SUPPORTING INFORMATION

A Rhodium Catalyzed C-H Activation/Cycloisomerization Tandem

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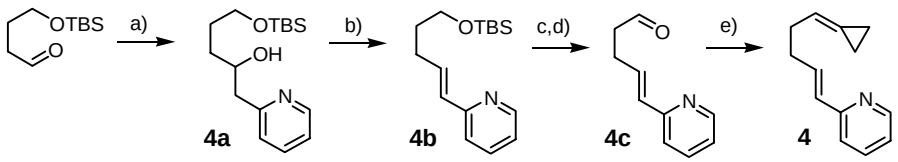
General. Unless stated otherwise, all reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-Anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF, DMA (Desmodur®, dibutyltin dilaurate), hexanes, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded with a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hertz. 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; CD_2Cl_2: δ_C = 53.8 ppm; residual CH_2Cl_2 in CD_2Cl_2: δ_H = 5.32 ppm). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determination: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds were used as received.

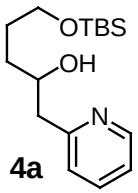
Substrates

Representative Sequence: Preparation of Compound 4



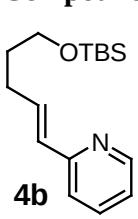
a) 2-methylpyridine, *n*-BuLi, THF; b) MsCl, pyridine, CH_2Cl_2, 80°C; c) HCl 5%, EtOH; d) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; e) 3-(bromopropyl)triphenylphosphonium bromide, *t*-BuOK, THF reflux.

Compound 4a. 2-Methylpyridine (0.27 mL, 2.70 mmol) was added to a cooled (–50°C) solution of *n*-BuLi (1.6 M in hexanes, 1.77 mL, 2.84 mmol) in THF (15 mL) at such a rate that the internal temperature did not exceed –45°C. Once the addition was complete, the mixture was allowed to stir at –20°C for 5 min before it was cooled to –50°C and a solution of 4-(*tert*-butyldimethylsilyloxy)butanal (600 mg, 2.97 mmol)[1] in THF (4 mL) was added via canula. The mixture was allowed to stir at –20°C for 2 h and at ambient temperature for 1 h before the reaction was quenched with aq. sat. $NaHCO_3$ and EtOAc. A standard extractive work up followed by flash chromatography (hexanes/EtOAc, 2/1) afforded product **4a** as a yellow oil (631 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (dd, *J* = 5.6, 2.0 Hz, 1H), 7.59 (td, *J* = 7.7, 1.9 Hz, 1H), 7.19-7.02 (m, 2H), 4.09-3.97 (m, 1H), 3.70-3.58 (m, 2H), 2.91 (dd, *J* = 14.8, 3.5 Hz, 1H), 2.84 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.78-1.49 (m, 4H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2, 148.5, 136.6, 123.7, 121.3, 70.8, 63.2, 43.5, 33.6, 29.0, 26.0 (3C), 18.3, –5.0, –5.4; IR (neat): $\tilde{\nu}$ = 3392 (broad), 3068, 2953, 2928, 2895, 2857, 1595, 1570, 1473, 1463, 1437, 1388, 1360, 1255, 1097, 836, 776, 662 cm^{-1}; MS (EI): *m*/*z* (%): 295 (3), 238 (100), 203 (7), 146 (63), 122 (40), 93 (90), 75 (54); HRMS (ESI+.) calcd for ($C_{16}H_{29}NO_2Si$ + Na): 318.18598; found: 318.18574; elemental analysis (%) calcd for $C_{16}H_{29}NO_2Si$: C 65.05, H 9.89, N 4.74; found: C 64.96, H 9.88, N 4.67.



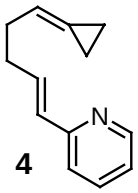
4a

Compound 4b. A mixture of alcohol **4a** (600 mg, 2.03 mmol), mesyl chloride (0.31 mL, 4.06 mmol) and pyridine (1.8 mL) in CH_2Cl_2 (6 mL) was heated in a Teflon-screw-cap Schlenk tube at 80°C for 7 h. All volatile materials were stripped off under high vacuum, the residue was dissolved in *tert*-butyl methyl ether (20 mL), and the organic phase was washed with aq. sat. $NaHCO_3$ and brine before it was dried over Na_2SO_4 and evaporated. Purification of the crude material by flash chromatography (hexanes/EtOAc, 15/1) afforded product **4b** as a yellow oil (279 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52-8.48 (m, 1H), 7.57 (td, *J* = 7.8, 1.9 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.06 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.73 (dt, *J* = 15.6, 7.0 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.31 (qd, *J* = 7.1, 1.4 Hz, 2H), 1.77-1.65 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 149.4, 136.3, 135.4, 130.1, 121.5, 120.9, 62.5, 32.0, 29.1, 25.9 (3C), 18.3, –5.3 (2C); IR (neat): $\tilde{\nu}$ = 3004, 2954, 2929, 2894, 2857, 1654, 1586, 1564, 1471, 1431, 1388, 1361, 1255, 1099, 971, 835, 776, 662 cm^{-1}; MS (EI): *m*/*z* (%): 277 (2), 262 (4), 220 (100), 204 (17); HRMS (EI): calcd for $C_{16}H_{27}NOSi$: 277.18620; found 277.18578; elemental analysis (%) calcd for $C_{16}H_{27}NOSi$: C 69.26, H 9.81, N 5.05, found: C 69.38, H 9.74, N 4.97.



4b

Compound 4. HCl (5% *w*/*w* in EtOH, 1 mL) was added via syringe to a solution of **4b** (284 mg, 1.03 mmol) in EtOH (10 mL) and the resulting solution was stirred for 90 min. The solvent was evaporated, the crude material was diluted with Et_2O (20 mL), the organic phase was washed with sat. aq. $NaHCO_3$, the aqueous layer was re-extracted Et_2O (2 x 10 mL), and the combined organic phases were dried over Na_2SO_4, filtered and evaporated. The resulting crude material was used in the next step without further purification.



4

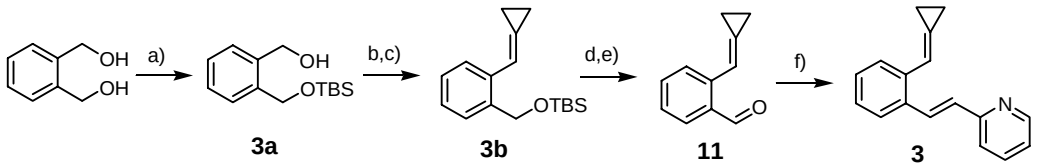
A solution of DMSO (185 µL, 2.6 mmol) in CH_2Cl_2 (0.3 mL) was added via canula to a solution of $(COCl)_2$ (113 µL, 1.3 mmol) in CH_2Cl_2 (3 mL) at –78°C. After 10 min, a solution of the crude alcohol obtained above in CH_2Cl_2 (1 mL) was introduced and the resulting mixture was stirred for 15 min at this temperature. Et_3N (0.7 mL, 5 mmol) was then rapidly added and stirring continued for 30 min at ambient temperature before the reaction was

[1] Kang, E. J.; Cho, E. J.; Ji, M. K.; Young, E. Shin, D. M.; Choi, S. Y.; Chung, Y. K.; Kim, J.-S.; Kim, H.-J.; Lee, S.-G.; Lah, M. S.; Lee, E. *J. Org. Chem.* **2005**, *70*, 6321-6329.

quenched with sat. aq. $NaHCO_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated.

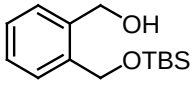
A solution of the resulting crude aldehyde **4c** in THF (2 mL) was added to a refluxing suspension of the freshly prepared ylide derived from 3-(bromopropyl)triphenylphosphonium bromide (511 mg, 1.1 mmol) and *t*-BuOK (246 mg, 2.2 mmol) in refluxing THF (11 mL)[2] and reflux was continued for 14 h. For work up, the mixture was allowed to reach ambient temperature before it was diluted with *tert*-butyl methyl ether (20 mL) and washed with water (20 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 x 10 mL), the combined organic phases were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 10/1) to give product **4** as a pale yellow oil (100 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 4.9 Hz, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.06 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.78-6.75 (m, 1H), 6.48 (d, *J* = 16.8 Hz, 1H), 5.85-5.76 (m, 1H), 2.47-2.30 (m, 4H), 1.02 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 149.4, 136.3, 135.4, 130.1, 121.8, 121.5, 120.9, 117.2, 32.6, 31.2, 2.1, 2.0; IR (neat): $\tilde{\nu}$ = 3049, 3002, 2978, 2927, 2844, 1653, 1585, 1564, 1469, 1430, 971, 756 cm^{-1}; MS (EI): *m/z* (%): 185 (10), 184 (41), 170 (19), 157 (22), 156 (24), 144 (31), 143 (11), 131 (17), 130 (32), 118 (100), 117 (68); HRMS (CI, *i*-butane) calcd for ($C_{13}H_{15}N$ + H): 186.12828; found: 186.12803; elemental analysis (%) calcd for $C_{13}H_{15}N$: C 84.28, H 8.16, N 7.56; found: C 84.15, H 8.08, N 7.64.

Representative Sequence: Preparation of Compounds 3 and 11



a) TBSCl, NaH, THF; b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; c) 3-(bromopropyl)triphenylphosphonium bromide, *t*–BuOK, THF reflux; d) TBAF, THF; e) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; f) (i) 2-methylpyridine, *n*-BuLi, THF; (ii) MsCl, pyridine, CH_2Cl_2, 80°C.

Compound 3a. Commercially available 1,2-bis(hydroxymethyl)benzene (1.38 g, 10 mmol) was added in portions to a vigorously stirred suspension of NaH (240 mg, 10 mmol) in THF (30 mL) at 0°C. After stirring for 16 h, TBSCl (1.5 g, 10 mmol) was added in portions and stirring was continued for 1 h at ambient temperature. A standard extractive work up followed by flash chromatography (hexanes/EtOAc, 10/1) gave compound **3a** as a colorless oil (2.42 g, 96%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.33 (m, 1H), 7.32-7.25 (m, 3H), 4.79 (s, 2H), 4.66 (d, *J* = 6.4 Hz, 2H), 3.20 (t, *J* = 6.4 Hz, 1H, -OH), 0.90 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 138.6, 126.4, 128.7, 128.3, 127.9, 64.7, 63.9, 25.9 (3C), 18.2, –5.3 (2C); IR (neat): $\tilde{\nu}$ = 3372 (br), 3069, 3025, 2955, 2929, 2884, 2857, 1606, 1471, 1462, 1389, 1361, 1255, 1079, 1041, 836, 776, 746 cm^{-1}; MS (EI) *m/z* (%) 195 (60), 119 (23), 75 (100), 57 (11); HRMS (ESI+): calcd for ($C_{14}H_{24}O_2Si$ + Na):

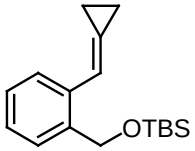


3a

[2] Phosphonium bromide and *t*-BuOK were mixed in THF at ambient temperature and the resulting mixture was refluxed for 2 h to give a suspension of the required ylide.

275.14378; found: 275.14365; elemental analysis (%) calcd for $C_{14}H_{24}O_2Si$: C 66.61, H 9.58; found: C 66.73, H 9.59.

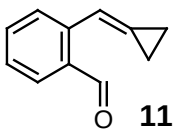
Compound 3b. A solution of DMSO (0.73 mL, 10.3 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $(COCl)_2$ (0.45 mL, 5.15 mmol) in CH_2Cl_2 (12 mL) at –78°C. After stirring for 10 min at this temperature, a solution of compound **3a** (1.0 g, 3.97 mmol) in CH_2Cl_2 (4 mL) was introduced and stirring was continued for 15 min at that temperature. Et_3N (2.8 mL, 20 mmol) was then rapidly added via syringe and the mixture was stirred for 30 min at ambient temperature before it was poured into aq. sat. $NaHCO_3$ (10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL), the combined organic layers were washed, dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 20/1) to give the corresponding aldehyde as a yellow oil (939 mg) which was used without further purification.



3b

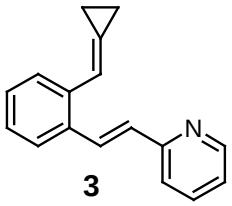
A solution of this crude material in THF (5 mL) and added to a refluxing suspension of the ylide prepared from (3-bromopropyl)triphenylphosphonium bromide (1.9 g, 1.1 mmol) and *t*–BuOK (269 mg, 2.4 mmol) in THF (25 mL).[2] Reflux was continued for 14 h before the mixture was allowed to reach ambient temperature. A standard extractive work up followed by flash chromatography (hexanes) afforded compound **3b** as a pale yellow oil (595 mg, 58% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74-7.70 (m, 1H), 7.45-7.40 (m, 1H), 7.23-7.18 (m, 2H), 6.94-6.90 (m, 1H), 4.84 (s, 2H), 1.43-1.35 (m, 2H), 1.20-1.13 (m, 2H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6, 135.4, 127.0, 126.9, 126.6, 125.9, 125.6, 114.7, 63.3, 26.0 (3C), 18.4, 4.2, 1.0, –5.2 (2C); IR (neat): $\tilde{\nu}$ = 3068, 3049, 3032, 2955, 2928, 2884, 2856, 1601, 1471, 1462, 1388, 1361, 1254, 1083, 1046, 836, 776, 750 cm^{-1}; MS (EI): *m/z* (%): 274 (10), 217 (51), 143 (66), 128 (43), 75 (100); HRMS (EI): calcd for $C_{17}H_{26}OSi$: 274.17529; found: 274.17556; elemental analysis (%) calcd for $C_{17}H_{26}OSi$: C 74.39, H 9.55; found: C 74.28, H 9.48.

Compound 11. A solution of compound **3b** (1.1 g, 4.02 mmol) and TBAF (1 M in THF, 4 mL) was stirred for 1 h at ambient temperature. For work up, the mixture was partitioned between Et_2O (10 mL) and sat. aq. NH_4Cl (10 mL), the aqueous layer was extracted with Et_2O (2 x 10 mL), the combined organic phases were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue was rapidly passed through a short pad of silica (hexanes/Et_2O, 10/1→3/1). An aliquot of the resulting alcohol (143.6 mg, 0.9 mmol) was dissolved in CH_2Cl_2 (1 mL) and this solution was added to a cooled (–78°C) solution of DMSO (140 mg, 1.8 mmol) and $(COCl)_2$ (85 µL, 1.0 mmol) in CH_2Cl_2 (4 mL). The resulting mixture was stirred for 15 min at –78°C before Et_3N (0.56 mL, 4.0 mmol) was introduced. Stirring was continued for 30 min at ambient temperature before the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), the combined organic phases were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 5/1) to give aldehyde **11** as a colorless oil (112 mg, 79% over two steps). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 10.31 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.68 (quint., *J* = 2.0 Hz, 1H), 7.56 (td, *J* = 7.7, 1.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H), 1.49-1.39 (m, 2H), 1.33-1.22 (m, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 192.9, 140.4, 133.7, 132.7, 131.7, 130.9, 127.9, 127.2, 114.3, 4.7, 1.8; IR (neat): $\tilde{\nu}$ = 3066, 2977, 2838, 2735, 1688, 1596, 1566, 1483, 1450, 1408, 1296, 1208, 1184, 1159, 975, 928, 868, 802, 791, 749 cm^{-1}; MS (EI): *m/z* (rel. intensity): 158 (60), 129 (100), 118 (31), 115 (40), 102 (16), 89 (11), 77 (10); HRMS (EI) calcd for $C_{11}H_{10}O$: 158.07316; found: 158.07306.



11

Compound 3. The alkylidenation reaction was performed as described for the preparation of compound **4a**, providing pyridine **3** as a yellow oil (388 mg, 42% over two steps). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.61-8.57 (m, 1H), 8.10 (d, *J* = 15.8 Hz, 1H), 7.76 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H), 7.66 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.4 (d, *J* = 7.9 Hz, 1H), 7.32-7.23 (m, 2H), 7.21 (quint., *J* = 2.0 Hz, 1H), 7.18 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 7.08 (d, *J* = 15.8 Hz, 1H), 1.47-1.39 (m, 2H), 1.28-1.21 (m, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 154.4, 148.2, 135.7, 133.2, 129.5, 12.3, 127.0, 126.0, 125.83 (2C), 125.81, 125.2, 121.1, 121.0, 114.2, 2.9, 0.0; IR (neat): $\tilde{\nu}$ = 3054, 3002, 2974, 1777, 1713, 1680, 1584, 1480, 1469, 1430, 970, 773, 740 cm^{-1}; MS (EI): *m/z* (%): 233 (29), 232 (100), 218 (35), 217 (36), 205 (12), 204 (15); HRMS (EI): calcd for $C_{17}H_{15}N$: 233.12045; found: 233.12026; elemental analysis (%) calcd for $C_{17}H_{15}N$: C 87.52, H 6.48, N 6.00; found: C 87.43, H 6.35, N 5.88.

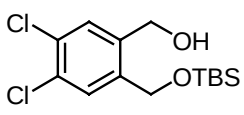


3

The deuterated compound **3-D** was obtained analogously; it showed the following spectroscopic properties: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (ddd, *J* = 5.0, 1.8, 0.8 Hz, 1H), 8.06 (d, *J* = 15.8 Hz, 0.07H), 7.72 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.37 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.31-7.17 (m, 3H), 7.12 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 7.05-7.01 (m, 1H), 1.43-1.35 (m, 2H), 1.24-1.17 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 149.6, 136.7, 136.5, 134.3, 130.1 (t, *J* = 23 Hz), 129.6, 128.0, 126.8 (2C), 126.7, 126.4, 122.00, 121.95, 115.4, 3.1, 1.2; MS (EI): *m/z* (%): 234 (33), 233 (100), 219 (26), 218 (38), 206 (12), 205 (12); HRMS (EI): calcd for ($C_{17}H_{14}DN$): 234.126727; found: 234.126460.

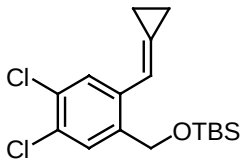
Unless stated otherwise, all other compounds were prepared analogously. Their analytical and spectroscopic date are compiled below:

Compound 1a. White solid (510 mg, 77%). m.p.: 52-54°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (s, 1H), 7.41 (s, 1H), 4.69 (s, 2H), 4.66 (d, *J* = 5.7 Hz, 2H), 2.78-2.69 (m, 1H, -OH), 0.91 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0, 138.6, 131.5, 131.4, 130.5, 129.9, 63.0, 62.4, 25.8 (3C), 18.2, –5.3 (2C); IR (neat): $\tilde{\nu}$ = 3354 (br), 2955, 2930, 2884, 2858, 1596, 1559, 1471, 1387, 1362, 1257, 1097, 1052, 1007, 937, 888, 838, 776, 681 cm^{-1}; MS (EI): *m/z* (%): 265 (18), 263 (26), 75 (100); HRMS (ESI+): calcd for ($C_{14}H_{22}Cl_2O_2Si$ + Na): 343.06584; found 343.06610; elemental analysis (%) calcd for $C_{14}H_{22}Cl_2O_2Si$: C 52.33, H 6.90; found: C 52.41, H 6.83.



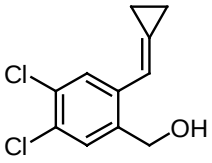
1a

Compound 1b. White solid (228 mg, 44 % over two steps). m.p.: 90-94°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.52 (s, 1H), 6.75 (quint., *J* = 2.0 Hz, 1H), 4.75 (s, 2H), 1.41-1.32 (m, 2H), 1.22-1.13 (m, 2H), 0.93 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 134.9, 130.6, 130.2, 128.5, 128.0, 127.3, 112.7, 62.1, 25.9 (3C), 18.3, 4.2, 1.1, –5.3 (2C); IR (KBr): $\tilde{\nu}$ = 3073, 3051, 1760 1739, 1554, 1485, 1471, 1456, 1385, 1366, 1261, 1090, 936, 860, 839, 779, 678 cm^{-1}; MS (EI): *m/z* (%): 342 (14), 307 (25), 285 (23), 211 (40), 176 (22), 141 (28), 75 (100); HRMS (ESI+): calcd for ($C_{17}H_{24}Cl_2OSi$ + Na): 365.08657; found 365.08671; elemental analysis (%) calcd for $C_{17}H_{24}Cl_2OSi$: C 59.47, H 7.05; found: C 59.30, H 6.94.



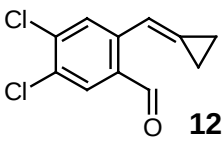
1b

Compound 1c. A solution of compound **1b** (930 mg, 2.7 mmol) and TBAF (1 M in THF, 2.7 mL) in THF (15 mL) was stirred for 1 h before the reaction was quenched with sat. aq. NH_4Cl. A standard extractive work up followed by flash chromatographic purification of the crude material gave product **4c** as a white solid (466 mg, 75%). m.p. 112-115°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.44 (s, 1H), 6.85 (quint., *J* = 2.0 Hz, 1H), 4.72 (s, 2H), 1.45-1.37 (m, 2H), 1.24-1.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.9, 135.9, 131.6, 130.2, 129.6, 128.6, 127.8, 112.6, 62.2, 4.2, 1.1; IR (KBr): $\tilde{\nu}$ = 3315, 3320, 3040, 2974, 2920, 1765, 1551, 1486, 1471, 1449, 1423, 1409, 1378, 1225, 1134, 1049, 986, 891, 678 cm^{-1}; MS (EI): *m/z* (%): 228 (7), 199 (37), 197 (56), 195 (32), 193 (100), 188 (11), 186 (17), 177 (10), 175 (30), 162 (37). HRMS (EI) calcd for $C_{11}H_{10}Cl_2O$: 228.01087; found: 228.01057; elemental analysis (%) calcd for $C_{11}H_{10}Cl_2O$: C 57.67, H 4.40; found: C 57.82, H 4.47.



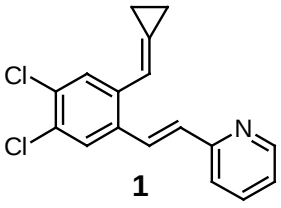
1c

Compound 12. White solid (329 mg, 78%). m.p.: 67-70°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.21 (s, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.54-7.50 (m, 1H), 1.47-1.46 (m, 2H), 1.32-1.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.0, 139.5, 138.2, 132.9, 132.4, 131.4, 131.2, 129.3, 112.1, 4.6, 1.9; IR (neat): $\tilde{\nu}$ = 3076, 3026, 2977, 2890, 1733, 1678, 1574, 1458, 1412, 1372, 1212, 1134, 977, 943, 922, 901, 878, 847 cm^{-1}; MS (EI) *m/z* (rel. intensity) 228 (31), 226 (48), 199 (19), 197 (26), 193 (32), 191 (100), 163 (54), 128 (74); HRMS (EI) calcd for $C_{11}H_8Cl_2O$: 225.99522; found: 225.99529; elemental analysis calcd for $C_{11}H_8Cl_2O$: C 58.18, H 3.55; found: C 58.06, H 3.51.



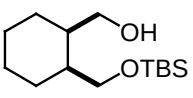
12

Compound 1. White solid (96 mg, 53% over two steps). m.p. 111-114°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 15.8 Hz, 1H), 7.77 (s, 1H), 7.67 (s, 1H), 7.65 (td, *J* = 7.8, 1.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 7.07 (quint., *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 15.8 Hz, 1H), 1.45-1.36 (m, 2H), 1.25-1.16 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.8, 149.6, 136.4, 136.3, 134.2, 131.6, 130.9, 130.3, 128.7, 128.1 (2C), 127.8, 122.5, 122.3, 113.5, 3.9, 1.2; IR (KBr): $\tilde{\nu}$ = 3046, 3022, 2973, 1735, 1630, 1582, 1563, 1475, 1465, 1431, 1230, 1139, 954, 883, 764 cm^{-1}; MS (EI): *m/z* (%): 303 (22), 302 (67), 301 (36), 300 (100), 288 (18), 287 (13), 286 (28), 285 (14); HRMS (EI): calcd for $C_{17}H_{13}Cl_2N$: 301.04251; found: 301.04242; elemental analysis (%) calcd for $C_{17}H_{13}Cl_2N$: C 67.38, H 4.30, N 4.70; found: C 67.57, H 4.34, N 4.63.



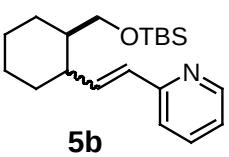
1

Compound 5a. Colorless oil (1.56 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (dd, *J* = 10.2, 8.5 Hz, 1H), 3.61 (ddd, *J* = 11.3, 8.5, 4.3 Hz, 1H), 3.52 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.51-3.33 (m, 2H), 1.96-1.81 (m, 2H), 1.61-1.23 (m, 8H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.0, 64.5, 40.7, 39.1, 28.0, 26.6, 25.8 (3C), 24.3, 23.8, 18.1, –5.6 (2C); IR (neat) $\tilde{\nu}$ = 3374, 2927, 2857, 1472, 1463, 1450, 1389, 1361, 1255, 1086, 837, 775 cm^{-1}; MS (EI): *m/z* (%): 201 (5), 109 (100), 105 (68), 75 (88); HRMS (ESI+): calcd for ($C_{14}H_{30}O_2Si$ + Na): 281.19073; found: 281.19083; elemental analysis (%) calcd for $C_{14}H_{30}O_2Si$: C 65.06, H 11.70; found: C 64.89, H 11.75.



5a

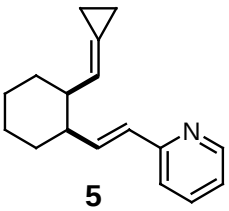
Compound 5b. Colorless oil (1.23 g, 64%, mixture of diastereomers ≈ 6:1). ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 8.51 (d, *J* = 4.3 Hz, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.06 (ddd, *J* = 7.5, 5.0, 1.1 Hz, 1H), 6.56 (dd, *J* = 15.8, 8.9 Hz, 1H), 6.41 (d, *J* = 15.5 Hz, 1H), 3.56 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.39 (dd, *J* = 9.9, 6.3 Hz, 1H), 2.13-1.99 (m, 1H), 1.91-1.82 (m, 1H), 1.79-1.61 (m, 3H), 1.42-1.06 (m, 5H), 0.85 (s, 9H),



5b

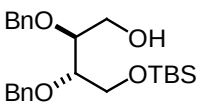
–0.04 (s, 6H); ^{13}C NMR (75MHz, $CDCl_3$): δ = 156.1, 149.4, 139.9, 136.3, 129.3, 121.5, 121.0, 66.3, 44.3, 43.5, 33.3, 29.3, 25.6 (3C), 18.1, –5.4 (2C); characteristic signals for the minor diastereomer: δ = 6.91 (dd, *J* = 15.5, 8.9 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H); IR (neat): $\tilde{\nu}$ = 2926, 2854, 1651, 1585, 1564, 1470, 1430, 1251, 1110, 1080, 1004, 972, 833, 772 cm^{-1}; MS (EI): *m/z* (%): 331 (2), 274 (100); HRMS (ESI+): calcd for ($C_{20}H_{33}NOSi$ + Na): 354.22236; found: 354.22246.

Compound 5. Yellow oil; the pure *cis* isomer was obtained by HPLC separation (253 mg, 31%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.46 (ddd, *J* = 4.6, 1.6, 0.8 Hz, 1H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.19 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.05 (ddd, *J* = 7.5, 4.8 Hz, 1.1 Hz, 1H), 6.61 (dd, *J* = 15.7, 7.7 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.72-5.64 (m, 1H), 2.23-2.03 (m, 1H), 1.94-1.69 (m, 4 H), 1.44-1.22 (m, 4H), 1.10-0.91 (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 156.7, 149.7, 140.8, 136.5, 129.2, 123.0, 121.7, 121.1, 120.9, 47.1, 45.9, 33.3, 33.2, 26.3, 26.2, 2.6, 1.9; IR (neat): $\tilde{\nu}$ = 3048, 3001, 2976, 2924, 2851, 1651, 1586, 1563, 1469, 1446, 1430, 971, 762 cm^{-1}; MS (EI): *m/z* (%): 239 (26), 238 (61), 224 (26), 210 (36), 196 (29), 182 (25), 170 (18), 157 (33), 144 (46), 130 (100), 117 (53), 106 (30), 93 (77), 79 (33); HRMS (ESI+): *calcd* for ($C_{17}H_{22}N$): 240.17467; found: 240.174765.



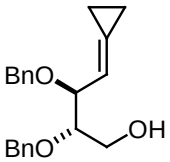
5

Compound 6b. Colorless oil (1.18 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.25 (m, 10H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.71-4.60 (m, 3H), 3.87.3.73 (m, 2H), 3.72-3-61 (m, 2H), 0.93 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.54, 138.52, 128.6 (2C), 128.5 (2C), 128.12 (2C), 128.07 (2C), 127.89, 127.86, 80.4, 79.5, 73.2, 73.0, 62.5, 61.7, 26.0 (3C), 18.4, –5.3 (2C); IR (neat): $\tilde{\nu}$ = 3451, 3089, 3064, 3031, 2953, 2928, 2883, 2857, 1606, 1496, 1471, 1462, 1454, 1255, 1094, 1028, 1006, 837, 777, 735, 698 cm^{-1}; MS (EI): *m/z* (%) 219 (6), 181 (29), 91 (100); HRMS (ESI+): calcd for ($C_{24}H_{36}O_4Si$ + Na): 439.22751; found 439.22725; elemental analysis (%) calcd for $C_{24}H_{36}O_4Si$: C 69.19, H 8.71; found: C 66.51, H 8.25.



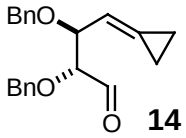
6b

Compound 6c. Dess-Martin periodinane (1.4 g, 3.29 mmol) was added to a solution of alcohol **6b** (1.14 g, 2.74 mmol) in CH_2Cl_2 (15 mL). After stirring for 40 min, the reaction was quenched with sat. aq. $Na_2S_2O_3$ and sat. aq. $NaHCO_3$, the aqueous phase was extracted with *tert*-butyl methyl ether, the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue rapidly passed through a short pad of silica gel. The resulting crude aldehyde was subjected to olefination, using (3-bromopropyl)triphenylphosphonium bromide (1.4 g, 3 mmol) and *t*-BuOK (674 mg, 6 mmol) in THF (20 mL). The crude material was desilylated with TBAF (1.28 mL, 1.28 mmol (1 M in THF) in THF (9 mL). A standard aqueous work up followed by purification via flash chromatography (hexanes/EtOAc, 10/1→7/1) afforded product **6c** as a pale yellow oil (215 mg, 24% over three steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.25 (m, 10H), 5.86 (dquint, *J* = 10.6, 1.9 Hz, 1H), 4.86 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.26 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.81-3-66 (m, 2H), 3.64-3.53 (m, 1H), 2.23-2.14 (m, 1H, -OH), 1.31-1.03 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.64, 138.6, 128.6, 128.5 (2C), 128.4 (2C), 128.0 (2C), 127.88 (2C), 127.85, 127.7, 115.6, 81.5, 80.1, 73.6, 70.5, 62.4, 2.7, 2.5; IR (neat): $\tilde{\nu}$ = 3451, 3087, 3062, 3030, 2989, 2923, 2870, 1605, 1496, 1454, 1089, 1055, 1028, 736, 698; MS (EI): *m/z* (%): 173 (7), 91 (100); HRMS (ESI+): calcd for ($C_{21}H_{24}O_3$ + Na): 347.16177; found: 347.16152; elemental analysis (%) calcd for $C_{21}H_{24}O_3$: C 77.75, H 7.46; found: C 77.63, H 7.35.



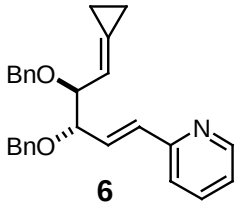
6c

Compound 14. Alcohol **6c** (52 mg, 0.16 mmol) in MeCN (1 mL) was added via canula to a suspension of MS 4Å (100 mg) in MeCN (4 mL). PDC (120 mg, 0.32 mmol) was then introduced in one portion and the suspension was stirred for 4 h at ambient temperature. For work up, all insoluble materials were filtered off through a short pad of Celite, the filtrate was evaporated and the product purified by flash chromatography (hexanes/EtOAc, 4/1) to give aldehyde **14** (42 mg, 81%), which was immediately used in the rearrangement step because of its low stability.



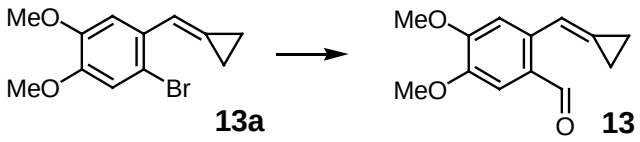
14

Compound 6. Colorless oil (79 mg, 50% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (ddd, *J* = 5.0, 1.9, 0.8 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41-7.23 (m, 10H), 7.14 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.75-6.72 (m, 2H), 5.95-5.87 (m, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.3 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.3 Hz, 1H), 4.27-4.18 (m, 2H), 1.21-0.98 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 149.7, 139.0, 138.7, 136.5, 132.7, 132.1, 128.4 (2C), 128.3 (2C), 128.2, 127.85 (2C), 127.82 (2C), 127.5, 127.4, 122.3, 121.5, 115.9, 81.90, 81.86, 71.3, 70.6, 2.6, 2.3; IR (neat): $\tilde{\nu}$ = 3061, 3030, 2979, 2863, 1653, 1585, 1564, 1496, 1469, 1454, 1431, 1112, 1090, 1067, 1028, 976, 737, 697 cm^{-1}; MS (EI): *m/z* (%): 306 (17), 224 (18), 173 (5), 91 (100); HRMS (ESI+): calcd for ($C_{27}H_{27}NO_2$ + Na): 420.19339; found 420.19324.



