

SUPPORTING INFORMATION

PtCl₂-Catalyzed Rearrangement of Methylenecyclopropanes

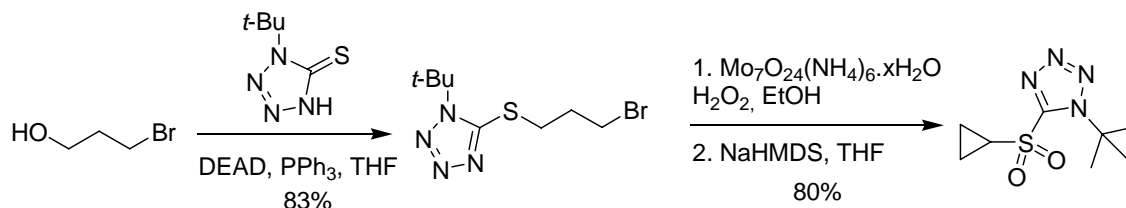
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General. All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O (Mg-anthracene), CH₂Cl₂ (P₄O₁₀), MeCN, Et₃N (CaH₂), MeOH (Mg), DMF, DMA (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on 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 Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_C \equiv 77.0$ ppm; residual CHCl₃ in CDCl₃: $\delta_H \equiv 7.24$ ppm; CD₂Cl₂: $\delta_C \equiv 53.8$ ppm; residual CH₂Cl₂ in CD₂Cl₂: $\delta_H \equiv 5.32$ 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 determinations: 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 (Fluka, Lancaster, Aldrich) were used as received.

Substrates



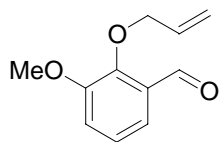
5-(3-Bromo-propylsulfanyl)-1-*tert*-butyl-1*H*-tetrazole. DEAD (1.73 mL, 11 mmol) was added to a solution of PPh₃ (2.89 g, 11 mmol) and 1-*tert*-butyl-1,4-dihydro-5-thio-1*H*-tetrazole (1.74 g, 11 mmol) in THF. The mixture was cooled to 0°C before 3-bromopropan-1-ol (0.9 mL, 10 mmol) was added via syringe. The resulting solution was stirred at ambient temperature for 30 min before all volatile materials were evaporated. The residue was purified by flash chromatography (hexanes/EtOAc gradient, 30/1→20/1→15/1→10/1) to give the title compound as a white solid (2.32 g, 83%). m.p.: 50-53°C. IR (film) 2982, 2938, 1507, 1473, 1431, 1409, 1375, 651, 544 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 3.54 (4H, q, *J* = 6.5 Hz), 2.42 (2H, quint., *J* = 6.7 Hz), 1.73 (9H, s). ¹³C NMR (CDCl₃, 75 MHz): δ = 152.2, 61.3, 32.2, 31.8, 31.7, 28.9 (3C). Anal. *calcd* for C₈H₁₅BrN₄S: C 34.42, H 5.42, N 20.07, *found*: C 34.74, H 5.52, N 20.14.

1-*tert*-Butyl-5-cyclopropanesulfonyl-1*H*-tetrazole. A solution of Mo₇O₂₄(NH₄)₆·xH₂O (2.1 g, 1.7 mmol) in H₂O₂ (30 % w/w, 21 mL) was added dropwise at 0°C within 5 minutes to a solution of 5-(3-bromo-propylsulfanyl)-1-*tert*-butyl-1*H*-tetrazole (5.54 g, 20.2 mmol) in EtOH (155 mL). After stirring for 90 min at room temperature, the solvent was evaporated. The crude material was dissolved in *tert*-butyl methyl ether, the organic phase was washed with water and brine, dried over Na₂SO₄ and concentrated.

A solution of the resulting colorless oil (5.77 g) in THF (45 mL) was slowly added via a dropping funnel within 9h to a solution of NaHMDS (3.74 g) in THF (900 mL) at -78°C. After the addition was complete, the reaction mixture was stirred for 1 h before it was quenched with sat. aq. NH₄Cl. The mixture was partitioned between water and *tert*-butyl methyl ether, the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc, 10/1) furnished compound **2** as a white solid (3.76 g, 80%). m.p. 93-95 °C. IR (KBr): 3067, 3000, 1336, 1161, 1052, 877, 709, 615 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.33-3.23 (1H, m), 1.86 (9H, s), 1.55-1.46 (2H, m), 1.46-1.33 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ = 154.9, 65.5, 33.5, 29.9 (3C), 7.1 (2C). MS (EI) *m/z* (rel. intensity): 111 (13), 110 (30), 82 (6), 67 (5), 57 (100), 41 (66). HRMS (ESIpos): *calcd* for C₈H₁₄N₄NaO₂S: 253.072966, *found*

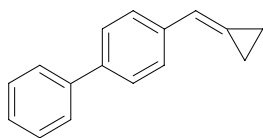
253.072974. Anal. *calcd* for $C_8H_{14}N_4O_2S$: C 41.73, H 6.13, N 24.33; *found* C 41.81, H 6.25, N 24.42.

2-Allyloxy-3-methoxy-benzaldehyde. 2-Hydroxy-3-methoxy-benzaldehyde (760 mg, 5 mmol) was added as a solid to a stirred suspension of NaH (150 mg, 6.25 mmol) in DMF (5 mL) at 0°C. After stirring at room temperature for 2 h, allyliodide (0.9 mL, 10 mmol) was introduced and stirring was continued for 20 h. For work up, the mixture was diluted with *tert*-butyl methyl ether and washed with sat. aq. NH_4Cl and brine. Drying of the organic layer over Na_2SO_4 , evaporation of the solvent, and purification of the residue by flash chromatography (hexanes/EtOAc, 15/1) gave the title compound as a pale yellow oil (737 mg, 68%). IR (neat): 3082, 3011, 2940, 2862, 2841, 2757, 1692, 1648, 1595, 1584, 1482, 1458, 1442, 1422, 1390, 1267, 1249, 1067, 983, 911, 786 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 10.46 (1H, s), 7.45-7.41 (1H, m), 7.16-7.14 (2H, m), 6.09 (1H, ddt, J = 17.2, 10.4, 5.8 Hz), 5.35 (1H, dq, J = 17.1, 1.6 Hz), 5.28 (1H, dq, J = 10.4, 1.2 Hz), 4.68 (2H), 3.92 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.7, 153.2, 151.4, 133.3, 130.3, 124.4, 119.2, 119.1, 118.2, 75.4, 56.2. MS (EI) m/z (rel. intensity): 192 (57), 151 (100), 136 (23), 131 (11), 122 (25), 108 (34), 93 (28), 65 (20), 52 (19), 41 (40). HRMS (EI): *calcd* for $C_{11}H_{12}O_3$: 192.078642, *found* 192.078848. Anal. *calcd* for $C_{11}H_{12}O_3$: C 53.55, H 4.87; *found* C 53.51, H 4.94.



Preparation of Alkylidenecyclopropanes by a Modified Julia-Kocienski Olefination

Representative procedure: 4-Cyclopropylidenemethyl-biphenyl (3). Cs_2CO_3 (1.95 g, 6 mmol) was added to a solution of 4-phenyl-benzaldehyde (364 mg, 2 mmol) and sulfone **2** (690 mg, 3 mmol) in THF (15 mL) and DMF (5 mL). The resulting suspension was stirred at 70°C for 40h. For work up, the mixture was poured into a saturated solution of NH_4Cl , the aqueous layer was extracted with *tert*-butyl methyl ether, the combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and evaporated. Purification of the residue by flash chromatography furnished product **3** as a white solid (313 mg, 76%). m.p. 66-68 °C. IR (KBr): 3086, 3033, 2971, 1747, 1596, 1580, 1558, 1521, 1488, 1450, 1427, 1408, 847, 757, 691 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.58 (6H, m), 7.46 (2H, t, J = 7.6 Hz), 7.38-7.33 (1H, m), 6.82-6.80 (1H, m), 1.51-1.46 (2H, m), 1.26-1.21 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0, 139.6, 137.5, 128.9 (2C), 127.3 (2C), 127.2, 127.1 (2C), 127.0 (2C), 124.8, 118.0, 4.4, 0.9. MS (EI) m/z (rel. intensity): 206 (100), 191 (55), 165 (23), 152 (12), 128 (30), 101 (7), 91 (22). HRMS (EI): *calcd* for $C_{16}H_{14}$: 206.109549, *found* 206.109351. The



deuterated compound **3-D** was obtained analogously. ^1H NMR (300 MHz, CDCl_3): δ = 7.68-7.56 (6H, m), 7.46 (2H, t, J = 7.6 Hz), 7.40-7.33 (1H, m), 1.48 (2H, dd, J = 10.1, 5.3 Hz), 1.24 (2H, dd, J = 9.7, 5.7 Hz). ^{13}C NMR (75 MHz, CDCl_3): δ = 141.1, 139.6, 137.4, 128.9 (2C), 127.3 (2C), 127.2, 127.1 (2C), 127.0 (2C), 124.7, 117.7 (1C, t, J = 24.0 Hz), 4.4, 0.9. MS (EI) m/z (rel. intensity): 207 (100), 192 (41), 166 (13), 152 (12), 129 (21), 102 (4), 91 (15). HRMS (EI): *calcd* for $\text{C}_{16}\text{H}_{13}\text{D}$: 207.115829, *found* 207.115890.

1-Benzyloxy-3-cyclopropylidenemethyl-benzene (5). Prepared analogously as a white solid (156 mg, 66%). m.p. 72-74°C. IR (KBr): 3066, 3033, 2966, 2939, 2886, 1751, 1595, 1585, 1495, 1446, 1419, 1411, 1388, 1253, 1177, 1016, 993, 936, 1862, 808, 744, 696 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.52-7.32 (5H, m), 7.31-7.24 (1H, m), 7.23-7.19 (1H, m), 7.14 (1H, d, J = 7.3 Hz), 6.87 (1H, dd, J = 8.0, 2.6 Hz), 6.74 (1H, quint, J = 1.8 Hz), 5.12 (2H, s), 1.46-1.37 (2H, m), 1.24-1.15 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): δ = 159.1, 139.8, 137.3, 129.5, 128.7 (2C), 128.0, 127.6 (2C), 124.9, 119.9, 118.2, 113.4, 112.9, 70.1, 4.4, 0.7. MS (EI) m/z (rel. intensity): 236 (7), 145 (24), 91 (100). HRMS (EI): *calcd* for $\text{C}_{17}\text{H}_{16}\text{O}$: 236.120112, *found* 236.120433. Anal. *calcd* for $\text{C}_{17}\text{H}_{16}\text{O}$: C 86.41, H 6.82; *found* C 86.31, H 6.85.

4-Cyclopropylidenemethyl-benzoic acid methyl ester (7). Prepared analogously as a white solid (113 mg, 60%). m.p. 53-55 °C. IR (KBr): 3077, 3037, 2977, 2951, 2844, 1720, 1606, 1436, 1278, 1109, 866, 759, 697 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 8.00 (2H, d, J = 8.4 Hz), 7.58 (2H, d, J = 8.4 Hz), 6.81 (1H, quint, J = 2.0 Hz), 3.92 (3H, s), 1.52-1.44 (2H, m), 1.27-1.18 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): δ = 167.2, 143.0, 130.2 (2C), 128.3, 126.6 (2C), 117.9, 52.2, 4.7, 0.9. MS (EI) m/z (rel. intensity): 188 (9), 157 (4), 129 (100). HRMS (EI): *calcd* for $\text{C}_{12}\text{H}_{12}\text{O}_2$: 188.083732, *found* 188.083656. Anal. *calcd* for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C 76.57, H 6.43; *found* C 76.62, H 6.24.

1-Bromo-2-cyclopropylidenemethyl-4,5-dimethoxy-benzene (9). Prepared analogously as a white solid (319 mg, 59%). m.p. 102-105 °C. IR (KBr): 2960, 2935, 2908, 2835, 1778, 1597, 1505, 1461, 1450, 1381, 1257, 1208, 1163, 1026, 857. ^1H NMR (300 MHz, CDCl_3): δ = 7.38 (1H, s), 7.05 (1H, qt, J = 2.0 Hz), 7.02 (1H, s), 3.89 (3H, s), 3.88 (3H, s), 1.45-1.39 (2H, m), 1.25-1.20 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): δ = 148.5, 148.3, 129.8, 124.9, 116.7, 115.2, 113.5, 109.4, 56.1, 55.8, 3.7, 0.7. MS (EI) m/z (rel. intensity): 270 (17), 268 (17), 239 (86), 237 (87), 189 (100), 145 (30). HRMS (ESIpos): *calcd* for $\text{C}_{12}\text{H}_{13}\text{BrO}_2 + \text{Na}$ 290.999126, *found* 290.998798. Anal. *calcd* for $\text{C}_{12}\text{H}_{13}\text{BrO}_2$: C 77.75, H 7.46; *found* C 77.63, H 7.51.

2-Cyclopropylidenemethyl-1,4-dimethoxy-benzene (11). Prepared analogously as a white solid (75 mg, 64%). m.p. 68-70 °C. IR (KBr): 3114, 3085, 3045, 3008, 2961, 2934, 2836, 1721, 1636, 1586, 1500, 1645, 1453, 1417, 1180, 1045, 861, 816, 804 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.34 (1H,

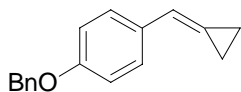
d, $J = 3.0$ Hz), 7.12 (1H, quint, $J = 2.0$ Hz), 6.84 (1H, d, $J = 8.9$ Hz), 6.75 (1H, dd, $J = 8.9, 3.1$ Hz), 3.83 (3H, s), 3.80 (3H, s), 1.45-1.38 (2H, m), 1.22-1.15 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 153.9, 150.9, 128.2, 125.0, 112.6, 112.4$ (2C), 112.2, 56.6, 55.8, 4.1, 0.9. MS (EI) m/z (rel. intensity): 190 (51), 175 (27), 159 (100). HRMS (EI): *calcd* for $\text{C}_{12}\text{H}_{14}\text{O}_2$: 190.099377, *found* 190.09950. Anal. *calcd* for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C 75.76, H 7.42; *found* C 75.60, H 7.42.

1-*tert*-Butyl-(4-cyclopropyliden-butoxy)-dimethyl-silane (13). Prepared analogously as a colorless oil (123 mg, 43%). IR (neat): 3052, 2980, 2955, 2929, 2895, 2857, 1256, 1101, 837, 775 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 5.77$ (1H, tt, $J = 6.7, 2.1$ Hz), 3.64 (2H, t, $J = 6.7$ Hz), 2.23 (2H, q, $J = 7.1$ Hz), 1.68 (2H, quint, $J = 6.8$ Hz), 1.04-1.01 (4H, m), 0.91 (9H, s), 0.06 (6H, s). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 121.4, 118.0, 63.0, 32.7, 28.3, 26.1$ (3C), 18.5, 2.2, 2.0, -5.1 (2C). MS (EI) m/z (rel. intensity): 226 (1), 169 (43), 139 (21), 75 (100). HRMS (ESIpos): *calcd* for $\text{C}_{13}\text{H}_{26}\text{OSi}$: 226.175297, *found* 226.175518.

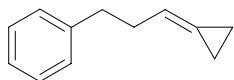
2-Allyloxy-1-cyclopropylidenemethyl-3-methoxy-benzene (17). Prepared analogously as a colorless oil (173 mg, 80%). IR (neat): 3077, 3046, 3007, 2975, 2936, 2836, 1769, 1743, 1647, 1596, 1579, 1475, 1439, 1420, 1271, 1208, 1092, 989, 927, 812, 746 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 7.42$ (1H, dd, $J = 7.9, 1.4$ Hz), 7.14 (1H, quint, $J = 2.0$ Hz), 7.03 (1H, t, $J = 8.0$ Hz), 6.79 (1H, dd, $J = 8.2, 1.4$ Hz), 6.14 (1H, ddt, $J = 17.2, 10.4, 5.8$ Hz), 5.40 (1H, dq, $J = 17.1, 1.6$ Hz), 5.24 (1H, dq, $J = 10.4, 1.2$ Hz), 4.51 (2H, dt, $J = 5.8, 1.3$ Hz), 3.87 (3H, s), 1.44-1.38 (2H, m), 1.20-1.15 (2H, m). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.2, 145.1, 134.5, 132.6, 125.4, 123.9, 118.5, 117.4, 112.5, 110.6, 74.4, 55.9, 4.2, 0.7$. MS (EI) m/z (rel. intensity): 216 (7), 175 (100), 159 (12), 147 (7), 132 (18), 115 (15), 103 (10), 91 (10), 77 (9). HRMS (ESIpos): *calcd* for $\text{C}_{14}\text{H}_{16}\text{NaO}_2$: 239.104248, *found* 239.104492. Anal. *calcd* for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C 68.74, H 6.29; *found* C 68.52, H 6.36.

4-Cyclopropylidenemethyl-1,2-dimethoxy-benzene (22). Prepared analogously as a white solid (73 mg, 62%). m.p. 78-81 °C. IR (KBr): 3084, 3044, 3008, 2963, 2925, 2840, 1781, 1600, 1585, 1516, 1471, 1455, 1419, 1229, 1158, 1141, 1027, 858, 827, 787, 776 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 7.16$ (1H, d, $J = 1.8$ Hz), 7.05 (1H, dd, $J = 8.3, 1.9$ Hz), 6.85 (1H, d, $J = 8.3$ Hz), 6.69 (1H, quint, $J = 2.0$ Hz), 3.92 (3H, s), 3.90 (3H, s), 1.45-1.37 (2H, m), 1.21-1.14 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 149.1, 148.2, 131.7, 122.2, 119.5, 118.0, 111.3, 109.4, 56.1, 55.9, 4.1, 0.7$. MS (EI) m/z (rel. intensity): 190 (31), 175 (14), 159 (100). HRMS (EI): *calcd* for $\text{C}_{12}\text{H}_{14}\text{O}_2$: 190.099383, *found* 190.099238. Anal. *calcd* for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C 75.76, H 7.42; *found* C 75.56, H 7.36.

1-Benzyloxy-4-cyclopropylidenemethyl-benzene (25). Prepared analogously as a white solid (145 mg, 56%). m.p. 72-74 °C. IR (KBr): 3060, 3037, 2968, 2942, 2922, 2865, 1764, 1606, 1573, 1510, 1452, 1414, 1381, 1249, 1012, 837, 741, 696 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.51-7.43 (3H, m), 7.42-7.38 (2H, m), 7.37-7.33 (1H, m), 6.96 (2H, d, J = 9.0 Hz), 6.70 (1H, quint, J = 2.0 Hz), 5.09 (2H, s), 1.42-1.36 (2H, m), 1.19-1.14 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): δ = 157.8, 137.2, 131.6, 128.7 (2C), 128.1, 127.8 (2C), 127.6 (2C), 122.0, 117.6, 115.0 (2C), 70.1, 4.1, 0.6. MS (EI) m/z (rel. intensity): 236 (6), 145 (52), 91 (100). HRMS (EI): *calcd* for $\text{C}_{17}\text{H}_{16}\text{O}$: 236.120118, *found* 236.120187. Anal. *calcd* for $\text{C}_{17}\text{H}_{16}\text{O}$: C 86.41, H 6.82; *found* C 86.35, H 6.84.

