Silicon as a Directing Group in the Phosphine- Catalyzed [2+3]-Cycloaddition of Aryl Allenones with Electron-Deficient Olefins.

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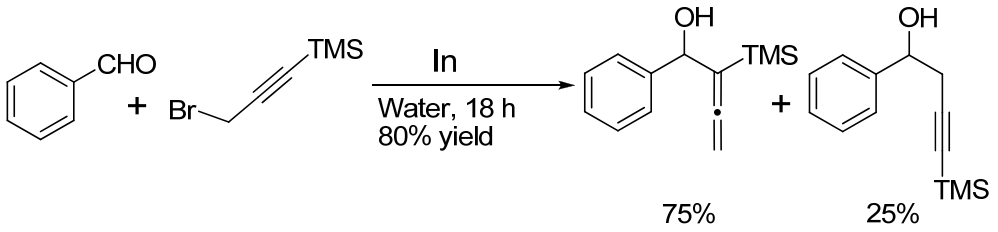
Supporting Information

I. General

Phosphine includes PPh_3, BINAP, (2*S*, 3*R*)-CHIRAPHOS, (*S*, *S*)-Et-DUPHOS, (*R*, *R*)-Et-DUPHOS, (+)-DIOP, (*S*)-(-)-2-[2-Diphenylphosphino)phenyl]-4-isopropyl-2-oxazoline were purchased from commercial suppliers. All reactions were carried out under nitrogen atmosphere unless otherwise stated. Commercial solvents and reagents were used without further purification with following exceptions: Toluene and Dichloromethane was distilled from calcium hydride prior to use. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. All HPLC chromatograms were recorded using Agilent 1100 and 1200 series. Infrared spectra were recorded on a Shimadzu IR Prestige-21 FT-IR. Liquid samples were examined as film between NaCl salt plates. HRMS spectra were recorded on a Waters Q – Tof Permier Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 300, 400 and 500MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.260, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet).

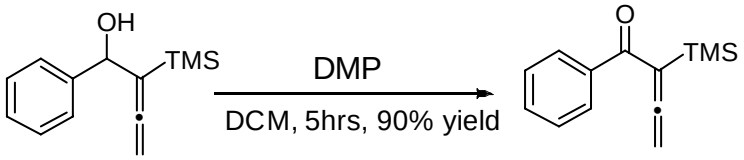
II. General Experimental Procedure for Aryl Allenone.

(a)



(3-bormoprop-1-ynyl) trimethylsilane (1.8 gm, 0.0103 mol) was added over 30 minutes to a mixture of Indium (1.2 g, 0.01037 mol) and benzaldehyde (1 g, 0.00943 mol) in water at 0 °C. After 18 h stirring, the reaction was quenched with 1 M HCl (30 mL) and extracted with ethylacetate (100 mL). The organic phase was then back washed with water (100 mL), brine (50 mL) and dried over Na_2SO_4 (anhydrous). The Allenic alcohol was purified through column chromatography (1% Ethylacetate in hexane) to give pale yellow oil of 1-phenyl-2-(trimethylsilyl) buta-2, 3-dien-1-one (1.3158 g, 80%).

(b)



Allenic alcohol (1.0 g, 0.0046 mol) obtained from the above reaction was added drop-wise to the round bottom flask containing Dess-Martin periodinane (2.14 g, 0.0050 mol) in dichloromethane (20 mL) at 0 °C under N_2 atmosphere. After 5 h stirring, the reaction mixture was diluted with dichloromethane (100mL), washed with 3M NaOH (50 mL) solution followed by water (100 mL) and brine (50 mL). The organic phase was dried over Na_2SO_4 (anhydrous) and concentrated to obtain the crude product. The Aryl allenone was purified through column chromatography (1% ethylacetate in hexane) to give colorless oil of 1- phenyl-2-(trimethylsilyl) buta-2, 3-dien-1-one (0.89 g, 90%).

^{1}H-NMR ($CDCl_3$, 300MHz): δ 7.80(m, 2H), 7.54(m, 1H), 7.45(m, 2H), 4.7(s, 2H), 0.24(s, 9H).

^{13}C-NMR ($CDCl_3$, 75MHz): δ 218.4, 195.1, 139.4, 132.0, 128.2 (2C), 127.4 (2C), 100.6, 70.3, 0.1.

HRMS (ESI) *m/z* calc. for $C_{13}H_{17}OSi^{+}$ $[M+H]^{+}$ 217.1049, found 217.1055.

FTIR (neat) ν = 1915, 1645, 1263, 1247, 842 cm^{-1}.

The same procedure was followed to synthesize **1-(furan-2-yl)-2-(trimethylsilyl) buta-2, 3-dien-1-one.**

^{1}H-NMR ($CDCl_3$, 300MHz): δ 7.58(brs, 1H), 7.27(m, 1H), 6.48(m, 1H), 4.82(s, 2H), 0.23(s, 9H).

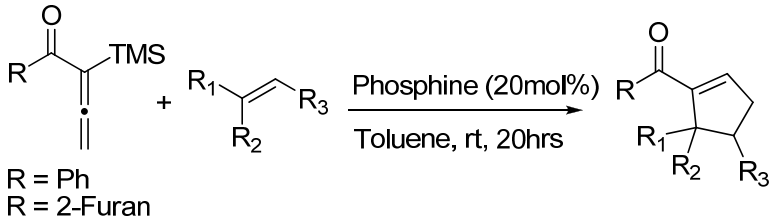
^{13}C-NMR ($CDCl_3$, 75MHz): δ 215.7, 181.4, 152.0, 146.2 (2C), 118.9, 111.6, 100.6, 99.7, -1.2.

HRMS (ESI) *m/z* calc. for $C_{11}H_{15}O_2Si^{+}$ $[M+H]^{+}$ 207.0841, found 207.0838.

FTIR (neat) ν = 1917, 1636, 1467, 1290, 1236, 748 cm^{-1}.

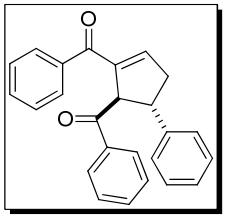
III. General Experimental Procedure for the [2+3] Cycloaddition Reaction

To a stirred solution of aryl allenone (50 mg; 0.23 mmol) and enone or enolate (0.25 mmol) in toluene (1.5 mL) was added drop-wise addition of phosphine (5.3 mg; 20 mol %) (Pre dissolved in toluene) at 0° C under nitrogen. After 20hrs stirring at room temperature under N_2 atmosphere, the reaction mixture was concentrated and purified using flash column chromatography (15-20% ethylacetate in Hexane).



This procedure is common for Tables 1 and 2, unless otherwise stated. For Table-3, CH_2Cl_2 (1.5mL) was used as solvent, unless otherwise stated.

(5-phenylcyclopent-2-ene-1,2-diyl)bis(phenylmethanone) (2a)



R_f: 0.6 (Hex: EA = 4:1)

^{1}H – NMR ($CDCl_3$, 300MHz) δ 7.8 (m, 2H), 7.7 (m, 2H), 7.45 (m, 1H), 7.4 (m, 3H), 7.25-7.35(m, 4H), 7.15 (m, 3H), 6.7(m, 1H), 5.1(m, 1H), 3.55(dt, *J* = 8.8, 5.4 Hz, 1H), 3.25(ddt, *J* = 19.0, 8.8, 2.3 Hz, 1H), 2.75(m, 1H).

^{13}C – NMR ($CDCl_3$, 75MHz) δ 200.8, 192.8, 146.1, 144.6, 143.7, 138.2, 136.5, 133.0, 132.2, 129.1 (2C), 128.9 (2C), 128.8 (2C), 128.3 (2C), 128.2 (2C), 127.0, 126.9 (2C), 60.9, 48.3, 43.1

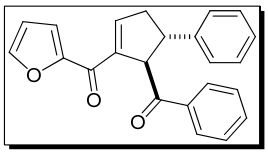
FTIR (neat) ν = 3018, 1674, 1641, 1598, 1251, 756 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{25}H_{21}O_2^+$ $[M+H]^+$ 353.1542, found 353.1544.

HPLC analysis [Table 3, entry 1]: 71% ee Daicel CHIRALPAK AD; Solvent system: 2% isopropanol/hexane; retention time: (minor) 15.0min, (major) 22.4min.

$[\alpha]_D^{20}$ = + 130° (*c* 0.2, CH_2Cl_2)

(5-benzoyl-4-phenylcyclopent-1-enyl)(furan-2-yl)methanone (4a)



R_f : 0.6 (Hex:EA = 4:1)

^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.8(m, 2H), 7.6(m, 1H), 7.5(m, 1H), 7.44(m, 1H), 7.35-7.15(m, 8H), 6.55(dd, *J* = 3.53, 1.69 Hz, 1H), 5.1(m, 1H), 3.55(dt, *J* = 8.8, 5.3 Hz, 1H), 3.35(ddt, *J* = 19.1, 8.9, 2.3 Hz, 1H), 2.88(m, 1H).

^{13}C-NMR ($CDCl_3$, 100MHz) δ 200.7, 177.7, 152.9, 146.1, 145.8, 144.7, 142.5, 136.4, 132.9, 128.9, 128.8 (2C), 128.3 (2C), 127.0, 126.9 (2C), 118.4, 112.1, 60.9, 53.4, 47.7, 43.4

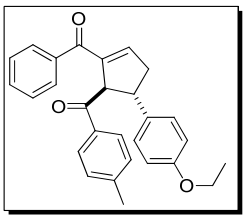
FTIR (neat) ν = 3018, 1629, 1560, 1467, 1215, 748 cm^{-1}.

HRMS (ESI) *m/z* calc. for $C_{23}H_{19}O_3^+$ $[M+H]^+$ 343.1344, found 343.1436.

HPLC analysis [Table 3, entry 2]: 92%ee [Daicel Chiralpak AD-H; solvent system: 2% isopropanol/hexane; retention time: (minor) 26.2min (major) 44.2min.

$[\alpha]_D^{20} = +55°$ (*c* 0.2, CH_2Cl_2)

(2-benzoyl-5-(4-ethoxyphenyl)cyclopent-2-enyl)(*p*-tolyl)methanone (2b)



R_f: 0.5 (Hex: EA = 4:1)

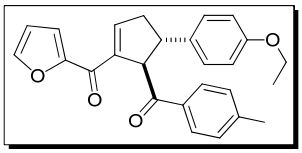
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.9(m, 2H), 7.7(m, 2H), 7.55(m, 1H), 7.45(m, 2H), 7.15(m, 4H), 6.85(m, 2H), 6.75(m, 1H), 5.11(m, 1H), 4.05(q, *J* = 6.9 Hz, 2H), 3.58(dt, *J* = 8.8, 5.4 Hz, 1H), 3.3(ddt, *J* = 18.9, 8.8, 2.2 Hz, 1H), 2.78(m, 1H), 2.36(s, 3H), 1.42(t, J = 6.9 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75MHz) δ 200.4, 192.8, 157.8, 146.0, 143.7, 143.7, 138.2, 136.7, 133.9, 132.1, 129.2 (2C), 129.1 (2C), 129.0 (2C), 128.1 (2C), 127.8 (2C), 114.7 (2C), 63.4, 61.0, 47.6, 43.2, 21.5, 14.8

FTIR (neat) ν = 3018, 1641, 1608, 1512, 1215, 756 cm^{-1}.

HRMS (ESI) *m/z* calc. for $C_{28}H_{27}O_3^+$ $[M+H]^+$ 411.1960, found 411.1943.

(5-(4-ethoxyphenyl)-2-(furan-2-carbonyl)cyclopent-2-enyl)(*p*-tolyl)methanone (4b)



R_f: 0.6 (Hex: EA = 4:1)

^{1}H-NMR ($CDCl_3$, 300Mz) δ 7.7(m, 2H), 7.58(brs, 1H), 7.39(brs, 1H), 7.25(brs, 1H), 7.13(m, 4H), 6.84(m, 2H), 6.53(dd, *J* = 3.3, 1.4 Hz, 1H), 5.05(m, 1H), 4.0(q, *J* = 6.9 Hz, 2H), 3.5(dt, *J* = 8.8, 5.1 Hz, 1H), 3.3(ddt, *J* = 19.2, 9.2, 1.9 Hz, 1H), 2.8(m, 1H), 2.3(s, 3H), 1.4(t, *J* = 6.9 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75MHz) δ 200.3, 177.8, 157.8, 153.0, 146.0, 145.7, 143.7, 142.5, 136.9, 133.9, 129.1 (2C), 129.0 (2C), 127.8, 118.4, 114.7, 112.1, 63.4, 61.0, 47.0, 43.5, 21.6, 14.8

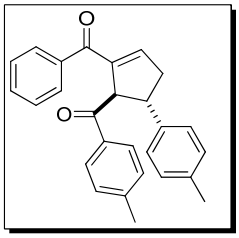
FTIR (neat) ν = 3016, 1672, 1631, 1608, 1512, 1467, 1246, 1217, 756 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{26}H_{25}O_4^+$ $[M+H]^+$ 401.1753, found 401.1751.

HPLC analysis [Table 3, entry 3]: 70% ee [Daicel Chiralpak AD-H, solvent system: 15% isopropanol/hexane, retention time: (minor) 11.8min. (major) 60.5min.

$[\alpha]_D^{20}$ = + 62° (*c* 0.2, CH_2Cl_2)

2-benzoyl-5-*p*-tolylcyclopent-2-enyl)(*p*-tolyl)methanone (2c)



R_f: 0.4 (Hex: EA = 4:1)

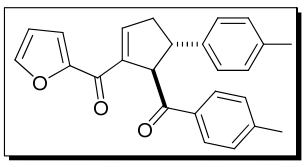
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.8(m, 2H), 7.7(m, 2H), 7.55(m, 1H), 7.45(m, 2H), 7.15(brs, 6H), 6.75(m, 1H), 5.13(m, 1H), 3.55(dt, *J* = 8.8, 5.24 Hz, 1H), 3.3(ddt *J* = 19.0, 8.8, 2.3 Hz, 1H), 2.8(m, 1H), 2.36(s, 3H), 2.35(s, 3H).

^{13}C-NMR ($CDCl_3$, 100MHz) δ 200.5, 192.9, 146.2, 143.9, 143.8, 143.7, 141.9, 138.3, 136.5, 134.0, 132.1, 129.5 (2C), 129.2 (2C), 129.1, 129.0 (2C), 128.2 (2C), 126.8 (2C), 60.8, 47.9, 43.3, 21.6, 21.0

FTIR (neat) ν = 3016, 1637, 1606, 1217, 756 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{27}H_{25}O_2^+$ $[M+H]^+$ 381.1855, found 381.1841.

2-(furan-2-carbonyl)-5-*p*-tolylcyclopent-2-enyl)(*p*-tolyl)methanone (4c)



R_f: 0.4(Hex: EA = 4:1)

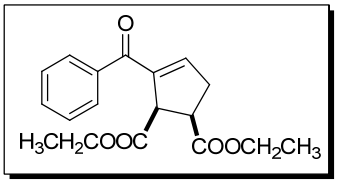
^{1}H-NMR ($CDCl_3$, 300Hz) δ 7.7(m, 2H), 7.5(m, 1H), 7.4(m, 1H), 7.25(m, 1H), 7.13(m, 6H), 6.53(dd, *J* = 3.3, 1.4 Hz, 1H), 5.0(m, 1H), 3.5(dt, *J* = 8.9, 5.0 Hz, 1H), 3.3(ddt, *J* = 19.0, 8.9, 2.3 Hz, 1H), 2.83(m, 1H), 2.35(s, 3H), 2.33(s, 3H).

^{13}C-NMR ($CDCl_3$, 100MHz) δ 200.3, 177.9, 153.0, 146.1, 145.9, 143.8, 142.6, 142.0, 136.5, 133.9, 129.5 (2C), 129.1 (2C), 129.0 (2C), 126.8 (2C), 118.5, 112.1, 60.9, 47.3, 43.6, 21.6, 21.0

FTIR (neat) ν = 3018, 2924, 1672, 1606, 1467, 1217, 756 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{25}H_{23}O_3^+$ $[M+H]^+$ 371.1647, found 371.1644.

Diethyl 3-benzoylcyclopent-3-ene-1,2-dicarboxylate (2d)



R_f: 0.6 (Hex: EA = 4:1)

^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.7(m, 2H), 7.54(m, 1H), 7.45(m, 2H), 6.62(m, 1H), 4.27(m, 1H), 4.18-4.08(m, 4H), 3.53(q, *J* =9.0 Hz, 1H), 3.33(ddt, *J* = 18.4, 8.7, 2.3 Hz, 1H), 2.85(ddd, *J* = 18.6, 8.7, 2.7 Hz, 1H), 1.29-1.2(m, 6H).

^{13}C-NMR ($CDCl_3$, 75MHz) δ 196.0, 172.0, 171.6, 145.9, 141.6, 137.8, 132.4, 129.0 (2C), 128.3 (2C), 61.0, 52.3, 46.0, 36.1, 30.9, 14.1, 14.0

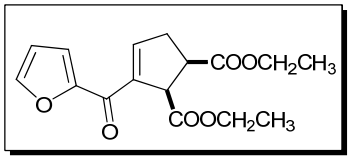
FTIR (neat) ν = 3018, 1734, 1635, 1629, 1215, 756 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{18}H_{21}O_5^+$ $[M+H]^+$ 317.1389, found 317.1375.

HPLC analysis [Table 3, entry 5]: 80%ee [Daicel Chiralpak AD-H, solvent system: 2% isopropanol/hexane, retention time: (major) 44.5min. (minor) 61.0min.

$[\alpha]_D^{20}$ = - 64° (*c* 0.5, CH_2Cl_2)

Diethyl 3-(furan-2-carbonyl)cyclopent-3-ene-1,2-dicarboxylate (4d)



R_f: 0.5 (Hex: EA = 4:1)

^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.59(brs, 1H), 7.25(m, 2H), 6.53(dd, *J* = 3.5, 1.6 Hz, 1H), 4.24(m, 1H), 4.18-4.08(m, 4H), 3.5(q, *J* = 9.0 Hz, 1H), 3.3(ddt, *J* = 18.6, 8.7, 2.2 Hz, 1H), 2.9(ddd, *J* = 18.6, 8.8, 2.9 Hz, 1H), 1.2(m, 6H).

^{13}C-NMR ($CDCl_3$, 75MHz) δ 177.4, 171.9, 171.6, 152.6, 146.2, 145.8, 140.6, 118.5, 112.1, 61.0 (2C), 52.1, 45.7, 36.3, 14.1, 14.0

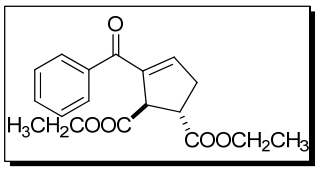
FTIR (neat) ν = 3018, 1734, 1635, 1467, 1215, 771 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{16}H_{19}O_6^+$ $[M+H]^+$ 307.1182, found 307.1173.

HPLC analysis [Table 3, entry 4]: 74% ee [Daicel Chiralpak AD-H, solvent system: 5% isopropanol/hexane, retention time: (major) 26.9min. (minor) 43.1min.

$[\alpha]_D^{20}$ = - 48° (*c* 0.5, CH_2Cl_2)

Diethyl 3-benzoylcyclopent-3-ene-1,2-dicarboxylate (2e)



R_f: 0.6 (Hex: EA = 4:1)

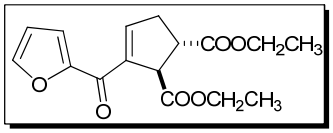
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.76(m, 2H), 7.55(m, 1H), 7.43(m, 2H), 6.51(m, 1H), 4.3(m, 1H), 4.26-4.15(m, 4H), 3.46(m, 1H), 2.9(m, 2H), 1.27(t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75MHz) δ 192.2, 173.3, 173.0, 144.3, 141.6, 137.9, 132.3, 128.9 (2C), 128.3 (2C), 61.3, 61.2, 53.8, 46.1, 36.7, 14.2, 14.1

FTIR (neat) ν = 3020, 2981, 1730, 1647, 1577, 1217, 754 cm^{-1}.

HRMS (ESI) *m*/*z* calc. for $C_{18}H_{21}O_5^+$ $[M+H]^+$ 317.1389, found 317.1377.

Diethyl 3-(furan-2-carbonyl)cyclopent-3-ene-1,2-dicarboxylate (4e)



R_f: 0.6 (Hex: EA = 4:1)

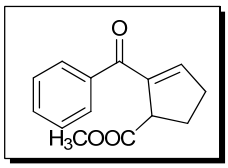
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.58(m, 1H), 7.22(m, 1H), 7.1(m, 1H), 6.52(dd, *J* = 3.5, 1.7 Hz, 1H), 4.32(m, 1H), 4.25-4.1(m, 4H), 3.37(m, 1H), 3.05(m, 2H), 1.26(t, *J* = 7.1 Hz, 3H), 1.25(t, *J* = 7.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75MHz) δ 177.4, 173.2, 173.0, 152.6, 146.2, 144.0, 144.9, 118.4, 112.1, 61.2, 61.1, 53.7, 45.7, 37.0, 14.1, 14.0

FTIR (neat) ν = 3020, 2983, 1732, 1635, 1467, 1217, 754 cm^{-1}.

HRMS (ESI) *m/z* calc. for $C_{16}H_{19}O_6^+$ $[M+H]^+$ 307.1182, found 307.1194.

Methyl 2-benzoylcyclopent-2-enecarboxylate (2f)



R_f: 0.4 (Hex: EA = 4:1)

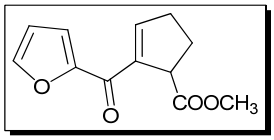
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.7(m, 2H), 7.55(m, 1H), 7.43(m, 2H), 6.64(m, 1H), 4.04(m, 1H), 3.7(s, 3H), 2.8(m, 1H), 2.6-2.7(m, 1H), 2.35-2.45(m, 1H), 2.1-2.2(m, 1H)

^{13}C-NMR ($CDCl_3$, 75MHz) δ 192.9, 175.0, 147.7, 142.8, 138.2, 132.2, 129.0 (2C), 128.2 (2C), 52.1, 49.9, 33.5, 28.0

FTIR (neat) ν = 3018, 1732, 1643, 1435, 1215, 167 cm^{-1}.

HRMS (ESI) *m/z* calc. for $C_{14}H_{15}O_3^+$ $[M+H]^+$ 231.1021, found 231.1017.

Methyl 2-(furan-2-carbonyl)cyclopent-2-enecarboxylate (4f)



R_f: 0.5 (Hex: EA = 4:1)

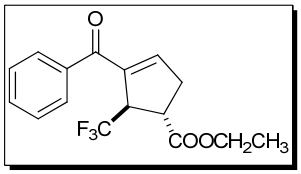
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.59(m, 1H), 7.23(m, 2H), 6.53(dd, *J* = 3.5, 1.7 Hz, 1H), 4.02(m, 1H), 3.68(s, 3H), 2.4-2.1(m, 2H), 2.35(m, 1H), 2.10(m, 1H).

^{13}C-NMR ($CDCl_3$, 100MHz) δ 178.1, 174.9, 152.8, 147.1, 146.1, 141.7, 118.2, 112.0, 52.0, 49.9, 33.8, 27.6

FTIR (neat) ν = 3018, 1734, 1629, 1215, 756 cm^{-1}.