6

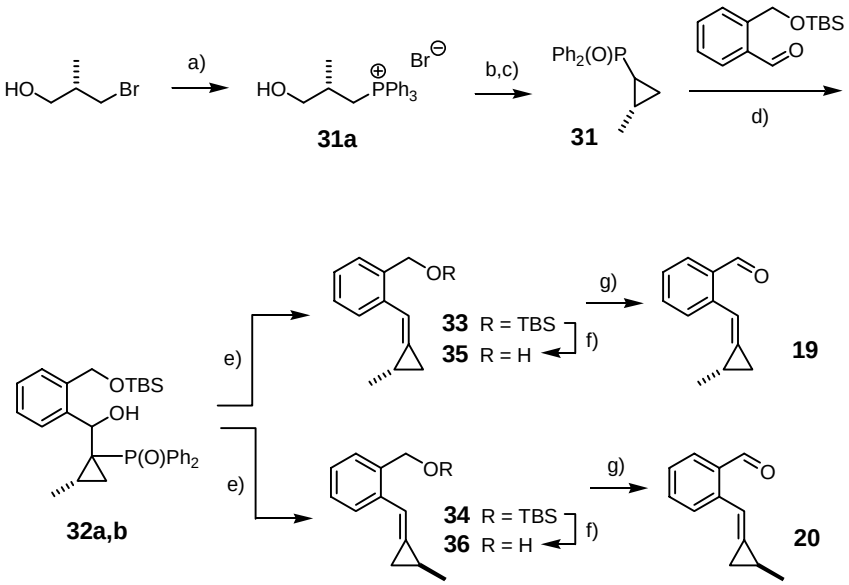
Compound 13. *t*-BuLi (1.7 M in pentane, 0.38 mL, 0.65 mmol) was slowly added via syringe to a solution of aryl bromide **13a**[3] in THF (6 mL) at –78°C. After stirring for 3 h at –78°C, DMF (69 μL, 0.89 mmol) was introduced and stirring continued for 1h. The reaction was quenched with water (5 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 5 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 15/1→4/1) to give aldehyde **13** as a yellow solid (85 mg, 66%). m.p.: 92-94°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.28 (s, 1H), 7.51 (quint., *J* = 2.0 Hz, 1H), 7.33 (s, 1H), 7.27 (s, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 1.45-1-41 (m, 2H), 1.34-1.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.0, 153.6, 148.3, 136.0, 129.0, 125.7, 113.0, 110.2, 109.0, 56.0, 55.9, 4.2, 1.6; IR (neat): $\tilde{\nu}$ = 2971, 2936, 2854, 1665, 1588, 1502, 1463, 1451, 1424, 1364, 1322, 1269, 1259, 1212, 1181, 1104, 1000, 872, 743 cm^{-1}; MS (EI): *m/z* (%): 218 (100), 203 (19), 189 (42), 187 (26), 175 (23), 159 (15), 145 (24), 132 (12), 115 (28), 103 (15), 91 (12), 77 (21); HRMS (EI) calcd for $C_{13}H_{14}O_3$: 218.09429; found: 218.09404.



13a **13**

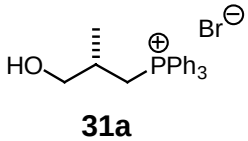
[3] Fürstner, A.; Aïssa, C. *J. Am. Chem. Soc*. **2006**, *128*, 6303-6307.

Preparation of Compounds 19 and 20



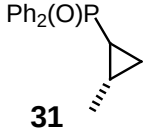
a) PPh_3, toluene, reflux, 72h. b) NaOH, water, reflux, 2h. c) 1) MsCl, DMAP, Et_3N, CH_2Cl_2, 0°C; 2) NaHMDS, THF, -50°C→r.t.; d) (i) *n*-Buli, THF, - 78°C; (ii) 2-(*tert*-butyldimethylsilyloxymethyl)benzaldehyde, –78°C, then separation of diastereomers. e) NaH, DMF/THF, 50°C; f) TBAF, THF. g) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2.

Compound 31a. A solution of commercially available (*S*)-(+)-3-bromo-2-methyl-1-propanol (2 mL, 19.1 mmol) and Ph_3P (5 g, 19.1 mmol) in toluene (20 mL) was stirred under reflux for 72 h. After reaching ambient temperature, the white precipitate was filtered off, carefully rinsed with toluene, and dried in vacuo to give the phosphonium salt **31a** as a white solid (5.1 g, 64%). m.p.: 177-179°C; $[\alpha]_D^{20} = -6.5$ (c = 0.45, CH_2Cl_2); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.96-7.76 (m, 9H), 7.75-7.64 (m, 6H), 4.63 (ddd, *J* = 16.1, 14.8, 2.3 Hz, 1H), 3.59 (dt, *J* = 11.5, 4.2 Hz, 1H), 3.48 (dd, *J* = 11.3, 8.4 Hz, 1H), 2.65 (ddd, *J* = 16.1, 12.1, 9.3 Hz, 1H), 2.30-2.04 (m, 1H), 0.58 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 137.3 (d, *J* = 3 Hz, 3C), 134.1 (d, *J* = 10 Hz, 6C), 130.8 (d, *J* = 13 Hz, 6C), 120.0 (d, *J* = 86 Hz, 3C), 66.7 (d, *J* = 13 Hz), 32.2 (d, *J* = 4 Hz), 26.6 (d, *J* = 51 Hz), 17.8 (d, *J* = 2 Hz); IR (neat): $\tilde{\nu}$ = 3313 (br), 2926, 2862, 1586, 1485, 1435, 1109, 161, 1039, 996, 812, 750, 717, 691 cm^{-1}; MS (EI): *m/z* (%): 262 (100), 257 (82), 201 (35), 183 (60), 108 (25); HRMS (ESI+) calcd for ($C_{22}H_{24}OP$ + Na): 335.15593; found: 335.15619.



31a

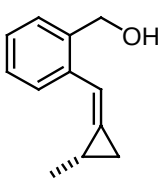
Compound 31. aq. NaOH (20% *w/w*, 110 mL) was added to a solution of phosphonium bromide **31a** (5.1 g, 12.22 mmol) in water (27 mL) and the resulting mixture was stirred under reflux for 2 h. For work up, the mixture was allowed to cool before it was extracted with CH_2Cl_2 (3 x 40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated to give a colorless oil which was dissolved in CH_2Cl_2 (50 mL). DMAP (149 mg, 1.22 mmol) and Et_3N (1.87 mL, 13.42 mmol) were added before mesyl chloride (0.94 mL, 12.2 mmol) was slowly introduced at 0°C. The resulting mixture was stirred for 1 h before the reaction was quenched with aq. sat. NH_4Cl. A standard extractive work up gave the crude



31

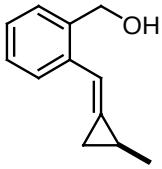
mesylate which was dissolved in THF (17 mL) and added via syringe pump to a cold solution of NaHMDS (2.47 g, 13.42 mmol) in THF (600 mL) over a period of 2.5 h at such as rate as to maintain the internal temperature between –50°C and –35°C. Once the addition was complete, the mixture was allowed to stir for an additional 2 h at 0-5°C. The reaction was quenched with aq. sat. NH_4Cl (20 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 30 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 1/10) to give product **31** as a white solid (1.43 g, 46% overall). m.p. 138-140°C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.79-7.65 (m, 4H), 7.59-7.41 (m, 6H), 1.51-1.32 (m, 1H), 1.26-0.97 (m, 2H), 1.21 (d, *J* = 5.8 Hz, 3H), 0.79-0.69 (m, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 136.3 (d, *J* = 115 Hz), 134.7 (d, *J* = 100 Hz), 131.85 (d, *J* = 2 Hz), 131.85 (d, *J* = 2 Hz), 131.3 (d, *J* = 9 Hz, 2C), 131.2 (d, *J* = 9 Hz, 2C), 128.84 (d, *J* = 11 Hz, 2C), 128.80 (d, *J* = 12 Hz, 2C), 18.5 (d, *J* = 3 Hz), 15.8 (d, *J* = 105 Hz), 12.0 (d, *J* = 4 Hz), 11.2 (d, *J* = 5 Hz); IR (neat): $\tilde{\nu}$ = 3052, 3000, 2959, 2925, 1486, 1438, 1178, 1122, 1110, 992, 919, 858, 718, 695 cm^{-1}; MS (EI): *m/z* (%): 256 (51), 255 (42), 212 (21), 202 (32), 201 (100), 77 (33); HRMS (EI) calcd for $C_{16}H_{17}OP$: 256.10171; found: 256.10172.

Compound 35. *n*-BuLi (1.6 M in hexanes, 0.63 mL, 1 mmol) was added dropwise to a solution of compound **31** (256 mg, 1 mmol) in THF (4 mL) at –78°C. After stirring at this temperature for 20 min, a solution of 2-(*tert*-butyldimethylsilyl-oxymethyl)benzaldehyde (250 mg, 1 mmol) in THF (1 mL) was added and stirring was continued for 30 min at that temperature. For work up, the reaction was diluted with *tert*-butyl methyl ether (10 mL) and quenched with water (10 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL), the combined organic layers were dried over Na_2SO_4, filtered and evaporated, and the residue purified by flash chromatography to give the two diastereomers of adduct **32** in pure form.



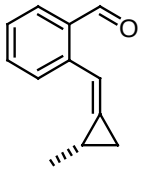
NaH (40 mg, 1.67 mmol) was added to a solution of the less polar fraction of **32** (268 mg, 0.53 mmol) in DMF (3.75 mL) and THF (1 mL) and the resulting mixture was stirred at 50°C for 1 h. For work up, the mixture was cooled to 0°C, the reaction was carefully quenched with water (5 mL), the organic phase was extracted with Et_2O (3 x 5 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue purified by flash chromatography (pentanes/Et_2O, 10/1→4/1) to give a first fraction containing product **33** and a second fraction of pure **35**. The fraction consisting of silyl ether **33** (44 mg, 0.15 mmol) was dissolved with THF (0.75 mL) and treated with TBAF (1 M in THF, 0.15 mL) for 30 min before it was diluted with Et_2O (5 mL) and washed with sat. aq. NH_4Cl and brine (5 mL each). The organic phase was dried over Na_2SO_4, filtered and evaporated, and the residue purified by flash chromatography (pentanes/Et_2O, 10/1→4/1) to give a second crop of product **35** which was obtained as a white solid (41 mg, 44%). m.p. 47-50°C; ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.67 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.34 (ddt, *J* = 7.5, 0.8, 0.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H), 7.02-6.99 (m, 1H), 4.81-4.76 (m, 2H), 1.81-1.75 (m, 1H), 1.76-1.73 (m, 1H, -OH), 1.37 (td, *J* = 8.9, 1.8 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 3H), 0.84 (ddd, *J* = 8.7, 5.1, 1.9 Hz, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 137.6, 136.5, 133.8, 128.8, 128.3, 127.0, 126.7, 115.1, 63.7, 17.4, 11.8, 9.2; IR (neat): $\tilde{\nu}$ = 3238, 3070, 3026, 2993, 2950, 2923, 2893, 2863, 1488, 1449, 1225, 1188, 993, 939, 743 cm^{-1}; MS (EI): *m/z* (%): 159 (10), 143 (100), 128 (60), 115 (31), 91 (21), 77 (14); HRMS (EI) calcd for ($C_{12}H_{14}O$ + H): 175.11229; found: 172.11207.

Compound 36. Obtained of the more polar fraction of **32** as described above. White solid



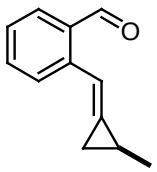
(70 mg, 55%). m.p. 50-52°C; $[\alpha]_D^{20}$ = –14 (c = 0.25, CH_2Cl_2) ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.82 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.35 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.32-7.17 (m, 2H), 7.11-7.05 (m, 1H), 4.78 (s, 2H), 1.86-1.58 (m, 1H, –OH), 1.66-1.48 (m, 2H), 1.21 (d, *J* = 5.7 Hz, 3H), 1.08-1.00 (m, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 138.2, 137.2, 134.3, 129.1, 128.5, 127.5, 126.9, 114.3, 65.0, 18.4, 12.4, 9.0; IR (neat): $\tilde{\nu}$ = 3235, 3071, 3025, 2993, 2950, 2923, 2893, 2863, 1488, 1448, 1225, 1188, 993, 939, 742 cm^{-1}; MS (EI): *m/z* (%): 159 (9), 143 (100), 128 (53), 115 (23), 91 (14), 77 (9); HRMS (EI) calcd for ($C_{12}H_{14}O$ + H): 175.11229; found: 172.11218.

Compound 19. Colorless oil (31 mg, 78 %). $[\alpha]_D^{20}$ = 135 (c = 0.9, CH_2Cl_2); ^{1}H NMR (400



MHz, CD_2Cl_2): δ = 10.34 (s, 1H), 7.80 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.66-7-63 (m, 1H), 7.56 (tdd, *J* = 7.4, 1.5, 0.5 Hz, 1H), 7.38 (td, *J* = 7.5, 0.9 Hz, 1H), 1.84-1.74 (m, 1H), 1.43 (td, *J* = 9.3, 1.8 Hz, 1H), 1.23 (d, *J* = 6.2 Hz, 3H), 0.90 (ddd, *J* = 8.9, 5.4, 2.0 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 192.8, 140.2, 138.0, 133.8, 132.6, 131.7, 128.0, 127.1, 114.4, 17.2, 12.0, 9.6; IR (neat): $\tilde{\nu}$ = 2957, 2926, 2864, 2732, 1688, 1596, 1566, 1483, 1450, 1406, 1377, 1209, 1184, 1006, 964, 869, 815, 748 cm^{-1}; MS (EI): *m/z* (%): 172 (28), 157 (55), 143 (92), 128 (100), 118 (32), 115 (48), 102 (15), 89 (17), 77 (16); HRMS (EI) calcd for $C_{12}H_{12}O$: 172.08881; found: 172.08867.

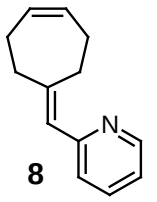
Compound 20. Pale yellow oil (26 mg, 48%). $[\alpha]_D^{20}$ = –3.5 (c = 1.25, CH_2Cl_2); ^{1}H NMR (300



MHz, CD_2Cl_2): δ = 10.33 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.72-7.67 (m, 1H), 7.55 (td, *J* = 7.6, 1.1 Hz, 1H), (td, *J* = 7.2, 1.1 Hz, 1H), 1.68-1.55 (m, 2H), (d, *J* = 6.1 Hz, 3H), 1.11-0.99 (m, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 192.9, 140.6, 138.1, 133.7, 132.8, 131.5, 127.7, 127.2, 113.4, 17.9, 12.2, 9.2; IR (neat): $\tilde{\nu}$ = 2959, 2925, 2865, 2736, 1689, 1595, 1566, 1483, 1450, 1410, 1377, 1209, 1185, 1006, 964, 869, 812, 754 cm^{-1}; MS (EI): *m/z* (%): 172 (21), 157 (50), 143 (87), 128 (100), 118 (32), 115 (47), 102 (13), 89 (15), 77 (12); HRMS (EI) calcd for $C_{12}H_{12}O$: 172.08881; found: 172.08894.

C-H-Activation / Cycloisomerization Tandem Reactions

Representative procedure for the pyridine directed, rhodium catalyzed C-H activation/cycloisomerization tandem. Preparation of compound 8. A Teflon-screw



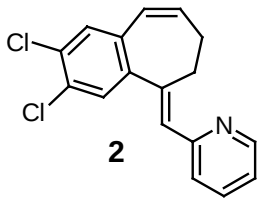
8

Schlenk tube equipped with a magnetic stir bar was charged with compound **4** (21 mg, 0.1 mmol), $RhCl(PPh_3)_3$ (4.6 mg, 0.005 mmol), $AgSbF_6$ (2.6 mg, 0.0075 mmol) and THF (2 mL). The flask was sealed and immersed into a pre-heated oil bath (120°C bath temperature). After stirring for 6 h at that temperature, the mixture was allowed to cool before it was filtered through a short pad of silica which was carefully rinsed with Et_2O. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/Et_2O, 20/1→10/1) to give product **8** as a colorless oil (13 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58-8.51 (m, 1H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.02 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 6.34 (s, 1H), 5.82-5.67 (m, 2H), 2.88-2.79 (m, 2H), 2.55-2.47 (m, 2H), 2.34-2.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.3, 150.0, 149.1, 135.7, 130.7, 130.5, 124.2, 123.8, 120.4, 38.2, 31.2, 29.4, 27.0; IR (neat): $\tilde{\nu}$ = 3012, 2925, 2842, 1642, 1585, 1559, 1471, 1427, 1148, 774, 742, 712 cm^{-1}; MS (EI): *m/z* (%): 185 (89), 184 (100), 170 (48), 157 (82), 144 (23), 130 (68), 118 (65), 93 (50), 79 (43). HRMS (EI): calcd

for $C_{13}H_{15}N$: 185.12045; found: 185.12029; elemental analysis (%) calcd for $C_{13}H_{15}N$: C 84.28, H 8.16, N 7.56; found: C 84.86, H 8.25, N 7.45.

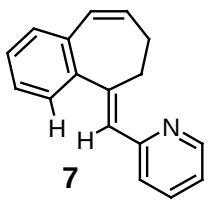
The following compounds were prepared analogously. Their analytical and spectral data are compiled below:

Compound 2. White solid (20 mg, 77%). m.p.: 78-79°C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.62 (ddd, *J* = 5.0, 1.8, 0.7 Hz, 1H), 7.68 (td, *J* = 7.6, 1.9 Hz, 1H), 7.49 (s, 1H), 7.30 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 6.58 (s, 1H), 6.28 (dt, *J* = 12.0, 2.0 Hz, 1H), 6.03 (dt, *J* = 12.0, 4.5 Hz, 1H), 3.21 (t, *J* = 6.2 Hz, 2H), 2.76-2.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3, 149.4, 146.3, 143.6, 136.1, 134.7, 134.5, 132.5, 130.8, 130.1, 128.8, 127.3, 127.2, 124.7, 121.3, 31.7, 28.7; IR (neat): $\tilde{\nu}$ = 3015, 2959, 2920, 2889, 2826, 1631, 1584, 1560, 1471, 1424, 1145, 888, 767, 741 cm^{-1}; MS (EI): *m/z* (%): 304 (19), 303 (59), 302 (75), 301 (94), 300 (100), 290 (10), 289 (12), 288 (61), 287 (28), 286 (94). 251 (38), 209 (20), 115 (23); HRMS (EI) calcd for $C_{17}H_{13}Cl_2N$: 301.04250 found: 301.04251.



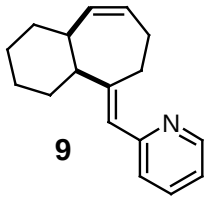
2

Compound 7. Colorless oil (19 mg, 68%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.61 (ddd, *J* = 4.8, 1.7, 0.7 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.26-7.18 (m, 3H), 7.13 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H), 6.59 (s, 1H), 6.38 (dt, *J* = 12.1, 2.1 Hz, 1H), 5.95 (dt, *J* = 12.1, 4.3 Hz, 1H), 3.24 (t, *J* = 6.2 Hz, 2H), 2.76-2.69 (m, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 157.2, 149.5, 149.1, 144.3, 136.5, 134.7, 133.0, 131.7, 129.6, 127.7, 127.5, 127.2, 126.4, 125.0, 121.4, 32.1, 29.4; IR (neat): $\tilde{\nu}$ = 3057, 3011, 2962, 2919, 2888, 2852, 2825, 1631, 1585, 1558, 1483, 1471, 1439, 1426, 775 cm^{-1}; MS (EI): *m/z* (%): 233 (79), 232 (86), 218 (100); HRMS (EI): calcd for $C_{17}H_{15}N$: 233.12045 found: 233.12025 The deuterated compound **7-D** was obtained analogously. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (dd, *J* = 4.9 Hz, 1H), 7.70 (td, *J* = 7.7, 1.9 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.34-7.24 (m, 4H), 7.17 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H), 6.68 (s, 1H), 6.44 (s, 1H), 6.00 (dt, *J* = 12.1, 4.4 Hz, 0.07 H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.79-2.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 149.2, 148.6, 143.8, 135.9, 134.2, 132.1 (t, *J* = 24 Hz), 131.3, 129.3, 127.3, 127.2, 126.8, 126.3, 124.4, 120.9, 31.6, 28.9; MS (EI): *m/z* (%): 234 (82), 233 (92), 219 (100); HRMS (EI): calcd for $C_{17}H_{14}DN$: 234.12672; found: 234.12692.



7

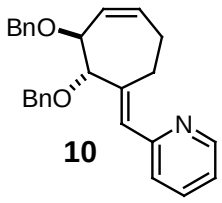
Compound 9. Colorless oil (18 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.52 (ddd, *J* = 5.0, 1.7, 0.8 Hz, 1H), 7.54 (td, *J* = 7.7, 1.9 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.99 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H), 6.30 (s, 1H), 5.48-5.46 (m, 1H), 5.29-5.21 (m, 1H), 3.14 (ddd, *J* = 12.9, 6.0, 3.3 Hz, 1H), 2.76 (ddd, *J* = 12.9, 11.0, 6.3 Hz, 1H), 2.58-2.19 (m, 4H), 1.87-1.66 (m, 4H), 1.53-1.08 (m, 4H); ^{13}C NMR (75 Hz, $CDCl_3$): δ = 157.4, 153.6, 149.0, 135.7, 134.3, 128.0, 124.8, 123.5, 120.3, 53.4, 40.8, 34.4, 33.6, 29.1, 27.2, 26.4, 26.3; IR (neat): $\tilde{\nu}$ = 3073, 3003, 2923, 2850, 1641, 1585, 1559, 1472, 1453, 1427, 740, 659 cm^{-1}; MS (EI): *m/z* (%): 239 (89), 224 (19), 210 (21), 196 (14), 182 (15), 168 (11), 157 (100), 144 (19), 130 (25), 117 (17), 106 (10), 93 (31); HRMS (ESI+) calcd for ($C_{17}H_{21}N$ + H): 240.17467; found: 240.17462 elemental analysis calcd (%) for $C_{17}H_{21}N$: C 85.30, H 8.84, N 5.85; found: C 85.26, H 8.74, N 5.72.



9

Compound 10. White solid (11 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64-8.60 (m, 1H), 7.64 (td, *J* = 7.7, 1.9 Hz, 1H), 7.45-7.25 (m, 10H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.11 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 6.63 (s, 1H), 5.75 (dtd, *J* = 11.9, 5.3, 1.5 Hz, 1H), 5.68-5.60 (m, 1H), 4.82-4.67 (m, 3H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.38-4.31 (m, 1H), 4.29 (d, *J* = 7.4 Hz, 1H),

3.03-2.90 (m, 2H), 2.60-2.45 (m, 1H), 2.44-2.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3, 149.2, 143.5, 138.9, 138.6, 136.0, 130.9, 129.2, 128.26 (2C), 128.22 (2C), 127.75 (3C), 127.67 (2C), 127.37, 127.33, 124.4, 121.1, 86.9, 85.5, 72.2, 70.6, 27.2, 26.7; IR (neat): $\tilde{\nu}$ = 3070, 3011, 2948, 2876, 2850, 1649, 1584, 1560, 1496, 1471, 1452, 1431, 1384, 1339, 1306, 1281, 1259, 1238, 1205, 1156, 1113, 1099, 1088, 1065, 1029, 988, 897, 742, 729, 717 cm^{-1}; MS (EI): *m/z* (%): 306 (56), 91 (100); HRMS (ESI+) calcd for ($C_{27}H_{27}NO_2$ + Na): 420.19340; found: 420.19341; elemental analysis calcd (%) for $C_{27}H_{27}NO_2$: C 81.58, H 6.85, N 3.52; found: C 81.42, H 6.86, N 3.41.

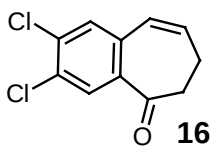


10

Representative procedure for the rhodium catalyzed C-H activation/cycloisomerization tandem of the aldehyde substrate. Preparation of compound 15. A Teflon-screw Schlenk flask equipped with a small stir bar was charged with compound **11** (18 mg, 0.11 mmol), $[Rh(coe)_2Cl]_2$ (4 mg, 0.005 mmol), (p-$MeOC_6H_4)_3P$ (7 mg, 0.02 mmol) and 1,2-dichloroethane (2 mL) under Ar. Ethylene was bubbled through the solution via a needle for 60 sec before the flask was sealed and immersed into a pre-heated oil bath (120°C bath temperature). After stirring for 2.5 h at that temperature, the mixture was allowed to cool before it was diluted with Et_2O (5 mL). Filtration through a short pad of silica, evaporation of the filtrate followed by flash chromatographic purification of the residue (hexanes/EtOAc, 20/1) afforded ketone **15** as a colorless oil (14 mg, 76%). Its analytical and spectroscopic data are in full agreement with those reported in the literature.[4]

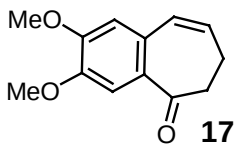
Compounds **16**-**18** were obtained analogously. Their analytical and spectroscopic data are compiled below:

Compound 16. White solid (37 mg, 82%). m.p.: 78-81°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.30 (s, 1H), 6.35 (d, J = 11.7 Hz, 1H), 6.25 (dt, J = 11.7, 5.2 Hz, 1H), 2.95-2-85 (m, 2H), 2.54-2.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 136.6, 135.7, 135.5, 135.2, 133.1, 131.5, 131.4, 129.4, 41.6, 23.9; IR (neat): $\tilde{\nu}$ = 2967, 2917, 1672, 1647, 1575, 1462, 1424, 1358, 1346, 1273, 1235, 1196, 1177, 1141, 1036, 928, 901, 879, 762, 672 cm^{-1}; MS (EI): *m/z* (%): 228 (64), 226 (100), 200 (23), 198 (33), 193 (16), 191 (50), 165 (18), 163 (52), 128 (50); HRMS (EI) calcd for $C_{11}H_8Cl_2O$: 225.99522; found: 225.99507; elemental analysis calcd for $C_{11}H_8Cl_2O$: C 58.18, H 3.55; found: C 58.08, H 3.64.



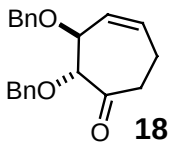
16

Compound 17. Pale yellow solid (23 mg, 72%). m.p.: 80-82°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 6.63 (s, 1H), 6.37 (d, J = 11.8 Hz, 1H), 6.20-6.10 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.91-2-85 (m, 2H), 2.45-2.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.2, 152.3, 147.7, 132.4, 131.4, 131.2, 129.1, 113.7, 112.2, 56.00, 55.97, 42.1, 23.2; IR (neat): $\tilde{\nu}$ = 3084, 2999, 2957, 2840, 1650, 1591, 1514, 1461, 1440, 1364, 1247, 1213, 1189, 1129, 1069, 1031, 875, 851, 783 cm^{-1}; MS (EI): *m/z* (%): 218 (100), 203 (11), 190 (24), 175 (21), 159 (23), 147 (11), 132 (6), 115 (16), 103 (8), 91 (8), 77 (8); HRMS (EI) calcd for $C_{13}H_{14}O_3$: 218.09430; found: 218.09407.



17

Compound 18. Pale yellow oil (28 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.27 (m, 10H), 5.97 (dt, J = 11.7, 5.8 Hz, 1H), 5.77 (ddt, J = 11.6, 4.7, 1.3 Hz, 1H), 4.71 (d, J = 11. 7 Hz, 1H), 4.70 (d, J = 11.7 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.36 (d, J = 7.3 Hz, 1H), 4.25 (ddd, J = 7.1, 4.7, 0.8 Hz, 1H), 2.72 (ddd, J = 14.3, 9.6, 4.7 Hz, 1H), 2.57-2.30 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.5, 138.3, 137.6, 132.1, 129.7, 128.6 (2C), 128.5 (2C), 128.2 (2C), 128.1, 127.9 (2C), 127.8, 86.4, 76.3, 72.8, 72.4, 40.0, 23.8; IR



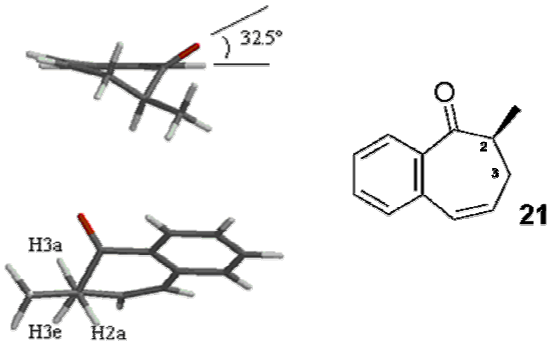
18

[4] Crich, D.; Gastaldi, S. *New. J. Chem*. **2000**, *24*, 249-250.

(neat): $\tilde{\nu}$ = 3030, 2866, 1716, 1496, 1454, 1205, 1087, 1067, 1027, 732, 695 cm^{-1}; MS (EI): *m/z* (%): 231 (11), 91 (100); HRMS (ESI+) calcd for ($C_{21}H_{22}O_3$ + Na): 345.14612; found: 345.14635; elemental analysis calcd for $C_{21}H_{22}O_3$: C 78.23, H 6.88; found: C 78.21, H 7.03.

Ketone 21. Colorless oil (21 mg, 53%).$[\alpha]_D^{20}$ = 167 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.23 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 (td, *J* = 7.6, 1.5 Hz, 1H), 7.32-7.20 (m, 2H); 6.45 (dd, *J* = 11.5, 2.0 Hz, 1H), 6.06 (ddd, *J* = 11.8, 6.6, 4.2 Hz, 1H), 3.07 (ddq, *J* = 11.1, 6.7, 3.9 Hz, 1H), 2.49 (dddd, *J* = 18.3, 6.4, 3.8, 1.0 Hz, 1H), 2.35 (dddd, *J* = 18.2, 11.1, 4.1, 2.3 Hz, 1H); 1.20 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 205.0, 137.6, 135.4, 132.2, 131.8, 130.8, 129.5, 127.4, 44.5, 33.6, 16.3; IR (neat): $\tilde{\nu}$ = 3024, 2971, 2932, 2825, 1677, 1593, 1481, 1445, 1424, 1376, 1291, 1278, 1242, 1207, 1004, 964, 781 cm^{-1}; MS (EI): *m/z* (%): 172 (100), 157 (33), 144 (21), 130 (92), 115 (35), 102 (22); HRMS (EI) calcd for $C_{12}H_{12}O$: 172.08882; found: 172.08863.

The UV spectrum showed 3 absorption bands: 316 (n→π*), 269, 234 nm. A positive circular dichroism was measured for the n→π* transition. The sign of the circular dichroism is in accordance with the absolute configuration indicated for **21**. As reported in the literature, the sign of the dihedral angle between the planes defined by the carbonyl group and the benzene ring (+32.5°) and the sign of the circular dichroism for the n→π* transition are identical.[5] The shown conformation is consistent with the observed coupling constants: $^3J_{H2a,H3a}$ = 11.1 Hz and $^3J_{H2a,H3e}$ = 3.9 Hz, which indicate that the methyl group is in equatorial position. This conformation was also calculated to be the most stable one (Spartan 02, 2001, MMFF level).



Ketone 22. Colorless oil (4 mg, 70%). $[\alpha]_D^{20}$ = –313 (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.40 (dd, *J* = 11.8, 1.8 Hz, 1H), 6.03 (dd, *J* = 11.9, 4.4 Hz, 1H), 2.88 (d, *J* = 6.4 Hz, 2H), 2.82-2.71 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 201.3, 140.0, 137.2, 136.1, 132.7, 132.1, 129.41, 129.38, 127.4, 49.6, 30.9, 20.6; IR (neat): $\tilde{\nu}$ = 3020, 296, 2929, 2874, 1672, 1595, 1482, 1456, 1443, 1428, 1375, 1357, 1312, 1279, 1123, 1106, 782, 751 cm^{-1}; MS (EI): *m/z* (%): 172 (100), 157 (54), 143 (28), 129 (73), 115 (26), 102 (16), 77 (17); HRMS (EI) calcd for $C_{12}H_{12}O$: 172.08881; found: 172.08904.

[5] Barry, J.; Kagan, H.-B.; Snatzke, G. *Tetrahedron* **1971**, *27*, 4737-4748.

