Diastereoselective Radical Mediated Alkylation of a Chiral Glycolic Acid Derivative†

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Experimental

General. Irradiations were performed using a sun lamp *Osram Ultra-Vitalux* 300 W. Flash column chromatography (FC) and filtration: *Baker* silica gel (0.063-0.200 mm), AcOEt, Et_2O and hexane as eluants. TLC: *Macherey-Nagel SIL G-25 UV*$_{254}$ anal. plates; detection with UV, I_2 or by spraying with a soln. of phosphomolybdic acid (25 g), $Ce(SO_4)_2 \bullet 4H_2O$ (10 g), conc. H_2SO_4 (60 ml), and H_2O (940 ml) with subsequent heating. IR: *Perkin-Elmer 16PC*. FT-IR: *Mattson Unicam 5000*. NMR: *Bruker AM 360* (^{1}H = 360 MHz ^{13}C = 90.5 MHz) and *Varian Gemini 200* (^{1}H = 200 MHz, ^{13}C = 50.3 MHz); chemical shift in ppm relative to tetramethylsilane = 0 ppm. MS: *Vacuum Generators Micromass VG 70/70E* and *DS 11-250*; CI (NH3), EI (70 eV); m/z (%). Elementary analysis: *Ilse Beetz*, Microanalytisches Laboratorium, D-8640 Kronach, Germany and *Ciba-Geigy*, Microlabor, CH-1700, Marly, Switzerland.

General Procedures

General Procedure 1. Radical reaction of 2 with Bu_3SnY
A soln. of **2** (1.0 mmol) and Bu_3SnY (4.0 mmol) in benzene (4 ml) was irradiated with a 300 W sun lamp. The reaction was monitored by TLC. After solvent evaporation, the crude product was purified by FC.

General Procedure 2. Radical addition of 2 to olefins
A soln. of **2** (1.5 mmol) and the olefin (1.0 mmol) in benzene (4.5 ml) was irradiated with a 300 W sun lamp at 80 °C. The reaction was monitored by TLC. After solvent evaporation, the crude product was purified by FC.

General Procedure 3. Radical addition of 2 to 4-substituted styrenes
A soln. of **2** (1.5 mmol) and 4-substituted styrene (1.0 mmol) in benzene (4 ml) was irradiated with a 300 W sun lamp under reflux. The reaction was monitored by TLC. After complete disapearance of the styrene derivative, the reaction was cooled down to rt. Bu_3SnH (3 mmol) and AIBN (10 mg) were added and the irradiation was continued for 2 h at rt. After solvent evaporation, the crude product was purified by FC.

General Procedure 4. Enolate alkylation of 1
Diisopropylamine (10 mmol) and 1.6 M BuLi (10 mmol) were added at –78 °C to THF (20 ml) containing HMPA (2 ml). After 5 min, a soln. of **1** (10 mmol) in THF (5 ml) was added dropwise. After 15 min at –78 °C, the electrophile (30 mmol) in THF (10 ml) was added. The reaction mixture was allowed to warm up to rt over 2 h. Sat. aq. $NaHCO_3$ (10 ml) and Et_2O (200 ml) were added and the organic layer was separated, washed with sat. $NaHCO_3$ (5 x 20 ml), dried (Na_2SO_4). After solvent evaporation, the crude product was purified by FC.

Product Description

2-(*tert*-Butyl)-2-methyl-5-phenylselanyl-1,3-dioxolan-4-one 2
A soln. of 1.6 M BuLi in hexane (62.5 ml, 100 mmol) was added to a soln. of (*i*-Pr)$_2$NH (14.2 ml, 100 mmol) in THF (250 ml) at –30 °C. After cooling at –78 °C, a soln. of **1** (7.9 g, 50 mmol) in THF (20 ml) was added dropwise. After 15 min, a soln. of $(PhSe)_2$ (15.6 g, 50 mmol) in THF (15 ml) was added and the solution was stirred for 2 h. Sat. aq. $NaHCO_3$ (10 ml) and Et_2O (200 ml) were added, the organic layers was separated, washed with sat. $NaHCO_3$ (5 x 20 ml) and dried (Na_2SO_4). FC (Et_2O/hexane, 1:20) gave **2** (14.16 g, 90%) as a 1:1 mixture of diastereomers. Diastereomer 1: ^{1}H-NMR (200 MHz, CDCl3): 7.70 (*m*, 2 arom. H); 7.30 (*m*, 3 arom. H); 5.97 (*s*, HC-Se); 1.46 (*s*, Me); 0.99 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 170.1 (*s*); 135.9 (*d*); 129.3 (*d*); 129.0 (*d*); 128.7 (*d*); 126.9 (*s*); 117.4 (*s*); 75.4 (*d*); 39.6 (*s*); 24.1 (*q*); 20.6 (*q*). Diastereomer 2: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.7 (*m*, 2 arom. H); 7.3 (*m*, 3 arom. H); 5.93 (*s*, HC-Se); 1.31 (*s*, Me); 0.95 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, CDCl3): 170.4 (*s*); 135.3 (*d*); 129.3 (*d*); 129.0 (*d*); 128.7 (*d*); 127.5 (*s*); 117.6 (*s*); 75.2 (*d*); 38.1 (*s*); 24.5 (*q*); 21.0 (*q*). Mixture of diastereomers: IR (Film): 2976, 1793, 1381, 1249, 1215, 1146, 1095, 952, 740. CI-MS: 314 (59,

[M+1]$^+$), 158 (25), 101 (100), 83 (49), 57 (26), 43 (57). Anal. calc. for $C_{14}H_{18}O_3Se$ (313.26): C 53.68, H 5.79; found: C 54.00, H 6.12.

2-(*tert*-Butyl)-2-methyl-5-$^2H_1$-1,3-dioxolan-4-one 3

According to General Procedure 1, from **2** (626 mg, 2.0 mmol) and Bu_3SnD (1.68 g, 4.0 mmol) in benzene (6 ml) at 0 °C (2 h). FC (Et_2O/hexane, 1:20) gave **3** (275 mg, 87%) as a trans/cis 6:1 mixture. Trans-**3**: ^{1}H-NMR (360 MHz, $CDCl_3$): 4.32 (*t*, *J* = 2.2, CH); 1.5 (*s*, Me); 1.02 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 171.6 (*s*); 118.0 (*s*); 64.1 (*t*); 39.1 (*s*); 24.3 (*q*); 20.3 (*q*); Cis-**3**: ^{1}H-NMR (360 MHz, $CDCl_3$): 4.36 (*t*, *J* = 2.4, CH); 1.5 (*s*, Me); 1.02 (*s*, *t*-Bu). Trans/cis-**3**: IR (Film): 2977, 2879, 1802, 1486, 1382, 1258, 1216, 1155, 1102, 933. CI-MS: 159 (35, M$^+$), 101 (75), 99 (9), 84 (16), 83 (100), 74 (9), 57 (11). Anal. calc. for $C_8H_{13}O_3D$ (159.20): C 60.35; found: C 60.32.

5-Allyl-2-(*tert*-butyl)-2-methyl-1,3-dioxolan-4-one 4

Radical procedure: According to General Procedure 1, from **2** (313 mg, 1.0 mmol) and allyltributylstannane (1.32 g, 4.0 mmol) at 80 °C. After evaporation, FC (Et_2O/hexane, 1:20) gave **4** (155 mg, 78%) as a trans/cis 3.5:1 mixture. Spectroscopic data are in accordance with literature (L. Parra Rapado, V. Bulugahapitiya and P. Renaud, *Helv. Chim. Acta*, 2000, **83**, 1625). The relative configuration of trans-**4** has been determined by n.O.e. measurements (see copy of spectra).

Enolate alkylation: Taken from: L. Parra Rapado, V. Bulugahapitiya and P. Renaud, *Helv. Chim. Acta*, 2000, **83**, 1625.

2-(*tert*-Butyl)-2-methyl-5-(2-trimethylsilylallyl)-1,3-dioxolan-4-one 5

According to the General Procedure 1, from **2** (313 mg, 1.0 mmol) and tributyl[2-(trimethylsilyl)-prop-2-enyl]stannane (1.61 g, 4.0 mmol) at 80 °C. FC (Et_2O/hexane, 1:20) gave **5** (230 mg, 85%) as a trans/cis 9.2:1 mixture. Trans-**5**: ^{1}H-NMR (360 MHz, $CDCl_3$): 5.74 (*s*, C=C*H*H); 5.5 (*s*, C=CH*H*); 4.48 (*dd*, *J* = 3.2, 10, H-C(5)); 2.74 (*dm*, J = 15, C*H*H); 2.44 (*dd*, J = 15, 10, CH*H*); 1.52 (*s*, Me); 1.0 (*s*, *t*-Bu); 0.12 (*s*, $SiMe_3$). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 173.5 (*s*); 147.0 (*s*); 127.4 (*t*); 116.5 (*s*); 75.7 (*d*); 40.1 (*s*); 39.8 (*t*); 24.5 (*q*); 23.1 (*q*); 1.6 (*q*). Cis-**5**: ^{1}H-NMR (360 MHz, $CDCl_3$): Significant peaks: 4.66 (*dd*, *J* = 2.6, 13.5, H-C(5)); 1.46 (*s*, Me); 1.1 (*s*, *t*-Bu). Trans/cis-**5**: IR (Film): 2963, 1913, 1796, 1380, 1251, 1214, 1152, 1108, 932, 759. CI-MS: 270 (56, M$^+$), 255 (31), 242 (10), 212 (50), 198 (19), 170 (100), 127 (50), 101 (38).

Methyl 2-[2-(*tert*-butyl)-2-methyl-5-oxo-1,3-dioxolan-4-yl-methyl]acrylate 6

According to the General Procedure 1, from **2** (313 mg, 1.0 mmol) and [2-(methoxycarbonyl)propenyl]tributylstannane (584 mg, 1.5 mmol) at 80 °C. FC (Et_2O/hexane, 1:20) gave **6** (236 mg, 87%) as a trans/cis 11.5:1 mixture. Trans-**6**: ^{1}H-NMR (360 MHz, $CDCl_3$): 6.3 (*s*, C=C*H*H); 5.7 (*s*, C=CH*H*); 4.6 (*dd*, *J* = 4.8, 8.3, H-C(5)); 3.8 (*s*, CO_2Me); 3.0 (*ddd*, *J* = 0.8, 4.8, 14.6, C*H*H); 2.6 (*ddd*, *J* = 0.8, 8.27, 14.6, CH*H*); 1.5 (*s*, Me); 1.0 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 172.6 (*s*); 166.8 (*s*); 135.1 (*s*); 128.6 (*t*); 116.5 (*s*); 74.6 (*d*); 51.9 (*d*); 40.1 (*s*); 35.7 (*t*); 24.4 (*q*); 22.8 (*q*). Cis-**6**: ^{1}H-NMR (360 MHz, $CDCl_3$): 6.3 (*s*, C=C*H*H); 5.7 (*s*, C=CH*H*); 4.6 (*dd*, *J* = 3.7, 9.8, H-C(5)); 3.8 (*s*, CO_2Me); 3.0 (*m*, C*H*H); 2.6 (*m*, CH*H*); 1.4 (*s*, Me); 0.98 (*s*, *t*-Bu).^{13}C-NMR (50.3 MHz, $CDCl_3$): 172.4 (*s*); 166.6 (*s*); 135.1 (*d*); 128.2 (*t*); 115.5 (*s*); 72.3 (*d*); 53.3 (*q*); 37.9 (*s*); 33.8 (*t*); 24.4 (*q*). Trans/cis-**6**: IR (Film): 2977, 2966, 1795, 1723, 1209, 1151, 929. CI-MS: 257 (41, [M+1]$^+$), 185 (15), 157 (100), 129 (22), 101 (13). Anal. calc. for $C_{13}H_{20}O_5$ (256.30): C 60.92, H 7.87; found: C 60.66, H 8.15. The relative configuration of trans-**6** has been attributed based on n.O.e. measurements (see spectra).

2-(*tert*-Butyl)-2-methyl-5-octyl-1,3-dioxolan-4-one 7

A soln. of **2** (626 mg, 2.0 mmol) in 1-octene (4 ml) was irradiated with a 300 W sun lamp for 4 h at 80 °C. After evaporation of the excess of 1-octene FC (Et_2O/hexane, 1:20) gave the intermediate selenide (624 mg, 74%) as a mixture of diastereomers. A soln. of the crude selenide (127 mg, 0.3 mmol) in benzene (1 ml), Bu_3SnH (174 mg, 0.6 mmol) and AIBN (10 mg) was irradiated with a 300 W sun lamp for 1 h at rt. After solvent evaporation, FC (Et_2O/hexane, 1:20) gave **7** (71 mg, 88%) as a trans/cis 10:1 mixture. Trans-**7**: ^{1}H-NMR (360 MHz, CDCl3): 4.36 (*dd*, *J* = 4.3, 8.2, H-C(5)); 1.93-1.83 (*m*, 1 H, OCHC*H*H); 1.75-1.64 (*m*, 1 H, OCHCH*H*); 1.54-1.23 (*m*, 12 H); 1.5 (*s*, Me); 1.15 (*s*, *t*-Bu); 0.9 (*t*, *J* = 6.8, Me). ^{13}C-NMR (50.3 MHz, CDCl3): 173.8 (*s*); 115.2 (*s*); 73.8 (*d*); 37.9 (*s*); 31.8 (*t*); 31.2 (*t*); 28.3 (*t*); 28.2 (*t*); 25.8 (*t*); 24.5 (*q*); 22.8 (*t*); 18.3 (*q*); 14.0 (*q*). IR (Film): 2926, 1796, 1254, 1154, 1104, 950, 932. CI-MS: 269 (3), 230 (15), 229 (100), 183 (36), 157 (16), 129 (10). Anal. calc. for $C_{16}H_{30}O_3$ (256.30): C 71.01, H 11.18; found: C 71.03, H 11.21.

Methyl 3-[2-(*tert*-butyl)-2-methyl-5-oxo-1,3-dioxolan-4-yl]-2-phenylselanyl propanoate

According to General Procedure 2, from **2** (939 mg, 3.0 mmol) and methyl acrylate (172 mg, 2.0 mmol) at 80 °C. After evaporation, FC (AcOEt/hexane, 1:20) gave the selenide (535 mg, 67%) as a mixture of diastereomers. A soln. of the crude selenide (203 mg, 0.5 mmol), Bu_3SnH (291 mg, 1 mmol) and AIBN (10 mg) was irradiated with a 300 W sun lamp for 1 h at rt. After evaporation of the solvent, FC (AcOEt/hexane, 1:10) gave **8** (124 mg,

quantitative) as a trans/cis 15:1 mixture of diastereomers. Trans-**8**: ^{1}H-NMR (200 MHz, $CDCl_3$): 4.42 (*dd*, *J* = 5.3, 7.6, H-C(5)); 3.7 (*s*, COOMe); 2.5 (*m*, CH_2CO_2Me); 2.3-1.9 (*m*, CH_2); 1.5 (*s*, Me); 0.99 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 172.9 (*s*); 172.7 (*s*); 116.5 (*s*); 74.8 (*d*); 51.7 (*q*); 40.1 (*s*); 29.5 (*t*); 28.5 (*t*); 24.5 (*q*); 22.8 (*q*). IR (Film): 2966, 2879, 1839, 1797, 1740, 1291, 1150, 920, 735. CI-MS: 244 (14, M^+), 187 (21), 173 (38), 145 (100), 117 (75), 101 (46). Anal. calc. for $C_{12}H_{20}O_5$ (244.29): C 59.00, H 8.25; found: C 58.79, H 8.12.

2-(*tert*-Butyl)-2-methyl-5-(2-phenylsulfonylethyl)-1,3-dioxolan-4-one 9

According to the General Procedure 2, from **2** (313 mg, 1.0 mmol) and phenylvinylsulfone (84 mg, 0.5 mmol) at 80 °C. FC (AcOEt/hexane, 1:5) gave the selenide (112 mg, 46%, 83% brsm) as a mixture of diastereomers and recovered phenylvinylsulfone (37 mg). Anal. calc. for $C_{22}H_{27}O_5SSe$ (482.48): C 54.77, H 5.64; found: C 54.82, H 5.76. A soln. of the crude selenide (172 mg, 0.36 mmol), Bu_3SnH (204 mg, 0.7 mmol) and AIBN (10 mg) was irradiated with a 300 W sun lamp for 2 h at rt. FC (AcOEt/hexane, 1:4) gave **9** (115 mg, quantitative) as a trans/cis 16:1 mixture of diastereomers. Trans-**9**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.91 (*m*, 2 arom. H); 7.62 (*m*, 3 arom. H); 4.41 (*dd*, *J* = 5.6, 7.8, H-C(5)); 3.25 and 3.32 (*dd*, *J* = 2.7, 6.5, C*H*$_2$S); 2.35-2.0 (*m*, CH_2); 1.47 (*s*, Me); 0.97 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 171.8 (*s*); 138.0 (*s*); 133.0 (*d*); 129.0 (*d*); 128.0 (*d*); 116.0 (*s*); 73.5 (*d*); 51.7 (*t*); 40.1 (*s*); 26.9 (*q*); 22.9 (*q*). IR (Film): 3369, 2959, 2922, 2873, 1791, 1307, 1086, 745, 689. CI-MS: 327 (100, M^+), 269 (15), 255 (12), 227 (47), 199 (19). Anal. calc. for $C_{16}H_{22}O_5S$ (326.41): C 58.88, H 6.79; found: C 59.03, H 5.83.

Dimethyl 2-[2-(*tert*-butyl)-2-methyl-5-oxo-1,3-dioxolan-4-yl]succinate 10

According to the General Procedure 2, from **2** (939 mg, 3.0 mmol) and dimethyl fumarate (288 mg, 2.0 mmol) at 80 °C. FC (AcOEt/hexane, 1:5) gave the selenide (558 mg, 61%, 79% brsm) as a mixture of diastereomers and recovered dimethyl fumarate (67 mg, 0.46 mmol). For caracterisation purpose the product was reduced with Bu_3SnH. A soln. of the crude selenide (200 mg, 0.44 mmol), Bu_3SnH (290 mg, 1.0 mmol) and AIBN (10 mg) was irradiated with a 300 W sun lamp for 2 h at rt. FC (AcOEt/hexane, 1:4) gave **10** (132 mg, quantitative) as a 35:23:1.5:1 mixture of diastereomers that cold not be separated. Trans-**10** (major): ^{1}H-NMR (200 MHz, $CDCl_3$): 4.74 (*d*, *J* = 4.3, H-C(5)); 3.76 and 3.69 (2*s*, 2 CO_2Me); 3.38 (*m*, $CHCO_2Me$); 3-2.8 (*m*, C*H*H); 2.75-2.5 (*m*, CH*H*); 1.50 (*s*, Me); 0.98 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 171.5 (*s*); 171.1 (*s*); 171.0(*s*); 116.9 (*s*); 75.6 (*d*); 52.3 (*q*); 52.0 (*q*); 43.8 (*d*); 40.6 (*s*); 31.6 (*t*); 24.5 (*q*); 21.8 (*q*). Trans-**10** (minor, selected peaks): ^{1}H-NMR (200 MHz, $CDCl_3$): 4.55 (*d*, *J* = 4.2, H-C(5)); 3.72 and 3.69 (2*s*, 2 CO_2Me); 1.45 (*s*, Me); 0.97 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 171.4 (*s*); 171.2 (*s*); 170.4 (*s*); 117.0 (*s*); 75.9 (*d*); 52.4 (*q*); 51.9 (*q*); 43.8 (*d*); 40.6 (*s*); 32.4 (*t*); 24.5 (*q*); 21.7 (*q*). Trans-**10** (minor/major)i: IR (Film): 2963, 2918, 1796, 1439, 1381, 1254, 1163, 954. CI-MS: 302 (6, M^+), 202 (100), 174 (95), 170 (10), 143 (32). Anal. calc. for $C_{14}H_{22}O_7$ (302.33): C 55.62, H 7.33; found: C 55.62, H 7.41.

3-[2-(*tert*-Butyl)-2-methyl-5-oxo-1,3-dioxolan-4-yl]-1-phenyl-2,5-azolandione 11

According to the General Procedure 2, from **2** (1.40 g, 4.5 mmol) and *N*-phenylmaleimide (519 mg, 3.0 mmol) at 80 °C. FC (AcOEt/hexane, 1:10) gave the selenide (938 mg, 64%, 79% brsm) as a 1.9:1 mixture of diastereomers and recovered *N*-phenylmaleimide (98 mg, 0.57 mmol). Anal. calc. for $C_{24}H_{25}O_5NSe$ (486.43): C 59.26, H 5.18, N 2.88; found: C 58.87, H 4.92, N 2.72. A soln. of the crude selenide (230 mg, 0.47 mmol), Bu_3SnH (290 mg, 1.0 mmol) and AIBN (10 mg) was irradiated with a 300 W sun lamp for 2 h at rt. FC (AcOEt/hexane, 1:4) gave **11** (154 mg, quantitative) as a 42:22:1.9:1 mixture of diastereomers. Further FC afforded pure samples of the two trans diastereomers. Trans-**11** (major): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.45 (*m*, 3 arom. H); 7.3 (*m*, 2 arom. H); 5.14 (*d*, *J* = 2.0, H-C(5)); 3.5 (*ddd*, *J* = 2, 5, 7, CHC(O)N); 2.98 (*dd*, J = 18, 9, C*H*H); 2.82 (dd, J = 18, 5, CH*H*); 1.6 (*s*, Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 174.9 (*s*); 173.9 (*s*); 170.9 (*s*); 131.6 (*s*); 126.4 (*d*); 117.6 (*s*); 74.9 (*d*); 42.3 (*d*); 40.8 (*s*); 29.4 (*t*); 24.6 (*q*); 22.4 (*q*). Trans-**11** (minor): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.45 (*m*, 3 arom. H); 7.25 (*m*, 2 arom. H); 4.75 (*d*, *J* = 2.5, H-C(5)); 3.59 (*ddd*, *J* = 2.5, 5.7, 9.4, CH); 3.10 (dd, J = 18.4, 9.5 C*H*H); 2.83 (dd, J = 18.4, 5.6, CH*H*); 1.5 (*s*, Me); 1.01 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 174.3 (*s*); 174.1 (*s*); 170.3 (*s*); 131.6 (*d*); 129.2 (*d*); 128.8 (*d*); 126.5 (*d*); 117.6 (*s*); 75.6 (*d*); 42.4 (*d*); 40.7 (*s*); 31.8 (*t*); 24.6 (*q*); 21.7 (*q*). Trans-**11** (major/minor): IR (Film): 3480, 2975, 2911, 1796, 1500, 1396, 1281, 1197, 973, 700. CI-MS: 332 (15, M^+), 232 (12), 205 (12), 103 (100), 101 (21), 85 (5). Anal. calc. for $C_{18}H_{21}O_5N$ (331.37): C 65.24, H 6.39, N 4.23; found: C 65.10, H 6.38, N 4.21.

2-(*tert*-Butyl)-2-methyl-5-phenethyl-1,3-dioxolan-4-one 12

According to General Procedure 3, from **2** (257 mg, 0.8 mmol), styrene (52 mg, 0.5 mmol) and Bu_3SnH (464 mg, 1.6 mmol). FC (Et_2O/hexane, 1:20) gave **12** (49 mg, 37%) as a trans/cis 10:1 mixture of diastereomers. Trans-**12**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.40-7.15 (*m*, 5 arom. H); 4.37 (*dd*, *J* = 4.9, 7.8, H-C(5)); 2.82 (*t*, *J* = 8.2, C*H*$_2$Ph); 2.3-1.95 (*m*, CH_2); 1.57 (*s*, Me); 1.02 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 173.5 (*s*); 136.4 (*s*); 128.5 (*d*); 126.5 (*d*); 116.4 (*s*); 74.9 (*d*); 40.1 (*s*); 35.0 (*t*); 31.6 (*t*); 24.5 (*q*); 22.6 (*q*). Cis-**12**: ^{1}H-NMR (200 MHz, $CDCl_3$):

Significant peak: 4.36 (*dd*, *J* = 5.6, 7.7, H-C(5)). Trans/cis-**12**: IR (Film): 2975, 2878, 1792, 1256, 1215, 1152, 1110, 952, 700. CI-MS: 263 (89, [M+1]+), 191 (11), 163 (22), 145 (15), 133 (12), 119 (11), 101 (100). Anal. calc. for $C_{16}H_{22}O_3$ (262.35): C 73.25, H 8.45; found: C 72.96, H 8.48.

