Supporting Information

C-C Bond Formation via 1,2-Addition of *tert*-Butylzinc Reagent and Carbonyls across Conjugated Dienes

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General procedures

Distillation were carried out in a Kugelrohr apparatus (SIBATA glass tube oven GTO-350RG). Boiling points are meant to refer to the oven temperature (± 1 °C). Microanalyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ± 0.4%. High resolution mass spectra (HRMS) were measured with JEOL JMSDX303. Infrared spectra were recorded with a JASCO A-100 or SHIMAZU FTIR-8700 infrared spectrophotometer. ^{1}H and ^{13}C magnetic resonance spectra were measured on JEOL-GX400 instrument with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard.

Tetrahydrofuran was dried and distilled from benzophenone-sodium immediately prior to use under nitrogen atmosphere. DMA were distilled over calcium hydride. Benzaldehyde, *p*-anisaldehyde, cyclohexanecarbaldehyde, *n*-hexanal, isoprene, 2,3-dimethyl-1,3-butadiene, myrcene, cyclohexadiene, methyl sorbate were distilled via Kugelrohr apparatus under reduced pressure prior to use. *t*-BuZnBr (0.5 M THF, Aldrich), *t*-BuI (Aldrich), Zinc dust (Aldrich), $Ni(cod)_2$ (KANTO Kagaku) were used without further purification. 1,3-Butadiene (Tokyo Kasei Kogyo Co., Ltd) was purchased, and was liquefied by cooling at -78 ˚C (dry ice/isopropanol) prior to use under argon atmosphere. 1,3-Butadiene could be measured by syringe kept cool in the freezer as well beforehand, and then was introduced into the reaction mixture at room temperature.

Typical procedure for the three-component coupling reaction of aldehydes, 1,3-butadiene, and *t*-BuZnBr (entry 1, Table 1): Into a nitrogen-purged flask were introduced successively THF (5 mL), 1,3-butadiene (0.4 mL, 4 mmol), benzaldehyde (106 mg, 1 mmol), and *t*-BuZnBr (2.4 mL, 0.5 M in THF) via syringe. The homogeneous mixture was stirred at room temperature for 6 h, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, sat. $NaHCO_3$, and brine, and then dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 32/1, v/v) to give an analytically pure sample of **1a** (213 mg, 98%).

Three-component coupling reaction of aldehydes, 1,3-butadiene, and *t*-BuZnI reagent prepared from *t*-BuI and Zn dust (entry 1, Table 2): Into a nitrogen-purged flask containing Zinc dust (78 mg, 1.2 mmol) were introduced successively THF (3 mL), and DMA (1 mL), *t*-BuI (220 mg, 1.2 mmol), 1,3-butadiene (0.4 mL, 4 mmol), and benzaldehyde (106 mg, 1 mmol) via syringes. The reaction mixture was stirred at room temperature for 24 h, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, sat. $NaHCO_3$, and brine, and then dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 32/1, v/v) to give **1a** (167 mg, 77%).

4,4-Dimethyl-1-phenyl-2-vinylpentan-1-ol (**1a**): (a mixture of 1,2-*anti* : *syn* = 7:1 ratio): IR (neat) 3423 (s), 2866 (s), 1495 (s), 1001 (s), 910 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.75 (s, 9 H), 1.18 (dd, J = 2.8, 13.9 Hz, 1 H), 1.24 (dd, J = 8.8, 13.9 Hz, 1 H), 2.34 (d, J = 2.1 Hz, 1 H), 2.45 (br dq, J = 2.8, 8.8 Hz, 1 H), 4.28 (br dd, J = 2.1, 8.1 Hz, 1 H), 5.20 (br dd, J = 1.8, 17.2 Hz, 1 H), 5.23 (br dd, J = 1.8, 10.3 Hz, 1 H), 5.72 (ddd, J = 9.5, 10.3, 17.2 Hz, 1 H), 7.13-7.53 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, *anti*-isomer) δ 30.0, 31.0, 44.1, 49.4, 77.4, 118.2, 127.4, 127.6, 128.2, 141.9, 142.3; ^1H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.81 (s, 9 H), 1.16 (dd, J = 9.5, 13.9 Hz, 1 H), 1.47 (dd, J = 2.2, 13.9 Hz, 1 H), 2.14 (br d, J = 5.3 Hz, 1 H), 2.54 (br dq, J = 2.2, 9.5 Hz, 1 H), 4.58 (br t, J = 5.3 Hz, 1 H), 5.08 (br d, J = 10.8, 1 H), 5.09 (br dd, J = 16.9 Hz, 1 H), 5.62 (ddd, J = 9.0, 10.8, 16.9 Hz, 1 H), 7.13-7.53 (m, 5 H); ^1H NMR (100 MHz, $CDCl_3$, *syn*-isomer) δ 30.1, 31.0, 42.9, 47.8, 77.4, 116.6, 126.8, 127.2, 127.9, 141.4, 142.4; High-resolution MS, Calcd for $C_{15}H_{22}O$: 218.1671. Found m/e (relative

intensity) 218.1692 (M^+, 100), 201 (88), 147 (34), 146 (32).

1-(4-Methoxyphenyl)-4,4-dimethyl-2-vinylpentan-1-ol (**1b**): (a mixture of 1,2-*anti* : *syn* = 6:1 ratio): IR (neat) 3452 (m), 2866 (m), 1612 (m), 1514 (s), 1248 (s), 1038 (s), 833 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*- isomer) δ 0.76 (s, 9 H), 1.17 (dd, J = 3.0, 14.0 Hz, 1 H), 1.23 (dd, J = 8.6, 14.0 Hz, 1 H), 2.27 (d, J = 1.7 Hz, 1 H), 2.42 (ddm, J = 3.0, 8.6 Hz, 1 H), 3.80 (s, 3 H), 4.22 (dd, J = 1.7, 8.1 Hz, 1 H), 5.20 (dd, J = 1.8, 17.1 Hz, 1 H), 5.23 (dd, J = 1.8, 10.2 Hz, 1 H), 5.72 (ddd, J = 9.3, 10.2, 17.1 Hz, 1 H), 6.86 (d, J = 8.5 Hz, 2 H), 7.24 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 30.0, 31.0, 44.1, 49.5, 55.2, 76.4, 113.4, 118.0, 128.3, 134.2, 142.1, 158.9; ^1H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.83 (s, 9 H), 2.51-2.53 (m, 1 H), 3.80 (s, 3 H), 4.53 (t, J = 5.1 Hz,1 H), 5.05 (dd, J = 1.9, 9.1 Hz, 1 H), 5.07 (dd, J = 1.9, 16.8 Hz, 1 H), 5.62 (ddd, J = 9.1, 10.5, 16.8 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 30.1, 43.2, 47.8, 113.2, 116.5, 127.8, 134.4, 141.2; High-resolution MS, Calcd for $C_{15}H_{21}ClO$: 248.1776, Found m/z (relative intensity): 248.1767 (M^+, 75), 215 (100).

1-(4-Chlorophenyl)-4,4-dimethyl-2-vinylpentan-1-ol (**1c**): (a mixture of 1,2-*anti* : *syn* = 9:1 ratio): IR (neat) 3433 (m), 2909 (s), 1638 (w), 1090 (s), 831 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.76 (s, 9 H), 1.16 (dd, J = 2.4, 13.9 Hz, 1 H), 1.25 (dd, J = 9.0, 13.9 Hz, 1 H), 2.32 (br s, 1 H), 2.39 (dddd, J = 2.4, 7.8, 9.0, 9.3 Hz, 1 H), 4.57 (d, J = 7.8 Hz, 1 H), 5.17 (dd, J = 1.3, 17.2 Hz, 1 H), 5.18 (dd, J = 1.3, 10.2 Hz, 1 H), 5.70 (ddd, J = 9.3, 10.2, 17.2 Hz, 1 H), 7.25 (d, J = 8.7 Hz, 2 H), 7.30 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 30.0, 31.0, 44.0, 49.4, 76.2, 118.5, 128.1, 128.6, 133.1, 140.6, 141.3; ^1H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.81 (s, 9 H), 2.50-2.52 (m, 1 H), 4.27 (t, J = 4.6 Hz,1 H), 5.08 (dm, J = 17.2 Hz, 1 H), 5.10 (dm, J = 10.4 Hz, 1 H), 5.60 (ddd, J = 9.3, 10.4,17.2 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 30.1, 42.8, 47.7, 116.9, 140.7, 140.8; High-resolution MS, Calcd for $C_{15}H_{21}ClO$: 252.1281, Found m/z (relative intensity): 252.1295 (M^+, 68), 219 (100).