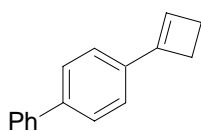


(3-Cyclopropylidene-propyl)-benzene (15). *t*-BuOK (750 mg, 6.6 mmol) was added in portions within 15 minutes to a stirred suspension of 3-bromopropyl triphenylphosphonium bromide (1.56 g, 3.3 mmol) in THF (20 mL). The orange mixture was then stirred at 70°C for 2h, before 3-phenyl-propionaldehyde (0.4 mL, 3 mmol) was added and reflux was continued for 2h. The reaction was quenched at room temperature with water, the aqueous layer was extracted twice with hexanes, and the combined organic layers were washed with brine and were dried over Na_2SO_4 . Evaporation of the solvent followed by flash chromatography (pentanes) of the residue gave the title compound as a colorless oil (274 mg, 58%). IR (neat): 3027, 2978, 2924, 2853, 1603, 1495, 1453, 1410, 743, 695 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.39-7.15 (5H, m), 5.81 (1H, tt, J = 6.7, 2.1 Hz), 2.78 (2H, dd, J = 8.4, 7.2 Hz), 2.51 (2H, q, J = 7.5 Hz), 1.07-0.93 (4H, m). ^{13}C NMR (75 MHz, CDCl_3): δ = 142.4, 128.6 (2C), 128.4 (2C), 125.8, 122.1, 117.5, 35.9, 33.8, 2.3, 2.0. MS (EI) m/z (rel. intensity): 158 (2), 143 (22), 130 (28), 91 (100). HRMS (EI): *calcd* for $\text{C}_{12}\text{H}_{14}$: 158.109548, *found* 158.109365.



PtCl₂ Catalyzed Rearrangement Reactions

Representative Procedure: 4-Cyclobuten-1-yl-biphenyl (4). PtCl₂ (1 mg, 0.0038 mmol) was added to a solution of 4-cyclopropylidenemethyl-biphenyl **3** (90 mg, 0.437 mmol) in toluene (4.3 mL). CO was bubbled into the solution via a needle for ca. 30 seconds and the resulting mixture was then stirred at 80 °C under CO atmosphere (1 atm). For work up, the mixture was filtered under Argon through a short pad of silica and the filtrate was evaporated to give product **4** as a white, air sensitive solid (69 mg, 77%). IR (KBr): 3054, 3030, 2949, 2915, 1867, 2834, 1672, 1596, 1580, 1485, 1448, 1407, 840, 745, 689 cm^{-1} . ^1H NMR (300 MHz, CD_3CN): δ = 7.68-7.60 (4H, m), 7.50-7.42 (4H, m), 7.40-7.33 (1H, m), 6.82-6.80 (1H, t, J = 1.4 Hz), 2.87-2.83 (2H, m), 2.57-2.53 (2H, m). ^{13}C NMR (75 MHz, CD_3CN): δ = 147.1, 141.4, 140.9, 135.1, 129.9 (2C), 128.6, 128.4, 127.9 (2C), 127.7 (2C), 125.7 (2C), 29.4, 27.0. MS (EI) m/z



(rel. intensity): 206 (100), 191 (38), 178 (37), 165 (16), 152 (15), 128 (17), 101 (8), 91 (15). HRMS (EI): *calcd* for $C_{16}H_{14}$: 206.109547, *found* 206.109387.

All other cyclobutenes were prepared analogously. Their analytical and spectroscopic data are compiled below:

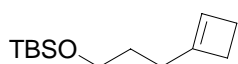
1-Benzyloxy-3-cyclobuten-1-yl-benzene (6). White, air sensitive solid (27 mg, 90%). IR (neat): 3041, 2948, 2918, 2838, 1591, 1576, 1485, 1464, 1455, 1433, 1383, 1324, 1286, 1241, 1220, 1205, 1183, 1160, 1012, 852, 803, 746, 696 cm^{-1} . 1H NMR (300 MHz, CD_3CN): δ = 7.49-7.32 (5H, m), 7.25 (1H, t, J = 7.8 Hz), 7.01-6.95 (2H, m), 6.92-6.86 (1H, m), 6.33 (1H, t, J = 1.4 Hz), 5.11 (2H, s), 2.82-2.77 (2H, m), 2.55-2.48 (2H, m). ^{13}C NMR (75 MHz, CD_3CN): δ = 160.0, 147.4, 138.5, 137.5, 130.5, 129.5 (2C), 128.9, 128.8, 128.7 (2C), 117.8, 115.3, 111.5, 70.6, 29.5, 26.8. MS (EI) m/z (rel. intensity): 236 (16), 145 (3), 91 (100). HRMS (EI): *calcd* for $C_{17}H_{16}O$: 236.120119, *found* 236.120340.

4-Cyclobuten-1-yl-benzoic acid methyl ester (8). White, air sensitive solid (25 mg, 80%). IR (neat): 2946, 2910, 2831, 1717, 1601, 1567, 1433, 1410, 1276, 1108, 1027, 735 cm^{-1} . 1H NMR (300 MHz, CD_3CN): δ = 7.96 (2H, d, J = 8.4 Hz), 7.47 (2H, d, J = 7.7 Hz), 6.51 (1H, t, J = 1.4 Hz), 3.86 (3H, s), 2.88-2.83 (2H, m), 2.58-2.53 (2H, m). ^{13}C NMR (75 MHz, CD_3CN): δ = 167.5, 146.6, 140.0, 131.9, 130.5 (2C), 130.0, 125.1 (2C), 52.6, 29.4, 27.2. MS (EI) m/z (rel. intensity): 188 (34), 157 (17), 129 (100), 59 (7). HRMS (EI): *calcd* for $C_{12}H_{12}O_2$: 188.083730, *found* 188.083494.

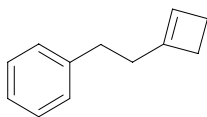
1-Bromo-2-cyclobuten-1-yl-4,5-dimethoxy-benzene (10). White, air sensitive solid (18 mg, 61%). IR (KBr): 3084, 3001, 2919, 2834, 1690, 1593, 1565, 1508, 1458, 1432, 1338, 1259, 1211, 1170, 1027, 852, 785 cm^{-1} . 1H NMR (300 MHz, CD_2Cl_2): δ = 6.99 (1H, s), 6.77 (1H, s), 6.56 (1H, s), 3.80 (6H, s), 2.92-2.89 (2H, m), 2.51-2.46 (2H, m). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 149.6, 149.1, 145.1, 132.5, 127.6, 117.3, 112.2, 111.3, 56.8, 56.7, 31.8, 27.0. MS (EI) m/z (rel. intensity): 270 (37), 268 (38), 242 (10), 240 (8), 189 (100), 158 (58). HRMS (EI): *calcd* for $C_{12}H_{13}BrO_2$: 268.009907, *found* 268.010036.

2-Cyclobuten-1-yl-1,4-dimethoxy-benzene (12). Pale yellow, air sensitive solid (50 mg, 50%). IR (KBr): 3001, 2956, 2911, 2832, 1613, 1586, 1497, 1464, 1452, 1442, 1397, 1315, 1279, 1215, 1044, 854, 821, 814, 766, 739 cm^{-1} . 1H NMR (300 MHz, CD_3CN): δ = 6.88 (1H, d, J = 8.8 Hz), 6.79 (1H, dd, J = 8.8, 2.9 Hz), 6.74 (1H, d, J = 3.3 Hz), 6.34 (1H, t, J = 1.3 Hz), 3.80 (3H, s), 3.74 (3H, s), 2.85-2.81 (2H, m), 2.56-2.51 (2H, m). ^{13}C NMR (75 MHz, CD_3CN): δ = 154.4, 153.6, 143.9, 133.4, 125.3, 114.0, 113.2, 112.8, 56.2 (2C), 30.6, 27.8. MS (EI) m/z (rel. intensity): 190 (100), 175 (51), 159 (75). HRMS (EI): *calcd* for $C_{12}H_{14}O_2$: 190.099384, *found* 190.099162.

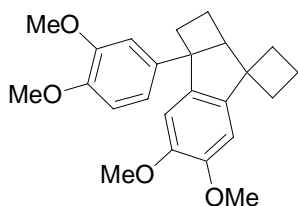
1-*tert*-Butyl-(4-cyclobuten-1-yl)-dimethyl-silane (14). Colorless, air sensitive oil (10 mg, 93%). IR (neat): 2928, 2857, 1631, 1472, 1254, 1099, 832, 773 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 5.69-5.67 (1H, m), 3.64 (2H, t, J = 6.6 Hz), 2.45-2.41 (2H, m), 2.36-2.32 (2H, m), 2.09-2.00 (2H, m), 1.66 (2H, quint, J = 6.7 Hz), 0.91 (9H, s), 0.06 (6H, s). ^{13}C NMR (75 MHz, CDCl_3): δ = 150.4, 126.9, 63.0, 31.3, 30.1, 27.5, 26.6, 26.1 (3C), 18.5, -5.1 (2C). MS (EI) m/z (rel. intensity): 169 (47), 141 (28), 75 (100). HRMS (CI): *calcd* for $\text{C}_{13}\text{H}_{17}\text{OSi}$: 227.183121, *found* 227.183220.



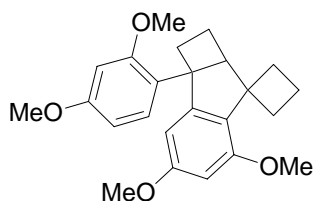
(3-Cyclobutenyl-propyl)-benzene (16). Colorless, air sensitive oil (30 mg, 95%). IR (neat): 3028, 2919, 2841, 1629, 1604, 1496, 1453, 1410, 853, 747, 696 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.32-7.27 (2H, m), 7.23-7.17 (3H, m), 5.71 (1H, s), 2.79 (2H, dd, J = 8.2, 7.2 Hz), 2.46-2.43 (2H, m), 2.38-2.30 (4H, m). ^{13}C NMR (75 MHz, CDCl_3): δ = 150.0, 142.3, 128.4 (4C), 127.4, 125.9, 33.3, 33.0, 31.4, 26.7. MS (EI) m/z (rel. intensity): 158 (2), 143 (10), 130 (29), 91 (100). HRMS (EI): *calcd* for $\text{C}_{12}\text{H}_{14}$: 158.109551, *found* 158.109352.



Compound 23. PtCl_2 (2 mg, 0.0075 mmol) was added to a solution of compound **22** (30 mg, 0.158 mmol) in toluene (0.1 M) and the resulting mixture was stirred at 80°C under CO atmosphere for 4h. Purification of the crude mixture by flash chromatography (hexanes, then hexanes/EtOAc, 4/1) gave a first fraction of pure compound **23** (10 mg) and second fraction of a mixture of **23** and its regioisomer **24** (16 mg), both as colorless oils (combined yield 87%). IR (neat): 2931, 1831, 1603, 1587, 1513, 1498, 1642, 1334, 1245, 1173, 1139, 1109, 1027, 849, 759 cm^{-1} . ^1H NMR (600 MHz, CDCl_3): δ = 6.94 (1H, s), 6.78 (1H, d, J = 8.3 Hz), 6.72 (1H, dd, J = 8.2, 2.1 Hz), 6.56 (1H, d, J = 2.1 Hz), 6.44 (1H, s), 3.93 (3H, s), 3.82 (3H, s), 3.76 (3H, s), 3.74 (3H, s), 3.10 (1H, t, J = 8.1 Hz), 2.69 (1H, dt, J = 11.1, 9.7 Hz), 2.39-2.33 (1H, m), 2.26-2.18 (4H, m), 2.08-1.94 (3H, m), 1.62-1.55 (1H, m). ^{13}C NMR (150 MHz, CDCl_3): δ = 149.2, 149.0, 148.8, 147.0, 142.2, 141.0, 140.8, 117.6, 111.0, 109.6, 106.9, 105.8, 57.5, 57.3, 56.1, 56.0, 55.9, 55.7, 53.4, 38.1, 29.6, 28.5, 19.5, 16.0. MS (EI) m/z (rel. intensity): 380 (42), 352 (74), 324 (100). HRMS (ESIpos): *calcd* for $\text{C}_{24}\text{H}_{28}\text{O}_4 + \text{Na}$: 403.187979, *found* 403.188368.



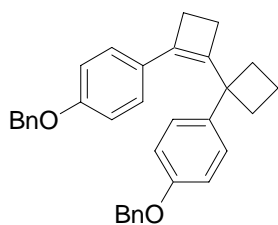
Regioisomer **24**: (resolved signals) ^1H NMR (400 MHz, CDCl_3): δ = 7.00-6.95 (2H, m), 6.60 (1H, d, J = 2.0 Hz), 3.83 (3H, s), 3.82 (3H, s), 3.80 (3H, s), 3.68 (3H, s), 2.66-2.56 (4H, m), 2.55-2.48 (2H, m), 2.47-2.41 (2H, m). ^{13}C NMR (100 MHz, CDCl_3): δ = 148.9, 147.9, 147.2, 145.9, 117.9, 110.6, 110.0, 109.9, 55.8, 55.6, 33.8, 26.6, 26.3, 25.4, 16.7.



Compound 21. This compound was obtained analogously from substrate **11** as a white solid (16 mg, 53%). m.p. 160-163°C. IR (neat): 2942, 2831, 1587, 1487, 1463, 1436, 1416, 1281, 1253, 1221, 1204, 1178, 1081, 1057, 1032, 874, 796, 725 cm^{-1} . ^1H NMR (600 MHz, CDCl_3): δ = 6.79 (1H, d, J = 2.9 Hz), 6.71 (1H, d, J =

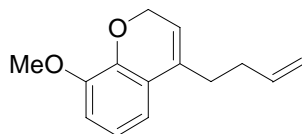
8.6 Hz), 6.66 (1H, d, $J = 8.8$ Hz), 6.63 (1H, dd, $J = 8.8, 2.9$ Hz), 6.57 (1H, d, $J = 8.6$ Hz), 3.86 (3H, s), 3.72 (3H, s), 3.51 (3H, s), 3.47 (3H, s), 3.21 (1H, dd, $J = 9.1, 7.5$ Hz), 2.86 (1H, dt, $J = 11.2, 9.9$ Hz), 2.83-2.77 (1H, m), 2.62-2.55 (1H, m), 2.21-2.09 (4H, m), 2.05 (1H, dddd, $J = 11.9, 10.1, 9.1, 3.1$), 1.85-1.77 (1H, m), 1.63 (1H, ddt, $J = 11.9, 9.5, 7.5$ Hz). ^{13}C NMR (150 MHz, CDCl_3): $\delta = 152.9, 152.1, 151.9, 150.8, 139.9, 137.8, 135.5, 116.3, 111.8, 111.0, 110.2, 110.1, 57.6, 55.9, 55.8, 55.7, 55.6, 55.5, 53.8, 35.4, 28.4, 27.2, 20.2, 15.3$. MS (EI) m/z (rel. intensity): 380 (30), 352 (36), 324 (100). HRMS (ESIpos): *calcd* for $\text{C}_{24}\text{H}_{28}\text{O}_4 + \text{Na}$: 403.187981, *found* 403.187676.

Compound 26. Obtained analogously from substrate **25** as a white solid (13 mg, 43%). m.p.

