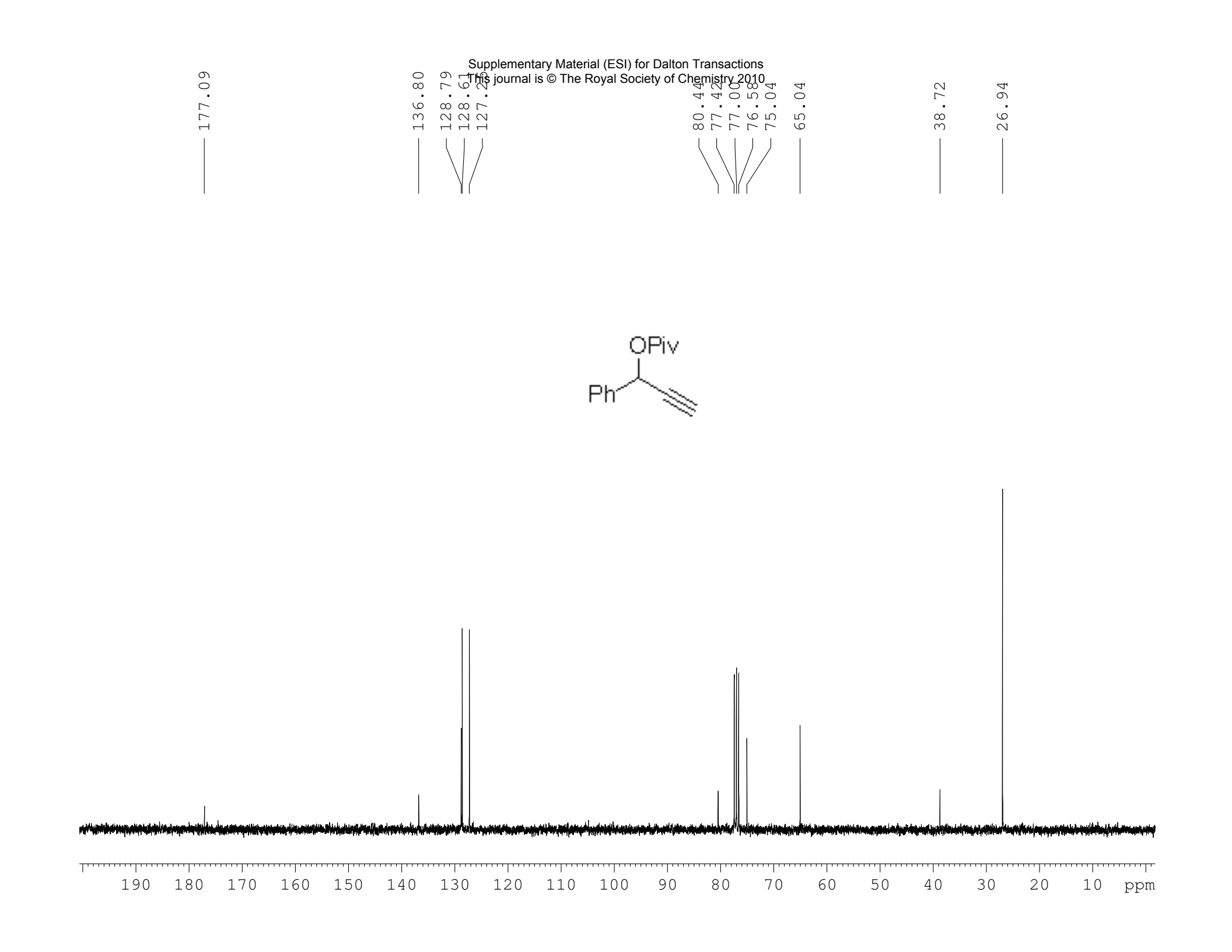

