Supporting Information for:

A Silicon-Based Approach to Oligoarenes by Iterative Cross-Coupling Reactions of Halogenated Organo[(2-hydroxymethyl)phenyl]dimethylsilanes

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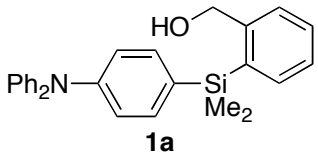
General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flush column chromatography was performed using Kanto Chemical silica gel 60 (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) spectrometer with solvent resonance (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm) as the internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad), coupling constants (Hz), and integration. IR spectra recorded on a Shimadzu FT-IR 8400 spectrometer are reported in cm^{-1}. Melting points (mp) were measured on a Yanaco Mp-500D and are uncorrected. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI) or JEOL JMS-HX110A (FAB+) spectrometer. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H using chloroform as an eluent.

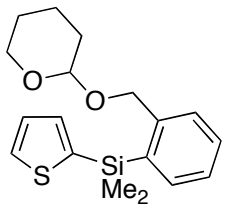
Chemicals. Unless otherwise noted, reagents were commercially available and were used without purification. Anhydrous DMF was purchased from Nacalai Tesque. Anhydrous toluene purchased from Kanto Chemical was degassed by purging vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[1] RuPhos was prepared according to the Buchwald's protocol.[2] Unless otherwise described below, preparation of organo[2-(hydroxymethyl)phenyl]dimethylsilanes is described in our previous publications.[3]



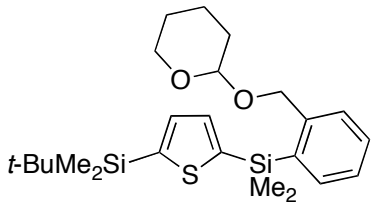
1a

Preparation of [4-(diphenylamino)phenyl][2-(hydroxymethyl)phenyl]dimethylsilane (1a).[4] To a suspension of Mg (1.9 g, 79 mmol) in Et_2O (160 mL) was added a solution of 4-bromo-*N*,*N*-diphenylaniline (25 g, 77 mmol) in THF (60 mL) at rt, and the resulting mixture was stirred at 60 °C for 4 h. The mixture was cooled to 0 °C, and then 1,1-dimethyl-2-oxa-1-silaindan **4** (12.1 g, 73 mmol) was added. After being stirred at rt overnight, the reaction mixture was quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **1a** (30 g, 95%) as a colorless viscous oil, R_f 0.70 (hexane–ethyl acetate = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 1H), 7.48–7.37 (m, 2H), 7.31 (d, *J* =8.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 5H), 7.08 (d, *J* = 8.2 Hz, 4H), 7.01

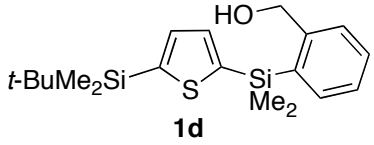
(t, J = 7.5 Hz, 4H), 4.58 (s, 2H), 1.33 (br, 1H), 0.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.2, 146.3, 136.2, 135.3, 134.6, 130.9, 129.8, 129.2, 128.2, 126.9, 124.7, 123.1, 122.1, 65.4, –0.8; IR (neat): 3398, 3057, 3011, 2955, 1585, 1489, 1327, 1315, 1279, 1254, 1196, 1109, 1076, 1028, 812, 754, 696, 665, 621 cm^{-1}; Anal. Calcd for $C_{27}H_{27}NOSi$; C, 79.17; H, 6.64. Found: C, 79.21; H, 6.80.



Preparation of dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl](2-thienyl)-silane. To a mixture of **1b** (20 g, 80 mmol) and 3,4-dihydro-2*H*-pyran (13.5 g, 160 mmol) were added 4 drops of conc. HCl at rt, and the resulting mixture was stirred for 4 h, diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (22 g, 82%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 4.6, 0.6 Hz, 1H), 7.53–7.46 (m, 2H), 7.40 (td, J = 7.5, 1.3 Hz, 1H), 7.29–7.22 (m, 2H), 7.17 (dd, J = 4.5, 3.4 Hz, 1H), 4.73 (d, J = 12.1 Hz, 1H), 4.53 (t, J = 3.5 Hz, 1H), 4.47 (d, J = 12.1 Hz, 1H), 3.85–3.77 (m, 1H), 3.50–3.42 (m, 1H), 1.88–1.75 (m, 1H), 1.72–1.42 (m, 5H), 0.652 (s, 3H), 0.651 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.2, 135.7, 135.20, 135.15, 130.9, 129.7, 128.5, 128.0, 126.7, 97.8, 68.7, 62.1, 30.6, 25.6, 19.5, 0.4, 0.3; IR (neat): 2943, 2870, 1437, 1406, 1350, 1252, 1213, 1202, 1119, 1078, 1026, 989, 907, 833, 812, 777, 756, 708, 656 cm^{-1}; Anal. Calcd for $C_{18}H_{24}O_2SSi$: C, 65.01; H, 7.27. Found: C, 64.88; H, 7.06.



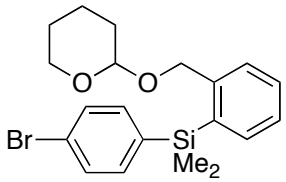
Preparation of 5-(*tert*-butyldimethylsilyl)-2-(dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl)thiophene. To a solution of dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl](2-thienyl)silane (1.56 g, 4.7 mmol) in Et_2O (5 mL) were added TMEDA (0.63 g, 5.4 mmol) and a 1.6 M solution of *n*-BuLi (5.2 mmol) in hexane at –40 °C. The resulting mixture was stirred at rt for 1 h, and then a solution of *t*-$BuMe_2SiCl$ in Et_2O (4 mL) was added at –40 °C. The resulting mixture was stirred at the same temperature for 30 min and then at rt overnight, diluted with diethyl ether, washed with water and brine, and then dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the title compound (1.74 g, 83%) as a colorless oil, R_f 0.37 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.43 (m, 2H), 7.39 (td, J = 7.5, 1.4 Hz, 1H), 7.32–7.18 (m, 3H), 4.72 (d, J = 12.1 Hz, 1H), 4.52 (t, J = 3.6 Hz, 1H), 4.46 (d, J = 12.1 Hz, 1H), 3.86–3.75 (m, 1H), 3.50–3.39 (m, 1H), 1.87–1.74 (m, 1H), 1.70–1.40 (m, 5H), 0.91 (s, 9H), 0.653 (s, 3H), 0.649 (s, 3H), 0.29 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.91, 143.85, 143.4, 136.04, 135.98, 135.9, 135.1, 129.6, 128.4, 126.7, 97.8, 68.8, 62.1, 30.6, 26.5, 25.6, 19.5, 17.0, 0.6, 0.4, –4.5; IR (neat): 2953, 2928, 2855, 1470, 1250, 1202, 1119, 1078, 1055, 1026, 1007, 976, 907, 835, 804, 773, 752, 675 cm^{-1}; Anal. Calcd for $C_{24}H_{38}O_2SSi_2$; C, 64.52; H, 8.57. Found: C, 64.51; H, 8.37.



1d

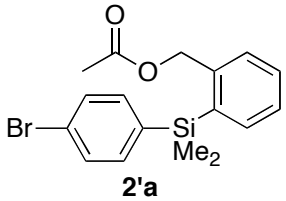
Preparation of 5-(*tert*-butyldimethylsilyl)-2-([2-(hydroxymethyl)-phenyl]dimethylsilyl)thiophene (1d). A solution of 5-(*tert*-Butyldimethylsilyl)-2-(dimethyl[2-(tetrahydro-2*H*-pyranoxymeth yl)phenyl]silyl)thiophene (1.51 g, 34 mmol) and pyridinium *p*-toluenesulfonate (PPTS, 171 mg, 0.68 mmol) in methanol (10 mL) was stirred at 40 °C for 2 h and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **1d** (1.13 g, 92%) as a white solid, mp 50.3–51.5 °C, R_f 0.26 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.3 Hz, 1H), 7.47–7.38 (m, 2H), 7.36–7.25 (m, 3H), 4.61 (d, J = 6.2 Hz, 2H), 1.38 (t, J = 6.0 Hz, 1H), 0.90 (s, 9H), 0.67 (s, 6H), 0.29 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 144.0, 143.9, 136.2, 136.0, 135.7, 135.1, 130.0,

128.3, 127.0, 65.4, 26.5, 17.0, 0.5, –4.6; IR (KBr): 3321, 2953, 2928, 2856, 1250, 1204, 1007, 835, 822, 808, 777 cm^{-1}; Anal. Calcd for $C_{19}H_{30}OSSi_2$; C, 62.92; H, 8.34. Found: C, 62.89; H, 8.17.



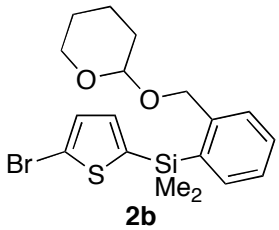
2a

Preparation of (4-bromophenyl)dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (2a). To a mixture of (4-bromophenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (6.4 g, 20 mmol) and 3,4-dihydro-2*H*-pyran (2.0 g, 24 mmol) was added a drop of conc. HCl at rt, and the resulting mixture was stirred overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **2a** (7.3 g, 90%) as a colorless oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.37 (m, 5H), 7.36–7.25 (m, 3H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.43 (t, *J* = 3.3 Hz, 1H), 4.33 (d, *J* = 11.9 Hz, 1H), 3.78–3.68 (m, 1H), 3.45–3.36 (m, 1H), 1.84–1.70 (m, 1H), 1.67–1.40 (m, 5H), 0.58 (s, 3H), 0.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 137.7, 135.5, 135.3, 130.8, 129.7, 128.6, 126.8, 123.7, 97.8, 68.7, 62.1, 30.6, 25.5, 19.5, –0.9, –1.0; IR (neat): 2943, 2870, 1570, 1479, 1439, 1377, 1258, 1202, 1119, 1078, 1067, 1026, 1011, 974, 907, 835, 818, 806, 775, 754, 723 cm^{-1}; Anal. Calcd for $C_{20}H_{25}BrO_2Si$: C, 59.25; H, 6.22. Found: C, 59.09; H, 6.22.



