Supporting Information

Benzothiazines in Synthesis. A Total Synthesis of Pseudopteroxazole

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General information:

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. THF was distilled over sodium-benzophenone before use. CH₂Cl₂ was distilled over CaH₂. Chromatographic separations were carried out using Silicycle ultra pure silica gel (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 nm silica gel 60-F plates.

Melting points were measured with a Fisher-Johns melting point apparatus. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. Optical rotations were measured on a Jasco DIP-370 digital polarimeter. ¹H NMR were recorded on a Bruker ARX-250 (250 MHz), DRX-300 (300 MHz), DRX-500 (500 MHz) spectrometer and are reported in ppm (δ) from tetramethylsilane (TMS: δ 0.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet), coupling constants (Hz), and integration. ¹³C NMR spectra were recorded on a Bruker ARX-250 (62.5 MHz), DRX-300 (75 MHz), and DRX-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with solvent resonance as the internal standard (CDCl₃: δ 77.0 ppm).

9: To 100 mL THF in 200 mL round bottomed flask was added **5** (392 mg, 1 mmol). After stirring at -45 °C for 10 minutes, 1.3 M LiHMDS (0.923 mL, 1.2 mmol) was added dropwise. After 1 hour, then allyl bromide (173 μL, 2.0 mmol) was added dropwise to the reaction mixture at -45 °C. The mixture was stirred for 1 hour, quenched with water, washed with brine, extracted with ethyl acetate (3 × 40 mL), dried over MgSO₄, filtered, and concentrated. The crude product was purified by flash chromatography (30%

Et₂O/Hexanes) to afford a colorless solid 435 mg (100%). Mp: 154-155 °C; IR: 2962, 2925, 2855, 1589, 1478, 1442, 1319, 1282, 1237 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.86-7.84 (m, 2H), 7.58-7.55 (m, 1H), 7.49-7.45 (m, 2H), 6.68 (s, 1H), 5.60-5.55 (m, 1H), 5.13-5.11 (m, 1H), 4.95-4.90 (m, 2H), 3.87 (s, 3H), 3.73-3.70 (m, 1H), 3.00-2.98 (m, 2H), 2.91-2.87 (m, 1H), 2.62-2.58 (m, 1H), 2.19 (s, 3H), 1.98-1.96 (m, 1H); 1.85 (dt, *J* = 13.4, 6.2 Hz, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.60 (ddd, *J* = 13.4, 5.0, 3.5 Hz, 1H), 1.12 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 149.6, 139.7, 134.1, 133.2, 131.9, 130.4, 130.0, 129.6, 129.1, 129.0, 128.1, 125.6, 117.7, 112.4, 62.0, 56.0, 40.4, 35.8, 34.4, 30.7, 29.6, 25.6, 23.6, 19.5, 17.6; HRMS calcd for C₂₇H₃₃NO₂SNa [M + Na]⁺ 458.2124; Found: 458.2138. [α]_D²⁵ = + 78.28 (c 1.28, CHCl₃).

(5S,7S,8R)-8-(but-3-enyl)-2-methoxy-4,7-dimethyl-5-(2-methylprop-1-enyl)-5,6,7,8-tetrahydronaphthalen-1-amine (8). To 100 mL round bottomed flask under N₂ was charged with 6% sodium amalgam (3.83 g, 10.0 mmol), and dispersed in dry MeOH (12 mL), followed by addition of solid Na₂HPO₄ (1.42 g, 10.0 mmol). The mixture was stirred at room temperature for a few minutes. **9** (435 mg, 1.0 mmol) was added into the well-stirred dispersion of buffered sodium amalgam as a solution in THF (3 mL). The reaction mixture was stirred at room temperature overnight. The mixture was filtered through a pad of Celite and concentrated in *vacuo*, to give crude product. Purification of the product by flash chromatography (5% EtOAc/Hexanes) afforded a colorless oil 288.2 mg (92%). IR: 3464, 3374, 2953, 2913, 2851, 1621, 1593, 1486, 1450, 1298 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 6.58 (s, 1H), 5.96-5.91 (m, 1H), 5.14-5.10 (m, 2H), 5.06-5.04 (m, 1H), 3.86 (s, 3H), 3.72 (s, 2H), 3.64 (t, *J* = 8.0 Hz, 1H), 2.43 (d, *J* = 10.6 Hz, 1H), 2.33-2.28 (m, 2H), 2.19-2.16 (m, 2H), 2.14 (s, 3H), 1.77 (s, 3H), 1.70 (s, 3H), 1.67-1.60 (m, 2H), 1.54-1.52 (m, 1H), 1.05 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 144.9, 138.4, 132.7, 131.4, 129.5, 128.5, 126.2, 125.3, 115.3, 110.7, 55.4, 39.7, 33.4,

