Supplementary Information for the Manuscript:

The Diels-Alder reactions of quinone-imine-ketals: A versatile synthesis of highly substituted 5-methoxy indoles.

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Experimental

General

Infrared spectra were obtained as thin films on NaCl plates using a BOMEM 100 MB FT-IR instrument. NMR experiments were performed on a Varian INOVA 400 or Mercury 400 instrument and spectra were obtained in $CDCl_3$ (referenced at 7.26 ppm for ^1H and 77.0 ppm for ^{13}C) or C_2D_6SO (referenced at 2.49 ppm for ^1H and 39.5 ppm for ^{13}C). Coupling values (*J*) are in Hz. Mass spectra were obtained on a Finnigan MAT 8200 spectrometer at 70 eV.

Hyperbaric conditions were achieved using a LECO^{TM} Tempres high pressure chemical reactor. Dichloromethane, toluene and THF were distilled prior to use according to the standard procedures.[1] All other reagents were used as purchased from Aldrich or Lancaster. Reactions were checked for completion by TLC (EM Science, silica gel 60 F_{254}) and/or ^1H NMR. Flash chromatography was performed using silica gel purchased from Silicycle Chemical Division Inc. (230-400 Mesh).

Procedures

N-(4-methoxy-8-methyl-5,8-dihydronaphthalen-1-yl)benzamide (13). The quinone imine ketal **10** (0.776 g, 3.0 mmol) and piperylene (0.613 g, 9.0 mmol) were taken up in dry methylene chloride (1.0 mL) in a 10 mL pear-shaped flask. This solution was transferred, with the aid of an additional 1.0 mL CH_2Cl_2, to a ~7 cm length of heat shrinkable Teflon tubing which was pinched and sealed at one end with a brass screw clamp. Excess air was squeezed from the tube and it was sealed with a brass screw clamp. The vessel was then pressurized in a LECO Tempres HPC 200 system at 13 kbar and 50^{o}C for a period of 12 hours, after which time the reaction mixture was concentrated and taken up in dry THF (20 mL). Concentrated HCl (1 drop) was added and the mixture was stirred under argon for 30 minutes, after which time solid $NaHCO_3$ was added. The mixture was then stirred for an additional 10 minutes and anhydrous $MgSO_4$ was then added, stirring for 10 minutes further. The mixture was filtered, washing with THF and concentrated. The crude residue was purified via trituration with cold hexanes, the solid filtered and dried. The yield was 0.857 g (97%) as a white solid. ^1H NMR (400 MHz, DMSO) δ = 9.79 (s, 1H), 7.97 (app d, J = 6.8 Hz, 2H), 7.59-7.49 (m, 3H), 7.12 (d, J = 8.6 Hz, 1H), 6.85 (d, J= 8.6 Hz, 1Hz), 5.91-5.84 (m, 2H), 3.80 (s, 3H), 3.63-3.56 (m, 1H), 3.28-3.24 (m, 1H), 3.09-3.02 (m, 1H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ = 165.9, 154.8, 137.7, 134.6, 131.4, 130.6, 128.4, 127.7, 127.5, 127.0, 122.8, 122.7, 107.5, 55.4, 29.9, 24.0, 22.4; IR (thin films) ν = 3276, 1643 cm^{-1}; MS *m/z* (relative intensity) 294 (14, M+1), 293 (66, M^+), 188 (21), 105 (100), 77 (43); HRMS (EI 70 eV) – calcd for $C_{19}H_{19}NO_2$: 293.1416, found: 293.1409.

N-(4-methoxy-6,7-dimethyl-5,8-dihydronaphthalen-1-yl)benzamide (14). The reaction between quinone imine ketal **10** (0.778 g, 3.0 mmol) and 2,3-dimethyl-1,3-butadiene (0.742 g, 9.0 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified via trituration with cold EtOAc / hexanes (30%), the solid filtered and dried. The yield was 0.791 g (87%) as a white solid. ^1H NMR (400 MHz, DMSO) δ = 9.73 (s, 1H), 7.97 (app d, J = 7.4 Hz, 2H), 7.59-7.45 (m, 3H), 7.11 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 3.78 (s, 3H), 3.16-3.14 (m, 4H), 1.73 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ

[1] Perrin, D. D.; Armarego, W. L. F. In *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988

= 165.5, 154.3, 134.6, 132.1, 131.5, 128.4, 127.8, 127.6, 125.3, 123.0, 122.1, 121.9, 107.3, 55.3, 32.1, 30.9, 18.5 (two overlapping signals); IR (thin film) ν = 3267, 1641 cm^{-1}, MS *m/z* (relative intensity) 308 (12, M+1), 307 (49, M^+), 172 (8), 105 (100), 77 (56); HRMS (EI 70eV) – calcd for $C_{20}H_{21}NO_2$: 307.1572, found: 307.1567.

N-(8-methoxy-1,4-dihydro-1,4-ethanonaphthalen-5-yl)benzamide (15). The reaction between quinone imine ketal **10** (0.7751 g, 3.0 mmol) and 1,3-cyclohexadiene (0.721 g, 9.0 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified via trituration with cold hexanes, the solid filtered and dired. The yield was 0.842 g (92%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ = 9.95 (s, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.60-7.50 (m, 3H), 6.98 (d, J = 8.6 Hz, 1H), 6.73 (d, J = 8.6 Hz, 1H), 6.49-6.42 (m, 2H), 4.35 (dd, J = 5.5, 2.0 Hz, 1H), 4.02 (dd, J = 5.5, 2.0 Hz, 1H), 3.78 (s, 3H), 1.48-1.34 (m, 3H), 1.31-1.23 (m, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 165.8, 151.1, 141.5, 135.3, 134.9, 134.5, 131.8, 131.5, 128.4, 127.7, 124.9, 123.6, 107.5, 55.5, 35.4, 32.4, 24.8, 24.3; IR (thin film) ν = 3286, 1645 cm^{-1}, MS *m/z* (relative intensity) 306 (7, M+1), 305 (33, M^+), 277 (56), 145 (9), 105 (100), 77 (37); HRMS (EI 70 eV) – calcd for $C_{20}H_{19}NO_2$: 305.1416, found: 305.1415.

N-(4-methoxy-7,8-dimethyl-5,8-dihydronaphthalen-1-yl)benzamide (**16**). The reaction between quinone imine ketal **10** (0.590 g, 2.3 mmol) and (3E)-3-methylpenta-1,3-diene (0.587 g, 6.9 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified via trituration with cold EtOAc / hexanes (1%). The yield was 0.572 g (81%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ = 9.77 (s, 1H), 7.97 (dd, J=1.6, 6.8 Hz, 2H), 7.58-7.50 (m, 3H), 7.11 (d, J=8.6 Hz, 1H), 6.84 (d, J=8.6 Hz, 1H), 5.59 (br. s, 1H), 3.80 (s, 3H), 3.42-3.28 (m, 2H), 3.03-2.98 (m, 1H), 1.77 (s, 3H), 1.06 (d, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ = 166.0, 154.7, 138.6, 136.8, 134.7, 131.4, 128.5, 127.5, 127.4, 127.0, 122.8, 118.3, 107.4, 55.4, 34.5, 24.4, 21.4, 20.4; IR (thin film) ν = 3278, 1643 cm^{-1}; MS *m/z* (relative intensity) 308 (25, M+1), 307 (96, M^+), 292 (63), 202 (27), 186 (100), 172 (27), 105 (75), 77 (65); HRMS (EI 70 eV) – calcd for $C_{20}H_{21}NO_2$: 307.1572, found: 307.1574.

N-(8-methoxy-6-methyl-1,4-dihydro-1,4-ethanonaphthalen-5-yl)benzamide (17). The reaction between quinone imine ketal **11** (0.845 g, 3.1 mmol) and 1,3-cyclohexadiene (0.721 g, 9.0 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified via trituration with cold EtOAc / hexanes (1%), the solid filtered and dried. The yield was 0.906 g (92%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ = 9.71 (s, 1H), 8.04-8.00 (m, 2H), 7.61-7.50 (m, 3H), 6.65 (s, 1H), 6.46 (ddd, J = 7.6, 6.1, 1.4 Hz, 1H), 6.41 (ddd, J = 7.6, 6.1, 1.5 Hz, 1H), 4.29 (dd, J = 6.1, 1.4 Hz, 1H), 3.94 (dd, J = 6.1, 1.5 Hz, 1H), 3.77 (s, 3H), 2.14 (s, 3H), 1.41-1.34 (m, 3H), 1.28-1.25 (m, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 165.7, 151.2, 143.0, 135.1, 135.1, 134.4, 132.3, 131.5, 129.1, 128.5, 127.6, 123.6, 109.1, 55.4, 35.5, 32.2, 24.9, 24.5, 18.2; IR (thin film) ν = 3293, 1645 cm^{-1}; MS *m/z* (relative intensity) 320 (7, M+1), 319 (28, M^+), 291 (83), 105 (100), 77 (61); HRMS (EI 70eV) – calcd for $C_{21}H_{21}NO_2$: 319.1572, found: 319.1566.

[8-(benzoylamino)-5-methoxy-7-methyl-1,4-dihydronaphthalen-1-yl]methyl pivalate (18). The reaction between quinone imine ketal **11** (0.380 g, 1.4 mmol) and diene (2*E*)-penta-2,4-dienyl pivalate (0.795 g, 4.73 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified by column chromatography on silica gel (elution

with 25% EtOAc/hexane). The yield was 0.399 g (70%) as a white solid. ^{1}H NMR(400 MHz, $CDCl_3$): 7.99-7.93(m, 2H), 7.57-7.46(m, 3H), 6.69(s, 1H), 6.08-6.04(m, 1H), 5.92-5.88(m, 1H), 4.14-4.11(m, 2H), 3.83(s, 3H), 3.82-3.79(m, 1H), 3.46-3.39(m, 1H), 3.11-3.05(m, 1H), 2.27(s, 3H), 1.05(s, 9H); ^{13}C NMR(100 MHz, $CDCl_3$): 178.7, 166.7, 155.5, 134.9, 134.4, 132.6, 131.6, 128.6, 127.4, 126.5, 126.0, 125.8, 122.7, 110.2, 68.3, 55.4, 38.6, 36.2, 27.0, 24.6, 18.8; IR (thin film) ν = 3292, 1727, 1645 cm^{-1}; MS *m/z* (relative intensity) 408 (0.2, M+1), 407 (0.6, M^+), 305 (5.5), 239 (12), 105 (100), 77 (42); HRMS (EI 70eV) – calcd for $C_{25}H_{29}NO_4$: 407.2097, found: 407.2097.

