SUPPORTING INFORMATION

Silver-catalysed Doyle-Kirmse reaction of allyl and propargyl sulfides.

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General Experimental

All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Na), Et_2O (Na), CH_2Cl_2 (P_4O_{10}), Et_3N (CaH_2), toluene (Na). Anhydrous $ClCH_2CH_2Cl$ was purchased from Aldrich.

Flash chromatography: Fluorochem silica gel 60 (40-63 u). IR: Perkin–Elmer Paragon 1600 FTIR spectrometer spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS and HRMS (EI): VG-ZabSpec, MS and HRMS (ES): Micromass LCT. Melting points: Kofler hot stage. Elemental analyses: Carlo Erba EA1110. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. Asynt DrySin heating blocks on stirrer hotplates were employed for reactions with temperature controlled via external probe. NMR: Spectra were recorded on Bruker AC300, AV300 and Bruker AV400 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm). 1D and 2D spectra were recorded using the following pulse sequences from the Bruker standard pulse program library: PENDANT, DEPT 45, DEPT 135; Gradient COSY 90; Gradient HSQC for $^1J(C,H) = 145$ Hz; Gradient HMBC for correlations via $^nJ(C,H)$. HPLC was performed on a Dionex Summit instrument.

Products

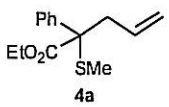
General procedure for the silver-catalysed Doyle Kirmse reaction

Silver triflate (10 mol%) was added to a solution of the sulfide (2 eq.) and diazo compound (1 eq.) in CH_2Cl_2 (0.05 M). The resulting mixture was stirred at 35 °C under an argon atmosphere until the reaction was complete (monitored by GC/MS or TLC). The crude mixture was rapidly filtered under a plug of silica and the solvent was evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate, 95/5) to give the desired sulfides.

The following compounds were prepared by this method:

From the 2,3-sigmatropic rearrangement of allyl sulfonium ylides: Products (4)

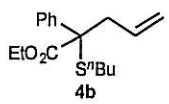
Ethyl 2-phenyl-2-(methylthio)-4-pentenoate (4a)



4a

Colourless oil (45 mg, 84%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* 7.1, 3 H), 1.90 (s, 3 H), 2.86 (m, 2 H), 4.24 (q, *J* 7.1, 2 H), 4.97 (m, 1 H), 5.00 (m, 1 H), 5.67 (m, 1 H), 7.18-7.40 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.1, 14.1, 42.5, 59.9, 61.5, 118.5, 127.2, 127.7 (2 C), 128.1 (2 C), 132.9, 138.7, 171.9; IR (NaCl): ν (cm^{-1}) = 3078, 2979, 2922, 1723, 1494, 1445, 1298, 1258, 1218, 1028, 918, 700; HR-MS (ES-TOF): m/z: calc for $C_{14}H_{18}O_2NaS$: 273.0925 found 273.0934 [*M* + *Na*].

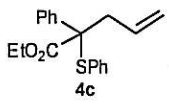
Ethyl 2-phenyl-2-(butylthio)-4-pentenoate (4b)



4b

Colourless oil (55 mg, 88%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.77 (t, *J* 7.2, 3 H), 1.20 (t, *J* 7.1, 3 H), 1.26 (m, 2 H), 1.38 (m, 2 H), 2.32 (m, 2 H), 2.80 (m, 2 H), 4.18 (q, *J* 7.1, 2 H), 4.90 (m, 1 H), 4.93 (m, 1 H), 5.61 (ddt, *J* 16.6, 10.5 and 7.1, 1 H), 7.18 (m, 1 H), 7.26 (m, 2 H), 7.34 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.6, 14.1, 22.1, 29.7, 30.7, 43.3, 60.2, 61.5, 118.5, 127.2, 127.7 (2 C), 128.0 (2 C), 133.0, 139.3, 172.2; IR (NaCl): ν (cm^{-1}) = 2960, 2931, 2872, 1723, 1445, 1258, 1212, 1028, 699; HR-MS (ES-TOF): m/z: calcd for $C_{17}H_{24}O_2NaS$: 315.1395, found 315.1389 [*M* + *Na*].

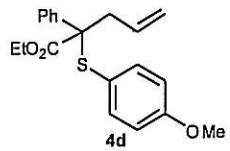
Ethyl 2-phenyl-2-(phenylthio)-4-pentenoate (4c)



4c

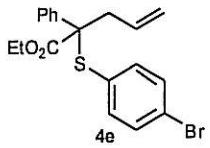
Colourless oil, 19 h (55 mg, 85%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, *J* 7.1, 3 H), 2.95 (m, 2 H), 4.26 (m, 2 H), 5.14 (m, 1 H), 5.22 (m, 1 H), 6.02 (m, 1 H), 7.23 (m, 5 H), 7.35 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 40.5, 61.7, 62.3, 118.7, 127.3, 127.4 (2 C), 128.0 (2 C), 128.4 (2 C), 129.1, 130.8, 133.2, 136.8 (2 C), 140.0, 171.8; IR (NaCl): ν (cm^{-1}) = 3059, 2979, 1727, 1472, 1438, 1212, 1024, 693; HR-MS (ES-TOF): m/z : calcd for $C_{19}H_{20}O_2NaS$: 335.1082, found 335.1078 [*M* + *Na*].

Ethyl 2-phenyl-2-(4-methoxyphenylthio)-4-pentenoate (4d)



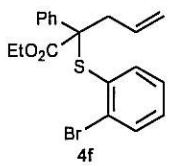
Colourless oil (62 mg, 85%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* 7.1, 3 H), 2.84 (m, 2 H), 3.76 (s, 3 H), 4.18 (m, 2 H), 5.08 (m, 1 H), 5.12 (m, 1 H), 5.93 (m, 1 H), 6.71 (d, *J* 8.8, 2 H), 7.06 (d, *J* 8.8, 2 H), 7.26 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 40.2, 55.2, 61.6, 64.2, 113.9 (2C), 118.6, 121.3, 127.3, 127.4 (2 C), 127.9 (2 C), 133.3, 138.5 (2 C), 140.0, 160.6, 171.8; IR (NaCl): ν (cm^{-1}) = 3058, 2924, 2853, 1731, 1591, 1492, 1315, 1291, 1248, 1208, 1030, 702; HR-MS (ES-TOF): m/z: calcd for $C_{20}H_{22}O_3NaS$: 365.1191, found 365.1187 [*M* + *Na*].

Ethyl 2-phenyl-2-(4-bromophenylthio)-4-pentenoate (4e)



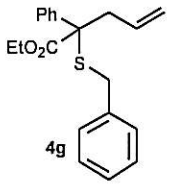
Colourless solid (80 mg, 97%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, *J* 7.1, 3 H), 2.78 (m, 1 H), 2.92 (m, 1 H), 4.18 (m, 2 H), 5.09 (m, 1 H), 5.14 (m, 1 H), 5.91 (m, 1 H), 6.93 (d, *J* 8.3, 2 H), 7.26 (m, 7 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 40.3, 61.9, 64.5, 119.0, 123.9, 127.4 (2 C), 127.5, 128.1 (2 C), 130.1, 131.5 (2 C), 132.9, 138.1 (2 C), 139.7, 171.5; IR (NaCl, Nujol): ν (cm^{-1}) = 3007, 2924, 2054, 1729, 1461, 1212, 1121, 1068, 1021, 932, 816, 731, 701; HR-MS (ES-TOF): m/z: calcd for $C_{19}H_{19}O_2NaSBr$: 413.0187 found 413.0194 [*M* + *Na*].

Ethyl 2-phenyl-2-(2-bromophenylthio)-4-pentenoate (4f)



Light pink solid, 24 h (70 mg, 83%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, *J* 7.1, 3 H), 3.20 (m, 2 H), 4.43 (m, 2 H), 5.25 (m, 1 H), 5.29 (m, 1 H), 6.16 (m, 1 H), 7.23-7.33 (m, 3 H), 7.47-7.60 (m, 5 H), 7.78 (d, *J* 7.5, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.9, 41.9, 61.9, 65.0, 118.8, 127.0, 127.5, 127.9 (2 C), 128.0 (3 C), 129.7, 130.3, 133.1 (2C), 137.0, 139.0, 171.3; IR (NaCl, nujol): ν (cm^{-1}) = 3082, 1721, 1259, 1212, 1123, 1022, 927, 759, 708; HR-MS (ES-TOF): m/z: calc for $C_{19}H_{19}O_2NaSBr$: 413.0187 found 413.0185 [*M* + *Na*].

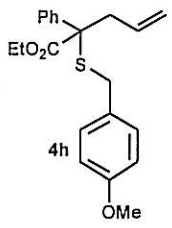
Ethyl 2-phenyl-2-(benzylthio)-4-pentenoate (4g)



Yellow oil (63 mg, 92%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, *J* 7.1, 3 H), 2.90 (m, 2 H), 3.49 (d, *J* 11.8, 1 H), 3.71 (d, *J* 11.8, 1 H), 4.27 (q, *J* 7.1, 2 H), 4.99 (m, 1 H), 5.02 (m, 1 H), 5.71 (ddt, *J* 17.0, 10.3 and 7.0, 1 H), 7.25 (m, 6 H, H-Ar), 7.37 (m, 2 H, H-Ar), 7.49 (m, 2 H, H-Ar); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.1, 35.1, 43.2, 61.1, 61.6, 118.7, 127.1, 127.4, 127.8 (2 C), 128.2 (2 C), 128.4 (2 C), 129.1 (2 C), 132.8, 136.9, 139.1, 172.1; IR (NaCl): ν (cm^{-1}) = 3425, 2980, 2935, 1721,

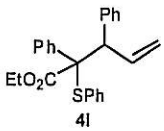
1495, 1446, 1219, 911, 733; HR-MS (ES-TOF): m/z: calcd for $C_{20}H_{22}O_2NaS$: 349.1238, found 349.1244 [*M* + *Na*].

Ethyl 2-phenyl-2-(4-methoxybenzylthio)-4-pentenoate (4h)



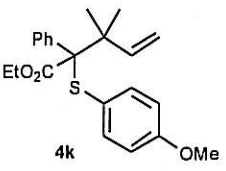
Colourless oil (48 mg, 64%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.30 (t, *J* 7.0, 3 H), 2.90 (d, *J* 7.0, 2 H), 3.44 (d, *J* 11.7, 1 H), 3.67 (d, *J* 11.7, 1 H), 3.77 (s, 3 H), 4.28 (q, *J* 7.0, 2 H), 5.00 (m, 2 H), 5.71 (m, 1 H), 6.79 (d, *J* 8.4, 2 H), 7.12 (d, *J* 8.4, 2 H), 7.28 (m, 1 H), 7.37 (m, 2 H), 7.48 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.1, 34.5, 43.2, 55.2, 61.1, 61.6, 113.9 (2 C), 118.7, 127.3, 127.7 (2 C), 128.2 (2 C), 128.7, 130.2 (2 C), 132.9, 139.1, 158.7, 172.1; IR (NaCl): ν (cm^{-1}) = 2979, 1724, 1610, 1511, 1445, 1301, 1249, 1217, 1176, 1034, 737, 700; HR-MS (ES-TOF): m/z: calcd for $C_{21}H_{24}O_3NaS$: 379.1344, found 379.1349 [*M* + *Na*].

Ethyl 2-phenyl-2-(phenylthio)-3-phenyl-4-pentenoate (4i)



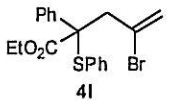
Isolated as a 35 : 65 mixture of diastereoisomers (50 mg, 62%); ^{1}H-NMR (400 MHz, $CDCl_3$): major isomer δ = 1.00 (t, *J* 7.1, 3 H), 3.79 (m, 1 H), 4.01 (m, 1 H), 4.59 (d, *J* 9.3, 1 H), 5,15 (m, *J* 10.1 and 1.7, 1 H), 5.21 (m, 1 H), 6.02 (m, 1 H), 6.74 (m, 2 H), 7.10-7.30 (m, 11 H), 7.52 (m, 2 H); minor isomer δ = 1.01 (t, *J* 7.1, 3 H), 3.84 (m, 1 H), 4.01 (m, 1 H), 4.59 (d, *J* 9.3, 1 H), 5.20 (m, 1 H), 5.24 (m, 1 H), 6.18 (m, 1 H), 6.78 (m, 2 H), 7.10-7.30 (m, 13 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.7, 56.2, 57.9, 61.2, 61.3, 69.6, 118.3, 118.4, 126.7, 127.2, 127.4, 127.5, 128.3, 130.4, 130.5, 131.0, 131.6, 134.5, 135.3, 135.4, 135.8, 136.3, 137.4, 137.8, 139.8, 170.3; IR (NaCl): ν (cm^{-1}) = 2979, 2934, 1724, 1440, 1219, 1026, 921, 746, 718, 701; HR-MS (ES-TOF): m/z: calc for $C_{25}H_{24}O_2NaS$: 411.1395 found 411.1392 [*M* + *Na*].

Ethyl 2-phenyl-2-(4-methoxyphenylthio)-3,3-dimethyl-4-pentenoate (4k)



Reaction was performed with additional 4Å molecular sieves; colourless solid (38.6 mg, 49%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, *J* 7.1, 3 H), 1.20 (s, 3 H), 1.30 (s, 3 H), 3.68 (m, 1 H), 3.71 (s, 3 H), 4.02 (m, 1 H), 4.92 (dd, *J* 17.4 and 1.1, 1 H), 5.03 (dd, *J* 10.8 and 1.1, 1 H), 6.42 (dd, *J* 17.4 and 10.8, 1 H), 6.66 (d, *J* 8.8, 2 H), 7.25 (m, 5 H), 7.61 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.6, 25.2 (2 C), 45.0, 55.2, 60.6, 72.9, 112.8, 113.7 (2 C), 123.5, 126.3 (2 C), 126.9, 131.5 (2 C), 137.3 (2 C), 137.5, 145.0, 160.1, 170.6; IR (NaCl, Nujol): ν (cm^{-1}) = 3088, 2954, 1714, 1590, 1490, 1288, 1250, 1220, 1036, 836, 627; HR-MS (ES-TOF): m/z: calcd for $C_{22}H_{26}O_3NaS$: 393.1500, found 393.1503 [*M* + *Na*].

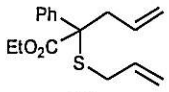
Ethyl 2-phenyl-2-(phenylthio)-4-bromo-4-pentenoate (4l)



4l

Yellow solid (73 mg, 89%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, *J* 7.1, 3 H), 3.41 (s, 1 H), 4.21 (m, 2 H), 5.64 (m, 1 H), 5.74 (m, 1 H), 7.24-7.33 (m, 10 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.8, 47.1, 62.0, 63.1, 121.3, 127.3, 127.6, 127.7 (2 C), 128.0 (2 C), 128.5 (2 C), 129.4, 130.6, 136.6 (2 C), 138.7, 170.9; IR (NaCl, Nujol): ν (cm^{-1}) = 3052, 1729, 1636, 1463, 1209, 1186, 1092, 1022, 901, 754, 707, 695; HR-MS (ES-TOF): m/z: calcd for $C_{19}H_{19}O_2NaSBr$: 413.0187 found 413.0192 [*M* + *Na*].

Ethyl 2-phenyl-2-(allylthio)-4-pentenoate (4m)

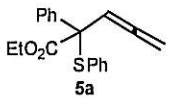


4m

Colourless oil (43 mg, 84%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, *J* 7.1, 3 H), 2.89 (m, 2 H), 2.99 (m, 1 H), 3.14 (m, 1 H), 4.26 (q, *J* 7.1, 2 H), 4.97-5.14 (m, 4 H), 5.73 (m, 2 H), 7.24-7.44 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.1, 33.6, 43.2, 60.7, 61.6, 117.7, 118.7, 127.3, 127.8 (2 C), 128.1 (2 C), 132.9, 133.2, 139.1, 172.1; IR (NaCl): ν (cm^{-1}) = 3080, 2980, 2934, 1725, 1683, 1446, 1297, 1214, 699; HR-MS (ES-TOF): m/z: calcd for $C_{16}H_{20}O_2NaS$: 299.1082, found 299.1074 [*M* + *Na*].

From the 2,3-sigmatropic rearrangement of propargyl sulfonium ylides: Products (5)

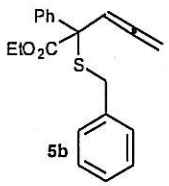
Ethyl 2-phenyl-2-(phenylthio)penta-3,4-dienoate (5a)



5a

Yellow oil (47 mg, 71%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, *J* 7.1, 3 H), 4.14 (m, 2 H), 4.69 (dd, *J* 11.3 and 6.6, 1 H), 4.74 (dd, *J* 11.3 and 6.6, 1 H), 5.75 (t, *J* 6.6, 1 H), 7.18-7.33 (m, 8 H), 7.43 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.9, 62.1, 64.2, 78.8, 94.0, 127.7, 127.9 (2 C), 128.0 (2 C), 128.3 (2 C), 128.9, 131.8, 136.4 (2 C), 139.0, 170.7, 208.3; IR (NaCl): ν (cm^{-1}) = 3059, 2982, 1955, 1729, 1472, 1229, 1026, 750, 693, 750; HR-MS (ES-TOF): m/z: calcd for $C_{19}H_{18}O_2NaS$: 333.0925, found 333.0920 [*M* + *Na*].

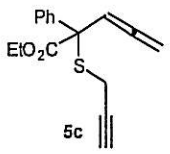
Ethyl 2-phenyl-2-(benzylthio)penta-3,4-dienoate (5b)



5b

Yellow oil (62 mg, 90%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, *J* 7.1, 3 H), 3.73 (d, *J* 11.6, 1 H), 3.78 (d, *J* 11.6, 1 H), 4.24 (q, *J* 7.1, 2 H), 4.91 (d, *J* 6.7, 2 H), 5.89 (t, *J* 6.7, 1 H), 7.19-7.40 (m, 8 H), 7.55 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.1, 36.1, 61.0, 62.1, 79.2, 94.2, 127.1, 127.7, 127.8 (2 C), 128.2 (2 C), 128.4 (2 C), 129.2 (2 C), 136.7, 138.7, 171.0, 208.4; IR (NaCl): ν (cm^{-1}) = 2980, 1955, 1727, 1600, 1494, 1446, 1222, 1030, 854, 696; HR-MS (ES-TOF): m/z: calcd for $C_{20}H_{20}O_2NaS$: 347.1082, found 347.1089 [*M* + *Na*].

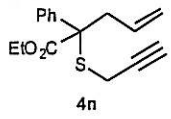
Ethyl 2-phenyl-2-(propargylthio)penta-3,4-dienoate (5c)



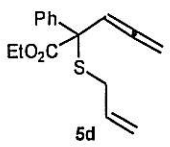
Yellow oil (43 mg, 63%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* 7.1, 3 H), 2.17 (t, *J* 2.7, 1 H), 3.27 (dd, *J* 16.0 and 2.7, 1 H), 3.33 (dd, *J* 16.0 and 2.7, 1 H), 4.25 (q, *J* 7.1, 2 H), 4.90 (dd, *J* 11.5 and 6.6, 1 H), 4.94 (dd, *J* 11.5 and 6.6, 1 H), 5.86 (t, *J* 6.6, 1 H), 7.34 (m, 3 H), 7.50 (m, 2 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.5, 29.7, 61.0, 62.3, 71.4, 79.4, 93.6, 127.8 (2 C), 128.0, 128.3 (2 C), 138.1, 170.7, 208.4; IR (NaCl): ν (cm^{-1}) = 3290, 2981, 2933, 1954, 1729, 1446, 1232, 1032, 855, 698, 642; HR-MS (ES-TOF): m/z: calcd for $C_{16}H_{16}O_2NaS$: 295.0769, found 295.0763 [*M* + *Na*].

Ethyl 2-phenyl-2-(propargylthio)-4-pentenoate (4n) / Ethyl 2-phenyl-2-(allylthio)penta-3,4-dienoate (5d)

(36.6 mg, 62%); Isolated as a 17 : 83 mixture of isomers **4n** : **5d**; HPLC separation was performed using a Phenomenex SEMI-PREP Luna 10u C18 column, size 250mm *10 mm, acetonitrile / water = 99 / 1 (3 mL/min).