24.05.2007
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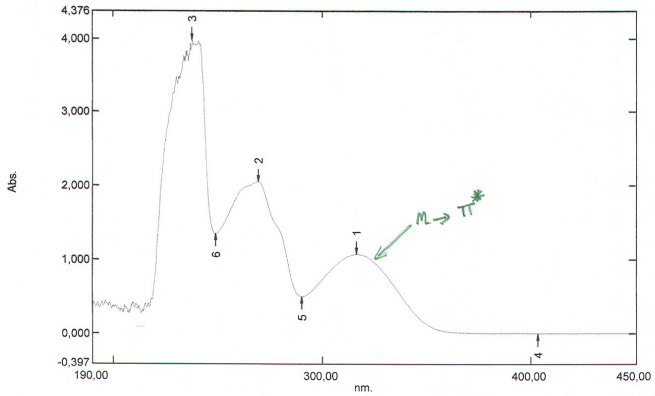

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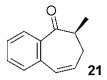

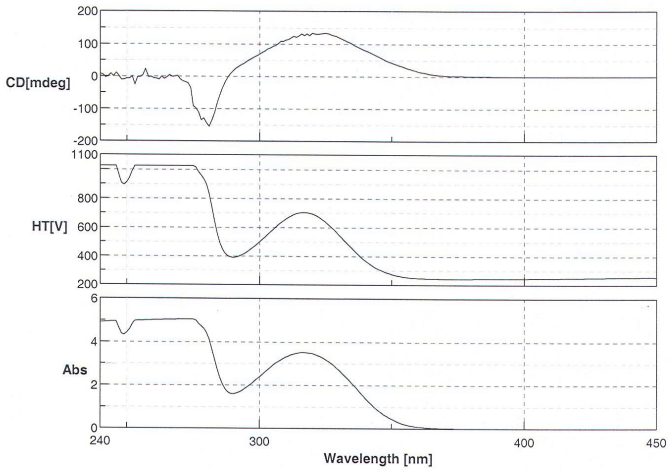

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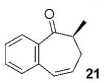

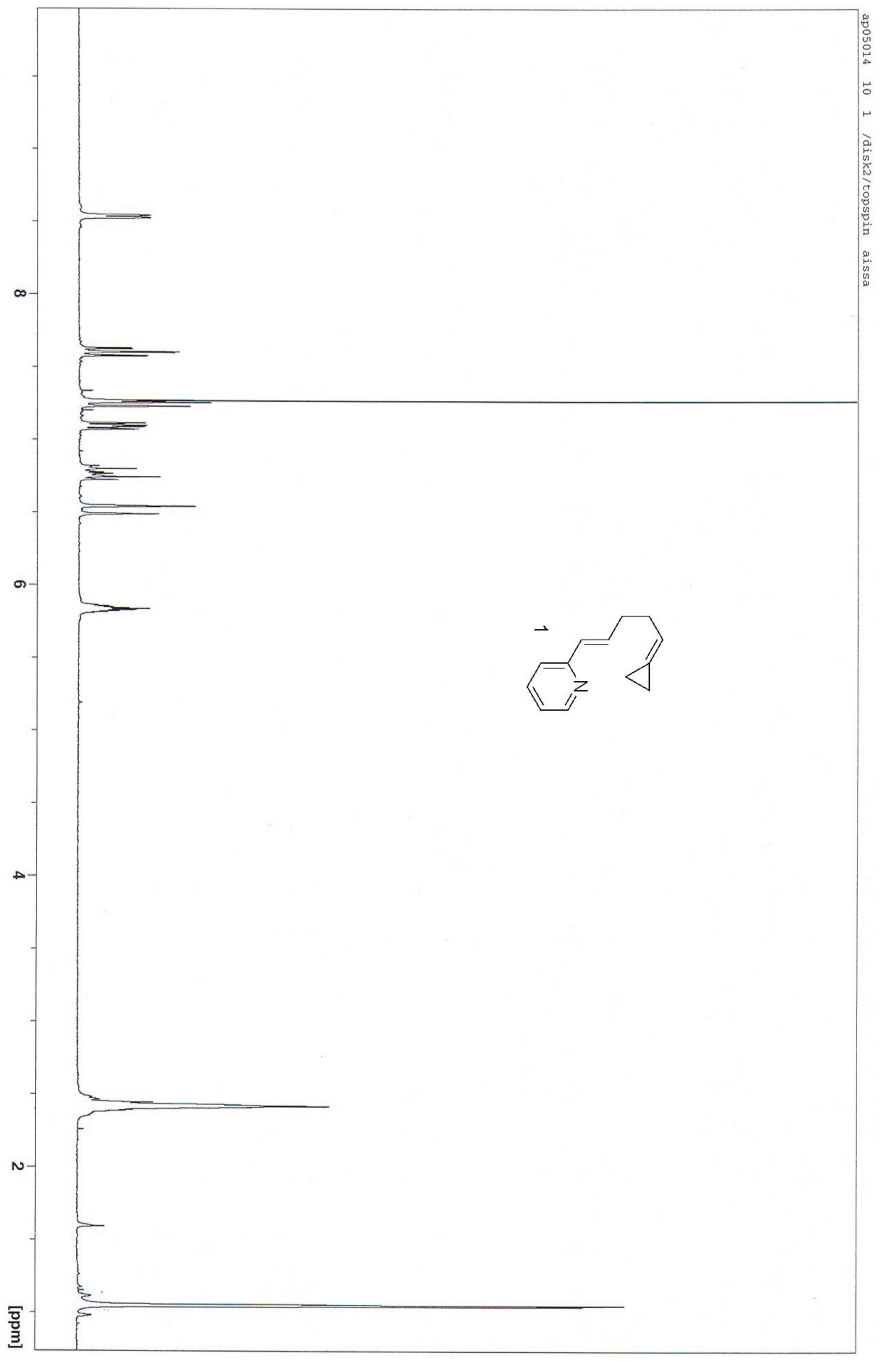
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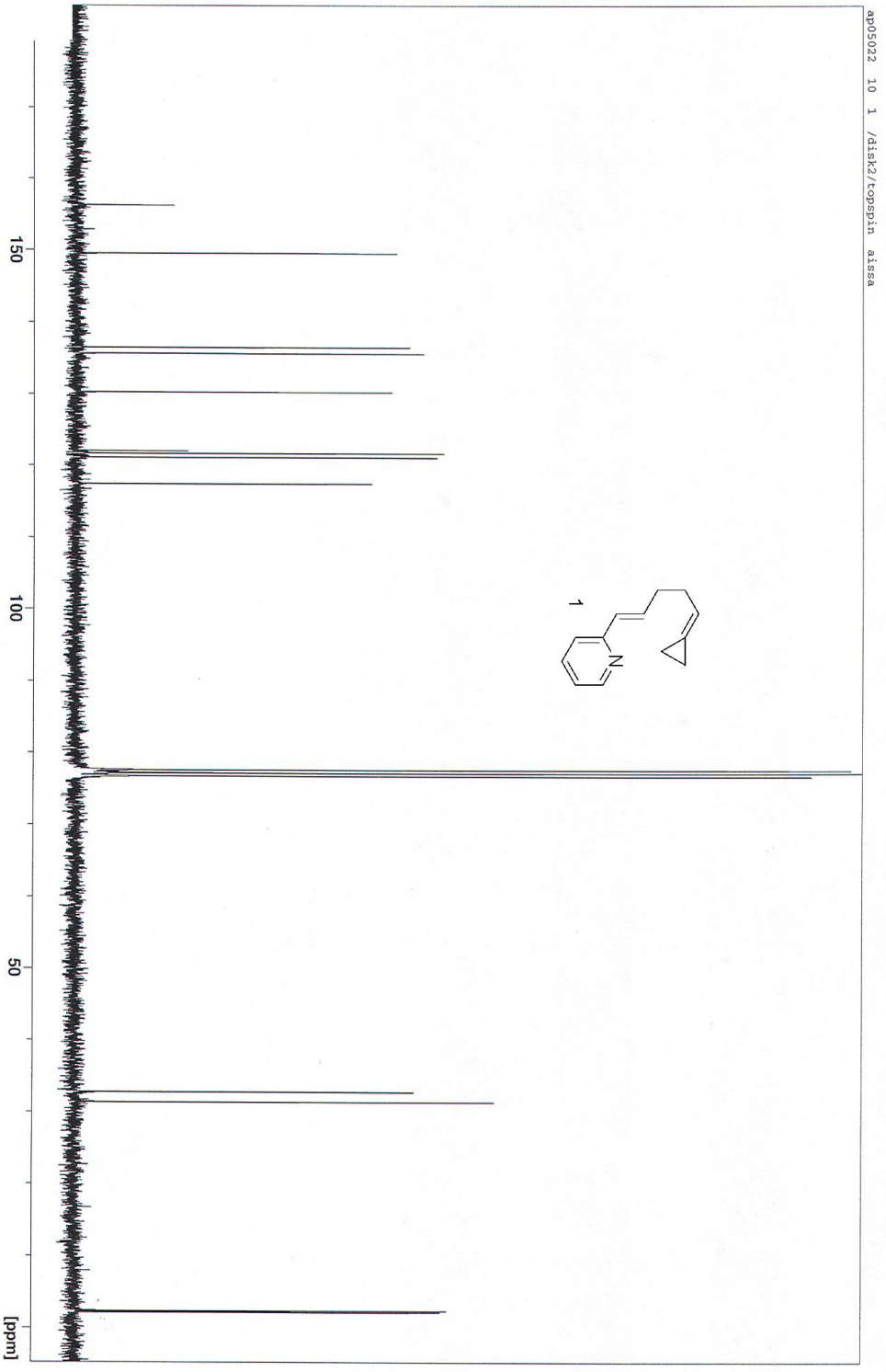
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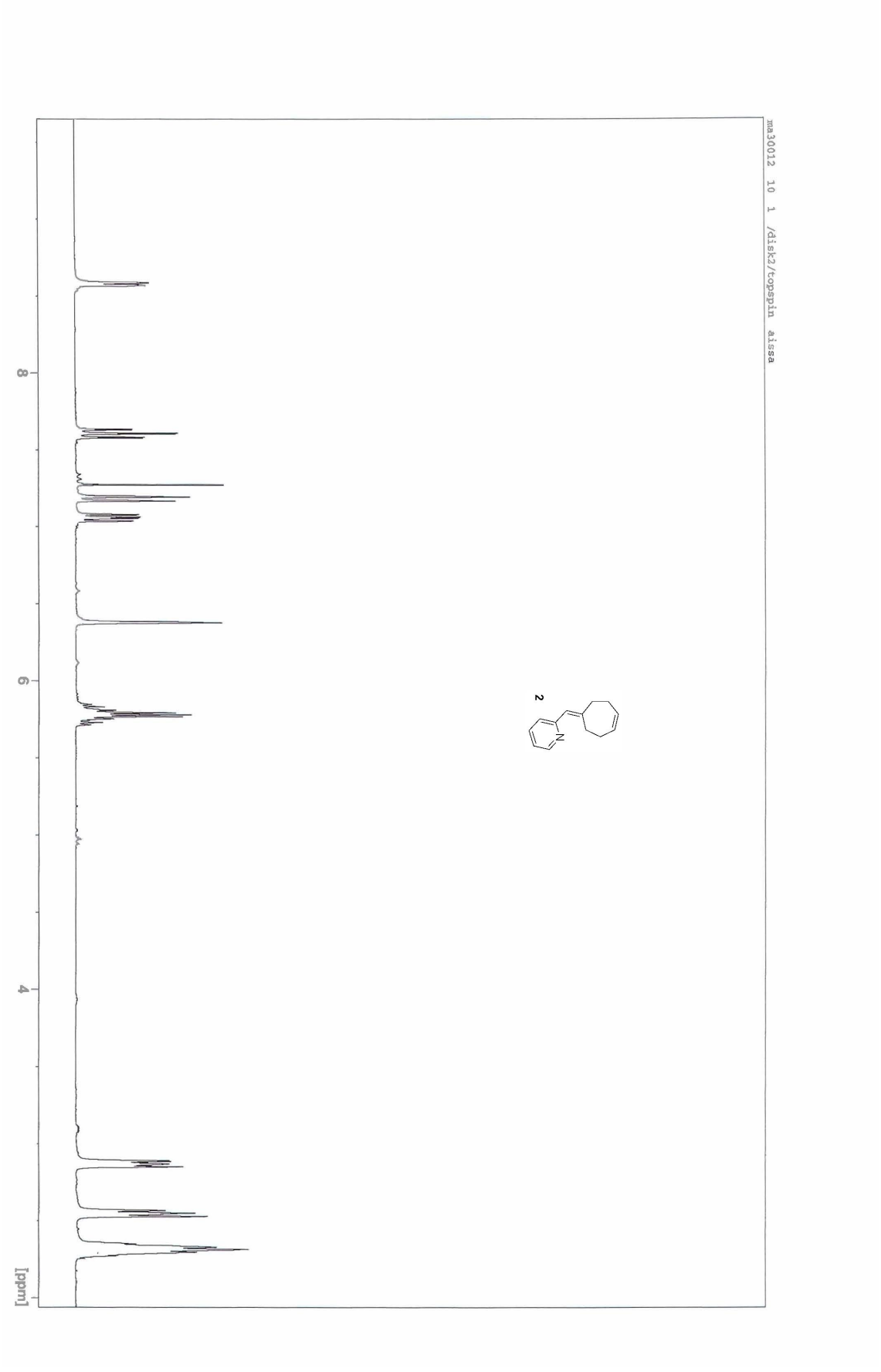
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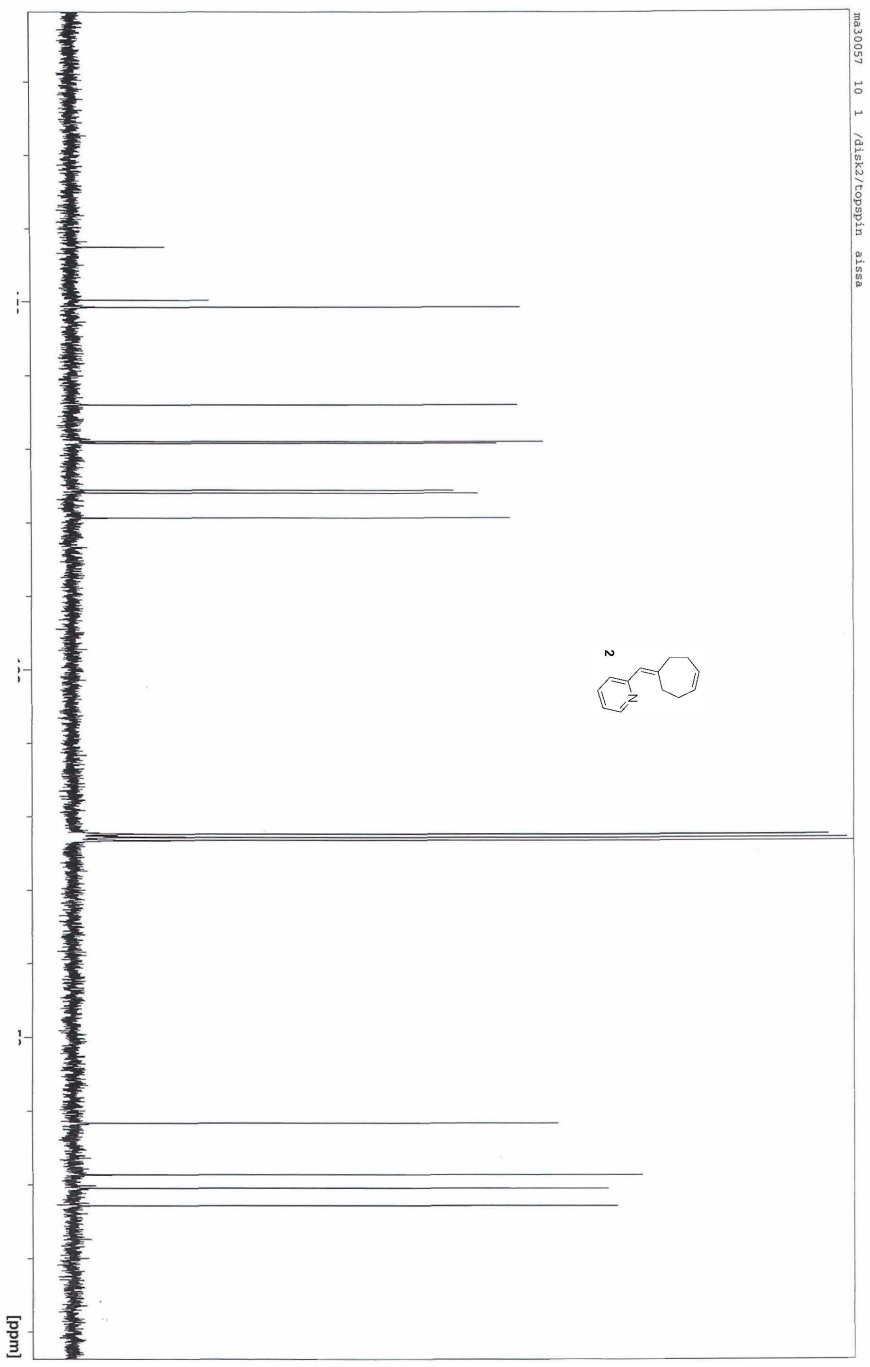
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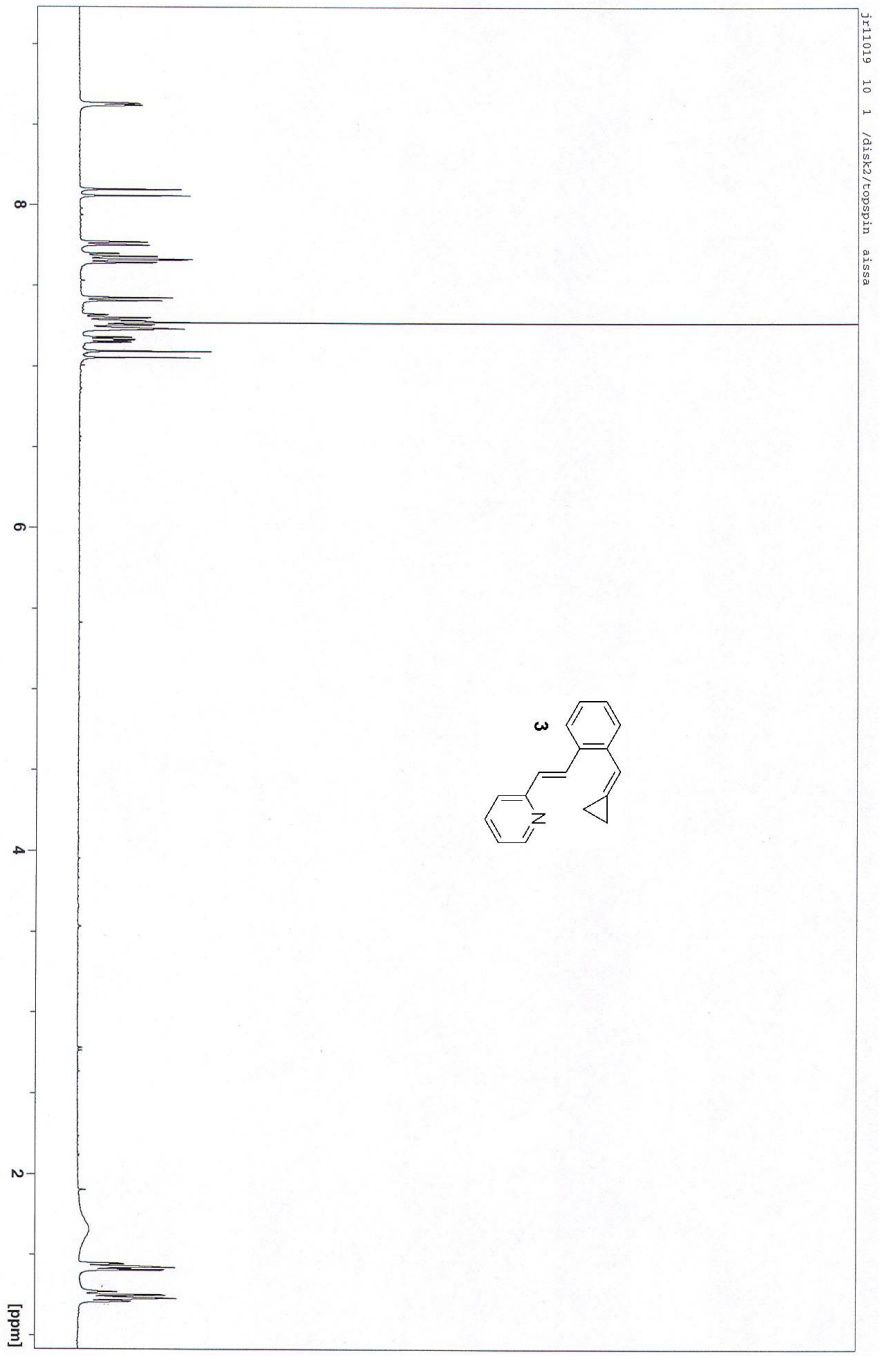
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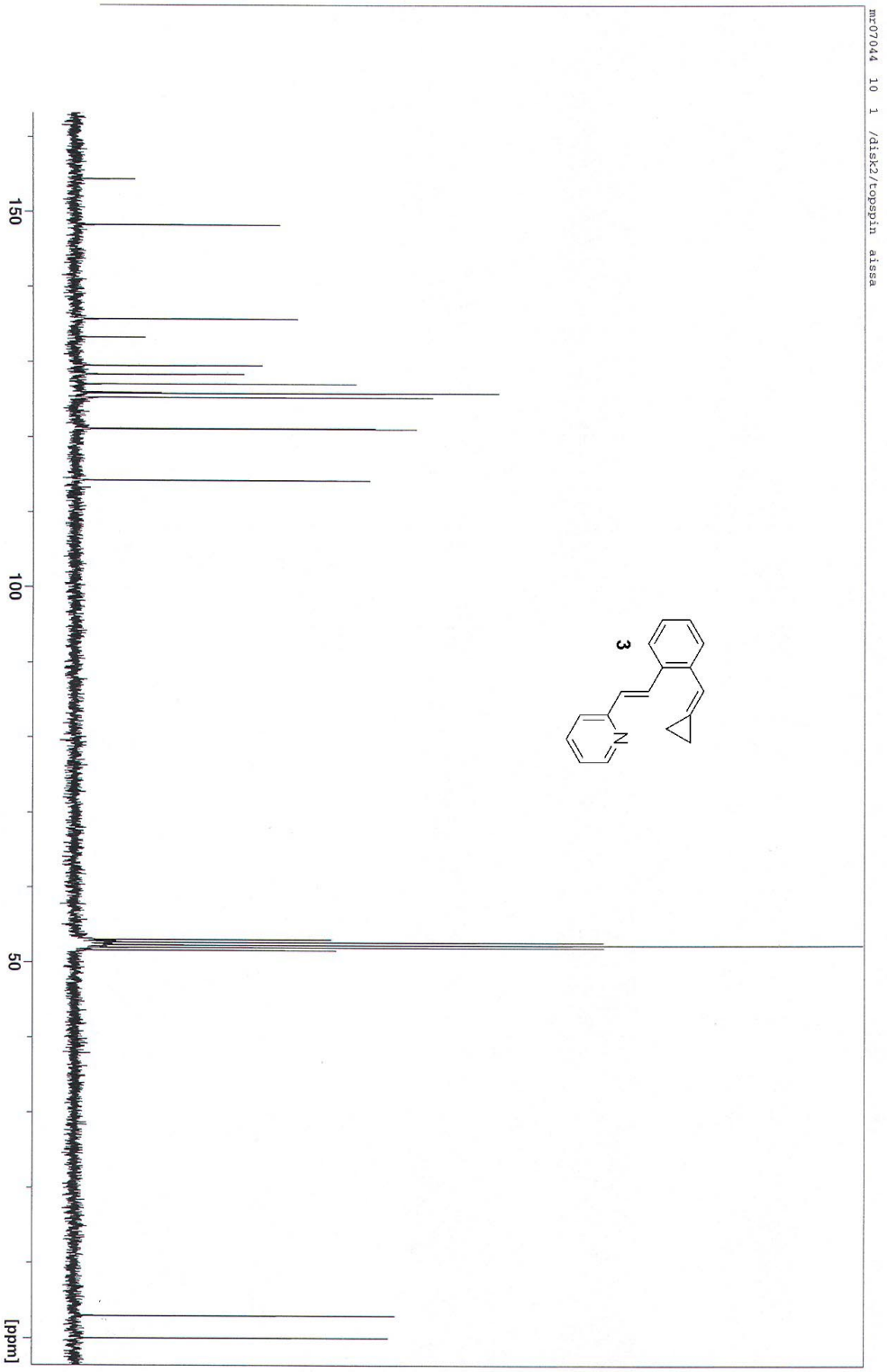
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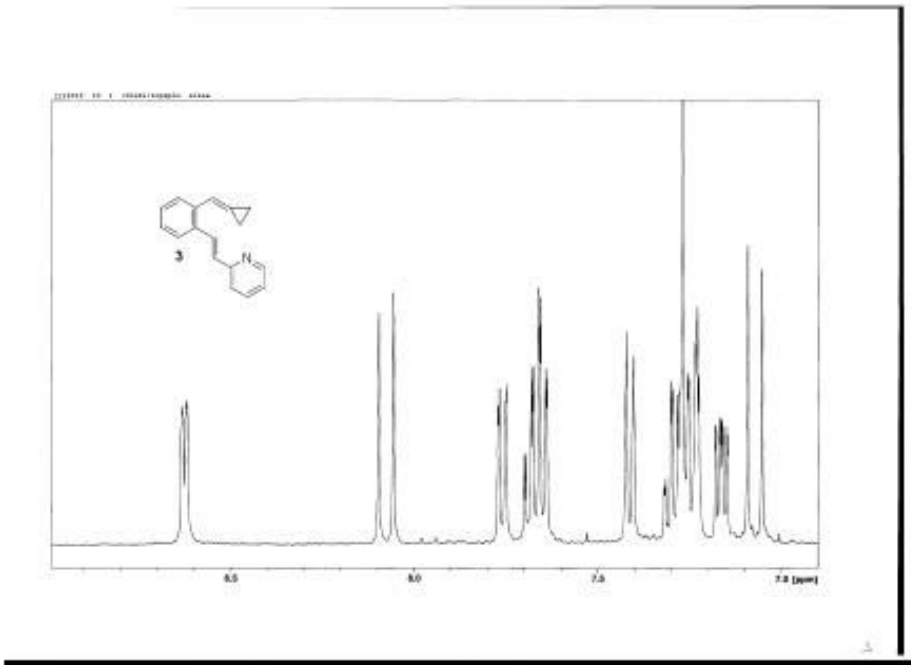
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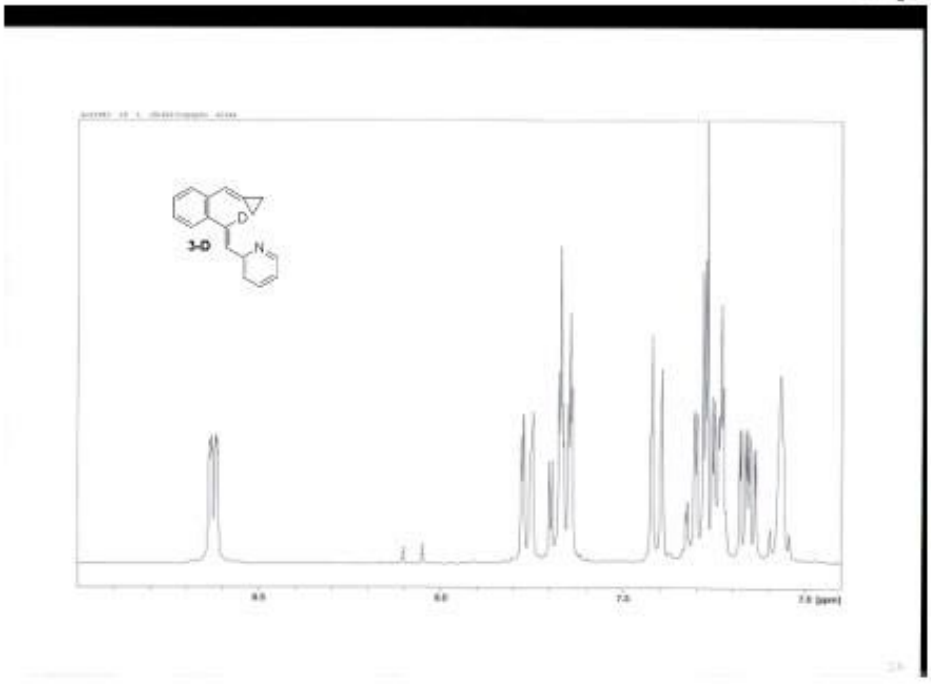
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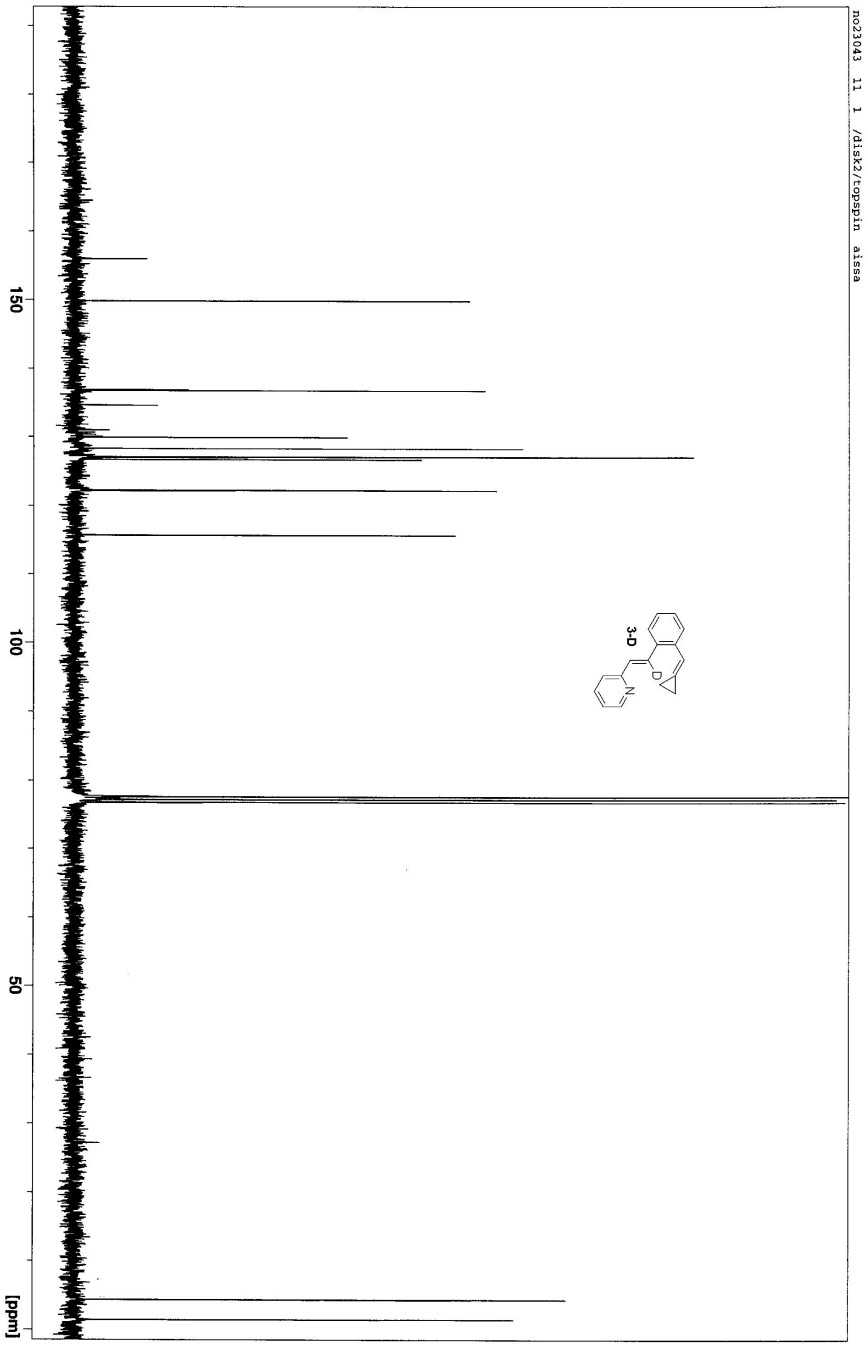
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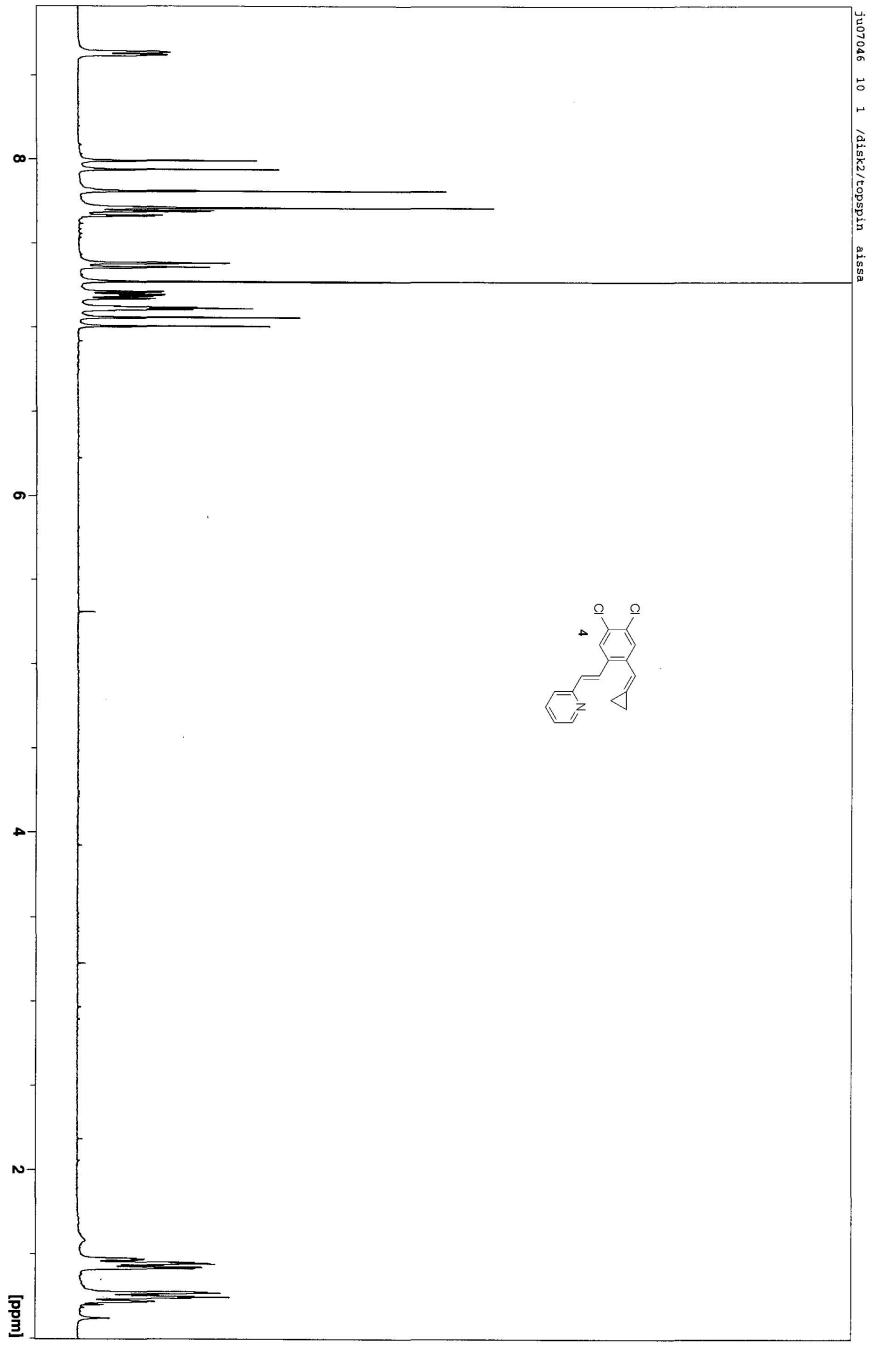
