Electronic Supplementary Information for

Coupling reaction of thioamides with sulfonyl azides: an efficient catalyst-free click-type ligation under mild conditions

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Synthetic Procedures

General. ^{1}H and ^{13}C NMR spectra were obtained at 500 and 125 MHz, respectively, on a Varian Gemini 500 spectrometer. IR spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ESI-HRMS analyses were carried out on a JEOL JMS-T100LC mass spectrometer or Thermo LTQ Orbitrap XL ETD. Melting points were determined with Yanako MP-S3 and not corrected.

Materials. The following compounds, mesyl azide,[S1] benzenesulfonyl azide,[S2] *N*-methyl thioacetamide,[S3] *N*,*N*-dimethyl thioacetamide,[S4] *N*-methyl-*N*-phenyl thioacetamide,[S5] thioacetanilide,[S6] *N*-methyl thioacetanilide,[S5] *N*-phenyl thioacetanilide,[S7] *N*,*N*-diphenyl thioacetamide,[S7] *N*-phenyl thiobenzamide,[S6] thiopyrrolidone,[S8] thiopiperidone,[S8] and *ε*-thiocaprolactam[S6] were prepared according to literature procedures. Other materials were all commercially available.

Detailed synthetic procedures for new compounds 1c, 1i, 1m, 1o, 1p, and 3b.

***N*-Methyl-*N*′-methanesulfonylacetamidine (1c).** An EtOH (1 mL) solution of *N*-methyl thioacetamide (89 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at reflux for 10 h (or at room temperature for 15 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 5) to give **1c** (147 mg (98%) for reflux or 12 mg (8%) for rt) as a colorless solid. Mp 137–138ºC; IR (KBr) 3314, 1600, 1561, 1250, 1118, 1092, 793 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.46 (brs, 1 H), 2.87 (s, 3 H), 2.66 (d, J = 4.5 Hz, 3 H), 2.34 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 165.5, 42.8, 42.7, 27.9, 27.8, 19.7, 19.6 ppm; HRMS calcd for MH^+, $C_4H_{11}N_2O_2S$: 151.0541; found 151.0533.

***N*-Phenyl-*N*′-methanesulfonylacetamidine (1i).** An EtOH (1 mL) solution of thioacetanilide (152 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent at that temperature, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1i** (155 mg (73%) for rt or 206 mg (97%) for reflux) as a colorless solid. **1i** also formed by using of H_2O as a solvent at room temperature for 5 h in 94% isolated yiled. Mp 109–110ºC; IR (KBr) 3315, 1583, 1551, 1265, 1123, 798 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.15 (brs, 1 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.36 (t, J = 8.0 Hz, 2 H), 7.15 (t, J = 8.0 Hz, 1 H), 2.99 (s, 3 H), 2.47 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 163.1, 138.2, 128.8, 128.7, 124.8, 124.7, 121.5, 121.4, 42.9, 42.8, 20.8, 20.7 ppm; HRMS calcd for MH^+, $C_9H_{13}N_2O_2S$: 213.0698; found 213.0690.

***N*-Methyl-*N*-phenyl-*N'*-methanesulfonylacetamidine (1m).** A H_2O (0.5 mL) suspension of *N*-methyl-*N*-phenyl thioacetamide (82 mg, 0.5 mmol) and mesyl azide (303 mg, 2.5 mmol) was vigorously stirred at room temperature for 8 h. After removal of the solvent at ambient temperature in vacuo, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 20 : 1) to give **1m** (97 mg, 87%) as a colorless solid. Mp 106–107ºC; IR (KBr) 1548, 1267, 1119, 1084, 807 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.51 (t, J = 7.5 Hz, 2 H), 7.43 (t, J = 7.5 Hz, 1 H), 7.38 (d, J = 7.5 Hz, 2 H), 3.28 (s, 3 H), 2.99 (s, 3 H), 2.14 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 165.1, 143.1, 130.0, 128.3, 127.1, 43.2, 43.1, 18.8 ppm; HRMS calcd for MH^+, $C_{10}H_{15}N_2O_2S$: 227.0854; found 227.0852.

***N*,*N*-Diphenyl-*N'*-methanesulfonylacetamidine (1o).** A H_2O (0.5 mL) suspension of *N*,*N*-diphenyl thioacetamide (113 mg, 0.5 mmol) and mesyl azide (303 mg, 2.5 mmol) was vigorously stirred at room temperature for 15 h. After removal of the solvent at ambient temperature in vacuo, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 5 : 1) to give **1o** (119 mg, 83%) as a colorless solid. Mp 192–193ºC; IR (KBr) 1538, 1491, 1274, 1123, 819 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.33–7.43 (brm, 10 H), 2.80 (s, 3 H), 2.32 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 166.2, 129.6 (br), 128.0 (br), 42.8, 42.6, 19.4, 19.3 ppm; HRMS calcd for MH^+, $C_{15}H_{17}N_2O_2S$: 289.1011; found 289.1014.

***N*,*N*-Diphenyl-*N'*-benzenesulfonylacetamidine (1p).** A H_2O (0.5 mL) suspension of *N*,*N*-diphenyl thioacetamide (113 mg, 0.5 mmol) and benzenesulfonyl azide (458 mg, 2.5 mmol) was vigorously stirred at room temperature for 15 h. After removal of the solvent at ambient temperature in vacuo, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 5 : 1) to give **1p** (173 mg, 99%) as a colorless solid. Mp 184–185ºC; IR (KBr) 1535, 1272, 1144, 1089, 807 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.28–7.64 (brm, 15 H), 2.35 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 166.8, 143.4, 143.1 (br), 142.1 (br), 131.68, 131.65, 131.60, 131.57, 129.9 (br), 129.1 (br), 128.7, 128.6, 128.2 (br), 127.3 (br), 125.5, 125.4, 19.7, 19.6 ppm; HRMS calcd for MH^+, $C_{20}H_{19}N_2O_2S$: 351.1167; found 351.1165.

***N*-(2-Piperidone-2-yl)benzenesulfonamide (3b).** A H_2O (1 mL) suspension of 2-thiopiperidone (115 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was vigorously stirred at room temperature for 1 h. After removal of the solvent at ambient temperature in vacuo, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 5) to give **3b** (236 mg, 99%) as a colorless solid. Mp 141–142ºC; IR (KBr) 3226, 3140, 3066, 2969, 1614, 1405, 1276, 1148, 847, 754 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.91 (brs, 1 H), 7.79 (dd, J = 6.8, 1.8 Hz, 2 H), 7.51–7.57 (m, 3 H), 3.22 (brd, J = 2.5 Hz, 2 H), 2.55 (brd, J = 6.5 Hz, 2 H), 1.62–1.64 ppm (m, 4 H); ^{13}C NMR (DMSO-d_6) δ 166.9, 143.8, 131.5, 128.7, 125.9, 125.8, 41.6, 28.6, 20.6, 18.7 ppm; HRMS calcd for MH^+, $C_{11}H_{15}N_2O_2S$: 239.0854; found 239.0851.

Synthetic procedures for known compounds with simple assignment.

***N*-Methanesulfonylacetamidine (1a).**[S9] [Method A] A H_2O, EtOH, MeOH, DMF, THF, MeCN, acetone, EtOAc, or $CHCl_3$ (1 mL) solution of thioacetamide (75 mg, 1 mmol) and mesyl azide (121 mg, 1 mmol) was stirred at room temperature for 15 h. After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1a** (86 mg (63%) for H_2O, 51 mg (37%) for EtOH, 40 mg (29%) for MeOH, 17 mg (12%) for DMF, 25 mg (18%) for THF, 22 mg (16%) for MeCN, 23 mg (17%) for acetone, 23 mg (17%) for EtOAc, or 19 mg (14%) for $CHCl_3$) as a colorless solid. [Method B]

An EtOH (1 mL) solution of thioacetamide (75 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent at that temperature, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1a** (90 mg (66%) for rt or 133 mg (98%) for reflux) as a colorless solid. **1a** also formed by using of H_2O as a solvent at room temperature for 15 h in 97% isolated yiled.^{1}H NMR (DMSO-d_6) δ 8.26 (brs, 1 H), 7.75 (brs, 1 H), 2.84 (s, 3 H), 2.06 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 167.0, 41.9, 41.8, 21.5 ppm; ESI-MS calcd for MH^+, $C_3H_9N_2O_2S$: 137.039; found 137.038.

***N*-Benzenesulfonylacetamidine (1b).**[S10] An EtOH (1 mL) solution of thioacetamide (75 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent at that temperature, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1b** (137 mg (69%) for rt or 194 mg (98%) for reflux) as a colorless solid. **1b** also formed by using of H_2O as a solvent at room temperature for 13 h in 98% isolated yiled.^{1}H NMR (DMSO-d_6) δ 8.46 (brs, 1 H), 8.05 (brs, 1 H), 7.80 (dd, J = 8.0, 2.0 Hz, 2 H), 7.59 (tt, J = 8.0, 2.0 Hz, 1 H), 7.53 (t, J = 8.0 Hz, 2 H), 2.05 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 167.8, 143.2, 131.8, 131.7, 128.9, 128.8, 126.0, 125.9, 21.5 ppm; ESI-MS calcd for MNa^+, $C_8H_{10}N_2O_2SNa$: 211.036; found 211.002.

***N*-Methyl-*N*′-benzenesulfonylacetamidine (1d).**[S11] An EtOH (1 mL) solution of *N*-methyl thioacetamide (89 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 3 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, hexane : EtOAc = 1 : 2) to give **1d** (32 mg (15%) for rt or 198 mg (94%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 8.73 (brs, 1 H), 7.80 (dd, J = 8.5, 1.5 Hz, 2 H), 7.52–7.58 (m, 5 H), 2.69 (d, J = 4.0 Hz, 3 H), 2.20 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 166.2, 144.0, 131.5, 128.84, 128.75, 125.83, 125.79, 28.1, 28.0, 19.9, 19.8 ppm; ESI-MS calcd for MNa^+, $C_9H_{12}N_2O_2SNa$: 235.052; found 235.057.

***N*,*N*-Dimethyl-*N*′-methanesulfonylacetamidine (1e).**[S12] An EtOH (1 mL) solution of *N*,*N*-dimethyl thioacetamide (103 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1e** (103 mg (62%) for rt or 156 mg (95%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 3.07 (s, 3 H), 2.97 (s, 3 H), 2.87 (s, 3 H), 2.39 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 165.5, 43.14, 43.05, 38.44, 38.39, 38.0, 37.9, 17.6, 17.5 ppm; ESI-MS calcd for MNa^+, $C_5H_{12}N_2O_2SNa$: 187.052; found 187.110.

***N*,*N*-Dimethyl-*N*′-benzenesulfonylacetamidine (1f).**[S12] An EtOH (1 mL) solution of *N*,*N*-dimethyl thioacetamide (103 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 5 : 1) to give **1f** (135 mg (77%) for rt or 221 mg (97%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 7.79 (dd, J = 7.8, 1.5 Hz, 2 H), 7.51–7.56 (m, 5 H), 3.09 (s, 3 H), 2.99 (s, 3 H), 2.36 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 166.0, 144.3, 131.4, 128.7, 125.70, 125.66, 38.74, 38.69, 38.4, 38.3, 17.7, 17.6 ppm; ESI-MS calcd for MH^+, $C_{10}H_{15}N_2O_2S$: 227.0854; found 227.0850.

***N*-Methanesulfonylbenzamidine (1g).**[S13] An EtOH (1 mL) solution of thiobenzamide (137 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 12 h).

After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1g** (8 mg (4%) for rt or 96 mg (96%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 8.93 (brs, 1 H), 8.02 (brs, 1 H), 7.89 (dd, J = 8.0, 1.0 Hz, 2 H), 7.60 (tt, J = 8.0, 1.0 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 2 H), 3.01 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 162.2, 133.5, 132.3, 132.2, 128.5, 128.4, 127.82, 127.79, 41.5, 41.4 ppm; ESI-MS calcd for MNa^+, $C_8H_{10}N_2O_2SNa$: 221.036; found 221.010.

***N*-Benzenesulfonylbenzamidine (1h).**[S13] An EtOH (1 mL) solution of thiobenzamide (137 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 12 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, hexane : EtOAc = 1 : 1) to give **1h** (11 mg (4%) for rt or 249 mg (96%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 9.10 (brs, 1 H), 8.27 (brs, 1 H), 7.94 (dd, J = 7.8, 1.3 Hz, 2 H), 7.85 (dd, J = 7.8, 1.3 Hz, 2 H), 7.55–7.64 (m, 4 H), 7.47 ppm (t, J = 7.8 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 162.7, 142.4, 133.2, 132.5, 132.2, 129.0, 128.9, 128.5, 128.4, 128.0, 127.9, 126.1 ppm; ESI-MS calcd for MNa^+, $C_{13}H_{12}N_2O_2SNa$: 283.052; found 282.964.

***N*-Phenyl-*N*′-benzenesulfonylacetamidine (1j).**[S14] An EtOH (1 mL) solution of thioacetanilide (152 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 5 : 1) to give **1j** (234 mg (85%) for rt or 274 mg (99%) for reflux) as a colorless solid. **1j** also formed by using of H_2O as a solvent at room temperature for 4 h in 97% isolated yiled.^{1}H NMR (DMSO-d_6) δ 10.39 (brs, 1 H), 7.83 (dd, J = 7.5, 1.5 Hz, 2 H), 7.55–7.61 (m, 5 H), 7.33 (t, J = 7.8 Hz, 2 H), 7.15 (t, J = 7.5 Hz, 1 H), 2.47 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 163.7, 143.3, 137.8, 131.9, 129.0, 128.8, 125.8, 125.1, 121.8, 121.7, 20.9, 20.8 ppm; ESI-MS calcd for MH^+, $C_{14}H_{15}N_2O_2S$: 275.0854; found 275.0853.

***N*-Phenyl-*N*′-methanesulfonylbenzamidine (1k).**[S13] An EtOH (1 mL) solution of *N*-phenyl thiobenzamide (213 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 12 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, hexane : EtOAc = 2 : 1) to give **1k** (14 mg (5%) for rt or 261 mg (95%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 10.33 (brs, 1 H), 7.73 (brd, J = 7.5 Hz, 2 H), 7.61 (dd, J = 7.5, 1.5 Hz, 2 H), 7.55 (tt, J = 7.8, 1.5 Hz, 1 H), 7.50 (t, J = 7.5 Hz, 2 H), 7.38 (t, J = 7.8 Hz, 2 H), 7.18 (t, J = 7.5 Hz, 1 H), 2.94 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 162.4, 138.4, 134.5, 130.6, 128.7, 128.6, 128.2, 127.9, 125.1, 125.0, 122.0, 43.3, 43.2 ppm; ESI-MS calcd for MH^+, $C_{14}H_{15}N_2O_2S$: 275.085; found 275.098.

***N*-Phenyl-*N*′-benzenesulfonylbenzamidine (1l).**[S15] An EtOH (1 mL) solution of *N*-phenyl thiobenzamide (213 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 12 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, hexane : EtOAc = 2 : 1) to give **1l** (48 mg (14%) for rt or 325 mg (97%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 10.56 (brs, 1 H), 7.65 (dd, J = 7.8, 1.5 Hz, 2 H), 7.45–7.60 (m, 10 H), 7.31 (t, J = 8.3 Hz, 2 H), 7.16 ppm (t, J = 7.3 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 162.9, 143.4, 138.1, 134.1, 131.6, 130.7, 128.8, 128.7, 128.6, 128.2, 127.9, 125.8, 125.3, 122.2 ppm; ESI-MS calcd for MNa^+, $C_{19}H_{16}N_2O_2SNa$: 359.083; found 359.076.

***N*-Methyl-*N*-phenyl-*N*′-benzenesulfonylacetamidine (1n).**[S16] A H_2O (0.5 mL) suspension of *N*-methyl-*N*-phenyl thioacetamide (82 mg, 0.5 mmol) and benzenesulfonyl azide (458 mg, 2.5 mmol) was

vigorously stirred at room temperature for 6 h. After removal of the solvent at ambient temperature in vacuo, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **1n** (143 mg, 99%) as a colorless oil. ^{1}H NMR (DMSO-d_6) δ 7.89 (d, J = 7.5 Hz, 2 H), 7.56–7.62 (m, 3 H), 7.50 (t, J = 7.5 Hz, 2 H), 7.39–7.44 (m, 3 H), 3.28 (s, 3 H), 2.16 ppm (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 165.6, 143.8, 142.8, 131.7, 129.9, 128.9, 128.8, 128.5, 127.0, 1268, 125.8, 40.0, 19.10, 19.05 ppm; ESI-MS calcd for MH^+, $C_{15}H_{17}N_2O_2S$: 289.1011; found 289.1008.

***N*-(2-Pyrrolidone-2-yl)methanesulfonamide (2a).**[S17] An EtOH (1 mL) solution of thiopyrrolidone (101 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 14 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 5) to give **2a** (12 mg (8%) for rt or 158 mg (97%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 8.73 (brs, 1 H), 3.38 (t, J = 7.0 Hz, 2 H), 2.84 (s, 3 H), 2.71 (t, J = 8.0 Hz, 2 H), 1.98 ppm (tt, J = 8.0, 7.0 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 171.5, 44.9, 41.8, 41.7, 31.3, 20.5 ppm; ESI-MS calcd for MH^+, $C_5H_{11}N_2O_2S$: 163.054; found 163.053.

***N*-(2-Pyrrolidone-2-yl)benzenesulfonamide (2b).**[S18] An EtOH (1 mL) solution of thiopyrrolidone (101 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 14 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **2b** (11 mg (5%) for rt or 213 mg (95%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 9.00 (brs, 1 H), 7.57 (dd, J = 7.5, 1.5 Hz, 2 H), 7.57 (tt, J = 7.5, 1.5 Hz, 1 H), 7.53 (t, J = 7.5 Hz, 2 H), 3.38 (t, J = 7.0 Hz, 2 H), 2.70 (t, J = 8.0 Hz, 2 H), 1.96 ppm (tt, J = 8.0, 7.5 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 172.2, 143.4, 131.6, 128.9, 128.8, 125.93, 125.87, 44.9, 31.4, 20.4 ppm; ESI-MS calcd for MH^+, $C_{10}H_{13}N_2O_2S$: 225.070; found 225.069.

***N*-(2-Piperidone-2-yl)methanesulfonamide (3a).**[S19] An EtOH (1 mL) solution of thiopiperidone (115 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 20 min). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 5) to give **3a** (162 mg (92%) for rt or 172 mg (97%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 8.54 (brs, 1 H), 3.23 (brd, J = 2.5 Hz, 2 H), 2.83 (s, 3 H), 2.56 (brs, 2 H), 1.65–1.67 ppm (m, 4 H); ^{13}C NMR (DMSO-d_6) δ 166.0, 42.14, 42.06, 41.5, 28.8, 20.8, 18.8 ppm; ESI-MS calcd for MH^+, $C_6H_{13}N_2O_2S$: 177.070; found 177.069.

***N*-(1-Aza-2-cycloheptanone-2-yl)methanesulfonamide (4a).**[S19] An EtOH (1 mL) solution of ε-thiocaprolactam (129 mg, 1 mmol) and mesyl azide (606 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent, the residue was chromatographed (SiO_2; eluent, CH_2Cl_2 : EtOAc = 1 : 1) to give **4a** (95 mg (50%) for rt or 171 mg (90%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 8.41 (brs, 1 H), 3.30–3.34 (m, 2 H), 2.85 (s, 3 H), 2.55–2.57 (m, 2 H), 1.65–1.70 (m, 2 H), 1.57–1.59 (m, 2 H), 1.50–1.52 ppm (m, 2 H); ^{13}C NMR (DMSO-d_6) δ 172.2, 43.8, 42.4, 42.3, 35.0, 29.9, 28.9, 24.0 ppm; ESI-MS calcd for MNa^+, $C_7H_{14}N_2O_2SNa$: 213.067; found 213.078.

