SUPPORTING INFORMATION

General:

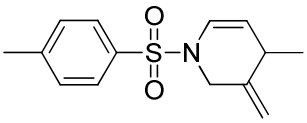
All reactions were carried out under argon atmosphere. HPLC grade solvents such as THF, methanol, and ethanol were used as received. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (300 / 400 MHz) spectrometer and carbon magnetic resonance (^{13}C NMR) spectra 75 / 100 / MHz Chemical shifts (δ) are reported in parts per million relative to C_6D_6. ^{1}H NMR assignment abbreviations are the following: singlet(s), doublet (d), triplet (t), quartet (q), broad singlet (bs), doublet of doublets (dd), doublet of triplets (dt), multiplet (m).

General Procedure for preparation of enamides 3 and hemiaminals 4

Under inert atmosphere, *N*-protected propargylamine **1** (0.478 mmol) diluted in 3 mL of solvent was slowly added to a stirred solution at 60°C containing allylic alcohol **2** (2.5 eq.), [Ru(Cp*)$(CH_3CN)_3PF_6$] (5 mol %) in 3 mL of solvent. The reaction mixture was stirred at 80°C overnight. Reaction completion was monitored using GC and TLC techniques. Crude reaction mixture was suspended onto alumina and purified by column chromatography over neutral alumina gel using Et_2O : pentane eluting mixture leading to compounds **3** using THF as solvent or **4** with methanol and ethanol.

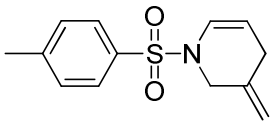
Analytical data

4-methyl-3-methylene-1-tosyl-1,2,3,4-tetrahydropyridine (3a)



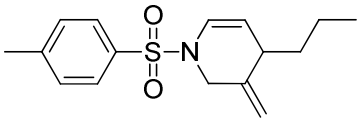
Prepared from *N*-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and crotylalcohol **2a** (2.5 equiv., 1.2 mmol) in THF (6 ml). Chromatography on alumina gel using pentane/Et_2O (70:30) as eluent afforded compound **3b** as colourless oil, 85 mg, (67%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.64 (d, *J* = 8.2 Hz, 2H), 6.77 (dd, *J* = 8.1 Hz, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 2H), 4.56 (s, 1H), 4.56-4.52 (m, 1H), 4.52 (s, 1H), 3.81 (s, 2H), 2.35-2.29 (m, 1H), 1.81 (s, 3H), 0.67 (d, *J*= 6.9 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 143.2, 142.4, 136.2, 129.6, 127.6, 125.0, 113.4, 111.2, 48.8, 33.6, 21.1, 20.9. HRMS calcd for $C_{14}H_{17}NO_2NaS$ ($[M+Na]^+$) 286.0878, found 286.0872.

3-methylene-1-tosyl-1,2,3,4-tetrahydeopyridine (3b)



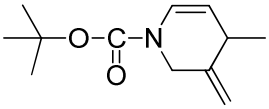
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and allylalcohol **2b** (2.5 equiv., 1.19 mmol) in THF (6 mL). Chromatography on alumina gel using pentane/Et_2O (70:30) as eluent afforded compound **3b** as colourless oil, 40 mg (34%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.63 (d, *J* = 8.2 Hz, 2H), 6.79 (dt, *J* = 8.2 Hz, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 2H), 4.58-4.52 (m, 3H), 3.78 (s, 2H), 2.15-2.12 (m, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 143.2, 137.1, 136.1, 129.6, 127.6, 125.9, 112.3, 107.1, 50.0, 29.5, 21.1. HRMS calcd for $C_{13}H_{15}NO_2NaS$ ($[M+Na]^+$) 272.0721, found 272.0722.

***3-methylene-4-propyl-1-tosyl-1,2,3,4-tetrahydropyridine* (3c)**



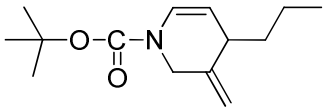
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and *n*-hex-2-en-1-ol **2c** (2.5 equiv., 1.2 mmol) in THF (6 mL). Chromatography on alumina gel using pentane/Et_2O (70:30) as eluent afforded compound **3c** as colourless oil, 85 mg (61%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.66 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J*= 7.9 Hz, 2H), 4.69 (dd, *J* = 7.9 Hz, *J* = 4.5 Hz, 1H), 4.60 (s, 1H), 4.53 (s, 1H), 4.07 (d, *J* = 12.9 Hz, 1H), 3.53 (d, *J* = 12.9 Hz, 1H), 2.25-2.15 (m, 1H), 1.83 (s, 3H), 1.00-0.87 (m, 4H), 0.64 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 143.2, 141.0, 136.1, 129.6, 127.6, 125.1, 112.4, 111.9, 48.1, 39.4, 38.6, 21.1, 20.0, 13.9. HRMS calcd for $C_{16}H_{21}NO_2NaS$ ($[M+Na]^+$) 314.1191, found 314.1188.

***tert-butyl 4-methyl-3-methylene-3,4-dihydropyridine-1(2H)-carboxylate* (3d)**



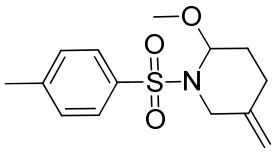
Prepared from N-Boc propargylamine **1b** (74 mg, 0.48 mmol) and crotylalcohol **2a** (2.5 equiv., 1.2 mmol) in THF (6 mL). Chromatography on alumina gel using pentane/Et_2O (80:20) as eluent afforded compound **3b** as colourless oil, 55 mg, (55%) as two conformers (ratio 67/33). Major conformer: ^{1}H NMR (400 MHz, C_6D_6) δ 6.86-6.80 (m, 1H), 4.79 (s, 1H), 4.72-4.68 (m, 1H), 4.55-4.50 (m, 1H), 4.20-4.13 (m, 1H), 4.00-3.95 (m, 1H), 2.67-2.58 (m, 1H), 1.37 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.9, 144.2, 125.1, 110.3, 109.6, 80.3, 46.9, 34.1, 28.2, 21.1. Minor conformer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.25-7.20 (m, 1H), 4.79 (s, 1H), 4.72-4.68 (m, 1H), 4.60-4.55 (m, 1H), 4.20-4.13 (m, 1H), 4.00-3.95 (m, 1H), 2.67-2.58 (m, 1H), 1.37 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 152.2, 144.4, 125.1, 110.0, 109.9, 80.3, 47.9, 33.9, 28.2, 21.1. HRMS calcd for $C_{12}H_{19}NO_2Na$ ($[M+Na]^+$) 232.1314 found 232.1322.

tert-butyl-3-methylene-4-propyl-3,4-didydropyridine-1(2H)-carboxylate **(3e)**



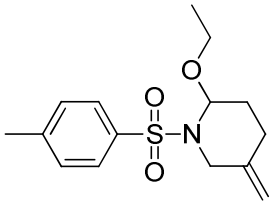
Prepared from N-Boc propargylamine **1b** (74 mg, 0.48 mmol) and *n*-hex-2-en-1-ol **2c** (2.5 equiv., 1.2 mmol) in THF (6 mL). Chromatography on alumina gel using pentane/Et_2O (80:20) as eluent afforded compound **3e** as colourless oil, 65 mg (57%) as two conformers (ratio 65/35). Major conformer: ^{1}H NMR (400 MHz, C_6D_6) δ 6.90-6.83 (m, 1H), 4.80 (s, 1H), 4.70 (s, 1H), 4.70-4.63 (m, 1H), 4.17 (d, *J*= 13.5 Hz, 1H), 3.77 (d, *J*= 13.5 Hz, 1H), 2.50-2.40 (m, 1H), 1.38 (s, 9H), 1.25-1.10 (m, 4H), 0.80-0.75 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.9, 142.7, 125.2, 111.5, 108.0, 80.3, 46.2, 40.0, 38.8, 28.6, 20.3, 14.1. Minor conformer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.28-7.22 (m, 1H), 4.80 (s, 1H), 4.70 (s, 1H), 4.70-4.63 (m, 1H), 4.50 (d, *J*= 13.5 Hz, 1H), 3.77 (d, *J*= 13.5 Hz, 1H), 2.50-2.40 (m, 1H), 1.38 (s, 9H), 1.25-1.10 (m, 4H), 0.80-0.75 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 152.2, 142.9, 125.1, 111.2, 108.2, 80.3, 47.2, 39.8, 38.8, 28.6, 20.3, 14.1. HRMS calcd for $C_{14}H_{23}NO_2Na$ ($[M+Na]^+$) 260.1627, found 260.1626.

2-methoxy-5-methylene-1-tosylpiperidine **(4a)**



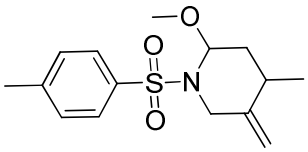
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and allylalcohol **2b** (2.5 equiv., 1.19 mmol) in MeOH (6 mL). Chromatography on alumina gel using PE/Et_2O (70:30) as eluent afforded compound **4a** as colourless oil, 38 mg (28%). ^{1}H NMR (300 MHz, C_6D_6) δ 7 .69 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 5.14 (s, 1H), 4.48 (s, 1H), 4.41 (s, 1H), 4.13 (d, *J* = 14.2, 1H), 3.69 (d, *J* = 14.2 Hz, 1H), 3.22 (s, 3H), 2.36-2.29 (m, 1H), 1.86 (s, 3H), 1.67-1.57 (m, 2H), 1.18-1.10 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 142.6, 141.2, 139.1, 129.5, 127.6, 110.1, 83.9, 54.9, 46.6, 30.7, 26.9, 21.1. HRMS calcd for $C_{14}H_{19}NO_3NaS$ ($[M+Na]^+$) 304.0983, found 304.0981.

2-ethoxy-5-methylene-1-tosylpiperidine **(4b)**



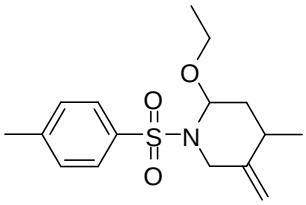
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and allylalcohol **2b** (2.5 equiv., 1.19 mmol) in EtOH (6 mL). Chromatography on alumina gel using pentane/Et_2O (70:30) as eluent afforded compound **4b** as colourless oil, 50 mg (35%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.70 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7. 9 Hz, 2H), 5.28 (s, 1H), 4.49 (s, 1H), 4.42 (s, 1H), 4.15 (d, *J* = 14.1 Hz, 1H), 3.75 (d, *J* = 14.1 Hz, 1H), 3.68-3.64 (m, 1H), 3.45-3.41 (m, 1H), 2.40-2.34 (m, 1H), 1.87 (s, 3H), 1.69-1.58 (m, 2H), 1.20-1.14 (m, 1H), 1.04 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 142.6, 141.3, 139.1, 129.5, 127.6, 110.1, 82.3, 63.0, 46.7, 30.9, 26.9, 21.1, 15.0. HRMS calcd for $C_{15}H_{21}NO_3NaS$ ($[M+Na]^+$) 318.1140, found 318.1139

2-methoxy-4-methyl-5-methylene-1-tosylpiperidine **(4c)**



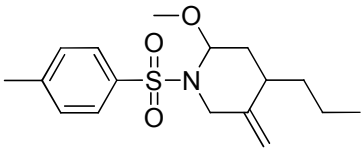
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and crotylalcohol **2a** (2.5 equiv., 1.2 mmol) in MeOH (6 mL). Chromatography on alumina gel using pentane/ Et_2O (70:30) as eluent afforded compound **4c** as colourless oil, 101 mg (72%) as two diastereomers (ratio 9/1). Major diastereomer : ^{1}H NMR (300 MHz, C_6D_6) δ 7.70 (d, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 7.4 Hz, 2H), 5.17 (s, 1H), 4.57 (s, 1H), 4.44 (s, 1H), 4.16 (d, *J* = 13.9 Hz, 1H), 3.70 (d, *J* = 13.9 Hz, 1H), 3.25 (s, 3H), 2.48-2.36 (m, 1H), 1.88 (s, 3H), 1.67-1.61 (m, 1H), 0.92-0.83 (m, 1H), 0.66 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 145.9, 142.8, 139.0, 129.5, 127.6, 108.0, 84.7, 55.1, 47.8, 39.3, 29.5, 21.1, 17.2. HRMS calcd for $C_{15}H_{21}NO_3NaS$ ($[M+Na]^+$) 318.1140, found 318.1137.

2-ethoxy-4-methyl-5-methyl-1-tosylpiperidine **(4d)**



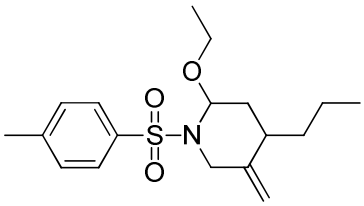
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and crotylalcohol **2a** (2.5 equiv., 1.2 mmol) in EtOH (6 mL). Chromatography on alumina gel using pentane/ Et_2O (70:30) as eluent afforded compound **4d** as colourless oil, 125 mg (85%) as two diastereomers (ratio 9/1). Major diastereomer: ^{1}H NMR (300 MHz, C_6D_6) δ 7.71 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* =8.0 Hz, 2H), 5.30 (s, 1H), 4.59 (s, 1H), 4.46 (s, 1H), 4.18 (d, *J* = 14.0 Hz, 1H), 3.75 (d, *J*= 14.0 Hz, 1H), 3.70-3.66 (m, 1H), 3.47-3.42 (m, 1H), 2.55-2.40 (m, 1H), 1.88 (s, 3H), 1.70-1.60 (m, 1H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.94-0.89 (m, 1H), 0.66 (d, *J*= 6.6 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 146.1, 142.7, 139.0, 129.5, 127.7, 108.0, 83.1, 63.1, 47.9, 39.5, 29.5, 21.1, 17.2, 15.1. HRMS calcd for $C_{16}H_{23}NO_3NaS$ ($[M+Na]^+$) 332.1296, found 332.1295.