HRMS (EI) *m/z* calc. for $C_{12}H_{12}O_4^+$ $[M]^+$ 220.0730, found 220.0733

Ethyl 3-benzoyl-2-(trifluoromethyl)cyclopent-3-enecarboxylate (2g)



R_f: 0.6 (Hex: EA = 4:1)

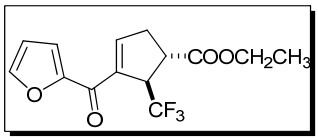
^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.7(m, 2H), 7.55(m, 1H), 7.45(m, 2H), 6.5(m, 1H), 4.2(m, 3H), 3.3(m, 1H), 3.0 (ddt, *J* = 19.0, 9.3, 2.5 Hz, 1H), 2.8(m, 1H), 1.25(t, *J* =7.1 Hz, 3H)

^{13}C-NMR ($CDCl_3$, 100MHz) δ 191.8, 172.3, 143.2, 141.5, 137.6, 132.5 (2C), 128.9 (2C), 128.4 (2C), 61.6, 51.1 (q), 45.1 (q), 33.9 (q), 14.0

FTIR (neat) ν = 3018, 1730, 1647, 1215, 1114, 756 cm^{-1}.

HRMS (ESI) *m/z* calc. for $C_{16}H_{16}O_3F_3^+$ $[M+H]^+$ 313.1052, found 313.1040.

Ethyl 3-(furan-2-carbonyl)-2-(trifluoromethyl)cyclopent-3-enecarboxylate (4g)



R_f: 0.5 (Hex: EA = 4:1)

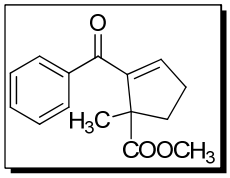
^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.6(m, 1H), 7.25(m, 1H), 7.15(m, 1H), 6.55(dd, *J* = 3.5, 1.7 Hz, 1H), 4.2(m, 3H), 3.25(m, 1H), 3.05(ddt, *J* = 19.0, 9.3, 2.5 Hz, 1H), 2.85(m, 1H), 1.25(t, *J* = 7.1 Hz, 3H)

^{13}C-NMR ($CDCl_3$, 75MHz) δ 176.9, 172.4, 152.6, 146.3, 143.1, 140.4, 118.6, 112.3 (2C), 61.5, 51.2 (q), 44.6 (q), 34.2 (q), 13.9

FTIR (neat) ν = 3016, 1633, 1618, 1215, 756 cm^{-1}.

HRMS (ESI) *m/z* calc. for $C_{14}H_{14}O_4F_3^+$ $[M+H]^+$ 303.0844, found 303.0862.

Methyl 2-benzoyl-1-methylcyclopent-2-enecarboxylate (2h)



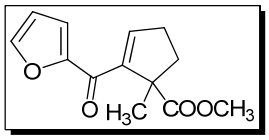
R_f: 0.6 (Hex: EA = 4:1)

^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.73(m, 2H), 7.53(m, 1H), 7.42(m, 2H), 6.54(t, *J* = 2.5 Hz, 1H), 3.68(s, 3H), 2.66(m, 2H), 2.3-2.4(m, 1H), 1.9-2.0(m, 1H), 1.53(s, 3H)

^{13}C-NMR ($CDCl_3$, 100MHz) δ 178.1, 176.5, 153.1, 146.5, 145.9, 145.9, 128.9 (2C), 128.7 (2C), 55.5, 52.1, 37.4, 32.3, 21.9

FTIR (neat) ν = 3018, 1728, 1622, 1469, 1214, 755 cm^{-1}.

Methyl 2-(furan-2-carbonyl)-1-methylcyclopent-2-enecarboxylate (4h)



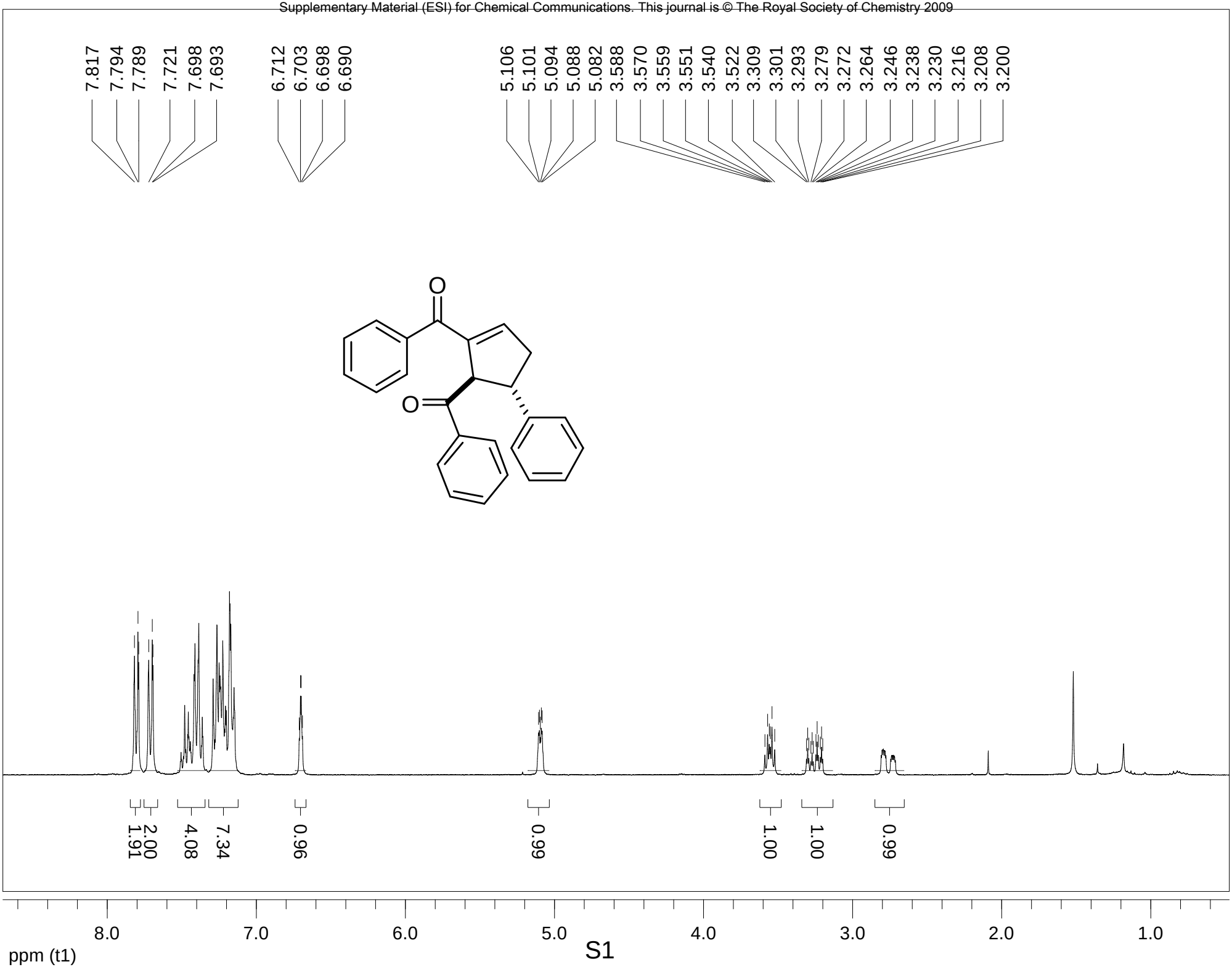
R_f: 0.6 (Hex: EA = 4:1)

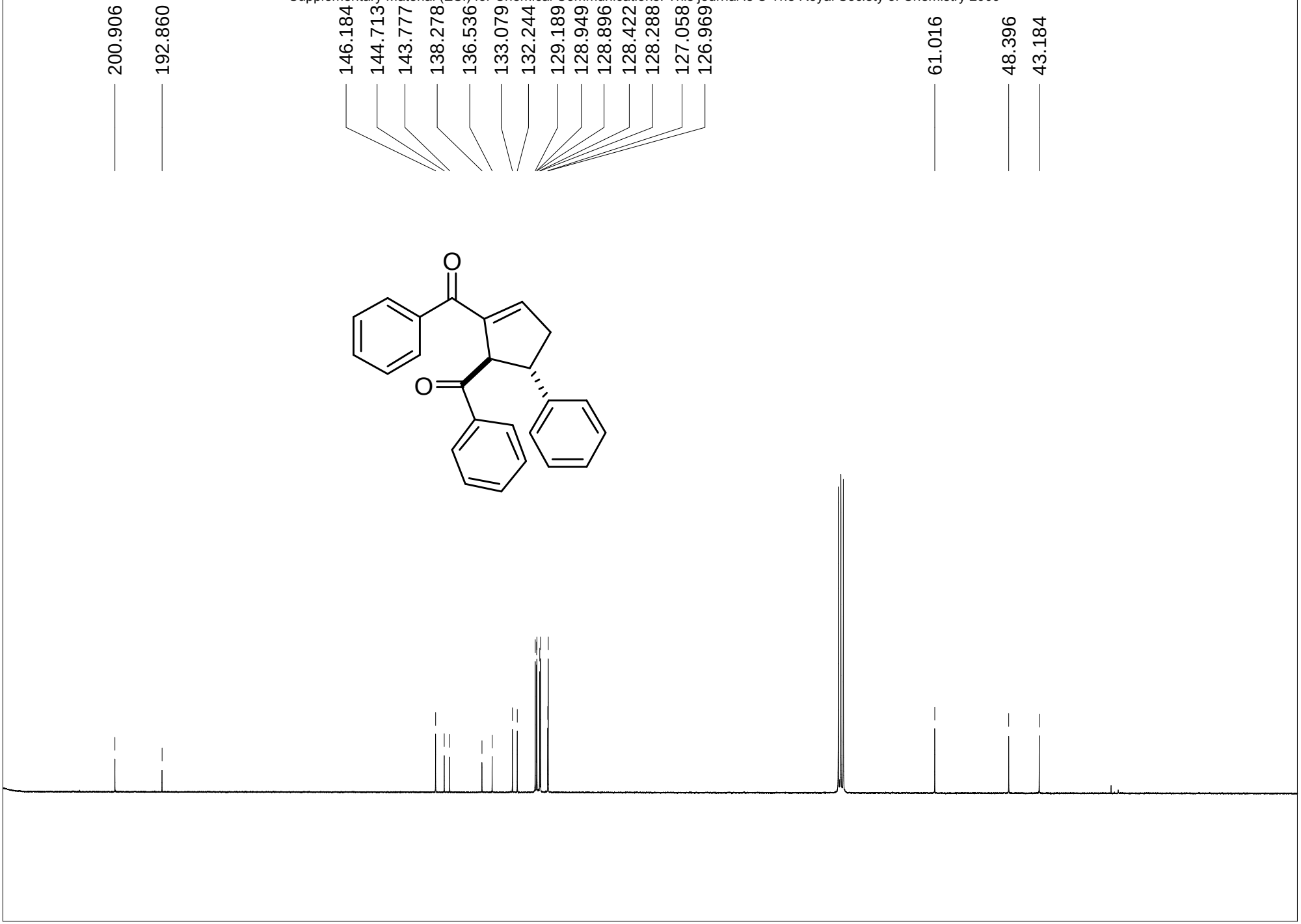
^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.58(m, 1H), 7.18(m, 2H), 6.52(dd, *J* =3.4, 1.6 Hz, 1H), 3.6(s, 3H), 2.7(m, 2H), 2.3(m, 1H), 1.95(m, 1H), 1.47(s, 3H).

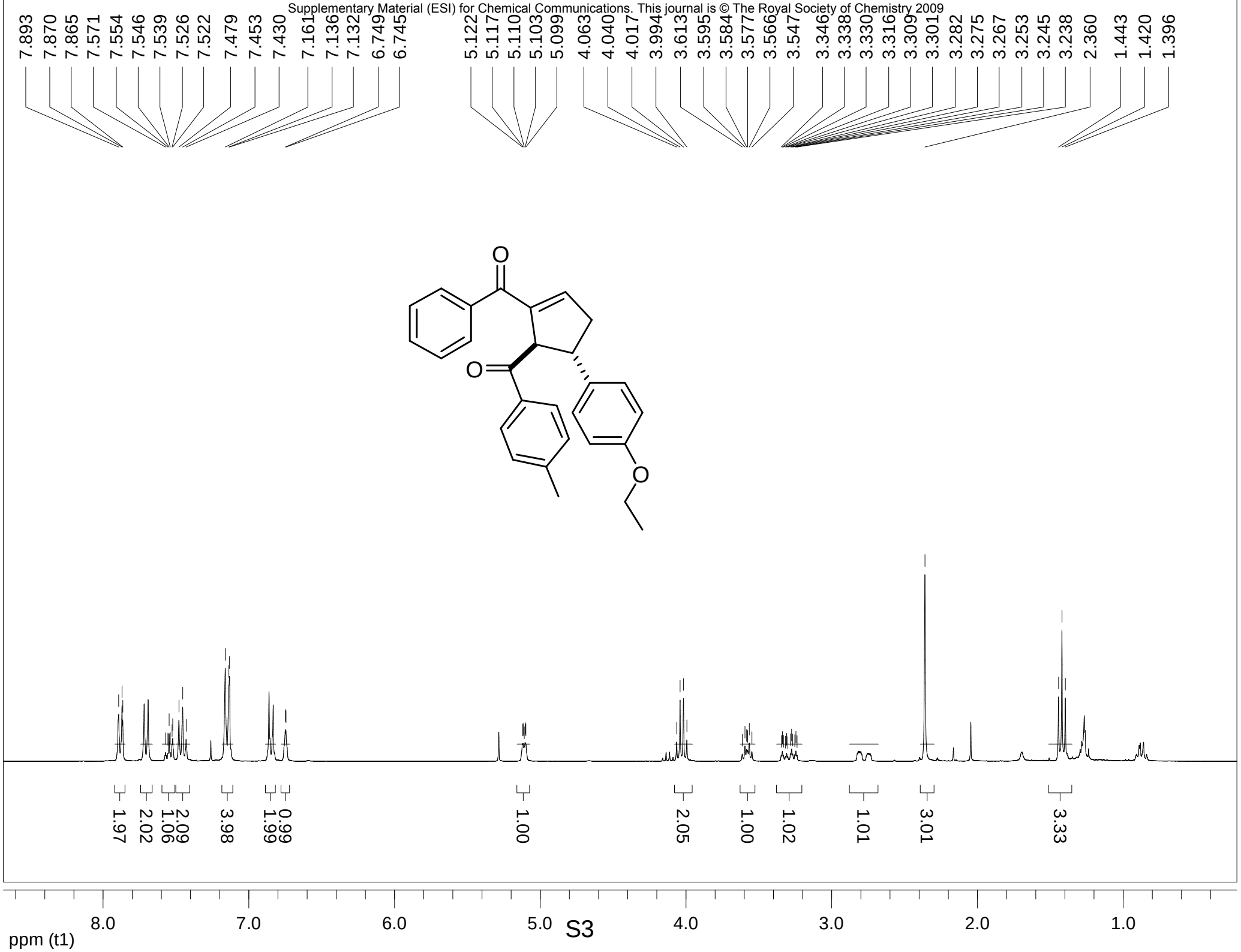
^{13}C-NMR ($CDCl_3$, 100MHz) δ 178.0, 176.5, 153.1, 146.5, 145.9 (2C), 118.0, 112.0, 55.5, 52.1, 37.3, 32.3, 21.9

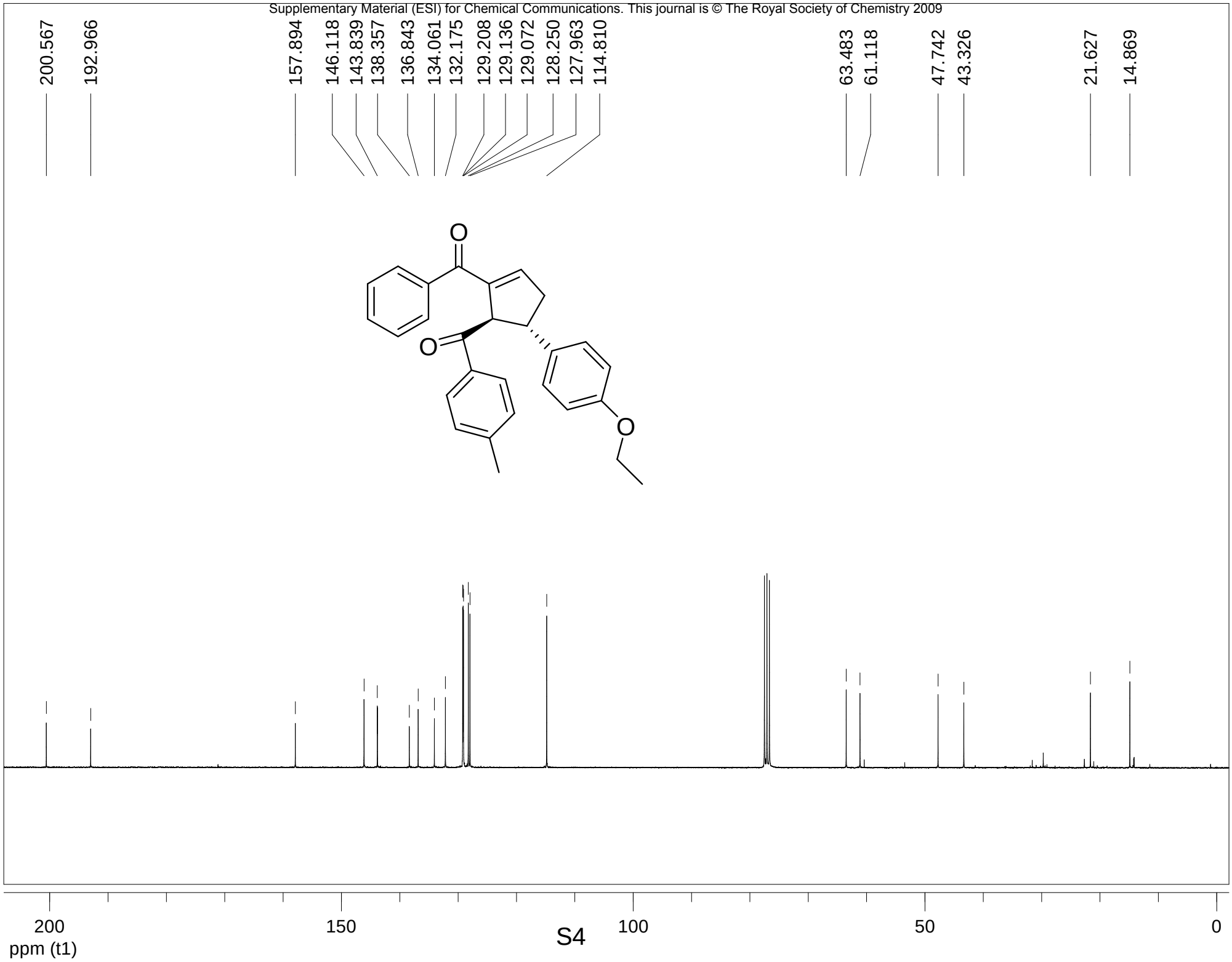
FTIR (neat) ν = 3020, 1728, 1629, 1467, 1215, 754 cm^{-1}.

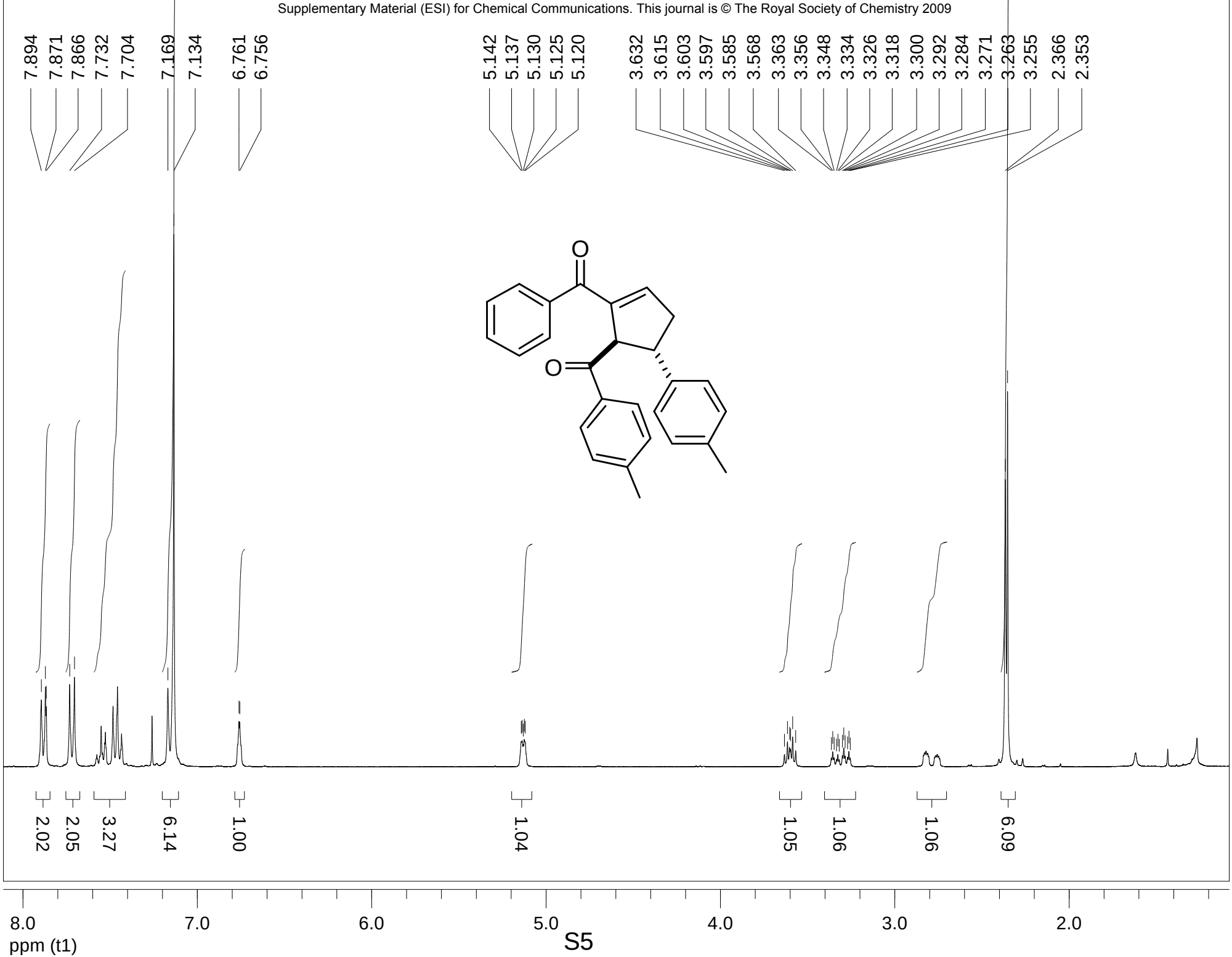
HRMS (ESI) *m*/*z* calc. for $C_{13}H_{15}O_4^+$ $[M+1]^+$ 235.0970, found 235.0969.