1-Cyclohexyl-4,4-dimethyl-2-vinylpentan-1-ol (**1d**): (a mixture of 1,2-*anti* : *syn* = 9:1 ratio): IR (neat) 3368 (br m), 3071 (s), 2853 (s), 1636 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.90 (s, 9 H), 0.96-1.30 (m, 5 H), 1.32-1.42 (m, 3 H), 1.64-1.76 (m, 4 H), 1.81-1.86 (m, 1 H), 2.37 (dq, J = 5.2, 9.2 Hz, 1 H), 3.07 (t, J = 5.2 Hz, 1 H),

5.08 (ddd, J = 0.7, 1.9, 17.3 Hz, 1 H), 5.14 (dd, J = 1.9, 10.4 Hz, 1 H), 5.73 (ddd, J = 9.2, 10.4, 17.3 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 26.1, 26.3, 26.5, 27.8, 30.0, 30.1, 31.3, 40.3, 42.9, 45.5, 79.1, 116.7, 140.8; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.86 (s, 9 H), 3.13 (m, 1 H), 5.02 (dm, J = 1.0 Hz,1 H), 5.07 (dm, J = 1.0 Hz, 1 H), 5.75 (dd, J = 8.5, 17.6 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 27.2, 29.2, 30.3, 30.4, 39.9, 42.7, 43.8, 80.2, 115.0, 143.1; High-resolution MS, Calcd for $C_{15}H_{28}O$: 224.2140, Found m/z (relative intensity): 224.2079 (M^+, 24), 223 (100).

2,2-Dimethyl-4-vinyldecan-5-ol (**1e**): (a mixture of 1,2-*anti* : *syn* = 1:1 ratio): IR (neat) 3362 (w), 2934 (s), 2862 (s), 1638 (w) cm^{-1}; (one isomer): ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.87 (t, J = 5.6 Hz, 3 H), 0.89 (s, 9 H), 1.21-1.39 (ddm, J = 4.6, 7.8 Hz, 10 H), 2.28 (dq, J = 4.1, 8.3 Hz, 1 H), 3.33-3.40 (m, 1 H), 5.08 (dd, J = 1.7, 18.5 Hz, 1 H), 5.13 (dd, J = 1.7, 10.0, Hz, 1 H), 5.69 (ddd, J = 8.3, 10.0, 18.5 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$, one isomer) δ 14.0, 22.6, 26.0, 30.1, 31.1, 33.2, 44.1, 75.7, 116.4, 141.5; (minor isomer): ^{1}H NMR (400 MHz, $CDCl_3$, other isomer) δ 0.90 (s, 9 H), 0.94 (t, J = 7.2 Hz, 3 H), 2.12-2.18 (dddm, J = 0.7, 4.6, 8.8 Hz, 1 H), 5.09 (dd, J = 0.7, 15.9 Hz,1 H), 5.09 (d, J = 11.5 Hz, 1 H), 5.68 (ddd, J = 8.8, 11.5, 15.9 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$, other isomer) δ 25.6, 30.2, 31.2, 31.9, 34.4, 44.9, 46.8, 74.9, 116.9, 141.2; High-resolution MS, Calcd for $C_{12}H_{24}O$: 212.214, Found m/z (relative intensity): 212.2099 (M^+, 46), 197 (100).

2,5,5-Trimethyl-3-vinylhexan-2-ol (**1f**): IR (neat) 3435 (w), 2959 (m), 2868 (w), 2345 (w), 1720 (w), 1466 (w), 1020 (m), 802 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9 H), 1.10 (s, 3 H), 1.18 (s, 3 H), 1.24 (dd, J = 9.5, 13.9 Hz, 1 H), 1.45 (dd, J = 1.6, 13.9 Hz, 1 H), 1.75 (s, 1 H), 2.12 (br td, J = 1.0, 9.5 Hz, 1 H), 5.12 (ddd, J = 1.0, 2.0, 17.3 Hz, 1 H), 5.15 (dd, J = 2.0, 10.2 Hz, 1 H), 5.67 (ddd, J = 9.5, 10.2, 17.3 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 26.4, 26.9, 30.2, 31.1, 43.6, 52.3, 71.9, 117.9, 141.9; High-resolution MS, Calcd for $C_{11}H_{22}O$: 170.1671, Found m/z (relative intensity): 171 (M^++1, 76), 170.1578 (M^+, 59), 169 (89).

2,4,4-Trimethyl-1-phenyl-2-vinylpentan-1-ol (**2a**): (a mixture of 1,2-*anti* : *syn* = 10:1 ratio): IR (neat) 3462 (br m), 3030 (m), 2953 (s), 1634 (w), 1454 (s), 1022 (s), 910 (s)

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.90 (s, 9 H), 1.10 (s, 3 H), 1.24 (d, J = 13.8 Hz, 1 H), 1.55 (d, J = 13.8 Hz, 1 H), 2.14 (d, J = 1.7 Hz, 1 H), 4.24 (d, J = 1.7 Hz, 1 H), 5.12 (dd, J = 1.2, 17.6 Hz, 1 H), 5.26 (dd, J = 1.2, 10.9 Hz, 1 H), 5.98 (dd, J = 10.9, 17.6 Hz, 1 H), 7.20 - 7.34 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 17.2, 29.7, 31.9, 46.9, 50.7, 80.7, 114.8, 126.2, 127.2, 128.3, 139.9, 145.9; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.76 (s, 9 H), 1.23 (s, 3 H), 1.23 (d, J = 4.3 Hz, 1 H), 1.41 (d, J = 4.3 Hz, 1 H), 2.04 (d, J = 6.0 Hz, 1 H), 4.27 (d, J = 6.0 Hz, 1 H), 5.01 (dd, J = 1.3, 17.6 Hz, 1 H), 5.15 (dd, J = 1.3, 11.8 Hz, 1 H), 5.97 (dd, J = 11.8, 17.6 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 19.9, 30.7, 32.2, 46.1, 50.1, 82.3, 113.9, 126.9, 127.3, 127.9, 141.3, 144.7; High-resolution MS, Calcd for $C_{16}H_{24}O$: 232.1827, Found m/z (relative intensity): 232.1823 (M^+, 2), 199 (100).

4,4-Dimethyl-1-phenyl-2-(prop-1-en-2-yl)pentan-1-ol (**3a**): (a mixture of 1,2-*anti* : *syn* = 9:1 ratio): IR (neat) 3470 (m), 3030 (w), 2866 (m), 1641 (w), 1196 (m), 1022 (m), 889 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.71 (s, 9 H), 0.97 (dd, J = 2.0, 14.1 Hz, 1 H), 1.39 (dd, J = 9.6, 14.1 Hz, 1 H), 1.78 (dd, J = 0.7, 1.5 Hz, 3 H), 2.35 (brs, 1 H), 2.52 (dt, J = 2.0, 9.6 Hz, 1 H), 4.27 (d, J = 9.6 Hz, 1 H), 5.04 (dd, J = 0.7, 1.8 Hz, 1 H), 5.07 (dd, J = 1.5, 1.8, Hz, 1 H), 7.33 (d, J = 4.4 Hz, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 18.9, 29.5, 31.0, 41.2, 52.6, 75.5, 116.1, 127.4, 127.5, 128.0, 142.5, 146.9; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.90 (s, 9 H), 0.97 (dm, J = 10.0 Hz, 1 H), 1.39 (dm, J = 10.0 Hz, 1 H), 1.69 (dd, J = 0.7, 1.5 Hz, 3 H), 4.99 (d, J = 0.7 Hz, 1 H), 5.03 (d, J = 1.5 Hz, 1 H); High-resolution MS, Calcd for $C_{16}H_{24}O$: 232.1827, Found m/z (relative intensity): 232.1823 (M^+, 13), 199 (100).

