Microwave Assisted Preparation of Aryltetrazoleboronate Esters

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General. Reagents were purchased from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were collected on either a Bruker-Biospin, Inc. DPX 300 MHz, DMX 400 MHz, DRX 500 MHz, or DMX 600 MHz NMR spectrometer. Chemical shift are reported with respect to tetramethylsilane (TMS) $\delta_{\text{H,C}} = 0.0$ ppm. Unless otherwise noted, spectra were acquired at ambient temperature using DMSO- d_6 or CDCl_3 . HPLC / mass spectral analyses were performed on an 1100 series Agilent HPLC driven Micromass electrospray TOF instrument utilizing a YMC column, 2 mm x 50 mm, 3 μm C18, (or Waters X-Terra MS 2.1 mm x 30 mm, 2.5 μm C18) 0.7 mL/min, 3 min gradient, 5 min run from 95% aqueous media (0.05% formic acid) to 95% CH_3CN (0.05% formic acid), 190 to 360 nm PDA detection. Microwave heating was performed with a single-mode cavity CEM Explorer utilizing 10 mL glass pressure vessels fitted with teflon-lined septa.

2-Methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzonitrile (5f). To a solution of 4-bromo-2-methylbenzonitrile (294 mg, 1.50 mmol) in THF (15 mL) at -78°C was added 1.7 M *t*-butyl lithium (1.94 mL, 3.30 mmol), dropwise. The mixture was stirred for 15 min at -78°C and 2-isopropoxy-pinacol borolane (0.61 mL, 3.00 mmol) was added. The reaction mixture was stirred at -78°C for 2 h and allowed to warm to room temperature then quenched with saturated aqueous NH_4Cl . The layers were separated and the aqueous layer was extracted with ether (3 X 25 mL). The combined organic layers were washed with brine, dried (MgSO_4), filtered, and concentrated. The residue was purified by Florisil column chromatography to furnish **5f** (160 mg, 44%). ^1H NMR (DMSO- d_6): δ 1.31 (s, 12H), 2.49 (s, 3H), 7.61 (d, 1H, $J = 7.6$ Hz), 7.73 (s, 1H), 7.76 (d, 1H, $J = 7.6$ Hz); ^{13}C NMR (DMSO- d_6): δ 19.6, 24.6, 84.2, 114.1, 117.7, 131.7, 131.9, 135.8, 140.6.

[2-Methoxy-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-acetonitrile (5g). To 3-bromo-2-methoxyphenyl acetonitrile (678 mg, 3.00 mmol) in DMF (18 mL) was added KOAc (883 mg, 9.00 mmol), bis(pinacolato) diboron (838 mg, 3.30 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (73 mg, 0.09 mmol). The reaction mixture was stirred at 80°C for 16 h. The mixture was filtered through celite and the filtrate was concentrated. The residue was by Florisil column chromatography to furnish **5g** (594 mg, 73%). ^1H NMR (DMSO- d_6): δ 1.29 (s, 12H), 3.87 (s, 5H), 7.07 (d, 1H, $J = 8.7$ Hz), 7.66 (s, 2H), 7.6 (s, 1H); ^{13}C NMR (DMSO- d_6): δ 18.1, 25.0, 56.1, 83.9, 111.0, 119.0, 119.1, 135.9, 136.7, 159.7.

2-Hydroxy-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzonitrile (5h). To 5-bromo-2-hydroxybenzonitrile (594 mg, 3.00 mmol) in DMF (18 mL) was added KOAc (883 mg, 9.00 mmol), bis(pinacolato) diboron (838 mg, 3.30 mmol), and Pd(dppf)Cl₂ (73 mg, 0.09 mmol). The reaction mixture was stirred at 80 °C for 16 h. The mixture was filtered through celite and the filtrate was concentrated. The residue was purified by Florisil column chromatography to furnish **5h** (437 mg, 60%). ¹H NMR (DMSO-*d*₆): δ 1.28 (s, 12H), 7.02 (d, 1H, *J* = 8.3 Hz), 7.73 (s, 1H), 7.76 (s, 1H); ¹³C NMR (DMSO-*d*₆): δ 24.5, 83.7, 99.0, 115.9, 116.6, 139.6, 140.4, 162.7.

2-Fluoro-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzonitrile (5i). To a 80 mL microwave reaction vessel containing 5-bromo-2-fluorobenzonitrile (600 mg, 3.00 mmol) in DME (18 mL) was added KOAc (883 mg, 9.00 mmol), bis(pinacolato) diboron (838 mg, 3.30 mmol), and Pd(dppf)Cl₂ (73 mg, 0.09 mmol). The reaction was irradiated (μW) for 10 min at 150 °C. The mixture was filtered through celite and the filtrate was concentrated. The residue was purified by Florisil column chromatography to furnish **5i** (160 mg, 22%). ¹H NMR (DMSO-*d*₆): δ 1.31 (s, 12H), 7.55 (m, 1H), 7.98-8.11 (m, 2H); ¹³C NMR (DMSO-*d*₆): δ 24.9, 84.8, 100.7, 114.0, 116.6, 140.1, 142.1, 163.0, 166.4.

5-[2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-1H-tetrazole (6a). To 2-cyanophenyl boronic acid, pinacol ester (344 mg, 1.50 mmol) was added DME (2.25 mL), azidotrimethylsilane (398 μL, 3.00 mmol), and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μW) for 10 min at 150 °C. After cooling to room temperature, additional azidotrimethylsilane (398 μL, 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μW) for 10 min at 150 °C. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH₂Cl₂/0.025% HOAc/heptane → 10% methanol/CH₂Cl₂ to furnish **6a** (265 mg, 65%(79%)). 2-cyanophenyl boronic acid, pinacol ester (47 mg, 0.21 mmol) was also obtained as recovered starting material. ¹H NMR (400 MHz, CDCl₃): δ 1.34 (s, 12H), 7.58 (dt, 1H, *J* = 1.3 and 7.6 Hz), 7.70 (dt, 1H, *J* = 1.2 and 7.9 Hz), 8.12 (dd, 1H, *J* = 1.0 and 7.6 Hz), 8.62 (d, 1H, *J* = 7.7 Hz); ¹³C NMR (400 MHz, CDCl₃): δ 25.1, 75.6, 85.7, 128.5, 129.8, 130.7, 131.9, 137.2, 156.4; HRMS *m/z* (M + H)⁺ calcd for C₁₃H₁₈BN₄O₂ 273.1523, found 273.1525.