2-methoxy-5-methylene-4-propyl-1-tosylpiperidine **(4e)**



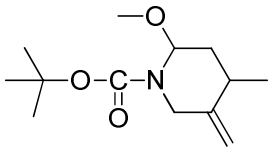
Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and n-hex-2-en-1-ol **2c** (2.5 equiv., 1.2 mmol) in MeOH (6 mL). Chromatography on alumina gel using pentane/Et_2O (70:30) afforded compound **4e** as colourless oil, 110 mg (71%) as two diastereomers (ratio 8/2). Major diastereomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.71 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 1H), 4.61 (s, 1H), 4.47 (s, 1H), 4.15 (d, *J* = 13.8 Hz, 1H), 3.71 (d, *J* = 13.8 Hz, 1H), 3.26 (s, 3H), 2.40-2.30 (m, 1H), 1.89 (s, 3H), 1.80-1.77 (m, 1H), 1.30-1.20 (m, 1H), 1.13-0.97 (m, 2H), 0.88-0.79 (m, 2H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 145.3, 142.7, 139.0, 129.5, 127.7, 108.4, 84.8, 55.0, 48.3, 36.9, 34.3, 33.6, 21.1, 19.9, 14.2. HRMS calcd for $C_{17}H_{25}NO_3NaS$ ($[M+Na]^+$) 346.1453, found 346.1451.

2-ethoxy-5-methylene-4-propyl-1-tosylpiperidine **(4f)**



Prepared from N-tosyl propargylamine **1a** (100 mg, 0.48 mmol) and n-hex-2-en-1-ol **2c** (2. 5 equiv., 1.2 mmol) in EtOH (6 mL). Chromatography afforded compound **4f** as colourless oil, 110 mg, (68%) as two diastereomers (ratio 3/1). Major diastereoisomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.72 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 5.34 (s, 1H), 4.63 (s, 1H), 4.48 (s, 1H), 4.18 (d, *J* = 13.9 Hz, 1H), 3.76 (d, *J* = 13.9 Hz, 1H), 3.73-3.65 (m, 1H), 3.52-3.42 (m, 1H), 2.45-2.35 (m, 1H), 1.89 (s, 3H), 1.81-1.77 (m, 1H), 1.31-1.22 (m, 1H), 1.06 (t, *J* = 6.9 Hz, 3H), 1.04-1.00 (m, 2H), 0.90-0.80 (m, 2H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 145.4, 142.7, 139.1, 129.5, 127.7, 108.3, 83.2, 63.1, 48.4, 37.2, 34.3, 33.7, 21.1, 19.9, 15.1, 14.3. HRMS calcd for $C_{18}H_{27}NO_3NaS$ ($[M+Na]^+$) 360.1609, found 360.1607.

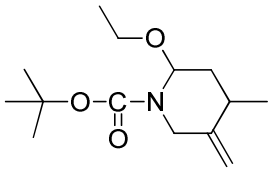
tert-butyl 2-methoxy-4-methyl-5-methylenepiperidine-1-carboxylate **(4g)**



Prepared from N-Boc propargylamine **1b** (74 mg, 0.48 mmol) and crotylalcohol **2a** (2.5 equiv., 1.2 mmol) in MeOH (6 mL). Chromatography on alumina gel afforded compound **4g** as colourless oil, 86 mg (75%) as two diastereomers (ratio 9/1) both in two conformers form (ratio 52/48). Major diastereomer in two conformers: ^{1}H NMR (300 MHz, C_6D_6) δ 5.70 (br s) & 5.31 (br s) for 1H, 4.84 (s, 1H), 4.63 (s) & 4.61 (s) for 1H, 4.79 (d, *J*= 13.7 Hz) & 4.37 (d, *J*= 13.6 Hz) for 1H, 3.68 (d, *J*= 13.7 Hz) & 3.60 (d, *J*= 13.6 Hz) for 1H, 3.22 (s) & 3.10 (s) for 3H, 2.70-2.60 (m, 1H, 1.84-1.82 (m) & 1.80-1.78 (m) for 1H, 1.42 (s) & 1.39 (s) for 9H, 1.20-1.10 (m, 1H), 0.84 (d, *J*= 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.8 & 154.3, 148.1 & 147.4, 107.5 & 106.9, 82.9 & 82.1, 79.6 & 79.5, 54.8 & 54.4, 47.0 & 45.7, 40.1 & 39.7, 30.0 & 29.9, 28.4, 17.5 & 17.4.

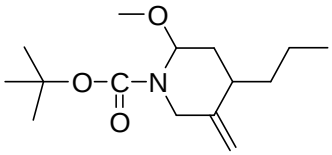
HRMS calcd for $C_{13}H_{23}NO_3Na$ ($[M+Na]^+$) 264.1576, found 264.1575.

tert-butyl 2-ethoxy-4-methyl-5-methylenepiperidine-1-carboxylate (4h)



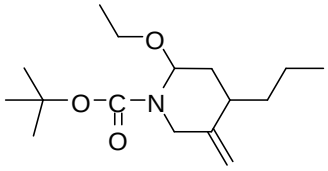
Prepared from N-Boc propargylamine **1b** (74 mg, 0.48 mmol) and crotylalcohol **2a** (2.5 equiv., 1.2 mmol) in EtOH (6 mL). Chromatography on alumina gel using pentane/Et_2O (80:20) as eluent afforded compound **4h** as colourless oil, 110 mg (91%) as two diastereomers (ratio 6/1) both in two conformers form (55/45 ratio). Major diastereomer in two conformers: ^{1}H NMR (400 MHz, C_6D_6) δ 5.82 (br s) & 5.45 (br s) for 1H, 4.85 (s, 1H), 4.65 (s) & 4.62 (s) for 1H, 4.79 (d, *J*= 13.5 Hz) & 4.39 (d, *J*= 13.5 Hz) for 1H, 3.73 (d, *J*= 13.5 Hz) & 3.64 (d, *J*= 13.5 Hz) for 1H, 3.55-3.30 (m, 2H), 2.74-2.64 (m, 1H), 1.85-1.79 (m, 1H), 1.43 (s) & 1.40 (s) for 9H, 1.22-1.16 (m, 1H), 1.15-1.06 (m, 3H), 0.85 (d, *J*= 6.0 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 154.6 & 154.2, 148.3 & 147.6, 107.5 & 106.8, 81.2 & 80.6, 79.5 & 79.4, 62.8 & 62.2, 47.1 & 45.7, 40.4 & 40.1, 30.1 & 30.0, 28.4, 17.5 & 17.4, 15.4 & 15.3. HRMS calcd for $C_{14}H_{25}NO_3Na$ ($[M+Na]^+$) 278.1732, found 278.1732.

tert-butyl 2-methoxy-5-methylene-4-propylpiperidine-1-carboxylate (4i)



Prepared from N-Boc propargylamine **1b** (74 mg, 0.48 mmol) and n-hex-2-en-1-ol **2c** (2.5 equiv., 1.2 mmol) in MeOH (6 mL). Chromatography on alumina gel using pentane/Et_2O (80:20) as eluent afforded compound **4i** as colourless oil, 91 mg (71%) as two diastereomers (ratio 4/1) both in two conformers form (ratio 55/45). Major diastereomer in two conformers: ^{1}H NMR (400 MHz, C_6D_6) δ 5.72 (br s) & 5.34 (br s) for 1H, 4.88 (s, 1H), 4.66 (s) & 4.64 (s) for 1H, 4.76 (d, *J*= 13.5 Hz) & 4.35 (d, *J*= 13.1 Hz) for 1H, 3.69 (d, *J*= 13.5 Hz) & 3.62 (d, *J*= 13.1 Hz) for 1H, 3.24 (s) & 3.12 (s) for 3H, 2.60-2.50 (m, 1H), 1.96-1.90 (m, 1H), 1.43 (s) & 1.40 (s) for 9H, 1.25-1.10 (m, 5H), 0.79 (d, *J*= 7.0 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.8 & 154.3, 147.8 & 146.9, 107.9 & 107.3, 82.9 & 82.1, 79.6 & 79.5, 54.8 & 54.4, 47.5 & 46.2, 37.7 & 37.3, 34.9 & 34.8, 34.2 & 34.1, 28.4, 20.2 & 20.1, 14.3. HRMS calcd for $C_{15}H_{27}NO_3Na$ ($[M+Na]^+$) 292.1889, found 292.1888.

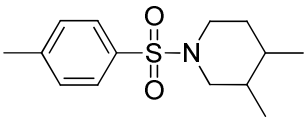
tert-butyl 2-ethoxy-5-methylene-4-propylpiperidine-1-carboxylate (4j)



Prepared from N-Boc propargylamine **1b** (74 mg, 0.48 mmol) and n-hex-2-en-1-ol **2c** (2.5 equiv., 1.2 mmol) in EtOH (6 mL). Chromatography on alumina gel using PE/Et_2O (80:20) as eluent afforded compound **4j** as colourless oil, 95 mg (70 %) two diastereomers (ratio 4/1) both in two conformers form (55/45 ratio). Major diastereomer in two conformers: ^{1}H NMR (400 MHz, C_6D_6) δ 5.84 (br s) & 5.49 (br s) for 1H, 4.90 (s, 1H, $=CH_2$), 4.68 (s) & 4.65 (s) for 1H, 4.77 (d, *J*= 13.3 Hz) & 4.37 (d, *J*= 13.0 Hz) for 1H, 3.75 (d, *J*= 13.0 Hz) & 3.65 (d, *J*= 13.3 Hz) for 1H, 3.60-3.30 (m, 2H), 2.62-2.52 (m, 1H), 2.00-1.90 (m, 1H), 1.43 (s) & 1.41 (s) for 9H, 1.30-1.00 (m, 8H), 0.79 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.7 & 154.2, 147.6 & 146.9, 107.8 & 107.2, 81.2 & 80.6, 79.5 & 79.4, 62.8 & 62.2, 47.6 & 46.3, 38.0 & 37.6, 35.0 & 34.9, 34.3 & 34.1, 28.4, 20.2 & 20.1, 15.4 & 15.3, 14.4. HRMS calcd for $C_{16}H_{29}NO_3Na$ ($[M+Na]^+$) 306.2045, found 306.2043.

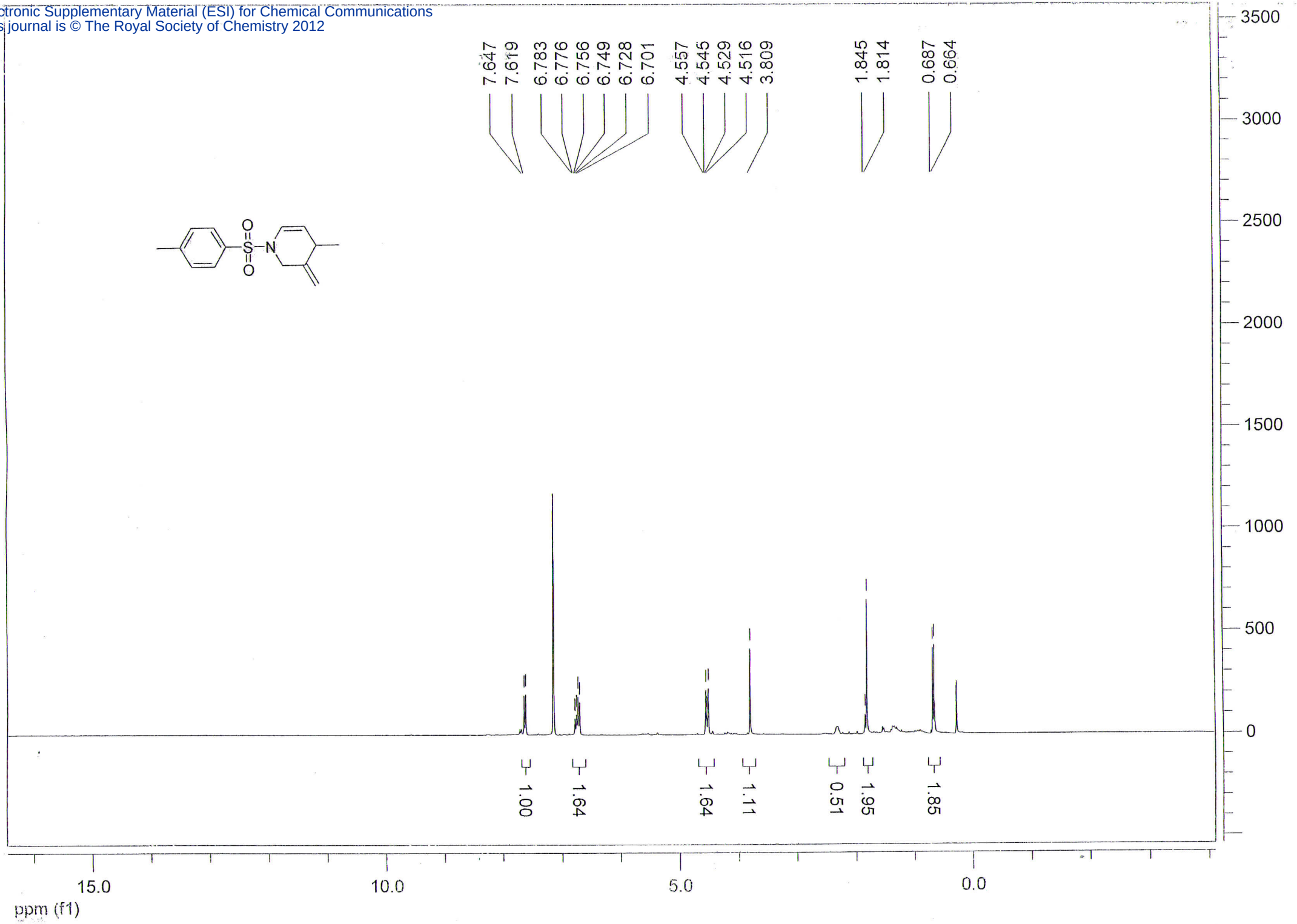
Procedure for the One Pot preparation 3,4 dimethyl *N*-tosylpiperidine 5