2'a

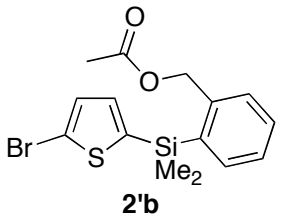
Preparation of [2-(acetoxymethyl)phenyl](4-bromophenyl)dimethylsilane (2'a). To a solution of (4-bromophenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (3.2 g, 10 mmol) in Et_2O (20 mL) were added DMAP (12.2 mg, 0.10 mmol), pyridine (1.58 g, 20 mmol), and acetyl chloride (0.86 g, 11 mmol) at 0 °C. The resulting mixture was stirred at rt overnight, diluted with Et_2O, neutralized with a 1M HCl aqueous solution (20 mL), and washed with water and brine. The organic layers were dried over anhydrous $MgSO_4$, filtered through a Celite pad, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **2'a** (3.7 g, 100%) as a white solid, mp 57.4–58.0 °C, R_f 0.44 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.49–7.28 (m, 7H), 4.94 (s, 2H), 1.92 (s, 3H), 0.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.1, 137.2, 136.4, 135.6, 135.4, 130.9, 129.9, 129.6, 127.6, 123.9, 66.5, 20.9, –1.0; IR (KBr): 2959, 1730, 1566, 1481, 1377, 1259, 1244, 1069, 1034, 1011, 837, 824, 800, 762, 721, 494 cm^{-1}; Anal. Calcd for $C_{17}H_{19}BrO_2Si$: C, 56.20; H, 5.27. Found: C, 56.19; H, 5.22.



2b

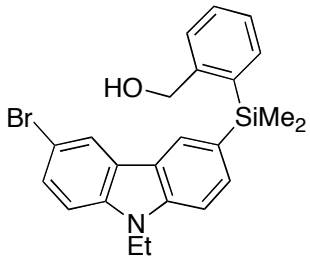
Preparation of (2-bromo-5-thienyl)dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (2b). To a solution of dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl](2-thienyl)silane (8.4 g, 25 mmol) in Et_2O (25 mL) were added TMEDA (3.4 g, 29 mmol) and a 1.6 M solution of *n*-BuLi (28 mmol) in hexane at –40 °C, after being stirred at rt for 2 h, 1,2-dibromo-1,1,2,2-tetrafluoroethane (7.8 g, 30 mmol) was added at –40 °C, and the resulting mixture was stirred at the same temperature for further 1 h, quenched with a saturated $Na_2S_2O_3$ aqueous solution (100 mL), and then diluted with diethyl ether (300 mL). The organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **2b** (9.3 g, 90%) as a yellowish oil, R_f 0.27 (hexane–ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 3.5 Hz, 1H), 6.97 (d, *J* = 3.5 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.54 (t, *J* = 3.5 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.87–3.75 (m, 1H), 3.52–3.42 (m, 1H), 1.88–1.75 (m, 1H), 1.72–1.41 (m, 5H), 0.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.6, 135.5,

135.2, 134.9, 131.1, 129.9, 128.7, 126.9, 117.3, 97.8, 68.7, 62.2, 30.6, 25.6, 19.5, 0.2, 0.1 cm^{-1}; IR (neat): 2943, 2870, 1439, 1406, 1350, 1259, 1204, 1119, 1078, 1026, 974, 953, 907, 870, 837, 812, 779, 754, 691, 656 cm^{-1}; Anal. Calcd for $C_{18}H_{23}BrO_2SSi$: C, 52.55; H, 5.63. Found: C, 52.72; H, 5.63.

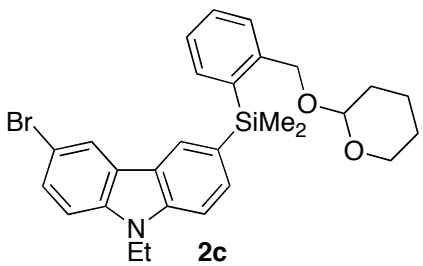


2'b

Preparation of [2-(acetoxymethyl)phenyl](2-bromo-5-thienyl)dimethylsilane (2'b). To a solution of diisopropylamine (0.53 g, 5.3 mmol) in THF (3 mL) was added a 1.6 M solution of *n*-BuLi (3.3 mmol) in hexane at –40 °C, and the resulting mixture was stirred for 30 min. To this was added 2-bromothiophene (0.82 g, 5.0 mmol) at –70 °C, and the resulting mixture was stirred at –40 °C for 30 min before addition of $MgBr_2$•Et_2O (1.4 g, 5.3 mmol) at –30 °C. After being stirred at –30 °C for further 30 min, **4** (0.82 g, 5.0 mmol) was added at the same temperature, and the resulting mixture was stirred at rt overnight. Acetyl chloride (0.39 g, 5.0 mmol) was added at 0 °C, and then the resulting mixture was stirred at rt for additional 6 h. The mixture was diluted with diethyl ether, washed with a saturated $NaHCO_3$ aqueous solution, water, and brine, and the organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **2b** (1.14 g, 62%) as a yellowish oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.48–7.31 (m, 3H), 7.09 (d, *J* = 3.5 Hz, 1H), 6.99 (d, *J* = 3.7 Hz, 1H), 5.07 (s, 2H), 2.02 (s, 3H), 0.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.0, 135.9, 135.6, 135.4, 131.2, 130.1, 129.6, 127.7, 117.6, 66.5, 21.0, 0.1 cm^{-1}; IR (neat): 3057, 2957, 1736, 1437, 1404, 1379, 1362, 1286, 1227, 1128, 1078, 1069, 1026, 999, 955, 837, 810, 779, 756, 692, 656 cm^{-1}; Anal. Calcd for $C_{15}H_{17}BrO_2SSi$: C, 48.78; H, 4.64. Found: C, 48.72; H, 4.67.



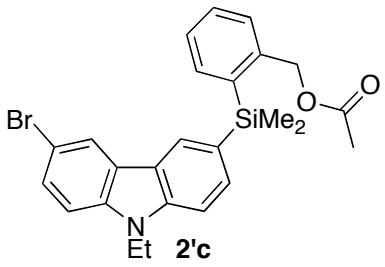
Preparation of (3-bromo-9-ethyl-9*H*-6-carbazolyl)[2-(hydroxymethyl)-phenyl]dimethylsilane. To a solution of 3,6-dibromo-9-ethyl-9*H*-carbazole[5] (7.7 g, 22 mmol) in THF (60 mL) was added a 1.6 M solution of *n*-BuLi in hexane (14 mL, 22 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h. To this was added **4** (3.6 g, 22 mmol) at –78 °C, and the resulting mixture was warmed slowly to rt, stirred overnight, and then quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (8.6 g, 90%) as a white solid, mp 49.2–51.0 °C, R_f 0.37 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48–7.22 (m, 4H), 4.55 (d, *J* = 4.4 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.24 (br, *J* = 5.3 Hz, 1H), 0.69 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 140.8, 138.4, 136.3, 135.4, 131.5, 129.8, 128.3, 128.1, 127.7, 126.9, 126.3, 124.3, 123.1, 121.9, 111.8, 109.8, 108.6, 65.3, 37.8, 13.9, 0.2; IR (KBr): 3418, 2972, 2951, 1587, 1474, 1435, 1346, 1286, 1275, 1232, 1157, 1097, 847, 802, 773, 754 cm^{-1}; HRMS (FAB+) Calcd for $C_{23}H_{24}BrNOSi$: M^+, 437.0811. Found: *m*/*z* 437.0807.



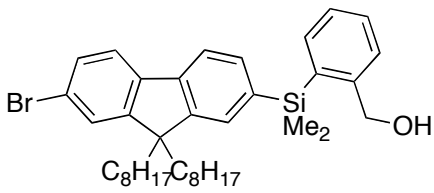
2c

Preparation of (3-bromo-9-ethyl-9*H*-6-carbazolyl)dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (2c). To a mixture of (3-bromo-9-ethyl-9*H*-6-carbazolyl)[2-(hydroxymethyl)phenyl]dimethylsilane (5.6 g, 13 mmol) and 3,4-dihydro-2*H*-pyran (1.29 g, 15.4 mmol) were added 3 drops of conc. HCl at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and

filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **2c** (6.1 g, 91%) as a colorless viscous oil, R_f 0.19 (hexane–ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.17 (s, 1H), 7.60–7.46 (m, 4H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.32–7.23 (m, 2H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.44–4.37 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.73–3.64 (m, 1H), 3.35–3.26 (m, 1H), 1.80–1.67 (m, 1H), 1.62–1.31 (m, 8H), 0.68 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 140.7, 138.3, 136.6, 135.4, 131.8, 129.5, 128.5, 128.1, 127.8, 126.7, 126.5, 124.4, 123.1, 121.7, 111.7, 109.7, 108.3, 97.8, 68.8, 62.0, 37.7, 30.5, 25.5, 19.4, 13.9, –0.3, –0.4; IR (neat): 3053, 3009, 2947, 2872, 1620, 1589, 1564, 1470, 1435, 1381, 1346, 1286, 1275, 1259, 1232, 1200, 1182, 1157, 1128, 1097, 1078, 1053, 1024, 976, 907, 870, 847, 800, 754, 689, 667, 635, 569 cm^{-1}; Anal. Calcd for $C_{28}H_{32}BrNO_2Si$: C, 64.36; H, 6.17. Found: C, 64.10; H, 6.05.

