Supporting Information for

Total Synthesis of Dragmacidin E

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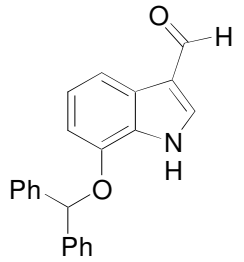
General Experimental. Unless stated otherwise, moisture and oxygen sensitive reactions were carried out in flame-dried glassware under a nitrogen or argon atmosphere using anhydrous, deoxygenated solvents. Tetrahydrofuran, toluene, dimethylformamide, and dichloromethane were dried by passage through an activated alumina column under a nitrogen atmosphere. Methanol was dried by passage through an activated alumina column under a nitrogen atmosphere or distillation from magnesium under a nitrogen atmosphere. Acetonitrile was dried by passage through an activated alumina column under a nitrogen atmosphere or distillation from calcium hydride under a nitrogen atmosphere. Ethyl acetate was dried over molecular sieves. Anhydrous carbon tetrachloride and 1,4-dioxane were used as received. All other commercially obtained reagents were used as received. Flash chromatography was performed on 32-63 μm silica gel. Melting points were taken with a Melt-Temp apparatus and are uncorrected. Chemical shifts of ^{1}H NMR spectra are reported relative to Me_4Si (δ 0.00), DMSO-d6 (δ 2.49), DMF-d7 (δ 2.74), CD_3OD (δ 3.30) or acetone-d6 (δ 2.04) if the former was absent. ^{13}C NMR spectra are reported relative to Me_4Si (δ 0.0), $CDCl_3$ (δ 77.0), DMSO-d6 (δ 39.5), DMF-d7 (δ 30.1), CD_3OD (δ 49.0) or acetone-d6 (δ 29.8) if the former was absent.

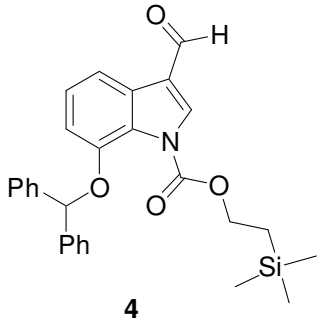


SM1

7-Benzhydryloxyindole-3-carboxaldehyde (SM1). Phosphorus(V) oxychloride (6.20 mL, 66.5 mmol) was added slowly to DMF (20 mL) at 0 ºC. The reaction mixture

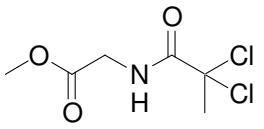
was stirred at this temperature for 30 min and a solution of 7-benzhydrylindole (16.62 g, 55.52 mmol) in DMF (50 mL) was added via cannula. The resulting dark brown solution was heated at 35-40 ºC for 20 h followed by cooling to room temperature and then in an ice bath. Ice (~50 g) was added to the reaction mixture followed by slow addition of a 1 M NaOH solution (100 mL). The mixture was heated at 95 ºC for 1 h and again allowed to cool to room temperature and then cooled in an ice bath. The liquid phase was slowly decanted off to leave a black syrup. This residue was dissolved in CH_2Cl_2 (200 mL). The black organic phase was poured into ice water (100 mL) and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/EtOAc) to give the desired aldehyde **SM1** as a yellow solid (13.00 g, 72% yield).

When a reaction was performed with a recrystallized starting material (125 mg, 0.42 mmol) by adding a solution of this compound in DMF (2 mL) to a reaction flask containing phosphorus(V) oxychloride (50 µL, 0.42 mmol) in DMF (0.5 mL) at 0 ºC, 127 mg (93% yield) of the desired aldehyde was obtained. mp 158-160 °C (recrystallized from EtOAc); IR (film) 3107, 1659 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.03 (br s, 1H), 9.84 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 3.1 Hz, 1H), 7.38 (d, *J* = 6.7 Hz, 4H), 7.18-7.28 (m, 6 H), 7.02 (t, *J* = 5.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1 H), 6.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 144.4, 140.6, 135.6, 128.6, 127.9, 127.7, 126.9, 125.9, 123.5, 119.5, 114.4, 107.4, 82.1; LRMS(ESI) *m/z* (relative intensity) 328.1 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{18}NO_2]^+$: 328.1338, found 328.1328.



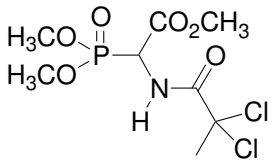
4

***N*-[(Trimethylsilylethoxy)carbonyl]-7-benzhydryloxyindole-3-carboxaldehyde (4)**. To an ice-cooled suspension of NaH (60% dispersion in mineral oil, 1.75 g, 43.75 mmol) in THF (50 mL) was added a solution of aldehyde **SM1** (13.00 g, 39.71 mmol) in THF (100 mL) via cannula. The suspension was stirred at 0 ºC for 30 min and then a solution of 4-nitrophenyl-2-(trimethylsilyl)ethyl carbonate (12.94 g, 45.67 mmol) in THF (50 mL) was added via cannula. The reaction mixture was stirred at room temperature for 12 h. The resulting orange suspension was poured into ice water (200 mL) and extracted with ether (3 x 100 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (2:1 hexanes/ether) to give the desired protected aldehyde **4** as a yellow solid (16.58 g, 89% yield). mp 101-102 °C (recrystallized from ether); IR (film) 1767, 1676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.09 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 4H), 7.31-7.16 (m, 6H), 7.09 (t, *J* = 5.3 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.28 (s, 1H), 4.30 (m, 2H), 1.02 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 149.9, 145.8, 141.0, 138.4, 128.7, 128.5, 127.7, 126.7, 125.7, 125.5, 121.3, 114.4, 110.7, 82.3, 67.2, 17.4, -1.7; LRMS(ESI) *m/z* (relative intensity) 494.2 (70%, $M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{28}H_{29}NO_4NaSi]^+$: 494.1764, found 494.1748.



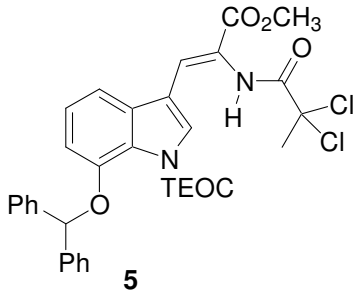
SM2

Methyl (2,2-Dichloropropionylamino)-acetate (SM2). To a solution of 2,2-dichloropropionic acid (90%, 13.6 mL, 119 mmol) in CH_2Cl_2 (100 mL) was added 2 drops of DMF followed by oxalyl chloride (20.8 mL, 238 mmol). The reaction mixture was stirred for 7.5 h until bubbling stopped. The resulting yellow acid chloride solution was concentrated under reduced pressure and then redissolved in CH_2Cl_2 (50 mL). The acid chloride solution was cannulated to an ice-cooled solution of glycine methyl ester hydrochloride (10.00 g, 79.64 mmol) and DMAP (20.43 g, 167.2 mmol) in CH_2Cl_2 (150 mL). The resulting red solution was stirred for 12 h (0 °C $\rightarrow$ room temperature) and it turned dark brown. The reaction mixture was poured into ice water (100 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/ether) to afford the dichloroamide **SM2** as a light yellow syrup (13.63 g, 80% yield). IR (film) 3368, 1753, 1686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (br s, 1H), 4.11 (d, J = 5.3 Hz, 2H), 3.80 (s, 3H), 2.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 166.6, 81.7, 52.5, 41.9, 33.8; LRMS(ESI) *m/z* (relative intensity) 214.0 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_6H_{10}NO_3Cl_2]^+$: 214.0038, found 214.0040.



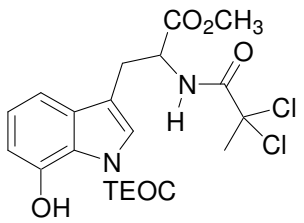
SM3

Methyl (2,2-Dichloropropionylamino)-(dimethoxyphosphoryl)-acetate (SM3). To a solution of dichloroamide **SM2** (10.71 g, 50.04 mmol) in CCl_4 (100 mL) was added *N*-bromosuccinimide (NBS) (9.51 g, 53.4 mmol). The reaction mixture was heated at reflux under sunlamp irradiation for 3 h. The precipitate was filtered off and washed with CCl_4 (20 mL). The filtrate was concentrated under reduced pressure to give a yellow liquid. This liquid was dissolved in CH_2Cl_2 (100 mL) and trimethyl phosphite ($P(OMe)_3$) (6.52 g, 52.6 mmol) was added. The reaction mixture was stirred at room temperature for 13 h. It was concentrated to dryness under reduced pressure to give the desired product as an off-white solid (16.12 g, 100% yield, crude). This phosphanate was carried on to the next step without purification. For characterization purpose, a portion was recrystallized from EtOAc to give the desired phosphanate **SM3** as a white solid. mp 93-94 °C; IR (film) 3206, 1756, 1696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (br d, *J* = 7.5 Hz, 1H), 5.12 (dd, *J* = 21.6, 8.7 Hz, 1H), 3.88 (s, 3H), 3.88 (d, *J* = 11.3 Hz, 3H), 3.85 (d, *J* = 11.3 Hz, 3H), 2.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 165.7 (d, *J* = 5.1 Hz), 81.3, 54.2 (d, *J* = 6.3 Hz), 53.9 (d, *J* = 6.9 Hz), 53.4, 51.0 (d, *J* = 147.2 Hz), 33.6; LRMS(ESI) *m/z* (relative intensity) 322.1 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_8H_{15}NO_6Cl_2P]^+$: 322.0014, found 322.0014.



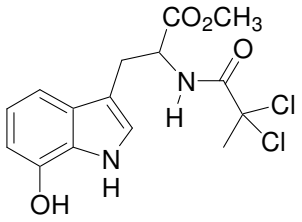
5

Methyl-2-(2,2-dichloropropionylamino)-3-(*N*[(trimethylsilylethoxy)carbonyl] -7-benzhydryloxyindol-3-yl)-acrylate (5). To an ice-cooled suspension of dimethylphosphoryl amide **SM3** (12.50 g, 38.8 mmol) in CH_2Cl_2 (100 mL) was added DBU (5.80 mL g, 38.8 mmol). The reaction mixture was stirred at 0 ºC for 20 min and then aldehyde **4** (12.20 g, 25.9 mmol) in CH_2Cl_2 (100 mL) was added via cannula. The reaction mixture was stirred at room temperature for 12 h. The resulting dark brown solution was poured into a mixture of ice water (100 mL) and brine (50 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/ether) to give the desired alkene **5** as a white solid (14.58 g, 84% yield). mp 140-142 °C (recrystallized from hexanes/ether); IR (film) 3306, 1760, 1721, 1706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.94 (s, 1H), 7.70 (s, 1H), 7.51 (d, *J* = 7.1 Hz, 4H), 7.30-7.16 (m, 7H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.26 (s, 1H), 4.28 (m, 2H), 3.77 (s, 3H), 2.32 (s, 3H), 1.00 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 163.7, 150.0, 146.2, 141.2, 132.2, 130.2, 128.5, 127.6, 126.7, 125.5, 124.43, 124.39, 121.5, 113.3, 111.0, 109.9, 82.17, 82.06, 66.6, 52.6, 33.5, 17.5, -1.7; LRMS(ESI) *m/z* (relative intensity) 689.2 (100%, $M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{34}H_{36}N_2O_6NaSiCl_2]^+$: 689.1617, found 689.1621



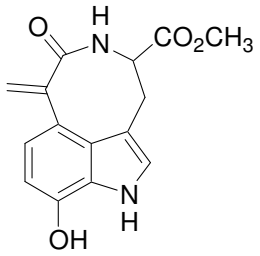
SM4

Methyl-2-(2,2-dichloropropionylamino)-3-(*N*[(trimethylsilylethoxy)carbonyl] -7-hydroxyindol-3-yl)-propionate (SM4). To a solution of the alkene **5** (10.40 g, 15.6 mmol) in a 1:1 mixture of MeOH and toluene (100 mL) was added $Rh(PPh_3)_3Cl$ (145 mg, 0.64 mmol) under an N_2 atmosphere. The reaction mixture was placed in a sealable metal container equipped with a gas inlet pressure gauge, and this vessel was pressurized with H_2 at 1250 psi with heating to 45 ºC for 50 h. The resulting dark brown solution was concentrated to dryness under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/ether) to give the desired dichloroamide **SM4** as a white solid (7.68 g, 98% yield). mp 96-97 °C (recrystallized from ether); IR (film) 3406, 1746, 1695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.32 (br d, *J* = 7.5 Hz, 1H), 7.31 (s, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 4.80 (ddd, *J* = 7.5, 5.6, 5.5 Hz, 1H) 4.45 (m, 2H), 3.67 (s, 3H), 3.24 (dd, *J* = 14.9, 5.5 Hz, 1H), 3.18 (dd, *J* = 14.9, 5.6 Hz, 1H), 2.24 (s, 3H), 1.13 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 165.7, 153.2, 144.7, 132.9, 125.4, 124.0, 123.2, 116.5, 113.2, 109.7, 81.9, 67.5, 52.9, 52.7, 33.7, 26.7, 17.5, -1.6; LRMS(ESI) *m/z* (relative intensity) 503.1 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{21}H_{29}N_2O_6SiCl_2]^+$: 503.1172, found 503.1200.



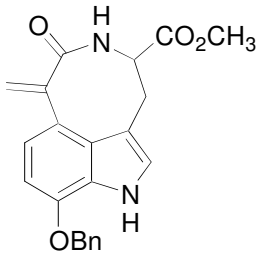
6

Methyl 2-(2,2-Dichloropropionylamino)-3-(7-hydroxyindol-3-yl)-propionate (6). To a solution of *N*-TEOC indolyl dichloroamide **SM4** (7.54 g, 15.0 mmol) in THF (70 mL) was added 1 M TBAF (15.0 mL, 15.0 mmol). The reaction mixture was stirred at room temperature for 1 h and then poured into ice water and extracted with EtOAc (3 x 70 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/EtOAc) to give the unprotected indole **6** as a white foamy solid (5.19 g, 96% yield). mp 55-57 °C; IR (film) 3396, 1738, 1679 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 10.65 (s, 1H), 9.46 (s, 1H), 8.70 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 4.51 (dt, *J* = 8.0, 5.9 Hz, 1H), 3.65 (s, 3H), 3.24 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d6) δ 171.5, 165.6, 143.6, 129.1, 126.2, 123.4, 119.3, 109.7, 109.2, 105.5, 82.9, 54.3, 52.2, 34.2, 26.2; LRMS(ESI) *m/z* (relative intensity) 359.1 (75%, $M+H^+$), 381.0 (100%, $M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{15}H_{17}N_2O_4Cl_2]^+$: 359.0565, found 359.0543.



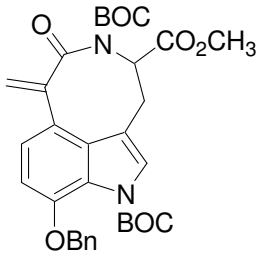
13

Methyl 10-Hydroxy-7-methylene-6-oxo-1,3,4,5,6,7-hexahydroazocino[4,5,6-*cd*]indole-4-carboxylate (13). A solution of dichloroamide **6** (157 mg, 0.44 mmol) in CH_3CN (87.5 mL) in a quartz vessel was degassed by passage of dry nitrogen for 30 min prior to, and during, irradiation. This solution was irradiated at 254 nm in a Rayonet photochemical reactor for 30 min. The resulting light brown solution was concentrated under reduced pressure and purified by flash chromatography on silica gel (1:4 hexanes/EtOAc and 100% EtOAc, respectively) to afford the bridged indole **13** as a yellow solid (83 mg, 66% yield). A larger scale reaction was carried out by dissolving 2.00 g (5.57 mmol) of **6** in CH_3CN (600 mL) and irradiated for 4 h to give 950 mg (60% yield) of the desired product. mp 232-234 °C; IR (film) 3320, 1736, 1635 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 11.09 (s, 1H), 9.80 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.18 (s, 1H), 6.76 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.50 (dd, *J* = 7.7, 1.9 Hz, 1H), 5.32 (s, 1H), 5.12 (s, 1H), 4.86 (app br s, 1H), 3.73 (s, 3H), 3.42 (d, *J* = 15.6 Hz, 1H), 3.21 (dd, *J* = 15.1, 13.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d6) δ 172.1, 171.5, 148.7, 144.3, 126.5, 124.8, 124.6, 121.4, 121.2, 112.6, 110.4, 104.9, 55.4, 52.4, 32.1; LRMS(CI) *m/z* (relative intensity) 287.1 (97%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{15}H_{15}N_2O_4]^+$: 287.1032, found 287.1048.



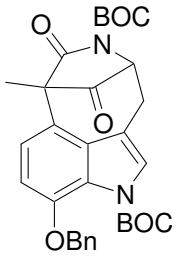
SM5

Methyl 10-Benzyloxy-7-methylene-6-oxo-1,3,4,5,6,7-hexahydroazocino[4,5,6-*cd*]indole-4-carboxylate (SM5). To a solution of hydroxy indole **13** (1.60 g, 5.59 mmol) in DMF (24 mL) was added K_2CO_3 (929 mg, 6.72 mmol) followed by benzyl bromide (810 μL, 6.77 mmol). The reaction mixture for stirred at room temperature for 14 h and then poured into ice water and extracted with EtOAc (3 x 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:3 hexanes/EtOAc) to afford the protected product **SM5** as a yellow solid (1.56 g, 74% yield). mp 216-217 °C (recrystallized from EtOAc/MeOH); IR (film) 3333, 1742, 1652 cm^{-1}; ^1H NMR (300 MHz, DMSO-d6) δ 11.39 (d, *J* = 2.1 Hz, 1H), 8.05 (br d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.42-7.32 (m, 3H), 7.23 (d, *J* = 2.5 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 5.27 (s, 2H), 5.16 (s, 1H), 4.86 (br t, *J* ~ 10 Hz, 1H), 3.73 (s, 3H), 3.44 (dd, *J* = 16.7, 2.6 Hz, 1H), 3.21 (dd, *J* = 16.3, 12.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d6) δ 171.8, 171.4, 148.3, 145.4, 137.2, 128.4, 127.8, 127.5, 126.6, 125.0, 124.3, 123.2, 120.8, 113.2, 110.5, 102.5, 69.1, 55.3, 52.4, 31.1; LRMS(ESI) *m/z* (relative intensity) 377.2 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{21}N_2O_4]^+$: 377.1501, found 377.1514.



SM6

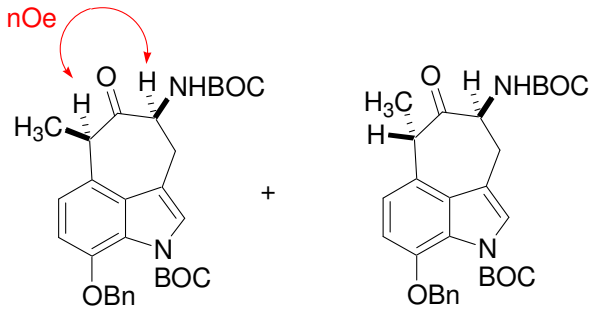
1,5-Di-*tert*-butyl 4-Methyl-10-benzyloxy-7-methylene-6-oxo-3,4,6,7-tetrahydroazocino[4,5, 6-*cd*]indole-1,4,5-tricarboxylate (SM6). A solution of BOC_2O (1.72 g, 7.87 mmol) in CH_3CN (10 mL) was cannulated into a suspension of benzyloxyindole **SM5** (1.22 g, 3.24 mmol) and DMAP (40 mg, 0.33 mmol) in CH_3CN (20 mL). The reaction mixture was stirred at room temperature for 20 min. The resulting dark brown solution was poured into ice water (30 mL) and extracted with ether (3 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/ether) to afford the desired protected product **SM6** as a white solid (1.29 g, 69% yield). mp 179-180 °C (recrystallized from ether); IR (film) 1732, 1692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.9 Hz, 2H), 7.41 (s, 1H), 7.37-7.26 (m, 4H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 5.92 (s, 1H), 5.21 (s, 2H), 4.77 (dd, *J* = 12.6, 4.1 Hz, 1H), 3.83 (s, 3H), 3.28 (dd, *J* = 15.3, 4.2 Hz, 1H), 3.09 (dd, *J* = 14.5, 12.9 Hz, 1H), 1.54 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 170.8, 151.3, 148.3, 148.1, 144.4, 136.7, 129.9, 128.3, 128.2, 128.0, 127.7, 127.2, 126.0, 125.3, 122.7, 115.2, 108.1, 83.5, 82.6, 70.8, 57.5, 52.5, 27.7, 27.4, 26.5; LRMS(AP+) *m/z* (relative intensity) 577.2 (95%, $M+H^+$); HRMS (AP+) *m/z* calcd for $[C_{32}H_{37}N_2O_8]^+$: 577.2250, found 577.2600.



15

Oxoimide 15. A solution of imide **SM6** (3.56 g, 6.17 mmol) in THF (60 mL) was cooled to -78 °C and a 1 M solution of *N*-selectride in THF (6.8 mL, 6.8 mmol) was added slowly. The reaction mixture was stirred for 14 h (-78 °C to room temperature). The resulting red solution was poured into ice water (60 mL) and extracted with EtOAc (3 x 60 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, passed through a SiO_2 pad, and concentrated under reduced pressure. The crude residue was suspended in CH_3CN (50 mL) and DMAP (75 mg, 0.61 mmol) was added followed by a solution of BOC_2O (2.69 g, 12.33 mmol) in CH_3CN (10 mL). The reaction mixture was stirred at room temperature for 10 min, then additional DMAP (75 mg, 0.61 mmol) was added. The reaction mixture was stirred for another 10 min. The resulting brown solution was poured into ice water (60 mL) and extracted with ether (3 x 60 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/ether) to afford the bridged amide **15** as a white solid (2.81 g, 83% yield). mp 96-98 °C (recrystallized from ether/hexanes); IR (film) 1798, 1763, 1744, 1721 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.42 (s, 1H), 7.37-7.25 (m, 3H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 5.17 (s, 2H), 4.86 (dd, *J* = 4.2, 2.9 Hz, 1H), 3.68 (ddd, *J* = 17.0, 4.3, 0.6 Hz, 1H), 3.14 (ddd, *J* = 16.9, 2.8, 2.0 Hz, 1H), 1.52 (s, 3H), 1.48 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 170.9,

149.4, 148.6, 147.8, 136.7, 128.9, 128.3, 127.8, 127.5, 127.4, 125.4, 120.2, 119.9, 112.5, 107.8, 84.3, 83.8, 70.8, 64.7, 58.3, 27.9, 27.7, 27.0, 13.5; LRMS(ESI) *m/z* (relative intensity) 569.2 (100%, M+Na^+); HRMS (ESI) *m/z* calcd for $[C_{31}H_{34}N_2O_7Na]^+$: 569.2264, found 569.2280.

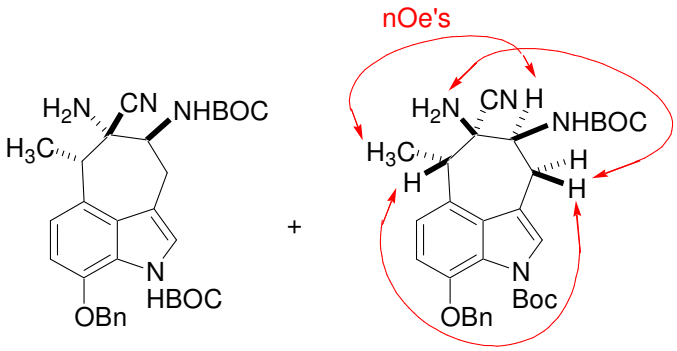


16a **16b**

(±)-*tert*-Butyl 3-Benzyloxy-8-*tert*-butoxycarbonylamino-6-methyl-7-oxo-6,7,8, 9-tetrahydro-2-azabenzo[*cd*]azulene-2-carboxylate (16a and **16b).** To an ice-cooled solution of imide **15** (2.10 g, 3.84 mmol) in THF (40 mL) was added a deoxygenated 1 M aq. LiOH solution (7.8 mL, 7.8 mmol). The reaction mixture was stirred for 1 h (0 °C to room temperature). The resulting slightly yellow solution was poured into ice water (40 mL) and extracted with ether (3 x 40 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:1 hexanes/ether) to afford a ~ 2:1 mixture of diastereomeric ketones **16a** and **16b** as a white solid (1.81 g, 91% yield). Major product (**16a**): mp 156-157 °C (recrystallized from ether); IR (film) 3417, 1756, 1710 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.44 (d, *J* = 6.9 Hz, 2H), 7.26 (s, 1H), 7.23-7.11 (m, 3H), 6.75 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 5.40 (br d, *J* = 5.9 Hz, 1 H), 4.91 (s, 2H), 4.64 (br dd, *J* ~ 4.0, 3.0 Hz, 1H), 4.11 (q, *J* = 6.7 Hz, 1H), 3.24 (dd, *J* =

15.9, 4.0 Hz, 1H), 3.11 (dd, *J* = 15.9, 3.0 Hz, 1H), 1.40 (s, 9H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4, 155.6, 148.7, 146.6, 137.0, 131.1, 128.2, 127.6, 127.2, 125.8, 124.9, 123.4, 119.7, 115.6, 109.1, 83.2, 79.6, 70.9, 61.4, 44.9, 28.2, 27.7, 27.6, 14.2; LRMS(ESI) *m/z* (relative intensity) 543.2 (100%, M+Na$^+$); HRMS (ESI) *m/z* calcd for $[C_{30}H_{36}N_2O_6Na]^+$: 543.2471, found 543.2467.

Minor product (**16b**): mp 161-162 °C (recrystallized from ether); IR (film) 3385, 1755, 1717 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.9 Hz, 2H), 7.40-7.26 (m, 4H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.50 (br s, 1 H), 5.19 (s, 2H), 4.48 (q, *J* = 6.8 Hz, 1H), 4.31 (br q, *J* = 6.4 Hz, 1H), 3.26 (app d, *J* = 7.0 Hz, 2H), 1.59 (d, *J* = 6.9 Hz, 3H), 1.53 (s, 9H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 155.5, 148.8, 146.6, 137.1, 131.1, 128.3, 127.7, 127.4, 125.8, 125.2, 123.3, 121.2, 116.0, 109.2, 83.4, 80.0, 71.1, 59.4, 47.8, 29.2, 28.3, 27.8, 15.8; LRMS(ESI) *m/z* (relative intensity) 543.3 (78%, M+Na$^+$); HRMS (ESI) *m/z* calcd for $[C_{30}H_{36}N_2O_6Na]^+$: 543.2471, found 543.2484.



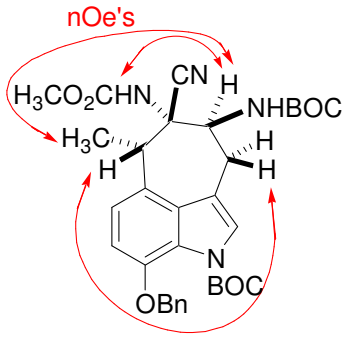
17a **17b**

(±)-*tert*-Butyl 7-Amino-3-benzyloxy-8-*tert*-butoxycarbonylamino-7-cyano-6-methyl-6,7,8,9-tetrahydro-2-azabenzo[*cd*]azulene-2-carboxylate (17a and **17b).** A

solution of the diastereomeric mixture of ketones **16a** and **16b** (1.736 g, 3.33 mmol) and NH_4Cl (368 mg, 6.88 mmol) in saturated NH_3/MeOH (15 mL) in a sealed tube was heated at 75 °C for 3 h. The reaction mixture was allowed to cool to room temperature and TMSCN (1.80 mL, 13.5 mmol) was added. The reaction mixture was stirred in a sealed tube at room temperature for 18 h. The resulting yellow suspension was diluted with CH_2Cl_2 (500 mL) and then poured into ice water (100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (2:1, 1:1 and 1:2 hexanes/EtOAc, respectively) to afford the aminonitriles **17a** (1.052 g, 58% yield) and **17b** (227 mg, 12% yield) as light yellow solids. Major product (**17a**): mp 143-144 °C (recrystallized from ether); IR (film) 3318, 2222, 1755, 1714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.0 Hz, 2H), 7.38-7.25 (m, 4H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.22 (br d, *J* = 9.4 Hz, 1H), 5.17 (s, 2H), 3.95 (t, *J* = 9.3 Hz, 1H), 3.68 (q, *J* = 7.0 Hz, 1H), 3.26 (dd, *J* = 15.4, 9.9 Hz, 1H), 2.92 (d, *J* = 14.3 Hz, 1H), 2.01 (br s, 2H), 1.60 (d, *J* = 7.1 Hz, 3H), 1.52 (s, 9H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 148.9, 147.0, 137.1, 132.2, 128.3, 127.6, 127.3, 125.1, 124.9, 124.0, 122.7, 122.3, 116.7, 108.9, 83.3, 80.5, 71.0, 65.7, 58.5, 42.0, 30.0, 28.2, 27.8, 15.2; LRMS(AP+) *m/z* (relative intensity) 547.3 (100%, $M+H^+$); HRMS (AP+) *m/z* calcd for $[C_{31}H_{39}N_4O_5]^+$: 547.2920, found 547.2881.

Minor product (**17b**): mp 149-150 °C (recrystallized from ether); IR (film) 3379, 1754, 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.0 Hz, 2H), 7.38-7.25 (m, 4H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.55 (br d, *J* ~ 8.8 Hz, 1H), 5.16

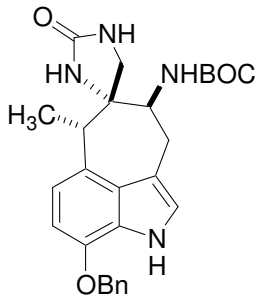
(s, 2H), 4.43 (br t, J ~ 9.3 Hz, 1H), 3.48 (q, J = 6.9 Hz, 1H), 3.11 (dd, J = 14.9, 10.5 Hz, 1H), 2.97 (dd, J = 15.9, 3.0 Hz, 1H), 1.92 (br s, 2H), 1.55 (d, J = 7.1 Hz, 3H), 1.51 (s, 9H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 148.8, 146.8, 137.0, 131.0, 128.2, 127.6, 127.3, 125.7, 125.2, 124.5, 123.7, 121.9, 115.5, 108.7, 83.3, 80.0, 70.9, 62.5, 52.9, 46.3, 28.4, 28.3, 27.7, 19.0; LRMS(ESI) *m/z* (relative intensity) 547.3 (100%, M+H$^+$); HRMS (ESI) *m/z* calcd for $[C_{31}H_{39}N_4O_5]^+$: 547.2920, found 547.2940.



SM7

(±)-*tert*-Butyl 3-Benzyloxy-8-*tert*-butoxycarbonylamino-7-cyano-7-methoxy-carbonylamino-6-methyl-6,7,8,9-tetrahydro-2-azabenzo[*cd*]azulene-2-carboxylate (SM7). To a mixture of aminonitrile **17a** (795 mg, 1.45 mmol) and K_2CO_3 (402 mg, 2.91 mmol) was added THF (20 mL) followed by methylchloroformate (740 µL, 8.79 mmol). The reaction mixture was heated at reflux for 20 h. The resulting yellow solution was allowed to cool to room temperature, poured into ice water (30 mL), and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (1:2 hexanes/ether) to afford the desired product **SM7** as a white solid (758 mg, 86% yield). mp 120-122 °C; IR (film) 3323, 2237, 1755, 1730, 1684 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 6.8 Hz, 2H), 7.37-7.25 (m, 4H),

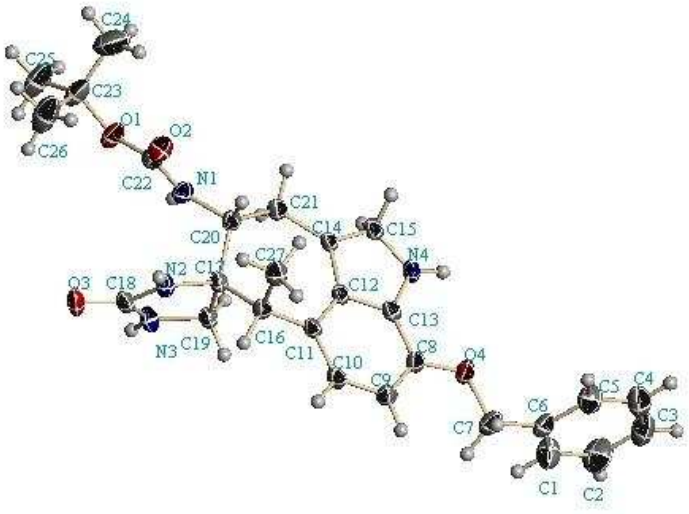
7.00 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 6.27 (br s, 1H), 5.40 (br d, J = 9.3 Hz, 1H), 5.17 (s, 2H), 4.33 (ddd, J = 8.9, 7.9, 5.1 Hz, 1H), 4.15 (q, J = 7.0 Hz, 1H), 3.70 (s, 3H), 3.31 (dd, J = 16.5, 4.8 Hz, 1H), 3.17 (dd, J = 15.9, 7.6 Hz, 1H), 1.50 (s, 9H), 1.46 (s, 9H), 1.44 (d, J = 7.0, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 155.2, 148.7, 146.9, 137.0, 131.1, 128.2, 127.6, 127.3, 125.7, 125.2, 125.0, 123.9, 117.6, 114.1, 108.9, 83.3, 81.2, 70.9, 65.5, 54.1, 52.3, 42.7, 30.1, 28.1, 27.7, 17.1; LRMS(ESI) *m/z* (relative intensity) 622.3 (55%, M+NH_4^+); HRMS (ESI) *m/z* calcd for $[C_{33}H_{44}N_5O_7]^+$: 622.3241, found 622.3260.

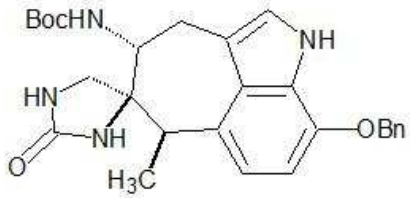


18

(±)-Spirocyclic Imidazolone 18. To a solution of aminonitrile **SM7** (570 mg, 0.94 mmol) in MeOH (50 mL) was added cobalt (II) chloride (3.06 g, 23.6 mmol). The resulting dark blue solution was cooled in an ice bath and sodium borohydride (892 mg, 23.6 mmol) was added in portions. The resulting black suspension was stirred at 0 °C for 30 min. Then additional sodium borohydride (892 mg, 23.6 mmol) was added in portions. The reaction mixture was stirred for 14 h (0 °C to room temperature). The resulting black suspension was diluted with CH_2Cl_2 (50 mL) and acidified with 1 M HCl solution (60 mL). The acidic solution was stirred vigorously for 1 h until it turned fuchsia and clear. The organic layer was separated and the aqueous layer was extracted

with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was dissolved in EtOH (9 ml) and a 1 M LiOH solution (9 mL) was added. The reaction mixture was heated at ~95 °C for 6 h. The resulting black suspension was diluted with CH_2Cl_2 (100 mL), and poured into ice water (50 mL) and brine (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (3% and 5% saturated NH_3/MeOH in CH_2Cl_2) to afford the desired product **18** as a yellow solid (348 mg, 78% yield). mp 222-224 °C IR (film) 3260, 1701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.59 (br s, 1H), 7.47-7.35 (m, 5H), 6.94 (s, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 5.43 (br s, 1 H), 5.24 (br d, *J* = 9.0 Hz, 1H), 5.15 (s, 2H), 4.96 (s, 1H), 4.55 (br m, 1H), 3.58 (q, *J* = 7.0 Hz, 1H), 3.38 (m, 2H), 3.13 (d, *J* = 9.5 Hz, 1H), 2.81 (dd, *J* = 15.9, 12.0 Hz, 1H), 1.46 (s, 9H), 1.36 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d6) δ 161.6, 155.9, 143.5, 137.5, 128.3, 127.8, 127.7, 127.5, 126.3, 125.0, 122.3, 119.1, 109.9, 102.9, 77.9, 69.1, 65.7, 49.6, 48.4, 44.6, 28.3, 28.2, 19.4; LRMS(ESI) *m/z* (relative intensity) 477.2 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{27}H_{33}N_4O_4]^+$: 477.2502, found 477.2505.



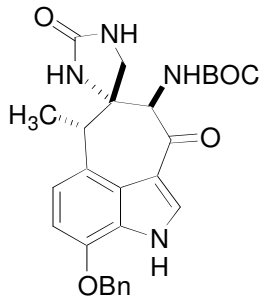


A colorless plate shaped crystal of **18** (CCDC 826169) [(C27 H33 N4 O4), 2.25(CH3-OH)] with approximate dimensions 0.06 x 0.21 x 0.29 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 143(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 20 seconds/frame. The total data collection time was about 18 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 22075 reflections to a maximum θ angle of 28.23° (0.90 Å resolution), of which 7217 were independent, completeness = 96.5%, R_{int} = 0.0848, R_{sig} = 0.0910 and 4218 were greater than 2σ(I). The final cell constants: a = 14.467(6)Å, b = 17.927(7)Å, c = 11.676(4)Å, α = 90°, β = 91.572(8)°, γ = 90°, volume = 3027(2)$Å^3$, are

based upon the refinement of the XYZ-centroids of 2613 reflections above 20σ(I) with 2.472° <θ <23.053°. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multi-scan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.6684.