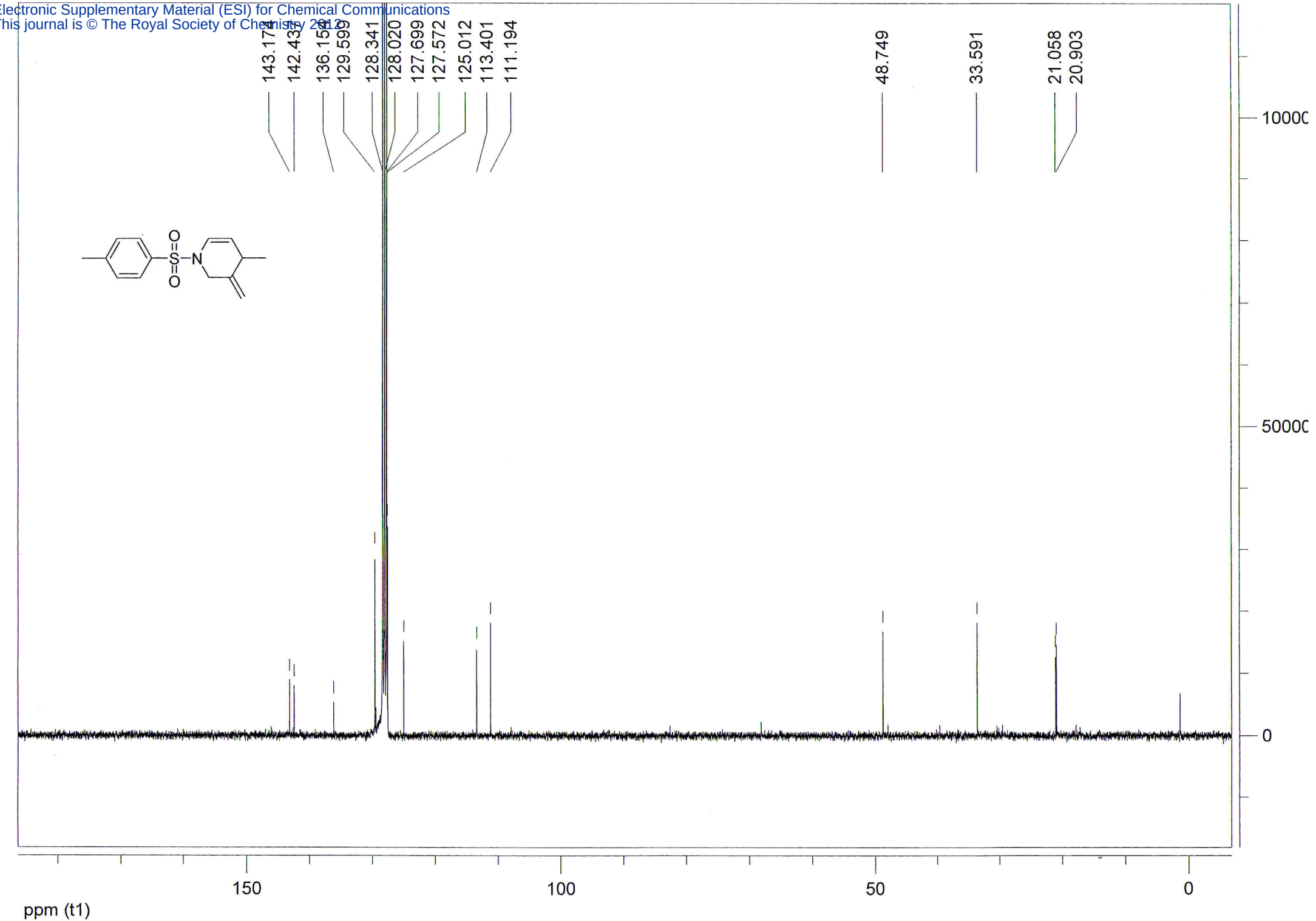
In an autoclave under an inert atmosphere, [Ru (Cp*)$(CH_3CN)_3PF_6$] (5 mol %) was added to a solution of *N*-protected propargylamine **1a** (100 mg, 0.48 mmol), crotyl alcohol **2a** (5 equiv.) in THF (4 mL) and the resulting solution was stirred at 90°C for 16 hours. After cooling down the reaction mixture, cat. **A** (5 mol %) and camphorsulfonic acid (CSA) (5 mol %) were then added and the autoclave was pressurized with 30 bars of molecular hydrogen and the reaction was stirred at 120 °C overnight. After evaporation, crude reaction mixture was suspended on silica and purification by column chromatography using pentane/Et_2O (85/15) as eluent afforded compound **5** as colorless oil in 60 % overall yield (76 mg) as two diastereoisomers (ratio 65/35):

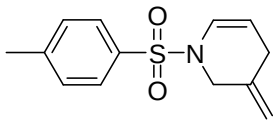


Major diastereomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.69-7.66 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 3.35-3.28 (m, 1H), 3.14 (dd, *J*= 11.3 Hz, *J*= 4.9 Hz, 1H), 2.44 (dd, *J*= 11.3 Hz, *J*= 3.1 Hz, 1H), 2.34 (td, *J*= 10.5 Hz, *J*= 3.2 Hz, 1H), 1.93 (s, 3H), 1.45-1.38 (m, 1H), 1.23-1.10 (m, 1H), 1.10-

1.00 (m, 2H), 0.76 (d, *J*= 7.0 Hz, 3H), 0.48 (d, *J*= 6.9 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 142.7, 134.9, 129.5, 128.1, 51.7, 45.4, 37.2, 33.4, 29.1, 21.1, 16.6, 12.4. Minor diastereomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.69-7.66 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 3.81-3.74 (m, 2H), 1.95-1.90 (m, 1H), 1.93 (s, 3H), 1.63 (dd, *J*= 11.3 Hz, *J*= 11.3 Hz, 1H), 1.23-1.10 (m, 1H), 1.10-1.00 (m, 2H), 0.58 (d, *J*= 6.5 Hz, 3H), 0.51 (d, *J*= 6.6 Hz, 3H), 0.40-0.30 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 142.8, 134.8, 129.5, 128.2, 53.2, 46.9, 36.8, 33.7, 32.3, 21.1, 18.9, 16.5.







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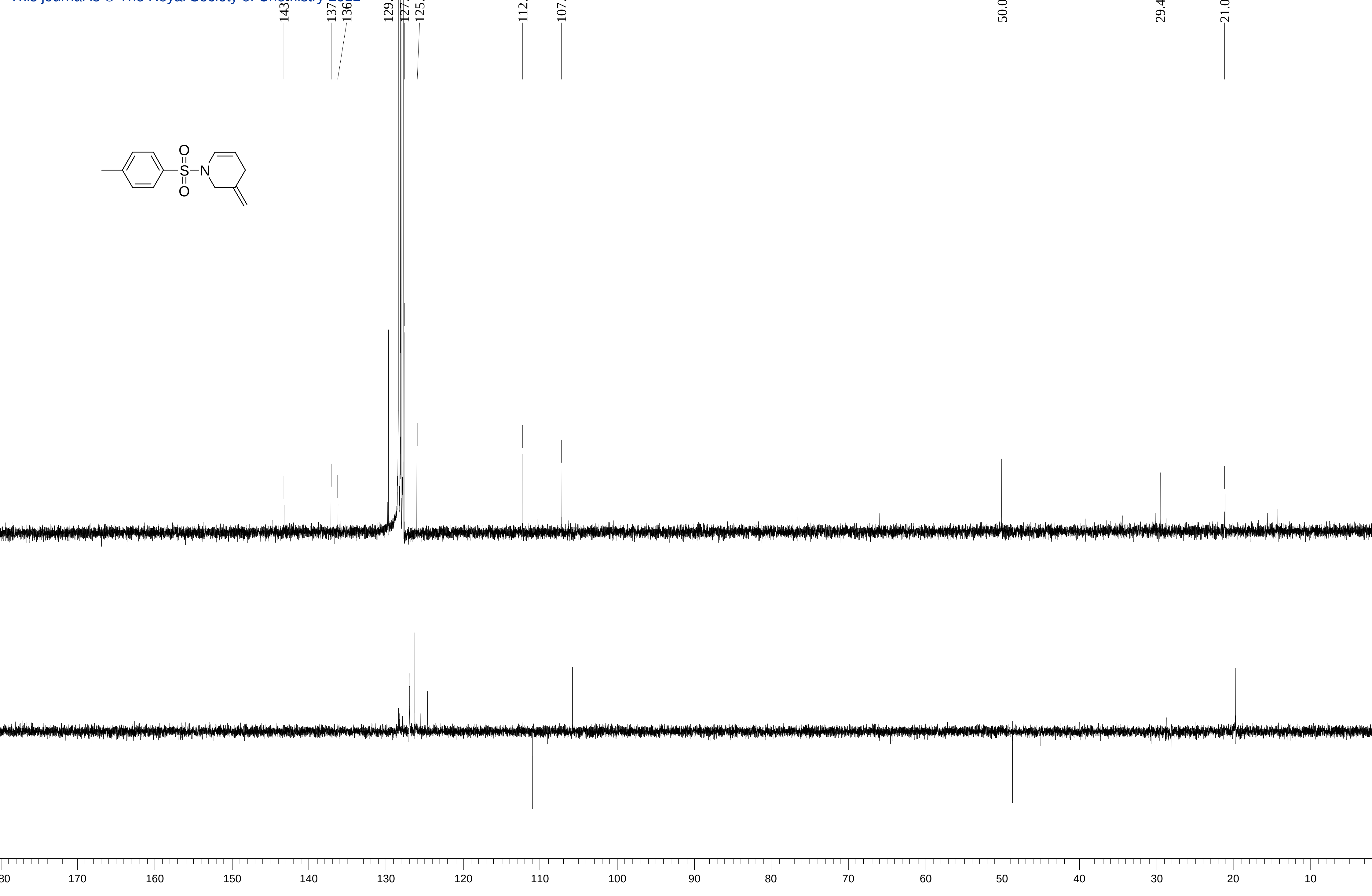
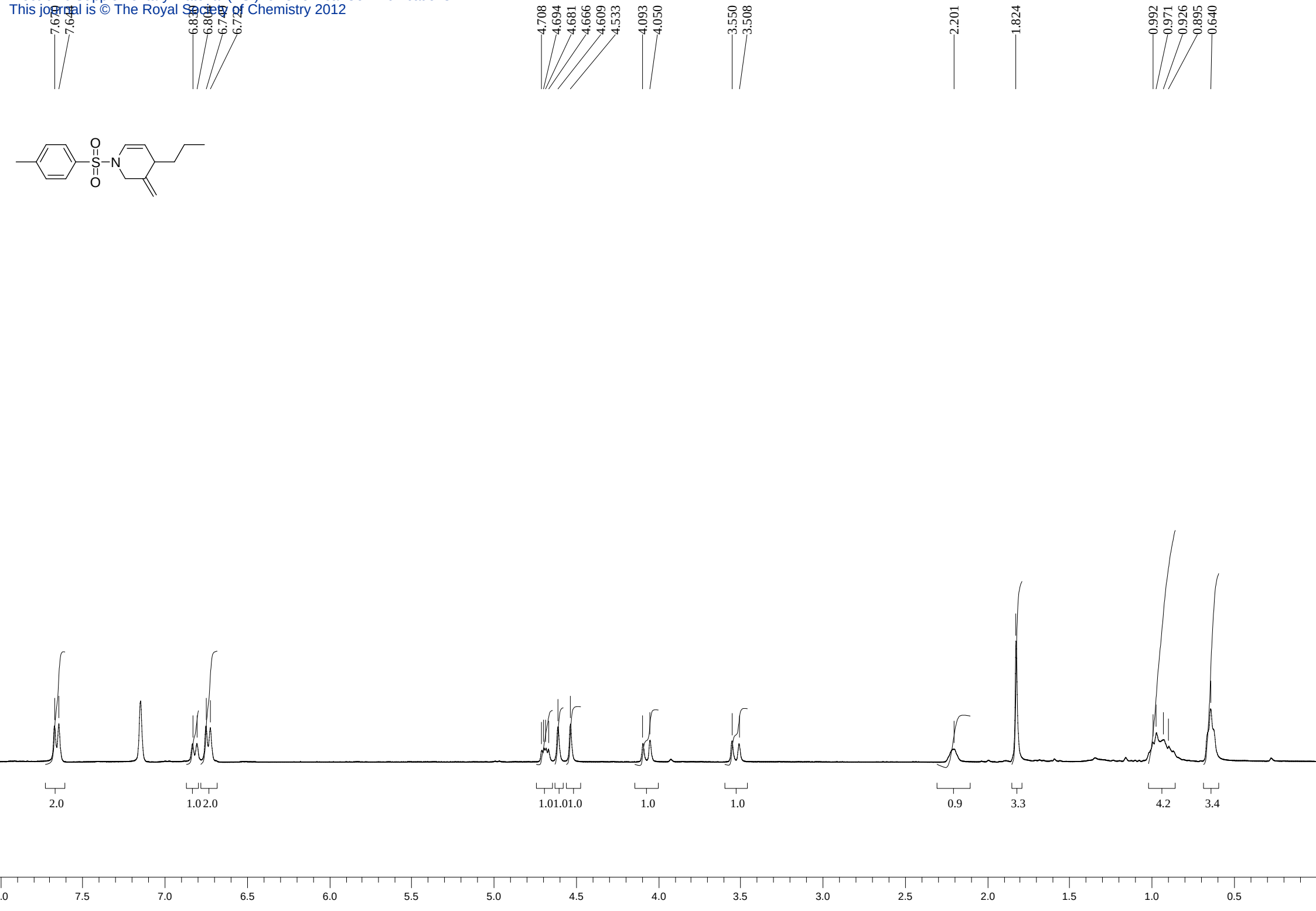
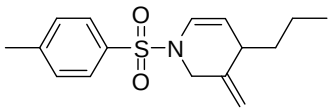
ppm (t1)

