SUPPORTING INFORMATION

Facile and Chemoselective Rhodium-Catalysed Intramolecular Hydroacylation of α,α-Disubstituted 4-Alkylidenecyclopropanals

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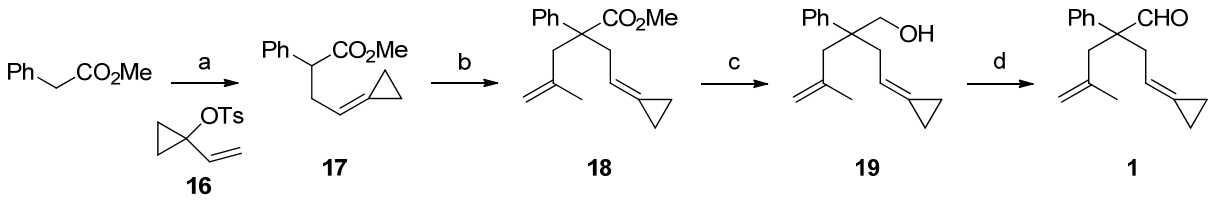
General. Otherwise noted, all reactions were carried out in flame-dried glassware under dry nitrogen atmosphere. The solvents were purified either with the solvent purification system Pure Solv MD-6 (THF, Et_2O, CH_2Cl_2, benzene, toluene, hexane) or by distillation over the drying agents indicated and were transferred under N_2: 1,2-DCE (CaH_2), acetone (Na_2SO_4). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DRX 500 spectrometer in $CDCl_3$; chemical shifts (δ) are given in ppm relative TMS and were converted to the TMS scale using the solvent signals as references ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.24 ppm). IR: PerkinElmer Spectrum 100 FT-IR spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. HRMS at the University of Liverpool: VG7070E (CI), micromass LCT mass spectrometer (ES+), except for compounds **2**, **4a**, **5**, **7**, **10**, and **15d** whose HMRS spectra were obtained from the EPSRC National Mass Spectrometry Service Centre at Swansea. Melting points: Griffin melting point apparatus (not corrected). Elemental analyses: University of Liverpool. All commercially available compounds were used as received. Compounds **16** and **22** are known compounds and were prepared according to literature.[1]

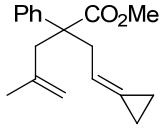
[1] Known compound, see: A. Stolle, J. Ollivier, P. P. Piras, J. Salaun, A. de Meijere, *J. Am. Chem. Soc.*, 1992, **114**, 4051.

Preparation of compound 1



[a] 1) NaH, methyl phenylacetate, DMF, 2) **16**, $Pd_2(dba)_3$, dppe, DMF, THF, 60 °C, 86%. [b] LiHMDS, methylallyl bromide, THF, –78 °C to r.t., 89%. [c] $LiAlH_4$, Et_2O, r.t., 84%. [d] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C, 94%.

Compound 17. Under N_2, methyl phenylacetate (1.27 mL, 8.82 mmol) was added at 0 °C to a suspension of sodium hydride (336 mg, 8.40 mmol) in DMF (16 mL) and the mixture was stirred at room temperature for 40 minutes. In another flask, tosylate **16** (1 g, 4.20 mmol) was added to a suspension of tris(dibenzylideneacetone)dipalladium (115 mg, 0.126 mmol) and dppe (100 mg, 0.252 mmol) in THF (24 mL) and the mixture was stirred at room temperature for 30 minutes. The palladium complex was cannulated to the enolate and the resulting mixture was stirred at 60 °C for 3 hours. The mixture was quenched with water (25 mL) and extracted with Et_2O (3 × 20 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/Et_2O, 50/1) gave **17** as a pale yellow oil (778 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 5H), 5.80–5.71 (m, 1H), 3.77 (t, *J* = 7.7 Hz, 2H), 3.68 (s, 3H), 3.09–2.93 (m, 1H), 2.76–2.63 (m, 1H), 1.14–0.98 (m, 3H), 0.97–0.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 138.9, 128.5 (2C), 128.0 (2C), 127.2, 124.0, 114.8, 51.9, 51.4, 35.8, 2.3, 1.9; IR (neat): $\tilde{\nu}$ = 3030, 2980, 2951, 2845, 1734, 1602, 1495, 1435, 1266, 1223, 1157, 836, 729, 697 cm^{-1}; MS (CI): *m/z* (rel. intensity): 234 (100), 217 (17); HRMS (CI) calcd for $(C_{14}H_{16}O_2 + NH_4)^+$: 234.14940; found: 234.14907; elemental analysis (%) calcd for $C_{14}H_{16}O_2$: C 77.75, H 7.46; found: C 77.86, H 7.48.

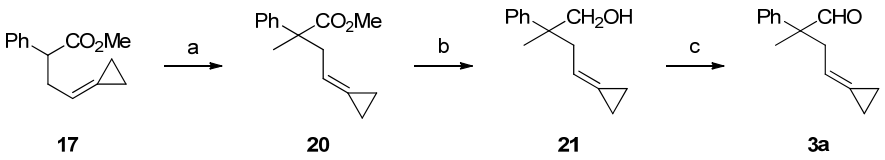


Compound 18. LiHMDS (1M in THF, 0.90 mL, 0.90 mmol) was added dropwise via syringe to **17** (150 mg, 0.69 mmol) in 5 mL THF at -78 °C under N_2. After stirring at that temperature for 1h, methylallyl bromide (91 µL, 0.90 mmol) was added via microsyringe. The mixture was allowed to slowly warm to room temperature overnight. The mixture was then quenched with a saturated solution of NH_4Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAC, 30/1) gave **18** as a colourless oil (167 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.23 (m, 4H), 7.23–7.18 (m, 1H), 5.57–5.49 (m, 1H), 4.82–4.80 (m, 1H), 4.63–4.60 (m, 1H), 3.61 (s, 3H), 2.97–2.93 (m, 2H), 2.88 (d, *J* = 13.7 Hz, 1H), 2.74 (d, *J* = 13.7 Hz, 1H), 1.40 (s, 3H), 1.01–0.90 (m, 2H), 0.89–0.80 (m, 1H), 0.80–0.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.1, 142.5, 141.8, 128.2 (2C), 126.7, 126.6 (2C), 125.5, 115.2, 113.1, 53.8, 51.9, 42.5, 37.0, 23.8, 2.7, 1.9; IR (neat): $\tilde{\nu}$ = 3058, 3023, 2980, 2949, 1729, 1644, 1600, 1580, 1498, 1446, 1257, 1200, 1081, 1031, 989, 959, 931, 893, 763, 729, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 293 (100); HRMS (ES+) calcd for $(C_{18}H_{22}O_2 + Na)^+$: 293.1517; found: 293.1518; elemental analysis calcd (%) for $C_{18}H_{22}O_2$: C 79.96, H 8.20; found: C 80.04, H 8.47.

Compound 19. Under N_2, ester **18** (154 mg, 0.57 mmol) in Et_2O (2.8 mL) was added to a suspension of lithium aluminium hydride (11 mg, 0.285 mmol) in Et_2O (4 mL) at 0 °C. After stirring for 20 minutes at room temperature, lithium aluminium hydride (11 mg, 0.285 mmol) was added at 0 °C. After stirring for another 30 minutes at room temperature, a saturated aqueous solution of Na_2SO_4 was added dropwise, first at 0 °C then at room temperature, until a white precipitate appeared. The mixture was filtered through a pad of celite and concentrated. Purification by flash chromatography (PE/EtOAc, 30/1 → 15/1) afforded **19** as a colourless oil (116 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 2H), 7.33–7.28 (m, 2H), 7.21–7.16 (m, 1H), 5.69–5.63 (m, 1H), 4.77–4.74 (m, 1H), 4.62–4.59 (m, 1H), 3.85 (d, *J* = 6.7 Hz, 2H), 2.72 (ddquint, *J* = 14.1 Hz, *J* = 6.7 Hz, *J* = 1.4 Hz, 1H), 2.63 (ddquint, *J* = 14.1 Hz, *J* = 7.7 Hz, *J* = 1.1 Hz, 1H), 2.47 (s, 2H), 1.43 (t, *J* = 6.7 Hz, 1H (OH)), 1.30 (s, 3H), 1.04–0.98 (m, 2H), 0.97–0.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.1, 143.1, 128.2 (2C), 127.0 (2C), 126.0, 124.6, 114.5, 114.2, 67.4, 46.2, 44.8, 38.3, 24.5, 2.8, 1.8; IR (neat): $\tilde{\nu}$ = 3436 (br), 3055, 2978, 2922, 1641, 1498, 1445, 1375, 1024, 964, 937, 892, 764, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 265 (100); HRMS (ES+) calcd for $(C_{17}H_{22}O + Na)^+$: 265.1568; found: 265.1560; elemental analysis calcd (%) for $C_{17}H_{22}O$: C 84.25, H 9.15; found: C 84.43, H 8.90.

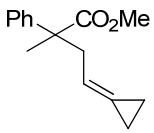
Compound 1. Under N_2, dimethyl sulfoxide (0.18 mL, 2.60 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of oxalyl chloride (0.11 mL, 1.30 mmol) in CH_2Cl_2 (5 mL) at –78 °C. After 10 minutes stirring at –78 °C, a solution of **19** (243 mg, 1 mmol) in CH_2Cl_2 (1 mL) was added. After 20 minutes stirring at –78 °C, triethylamine (0.70 mL, 5 mmol) was added rapidly and the mixture was stirred at room temperature during 20 minutes. A saturated solution of NH_4Cl (10 mL) was added to the reaction mixture which was then extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography PE/EtOAc, 80/1) gave **1** as colourless oil (225 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.54 (s, 1H), 7.37–7.32 (m, 2H), 7.29–7.21 (m, 3H), 5.65–5.59 (m, 1H), 4.81–4.78 (m, 1H), 4.62–4.58 (m, 1H), 2.89 (d, *J* = 7.2 Hz, 2H), 2.74 (d, *J* = 14.2 Hz, 1H), 2.67 (d, *J* = 14.4 Hz, 1H), 1.37 (s, 3H), 1.04–0.94 (m, 2H), 0.92–0.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.3, 141.3, 138.6, 128.6 (2C), 127.9 (2C), 127.3, 126.0, 115.3, 112.5, 57.6, 41.0, 34.8, 24.3, 2.8, 2.0; IR (neat): $\tilde{\nu}$ = 3057, 2979, 2709, 1721, 1643, 1544, 1495, 1446, 1377, 1091, 1030, 1002, 967, 930, 894, 759, 697 cm^{-1}; MS (CI) : *m/z* (rel. intensity) : 259 (17), 258 (100), 242 (12), 241 (69), 173 (14); elemental analysis calcd (%) for $C_{17}H_{20}O$: C 84.16, H 8.83; found: C 83.20, H 8.44.

Preparation of compound 3a

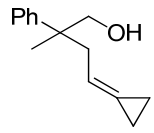


[a] NaHMDS, MeI, THF, r.t., 79%. [b] $LiAlH_4$, Et_2O, r.t., 95%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C, 91%.

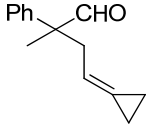
Compound 20. Under N_2, NaHMDS (407 mg, 2.22 mmol) was added as solid in one portion to a solution of **17** (320 mg, 1.48 mmol) in THF (15 mL) at 0 °C. The mixture was stirred at room temperature during 1 hour. Then iodomethane (0.55 mL, 8.88 mmol) was added via syringe and the mixture was stirred for another 4 hours at room temperature. The reaction mixture was quenched with a saturated solution of NH_4Cl (10 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 60/1) gave **20** as a colourless oil (270 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.31 (m, 4H), 7.24–7.20 (m, 1H), 5.62-5.56 (m, 1H), 3.64 (s, 3H), 2.94 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H), 2.77 (dd, *J* = 13.2 Hz, *J* = 7.6 Hz, 1H), 1.52 (s, 3H), 1.06–0.98 (m, 2H), 0.95–0.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.5, 143.5, 128.3 (2C), 126.7, 126.0 (2C), 125.6, 113.4, 52.1, 50.5, 41.6, 22.7, 2.8, 1.7; IR (neat): $\tilde{\nu}$ = 3053, 3023, 2980, 2950, 1729, 1601, 1497, 1446, 1434, 1377, 1268, 1227, 1203, 1147, 1120, 1074, 1031, 986, 968, 935, 857, 810, 764, 732, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 253 (100); HRMS (ES+) calcd for $(C_{15}H_{18}O_2 + Na)^+$: 253.1204; found: 253.1194; elemental analysis (%) calcd for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found: C 77.32, H 7.74.



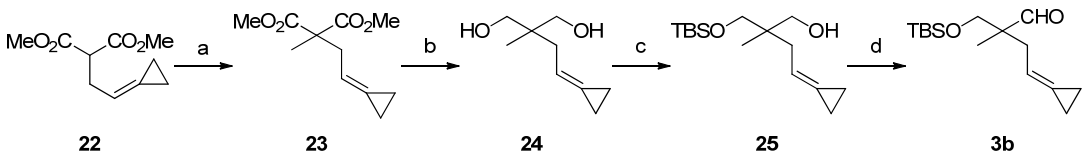
Compound 21. This compound was prepared from **20** (117 mg, 0.508 mmol) according to the procedure described for the preparation of **19**. Colourless oil (81 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 5.61–5.53 (m, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.60 (dd, *J* = 10.8 Hz, *J* = 4.7 Hz, 1H), 2.63 (dd, *J* = 13.9 Hz, *J* = 6.5 Hz, 1H), 2.47 (dd, *J* = 13.9 Hz, *J* = 7.9 Hz, 1H), 1.33 (s, 3H), 1.30–1.22 (br s, 1H), 1.04–0.82 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.8, 128.4 (2C), 126.7 (2C), 126.2, 124.5, 113.9, 71.8, 43.9, 40.9, 21.9, 2.8, 1.7; IR (neat): $\tilde{\nu}$ = 3367 (br), 3053, 2977, 2926, 2871, 1601, 1497, 1445, 1373, 1296, 1156 1024, 966, 935, 894, 830, 760, 697 cm^{-1}; MS (CI): *m/z* (rel. intensity): 221 (15), 220 (100), 185 (5); HRMS (CI) calcd for $(C_{14}H_{18}O + NH_4)^+$: 220.1696; found: 220.1692.



Compound 3a. This compound was prepared from **21** (50 mg, 0.25 mmol) according to the procedure described for the preparation of **1**. Colourless oil (45 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.56 (s, 1H), 7.39–7.36 (m, 2H), 7.31–7.25 (m, 3H), 5.61–5.55 (m, 1H), 2.80 (d, *J* = 7.2 Hz, 2H), 1.44 (s, 3H), 1.08-0.98 (m, 2H), 0.96–0.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.4, 139.8, 128.7 (2C), 127.2 (3C), 125.9, 112.6, 54.4, 38.4, 19.0, 2.9, 1.7; IR (neat): $\tilde{\nu}$ = 3056, 2979, 2934, 2806, 2707, 1722, 1600, 1495, 1446, 1389, 1372, 1267, 1075, 1029, 967, 935, 837, 760, 733, 698 cm^{-1}; MS (CI): *m/z* (rel. intensity): 219 (12), 218 (100), 201 (3), 200 (1); HRMS (CI) calcd for $(C_{14}H_{16}O + NH_4)^+$: 218.1539; found: 218.1539.



Preparation of compound 3b



[a] NaH, MeI, THF, r.t., 80%. [b] $LiAlH_4$, Et_2O, r.t., 89%. [c] NaH, TBSCl, CH_2Cl_2, r.t., 84%. [d] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 82%.

Compound 23. Under N_2, **22** (300 mg, 1.51 mmol) in THF (4 mL) was added to a suspension of sodium hydride (44 mg, 1.82 mmol) in THF (12 mL) cooled at 0 °C. The mixture was stirred at room temperature for 1 hour, then iodomethane (141 µL, 2.27 mmol) was added and the mixture was stirred for another 40 minutes at room temperature. The mixture was quenched with brine (10 mL) and extracted with Et_2O (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/Et_2O, 40/1 → 30/1) afforded **23** as a colourless oil (257 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.63–5.57 (m, 1H), 3.67 (s, 6H), 2.70 (d, *J* = 7.6 Hz, 2H), 1.35 (s, 3H), 1.06–1.01 (m, 2H), 0.98–0.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.5 (2C), 126.5, 112.0, 53.9, 52.4 (2C), 38.2, 19.8, 2.9, 1.7; IR (neat): $\tilde{\nu}$ = 2985, 2954, 1731, 1454, 1434, 1377, 1287, 1242, 1202, 1159, 1110, 982, 936, 874, 755 cm^{-1}; MS (CI): *m/z* (rel. intensity): 232 (42), 230 (95), 215 (82), 213 (100), 164 (93), 147 (10); HRMS (CI) calcd for ($C_{11}H_{16}O_4$ + H): 213.11268; found: 213.11277; elemental analysis (%) calcd for $C_{11}H_{16}O_4$: C 62.25, H 7.60; found: C 62.32, H 7.63.

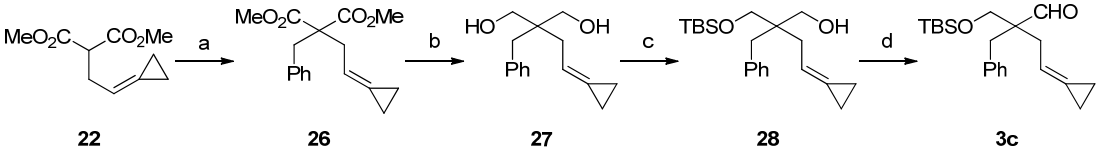
Compound 24. To a suspension of lithium aluminum hydride (67 mg, 1.77 mmol) in Et_2O (12 mL), a solution of **23** (250 mg, 1.18 mmol) in Et_20 (6 mL) was added at 0°C. The mixture was stirred during 20 minutes at room temperature then lithium aluminum hydride (67 mg, 1.77 mmol) was added at 0°C. After 30 minutes of stirring at room temperature, few drops of a saturated solution of Na_2SO_4 was added until a white precipitate appeared. The mixture was filtered through a pad of celite and evaporated. Colourless oil (164 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.82–5.72 (m, 1H), 3.53 (d, *J* = 10.6 Hz, 2H), 3.47 (d, *J* = 10.6 Hz, 2H), 2.90 (s, 2H (OH)), 2.16 (d, *J* = 7.7 Hz, 2H), 1.09–0.94 (m, 4H), 0.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.6, 113.5, 70.0 (2C), 40.0, 36.4, 18.5, 2.8, 1.7; IR (neat): $\tilde{\nu}$ = 3246 (br), 2962, 2936, 2877, 1470, 1429, 1387, 1367, 1295, 1251, 1223, 1156, 1096, 1044, 1018, 988, 964, 941, 887, 871, 807, 755, 715 cm^{-1}; MS (CI): *m/z* (rel. intensity): 176 (24), 174 (100), 159 (16), 157 (43), 139 (14), 132 (13), 128 (16), 126 (23), 115 (17), 109 (16); HRMS (CI) calcd for ($C_9H_{16}O_2$ + H): 157.12285; found: 157.12310; elemental analysis (%) calcd for $C_9H_{16}O_2$: C 69.19, H 10.32; found: C 69.32, H 10.37.

Compound 25. Under N_2, a solution of **24** (170 mg, 1.088 mmol) in THF (2 mL) was added to a suspension of sodium hydride (26 mg, 1.088 mmol) in THF (8 mL) cooled at 0 °C. The mixture was stirred at room temperature during 18 hours then *tert*-butyldimethylsilyl chloride (163 mg, 1.088 mmol) was added. The mixture was sirred at room temperature during 1 hour then quenched with water (10 mL) and extracted with Et_2O (3 × 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/Et_2O, 35/1 → 30/1) gave **25** as a colourless oil (247 mg, 84%). ^{1}H NMR

(500 MHz, $CDCl_3$): δ = 5.79–5.70 (m, 1H), 3.51 (d, *J* = 9.7 Hz, 2 H), 3.49–3.42 (m, 2H), 3.02–2.56 (m, 1H (OH)), 2.19 (dd, *J* = 13.6 Hz, 7.5 Hz, 1H), 2.13 (dd, *J* = 13.7 Hz, 7.6 Hz, 1H), 1.08–1.00 (m, 2H), 0.99–0.93 (m, 2H), 0.86 (s, 9H), 0.78 (s, 3H), -0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.3, 113.7, 71.2, 70.6, 39.9, 36.4, 25.8 (3C), 18.6, 18.1, 2.8, 1.8, -5.7 (2C); IR (neat): $\tilde{\nu}$ = 3436, 2955, 2929, 2857, 1472, 1389, 1362, 1252, 1088, 1039, 1006, 968, 937, 834, 774, 667 cm^{-1}; MS (CI): *m/z* (rel. intensity): 273 (61), 271 (100), 132 (20), 109 (13); HRMS (CI) calcd for ($C_{15}H_{30}O_2Si$ + H): 271.20933; found: 271.20890; elemental analysis (%) calcd for $C_{58}H_{30}O_2Si$: C 66.61, H 11.18; found: C 67.06, H 11.26.

Compound 3b. This compound was prepared from **25** (210 mg, 0.78 mmol) according to the procedure described for the preparation of **1**. Colourless oil (181 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.57 (s, 1H), 5.68–5.62 (m, 1H), 3.66 (d, *J* = 9.7 Hz, 1H), 3.56 (d, *J* = 9.7 Hz, 1H), 2.39–2.44 (m, 1H), 2.35–2.30 (m, 1H), 1.07–1.02 (m, 2H), 0.99 (s, 3H), 0.97–0.93 (m, 2H), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.3, 125.5, 112.4, 66.6, 51.9, 34.6, 25.7 (3C), 18.1, 16.0, 2.8, 1.8, -5.7 (2C); IR (neat): $\tilde{\nu}$ = 2952, 2930, 2886, 2857, 1730, 1472, 1464, 1391, 1363, 1252, 1102, 1004, 969, 936, 835, 777, 670 cm^{-1}; MS (CI): *m/z* (rel. intensity): 286 (14), 271 (32), 269 (100), 268 (18), 251 (18), 136 (33), 132 (35), 119 (28); HRMS (CI) calcd for ($C_{15}H_{28}O_2Si$ + H): 269.19368; found: 269.19364; elemental analysis (%) calcd for $C_{15}H_{28}O_2Si$: C 67.11, H 10.51; found: C 67.00, H 10.54.

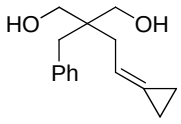
Preparation of compound 3c



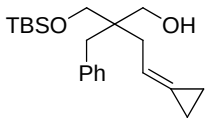
22 **26** **27** **28** **3c**

[a] NaH, BnBr, Bu_4NI, THF, r.t., 71%. [b] $LiAlH_4$, Et_2O, r.t., 99%. [c] TBSCl, Pyridine, CH_2Cl_2, 40 °C, 90%. [d] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 95%.

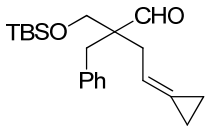
Compound 26. Under N_2, a solution of ester **22** (200 mg, 1.01 mmol) in THF (3 mL) was added to a suspension of sodium hydride (29 mg, 1.21 mmol) in THF (3 mL) at 0 °C. The resulting mixture was stirred at room temperature during 2 hours then benzyl bromide (145 µL, 1.21 mmol) followed by tetrabutylammonium iodide (149 mg, 0.40 mmol) were added. The resulting mixture was stirred at room temperature during 14 hours. The mixture was quenched with a saturated solution of NH_4Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 60/1 → 40/1) gave **26** as a colourless oil (445 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.18 (m, 3H), 7.09–7.04 (m, 2H), 5.74–5.68 (m, 1H), 3.67 (s, 6H), 3.23 (s, 2H), 2.68 (d, *J* = 7.5 Hz, 2H), 1.11–1.06 (m, 2H), 1.02–0.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.4 (2C), 136.0, 129.8 (2C), 128.2 (2C), 126.9, 126.4, 112.0, 59.1, 52.3 (2C), 38.1, 34.5, 2.9, 2.0; IR (neat): $\tilde{\nu}$ = 3031, 2977, 2952, 1732, 1497, 1434, 1328, 1278, 1242, 1201, 1175, 1084, 1044, 1003, 953, 899, 862, 821, 780, 743, 700 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 311 (100); HRMS (ES+) calcd for $(C_{17}H_{20}O_4 + Na)^+$: 311.1259; found: 311.1260; elemental analysis (%) calcd for $C_{17}H_{20}O_4$: C 70.81, H 6.99; found: C 70.25, H 6.97.

Compound 27. This compound was prepared from **26** (197 mg, 0.68 mmol) according to the procedure described for the preparation of **24**. Colourless oil (157 mg, 99%). 

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 3H), 7.23–7.19 (m, 2H), 5.91–5.85 (m, 1H), 3.60 (d, *J* = 10.7 Hz, 2H), 3.54 (d, *J* = 10.7 Hz, 2H), 2.98 (s, 2H), 2.71 (s, 2H), 2.11 (d, *J* = 7.5 Hz, 2H), 1.14–1.08 (m, 2H), 1.04–0.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.6, 130.4 (2C), 128.0 (2C), 126.1, 124.9, 113.4, 67.8 (2C), 43.3, 37.4, 34.0, 2.9, 2.0; IR (neat): $\tilde{\nu}$ = 3349, 3058, 3028, 2978, 2923, 2876, 1603, 1496, 1453, 1333, 1211, 1089, 1064, 1027, 967, 933, 870, 797, 722, 701 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 255 (100); HRMS (ES+) calcd for $(C_{15}H_{30}O_2 + Na)^+$: 255.1361; found: 255.1366.

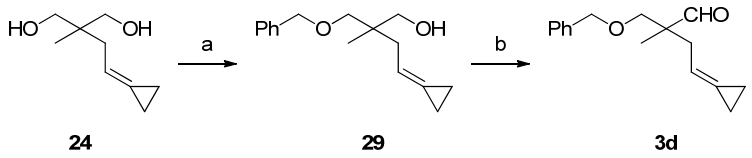
Compound 28. Under N_2, pyridine (51 µL, 0.698 mmol) was added to a solution of **27** (135 mg, 0.582 mmol) in CH_2Cl_2 (4 mL) at room temperature. The mixture was stirred at room temperature during 2 hours before adding *tert*-butyldimethylsilyl chloride (85 mg, 0.564 mmol). The resulting mixture was stirred at 40 °C during 14 hours. The mixture was quenched with a saturated solution of NH_4Cl (4 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 70/1 → 50/1) afforded **28** as a colourless oil (181 mg, 90%). 

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.19 (m, 5H), 5.90–5.83 (m, 1H), 3.63–3.54 (m, 2H), 3.52–3.44 (m, 2H), 2.81 (d, *J* = 12.7 Hz, 1H), 2.78–2.73 (m, 1H (OH)), 2.67 (d, *J* = 12.9 Hz, 1H), 2.15–2.03 (m, 2H), 1.14–1.08 (m, 2H), 1.04–0.98 (m, 2H), 0.94 (s, 9H), -0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.9, 130.6 (2C), 127.9 (2C), 126.0, 124.6, 113.6, 68.7, 68.1, 43.4, 37.3, 34.0, 25.8 (3C), 18.1, 2.8, 2.0, -5.6, -5.7; IR (neat): $\tilde{\nu}$ = 3454 (br), 3028, 2953, 2928, 2857, 1603, 1492, 1471, 1391, 1360, 1252, 1070, 1034, 1006, 967, 938, 834, 774, 723, 701, 669 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 369 (100); HRMS (ES+) calcd for $(C_{21}H_{34}O_2Si + Na)^+$: 369.2226; found: 369.2236.

Compound 3c. This compound was prepared from **28** (166 mg, 0.48 mmol) according to the procedure described for the preparation of **1**. Colourless oil (157 mg, 95%). 

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.64 (s, 1H), 7.26–7.22 (m, 2H), 7.21–7.18 (m, 1H), 7.15–7.12 (m, 2H), 5.76–5.71 (m, 1H), 3.62 (d, *J* = 10.1 Hz, 1H), 3.55 (d, *J* = 10.1 Hz, 1H), 2.98 (d, *J* = 13.9 Hz, 1H), 2.87 (d, *J* = 13.9 Hz, 1H), 2.37 (d, *J* = 7.1 Hz, 2H), 1.10–1.05 (m, 2H), 1.00–0.95 (m, 2H), 0.90 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.0, 136.7, 130.3 (2C), 128.1 (2C), 126.4, 125.8, 112.3, 62.8, 56.0, 35.8, 32.7, 25.8 (3C), 18.1, 2.9, 2.1, -5.6 (2C); IR (neat): $\tilde{\nu}$ = 3053, 3028, 2954, 2929, 2857, 2714, 1726, 1603, 1496, 1471, 1390, 1360, 1252, 1095, 1031, 1006, 968, 937, 835, 775, 723, 700, 669 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 367 (100); HRMS (ES+) calcd for $(C_{21}H_{32}O_2Si + Na)^+$: 367.2069; found: 367.2075; elemental analysis (%) calcd for $C_{21}H_{32}O_2Si$: C 73.20, H 9.36; found: C 72.12, H 9.42.

Preparation of compound 3d



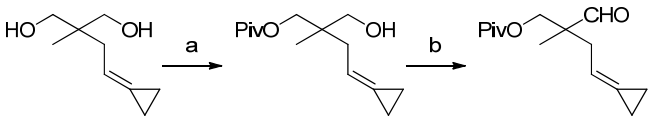
24 **29** **3d**

[a] NaH, BnBr, Bu_4NI, DMF, r.t., 63%. [b] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 86%.

Compound 29. Under N_2, a solution of **24** (153 mg, 0.979 mmol) in DMF (0.4 mL) was added to a suspension of sodium hydride (24 mg, 0.979 mmol) in DMF (1 mL). The resulting mixture was stirred at room temperature during 2 hours. Then, benzyl bromide (117 µL, 0.979 mmol) followed by tetrabutylammonium iodide (217 mg, 0.588 mmol) were added. The mixture was stirred at room temperature during 16 hours. The mixture was quenched with water (10 mL) and extracted with Et_2O (3 × 15 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 40/1 → 10/1) afforded **29** as a colourless oil (152 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 5H), 5.78–5.71 (m, 1H), 4.49 (s, 2H), 3.50 (s, 2H), 3.39 (d, *J* = 9.1 Hz, 1H), 3.33 (d, *J* = 8.8 Hz, 1H), 2.73–2.50 (m, 1H (OH)), 2.29–2.17 (m, 2H), 1.10–1.03 (m, 2H), 1.00–0.93 (m, 2H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.0, 128.4 (2C), 127.7, 127.4 (2C), 124.6, 113.6, 78.1, 73.5, 70.5, 39.8, 36.8, 19.0, 2.8, 1.8; IR (neat): $\tilde{\nu}$ = 3434 (br), 3031, 2977, 2916, 2856, 1497, 1454, 1406, 1362, 1307, 1292, 1249, 1206, 1095, 1075, 1028, 967, 936, 902, 801, 734, 696 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 269 (100); HRMS (ES+) calcd for $(C_{16}H_{22}O_2 + Na)^+$: 269.1517; found: 269.1508; elemental analysis (%) calcd for $C_{16}H_{22}O_2$: C 78.01, H 9.00; found: C 77.17, H 9.40.

Compound 3d. This compound was prepared from **29** (166 mg, 0.67 mmol) according to the procedure described for the preparation of **1**. Colourless oil (141 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.58 (s, 1H), 7.35–7.31 (m, 2H), 7.29–7.25 (m, 3H), 5.67–5.61 (m, 1H), 4.48 (s, 2H), 3.53 (d, *J* = 9.3 Hz, 1H), 3.43 (d, *J* = 9.2 Hz, 1H), 2.44 (dd, *J* = 13.8 Hz, *J* = 7.6 Hz, 1H), 2.38 (dd, *J* = 13.8 Hz, *J* = 7.6 Hz, 1H), 1.06 (s, 3H), 1.07–1.02 (m, 2H), 0.98–0.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.6, 138.0, 128.3 (2C), 127.6, 127.4 (2C), 125.9, 112.1, 73.4 (2C), 51.0, 35.0, 16.5, 2.9, 1.8; IR (neat): $\tilde{\nu}$ = 3027, 2979, 2857, 2704, 1726, 1492, 1454, 1406, 1361, 1305, 1257, 1205, 1093, 1028, 967, 934, 900, 798, 735, 697 cm^{-1}. MS (ES+): *m/z* (rel. intensity): 267 (100); HRMS (ES+) calcd for $(C_{16}H_{20}O_2 + Na)^+$: 267.1361; found: 267.1359.

Preparation of compound 3e



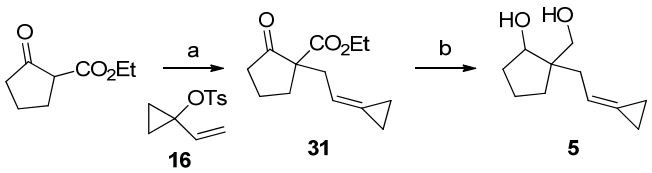
24 **30** **3e**

[a] Pyridine, pivaloyl chloride, CH_2Cl_2, reflux, 85%. [b] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 94%.

Compound 30. Under N_2, pyridine (42 µL, 0.518 mmol) was added to a solution of **24** (140 mg, 0.896 mmol) in CH_2Cl_2 (14 mL). The resulting mixture was stirred at room temperature during 2 hours. Then, pivaloyl chloride (111 µL, 0.905 mmol) was added and the mixture was stirred under reflux for 14 hours. The mixture was quenched with brine (10 mL) and extracted with Et_2O (3 × 15 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 50/1 → 25/1 → 10/1) afforded **30** as a colourless oil (183 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.80–5.70 (m, 1H), 3.95 (d, *J* = 11.2 Hz, 1H), 3.90 (d, *J* = 11.2 Hz, 1H), 3.30 (d, *J* = 11.5 Hz, 1H), 3.26 (d, *J* = 11.6 Hz, 1H), 2.65–2.35 (m, 1H (OH)), 2.16 (dd, *J* = 13.6 Hz, *J* = 7.9 Hz, 1H), 2.10 (dd, *J* = 13.5 Hz, *J* = 7.6 Hz, 1H), 1.19 (s, 9H), 1.09–1.02 (m, 2H), 1.00–0.93 (m, 2H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.4, 125.2, 112.9, 67.5, 66.9, 40.2, 39.0, 36.5, 27.2 (3C), 18.6, 2.8, 1.7; IR (neat): $\tilde{\nu}$ = 3452 (br), 2976, 2937, 2876, 1728, 1710, 1481, 1462, 1398, 1366, 1284, 1155, 1096, 1034, 986, 968, 937, 890, 793, 771, 750, 714 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 263 (100); HRMS (ES+) calcd for $(C_{14}H_{24}O_3 + Na)^+$: 263.1623; found: 263.1617.

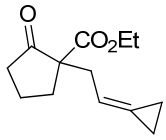
Compound 3e. This compound was prepared from **30** (207 mg, 0.86 mmol) according to the procedure described for the preparation of **1**. Colourless oil (194 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.54 (s, 1H), 5.68–5.61 (m, 1H), 4.14 (d, *J* = 11.3 Hz, 1H), 4.05 (d, *J* = 11.1 Hz, 1H), 2.39 (d, *J* = 7.7 Hz, 2H), 1.14 (s, 9H), 1.07 (s, 3H), 1.08–1.03 (m, 2H), 0.98–0.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.6, 178.0, 126.7, 111.3, 66.2, 50.3, 38.8, 34.9, 27.0 (3C), 16.3, 2.9, 1.8; IR (neat): $\tilde{\nu}$ = 2978, 2937, 2906, 2871, 2709, 1728, 1481, 1461, 1398, 1366, 1282, 1144, 1036, 993, 936, 872, 787, 769, 718 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 261 (100); HRMS (ES+) calcd for $(C_{14}H_{22}O_3 + Na)^+$: 261.1467; found: 261.1468.

Preparation of compound 5

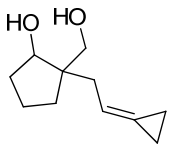


[a] 1) NaH, DMF, 2) $Pd_2(dba)_3$, dppe, **16**, THF, r.t., 99%. [b] $LiAlH_4$, Et_2O, r.t., 70%.

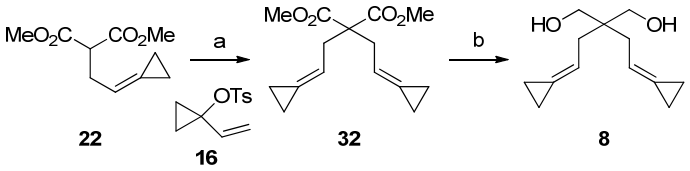
Compound 31. This compound was prepared from **16** (200 mg, 0.84 mmol) and commercially available 2-ethoxycarbonylcyclopentanone according to the procedure described for the preparation of **17**. Colourless oil (184 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.68–5.61 (m, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.76 (dd, *J* = 13.7 Hz, *J* = 7.0 Hz, 1H), 2.49 (dd, *J* = 13.7 Hz, *J* = 7.5 Hz, 1H), 2.46–2.34 (m, 2H), 2.29–2.17 (m, 1H), 2.04–1.82 (m, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.09–1.03 (m, 2H), 1.01–0.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.8, 171.0, 126.1, 112.5, 61.2, 60.3, 38.0, 35.7, 32.0, 19.4, 13.9, 2.8, 1.8; IR (neat): $\tilde{\nu}$ = 2980, 2906, 1749, 1718, 1448, 1406, 1366, 1278, 1223, 1146, 1117, 1094, 1028, 965, 934, 921, 861, 788, 761, 722 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 245 (100); HRMS (ES+) calcd for $(C_{13}H_{18}O_3 + Na)^+$: 245.1154; found: 245.1157; elemental analysis (%) calcd for $C_{13}H_{18}O_3$: C 70.24, H 8.16; found: C 70.33, H 8.29.



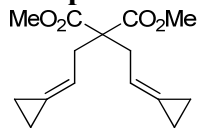
Compound 5. This compound was prepared from **31** (64 mg, 0.29 mmol) according to the procedure described for the preparation of **19**, using 2 equivalents of lithium aluminium hydride. White solid (37 mg, 70%). m.p.: 53–55°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.90–5.80 (m, 1H), 4.05 (m, 1H), 3.61 (d, *J* = 10.3 Hz, 1H), 3.34 (d, *J* = 10.9 Hz, 1H), 2.51 (dd, *J* = 14.2 Hz, *J* = 7.8 Hz, 1H), 2.29–2.24 (n, 1H (OH)), 2.20 (dd, *J* = 14.2 Hz, *J* = 7.1 Hz, 1H), 2.06–1.94 (m, 2H), 1.79–1.68 (m, 1H), 1.66–1.584 (m, 1H), 1.582–1.47 (m, 2H), 1.27–1.17 (m, 1H), 1.11–1.05 (m, 2H), 1.04–0.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.2, 114.9, 79.4, 68.9, 49.4, 32.3, 31.1, 30.4, 19.6, 2.9, 1.8; IR (neat): $\tilde{\nu}$ = 3320, 3038, 2962, 2922, 2901, 2871, 2860, 1467, 1440, 1356, 1319, 1254, 1202, 1136, 1090, 1048, 1036, 1017, 962, 948, 929, 905, 878, 850, 792, 766, 719 cm^{-1}; MS (CI): *m/z* (rel. intensity): 201 (11), 200 (100), 183 (31), 165 (31), 158 (12), 147 (38), 141 (22); HRMS (CI) calcd for $(C_{11}H_{18}O_2 + NH_4)^+$: 200.1645; found: 200.1643; elemental analysis (%) calcd for $C_{11}H_{18}O_2$: C 72.49, H 9.95; found: C 71.99, H 9.90.



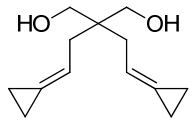
Preparation of compound 8



[a] 1) NaH, DMF; 2) $Pd_2(dba)_3$, dppe, **16**, THF, r.t., 71%. [b] $LiAlH_4$, Et_2O, r.t., 95%. [c] $(COCl)_2$, DMSO, ET_3N, CH_2Cl_2, -78 °C, full conversion.

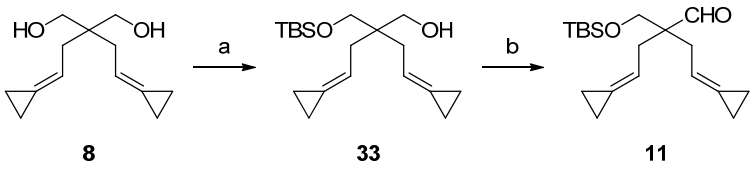


Compound 32. Under N_2, at room temperature, a solution of **22** (470 mg, 2.37 mmol) was added to a suspension of sodium hydride (56 mg, 2.37 mmol) in DMF (8 mL). The mixture was stirred at room temperature during 1 hour. In another flask, under N_2, **16** (564 mg, 2.37 mmol) was added to a solution of tris(dibenzylideneacetone)dipalladium (66 mg, 0.071 mmol) and dppe (28 mg, 0.071 mmol) in THF (15 mL) at room temperature. The resulting mixture was stirred at room temperature during 30 minutes before being canulated to the enolate. The resulting mixture was stirred during 48 hours at room temperature. The mixture was quenched with water (15 mL) and extracted with Et_2O (3 × 20 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/Et_2O, 50/1 → 20/1) gave **32** as a colourless oil (445 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.65–5.57 (m, 2H), 3.65 (s, 6H), 2.75 (d, *J* = 7.8 Hz, 4H), 1.07–1.00 (m, 4H), 0.96–0.90 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.6 (2C), 126.2 (2C), 111.9 (2C), 58.0, 52.3 (2C), 35.0 (2C), 2.9 (2C), 1.7 (2C); IR (neat): $\tilde{\nu}$ = 3053, 2982, 2953, 2841, 1732, 1436, 1411, 1307, 1281, 1245, 1198, 1180, 1109, 1071, 1000, 969, 947, 931, 861, 826, 794, 756 733 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 287 (100); HRMS (ES+) calcd for $(C_{15}H_{20}O_4 + Na)^+$: 287.1259; found: 287.1266; elemental analysis (%) calcd for: C 68.16, H 7.63; found: C 68.15, H 7.69.



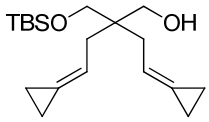
Compound 8. This compound was prepared from **32** (286 mg, 1.08 mmol) according to the procedure described for the preparation of **24**. White solid (214 mg, 95%). m.p.: 39–41°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.86–5.78 (m, 2H), 3.59 (s, 4H), 2.20 (d, *J* = 7.9 Hz, 4H), 2.11–1.96 (m, 2H), 1.11–1.06 (m, 4H), 1.03–0.97 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.7 (2C), 113.5 (2C), 68.6 (2C), 43.4, 33.9 (2C), 2.9 (2C), 1.8 (2C); IR (neat): $\tilde{\nu}$ = 3346 (br), 3051, 2978, 2923 1464, 1438, 1408, 1312, 1211, 1091, 1025, 965, 933, 871, 785, 748, 717 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 231 (100); HRMS (ES+) calcd for $(C_{13}H_{20}O_2 + Na)^+$: 231.1361; found: 231.1364; elemental analysis (%) calcd for: C 74.96, H 9.68; found: C 75.09, H 9.82.

Preparation of compound 11

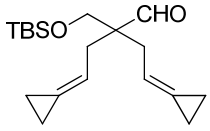


[a] TBSCl, DMAP, Et_3N, CH_2Cl_2, r.t., 83%. [b] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 97%.

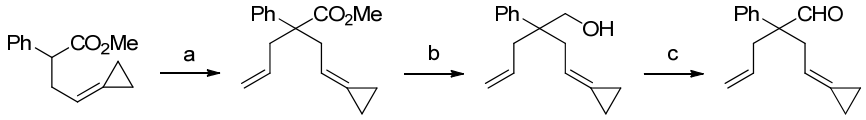
Compound 33. 4-(dimethylamino)pyridine (6 mg, 0.049 mmol) followed by triethylamine (70 µL, 0.504 mmol) and *t*-butyldimethylsilyl chloride (72 mg, 0.480 mmol) were added to a solution of **8** (100 mg, 0.480 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The resulting mixture was stirred at room temperature for 16 hours. The mixture was quenched with a saturated solution of NH_4Cl (4 mL) then extracted with CH_2Cl_2 (3 × 5 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 10/1 → 5/1) afforded **33** as a colourless oil (129 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.81–5.75 (m, 2H), 3.55 (s, 2H), 3.53 (d, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 5.9 Hz, 1H), 2.23–2.13 (m, 4H), 1.09–1.03 (m, 4H), 1.01–0.94 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.2 (2C), 113.8 (2C), 69.2, 68.9, 43.2, 34.0 (2C), 25.8 (3C), 18.1, 2.8 (2C), 1.8 (2C), -5.7 (2C); IR (neat): $\tilde{\nu}$ = 3463 (br), 3052, 2980, 2954, 2929, 2896, 2857, 1472, 1462, 1438, 1411, 1389, 1361, 1255, 1083, 1039, 1005, 966, 937, 834, 774, 668 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 345 (100); HRMS (ES+) calcd for $(C_{19}H_{34}O_2Si + Na)^+$: 345.2226; found: 345.2223; elemental analysis (%) calcd for $C_{19}H_{34}O_2Si$: C 70.75, H 10.62; found: C 70.45, H 10.60.