32.9, 31.2, 27.6, 25.3, 22.5, 19.5, 17.5; HRMS Calcd for C₂₁H₃₁NOH [M + H]⁺ 314.2478; Found: 314.2475. $[\alpha]_D^{25} = +38.05$ (c 1.64, CHCl₃).

(Z)-1-((5S,7S,8R)-8-(but-3-enyl)-2-methoxy-4,7-dimethyl-5-(2-methylprop-1-enyl)-5,6,7,8-tetrahydronaphthalen-1-yl)-3,3-diethyltriazen-1-ene (10). To 50 mL round bottomed flask was charged with aniline **8** (282 mg, 0.9 mmol), 4.5 M aq. HCl (0.9 mL), Et₂O/THF/CH₃CN 7:6:1 (5 mL), and chilled to 5 °C in an ice bath. A solution of NaNO₂ (211 mg, 3.06 mmol) in CH₃CN/H₂O 2:3 (4 mL) was added and the reaction mixture was stirred at 0-5 °C for 1h. A second 50 mL round bottomed flask was charged with diethylamine (464 μL, 4.5 mmol), K₂CO₃ (621 mg, 4.5 mmol) and CH₃CN/H₂O 2:1 (5 mL) which was chilled to 0-5 °C in an ice bath. The solution of aniline was transferred over 15 minutes, and stirred for additional 1h at 0-5 °C. The solution was extracted with 3 x 10 mL Et₂O. The combined organic phase was dried over Na₂SO₄, filtered, and concentrated in *vacuo*, to give a brown oil. Purification of the product by basic aluminum oxide chromatography (5% Et₂O/Pentanes) afforded a colorless oil 344 mg (100%). IR: 2966, 2917, 1634, 1589, 1462, 1061 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 6.62 (s, 1H), 5.74-5.69 (m, 1H), 5.09-5.07 (m, 1H), 4.95-4.91 (m, 1H), 4.86-4.84 (m, 1H), 3.77-3.71 (m, 4H), 3.70 (s, 3H), 3.61 (t, *J* = 8.0 Hz, 1H), 2.72 (d, *J* = 10.6 Hz, 1H), 2.28-2.23 (m, 1H), 2.15-1.98 (m, 2H), 2.13 (s, 3H), 1.97-1.93 (m, 1H), 1.74 (s, 3H), 1.70 (s, 3H), 1.57-1.54 (m, 2H), 1.43-1.30 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 6H), 0.99 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 149.0, 139.1, 138.0, 134.6, 134.1, 133.0, 129.7, 128.4, 113.8, 113.1, 56.2, 40.0, 34.5, 33.4, 32.4, 31.4, 27.1, 25.4, 22.3, 20.0, 17.6; HRMS Calcd for C₂₅H₃₉N₃ONa [M + Na]⁺ 420.2985; Found: 420.2975. $[\alpha]_D^{25} = +280.11$ (c 5.23, CHCl₃).

