Multiple Rhodium-Catalysed Cleavages of Single C–C bonds

SUPPORTING INFORMATION

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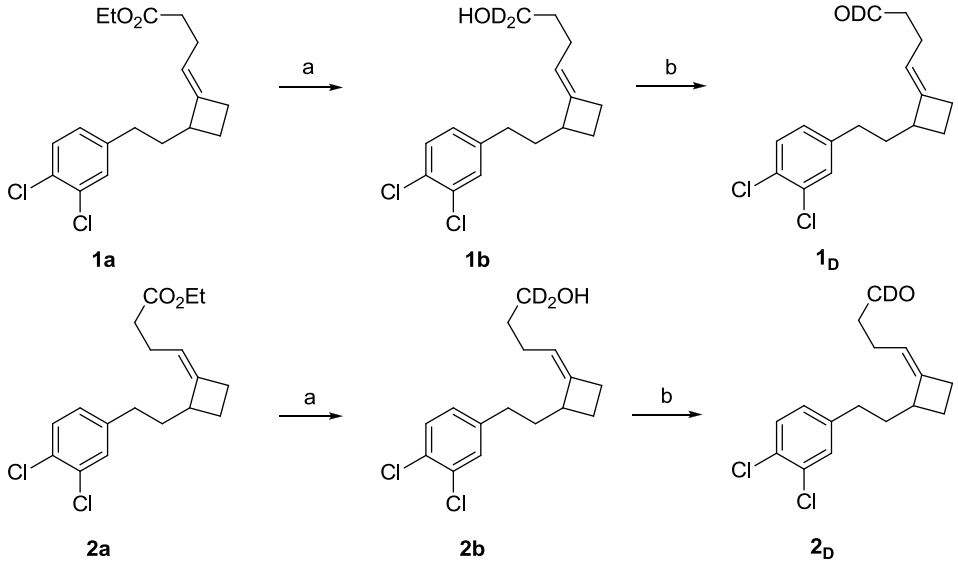
General. Otherwise noted, all reactions were carried out in flame-dried glassware under dry nitrogen atmosphere. The solvents were purified either with the solvent purification system Pure Solv MD-6 (THF, Et_2O, CH_2Cl_2, benzene, toluene, hexane). Dry acetone was purchased from VWR. Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DRX 500 and a Bruker DPX 400 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative TMS. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: 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: micromass LCT mass spectrometer (ES+). Melting points: Griffin melting point apparatus (not corrected). Elemental analyses: University of Liverpool. All commercially available compounds were used as received.

Syntheses of compounds **1_D** and **2_D** S2
Syntheses of compounds **4** and **6** S4
Syntheses of compounds **8a**–**8g** and **11** S8
General procedure for Rh-catalyzed reactions S26
Description of compounds **3_D**, **5**, **7**, **9a**–**9g**, **10c**–**10g**, **12** and **13** S26
NMR spectra for **1_D**, **2_D**, **4**, **6**, **8a**–**8g** and **11** S31
NMR spectra for **3_D**, **5**, **7**, **9a**–**9g**, **10c**–**10g**, **12** and **13** S61

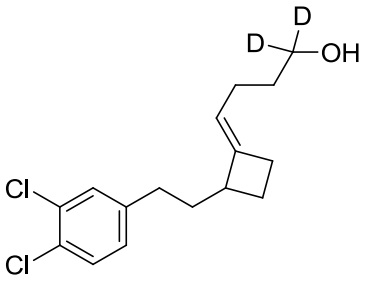
Preparation of compounds $\mathbf{1_D}$ and $\mathbf{2_D}$



[a] $LiAlD_4$, Et_2O, 0 °C to r.t.; 69% (**1b**) and 95% (**2b**). [b] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 64% ($\mathbf{1_D}$) and 85% ($\mathbf{2_D}$).

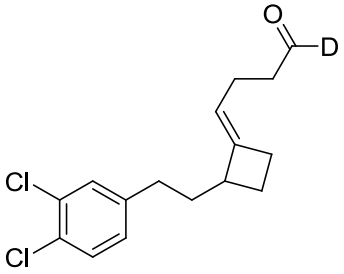
Compounds **1a** and **2a** were described previously.[1]

Compound 1b. Ester **1a** (49 mg, 0.144 mmol) in Et_2O (0.3 mL) was added under N_2 to a suspension of $LiAlD_4$ (3.3 mg, 0.079 mmol) in Et_2O (1 mL) at 0°C (bath temperature). After stirring for 20 minutes at r.t., $LiAlD_4$ (3.3 mg, 0.079 mmol) was added as solid. After stirring for 15 minutes at r.t., few drops of a saturated solution of Na_2SO_4 was added until a white precipitate appeared. The mixture was then allowed to stir at room temperature before being filtered through a pad of Celite and concentrated. Purification by flash chromatography (petroleum ether/EtOAc, 5/1) afforded **1b** as a colorless oil (30 mg, 69%).



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 6.97 (dd, *J* = 8.2, 1.6 Hz, 2H), 5.10 (tq, *J* = 7.3, 2.3 Hz, 1H), 2.91-2.78 (m, 1H), 2.62-2.46 (m, 4H), 2.07 (dtd, *J* = 10.7, 9.0, 5.3 Hz, 1H), 1.95 (q, *J* = 7.3 Hz, 2H), 1.85 (ddt, *J* = 13.1, 9.6, 6.4 Hz, 1H), 1.64 (dtd, *J* = 13.5, 9.0, 6.1 Hz, 1H), 1.57 (t, *J* = 7.2 Hz, 2H), 1.55-1.49 (m, 1H), 1.35 (s, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.6, 142.8, 132.1, 130.3, 130.1, 129.5, 127.9, 118.8, 61.9 (quint, *J* = 21.3 Hz), 42.8, 36.0, 32.5, 32.4, 26.4, 24.1, 23.6; IR (neat): $\tilde{\nu}$ = 3324 (br), 2926, 2854, 2198, 2092, 1593, 1562, 1473, 1396, 1258, 1206, 1132, 1098, 1031, 965, 890, 871, 847, 817, 703, 684, 663 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 325 (65), 323 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}{}^{35}Cl_2D_2O$ + Na): 323.0914; found: 323.0915; calcd for ($C_{16}H_{18}{}^{35}Cl^{37}ClD_2O$ + Na): 325.0885; found: 325.0891.

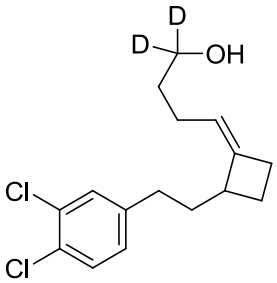
Compound $\mathbf{1_D}$. A solution of DMSO (18 µL, 0.259 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of $(COCl)_2$ (11 µL, 0.130 mmol) in CH_2Cl_2 (1 mL) at -78 °C under N_2. After stirring for 10 minutes at this temperature, a solution of **1b** (30 mg, 0.100 mmol) in CH_2Cl_2 (0.5 mL) was added via canula. After stirring for 15 minutes at -78 °C, Et_3N (69 µL, 0.497 mmol) was added via syringe. After stirring for 30 minutes at r.t., the mixture was quenched with a saturated solution of NH_4Cl (5 mL). The aqueous layer was extracted with CH_2Cl_2 (1 × 10 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4,



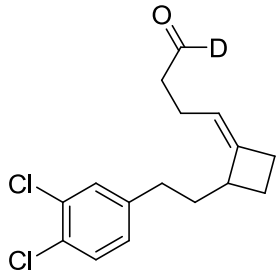
[1] Crépin, D.; Dawick, J.; Aïssa, C. *Angew. Chem. Int. Ed.* **2010**, *47*, 620.

filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 80/1 → 60/1 → 40/1) gave **1_D** as colorless oil (19 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 8.2, 2.0 Hz, 2H), 5.06 (tq, *J* = 7.3 Hz, *J* = 2.4 Hz, 1H), 2.88–2.78 (m, 1H), 2.58-2.46 (m, 4H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.20 (q, *J* = 7.3 Hz, 2H), 2.07 (dtd, *J* = 10.9, 9.0, 5.4 Hz, 1H), 1.83 (ddt, *J* = 13.2, 9.5, 6.5 Hz, 1H), 1.63 (dtd, *J* = 13.2, 9.3, 5.8 Hz, 1H), 1.58-1.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.3 (t, *J* = 25.6 Hz), 145.8, 142.7, 132.0, 130.3, 130.1, 129.5, 127.9, 117.1, 43.6 (t, *J* = 3.8 Hz), 42.7, 35.8, 32.5, 26.4, 23.5, 20.7; IR (neat): $\tilde{\nu}$ = 2917, 2855, 2069, 1713, 1596, 1561, 1473, 1397, 1352, 1259, 1207, 1131, 1094, 1030, 870, 816, 706, 684 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 354 (64), 352 (100) [M + MeOH + Na]; HRMS (ES+) calcd for ($C_{16}H_{17}{}^{35}Cl_2DO$ + MeOH +Na): 352.0957; found: 352.0941; calcd for ($C_{16}H_{17}{}^{35}Cl^{37}ClDO$ + MeOH +Na): 354.0928; found: 354.0914.

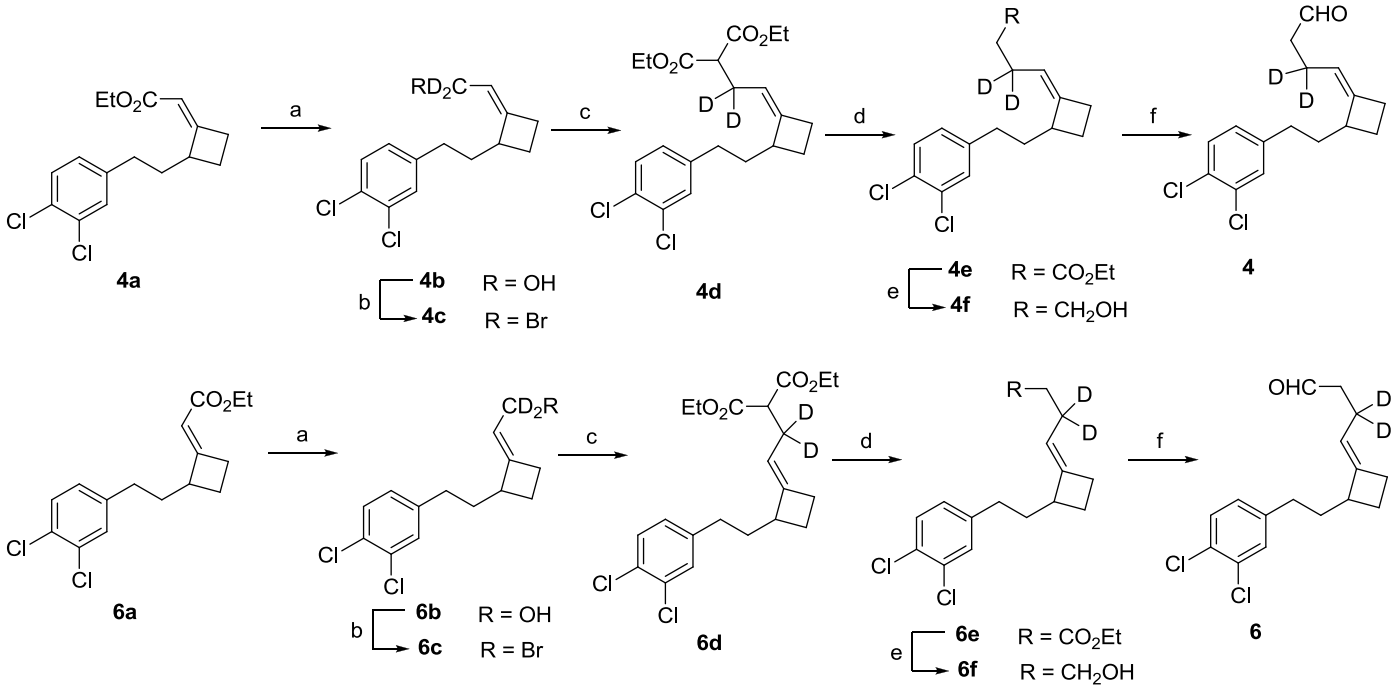
Compound 2b. This compound was obtained from **2a** according to the procedure described for the preparation of **1b**. Colorless oil (38 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 6.99 (dd, *J* = 8.2 Hz, *J* = 1.9 Hz, 2H), 5.05 (tq, *J* = 7.2, 2.3 Hz, 1H), 2.99-2.88 (m, 1H), 2.67-2.541 (m, 2H), 2.536-2.42 (m, 2H), 2.08 (dtd, *J* = 11.0, 9.1, 7.0 Hz, 1H), 1.98 (q, *J* = 7.2 Hz, 2H), 1.95-1.87 (m, 1H), 1.74 (dtd, *J* = 13.4, 10.2, 4.9 Hz, 1H), 1.62-1.52 (m, 3H), 1.56 (t, *J* = , 2H), 1.33–1.27 (m, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.0, 142.7, 132.1, 130.3, 130.2, 129.5, 127.8, 120.9, 61.9 (quint, *J* = 21.3 Hz), 42.1, 35.7, 32.7, 32.5, 28.0, 24.5, 22.7; IR (neat): $\tilde{\nu}$ = 3345 (br), 2922, 2851, 2206, 2100, 1593, 1562, 1473, 1454, 1424, 1374, 1290, 1259, 1206, 1131, 1093, 1030, 965, 871, 851, 816, 686, 660 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 325 (65), 323 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}{}^{35}Cl_2D_2O$ + Na): 323.0914; found: 323.0924; calcd for ($C_{16}H_{18}{}^{35}Cl^{37}ClD_2O$ + Na): 325.0885; found: 325.0891.



Compound 2_D. This compound was obtained from **2b** according to the Swern procedure described for the preparation of **1_D**. Colorless oil (26 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.2, 2.0 Hz, 2H), 5.00 (tq, *J* = 7.2 Hz, *J* = 2.4 Hz, 1H), 3.01-2.88 (m, 1H), 2.67-2.55 (m, 2H), 2.54-2.46 (m, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.31-2.17 (m, 2H), 2.09 (dtd, *J* = 11.0, 9.1, 6.9 Hz, 1H), 2.00-1.88 (m, 1H), 1.75 (dtd, *J* = 13.3, 10.1, 5.0 Hz, 1H), 1.63-1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9 (t, *J* = 26.5 Hz), 144.2, 142.6, 132.1, 130.3, 130.2, 129.6, 127.8, 119.2, 43.9 (t, *J* = 3.5 Hz), 42.1, 35.6, 32.5, 28.0, 22.7, 21.0; IR (neat): $\tilde{\nu}$ = 2921, 2855, 2070, 1712, 1593, 1562, 1472, 1421, 1397, 1355, 1260, 1208, 1132, 1094, 1030, 948, 872, 850, 819, 706, 686, 659 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 354 (65), 352 (100) [M + MeOH + Na]; HRMS (ES+) calcd for ($C_{16}H_{17}{}^{35}Cl_2DO$ + MeOH +Na): 352.0957; found: 352.0954; calcd for ($C_{16}H_{17}{}^{35}Cl^{37}ClDO$ + MeOH +Na): 354.0928; found: 354.0925.



Preparation of compounds 4 and 6



[a] $LiAlD_4$, Et_2O, –20 °C; 61% (**6b**) and 77% (**4b**). [b] PBr_3, Et_2O, 0 °C; quantitative. [c] 1) Diethyl malonate, NaH, THF, –78 °C; 2) **6c** or **4c**, THF, 0 °C to r.t.; 75% (**6d**) and 74% (**4d**). [d] LiCl, H_2O, DMSO, reflux; 79% (**6e**) and 71% (**4e**). [e] $LiAlH_4$, Et_2O, 0 °C to r.t.; 98% (**6f**) and 61% (**4f**). [f] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 66% (**6**) and 64% (**4**).

Compounds **6a** and **4a** were prepared as described previously.[1]

Compound 6b. Ester **6a** (634 mg, 2.02 mmol) in Et_2O (2 mL) was added under N_2 to a suspension of $LiAlD_4$ (46 mg, 1.11 mmol) in Et_2O (8 mL) at -20°C (bath temperature). After stirring for 20 minutes at –20 °C, $LiAlD_4$ (46 mg, 1.11 mmol) was added as solid. After stirring for 35 minutes at –20 °C, few drops of a saturated solution of Na_2SO_4 was added until a white precipitate appeared. The mixture was then allowed to stir at room temperature before being filtered through a pad of Celite and concentrated. Purification by flash chromatography (PE/EtOAc, 10/1 → 5/1 → 5/2) afforded **6b** as a colorless oil (333 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.5 Hz, 1H), 7.26–7.24 (m, 1H), 7.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.38–5.33 (m, 1H), 2.93–2.84 (m, 1H), 2.68–2.45 (m, 4H), 2.09 (dtd, *J* = 10.9, 9.1, 5.3 Hz, 1H), 1.88 (ddt, *J* = 13.4, 9.4, 6.6 Hz, 1H), 1.68 (dtd, *J* = 13.5, 9.1, 6.1 Hz, 1H), 1.62–1.53 (m, 1H), 1.15–1.05 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.8, 142.5, 132.0, 130.2, 130.1, 129.5, 127.8, 118.1, 58.6 (quint., *J* = 21.0 Hz), 42.9, 35.4, 32.4, 26.5, 23.6; IR (neat): $\tilde{\nu}$ = 3312, 2926, 2857, 2187, 2083, 1693, 1593, 1561, 1472, 1396, 1353, 1312, 1257, 1207, 1131, 1094, 1071, 1030, 953, 905, 870, 816, 704, 684, 661 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 297 (68), 295 (100) [M + Na]; HRMS (ES+) calcd for ($C_{14}H_{14}D_2{}^{35}Cl_2O$ + Na): 295.0601; found: 295.0594; calcd for ($C_{14}H_{14}D_2{}^{35}Cl^{37}ClO$ + Na): 297.0572; found: 297.0572.

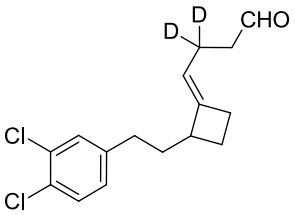
Compound 6d. Under N_2, PBr_3 (114 µL, 1.21 mmol) was added to a solution of **6b** (330 mg, 1.21 mmol) in Et_2O at 0 °C. After stirring at this temperature for 2.5 hours, the mixture was quenched with brine, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. Diethyl malonate (0.25 mL, 1.63 mmol) was added to a suspension of NaH (58 mg, 1.45 mmol (60% in oil)) in THF (9 mL) at 0 °C under N_2. After stirring at r.t. for 30 minutes, this solution was added via canula to a solution of crude **6c** in THF (6.5 mL) at 0 °C under N_2. After stirring at r.t. for 90 minutes, the mixture was quenched with a saturated solution of NH_4Cl (10 mL) and diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 50/1 → 30/1) gave **6d** as colourless oil (375 mg, 75% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.08–5.01 (m, 1H), 4.21–4.11 (m, 4H), 3.29 (s, 1H), 2.86–2.76 (m, 1H), 2.63–2.43 (m, 4H), 2.05 (dtd, *J* = 10.9, 9.1, 5.2 Hz, 1H), 1.81 (ddt, *J* = 13.5, 9.5, 6.5 Hz, 1H), 1.61 (dtd, *J* = 13.6, 9.2, 6.0 Hz, 1H), 1.55–1.47 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1 (2C), 147.5, 142.6, 132.0, 130.2, 130.1, 129.5, 127.8, 114.6, 61.2 (2C), 51.9, 42.7, 35.7, 32.3, 26.6 (quint., *J* = 21.1 Hz) 26.4, 23.4, 14.1 (2C); IR (neat): $\tilde{\nu}$ = 2980, 2937, 2861, 1730, 1590, 1560, 1473, 1394, 1368, 1318, 1210, 1175, 1150, 1131, 1096, 1030, 952, 868, 818, 684, 658 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 439 (63), 437 (100) [M + Na]; HRMS (ES+) calcd for ($C_{21}H_{24}D_2{}^{35}Cl_2O_4$ + Na): 437.1231; found: 437.1215; calcd for ($C_{21}H_{24}D_2{}^{35}Cl^{37}ClO_4$ + Na): 439.1202; found: 439.1203.

Compound 6e. Lithium chloride (73 mg, 1.727 mmol) was added to a solution of **6d** (326 mg, 0.785 mmol) in DMSO (5 mL). Seven drops of water were added via pipette then the mixture was stirred at 155°C (oil bath temperature) during 16 hours. At room temperature, the mixture was partitioned between brine (5 mL) and EtOAc (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated. Purification by flash chromatography (PE/EtOAc, 1/0 → 90/1) gave **7e** as colourless oil (212 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.09–5.04 (m, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.87–2.78 (m, 1H), 2.61–2.46 (m, 4H), 2.28 (s, 2H), 2.05 (dtd, *J* = 10.9, 9.0, 5.3 Hz, 1H), 1.83 (ddt, *J* = 13.4, 9.5, 6.5 Hz, 1H), 1.62 (dtd, *J* = 13.5, 9.1, 5.9 Hz, 1H), 1.57–1.49 (m, 1H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.2, 145.5, 142.7, 132.0, 130.2, 130.1, 129.4, 127.8, 117.2, 60.2, 42.7, 35.8, 34.2, 32.4, 26.3, 23.5, 22.8 (quint., *J* = 19.0 Hz), 14.2; IR (neat): $\tilde{\nu}$ = 2972, 2931, 2851, 2203, 2106, 1732, 1593, 1562, 1473, 1395, 1369, 1339, 1263, 1182, 1131, 1031, 871, 817, 684, 658 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 367 (63), 365 (100) [M + Na]; HRMS (ES+) calcd for ($C_{18}H_{20}D_2{}^{35}Cl_2O_2$ + Na): 365.1020; found: 365.1012; calcd for ($C_{18}H_{20}D_2{}^{35}Cl^{37}ClO_2$ + Na): 367.0991; found: 367.0997.

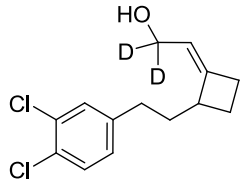
Compound 6f. Ester **6e** (250 mg, 0.728 mmol) in Et_2O (1 mL) was added under N_2 to a suspension of $LiAlH_4$ (14 mg, 0.364 mmol) in Et_2O (4 mL) at 0 °C (bath temperature). After stirring for 20 minutes at 0 °C, $LiAlH_4$ (14 mg, 0.364 mmol) was added as solid. After stirring for 35 minutes at r.t., few drops of a saturated solution of Na_2SO_4 were added until a white precipitate appeared. The mixture was then allowed to stir at room temperature before being filtered through a pad of Celite and concentrated. Purification by flash chromatography (PE/EtOAc, 15/1 → 10/1 → 5/1 → 3/1) afforded **6f** as a colourless oil (215 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 1.6 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.11–5.05 (m, 1H), 3.59 (t, *J* = 6.6 Hz, 2H),

2.87–2.77 (m, 1H), 2.60–2.44 (m, 4H), 2.06 (dtd, *J* = 10.9, 9.0, 5.4 Hz, 1H), 1.85 (ddt, *J* = 13.1, 9.5, 6.5 Hz, 1H), 1.64 (dtd, *J* = 13.4, 9.1, 5.9 Hz, 1H), 1.59–1.50 (m, 1H), 1.57 (t, *J* = 6.5 Hz, 2H), 1.31–1.24 (m, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.6, 142.7, 132.0, 130.2, 130.1, 129.4, 127.8, 118.6, 62.5, 42.7, 35.9, 32.5, 32.3, 26.4, 23.5, 23.4 (quint., *J* = 18.8 Hz); IR (neat): $\tilde{\nu}$ = 3323 (br), 2929, 2859, 2187, 2100, 1593, 1561, 1472, 1396, 1350, 1258, 1207, 1131, 1052, 1030, 906, 870, 816, 684, 658 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 325 (65), 323 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}D_2{}^{35}Cl_2O$ + Na): 323.0914; found: 323.0902; calcd for ($C_{16}H_{18}D_2{}^{35}Cl^{37}ClO$ + Na): 325.0885; found: 325.0884.

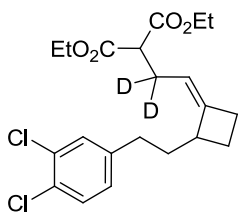
Compound 6. A solution of DMSO (61 µL, 0.863 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of $(COCl)_2$ (37 µL, 0.432 mmol) in CH_2Cl_2 (3 mL) at -78 °C under N_2. After stirring for 10 minutes at this temperature, a solution of **6f** (100 mg, 0.332 mmol) in CH_2Cl_2 (1 mL) was added via canula. After stirring for 15 minutes at -78 °C, Et_3N (0.23 mL, 1.66 mmol) was added via syringe. After stirring for 30 minutes at r.t., the mixture was quenched with a saturated solution of NH_4Cl (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 70/1 → 30/1 → 15/1) gave **7** as colourless oil (65 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.73 (t, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 6.97 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.08–5.03 (m, 1H), 2.89–2.77 (m, 1H), 2.62–2.44 (m, 4H), 2.41 (s, 2H), 2.06 (dtd, *J* = 10.9, 9.0, 5.4 Hz, 1H), 1.83 (ddt, *J* = 13.4, 9.5, 6.3 Hz, 1H), 1.62 (dtd, *J* = 13.5, 9.1, 6.0 Hz, 1H), 1.57–1.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.4, 145.8, 142.7, 132.0, 130.3, 130.1, 129.5, 127.9, 116.9, 43.6, 42.7, 35.8, 32.5, 26.4, 23.5, 20.1 (quint, *J* = 19.8 Hz); IR (neat): $\tilde{\nu}$ = 3027, 2918, 2856, 2820, 2720, 2197, 2111, 1722, 1593, 1561, 1472, 1395, 1350, 1327, 1257, 1208, 1131, 1071, 1030, 872, 817, 705, 684, 660 cm^{-1}; MS (CI): *m/z* (rel. intensity): 320 (13), 318 (65), 316 (100); HRMS (CI) calcd for ($C_{16}H_{16}D_2{}^{35}Cl_2O$ + H): 299.0933; found: 299.0937.



Compound 4b. This compound was prepared from **4a** (324 mg, 1.034 mmol) according to the procedure described for the preparation of **6b**. Colourless oil (217 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 6.97 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.32–5.27 (m, 1H), 3.02–2.93 (m, 1H), 2.70–2.61 (m, 1H), 2.60–2.49 (m, 2H), 2.45 (ddd, *J* = 13.8 Hz, 10.3, 6.8 Hz, 1H), 2.10 (dtd, *J* = 11.0, 9.1, 6.9 Hz, 1H), 1.94–1.85 (m, 1H), 1.76 (dtd, *J* = 13.4, 10.0, 5.0 Hz, 1H), 1.69–1.62 (m, 1H(OH)), 1.62–1.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.9, 142.5, 132.1, 130.3, 130.2, 129.7, 127.9, 120.3, 58.6 (quint., *J* = 21.9 Hz), 42.3, 36.2, 32.5, 28.3, 22.8; IR (neat): $\tilde{\nu}$ = 3321 (br), 2937, 2857, 2187, 2096, 1694, 1593, 1562, 1473, 1396, 1348, 1208, 1131, 1070, 1030, 969, 951, 872, 817, 703, 686, 659 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 297 (81), 295 (100) [M + Na]; HRMS (ES+) calcd for ($C_{14}H_{14}D_2{}^{35}Cl_2O$ + Na): 295.0601; found: 295.0601; calcd for ($C_{14}H_{14}D_2{}^{35}Cl^{37}ClO$ + Na): 297.0572; found: 297.0569.



Compound 4d. Intermediate allylic bromide **4c** was prepared from **4b** (315 mg, 1.15 mmol) according to the procedure described for the preparation of **6c**. Compound **4d** was then prepared from 9c according to the procedure described for the preparation of **6d**. Colourless oil (353 mg, 74% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.01–4.96 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 1H), 3.01–2.91 (m, 1H), 2.66–2.54 (m, 2H), 2.52–2.42 (m, 2H), 2.07 (dtd, *J* = 11.0, 9.1, 7.0 Hz, 1H), 2.01–1.92 (m, 1H), 1.73 (dtd, *J* = 13.4, 10.4, 4.9 Hz, 1H), 1.61–1.53 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125



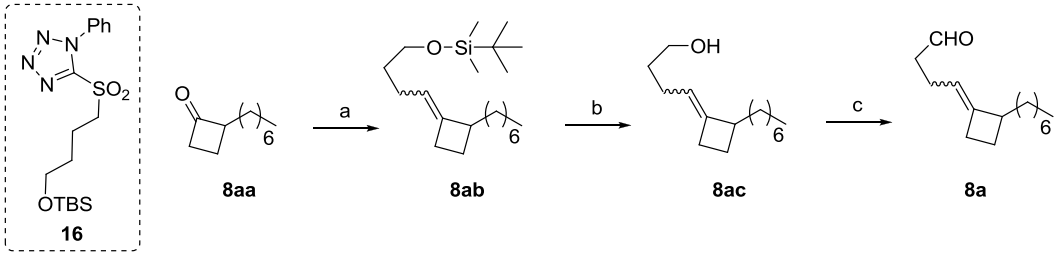
MHz, $CDCl_3$): δ = 169.0 (2C), 145.8, 142.5, 131.9, 130.2, 130.1, 129.4, 127.8, 116.6, 61.22, 61.16, 52.1, 42.0, 35.4, 32.4, 28.0, 26.9 (quint., *J* = 19.4 Hz), 22.5, 14.0 (2C); IR (neat): $\tilde{\nu}$ = 2979, 2938, 2856, 1730, 1590, 1562, 1473, 1393, 1368, 1319, 1209, 1175, 1151, 1131, 1096, 1030, 942, 868, 818, 686, 659 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 439 (65), 437 (100); HRMS (ES+) calcd for ($C_{21}H_{24}D_2{}^{35}Cl_2O_4$ + Na): 437.1231; found: 437.1215; calcd for ($C_{21}H_{24}D_2{}^{35}Cl^{37}ClO_4$ + Na): 439.1202; found: 439.1184.

Compound 4e. This compound was prepared from **4d** (353 mg, 0.85 mmol) according to the procedure described for the preparation of **6e**. Colourless oil (242 mg, 71%). Under these conditions, partial isomerisation of the C–C double bond was observed (*E*/*Z*, 4:96). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.03–4.98 (m, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.01–2.90 (m, 1H), 2.66–2.54 (m, 4H), 2.27 (s, 2H), 2.07 (dtd, *J* = 11.0, 9.1, 6.9 Hz, 1H), 1.99–1.90 (m, 1H), 1.73 (dtd, *J* = 13.4, 10.2, 4.9 Hz, 1H), 1.61–1.52 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.2, 143.9, 142.6, 132.0, 130.2, 130.0, 129.5, 127.8, 119.3, 60.2, 42.0, 35.6, 34.5, 32.5, 28.0, 23.1 (quint., *J* = 19.9 Hz), 22.6, 14.2; IR (neat): $\tilde{\nu}$ = 2967, 2937, 2856, 2203, 2106, 1732, 1593, 1563, 1473, 1395, 1369, 1339, 1263, 1182, 1130, 1030, 949, 871, 817, 706, 686, 659 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 367 (67), 365 (100) [M + Na]; HRMS (ES+) calcd for ($C_{18}H_{20}D_2{}^{35}Cl_2O_2$ + Na): 365.1020; found: 365.1019; calcd for ($C_{18}H_{20}D_2{}^{35}Cl^{37}ClO_2$ + Na): 367.0991; found: 367.1001.

Compound 4f. This compound was prepared from **4e** (240 mg, 0.699 mmol) according to the procedure described for the preparation of **6f**. Colourless oil (128 mg, 61%, *Z* isomer only). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.07–5.02 (m, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 3.01–2.89 (m, 1H), 2.67–2.55 (m, 2H), 2.54–2.42 (m, 2H), 2.08 (dtd, *J* = 11.1, 9.2, 7.0 Hz, 1H), 2.01–1.90 (m, 1H), 1.74 (dtd, *J* = 13.5, 10.1, 5.0 Hz, 1H), 1.63–1.51 (m, 3H), 1.28–1.17 (m, 1H(OH)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 142.7, 132.0, 130.2, 130.1, 129.5, 127.8, 120.8, 62.5, 42.1, 35.6, 32.7, 32.5, 28.0, 23.8 (quint., *J* = 19.0 Hz), 22.7; IR (neat): $\tilde{\nu}$ = 3320 (br), 2933, 2861, 2187, 2106, 1593, 1562, 1473, 1396, 1347, 1259, 1208, 1131, 1051, 1030, 949, 907, 871, 816, 732, 686, 659 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 325 (67), 323 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}D_2{}^{35}Cl_2O$ + Na): 323.0914; found: 323.0916; calcd for ($C_{16}H_{18}D_2{}^{35}Cl^{37}ClO$ + Na): 325.0885; found: 325.0898.

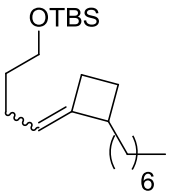
Compound 4. This compound was prepared from **4f** (54 mg, 0.179 mmol) according to the procedure described for the preparation of **6**. Colourless oil (35 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.74 (t, *J* = 1.5 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.02–4.97 (m, 1H), 3.00–2.90 (m, 1H), 2.65–2.59 (m, 2H), 2.53–2.43 (m, 2H), 2.42 (s, 2H), 2.09 (dtd, *J* = 11.0, 9.1, 6.9 Hz, 1H), 1.99–1.89 (m, 1H), 1.75 (dtd, *J* = 13.5, 10.2, 5.0 Hz, 1H), 1.63–1.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.3, 144.2, 142.6, 132.1, 130.3, 130.2, 129.6, 127.8, 119.1, 43.9, 42.1, 35.6, 32.5, 28.1, 22.6, 20.4 (quint., *J* = 19.7 Hz); IR (neat): $\tilde{\nu}$ = 2936, 2856, 2820, 2719, 2208, 2106, 1724, 1593, 1560, 1473, 1396, 1322, 1257, 1204, 1131, 1077, 1030, 956, 872, 819, 685, 658 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 355 (60), 353 (100) [M + MeOH + Na]; HRMS (ES+) calcd for ($C_{16}H_{16}D_2{}^{35}Cl_2O$ + MeOH + Na): 353.1020; found: 353.1022; calcd for ($C_{16}H_{16}D_2{}^{35}Cl^{37}ClO$ + MeOH + Na): 355.0991; found: 355.0997.

Preparation of compound 8a

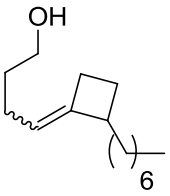


[a] **16**, NaHMDS, THF, –78 °C to r.t.; 51%. [b] TBAF, THF; 95%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 84%.

Compound 8ab. Sodium bis(trimethylsilyl)amide (320 mg, 1.8 mmol) was added as solid in one portion under N_2 to a solution of **16** (653 mg, 1.65 mmol)[1] and **8aa** (252 mg, 1.5 mmol)[2] in THF (21 mL) at –78 °C. The mixture was slowly allowed to warm to room temperature overnight while stirring by maintaining the flask dipped in the dry ice bath. The mixture was quenched with a saturated solution of NH_4Cl (10 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (petroleum ether/EtOAc, 150:1) gave **8ab** as a colorless oil (180 mg, 51%, partially inseparable mixture of *E*/*Z* isomers, ratio = 7:3). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 5.09–5.03 (m, 0.7H), [5.03–4.97 (m, 0.3H)], [3.59 (t, *J* = 6.5 Hz, 0.6H)], 3.58 (t, *J* = 6.5 Hz, 1.4H), [2.94–2.86 (m, 0.3H)], 2.85–2.76 (m, 0.7H), 2.62–2.40 (m, 2H), 2.07–1.98 (m, 1H), [1.95 (q, *J* = 7.5 Hz, 0.6H)], 1.90 (q, *J* = 7.5 Hz, 1.4H), 1.69–1.38 (m, 5H), 1.37–1.15 (m, 10H), 0.88 (s, 9H), 0.86 (t, *J* = 6.7 Hz, 3H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 145.2, [143.7], [120.4], 118.3, [62.8], 62.7, 43.7, [42.8], 34.7, [34.4], [33.4], 33.0, 31.9, [29.75], 29.73, [29.40], 29.35, [28.1], 27.15, [27.11], 26.4, 26.0 (3C), [24.5], 24.0, 23.9, [22.9], 22.7, 18.3, 14.1, -5.3 (2C); IR (neat): $\tilde{\nu}$ = 2955, 2925, 2855, 1463, 1254, 1099, 834, 773 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{42}OSi$ + Na): 361.2903; found: 361.2915.



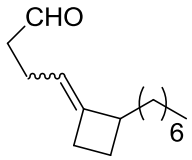
Compound 8ac. TBAF (1.64 mL, 1.64 mmol (1M in THF)) was added via syringe to a solution of **8ab** (503 mg, 1.49 mmol) in THF (15 mL) at 0 °C under N_2. After stirring for 1h at room temperature, the mixture was quenched with a saturated solution of NH_4Cl (5 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (petroleum ether/EtOAc, 15:1 → 12:1 → 10:1 → 7:1) gave two fractions of colourless oil (150 mg, *E*/*Z* = 10:1 and 168 mg, *E*/*Z* = 1:1, 95% combined) which enabled the attributions of peaks to each isomers in the NMR spectra. ^{1}H NMR (500 MHz, $CDCl_3$): (isomer *E*) δ = 5.08 (tq, *J* = 7.3, 2.4 Hz, 1H), 3.68–3.59 (m, 2H), 2.85–2.76 (m, 1H), 2.56–2.42 (m, 2H), 2.03 (ddt, *J* = 11.0, 5.4, 8.9 Hz, 1H), 1.95 (q, *J* = 7.3 Hz, 2H), 1.59 (quint, *J* = 6.9 Hz, 2H), 1.55–1.45 (m, 2H), 1.36–1.12 (m, 11H), 0.86 (t, *J* = 7.0 Hz, 3H); characteristic signals of *Z* isomer: δ = 5.02 (tq, *J* = 7.5, 2.2 Hz, 1H), 2.95–2.85 (m, 1H), 2.63–2.50 (m, 2H), 1.99 (q, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 145.8, [144.3], [120.1], 118.0, 62.79, [62.77], 43.6, [42.8], 34.6, [34.4], [33.0], 32.6, 31.9, [29.71], 29.68, [29.4], 29.3, [28.1], 27.09, [27.07], 26.4, [24.5], 24.2, 23.8, [22.8], 22.7, 14.1; IR (neat): $\tilde{\nu}$ = 3328 (br), 2922, 2853, 1456, 1054 cm^{-1}; MS (CI): *m*/*z* (rel. intensity): 242 (39) [M + NH_4], 225 (25) [M + H], 207 (12), 85 (100); elemental analysis (%) calcd for $C_{15}H_{28}O$: C 80.29, H 12.58; found: C 80.17, H 12.47.



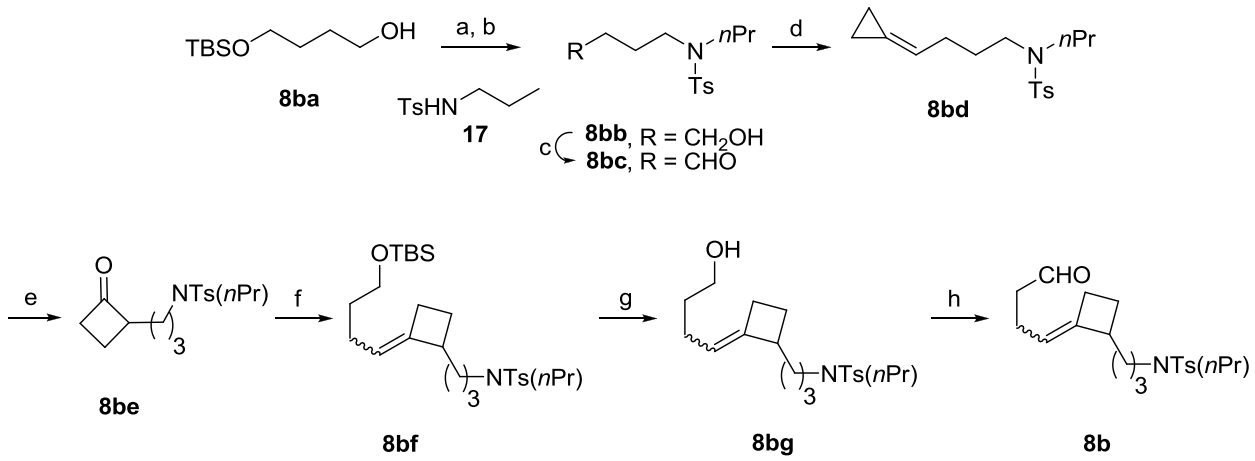
[2] Nemoto, H.; Shiraki, M.; Fukumoto, K. *J. Org. Chem.* **1996**, *61*, 1347.

[3] Underlined chemical shifts are common to the *E* and *Z* isomers. Chemical shifts attributed to the *Z* isomer are given in brackets.

Compound 8a. This compound was obtained from **8ac** (224 mg, 1 mmol) using the Swern procedure followed for the preparation of **6**. (Colourless oil, 186 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = [9.75 (t, *J* = 1.7 Hz, 0.4H)], 9.73 (t, *J* = 1.8 Hz, 0.6H), 5.04 (tq, *J* = 7.2, 2.4 Hz, 0.6H), [4.97 (tq, *J* = 7.4, 2.1, 0.4H)], [2.95–2.87 (m, 0.4H)], 2.85–2.76 (m, 0.6H), [2.63–2.44 (m, 1.2H)], 2.56–2.46 (m, 1.2H), 2.45–2.40 (m, 1.2H), [2.30–2.20 (m, 0.8H)], 2.21–2.15 (m, 1.2H), 2.08–1.97 (m, 1H), [1.70–1.59 (m, 0.4H)], 1.55–1.48 (m, 0.6H), [1.47–1.36 (m, 0.4H)], 1.34–1.14 (m, 12H), 0.89–0.82 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 202.7, [202.5], 146.8, [145.4], [118.3], 116.2, [44.2], 43.8, 43.6, [42.7], 34.5, [34.3], [31.9], 31.8, [29.67], 29.64, [29.33], 29.27, 27.0, 26.3, 23.7, [22.7], 22.6, [21.0], 20.8, 14.1; IR (neat): $\tilde{\nu}$ = 2923, 2853, 2715, 1727, 1465, 1388, 1047, 821, 723 cm^{-1}; MS (CI): *m*/*z* (rel. intensity): 240 (100) [M + NH_4], 223 (74) [M + H], 205 (31), 95 (25); elemental analysis (%) calcd for $C_{15}H_{26}O$: C 81.02, H 11.79; found: C 81.16, H 12.41.

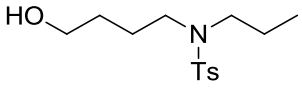


Preparation of compound 8b



[a] PPh_3, **17**, DEAD, THF, 0 °C to r.t.. [b] TBAF, THF; 40% over two steps. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 90%. [d] 1) $BrCH_2CH_2CH_2PPH_3$,Br, *t*BuONa, THF, reflux; 2) **8bd**, reflux; 45%. [e] 1) mCPBA, CH_2Cl_2, 0 °C to r.t.; 2) LiI, CH_2Cl_2, reflux; 55%.[f] **16**, NaHMDS, THF, –78 °C to r.t.; 50%. [g] TBAF, THF; 93%. [h] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 93%.

Compound 8bb. A solution of commercially available **8ba** (1.5g, 7.35 mmol) in THF (5 mL) was added via canula to a solution of PPh_3 (2.12 g, 8.09 mmol) and **17** (1.73 g, 8.09 mmol) in THF (70 mL) at 0 °C under N_2. Then diethyldiazodicarboxylate (DEAD) (1.27 mL, 8.09 mmol) was added via syringe within 2 minutes. After stirring overnight at r.t., all volatiles were evaporated and purification by flash chromatography (PE/EtOAC, 20/1 → 15/1 → 10/1 → 7/1 → 4/1) gave 1.36 g of colourless oil which immediately dissolved in THF (10 mL) and treated at 0 °C with TBAF (3.6 mL). After stirring for 1h, the mixture was quenched with a saturated solution of NH_4Cl (10 mL) and diluted with EtOAc (30 mL). The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 3/1 → 2/1 → 1/1) gave **8bb** as a pale yellow oil (828 mg, 40% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 3.13–3.08 (m, 2H), 3.06–3.01 (m, 2H), 2.39 (s, 3H), 2.06–1.95 (m, 1H(*OH*)), 1.67 (m, 2H), 1.57–1.47 (m, 4H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.9, 136.8, 129.5 (2C), 126.9 (2C), 62.1, 50.0, 48.0, 29.5, 25.2, 21.9, 21.4, 11.1; IR (neat): $\tilde{\nu}$ = 3480 (br), 2935, 2875, 1598, 1494, 1459, 1381, 1331, 1152, 1089, 1002, 845, 727 cm^{-1}; HRMS (ES+) calcd for ($C_{14}H_{23}NO_3S$ + Na): 308.1296; found: 308.1291.



Compound 8bc. This compound was obtained from **8bb** (800 mg, 2.81 mmol) using the Swern procedure followed for the preparation of **6**. Purification by flash chromatography (PE/EtOAc, 3/1) gave **8bc** as a pale yellow oil (717 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.78–9.76 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 3.06–3.00 (m, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.85 (quint., *J* = 7.1 Hz, 2H), 1.56–1.47 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.4, 143.1, 136.6, 129.6 (2C), 127.0 (2C), 50.5, 47.4, 40.6, 21.9, 21.4, 21.2, 11.1; IR (neat): $\tilde{\nu}$ = 2966, 2935, 2876, 2726, 1721, 1598, 1494, 1459, 1333, 1154, 1089, 980, 815, 731 cm^{-1}; HRMS (ES+) calcd for ($C_{14}H_{21}NO_3S$ + Na): 306.1140; found: 306.1140; elemental analysis (%) calcd for $C_{14}H_{21}NO_3S$: C 59.34, H 7.47, N 4.94; found: C 58.70, H 7.42, N 5.46.

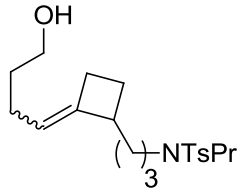
Compound 8bd. *t*-BuONa (485 mg, 5.05 mmol) was added as solid in 3 portions at room temperature and under N_2 to a solution of 3-(bromopropyl)triphenylphosphonium bromide (1.17 g, 2.53 mmol) in THF (15 mL). Then, the suspension was heated to reflux for 2 hours (oil bath temperature = 74 °C), before adding a solution of **8bc** (650 mg, 2.27 mmol) in THF (2 mL) via canula. After 2.5 hours heating, the crude mixture was quenched at room temperature with H_2O (5 mL). The aqueous layer was extracted with ethyl acetate (2 × 20 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc: 200/1 → 10/1 → 3/1) gave compound **8bd** as colorless oil (312 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.72– 5.66 (m, 1H), 3.12–3.00 (m, 4H), 2.39 (s, 3H), 2.13 (q, *J* = 7.3 Hz, 2H), 1.65 (quint., *J* = 7.7 Hz, 2H), 1.57–1.48 (m, 2H), 1.03–0.94 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.8, 137.0, 129.5 (2C), 127.0 (2C), 122.0, 116.8, 50.0, 48.0, 29.0, 28.3, 22.0, 21.4, 11.1, 2.1, 1.8; IR (neat): $\tilde{\nu}$ = 2971, 2934, 2875, 1599, 1494, 1459, 1337, 1154, 1090, 962, 814, 730 cm^{-1}; HRMS (ES+) calcd for ($C_{16}H_{25}NO_2S$ + Na): 330.1504; found: 330.1505.

Compound 8be. mCPBA (202 mg, 1.18 mmol) was added as solid in one portion to a solution of **8bd** (300 mg, 0.98 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After stirring at r.t. for 20 hours, the mixture was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. This material was diluted in CH_2Cl_2 (1 mL) and LiI (5 mg, 0.037 mmol) was added under N_2. After heating at reflux for 3h, the mixture was diluted with CH_2Cl_2, washed with brine and concentrated. Purification by flash chromatography (PE/EtOAc, 4/1) gave **8be** as a colorless oil (172 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.29– 3.19 (m, 1H), 3.12–2.95 (m, 5H), 2.92–2.82 (m, 1H), 2.39 (s, 3H), 2.15 (qd, *J* = 10.6, 5.2 Hz, 1H), 1.67–1.54 (m, 4H), 1.54–1.44 (m, 3H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 211.5, 143.0, 136.8, 129.6 (2C), 127.0 (2C), 59.7, 50.1, 47.9, 44.4, 26.6, 26.2, 21.9, 21.4, 16.8, 11.1; IR (neat): $\tilde{\nu}$ = 2967, 2932, 2875, 1773, 1598, 1494, 1459, 1335, 1154, 1089, 960, 815, 719 cm^{-1}; HRMS (ES+) calcd for ($C_{16}H_{25}NO_3S$ + Na): 346.1453; found: 346.1447.

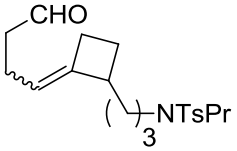
Compound 8bf. This compound was obtained from **8be** (160 mg, 0.49 mmol), using the procedure described for the preparation of **8ab**. Purification by flash chromatography (PE/EtOAc, 15/1) gave **8bf** as a inseparable mixture of *E* and *Z* isomers (6:4) (Colorless oil, 122 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.66 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 5.05–4.97 (m, 1H), 3.61–3.53 (m, 2H), 3.10–3.00 (m, 4H), [2.91–2.83 (m, 0.4H)], 2.82–2.73 (m, 0.6 H), 2.60–2.42 (m, 2H), 2.39 (s, 3H), 2.06–1.96 (m, 1H), 1.95–1.85 (m, 2H), 1.63–1.25 (m, 9H), 0.871 (s, 5H), [0.865 (s, 4H)], 0.85 (t, *J* = 7.3 Hz, 3H), 0.02 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 144.3, 142.8, [142.7], 137.1, 129.5 (2C), 127.1 (2C), [120.9], 118.8, [62.7], 62.6, [50.0], 49.9, [48.34], 48.25, 43.0, [42.1], [33.2], 32.9, 31.6, [31.3], [28.0], 26.33, [26.30], 26.2, 25.9 (3C), [24.4], 24.0, 23.6, [22.7], [21.99], 21.95, 21.4, [18.30], 18.28, 11.2, -5.3 (2C); IR (neat): $\tilde{\nu}$ = 2929, 2856, 1599, 1495, 1463, 1341, 1253, 1157, 1091, 1040, 1020, 1005, 959, 834, 814, 774, 724 cm^{-1}; HRMS (ES+) calcd for ($C_{27}H_{47}NO_3SSi$ + Na): 516.2944; found: 516.2956.

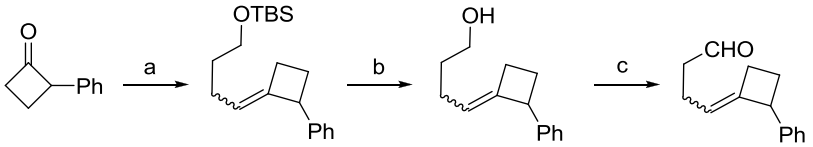
Compound 8bg. This compound was obtained from 11bf (144 mg, 0.292 mmol) using the procedure described for the preparation of **8ac**. Purification by flash chromatography (PE/EtOAc, 4/1 → 3/1) gave **8bg** as an inseparable mixture of *E* and *Z* isomers (6:4) (colorless oil, 103 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.65 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 5.08–4.98 (m, 1H), 3.66–3.54 (m, 2H), 3.15–2.98 (m, 4H), [2.95–2.86 (m, 0.4H)], 2.83–2.73 (m, 0.6 H), 2.61–2.40 (m, 2H), 2.38 (s, 3H), 2.06–1.85 (m, 4H), [1.70–1.61 (m, 0.4H)], 1.60–1.39 (m, 8H), 1.34–1.25 (m, 0.6H), 0.89–0.78 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 144.6, [143.03], [142.85], 142.8, 136.93, [136.89], [129.46 (2C)], 129.44 (2C), 126.94 (2C), [126.92 (2C)], [120.7], 118.5, [62.4], 62.3, [49.9], 49.8, [48.3], 48.2, 42.9, [42.1], [32.9], 32.5, 31.4, [31.3], [27.9], 26.3, 26.1, [26.0], [24.4], 24.0, 23.5, [22.5], 21.9, 21.3, 11.1; IR (neat): $\tilde{\nu}$ = 3403 (br), 2932, 2874, 1598, 1494, 1457, 1379, 1334, 1305, 1153, 1090, 1042, 1020, 960, 814, 724 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{33}NO_3S$ + Na): 402.2079; found: 402.2075.



Compound 8b. This compound was obtained from **8bg** (100 mg, 0.263 mmol) using the Swern procedure followed for the preparation of **6**. Purification by flash chromatography (PE/EtOAc, 10/1) gave **8b** as an inseparable mixture of *E* and *Z* isomers (6:4) (colorless oil, 92 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = [9.73–9.71 (m, 0.4H)], 9.71–9.69 (m, 0.6H), 7.66–7.60 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 5.03–4.93 (m, 1H), 3.12–2.97 (m, 4H), [2.93–2.83 (m, 0.4H)], 2.71–2.59 (m, 0.6H), 2.59–2.34 (m, 4H), 2.37 (s, 3H), 2.25–2.11 (m, 2H), 2.06–1.94 (m, 1H), [1.66–1.57 (m, 0.4H)], 1.56–1.36 (m, 6H), 1.34–1.23 (m, 0.6H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 202.45, [202.38], 145.8, [144.4], [142.84], 142.81, 136.9, [129.47 (2C)], 129.45 (2C), 127.0 (2C), [118.9], 116.8, [50.0], 49.9, [48.3], 48.2, [44.0], 43.7, 42.8, [42.0], 31.3, [31.1], [27.9], 26.3, [26.2], 26.1, 23.4, [22.5], [21.93], 21.89, 21.4, [20.9], 20.6, 11.1; IR (neat): $\tilde{\nu}$ = 2934, 2875, 2722, 1722, 1599, 1494, 1459, 1381, 1336, 1154, 1090, 1041, 1020, 993, 960, 815, 724 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 432 (54) [M + MeOH +Na], 400 (100) [M + Na]; HRMS (ES+) calcd for ($C_{21}H_{31}NO_3S$ + Na): 400.1922; found: 400.1905.



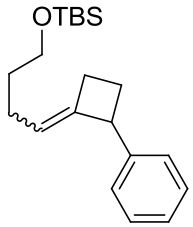
Preparation of compound 8c



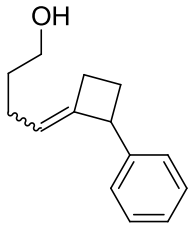
8ca **8cb** **8cc** **8c**

[a] **16**, LiHMDS, toluene, –78 °C to r.t.; 66%. [b] TBAF, THF; 90%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 55–63%.

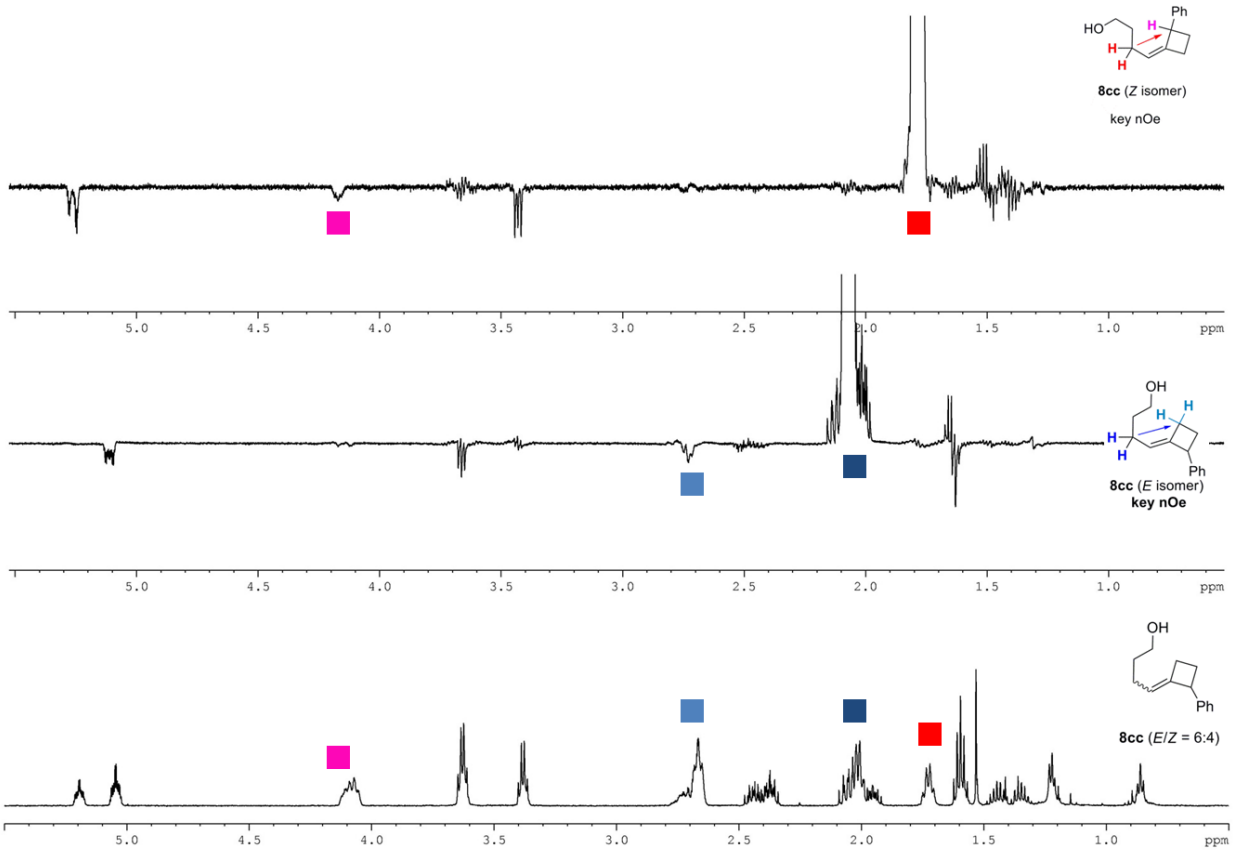
Compound 8cb. Lithium bis(trimethylsilyl)amide (327 mg, 2.01 mmol) was added as solid in one portion under N_2 to a solution of **16** (650 mg, 1.64 mmol)[1] and commercially available **8ca** (184 mg, 1.26 mmol) in toluene (12 mL) at –78 °C. The mixture was slowly allowed to warm to room temperature overnight while stirring by maintaining the flask dipped in the dry ice bath. The mixture was quenched with a saturated solution of NH_4Cl (10 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (petroleum ether/EtOAc, 50:1) gave **8cb** as an inseparable mixture of *E* and *Z* isomers (1:1) (Colorless oil, 265 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.31–7.23 (m, 4H), 7.19–7.14 (m, 1H), [5.20 (tq, *J* = 7.4, 2.3 Hz, 0.5H], 5.03 (tq, *J* = 7.4, 2.5 Hz, 0.5H), 4.13–4.02 (m, 1H), 3.58 (t, *J* = 6.6 Hz, 1H), [3.41 (dt, *J* = 10.2, 6.8 Hz, 0.5H)], [3.35 (dt, *J* = 10.1, 6.6 Hz, 0.5H)], [2.77–2.61 (m, 1H)], 2.68–2.62 (m, 1H), [2.43 (dtd, *J* = 11.3, 9.4, 6.4 Hz, 0.5H)], 2.37 (ddt, *J* = 10.8, 9.3, 6.9 Hz, 0.5H), 2.08–1.93 (m, 1.5H), [1.91 (ddt, *J* = 11.2, 10.1, 6.1 Hz, 0.5H)], [1.76–1.68 (m, 0.5H)], [1.66–1.58 (m, 0.5H)], 1.53 (quint., *J* = 7.0 Hz, 1H), 1.43–1.32 (m, 0.5H), 0.87 (s, 4.5H), [0.82 (s, 4.5H)], 0.02 (s, 3H), [-0.04 (s, 1.5H)], [-0.05 (s, 1.5H)]; ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = [144.5], 143.8, 143.3, [141.7], [128.3 (2C)], 128.2 (2C), 127.4 (2C), [127.2 (2C)], 126.0, [125.9], [122.4], 120.7, [62.8], 62.6, 48.6, [47.7], 32.8, [32.6], [28.3], [27.1], 26.8, 26.4, 26.0 (3C), [25.9 (3C)], [24.1], 24.0, 18.32, [18.28], -5.28 (2C), [-5.33 (2C)]; IR (neat): $\tilde{\nu}$ = 3062, 3027, 2950, 2929, 2856, 1603, 1494, 1472, 1463, 1388, 1361, 1254, 1097, 1031, 1006, 963, 939, 833, 773, 697, 661, 597, 542, 531, 522 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 339 (100); HRMS (ES+) calcd for ($C_{20}H_{32}OSi$ + Na): 339.2120; found: 339.2117.