5-[3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-1H-tetrazole (6b). To 3-cyanophenylboronic acid (220 mg, 1.50 mmol) was added DME (1.5 mL), pinacol (186 mg, 1.58 mmol), and MgSO_4 (660 mg). The mixture was agitated at room temperature for 18 h, then filtered and rinsed with DME (0.75 mL). To the filtrate was added azidotrimethylsilane (398 μL , 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. After cooling to room temperature, additional azidotrimethylsilane (398 μL , 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH_2Cl_2 /heptane $\rightarrow$ 10% methanol/ CH_2Cl_2 to furnish **6b** (338 mg, 83%). ^1H NMR ($\text{DMSO}-d_6$): δ 1.34 (s, 12H), 7.58 (t, 1H, $J = 7.6$ Hz), 7.80 (d, 1H, $J = 7.2$ Hz), 8.16 (d, 1H, $J = 7.9$ Hz), 8.37 (s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.7, 83.9, 125.6, 128.8, 129.6, 132.6, 136.1, 156.5; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{BN}_4\text{O}_2$ 273.1523, found 273.1519.

5-[4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-1H-tetrazole (6c). To 4-cyanophenylboronic acid (220 mg, 1.50 mmol) was added DME (1.5 mL), pinacol (186 mg, 1.58 mmol), and MgSO_4 (660 mg). The mixture was agitated at room temperature for 18 h, then filtered and rinsed with DME (0.75 mL). To the filtrate was added azidotrimethylsilane (398 μL , 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. After cooling to room temperature, additional azidotrimethylsilane (398 μL , 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH_2Cl_2 /heptane $\rightarrow$ 10% methanol/ CH_2Cl_2 to furnish **6c** (342 mg, 84%). ^1H NMR ($\text{DMSO}-d_6$): δ 1.32 (s, 12H), 7.84 (d, 2H, $J = 7.9$ Hz), 8.06 (d, 2H, $J = 7.9$ Hz); ^{13}C NMR ($\text{DMSO}-d_6$): δ 25.3, 84.3, 126.4, 129.2, 135.4, 157.2; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{BN}_4\text{O}_2$ 273.1523, found 273.1530.

5-[3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzyl]-1H-tetrazole (6d). To (3-cyanomethylphenyl) boronic acid, pinacol ester (365 mg, 1.50 mmol) was added DME (2.25 mL), azidotrimethylsilane (398 μL , 3.00 mmol), and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. After cooling to room temperature, additional azidotrimethylsilane (398 μL , 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH_2Cl_2 /heptane $\rightarrow$ 10% methanol/ CH_2Cl_2 to furnish **6d** (301 mg, 70%). ^1H NMR ($\text{DMSO}-d_6$): δ 1.29 (s, 12H), 4.29 (s, 2H), 7.32-7.42 (m, 2H), 7.57 (d, 1H, $J = 7.0$ Hz), 7.59 (s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.6, 28.8, 83.7, 128.3, 131.8, 133.0, 134.6, 135.6, 155.5; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{BN}_4\text{O}_2$ 287.1679, found 287.1689.

5-[4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzyl]-1H-tetrazole (6e). To (4-cyanomethylphenyl) boronic acid, pinacol ester (365 mg, 1.50 mmol) was added DME (2.25 mL), azidotrimethylsilane (398 μ L, 3.00 mmol), and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. After cooling to room temperature, additional azidotrimethylsilane (398 μ L, 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH_2Cl_2 /heptane $\rightarrow$ 10% methanol/ CH_2Cl_2 to furnish **6e** (301 mg, 65%). ^1H NMR ($\text{DMSO}-d_6$): δ 1.28 (s, 12H), 4.28 (s, 2H), 7.27 (d, 2H, $J = 7.9$ Hz), 7.63 (d, 2H, $J = 7.9$ Hz); ^{13}C NMR ($\text{DMSO}-d_6$): δ 25.8, 30.3, 84.5, 129.0, 135.6, 140.5, 159.5; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{BN}_4\text{O}_2$ 287.1679, found 287.1670.

5-[2-Methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-1H-tetrazole (6f). To compound **5f** (365 mg, 1.50 mmol) was added DME (2.25 mL), azidotrimethylsilane (398 μ L, 3.00 mmol), and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. After cooling to room temperature, additional azidotrimethylsilane (398 μ L, 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 25% CH_2Cl_2 /heptane $\rightarrow$ 10% methanol/ CH_2Cl_2 to furnish **6f** (373 mg, 87%). ^1H NMR ($\text{DMSO}-d_6$): δ 1.31 (s, 12H), 2.54 (s, 3H), 7.58 (d, 1H, $J = 7.8$ Hz), 7.64 (s, 1H), 7.80 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR ($\text{DMSO}-d_6$): δ 21.4, 25.0, 84.1, 128.8, 130.4, 132.1, 136.0, 137.5, 158.2; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{BN}_4\text{O}_2$ 287.1679, found 287.1685.

5-[2-Methoxy-5-(boronic acid)-benzyl]-1H-tetrazole (6g). To compound **5g** (136 mg, 0.50 mmol) was added DME (1.00 mL), azidotrimethylsilane (134 μ L, 1.00 mmol), and dibutyltin oxide (12 mg, 0.05 mmol). The mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. After cooling to room temperature, additional azidotrimethylsilane (134 μ L, 1.00 mmol) and dibutyltin oxide (12 mg, 0.05 mmol) were added and the mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. The reaction mixture was concentrated and the residue was taken up in ether. The ether was extracted with 2N NaOH (2 X 6 mL) and then the combined aqueous layers were washed with ether. The aqueous layer was acidified to pH 3-4 with 6N HCl and the resulting precipitate was collected to furnish **6g** (109 mg, 93%). ^1H NMR ($\text{DMSO}-d_6$): δ 3.77 (s, 3H), 4.17 (s, 2H), 6.98 (d, 1H, $J = 8.3$ Hz), 7.58 (s, 1H), 7.75 (d, 1H, $J = 8.3$ Hz); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.4, 55.7, 110.4, 122.9, 125.9, 135.6, 136.6, 155.2, 159.0; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_9\text{H}_{12}\text{BN}_4\text{O}_3$ 235.1002, found 235.1007.