***N*-(1-Aza-2-cycloheptanone-2-yl)benzenesulfonamide (4b).**[S20] An EtOH (1 mL) solution of ε-thiocaprolactam (129 mg, 1 mmol) and benzenesulfonyl azide (916 mg, 5 mmol) was stirred at room temperature for 15 h (or at reflux for 1 h). After removal of the solvent, the residue was chromatographed

(SiO_2; eluent, hexane : EtOAc = 1 : 1) to give **4b** (132 mg (52%) for rt or 230 mg (91%) for reflux) as a colorless solid. ^{1}H NMR (DMSO-d_6) δ 8.77 (brs, 1 H), 7.84 (dd, J = 7.0, 2.0 Hz, 2 H), 7.59 (tt, J = 7.0, 2.0 Hz, 1 H), 7.54 (t, J = 7.0 Hz, 2 H), 3.34 (dd, J = 10.5, 5.5 Hz, 2 H), 2.59 (dd, J = 11.0, 5.5 Hz, 2 H), 1.60–1.64 (m, 2 H), 1.42–1.45 ppm (m, 2 H); ^{13}C NMR (DMSO-d_6) δ 173.0, 143.9, 132.5, 129.52, 129.45, 126.6, 43.8, 34.5, 29.8, 28.7, 23.7 ppm; ESI-MS calcd for MNa^+, $C_{10}H_{13}N_2O_2SNa$: 275.083; found 274.999.

References for ESI

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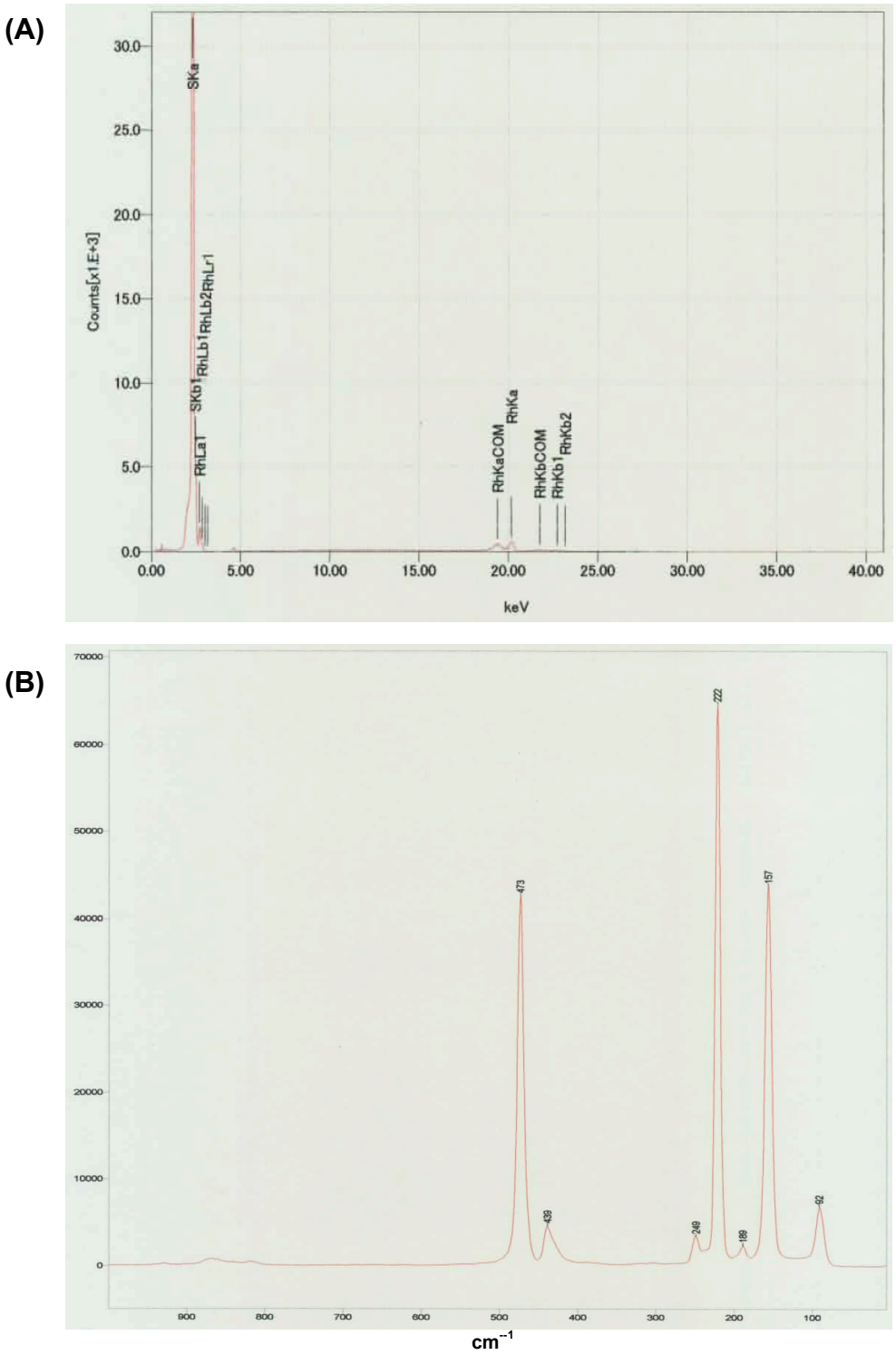


Figure S1. (A) Energy dispersive X-ray fluorescence (JEOL JSX3201A) and (B) Raman (RENISHAW JRS-SYSTEM1000) spectra for yellow precipitation formed in the coupling reaction mixture.

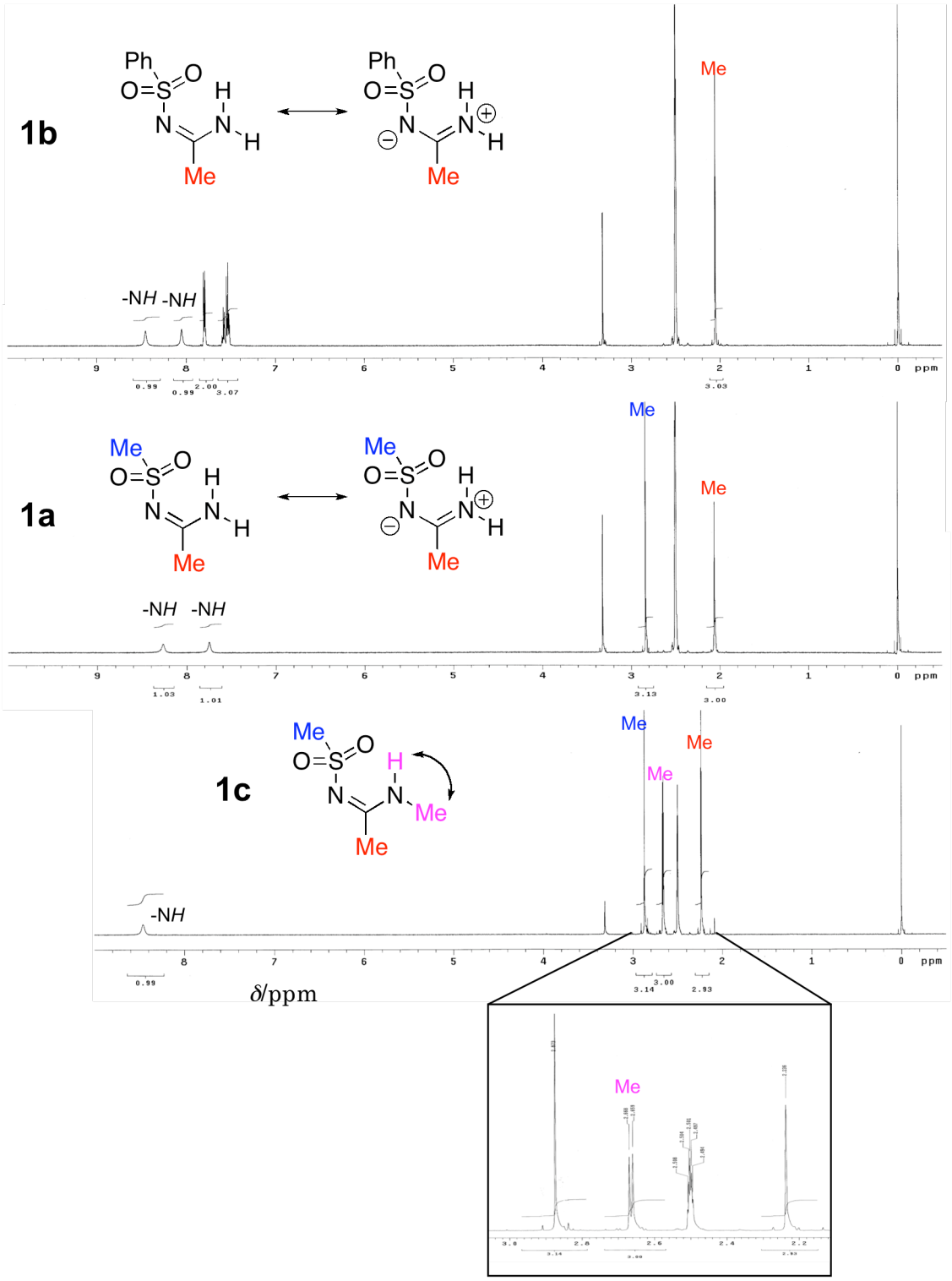


Figure S2. Assignment of Me groups of R^1, R^2, and R^3 for **1a–c** in ^{1}H NMR spectra (500 MHz, 25ºC, DMSO-d_6). Due to the 'C=N double-bond character' of the resonance structures in the amine-type tautomers, **1a** and **1b** have the two distinct -N*H* protons. The -N*Me* protons of **1c** are observed as doublet indicating coupling to the N-H proton in the amine-type form. For amidine **1c**, predominant "amine-type tautomer" was also assigned by ^{1}H-^{1}H COSY (see Figure S3).

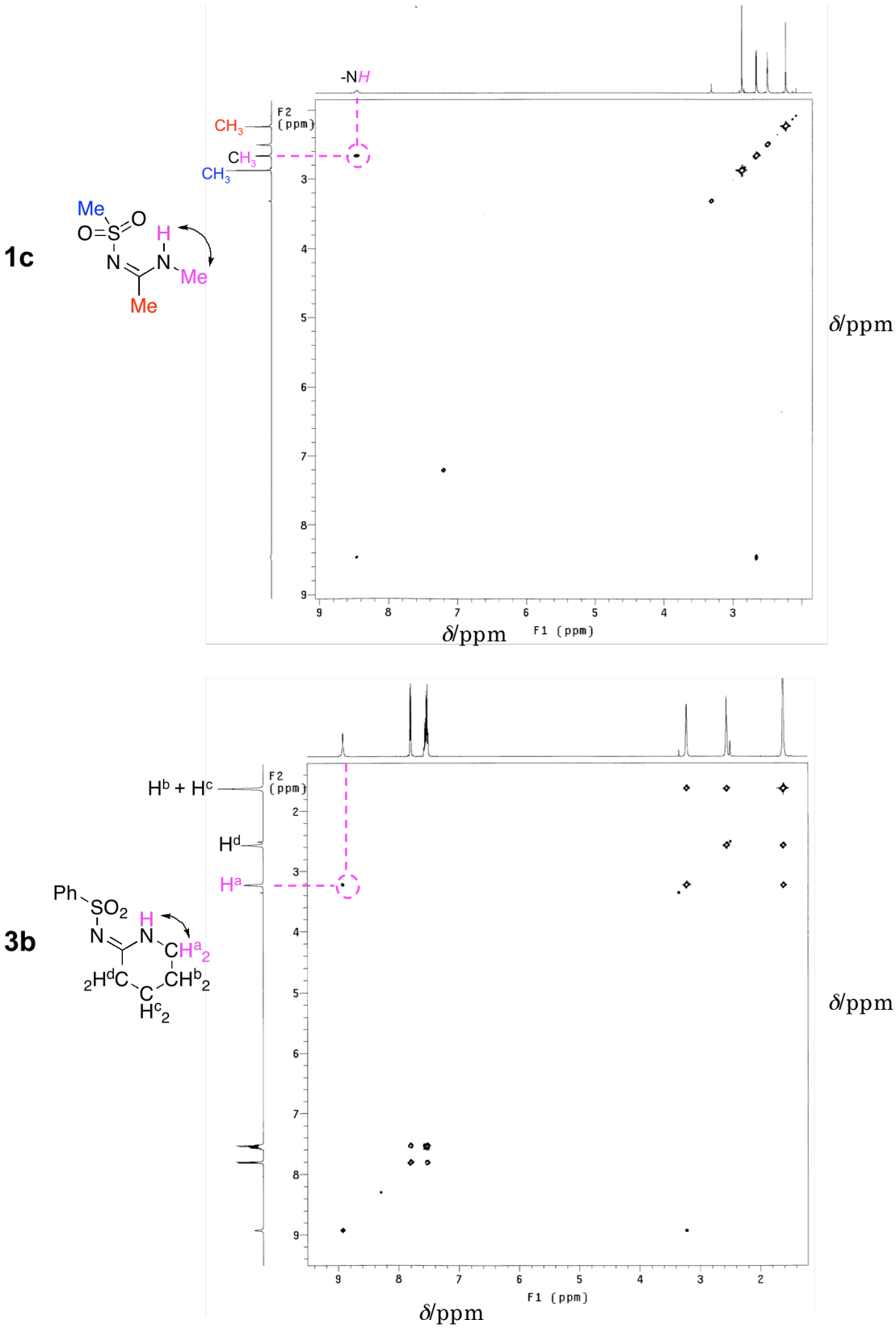
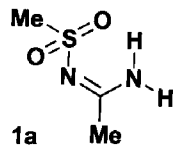


Figure S3. ^{1}H-^{1}H COSY spectra for **1c** and **3b** (500 MHz, DMSO-d_6).



1a

STANDARD CARBON PARAMETERS

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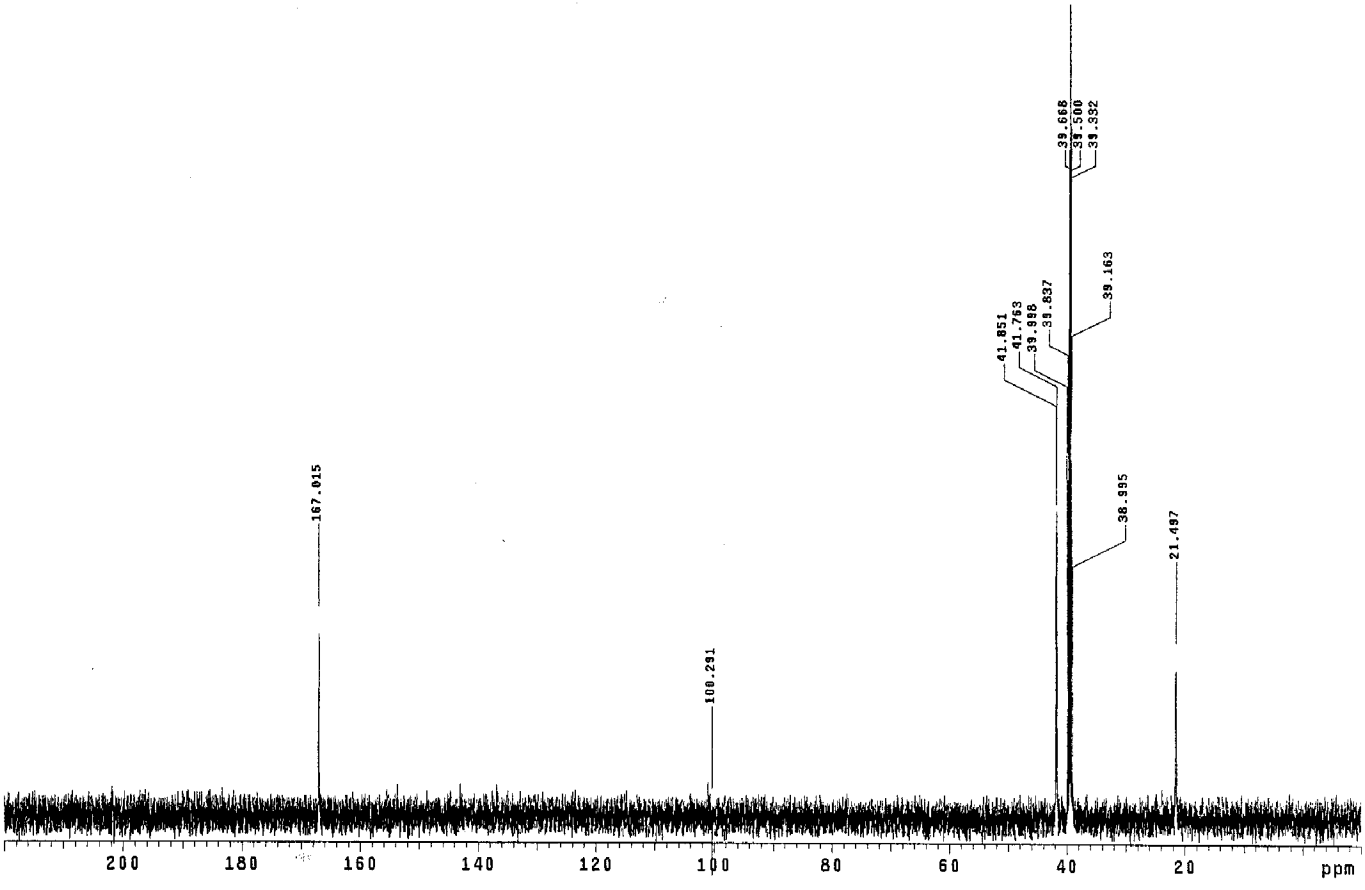