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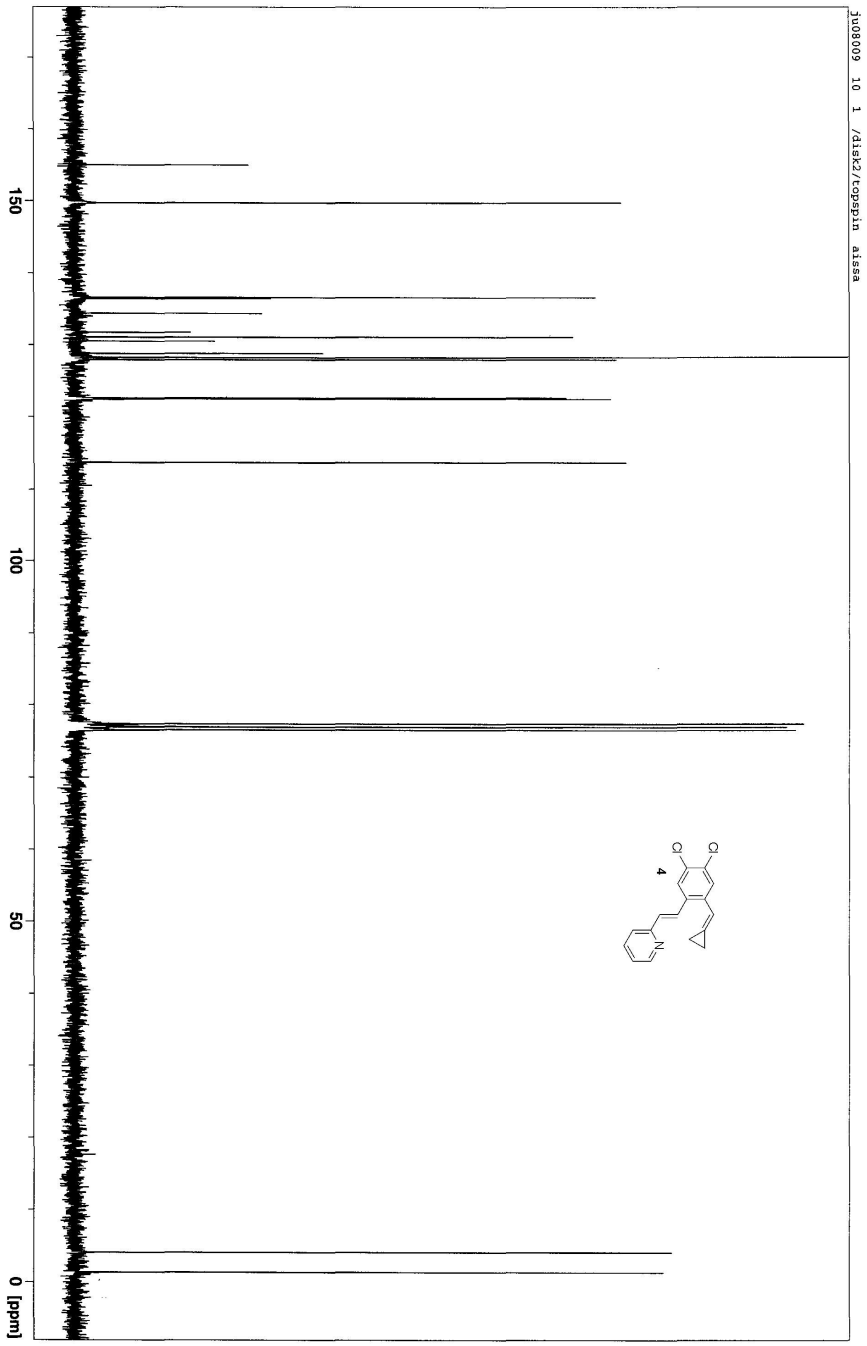
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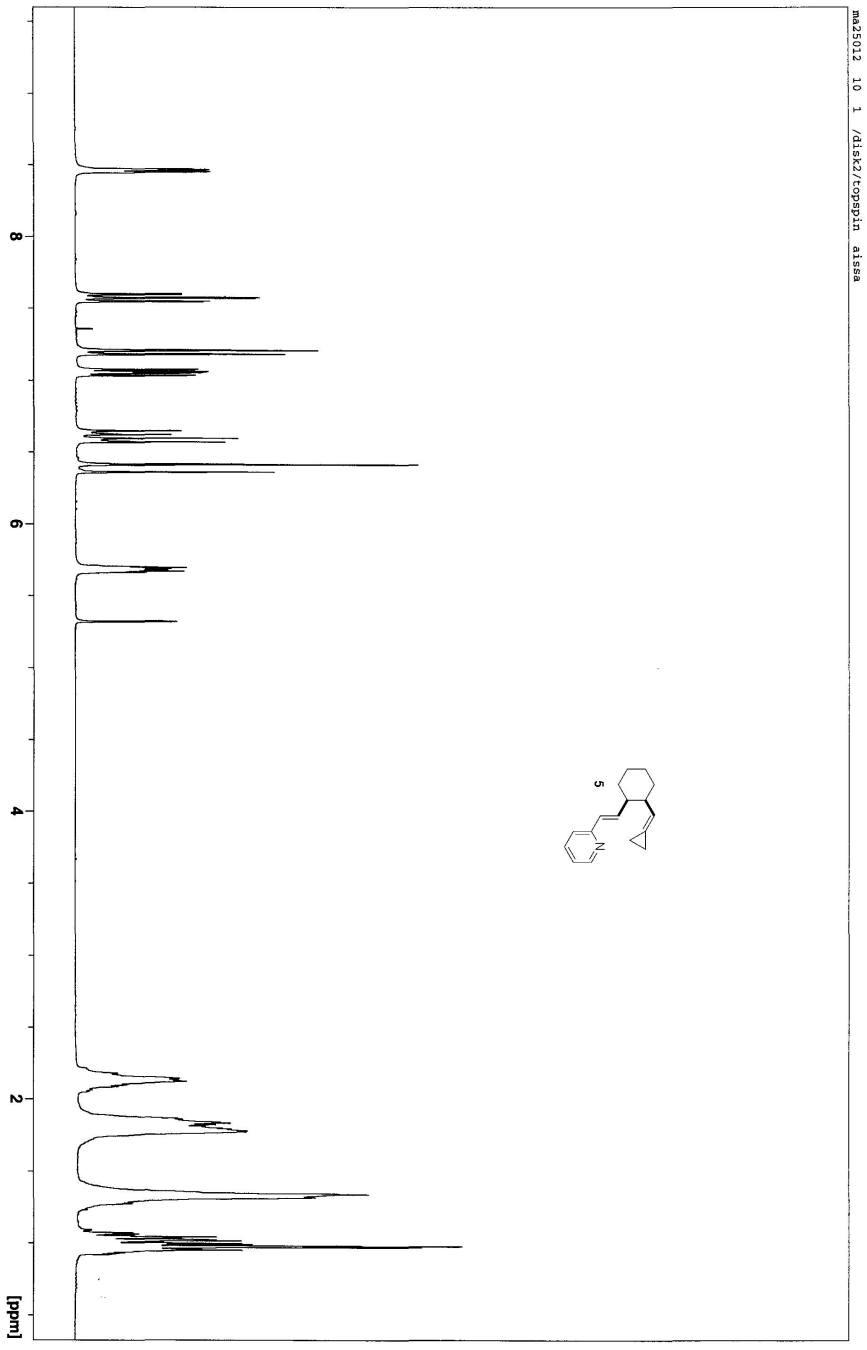
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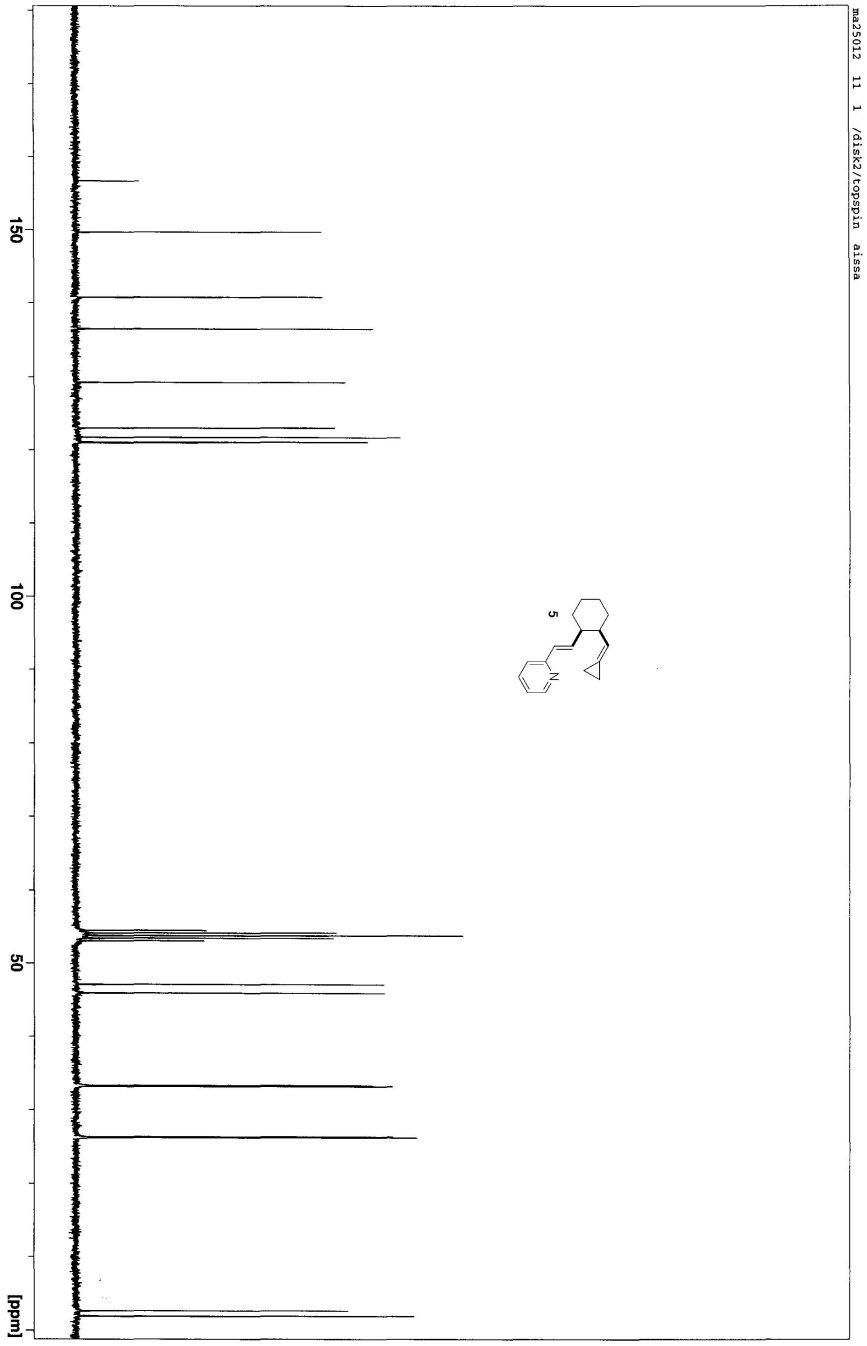
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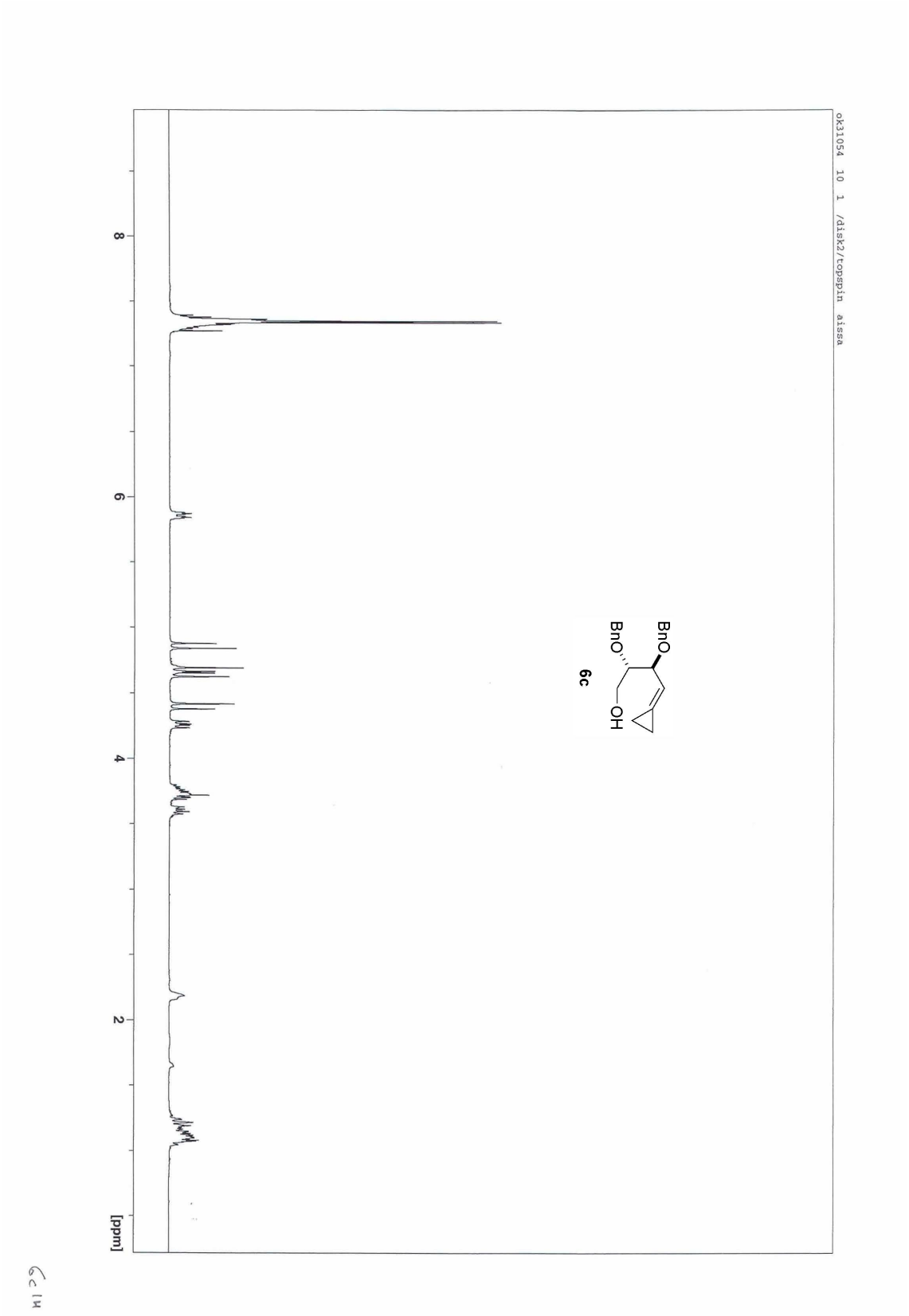
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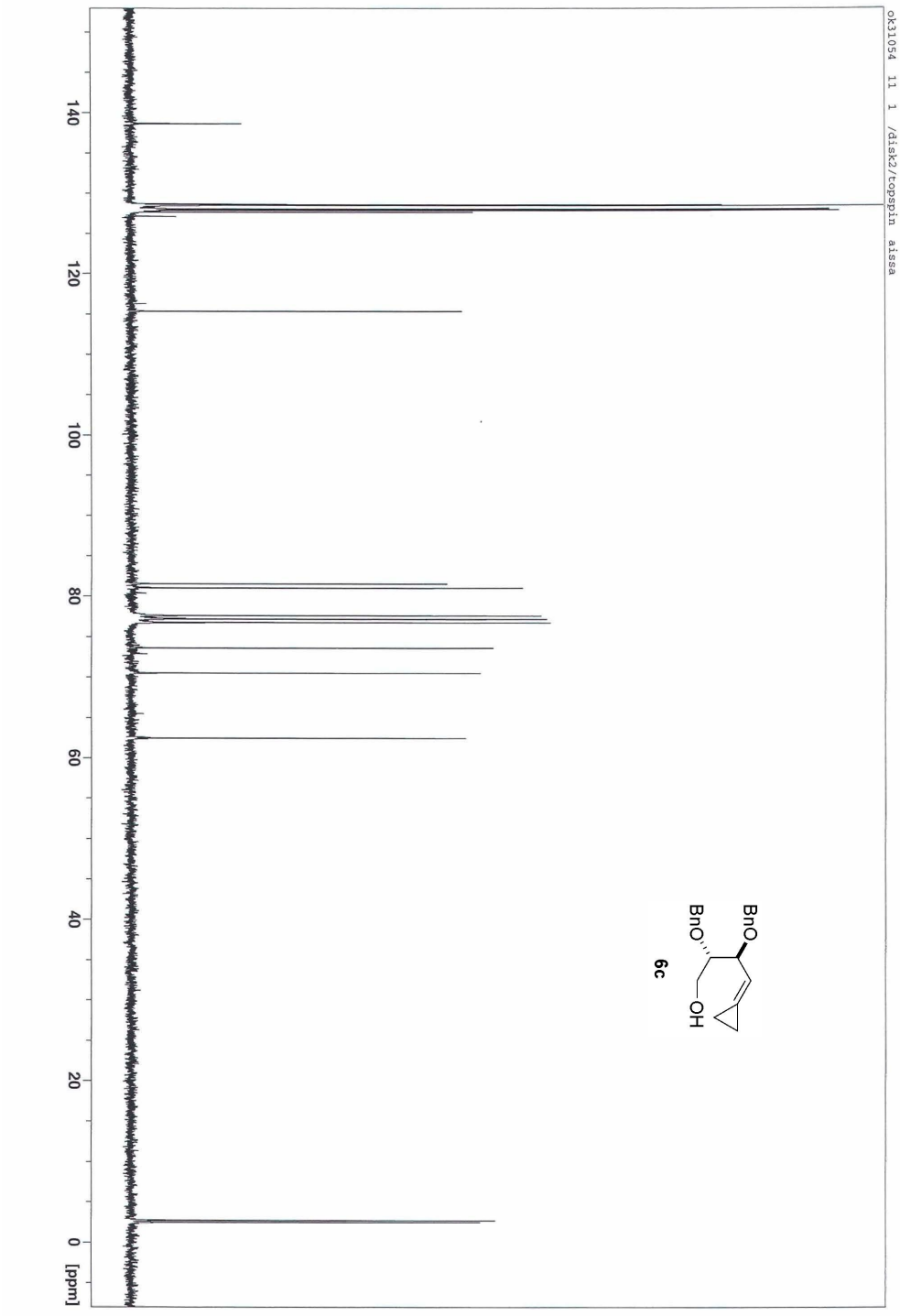
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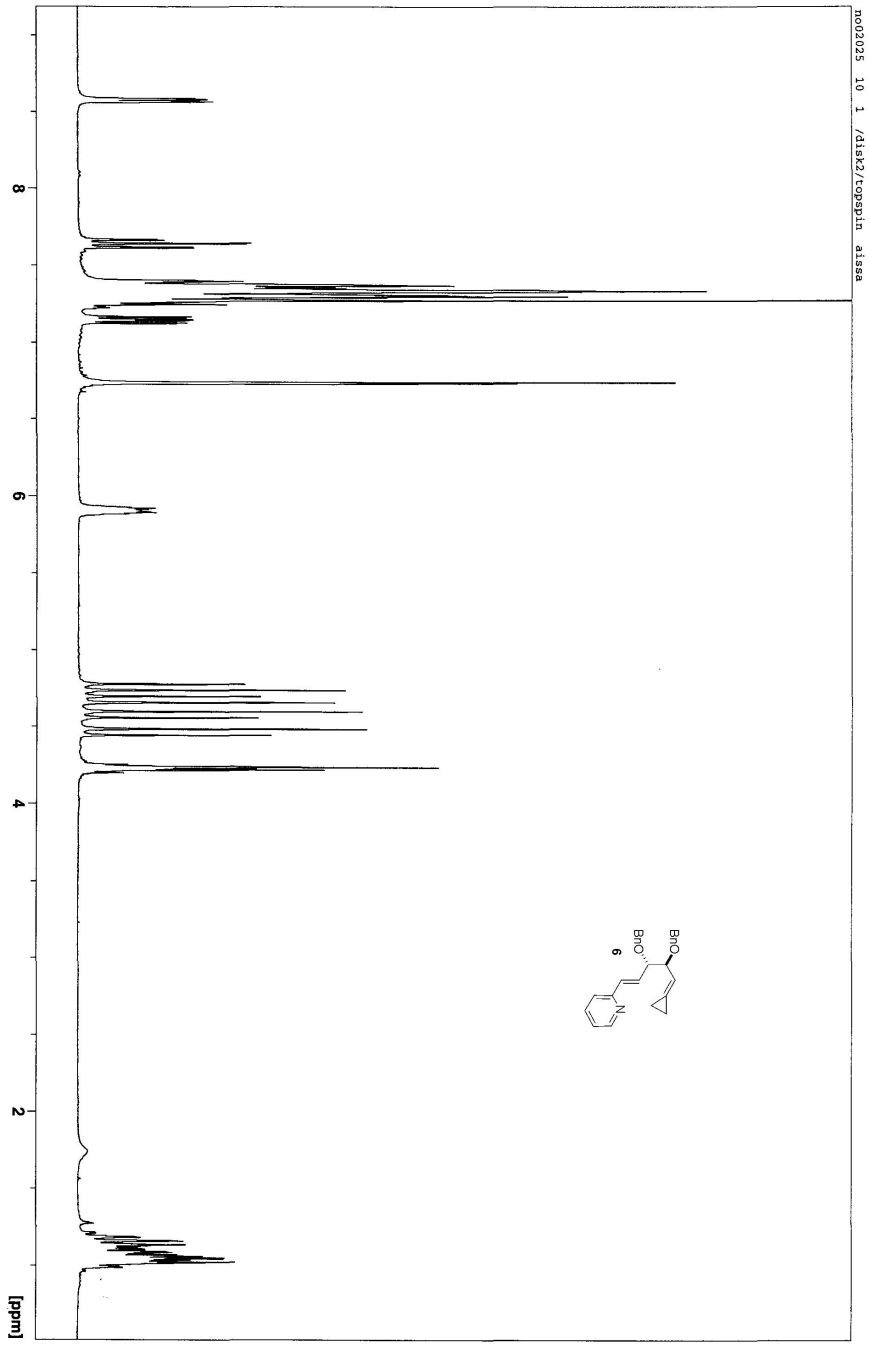
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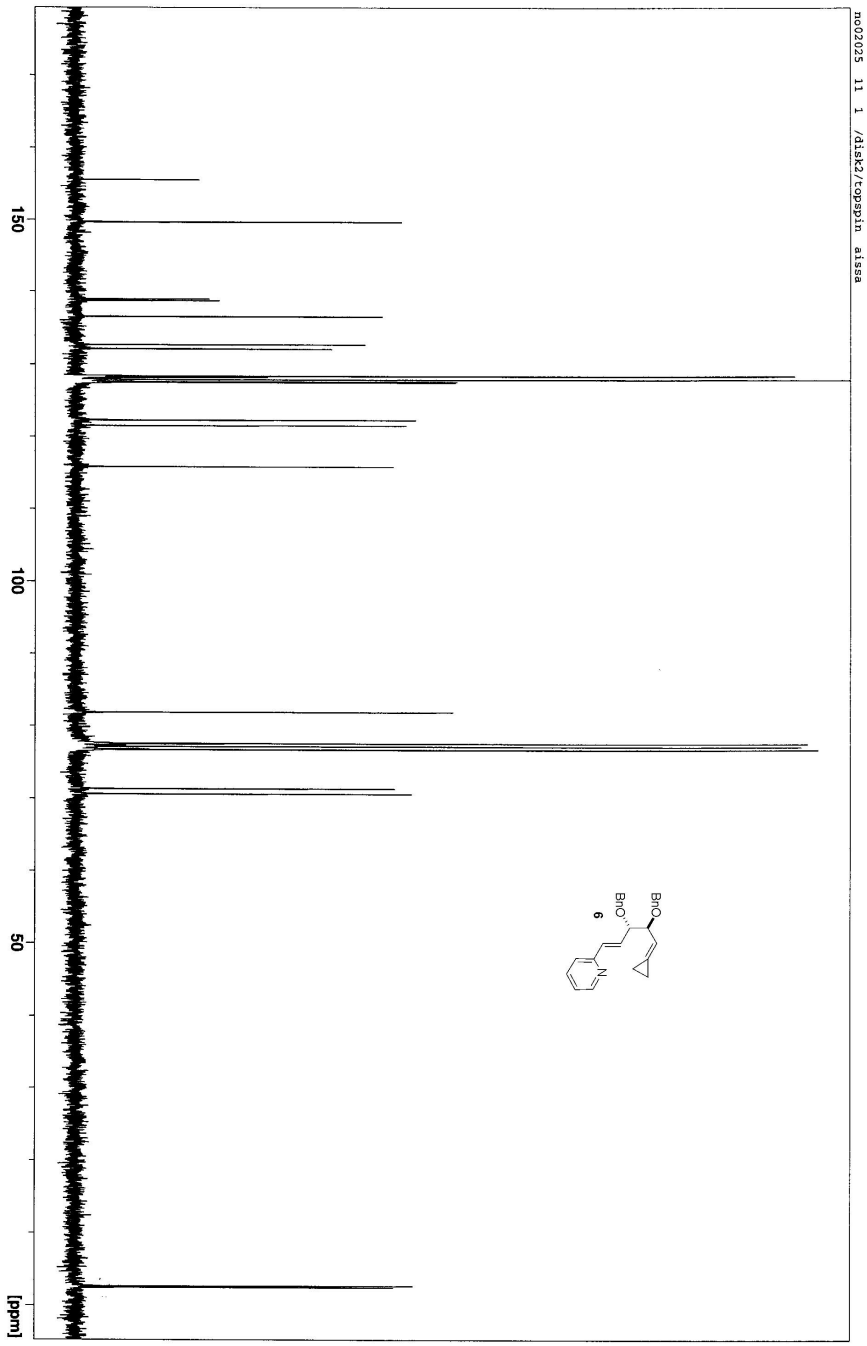
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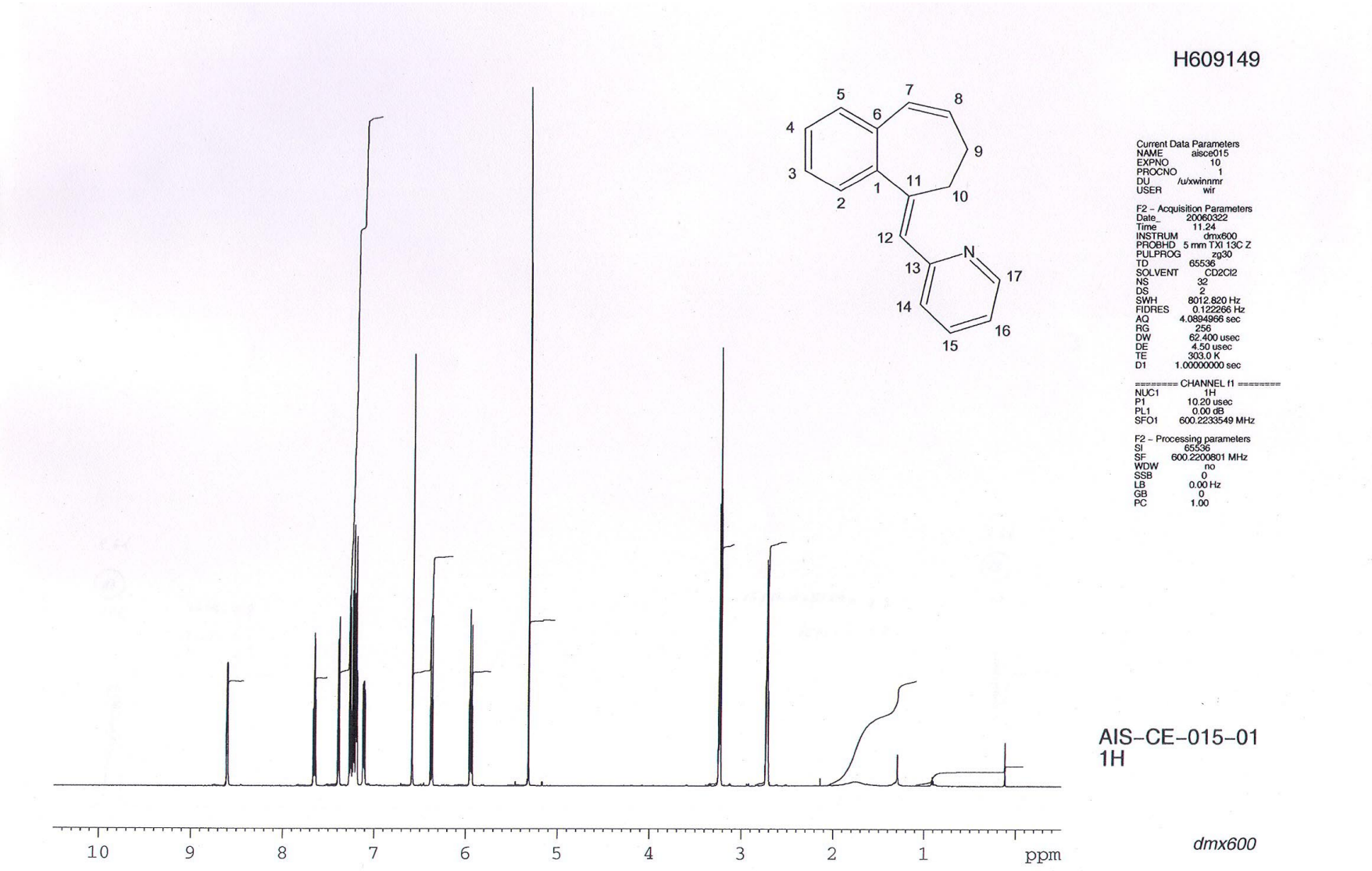
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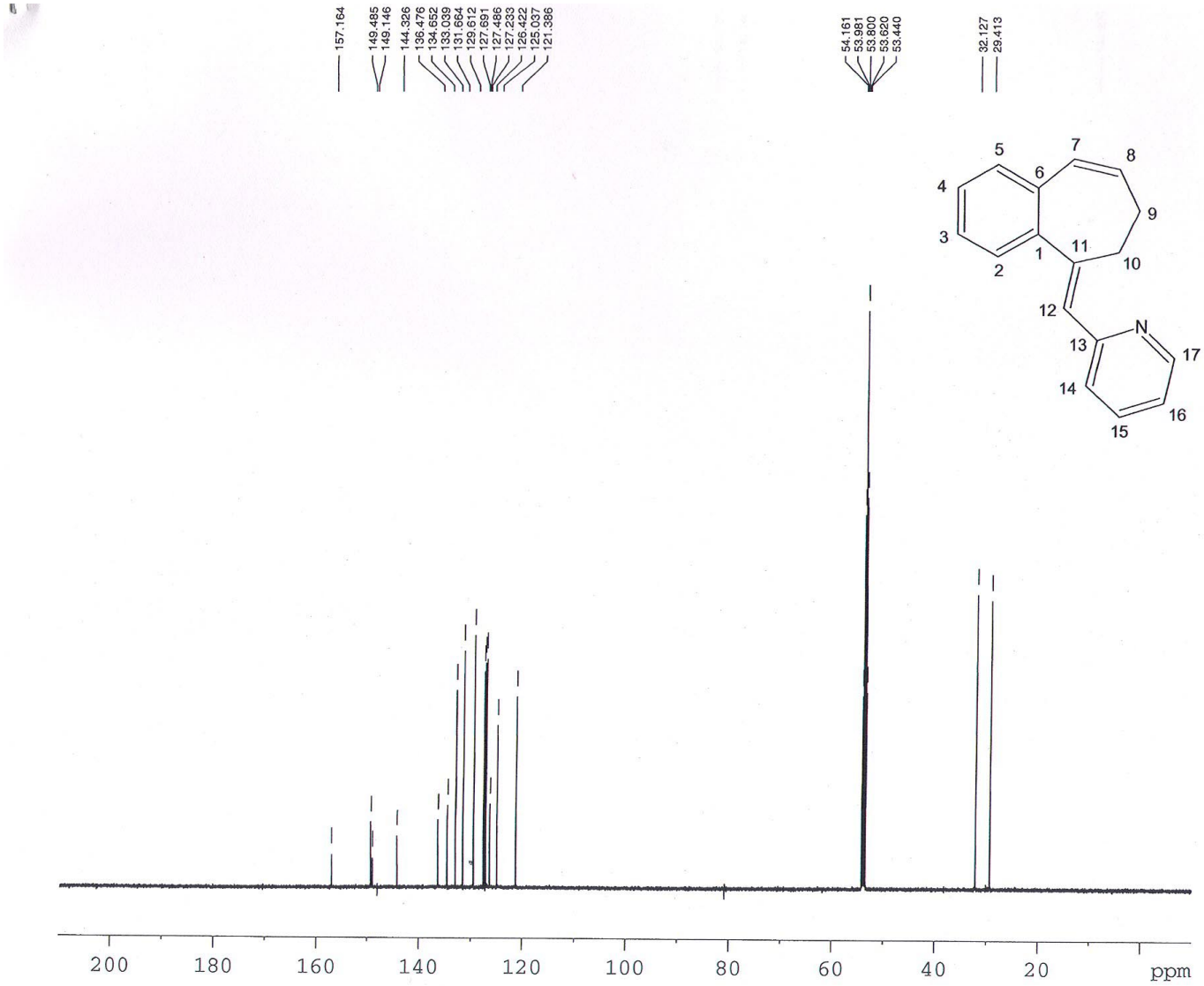
PROBHD 5 mm TXI 13C Z
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 32
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 256
DW 62.400 usec
DE 4.50 usec
TE 303.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PL1 0.00 dB
SFO1 600.2233549 MHz
F2 - Processing parameters
SI 65536
SF 600.2200801 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 N
10 9 8 7 6 5 4 3 2 1 ppm
AIS-CE-015-01
1H
dmx600