(1*R*,2*S*,4*S*)-1-(but-3-enyl)-8-iodo-7-methoxy-2,5-dimethyl-4-(2-methylprop-1-enyl)-1,2,3,4-tetrahydronaphthalene (11). A 15 mL sealed tube under Ar₂ was charged with triazene **10** (100 mg, 0.251 mmol) in diiodomethane (6 mL). The solution was degassed, sealed and stirred at 80-81 °C for 20 hours. The solvent was removed under reduced pressure and the red residue was dissolved in Et₂O (20 mL), washed with saturated Na₂S₂O₃ solution, water and dried over MgSO₄. Removal of the solvent gave crude product. Purification of the product by flash chromatography (Pentanes to 2% Et₂O/Pentanes) afforded a colorless oil **11** 79.8 mg (75%). IR: 2962, 2925, 2851, 1642, 1568, 1066 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 6.57 (s, 1H), 5.93-5.88 (m, 1H), 5.06-5.01 (m, 2H), 4.97-4.95 (m, 1H), 3.87 (s, 3H), 3.62 (t, *J* = 8.1 Hz, 1H), 2.92 (d, *J* = 11.2 Hz, 1H), 2.37-2.28 (m, 1H), 2.25-2.20 (m, 2H), 2.19-2.18 (m, 1H), 2.17 (s, 3H), 1.75 (s, 3H), 1.66 (s, 3H), 1.64-1.56 (m, 2H), 1.31-1.21 (m, 1H), 1.0 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 155.9, 143.3, 138.8, 138.6, 132.3, 131.8, 129.2, 114.3, 111.7, 93.1, 56.3, 49.8, 34.7, 33.6, 32.3, 31.8, 27.4, 25.3, 22.1, 20.2, 17.7; HRMS Calcd for C₂₁H₂₉IO 424.1257; Found 424.1243. [α]_D²⁵ = + 45.92 (c 1.52, CHCl₃).

(1*S*,3*S*,9*aR*)-6-methoxy-1,4,7-trimethyl-3-(2-methylprop-1-enyl)-2,3,9,9a-tetrahydro-1*H*-phenalene (7). An 80 mL sealed tube under Ar₂ was charged with iodide (300 mg, 0.707 mmol), Pd(OAc)₂ (8.0 mg, 0.035 mmol), tri-*o*-tolylphosphine (21.5 mg, 0.0707 mmol) in triethylamine (20 mL). The solution was degassed by Ar₂ for 20 minutes. The sealed tube was warmed until it was homogeneous and then heated at 120 °C for 38 h. The cooled reaction mixture was diluted with 15 mL of 6 N sodium hydroxide and 15 mL of ether. After shaking, the aqueous layer was extracted twice more with ether. The combined ether extracts were washed with water, dried (MgSO₄), and concentrated under reduced pressure. Purification of the crude product by chromatotron (Pentanes to 2% Et₂O/Pentanes) afforded a colorless oil **7** 129.4 mg (62%) and a colorless oil 30 mg (14%). Compound **7'** is not stable, which can be isomerized into compound **7** in 81% yield when we attempted to further purify the small amount of impurity by biotage technology. IR: 2962, 2913, 2868, 1585, 1552, 1466, 1294 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 6.62 (s, 1H), 5.86-5.83 (m, 1H), 4.90-4.86 (m, 1H), 3.78(s, 3H), 3.81-3.69 (m, 1H), 2.35-2.24 (m, 1H), 2.10 (s, 3H), 2.19 (s, 3H), 2.08-2.01 (m, 1H), 1.93 (ddd, *J* = 13.3, 7.6, 2.3 Hz, 1H), 1.74 (d, *J* = 0.9 Hz, 3H), 1.68 (d, *J* = 0.9 Hz, 3H), 1.58-1.26 (m, 2H), 1.21-1.13 (m, 1H), 1.04 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 154.4, 139.7, 137.5, 133.1, 131.0, 129.8, 128.7, 124.7, 122.7, 113.2, 55.6, 43.7, 39.5, 37.0, 32.9, 27.6, 25.4, 22.8, 21.0, 20.0, 17.5; HRMS Calcd for C₂₁H₂₈ONa [M + Na]⁺ 319.2032; Found: 319.2022; [α]_D²⁵ = + 56.88 (c 1.54, CHCl₃).