N-(3-chloro-4-methoxy-8-methyl-5,8-dihydronaphthalen-1-yl)benzamide (19). The reaction between quinone imine ketal **12** (0.925 g, 3.2 mmol) and piperylene (0.641 g, 9.4 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified via trituration with cold hexanes, the solid filtered and dried. The yield was 0.872 (85%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ = 9.93 (s, 1H), 7.97-7.94 (m, 2H), 7.62-7.57 (m, 1H), 7.55-7.51 (m, 2H), 7.33 (s, 1H), 5.95-5.87 (m, 2H), 3.79 (s, 3H), 3.68-3.64 (m, 1H), 3.47-3.46 (m, 1H), 3.31-3.25 (m, 1H), 1.05 (d, J = 7.0 Hz, 3H); ^{13} C NMR (100 MHz, DMSO) δ = 166.0, 151.1, 137.3, 134.2, 131.8, 131.7, 130.4, 130.3, 128.5, 127.6, 127.4, 123.4, 122.6, 59.9, 29.8, 24.3, 21.8; IR (thin film) ν = 3266, 1645 cm^{-1}; MS *m/z* (relative intensity) 328 (9, M+1), 327 (29, M^+), 172 (8), 105 (100), 77 (53), 49 (21); HRMS (EI 70eV) – calcd for $C_{19}H_{18}ClNO_2$: 327.1026, found: 327.1031.

N-(3-chloro-4-methoxy-7,8-dimethyl-5,8-dihydronaphthalen-1-yl)benzamide (**20**). The reaction between quinone imine ketal **12** (0.628 g, 2.2 mmol) and (3E)-3-methylpenta-1,3-diene (0.568 g, 6.5 mmol) was performed in a similar manner as in the preparation of compound **13**. The crude residue was purified by column chromatography on silica gel (elution with 20% EtOAc/hexane). The yield was 0.662 g (90%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ = 9.91 (s, 1H), 7.97-7.95 (m, 2H), 7.62-7.58 (m, 1H), 7.55-7.51 (m, 2H), 7.32 (s, 1H), 5.62-5.61 (m, 1H), 3.78 (s, 3H), 3.48-3.46 (m, 1H), 3.43 (dd, J = 21.5, 5.3 Hz, 1H), 3.23 (dd, J = 21.5, 2.3 Hz, 1H), 1.79 (s, 3H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ = 166.1, 151.0, 138.2, 137.0, 134.3, 131.7, 131.4, 130.5, 128.5, 127.6, 127.3, 123.2, 118.0, 60.0, 34.4, 24.6, 21.3, 19.8; IR (thin film) ν = 3426, 1645 cm^{-1}; MS *m/z* (relative intensity) 342 (M+1, 12), 341 (M^+, 72), 186 (20), 105 (100), 77 (49); HRMS (EI 70 eV) – calcd for $C_{20}H_{20}ClNO_2$: 341.1183, found: 341.1181.

(1-benzoyl-5-methoxy-3-methyl-1H-indol-4-yl)acetaldehyde (21). The dihydronaphthalene **13** (0.147 g, 0.50 mmol) was suspended in a mixture of THF (3 mL) and H_2O (2 mL). A crystal of osmium tetroxide (< 1 mg) was added, and the mixture stirred for 5 min giving a black solution, after which NMO (0.070 g, 0.60 mmol) was added. The solution was stirred until starting material was consumed by TLC (~ 1 h), at which point Na_2SO_3 (0.756 g, 6 mmol) was added, and the mixture stirred for a further 10 min. The mixture was extracted with EtOAc (3 times), and the combined organic layers were then washed with brine, dried with $MgSO_4$, filtered and concentrated to yield 0.157 g (ca. 93%) of the crude diol (R_F = 0.01, 30% EtOAc/hexane) as an off-white solid. The crude diol was used without further purification, and suspended in CH_2Cl_2 (9.0 mL). This suspension was added dropwise, via Pasteur pipette, to a vigorously stirred mixture of $NaIO_4$ / SiO_2 (1.17 g) in CH_2Cl_2 (3.5 mL). The mixture was stirred for three hours, filtered and concentrated to yield 0.135 g (ca. 89%) of the crude dialdehyde (R_F = 0.47, 70%

EtOAc/hexane) as a yellow oil, which was taken up in dry toluene. *p*-Toluenesulfonic acid (ca. 15 mg) was added to the solution, and the mixture stirred under argon until consumption of the dialdehyde was indicated by TLC (~ 2 h). Solid $NaHCO_3$ was then added with stirring, the mixture filtered, washing with CH_2Cl_2, and concentrated to a volume of approximately 5 mL. The crude indole (R_F = 0.54, 80% CH_2Cl_2/hexane) was purified by column chromatography on silica gel (elution with 60% CH_2Cl_2/hexane). The yield was 0.112 g (73%, over 3 steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.74 (t, J = 2.0 Hz, 1H), 8.43 (d, J = 9.0 Hz, 1H), 7.70-7.68 (m, 2H), 7.61-7.57) (m, 1H), 7.54-7.50 (m, 2H), 7.03 (d, J = 9.0 Hz, 1H), 7.02 (s, 1H), 4.11 (d, J = 2.0 Hz, 2H), 3.91 (s, 3H), 2.32 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 167.9, 154.4, 134.8, 131.9, 131.6, 131.3, 128.9, 128.5, 126.9, 117.4, 116.3, 112.7, 108.8, 56.4, 40.8, 13.4; IR (thin film) ν = 1708, 1679 cm^{-1}; MS *m/z* (relative intensity) 308 (40, M+1), 307 (45, M^+), 278 (37), 105 (100), 77 (38); HRMS (EI 70 eV) – calcd for $C_{19}H_{17}NO_3$: 307.1208, found: 307.1213.

1-(1-benzoyl-5-methoxy-2-methyl-1H-indol-4-yl)acetone (22). The dihydronaphthalene **14** (0.154 g, 0.50 mmol) was reacted following the same procedure for the formation of indole **21**. Note that in the acid catalyzed closure of the benzopyrole ring CH_2Cl_2 (10 mL) was used as a co-solvent. The crude indole was purified by column chromatography (elution with CH_2Cl_2). The yield was 0.060 g (37%, over 3 steps) as a off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (app d, J = 8.2 Hz, 2H), 7.64-7.60 (m, 1H), 7.51-7.47 (m, 2H), 6.96 (d, J = 9.0 Hz, 1H), 6.68 (d, J = 9.0 Hz, 1H), 6.36 (s, 1H), 3.89 (s, 2H), 3.82 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.2, 169.6, 153.0, 139.3, 135.6, 132.7, 132.0, 130.7, 129.5, 128.7, 113.8, 112.9, 107.1, 106.8, 56.3, 42.1, 29.0, 16.1; IR (thin film) ν = 1709, 1684 cm^{-1}; MS *m/z* (relative intensity) 322 (M+1, 6), 321 (M^+, 26), 278 (57), 105 (100), 77 (59); HRMS (EI 70 eV) – calcd for $C_{20}H_{19}NO_3$: 321.1365, found: 321.1368.

1-benzoyl-6-methoxy-1,3,4,5-tetrahydrobenzo[cd]indole-5-carbaldehyde (23). The dihydronaphthalene **15** (0.153 g, 0.50 mmol) was reacted following the same procedure for the formation of indole **21**. The crude indole was purified by column chromatography (elution with 70% CH_2Cl_2/hexane). The yield was 0.114 g (71%, over 3 steps) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.77 (d, J = 0.8 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.72-7.70 (m, 2H), 7.61-7.57 (m, 1H), 7.53-7.49 (m, 2H), 7.00 (d, J = 8.6 Hz, 1H), 7.00 (s, 1H), 4.09-4.07 (m, 1H), 3.92 (s, 3H), 2.78-2.72 (m, 2H), 2.59-2.53 (m, 1H), 1.95-1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.7, 168.2, 152.9, 134.8, 131.5, 131.1, 129.4, 128.8, 128.5, 122.2, 118.1, 116.2, 112.5, 109.2, 56.2, 45.7, 22.9, 18.6; IR (thin film) ν = 1720, 1676 cm^{-1}; MS *m/z* (relative intensity) 320 (5, M+1), 319 (21, M^+), 290 (33), 105 (100) 77 (43); HRMS (EI 70 eV) – calcd for $C_{20}H_{17}NO_3$: 319.1208, found: 319.1209

(1-benzoyl-5-methoxy-2,3-dimethyl-1H-indol-4-yl)acetaldehyde (24). The dihydronaphthalene **16** (0.155 g, 0.5 mmol) was reacted following the same procedure for the formation of indole **21**. The crude indole was purified by column chromatography (elution with 70% CH_2Cl_2 /hexane). The yield was 0.130 g (80%, over 3 steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.74(t, J=2.0 Hz, 1H), 7.70-7.68(m, 2H), 7.63-7.59(m, 1H), 7.51-7.46(m, 2H), 7.11(d, J=9.0 Hz, 1H), 6.71(d, J=9.2 Hz, 1H), 4.13(d, J=2.0 Hz, 2H), 3.82(s, 3H), 2.32(s, 3H), 2.22(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.8, 169.4, 153.5, 136.0, 134.7, 132.7, 131.9, 130.4, 129.7, 128.7, 114.5, 113.7, 111.6, 106.9, 56.4, 41.0, 13.2, 12.1; IR (thin film) ν = 1722,

1679 cm^{-1}; MS *m/z* (relative intensity) 322 (14, M+1), 321 (56, M^+), 292 (42), 105 (100), 77 (34); HRMS (EI 70eV) – calcd for $C_{20}H_{19}NO_3$: 321.1365, found: 321.1357.