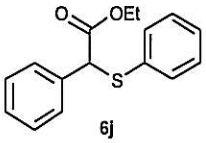
4n, colourless oil, ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, *J* 7.1, 3 H), 2.15 (t, *J* 2.7, 1 H), 2.93 (m, 2 H), 3.00 (dd, *J* 16.1 and 2.7, 1 H), 3.23 (dd, *J* 16.1 and *J* 2.7, 1 H), 4.27 (q, *J* 7.1, 2 H), 5.04 (m, 2 H), 5.74 (m, 1 H), 7.25-7.34 (m, 5 H, H-Ar); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 18.4, 42.9, 61.3, 61.8, 71.3, 79.6, 119.1, 127.6 (3 C), 128.4 (2 C), 132.6, 138.4, 171.8; IR (NaCl): ν (cm^{-1}) = 3286, 3070, 2980, 1725, 1446, 1213, 1023; HR-MS (ES-TOF): m/z: calcd for $C_{16}H_{18}O_2NaS$: 297.0925, found 297.0920 [*M* + *Na*].



5d; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* 7.1, 3 H), 3.21 (m, 2 H), 4.24 (q, *J* 7.1, 2 H), 4.87 (dd, *J* 11.5 and 6.6, 1 H), 4.91 (dd, *J* 11.5 and 6.6, 1 H), 5.05 (m, 1 H), 5.15 (ddt, *J* 17.0, 1.5 and 1.4, 1 H), 5.79 (ddt, *J* 17.0, 9.9 and 7.2, 1 H), 5.85 (t, *J* 6.6, 1 H), 7.37-7.25 (m, 3 H, H-Ar), 7.50 (m, 2 H, H-Ar); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 34.7, 60.7, 62.1, 79.1, 94.3, 117.9, 127.7, 127.8 (2 C), 128.2 (2 C), 133.2, 138.8, 171.0, 208.4; IR (NaCl): ν (cm^{-1}) = 3248, 3062, 2980, 2935, 1767, 1715, 1218 ; HR-MS (ES-TOF): m/z: calcd for $C_{16}H_{18}O_2NaS$: 297.0925 found 297.0933 [*M* + *Na*].

From deprenylation of sulfonium ylides: Products (6)

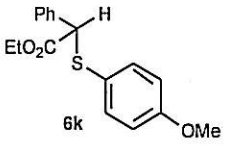
Ethyl 2-phenyl-2-(phenylthio)-ethanoate (6j)



6j

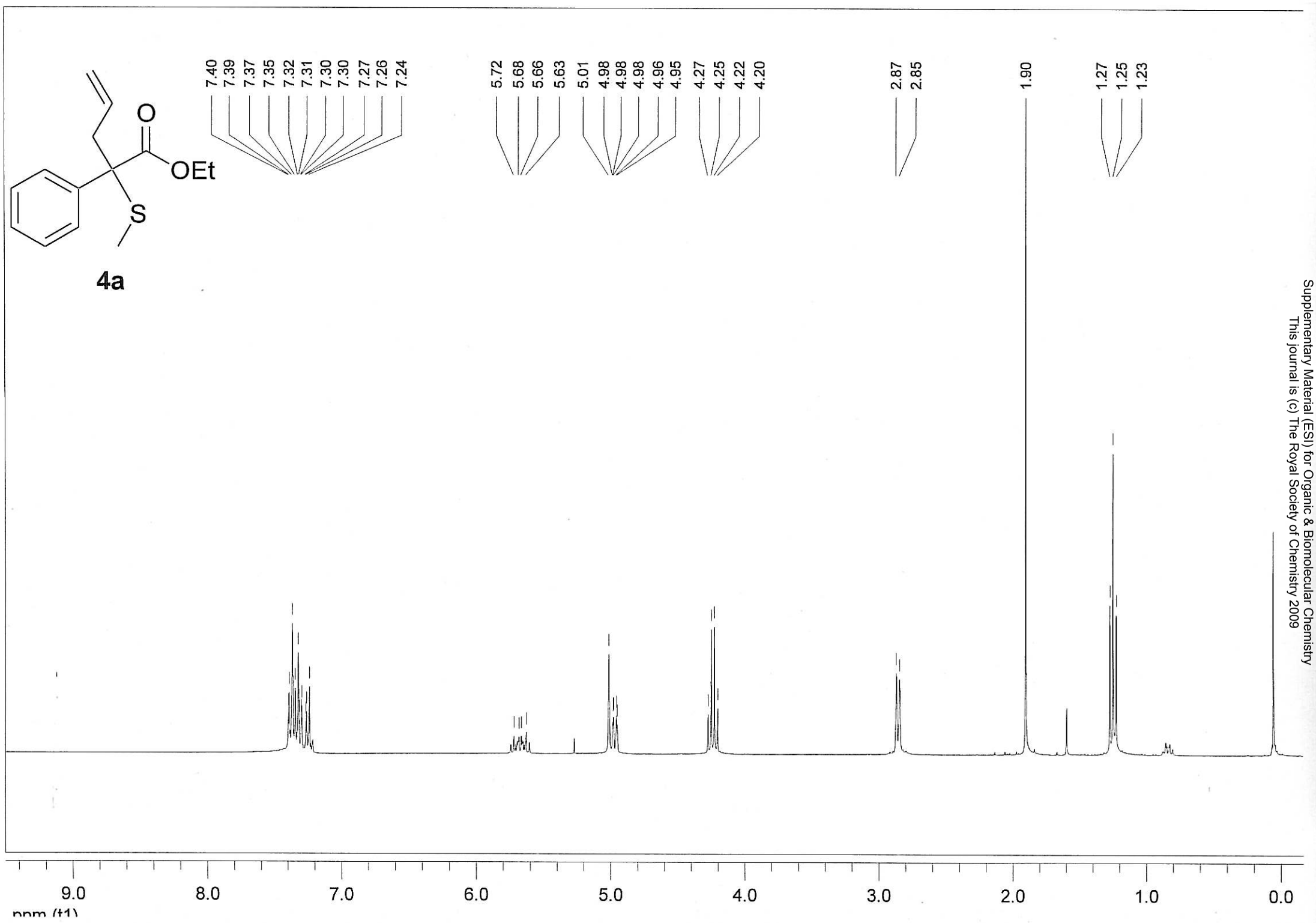
Colourless oil, 24 h (40 mg, 69%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, *J* 7.1, 3 H), 4.11 (m, 2 H), 4.89 (s, 1 H), 7.24 (m, 3 H), 7.28 (m, 3 H), 7.36 (m, 2 H), 7.43 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.0, 56.3, 61.7, 128.0, 128.2, 128.5 (2 C), 128.6 (2 C), 128.9 (2 C), 132.6 (2 C), 133.8, 135.6, 170.4; IR (NaCl): ν (cm^{-1}) = 3452, 3060, 2980, 1735, 1303, 1281, 1212, 1147, 1025, 693; HR-MS (ES-TOF): m/z: calcd for $C_{16}H_{16}O_2NaS$: 295.0769, found 295.0770 [*M* + *Na*].

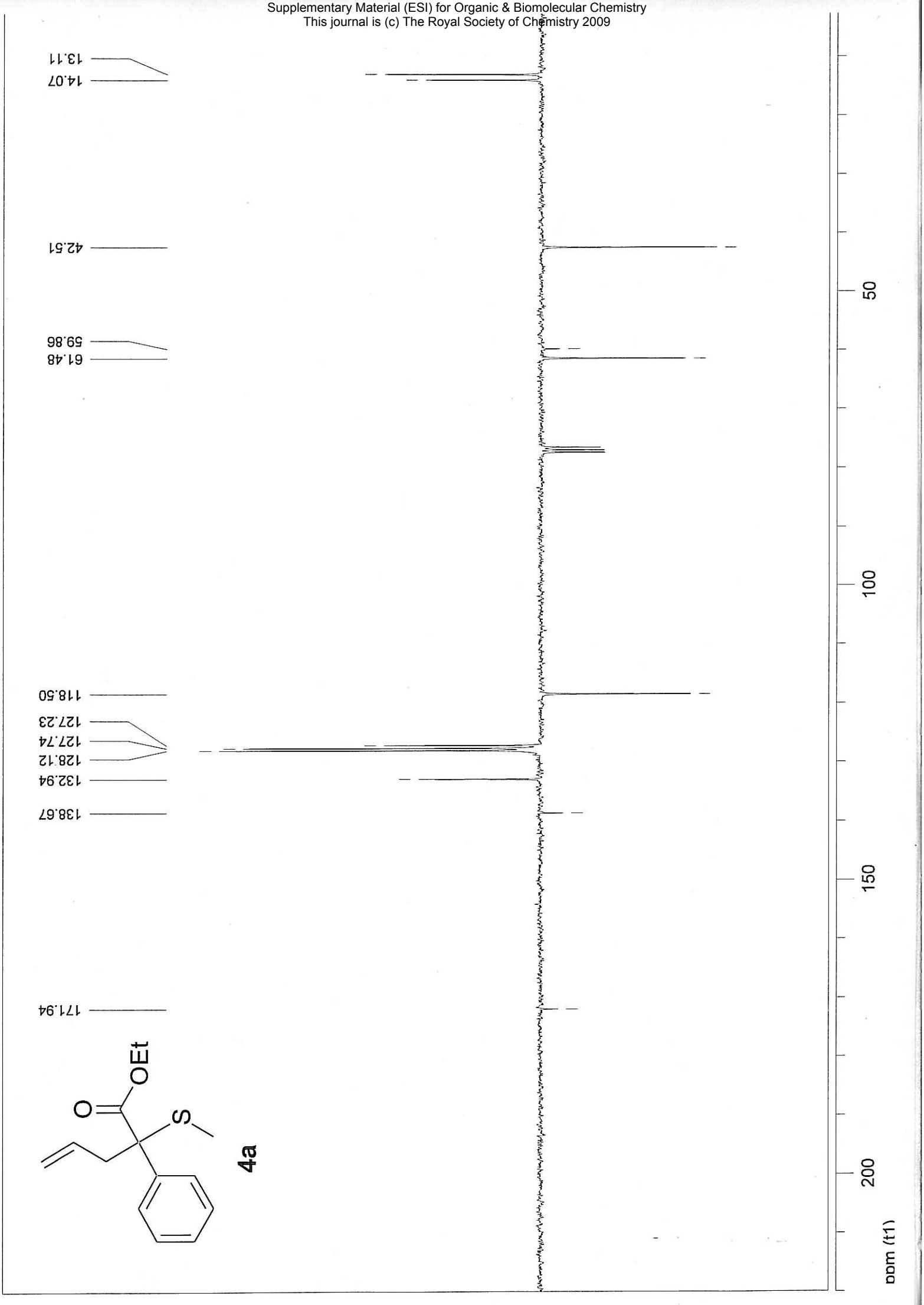
Ethyl 2-phenyl-2-(4-methoxyphenylthio)-ethanoate (6k)



6k

Reaction performed under molecular sieves, colourless oil (7.5 mg, 12%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, *J* 7.1, 3 H), 3.78 (s, 3 H), 4.12 (m, 2 H), 4.74 (s, 1 H), 6.79 (d, *J* 8.8, 2 H), 7.31 (m, 5 H), 7.23-7.42 (m, 2 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.0, 55.3, 57.4, 61.6, 114.4 (2 C), 123.8, 128.1, 128.5 (2 C), 128.6 (2 C), 135.9, 136.2 (2 C), 160.2, 170.5; IR (NaCl): ν (cm^{-1}) = 3064, 2979, 2837, 1733, 1592, 1493, 1286, 1248, 1146, 1029, 697, 640; HR-MS (ES-TOF): m/z: calcd for $C_{17}H_{18}O_3NaS$: 325.0874, found 325.0880 [*M* + *Na*].

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14.07
42.51
59.86
61.48
118.50
127.23
127.74
128.12
132.94
138.67
171.94
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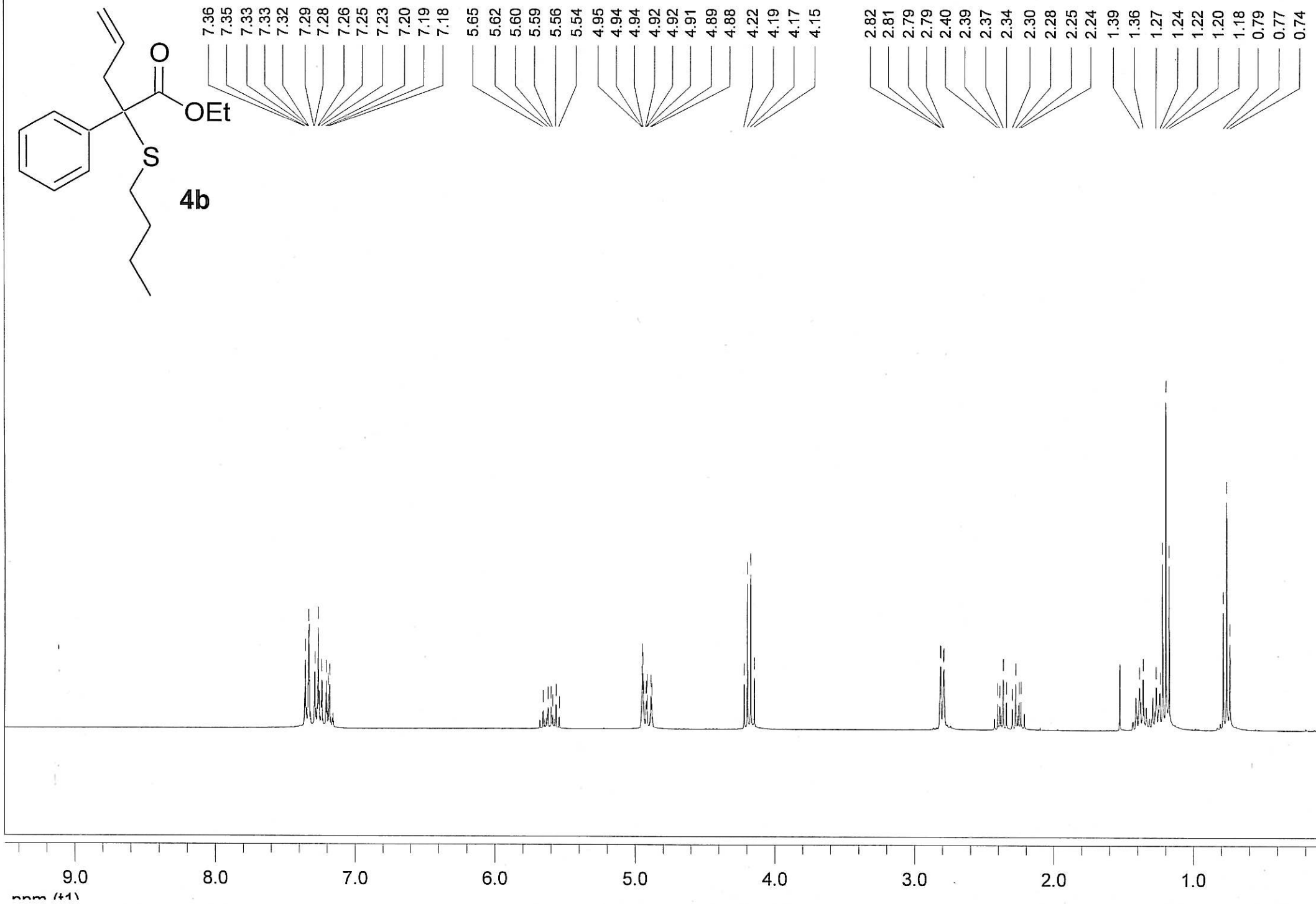
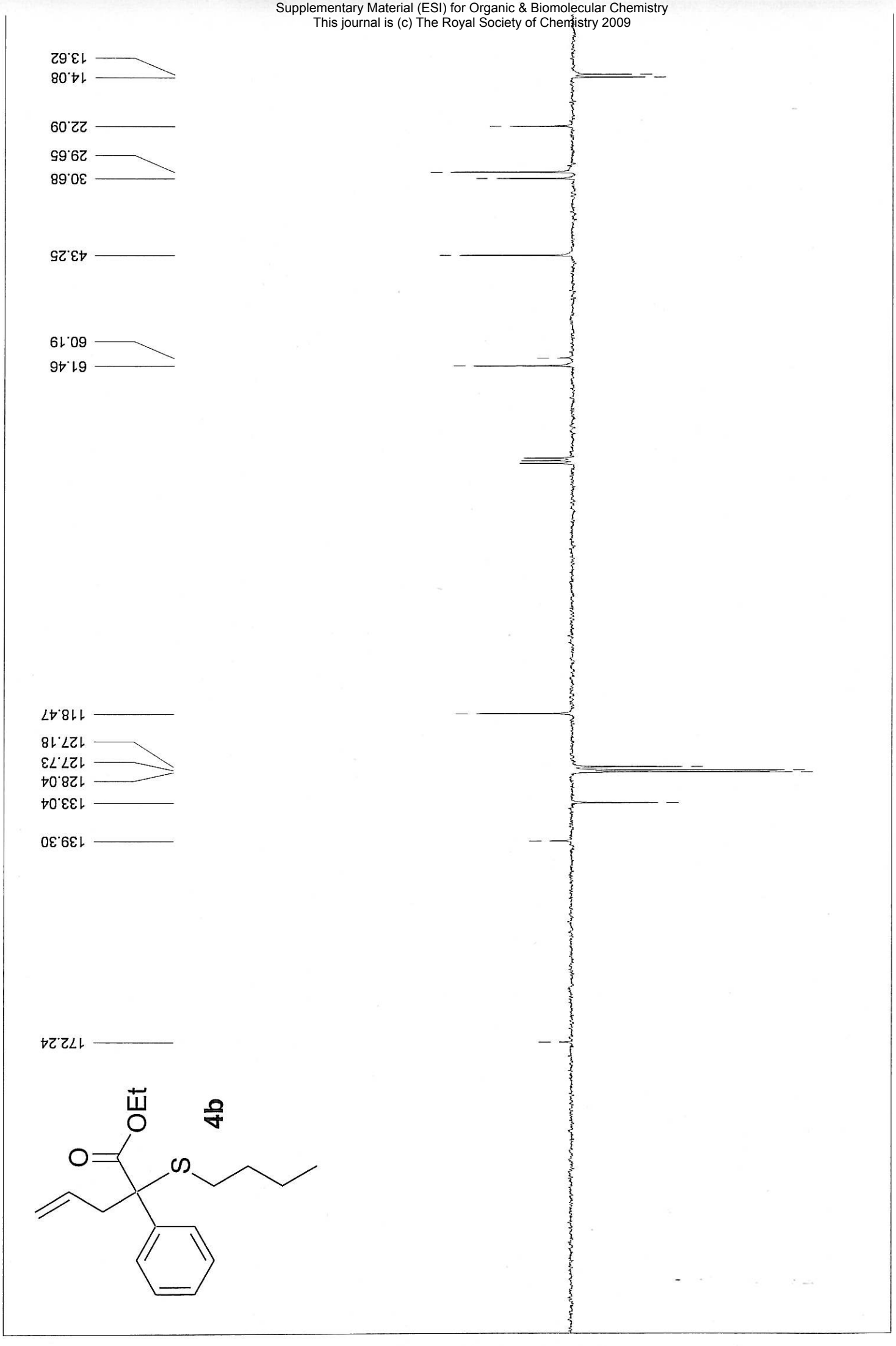
O
S
4a
50
100
150
200
ppm (t1)