5-[2-Hydroxy-5-(boronic acid)-phenyl]-1H-tetrazole (6h). To compound **5h** (122 mg, 0.50 mmol) was added DME (1.00 mL), azidotrimethylsilane (134 μ L, 1.00 mmol), and dibutyltin oxide (12 mg, 0.05 mmol). The mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. After cooling to room temperature, additional azidotrimethylsilane (134 μ L, 1.00 mmol) and dibutyltin oxide (12 mg, 0.05 mmol) were added and the mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. The reaction mixture was concentrated and the residue was taken up in ether. The ether was extracted with 2N NaOH (2 X 6 mL) and then the combined aqueous layers were washed with ether. The aqueous layer was acidified to pH 3-4 with 6N HCl and the resulting precipitate was collected to furnish **6h** (58 mg, 56%). ^1H NMR (DMSO- d_6): δ 3.45 (br, 1H), 7.02 (s, 1H), 7.82 (s, 1H), 8.46 (s, 1H); ^{13}C NMR (DMSO- d_6): δ 109.8, 115.3, 124.9, 135.7, 138.4, 151.8, 156.9; HRMS m/z (M + H) $^{+}$ calcd for $\text{C}_7\text{H}_8\text{BN}_4\text{O}_3$ 207.0689, found 207.0694.

5-[2-Fluoro-5-(boronic acid)-phenyl]-1H-tetrazole (6i). To compound **5i** (124 mg, 0.50 mmol) was added DME (1.00 mL), azidotrimethylsilane (134 μ L, 1.00 mmol), and dibutyltin oxide (12 mg, 0.05 mmol). The mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. After cooling to room temperature, additional azidotrimethylsilane (134 μ L, 1.00 mmol) and dibutyltin oxide (12 mg, 0.05 mmol) were added and the mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. The reaction mixture was concentrated and the residue was taken up in ether. The ether was extracted with 2N NaOH (2 X 6 mL) and then the combined aqueous layers were washed with ether. The aqueous layer was acidified to pH 3-4 with 6N HCl and the resulting precipitate was collected to furnish **6i** (88 mg, 85%). ^1H NMR (DMSO- d_6): δ 7.48 (t, 1H, J = 9.7 Hz), 8.06 (t, 1H, J = 7.2 Hz), 8.37 (br, 2H), 8.51 (d, 1H, J = 7.8 Hz); ^{13}C NMR (DMSO- d_6): δ 111.8, 115.7 (d, $^2J_{\text{CF}}$ = 19.4 Hz), 131.5, 136.2, 139.3 (d, $^3J_{\text{CF}}$ = 8.3 Hz), 150.9, 160.4 (d, $^1J_{\text{CF}}$ = 254.5 Hz); HRMS m/z (M + H) $^{+}$ calcd for $\text{C}_7\text{H}_7\text{BFN}_4\text{O}_2$ 209.0646, found 209.0654.

5-[3-Nitro-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-1H-tetrazole (6j). To 4-cyano-2-nitrophenyl boronic acid (288 mg, 1.50 mmol) was added DME (1.5 mL), pinacol (186 mg, 1.58 mmol), and MgSO_4 (660 mg). The mixture was agitated at room temperature for 18 h, then filtered and rinsed with DME (0.75 mL). To the filtrate was added azidotrimethylsilane (398 μ L, 3.00 mmol), and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. After cooling to room temperature, additional azidotrimethylsilane (398 μ L, 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μ W) for 10 min at 150 $^{\circ}$ C. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH_2Cl_2 /0.025% HOAc/heptane $\rightarrow$ 10% methanol/ CH_2Cl_2 to furnish **6j** (265 mg, 56%). ^1H NMR (300 MHz, DMSO- d_6): δ 1.37 (s, 12H), 7.88 (d, 1H, J = 7.7 Hz), 8.49 (d, 1H, J = 7.6 Hz), 8.81 (s, 1H); ^{13}C NMR (300 MHz, DMSO- d_6): δ 24.7, 84.9, 121.6, 127.5, 132.5, 134.7, 151.5, 155.2; HRMS m/z (M + H) $^{+}$ calcd for $\text{C}_{13}\text{H}_{17}\text{BN}_5\text{O}_4$ 318.1374, found 318.1369.

3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-N-[2-(1H-tetrazol-5-yl)-ethyl]-benzamide (6k). To 3-(2-cyanoethylaminocarbonyl) phenyl boronic acid (327 mg, 1.50 mmol) was added DME (1.5 mL), pinacol (186 mg, 1.58 mmol), and MgSO_4 (660 mg). The mixture was agitated at room temperature for 18 h, then filtered and rinsed with DME (0.75 mL). To the filtrate was added azidotrimethylsilane (398 μL , 3.00 mmol), and dibutyltin oxide (37 mg, 0.15 mmol). The mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. After cooling to room temperature, additional azidotrimethylsilane (398 μL , 3.00 mmol) and dibutyltin oxide (37 mg, 0.15 mmol) were added and the mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. The reaction solution was loaded onto a Florisil column (35 g) and eluted with 20% CH_2Cl_2 /0.025% HOAc/heptane $\rightarrow$ 20% methanol/ CH_2Cl_2 to furnish **6k** (476 mg, 93%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.32 (s, 12H), 2.95 (t, 2H, $J = 7.4$ Hz), 3.55 (dt, 2H, $J = 5.9$ and 7.3 Hz), 7.48 (dd, 1H, $J = 7.6$ and 7.6 Hz), 7.80 (d, 1H, $J = 7.3$ Hz), 7.96 (d, 1H, $J = 7.8$ Hz), 8.15 (s, 1H), 8.72 (t, 1H, $J = 5.5$ Hz); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$): δ 25.1, 25.6, 39.2, 84.0, 128.1, 129.8, 130.2, 133.3, 134.3, 137.2, 158.1, 166.5; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{16}\text{H}_{23}\text{BN}_5\text{O}_3$ 344.1894, found 344.1884.