2,4,4-Trimethyl-1-phenyl-2-(prop-1-en-2-yl)pentan-1-ol (**2b**): (a mixture of 1,2-*anti* : *syn* = 3:1 ratio): IR (neat) 3462 (w), 2953 (s), 2872 (s), 1630 (w), 1452 (m), 1364 (m), 1242 (m), 1190 (m), 1043 (m), 1022 (m), 894 (m), 702 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.87 (s, 9 H), 1.05 (d, J = 14.5 Hz, 1 H), 1.10 (s, 3 H), 1.72 (d, J = 14.5 Hz, 1 H), 1.95 (br s, 3 H), 4.45 (br s, 1 H), 5.10 (br s, 1 H), 5.18 (br s, 1 H), 7.24 - 7.35 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 18.5, 21.9, 26.5, 32.2, 48.5, 49.0, 80.4, 114.0, 127.2, 128.1, 141.0, 148.9; (1,2-*syn* isomer): ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 17.9, 20.3, 26.4, 31.6, 45.8, 47.4, 78.2, 115.9, 127.4, 128.9, 140.3, 149.7; High-resolution MS, Calcd for $C_{17}H_{26}O$: 246.1984, Found m/z (relative

intensity): 246.1992 (M^+, 1), 245 (4), 244 (6), 229 (100).

6-Methyl-2-neopentyl-1-phenyl-2-vinylhept-5-en-1-ol (**2c**): (a mixture of 1,2-*anti* : *syn* = 1:1 ratio): IR (neat) 3470 (br m), 3030 (m), 2934 (s), 1634 (w), 1196 (m), 899 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 1.02 (s, 9 H), 1.42 (ddd, J = 2.4, 8.4, 19.8, Hz, 1 H), 1.43 (dd, J = 8.4, 19.8, Hz, 1 H), 1.57 (s, 3 H), 1.64 (d, J = 1.2 Hz, 3 H), 1.75 (s, 2 H), 1.89 (d, J = 4.1 Hz, 1 H), 2.04 (ddm, J = 7.1, 8.4, Hz, 2 H), 4.64 (d, J = 4.1 Hz, 1 H), 4.96 (dt, J = 1.2, 7.1 Hz, 1 H), 4.96 (dd, J = 18.1, 1.3 Hz, 1 H), 5.20 (dd, J = 11.2, 1.3 Hz, 1 H), 5.94 (dd, J = 18.1, 11.2 Hz, 1 H), 7.25 - 7.31 (dm, J = 6.1 Hz, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 23.0, 25.7, 32.1, 32.1, 33.0, 44.1, 48.6, 79.1, 114.6, 124.6, 127.3, 128.2, 141.2, 143.3; High-resolution MS, Calcd for $C_{21}H_{32}O$: 300.2453, Found m/z (relative intensity): 300.2461 (M^+, 11), 282 (100).

7-Methyl-3-methylene-2-neopentyl-1-phenyloct-6-en-1-ol (**3c**): (a mixture of 1,2-*anti* : *syn* = 1:1 ratio): IR (neat) 3470 (br m), 3030 (m), 2866 (m), 1634 (w), 1196 (m), 899 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.71 (s, 9 H), 1.03 (dd, J = 2.0, 14.1 Hz, 1 H), 1.44 (dd, J = 9.8, 14.1 Hz, 1 H), 1.63 (s, 3 H), 1.70 (d, J = 1.2 Hz, 3 H), 2.04 (dt, J = 6.8, 8.2 Hz, 2 H), 2.16 – 2.24 (m, 2 H), 2.34 (d, J = 2.4 Hz, 1 H), 2.51 (ddd, J = 2.0, 9.0, 9.8 Hz, 1 H), 4.32 (dd, J = 2.4, 9.0 Hz, 1 H), 5.11 (d, J = 1.7 Hz, 1 H), 5.12 (d, J = 1.2 Hz, 1 H), 5.14 (tq, J = 1.2, 6.8 Hz, 1 H), 7.31 (d, J = 4.4 Hz, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 17.7, 25.6, 26.1, 29.6, 31.0, 32.3, 41.9, 52.9, 75.9, 113.9, 123.9, 127.3, 127.5, 128.0, 132.0, 142.6, 150.7; High-resolution MS, Calcd for $C_{21}H_{32}O$: 300.2453, Found m/z (relative intensity): 300.2461 (M^+, 11), 282 (100).

Hetero Diels-Alder reaction of PhCHO and 2,3-dimethyl-1,3-butadiene (Scheme 4): Into a nitrogen-purged flask containing Zinc dust (13 mg, 0.2 mmol) were introduced benzene (3 mL), 2,3-dimethyl-1,3-butadiene (0.45 mL, 4 mmol), benzaldehyde (106 mg, 1 mmol), and *t*-BuI (37 mg, 0.2 mmol) via syringes. The reaction mixture was stirred at room temperature for 24 h, during which the reaction was monitored by TLC. After dilution with ethyl acetate (20 mL), the mixture was washed successively with 2 N-HCl, sat. $NaHCO_3$, and brine, and then dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 32/1, v/v) to give **4** (164 mg, 87%).

3,6-Dihydro-4,5-dimethyl-2-phenyl-2*H*-pyran (**4**): IR (neat) 2916 (s), 2812 (m), 1495 (m), 1103 (s), 758 (s), 698 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 3 H), 1.69 (s, 3 H), 2.09 (dm, J = 16.3 Hz, 1 H), 2.30 (br m, 1 H), 4.15 (br m, 2 H), 4.54 (dd, J = 3.5, 10.6 Hz, 1 H), 7.20 - 7.38 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 13.8, 18.3, 38.5, 70.2, 123.7, 124.4, 125.7, 127.2, 128.2, 139.0. High-resolution MS, Calcd for $C_{13}H_{16}O$: 188.1201, Found m/z (relative intensity): 188.1169 (M^+, 100), 187 (6).

Structure determination of 2,2-dimethyl-5-neopentyl-4-phenyl-1,3-dioxane (**5**): A solution of 4,4-Dimethyl-1-phenyl-2-vinylpentan-1-ol (**1a**) (218 mg, 1 mmol) in dichloromethane (10 mL) was cooled to – 78 ˚C, and ozone was bubbled through for 20 min until a blue color appeared. The excess of ozone was removed by a flow of nitrogen and the solvent was removed by a rotary evaporator. The residue was dissolved in EtOH (3 mL) and treated with $NaBH_4$ (152 mg, 4 mmol) at 0 ˚C and then at room temperature for 6 h. The reaction mixture was concentrated in vacuo and the residue was diluted with ethyl acetate (30 mL) and washed with 2 M HCl, sat. $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Into a solution of the residue dissolved in 2,2-dimethoxypropane (10 mL, 80 mmol) was added *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol), and the reaction mixture was stirred at room temperature for 12 h. After dilution with ethyl acetate (10 mL), the mixture was washed with sat. $NaHCO_3$ and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by means of column chromatography over silica gel (hexane/ethyl acetate = 24/1, v/v) to provide 1,3-dioxane **5** in 86% yield. **2,2-Dimethyl-5-neopentyl-4-phenyl-1,3-dioxane** (**5**): (a mixture of *anti* and *syn* = 10:1, major isomer was assigned): mp = 79.5 – 80.1 ˚C. IR (KBr) 2995 (s), 2955 (s), 1059 (s), 1026 (s) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.58 (s, 9 H), 0.78 (dd, J = 7.5, 14.5 Hz, 1 H), 0.99 (dd, J = 1.5, 14.5 Hz, 1 H), 1.48 (s, 3 H), 1.56 (s, 3 H), 1.86 – 1.95 (m, 1 H, coalescing to ddm, J = 1.5, 5.3, 7.5 Hz by irradiation at 4.41), 3.70 (t, J = 11.6 Hz, 1 H), 4.00 (dd, J = 5.3, 11.6 Hz, 1 H), 4.41 (d, J = 10.3 Hz, 1 H), 7.20-7.43 (m, 5 H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 29.5, 29.9, 30.4, 37.8, 40.6, 66.8, 78.0, 98.5, 128.1, 128.2, 128.3, 140.3; High-resolution MS, Calcd for $C_{17}H_{26}O_2$: 262.1933. Found m/e (relative intensity) 262.1934 (M^+, 25), 247 (79), 165 (94), 163 (100).

