Supporting Information

Palladium-Catalyzed Direct Hydroxymethylation of Aryl Halides and Triflates with Potassium Acetoxymethyltrifluoroborate

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1. General

Nuclear magnetic resonance (^1H NMR (400 MHz), ^{13}C NMR (100MHz)) spectra were determined on a Varian Mercury plus 400 MHz or Varian Mercury 400 MHz. Chemical shifts for ^1H NMR are reported in parts per million down fields from tetramethylsilane (δ) as the internal standard and coupling constants are in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts for ^{13}C NMR were reported in ppm relative to the center line of a triplet at 77.16 ppm for deuteriochloroform and a septet at 39.52 ppm for hexadeuterodimethyl sulfoxide. ^{19}F and ^{11}B spectra were determined on a Avance 400 MHz. ^{19}F NMR chemical shifts were referenced to external trifluorotoluene (-67.73 ppm). ^{11}B NMR chemical shifts were referenced to external $\text{BF}_3 \cdot \text{OEt}_2$ (0.0 ppm).

Infrared (IR) spectra were recorded on a JASCO FT/IR-620 Spectrophotometer and were reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a Waters GCT Premier using electron ionization (EI) method. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254. Preparative TLC separations were performed on Merck analytical plates 0.50 mm thick precoated with silica gel 60 F254 or NH_2 F254s. Flash chromatography separations were performed on Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh ASTM).

$\text{Pd}(\text{OAc})_2$, Bedford's catalyst, $\text{Pd}(t\text{-Bu}_3\text{P})_2$, $\text{Pd}(\text{dppe})_2$, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $\text{Pd}_2(\text{dba})_3$, PCy_3 , S-phos, Ru-phos, Dave-phos, X-phos, *t*-BuX-phos, Cy-vBRIDP, Cs_2CO_3 , K_3PO_4 were purchased from Sigma-Aldrich and were used without further purification. $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , KF were purchased from Kanto Chemicals Co., Inc., and were used without further purification. $\text{Pd}(\text{dba})_2$ was purchased from Sigma-Aldrich or Tokyo Chemical Industry Co., Ltd., and was used without further purification. DPE-phos was purchased from ACROS Organics and were used without further purification. (s)-BINAP was purchased from Tokyo Chemical Industry Co., Ltd., and was used without further purification. BI-DIME was synthesized by Tang's procedure.¹ All Substrates except Table 2 entries 9 and 11 were purchased from Sigma-Aldrich or Tokyo Chemical Industry Co., Ltd., or Kanto Chemicals Co., Inc., and were used without further purification. 1,4-Dioxane hydrate and Distilled water were purchased from Kanto Chemicals Co., Inc., and were used without further purification.

2. Preparation of potassium acetoxymethyltrifluoroborate **1** (Scheme 1)

Preparation of potassium acetoxymethyltrifluoroborate **1**

To a mixture of 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18.0 g, 75.0 mmol) and tetrahydrofuran (150 mL) were added potassium acetate (8.83 g, 90.0 mmol) at 0 °C. Then, the reaction mixture was stirred at 50 °C for 14 hours. After the reaction mixture was cooled at 0 °C, to the reaction mixture was added potassium hydrogen fluoride (8.83 g, 90.0 mmol). Distilled water (75.0 mL) was added dropwise to the stirring solution at same temperature over 1.5 hours, and then reaction mixture was stirred at room temperature for 30 min. The reaction mixture was concentrated under reduced pressure. Moreover residual water was removed by azeotrope with toluene before drying in vacuo over 5 hours. The resulting solid was added acetone (400 mL) and methanol (90.0 mL), and then the reaction mixture was stirred at 50 °C for 30 min, and then filtered, concentrated under reduced pressure. The resulting solid was added acetonitrile/methanol (3/1) solution, and then the mixture was stirred at 60 °C for 30 min, and then filtered. The filtrate was added ethyl acetate until the appearance of the solid. The resulting solid was filtered and dried under reduced pressure to obtain the potassium acetoxymethyltrifluoroborate **1** as a white solid (10.9 g, 60.6 mmol, 80.8%).

^1H NMR (400 MHz, DMSO- d_6) δ 3.00-3.12 (m, 2H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 171.6, 21.2; ^{19}F NMR (376.5 MHz, DMSO- d_6) δ -149.0; ^{11}B NMR (128.4 MHz, DMSO- d_6) δ 3.2; IR (ATR, cm^{-1}) 1725, 1381, 1335, 1272, 1103, 1005, 957, 882, 785; HRMS (ESI-) calcd for $\text{C}_3\text{H}_5\text{BF}_3\text{O}_2$ (M-H) $^-$ 141.0329, found 141.0334.

Preparation of 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

To a mixture of triisopropyl borate (20.0 g, 110 mmol), dibromomethane (8.60 mL, 120 mmol) and tetrahydrofuran (150 mL) was added *n*-butyllithium (2.6M *n*-hexane solution, 39 mL, 100 mmol) at -78 °C (external temperature) over 1.5 hours. The reaction mixture was stirred at the same temperature for 1.5 hours, and then the reaction mixture was stirred at room temperature for 2 hours. After the mixture was cooled at 0 °C (external temperature), to the reaction mixture was added methanesulfonic acid (6.50 mL, 100 mmol), and then the reaction mixture was stirred at room temperature for 1

hour. After the mixture was cooled at 0 °C (external temperature), to the reaction mixture was added pinacol (12.0g, 100 mmol), and then the reaction mixture was stirred at room temperature for 1 hour. After the solvent was concentrated, the resulting residue was distilled under reduce pressure (74-76 °C, 8 mmHg), to obtain the title compound (16.0 g, 72.4 mmol, 72.4%).

^1H NMR (400 MHz, CDCl_3) δ 2.57 (s, 2H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 84.6, 24.7; IR (ATR, cm^{-1}) 2979, 1415, 1372, 1336, 1272, 1214, 1135, 1055, 967, 886, 845, 673; HRMS (EI+) calcd for $\text{C}_7\text{H}_{14}\text{BBrO}_2$ (M) $^+$ 220.0270, found 220.0315.

3. General experimental procedure for Suzuki-Miyaura cross-coupling reaction using microwave irradiation (Table1)

A Biotage microwave vial was charged with 2-chloronaphthalene, palladium, ligand, base, potassium acetoxymethyltrifluoroborate **1**, 1,4-dioxane/distilled water (10/1). The test tube was sealed with a disposable cap, and the reaction mixture was stirred and irradiated at 120 °C (maximum 200 W) in the microwave reactor for 35 min. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford naphthalene-2-yl-methanol.

4. Experimental procedure for Suzuki-Miyaura cross-coupling reaction 2a–3f (Table 2 and 3)

Preparation of naphthalene-2-yl-methanol (2a)²

A Biotage microwave vial was charged with 2-chloronaphthalene (15.0 mg, 0.092 mmol), bis(dibenzylideneacetone)palladium (2.65 mg, 0.005 mmol), Ru-phos (5.44 mg, 0.012 mmol, 95% purity), sodium carbonate (14.7 mg, 0.138 mmol), potassium acetoxymethyltrifluoroborate **1** (24.9 mg, 0.138 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2a** (12.4 mg, 85.0%).

Commercially available compound: CAS [1592-38-7]

¹H NMR (400 MHz, CDCl₃) δ 7.70-7.89 (m, 1H), 7.37-7.55 (m, 1H), 4.81 (d, *J*=5.32 Hz, 1H), 2.00 (t, *J*=5.59 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 133.5, 133.0, 128.4, 128.0, 127.8, 126.3, 126.0, 125.5, 125.3, 65.6; HRMS (EI⁺) calcd for C₁₁H₁₀O (M)⁺ 158.0732, found 158.0762.

1.00 gram scale synthesis of naphthalene-2-yl-methanol (2a) from 2-chloronaphthalene

To a mixture of 2-chloronaphthalene (1.00 g, 6.15 mmol), bis(dibenzylideneacetone)palladium (177 mg, 0.307 mmol), Ru-phos (362 mg, 0.738 mmol, 95% putity), sodium carbonate (978 mg, 9.22 mmol), potassium acetoxymethyl trifluoroborate **1** (1.66 g, 9.22 mmol), 1,4-dioxane (90.0 mL), distilled water (9.00 mL). The reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature and filtered, and then the filtrate was added water and ethyl acetate. The residue was extracted with ethyl acetate, washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual was purified by silica gel column chromatography (heptane/ethyl acetate = 4/1) to afford **2a** (768 mg, 78.9%).

Preparation of naphthalene-2-yl-methanol (2a) from 2-bromonaphthalene

A Biotage microwave vial was charged with 2-bromonaphthalene (21.3 mg, 0.100 mmol, 97% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyltrifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2a** (9.00 mg, 56.9%).