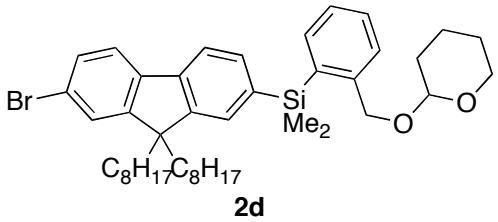


Preparation of [2-(acetoxymethyl)phenyl](3-bromo-9-ethyl-9*H*-6-carbazolyl)dimethylsilane (2'c). To a solution of 3,6-dibromo-9-ethyl-9*H*-carbazole (7.0 g, 20 mmol) in THF (60 mL) was added a 1.6 M solution of *n*-BuLi in hexane (12.5 mL, 20 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h. To this was added **4** (3.3 g, 20 mmol) at –78 °C. The resulting mixture was warmed slowly to rt and stirred for further 17 h. Acetyl chloride (1.6 g, 20 mmol) was added at 0 °C, and the resulting mixture was stirred at rt for 6 h. The reaction mixture was diluted with Et_2O and washed with a saturated $NaHCO_3$ aqueous solution, water, and then brine. The organic layers were dried over anhydrous $MgSO_4$ before concentration in vacuo, and the residue was purified by flash chromatography on silica gel to afford **2'c** (8.8 g, 92%) as a colorless viscous oil, R_f 0.44 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.6 Hz, 1H), 8.14 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.45–7.32 (m, 4H), 7.28–7.23 (m, 1H), 4.99 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.84 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.69 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.2, 140.8, 138.3, 137.7, 135.7, 131.6, 129.6, 129.4, 128.2, 127.5, 127.3, 126.5, 124.4, 123.1, 121.8, 111.7, 109.8, 108.5, 66.6, 37.7, 20.9, 13.9, –0.4; IR (neat): 3055, 2974, 2897, 1732, 1622, 1589, 1474, 1435, 1379, 1346, 1286, 1275, 1232, 1157, 1128, 1097, 1024, 849, 802, 773, 756, 691, 635 cm^{-1}; Anal. Calcd for $C_{25}H_{26}BrNO_2Si$: C, 62.49; H, 5.45. Found: C, 62.79; H, 5.44.



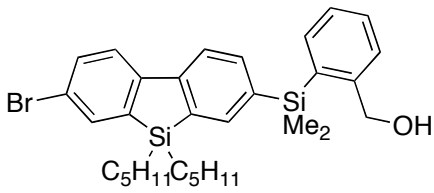
Preparation of (2-bromo-9,9'-dioctyl-9*H*-7-fluorenyl)[2-(hydroxymethyl)phenyl]dimethylsilane. To a solution of 2,7-dibromo-9,9'-dioctyl-9*H*-fluorene (22 g, 40 mmol) in THF (120 mL) was added a 1.6 M solution of *n*-BuLi in hexane (25 mL, 40 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h. To this was added **4** (6.6 g, 40 mmol) at –78 °C, and the resulting mixture was warmed slowly to rt, stirred overnight, and then quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (25 g, 100%) as a colorless viscous oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.57–7.50 (m, 2H), 7.48–7.38 (m, 6H), 7.28 (td, *J* = 7.1, 2.0 Hz, 1H), 4.52 (d, *J* = 5.7 Hz, 2H), 1.97–1.80 (m, 4H), 1.30–0.94 (m, 21H), 0.83 (t, *J* = 7.1 Hz, 6H), 0.68–0.48 (m, 4H), 0.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 149.6, 146.4, 141.0, 139.7, 137.8, 136.2, 135.5, 132.5, 129.81, 129.79, 128.1, 128.0, 126.9, 126.1, 121.2, 121.1, 119.3, 65.3, 55.4, 40.1, 31.9, 30.0, 29.28, 29.25, 23.8, 22.7, 14.2, –0.7; IR (neat): 3393, 3053, 2955, 2926, 2855, 1601, 1560, 1454, 1396, 1377, 1256, 1200,

1126, 1092, 1078, 1061, 1003, 876, 814, 777, 752, 689, 646 cm^{-1}; Anal. Calcd for $C_{38}H_{53}BrOSi$: C, 72.01; H, 8.43. Found: C, 71.90; H, 8.39.

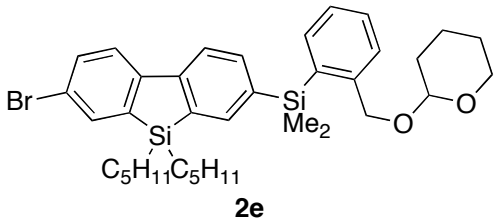


2d

Preparation of (2-bromo-9,9'-dioctyl-9*H*-7-fluorenyl)dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (2d). To a mixture of (2-bromo-9,9'-dioctyl-9*H*-7-fluorenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (21 g, 32 mmol) and 3,4-dihydro-2*H*-pyran (3.3 g, 39 mmol) were added 2 drops of conc. HCl at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **2d** (22 g, 95%) as a colorless viscous oil, R_f 0.34 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.50–7.35 (m, 7H), 7.26–7.20 (m, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.50 (t, *J* = 3.2 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 3.84–3.74 (m, 1H), 3.47–3.39 (m, 1H), 1.96–1.75 (m, 5H), 1.69–1.41 (m, 5H), 1.28–0.94 (m, 20H), 0.83 (t, *J* = 7.2 Hz, 6H), 0.68–0.52 (m, 4H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 149.4, 144.0, 140.7, 139.8, 137.8, 136.4, 135.5, 132.7, 129.7, 129.4, 128.4, 128.2, 126.6, 126.1, 121.0, 119.1, 109.7, 97.6, 68.8, 61.9, 55.4, 40.1, 31.9, 30.6, 30.0, 29.31, 29.28, 25.6, 23.9, 22.7, 19.4, 14.2, –0.65, –0.73; IR (neat) 2926, 2853, 1452, 1258, 1200, 1119, 1092, 1078, 1055, 1026, 1003, 836, 814, 777, 752, 646 cm^{-1}; Anal. Calcd for $C_{43}H_{61}BrO_2Si$; C, 71.94; H, 8.56. Found: C, 71.96; H, 8.73.



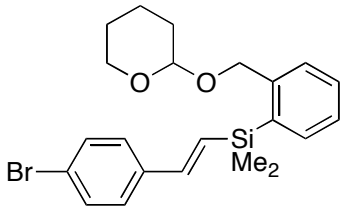
Preparation of (2-bromo-9,9'-dipentyl-9*H*-9-silafluoren-7-yl)[2-(hydroxymethyl)phenyl]dimethylsilane. To a solution of 2,7-dibromo-9,9'-dioctyl-9*H*-9-silafluorene[6] (2.5 g, 5.2 mmol) in THF (16 mL) was added a 1.6 M solution of *n*-BuLi in hexane (3.3 mL, 5.2 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h. To this was added **4** (0.85 g, 5.2 mmol) at –78 °C. The resulting mixture was warmed slowly to rt, stirred overnight, and the quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (1.79 g, 61%) as a viscous oil, R_f 0.32 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.57–7.46 (m, 3H), 7.45–7.36 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 7.5 Hz, 2H), 1.34–1.13 (m, 13H), 0.92–0.84 (m, 4H), 0.77 (t, *J* = 6.8 Hz, 6H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 146.6, 146.4, 141.0, 138.6, 137.7, 136.8, 135.86, 135.83, 135.6, 135.4, 132.7, 129.8, 128.1, 126.9, 122.5, 122.0, 120.3, 65.4, 35.5, 23.6, 22.2, 14.1, 12.1, –0.8; IR (neat): 3377, 3057, 2955, 2922, 2870, 2856, 1582, 1458, 1443, 1379, 1366, 1250, 1113, 1076, 999, 837, 827, 775, 750, 646 cm^{-1}; Anal. Calcd for $C_{31}H_{41}BrOSi_2$; C, 65.81; H, 7.30. Found: C, 65.94; H, 7.51.



2e

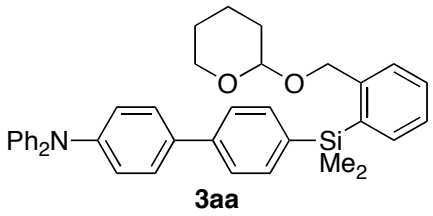
Preparation of (2-bromo-9,9'-dipentyl-9*H*-9-silafluoren-7-yl)dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (2e). To a solution of (2-bromo-9,9'-dipentyl-9*H*-9-silafluoren-7-yl)[2-(hydroxymethyl)phenyl]dimethylsilane (1.36 g, 2.4 mmol) and 3,4-dihydro-2*H*-pyran (0.4 g, 4.8 mmol) in Et_2O (2.4 mL) were added 2 drops of conc. HCl at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a

Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **2e** (1.47 g, 94%) as a colorless oil, R_f 0.35 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.62 (m, 4H), 7.57–7.44 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30–7.22 (m, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.47 (t, *J* = 3.2 Hz, 1H), .4.41 (d, *J* = 12.1 Hz, 1H), 3.80–3.70 (m, 1H), 3.44–3.25 (m, 1H), 1.84–1.70 (m, 1H), 1.66–1.02 (m, 17H), 0.95–0.85 (m, 6H), 0.84–0.74 (m, 4H), 0.620 (s, 3H), 0.617 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.8, 144.0, 141.1, 138.7, 137.8, 136.4, 136.1, 136.0, 135.6, 135.4, 132.7, 129.5, 128.5, 126.7, 122.4, 121.9, 120.0, 97.7 68.8, 61.9, 35.6, 30.6, 25.5, 23.6, 22.2, 19.4, 14.1, 12.2, –0.7, –0.8; IR (neat): 2955, 2922, 2870, 2856, 1441, 1250, 1200, 1115, 1078, 1026, 837, 816, 775, 750 cm^{-1}; Anal. Calcd for $C_{36}H_{49}BrO_2Si_2$; C, 66.54; H, 7.60. Found: C, 66.39; H, 7.42.



2f

(*E*)-2-[(4-Bromophenyl)ethenyl][2-(tetrahydro-2*H*-pyranoxymethyl)-phenyl]dimethylsilane (2f). To a solution of dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (0.79 g, 3.2 mmol) and 1-bromo-4-ethynylbenzene (0.54 g, 3.0 mmol) in hexane (0.3 mL) were slowly added a 10 wt% hexane solution of *t*-Bu_3P (6.1 mg, 3.0 μmol) and a 0.01 M solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.3 mL, 3.0 μmol) in hexane at –40 °C over 30 min. The resulting mixture was stirred at the same temperature for further 30 min and then at rt for 23 h, filtered through a Florisil pad. Concentration in vacuo followed by flash chromatography on silica gel gave **2f** (1.23 g, 95%) as a yellow oil, R_f 0.13 (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.47–7.37 (m, 3H), 7.32–7.27 (m, 3H), 6.86 (d, *J* = 19.0 Hz, 1H), 6.65 (d, *J* = 19.0 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.65 (t, *J* = 3.6 Hz, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 3.98–3.82 (m, 1H), 3.52–3.42 (m, 1H), 1.91–1.77 (m, 1H), 1.76–1.43 (m, 5H), 0.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.3, 137.0, 136.3, 134.9, 131.4, 129.4, 128.9, 128.4, 127.8, 126.8, 121.8, 97.9, 68.9, 62.2, 30.7, 25.6, 19.5, –1.1, –1.2; IR (neat): 2947, 2870, 1603, 1485, 1439, 1396, 1350, 1248, 1200, 1117, 1074, 1026, 1009, 988, 961, 907, 845, 818, 785, 752 cm^{-1}; Anal. Calcd for $C_{22}H_{27}BrO_2Si$; C, 61.25; H, 6.31. Found: C, 61.52 ; H, 6.32.