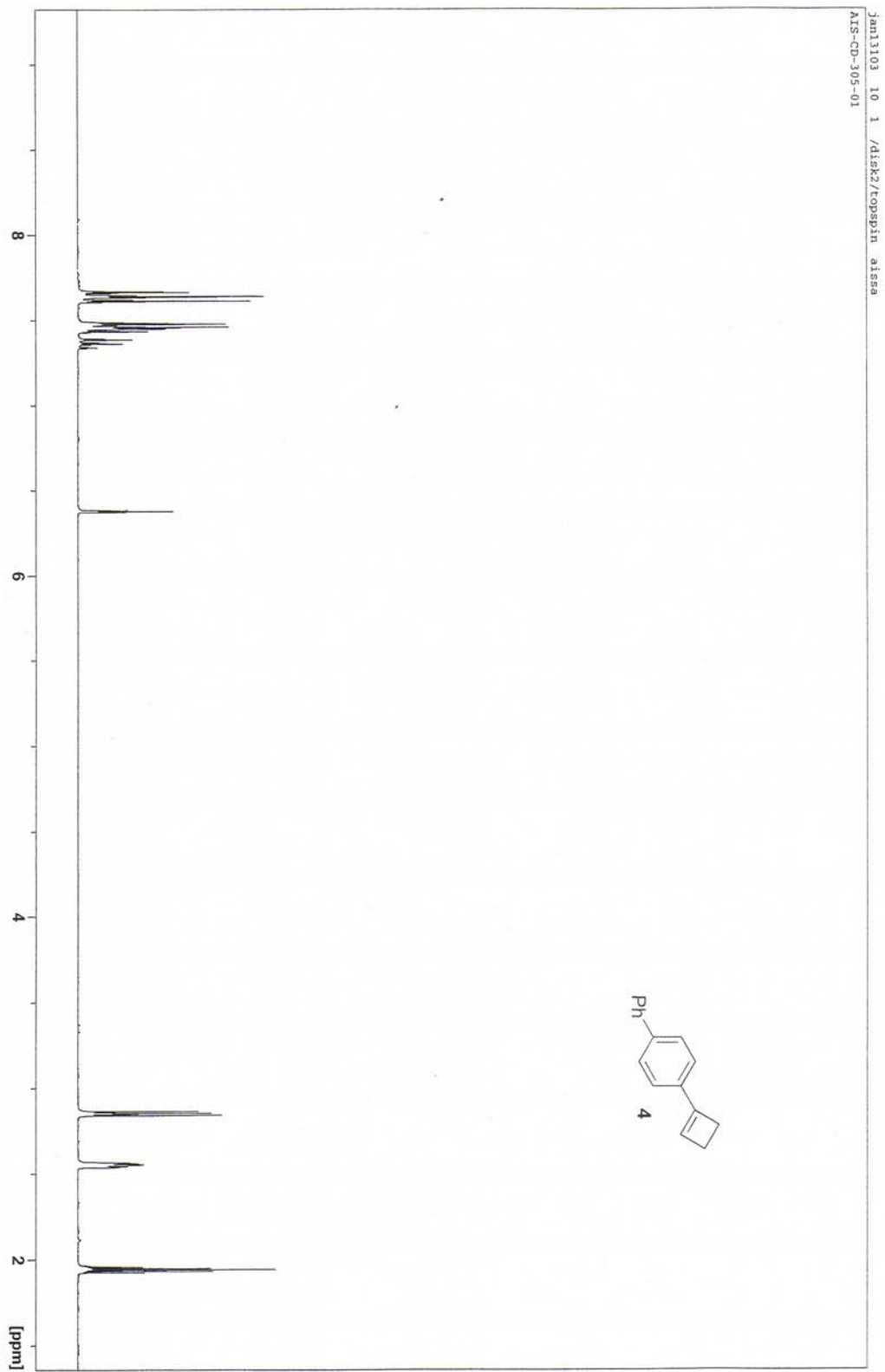


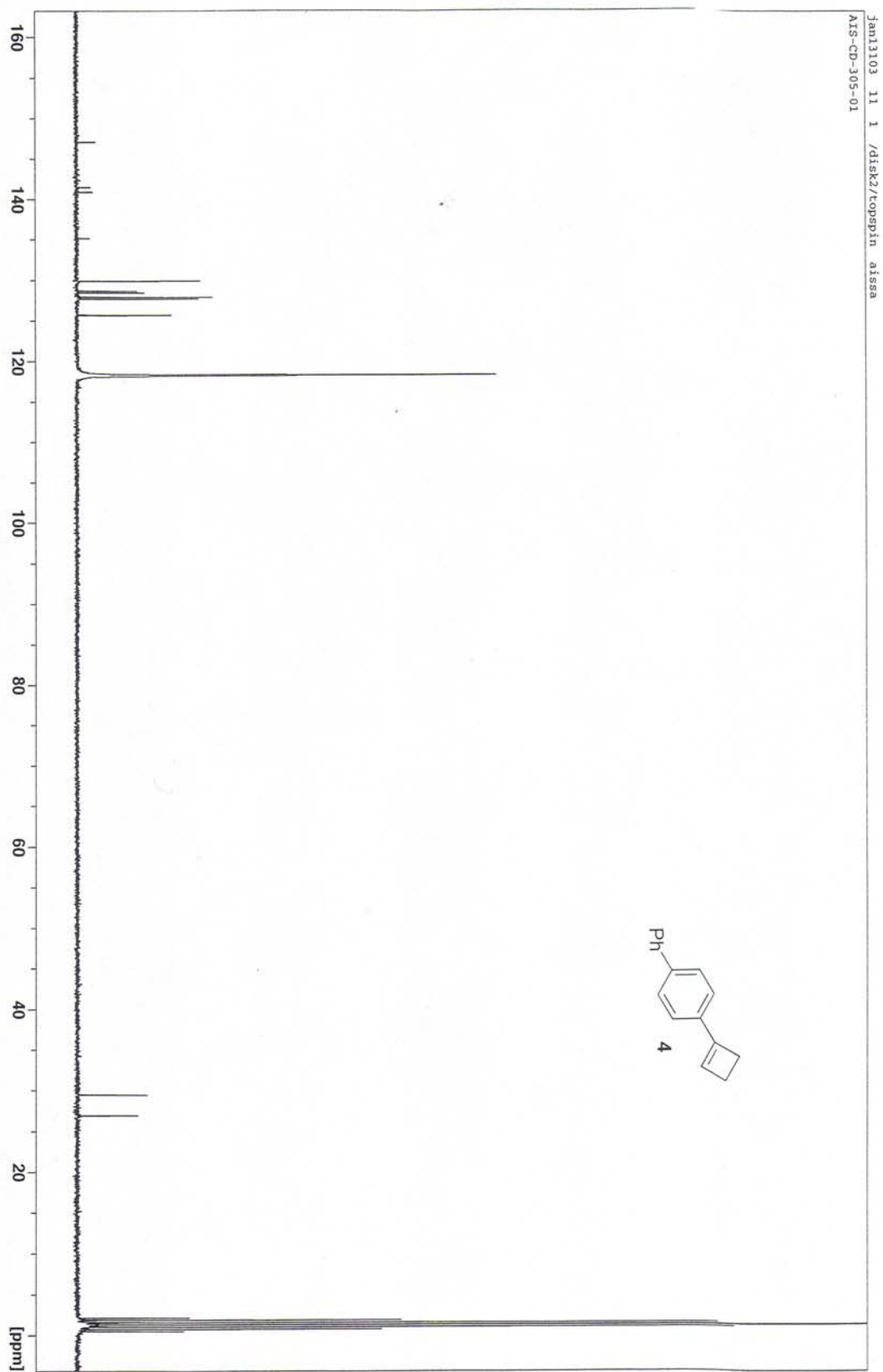
113-117°C. IR (neat): 3033, 2937, 2915, 2899, 2830, 1605, 1571, 1506, 1467, 1454, 1380, 1287, 1235, 1173, 1013, 835, 811, 745, 698 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 7.49\text{--}7.31$ (10H, m), 7.09 (2H, d, $J = 8.8$ Hz), 6.97 (2H, d, $J = 8.3$ Hz), 6.87 (2H, d, $J = 8.8$ Hz), 5.07 (2H, s), 5.05 (2H, s), 2.68-2.63 (2H, m), 2.61-2.52 (4H, m), 2.51-2.42 (2H, m), 1.99-1.90 (2H, m). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 157.2, 156.6, 145.3, 139.4, 136.9, 136.7, 136.3, 128.7, 128.2$ (4C), 127.6, 127.58, 127.5 (2C), 127.2 (2C), 127.1 (2C), 126.8 (2C), 114.3 (2C), 114.0 (2C), 69.7, 69.6, 47.3, 33.6 (2C), 25.9, 25.1, 16.3. MS (EI) m/z (rel. intensity): 472 (8), 444 (4), 381 (21), 91 (100). HRMS (EI): *calcd* for $\text{C}_{34}\text{H}_{32}\text{O}_2$: 472.240592, *found* 472.240233.

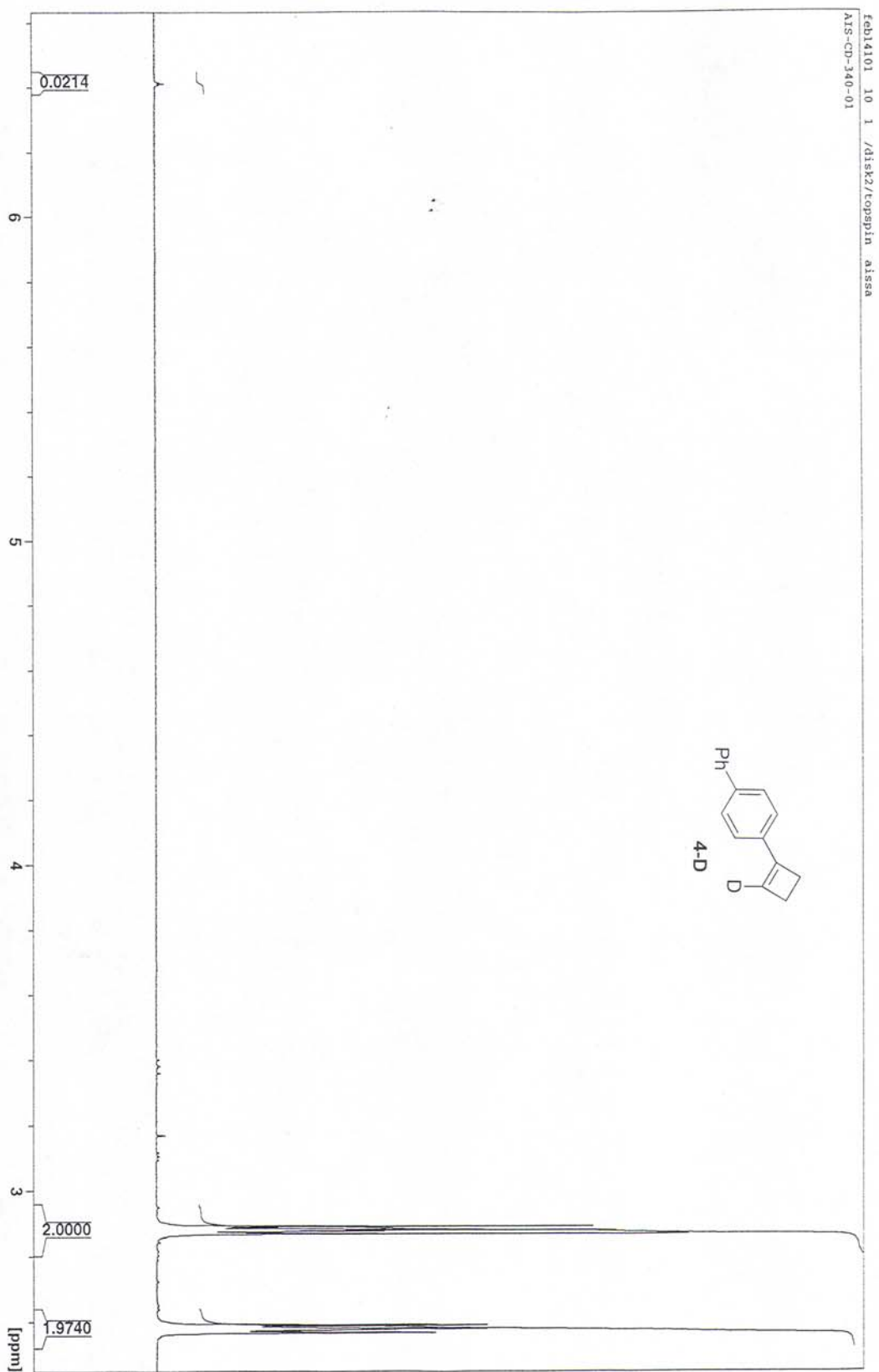
4-But-3-enyl-8-methoxy-2H-chromene (19). PtCl_2 (3.5 mg, 0.0132 mmol) was added to a solution of substrate **17** (33 mg, 0.139 mmol) in toluene (1.4 mL).

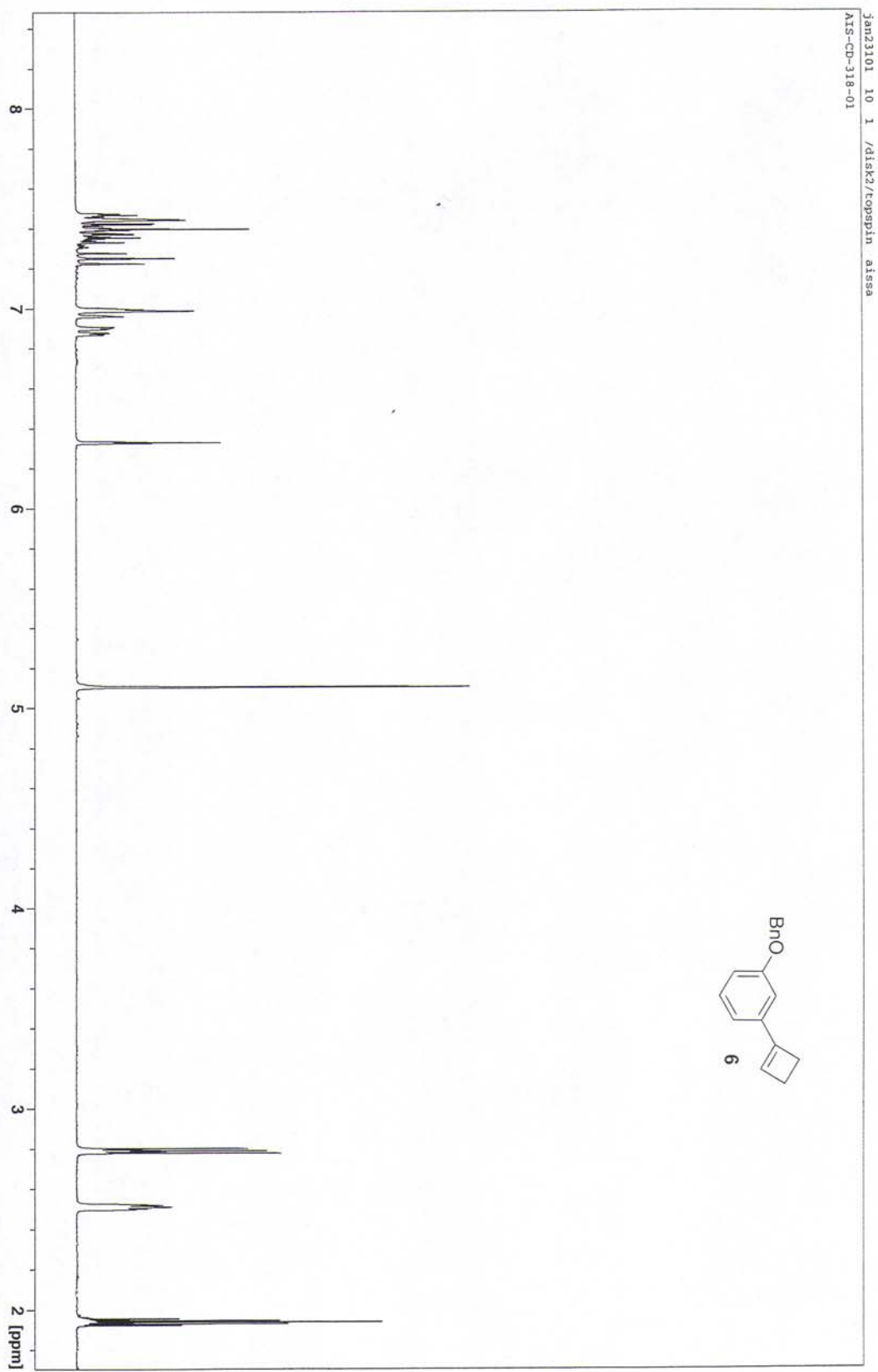


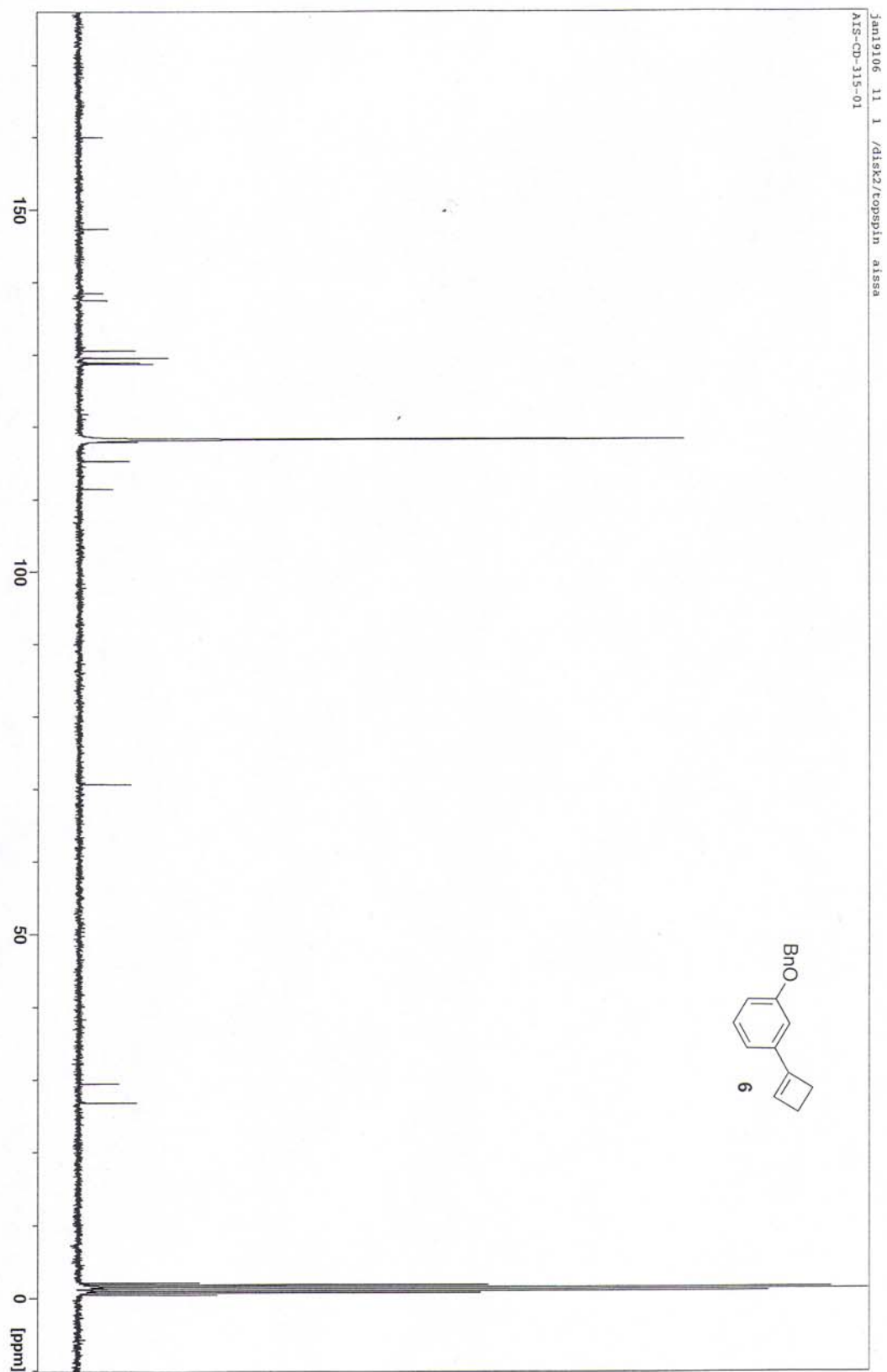
The solution was stirred for 4.5 h at 80°C before it was transferred at room temperature into a flask containing a solution of the Grubbs catalyst $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$ (5.7 mg, 0.00695 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was refluxed for 30 min, the reaction was quenched with a few drops of ethyl vinyl ether, the solvent was evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 20/1) to give chromene **19** as a yellow oil (21 mg, 64%). IR (neat): 3075, 2997, 2934, 2836, 1641, 1603, 1576, 1477, 1440, 1270, 1220, 1199, 1176, 1152, 1091, 1050, 1007, 913 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 6.95\text{--}6.79$ (3H, m), 5.88 (1H, ddt, $J = 17.0, 10.2, 6.5$ Hz), 5.65-5.60 (1H, m), 5.07 (1H, dq, $J = 17.0, 1.7$ Hz), 5.01 (1H, dq, $J = 10.1, 1.0$ Hz), 4.83-4.79 (2H, m), 3.88 (3H, s), 2.52-2.44 (2H, m), 2.35-2.26 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 148.2, 143.5, 138.1, 133.9, 124.4, 120.7, 117.9, 115.7, 115.1, 111.8, 65.7, 56.2, 32.2, 31.1$. MS (EI) m/z (rel. intensity): 216 (100), 201 (19), 175 (30). HRMS (EI) : *calcd* for $\text{C}_{14}\text{H}_{16}\text{O}_2$: 216.115032, *found* 216.115269.