Preparation of naphthalene-2-yl-methanol (2a) from 2-naphthyl trifluoromethanesulfonate

A Biotage microwave vial was charged with 2-naphthyl trifluoromethanesulfonate (25.0 mg, 0.091 mmol), bis(dibenzylideneacetone)palladium (2.60 mg, 0.005 mmol), Ru-phos (5.33 mg, 0.011 mmol, 95% putity), sodium carbonate (14.4 mg, 0.136 mmol), potassium acetoxymethyl trifluoroborate **1** (24.4 mg, 0.136 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the

reaction mixture was stirred at reflux for 7 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2a** (12.0 mg, 83.8%).

Preparation of (3,5-dimethoxyphenyl)methanol (**2b**)³

A Biotage microwave vial was charged with 1-chloro-3,5-dimethoxybenzene (17.3 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 1/1) to afford **2b** (13.6 mg, 80.9%).

Commercially available compound: CAS [705-76-0]

¹H NMR (400 MHz, CDCl₃) δ 6.47-6.53 (m, 2H), 6.37 (t, *J*=2.29 Hz, 1H), 4.60 (d, *J*=4.95 Hz, 2H), 3.77 (d, *J*=0.55 Hz, 6H), 2.09-2.17 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 143.5, 104.6, 99.7, 65.3, 55.4; HRMS (EI+) calcd for C₉H₁₂O₃ (M)⁺ 168.0786, found 168.0766.

Preparation of (3,5-dimethoxyphenyl)methanol (**2b**) from 3,5-dimethoxyphenyl trifluoromethanesulfonate

A Biotage microwave vial was charged with 3,5-dimethoxyphenyl trifluoromethanesulfonate (29.5 mg, 0.100 mmol, 97% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 10 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 1/1) to afford **2b** (13.6 mg, 80.9%).

Preparation of (4-nitrophenyl)methanol (2c)²

A Biotage microwave vial was charged with 4-chloronitrobenzene (15.8 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 2/1) to afford **2c** (14.5 mg, 94.4%).

Commercially available compound: CAS [619-73-8]

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J*=8.78 Hz, 2H), 7.49-7.57 (m, 2H), 4.83 (d, *J*=3.66 Hz, 2H), 2.26 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.4, 147.4, 127.1, 123.8, 64.1; HRMS (EI⁺) calcd for C₇H₇NO₃ (M)⁺ 153.0426, found 153.0453.

Preparation of (4-nitrophenyl)methanol (2c) from 4-bromonitrobenzene

A Biotage microwave vial was charged with 4-bromonitrobenzene (20.2 mg, 0.100 mmol, 99% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2c** (9.50 mg, 62.0%).

Preparation of (4-nitrophenyl)methanol (2c) from 4-nitrophenyl trifluoromethanesulfonate

A Biotage microwave vial was charged with 4-nitrophenyl trifluoromethanesulfonate (27.4 mg, 0.100 mmol, 99% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a

disposable cap, and the reaction mixture was stirred at reflux for 10 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2c** (12.8 mg, 83.7%).

Preparation of 3-(hydroxymethyl)benzonitrile (**2d**)²

A Biotage microwave vial was charged with 3-chlorobenzonitrile (14.1 mg, 0.100 mmol, 98% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 36 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2d** (11.6 mg, 87.1%).

Commercially available compound: CAS [874-97-5]

¹H NMR (400 MHz, CDCl₃) δ 7.67 (td, J =1.10, 1.83 Hz, 1H), 7.54-7.63 (m, 2H), 7.44-7.50 (m, 1H), 4.75 (s, 2H), 2.20 (br. s., 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 131.2, 131.2, 130.2, 129.4, 118.9, 112.4, 63.9; HRMS (EI⁺) calcd for C₈H₇NO (M)⁺ 133.0528, found 133.0550.

Preparation of ethyl 4-(hydroxymethyl)benzoate (**2e**)⁴

A Biotage microwave vial was charged with ethyl 4-chlorobenzoate (18.5 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to

afford **2e** (15.4 mg, 85.5%).

^1H NMR (400 MHz, CDCl_3) δ 7.93-8.07 (m, 2H), 7.34-7.45 (m, 2H), 4.74 (d, $J=4.03$ Hz, 2H), 4.36 (q, $J=7.32$ Hz, 2H), 2.36 (br. s., 1H), 1.36-1.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 146.1, 129.9, 129.7, 126.5, 64.7, 61.1, 14.4; HRMS (EI $^+$) calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3$ (M) $^+$ 180.0786, found 180.0822.

Preparation of (4-benzoylphenyl)methanol (**2f**)⁵

A Biotage microwave vial was charged with 4-chlorobenzophenone (21.7 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2f** (19.4 mg, 91.4%).

^1H NMR (400 MHz, CDCl_3) δ 7.73-7.81 (m, 4H), 7.55-7.62 (m, 1H), 7.44-7.51 (m, 4H), 4.78 (s, 2H), 2.43 (br. s., 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 145.8, 137.7, 136.7, 132.6, 130.5, 130.1, 128.4, 126.5, 64.7; HRMS (EI $^+$) calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$ (M) $^+$ 212.0837, found 212.0845.

Preparation of 4-(hydroxymethyl)benzamide (**2g**)

A Biotage microwave vial was charged with 4-chlorobenzamide (15.6 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 1/5) to

afford **2g** (12.4 mg, 82.0%).

Commercially available compound: CAS [87128-27-6].

^1H NMR (400 MHz, DMSO- d_6) δ 7.92 (br. s., 1H), 7.82 (d, $J=8.42$ Hz, 2H), 7.36 (d, $J=8.05$ Hz, 2H), 7.30 (br. s., 1H), 5.28 (t, $J=5.85$ Hz, 1H), 4.53 (d, $J=5.86$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.9, 146.0, 132.6, 127.4, 126.0, 62.5; IR (ATR, cm^{-1}) 3361, 2360, 1620, 1558, 1417, 1044, 1014, 773; HRMS (EI+) calcd for $\text{C}_8\text{H}_9\text{NO}_2$ (M) $^+$ 151.0633, found 151.0644.

Preparation of [4-(1H-pyrrol-1-yl)phenyl]methanol (**2h**)

A Biotage microwave vial was charged with 1-(4-chlorophenyl)-1H-pyrrole (18.3 mg, 0.100 mmol, 97% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =3/2) to afford **2h** (14.7 mg, 84.9 %).

^1H NMR (400 MHz, CDCl_3) δ 7.32-7.48 (m, 4H), 7.10 (t, $J=2.20$ Hz, 2H), 6.37 (t, $J=2.20$ Hz, 2H), 4.69 (s, 2H), 2.04 (br. s., 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 138.3, 128.3, 120.6, 119.4, 110.6, 64.8; IR (ATR, cm^{-1}) 3250, 1611, 1524, 1473, 1331, 1186, 1126, 1080, 1065, 1036, 1001, 918, 839, 802, 715; HRMS (EI+) calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$ (M) $^+$ 173.0841, found 173.0888.

Preparation of 3-(hydroxymethyl)benzaldehyde (**2i**)⁶

A Biotage microwave vial was charged with 3-chlorobenzaldehyde (14.5 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the

reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =3/2) to afford **2i** (13.0 mg, 95.5%).

Commercially available compound: CAS [52010-98-7]

¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 7.85-7.88 (m, 1H), 7.76-7.81 (m, 1H), 7.60-7.66 (m, 1H), 7.48-7.55 (m, 1H), 4.77 (d, *J*=2.93 Hz, 2H), 2.27 (br. s., 1H); ¹³C NMR (100 MHz, CDCl₃) δ 192.6, 142.1, 136.7, 133.0, 129.4, 129.2, 127.9, 64.6; HRMS (EI+) calcd for C₈H₈O₂ (M)⁺ 136.0524, found 136.0564.

Preparation of (3-aminophenyl)methanol (**2j**)⁷

A Biotage microwave vial was charged with 3-chloroaniline (12.8 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/3) to afford **2j** (6.90 mg, 56.0%).

Commercially available compound: CAS [1877-77-6]

¹H NMR (400 MHz, DMSO-*d*₆) δ 6.86-7.02 (m, 1H), 6.55 (d, *J*=1.10 Hz, 1H), 6.38-6.49 (m, 2H), 4.99 (dt, *J*=1.46, 5.86 Hz, 1H), 4.94 (s, 2H), 4.35 (d, *J*=5.86 Hz, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 148.5, 143.2, 128.6, 114.2, 112.5, 112.2, 63.3; HRMS (EI+) calcd for C₇H₉NO (M)⁺ 123.0684, found 123.0781.