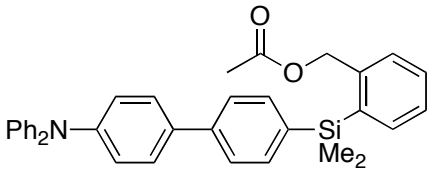


3aa

Gram-scale Cross-coupling reaction of 1a with 2a. To a solution of **1a** (4.9 g, 12 mmol), K_2CO_3 (3.5 g, 2.5 mmol), [(η^3- C_3H_5)PdCl]$_2$ (18 mg, 50 μmol, measured in a glove box), RuPhos (98 mg, 0.21 mmol), and CuI (57 mg, 0.30 mmol) in DMF (8 mL) and THF (22 mL) in a Schlenk tube was added **2a** (4.1 g, 10 mmol), and the resulting mixture was stirred at 75 °C for 7 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water for 5 times and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by distillation under vacuum (3.0 mmHg) to gave cyclic silyl ether **4** (1.50 g, 86% based on consumed **1a**). The residue was further purified by flash chromatography on silica gel (hexane–ethyl acetate = 20:1, 10:1, then 2:1 as eluents) to give 4'-(diphenylamino)-4-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)biphenyl (**3aa**, 5.0 g, 88%) and unreacted **1a** (0.58 g, 12%). **3aa**: A white solid, mp 52.6–53.5 °C, R_f 0.18 (hexane–ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.37 (m, 8H), 7.34–7.20 (m, 6H), 7.16–7.07 (m, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.46–4.37 (m, 2H), 3.80–3.70 (m, 1H), 3.45–3.35 (m, 1H), 1.84–1.69 (m, 1H), 1.66–1.38 (m, 5H), 0.62 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 147.1, 144.0, 141.0, 136.9, 136.0, 135.4, 134.7, 134.4, 129.5, 129.1, 128.4, 127.6, 126.7, 125.9, 124.4, 123.6, 122.8, 97.8, 68.8, 62.0, 30.6, 25.5, 19.4, –0.7, –0.8; IR (KBr): 3470, 2945, 1589, 1489, 1325, 1277, 1115, 1026, 835, 812, 775, 754, 696, 521 cm^{-1}; Anal. Calcd for

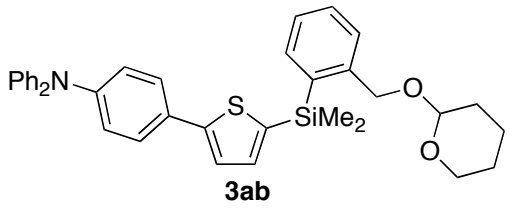
$C_{38}H_{39}NO_2Si$: C, 80.10; H, 6.90. Found: C, 80.07; H, 6.80.

Cross-coupling reaction of 1 with halogenated organo[2-(alkoxymethyl)phenyl]dimethylsilanes (2). *A general procedure*. To a mixture of **1** (1.2–1.5 mmol), K_2CO_3 (0.35 g, 2.5 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (1.8 mg, 5.0 μmol, measured in a glove box), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) in a Schlenk tube was added **2** (1.0 mmol), and the resulting mixture was stirred at 75 °C. After the time specified in Table 1, the mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding coupling product in a yield listed in Table 1.



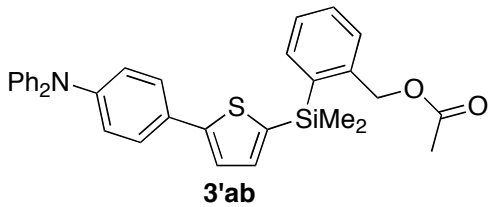
3'aa

4-([2-Acetoxymethyl]phenyl)dimethylsilyl-4'-(diphenylamino)-biphenyl (3'aa). A white solid, mp 43.4–45.3 °C, R_f 0.26 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.1 Hz, 1H), 7.56–7.31 (m, 9H), 7.29–7.21 (m, 4H), 7.17–7.08 (m, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 5.00 (s, 2H), 1.91 (s, 3H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 147.4, 147.2, 141.1, 137.2, 136.4, 135.6, 134.5, 134.3, 129.7, 129.5, 129.1, 127.58, 127.56, 126.0, 124.4, 123.6, 122.9, 66.7, 21.0, –0.8; IR (KBr): 3456, 3057, 3032, 2955, 1736, 1589, 1518, 1489, 1379, 1327, 1317, 1277, 1250, 1234, 1113, 1026, 835, 810, 775, 754, 696, 521 cm^{-1}; Anal. Calcd for $C_{35}H_{33}NO_2Si$: C, 79.66; H, 6.30. Found: C, 79.48; H, 6.27.



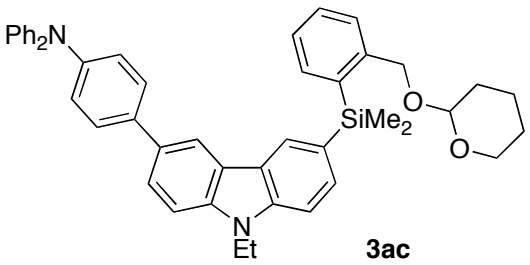
3ab

2-(Dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]sil-yl)-5-[4-(diphenylamino)phenyl]thiophene (3ab). A pale yellow viscous liquid, R_f 0.13 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.53–7.43 (m, 3H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31–7.22 (m, 6H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.14–7.08 (m, 4H), 7.07–6.99 (m, 4H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.58 (t, *J* =3.6 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.88–3.79 (m, 1H), 3.54–3.42 (m, 1H), 1.90–1.76 (m, 1H), 1.73–1.44 (m, 5H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.3, 147.1, 143.9, 137.2, 136.3, 135.7, 135.2, 129.7, 129.1, 128.5, 128.3, 126.8, 126.6, 124.3, 123.54, 123.45, 122.9, 97.8, 68.8, 62.1, 30.6, 25.6, 19.5, 0.3, 0.2; IR (neat): 3055, 2941, 2868,1589, 1529, 1489, 1431, 1327, 1313, 1277, 1277, 1200, 1117, 1076, 1026, 955, 949, 835, 810, 773, 752, 731, 696 cm^{-1}; HRMS (FAB+) Calcd for $C_{36}H_{37}BrNO_2SSi$: M^+, 575.2314. Found: *m*/*z* 575.2327.



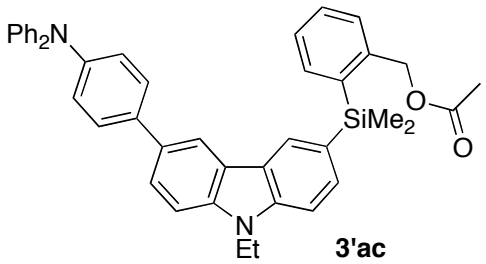
3'ab

2-([2-(Acetoxymethyl)phenyl]dimethylsilyl)-5-[4-(diphenyl-amino)phenyl]thiophene (3'ab). A pale yellow viscous oil, R_f 0.13 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.59–7.37 (m, 5H), 7.34 (td, *J* = 7.1, 1.9 Hz, 1H), 7.29–7.22 (m, 5H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.13–7.08 (m, 4H), 7.06–7.00 (m, 4H), 5.10 (s, 2H), 2.02 (s, 3H), 0.68 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 150.3, 147.3, 147.1, 141.1, 136.7, 136.6, 136.3, 135.4, 129.9, 129.5, 129.1, 128.2, 127.6, 126.6, 124.4, 123.5, 122.9, 66.6, 21.1. 0.2; IR (neat) 3057, 3034, 2961, 1738, 1591, 1529, 1495, 1433, 1327, 1315, 1279, 1259, 1234, 1078, 1026, 995, 951, 835, 808, 779, 754, 696 cm^{-1}; HRMS (EI) Calcd for $C_{33}H_{31}NO_2SSi_2$: M^+, 533.1845. Found: *m*/*z* 533.1846.



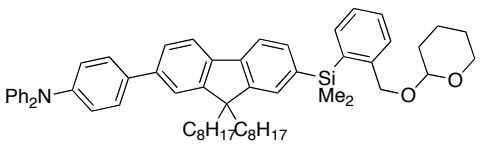
3ac

6-[4-(Diphenylamino)phenyl]-3-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)-9-ethyl-9*H*-carbazole (3ac). A pale yellow viscous oil, R_f 0.42 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.25 (d, *J* = 1.1 Hz, 1H), 7.67 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.61–7.53 (m, 4H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.46–7.35 (m, 3H), 7.32–7.22 (m, 5H), 7.20–7.11 (m, 6H), 7.01 (t, *J* = 7.3 Hz, 2H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.46–4.32 (m, 4H), 3.74–3.65 (m, 1H), 3.35–3.27 (m, 1H), 1.80–1.67 (m, 1H), 1.62–1.23 (m, 8H), 0.688 (s, 3H), 0.685 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.1, 144.0, 140.9, 139.0, 136.9, 136.4, 135.5, 131.9, 131.3, 129.4, 129.1, 128.4, 127.8, 127.2, 126.6, 126.3, 124.7, 124.4, 124.0, 123.2, 122.8, 122.5, 118.5, 108.5, 108.2, 97.8, 68.9, 62.0, 37.7, 30.6, 25.5, 19.4, 14.0, –0.3, –0.4; IR (neat): 2947, 2870, 1593, 1479, 1275, 1232, 1128, 1117, 1078, 1026, 837, 806, 752, 696 cm^{-1}; Anal. Calcd for $C_{46}H_{46}N_2O_2Si$: C, 80.43; H, 6.75. Found: C, 80.20; H, 6.77.