N-[3'-(1H-Tetrazol-5-yl)-biphenyl-4-yl]-acetamide (7). To 4-bromoacetanilide (214 mg, 1.00 mmol) in ethanol (2 mL) was added K_2CO_3 (207 mg, 1.50 mmol) in H_2O (0.4 mL), 5-[5-(boronic acid)-phenyl]-1H-tetrazole (190 mg, 1.00 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (41 mg, 0.05 mmol). The reaction mixture was irradiated (μW) for 6 min at 150 $^\circ\text{C}$. The mixture was concentrated and the resulting residue was purified by flash chromatography (0-10% methanol/ CH_2Cl_2) to furnish **7** (207mg, 74%). ^1H NMR ($\text{DMSO}-d_6$): δ 2.10 (s, 3H), 7.77-7.66 (m, 5H), 7.75 (d, 1H, $J = 7.9$ Hz), 7.87 (d, 1H, $J = 7.7$ Hz), 8.01 (m, 1H), 8.32 (s, 1H), 10.12 (s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.0, 120.1, 125.2, 125.4, 127.0, 129.5, 130.3, 133.4, 139.3, 140.7, 155.0, 168.4; HRMS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{N}_5\text{O}$ 280.1198, found 280.1188.

(4). To 4-cyanophenyl boronic acid (100 mg, 0.68 mmol) and dibutyltin oxide (169 mg, 0.68 mmol) was added DME (1.0 mL). The mixture was irradiated (μW) for 10 min at 150 $^\circ\text{C}$. After cooling to room temperature, the solution was concentrated to a residue then purified by reverse-phase chromatography (from 90% aqueous media (0.1% TFA) to 90% CH_3CN (0.1% TFA)) to furnish **4** (225 mg, 74%). ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, 2H, $J = 8.0$ Hz), 7.65 (d, 2H, $J = 7.8$ Hz), 1.77-1.61 (m, 8H),

1.43-1.38 (m, 4H), 0.91 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3 ,): δ 13.9, 18.8, 27.3, 27.8, 113.4, 115.7 (q, $J = 288.4$ Hz), 119.0, 132.0, 137.0, 148.8, 161.5 (q, $J = 39.7$ Hz); MS m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{F}_3\text{NO}_2\text{Sn}$ 450.1, found 450.1.

Evaluation of the above reaction before or after reverse phase purification resulted in the acetonitrile adduct being detected by LC/MS analysis (Mass spectral analyses were performed on a Micromass TOF instrument (Hewlett-Packard HPLC driven electrospray MS instrument, Waters X-terra column, 2 mm x 30 mm, 2.5 μm C18, 0.5 mL/min, 3 min gradient, 5 min run from 95% aqueous media (0.1% formic acid) to 95% CH_3CN (0.1% formic acid), 190 to 360 nm PDA detection).

HRMS m/z (M) $^+$ calcd for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{Sn}$ 377.1040, found 377.1028.

X-ray Analysis of Structure (4)

Single crystals of $\text{Sn}(\text{O}_2\text{CCF}_3)(\text{C}_6\text{H}_4\text{CN})(\text{C}_4\text{H}_9)_2(\text{H}_2\text{O})$ are, at -80 ± 2 °C, monoclinic, space group $\text{P}2_1/\text{n}$ with $a = 11.5732(7)$ Å, $b = 13.1817(8)$ Å, $c = 13.4093(8)$ Å, $\beta = 94.826(1)^\circ$, $V = 2038.4(2)$ Å 3 and $Z = 4$ molecules { $d_{\text{calcd}} = 1.519$ gcm $^{-3}$; μ_a (MoK α) = 1.294 mm $^{-1}$ }. A full hemisphere of diffracted intensities (1868 10-second frames with an omega scan width of 0.30°) was measured using graphite monochromated MoK α radiation on a Bruker SMART APEX CCD Single Crystal Diffraction System. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 35mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 6757 reflections. A total of 20878 integrated reflection intensities having $2\theta(\text{MoK}\alpha) < 61.0^\circ$ were produced using the Bruker SAINT; 6026 of these were independent and gave $R_{\text{int}} = 0.033$. The Bruker SHELXTL-PC software package was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL-PC Version 5 software package. Final agreement factors at convergence are: R_1 (unweighted, based on F) = 0.029 for 5418 independent absorption-corrected reflections having $2\theta(\text{MoK}\alpha) < 61.0^\circ$ and $I > 2\sigma(I)$; R_1 (unweighted, based on F) = 0.032 and wR_2 (weighted, based on F^2) = 0.082 for all 6026 independent absorption-corrected reflections having $2\theta(\text{MoK}\alpha) < 61.0^\circ$.

The $-\text{CF}_3$ group is disordered with two preferred orientations about the $\text{C}_8\text{-C}_9$ bond. The major and minor rotational conformers of the $-\text{CF}_3$ group are present in the lattice 60% and 40% of the time, respectively. The structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms except the three minor-occupancy fluorine sites (F_1 , F_2 , and F_3) associated with the alternate rotational conformation of the disordered $-\text{CF}_3$ group. All hydrogen atoms were located from a difference Fourier synthesis. The three minor-occupancy fluorines (F_1 , F_2 , and F_3) and all hydrogen atoms were included in the structural model as individual isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles.