Preparation of 3-(hydroxymethyl)phenol (**2k**)⁸

A Biotage microwave vial was charged with 3-chlorophenol (19.2 mg, 0.150 mmol), bis(dibenzylideneacetone)palladium (4.29 mg, 0.007 mmol), Ru-phos (8.80 mg, 0.018 mmol, 95% putity), sodium carbonate (23.8 mg, 0.225 mmol), potassium acetoxymethyl trifluoroborate **1** (40.5 mg, 0.225 mmol), 1,4-dioxane (2.00 mL), distilled water (200 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred

at reflux for 36 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/1) to afford **2k** (11.5 mg, 61.8%).

Commercially available compound: CAS [620-24-6]

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.07 (t, *J*=7.87 Hz, 1H), 6.73 (d, *J*=1.46 Hz, 1H), 6.66-6.71 (m, 1H), 6.57-6.62 (m, 1H), 5.08 (br. s., 1H), 4.39 (br. s., 2H) (400 MHz, CDCl₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 157.3, 144.1, 129.0, 117.0, 113.6, 113.3, 62.9; HRMS (EI⁺) calcd for C₇H₈O₂ (M)⁺ 124.0524, found 124.0550.

Preparation of (2-methoxy-4-nitrophenyl)methanol (**2l**)⁹

A Biotage microwave vial was charged with 2-chloro-5-nitroanisole (19.1 mg, 0.100 mmol, >98% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =3/2) to afford **2l** (16.1 mg, 87.9%).

Commercially available compound: CAS [136507-14-7]

¹H NMR (400 MHz, CDCl₃) δ 7.83-7.88 (m, 1H), 7.69-7.71 (m, 1H), 7.52 (dd, *J*=0.92, 8.25 Hz, 1H), 4.76 (d, *J*=5.13 Hz, 2H), 3.95 (d, *J*=0.73 Hz, 3H), 2.34-2.49 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 148.4, 136.8, 128.0, 116.1, 105.1, 60.8, 56.0; HRMS (EI⁺) calcd. for C₈H₉NO₄ (M)⁺ 183.0532, found 183.0544.

Preparation of (2,4,6-trimethylphenyl)methanol (**2m**)²

A Biotage microwave vial was charged with mesityl chloride (15.5 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (25.8 mg, 0.010 mmol), Ru-phos (11.8 mg, 0.024 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl

trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2m** (8.80 mg, 58.6%). Commercially available compound: CAS [4170-90-5]

¹H NMR (400 MHz, CDCl₃) δ 6.87 (s, 2H), 4.71 (s, 2H), 2.40 (s, 6H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 137.4, 133.9, 129.3, 59.3, 21.1, 19.5; HRMS (EI+) calcd for C₁₀H₁₄O (M)⁺ 150.1045, found 150.1066.

Preparation of {4-[(methoxymethoxy)methyl]phenyl}methanol (**2n**)¹⁰

A Biotage microwave vial was charged with 1-chloro-4-[(methoxymethoxy)methyl]benzene (18.7 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 1/1) to afford **2n** (13.3 mg, 73.0%).

¹H NMR (400 MHz, CDCl₃) δ 7.34 (s, 4H), 4.69 (s, 2H), 4.66 (s, 2H), 4.58 (s, 2H), 3.40 (s, 3H), 2.07 (br. s., 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 137.3, 128.2, 127.2, 95.7, 69.0, 65.1, 55.5; HRMS (EI+) calcd for C₁₁H₁₆O₃ (M)⁺ 182.0943, found 182.0962.

Preparation of 1-chloro-4-[(methoxymethoxy)methyl]benzene¹¹

To a solution of 4-chlorobenzyl alcohol (500 mg, 3.51 mmol) and diisopropylethylamine (6.30 mL, 35.1 mmol) in dichloromethane (20.0 mL) was added methoxymethylchloride (1.30 mL, 17.5 mmol) at 0 °C. The reaction mixture was stirring at room temperature for 12 hours. The reaction mixture was quenched with water, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and

concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (heptane/ethyl acetate = 10/1) to afford 1-chloro-4-[(methoxymethoxy)methyl]benzene (524 mg, 80.1%).

^1H NMR (400 MHz, CDCl_3) δ 7.27-7.35 (m, 4H), 4.69 (s, 2H), 4.56 (s, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 133.6, 129.3, 128.7, 95.8, 68.5, 55.5; HRMS (EI+) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_2$ (M) $^+$ 186.0448, found 186.0271.

Preparation of (4-[(*tert*-butyldimethylsilyl)oxy]methyl)phenylmethanol (**2o**)¹²

A Biotage microwave vial was charged with *tert*-butyl[(4-chlorophenyl)methoxy]dimethylsilane (25.7 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 ml), distilled water (150 μl). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 36 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 2/1) to afford **2o** (16.7 mg, 66.2 %).

^1H NMR (400 MHz, CDCl_3) δ 7.32 (s, 4H), 4.74 (s, 2H), 4.65 (s, 2H), 0.95 (s, 10H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 139.6, 127.1, 126.4, 65.3, 64.9, 26.1, 18.5, -5.1; HRMS (EI+) calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$ (M- C_4H_9) $^+$ 195.0836, found 195.0841.

Preparation of *tert*-butyl[(4-chlorophenyl)methoxy]dimethylsilane¹³

To a solution of 4-chlorobenzyl alcohol (200 mg, 1.40 mmol) and imidazole (229 mg, 3.37 mmol) in dichloromethane (10.0 mL) was added *t*-butyldimethylsilylchloride (254 mg, 1.68 mmol) at 0 $^\circ\text{C}$. The reaction mixture was stirring at room temperature for 12 hours. The reaction mixture was quenched with water, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (heptane/ethyl acetate = 50/1 to 20/1) to afford *tert*-butyl[(4-chlorophenyl)methoxy]dimethylsilane (328 mg,

91.0%).

^1H NMR (400 MHz, CDCl_3) δ 7.23-7.33 (m, 4H), 4.70 (s, 2H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 132.6, 128.5, 127.5, 64.4, 26.1, 18.5, -5.1; HRMS (EI⁺) calcd for $\text{C}_{13}\text{H}_{21}\text{ClOSi}$ (M)⁺ 256.1050, found 256.1151.

Preparation of 3-(hydroxymethyl)-2H-chloro-2-one (2p)

A Biotage microwave vial was charged with 3-chlorocoumarin (18.1 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 ml), distilled water (150 μl). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 3/2) to afford **2p** (15.0 mg, 85.1 %).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.94 (s, 1H), 7.70-7.79 (m, 1H), 7.49-7.59 (m, 1H), 7.37 (d, J =8.05 Hz, 1H), 7.32 (t, J =7.50 Hz, 1H), 5.44 (t, J =5.49 Hz, 1H), 4.35 (dd, J =1.46, 5.49 Hz, 2H) (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 159.7, 152.4, 137.1, 131.0, 129.2, 128.1, 124.5, 119.1, 116.0, 58.2; IR (ATR, cm^{-1}) 3447, 2360, 1690, 1608, 1449, 1400, 1284, 1173, 1153, 1090, 1018, 988, 918, 774, 759, 726, 681; HRMS (EI⁺) calcd for $\text{C}_{10}\text{H}_8\text{O}_3$ (M)⁺ 176.0473, found 176.0478.

Preparation of 4-(hydroxymethyl)-2,6,6-trimethylcyclohexa-2,4-dien-1-one (2q)

A Biotage microwave vial was charged with 3,3,5-trimethyl-4-oxocyclohexa-1,5-dien-1-yl-trifluoromethanesulfonate (28.4 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the

reaction mixture was stirred at reflux for 7 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =3/2) to afford **2q** (12.6 mg, 75.8 %).

¹H NMR (400 MHz, CDCl₃) δ 6.88 (dd, *J*=1.46, 2.20 Hz, 1H), 6.08 (s, 1H), 4.24 (br. s., 2H), 1.90 (s, 3H), 1.18 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 206.2, 141.3, 138.7, 133.3, 130.4, 64.8, 46.1, 26.1, 15.7; IR (ATR, cm⁻¹) 3422, 2966, 2925, 2866, 1666, 1634, 1591, 1451, 1377, 1271, 1238, 1207, 1128, 1033, 963, 914, 849, 771; HRMS (EI⁺) calcd for C₁₀H₁₄O₂ (M)⁺ 166.0994, found 166.1015.