Compound 11. This compound was prepared from **33** (30 mg, 0.093 mmol) according to the procedure described for the preparation of **1**. Colourless oil (29 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.57 (s, 1H), 5.71–5.65 (m, 2H), 3.67 (s, 2H), 2.49–2.37 (m, 4H), 1.08–1.01 (m, 4H), 0.99–0.92 (m, 4H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.3, 125.3 (2C), 112.5 (2C), 64.0, 55.5, 32.3 (2C), 25.7 (3C), 18.1, 2.8 (2C), 1.9 (2C), -5.7 (2C); IR (neat): $\tilde{\nu}$ = 3054, 2981, 2954, 2929, 2896, 2857, 2704, 1725, 1472, 1438, 1410, 1386, 1362, 1252, 1100, 1006, 967, 934, 836, 815, 776, 670 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 343 (100); HRMS (ES+) calcd for $(C_{19}H_{32}O_2Si + Na)^+$: 343.2069; found: 343.2073.

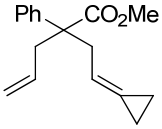


Preparation of compound 14a

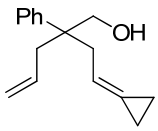


17 **34** **35** **14a**

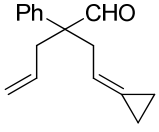
[a] NaHMDS, allyl bromide, THF, -78 °C to r.t., 74%. [b] $LiAlH_4$, Et_2O, r.t., 97%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 89%.



Compound 34. Under N_2, NaHMDS (188 mg, 1.023 mmol) was added as solid in one portion to a solution of **17** (170 mg, 0.787 mmol) in THF (5 ml) at -78 °C. The mixture was stirred for 1.5 hour at -78 °C then allyl bromide (89 µL, 1.023 mmol) and tetrabutylammonium iodide (116 mg, 0.315 mmol) were added. The mixture was slowly warmed at room temperature overnight. The mixture was quenched with a saturated solution of NH_4Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAC, 30/1) gave **34** as a colourless oil (150 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.27 (m, 2H), 7.26-7.20 (m, 3H), 5.57 (ddt, *J* = 17.2 Hz, 10.5 Hz, 7.1 Hz, 1H), 5.51–5.47 (m, 1H), 5.04–5.01 (m, 1H), 5.01–4.97 (m, 1H), 3.62 (s, 3H), 2.93 (dd, *J* = 13.7 Hz, *J* = 7.7 Hz, 1H), 2.85 (dd, *J* = 13.7 Hz, *J* = 7.0 Hz, 1H), 2.79 (dd, *J* = 13.9 Hz, 7.9 Hz, 1H), 2.75 (dd, *J* = 13.9 Hz, 7.0 Hz, 1H), 1.05–0.94 (m, 2H), 0.92–0.85 (m, 1H), 0.85–0.77 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.7, 142.0, 133.6, 128.2 (2C), 126.7, 126.5 (2C), 125.6, 118.3, 112.8, 54.2, 51.9, 39.1, 37.2, 2.8, 1.9; IR (neat): $\tilde{\nu}$ = 2980, 2950, 1729, 1640, 1600, 1581, 1498, 1445, 1320, 1301, 1268, 1206, 1138, 1108, 1088, 1035, 996, 916, 889, 847, 811, 763, 729, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 295 (16), 280 (19), 279 (100); HRMS (ES+) calcd for $(C_{17}H_{20}O_2 + Na)^+$: 279.1361; found: 279.1362; Elemental analysis calcd (%) for $C_{17}H_{20}O_2$: C 79.65, H 7.86; found: C 79.59, H 7.87.



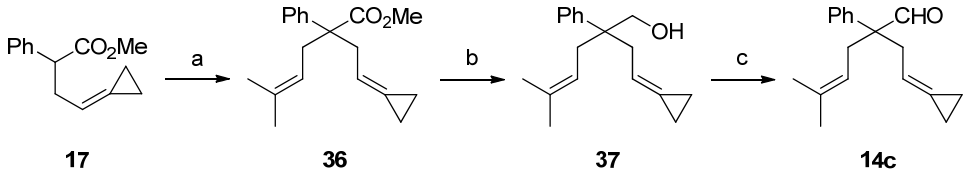
Compound 35. This compound was prepared from 34 following the procedure described for the preparation of **19**. Colourless oil (217 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.29 (m, 3H), 7.23–7.18 (m, 2H), 5.74–5.57 (m, 2H), 5.07 (d, *J* = 16.9 Hz, 1H), 5.01 (d, *J* = 10.2 Hz, 1H), 3.78 (s, 2H), 2.64 (dd, *J* = 13.8 Hz, *J* = 7.4 Hz, 1H), 2.59–2.53 (m, *2*H), 2.48 (dd, *J* = 13.3 Hz, *J* = 7.3 Hz, 1H), 1.48–1.30 (s, 1H), 1.06–0.98 (m, 2H), 0.97–0.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6, 134.6, 128.3 (2C), 126.9 (2C), 126.2, 124.7, 117.6, 113.7, 68.1, 46.5, 39.7, 37.7, 2.8, 1.9; IR (neat): $\tilde{\nu}$ = 3403 (br), 3057, 2977, 2925, 1638, 1498, 1446, 1413, 1043, 997, 963, 697 cm^{-1}; MS (CI): *m/z* (rel. intensity): 246 (100); HRMS (CI) calcd for $(C_{14}H_{16}O + NH_4)^+$: 246.1852; found: 246.1855.



Compound 14a. Under N_2, dimethyl sulfoxide (29 µL, 0.410 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of oxalyl chloride (18 µL, 0.205 mmol) in CH_2Cl_2 (1.9 mL) at –78 °C. After 10 minutes stirring at –78 °C, a solution of **35** (36 mg, 0.158 mmol) in CH_2Cl_2 (0.7 mL) was added. After 20 minutes stirring at –78 °C, triethylamine (0.11 mL, 0.788 mmol) was added rapidly and the mixture was stirred at room temperature during 15 minutes. A saturated solution of NH_4Cl (4 mL) was added to the reaction mixture which was then extracted with CH_2Cl_2 (3 × 5 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography PE/EtOAc, 80/1) gave **1** as a colourless oil (32 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.53 (s, 1H), 7.39–7.32 (m, 2H), 7.30–7.25 (m, 1H), 7.24–7.19 (m, 2H), 5.61–5.50 (m, 2H), 5.02 (d, *J* = 16.2 Hz, 1H), 5.01 (d, *J* = 12.9 Hz, 1H), 2.85 (dd, *J* = 14.2 Hz,

J = 7.7 Hz, 1H), 2.79 (dd, J = 14.2 Hz, J = 7.0 Hz, 1H), 2.69 (d, J = 7.5 Hz, 2H), 1.07–0.96 (m, 2H), 0.93–0.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.3, 138.3, 133.1, 128.7 (2C), 127.7 (2C), 127.3, 126.1, 118.6, 112.2, 57.7, 37.1, 34.8, 2.9, 2.0; IR (neat): $\tilde{\nu}$ = 3057, 2980, 2921, 2804, 2709, 1722, 1640, 1599, 1580, 1496, 1446, 997, 967, 918, 875, 842, 759, 738, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 249 (100); HRMS (ES+) calcd for ($C_{16}H_{18}O$ + Na)$^+$: 249.1255; found: 249.1258.

Preparation of compound 14c



17 **36** **37** **14c**

[a] KHMDS, 3,3-dimethylallyl bromide, THF, -78 °C to r.t., 82%. [b] $LiAlH_4$, Et_2O, r.t., 94%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 90%.

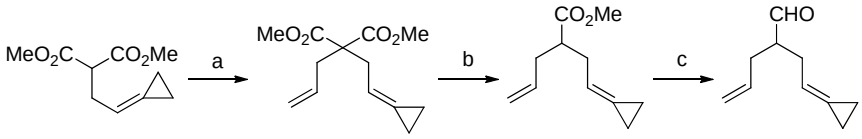
Compound 36. This compound was prepared from **17** (119 mg, 0.551 mmol) according to the procedure described for the preparation of **18** and using 3,3-dimethylallyl bromide. Colourless oil (128 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (t, J = 7.7 Hz, 1H), 7.26–7.18 (m, 4H), 5.53–5.45 (m, 1H), 4.94 (t, J = 6.7 Hz, 1H), 3.61 (s, 3H), 2.91 (dd, J = 13.3 Hz, J = 7.7 Hz, 1H), 2.83 (dd, J = 13.5 Hz, J = 6.5 Hz, 1H), 2.76 (dd, J = 14.3 Hz, J = 7.6 Hz, 1H), 2.64 (dd, J = 14.3 Hz, J = 6.4 Hz, 1H), 1.63 (s, 3H), 1.47 (s, 3H), 1.02–0.91 (m, 2H), 0.88–0.80 (m, 1H), 0.80–0.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.2, 142.4, 134.4, 128.1 (2C), 126.63 (2C), 125.59, 125.4, 119.0, 113.1, 54.5, 51.9, 37.5, 33.3, 26.0, 17.8, 2.8, 1.7; IR (neat) : $\tilde{\nu}$ = 2980, 2916, 1730, 1601, 1498, 1446, 1377, 1311, 1268, 1202, 1069, 1031, 1002, 852, 765, 737, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 307 (100); HRMS (ES+) calcd for ($C_{19}H_{24}O_2$ + Na)$^+$: 307.1674; found : 307.1685; elemental analysis calcd (%) for $C_{19}H_{24}O_2$: C 80.28, H 8.45; found: C 79.92, H 8.77.

Compound 37. This compound was prepared from **36** (119 mg, 0.419 mmol) according to the procedure described for the preparation of **19**. Colourless oil (101 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 4H), 7.22–7.17 (m, 1H), 5.63–5.57 (m, 1H), 5.04–4.98 (m, 1H), 3.77 (d, J = 6.0 Hz, 2H), 2.64 (ddquint, J = 13.9 Hz, J = 7.2 Hz, J = 1.3 Hz, 1H), 2.56 (ddquint, J = 13.9 Hz, J = 7.3 Hz, J = 1.3 Hz, 1H), 2.47 (dd, J =14.6 Hz, J = 7.3 Hz, 1H), 2.40 (dd, J =14.6 Hz, J = 7.3 Hz, 1H), 1.63 (s, 3H), 1.57 (s, 3H), 1.30 (t, J = 6.0 Hz, 1H), 1.03–0.96 (m, 2H), 0.96–0.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.1, 133.8, 128.7 (2C), 127.1 (2C), 126.0, 124.4, 120.0, 114.1, 68.5, 47.0, 38.0, 33.9, 26.0, 17.9, 2.8, 1.8; IR (neat) : $\tilde{\nu}$ = 3432 (br), 3054, 2978, 2914, 1601, 1498, 1445, 1376, 1028, 965, 936, 760, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 279 (100); HRMS (ES+) calcd for ($C_{18}H_{24}O$ + Na)$^+$: 279.1725; found: 279.1729; elemental analysis calcd (%) for $C_{18}H_{24}O$: C 84.38, H 9.38; found: C 84.50, H 9.79.

Compound 14c. This compound was prepared from **37** (89 mg, 0.348 mmol) according to the procedure described for the preparation of **1**. Colourless oil (79 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.53 (s, 1H), 7.38–7.32 (m, 2H), 7.29–7.19 (m, 3H), 5.56–5.50 (m, 1H), 4.99–4.92 (m, 1H), 2.83 (dd, J = 14.1 Hz, J = 7.6 Hz, 1H), 2.76 (J = 14.1 Hz, J = 6.9 Hz, 1H), 2.67 (dd, J = 15.0 Hz, J = 7.5 Hz,

1H), 2.58 (dd, *J* = 15.0 Hz, *J* = 6.9 Hz, 1H), 1.62 (s, 3H), 1.49 (s, 3H), 1.04–0.93 (m, 2H), 0.89–0.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.8, 138.8, 134.7, 128.6 (2C), 127.8 (2C), 127.2, 125.7, 118.3, 112.6, 58.2, 35.2, 31.1, 26.1, 18.0, 3.0, 1.9; IR (neat): $\tilde{\nu}$ = 3055, 2980, 2916, 2707, 1722, 1599, 1496, 1446, 1377, 1088, 1030, 1002, 967, 932, 880, 858, 759, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 277 (100); HRMS (ES+) calcd for $(C_{18}H_{24}O + Na)^+$: 277.1568; found: 277.1566.

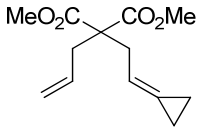
Preparation of compound 14d



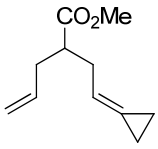
22 **38** **39** **14d**

[a] NaH, allyl bromide, Bu_4NI, THF, 0 °C to r.t., 76%. [b] LiCl, DMSO, water, 150 °C, 66%. [c] 1) $LiAlH_4$, Et_2O, r.t. 2) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 59%.

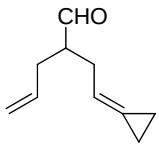
Compound 38. Under N_2, A solution of **22** (500 mg, 2.52 mmol) in THF (7 mL) was added to a suspension of sodium hydride (61 mg, 2.55 mmol) in THF (7 mL) at 0°C. The resulting mixture was stirred at room temperature during 40 minutes then cooled down at 0°C. Allyl bromide (0.22 mL, 2.55 mmol) followed by tetrabutylammonium iodide (186 mg, 0.50 mmol) were added and the mixture was stirred at room temperature for 1 hour. The mixture was quenched with brine (10 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were dried over Na_2SO_4, filtered and evaporated. Purification by flash chromatography (PE/EtOAc, 40/1) gave **38** as colourless oil (396 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.71–5.61 (m, 1H), 5.60–5.54 (m, 1H), 5.07–5.04 (m, 2H), 3.68 (s, 6H), 2.75 (d, *J* = 7.4 Hz, 2H), 2.60 (d, *J* = 7.4 Hz, 2H), 1.07–1.02 (m, 2H), 0.98–0.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.4 (2C), 132.5, 126.5, 118.9, 111.7, 57.9, 52.3 (2C), 36.9, 34.9, 2.9, 1.8; IR (neat): $\tilde{\nu}$ = 3078, 3048, 2983, 2954, 2841, 1731, 1642, 1436, 1284, 1249, 1198, 1142, 1082, 1043, 996, 968, 921, 859, 823, 756, 721 cm^{-1}; MS (CI): *m/z* (rel. intensity): 257 (10), 256 (84), 240 (12), 239 (100); HRMS (CI) calcd for $(C_{13}H_{18}O_4 + H)^+$: 239.1278; found: 239.1275; elemental analysis (%) calcd for $C_{13}H_{18}O_4$: C 65.53, H 7.61; found: C 65.52, H 7.62.



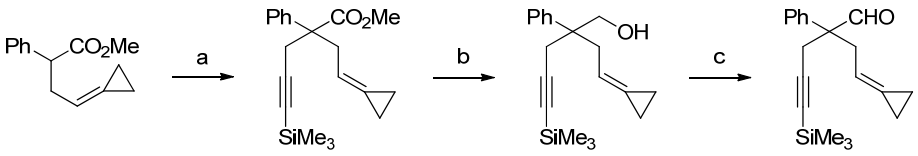
Compound 39. Lithium chloride (149 mg, 3.51mmol) was added to a solution of **38** (380 mg, 1.60 mmol) in DMSO (11 mL). Water (100 µL) was added then the mixture was stirred at 150 °C (oil bath temperature) during 6 hours. At room temperature, the mixture was partitioned between brine (10 mL) and Et_2O and extracted with Et_2O (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (pentane/Et_2O, 50/1) gave **39** as a colourless oil (188 mg, 66%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.77–5.64 (m, 2H), 5.02 (dd, *J* = 17.2 Hz, *J* = 1.8 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 3.62 (s, 3H), 2.62–2.54 (m, 1H), 2.51–2.42 (m, 1H), 2.39–2.29 (m, 2H), 2.27–2.20 (m, 1H), 1.05–0.94 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.6, 135.4, 123.9, 116.7, 114.7, 51.4, 45.2, 35.8, 33.8, 2.5 1.9; IR (neat): $\tilde{\nu}$ = 3078, 3053, 2982, 2951, 2911, 2846, 1736, 1642, 1436, 1370, 1340, 1262, 1232, 1164, 1120, 1067, 1046, 995, 964, 916, 857, 834, 754, 718 cm^{-1}; MS (CI): *m/z* (rel. intensity): 198 (100), 181 (73), 121 (26); HRMS (CI) calcd for $(C_{11}H_{16}O_2 + H)^+$: 181.12285; found: 181.12233; elemental analysis (%) calcd for $C_{11}H_{16}O_2$: C 73.30, H 8.95; found: C 73.25, H 8.99;



Compound 14d. This compound was prepared from **39** (160 mg, 0.89 mmol) according to the procedure described for the preparation of **19**. The crude alcohol was then oxidised according to the procedure described for the preparation of **1**. Colourless oil (79 mg, 59% over two steps). ^{1}H NMR (500 MHz, C_3D_6O): δ = 9.64 (s, 1H), 5.79 (ddt, *J* = 17.3 Hz, *J* = 10.4 Hz, *J* = 6.9 Hz, 1H), 5.78–5.70 (m, 1H), 5.06 (d, *J* = 17.5 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 2.55–2.63 (m, 1H), 2.48–2.55 (m, 1H), 2.46–2.36 (m, 2H), 2.30–2.22 (m, 1H), 1.07–0.98 (m, 4H); ^{13}C NMR (125 MHz, C_3D_6O): δ = 204.5, 136.5, 124.6, 117.1, 115.4, 51.7, 32.2, 31.2, 2.7, 2.3; IR (neat): $\tilde{\nu}$ = 3078, 3048, 2981, 2922, 2849, 2718, 1725, 1641, 1440, 1413, 1393, 1070, 994, 966, 915, 835, 776, 749, 719; MS (CI): *m/z* (rel. intensity): 168 (100), 152 (21), 150 (22), 135 (17), 133 (14); HRMS (CI) calcd for $(C_{10}H_{14}O + NH_4)^+$: 168.13884; found: 168.13860.



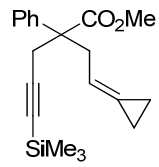
Preparation of compound 14e



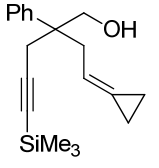
17 **40** **41** **14e**

[a] KHMDS, 3-bromo-1-(trimethylsilyl)-1-propyne, THF, -78 °C to r.t., 77%. [b] $LiAlH_4$, Et_2O, r.t., 96%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 94%.

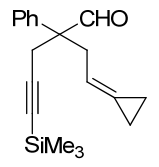
Compound 40. This compound was prepared from **17** (233 mg, 1.08 mmol) according to the procedure described for the preparation of **18** and using 3-bromo-1-(trimethylsilyl)-1-propyne. Colourless oil (271 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 2H), 7.26–7.21 (m, 3H), 5.48 (tquint, *J* = 7.3 Hz, *J* = 2.0 Hz, 1H), 3.66 (s, 3H), 3.14–3.01 (m, 2H), 2.93 (d, *J* = 16.5 Hz, 1H), 2.80 (d, *J* = 16.7 Hz, 1H), 1.08–0.92 (m, 4H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.8, 141.1, 128.2 (2C), 127.1, 126.7, 126.3 (2C), 112.5, 103.6, 87.5, 54.0, 52.2, 37.2, 26.9, 2.9, 2.0, 0.0 (3C); IR (neat) : $\tilde{\nu}$ = 2955, 2178, 1733, 1601, 1498, 1435, 1316, 1250, 1205, 1037, 839, 759, 733, 696 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 349 (100); HRMS (ES+) calcd for $(C_{20}H_{26}O_2Si + Na)^+$: 349.1600; found: 349.1609; elemental analysis calcd (%) for $C_{17}H_{26}O_2Si$: C 73.62, H 7.98; found: C 72.79, H 8.21.



Compound 41. This compound was prepared from **40** (255 mg, 0.782 mmol) according to the procedure described for the preparation of **19**. Colourless oil (224 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 4H), 7.26–7.19 (m, 1H), 5.54–5.44 (m, 1H), 3.95–3.83 (m, 2H), 2.79–2.71 (m, 2H), 2.68–2.58 (m, 2H), 1.59–1.44 (m, 1H (OH)), 1.03–0.94 (m, 3H), 0.94–0.85 (m, 1H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.6, 128.4 (2C), 126.8 (2C), 126.5, 125.3, 113.1, 104.6, 87.7, 68.9, 46.8, 38.1, 26.0, 2.8, 1.9, 0.0 (3C). IR (neat): $\tilde{\nu}$ = 3436, 3055, 2958, 2173, 1741, 1602, 1499, 1445, 1249, 1080, 1025, 838, 759, 696 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 321 (100); HRMS (ES+) calcd for $(C_{19}H_{26}OSi + Na^+)$: 321.1651; found: 321.1660; elemental analysis calcd (%) for $C_{19}H_{26}OSi$: C 76.51, H 8.72; found: C 75.96, H 9.04.

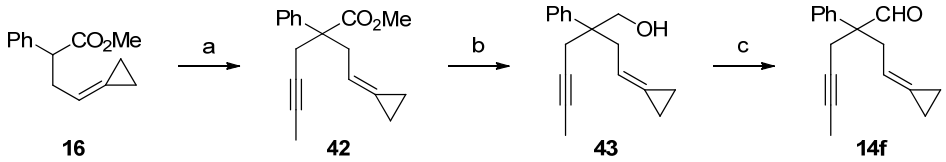


Compound 14e. This compound was prepared from **41** (127 mg, 0. 426 mmol) according to the procedure described for the preparation of **1**. The crude material was purified by flash chromatography (PE only → PE/EtOAc = 30/1). However, an unidentified small impurity was still visible by NMR. Further purification was not attempted. Colourless oil (107 mg, 85%).^{1}H NMR (500 MHz, $CDCl_3$): δ =



9.58 (s, 1H), 7.39–7.33 (m, 2H), 7.32–7.20 (m, 2H), 5.55 (tquint, J = 7.4 Hz, J = 2.0 Hz, 1H), 3.05–2.93 (m, 2H), 2.83 (d, J = 17.0 Hz, 1H), 2.72 (d, J = 17.2 Hz, 1H), 1.09–0.91 (m, 4H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.9, 137.5, 125.7 (2C), 127.6, 127.5 (2C), 127.0, 111.9, 102.7, 88.5, 57.3, 34.9, 24.5, 3.0, 2.0, -0.1 (3C); IR (neat): $\tilde{\nu}$ = 2959, 2702, 2178, 1725, 1496, 1447, 1249, 107, 838, 758, 697 cm^{-1}; HRMS (ES+) calcd for ($C_{19}H_{24}OSi$ + Na^+): 319.1494; found: 319.1496.

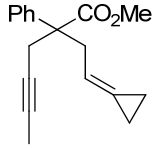
Preparation of compound 14f



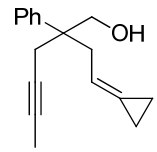
16 42 43 14f

[a] LDA, 4-bromo-1-butyne, THF, -78°C, 73%. [b] $LiAlH_4$, Et_2O, 0°C to r.t., 85%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78°C, 96%.

Compound 42. Under N_2, a solution of LDA (1.80 mmol), prepared from 0.72 mL of a 2.5 M of nBuLi and 0.25 mL of diisopropylamine in THF (3.60 mL) at 0°C, was added to a solution of **17** (150 mg, 0.694 mmol) in THF (3.30 mL) at -78°C. The resulting solution was stirred at -78°C for 1.5 hour then 4-bromo-1-butyne (0.16 mL, 1.80 mmol) was slowly added. The mixture was stirred at -78°C for another 30 minutes before being quenched with few drops of methanol and allowed to warm at room temperature. The mixture was diluted with a saturated solution of NH_4Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 200/1 → 175/1 → 150/1) afforded **35** as a colourless oil (136 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 2H), 7.26–7.21 (m, 3H), 5.53–5.46 (m, 1H), 3.64 (s, 3H), 3.10–3.01 (m, 2H), 2.88 (dq, J = 16.3 Hz, J = 2.5 Hz, 1H), 2.75 (dq, J = 16.3 Hz, J = 2.5 Hz, 1H), 1.71 (t, J = 2.5 Hz, 3H), 1.05–0.91 (m, 3H), 0.91–0.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 141.3, 128.2 (2C), 126.9, 126.34 (2C), 126.31, 112.7, 78.1, 75.1, 54.0, 52.2, 37.4, 25.6, 3.5, 2.9, 1.8; IR (neat): $\tilde{\nu}$ = 3053, 3023, 2981, 2951, 2921, 2851, 1731, 1601, 1580, 1498, 1436, 1322, 1302, 1270, 1207, 1070, 1002, 964, 910, 849, 764, 731, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 291 (100); HRMS (ES+) calcd for ($C_{18}H_{20}O_2$ + Na)$^+$: 291.1361; found: 291.1357; elemental analysis (%) calcd for $C_{18}H_{20}O_2$: C 80.56, H 7.51; found: C 80.85, H 7.59.



Compound 43. This compound was prepared from **42** (83 mg, 0.310 mmol) according to the procedure described for the preparation of **19**. Colourless oil (63 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 4H), 7.23–7.15 (m, 1H), 5.55–5.45 (m, 1H), 3.87 (d, J = 5.8 Hz, 2H), 2.75–2.65 (m, 2H), 2.63–2.57 (m, 1H), 2.56 (dq, J = 16.4 Hz, J = 2.6 Hz, 1H), 1.75 (t, J = 2.6 Hz, 3H), 1.60–1.56 (m, 1H (OH)), 1.03–0.90 (m, 3H), 0.89–0.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 128.3 (2C), 126.9 (2C), 126.3, 125.0, 113.3, 78.2, 76.1, 68.9, 46.7, 38.4, 24.9, 3.5, 2.8, 1.8; IR (neat): $\tilde{\nu}$ = 2412, 3084, 3048, 2978, 2918, 1602, 1580, 1498, 1445, 1378, 1075, 1028, 966, 937, 860, 846, 761, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 263 (100); HRMS (ES+) calcd for ($C_{17}H_{20}O$ + Na)$^+$: 263.1412; found: 263.1410.



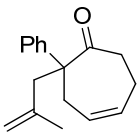
Compound 14f. This compound was prepared from **43** (32 mg, 0.133 mmol) according to the procedure described for the preparation of **1**. Colourless oil (29 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.57 (s, 1H), 7.39–7.32 (m, 2H), 7.30–7.26 (m, 1H), 7.24–7.21 (m, 2H), 5.57–5.49 (m, 1H), 2.99–2.88 (m, 2H), 2.79 (dq, *J* = 16.8 Hz, *J* = 2.6 Hz, 1H), 2.67 (dq, *J* = 16.8 Hz, *J* = 2.6 Hz, 1H), 1.70 (t, *J* = 2.6 Hz, 3H), 1.06-0.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 137.8, 128.7 (2C), 127.5 (2C), 127.4, 126.5, 112.0, 79.0, 74.4, 57.4, 35.3, 23.2, 3.5, 2.9, 1.9; IR (neat): $\tilde{\nu}$ = 3055, 2980, 2919, 2854, 2800, 2712, 1723, 1599, 1580, 1496, 1446, 1384, 1317, 1257, 1231, 1090, 1070, 1002, 967, 933, 910, 874, 837, 759, 733, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 261 (100); HRMS (ES+) calcd for $(C_{17}H_{18}O + Na)^{+}$: 261.1255; found: 261.1257.

Representative procedure for rhodium-catalysed rearrangement

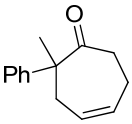
A Teflon-screw Schlenk flask equipped with a small stirring bar was charged with $[Rh(nbd)_2]BF_4$ (3.4 mg, 0.0091 mmol), BINAP (5.7 mg, 0.0091 mmol), and acetone (1.8 mL) under N_2 before bubbling H_2 (3.8 mL, 0.153 mmol) via syringe and sealing the flask under N_2. After stirring for 1h at room temperature, this solution was added to aldehyde **1a** (20.8 mg, 0.091 mmol) in acetone (0.83 mL) was added under N_2 and the flask was again sealed. After stirring for 4 h at room temperature, the mixture was allowed to cool before evaporation. Purification by flash chromatography (PE/EtOAc: 250/1) gave ketone **2** (15.6 mg, 75%).

Compounds **4a**–**4e**, **12**, and **15c**–**15e** were obtained according to this procedure using purified aldehydes as starting material and the catalyst loadings specified in the manuscript. Compounds **7**, **10**, **15a** and **15b** were obtained from crude aldehydes and after treating this crude material with the active catalyst prepared according to this general and representative procedure. Compound **15f** was obtained according to this general procedure, except that BINAP was replaced with dppf.

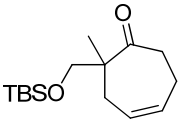
Compound 2. White solid (25 mg, 89%). m.p.: 41–43 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.16 (m, 5H), 5.83–5.73 (m, 1H), 5.64–5.56 (m, 1H), 4.76–4.71 (m, 1H), 4.54–4.49 (m, 1H), 3.15–3.06 (m, 1H), 3.00–2.91 (m, 1H), 2.70 (d, *J* = 13.6 Hz, 1H), 2.59 (dd, *J* = 15.0 Hz, *J* = 7.5 Hz, 1H), 2.53 (d, *J* = 13.6 Hz, 1H), 2.36-2.21 (m, 3H), 1.06 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.2, 143.2, 140.6, 130.3, 128.4 (2C), 127.2 (2C), 127.0, 126.9, 115.0, 61.8, 44.9, 37.9, 29.1, 27.1, 23.9; IR (neat): $\tilde{\nu}$ = 3069, 3022, 2947, 2918, 2851, 1702, 1641, 1597, 1580, 1497, 1472, 1445, 1375, 1343, 1308, 1267, 1196, 1139, 1032, 963, 893, 793, 770, 728, 698, 680, 661 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 263 (100); HRMS (ES+) calcd for $(C_{17}H_{20}O + Na)^+$: 263.1412; found: 263.1408.



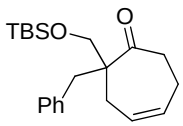
Compound 4a. Colourless oil (25.2 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 2H), 7.24–2.20 (m, 3H), 5.85–5.77 (m, 1H), 5.68–5.61 (m, 1H), 3.09 (dd, *J* = 15.4 Hz, *J* = 5.9 Hz, 1H), 2.98 (ddd, *J* = 12.2 Hz, *J* = 9.5 Hz, *J* = 6.9 Hz, 1H), 2.47–2.38 (m, 2H), 2.32–2.24 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.6, 143.5, 130.3, 128.6 (2C), 127.0, 126.7, 126.1 (2C), 58.6, 38.7, 34.7, 26.7, 26.4; IR (neat): $\tilde{\nu}$ = 3053, 3022, 2969, 2928, 2851, 1706, 1600, 1580, 1495, 1445, 1371, 1309, 1194, 1153, 1075, 1031, 894, 766, 699, 678, 656 cm^{-1}; MS (CI): *m/z* (rel. intensity) 219 (13), 218 (100), 201 (9), 200 (3); HRMS (CI) calcd for $(C_{14}H_{16}O + NH_4)^+$: 218.1539; found: 218.1542; elemental analysis (%) calcd for $C_{14}H_{16}O$: C 83.96 H 8.05; found: C 83.17, H 8.17.



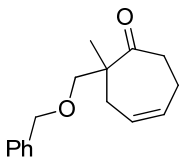
Compound 4b. Colourless oil (17.8 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.73–5.65 (m, 1H), 5.59–5.53 (m, 1H), 3.65 (d, *J* = 9.3 Hz, 1H), 3.37 (d, *J* = 9.3 Hz, 1H), 3.03 (td, *J* = 11.2 Hz, *J* = 5.3 Hz, 1H), 3.00–2.93 (m, 1H), 2.56–2.49 (m, 1H), 2.44–2.21 (m, 2H), 1.91 (dd, *J* = 15.9 Hz, *J* = 7.7 Hz, 1H), 1.00 (s, 3H), 0.84 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 217.4, 129.0, 126.7, 70.1, 56.0, 39.9, 31.5, 27.6, 25.8 (3C), 19.9, 18.2, -5.86 (2C); IR (neat): $\tilde{\nu}$ = 2954, 2929, 2896, 2857, 1706, 1464, 1383, 1362, 1311, 1251, 1203, 1089, 1006, 939, 907, 834, 774, 734, 657 cm^{-1}; MS (CI): *m/z* (rel. intensity): 271 (12), 269 (100); HRMS (CI) calcd for $(C_{15}H_{28}O_2Si + H)$: 269.19368; found: 255.19440; elemental analysis (%) calcd for $C_{15}H_{28}O_2Si$: C 67.11, H 10.51; found: C 68.00, H 10.70.



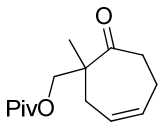
Compound 4c. Colourless oil (23.4 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24–7.16 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.70–5.61 (m, 1H), 5.53 (dt, *J* = 11.4 Hz, 3.8 Hz, 1H), 3.65 (d, *J* = 9.2 Hz, 1H), 3.46 (d, *J* = 9.2 Hz, 1H), 2.87 (s, 2H), 2.69 (ddd, *J* = 11.3 Hz, *J* = 7.9 Hz, *J* = 6.0 Hz, 1H), 2.62 (dd, *J* = 15.6 Hz, *J* = 6.5 Hz, 1H), 2.55 (ddd, *J* = 11.3 Hz, *J* = 7.7 Hz, *J* = 6.0 Hz, 1H), 2.36–2.23 (m, 2H), 2.16 (dd, *J* = 15.6 Hz, *J* = 6.3 Hz, 1H), 0.87 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 216.6, 137.5, 130.2 (2C), 129.2, 128.0 (2C), 126.3 (2C), 66.5, 60.4, 40.0, 39.9, 27.7, 27.4, 25.8 (3C), 18.2, -5.6, -5.7; IR (neat): $\tilde{\nu}$ = 3026, 2952, 2928, 2856, 1702, 1603, 1495, 1471, 1441, 1388, 1361, 1311, 1251, 1195, 1095, 1031, 1022, 1004, 939, 900, 834, 775, 733, 701, 667 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 367 (100); HRMS (ES+) calcd for $(C_{21}H_{32}O_2Si + Na)^+$: 367.2069; found: 367.2066; elemental analysis (%) calcd for $C_{21}H_{32}O_2Si$: C 73.20, H 9.36; found: C 72.98, H 9.30.



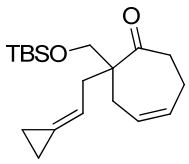
Compound 4d. Colourless oil (15.3 mg, 77%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.22-7.17 (m, 4H), 7.10-7.08 (m, 1H), 5.58-5.49 (m, 1H), 5.38-5.30 (m, 1H), 4.24 (d, *J* = 12.0 Hz, 1H), 4.17 (d, *J* = 12.0 Hz, 1H), 3.52 (d, *J* = 8.6 Hz, 1H), 3.17 (d, *J* = 8.6 Hz, 1H), 2.97-2.91 (m, 1H), 2.88 (dt, *J* = 11.6 Hz, 8.2 Hz, 1H), 2.42 (dt, *J* = 11.5 Hz, 5.7 Hz, 1H), 2.04-1.96 (m, 2H), 1.75 (dd, *J* = 15.7 Hz, *J* = 7.8 Hz, 1H), 1.09 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ = 214.4, 138.9, 129.6, 128.6 (2C), 127.73, 127.66 (2C), 126.7, 77.6, 73.4, 54.9, 39.7, 32.2, 27.7, 20.6; IR (neat): $\tilde{\nu}$ = 3064, 3023, 2967, 2928, 2901, 2855, 1704, 1494, 1454, 1371, 1312, 1252, 1205, 1100, 1029, 907, 776, 737, 698 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 267 (100); HRMS (ES+) calcd for $(C_{16}H_{20}O_2 + Na)^+$: 267.1361; found: 267.1356; elemental analysis (%) calcd for $C_{16}H_{20}O_2$: C 78.65, H 8.25; found: C 77.99, H 8.41.



Compound 4e. Colourless oil (5.4 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.74-5.60 (m, 2H), 4.06 (d, *J* = 10.7 Hz, 1H), 4.03 (d, *J* = 10.7 Hz, 1H), 2.91 (ddd, *J* = 15.2 Hz, *J* = 10.0 Hz, *J* = 5.2 Hz, 1H), 2.69-2.62 (m, 2H), 2.45-2.363 (m, 1H), 2.356-2.58 (m, 1H), 2.11 (dd, *J* = 15.6 Hz, *J* = 6.5 Hz, 1H), 1.16 (s, 9H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.6, 178.1, 129.8, 125.9, 69.8, 53.7, 39.0, 32.0, 29.7, 27.3, 27.1 (3C), 20.5; IR (neat): $\tilde{\nu}$ = 3023, 2967, 2929, 2871, 2856, 1732, 1708, 1479, 1463, 1396, 1365, 1283, 1152, 1080, 1035, 989, 905, 769 cm^{-1}; MS (ES+): *m/z* (rel. intensity): HRMS (ES+) calcd for $(C_{14}H_{22}O_3 + Na)^+$: 261.1467; found: 261.1355.



Compound 12. Colourless oil (34.5 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.69–5.61 (m, 2H), 5.59–5.52 (m, 1H), 3.64 (d, *J* = 9.6 Hz, 1H), 3.55 (d, *J* = 9.6 Hz, 1H), 2.82–2.75 (m, 1H), 2.74–2.64 (m, 2H), 2.45–2.37 (m, 2H), 2.35–2.28 (m, 2H), 2.21 (dd, *J* = 15.7 Hz, *J* = 6.7 Hz, 1H), 1.06–1.01 (m, 2H), 0.99–0.90 (m, 2H), 0.85 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 216.6, 129.2, 126.7, 124.9, 113.4, 66.9, 59.8, 39.9, 36.1, 28.4, 27.5, 25.8 (3C), 18.1, 2.8, 1.8, -5.65, -5.69; IR (neat): $\tilde{\nu}$ = 3018, 2953, 2929, 2856, 1703, 1464, 1440, 1408, 1386, 1361, 1312, 1251, 1197, 1095, 1005, 960, 938, 902, 834, 775, 667 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 343 (100); HRMS (ES+) calcd for $(C_{19}H_{32}O_2Si + Na)^+$: 343.2069; found: 343.2067; elemental analysis (%) calcd for $C_{19}H_{32}O_2Si$: C 71.19, H 10.06; found: C 71.30, H 10.30.

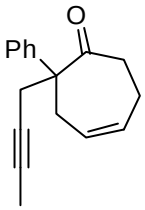


Compound 15a. This compound was obtained from crude aldehyde obtained according to the procedure and aqueous work up described for the preparation of compound **9**. Colourless oil (15.6 mg, 75% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.28 (m, 2H), 7.23–7.18 (m, 3H), 5.81–5.73 (m, 1H), 5.66–5.59 (m, 1H), 5.39–5.28 (m, 1H), 4.94 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 9.0 Hz, 1H), 3.07 (dd, *J* = 15.4 Hz, 5.5 Hz, 1H), 2.98–2.91 (m, 1H), 2.78 (dd, *J* = 14.2 Hz, 5.9 Hz, 1H), 2.54 (dd, *J* = 14.5 Hz, 12.2 Hz, 1H), 2.53 (t, *J* = 14.3 Hz, 1H), 2.35–2.25 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.4, 140.3, 134.7, 130.4, 128.5, 126.9, 126.8, 117.8, 61.8, 42.2, 38.3, 29.8, 26.7; IR (neat): $\tilde{\nu}$ = 3063, 3022, 2972, 2927, 2856, 1705, 1638, 1598, 1578, 1495, 1472, 1445, 1345, 1308, 1196, 1134, 1090, 1075, 1035, 998, 948, 913, 840, 785, 761, 727, 698, 673 cm^{-1}; MS (CI): *m/z* (rel. intensity): 245 (16), 244 (100), 228 (10), 227 (70); HRMS (CI) calcd for $(C_{16}H_{18}O + H)^+$: 227.1430; found: 227.1433; elemental analysis (%) calcd for $C_{16}H_{18}O$: C 84.91, H 8.02; found: C 84.96, H 8.18.

Compound 15c. Colourless oil (17.2 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 2H), 7.23–7.16 (m, 3H), 5.81–5.71 (m, 1H), 5.66–5.57 (m, 1H), 4.76–4.67 (m, 1H), 2.98 (dd, *J* = 15.3 Hz, *J* = 5.8 Hz, 1H), 2.91 (dt, *J* = 16.4 Hz, 8.1 Hz, 1H), 2.58 (dd, *J* = 14.8 Hz, 6.6 Hz, 1H), 2.52 (dd, *J* = 15.0 Hz, 8.7 Hz, 1H), 2.49 (dd, *J* = 15.3 Hz, 6.9 Hz), 2.39–2.32 (m, 1H), 2.31–2.22 (m, 2H), 1.58 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.0, 140.8, 134.3, 130.3, 128.3 (2C), 127.09, 127.05 (2C), 126.7, 119.8, 62.3, 38.6, 36.1, 30.1, 26.7, 25.9, 17.8; IR (neat): $\tilde{\nu}$ = 3084, 3053, 3022, 2967, 2914, 2851, 1706, 1599, 1580, 1496, 1445, 1376, 1345, 1308, 1195, 1140, 1110, 1031, 1002, 981, 948, 899, 844, 774, 751, 724, 698, 681, 667 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 277 (100); HRMS (ES+) calcd for $(C_{18}H_{22}O + Na)^+$: 277.1568; found: 277.1568; elemental analysis (%) calcd for $C_{18}H_{22}O_2$: C 84.99, H 8.72; found: C 84.94, H 8.71.

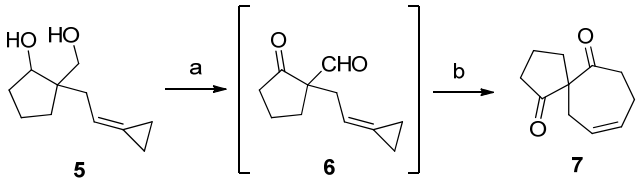
Compound 15d. Colourless oil (99% conversion was obtained when the reaction was performed in NMR tube). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.80–5.65 (m, 3H), 5.018 (dq, *J* = 17.1 Hz, *J* = 1.6 Hz, 1H), 5.017–4.98 (m, 1H), 2.91–2.83 (m, 1H), 2.68 (ddd, *J* = 15.1 Hz, *J* = 11.3 Hz, *J* = 3.9 Hz, 1H), 2.53 (dd, *J* = 6.5 Hz, *J* = 3.7 Hz, 1H), 2.52–2.43 (m, 2H), 2.37–2.29 (m, 1H), 2.23–2.15 (m, 1H), 2.12–2.00 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.0, 136.0, 129.5, 128.8, 116.8, 50.3, 42.2, 35.1, 30.1, 24.1; IR (neat): $\tilde{\nu}$ = 3073, 3018, 2916, 2851, 1706, 1641, 1436, 1373, 1259, 1219, 1194, 991, 913 cm^{-1}; MS (EI): *m/z* (rel. intensity): 150 (6), 96 (48), 95 (27), 81 (24), 79 (53), 67 (44), 65 (18), 53 (44), 51 (21), 41 (59), 39 (100); HRMS (CI) calcd for $(C_{10}H_{14}O)^+$: 150.1030; found: 150.1037.