Typical procedure for the three-component coupling reaction of diene, carbon dioxide, and *t*-BuZnBr (entry 1, Table 4, condition A): Into a carbon dioxide-purged flask were introduced successively THF (2 mL), 1,3-butadiene (0.4 mL, 4 mmol), and *t*-BuZnBr (2.4 mL, 0.5 M in THF, 1.2 mmol) via syringes. The homogeneous mixture was stirred at room temperature for 24 h under carbon dioxide atmospheric pressure, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, and brine, and then dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to give an analytically pure sample of **6a** (161 mg, 86%).

Typical procedure for the three-component coupling reaction of diene, carbon dioxide, and *t*-BuZnI reagent prepared from *t*-BuI and Zn dust (entry 1, Table 4, condition B): Into a carbon dioxide-purged flask containing Zinc dust (78 mg, 1.2 mmol) were introduced successively THF (2 mL), *t*-BuI (220 mg, 1.2 mmol), 1,3-butadiene (0.4 mL, 4 mmol) via syringes. The reaction mixture was stirred at room temperature for 24 h under carbon dioxide atmospheric pressure, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, and brine, and then dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to give an analytically pure sample of **6a** (114 mg, 61%). **4,4-Dimethyl-2-vinylpentanoic acid** (**6a**): IR (neat) 2957 (s), 2870 (s), 1709 (s), 1638 (m), 922 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.92 (s, 9 H), 1.37 (dd, J = 4.3, 13.9 Hz, 1 H), 1.87 (dd, J = 8.5, 13.9 Hz, 1 H), 3.09 (ddt, J = 0.7, 4.3, 8.5 Hz, 1 H), 5.04 (ddd, J = 0.7, 1.3, 10.1 Hz, 1 H), 5.13 (dd, J = 1.3, 17.2 Hz, 1 H), 5.81 (ddd, J = 8.5, 10.1, 17.2 Hz, 1 H); ^{13}C NMR (400 MHz, CD_3OD) δ 30.0, 31.8, 47.2, 48.6, 116.1, 139.6, 178.5; High-resolution MS, Calcd for $C_9H_{16}O_2$: 156.1150, Found m/z (relative intensity): 156.1129 (M^+, 24), 141 (100).

2,4,4-Trimethyl-2-(prop-1-en-2-yl)pentanoic acid (**6b**): IR (neat) 2955 (s), 2876 (s), 1701 (s), 1638 (w), 897 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.99 (s, 9 H), 1.39 (s, 3 H), 1.67 (d, J = 14.4 Hz, 1 H), 1.76 (d, J = 1.2 Hz, 3 H), 2.04 (d, J = 14.4 Hz, 1 H), 4.85 (q, J = 1.2 Hz, 1 H), 4.94 (s, 1 H); ^{13}C NMR (400 MHz, CD_3OD) δ 20.5, 23.0, 31.8,

32.5, 49.5, 52.4, 111.4, 150.0, 180.1; High-resolution MS, Calcd for $C_{11}H_{20}O_2$: 184.1463, Found m/z (relative intensity): 184.1437 (M^+, 25), 169 (100).

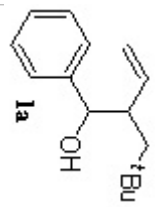
2,4,4-Trimethyl-2-vinylpentanoic acid (**6c**): IR (neat) 2955 (br s), 2874 (s), 1703 (s), 1643 (w), 918 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.96 (s, 9 H), 1.34 (s, 3 H), 1.65 (d, J = 14.4 Hz, 1 H), 1.84 (d, J = 14.4 Hz, 1 H), 5.01 (dd, J = 1.0, 10.7 Hz, 1 H), 5.07 (dd, J = 1.0, 17.6, Hz, 1 H), 6.17 (dd, J = 10.7, 17.6 Hz, 1 H); ^{13}C NMR (400 MHz, CD_3OD) δ 23.4, 31.6, 32.7, 49.5, 54.0, 112.5, 145.2, 180.2; High-resolution MS, Calcd for $C_{10}H_{18}O_2$: 170.1307, Found m/z (relative intensity): 170.1303 (M^+, 100), 155 (60).

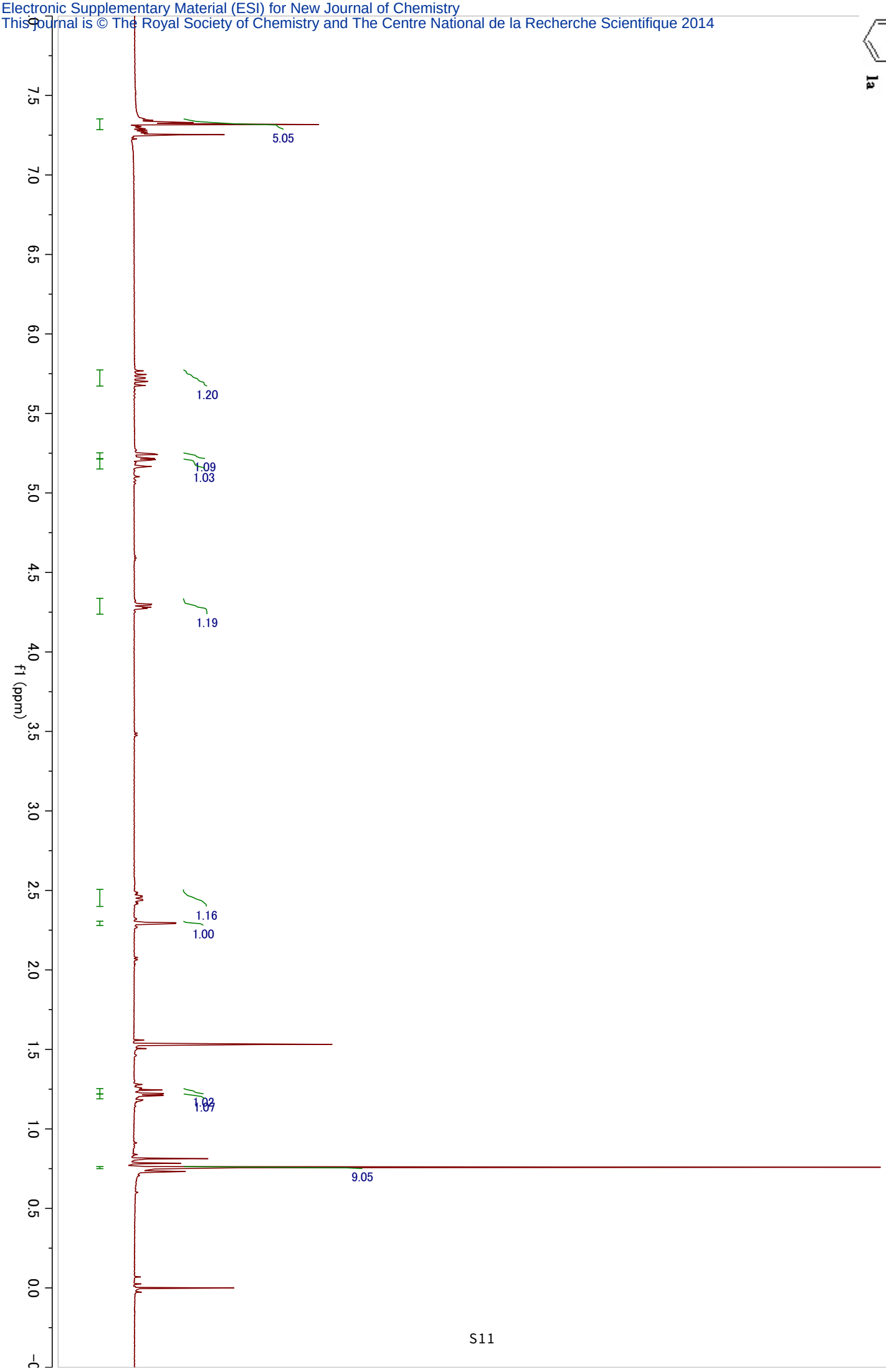
4,4-Dimethyl-2-(prop-1-en-2-yl)pentanoic acid (**7c**): IR (neat) 2955 (br s), 2874 (s), 1703 (s), 1643 (w), 918 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.91 (s, 9 H), 1.35 (dd, J = 3.3, 14.0 Hz, 1 H), 1.77 (dd, J = 0.9, 1.5 Hz, 3 H), 1.98 (dd, J = 9.0, 14.0 Hz, 1 H), 3.08 (dd, J = 3.3, 9.0 Hz, 1 H), 4.81 (q, J = 1.5 Hz, 1 H), 4.88 (q, J = 0.9 Hz, 1 H); ^{13}C NMR (400 MHz, CD_3OD) δ 20.8, 29.7, 31.4, 45.5, 50.8, 112.9, 146.0, 177.8; High-resolution MS, Calcd for $C_{10}H_{18}O_2$: 170.1307, Found m/z (relative intensity): 170.1303 (M^+, 100), 155 (60).