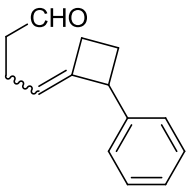


Compound 8cc. This compound was obtained from **8cb** (348 mg, 1.1 mmol) using the procedure followed for the preparation of **8ac**. Partial separation by flash chromatography (petroleum ether/Et_2O, 10/1 → 3/1) and purification by preparative TLC (petroleum ether/EtOAc, 3/1) gave two fractions of **8cc**, both as colorless oil: 1) *E*/*Z* = 3:1 (147 mg, 66%), 2) *Z* isomer only (54 mg, 24%). This enabled the attribution of NMR signals for *E* and *Z* isomers for **8cc** and the mixture of isomers of **8cb**. ^{1}H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 7.25–7.21 (m, 4H), 7.20–7.15 (m, 1H), 5.05 (tq, *J* = 7.4, 2.5 Hz, 1H), 4.10–4.03 (m, 1H), 3.63 (q, *J* = 6.2 Hz, 2H), 2.76–2.62 (m, 2H), 2.37 (ddt, *J* = 11.0, 9.3, 6.9 Hz, 1H), 2.10–1.98 (m, 3H), 1.60 (quint., *J* = 6.9 Hz, 2H), 1.22 (t, *J* = 5.4 Hz, 1H(OH)); (*Z* isomer) δ = 7.31–7.26 (m, 4H), 7.20–7.15 (m, 1H), 5.19 (tq, *J* = 7.5, 2.3 Hz, 1H), 4.14–4.08 (m, 1H), 3.38 (q, *J* = 6.0 Hz, 2H), 2.80–2.62 (m, 2H), 2.44 (dtd, *J* = 11.3, 9.4, 6.3 Hz, 1H), 1.95 (ddt, *J* = 11.3, 10.1, 6.7 Hz, 1H), 1.77–1.68 (m, 2H), 1.49–1.40 (m, 1H), 1.39–1.30 (m, 1H), 0.86 (t, *J* = 5.9 Hz, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 143.9, 143.5, 128.2 (2C), 127.3 (2C), 126.0, 120.3, 62.5, 48.6, 32.4, 26.7, 26.2, 24.1; (*Z* isomer) δ = 144.5, 142.6, 128.4 (2C), 127.2 (2C), 126.0, 122.1, 62.3, 47.8, 32.2, 28.3, 26.9, 23.8; IR (neat): $\tilde{\nu}$ = 3343 (br), 3061, 3026, 2938, 2876, 1699, 1602, 1492, 1452, 1047, 1031, 917, 868, 837, 758, 744, 698 cm^{-1}; MS (CI): *m/z* (rel. intensity): 220 (100) [M + NH_4], 203 (15) [M + H], 85 (23); elemental analysis (%) calcd for $C_{14}H_{18}O$: C 83.12, H 8.97; found: C 83.57, H 9.11.



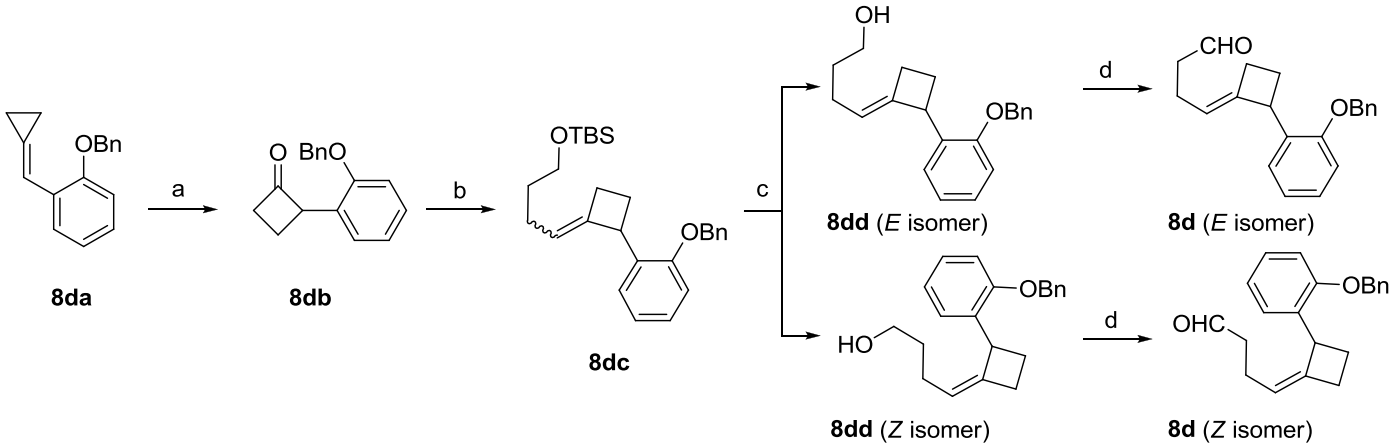
The geometry of the olefin in **8cc** was confirmed on a *E*/*Z* (6:4) mixture by nOe experiments.



Compound 8c. Two batches of this compound were obtained by Swern oxidation of alcohol **8cb**: 1) a *E*/*Z* (3:1) mixture (pale yellow oil, 81 mg, 55%), 2) the pure *Z* isomer (colourless oil, 28 mg, 63%). 

^{1}H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 9.74 (t, *J* = 1.7 Hz, 1H), 7.24–7.21 (m, 4H), 7.20–7.15 (m, 1H), 5.01 (tq, *J* = 7.3, 2.5 Hz, 1H), 4.10–4.03 (m, 1H), 2.76–2.62 (m, 2H), 2.44 (td, *J* = 7.2, 1.8 Hz, 2H), 2.38 (ddt, *J* = 11.0, 9.3, 6.9 Hz, 1H), 2.29–2.23 (m, 2H), 2.06 (dtd, *J* = 10.8, 8.9, 8.0 Hz, 1H); (*Z* isomer) δ = 9.49 (t, *J* = 1.9 Hz, 1H), 7.31–7.24 (m, 4H), 7.20–7.15 (m, 1H), 5.18 (tq, *J* = 7.5, 2.2 Hz, 1H), 4.15–4.08 (m, 1H), 2.78–2.62 (m, 2H), 2.44 (dtd, *J* = 11.2, 9.4, 6.4 Hz, 1H), 2.29–2.12 (m, 2H), 2.04–1.89 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 202.3, 145.2, 143.2, 128.3 (2C), 127.3 (2C), 126.1, 118.6, 48.6, 43.6, 26.7, 26.1, 20.7; (*Z* isomer) δ = 202.4, 144.2, 143.9, 128.5 (2C), 127.2 (2C), 126.2, 120.3, 47.8, 43.4, 28.3, 26.9, 20.6; IR (neat): $\tilde{\nu}$ = 3058, 3026, 2947, 2916, 2851, 2825, 2719, 1724, 1601, 1493, 1454, 1408, 1389, 1078, 1031, 838, 747, 700 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 255 (100) [M + MeOH + Na]; HRMS (ES+) calcd for ($C_{14}H_{17}O$ + MeOH + Na): 255.1361; found: 255.1357.

Preparation of compound 8d



[a] mCPBA, CH_2Cl_2, r.t.; 45%. [b] **16**, NaHMDS, THF, –78 °C to r.t.; 39%. [c] TBAF, THF, then separation by preparative TLC; 22% (*E*) + 16% (*Z*). [d] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 47% (*E*); 56% (*Z*).

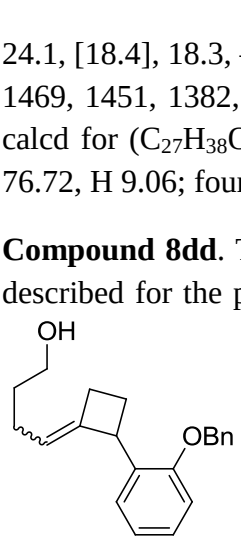
Compound 8db. mCPBA (3.35g, 14.7 mmol, 75% w/w) was added in one portion to **8da**[4] (2.89 g, 12.3 mmol) in CH_2Cl_2 (45 mL). After stirring for 2h at r.t., the mixture was quenched carefully with a saturated solution of $NaHCO_3$ (30 mL) and diluted with CH_2Cl_2 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (15 mL). The combined organic layers were washed with brine (10 mL), dired over Na_2SO_4, filtered and concentrated. Purification by flash chromatography after solid deposition (petroleum ether/EtOAc, 15/1 → 10/1) gave **8db** as a white solid (1.38 g, 45%). m.p.: 56–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.35 (m, 4H), 7.34–7.30 (m, 1H), 7.23–7.18 (m, 1H), 7.12 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.89 (td, *J* = 7.4, 1.0 Hz, 1H), 5.02 (s, 2H), 4.46 (ddt, *J* = 10.6, 8.1, 2.5 Hz, 1H), 3.01 (dddd, *J* = 18.1, 10.3, 7.9, 2.3 Hz, 1H), 2.80 (dddd, *J* = 17.6, 9.7, 4.8, 2.8 Hz, 1H), 2.34 (qd, *J* = 10.7, 4.9 Hz, 1H), 2.21 (ddt, *J* = 10.8, 9.7, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.3, 156.5, 136.5, 129.5, 128.6, 128.5 (2C), 128.1, 127.8 (2C), 126.1, 120.8, 111.7, 70.3, 62.0, 44.9, 18.1; IR (neat): $\tilde{\nu}$ = 3058, 3028, 2997, 2952, 2920, 2886, 1779, 1597, 1583, 1491, 1467, 1454, 1381, 1336, 1295, 1264, 1233, 1211, 1180, 1158, 1117, 1078, 1034, 1009, 960, 918, 882, 854, 811, 765, 747, 730, 695 cm^{-1}; MS (CI): *m/z* (rel. intensity): 270 (100), 253 (9); HRMS (CI) calcd for ($C_{17}H_{16}O_2$ + NH_4): 270.1489; found: 270.1488; elemental analysis (%) calcd for $C_{17}H_{16}O_2$: C 80.93, H 6.39; found: C 80.73, H 6.41.

Compound 8dc. This compound was obtained from **8db** (504 mg, 2 mmol) according the procedure described for **8ab**. Colorless oil (316 mg, 39%, mixture of *E* and *Z* isomers (7:3)). ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.47–7.42 (m, 2H), 7.41–7.36 (m, 3H), 7.35–7.29 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), [5.27 (tq, *J* = 7.4, 2.3 Hz, 0.3H)], 5.12 (tq, *J* = 7.5, 2.3 Hz, 0.7H), 5.07 (s, 2H), 4.59–4.45 (m, 1H), 3.62 (t, *J* = 6.6 Hz, 1.4H), [3.50–3.42 (m, 0.6H)], [2.77–2.57 (m, 0.6H)], 2.69–2.62 (m, 1.4H), [2.53–2.44 (m, 0.3H)], 2.46–2.35 (m, 0.7H), 2.06–1.94 (m, 2.1H), [1.90–1.82 (m, 0.3H)], [1.81–1.70 (m, 0.6H)], 1.57 (quint., *J* = 7.0 Hz, 1.4H), [1.46 (quint., *J* = 7.0 Hz, 0.6H)], 0.90 (s, 6.3H), [0.84 (s, 2.7H)], 0.052 (s, 2.1H), 0.051 (s, 2.1H), [–0.02 (s, 0.9H)], [–0.03 (s, 0.9H)]; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.3, [155.9], 142.5, [141.1], 137.5, [132.7], 132.6, 128.5 (2C), 127.7, 127.67, [127.62], 127.4, 127.1 (2C), 127.0, [122.5], 121.1, 120.7, 111.6, [111.5], 69.9, [69.8], [62.9], 62.8, 42.5, [41.7], 32.9, [32.7], [28.1], 26.6, [26.2], 26.0 (3C), [25.9 (3C)], 25.7, [24.3],

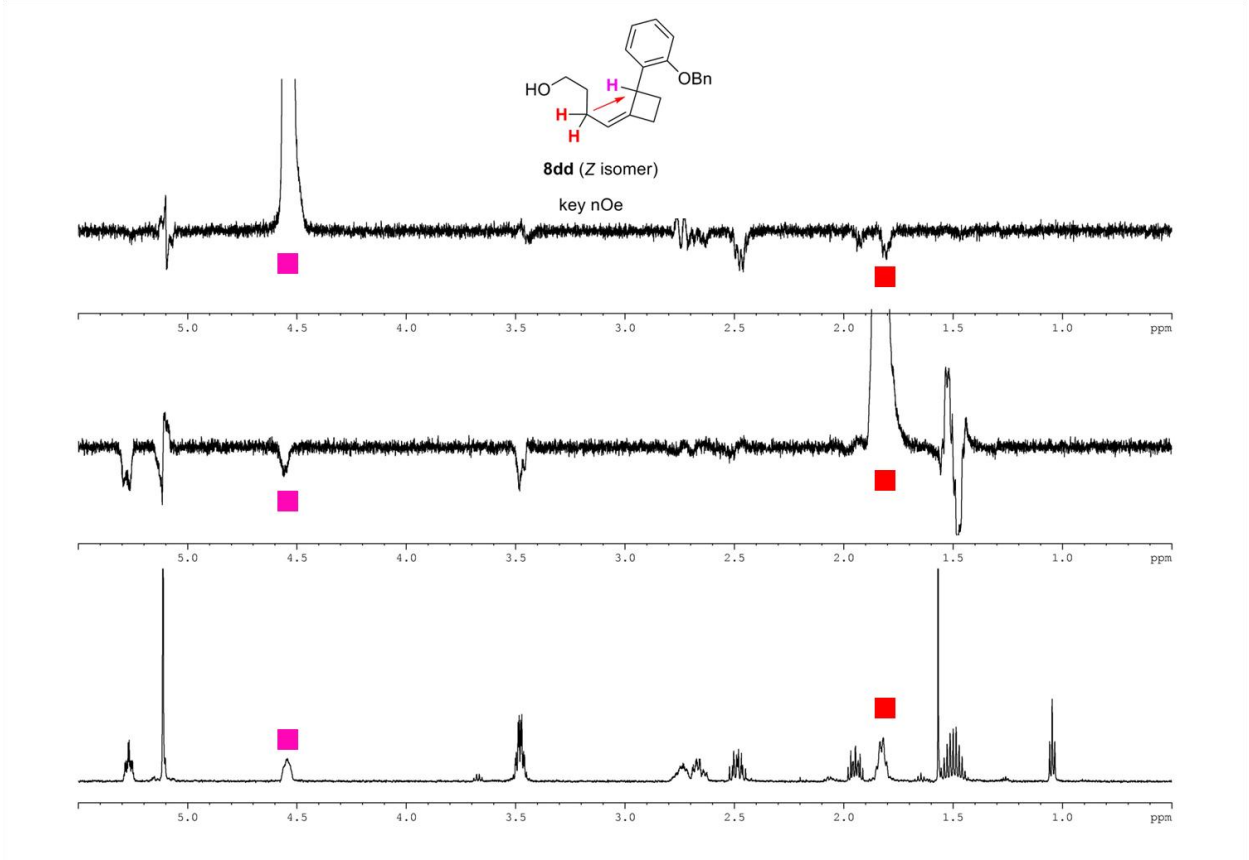
[4] Shi, M.; Liu, L. P.; Tang, J. *J. Am. Chem. Soc.* **2006**, *128*, 7430.

24.1, [18.4], 18.3, –5.25 (2C), [–5.31 (2C)]; IR (neat): $\tilde{\nu}$ = 3064, 3028, 2942, 2929, 2857, 1599, 1583, 1490, 1469, 1451, 1382, 1360, 1285, 1241, 1100, 1052, 1026, 963, 835, 812, 775, 750, 696 cm^{-1}; HRMS (ES+) calcd for ($C_{27}H_{38}O_2Si$ + Na): 445.2539; found: 445.2522; elemental analysis (%) calcd for $C_{27}H_{38}O_2Si$: C 76.72, H 9.06; found: C 76.51, H 9.11.

Compound 8dd. This compound was prepared from **8dc** (475 mg, 1.16 mmol) according to the procedure described for the preparation of **8ac**. Purification by flash chromatography (petroleum ether/EtOAc, 5.5/1) followed by preparative TLC (petroleum ether/EtOAc, 4:1 (2 migrations)) gave 2 fractions (77 mg, 22%, *E*/*Z* = 20:1) and (56 mg, 16%, *E*/*Z* = 1:14), both obtained as colorless oils. ^{1}H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 7.42–7.39 (m, 2H), 7.38–7.34 (m, 3H), 7.32–7.27 (m, 1H), 7.18–7.12 (m, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.11 (tq, *J* = 7.5, 2.5 Hz, 1H), 5.06 (s, 2H), 4.53–4.45 (m, 1H), 3.62 (q, *J* = 6.1 Hz, 2H), 2.69–2.58 (m, 2H), 2.38 (ddt, *J* = 10.7, 9.7, 7.2, 1H), 2.06–1.97 (m, 3H), 1.60 (quint., *J* = 6.9 Hz, 2H), 1.21 (t, *J* = 5.1 Hz, 1H(OH)); (*Z* isomer) δ = 7.44 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.36–7.29 (m, 2H), 7.18 (td, *J* = 7.8, 1.7 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.24 (tq, *J* = 7.4, 2.3 Hz, 1H), 5.08 (s, 2H), 4.56–4.48 (m, 1H), 3.44 (td, *J* = 6.4, 2.4 Hz, 2H), 2.77–2.67 (m, 1H), 2.67–2.59 (m, 1H), 2.46 (dtd, *J* = 11.1, 9.5, 6.8 Hz, 1H), 1.92 (tt, *J* = 10.9, 6.0 Hz, 1H), 1.85–1.74 (m, 2H), 1.55–1.39 (m, 2H), 1.37–1.21 (m, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 156.2, 143.1, 137.3, 132.3, 128.4 (2C), 127.6, 127.4, 127.04 (2C), 127.01, 120.7, 120.6, 111.5, 69.8, 62.6, 42.6 ,32.4, 26.6, 25.4, 24.2; (*Z* isomer) δ = 155.8, 142.1, 137.3, 132.6, 128.5 (2C), 127.73, 127.66, 127.13 (2C), 127.10, 122.0, 120.8, 111.6, 69.9, 62.5, 41.5, 32.4, 28.1, 25.9, 24.1; IR (neat): $\tilde{\nu}$ = 3334 (br), 3063, 3033, 2934, 2866, 1598, 1585, 1489, 1449, 1380, 1330, 1288, 1237, 1161, 1110, 1049, 1024, 914, 848, 813, 749, 695 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{24}O_2$ + Na): 331.1674; found: 331.1679; elemental analysis (%) calcd for $C_{21}H_{24}O_2$: C 81.78, H 7.84; found: C 81.45, H 7.85.



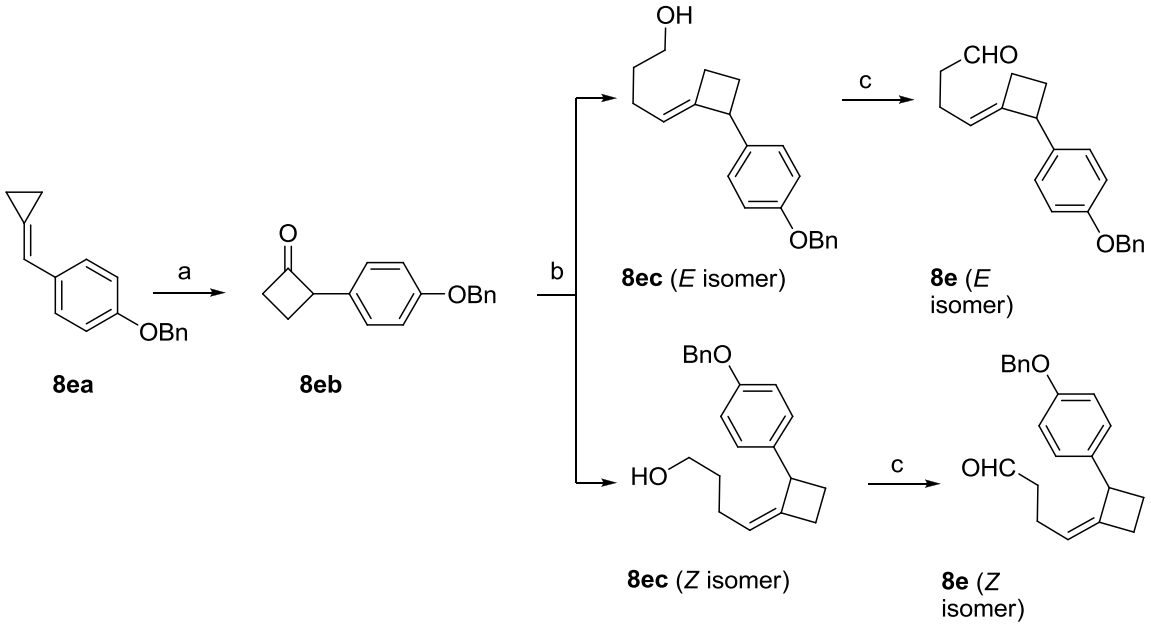
The geometry of the olefin in **8dd** was confirmed on the *Z* isomer by nOe experiments.



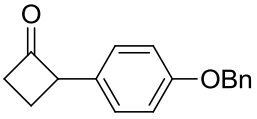
Compound 8d (*E* isomer). This compound was obtained from the *E* isomer of **8dd** (77 mg, 0.25 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (36 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.74 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.39–7.35 (m, 2H), 7.34–7.27 (m, 2H), 7.15 (td, *J* = 7.8, 1.8 Hz, 1H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (dd, *J* = 8.2, 0.8 Hz, 1H), 5.07 (tq, *J* = 7.3, 2.5 Hz, 1H), 5.05 (s, 2H), 4.53–4.45 (m, 1H), 2.69–2.61 (m, 2H), 2.43 (td, *J* = 7.1, 1.7 Hz, 2H), 2.38 (ddt, *J* = 10.9, 9.5, 7.1 Hz, 1H), 2.30–2.23 (m, 2H), 2.07–1.97 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.4, 156.2, 144.3, 137.3, 131.9, 128.4 (2C), 127.6, 127.4, 127.1, 127.0 (2C), 120.6, 118.8, 111.5, 69.8, 43.6, 42.6, 26.6, 25.3, 20.8; IR (neat): $\tilde{\nu}$ = 3063, 3033, 2941, 2917, 2856, 2825, 2721, 1721, 1598, 1585, 1489, 1450, 1382, 1330, 1289, 1237, 1161, 1110, 1050, 1024, 912, 852, 750, 696 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{22}O_2$: C 82.32, H 7.24; found: C 81.65, H 7.18.

Compound 8d (*Z* isomer). This compound was obtained from the *Z* isomer of **8dd** (56 mg, 0.18 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (31 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.53 (t, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.35–7.29 (m, 2H), 7.17 (dt, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.22 (tq, *J* = 7.4, 2.3 Hz, 1H), 5.07 (s, 2H), 4.58–4.46 (m, 1H), 2.77–2.672 (m, 1H), 2.667–2.57 (m, 1H), 2.46 (dtd, *J* = 11.5, 9.6, 6.8 Hz, 1H), 2.35–2.18 (m, 2H), 2.09–2.01 (m, 2H), 1.92 (t, *J* = 10.8, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.6, 155.8, 143.5, 137.3, 132.3, 128.5 (2C), 127.8, 127.6, 127.21, 127.15 (2C), 120.8, 120.1, 111.7, 69.9, 43.5, 41.5, 28.1, 25.9, 20.8; IR (neat): $\tilde{\nu}$ = 3064, 3032, 2942, 2918, 2856, 2721, 1722, 1598, 1585, 1489, 1450, 1407, 1381, 1319, 1288, 1236, 1178, 1161, 1108, 1050, 1024, 935, 915, 853, 751, 696 cm^{-1}; MS (ES+): *m/z* (rel. intensity): 361 (100) [M + MeOH + Na], 329 (33) [M + Na]; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$ + Na): 329.1517; found: 329.1531; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$ + MeOH + Na): 361.1780; found: 361.1778.

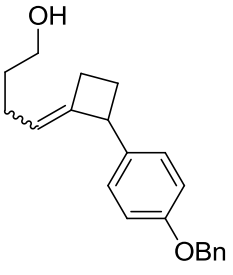
Preparation of compound 8e



[a] mCPBA, CH_2Cl_2, r.t.; 65%. [b] 1) **16**, NaHMDS, THF, –78 °C to r.t.; 2) TBAF, THF, then separation; 43% over two steps. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 71% (*E*); 74% (*Z*).



Compound 8eb.This compound was obtained from **8ea**[5] (2.75 g, 11.65 mmol) according to the procedure described for the preparation of **8db**. White solid (1.9 g, 65%). m.p.: 40–43 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.1 Hz, 2H), 7.39–7.34 (m, 2H), 7.33–7.31 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.03 (s, 2H), 4.45 (ddt, *J* = 10.6, 8.2, 2.5 Hz, 1H), 3.19 (dddd, *J* = 18.8, 10.7, 8.3, 2.4 Hz, 1H), 3.00 (dddd, *J* = 17.5, 9.8, 4.9, 2.6 Hz, 1H), 2.50 (qd, *J* = 10.7, 4.9 Hz, 1H), 2.16 (ddt, *J* = 11.2, 9.8, 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.2, 157.7, 136.9, 128.9, 128.5 (2C), 128.0, (2C), 127.8, 127.3 (2C), 114.9 (2C), 69.9, 63.8, 44.6, 17.9; IR (neat): $\tilde{\nu}$ = 3057, 3035, 2984, 2904, 2864, 1762, 1610, 1580, 1509, 1469, 1455, 1400, 1378, 1335, 1298, 1243, 1225, 1210, 1175, 1112, 1072, 1014, 993, 970 ,929, 916, 906, 857, 821, 759, 743, 695 cm^{-1}; HRMS (ES+) calcd for ($C_{17}H_{16}O_2$ + Na): 275.1048; found: 275.1049; elemental analysis (%) calcd for $C_{17}H_{16}O_2$: C 80.93, H 6.39; found: C 80.76, H 6.42.

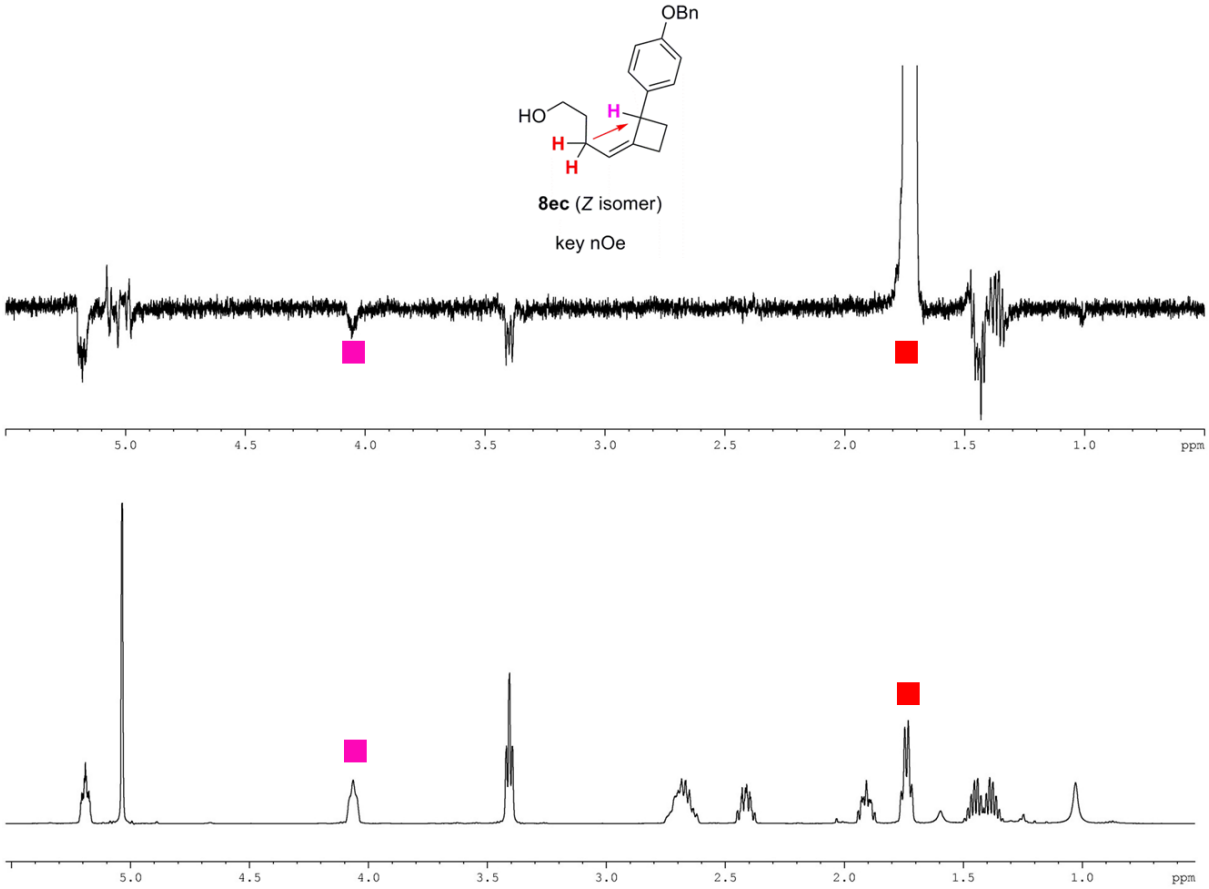


Compound 8ec. This compound was obtained from **8eb** (400 mg, 1.58 mmol) according the procedures described for **8ab** and **8ac**. *E* (90 mg, 18%) and *Z* (72 mg, 14%) isomers of **8ec** could be separated by flash chromatography (petroleum ether/EtOAc, 4:1) and were both obtained as white solids. A fraction of mixture of *E* and *Z* isomers was also obtained (57 mg, 11%). *E* isomer, m.p.: 29–31 ºC; *Z* isomer, m.p.: 31–34 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 7.43 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33– 7.29 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.08–5.00 (m, 1H), 5.04 (s, 2H), 4.07–4.01 (m, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.72–2.60 (m, 2H), 2.42–2.31 (m, 1H), 2.08–1.95 (m, 3H), 1.60 (quint., *J* = 6.8 Hz, 2H), 1.50–1.34 (m, 1H(OH)); (*Z* isomer) δ = 7.42 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33– 7.29 (m, 1H), 7.19 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 2H), 5.16 (tq, *J* = 7.5, 2.3 Hz, 1H), 5.03 (s, 2H), 4.10–4.03 (m, 1H), 3.41 (t, *J* = 6.4 Hz, 2H), 2.76–2.60 (m, 2H), 2.46–2.37 (m, 1H), 1.95–1.86 (m, 1H), 1.74 (q, *J* = 7.3 Hz, 2H), 1.45 (dquint., *J* = 13.7, 6.8 Hz, 1H), 1.37 (dquint., *J* = 13.8, 6.9 Hz, 1H), 1.10–0.95 (m, 1H (OH)); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 157.2, 144.6,

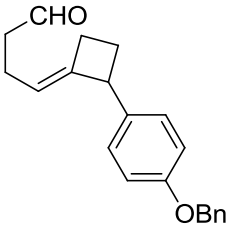
[5] Fürstner, A.; Aïssa, C. *J. Am. Chem. Soc.* **2006**, *128*, 6306.

137.2, 136.1, 128.5 (2C), 128.3 (2C), 127.9, 127.4 (2C), 120.0, 114.6 (2C), 70.0, 48.0, 32.5, 26.7, 26.5, 24.1; (*Z* isomer) δ = 157.1, 143.1, 137.2, 137.0, 128.5 (2C), 128.2 (2C), 127.9, 127.5 (2C), 121.9, 114.8 (2C), 70.0, 62.5, 47.1, 32.4, 28.3, 27.1, 23.8; IR (neat): $\tilde{\nu}$ = 3340 (br), 3032, 2936, 1609, 1581, 1508, 1454, 1380, 1300, 1278, 1236, 1174, 1110, 1039, 1024, 914, 858, 825, 734, 695 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{24}O_2$ + Na): 331.1674; found: 331.1683; elemental analysis (%) calcd for $C_{21}H_{24}O_2$: C 81.78, H 7.84; found: C 80.64, H 7.68.

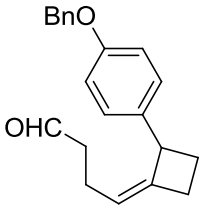
The geometry of the olefin in **8ec** was confirmed on the *Z* isomer by nOe experiments.



Compound 8e (*E* isomer). This compound was obtained from the *E* isomer of **8ec** (126 mg, 0.43 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (94 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.74 (t, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.39–7.34 (m, 2H), 7.33–7.31 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.03 (s, 2H), 4.99 (tq, *J* = 7.4, 2.5 Hz, 1H), 4.04–3.97 (m, 1H), 2.68–2.61 (m, 2H), 2.44 (td, *J* = 7.3, 1.7 Hz, 2H), 2.35 (ddt, *J* = 10.9, 9.2, 6.8 Hz, 1H), 2.31–2.25 (m, 2H), 2.10–1.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.3, 157.2, 145.7, 137.2, 135.7, 128.5 (2C), 128.3 (2C), 127.8, 127.4 (2C), 118.3, 114.6 (2C), 70.0, 47.9, 43.6, 26.7, 26.4, 20.7; IR (neat): $\tilde{\nu}$ = 3043, 2942, 2721, 1721, 1609, 1581, 1508, 1454, 1382, 1301, 1282, 1236, 1174, 1110, 1016, 913, 857, 826, 735, 696 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 361 (100) [M + MeOH + Na], 329 (57) [M + Na]; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$ + Na): 329.1517; found: 329.1530.

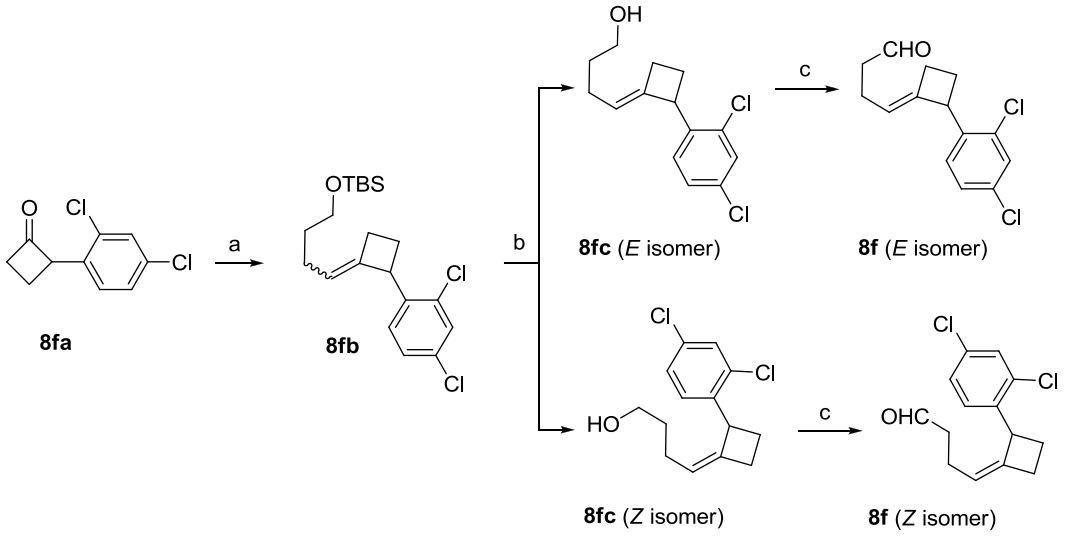


Compound 8e (Z isomer). This compound was obtained from the *Z* isomer of **8ec** (88 mg, 0.29 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (65 mg, 74%).



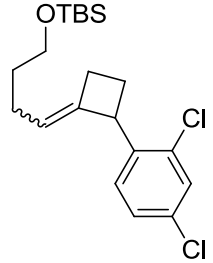
^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.52–9.50 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.33–7.29 (m, 1H), 7.17 (d, *J* = 9.1 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.16 (tq, *J* = 7.5, 2.3 Hz, 1H), 5.03 (s, 2H), 4.11–4.02 (m, 1H), 2.75–2.59 (m, 2H), 2.41 (dtd, *J* = 11.1, 9.4, 6.3 Hz, 1H), 2.28–2.13 (m, 2H), 2.05–1.92 (m, 2H), 1.96–1.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.4, 157.2, 144.4, 137.1, 136.6, 128.5 (2C), 128.2 (2C), 127.9, 127.4 (2C), 120.0, 114.8 (2C), 70.0, 47.1, 43.4, 28.2, 27.1, 20.5; IR (neat): $\tilde{\nu}$ = 3032, 2945, 2721, 1721, 1609, 1580, 1508, 1454, 1382, 1299, 1272, 1233, 1174, 1110, 1023, 915, 858, 826, 734, 695 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 361 (100) [M + MeOH + Na], 329 (40) [M + Na]; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$ + Na): 329.1517; found: 329.1503.

Preparation of compound 8f



[a] **16**, LiHMDS, toluene, –78 °C to r.t.; 75%. [b] TBAF, THF; then separation: *E* isomer (48%) + *Z* isomer (34%). [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; *E* isomer (71%), *Z* isomer (79%).

Compound 8fb. This compound was prepared from **8fa**[6] (271 mg, 1.26 mmol) according to the procedure described for the preparation of **8cb**. Purification by flash chromatography (petroleum ether/EtOAc, 200/1 → 150/1 → 50/1 → 15/1) gave **8fb** as an equimolar mixture of *E* and *Z* isomers (360 mg, 75%). Colorless oil.

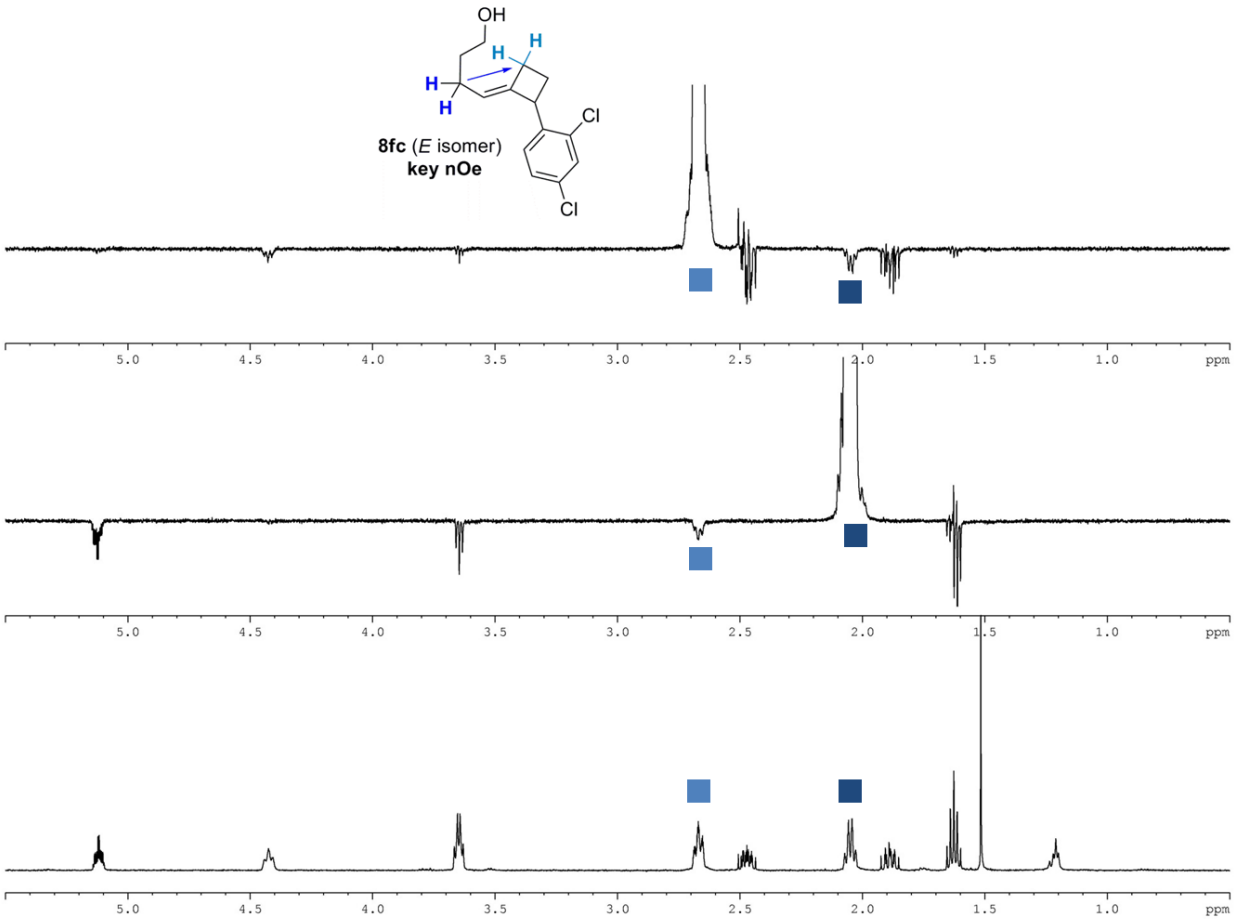


^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.39 (d, *J* = 8.4 Hz, 0.55H), 7.33 (d, *J* = 2.4 Hz, 1H), [7.31 (d, *J* = 8.4 Hz, 0.45H)], 7.19–7.15 (m, 1H), [5.32 (tq, *J* = 7.4, 2.3 Hz, 0.45H)], 5.11 (tq, *J* = 7.4, 2.5 Hz, 0.55H), 4.45–4.36 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 1.1H), [3.47 (t, *J* = 6.6 Hz, 0.9H)], 2.76–2.59 (m, 2H), [2.57–2.49 (m, 0.45H)], 2.51–2.42 (m, 0.55H), 2.06–1.95 (m, 1.1H), 1.91–1.81 (m, 0.55H), [1.78–1.65 (m, 1.35H)], 1.56 (quint., *J* = 6.9 Hz, 1.1H), [1.44 (quint., *J* = 7.1 Hz, 0.9H)], 0.88 (s, 5H), [0.82 (s, 4H)], 0.03 (s, 3.3H), [-0.03 (s, 1.4H)],[-0.04 (s, 1.4H)]; ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 140.7, [140.0], [139.9], 139.3, 134.4, [134.0], 132.1, [129.04], 129.01, [128.9], 128.8, [127.0], 126.9, [123.8], 122.6, [62.7], 62.6, 44.9, [43.9], 32.7, [32.5], [27.8], 26.4, [26.2], 26.0 (3C), [25.9 (3C)], [24.6], 24.2, 18.33, [18.27], -5.3 (2C), [-5.4 (2C)]; IR (neat): $\tilde{\nu}$ = 2952, 2928, 2856, 1588, 1558, 1470, 1384, 1361, 1254, 1098, 1049, 1006, 964, 939, 865, 833, 810, 773 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 409 (72), 407 (100) [M + Na], 387 (36), 385 (51) [M + H]; HRMS (ES+) calcd for ($C_{20}H_{30}{}^{35}Cl_2SiO$+ Na): 407.1341; found: 407.1326.

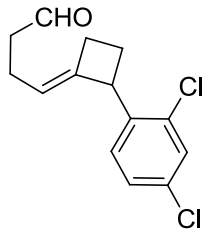
[6] Schweinitz, A.; Chtchemelimine, A.; Orellana, A. *Org. Lett.* **2011**, *13*, 232.

Compound 8fc. This compound was obtained from **8fb** (360 mg, 0.94 mmol) according the procedure described **8ac**. Purification by flash chromatography (petroleum ether/EtOAc, 10/1 → 5/1) enabled partial separation of *E* (123 mg, 48%) and *Z* (87 mg, 34%) isomers of **8fc**, both obtained as colorless oils. ^{1}H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 7.37 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.12 (tq, *J* = 7.4, 2.5 Hz, 1H), 4.46–4.39 (m, 1H), 3.65 (q, *J* = 6.0 Hz, 2H), 2.71–2.62 (m, 2H), 2.51–2.43 (m, 1H), 2.09–2.01 (m, 2H), 1.89 (dtd, *J* = 11.1, 8.8, 7.5 Hz, 1H), 1.63 (quint., *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 5.6 Hz, 1H(OH)); (*Z* isomer) δ = 7.35 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.32 (tq, *J* = 7.4, 2.3 Hz, 1H), 4.46–4.37 (m, 1H), 3.52 (q, *J* = 6.1 Hz, 2H), 2.77–2.61 (m, 2H), 2.54 (dtd, *J* = 11.3, 9.3, 7.1 Hz, 1H), 1.81–1.72 (m, 3H), 1.57–1.45 (m, 2H), 1.10 (t, *J* = 5.3 Hz, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 141.3, 139.7, 134.3, 132.1, 129.0, 128.7, 122.1, 62.5, 44.8, 32.4, 26.4, 25.7, 24.2; (*Z* isomer) δ = 140.0, 134.1, 132.2, 129.1, 128.9, 127.0, 123.4, 62.5, 43.9, 32.3, 27.8, 26.1, 24.4; IR (neat): $\tilde{\nu}$ = 3318 (br), 2936, 1586, 1557, 1468, 1426, 1381, 1333, 1100, 1048, 916, 865, 841, 819, 809 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 295 (67), 293 (100) [M + Na]; HRMS (ES+) calcd for ($C_{14}H_{16}{}^{35}Cl_2O$+ Na): 293.0476; found: 293.0463.

The geometry of the olefin in **8fc** was confirmed on the *E* isomer by nOe experiments.

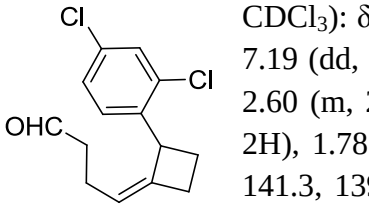


Compound 8f (*E* isomer). This compound was obtained from the *E* isomer of **8fc** (123 mg, 0.46 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (88 mg, 71%).

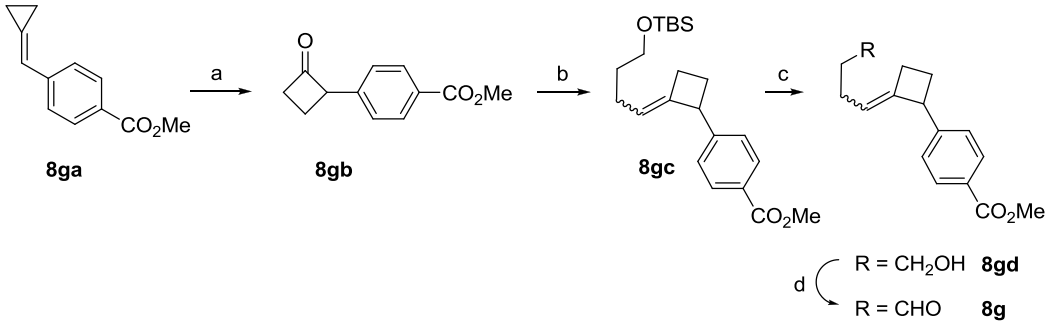


^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.76 (t, *J* = 1.6 Hz, 1H), 7.34 (d, *J* = 2.3 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.08 (tq, *J* = 7.2, 2.6 Hz, 1H), 4.45–4.38 (m, 1H), 2.73–2.64 (m, 1H), 2.52–2.44 (m, 3H), 2.33–2.24 (m, 2H), 1.90 (dtd, *J* = 11.1, 8.7, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.0, 142.5, 139.4, 134.3, 132.2, 129.0, 128.7, 127.0, 120.4, 44.8, 43.6, 26.5, 25.6, 20.8; IR (neat): $\tilde{\nu}$ = 2949, 2822, 2720, 1723, 1587, 1557, 1468, 1443, 1407, 1382, 1194, 1141, 1100, 1048, 865, 803 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 325 (66), 323 (100) [M + MeOH +Na], 293 (5), 291 (8) [M + Na]; HRMS (ES+) calcd for ($C_{14}H_{14}{}^{35}Cl_2O$+ Na): 291.0319; found: 291.0313.

Compound 8f (*Z* isomer). This compound was obtained from the *Z* isomer of **8fc** (85 mg, 0.31 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (66 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.63 (t, *J* = 1.7 Hz, 1H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.19 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.28 (tq, *J* = 7.4, 2.3 Hz, 1H), 4.46–4.40 (m, 1H), 2.77–2.60 (m, 2H), 2.54 (dtd, *J* = 11.2, 9.3, 7.1 Hz, 1H), 2.38–2.31 (m, 2H), 2.07–1.95 (m, 2H), 1.78 (ddt, *J* = 11.3, 10.1, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.9, 141.3, 139.6, 134.0, 132.3, 129.2, 128.8, 127.1, 121.6, 43.8, 43.3, 27.8, 26.1, 20.1; IR (neat): $\tilde{\nu}$ = 2949, 2824, 2720, 1724, 1586, 1557, 1468, 1440, 1407, 1382, 1194, 1143, 1100, 1048, 865, 819, 803 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 325 (61), 323 (100) [M + MeOH +Na], 293 (5), 291 (8) [M + Na]; HRMS (ES+) calcd for ($C_{14}H_{14}{}^{35}Cl_2O$ + MeOH + Na): 323.0582; found: 323.0569.

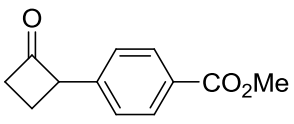


Preparation of compound 8g



[a] mCPBA, CH_2Cl_2, r.t.; 66%. [b] **16**, LiHMDS, toluene, –78 °C to r.t.; 37%. [c] TBAF, THF; 78%. [d] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 69%.

Compound 8gb. This compound was obtained from **8ga**[5] (0.90 g, 4.78 mmol) according to the procedure described for the preparation of **8db**. Pale yellow solid (0.65 g, 66%). m.p.: 78–80 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.58 (ddt, *J* = 10.5, 8.2, 2.3 Hz, 1H), 3.88 (s, 3H), 3.30–3.21 (m, 1H), 3.05 (dddd, *J* = 17.3, 9.7, 4.8, 2.4 Hz, 1H), 2.56 (qd, *J* = 10.8, 4.9 Hz, 1H), 2.26 (ddt, *J* = 11.0, 9.8, 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.6, 166.8, 141.4, 129.9 (2C), 128.7, 126.8 (2C), 64.2, 52.1, 44.9, 17.3; IR (neat): $\tilde{\nu}$ = 3000, 2954, 1780, 1717, 1610, 1572, 1509, 1435, 1010, 1313, 1275, 1180, 1108, 1069, 1019, 962, 851, 826, 769, 748, 724, 699 cm^{-1}; MS (CI): *m*/*z* (rel. intensity): 222 (100) [M + NH_4], 205 (10) [M + H], 162 (19), 131 (14); elemental analysis (%) calcd for $C_{12}H_{12}O_3$: C 70.57, H 5.92; found: C 69.29, H 6.00.

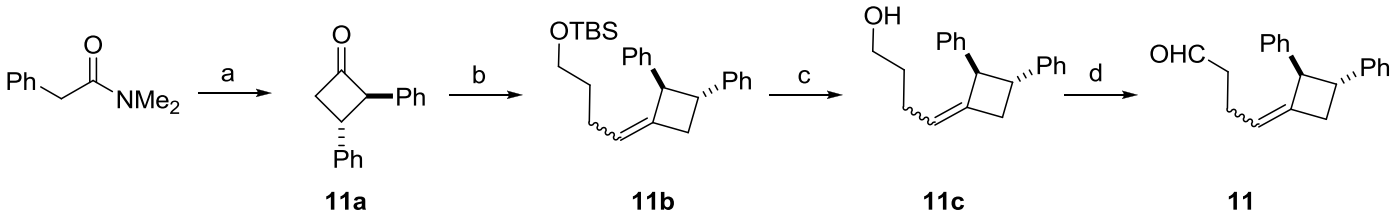


Compound 8gc. This compound was prepared from **8gb** (350 mg, 1.71 mmol) according to the procedure described for the preparation of **8cb**. Purification by flash chromatography (petroleum ether/Et_2O, 100/1 → 50/1) gave **8gb** as an equimolar mixture of *E* and *Z* isomers (242 mg, 37%). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.96–7.93 (m, 2H), 7.33–7.29 (m, 2H), [5.22 (tq, *J* = 7.4, 2.4 Hz, 0.5H)], 5.01 (tq, *J* = 7.6, 2.4 Hz, 0.5H), 4.17–4.09 (m, 1H), 3.89 (s, 3H), 3.57 (t, *J* = 6.5 Hz, 1H), [3.43–3.32 (m, 1H)], 2.78–2.64 (m, 2H), [2.46 (dtd, *J* = 11.3, 9.4, 6.5 Hz, 0.5H)], 2.39 (ddt, *J* = 10.9, 9.3, 7.0 Hz, 0.5H), 2.08–2.00 (m, 0.5H), 1.97 (q, *J* = 7.3 Hz, 1H), [1.91 (ddt, *J* = 11.2, 10.1, 6.6 Hz, 0.5H)], [1.72–1.55 (m, 1H)], 1.55–1.49 (m, 1H), [1.40–1.30 (m, 1H)], 0.87 (s, 4.5H), [0.80 (s, 4.5H)], 0.02 (s, 3H), [-0.05 (s, 1.5H)],[-0.06 (s, 1.5H)]; ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = 167.13, [167.10], [150.0], 149.2, 142.6, [140.8], [129.8 (2C)], 129.7 (2C), 127.9, [127.8], 127.4 (2C), [127.3 (2C)], [123.1], 121.4, 62.7, [62.6], 51.95, [51.92], 48.5, [47.6], 32.7, [32.4], [28.3], [27.0], 26.8, 26.1, 26.0 (3C), [25.9 (3C)], 24.2, [24.0], 18.31, [18.25], -5.3 (2C), [-5.4 (2C)]; IR (neat): $\tilde{\nu}$ = 2951, 2929, 2856, 1724, 1610, 1472, 1463, 1435, 1415, 1388, 1361, 1310, 1277, 1255, 1192, 1177, 1101, 1020, 1006, 965, 940, 835, 774, 705 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 397 (100) [M + Na]; HRMS (ES+) calcd for ($C_{22}H_{34}O_3$+ Na): 397.2175; found: 397.2186.

Compound 8gd. This compound was obtained from **8gc** (242 mg, 0.65 mmol) according the procedure described **8ac**. After purification by flash chromatography (petroleum ether/Et_2O, 3/1 → 2/1 → 1/1), a first batch of **8gd** (131 mg, 78%) was obtained as colourless oil (*E*/*Z* = 1:1.3). However, further attempts to separate the isomers led to partial decomposition and contamination by an unidentified compound. The data given below was obtained for a mixture of *E*/*Z* = 1:4, and this material was also used in the next step. ^{1}H NMR (500 MHz, $CDCl_3$): (*Z* isomer) δ = 7.94 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.23 (tq, *J* = 7.6, 2.3 Hz, 1H), 4.18–4.13 (m, 1H), 3.87 (s, 3H), 3.40 (t, *J* = 6.1 Hz, 2H), 2.79–2.64 (m, 2H), 2.50–2.42 (m, 1H), 1.92 (ddt, *J* = 11.2, 10.2, 6.6 Hz, 1H), 1.74–1.63 (m, 2H), 1.47–1.32 (m, 2H); characteristic signals of *E* isomer: δ = 7.30 (d, *J* = 8.6 Hz, 2H), 5.02 (tq, *J* = 7.4, 2.5 Hz, 1H), 4.15–4.09 (m, 1H), 3.61 (t, *J* = 6.1 Hz, 2H), 2.11–2.03 (m, 1H), 2.01 (q, *J* = 7.2 Hz, 2H), 1.62–1.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): (only *Z* isomer described for clarity) δ = 167.0, 149.9, 141.5, 129.8 (2C), 127.9, 127.2 (2C), 122.6, 62.4, 51.9, 47.5, 32.2, 28.3, 26.8, 24.0; IR (neat): $\tilde{\nu}$ = 3357 (br), 2947, 1719, 1608, 1571, 1434, 1415, 1309, 1276, 1191, 1177, 1104, 1048, 1019, 965, 918, 851, 826, 771 and 705 cm^{-1}; MS (CI): *m*/*z* (rel. intensity): 278 (100) [M + NH_4], 261 (43) [M + H], 229 (39), 85 (42).

Compound 8g. This compound was obtained from a *E*/*Z* = 1:4 mixture of **8gd** (27 mg, 0.10 mmol) using the Swern procedure followed for the preparation of **6**. Colorless oil (20 mg, 69% (*E*/*Z* = 1:4)). This reaction was repeated on similar scale with similar results using several batches of **8gd** (*E*/*Z* = 1:2 to 1:5). ^{1}H NMR (500 MHz, $CDCl_3$): (*Z* isomer) δ = 9.53–9.51 (m, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.19 (tq, *J* = 7.4, 2.3 Hz, 1H), 4.19–4.13 (m, 1H), 3.88 (s, 3H), 2.79–2.64 (m, 2H), 2.51–2.42 (m, 1H), 2.29–2.15 (m, 2H), 2.00–1.85 (m, 3H); characteristic signals of *E* isomer: δ = 9.74–9.72 (m, 1H), 7.29 (d, J = 8.6 Hz, 2H), 4.98 (tq, *J* = 7.3, 2.5 Hz, 1H), 4.13–4.08 (m, 1H), 2.11–2.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.1, [202.0], 167.04, [166.98], [149.5], 148.6, 144.3, [142.8], [129.9 (2C)], 129.7 (2C), [128.1], 127.3 (2C), [127.2 (2C)], 125.3, [120.9], 119.3, 52.0, 48.4, [47.6], 43.5, [43.2], [28.3], [26.83], 26.79, 25.9, 20.6, [20.5]; IR (neat): $\tilde{\nu}$ = 2950, 2846, 2720, 1718, 1609, 1572, 1435, 1415, 1310, 1277, 1177, 1104, 1019, 965, 852, 825, 773, 705 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 281 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}O_3$+ Na): 281.1154; found: 281.1154.

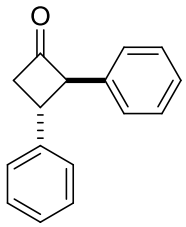
Preparation of compound (±)-11



11a **11b** **11c** **11**

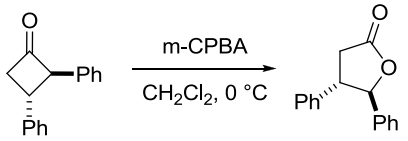
[a] *N*,*N*-Dimethyl-2-phenyl-acetamide, *sym*-collidine, styrene, Tf_2O, $CHCl_3$, reflux, 52%. [b] **16**, LiHMDS, toluene, –78 °C to r.t.; 49%. [c] TBAF, THF; 53%. [c] $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; 79–84%.