C609150

Current Data Parameters
NAME aisce015
EXPNO 11
PROCNO 1
DU /u/xwinnmr
USER wir

F2 - Acquisition Parameters
Date_ 20060323
Time 8.34
INSTRUM dmx600
PROBHD 5 mm TXI 13C Z
PULPROG zgdc30
TD 65536
SOLVENT CD2Cl2
NS 23356
DS 200
SWH 37594.402 Hz
FIDRES 0.573645 Hz
AQ 0.8716691 sec
RG 16384
DW 13.300 usec
DE 4.50 usec
TE 303.0 K
D1 0.03000000 sec
D11 0.03000000 sec

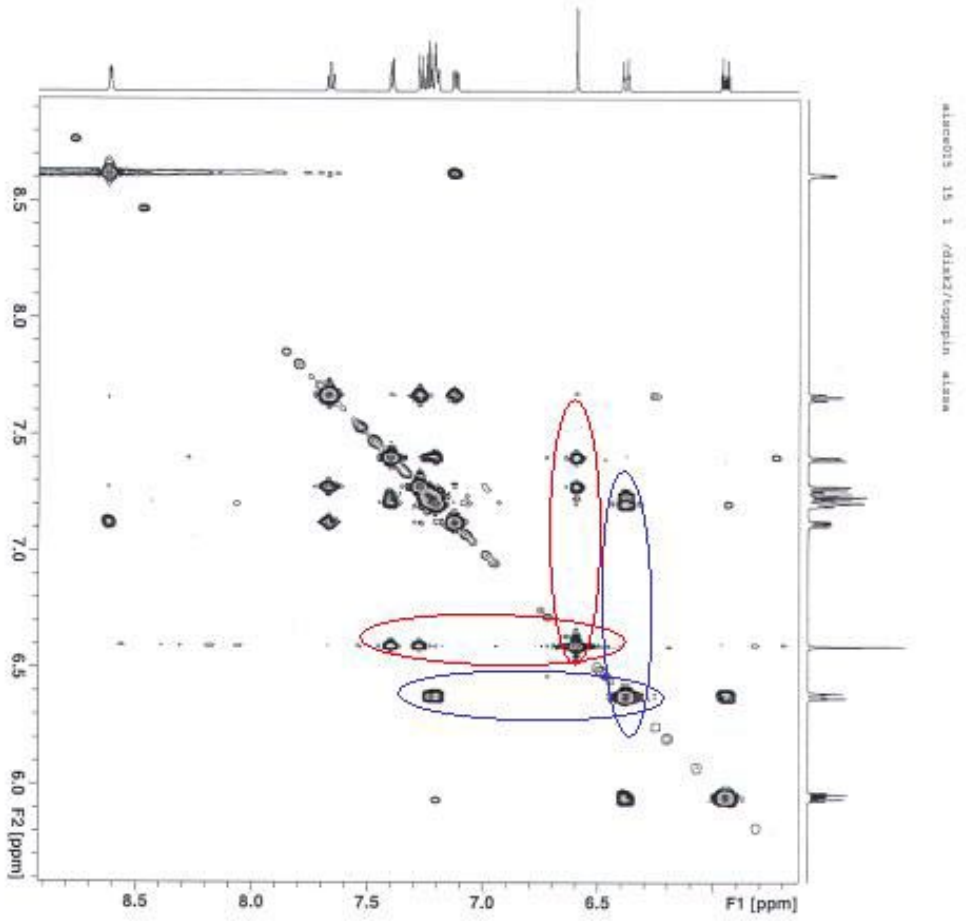
======== CHANNEL f1 ========
NUC1 13C
P1 16.90 usec
PL1 0.00 dB
SFO1 150.9419346 MHz

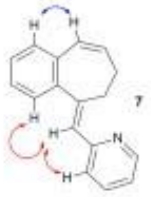
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0.00 dB
PL12 16.31 dB
SFO2 600.2234213 MHz

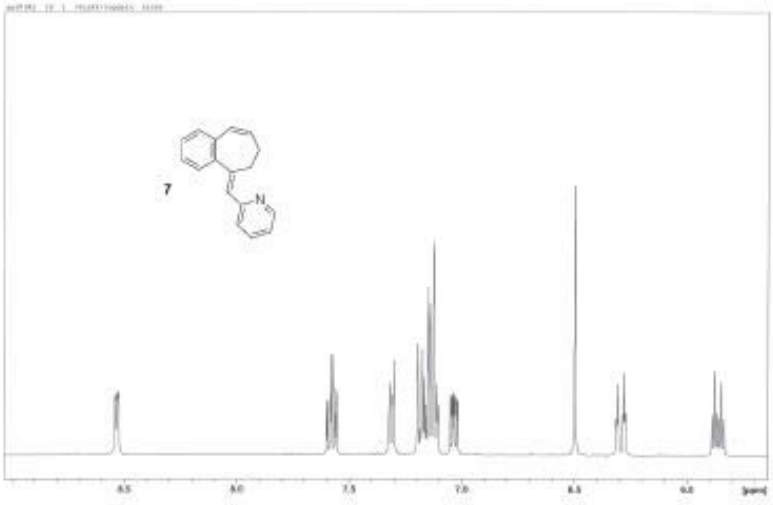
F2 - Processing parameters
SI 65536
SF 150.9253793 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 2.00

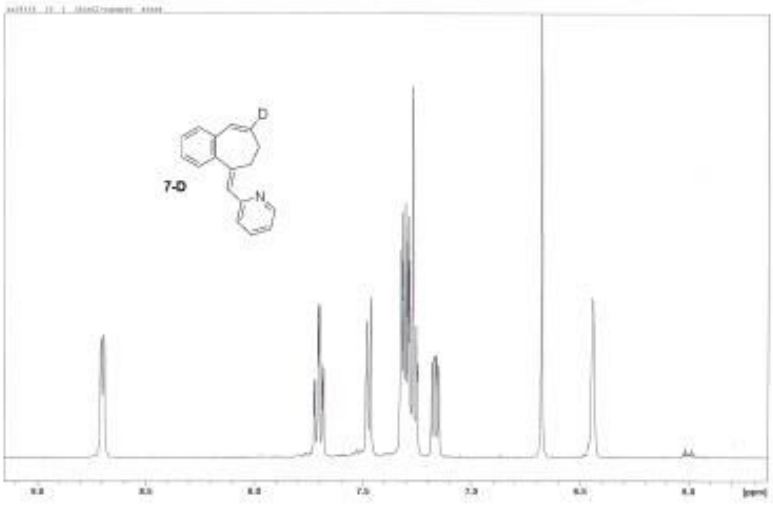
AIS-CE-015-01
13C

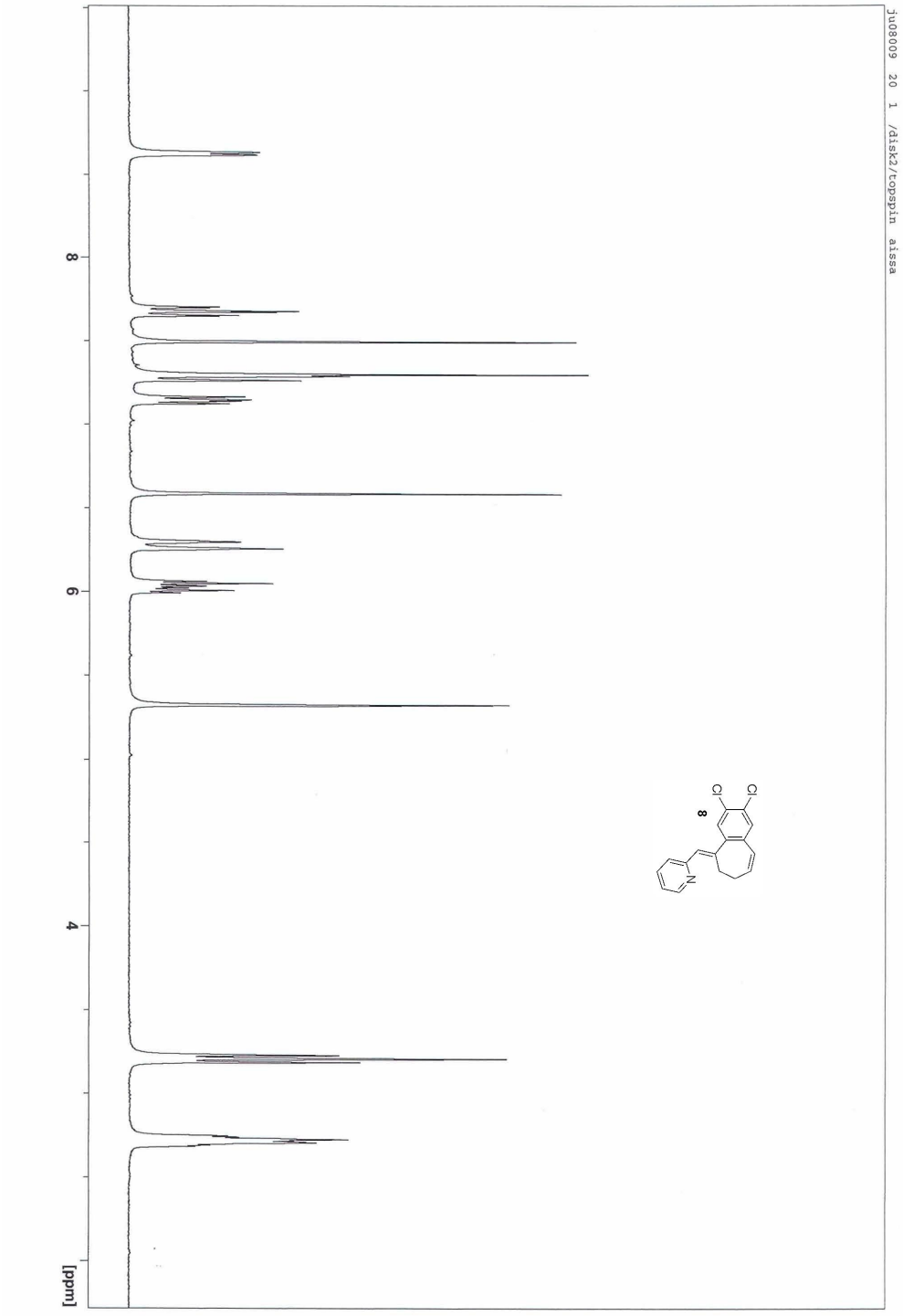
dmx600

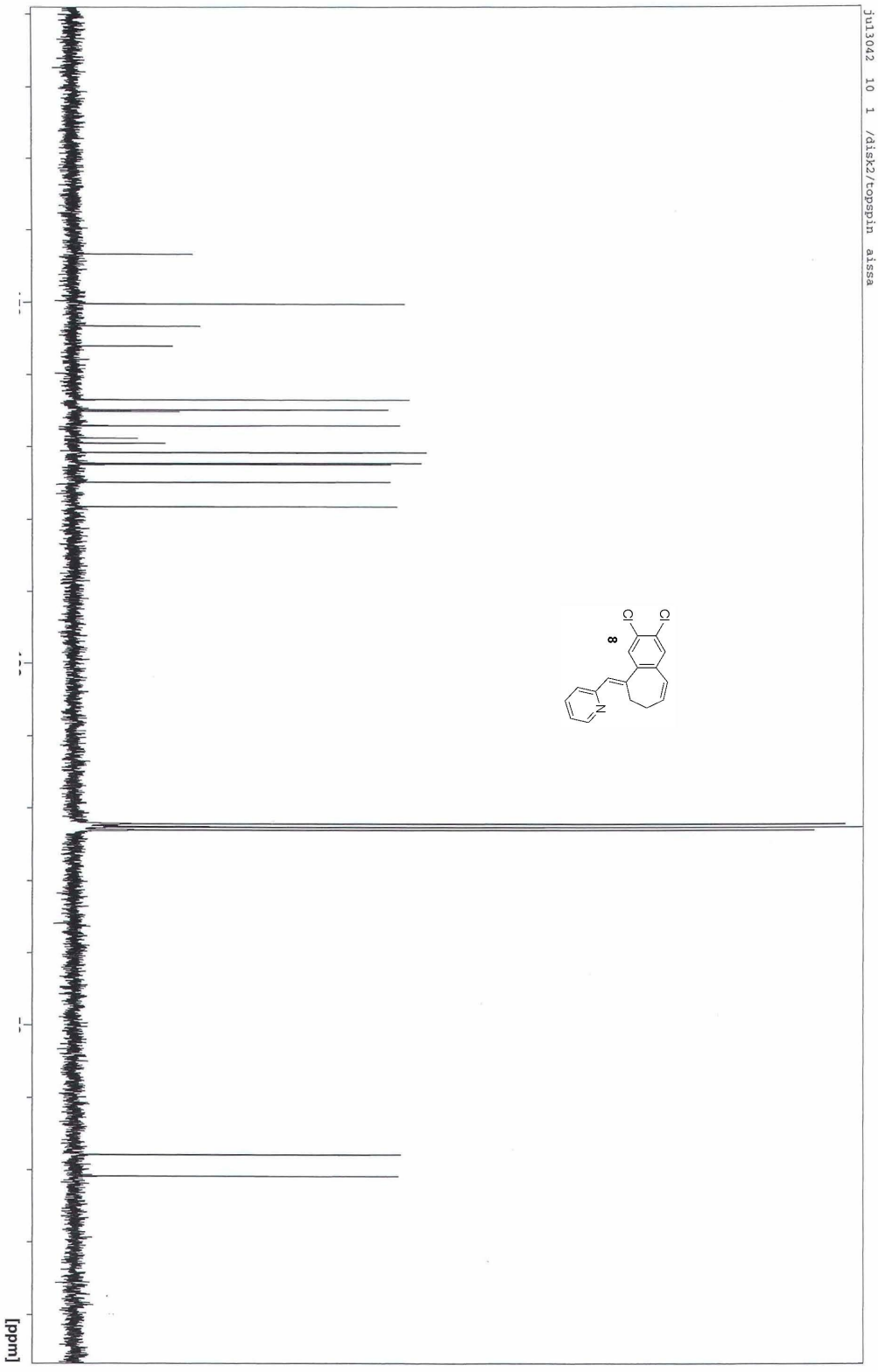

8.5
8.0
7.5
7.0
6.5
6.0 F2 [ppm]
8.5
8.0
7.5
7.0
6.5
F1 [ppm]

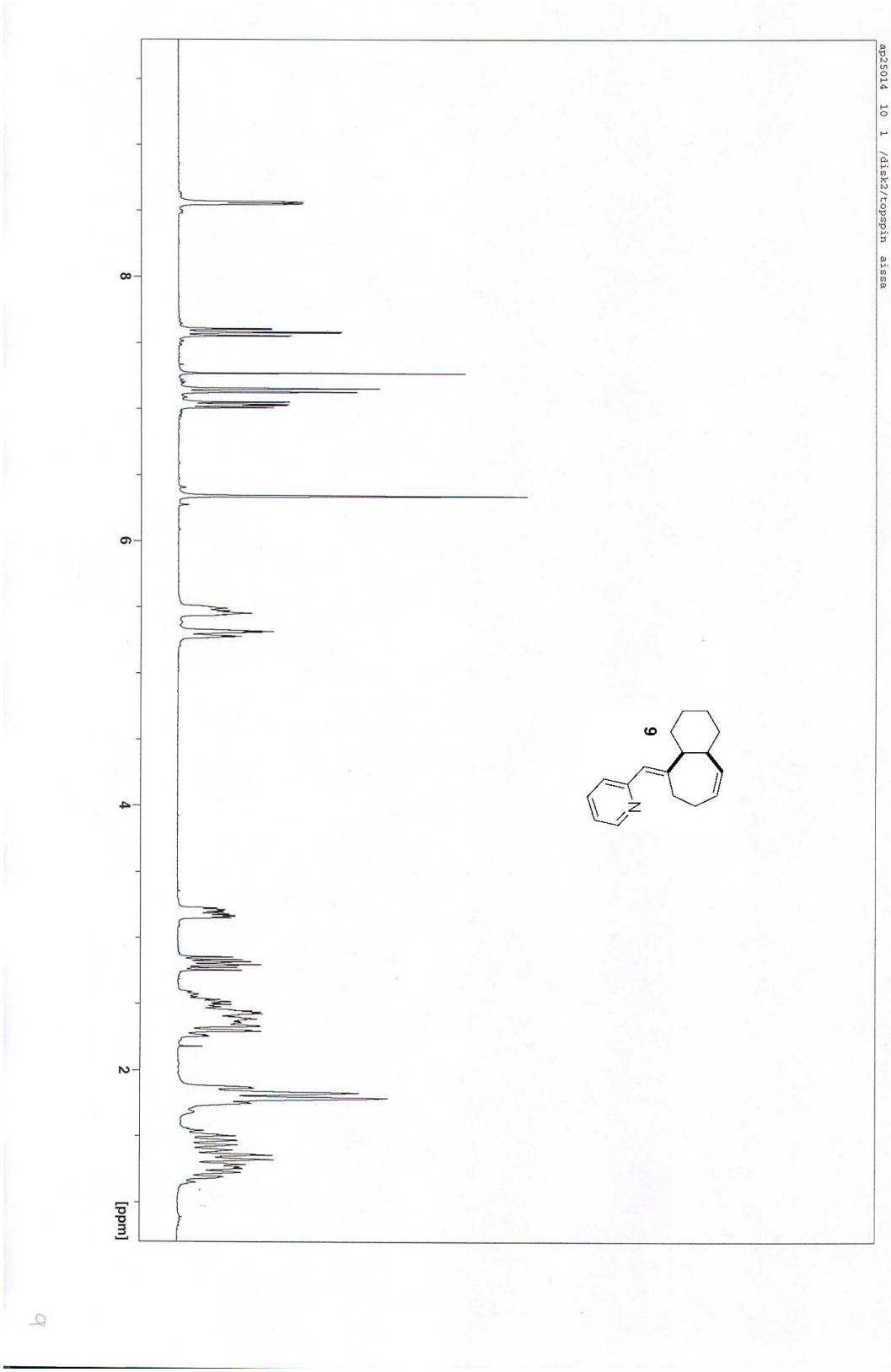

H
H
H
H
N
H
7

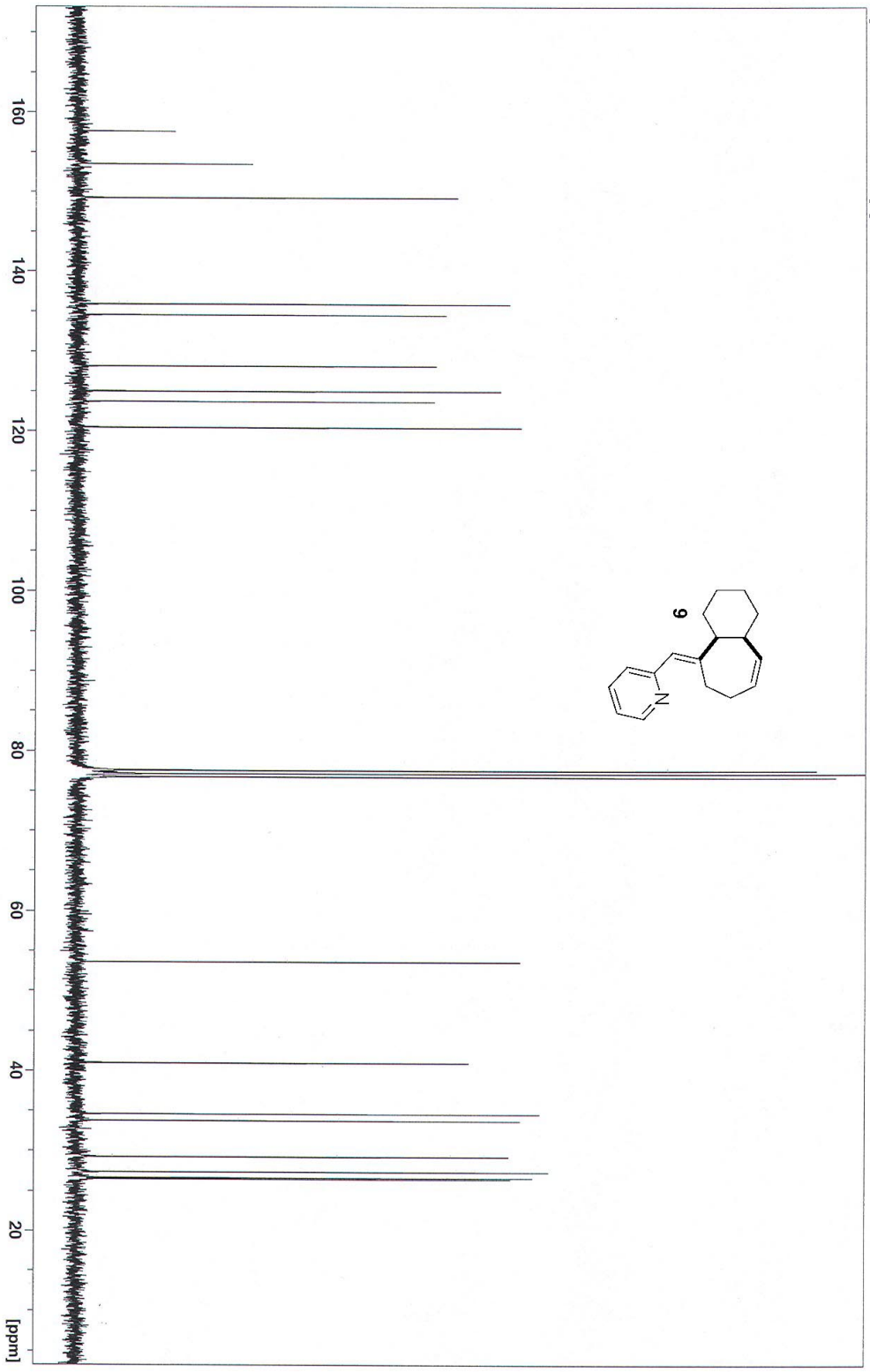

7
N

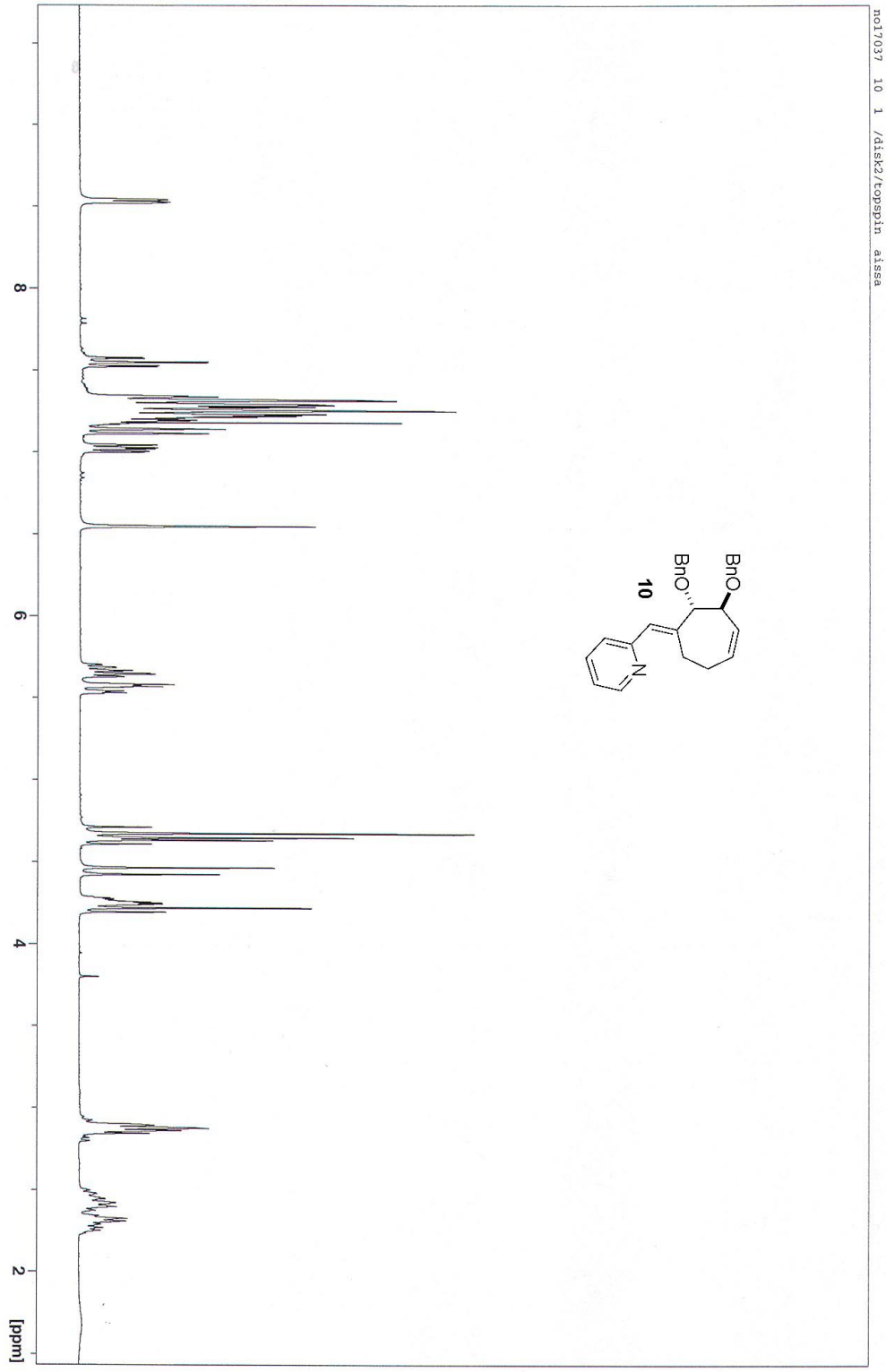

D
7-D
N

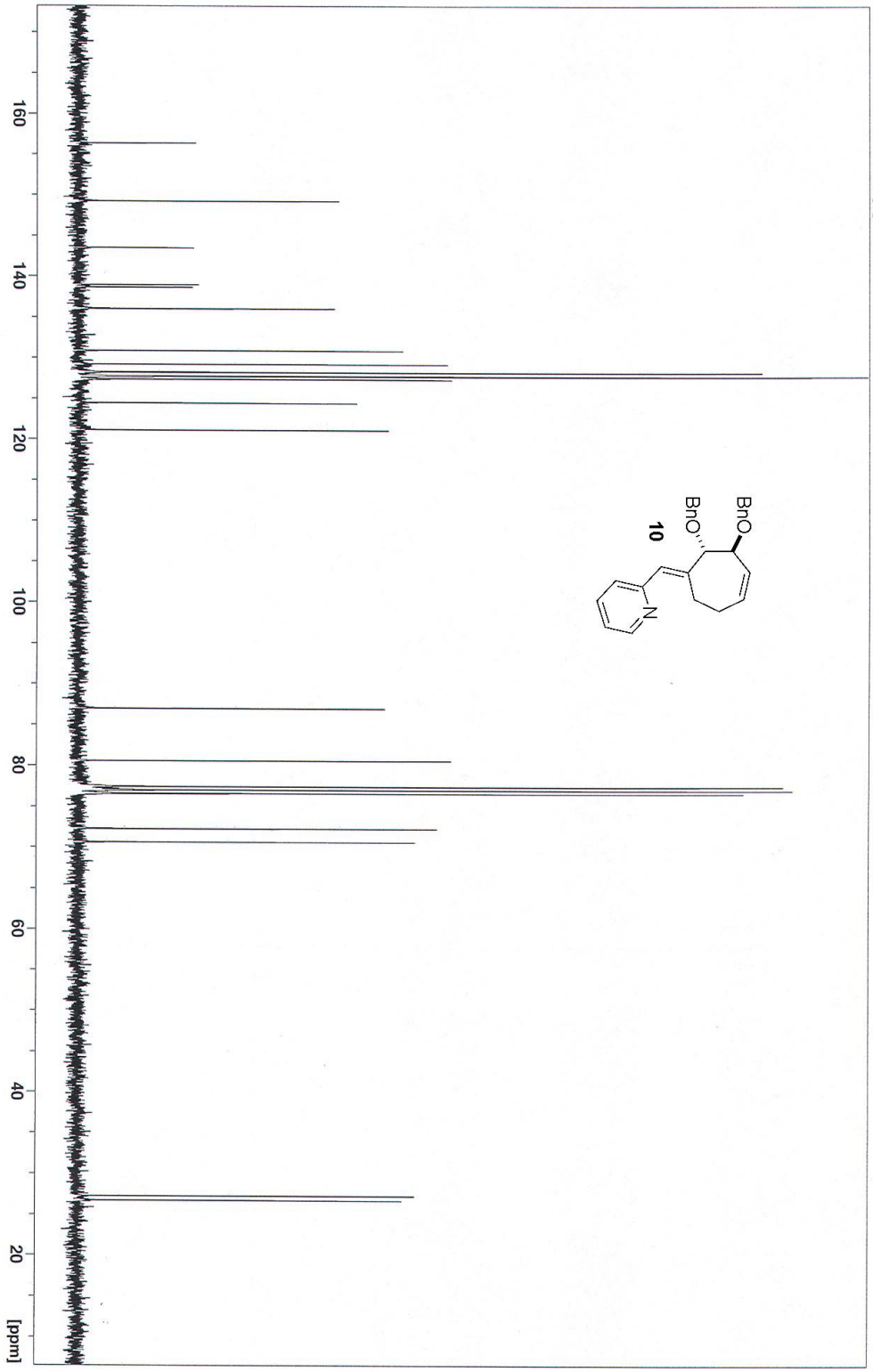

ju08009 20 1 /disk2/topspin aissa
8
6
4
[ppm]
Cl
Cl
8
N

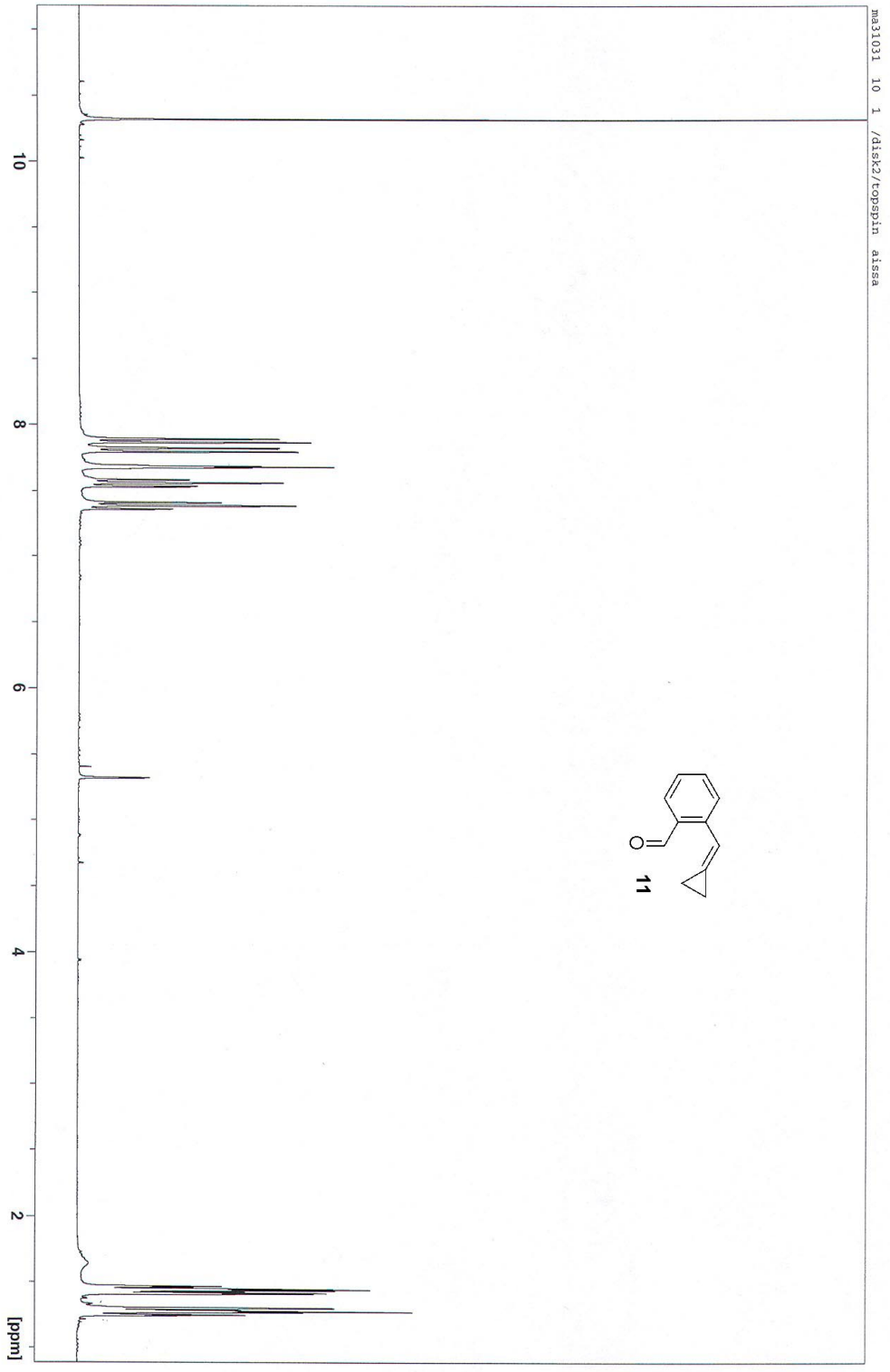

ju13042 10 1 /disk2/topspin aissa
Cl
Cl
8
N
[ppm]