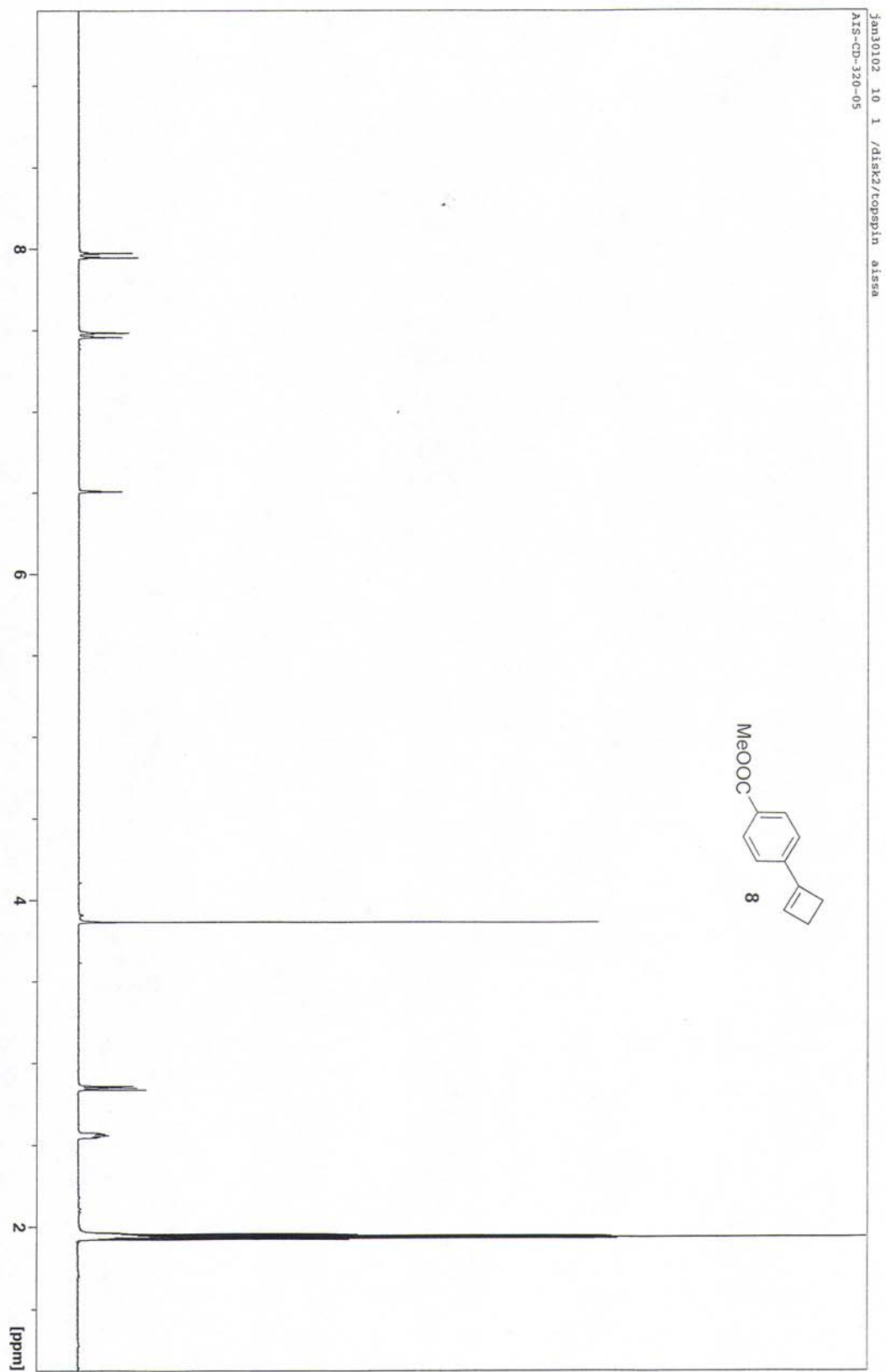


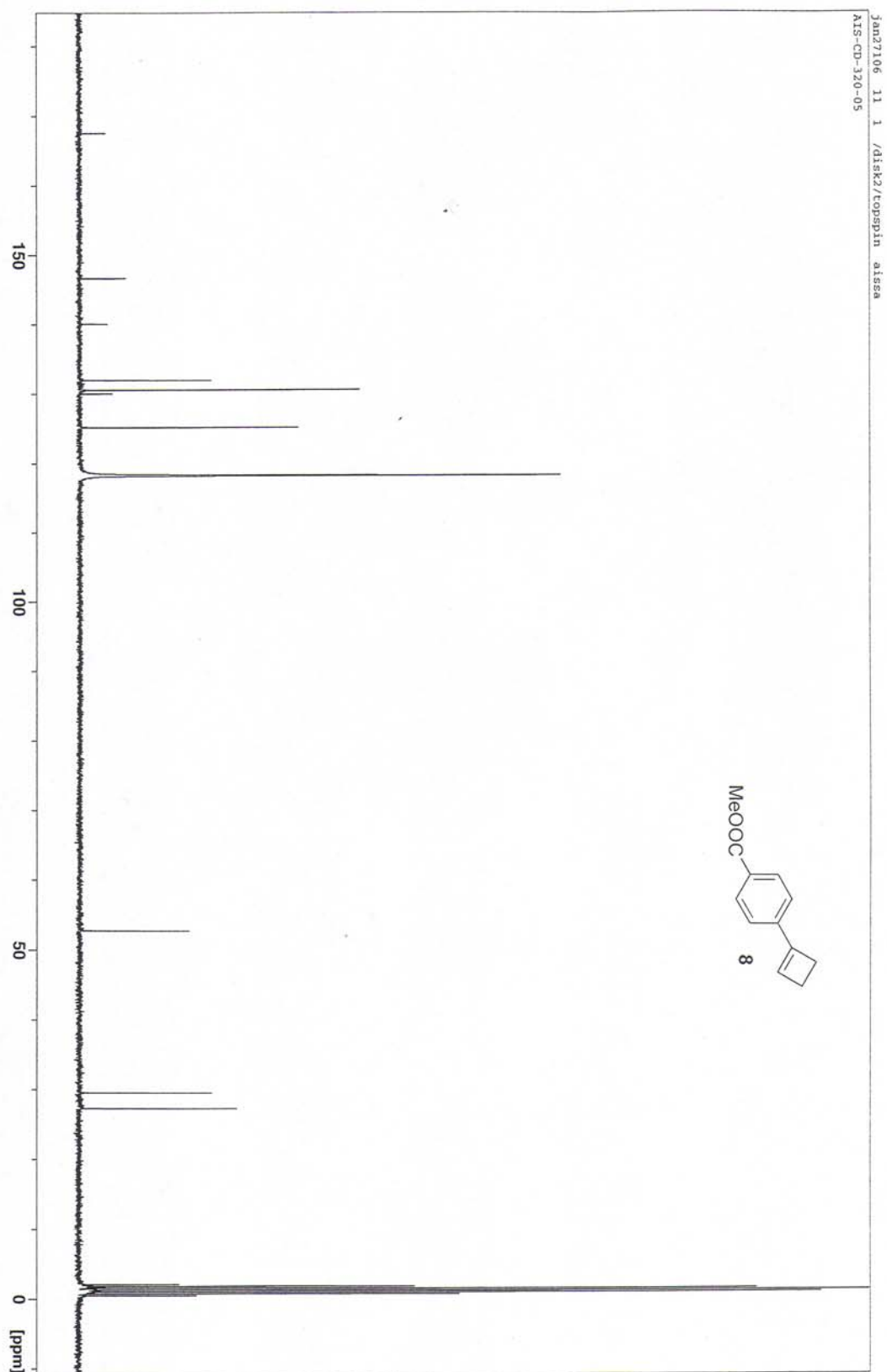


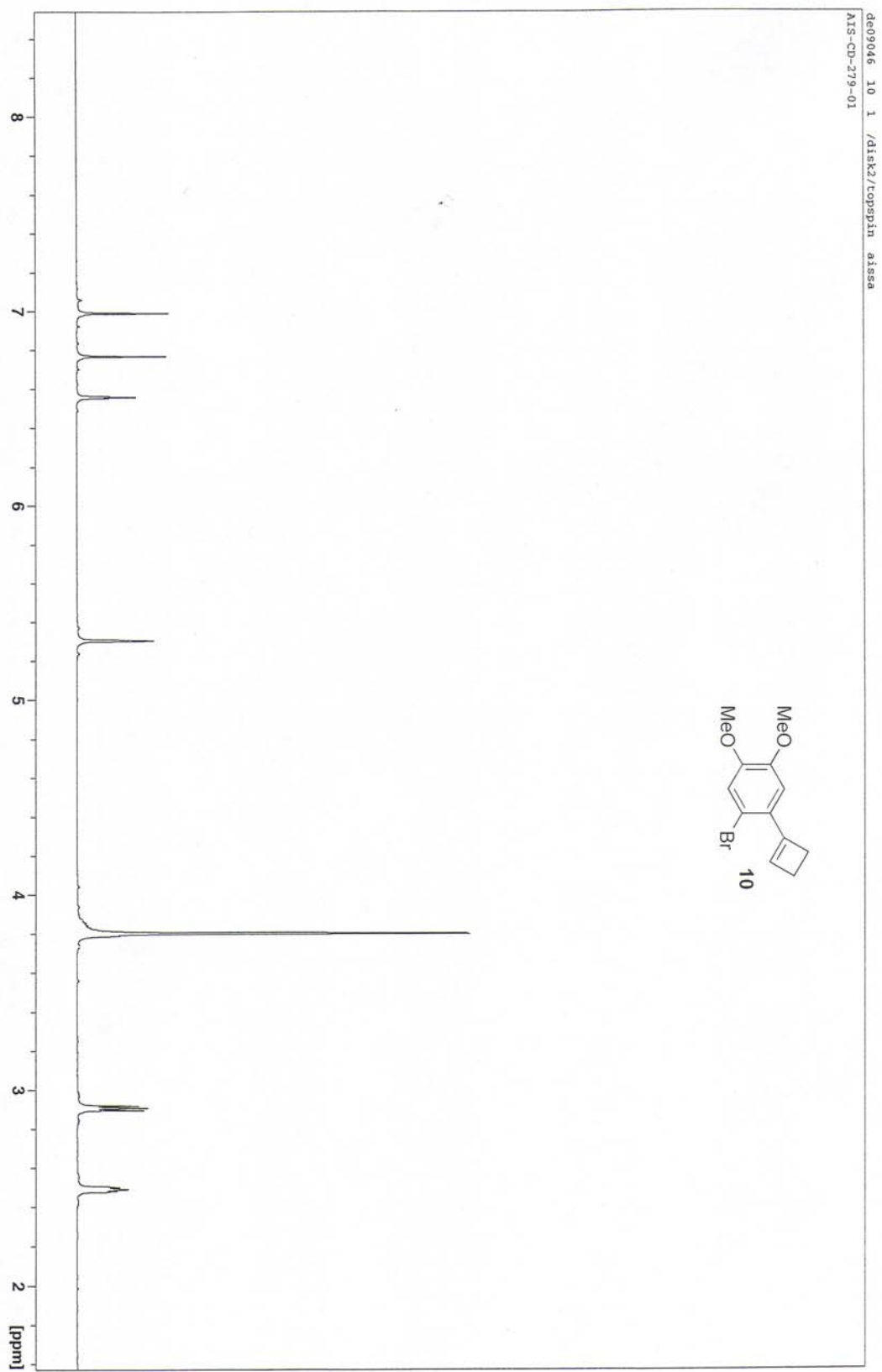


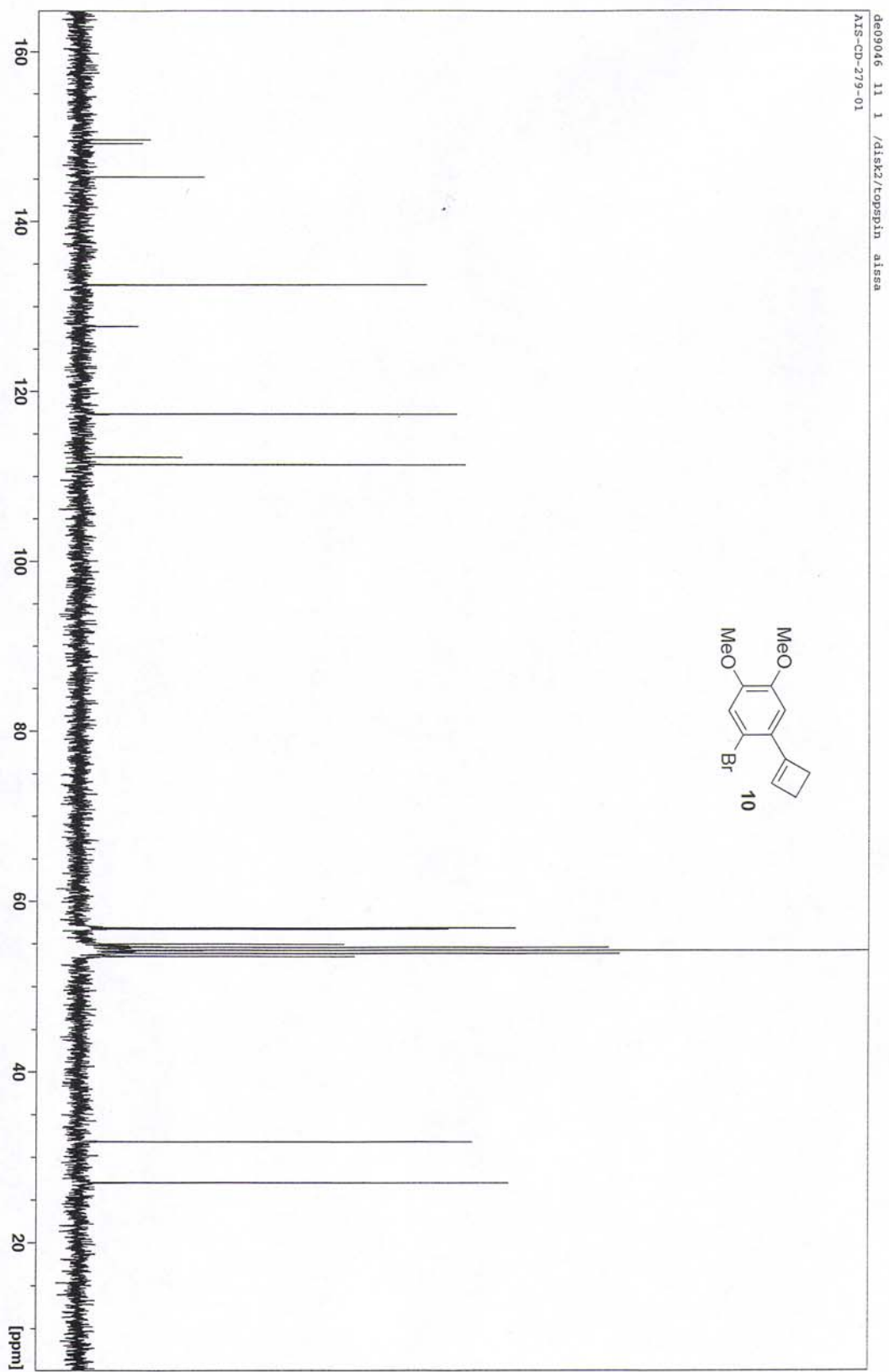


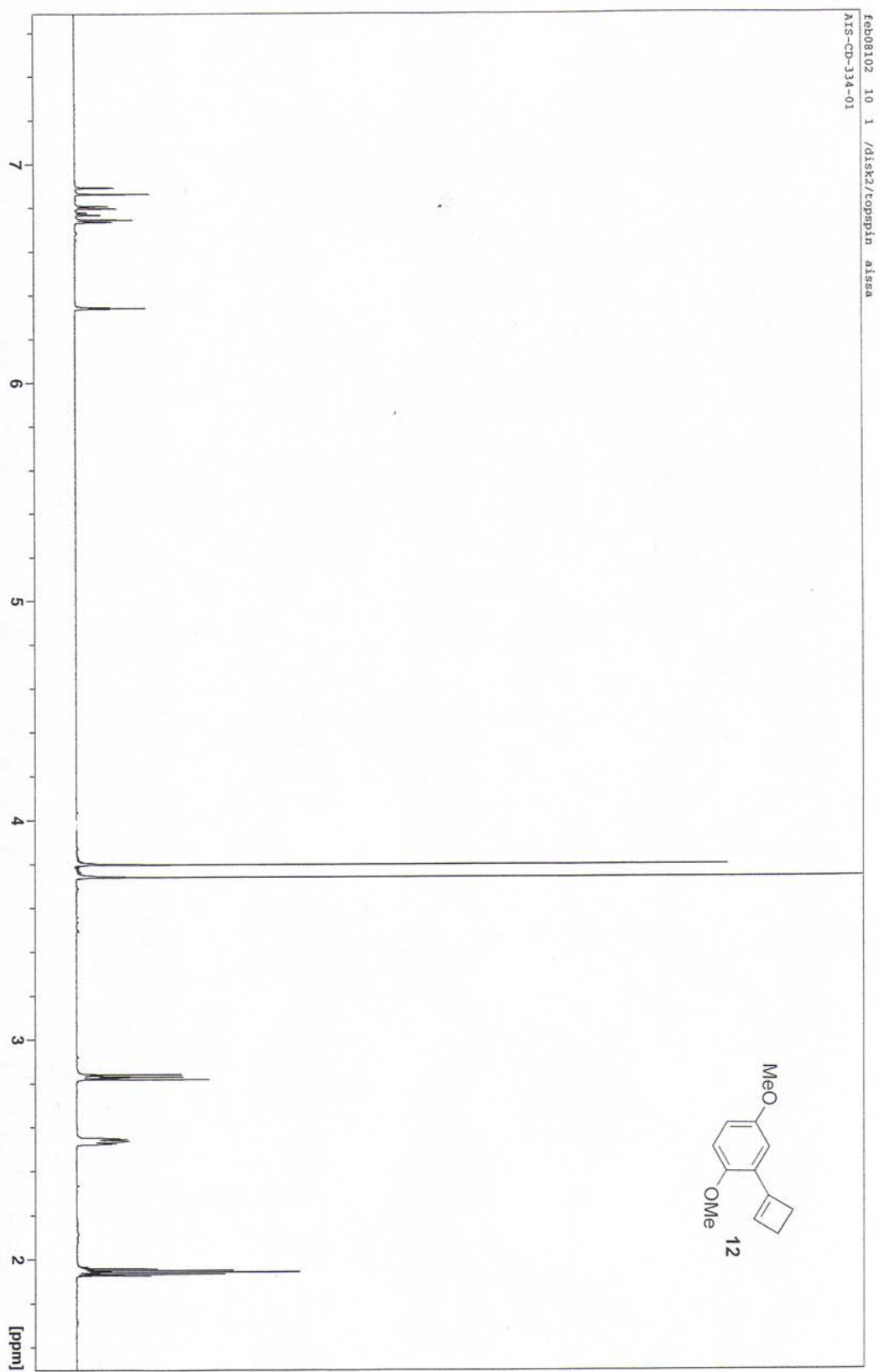


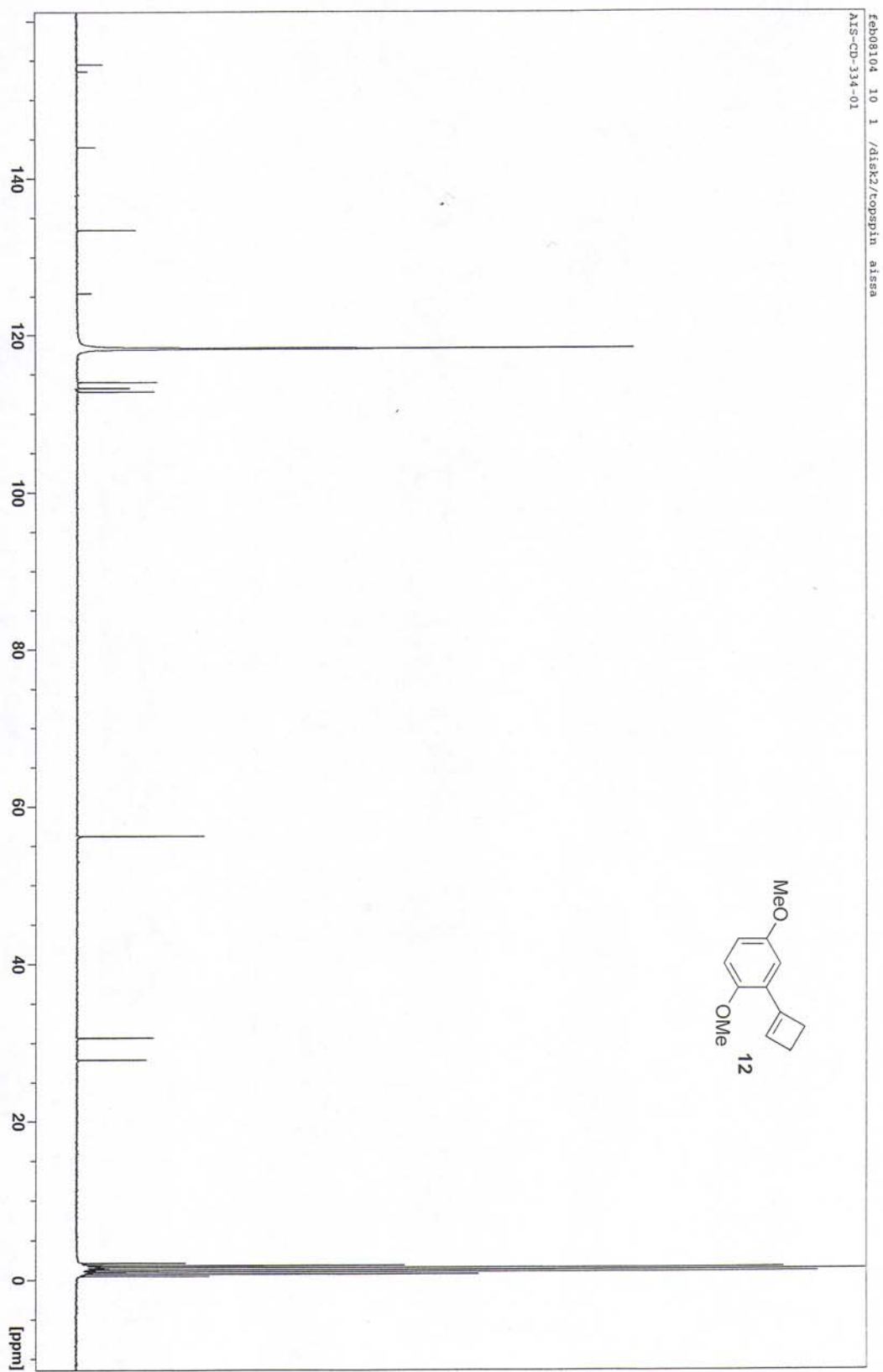


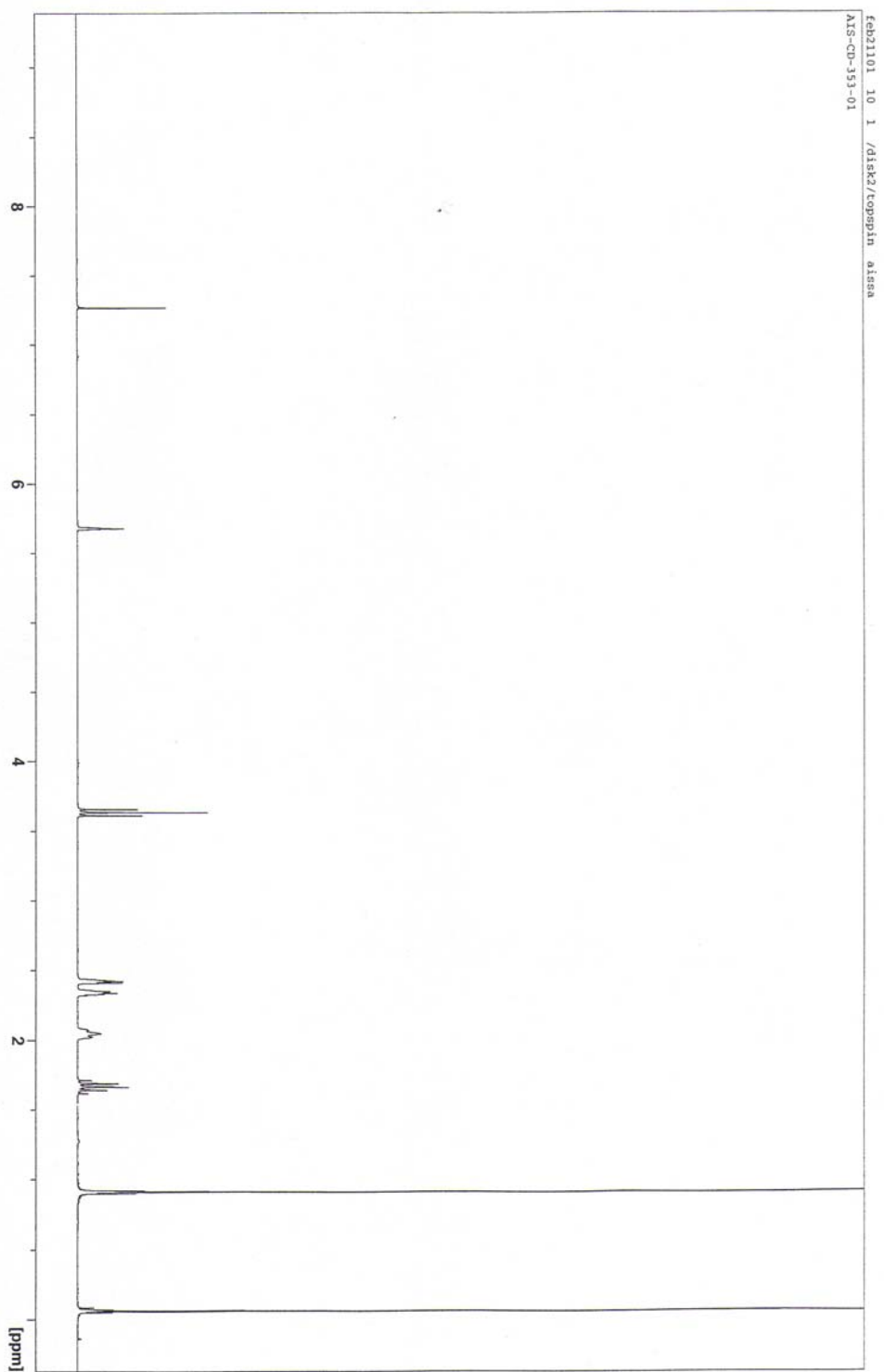
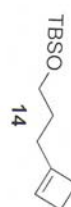