Compound 11a. This compound was prepared by slightly modifying the original procedure.[7] To a refluxing



mixture of *N*,*N*-Dimethyl-2-phenyl-acetamide[8] (0.485 g, 2.98 mmol), *sym*-collidine (0.47 mL, 3.55 mmol) and styrene (3.42 mL, 29.8 mmol) in $CHCl_3$ (10 mL) under argon was added Tf_2O (0.59 mL, 3.55 mmol) in $CHCl_3$ (20 mL) dropwise over 16 hours (*via* addition funnel). The reaction mixture was cooled to room temperature diluted with CH_2Cl_2 (50 mL) and water (50 mL). The biphasic mixture was stirred for 30 minutes, separated and the aqueous layer extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by flash column chromatography (petroleum ether/Et_2O, 40:1 → 10:1) gave racemic **11a** as a colourless oil (0.34 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.34 (m, 4H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.29-7.25 (m, 4H), 4.58 (d, *J* = 8.8 Hz, 1H), 3.82 (q, *J* = 8.9 Hz, 1H), 3.44 (ddd, *J* = 17.2, 8.8, 1.8 Hz, 1H), 3.37 (ddd, *J* = 17.2, 9.1, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.1, 142.4, 135.6, 128.8 (2C), 128.7 (2C), 127.3, 127.0 (2C), 126.9, 126.6 (2C), 71.5, 51.4, 36.8; IR (neat): $\tilde{\nu}$ = 3028, 2923, 1779, 1670, 1601, 1495, 1448, 1397, 1207, 1170, 1114, 1074, 1030, 953, 747, 697 cm^{-1}; MS (CI): *m/z* (rel. intensity): 240 (100) [M + NH_4], 223 (9) [M + H].

The relative configuration of the stereogenic centres in (±)-**11a** was established unambiguously after its Baeyer-Villiger oxidation into β,γ-Diphenylbutyrolactone (±)-**18** and by comparison to literature ^{1}H NMR data[9] {^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 6H), 7.19–7.13 (m, 4H), 5.41 (d, *J* = 8.5 Hz, 1H), 3.61–3.54 (m, 1H), 3.05 (dd, *J* = 17.5, 8.5 Hz, 1H) and 2.91 (dd, *J* = 17.5, 10.7 Hz, 1H)}.



(±)-**11a** (±)-**18**

[7] Falmagne, V. J-B.; Escudero, J.; Taleb-Sahraoui, S.; Ghosez, L. *Angew. Chem.* **1981**, *93*, 926.

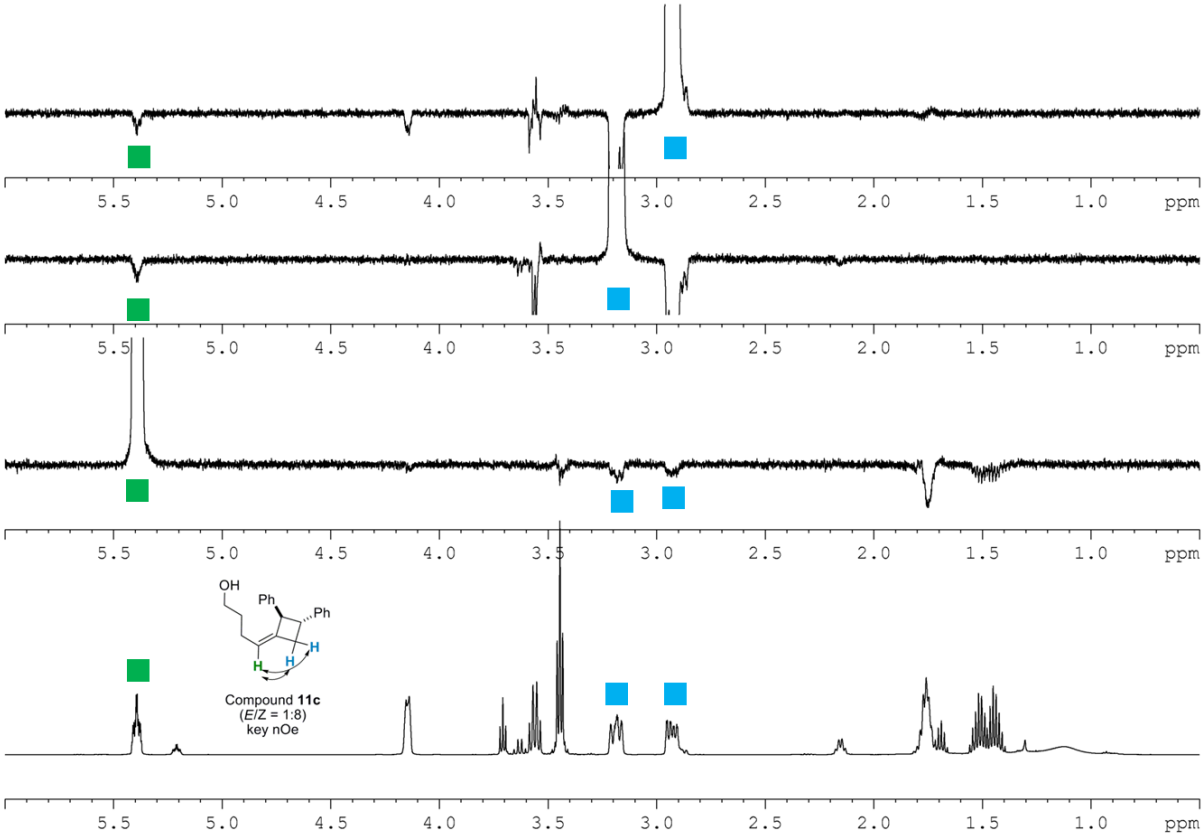
[8] Prepared according to Pintori, D.G.; Greaney, M.F. *Org. Lett.* **2011,** *13*, 5713.

[9] Pippel, D.J.; Curtis, M.D.; Du, H.; Beak, P. *J. Org. Chem.* **1998**, *63*, 2. For ^{1}H NMR data of the other diastereomer, see: Katritzky, A. R.; Feng, D.; Lang, H. *J. Org. Chem.* **1997**, *62*, 706.

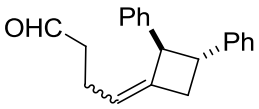
Compound 11b. This compound was prepared from **11a** (0.27 g, 1.21 mmol) according to the procedure described for the preparation of **8cb**. Purification by flash chromatography (petroleum ether/Et_2O, 100:1 → 50:1) gave (±)-**11b** as an inseparable mixture of *E* and *Z* isomers (232 mg, 49%, *E*/*Z* = 45:55). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$):[3] δ = 7.32–7.25 (m, 6H), 7.24–7.15 (m, 4H), [5.34 (tq, *J* = 7.5, 2.0 Hz, 0.55H)], 5.14 (tq, *J* = 7.4, 2.5 Hz, 0.45H), 4.13–4.03 (m, 1H), 3.62 (t, *J* = 6.6 Hz, 0.9H), 3.55 (q, *J* = 8.7 Hz, 0.45H), [3.45 (q, *J* = 8.4 Hz, 0.55H)], [3.43–3.33 (m, 1.1H)], 3.16–3.06 (m, 1H), 2.89–2.77 (m, 1H), 2.12–1.98 (m, 0.9H), [1.73–1.59 (m, 1.1H)], 1.58 (quint., *J* = 7.0 Hz, 0.9H), [1.42–1.34 (m, 1.1H)], 0.89 (s, 4H), [0.82 (s, 5H)], 0.04 (s, 2.7H), [-0.04 (s, 1.65H)], [-0.05 (s, 1.65H)]; ^{13}C NMR (125 MHz, $CDCl_3$):[3] δ = [144.9], 144.4, [142.9], 142.1, 139.5, [137.9], [128.5 (2C)], 128.41 (2C), 128.35 (2C), 127.8 (2C), [127.6 (2C)], 126.6 (2C), [126.5 (2C)], 126.4, [126.3], 126.2, [126.1], [123.1], 120.8, 62.8, [62.7], 57.3, [56.9], [45.7], 44.9, [35.3], 34.0, 32.8, [32.6], 25.99 (3C), [25.97 (3C)], 24.4, [24.3], 18.4, [18.3], -5.2 (2C), [-5.3 (2C)]; IR (neat): $\tilde{\nu}$ = 3061, 3027, 2951, 2927, 2855, 1602, 1494, 1471, 1462, 1452, 1387, 1360, 1254, 1099, 1030, 1005, 960, 938, 909, 835, 774, 734, 697, 662 cm^{-1}; MS (ES+) *m/z* (rel. intensity) 415 (100) [M+Na]; HRMS (ES+) calcd for ($C_{26}H_{36}OSiNa$): 415.2433; found: 415.2433.

Compound 11c. This compound was obtained from (±)-**11b** (219 mg, 0.55 mmol) according the procedure described **8ac**. Purification by flash chromatography (petroleum ether/Et_2O, 3:1 → 2:1 → 1:1) enabled partial separation of *E* and *Z* isomers, giving two fractions (43 mg, 28%, *E:Z* = 1:8) and (39 mg, 25%, *E:Z* = 3.3:1), both as colorless oils. ^{1}H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 7.32–7.25 (m, 6H), 7.24–7.15 (m, 4H), 5.14 (tq, *J* = 7.4, 2.4 Hz, 1H), 4.11–4.15 (m, 1H), 3.66 (t, *J* = 6.6 Hz, 2H), 3.56 (q, *J* = 8.8 Hz, 1H), 3.15–3.08 (m, 1H), 2.88–2.78 (m, 1H), 2.09 (q, *J* = 7.4 Hz, 2H), 1.63 (quint., *J* = 6.9 Hz, 2H), 1.58–1.47 (m, 1H(OH)); (Z isomer): δ = 7.40–7.32 (m, 6H), 7.31–7.22 (m, 4H), 5.40 (tq, *J* = 7.5, 2.3 Hz, 1H), 4.18–4.13 (m, 1H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.23–3.16 (m, 1H), 2.97–2.90 (m, 1H), 1.83–1.72 (m, 2H), 1.60–1.47 (m, 1H), 1.55–1.39 (m, 1H), 1.25–0.93 (m, 1H(OH)); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 144.2, 141.8, 140.0, 128.4 (2C), 128.3 (2C), 127.7 (2C), 126.5 (2C), 126.4, 126.1, 120.3, 62.5, 57.2, 44.7, 33.9, 32.4, 24.3; (Z isomer): δ = 144.6, 142.9, 138.8, 128.5 (2C), 128.3 (2C), 127.6 (2C), 126.4 (2C + 1C), 126.1, 122.6, 62.4, 56.9, 45.4, 35.3, 32.3, 24.0; IR (neat): $\tilde{\nu}$ = 3340 (br), 3059, 3025, 2932, 1601, 1493, 1451, 1180, 1049, 1030, 924, 844, 746, 698 cm^{-1}; MS (ES+) *m/z* (rel. intensity) 301 (100), [M + Na]; HRMS calcd for ($C_{20}H_{22}ONa$): 301.1568, found: 301.1570.

The geometry of the olefin in (±)-**11c** was confirmed on the *Z* isomer by nOe experiments



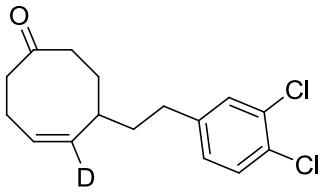
Compound 11. Two batches of this compound were obtained by Swern oxidation of alcohol (±)-**11c**: 1) a *E*/*Z* (3.3:1) mixture (colorless oil, 33 mg, 84%), 2) a *E*/*Z* (1:8) mixture (colorless oil, 39 mg, 79%).[1]H NMR (500 MHz, $CDCl_3$): (*E* isomer) δ = 9.78 (t, *J* = 1.6 Hz, 1H), 7.34–7.26 (m, 6H), 7.25–7.18 (m, 4H), 5.12 (tq, *J* = 7.3, 2.5 Hz, 1H), 4.15–4.05 (m, 1H), 3.59 (q, *J* = 8.9 Hz, 1H), 3.19–3.12 (m, 1H), 2.88–2.81 (m, 1H), 2.50 (td, *J* = 7.2, 1.5 Hz, 2H), 2.35 (q, *J* = 7.2 Hz, 2H); (Z isomer): δ = 9.55 (t, *J* = 2.0 Hz, 1H), 7.37-7.34 (m, 4H), 7.39-7.30 (m, 2H), 7.29-7.21 (m, 4H), 5.36 (tq, *J* = 7.6 and 2.3 Hz, 1H), 4.16-4.12 (m, 1H), 3.55 (q, *J* = 8.4 Hz, 1H), 3.20-3.13 (m, 1H), 2.95-2.88 (m, 1H), 2.32 (dtd, J_{ABX} = 17.0, 7.5 and 2.0 Hz, 1H), 2.25 (dtd, J_{ABX} = 17.1, 7.1 and 2.0 Hz, 1H) and 2.06-1.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): (*E* isomer) δ = 202.2, 144.0, 141.6, 141.3, 128.44 (2C), 128.35 (2C), 127.7 (2C), 126.5 (2C + 1C), 126.2, 118.7, 57.2, 44.6, 43.7, 33.9, 20.9; (Z isomer): δ = 202.3, 144.4, 142.5, 140.1, 128.6 (2C), 128.3 (2C), 127.6 (2C), 126.6, 126.4 (2C), 126.2, 120.8, 56.8, 45.4, 43.3, 35.2, 20.7; IR (neat): $\tilde{\nu}$ = 3059, 3026, 2913, 2823, 2720, 1721, 1601, 1493, 1451, 1407, 1388, 1358, 1191, 1155, 1070, 1048, 1029, 993, 902, 843, 748, 697 cm^{-1}; MS (ES+) *m/z* (rel. intensity) 331 (100) [M + MeOH + Na], 299 (20) [M + Na]; HRMS calcd for ($C_{21}H_{24}O_2Na$): 331.1674, found: 331.1682; HRMS calcd for ($C_{20}H_{20}ONa$): 299.1412, found: 299.1413.



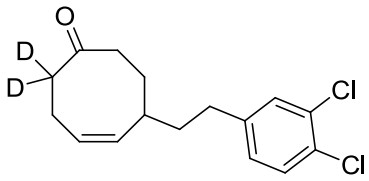
General procedure for rhodium-catalysed hydroacylations

At room temperature, hydrogen gas (2.2 mL, 0.09 mmol) was added slowly (within 10 min) via syringe to a solution [Rh(nbd)(BINAP)]BF_4[10] (10.2 mg, 0.0113 mmol) in dry acetone (1.65 mL) in a Schlenk flask equipped with a J-Young key. The flask was then closed. After stirring for 1h, volatiles were evaporated until dryness under high vacuum. Under N_2, a solution of **8c** (*E*/*Z* = 3:1) (15.5 mg, 0.075 mmol) in acetone (1.5 mL) was added via canula to the dry active catalyst thus prepared, and the mixture was heated in a oil bath set a 60 °C. After 44h, the solvent was evaporated and purification by flash chromatography (petroleum ether/EtOAc: 30/1 → 20/1 → 10/1) gave **9c** (11.6 mg, 75%) and **10c** (2.7 mg, 17%), both as colorless oils. See below for analytical data.

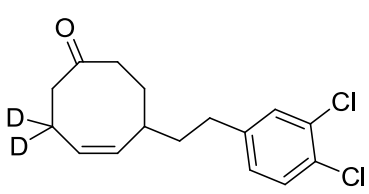
Compound 3_D. This compound was obtained using the standard from aldehyde $\mathbf{1_D}$ (17 mg, 0.057 mmol) procedure {15.8 mg, 93%} or from aldehyde $\mathbf{2_D}$ (10 mg, 0.0335 mmol) {3 mg, 30% + 4.6 mg, 46% of recovered $\mathbf{2_D}$}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.94 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.81 (t, *J* = 7.8 Hz, 1H), 2.58–2.54 (m, 1H), 2.55–2.50 (m, 1H), 2.50–2.36 (m, 5H), 2.27–2.14 (m, 2H), 1.67 (ddt, *J* = 13.1, 8.9, 4.0 Hz, 1H), 1.63–1.54 (m, 2H), 1.30–1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.4, 142.3, 135.4 (t, *J* = 23.5 Hz), 132.1, 130.3, 130.2, 129.7, 129.6, 127.8, 47.4, 39.8, 37.8, 36.4, 32.9, 30.1, 22.8; IR (neat): $\tilde{\nu}$ = 2934, 2910, 2865, 2848, 1690, 1593, 1561, 1468, 1456, 1433, 1417, 1400, 1368, 1342, 1260, 1238, 1210, 1190, 1176, 1158, 1141, 1132, 1076, 1028, 984, 959, 937, 917, 903, 893, 866, 815, 715, 675 cm^{-1}; MS (ES+):*m/z* (rel. intensity): 323 (70), 321 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{17}D^{35}Cl_2O$ + Na): 320.0695; found: 320.0692; calcd for ($C_{16}H_{17}D^{35}Cl^{37}ClO$ + Na): 322.0666; found: 322.0672.



Compound 5. This compound was obtained from aldehyde **4** (23 mg, 0.0769 mmol) using the standard procedure, except that the reaction was carried out for 96h. White solid (15.2 mg, 66%). m.p.: 41–43 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 6.94 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.86–5.78 (m, 1H), 5.35 (ddd, *J* = 10.2, 8.8, 1.3 Hz, 1H), 2.58 (ddd, *J* = 14.0, 8.7, 5.5 Hz, 1H), 2.52–2.36 (m, 4H), 2.29–2.20 (m, 1H), 2.17 (dd, *J* = 13.7, 7.1 Hz, 1H), 1.68 (ddt, *J* = 13.0, 8.6, 4.3 Hz, 1H), 1.64–1.50 (m, 2H), 1.30–1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.6, 142.3, 135.8, 132.1, 130.3, 130.2, 129.7, 129.7, 127.8, 46.8 (quint., *J* = 20.3 Hz), 39.8, 37.8, 36.5, 32.9, 30.1, 22.7; IR (neat): $\tilde{\nu}$ = 3053, 3010, 2926, 2854, 2218, 1703, 1593, 1561, 1472, 1456, 1397, 1346, 1317, 1261, 1198, 1132, 1097, 1030, 893, 874, 820, 726, 688, 664 cm^{-1}; MS (ES+):*m/z* (rel. intensity): 323 (70), 321 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{16}D_2{}^{35}Cl_2O$ + Na): 321.0758; found: 321.0772; calcd for ($C_{16}H_{16}D_2{}^{35}Cl^{37}ClO$ + Na): 323.0728; found: 323.0716.



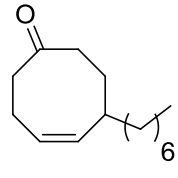
Compound 7. This compound was obtained from aldehyde **6** (16.4 mg, 0.0548 mmol) using the standard procedure, except that the reaction was carried out for 24h. White solid (14.7 mg, 90%). m.p.: 42–44 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 1.8 Hz, 1H), 6.94 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.81 (d, *J* = 10.6 Hz, 1H), 5.34 (dd, *J* = 10.6, 8.8 Hz, 1H), 2.57 (ddd, *J* = 14.2, 9.0, 5.4 Hz, 1H), 2.51 (d, *J* = 12.3 Hz, 1H), 2.49–2.35 (m, 4H), 2.30–2.17 (m, 1H), 1.67 (ddt, *J* = 13.3, 8.3, 4.1 Hz, 1H), 1.64–1.53 (m, 2H), 1.32–1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.5, 142.3, 135.7, 132.1, 130.3, 130.2, 129.63, 129.59, 127.8, 47.3, 39.8, 37.8, 36.5, 32.8, 30.1, 22.1



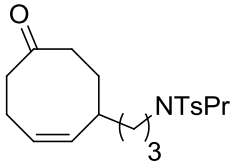
[10] This compound was prepared according to Itooka, R.; Iguchi, Y.; Miyaura, N. *J. Org. Chem.* **2003**, *68*, 6000.

(quint., J = 20.0 Hz); IR (neat): $\tilde{\nu}$ = 3053, 3011, 2932, 2910, 2861, 2850, 2216, 2106, 1692, 1593, 1560, 1470, 1456, 1439, 1417, 1399, 1350, 1291, 1259, 1193, 1142, 1129, 1098, 1079, 1027, 1001, 966, 952, 916, 902, 879, 854, 815, 805, 761, 728, 688, 664 cm^{-1}; MS (ES+):*m/z* (rel. intensity): 323 (68), 321 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{16}D_2{}^{35}Cl_2O$ + Na): 321.0758; found: 321.0762; calcd for ($C_{16}H_{16}D_2{}^{35}Cl^{37}ClO$ + Na): 323.0728; found: 323.0731.

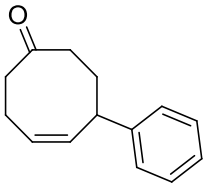
Compound 9a. This compound was obtained from **8a** (8.9 mg, 0.041 mmol) using the general procedure (5.4 mg, 61%). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.76–5.68 (m, 1H), 5.34–5.27 (m, 1H), 2.65–2.50 (m, 2H), 2.49–2.43 (m, 1H), 2.42–2.35 (m, 1H), 2.31–2.21 (m, 1H), 2.19–2.11 (m, 1H), 1.69 (ddt, J = 13.1, 9.1, 3.9 Hz, 1H), 1.38–1.13 (m, 14H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 215.1, 136.9, 128.6, 47.6, 40.0, 37.3, 36.6, 31.8, 30.3, 29.6, 29.3, 27.5, 22.8, 22.6, 14.1; IR (neat): $\tilde{\nu}$ = 3010, 2923, 2853, 1705, 1457, 1345, 1201, 1167, 1109, 874, 738 cm^{-1}; MS (CI): *m/z* (rel. intensity): 240 (100) [M+ NH_4]; elemental analysis (%) calcd for $C_{15}H_{26}O$: C 81.02, H 11.79; found: C 81.08, H 11.85.



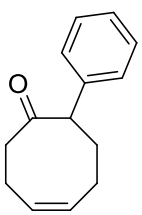
Compound 9b. This compound was obtained from **8b** (13 mg, 0.0345 mmol) using the general procedure (9 mg, 69%). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.78–5.70 (m, 1H), 5.28–5.21 (m, 1H), 3.10–2.98 (m, 3H), 2.60–2.50 (m, 2H), 2.48–2.35 (m, 3H), 2.40 (s, 3H), 2.30–2.21 (m, 1H), 2.20–2.12 (m, 1H), 1.66 (ddt, J = 13.2, 9.0, 4.1 Hz, 1H), 1.54–1.39 (m, 4H), 1.36–1.13 (m, 3H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.5, 142.9, 137.1, 136.0, 129.5 (2C), 129.2, 127.1 (2C), 50.0, 48.1, 47.5, 39.8, 36.9, 33.4, 30.2, 26.7, 22.8, 21.9, 21.4, 11.2; IR (neat): $\tilde{\nu}$ = 2930, 2874, 1702, 1598, 1494, 1457, 1335, 1305, 1154, 1090, 1042, 976, 874, 815, 736 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{31}NO_3S$+ Na): 400.1922; found: 400.1924.



Compound 9c. This compound was obtained from **8c** (*E*/*Z* = 3:1) (15.5 mg, 0.075 mmol) using the general procedure (11.6 mg, 75%). It was also obtained in lower yield (2.1 mg, 13%) from **8c** (*E*/*Z* <1:20) (16 mg, 0.079 mmol). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 2H), 7.22–7.16 (m, 3H), 5.81–5.74 (m, 1H), 5.69 (ddd, J = 10.6, 8.6, 1.3 Hz, 1H), 3.59 (ddd, J = 12.1, 8.5, 3.3 Hz, 1H), 2.77 (tddd, J = 13.5, 9.3, 4.1, 1.0 Hz, 1H), 2.68–2.60 (m, 2H), 2.55–2.46 (m, 2H), 2.26 (ddt, J = 13.6, 7.0, 4.2 Hz, 1H), 1.95 (ddt, J = 13.1, 8.8, 3.7 Hz, 1H), 1.77 (tdd, J = 12.5, 8.7, 3.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.1, 145.2, 135.7, 128.6 (2C), 128.4, 127.0 (2C), 126.4, 47.6, 43.7, 40.0, 31.4, 22.5; IR (neat): $\tilde{\nu}$ = 3063, 3026, 2924, 2854, 1703, 1602, 1492, 1454, 1342, 1164, 1062, 885, 874, 760, 737, 701 cm^{-1}; MS (CI): *m/z* (rel. intensity): 218 (100) [M+ NH_4], 183 (14); elemental analysis (%) calcd for $C_{14}H_{16}O$: C 83.96, H 8.05; found: C 84.61, H 8.50.

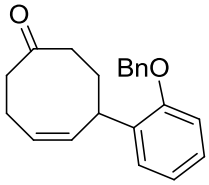


Compound 10c. This compound was obtained from **8c** (*E*/*Z* = 3:1) (15.5 mg, 0.075 mmol) using the general procedure (2.7 mg, 17%). It was also obtained (2.1 mg, 13%) from **8c** (*E*/*Z* <1:20) (16 mg, 0.079 mmol) after difficult separation from the recovered starting material (2.1 mg, 13%) by preparative TLC (petroleum ether/EtOAc = 20:1, two elutions) (6.1 mg, 38%). White solid. m.p.: 27–30 °C.^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.32 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.18 (m, 1H), 5.85 (td, J = 9.7, 7.1 Hz, 1H), 5.75 (td, J = 10.2, 7.6 Hz, 1H), 3.97 (dd, J = 12.2, 3.5 Hz, 1H), 2.76–2.70 (m, 1H), 2.67 (ddd, J = 13.6, 9.2, 4.5 Hz, 1H), 2.39–2.24 (m, 3H), 2.17 (dtd, J = 13.6, 9.2, 3.8 Hz, 1H), 1.94 (tdd, J = 12.5, 8.4, 3.9 Hz, 1H), 1.63 (ddt, J = 12.9, 9.2, 3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.5, 140.1, 130.7, 129.8, 128.4 (2C), 128.1 (2C), 126.9, 55.6, 46.7, 31.7, 25.9, 22.4; IR (neat): $\tilde{\nu}$ = 3061, 3021, 2855, 2926, 1708, 1650, 1600, 1496, 1464, 1453, 1360, 1328,

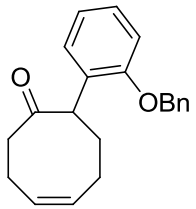


1210, 1184, 1152, 1097, 1032, 974, 892, 734, 699 cm^{-1}; elemental analysis (%) calcd for $C_{14}H_{16}O$: C 83.96, H 8.05; found: C 83.75, H 8.15.

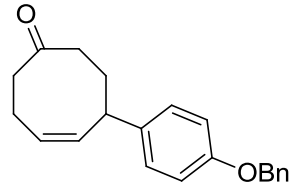
Compound 9d. This compound was obtained from **8d** (*E*/*Z* = 19:1) (15mg, 0.049 mmol) using the general procedure (14 mg, 93%). It was also obtained in lower yield (8 mg, 27%) from **8d** (*E*/*Z* <1:20) (30 mg, 0.098 mmol). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.35 (m, 4H), 7.33–7.28 (m, 1H), 7.23 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.16 (td, *J* = 7.8, 1.6 Hz, 1H), 6.94 (td, *J* = 7.5, 1.1 Hz, 1H), 6.90 (dd, *J* = 8.3, 0.8 Hz, 1H), 5.78–5.63 (m, 2H), 5.05 (s, 2H), 4.25 (ddd, *J* = 11.4, 8.3, 4.0 Hz, 1H), 2.81 (tdd, *J* = 13.7, 9.2, 4.4 Hz, 1H), 2.71–2.59 (m, 2H), 2.51–2.41 (m, 2H), 2.18 (ddt, *J* = 13.7, 6.7, 4.2 Hz, 1H), 1.95–1.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.3, 155.8, 137.3, 135.5, 133.9, 128.47 (2C), 128.45, 127.7, 127.3, 127.14, 127.06 (2C), 121.2, 112.2, 70.2, 47.7, 40.3, 37.0, 30.3, 22.3; IR (neat): $\tilde{\nu}$ = 3062, 3031, 2923, 1702, 1599, 1583, 1490, 1450, 1380, 1343, 1291, 1239, 1163, 1105, 1047, 1024, 972, 875, 849, 800, 751, 735, 697 cm^{-1}; HRMS (ES+) calcd for $(C_{21}H_{22}O_2 + Na)^+$: 329.1517; found: 329.1509.



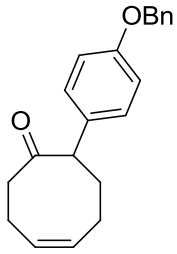
Compound 10d. This compound was obtained from **8d** (*E*/*Z* <1:20) (30 mg, 0.098 mmol) using the general procedure. Initially a mixture of **8d**/**9d**/**10d** = 1:1:5.75 (18.6 mg, 62%) was obtained and an analytically pure sample was then obtained by preparative TLC (petroleum ether/EtOAc: 4/1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.36 (m, 5H), 7.35–7.31 (m, 1H), 7.16 (td, *J* = 7.8, 1.7 Hz, 1H), 6.96 (td, *J* = 7.6, 1.1 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.82–5.68 (m, 2H), 5.04 (d, *J* = 11.6 Hz, 1H), 5.01 (d, *J* = 11.5 Hz, 1H), 4.46 (dd, *J* = 12.3, 3.5 Hz, 1H), 2.69 (ddd, *J* = 11.7, 7.6, 4.0 Hz, 1H), 2.56 (dtd, *J* = 13.9, 9.1, 4.4 Hz, 1H), 2.31 (dtd, *J* = 14.3, 7.3, 3.7 Hz, 1H), 2.24–2.10 (m, 3H), 1.92 (tdd, *J* = 12.4, 8.4, 3.9 Hz, 1H), 1.73 (ddt, *J* = 12.8, 9.3, 3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.9, 155.5, 136.8, 130.4, 130.2, 129.6, 128.6 (2C), 128.10, 128.07, 127.6 (2C), 127.5, 121.1, 111.1, 70.2, 47.5, 46.7, 28.7, 25.5, 22.3; IR (neat): $\tilde{\nu}$ = 3064, 3018, 2932, 2861, 1707, 1599, 1586, 1489, 1451, 1380, 1322, 1290, 1236, 1189, 1152, 1118, 1100, 1082, 1051, 1012, 895, 855, 747, 732, 696 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$ + Na): 329.1517; found: 329.1510.



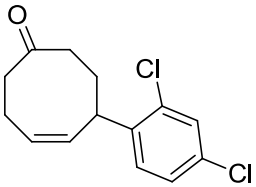
Compound 9e. This compound was obtained from **8e** (*E*/*Z* >20:1) (21 mg, 0.0686 mmol) using the standard procedure. White solid (19 mg, 90%). m.p.: 53–55 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.80–5.72 (m, 1H), 5.66 (dd, *J* = 10.4, 8.9 Hz, 1H), 5.03 (s, 2H), 3.54 (ddd, *J* = 12.2, 9.0, 3.1 Hz, 1H), 2.75 (tdd, *J* = 13.4, 9.4, 4.1 Hz, 1H), 2.67–2.59 (m, 2H), 2.55–2.45 (m, 2H), 2.25 (ddt, *J* = 13.6, 7.0, 4.2 Hz, 1H), 1.93 (ddt, *J* = 13.0, 9.1, 3.9 Hz, 1H), 1.73 (tdd, *J* = 12.6, 8.6, 3.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.1, 157.3, 137.6, 137.1, 136.0, 128.5 (2C), 128.1, 127.93 (2C), 127.89, 127.4 (2C), 114.9 (2C), 70.1, 47.6, 42.8, 40.0, 31.5, 22.5; IR (neat): $\tilde{\nu}$ = 3066, 3026, 2925, 2876, 1694, 1609, 1583, 1511, 1452, 1417, 1386, 1347, 1242, 1225, 1182, 1165, 1109, 1065, 1025, 871, 881, 832, 819, 735, 695 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$+ Na): 329.1517; found: 329.1528.



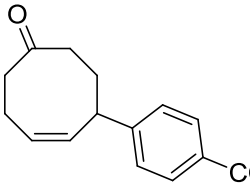
Compound 10e. This compound was obtained from **8e** (*E*/*Z* <20:1) (7 mg, 0.0229 mmol) using the standard procedure. Colorless oil (4.2 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 2H), 7.38–7.33 (m, 2H), 7.32–7.27 (m, 1H), 7.27–7.24 (m, 2H), 6.92–6.85 (m, 2H), 5.83 (td, *J* = 10.3, 7.2 Hz, 1H), 5.73 (td, *J* = 9.9, 7.4 Hz, 1H), 5.01 (s, 2H), 3.91 (dd, *J* = 12.2, 3.5 Hz, 1H), 2.74–2.60 (m, 2H), 2.97–2.27 (m, 3H), 2.15 (dtd, *J* = 13.1, 9.1, 3.3 Hz, 1H), 1.90 (tdd, *J* = 12.4, 8.1, 3.6 Hz, 1H), 1.60 (ddt, *J* = 12.9, 9.2, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.0, 157.9, 137.1, 132.5, 130.7, 129.8, 129.0 (2C), 128.6 (2C), 127.9, 127.4 (2C), 114.8 (2C), 70.0, 54.6, 46.6, 31.8, 25.9, 22.3; IR (neat): $\tilde{\nu}$ = 3016, 2972, 2936, 2918, 2895, 1707, 1068, 1581, 1508, 1460, 1452, 1436, 1385, 1363, 1331, 1303, 1272, 1235, 1195, 1180, 1119, 1106, 1080, 1069, 1040, 1030, 1007, 976, 923, 892, 847, 820, 800, 754 ,736, 702 cm^{-1}; HRMS (ES+) calcd for ($C_{21}H_{22}O_2$ + Na): 329.1517; found: 329.1511.



Compound 9f. This compound was obtained from **8f** (*E*/*Z* >20:1) (15 mg, 0.056 mmol) using the standard procedure. Colorless oil (14 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.33 (m, 1H), 7.23–7.20 (m, 2H), 5.85–5.76 (m, 1H), 5.49 (ddd, *J* = 10.2, 8.5, 1.2 Hz, 1H), 4.12–4.03 (m, 1H), 2.91 (tddd, *J* = 13.7, 9.7, 4.2, 1.2 Hz, 1H), 2.86–2.75 (m, 2H), 2.65–2.44 (m, 2H), 2.29 (ddt, *J* = 13.6, 7.0, 4.2 Hz, 1H), 1.88–7.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.5, 140.9, 134.1, 133.4, 132.6, 129.9, 129.3, 128.3, 127.5, 47.6, 39.9, 39.6, 30.4, 22.5; IR (neat): $\tilde{\nu}$ = 3020, 2928, 2869, 1702, 1587, 1560, 1473, 1439, 1383, 1343, 1191, 1165, 1145, 1103, 1070, 1046, 969, 867, 846, 812, 774, 728 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 293 (60), 291 (100) [M + Na]; HRMS (ES+) calcd for ($C_{14}H_{14}{}^{35}Cl_2O$+ Na): 291.0319; found: 291.0319.



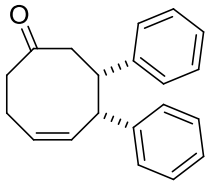
Compound 9g. This compound was obtained from **8g** (*E*/*Z* = 1:3) (28 mg, 0.11 mmol) using the standard procedure except that the reaction was stopped after 90h. White solid (8 mg, 29%). m.p.: 52–55 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.85–5.77 (m, 1H), 5.65 (ddd, *J* = 10.4, 8.9, 1.3 Hz 1H), 3.88 (s, 3H), 3.64 (ddd, *J* = 12.1, 8.8, 3.2 Hz, 1H), 2.76 (tddd, *J* = 13.6, 9.5, 4.0, 0.9 Hz, 1H), 2.69–2.62 (m, 2H), 2.56–2.47 (m, 2H), 2.28 (ddt, *J* = 13.6, 7.2, 4.1 Hz, 1H), 1.95 (ddt, *J* = 13.0, 9.0, 3.8 Hz, 1H), 1.77 (tdd, *J* = 12.7, 8.8, 3.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.9, 166.9, 150.3, 134.6, 130 (2C), 129.1, 128.4, 127.1 (2C), 52.0, 47.5, 43.7, 39.9, 31.0, 22.6; IR (neat): $\tilde{\nu}$ = 2954, 2863, 1710, 1693, 1608, 1436, 1418, 1396, 1338, 1311, 1279, 1251, 1192, 1179, 1165, 1107, 1070, 1018, 968, 957, 895, 878, 855, 815, 771, 746, 710 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 281 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}O_3$+ Na): 281.1154; found: 281.1153.



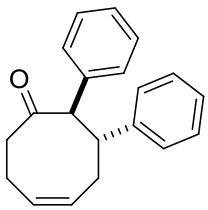
Compound 10g. This compound was obtained from **8g** (*E*/*Z* = 1:3.3) (28 mg, 0.11 mmol) using the standard procedure except that the reaction was stopped after 90h. Colorless oil (12 mg, 38%). This sample was obtained as an inseparable **8g**/**10g** = 1:7.3 mixture and the indicated yield reflects this ratio. Further purification by preparative TLC (petroleum ether/EtOAc = 6:1) gave a sample of **8g**/**10g** = 1:20 which was used for characterization. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.2 Hz, 2H), 7.41 (*J* = 8.2 Hz, 2H), 5.86 (td, *J* = 9.8, 7.3 Hz, 1H), 5.75 (td, *J* = 9.7, 7.7 Hz, 1H), 4.04 (dd, *J* = 12.1, 3.4 Hz, 1H), 3.87 (s, 3H), 2.77–2.63 (m, 2H), 2.42–2.34 (m, 1H), 2.34–2.25 (m, 2H), 2.18 (dtd, *J* = 13.3, 9.3, 3.7 Hz, 1H), 1.93 (tdd, *J* = 12.4, 8.3, 3.7 Hz, 1H), 1.63 (ddt, *J* = 12.9, 9.1, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.8, 167.0, 145.1, 130.6, 129.9, 129.7 (2C), 128.8, 128.1 (2C), 55.5, 52.0, 46.8, 31.8, 25.8, 22.2; IR (neat): $\tilde{\nu}$ = 3026, 2951, 2909, 2849, 1720, 1700, 1608, 1573, 1437, 1420, 1349, 1323, 1310, 1280, 1265, 1246, 1185, 1171, 1063, 1017, 977, 968, 898, 874, 855, 839, 813, 779, 752, 736, 709 cm^{-1}; MS (ES+):

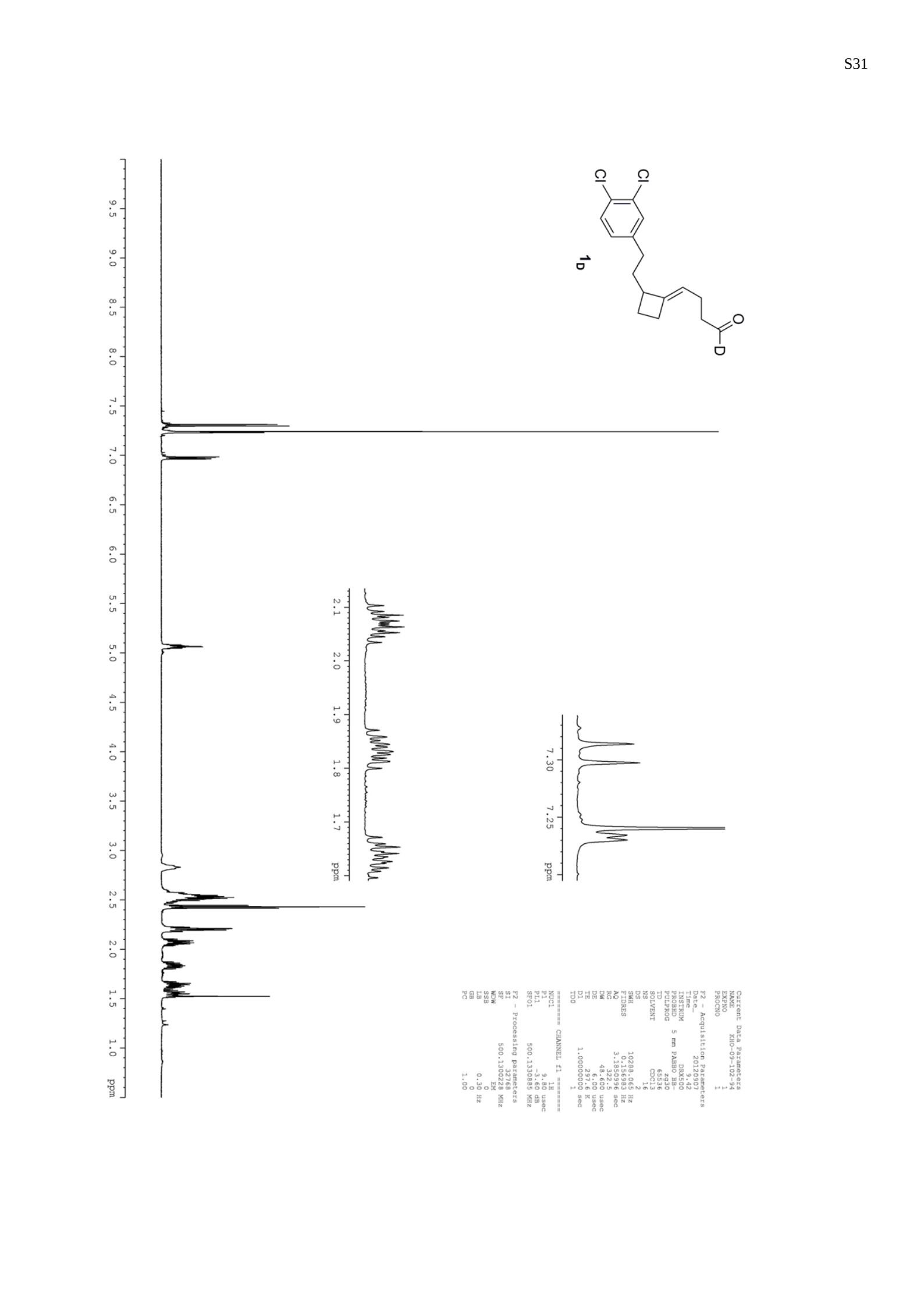
m/*z* (rel. intensity): 281 (100) [M + Na]; HRMS (ES+) calcd for ($C_{16}H_{18}O_3$+ Na): 281.1154; found: 281.1153.

Compound 12. This compound was obtained from **11** (*E*/*Z* = 3.3:1) (15 mg, 0.0543 mmol) using the standard procedure. White solid (11.2 mg, 75%). m.p.: 127–130 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–6.89 (m, 10H), 5.74 (td, *J* = 10.8, 7.4 Hz, 1H), 5.70 (tdd, *J* = 10.7, 6.3, 1.1 Hz, 1H), 4.02 (dd, *J* = 10.6, 7.2 Hz, 1H), 3.27–3.14 (m, 3H), 2.79 (ddd, *J* = 13.0, 5.0, 3.1 Hz, 1H), 2.54–2.48 (m, 1H), 2.46 (td, *J* = 13.3, 4.9 Hz, 1H), 2.38–2.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 211.7, 143.8, 143.6, 136.4, 129.2, 128.1 (4C), 128.1 (2C), 127.7 (2C), 125.9, 125.8, 50.7, 48.7, 47.9, 47.2, 22.2; IR (neat): $\tilde{\nu}$ = 3030, 2937, 1698, 1602, 1494, 1454, 1421, 1331, 1221, 1184, 1164, 1123, 1103, 1075, 1022, 787, 765, 754, 732, 702 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 299 (100) [M + Na]; HRMS (ES+) calcd for ($C_{20}H_{20}O$+ Na): 299.1412; found: 299.1414.



Compound 13. This compound was obtained from **11** (*E*/*Z* = 1:8) (18 mg, 0.0652 mmol) using the standard procedure. White solid (6 mg, 33%). m.p.: 124–126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ =7.24–7.21 (m, 2H), 7.12–6.97 (m, 8H), 6.11–6.01 (m, 1H), 5.80 (td, *J* = 10.2, 7.3 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 3.32 (dt, *J* = 11.5, 5.1 Hz, 1H), 2.86 (td, *J* = 10.9, 4.3 Hz, 1H), 2.71–2.60 (m, 1H), 2.49 (ddd, *J* = 14.1, 9.7, 4.5 Hz, 1H), 2.45–2.34 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.1, 142.7, 137.3, 130.8, 129.1, 129.0 (2C), 128.10 (2C), 128.05 (2C), 127.9 (2C), 126.7, 126.1, 60.2, 47.3, 46.0, 33.9, 23.4; IR (neat): $\tilde{\nu}$ = 3060, 3028, 2970, 2934, 2859, 1701, 1601, 1493, 1454, 1434, 1342, 1318, 1292, 1227, 1193, 1164, 1099, 1071, 1030, 1015, 846, 770, 736, 722, 707, 695 cm^{-1}; MS (ES+): *m*/*z* (rel. intensity): 299 (100) [M + Na]; HRMS (ES+) calcd for ($C_{20}H_{20}O$+ Na): 299.1412; found: 299.1414.

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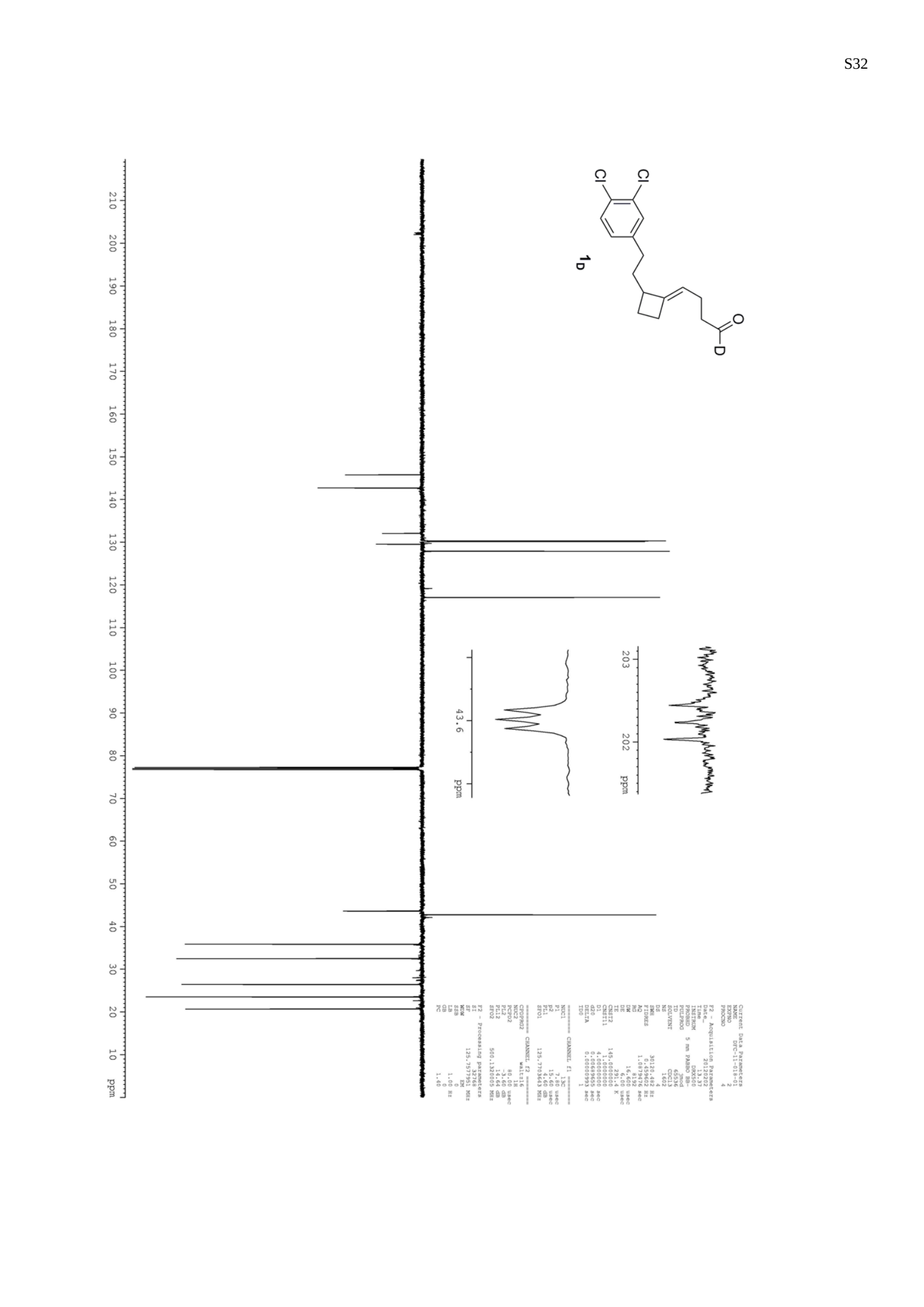
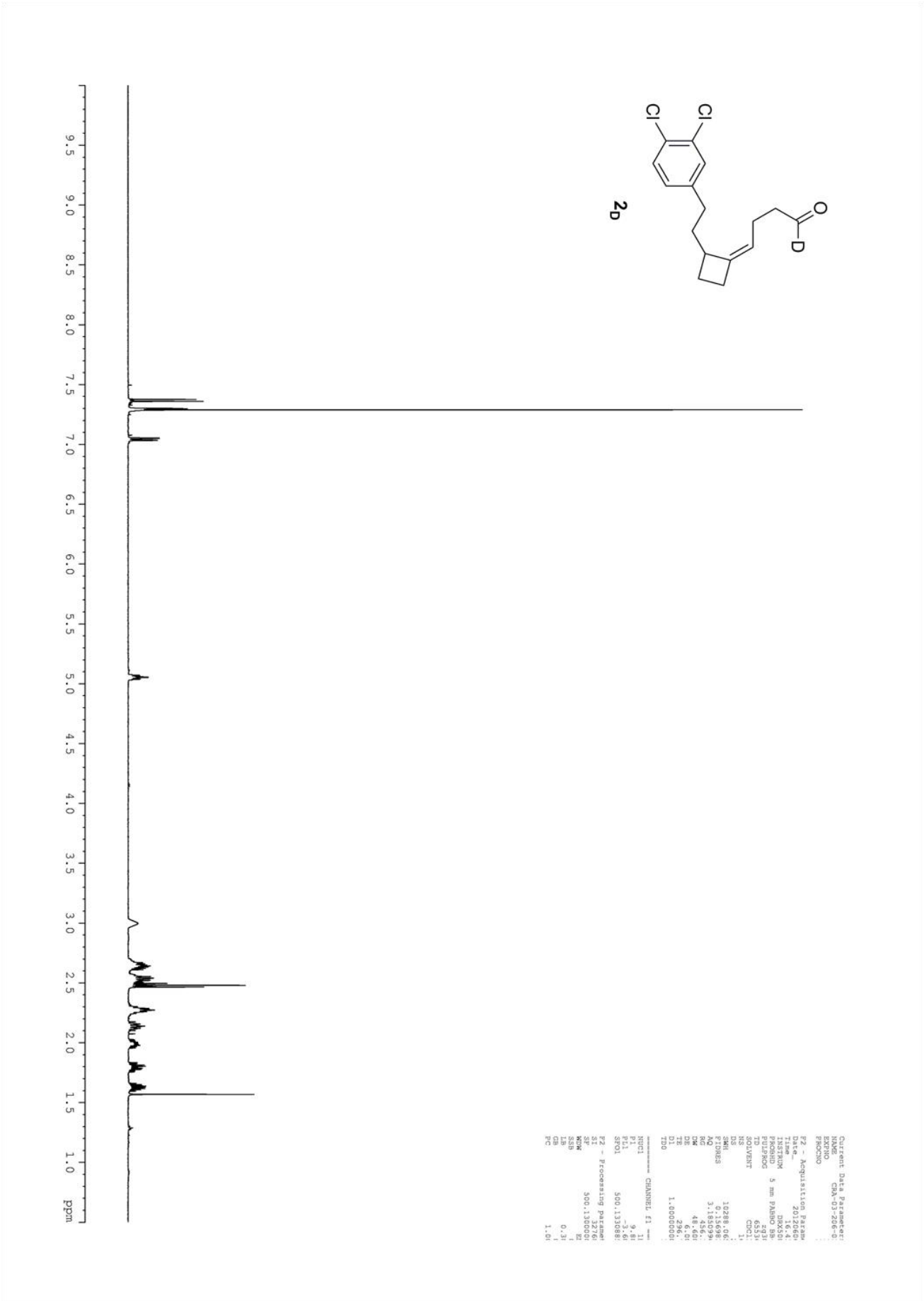
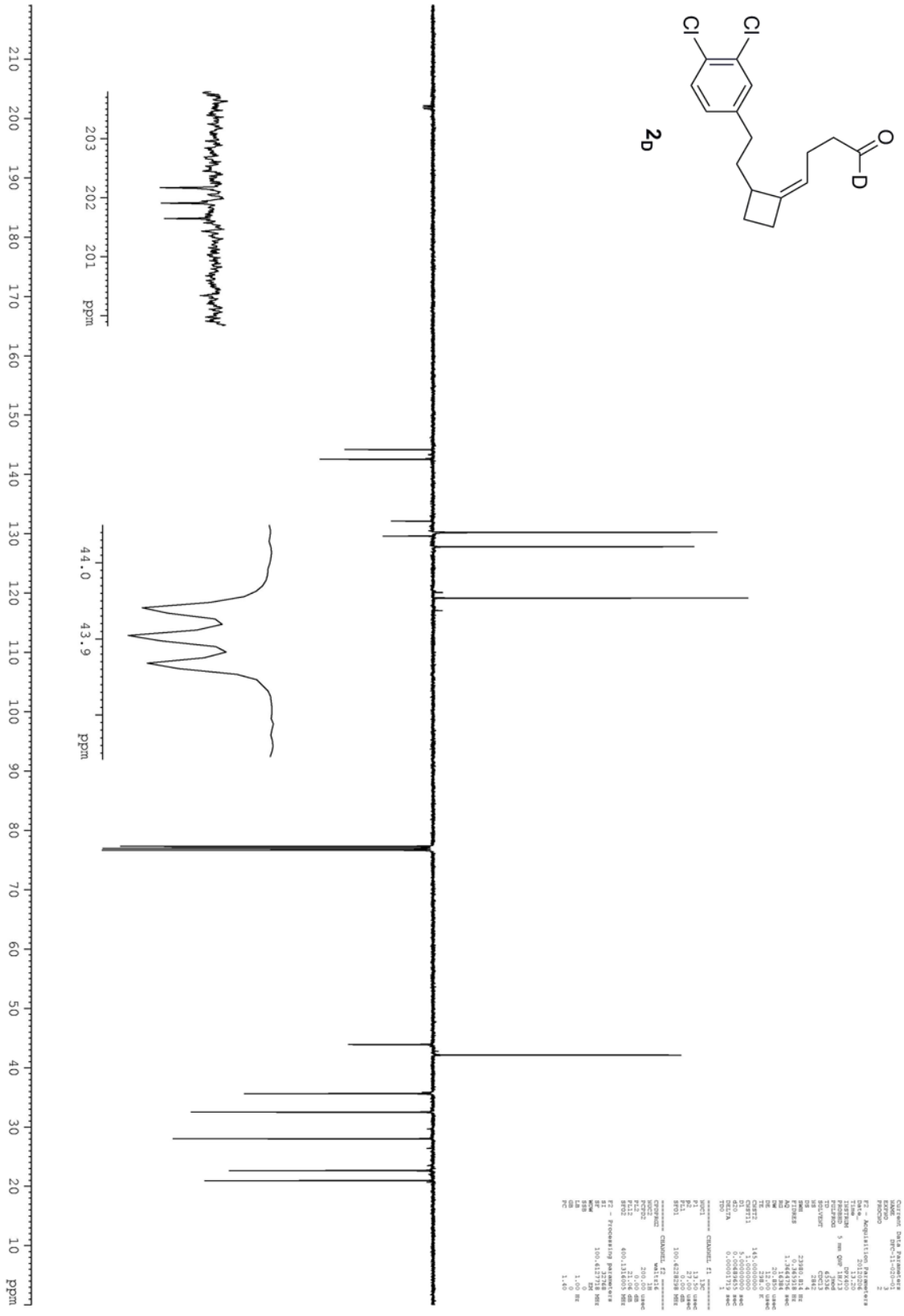
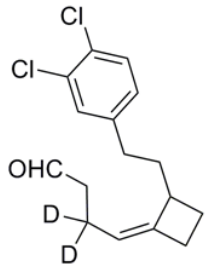
1D
Current Data Parameters
NAME KHO-09-102-94
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120907
Time 9.42
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 322.5
DW 48.600 usec
DE 6.00 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300228 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.30
7.25
ppm
2.1
2.0
1.9
1.8
1.7
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


Cl
Cl
O
D
1D
203
202
ppm
43.6
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

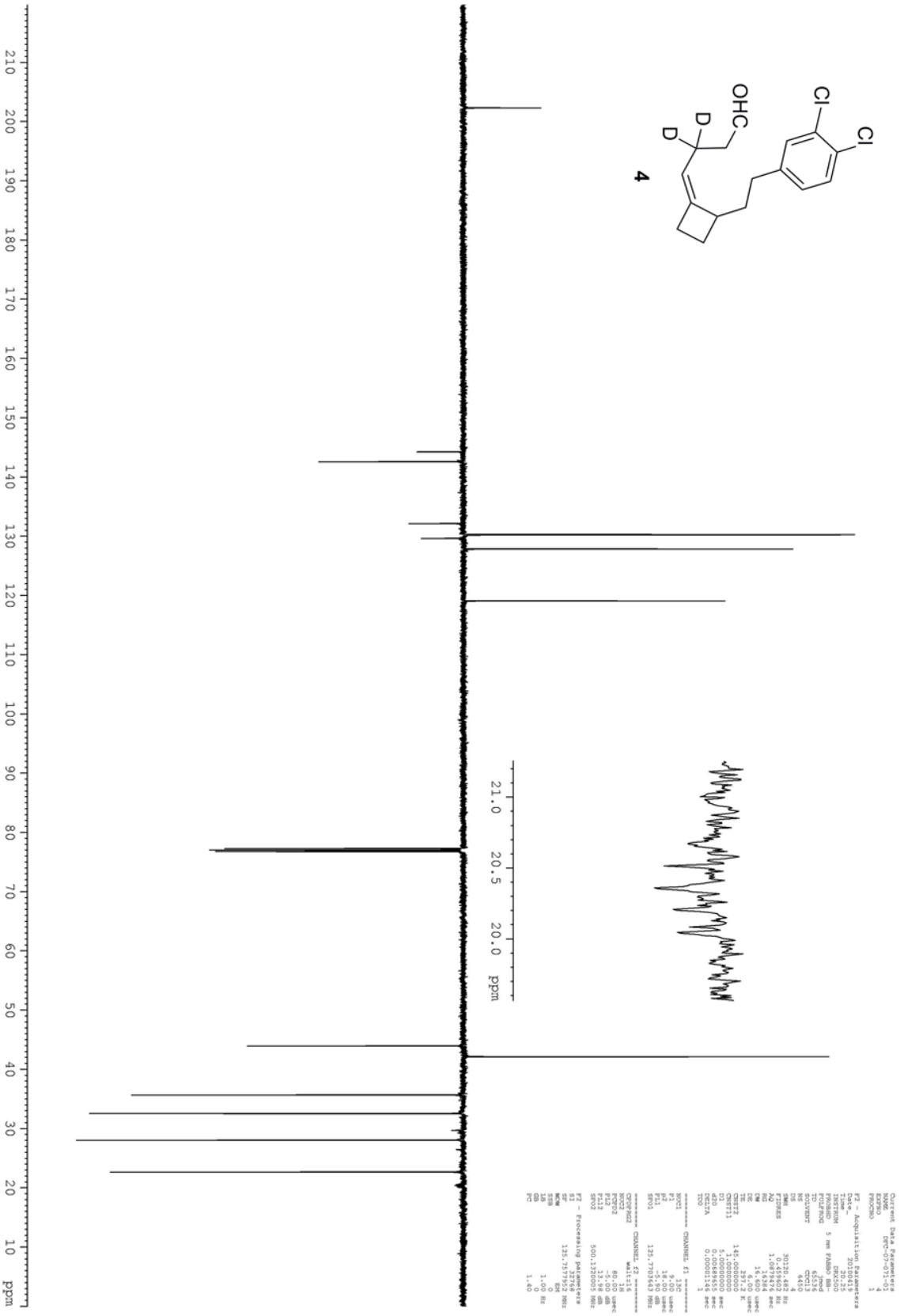

Cl
Cl
O
D
2D
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

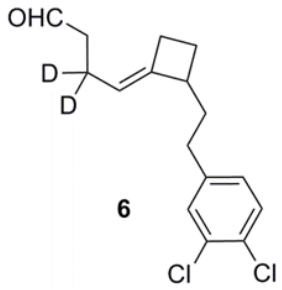

Cl
Cl
O
D
2D
203
202
201
ppm
44.0
43.9
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Cl
Cl
OHC
D
D