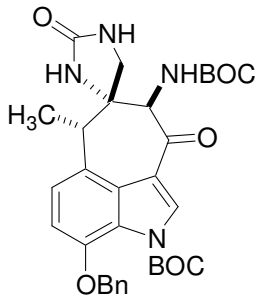
The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P21/c, with Z = 4 for the formula unit, C29.25 H42 N4 O6.25. The final anisotropic full-matrix least-squares refinement on F^2 with 380 variables converged at R1 = 7.33%, for the observed data and wR2 = 20.70% for all data. The goodness-of-fit was 1.032. The largest peak on the final difference map was 0.596 $e^-/Å^3$ and the largest hole was -0.656 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.206 g/cm^3 and F(000) amounts to 1182 electrons.



SM8

(±)-Spirocyclic Imidazolone SM8. To an ice-cooled solution of the cyclic imidazolone **18** (305 mg, 0.64 mmol) in a mixture of THF (6 mL) and H_2O (2 mL) was added DDQ (872 mg, 3.84 mmol). The reaction mixture was stirred for 30 min at 0 °C. The resulting dark yellow solution was diluted with EtOAc (100 mL) and washed with saturated $NaHCO_3$ solution (3 x 30 mL). The aqueous layer was extracted with EtOAc (2 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and

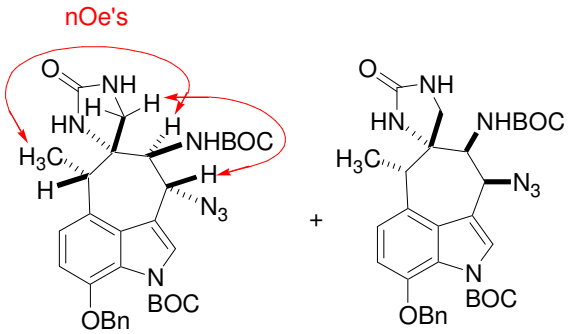
concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (3% and 5% saturated NH_3/MeOH in CH_2Cl_2) to afford the desired product **SM8** as a dark yellow solid (224 mg, 71% yield). mp 240 °C (dec.); IR (film) 3368, 1704, 1641 cm^{-1}; ^1H NMR (300 MHz, acetone-d6) δ 11.76 (br s, 1H), 8.14 (d, *J* = 3.1 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.44-7.34 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 6.1 Hz, 1H), 5.75 (s, 1H), 5.42 (s, 1H), 5.28 (s, 2H), 5.08 (d, *J* = 6.3 Hz, 1H), 3.61 (q, *J* = 7.1 Hz, 1H), 3.16 (d, *J* = 9.3 Hz, 1H), 3.05 (d, *J* = 9.7 Hz, 1H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, acetone-d6) δ 189.2, 162.6, 158.7, 145.3, 138.1, 132.8, 129.3, 128.8, 128.6, 128.0, 127.7, 124.5, 123.9, 116.1, 106.0, 80.1, 70.8, 64.5, 62.4, 50.3, 48.7, 28.5, 20.9; LRMS(ESI) *m/z* (relative intensity) 491.1 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{27}H_{31}N_4O_5]^+$: 491.2294, found 491.2278.



19

(±)-***N*-Boc Ketoindole 19**. A solution of BOC_2O (106 mg, 0.49 mmol) in CH_3CN (2 mL) was slowly added to a suspension of the keto indole **SM8** (224 mg, 0.46 mmol) and DMAP (6 mg, 0.05 mmol) in CH_3CN (5 mL). The reaction mixture immediately turned yellow and clear. It was stirred at room temperature for 10 min and then concentrated to dryness under reduced pressure. The crude residue was purified by flash

chromatography on silica gel (gradient 1-3% saturated NH_3/MeOH in CH_2Cl_2) to afford the desired Boc-protected product **19** as a yellow solid (241 mg, 89% yield). mp 250 °C (dec.); IR (film) 3384, 1768, 1711, 1659 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.40-7.2 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.13 (d, *J* = 5.8 Hz, 1H), 5.79 (s, 1H), 5.25 (d, *J* = 19.7 Hz, 1H), 5.18 (d, *J* = 11.7 Hz, 1H), 5.13 (d, *J* = 5.7 Hz, 1H), 4.54 (s, 1H), 3.69 (q, *J* = 7.0 Hz, 1H), 3.13 (app s, 2H), 1.62 (d, *J* = 7.1 Hz, 3H), 1.53 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 161.9, 157.9, 147.8, 146.0, 136.5, 135.1, 128.4, 128.0, 127.6, 126.8, 126.7, 125.3, 124.8, 116.9, 109.3, 85.7, 80.7, 71.1, 64.2, 64.5, 48.8, 47.7, 28.3, 27.6, 20.8; LRMS(ESI) *m/z* (relative intensity) 591.3 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{32}H_{39}N_4O_7]^+$: 591.2819, found 591.2872.



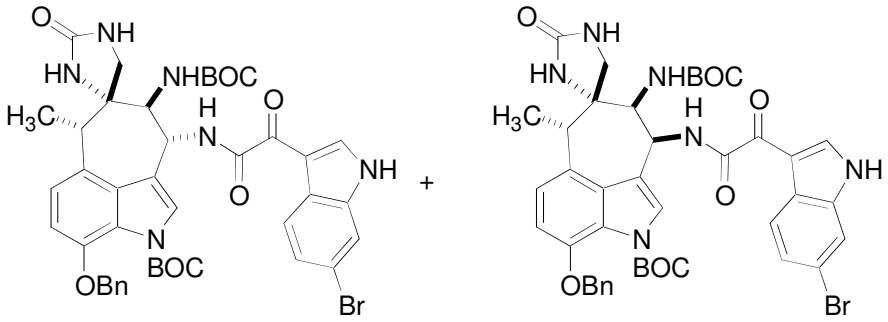
20a **20b**

(±)-**Azido Indoles 20a** and **20b**. To an ice-cooled solution of keto indole **17** (241 mg, 0.41 mmol) in MeOH (5 mL) was added $NaBH_4$ (154 mg, 4.07 mmol). The resulting clear and colorless solution was stirred for 20 min (0 ºC to room temperature), poured into ice water (30 mL) and extracted with EtOAc (3 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was dissolved in a mixture of toluene (5 mL) and DMF (0.5 mL) and

DPPA (440 μL, 2.04 mmol) was added followed by DBU (370 μL, 2.47 mmol). The reaction mixture was stirred at room temperature for 14 h. The resulting dark brown solution was poured into ice water (30 mL) and extracted with EtOAc (3 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (gradient 1-5% saturated NH_3/MeOH in CH_2Cl_2) to afford a 2:1 mixture of the desired azides **20a** and **20b** as a slightly yellow solid (197 mg, 78% yield). Major product (**20a**): mp 200 °C (dec.); IR (film) 3259, 2098, 1761, 1713 cm^{-1}; ^1H NMR (300 MHz, acetone-d6) δ 7.79 (d, *J* = 1.2 Hz, 1H), 7.60 (d, *J* = 6.7 Hz, 2H), 7.42-7.29 (m, 3H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.78 (br d, *J* = 9.7 Hz, 1H), 5.76 (br s, 1H), 5.58 (br s, 1H), 5.26 (s, 2H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.52 (t, *J* = 9.1 Hz, 1H), 3.52 (q, *J* = 7.0 Hz, 1H), 3.51 (d, *J* = 9.4 Hz, 1H), 3.00 (d, *J* = 9.7 Hz, 1H), 1.54 (s, 9H), 1.46 (d, *J* = 7.0 Hz, 3H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, acetone-d6) δ 162.5, 157.4, 149.4, 147.0, 138.3, 129.7, 129.1, 128.49, 128.46, 128.44, 127.9, 125.9, 125.6, 116.0, 109.4, 84.5, 79.6, 71.3, 65.5, 61.9, 57.7, 50.0, 46.6, 28.6, 27.8, 19.4; LRMS(ESI) *m/z* (relative intensity) 640.3 (50%, M+Na^+); HRMS (ESI) *m/z* calcd for $[C_{32}H_{40}N_7O_6]^+$: 618.3040, found 618.3038.

Minor product (**20b**): mp 200 °C (dec.); IR (film) 3257, 2102, 1760, 1707 cm^{-1}; ^1H NMR (300 MHz, acetone-d6) δ 7.85 (s, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.41-7.29 (m, 3H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.46 (br d, *J* = 8.7 Hz, 1H), 5.60 (br s, 1H), 5.52 (br s, 1H), 5.27 (s, 2H), 5.25 (d, *J* = 1.7 Hz, 1H), 4.22 (d, *J* = 9.0 Hz, 1H), 3.98 (dd, *J* = 10.4, 1.4 Hz, 1H), 3.51 (q, *J* = 7.1 Hz, 1H), 3.31 (d, *J* = 11.0 Hz, 1H), 1.53 (s, 9H), 1.43 (d, *J* = 7.0 Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, acetone-d6) δ 162.7, 156.8, 149.5, 147.2, 138.4, 131.1, 129.1, 128.9, 128.5, 128.4, 127.6, 125.8, 124.6, 116.9,

109.5, 84.4, 79.5, 71.3, 67.3, 62.0, 58.5, 48.6, 45.5, 28.5, 27.8, 15.8; LRMS(ESI) *m/z* (relative intensity) 640.2 (50%, M+Na^+); HRMS (ESI) *m/z* calcd for $[C_{32}H_{40}N_7O_6]^+$: 618.3040, found 618.3063.



22a **22b**

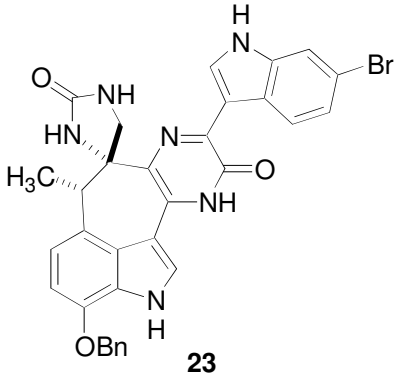
(±)-**Bisindoles 22a and 22b**. To a solution of a 2:1 mixture of azido indoles **20a** and **20b** (197 mg, 0.32 mmol) in MeOH (5 mL) was added nickle (II) chloride (42 mg, 0.32 mmol). The reaction mixture was cooled in an ice bath and $NaBH_4$ (235 mg, 6.21 mmol) was added in portions. The resulting black suspension was stirred for 1 h (0 °C to room temperature). The reaction mixture was filtered through a Celite pad and washed with EtOAc (60 mL). The organic filtrate was washed with 0.01 M EDTA (2 x 30 mL) and brine solution (30 ml). The aqueous layer was extracted with EtOAc (2 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude residue was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. Then, 6-bromoindol-3-yl-oxo-acetyl chloride (**21**)[1] (110 mg, 0.38 mmol) was added followed by Et_3N (90 µL, 0.64 mmol). The reaction mixture was stirred for 12 h (0 °C to room temperature), and then diluted with EtOAc (60 mL) and poured into ice water (30 mL). The organic layer was separated and the aqueous layer was extracted

[1] Guinchard, X.; Vallée, Y.; Denis, J. *Org; Lett*. **2007**, *9*, 3761-3764.

with EtOAc (2 x 30 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (gradient 1-5% saturated NH_3/MeOH in CH_2Cl_2) to afford a 2:1 mixture of the desired bisindoles **22a** and **22b** as a white solid (152 mg, 57% yield). The stereochemistry of **22a** was confirmed by transformation of **20a** to **22a**. Major Product (**22a**): mp 250 °C (dec.); IR (film) 3292, 1696 cm^{-1}; ^1H NMR (300 MHz, acetone-d6) δ 11.50 (br s, 1H), 9.07 (s, 1H), 8.58 (br d, *J* = 7.8 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.60-7.56 (m, 3H), 7.41-7.31 (m, 4H), 7.10 (d , *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.08 (br d, *J* = 9.0 Hz, 1H), 5.73 (s, 1H), 5.48 (s, 1H), 5.45 (t, *J* = 9.1 Hz, 1H), 5.26 (s, 2H), 4.54 (t, *J* = 10.3 Hz, 1H), 3.78 (d, *J* = 10.0 Hz, 1H), 3.56 (q, *J* = 7.1 Hz, 1H), 3.29 (d, *J* = 9.9 Hz, 1H), 1.48 (d, *J* = 7.1 Hz, 3H), 1.46 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, acetone-d6) δ 181.7, 163.9, 162.7, 158.0, 149.7, 147.0, 140.2, 138.4, 138.2, 129.1, 128.5, 128.2, 126.7, 126.5, 126.0, 124.8, 124.2, 117.4, 116.1, 113.7, 109.2, 84.2, 79.6, 71.3, 65.9, 48.9, 46.9, 28.5, 27.8, 18.0; ^{13}C NMR (75 MHz, DMF-d7) δ 182.3, 164.1, 157.8, 149.5, 146.6, 140.1, 138.3, 138.2, 128.9, 128.3, 128.23, 128.15, 126.7, 126.4, 126.2, 125.3, 124.7, 123.8, 119.9, 116.9, 116.1, 113.4, 108.9, 84.2, 79.0, 70.9, 65.7, 57.3, 48.7, 47.9, 46.6, 28.4, 27.6, 17.9 (one C=O peak at ~163 ppm is obscured by the solvent peak); LRMS(ESI) *m/z* (relative intensity) 863.2 (61%, $M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{42}H_{45}N_6O_8NaBr]^+$: 863.2380, found 863.2353.

Minor Product (**22b**): mp 250 °C (dec.); IR (film) 3296, 1702 cm^{-1}; ^1H NMR (300 MHz, acetone-d6) δ 11.54 (br s, 1H), 9.05 (s, 1H), 8.44 (br d, *J* = 8.3 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 1.4 Hz, 1H), 7.61-7.59 (m, 3H), 7.43-7.31 (m, 4H), 7.15 (d , *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.37 (br d, *J* = 11.0 Hz, 1H), 5.81 (s, 1H), 5.69 (s,

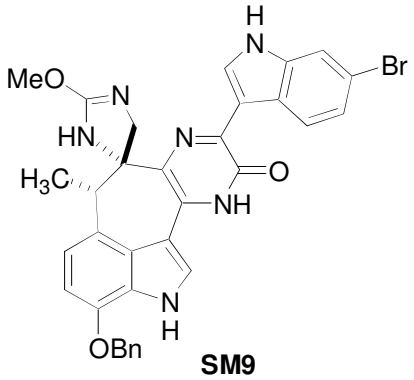
1H), 5.37 (s, 1H), 5.27 (s, 2H), 4.43 (dd, *J* = 9.9, 4.0 Hz, 1H), 3.48 (m, 2H), 3.11 (d, *J* = 9.5 Hz, 1H), 1.62 (d, *J* = 7.1 Hz, 3H), 1.50 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, acetone-d6) δ 181.3, 163.6, 162.8, 157.1, 149.6, 147.2, 140.4, 138.4, 138.3, 131.3, 129.1, 128.5, 128.4, 128.1, 127.0, 126.7, 126.5, 125.9, 125.2, 124.1, 118.8, 117.4, 116.2, 113.5, 109.4, 84.1, 79.5, 71.3, 66.8, 60.8, 49.4, 49.0, 46.8, 28.5, 27.9, 17.4; LRMS(ESI) *m/z* (relative intensity) 863.2 (92%, M+Na$^+$); HRMS (ESI) *m/z* calcd for $[C_{42}H_{45}N_6O_8NaBr]^+$: 863.2380, found 863.2349.



23

(±)-Bisindolyl Pyrazinone 23. To an ice-cooled solution of bisindole **22** (91 mg, 0.11 mmol) in CH_2Cl_2 (4 mL) was added TFA (2 mL). The resulting orange solution was stirred at 0°C for 1 h. At that point, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and then saturated $NaHCO_3$ solution (20 mL) was slowly added at 0°C. The resulting mixture was stirred at this temperature for 10 min and then EtOAc (60 mL) was added followed by additional saturated $NaHCO_3$ solution (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (40 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was dissolved in MeOH (30 mL) and stirred at room temperature for 16 h to let the cyclization go to completion. This solution then was

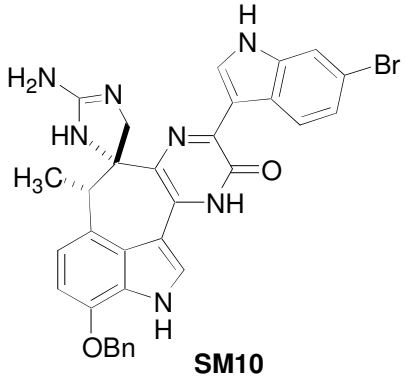
concentrated under reduced pressure to give a pale yellow solid. This solid was dissolved in 1,4-dioxane (5 mL) and DDQ (49 mg, 0.22 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and then diluted with EtOAc (100 mL) and washed with saturated $NaHCO_3$ solution (3 x 50 mL). The aqueous layer was extracted with EtOAc (2 x 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (gradient 1-10% saturated NH_3/MeOH in CH_2Cl_2) to afford the desired bisindolyl pyrazinone **23** as a bright yellow solid (44 mg, 65% overall yield). mp 250 °C (dec.); IR (film) 3235, 1686, 1633 cm^{-1}; ^1H NMR (400 MHz, DMF-d7) δ 12.33 (s, 1H), 12.28 (br s, 1H), 11.68 (s, 1H), 8.98 (d, *J* = 8.6 Hz, 1H), 8.88 (s, 1H), 8.49 (s, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.25 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.09 (s, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.09 (s, 1H), 5.34 (s, 2H), 3.57 (q, *J* = 6.9 Hz, 1H), 3.20 (d, *J* = 8.9 Hz, 1H), 3.02 (d, *J* = 8.9 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, DMF-d7) δ 164.2, 155.9, 145.3, 138.3, 138.2, 131.7, 129.1, 129.0, 128.5, 128.4, 127.8, 126.7, 126.4, 125.9, 123.9, 123.7, 121.7, 115.7, 114.5, 113.8, 104.9, 70.4, 67.3, 53.2, 51.3, 20.1; LRMS(ESI) *m/z* (relative intensity) 621.2 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{32}H_{26}BrN_6O_3]^+$: 621.1250, found 621.1246.



SM9

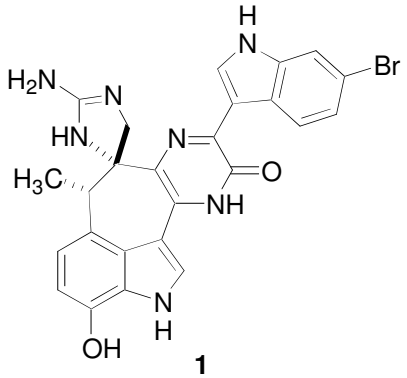
(±)-Iso-urea SM9. To a yellow suspension of urea **23** (6.0 mg, 0.010 mmol) in EtOAc (10 mL) at room temperature was added $NaHCO_3$ (17 mg, 0.20 mmol) followed by Me_3OBF_4 (29 mg, 0.20 mmol). The reaction mixture was stirred at room temperature for 1 h and then diluted with EtOAc (100 mL). This mixture was poured into a mixture of saturated $NaHCO_3$ solution (25 mL) and water (25 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. TLC analysis showed that urea **23** was not all consumed and so the reaction was repeated under the same reaction conditions for 1 h to give a clear and bright yellow solution. The reaction mixture was worked up as previously described. The crude residue was purified by preparative TLC (7% saturated NH_3/MeOH in CH_2Cl_2) to afford the desired iso-urea **SM9** as a bright yellow solid (4.2 mg, 69%). mp 250 °C (dec.); IR (film) 3142, 1630 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 8.7 (s, 1H), 8.56 (d, *J* = 8.6 Hz, 1H), 8.03 (s, 1H), 7.61 (d, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 6.8 Hz, 2H), 7.42-7.27 (m, 4H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 5.28 (s, 2H), 3.89 (s, 3H), 3.57 (q, *J* = 6.9 Hz, 1H), 3.40 (d, *J* = 12.5 Hz, 1H), 3.26 (d, *J* = 12.5 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 3H); LRMS(ESI) *m/z* (relative intensity) 635.2 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{33}H_{28}BrN_6O_3]^+$: 635.1406, found 635.1385. Since the iso-urea precipitated quickly

in MeOD and was gradually converted back to the urea in DMF-d7, we could not obtain a good ^{13}C NMR spectrum of this compound.



SM10

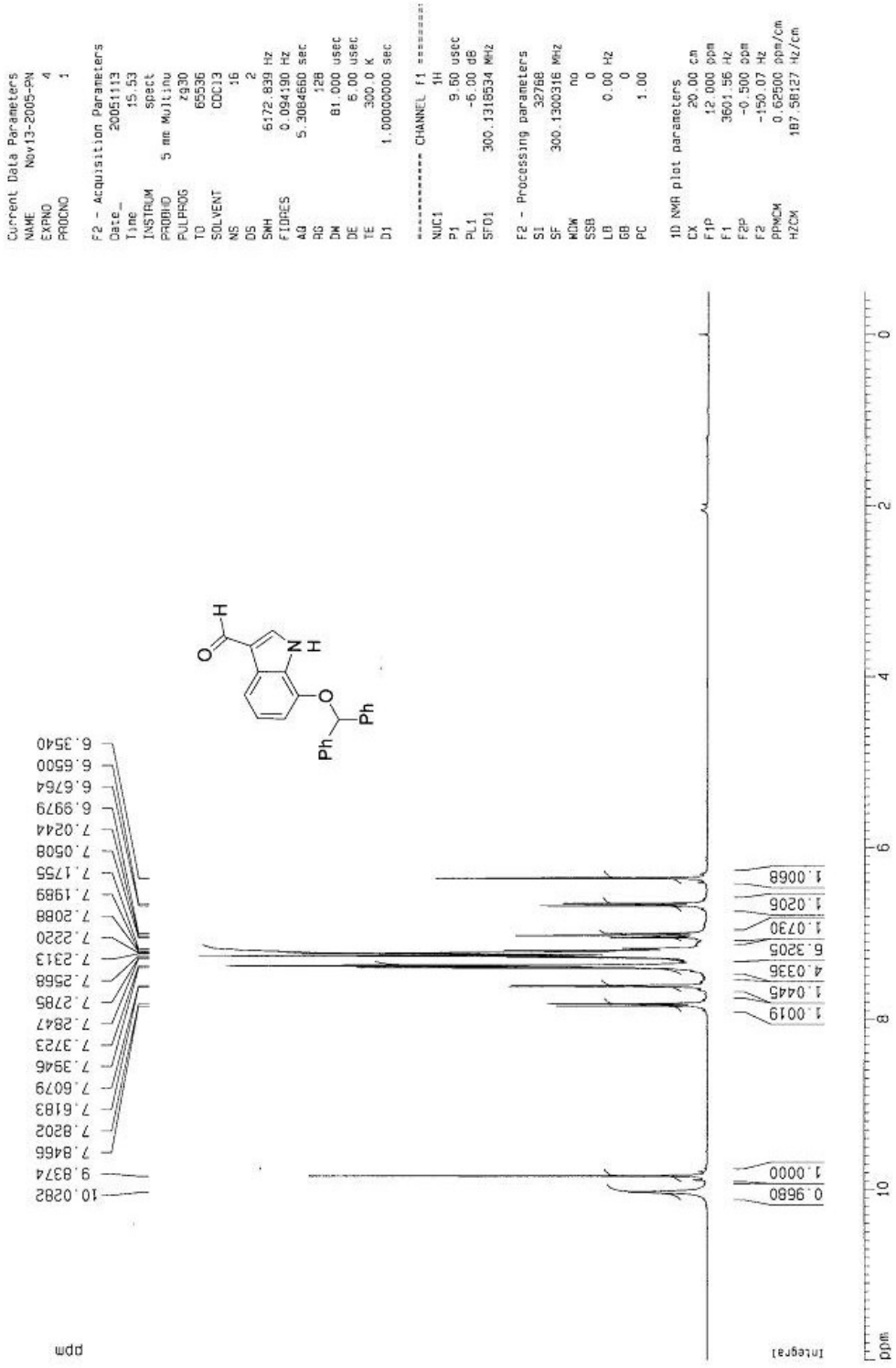
(±)-Guanidine SM10. A solution of iso-urea **SM9** (8.8 mg, 0.014 mmol) in saturated NH_3/MeOH (2 mL) in a sealed tube was heated at 95 °C for 3 h. The reaction mixture then was allowed to cool to room temperature and concentrated to dryness under reduced pressure. The crude residue was purified by flash chromatography on silica gel (gradient 5-40% saturated NH_3/MeOH in CH_2Cl_2) to afford the desired guanidine **SM10** as a bright yellow solid (5.7 mg, 66%). mp 250 °C (dec.); IR (neat) 3182, 1686, 1626 cm^{-1}; ^1H NMR (850 MHz, CD_3OD) δ 8.61 (s, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.02 (s, 1H), 7.55-7.54 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.27 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.26 (s, 2H), 3.55 (q, *J* = 6.9 Hz, 1H), 3.42 (d, *J* = 10.2 Hz, 1H), 3.25 (d, *J* = 10.1 Hz, 1H), 1.10 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (212.5 MHz, CD_3OD) δ 161.5, 161.0, 146.1, 138.84, 138.76, 132.8, 130.2, 129.5, 128.9, 128.7, 128.5, 128.4, 127.1, 126.5, 125.3, 124.5, 123.7, 121.5, 116.0, 115.2, 114.8, 104.7, 72.3, 71.3, 56.6, 51.6, 20.0; LRMS(ESI) *m/z* (relative intensity) 620.3 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{32}H_{27}BrN_7O_2]^+$: 620.1410, found 620.1390.



1

(±)-Dragmacidin E (1). To a suspension of guanidine **SM10** (3.9 mg, 0.0063 mmol) in CH_3CN (0.5 mL) was added TMSI (110 μL, 0.77 mmol). The reaction mixture was heated at 50°C for 2 h and then it was allowed to cool to room temperature. This solution then was diluted with EtOAc (20 mL) and saturated sodium metabisulfite (20 mL) was added. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (gradient 10-50% saturated NH_3/MeOH in CH_2Cl_2) to afford dragmacidin E (**1**) as a bright yellow solid (1.8 mg, 55%). mp 200 °C (dec.); IR (film) 3401, 1690, 1637 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 8.66 (s, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.02 (s, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 3.54 (q, *J* = 7.0 Hz, 1H), 3.41 (d, *J* = 10.0 Hz, 1H), 3.24 (d, *J* = 10.1 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (212.5 MHz, CD_3OD) δ 160.6, 157.3, 144.9, 138.8, 132.0, 128.4, 126.4, 126.1, 125.9, 125.3, 124.6, 123.9, 122.9, 116.8, 115.2, 113.8, 108.2, 72.1, 56.3, 51.1, 19.7; LRMS(ESI) *m/z* (relative intensity) 530.3 (100%, $M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{25}H_{21}BrN_7O_2]^+$: 530.0940, found 530.0959.

^{1}H NMR **SM1**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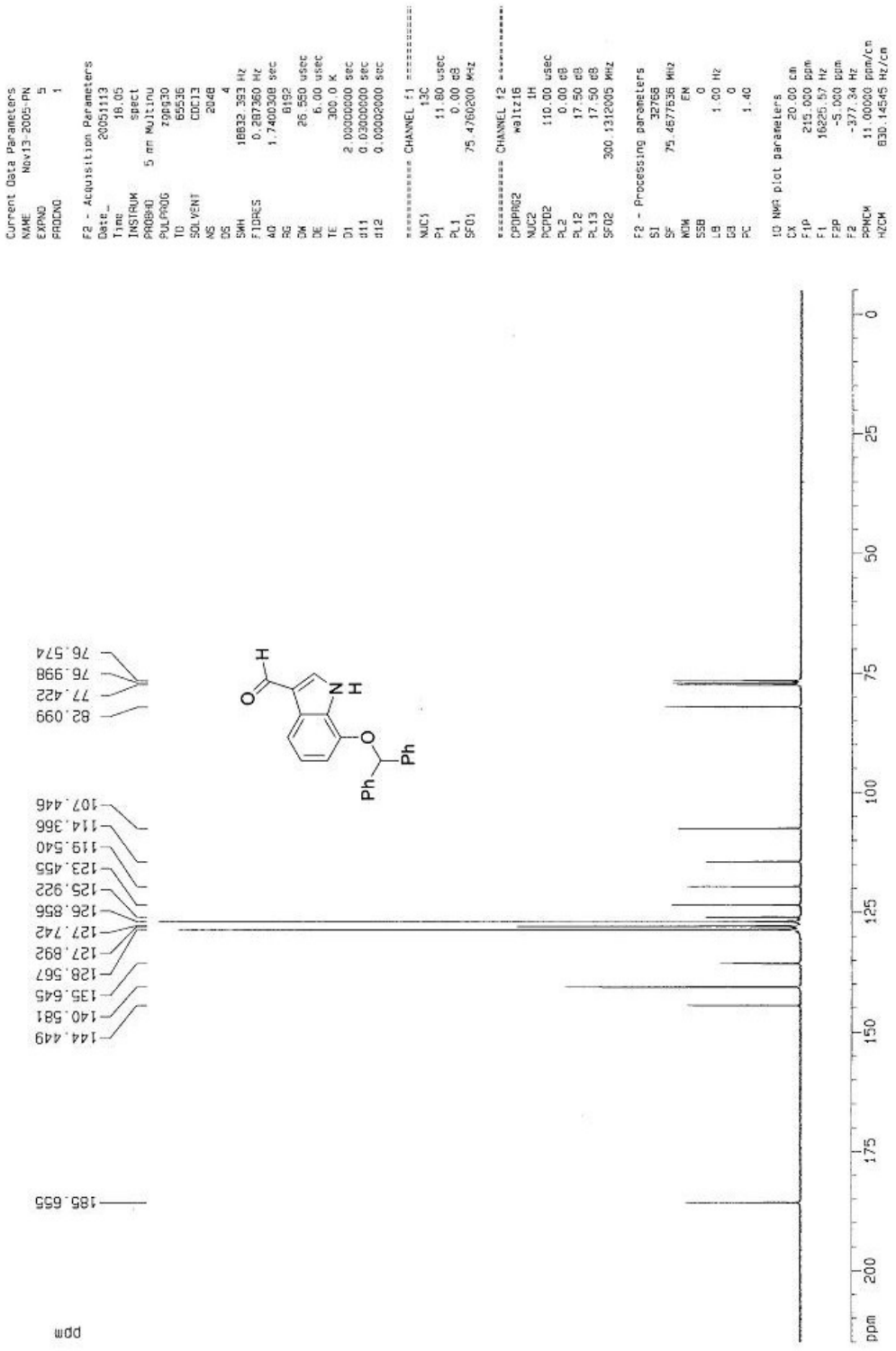
^{13}C NMR **SM1**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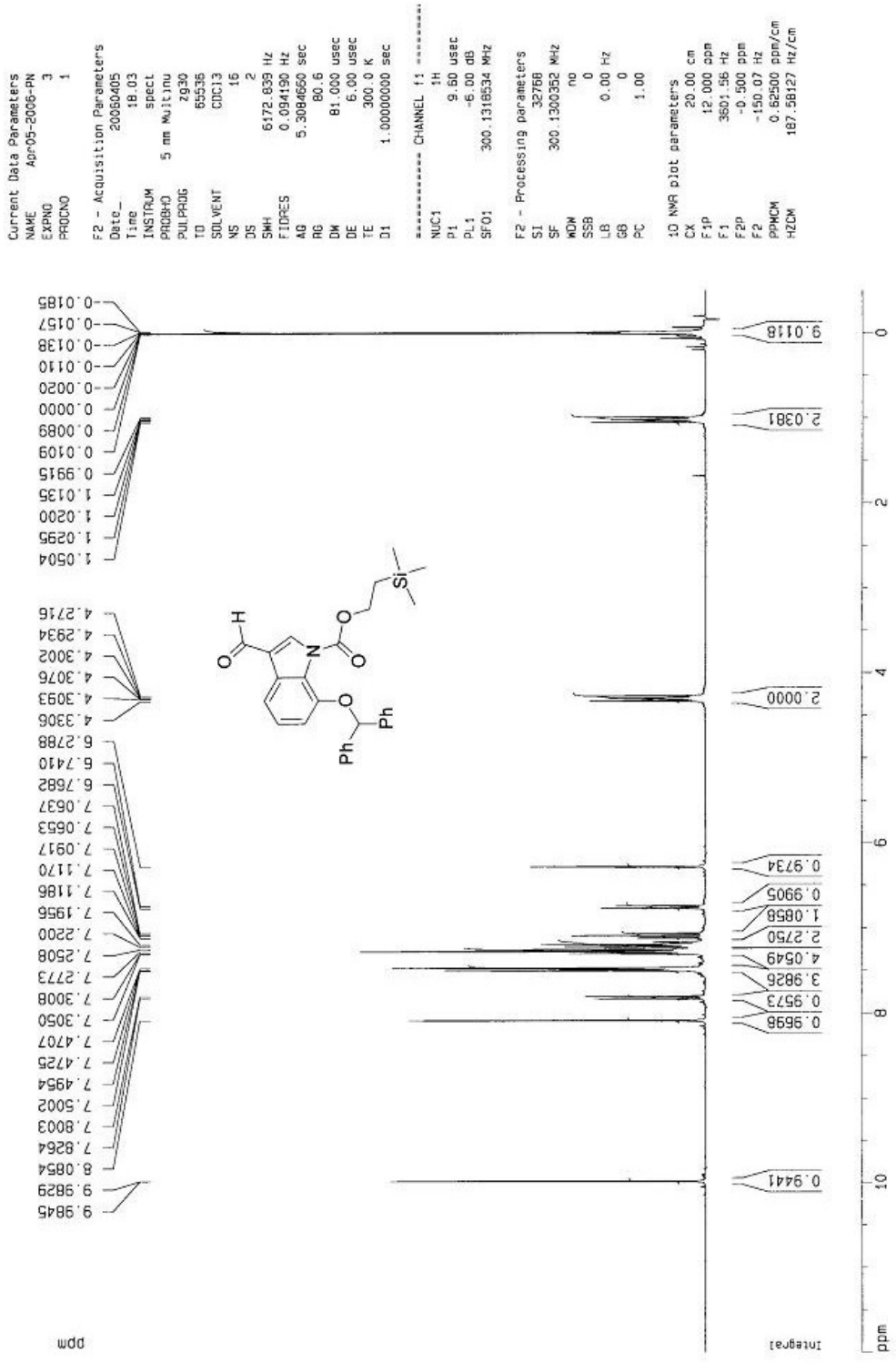
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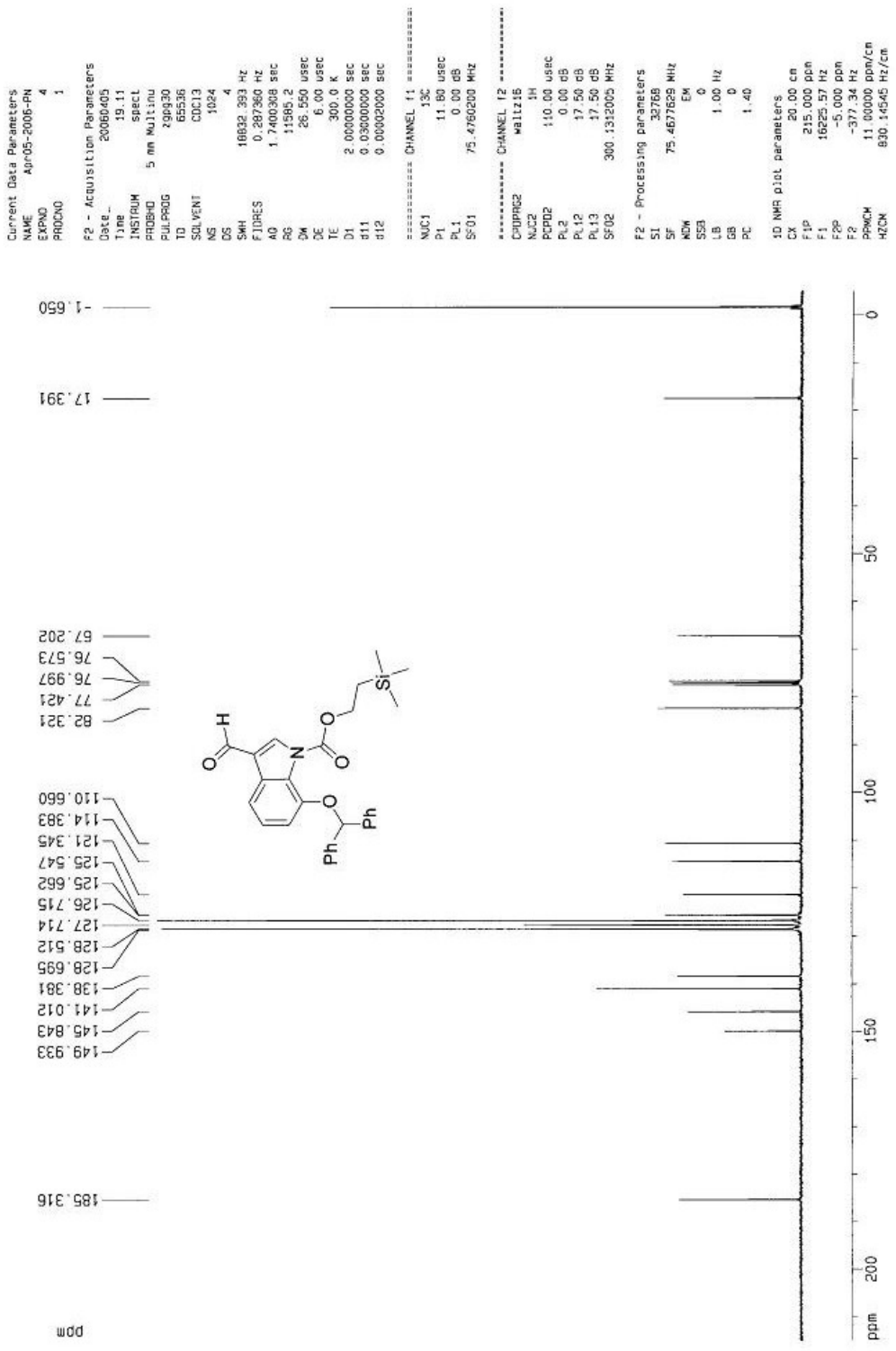
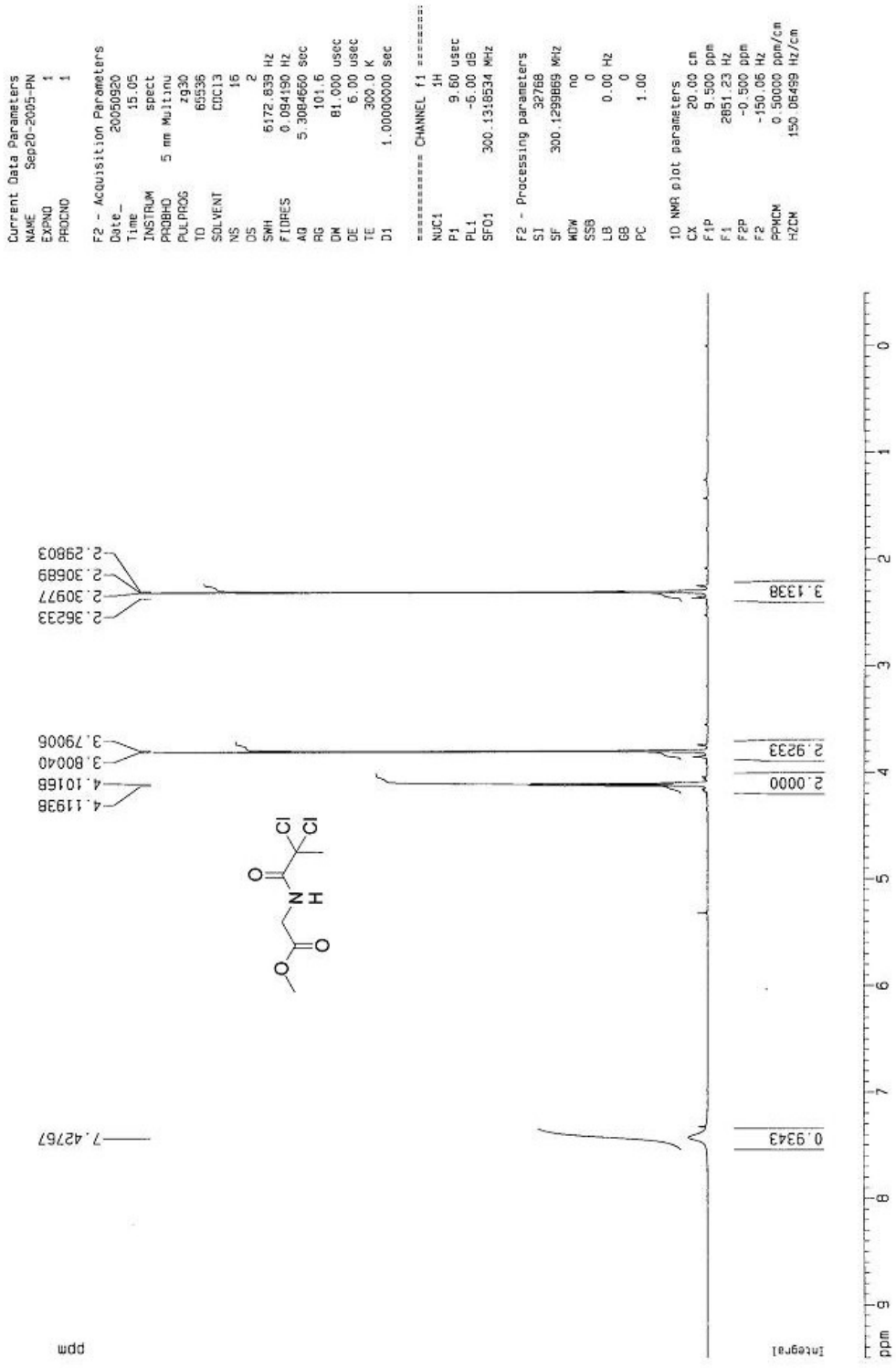
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300352 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.58127 Hz/cm
9.0118
2.0381
2.0000
0.9734
0.9905
1.0858
2.2750
4.0549
3.9825
0.9573
0.9698
0.9441
Integral
ppm
Si
O
H
N
Ph
Ph