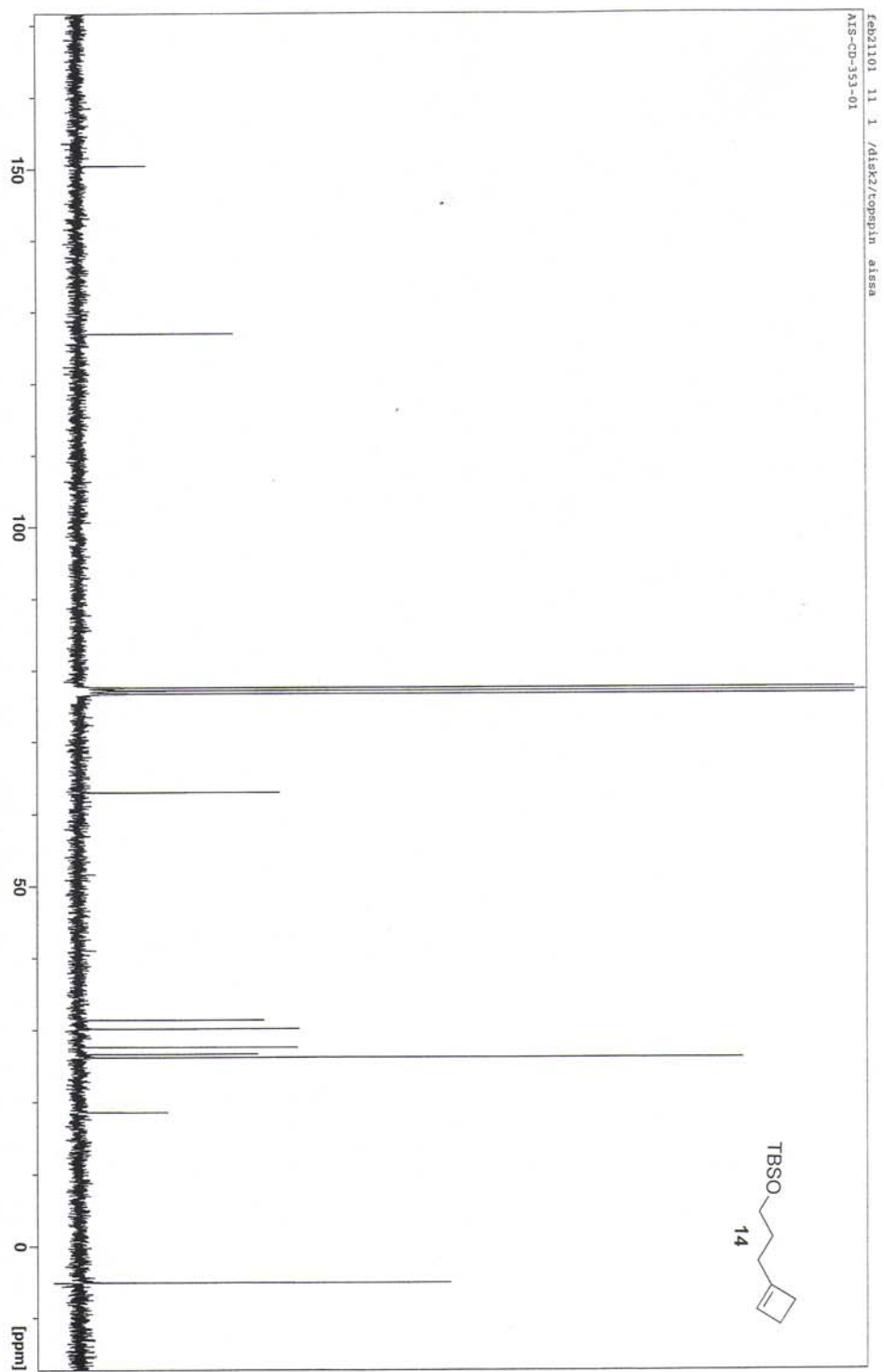


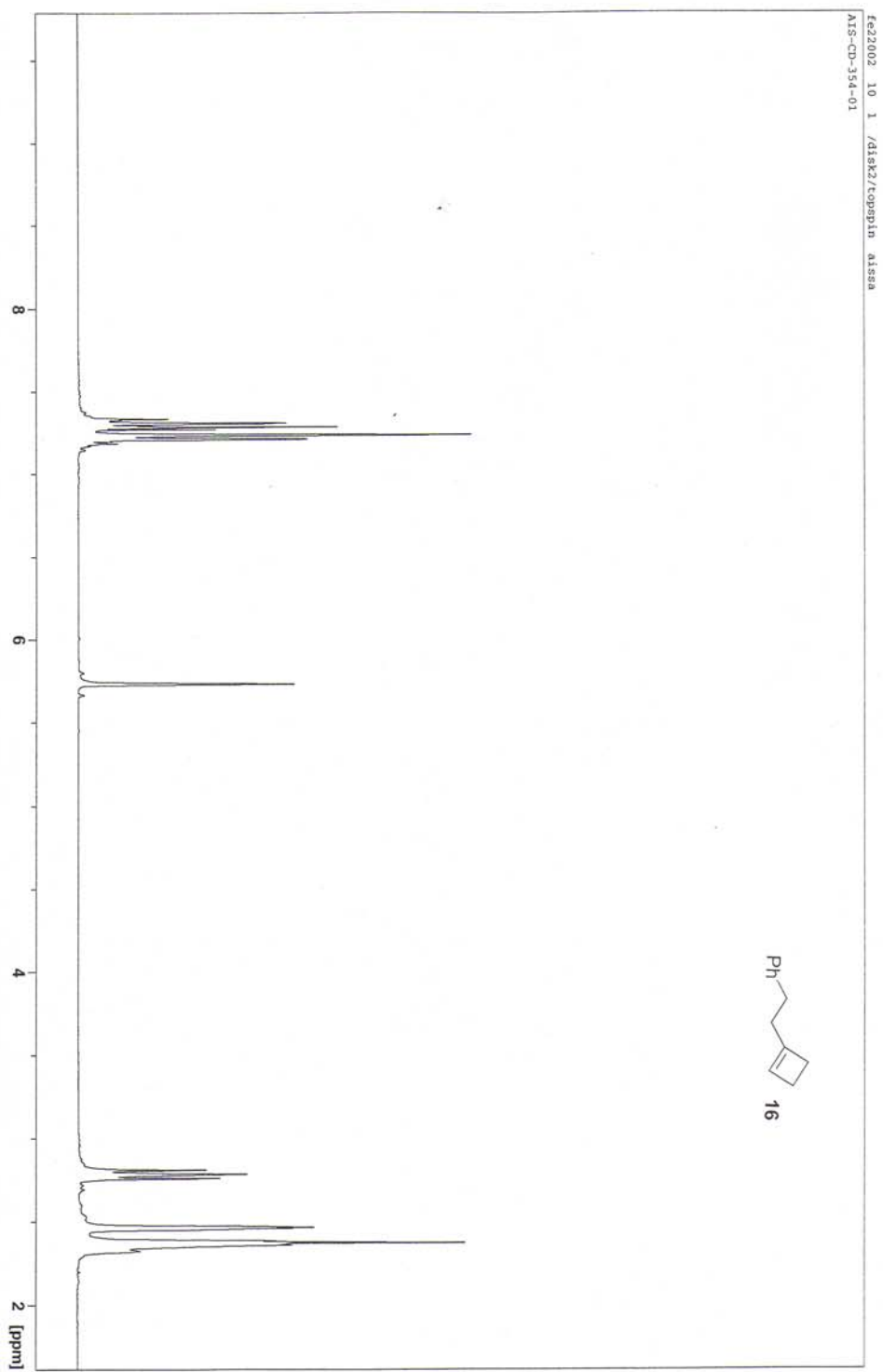


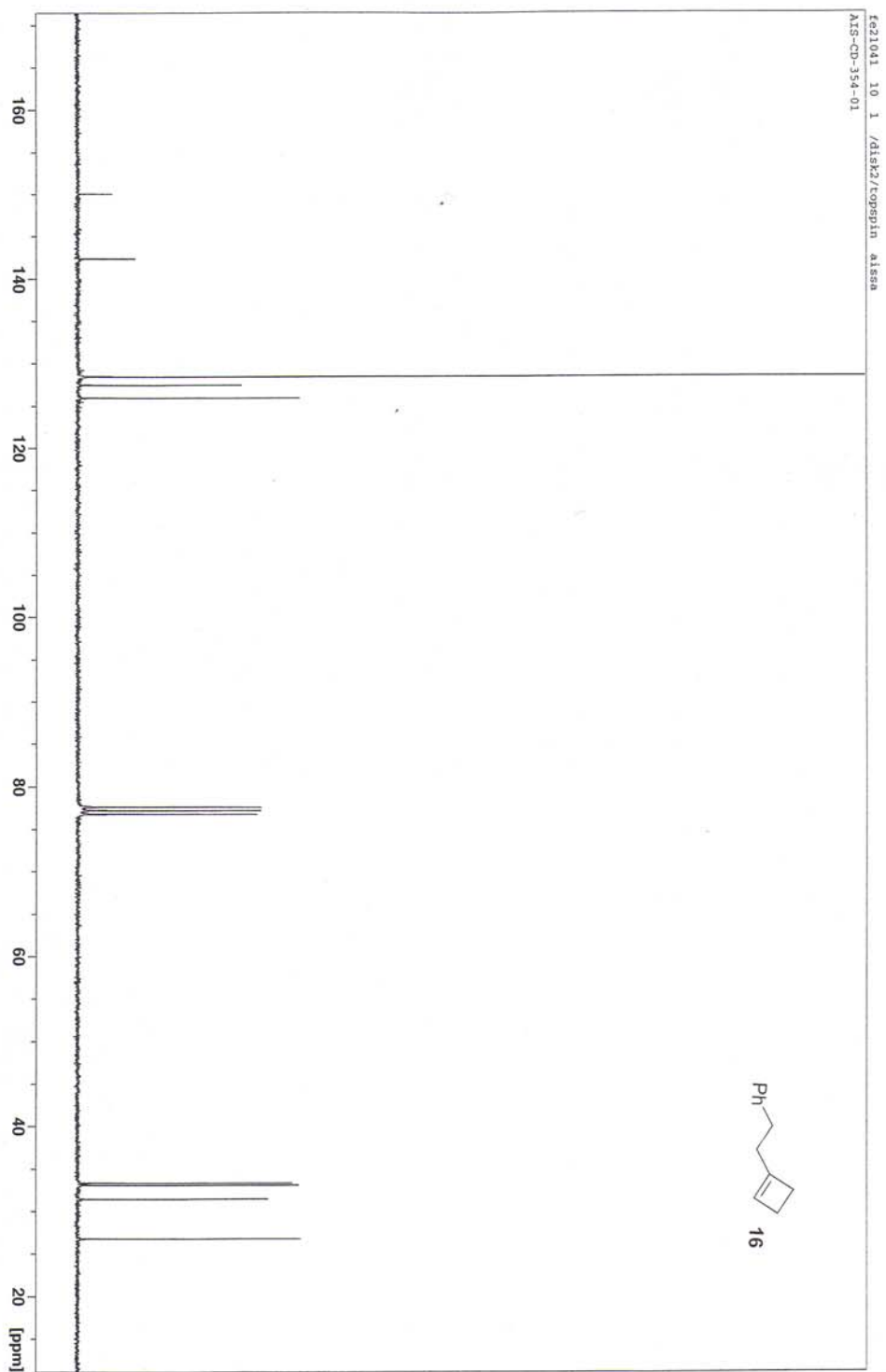


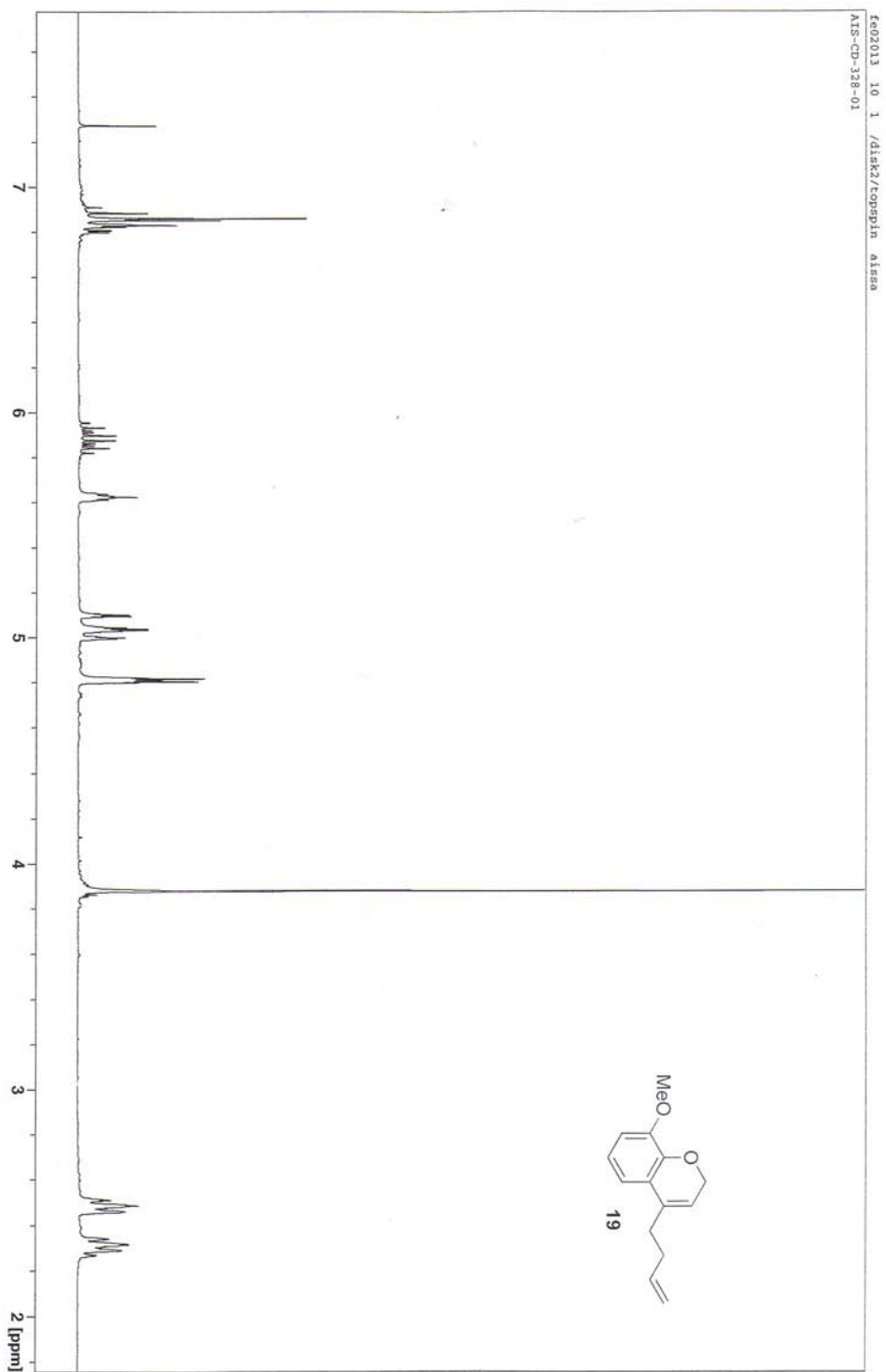


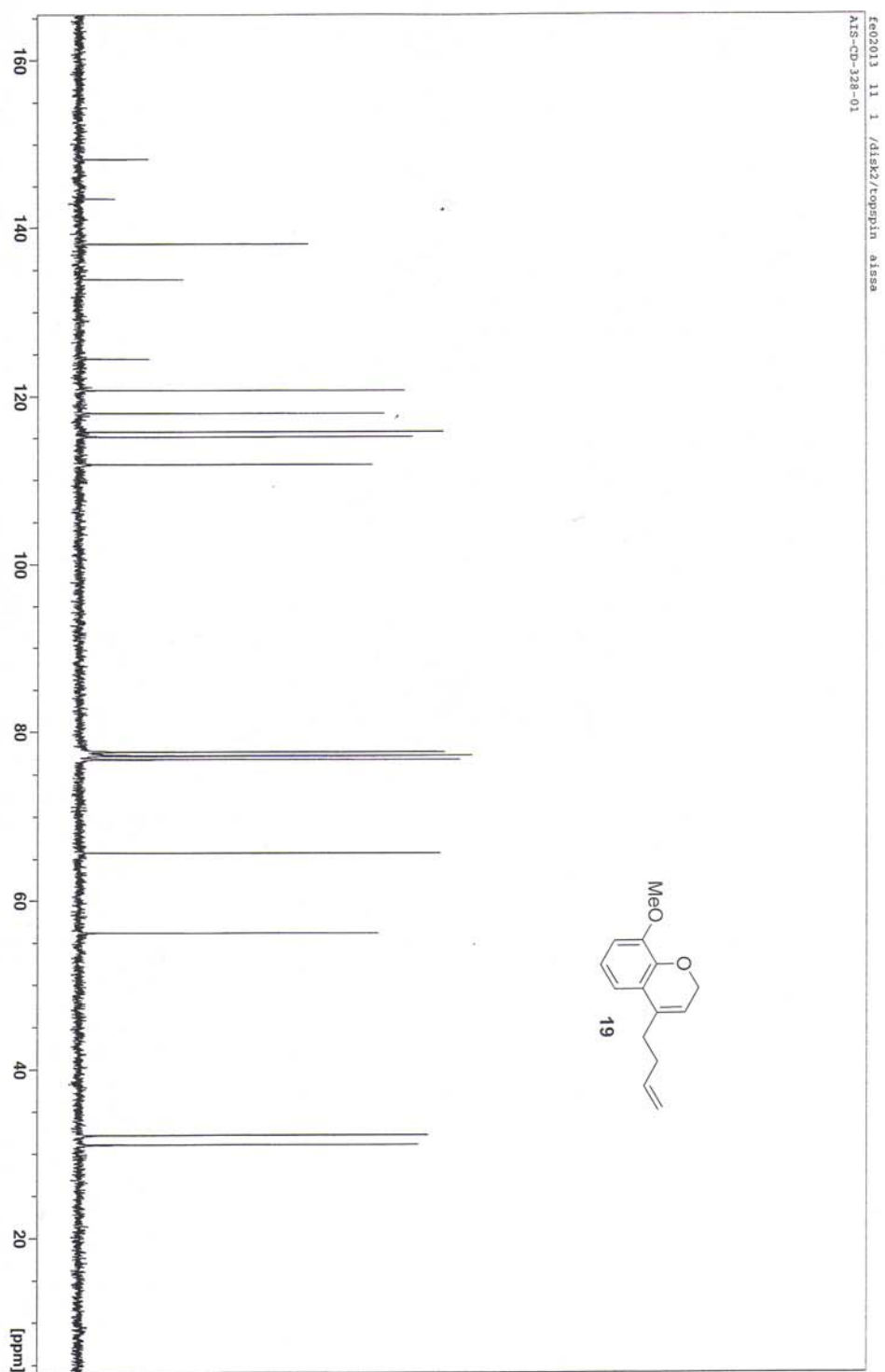


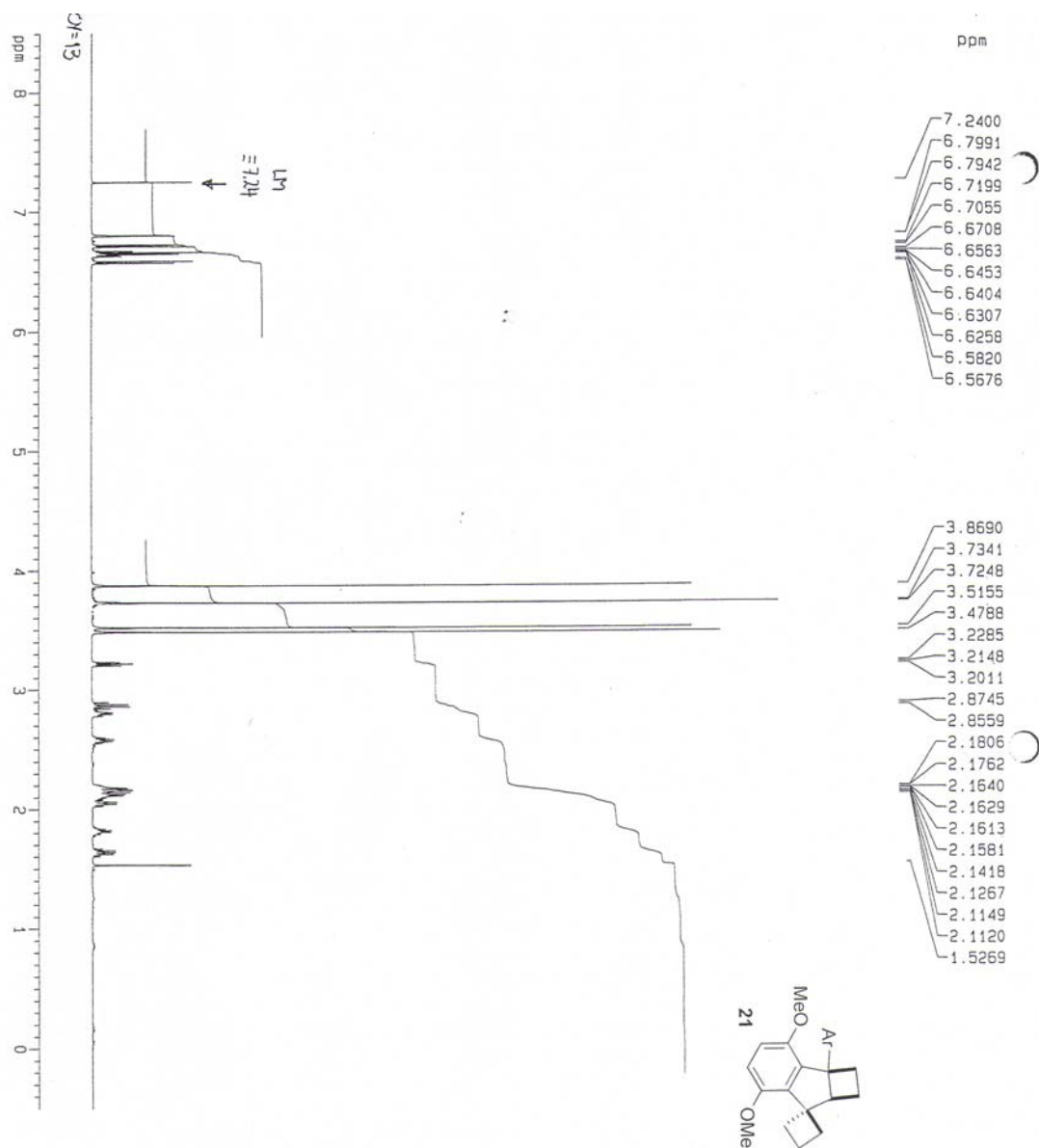