Electronic Supplementary Material (ESI) for Chemical Communications







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13.909

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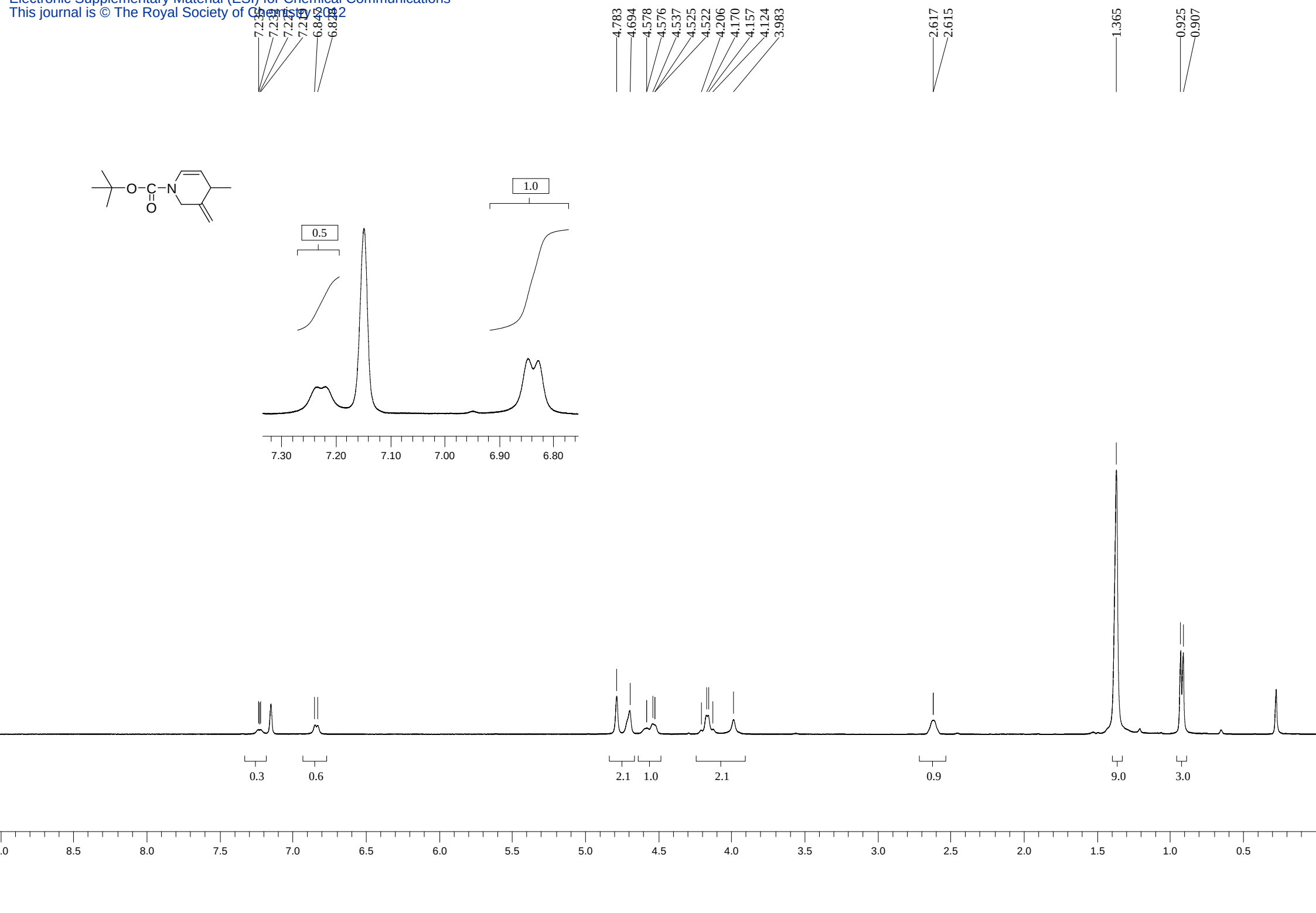