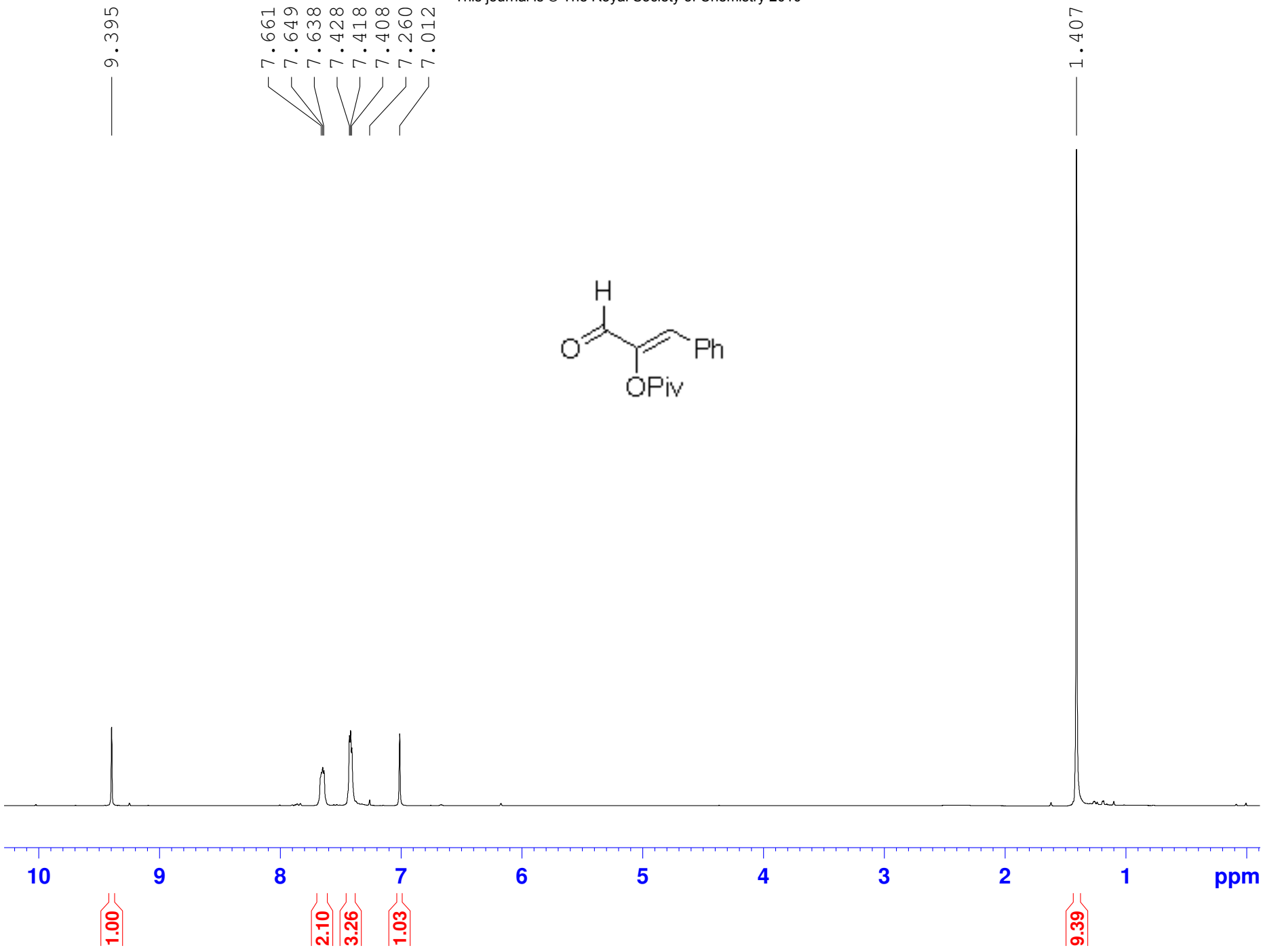

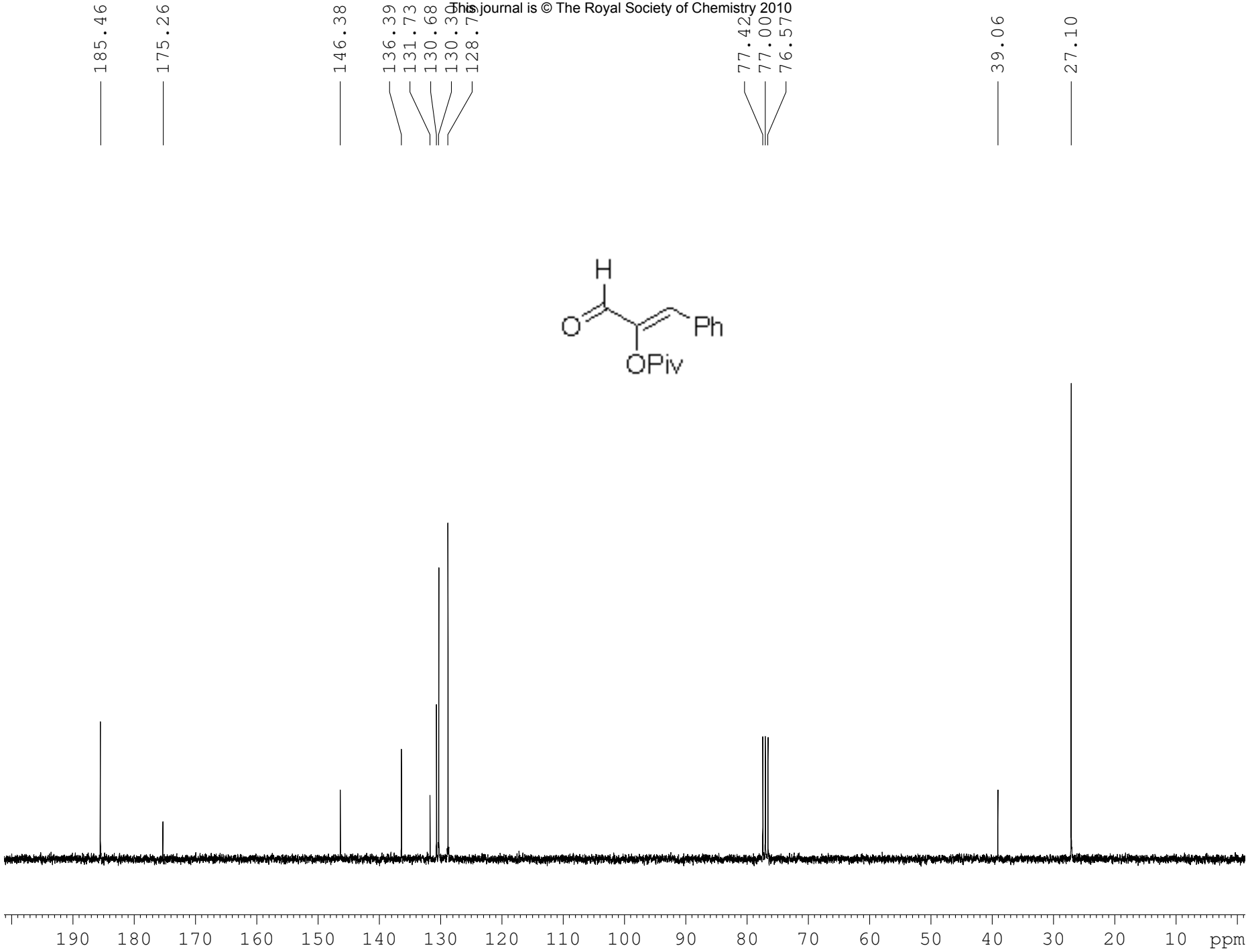