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29.65
30.68
43.25
60.19
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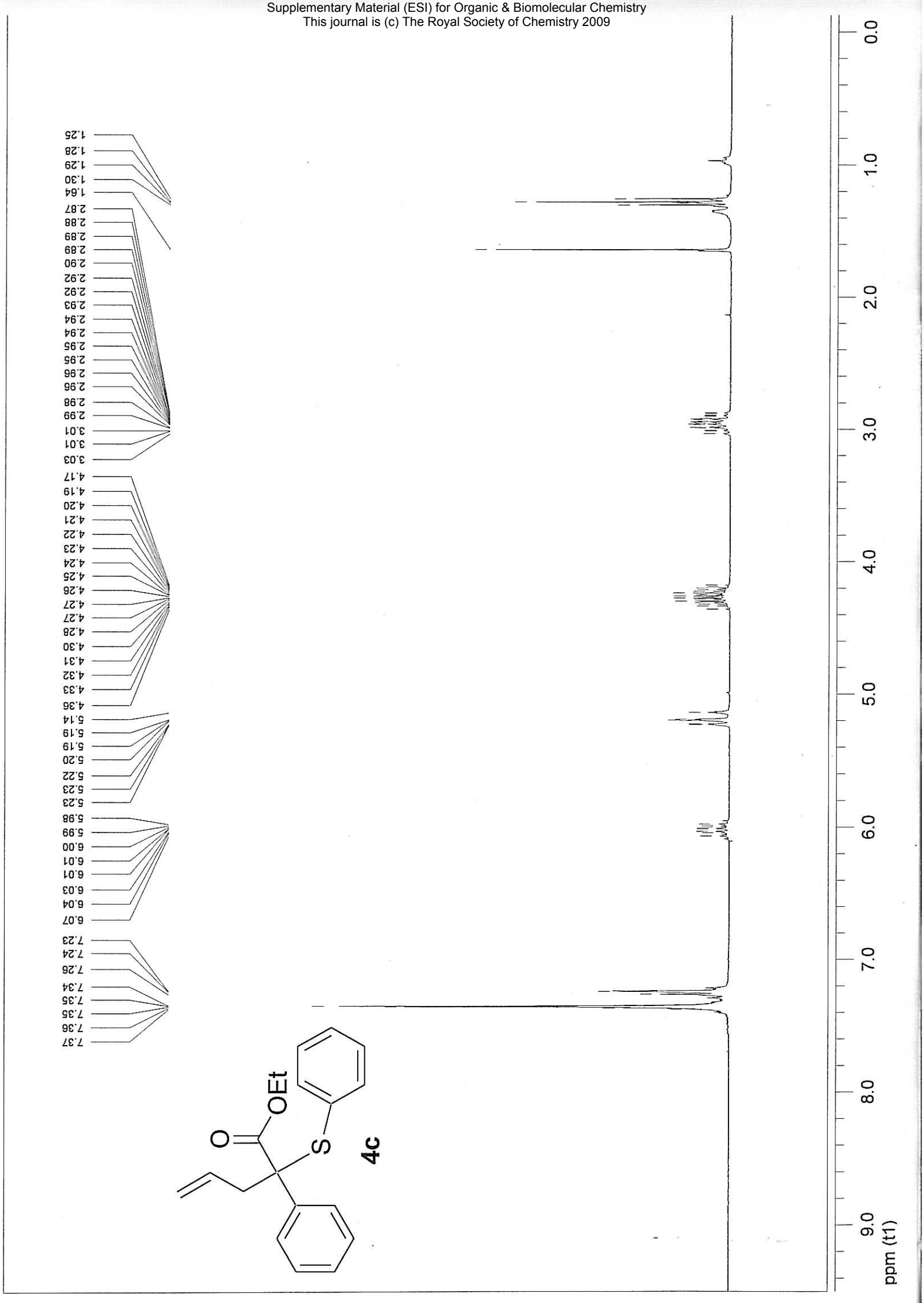
127.18
127.73
128.04
133.04
139.30
172.24
OEt
O
S
4b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1.30
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2.88
2.89
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2.90
2.92
2.92
2.93
2.94
2.94
2.95
2.95
2.96
2.96
2.98
2.99
3.01
3.01
3.03
4.17
4.19
4.20
4.21
4.22
4.23
4.24
4.25
4.26
4.27
4.27
4.28
4.30
4.31
4.32
4.33
4.36
5.14
5.19
5.19
5.20
5.22
5.23
5.23
5.98
5.99
6.00
6.01
6.01
6.03
6.04
6.07
7.23
7.24
7.26
7.34
7.35
7.35
7.36
7.37
O
OEt
S
4c
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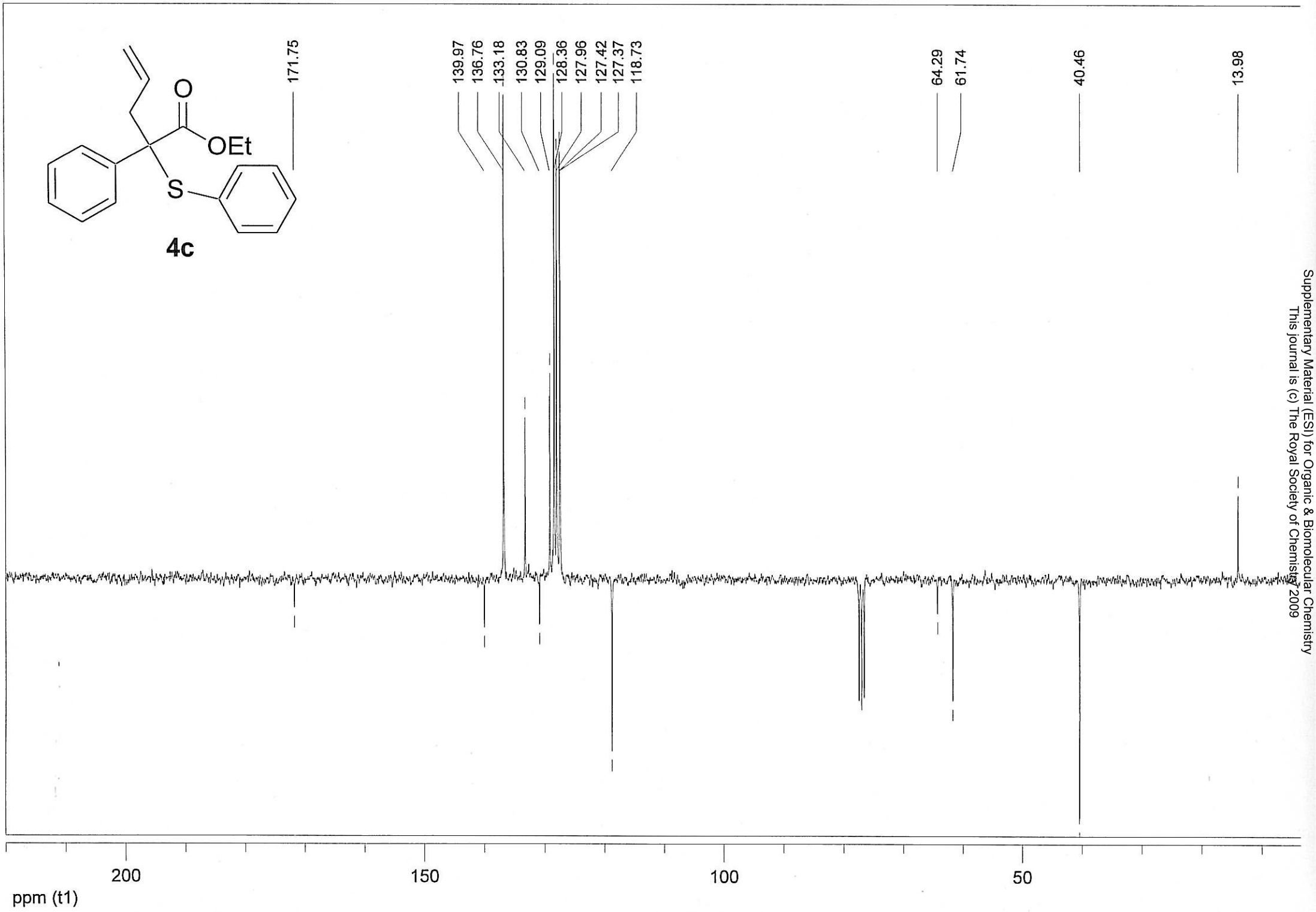
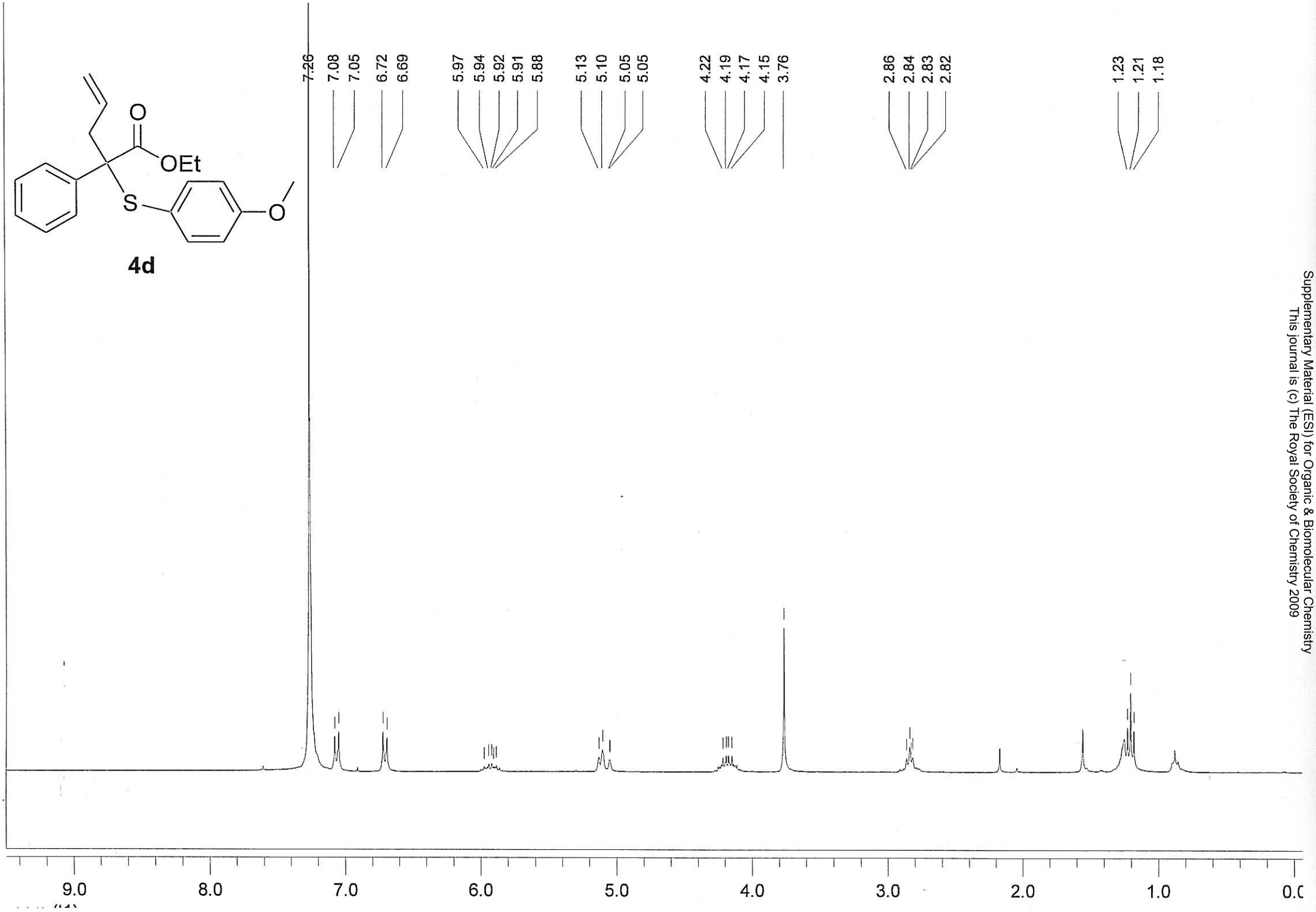
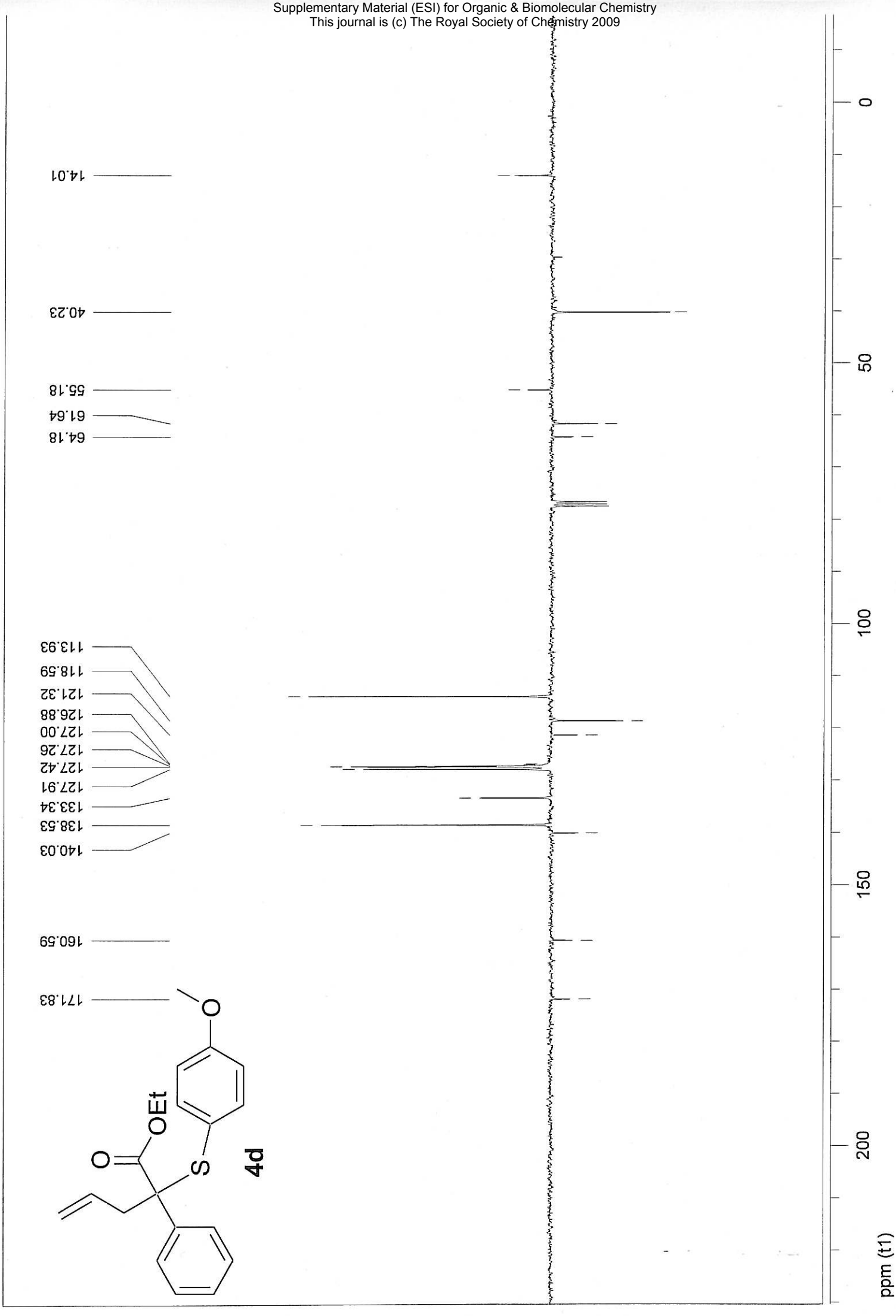
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)



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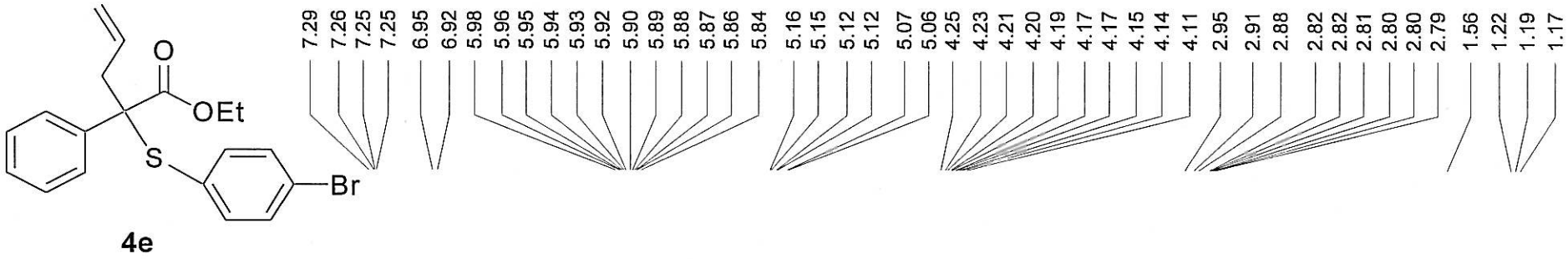
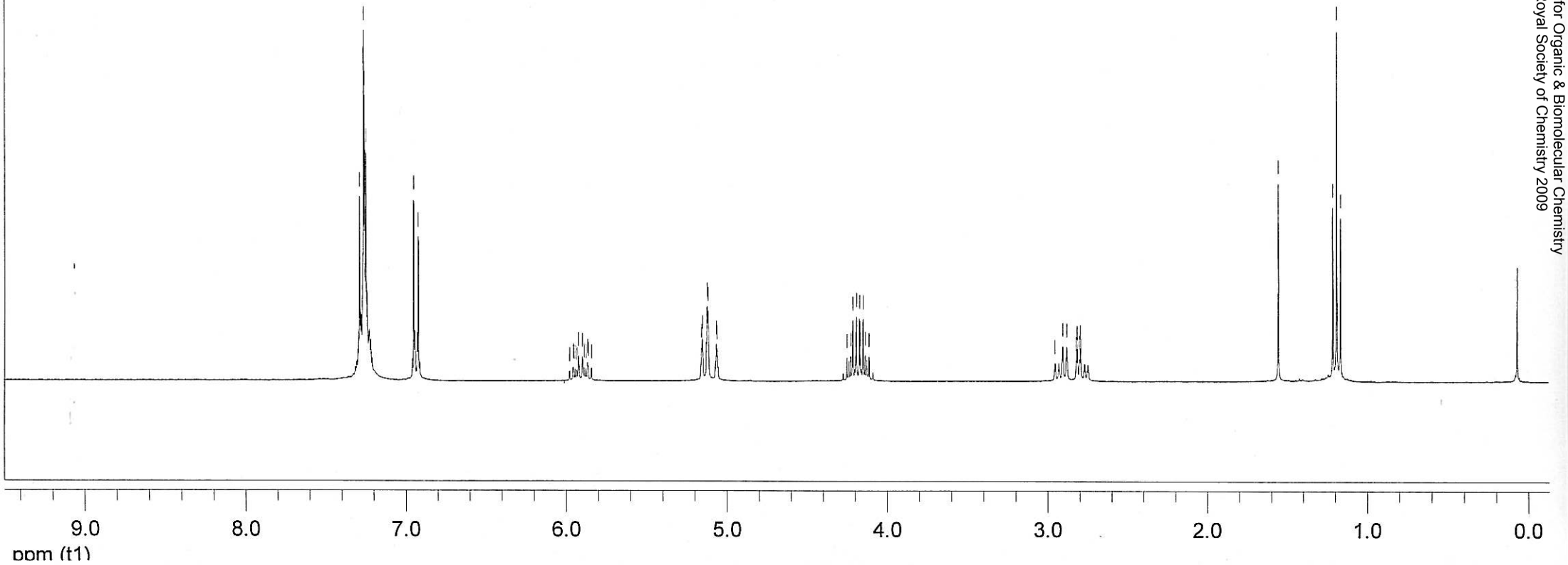
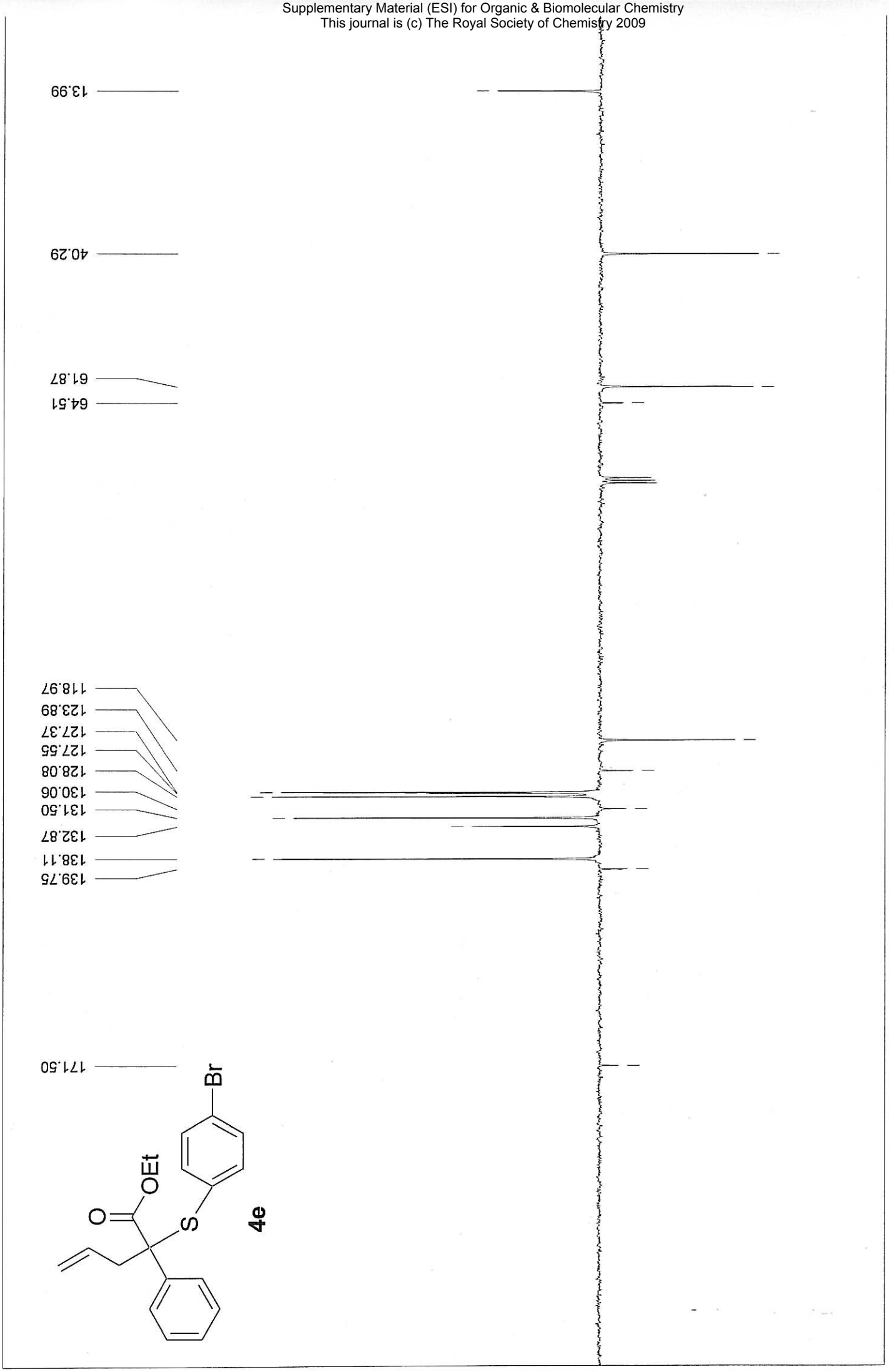
121.32
126.88
127.00
127.26
127.42
127.91
133.34
138.53
140.03
160.59
171.83
O
OEt
O
S
4d
0
50
100
150
200
ppm (t1)