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7.169
7.134
6.761
6.756
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5.137
5.130
5.125
5.120
3.632
3.615
3.603
3.597
3.585
3.568
3.363
3.356
3.348
3.334
3.326
3.318
3.300
3.292
3.284
3.271
3.263
3.255
2.366
2.353
O
O
2.02
2.05
3.27
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1.00
1.04
1.05
1.06
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6.09
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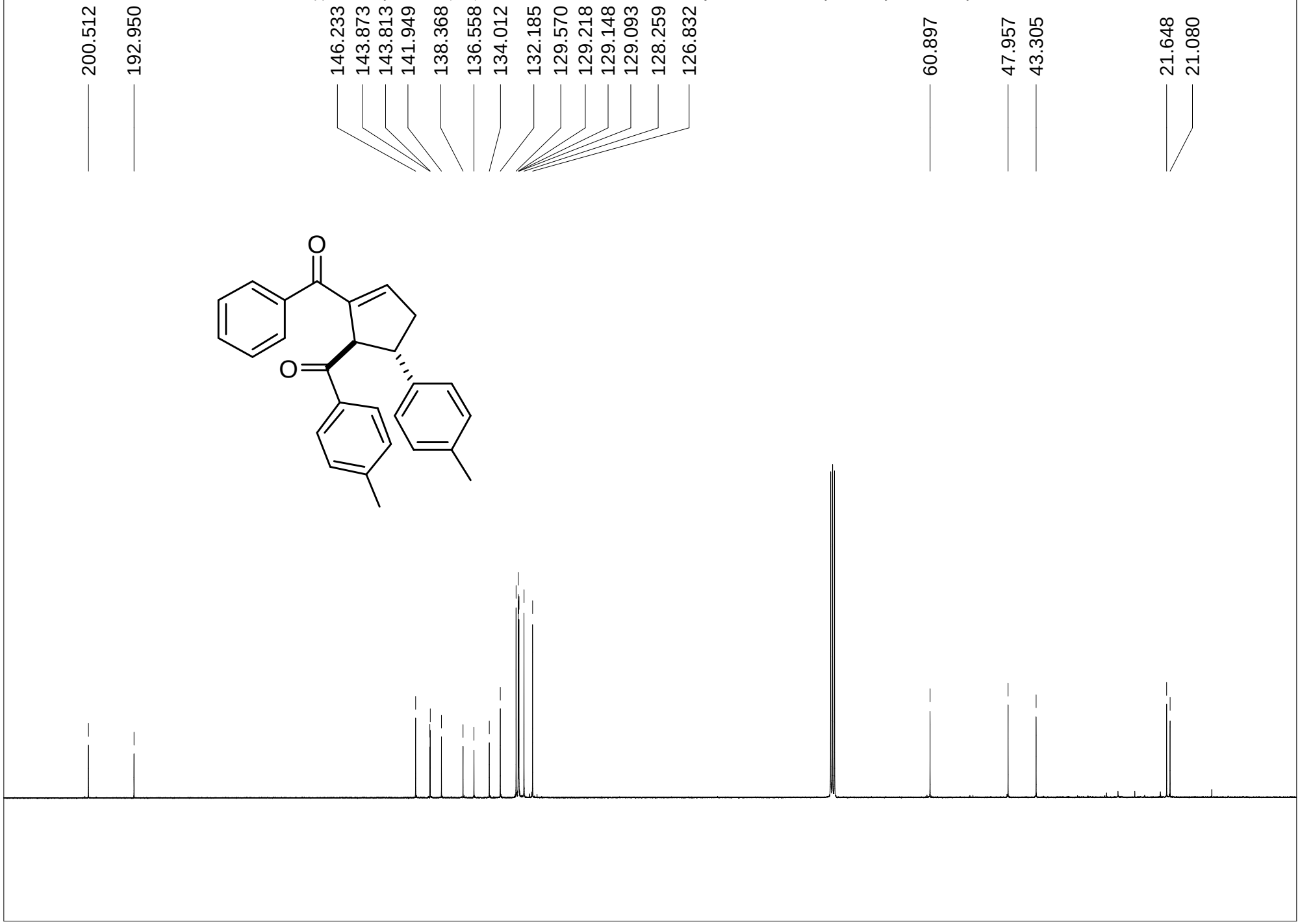
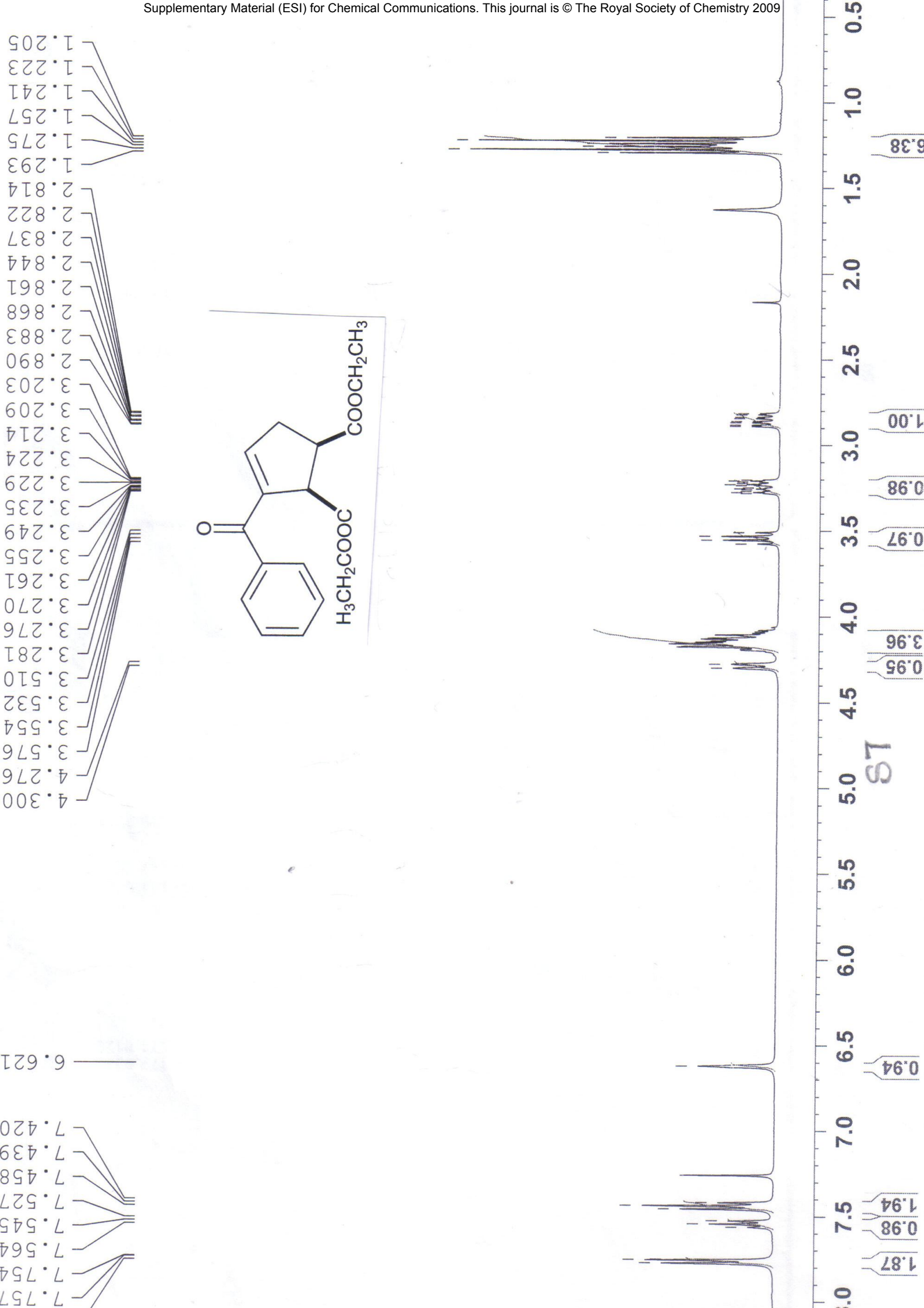
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

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1.241
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1.293
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2.822
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2.868
2.883
2.890
3.203
3.209
3.214
3.224
3.229
3.235
3.249
3.255
3.261
3.270
3.276
3.281
3.510
3.532
3.554
3.576
4.276
4.300
6.621
7.420
7.439
7.458
7.527
7.545
7.564
7.754
7.757
O
COOCH2CH3
H3CH2COOC
6.38
1.00
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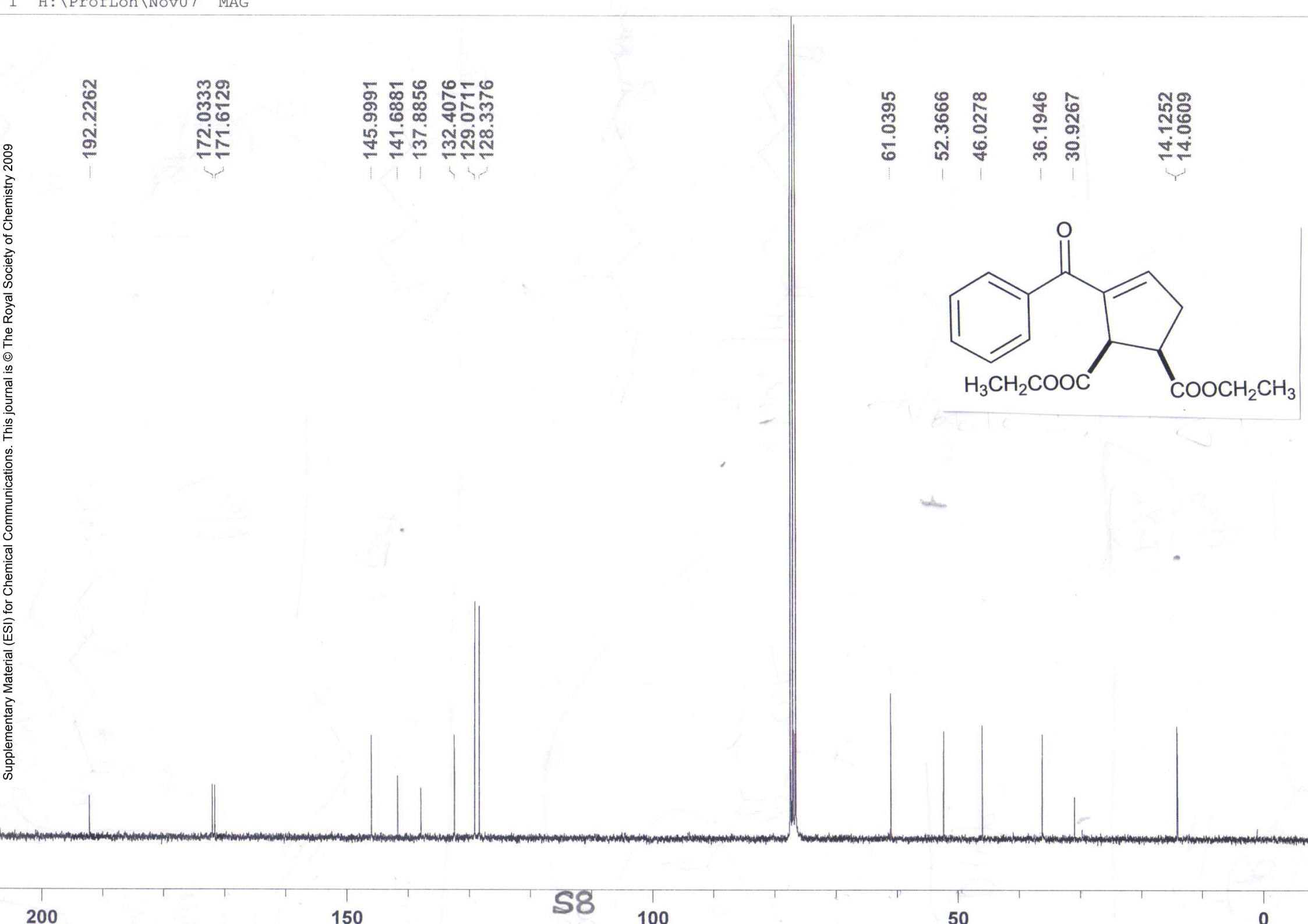
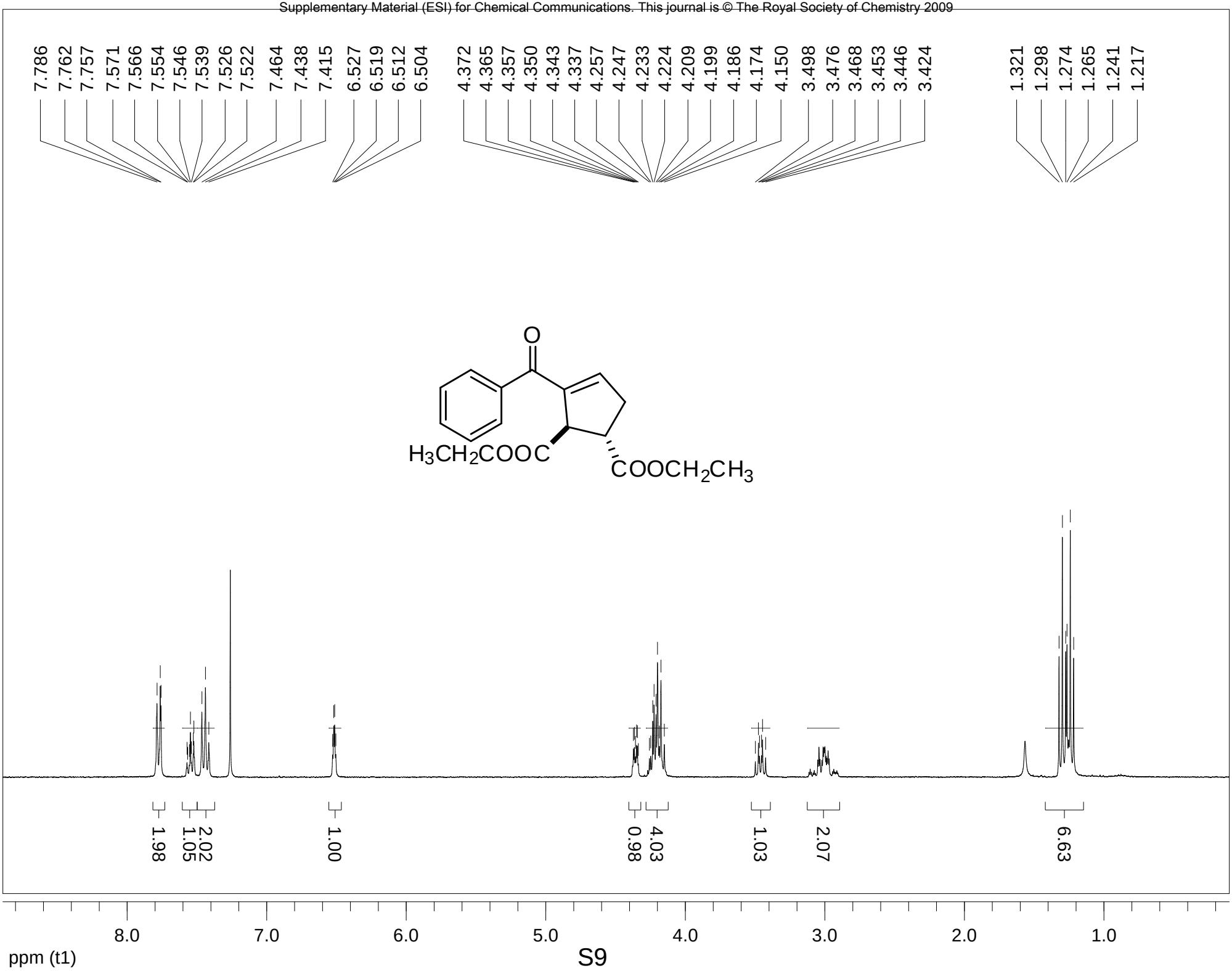
0.97
3.96
0.95
0.94
1.94
0.98
1.87
ST

1 H:\ProTon\Nov07 MAG

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7.522
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6.527
6.519
6.512
6.504
4.372
4.365
4.357
4.350
4.343
4.337
4.257
4.247
4.233
4.224
4.209
4.199
4.186
4.174
4.150
3.498
3.476
3.468
3.453
3.446
3.424
1.321
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1.274
1.265
1.241
1.217
O
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COOCH2CH3
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2.02
1.00
0.98
4.03
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6.0
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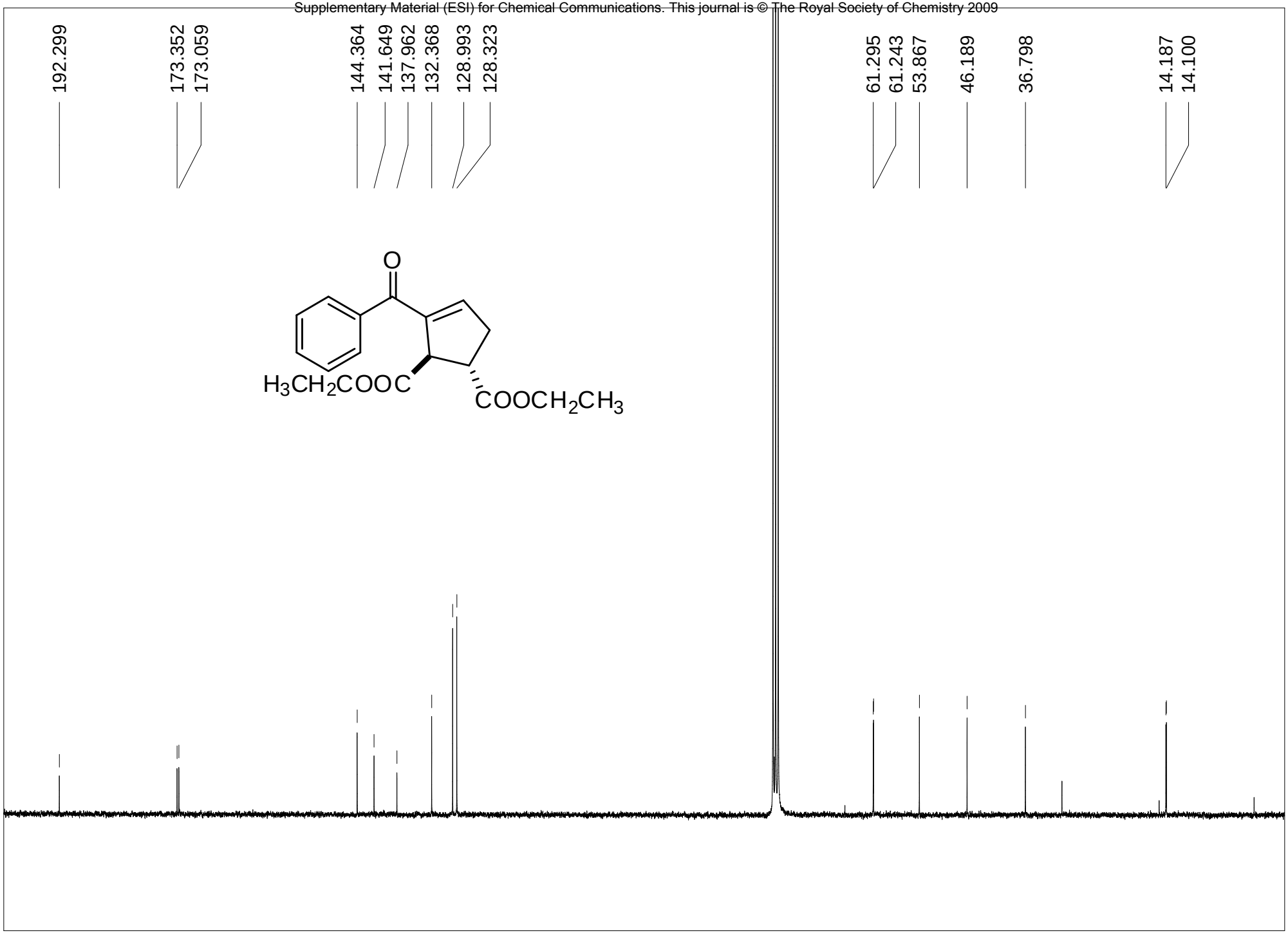
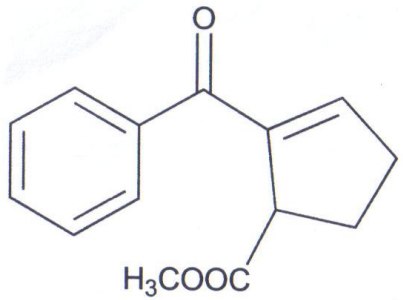
4.0
3.0
2.0
1.0
ppm (t1)



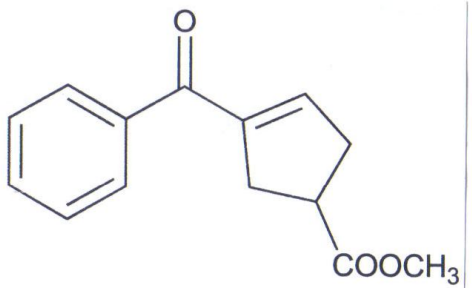
AG 042 400MHz CDCl3

7.795 7.775 7.737 7.718 7.557 7.539 7.522 7.457 7.439 7.420 6.642 6.639 6.458

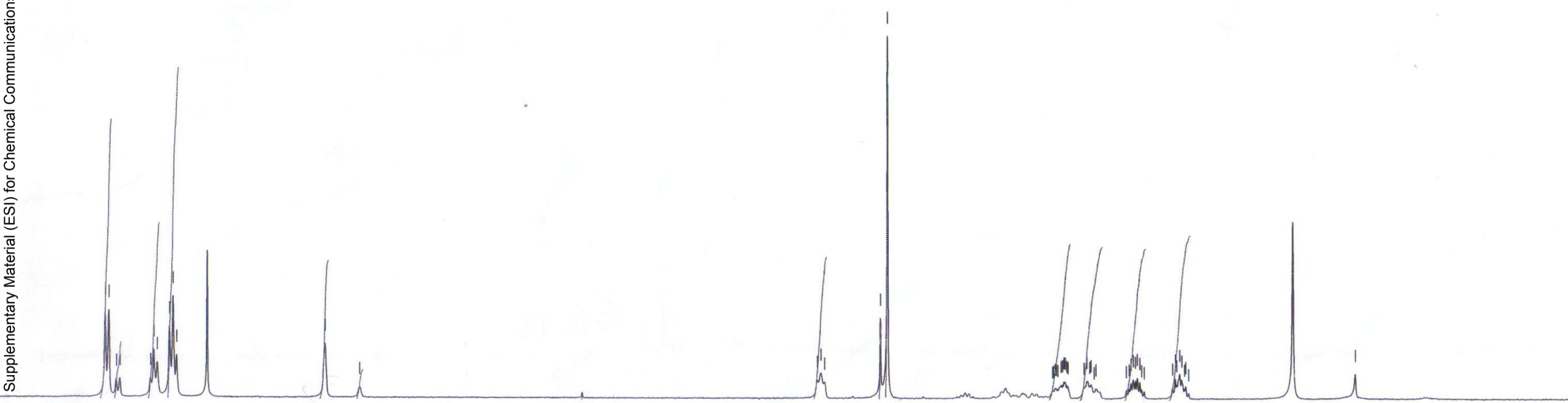
4.066 4.047 4.029 3.737 3.700 2.838 2.832 2.824 2.817 2.809 2.793 2.785 2.778 2.771 2.763 2.756 2.673 2.659 2.644 2.638 2.621 2.612 2.452 2.438 2.428 2.416 2.405 2.395 2.382 2.372 2.359 2.210 2.195 2.187 2.171 2.161 2.147