2-(*tert*-Butyl)-2-methyl-5-(4-trifluoromethylphenethyl-1,3-dioxolan-4-one 13

According to the General Procedure 3, from **2** (251 mg, 0.8 mmol), 4-trifluoromethylstyrene (86 mg, 0.5 mmol) and Bu_3SnH (464 mg, 1.6 mmol). FC (Et_2O/hexane, 1:20) gave **13** (64 mg, 40%) as a trans/cis 10:1 mixture. Trans-**13**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.55 (*m*, 2 arom. H); 7.32 (*m*, 2 arom. H); 4.35 (*dd*, *J* = 5, 7.7, H-C(5)); 2.87 (*m*, CH_2Ph); 2.3-1.9 (*m*, *C*$H_2$$CH_2$Ph); 1.56 (*s*, Me); 1.02 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 173.2 (*s*); 144.5 (*s*); 128.8 (*d*); 125.5 (*d*); 116.6 (*s*); 74.8 (*d*); 40.2 (*s*); 34.6 (*t*); 30.9 (*t*); 24.5 (*q*); 22.9 (*q*). Cis-**13**: ^{1}H-NMR (200 MHz, $CDCl_3$): Significant peak: 4.22 (*dd*, *J* = 1.4, 5.6, H-C(5)). Trans/cis-**13**: IR (Film): 2982, 2882, 1784, 1380, 1330, 1266, 1158, 1122, 1069, 1017, 932. CI-MS: 330 (100, M^+), 311 (65), 272 (4), 210 (3), 101 (6). Anal. calc. for $C_{17}H_{21}O_3F$ (330.35): C 61.81, H 6.41; found: C 61.57, H 6.41.

4-(2-(2-(*tert*-Butyl)-2-methyl-5-oxo-1,3-dioxolan-4-yl)ethyl)phenyl acetate 14

According to the General Procedure 3, from **2** (123 mg, 0.4 mmol), 4-acetoxystyrene (40 mg, 0.25 mmol) and Bu_3SnH (175 mg, 0.6 mmol). FC (Et_2O/hexane, 1:20) gave **14** (32 mg, 40%) as a trans/cis 10:1 mixture. Trans-**14**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.2 (*m*, 2 arom. H); 7.0 (*m*, 2 arom. H); 4.36 (*dd*, *J* = 5.0, 7.6, H-C(5)); 2.8 (*t*, *J* = 8.4, CH_2-Ph); 2.3 (*s*, OAc); 2.2-1.9 (*m*, CH_2); 1.54 (*s*, Me); 1.01 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 173.4 (*s*); 169.4 (s); 149.1 (*s*); 137.9 (*s*); 129.4 (*d*); 121.5 (*d*); 116.4 (*s*); 74.9 (*d*); 40.1 (*s*); 34.9 (*t*); 30.5 (t); 24.5 (*q*); 22.9 (*q*). Cis-**14**: ^{1}H-NMR (360 MHz, $CDCl_3$): Significant peak: 4.33 (*dd*, *J* = 4.5, 7.7, H-C(5)). Trans/cis-**14**: IR (Film): 2975, 2878, 1791, 1767, 1508, 1216, 1155, 911, 733. CI-MS: 320 (100, M^+), 218 (13), 178 (14), 107 (12), 101 (17), 86 (13). Anal. calc. for $C_{18}H_{24}O_5$ (320.39): C 67.48, H 7.55; found: C 67.16, H 7.66.

2-(*tert*-Butyl)-2-methyl-5-(4-methoxyphenethyl)-1,3-dioxolan-4-one 15

According to the General Procedure 3, from **2** (257 mg, 0.8 mmol), 4-methoxystyrene (67 mg, 0.5 mmol) and Bu_3SnH (465 mg, 1.6 mmol). FC (Et_2O/hexane, 1:20) gave **15** (146 mg, 50%) as a trans/cis 8.8:1 mixture. Trans-**15**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.13 (*dm*, *J* = 8.8, 2 arom. H); 6.84 (*dm*, *J* = 8.8, 2 arom. H); 4.33 (*dd*, *J* = 3.9, 7.3, H-C(5)); 3.79 (*s*, Me-O); 2.75 (*t*, *J* = 7.8, CH_2Ph); 2.2-1.9 (*m*, CH_2); 1.55 (*s*, Me); 1.01 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 173.6 (*s*); 158.1 (*s*); 132.4 (*s*); 129.4 (*d*); 116.3 (*s*); 113.9 (*d*); 74.9 (*d*); 55.2 (*q*); 40.1 (*s*); 35.2 (*t*); 30.2 (*t*); 24.5 (*q*); 22.9 (*q*). Cis-**15**: 4.74 (d, J = 7, H-C(5)), Trans/cis-**15**: IR (Film): 2963, 2878, 1791, 1613, 1513, 1250, 1152, 1036, 830. CI-MS: 293 (100, $[M+1]^+$), 235 (10), 193 (21), 191 (15), 147 (43), 121 (81), 101 (34). Anal. calc. for $C_{17}H_{24}O_3$ (292.38): C 69.84, H 8.27; found: C 69.49, H 8.82.

5-Bromo-2-(*tert*-butyl)-2-methyl-1,3-dioxolan-4-one 16

Compound **1** (798 mg, 5.0 mmol), *N*-bromosuccinimide (978 mg, 5.5 mmol) and AIBN (10 mg) were heated in dry carbon tetrachloride (20 ml) under reflux for 2 h. The mixture was then cooled at 0 °C, succinimide was removed by filtration and the solvent was evaporated under reduced pressure. FC (Et_2O/hexane, 1:20) gave **16** (1.05 g, 89%) as a trans/cis 21:1 mixture of diastereomers. Trans-**16**: ^{1}H-NMR (200 MHz, $CDCl_3$): 6.50 (*s*, H-C(5)); 1.75 (*s*, Me); 0.96 (*s*, *t*-Bu); ^{13}C-NMR (50.3 MHz, $CDCl_3$): 166.4 (*s*); 119.8 (*s*); 72.5 (*d*); 39.1 (*s*); 23.8 (*q*); 18.5 (*q*). IR (Film): 2978, 2880, 1808, 1484, 1252, 1151, 1052, 952, 891. CI-MS: 237 (33, M+), 178 (10), 164 (92), 157 (18), 101 (100), 83 (86). Cis-**16**. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.54 (*s*, H-C(5)); 1.69 (*s*, Me); 1.0 (*s*, *t*-Bu).

2-(*tert*-butyl)-2,5-dimethyl-1,3-dioxolan-4-one 17

Taken from: P. Renaud and S. Abazi, *Helv. Chim. Acta,* 1996, **79**, 1696.

5-Benzyl-2-(*tert*-butyl-)2-methyl-1,3-dioxolan-4-one 18

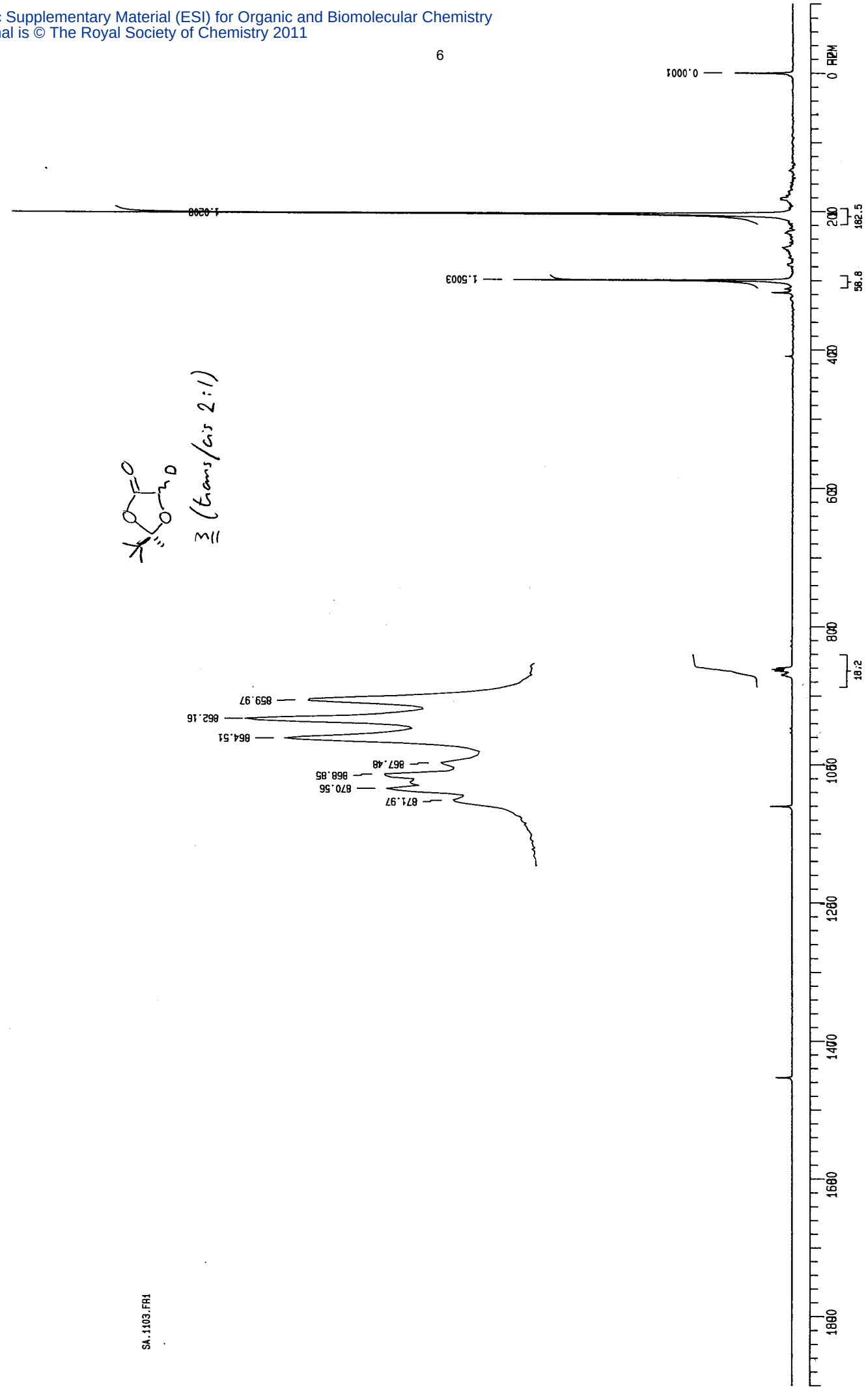
According to the General Procedure 4, from **1** (790 mg, 5.0 mmol) and benzyl bromide (1.71 g, 10 mmol). FC (AcOEt/hexane, 1:20) gave **18** (867 mg, 70%) as a trans/cis 3.6:1 mixture. Trans-**18**: ^{1}H-NMR (360 MHz, $CDCl_3$): 7.28 (*m*, 5 arom. H); 4.66 (*t*, *J* = 4.9, H-C(5)); 3.14 (A part of ABX, J_{AB} = 14, J_{AX} = 4.6, C*H*H); 3.10 (B part of ABX, J_{AB} = 14, J_{BX} = 5.2, CH*H*); 1.04 (*s*, Me); 0.96 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 172.9 (*s*); 135.8 (*s*); 130.1 (*d*); 128.4 (*d*); 127.1 (*d*); 116.6 (*s*); 77.0 (*d*); 40.2 (*d*); 38.6 (*t*); 24.6 (*q*); 22.0 (*q*). Cis-**18**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.29 (*m*, 5 arom. H); 4.59 (*dd*, *J* = 3.9, 8.2, H-C(5)); 3.20 (*dd*, J = 3.9, 14.6, C*H*H); 3.02 (*dd*, J = 8.2, 14.4, CH*H*); 1.45 (*s*, Me); 0.96 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 172.6 (*s*); 136.5 (*s*); 129.4 (*d*); 128.4 (*d*); 126.9 (*d*); 115.5 (*s*); 74.7 (*d*); 38.5 (*d*); 37.2 (*t*); 24.3 (*q*); 19.3 (*q*). Trans/cis-**18**: IR (Film): 2975, 2878, 1791, 1254, 1149, 1104, 926, 700. CI-MS: 249 (48, $[M+1]^+$), 223 (3), 191 (21), 177 (18), 149 (100), 131 (11). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.64, H 8.18.

2-(*tert*-Butyl)-5-(1-hydroxy-1-methylethyl)-2-methyl-1,3-dioxolan-4-one 19

According to the General Procedure 4, from **1** (790 mg, 5.0 mmol) and acetone (2.9 g, 50 mmol). The reaction mixture was stirred for 15 min at –78 °C and a sat. aq. $NaHCO_3$ (10 ml) soln. was added to the cold solution. FC (AcOEt/hexane, 1:10) gave **19** (922 mg, 85%) as a trans/cis 3.8:1 mixture that could not be separated. Trans/cis-**19**: ^{1}H-NMR (200 MHz, $CDCl_3$): 4.17 (*s*, H-C(5), cis); 4.15 (*s*, H-C(5), trans); 2.81 (*s*, OH, cis); 2.58 (*s*, OH, trans); 1.54 (*s*, Me, trans); 1.47 (*s*, Me, trans); 1.34 and 1.29 (2*s*, $(Me)_2C$, cis); 1.33 and 1.29 (2*s*, $(Me)_2C$, trans); 1.02 (*s*, *t*-Bu, cis); 0.98 (*s*, *t*-Bu, trans). ^{13}C-NMR (50.3 MHz, $CDCl_3$): trans: 171.7 (*s*); 116.1 (*s*); 82.1 (*d*); 71.4 (*s*); 40.5 (*s*); 25.2 (*q*); 24.4 (*q*); 21.9 (*q*); cis: 172.0 (*s*); 114.1 (*s*); 79.2 (*d*); 71.1 (*s*); 37.8 (*s*); 25.7 (*q*); 24.6 (*q*); 18.7 (*q*). IR (Film): 3540, 3534, 2980, 2881, 1770, 1365, 1319, 1140, 970, 961. CI-MS: 217 (100, $[M+1]^+$); 199 (72), 171 (22), 155 (33), 101 (56), 71 (16). Anal. calc. for $C_{11}H_{20}O_4$ (216.28): C 61.09, H 9.32; found: C 61.00, H 9.55.

5-Benzyl-2-(*tert*-butyl)-2,5-dimethyl-1,3-dioxolan-4-one 20

According to the General Procedure 4, from **17** (516 mg, 3.0 mmol) and benzyl bromide (1.02 g, 6.0 mmol). FC (AcOEt/hexane, 1:20) gave **20** (668 mg, 85%) as a trans/cis 16:1 mixture. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.3 (*m*, 5 arom. H); 3.2 (*d*, J = 14, CH*H*Ph); 2.9 (*d*, J_{AB} = 14, C*H*HPh); 1.39 (*s*, Me-C(2)); 1.27 (*s*, Me-C(5)); 0.98 (*s*, *t*-Bu). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 175.6 (*s*); 135.4 (*s*); 130.6 (*d*); 128.3 (*d*); 127.0 (*d*); 114.9 (*s*); 80.5 (*s*); 44.8 (*t*); 38.8 (*s*); 24.8 (*q*); 23.3 (*q*); 22.5 (*q*). IR (Film): 2979, 2965, 1789, 1377, 1285, 1152, 931, 699. CI-MS: 163 (100, $[M+1]^+$), 205 (26), 163 (98), 135 (52), 101 (76). Anal. calc. for $C_{16}H_{22}O_3$ (262.35): C 73.25, H 8.43; found: C 72.93, H 8.56.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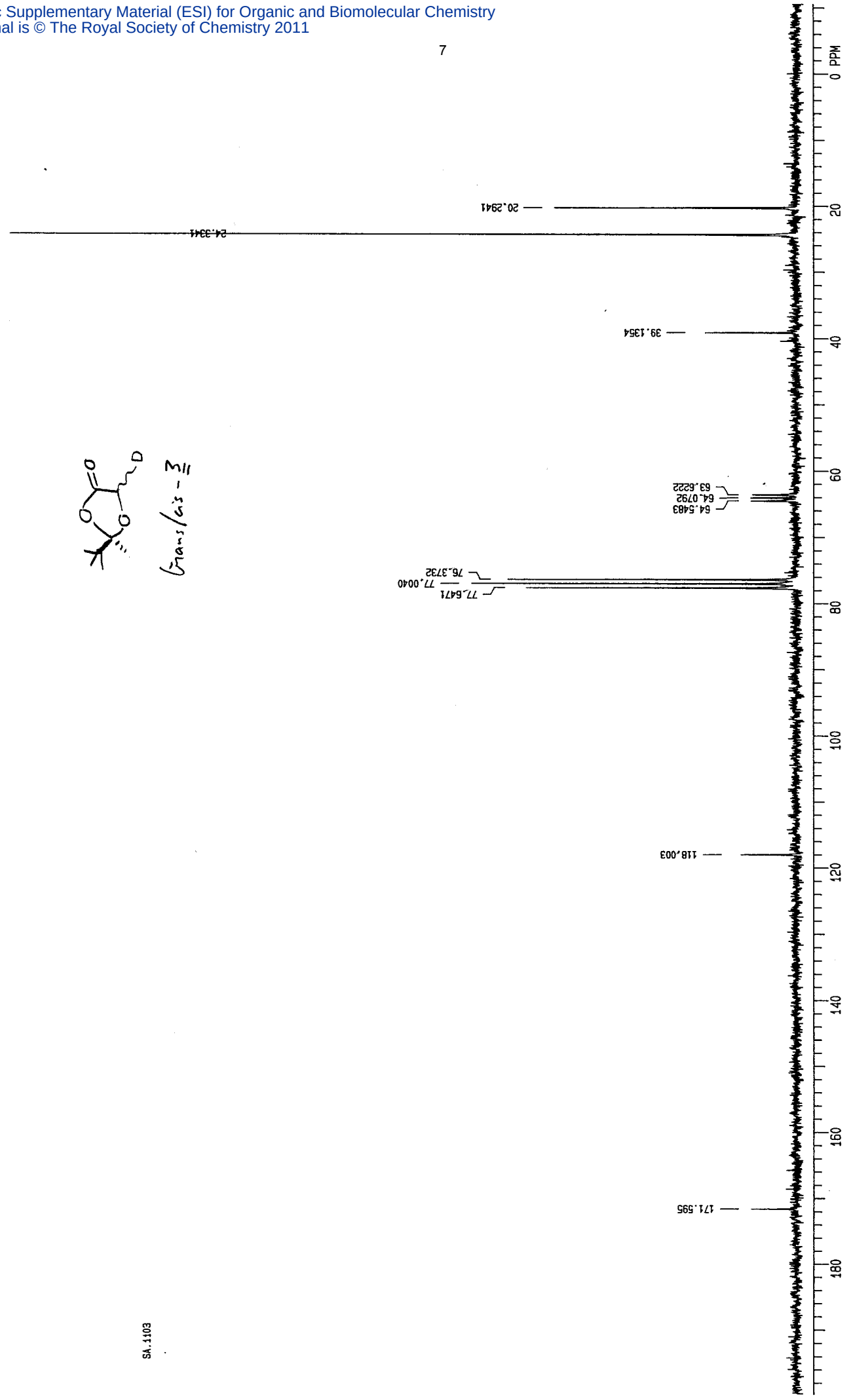
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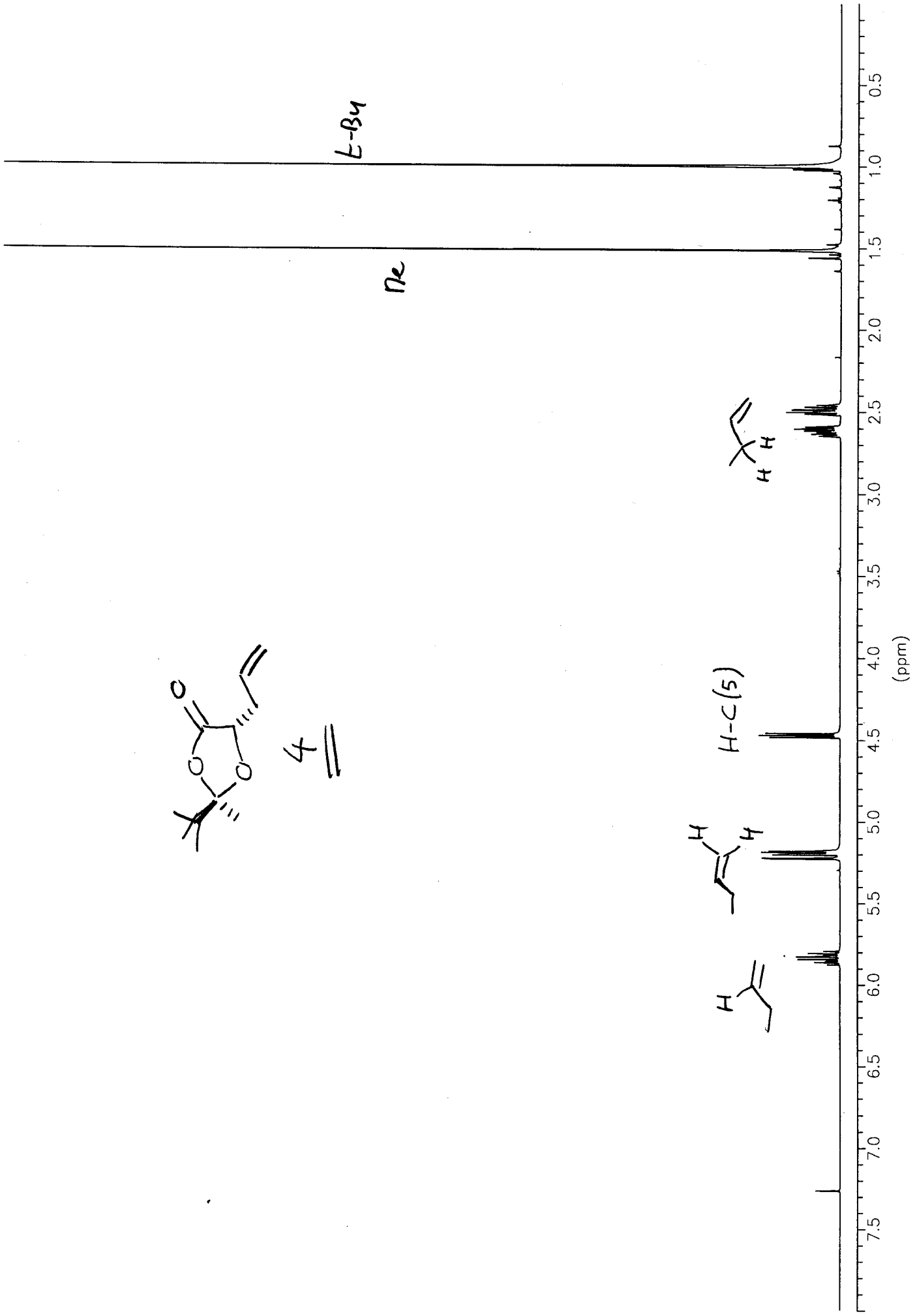
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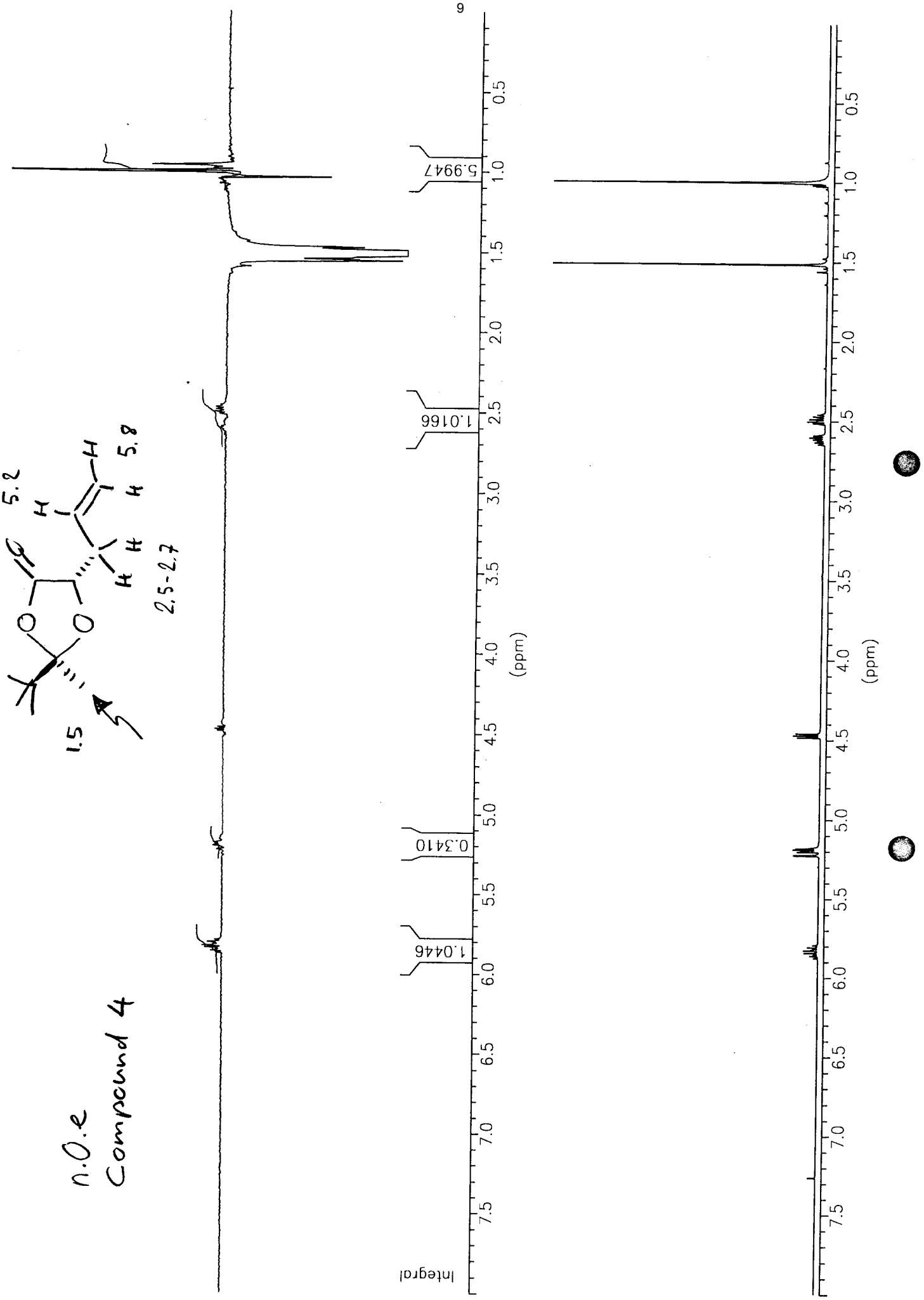