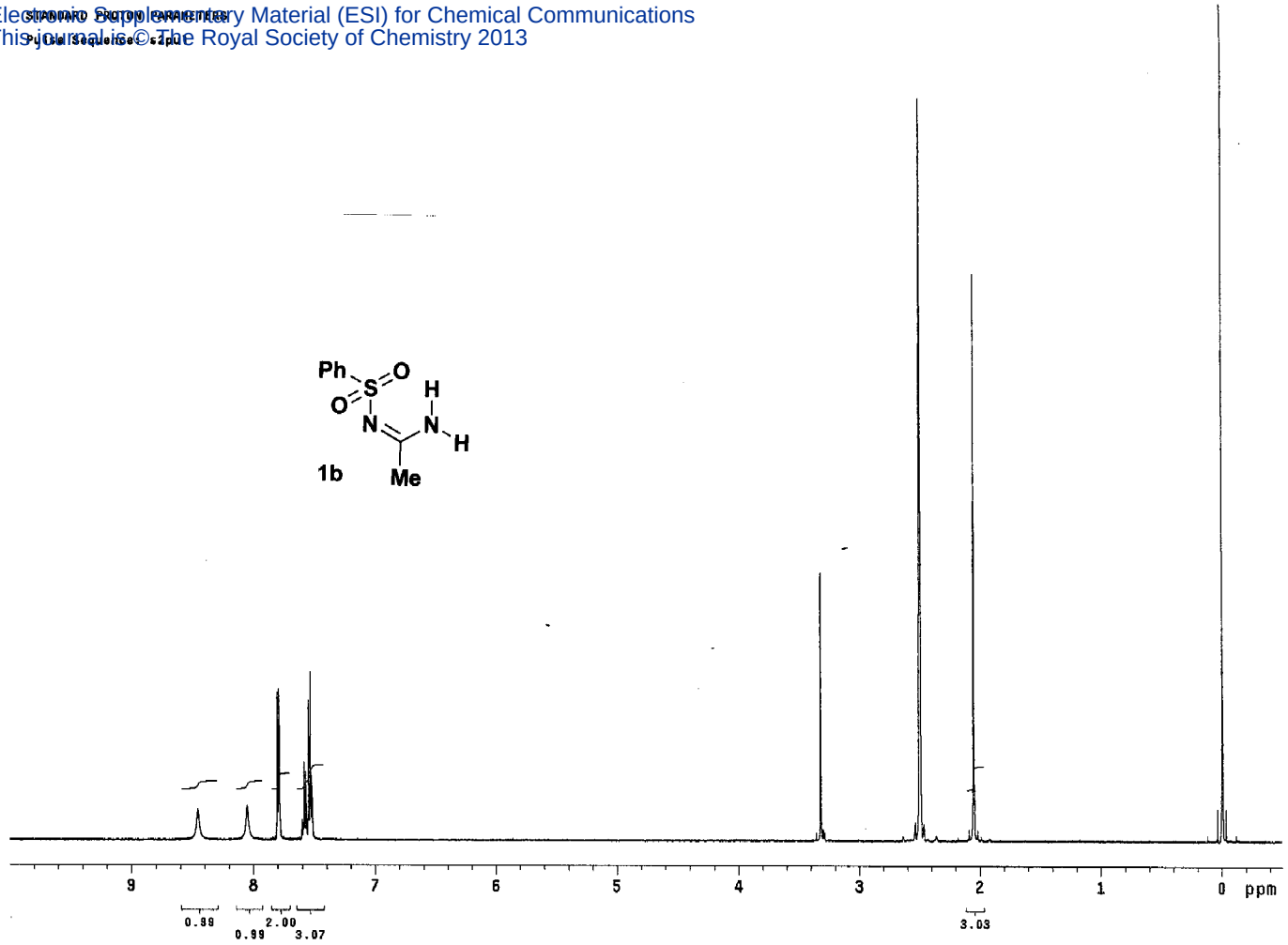

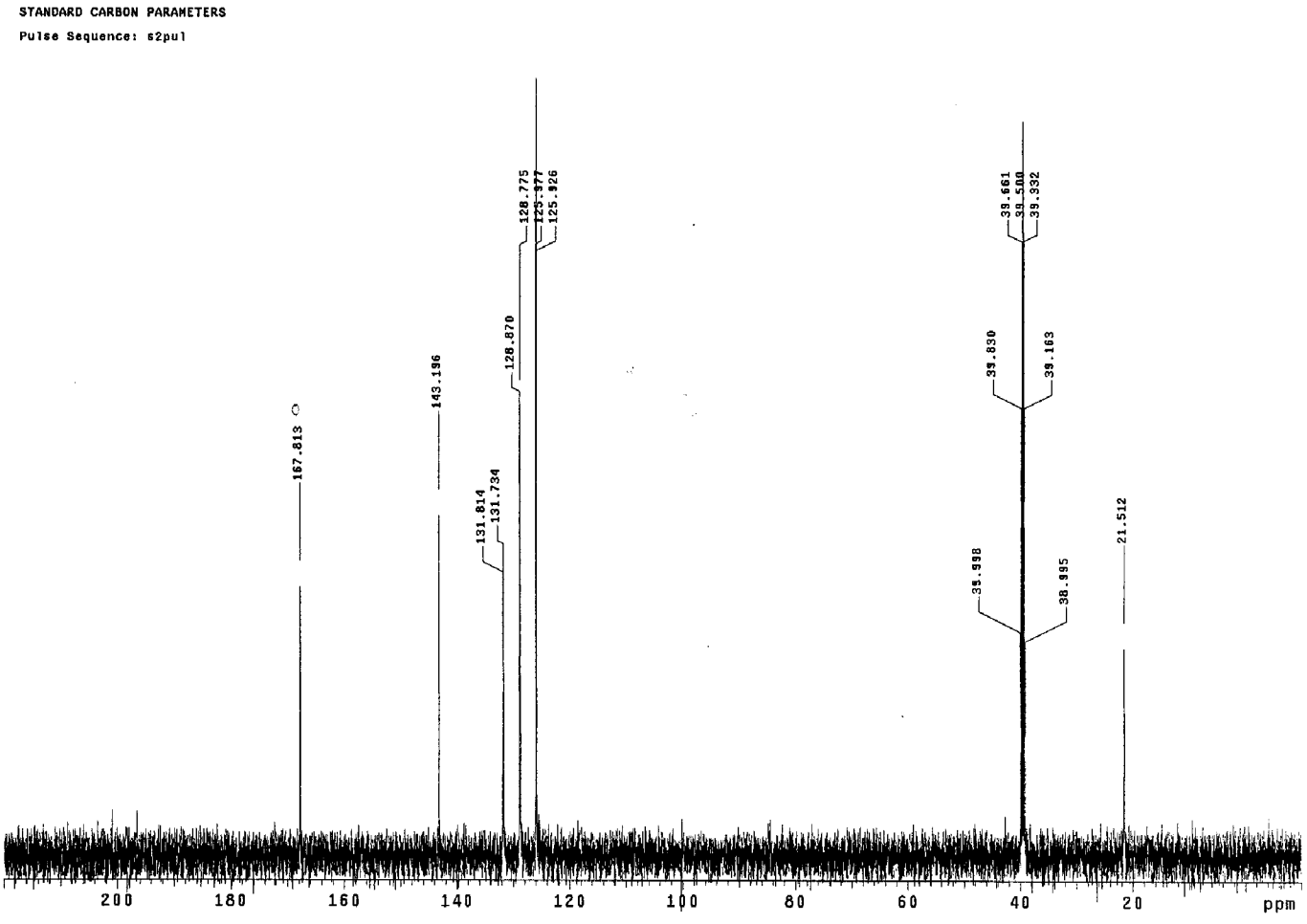

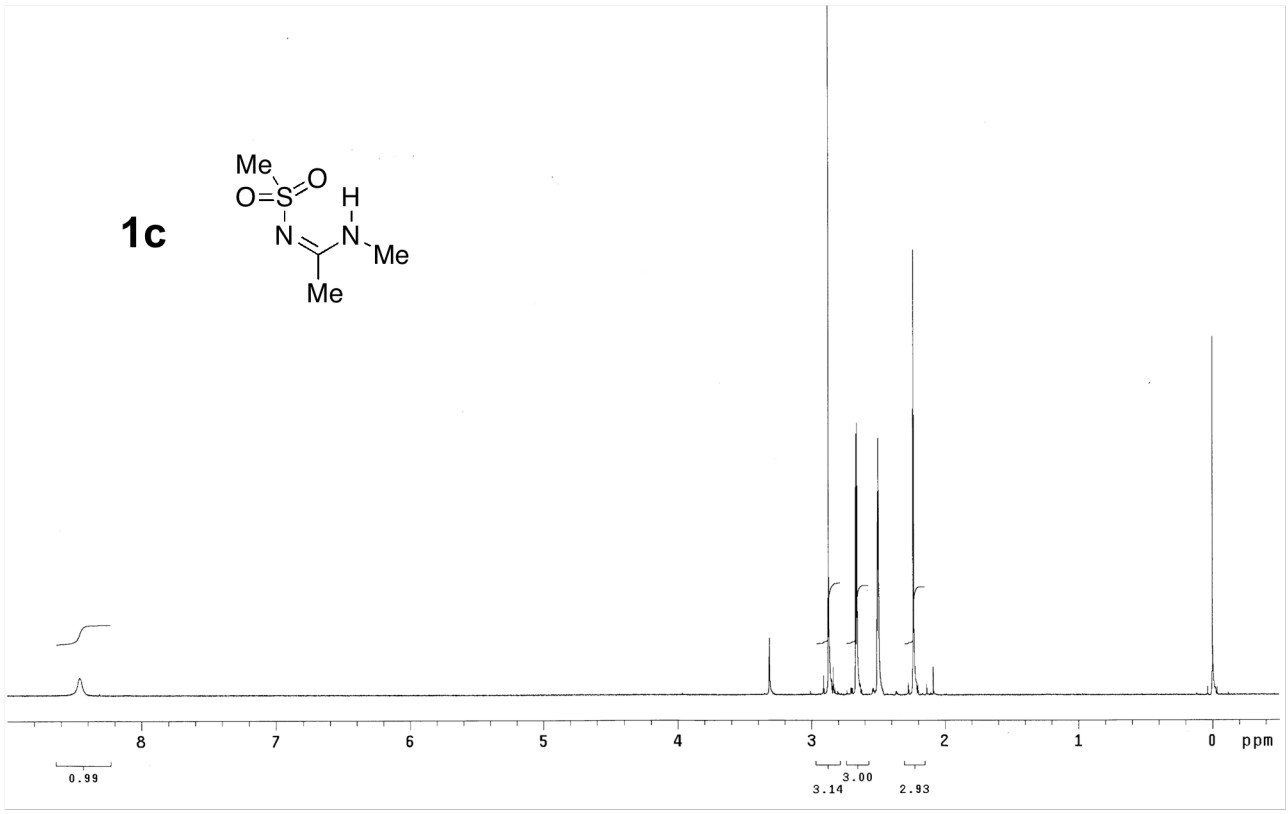

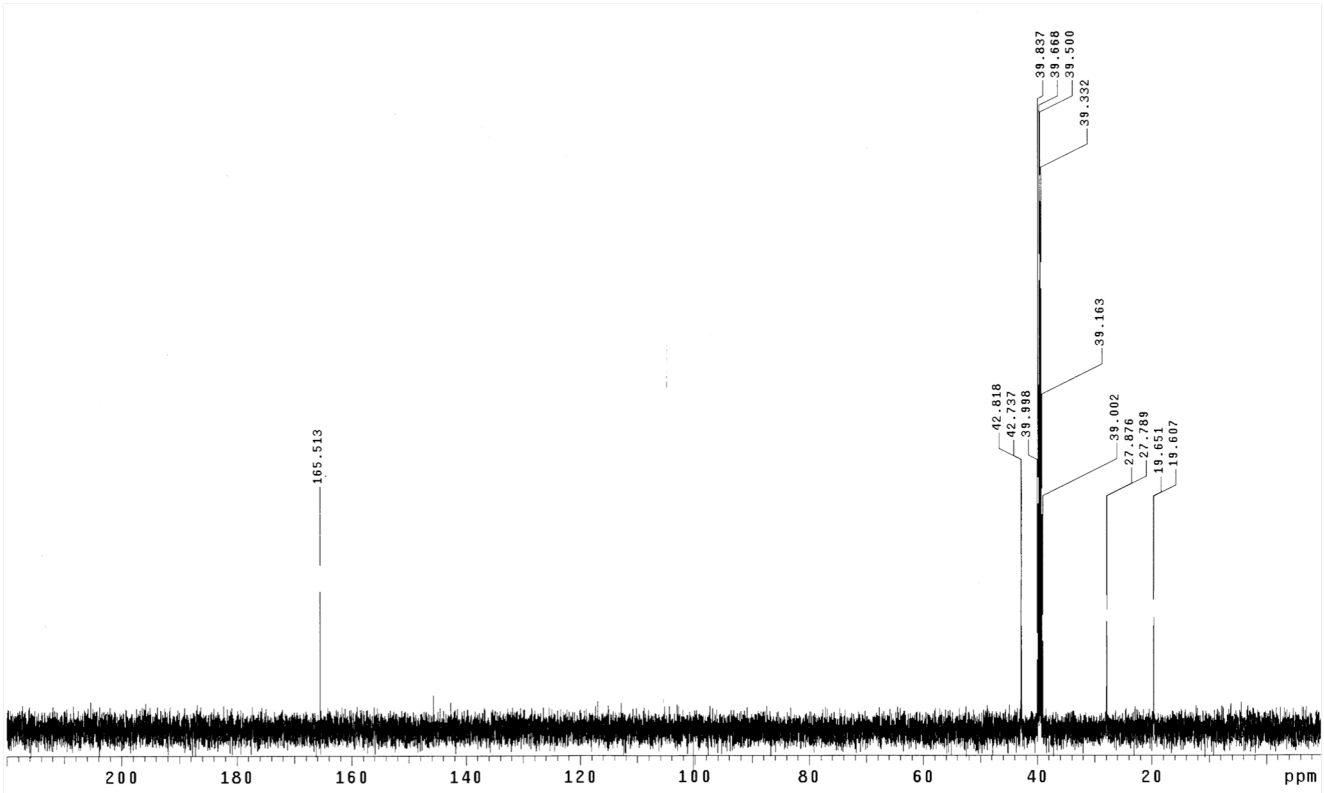

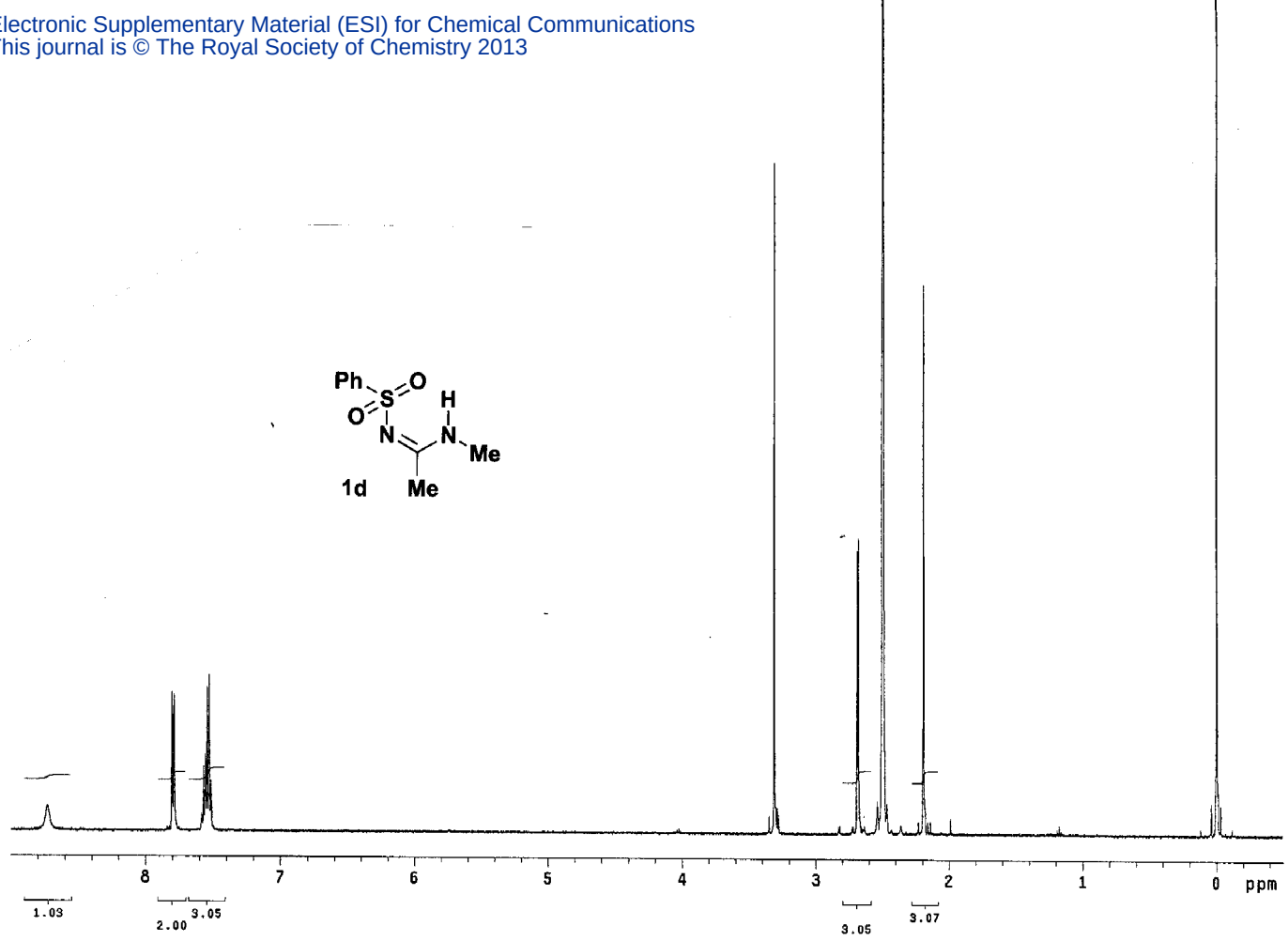
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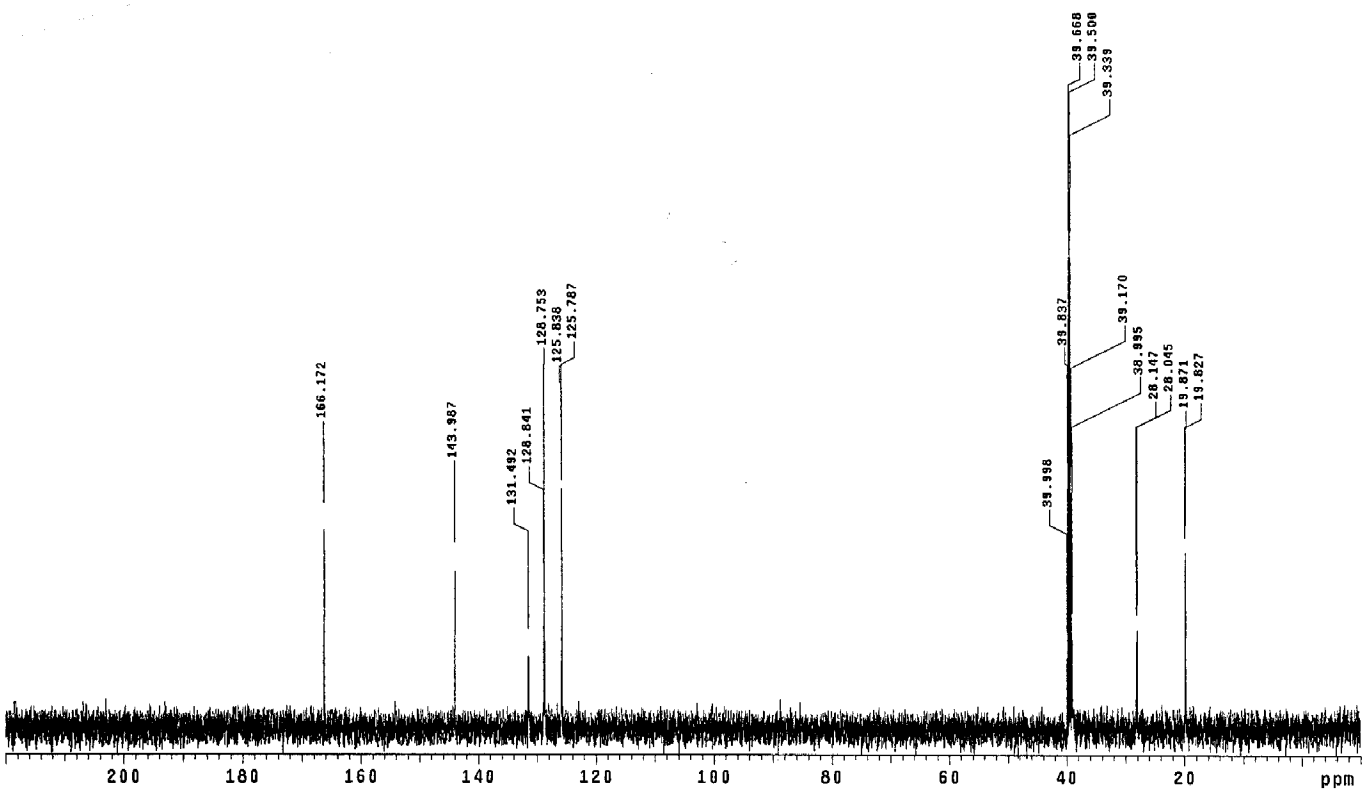
3.05
3.05
3.07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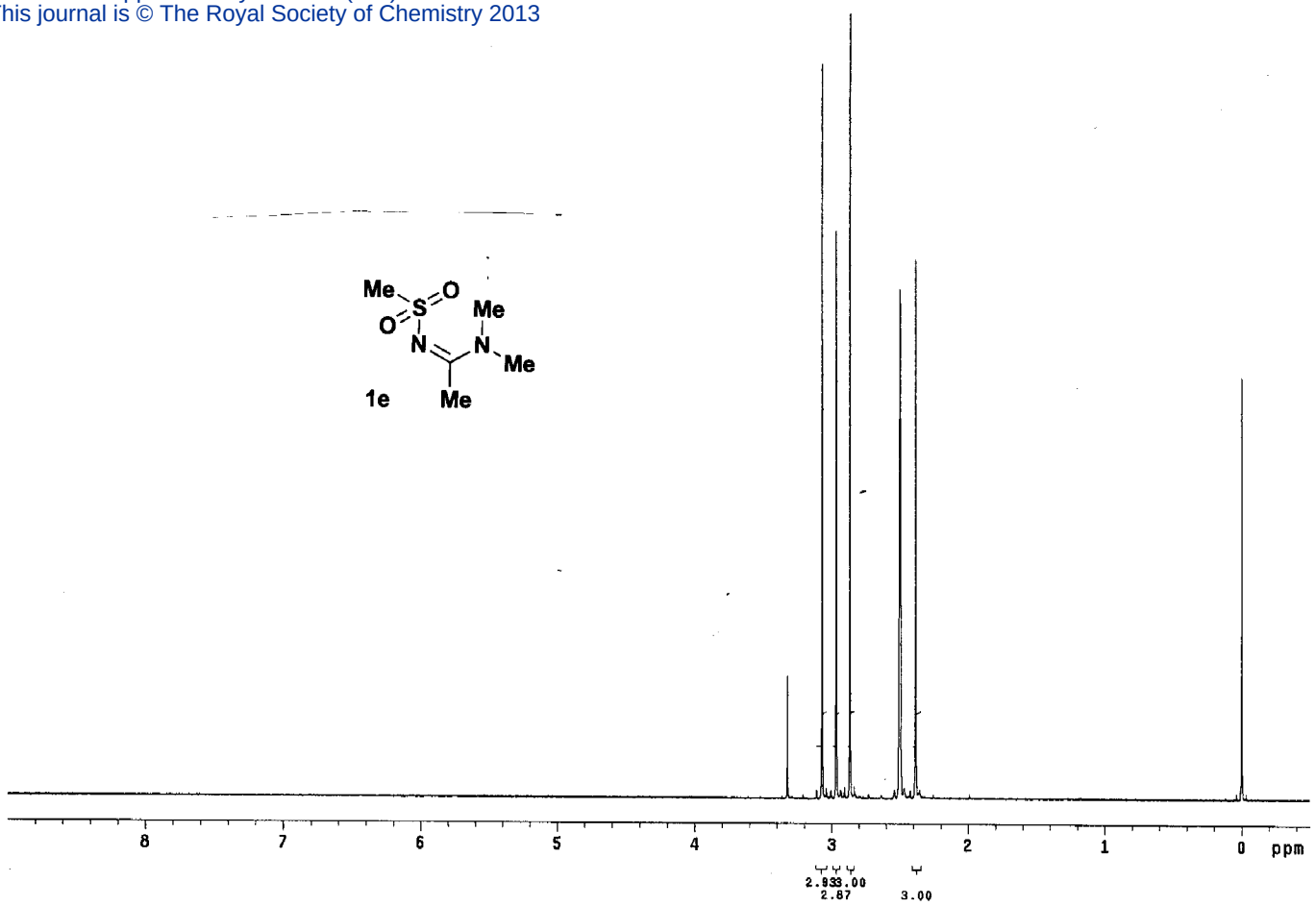