Major



Minor



8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

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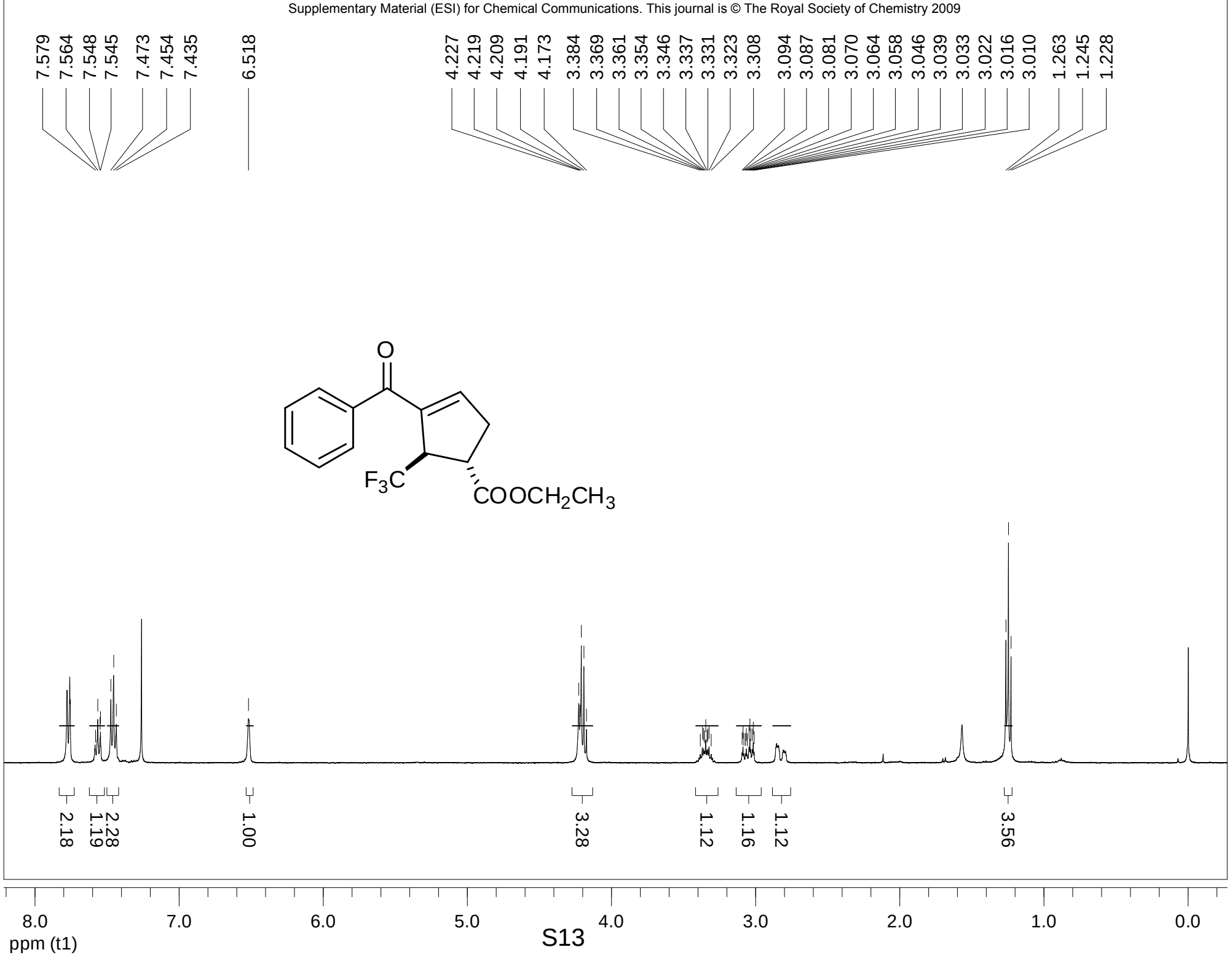
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7.473
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7.435
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4.219
4.209
4.191
4.173
3.384
3.369
3.361
3.354
3.346
3.337
3.331
3.323
3.308
3.094
3.087
3.081
3.070
3.064
3.058
3.046
3.039
3.033
3.022
3.016
3.010
1.263
1.245
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F3C
COOCH2CH3
2.18
1.19
2.28
1.00
3.28
1.12
1.16
1.12
3.56
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7.0
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5.0
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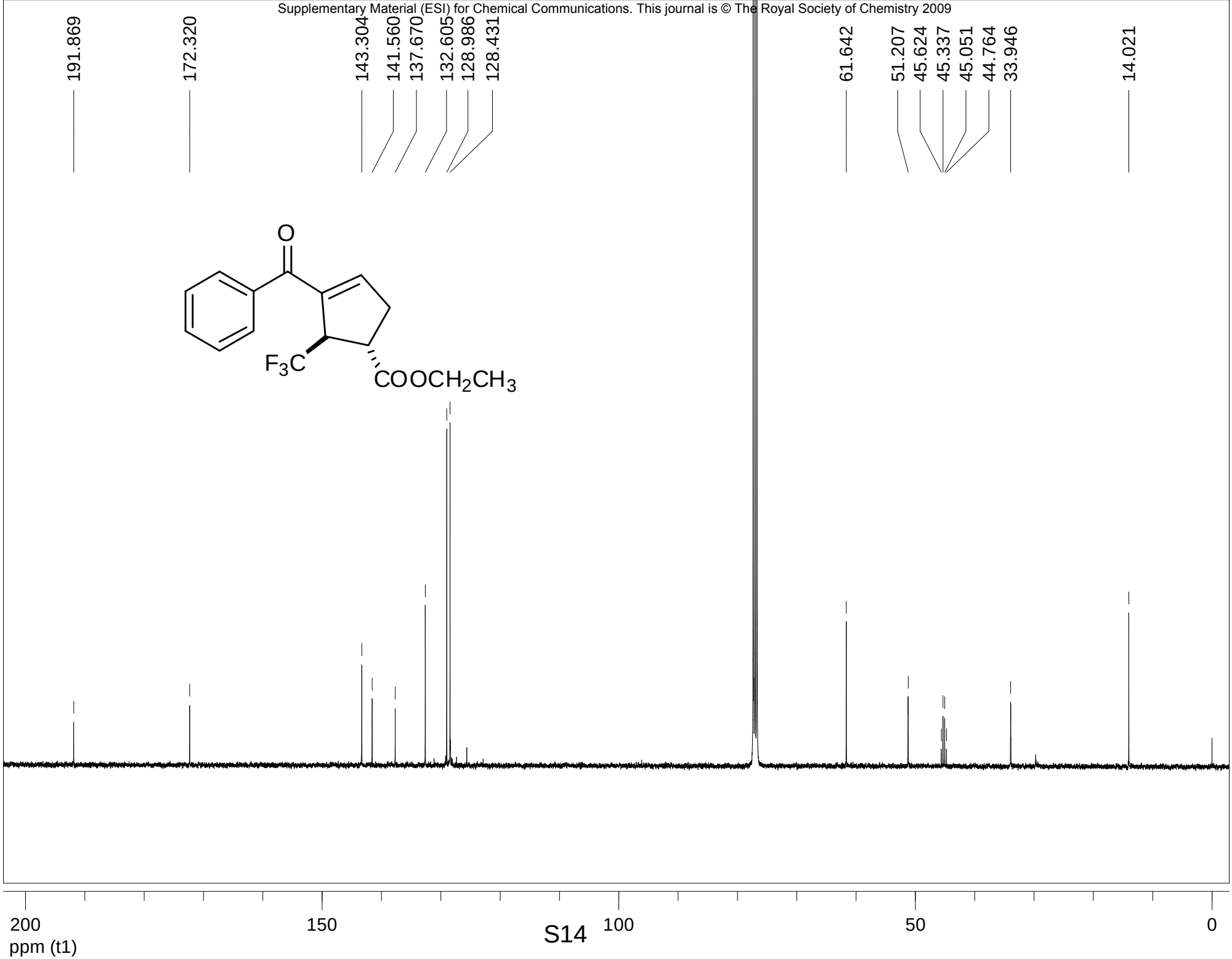
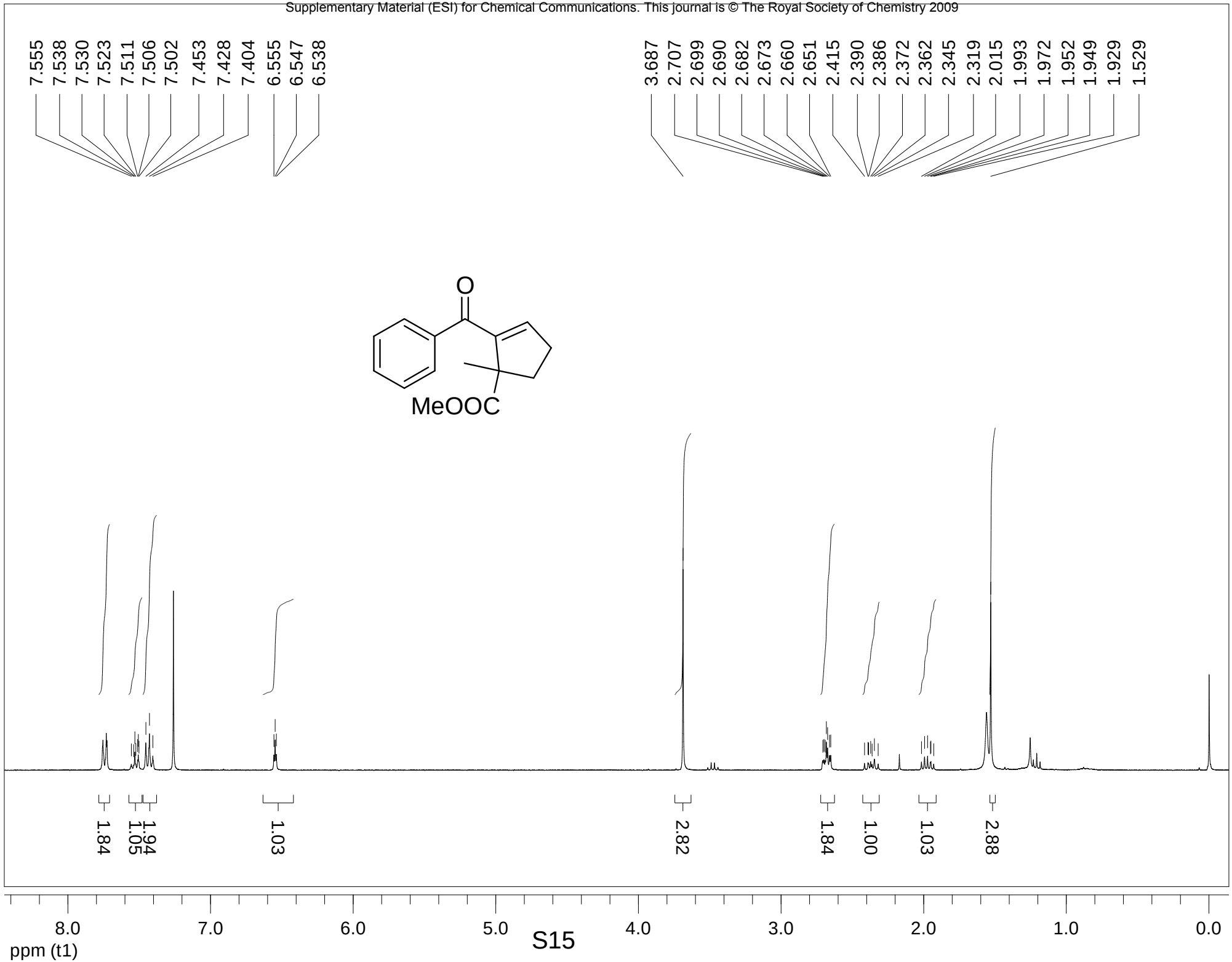
3.0
2.0
1.0
0.0
ppm (t1)

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7.453
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7.404
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6.538
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2.707
2.699
2.690
2.682
2.673
2.660
2.651
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2.390
2.386
2.372
2.362
2.345
2.319
2.015
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1.972
1.952
1.949
1.929
1.529
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MeOOC
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1.05
1.94
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2.82
1.84
1.00
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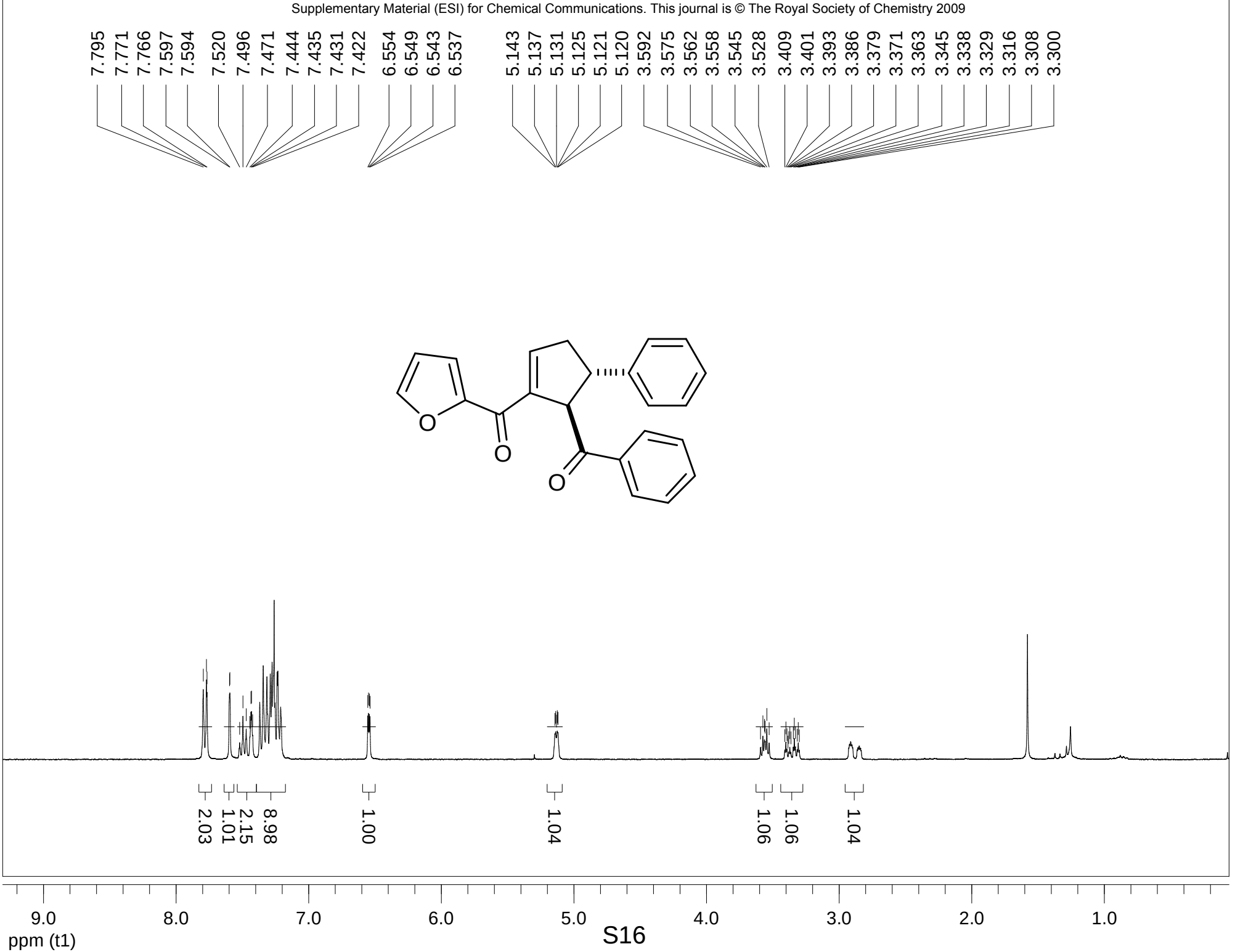
ppm (t1)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7.520
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7.431
7.422
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6.543
6.537
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5.120
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3.575
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3.401
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1.04
1.06
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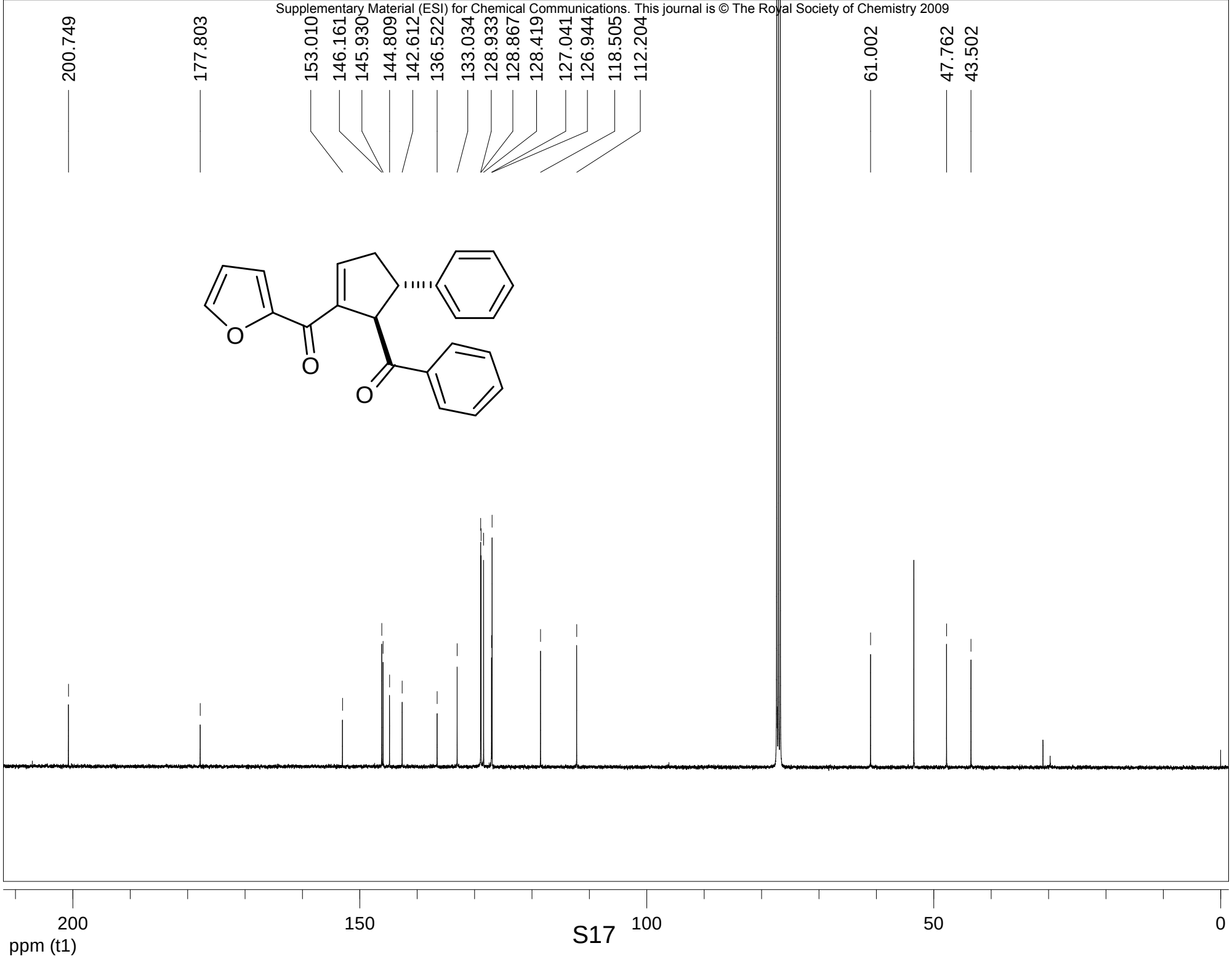
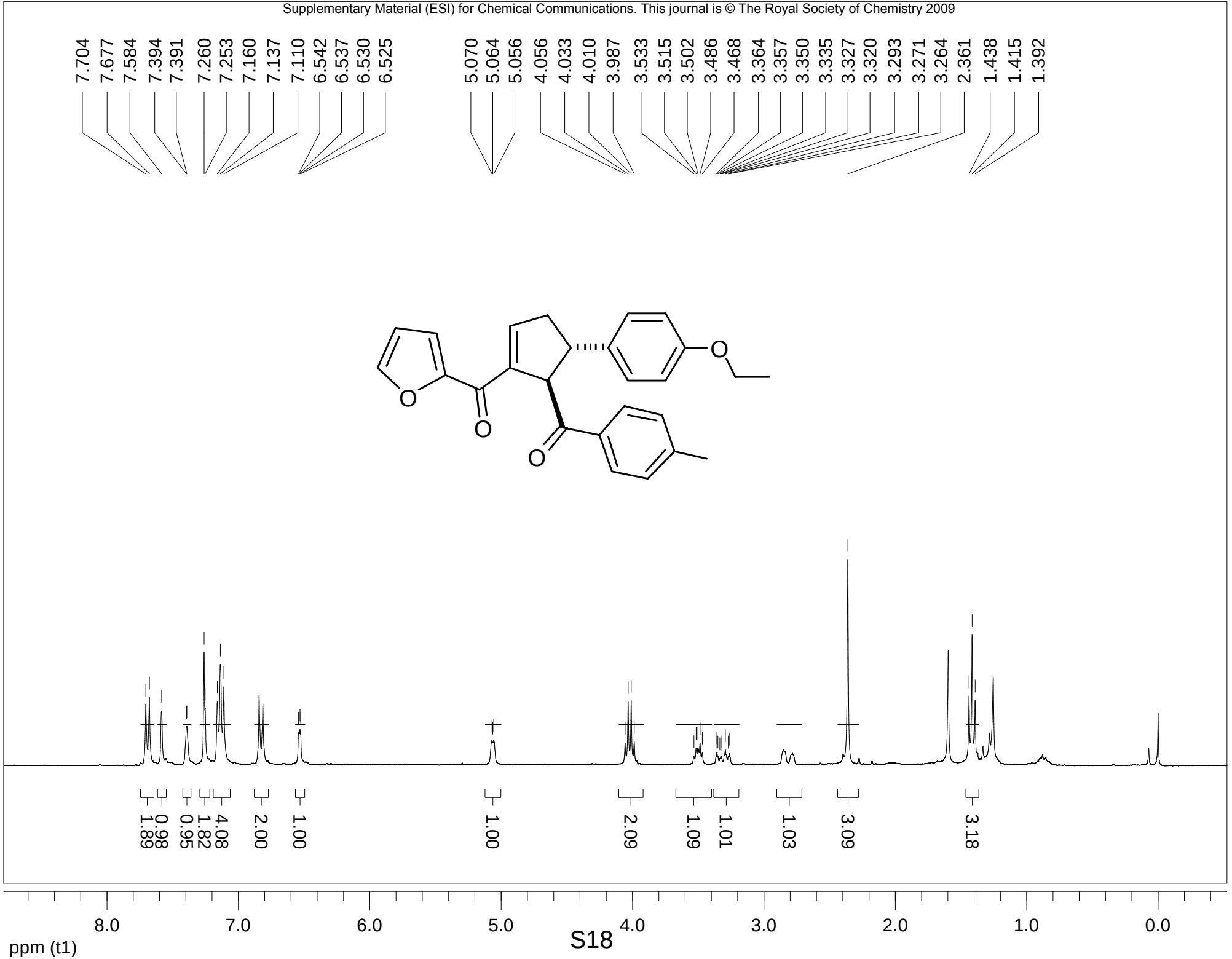
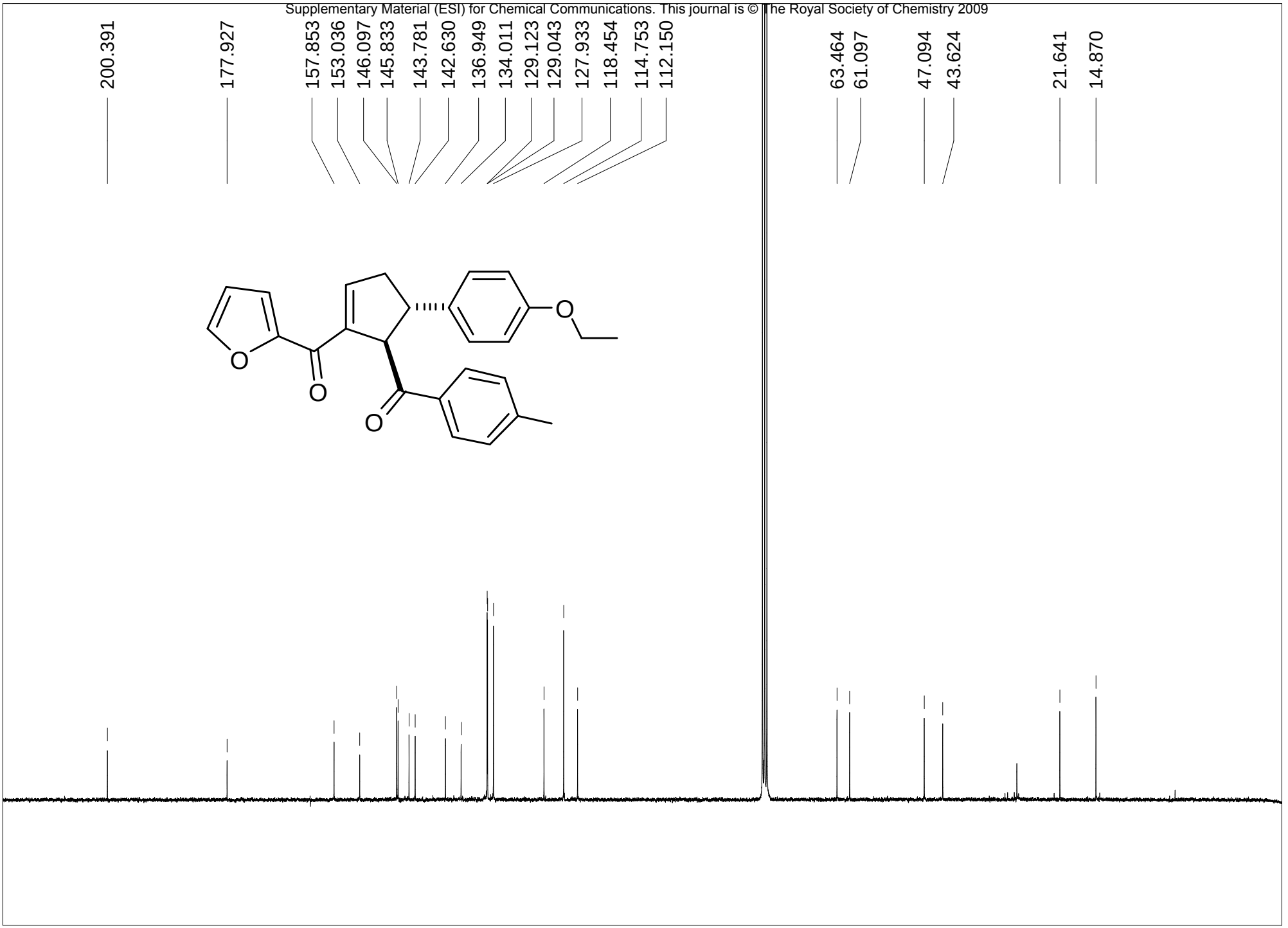
1.0
ppm (t1)