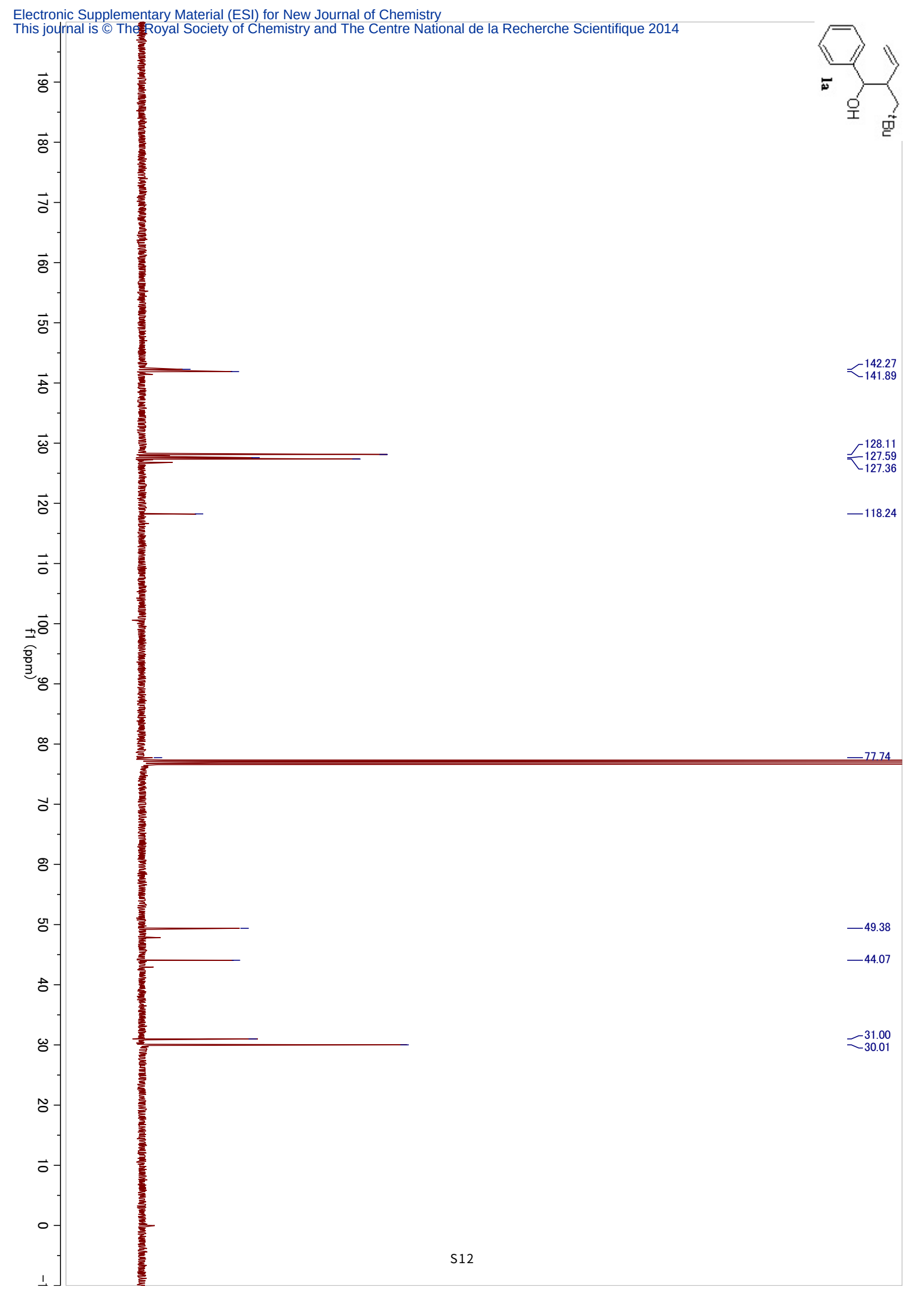
6-Methyl-2-neopentyl-2-vinylhept-5-enoic acid (6d): IR (neat) 2955 (s), 2876 (s), 2608 (w), 1699 (s), 1638 (m), 914 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.92 (s, 9 H), 1.55 (s, 3 H), 1.62 (d, J = 14.1 Hz, 1 H), 1.65 (d, J = 1.2 Hz, 3 H), 1.67 (dd, J = 4.9, 12.2 Hz, 1 H), 1.71-1.81 (m, 1 H), 1.85 (dd, J = 3.9, 12.2 Hz, 1 H), 1.94-2.01 (m, 1 H), 1.99 (d, J = 14.1 Hz, 1 H), 2.16 (s, 1 H), 5.05 (dq, J = 1.2, 7.0 Hz, 1 H), 5.17 (dd, J = 1.0, 17.8 Hz, 1 H), 5.22 (dd, J = 1.0, 11.2 Hz, 1 H), 6.31 (dd, J = 11.2, 17.8 Hz, 1 H); ^{13}C NMR (400 MHz, CD_3OD) δ 17.6, 22.9, 25.6, 31.3, 31.9, 40.2, 51.2, 53.9, 114.1, 123.6, 131.8, 139.4, 181.0; High-resolution MS, Calcd for $C_{15}H_{26}O_2$: 238.1933, Found m/z (relative intensity): 238.1915 (M^+, 30), 195 (100).

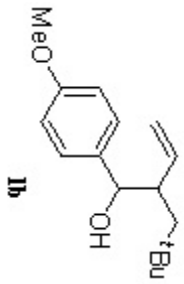
7-Methyl-3-methylene-2-neopentyloct-6-enoic acid (**7d**): IR (neat) 2955 (s), 2874 (s), 2608 (w), 1699 (s), 1638 (m), 916 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.90 (s, 9 H), 1.38 (dd, J = 2.8, 14.1 Hz, 1 H), 1.61 (s, 3 H), 1.68 (s, 3 H), 2.02 (dd, J = 9.5, 14.1 Hz, 1 H), 2.08-2.17 (m, 4 H), 3.07 (dd, J = 2.8, 9.5 Hz, 1 H), 4.89 (s, 1 H), 5.01 (s, 1 H), 5.09-5.14 (m, 1 H); ^{13}C NMR (400 MHz, CD_3OD) δ 17.7, 25.6, 26.3, 29.2, 30.8, 44.9,

47.9, 111.4, 123.6, 131.8, 147.8, 179.7; High-resolution MS, Calcd for $C_{15}H_{26}O_2$: 238.1933, Found m/z (relative intensity): 238.1915 (M^+, 30), 195 (100).