(1*S*,3*S*,7*S*,9*aR*)-6-methoxy-1,4,7-trimethyl-3-(2-methylprop-1-enyl)-2,3,7,8,9,9a-hexahydro-1*H*-phenalene (6). A solution of **7** (16 mg, 0.054 mmol) and iridium catalyst **12** (2.53 mg, 0.0016 mmol) in dry dichloromethane was degassed for 10 minutes, then was stirred in a high-pressure autoclave under 200 psi hydrogen for 1h. Removal of the solvent gave crude product. Purification of the product by flash chromatography

(Pentanes to 2% Et₂O/Pentanes) afforded a colorless oil 14.4 mg (90%). IR: 2953, 2921, 2851, 1589, 1458, 1437, 1098 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ: 6.57 (s, 1H), 4.98-4.96 (m, 1H), 3.80 (s, 3H), 3.76-3.71 (m, 1H), 3.21 (Hex, *J* = 7.0 Hz, 1H), 2.19 (s, 3H), 2.18-2.14 (m, 1H), 2.09-2.06 (m, 2H), 2.01-1.97 (m, 1H), 1.75 (d, *J* = 1.2 Hz, 3H), 1.69 (d, *J* = 1.2 Hz, 3H), 1.35-1.20 (m, 3H), 1.23 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.0 Hz, 3H), 0.98-0.95 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 155.3, 140.5, 134.9, 131.1, 129.9, 128.4, 127.8, 110.9, 55.0, 44.8, 40.0, 36.5, 34.0, 31.7, 28.0, 27.6, 25.4, 23.5, 20.6, 20.1, 17.5; HRMS Calcd for C₂₁H₃₀O 298.2291; Found: 298.2266. [α]_D²⁵ = + 104.86 (c 0.74, CHCl₃).

(4*S*,6*S*,6*aR*,9*S*)-3,6,9-trimethyl-4-(2-methylprop-1-enyl)-5,6,6*a*,7,8,9-hexahydro-4*H*-phenalen-1-ol (13). To a suspension of 60% NaH (131.3 mg, 3.28 mmol) in 10 mL dry DMF was added EtSH (210.6 μ L, 2.81 mmol) dropwise at 0 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 15 minutes. **6** in 10 mL dry DMF was added dropwise, and the mixture was then heated to reflux for overnight. The reaction was cooled to room temperature, and diluted with water, neutralized with concentrated HCl, extracted with Et₂O (4 x 20 mL). The combined organic layer was dried over MgSO₄. Removal of the solvent gave crude product. Purification of the product by flash chromatography (5% Et₂O/Pentanes) afforded a colorless oil 115.4 mg (87%). IR: 3481, 2949, 2913, 2851, 1593, 1433, 1409, 1368, 1294, 1217, 1041 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 6.46 (s, 1H), 4.98-4.96 (m, 1H), 4.50 (s, 1H), 3.70 (q, *J* = 9.0 Hz, 1H), 3.14 (Hex, *J* = 7.2 Hz, 1H), 2.25-2.15 (m, 1H), 2.12 (s, 3H), 2.10-1.95 (m, 3H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.43-1.18 (m, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 5.9 Hz, 3H), 0.95-0.89 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 151.3, 140.7, 135.4, 131.1, 130.3, 128.5, 125.3, 115.7, 44.9, 40.0, 36.5,

34.0, 31.8, 28.0, 27.6, 25.4, 23.2, 20.1, 20.0, 17.5; HRMS Calcd for C₂₀H₂₈OLi 291.2306; Found 291.2301. $[\alpha]_D^{25} = +111.15$ (c 3.3, CHCl₃).