Preparation of 3,3,5-trimethyl-4-oxocyclohexa-1,5-dien-1-yl-trifluoromethanesulfonate¹⁴

To a solution of 4-ketoisophorone (1.00 g, 6.57 mmol) in Tetrahydrofuran (20.0 mL) was added lithium hexamethyldisilazide (ca. 1.6M tetrahydrofuran solution, 4.9 mL, 7.89 mmol) at -78 °C. The reaction mixture was stirring at same temperature for 20 min, and then, added N-phenylbis(trifluoromethanesulfonate) (2.60 g, 7.23 mmol). The reaction mixture was stirring at same temperature for 20 min, and then, stirred at room temperature for 9 h. The reaction mixture was quenched with saturated aqueous ammonium chloride, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (heptane/ethyl acetate = 50/1 to 20/1) to afford 3,3,5-trimethyl-4-oxocyclohexa-1,5-dien-1-yl-trifluoromethanesulfonate (1.66 g, 88.8%).

¹H NMR (400 MHz, CDCl₃) δ 6.73 (dd, *J*=1.56, 3.21 Hz, 1H), 6.10 (dd, *J*=0.64, 3.21 Hz, 1H), 1.94 (dd, *J*=0.82, 1.56 Hz, 3H), 1.27 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 202.7, 141.7, 136.7, 133.4, 132.9, 117.1, 46.8, 26.0, 15.7; HRMS (EI⁺) calcd for C₁₀H₁₁F₃O₄S (M)⁺ 284.0330, found 284.0274.

Preparation of quinolin-6-yl-methanol (**3a**)¹⁵

A Biotage microwave vial was charged with 6-chloroquinoline (16.4 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/3) to afford **3a** (12.9 mg, 81.0 %).

Commercially available compound: CAS [100516-88-9]

¹H NMR (400 MHz, CDCl₃) δ 8.83 (dd, *J*=1.65, 4.21 Hz, 1H), 8.08-8.14 (m, 1H), 8.04 (d, *J*=8.42 Hz, 1H), 7.78 (s, 1H), 7.67 (dd, *J*=1.83, 8.78 Hz, 1H), 7.37 (dd, *J*=4.21, 8.23 Hz, 1H), 4.89 (s, 2H), 3.11 (br. s., 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 147.8, 139.7, 136.3, 129.6, 128.9, 128.3, 125.0, 121.4, 64.8; HRMS (EI+) calcd for C₁₀H₉NO (M)⁺ 159.0684, found 159.0702.

Preparation of quinolin-6-yl-methanol (**3a**) from 6-quinolinyl trifluoromethanesulfonate

A Biotage microwave vial was charged with 6-quinolinyl trifluoromethanesulfonate (28.6 mg, 0.100 mmol, 97% purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/5, twice) to afford **3a** (13.3 mg, 83.6 %).

Preparation of pyridine-3-yl-methanol (**3b**)²

A Biotage microwave vial was charged with 3-Chloropyridine (17.0 mg, 0.150 mmol), bis(dibenzylideneacetone)palladium (8.61 mg, 0.015 mmol), Ru-phos (17.6 mg, 0.036 mmol, 95% putity), sodium carbonate (23.8 mg, 0.225 mmol), potassium acetoxymethyl trifluoroborate **1** (40.5 mg, 0.225 mmol), 1,4-dioxane (2.00 mL), distilled water (200

μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 1/5) to afford **3b** (8.50 mg, 51.9 %).

Commercially available compound: CAS [100-55-0]

^1H NMR (400 MHz, CDCl_3) δ 8.33-8.50 (m, 1H), 7.64-7.76 (m, 1H), 7.17-7.32 (m, 1H), 4.68 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.4, 148.2, 137.0, 135.3, 123.7, 62.3; HRMS (EI+) calcd for $\text{C}_6\text{H}_7\text{NO}$ (M) $^+$ 109.0528, found 109.0559.

Preparation of (2-methyl-1,3-benzoxazol-5-yl)methanol (**3c**)

(**3c**) A Biotage microwave vial was charged with 5-chloro-2-methylbenzoxazole (16.8 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate = 1/1) to afford **3c** (13.0 mg, 79.7 %).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.48-7.63 (m, 2H), 7.28 (dd, J =1.65, 8.25 Hz, 1H), 5.29 (t, J =5.77 Hz, 1H), 4.59 (d, J =5.87 Hz, 2H), 2.59 (s, 3H) (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 164.1, 149.4, 141.2, 139.0, 123.2, 116.8, 109.7, 62.9, 14.1; IR (ATR, cm^{-1}) 3367, 2928, 1680, 1624, 1577, 1437, 1381, 1258, 1179, 1012, 936, 876, 824, 779, 672; HRMS (EI+) calcd for $\text{C}_9\text{H}_9\text{NO}_2$ (M) $^+$ 163.0633, found 163.0644.

Preparation of 1-[5-(hydroxymethyl)thiophen-2-yl]ethan-1-one (**3d**)

A Biotage microwave vial was charged with 2-acetyl-5-chlorothiophene (16.2 mg, 0.100 mmol, 99 % purity), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N_2 . The reaction mixture was

cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/1) to afford **3d** (13.1 mg, 83.9 %).

^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J=3.66$ Hz, 1H), 6.95-7.07 (m, 1H), 4.84 (d, $J=5.49$ Hz, 2H), 2.63-2.74 (m, 1H), 2.43-2.59 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 153.9, 143.6, 132.8, 125.6, 60.4, 26.8; IR (ATR, cm^{-1}) 3331, 2927, 1636, 1616, 1532, 1458, 1358, 1278, 1167, 1020, 930, 812; HRMS (EI+) calcd for $\text{C}_7\text{H}_8\text{O}_2\text{S}$ (M) $^+$ 156.0245, found 156.0269.

Preparation of 5-(hydroxymethyl)furan-2-carbaldehyde (**3e**)¹⁶

A Biotage microwave vial was charged with 5-chloro-2-furaldehyde (13.1 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% putity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 24 h under N_2 . The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/1) to afford **3e** (10.1 mg, 80.2 %).

Commercially available compound: CAS [67-47-0]

^1H NMR (400 MHz, CDCl_3) δ 9.53 (s, 1H), 7.20 (d, $J=3.66$ Hz, 1H), 6.41-6.54 (m, 1H), 4.68 (d, $J=5.86$ Hz, 2H), 3.38 (t, $J=5.67$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.9, 161.0, 152.3, 123.3, 110.1, 57.6; HRMS (EI+) calcd for $\text{C}_6\text{H}_6\text{O}_3$ (M) $^+$ 126.0317, found 126.0357.

Preparation of ethyl 5-(hydroxymethyl)-1H-indole-2-carboxylate (**3f**)

A Biotage microwave vial was charged with ethyl 5-chloroindole-2-carboxylate (22.4 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (5.75 mg, 0.010 mmol), Ru-phos (11.8 mg, 0.024 mmol, 95% putity), sodium carbonate (21.2 mg, 0.200 mmol), potassium acetoxymethyl trifluoroborate **1** (36.0 mg, 0.200 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the

reaction mixture was stirred at reflux for 24 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/1) to afford **3f** (12.5 mg, 57.0 %).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.79 (br. s., 1H), 7.56 (s, 1H), 7.39 (d, *J*=8.42 Hz, 1H), 7.22 (dd, *J*=1.46, 8.78 Hz, 1H), 7.10 (d, *J*=1.10 Hz, 1H), 5.08 (t, *J*=5.86 Hz, 1H), 4.53 (d, *J*=5.86 Hz, 2H), 4.31 (q, *J*=7.32 Hz, 2H), 1.32 (t, *J*=7.14 Hz, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 161.4, 136.6, 134.4, 127.4, 126.6, 124.5, 119.6, 112.3, 107.7, 63.5, 60.4, 14.3; IR (ATR, cm⁻¹) 3318, 2475, 1694, 1531, 1333, 1299, 1252, 1210, 1154, 1010, 991, 887, 808, 766, 742; HRMS (EI⁺) calcd for C₁₂H₁₃NO₃ (M)⁺ 219.0895, found 219.0872.

5. Experimental procedure for preparing compound 4 and Suzuki-Miyaura cross-coupling reaction (Scheme 2)

Preparation of (4-chlorophenyl)methanol (**5**)²

A Biotage microwave vial was charged with 4-chlorophenyl trifluoromethanesulfonate (26.1 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (2.88 mg, 0.005 mmol), Ru-phos (5.89 mg, 0.012 mmol, 95% purity), sodium carbonate (15.9 mg, 0.150 mmol), potassium acetoxymethyl trifluoroborate **1** (27.0 mg, 0.150 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μL). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 5 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/1) to afford **5** (9.30 mg, 65.2 %).

Commercially available compound: CAS [873-76-7]

¹H NMR (400 MHz, CDCl₃) 7.21-7.38 (m, 4H), 4.64 (d, *J*=3.29 Hz, 2H), 1.97 (br. s., 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 133.5, 128.8, 128.4, 64.6; HRMS (EI⁺) calcd For C₇H₇ClO (M)⁺ 142.0185, found 142.0219.