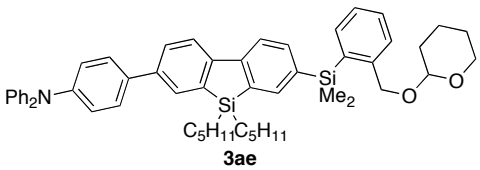
3'ac

3-([2-(Acetoxymethyl)phenyl]dimethylsilyl)-6-[(4-diphenylamino)phenyl]-9-ethyl-9*H*-carbazole (3'ac). A white solid, mp 75.3–76.4 °C, R_f 0.29 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.5 Hz, 1H), 8.24 (s, 1H), 7.67 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.63 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.60–7.52 (m, 3H), 7.45–7.31 (m, 5H), 7.30–7.22 (m, 4H), 7.19–7.11 (m, 6H), 7.01 (tt, *J* = 7.2, 1.1 Hz, 2H), 5.01 (s, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.84 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H), 0.70 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 147.6, 146.1, 141.2, 141.0, 139.0, 138.0, 136.3, 135.7, 132.0, 131.1, 129.5, 129.4, 129.1, 127.8, 127.5, 126.7, 126.3, 124.8, 124.4, 124.0, 123.1, 122.9, 122.5, 118.5, 108.5, 108.3, 66.7, 37.7, 21.0, 14.0, –0.4; IR (KBr): 3452, 1736, 1591, 1479, 1277, 1232, 837, 806, 754, 696 cm^{-1}; Anal. Calcd for $C_{43}H_{40}N_2O_2Si$: C, 80.09; H, 6.25. Found: C, 80.07; H, 6.34.



3ad

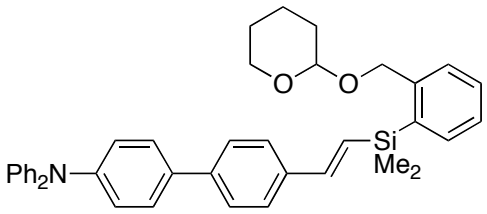
7-[(4-Diphenylamino)phenyl]-2-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)-9,9'-dioctyl-9*H*-fluorene (3ad). A pale yellow viscous oil, R_f 0.22 (hexane–ethyl acetate = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.57–7.42 (m, 8H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30–7.20 (m, 5H), 7.14 (t, *J* = 7.4 Hz, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.51 (t, *J* = 3.4 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 3.86–3.74 (m, 1H), 3.48–3.39 (m, 1H), 2.00–1.75 (m, 5H), 1.70–1.40 (m, 5H), 1.34–0.93 (m, 20H), 0.81 (t, *J* = 7.2 Hz, 6H), 0.74–0.58 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 145.0, 147.5, 146.9, 144.0, 141.6, 139.7, 139.5, 137.0, 136.7, 135.52, 135.47, 132.6, 129.4, 129.1, 128.4, 128.1, 127.6, 126.6, 125.3, 124.2, 123.9, 122.8, 120.8, 119.9, 119.0, 97.6, 68.8, 61.9, 55.1, 40.3, 31.9, 30.6, 30.1, 29.34, 29.31, 25.6, 24.0, 22.7, 19.4, 14.2, –0.6, –0.7; IR (KBr): 3458, 2926, 2853, 1591, 1514, 1493, 1464, 1281, 1028, 837, 816, 752, 696 cm^{-1}; Anal. Calcd for $C_{61}H_{75}NO_2Si$: C, 83.04; H, 8.57. Found: C, 83.14; H, 8.55.



3ae

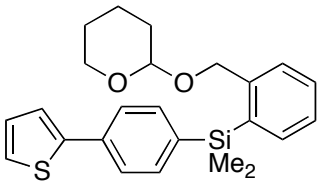
7-[4-(Diphenylamino)phenyl]-2-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)-9,9'-dipentyl-9*H*-9-silafluorene (3ae). A pale yellow viscous liquid, R_f 0.27 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.81–7.71 (m, 1H), 7.61 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.57–7.46 (m, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31–7.21 (m, 5H), 7.18–7.09 (m, 6H), 7.02 (t, *J* = 7.2 Hz,

2H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.48 (t, *J* = 3.4 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 3.82–3.71 (m, 1H), 3.46–3.36 (m, 1H), 1.85–1.72 (m, 1H), 1.67–1.16 (m, 17H), 0.98–0.89 (m, 4H), 0.85–0.75 (m, 6H), 0.630 (s, 3H), 0.626 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.8, 147.2, 147.1, 144.3, 139.6, 139.01, 139.03, 137.33, 137.30, 136.6, 136.2, 135.8, 135.4, 131.5, 129.7, 129.4, 128.7, 128.6, 127.8, 127.0, 124.5, 124.2, 123.1, 121.4, 120.4, 98.0, 69.1, 62.3, 35.9, 30.9, 25.9, 24.0, 22.6, 19.7, 14.4, 12.7, –0.3, –0.4; IR (KBr): 3450, 2953, 2922, 2870, 2855, 1591, 1510, 1493, 1452, 1325, 1279, 1117, 1076, 1026, 837, 816, 752, 696, 498 cm^{-1}; Anal. Calcd for $C_{54}H_{63}NO_2Si_2$: C, 79.65; H, 7.80. Found: C, 79.65; H, 7.80.



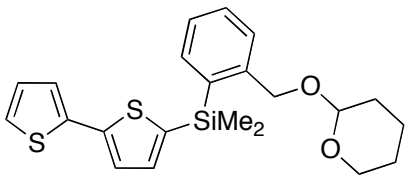
3af

(*E*)-4-(Diphenylamino)-4'-[2-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)ethenyl]biphenyl (3af). A yellow solid, mp 47.0–49.2 °C, R_f 0.21 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.57–7.44 (m, 7H), 7.40 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33–7.22 (m, 5H), 7.16–7.08 (m, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.96 (d, *J* =19.0 Hz, 1H), 6.68 (d, *J* =19.0 Hz, 1H), 4.88 (d, *J* =11.9 Hz, 1H), 4.67 (t, *J* =3.5 Hz, 1H), 4.63 (d, *J* =11.9 Hz, 1H), 3.94–3.84 (m, 1H), 3.53–3.43 (m, 1H), 1.90–1.78 (m, 1H) 1.75–1.43 (m, 5H), 0.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 147.1, 144.2, 143.8, 140.1, 136.63, 136.60, 134.9, 134.3, 129.4, 129.1, 128.4, 127.5, 127.4, 126.81, 126.76, 126.5, 124.3, 123.7, 122.8, 97.9, 68.9, 62.2, 30.7, 25.6, 19.5, –1.0, –1.1; IR (KBr): 3055, 3032, 2943, 2868, 1589, 1489, 1325, 1277, 1200, 1180, 1117, 1076, 1024, 988, 905, 818, 752, 694 cm^{-1}; HRMS (EI) Calcd for $C_{40}H_{41}NO_2Si$: M^+, 595.2907. Found: *m*/*z* 595.2902.



3ba

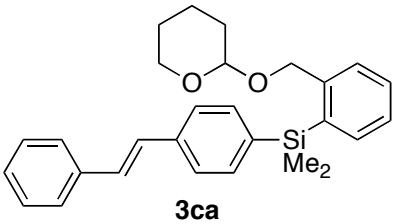
Dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl][4-(2-thienyl)phenyl]silane (3ba). A pale yellow viscous oil, R_f 0.13 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.46 (m, 6H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34–7.24 (m, 3H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.45 (t, *J* = 3.6 Hz, 1H) , 4.40 (d, *J* = 11.9 Hz, 1H) , 3.79–3.71 (m, 1H), 3.45–3.37 (m, 1H), 1.84–1.72 (m, 1H), 1.67–1.39 (m, 5H), 0.620 (s, 3H), 0.615 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 144.0, 138.0, 135.8, 135.3, 134.7, 134.5, 129.6, 128.5, 127.9, 126.7, 125.1, 124.8, 123.1, 97.8, 68.8, 62.0, 30.6, 25.5, 19.4, –0.8, –0.9; IR (neat): 3055, 3013, 2945, 2870, 1597, 1433, 1394, 1350, 1258, 1200, 1117, 1078, 1026, 974, 907, 870, 833, 812, 775, 756, 729, 696, 654, 534 cm^{-1}; Anal. Calcd for $C_{24}H_{28}O_2SSi_2$: C, 70.54; H, 6.91. Found: C, 70.46; H, 6.84



3bb

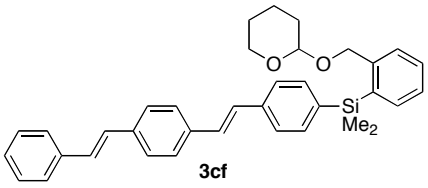
5-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)-2,2'-bithiophene (3bb). To a mixture of **1b** (6.0 g, 24 mmol), K_2CO_3 (6.9 g, 50 mmol), (dppf)$PdCl_2$•CH_2Cl_2 (163 mg, 0.20 mmol), and CuI (114 mg, 0.60 mmol) in DMF (16 mL) and THF (44 mL) in a Schlenk tube was added **2b** (20 mmol), and the resulting mixture was stirred at 75 °C for 6 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **3bb** (8.0 g, 96%) as a colorless viscous oil, R_f 0.20 (hexane–ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.28 (td, *J* = 7.3, 1.1 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.19 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 3.6 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.86–3.77 (m, 1H), 3.51–3.41 (m, 1H),

1.88–1.75 (m, 1H), 1.72–1.41 (m, 5H), 0.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.9, 137.9, 137.1, 135.9, 135.4, 135.2, 129.8, 128.6, 127.7, 126.8, 124.9, 124.3, 123.7, 97.8, 68.8, 62.1, 30.6, 25.6, 19.5, 0.3, 0.2; IR (neat): 2943, 2870, 2849, 1439, 1252, 1200, 1119, 1078, 1026, 988, 907, 837, 812, 777, 756, 692 cm^{-1}; Anal. Calcd for $C_{22}H_{26}O_2S_2Si$: C, 63.72; H, 6.32. Found: C, 63.47; H, 6.32.