1-benzoyl-6-methoxy-8-methyl-1,3,4,5-tetrahydrobenzo[cd]indole-5-carbaldehyde (25). The dihydronaphthalene **17** (0.160 g, 0.50 mmol) was reacted following the same procedure for the formation of indole **21**. Note that in the acid catalyzed closure of the benzopyrole ring CH_2Cl_2 (6 mL) was used as a co-solvent. The crude indole was purified by column chromatography (elution with 70% CH_2Cl_2/hexane). The yield was 0.115 g (69%, over 3 steps) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.74 (br t, J = 1.0 Hz, 1H), 7.88-7.86(m, 2H), 7.64-7.60 (m, 1H), 7.55-7.50 (m, 2H), 6.91 (br t, J = 1.2 Hz, 1H), 6.82 (s, 1H), 4.03 (br t, J = 4.4 Hz, 1H), 3.92 (s, 3H), 2.74-2.69 (m, 2H), 2.58 (s, 3H), 2.55-2.49 (m, 1H), 1.93-1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.1, 167.6, 153.0, 134.5, 132.5, 132.0, 130.0, 129.2, 128.6, 126.6, 124.2, 117.1, 112.1, 109.8, 56.3, 45.6, 22.8, 21.9, 18.7; IR (thin film) ν = 1721, 1686 cm^{-1}; MS *m/z* (relative intensity) 334 (4, M+1), 333 (31, M^+), 105 (100), 77 (71); HRMS (EI 70eV) – calcd for $C_{21}H_{19}NO_3$: 333.1365, found: 333.1363.

[1-benzoyl-5-methoxy-7-methyl-4-(2-oxoethyl)-1H-indol-3-yl]methyl pivalate (26). The dihydronaphthalene **18** (0.204 g, 0.5 mmol) was reacted following the same procedure for the formation of indole **21**. Note that in the acid catalyzed closure of the benzopyrole ring CH_2Cl_2 (6 mL) was used as a co-solvent. The crude indole was purified by column chromatography (elution with CH_2Cl_2). The yield was 0.098 g (46%, over 3 steps) as a white solid. ^{1}H NMR(400 MHz, $CDCl_3$): 9.73(t, J=1.9 Hz, 1H), 7.92(d, J=8.2 Hz, 2H), 7.67(t, J=7.4 Hz, 1H), 7.55(t, J=7.9 Hz, 2H), 7.29(s, 1H), 6.89(s, 1H), 5.14(s, 2H), 4.06(d, J=1.6 Hz, 2H), 3.90(s, 3H), 2.47(s, 3H), 1,14(s, 9H); ^{13}C NMR(100 MHz, $CDCl_3$): 200.5, 178.0, 167.0, 154.7, 133.3, 132.2, 131.8, 131.0, 130.4, 128.9, 127.3, 126.4, 115.3, 112.0, 109.8, 58.8, 56.5, 40.9, 38.8, 27.1, 21.9; IR (thin film) ν = 1727, 1698 cm^{-1}; MS *m/z* (relative intensity) 422 (11, M+1), 421 (36, M^+), 319 (47), 291 (8), 215 (17), 105 (100), 77 (23); HRMS (EI 70eV) – calcd for $C_{25}H_{27}NO_5$: 421.1889, found: 421.1890.

(1-benzoyl-6-chloro-5-methoxy-1H-indol-4-yl)acetaldehyde (27). The dihydronaphthalene **19** (0.163 g, 0.50 mmol) was reacted following the same procedure for the formation of indole **21**. Note that in the acid catalyzed closure of the benzopyrole ring CH_2Cl_2 (6 mL) was used as a co-solvent. The crude indole was purified by column chromatography (elution with 70% CH_2Cl_2/hexane). The yield was 0.132 g (77%, over 3 steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.84 (t, J = 1.7 Hz, 1H), 8.57 (s, 1H), 7.71-7.68 (m, 2H), 7.64-7.59 (m, 1H), 7.55-7.51 (m, 2H), 7.03 (q, J = 1.2 Hz, 1H), 4.17 (d, J = 1.7 Hz, 2H), 3.85 (s, 3H), 2.28 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.1, 167.9, 151.1, 134.1, 133.3, 132.0, 129.7, 129.0, 128.6, 126.9, 125.3, 119.3, 117.7, 117.2, 61.2, 41.8, 13.0; IR (thin film) ν = 1722, 1684 cm^{-1}; MS *m/z* (relative intensity) 342 (M+1, 5), 341 (M^+, 19), 105 (100), 77 (35); HRMS (EI 70eV) – calcd for $C_{19}H_{16}ClNO_3$: 341.0819, found: 341.0815.

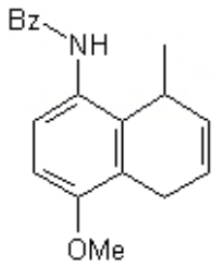
(1-benzoyl-6-chloro-5-methoxy-2,3-dimethyl-1H-indol-4-yl)acetaldehyde (**28**). The dihydronaphthalene **20** (0.171 g, 0.5 mmol) was reacted following the same procedure for the formation of indole **21**. Note that in the acid catalyzed closure of the benzopyrole ring CH_2Cl_2 (6 mL) was used as a co-solvent. The crude indole was purified by column chromatography (elution with 1% ACETONE/CH_2Cl_2). The yield was 0.125 g (70%, over 3 steps) as a white solid. ^{1}H

NMR (400 MHz, $CDCl_3$) δ = 9.84 (t, J = 1.7 Hz, 1H), 7.70-7.66 (m, 2H), 7.65-7.62 (m, 1H), 7.53-7.49 (m, 2H), 7.29 (s, 1H), 4.19 (d, J = 1.7 Hz, 2H), 3.79 (s, 3H), 2.27 (d, J = 0.6 Hz, 3H), 2.16 (d, J = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.5, 169.3, 150.2, 135.2, 134.7, 133.3, 133.2, 129.8, 128.9, 128.7, 123.1, 118.3, 115.0, 114.2, 61.1, 41.9, 13.2, 11.7; IR (thin film) ν = 1723, 1684 cm^{-1}; MS *m/z* (relative intensity) 356 (M+1, 9), 355 (M^+, 35), 105 (100), 77 (35); HRMS (EI 70eV) – calcd for $C_{20}H_{18}ClNO_3$: 355.0975, found: 355.0974.

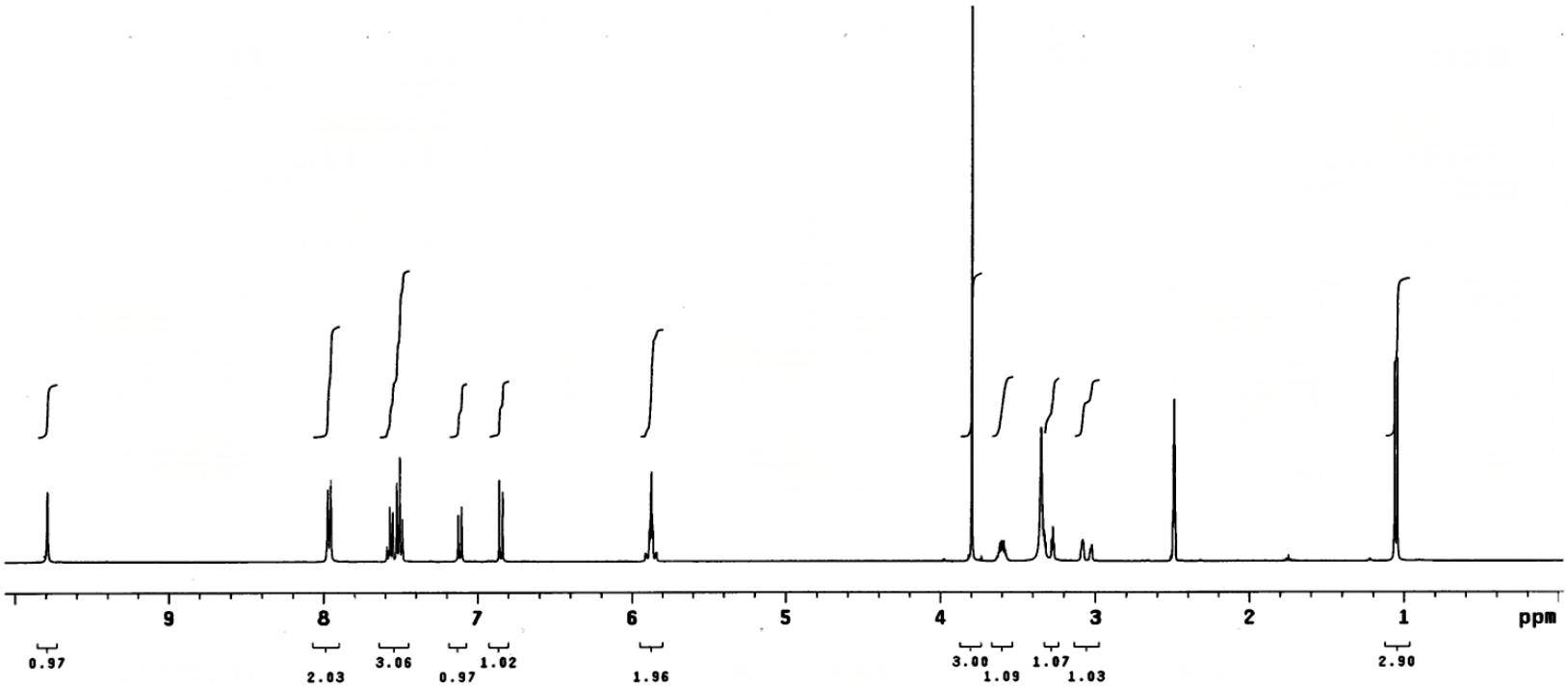
[SB-5-123] in DMSO, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb5123_30Jun2001-12:04:22