4e

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64.51
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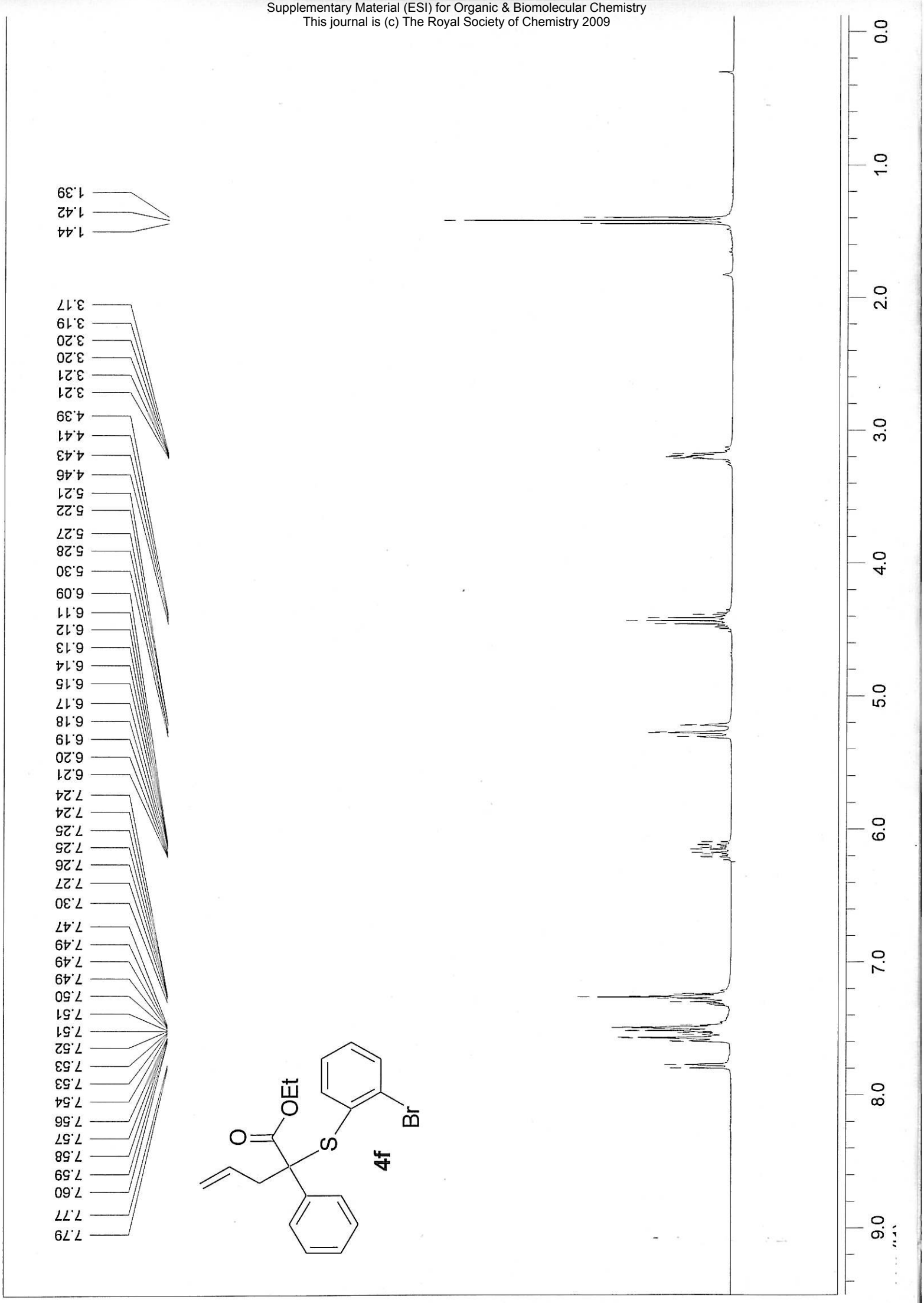
123.89
127.37
127.55
128.08
130.06
131.50
132.87
138.11
139.75
171.50
Br
S
O
OEt
4e
50
100
150
200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3.21
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4.39
4.41
4.43
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5.21
5.22
5.27
5.28
5.30
6.09
6.11
6.12
6.13
6.14
6.15
6.17
6.18
6.19
6.20
6.21
7.24
7.24
7.25
7.25
7.26
7.27
7.30
7.47
7.49
7.49
7.49
7.50
7.51
7.51
7.52
7.53
7.53
7.54
7.56
7.57
7.58
7.59
7.60
7.77
7.79
O
OEt
S
Br
4f
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1.0
2.0
3.0
4.0
5.0
6.0
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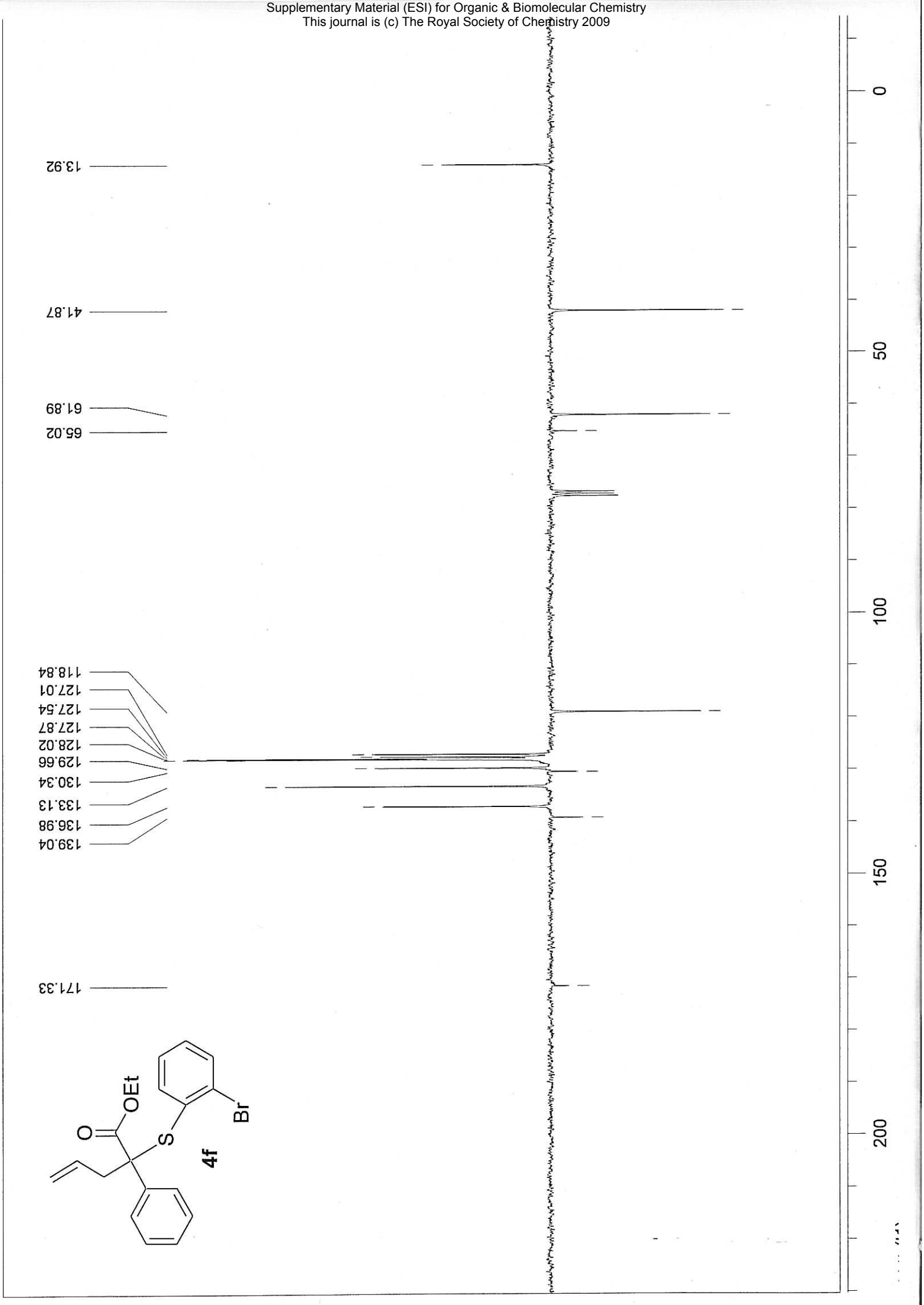
8.0
9.0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127.01
127.54
127.87
128.02
129.66
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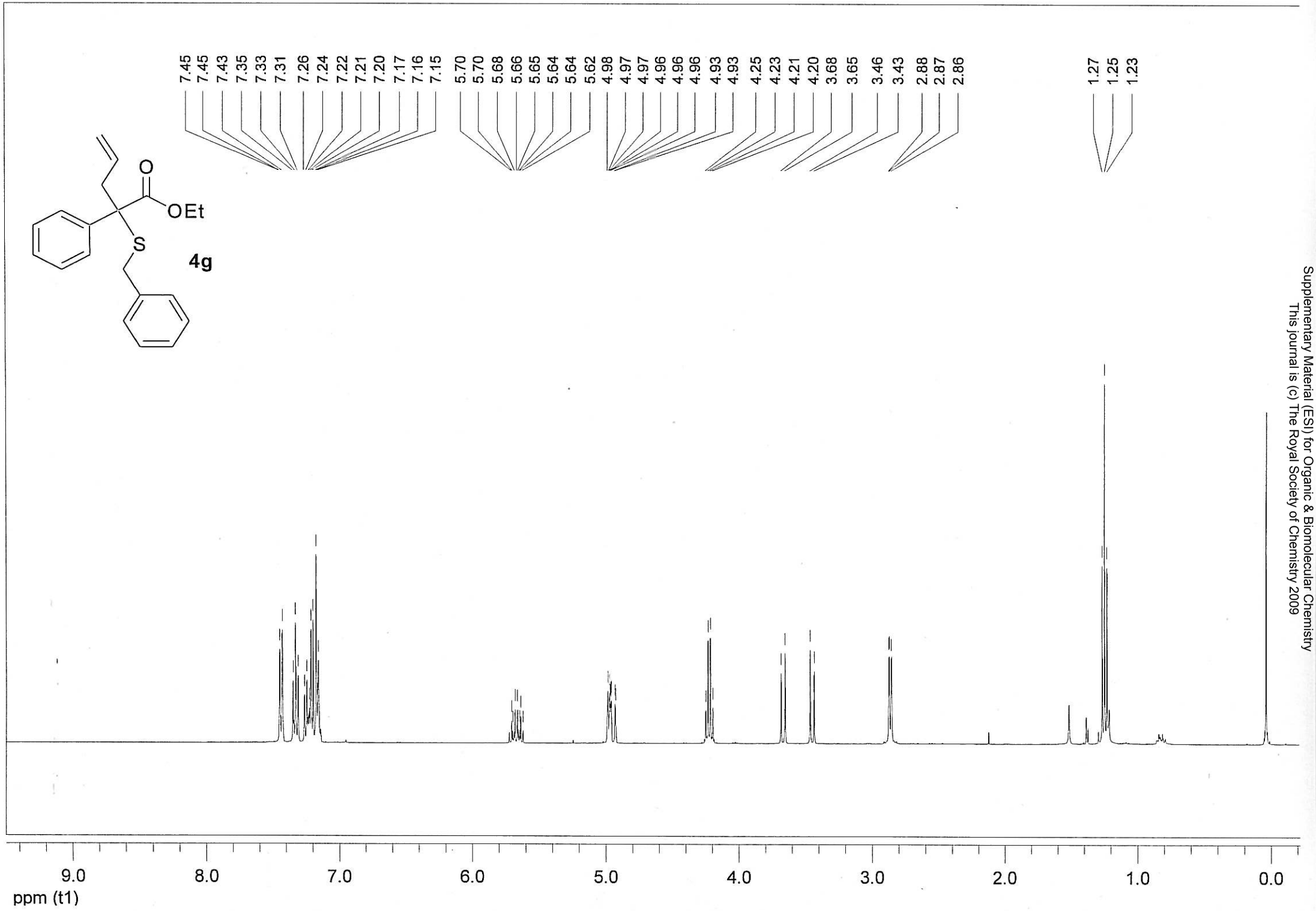
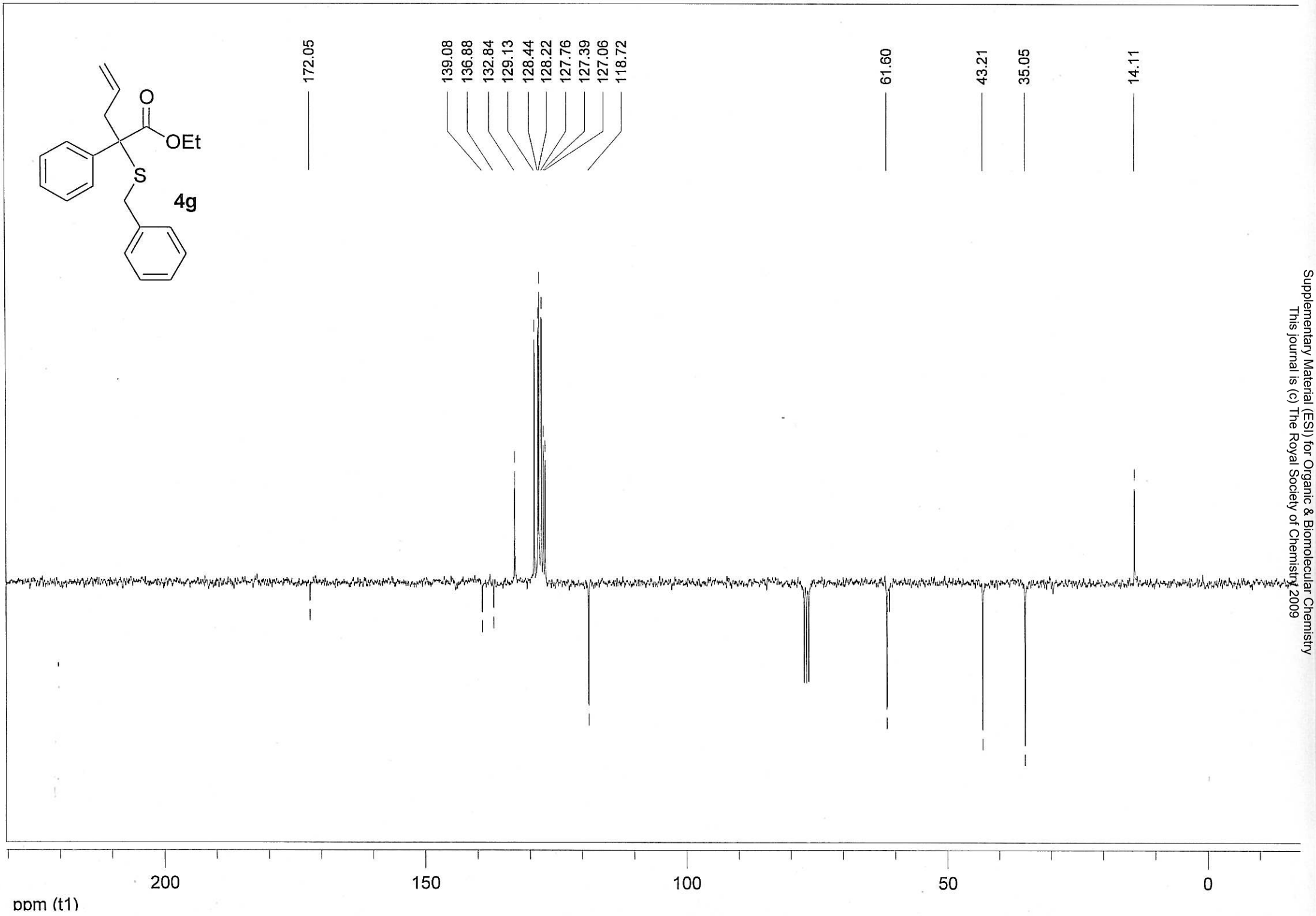
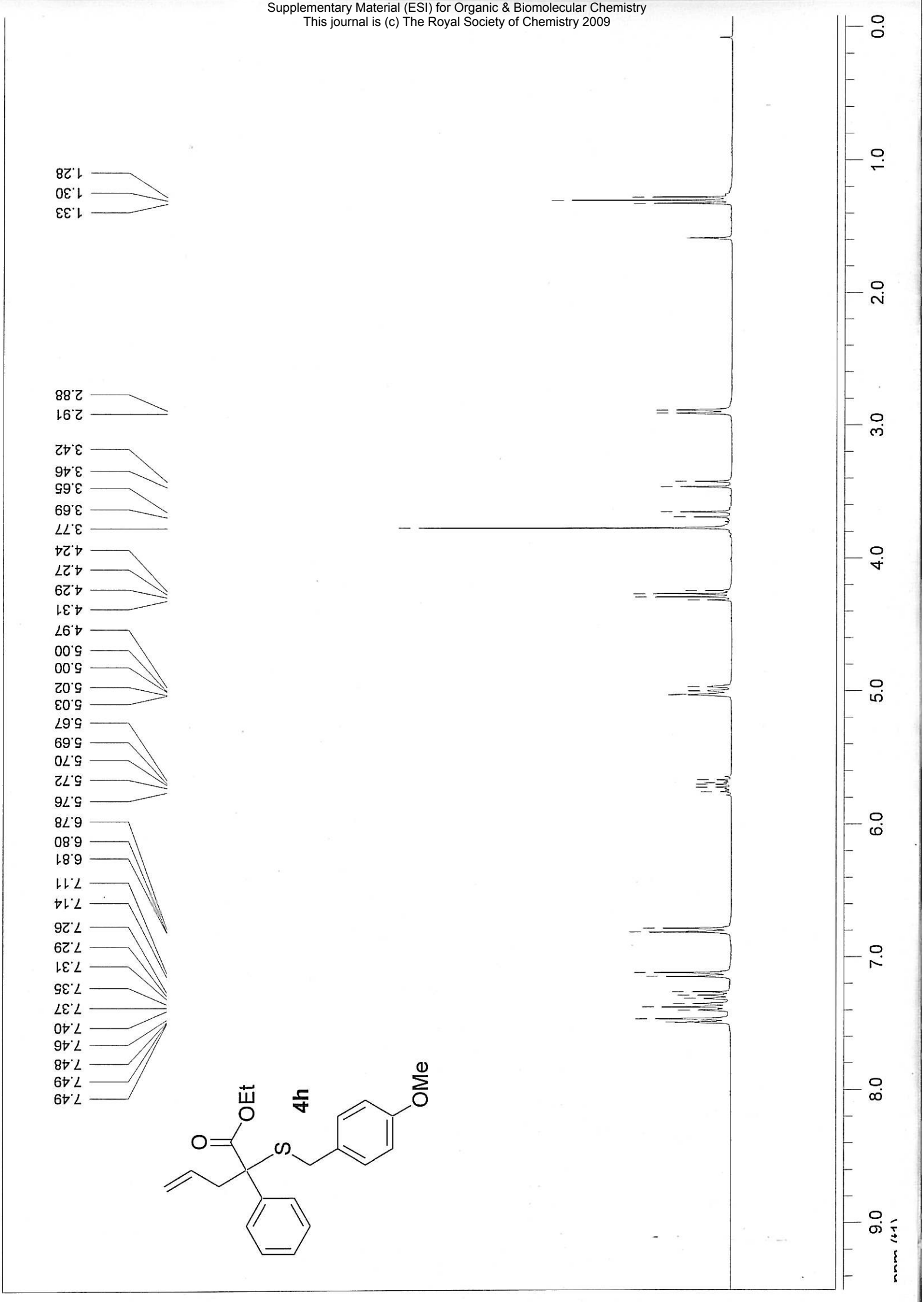
133.13
136.98
139.04
171.33
0
50
100
150
200
O
OEt
S
Br
4f