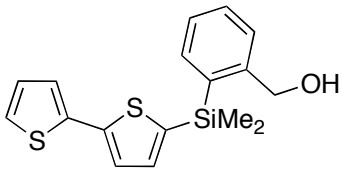
3ca

(*E*)-4-(Dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl)-stilbene (3ca). A pale yellow viscous oil, R_f 0.10 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.45 (m, 8H), 7.42 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39–7.33 (m, 2H), 7.32–7.23 (m, 2H), 7.14 (d, *J* = 16.3, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.59 (t, *J* = 3.5, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 3.80–3.71 (m, 1H), 3.46-3.37 (m, 1H), 1.82–1.73 (m, 1H), 1.69–1.41 (m, 5H), 0.62 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 138.2, 137.7, 137.1, 135.9, 135.3, 134.3, 129.5, 128.9, 128.54, 128.48, 128.4, 127.5, 126.7, 126.4, 125.7, 97.8, 68.8, 62.0, 30.6, 25.5, 19.4, –0.8, –0.9; IR (neat) 3057, 3024, 2949, 2870, 1597, 1495, 1466, 1448, 1439, 1396, 1348, 1258, 1200, 1117, 1078, 1026, 964, 907, 870, 835, 806, 775, 754, 718, 692, 646, 577, 536 cm^{-1}; Anal. Calcd for $C_{28}H_{32}O_2Si$: C, 78.46; H, 7.52. Found: C, 78.40; H, 7.59



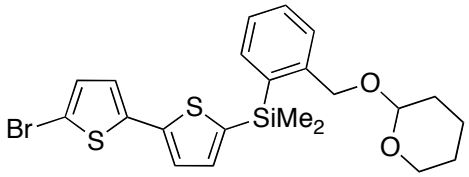
3cf

(*E*)-1-(2-[4-(Dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl)phenyl]ethenyl)-4-(2-phenyl)ethenylbenzene (3cf). A yellow solid, mp 53.2–56.5 °C, R_f 0.13 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.56–7.22 (m, 8H), 7.13 (d, *J* =16.3 Hz, 1H), 7.08 (d, *J* =16.3 Hz, 1H), 6.93 (d, *J* =19.2 Hz, 1H), 6.67 (d, *J* =19.0 Hz, 1H), 4.87 (d, *J* =11.9 Hz, 1H), 4.67 (t, *J* =3.5 Hz, 1H), 4.62 (d, *J* =11.9 Hz, 1H), 3.93–3.84 (m, 1H), 3.52–3.44 (m, 1H), 1.92–1.78 (m, 1H), 1.76–1.43 (m, 5H), 0.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.8, 137.4, 137.1, 137.0, 136.6, 134.9, 129.4, 128.6, 128.4, 128.1, 127.7, 127.5, 126.8, 126.7, 126.5, 126.4, 97.9, 68.9, 62.2, 30.7, 25.6, 19.5, –1.0, –1.1; IR (KBr): 3053, 3022, 2941, 2891, 2868, 1597, 1508, 1448, 1437, 1342, 1250, 1200, 1117, 1076, 1055, 1028, 991, 966, 907, 868, 837, 820, 793, 752, 731, 708, 689, 534 cm^{-1}; Anal. Calcd for $C_{30}H_{34}O_2Si_2$: C, 79.25; H, 7.54. Found: C, 79.10; H, 7.46.



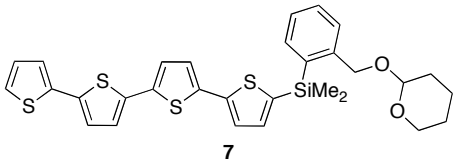
5

Deprotection of 3bb. A solution of **3bb** (3.4 g, 8.3 mmol) and PPTS (0.42 g, 1.65 mmol) in MeOH (41 mL) was stirred at 40 °C for 2 h, and then concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to give 5-([2-(hydroxymethyl)phenyl]dimethylsilyl)-2,2'-bithiophene (**5,** 2.4 g, 89%) as a white solid, mp 47.2–48.0 °C, R_f 0.30 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.50–7.39 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 5.1 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.98 (dd, *J* = 4.8, 3.8 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 2H), 1.53 (t, *J* = 5.8 Hz, 1H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 143.1, 137.8, 136.9, 135.9, 135.2, 135.0, 130.1, 128.0, 127.7, 127.0, 125.0, 124.5, 123.9, 65.3, 0.3; IR (KBr): 3329, 3057, 2947, 1439, 1418, 1217, 1200, 1126, 1078, 1015, 989, 839, 810, 779, 758, 746, 708, 691 cm^{-1}; Anal. Calcd for $C_{17}H_{18}OS_2Si$: C, 61.77; H, 5.49. Found: C, 61.58; H, 5.48.



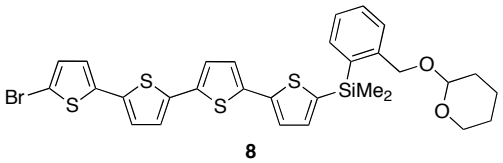
6

Bromination of 3bb. To a solution of **3bb** (4.6 g, 11 mmol) in Et_2O (33 mL) was added TMEDA (1.41 g, 12.1 mmol) and a 1.6 M solution of *n*-BuLi (7.2 mL, 11.6 mmol) in hexane at –40 °C, and the resulting mixture was stirred at –40 °C for 30 min and then at rt for 30 min. To this was added 1,2-dibromo-1,1,2,2-tetrafluoroethane (3.1 g, 12.1 mmol) at –40 °C, and the resulting mixture was stirred at the same temperature for 1 h. The reaction was quenched with a saturated $Na_2S_2O_3$ aqueous solution (20 mL), and the aqueous layer was extracted with diethyl ether (120 mL). The organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo, and then purified by flash chromatography on silica gel to give 5-bromo-5'-(dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl)-2,2'-bithiophene (**6**, 4.9 g, 90%) as a colorless oil, R_f 0.22 (hexane–ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42 (td, *J* = 7.4, 1.0 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.95 (d, *J* = 3.8 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.56 (t, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 3.88–3.76 (m, 1H), 3.52–3.42 (m, 1H), 1.73–1.42 (m, 5H), 1.88–17.5 (m, 1H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.8, 138.63, 138.60, 135.9, 135.22, 135.17, 130.5, 129.9, 128.6, 126.8, 125.1, 123.8, 110.9, 97.8, 68.7, 62.1, 30.6, 25.5, 19.5, 0.3, 0.2 ; IR (neat): 3055, 2943, 2870, 2849, 1441, 1418, 1350, 1252, 1200, 1119, 1078, 1026, 988, 970, 905, 870, 835, 812, 754, 691, 654, 530 cm^{-1}; Anal. Calcd for $C_{22}H_{25}BrO_2S_2Si$: C, 53.54; H, 5.11. Found: C, 53.77; H, 5.19.



7

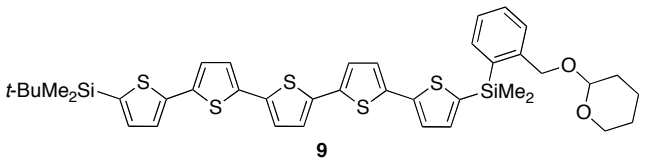
Synthesis of 7. To a solution of **5** (3.9 g, 11.9 mmol), K_2CO_3 (3.4 g, 25 mmol), (dppf)$PdCl_2$•CH_2Cl_2 (0.25 g, 0.30 mmol), and CuI (0.17 g, 0.89 mmol) in DMF (7.9 mL) and THF (22 mL) in a Schlenk tube was added **6** (4.9 g, 9.9 mmol), and the resulting mixture was stirred at 75 °C for 10 h before filtration through a Frolisile pad. After concentration in vacuo, the residue was filtered through a short silica gel column and further purified by preparative GPC to afford 5-([2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]dimethylsilyl)-2,2':5',2'':5'',2'''-quarterthiophene (**7**, 4.7 g, 82%) as a yellow solid, mp 111.0–111.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.3, 1.3 Hz, 1H), 7.23–7.18 (m, 2H), 7.16 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.09–7.03 (m, 4H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 3.6 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.85–3.77 (m, 1H), 3.51–3.42 (m, 1H), 1.87–1.75 (m, 1H), 1.72–1.42 (m, 5H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.5, 138.3, 136.9, 136.1, 136.03, 136.01, 135.8, 135.7, 135.3, 135.2, 129.8, 128.6, 127.8, 126.8, 124.9, 124.43, 124.40, 124.3, 124.2, 124.1, 123.6, 97.8, 68.8, 62.1, 30.6, 25.6, 19.5, 0.3, 0.2; IR (KBr): 3452, 2949, 833, 793, 687 cm^{-1}; Anal. Calcd for $C_{30}H_{30}O_2S_4Si$: C, 62.24; H, 5.22. Found: C, 62.00; H, 4.95.



8

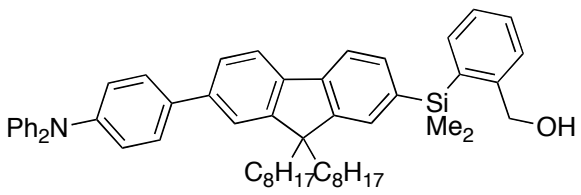
Bromination of 7. To a solution of **7** (0.70 g, 1.2 mmol) in THF (14 mL) were added TMEDA (153 mg, 1.32 mmol) and a 1.6 M solution of *n*-BuLi (1.32 mmol) in hexane at –78 °C, and the resulting mixture was stirred at the same temperature for 5 min. To this was added $BrCF_2CF_2Br$ (0.37 g, 1.44 mmol), and the resulting mixture was stirred at –40 °C for 1 h and then quenched with a saturated $Na_2S_2O_3$ aqueous solution (2 mL). The aqueous layer was extracted with diethyl ether (20 mL), and the organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by preparative GPC to give

5-bromo-5’’’-(dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl)-2,2’:5’,2’’:5’’,2’’’-quarterthiophene (**8**, 0.71 g, 90%) as a yellow solid, mp 112.4–115.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.4, 1.0 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.08–7.02 (m, 3H), 7.00 (d, *J* = 3.7 Hz, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.56 (t, *J* = 3.5 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.86–3.77 (m, 1H), 3.51–3.43 (m, 1H), 1.86–1.74 (m, 1H), 1.72–1.42 (m, 5H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.3, 138.4, 138.3, 136.3, 136.2, 136.0, 135.4, 135.3, 135.2, 134.9, 130.5, 129.8, 128.6, 126.8, 124.9, 124.5, 124.38, 124.37, 124.0, 123.6, 111.0, 97.8, 68.7, 62.1, 30.6, 25.5, 19.5, 0.3, 0.2; IR (KBr): 3450, 3061, 2943, 2870, 1427, 1254, 1117, 1078, 1028, 989, 843, 835, 814, 789, 756, 465 cm^{-1}; HRMS (FAB+) Calcd for $C_{30}H_{29}BrO_2S_4Si$: M^+, 656.0003. Found: *m*/*z* 656.0024.