Preparation of [4-(hydroxymethyl)phenyl]methanol (**6**)¹⁷

A Biotage microwave vial was charged with 4-chlorophenyl trifluoromethanesulfonate

(26.1 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (5.75 mg, 0.010 mmol), Ru-phos (11.8 mg, 0.024 mmol, 95% putity), sodium carbonate (31.8 mg, 0.300 mmol), potassium acetoxymethyl trifluoroborate **1** (54.0 mg, 0.300 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred at reflux for 48 h under N₂. The reaction mixture was cooled to room temperature, then filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =1/1) to afford **6** (10.1 mg, 73.1 %).

Commercially available compound: CAS [589-29-7]

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.24 (s, 1H), 5.12 (t, *J*=5.67 Hz, 1H), 4.46 (d, *J*=5.86 Hz, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 140.9, 126.3, 62.8; HRMS (EI+) calcd for C₈H₁₀O₂ (M)⁺ 138.0681, found 138.0706.

Preparation of 4-chlorophenyl trifluoromethanesulfonate (**4**)¹⁸

To a solution of 4-chlorophenol (250 mg, 1.95 mmol) and 2,6-lutidine (451 μ L, 3.89 mmol) in dichloromethane (10.0 mL) was added trifuric anhydride (1.5 mL, 2.53 mmol) at 0 °C. The reaction mixture was stirring for 1 hour. The reaction mixture was quenched with saturated aqueous ammonium chloride, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (heptane/ethyl acetate = 20/1) to afford **4** (280 mg, 55.2%).

¹H NMR (400 MHz, CDCl₃) δ 7.35-7.47 (m, 2H), 7.17-7.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 148.0, 134.4, 130.5, 122.9, 120.4; HRMS (EI+) calcd for C₇H₄ClF₃O₃S (M)⁺ 259.9522, found 259.9541.

6. Experimental procedure for preparing compounds **7** and **8**, and Suzuki-Miyaura cross-coupling reaction (Scheme 3)

Suzuki-Miyaura cross-coupling reaction of compound **7**

A Biotage microwave vial was charged with naphthalene-2-yl methanesulfonate **7** (22.2 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (5.75 mg, 0.010 mmol), Ru-phos (11.8 mg, 0.024 mmol, 95% putity), sodium carbonate (21.2 mg, 0.200 mmol),

potassium acetoxymethyl trifluoroborate **1** (31.8 mg, 0.200 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred and irradiated at 130 °C (maximum 200 W) in the microwave reactor for 4 h. The reaction mixture was cooled to room temperature, then filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =3/2) to afford naphthalene-2-yl-methanol (11.6 mg, 73.3 %).

Suzuki-Miyaura cross-coupling reaction of compound **8**

A Biotage microwave vial was charged with naphthalene-2-yl 4-methylbenzenesulfonate **8** (29.8 mg, 0.100 mmol), bis(dibenzylideneacetone)palladium (5.75 mg, 0.010 mmol), Ru-phos (11.8 mg, 0.024 mmol, 95% purity), sodium carbonate (21.2 mg, 0.200 mmol), potassium acetoxymethyl trifluoroborate **1** (36.0 mg, 0.200 mmol), 1,4-dioxane (1.50 mL), distilled water (150 μ L). The test tube was sealed with a disposable cap, and the reaction mixture was stirred and irradiated at 130 °C (maximum 200 W) in the microwave reactor for 4 h. The reaction mixture was cooled to room temperature, then filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, heptane/ethyl acetate =3/2) to afford naphthalene-2-yl-methanol (12.0 mg, 75.9 %).

Preparation of naphthalene-2-yl methanesulfonate (**7**)¹⁹

To a solution of 2-naphtol (3.00 g, 20.8 mmol) and pyridine (10.0 mL) in dichloromethane (20.0 mL) was added methanesulfonyl chloride (2.10 mL, 27.0 mmol) at 0 °C. The reaction mixture was stirring at room temperature for 12 hours. The reaction mixture was quenched with saturated aqueous ammonium chloride, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (heptane/ethyl acetate = 4/1 to 2/1) to afford **7** (4.10 g, 89.1%).

¹H NMR (400 MHz, CDCl₃) δ 7.82-7.92 (m, 3H), 7.76 (d, J =2.20 Hz, 1H), 7.49-7.58 (m, 2H), 7.41 (ddd, J =1.10, 2.38, 8.97 Hz, 1H), 3.18 (d, J =1.10 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 133.7, 132.2, 130.4, 128.0, 128.0, 127.3, 126.7, 120.9, 119.6, 37.5; HRMS (EI⁺) calcd for C₁₁H₁₀O₃S (M)⁺ 222.0351, found 222.0370.

Preparation of naphthalene-2-yl 4-methylbenzenesulfonate (**8**)¹⁹

To a solution of 2-naphthol (3.00 g, 20.8 mmol) and pyridine (10.0 mL) in CH₂Cl₂ (20.0 mL) was added methanesulfonyl chloride (5.20 g, 27.3 mmol) at 0 °C. The reaction mixture was stirring at room temperature for 12 hours. The reaction mixture was quenched with saturated aqueous ammonium chloride, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (heptane/ethyl acetate = 4/1 to 2/1) to afford **8** (3.20 g, 51.6%).

¹H NMR (400 MHz, CDCl₃) δ 7.77-7.84 (m, 1H), 7.70-7.77 (m, 4H), 7.44-7.51 (m, 3H), 7.29 (d, *J*=8.05 Hz, 2H), 7.09 (dd, *J*=2.38, 8.97 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 145.5, 133.6, 132.6, 132.0, 129.9, 129.9, 128.7, 128.0, 127.9, 127.0, 126.5, 121.3, 120.1, 21.9; HRMS (EI⁺) calcd for C₁₇H₁₄O₃S (M)⁺ 298.0664, found 298.0612.

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7. Spectra for Compounds

Formula C ₃ H ₅ BF ₃ KO ₂		FW 179.9751 (140.8774+39.0978)
Acquisition Time (sec) 2.7320	Comment	STANDARD 1H OBSERVE
Date Stamp Oct 23 2011	File Name	C:\USR\NMR\FID
Nucleus 1H	Original Points Count 16379	Points Count 16384
Receiver Gain 12.00	Spectrum Offset (Hz) 2247.6611	Spectrum Type STANDARD
Temperature (degree C) AMBIENT TEMPERATURE		Sweep Width (Hz) 5995.20

¹H NMR (400 MHz, DMSO-d₆) δ 3.00-3.12 (m, 2H), 1.87 (s, 3H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-32

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

640 repetitions

OBSERVE C13, 100.5611376 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FF size 65536

Total time 3 hr, 34 min, 58 sec

1

C09396 KT-4 079226-076141 DMSO 19F-NMR TXO 091224 d1=2

1

-148.84
-148.94
-149.09
-149.21

Current Data Parameters
NAME C09396 KT-4
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 2005124
Time 11:22
INSTRUM spect
PROBHD 5 mm PACTO 19F
PULPROG zgpg30
TD 131072
SOLVENT DMSO
NS 32
DS 4
SWH 75187.965 Hz
FIDRES 0.573639 Hz
AQ 0.8716788 sec
RG 4096
DN 6.650 usec
DR 1.000 usec
TE 303.2 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 19F
P1 11.50 usec
PL1 -5.00 dB
SFO1 376.4607160 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.50 dB
PL2 -19.70 dB
SFO2 400.1316000 MHz

F2 - Processing Parameters
SI 131072
SF 376.500843 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

C09396 KT-4 079226-076141 DMSO 11B-NMR(aring) DE=1000us BBO

1

2.58
3.00
3.44
3.86

14

12

10

8

6

4

2

0

-2

-4

-6

-8

ppm

495.52
441.22
385.13
331.34

14

12

10

8

6

4

2

0

-2

-4

-6

-8

ppm

Current Data Parameters
NAME C09396 KT-4
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091225
Time 11:14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 256
DS 4
SWH 25641.025 Hz
FIDRES 3.130008 Hz
AQ 0.1597940 sec
RG 4597.6
DW 19.500 usec
DE 1000.000 usec
TE 303.1 K
D1 2.00000000 sec
d13 0.0000400 sec
TD0 1

===== CHANNEL f1 =====
NUC1 11B
P1 10.40 usec
PL1 -0.50 dB
SFO1 128.3775371 MHz

F2 - Processing parameters
SI 32768
SF 128.3775381 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Formula	C ₂ H ₁₄ BBrO ₂	FW	220.8999
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Oct 23 2011	Date Stamp	Oct 23 2011
File Name	C:\USR\NMR\FID			Nucleus	1H	Number of Transients	32
Original Points Count	16379	Points Count	16384	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Temperature (degree C)	AMBIENT TEMPERATURE		