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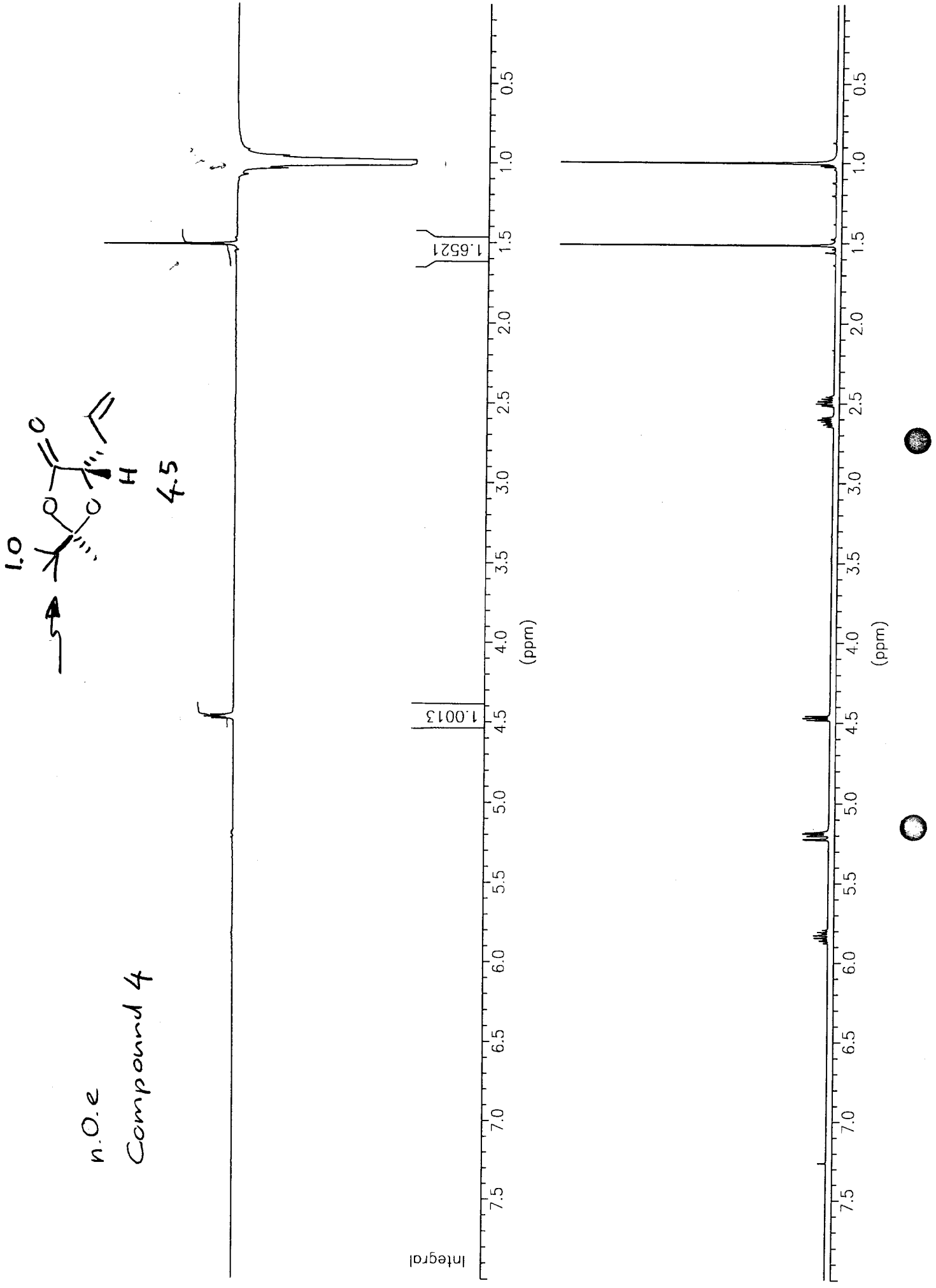
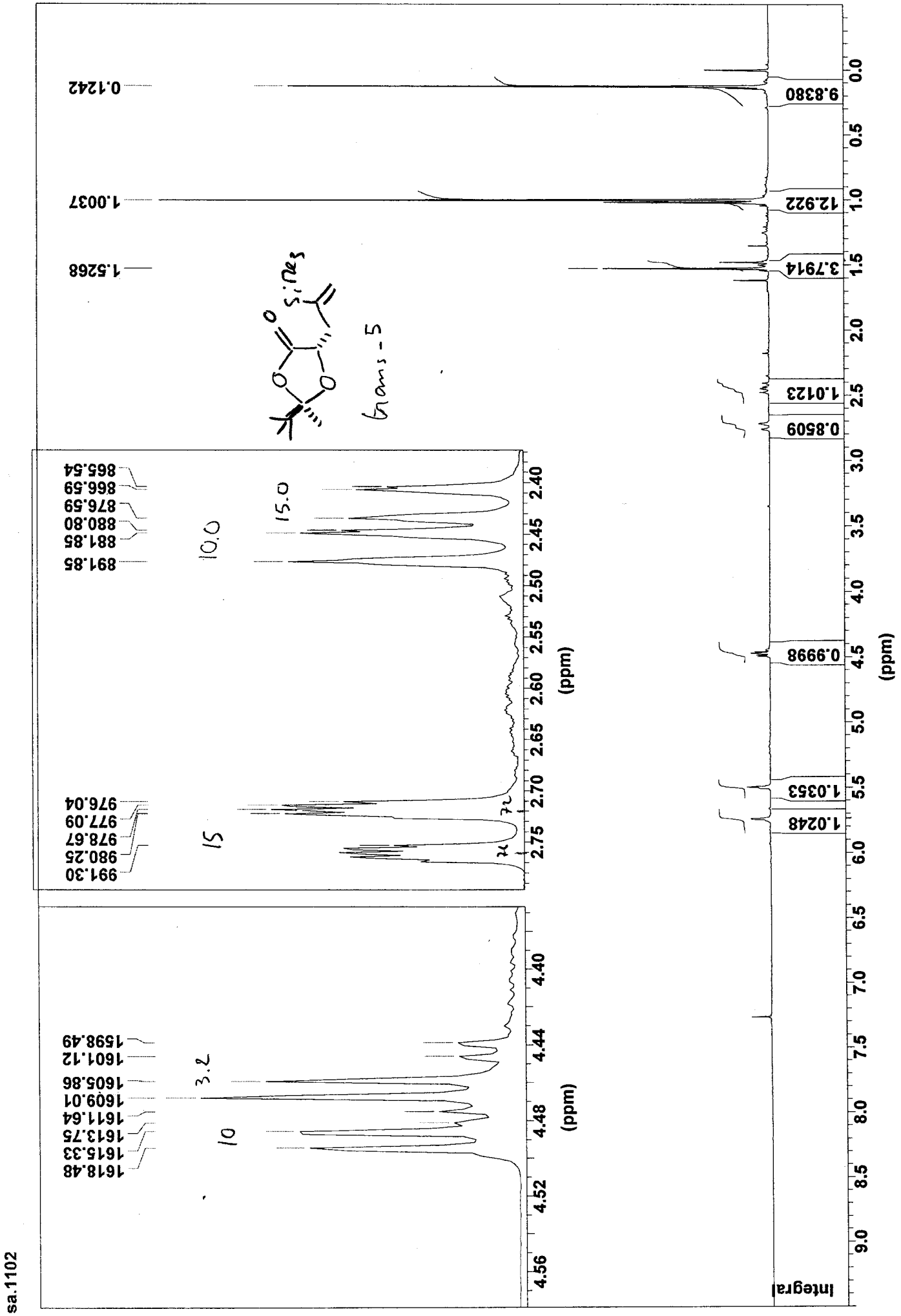
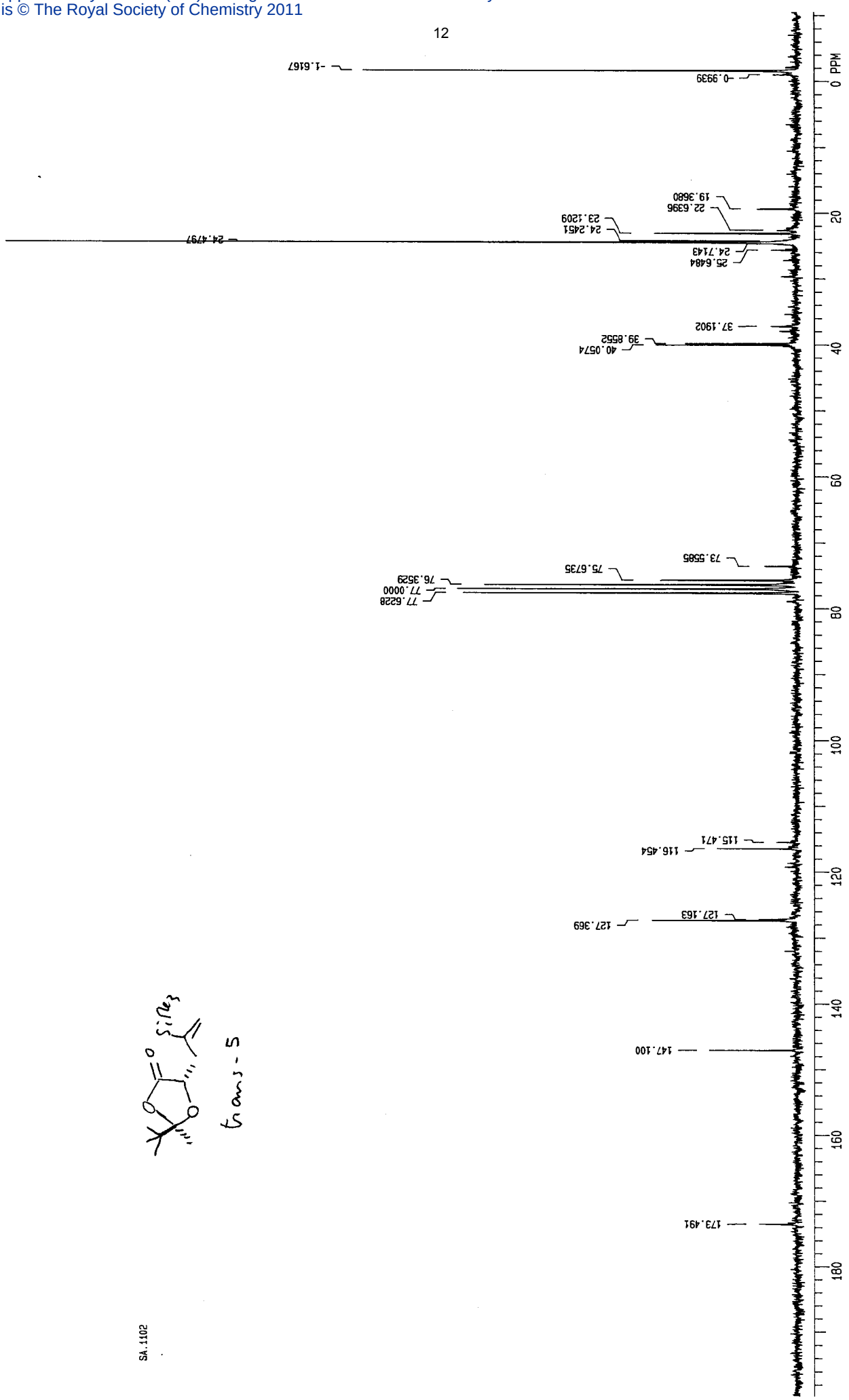
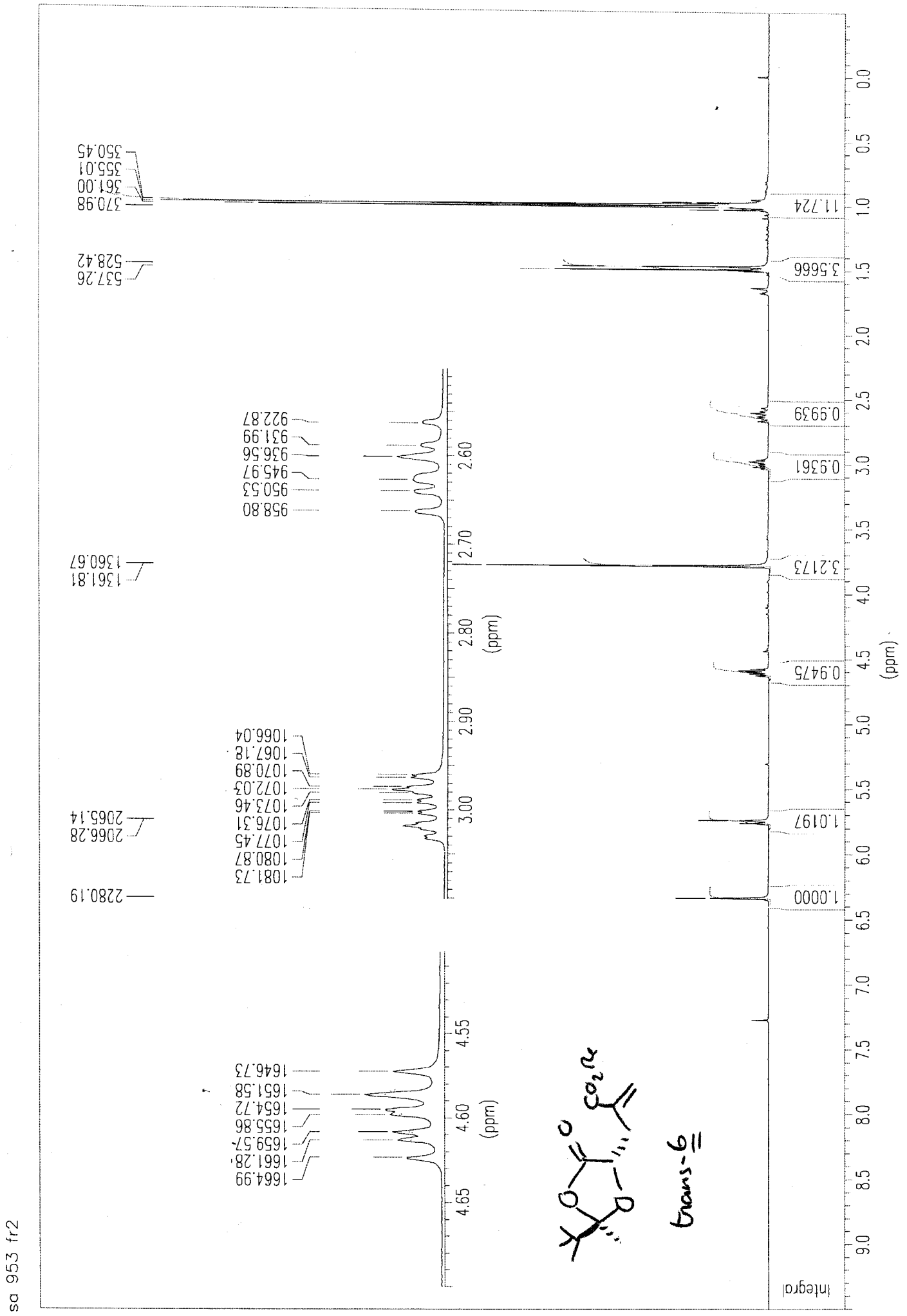
Compound 4





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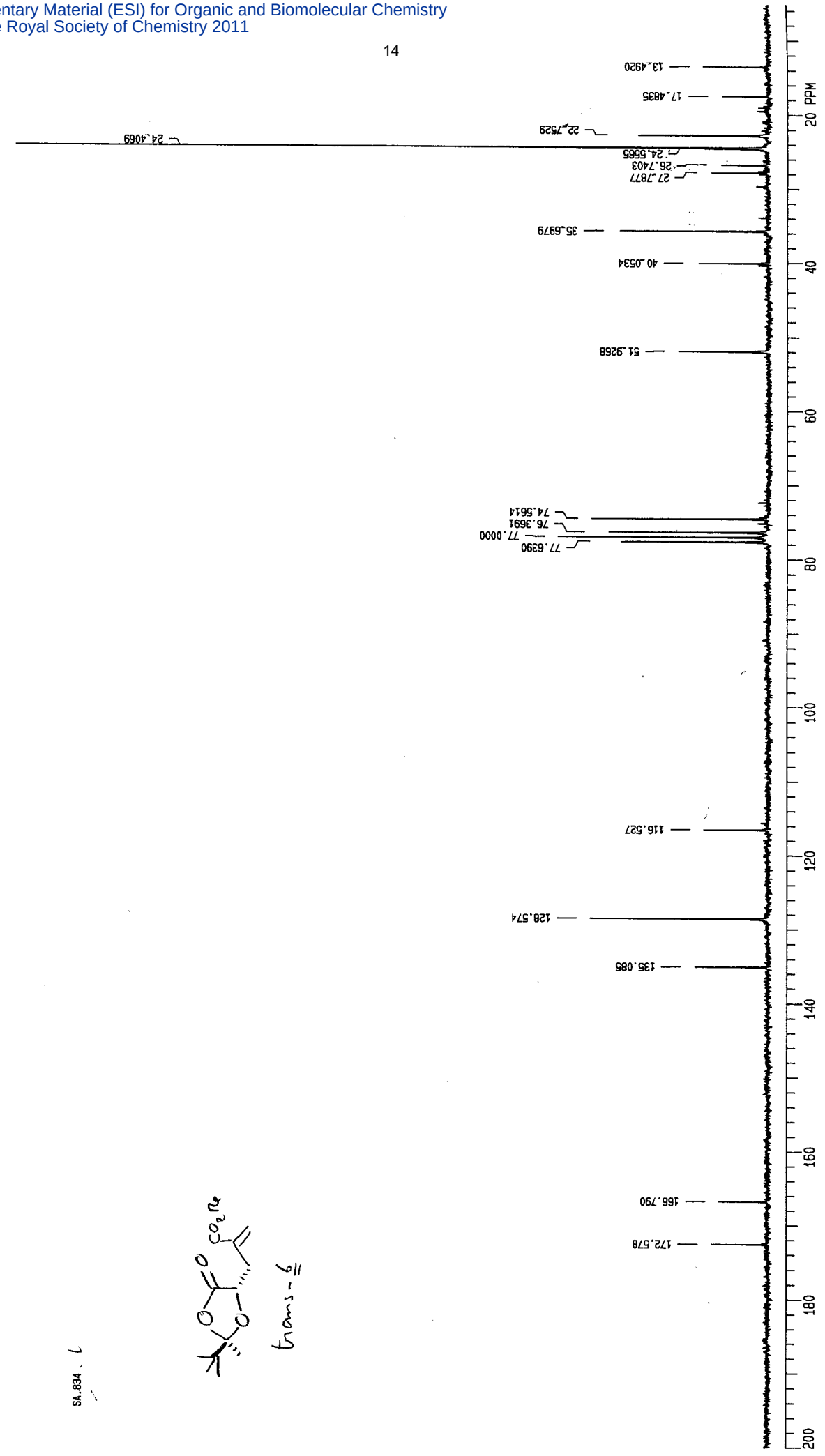