(4*S*,6*S*,6*aR*,9*S*)-3,6,9-trimethyl-4-(2-methylprop-1-enyl)-2-nitro-5,6,6*a*,7,8,9-hexahydro-4*H*-phenalen-1-ol (14). To a stirred solution of **13** (30 mg, 0.106 mmol) in Hexanes (7 mL) at room temperature was added 70% HNO₃ (1 mL) dropwise. The reaction was stirred for 1.5 minutes and then quenched by saturated NaHCO₃. The reaction mixture was extracted with ether (4 x 10 mL). The combined organic layer was dried over MgSO₄. Removal of the solvent gave crude product. Purification of the product by flash chromatography (5% Et₂O/Pentanes) afforded a yellow oil 35 mg (84%). IR: 2949, 2921, 2847, 1580, 1503, 1442, 1392, 1221 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.50 (s, 1H), 4.91-4.88 (m, 1H), 3.74 (q, *J* = 8.7 Hz, 1H), 3.30 (Hex, *J* = 7.4 Hz, 1H), 2.25 (s, 3H), 2.20-2.19 (m, 1H), 2.11-2.00 (m, 3H), 1.73 (d, *J* = 1.2 Hz, 3H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.39-1.36 (m, 1H), 1.28-1.20 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 5.9 Hz, 3H), 0.98-0.95 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 149.2, 147.8, 136.2, 132.1, 130.6, 129.8, 129.7, 129.2, 45.0, 39.5, 36.9, 33.3, 30.9, 28.1, 26.9, 25.4, 22.7, 20.1, 17.5, 17.1; HRMS Calcd for C₂₀H₂₇NO₃Li 336.2151; Found 336.2148. $[\alpha]_D^{25} = +298.0$ (c 0.4, CHCl₃).

Pseudopteroxazole (1). To a stirred solution of **14** (25 mg, 0.063 mmol) in 90% MeOH (10 mL) at room temperature was added solid NH_4Cl (30 mg), followed by Zinc dust (100 mg), and the reaction mixture was stirred for 1 hour. The mixture was filtered through Celite, washing with MeOH. The MeOH solution was concentrated under reduce pressure, washed with water, extracted with Et_2O (4 x 10 mL), dried over MgSO_4 . Removal of the combined organic solvent afforded the crude aniline, which was used in next step without purification. The aniline was dissolved in trimethyl orthoformate (2 mL) and cat. TSOH. The reaction mixture was stirred at room temperature for 1h. The solvent was removed by reduced pressure, then the remaining was removed with benzene under reduce pressure too. Purification of the crude product by flash chromatography (20% Et_2O /Pentanes) afforded a pale yellow oil 12.7 mg (65%). IR: 2954, 2917, 2835, 1666, 1511, 1450, 1368 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.98 (s, 1H), 4.97 (d, $J = 9.3\text{Hz}$, 1H), 3.95 (q, $J = 8.8\text{ Hz}$, 1H), 3.27–3.20 (m, 1H), 2.44 (s, 3H), 2.28–2.11 (m, 4H), 1.78 (d, $J = 0.9\text{ Hz}$, 3H), 1.67 (d, $J = 0.9\text{ Hz}$, 3), 1.45 (d, $J = 6.8\text{ Hz}$, 3H), 1.44–1.38 (m, 1H), 1.12–1.03 (m, 1H), 1.32–1.25 (m, 2H), 1.12–1.07 (m, 1H), 1.05 (d, $J = 5.9\text{ Hz}$, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 151.0, 147.1, 137.8, 136.7, 134.7, 130.6, 128.8, 126.6, 122.4, 44.7, 40.0, 36.4, 34.5, 32.2, 30.2, 28.0, 25.4, 22.2, 19.8, 17.6, 13.5; HRMS Calcd for $\text{C}_{21}\text{H}_{27}\text{NOLi}$ 316.2258; Found 316.2270. $[\alpha]_{\text{D}}^{25} = +124.8$ (c 0.5, CHCl_3).

9

Current Data Parameters
NAME XH-VII-44-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20031216
Time 19.15
INSTRUM DRX500
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 57344
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.180151 Hz
AQ 2.7754996 sec
RG 64
DM 48.400 usec
DE 6.00 usec
TE 296.7 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 13.25 usec
PL1 -3.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300115 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40

Current Data Parameters
 NAME XH-VII-44-A1
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20031216
 Time 19.21
 INSTRUM DRX500
 PROBHD 5 mm Multinuc1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 232
 DS 4
 SMH 39681.812 Hz
 FIDRES 0.605496 Hz
 AQ 0.8258188 sec
 RG 16384
 DM 12.600 usec
 DE 6.00 usec
 TE 298.0 K
 D1 2.0000000 sec
 d11 0.0300000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 8.10 usec
 PL1 3.00 dB
 SF01 125.7713108 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 88.00 usec
 PL2 0.00 dB
 PL12 21.00 dB
 SF02 500.1320005 MHz