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3.77
4.24
4.27
4.29
4.31
4.97
5.00
5.00
5.02
5.03
5.67
5.69
5.70
5.72
5.76
6.78
6.80
6.81
7.11
7.14
7.26
7.29
7.31
7.35
7.37
7.40
7.46
7.48
7.49
7.49
OEt
O
S
4h
OMe
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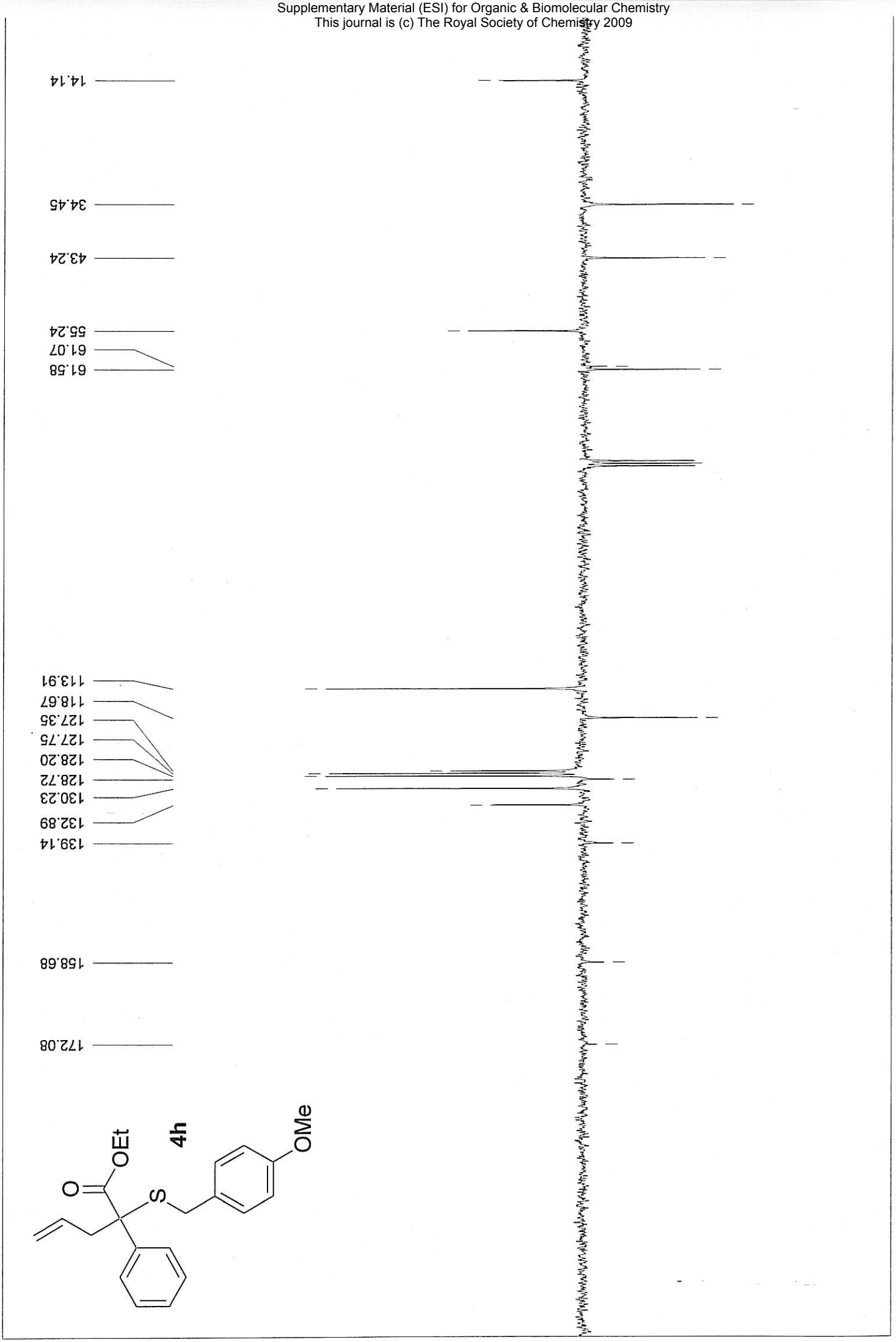
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61.58
113.91
118.67
127.35
127.75
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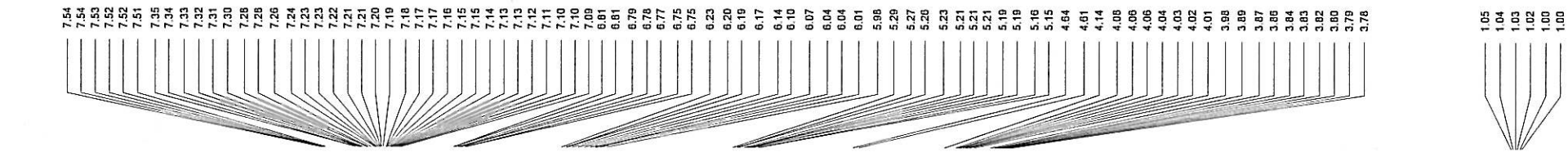
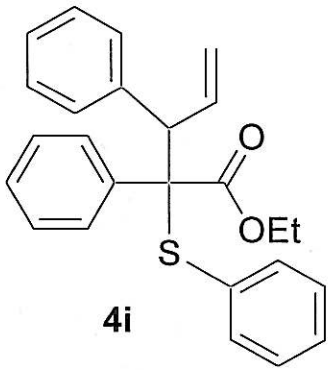
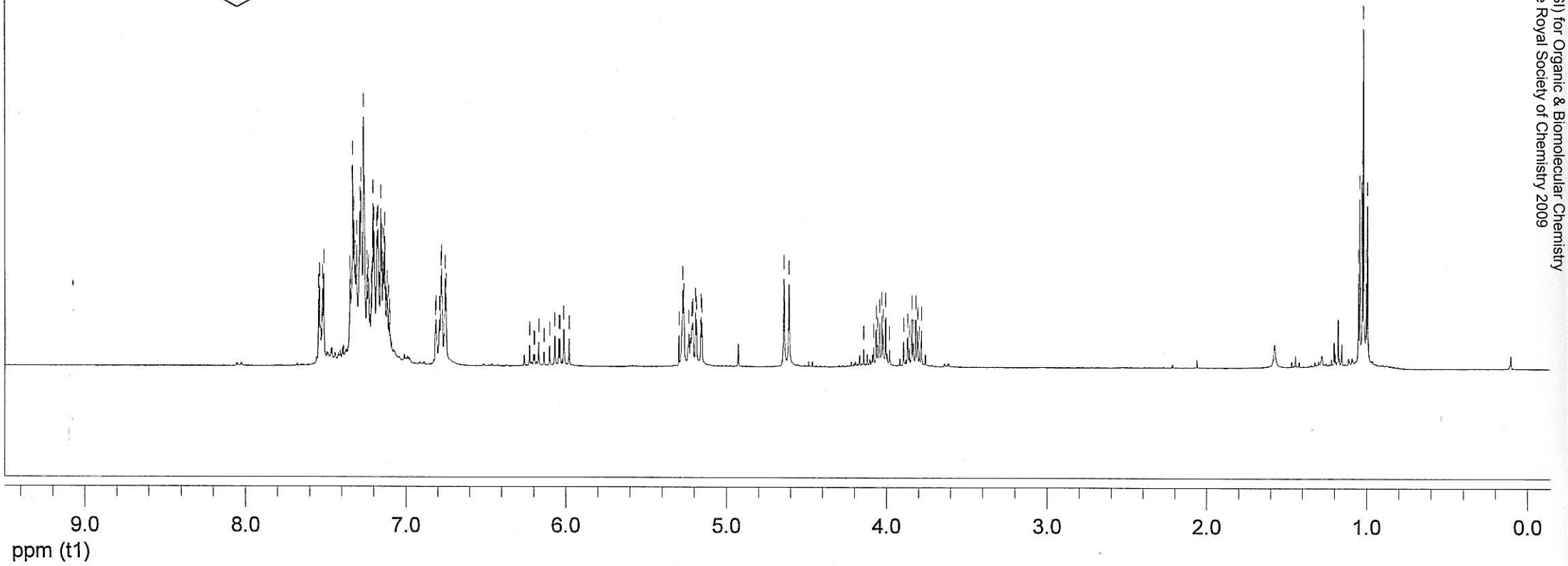
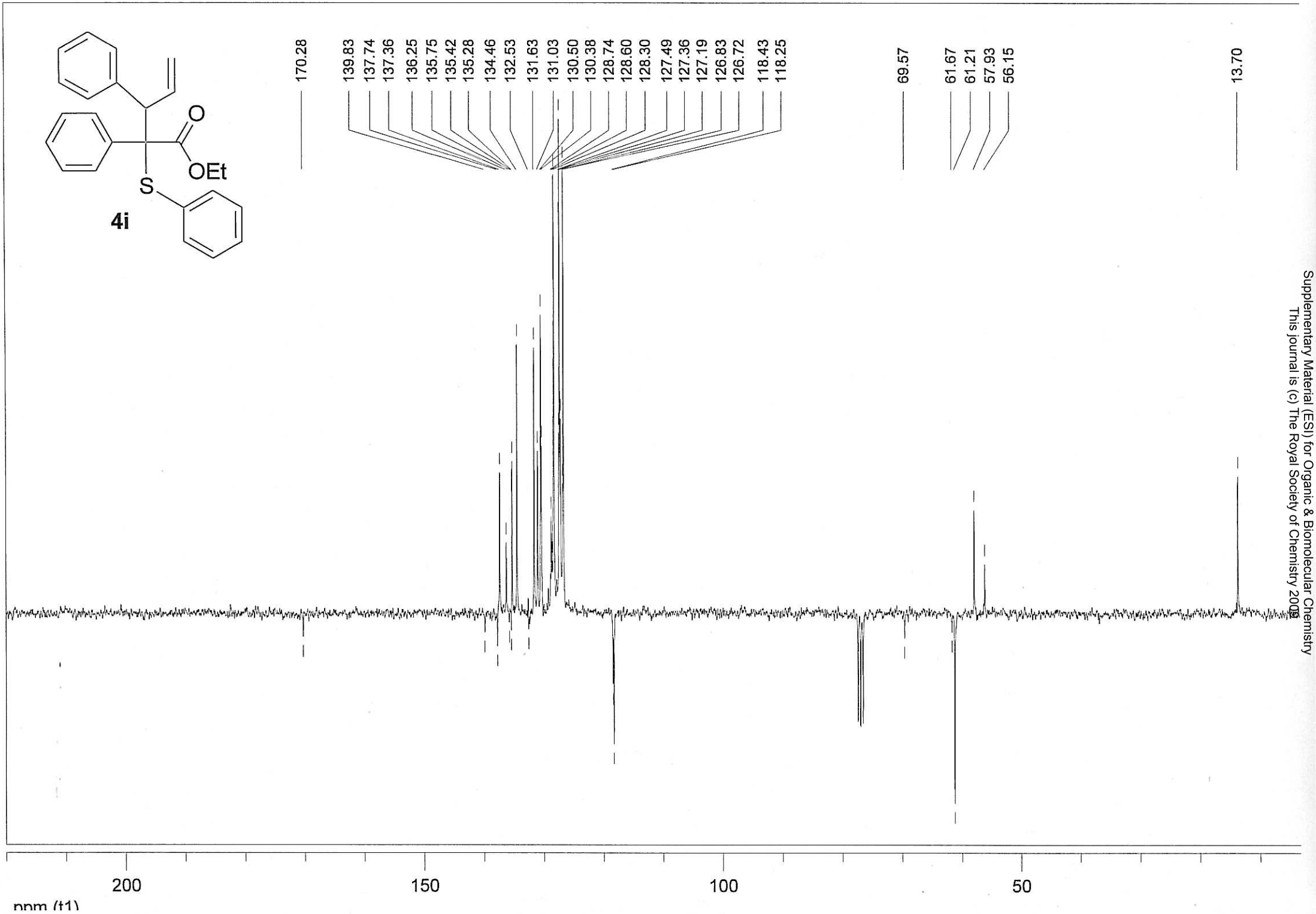
128.72
130.23
132.89
139.14
158.68
172.08
4h
OEt
O
S
OMe