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USER bara

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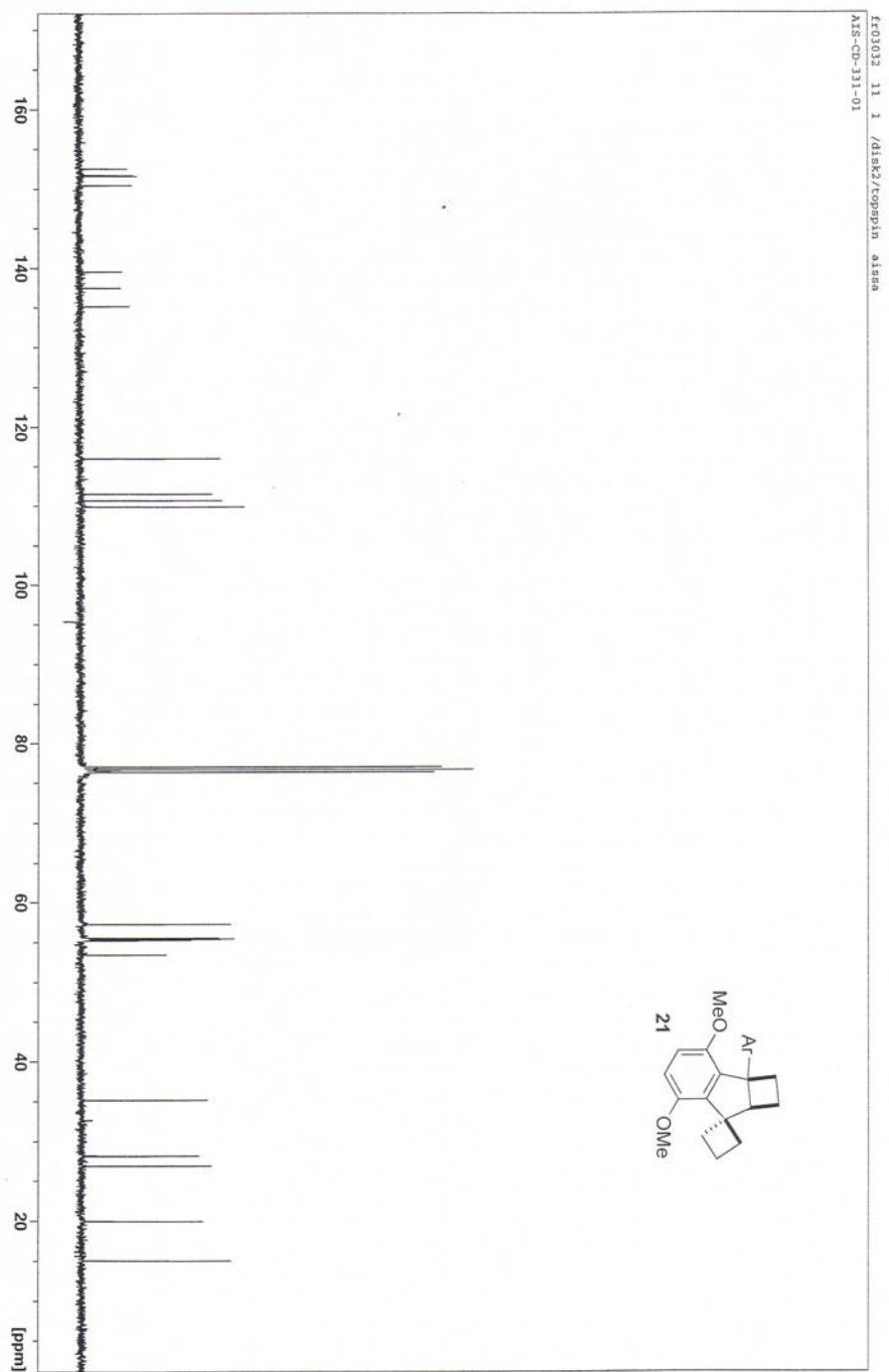
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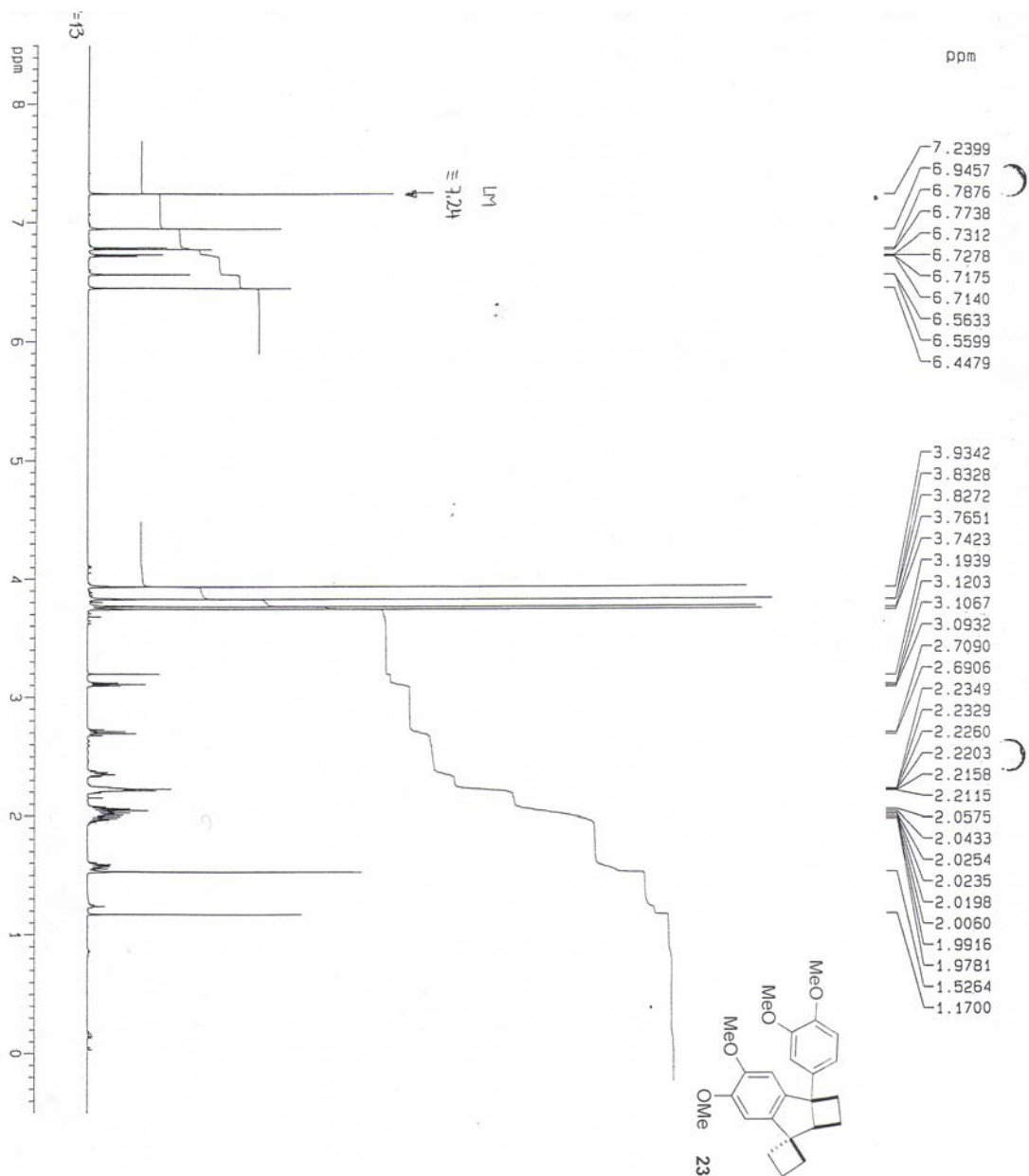
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H609 078