Pulse Sequence: s2pul



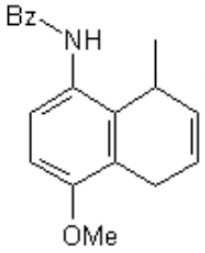
13



[SB-4-179]
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_24Mar2001

Pulse Sequence: s2pul

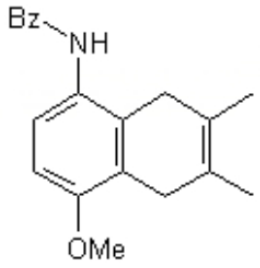


13

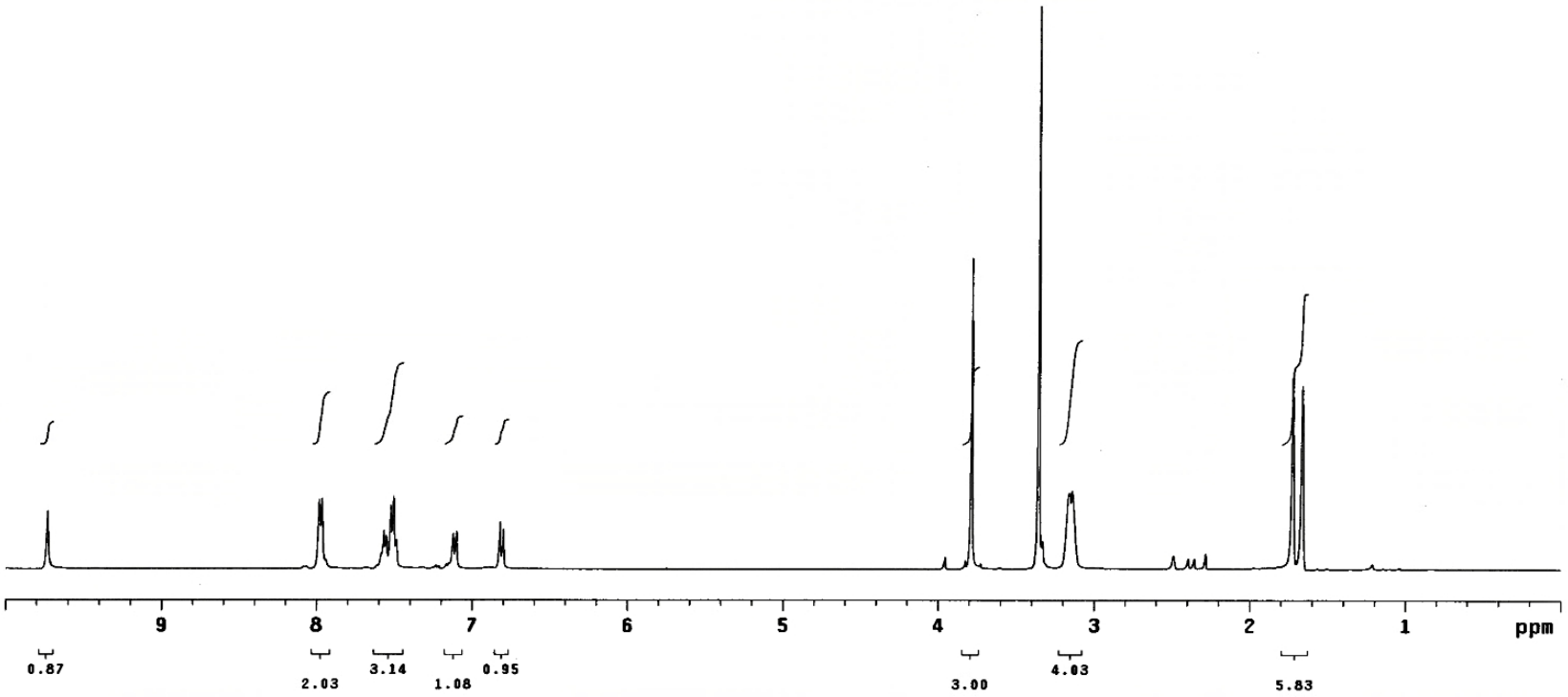
[Sb-5-33]
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_24Mar2001

Pulse Sequence: s2pul



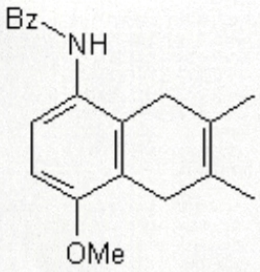
14



[Sb-5-33]
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_24Mar2001

Pulse Sequence: s2pul

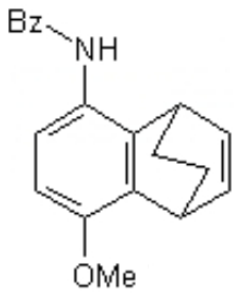


14

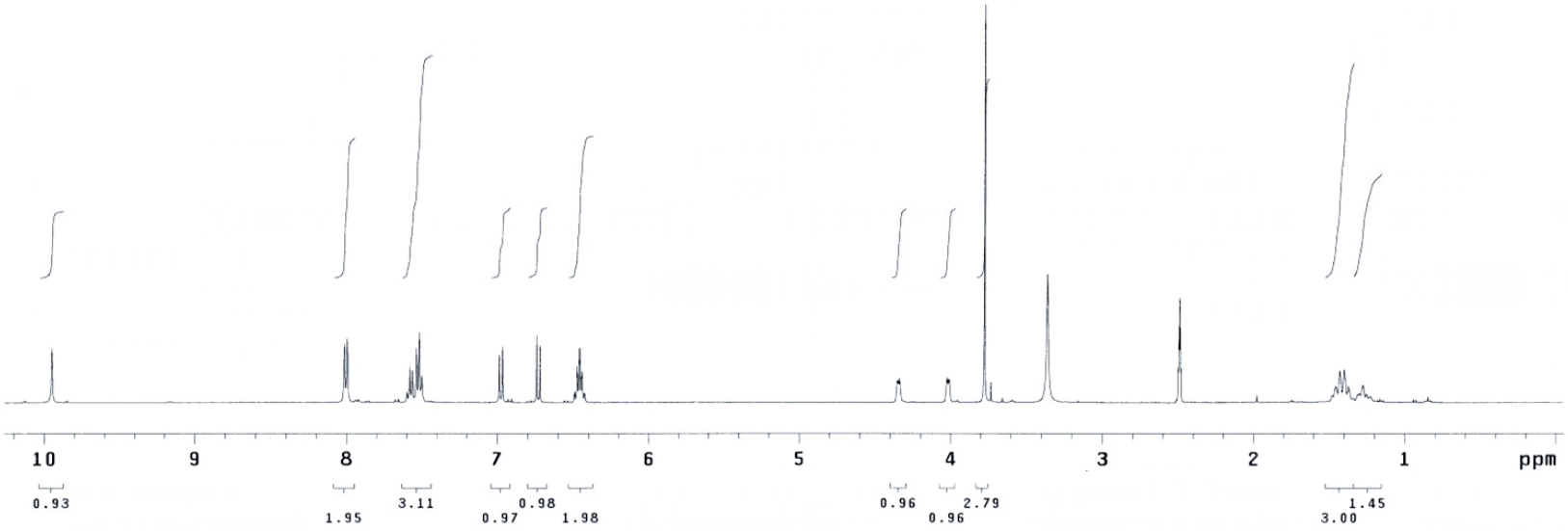
[SB-5-105] in DMSO, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb5105_30Jun2001

Pulse Sequence: s2pul



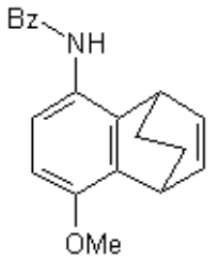
15



[SB-5-105] in DMSO, Mercury 400
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul

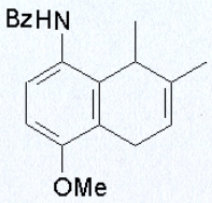


15

Dylan rxn 3-85 Invova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: DE3-85_02Aug2001-16:07:52