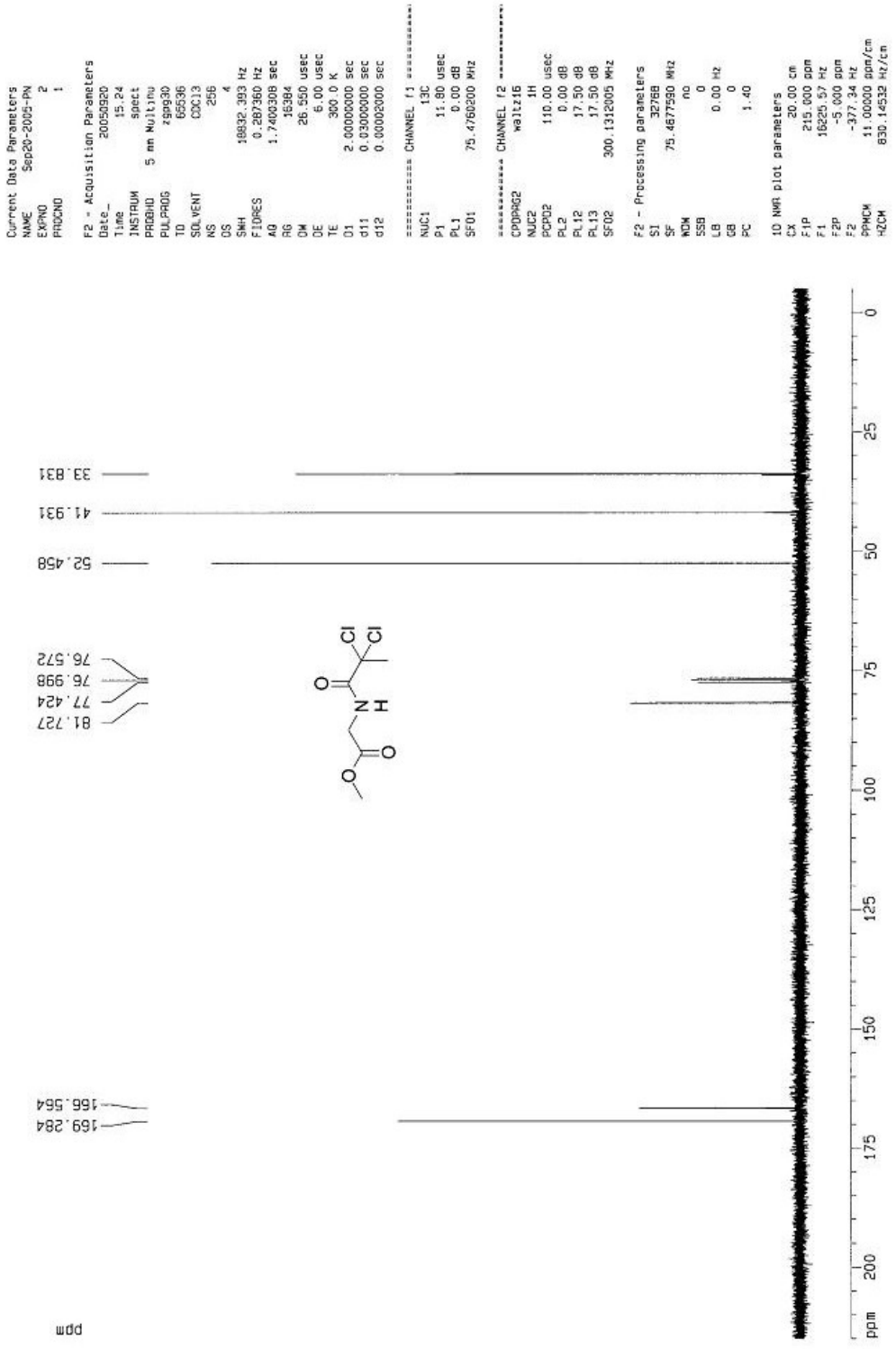
^{13}C NMR **4**


Current Data Parameters
NAME Apr05-2006-PN
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060405
Time 19.11
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 11585.2
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677629 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14545 Hz/cm
-1.650
17.391
67.202
76.573
76.997
77.421
82.321
110.660
114.383
121.345
125.547
125.662
126.715
127.714
128.512
128.695
138.381
141.012
145.843
149.933
185.316
ppm
0
50
100
150
200
ppm
O
H
N
O
O
Si
O
Ph
Ph

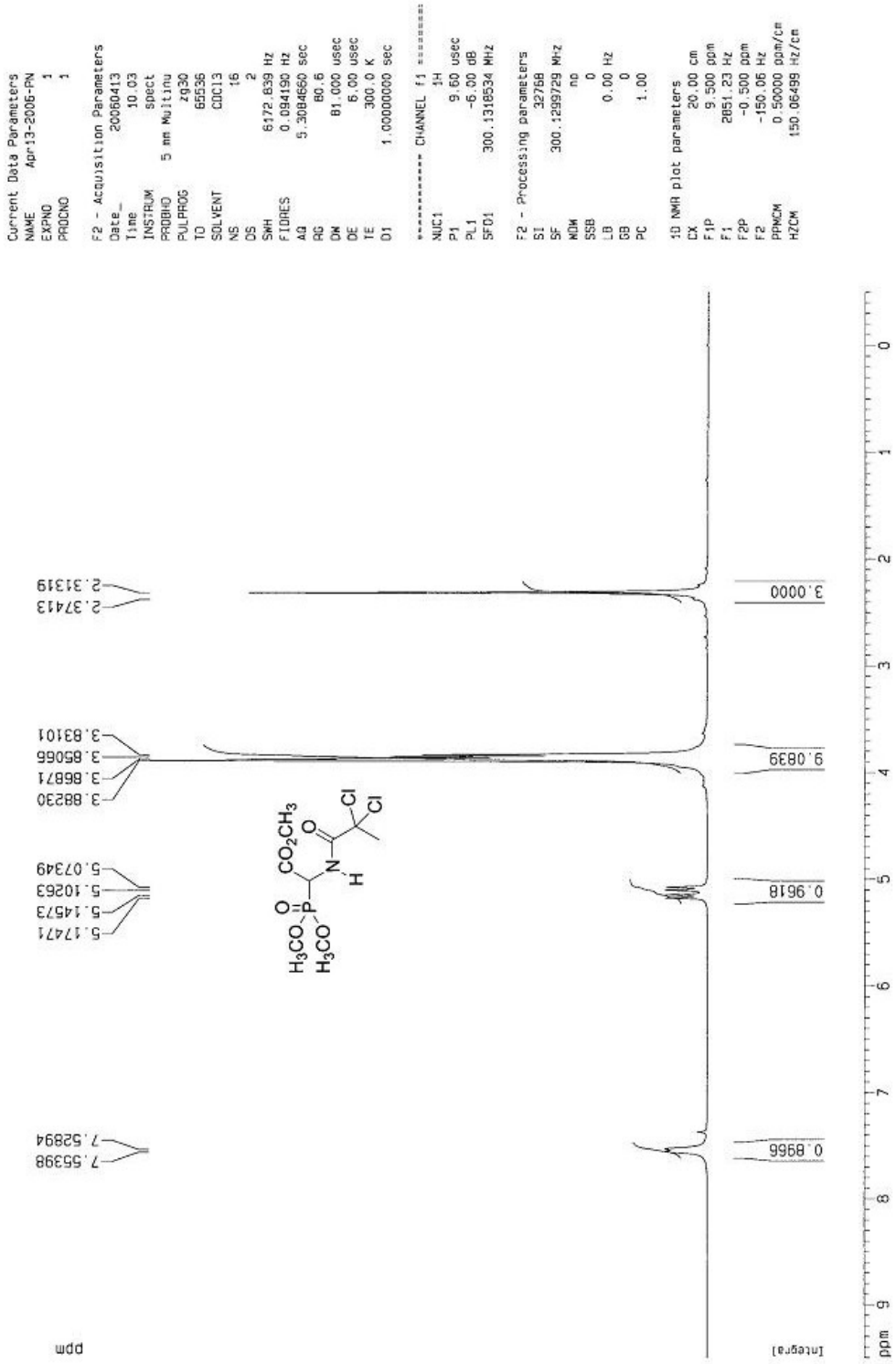
^{1}H NMR **SM2**


Current Data Parameters
NAME Sep20-2005-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050920
Time 15.05
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084650 sec
RG 101.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1316534 MHz
F2 - Processing parameters
SI 32768
SF 300.1299869 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.23 Hz
F2P -0.500 ppm
F2 -150.05 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06499 Hz/cm
2.29803
2.30689
2.30977
2.36233
3.79006
3.80040
4.10168
4.11938
7.42767
3.1338
2.9233
2.0000
0.9343
Cl
Cl
O
N
H
O
O
O
ppm
Integral

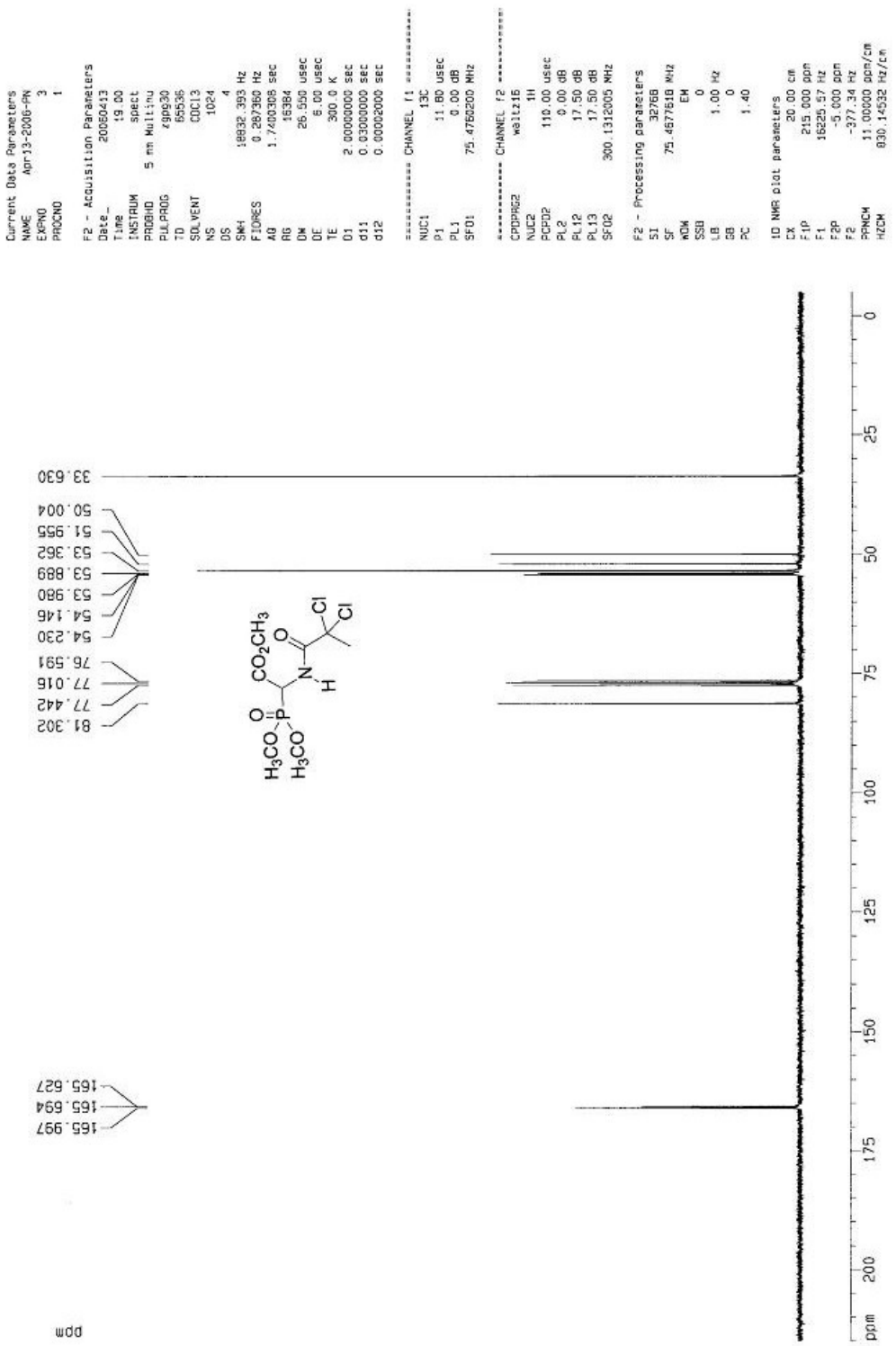
^{13}C NMR **SM2**


Current Data Parameters
NAME Sep20-2005-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050920
Time 15.24
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677590 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14532 Hz/cm
33.831
41.931
52.458
76.572
76.998
77.424
81.727
166.564
169.284
ppm
0
25
50
75
100
125
150
175
200
ppm

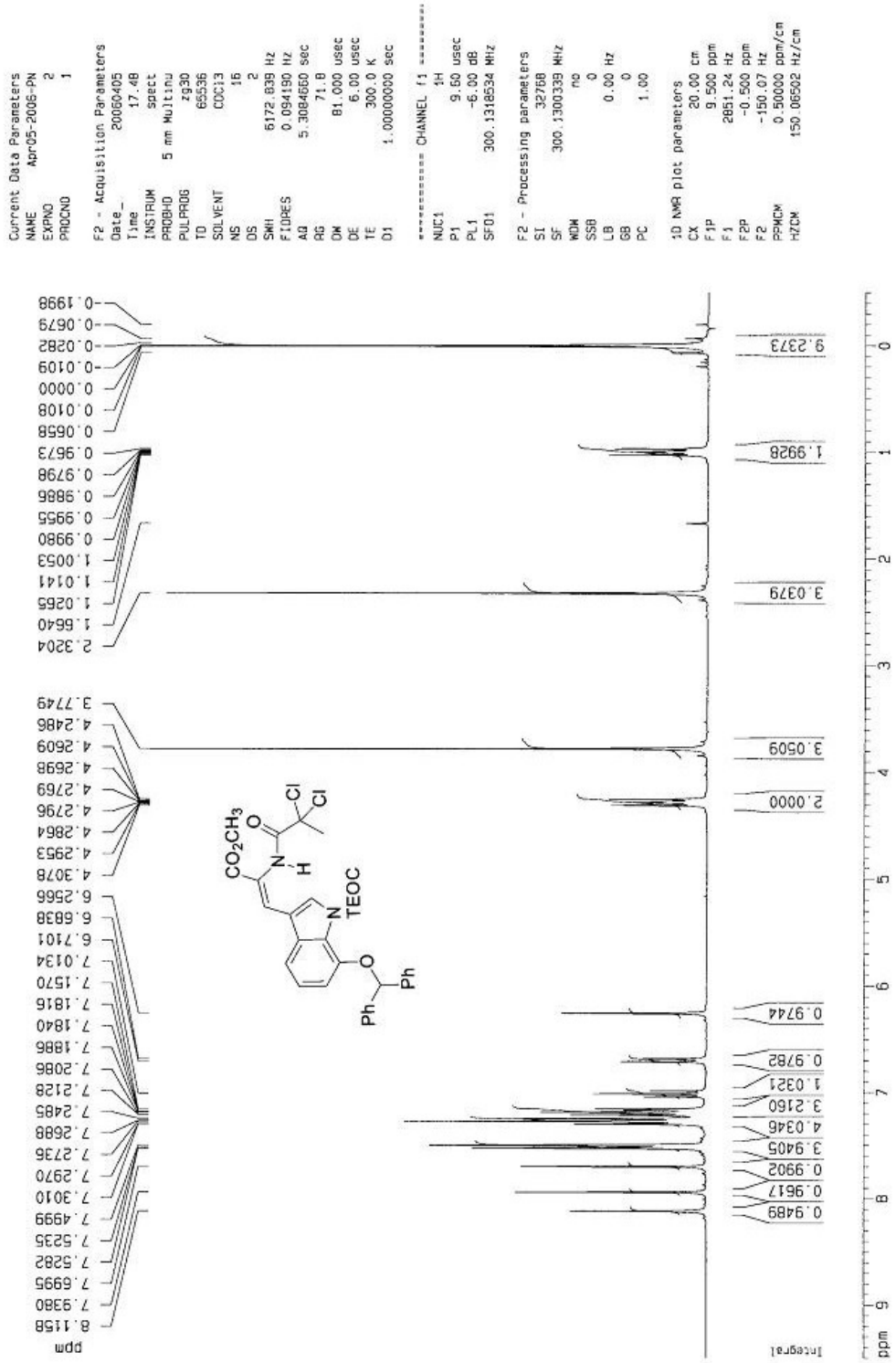
^{1}H NMR **SM3**


Current Data Parameters
NAME Apr13-2006-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060413
Time 10.03
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 80.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1299729 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.23 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06499 Hz/cm
7.55398
7.52894
5.17471
5.14573
5.10263
5.07349
3.88230
3.86871
3.85066
3.83101
2.37413
2.31319
0.8956
0.9618
9.0839
3.0000
ppm
[Integral]

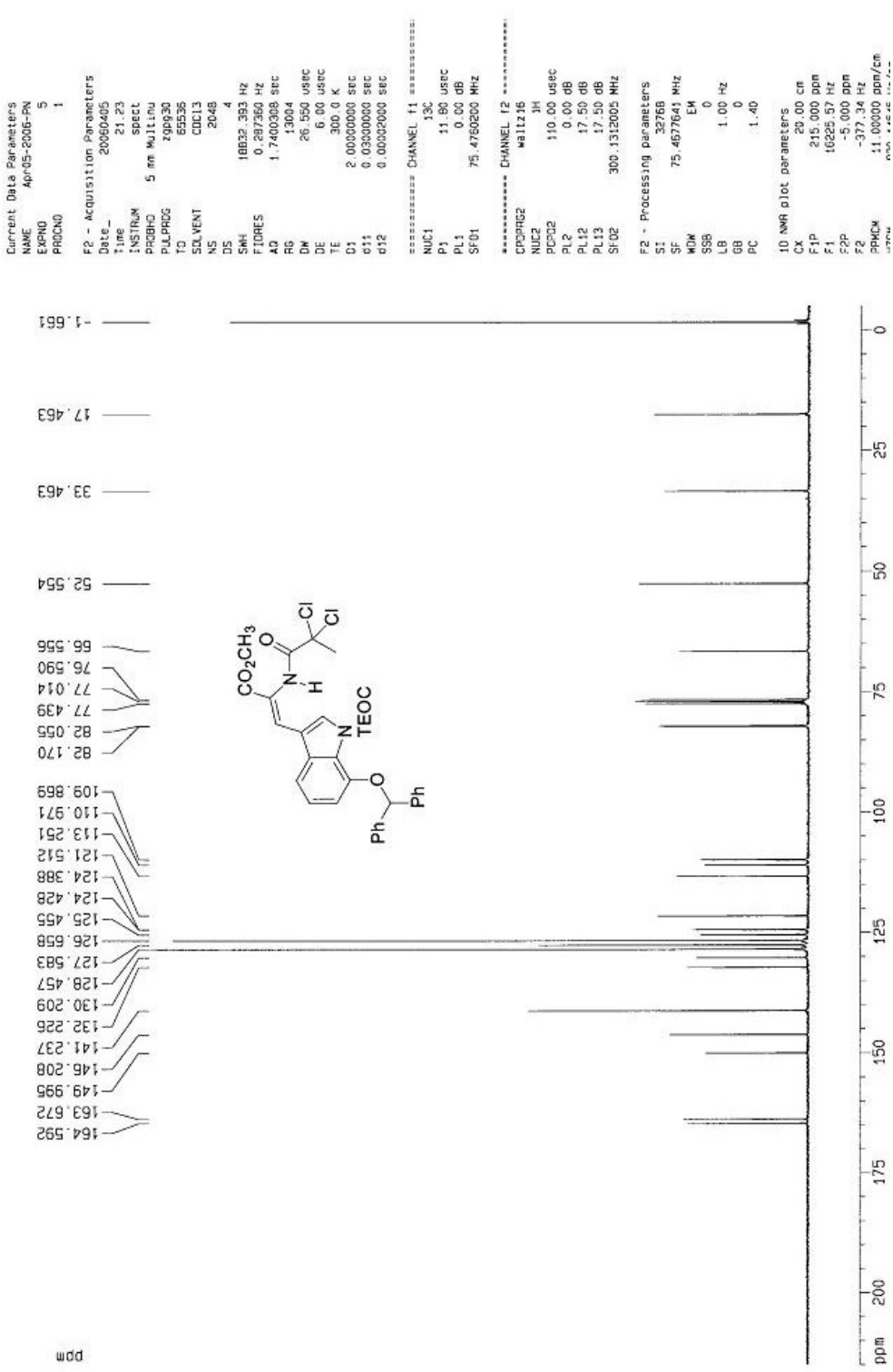
^{13}C NMR **SM3**


Current Data Parameters
NAME Apr13-2006-PA
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060413
Time 19.00
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677618 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14532 Hz/cm
165.997
165.694
165.627
81.302
77.442
77.016
76.591
54.230
53.980
53.889
53.362
51.955
50.004
33.630
ppm
200
175
150
125
100
75
50
25
0

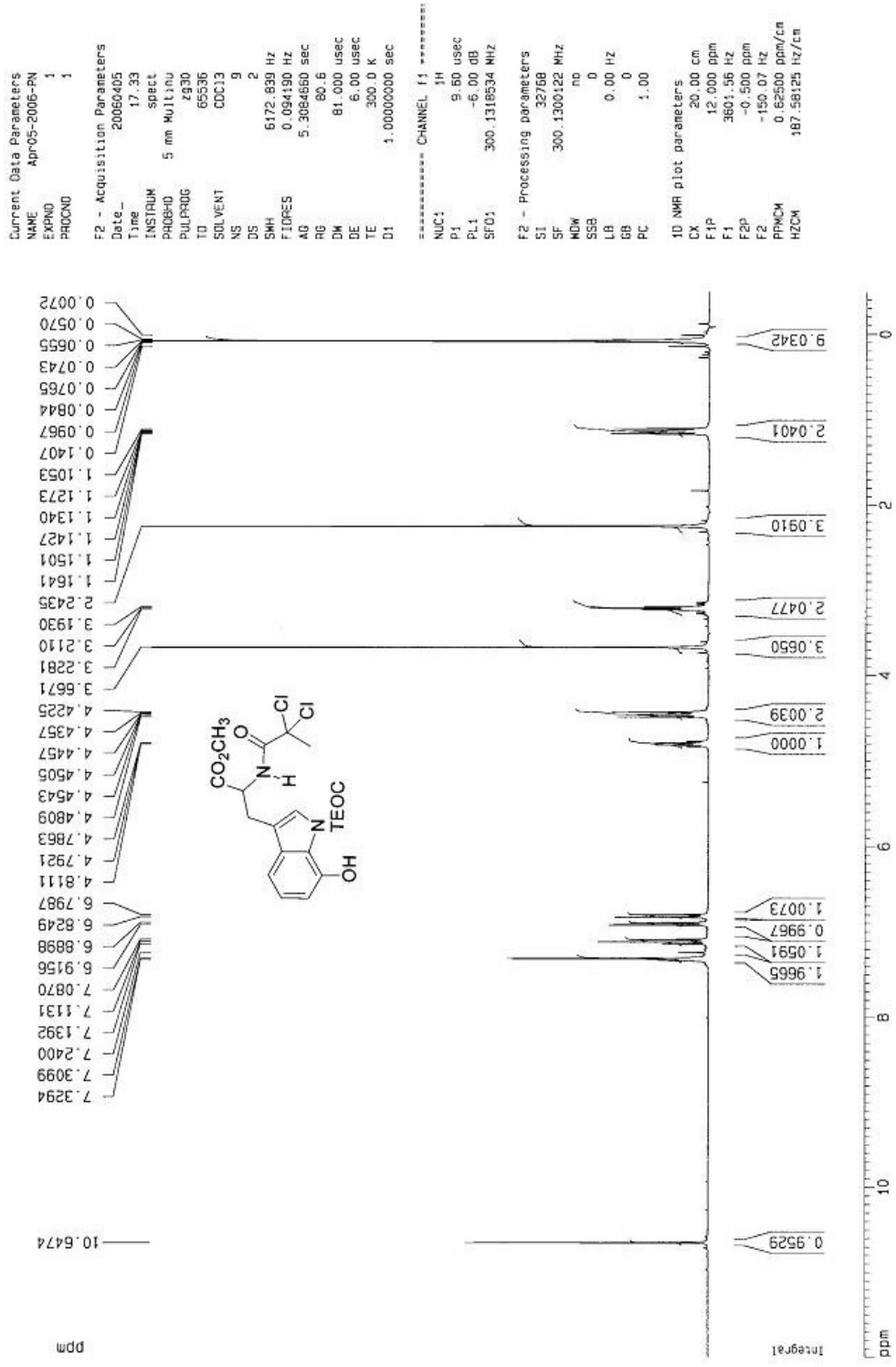
^{1}H NMR **5**


Current Data Parameters
NAME Apr05-2006-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060405
Time 17.48
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084650 sec
RG 71.8
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300339 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06502 Hz/cm
ppm
Integral
CO2CH3
O
Cl
Cl
N
H
N
TEOC
O
Ph
Ph

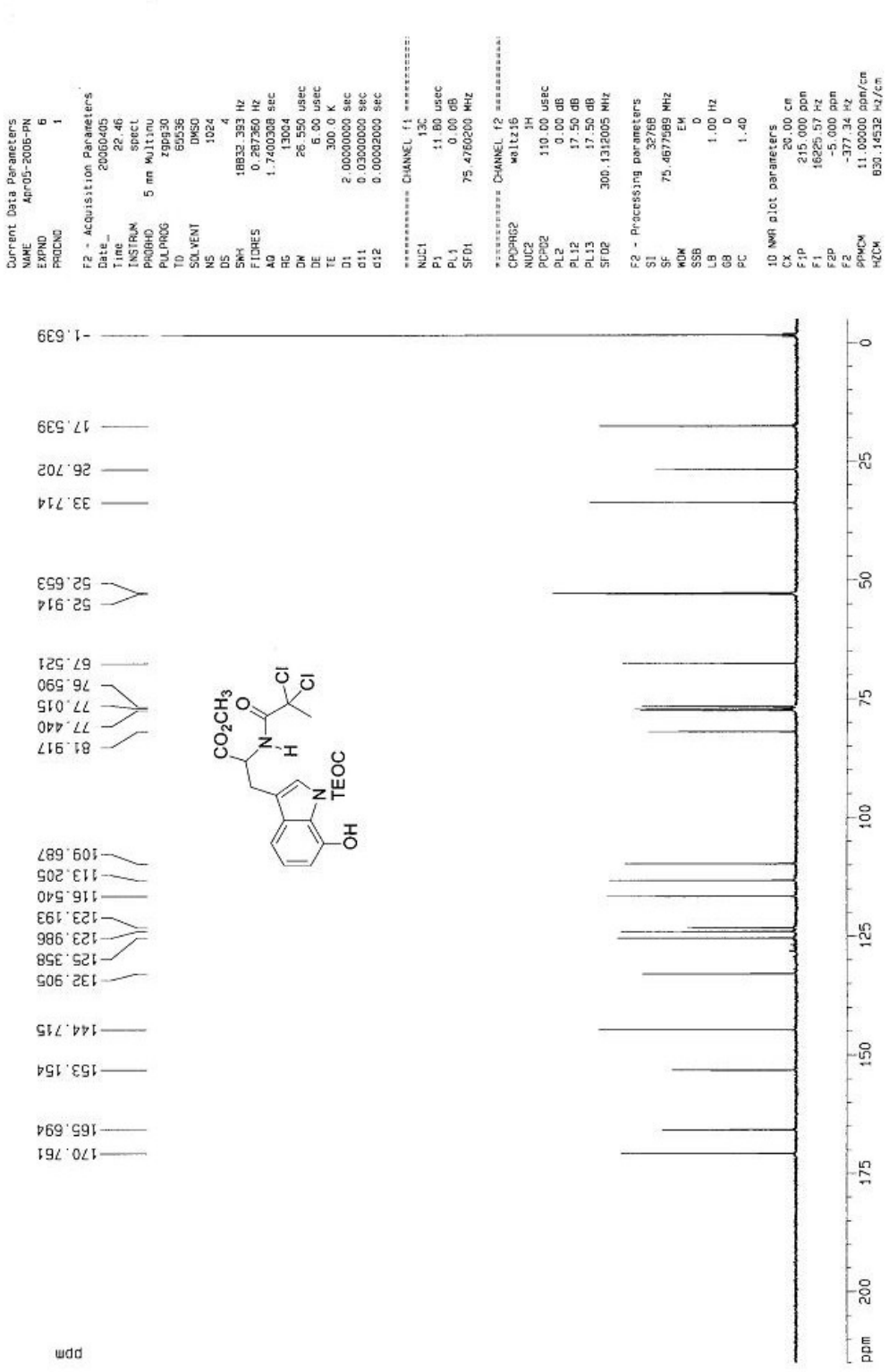
^{13}C NMR **5**


Current Data Parameters
NAME Apr05-2006-PN
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060405
Time 21.23
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SF01 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677641 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
-1.661
17.463
33.463
52.554
66.556
76.590
77.014
77.439
82.055
82.170
109.869
110.971
113.251
121.512
124.388
124.428
125.455
126.658
127.583
128.457
130.209
132.226
141.237
146.208
149.995
163.672
164.592
CO2CH3
Cl
Cl
N
H
TEOC
O
Ph
Ph
ppm