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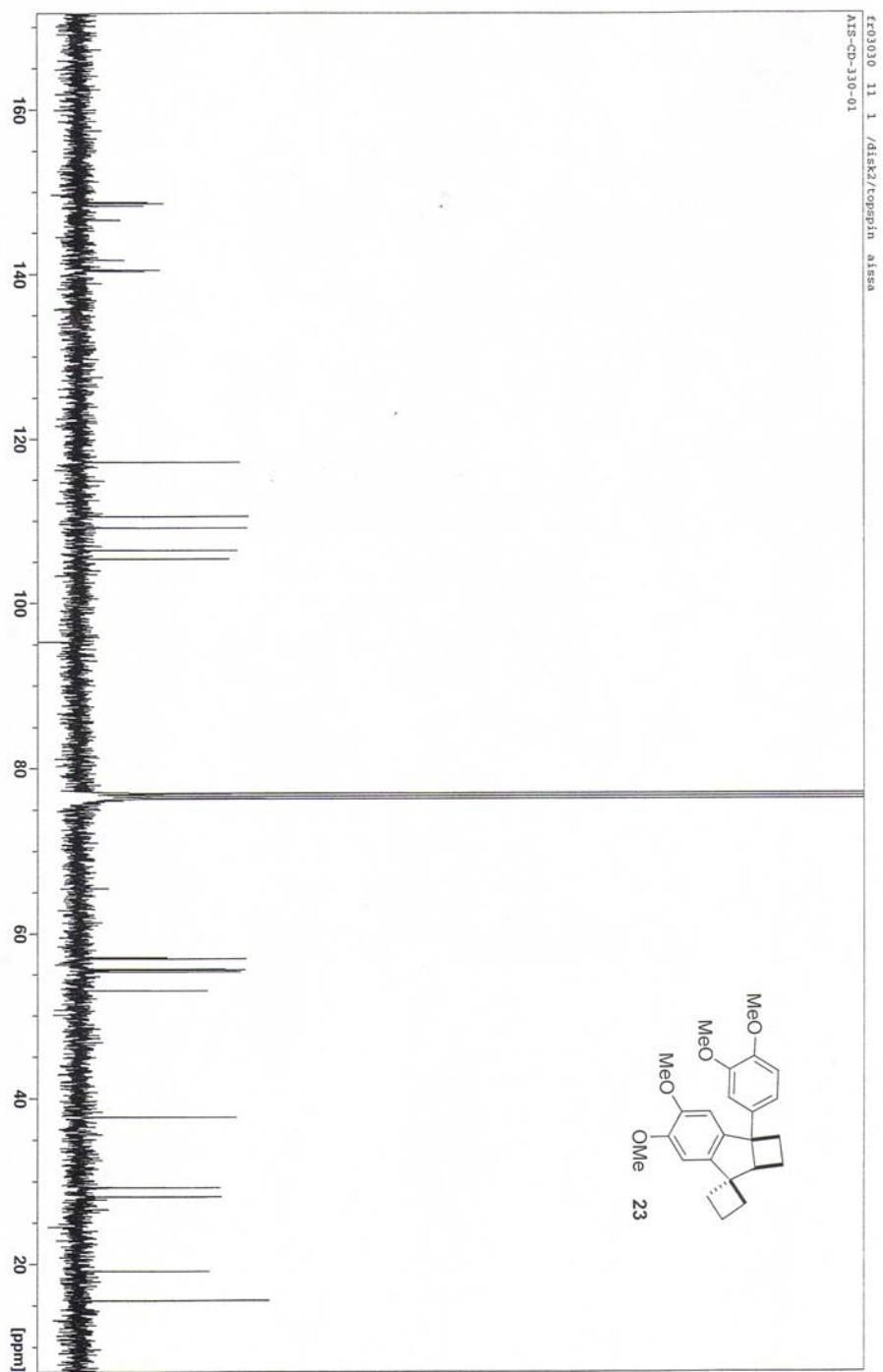
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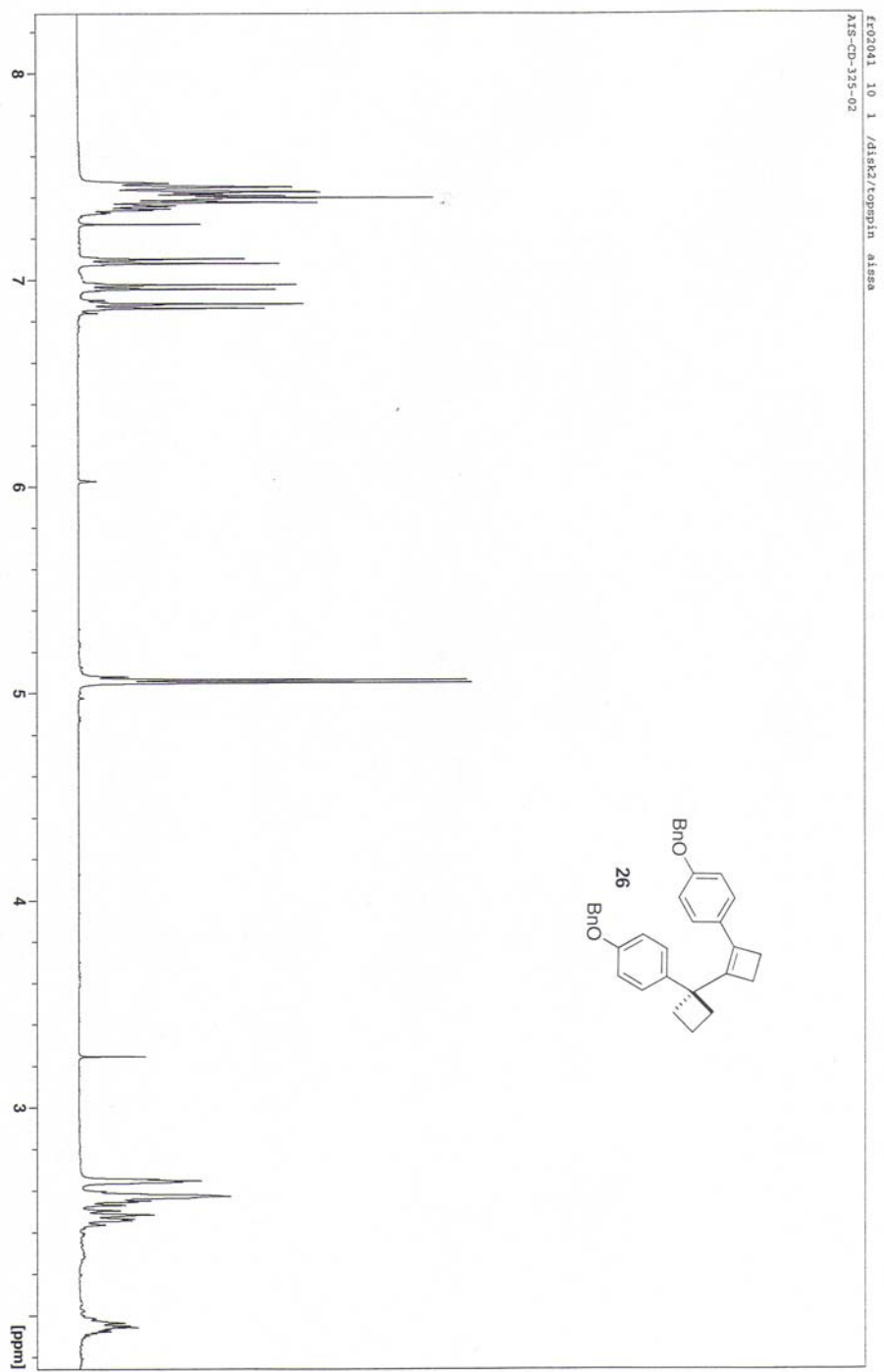
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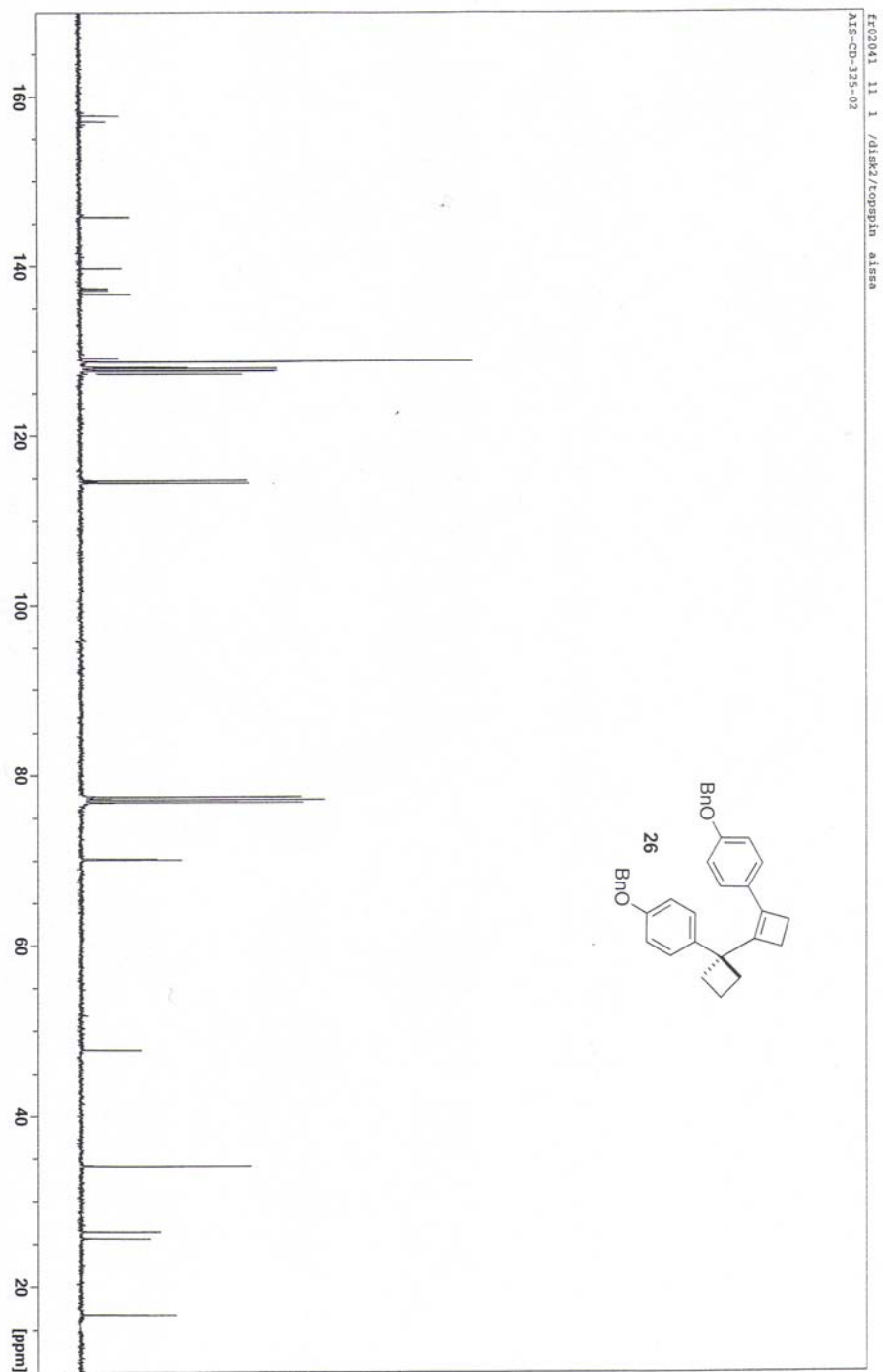
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H609 091

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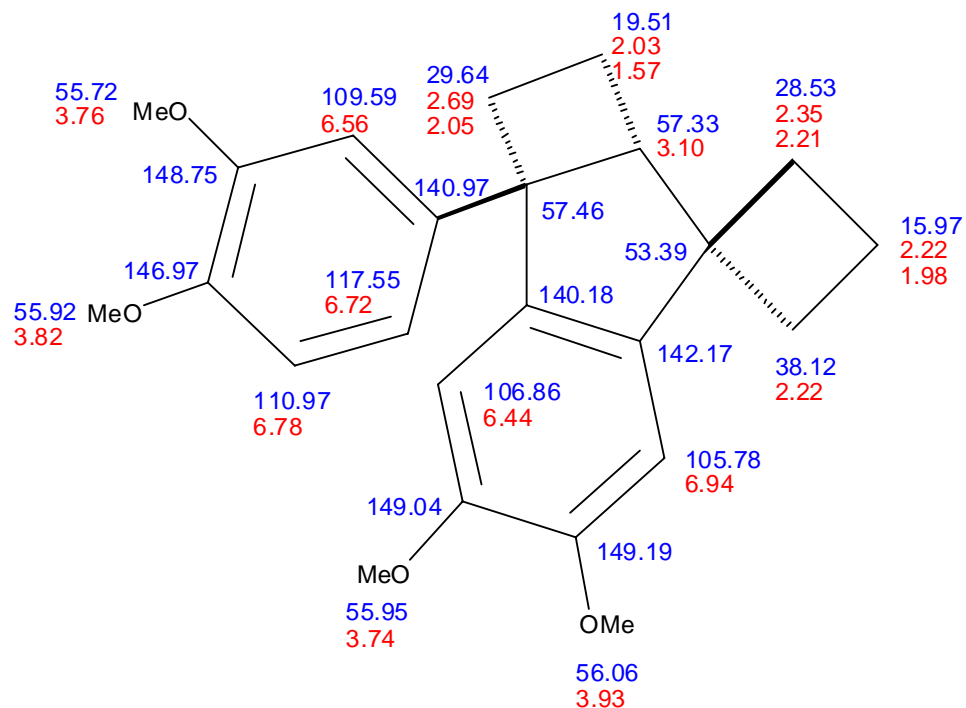
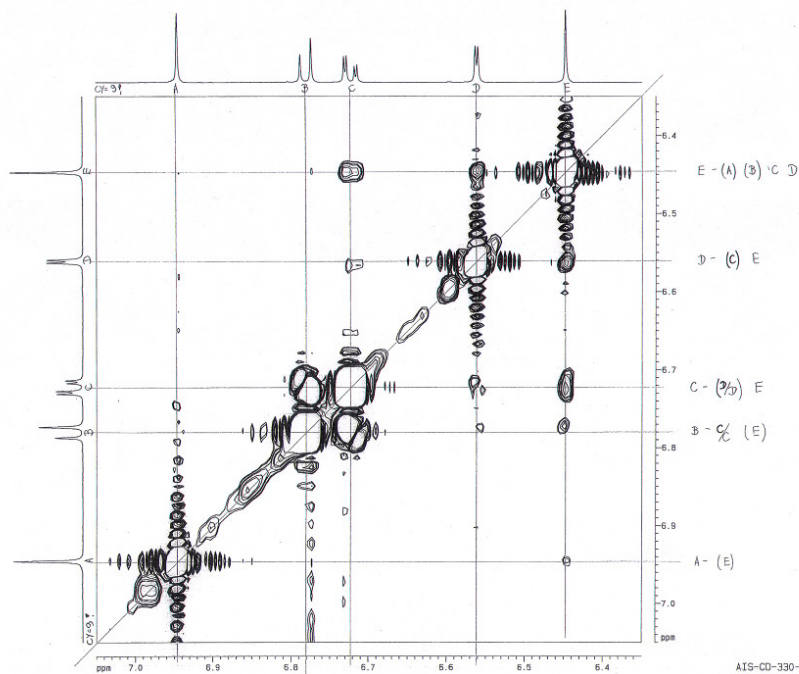
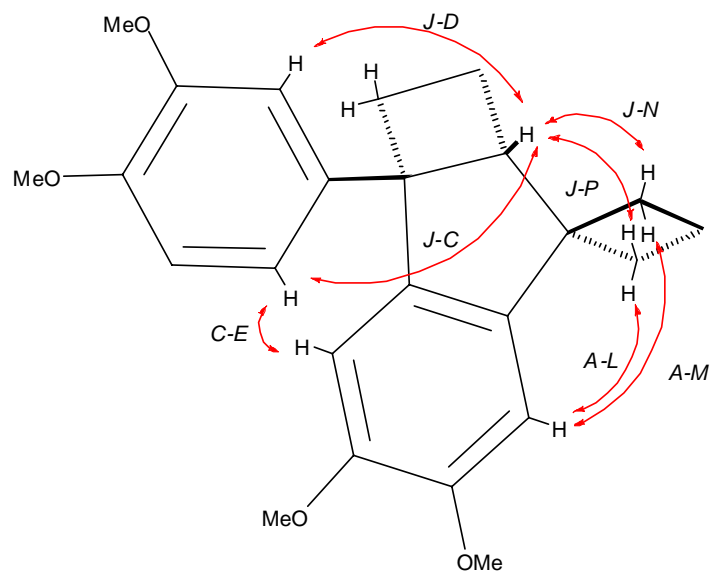


Figure S-1. Overview over the spectral data recorded for compound **23** (DMX 600 spectrometer, CDCl_3). ^1H NMR shifts are given in red, ^{13}C NMR shifts are shown in blue. The signal assignments are unambiguous, based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosyqtp*); HSQC (*invietgssi*) optimized for $^1J(\text{C,H}) = 145$ Hz; HMBC (*inv4gslplrnd*) for correlations via $^nJ(\text{C,H})$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

Figure S-2. Selected NOESYs for compound 23.



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DS	10
SWH	3633.188 Hz
F2FREQ	3.335670 Hz
AD	0.141900 sec
RG	256
AW	138.500 MHz
DE	4.00 MHz
TE	300.2 K
DQ	0.0000000 sec
DS	4.1888881 sec
DB	1.2000000 sec
DS	0.0000000 sec
DD	0.0000000 sec
DE	0.0013000 sec

===== CHANNEL f1 =====

NUC1	13
P1	10.00 MHz
RF	50.00 MHz
PL1	0.00 dB
PL2	0.00 dB

===== GRABBER CHANNEL =====

GRAB1	13
GRAB2	13
GRAB3	13
GRAB4	13
GRAB5	13
GRAB6	13
GRAB7	13
GRAB8	13
GRAB9	13
GRAB10	13
GRAB11	13
GRAB12	13
GRAB13	13
GRAB14	13
GRAB15	13
GRAB16	13
GRAB17	13
GRAB18	13
GRAB19	13
GRAB20	13
GRAB21	13
GRAB22	13
GRAB23	13
GRAB24	13
GRAB25	13
GRAB26	13
GRAB27	13
GRAB28	13
GRAB29	13
GRAB30	13
GRAB31	13
GRAB32	13
GRAB33	13
GRAB34	13
GRAB35	13
GRAB36	13
GRAB37	13
GRAB38	13
GRAB39	13
GRAB40	13
GRAB41	13
GRAB42	13
GRAB43	13
GRAB44	13
GRAB45	13
GRAB46	13
GRAB47	13
GRAB48	13
GRAB49	13
GRAB50	13
GRAB51	13
GRAB52	13
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GRAB55	13
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GRAB57	13
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GRAB63	13
GRAB64	13
GRAB65	13
GRAB66	13
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GRAB68	13
GRAB69	13
GRAB70	13
GRAB71	13
GRAB72	13
GRAB73	13
GRAB74	13
GRAB75	13
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GRAB77	13
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GRAB79	13
GRAB80	13
GRAB81	13
GRAB82	13
GRAB83	13
GRAB84	13
GRAB85	13
GRAB86	13
GRAB87	13
GRAB88	13
GRAB89	13
GRAB90	13
GRAB91	13
GRAB92	13
GRAB93	13
GRAB94	13
GRAB95	13
GRAB96	13
GRAB97	13
GRAB98	13
GRAB99	13
GRAB100	13

F1 - Acquisition parameters

NUC1	13
TD	1024
SWH	3633.188 Hz
RG	256
AW	138.500 MHz
DE	4.00 MHz
TE	300.2 K
DQ	0.0000000 sec
DS	4.1888881 sec
DB	1.2000000 sec
DS	0.0000000 sec
DD	0.0000000 sec
DE	0.0013000 sec

F2 - Processing parameters

SI	1024
SF	600.280250 MHz
SR	25.00 Hz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

F1 - Processing parameters

SI	1024
SF	600.280250 MHz
SR	25.00 Hz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

2D NMR plot parameters

DS	25.00 Hz
SR	25.00 Hz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

AIS-CD-330-01
 NOESYGPFP DB=1.2
 10mg CDCl3/30 C

AIS-CD-330-01
NDESY6PTP 08=1.2
10mg CDC13/30 C

[illegible]