200.391
177.927
157.853
153.036
146.097
145.833
143.781
142.630
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134.011
129.123
129.043
127.933
118.454
114.753
112.150
63.464
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47.094
43.624
21.641
14.870
O
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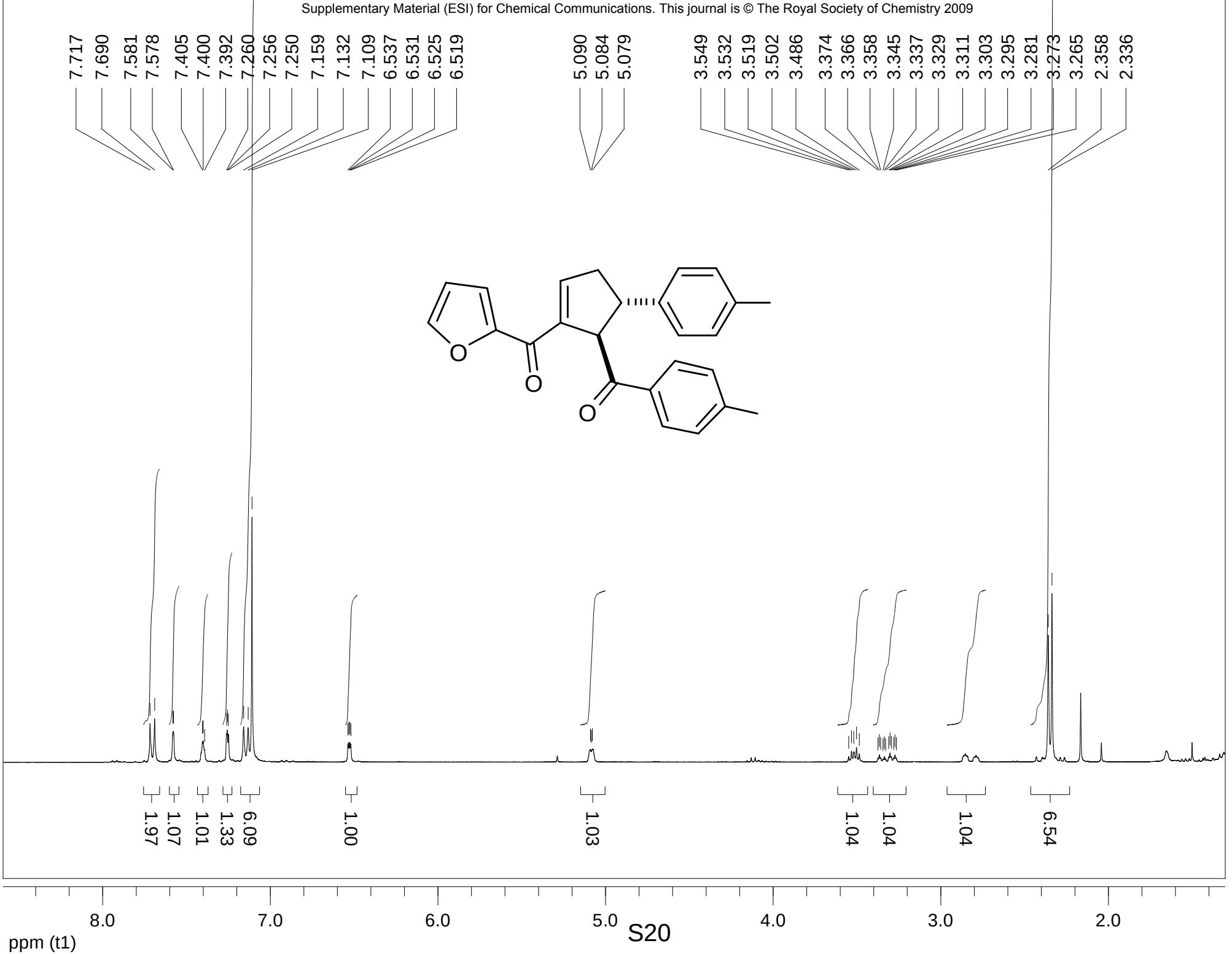
O
200
150
100
50
0
ppm (t1)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7.132
7.109
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6.531
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3.358
3.345
3.337
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3.303
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3.265
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1.33
6.09
1.00
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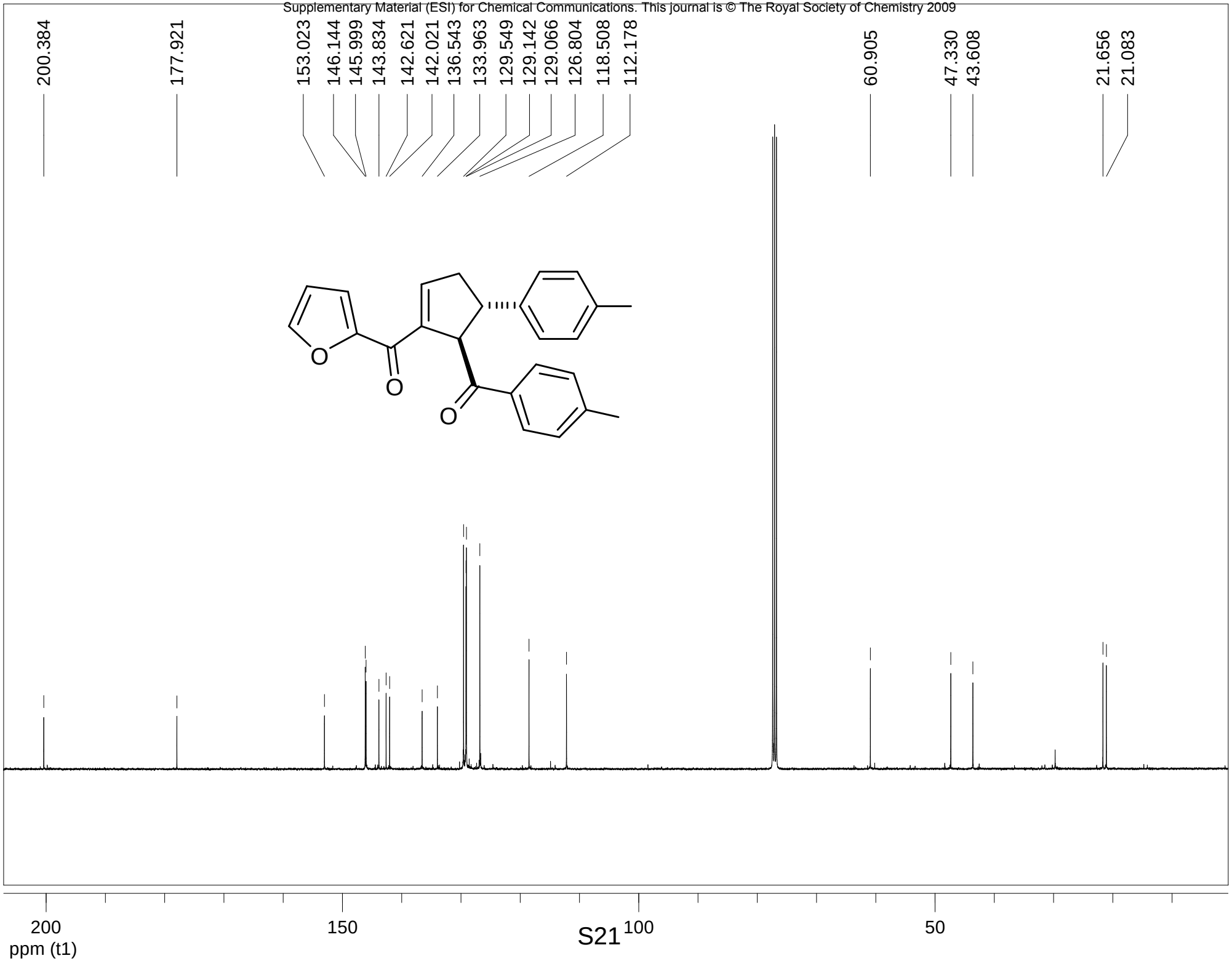
6.54
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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145.999
143.834
142.621
142.021
136.543
133.963
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129.142
129.066
126.804
118.508
112.178
60.905
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43.608
21.656
21.083
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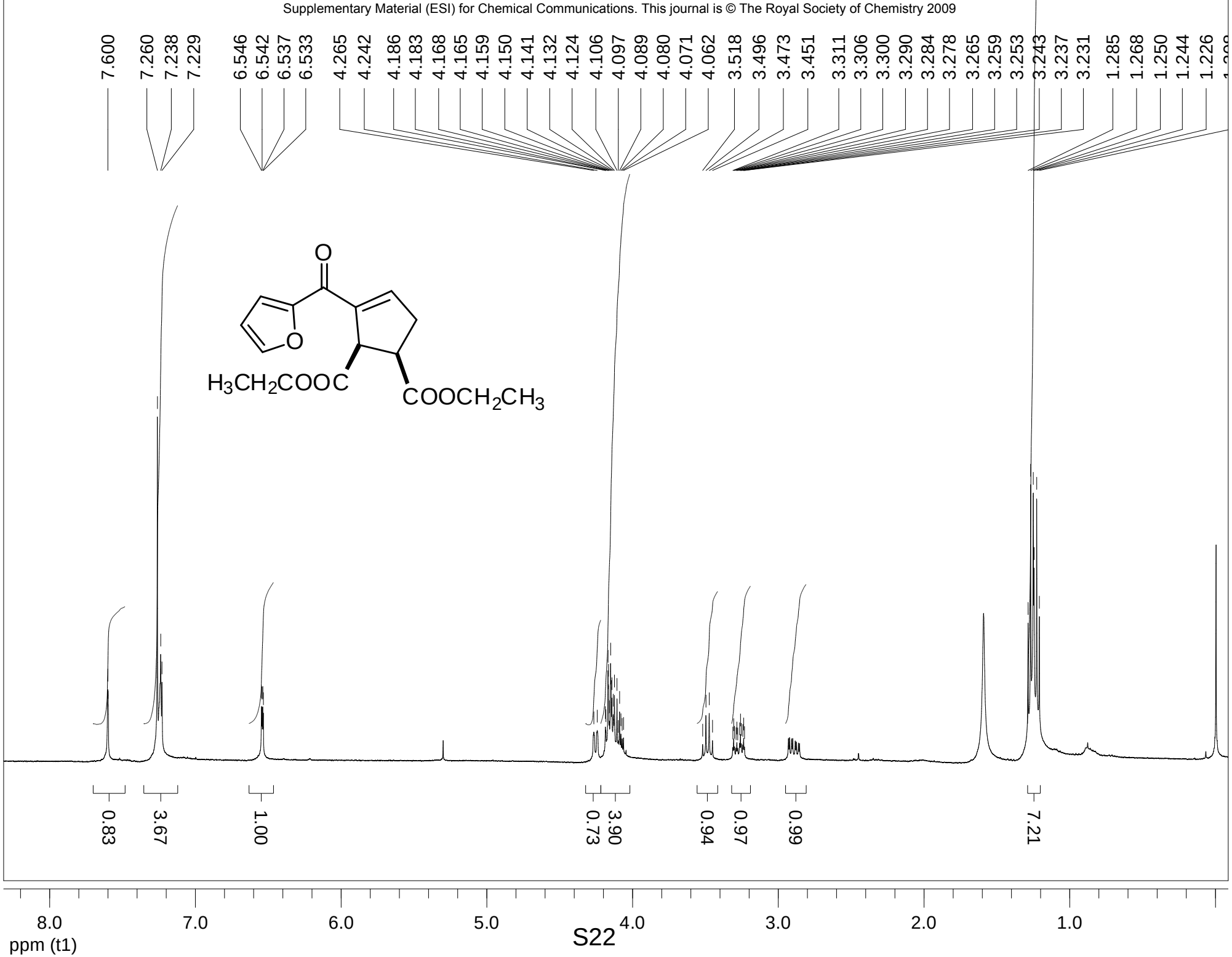
O
O
200
150
100
50
ppm (t1)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6.537
6.533
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4.242
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4.183
4.168
4.165
4.159
4.150
4.141
4.132
4.124
4.106
4.097
4.089
4.080
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3.253
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3.237
3.231
1.285
1.268
1.250
1.244
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COOCH2CH3
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0.73
3.90
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0.97
0.99
7.21
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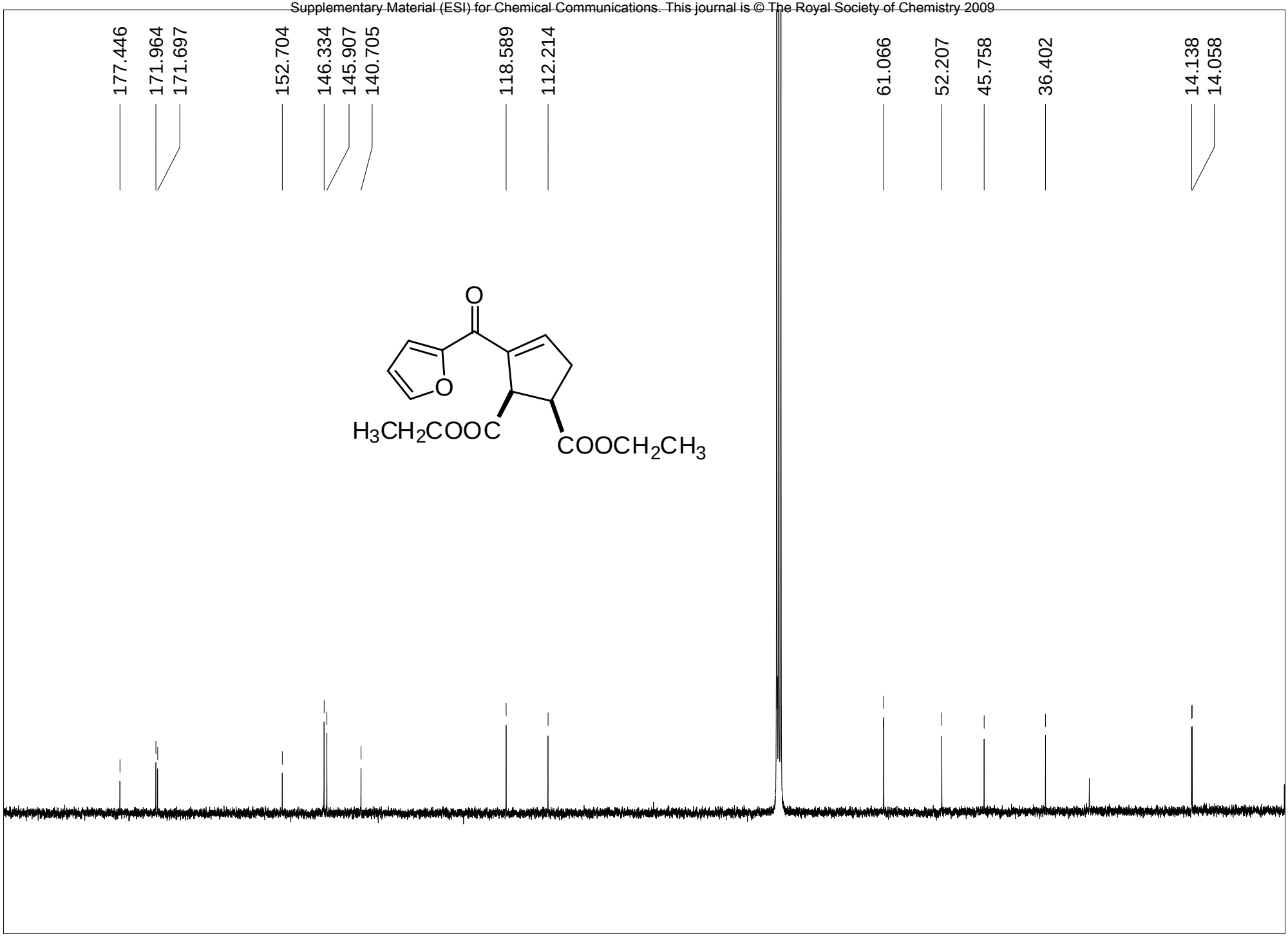
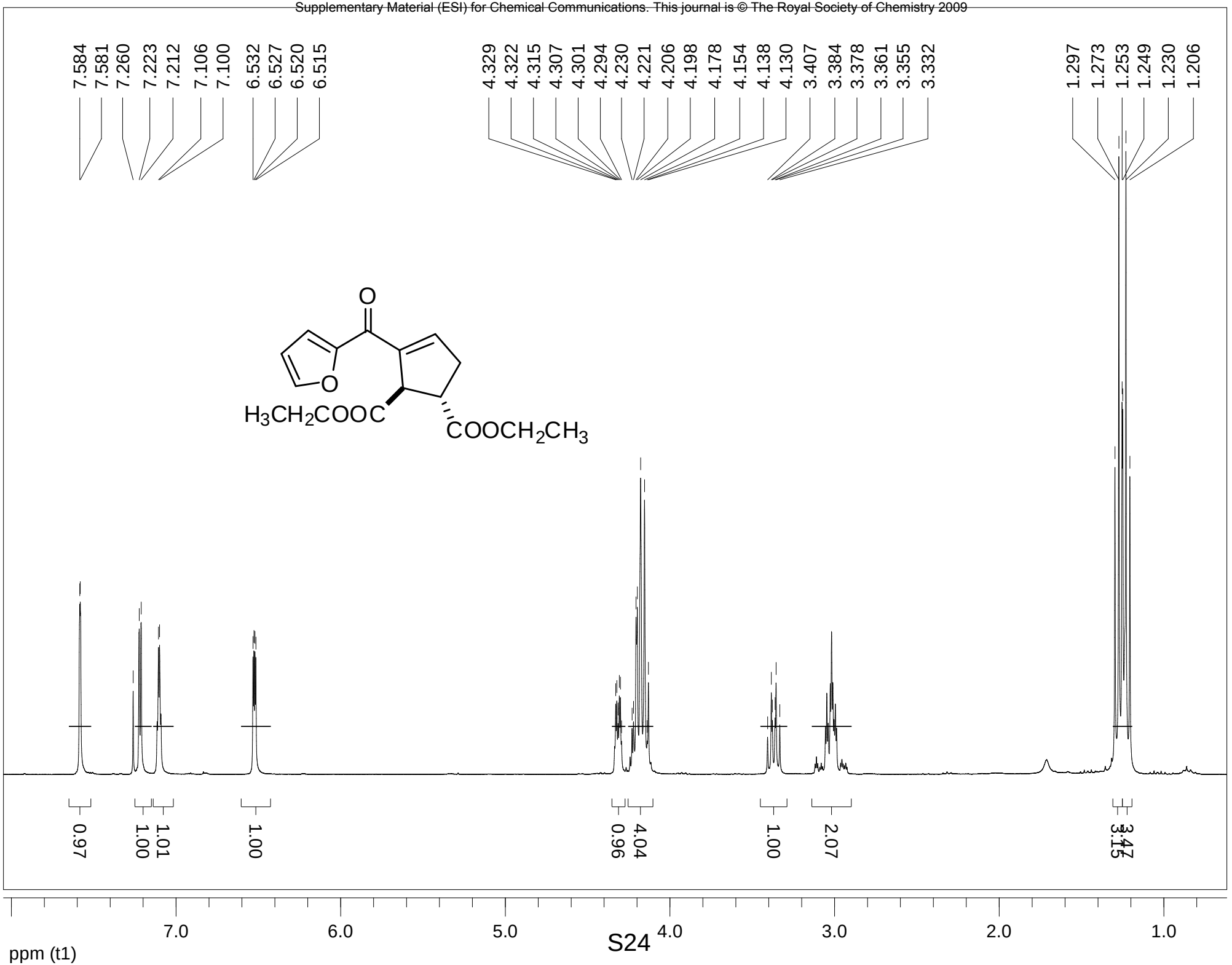
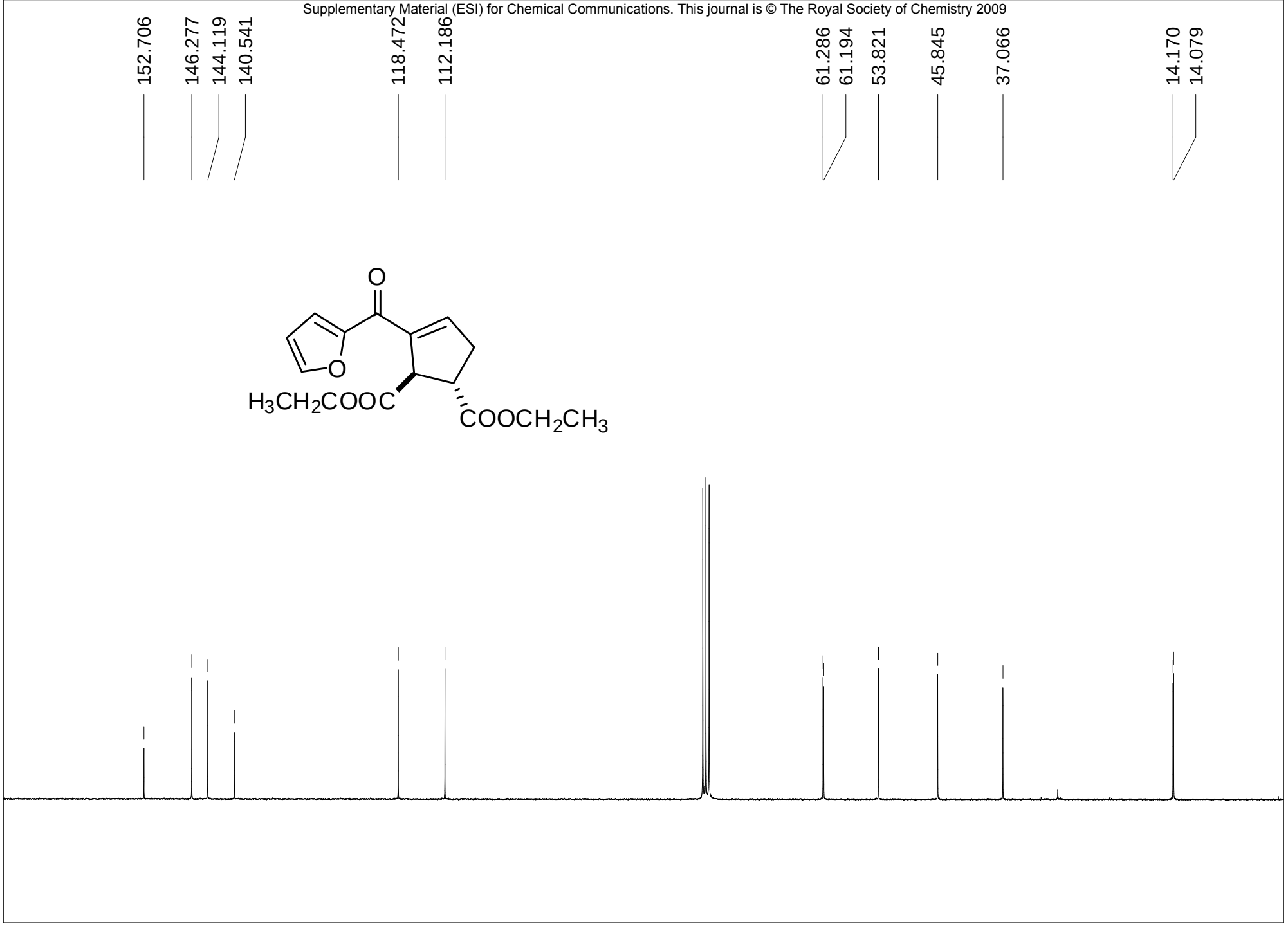
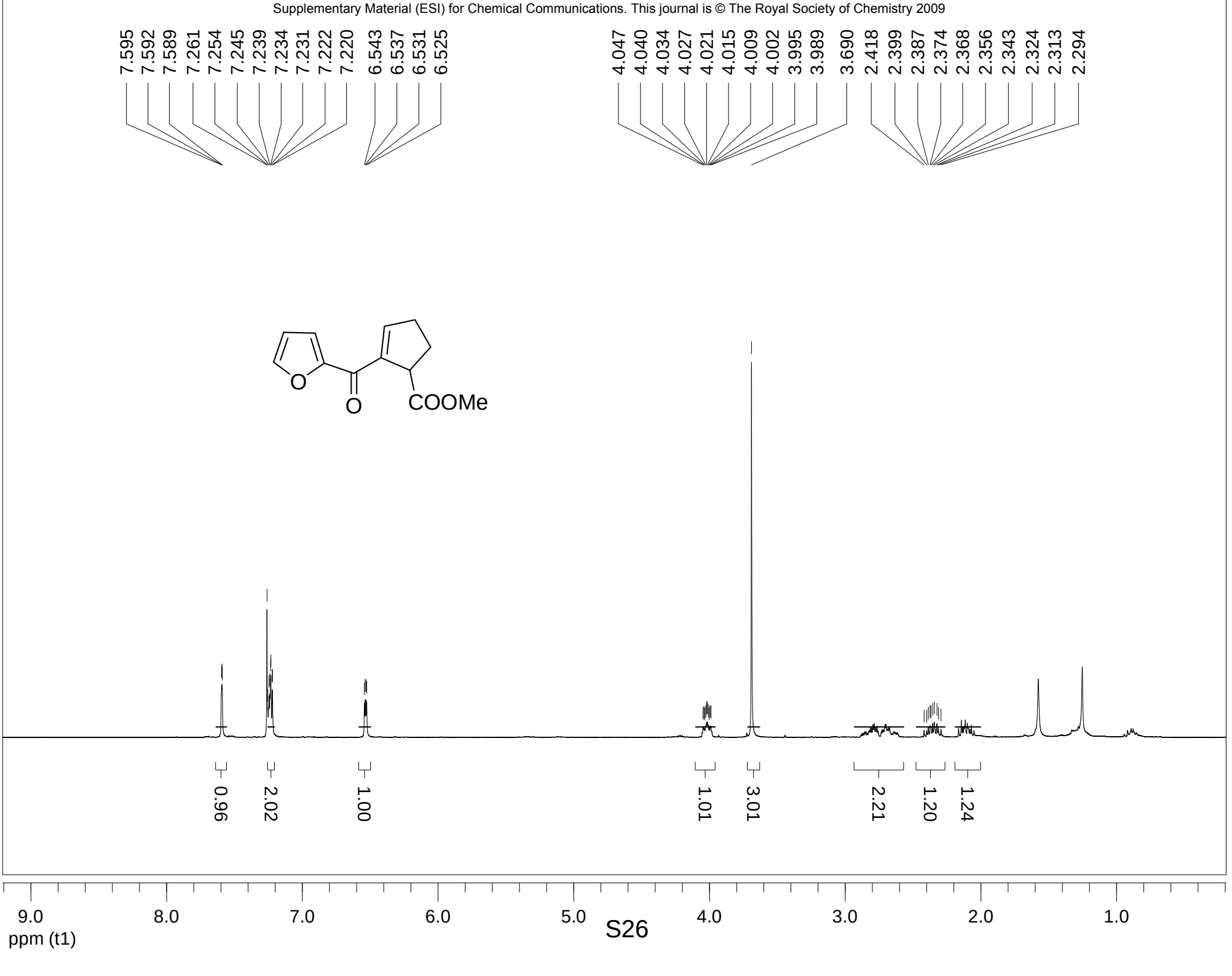
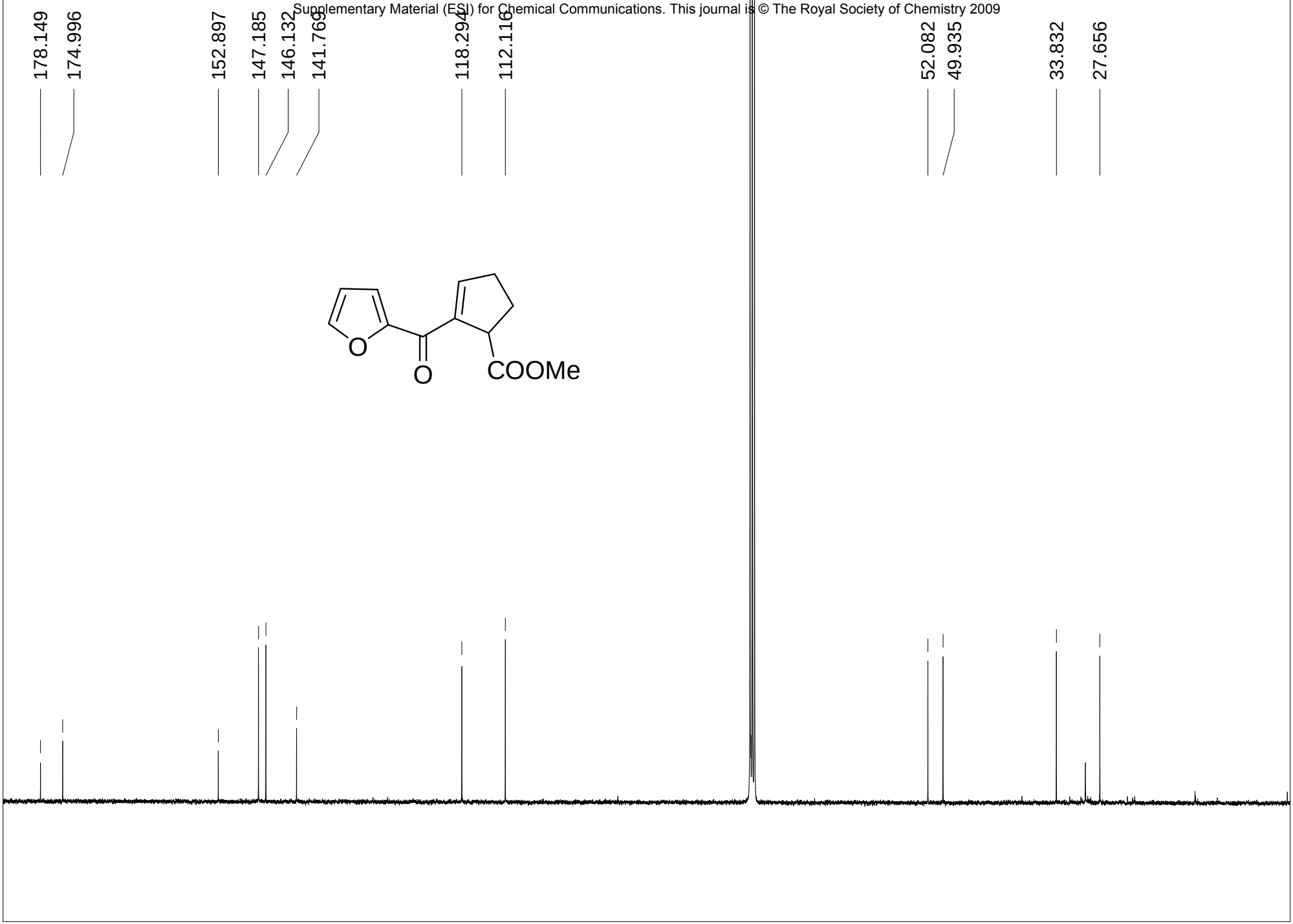
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