Pulse Sequence: s2pul

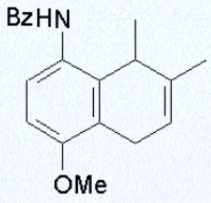


16

Dylan rxn 3-85
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_31Jul2001

Pulse Sequence: s2pul

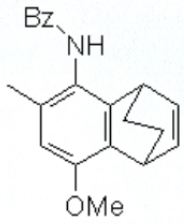


16

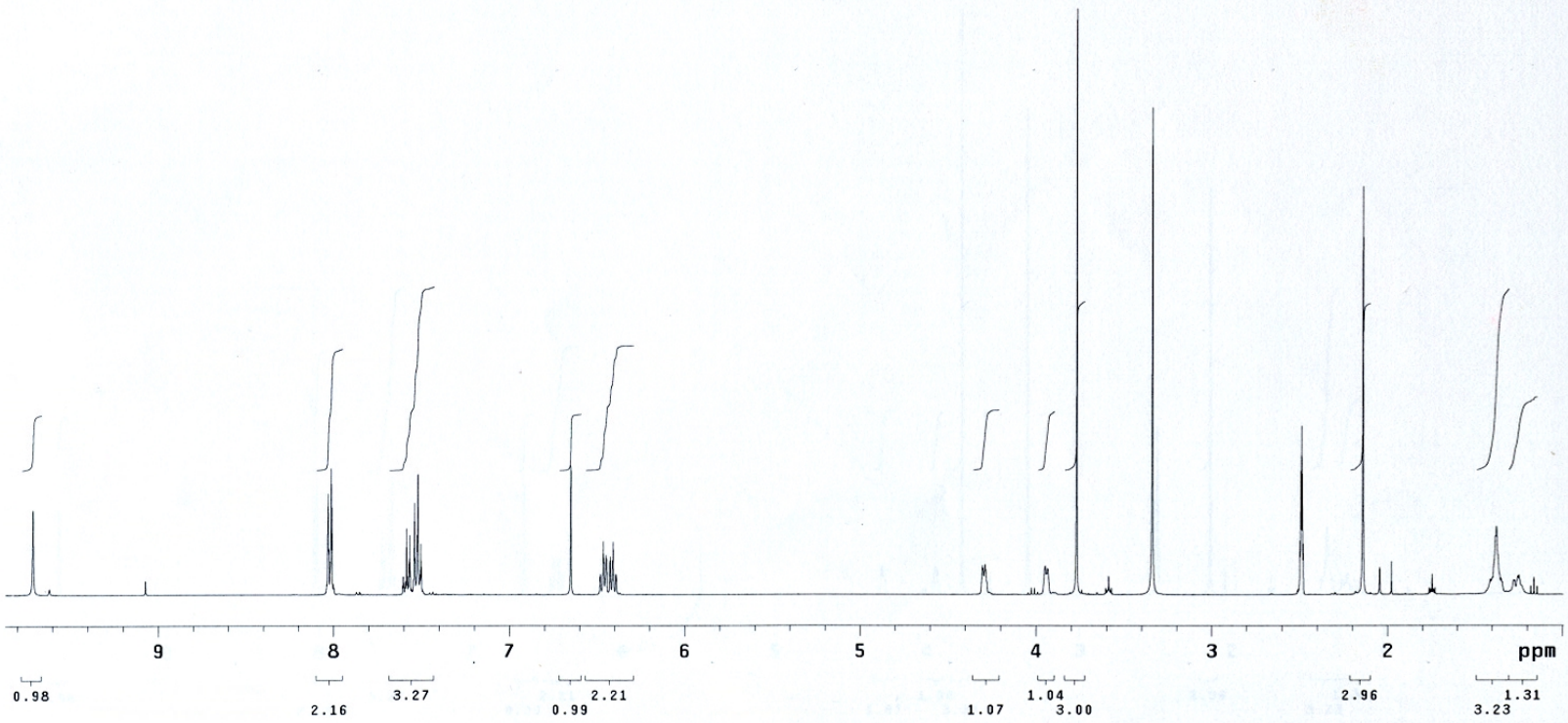
[SB-5-121] in DMSO, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb5121_30Jun2001

Pulse Sequence: s2pul



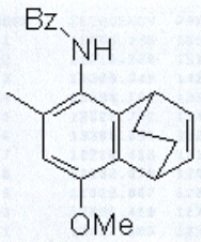
17



[SB-5-121] in DMSO, Mercury 400
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_01Jul2001

Pulse Sequence: s2pul

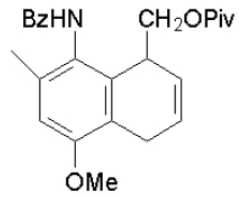


17

Dylan rxn 3-59 Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: DE3-59_07Aug2001

Pulse Sequence: s2pul

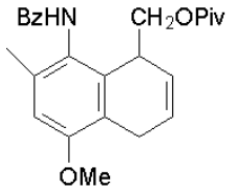


18

Dylan rxn 3-59
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_08Aug2001-16:25:30

Pulse Sequence: s2pul

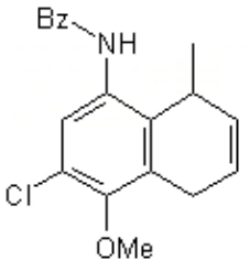


18

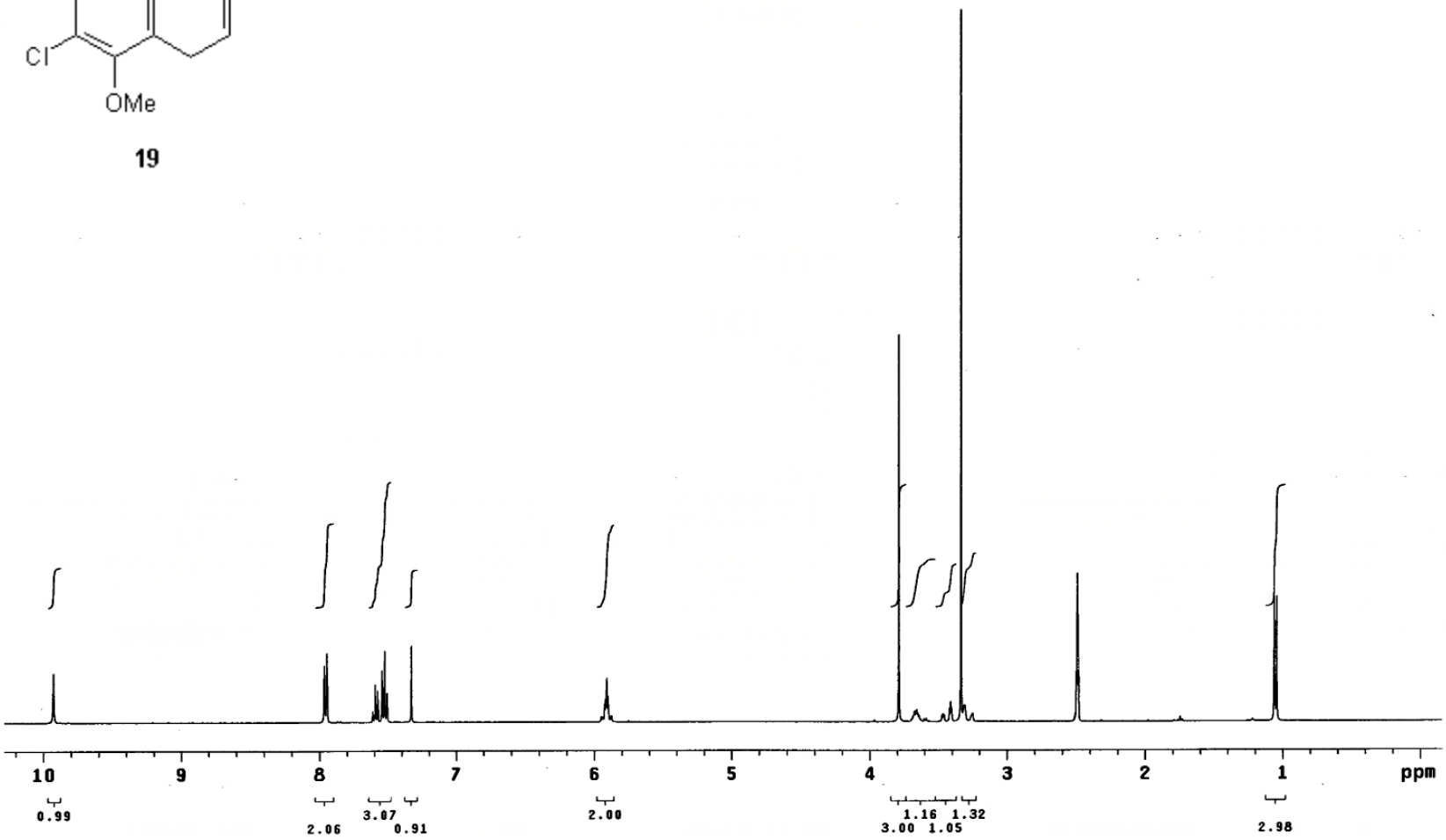
[SB-5-151] in DMSO, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb5151_30Jun2001