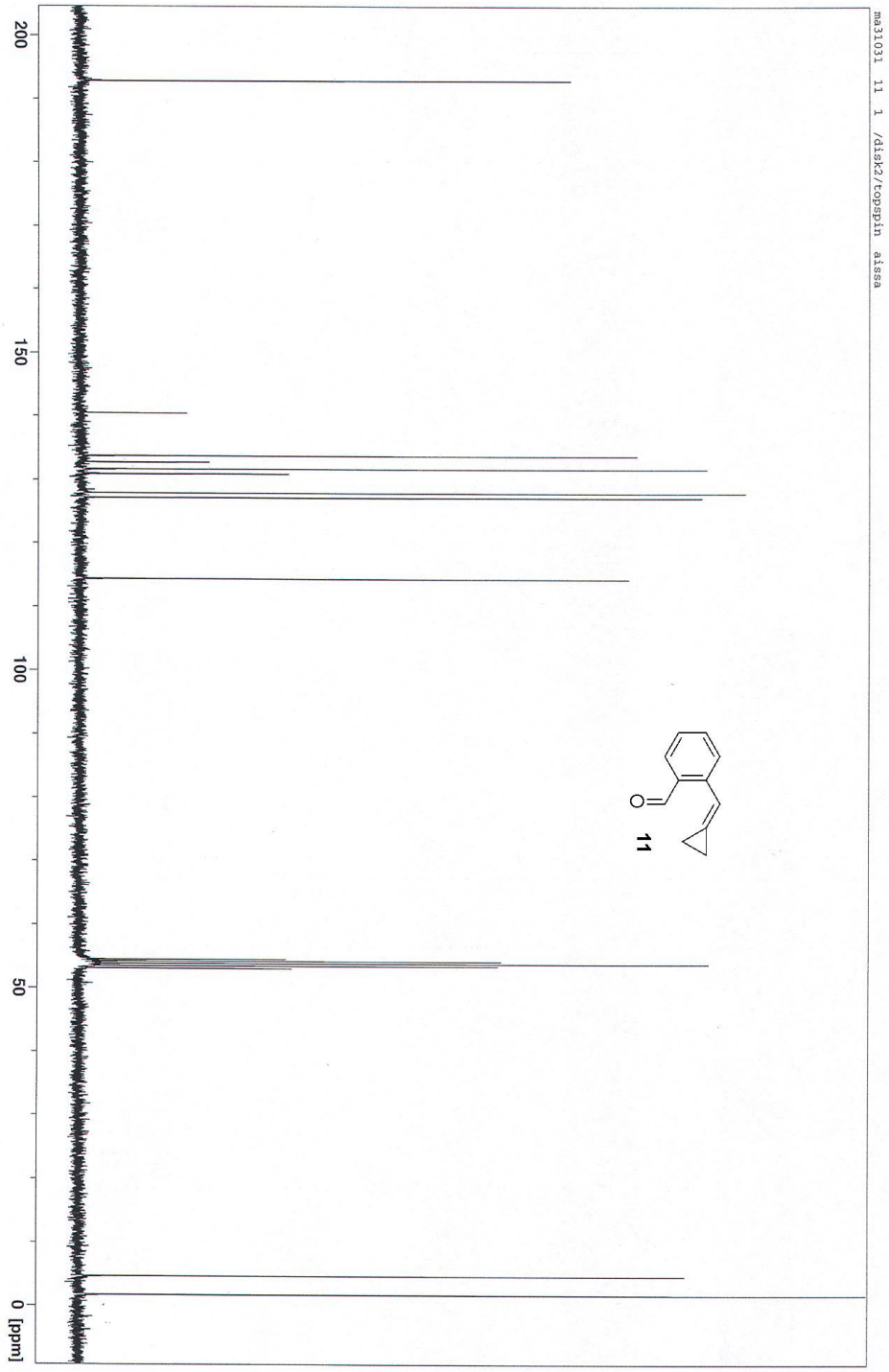

ap25014 10 1 /disk2/topspin aissa
9
N
8
6
4
2
[ppm]

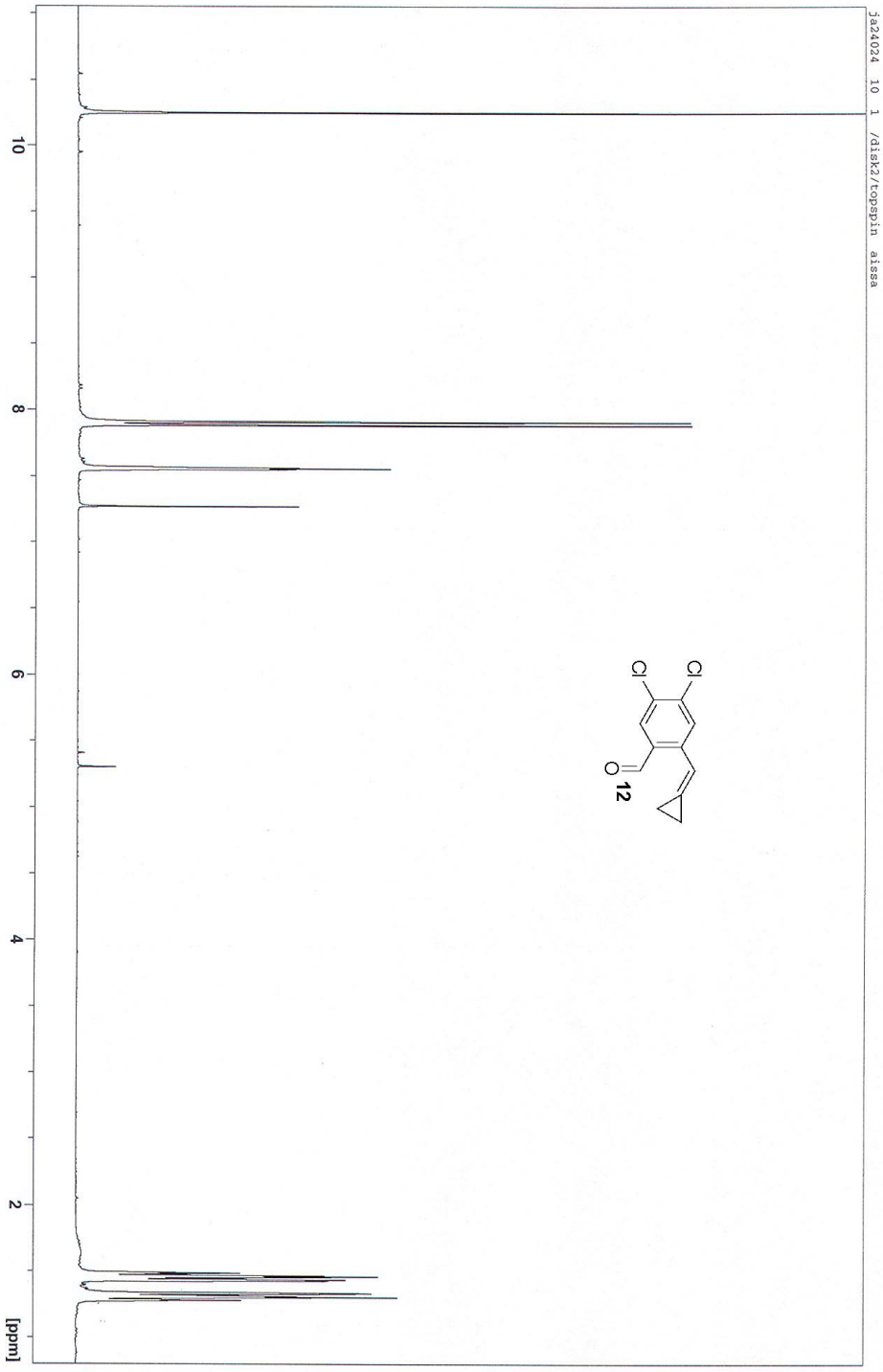

ap25016 10 1 /disk2/topspin aissa
9
N
160
140
120
100
80
60
40
20
[ppm]

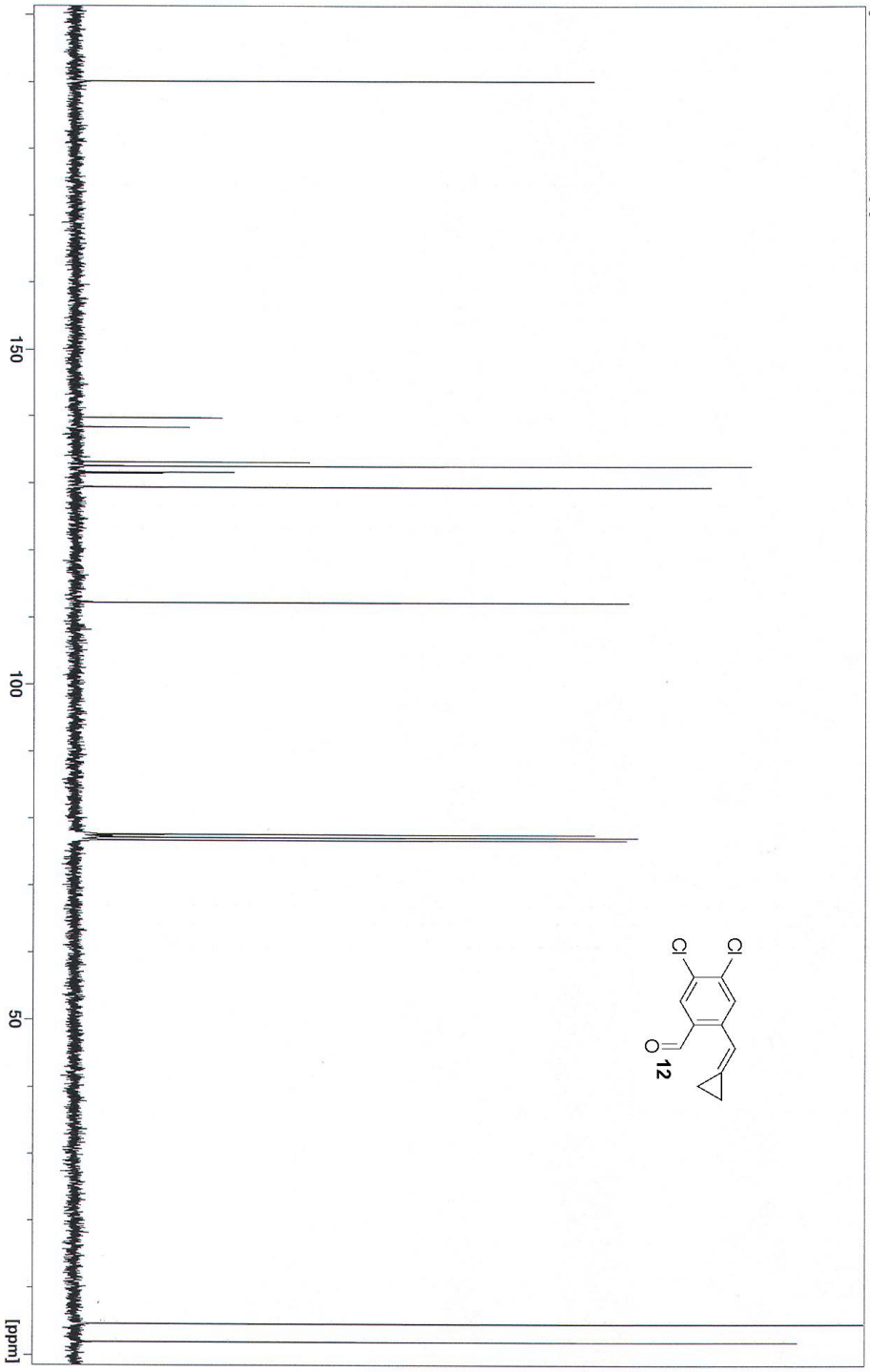

no17037 10 1 /disk2/topspin aissa
BnO
BnO
10
N
8
6
4
2
[ppm]

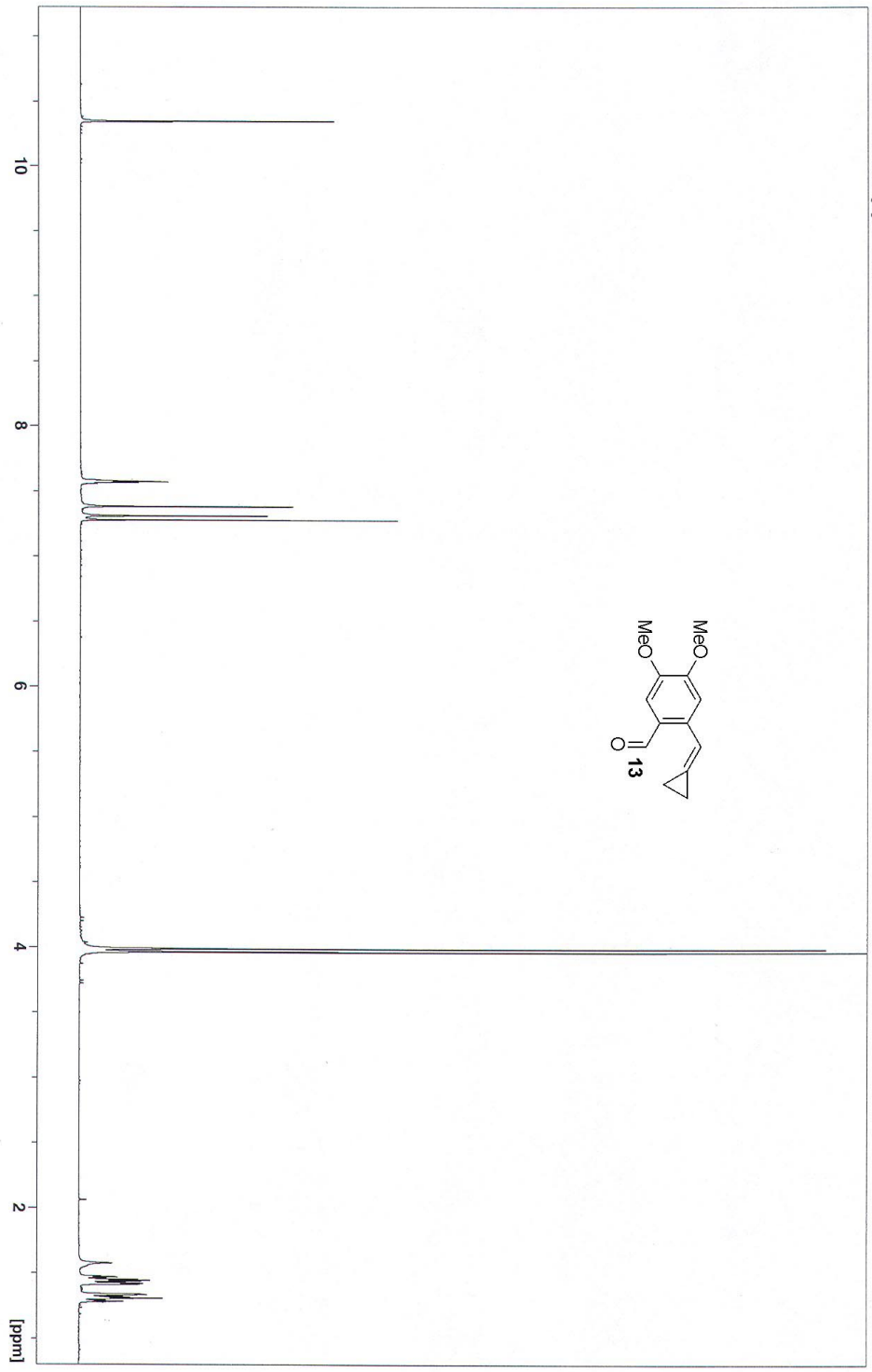

no17037 11 1 /disk2/topspin aisa
160
140
120
100
80
60
40
20
[ppm]
BnO
BnO
10
N

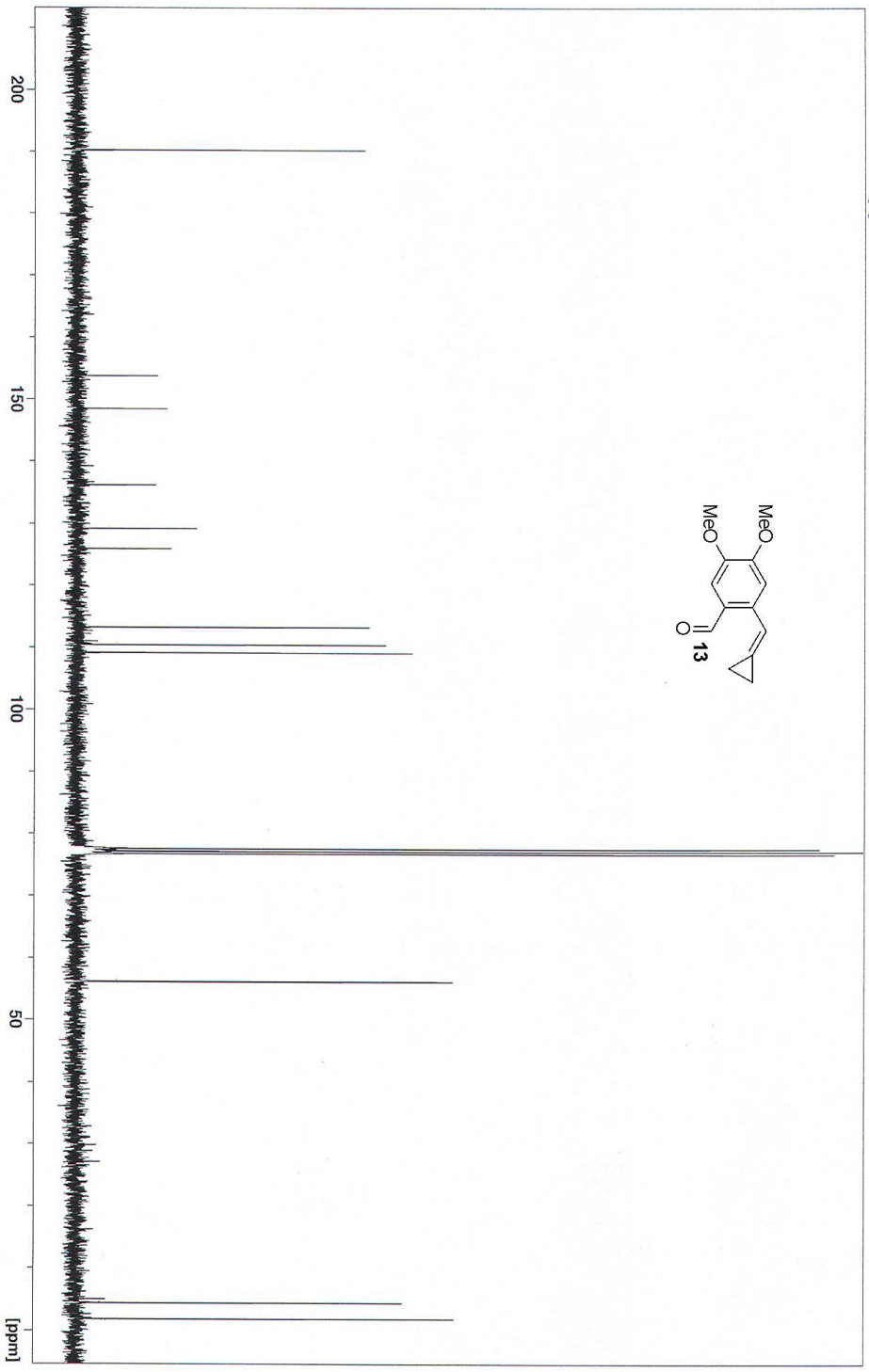

ma31031 10 1 /disk2/topspin aissa
10
8
6
4
2
[ppm]
O
11

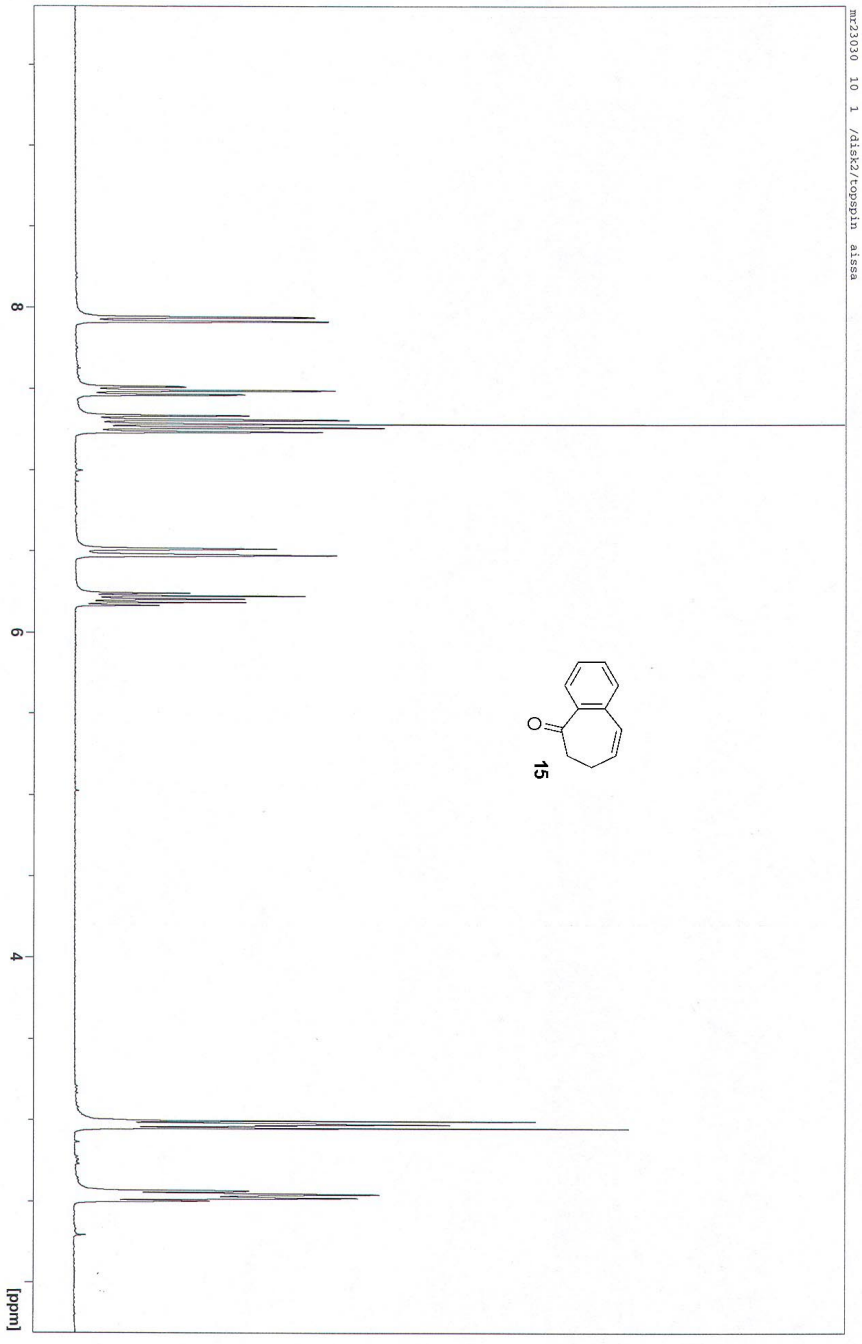

ma31031 11 1 /disk2/topspin aissa
200
150
100
50
0 [ppm]
O
11

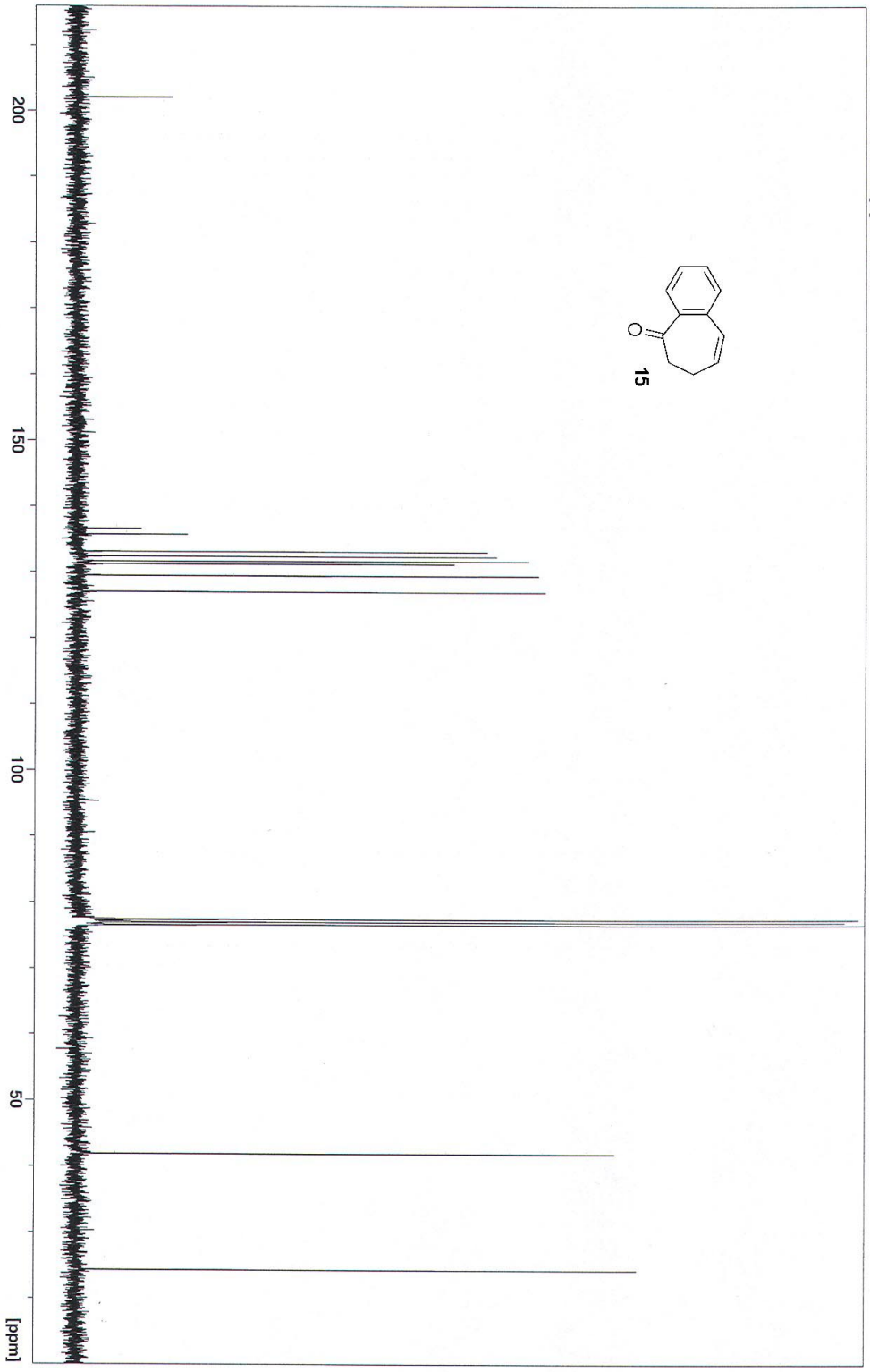

ja24024_10_1 /disk2/topspin aissa
Cl
Cl
O
12
10
8
6
4
2
[ppm]

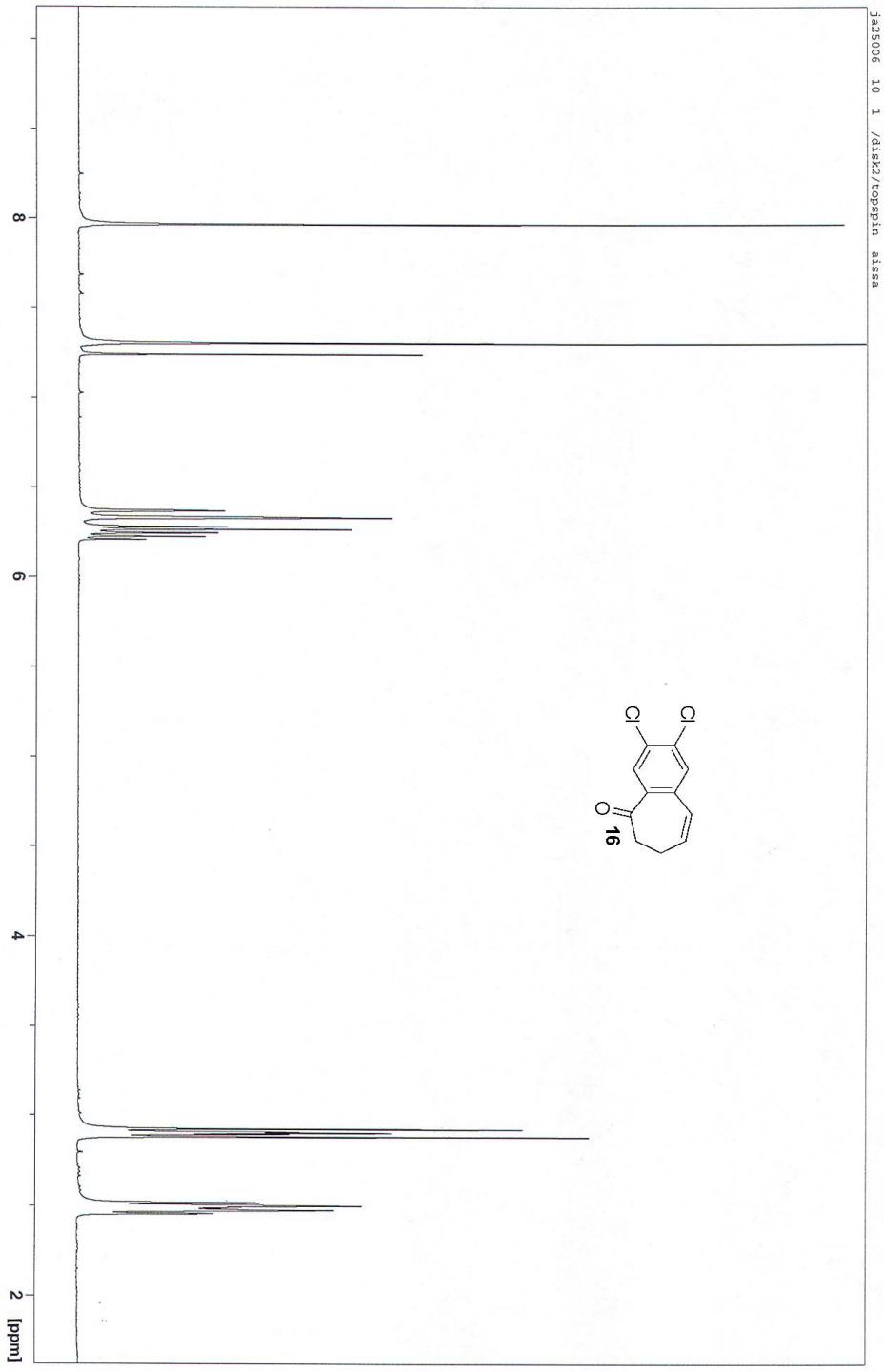

ja24024 11 1 /disk2/topspin aissa
150
100
50
[ppm]
Cl
Cl
O
12

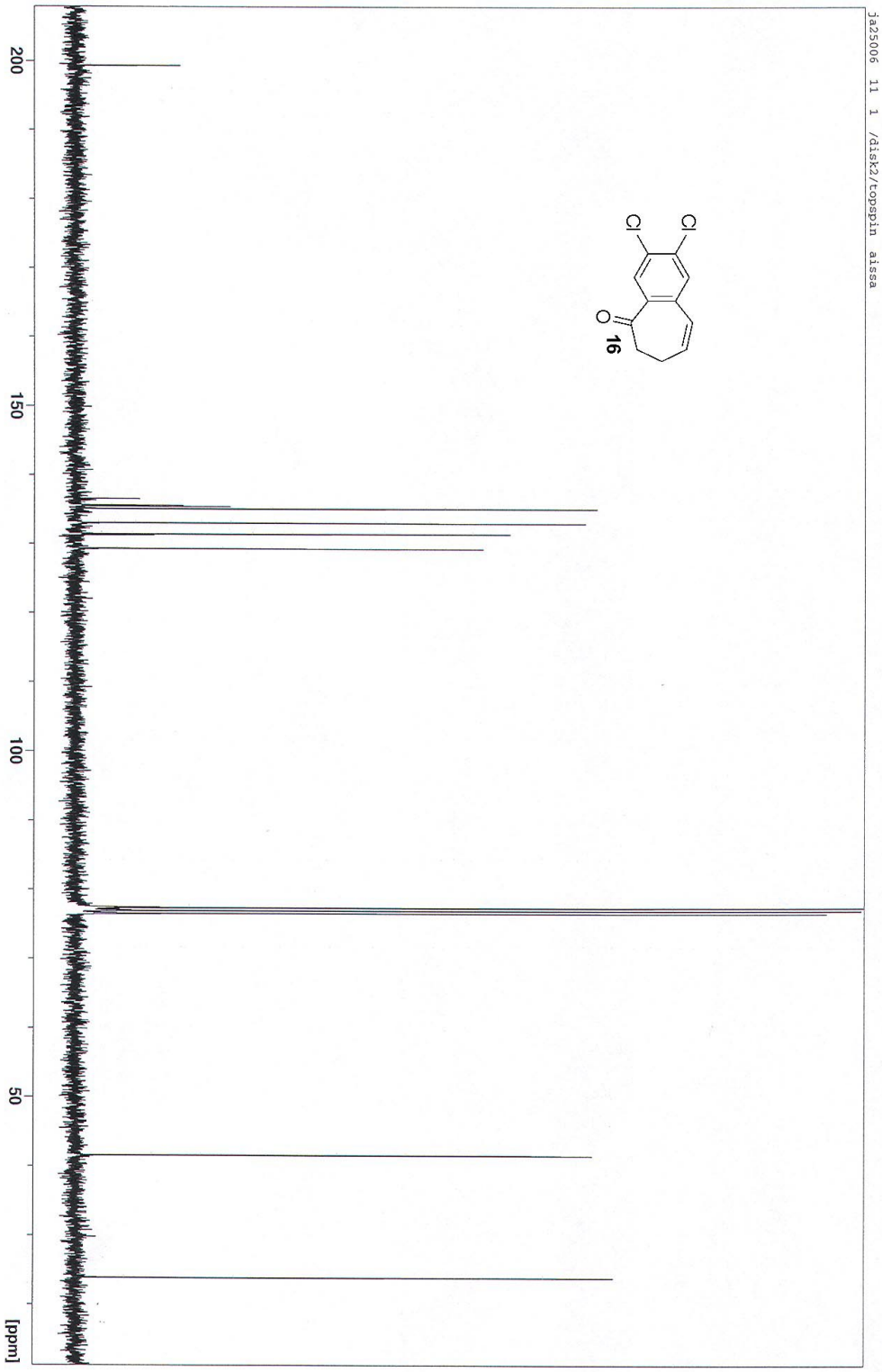

mr21024 10 1 /disk2/topspin aissa
MeO
MeO
O
13
10
8
6
4
2
[ppm]