F2 - Processing Parameters
 SI 32768
 SF 125.7577947 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 15.00 cm
 F1P 200.000 ppm
 F1 25151.56 Hz
 F2P -10.000 ppm
 F2 -1257.58 Hz
 PPMCM 10.50000 ppm/cm
 HZCM 1320.45691 Hz/cm

Current Data Parameters

NAME	EXPNO	PROCNO
XH-VII-65-A1	1	1

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AG	RG	DW	DE	TE	D1
20040102	17.03	DRX500	5 mm Multinuc1	zg30	57344	CDCl3	16	2	10330.578 Hz	0.180151 Hz	2.7754996 sec	35.9	48.400 usec	6.00 usec	296.7 K	1.00000000 sec

==== CHANNEL f1 =====

NUC1	P1	PL1	SFO1
¹ H	13.25 usec	-3.00 dB	500.1330885 MHz

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
32768	500.1300131 MHz	EM	0	0.20 Hz	0	1.40

1D NMR plot parameters

CX	CY	F1P	F1	F2P	F2	PPMCM	HZCM
20.00 cm	12.50 cm	8.000 ppm	4001.04 Hz	-0.500 ppm	-250.07 Hz	0.42500 ppm/cr	212.55525 Hz/cm

ppm

144.905
138.371
132.688
131.377
129.528
128.479
126.178
125.292
115.306
110.722

77.257
77.001
76.748

55.373

39.696
33.426
32.963
32.308
31.172
27.603
25.337
22.490
19.482
17.558

Current Data Parameters
NAME XH-VII-65-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20040102
Time 17.10
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 117
DS 4
SWH 39681.812 Hz
FIDRES 0.605496 Hz
AQ 0.8258188 sec
RG 16384
DM 12.600 usec
DE 5.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec

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

NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SF01 125.7713108 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SF02 500.1320005 MHz

F2 - Processing parameters

SI 32768
SF 125.7578032 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
CY 8.00 cm
F1P 200.000 ppm
F1 25151.56 Hz
F2P -10.000 ppm
F2 -1257.58 Hz
PPMCM 10.50000 ppm/cm
HZCM 1320.45691 Hz/cm

10

Current Data Parameters
NAME XH-XI-22-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050418
Time 15.22

INSTRUM drx300
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 64
DM 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.05 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.130062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.30

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 9.000 ppm
F1 2701.17 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PNUCM 0.47500 ppm/cm
HZCM 142.56175 Hz/cm

10

Current Data Parameters
NAME XH-XI-22-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050418
Time 15.23

INSTRUM drx300
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 4

SMH 18832.393 Hz
FIDRES 0.267360 Hz
AQ 1.7400308 sec

RG 22528
DM 26.550 usec
DE 6.00 usec

TE 297.1 K
D1 1.79999995 sec
d11 0.03000000 sec
d31 0.00000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.50 usec
PL1 5.00 dB
SF01 75.4760107 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 25.60 dB
SF02 300.1312005 MHz

F2 - Processing Parameters
SI 32768
SF 75.4677565 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

10 NMR plot parameters
CX 20.00 cm
CY 11.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PRMCM 10.50000 ppm/cm
HZCM 792.41144 Hz/cm

¹H NMR

Current Data Parameters

NAME	XH-VI-24-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050421
Time	21.49
INSTRUM	gpc250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	256
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.0000000 sec
P1	8.25 use
SFO1	250.1315321 MHz
NUCLEUS	¹ H

F2 - Processing parameters

SI	16384
SF	250.130073 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	8.00 cm
F1P	9.000 ppm
F1	2251.17 Hz
F2P	-0.500 ppm
F2	-125.07 Hz
PPMCM	0.47500 ppm
HZCM	118.81175 Hz/

¹³C NMR

Current Data Parameters
NAME XH-VI-25-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050421

Time 21.32
INSTRUM arx250
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 36864
SOLVENT CDCl3
NS 117
DS 4
SWH 17241.379 Hz
FIDRES 0.467702 Hz
AQ 1.0691060 sec
RG 22800
DM 29.000 use
DE 41.43 use
TE 300.0 K
D12 0.000200 sec
DLS 23.05 dB
CPDPRG waltz16
P31 103.00 use
D1 2.0000000 sec
P1 6.00 use
SFO1 62.9023694 MHz
NUCLEUS 13C
D11 0.0300000 sec