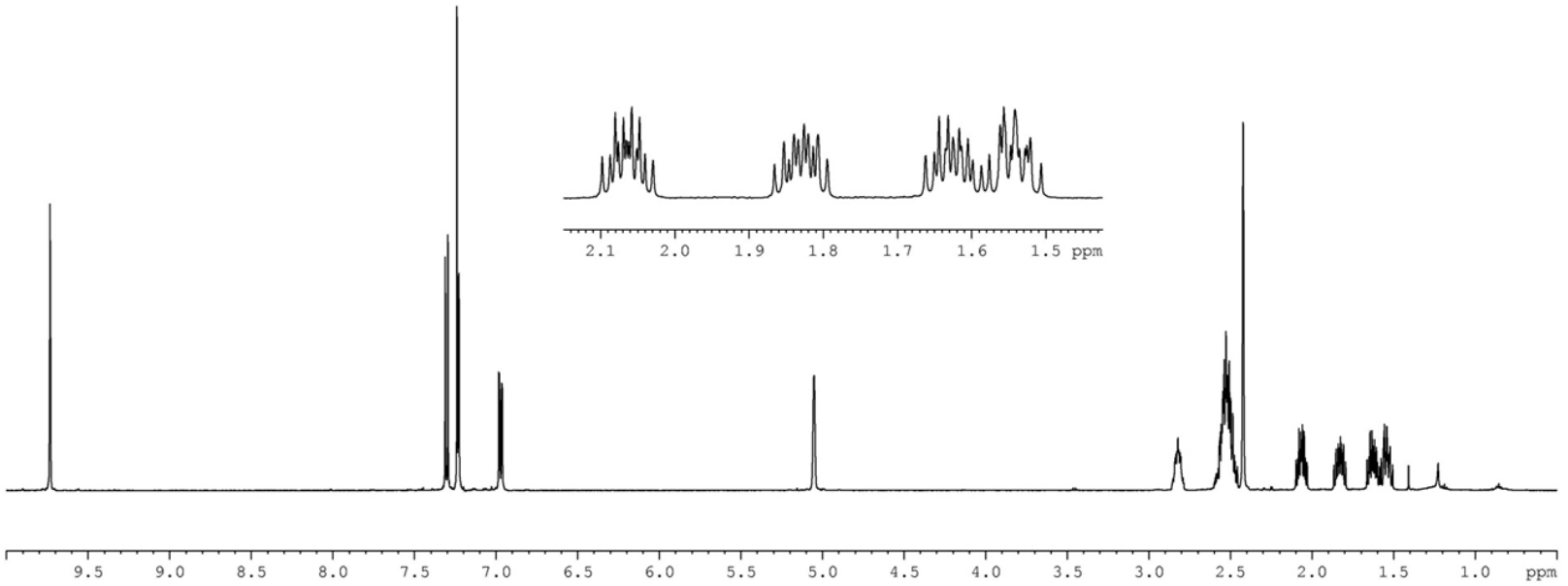
4

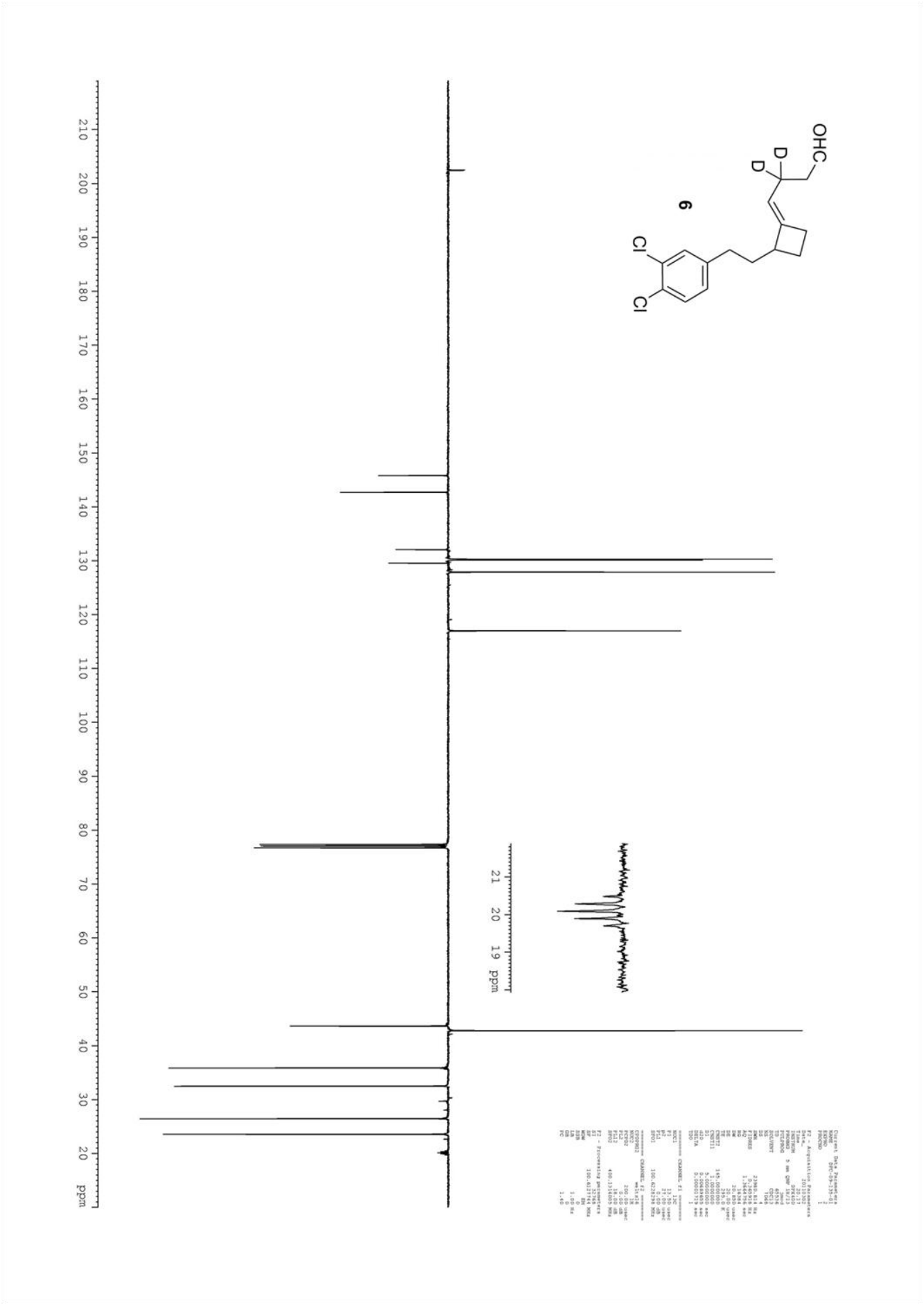
Current Data Parameters
NAME DFC-09-139-01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110307
Time 16.04
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 406.4
DW 48.600 usec
DE 6.00 usec
TE 289.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -2.70 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300246 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.10 2.05 2.00 1.95 1.90 1.85 1.80 1.75 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 ppm

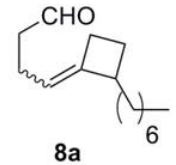

OHC
D
D
Cl
Cl
4
21.0
20.5
20.0
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OHC
D
D
6
Cl
Cl


Current Data Parameters
NAME DFC-09-135-01
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110302
Time 10.45
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156963 Hz
AQ 3.1850996 sec
RG 256
DW 48.600 usec
DE 6.00 usec
TE 289.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -2.70 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300246 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


2.1
2.0
1.9
1.8
1.7
1.6
1.5 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
ppm

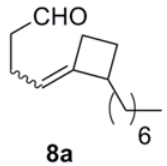

OHC
D
D
Cl
Cl
6
21 20 19 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


CHO
6

8a

(*E*/*Z* = 6:4)

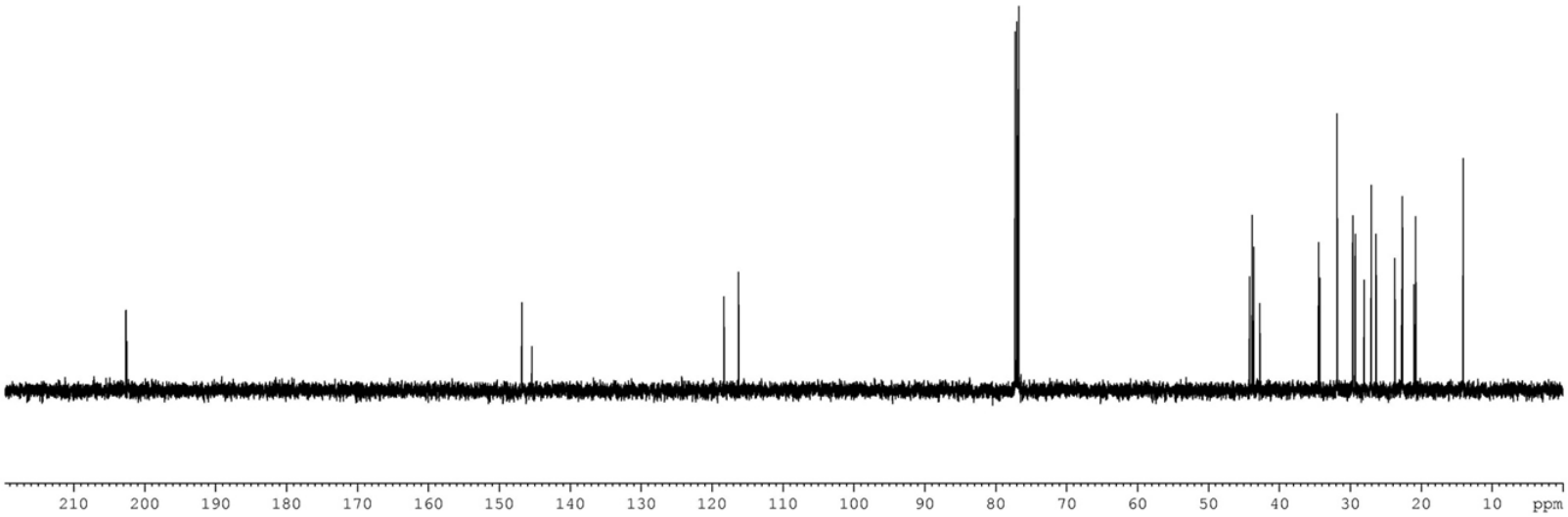
Current Data Parameter
NAME CRA-03-178-0
EXPNO
PROCNO
F2 - Acquisition Param
Date_ 2012042
Time 18.4
INSTRUM DRX50
PROBHD 5 mm PABBO BB
PULPROG zg3
TD 6553
SOLVENT CDCl
NS 1
DS
SWH 10288.06
FIDRES 0.15698
AQ 3.185099
RG 406.
DW 48.60
DE 6.0
TE 294.
D1 1.0000000
TD0
CHANNEL f1
NUC1 1
P1 9.8
PL1 -3.6
SFO1 500.133088
F2 - Processing parame
SI 3276
SF 500.130022
WDW E
SSB
LB 0.3
GB
PC 1.0
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

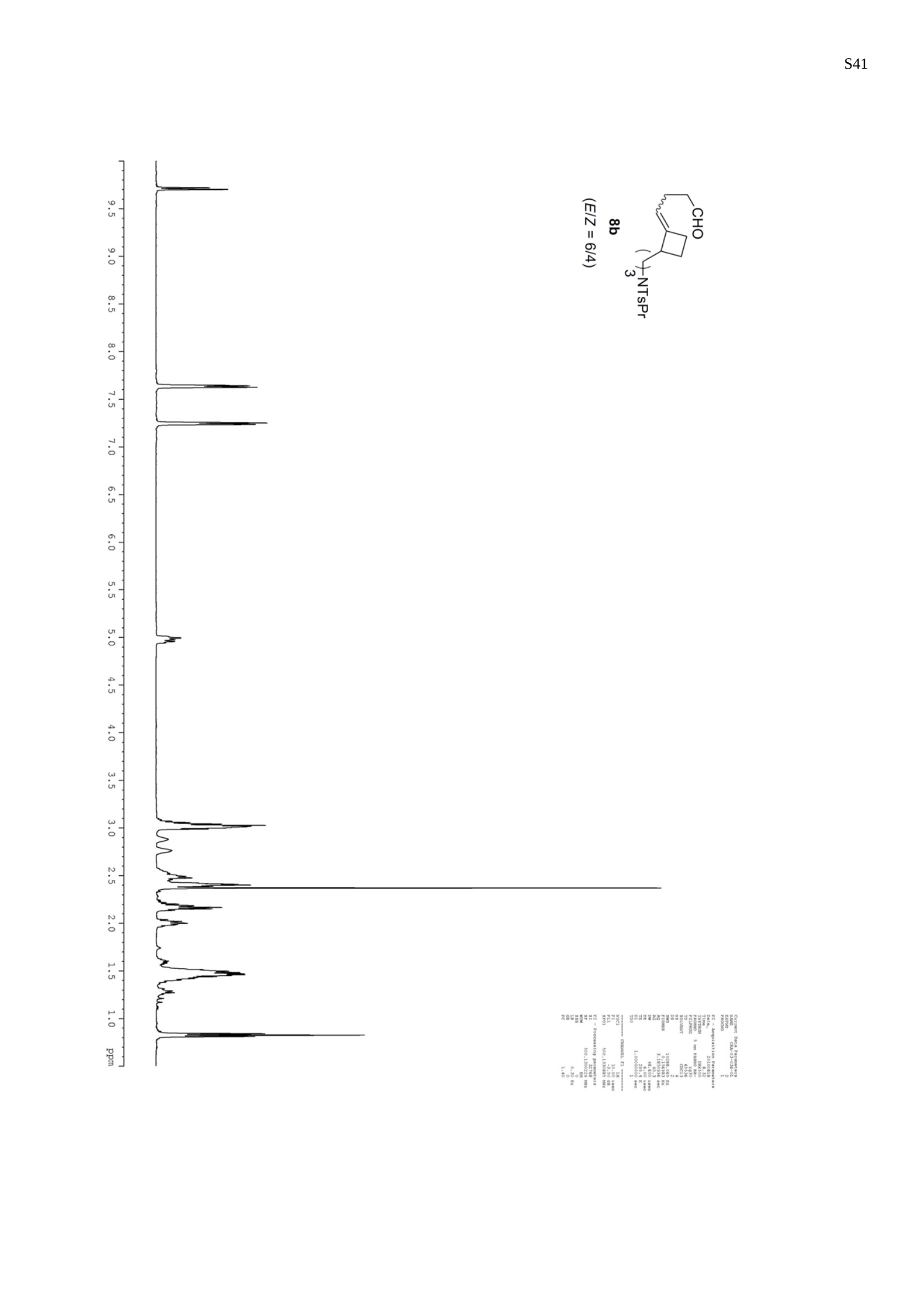


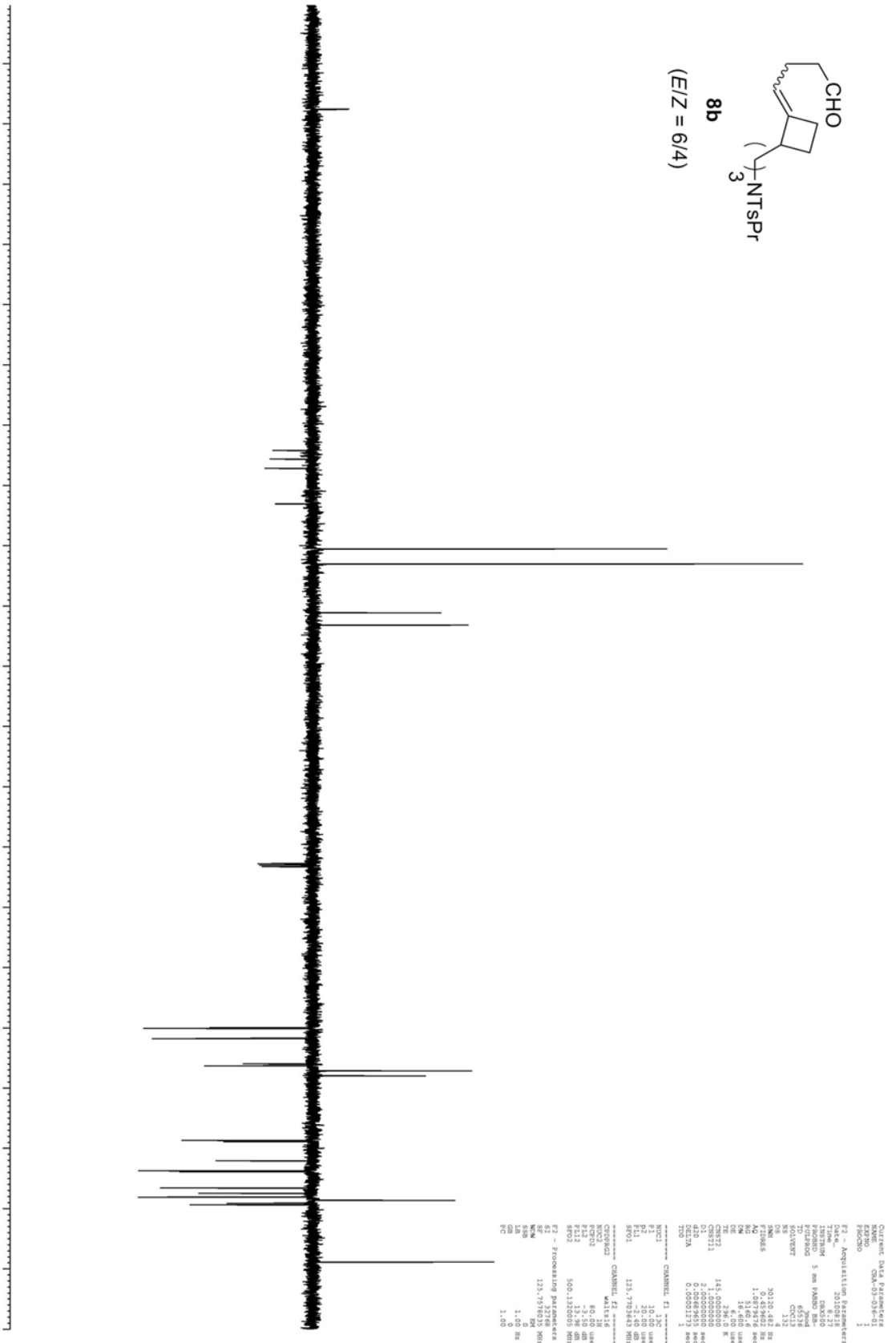
8a

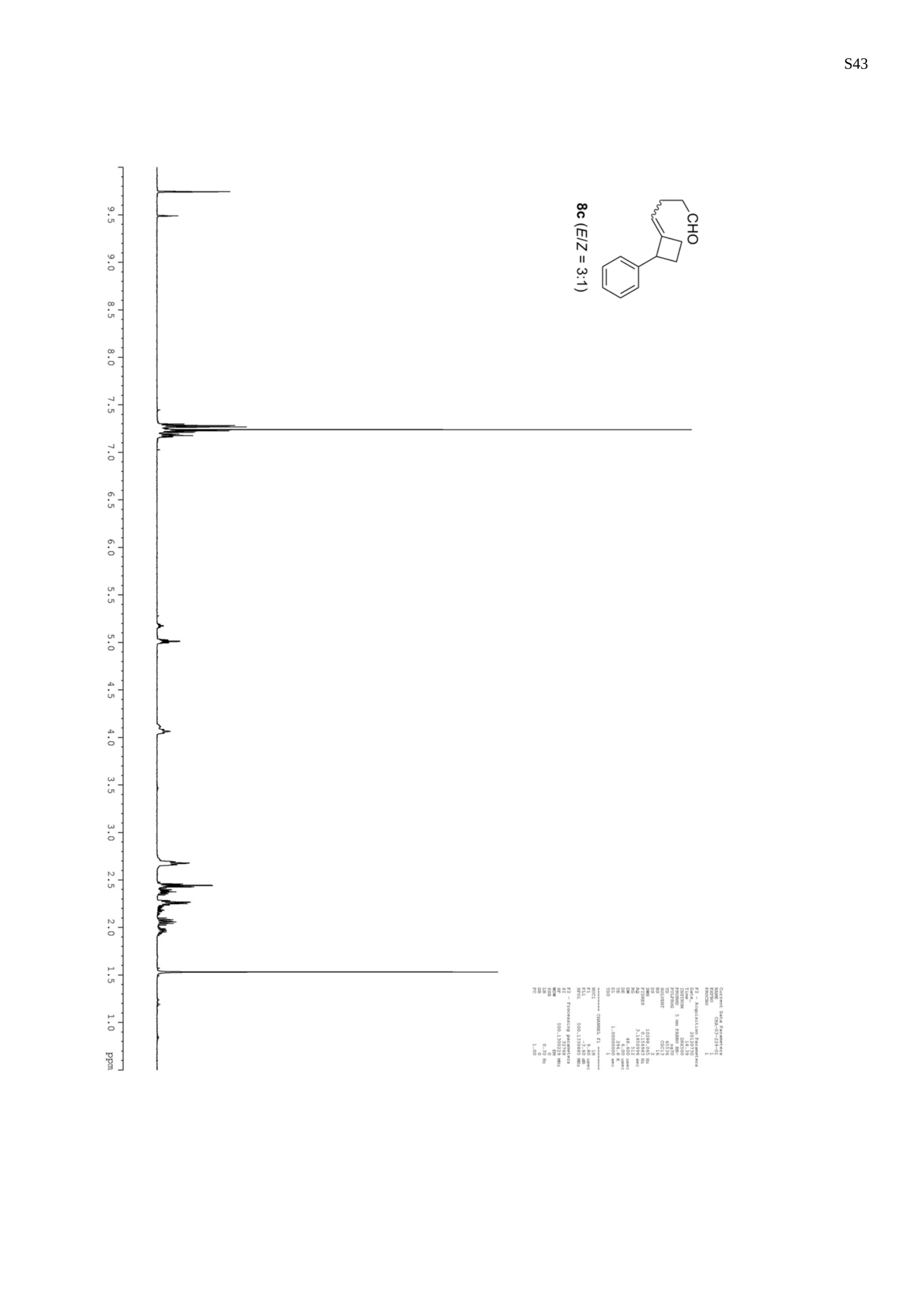
(*E*/*Z* = 6:4)

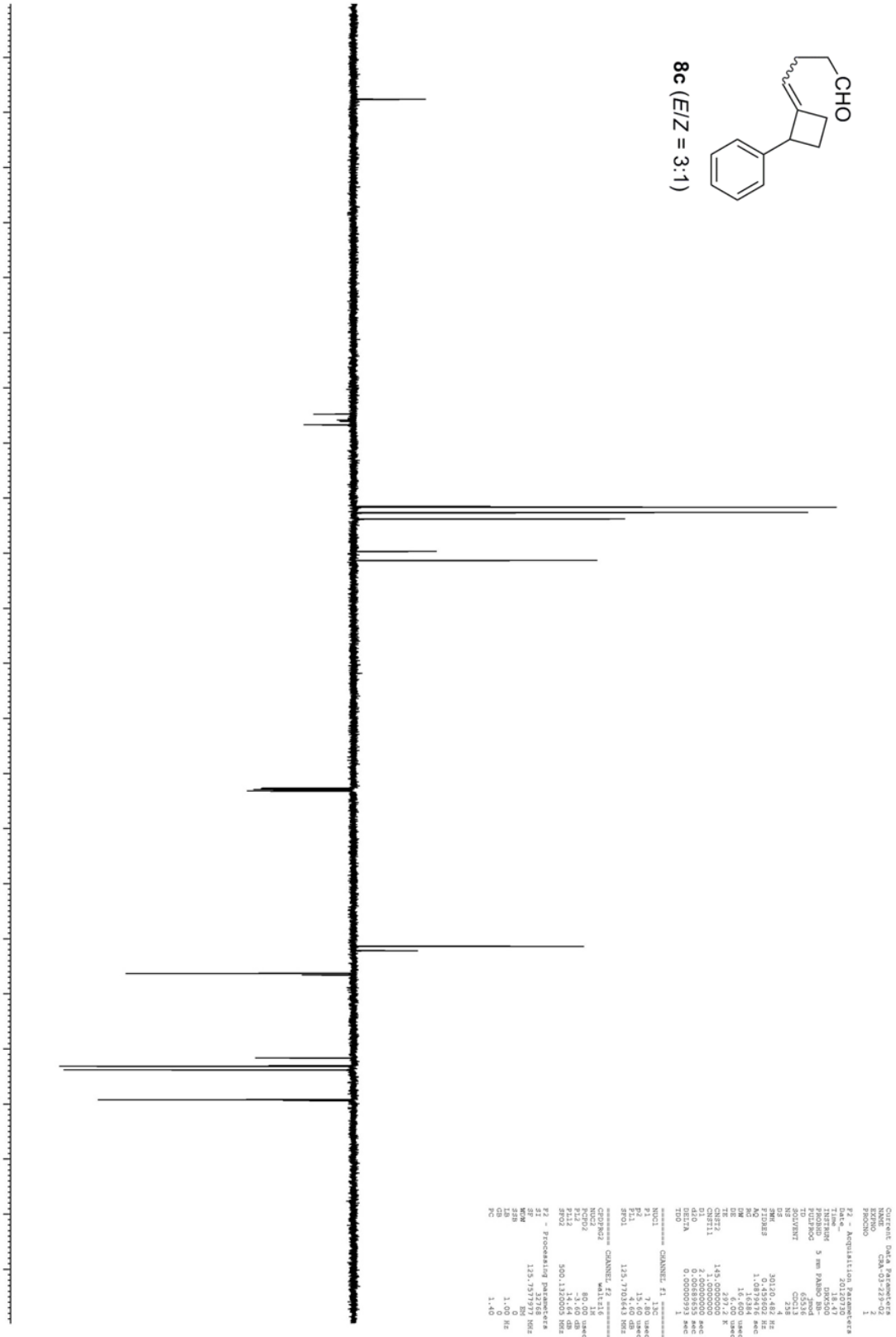
```
Current Data Parameters
NAME        CRA-03-178-04
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120427
Time                18.58
INSTRUM          DRX500
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                   22
DS                    4
SWH           30120.482 Hz
FIDRES        0.459602 Hz
AQ            1.0879476 sec
RG               11585.2
DW               16.600 usec
DE                6.00 usec
TE                295.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                7.80 usec
PL1               4.60 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -3.60 dB
PL12             14.64 dB
PL13             14.64 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                  32768
SF          125.7577949 MHz
WDW                    EM
SSB                     0
LB                1.00 Hz
GB                      0
PC                1.00
```

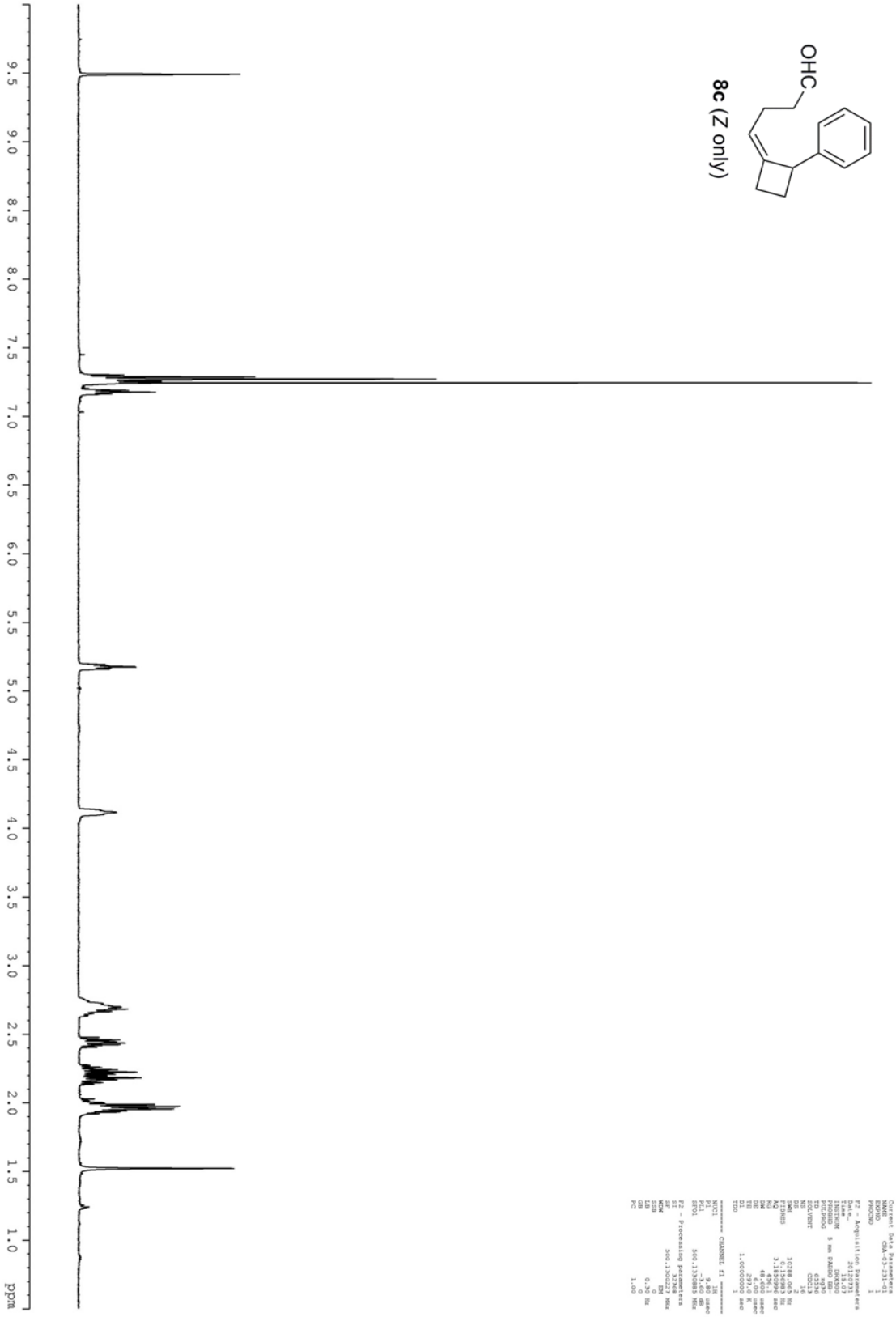


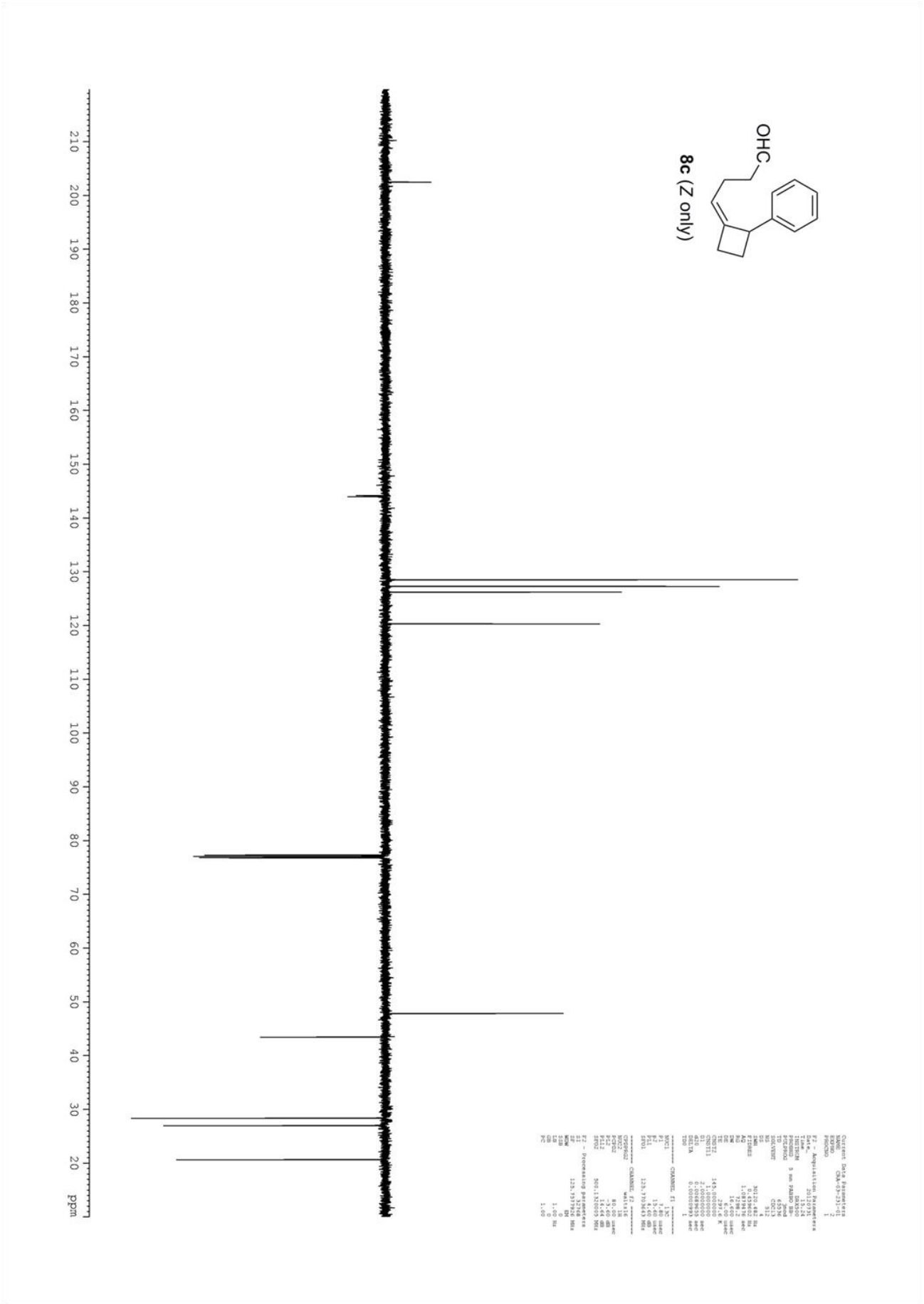

CHO
NTsPr
3
8b
(E/Z = 6/4)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

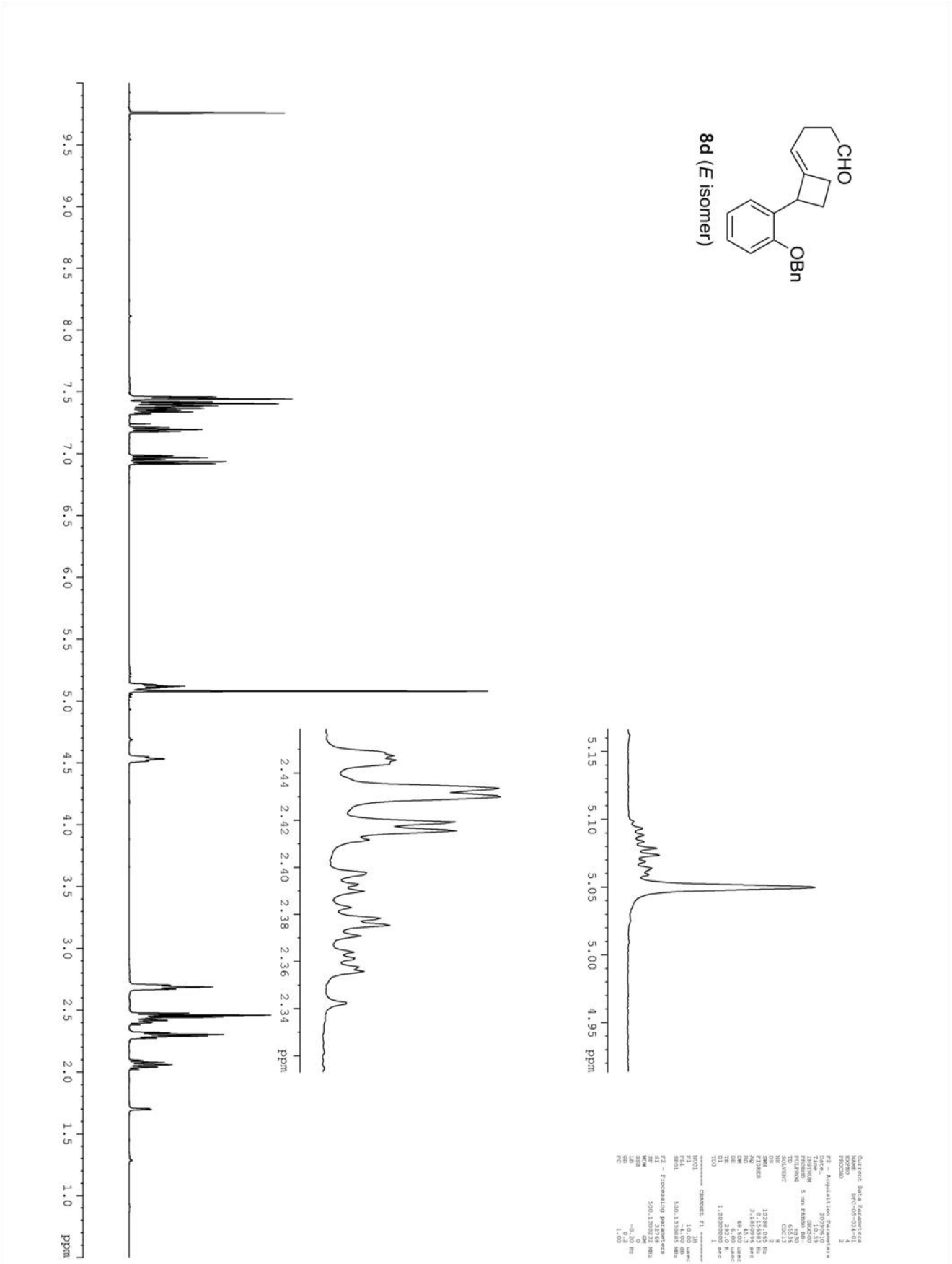

CHO
NTsPr
3
8b
(E/Z = 6/4)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

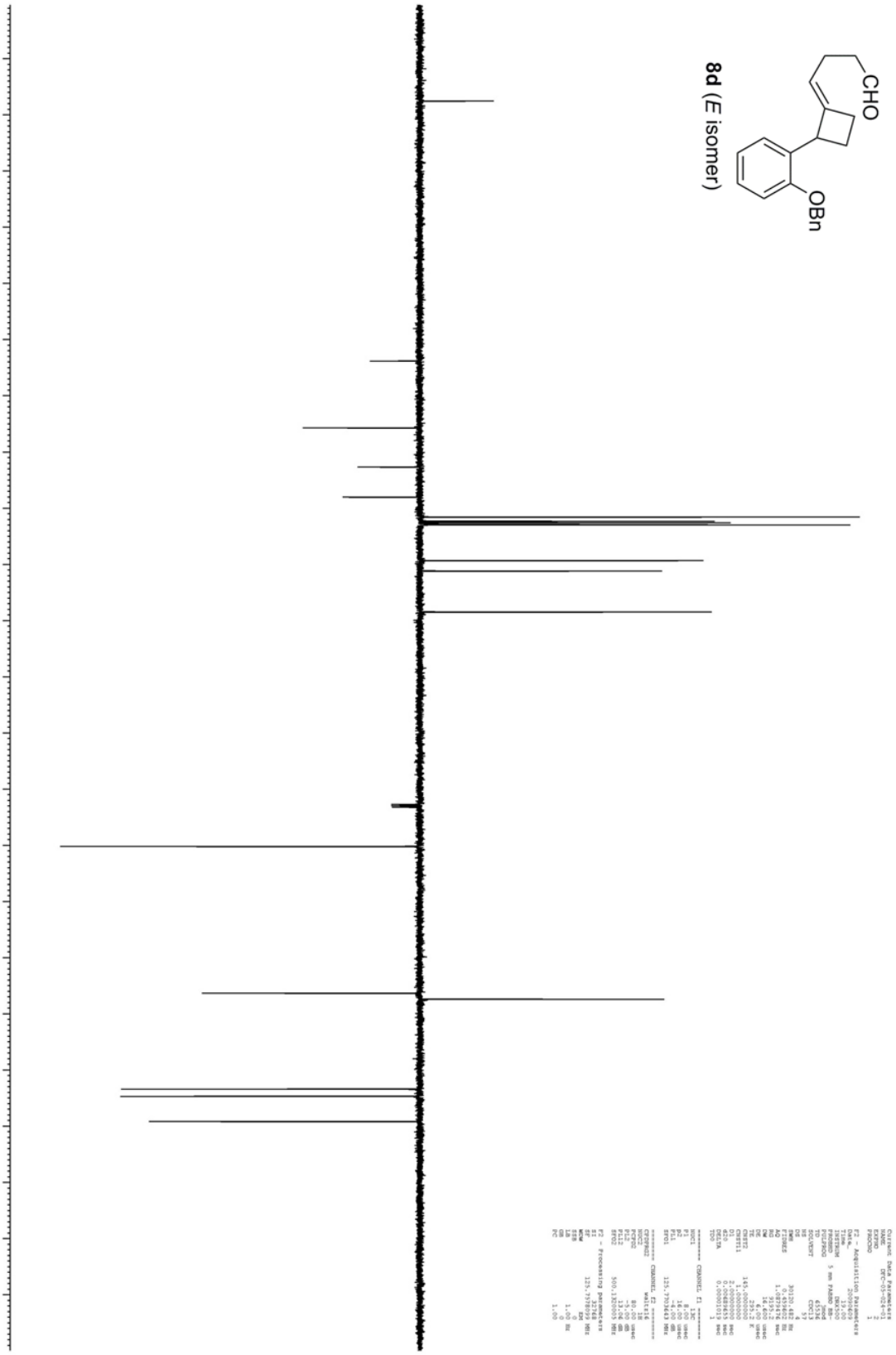

CHO
8c (E/Z = 3:1)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

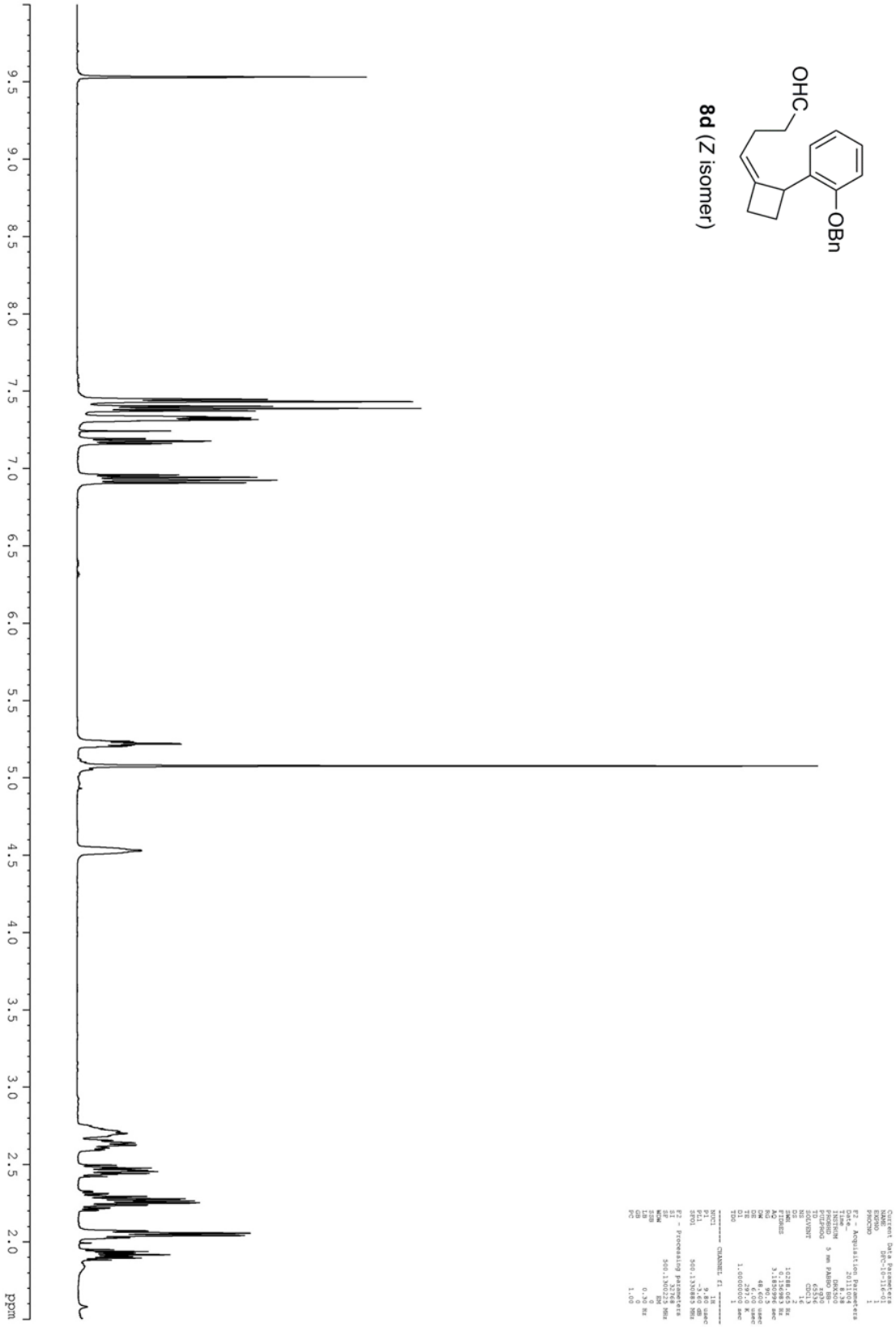

CHO
8c (E/Z = 3:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

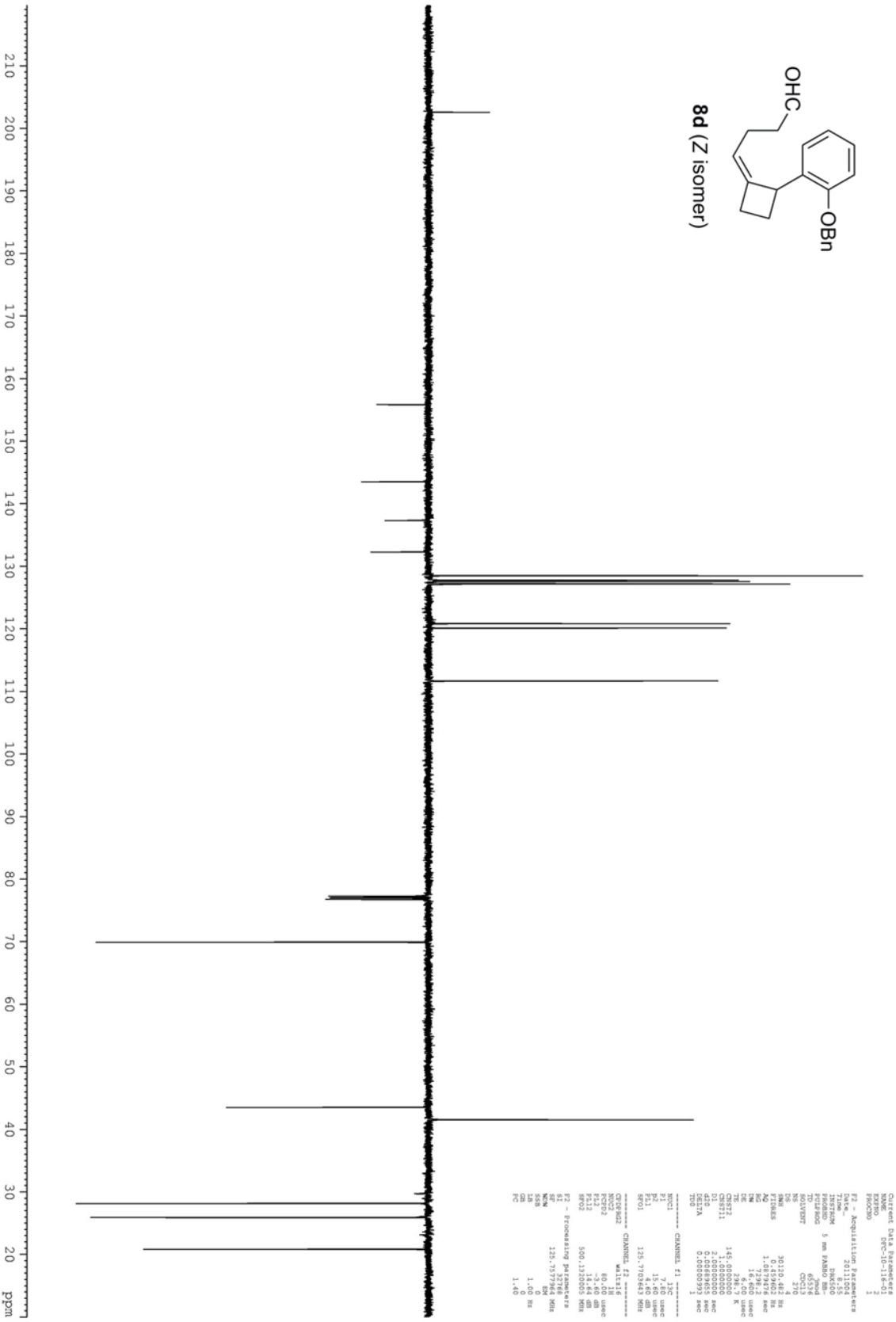

OHC
8c (Z only)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

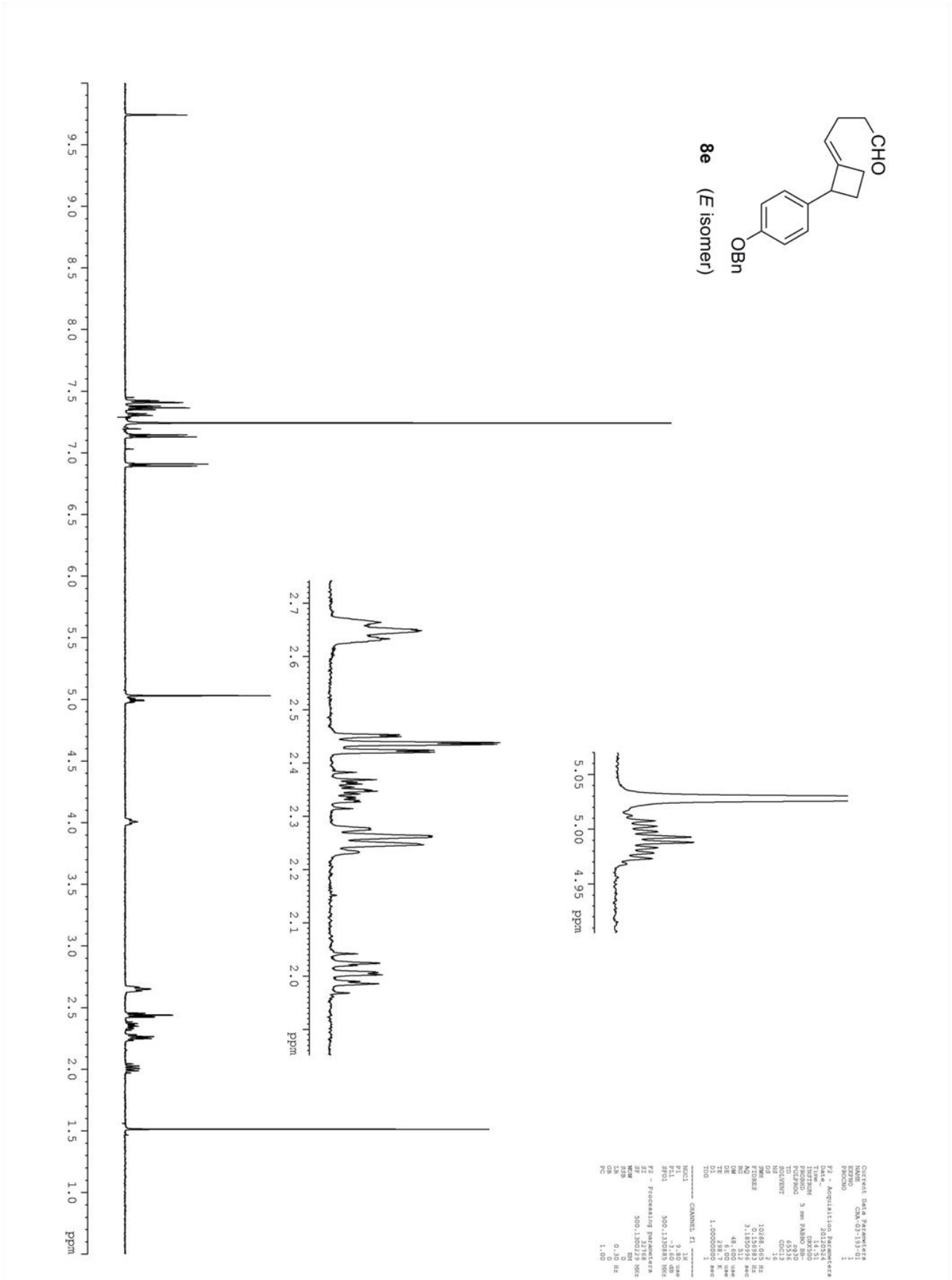

OHC
8c (Z only)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

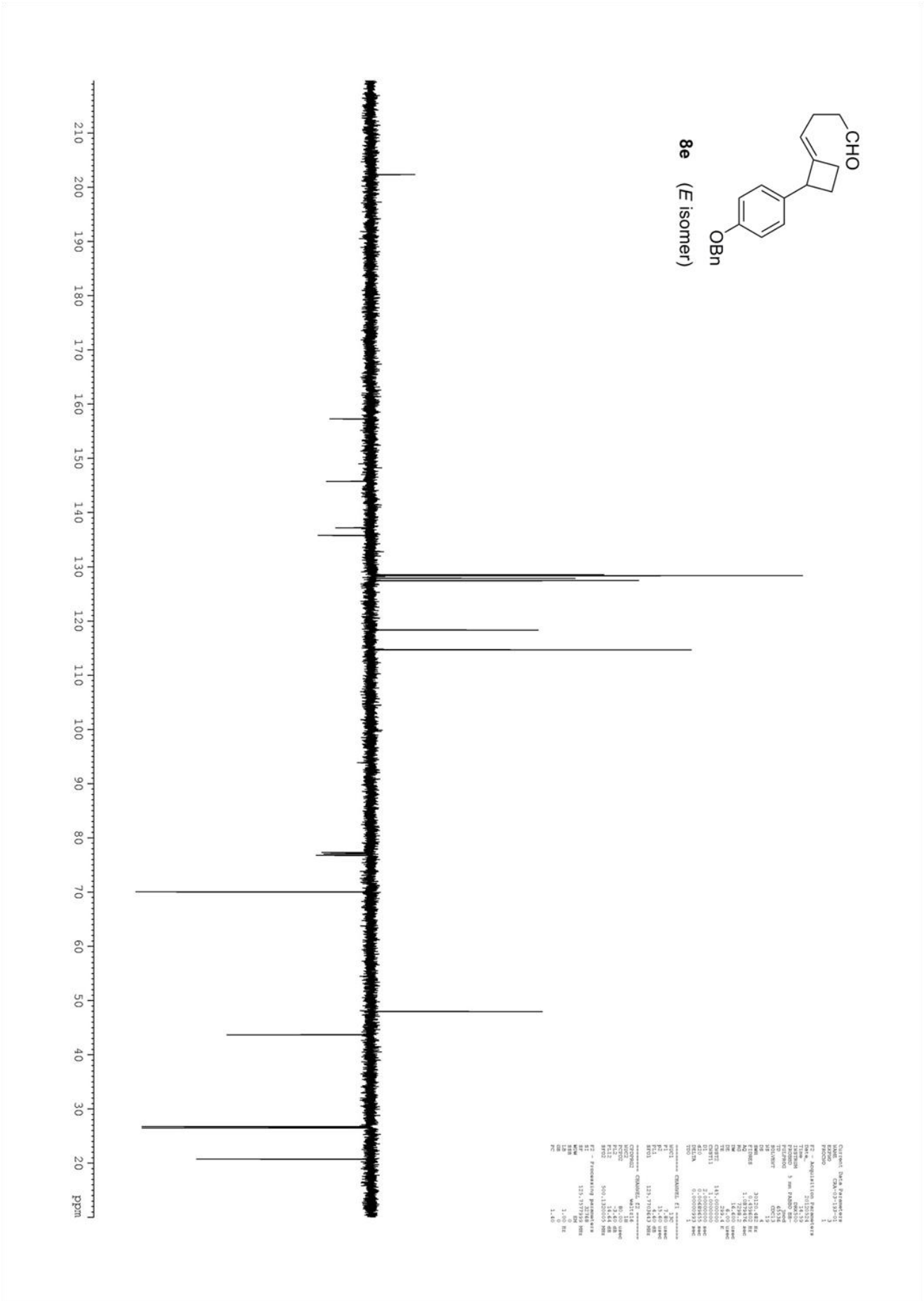

CHO
OBn
8d (E isomer)
5.15
5.10
5.05
5.00
4.95
ppm
2.44
2.42
2.40
2.38
2.36
2.34
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