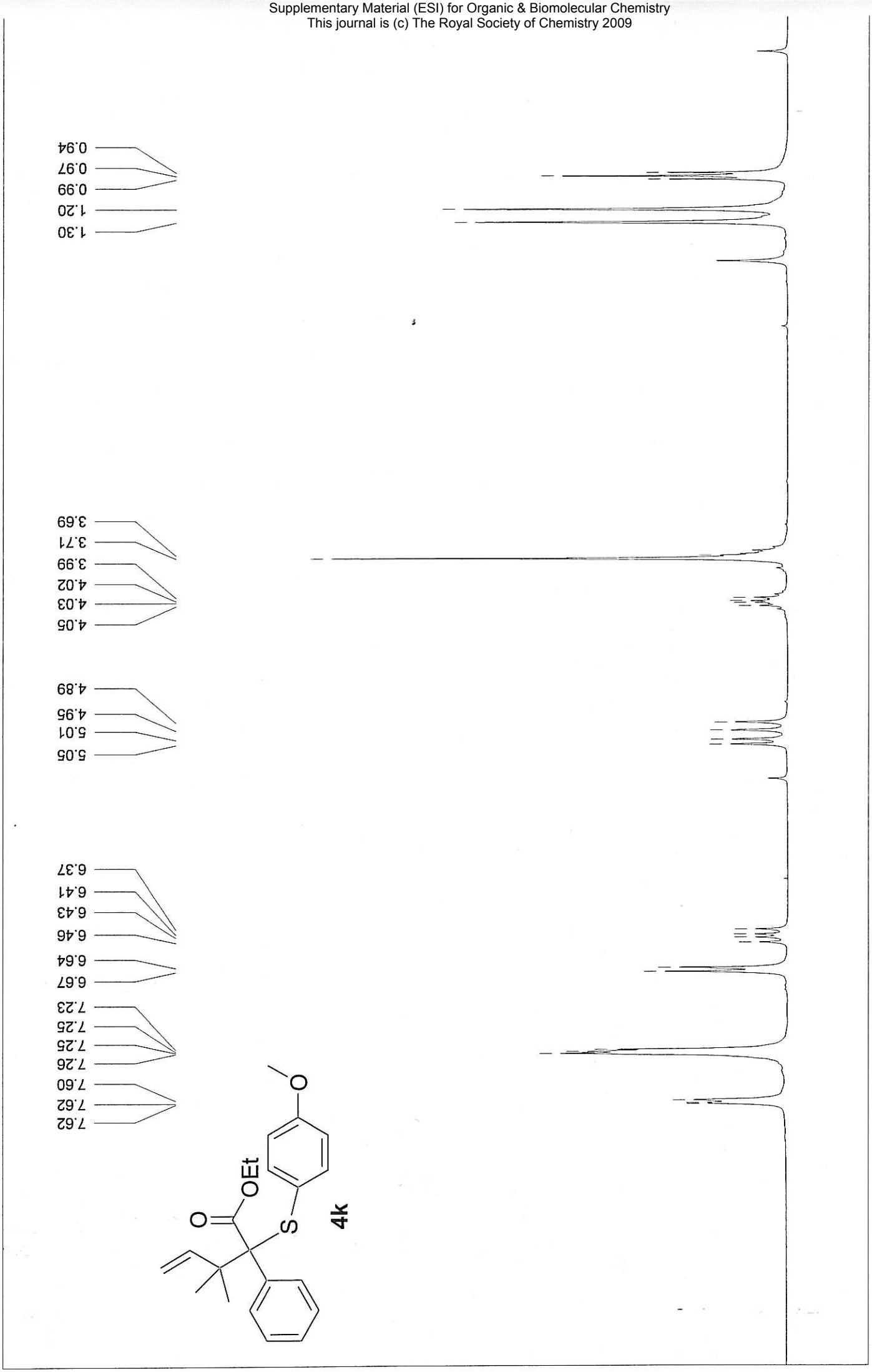




4i



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3.99
4.02
4.03
4.05
4.89
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5.01
5.05
6.37
6.41
6.43
6.46
6.64
6.67
7.23
7.25
7.25
7.26
7.60
7.62
7.62
O
OEt
O
S
4k
0.0
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2.0
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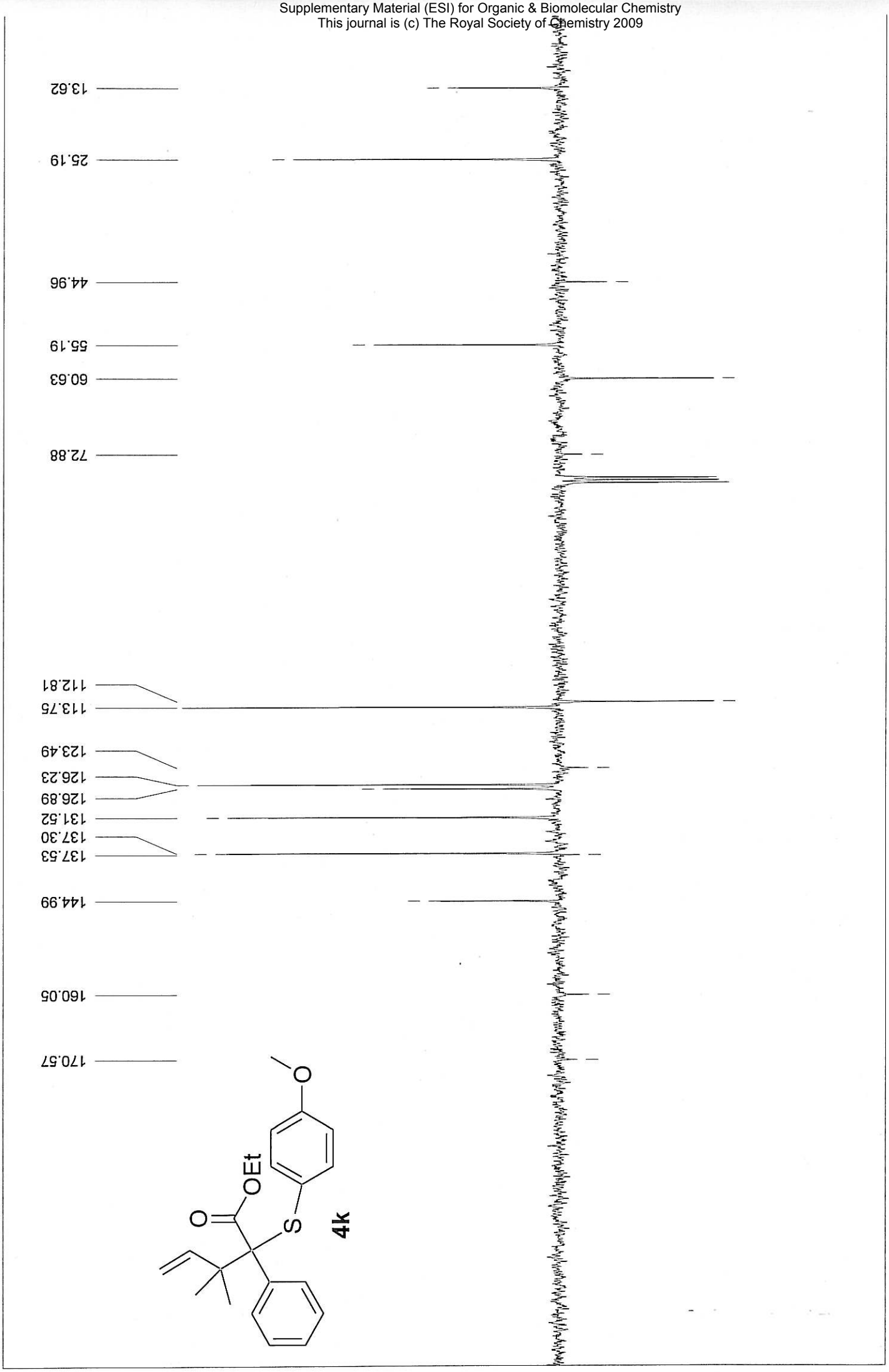
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)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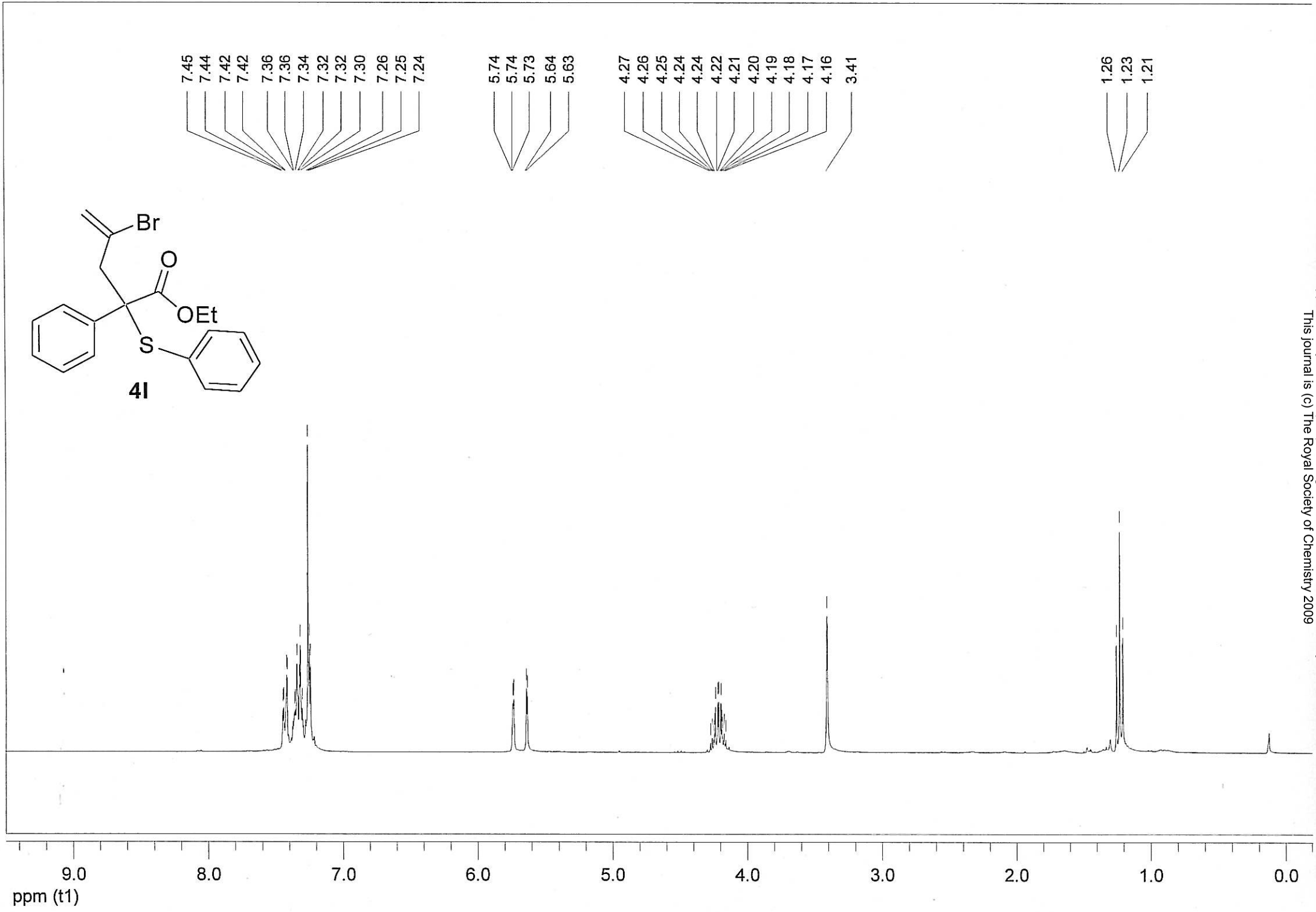
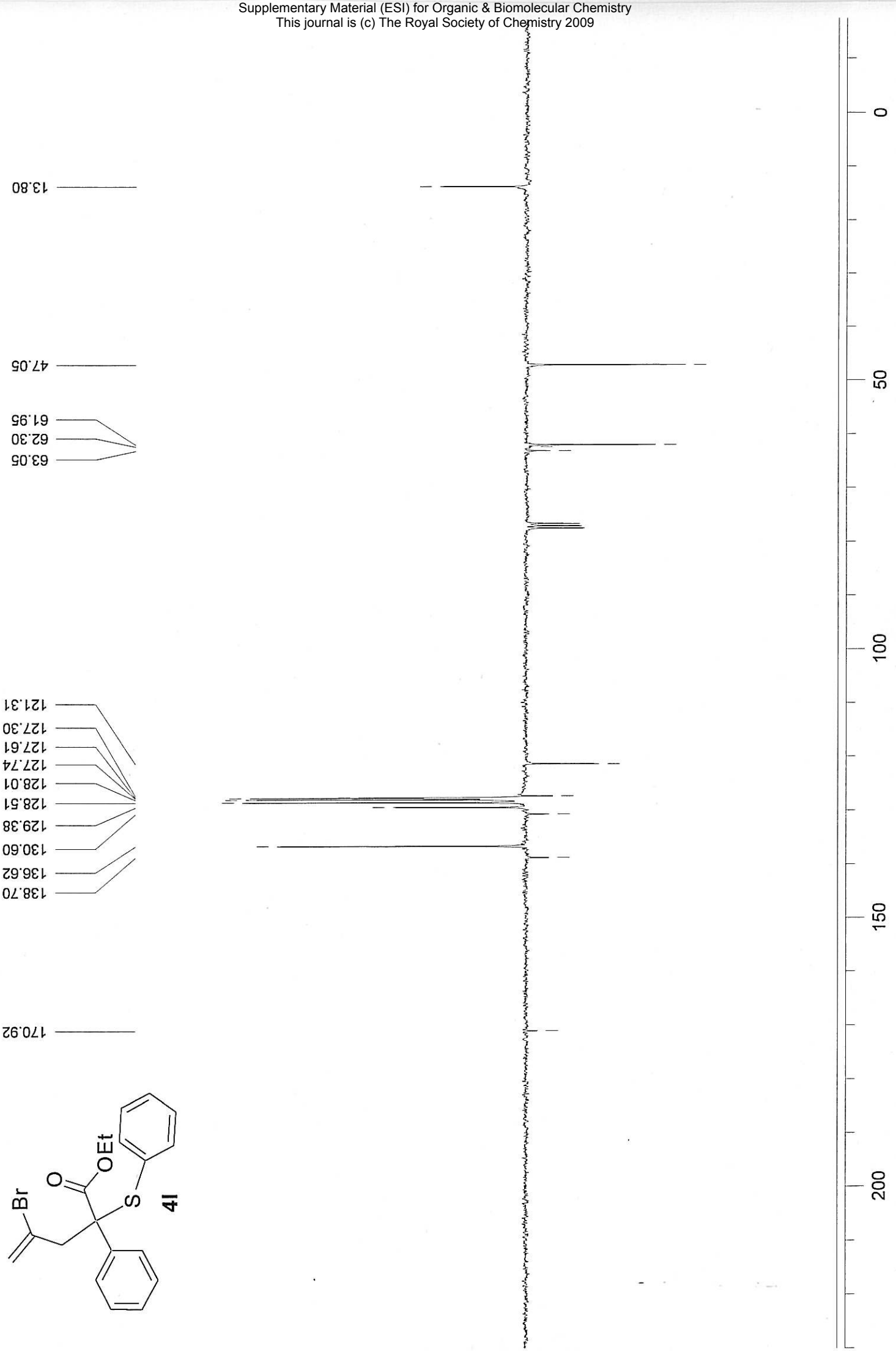
100
150
200
O
OEt
O
S
4k

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63.05
121.31
127.30
127.61
127.74
128.01
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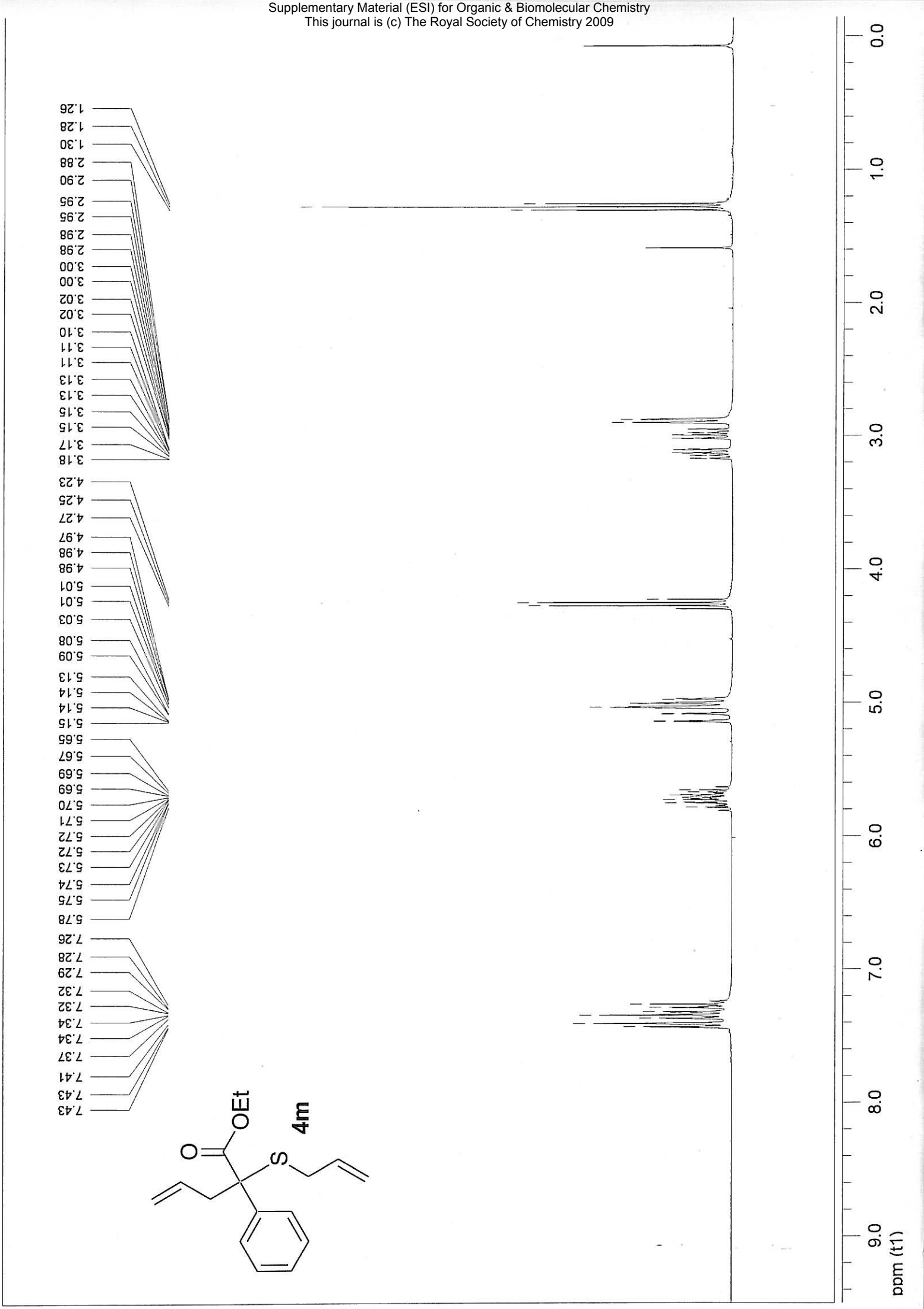
136.62
138.70
170.92
0
50
100
150
200
Br
O
OEt
S
4l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3.00
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4.98
4.98
5.01
5.01
5.03
5.08
5.09
5.13
5.14
5.14
5.15
5.65
5.67
5.69
5.69
5.70
5.71
5.72
5.72
5.73
5.74
5.75
5.78
7.26
7.28
7.29
7.32
7.32
7.34
7.34
7.37
7.41
7.43
7.43
OEt
O
S
4m
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3.0
4.0
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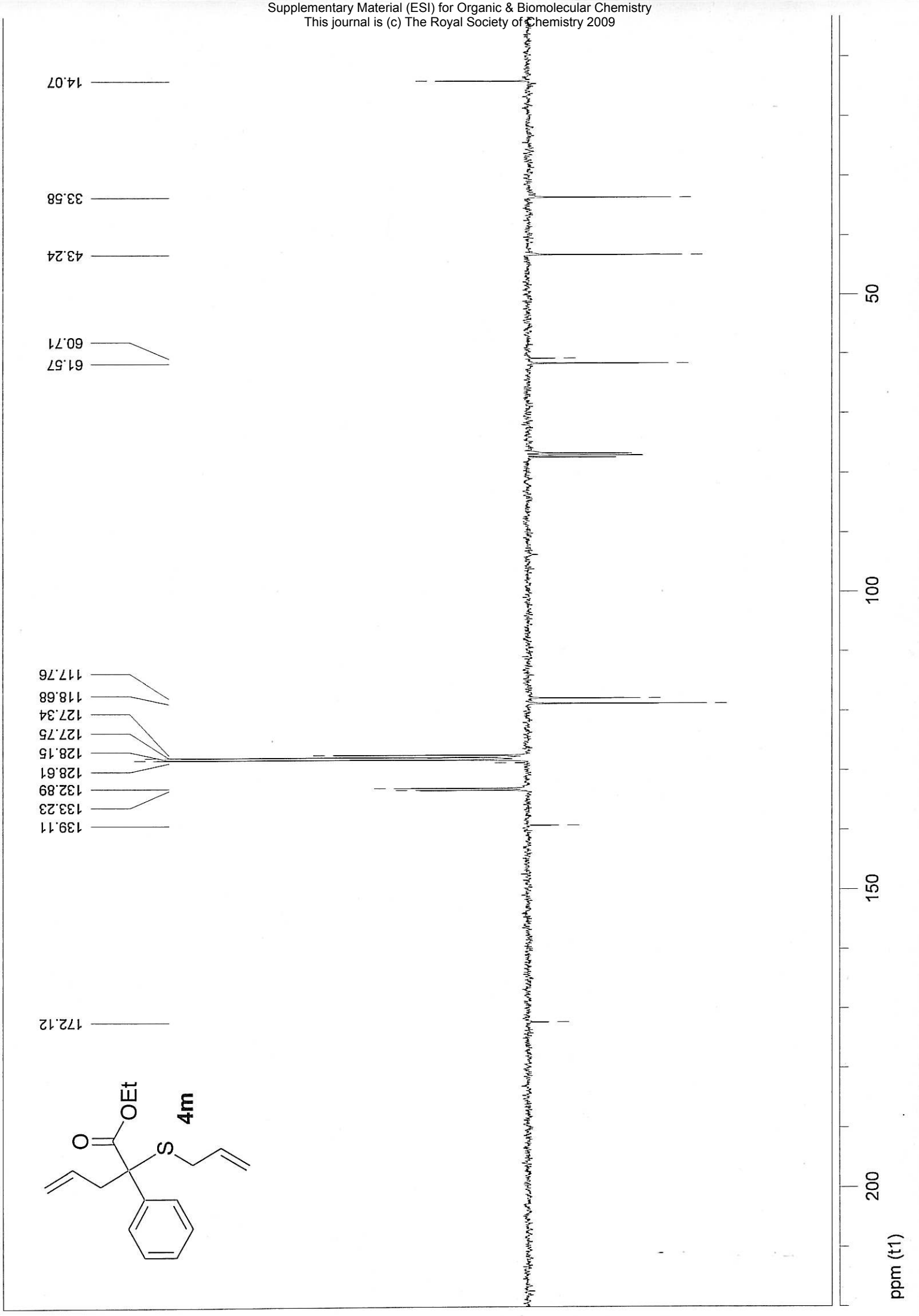
8.0
9.0
ppm (t1)