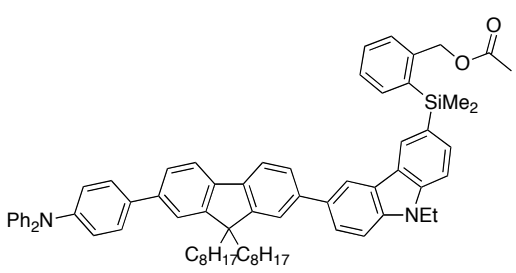


9

Synthesis of 9. To a solution of **1d** (44 mg, 0.12 mmol), K_2CO_3 (3.5 mg, 0.25 mmol), (dppf)$PdCl_2$•CH_2Cl_2 (4.1 mg, 5.0 μmol), and CuI (1.0 mg, 5.0 μmol) in DMF (0.16 mL) and THF (0.44 mL) in a Schlenk tube was added **8** (66 mg, 0.10 mmol), and the resulting mixture was stirred at 50 °C for 5 h before filtration through a Florisil pad. After concentration in vacuo, the residue was filtered through a short silica gel column and further purified by preparative GPC to give 5’’’’-(*tert*-butyldimethylsilyl)-5-(dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl)-2,2’:5’,2’’:5’’,2’’’:5’’’,2’’’’-quinquethiophene (**9**, 62 mg, 80%) as an orange solid, mp 128.5–130.3 °C, R_f 0.32 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 3.3 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.11–7.01 (m, 7H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 3.4 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.87–3.77 (m, 1H), 3.51–3.42 (m, 1H), 1.88–1.75 (m, 1H), 1.73–1.43 (m, 5H), 0.95 (s, 9H), 0.67 (s, 6H), 0.31 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.5, 141.9, 138.3, 137.0, 136.2, 136.1, 136.0, 135.9, 135.79, 135.76, 135.7, 135.6, 135.3, 135.2, 129.8, 128.6, 126.8, 124.9, 124.7, 124.4, 124.3, 124.23, 124.21, 124.17, 124.12, 97.8, 68.8, 62.1, 30.6, 26.4, 25.6, 19.5, 17.1, 0.3, 0.20, –4.8; IR (KBr): 3059, 2951, 2926, 2855, 1427, 1078, 986, 833, 804, 791, 773, 473 cm^{-1}; Anal. Calcd for $C_{40}H_{46}O_2S_5Si_2$: C, 61.97; H, 5.98. Found: C, 61.85; H, 6.08.

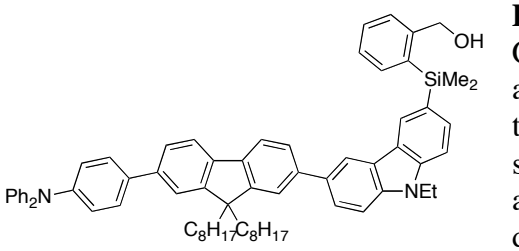


Deprotection of 3ad. To a solution of **3ad** (0.88 g, 1.0 mmol) in MeOH (3 mL) and CH_2Cl_2 (3 mL) was added *p*-TsOH•H_2O (3.8 mg, 20 μmol), and the resulting mixture was stirred at rt overnight. Concentration in vacuo followed by flash chromatography on silica gel to afford OH-free **3ad** (0.74 g, 93%) as a viscous oil, R_f 0.27 (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.59–7.38 (m, 9H), 7.32–7.21 (m, 5H), 7.18–7.09 (m, 6H), 7.02 (t, *J* = 7.2 Hz, 2H), 4.54 (d, *J* = 5.9 Hz, 2H), 2.01–1.98 (m, 4H), 1.30–0.94 (m, 21H), 0.81 (t, *J* = 7.0 Hz, 6H), 0.74–0.54 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 150.2, 147.5, 146.9, 146.5, 141.8, 139.6, 139.5, 136.9, 136.4, 135.5, 135.4, 132.4, 129.8, 129.1, 128.2, 128.0, 127.6, 126.8, 125.3, 124.2, 123.9, 122.8, 120.8, 120.0, 119.2, 65.4, 55.2, 40.3, 31.9, 30.1, 29.31, 29.28, 23.9, 22.7, 14.2, –0.7; IR (neat): 3450, 2953, 2926, 2853, 1591, 1514, 1493, 1464, 1331, 1315, 1279, 837, 816, 752, 696, 502 cm^{-1}; Anal. Calcd for $C_{56}H_{67}NOSi$: C, 84.26; H, 8.46. Found: C, 84.24; H, 8.23.

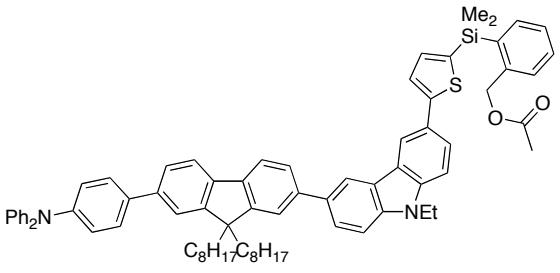


10

Preparation of 10. To a mixture of deproteced **3ad** (8.0 g, 10 mmol), K_2CO_3 (3.5 g, 25 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (18 mg, 50 μmol, measured in a glove box), RuPhos (98 mg, 0.21 mmol), and CuI (57 mg, 0.30 mmol) in DMF (8 mL) and THF (22 mL) in a Schlenk tube was added **2'c** (4.8 g, 10 mmol), and the resulting mixture was stirred at 75 °C for 17 h, filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, and then dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel gave **10** (9.0 g, 87%) as a white solid, mp 70.8–73.6 °C, R_f 0.37 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.30 (s, 1H), 7.81–7.72 (m, 3H), 7.71–7.62 (m, 3H), 7.61–7.51 (m, 5H), 7.50–7.32 (m, 5H), 7.31–7.22 (m, 4H), 7.20–7.11 (m, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 5.03 (s, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.13–1.99 (m, 4H), 1.86 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.23–0.98 (m, 20H), 0.84–0.68 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 151.5, 151.4, 147.5, 146.8, 141.2, 141.0, 139.8, 139.2, 139.1, 139.0, 138.0, 135.8, 135.6, 133.0, 131.2, 129.6, 129.4, 129.1, 127.6, 127.5, 126.7, 126.4, 126.0, 125.34, 125.31, 124.2, 123.9, 123.2, 123.0, 122.7, 121.5, 120.8, 119.74, 119.71, 118.9, 108.5, 108.4, 66.7, 55.3, 40.6, 37.8, 31.9, 30.2, 29.35, 29.32, 24.0, 22.7, 21.0, 14.2, 14.1, –0.4; IR (KBr): 3452, 2926, 2852, 1738, 1593, 1493, 1464, 1275, 1232, 818, 806, 754, 696 cm^{-1}; Anal. Calcd for $C_{72}H_{80}N_2O_2Si$: C, 83.67; H, 7.80. Found: C, 83.92; H, 7.91.



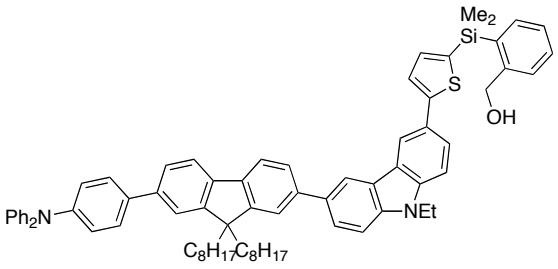
Deprotection of 10. To a solution of **10** (9.0 g, 8.7 mmol) in CH_2Cl_2 (17.4 mL) was added DIBAL–H (9.6 mmol) in toluene at –78 °C, and the resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched with a saturated NH_4Cl aqueous solution at –78 °C, diluted with Et_2O, and slowly warmed to rt. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded OH-free **10** (0.82 g, 95%) as a white solid, mp 81.9–83.5 °C, R_f 0.52 (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.34 (s, 1H), 7.81–7.72 (m, 3H), 7.71–7.62 (m, 3H), 7.61–7.52 (m, 5H), 7.51–7.40 (m, 4H), 7.37–7.22 (m, 5H), 7.20–7.11 (m, 6H), 7.03 (t, *J* = 7.2 Hz, 2H), 4.57 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.13–1.97 (m, 4H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.29–0.98 (m, 21H), 0.82–0.66 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 147.5, 146.8, 146.5, 141.0, 140.7, 139.8, 139.2, 139.1, 139.0, 136.7, 135.6, 135.5, 133.0, 131.0, 129.8, 129.1, 128.2, 127.6, 127.2, 126.9, 126.2, 126.0, 125.4, 125.3, 124.2, 123.9, 123.1, 122.7, 121.5, 120.8, 119.8, 119.7, 118.9, 108.6, 65.4, 55.3, 40.6, 37.8, 31.9, 30.2, 29.35, 29.32, 24.0, 22.7, 14.2, 14.1, –0.4; IR (KBr): 3450, 2926, 2853, 1593, 1493, 1464, 1275, 1232, 820, 804, 752, 696 cm^{-1}; Anal. Calcd for $C_{70}H_{78}N_2OSi$: C, 84.80; H, 7.93. Found: C, 84.79; H, 7.84.