F2 - Processing parameters

SI 32768
SF 62.8952434 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
CY 10.00 cm
F1P 200.000 ppm
F1 12579.05 Hz
F2P -10.000 ppm
F2 -628.95 Hz
PWCW 10.50000 ppm
HZCW 660.40009 Hz/

¹H NMR

Current Data Parameters
NAME XH-XI-27-2-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050505
Time 0.17

INSTRUM drx300
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SMH 6172.839 HZ
FIDRES 0.188380 HZ
AQ 2.6542580 sec
RG 64
DM 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 7.05 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300064 MHz
MDW EM
SSB 0
LB 0.30 HZ
GB 0
PC 1.30

1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 9.000 ppm
F1 2701.17 HZ
F2P -0.500 ppm
F2 -150.06 HZ
PPMCM 0.47500 ppm/cm
HZCM 142.56175 HZ/cm

13C NMR

Current Data Parameters
NAME XH-XI-27-2-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050505
Time 0.23

INSTRUM drx300
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8752
DS 4
SWH 18832.393 HZ
FIDRES 0.287360 HZ
AQ 1.7400308 sec
RG 22528
DM 26.550 usec
DE 6.00 usec
TE 297.1 K
D1 1.7999995 sec
d11 0.03000000 sec
D31 0.00000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.50 usec
PL1 5.00 dB
SFO1 75.4760107 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 25.50 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677502 MHz
WDW EM
SSB 0
LB 1.00 HZ
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 50.00 cm
F1P 200.000 ppm
F1 15093.55 HZ
F2P -10.000 ppm
F2 -754.68 HZ
PPMCM 10.50000 ppm/cm
HZCM 792.4138 HZ/cm

Current Data Parameters
 NAME XH-XI-36-A1
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050510
 Time 22.21
 INSTRUM DRX500
 PROBD 5 mm Multinuc1
 PULPROG zg30
 TD 57344
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.180151 Hz
 AQ 2.775496 sec
 RG 64
 DW 48.400 usec
 DE 6.00 usec
 TE 296.7 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 13.25 usec
 PL1 -3.00 dB
 SF01 500.130085 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300134 MHz
 MDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P -0.500 ppm
 F2 -250.07 Hz
 PPMCM 0.47500 ppm/cr
 HZCM 237.56175 Hz/cm

6

Current Data Parameters
NAME XH-XI-36-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050510
Time 22.30
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 204
DS 4
SMH 39681.812 Hz
FIDRES 0.605496 Hz
AQ 0.8258188 sec
RG 16384
DW 12.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7713108 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577947 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 200.000 ppm
F1 25151.56 Hz
F2P -10.000 ppm
F2 -1257.58 Hz
PPMCM 10.50000 ppm/cm
HZCM 1320.45691 Hz/cm

13

Current Data Parameters
NAME XH-XI-43-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050511

Time 16.33

INSTRUM apx250

PROBHD 5 mm QNP 1H

PULPROG zg30

TD 32768

SOLVENT CDCl3

NS 16

DS 2

SMH 5208.333 Hz

FIDRES 0.158946 Hz

AQ 3.1457779 sec

RG 256

DW 96.000 use

DE 137.14 use

TE 300.0 K

D1 1.00000000 sec

P1 8.70 use

SF01 250.1315321 MHz

NUCLEUS 1H

F2 - Processing parameters

SI 16384

SF 250.1300073 MHz

WDW EM

SSB 0

LB 0.20 Hz

GB 0

PC 1.50

1D NMR plot parameters

CX 20.00 cm

CY 12.50 cm

F1P 9.000 ppm

F1 2251.17 Hz

F2P -0.500 ppm

F2 -125.07 Hz

PPMCM 0.47500 ppm

HZCM 118.81175 Hz

13

Current Data Parameters
NAME XH-XI-43-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050511
Time 16.35