Compound 15e. Colourless oil (14 mg, 58%). 7.33–7.28 (m, 2H), 7.26–7.24 (m, 1H), 7.22–7.19 (m, 1H), 5.88–5.80 (m, 1H), 5.65 (dt, *J* = 11.4 Hz, 4.2 Hz, 1H), 3.12 (ddquint, *J* = 15.4 Hz, 6.1 Hz, 1.6 Hz, 1H), 2.94 (dt, *J* = 12.4 Hz, 8.2 Hz, 1H), 2.84 (dd, *J* = 17.2 Hz, *J* = 1.1 Hz, 1H), 2.80 (dd, *J* = 15.5 Hz, 7.0 Hz, 1H), 2.63 (d, *J* = 17.2 Hz, 1H), 2.40 (dt, *J* = 12.4 Hz, 5.6 Hz, 1H), 2.31–2.22 (m, 2H) 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 211.4, 139.7, 130.9, 128.3 (2C), 127.2, 127.0 (2C), 126.7, 104.1, 87.7, 61.2, 38.8, 30.4, 29.7, 26.5, 0.0; IR (neat): $\tilde{\nu}$ = 3058, 3024, 2958, 2901, 2851, 2177, 1709, 1598, 1497, 1472, 1446, 1308, 1249, 1199, 1142, 1051, 1037, 1025, 1001, 976, 943, 842, 759, 729, 698, 670 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 319 (100); HRMS (ES+) calcd for $(C_{19}H_{24}OSi + Na)^+$: 319.1494; found: 319.1487; elemental analysis (%) calcd for $C_{19}H_{24}OSi$: C 76.97, H 8.16; found: C 71.11, H 8.46.



Compound 15f. Colourless oil (7.5 mg, 75%). 7.33–7.28 (m, 2H), 7.26–7.20 (m, 3H), 5.87–5.79 (m, 1H), 5.64 (dt, J = 11.4 Hz, J = 4.3 Hz, 1H), 3.13–3.06 (m, 1H), 2.92 (dt, J = 12.5 Hz, J = 8.0 Hz, 1H), 2.81 (dd, J = 15.5 Hz, J = 6.8 Hz, 1H), 2.75–2.69 (m, 1H), 2.60 (dq, J = 16.9 Hz, J = 2.6 Hz, 1H), 2.40 (dt, J = 12.5 Hz, J = 5.8 Hz, 1H), 2.28–2.21 (m, 2H), 1.66 (t, J = 2.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 211.9, 140.1, 130.6, 128.3 (2C), 127.1, 126.9 (2C), 126.8, 78.4, 75.7, 61.3, 38.9, 30.5, 28.7, 26.5, 3.5; IR (neat): $\tilde{\nu}$ = 3053, 3023, 2920, 2853, 1702, 1598, 1578, 1497, 1446, 1308, 1196, 1142, 1037, 758, 698, 670 cm^{-1}; HRMS (ES+) calcd for $(C_{17}H_{18}O + Na)^+$: 261.1255; found: 261.1264.

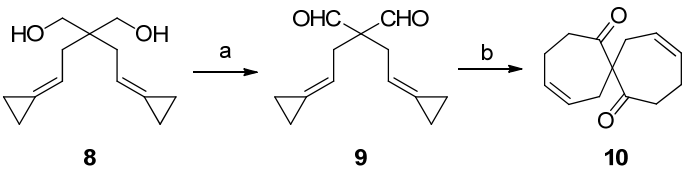
Oxidation of diol 5 and hydroacylation of 1,3-keto-aldehyde 6



[a] Dess-Martin periodinane, $NaHCO_3$, CH_2Cl_2, 0 °C, full conversion. [b] 10 mol% $[Rh(BINAP)]BF_4$, acetone, 60 °C. 80% over two steps.

Compound 7. Under N_2, **5** (14 mg, 0.0768 mmol) was added to a suspension of Dess Martin periodinane (137 mg, 0.323 mmol) and $NaHCO_3$ (84 mg, 0.999 mmol) in CH_2Cl_2 (1 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 2 hours. The mixture was filtered through deactivated neutral alumina and rinsed with a mixture PE/Et_2O (2:1). The filtrate was evaporated and the filtration was repeated. Crude compound **6** was obtained as colourless oil [^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.58–5.50 (m, 1H), 2.76 (dd, *J* = 14.0 Hz, 7.6 Hz, 1H), 2.55 (dd, *J* = 14.1 Hz, 7.1 Hz, 1H), 2.48 (dd, *J* = 11.7 Hz, 5.9 Hz, 1H), 2.53–2.17 (m, 2H), 1.98–1.76 (m, 3H), 1.09–1.03 (m, 2H), 1.02–0.94 (m, 2H)]. This crude material was not further purified due to its inherent instability. Instead, a solution of $[Rh(BINAP)]BF_4$ (0.00768 mmol) in 1.5 mL acetone prepared according to the general procedure was added under N_2 to crude ketoaldehyde **6**. After 12 h at 60 °C and purification by flash chromatography (PE/Et_2O = 70/1 → 50/1 → 30/1), spirobisketone **7** was obtained as colourless oil (10.8 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.72–5.64 (m, 1H), 5.63–5.56 (m, 1H), 3.28 (dt, *J* = 11.7 Hz, *J* = 5.6 Hz, 1H), 3.03–2.95 (m, 1H), 2.65–2.57 (m, 1H), 2.56–2.49 (m, 1H), 2.46 (dt, *J* = 11.6 Hz, 4.9 Hz, 1H), 2.42–2.35 (m, 2H), 2.33–2.23 (m, 1H), 2.08–2.04 (m, 1H), 2.03 (dd, *J* = 15.6 Hz, 8.0 Hz, 1H), 1.89–1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 215.6, 210.0, 130.2, 125.5, 69.5, 39.1, 38.2, 33.2, 30.7, 27.3, 19.3; IR (neat): $\tilde{\nu}$ = 3018, 2961, 2854, 1736, 1699, 1626, 1608, 1442, 1405, 1349, 1312, 1274, 1199, 1147, 1089, 1044, 1011, 951, 916, 860, 824, 774, 693, 662 cm^{-1}; MS (CI): *m/z* (rel. intensity): 196 (100), 179 (12), 151 (10); HRMS (CI) calcd for $(C_{11}H_{14}O_2 + H)^+$: 179.1067; found: 179.1069.

Oxidation of diol 8 and hydroacylation of 1,3-keto-aldehyde 9



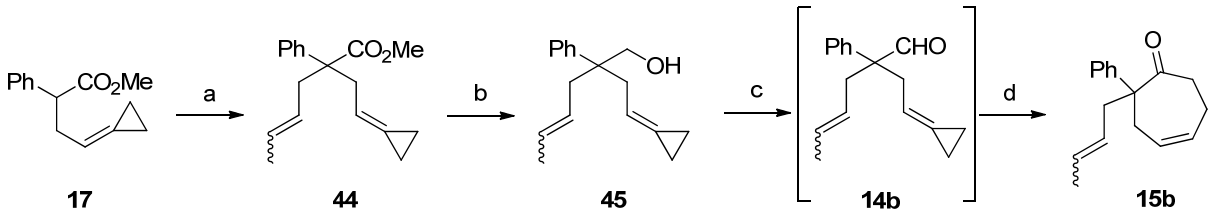
8 **9** **10**

[a] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, full conversion. [b] 10 mol% $[Rh(BINAP)]BF_4$, acetone, r.t., 82% over two steps

Compound 10. Under N_2, dimethyl sulfoxide (30 µL, 0.425 mmol) was added to a solution of oxalyl chloride (18 µL, 0.210 mmol) in CH_2Cl_2 (1.5 mL) at -78 °C. After 10 minutes stirring at -78 °C, a solution of alcohol **8** (21 mg, 0.103 mmol) in CH_2Cl_2 (0.6 mL) was added. After 20 minutes stirring at -78°C, triethylamine (0.12 mL, 0.83 mmol) was added rapidly and the mixture was stirred at room temperature during 30 minutes. The mixture was quenched with a saturated aqueous solution of $CuSO_4$ (4 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic layers were concentrated before being dissolved in CH_2Cl_2 (5 mL) and washed with water (2 x 3 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated, affording **9** as colourless oil. This aqueous work up[2] was repeated until no Me_2S was visible by NMR [^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.71 (s, 2H), 5.73–5.62 (m, 2H), 2.70 (d, *J* = 7.2 Hz, 4H), 1.10–1.03 (m, 4H), 1.01–0.93 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.5 (2C), 127.2 (2C), 110.9 (2C), 65.5, 33.2 (2C), 3.0 (2C), 2.1 (2C)]. This crude material was not further purified due to its inherent instability. Instead, a solution of $[Rh(BINAP)]BF_4$ (0.01 mmol) in 2 mL acetone prepared according to the general procedure was added under N_2 to crude bisaldehyde **9**. After stirring at room temperature for 12h, evaporation of volatiles and purification by flash chromatography gave **10**. Colourless oil (16.7 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.73–5.59 (m, 4H), 3.23 (td, *J* = 11.4 Hz, *J* = 5.5 Hz, 2H), 3.20–3.14 (m, 2H), 2.48–2.40 (m, 2H), 2.35 (dt, *J* = 11.4 Hz, *J* = 5.1 Hz, 2H), 2.33–2.23 (m, 2H), 2.18 (dd, *J* = 15.7 Hz, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.6 (2C), 130.2 (2C), 126.1 (2C), 75.6, 38.5 (2C), 28.5 (2C), 27.4 (2C); IR (neat): $\tilde{\nu}$ = 3023, 2973, 2896, 2856, 1709, 1691, 1469, 1440, 1382, 1349, 1311, 1195, 1140, 1112, 1076, 1043, 980, 934, 902, 836, 794, 746, 669 cm^{-1}; MS (CI): *m/z* (rel. intensity): 222 (100), 205 (32); HRMS (CI) calcd for ($C_{13}H_{16}O_2$ + H): 205.1223; found: 205.1221; elemental analysis (%) calcd for $C_{13}H_{16}O_2$: C 76.44, H 7.90; found: C 75.49, H 7.81.

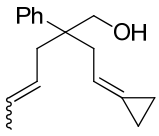
[2] M. L. Grachan, M. T. Tudge, E. N. Jacobsen, *Angew. Chem. Int. Ed.*, 2008, **47**, 1469

Preparation of compound 14b and hydroacylation to obtain 15b



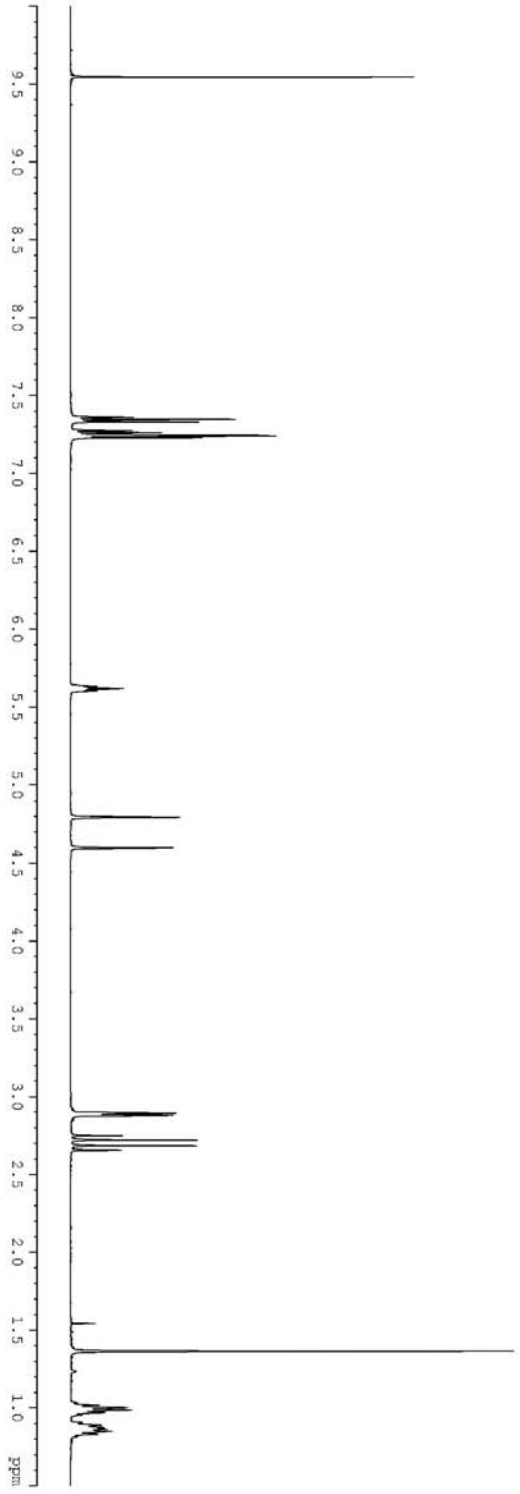
[a] LiHMDS, crotyl chloride, THF, -78 °C to r.t., 83%. [b] $LiAlH_4$, Et_2O, r.t., 94%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, $CuSO_4$ aqueous work up, full conversion. [d] 10 mol% [Rh(BINAP)]BF_4, acetone, r.t., 70% over two steps

Compound 44. This compound was prepared from **17** (152 mg, 0.698 mmol) according to the procedure described for the preparation of **18** and using crotyl chloride (*E*/*Z* = 6:1). This compound was obtained as an inseparable mixture of stereoisomers (*E*/*Z* = 5:1 (determined by ^{1}H NMR)). Colourless oil (157 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 2H), 7.26–7.19 (m, 3H), 5.52–5.36 (m, 2H), 5.23–5.14 (m, 1H), 3.61 (s, 3H), 2.89 (dd, *J* = 13.8 Hz, *J* = 7.7 Hz, 1H), 2.82 (dd, *J* = 14.1 Hz, *J* = 6.9 Hz, 1H), 2.72 (dd, *J* = 13.7 Hz, *J* = 7.6 Hz, 1H,), 2.64 (dd, *J* = 13.8 Hz, *J* = 6.7 Hz, 1H), 1,59 (dd, *J* = 6.6Hz, *J* = 0.9Hz, 3H), 1.02–0.92 (m, 2H), 0.89–0.82 (m, 1H), 0.82–0.74 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.9, 142.3, 129.0, 128.18 (2C), 126.63, 126.53 (2C), 125.8, 125.4, 112.97, 54.4, 51.9, 37.8, 37.2, 18.1, 2.75, 1.79; Additional signals for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.93 (dd, *J* = 14.1 Hz, 7.8 Hz, 1H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 128.21 (2C), 126.9, 126.7, 126.57 (2C), 125.6, 125.1, 113.05, 52.0, 37.4, 32.0, 12.8, 2.80, 1.76; IR (neat): $\tilde{\nu}$ = 3026, 2981, 2949, 1730, 1600, 1498, 1439, 1260, 1201, 1130, 1092, 1068, 1036, 1002, 967, 934, 919, 847, 763, 736, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 293 (100); HRMS (ES+) calcd for $(C_{18}H_{22}O_2 + Na)^+$: 293.1517; found: 293.1525; elemental analysis calcd (%) for $C_{18}H_{22}O_2$: C 79.96, H 8.20; found: C 80.41, H 8.46.



Compound 45. This compound was prepared from **44** (122 mg, 0.452 mmol) according to the procedure described for the preparation of **19**. This compound was obtained as an inseparable mixture of stereoisomers (*E*/*Z* = 5:1 (determined by ^{1}H NMR)). Colourless oil (103 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.29 (m, 4H), 7.23–7.17 (m, 1H), 5.66–5.56 (m, 1H), 5.54–5.44 (m, 1H), 5.34–5.24 (m, 1H), 3.78 (s, 2H), 2.61 (dd, *J* = 13.9 Hz, *J* = 7.5 Hz, 1H), 2.54 (dd, *J* = 13.8 Hz, *J* = 7.2 Hz, 1H), 2.49 (dd, *J* = 13.8 Hz, *J* = 7.2 Hz, 1H), 2.41 (dd, *J* = 14.1 Hz, *J* = 7.2 Hz, 1H), 1.61 (dd, *J* = 6.0 Hz, *J* = 1.0 Hz, 3H), 1.41–1.31 (m, 1H (OH)), 1.05–0.96 (m, 2H), 0.96–0.86 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.9, 128.3 (2C), 128.1, 127.0 (2C), 126.8, 126.0, 124.4, 113.9, 68.26, 46.6, 38.4, 37.8, 18.0, 2.7, 1.8; Additional signals for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.67 (dd, *J* = 13.9 Hz, 7.2 Hz, 1H), 1.58 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.2, 126.1, 124.6, 114.0, 68.32, 46.8, 32.6, 12.9, 2.8; IR (neat): $\tilde{\nu}$ = 3413 (br), 3024, 2978, 2917, 1601, 1498, 1445, 1027, 967, 937, 759, 697 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 265 (100); HRMS (ES+) calcd for $(C_{17}H_{22}O + Na)^+$: 265.1568; found: 265.1569; elemental analysis calcd (%) for $C_{17}H_{22}O$: C 84.25, H 9.15; found: C 83.94, H 9.48.

Compound 15b. Aldehyde **14b** prepared from **45** (23.5 mg, 0.093 mmol) according to the procedure described for the preparation of **9** was not further purified due to its inherent instability [^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.52 (s, 1H), 7.40–7.32 (m, 2H), 7.31–7.17 (m, 3H), 5.62–5.39 (m, 2H), 5.26–5.14 (m, 1H), 2.90–2.56 (m, 4H), 1.58 (d, *J* = 6.5 Hz, 3H), 1.05–0.94 (m, 2H), 0.92-0.78 (m, 2H); Additional signal for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.5 Hz, 3H)]. Instead, a solution of [Rh(BINAP)]BF_4 (0.0093 mmol) in 1.9 mL acetone prepared according to the general procedure was added under N_2 to the crude aldehyde. After stirring at room temperature for 12h, evaporation of volatiles and purification by flash chromatography gave **15b** as inseparable mixture of stereoisomers (*E*/*Z* = 4:1, ratio determined by ^{1}H NMR). Colourless oil (16.3 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 2H), 7.24–7.16 (m, 3H), 5.81–5.71 (m, 1H), 5.66–5.57 (m, 1H), 5.39 (dq, *J* = 15.1 Hz, *J* = 6.5 Hz, 1H), 5.03–4.92 (m, 1H), 3.05–2.92 (m, 1H), 2.92 (dt, *J* = 11.9 Hz, *J* = 8.2 Hz, 1H), 2.67–2.58 (m, 1H), 2.49 (dd, *J* = 15.3 Hz, *J* = 7.0 Hz, 1H), 2.43 (dd, *J* = 14.1 Hz, *J* = 8.6 Hz, 1H), 2.37–2.301 (m, 1H), 2.297–2.22 (m, 2H), 1.54 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.8, 140.7, 130.2, 128.4 (2C), 128.3, 126.96, 126.92 (2C), 126.9, 126.7, 62.1, 41.2, 38.6, 30.04, 26.7, 17.96; Additional signals for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): 5.49 (dqt, *J* = 11.0 Hz, *J* = 6.8 Hz, *J* = 1.5 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.5, 130.5, 127.04, 126.8, 125.9, 38.4, 34.7, 30.05, 26.8, 17.97; IR (neat): $\tilde{\nu}$ = 3058, 3022, 2916, 2854, 1706, 1598, 1578, 1495, 1467, 1445, 1377, 1345, 1308, 1196, 1142, 1074, 1036,1002, 970, 912, 770, 753, 728, 698, 665 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 263 (100); HRMS (ES+) calcd for $(C_{17}H_{20}O + Na)^+$: 263.1412; found: 263.1410.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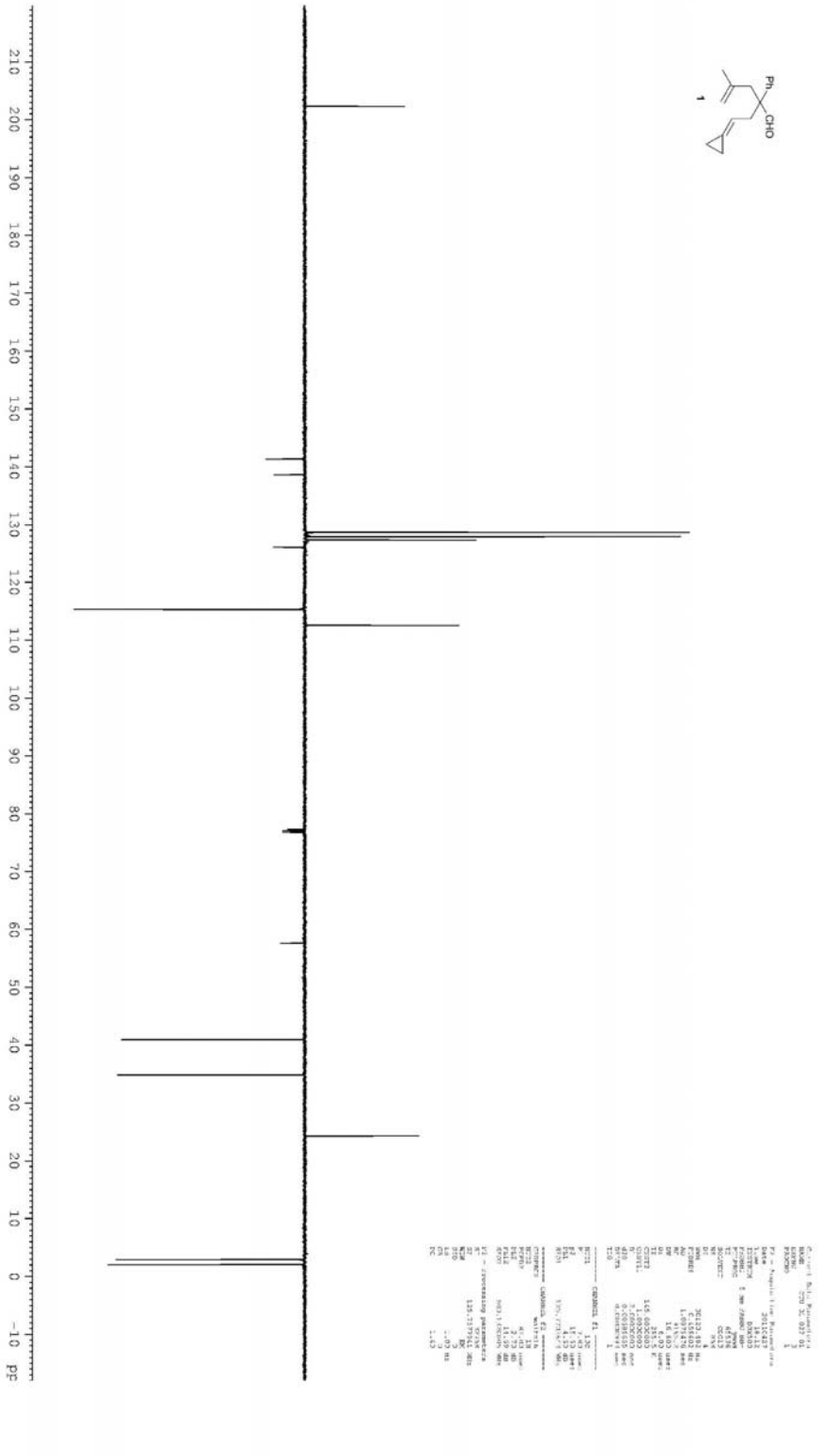
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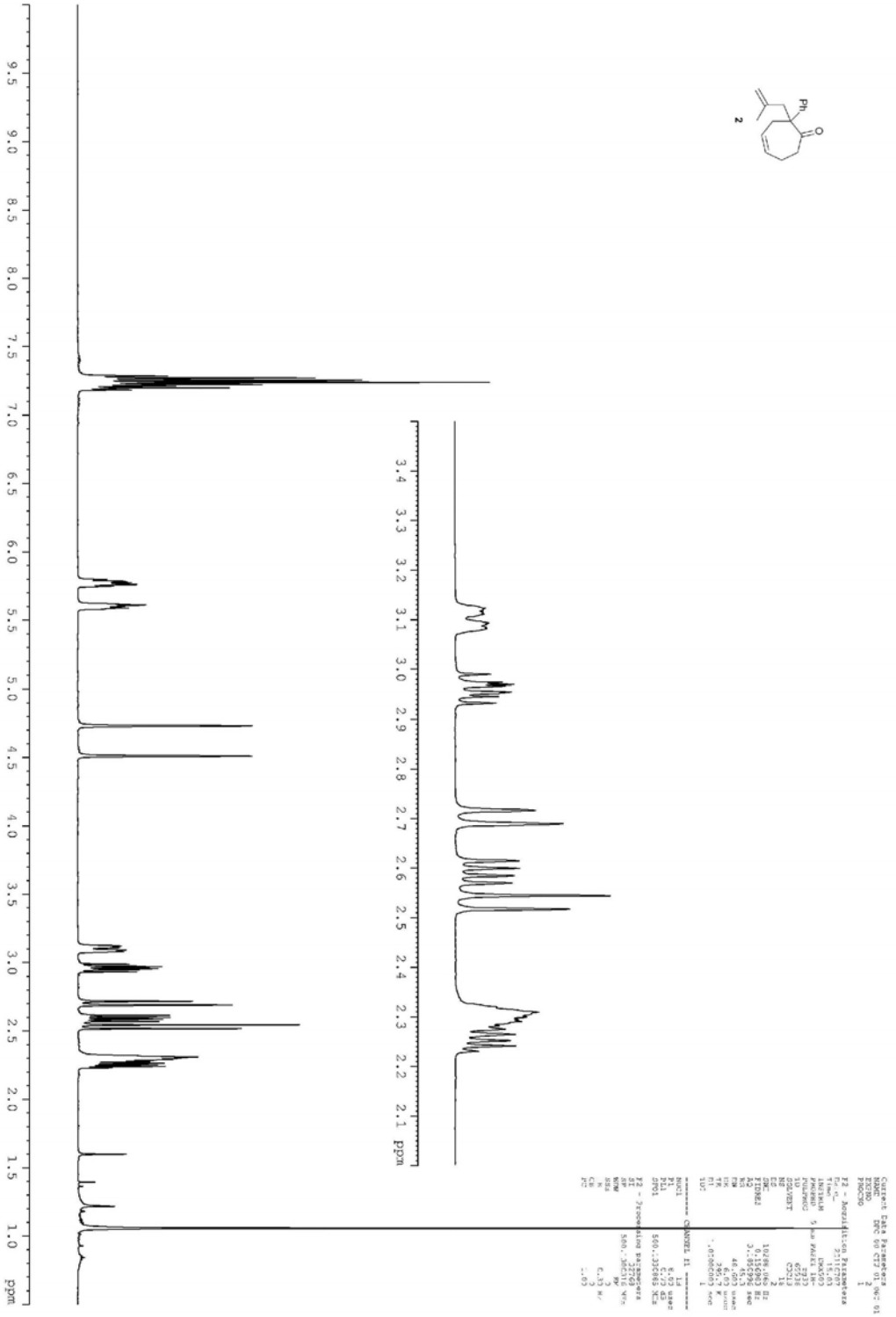