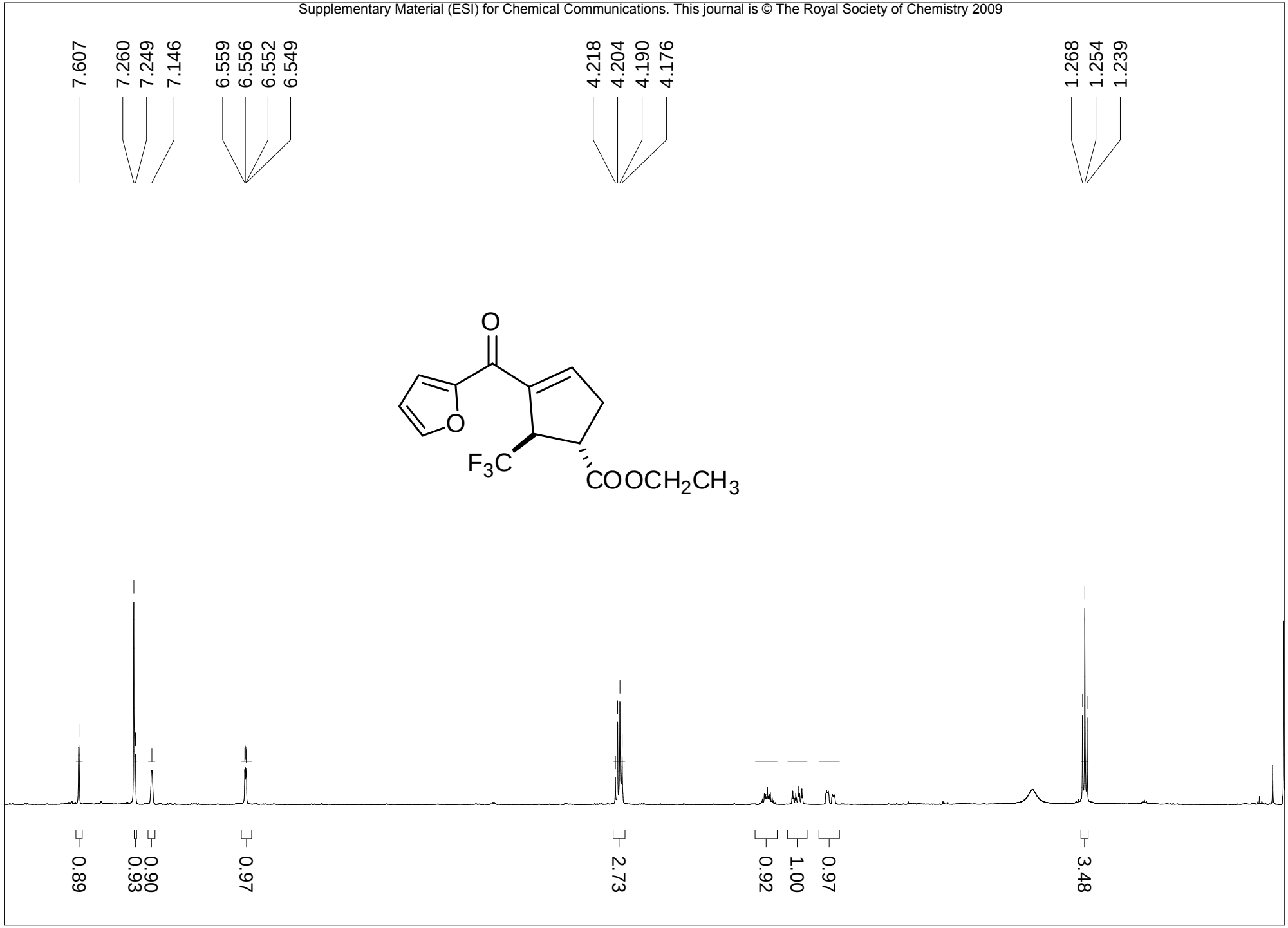


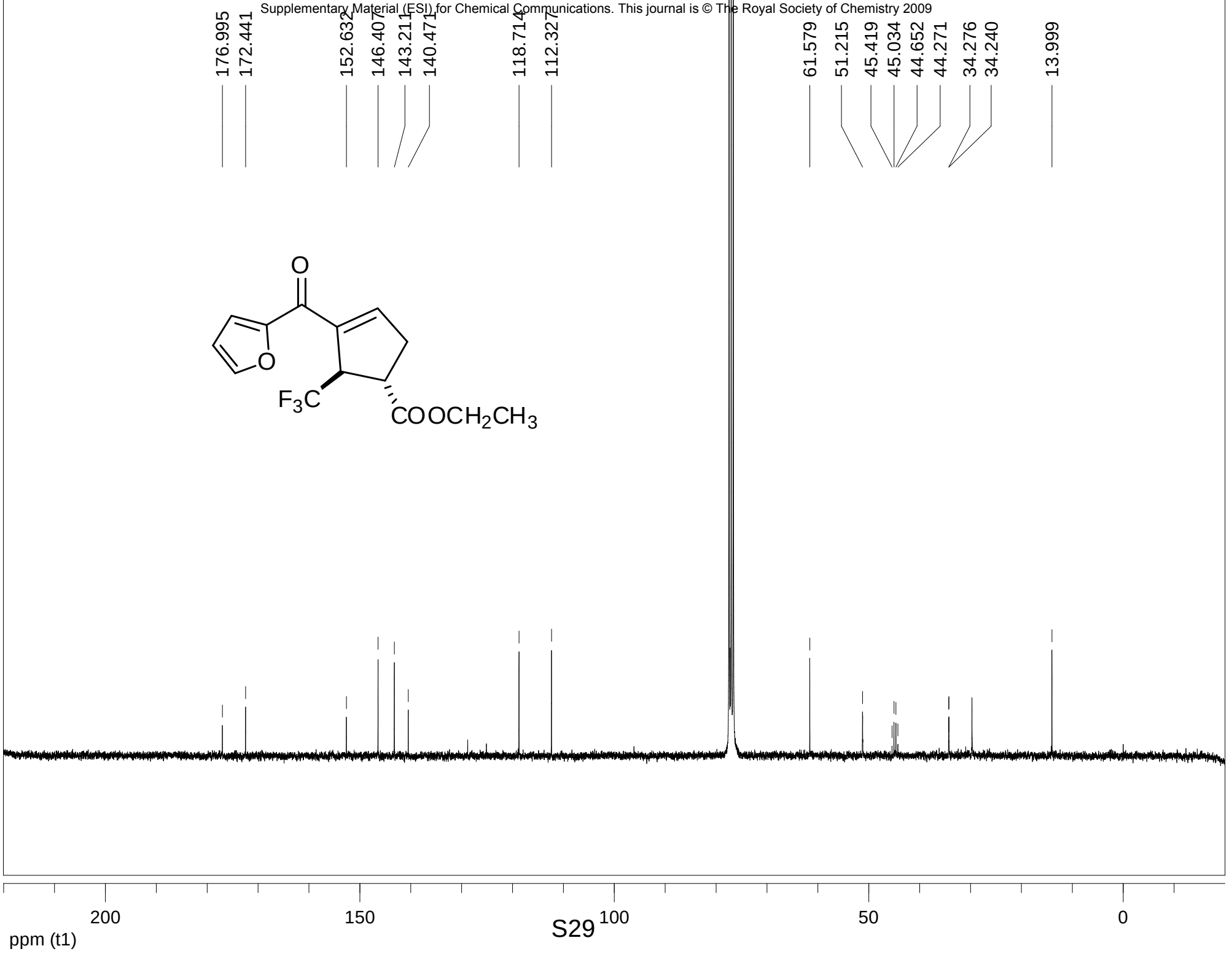


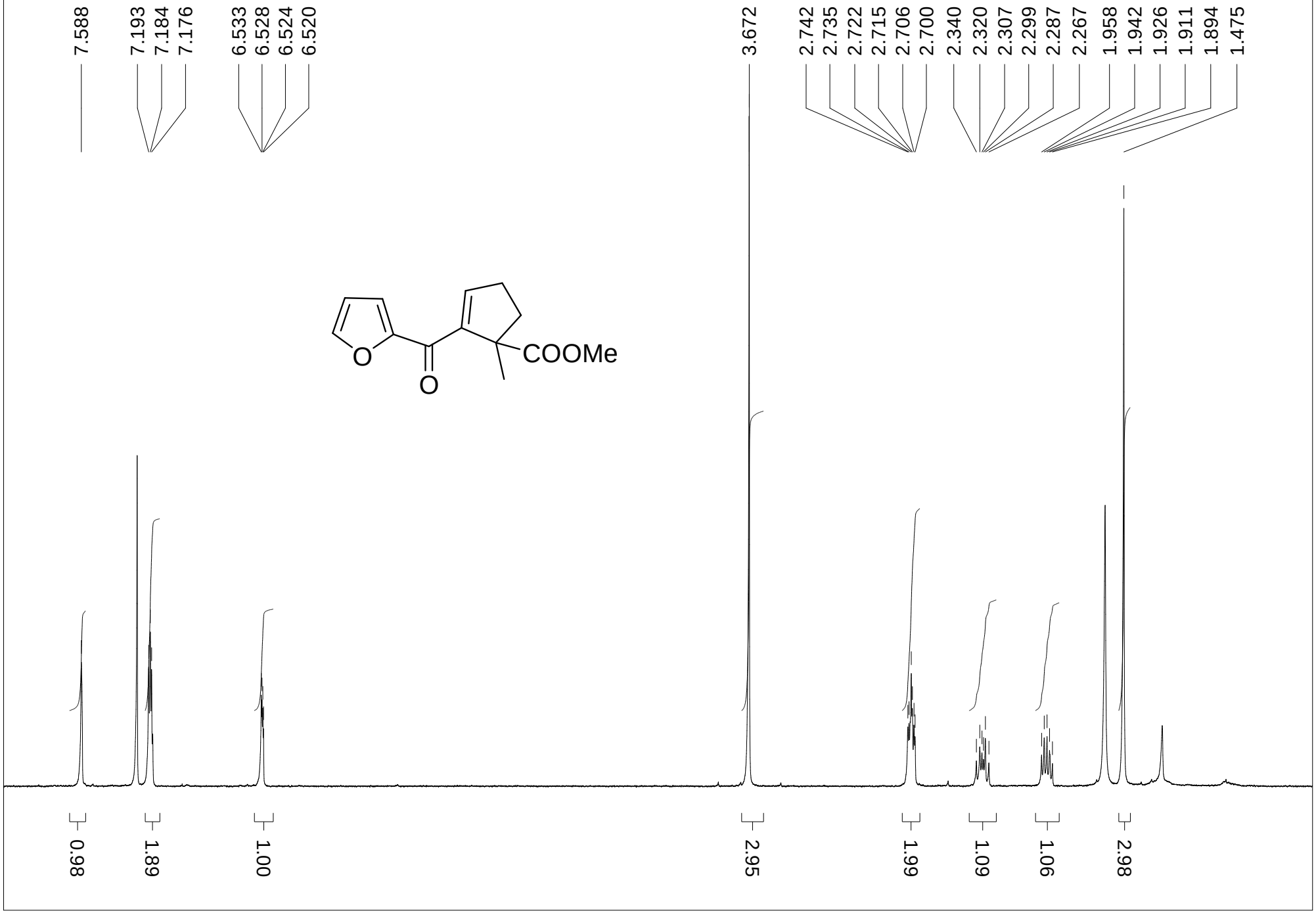


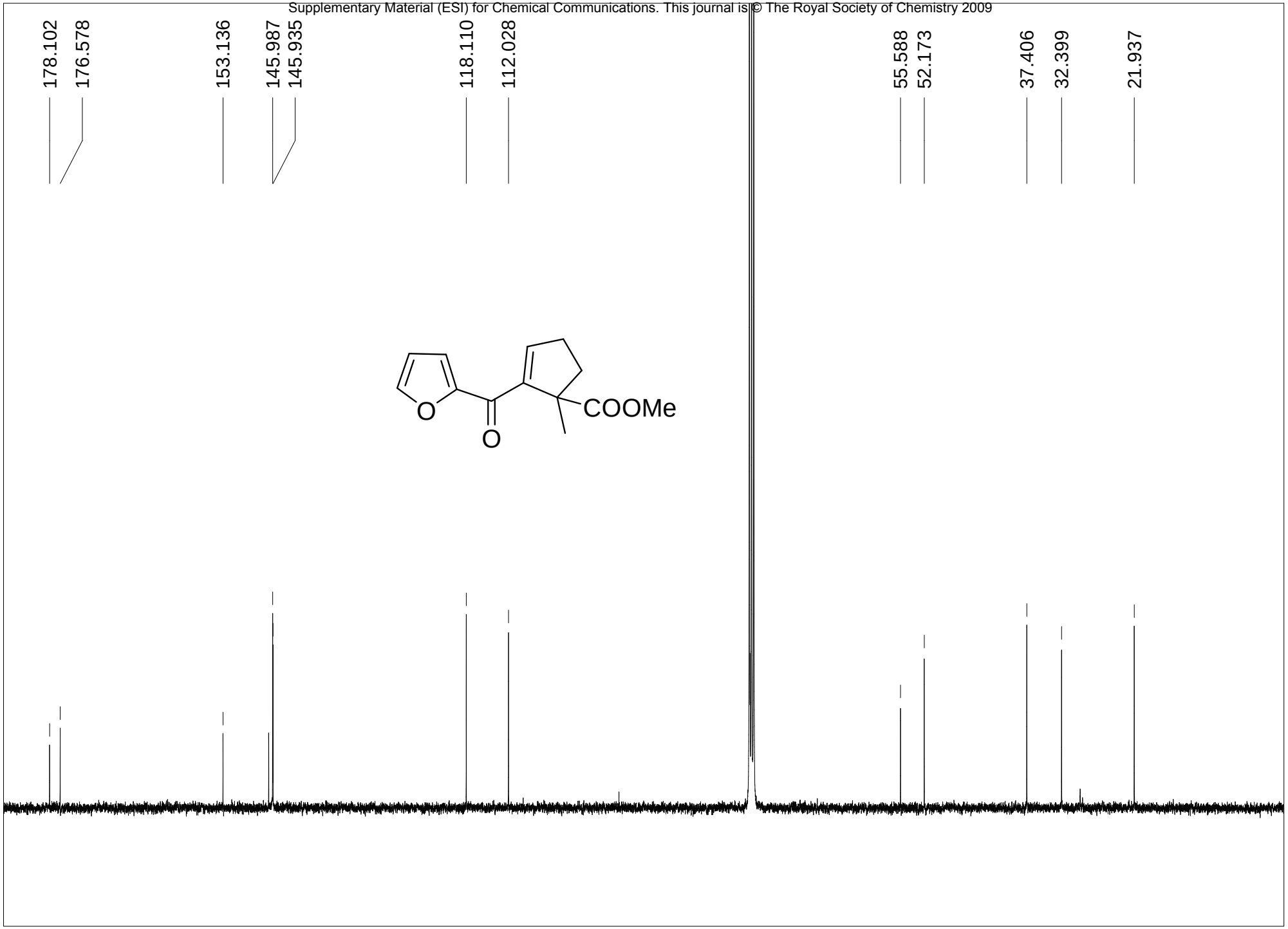





7.607
7.260
7.249
7.146
6.559
6.556
6.552
6.549
4.218
4.204
4.190
4.176
1.268
1.254
1.239
O
O
F3C
COOCH2CH3
0.89
0.93
0.90
0.97
2.73
0.92
1.00
0.97
3.48
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)







```
Injection Date  : 2/27/2008 3:33:27 PM
Sample Name     : 049-1                          Location : Vial 4
Acq. Operator   : MAG
Acq. Instrument : Instrument 1                   Inj Volume : 100 µl
Acq. Method     : C:\HPCHEM\1\METHODS\WSM.M
Last changed    : 2/27/2008 3:31:02 PM by MAG
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\WSM.M
Last changed    : 2/27/2008 4:35:07 PM by MAG
                  (modified after loading)
NN
```