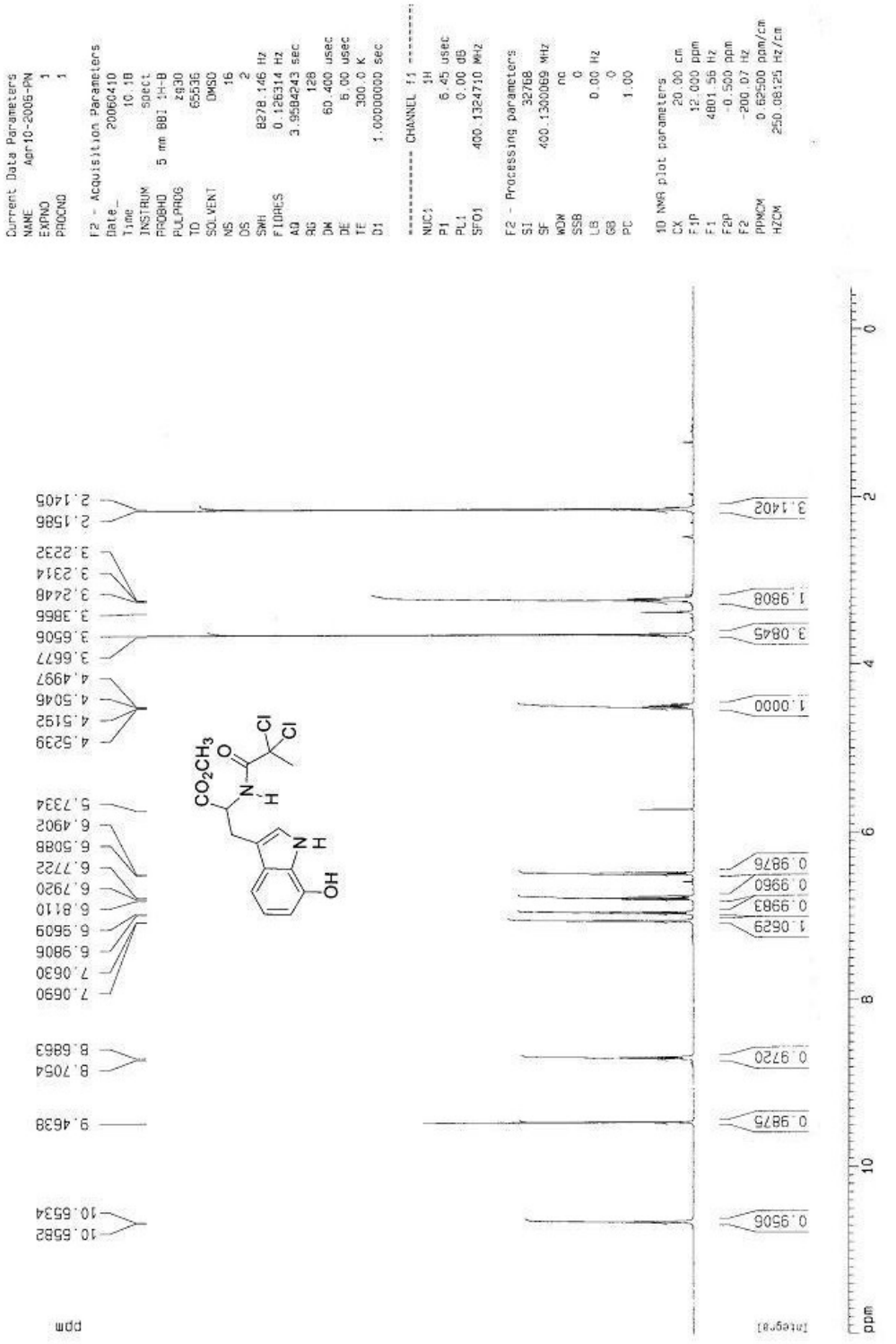
^{1}H NMR **SM4**


Current Data Parameters
NAME Apr05-2006-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060405
Time 17.33
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 80.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -6.00 dB
SFO1 300.1316534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.82500 ppm/cm
HZCM 187.58125 Hz/cm
0.0072
0.0570
0.0655
0.0743
0.0765
0.0844
0.0967
0.1407
1.1053
1.1273
1.1340
1.1427
1.1501
1.1641
2.2435
3.1930
3.2110
3.2281
3.6671
4.4225
4.4357
4.4457
4.4505
4.4543
4.4809
4.7863
4.7921
4.8111
6.7987
6.8249
6.8898
6.9156
7.0870
7.1131
7.1392
7.2400
7.3099
7.3294
10.6474
9.0342
2.0401
3.0910
2.0477
3.0650
2.0039
1.0000
1.0073
0.9967
1.0591
1.9665
0.9529
CO2CH3
TEOC
OH
ppm
Integral

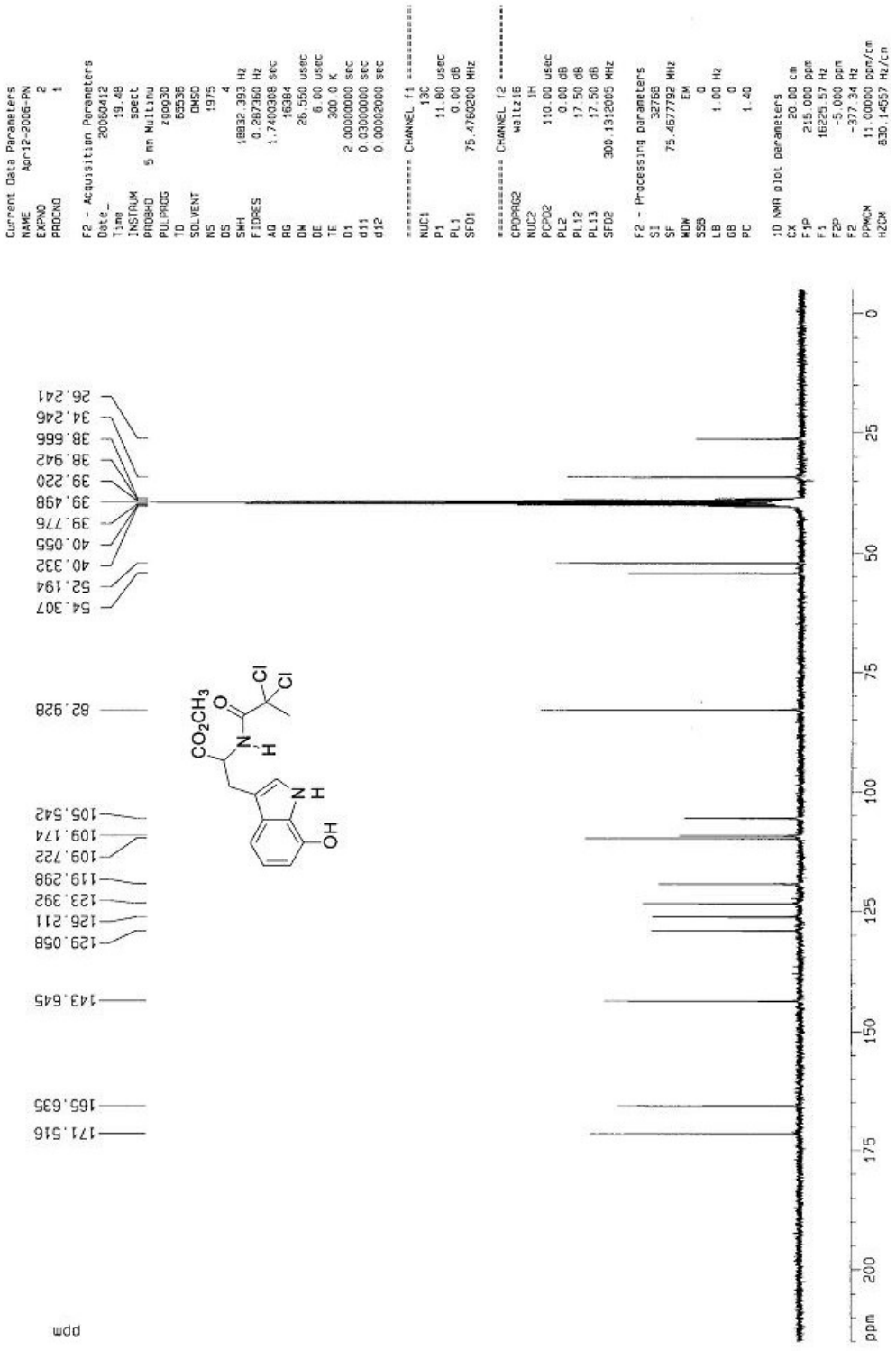
^{13}C NMR **SM4**


Current Data Parameters
NAME Apr05-2006-PN
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060405
Time 22.46
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677689 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.02000 ppm/cm
HZCM 830.14532 Hz/cm
-1.639
17.539
26.702
33.714
52.653
52.914
67.521
76.590
77.015
77.440
81.917
109.687
113.205
116.540
123.193
123.986
125.358
132.905
144.715
153.154
165.694
170.761
ppm
0
25
50
75
100
125
150
175
200
ppm

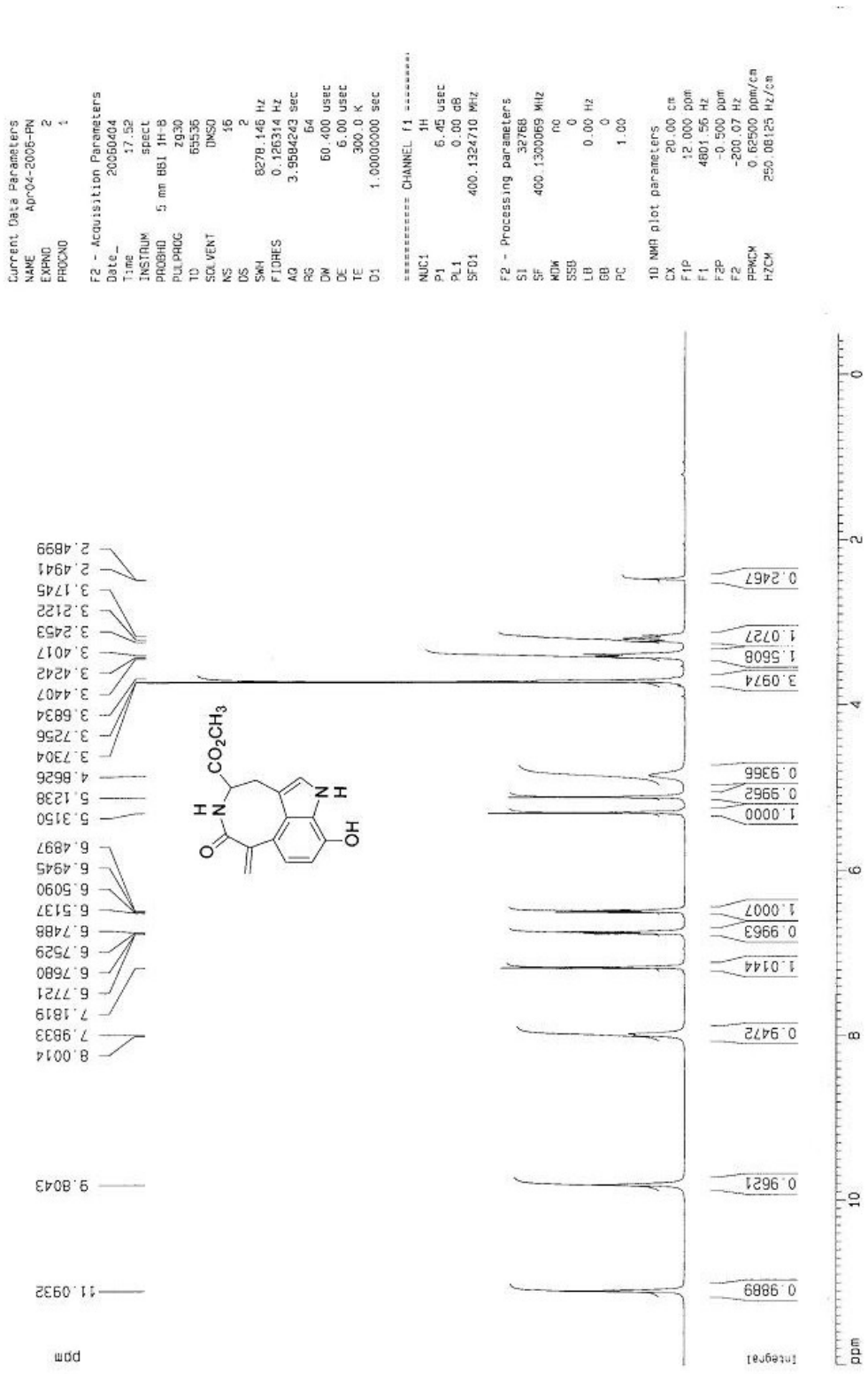
^{1}H NMR **6**


Current Data Parameters
NAME Apr10-2006-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060410
Time 10.18
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
---------- CHANNEL f1 ----------
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300069 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 4801.55 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 250.08125 Hz/cm
2.1405
2.1586
3.2232
3.2314
3.2448
3.3866
3.6506
3.6677
4.4997
4.5046
4.5192
4.5239
5.7334
6.4902
6.5088
6.7722
6.7920
6.8110
6.9609
6.9806
7.0630
7.0690
8.6863
8.7054
9.4638
10.6534
10.6582
3.1402
1.9808
3.0845
1.0000
0.9876
0.9960
0.9983
1.0629
0.9720
0.9875
0.9506
integral
ppm

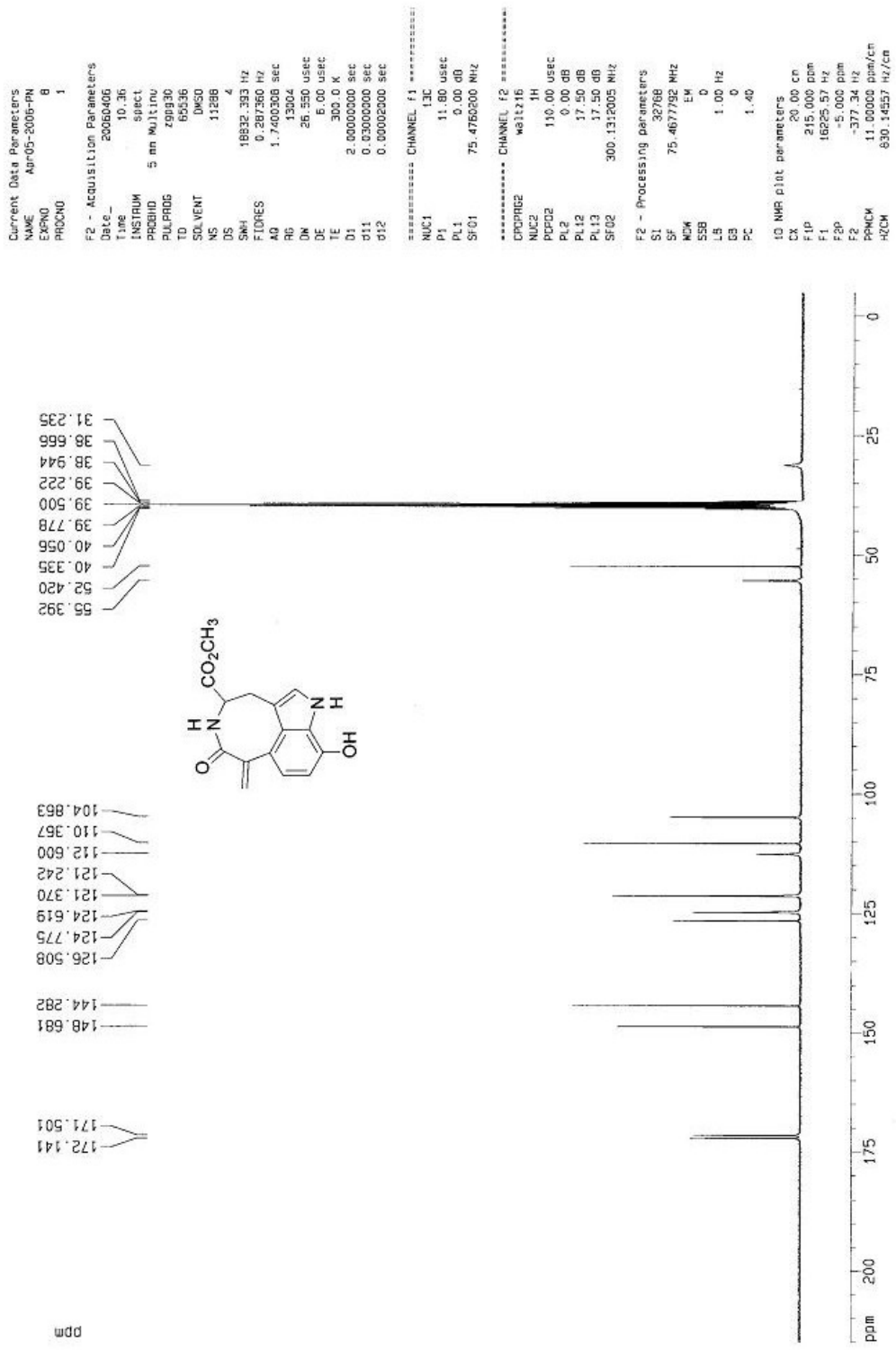
^{13}C NMR **6**


Current Data Parameters
NAME Apr12-2006-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060412
Time 19.48
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1975
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677792 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14557 Hz/cm
26.241
34.246
38.666
38.942
39.220
39.498
39.775
40.055
40.332
52.194
54.307
82.928
105.542
109.174
109.722
119.298
123.392
126.211
129.058
143.645
165.635
171.516
ppm
0
25
50
75
100
125
150
175
200

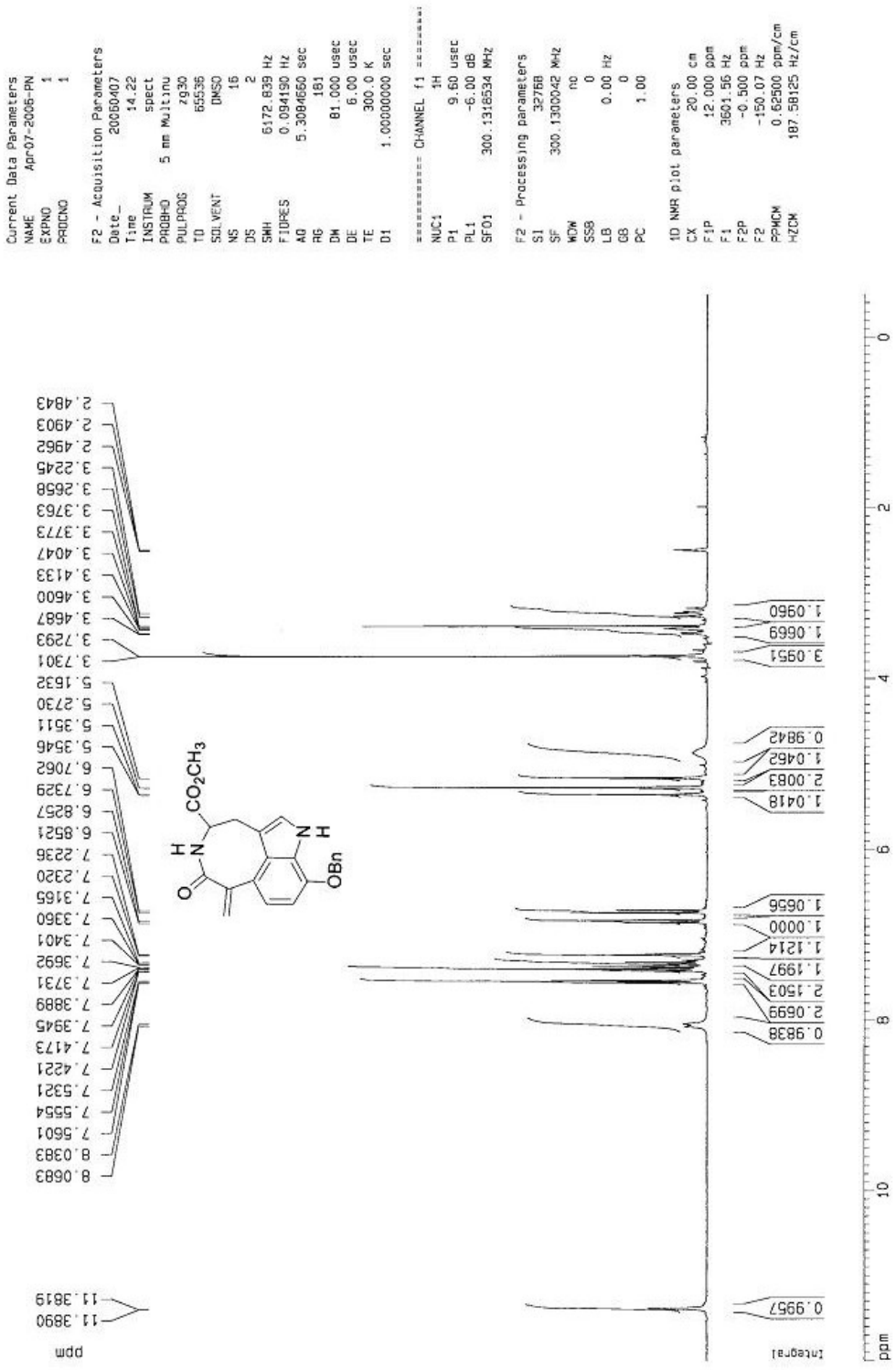
^{1}H NMR **13**


Current Data Parameters
NAME Apr04-2006-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060404
Time 17.52
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 64
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300069 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 4801.56 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 250.08125 Hz/cm
2.4899
2.4941
3.1745
3.2122
3.2453
3.4017
3.4242
3.4407
3.6834
3.7256
3.7304
4.8626
5.1238
5.3150
6.4897
6.4945
6.5090
6.5137
6.7488
6.7529
6.7680
6.7721
7.1819
7.9833
8.0014
9.8043
11.0932
0.2467
1.0727
1.5608
3.0974
0.9366
0.9962
1.0000
1.0007
0.9963
1.0144
0.9472
0.9621
0.9889
ppm
Integral

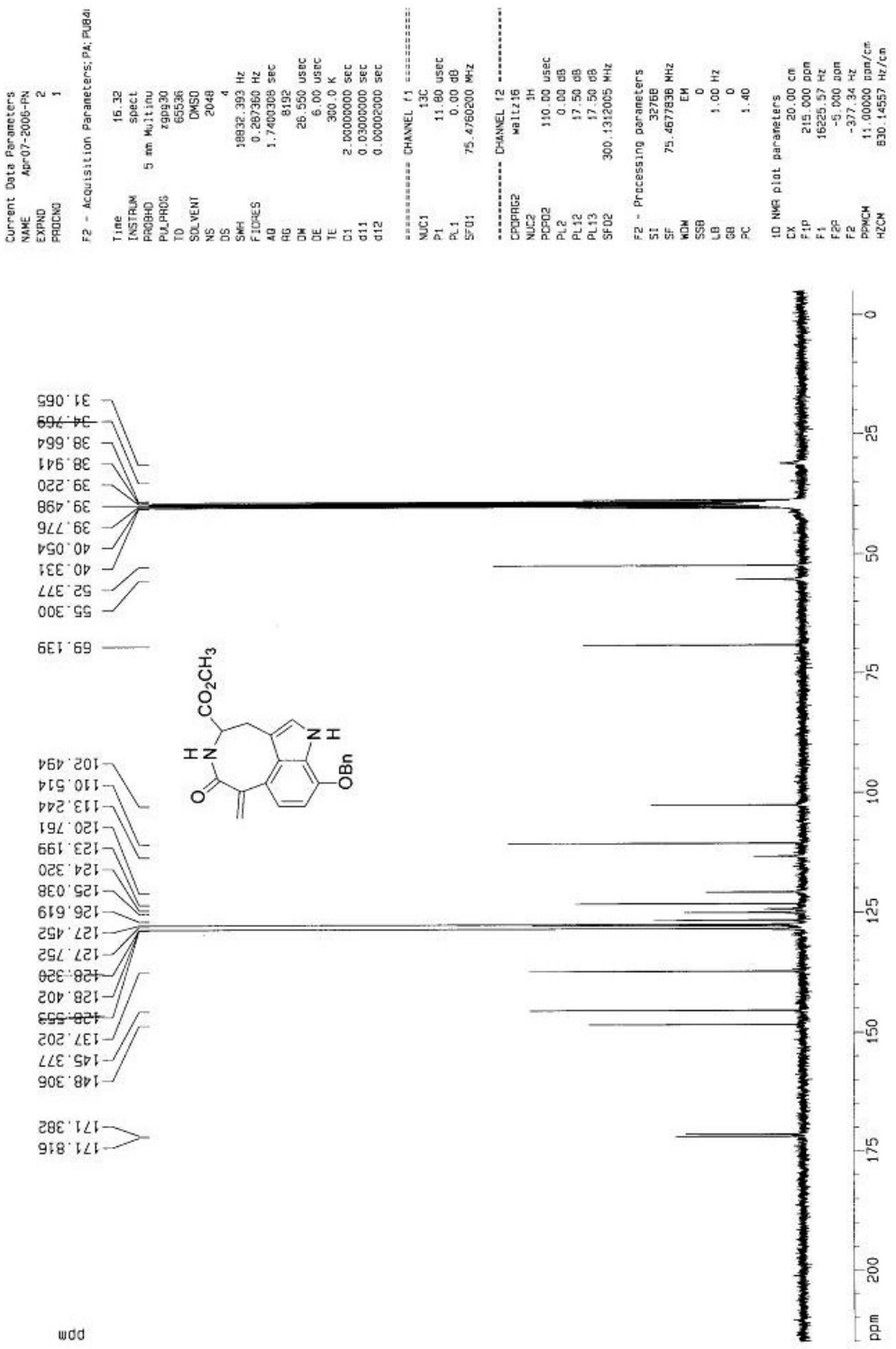
^{13}C NMR **13**


Current Data Parameters
NAME Apr05-2006-PN
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060406
Time 10.36
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 11288
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SF01 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SF02 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677792 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14557 Hz/cm
31.235
38.666
38.944
39.222
39.500
39.778
40.056
40.335
52.420
55.392
104.863
110.367
112.600
121.242
121.370
124.619
124.775
126.508
144.282
148.681
171.501
172.141
ppm
0
25
50
75
100
125
150
175
200

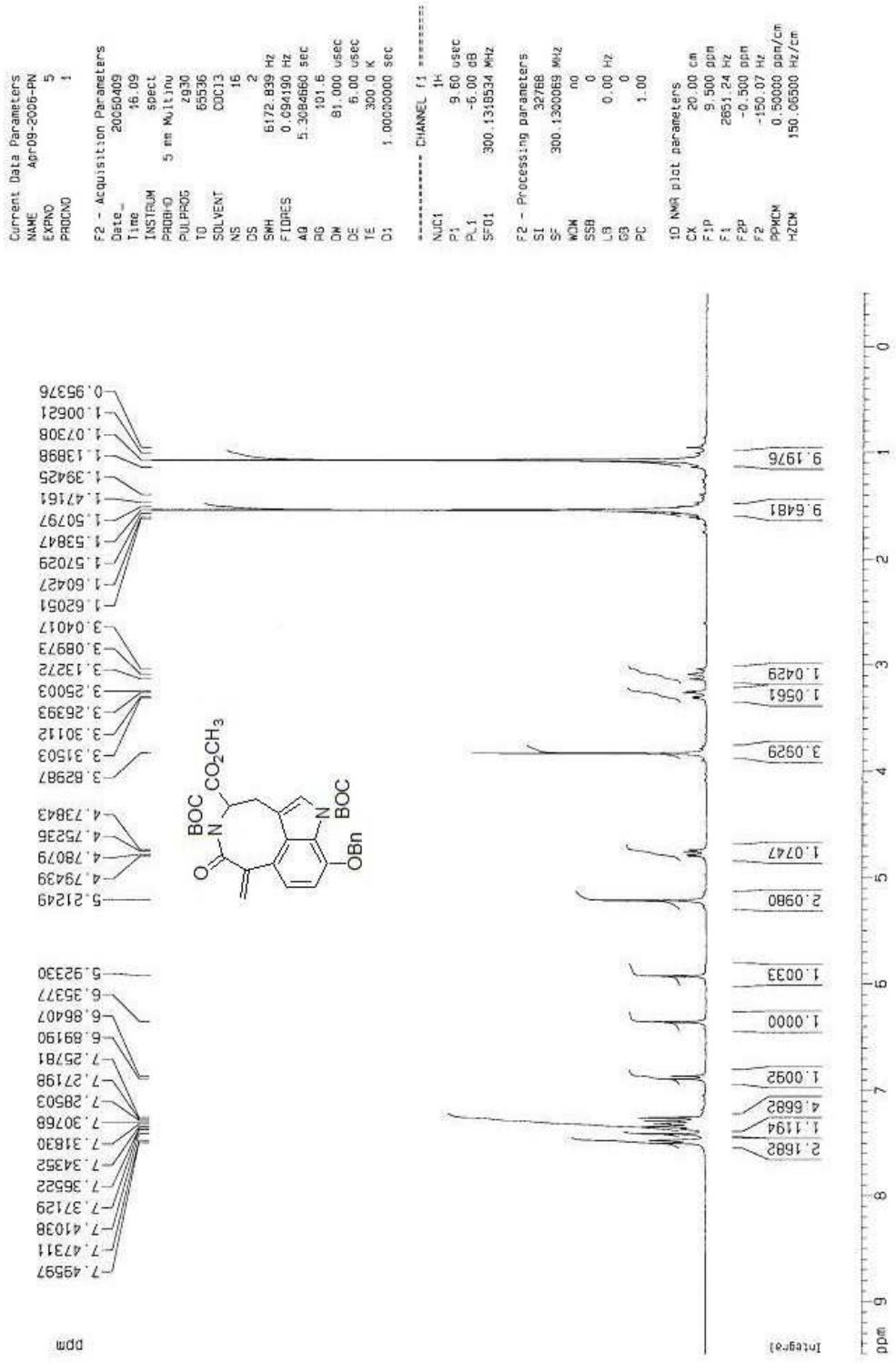
^{1}H NMR **SM5**


Current Data Parameters
NAME Apr07-2006-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060407
Time 14.22
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1316534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300042 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.58125 Hz/cm
11.3819
11.3890
8.0683
8.0383
7.5601
7.5554
7.5321
7.4221
7.4173
7.3945
7.3889
7.3731
7.3692
7.3401
7.3360
7.3165
7.2320
7.2236
6.8521
6.8257
6.7329
6.7062
5.3546
5.3511
5.2730
5.1532
3.7301
3.7293
3.4687
3.4600
3.4133
3.4047
3.3773
3.3763
3.2658
3.2245
2.4962
2.4903
2.4843
0.9957
0.9838
2.0699
2.1503
1.1997
1.2214
1.0000
1.0656
1.0418
2.0083
1.0462
0.9842
3.0951
1.0669
1.0960
ppm
Integral

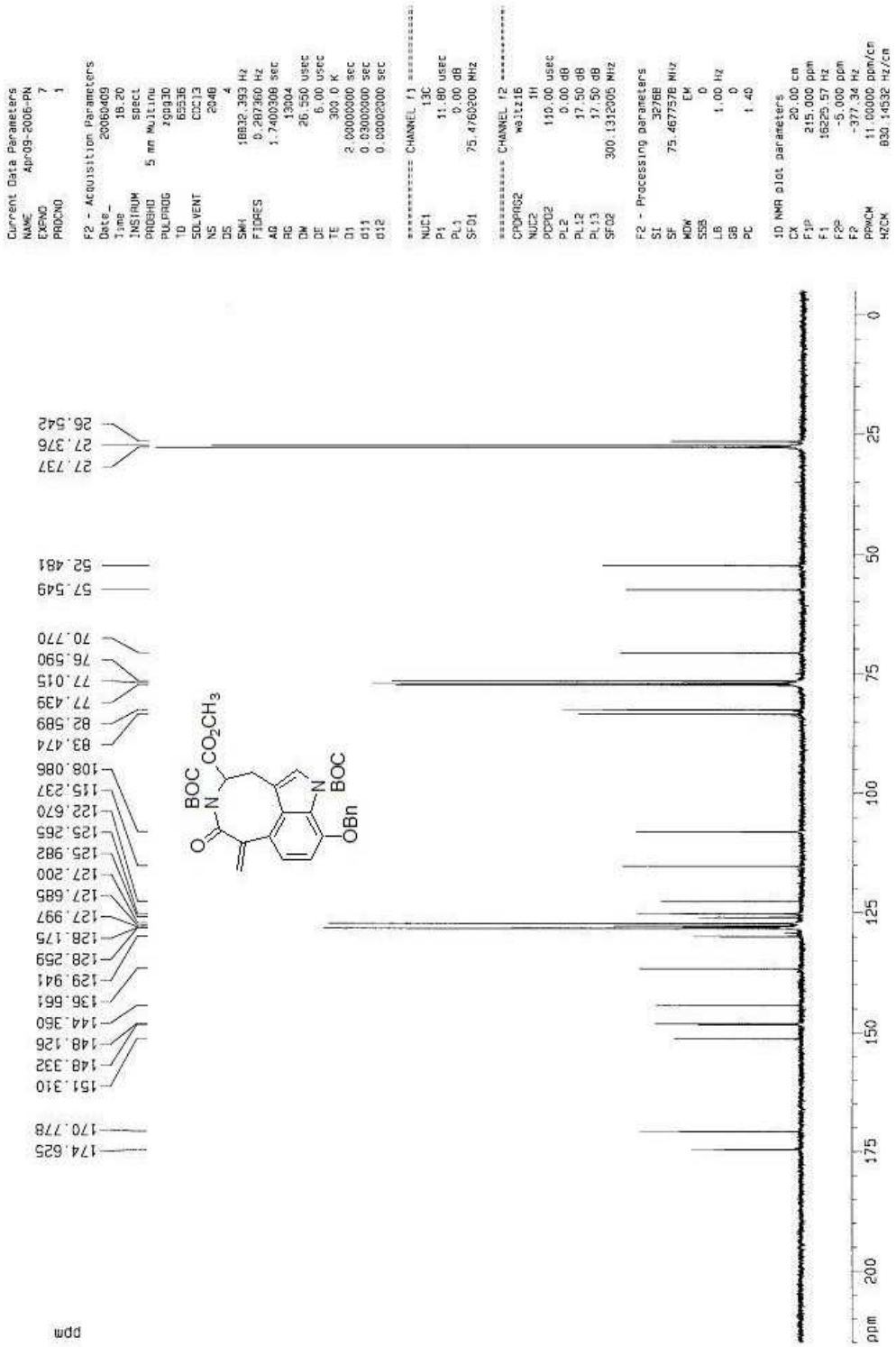
^{13}C NMR **SM5**


Current Data Parameters
NAME Apr07-2006-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters; PA; PUBA
Time 16.32
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2048
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 8192
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677836 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14557 Hz/cm
31.065
34.769
38.664
38.941
39.220
39.498
39.776
40.054
40.331
52.377
55.300
69.139
102.494
110.514
113.244
120.761
123.199
124.320
125.038
126.619
127.452
127.752
128.320
128.402
128.553
137.202
145.377
148.306
171.382
171.816
CO_2CH_3
OBn
ppm

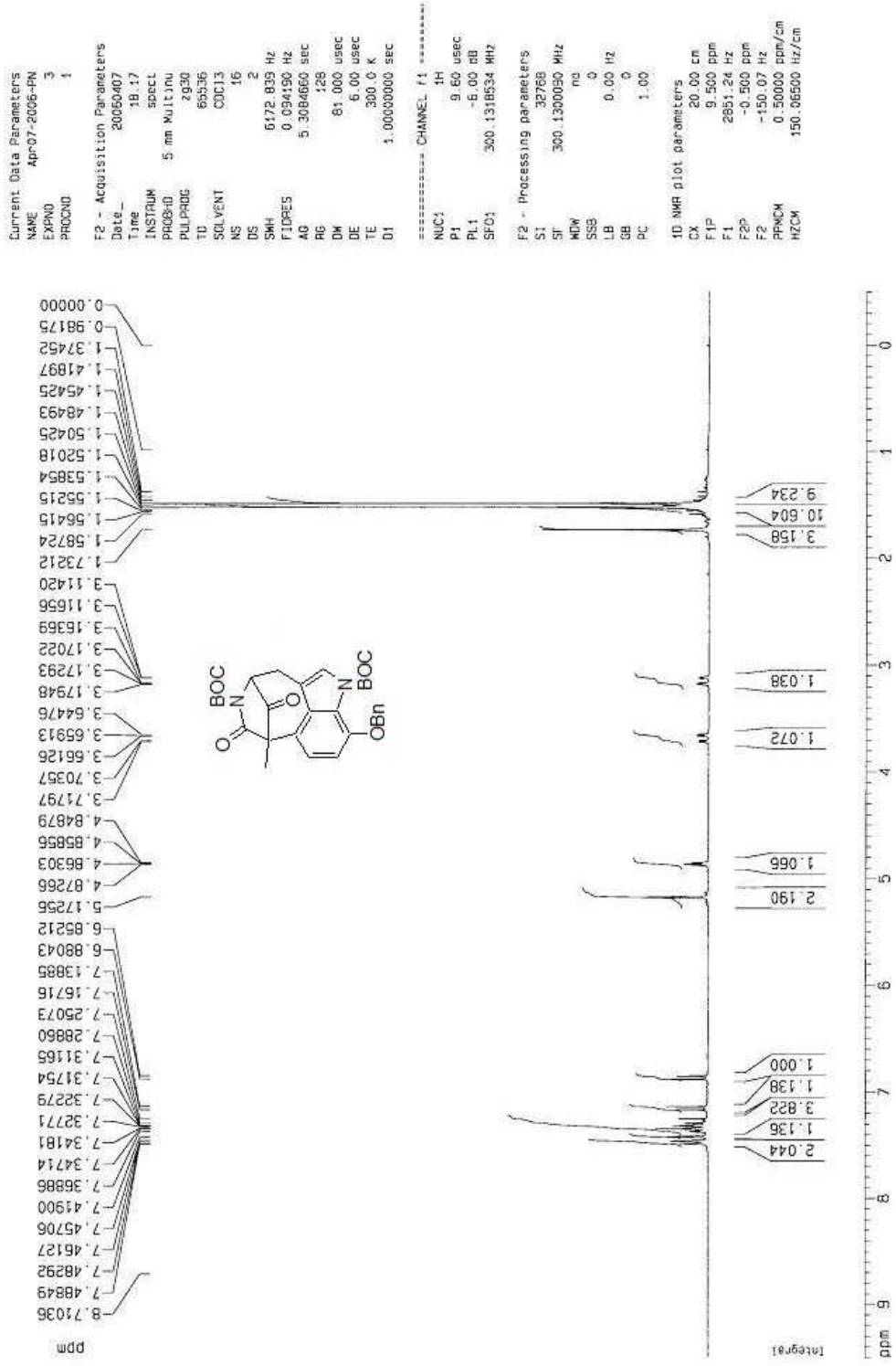
^{1}H NMR **SM6**


Current Data Parameters
NAME Apr09-2006-PN
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060409
Time 16.09
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 101.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
---------- CHANNEL f1 ----------
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300069 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm
BOC
CO2CH3
N
O
N
BOC
OBn
0.95376
1.00621
1.07308
1.13898
1.39425
1.47161
1.50797
1.53847
1.57029
1.60427
1.62051
3.04017
3.08973
3.13272
3.25003
3.26393
3.30112
3.31503
3.82987
4.73843
4.75236
4.78079
4.79439
5.21249
5.92330
6.35377
6.86407
6.89190
7.25781
7.27198
7.28503
7.30768
7.31830
7.34352
7.36522
7.37129
7.41038
7.47311
7.49597
9.1976
9.6481
1.0429
1.0561
3.0929
1.0747
2.0980
1.0033
1.0000
1.0092
4.6682
1.1194
2.1682
ppm
Integral