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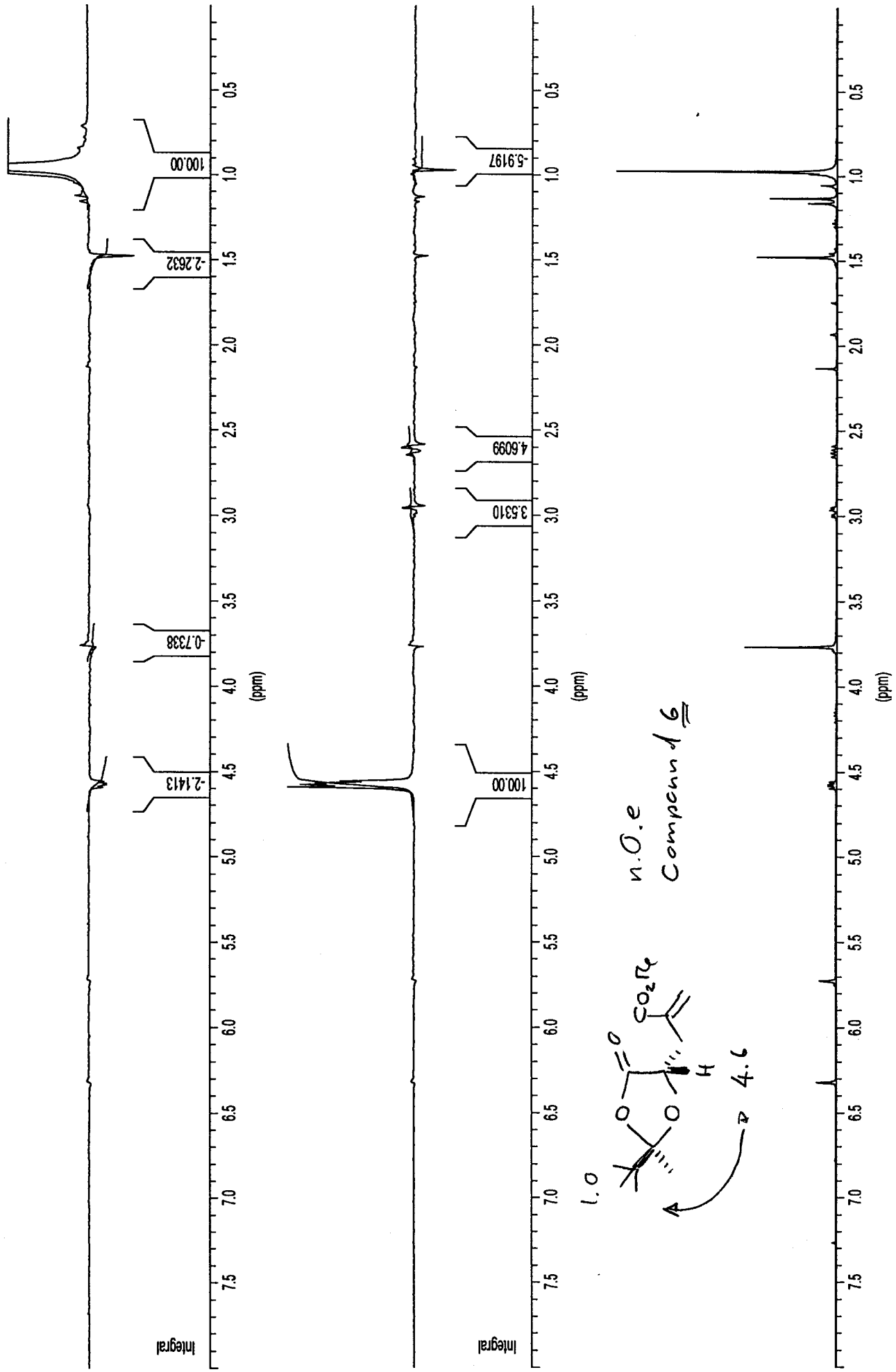

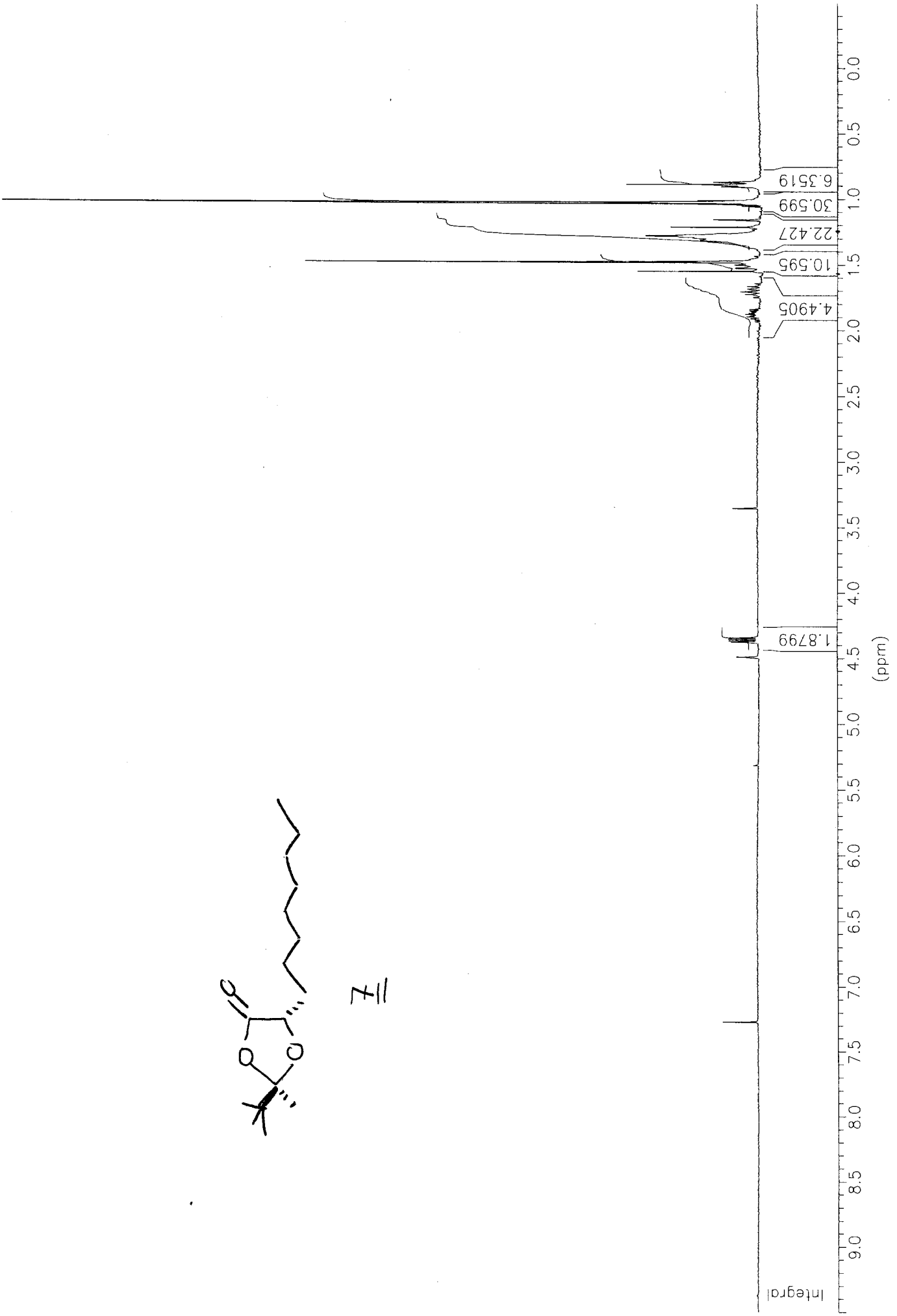

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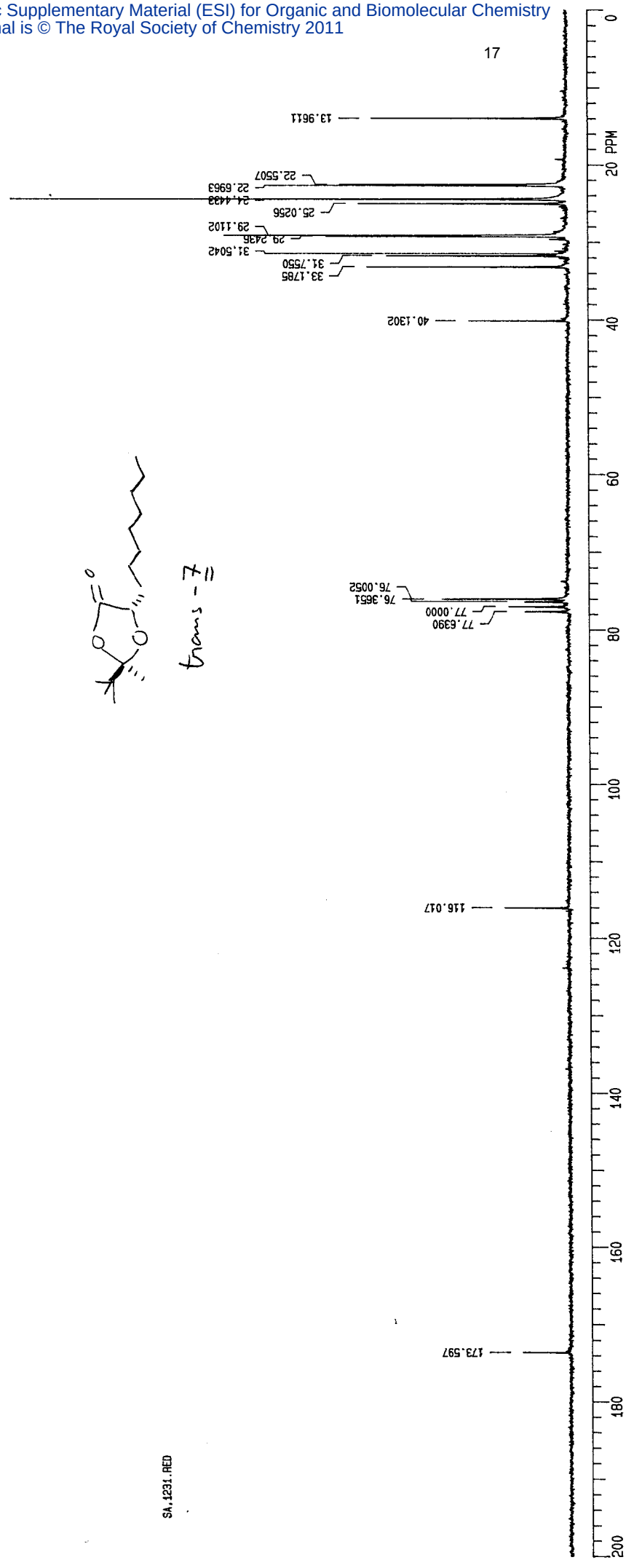
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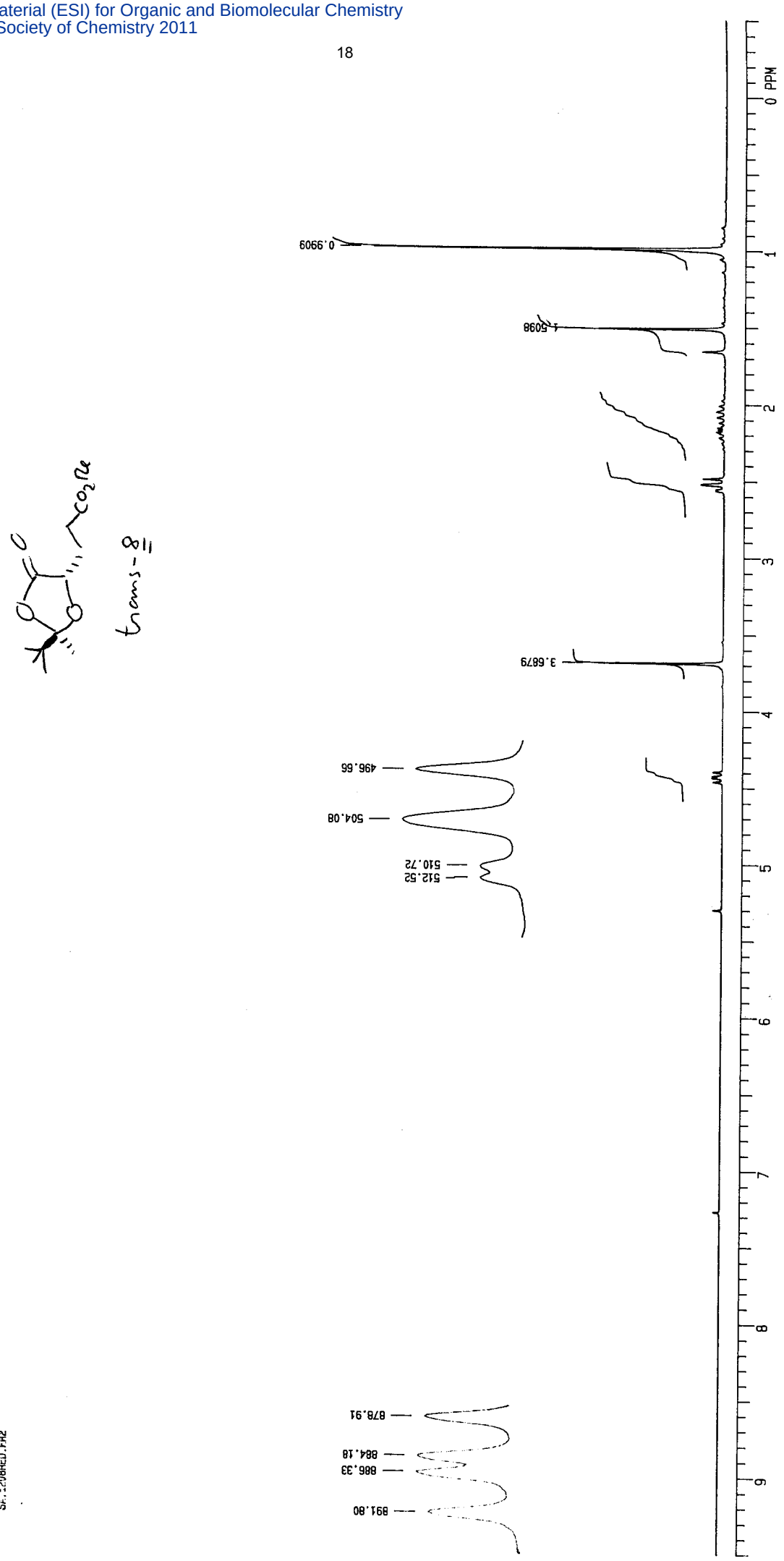
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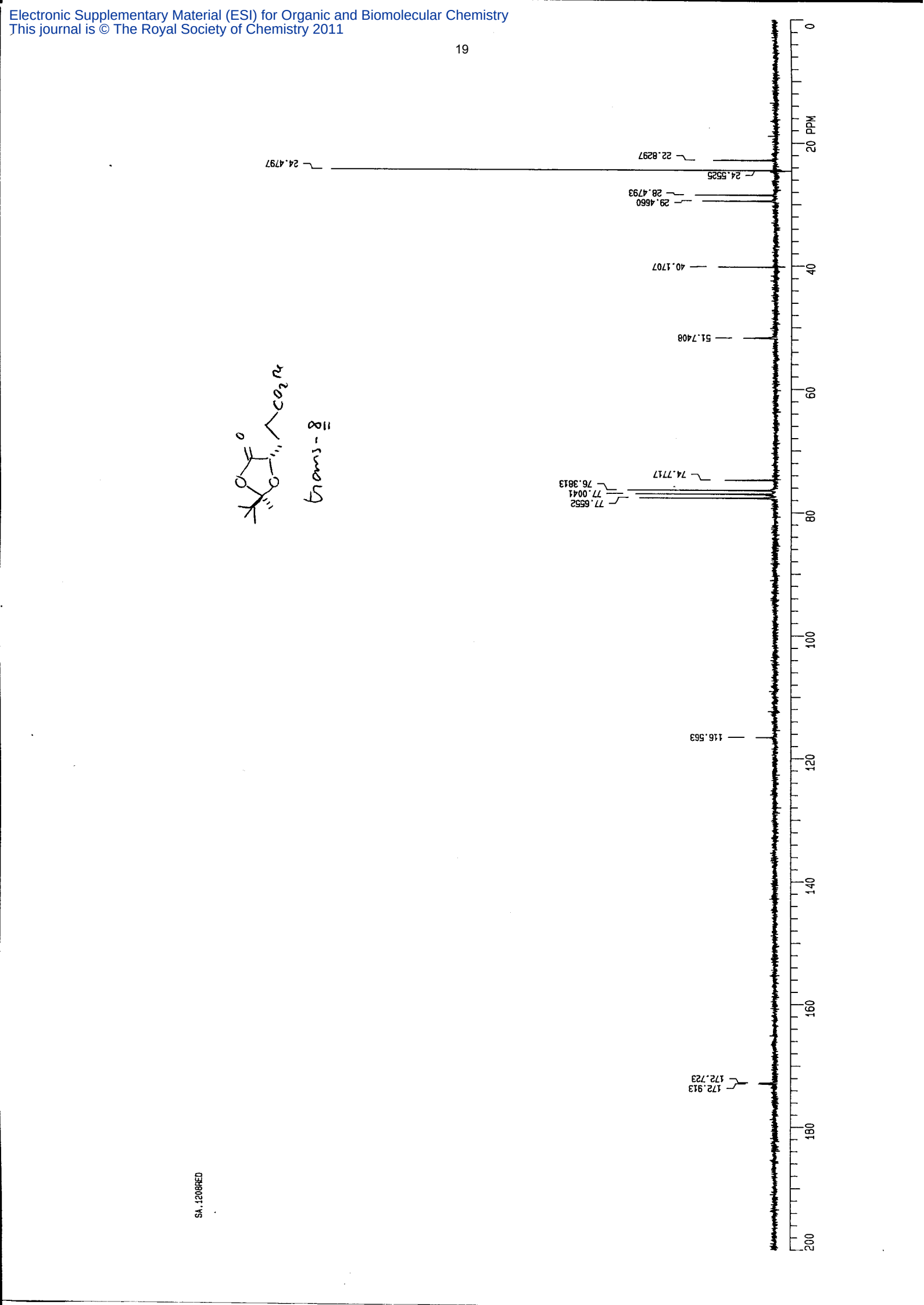
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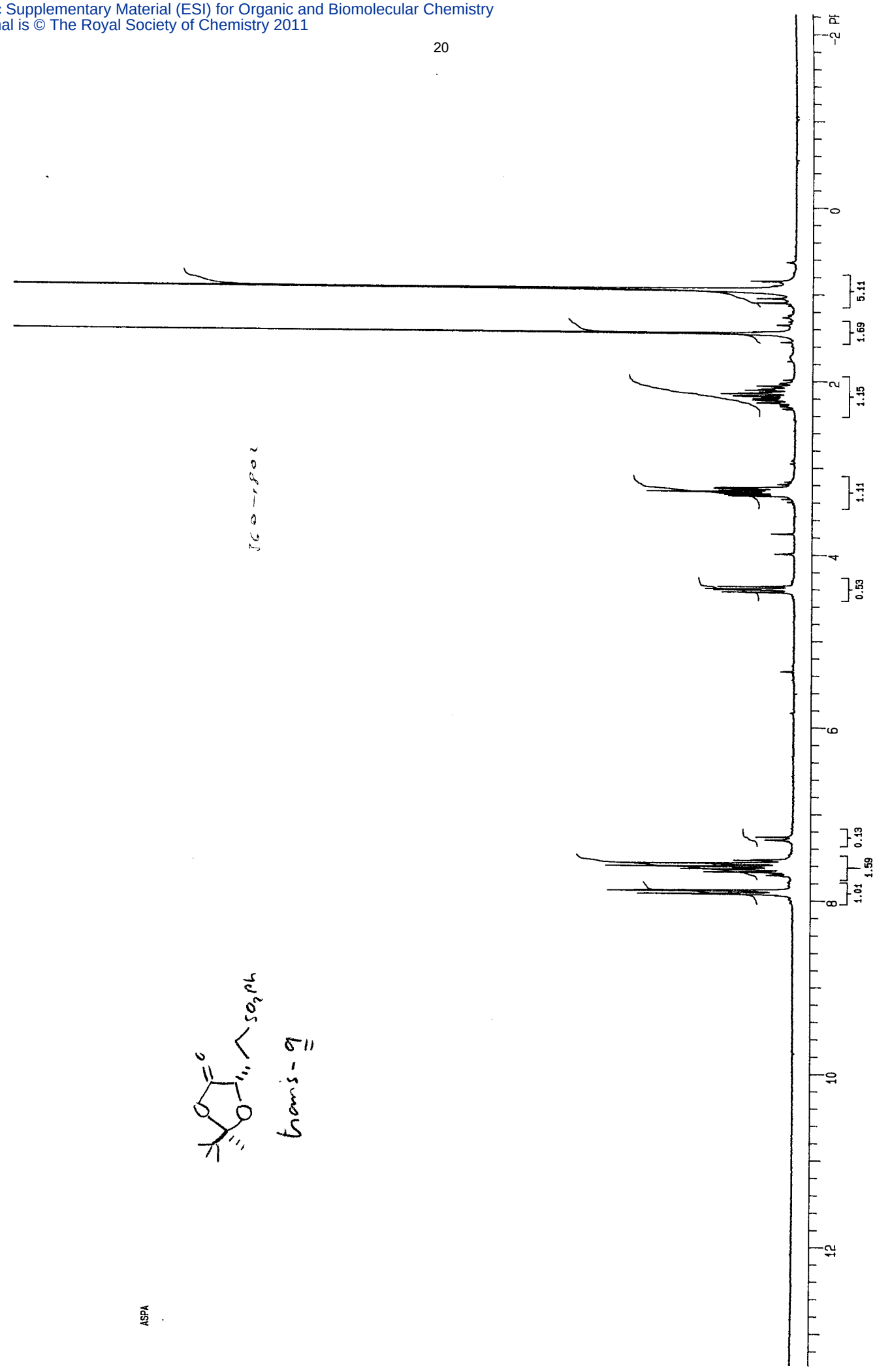