SC-15312-130

Current Data Parameters
NAME 500.13012-1302
EXNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20/02/03
Time 15:21
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 14
DS 2
SWH 10360.575 Hz
FIDRES 0.157632 Hz
AQ 3.1719223 sec
RG 57
WB 40.400 uspc
DE 5.00 uspc
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.50 uspc
PL1 0.00 dB
SFO1 500.130125 MHz

F2 - Processing parameters
SI 32768
SF 500.130125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
FIP 9.500 cm
F1 4791.24 Hz
F2 -250.07 Hz
FREQH 0.05455 GHz/cm
HZH 227.33103 Hz/cm

138
SC-15312-135

Current Data Parameters
NAME 500_Apr30-2002
EXNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020430
Time 10:32
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2049
DS 4
SWH 31446.541 Hz
FIDRES 0.47936 Hz
AQ 1.0420724 sec
RG 1440 2
DM 15.500 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.70 usec
PL1 5.00 dB
SFO1 125.7715719 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 6.00 dB
PL12 24.00 dB
PL13 27.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
FAP 215.000 DDM
F1 27037.92 Hz
F2p -5.000 DDM
F2 -628.79 Hz
PDMCH 11.00000 GDM/cm
HZCM 1303.3500 Hz/cm

mjs 10217_59

Current Data Parameters
NAME R4_Sep24-2002
EXPNO 360
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020924
Time 13.45
INSTRUM spect
PROBHD 5 mm Dnl 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 15
DS 2
SWH 6172.039 Hz
FIDRES 0.100360 Hz
AQ 2.0542580 sec
RG 912.3
DM 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing parameters
SI 16384
SF 300.1300007 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
FAP 9.500 ppm
F1 2051.24 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.45455 ppm/cm
HZCM 135.42273 Hz/cm

mjs 10217_59

140.647
135.819
131.889
131.709
117.717
114.119

84.199

40.325
40.047
39.769
39.491
39.213
38.935
38.657
24.551
19.625

-0.000

Current Data Parameters
NAME R4_mj16-2003
EXPNO 500
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030616
Time 20.25
INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 10932.363 Hz
FIDRES 0.267360 Hz
AQ 1.7400308 sec
RG 16364
RW 26.550 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.0002000 sec

CHANNEL f1
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 75.476200 MHz

CHANNEL f2
GCPROB2 waltz16
NUC2 1H
PCPO2 100.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677992 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 16225.50 Hz
F2P -5.000 ppm
F2 -377.34 Hz
FPCNCH 11.00000 ppm/cm
HZCH 830.14563 Hz/cm

mjs 18217_165

Current Data Parameters
NAME R4_Mj05-2003
EXPNO 60
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030505
Time 9.32

INSTRUM spect
PROBHD 5 mm Dual 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2

SWH 6172.839 Hz
FIDRES 0.100300 Hz
AQ 2.6542500 sec

RG 512
DM 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing parameters
SI 16384
SF 300.1300000 MHz
KHM EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
F1P 9.500 DPM
F1 2551.24 Hz
F2P -0.500 DPM
F2 -150.06 Hz
PPMCH 0.45455 DPM/cm
HZCM 136.42273 Hz/cm

10217_165

Current Data Parameters
NAME R4_May05-2003
EXPNO 500
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030505
Time 10.10
INSTRUM spect
PROBHD 5 mm Dm1 13
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 10932.309 Hz
FIDRES 0.207360 Hz
AQ 1.7400309 sec
RG 16384
WB 26.550 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 75.4750200 MHz

===== CHANNEL f2 =====
GPROB2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677657 MHz
WDM EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
FAP 215.000 ppm
F1 10225.57 Hz
F2 -5.000 ppm
F2 -377.34 Hz
PPMCM 11.00000 ppm/cm
HZCM 030.14532 Hz/cm

mjs 18217_167

Current Data Parameters
 NAME R4_M012-2003
 EXPNO 60
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030512
 Time 9.12
 INSTRUM spect
 PROBD 5 mm Dui1 13
 PULPROG zg30
 TD 32768
 SOLVENT DMSO
 NS 16
 DS 2
 SMH 6172.899 Hz
 FIDRES 0.109360 Hz
 AQ 2.6542560 sec
 RG 645.1
 DM 01.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 0.00 dB
 SF01 300.1310534 MHz

F2 - Processing parameters
 SI 16384
 SF 300.1300009 MHz
 WDM EN
 SSF 0
 LB 0.30 Hz
 GB 0
 PC 4.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.500 ppm
 F1 2051.24 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.45455 ppm/cm
 HZCM 135.42273 Hz/cm

mjs 18217_167

Current Data Parameters
 NAME R4_M012-2003
 EXPNO 590
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030512
 Time 20.19
 INSTRUM spect
 PROCH0 5 mm Dual 13
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 1024
 DS 4
 SWH 18382.363 Hz
 FIDRES 0.267360 Hz
 AQ 1.7400309 sec
 RB 16364
 DE 26.550 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.50 usec
 PL1 0.00 dB
 SFO1 75.4760200 MHz

===== CHANNEL f2 =====
 GPCPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 0.00 dB
 PL12 18.00 dB
 PL13 18.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677091 MHz
 WDM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

3D NMR plot parameters
 CX 20.00 cm
 F1P 215.000 ppm
 F1 16226.55 Hz
 F2P -377.34 Hz
 F2 11.00000 ppm/cm
 PCNCH 930.14563 Hz/cm

mjs 10217_179

Current Data Parameters
NAME R4_May22-2003
EXPNO 320
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030522
Time 13.08
INSTRUM spect
PROBHD 5 mm QNP1 13
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 6172.039 Hz
FIDRES 0.189380 Hz
AQ 2.6542560 sec
RG 574.7
DM 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing parameters
SI 16384
SF 300.129997 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
F1P 9.500 ppm
F1 2551.24 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCH 0.45455 ppm/cm
HZCM 136.42273 Hz/cm

mjs 10217_179

Current Data Parameters
 NAME R4_10217-2003
 EXPNO 330
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030619
 Time 21.35
 INSTRUM spect
 PROCRD 5 mm Dui1 13
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 1024
 DS 4
 SWH 18332.363 Hz
 FIDRES 0.267360 Hz
 AQ 1.7400300 sec
 RG 16394
 DW 26.550 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.30 usec
 PL1 0.00 dB
 SF01 75.476200 MHz