Pulse Sequence: s2pul



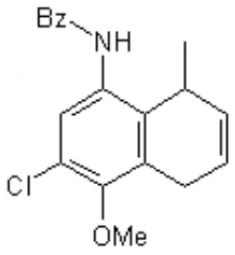
19



[SB-5-151]
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul

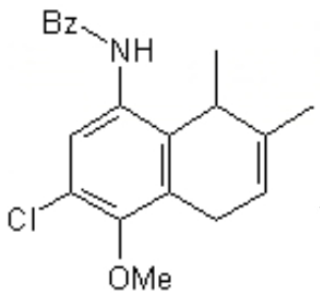


19

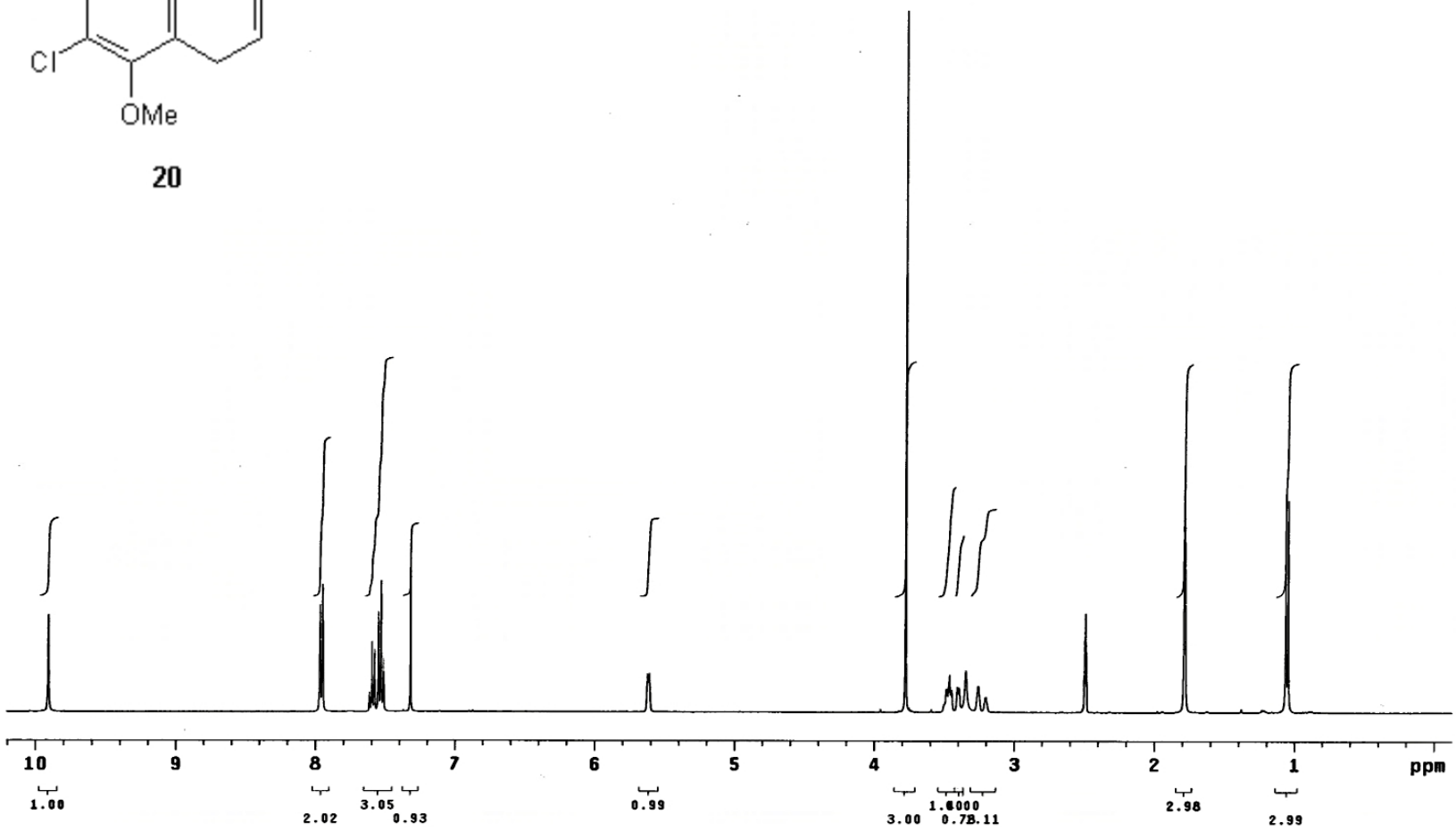
[SB-6-129] in DMSO, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb6129_02Aug2001

Pulse Sequence: s2pul



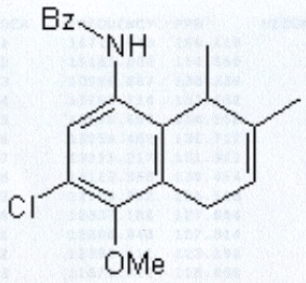
20



[SB-6-129] in DMSO, Mercury
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_02Aug2001

Pulse Sequence: s2pul

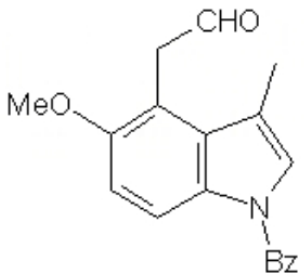


20

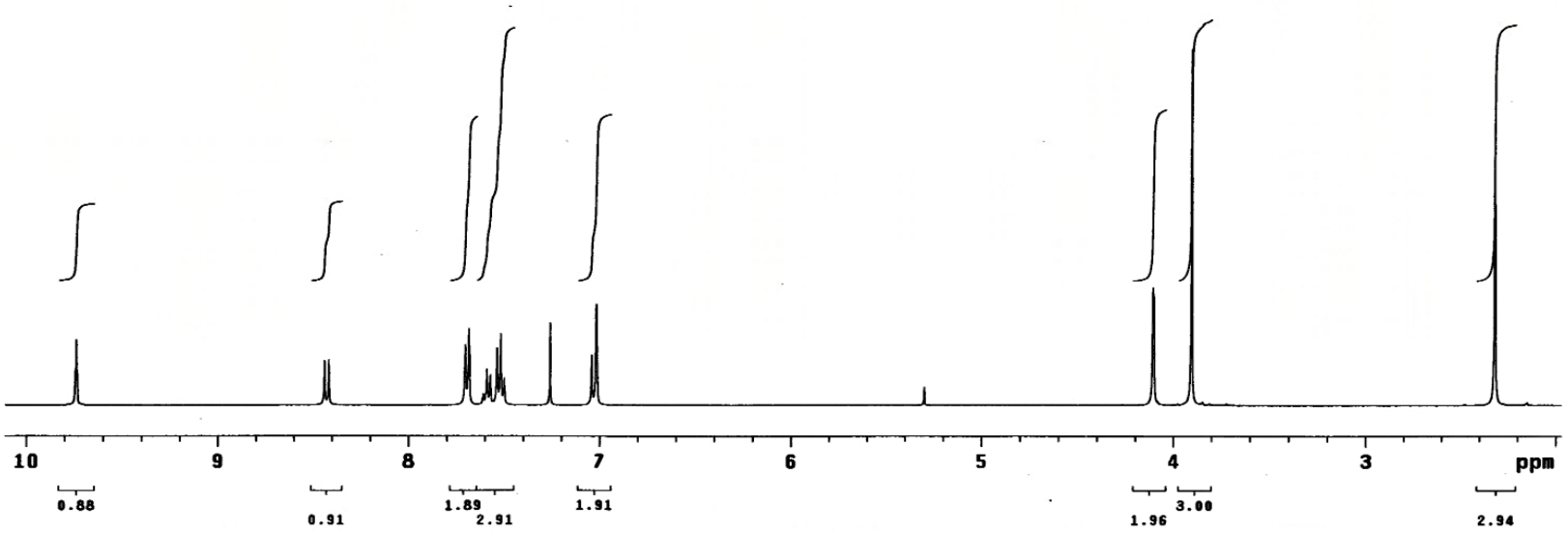
[SB-6-37] in CDCl3, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb637_30Jun2001

Pulse Sequence: s2pul



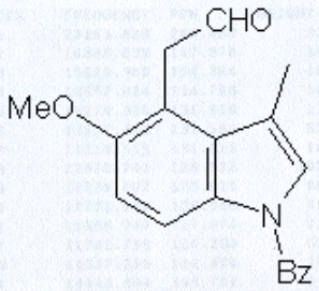
21



[SB-6-37] in CDCl3, Mercury 400
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul

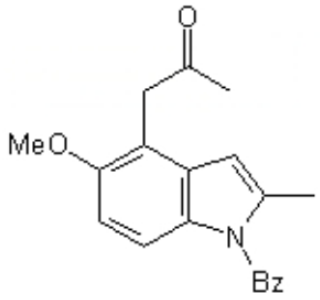


21

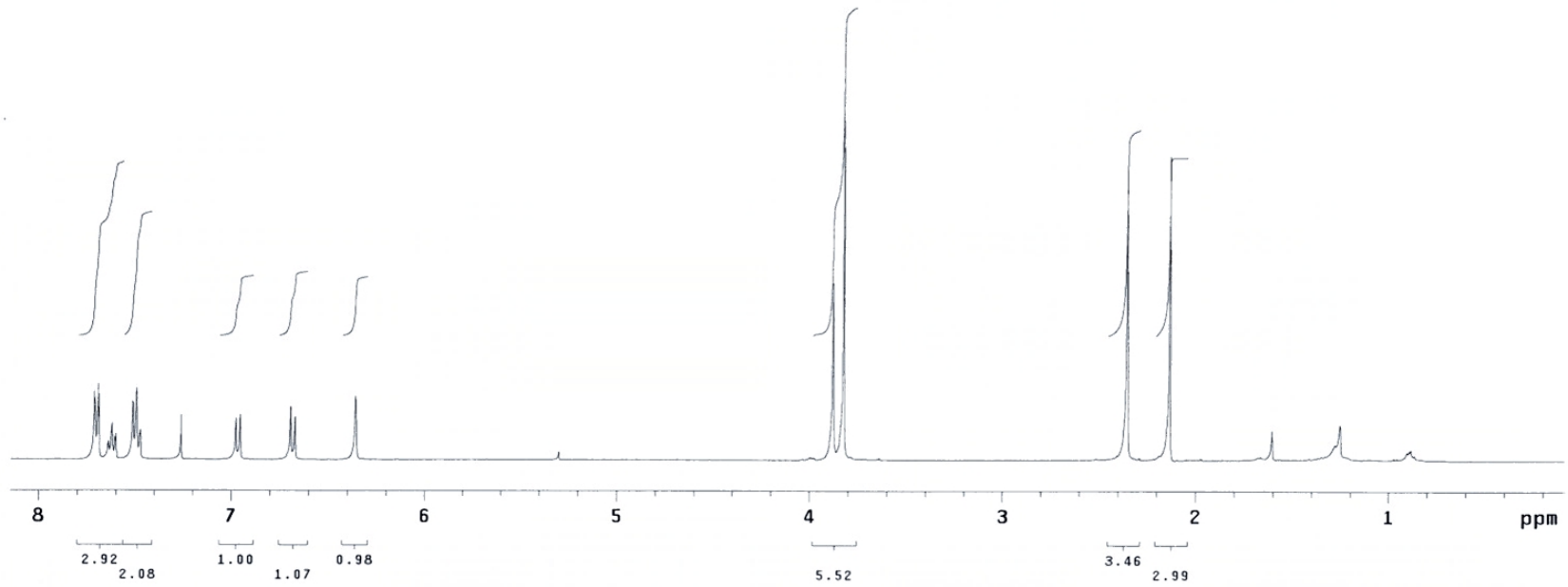
Dylan rxn 3-61
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_20Jul2001