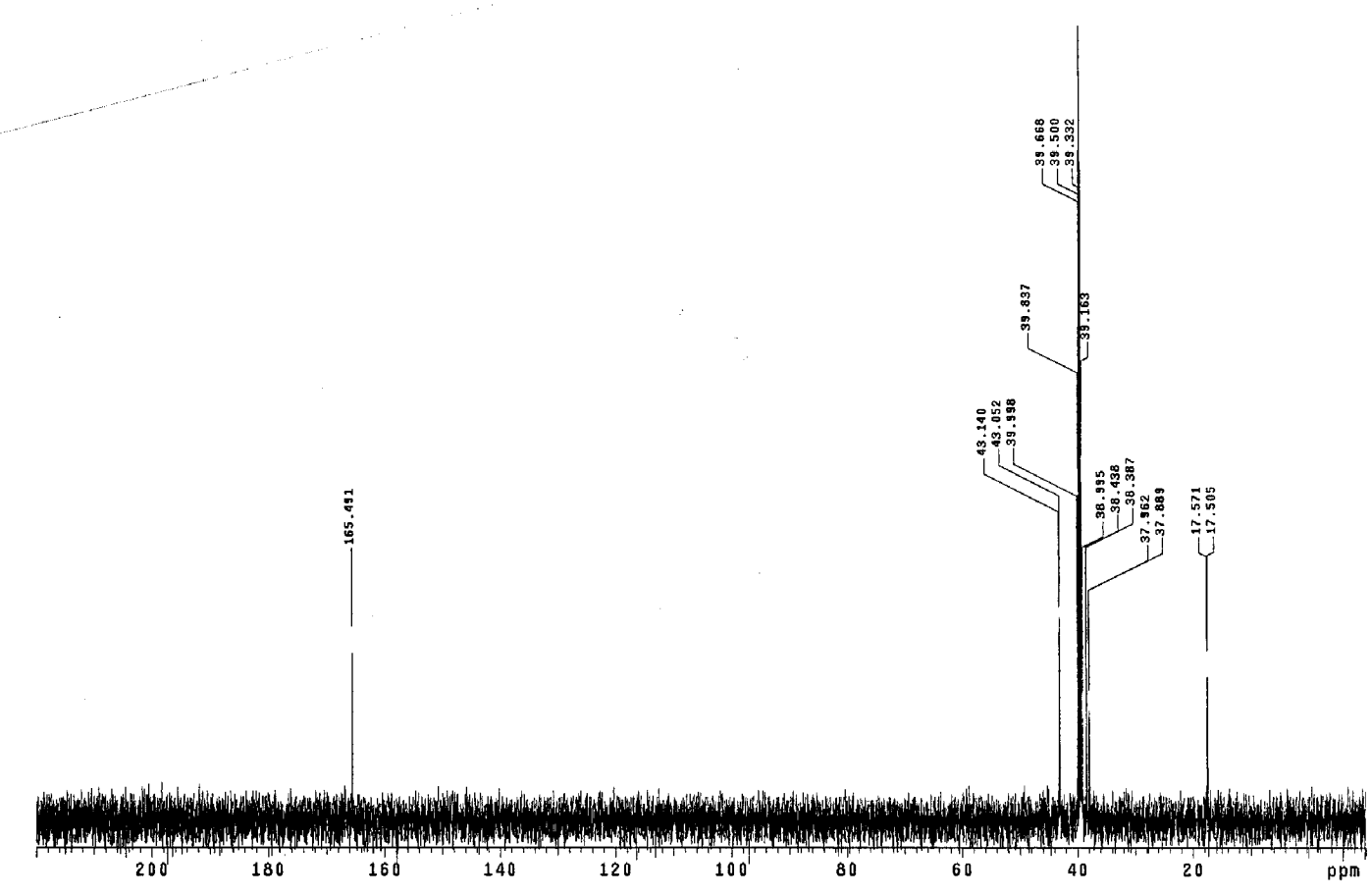

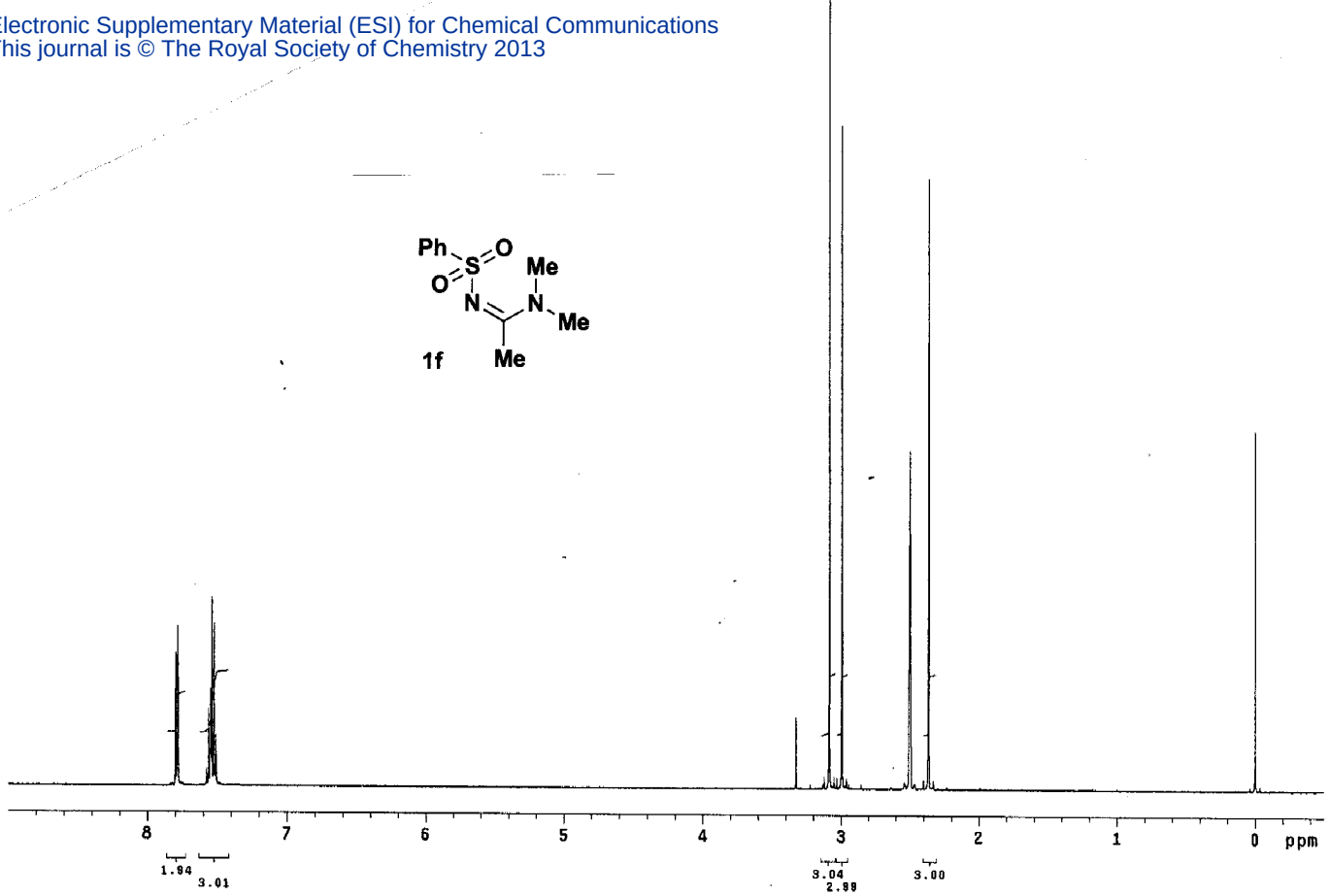

STANDARD CARBON PARAMETERS
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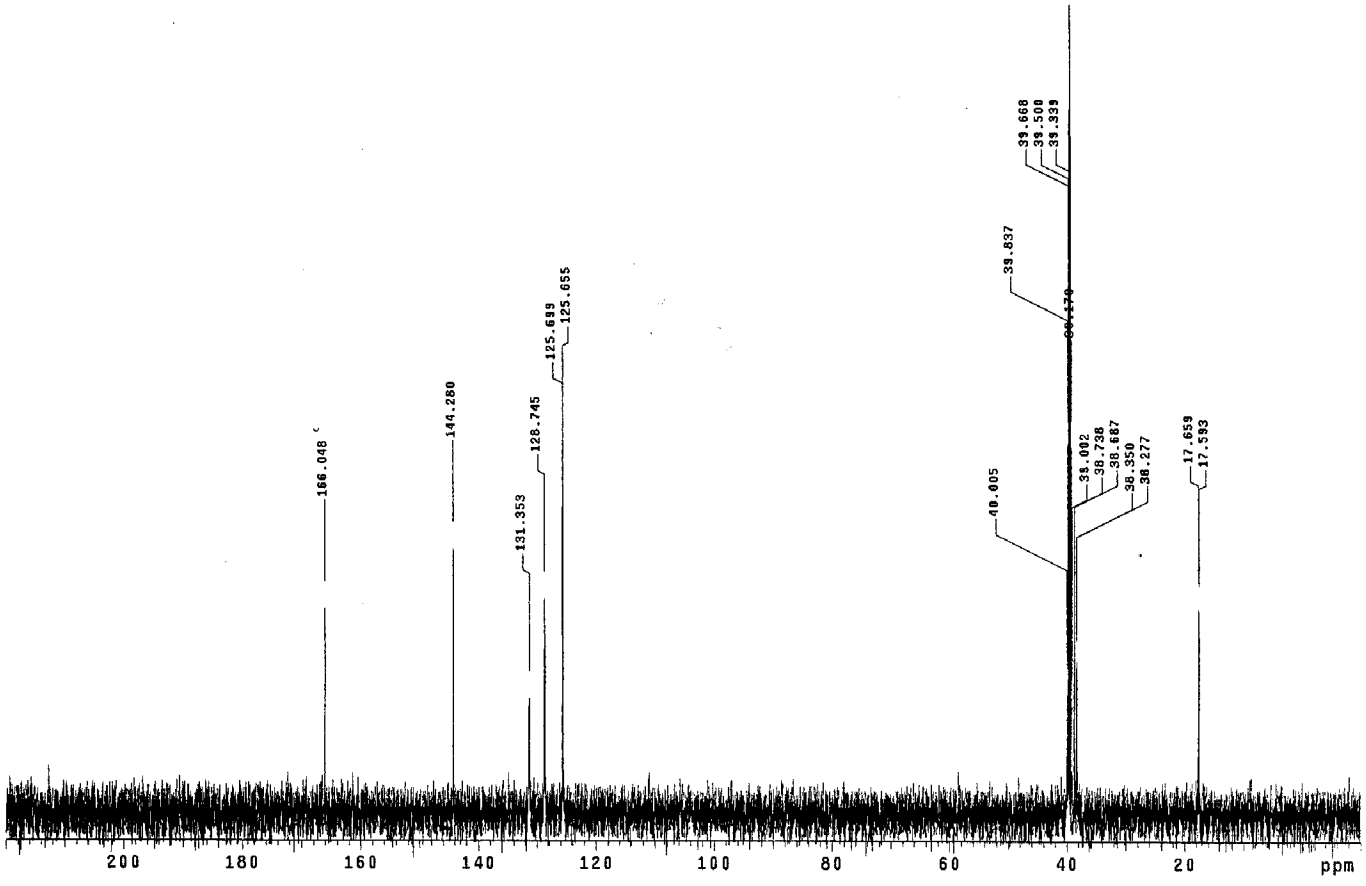