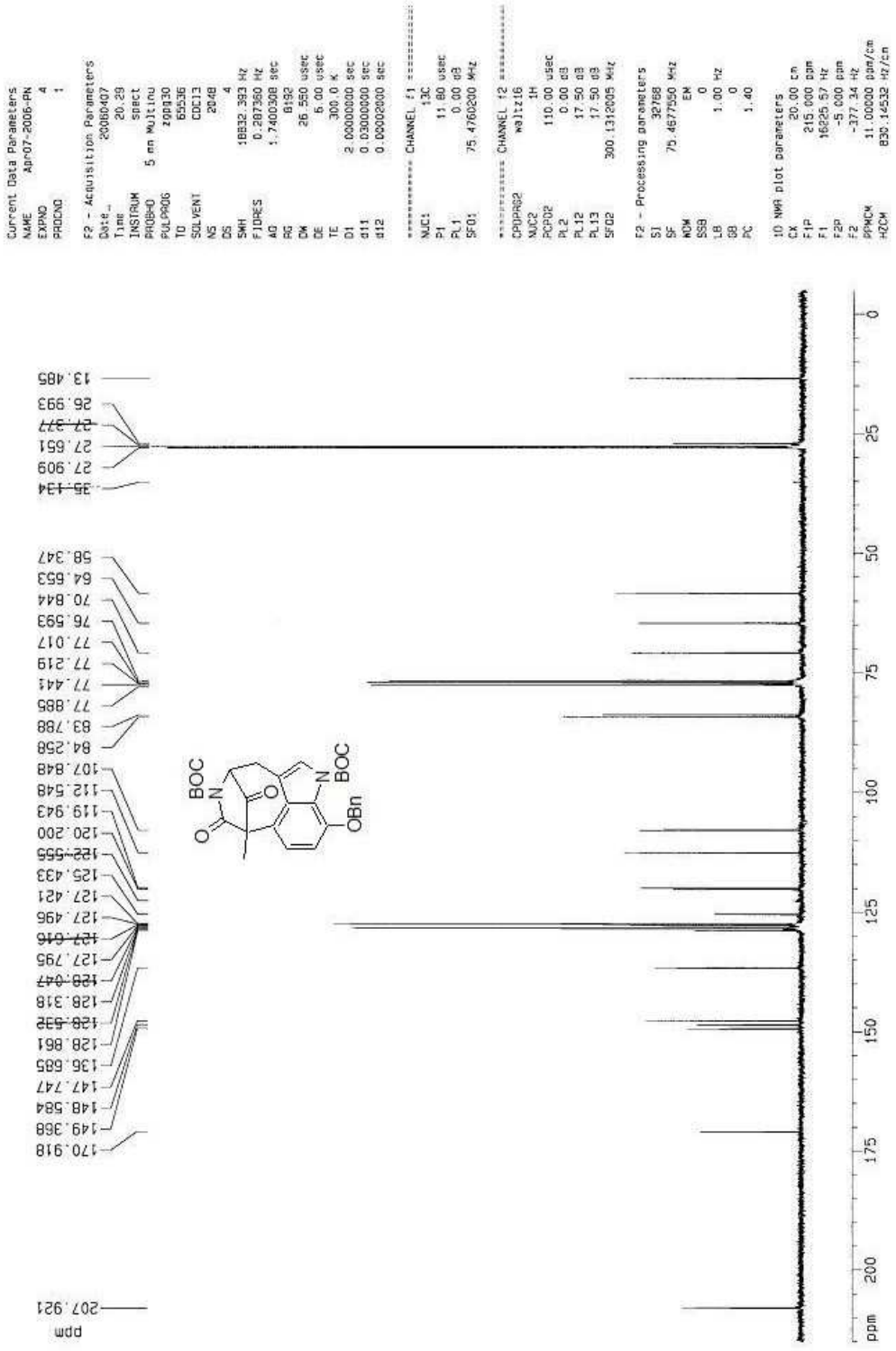
^{13}C NMR **SM6**


Current Data Parameters
NAME Apr09-2006-PN
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060409
Time 18.20
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400300 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677378 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14532 Hz/cm
26.542
27.376
27.737
52.481
57.549
70.770
76.590
77.015
77.439
82.589
83.474
108.086
115.237
122.670
125.265
125.982
127.200
127.685
127.997
128.175
128.259
129.941
136.661
144.360
148.126
148.332
151.310
170.778
174.625
BOC
CO2CH3
N
O
N
BOC
OBn
ppm
0
25
50
75
100
125
150
175
200

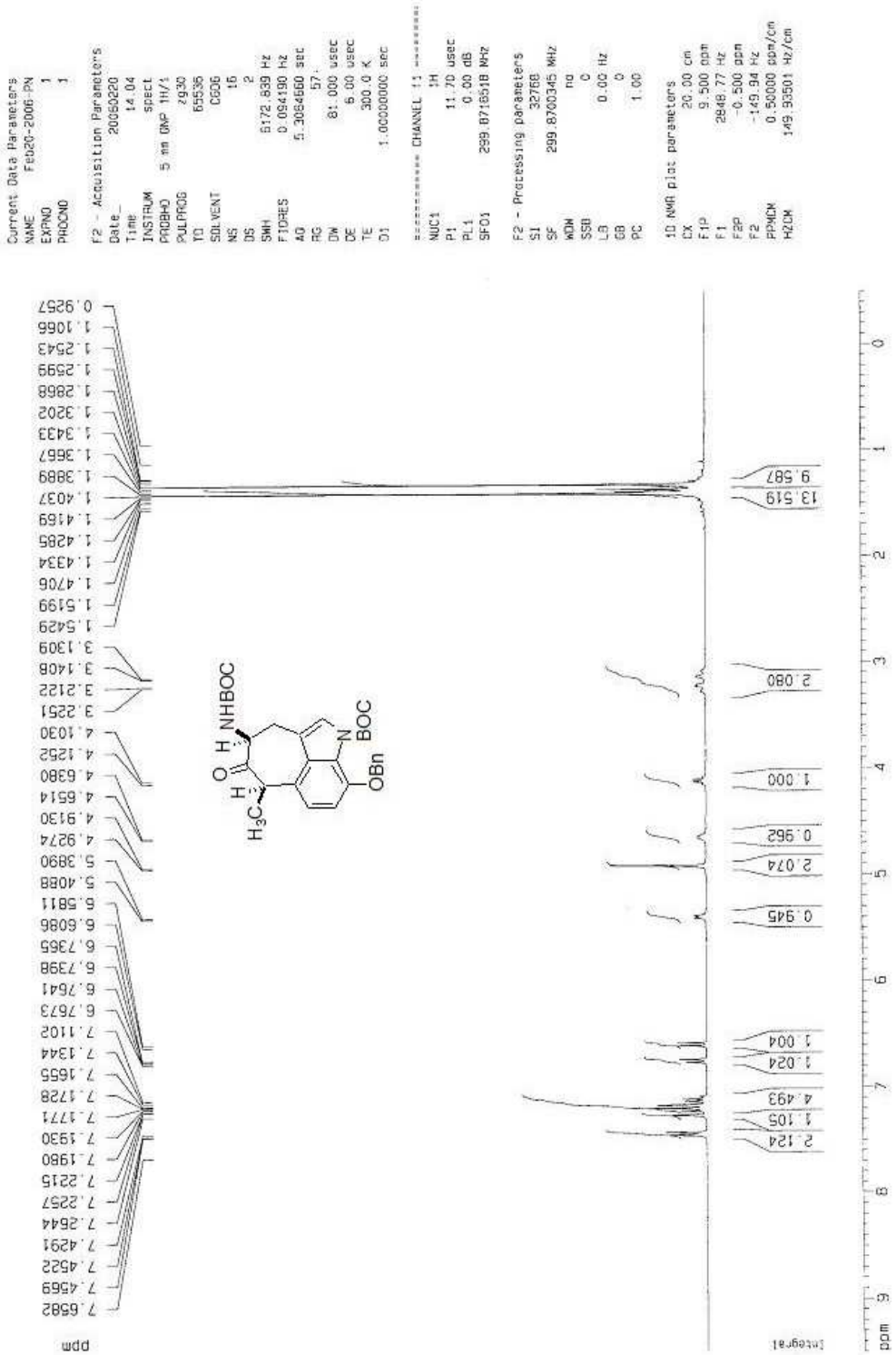
^{1}H NMR **15**


Current Data Parameters
NAME Apr07-2006-PN
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060407
Time 18.17
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300090 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm
BOC
N
O
O
N
BOC
OBn
9.234
10.604
3.158
1.038
1.072
1.065
2.190
1.000
1.138
3.822
1.136
2.044
integral
ppm

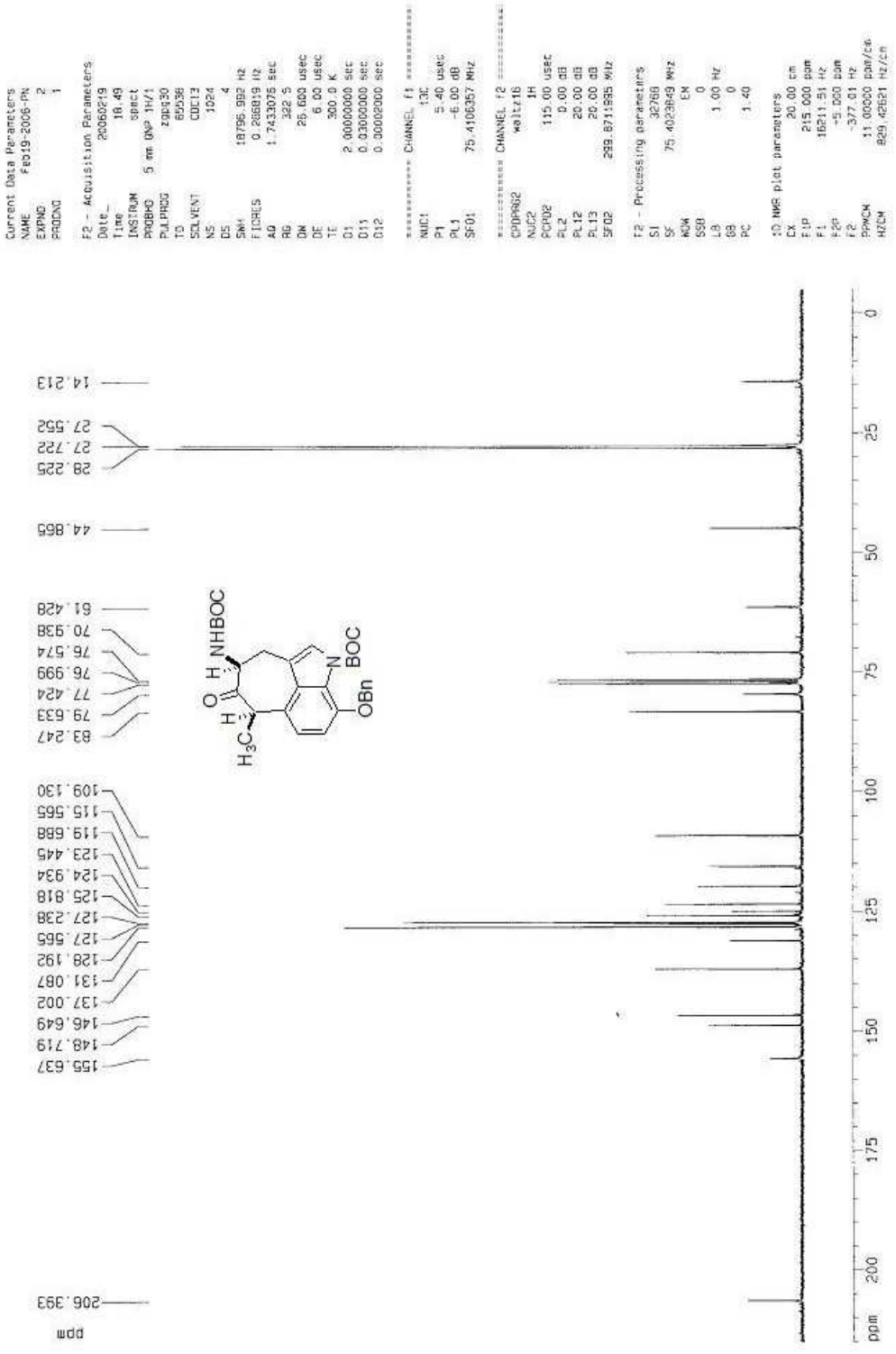
^{13}C NMR **15**


Current Data Parameters
NAME Apr07-2006-PN
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060407
Time 20.29
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 8192
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677950 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14532 Hz/cm
13.485
26.993
27.377
27.651
27.909
35.134
58.347
64.653
70.844
76.593
77.017
77.219
77.441
77.885
83.788
84.258
107.848
112.548
119.943
120.200
122.555
125.433
127.421
127.496
127.616
127.795
128.047
128.318
128.532
128.861
136.685
147.747
148.584
149.368
170.918
207.921
BOC
N
O
O
N
BOC
OBn
ppm
0
25
50
75
100
125
150
175
200

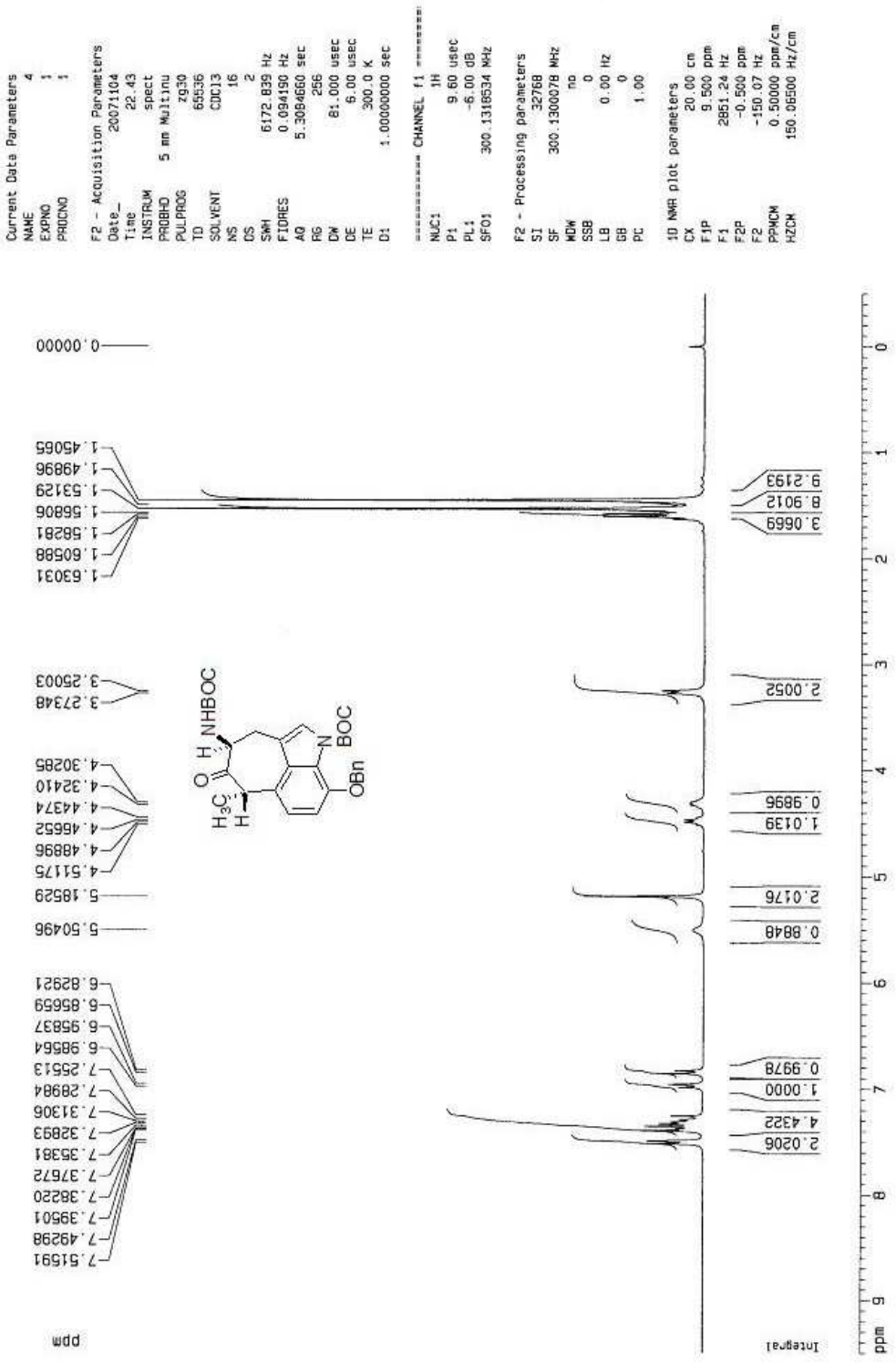
^{1}H NMR **16a**


Current Data Parameters
NAME Feb20-2006-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050220
Time 14.04
INSTRUM spect
PROBHD 5 mm BMP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 57
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.70 usec
PL1 0.00 dB
SFO1 299.8716518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700345 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2848.77 Hz
F2P -0.500 ppm
F2 -149.94 Hz
PPMCM 0.50000 ppm/cm
HZCM 149.93501 Hz/cm
NHBOC
OBn
BOC
ppm
Integral

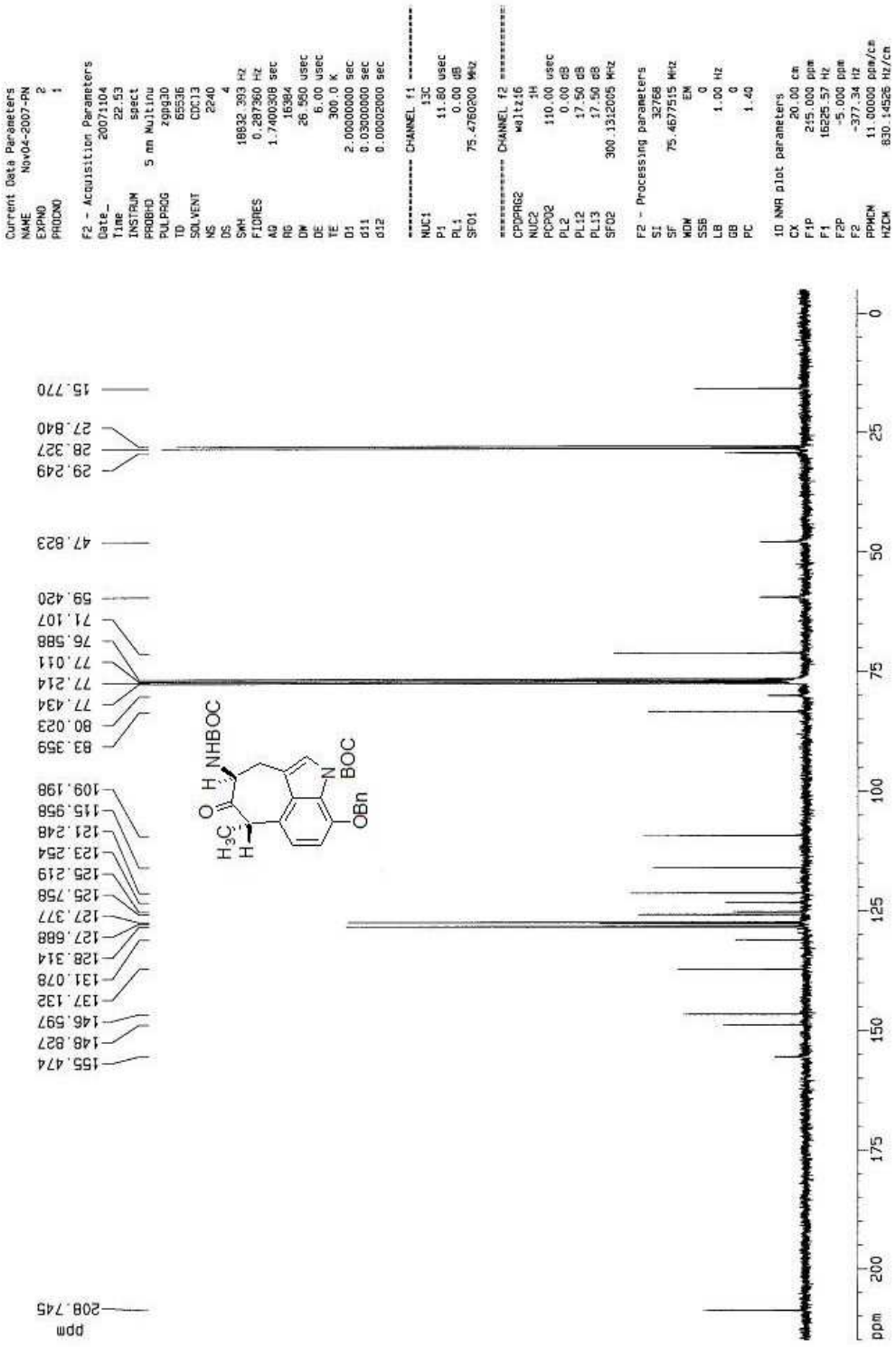
^{13}C NMR **16a**


14.213
27.552
27.722
28.225
44.865
61.428
70.938
76.574
76.999
77.424
79.633
83.247
109.130
115.565
119.688
123.445
124.934
125.818
127.238
127.565
128.192
131.087
137.002
146.649
148.719
155.637
206.393
ppm
NHBOC
BOC
OBn
H3C
0
25
50
75
100
125
150
175
200
ppm

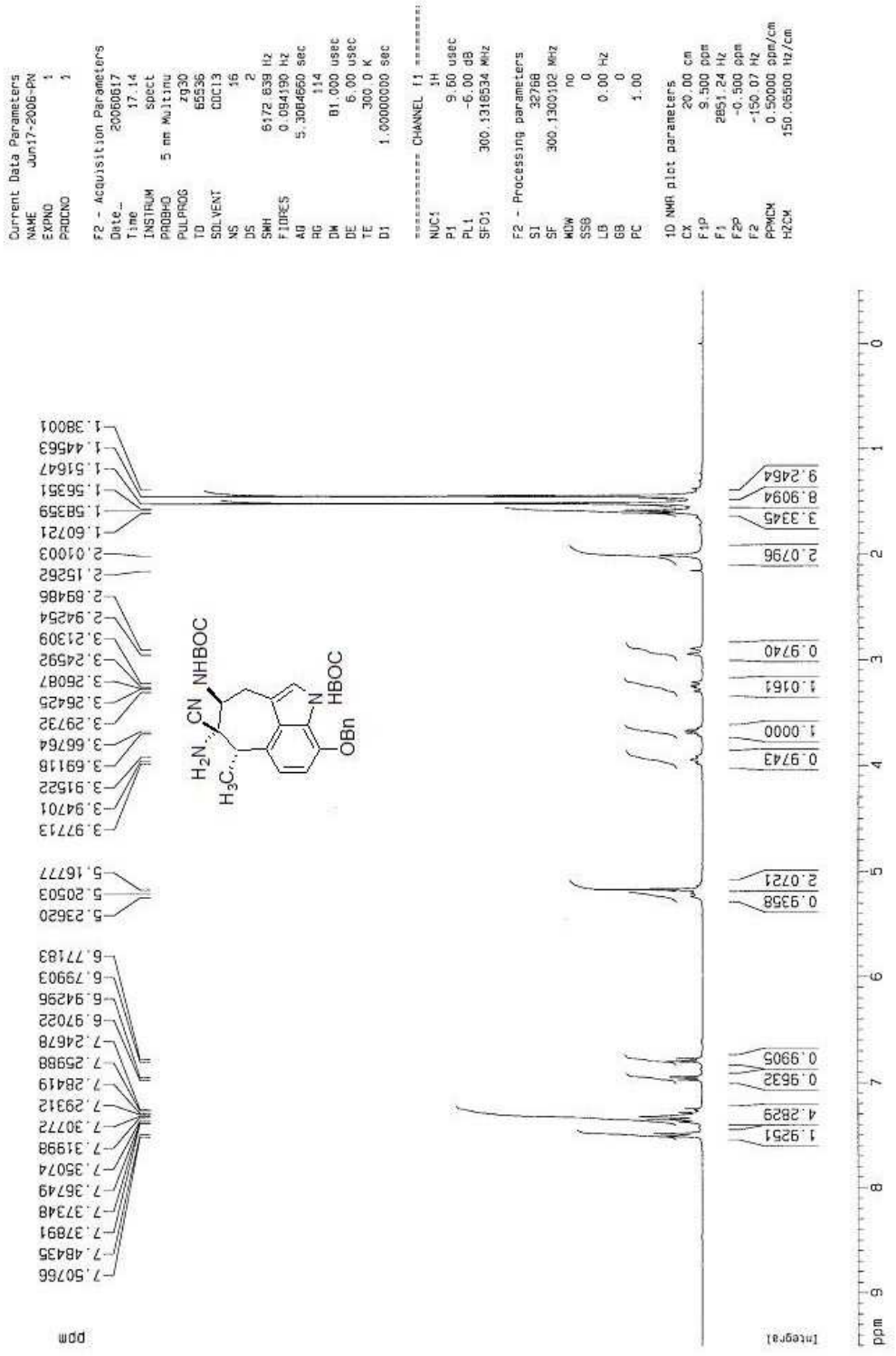
^{1}H NMR **16b**


Current Data Parameters
NAME 4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071104
Time 22.43
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300078 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm
0.00000
1.45065
1.48896
1.53129
1.56806
1.58281
1.60588
1.63031
3.25003
3.27348
4.30285
4.32410
4.43774
4.46652
4.48896
4.51175
5.18529
5.50496
6.82921
6.85659
6.95837
6.98564
7.25513
7.28984
7.31306
7.32893
7.35381
7.37672
7.38220
7.39501
7.49298
7.51591
9.2193
8.9012
3.0669
2.0052
0.9896
1.0139
2.0176
0.8848
0.9978
1.0000
4.4322
2.0206
NHBOC
BOC
OBn
ppm
Integral

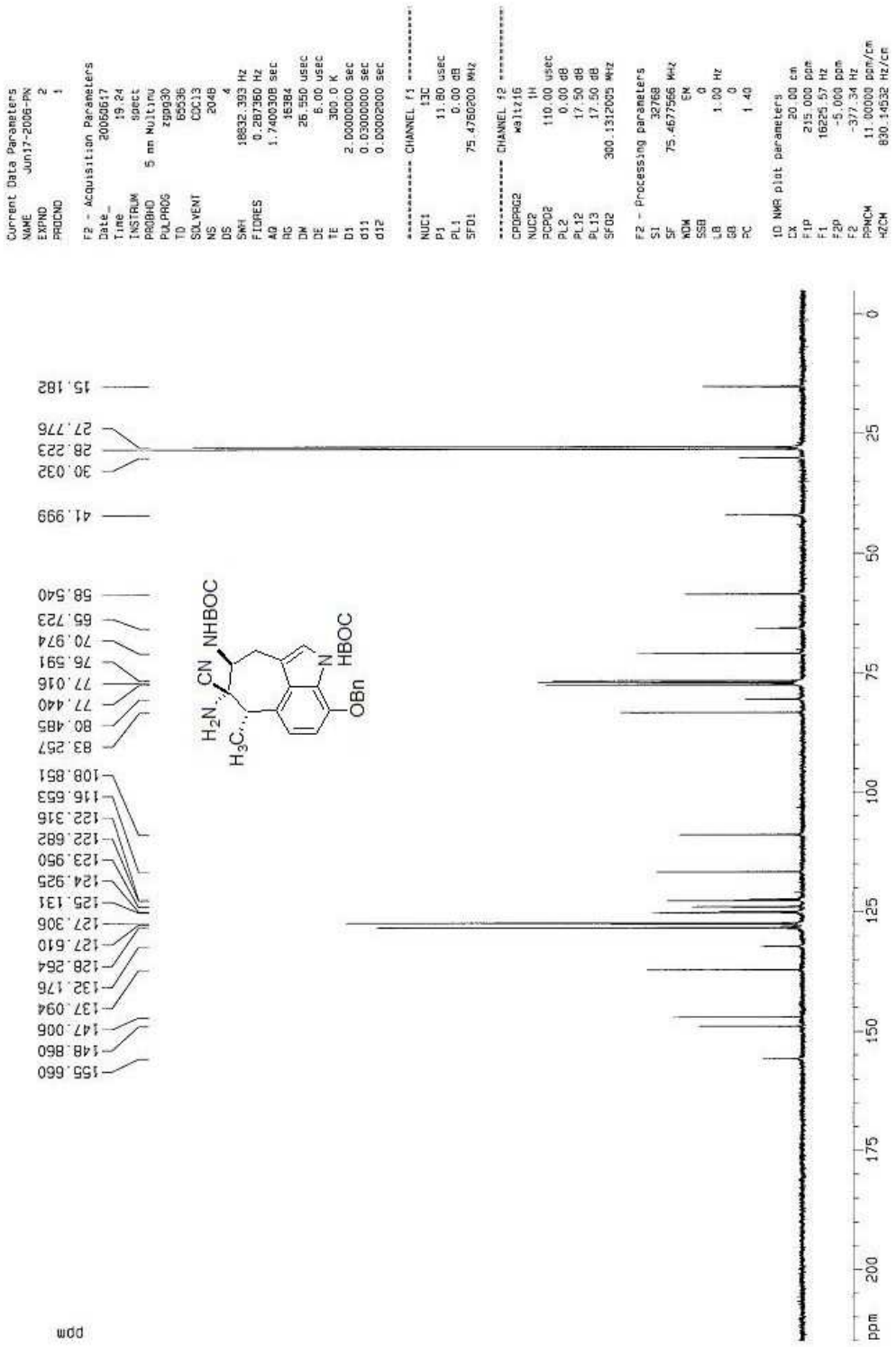
^{13}C NMR **16b**


Current Data Parameters
NAME Nov04-2007-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071104
Time 22.53
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2240
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677515 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14526 Hz/cm
15.770
27.840
28.327
29.249
47.823
59.420
71.107
76.588
77.011
77.214
77.434
80.023
83.359
109.198
115.958
121.248
123.254
125.219
125.758
127.377
127.688
128.314
131.078
137.132
146.597
148.827
155.474
208.745
ppm
NHBOC
BOC
OBn
0
25
50
75
100
125
150
175
200
ppm

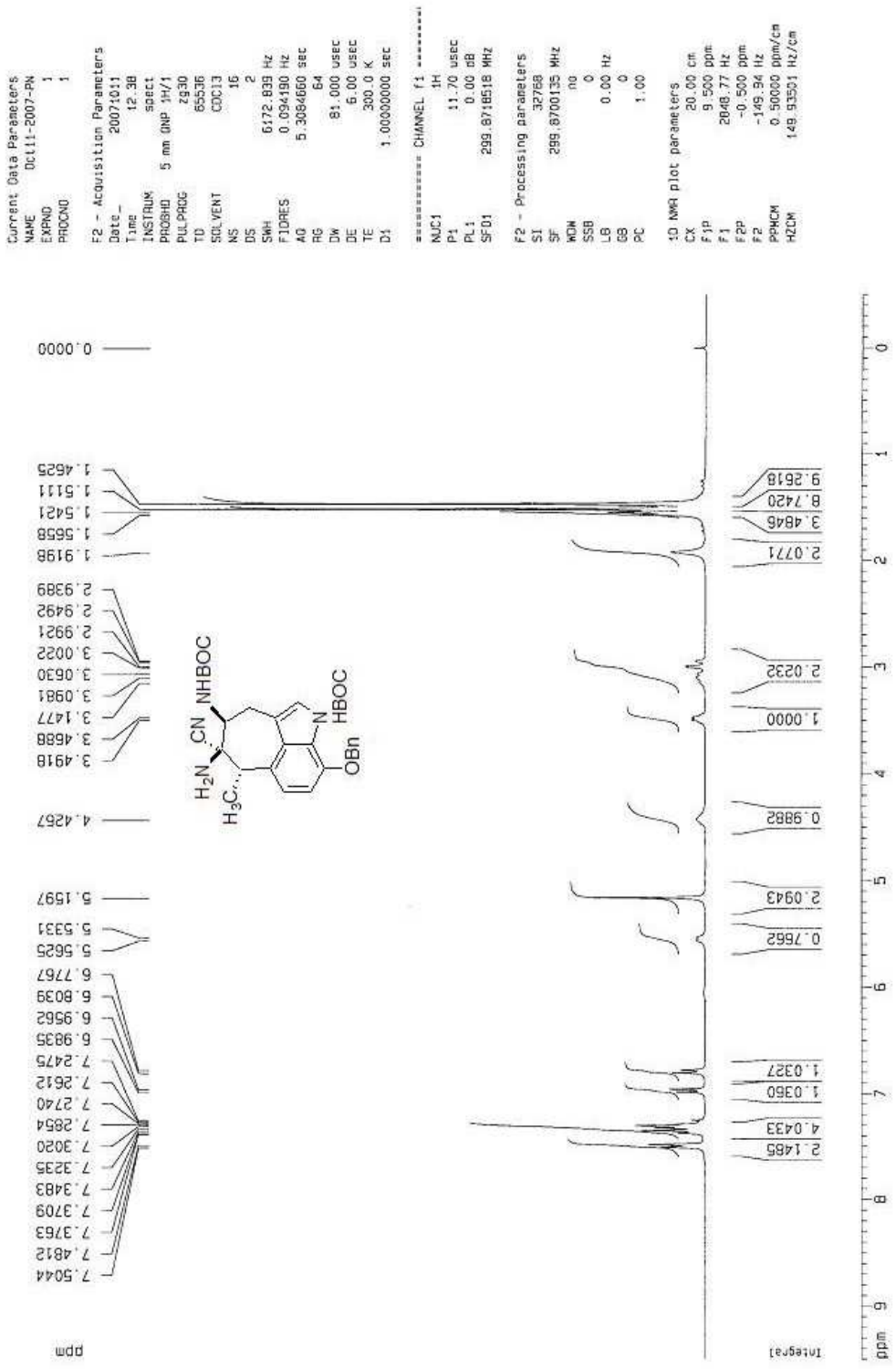
^{1}H NMR **17a**


Current Data Parameters
NAME Jun17-2006-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060617
Time 17.14
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084650 sec
RG 114
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1316534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300102 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm
NHBOC
CN
H_2N
H_3C
N
HBOC
OBn
ppm
Integral

^{13}C NMR **17a**


Current Data Parameters
NAME Jun17-2006-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060617
Time 19.24
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
---------- CHANNEL f1 ----------
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
---------- CHANNEL f2 ----------
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14532 Hz/cm
15.182
27.776
28.223
30.032
41.999
58.540
65.723
70.974
76.591
77.016
77.440
80.485
83.257
108.851
116.653
122.316
122.682
123.950
124.925
125.131
127.306
127.610
128.264
132.176
137.094
147.006
148.860
155.660
NHBOC
CN
H_2N
H_3C
N
HBOC
OBn
ppm
0
25
50
75
100
125
150
175
200
ppm