14.07
33.58
43.24
60.71
61.57
117.76
118.68
127.34
127.75
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128.61
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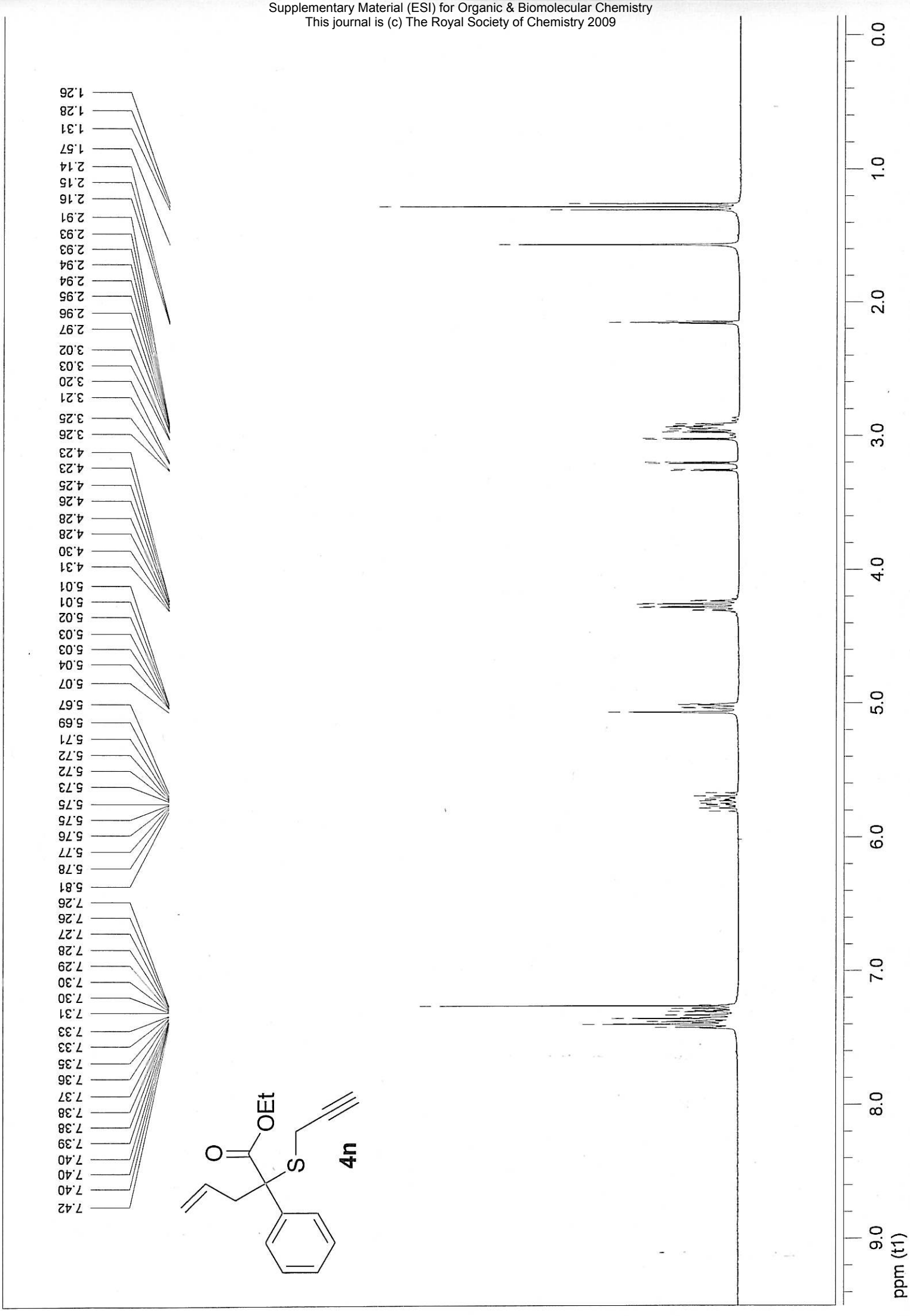
133.23
139.11
172.12
OEt
O
S
4m
50
100
150
200
ppm (t1)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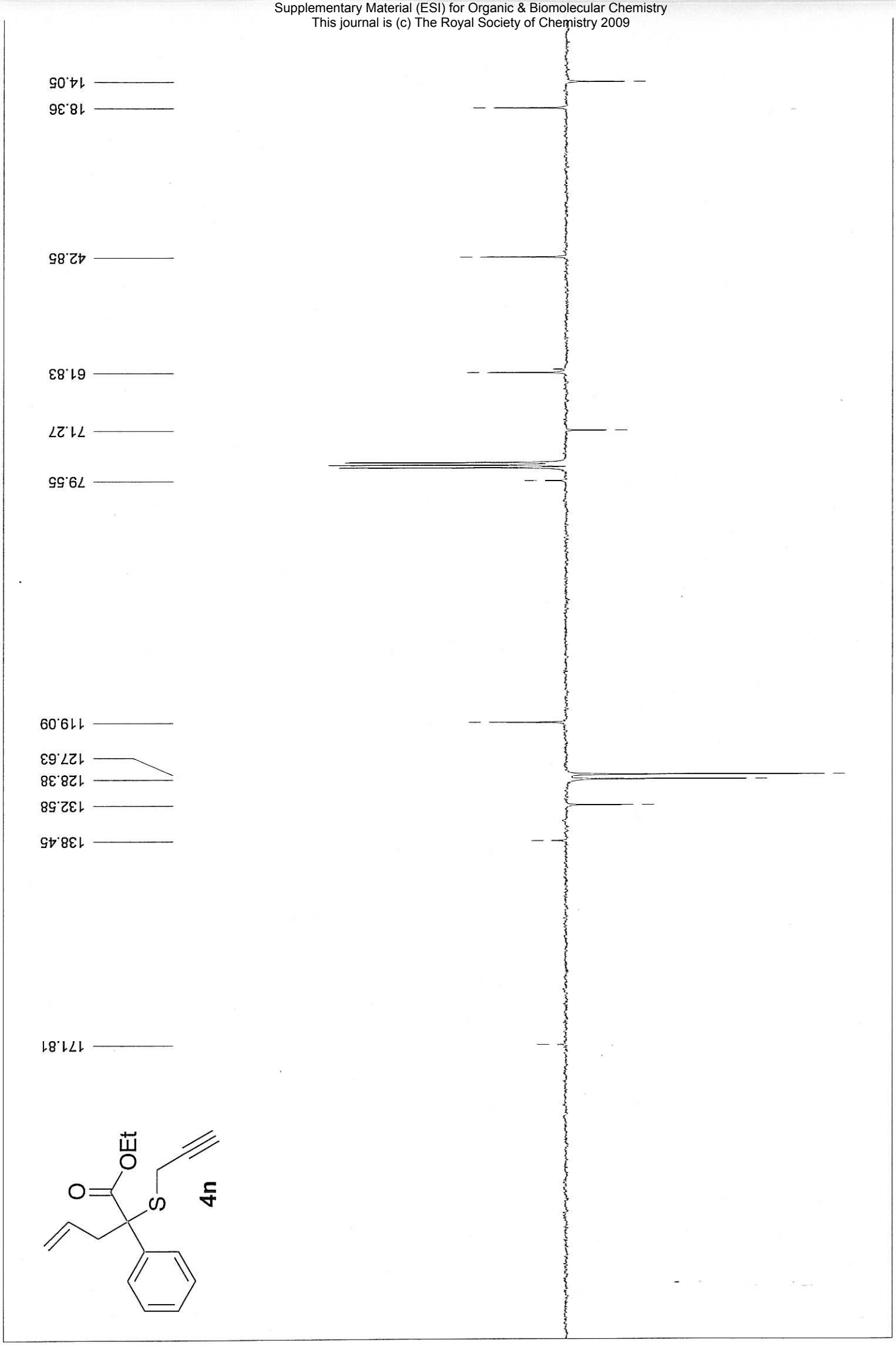
1.28
1.31
1.57
2.14
2.15
2.16
2.91
2.93
2.93
2.94
2.94
2.95
2.96
2.97
3.02
3.03
3.20
3.21
3.25
3.26
4.23
4.23
4.25
4.26
4.28
4.28
4.30
4.31
5.01
5.01
5.02
5.03
5.03
5.04
5.07
5.67
5.69
5.71
5.72
5.72
5.73
5.75
5.75
5.76
5.77
5.78
5.81
7.26
7.26
7.27
7.28
7.29
7.30
7.30
7.31
7.33
7.33
7.35
7.36
7.37
7.38
7.38
7.39
7.40
7.40
7.40
7.42
O
OEt
S
4n
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)


14.05
18.36
42.85
61.83
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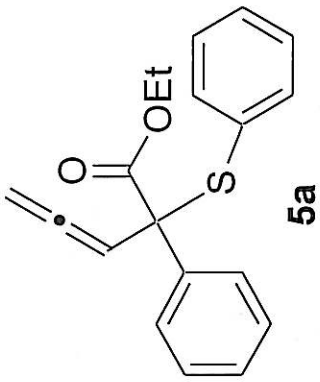
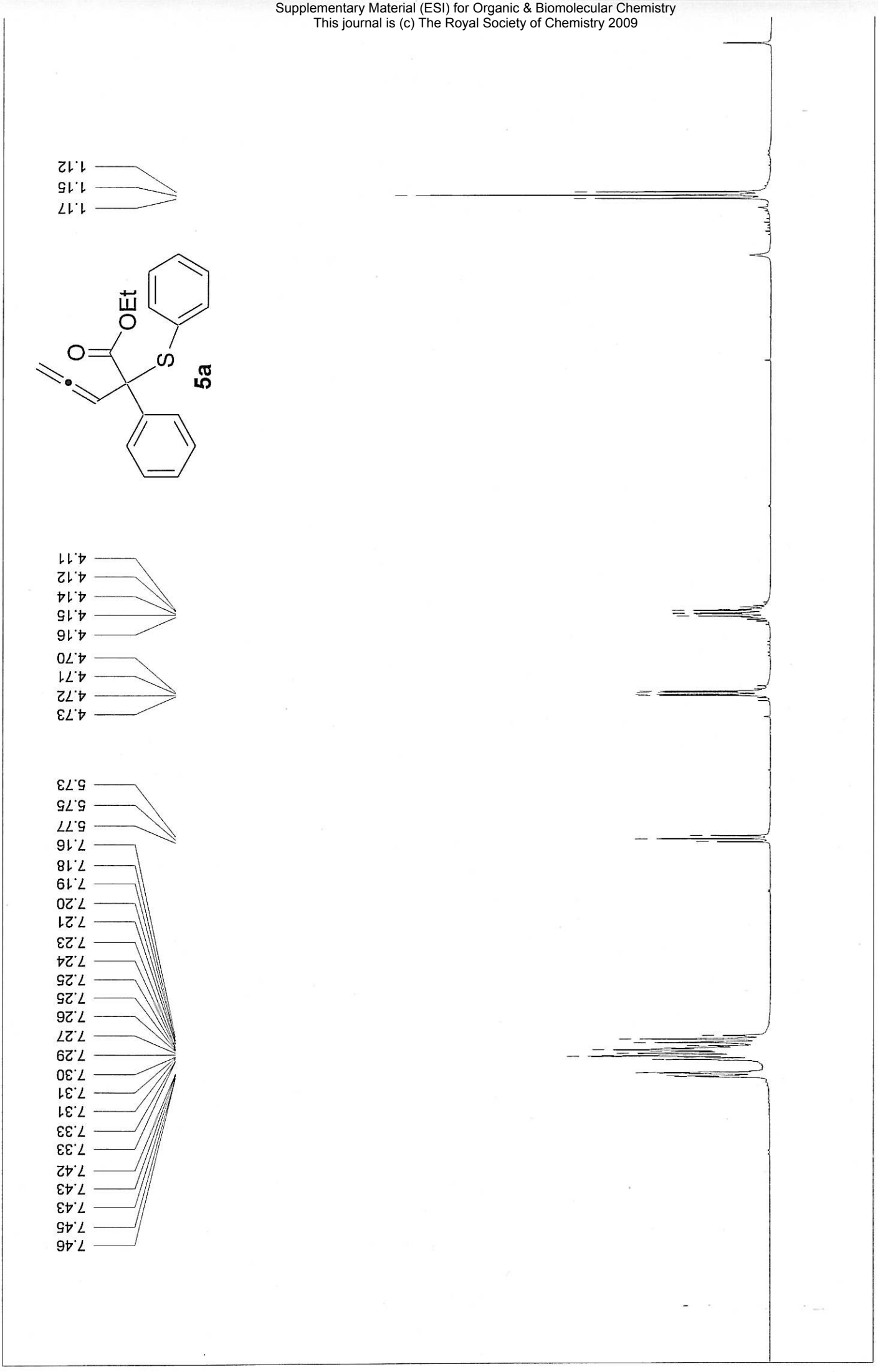
79.55
119.09
127.63
128.38
132.58
138.45
171.81
OEt
O
S
4n

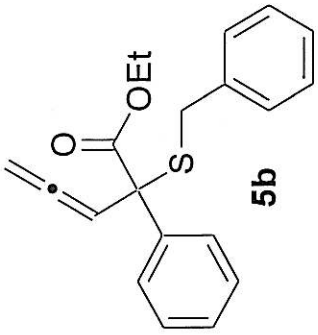


5a

13.94
14.08
62.06
64.18
78.80
93.98
127.68
127.96
128.03
128.30
128.47
128.92
131.75
136.44
138.99
170.58
170.67
208.32

50
100
150
200
ppm (t1)

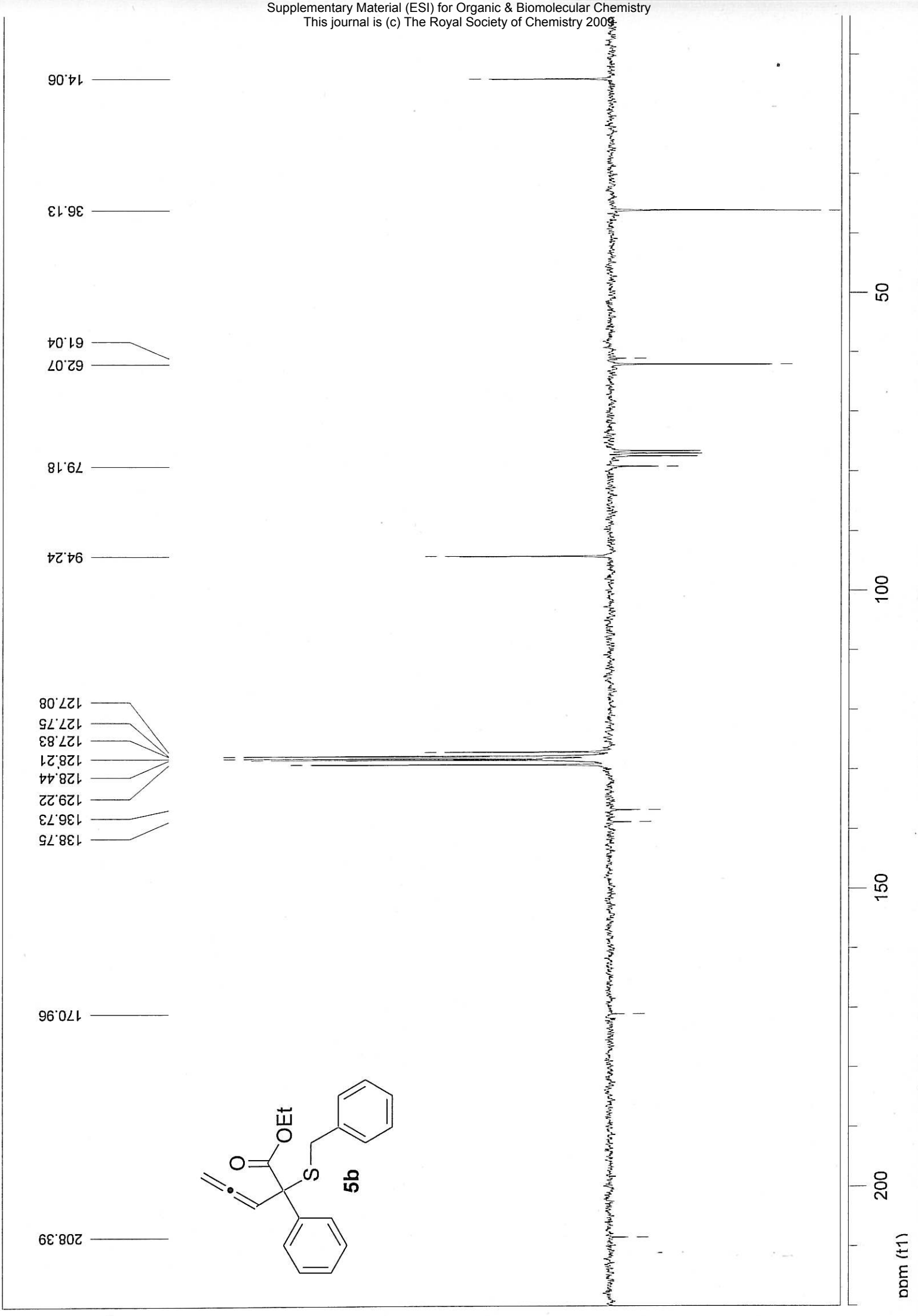

1.12
1.15
1.17
OEt
O
S
5a
4.11
4.12
4.14
4.15
4.16
4.70
4.71
4.72
4.73
5.73
5.75
5.77
7.16
7.18
7.19
7.20
7.21
7.23
7.24
7.25
7.25
7.26
7.27
7.29
7.30
7.31
7.31
7.33
7.33
7.42
7.43
7.43
7.45
7.46
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)



5b

1.24
1.27
1.29
3.75
3.76
4.20
4.23
4.25
4.27
4.90
4.92
5.87
5.89
5.91
7.21
7.22
7.23
7.24
7.25
7.26
7.27
7.29
7.30
7.31
7.32
7.32
7.34
7.36
7.37
7.39
7.53
7.55
7.56
7.56