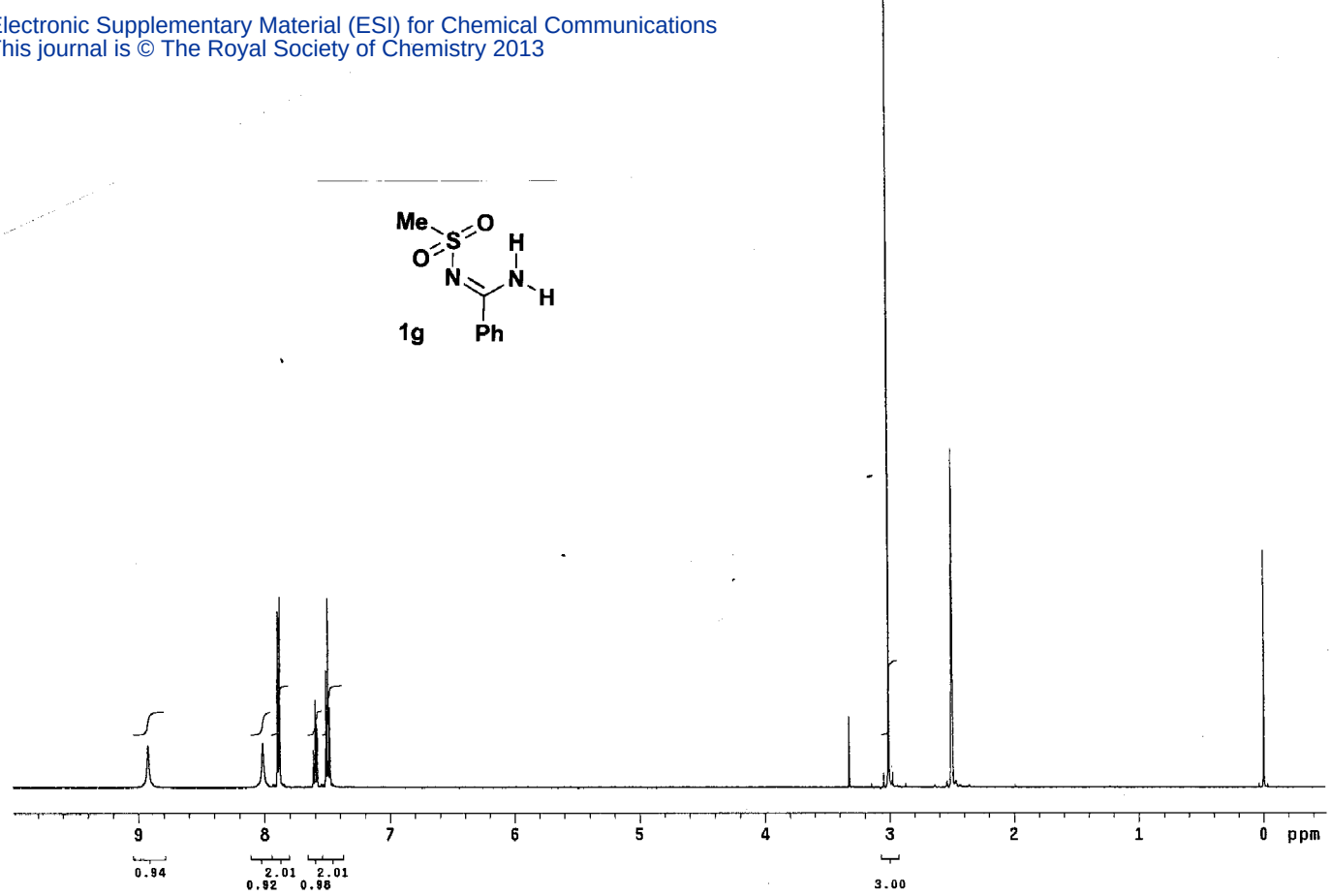

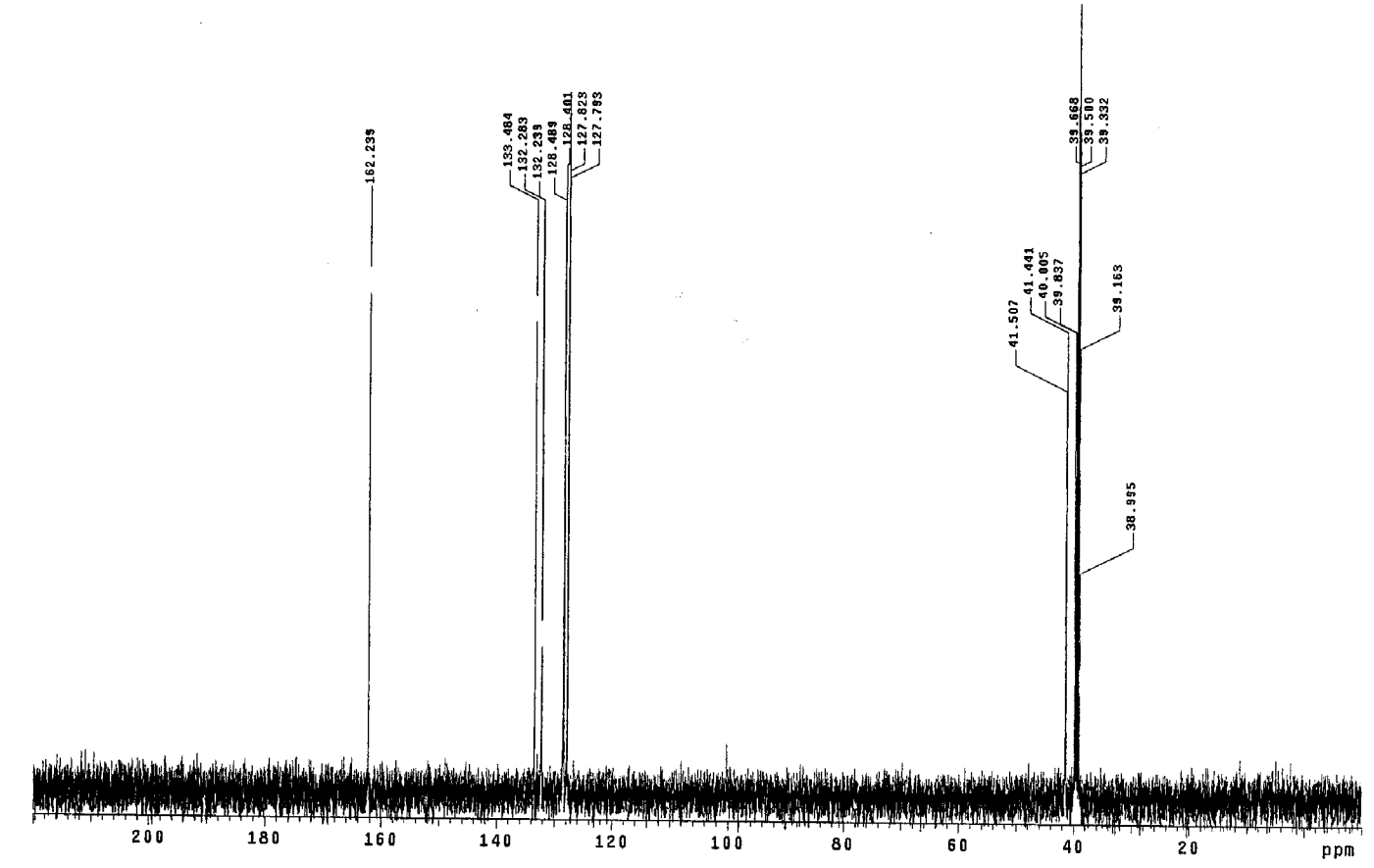

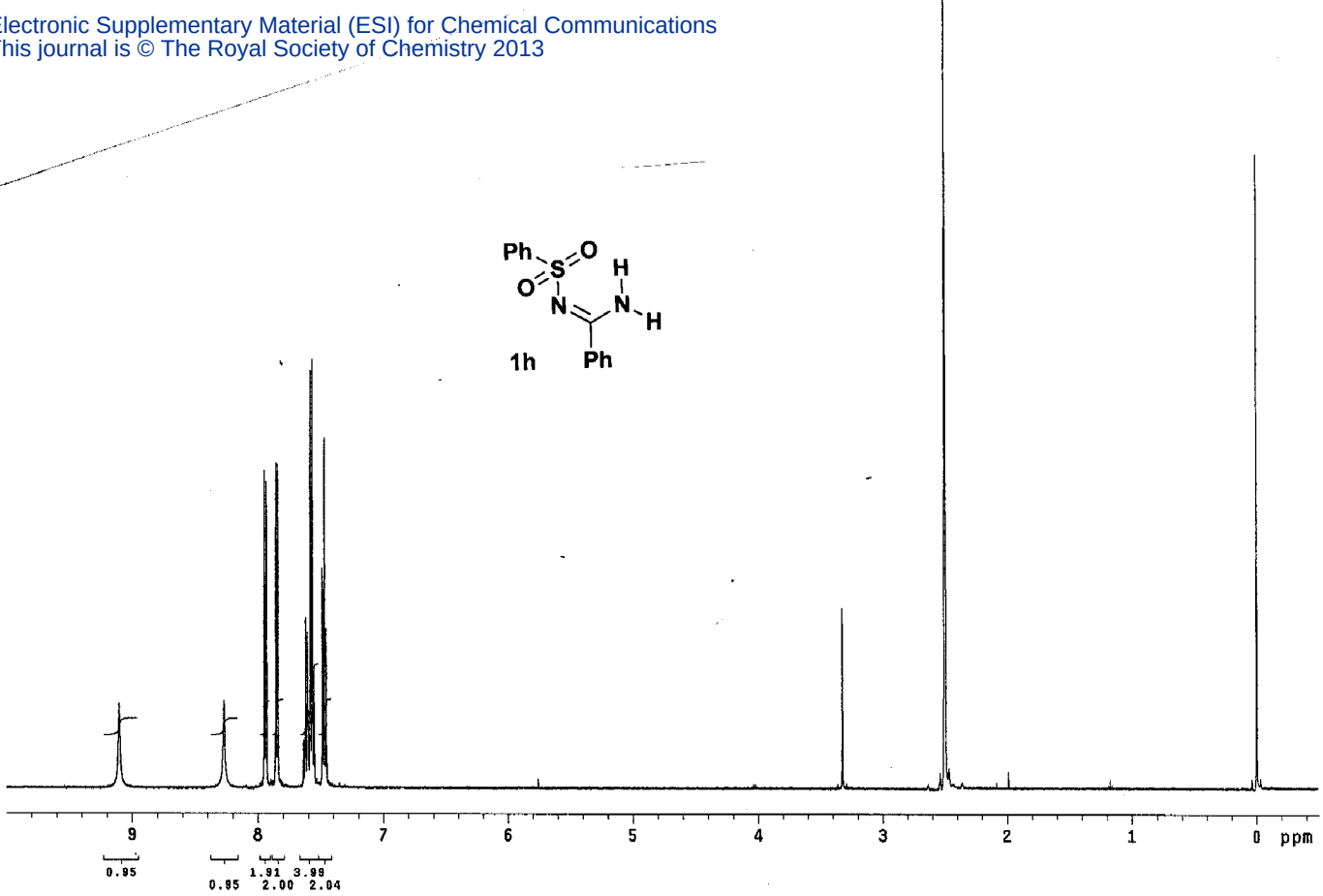

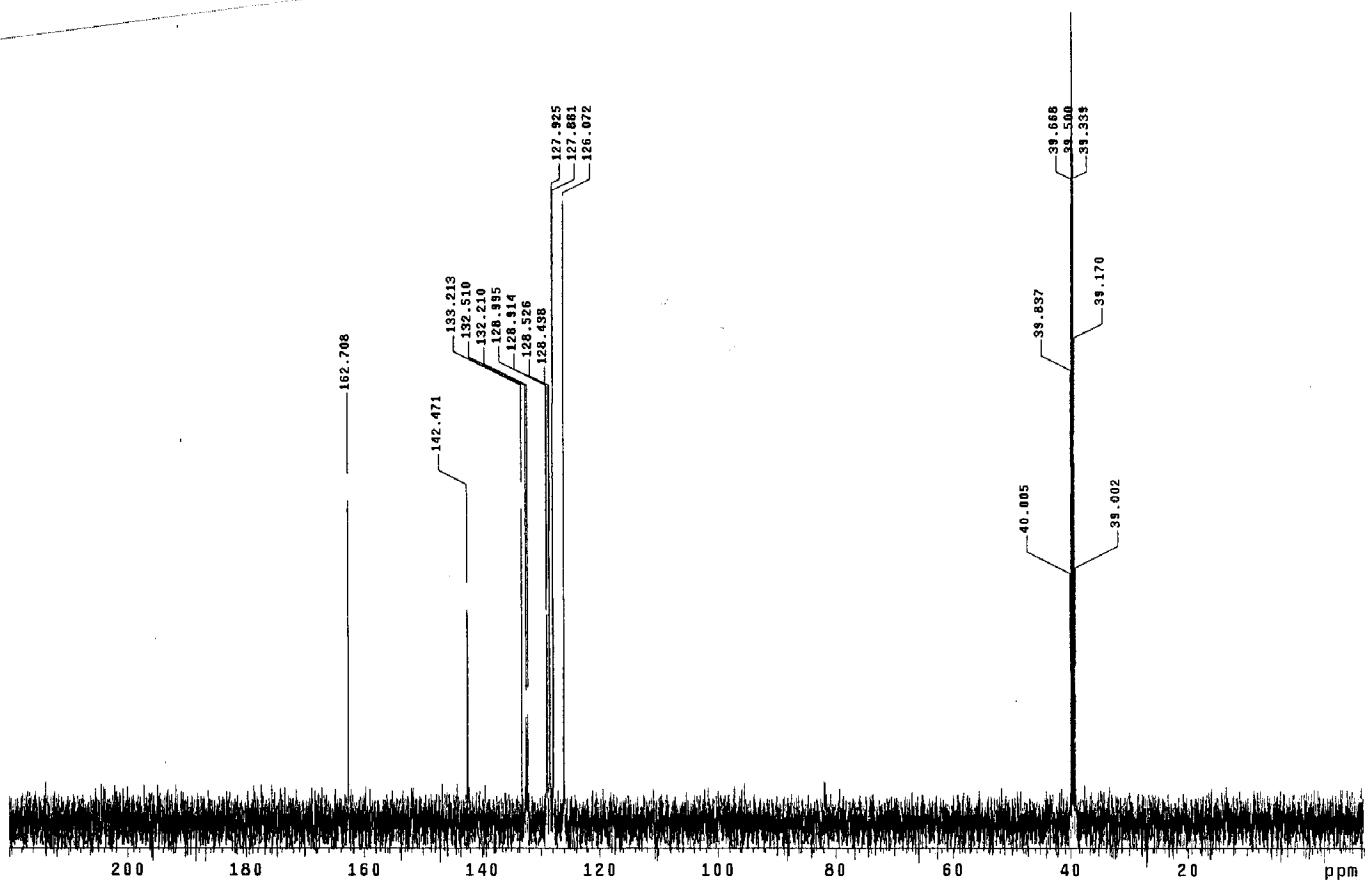

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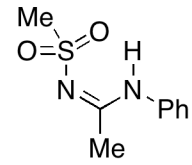

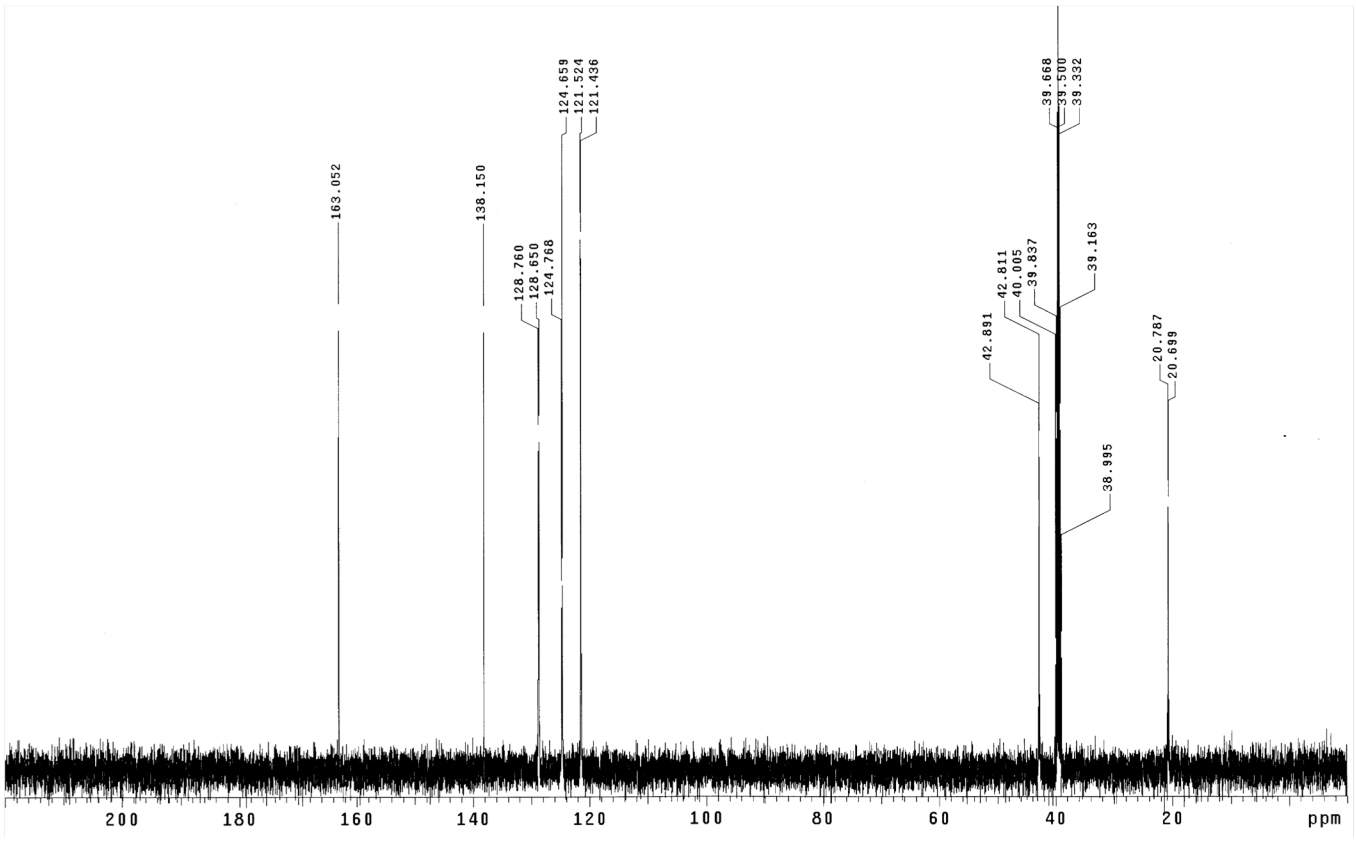

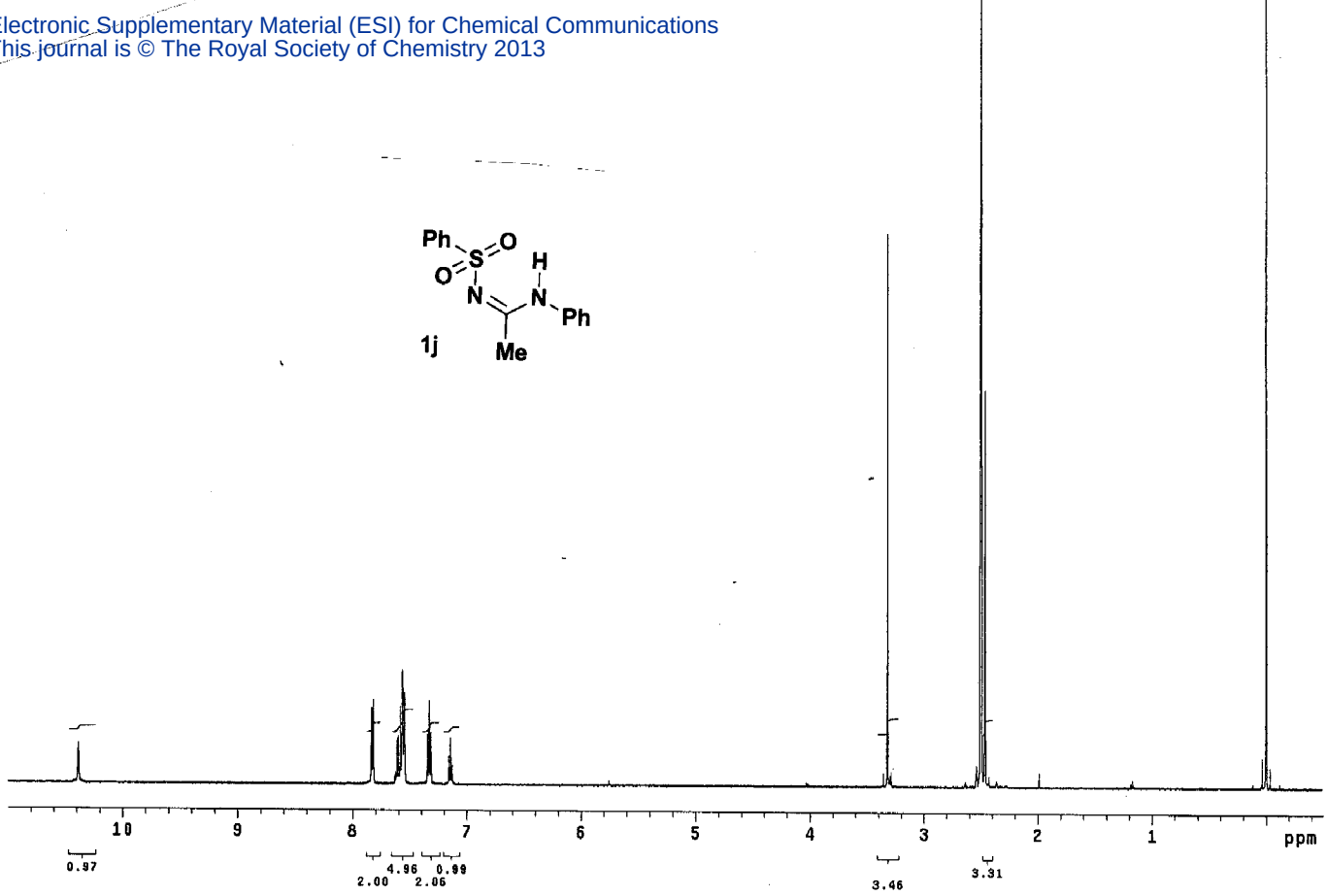

STANDARD CARBON PARAMETERS

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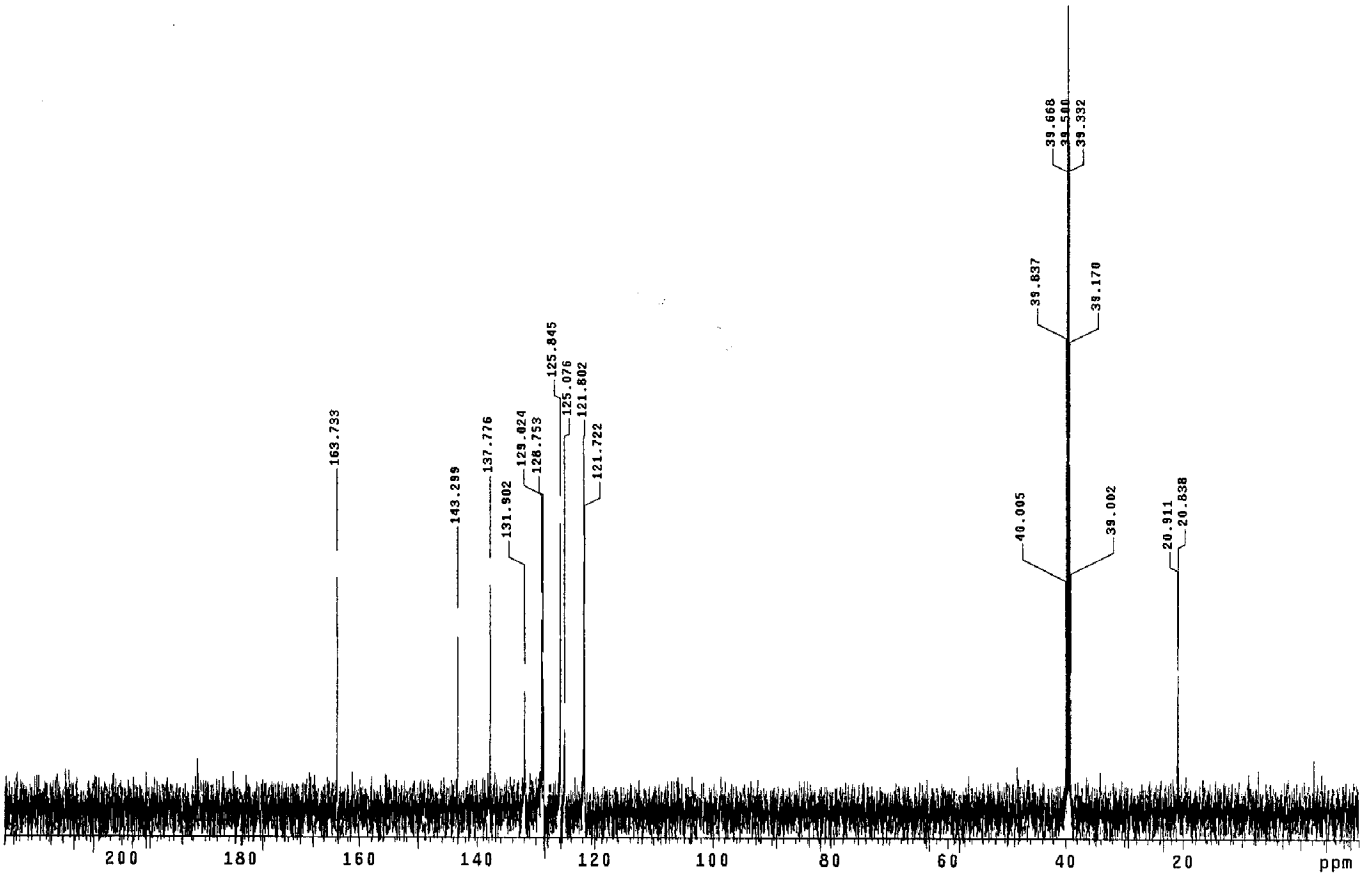