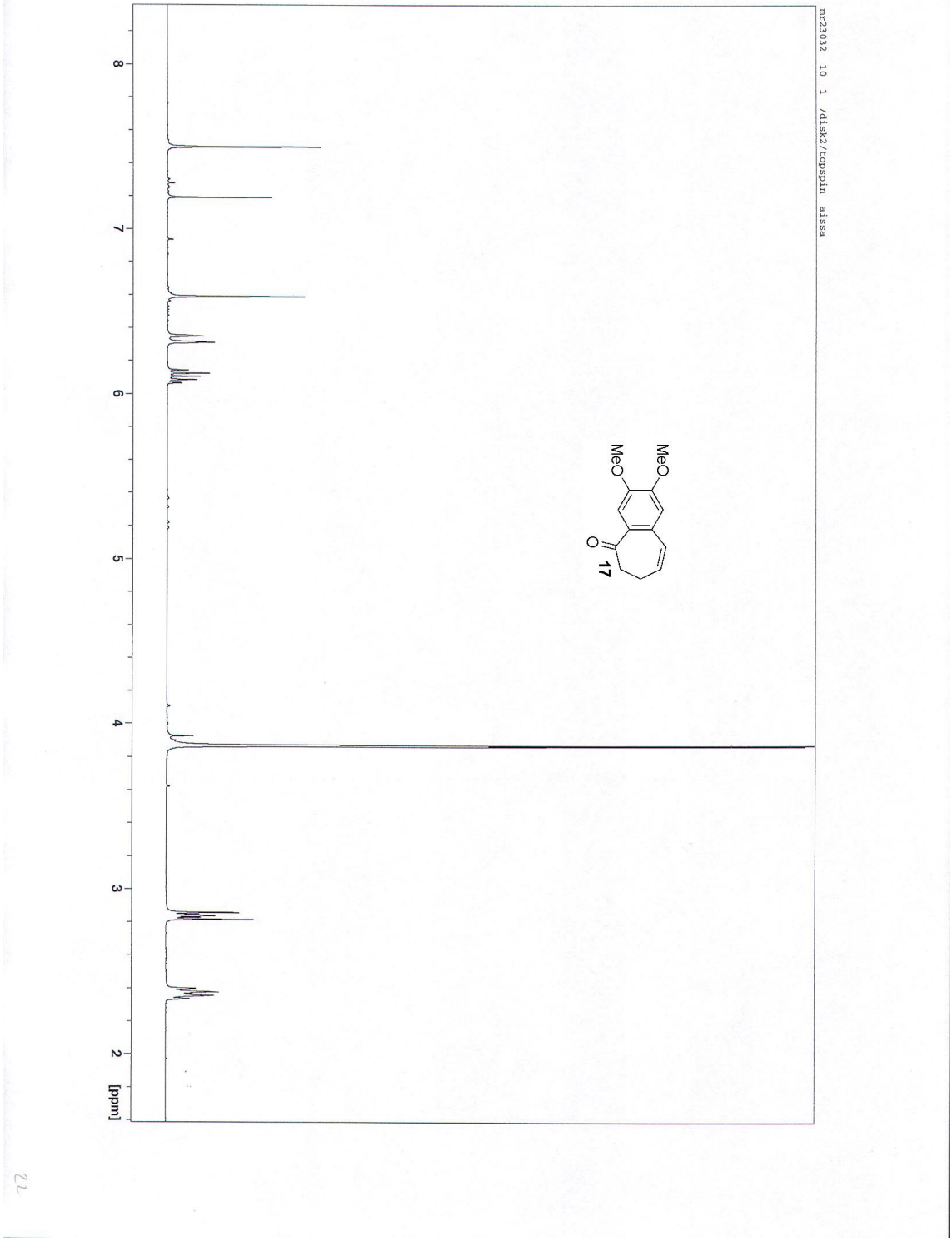

mr12023 11 1 /disk2/topspin aissa
MeO
MeO
O
13
200
150
100
50
[ppm]

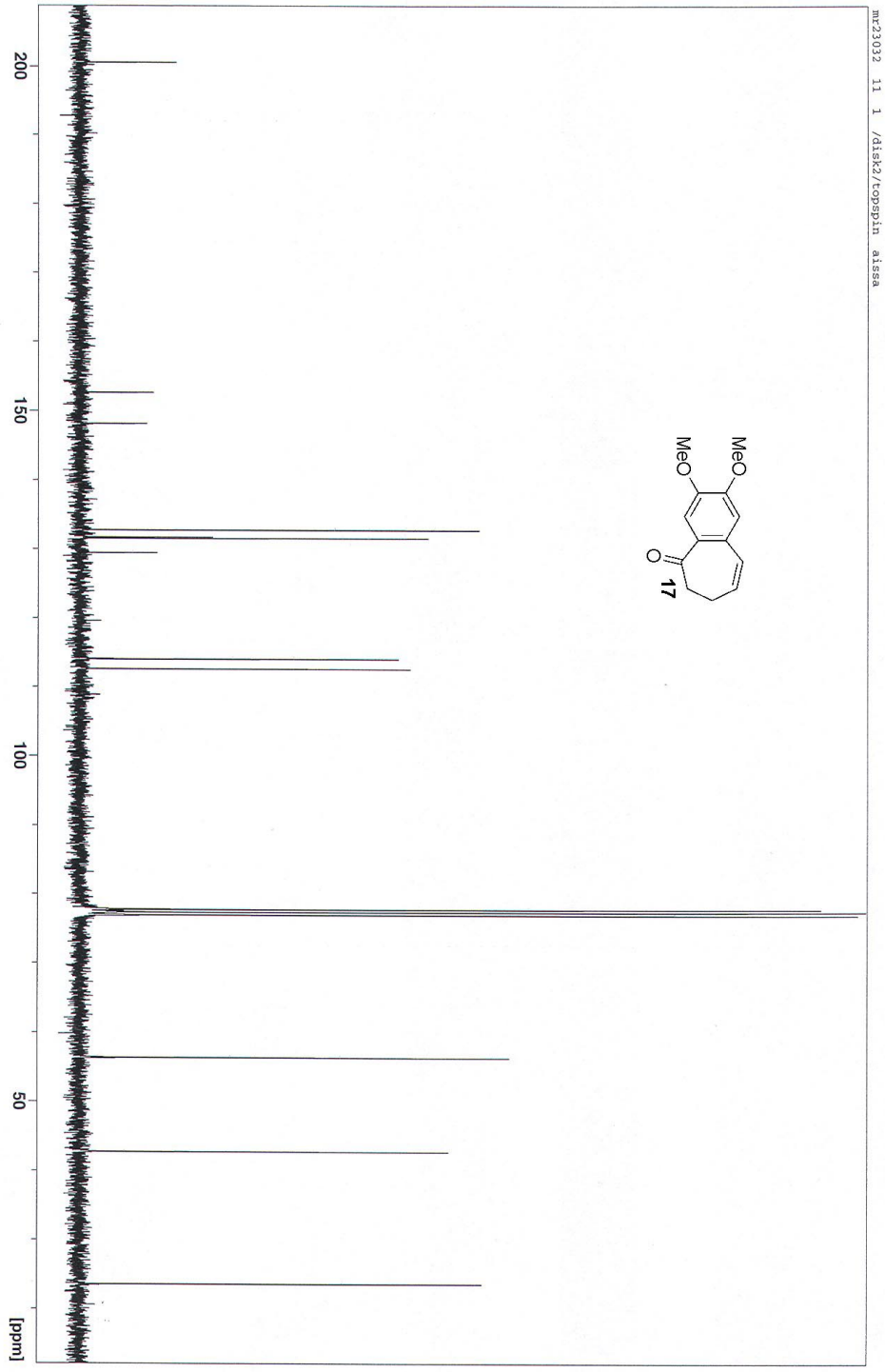

mr23030 10 1 /disk2/topspin aissa
8
6
4
[ppm]
O
15

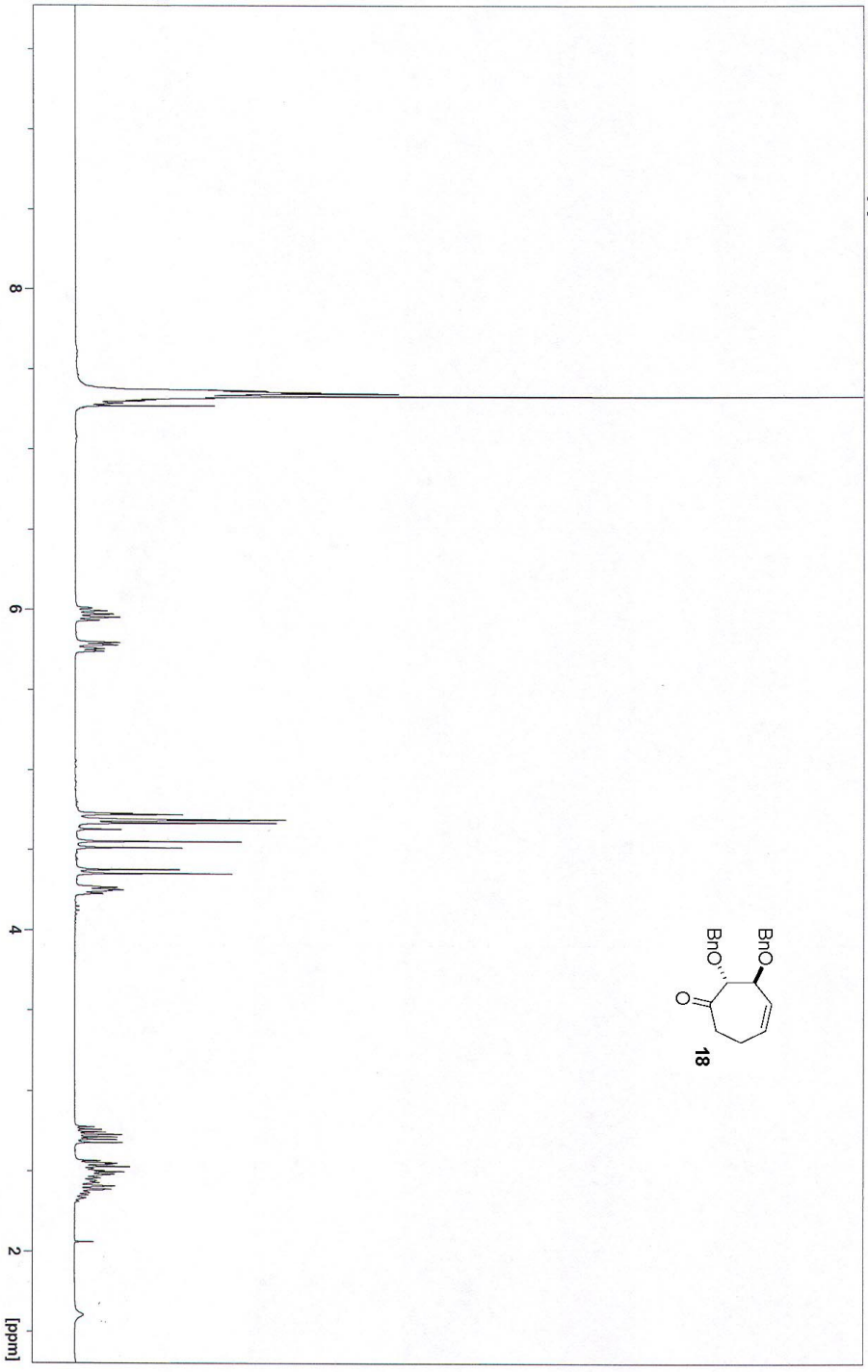

no07034 11 1 /disk2/topspin aissa
O
15
200
150
100
50
[ppm]

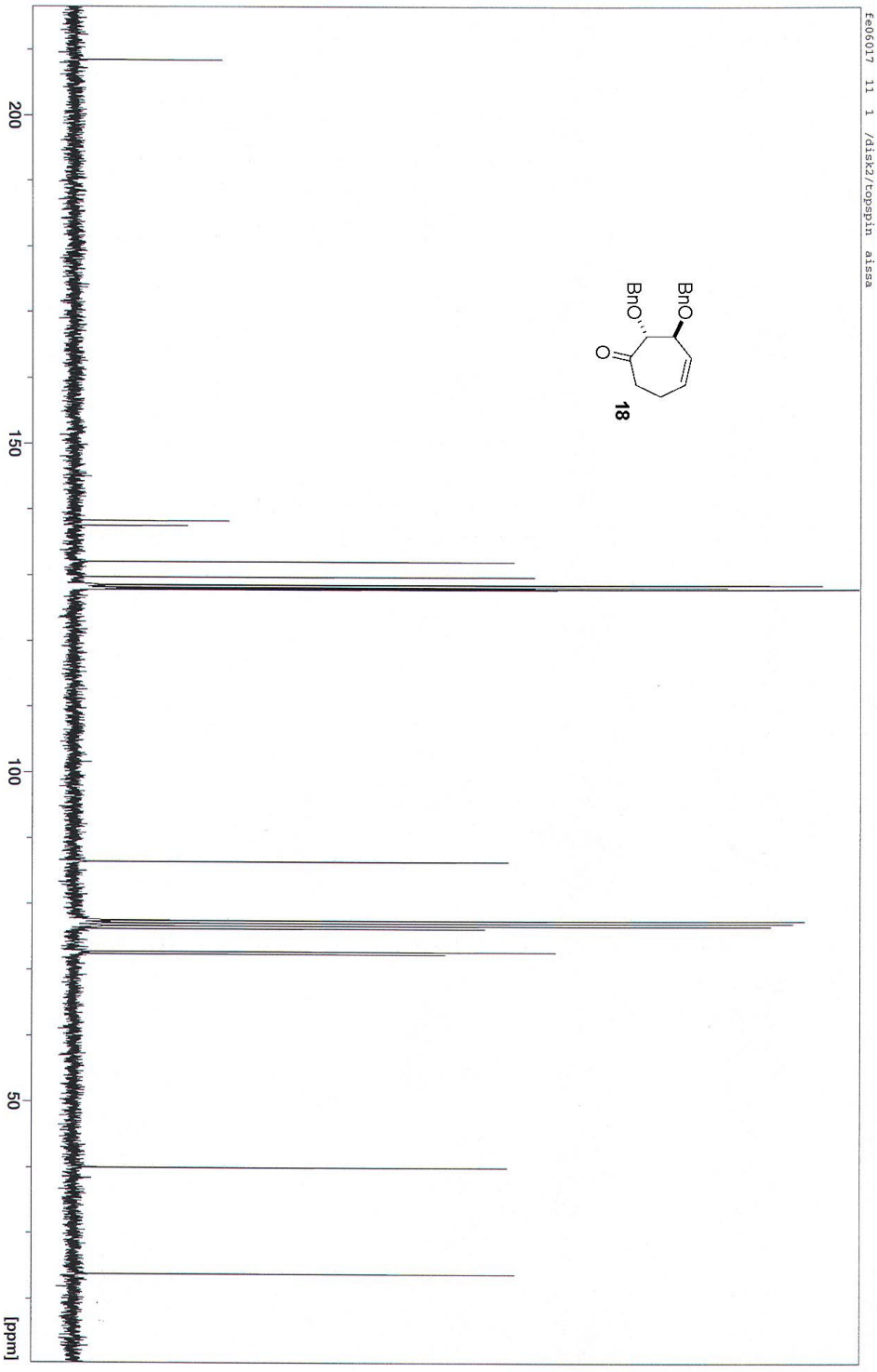

ja25006 10 1 /disk2/topspin aissa
8
6
4
2
[ppm]
Cl
Cl
O
16

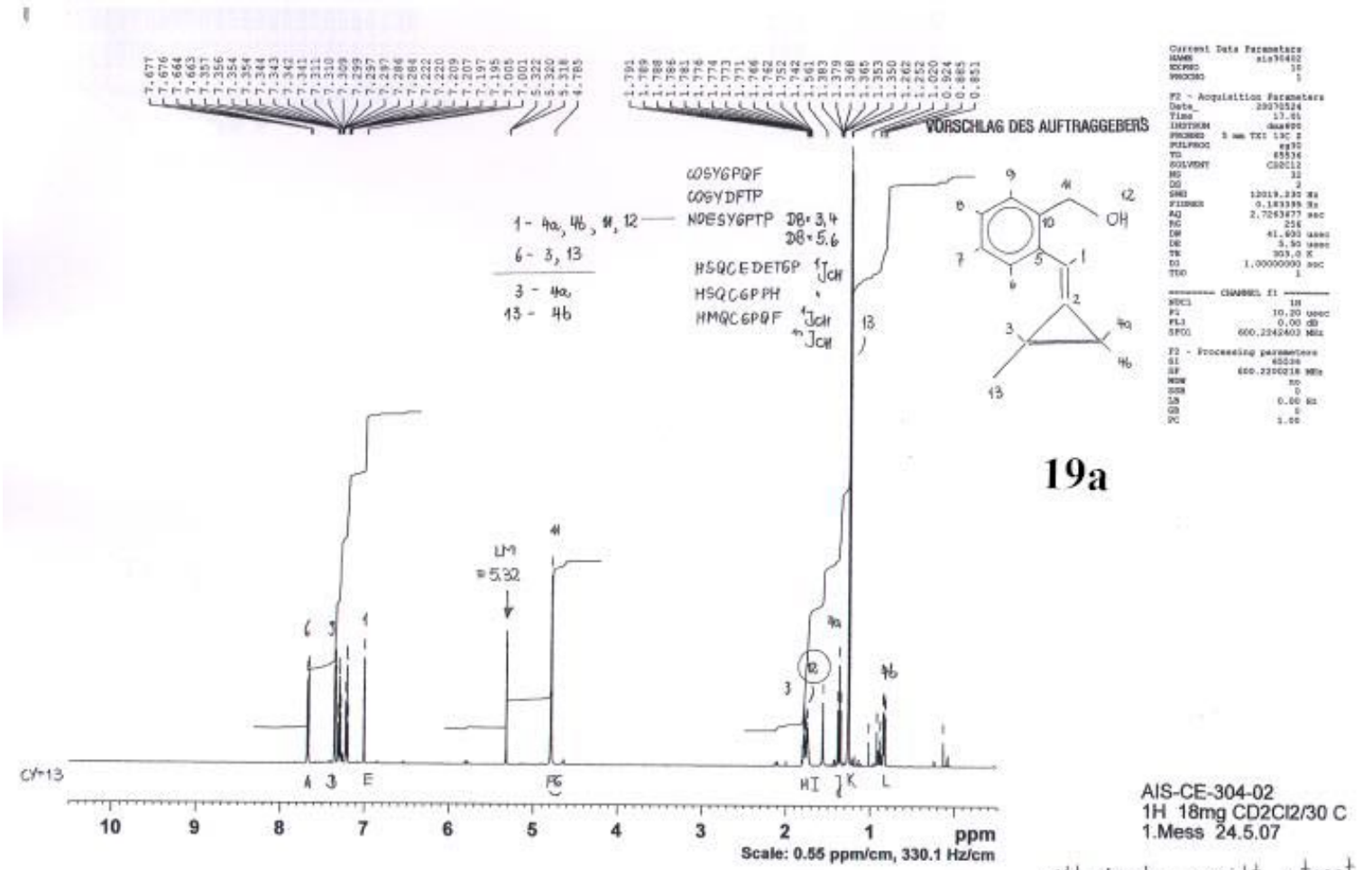

ja25006 11 1 /disk2/topspin aissa
Cl
Cl
O
16
200
150
100
50
[ppm]

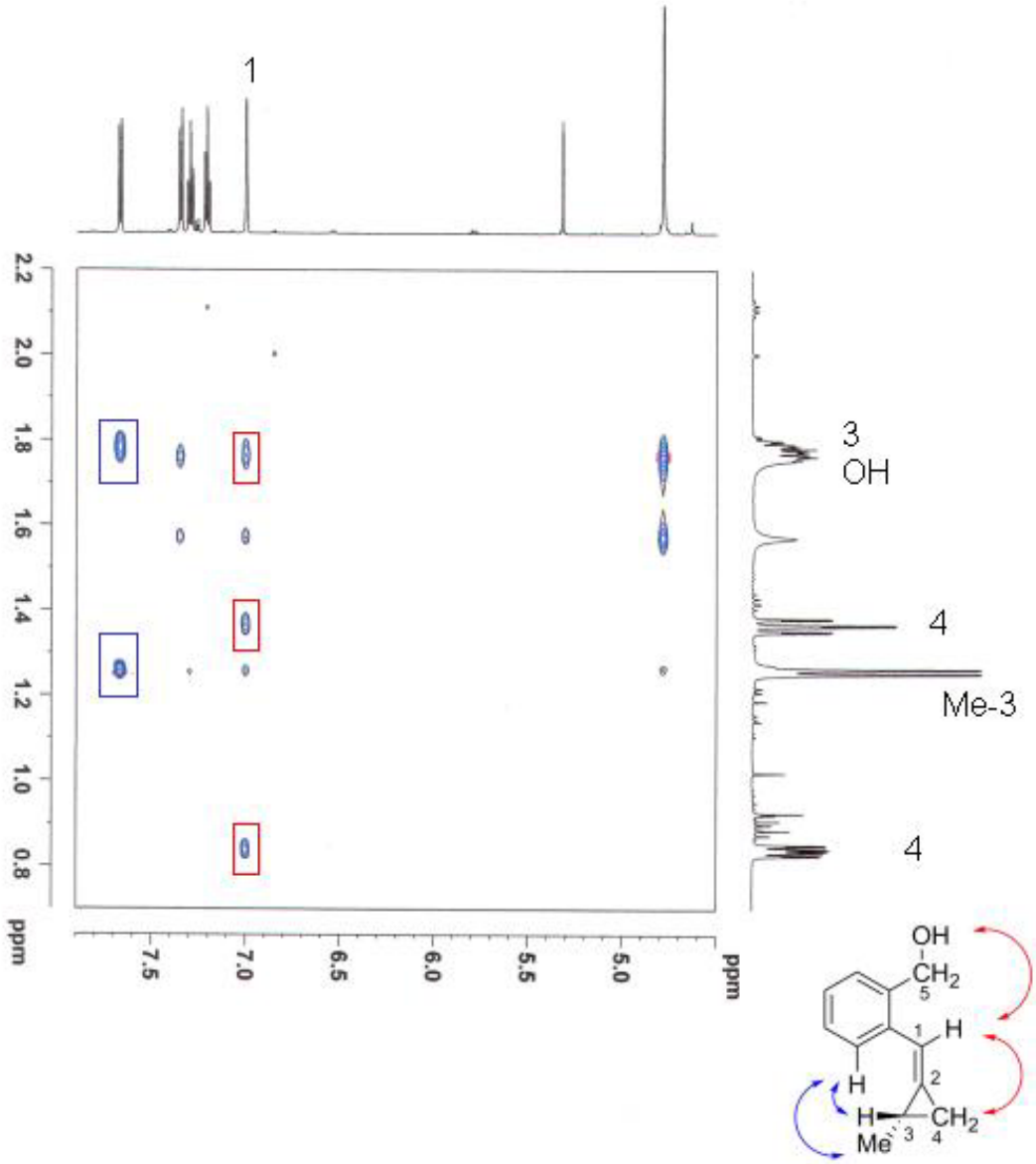

mr23032 10 1 /disk2/topspin aissa
MeO
MeO
O
17
8
7
6
5
4
3
2
[ppm]


mr23032 11 1 /disk2/topspin aissa
MeO
MeO
O
17
200
150
100
50
[ppm]


fe06017 10 1 /disk2/topspin aissa
8
6
4
2
[ppm]
BnO
BnO
O
18

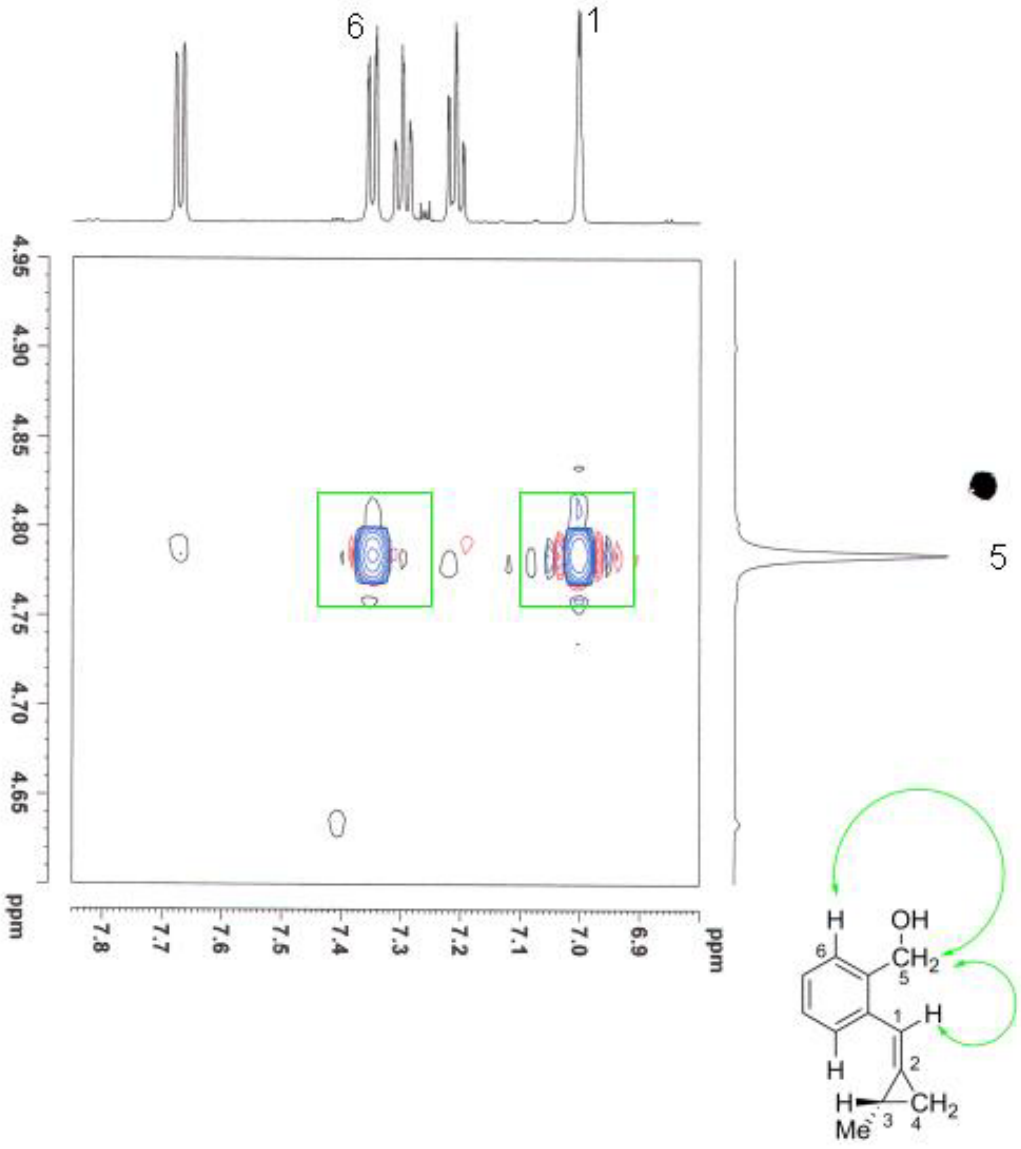

fe06017 11 1 /disk2/topspin aissa
BnO
BnO
O
18
200
150
100
50
[ppm]


VORSCHLAG DES AUFTRAGGEBERS
COSYGPQF
COSYDFTP
NOESYGPTP
HSQCEDETGP
HSQCGPPH
HMQCGPQF
1 - 4a, 4b, 11, 12
6 - 3, 13
3 - 4a,
13 - 4b
OH
19a
AIS-CE-304-02
1H 18mg CD2Cl2/30 C
1.Mess 24.5.07
nicht abgeschm. ; nicht entgast
ppm
Scale: 0.55 ppm/cm, 330.1 Hz/cm



19a

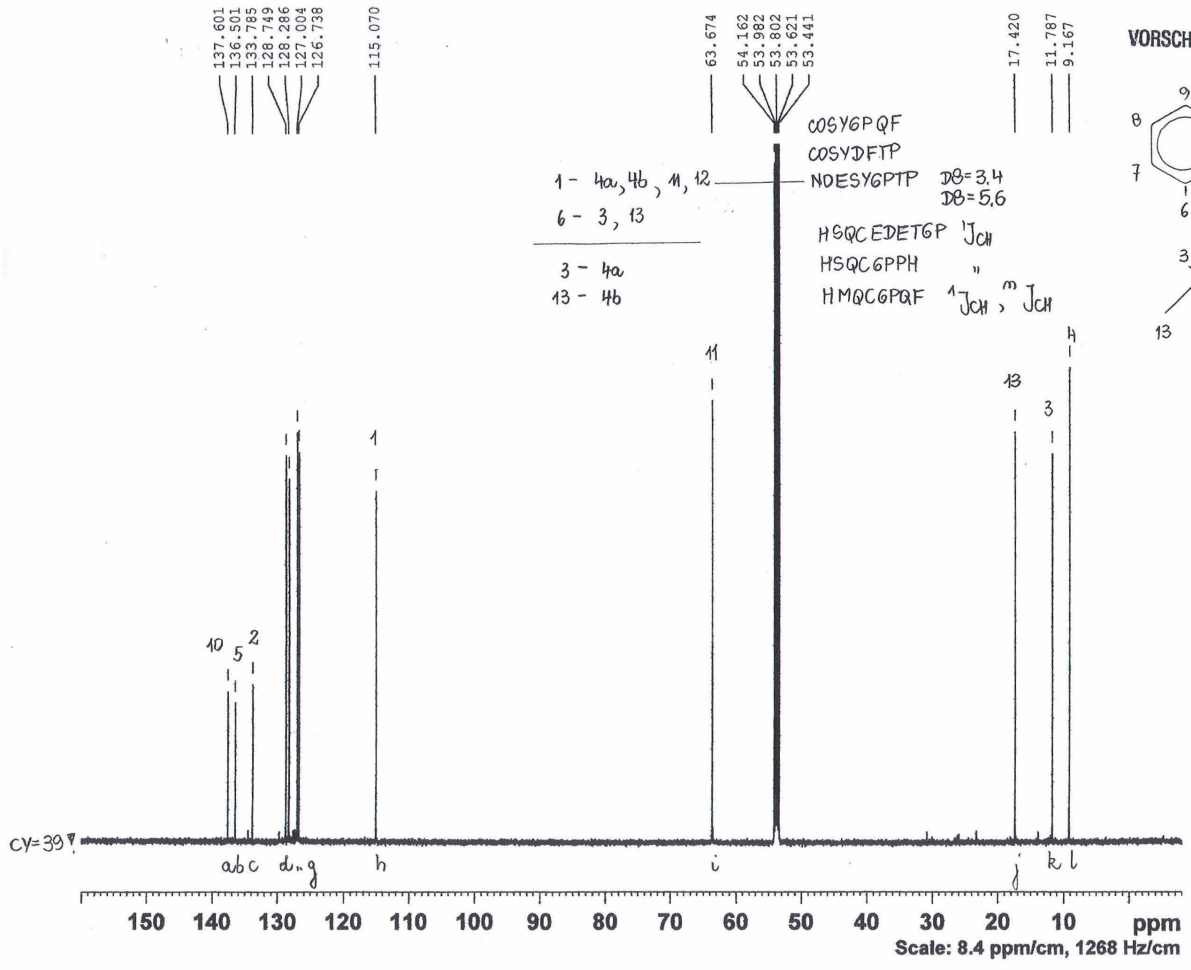
AIS-CE-304-02
NOESYGPTP D8=5.6
18mg CDCl3/30 C