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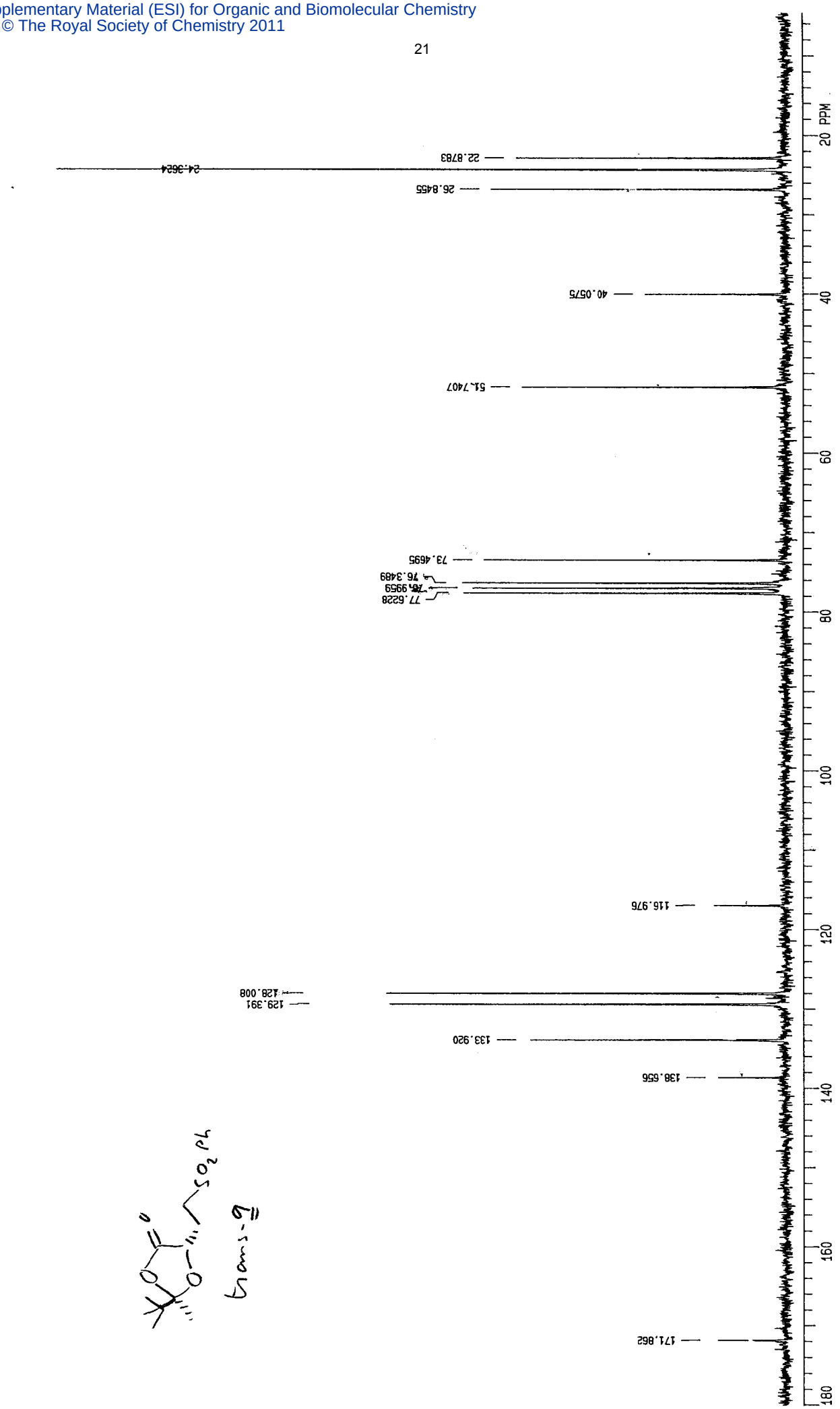
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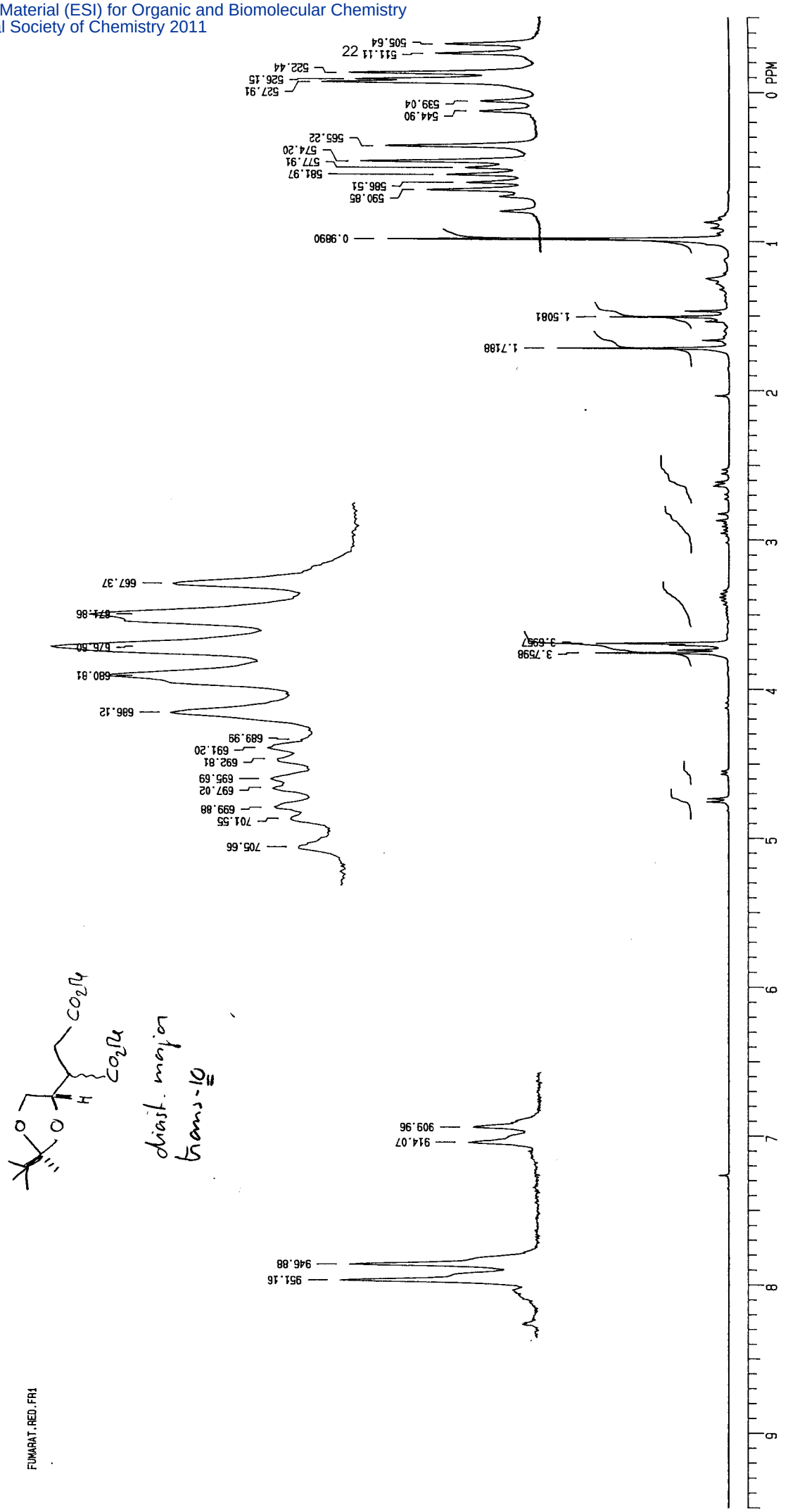

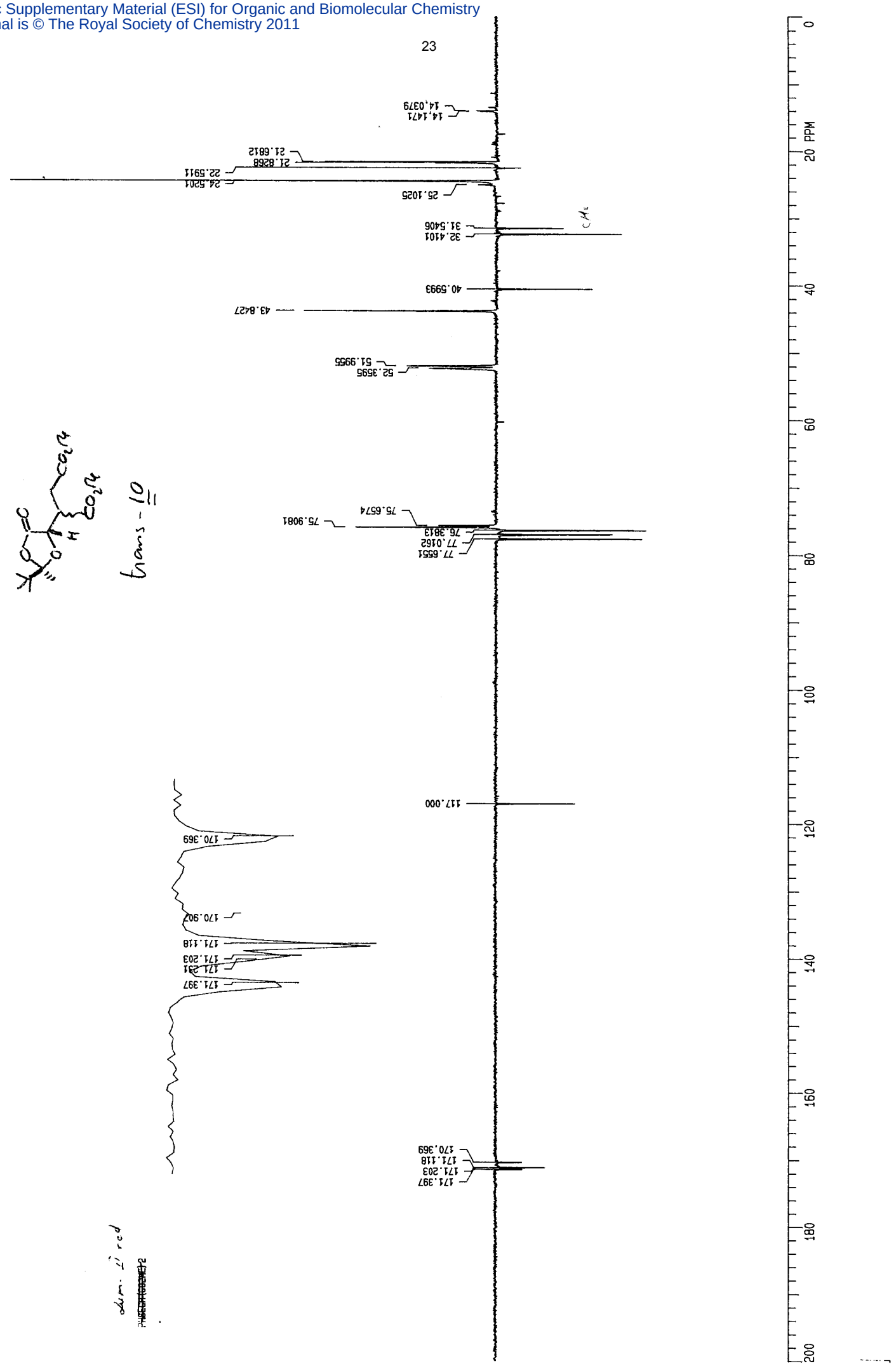
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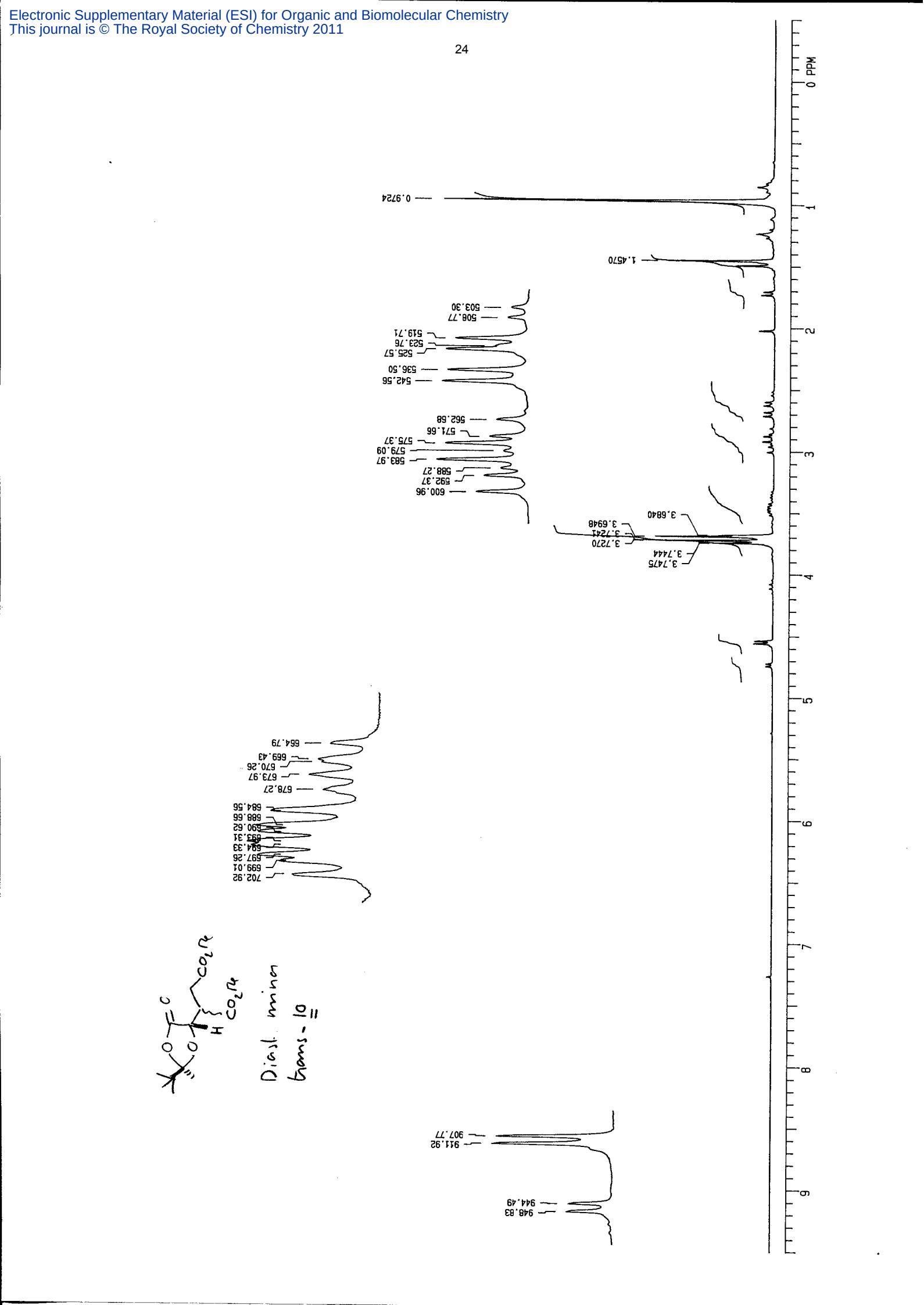
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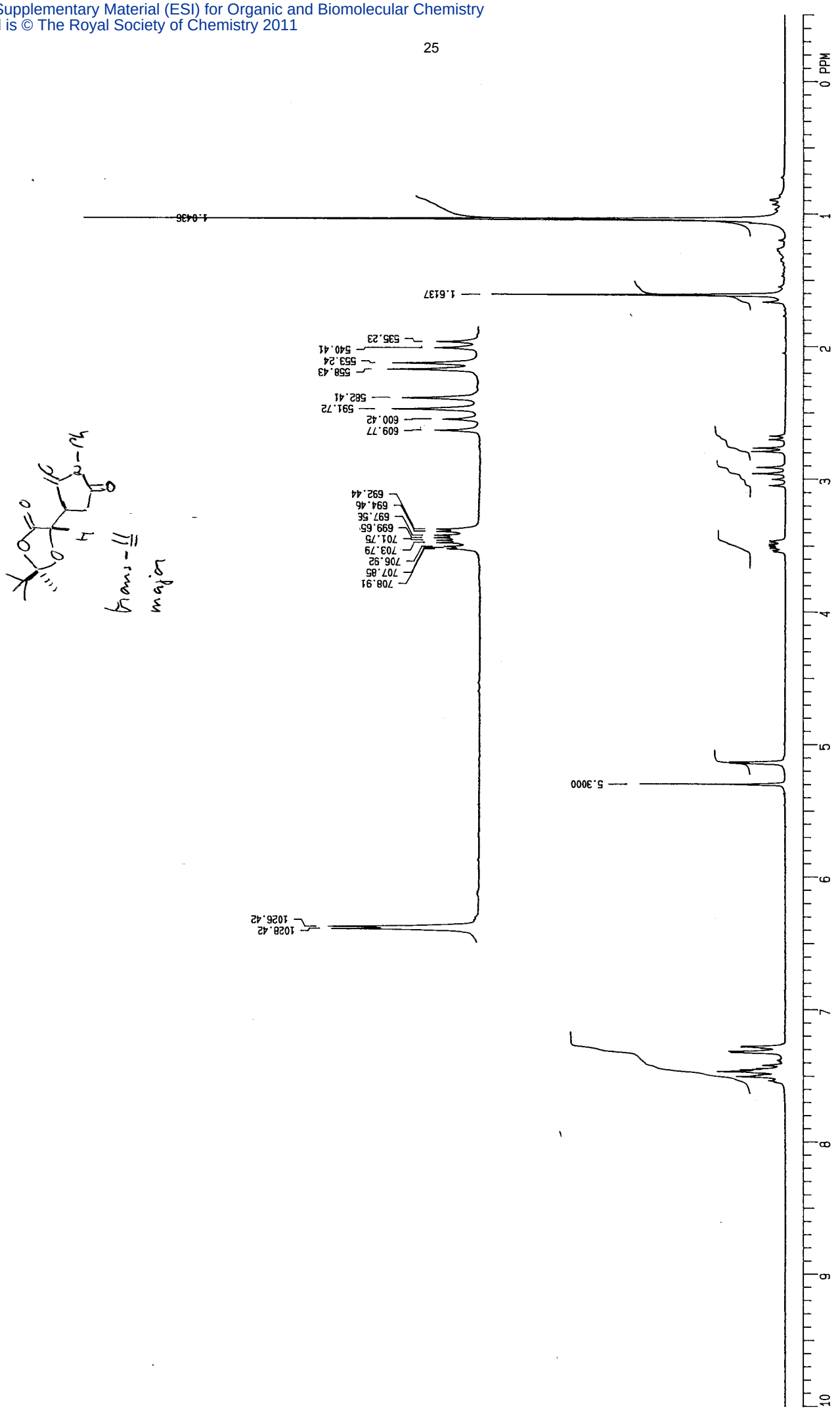
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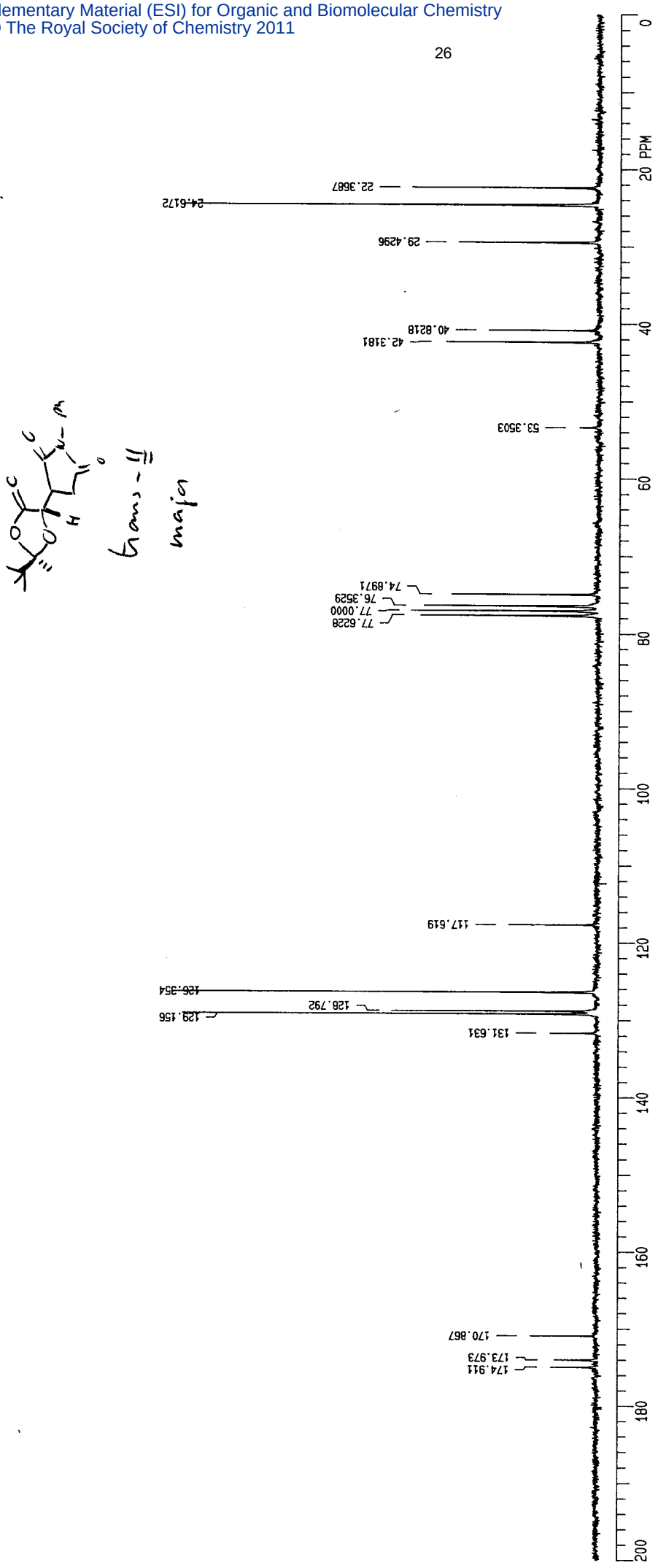
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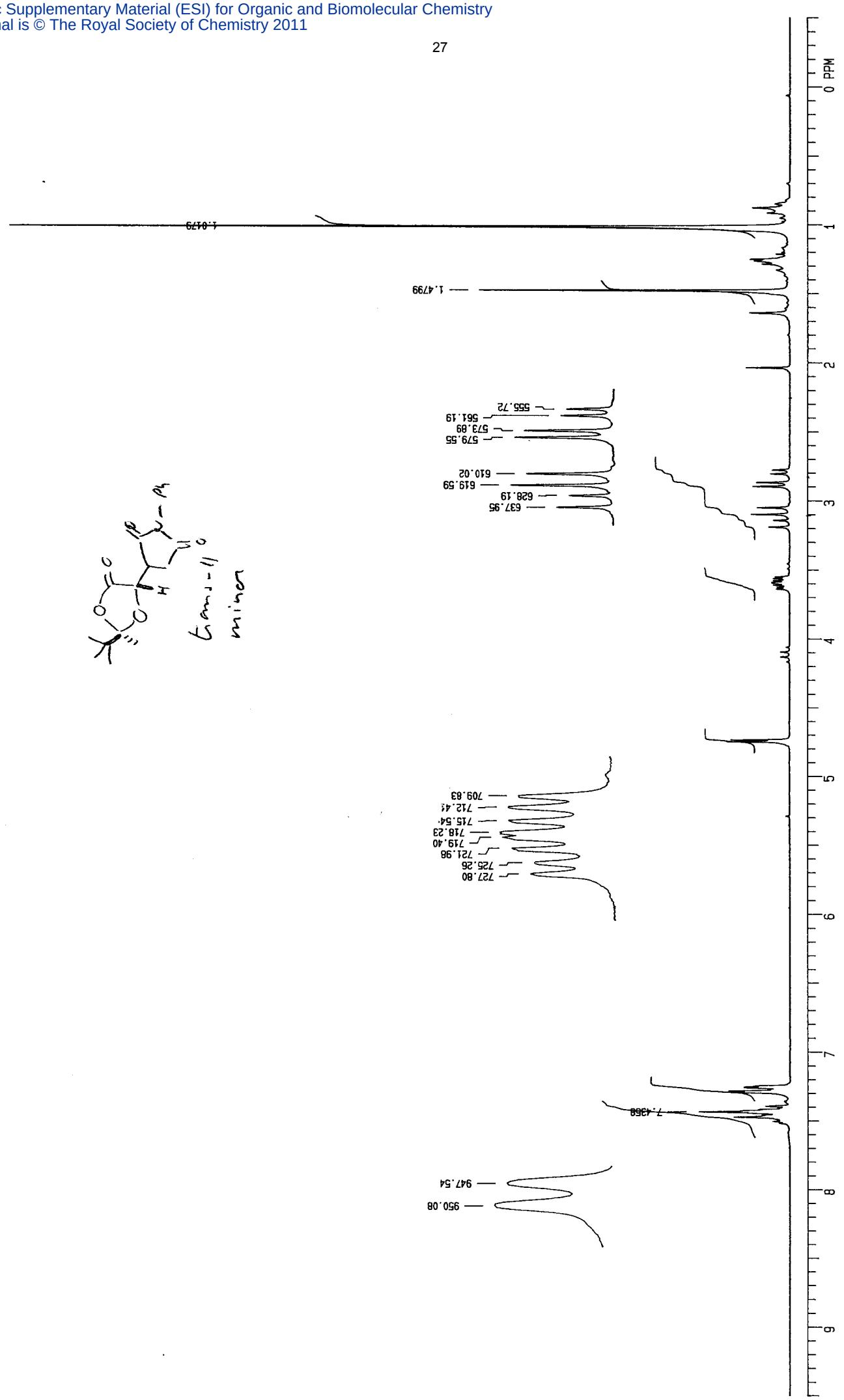
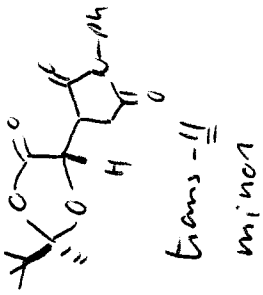
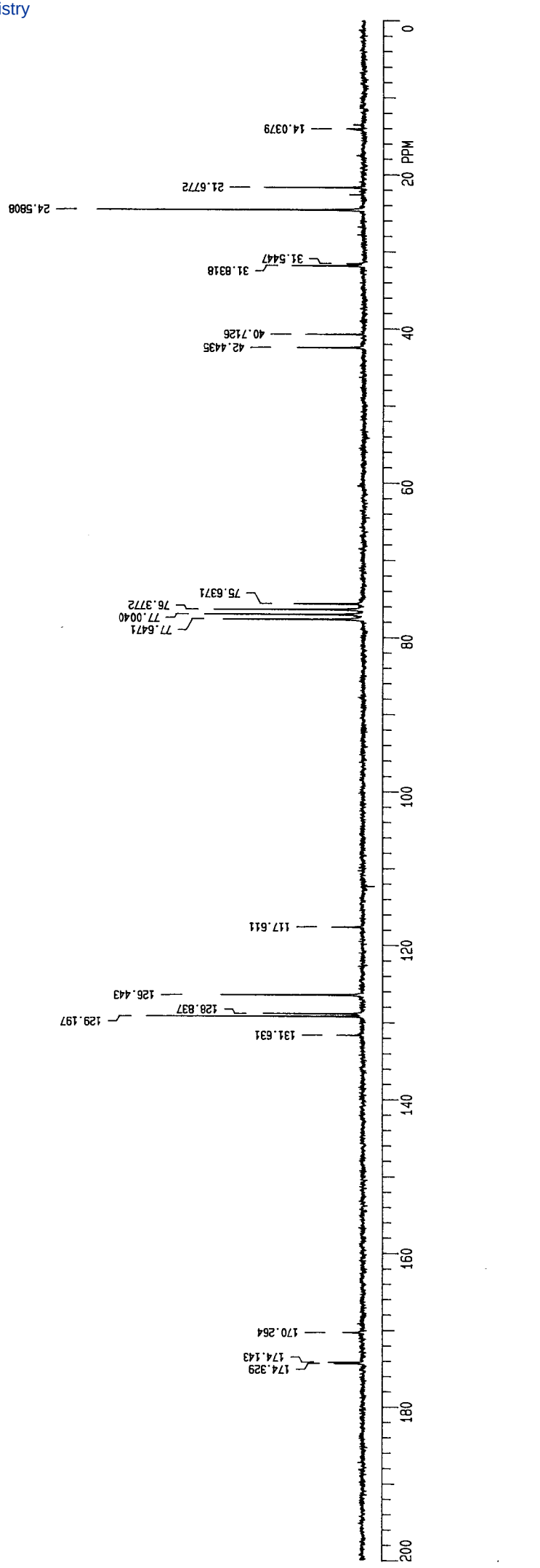
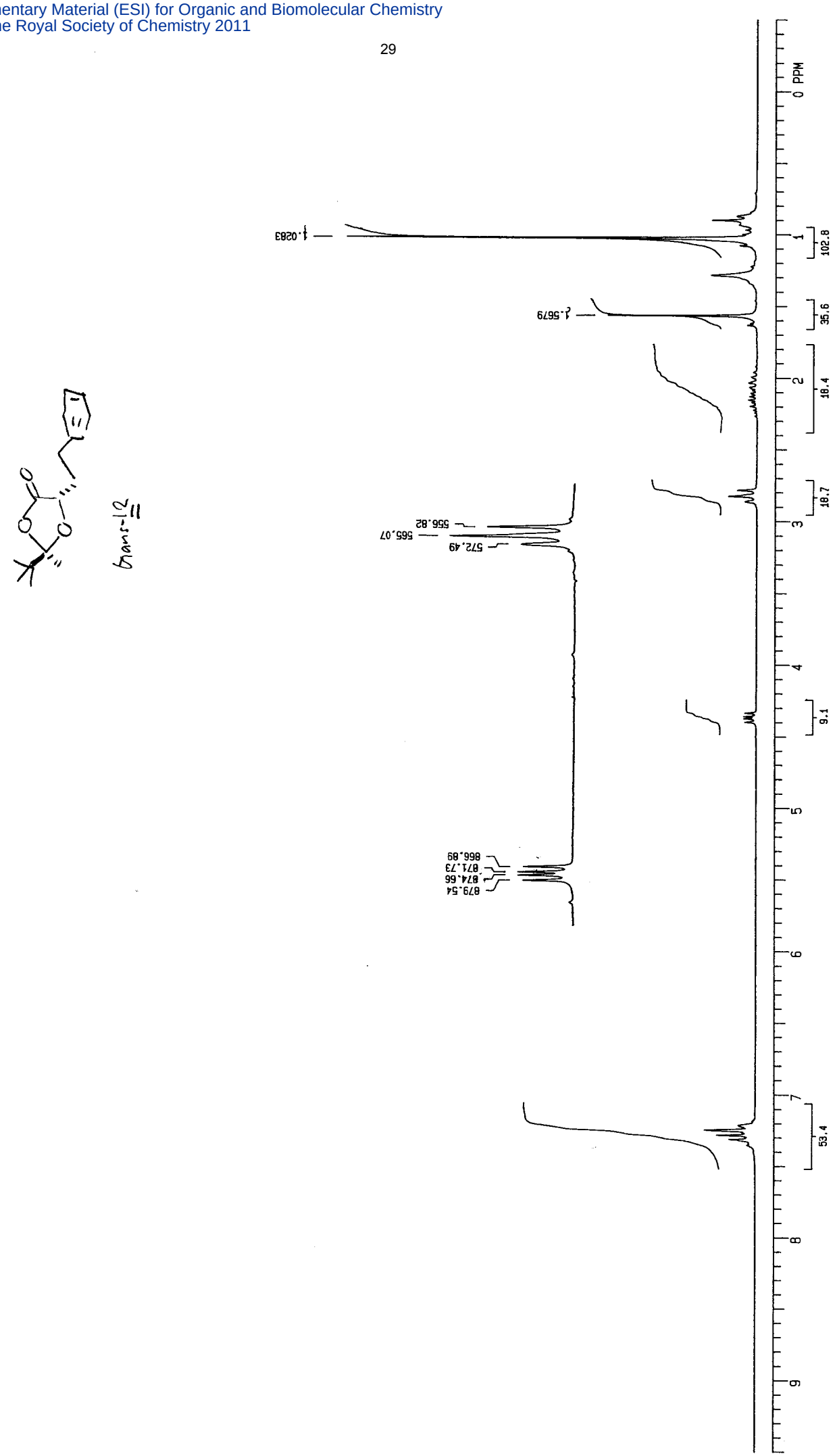
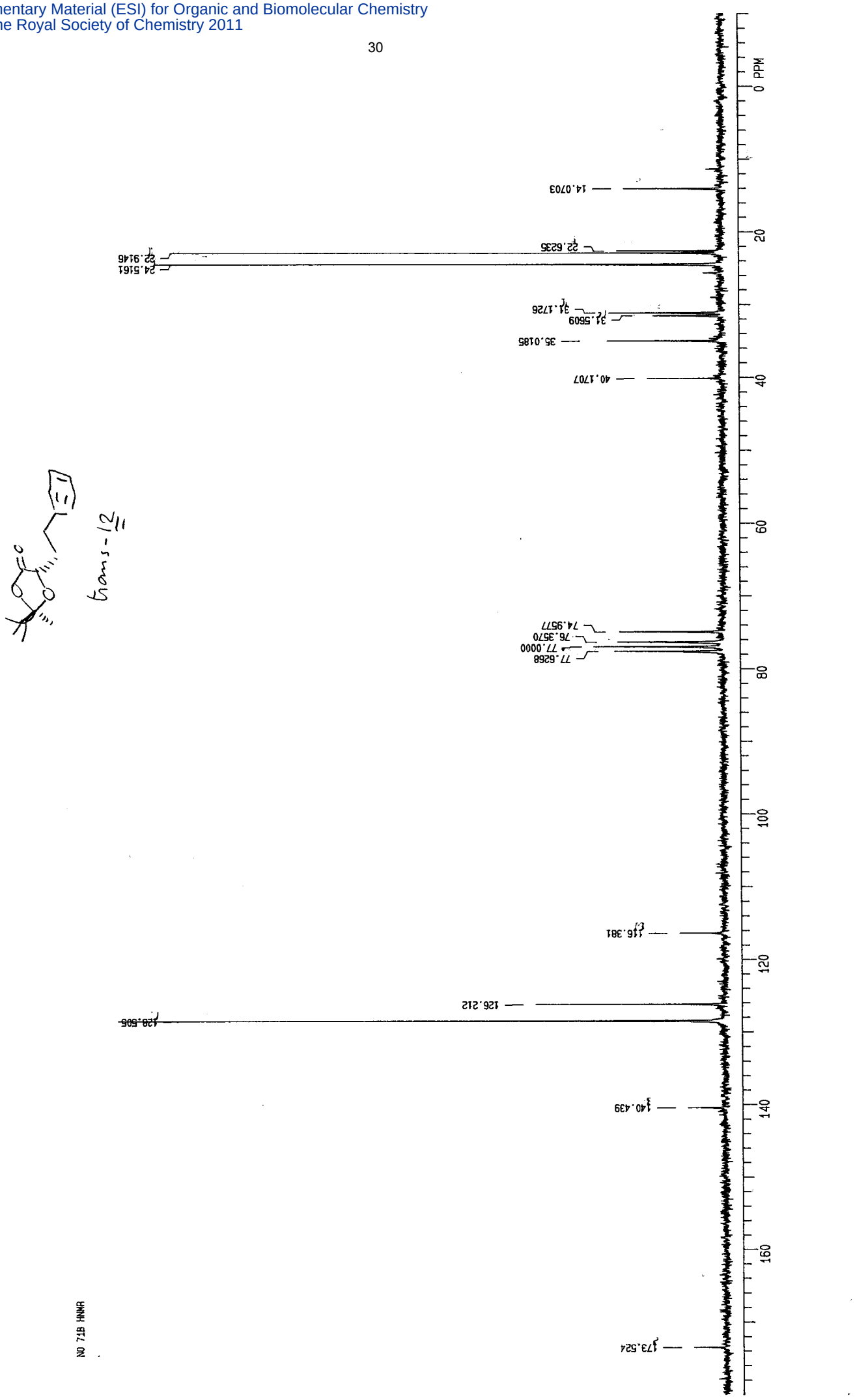
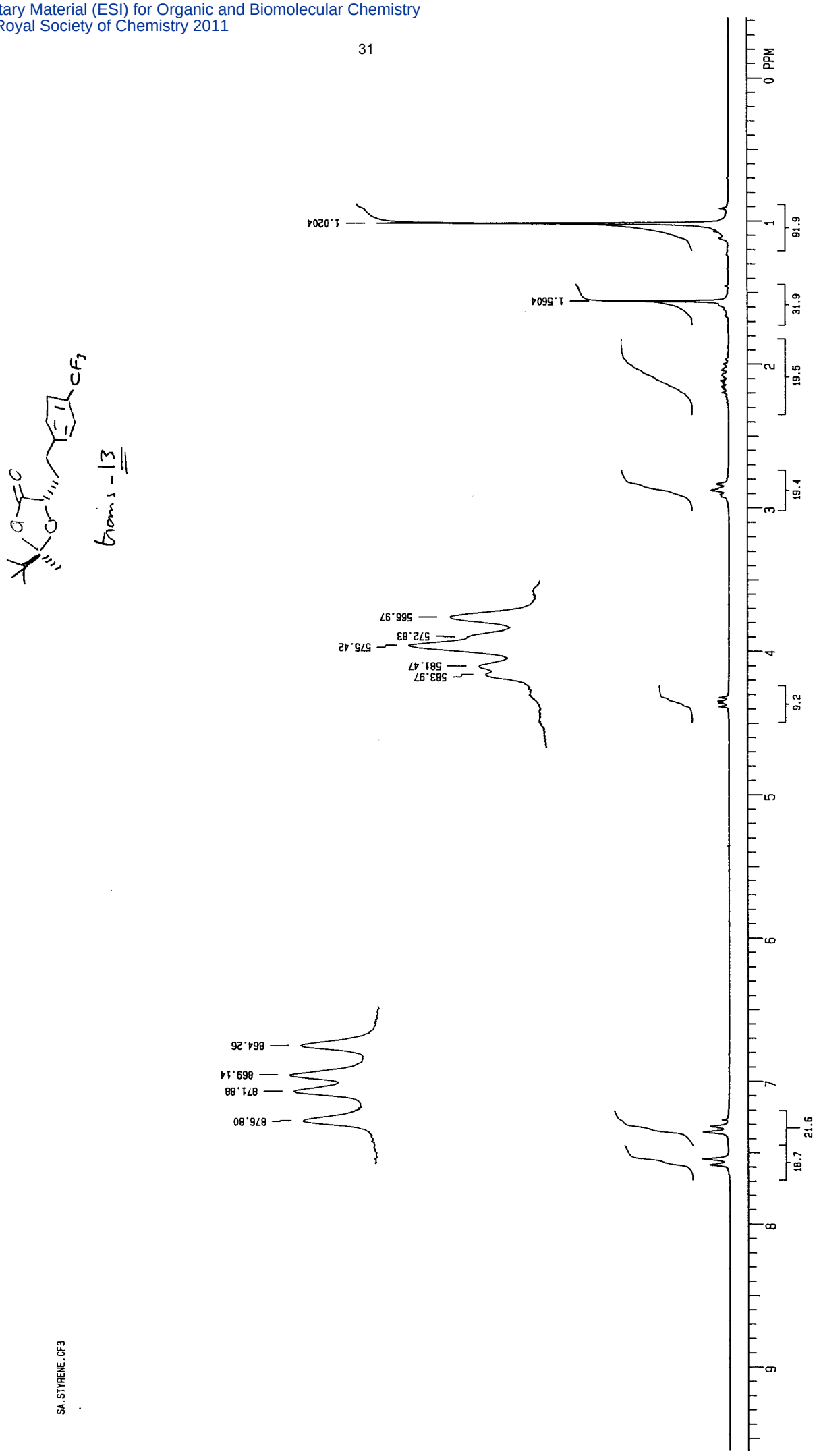