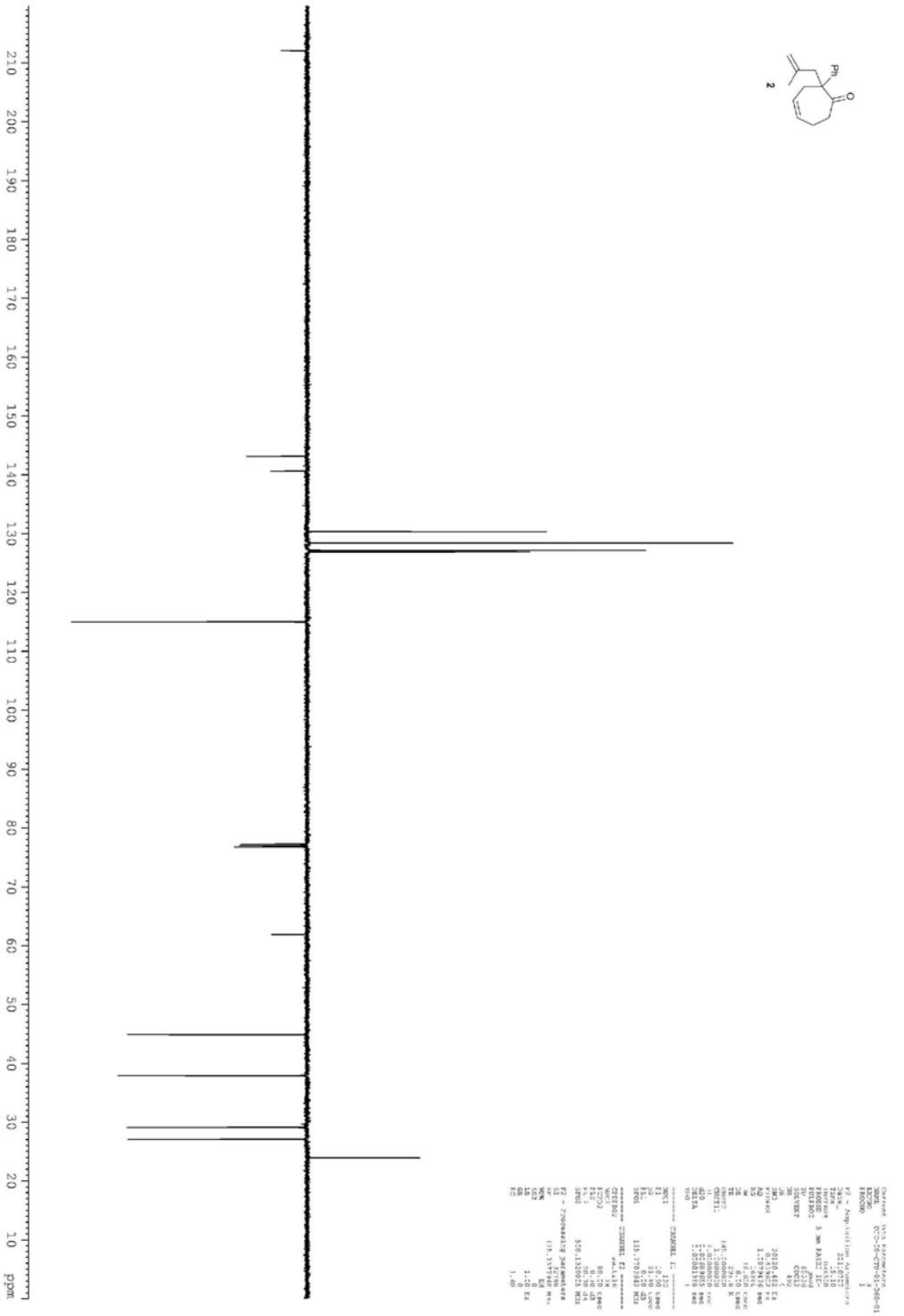
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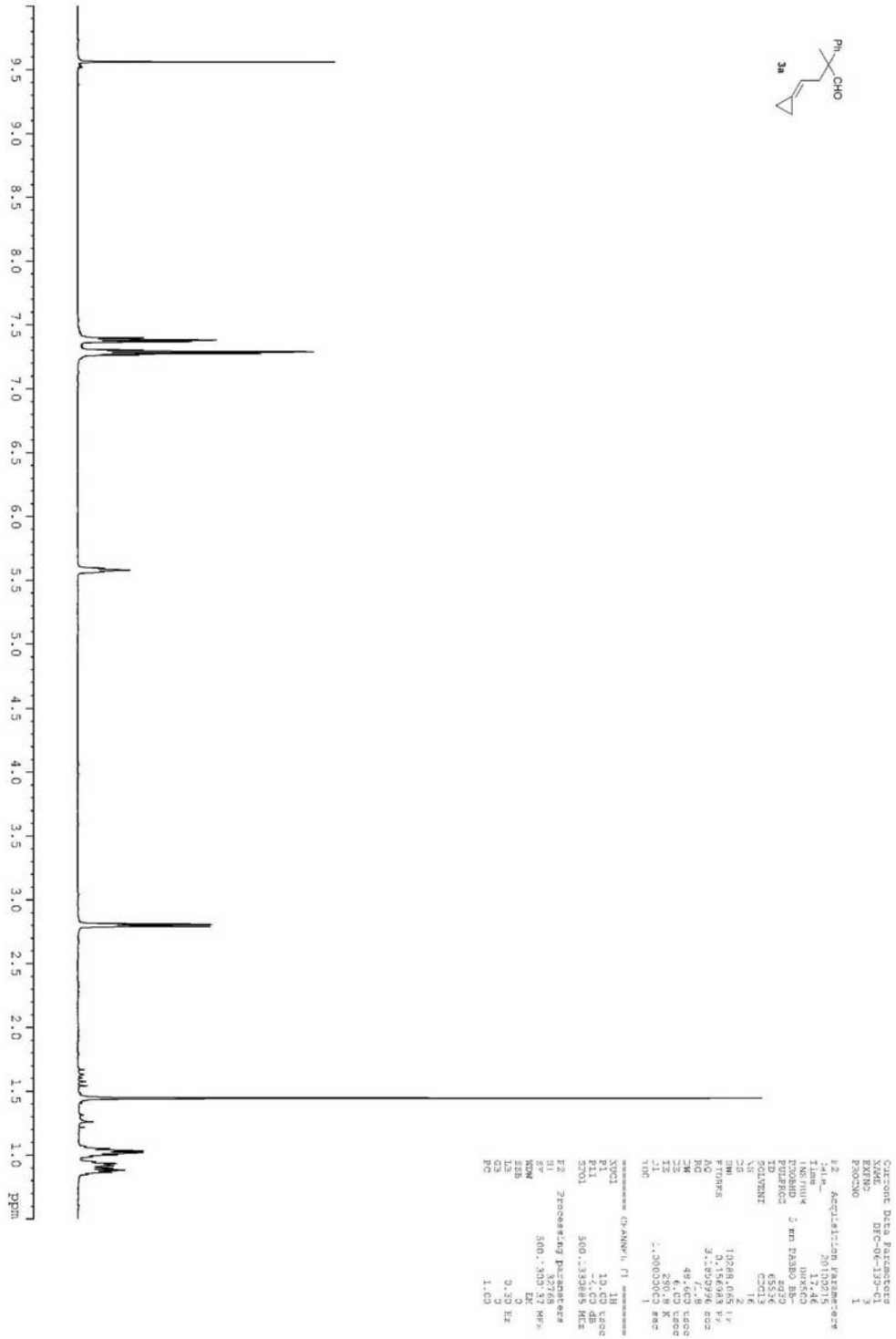
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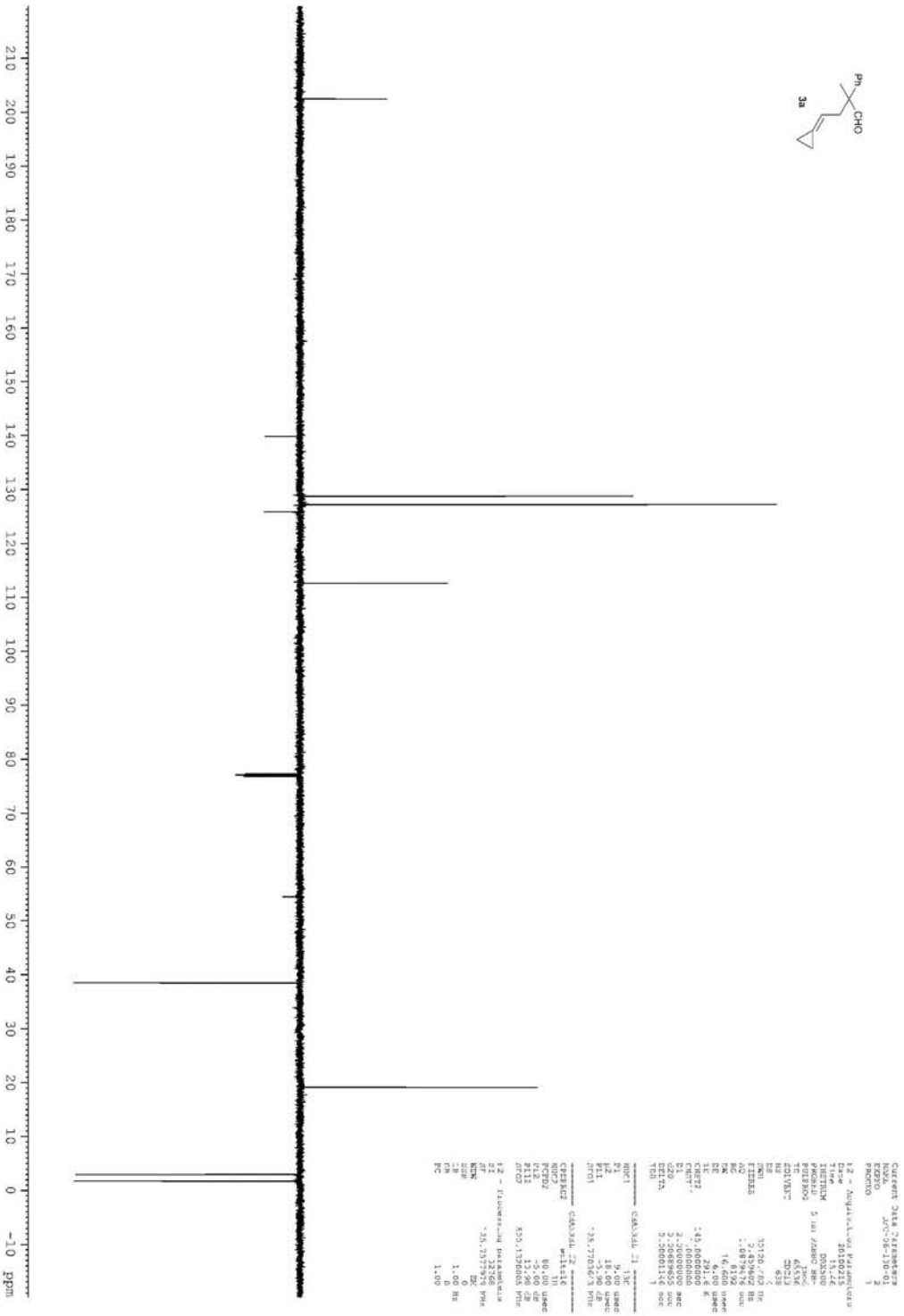
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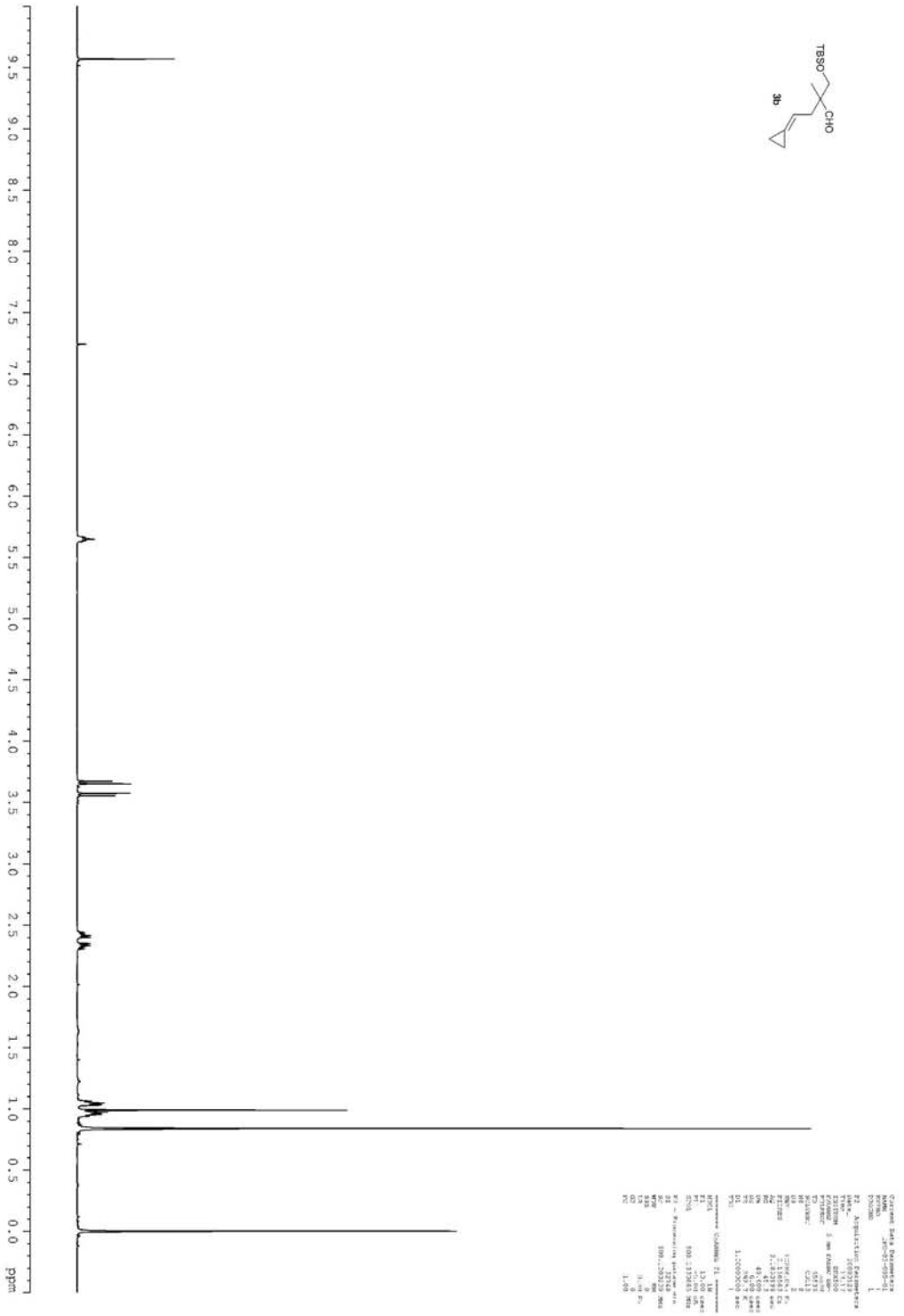
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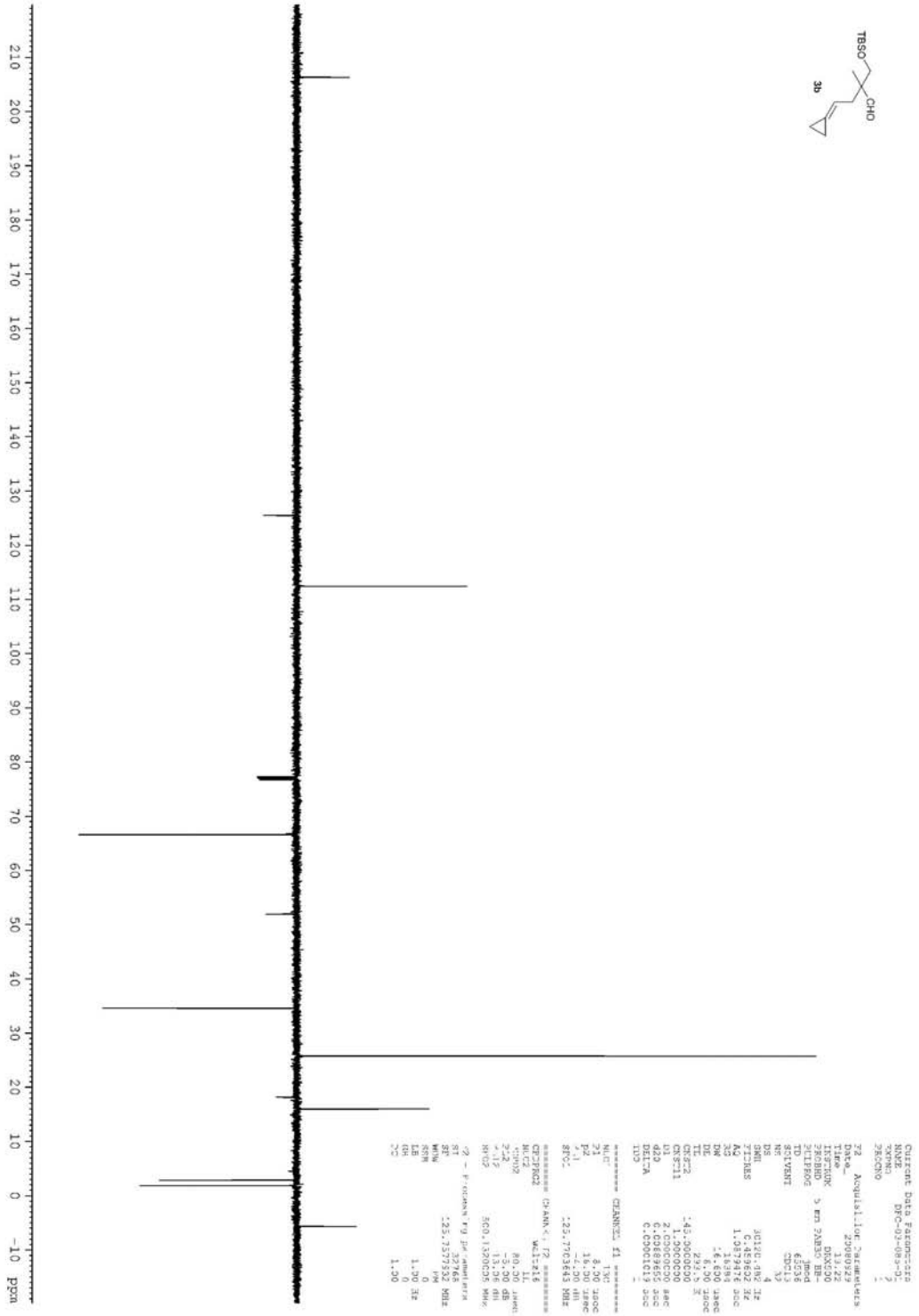
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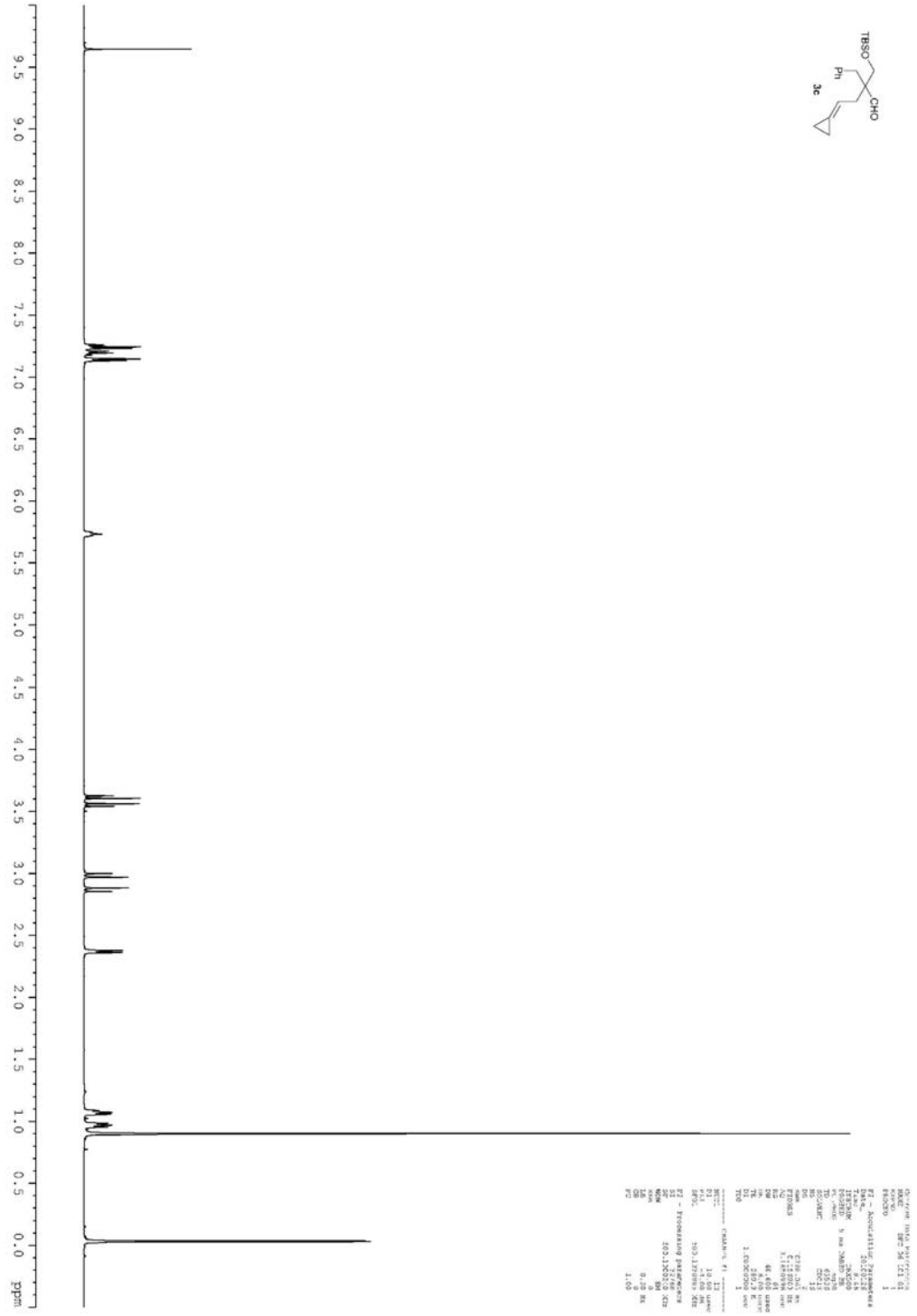
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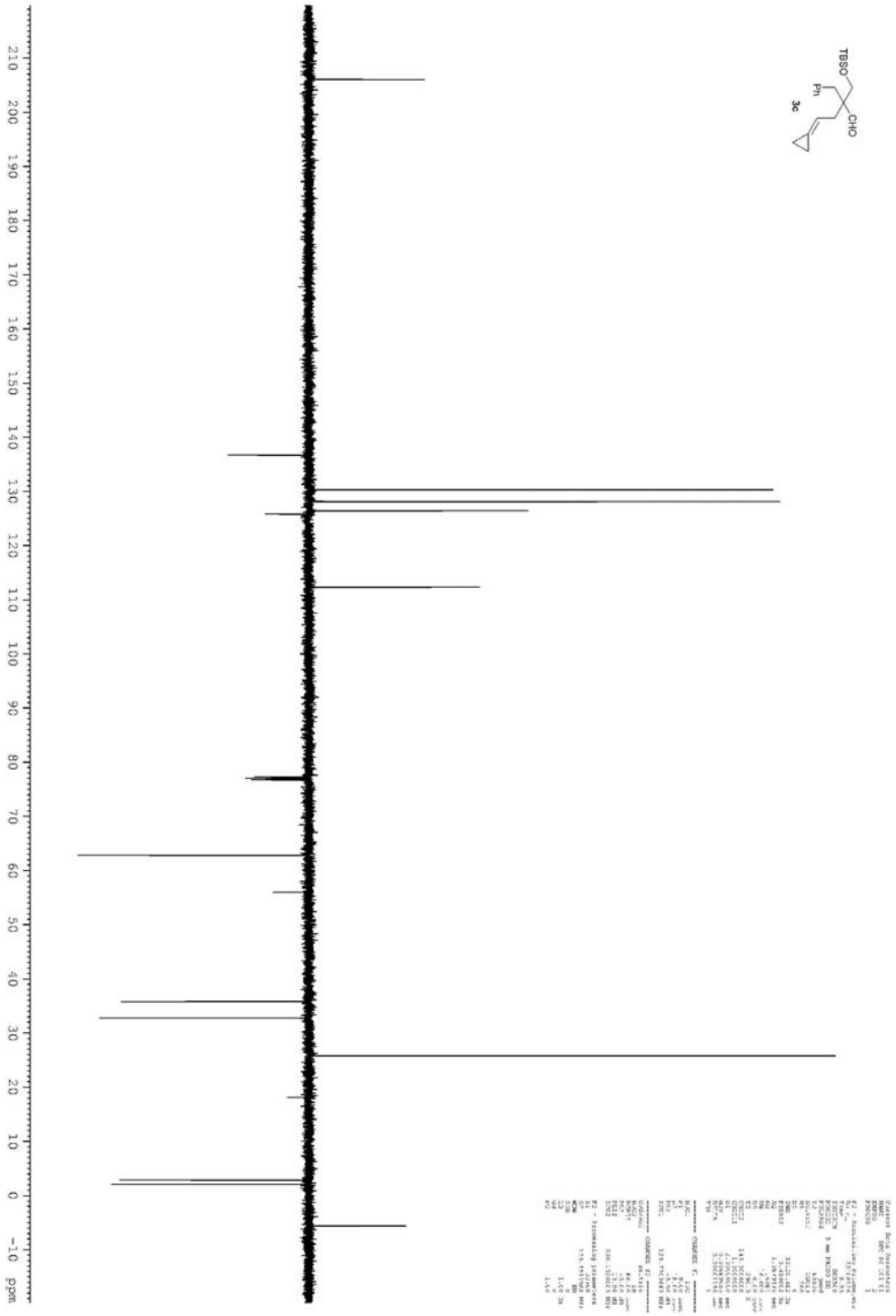
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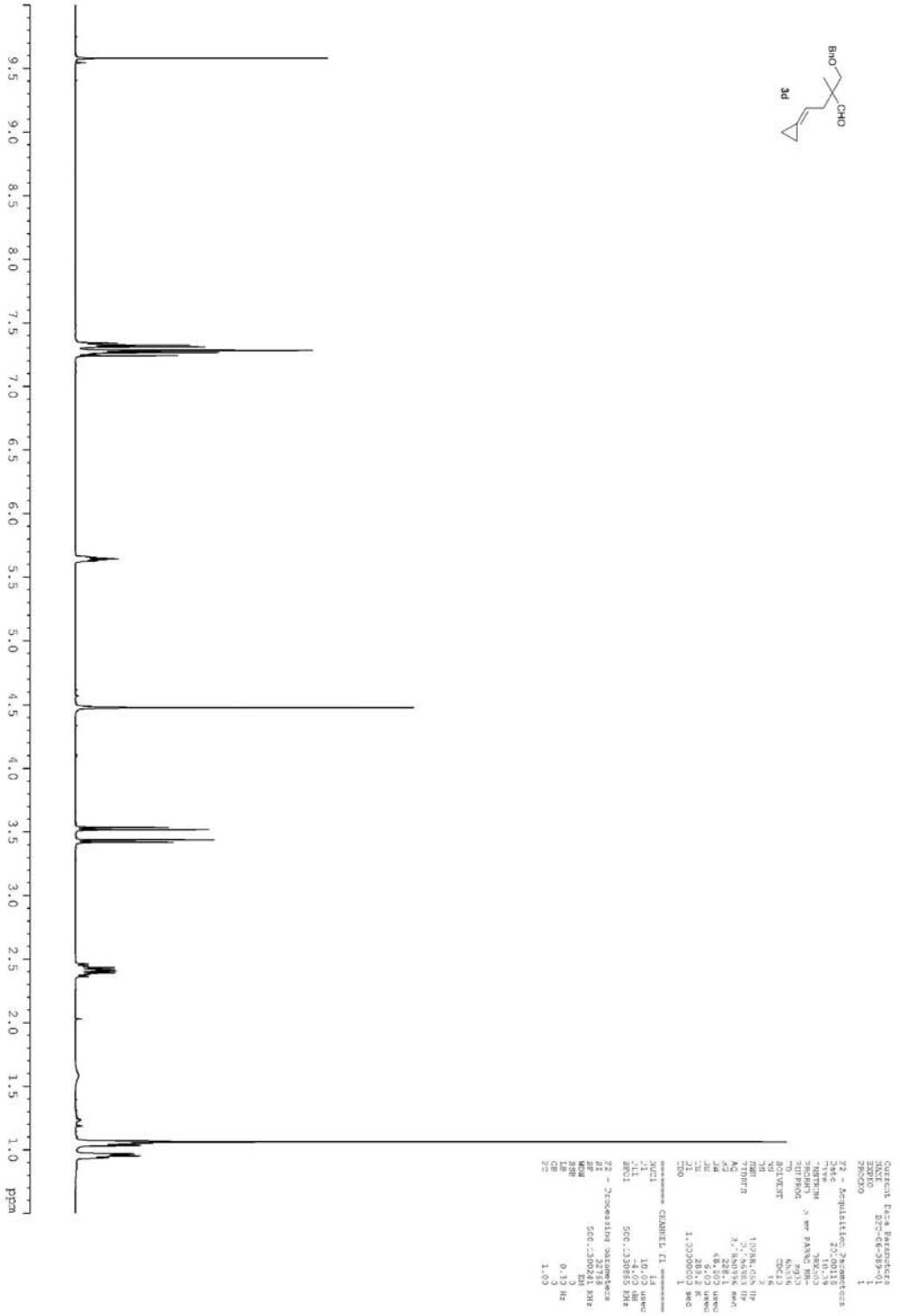
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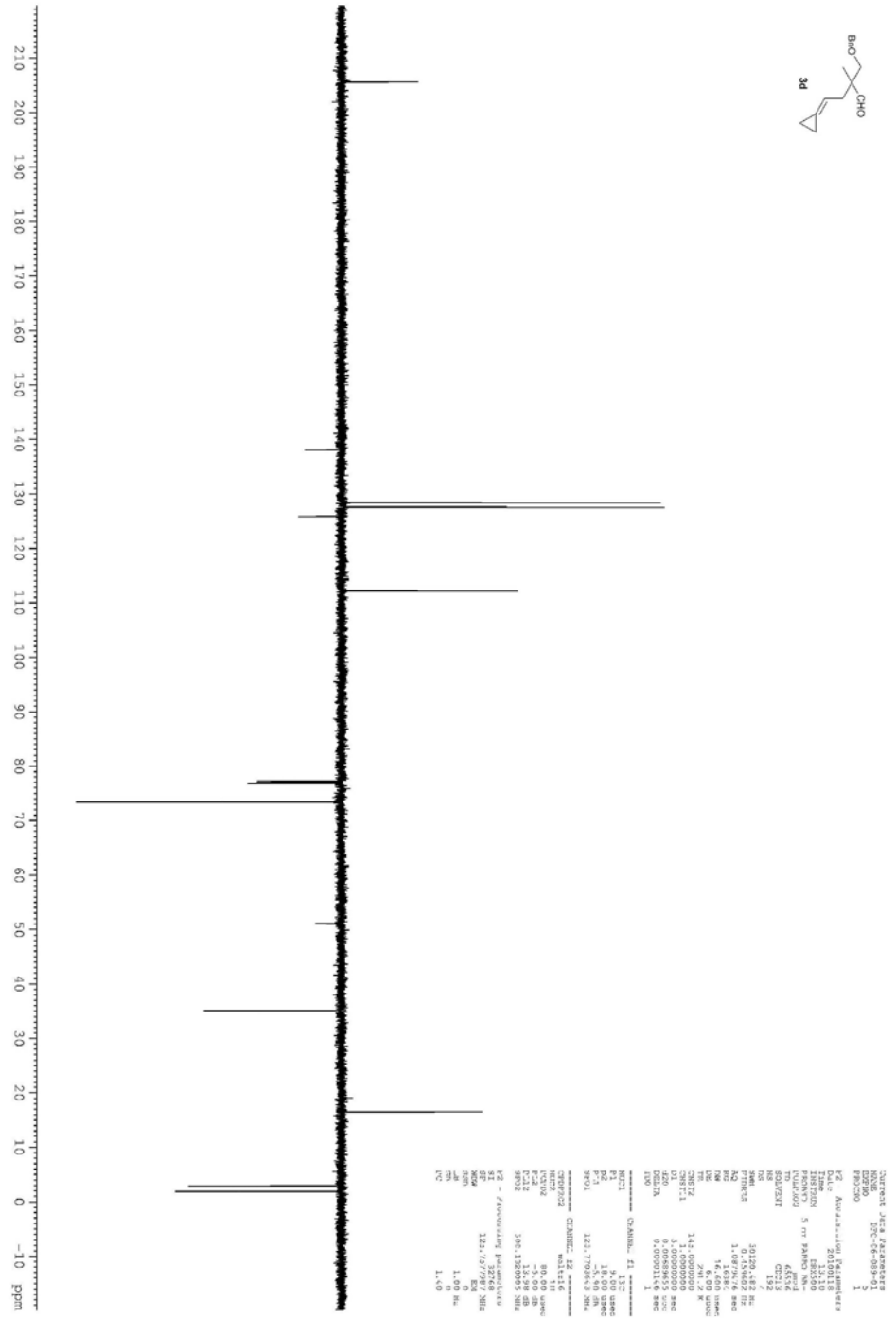
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3d
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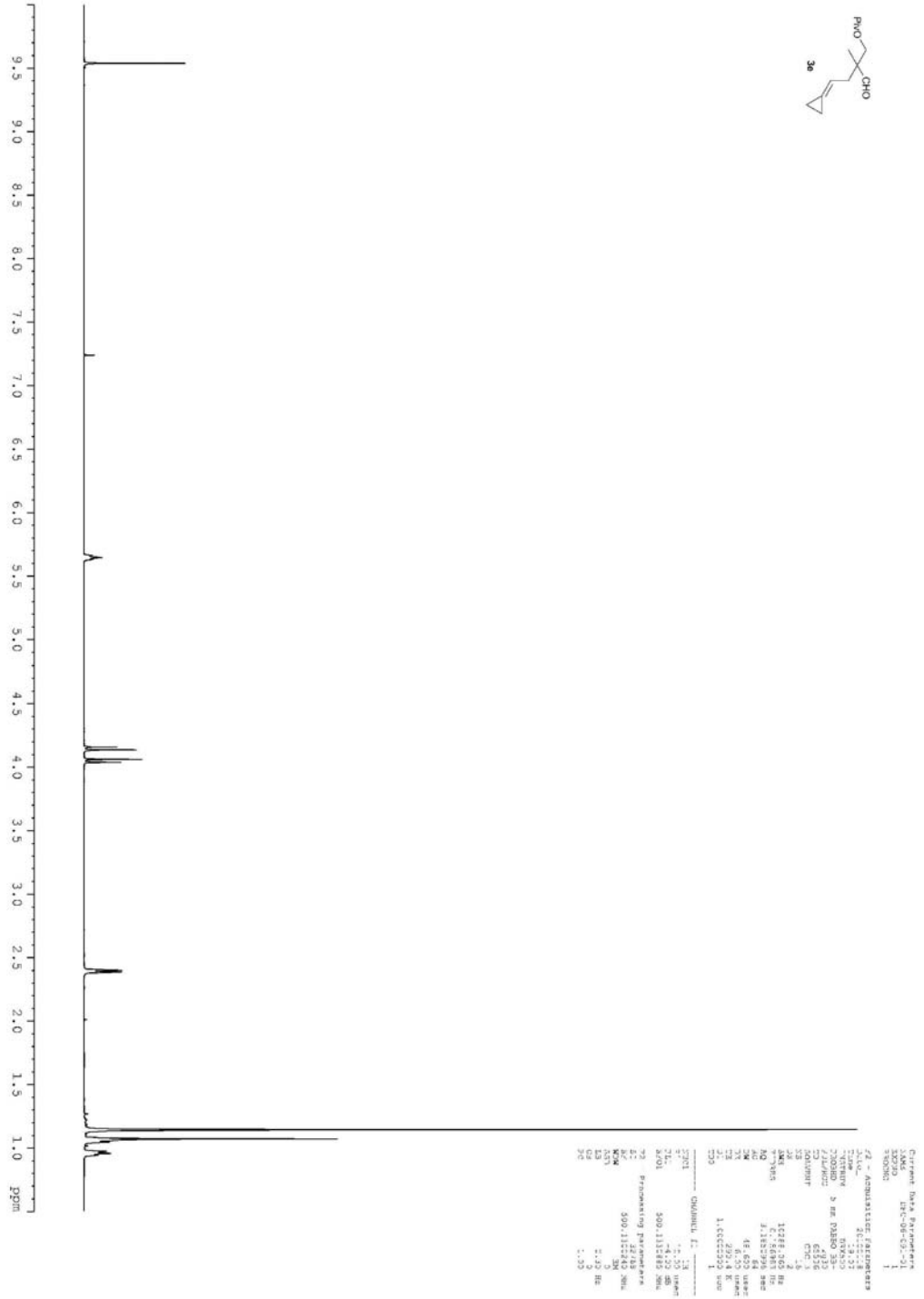
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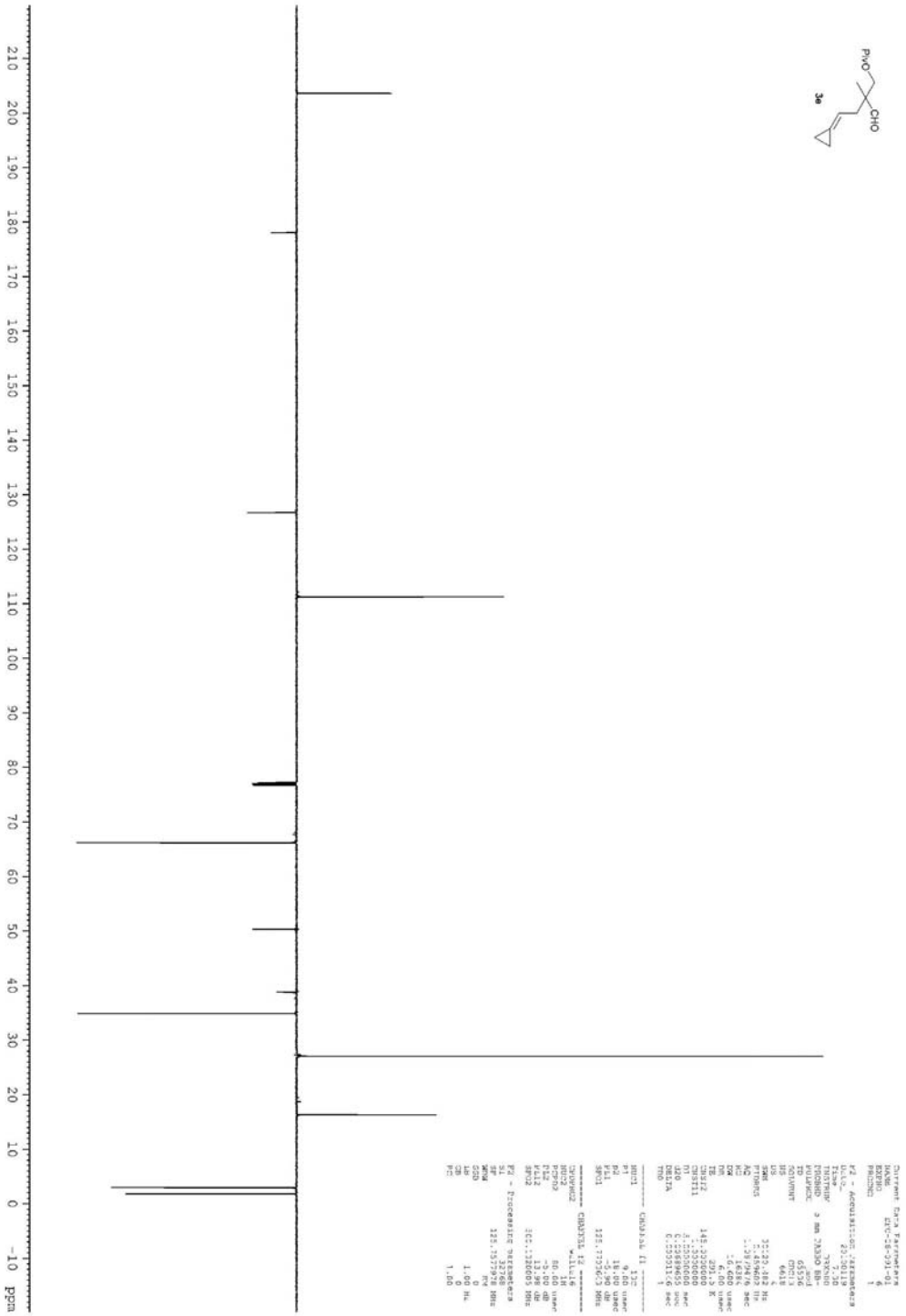
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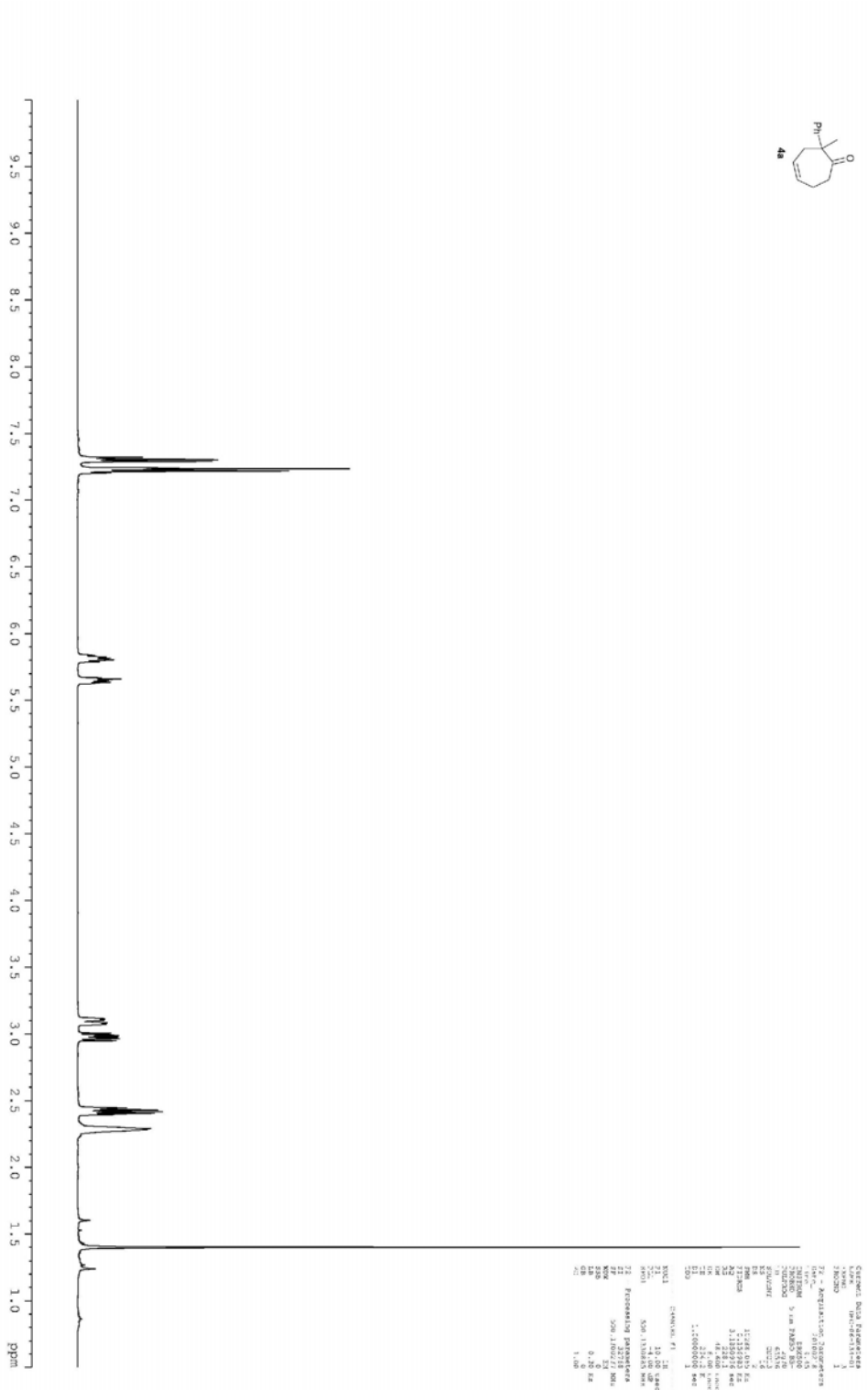
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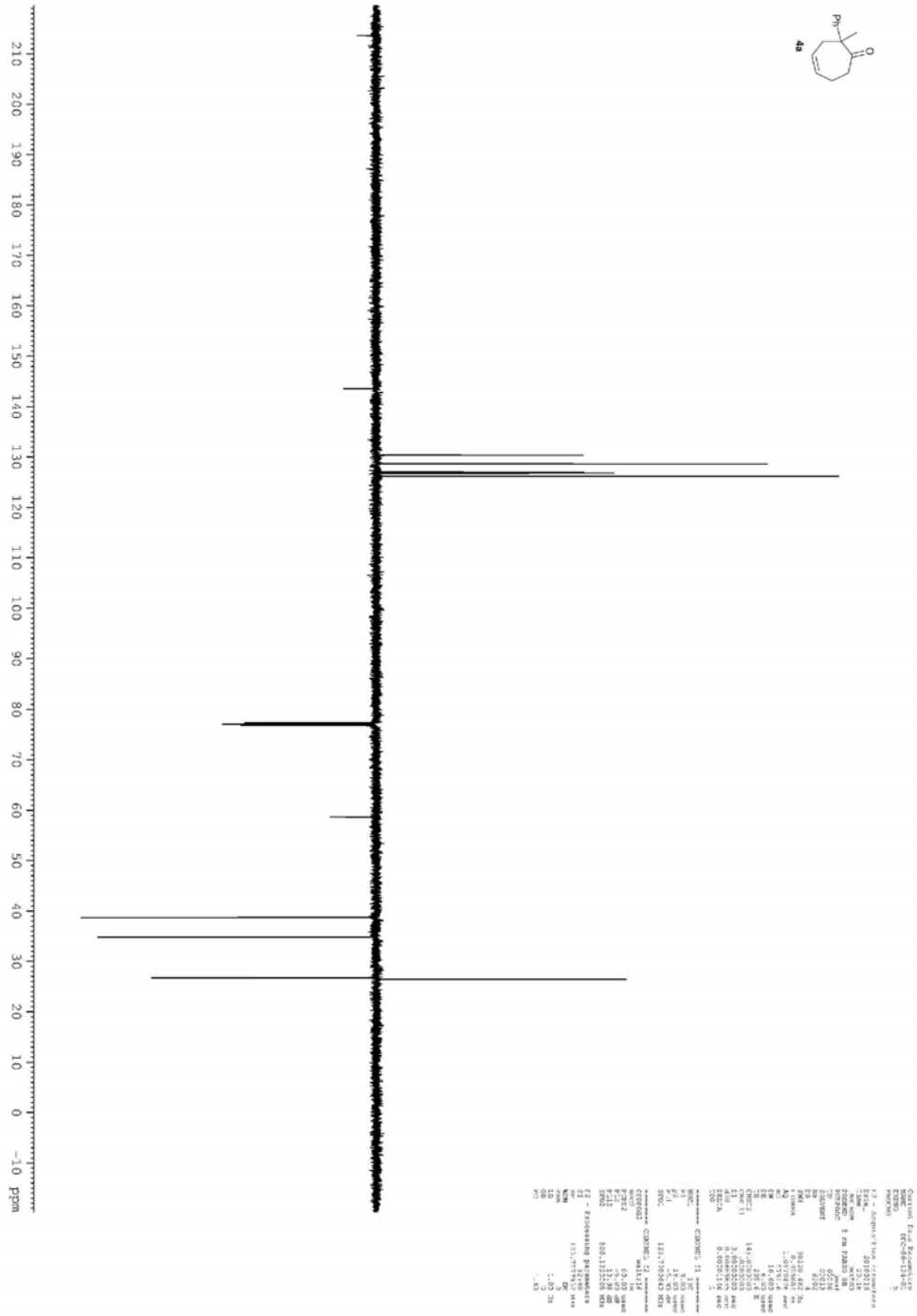
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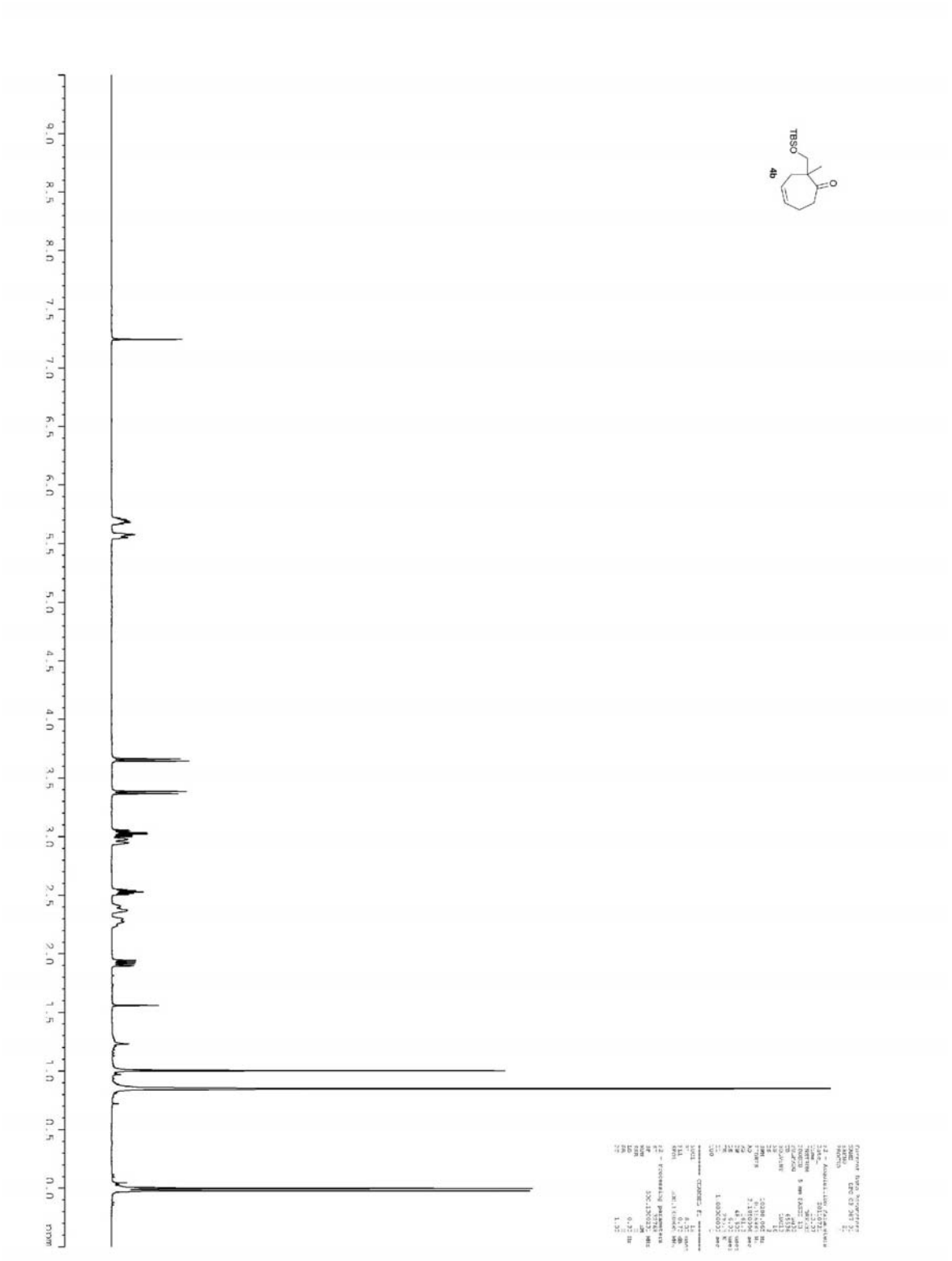

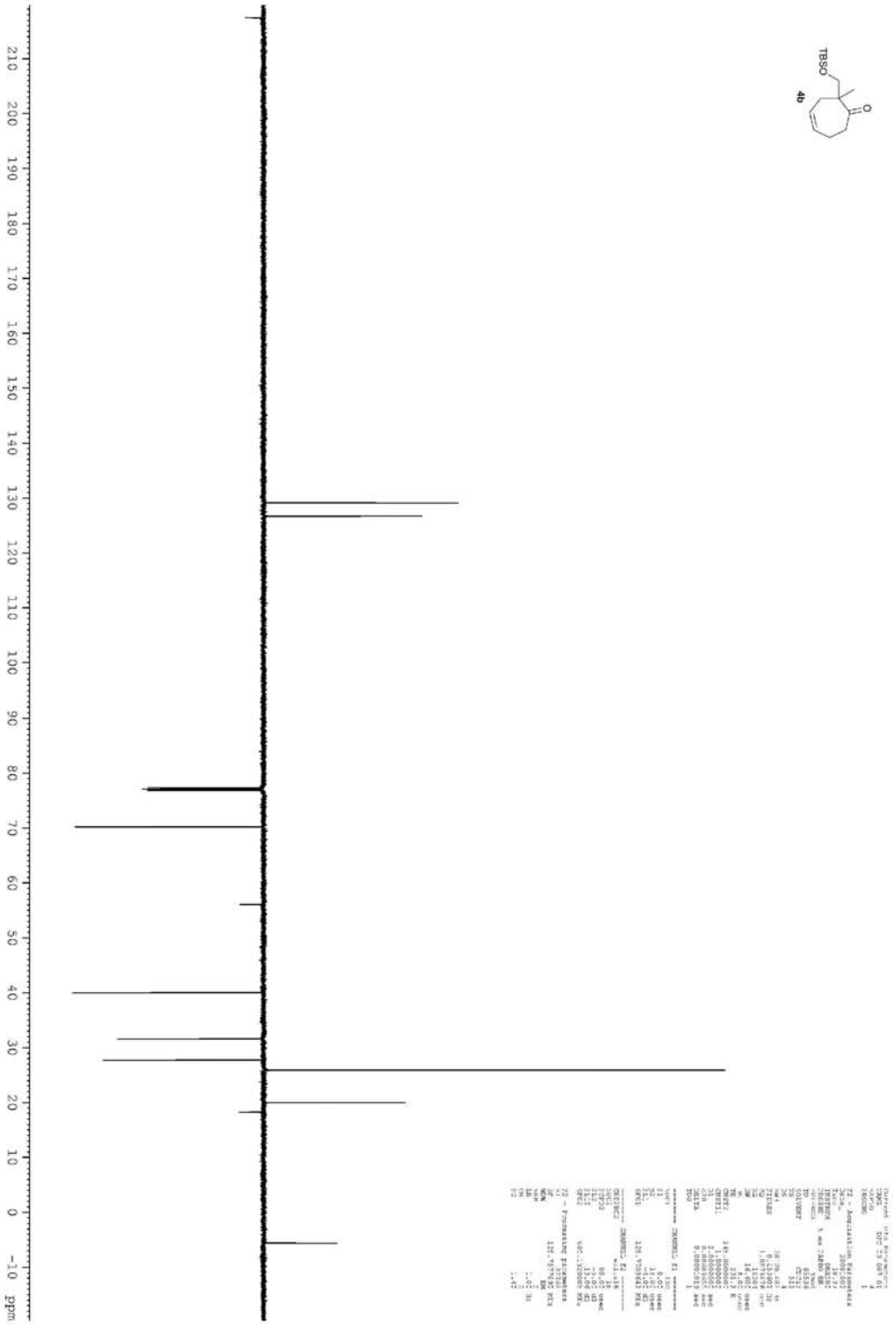
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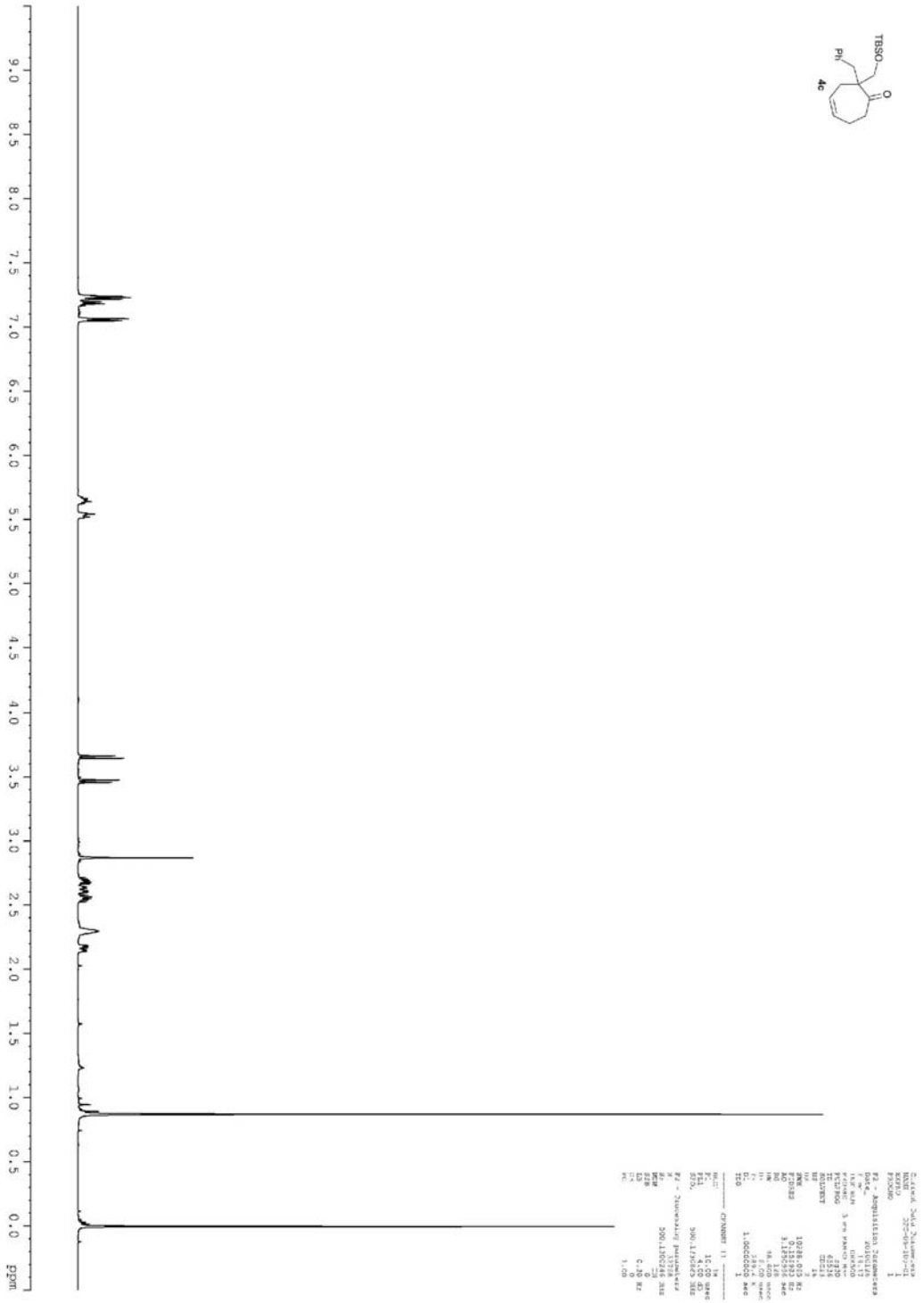
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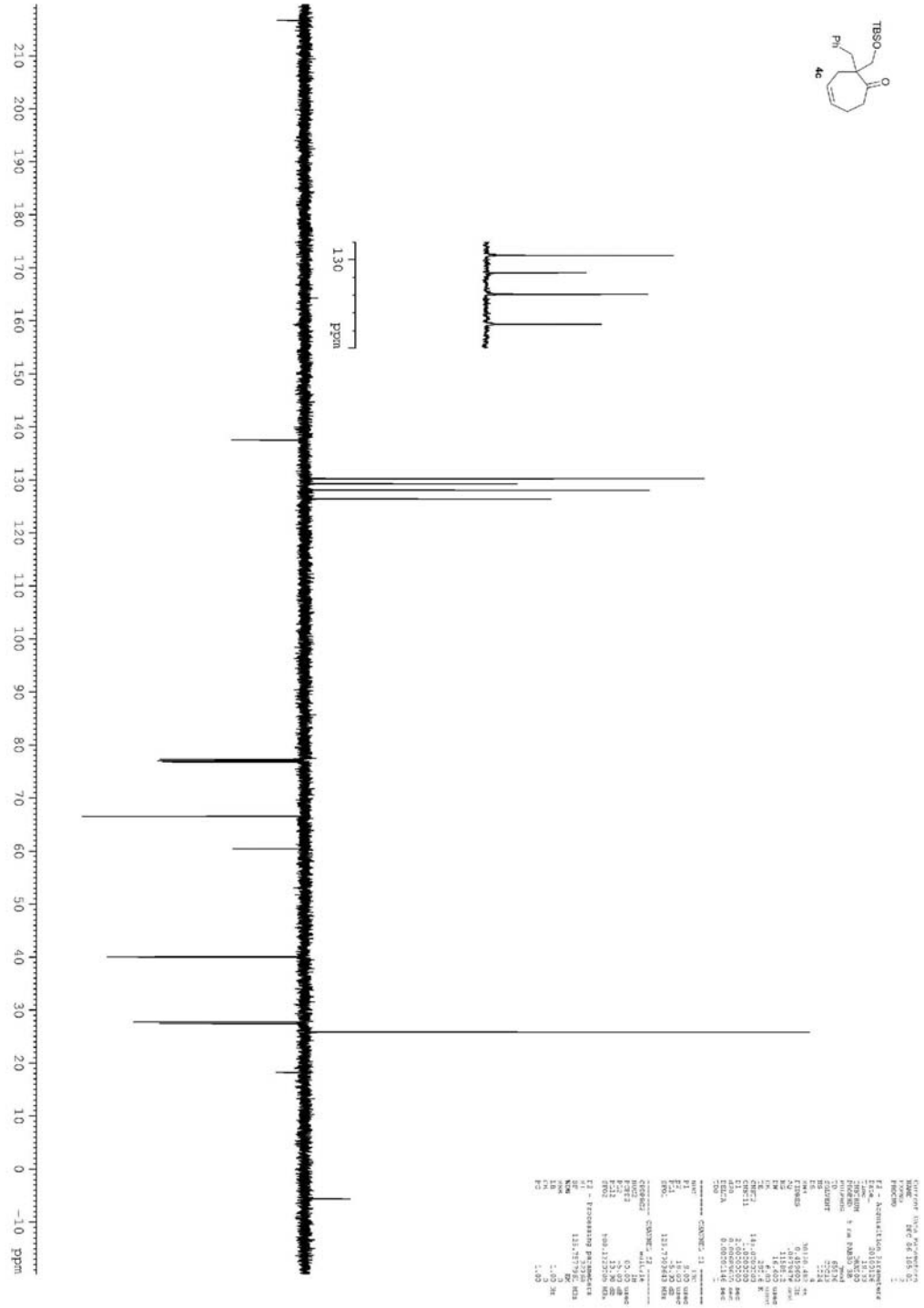
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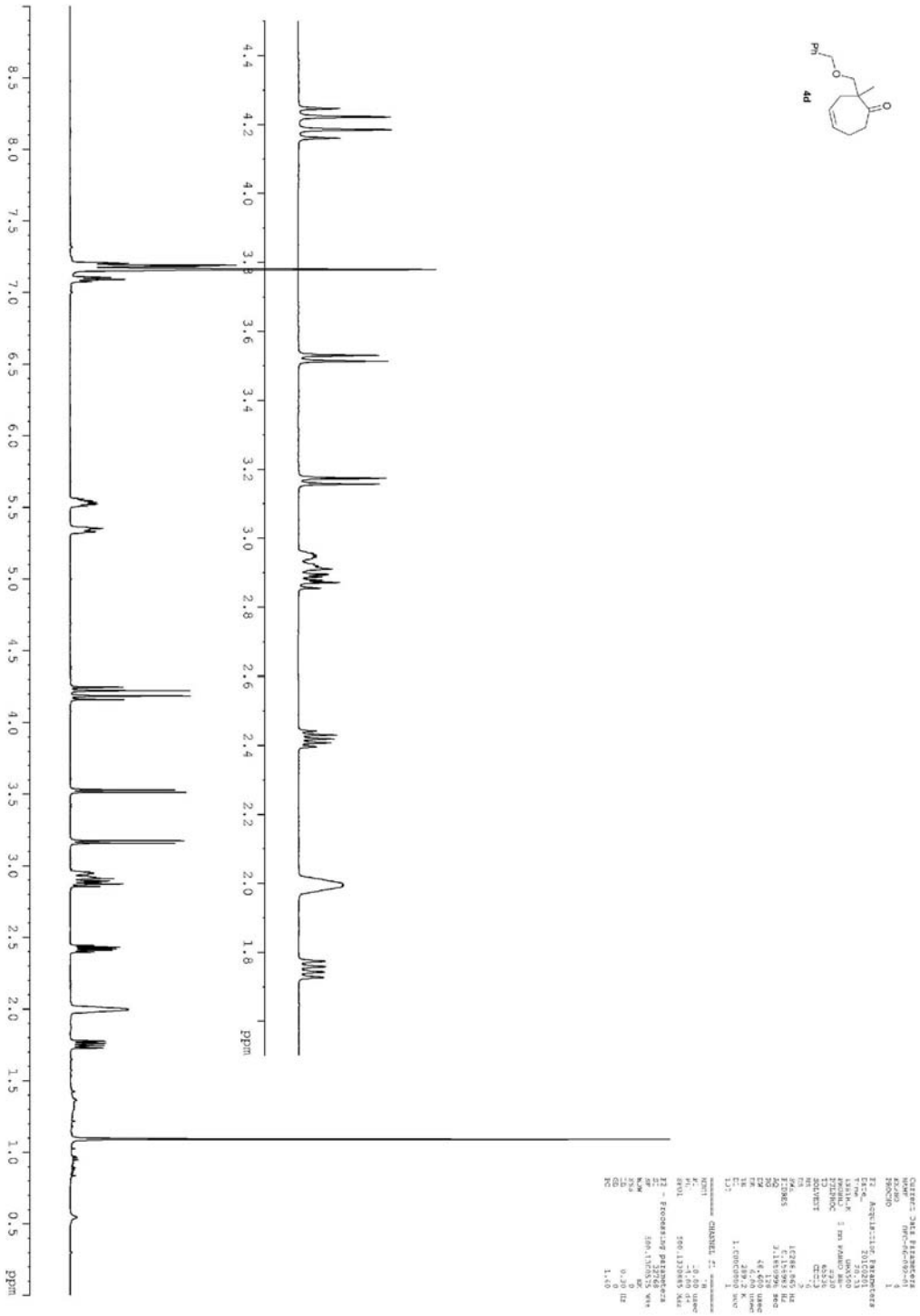