Pulse Sequence: s2pul



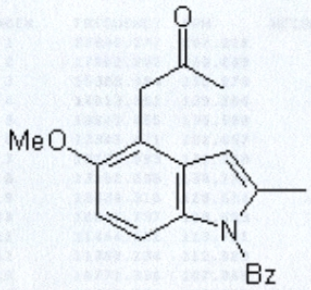
22



Dylan rxn 3-61
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_21Jul2001

Pulse Sequence: s2pul

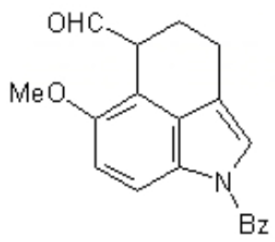


22

[SB-6-77] in CDCl3, Mercury 400
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul

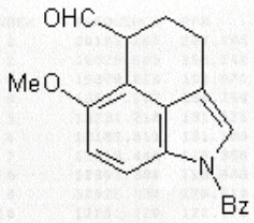


23

[SB-6-77] in CDCl3, Mercury 400
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul

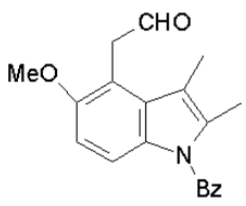


23

Dylan rxn 3-91 Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: DE3-91_03Aug2001

Pulse Sequence: s2pul

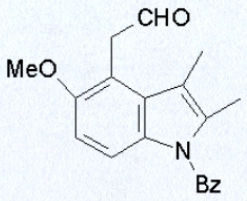


24

Dylan rxn 3-91
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_03Aug2001

Pulse Sequence: s2pul

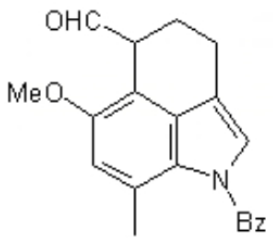


24

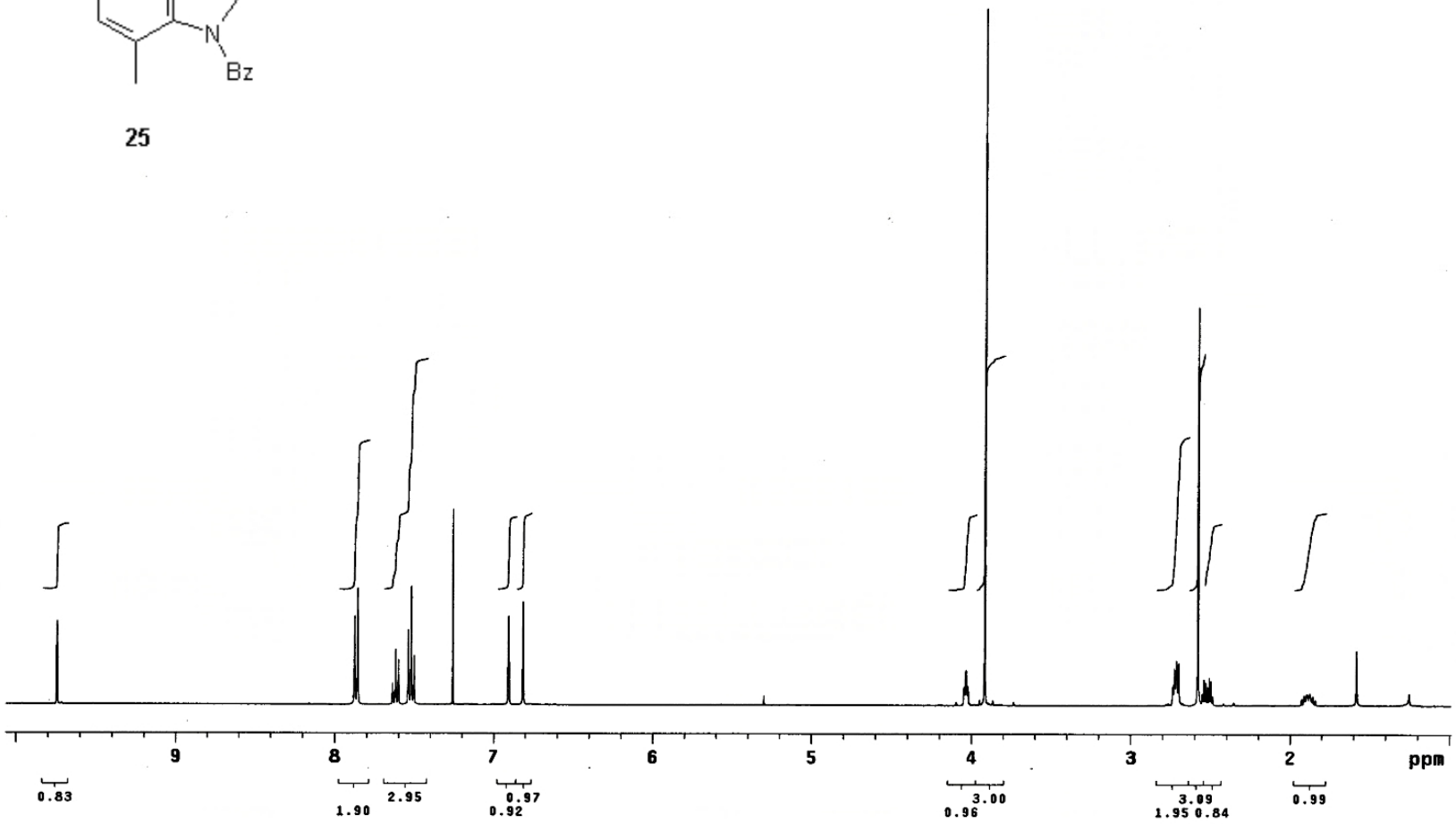
[SB-6-99] in CDCl3, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb699_30Jun2001

Pulse Sequence: s2pul



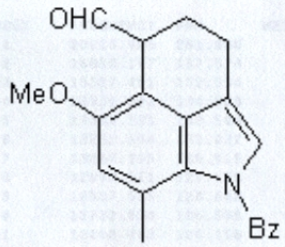
25



[SB-6-99]
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul

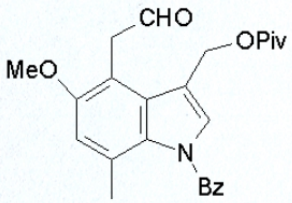


25

Dylan rxn 3-69
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_23Jul2001

Pulse Sequence: s2pul

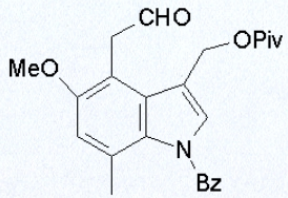


26

Dylan rxn 3-69
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_25Jul2001

Pulse Sequence: s2pul

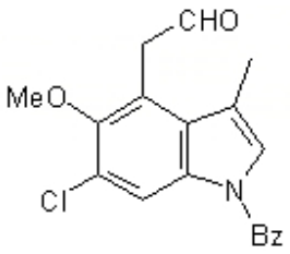


26

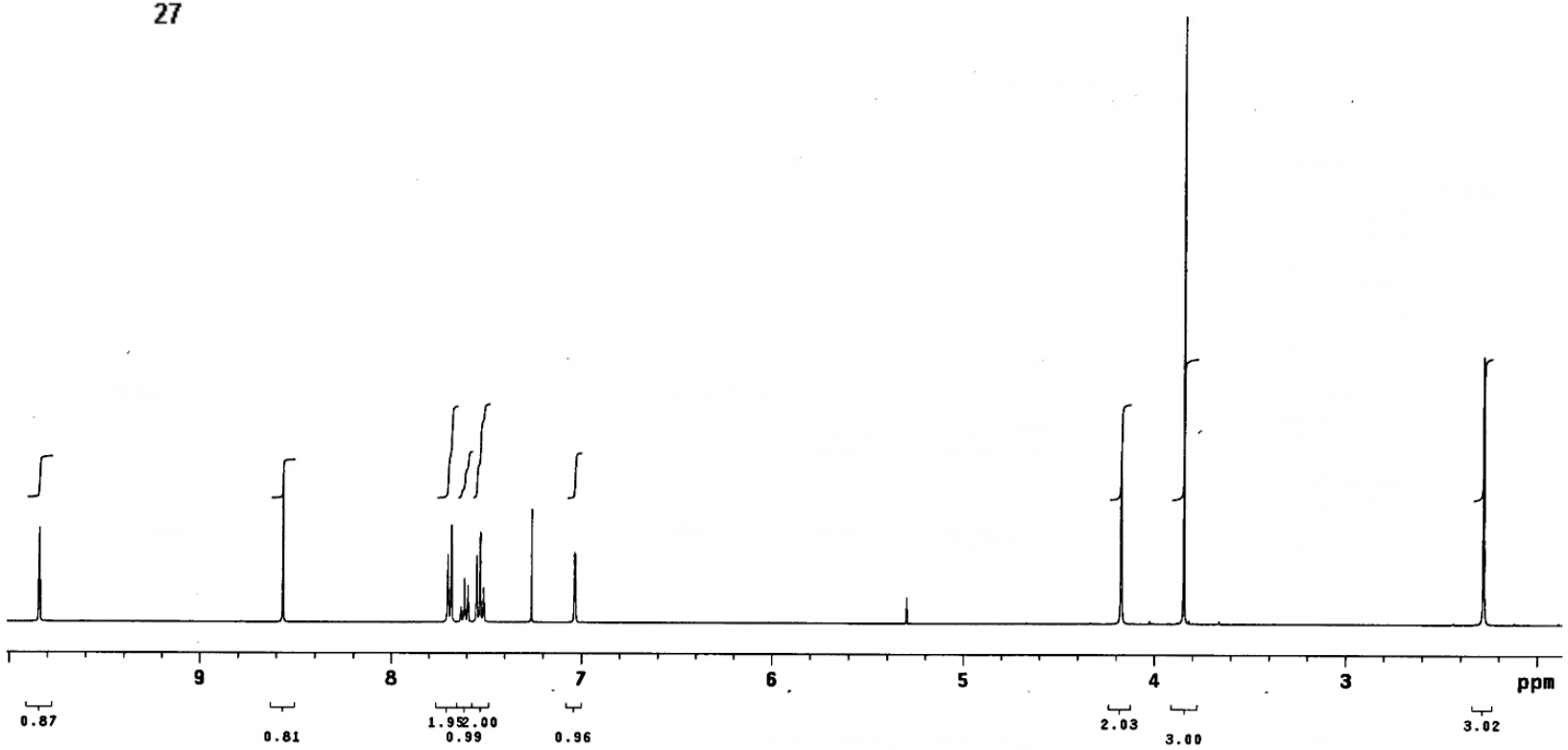
[SB-6-83] in CDCl3, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb683_30Jun2001