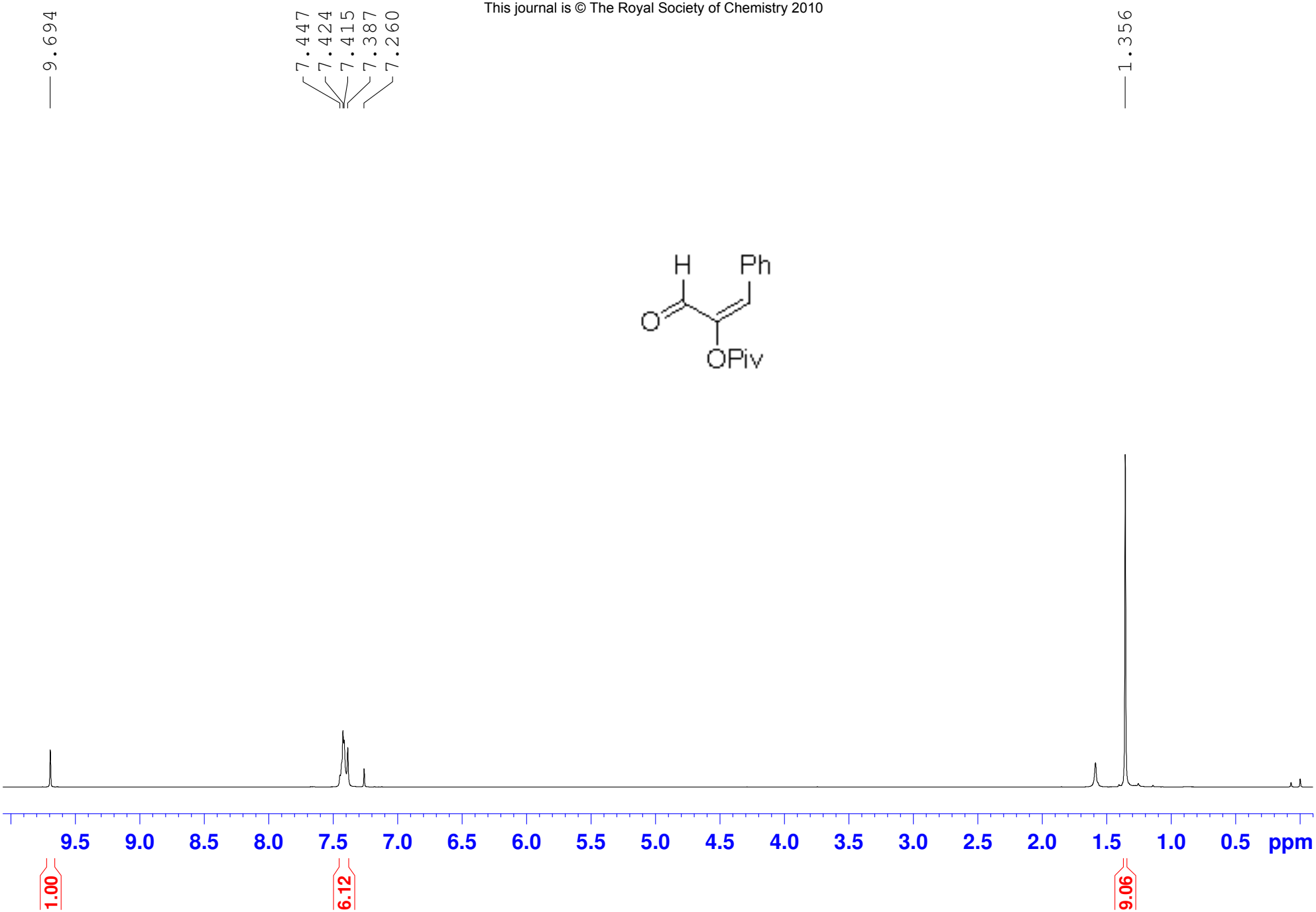
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