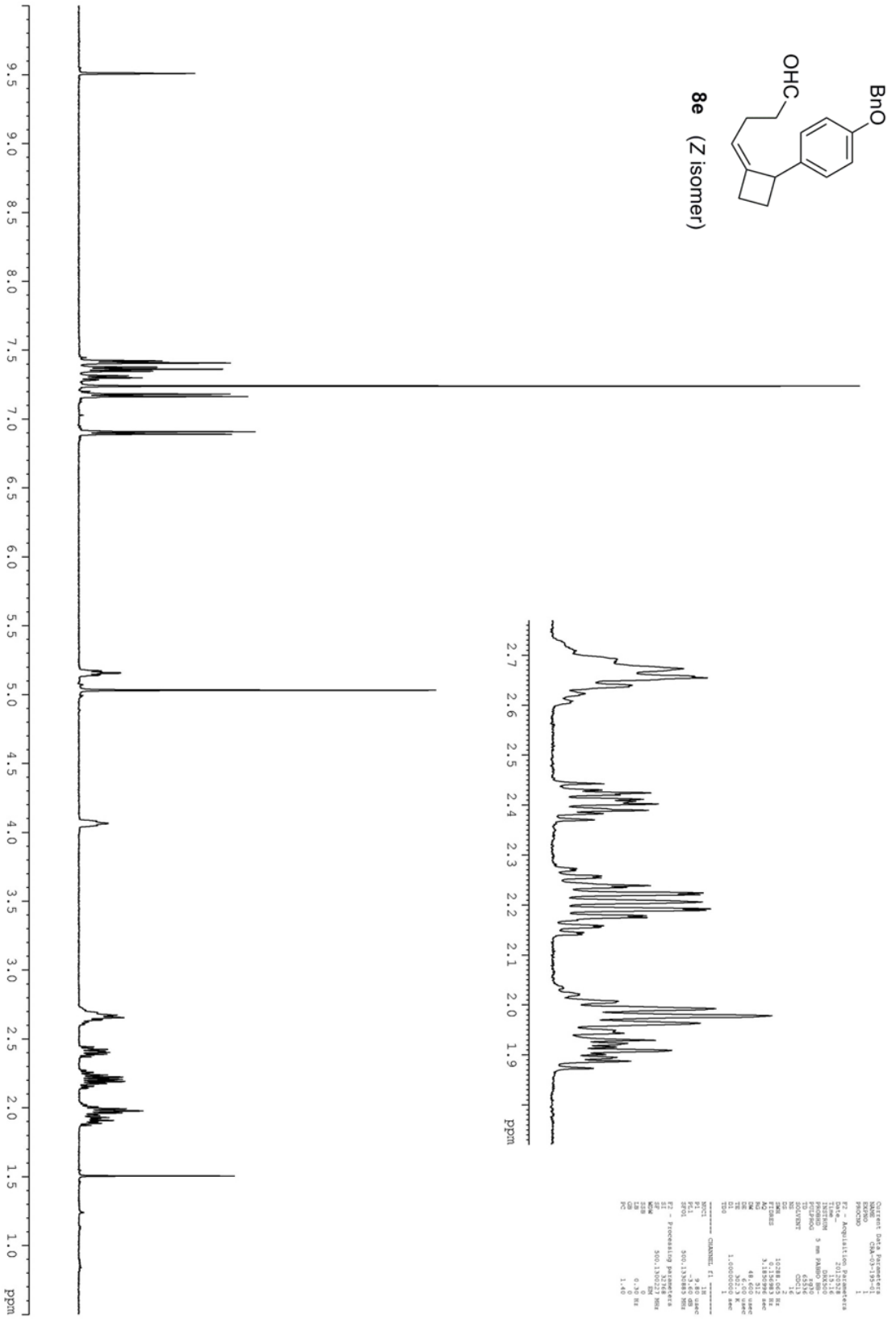

CHO
OBn
8d (E isomer)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm

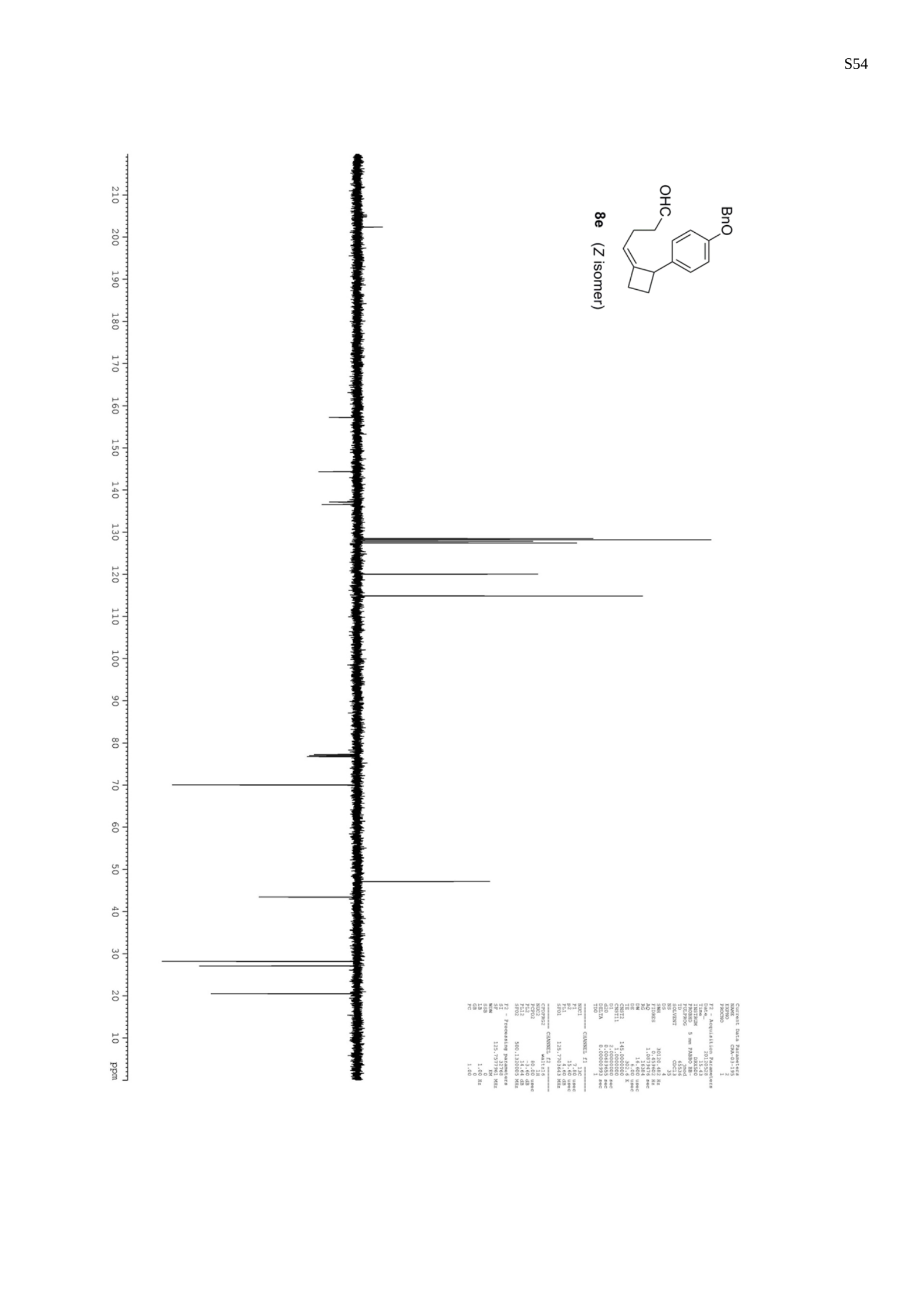

OHC
OBn
8d (Z isomer)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

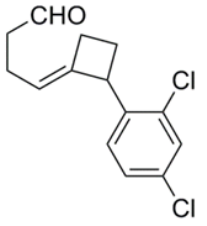

OHC
OBn
8d (Z isomer)
ppm


CHO
OBn
8e (E isomer)
5.05
5.00
4.95 ppm
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
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


CHO
OBn
8e (E isomer)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

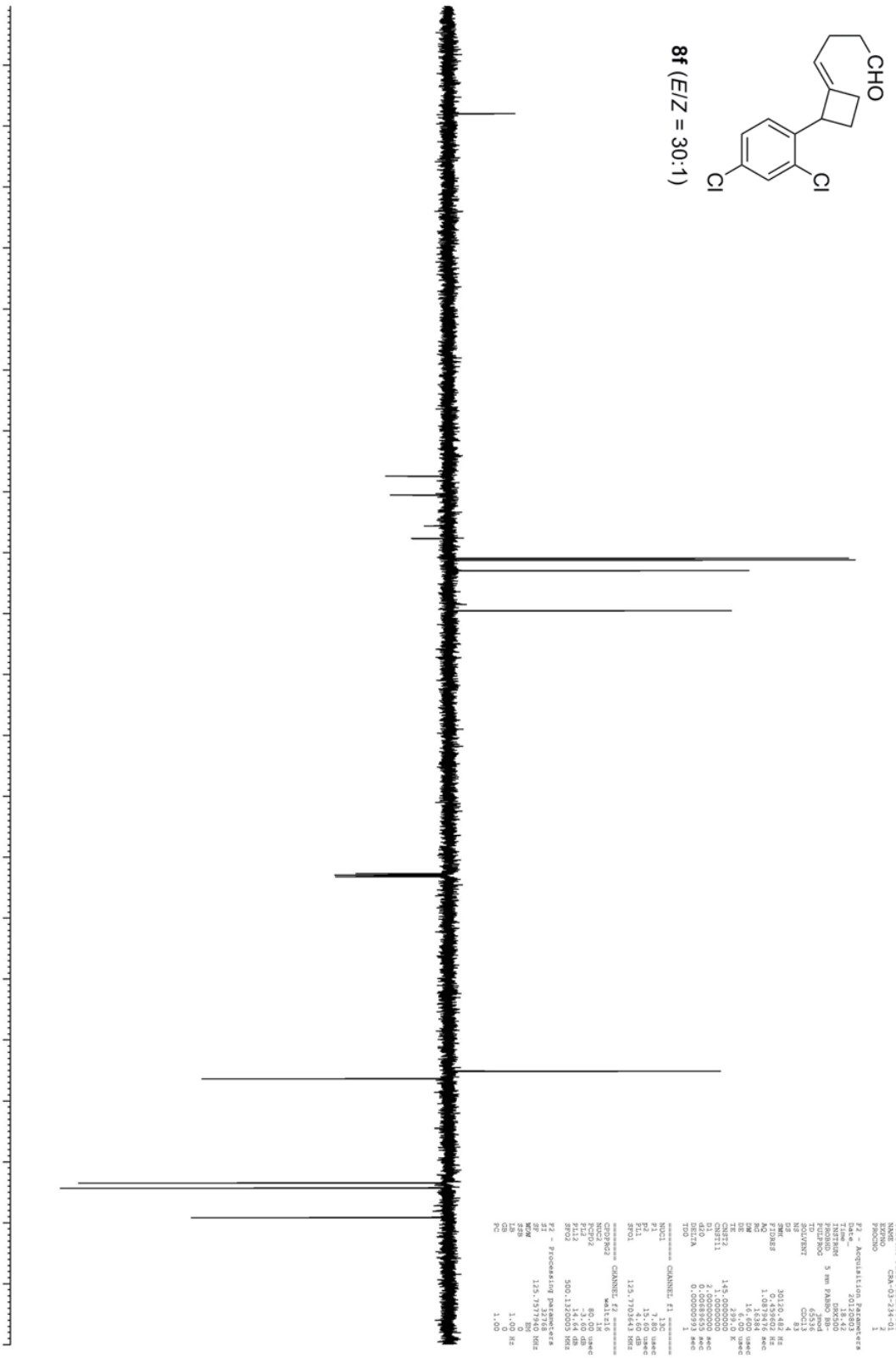

BnO
OHC
8e (Z isomer)
ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

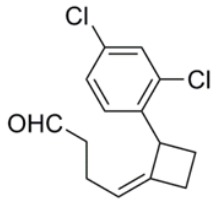

BnO
OHC
8e (Z isomer)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



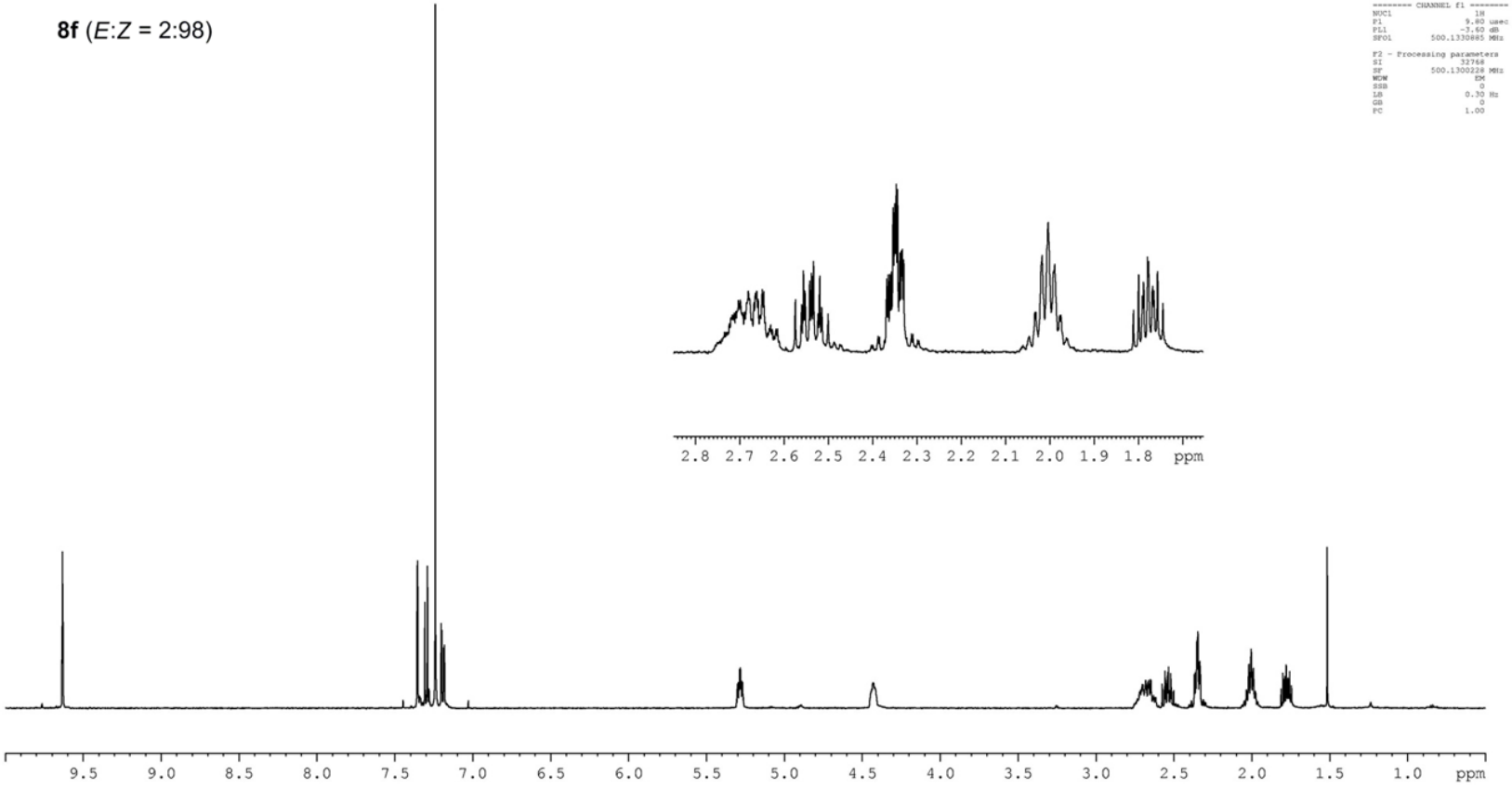
8f (*E*/*Z* = 30:1)


```
Current Data Parameters
NAME                  CRA-03-234-01
EXPNO                            1
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20120803
Time                         18.33
INSTRUM                     DRX500
PROBHD   5 mm PABBO BB-
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                     10288.065 Hz
FIDRES                   0.156983 Hz
AQ                       3.1850996 sec
RG                            512
DW                         48.600 usec
DE                          6.00 usec
TE                         298.6 K
D1                    1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          1H
P1                          9.80 usec
PL1                        -3.60 dB
SFO1                500.1330885 MHz

F2 - Processing parameters
SI                          32768
SF                  500.1300226 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```

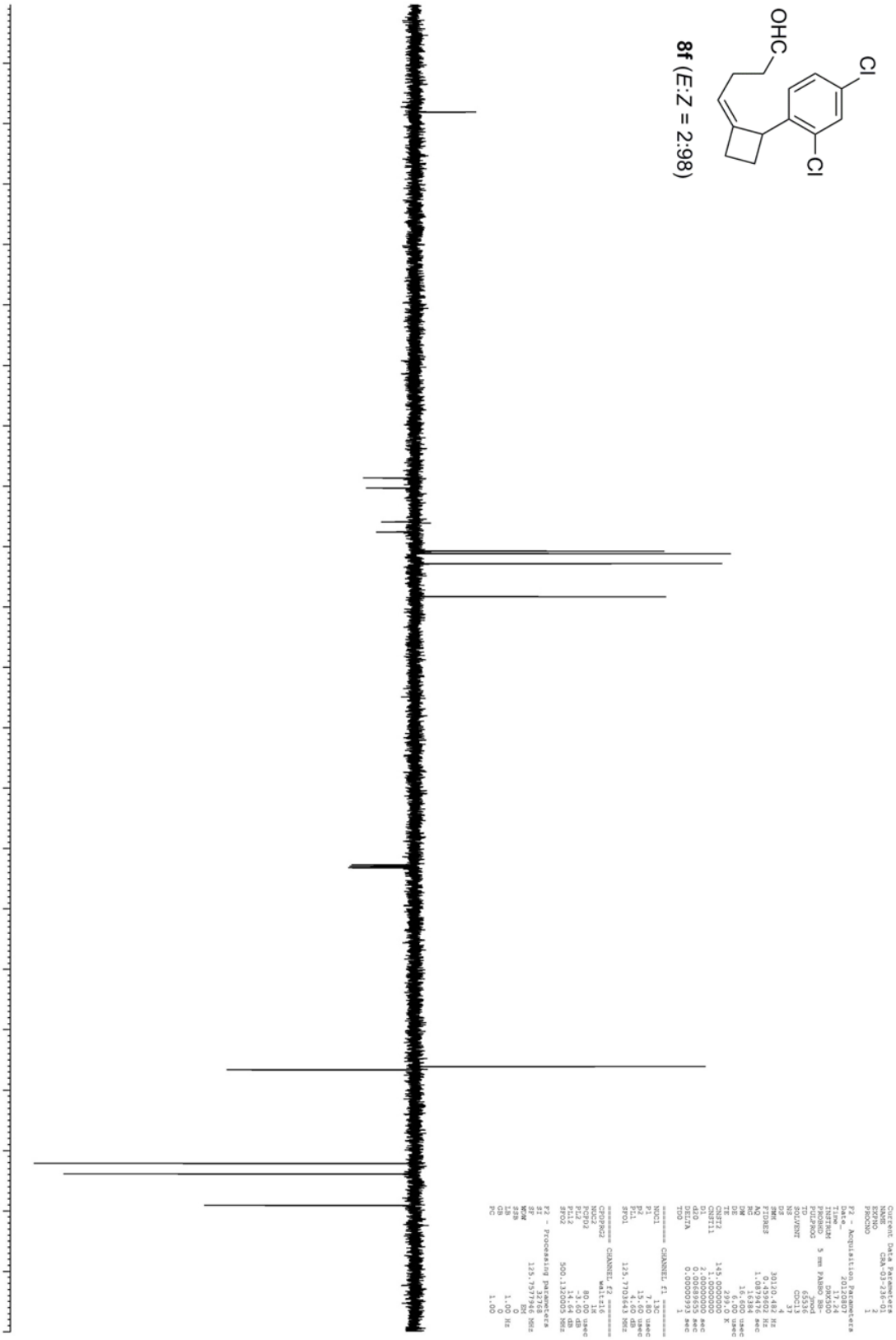

CHO
Cl
Cl
8f (E/Z = 30:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

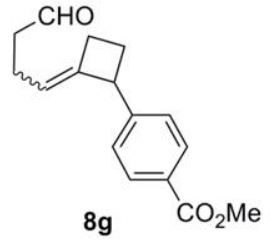

Cl
Cl
OHC

8f (*E*:*Z* = 2:98)


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
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 ppm

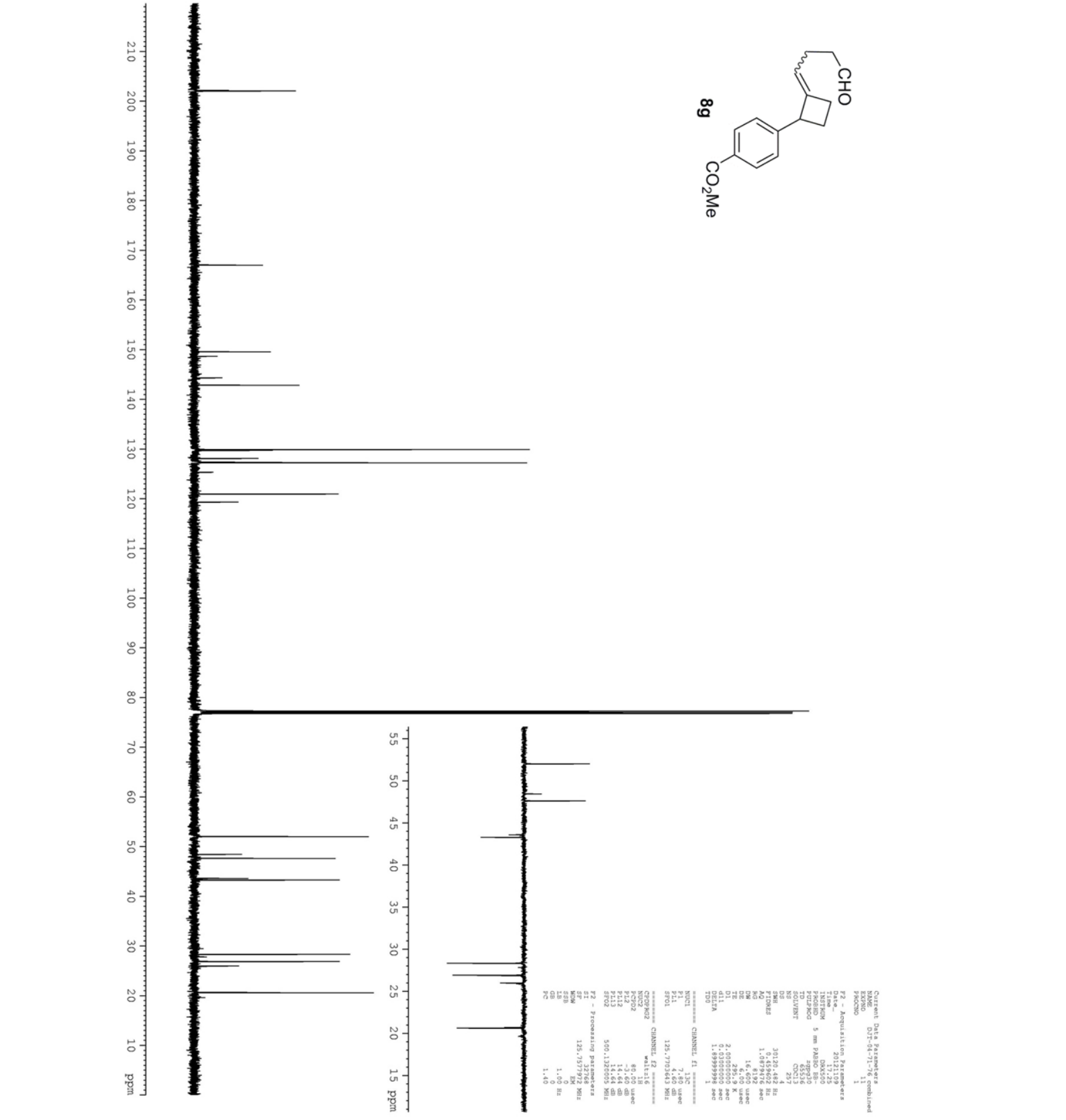

Current Data Parameters
NAME CRA-03-236-01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120807
Time 17.05
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 456.1
DW 48.600 usec
DE 6.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.60 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300228 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

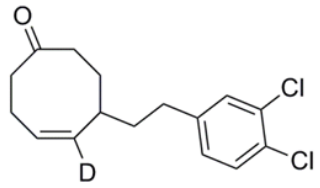

OHC
Cl
Cl
8f (E:Z = 2:98)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CHO
CO2Me

8g

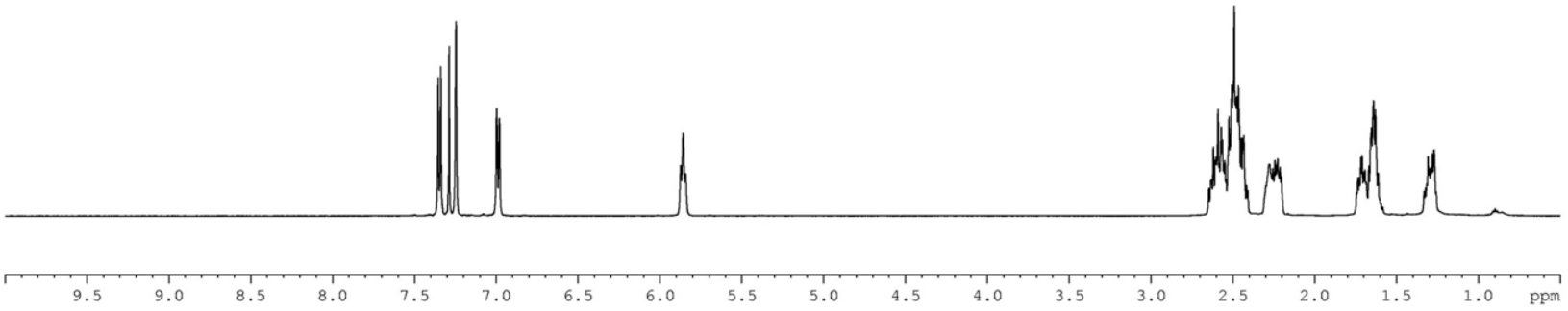
Current Data Parameters
NAME DJT-04-69-01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121105
Time 16.57
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 181
DW 48.600 usec
DE 6.00 usec
TE 292.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.60 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300238 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm

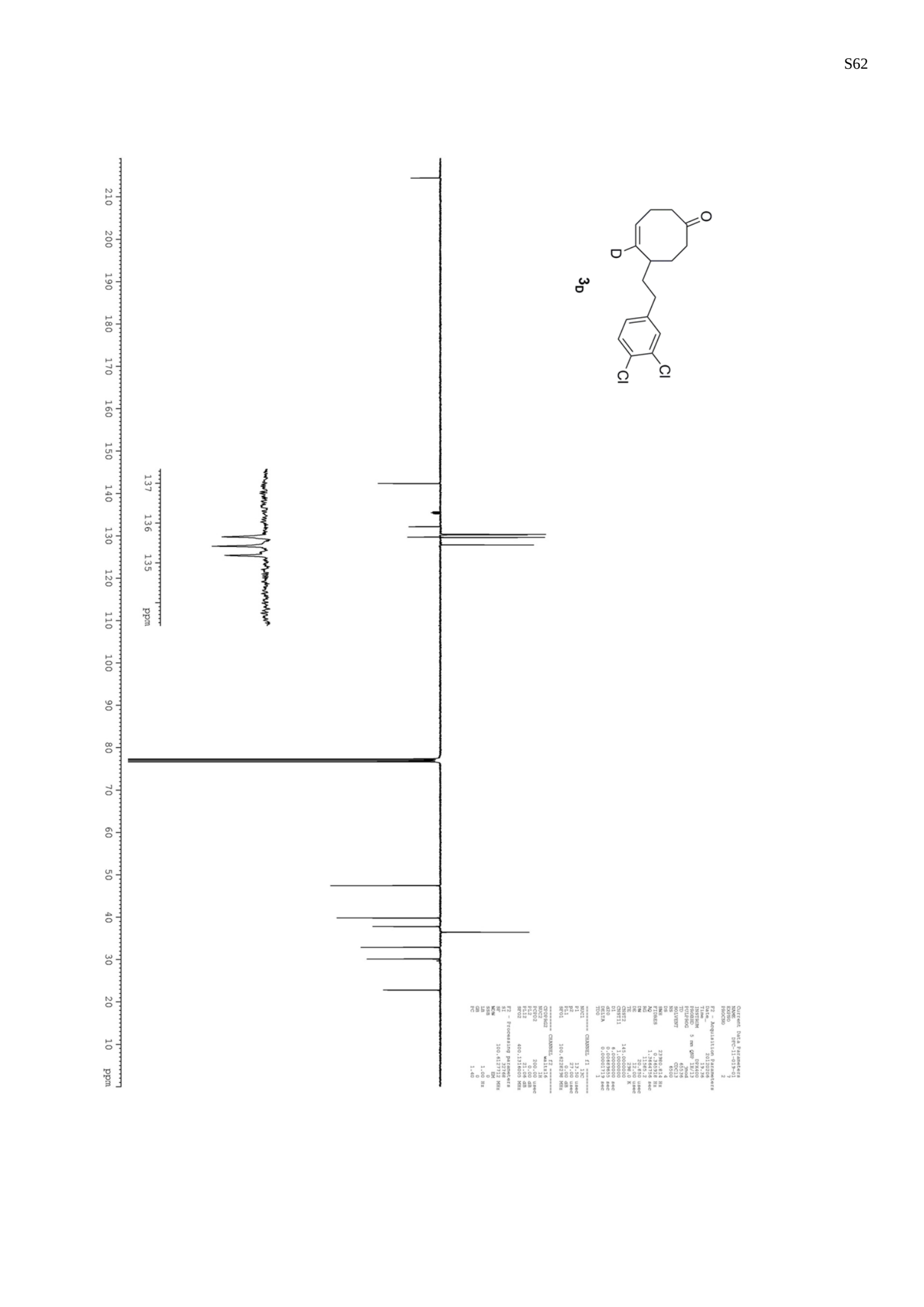

CHO
8g
CO2Me
Current Data Parameters
NAME DJT-04-71-76 combined
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111129
Time 17.25
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 23
DS 4
SWH 30120.482 Hz
FIDRES 0.459502 Hz
AQ 1.0895902 sec
RG 8192
DW 16.600 usec
DE 6.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 7.80 usec
PL1 4.60 dB
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.60 dB
PL12 14.64 dB
PL13 14.64 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577972 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
55 50 45 40 35 30 25 20 15 ppm

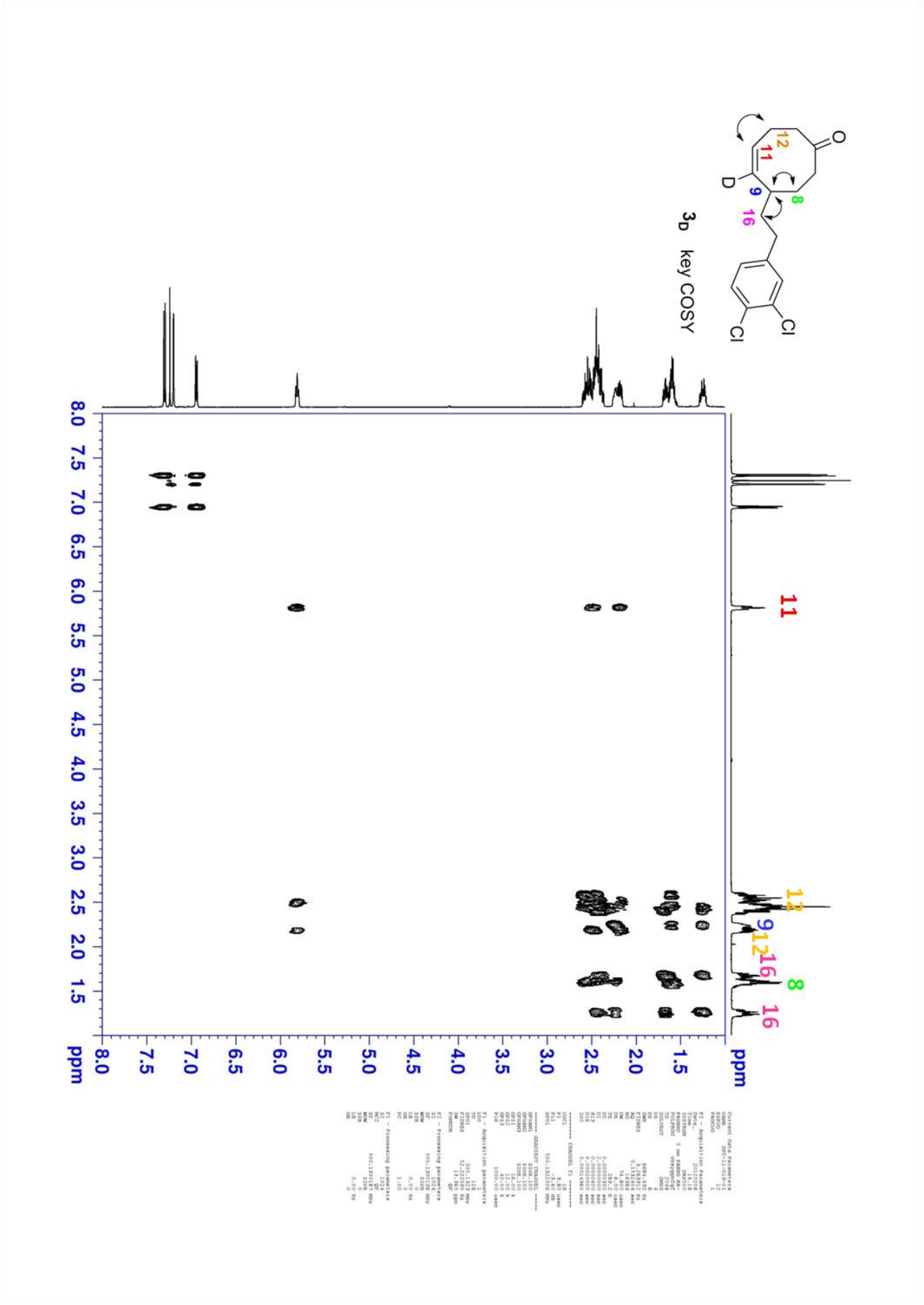


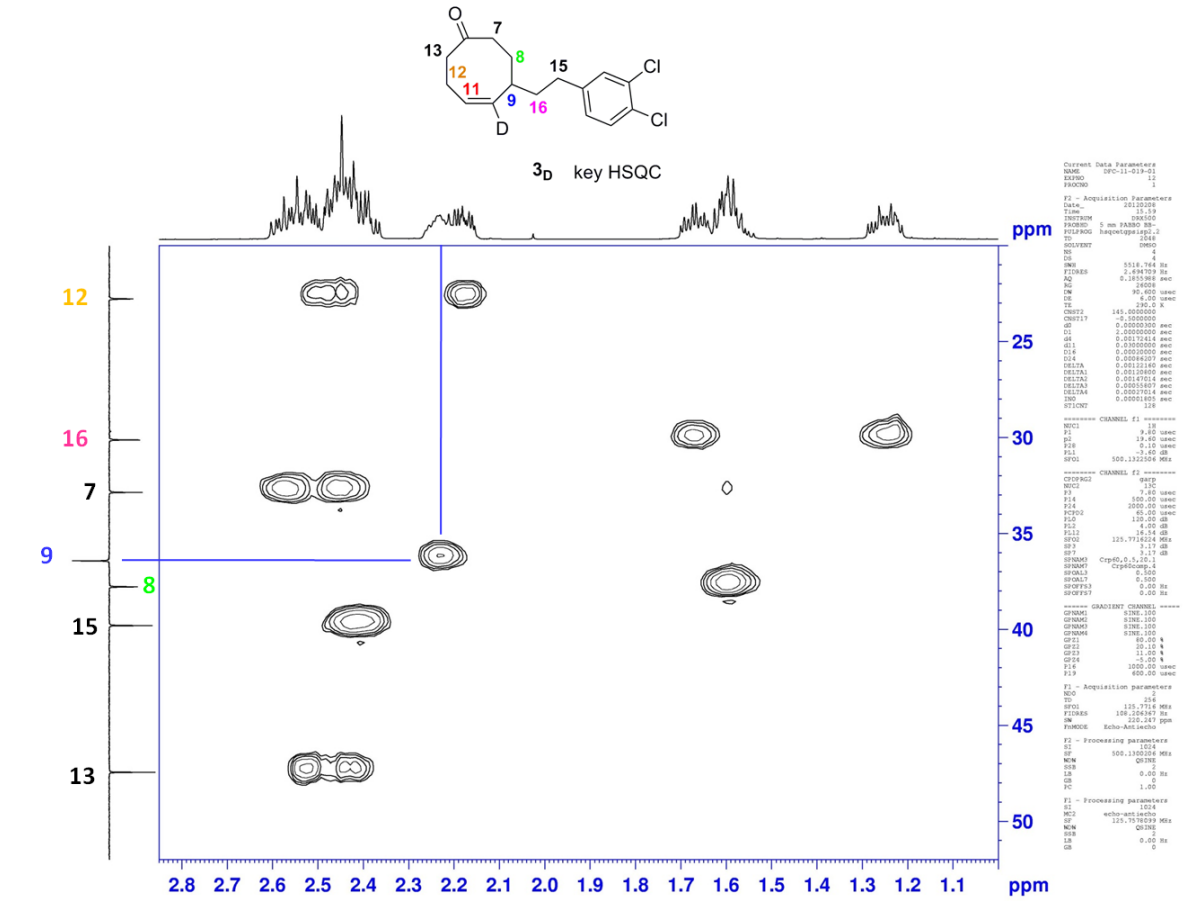
3_D

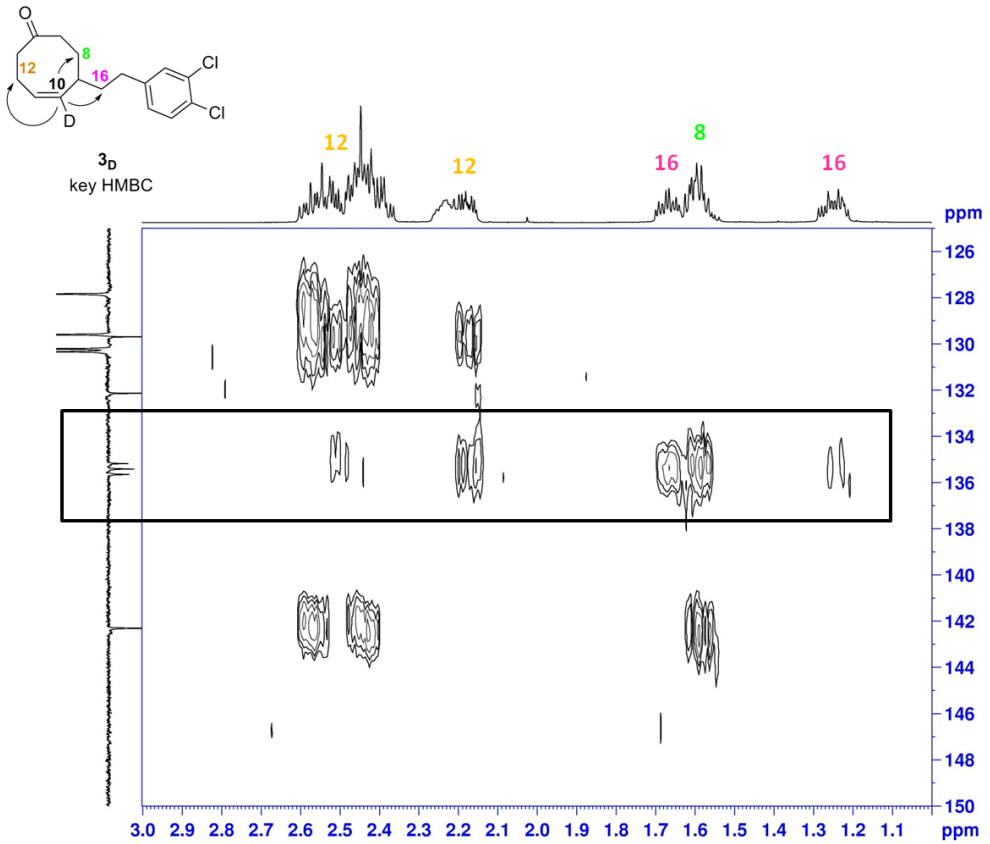
```
Current Data Parameters
NAME          DFC-11-019-01
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120208
Time                  14.39
INSTRUM              DRX500
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10288.065 Hz
FIDRES            0.156983 Hz
AQ                3.1850996 sec
RG                    228.1
DW                   48.600 usec
DE                    6.00 usec
TE                   289.3 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.80 usec
PL1                  -3.60 dB
SFO1          500.1330885 MHz

F2 - Processing parameters
SI                    32768
SF            500.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.40
```

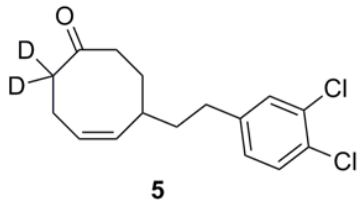



O
D
Cl
Cl
3D
ppm

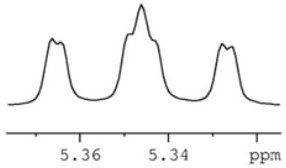

3D key COSY
O
12
11
D
9
8
16
Cl
Cl
11
12
9
12
16
8
16
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


3D key HSQC
ppm
12
16
7
9
8
15
13
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 ppm
25
30
35
40
45
50

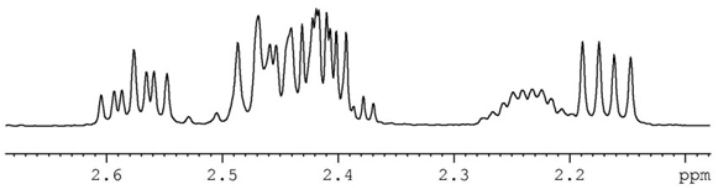

3D
key HMBC
12
12
8
16
16
ppm
126
128
130
132
134
136
138
140
142
144
146
148
150
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 ppm

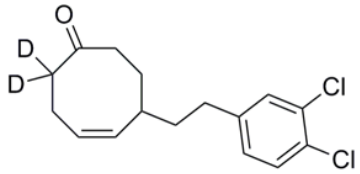


5



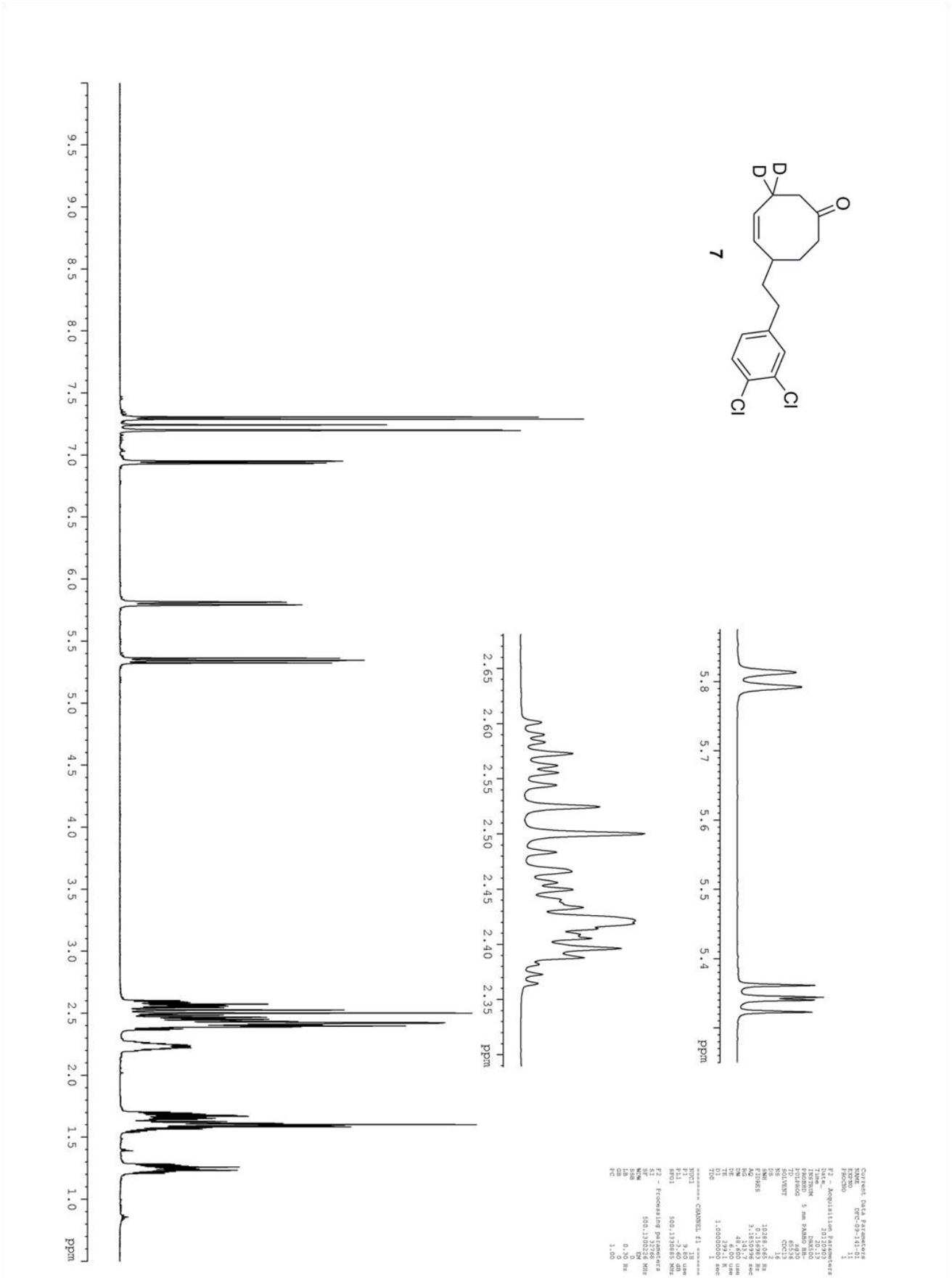

```
Current Data Parameters
NAME        DFC-09-151-03
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120905
Time              18.56
INSTRUM         DRX500
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10288.065 Hz
FIDRES        0.156983 Hz
AQ            3.1850996 sec
RG                287.4
DW               48.600 usec
DE                6.00 usec
TE                298.2 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.80 usec
PL1              -3.60 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300228 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

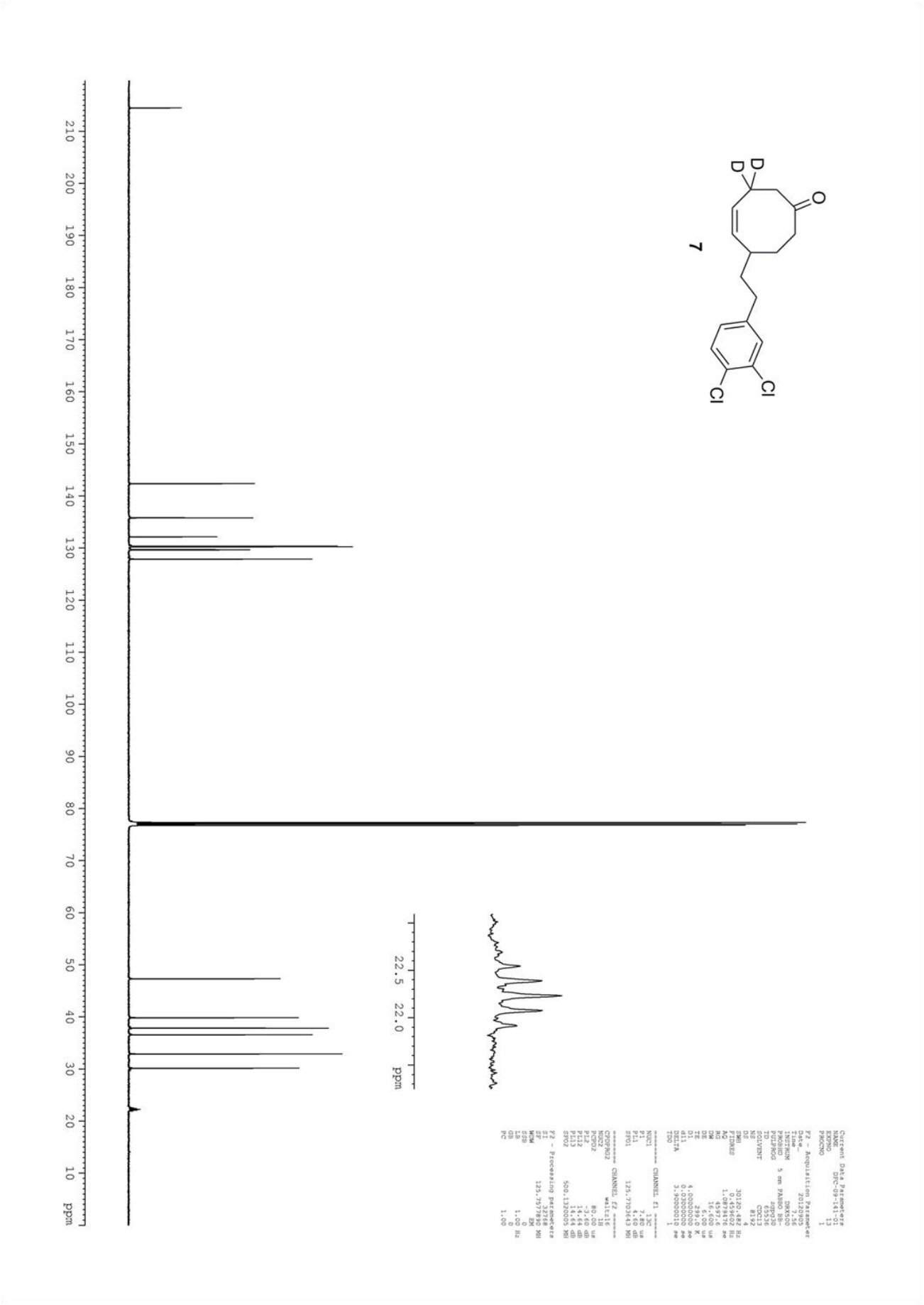


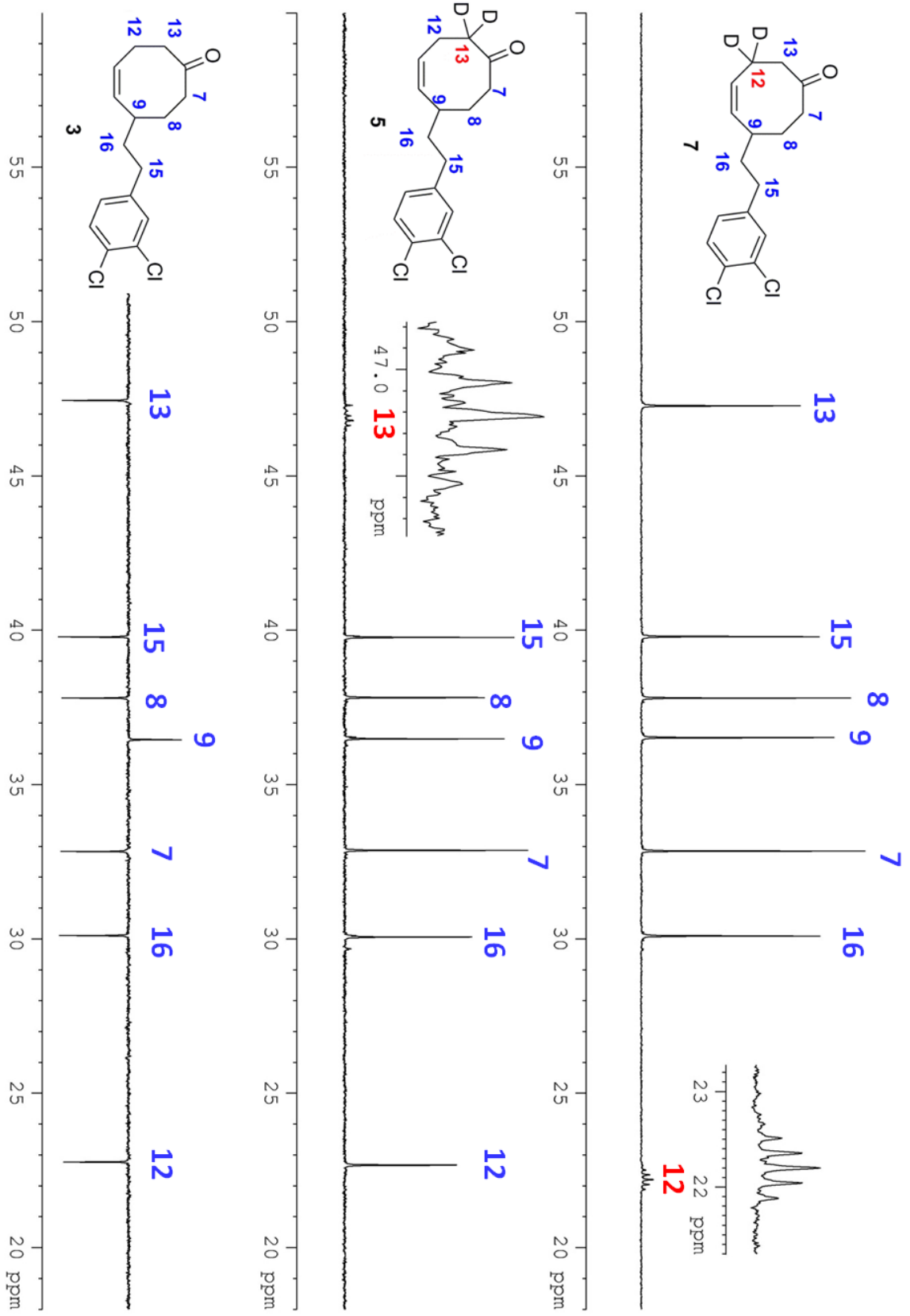


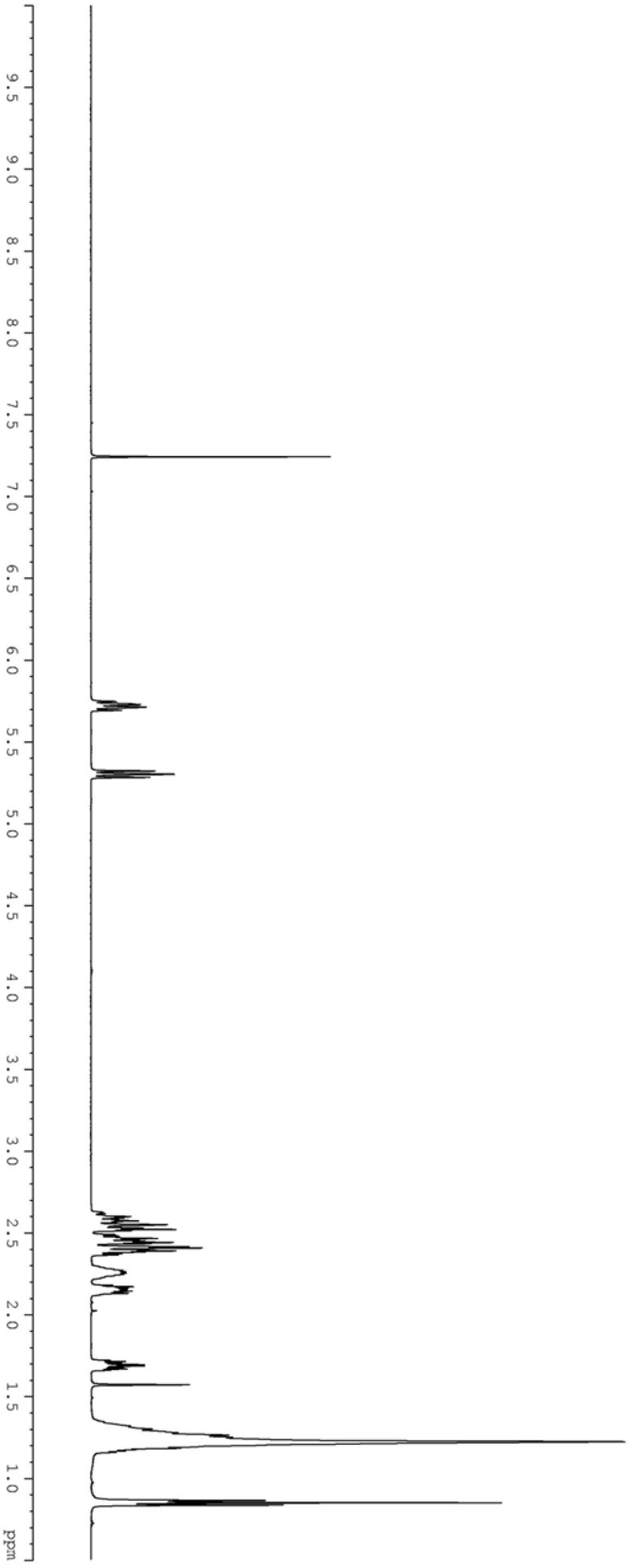
5

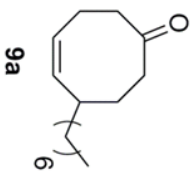

```
Current Data Parameters
NAME                  DFC-09-151-03
EXPNO                           12
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20120906
Time                          7.49
INSTRUM                     DRX500
PROBHD     5 mm PABBO BB-
PULPROG                   zgpg30
TD                             65536
SOLVENT                      CDCl3
NS                              8192
DS                                 4
SWH                       30120.482 Hz
FIDRES                    0.459602 Hz
AQ                        1.0879476 sec
RG                           11585.2
DW                           16.600 usec
DE                            6.00 usec
TE                           298.4 K
D1                        4.00000000 sec
d11                       0.03000000 sec
DELTA                     3.90000010 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                           13C
P1                            7.80 usec
PL1                           4.60 dB
SFO1                  125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                            1H
PCPD2                        80.00 usec
PL2                          -3.60 dB
PL12                         14.64 dB
PL13                         14.64 dB
SFO2                  500.1320005 MHz

F2 - Processing parameters
SI                             32768
SF                    125.7577914 MHz
WDW                               EM
SSB                                0
LB                            1.00 Hz
GB                                 0
PC                            1.00
```


D
D
O
Cl
Cl
7
ppm
2.65 2.60 2.55 2.50 2.45 2.40 2.35 ppm
5.8 5.7 5.6 5.5 5.4 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