¹H NMR (400 MHz, CHLOROFORM-d) δ 2.57 (s, 2H), 1.27 (s, 12H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-33

Mercury-400HB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

768 repetitions

OBSERVE C13, 100.5606087 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₁ H ₁₀ O	FW	158.1965
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STANDARD 1H OBSERVE				Date		Date Stamp	
Acquisition Time (sec)	3.5000	Comment		Nucleus	1H	Number of Transients	8
File Name	C:\USR\NMR\FID	Frequency (MHz)	399.89	Receiver Gain	10.00	Solvent	CHLOROFORM-d
Original Points Count	21021	Pulse Sequence	s2pul	Temperature (degree C)	AMBIENT TEMPERATURE		
Spectrum Offset (Hz)	2756.4719	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01		

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.70-7.89 (m, 1H), 7.37-7.55 (m, 1H), 4.81 (d, *J*=5.32 Hz, 1H), 2.00 (t, *J*=5.59 Hz, 1H)

2a

2a

13C OBSERVE

Pulse Sequence: s2pul

DATE: Oct 21 2011

Solvent: CDCl₃

Ambient temperature

File: 08606-01

Mercury-400BB "7Fback"

Relax. delay 1.801 sec

Pulse 49.1 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

128 repetitions

OBSERVE C13, 100.5524222 MHz

DECOUPLE H1, 399.8920149 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 6 min, 58 sec

Formula	C ₉ H ₁₂ O ₃	FW	168.1898
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STANDARD 1H OBSERVE			
Acquisition Time (sec)	3.5000	Comment	
File Name	C:\USR\NMR\FID	Frequency (MHz)	399.89
Original Points Count	21021	Pulse Sequence	s2pul
Spectrum Offset (Hz)	2765.3716	Spectrum Type	STANDARD
		Sweep Width (Hz)	6006.01
		Temperature (degree C)	AMBIENT TEMPERATURE
		Receiver Gain	10.00
		Nucleus	1H
		Date	Oct 22 2011
		Date Stamp	Oct 22 2011
		Number of Transients	32
		Solvent	CHLOROFORM-d

¹H NMR (400 MHz, CHLOROFORM-d) δ 6.47-6.53 (m, 2H), 6.37 (t, J =2.29 Hz, 1H), 4.60 (d, J =4.95 Hz, 2H), 3.77 (d, J =0.55 Hz, 6H), 2.09-2.17 (m, 1H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-02re

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

480 repetitions

OBSERVE C13, 100.5606126 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₇ H ₇ NO ₃	FW	153.1354
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE				Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients		32	
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	12.00	Solvent	CHLOROFORM-d	
Spectrum Offset (Hz)	2253.2788	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE			

¹H NMR (400 MHz, CHLOROFORM-d) δ 8.20 (d, *J*=8.78 Hz, 2H), 7.49-7.57 (m, 2H), 4.83 (d, *J*=3.66 Hz, 2H), 2.26 (s, 1H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-03

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

512 repetitions

OBSERVE C13, 100.5606103 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 65536

Total time 26 min, 52 sec

2c

Formula	C ₈ H ₇ NO	FW	133.1473
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Number of Transients	32
Original Points Count	21021	Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	20.00	Solvent
Spectrum Offset (Hz)	2770.0359	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01	Temperature (degree C)	AMBIENT TEMPERATURE	
								CHLOROFORM-d

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.67 (td, $J=1.10, 1.83$ Hz, 1H), 7.54-7.63 (m, 2H), 7.44-7.50 (m, 1H), 4.75 (s, 2H), 2.20 (br. s., 1H)

2d

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-04re

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

416 repetitions

OBSERVE C13, 100.5606133 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₀ H ₁₂ O ₃	FW	180.2005
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Acquisition Time (sec)		2.7320	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USRX\NMR\FID			Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379		Points Count	16384		Receiver Gain	10.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2252.5469		Spectrum Type	STANDARD		Temperature (degree C)	AMBIENT TEMPERATURE		
						Sweep Width (Hz)	5995.20		

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.93-8.07 (m, 2H), 7.34-7.45 (m, 2H), 4.74 (d, J =4.03 Hz, 2H), 4.36 (q, J =7.32 Hz, 2H), 2.36 (br. s., 1H), 1.36-1.42 (m, 3H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-05

Mercury-400BB "67back"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

736 repetitions

OBSERVE C13, 100.5606103 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₄ H ₁₂ O ₂	FW	212.2439
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Number of Transients	32
Original Points Count	21021	Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	10.00	Solvent
Spectrum Offset (Hz)	2767.8362	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01	Temperature (degree C)	AMBIENT TEMPERATURE	
								CHLOROFORM-d

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.73-7.81 (m, 4H), 7.55-7.62 (m, 1H), 7.44-7.51 (m, 4H), 4.78 (s, 2H), 2.43 (br. s., 1H)

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 08606-06re

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

960 repetitions

OBSERVE C13, 100.5606118 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₈ H ₉ NO ₂	FW	151.1626
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Nov 12 2011
Date Stamp	Nov 12 2011	File Name	C:\USR\NMR\FID	Frequency (MHz)	399.93
Nucleus	1H	Number of Transients	32	Original Points Count	16379
Receiver Gain	10.00	Solvent	DMSO-d ₆	Spectrum Type	STANDARD
Temperature (degree C)	AMBIENT TEMPERATURE	Spectrum Offset (Hz)	2247.6611	Pulse Sequence	s2bul
				Sweep Width (Hz)	5995.20

¹H NMR (400 MHz, DMSO-d₆) δ 7.92 (br. s., 1H), 7.82 (d, *J*=8.42 Hz, 2H), 7.36 (d, *J*=8.05 Hz, 2H), 7.30 (br. s., 1H), 5.28 (t, *J*=5.85 Hz, 1H), 4.53 (d, *J*=5.86 Hz, 2H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-07-1

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

512 repetitions

OBSERVE C13, 100.5611391 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 26 min, 52 sec

Formula	C ₁₁ H ₁₁ NO	FW	173.2111
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	10.00	Solvent
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE	
								CHLOROFORM-d

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.32-7.48 (m, 4H), 7.10 (t, $J=2.20$ Hz, 2H), 6.37 (t, $J=2.20$ Hz, 2H), 4.69 (s, 2H), 2.04 (br. s., 1H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-22

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

576 repetitions

OBSERVE C13, 100.5606141 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₈ H ₈ O ₂	FW	136.1479
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE				Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients		32	
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	16.00	Solvent	CHLOROFORM-d	
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C) AMBIENT TEMPERATURE				

¹H NMR (400 MHz, CHLOROFORM-d) δ 9.99 (s, 1H), 7.85-7.88 (m, 1H), 7.76-7.81 (m, 1H), 7.60-7.66 (m, 1H), 7.48-7.55 (m, 1H), 4.77 (d, J =2.93 Hz, 2H), 2.27 (br. s., 1H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 08606-08

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

736 repetitions

OBSERVE C13, 100.5606095 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 Modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 47 min, 29 sec

2i

Formula	C ₇ H ₉ NO	FW	123.1525
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STANDARD 1H OBSERVE			
Acquisition Time (sec)	2.7320	Comment	
File Name	C:\USRX\NMR\FID	Frequency (MHz)	399.93
Original Points Count	16379	Pulse Sequence	s2pul
Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20
		Temperature (degree C)	AMBIENT TEMPERATURE
		Date	Nov 12 2011
		Nucleus	1H
		Number of Transients	16
		Spectrum Offset (Hz)	2247.6611

¹H NMR (400 MHz, DMSO-d₆) δ 6.86-7.02 (m, 1H), 6.55 (d, *J*=1.10 Hz, 1H), 6.38-6.49 (m, 2H), 4.99 (dt, *J*=1.46, 5.86 Hz, 1H), 4.94 (s, 2H), 4.35 (d, *J*=5.86 Hz, 2H)

2j

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-09-1

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

256 repetitions

OBSERVE C13, 100.5611376 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FF size 65536

Total time 26 min, 52 sec

Formula	C ₇ H ₈ O ₂	FW	124.1372
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Nov 12 2011
Date Stamp	Nov 12 2011	File Name	C:\USR\NMR\FID	Frequency (MHz)	399.93
Nucleus	1H	Number of Transients	16	Original Points Count	16384
Receiver Gain	10.00	Solvent	DMSO-d ₆	Spectrum Type	STANDARD
Temperature (degree C)	AMBIENT TEMPERATURE	Spectrum Offset (Hz)	2247.6611	Pulse Sequence	s2bul
				Sweep Width (Hz)	5995.20