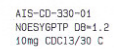
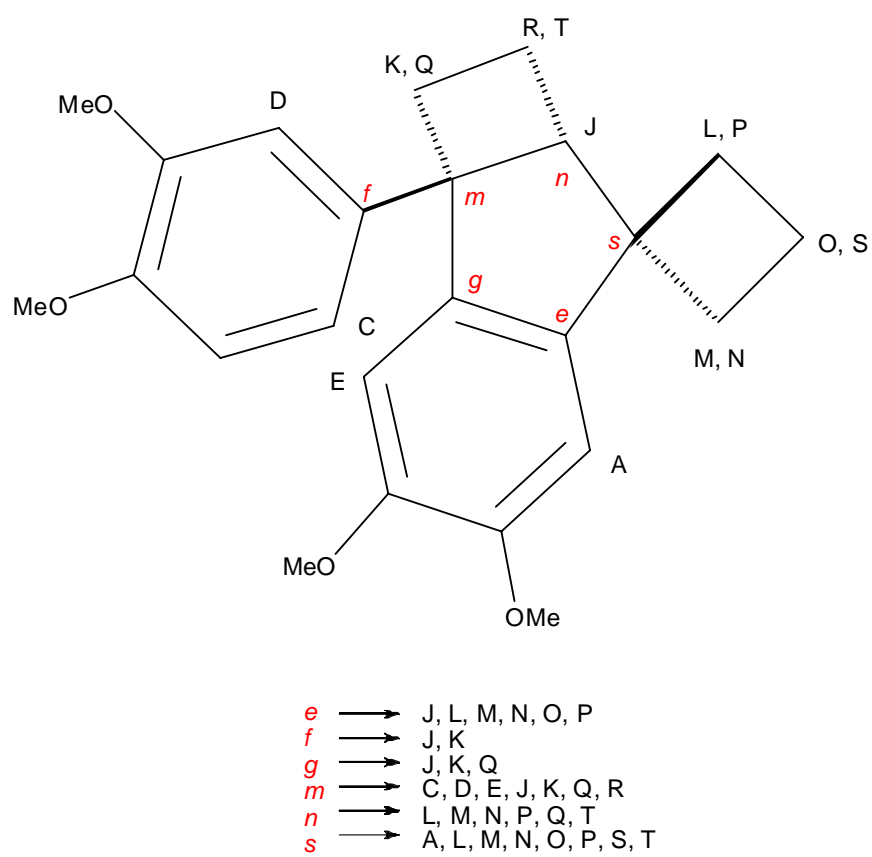
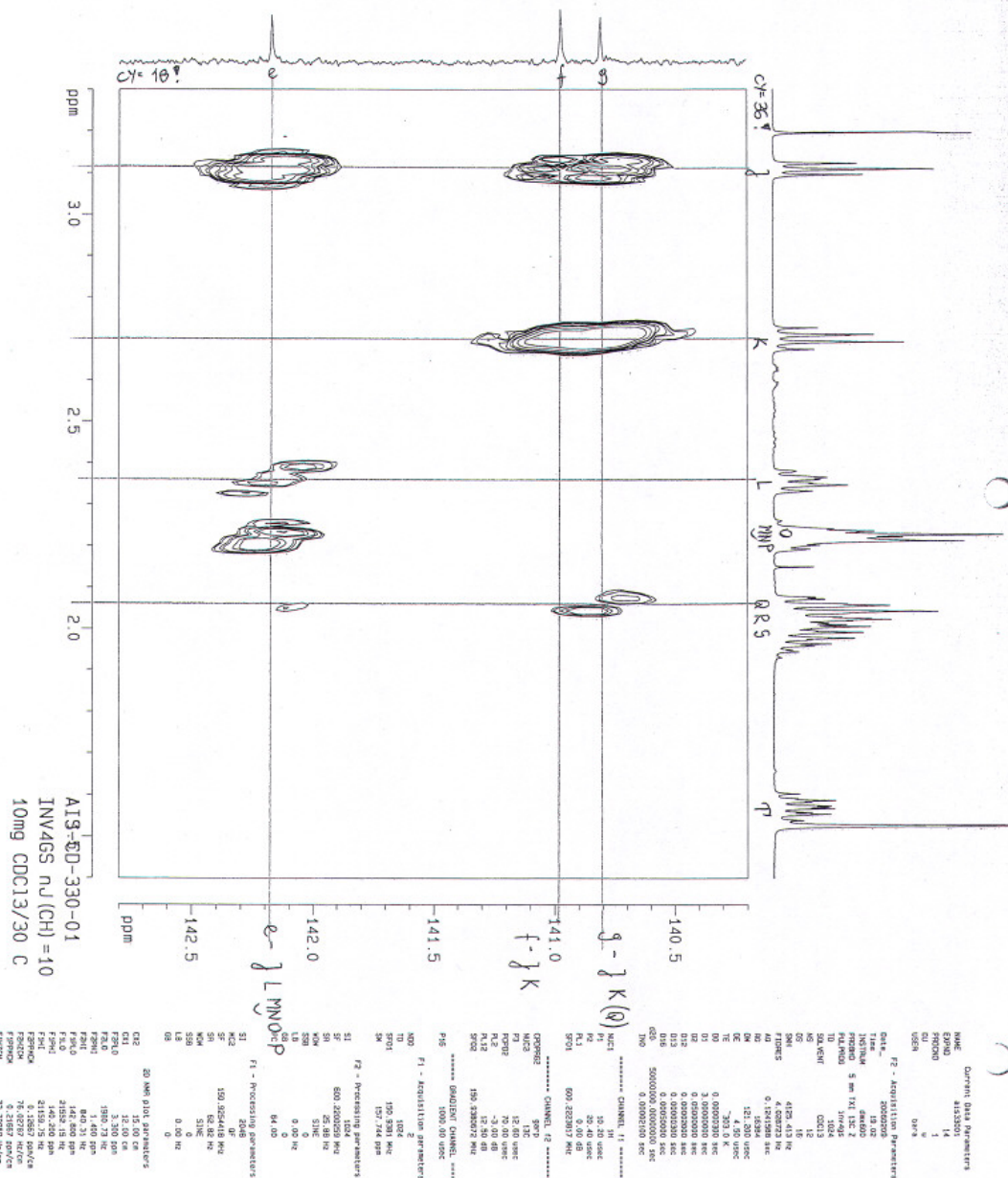
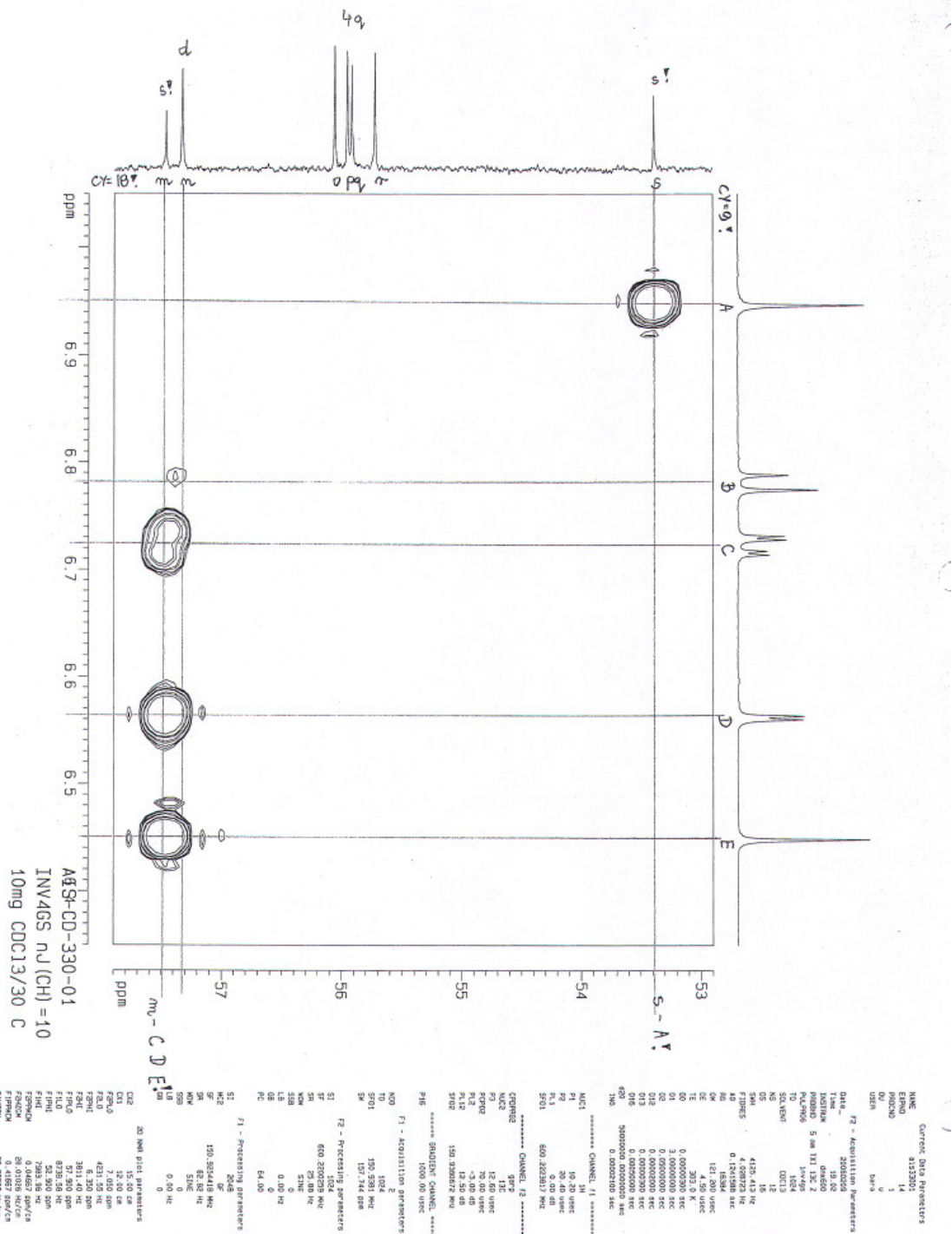
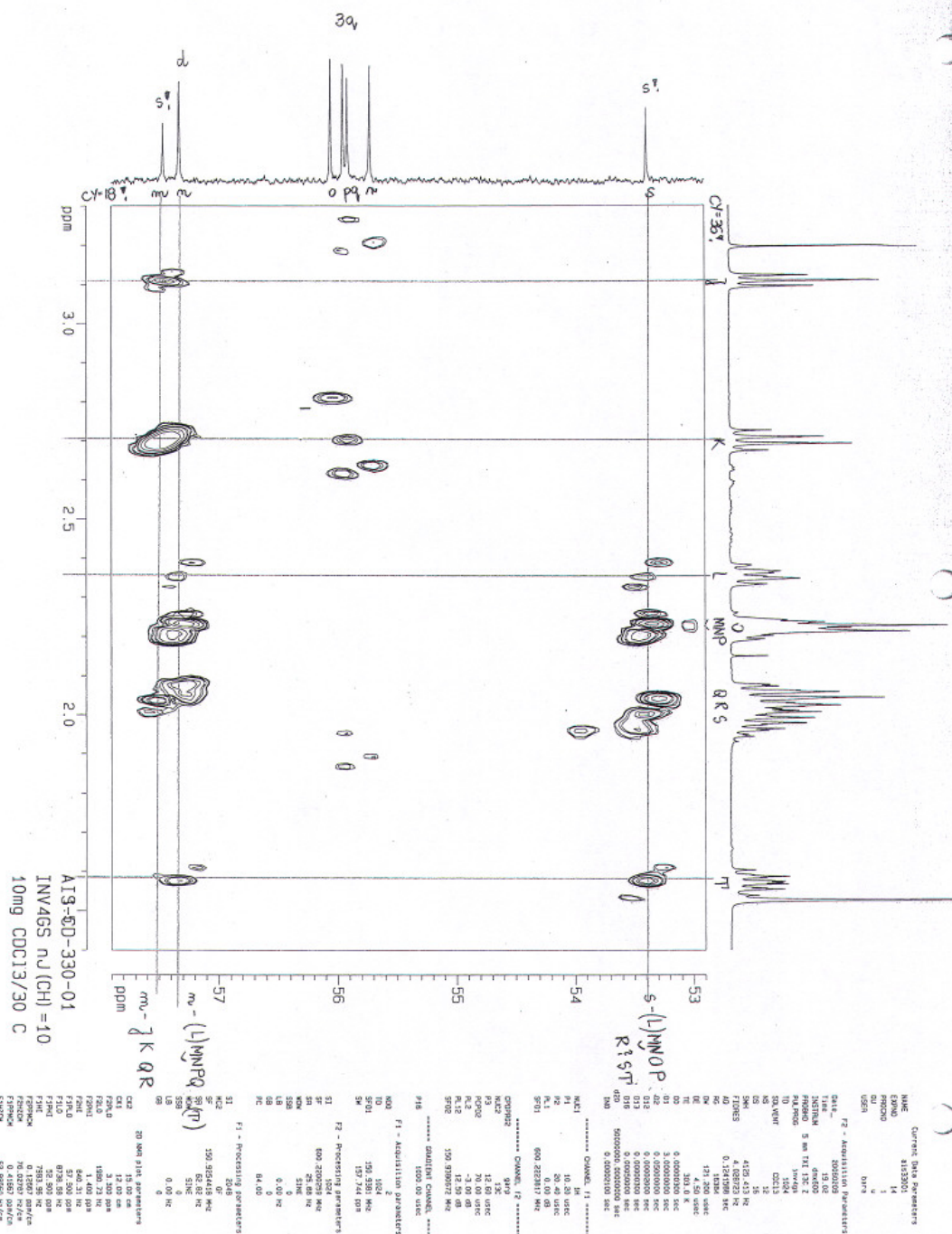


Figure S-3. Selected long range couplings for compound **23**.







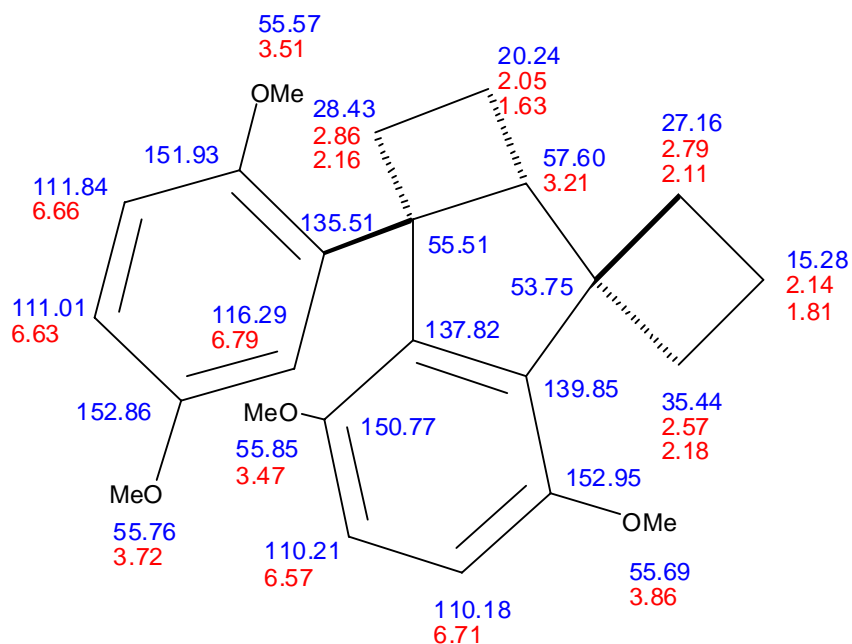


Figure S-4. Overview over the spectral data recorded for compound **21** (DMX 600 spectrometer, CDCl_3). ^1H NMR shifts are given in red, ^{13}C NMR shifts are shown in blue. The signal assignments are unambiguous, based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydtq*); HSQC (*invietgssi*) optimized for $^1J(\text{C},\text{H}) = 145$ Hz; HMBC (*inv4gslplrnd*) for correlations via $^nJ(\text{C},\text{H})$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

Figure S-5. Selected NOESYs for compound 21.

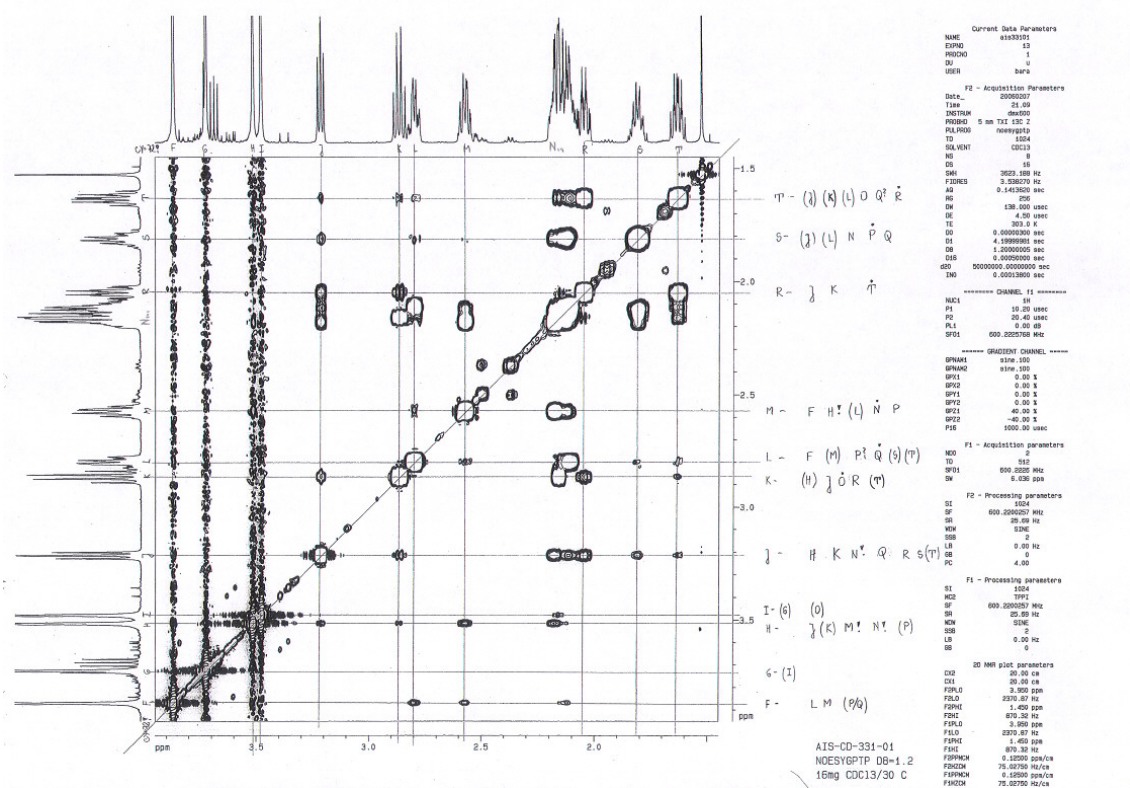
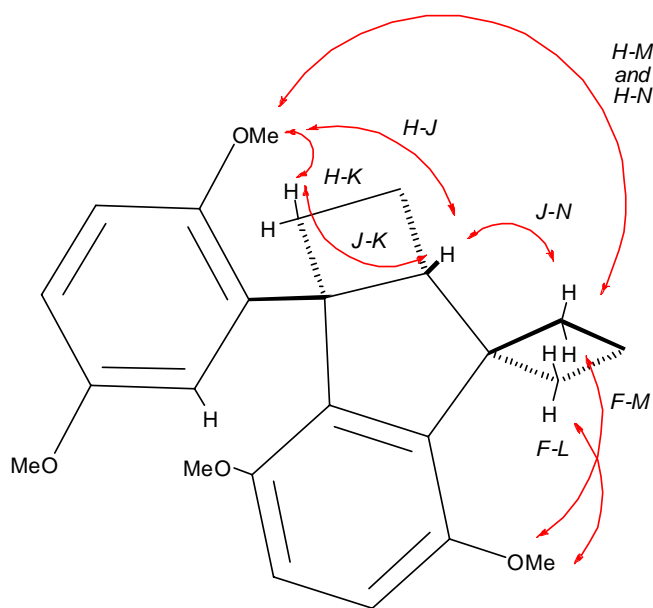


Figure S-6. Selected long range couplings for compound **21**.