^{1}H NMR **17b**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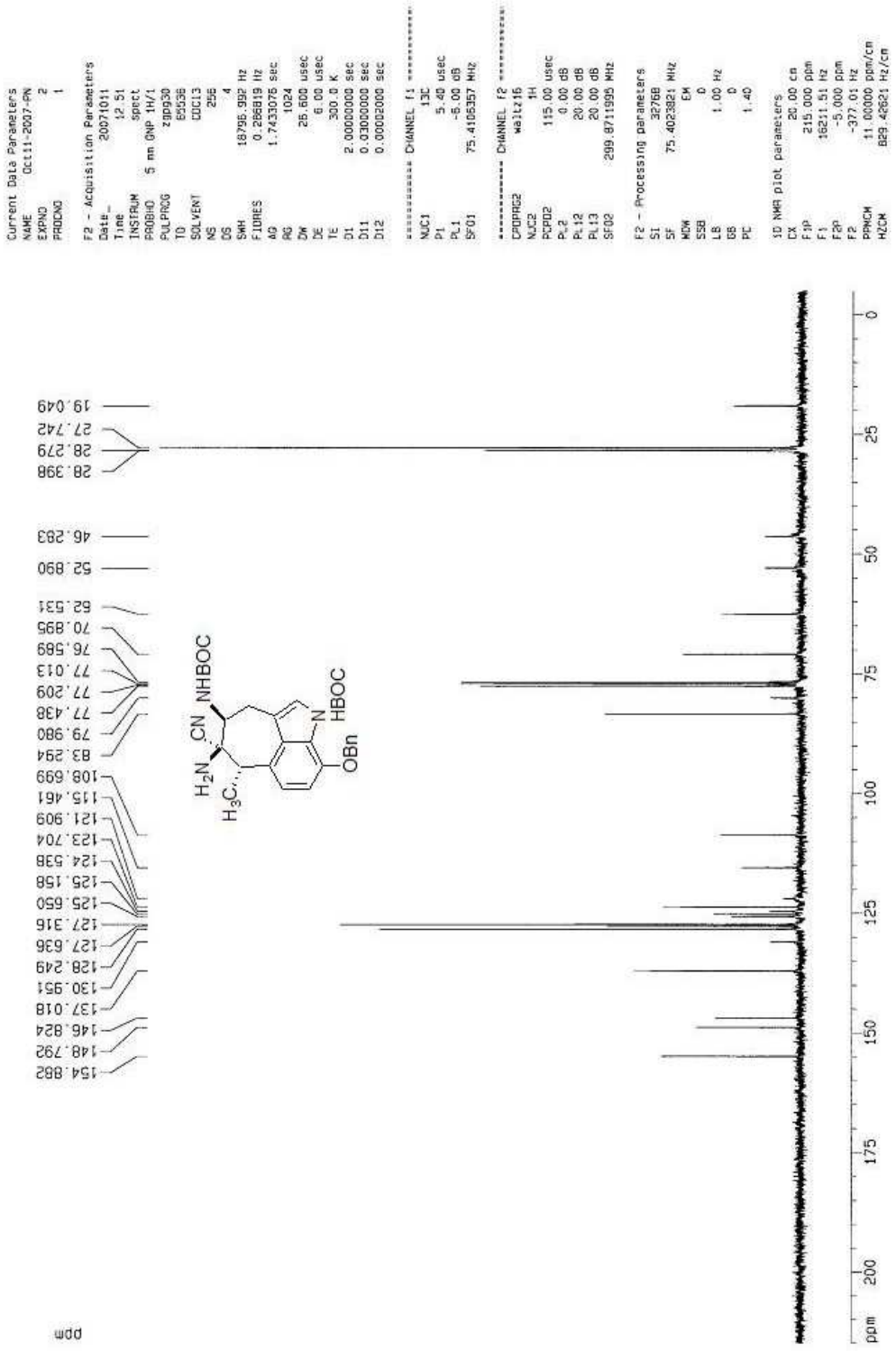
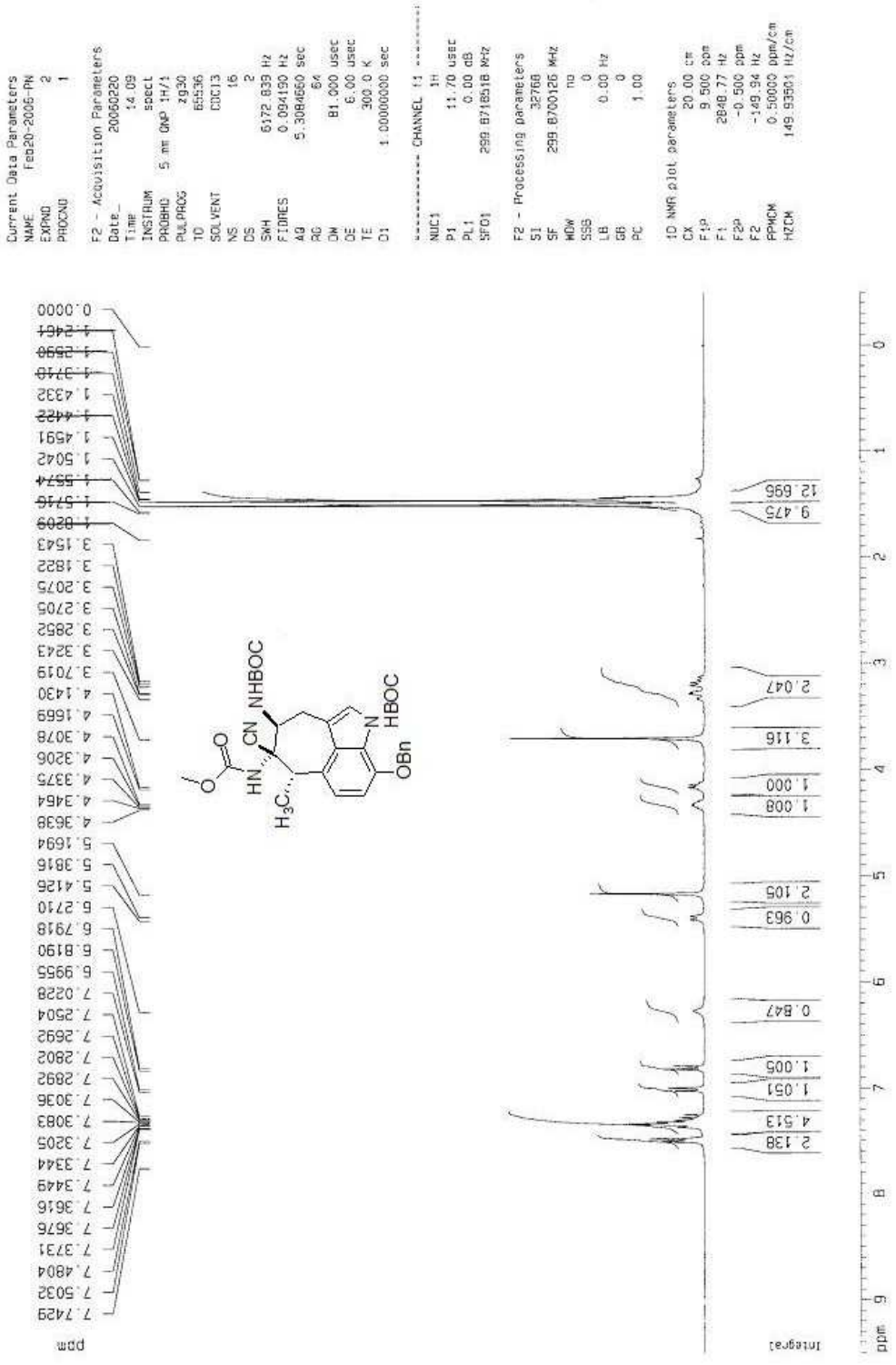
NAME Oct11-2007-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071011
Time 12.38
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 64
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.70 usec
PL1 0.00 dB
SFO1 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700135 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
FIP 9.500 ppm
F1 2848.77 Hz
F2P -0.500 ppm
F2 -149.34 Hz
PPMCM 0.50000 ppm/cm
HZCM 149.93501 Hz/cm
NHBOC
CN
H_2N
H_3C
N
HBOC
OBn
ppm
Integral

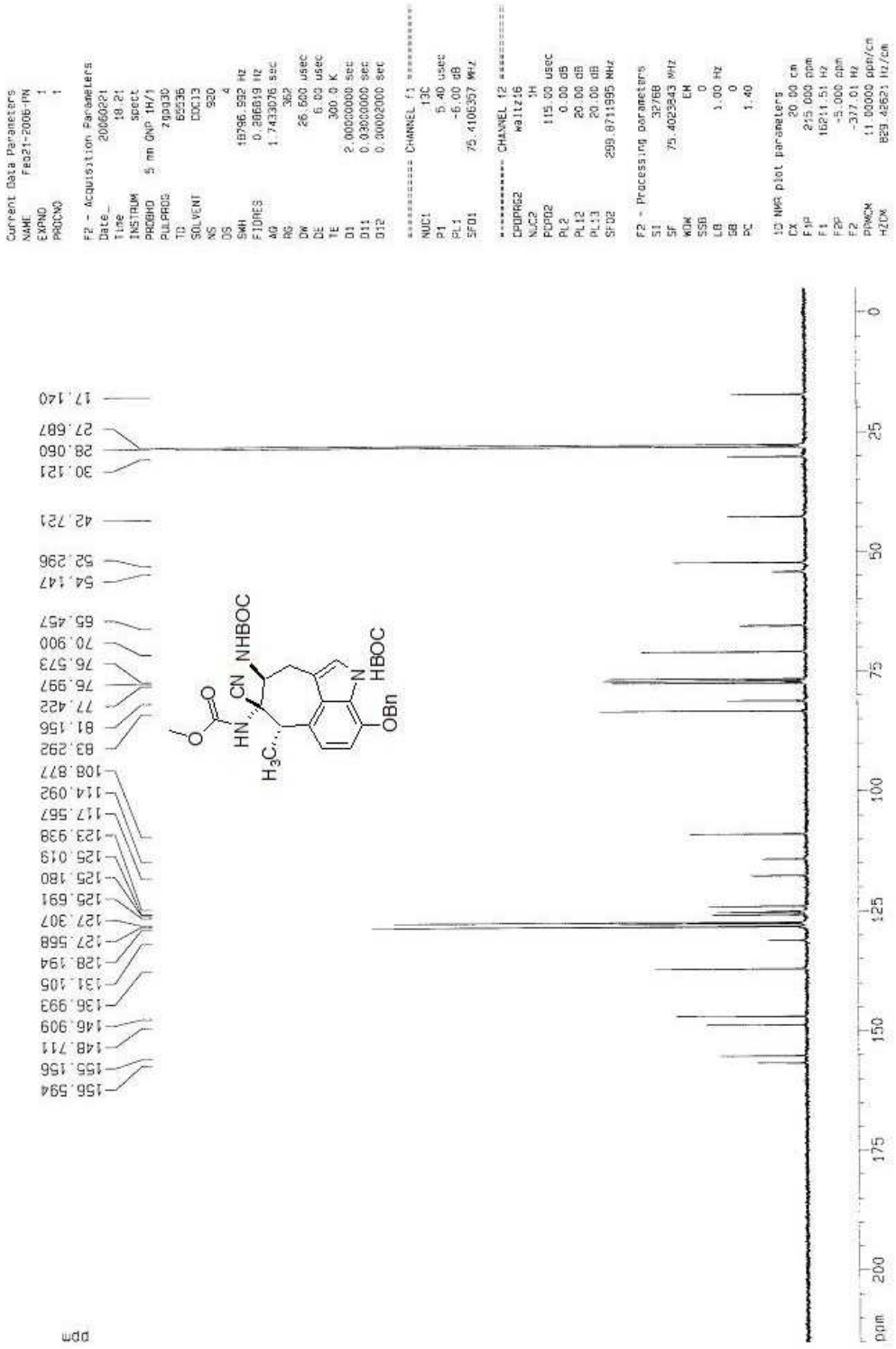
^{13}C NMR **17b**


Current Data Parameters
NAME Oct11-2007-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071011
Time 12.51
INSTRUM spect
PROBHD 5 mm GNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433075 sec
RG 1024
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.40 usec
PL1 -5.00 dB
SF01 75.4106357 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SF02 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4023821 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16211.51 Hz
F2P -5.000 ppm
F2 -377.01 Hz
PPMCM 11.00000 ppm/cm
HZCM 829.42621 Hz/cm
19.049
27.742
28.279
28.398
46.283
52.890
62.531
70.895
76.589
77.013
77.209
77.438
79.980
83.294
108.699
115.461
121.909
123.704
124.538
125.158
125.650
127.316
127.636
128.249
130.951
137.018
146.824
148.792
154.882
NHBOC
CN
HBOC
OBn
H_2N
H_3C
ppm
0
25
50
75
100
125
150
175
200
ppm

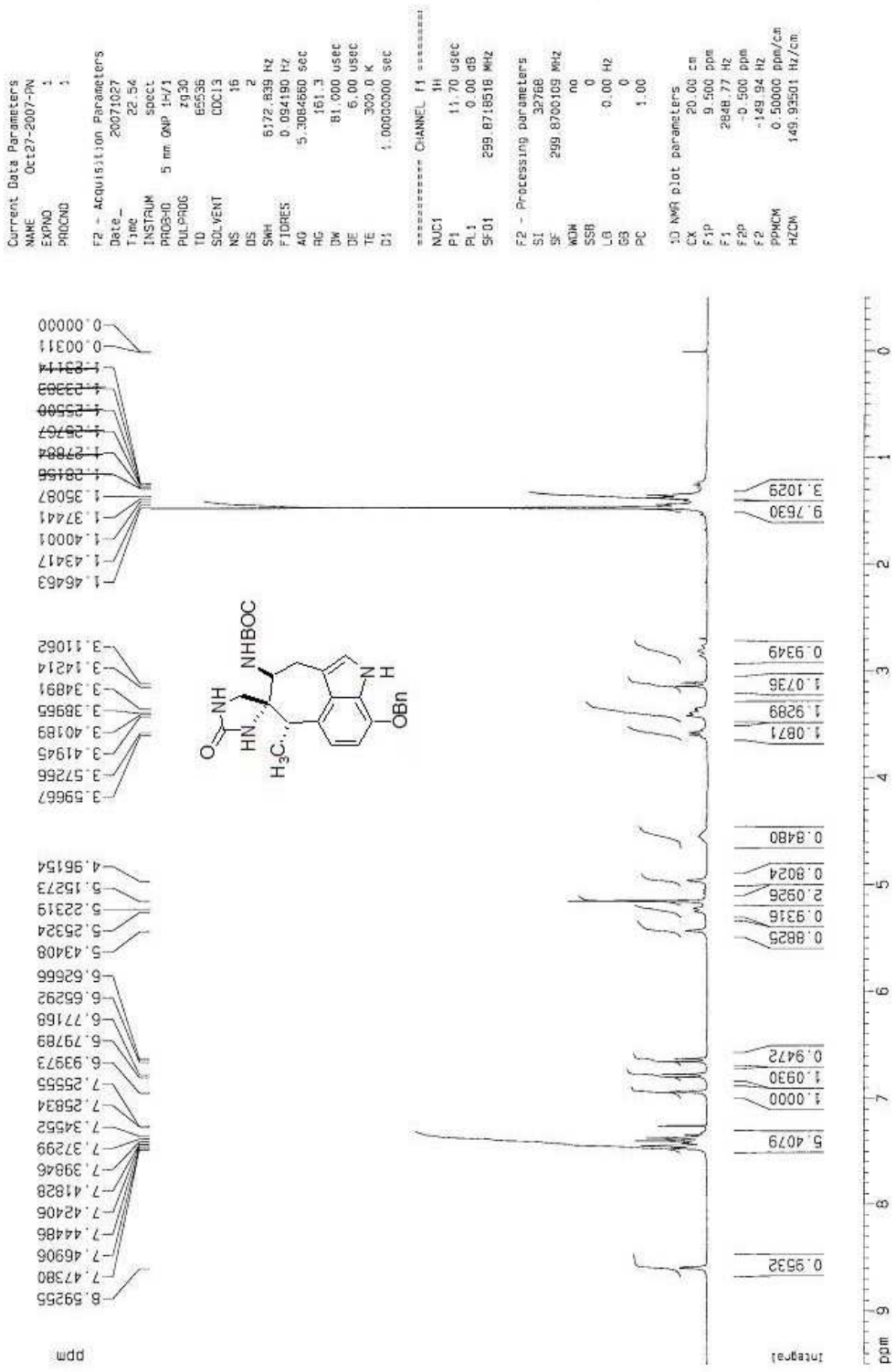
^{1}H NMR **SM7**


NHBOC
CN
HBOC
OBn
HN
O
O
H_3C
12.696
9.475
2.047
3.116
1.000
1.008
0.963
2.105
0.847
1.005
1.051
4.513
2.138
ppm

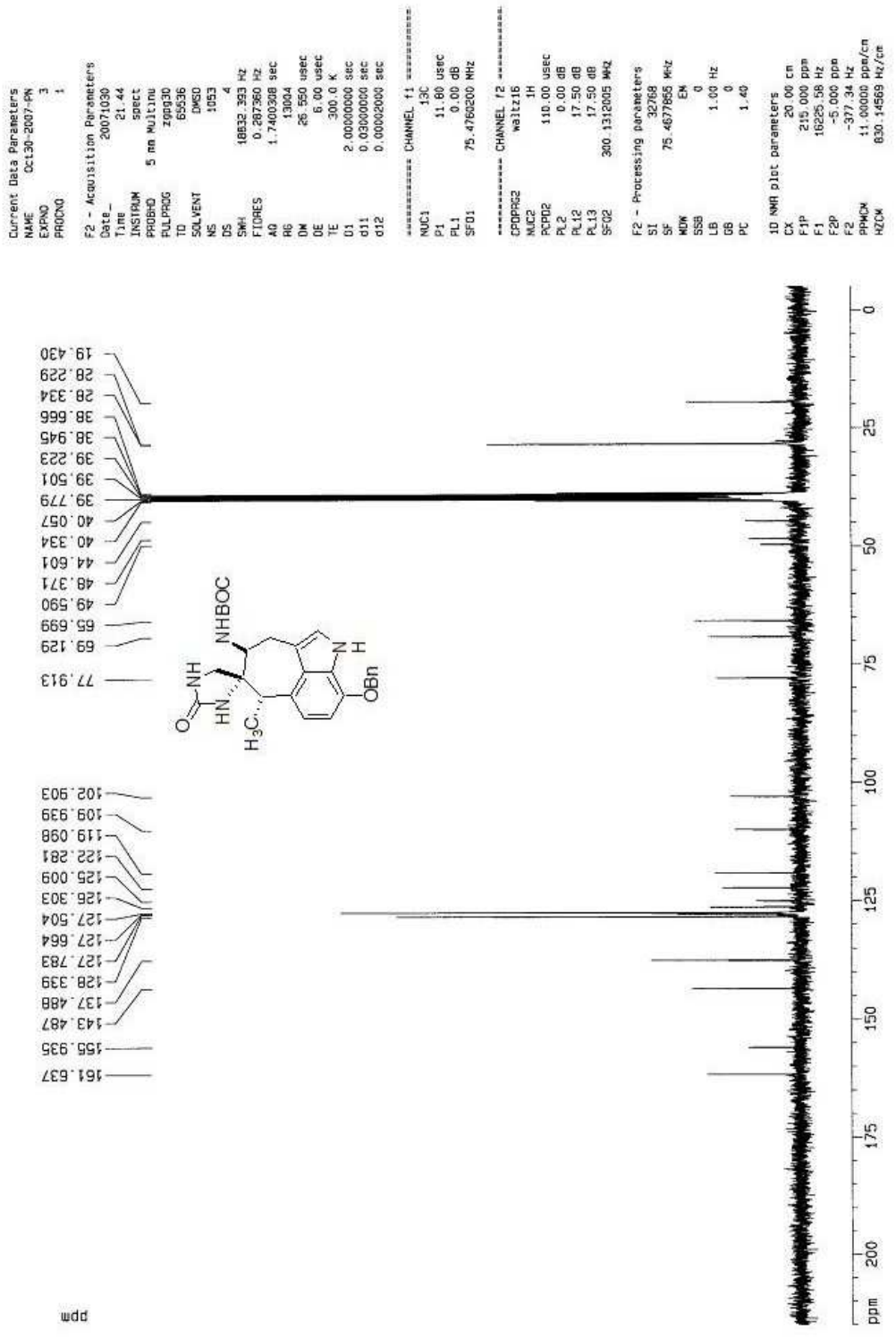
^{13}C NMR **SM7**


Current Data Parameters
NAME Fe221-2006-1PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060221
Time 18.21
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 930
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 362
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.40 usec
PL1 -6.00 dB
SFO1 75.4106357 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4029843 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
FP 215.000 ppm
F1 16211.51 Hz
FP -5.000 ppm
F2 -377.01 Hz
PPMCM 11.00000 ppm/cm
HZCM 829.48621 Hz/cm
17.140
27.687
28.060
30.121
42.721
52.296
54.147
65.457
70.900
76.573
76.997
77.422
81.156
83.292
108.877
114.092
117.567
123.938
125.019
125.180
125.691
127.307
127.568
128.194
131.105
136.993
146.909
148.711
155.156
156.594
NHBOC
CN
HN
O
O
H_3C
N
HBOC
OBn
ppm
0
25
50
75
100
125
150
175
200

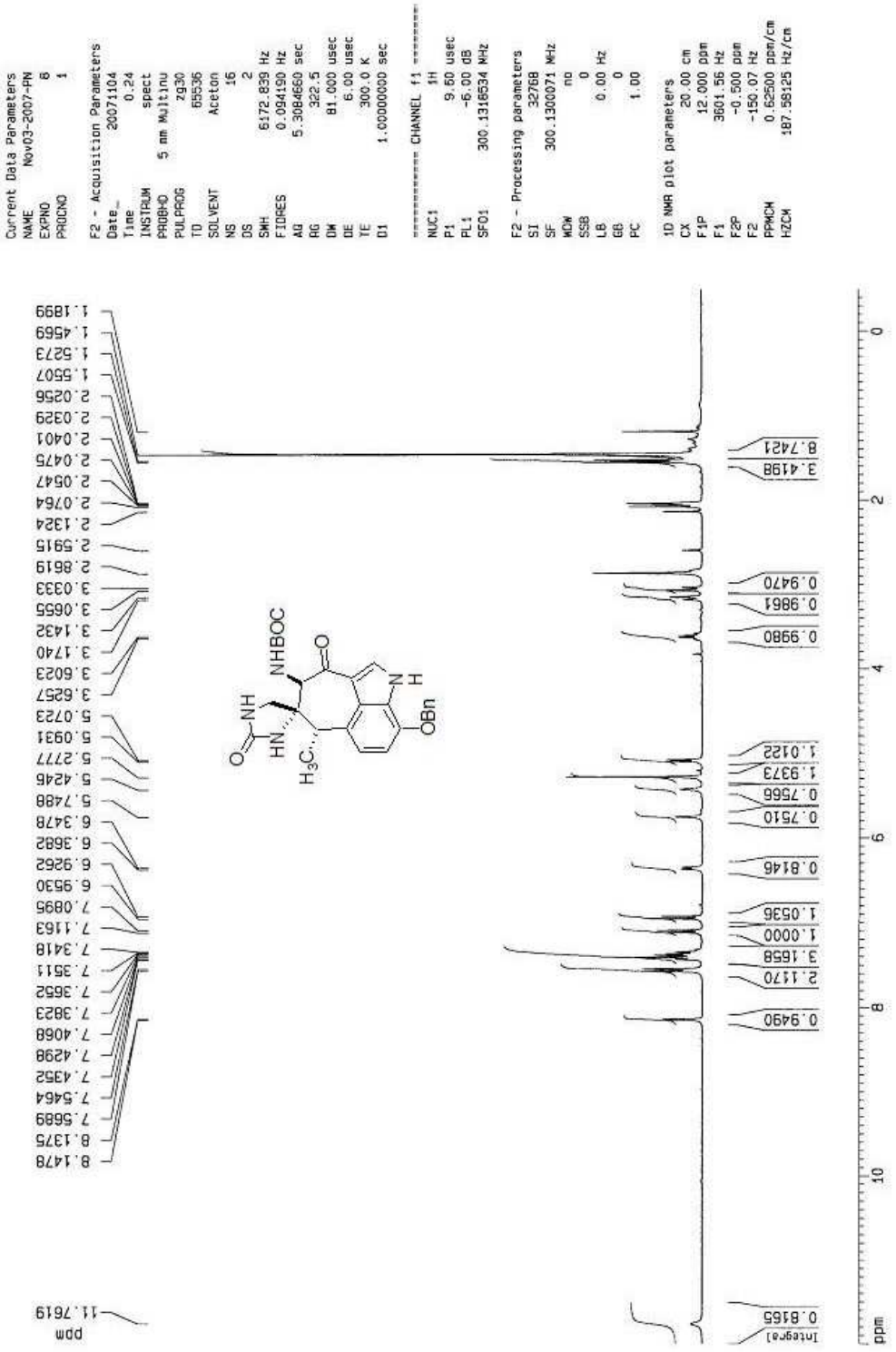
^{1}H NMR **18**



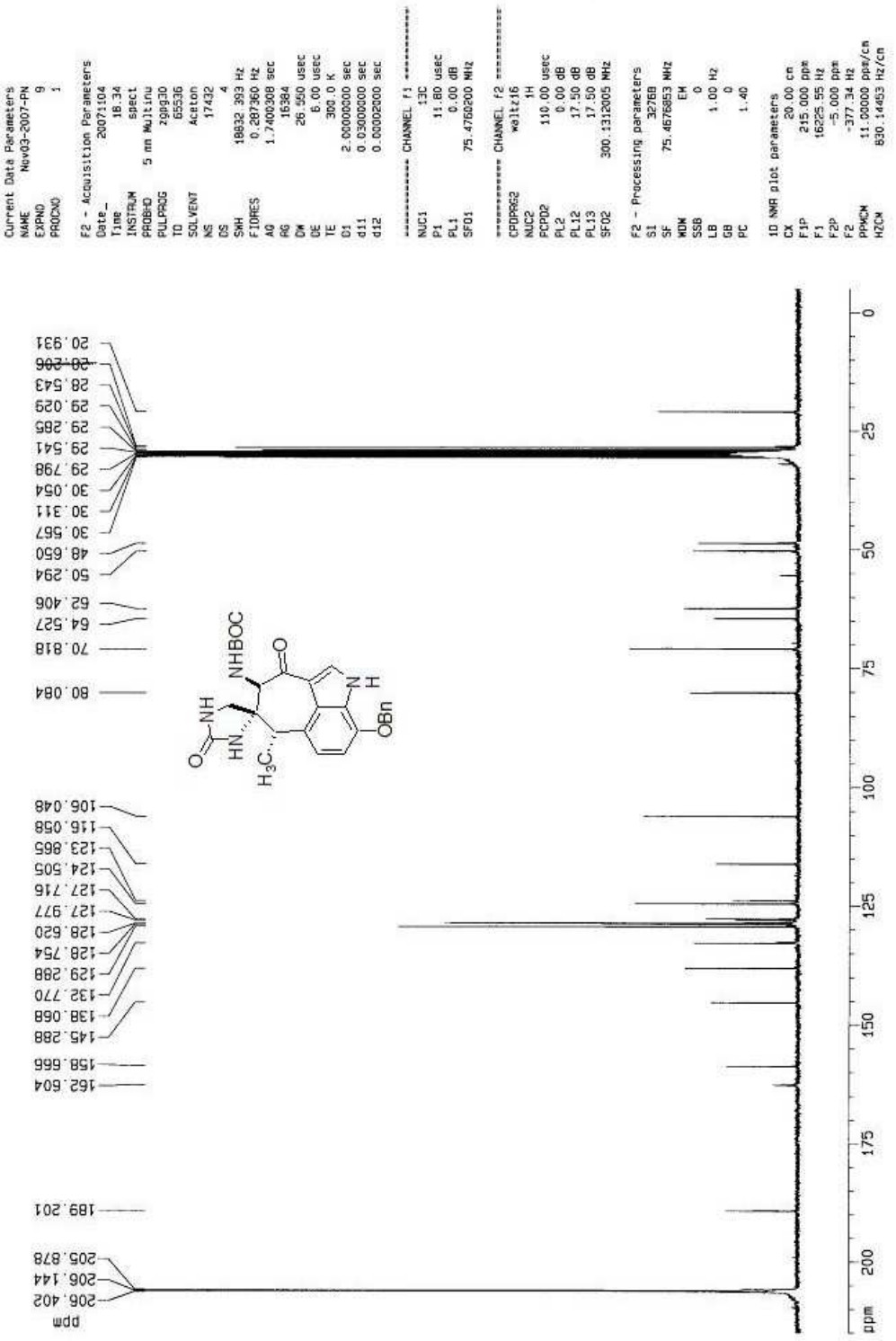
^{13}C NMR **18**


Current Data Parameters
NAME Oct30-2007-PN
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071030
Time 21.44
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1053
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677865 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.58 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14569 Hz/cm
NHBOC
OBn
ppm

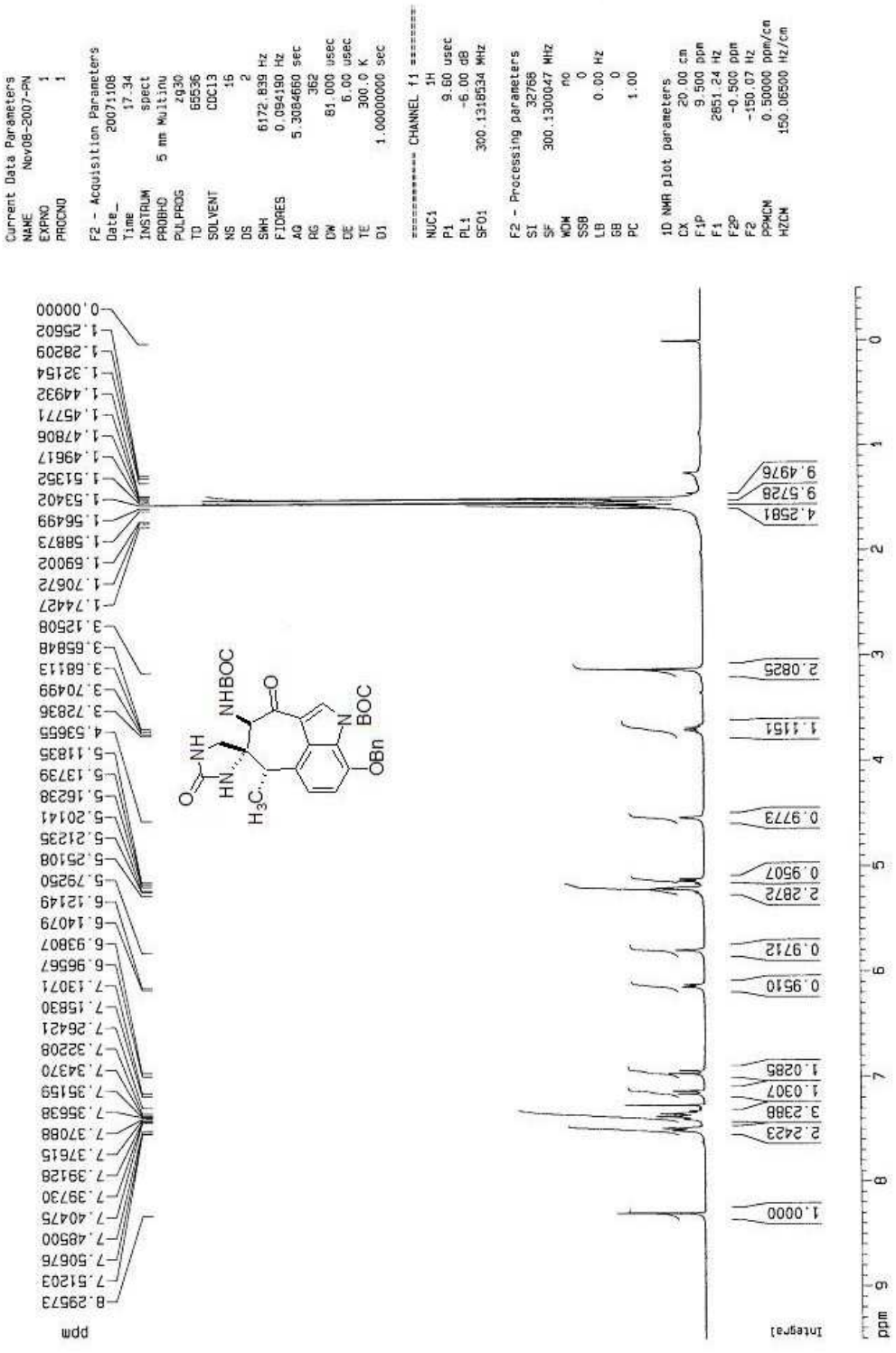
^{1}H NMR **SM8**


Current Data Parameters
NAME Nov03-2007-PN
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071104
Time 0.24
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT Aceton
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 322.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1316534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300071 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.58125 Hz/cm
NHBOC
OBn
ppm
Integral
ppm

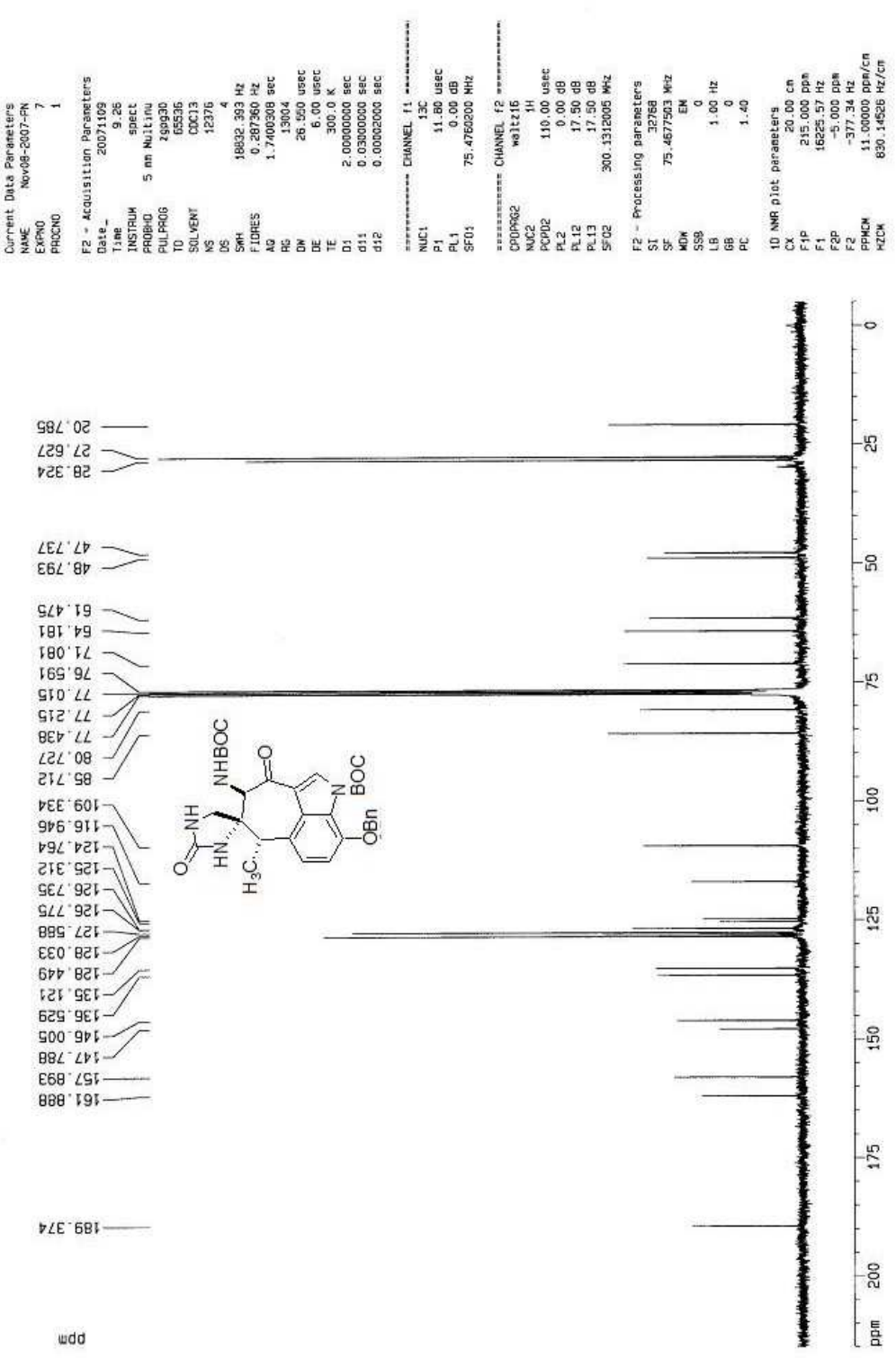
^{13}C NMR **SM8**


Current Data Parameters
NAME Nov03-2007-PN
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071104
Time 16.34
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT Aceton
NS 17432
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SF01 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SF02 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4676853 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.55 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14453 Hz/cm
20.931
28.206
28.543
29.029
29.285
29.541
29.798
30.054
30.311
30.567
48.650
50.294
62.406
64.527
70.818
80.084
106.048
116.058
123.865
124.505
127.716
127.977
128.620
128.754
129.288
132.770
138.068
145.288
158.666
162.604
189.201
205.878
206.144
206.402
NHBOC
NH
HN
O
O
N
H
OBn
H3C
ppm
0
25
50
75
100
125
150
175
200