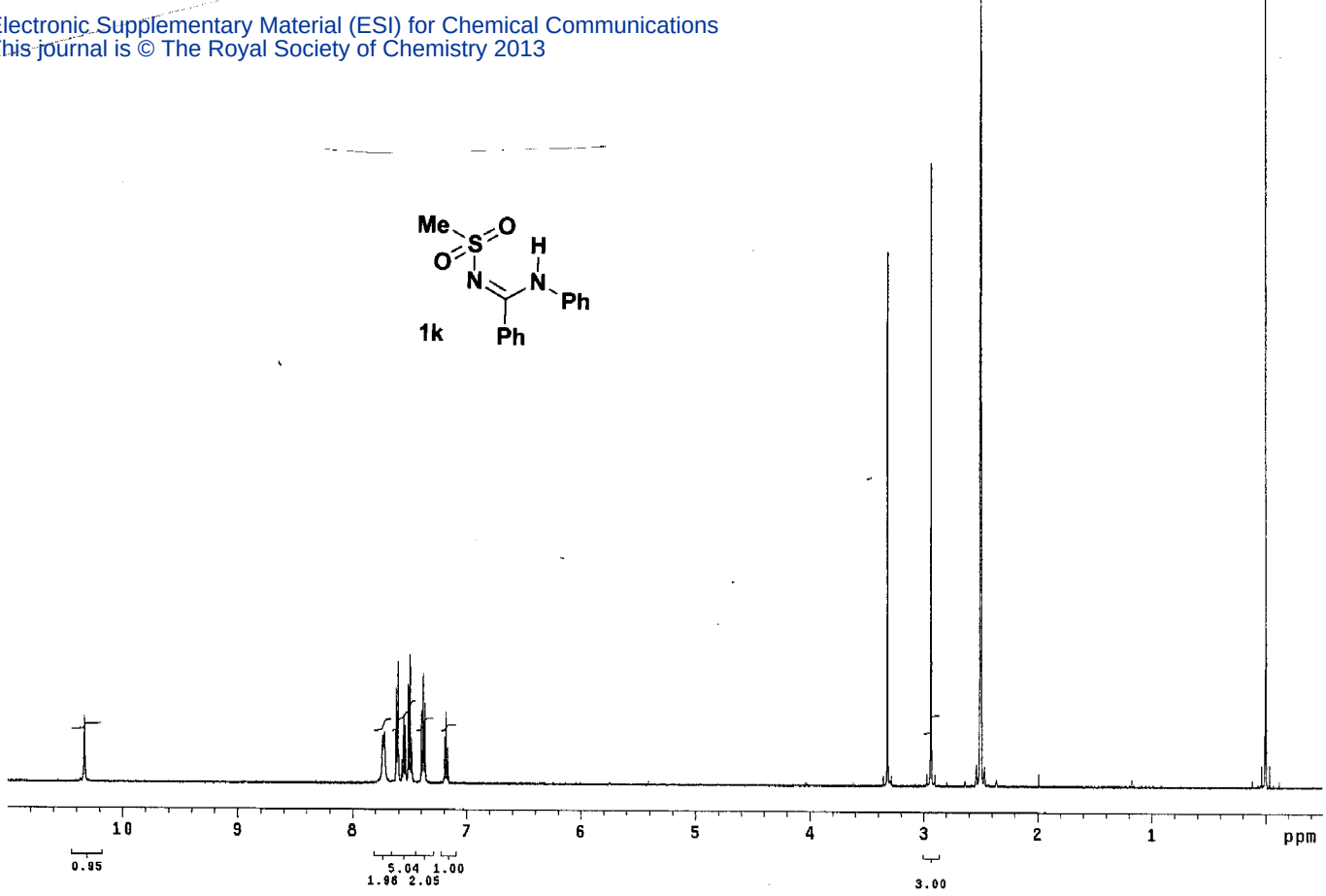

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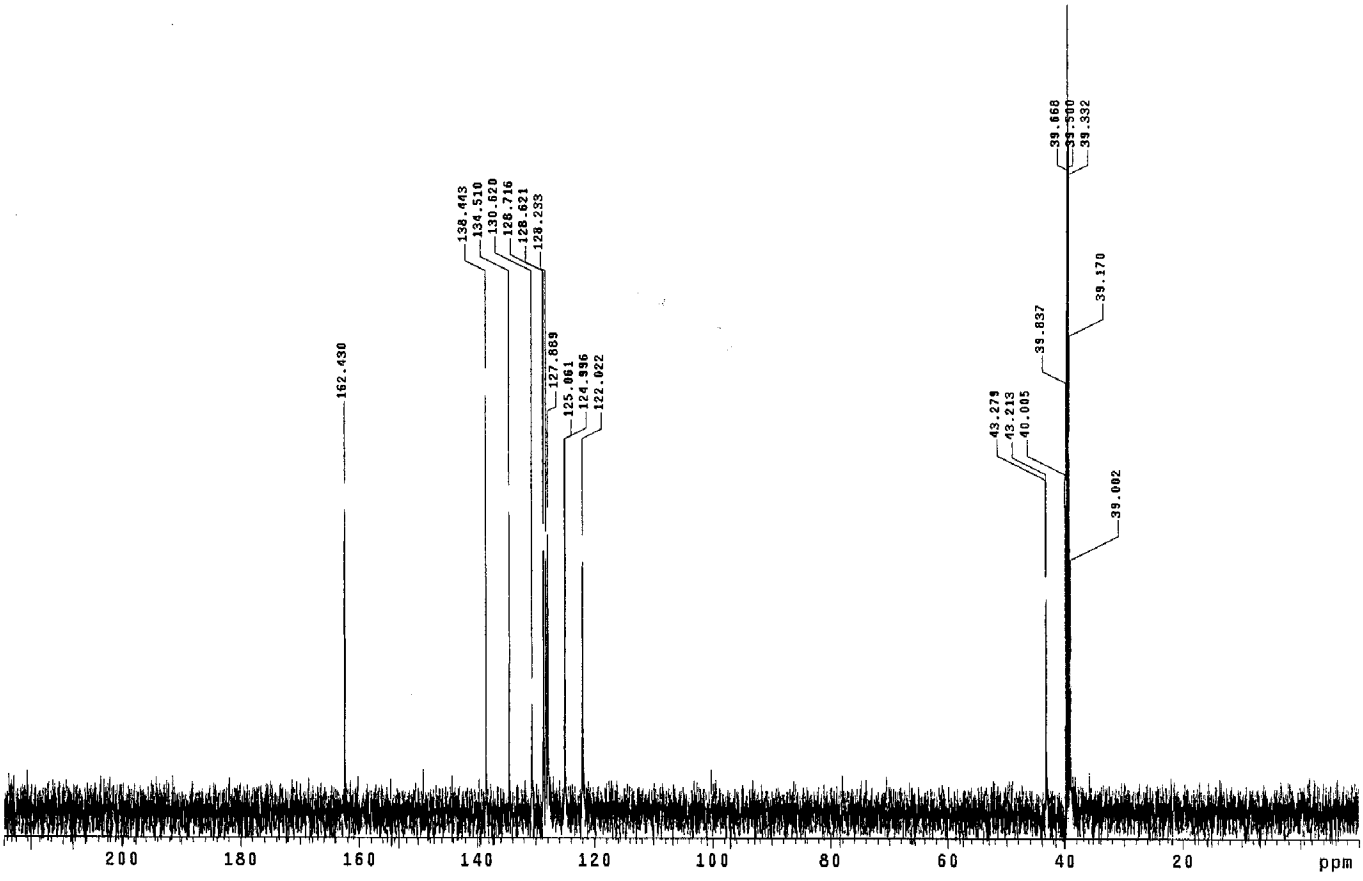