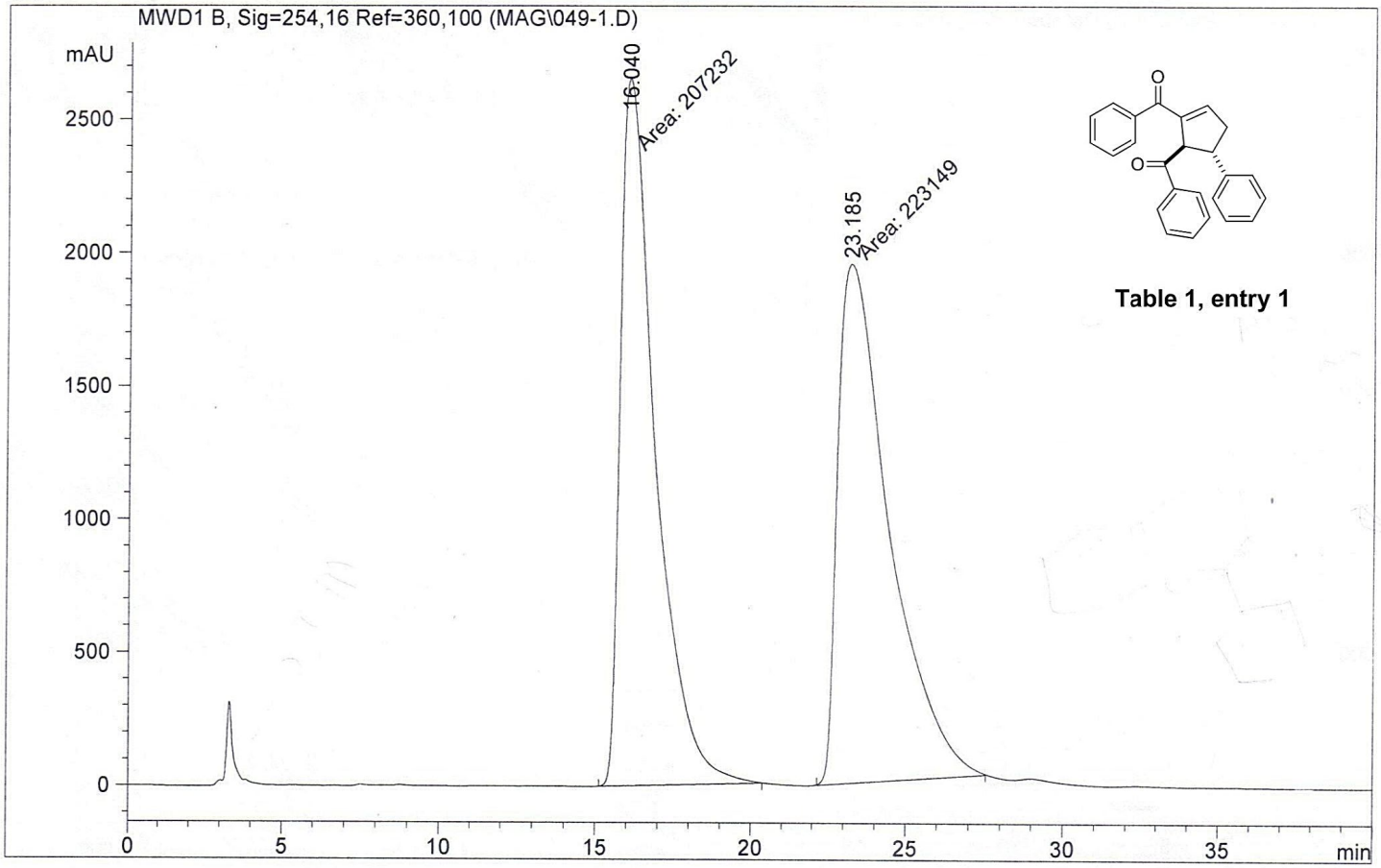


Table 1, entry 1

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.040 MM    1.3014 2.07232e5  2653.96680  48.1508
   2  23.185 MM    1.9102 2.23149e5  1946.95654  51.8492

Totals :                  4.30380e5  4600.92334

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

Sample Name: 106

Acq. Operator : MAGESH
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 3/18/2008 10:25:41 PM
Inj Volume : 50 µl

Acq. Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/18/2008 10:23:48 PM by MAGESH
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\ZJF.M
Last changed : 8/19/2008 10:54:58 PM by ZJF
(modified after loading)
Method Info : WAP254nm

Sample Info : Chiralpak AD

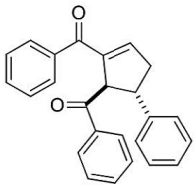
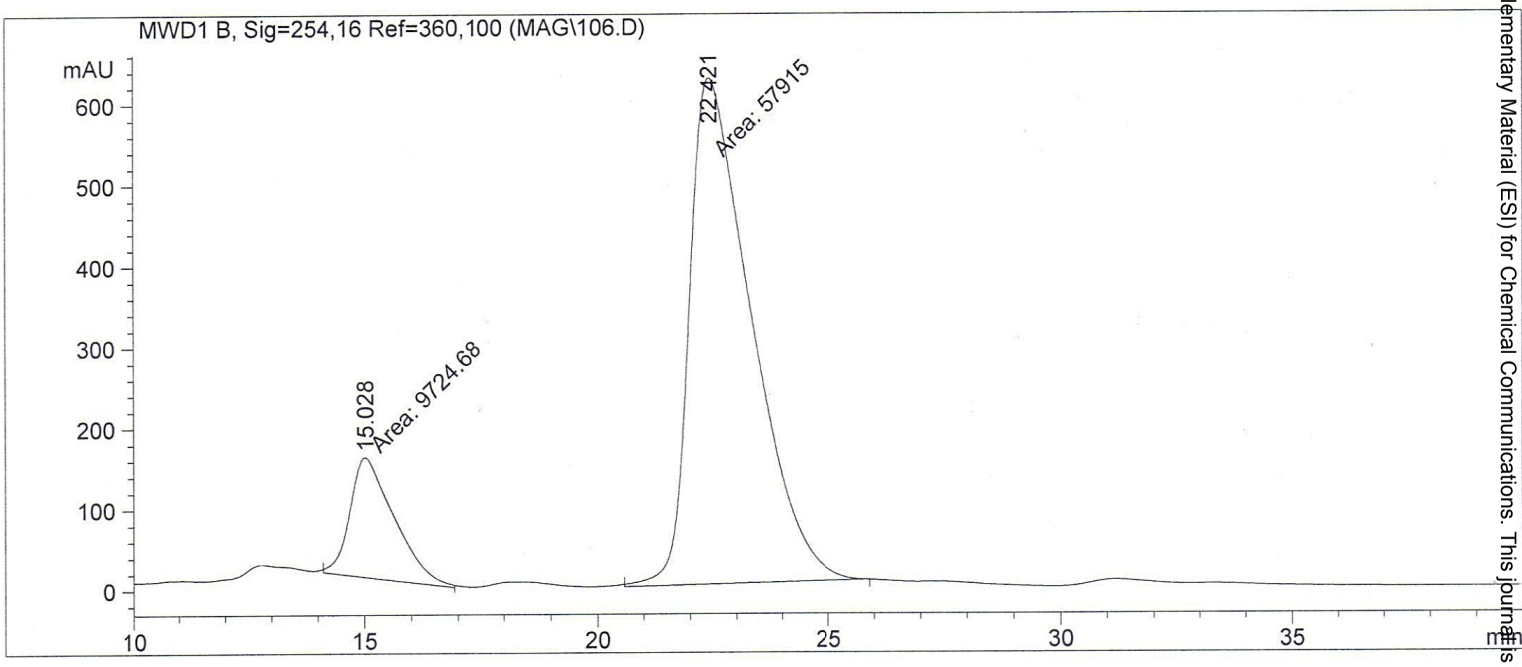


Table 3, entry 1



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.028	MM	1.0960	9724.68262	147.88405	14.3772
2	22.421	MM	1.5442	5.79150e4	625.07318	85.6228

Totals : 6.76397e4 772.95723

*** End of Report ***

Data File C:\CHEM32\1\DATA\MAG\065C.D
Sample Name: 065C

==========

Acq. Operator : Magesh
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 3/28/2008 10:17:45 PM
Inj Volume : 100 µl
Acq. Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/28/2008 10:16:01 PM by Magesh
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/29/2008 10:57:55 AM by Magesh
(modified after loading)
Method Info : weijuan290nm

Sample Info : Chiralpak ADH

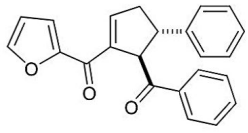
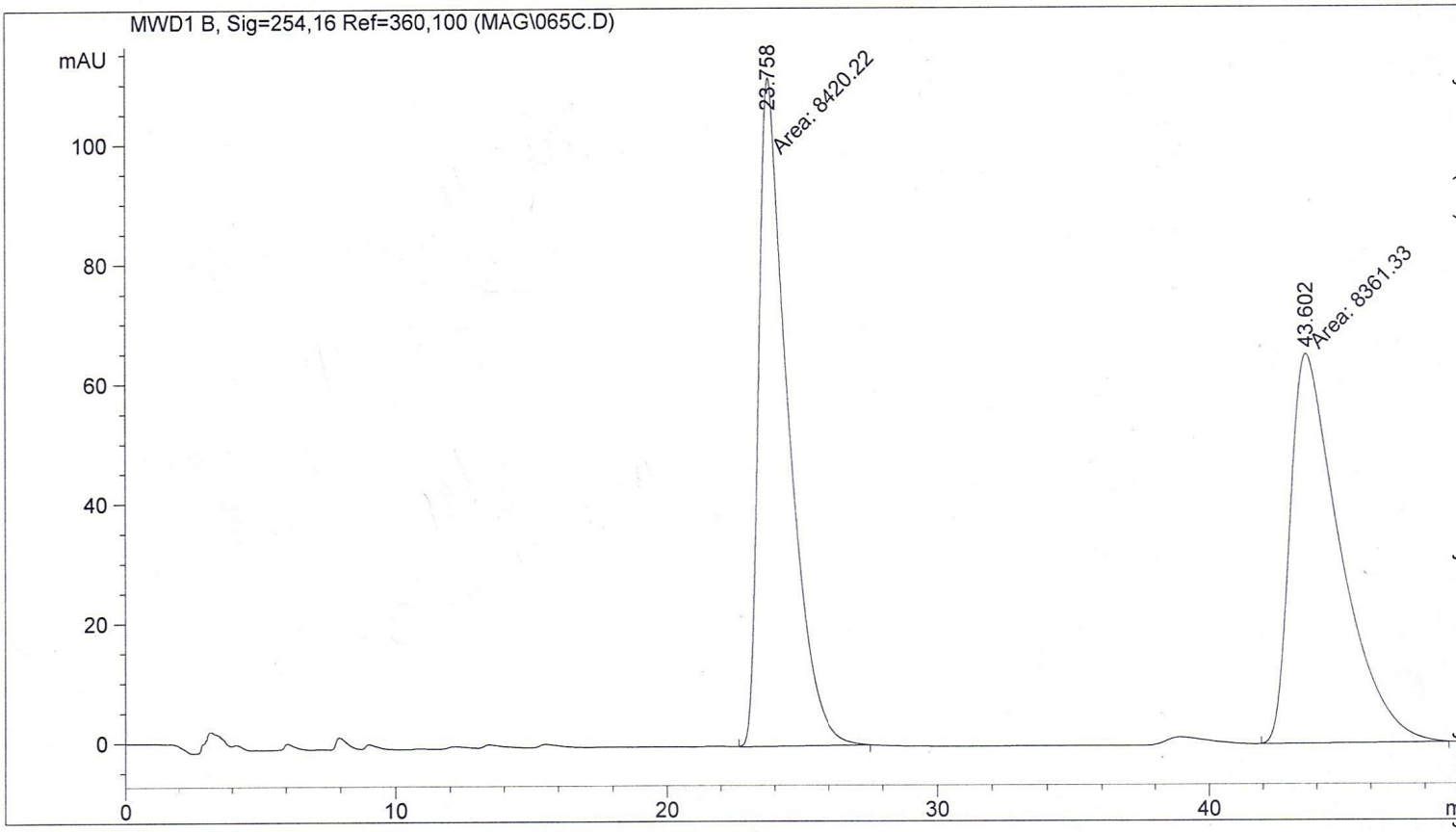


Table 2, entry 1



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Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.758	MM	1.2567	8420.21680	111.66999	50.1754
2	43.602	MM	2.1448	8361.33398	64.97339	49.8246
Totals :				1.67816e4	176.64338	

Data File C:\CHEM32\1\DATA\MAG\121.D
Sample Name: 121

==========

Acq. Operator : Magesh
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 3/26/2008 2:18:18 PM
Inj Volume : 50 µl
Acq. Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/26/2008 2:17:05 PM by Magesh
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/26/2008 3:24:55 PM by Magesh
(modified after loading)
Method Info : weijuan290nm

Sample Info : Chiralpak ADH

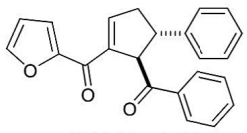
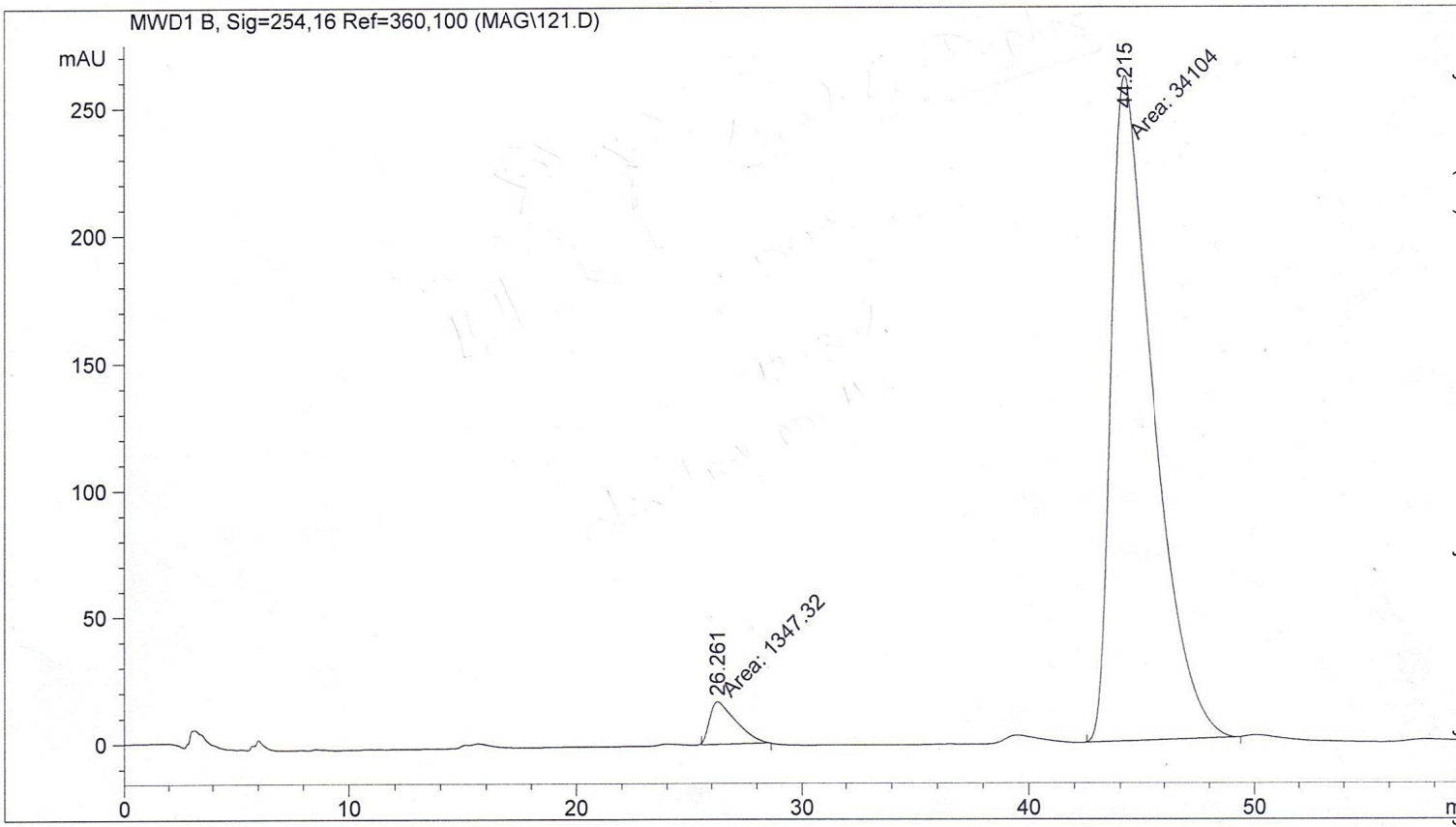


Table 3, entry 2



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.261	MM	1.3461	1347.32349	16.68237	3.8005
2	44.215	MM	2.1751	3.41040e4	261.32260	96.1995
Totals :				3.54513e4	278.00497	

Data File C:\CHEM32\1\DATA\MAG\108B.D
Sample Name: 108B

==========

Acq. Operator : Magesh
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 3/30/2008 2:18:58 PM
Inj Volume : 50 µl
Acq. Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/30/2008 2:17:20 PM by Magesh
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 3/30/2008 3:54:21 PM by Magesh
(modified after loading)
Method Info : weijuan290nm

Sample Info : Chiralpak ADH

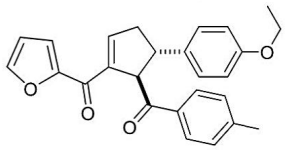
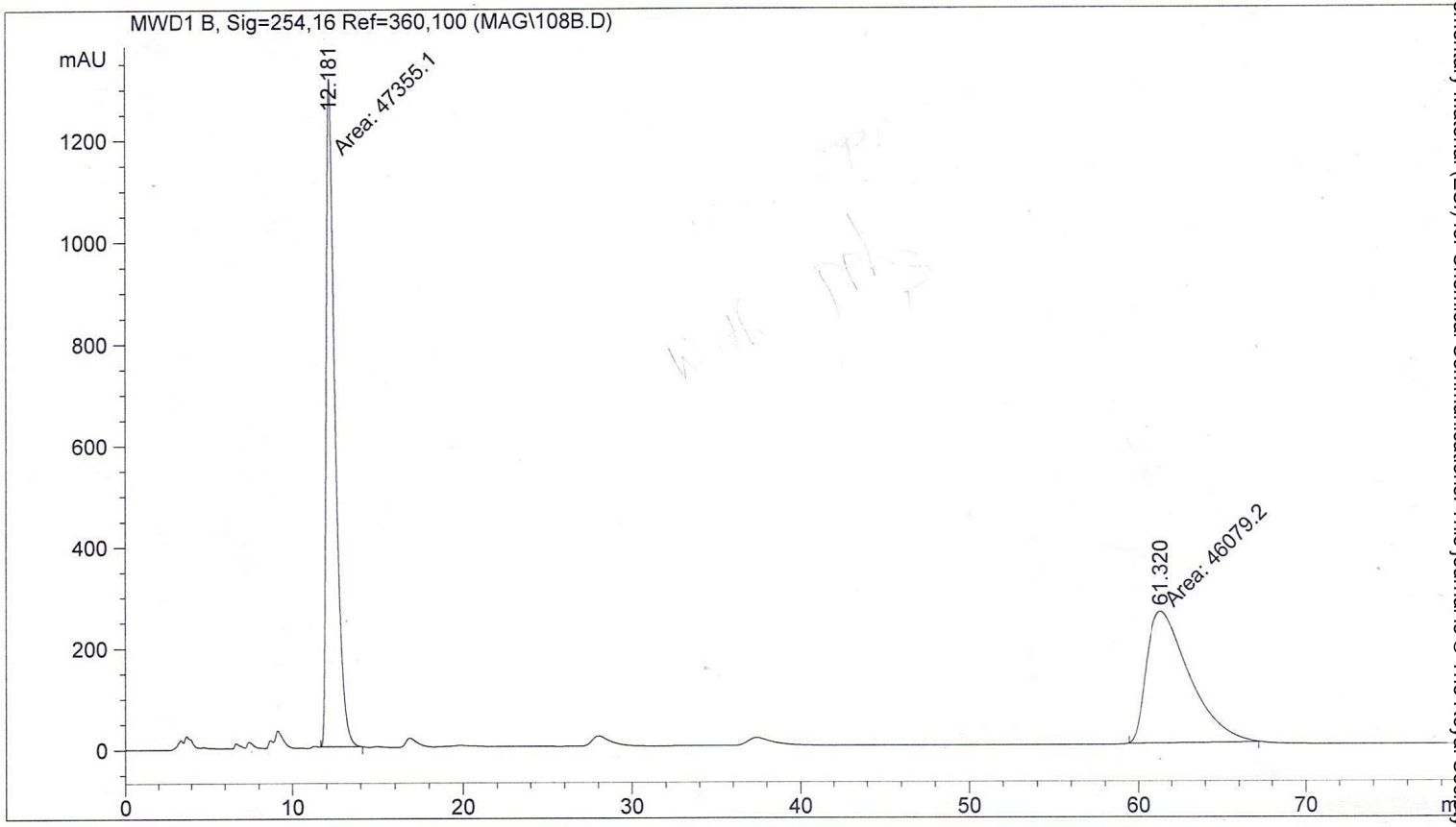