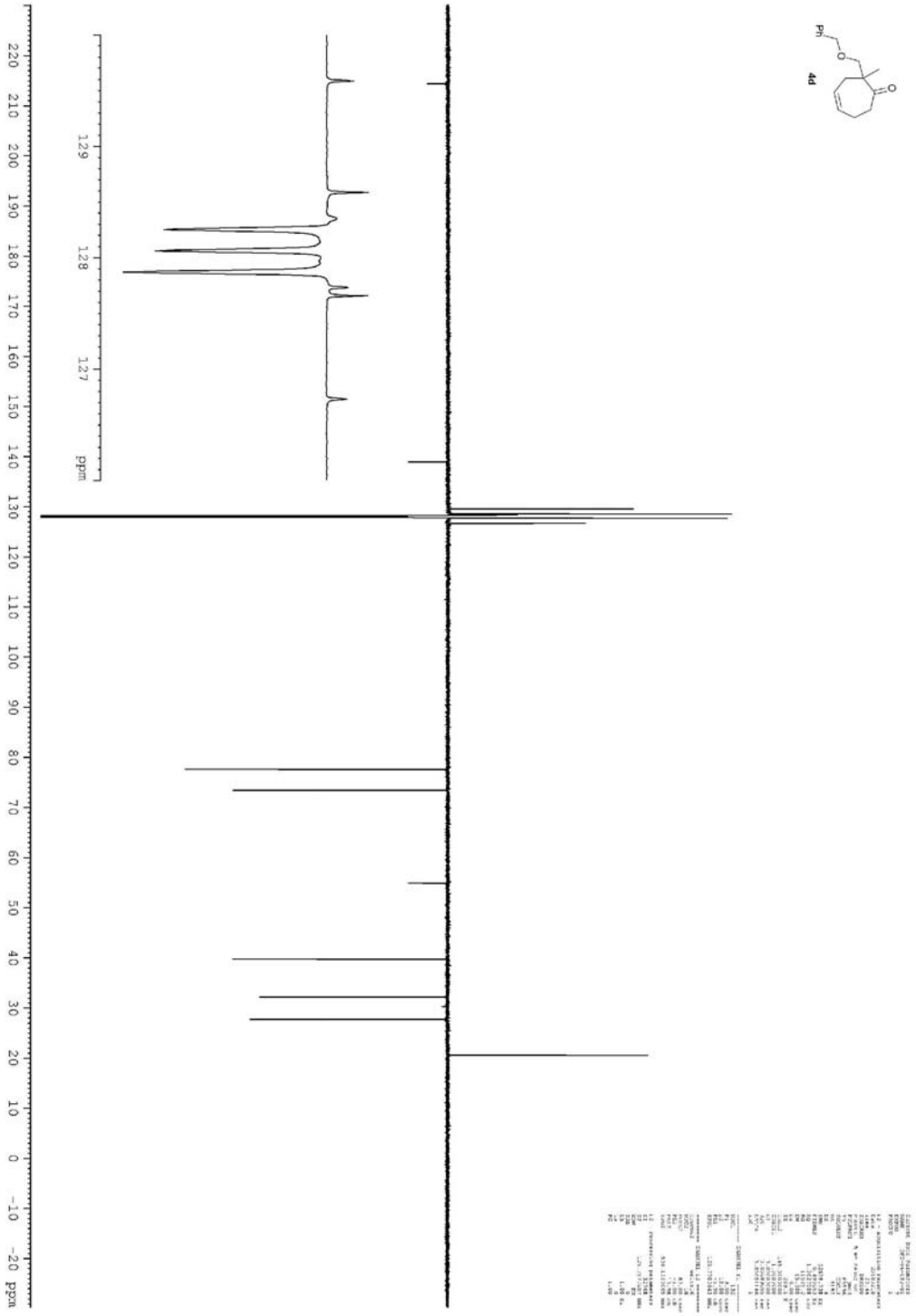
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O
4d
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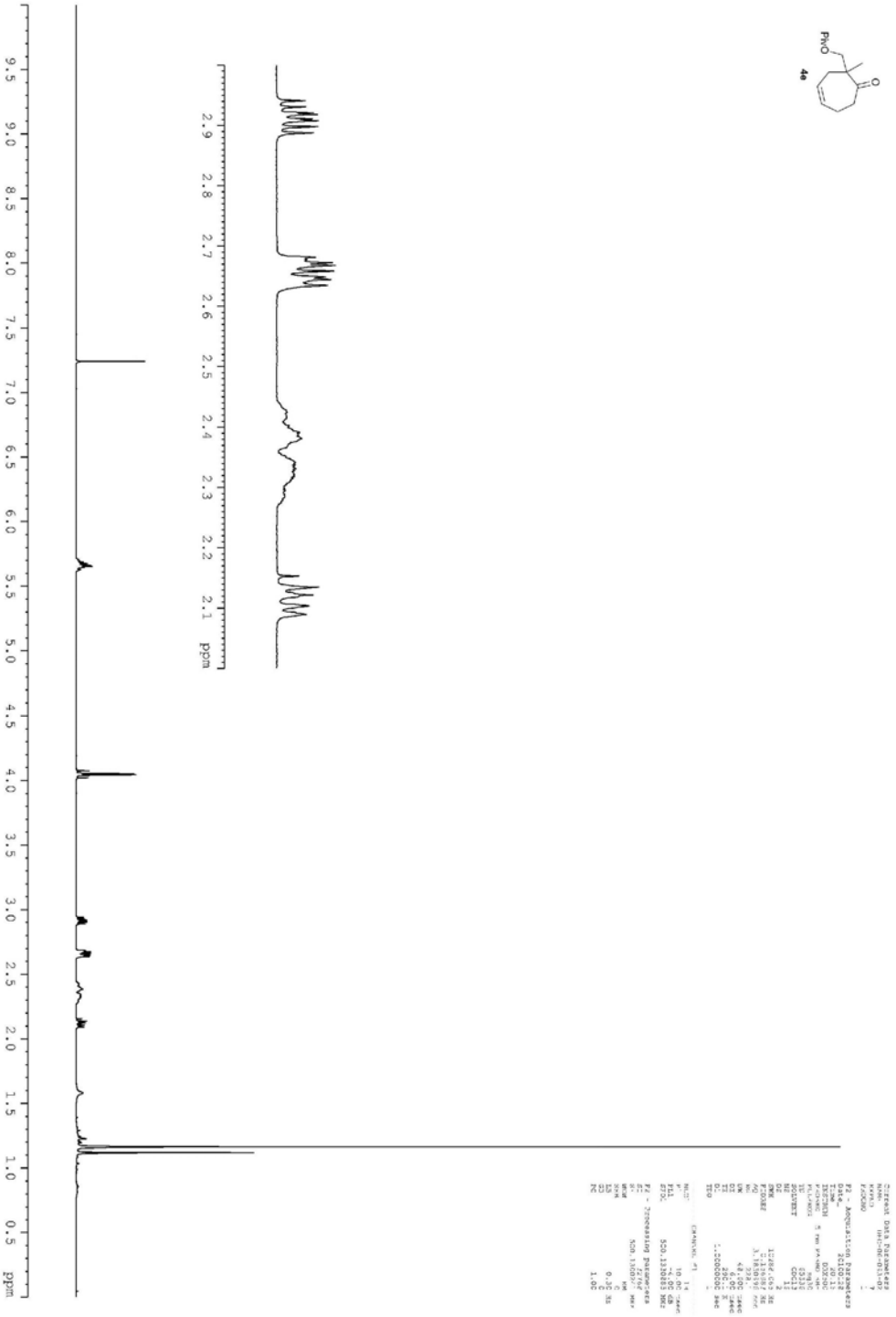
127
ppm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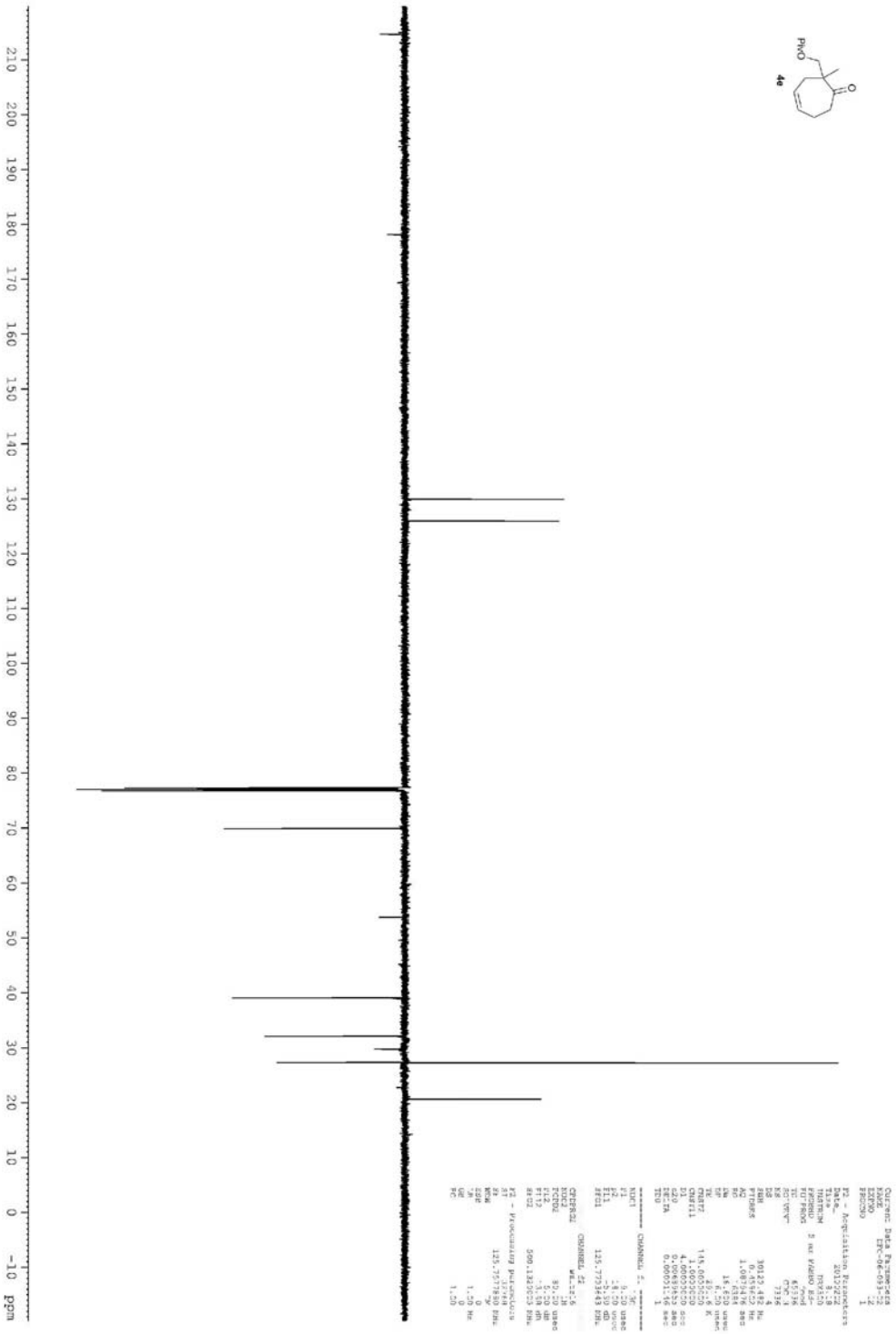
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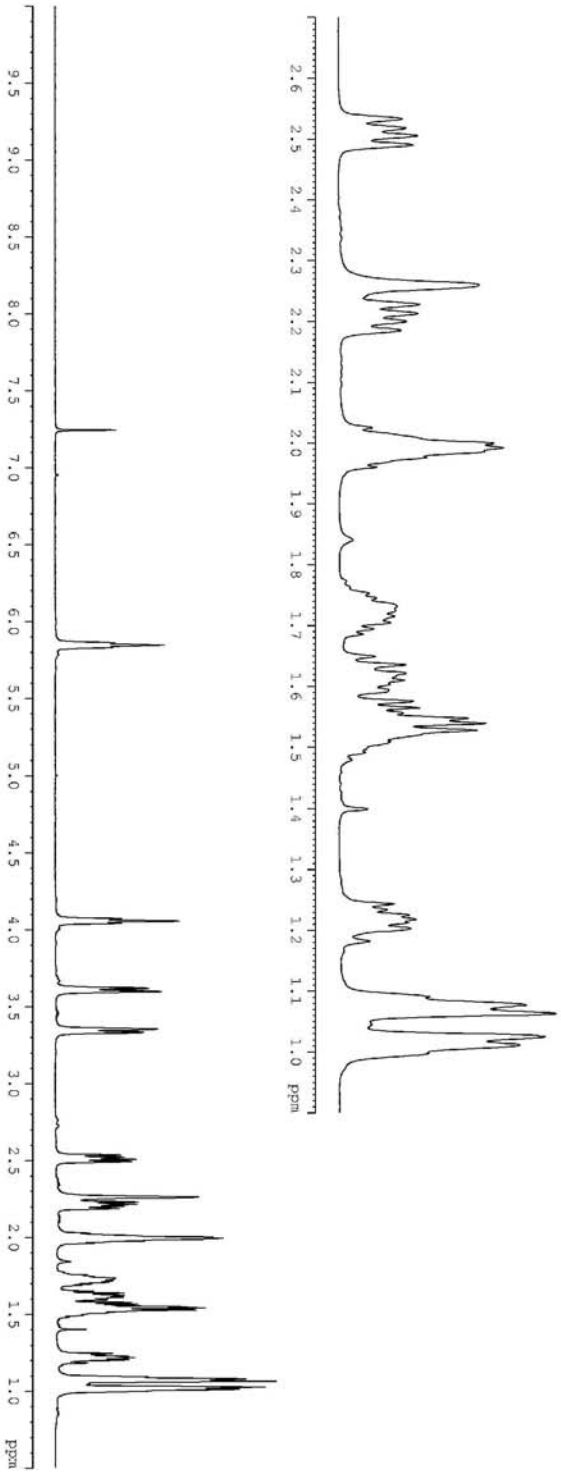

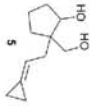

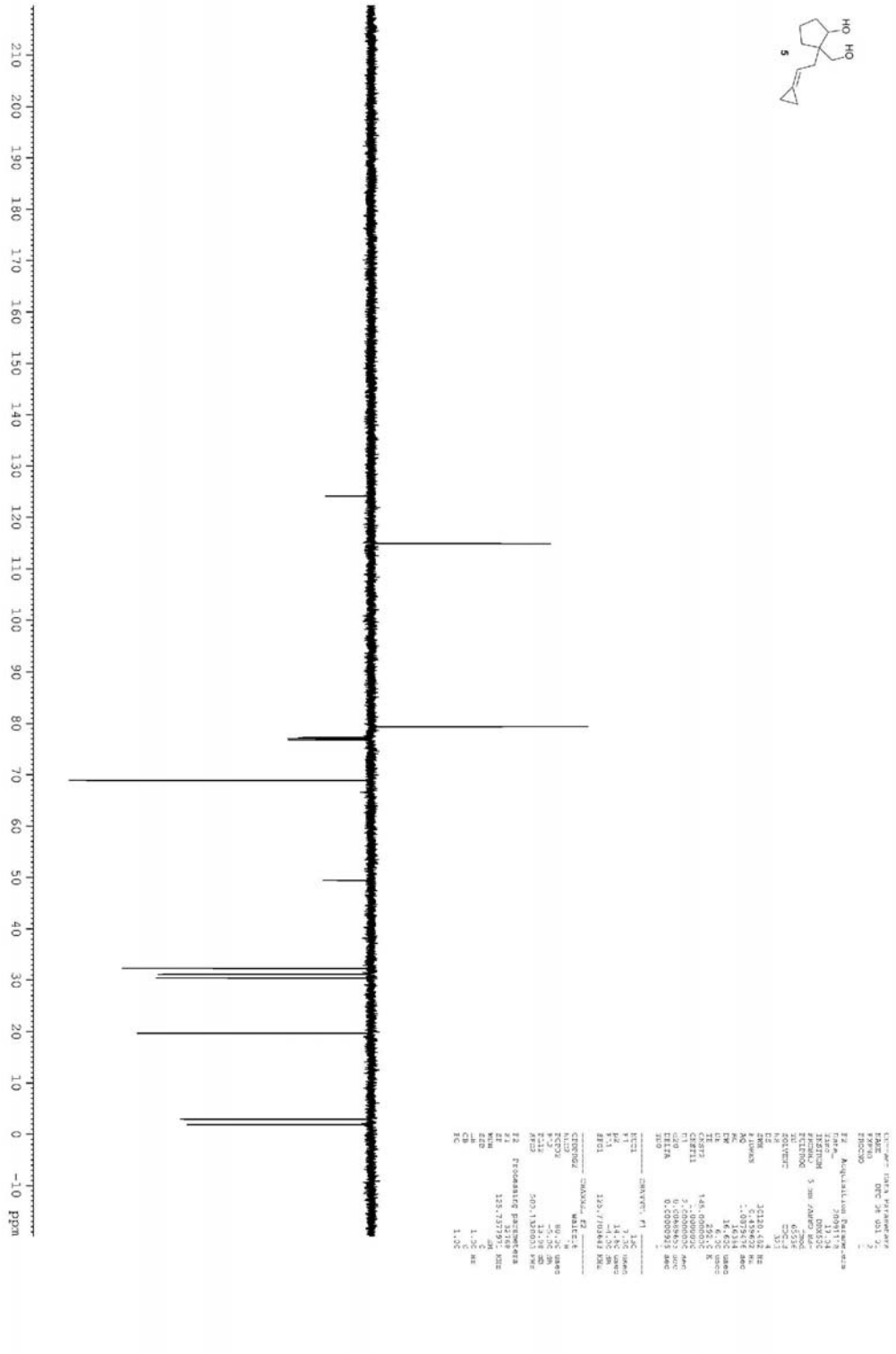
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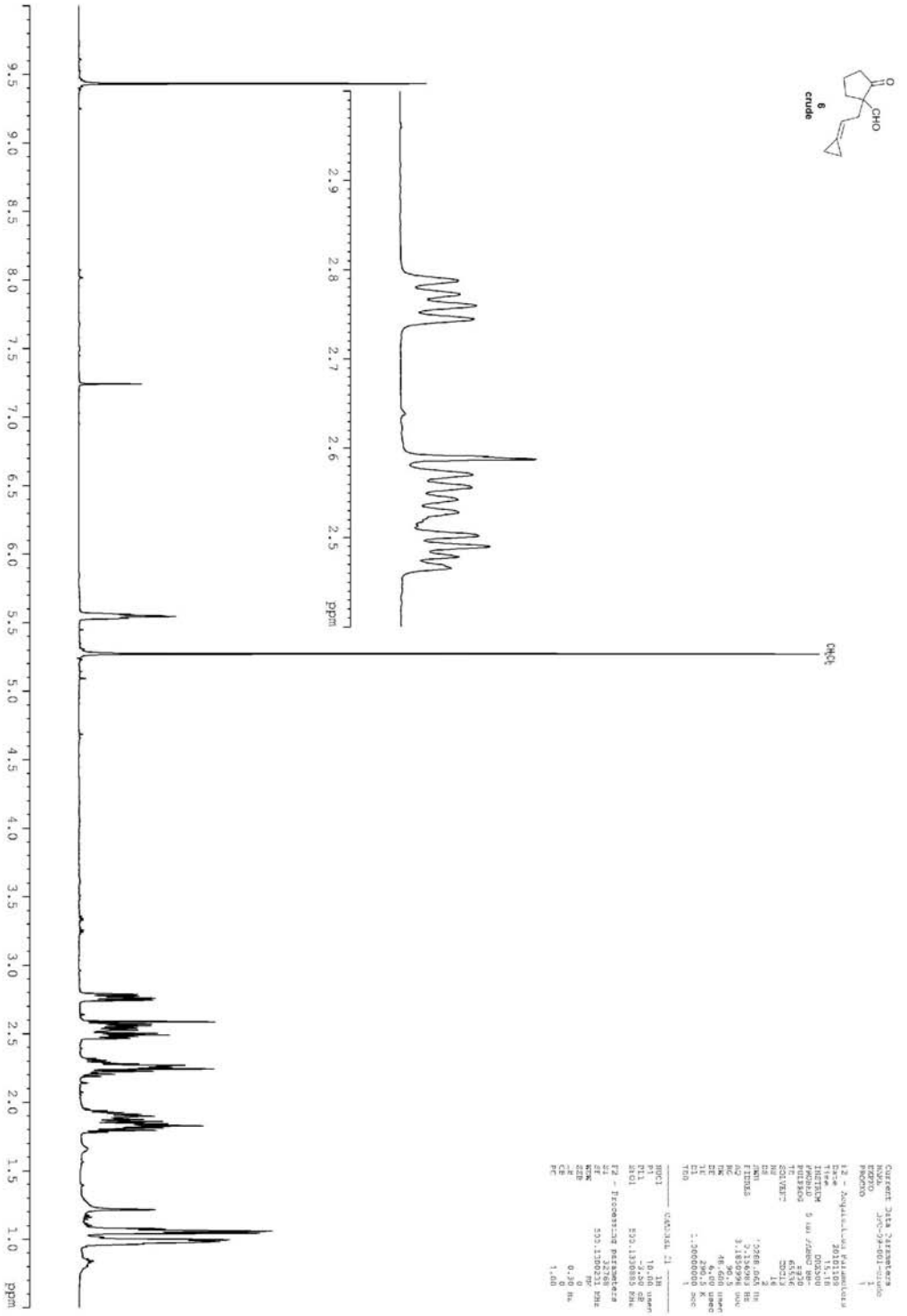
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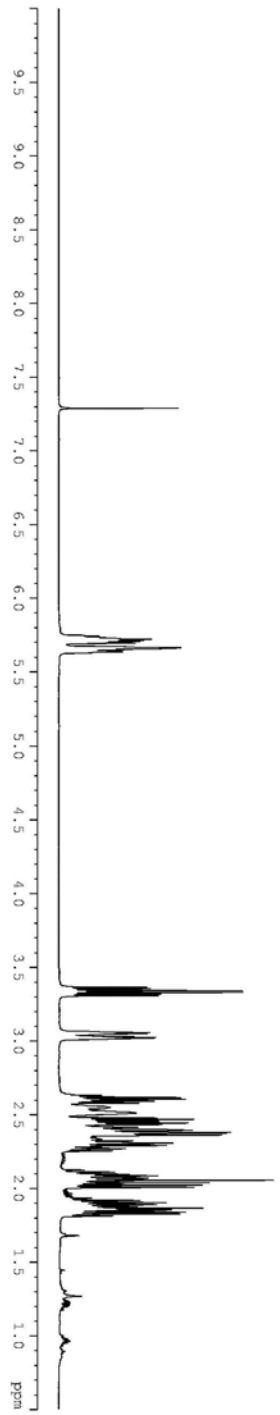
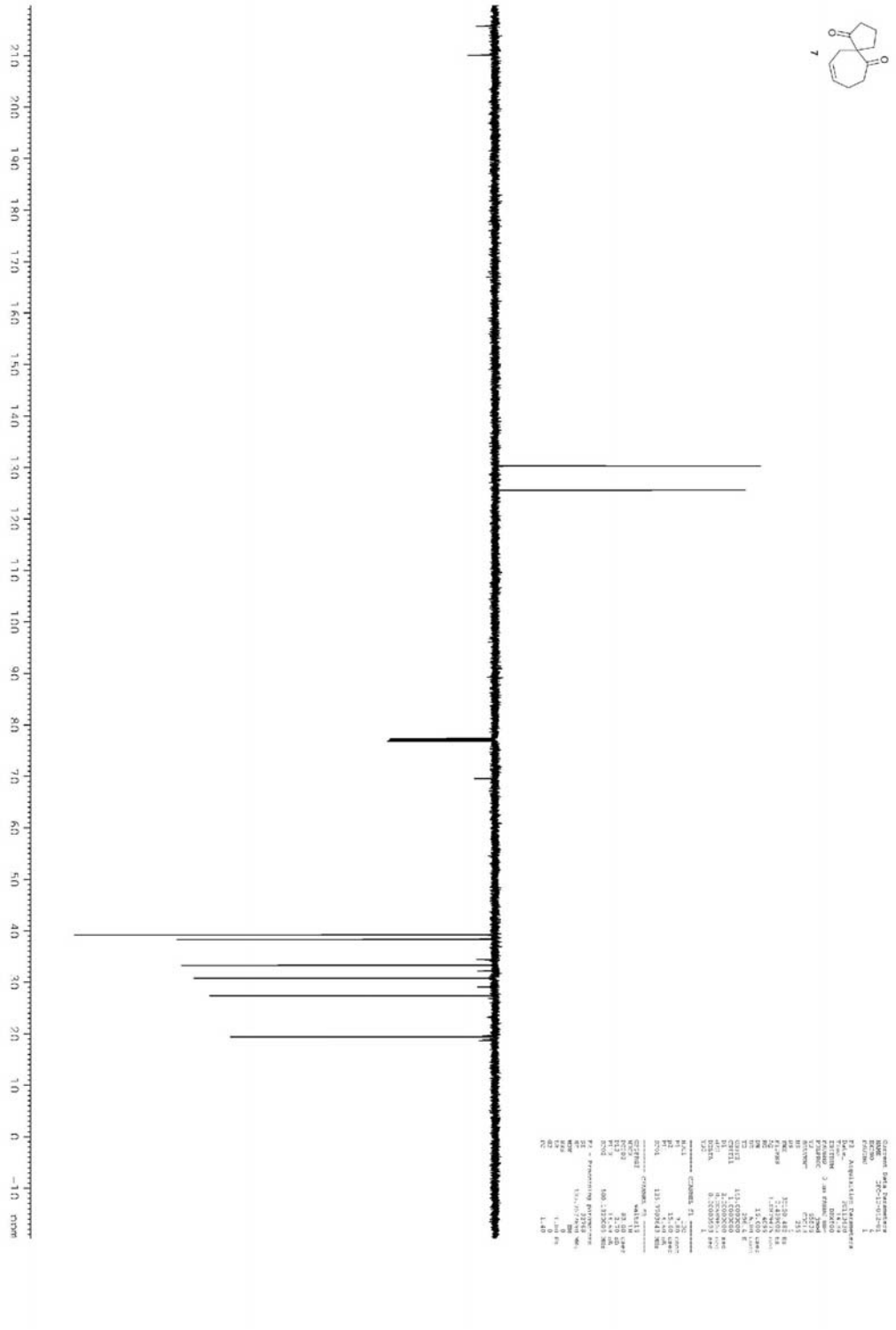
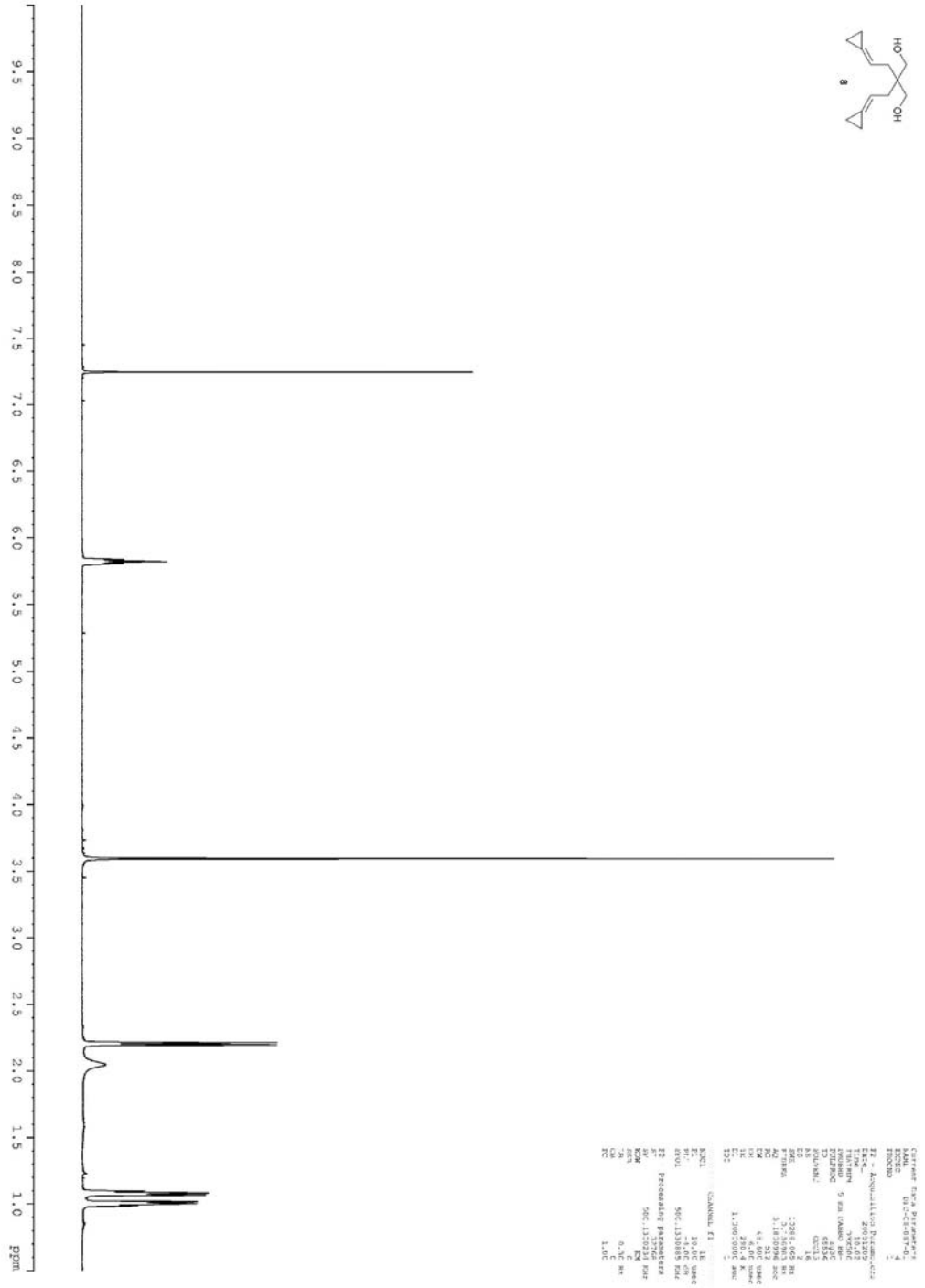
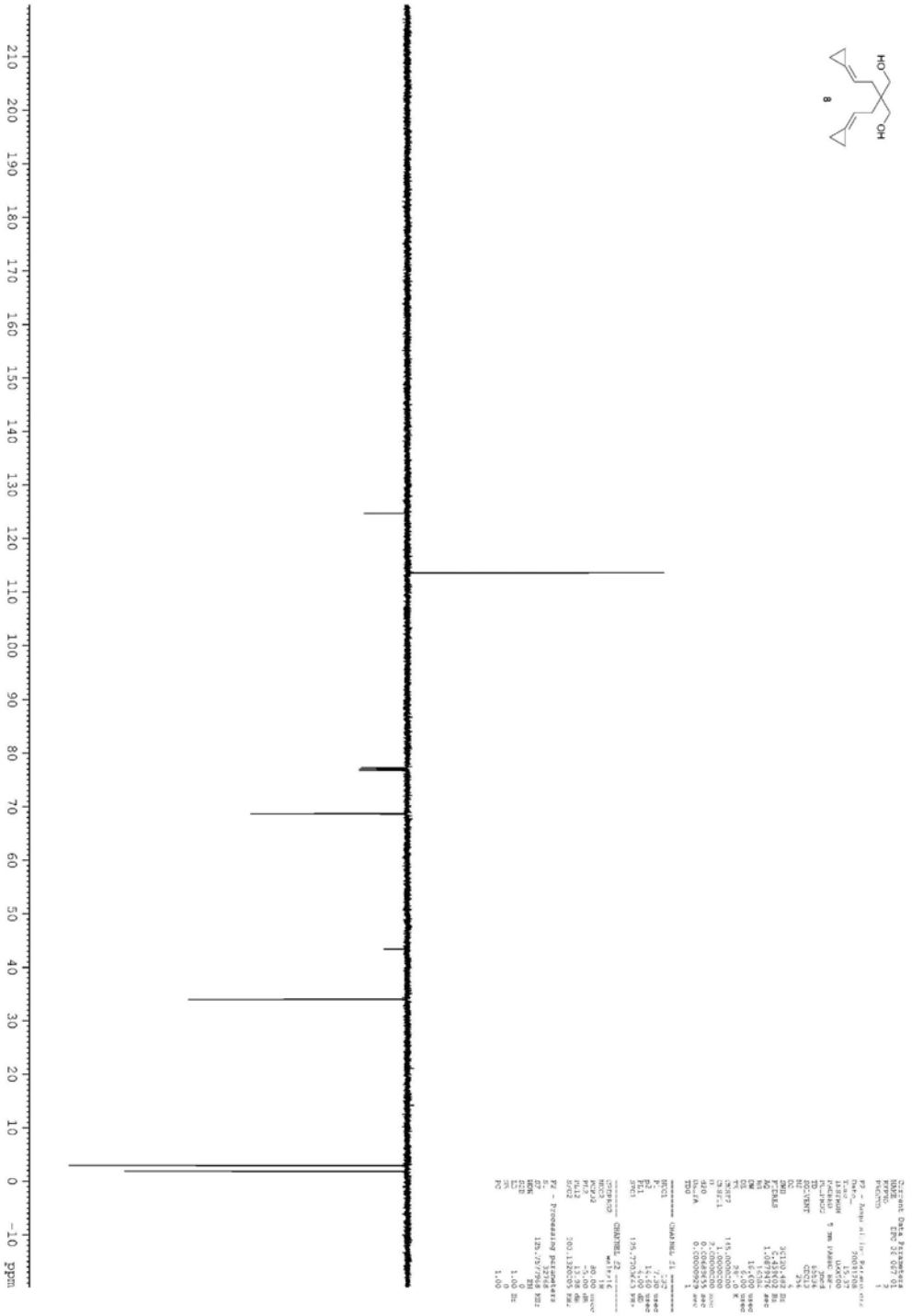
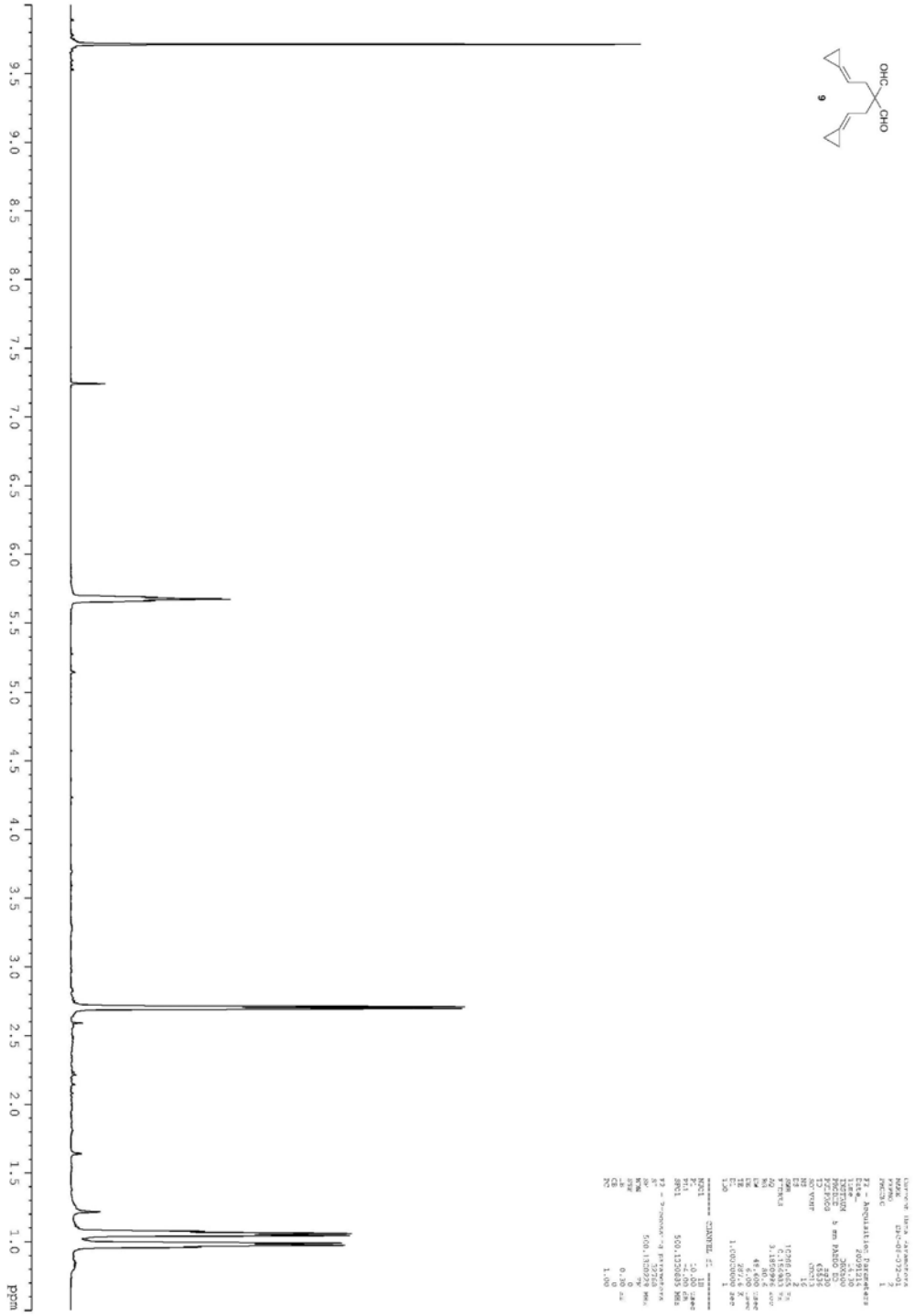
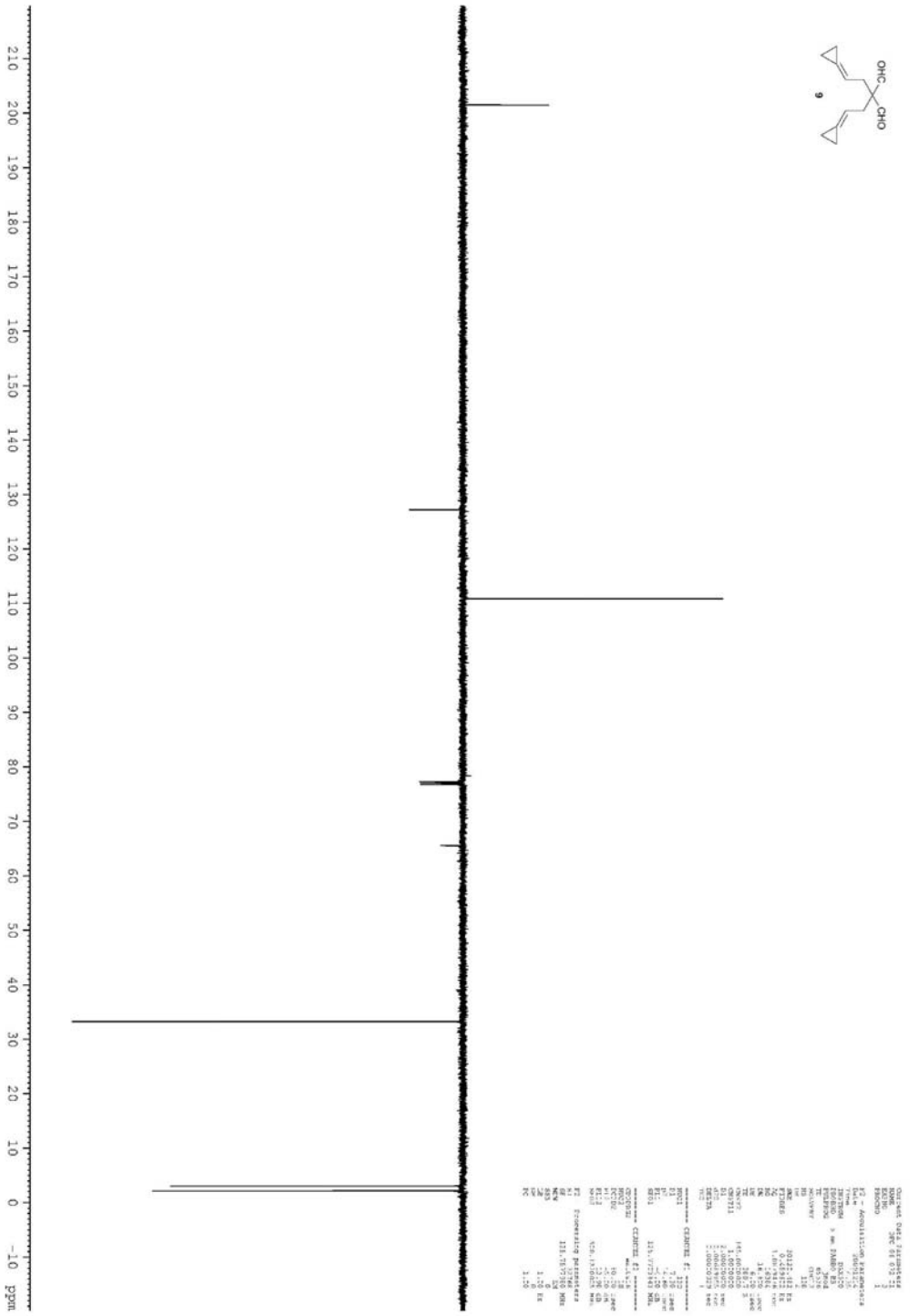