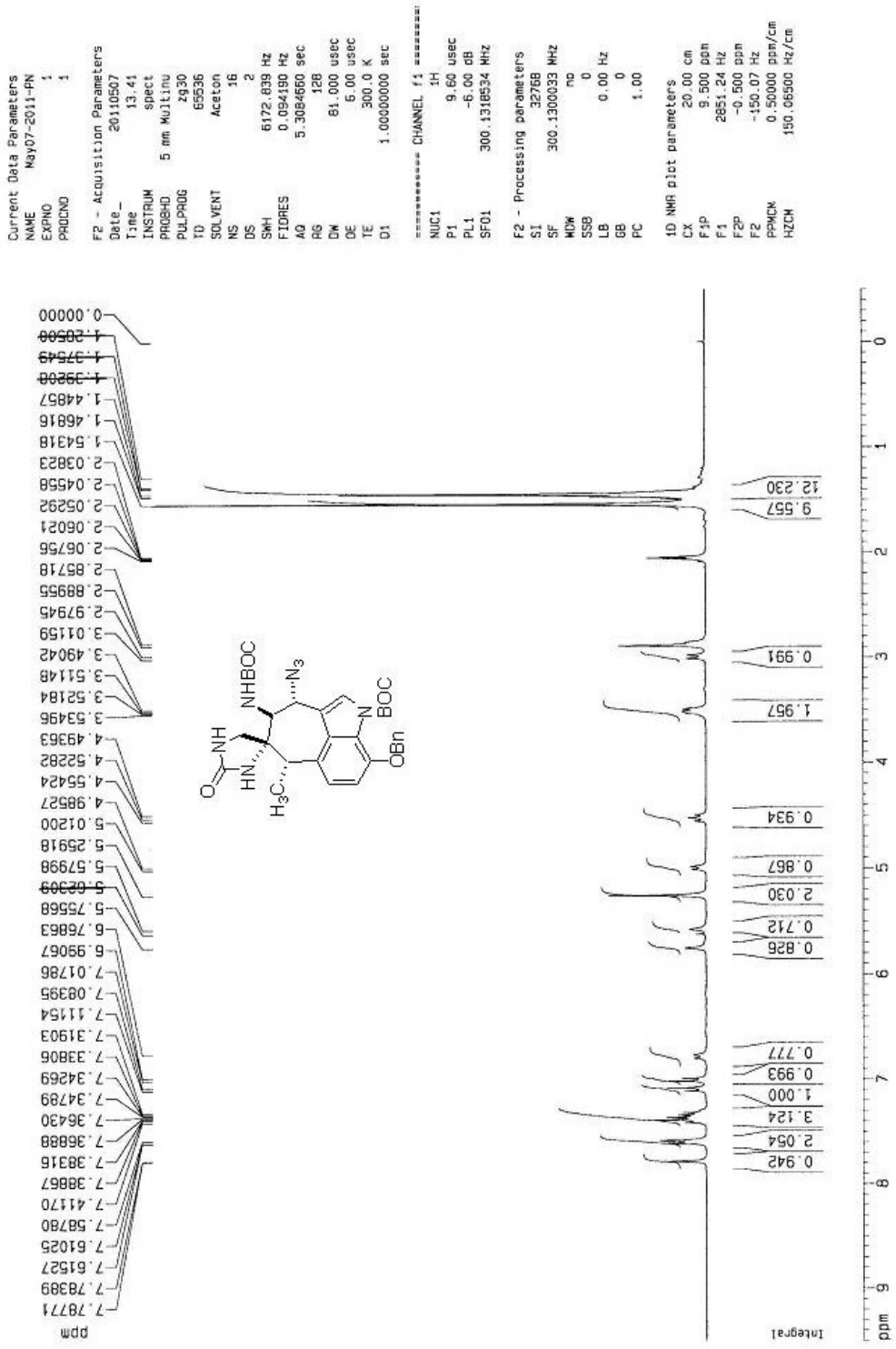
^{1}H NMR **19**


Current Data Parameters
NAME Nov08-2007-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071108
Time 17.34
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 362
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300047 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm
NHBOC
BOC
OBn
NH
HN
O
O
N
H_3C
ppm
Integral
9.4976
9.5728
4.2581
2.0825
1.1151
0.9773
0.9507
2.2872
0.9712
0.9510
1.0285
1.0307
3.2388
2.2423
1.0000

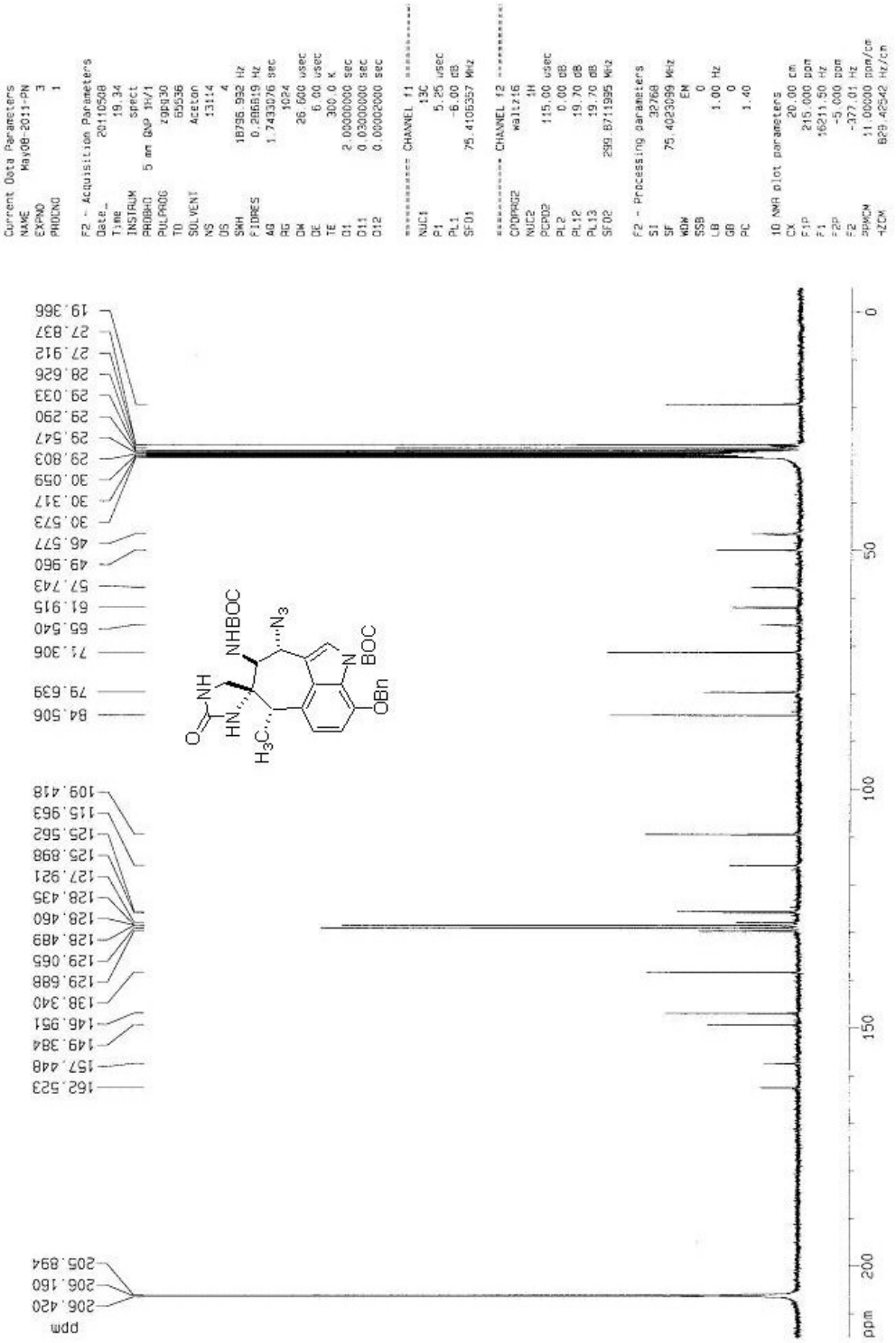
^{13}C NMR **19**


Current Data Parameters
NAME Nov08-2007-FN
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071109
Time 9.26
INSTRUM spect
PROBHD 5 mm Nuitinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 12376
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677503 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 830.14526 Hz/cm
20.785
27.627
28.324
47.737
48.793
61.475
64.181
71.081
76.591
77.015
77.215
77.438
80.727
85.712
109.334
116.946
124.764
125.312
126.735
126.775
127.588
128.033
128.449
135.121
136.529
146.005
147.788
157.893
161.888
189.374
NHBOC
NH
HN
O
O
N
BOC
OBn
H_3C
ppm
0
25
50
75
100
125
150
175
200
ppm

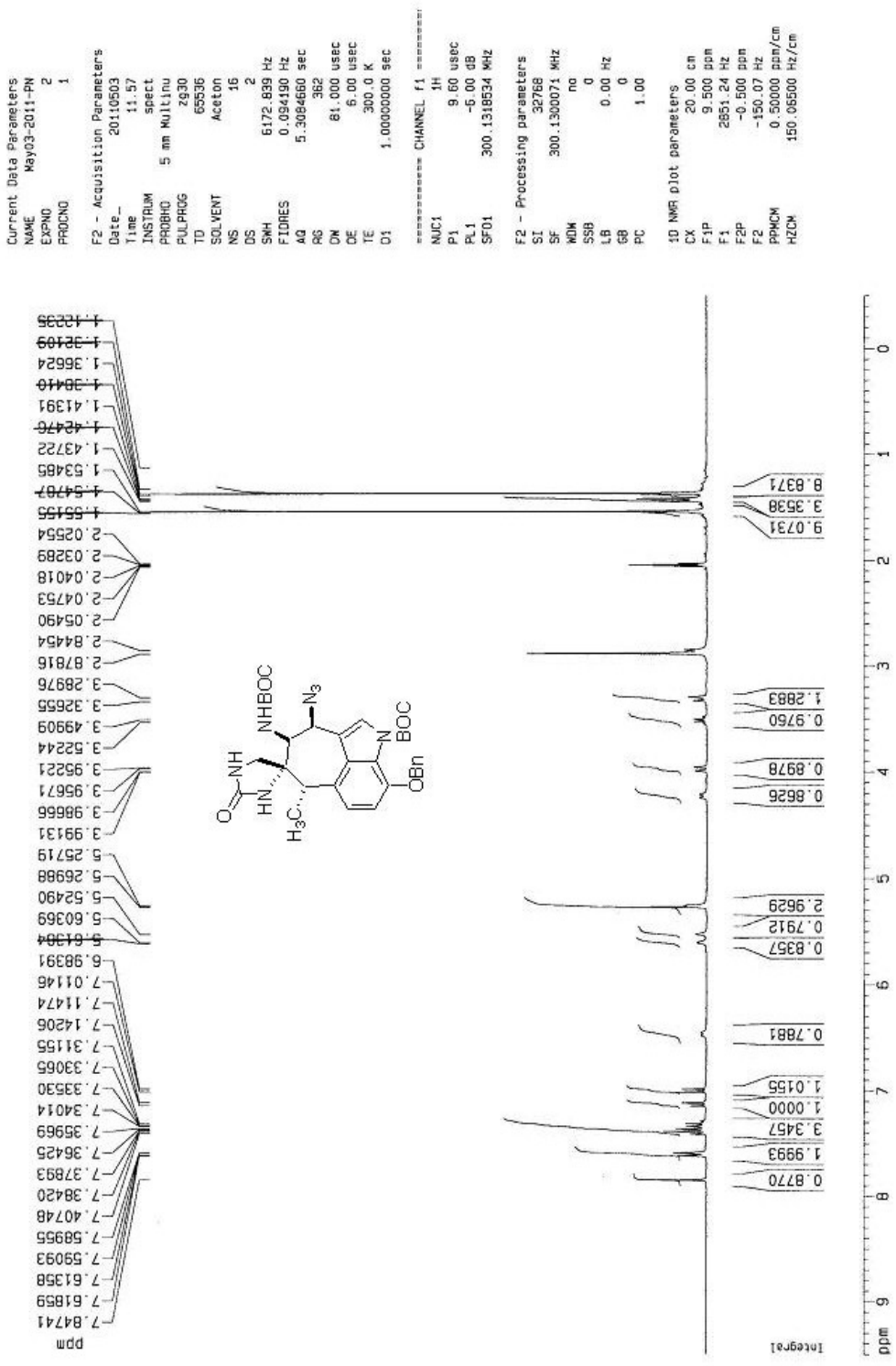
^{1}H NMR **20a**


Current Data Parameters
NAME May07-2011-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110507
Time 13.41
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT Aceton
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300033 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm
NHBOC
N3
BOC
OBn
NH
HN
H3C
12.230
9.557
0.991
1.957
0.934
0.867
2.030
0.712
0.826
0.777
0.993
1.000
3.124
2.054
0.942
Integral
ppm

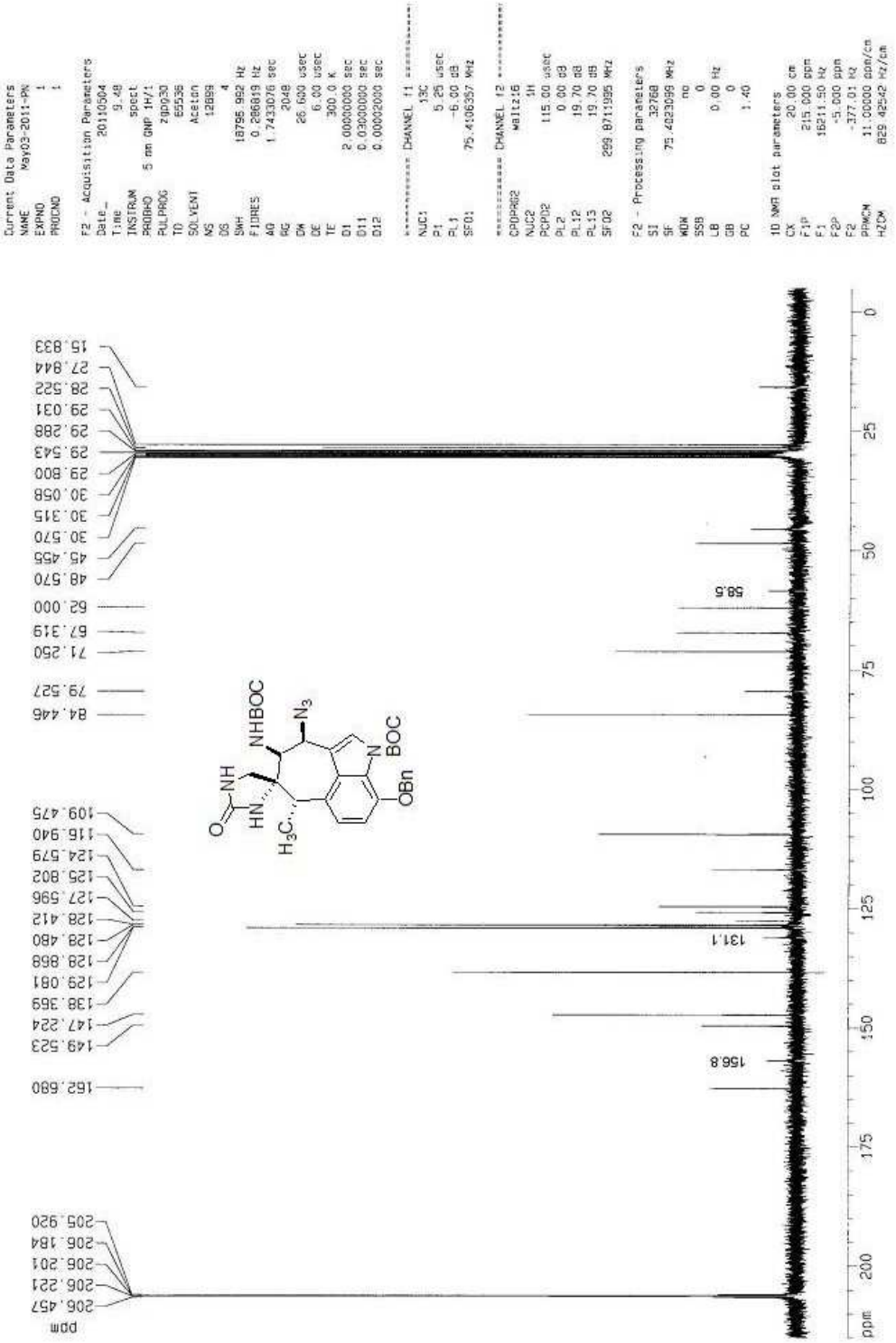
^{13}C NMR **20a**


Current Data Parameters
NAME May08-2011-PN
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110508
Time 19.34
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1314
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 1024
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.25 usec
PL1 -6.00 dB
SF01 75.4106357 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 19.70 dB
PL13 19.70 dB
SF02 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4023099 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16211.50 Hz
F2P -5.000 ppm
F2 -377.01 Hz
PPMCM 11.00000 ppm/cm
HZCM 829.42542 Hz/cm
19.366
27.837
27.912
28.626
29.033
29.290
29.547
29.803
30.059
30.317
30.573
46.577
49.960
57.743
61.915
65.540
71.306
79.639
84.506
109.418
115.963
125.562
125.898
127.921
128.435
128.460
128.489
129.065
129.688
138.340
146.951
149.384
157.448
162.523
205.894
206.160
206.420
NHBOC
NH
HN
O
H_3C
N_3
N
BOC
OBn
ppm
0
50
100
150
200

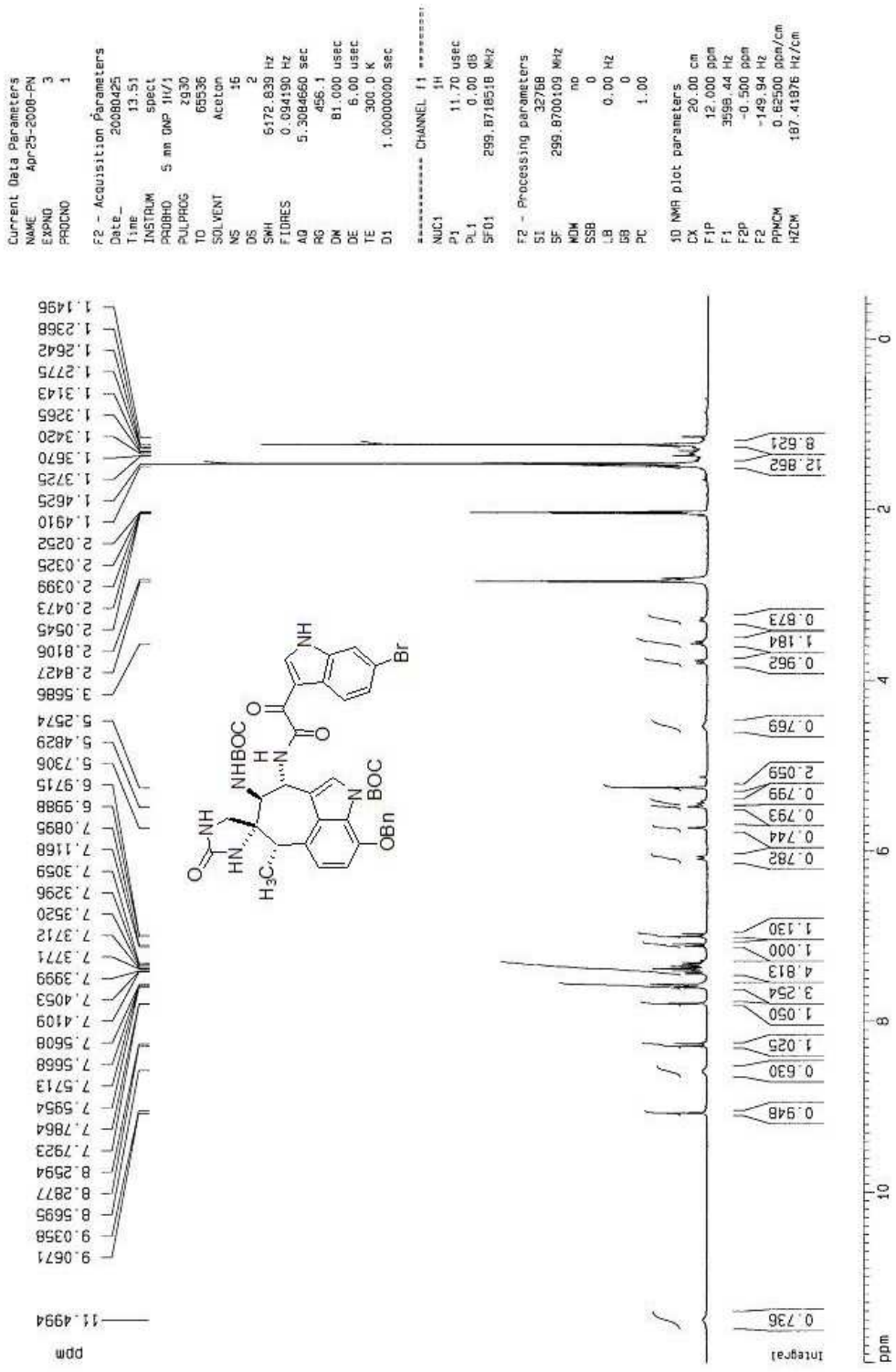
^{1}H NMR **20b**



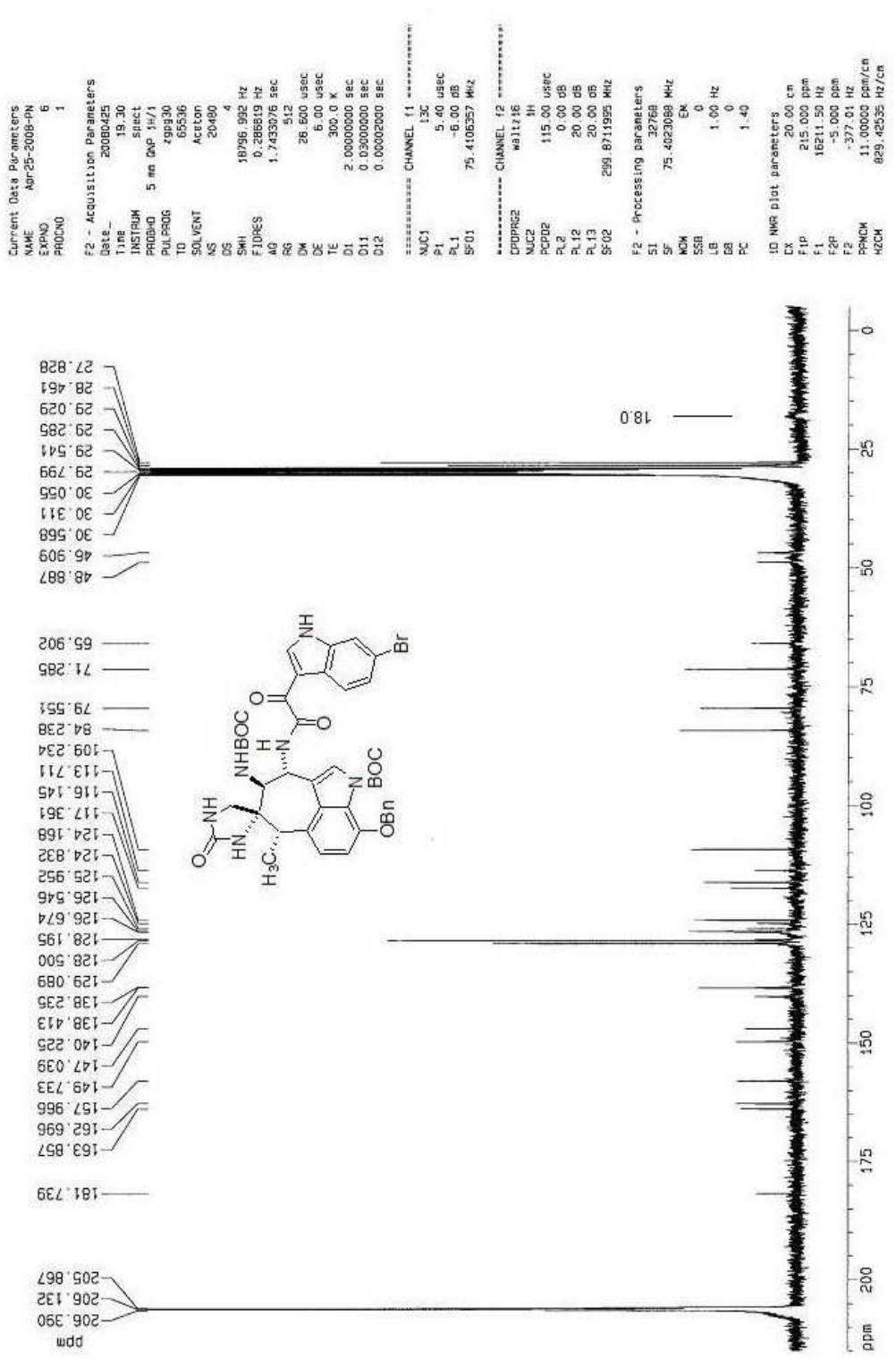
^{13}C NMR **20b**


Current Data Parameters
NAME May03-2011-PK
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110504
Time 9.48
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT Aceton
NS 1088
DS 4
SWH 18796.982 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 2048
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.25 usec
PL1 -6.00 dB
SF01 75.4706357 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 19.70 dB
PL13 19.70 dB
SF02 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4823099 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16211.50 Hz
F2P -5.000 ppm
F2 -377.01 Hz
PPMCM 11.00000 ppm/cm
HZCM 829.42542 Hz/cm
15.833
27.844
28.522
29.031
29.288
29.543
29.800
30.058
30.315
30.570
45.455
48.570
62.000
67.319
71.250
79.527
84.446
109.475
116.940
124.579
125.802
127.596
128.412
128.480
128.868
129.081
138.369
147.224
149.523
162.680
205.920
206.184
206.201
206.221
206.457
58.5
131.1
156.8
NHBOC
N3
BOC
OBn
NH
HN
H3C
ppm
0
25
50
75
100
125
150
175
200

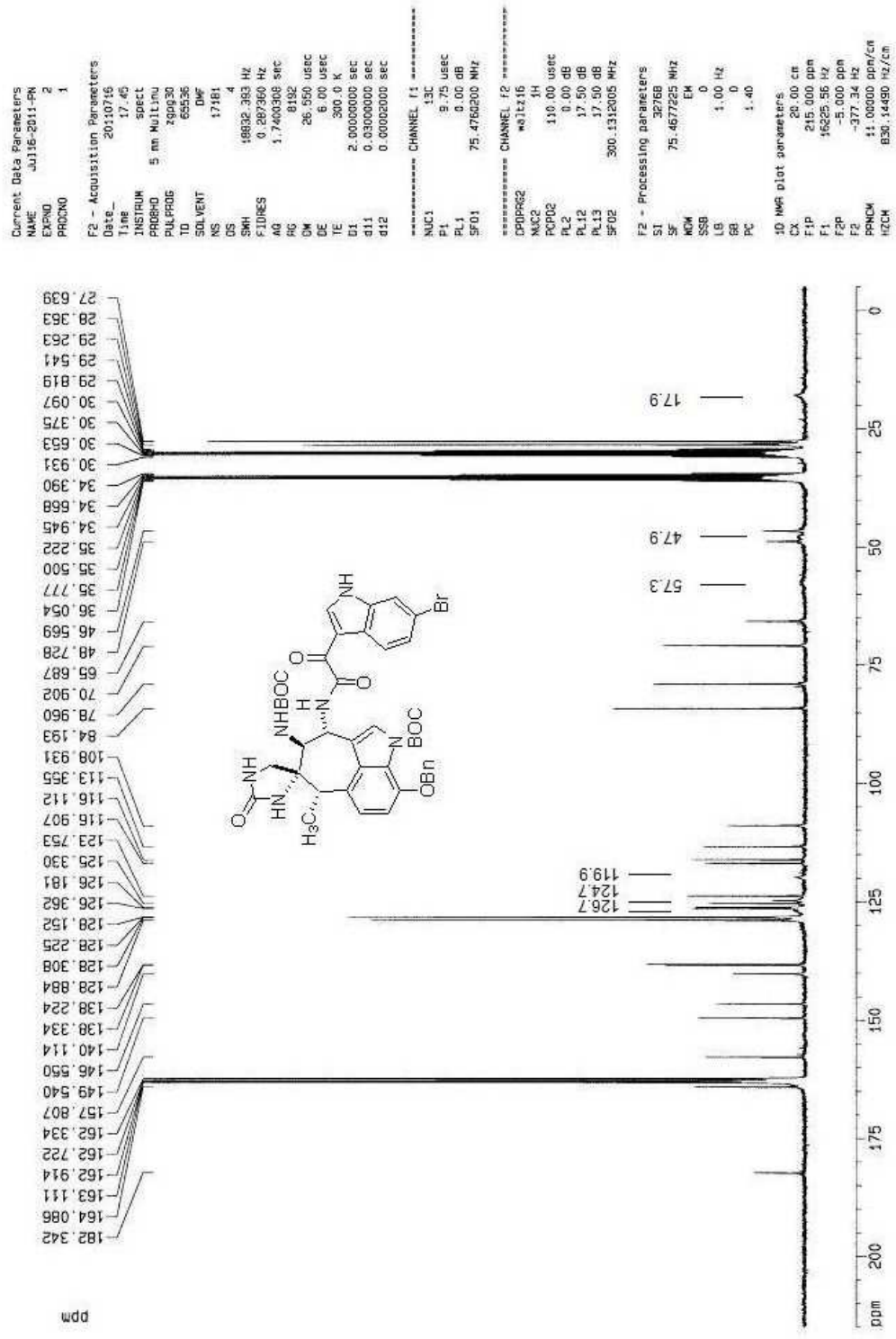
^{1}H NMR **22a**


Current Data Parameters
NAME Apr25-2008-PN
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080425
Time 13.51
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT Aceton
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.70 usec
PL1 0.00 dB
SF01 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700109 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 3599.44 Hz
F2P -0.500 ppm
F2 -149.94 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.41876 Hz/cm
NHBOC
BOC
OBn
Br
ppm
Integral

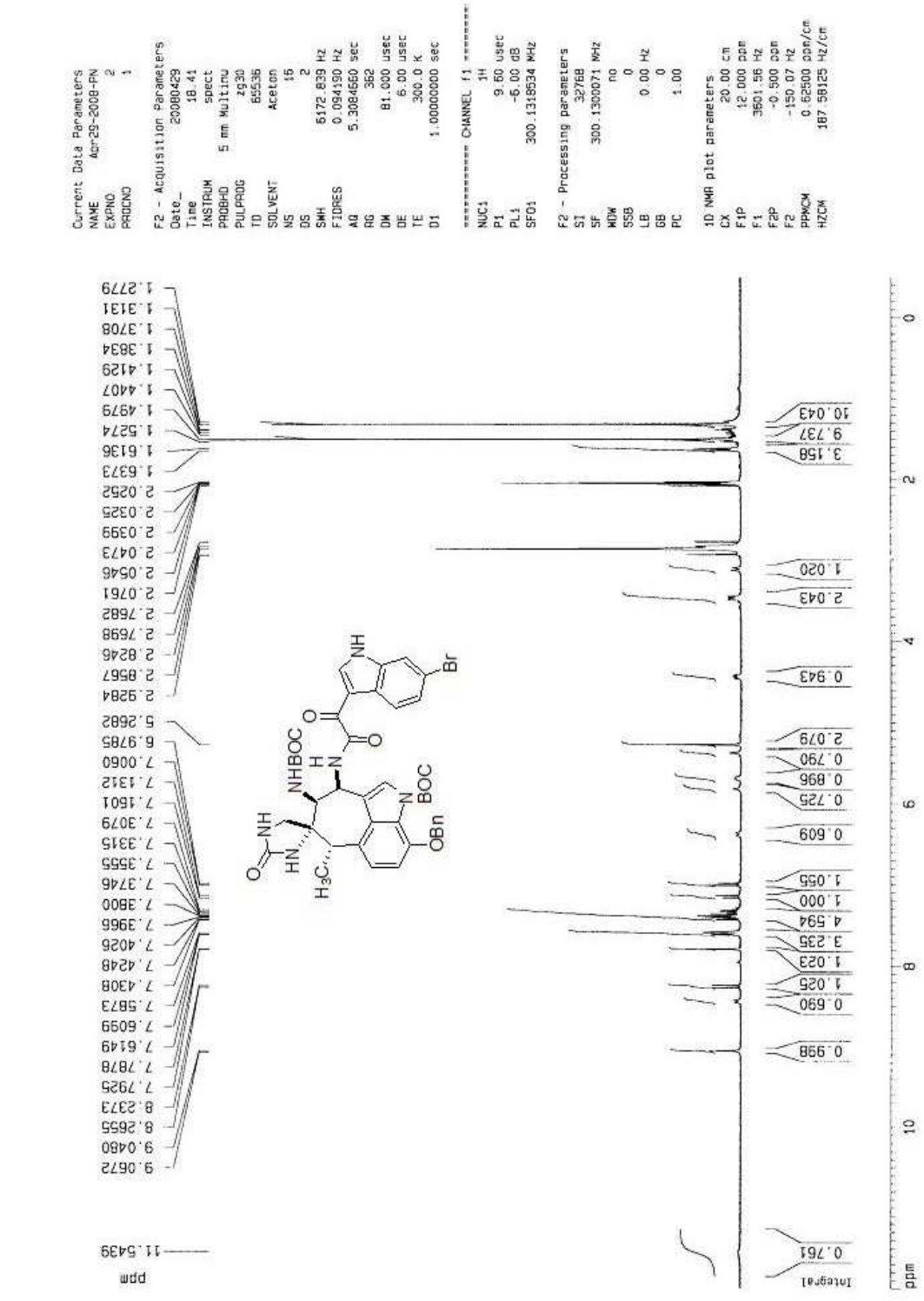
^{13}C NMR **22a** (acetone-d6)



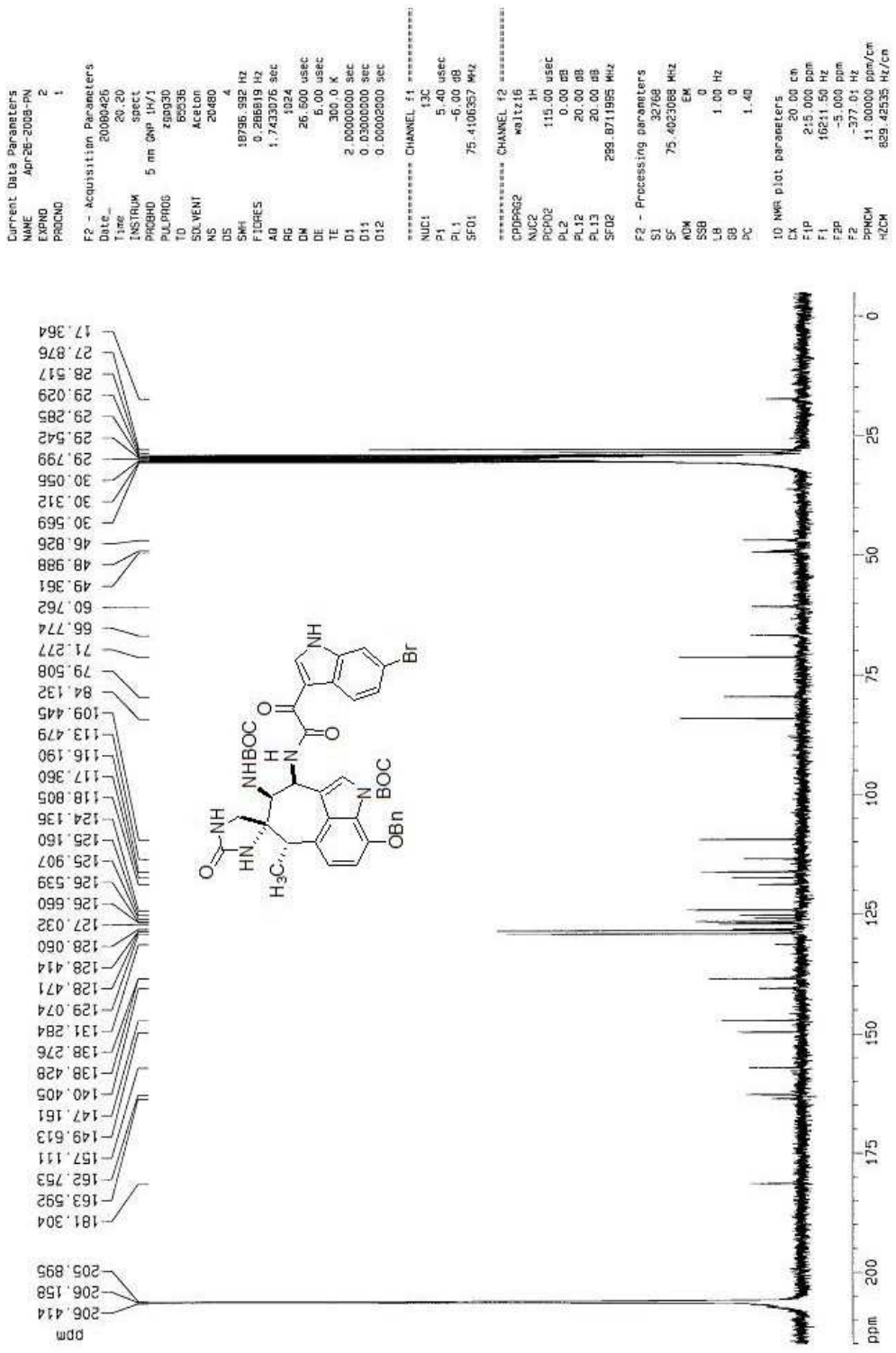
^{13}C NMR **22a** (DMF-d7)