1.0179
1.4799
555.72
561.19
573.89
579.55
610.02
619.59
628.19
637.95
709.83
712.41
715.54
718.23
719.40
721.98
725.26
727.80
947.54
950.08
7.4368
0 PPM
1
2
3
4
5
6
7
8
9
trans-II
minor

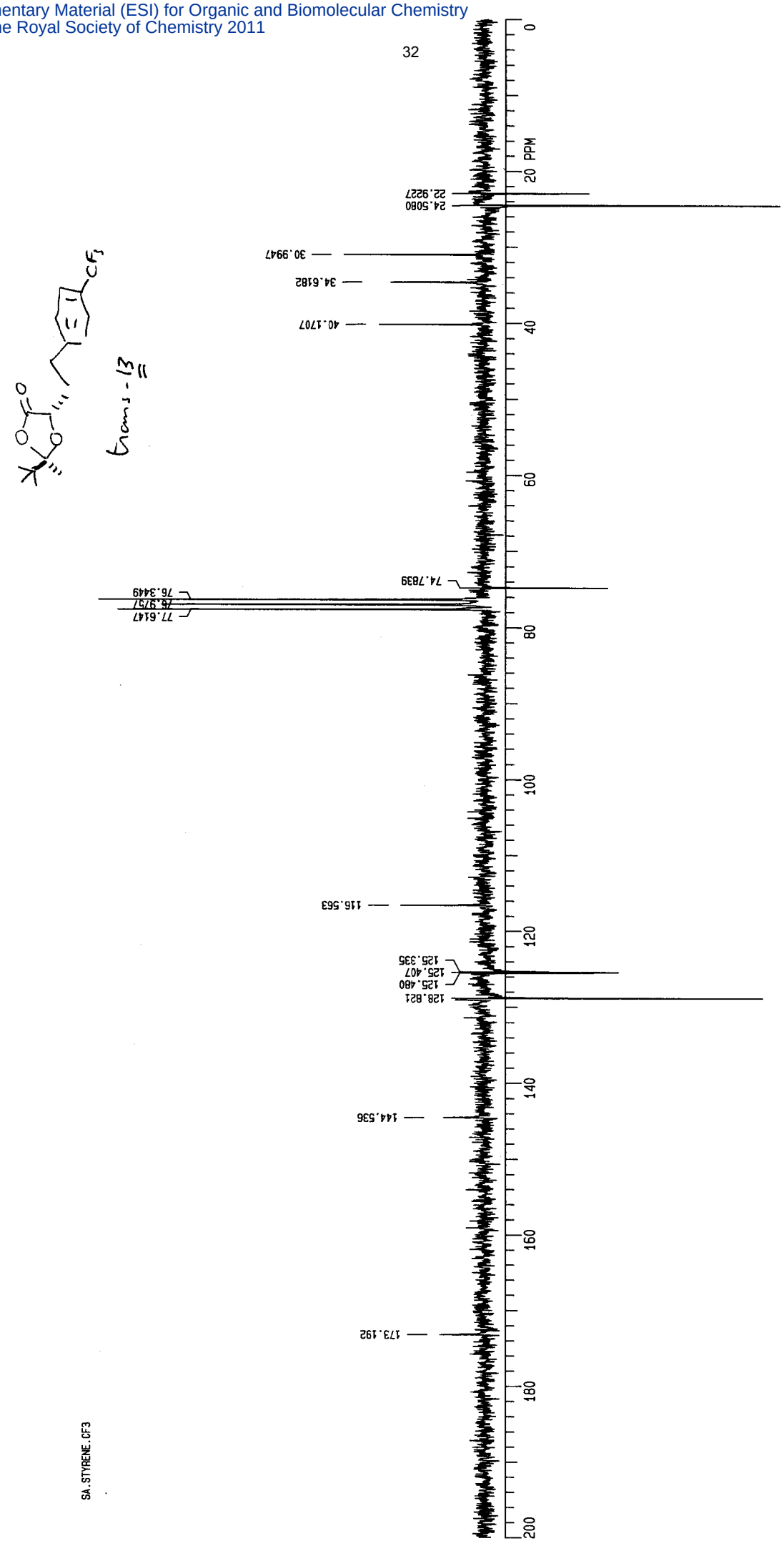

trans-II
major

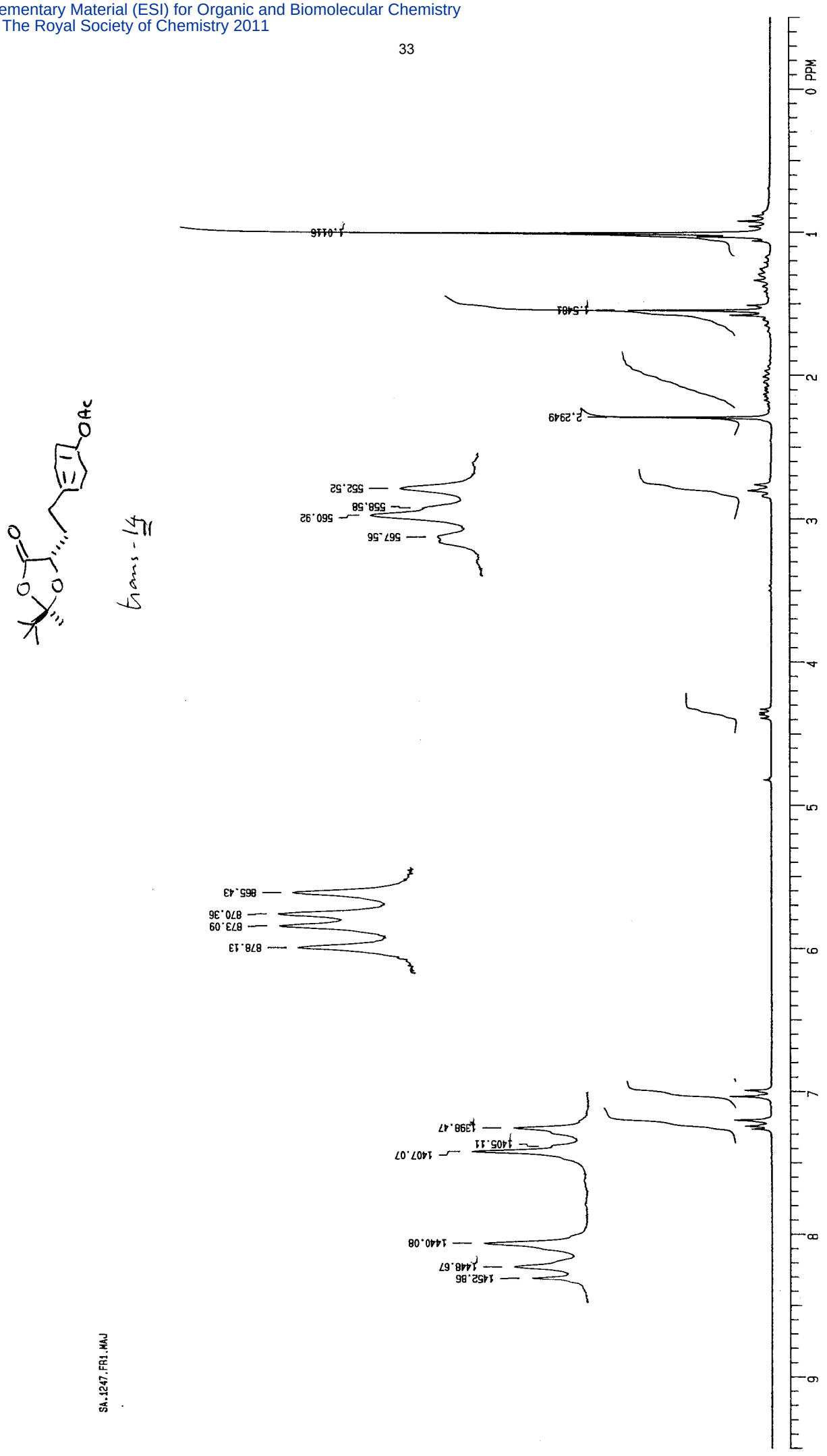

14.0379
21.6772
24.5808
31.5447
31.8318
40.7126
42.4435
75.6371
76.3772
77.0040
77.6471
117.611
126.443
128.837
129.197
131.631
170.264
174.329
174.143
0
20 PPM
40
60
80
100
120
140
160
180
200

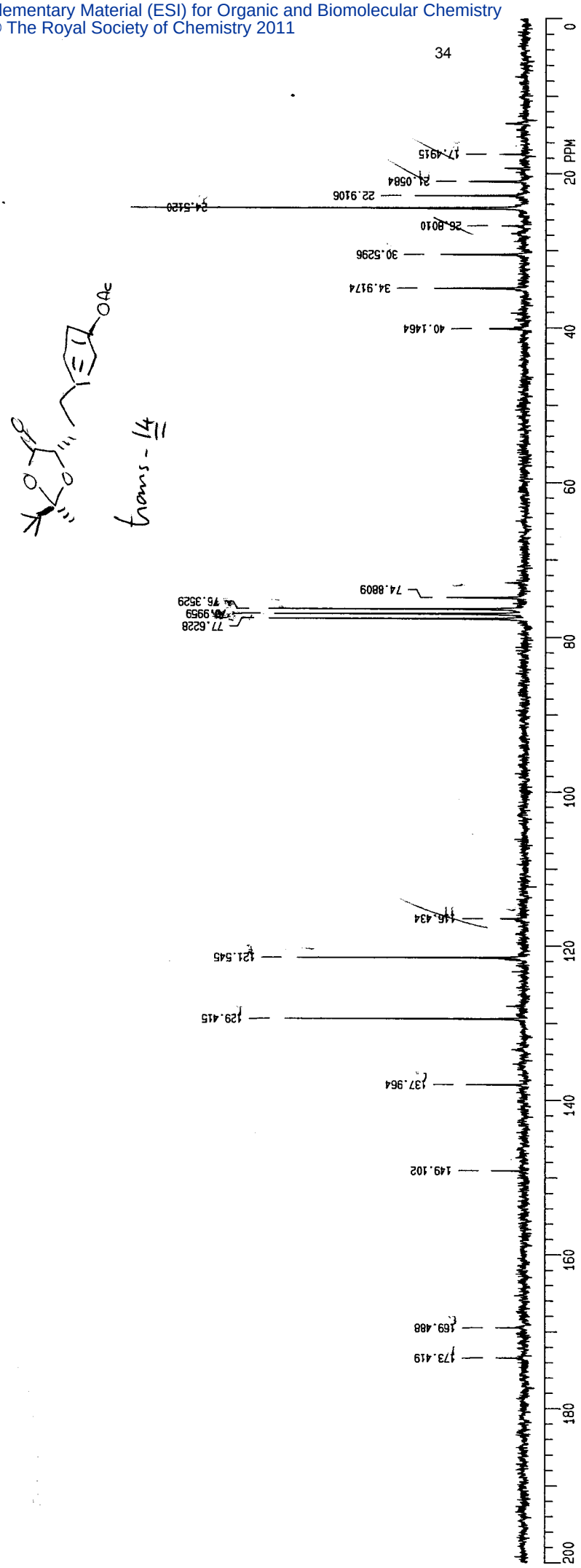

trans-12
1.0283
2.5679
572.49
565.07
556.82
879.54
874.66
871.73
866.89
0 PPM
1
2
3
4
5
6
7
8
9
102.8
35.6
18.4
18.7
9.1
53.4