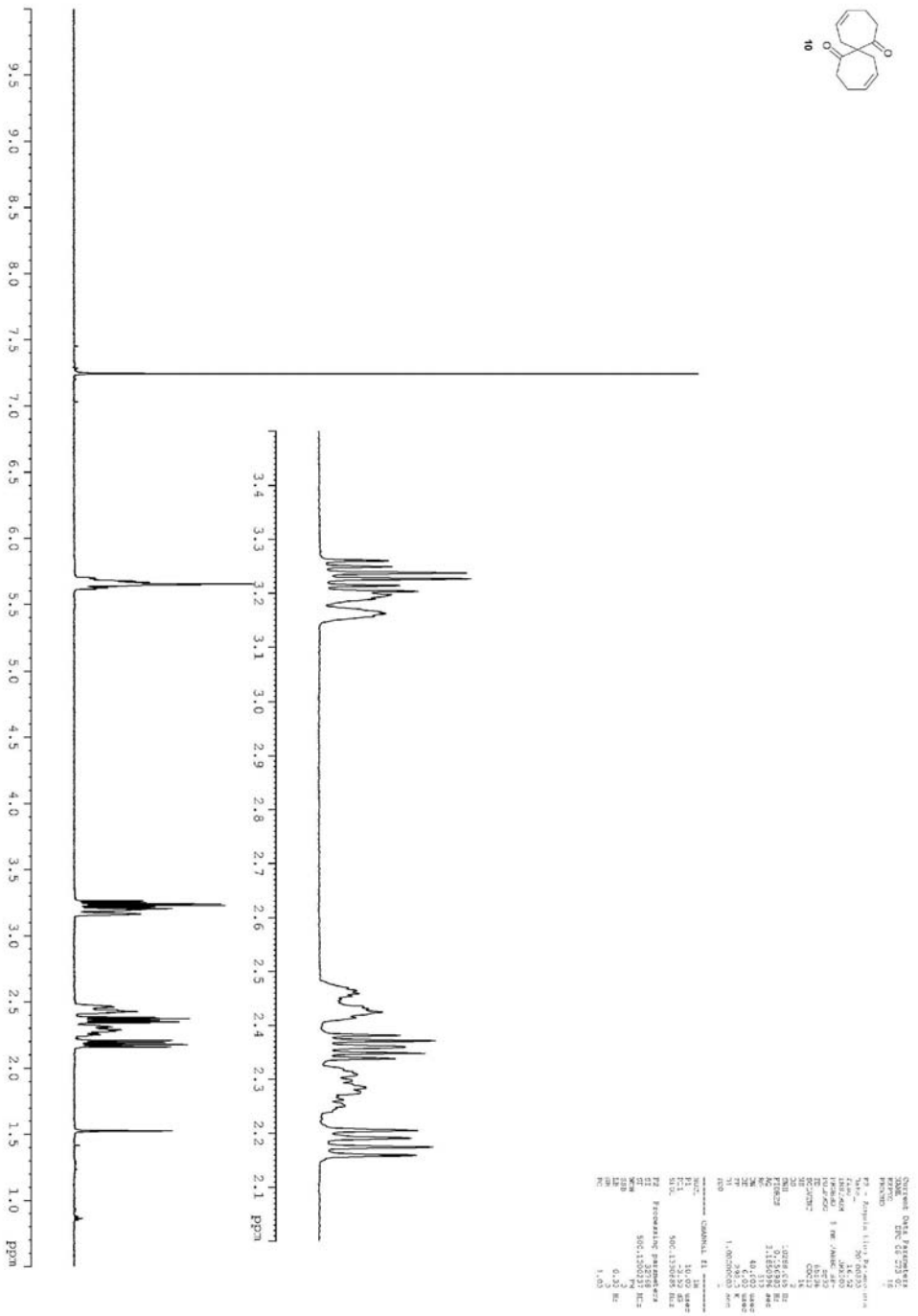


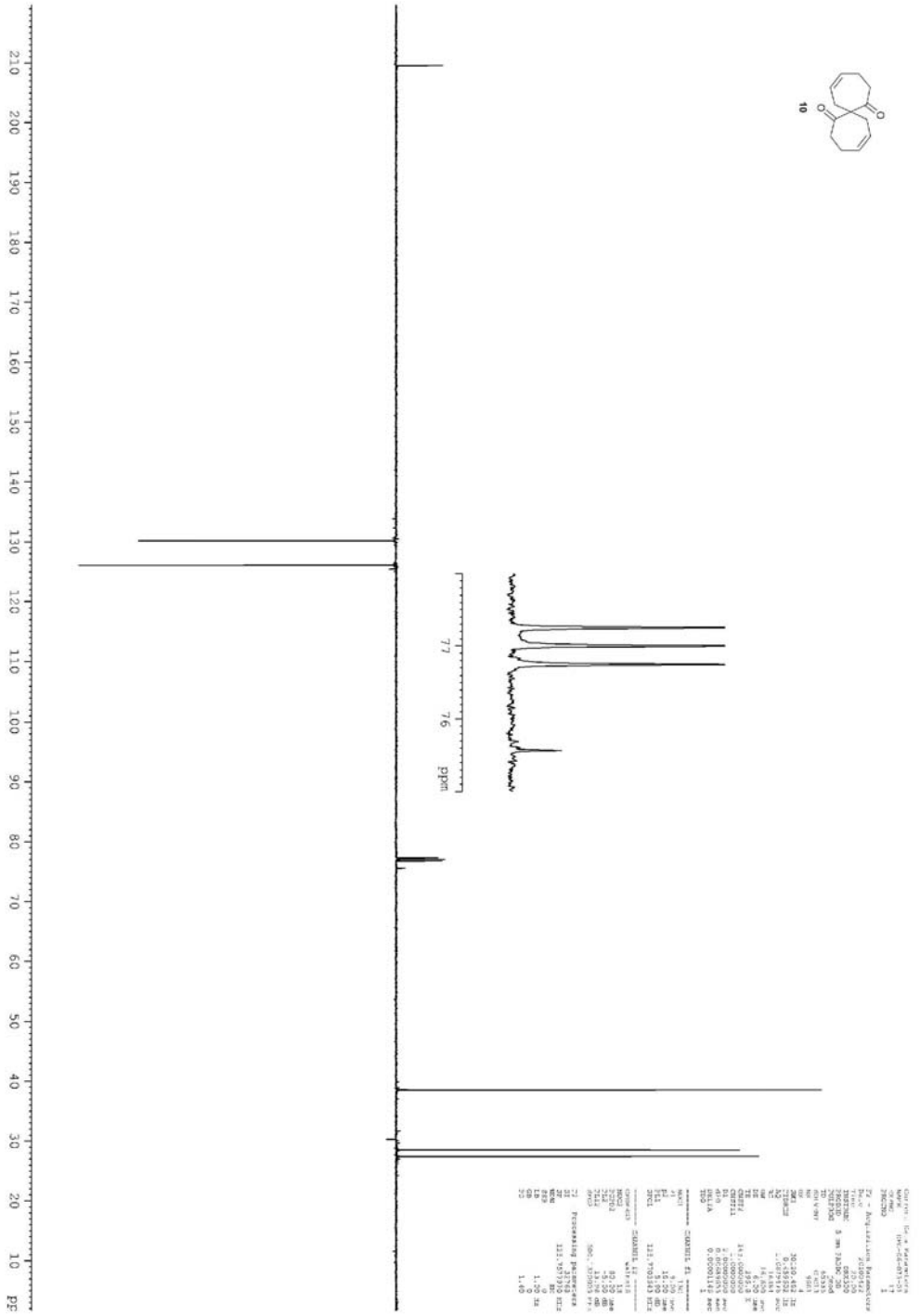

HO
OH
8
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

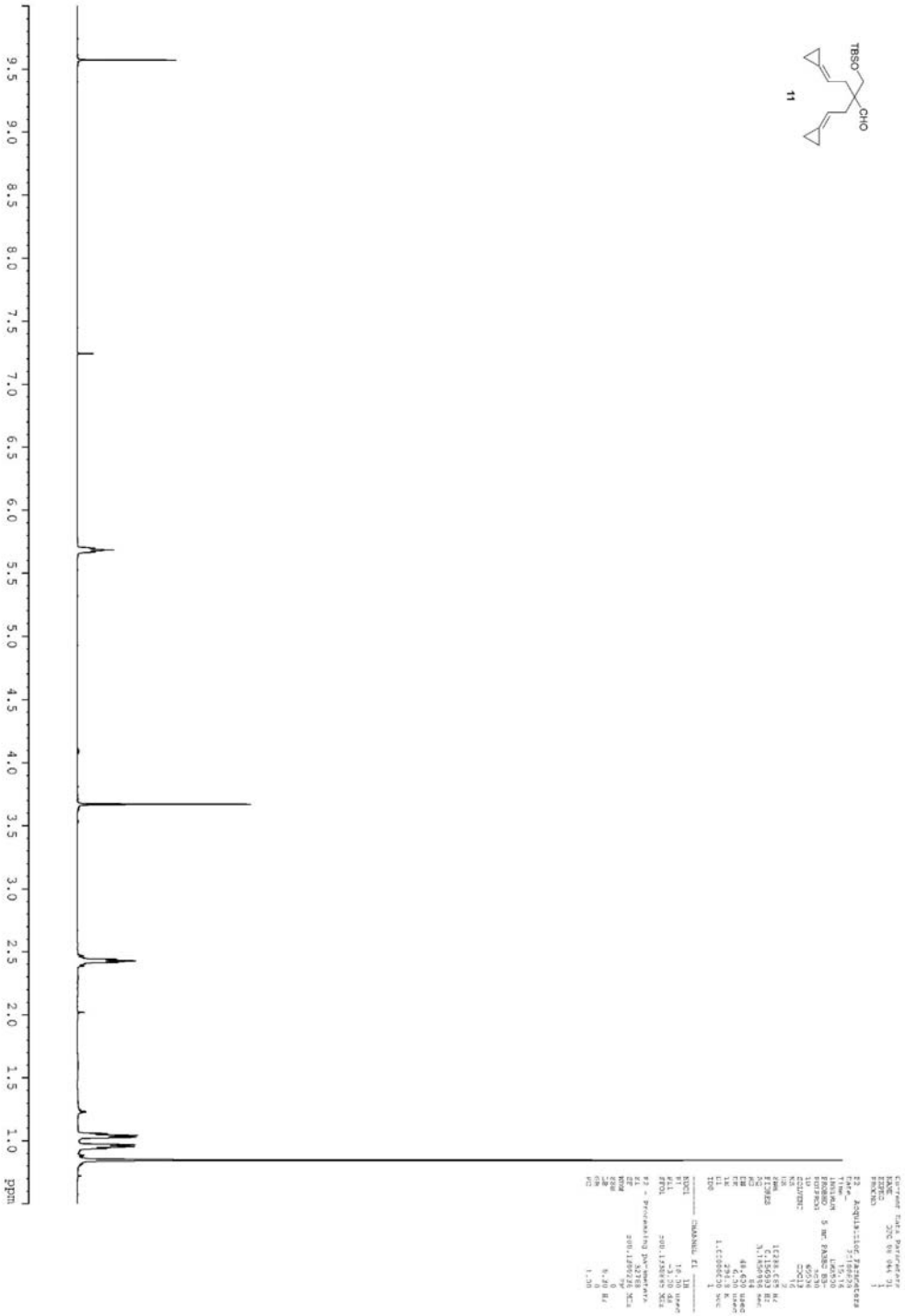

HO
OH
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

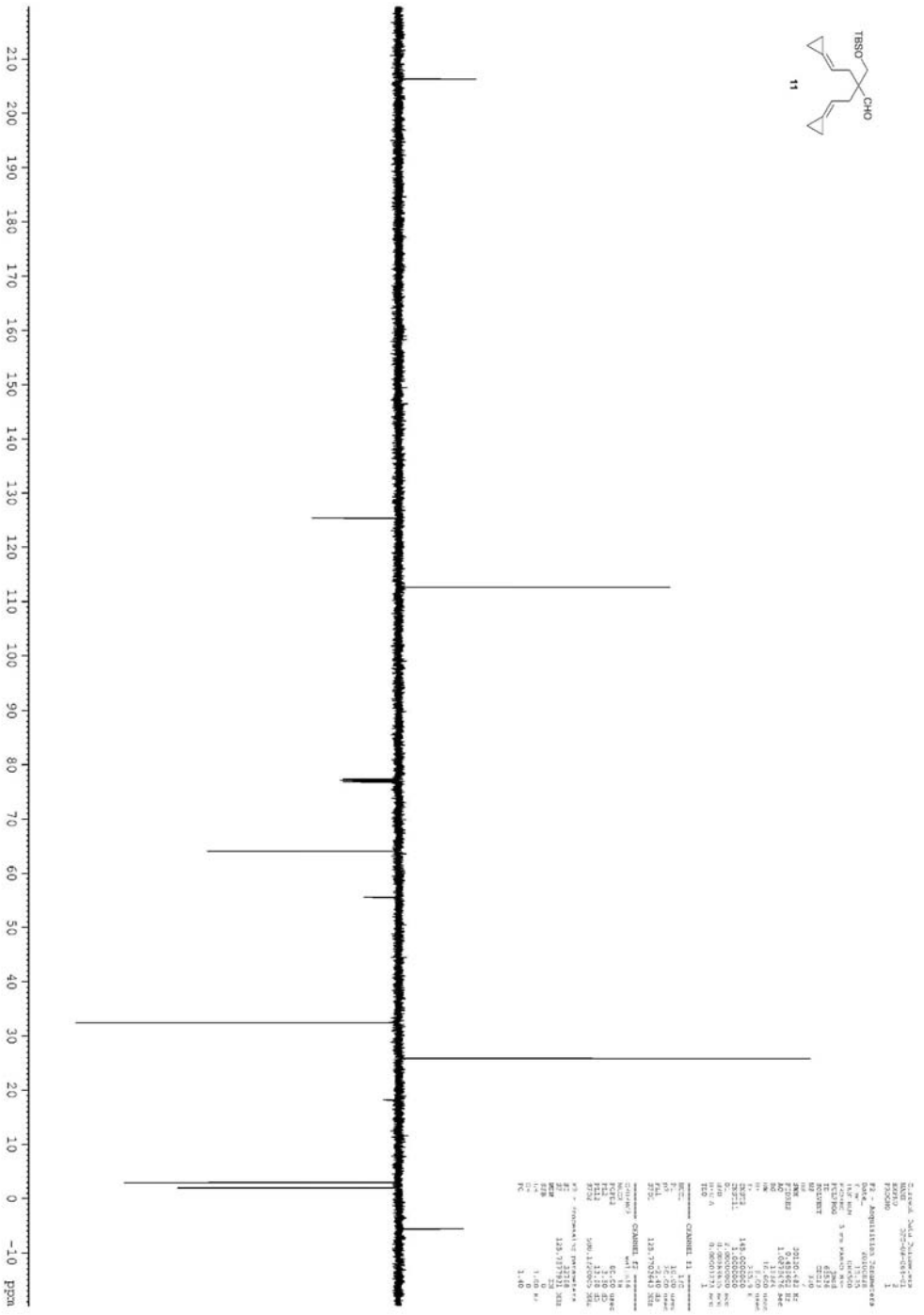

OHC
CHO
9
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

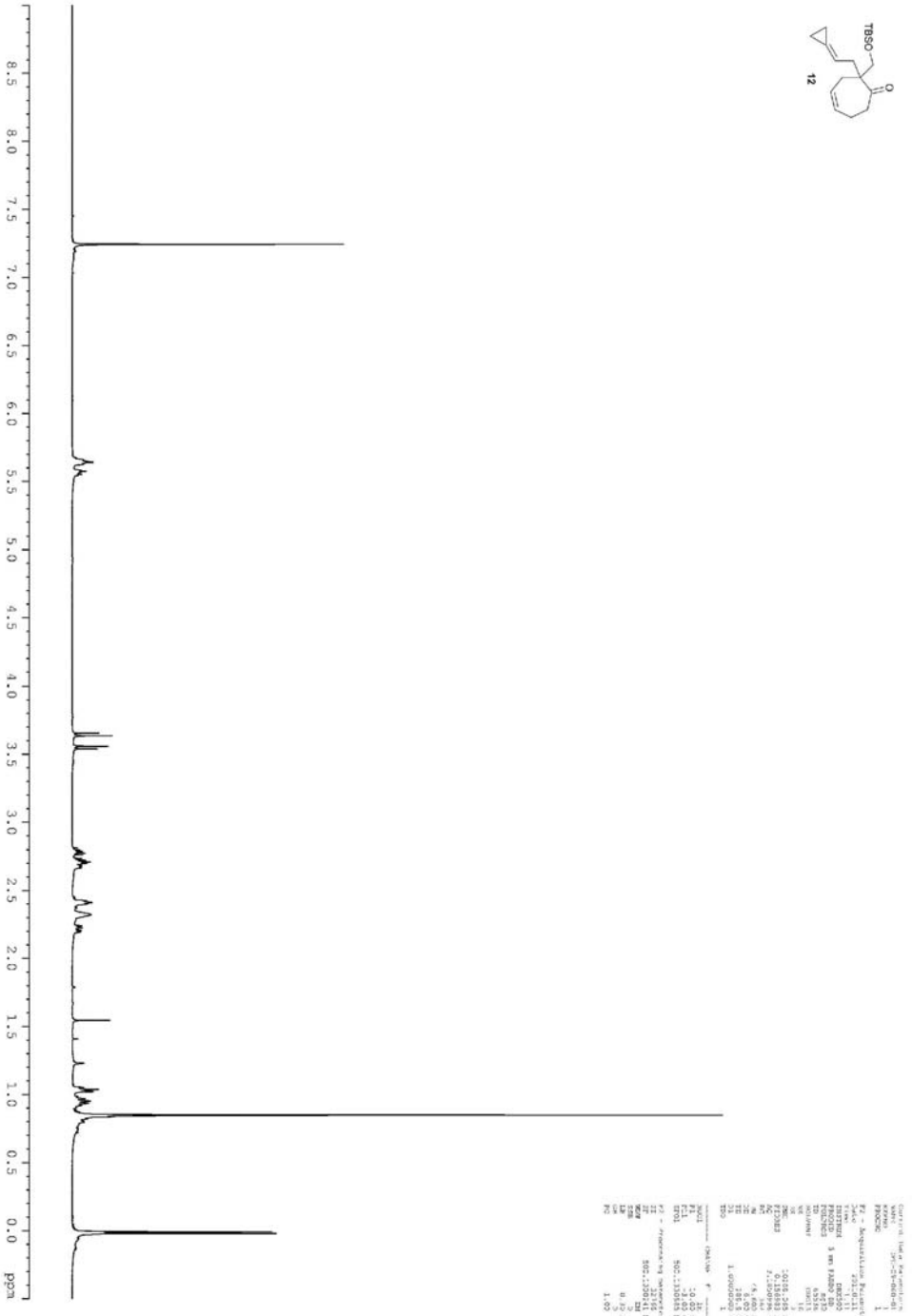

OHC
CHO
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

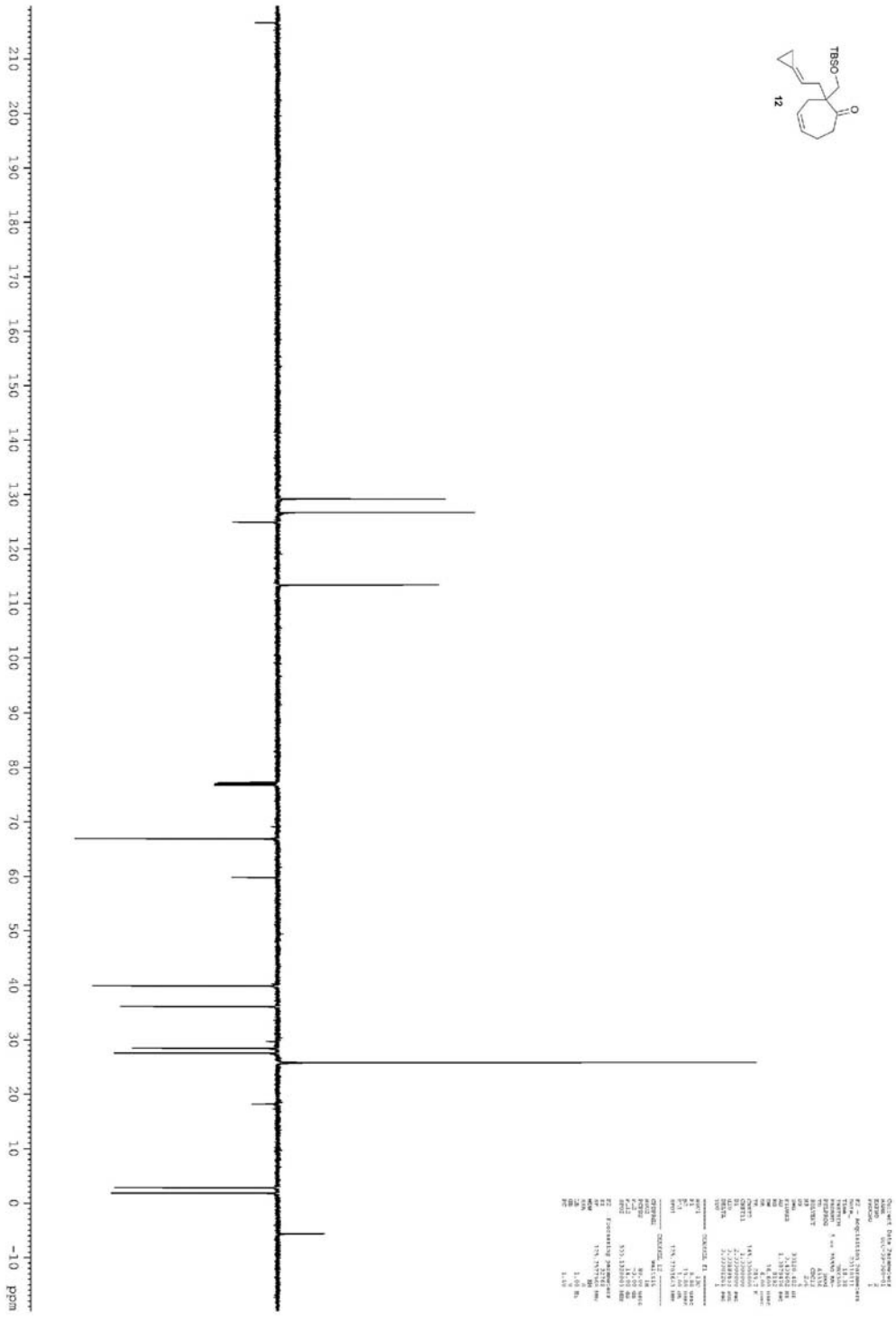

10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 ppm

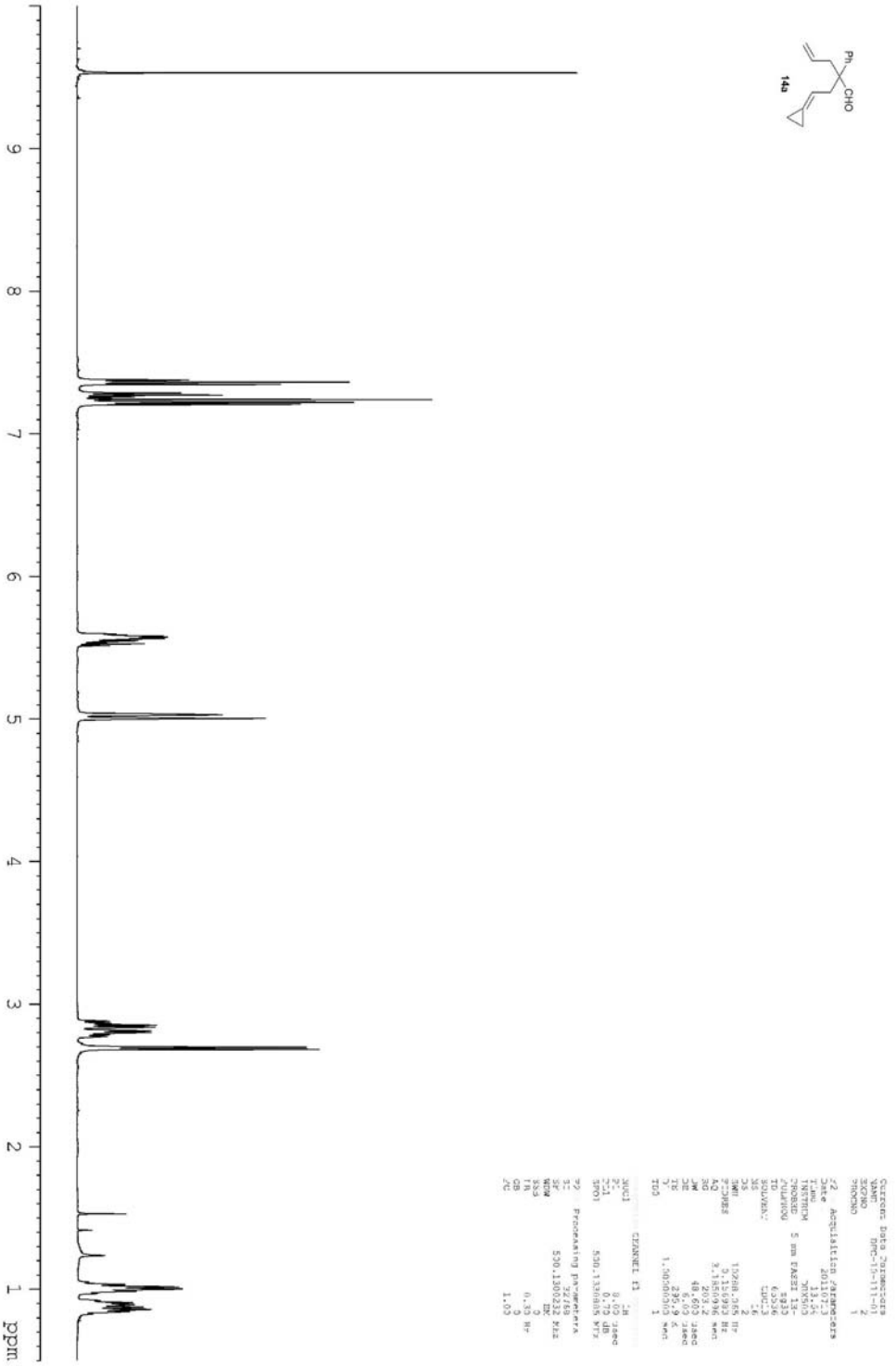

10
77
76
ppm

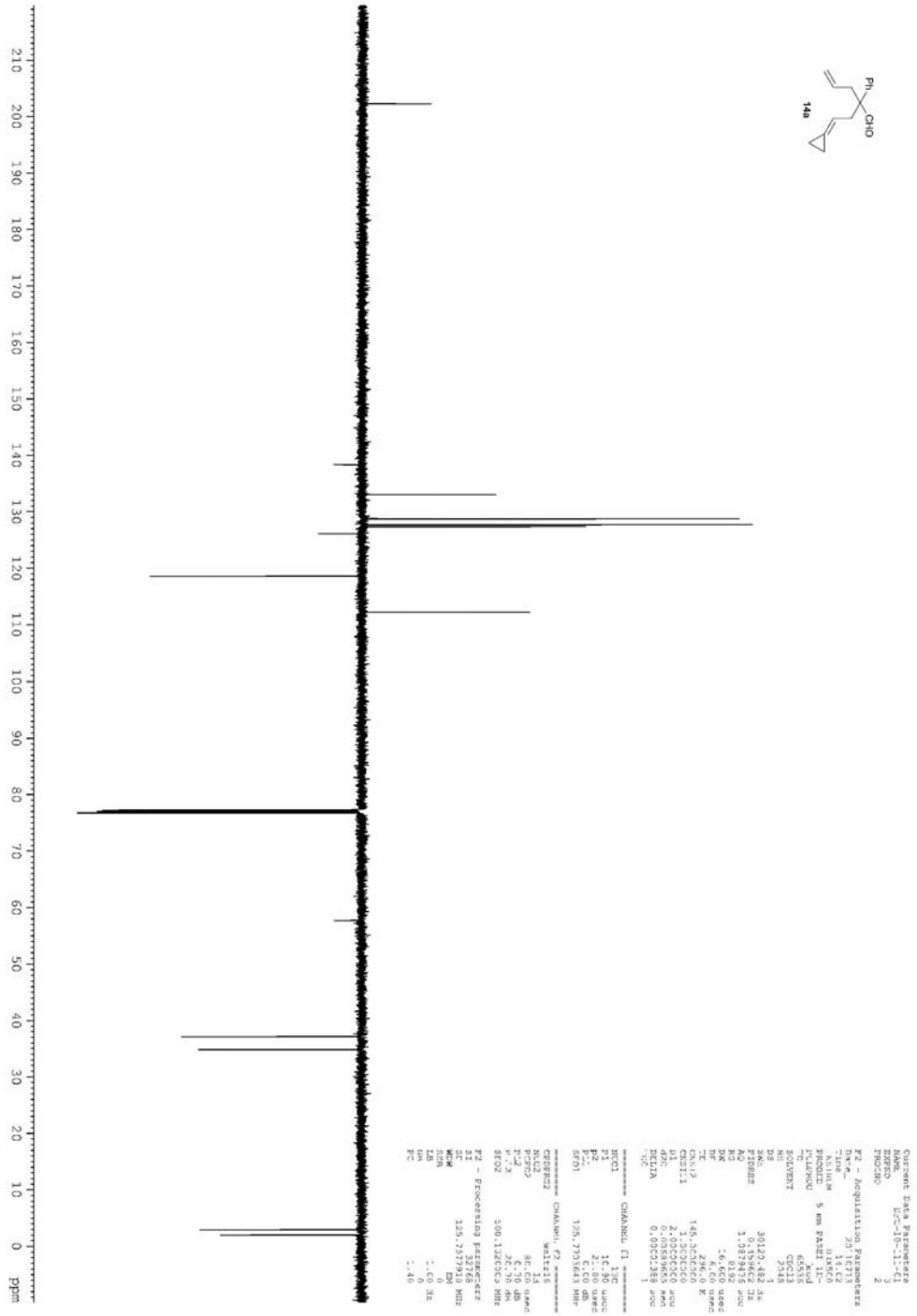

TBSO
CHO
11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

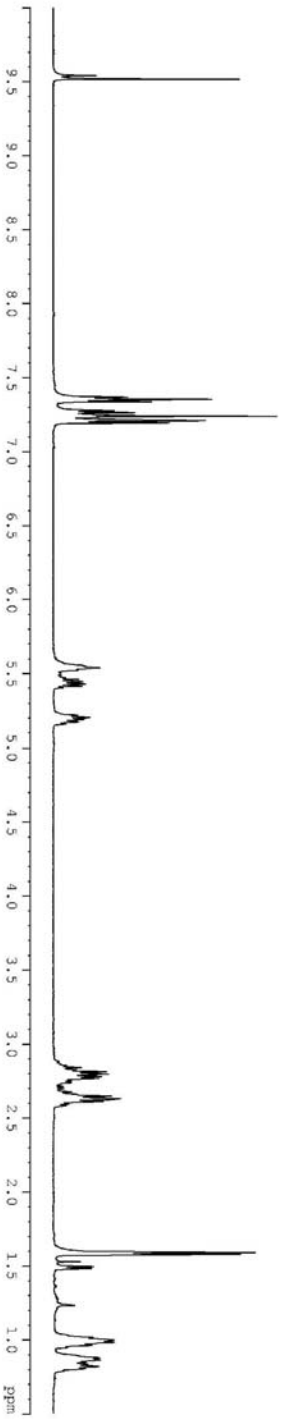

TBSO
CHO
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

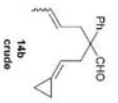

TBSO
O
12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


TBSO
O
12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

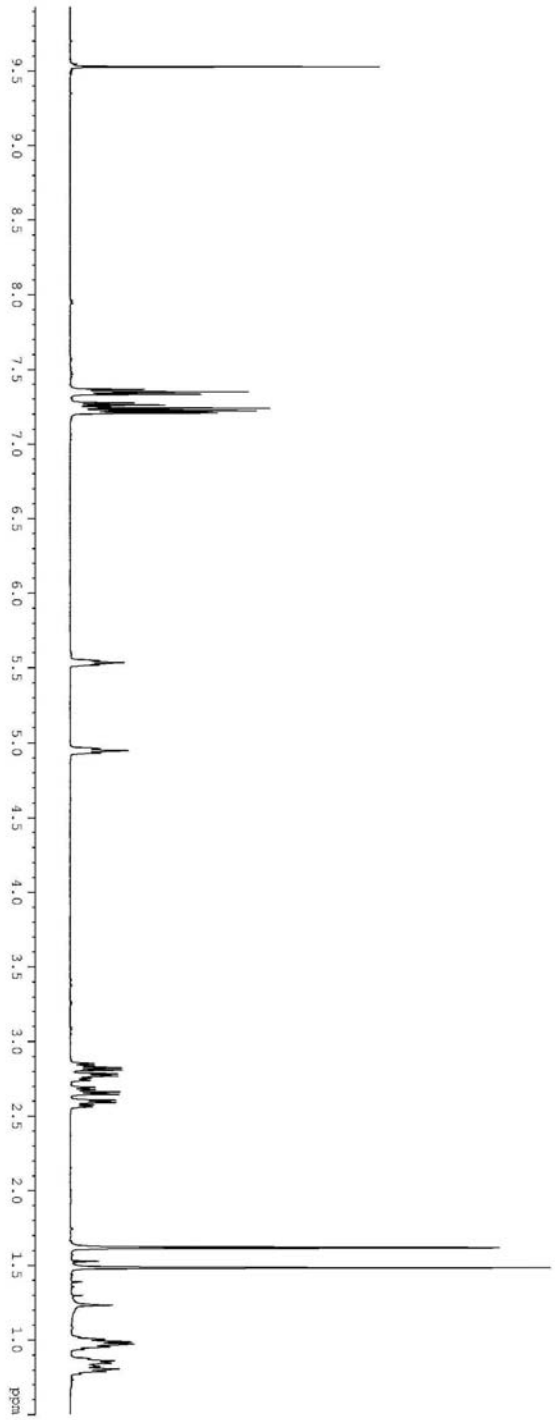

Ph
CHO
14a
ppm
1
2
3
4
5
6
7
8
9

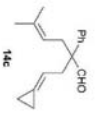

Ph
CHO
14a
ppm

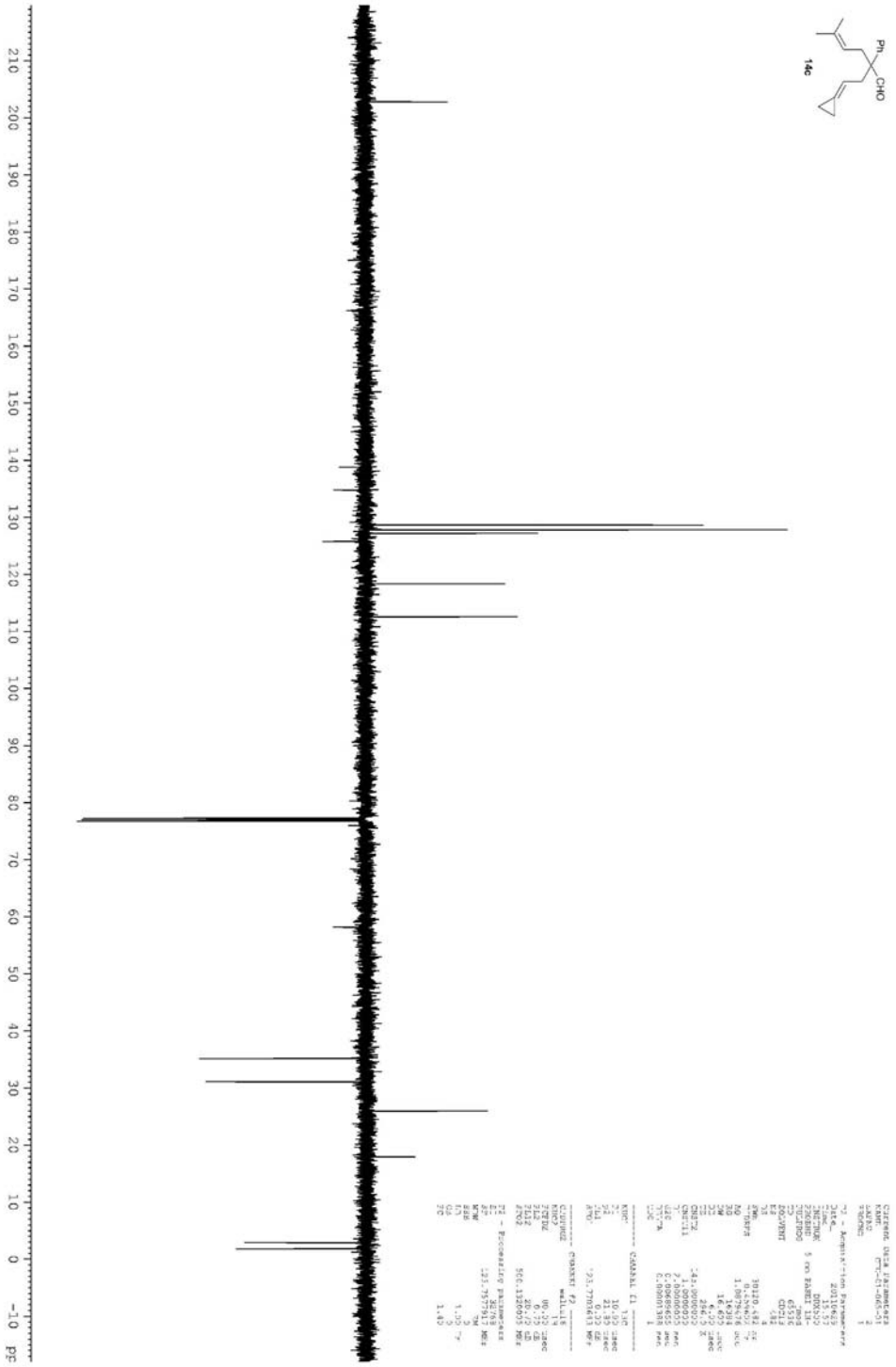


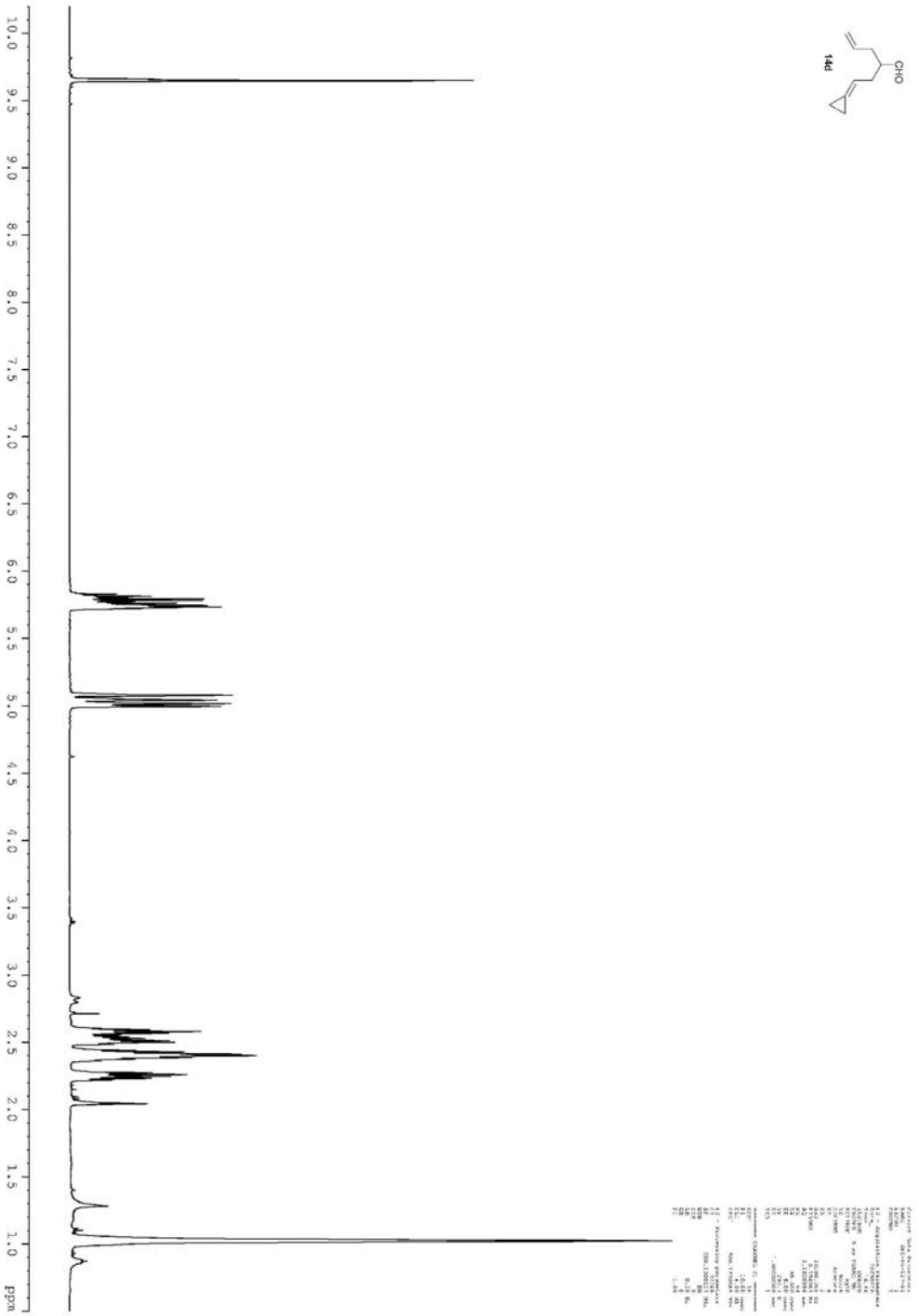


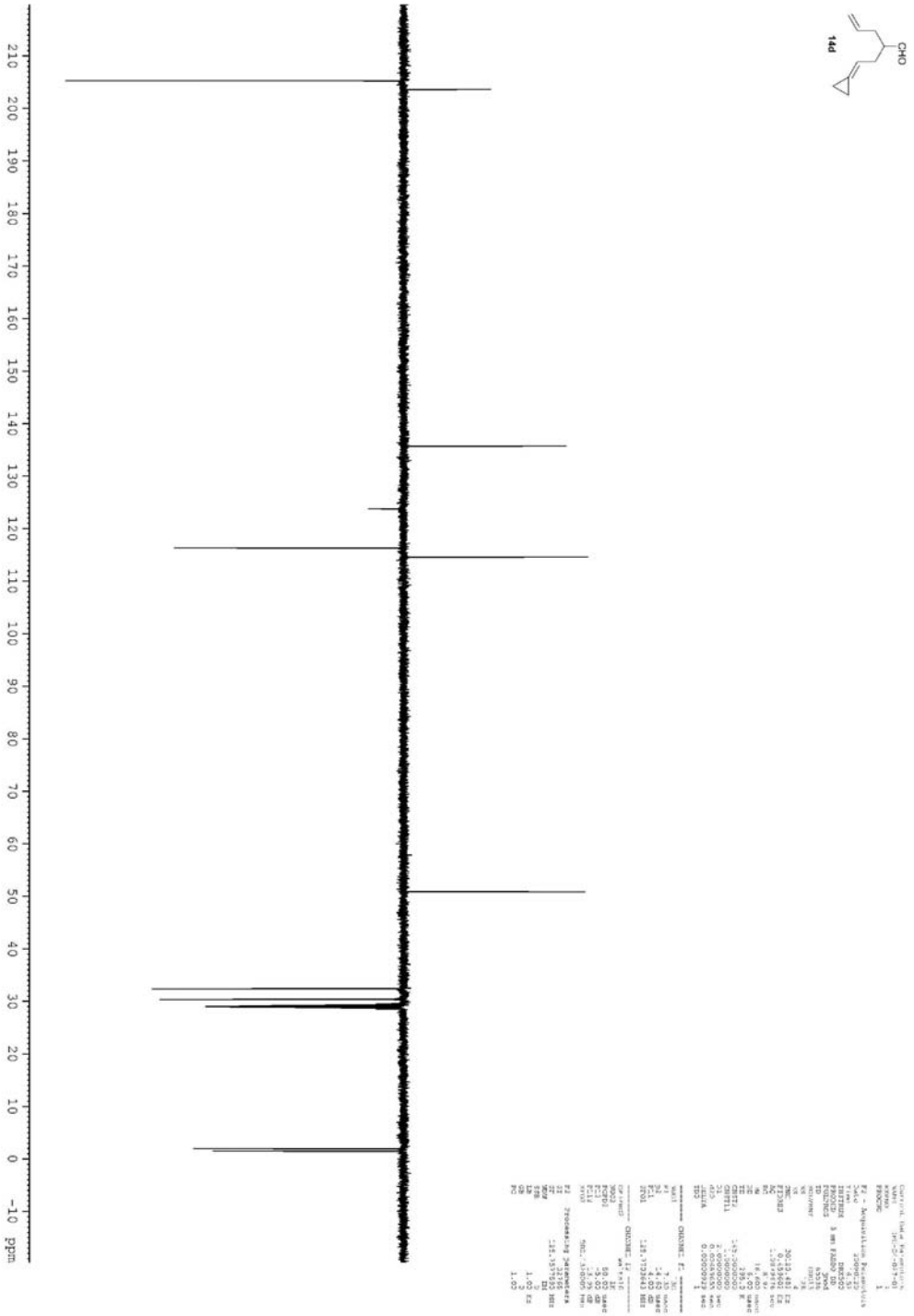
14b
crude

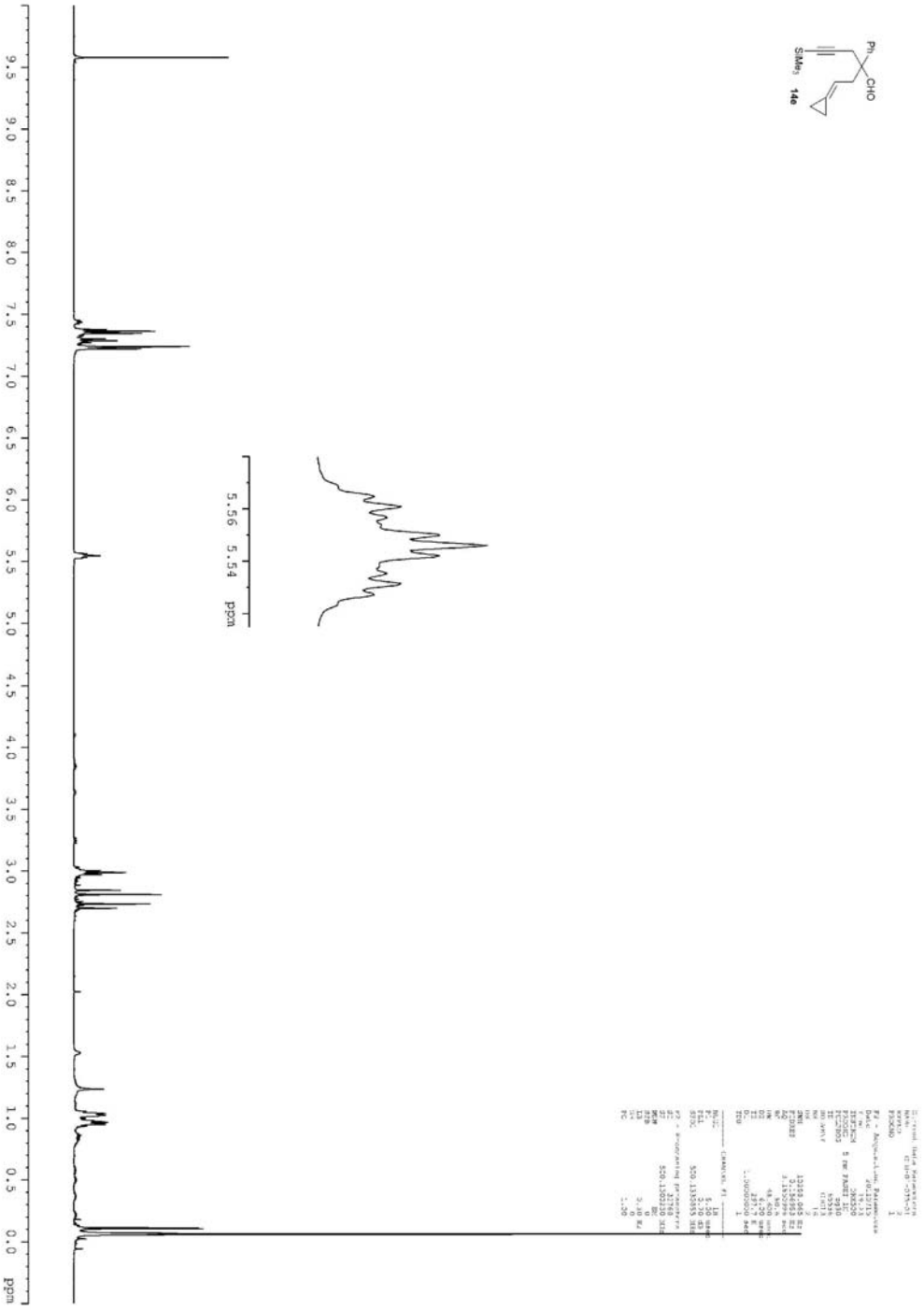

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