¹H NMR (400 MHz, DMSO-d₆) δ 7.07 (t, *J*=7.87 Hz, 1H), 6.73 (d, *J*=1.46 Hz, 1H), 6.66-6.71 (m, 1H), 6.57-6.62 (m, 1H), 5.08 (br. s., 1H), 4.39 (br. s., 2H)

2k

2k

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-10-1

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

320 repetitions

OBSERVE C13, 100.5611384 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 65536

Total time 26 min, 52 sec

Formula	C ₈ H ₉ NO ₄	FW	183.1614
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Acquisition Time (sec)		Comment	STANDARD 1H OBSERVE		Date	Date Stamp	
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Oct 22 2011
Original Points Count	21021	Points Count	Pulse Sequence	s2pul	Receiver Gain	10.00	Number of Transients
Spectrum Offset (Hz)	2773.3352	Spectrum Type	STANDARD	6006.01	Temperature (degree C)	AMBIENT	Solvent
		Sweep Width (Hz)					

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.83-7.88 (m, 1H), 7.69-7.71 (m, 1H), 7.52 (dd, $J=0.92, 8.25$ Hz, 1H), 4.76 (d, $J=5.13$ Hz, 2H), 3.95 (d, $J=0.73$ Hz, 3H), 2.34-2.49 (m, 1H)

21

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-11re

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

352 repetitions

OBSERVE C13, 100.5606103 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₀ H ₁₄ O	FW	150.2176
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	12.00	Solvent
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE	
CHLOROFORM-d								

¹H NMR (400 MHz, CHLOROFORM-d) δ 6.87 (s, 2H), 4.71 (s, 2H), 2.40 (s, 6H), 2.27 (s, 3H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-12

Mercury-400EBB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

736 repetitions

OBSERVE C13, 100.5606087 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 47 min, 29 sec

2m

Formula	C ₁₀ H ₁₄ O ₃	FW	182.2164
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE				Date	Oct 22 2011	Date Stamp	Oct 22 2011	
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Number of Transients				32
Original Points Count	21021	Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	10.00	Solvent			CHLOROFORM-d
Spectrum Offset (Hz)	2766.3699	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01	Temperature (degree C)		AMBIENT TEMPERATURE			

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.34 (s, 4H), 4.69 (s, 2H), 4.66 (s, 2H), 4.58 (s, 2H), 3.40 (s, 3H), 2.07 (br. s., 1H)

2n

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

File: 08606-13re

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

352 repetitions

OBSERVE C13, 100.5606110 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FR size 65536

Total time 3 hr, 34 min, 58 sec

2n

Formula	C ₉ H ₁₁ ClO ₂	FW	186.6354
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE			Date	Oct 22 2011	Date Stamp	Oct 22 2011	
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Number of Transients			32
Original Points Count	21021	Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	10.00	Solvent	CHLOROFORM-d	
Spectrum Offset (Hz)	2765.3716	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01	Temperature (degree C)	AMBIENT TEMPERATURE			

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.27-7.35 (m, 4H), 4.69 (s, 2H), 4.56 (s, 2H), 3.40 (s, 3H)

13C OBSERVE

Pulse Sequence: s2pul
 DATE: Oct 22 2011
 Solvent: CDCl3
 Ambient temperature
 File: 08606-15
 Mercury-400BB "7Fback"

Relax. delay 1.801 sec
 Pulse 49.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 768 repetitions
 OBSERVE C13, 100.5524199 MHz
 DECOUPLE H1, 399.8920149 MHz
 Power 34 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 1 hr, 47 min, 35 sec

129.280
 128.696
 136.526
 133.567

95.833
 77.479
 77.160
 76.849
 68.495
 55.543

180 160 140 120 100 80 60 40 20 ppm

Formula	C ₁₄ H ₂₆ O ₂ Si	FW	252.4247
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE			Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients 32		
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul				
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C) AMBIENT TEMPERATURE			

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.32 (s, 4H), 4.74 (s, 2H), 4.65 (s, 2H), 0.95 (s, 10H), 0.11 (s, 6H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

File: 08606-14

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

800 repetitions

OBSERVE C13, 100.5606110 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FF size 65536

Total time 1 hr, 47 min, 35 sec

Formula	C ₁₃ H ₂₁ ClOSi	FW	256.8437
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USRX\NMR\FID			Nucleus	1H	Number of Transients	32
Original Points Count	16379	Points Count	16384	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Temperature (degree C)	AMBIENT TEMPERATURE		

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.23-7.33 (m, 4H), 4.70 (s, 2H), 0.94 (s, 9H), 0.10 (s, 6H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-16

Mercury-400EB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

736 repetitions

OBSERVE C13, 100.5606072 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 47 min, 35 sec

Formula	C ₁₀ H ₈ O ₃	FW	176.1687
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Nov 12 2011
Date Stamp	Nov 12 2011	File Name	C:\USR\NMR\FID	Frequency (MHz)	399.93
Nucleus	1H	Number of Transients	32	Pulse Sequence	s2bul
Receiver Gain	20.00	Solvent	DMSO-d6	Spectrum Type	STANDARD
Temperature (degree C)	AMBIENT TEMPERATURE	Original Points Count	16379	Sweep Width (Hz)	5995.20
		Spectrum Offset (Hz)	2247.6611		

¹H NMR (400 MHz, DMSO-d₆) δ 7.94 (s, 1H), 7.70-7.79 (m, 1H), 7.49-7.59 (m, 1H), 7.37 (d, *J*=8.05 Hz, 1H), 7.32 (t, *J*=7.50 Hz, 1H), 5.44 (t, *J*=5.49 Hz, 1H), 4.35 (dd, *J*=1.46, 5.49 Hz, 2H)

2p

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-17-1

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

384 repetitions

OBSERVE C13, 100.5611437 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 53 min, 44 sec

2p

Formula	C ₁₀ H ₁₄ O ₂	FW	166.2170
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Acquisition Time (sec)		Comment	STANDARD 1H OBSERVE		Date	Date Stamp	
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Oct 22 2011
Original Points Count	16379	Points Count	Pulse Sequence	s2pul	Receiver Gain	12.00	Number of Transients
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE	32
					Solvent	CHLOROFORM-d	

¹H NMR (400 MHz, CHLOROFORM-d) δ 6.88 (dd, *J*=1.46, 2.20 Hz, 1H), 6.08 (s, 1H), 4.24 (br. s., 2H), 1.90 (s, 3H), 1.18 (s, 6H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 08606-18

Mercury-400BB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

672 repetitions

OBSERVE C13, 100.5606080 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 47 min, 29 sec

2q

Formula	$C_{10}H_{11}F_3O_3S$	FW	284.2521
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Number of Transients	32
Original Points Count	21021	Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	10.00	Solvent
Spectrum Offset (Hz)	2765.3716	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01	Temperature (degree C)	AMBIENT TEMPERATURE	
CHLOROFORM-d								

1H NMR (400 MHz, CHLOROFORM-d) δ 6.73 (dd, $J=1.56, 3.21$ Hz, 1H), 6.10 (dd, $J=0.64, 3.21$ Hz, 1H), 1.94 (dd, $J=0.82, 1.56$ Hz, 3H), 1.27 (s, 6H)

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 08606-19re

Mercury-400RB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

608 repetitions

OBSERVE C13, 100.5606065 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₀ H ₉ NO	FW	159.1846
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE			Date	Oct 22 2011	Date Stamp	Oct 22 2011	
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients			32
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	16.00	Solvent	CHLOROFORM-d	
Spectrum Offset (Hz)	2247.6414	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE			

¹H NMR (400 MHz, CHLOROFORM-d) δ 8.83 (dd, $J=1.65, 4.21$ Hz, 1H), 8.08-8.14 (m, 1H), 8.04 (d, $J=8.42$ Hz, 1H), 7.78 (s, 1H), 7.67 (dd, $J=1.83, 8.78$ Hz, 1H), 7.37 (dd, $J=4.21, 8.23$ Hz, 1H), 4.89 (s, 2H), 3.11 (br. s., 1H)

3a

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-20

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

2176 repetitions

OBSERVE C13, 100.5606087 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₈ H ₇ NO	FW	109.1259
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE				Date	Oct 22 2011	Date Stamp	Oct 22 2011	
File Name	C:\USRX\NMR\FID		Frequency (MHz)	399.89	Nucleus	1H	Number of Transients				32
Original Points Count	21021	Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	16.00	Solvent			CHLOROFORM-d
Spectrum Offset (Hz)	2765.3716	Spectrum Type	STANDARD	Sweep Width (Hz)	6006.01	Temperature (degree C)					AMBIENT TEMPERATURE

¹H NMR (400 MHz, CHLOROFORM-d) δ 8.33-8.50 (m, 1H), 7.64-7.76 (m, 1H), 7.17-7.32 (m, 1H), 4.68 (s, 2H)