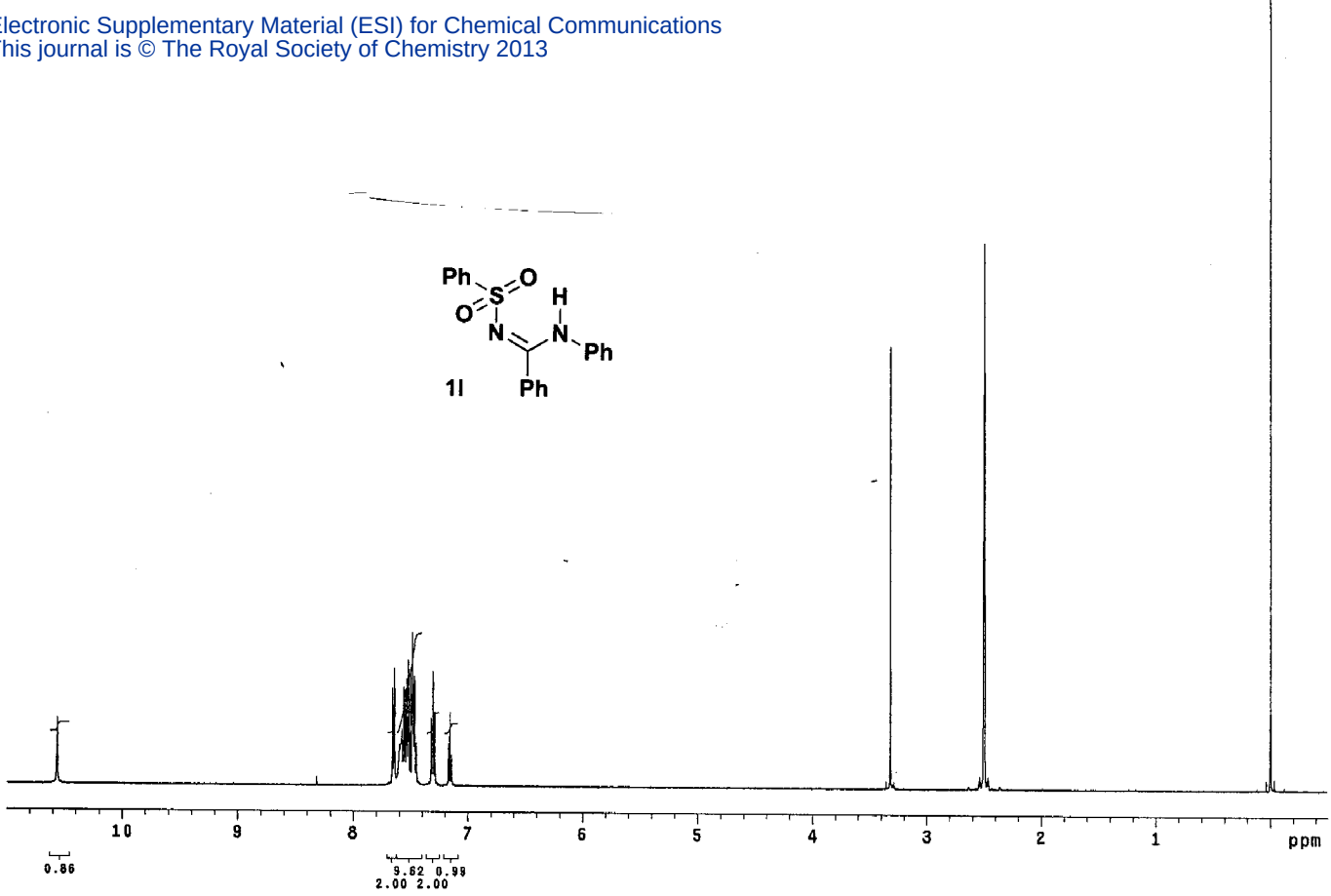

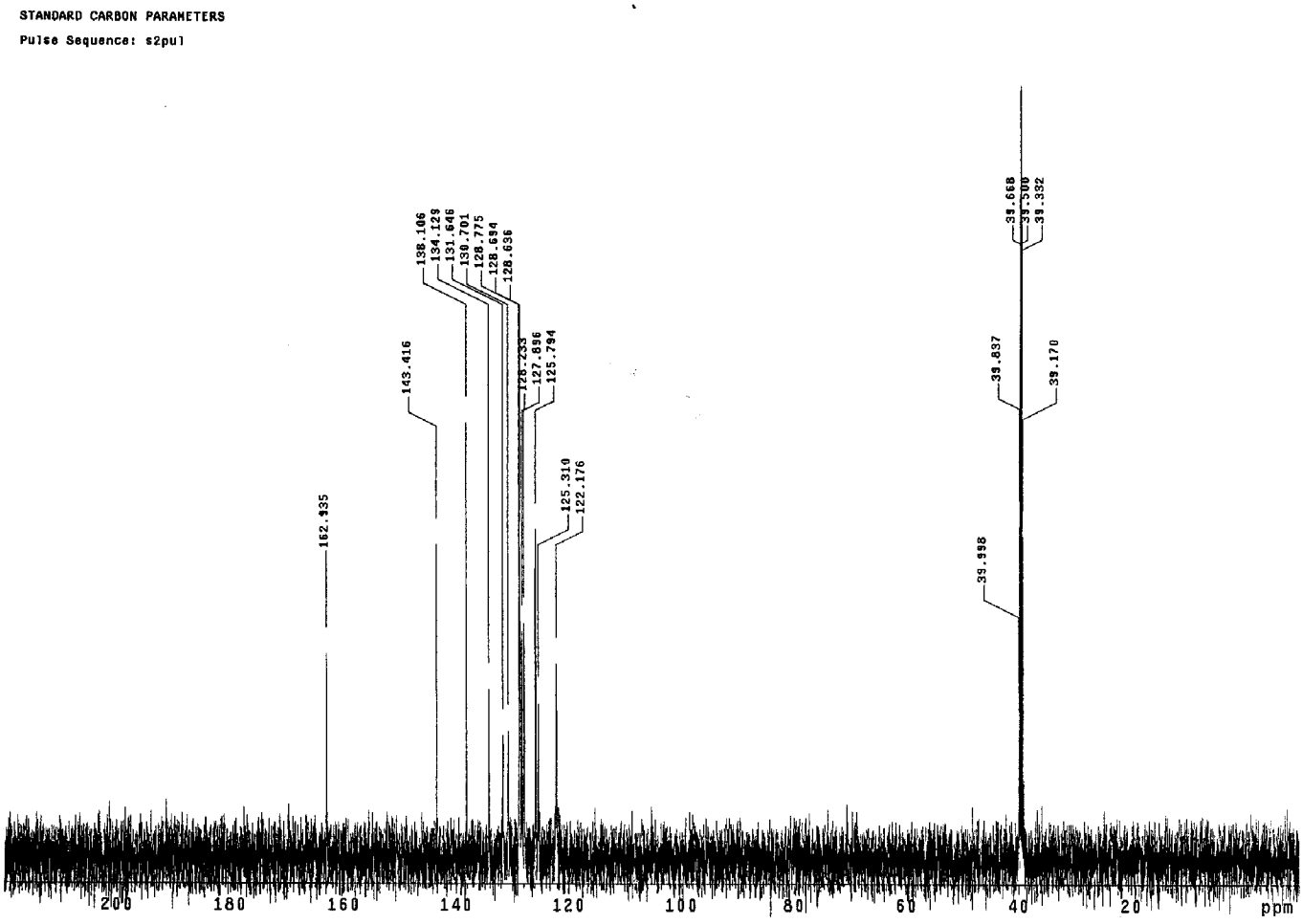

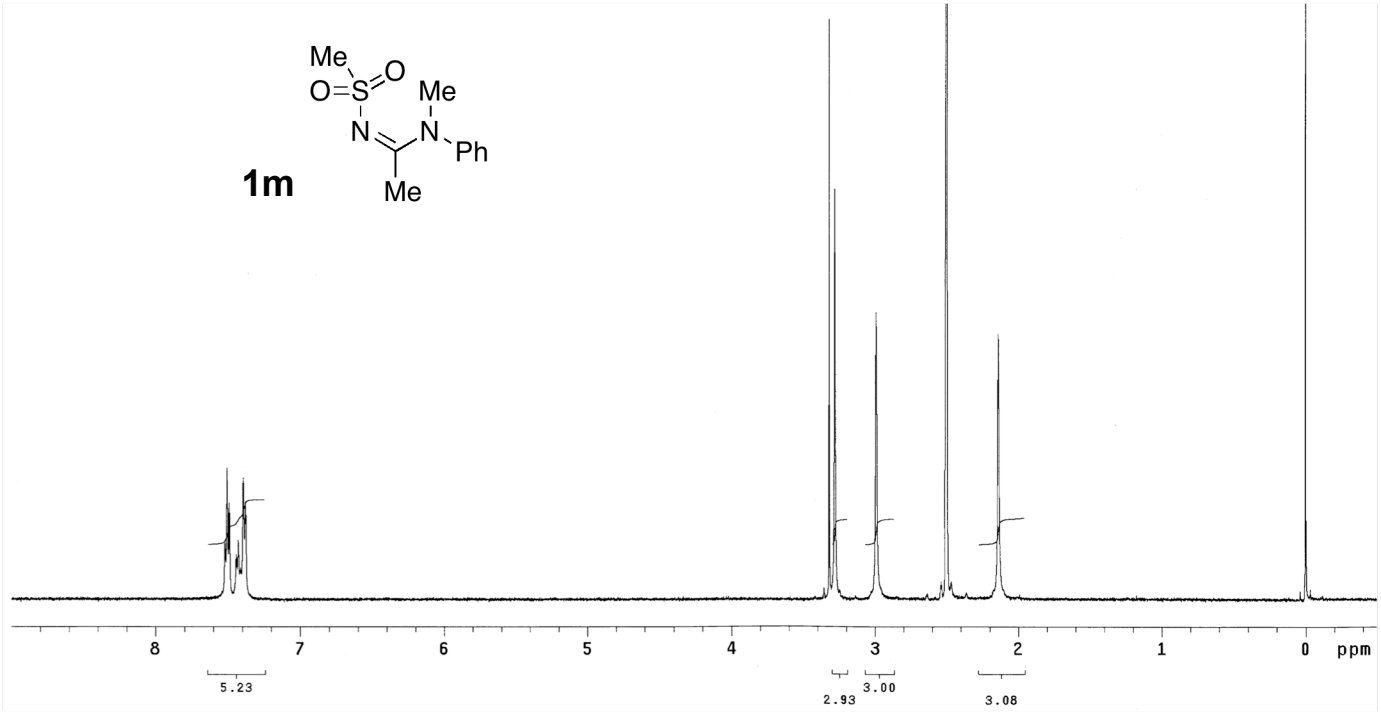

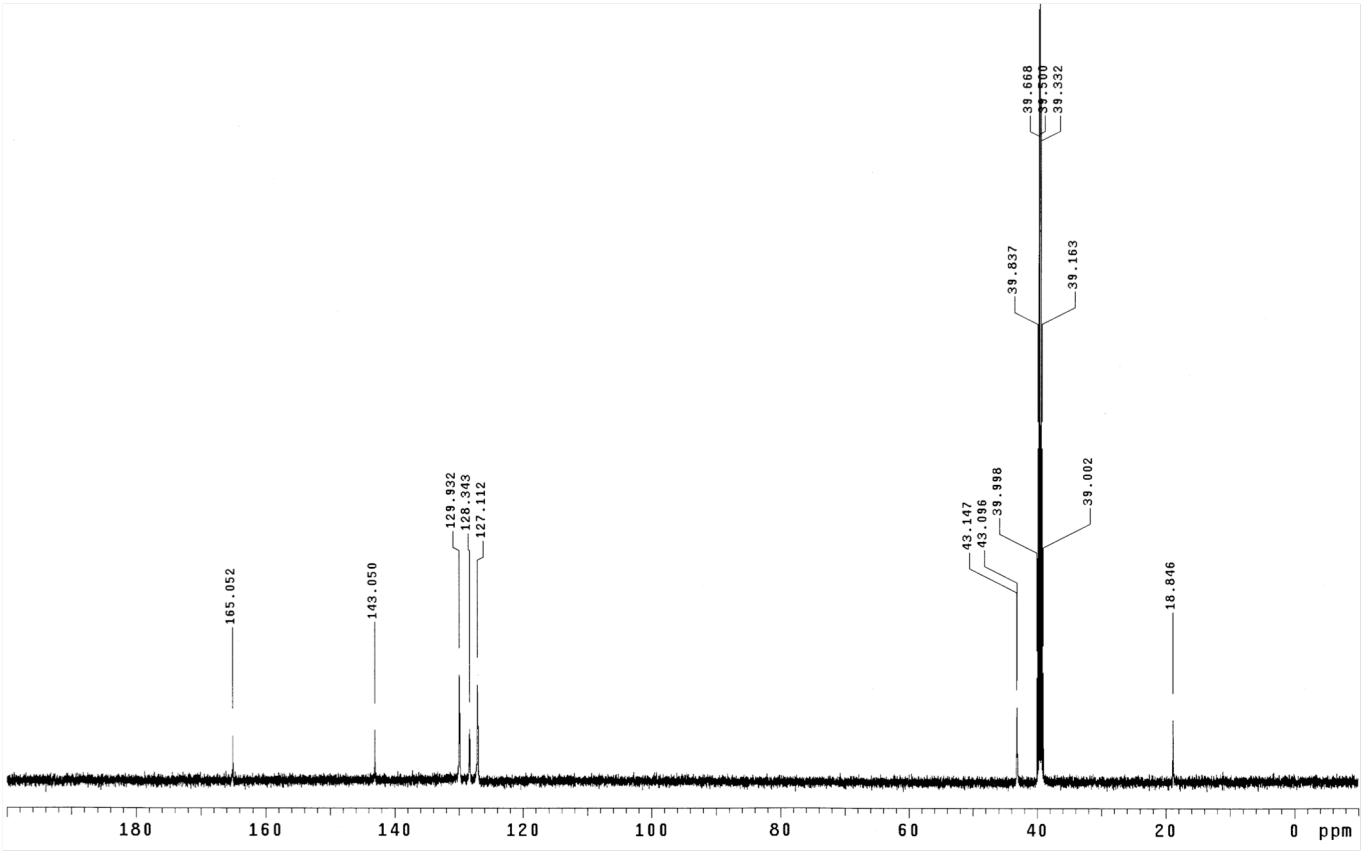

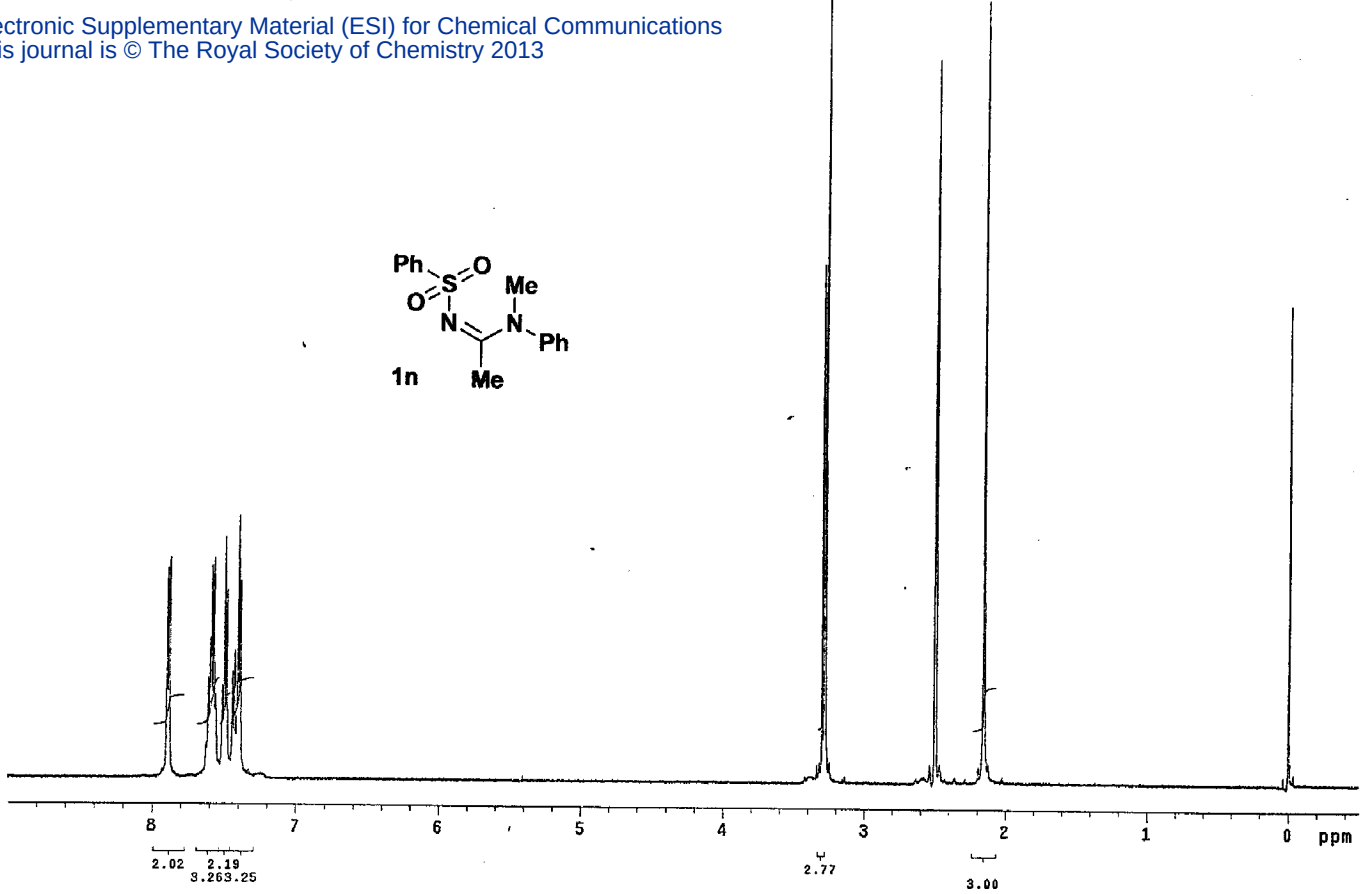
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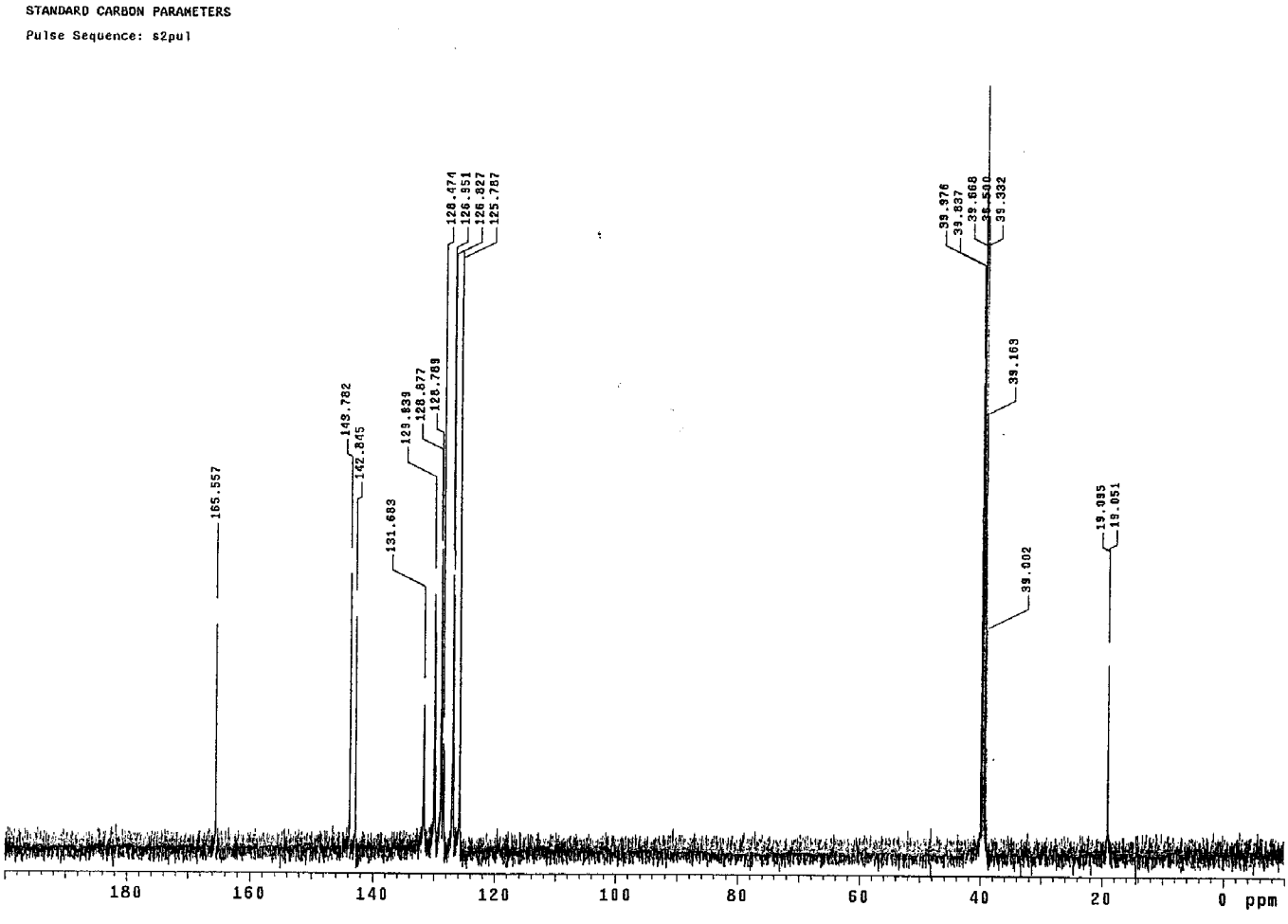
STANDARD CARBON PARAMETERS
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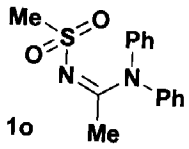

1o

STANDARD CARBON PARAMETERS

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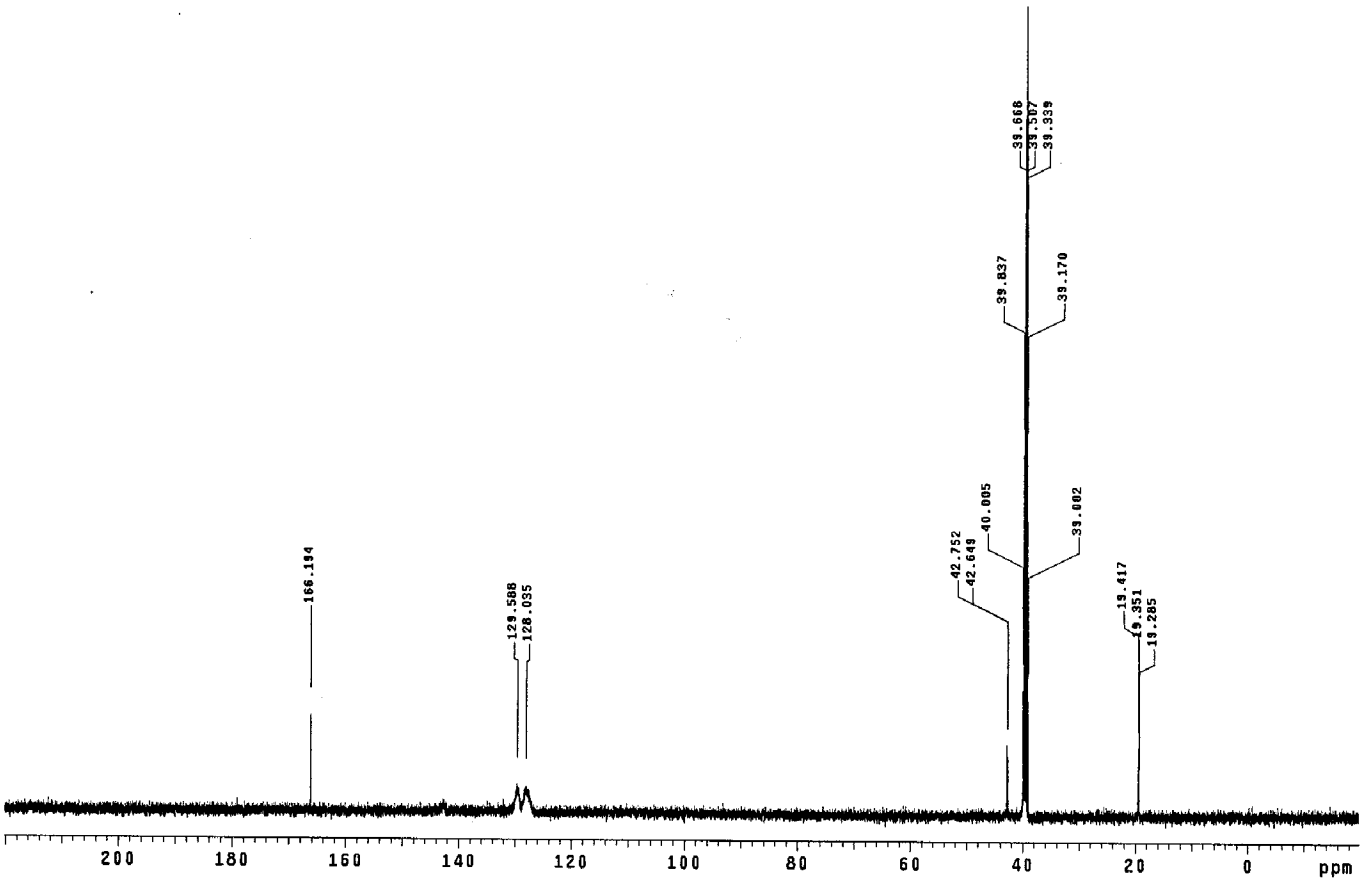

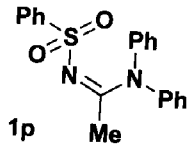

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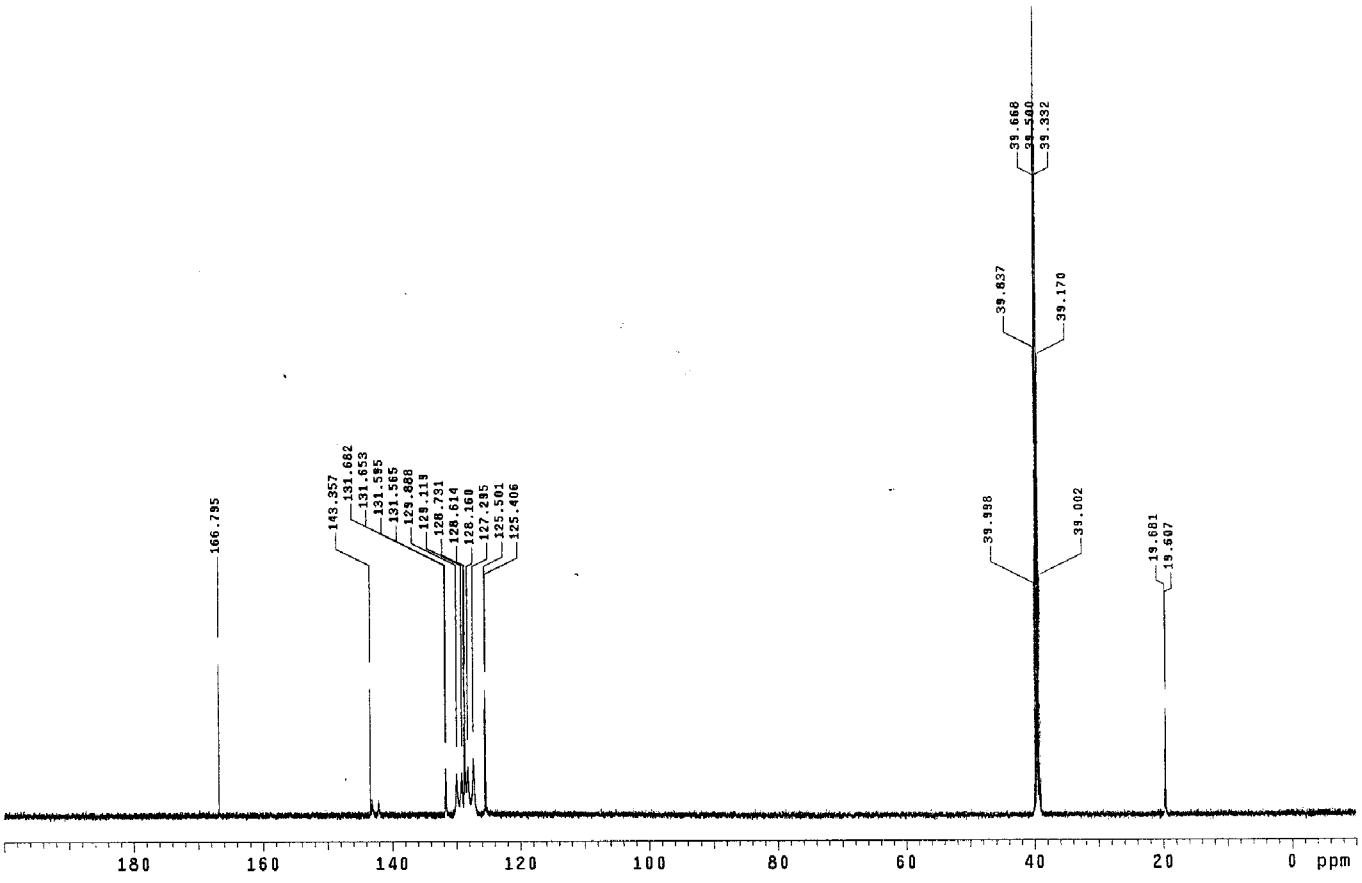