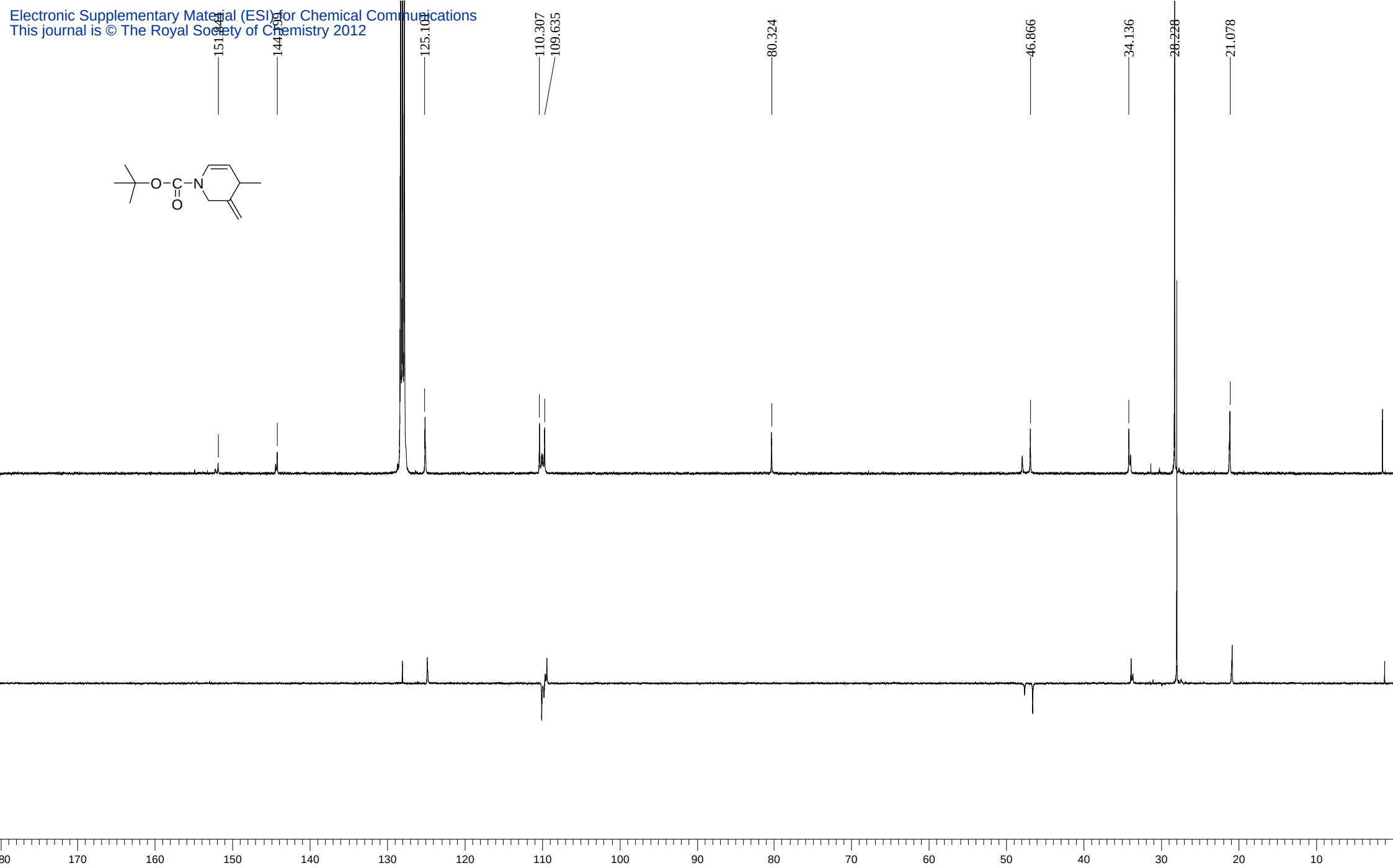

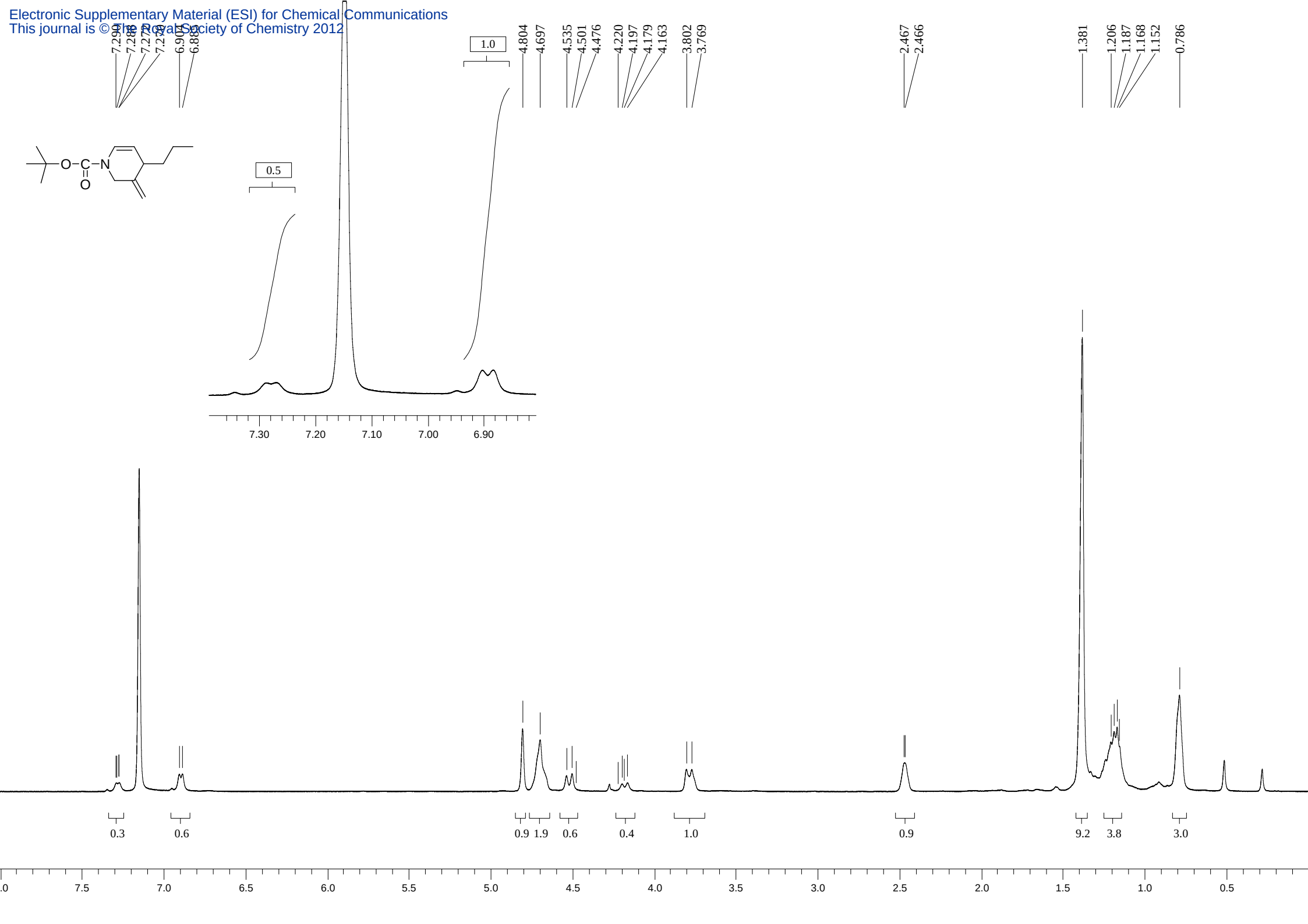

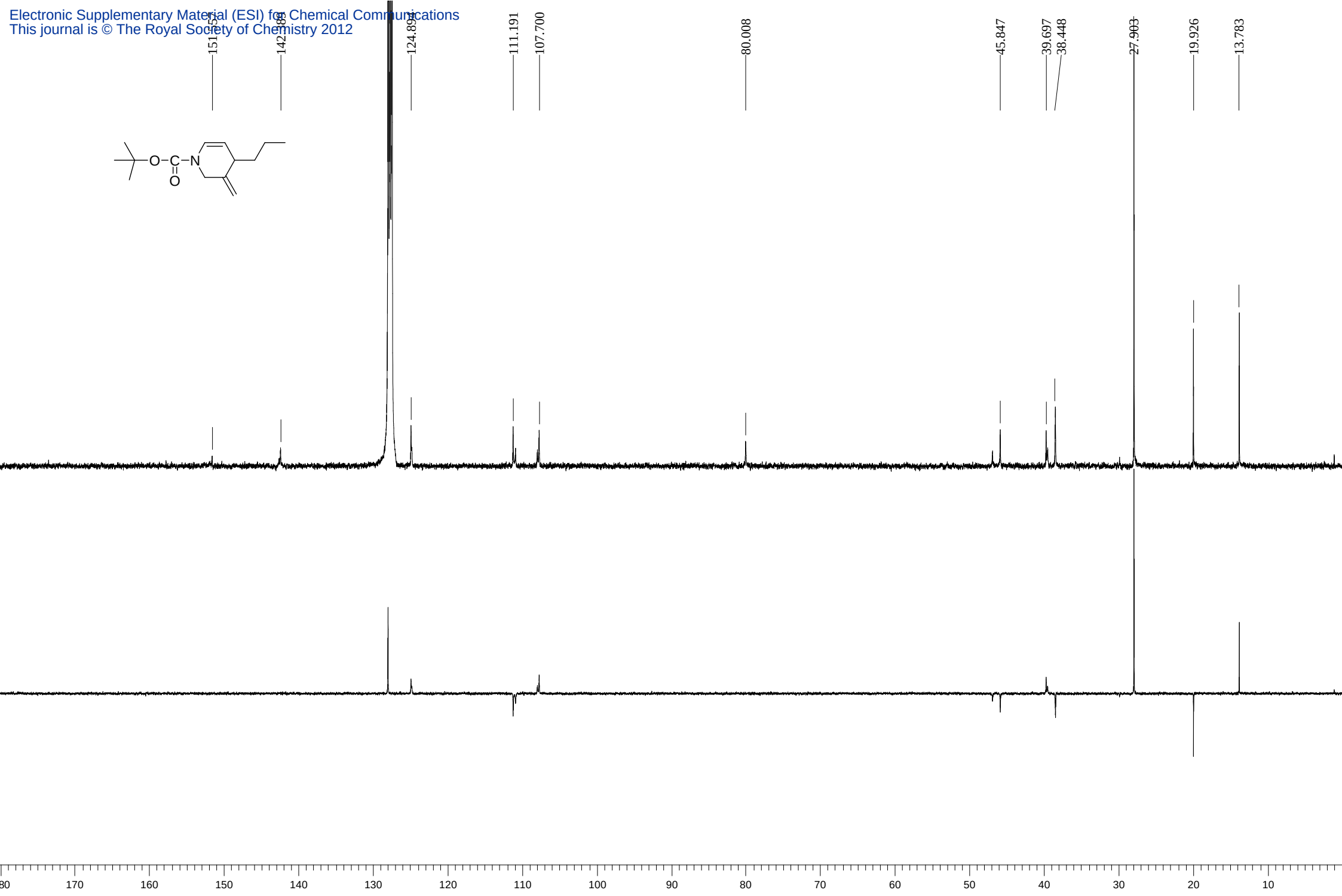

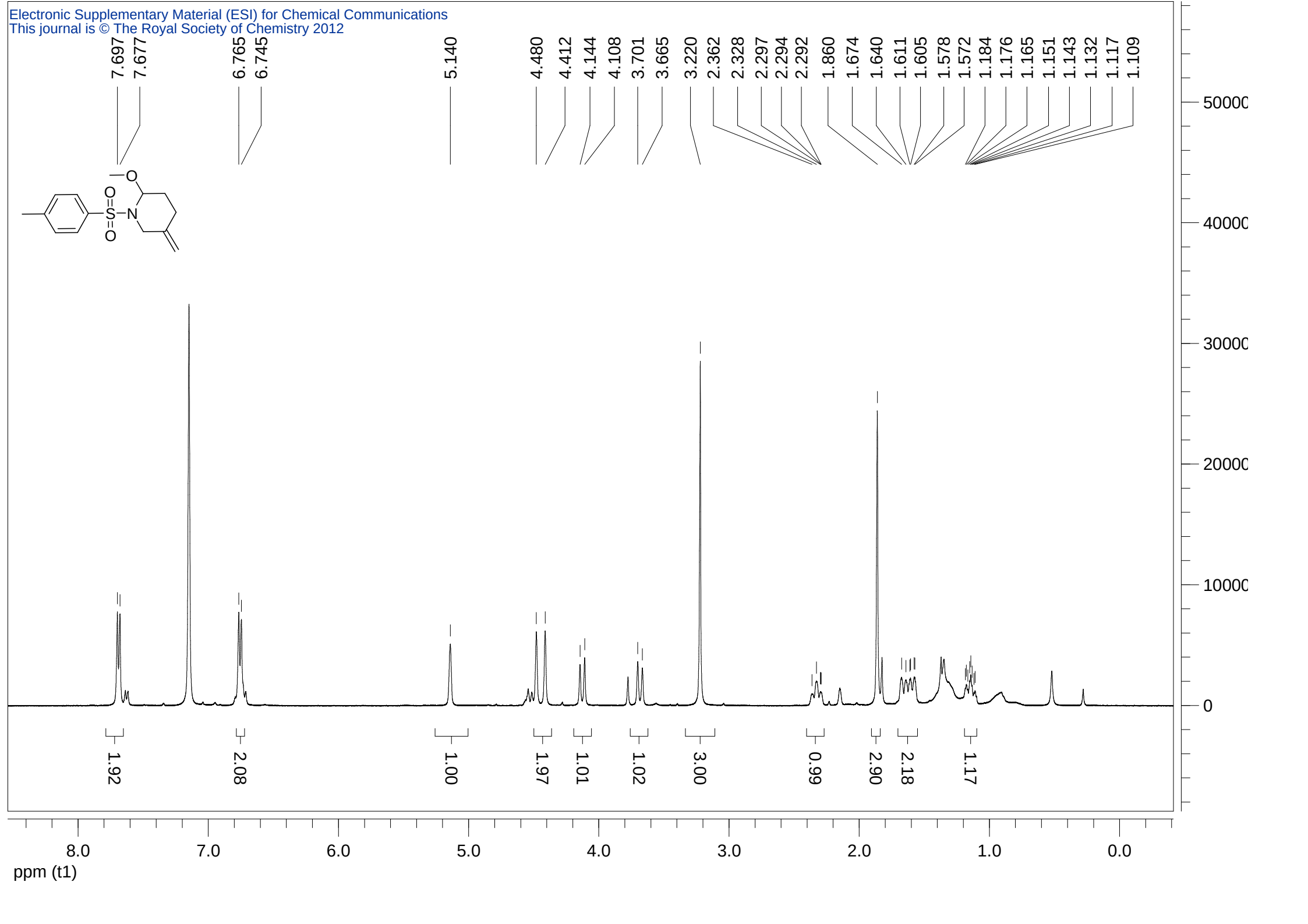

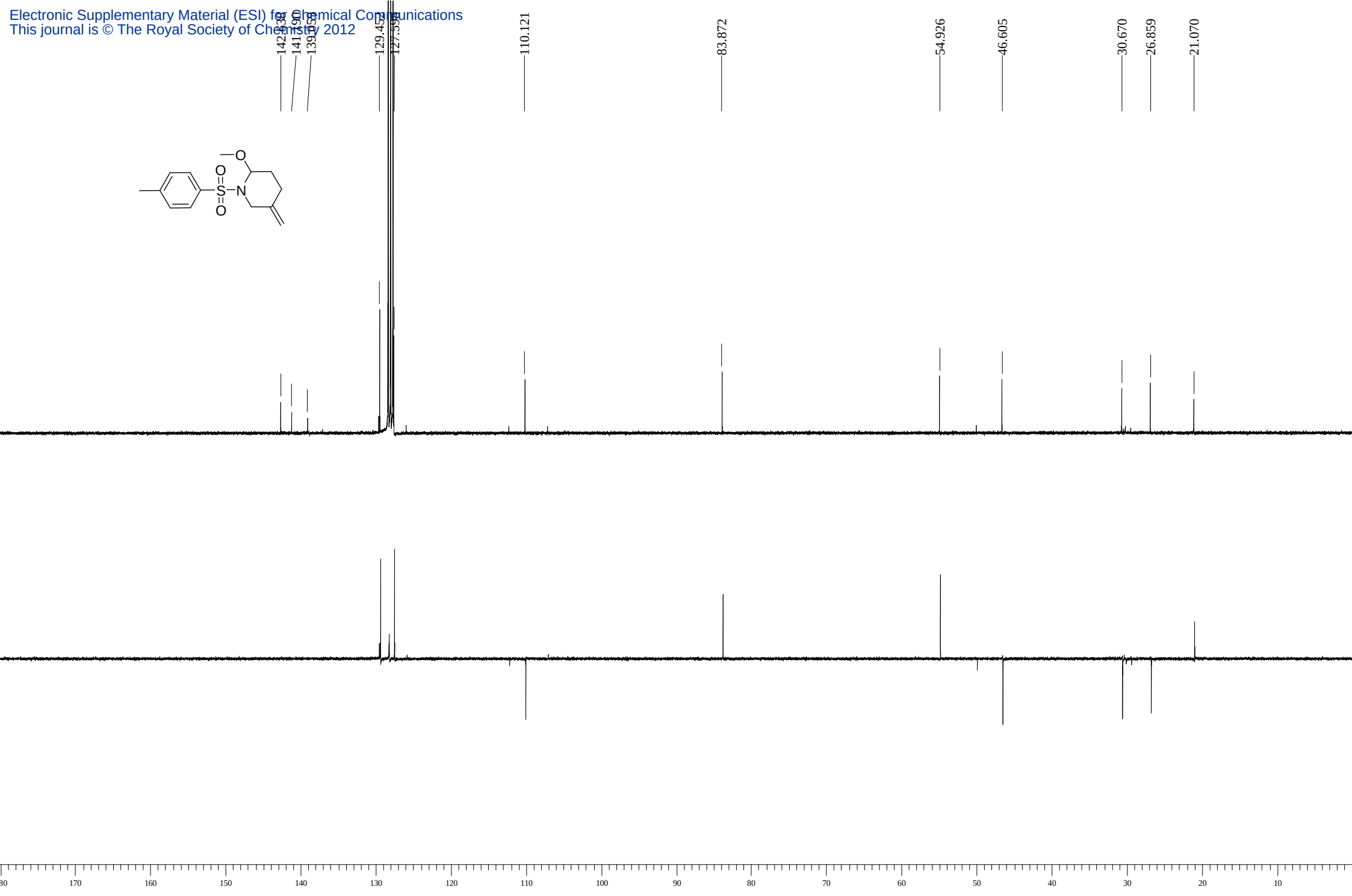

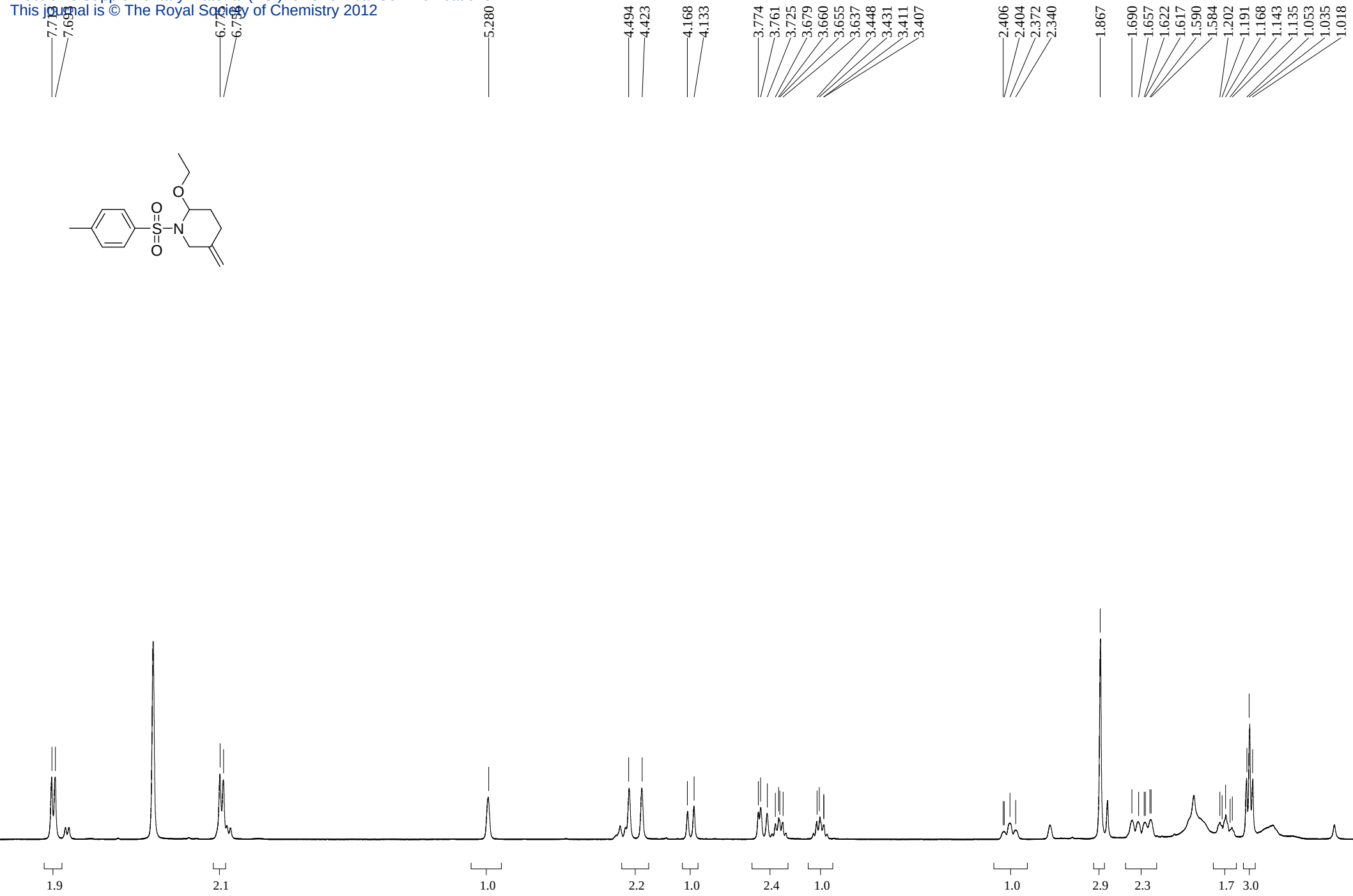