INSTRUM arx250
PROBHD 5 mm QNP 1H
PULPROG zgpg30

TD 36864
SOLVENT CDCl3
NS 433

DS 4
SWH 17241.379 HZ
FIDRES 0.467702 HZ

RG 22800
AQ 1.0691060 sec
RG 22800

DW 29.000 use
DE 41.43 use
TE 300.0 K

D12 0.00002000 sec
DL5 23.00 dB
CPDPRG waltz16

P31 103.00 use
D1 2.00000000 sec
P1 6.00 use

SF01 62.9023694 MHz
NUCLEUS 13C
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 62.8952419 MHz

WDW EM
SSB 0
LB 1.00 HZ

GB 0
PC 1.40

10 NMR plot parameters
CX 20.00 cm
CY 12.50 cm

F1P 200.000 ppm
F1 12579.05 HZ
F2P -10.000 ppm

F2 -628.95 HZ
PPMCM 10.50000 ppm
HZCM 650.40002 HZ/

Current Data Parameters

NAME	XH-XI-44-5
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050519
Time	14.23
INSTRUM	DRX500
PROBHD	5 mm Multinuc1
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
DS	16
NS	2
SMH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	64
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1 1H

P1	13.25 usec
PL1	-3.00 dB
SFO1	500.130085 MHz

F2 - Processing parameters

SI	32768
SF	500.1300134 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	8.00 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	-0.500 ppm
F2	-250.07 Hz
PPMCM	0.52500 ppm/cr
HZCM	262.56824 Hz/cm

ppm

149.232
147.767
136.204
132.062
130.598
129.827
129.729
129.210

77.251
76.998
76.742

45.006
39.524
36.910
33.281
30.914
28.084
26.886
25.444
22.737
20.070
17.551
17.137

Current Data Parameters
NAME XH-XI-44-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050513

Time 8.32

INSTRUM DRX500

PROBHD 5 mm Multinuc1

PULPROG zgpg30

TD 65536

SOLVENT CDCl3

NS 203

DS 4

SWH 39681.812 Hz

FIDRES 0.605496 Hz

AQ 0.8258188 sec

RG 16384

DW 12.600 usec

DE 5.00 usec

TE 298.0 K

D1 2.00000000 sec

d11 0.03000000 sec

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

NUC1 13C

P1 8.10 usec

PL1 3.00 dB

SFO1 125.7713108 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16

NUC2 1H

PCPD2 88.00 usec

PL2 0.00 dB

PL12 21.00 dB

SFO2 500.1320005 MHz

F2 - Processing parameters

SI 32768

SF 125.7577935 MHz

WDW EM

SSB 0

LB 1.00 Hz

GB 0

PC 1.40

10 NMR plot parameters

CX 20.00 cm

CY 25.00 cm

F1P 200.000 ppm

F1 25151.56 Hz

F2P -10.000 ppm

F2 -1257.58 Hz

PPMCM 10.50000 ppm/cm

HZCM 1320.45691 Hz/cm

Current Data Parameters
 NAME XH-XI-48-A1
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050516
 Time 15.30
 INSTRUM DRX500
 PROBHD 5 mm Multinuc1
 PULPROG zg30
 TD 57344
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 10330.578 Hz
 FIDRES 0.180151 Hz
 AQ 2.7754996 sec
 RG 64
 DW 48.400 usec
 DE 6.00 usec
 TE 296.7 K
 D1 1.00000000 sec

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

NUC1 1H
 P1 13.25 usec
 PL1 -3.00 dB
 SFO1 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300134 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P -0.500 ppm
 F2 -250.07 Hz
 PPMCM 0.47500 ppm/cr
 HZCM 237.56175 Hz/cm

Current Data Parameters

NAME	XI-XI-48-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050516
Time	15.39
INSTRUM	DRX500
PROBHD	5 mm Multinuc1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	6706
DS	4
SMH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	16384
DW	12.600 usec
DE	5.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SFO1	125.7713108 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	500.1320005 MHz

F2 - Processing parameters

SI	32768
SF	125.7577923 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	200.00 cm
F1P	200.000 ppm
F1	25151.56 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCM	10.50000 ppm/cm
HZCM	1320.45679 Hz/cm