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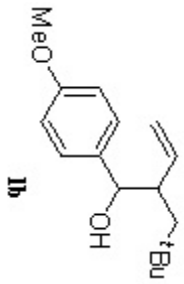

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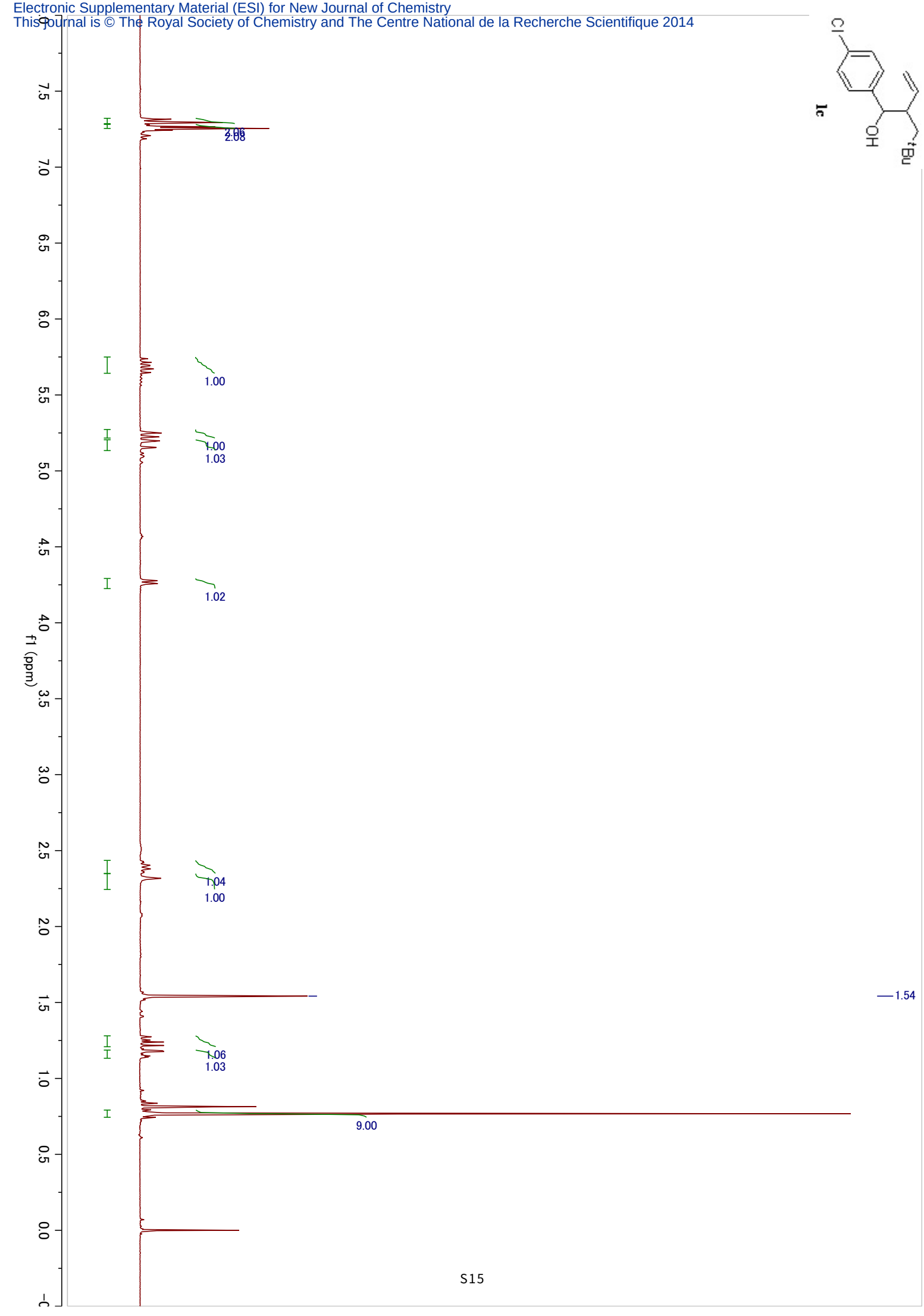