D
D
O
Cl
Cl
7
22.5
22.0
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

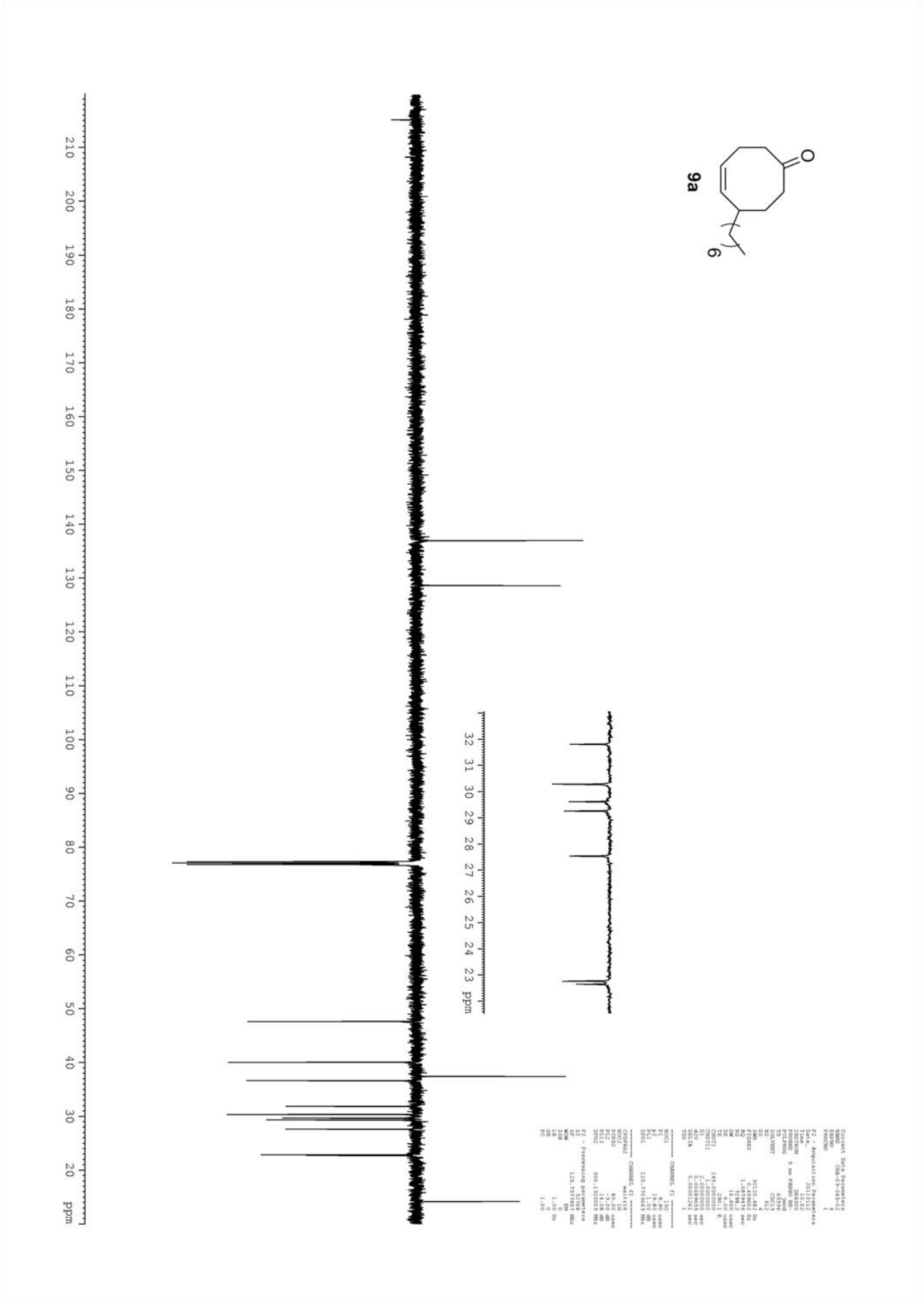

7
5
3
13
15
8
9
7
16
12
47.0
23
22
ppm
55
50
45
40
35
30
25
20

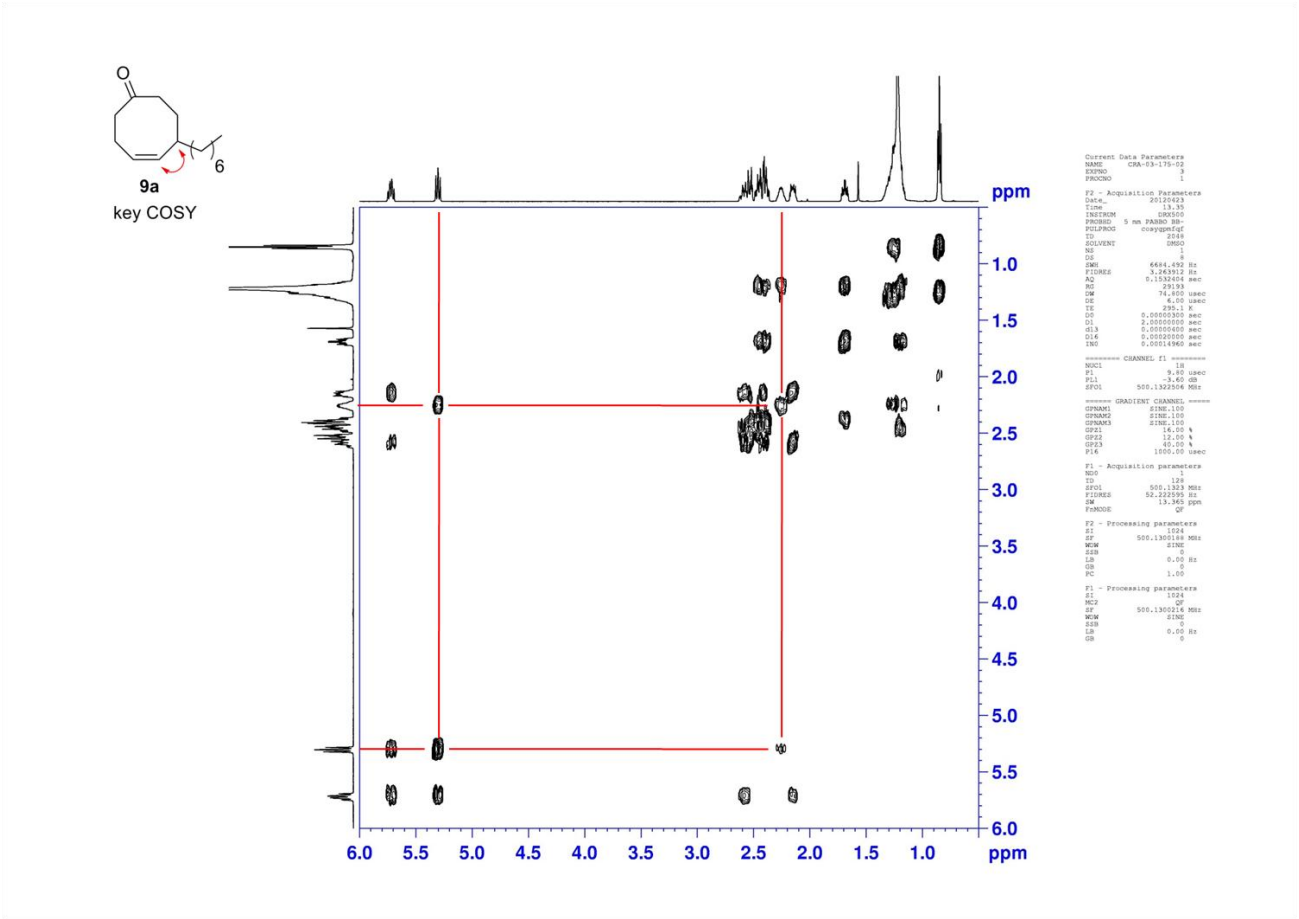


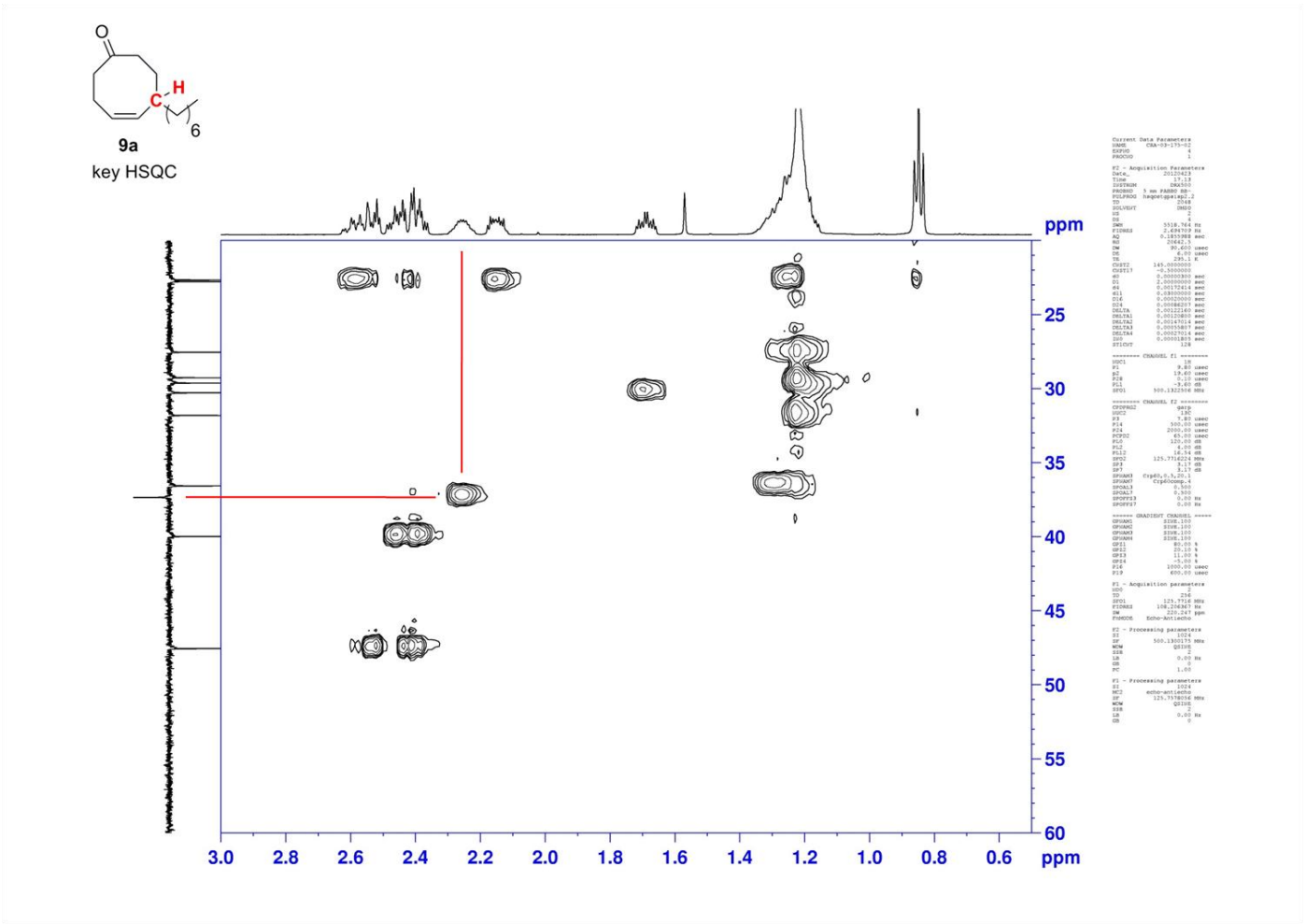


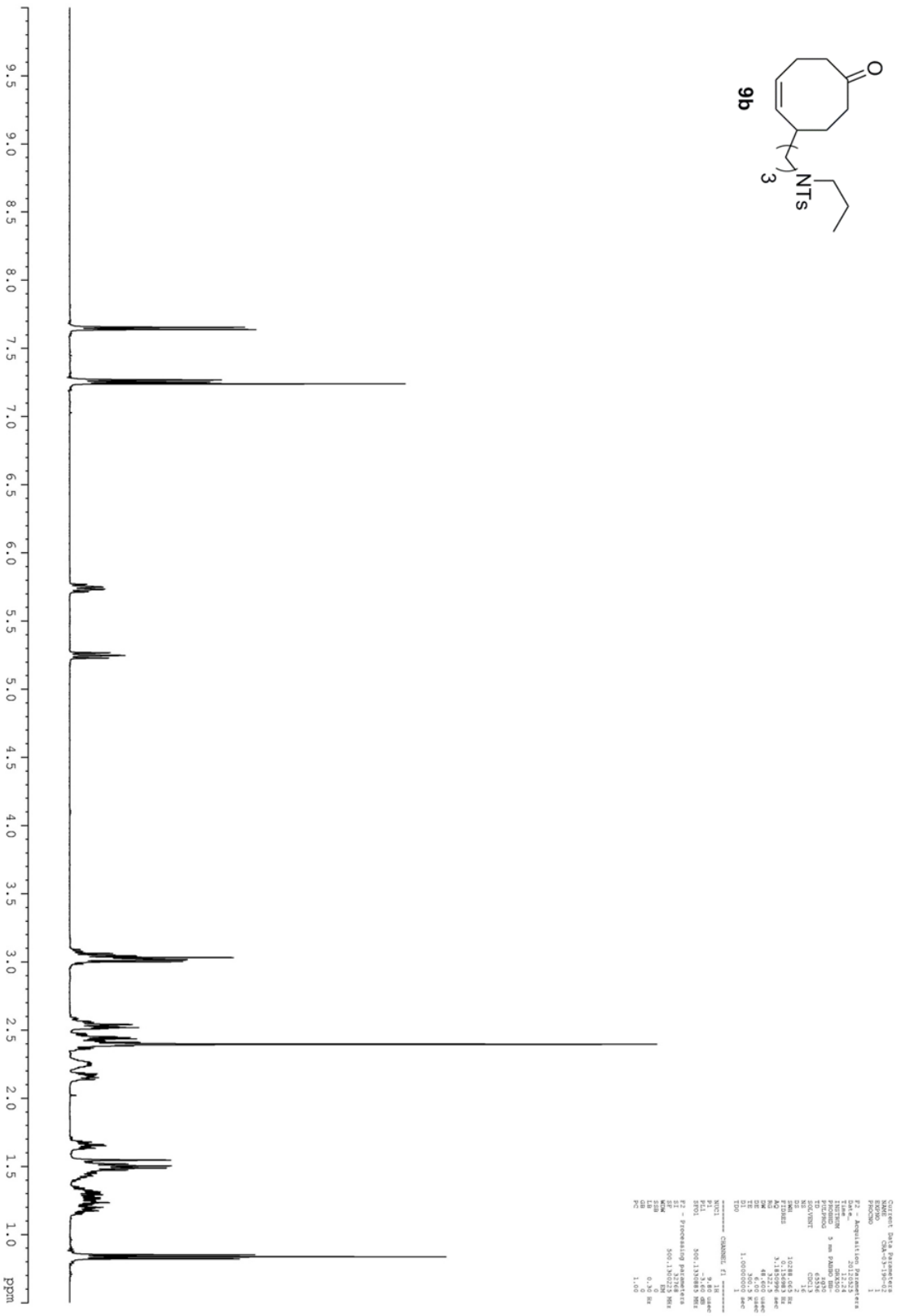
9a

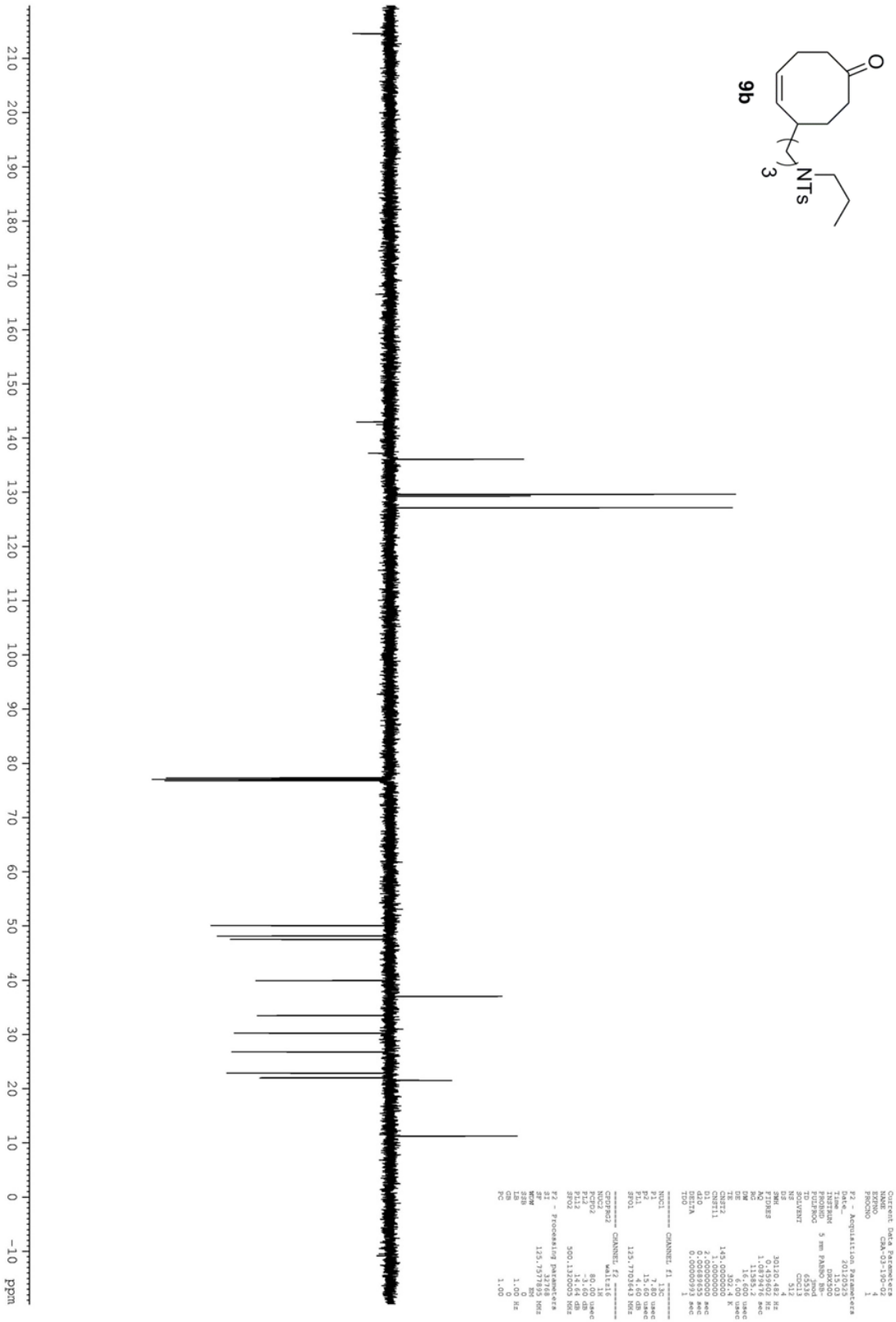
```
Current Data Parameters
NAME            CRA-03-172-B1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20120419
Time            17.03
INSTRUM         DRX500
PROBHD     5 mm PABBO BB-
PULPROG         zg30
TD              65536
SOLVENT         CDCl3
NS              16
DS              4
SWH             10288.065 Hz
FIDRES          0.156993 Hz
AQ              3.1850996 sec
RG              114.16
DW              48.600 usec
DE              6.00 usec
TE              297.5 K
D1              1.00000000 sec
TD0             1

======== CHANNEL f1 ========
NUC1            1H
P1              9.80 usec
PL1             -3.00 dB
SFO1            500.1330885 MHz

F2 - Processing parameters
SI              32768
SF              500.1300028 MHz
WDW             EM
SSB             0
LB              0.30 Hz
GB              0
PC              1.00
```

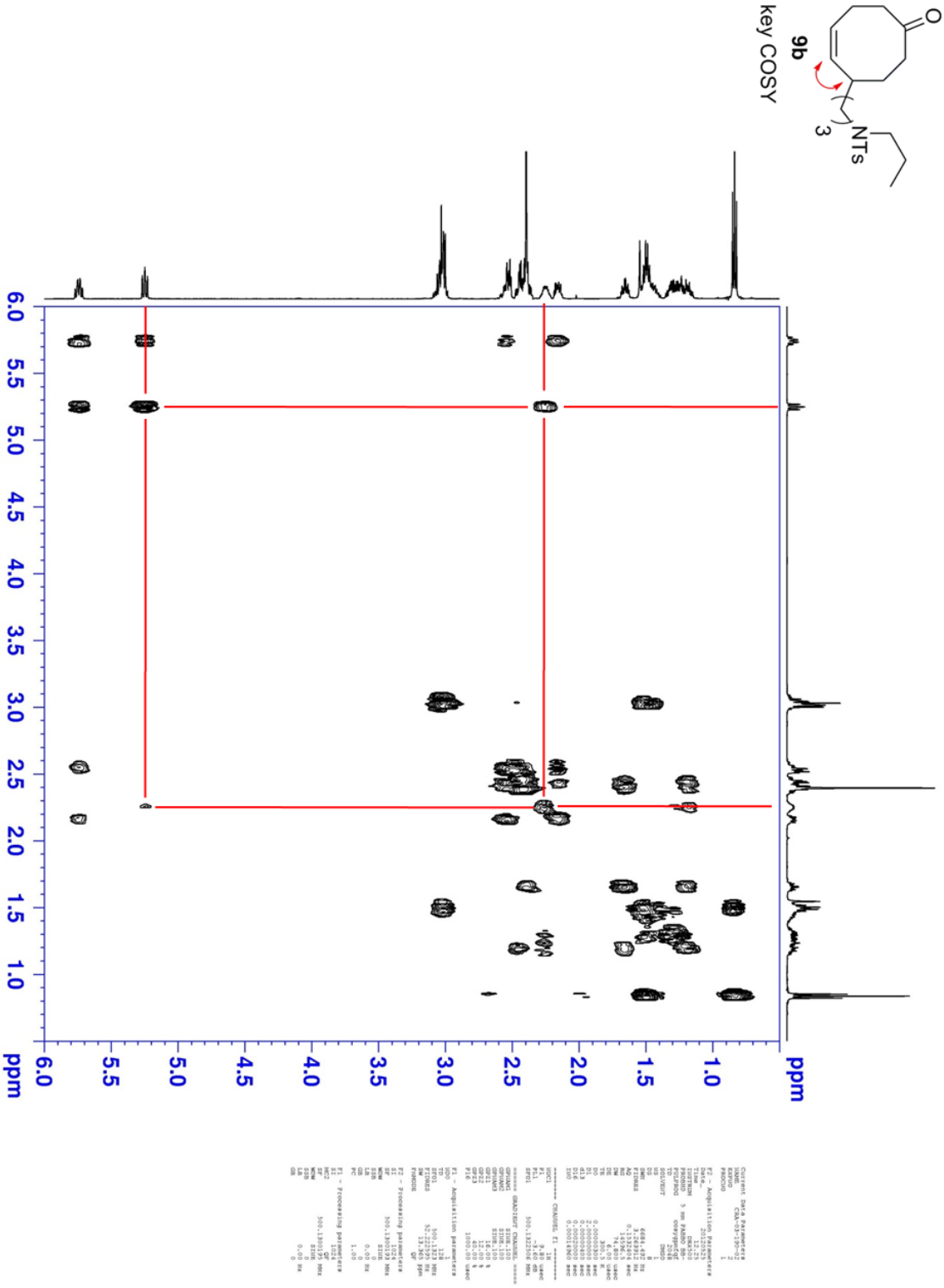

9a
O
6
32 31 30 29 28 27 26 25 24 23 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

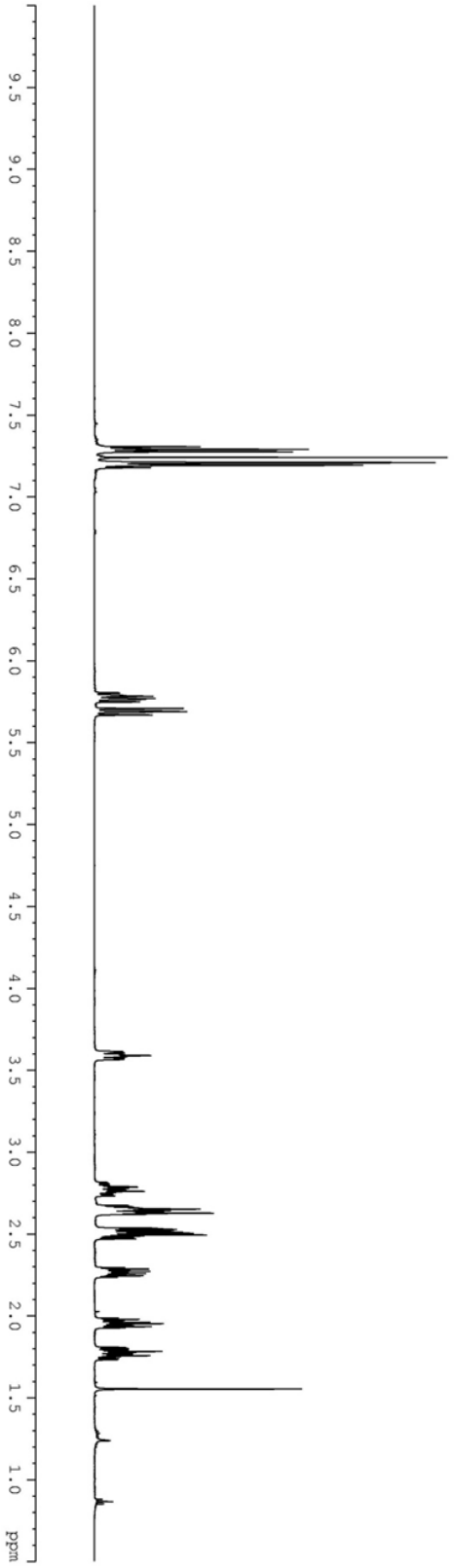

9a
key COSY
ppm
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

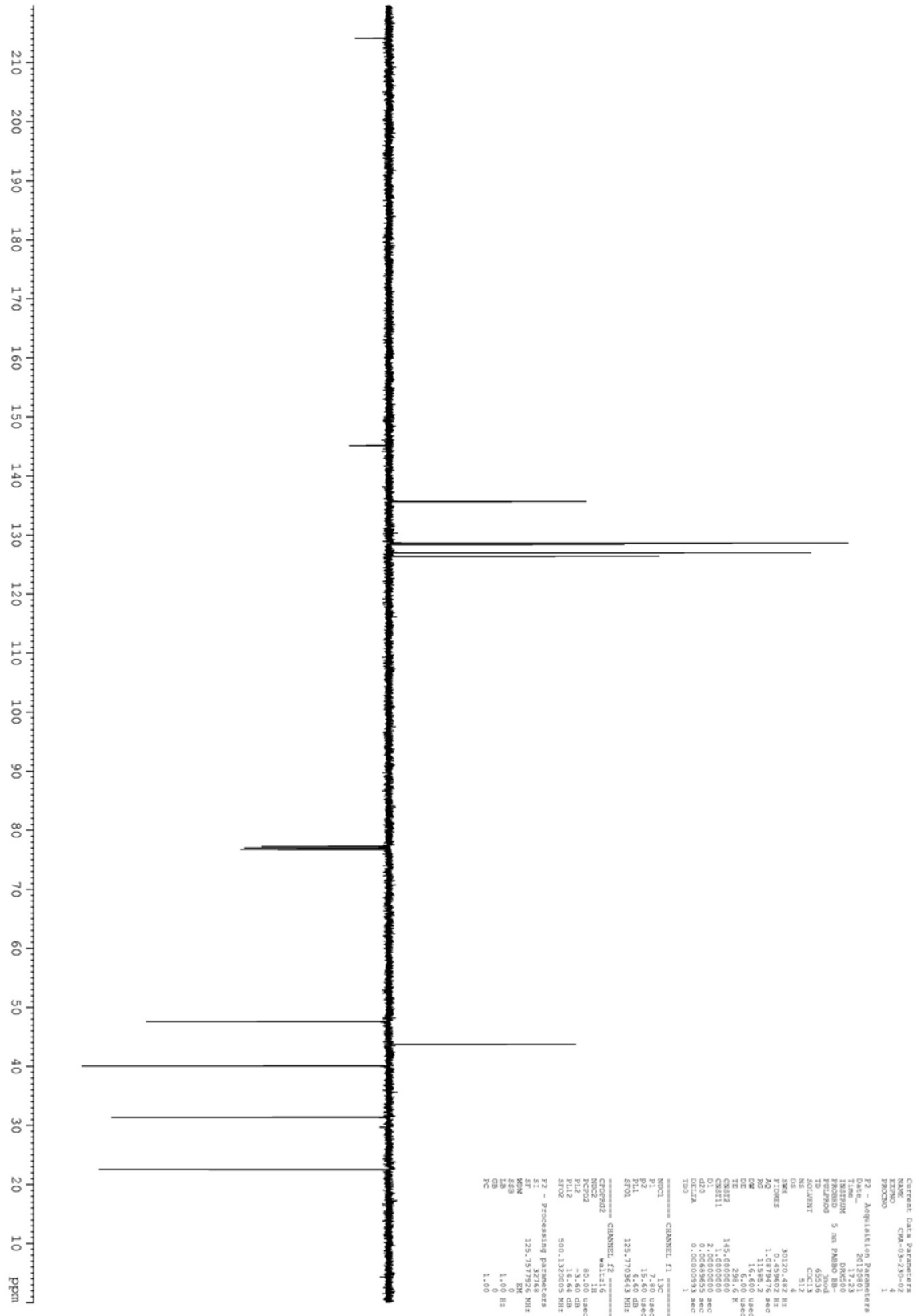

9a
key HSQC
ppm
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 ppm

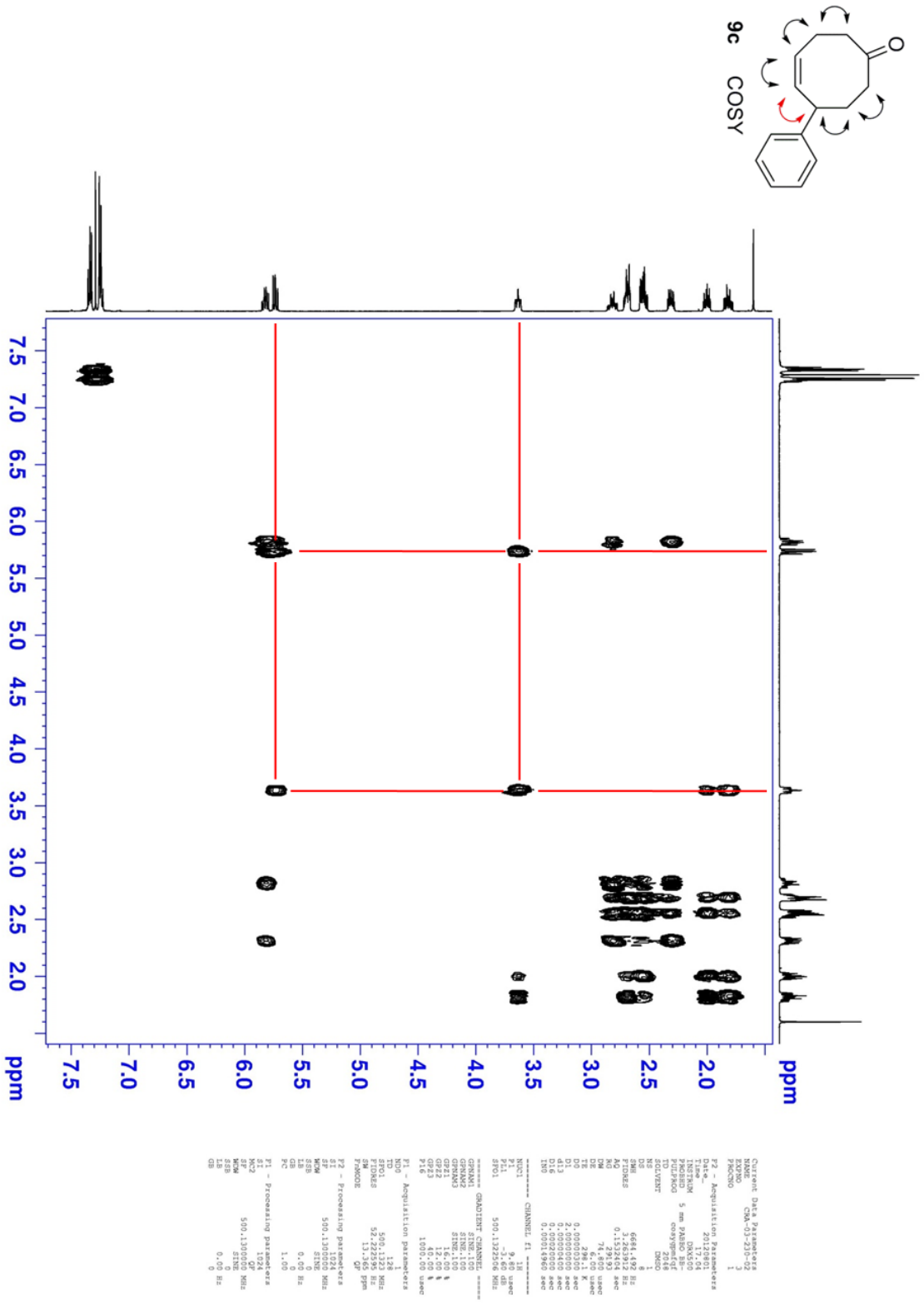

O
NTs
3
9b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

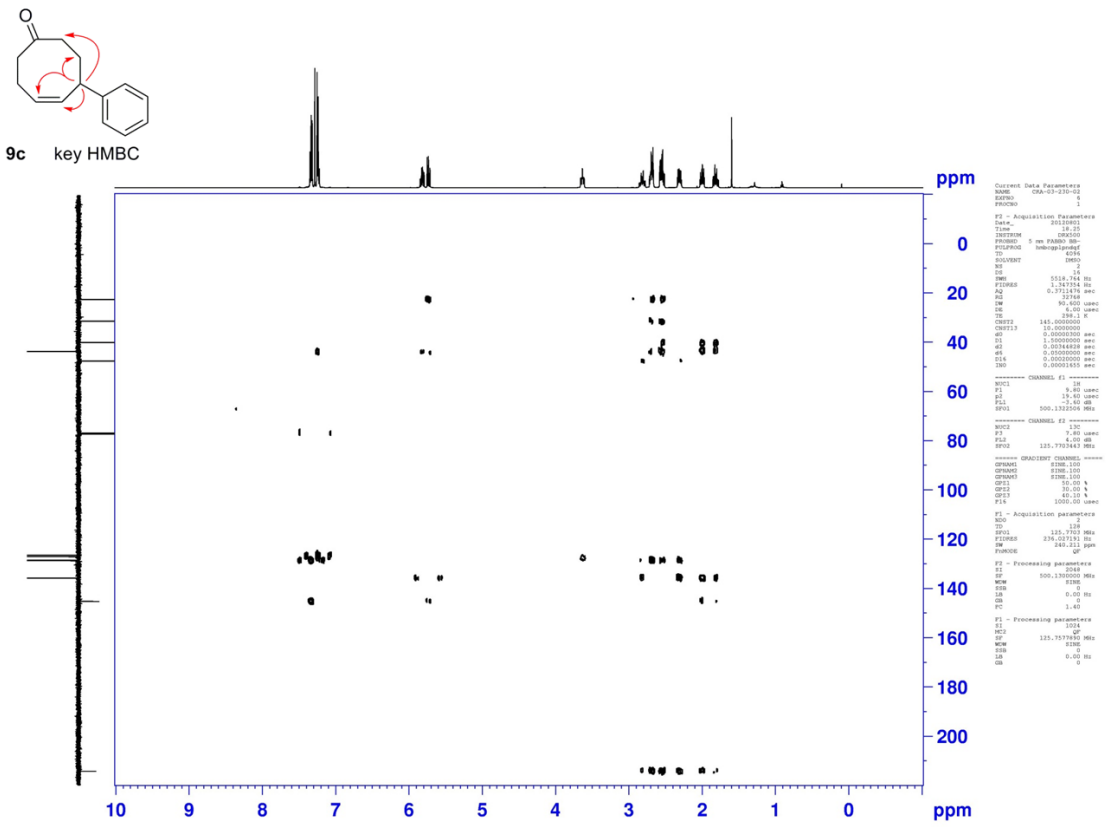

9b
O
NTs
3
Current Data Parameters
NAME CAA-03-190-02
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151103
Time_ 10.53
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.0873476 sec
RG 114
DW 16.600 usec
DE 6.00 usec
TE 301.1 K
CNST2 145.0000000
CNST11 2.0000000
D1 1.0000000 sec
d20 0.0089655 sec
DELTA 0.0000993 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
P2 15.60 usec
PL1 0.00 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 14.64 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 131072
SF 125.7577895 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

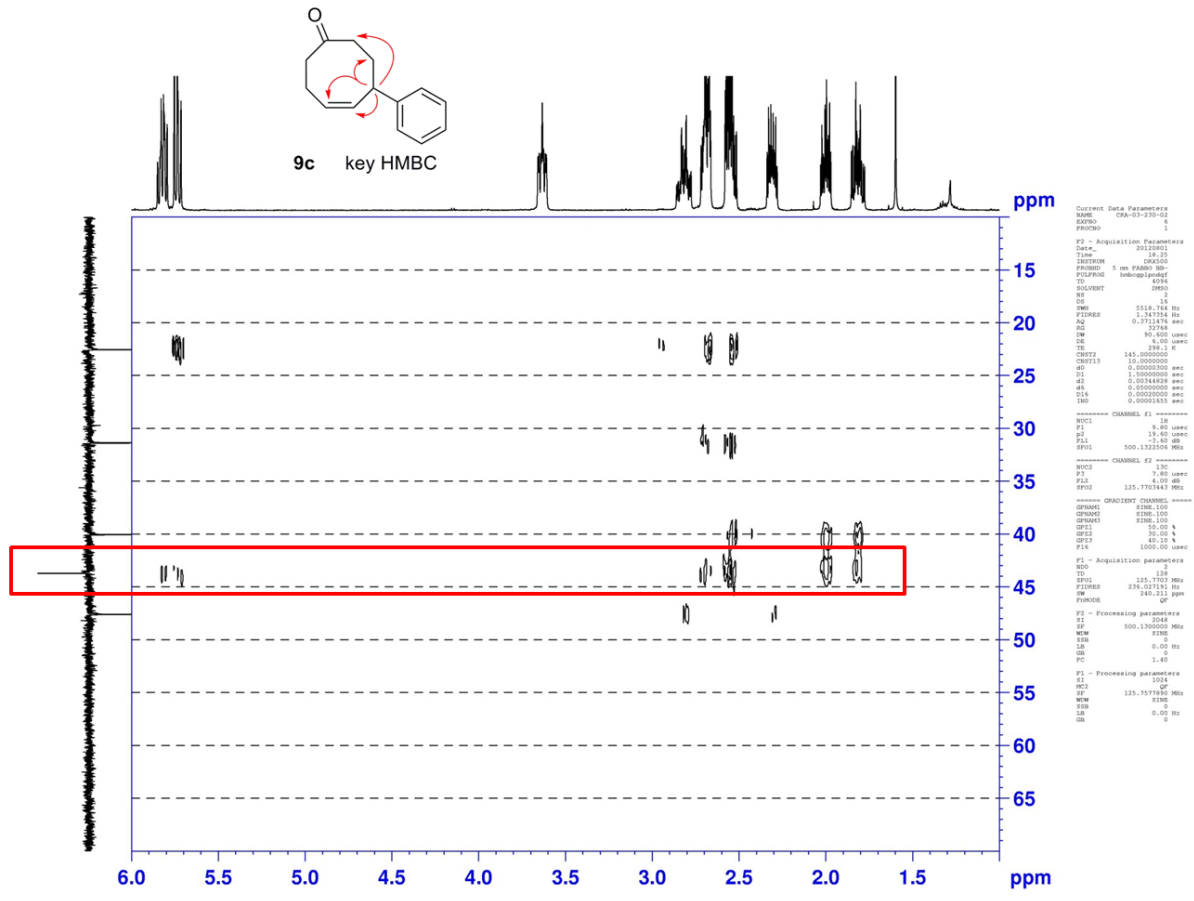

O
9b
NTs
3
key COSY
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

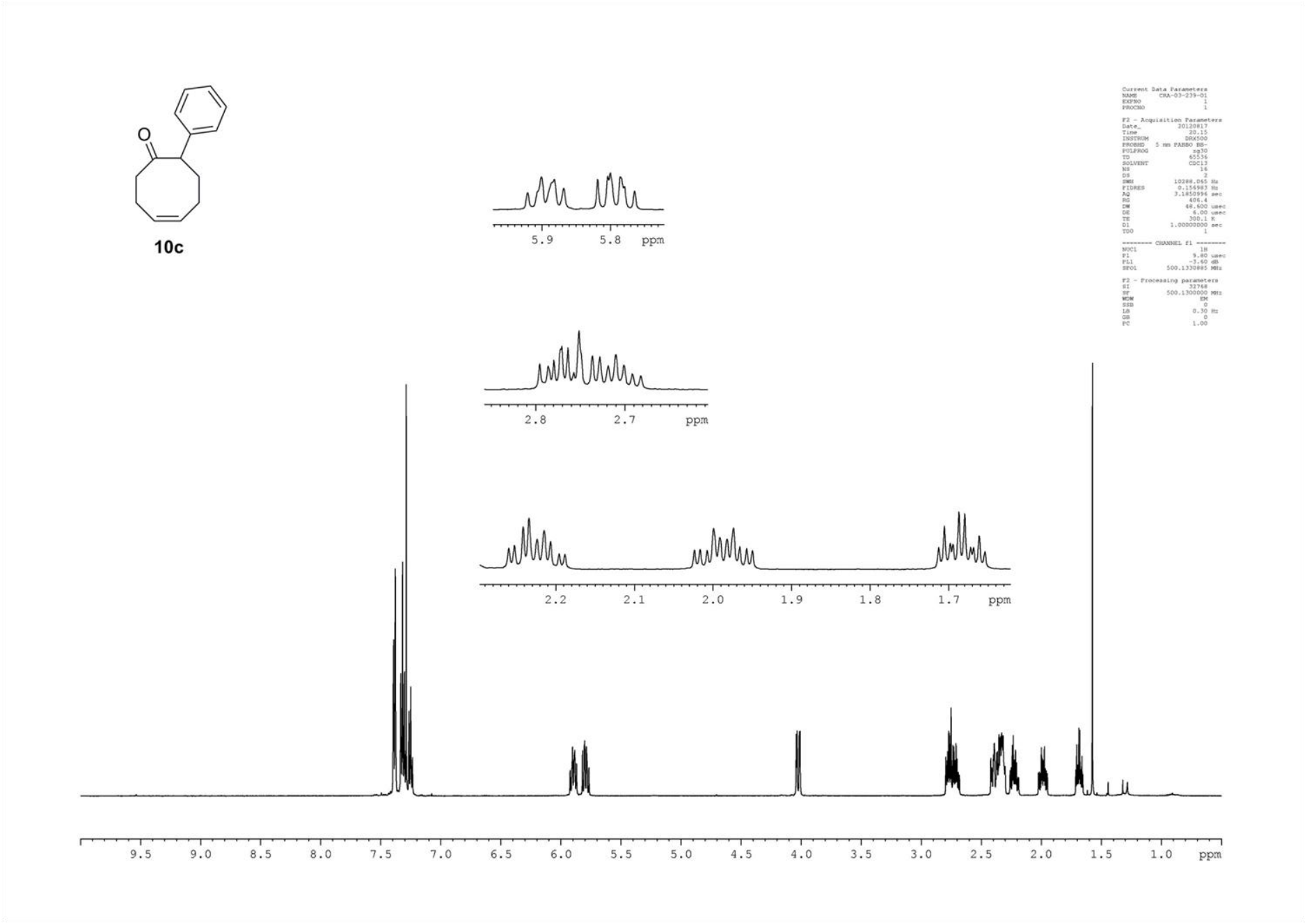

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

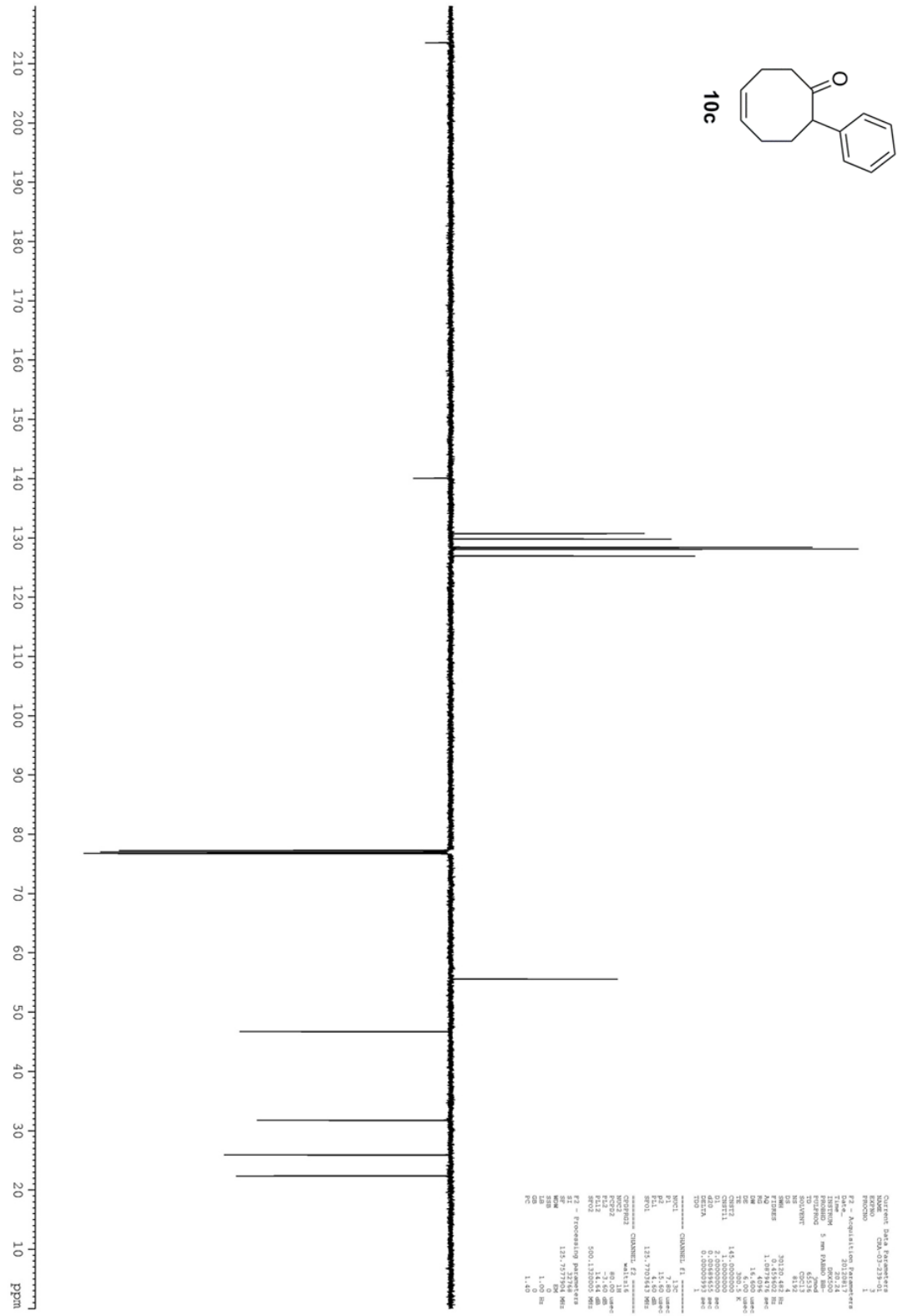

Current Data Parameters
NAME CRA-63-230-02
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120831
Time 21.21
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 16384
DW 16.600 usec
DE 6.00 usec
TE 298.6 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
DELTA 0.00000931 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
P2 15.60 usec
PL1 4.60 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 13.60 dB
PL12 18.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 131072
SF 125.7577926 MHz
WDW EM
SSB 1.0
LB 0 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

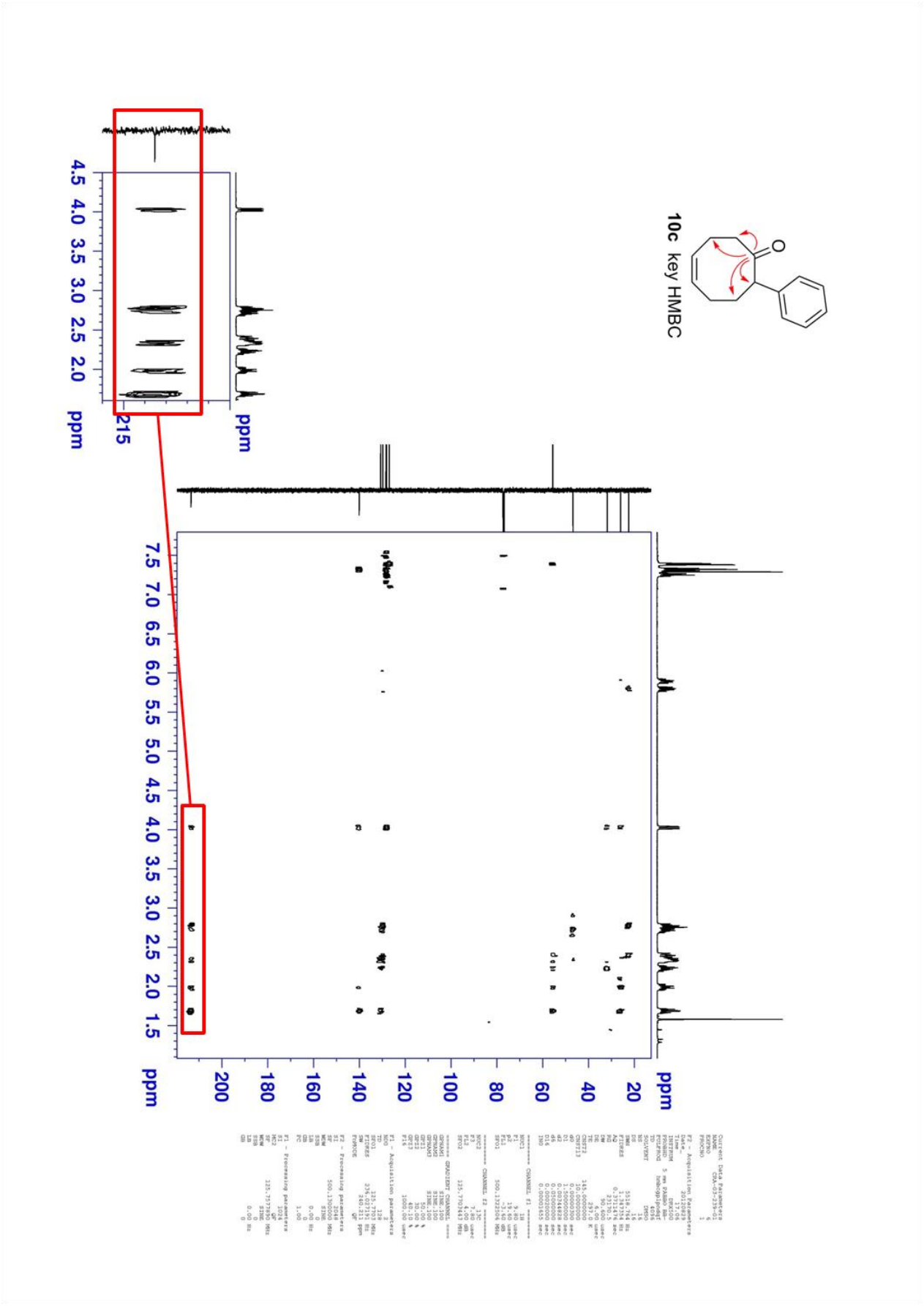

9c
COSY
O
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

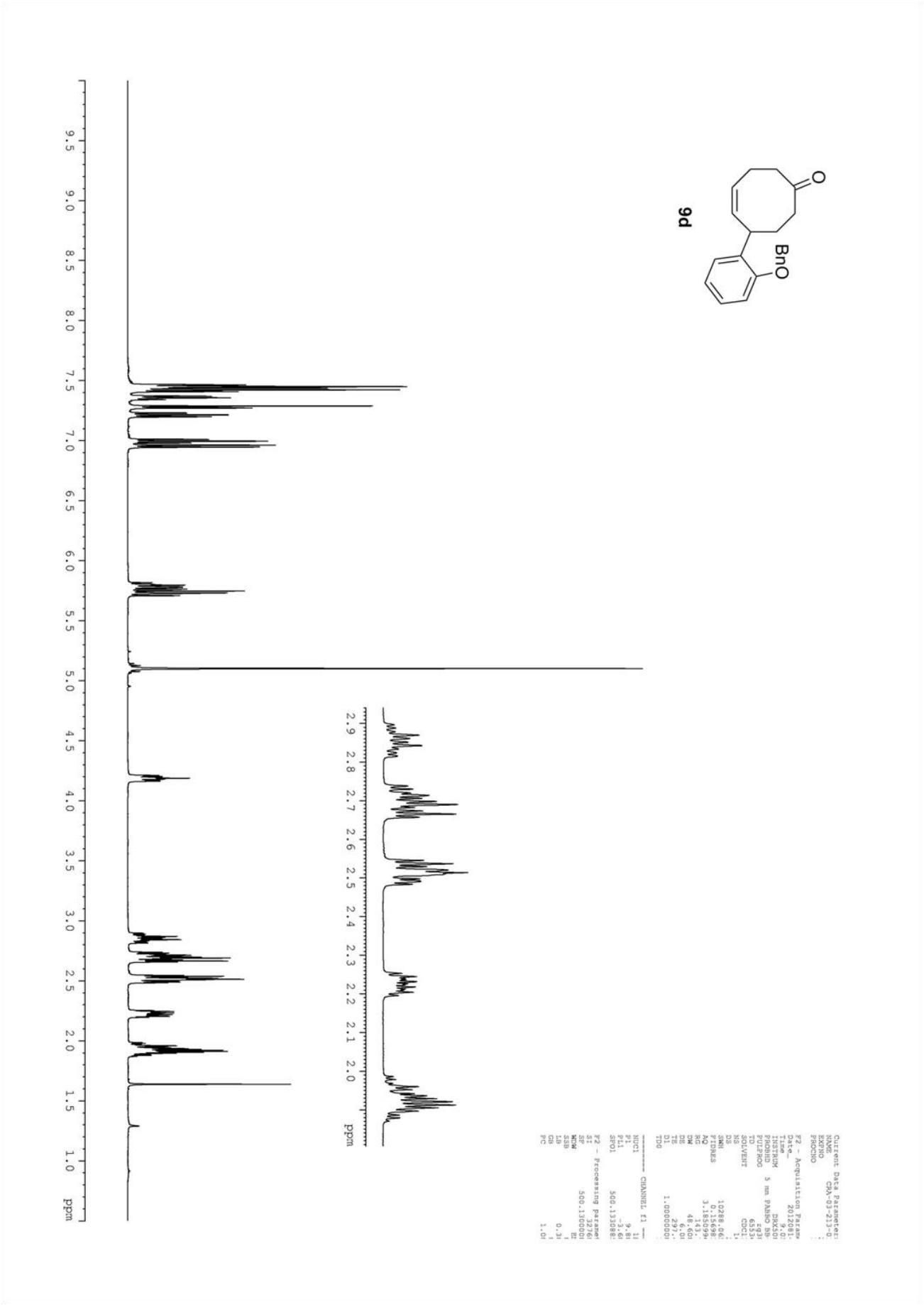

9c
key HMBC
ppm
0
20
40
60
80
100
120
140
160
180
200
10
9
8
7
6
5
4
3
2
1
0
ppm

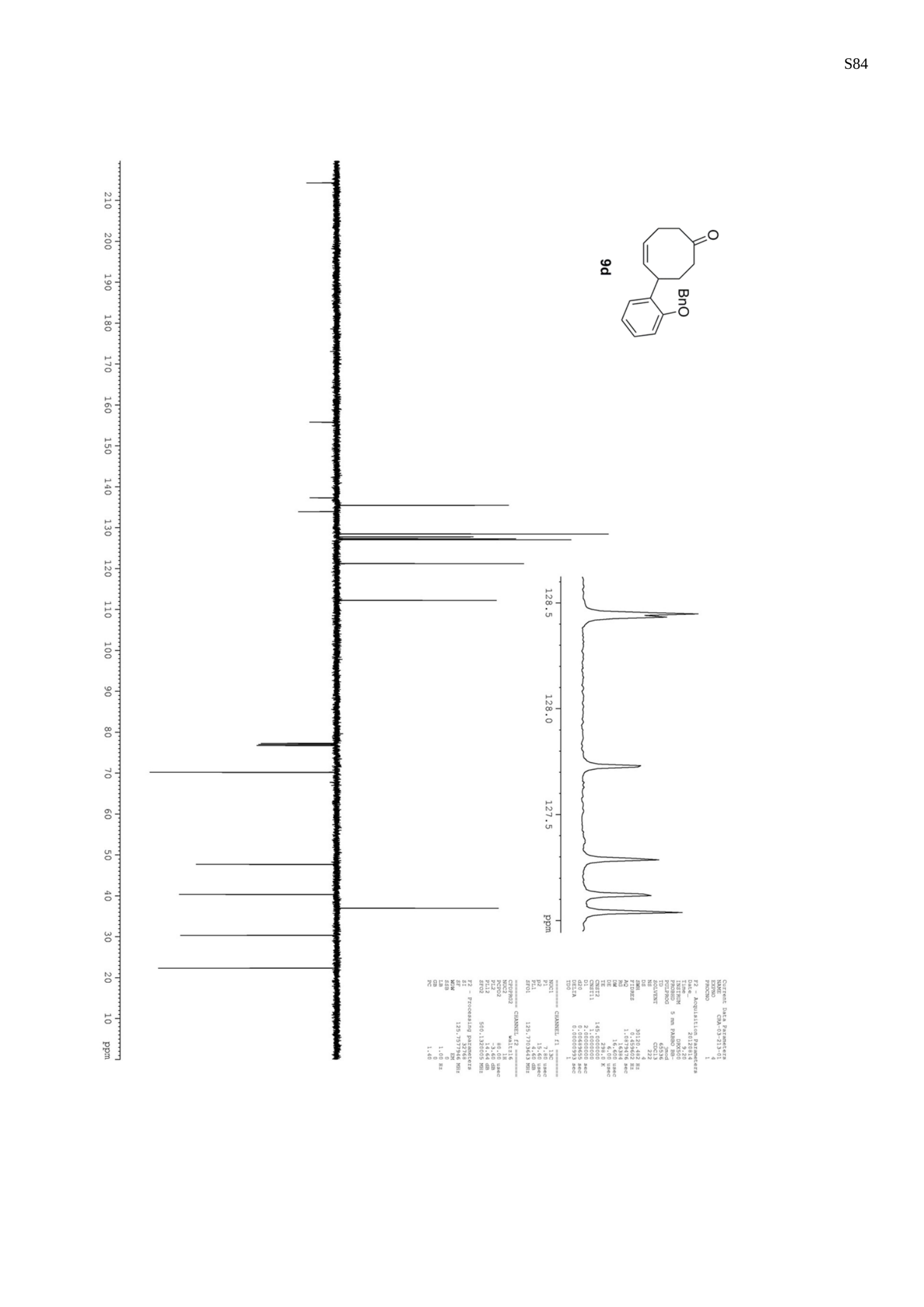

9c
key HMBC
ppm
15
20
25
30
35
40
45
50
55
60
65
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

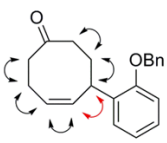

O
10c
5.9
5.8
ppm
2.8
2.7
ppm
2.2
2.1
2.0
1.9
1.8
1.7
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
Current Data Parameters
NAME CKA-03-239-01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120817
Time 20.15
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 406.4
DW 48.600 usec
DE 6.00 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.60 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


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

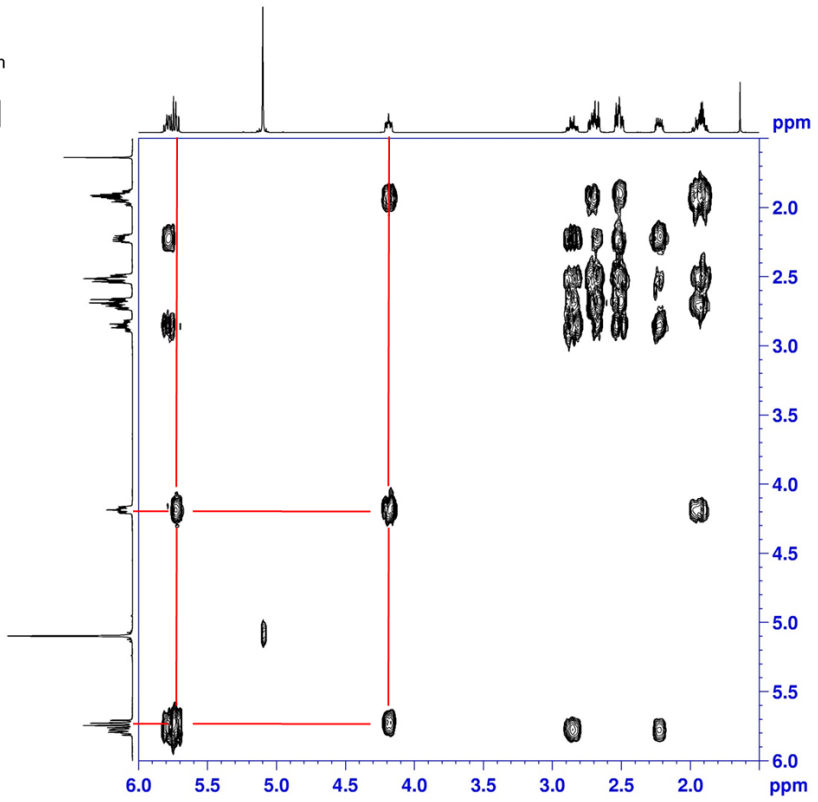

10c key HMBC
O
4.5 4.0 3.5 3.0 2.5 2.0
ppm
215
ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm
200 180 160 140 120 100 80 60 40 20
ppm