Pulse Sequence: s2pul



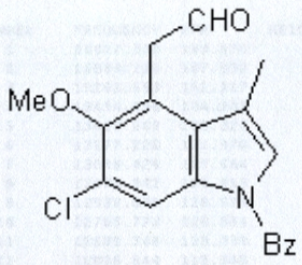
27



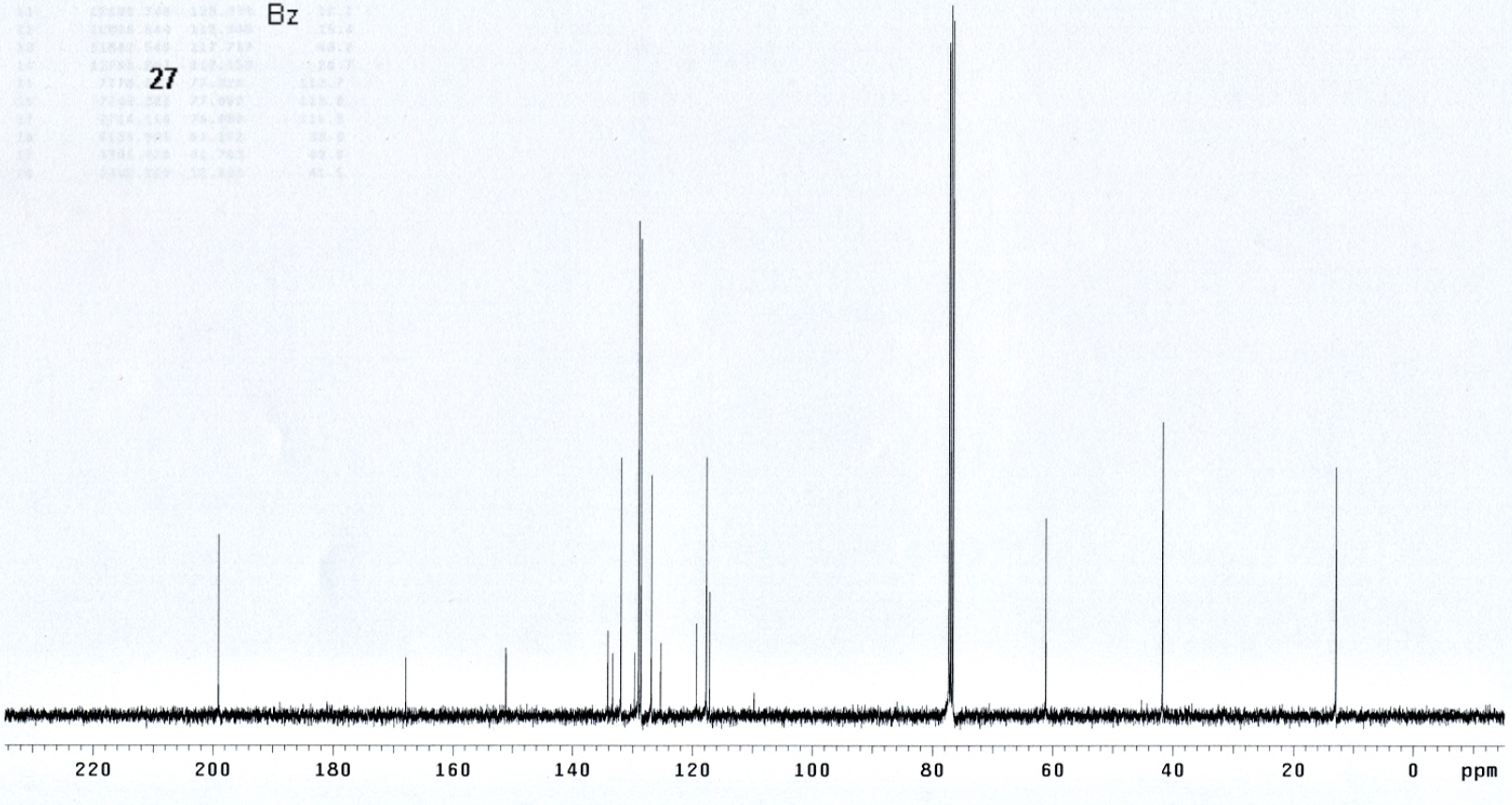
[SB-6-83] in CDCl3, Mercury 400
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_30Jun2001

Pulse Sequence: s2pul



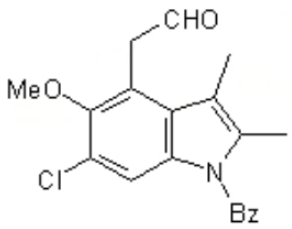
27



[SB-6-135] in CDCl3, Inova 400

Archive directory: /export/home/kerr/vnmrsys/data
Sample directory: sb6135_02Aug2001

Pulse Sequence: s2pul



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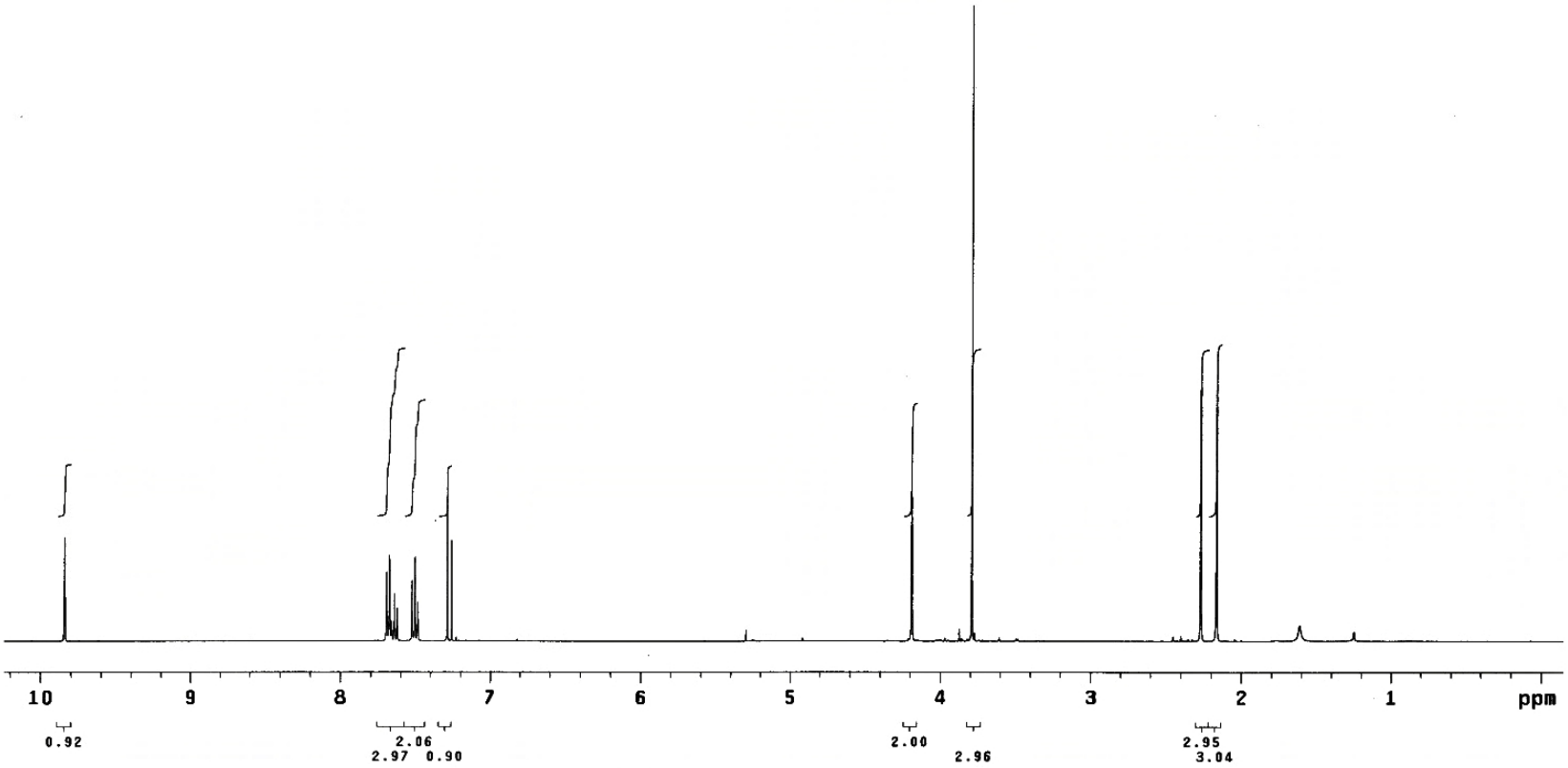
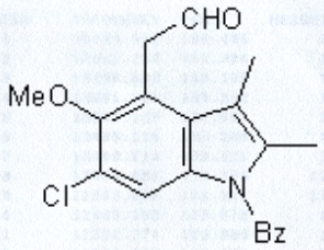


[SB-6-135] in CDCl3, Mercury
STANDARD 1H OBSERVE

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: auto_02Aug2001

Pulse Sequence: s2pul



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