===== CHANNEL f2 =====
 GPCPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 0.00 dB
 PL12 19.00 dB
 PL13 19.00 dB
 SF02 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.467567 MHz
 WDM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 FXP 215.000 ppm
 F1 16225.57 Hz
 F2P -5.000 ppm
 F2 -377.34 Hz
 FPMCM 11.00000 ppm/cm
 HZCM 830.14532 Hz/cm

15917-2

Current Data Parameters
NAME 1053-Jan23-2004
EXPNO 80
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040123
Time 9.16

INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
FIDRES 0.125099 Hz
AQ 3.9715316 sec
RG 512
DM 60.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.000000000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 8.60 usec
PL1 6.00 dB
SFO1 399.9024656 MHz

F2 - Processing parameters
SI 32768
SF 399.9000094 MHz
KON EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
FAP 9.800 ppm
F1 3919.02 Hz
F2 -0.200 ppm
FPCMH 0.50000 ppm/cm
HZCM 199.95001 Hz/cm

15817-2

Current Data Parameters
 NAME 1053-Jun23-2004
 EXPNO 100
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 2000123
 Time 10:35
 INSTRUM spect
 PROBO 5 mm Multinucl
 PULPROG zgpg30
 TO FSS35
 SOLVENT CDCl3
 NS 64
 DS 4
 SWH 24030.461 Hz
 FIDRES 0.366793 Hz
 AQ 1.3631933 sec
 RG 32755
 DW 20.600 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 13.00 usec
 PL1 2.00 dB
 SF01 100.625505 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 105.00 usec
 PL2 6.00 dB
 PL12 27.73 dB
 PL13 29.00 dB
 SF02 399.9015996 MHz

F2 - Processing parameters
 SI 32755
 SF 100.5943560 MHz
 ICW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 215.000 ppm
 F1 21619.30 Hz
 F2P -5.000 ppm
 F2 -502.77 Hz
 PRNOM 11.0000 ppm/cm
 HZCM 1105.10383 Hz/cm

mjs 18217_45_2

Current Data Parameters
NAME R4_Sep05-2002
EXPNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020905
Time 9.41

INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2

SWH 6172.839 Hz
FIDRES 0.100300 Hz
AQ 2.6542500 sec
RG 645.1
DM 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing Parameters
SI 16384
SF 300.1300001 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
F1P 9.500 ppm
F1 2051.24 Hz
F2P -0.500 ppm
F2 -150.05 Hz
PPHOM 0.45455 ppm/cm
HZCM 136.42273 Hz/cm

MUS 45-2 T=25C

Current Data Parameters
NAME 500_5000-2002
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020906
Time 12.14

INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1745
DS 4
SMH 20243.500 Hz
FIDRES 0.431039 Hz
AQ 1.1600372 sec
RG 1290.2
DM 17.700 usec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 2.00 dB
SF01 125.7709496 MHz

===== CHANNEL f2 =====
CROSSP2 waltz16
NUC2 1H
PCPD2 93.60 usec
PL2 6.00 dB
PL12 27.00 dB
PL13 30.00 dB
SF02 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7575902 MHz
KON EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 100.000 ppm
F1 22636.41 Hz
F2P 0.000 ppm
F2 0.00 Hz
FPCMH 9.00000 ppm/cm
HZCM 1131.32096 Hz/cm

mjs 18217_45_1

Current Data Parameters
NAME R4_Jun19-2003
EXPNO 300
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030619
Time 15.32
INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 6172.039 Hz
FIDRES 0.100300 Hz
AQ 2.6542560 sec
RG 645.1
DM 01.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SF01 300.1310534 MHz

F2 - Processing parameters
SI 16384
SF 300.1300001 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
F1P 9.500 ppm
F1 2651.24 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PCPICH 0.45455 ppm/cm
HZCM 135.42273 Hz/cm

mjs 10217_45_1

Current Data Parameters
 NAME R4_Junit5-2003
 EXPNO 350
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030519
 Time 18.10
 INSTRUM spect
 PROBO 5 mm Dui1 13
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 1024
 DS 4
 SWH 18332.353 Hz
 FIDRES 0.267360 Hz
 AQ 1.7403300 sec
 RB 16354
 DM 26.550 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.30 usec
 PL1 0.00 dB
 SFO1 75.4750200 MHz

===== CHANNEL f2 =====
 CQCPRO2 waltz16
 NUC2 1H
 PCP02 100.00 usec
 PL2 0.00 dB
 PL12 19.00 dB
 PL13 19.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677567 MHz
 WDM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 FLIP 215.000 ppm
 F1 16225.57 Hz
 F2 -5.000 ppm
 F2 -377.34 Hz
 PPMCH 11.00000 ppm/cm
 HZCH 630.14532 Hz/cm

mjs 18217_48_1

Current Data Parameters
 NAME R4_Sep05-2002
 EXPNO 100
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020905
 Time 9.47
 INSTRUM spect
 PROCNO 5 mm Dnl 13
 PULPROG zg30
 TD 32768
 SOLVENT DMSO
 NS 16
 DS 2
 SWH 6172.039 Hz
 FIDRES 0.106300 Hz
 AQ 2.6542500 sec
 RG 645.1
 DW 81.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 0.00 dB
 SF01 300.1310534 MHz

F2 - Processing parameters
 SI 16384
 SF 300.1300000 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 4.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.500 ppm
 F1 2851.24 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 FFCM 0.45/55 ppm/cm
 HZCM 135.42273 Hz/cm

MUS 48-1 T=25C

Current Data Parameters
 NAME 500_Sep05-2002
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020906
 Time 13.33
 INSTRUM spect
 PROBO 5 mm Multinu
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 1213
 DS 4
 SMH 20240.569 Hz
 FIDRES 0.431059 Hz
 AQ 1.1600372 sec
 RG 3251
 DM 17.700 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.50000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 15.00 usec
 PL1 2.00 dB
 SF01 125.7709436 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 93.60 usec
 PL2 6.00 dB
 PL12 27.00 dB
 PL13 30.00 dB
 SF02 500.1320005 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7570510 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1p 100.000 ppm
 F1 22636.41 Hz
 F2p 0.000 ppm
 F2 0.00 Hz
 PPM0H 9.00000 ppm/cm
 HZ0H 1131.02056 Hz/cm

ms 18217_48_2

Current Data Parameters
NAME R4_Sep05-2002
EXNO 110
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020905
Time 9.54

INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zg30

TD 32769
SOLVENT DMSO

NS 16
DS 2

SNH 6172.039 Hz
FIDRES 0.18030 Hz

RG 2.654280 sec
F6 645.1

DW 81.000 usec
DE 6.50 usec

TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing parameters
SI 16384
SF 300.1300005 MHz

WDW EM
SSB 0
LB 0.30 Hz
GB 0

PC 4.00

1D NMR plot parameters
CX 22.00 cm
F1P 9.500 ppm

F1 2651.24 Hz
F2P -0.500 ppm

F2 -150.06 Hz
PPMCM 0.45455 ppm/cm
HZCM 135.42273 Hz/cm

MS-48.2, DMSO, te = 60C

Current Data Parameters
NAME MS-48.2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020912
Time 6.50
INSTRUM spect
PROBHD 5 mm TXI (H)
PULPROG zgpg30
TO 65536
SOLVENT DMSO
NS 20000
DS 4
SWH 3753.924 Hz
FIDRES 0.572639 Hz
AQ 0.0716783 sec
RG 16384
DM 13.300 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 -2.00 dB
SFO1 150.9193778 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 5.00 dB
PL12 25.20 dB
PL13 30.00 dB
SFO2 600.1324005 MHz

F2 - Processing parameters
SI 32768
SF 150.9027450 MHz
WDW EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
FAP 215.000 ppm
F1 32444.10 Hz
F2 -5.000 ppm
F2 -754.51 Hz
PCNCH 11.000000 ppm/cm
HZCM 1659.98030 Hz/cm

mjs 18217_166

Current Data Parameters
NAME R4_Mhy12-2003
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030512
Time 9.05
INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.10360 Hz
AQ 2.654250 sec
RG 645.1
DM 64.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing Parameters
SI 16384
SF 300.1300009 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
F1P 9.500 ppm
F1 2051.24 Hz
F2P -0.500 ppm
F2 -150.06 Hz
FPMCM 0.45455 ppm/cm
HZCM 136.42273 Hz/cm

mjs 18217_166

Current Data Parameters
NAME R4_May12-2003
EXPNO 540
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030512
Time 19.09

INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024

DS 4
SWH 10332.363 Hz
FIDRES 0.26760 Hz
AQ 1.740300 sec
RG 16394
DM 26.560 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 75.476200 MHz

===== CHANNEL f2 =====
GCPROG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 49.00 dB
PL13 19.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.467967 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 16226.57 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCH 11.00000 ppm/cm
HZCH 830.14532 Hz/cm

mjs 19393_418

Current Data Parameters
 NAME R4_Sep24-2003
 EXNO 200
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030924
 Time 11.40
 INSTRUM spect
 PROHD 5 mm Dnl 13
 PULPROG zg30
 TD 32768
 SOLVENT DMSO
 NS 16
 DS 2
 SMI 6172.839 Hz
 FIDRES 0.18830 Hz
 AQ 2.6542800 sec
 RG 406.4
 DW 61.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 0.00 dB
 SFO1 300.1310534 MHz

F2 - Processing parameters
 SI 16384
 SF 300.1300000 MHz
 KDN EN
 SSF 0
 LB 0.30 Hz
 GB 0
 PC 4.00

1D NMR plot parameters
 CX 22.00 cm
 FLP 9.500 ppm
 F1 2651.24 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PPMCM 0.45455 ppm/cm
 HZCM 136.42273 Hz/cm

m/s 19393_48

Current Data Parameters
NAME R4_Sep26-2003
EXPNO 730
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030927
Time 5.04
INSTRUM spect
PROBHD 5 mm QNP 13
PULPROG zgpg30
TD 65535
FIDRES 1.7400303 sec
AQ 1.7400303 sec
RG 16384
DM 26.550 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.80 usec
PL1 0.00 dB
SF01 75.4760200 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 18.00 dB
SF02 300.1312005 MHz

F2 - Processing Parameters
SI 32768
SF 75.4677567 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 130.14532 Hz/cm

MS-19393_67 T=40C

Current Data Parameters
 Name: 500_06127-2003
 ExpNO: 10
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20031027
 Time: 15:56
 Instrument: spect
 PROBHD: 5 mm Maltinn
 PULPROG: zgpg30
 TO: 2030
 SOLVENT: DMSO
 NS: 16
 DS: 2
 SWH: 10330.570 Hz
 FIDRES: 0.197632 Hz
 AQ: 3.1719223 sec
 RG: 120
 DW: 40.400 usec
 DE: 11.90 usec
 TE: 300.0 K
 D1: 1.0000000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.50 usec
 PL1: 0.00 dB
 SFO1: 500.136000 MHz

F2 - Processing parameters
 SI: 32768
 SF: 500.136000 MHz
 KW: EN
 SS3: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.00

1D NMR plot parameters
 CX: 22.00 cm
 CK: 10.000 ppm
 F1: 5002.34 Hz
 F2: 0.000 ppm
 FREQN: 0.00016 GHz/cm
 WIDN: 409.19727 Hz/cm

MS-19393_67 T=40C

Current Data Parameters
NAME 500_06127-2003
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20031027
Time 16:15

INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 24576
DS 4

SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.307492 sec
RG 6192
DM 19.950 usec
DE 11.50 usec
TE 300.0 K

D1 1.5000000 sec
d11 0.0300000 sec
d12 0.0002000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 15.00 usec
PL1 2.00 dB
SFO1 125.759600 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 93.60 usec
PL2 6.00 dB
PL12 27.00 dB
PL13 30.00 dB
SFO2 500.132005 MHz