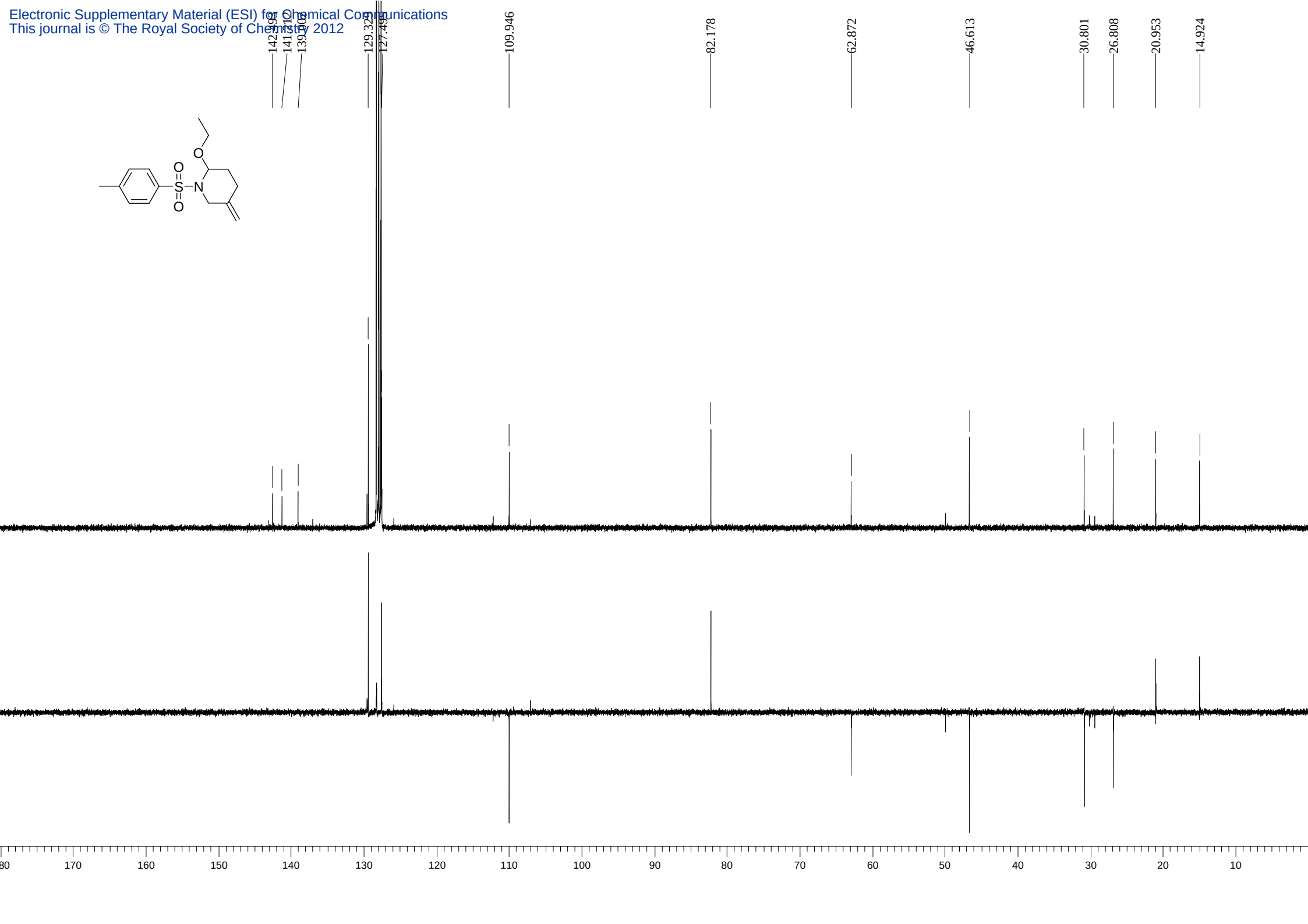

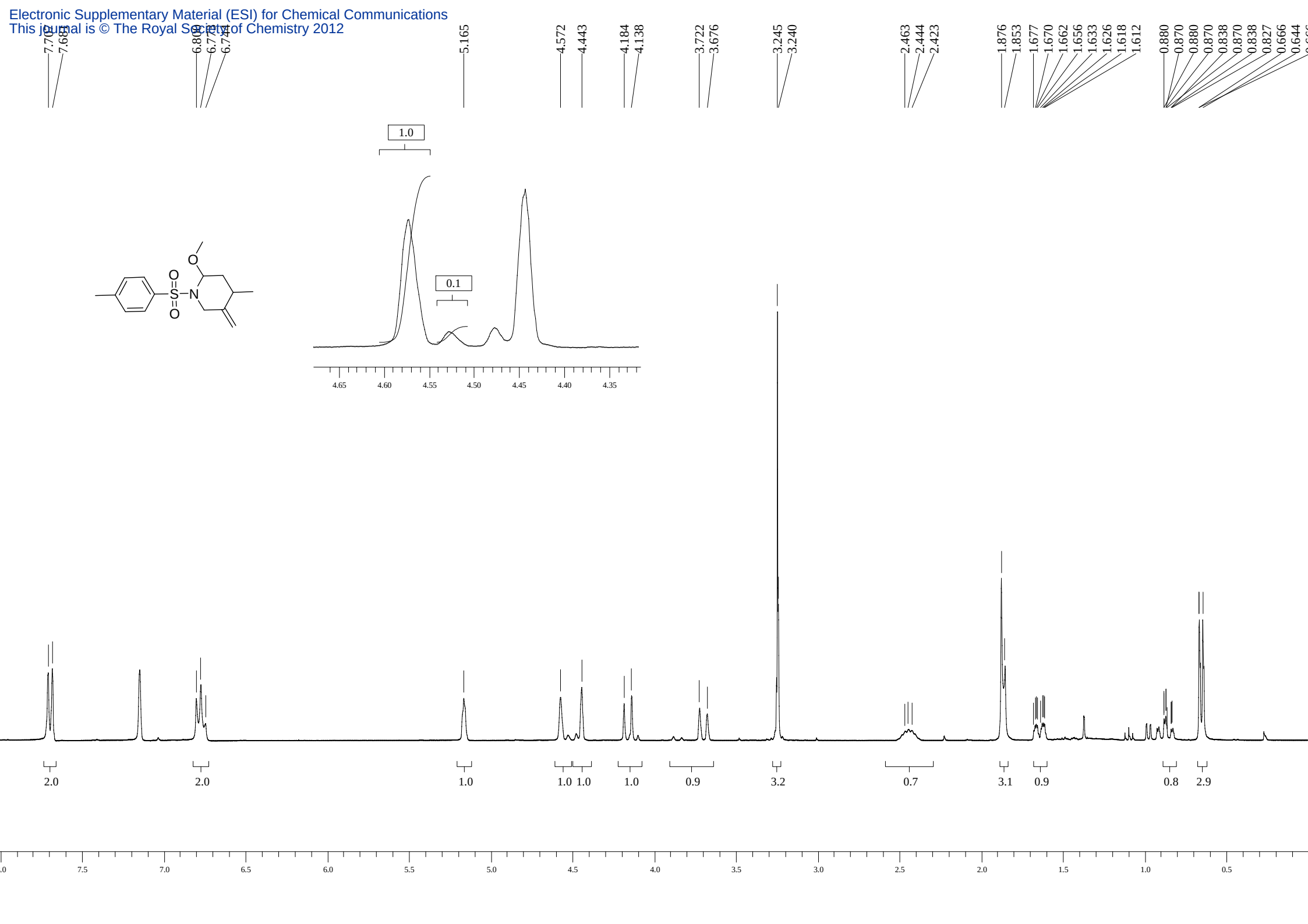

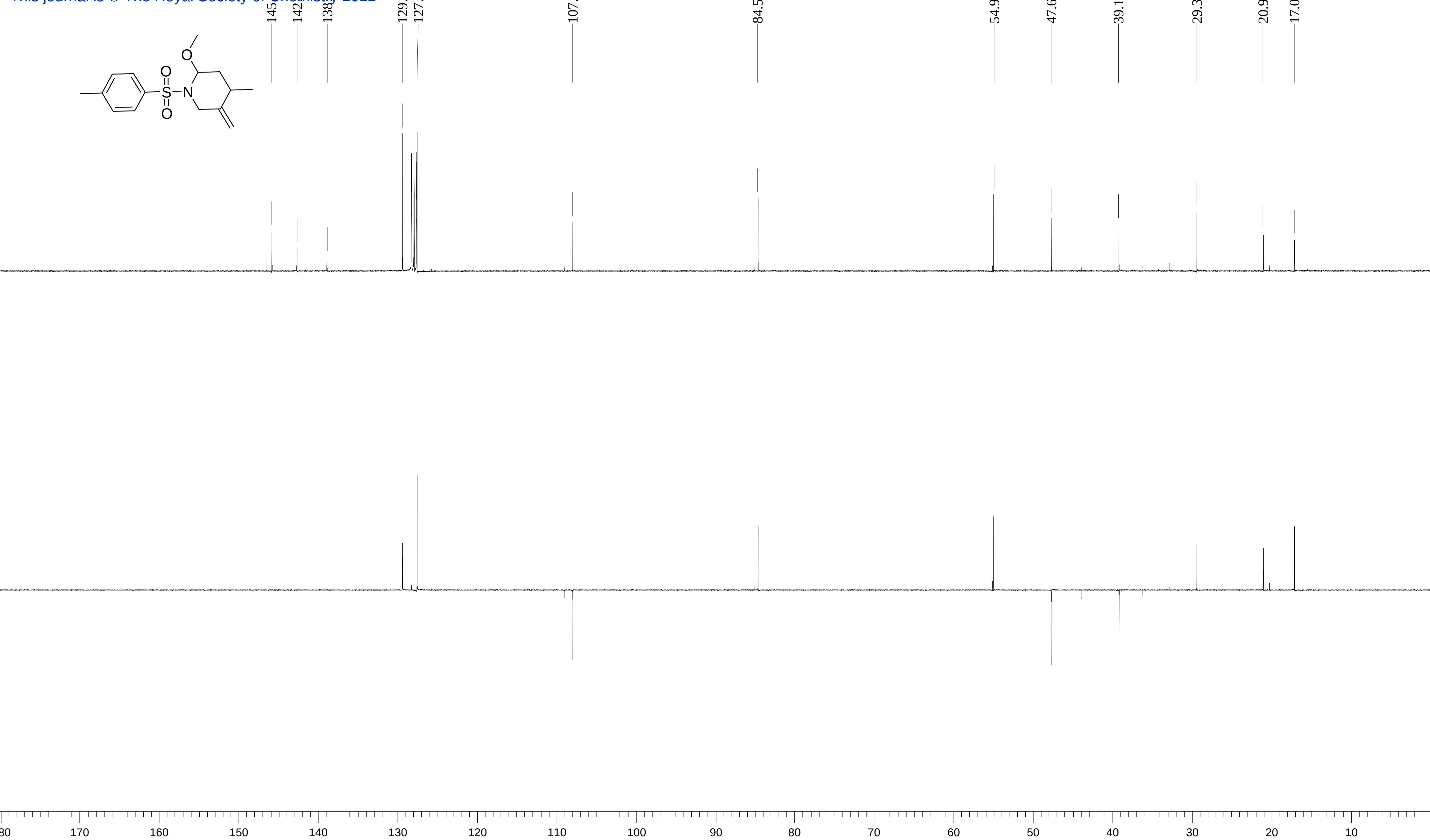
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17.066
O
O
S
N