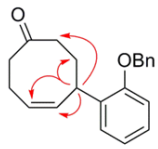

9d
BnO
O
ppm
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


9d
BnO
O
128.5
128.0
127.5
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

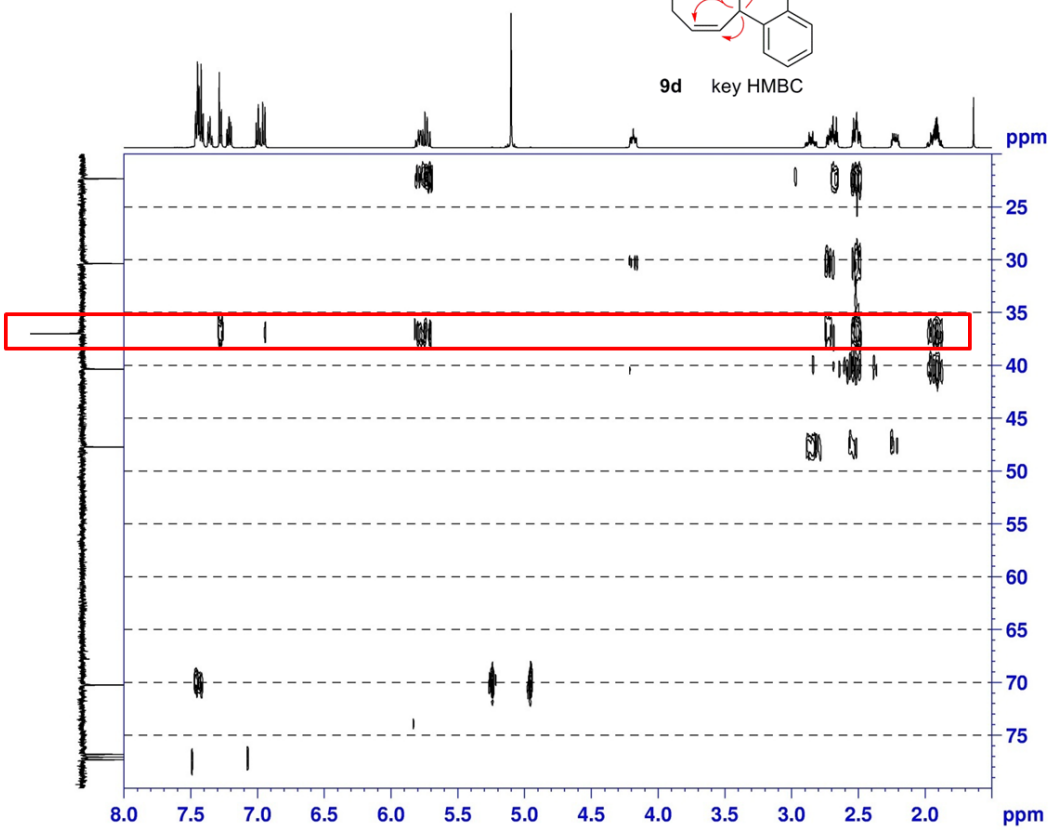


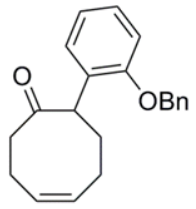
9d COSY





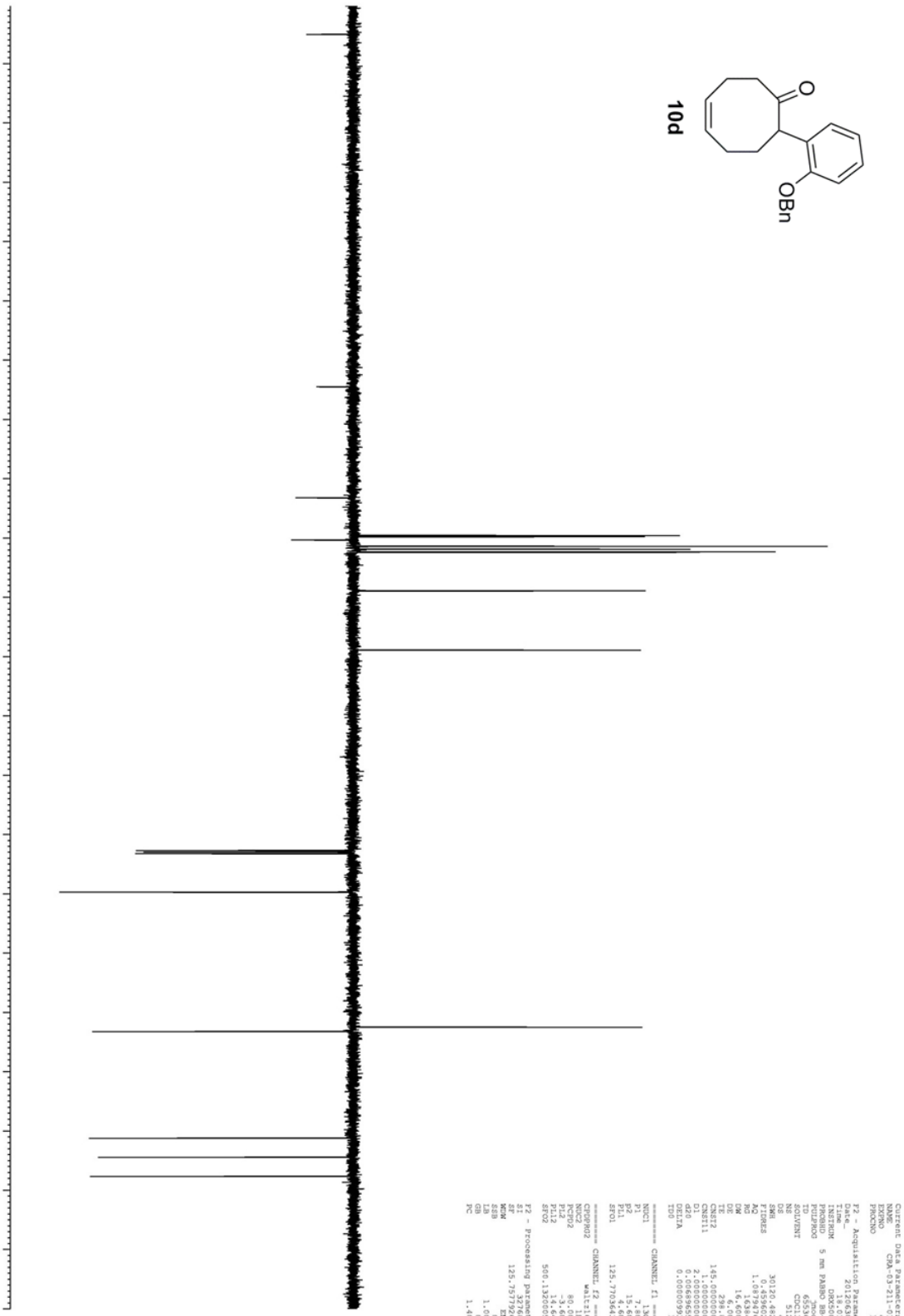
9d key HMBC

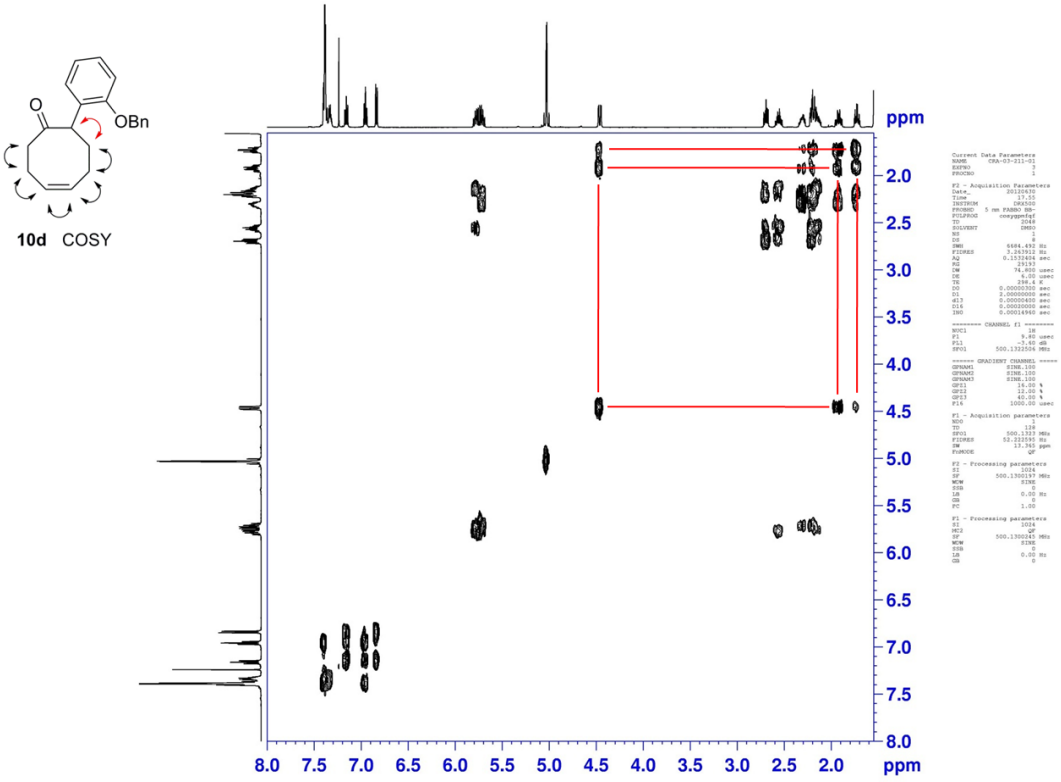


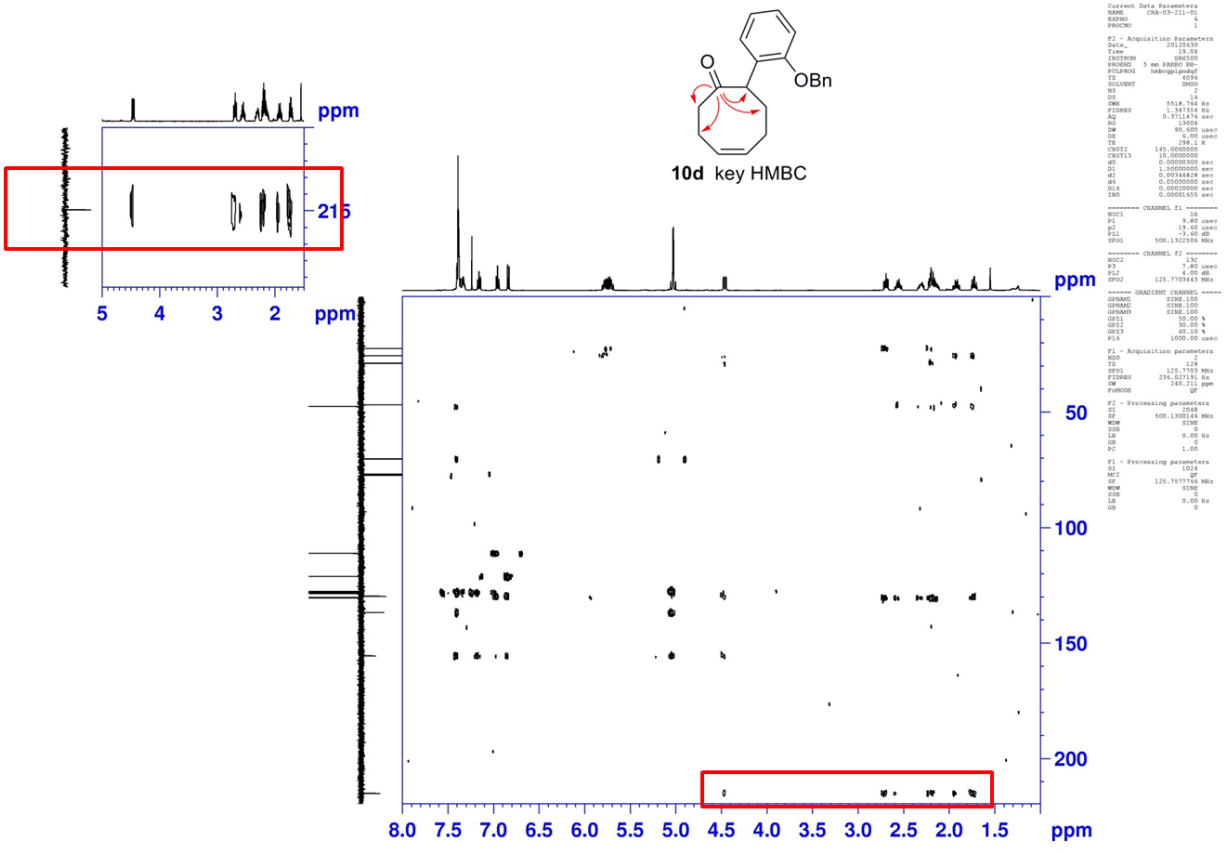

O
OBn

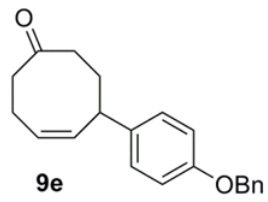
10d

Current Data Parameters
NAME CRA-03-211-01
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120630
Time 17.54
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 203.2
DW 48.600 usec
DE 6.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.50 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300227 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 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


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

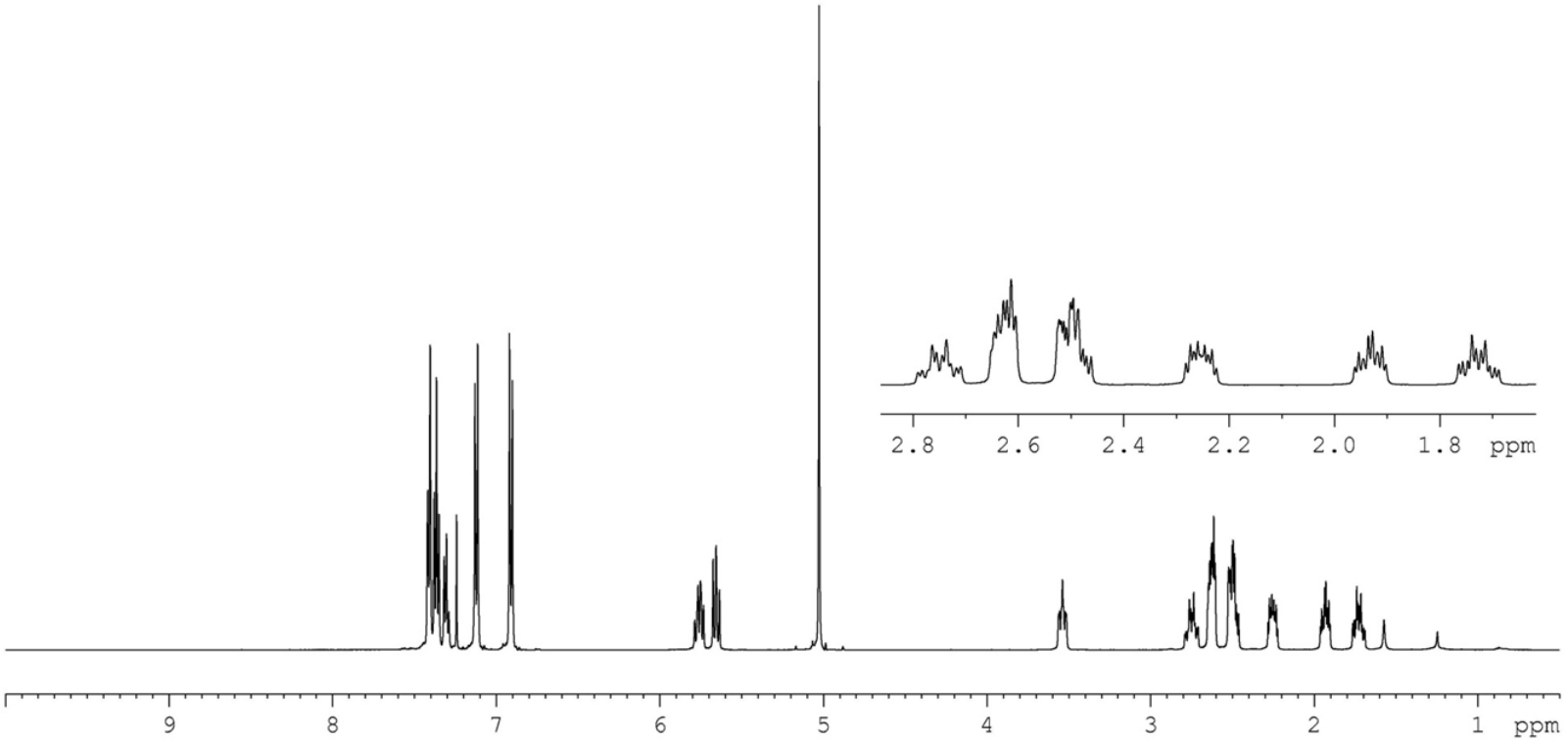

O
OBn
10d COSY
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm

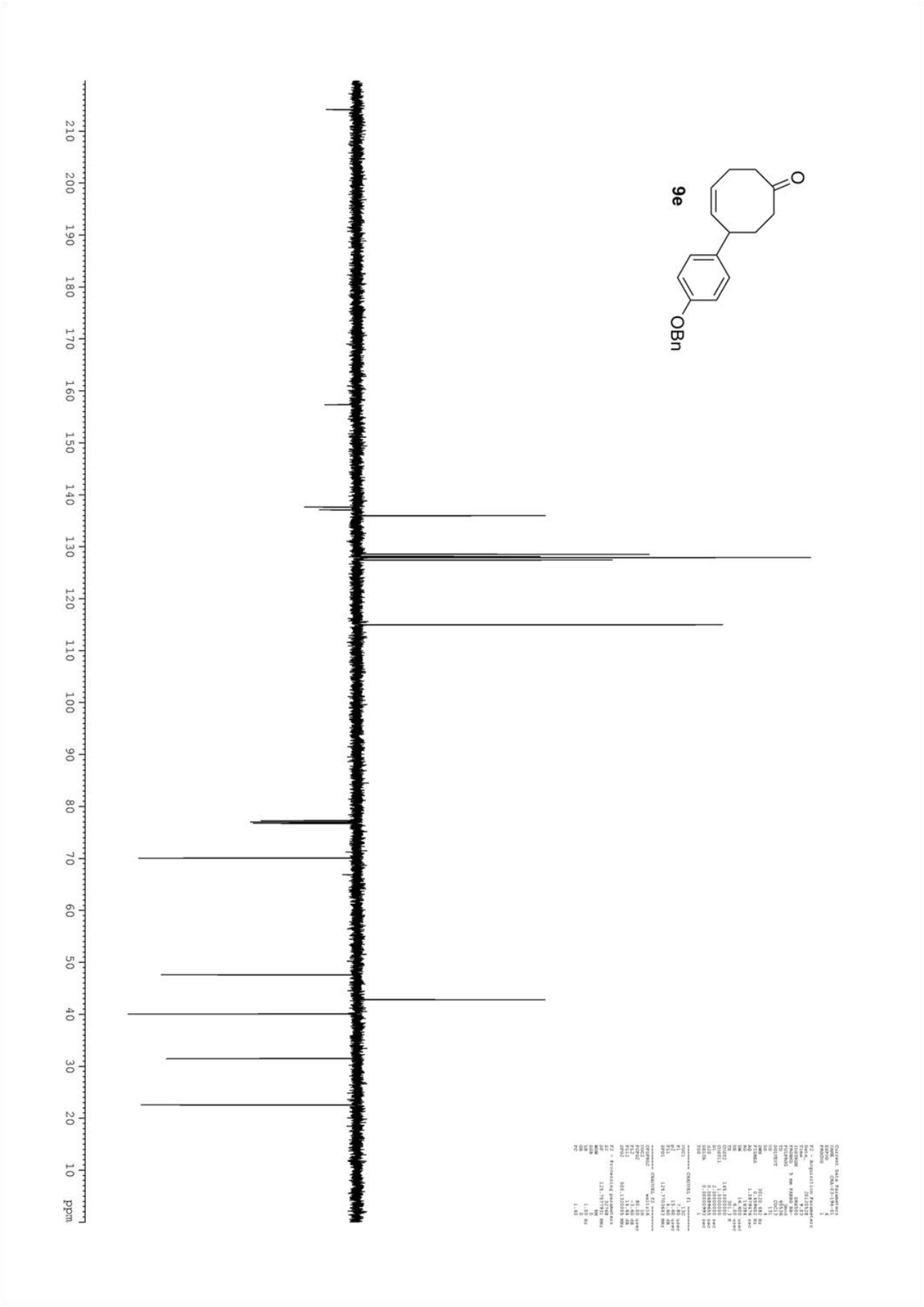

O
OBn
10d key HMBC
ppm
215
5 4 3 2 ppm
ppm
50
100
150
200
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

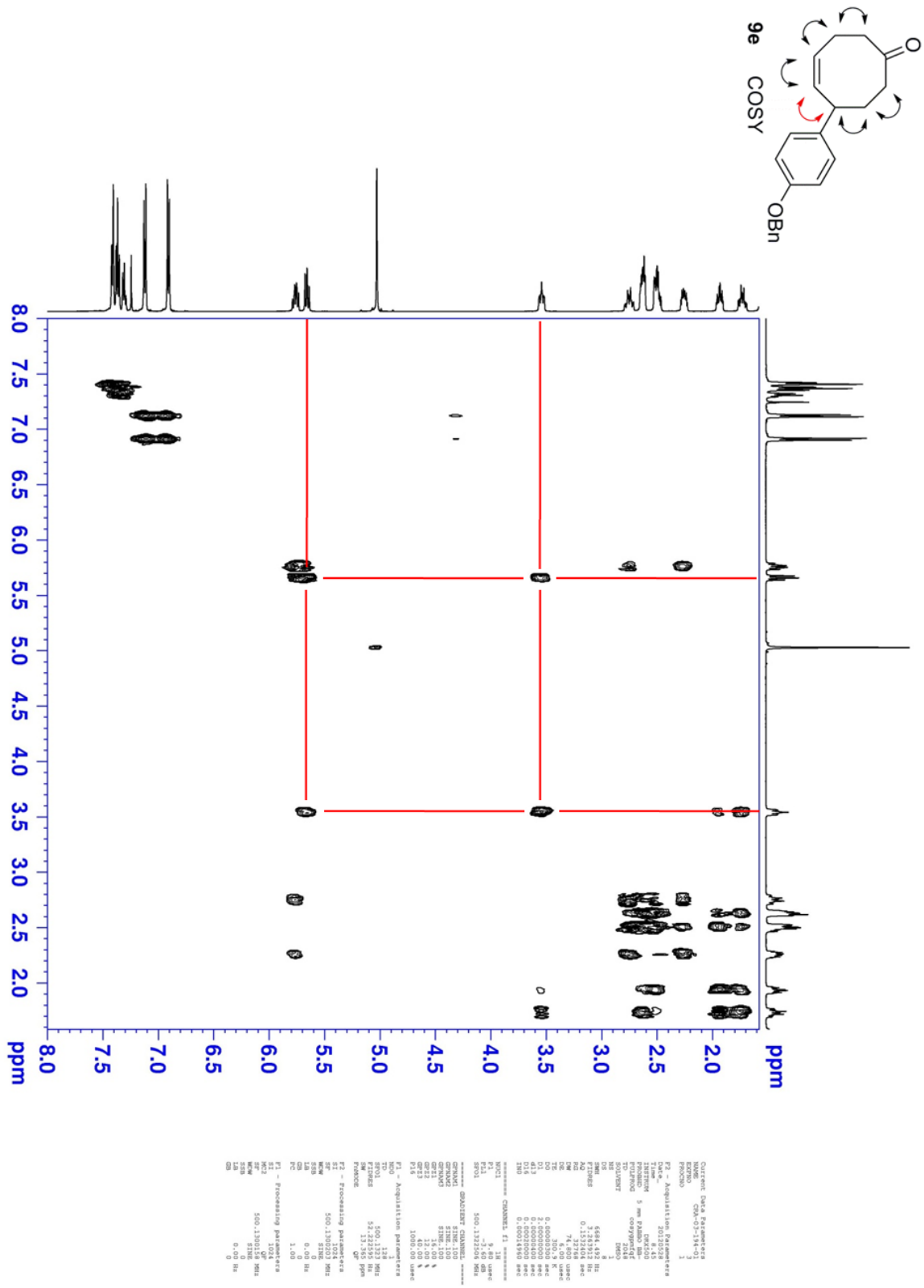

O
OBn

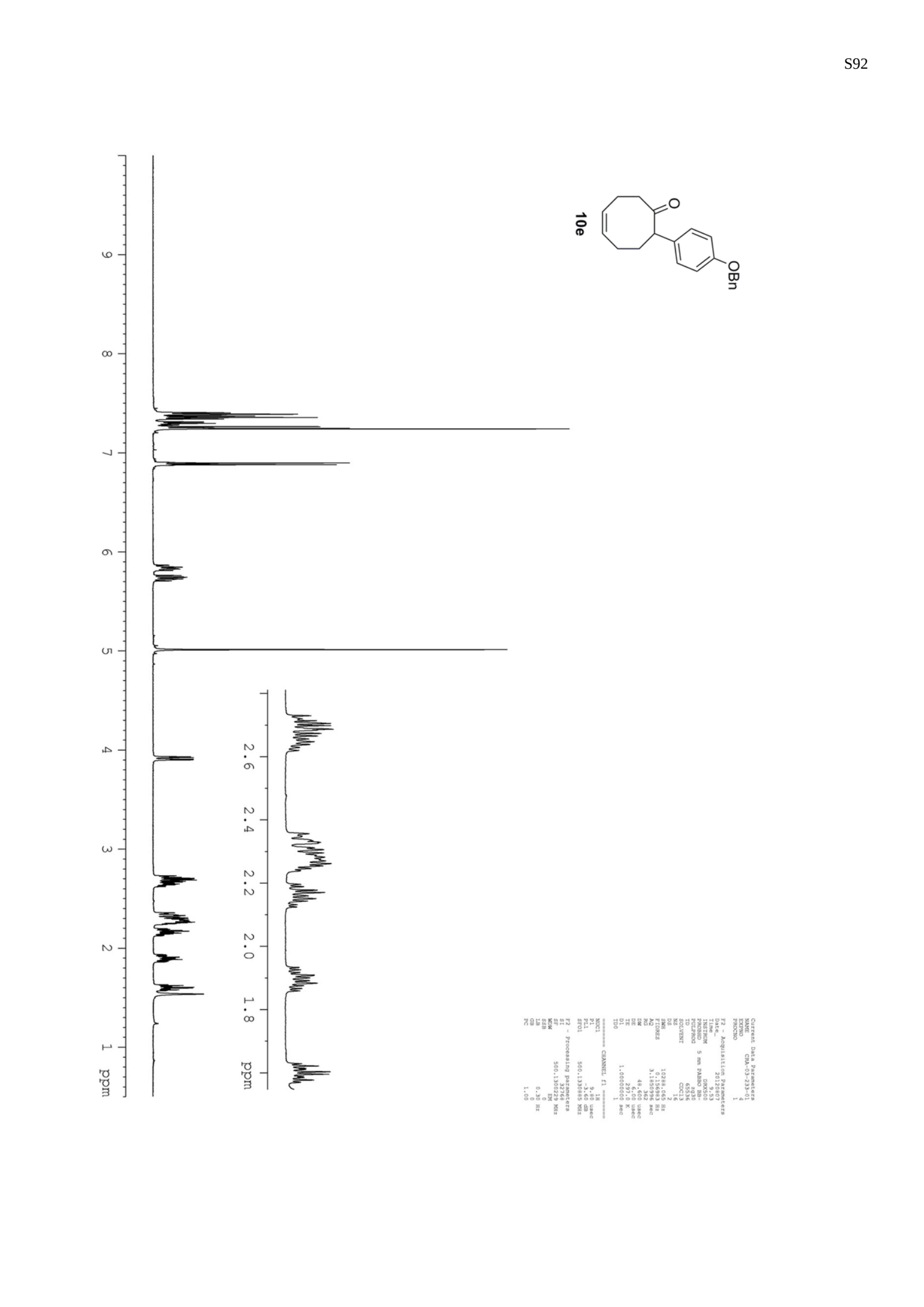
9e

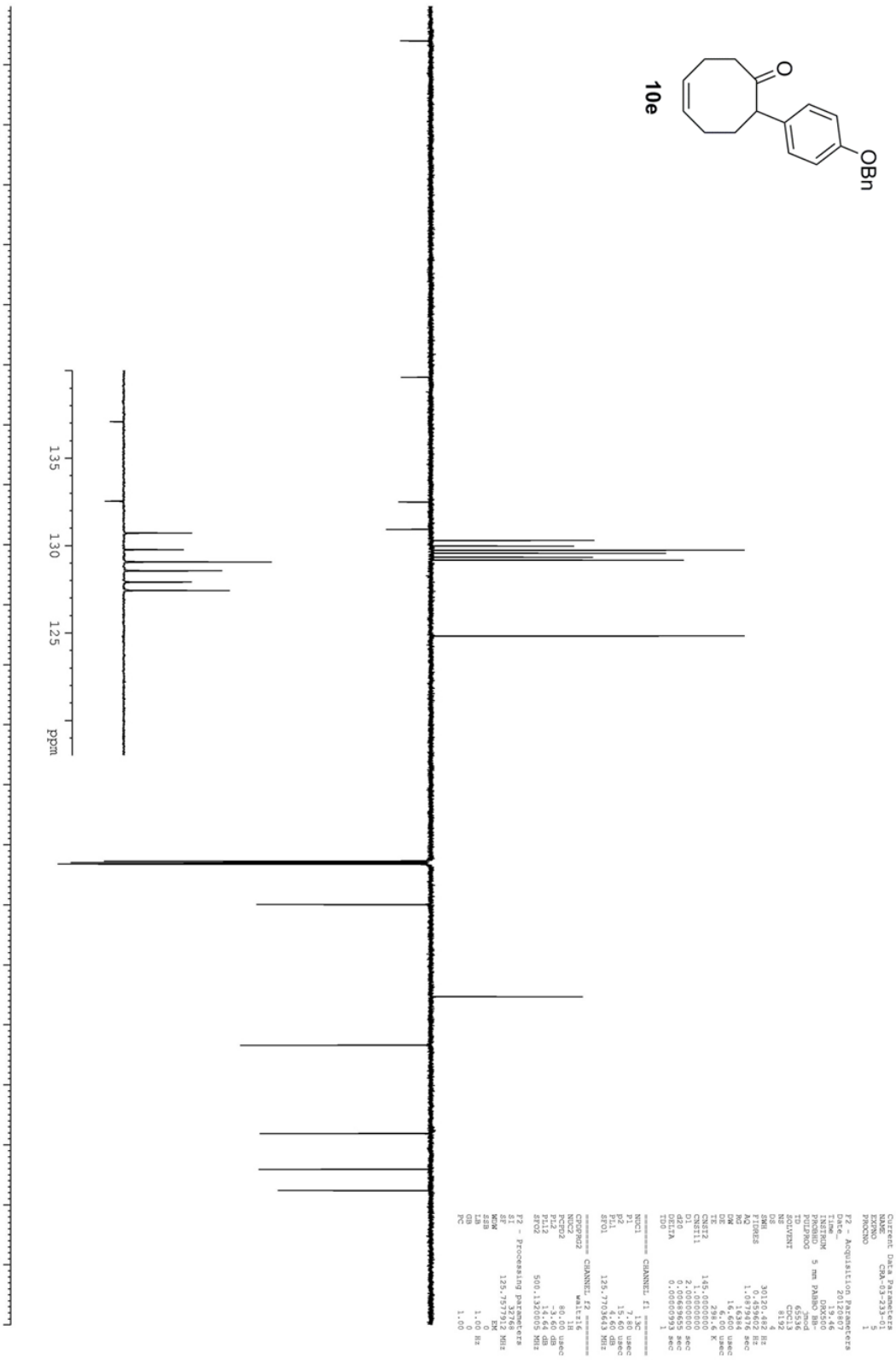

Current Data Parameters
NAME CRA-03-194-01
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120528
Time 8.43
INSTRM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156983 Hz
AQ 3.1850996 sec
RG 161.3
DW 48.600 usec
DE 6.00 usec
TE 300.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.60 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300226 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

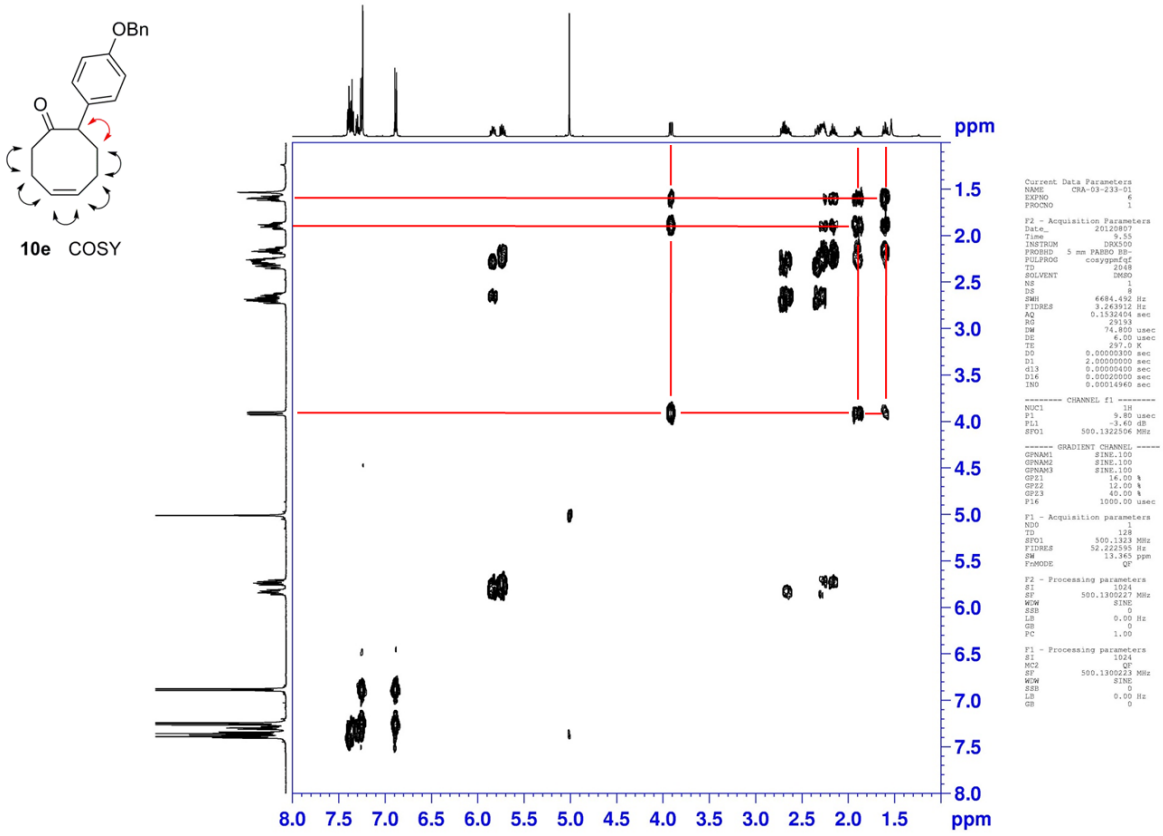

2.8
2.6
2.4
2.2
2.0
1.8
ppm
9
8
7
6
5
4
3
2
1
ppm

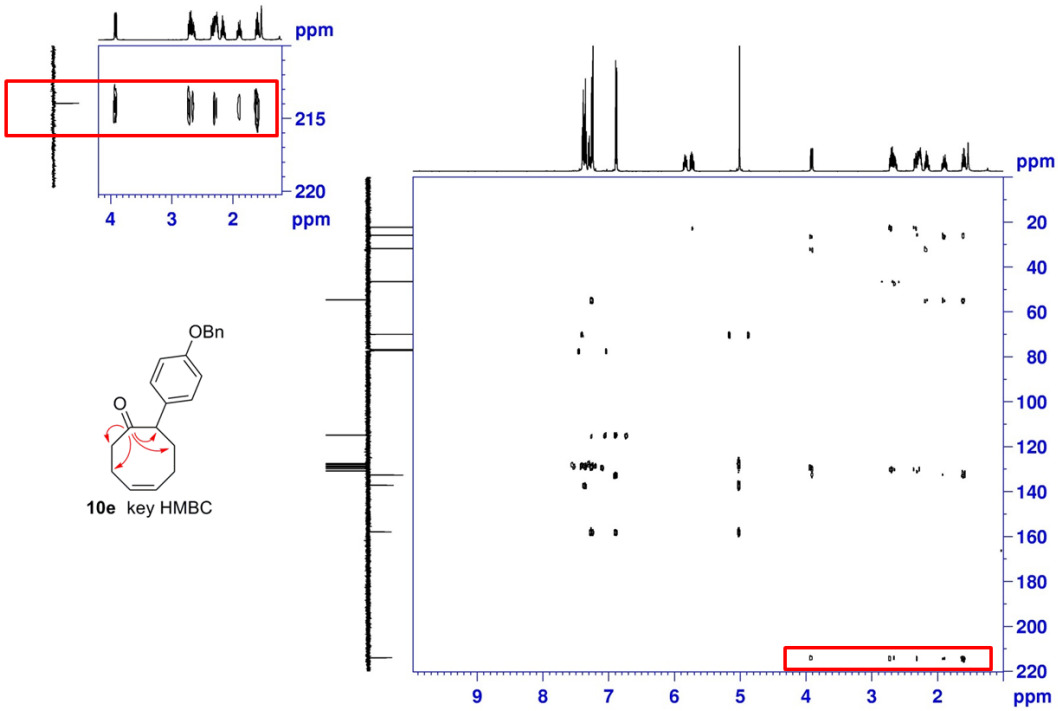

9e
O
OBn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

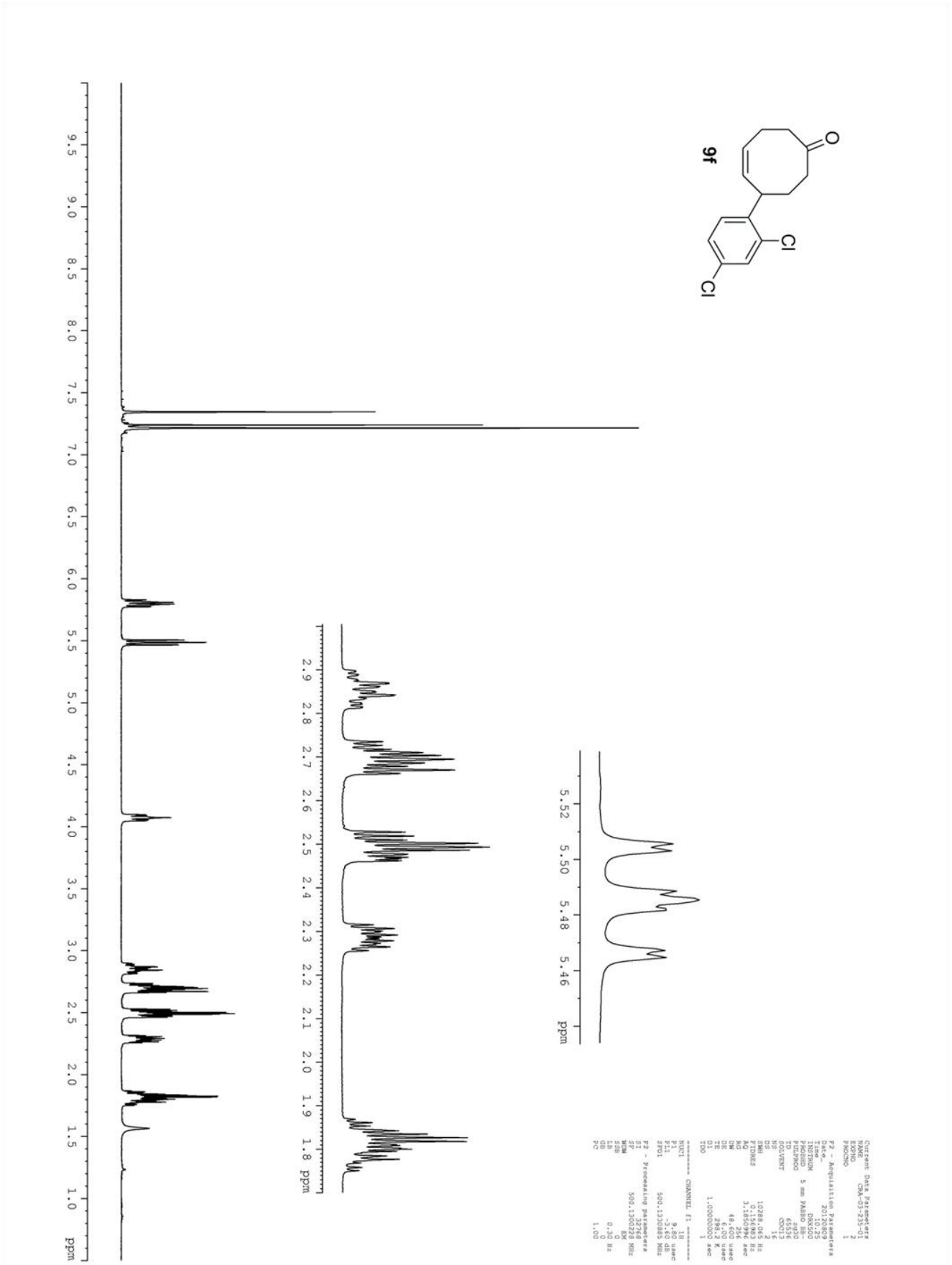

9e
COSY
O
OBn
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

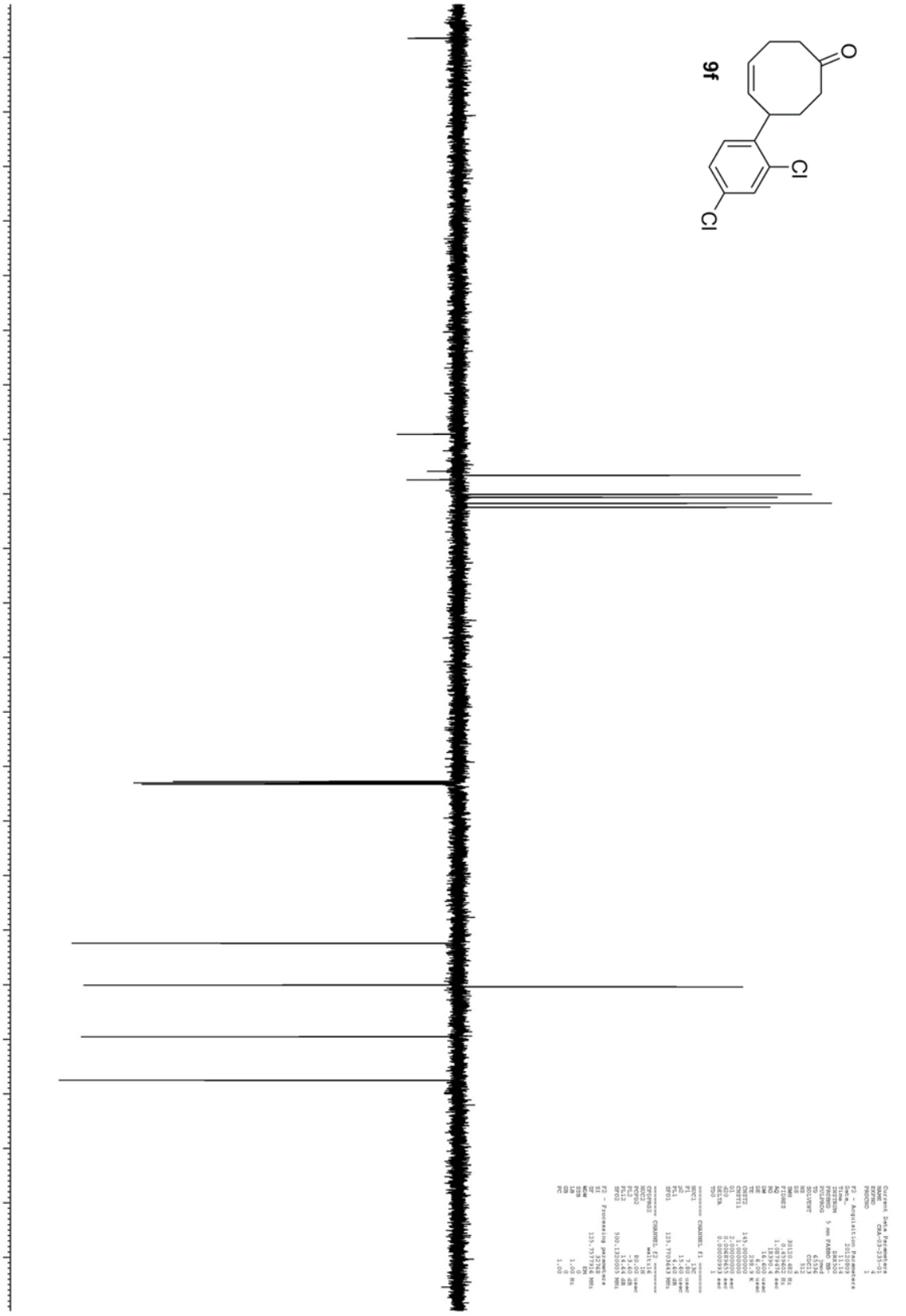

10e
OBn
Current Data Parameters
NAME CRA-03-233-01
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180703
Time 9.53
INSTRUM DRX500
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10288.065 Hz
FIDRES 0.156893 Hz
AQ 3.1853362 sec
RG 203
DW 48.600 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
D0 0.00003000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300229 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1 ppm
2.6
2.4
2.2
2.0
1.8 ppm

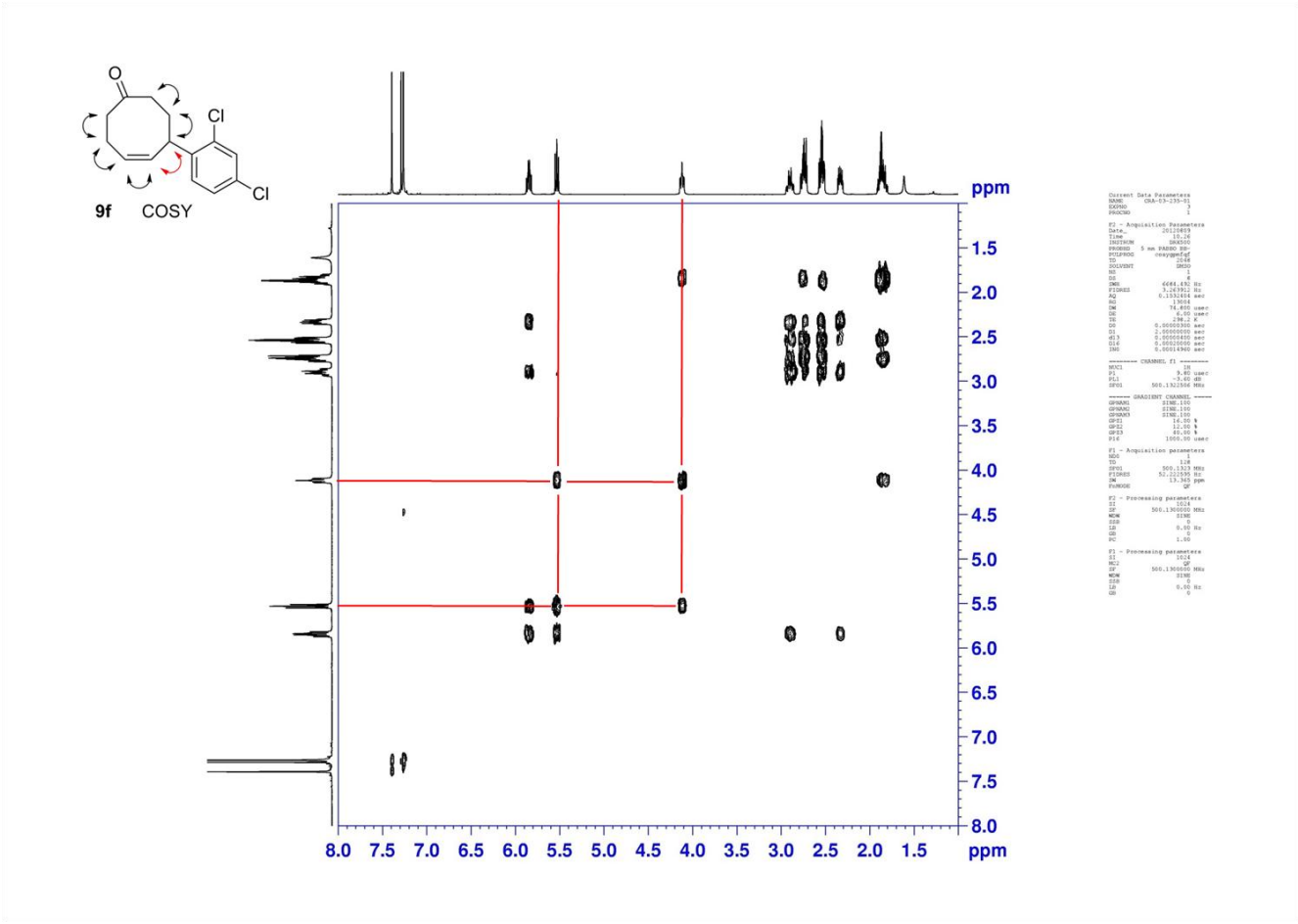

10e
O
OBn
ppm
ppm

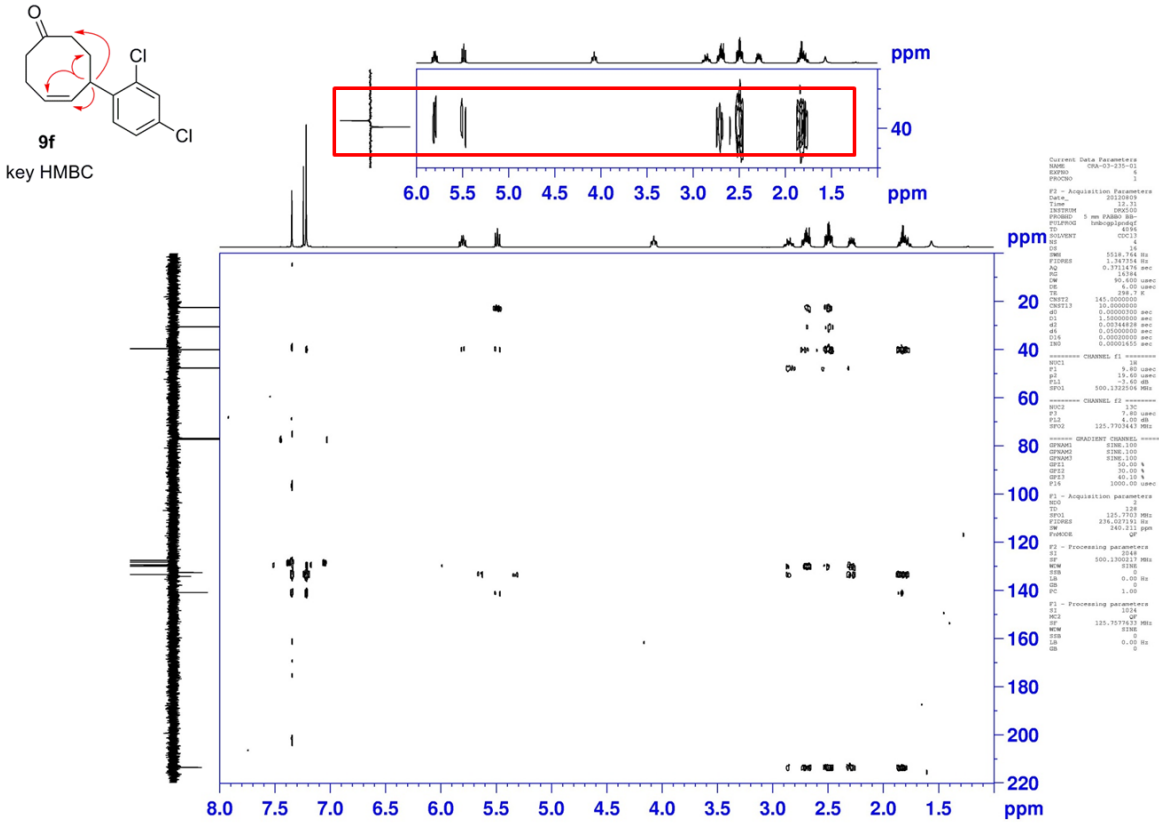

OBn
O
10e COSY
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

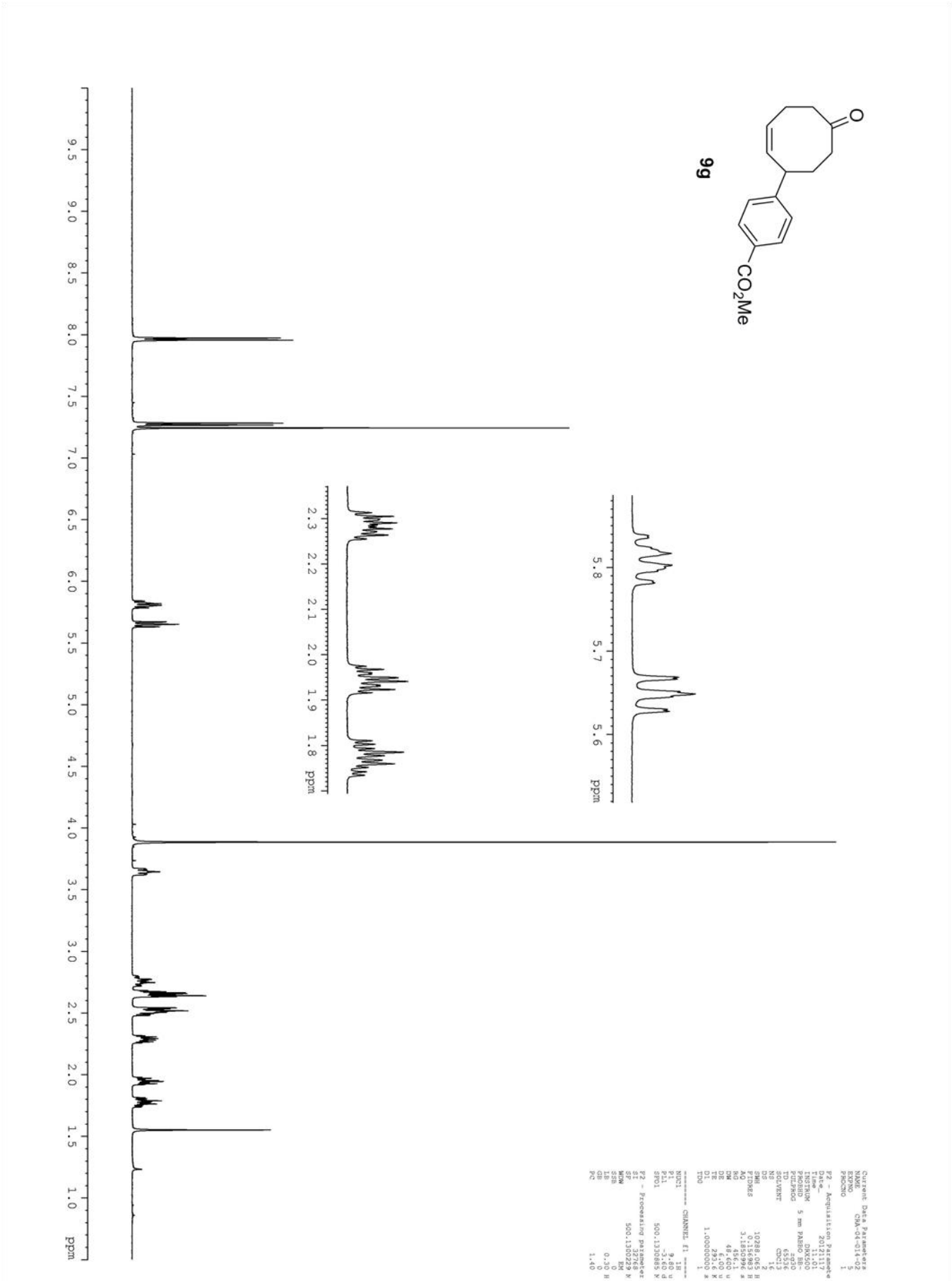

ppm
215
220
4 3 2 ppm
OBn
O
10e key HMBC
ppm
20
40
60
80
100
120
140
160
180
200
220
9 8 7 6 5 4 3 2 ppm

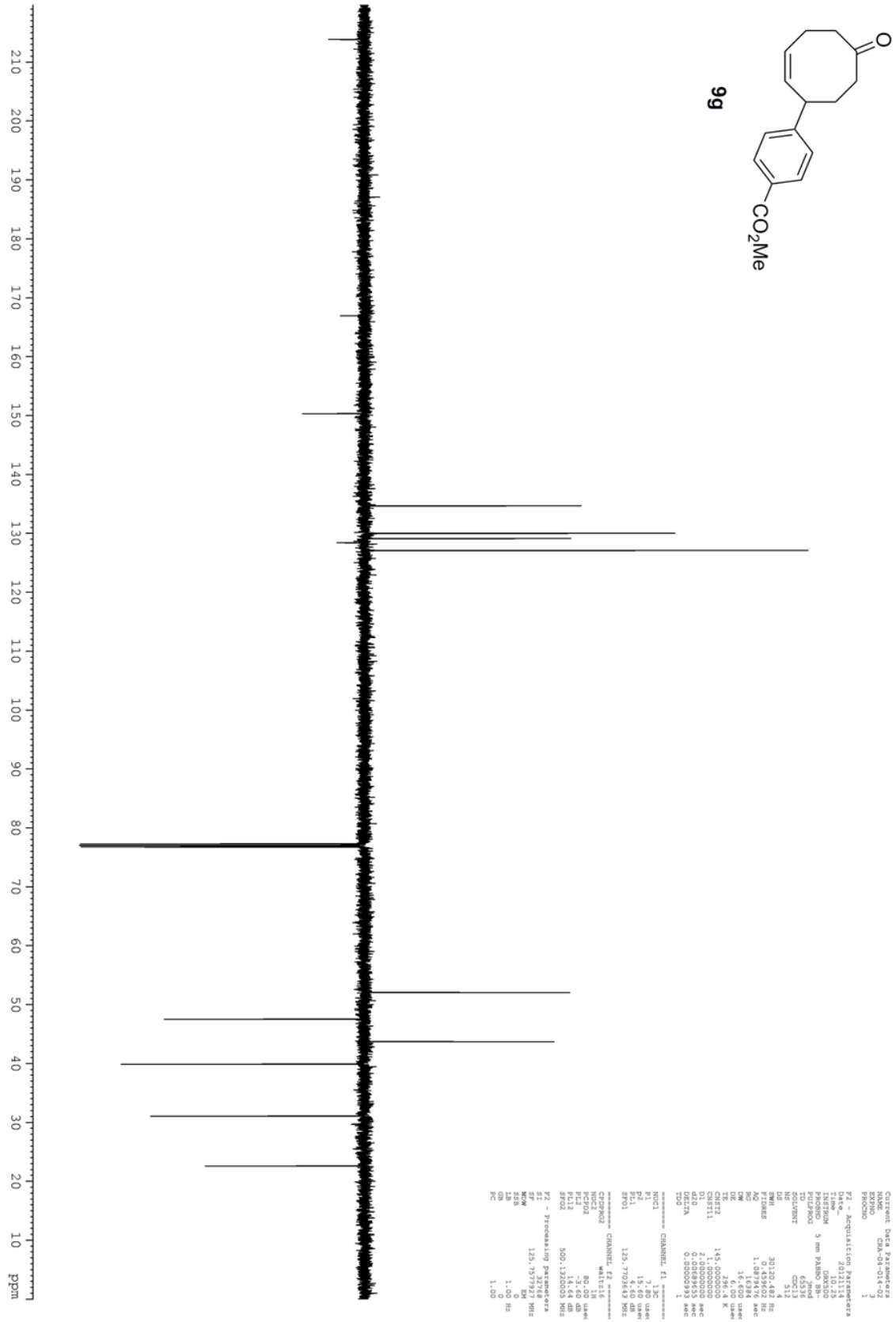

9f
Cl
Cl
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 ppm
5.52 5.50 5.48 5.46 ppm