Table 2, entry 2



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.181	MM	0.6004	4.73551e4	1314.43652	50.6828
2	61.320	MM	2.9732	4.60792e4	258.30197	49.3172
Totals :				9.34342e4	1572.73849	

Data File C:\CHEM32\1\DATA\MAG\126-1.D
Sample Name: 126-1

==========

Acq. Operator : Magesh
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 4/3/2008 10:01:22 PM
Inj Volume : 100 µl

Acq. Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 4/3/2008 9:59:44 PM by Magesh
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed : 4/3/2008 11:25:04 PM by Magesh
(modified after loading)
Method Info : weijuan290nm

Sample Info : Chiralpak ADH

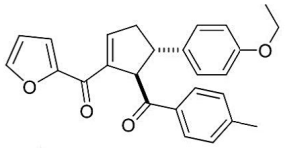
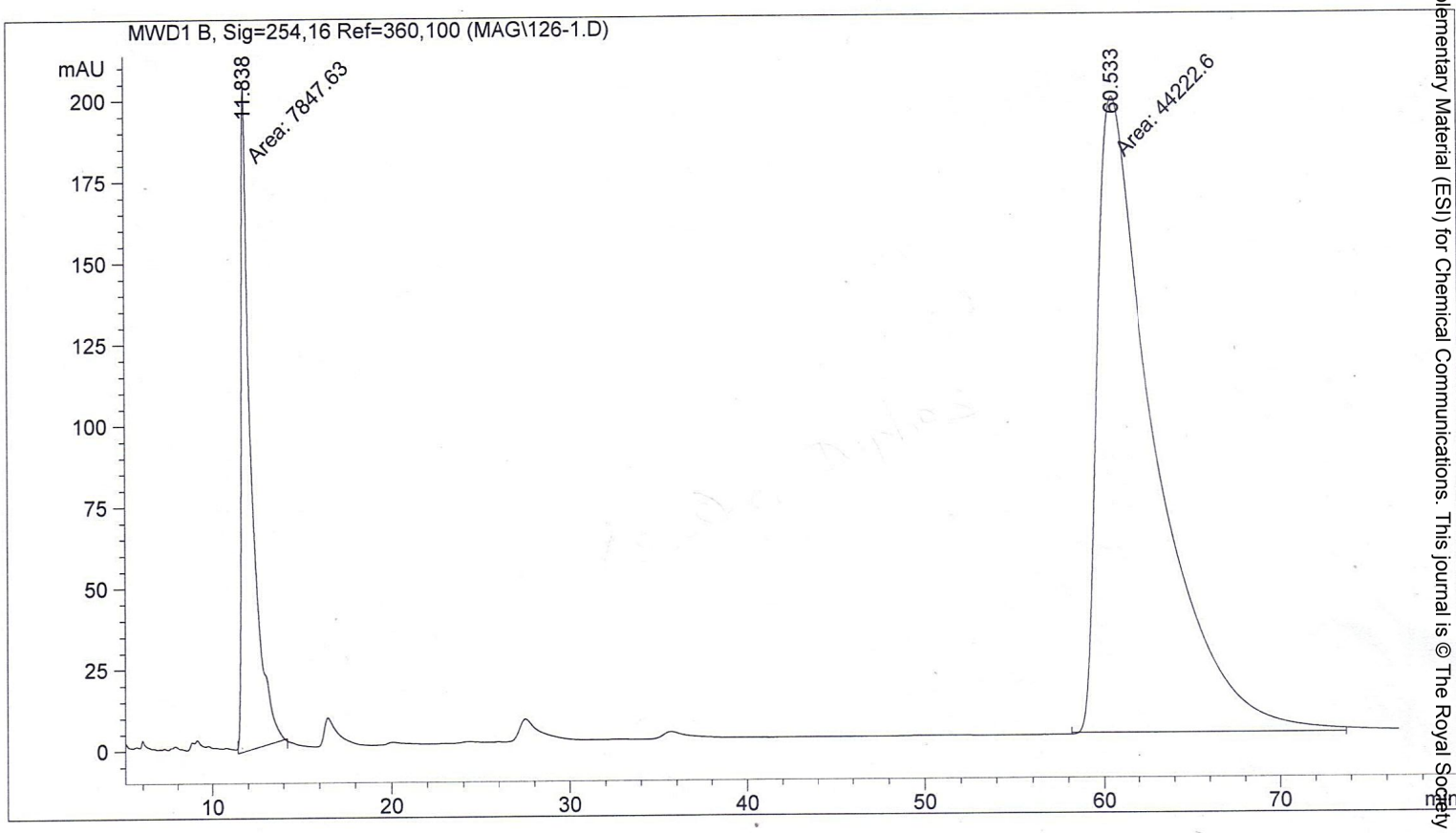


Table 3, entry 3



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.838	MM	0.6412	7847.62646	203.97250	15.0712
2	60.533	MM	3.7690	4.42226e4	195.55606	84.9288
Totals :				5.20703e4	399.52856	

Chiral pak ADH
5%IPA

==========

Injection Date : 5/2/2008 3:54:21 PM
Sample Name : 112-3 Location : Vial 4
Acq. Operator : Magesh
Acq. Instrument : Instrument 1 Inj Volume : 100 µl
Acq. Method : C:\HPCHEM\1\METHODS\WSM.M
Last changed : 5/2/2008 3:48:53 PM by Magesh
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\WSM.M
Last changed : 5/2/2008 5:00:57 PM by Magesh
(modified after loading)

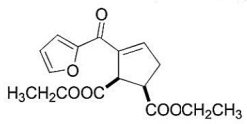
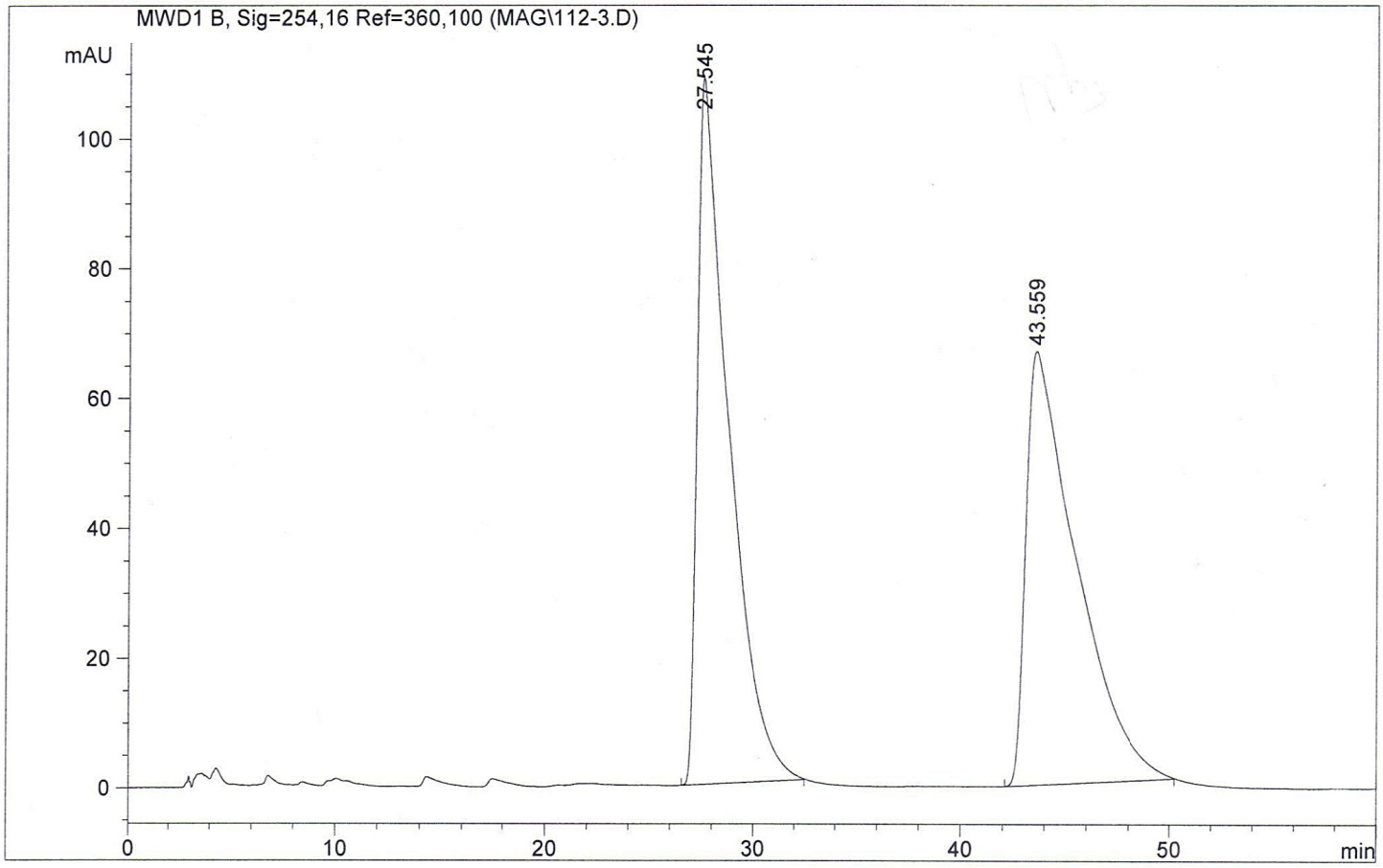


Table 2, entry 4

NN



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.545	BB	1.3799	1.14541e4	108.82535	50.5247
2	43.559	BB	2.1314	1.12162e4	66.71463	49.4753
Totals :				2.26703e4	175.53998	

Results obtained with enhanced integrator!

==========

*** End of Report ***

Data File C:\HPCHEM\1\DATA\MAG\155-1.D Sample Name: 155-1

Chiral pak ADH
5% IPA

75%

==========

Injection Date : 5/2/2008 5:35:19 PM
Sample Name : 155-1 Location : Vial 4
Acq. Operator : Magesh
Acq. Instrument : Instrument 1 Inj Volume : 100 µl
Acq. Method : C:\HPCHEM\1\METHODS\WSM.M
Last changed : 5/2/2008 5:31:41 PM by Magesh
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\WSM.M
Last changed : 5/2/2008 6:27:37 PM by Magesh
(modified after loading)

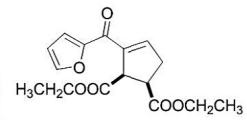
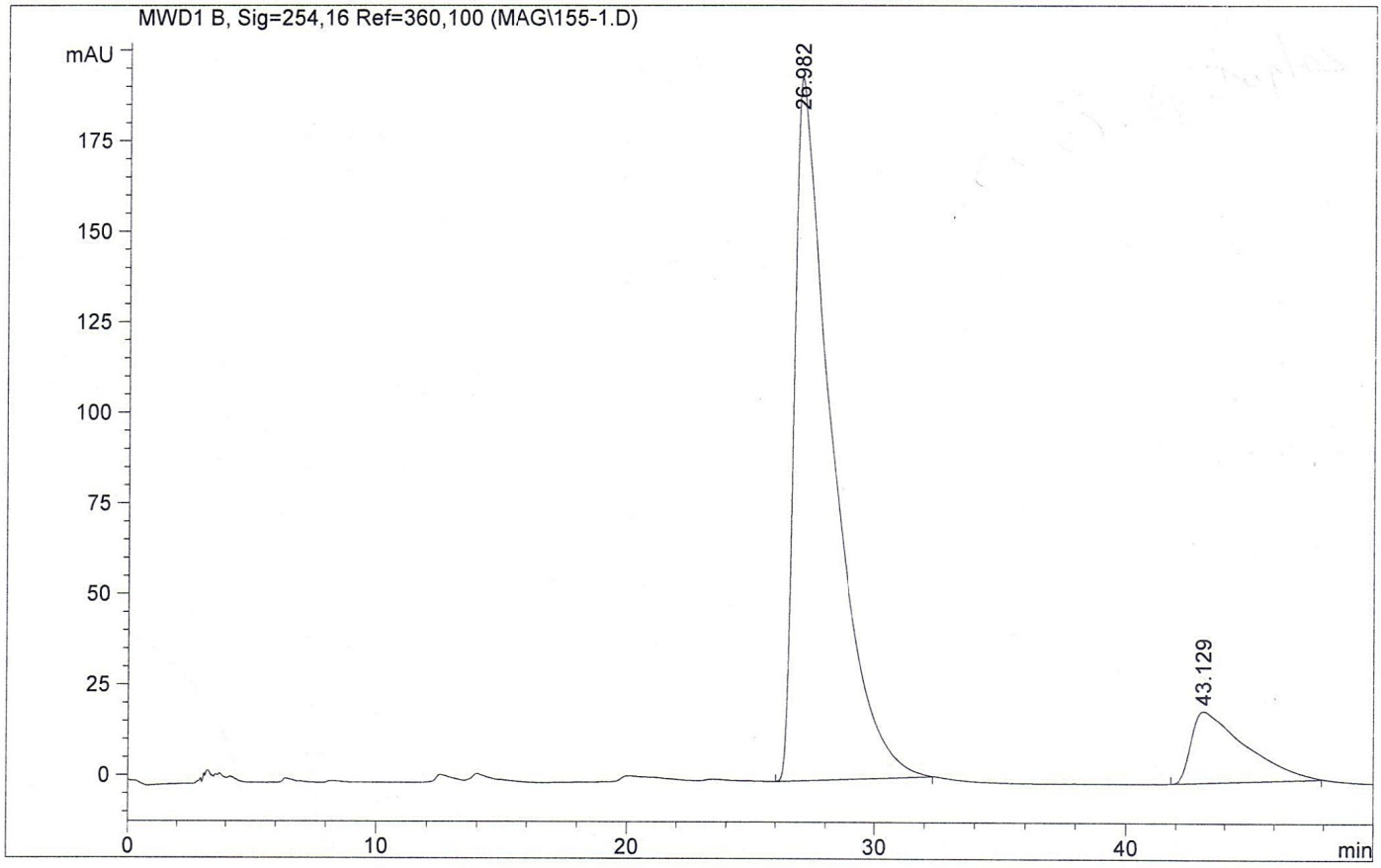


Table 3, entry 4

NN



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.982	PB	1.3730	2.03683e4	193.66440	87.3165
2	43.129	BB	1.7651	2958.68018	19.64435	12.6835
Totals :				2.33270e4	213.30875	

Results obtained with enhanced integrator!

==========

*** End of Report ***

Data File C:\CHEM32\1\DATA\MAG\048-3.D
Sample Name: 048-3

```
==========================================================================
Acq. Operator   : MAG
Acq. Instrument : Instrument 1                    Location : Vial 4
Injection Date  : 8/22/2008 11:27:52 AM
                                                  Inj Volume : 50 µl
Acq. Method     : C:\CHEM32\1\METHODS\WSM.M
Last changed    : 8/22/2008 11:25:25 AM by MAG
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\WSM.M
Last changed    : 10/11/2007 11:41:32 AM by SM
Method Info     : weijuan290nm

Sample Info     : 048-3 repeat
```

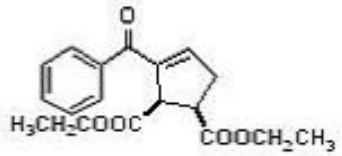
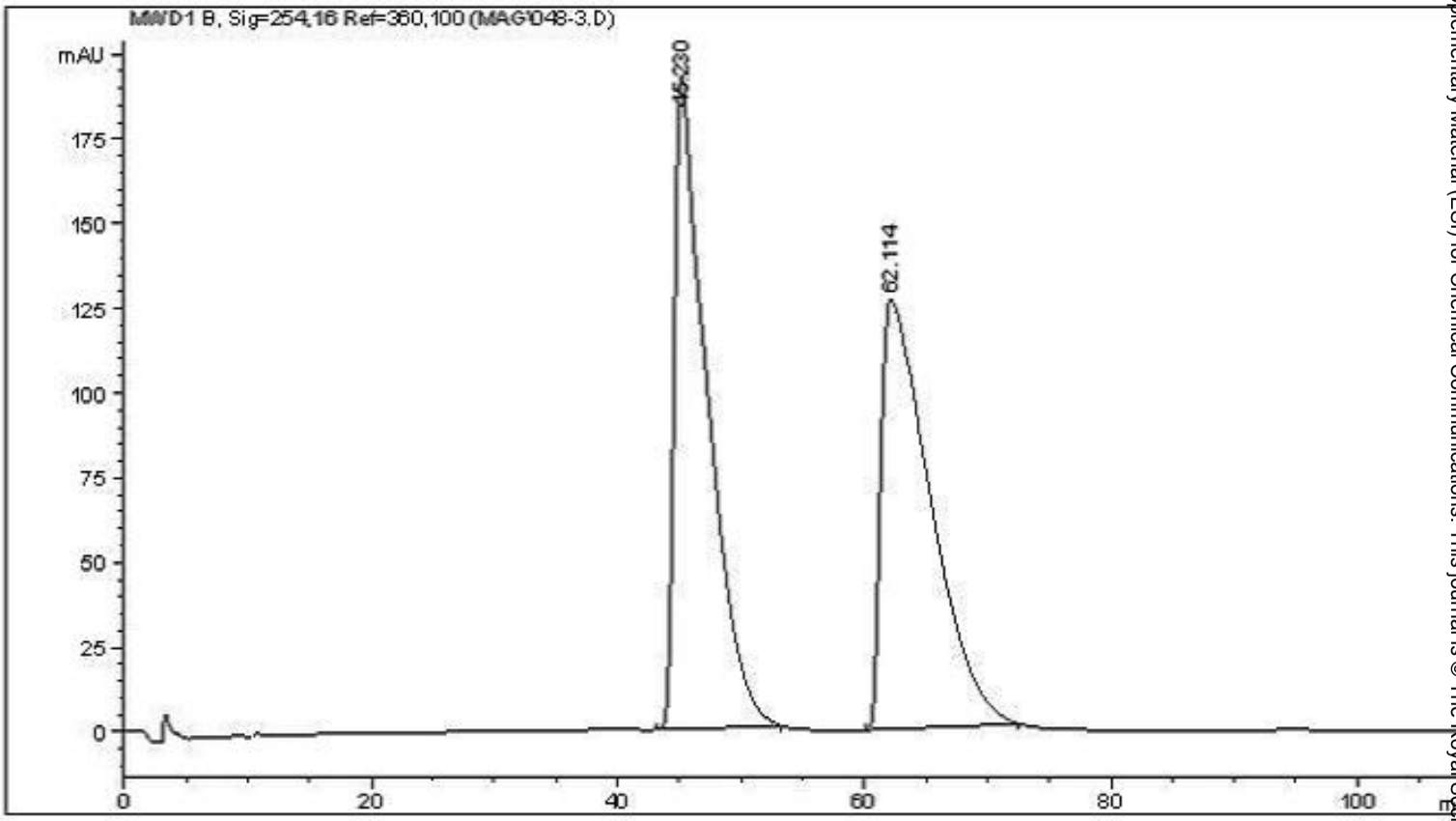


Table 1, entry 4




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  45.230 BB    2.4599 3.55767e4   193.06064  50.1337
   2  62.114 BB    3.5612 3.53870e4   126.98512  49.8663

Totals :                  7.09638e4   320.04575
```

Sample Name: 148

```
Acq. Operator    : Magesh
Acq. Instrument  : Instrument 1                    Location : Vial 4
Injection Date   : 4/25/2008 8:30:52 PM
                                                   Inj Volume : 50 µl
Acq. Method      : C:\CHEM32\1\METHODS\WSM.M\WSM.M
Last changed     : 4/25/2008 8:29:18 PM by Magesh
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\ZJF.M
Last changed     : 8/19/2008 11:06:45 PM by ZJF
                   (modified after loading)
Method Info      : WAP254nm

Sample Info      : Chiralpak ADH
                   2% IPA
```

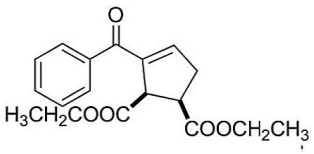
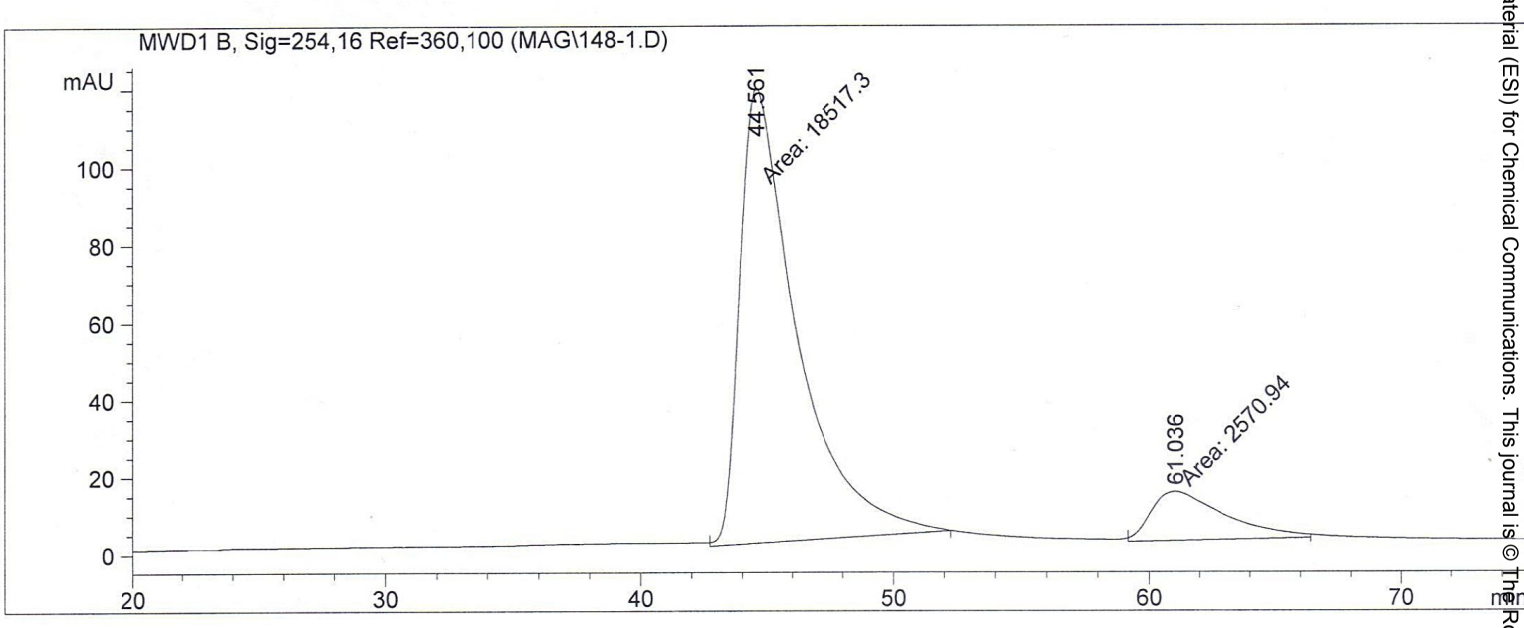


Table 2, entry 5



Height Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height    Height
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  44.561 MM    2.6629 1.85173e4   117.37875  90.2358
   2  61.036 MM    3.3736 2570.93774   12.70125   9.7642

Totals :                  2.10882e4   130.08000
```

*** End of Report