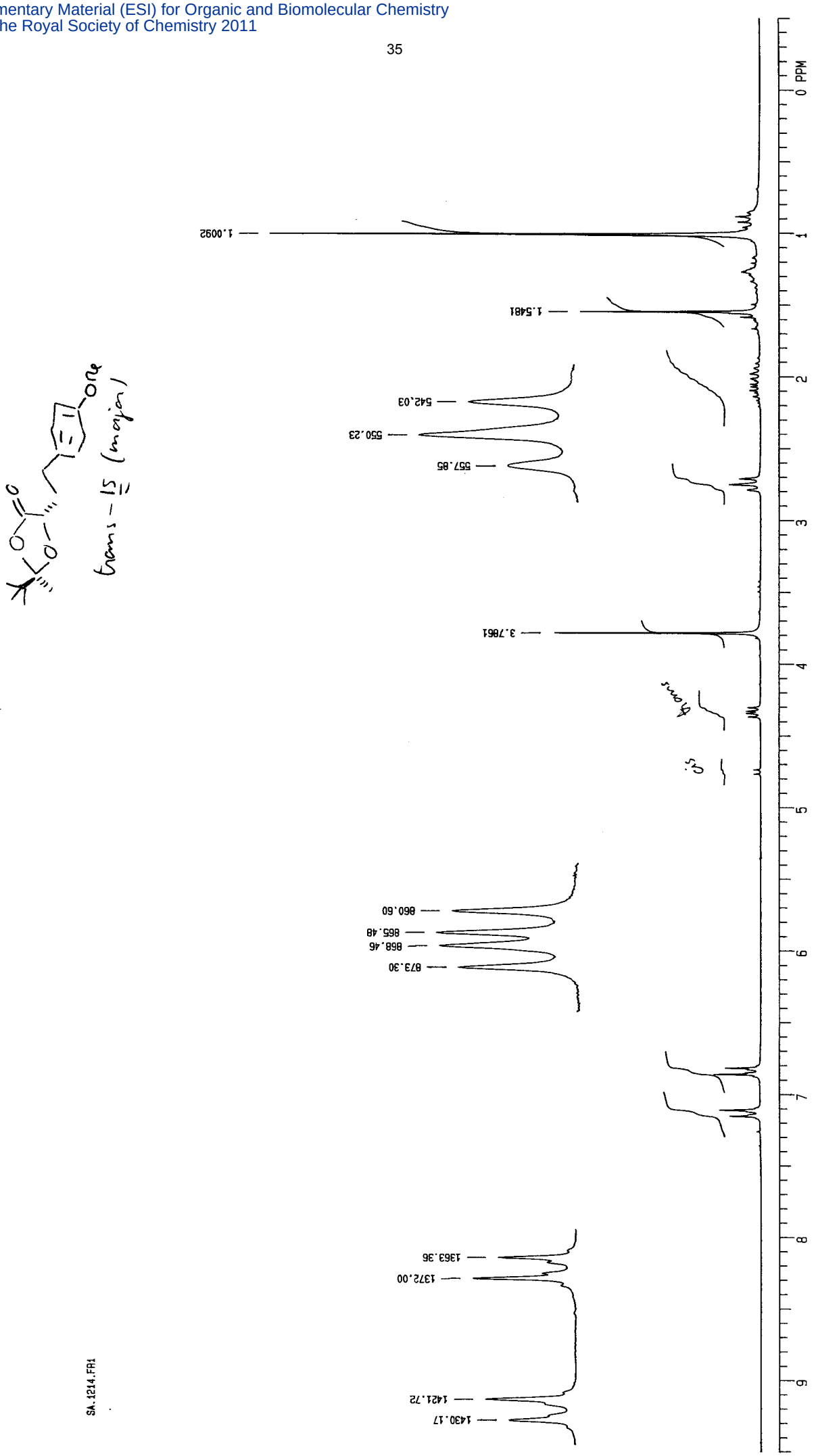

trans-12
NO 71B HNMR
14.0703
22.6235
22.9146
24.5161
31.1726
31.5609
35.0185
40.1707
74.9577
76.3570
77.0000
77.6268
116.381
126.212
128.506
140.439
173.524
0 PPM
20
40
60
80
100
120
140
160

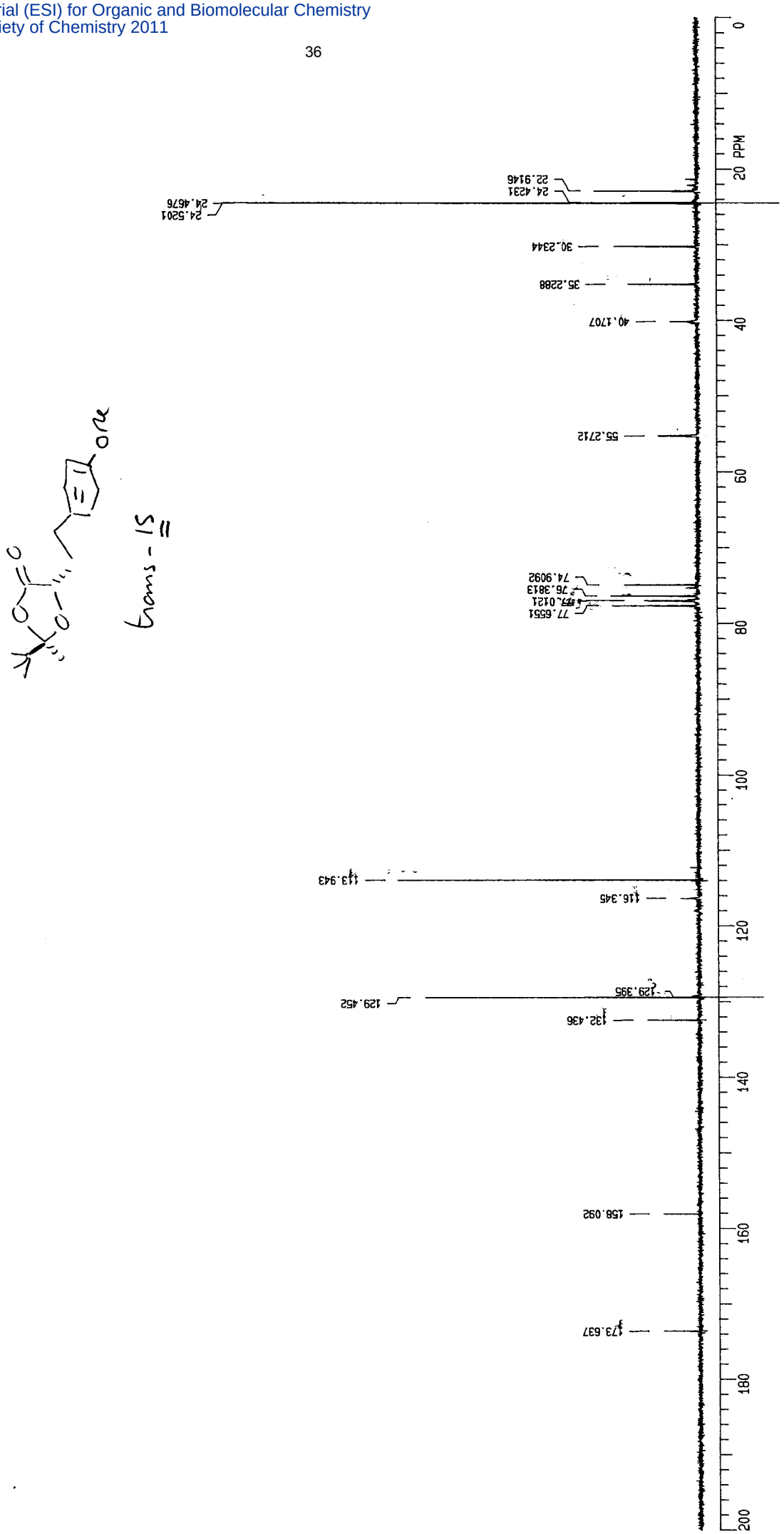


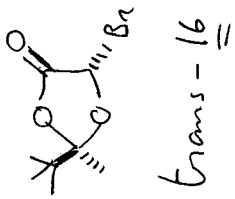



OAc
trans - 14
1.0116
1.5481
2.2949
552.52
558.58
560.92
567.56
865.43
870.36
873.09
878.13
1398.47
1405.11
1407.07
1440.08
1448.67
1452.86
0 PPM
SA.1247.FR1.MAJ

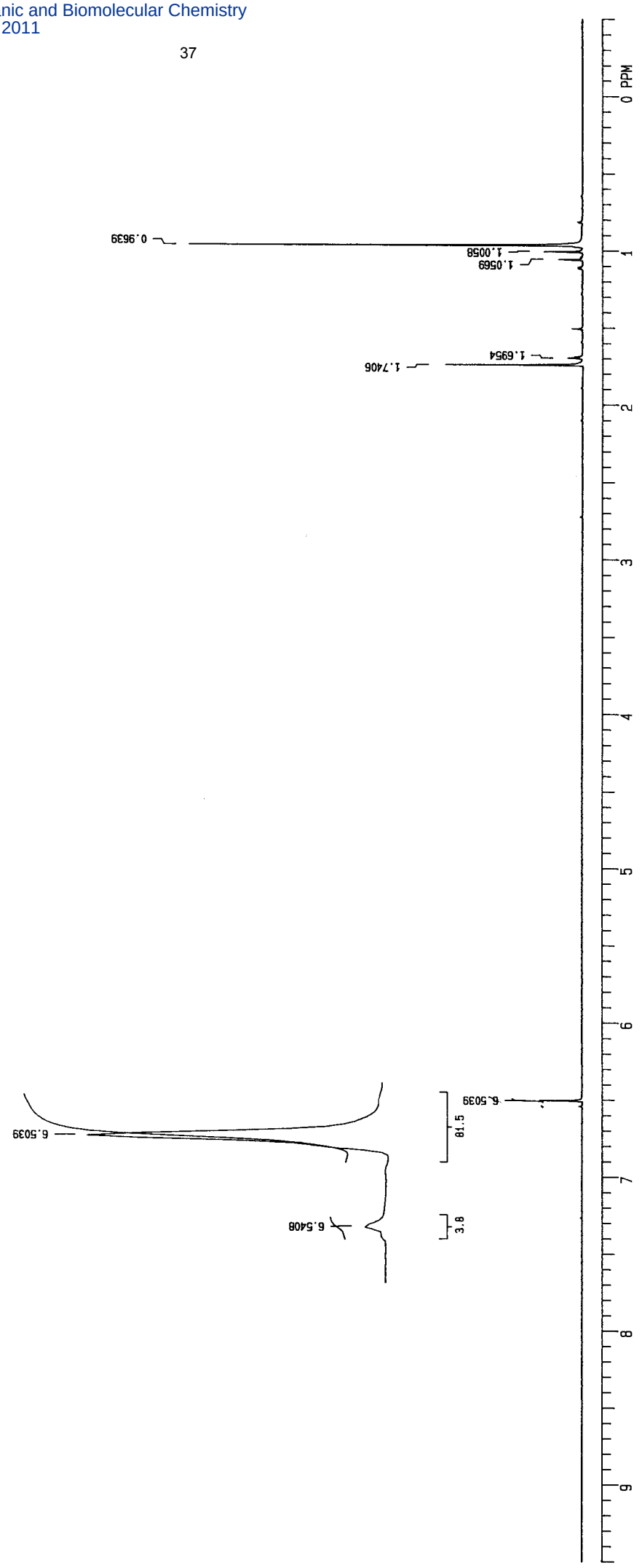



trans - 15 (major)
1.0092
1.5481
542.03
550.23
557.85
3.7861
trans
cis
860.60
865.48
868.46
873.30
1363.36
1372.00
1421.72
1430.17
0 PPM
SA.1214.FR1