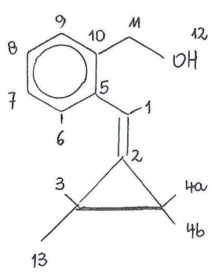


19a

AIS-CE-304-02
NOESYGPTP D8=5.6
18mg CDCl3/30 C

C610094





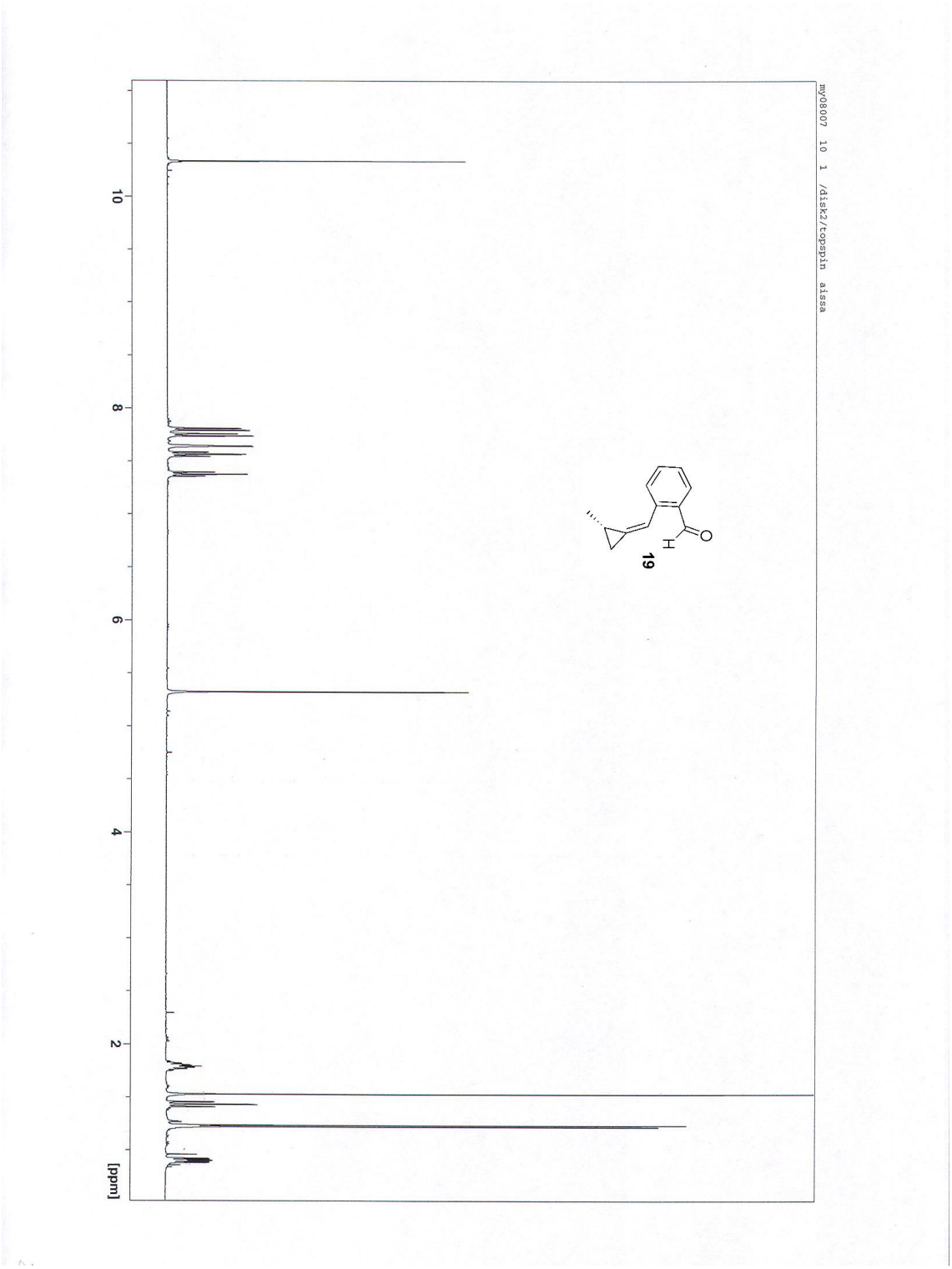
VORSCHLAG DES AUFTRAGGEBERS

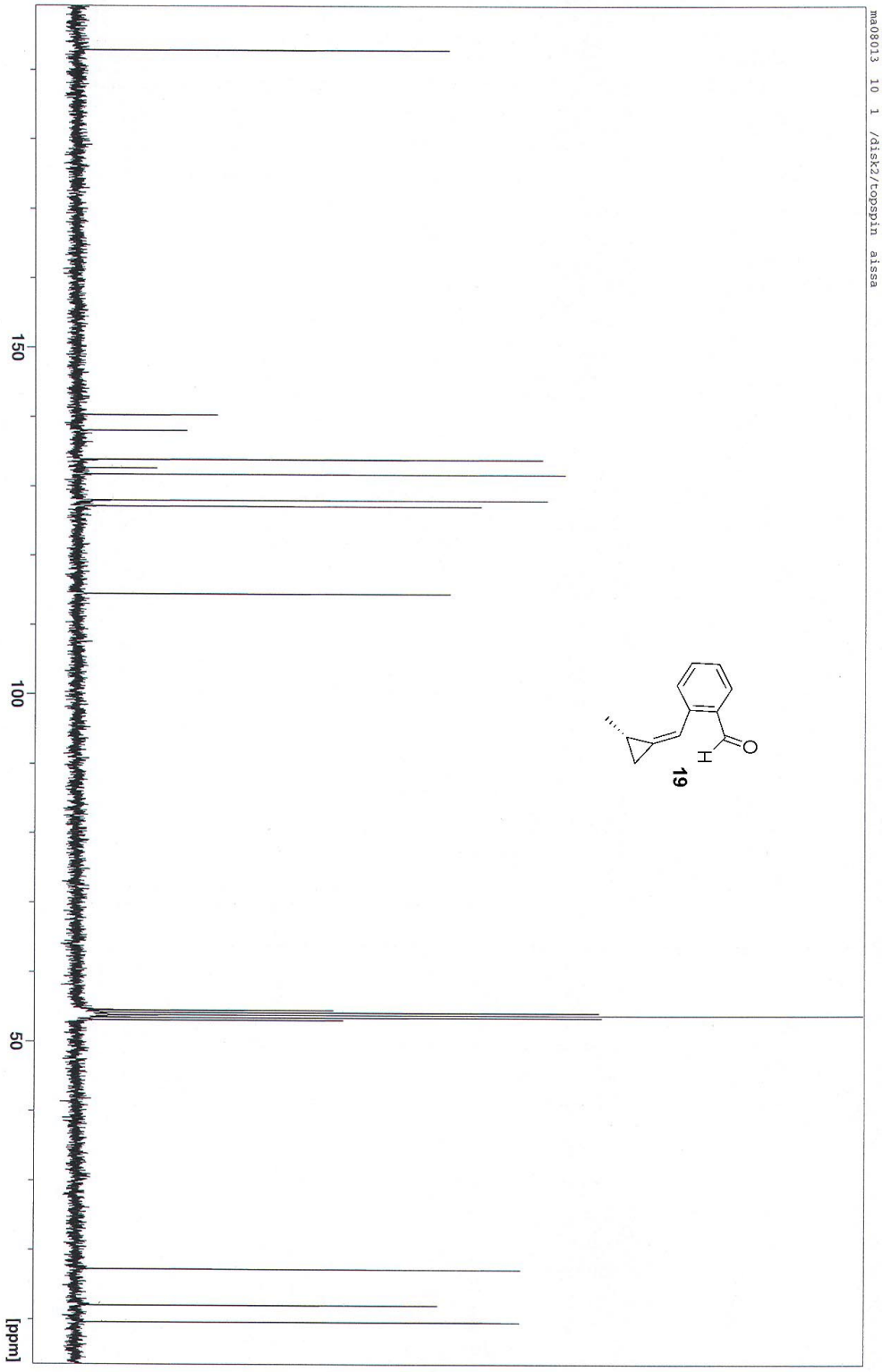
```
Current Data Pa     ters
NAME                0402
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070524
Time               22.37
INSTRUM           dmx600
PROBHD   5 mm TXI 13C z
PULPROG          zgdc30
TD                65536
SOLVENT          CD2Cl2
NS                20000
DS                  640
SWH           37593.984 Hz
FIDRES        0.573639 Hz
AQ            0.8716788 sec
RG                16384
DW               13.300 usec
DE                5.50 usec
TE               303.0 K
D1            0.03000000 sec
d11           0.03000000 sec
TD0                   1

========== CHANNEL f1 ========
NUC1                 13C
P1                16.90 usec
PL1                0.00 dB
SFO1         150.9419356 MHz

========== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2                0.00 dB
PL12              16.31 dB
SFO2         600.2223000 MHz

F2 - Processing parameters
SI                  65536
SF           150.9253799 MHz
WDW                   EM
SSB                    0
LB                 0.80 Hz
GB                     0
PC                  1.00
```

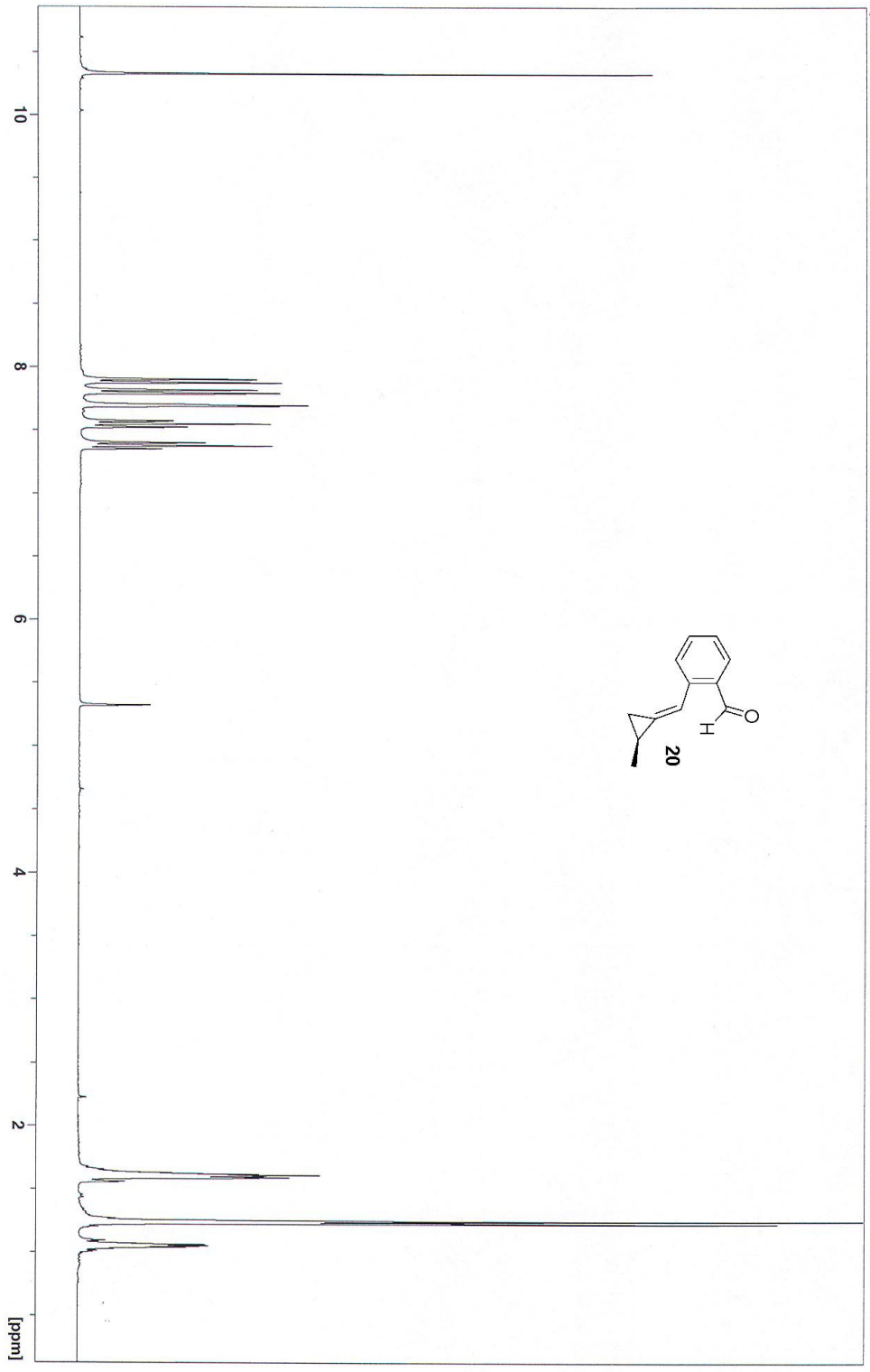
AIS-CE-304-02
13C{1H} 18mg CD2Cl2/30 C

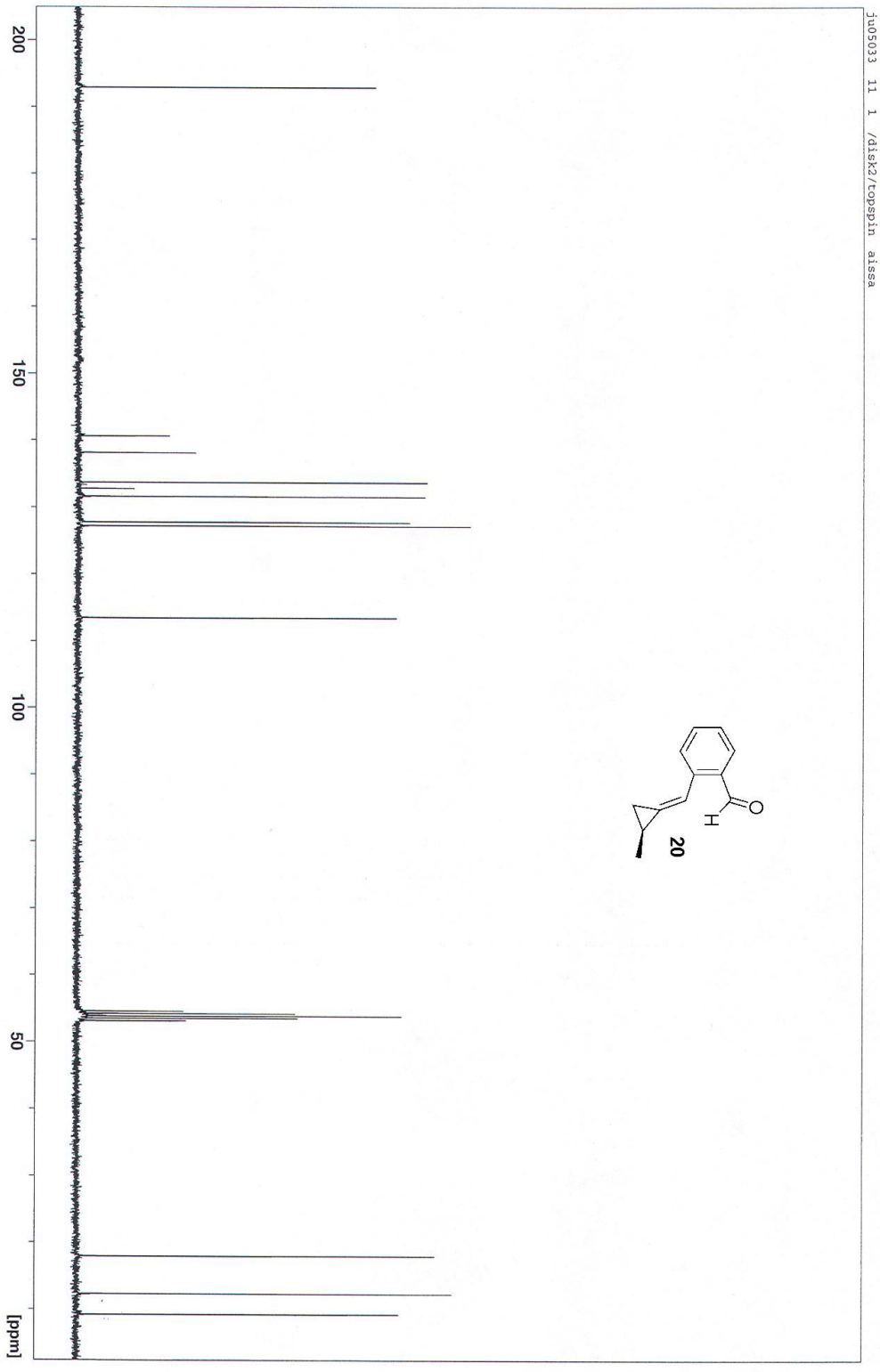
19a 13C

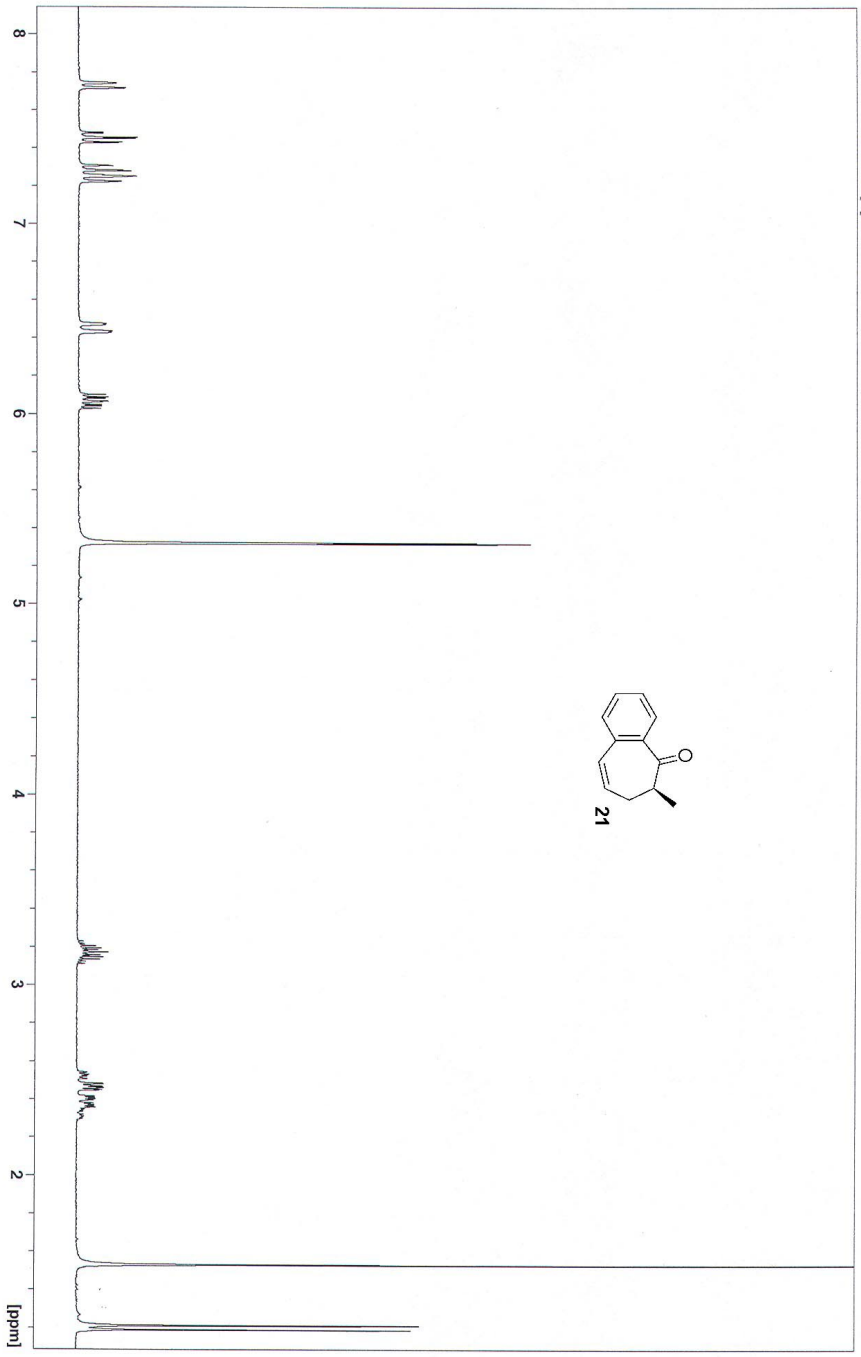
nicht abgedrm. ; nicht entgast

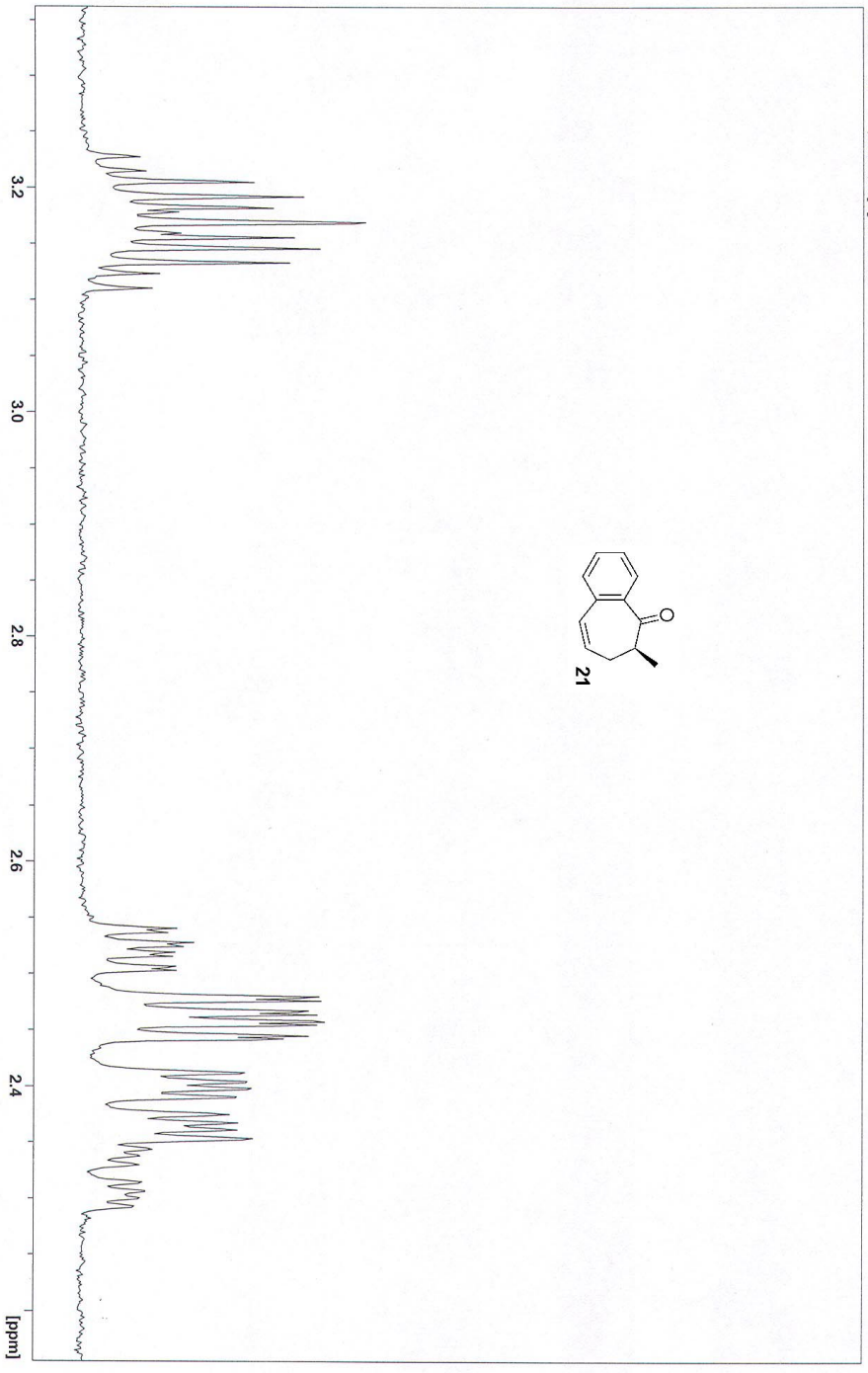

my08007 10 1 /disk2/topspin aissa
10
8
6
4
2
[ppm]
19

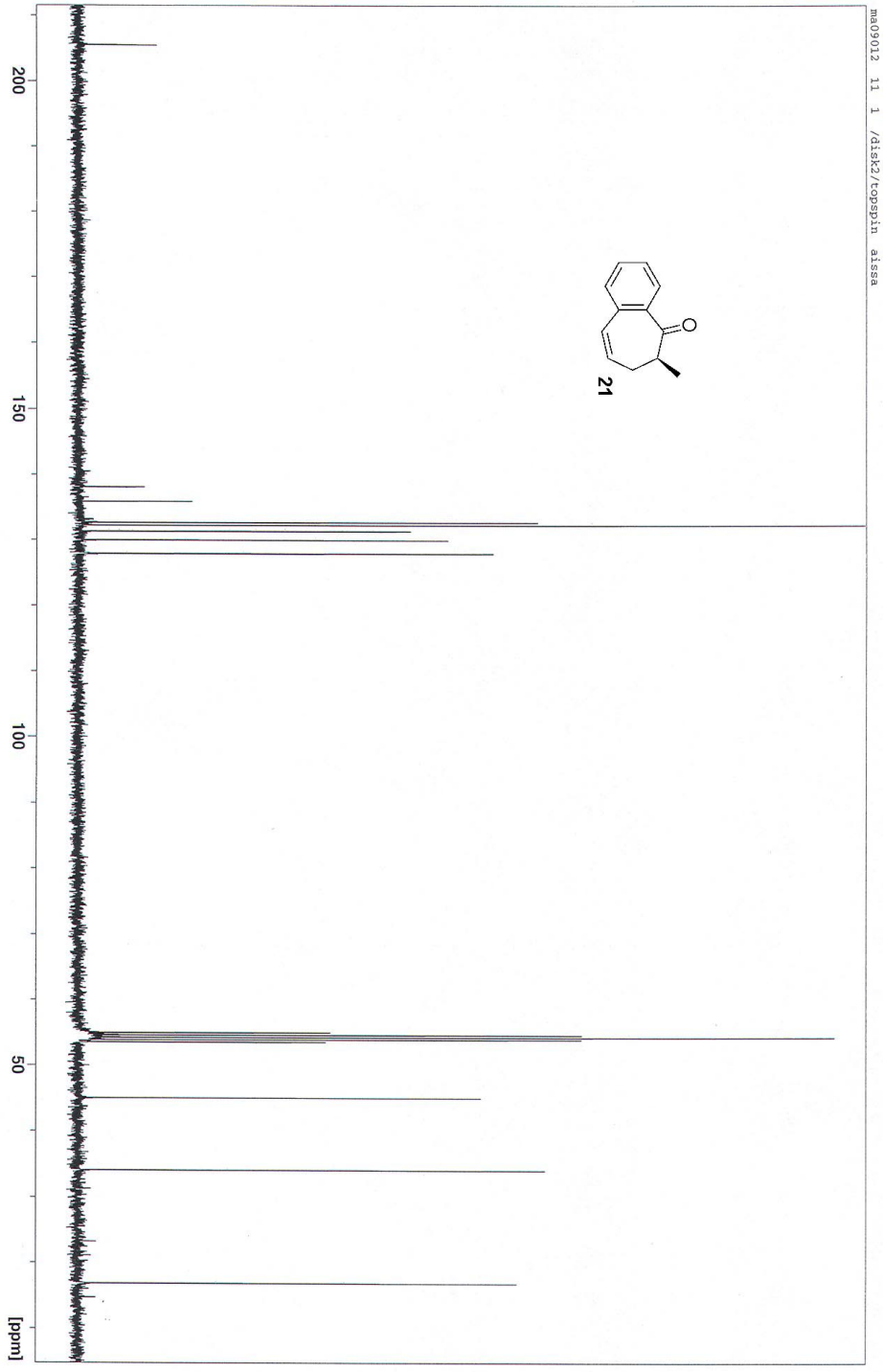

ma08013 10 1 /disk2/topspin aissa
150
100
50
[ppm]
O
H
19

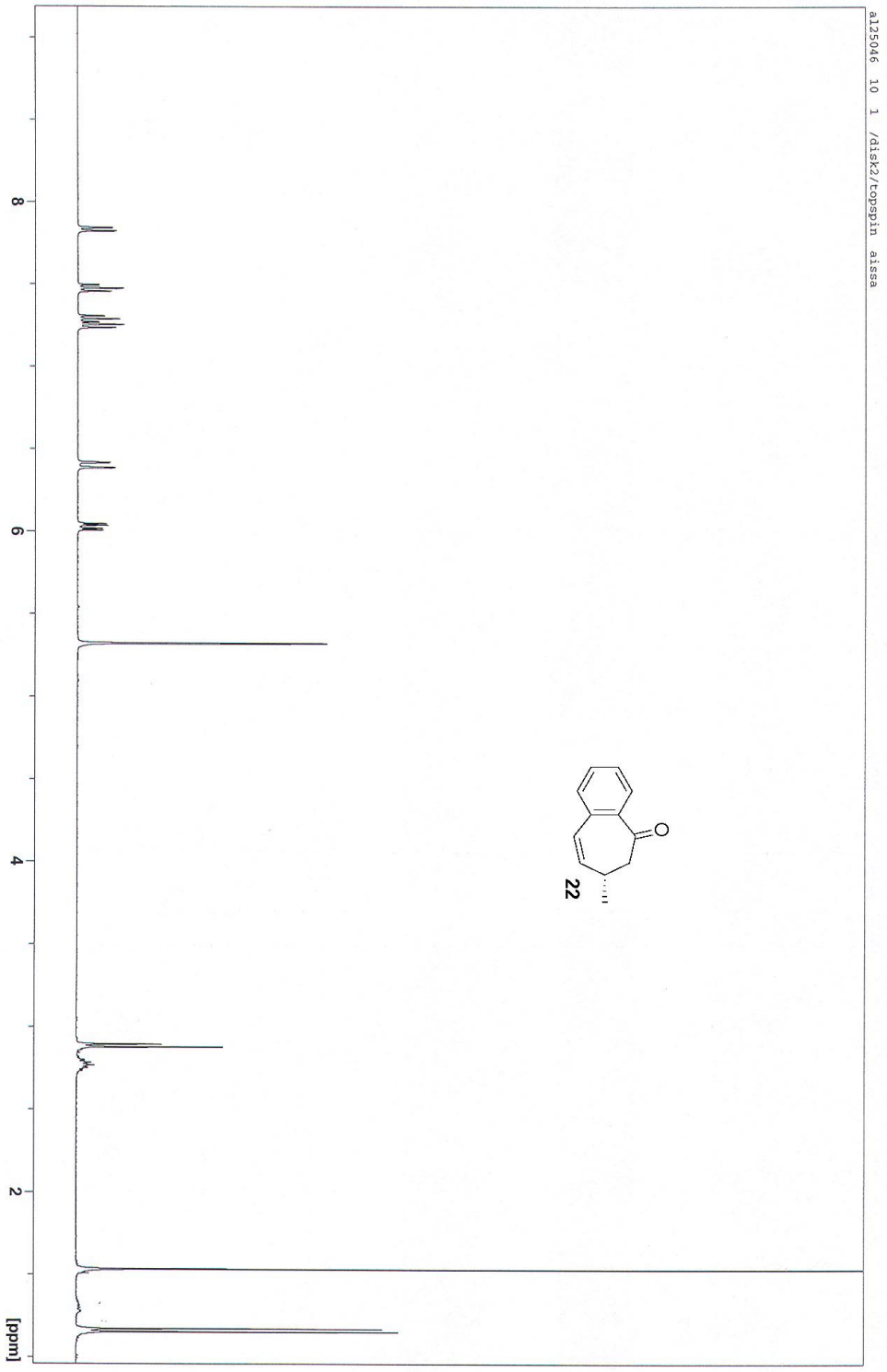

ju05033 10 1 /disk2/topspin aissa
10
8
6
4
2
[ppm]
O
H
20

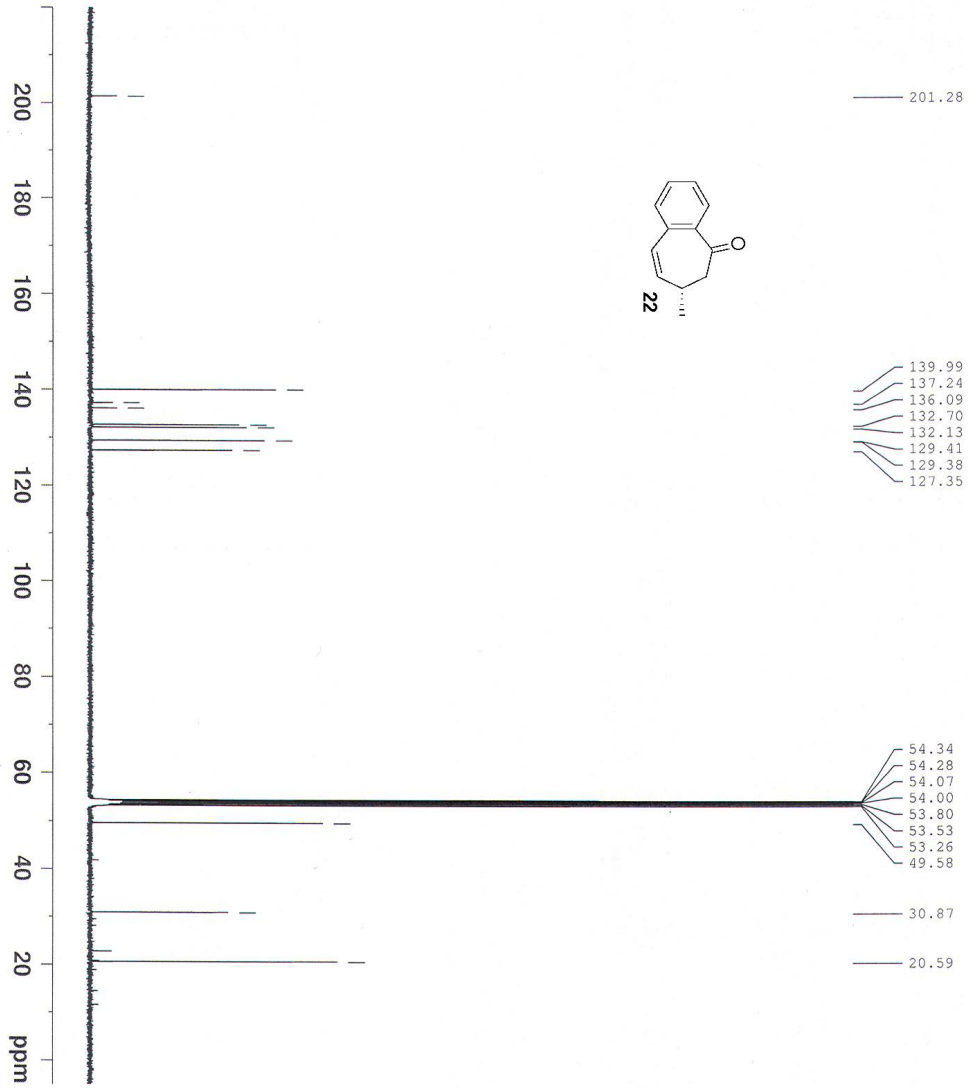

ju05033 11 1 /disk2/topspin aissa
200
150
100
50
[ppm]
O
H
20


ma09013 10 1 /disk2/topspin aissa
8
7
6
5
4
3
2
[ppm]
O
21


ma09013 10 1 /disk2/topspin aissa
3.2
3.0
2.8
2.6
2.4
[ppm]
O
21


ma09012 11 1 /disk2/topspin aissa
21
200
150
100
50
[ppm]


a125046 10 1 /disk2/topspin aissa
8
6
4
2
[ppm]
O
22




```
Current Data Parameters
NAME                  AIS30501
EXPNO                        1
PROCNO                       1
DU              /opt/topspin
USER                    wiswo

F2 - Acquisition Parameters
Date_              20070427
Time_                 15.30
INSTRUM                spect
PROBHD     5 mm BBI 1H-BB
PULPROG             zgdc30
TD                       65536
SOLVENT             CD2Cl2
NS                       372523
DS                           4
SWH                31250.000 Hz
FIDRES                0.476837 Hz
AQ                    1.0486259 sec
RG                       11585.2
DW                      16.000 usec
DE                       7.50 usec
TE                     300.0 K
O1                   12576.60 Hz
O2                    1600.52 Hz
d11                0.03000000 sec
D1                 0.01000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                      14.75 usec
PL1                    -2.00 dB
SFO1          100.6253456 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL12                   22.00 dB
PL2                     0.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF            100.6127283 MHz
WDW                        EM
SSB                         0
LB                       0.80 Hz
GB                          0
PC                       1.40
SR                    -40.75 Hz
HzpPT                 0.953674 Hz
```

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