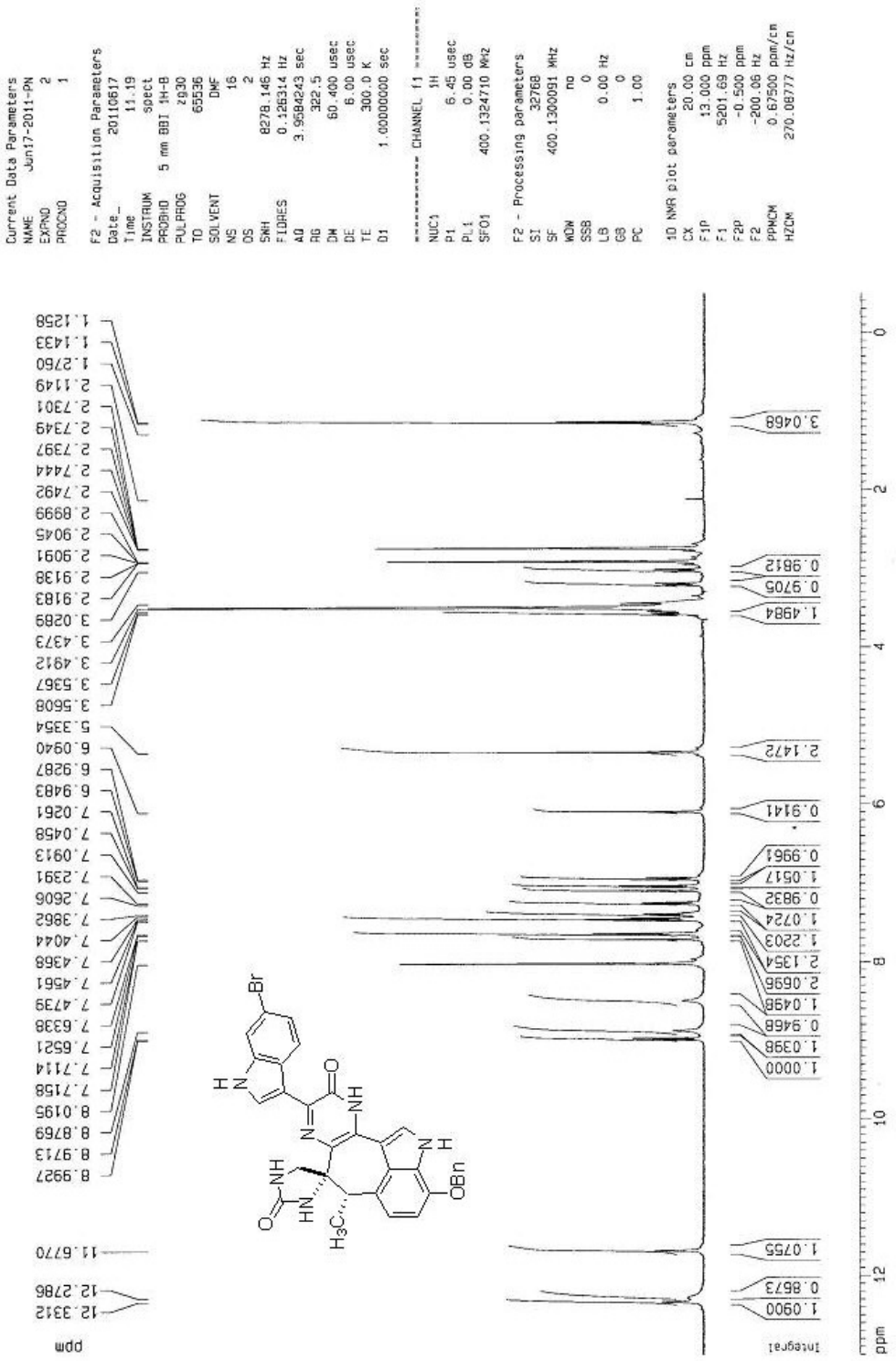
^{1}H NMR **22b**


Current Data Parameters
NAME Apr29-2008-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080429
Time 18.41
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT Aceton
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084560 sec
RG 362
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300071 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.58125 Hz/cm
NH
Br
O
NHBOC
H
N
O
O
NH
HN
H3C
N
BOC
OBn
ppm
Integral
11.5439
9.0672
9.0480
8.2655
8.2373
7.7925
7.7878
7.6149
7.5873
7.4308
7.4248
7.4026
7.3966
7.3800
7.3555
7.3315
7.3079
7.1501
7.1312
7.0060
6.9785
5.2682
2.9284
2.8567
2.8246
2.7698
2.7682
2.0761
2.0546
2.0473
2.0399
2.0325
2.0252
1.6373
1.6136
1.5274
1.4979
1.4407
1.4129
1.3834
1.3708
1.3131
1.2779
10.043
9.737
3.158
2.043
1.020
0.943
2.079
0.790
0.896
0.725
0.609
1.055
1.000
4.594
3.235
1.023
1.025
0.690
0.988
0.761

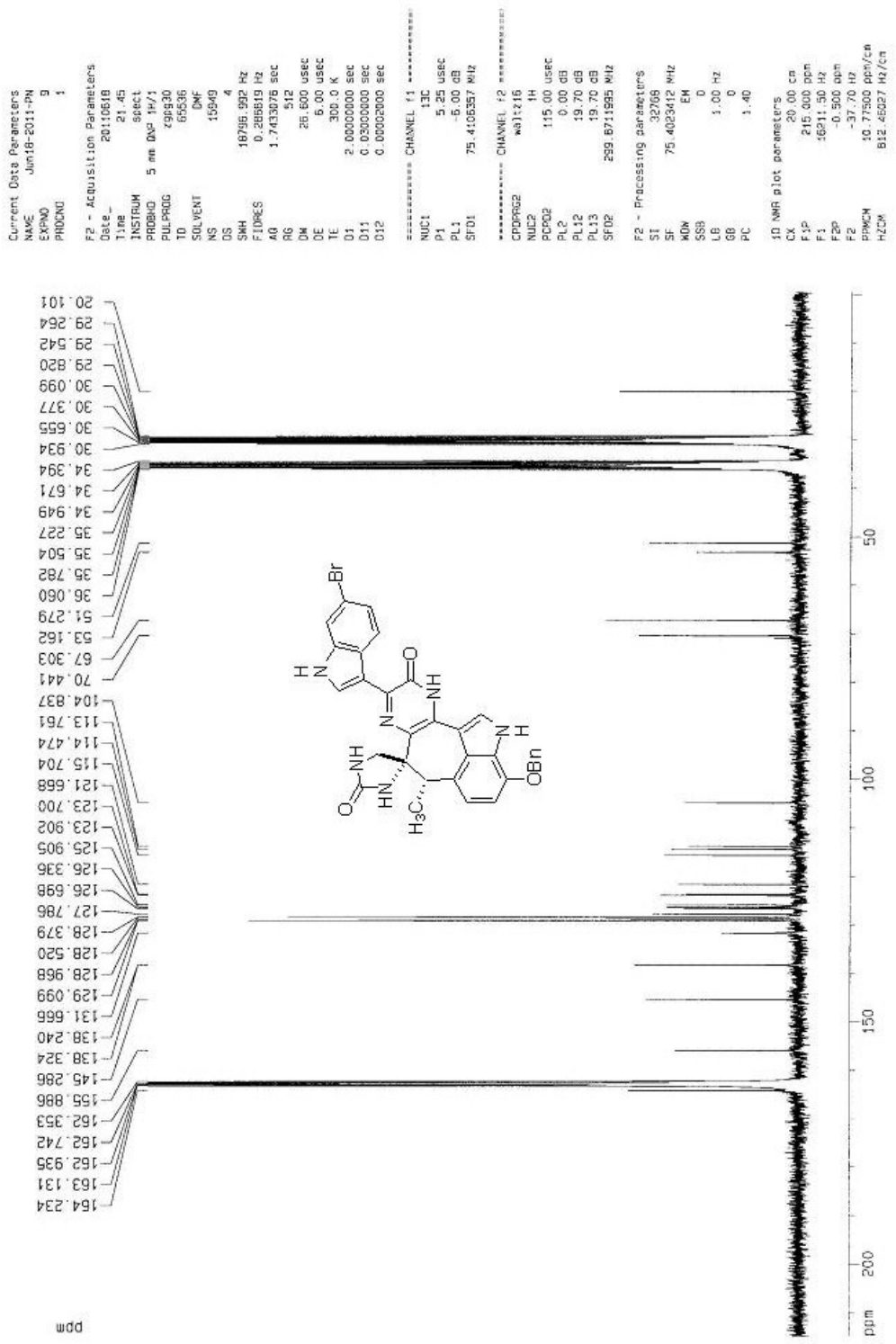
^{13}C NMR **22b**


Current Data Parameters
NAME Apr26-2008-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080426
Time 20.20
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT Aceton
NS 20480
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 1024
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.40 usec
PL1 -6.00 dB
SFO1 75.4106357 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4623088 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16211.50 Hz
F2P -5.000 ppm
F2 -377.01 Hz
PPMCM 11.00000 ppm/cm
HZCM 829.42535 Hz/cm
17.364
27.876
28.517
29.029
29.285
29.542
29.799
30.056
30.312
30.569
46.826
48.988
49.361
60.762
66.774
71.277
79.508
84.132
109.445
113.479
116.190
117.360
118.805
124.136
125.160
125.907
126.539
126.660
127.032
128.060
128.414
128.471
129.074
131.284
138.276
138.428
140.405
147.161
149.613
157.111
162.753
163.592
181.304
205.895
206.158
206.414
ppm
NH
Br
NHBOC
O
H
N
O
NH
HN
H3C
N
BOC
OBn

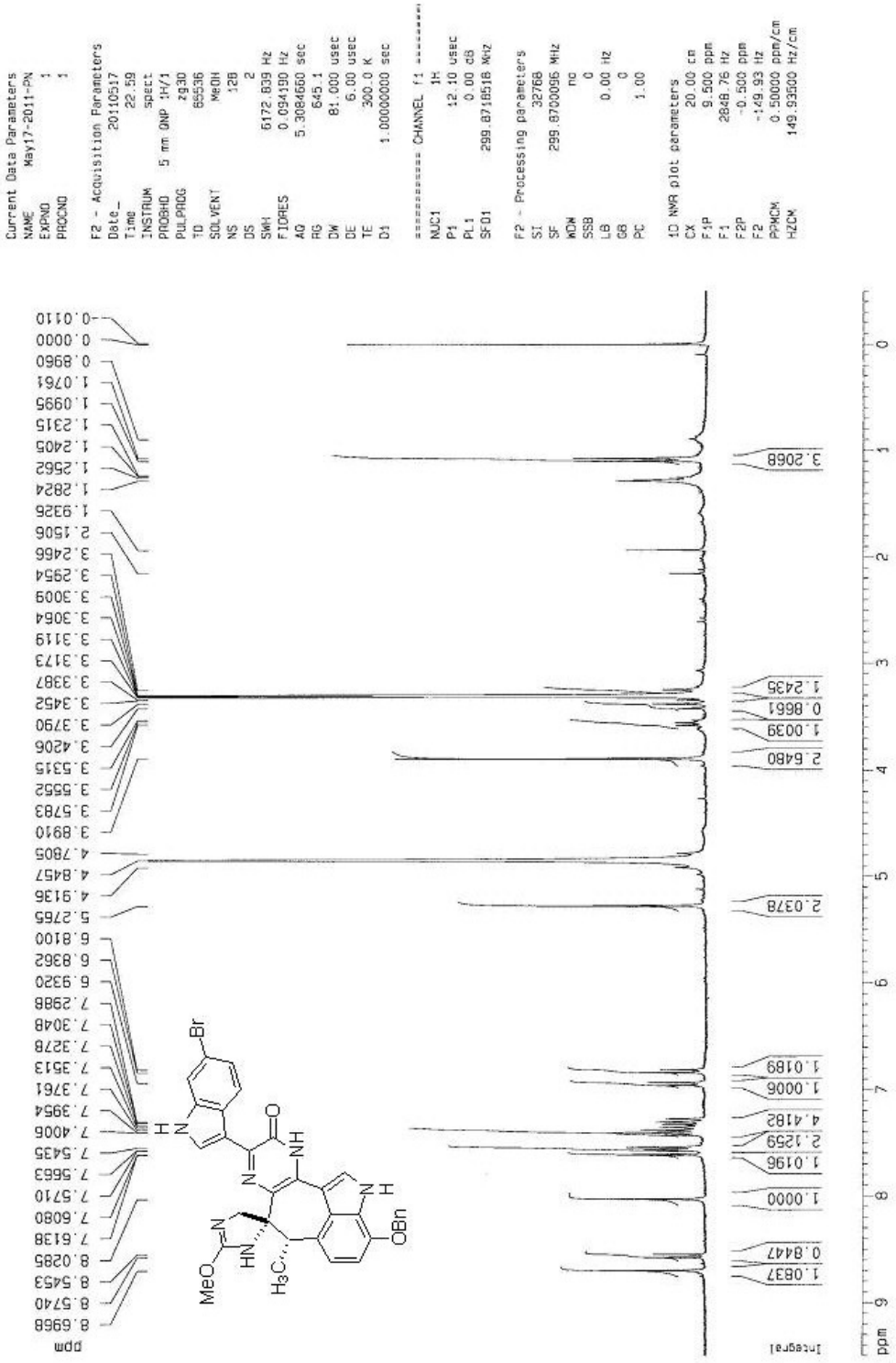
^{1}H NMR **23**


Current Data Parameters
NAME Jun17-2011-PN
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110617
Time 11.19
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG 2930
TD 65536
SOLVENT DMF
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 13.000 ppm
F1 5201.69 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.67500 ppm/cm
HZCM 270.08777 Hz/cm
ppm
Integral
OBn
Br

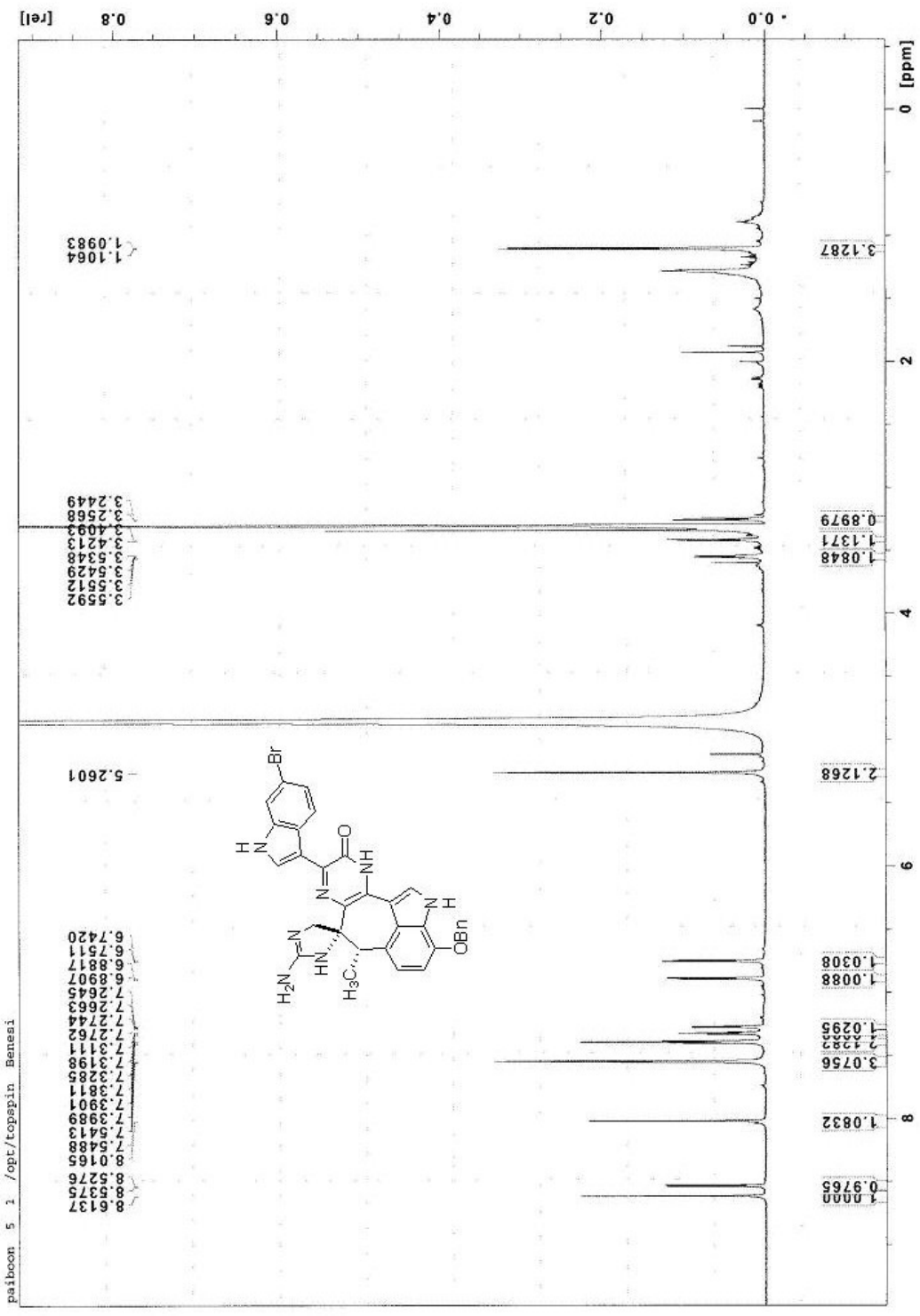
^{13}C NMR **23**


Current Data Parameters
NAME Jun16-2011-PN
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110616
Time 21.45
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT DMF
NS 1540
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 512
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.25 usec
PL1 -5.00 dB
SFO1 75.4106357 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 19.70 dB
PL13 19.70 dB
SFO2 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4023412 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16211.50 Hz
F2P -0.500 ppm
F2 -37.70 Hz
PPMCM 10.77500 ppm/cm
HZCM 812.46027 Hz/cm
20.101
29.264
29.542
29.820
30.099
30.377
30.655
30.934
34.394
34.671
34.949
35.227
35.504
35.782
36.060
51.279
53.162
67.303
70.441
104.837
113.761
114.474
115.704
121.668
123.700
123.902
125.905
126.336
126.698
127.786
128.379
128.520
128.968
129.099
131.665
138.240
138.324
145.286
155.886
162.353
162.742
162.935
163.131
164.234
Br
H
N
NH
O
N
NH
O
HN
H3C
N
H
OBn
ppm
200
150
100
50

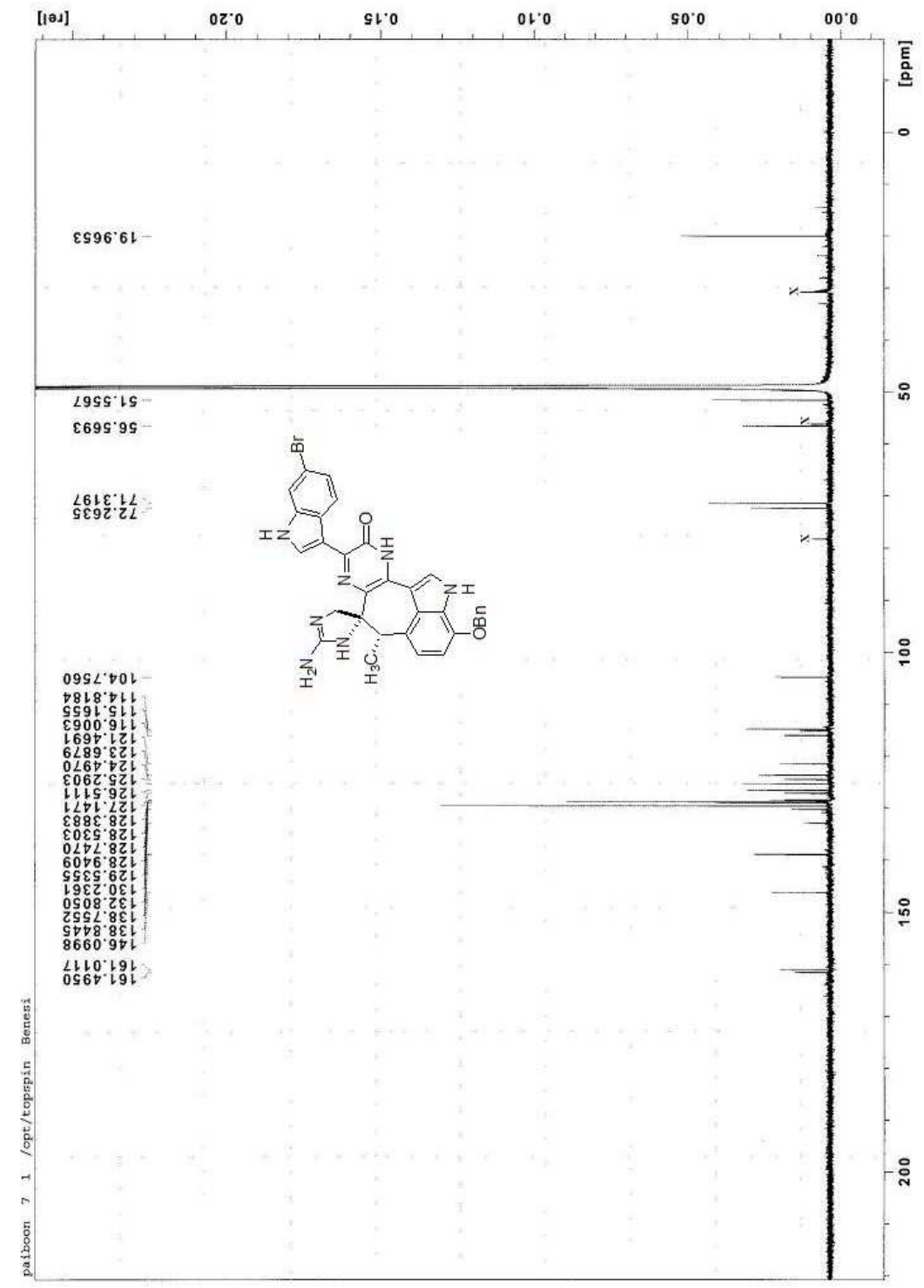
^{1}H NMR **SM9**


Current Data Parameters
NAME May17-2011-PN
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110517
Time 22.59
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOH
NS 128
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 12.10 usec
PL1 0.00 dB
SF01 299.87186518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700096 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.500 ppm
F1 2848.76 Hz
F2P -0.500 ppm
F2 -149.93 Hz
PPMCM 0.50000 ppm/cm
HZCM 149.93500 Hz/cm
ppm
Integral
8.6968
8.5740
8.5453
8.0285
7.6138
7.6080
7.5710
7.5663
7.5435
7.4006
7.3954
7.3761
7.3513
7.3278
7.3048
7.2988
6.9320
6.8362
6.8100
5.2765
4.9136
4.8457
4.7805
3.8910
3.5783
3.5552
3.5315
3.4206
3.3790
3.3452
3.3387
3.3173
3.3119
3.3064
3.3009
3.2954
3.2466
2.1506
1.9326
1.2824
1.2562
1.2405
1.2315
1.0995
1.0761
0.8960
0.0000
0.0110
3.2068
1.2435
0.8661
1.0039
2.6480
2.0378
1.0189
1.0006
4.4182
2.1259
1.0196
1.0000
0.8447
1.0837
Br
N
H
O
NH
N
N
H
OBn
MeO
N
HN
H3C
0
1
2
3
4
5
6
7
8
9

^{1}H NMR **SM10**



^{13}C NMR **SM10**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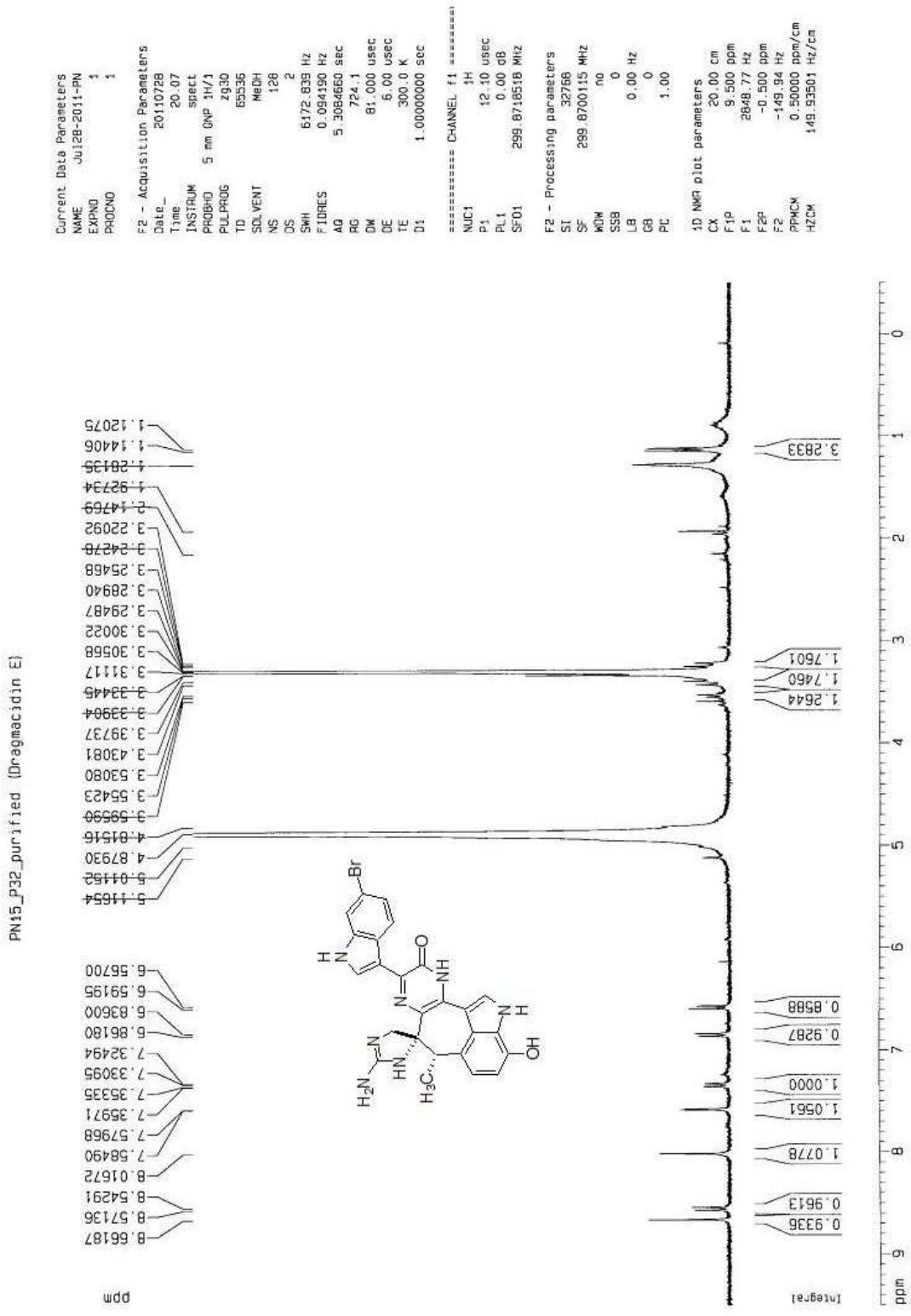
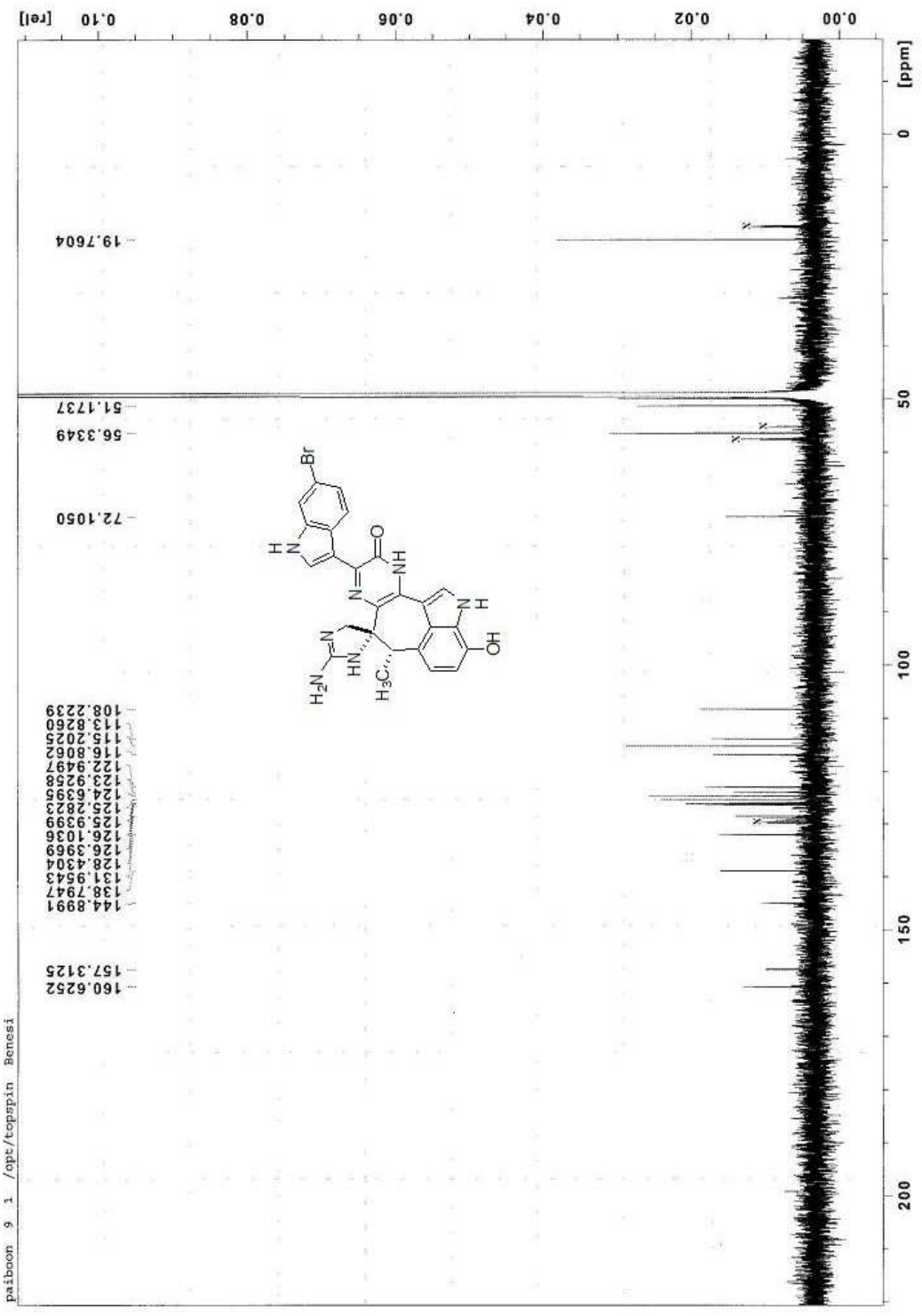
0.20
0.15
0.10
0.05
0.00
[ppm]
0
50
100
150
200
19.9653
51.5567
56.5693
72.2635
71.3197
104.7560
114.8184
115.1655
116.0063
121.4691
123.6879
124.4970
125.2903
126.5111
127.1471
128.3883
128.5303
128.7470
128.9409
129.5355
130.2361
132.8050
138.7552
138.8445
146.0998
161.0117
161.4950
Br
H
N
O
NH
N
N
H
N
OBn
H_2N
HN
H_3C
paiboon 7 1 /opt/topspin Benesi

^{1}H NMR **1** (±)-dragmacidin E

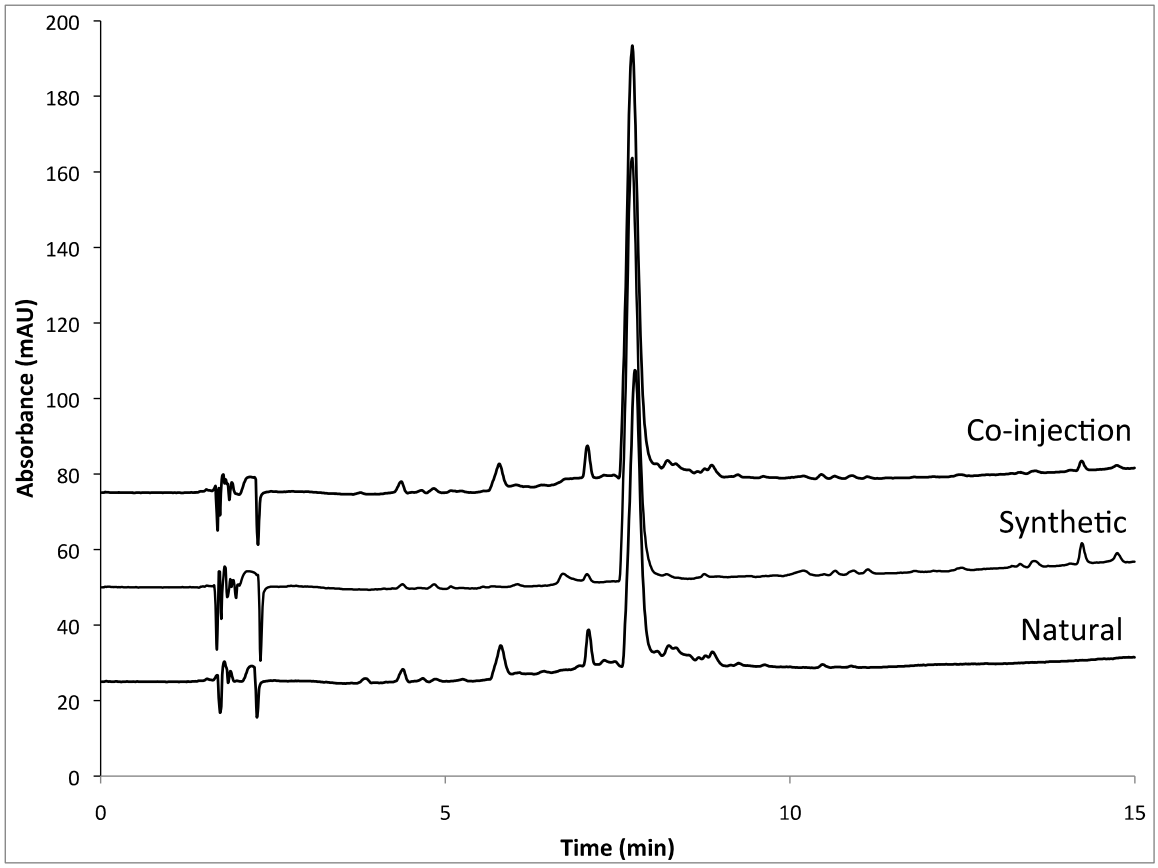


^{13}C NMR **1** (±)-dragmacidin E



HPLC assay of synthetic dragmacidin E vs. natural dragmacidin E, conducted by Dr. R. Capon, The University of Queensland

HPLC conditions: Zorbax SB-C8 150 x 4.6 mm, 5 uM column, 1 mL/min, gradient 10 – 100% CH_3CN:H_2O (with isocratic 0.05 % formic acid) over 15 min.; UV detection at 254 nm.



UV comparison of synthetic dragmacidin E and natural dragmacidin E, conducted by Dr. R. Capon, The University of Queensland.