13C OBSERVE

Pulse Sequence: s2pul

DATE: Oct 22 2011

Solvent: CDCl3

Ambient temperature

File: 08606-21

Mercury-400BB "7fback"

Relax. delay 1.801 sec

Pulse 49.1 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

576 repetitions

OBSERVE C13, 100.5524206 MHz

DECOUPLE H1, 399.8920149 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 47 min, 29 sec

3b

Formula	C ₉ H ₉ NO ₂	FW	163.1733
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Acquisition Time (sec)	3.5000	Comment	STANDARD 1H OBSERVE	Date	Nov 12 2011	Frequency (MHz)	399.89
Date Stamp	Nov 12 2011		File Name	C:\USR\NMR\FID		Pulse Sequence	s2bul
Nucleus	1H	Number of Transients	32	Original Points Count	21021	Points Count	32768
Receiver Gain	10.00	Solvent	DMSO-d ₆	Spectrum Offset (Hz)	2772.6514	Spectrum Type	STANDARD
Temperature (degree C)	AMBIENT TEMPERATURE					Sweep Width (Hz)	6006.01

¹H NMR (400 MHz, DMSO-d₆) δ 7.48-7.63 (m, 2H), 7.28 (dd, *J*=1.65, 8.25 Hz, 1H), 5.29 (t, *J*=5.77 Hz, 1H), 4.59 (d, *J*=5.87 Hz, 2H), 2.59 (s, 3H)

3c

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-23-1

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

320 repetitions

OBSERVE C13, 100.5611407 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FF size 65536

Total time 53 min, 44 sec

3c

Formula	C ₇ H ₈ O ₂ S	FW	156.2022
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Acquisition Time (sec)		2.7320	Comment	STANDARD 1H OBSERVE		Date	Oct 22 2011	Date Stamp	Oct 22 2011
File Name	C:\USR\NMR\FID			Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379		Points Count	16384	Pulse Sequence	Receiver Gain	16.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2247.6414		Spectrum Type	STANDARD	Sweep Width (Hz)	Temperature (degree C)	AMBIENT TEMPERATURE		

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.56 (d, *J*=3.66 Hz, 1H), 6.95-7.07 (m, 1H), 4.84 (d, *J*=5.49 Hz, 2H), 2.63-2.74 (m, 1H), 2.52 (s, 3H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 08606-24

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

448 repetitions

OBSERVE C13, 100.5606103 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

3d

Formula	C ₈ H ₆ O ₃	FW	126.1100
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Acquisition Time (sec)		2.7320	Comment	STANDARD 1H OBSERVE		Date	Date Stamp	
File Name	C:\USR\NMR\FID			Frequency (MHz)	399.92	Oct 22 2011	Oct 22 2011	
Original Points Count	16379		Points Count	Pulse Sequence	s2pul	Nucleus	1H	Number of Transients
Spectrum Offset (Hz)	2247.6414		Spectrum Type	STANDARD		Receiver Gain	10.00	32
						Temperature (degree C)	AMBIENT	Solvent
						Sweep Width (Hz)	5995.20	CHLOROFORM-d

¹H NMR (400 MHz, CHLOROFORM-d) δ 9.53 (s, 1H), 7.20 (d, *J*=3.66 Hz, 1H), 6.41-6.54 (m, 1H), 4.68 (d, *J*=5.86 Hz, 2H), 3.38 (t, *J*=5.67 Hz, 1H)

3e

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-25

Mercury-400BB "6ftback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

384 repetitions

OBSERVE C13, 100.5606133 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₂ H ₁₃ NO ₃	FW	219.2365
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Nov 12 2011	Frequency (MHz)	399.93
Date Stamp	Nov 12 2011		File Name	C:\USR\NMR\FID		Pulse Sequence	s2bul
Nucleus	1H	Number of Transients	32	Original Points Count	16379	Points Count	16384
Receiver Gain	10.00	Solvent	DMSO-d6	Spectrum Offset (Hz)	2247.6611	Spectrum Type	STANDARD
Temperature (degree C)	AMBIENT TEMPERATURE			Spectrum Offset (Hz)	2247.6611	Sweep Width (Hz)	5995.20

¹H NMR (400 MHz, DMSO-d₆) δ 11.79 (br. s., 1H), 7.56 (s, 1H), 7.39 (d, *J*=8.42 Hz, 1H), 7.22 (dd, *J*=1.46, 8.78 Hz, 1H), 7.10 (d, *J*=1.10 Hz, 1H), 5.08 (t, *J*=5.86 Hz, 1H), 4.53 (d, *J*=5.86 Hz, 2H), 4.31 (q, *J*=7.32 Hz, 2H), 1.32 (t, *J*=7.14 Hz, 3H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-26-1

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

960 repetitions

OBSERVE C13, 100.5611422 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

3f

Formula	C ₇ H ₇ ClO	FW	142.5829
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Acquisition Time (sec)		2.7320	Comment	STANDARD 1H OBSERVE		Date	Oct 23 2011	Date Stamp	Oct 23 2011
File Name	C:\USR\NMR\FID			Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379			Pulse Sequence	s2pul	Receiver Gain	16.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2248.1555			Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE		

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.21-7.38 (m, 4H), 4.64 (d, *J*=3.29 Hz, 2H), 1.97 (br. s., 1H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-28

Mercury-400RB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

800 repetitions

OBSERVE C13, 100.5606095 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

5

Formula	C ₈ H ₁₀ O ₂	FW	138.1638
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE	Date	Nov 12 2011	Frequency (MHz)	399.93
Date Stamp	Nov 12 2011	File Name	C:\USR\NMR\FID	Points Count	16384	Pulse Sequence	s2bul
Nucleus	1H	Number of Transients	16	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20
Receiver Gain	6.00	Solvent	DMSO-d ₆				
Temperature (degree C)	AMBIENT TEMPERATURE						

¹H NMR (400 MHz, DMSO-d₆) δ 7.24 (s, 1H), 5.12 (t, *J*=5.67 Hz, 1H), 4.46 (d, *J*=5.86 Hz, 2H)

6

13C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 08606-29-1

Mercury-400HB "6fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

160 repetitions

OBSERVE C13, 100.5611407 MHz

DECOUPLE H1, 399.9264685 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 26 min, 52 sec

Formula	C ₇ H ₄ ClF ₃ O ₃ S	FW	260.6181
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE				
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.92	Date	Oct 23 2011	
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Nucleus	1H
Spectrum Offset (Hz)	2248.5215	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Receiver Gain	16.00
				Temperature (degree C)			AMBIENT TEMPERATURE
				Solvent			CHLOROFORM-d
				Number of Transients			32
				Date Stamp			Oct 23 2011

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.35-7.47 (m, 2H), 7.17-7.30 (m, 2H)

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 08606-27

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

544 repetitions

OBSERVE C13, 100.5606065 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

Formula	C ₁₁ H ₁₀ O ₃ S	FW	222.2603
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Acquisition Time (sec)		Comment		STANDARD 1H OBSERVE		Date		Date Stamp	
File Name	C:\USR\NMR\FID			Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	14.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2246.3259	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE		

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.82-7.92 (m, 3H), 7.76 (d, *J*=2.20 Hz, 1H), 7.49-7.58 (m, 2H), 7.41 (ddd, *J*=1.10, 2.38, 8.97 Hz, 1H), 3.18 (d, *J*=1.10 Hz, 3H)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-31

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

448 repetitions

OBSERVE C13, 100.5606103 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

7

Formula	C ₁₇ H ₁₄ O ₃ S	FW	298.3563
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Acquisition Time (sec)	2.7320	Comment	STANDARD 1H OBSERVE		Date	Oct 23 2011	Date Stamp	Oct 23 2011
File Name	C:\USR\NMR\FID		Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	32
Original Points Count	16379	Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	14.00	Solvent
Spectrum Offset (Hz)	2246.6919	Spectrum Type	STANDARD	Sweep Width (Hz)	5995.20	Temperature (degree C)	AMBIENT TEMPERATURE	
CHLOROFORM-d								

¹H NMR (400 MHz, CHLOROFORM-d) δ 7.77-7.84 (m, 1H), 7.70-7.77 (m, 4H), 7.44-7.51 (m, 3H), 7.29 (d, *J*=8.05 Hz, 2H), 7.09 (dd, *J*=2.38, 8.97 Hz, 1H), 2.44 (s, 3H)

8

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 08606-30

Mercury-400BB "6Fback"

Relax. delay 1.801 sec

Pulse 37.5 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

512 repetitions

OBSERVE C13, 100.5606087 MHz

DECOUPLE H1, 399.9245689 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 3 hr, 34 min, 58 sec

8