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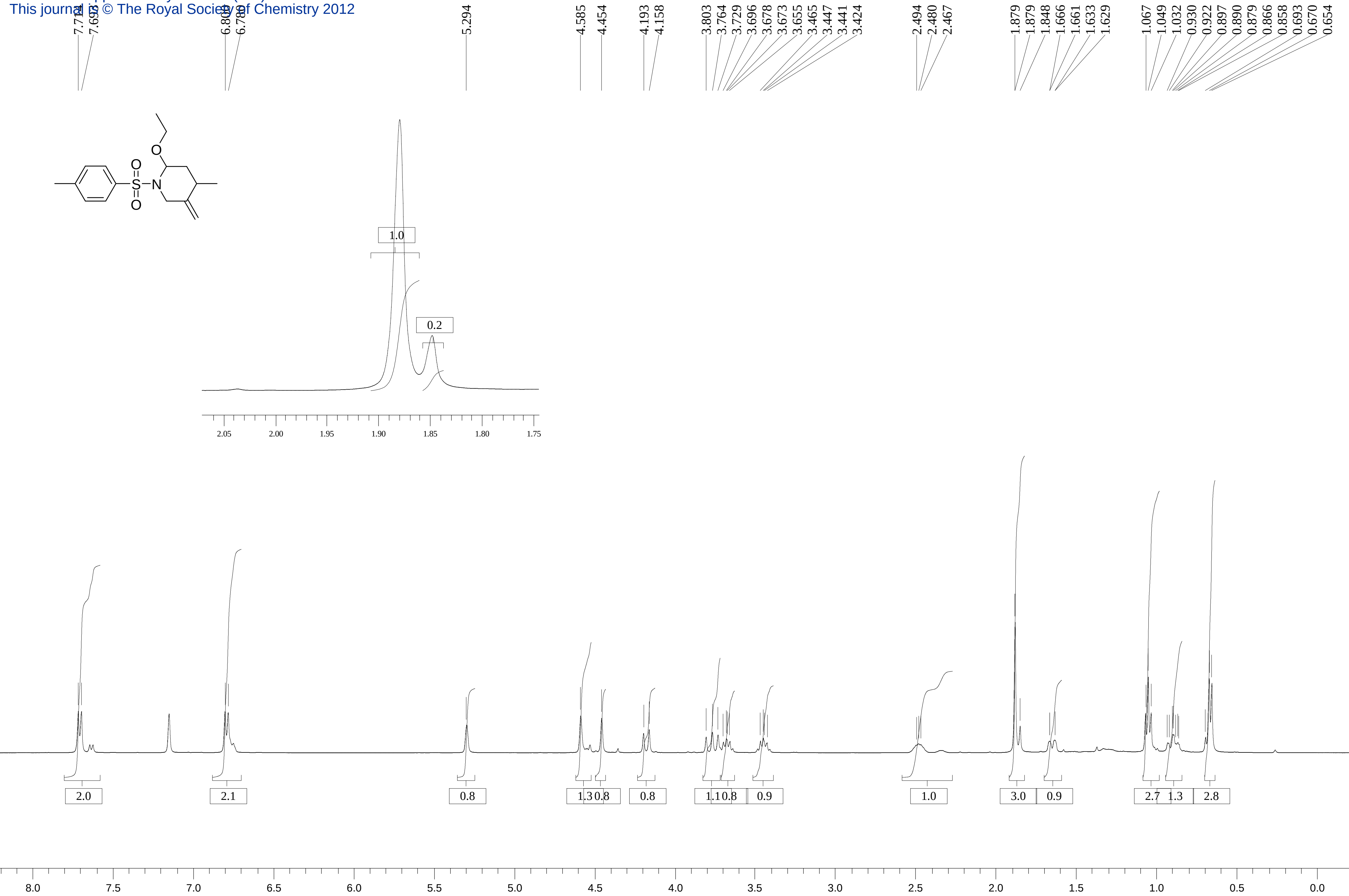
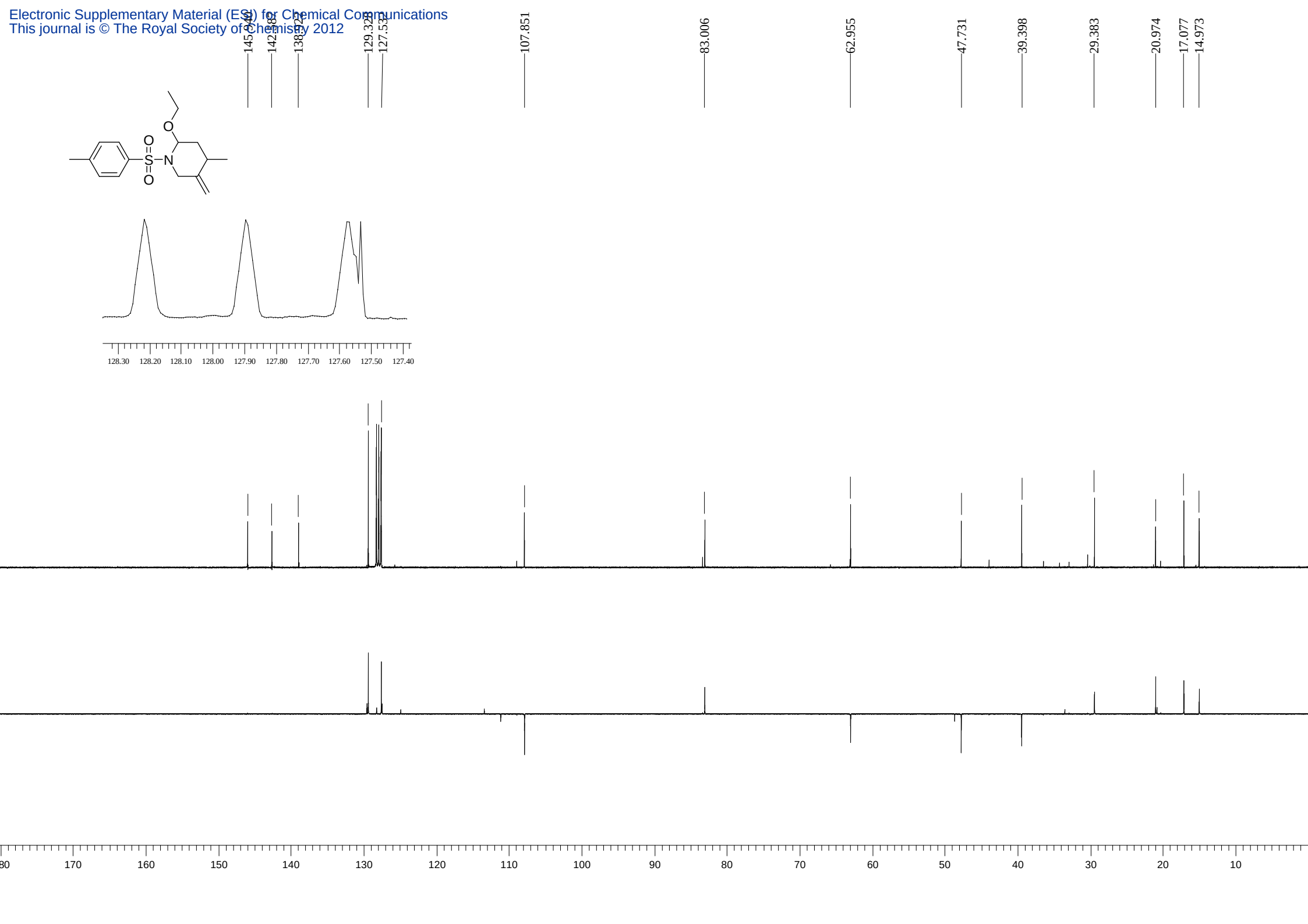
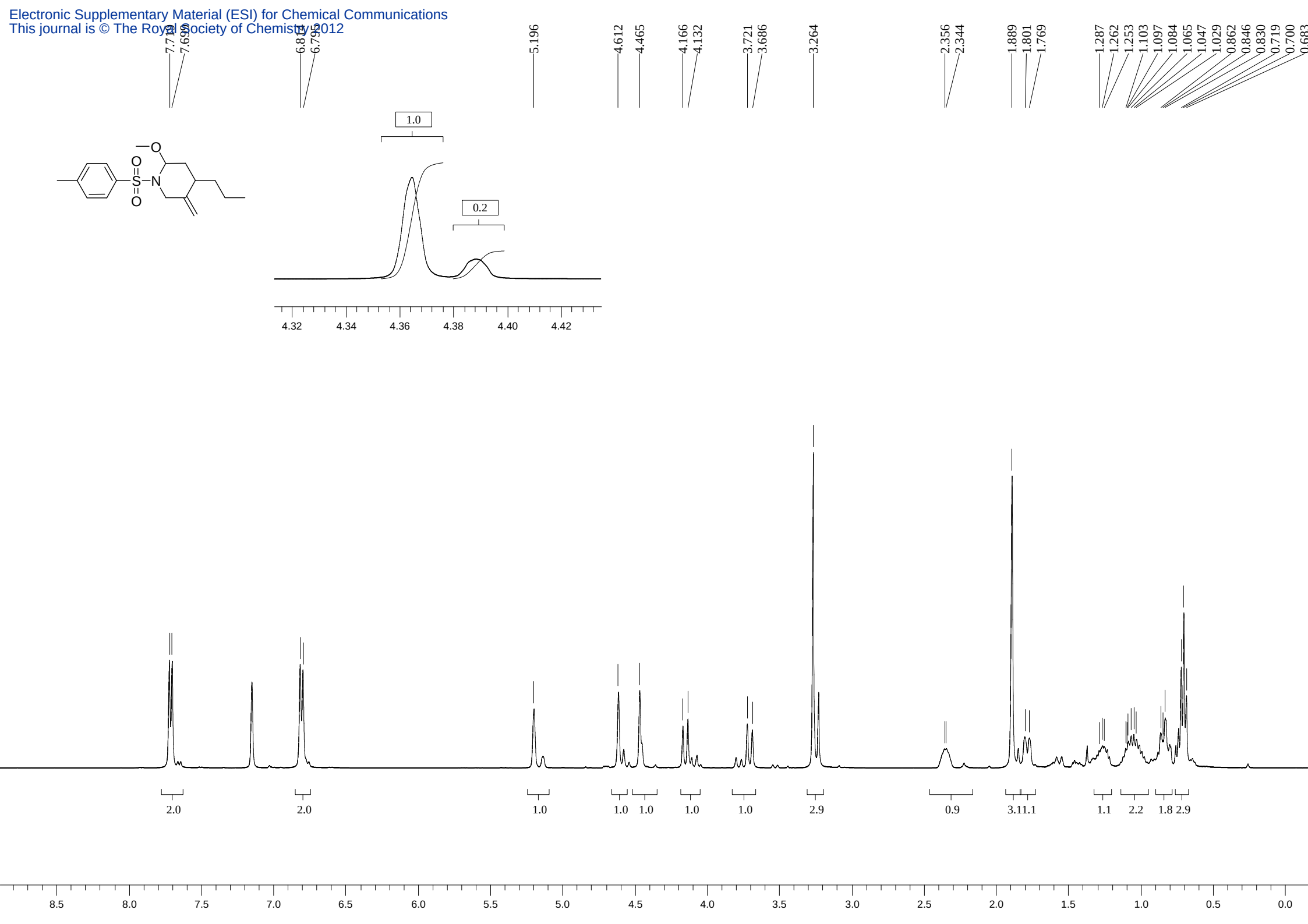
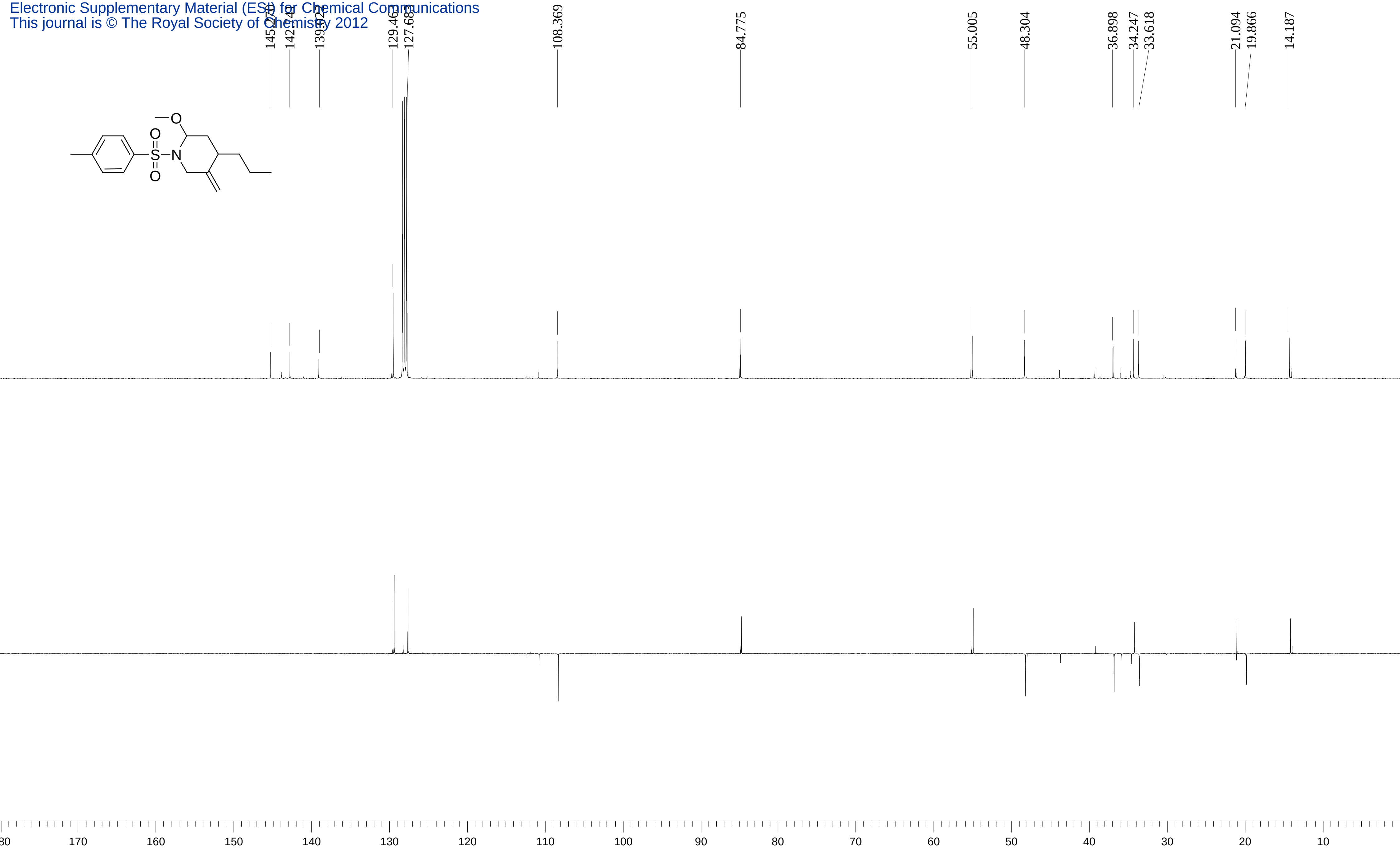
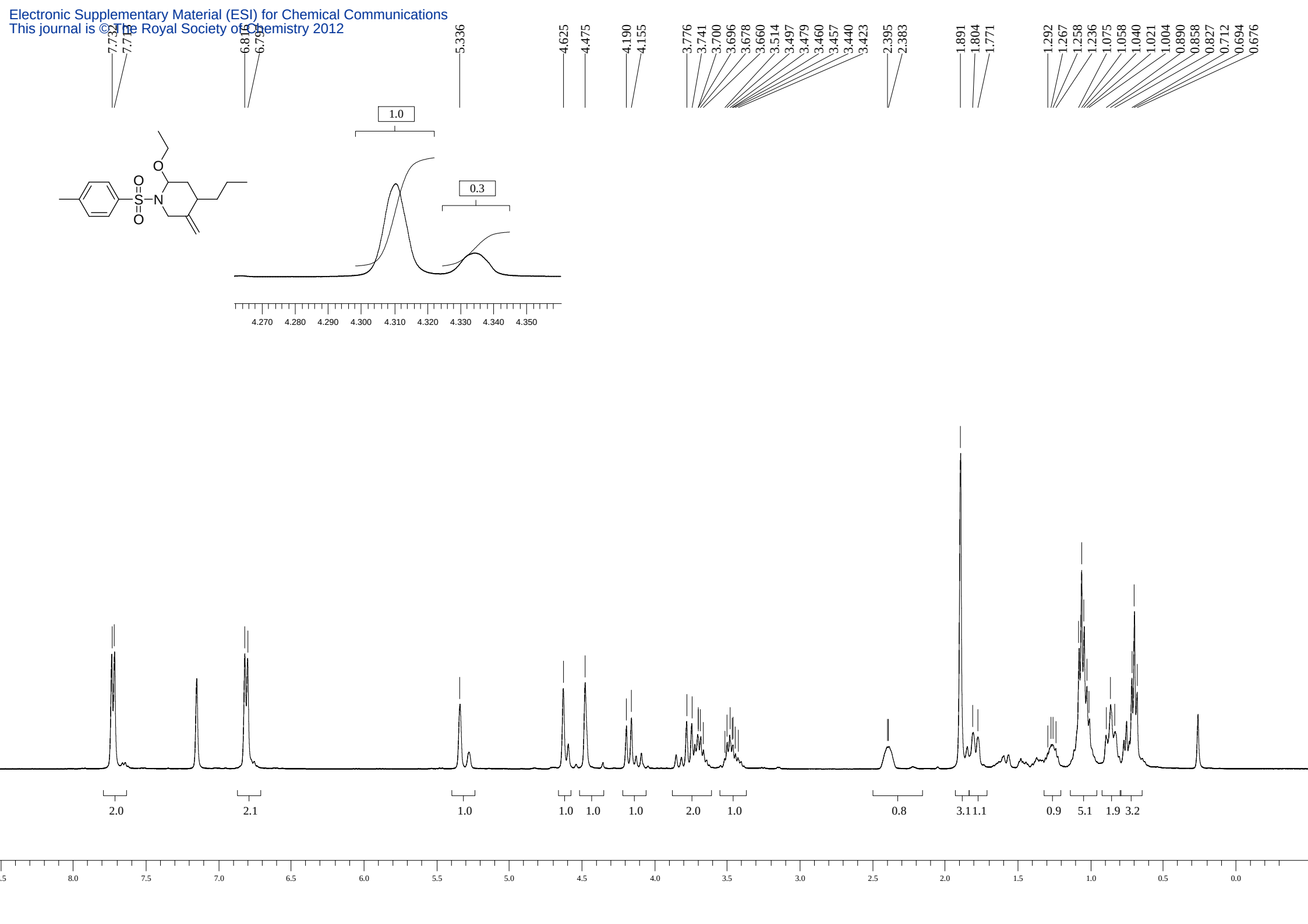
10