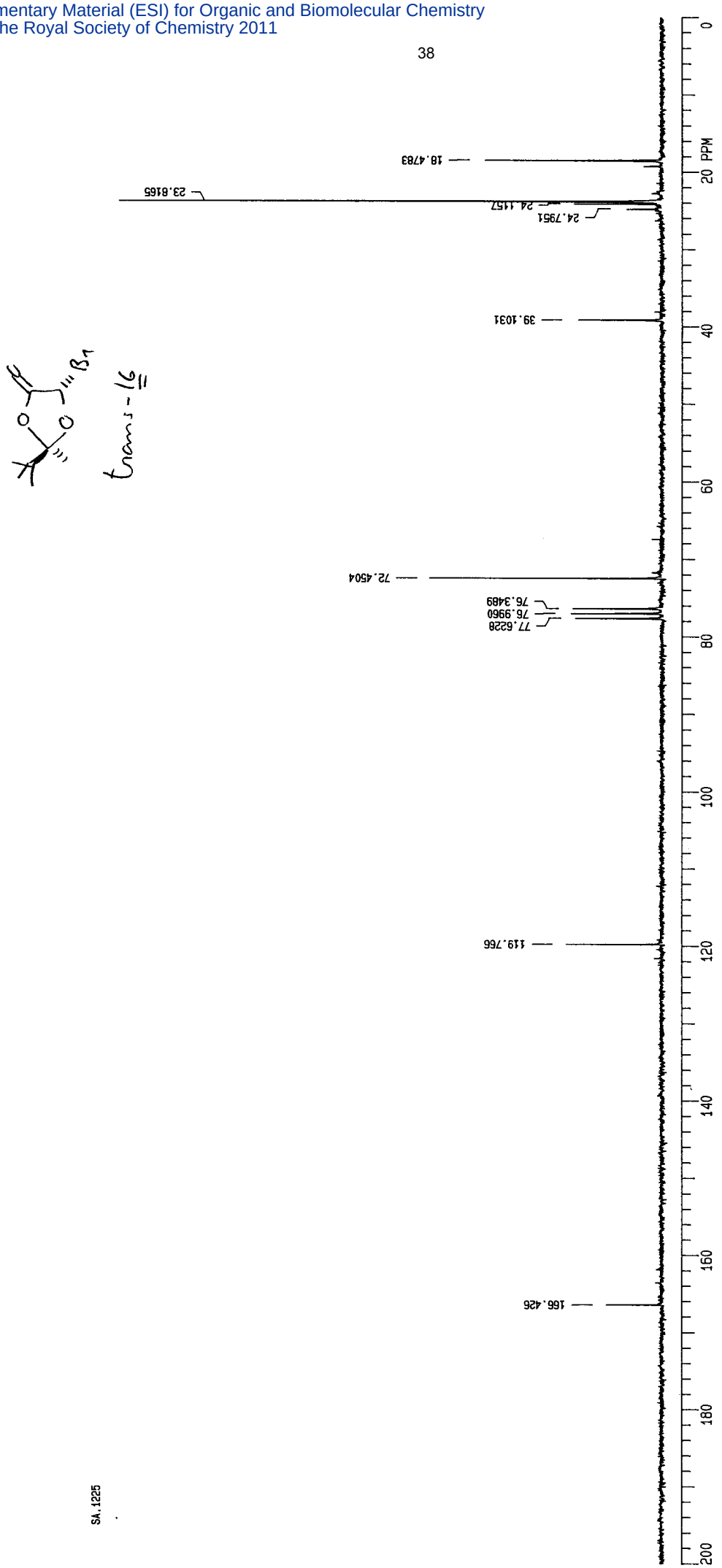


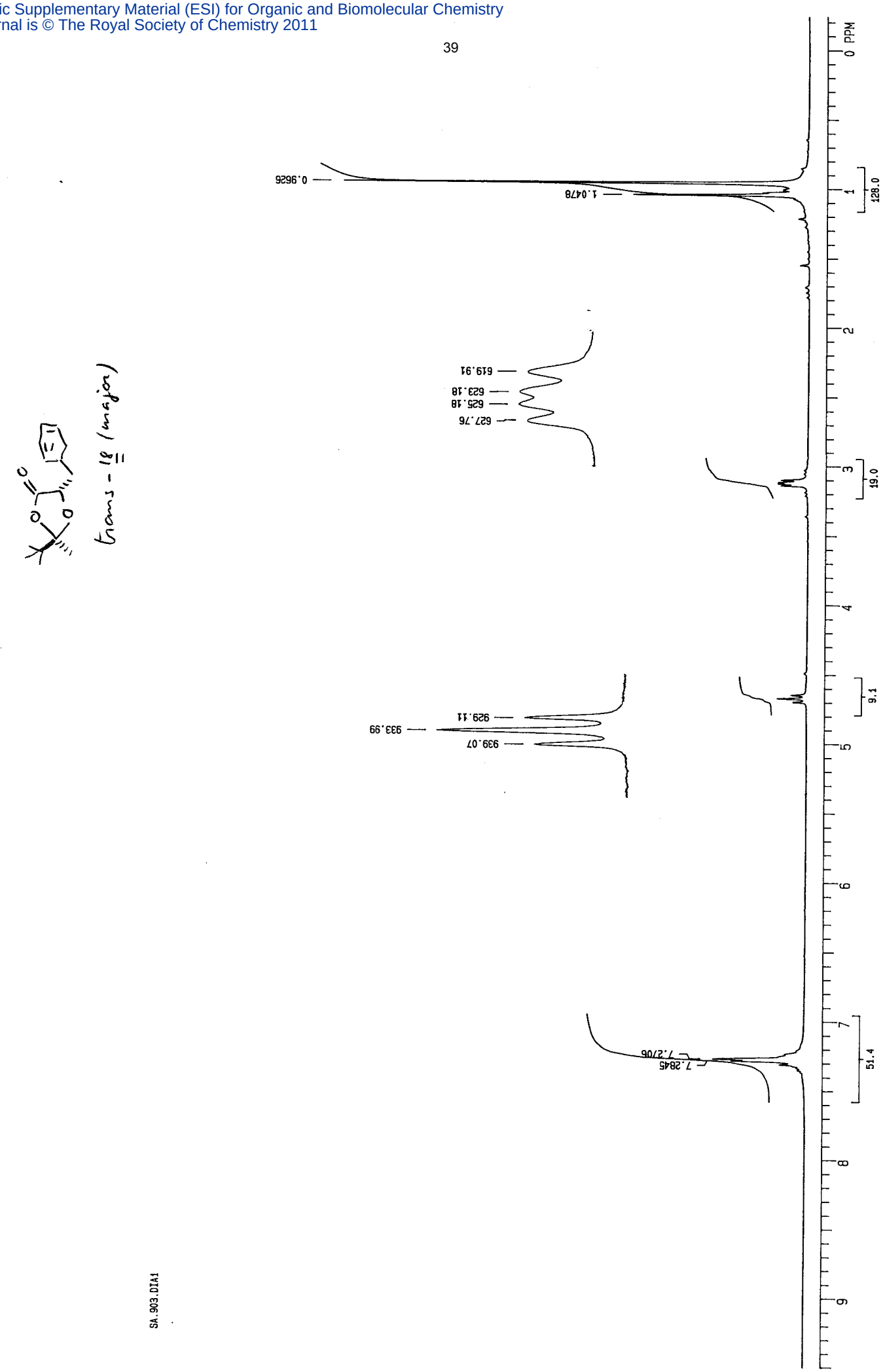


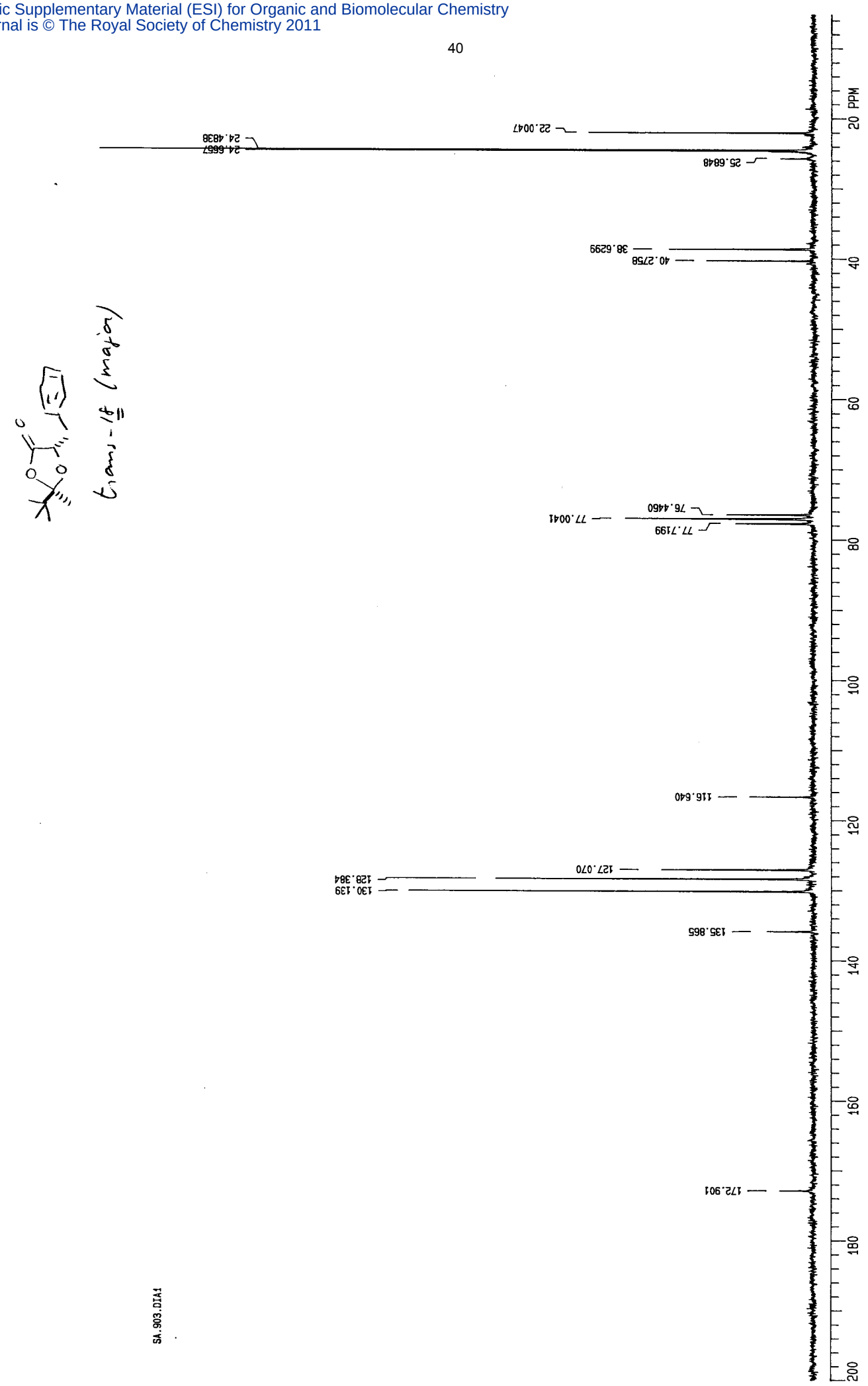
trans - 16

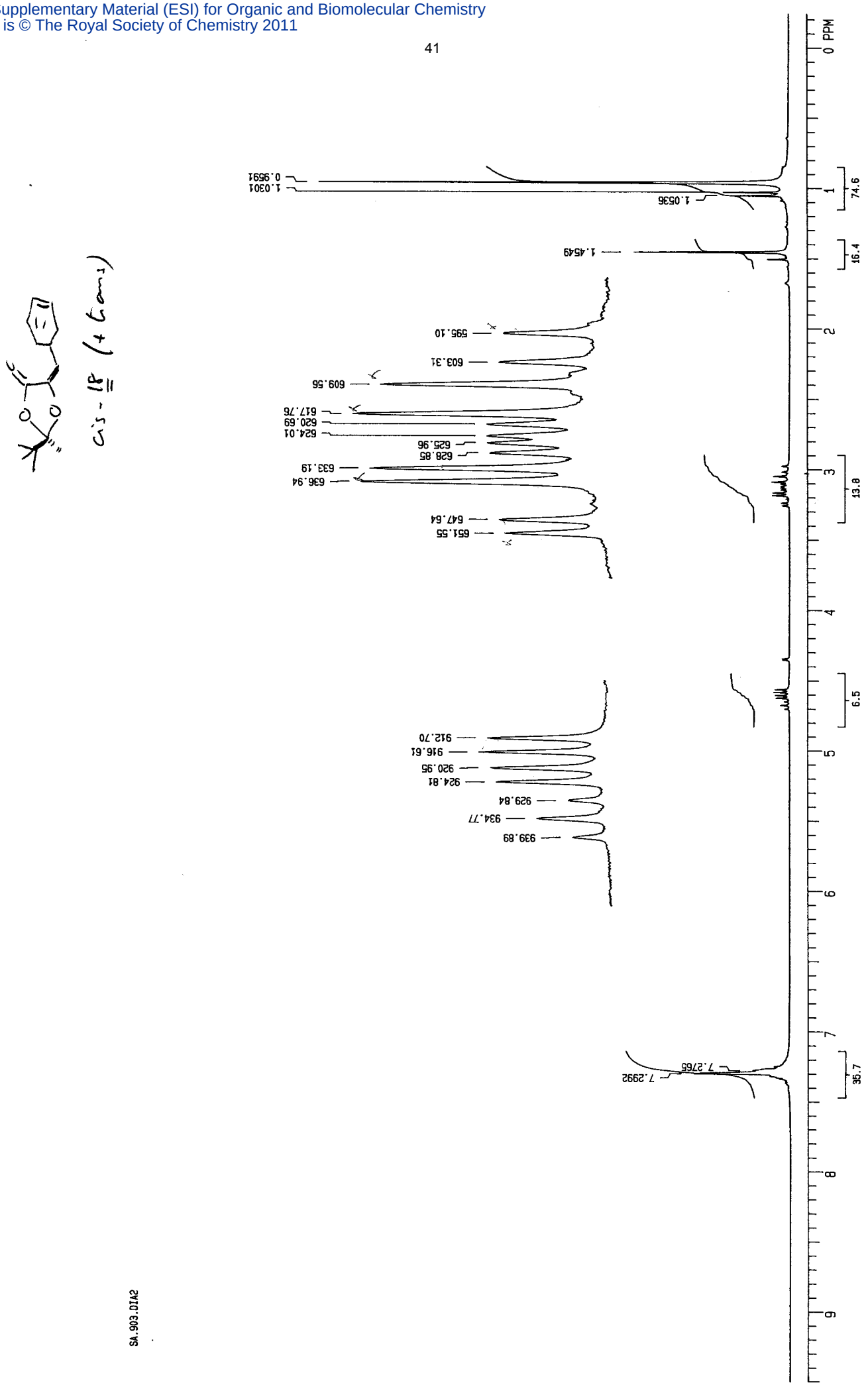


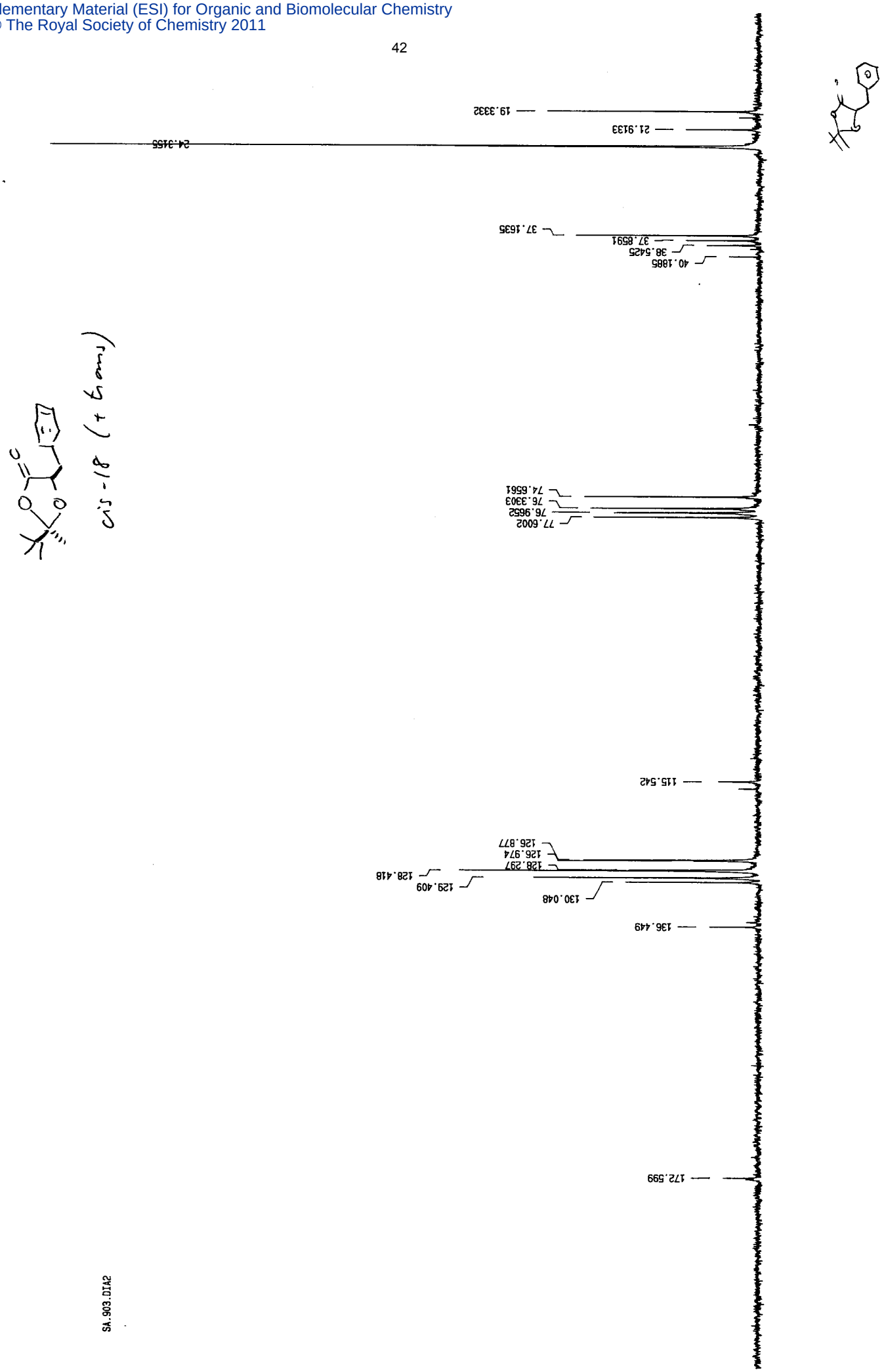
SA.1225

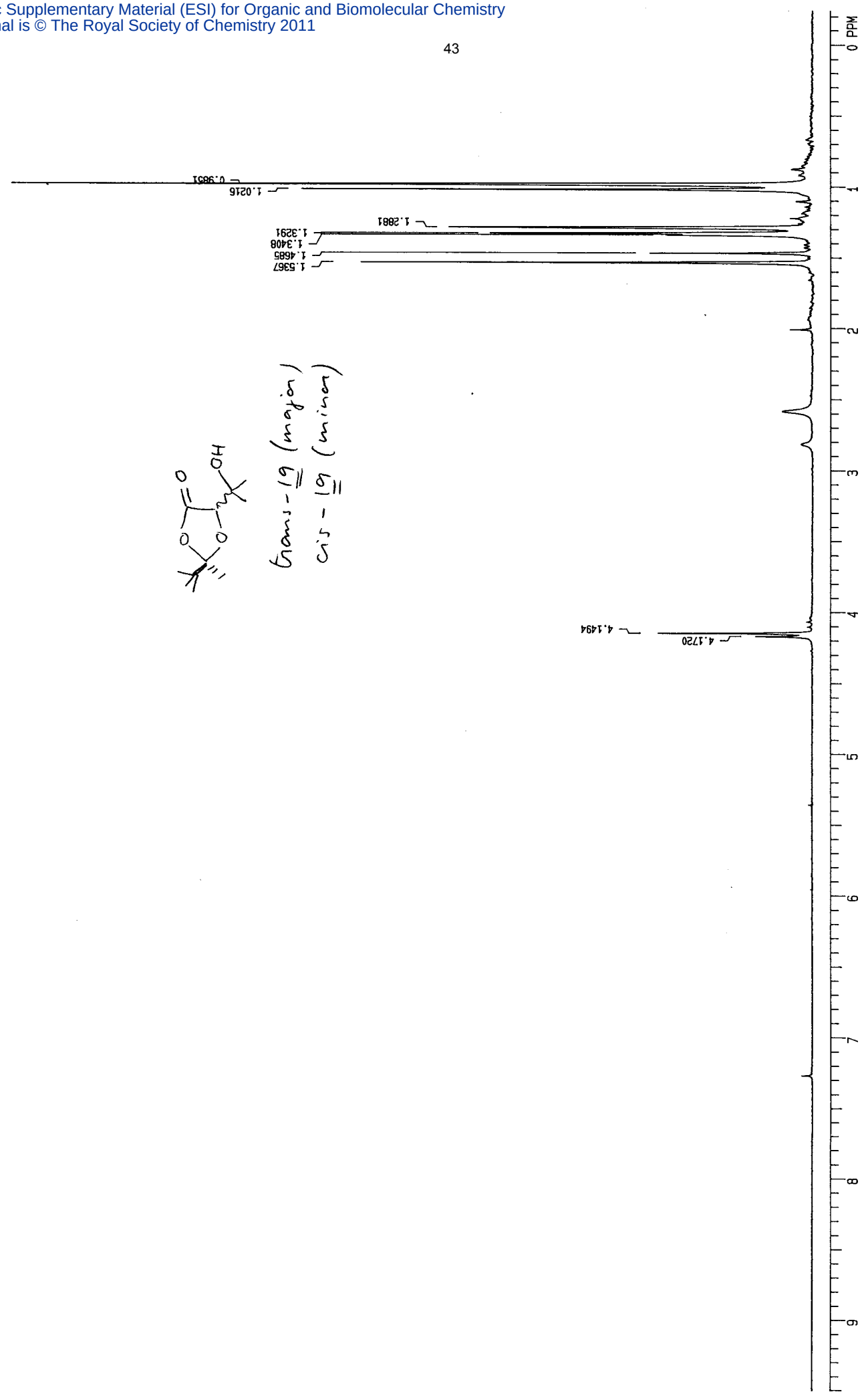

18.4783
23.8165
24.1457
24.7951
39.1031
72.4504
76.3489
76.9960
77.6228
119.766
166.426
0
20
40
60
80
100
120
140
160
180
200
PPM
trans-16
SA.1225

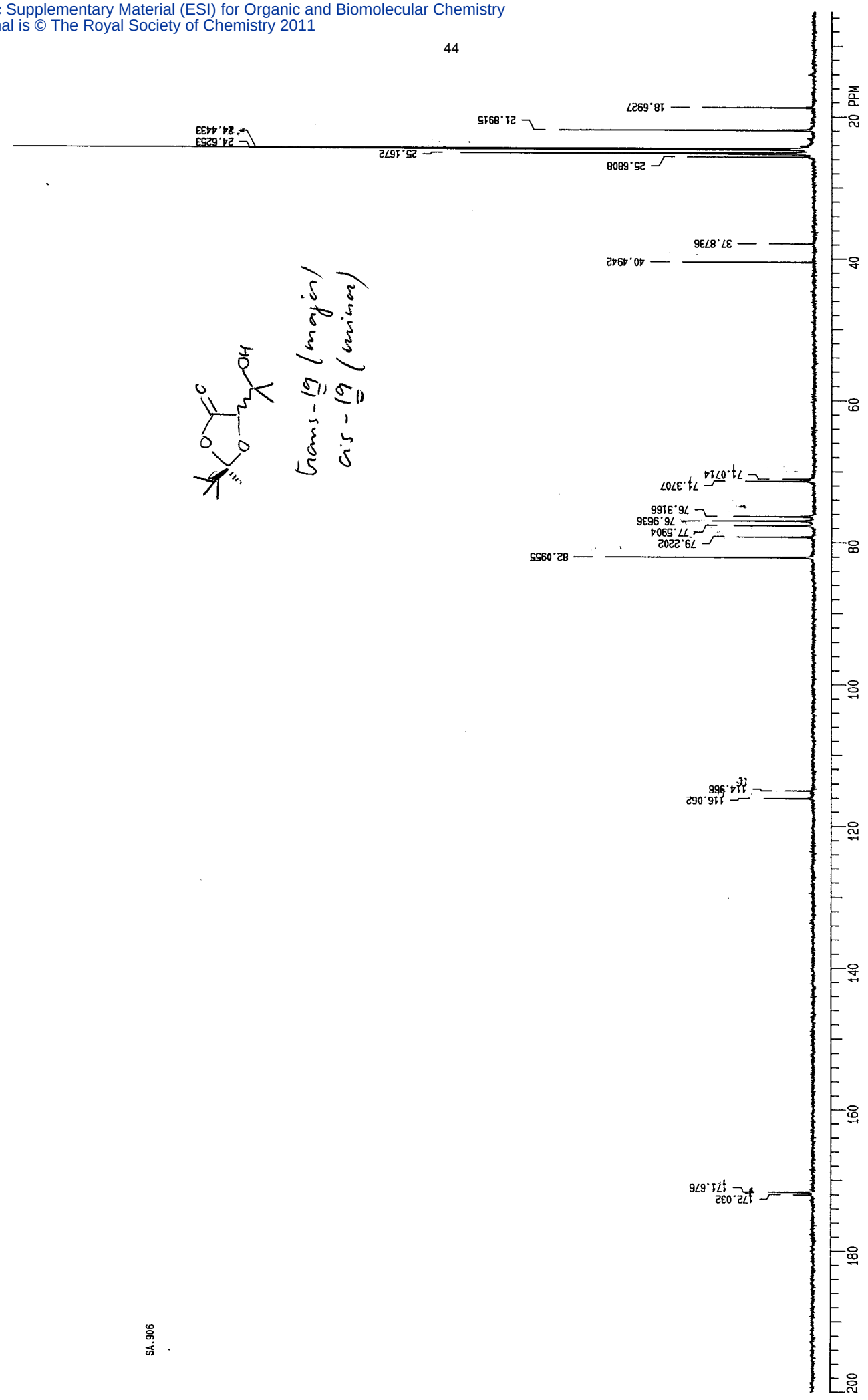

trans - 1g (major)
0.9626
1.0478
619.91
623.18
625.18
627.76
929.11
933.99
939.07
7.2706
7.2845
0 PPM
1
2
3
4
5
6
7
8
9
128.0
19.0
9.1
51.4
SA.903.DIA1

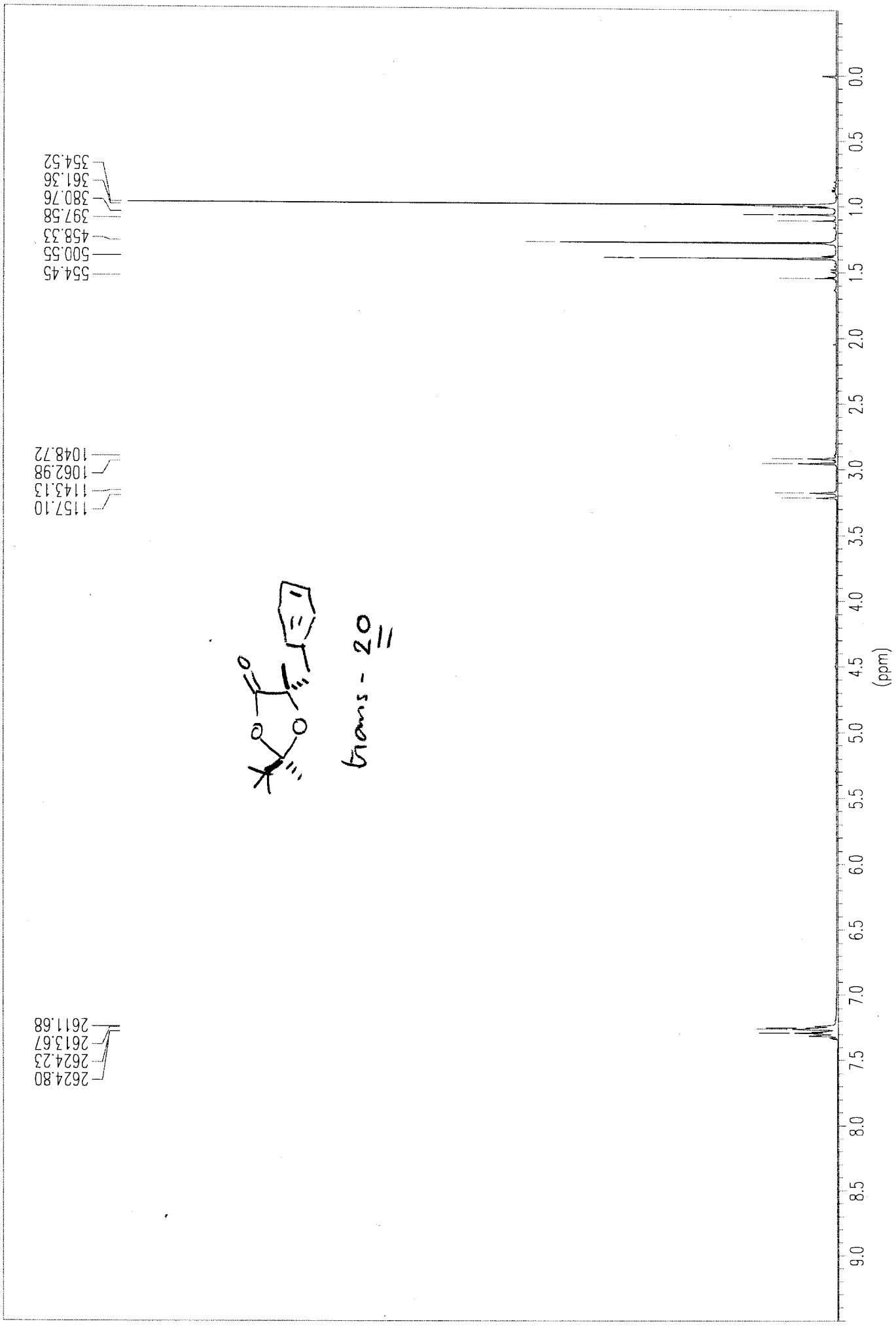

trans-1ff (major)
22.0047
24.4838
24.6857
25.6848
38.6299
40.2758
76.4460
77.0041
77.7199
116.640
127.070
128.384
130.139
135.865
172.901
20 PPM
40
60
80
100
120
140
160
180
200
SA.903.DIA1

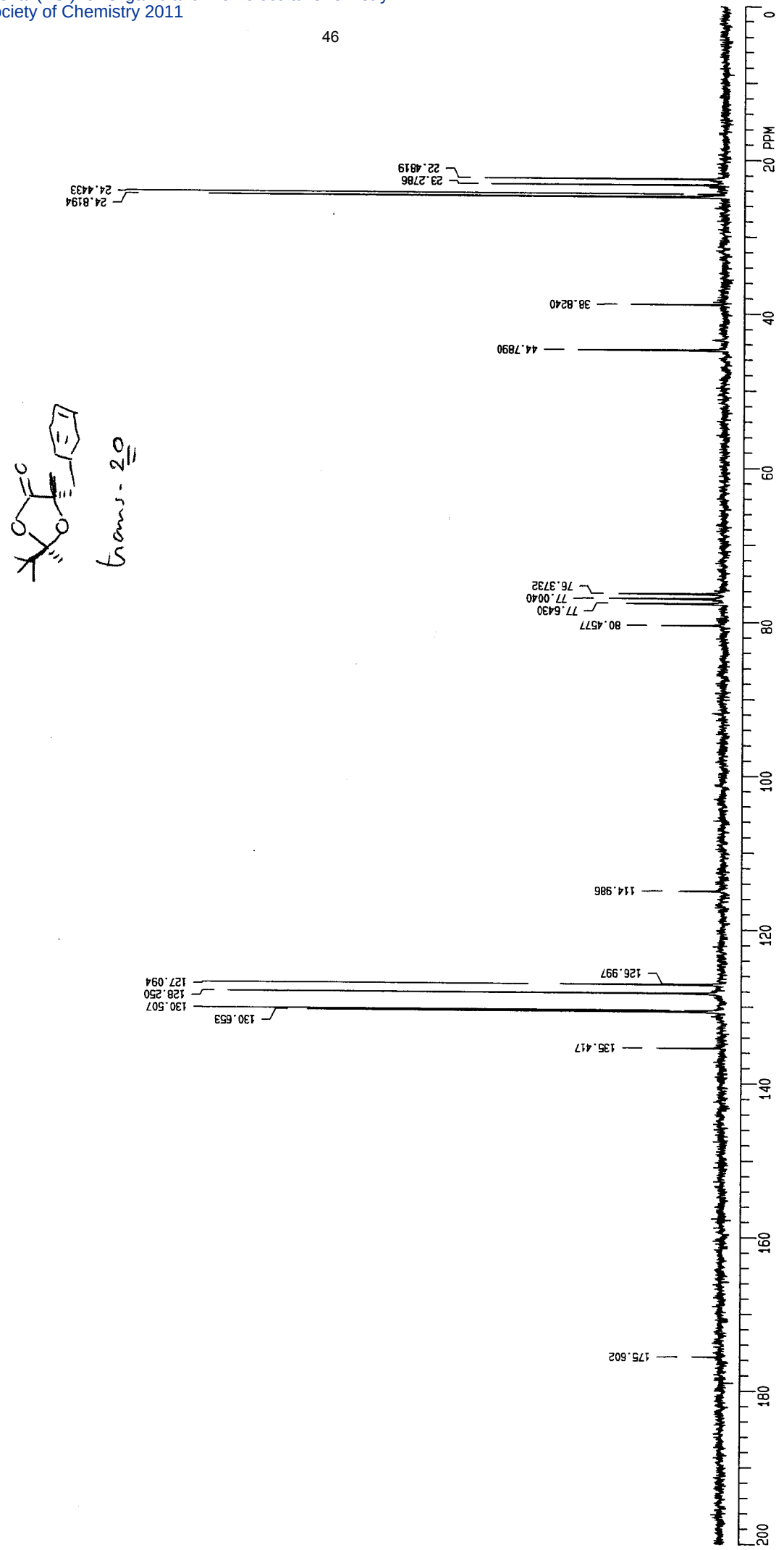

cis - IP (1 isomer)
0.9891
1.0301
1.0536
1.4549
595.10
603.31
609.56
617.76
620.69
624.01
625.96
628.85
633.19
636.94
647.64
651.55
912.70
916.61
920.95
924.81
929.84
934.77
939.89
7.2766
7.2992
0 PPM
1
2
3
4
5
6
7
8
9
74.6
16.4
13.8
6.5
35.7
SA.903.DIA2


19.3332
21.9133
24.3455
37.1635
37.8591
38.5425
40.1885
74.6561
76.3303
76.9652
77.6002
115.542
126.877
126.974
128.297
128.418
129.409
130.048
136.449
172.599
SA.903.DIA2


0.9851
1.0216
1.2881
1.3291
1.3408
1.4685
1.5367
4.1494
4.1720
0 PPM
1
2
3
4
5
6
7
8
9
trans-19 (major)
cis-19 (minor)
OH
O
O
O


18.6927
21.8915
24.4433
24.6253
25.1572
25.6808
37.8736
40.4942
71.0714
71.3707
76.3166
76.9636
77.5904
79.2202
82.0955
114.966
116.062
172.032
172.676
20 PPM
40
60
80
100
120
140
160
180
200
trans - 19 (major)
cis - 19 (minor)
SA.306





trans - 20