F2 - Processing Parameters
SI 32768
SF 125.757035 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
FAP 155.000 ppm
F1 20750.05 Hz
F2 12575.79 Hz
PUNCH 3 25000 ppm/cm
HZCM 400 71307 Hz/cm

mjs 19393_47

Current Data Parameters
NAME R4_Sep25-2003
EXPNO 340
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030925
Time 13.42
INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188360 Hz
AQ 2.6542500 sec
RG 574.7
DM 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing parameters
SI 16364
SF 300.129925 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
FAP 9.500 ppm
F1 2851.24 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.45455 ppm/cm
HZCM 136.42273 Hz/cm

MUS 19393_47

ppm

161.468
159.445

150.95

139.314
139.249
136.191

131.497

115.768
115.612
111.752

Current Data Parameters
NAME 500_Sep29-2003
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030929
Time 10.17

INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 6753
DS 4
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 16394
DM 22.000 usec
DE 11.50 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 2.00 dB
SF01 125.7694284 MHz

===== CHANNEL f2 =====
CROSSPRG2 waltz16
NUC2 1H
PCPD2 93.60 usec
PL2 5.00 dB
PL12 27.00 dB
PL13 30.00 dB
SF02 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.769427 MHz
WDW EM
SS3 0
LB 2.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 170.000 DPM
F1 21378.03 Hz
F2P 100.000 DPM
F2 12575.79 Hz
FPCMH 3.50000 DPM/cm
HZCM 440.15227 Hz/cm

15465-143-1

Current Data Parameters
NAME H4_Sep26-2003
EXPNO 140
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030926
Time 9.20

INSTRUM spect
PROBHD 5 mm Dui1 13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2

SWH 6172.039 Hz
FIDRES 0.100300 Hz
AQ 2.0542800 sec
RG 1149.4
DM 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 300.1310534 MHz

F2 - Processing Parameters
SI 16304
SF 300.1300005 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.00 cm
FLP 9.500 ppm
F1 2951.24 Hz
F2 -0.500 ppm
F2P -150.06 Hz
PPMCH 0.45455 ppm/cm
HZCH 136.42273 Hz/cm

15405-143-1

Current Data Parameters
 NAME R4_Sep26-2003
 EXPNO 230
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030926
 Time 11.04
 INSTRUM spect
 PROBO 5 mm Dual 13
 PULPROG zgpg30
 TO 65536
 SOLVENT DMSO
 NS 64
 DS 4
 SWH 18332.323 Hz
 FIDRES 0.267350 Hz
 AQ 1.7400300 sec
 RB 16304
 DW 26.550 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.09000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.30 usec
 PL1 0.00 dB
 SFO1 75.4760200 MHz

===== CHANNEL f2 =====
 GPCPRG2 waltz16
 NUC2 1H
 PCPRG2 100.00 usec
 PL2 0.00 dB
 PL12 18.00 dB
 PL13 18.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677957 MHz
 NCM 64
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR Plot parameters
 CX 20.00 cm
 F1P 215.000 ppm
 F1 16825.57 Hz
 F2P -5.000 ppm
 F2 -377.34 Hz
 FREQN 11.00000 ppm/cm
 HZCM 930.14532 Hz/cm

15617-5-2

Current Data Parameters
NAME 1053-fab04-2004
EXPNO 120
PROCNO 1

F2 - Acquisition Parameters
Date_ 2004/02/04
Time 9.35
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8250.825 Hz
FIDRES 0.126398 Hz
AQ 3.9715316 sec
RG 1024
DM 60.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.60 usec
PL1 6.00 dB
SFO1 399.9024658 MHz

F2 - Processing parameters
SI 32768
SF 399.900036 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
FAP 9.800 ppm
F1 3919.02 Hz
F2 -79.98 Hz
PPMCH 0.50000 ppm/cm
HZCM 199.95000 Hz/cm

15817-5-2

Current Data Parameters

NAME	1053-F0104-2004
EXPNO	160
PROCNO	1

F2 - Acquisition Parameters

Date_	20040204
Time	10.43
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	120
DS	4
SWH	24036.461 Hz
FIDRES	0.366793 Hz
AQ	1.3631933 sec
RG	40964
DM	20.800 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.0002000 sec

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

NUC1	13C
P1	13.00 usec
PL1	2.00 dB
SFO1	100.625005 MHz

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

CPDPRG2	molczi6
NUC2	1H
PCPD2	105.00 usec
PL2	6.00 dB
PL12	27.73 dB
PL13	29.00 dB
SFO2	399.9015596 MHz

F2 - Processing parameters

SI	32768
SF	100.5949493 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	12.50 cm
F1	215.000 ppm
F2P	21519.31 Hz
F2	-5.000 ppm
PPHOM	-502.77 Hz
HZCM	11.0000 ppm/cm
	1105.10437 Hz/cm

MS_19393-109

Current Data Parameters
NAME 500_F0013-2004
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20000213
Time 11.50
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1
DS 2
SWH 6000.615 Hz
FIDRES 0.0941023 Hz
AQ 5.4267453 sec
RG 401.3
DE 19.200 umsec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.50 umsec
PL1 0.00 dB
SFO1 500.135005 MHz

F2 - Processing parameters
SI 32768
SF 500.135005 MHz
SD 64
SFO 500.135005 MHz
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CZ 10.500 ppm
F1 5261.37 Hz
F2 -250.07 Hz
FREQM 0.50000 ppm/cm
HDCM 250.02500 Hz/cm

Current Data Parameters
NAME 1069-Feb13-2004
EXNO 470
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040216
Time 6.08
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 65536
DS 4
SWH 24030.461 Hz
FIDRES 0.365793 Hz
AQ 1.3531933 sec
RG 32769
DM 20.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.0002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 13.00 usec
PL1 2.00 dB
SFO1 100.5645905 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 105.00 usec
PL2 6.00 dB
PL12 27.73 dB
PL13 25.00 dB
SFO2 399.9015596 MHz

F2 - Processing parameters
SI 32769
SF 100.5549039 MHz
WDW EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR Plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 215.000 ppm
F1 21519.32 Hz
F2P -5.000 ppm
F2 -502.77 Hz
PPH0 11.00000 ppm/cm
HZ0 1105.10489 Hz/cm