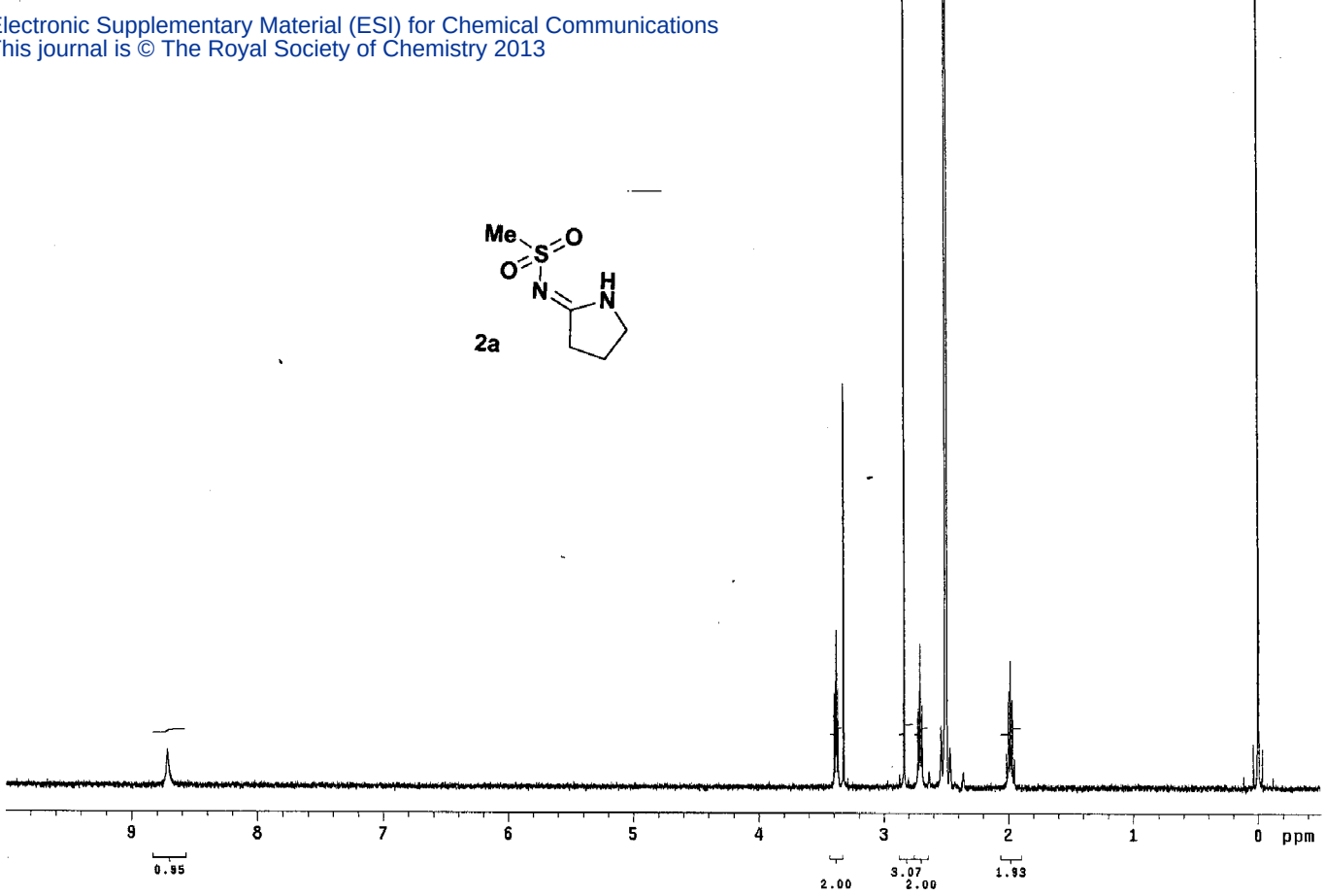
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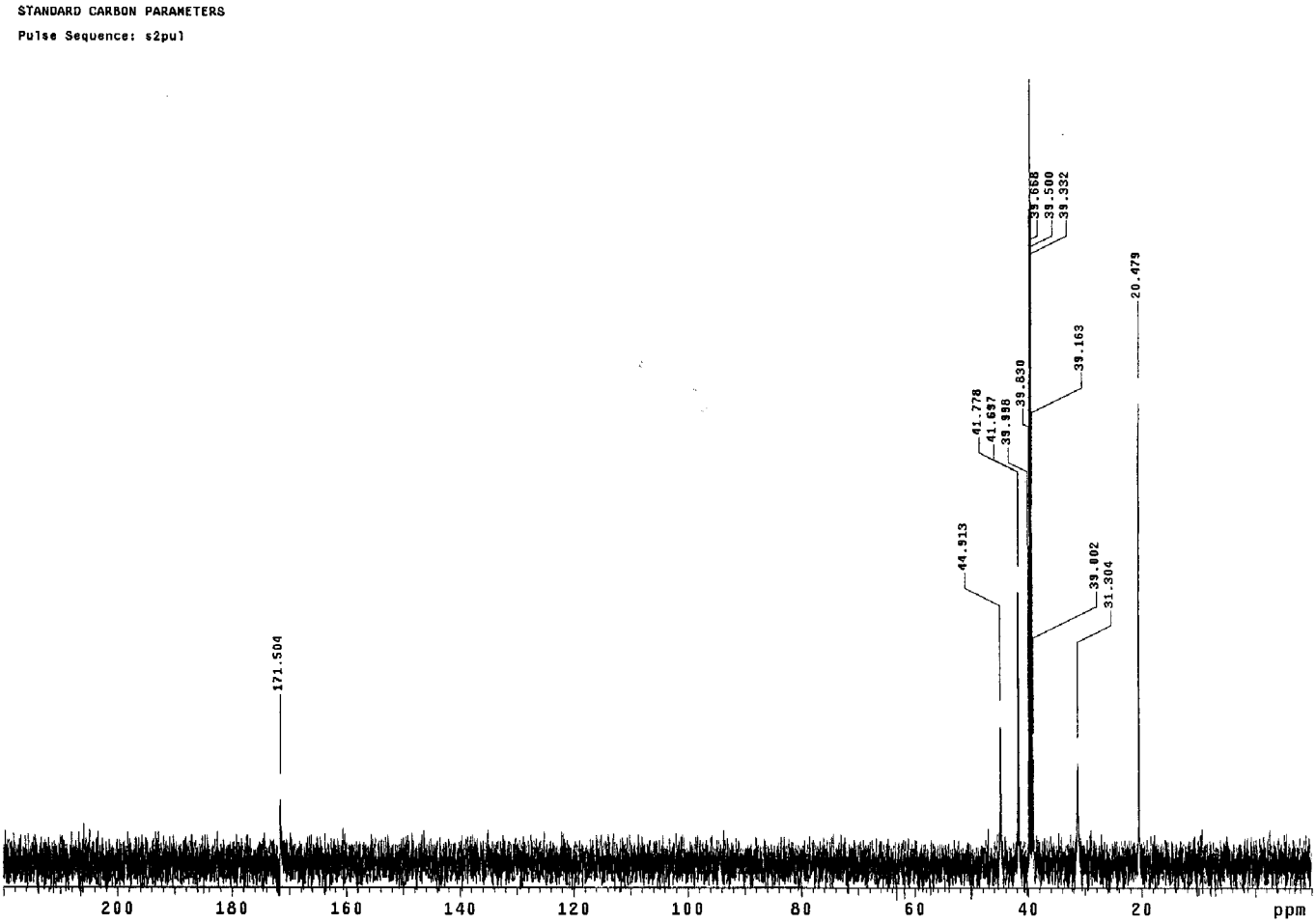
STANDARD CARBON PARAMETERS
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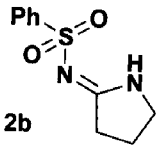
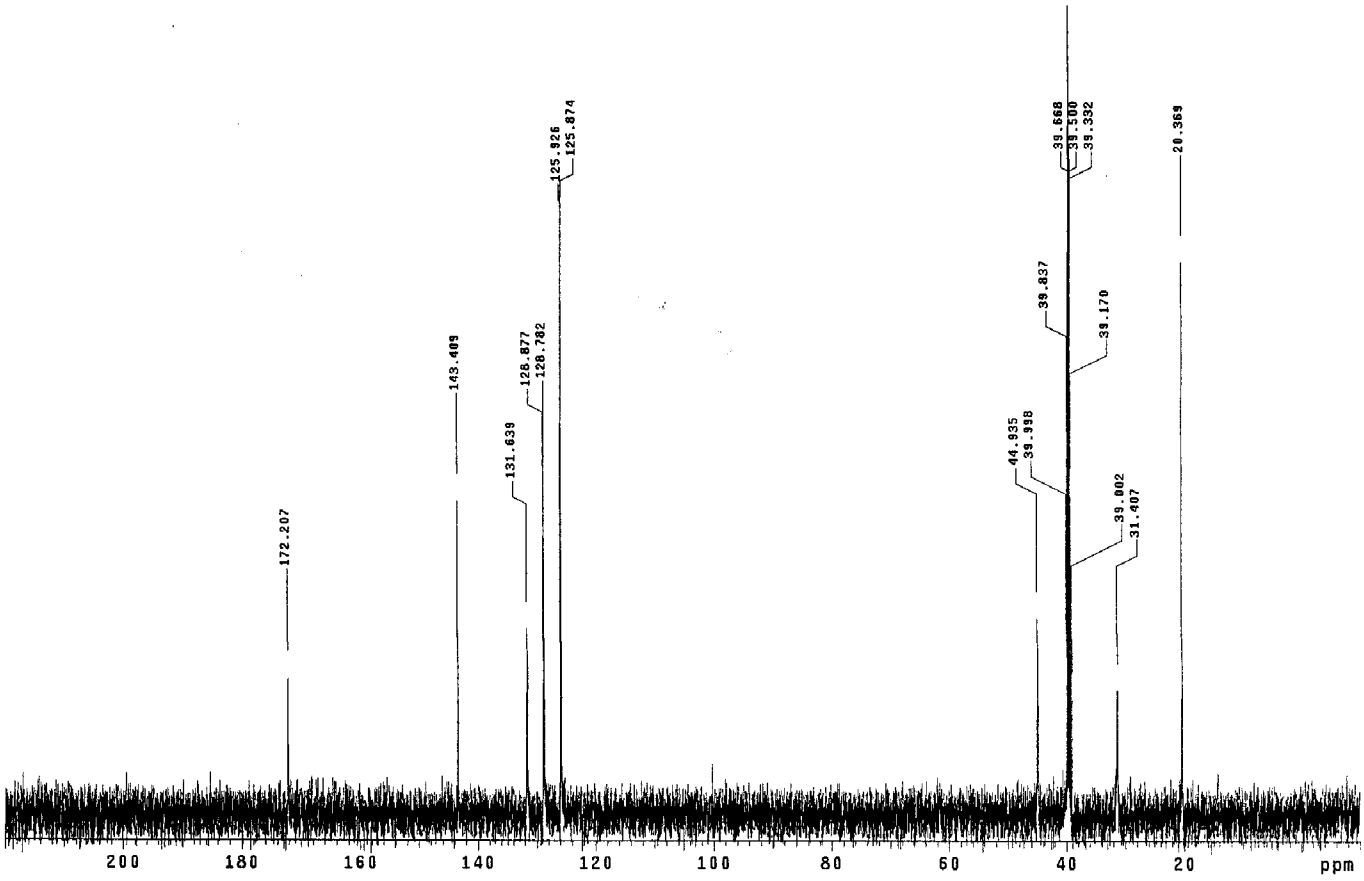
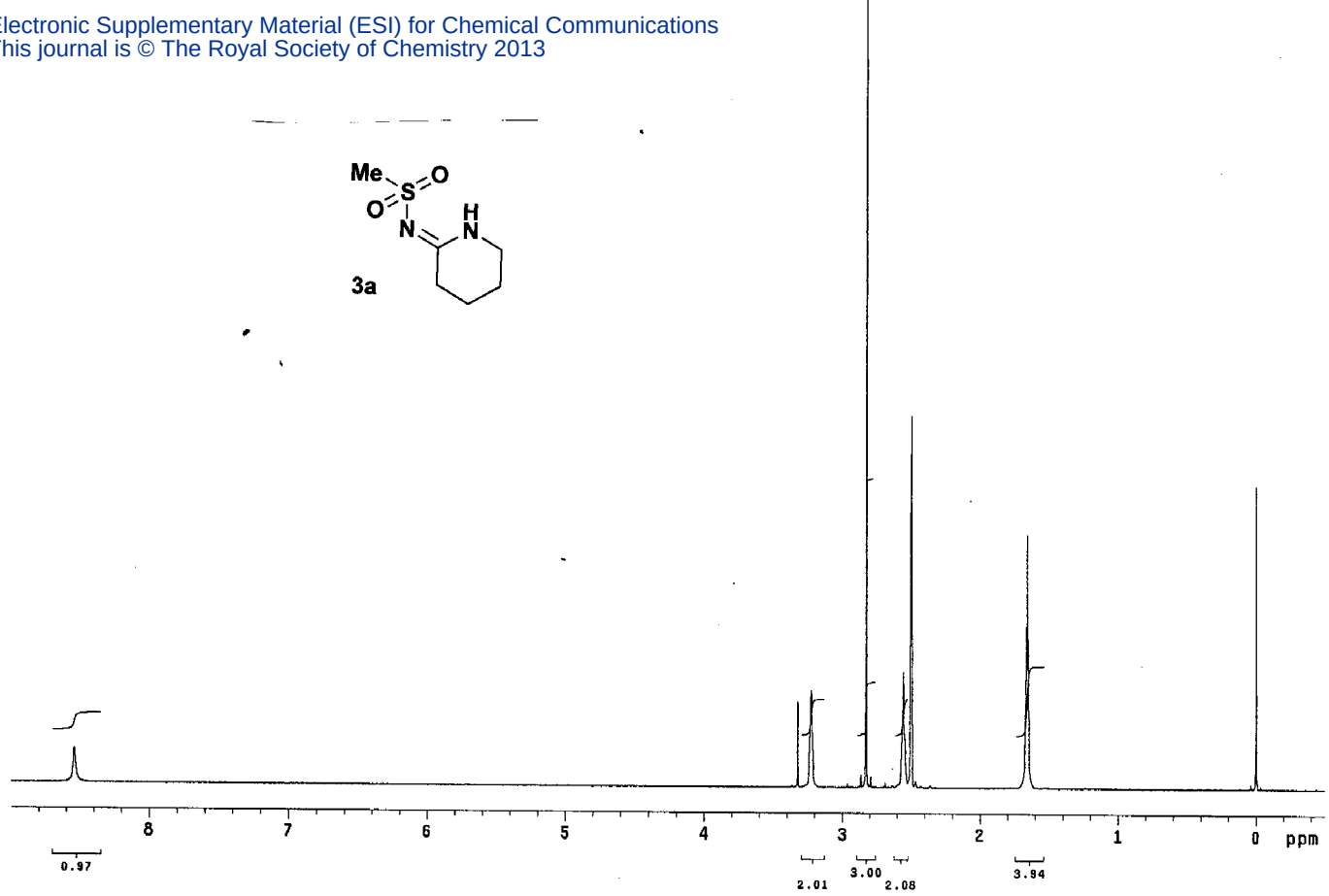
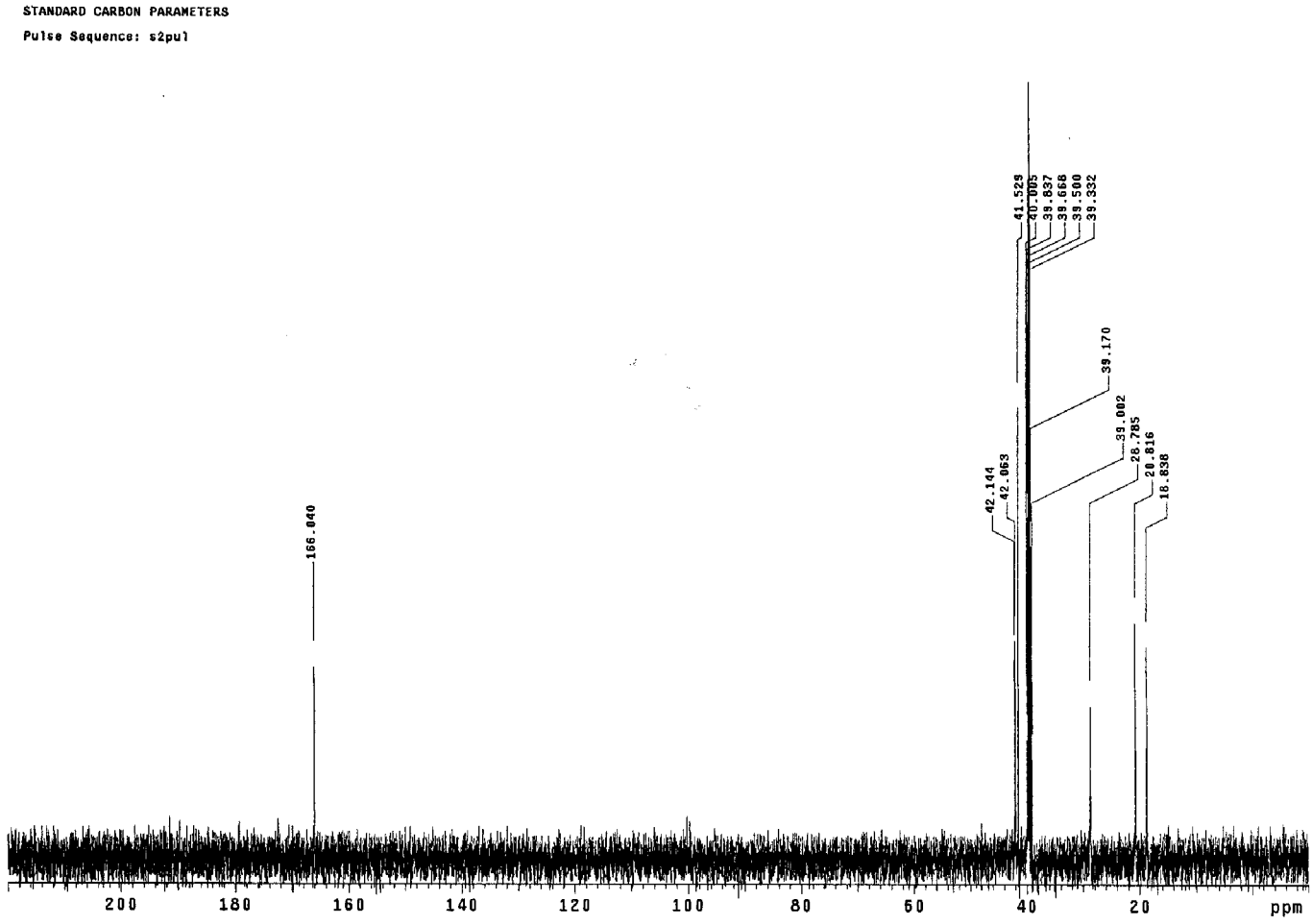


2b







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