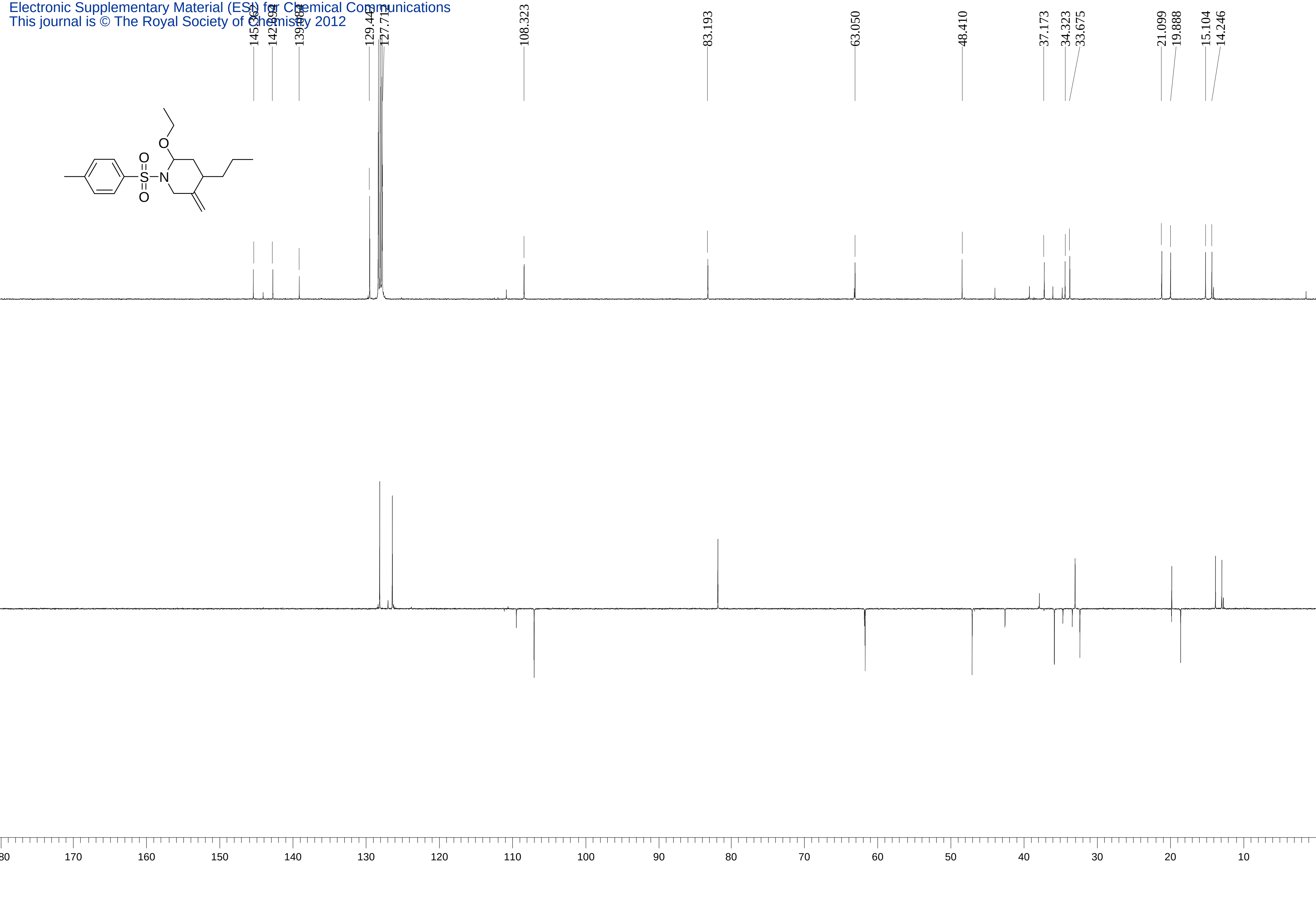


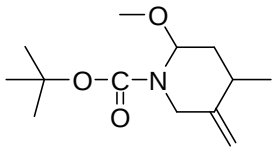












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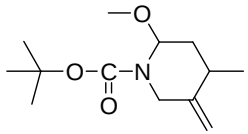

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45.315
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17.106

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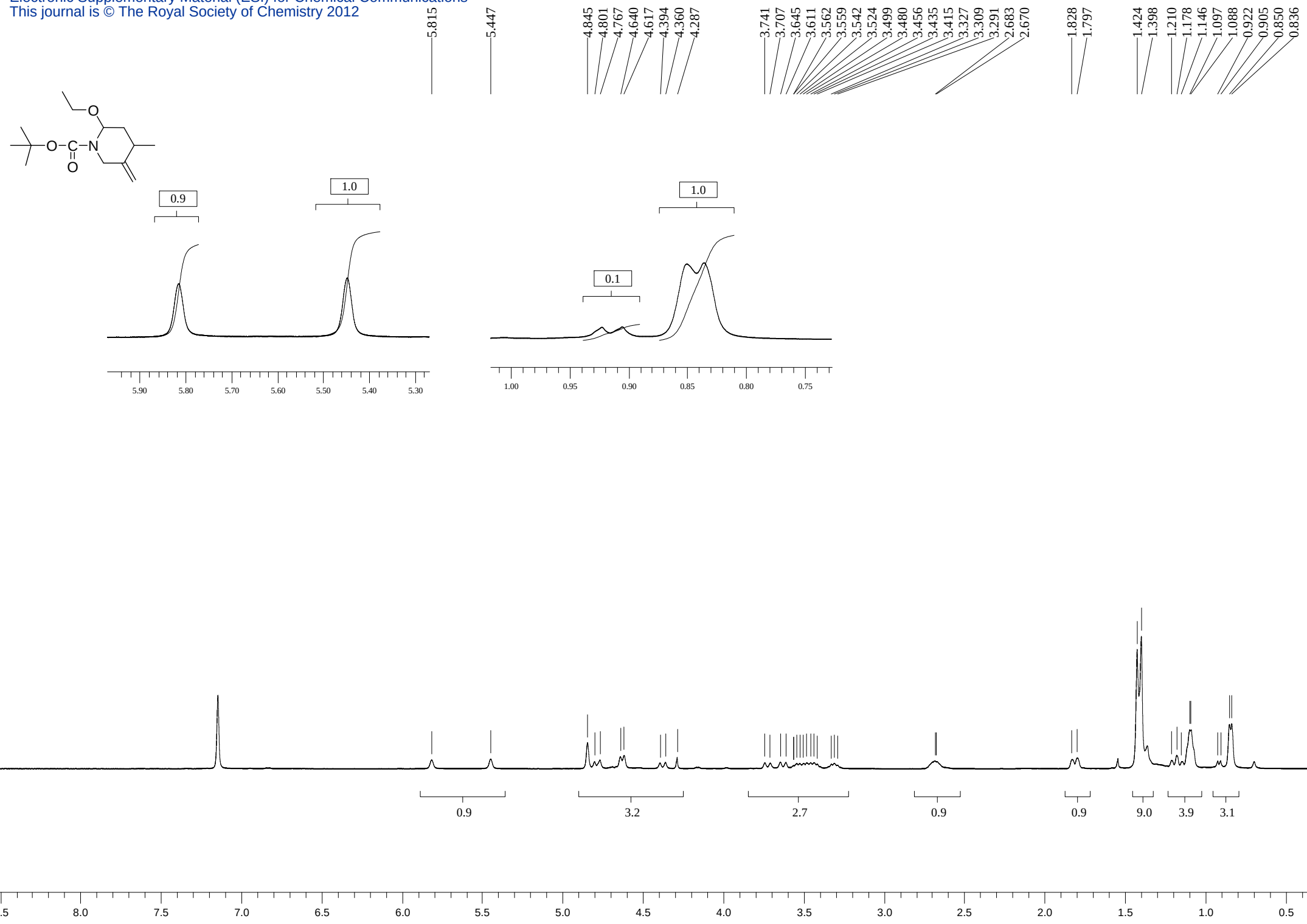

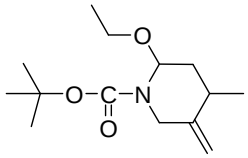

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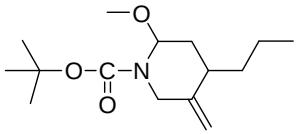

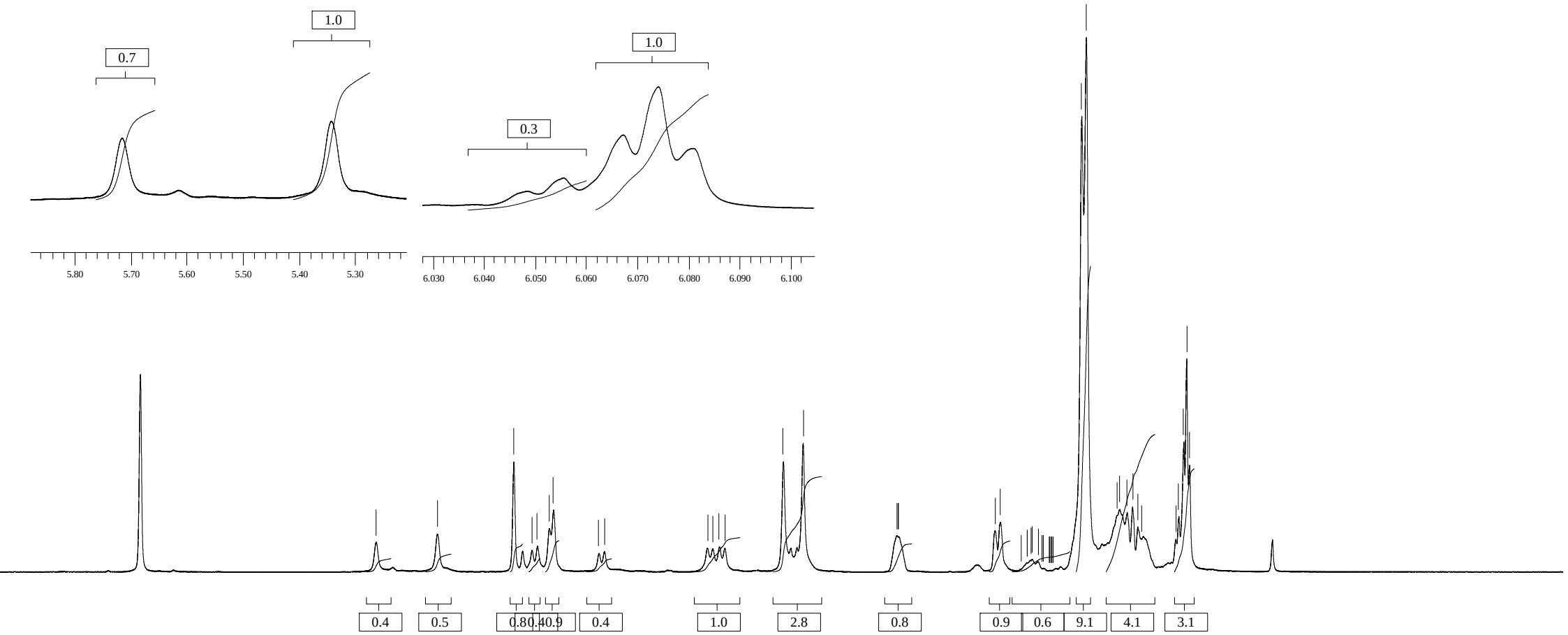

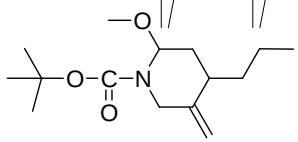

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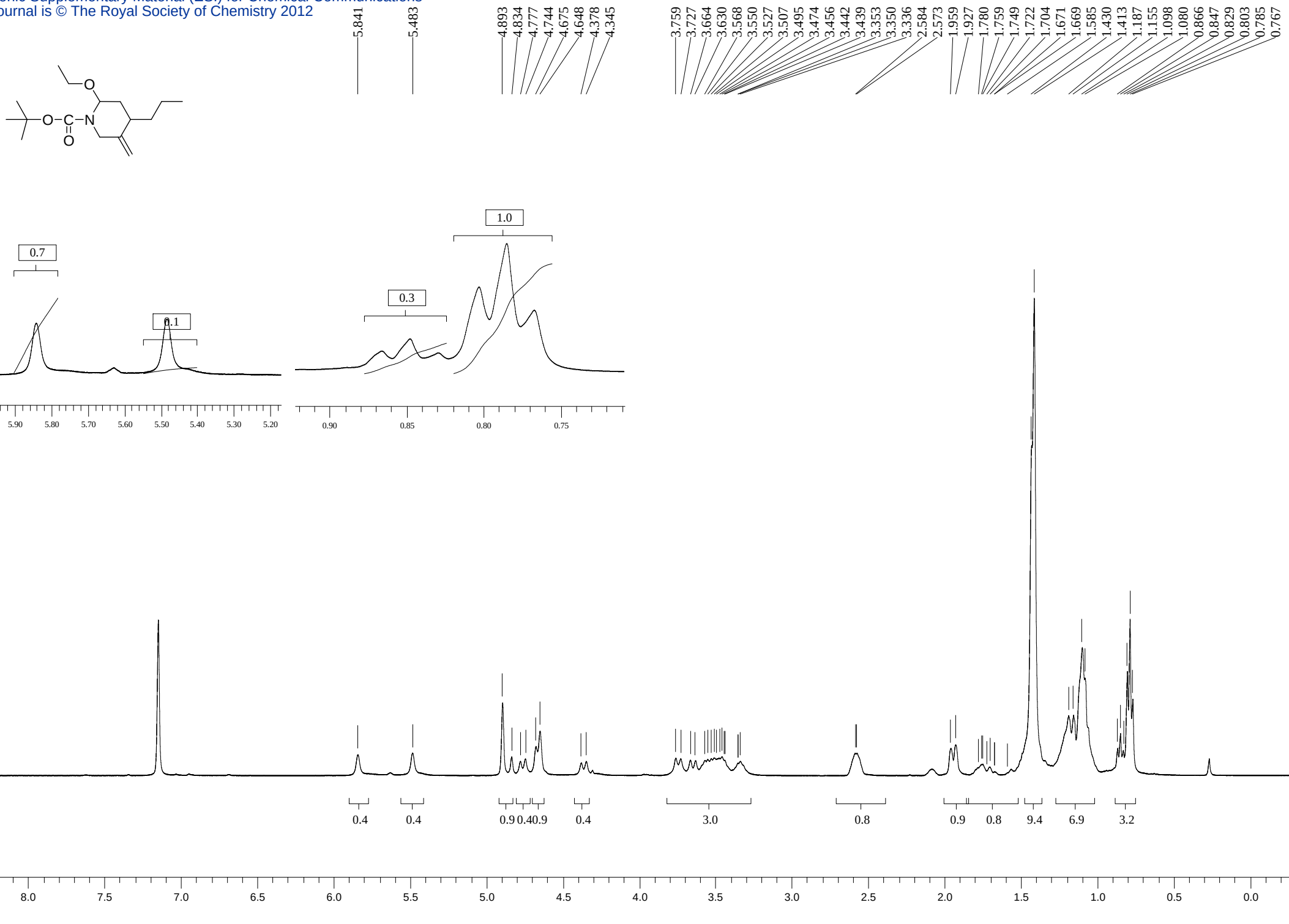

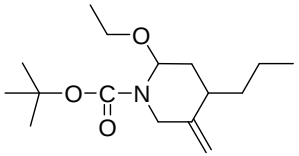

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20.185
20.138
15.401
15.344
14.396
14.248

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10