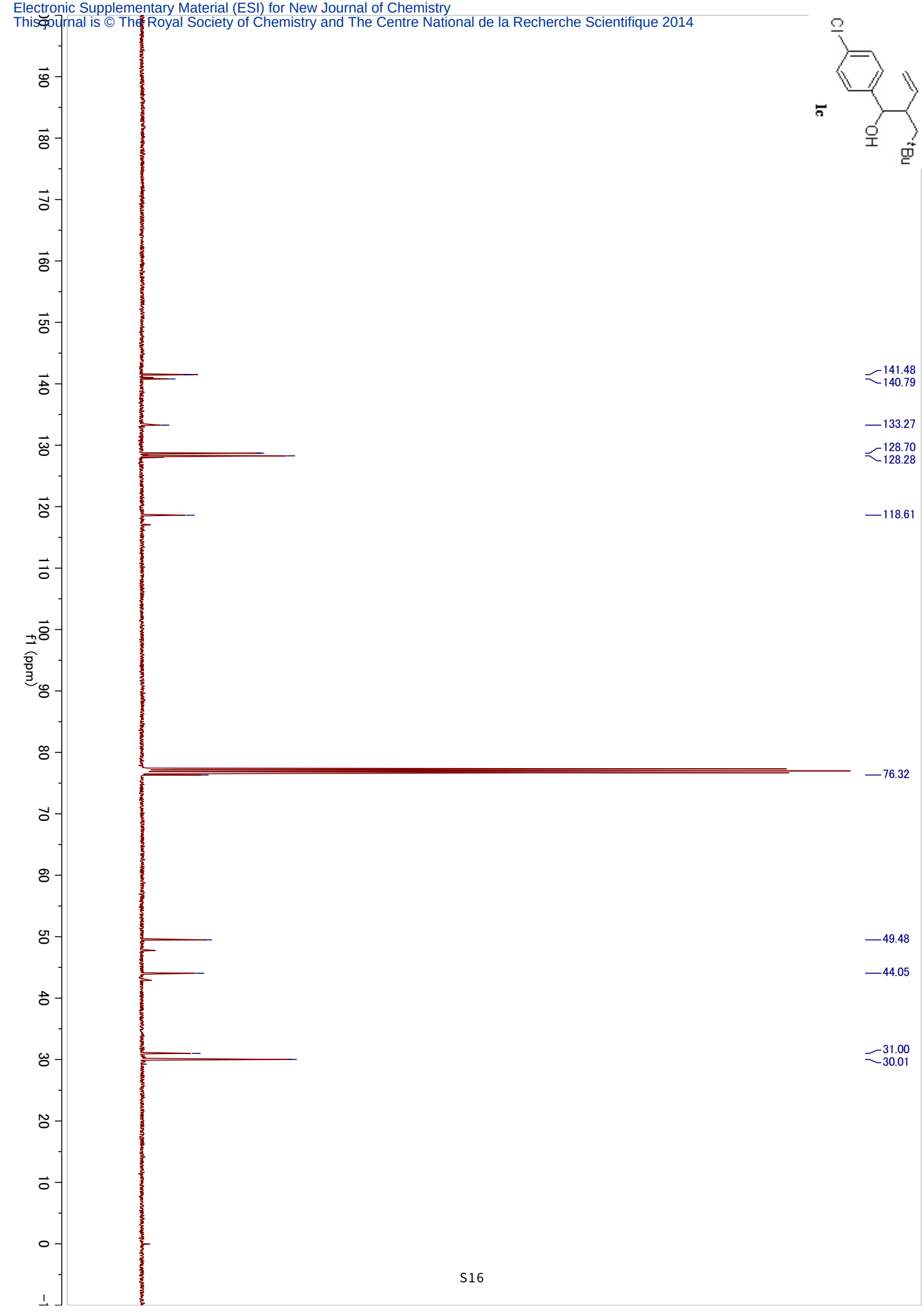

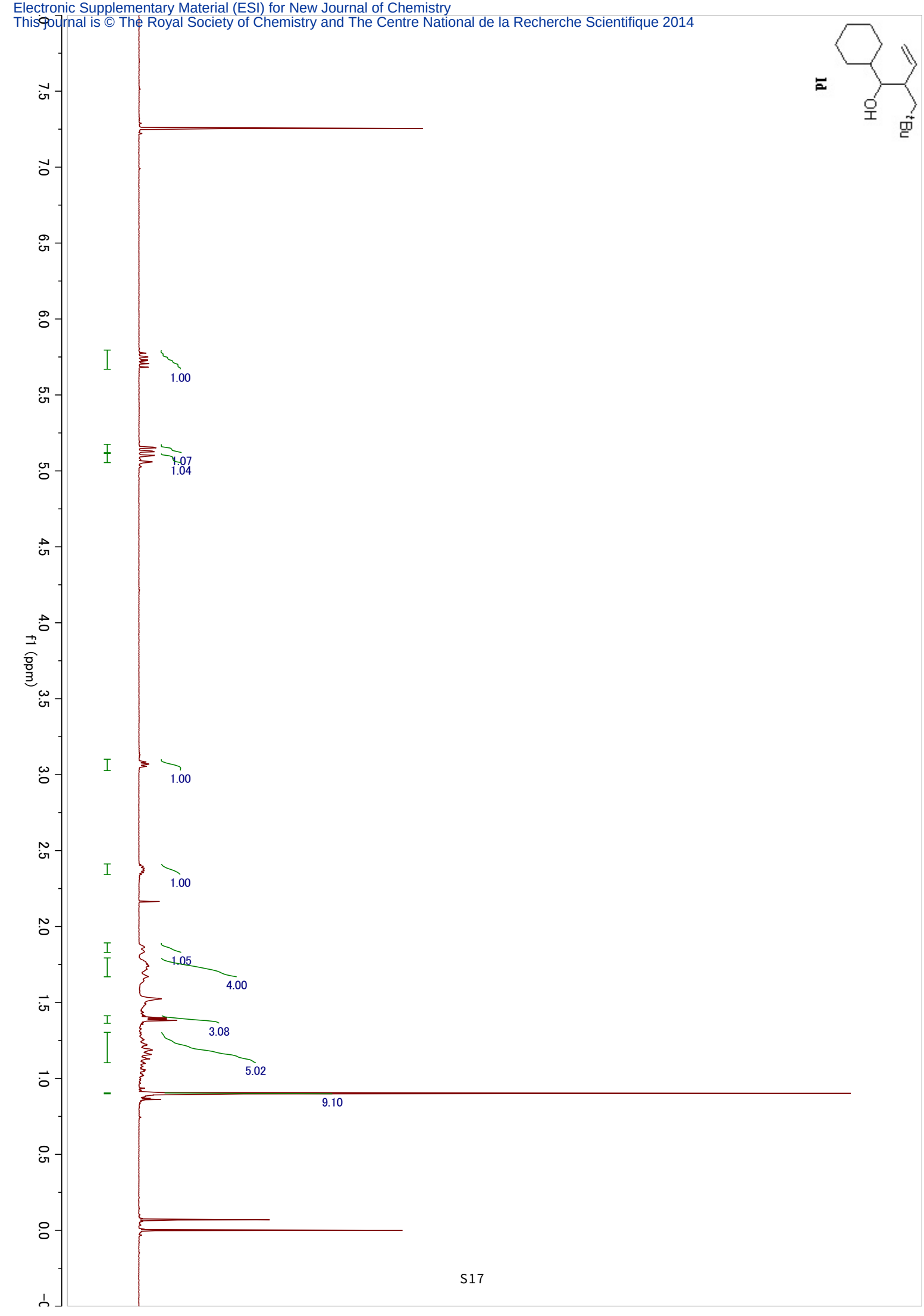

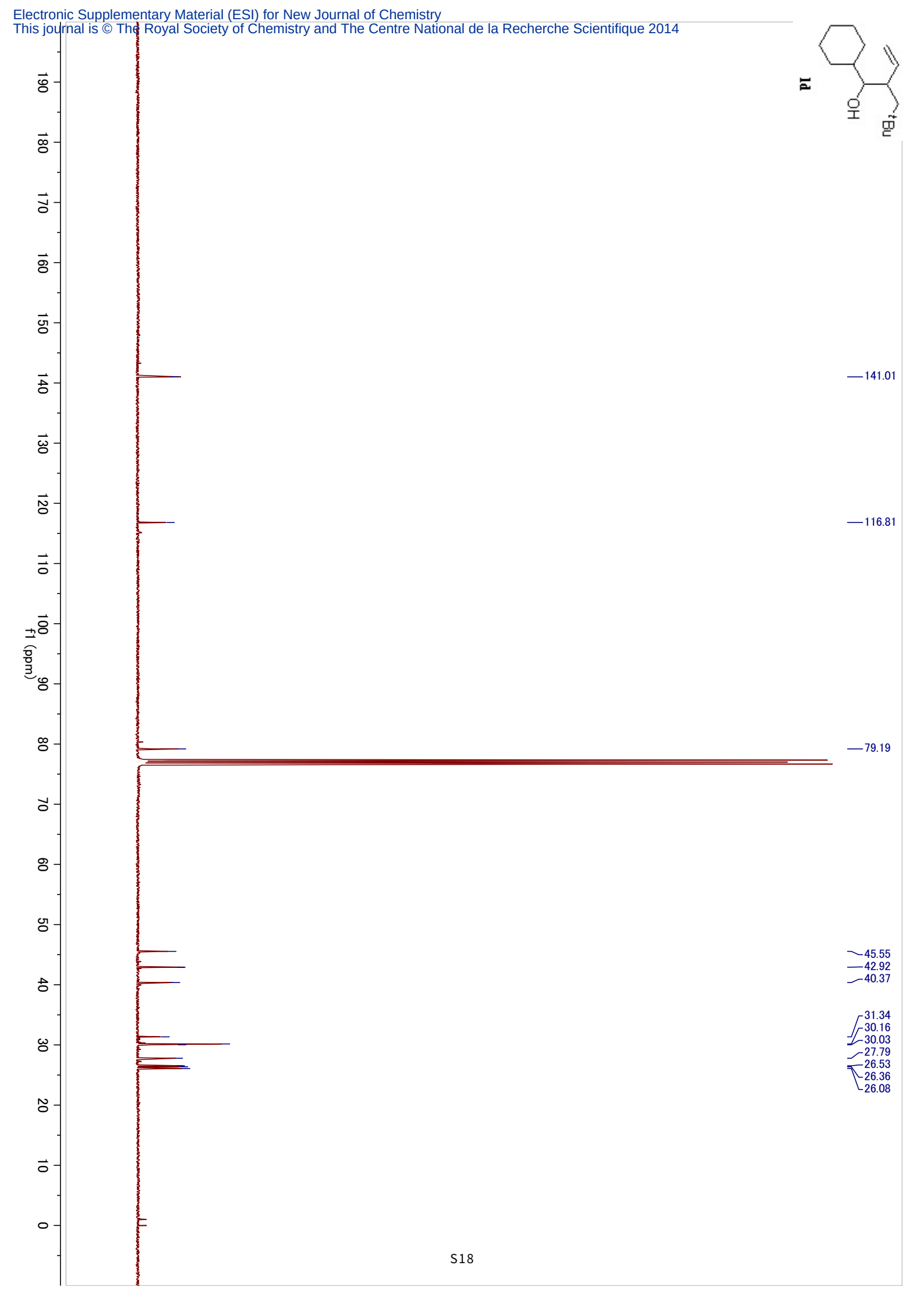

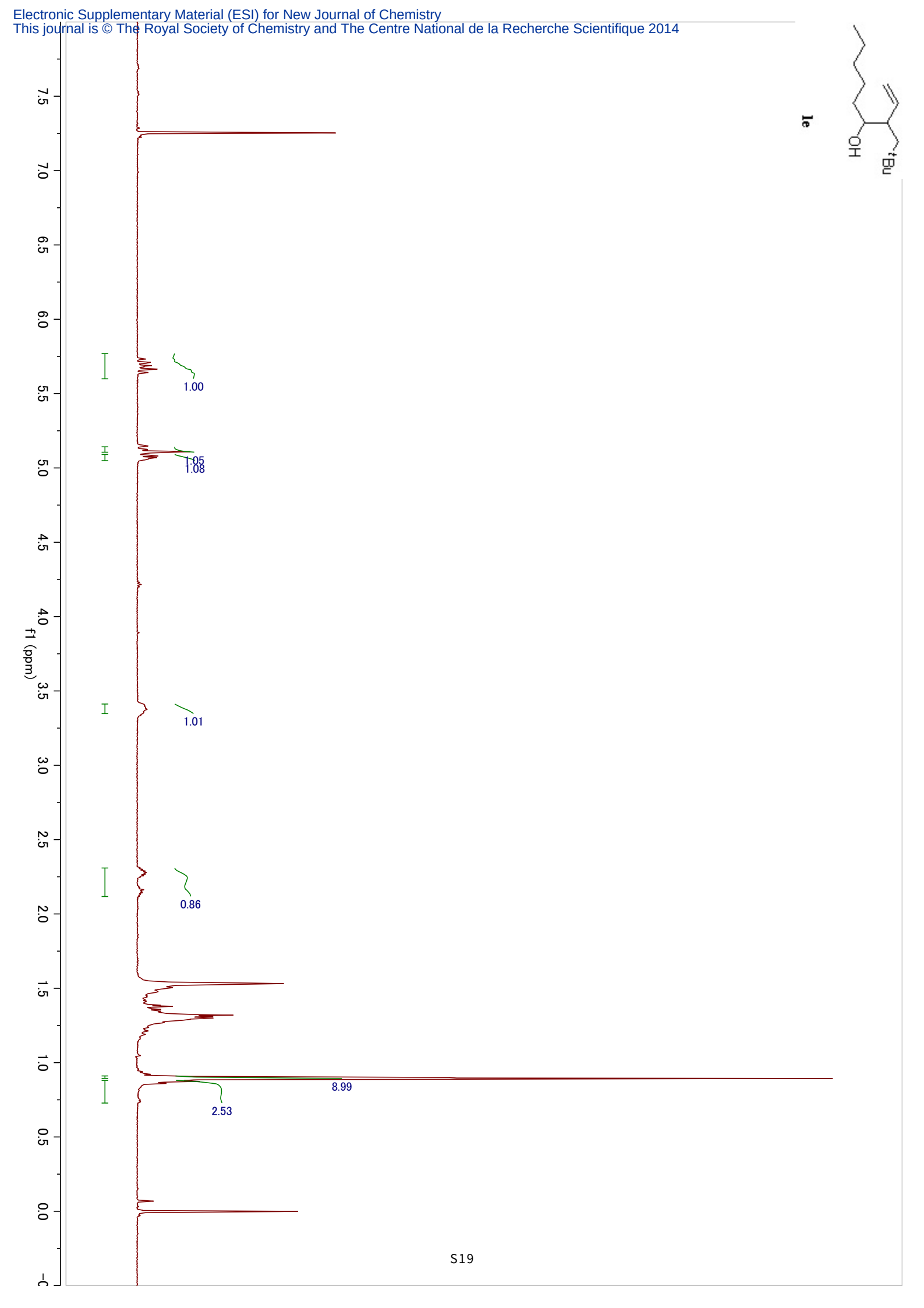