1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)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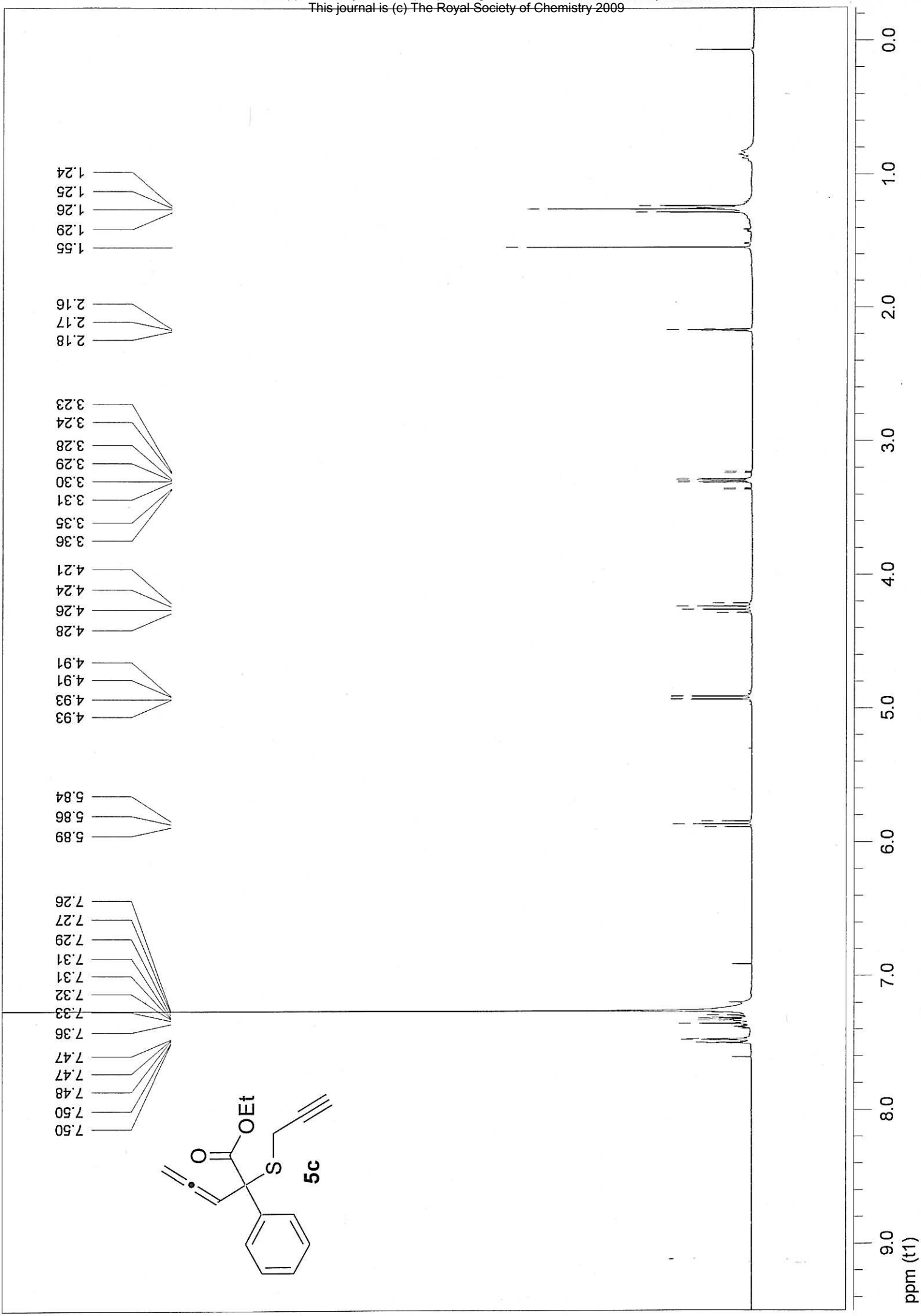
36.13
61.04
62.07
79.18
94.24
127.08
127.75
127.83
128.21
128.44
129.22
136.73
138.75
170.96
208.39
50
100
150
200
ppm (t1)
OEt
O
S
5b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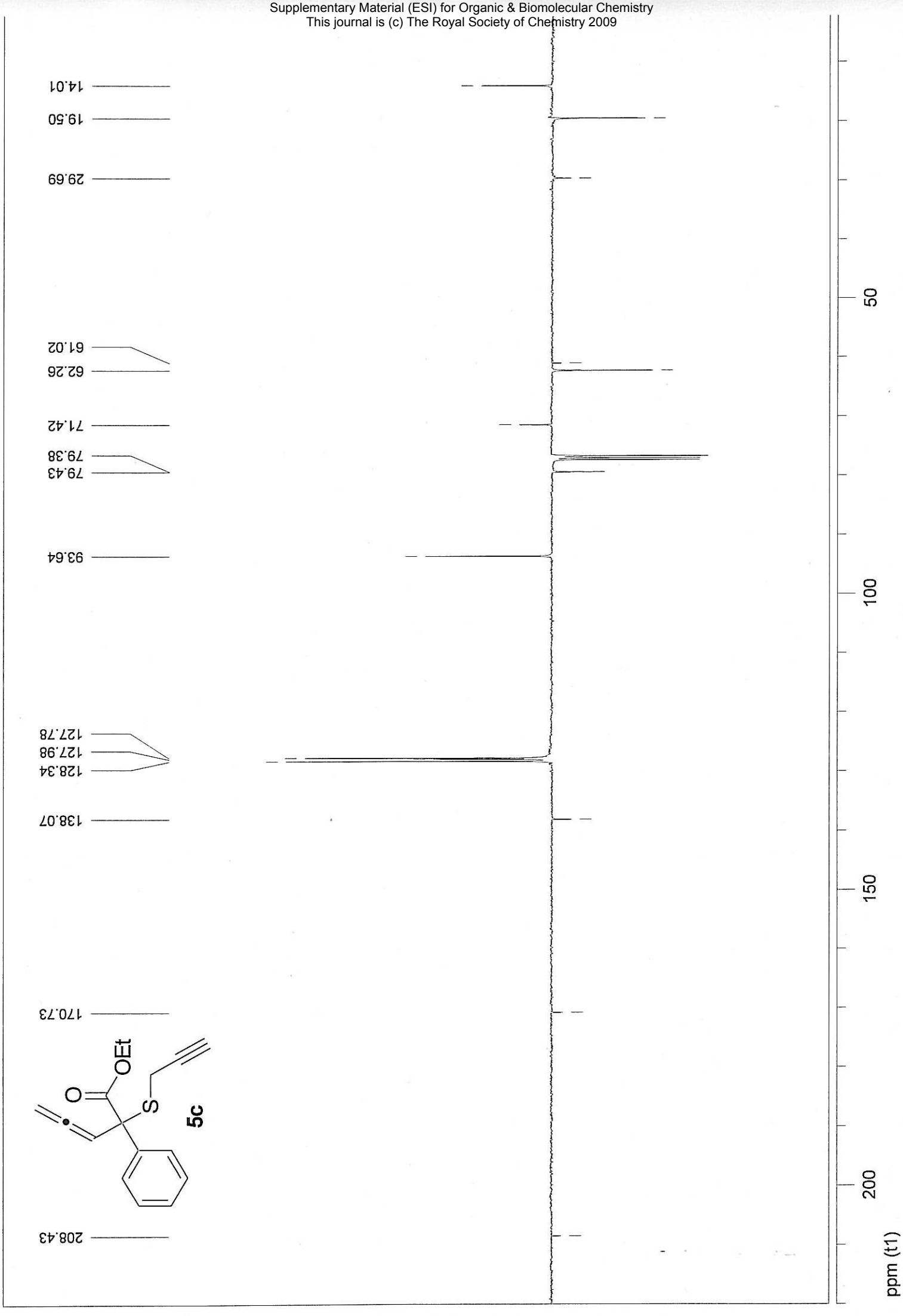
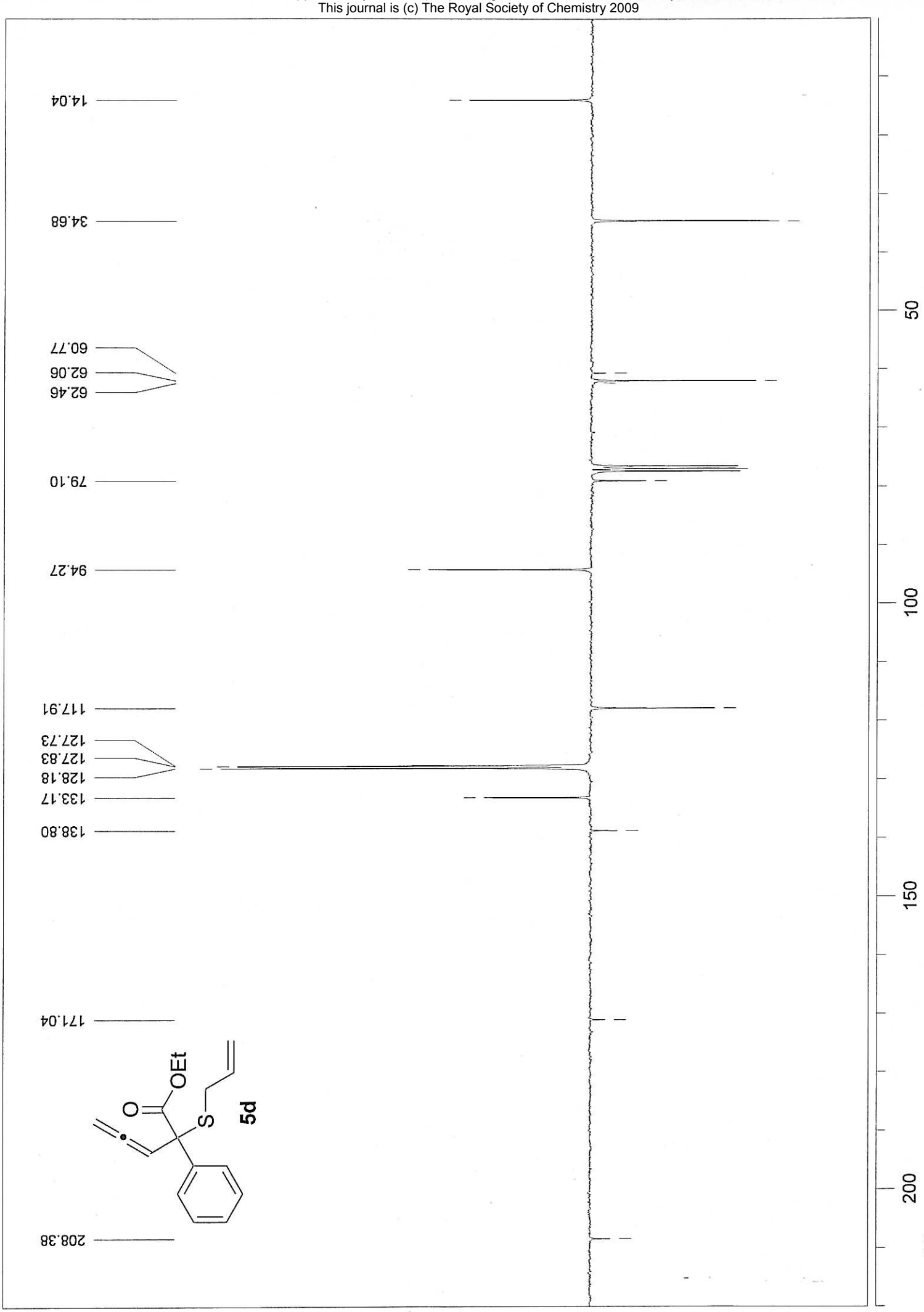
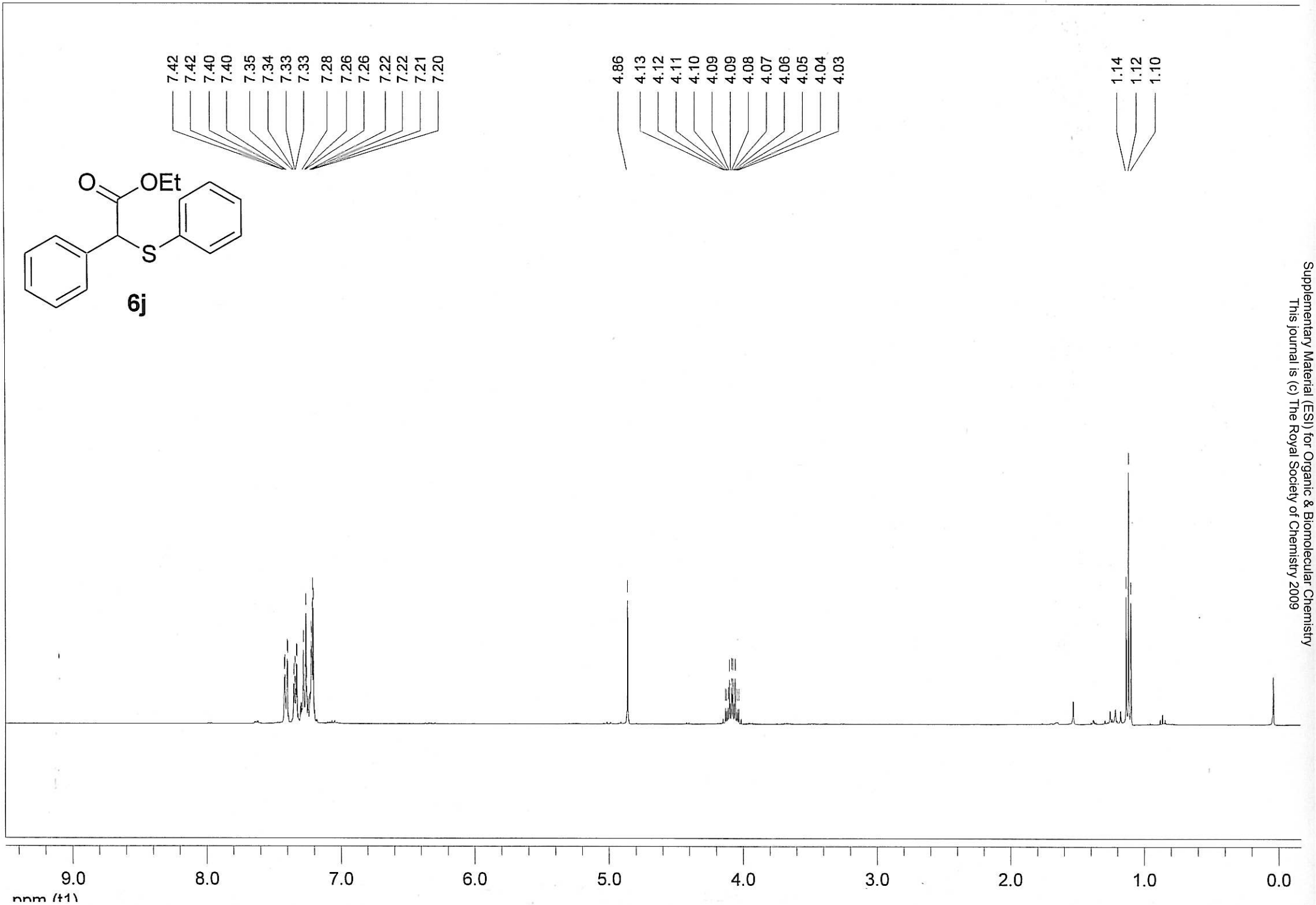
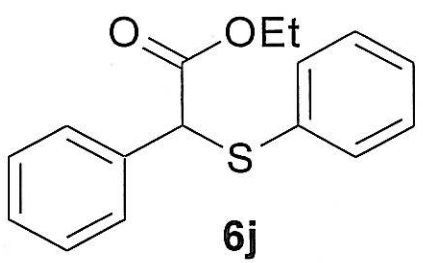
1.25
1.26
1.29
1.55
2.16
2.17
2.18
3.23
3.24
3.28
3.29
3.30
3.31
3.35
3.36
4.21
4.24
4.26
4.28
4.91
4.91
4.93
4.93
5.84
5.86
5.89
7.26
7.27
7.29
7.31
7.31
7.32
7.33
7.36
7.47
7.47
7.48
7.50
7.50
OEt
O
S
5c
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)


14.01
19.50
29.69
61.02
62.26
71.42
79.38
79.43
93.64
127.78
127.98
128.34
138.07
170.73
208.43
OEt
O
S
5c
50
100
150
200
ppm (t1)

1.24
1.26
1.28
3.19
3.22
4.20
4.23
4.25
4.28
4.88
4.90
4.90
5.03
5.03
5.06
5.07
5.12
5.12
5.17
5.18
5.72
5.74
5.75
5.77
5.78
5.80
5.81
5.83
5.83
5.85
5.86
5.87
7.25
7.26
7.28
7.29
7.30
7.30
7.31
7.32
7.33
7.34
7.35
7.35
7.36
7.37
7.37
7.48
7.48
7.49
7.50
7.51
7.51
OEt
O
S
5d


14.04
34.68
60.77
62.06
62.46
79.10
94.27
117.91
127.73
127.83
128.18
133.17
138.80
171.04
208.38
O
OEt
S
5d
50
100
150
200
ppm (f1)





6j

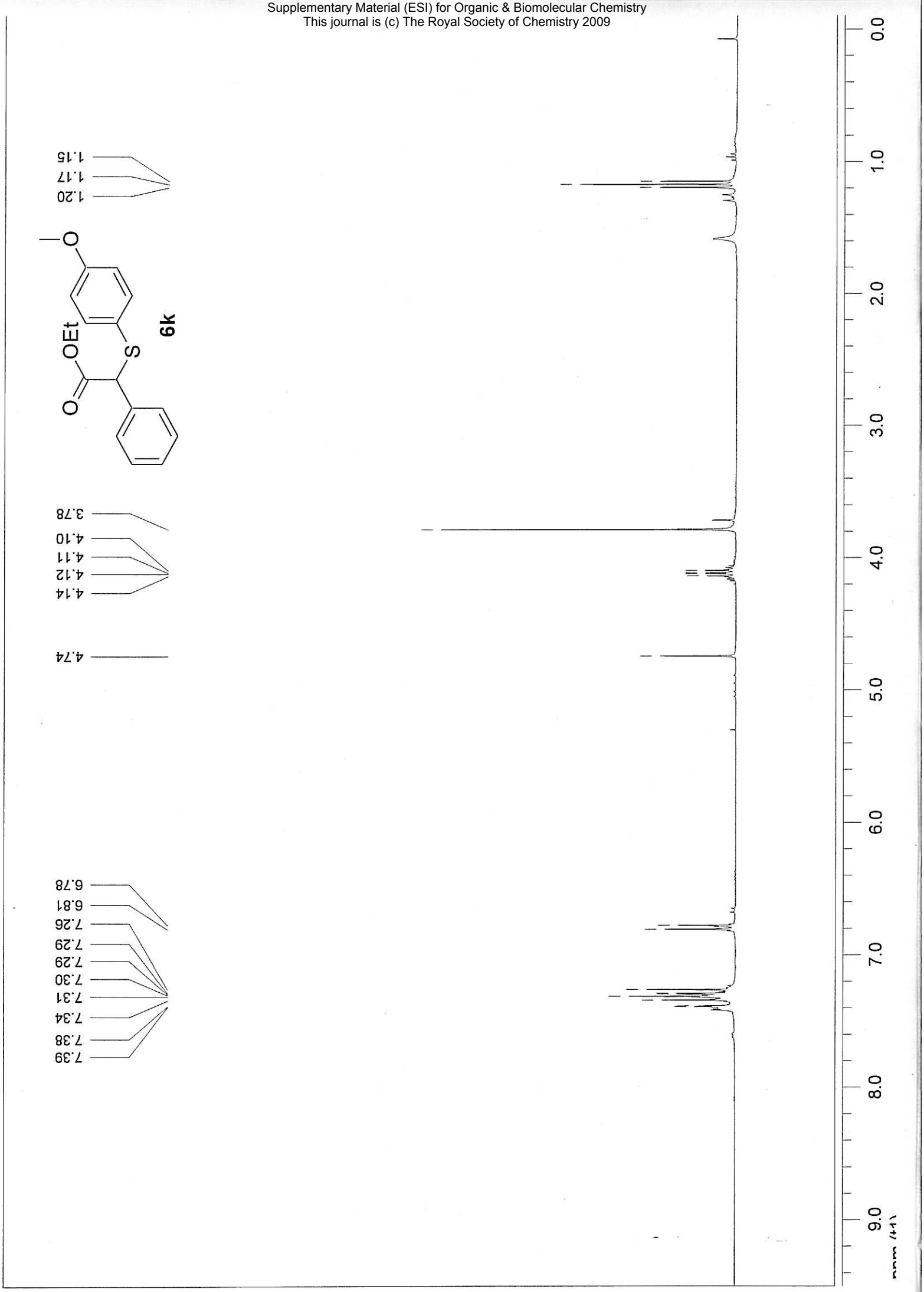
170.37

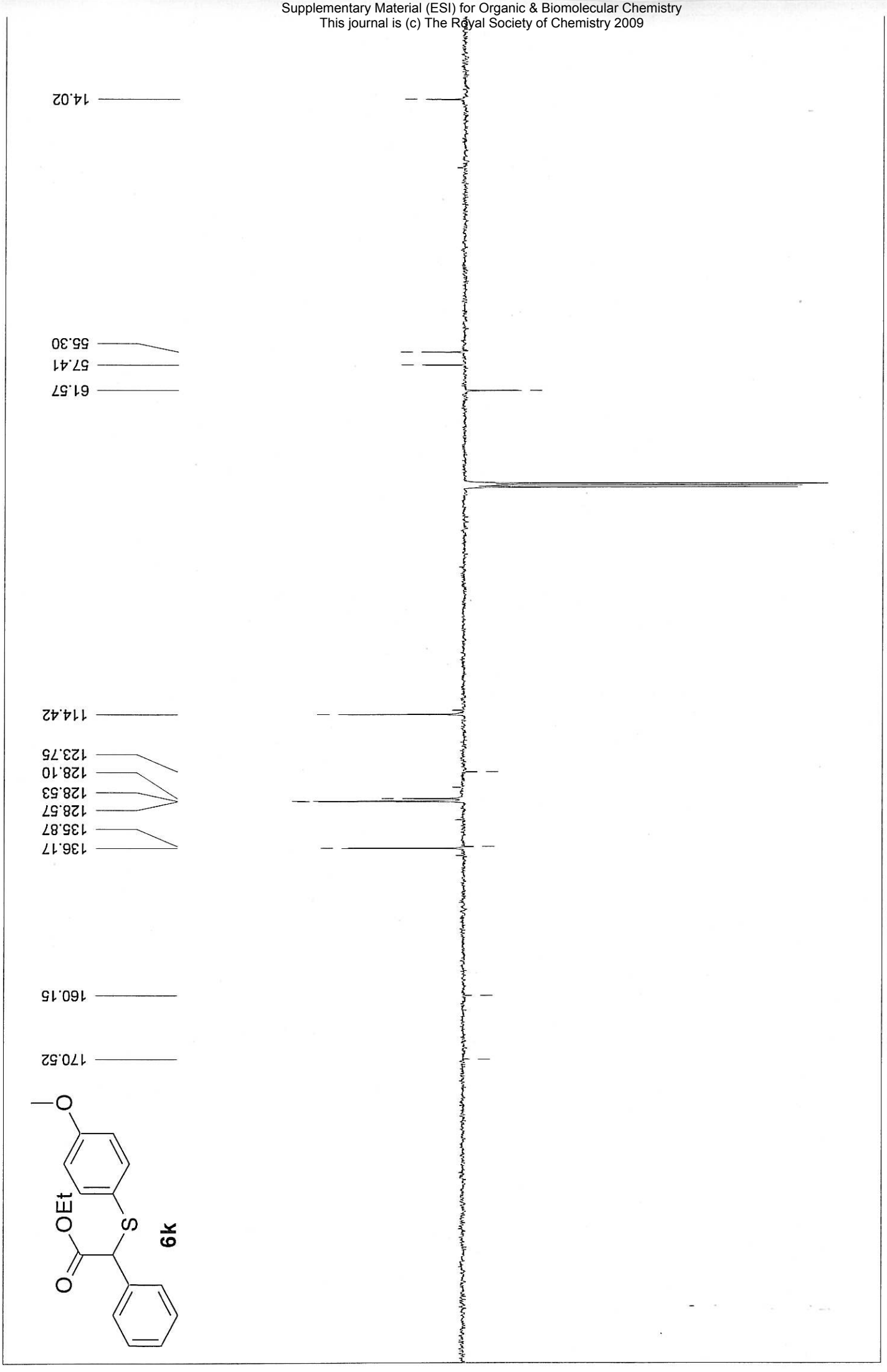
135.64
132.60
128.90
128.61
128.49
128.24
127.90

61.69
56.33

13.97

200
150
100
50
ppm (t1)


1.15
1.17
1.20
O
OEt
O
S
6k
3.78
4.10
4.11
4.12
4.14
4.74
6.78
6.81
7.26
7.29
7.29
7.30
7.31
7.34
7.38
7.39
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)


14.02
55.30
57.41
61.57
114.42
123.75
128.10
128.53
128.57
135.87
136.17
160.15
170.52
O
OEt
O
S
6k
50
100
150
200
ppm (t1)