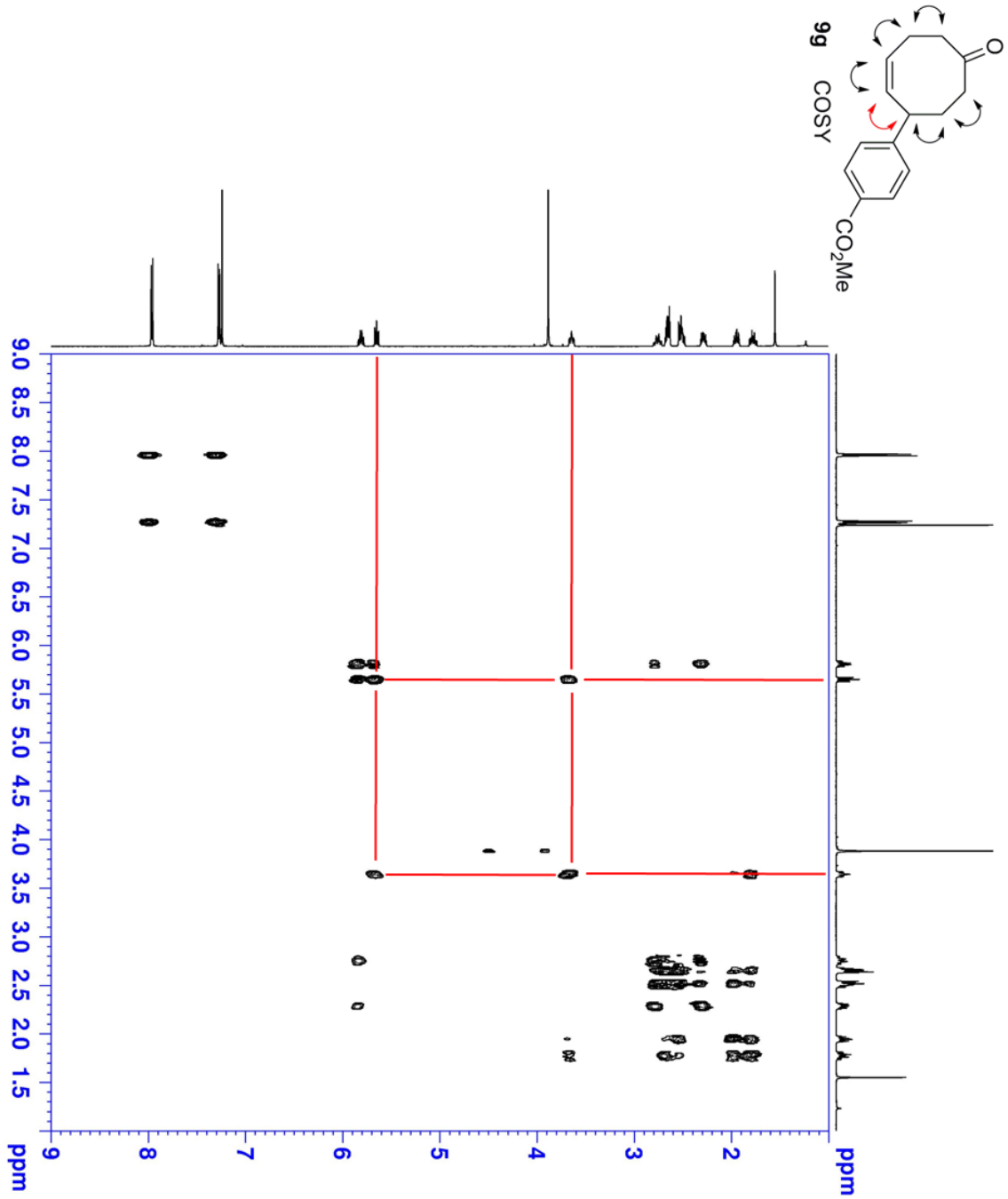

O
Cl
Cl
9f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm


O
Cl
Cl
9f COSY
ppm
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

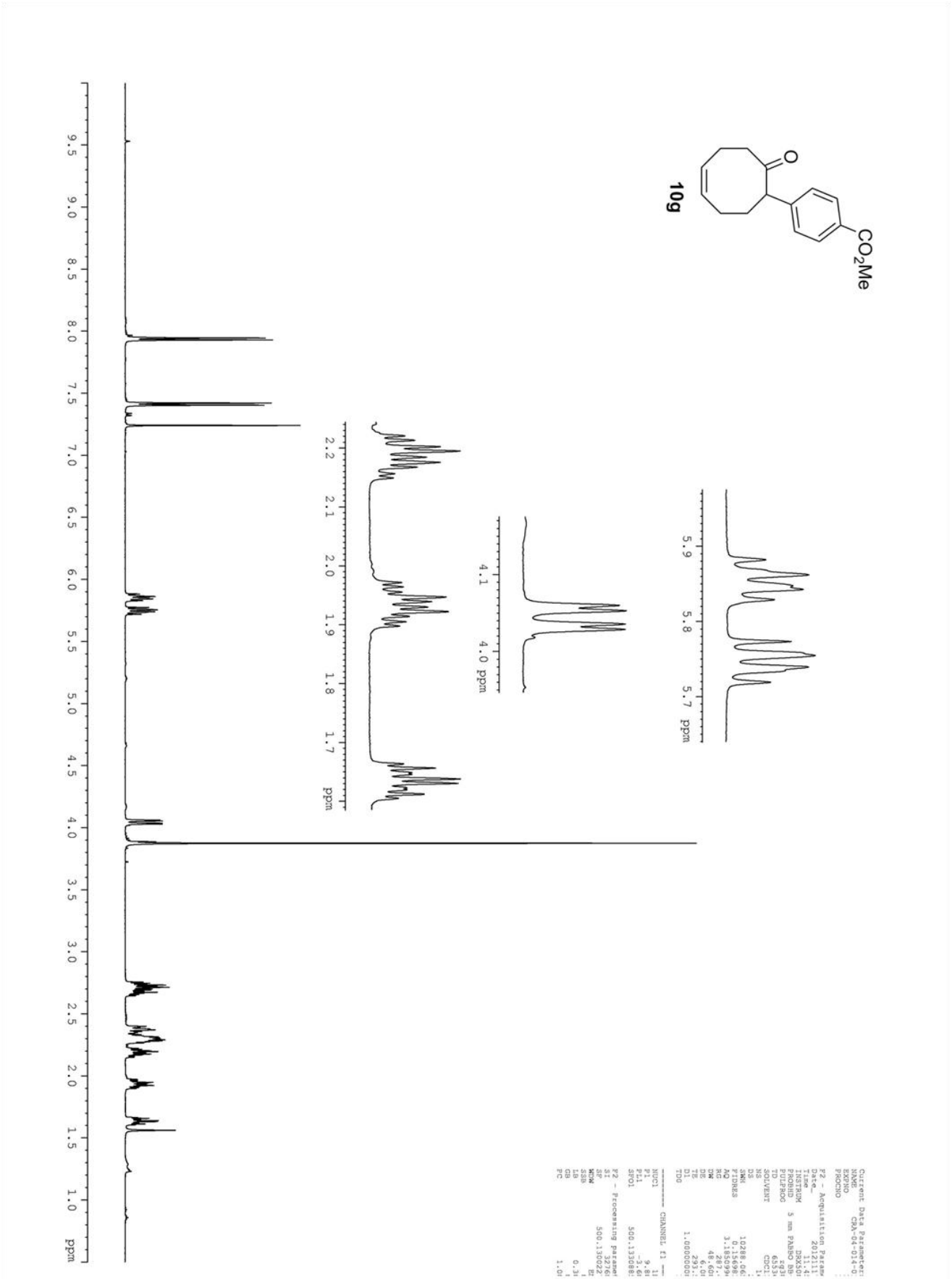

O
Cl
Cl
9f
key HMBC
ppm
40
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
ppm
20 40 60 80 100 120 140 160 180 200 220
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

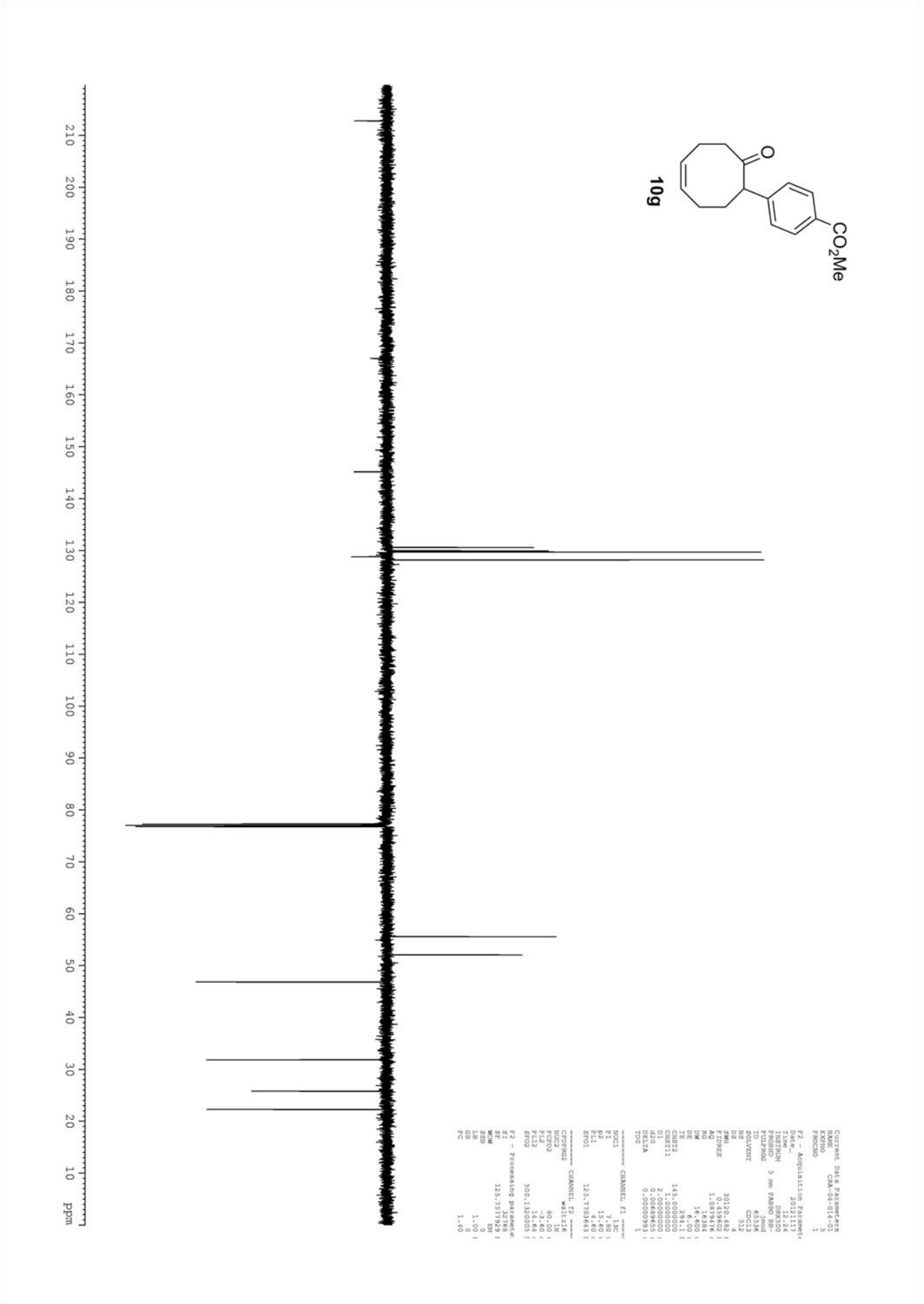

O
CO2Me
9g
5.8
5.7
5.6
ppm
2.3
2.2
2.1
2.0
1.9
1.8
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

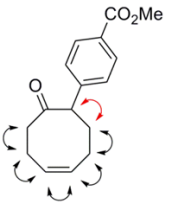

9g
O
CO2Me
Current Data Parameters
NAME CRA-04-014-02
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171115
Time 10.25
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 314
DS 4
SWH 30120.482 Hz
FIDRES 0.459476 Hz
AQ 1.0879476 sec
RG 16384
DW 16.600 usec
DE 6.00 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00020000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -1.60 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.60 dB
PL12 14.64 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577919 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



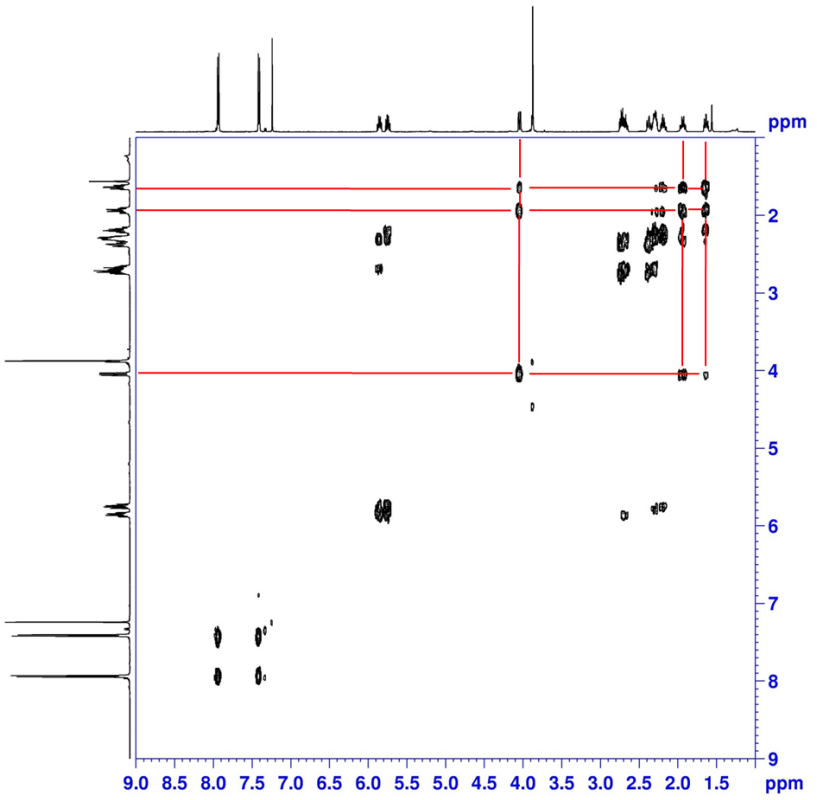

```
Current Data Parameters
NAME                  CRA-04-014-02
EXPNO                            6
PROCNO                           1

F2 - Acquisition Parameters
Date_               20121127
Time                    DRX500
INSTRUM                 5 mm PABBO BB-
PROBHD
PULPROG                 cosygpmfqf
TD                        2048
SOLVENT                   DMSO
NS                           1
DS                           8
SWH                  6684.492 Hz
FIDRES               3.263912 Hz
AQ                   0.1532404 sec
RG                       16384
DW                    74.800 usec
DE                     6.00 usec
TE                     293.6 K
D0                   0.00000300 sec
D1                   2.00000000 sec
d13                  0.00000400 sec
D16                  0.00020000 sec
IN0                  0.00014960 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      9.80 usec
PL1                     -3.00 dB
SFO1                500.1322506 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPNAM2               SINE.100
GPNAM3               SINE.100
GPZ1                    16.00 %
GPZ2                    11.00 %
GPZ3                    40.00 %
P16                   1000.00 usec

F1 - Acquisition parameters
ND0                          1
TD                         128
SFO1                500.1323 MHz
FIDRES               52.223549 Hz
SW                   13.365 PPM
FnMODE                       QF

F2 - Processing parameters
SI                        1024
SF                500.1300225 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.00

F1 - Processing parameters
SI                        1024
SF2               500.1300059 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
```

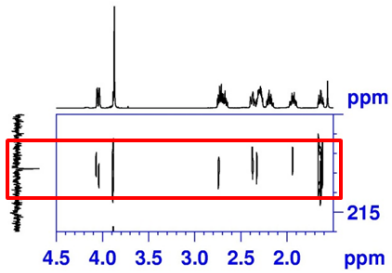

10g
CO2Me
O
5.9
5.8
5.7 ppm
4.1
4.0 ppm
2.2
2.1
2.0
1.9
1.8
1.7
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

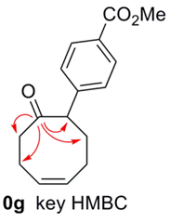

10g
O
CO2Me
ppm



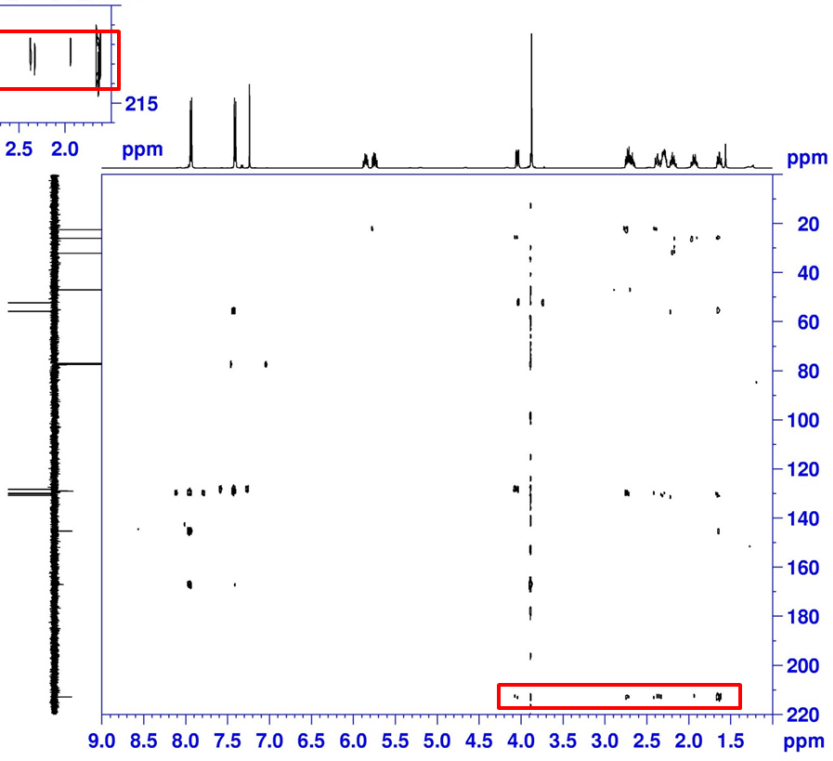
10g COSY

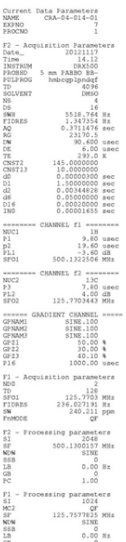


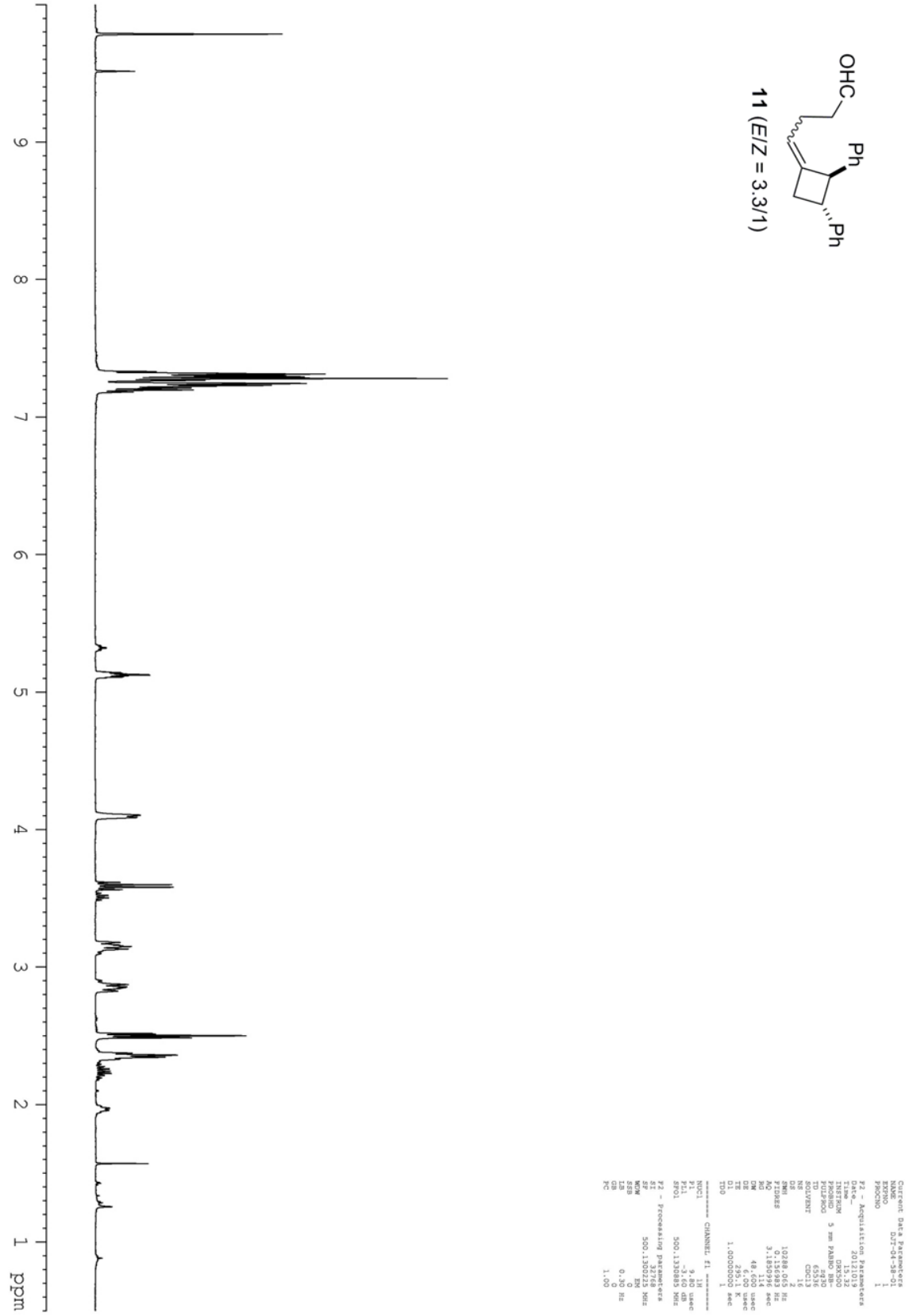


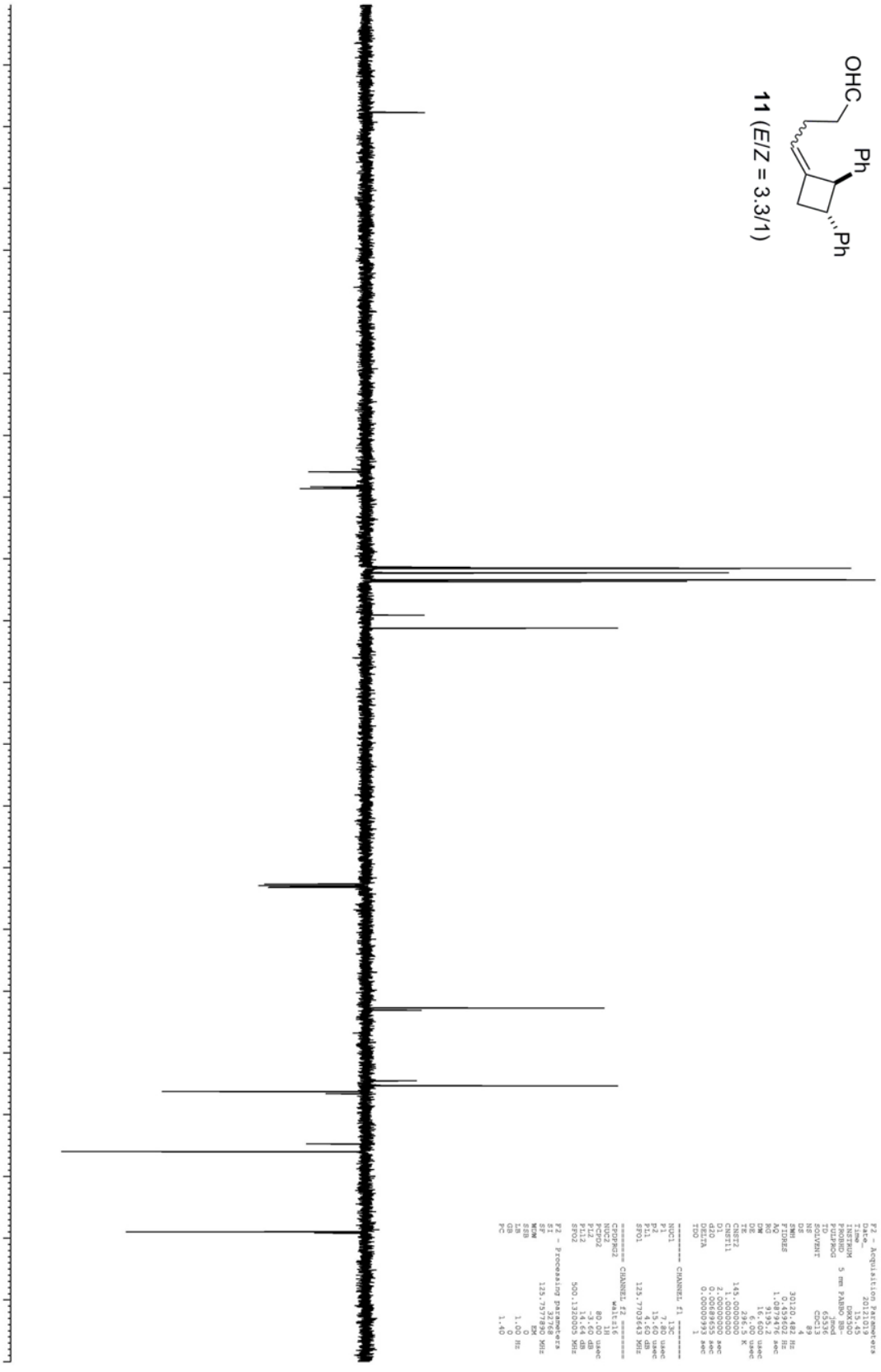


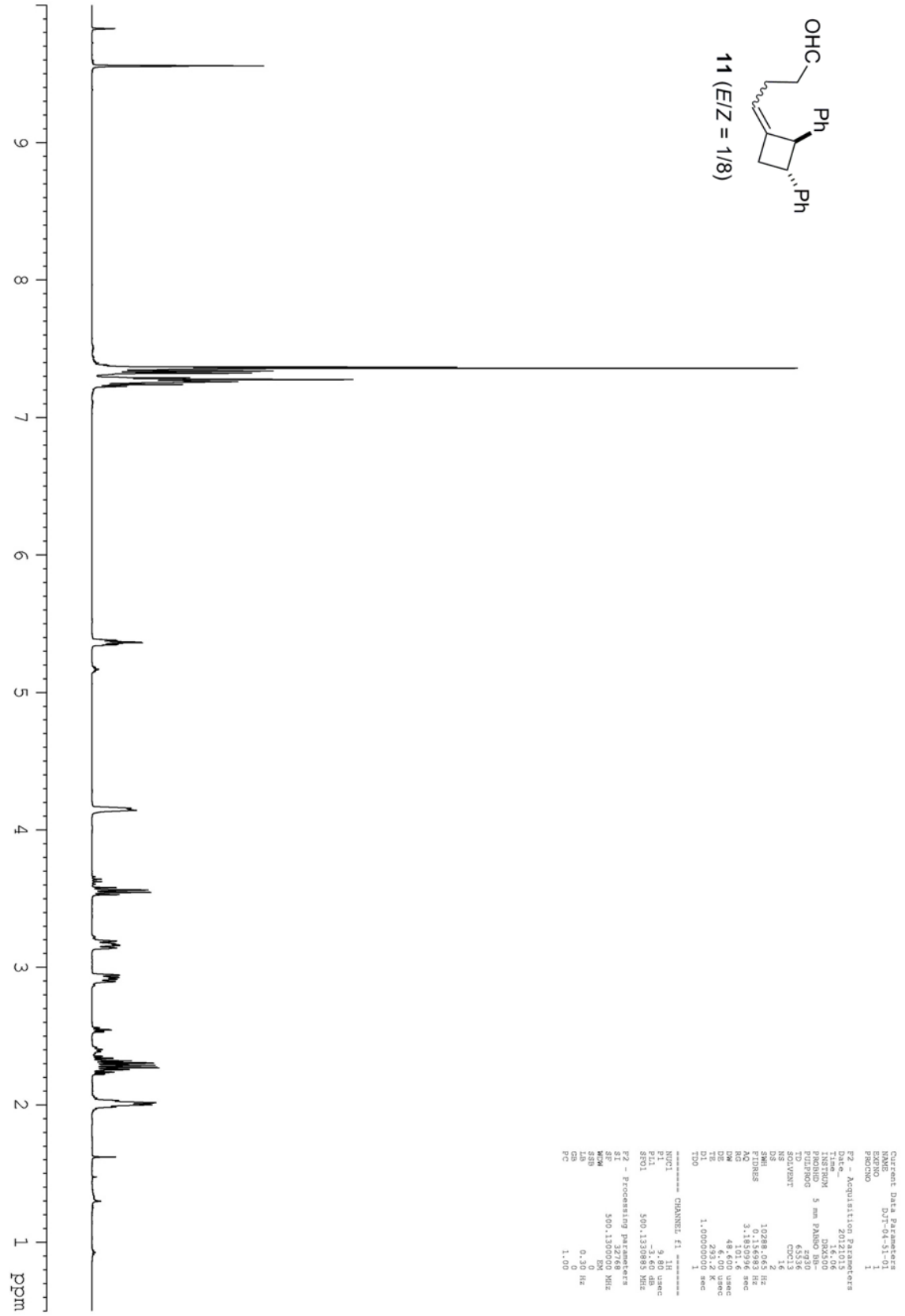
10g key HMBC

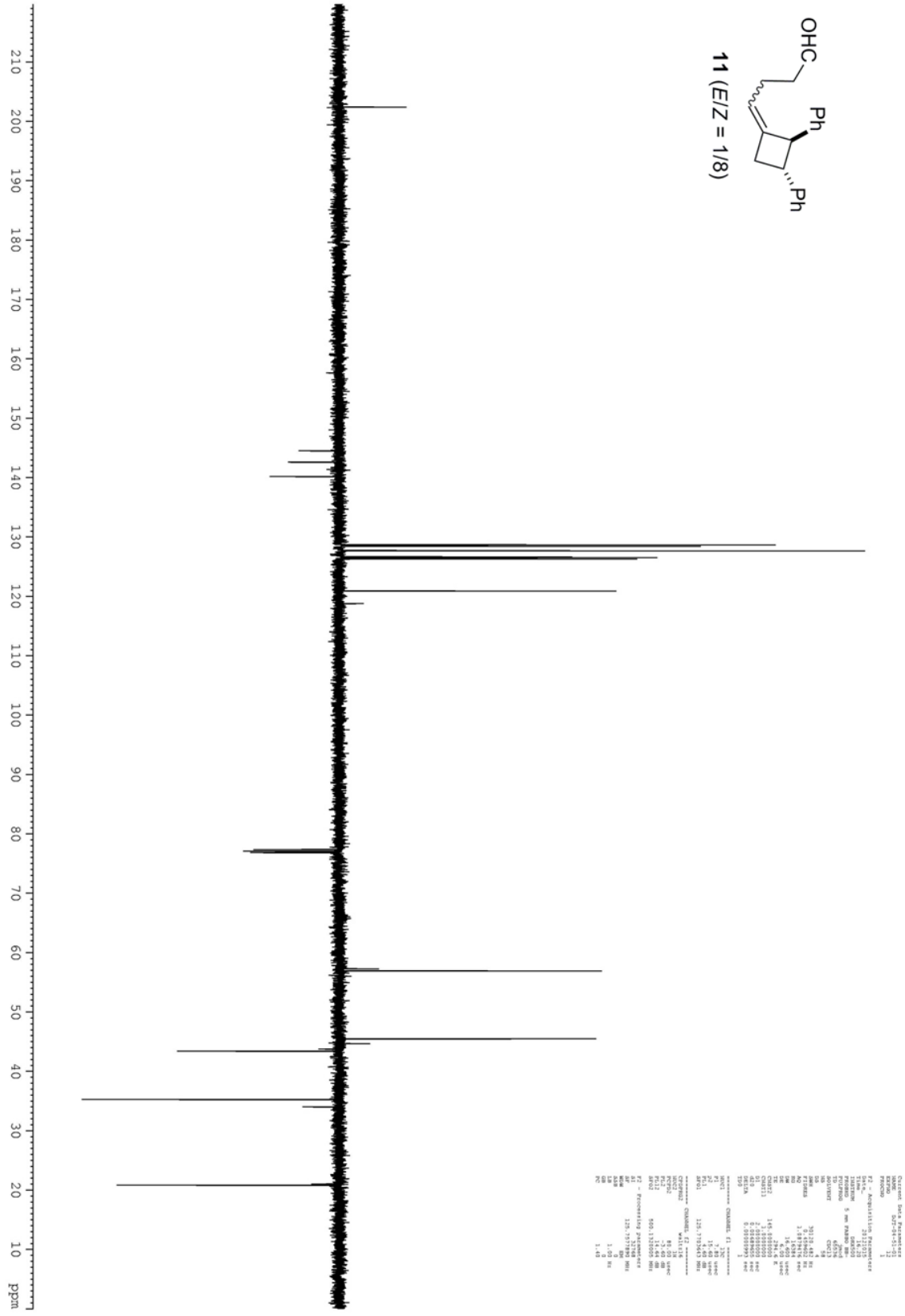


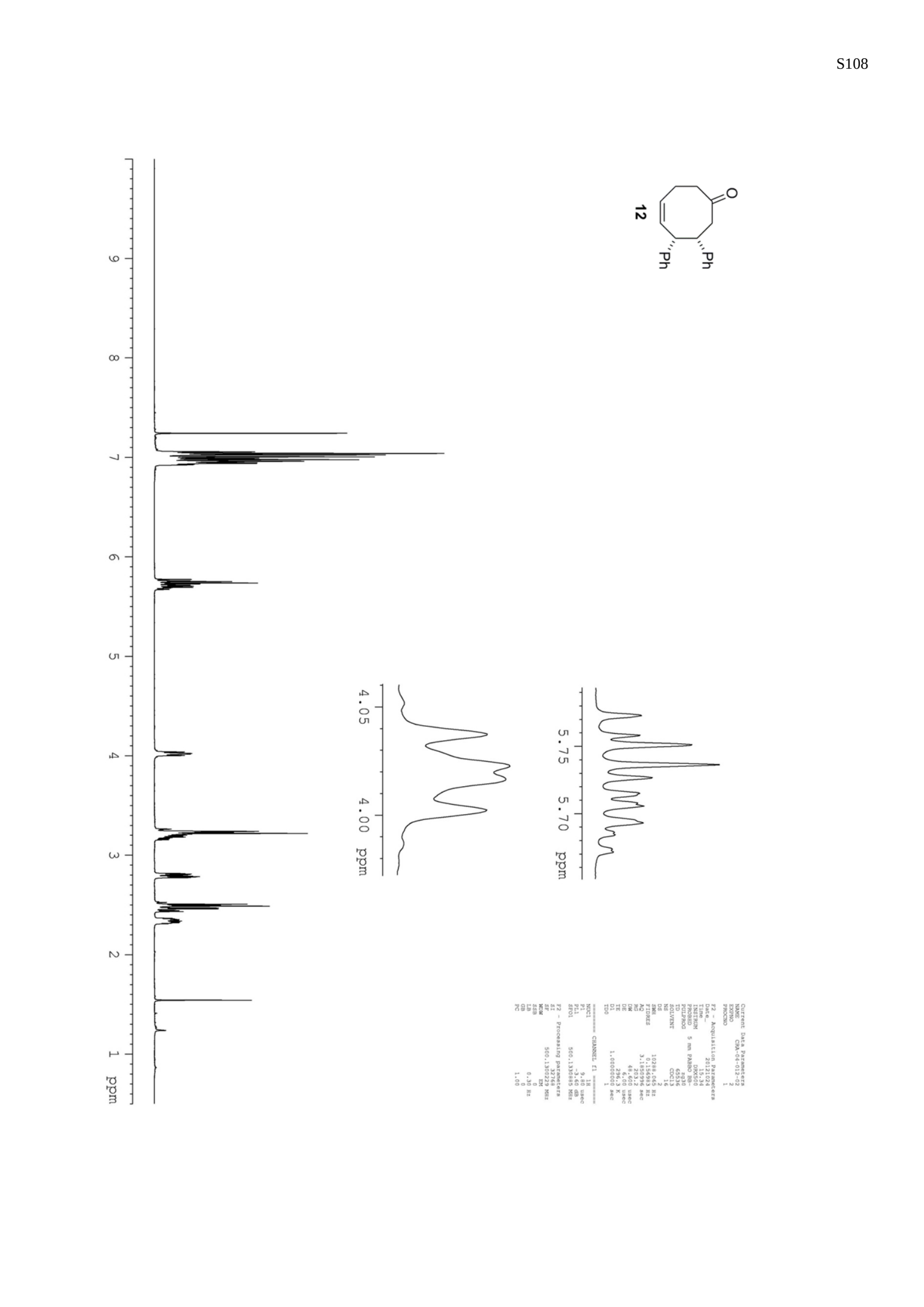


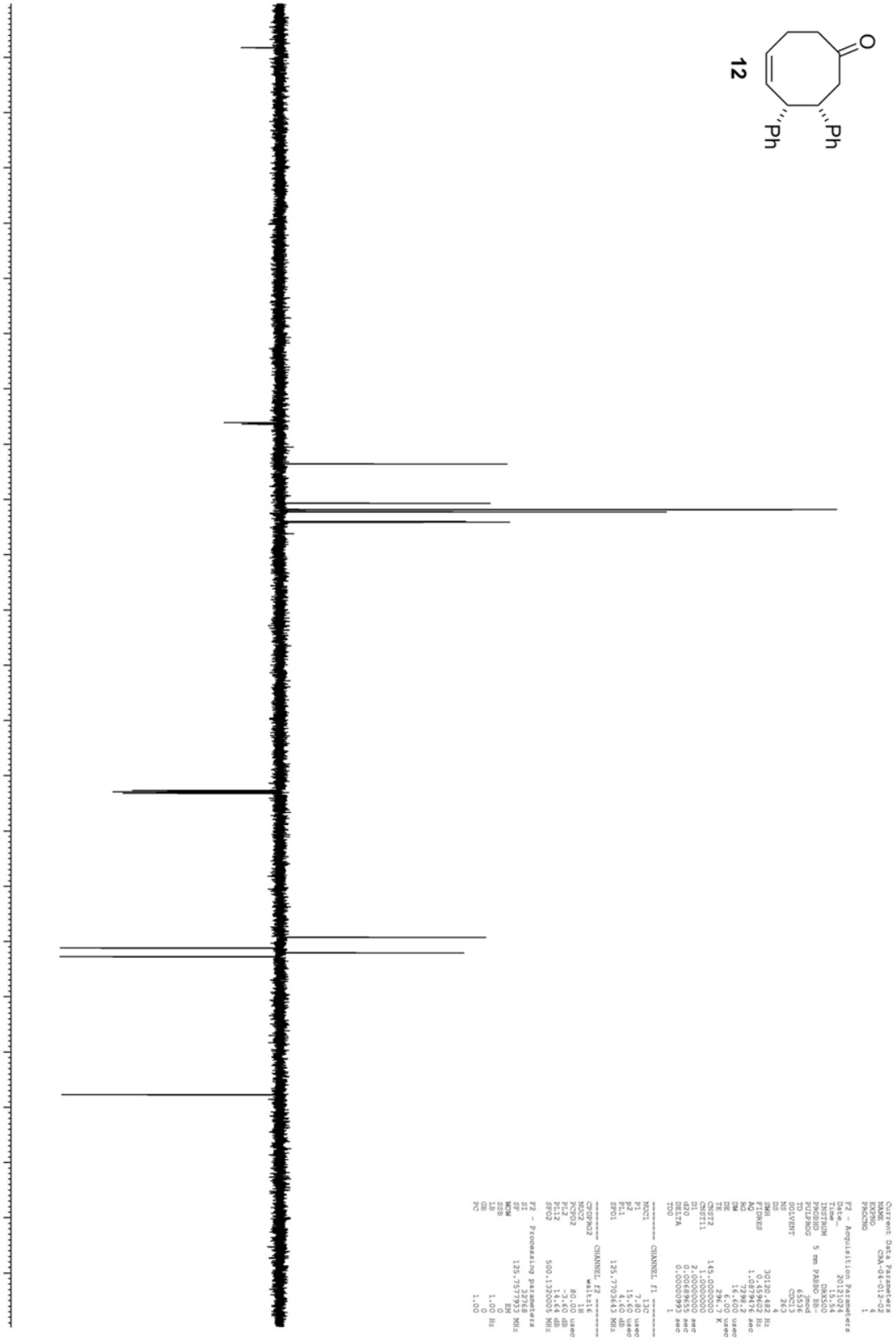

OHC
Ph
Ph
11 (E/Z = 3.3/1)
9
8
7
6
5
4
3
2
1
ppm

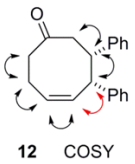

OHC
Ph
Ph
11 (E/Z = 3.3/1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OHC
Ph
Ph
11 (E/Z = 1/8)
9
8
7
6
5
4
3
2
1
ppm

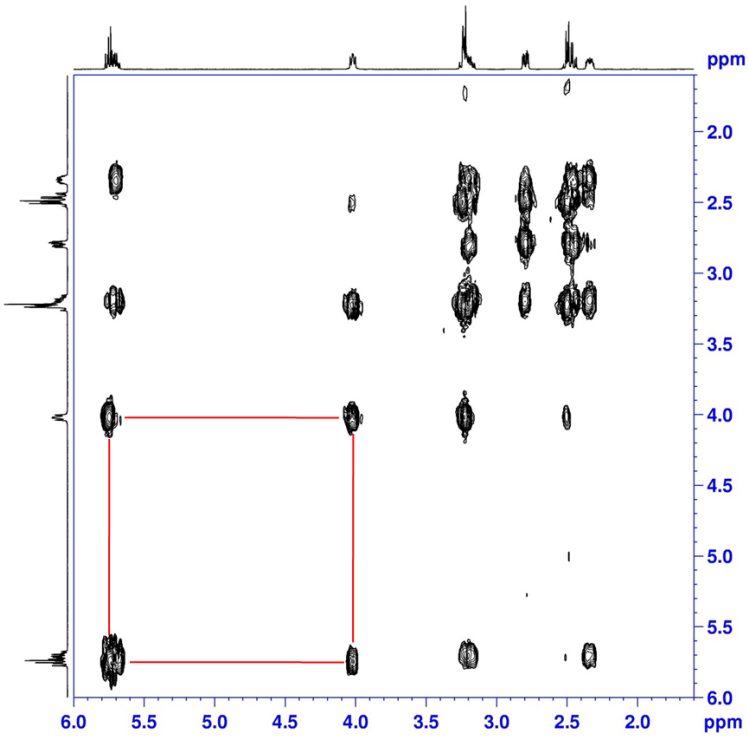

OHC
Ph
Ph
11 (E/Z = 1/8)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

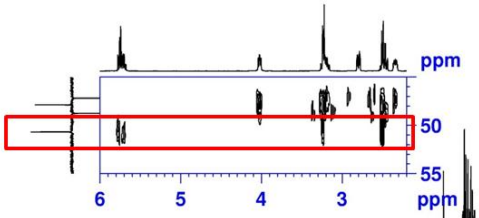

O
Ph
Ph
12
5.75
5.70 ppm
4.05
4.00 ppm
9
8
7
6
5
4
3
2
1 ppm

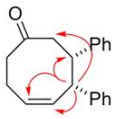

O
Ph
Ph
12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



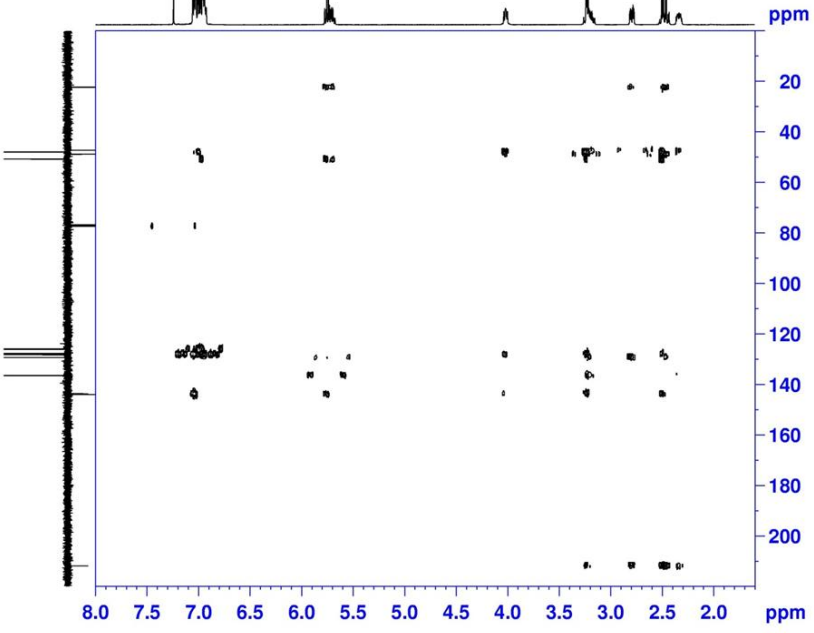
12 COSY

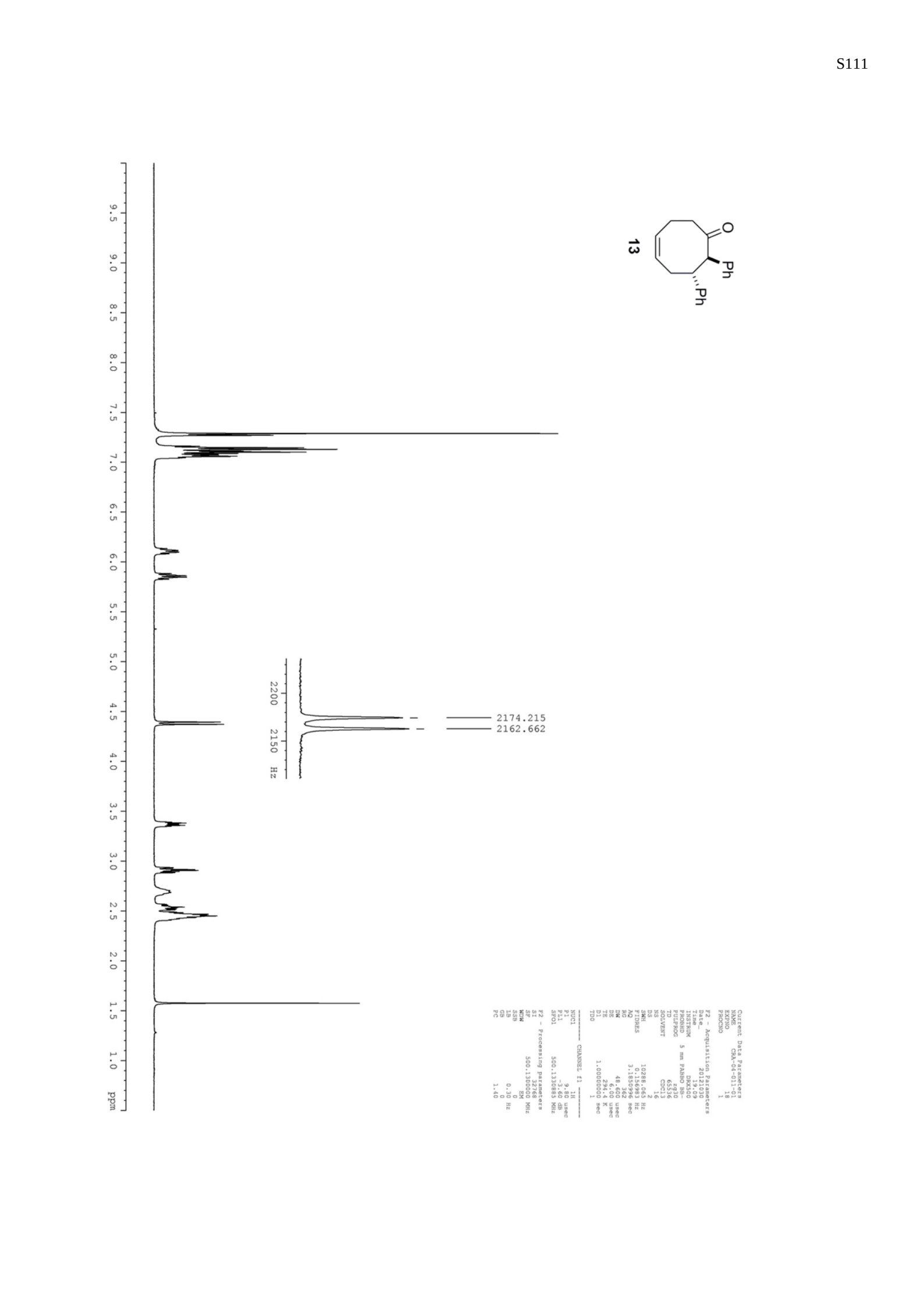


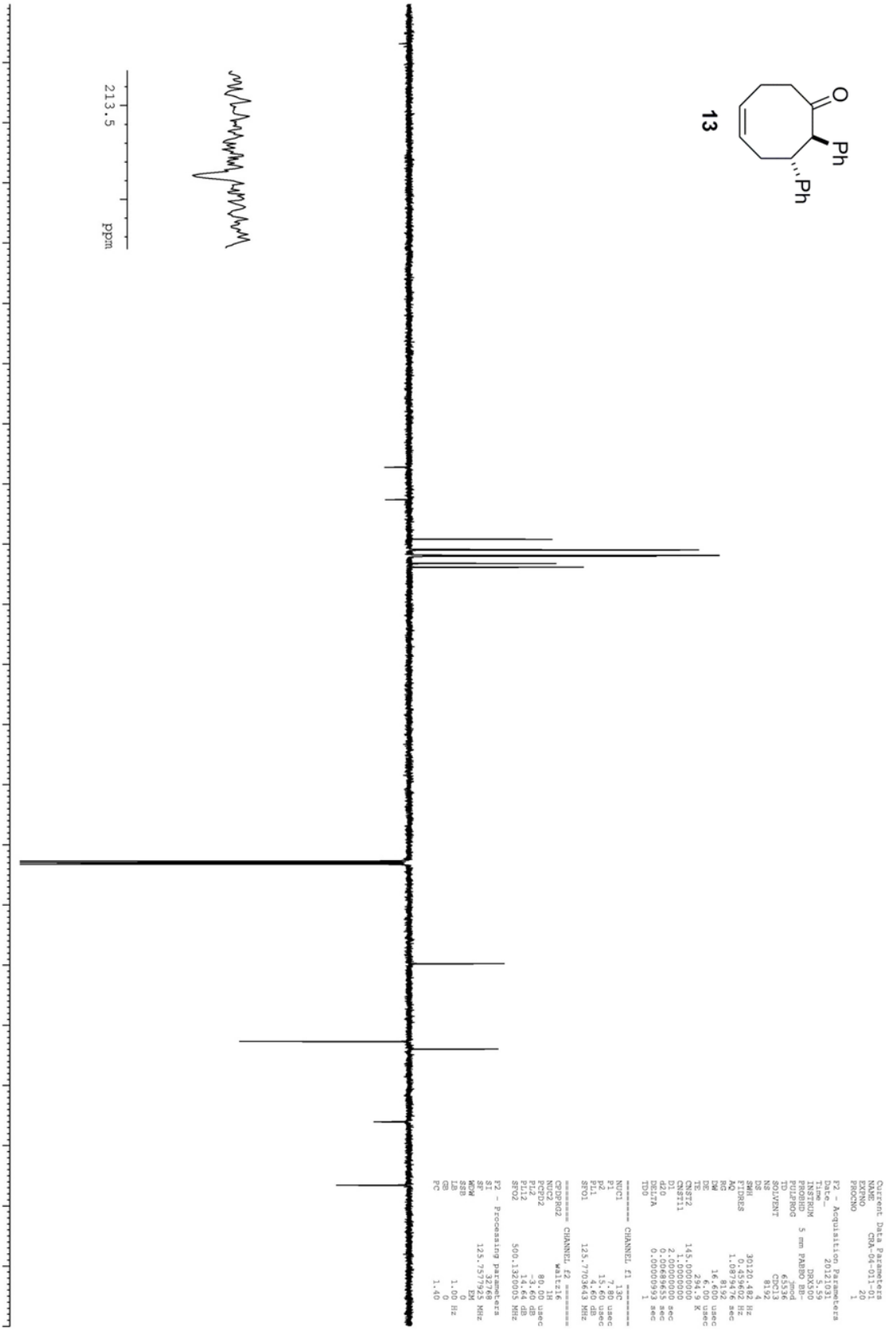


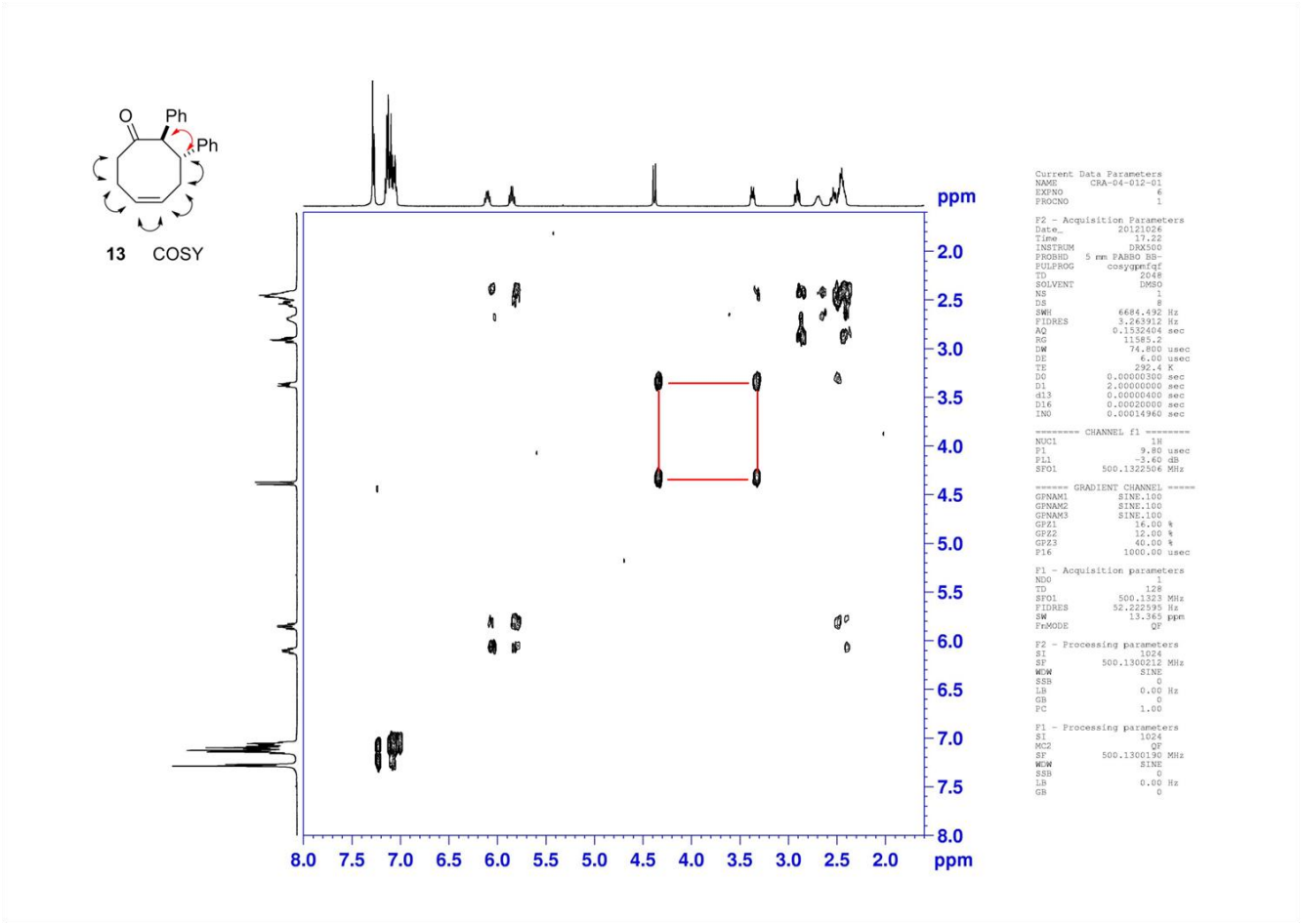


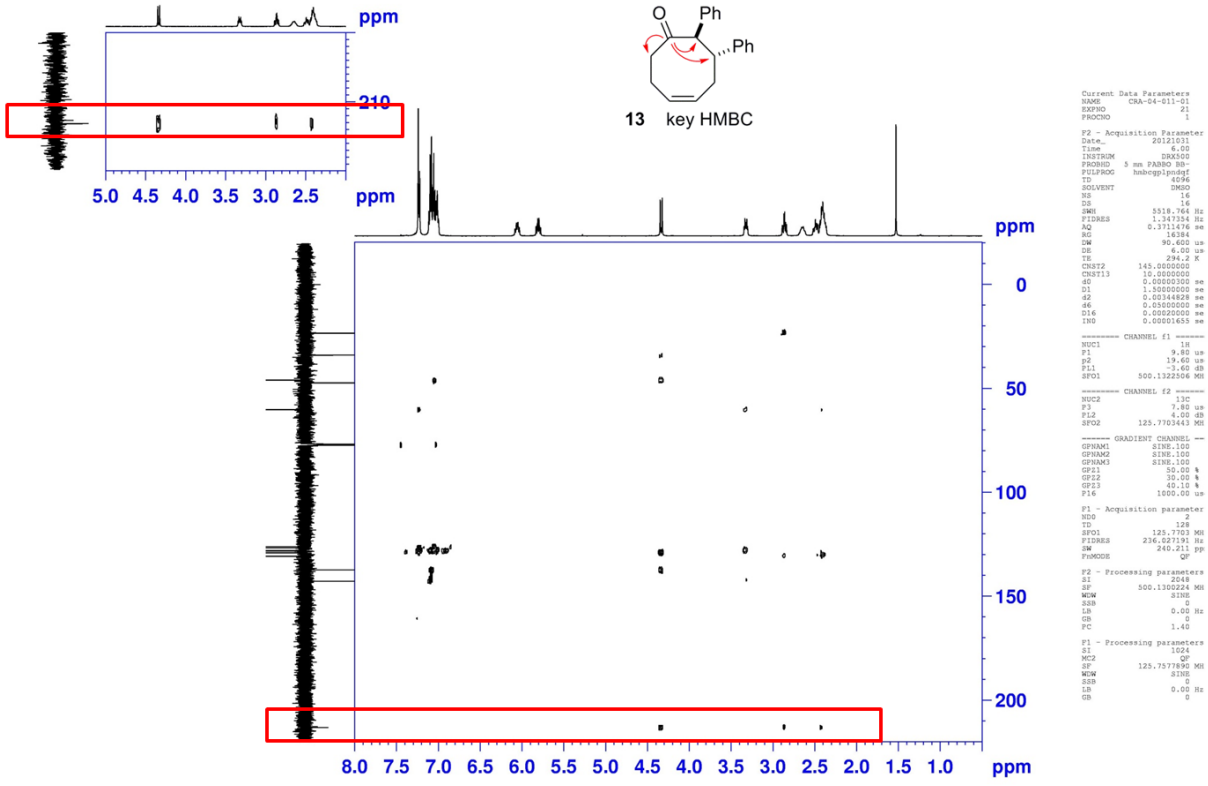
12 key HMBC




13
Ph
Ph
O
2174.215
2162.662
2200
2150
Hz
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
Ph
O
13
213.5
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


13 COSY
ppm
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 ppm
Current Data Parameters
NAME CRA-04-012-01
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121026
Time 17.22
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG cosygpmfqf
TD 2048
SOLVENT DMSO
NS 1
DS 8
SWH 6684.492 Hz
FIDRES 3.263912 Hz
AQ 0.1532404 sec
RG 11585.2
DW 74.800 usec
DE 6.00 usec
TE 292.4 K
D0 0.00000300 sec
D1 2.00000000 sec
d13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00014960 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -3.60 dB
SFO1 500.1322506 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 16.00 %
GPZ2 12.00 %
GPZ3 40.00 %
P16 1000.00 usec
F1 - Acquisition parameters
ND0 1
TD 128
SFO1 500.1323 MHz
FIDRES 52.222595 Hz
SW 13.365 ppm
FnMODE QF
F2 - Processing parameters
SI 1024
SF 500.1300212 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 500.1300190 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0


13 key HMBC
ppm
210
5.0 4.5 4.0 3.5 3.0 2.5 ppm
ppm
0
50
100
150
200
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
Current Data Parameters
NAME CRA-04-011-01
EXPNO 21
PROCNO 1
F2 - Acquisition Parameter
Date_ 20121031
Time 6.00
INSTRUM DRX500
PROBHD 5 mm PABBO BB-
PULPROG hmbcgplpndqf
TD 4096
SOLVENT DMSO
NS 16
DS 16
SWH 5518.764 Hz
FIDRES 1.347354 Hz
AQ 0.3711476 se
RG 16384
DW 90.600 us
DE 6.00 us
TE 294.2 K
CNST2 145.0000000
CNST13 10.0000000
d0 0.00000300 se
D1 1.50000000 se
d2 0.00344828 se
d6 0.05000000 se
D16 0.00020000 se
IN0 0.00001655 se
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 us
p2 19.60 us
PL1 -3.60 dB
SFO1 500.1322506 MH
======== CHANNEL f2 ========
NUC2 13C
P3 7.80 us
PL2 4.00 dB
SFO2 125.7703443 MH
====== GRADIENT CHANNEL ==
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 50.00 %
GPZ2 30.00 %
GPZ3 40.10 %
P16 1000.00 us
F1 - Acquisition parameter
ND0 2
TD 128
SFO1 125.7703 MH
FIDRES 236.627191 Hz
SW 240.211 pp
FnMODE QF
F2 - Processing parameters
SI 2048
SF 500.1300224 MH
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 125.7577890 MH
WDW SINE
SSB 0
LB 0.00 Hz
GB 0