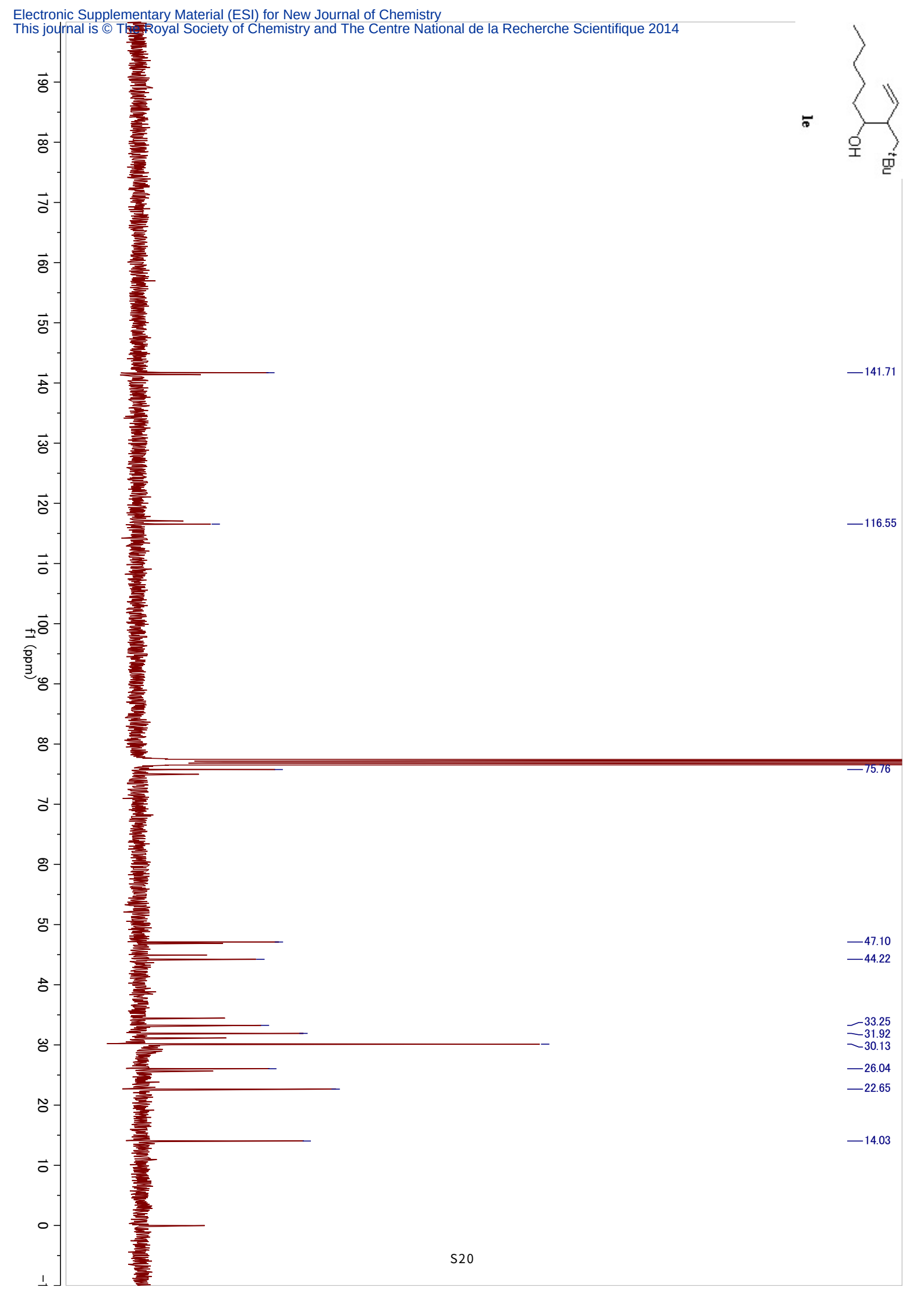

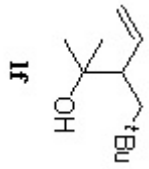

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