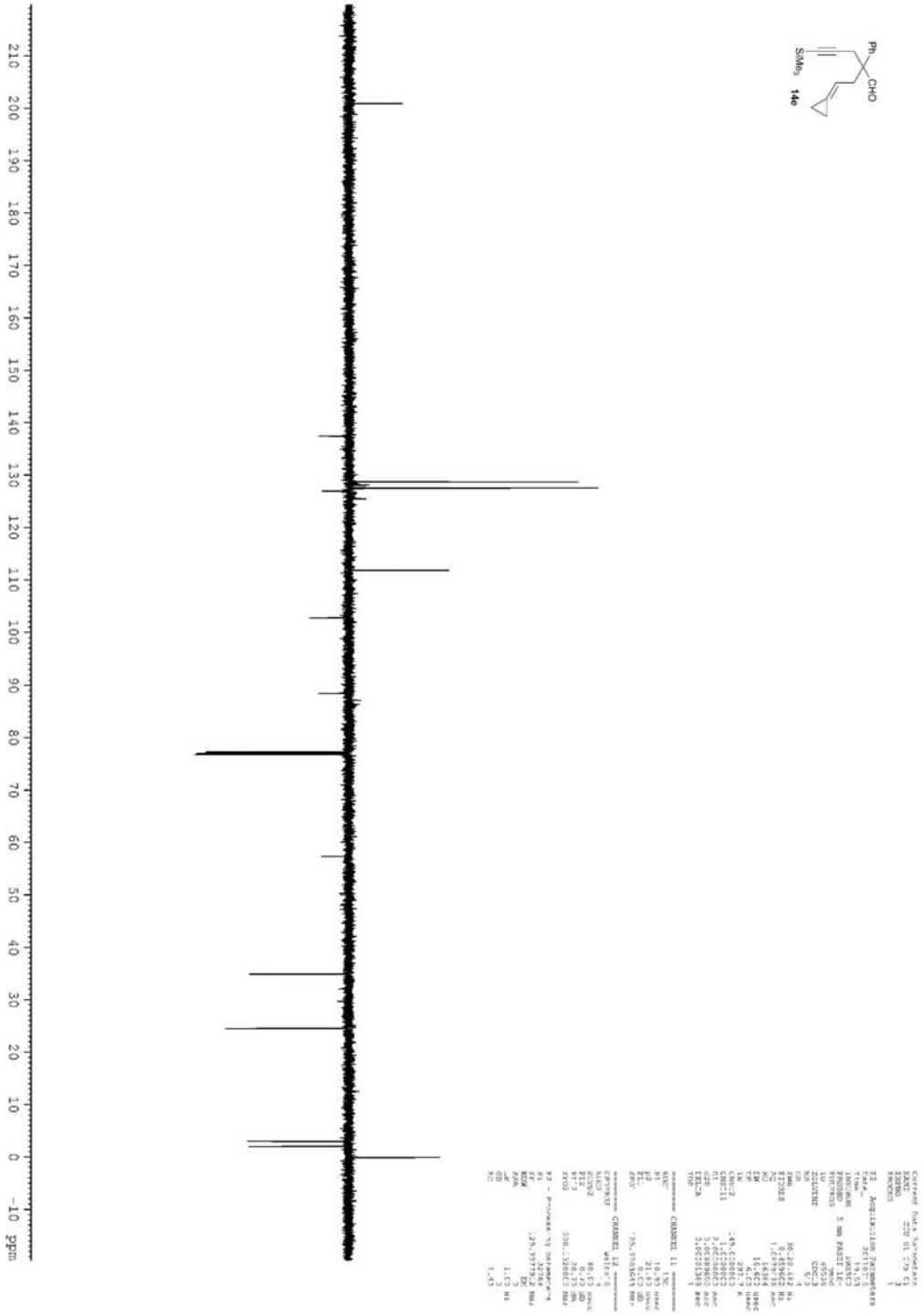

Ph
CHO
14c

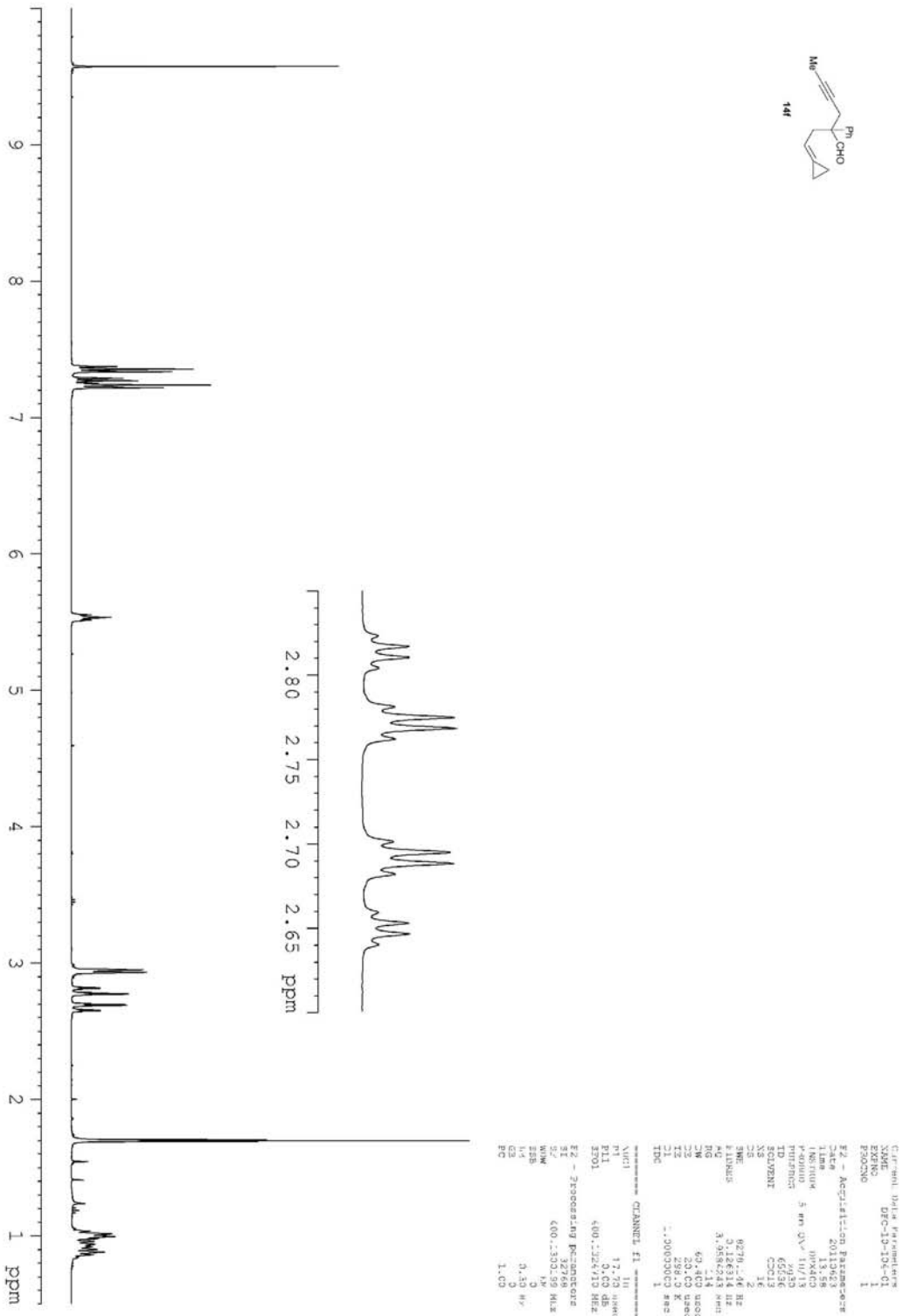

Ph
CHO
14c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

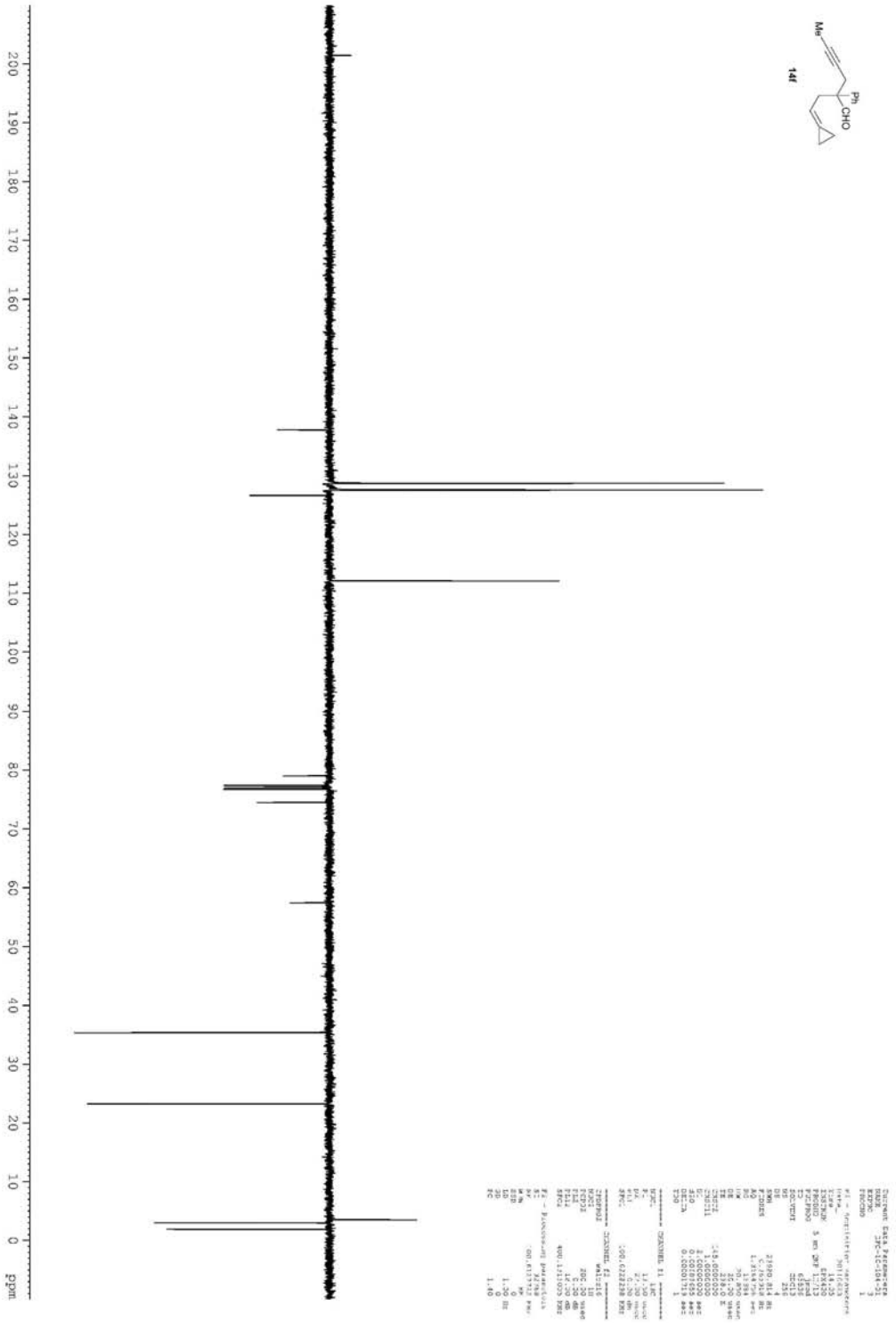

14d
CHO
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

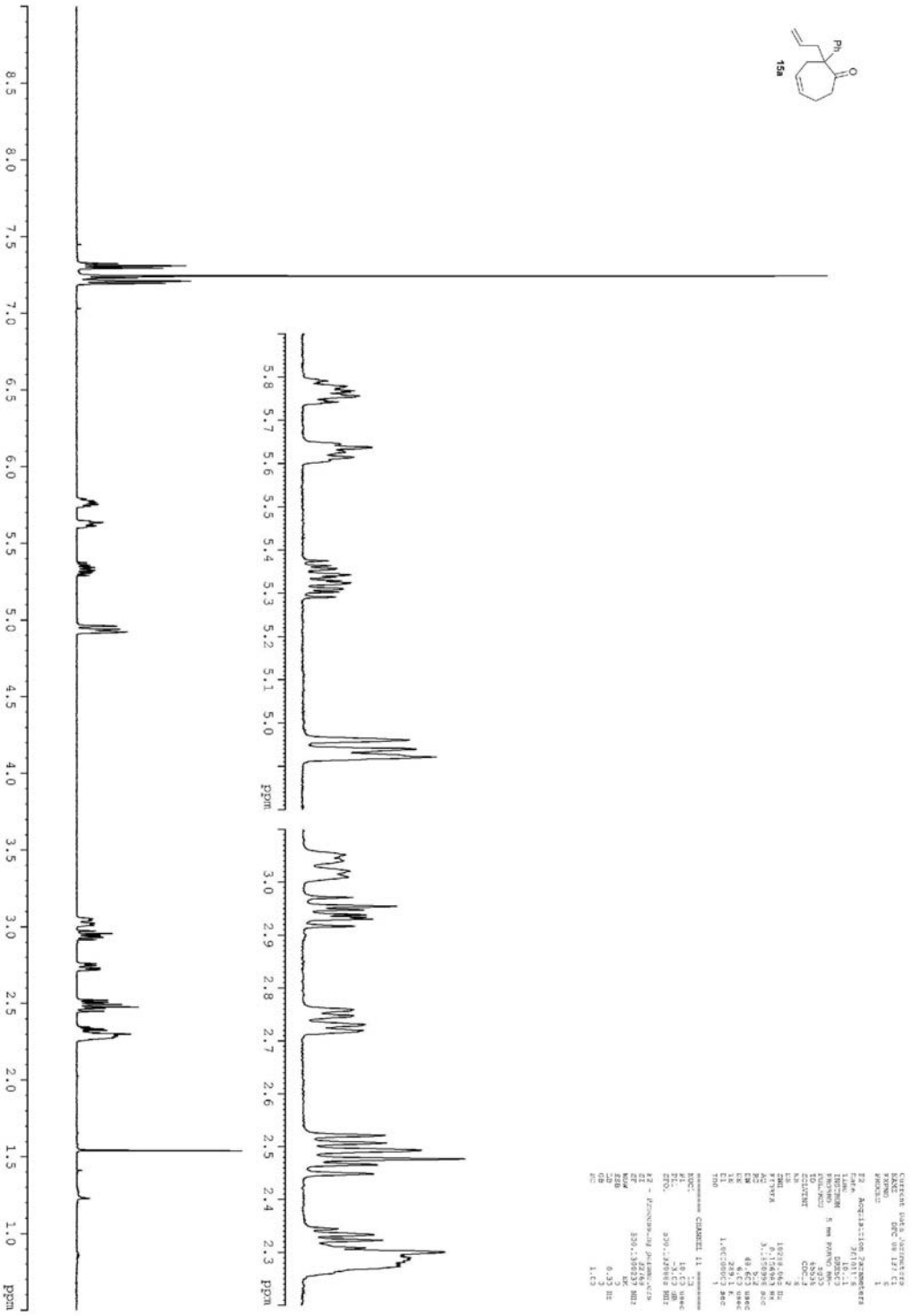

14d
CHO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

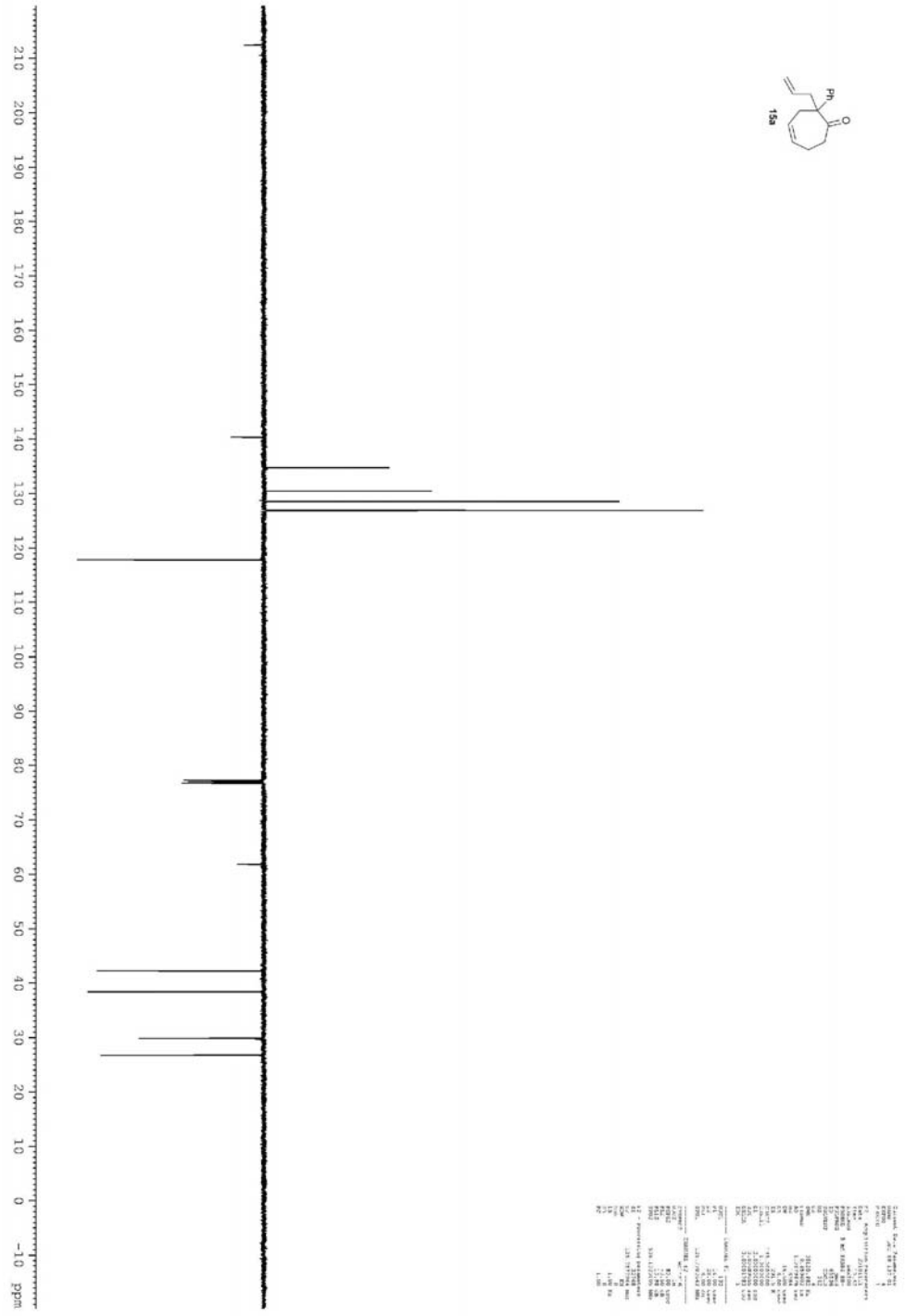

Ph
CHO
SiMe3
14e
5.56
5.54
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

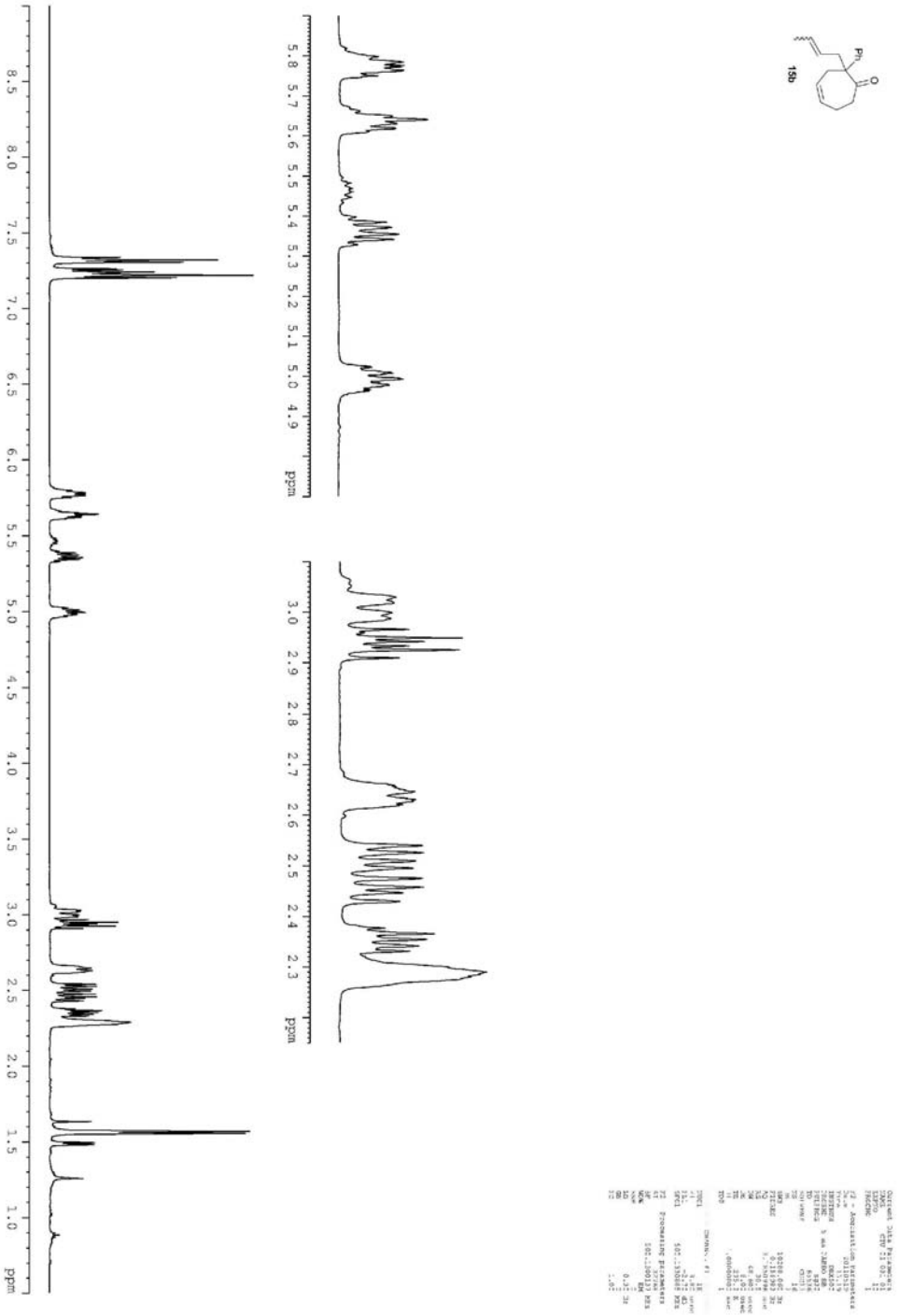

Ph
CHO
SiMe3
14e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

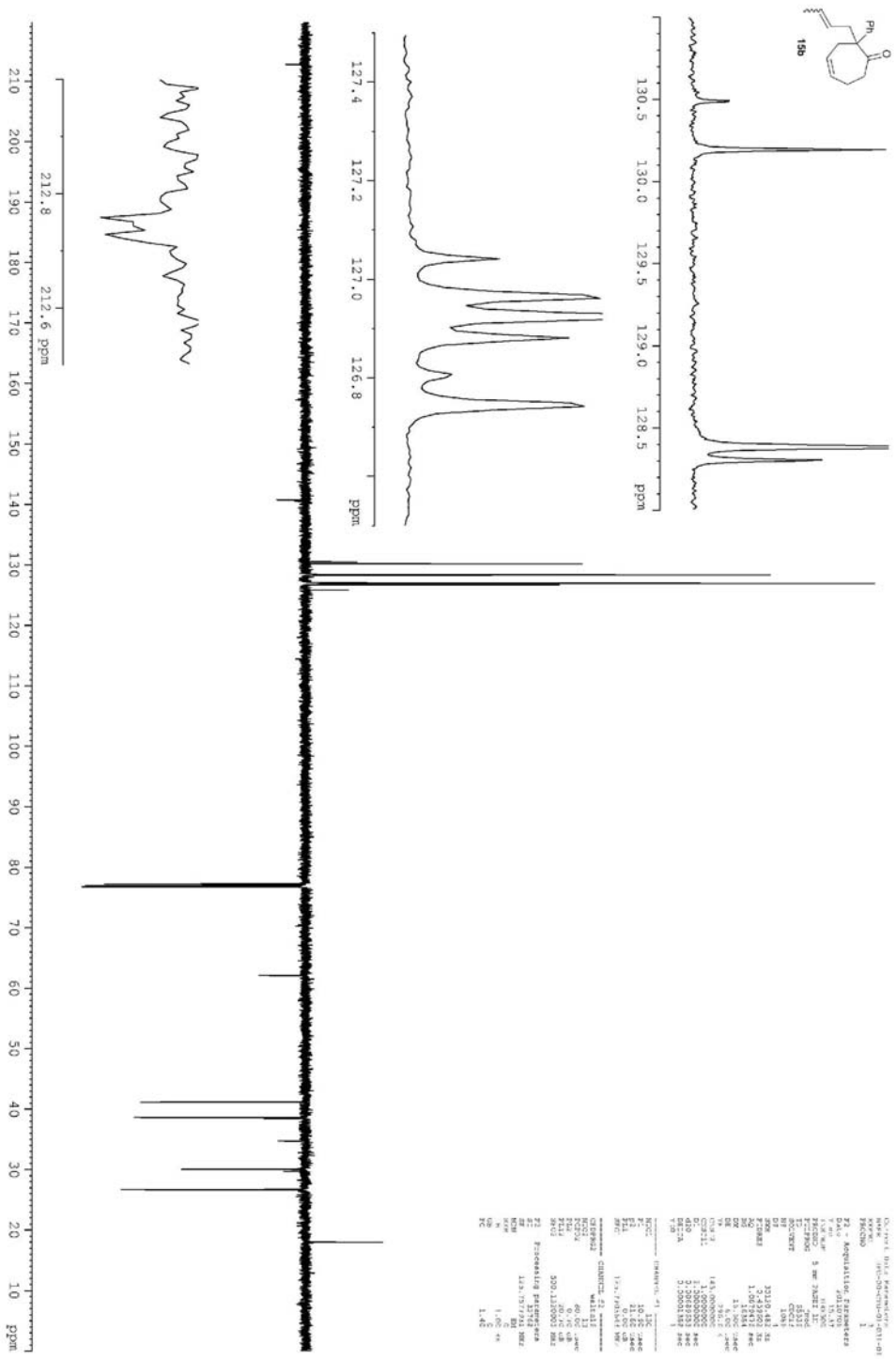

Mg
Ph
CHO
14f
2.80
2.75
2.70
2.65
ppm
9
8
7
6
5
4
3
2
1
ppm

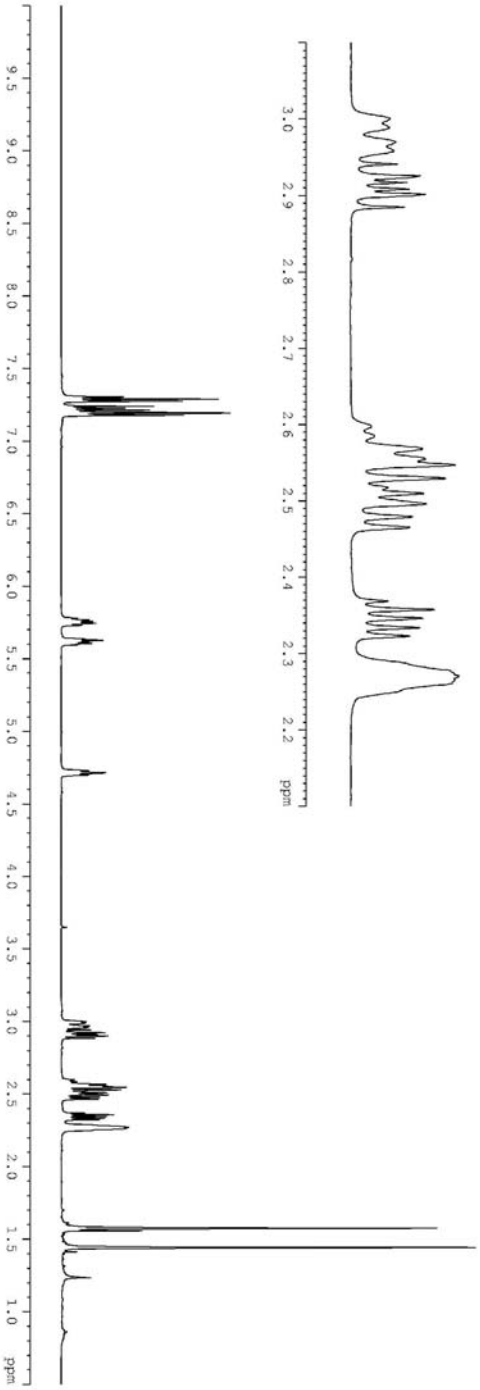

Me
Ph
CHO
14f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

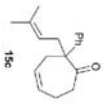

Ph
O
15a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
ppm
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
ppm


Ph
O
15a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

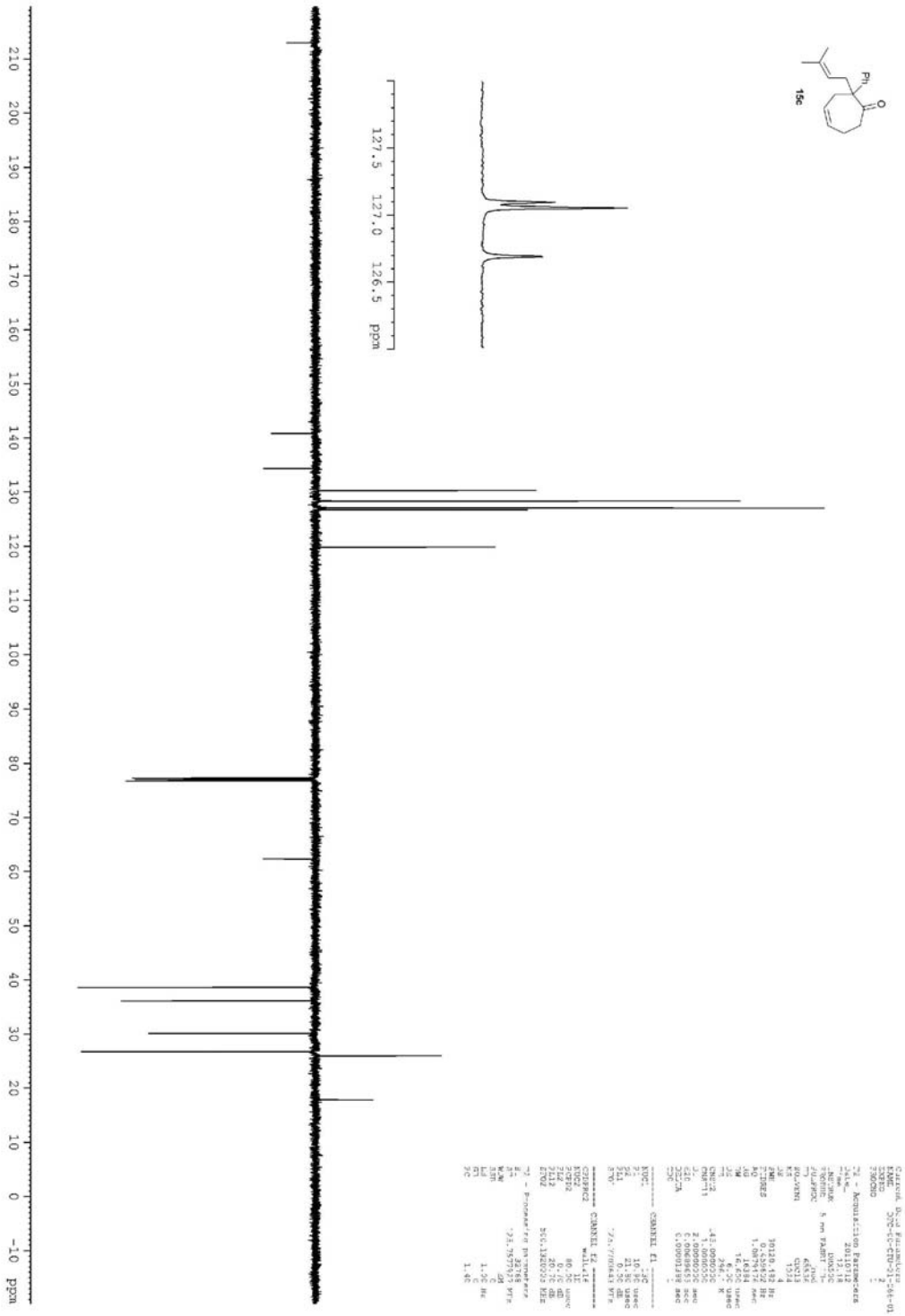

Ph
O
O
15b
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 ppm
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 ppm

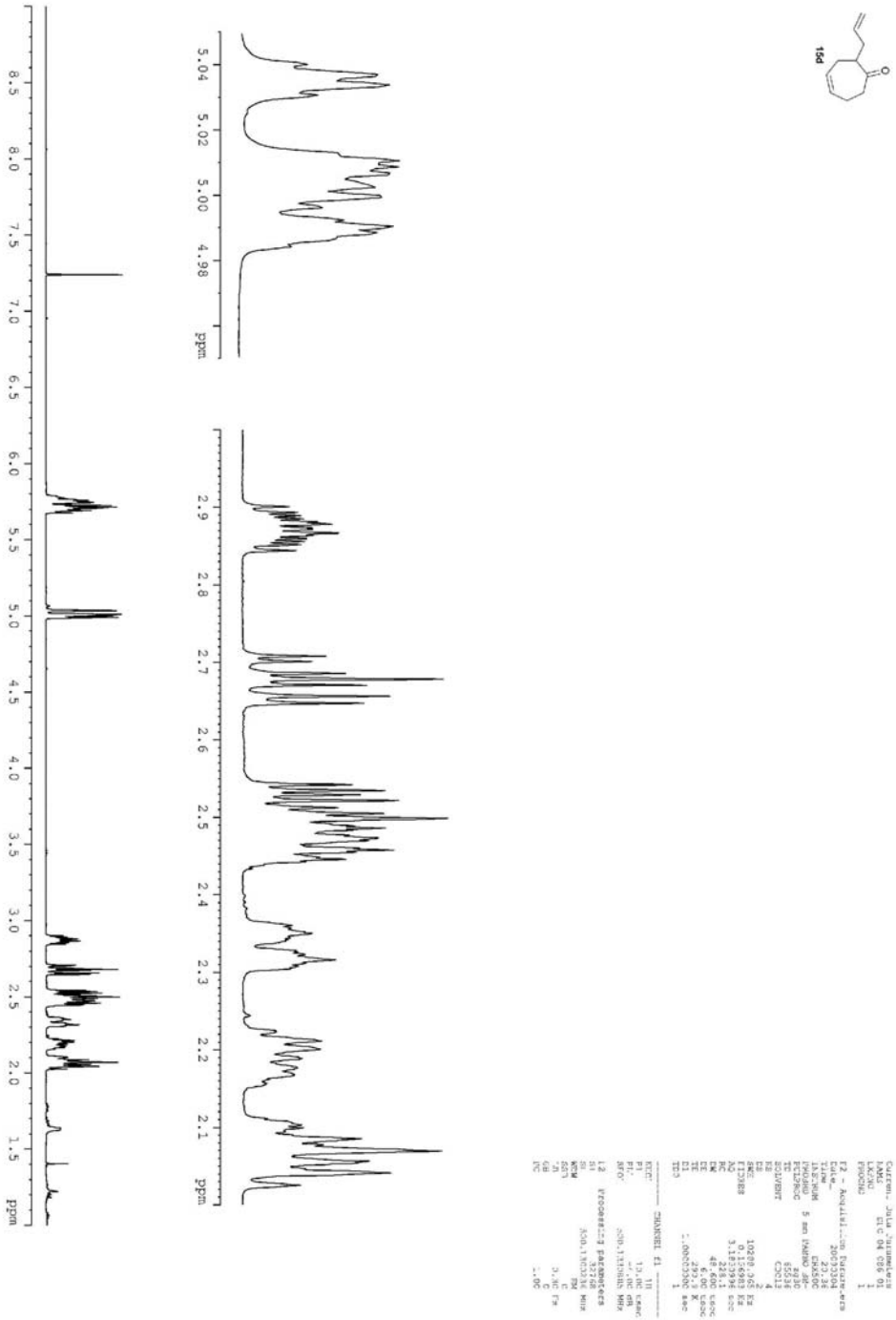

Ph
O
15b
130.5
130.0
129.5
129.0
128.5
ppm
127.4
127.2
127.0
126.8
ppm
212.8
212.6 ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

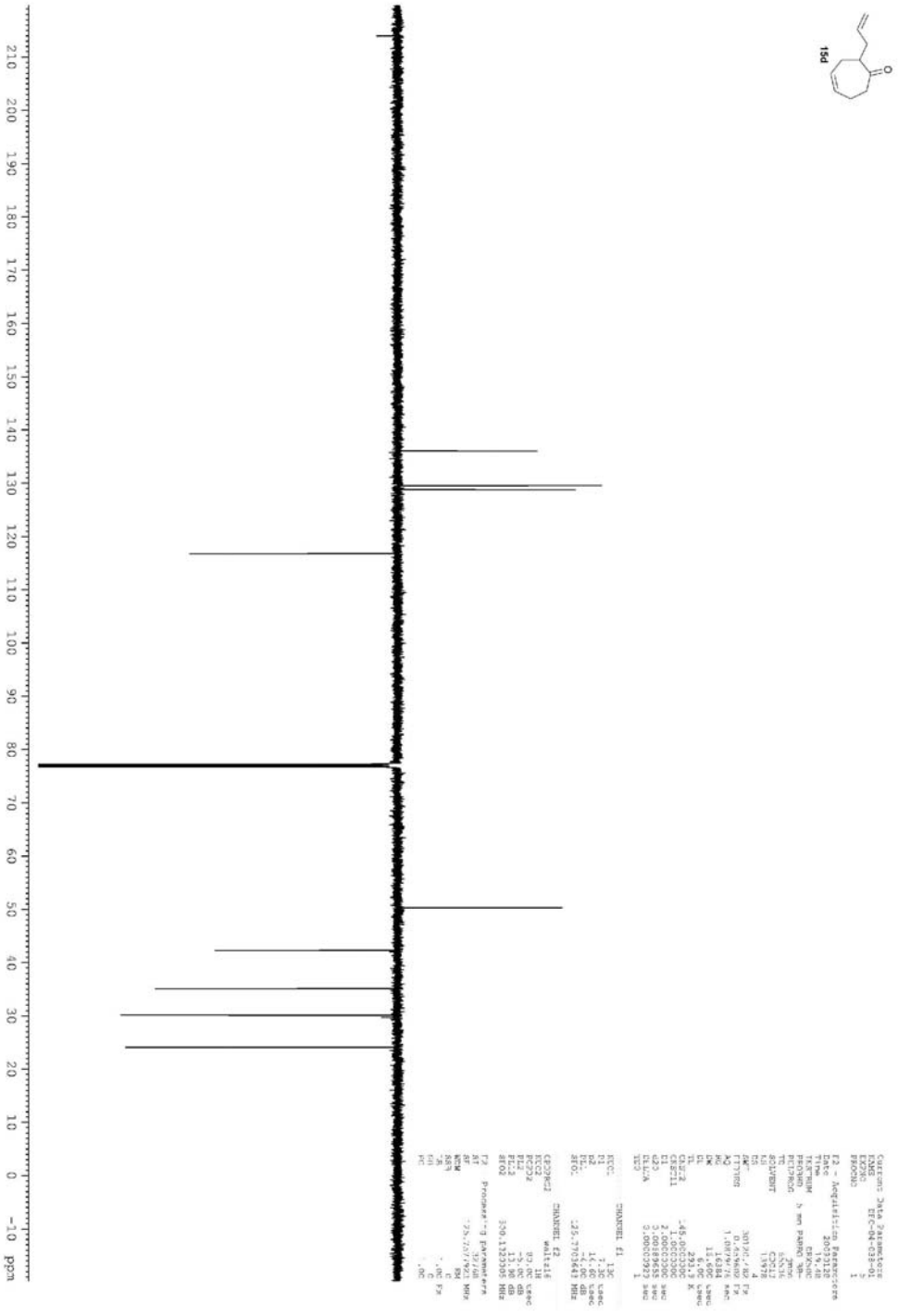

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
ppm

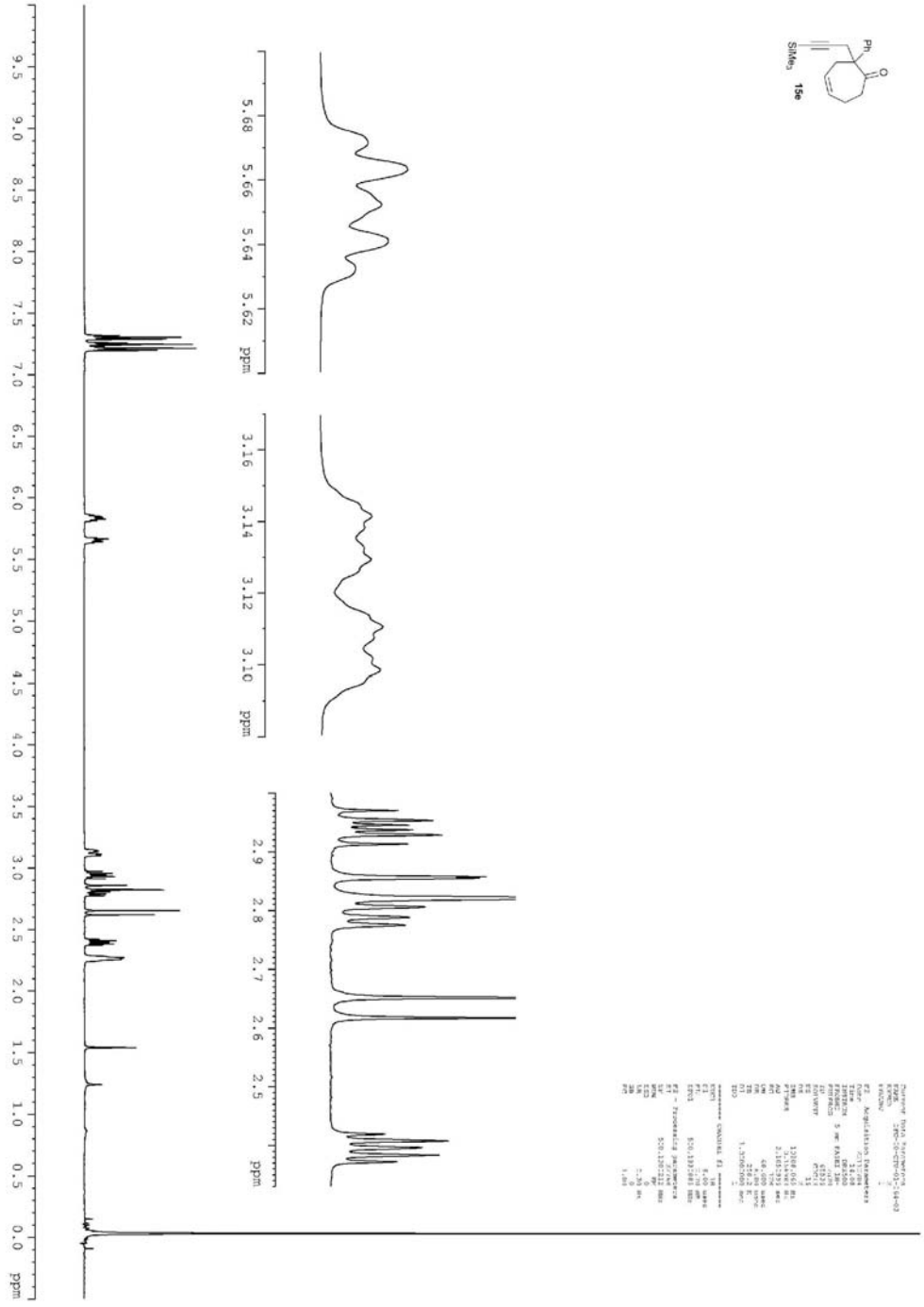

Ph
O

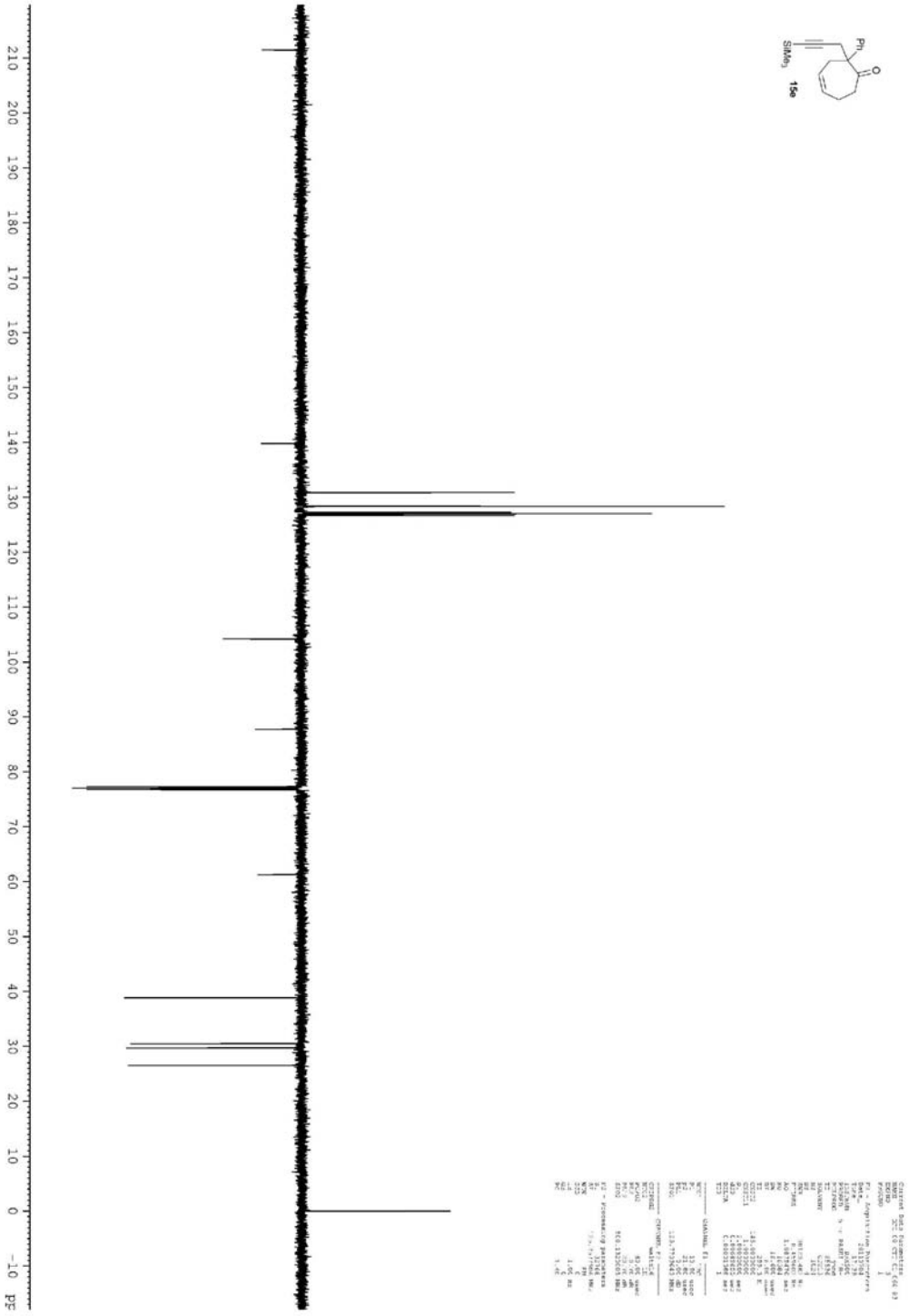
15c

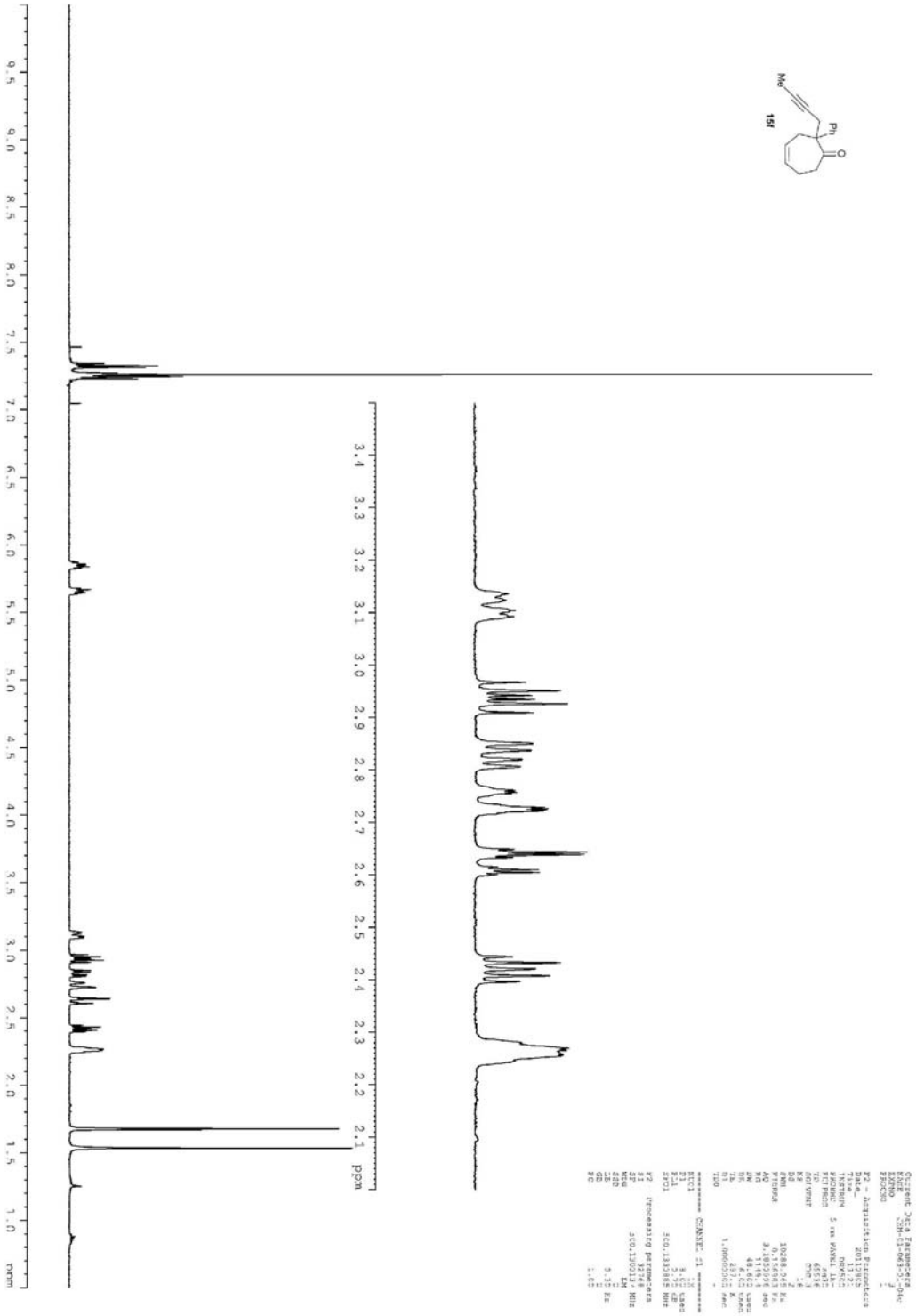

Ph
O
15c
127.5
127.0
126.5
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

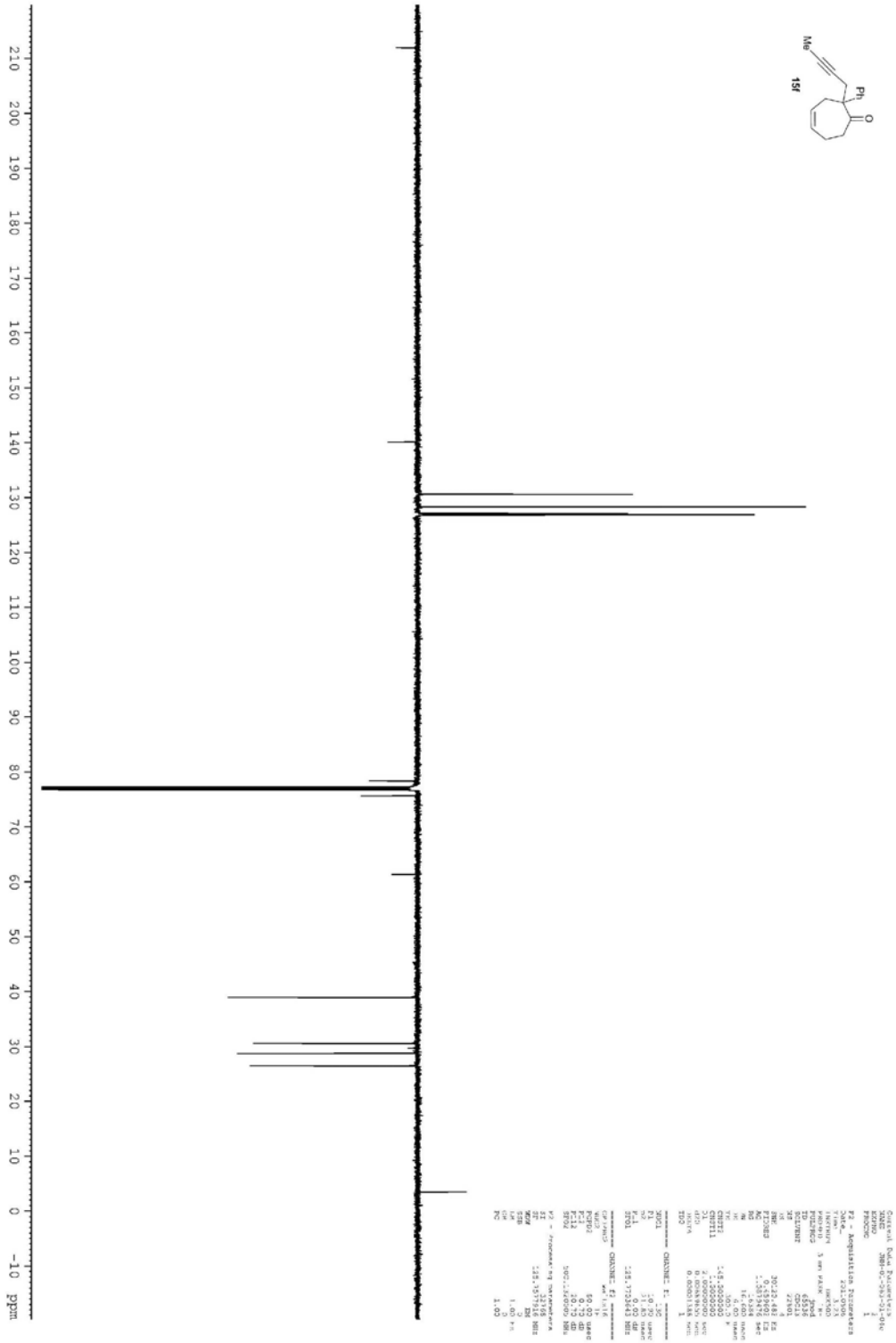

15d
5.04
5.02
5.00
4.98
ppm
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


15d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

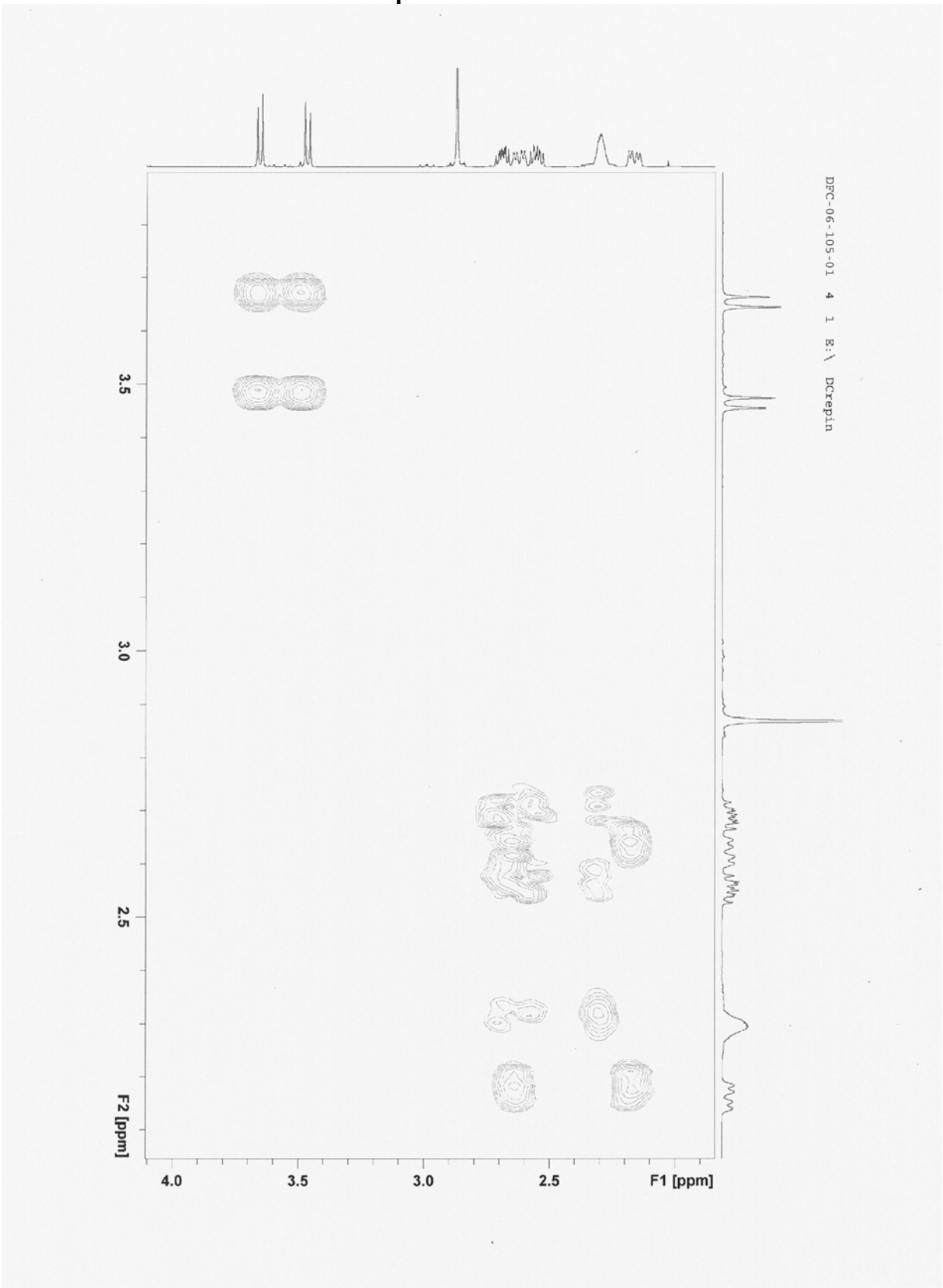

Ph
O
SiMe3
15e
5.68
5.66
5.64
5.62
ppm
3.16
3.14
3.12
3.10
ppm
2.9
2.8
2.7
2.6
2.5
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Ph
SiMe3
O
15e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
PPM

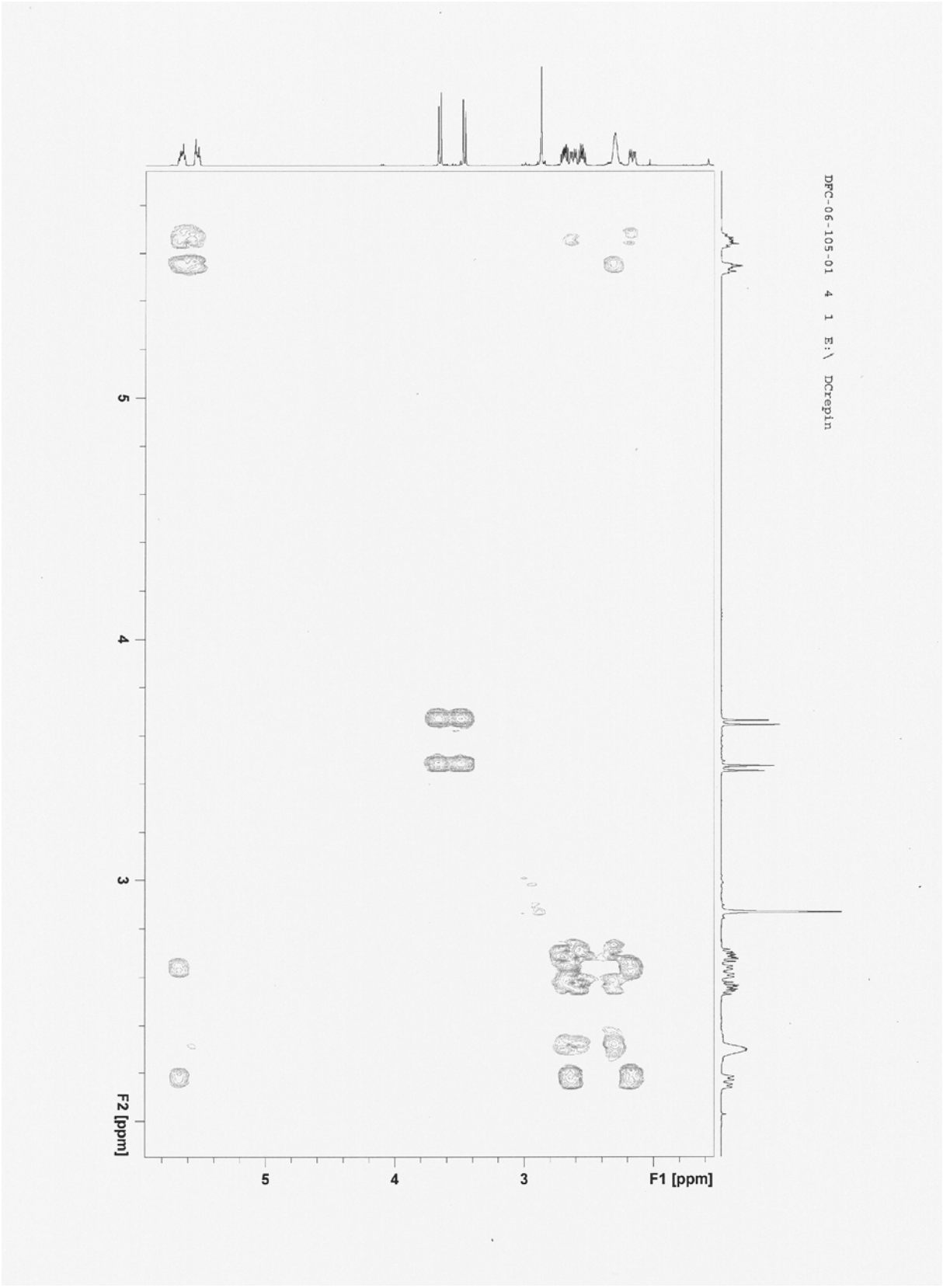

Me
Ph
O
15f
ppm


Me
Ph
O
15f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

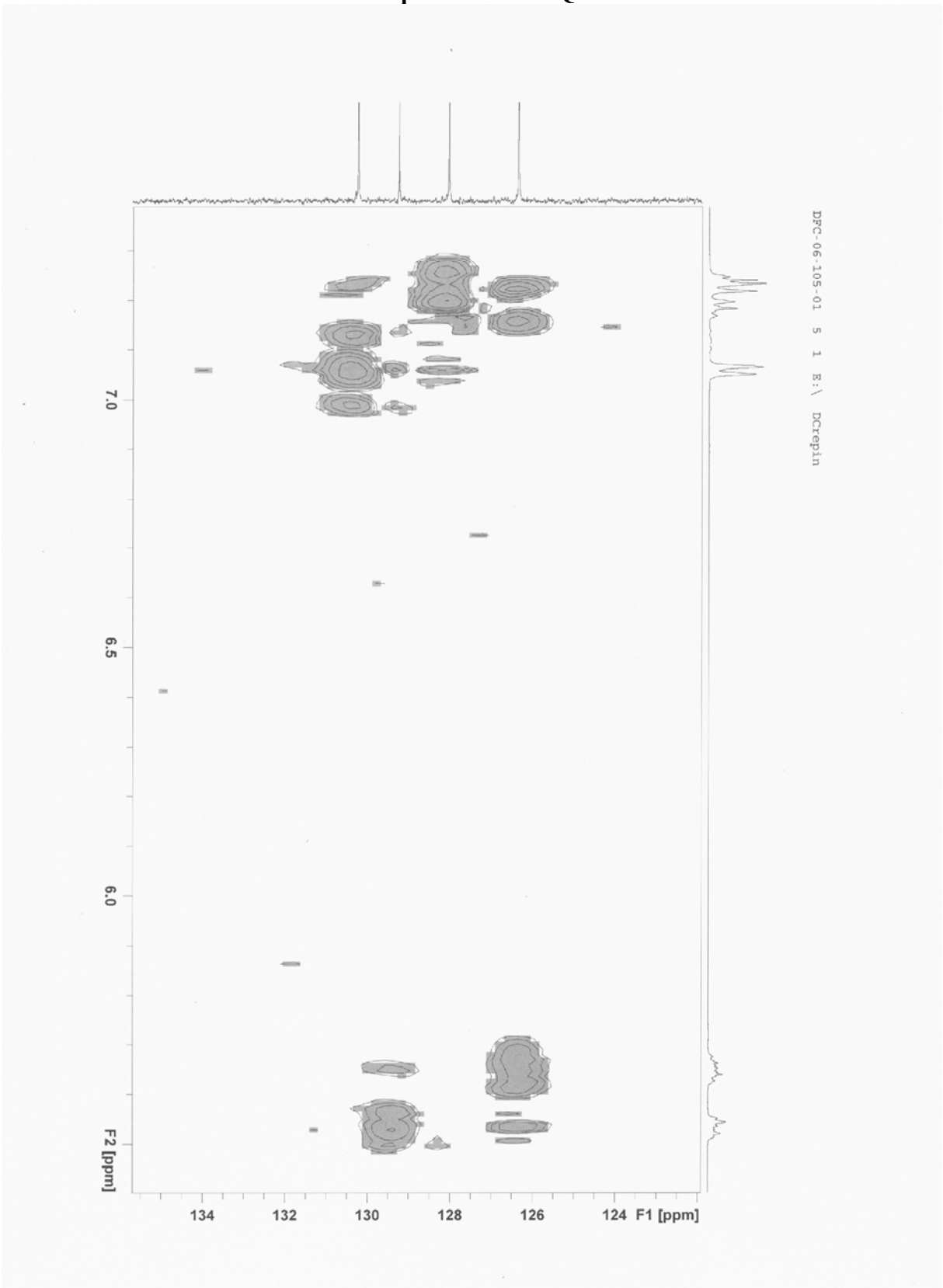
Compound 4c – COSY1



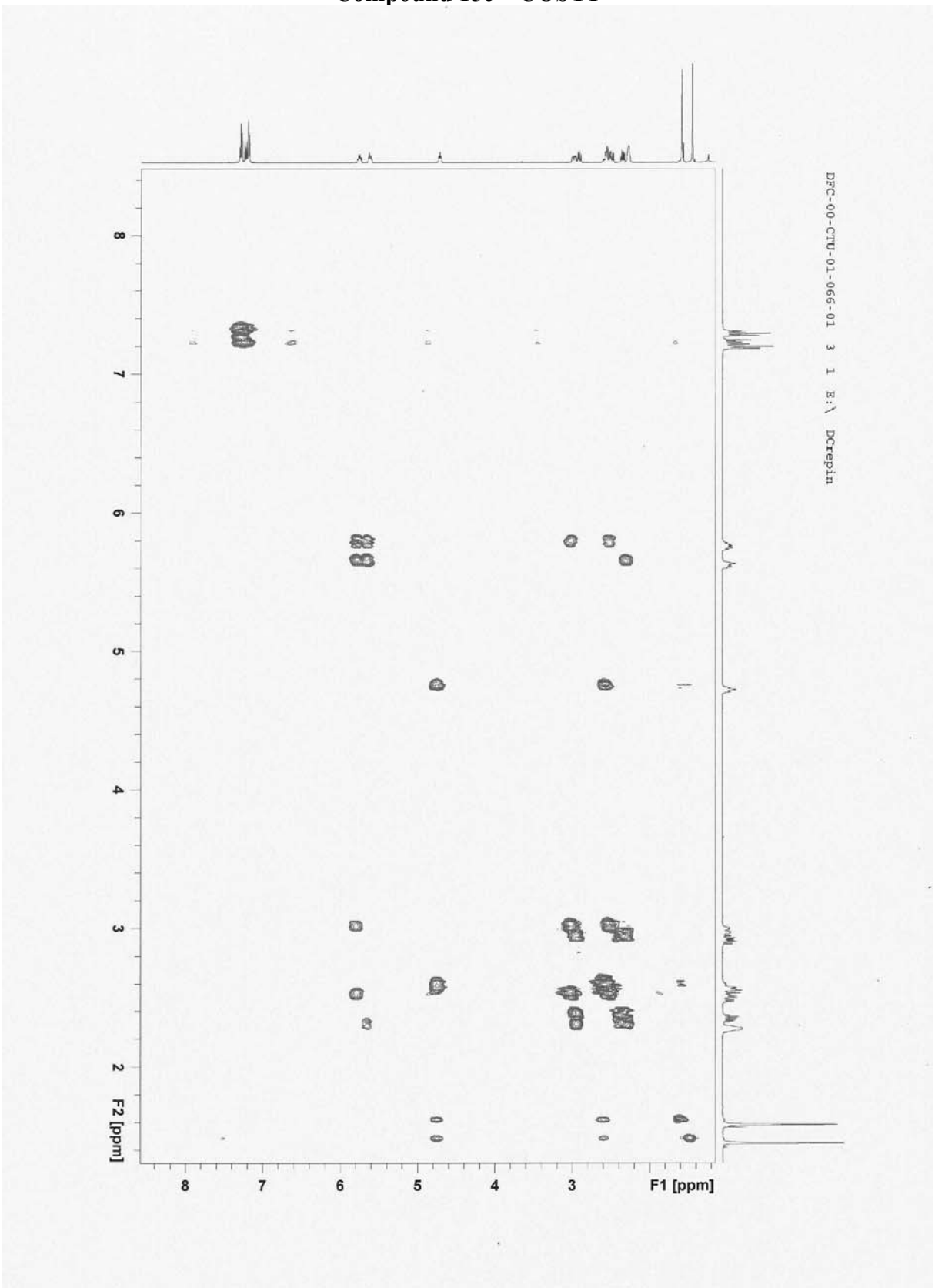
Compound 4c – COSY2



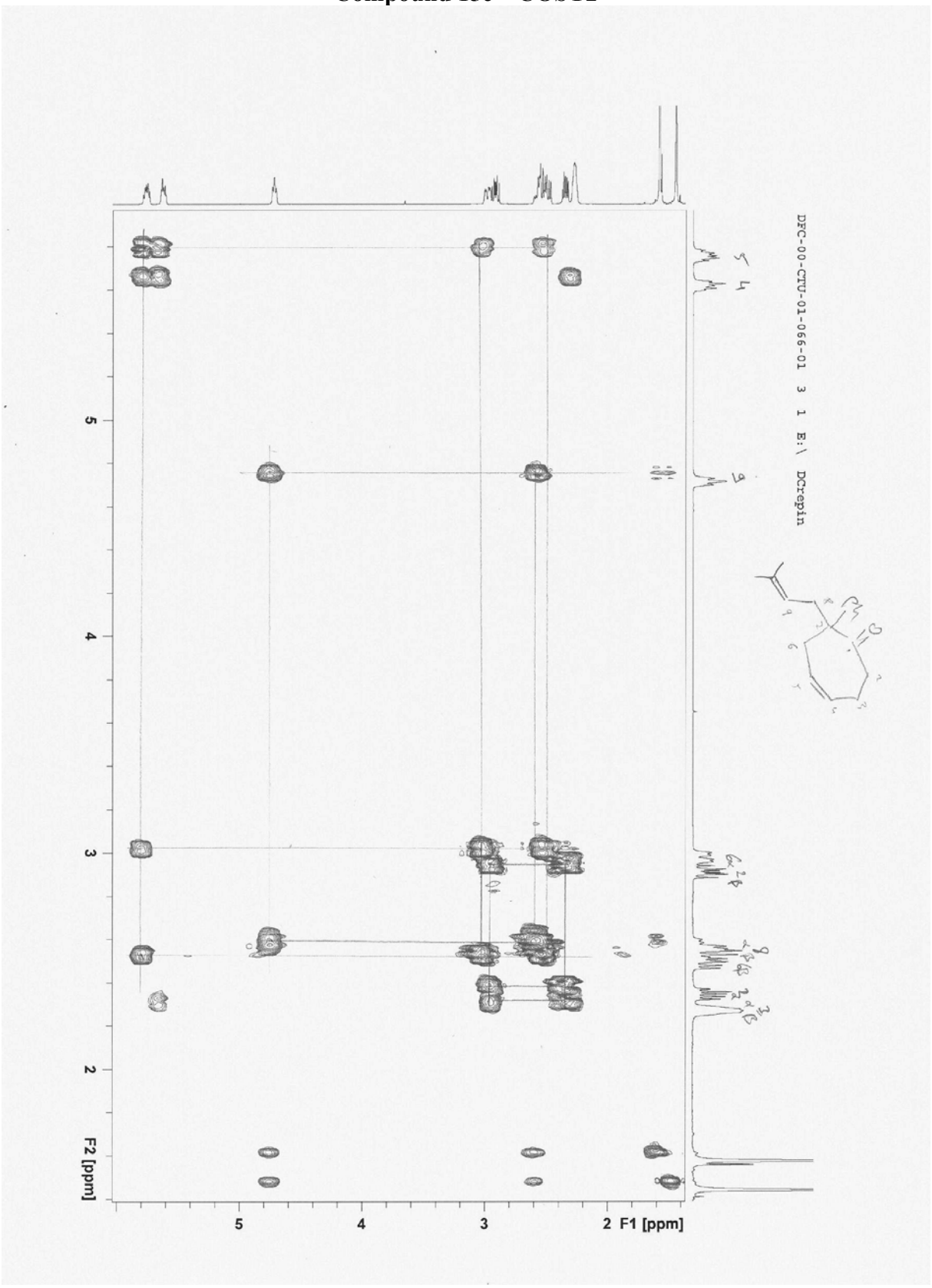
Compound 4c – HSQC



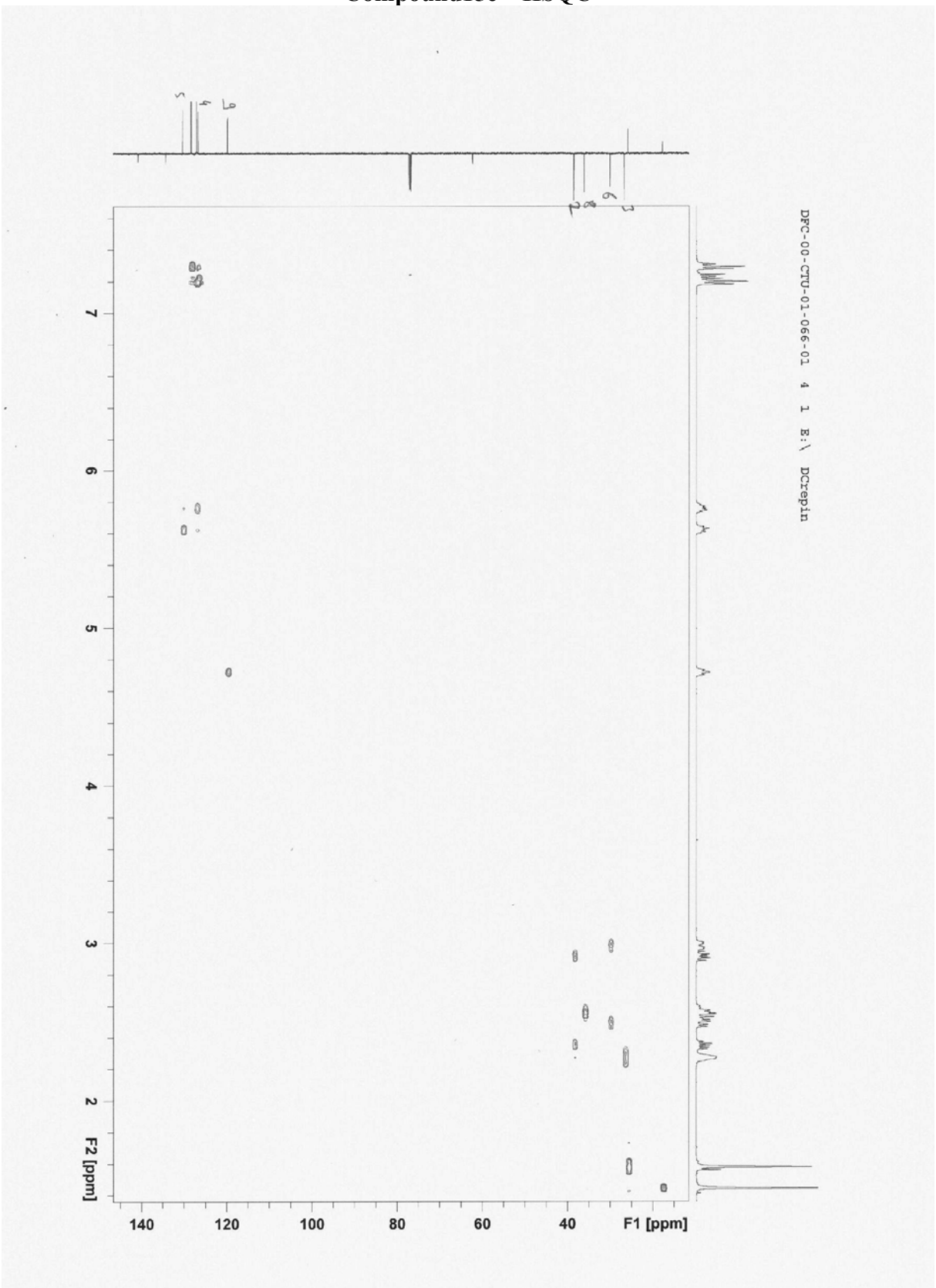
Compound 15c – COSY1



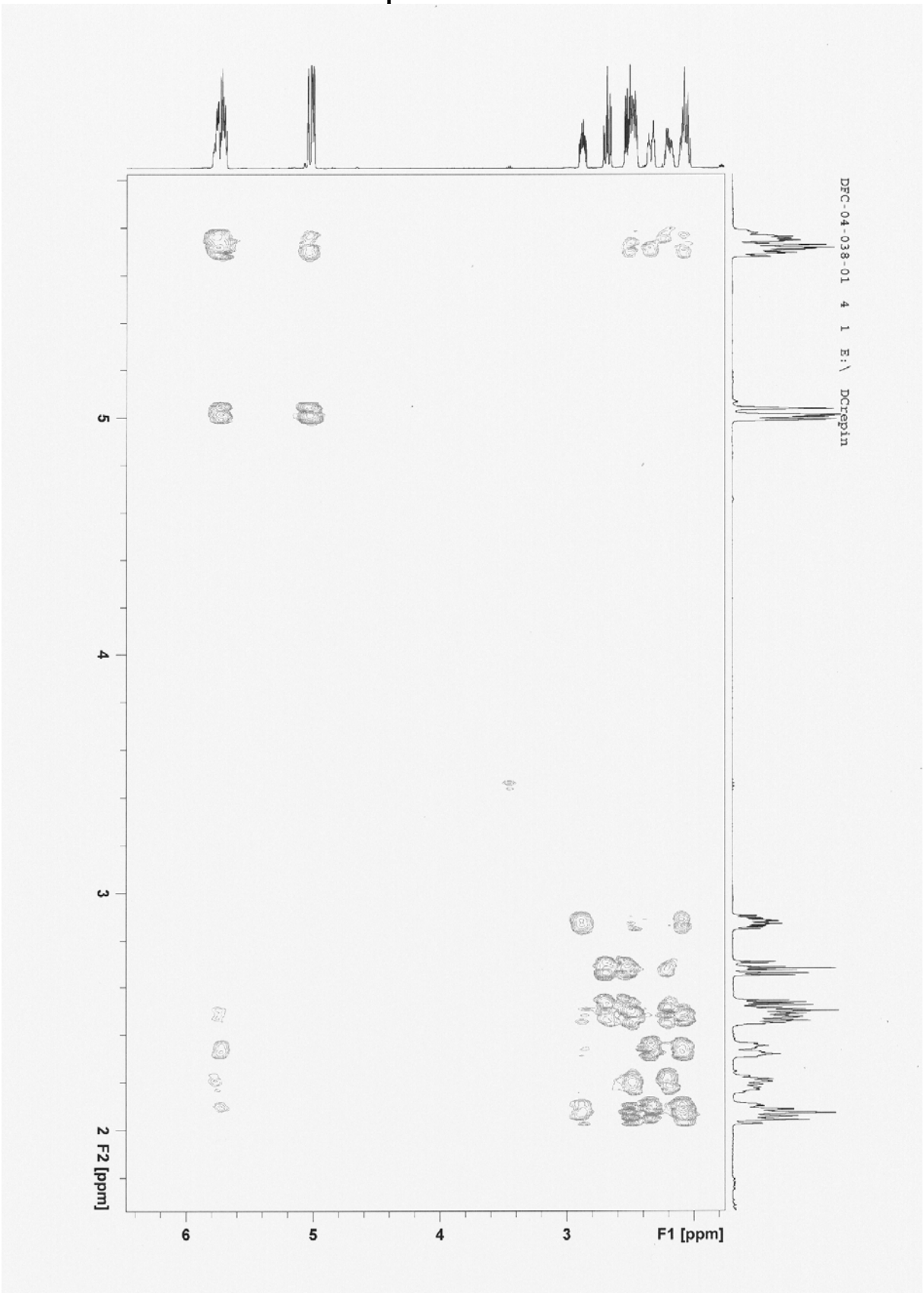
Compound 15c – COSY2



Compound15c – HSQC



Compound 15d – COSY



Compound 15d – HSQC