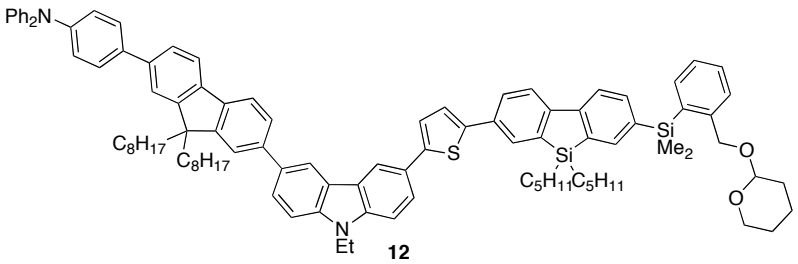
11

Synthesis of 11. To a mixture of deacetylated **10** (0.99 g, 1.0 mmol), K_2CO_3 (0.99 g, 1.0 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (9.1 mg, 25 μmol, measured in a glove box), RuPhos (49 mg, 0.10 mmol), and CuI (9.5 mg, 50 μmol) in DMF (0.8 mL) and THF (2.2 mL) in a Schlenk tube was added **2'b** (0.37 g, 1.0 mmol), and the resulting mixture was stirred at 75 °C for 24 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash

chromatography on silica gel to give **11** (0.87 g, 78%) as a yellow solid, mp 71.8–73.6 °C, R_f 0.38 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.1 Hz, 1H), 8.39 (s, 1H), 7.83–7.52 (m, 11H), 7.51–7.32 (m, 6H), 7.31–7.21 (m, 5H), 7.20–7.11 (m, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 5.14 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.15–1.96 (m, 7H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.22–0.99 (m, 24H), 0.77 (t, *J* = 7.0 Hz, 6H), 0.72 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 151.8, 151.5, 151.4, 147.5, 146.8, 141.1, 140.6, 139.9, 139.7, 139.6, 139.2, 139.0, 136.9, 136.4, 136.1, 135.6, 135.5, 133.0, 129.9, 129.5, 129.1, 127.6, 126.0, 125.5, 125.3, 124.4, 124.2, 123.9, 123.40, 123.36, 122.7, 121.4, 120.8, 119.8, 119.7, 118.9, 118.0, 108.8, 66.6, 55.3, 40.6, 37.9, 31.9, 30.2, 29.34, 29.32, 24.0, 22.7, 21.1, 14.2, 14.1, 0.3; IR (KBr): 3466, 2926, 2855, 1736, 1593, 1493, 1483, 1466, 1275, 1252, 1231, 804, 752, 696 cm^{-1}; Anal. Calcd for: C, 81.82; H, 7.41. Found: C, 81.57; H, 7.51.



Deprotection of 11. To a solution of **11** (0.82 g, 0.74 mmol) in CH_2Cl_2 (2 mL) was added a 1.5 M solution of DIBAL–H (0.81 mmol) in toluene at –78 °C, and the resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched with a saturated NH_4Cl aqueous solution at –78 °C, diluted with Et_2O, and slowly warmed to rt The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford deacetylated **11** (0.68 g, 85%) as a yellow solid, mp 86.7–88.0 °C, R_f 0.50 (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.39 (s, 1H), 7.83–7.37 (m, 15H), 7.36–7.21 (m, 7H), 7.20–7.10 (m, 6H), 7.03 (td, *J* = 7.3, 1.0 Hz, 2H), 4.72 (d, *J* = 5.9 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.14–1.98 (m, 4H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.22–0.99 (m, 25H), 0.77 (t, *J* = 6.8 Hz, 6H), 0.72 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 149.5, 147.5, 146.8, 145.6, 140.6, 139.8, 139.72, 139.65, 139.2, 139.0, 135.6, 134.9. 133.0, 130.8, 129.4, 129.1, 127.9, 127.6, 126.7, 126.0, 125.7, 125.6, 125.4, 124.4, 124.2, 123.9, 123.5, 123.4, 123.3, 122.7, 121.9, 121.51, 121.48, 120.8, 119.8, 119.7, 118.9, 118.0, 108.80, 108.77, 71.5, 55.3, 40.6, 37.9, 31.9, 30.2, 29.4, 29.3, 24.0, 22.7, 14.2, 14.0, 0.7; IR (KBr): 3452, 2926, 2853, 1593, 1493, 1466, 1275, 804, 752, 696 cm^{-1}; Anal. Calcd for $C_{74}H_{80}N_2OSSi$: C, 82.79; H, 7.51. Found: C, 82.53; H, 7.54.



12

Synthesis of 12. To a mixture of deprotected **11** (107 mg, 0.10 mmol), K_2CO_3 (35 mg, 0.25 mmol), (dppf)$PdCl_2$•CH_2Cl_2 (4.1 mg, 5.0 μmol), and CuI (1.0 mg, 5.0 μmol) in DMF (80 μL) and THF (0.22 mL) in a Schlenk tube was added **2e** (65 mg, 0.10 mmol), and the resulting mixture was stirred at 75 °C for 24 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel gave **12** (0.118 g, 80%) as a yellow solid, mp 91.7–94.0 °C, R_f 0.35 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.43 (s, 1H), 7.91–7.65 (m, 10H), 7.62–7.33 (m, 12H), 7.32–7.11 (m, 12H), 7.03 (t, *J* = 7.2 Hz, 2H), 4.70 (d, *J* = 11.9 Hz, 2H), 4.51–4.38 (m, 4H), 3.82–3.72 (m, 1H), 3.46–3.36 (m, 1H), 2.18–1.99 (m, 4H), 1.85–1.72 (m, 1H), 1.68–0.91 (m, 47H), 0.89–0.70 (m, 12H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 148.5, 147.5, 147.2, 146.8, 144.7, 144.0, 142.5, 140.6, 139.8, 139.72, 139.68, 139.2, 139.1, 138.9, 138.7, 137.2, 136.9, 136.3, 136.0, 135.6, 135.5, 133.3, 133.0, 129.9, 129.4, 129.1, 128.4, 127.6, 127.1,

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Reference

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2. Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028.
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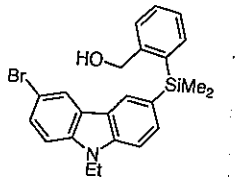
STANDARD 1H OBSERVE



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Mercury-400BB "m400"

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Pulse 45.0 degrees
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Width 5995.2 Hz
16 repetitions
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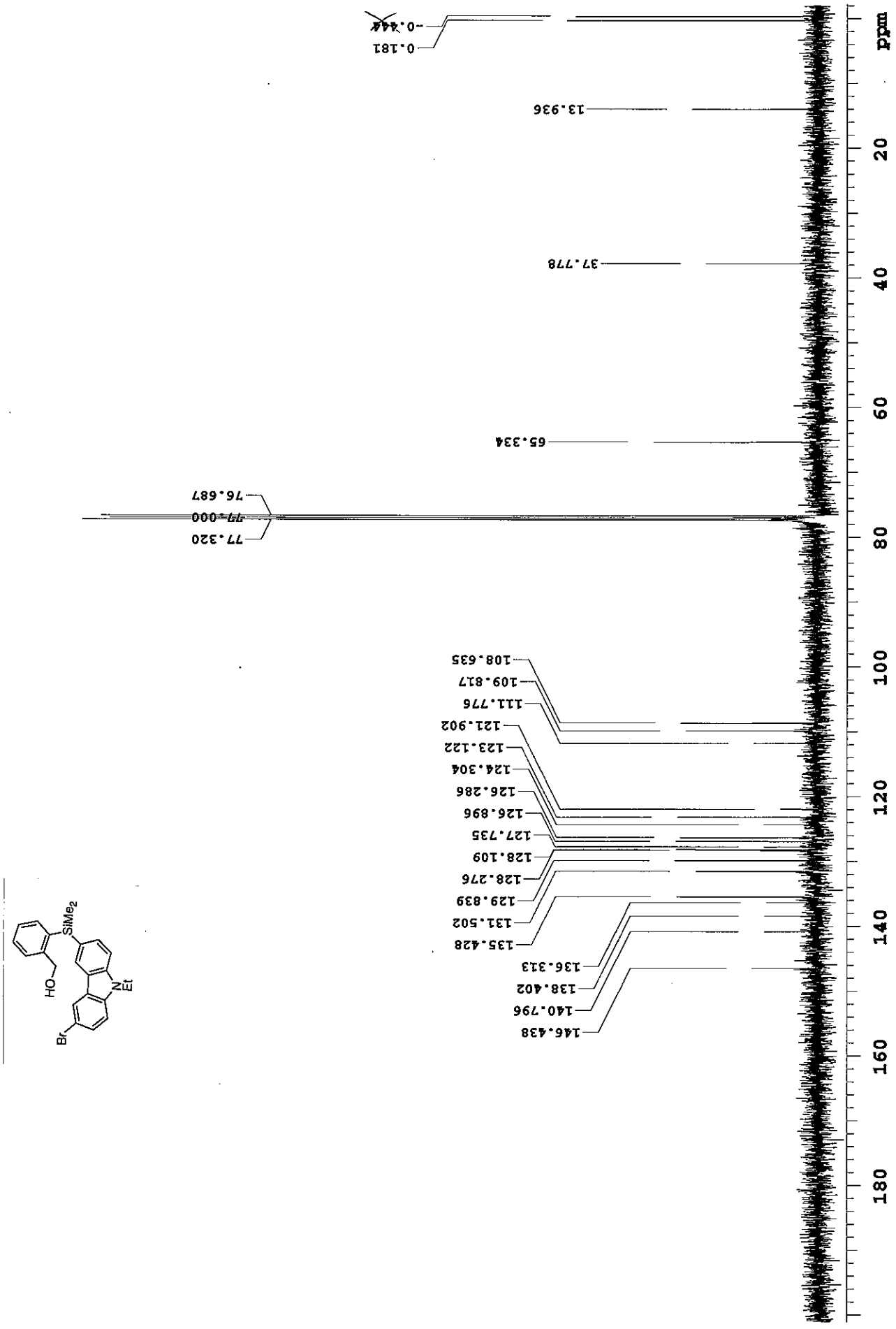
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec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123.122
124.304
126.286
126.896
127.735
128.109
128.276
129.839
131.502
135.428
136.313
138.402
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ppm
20
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60
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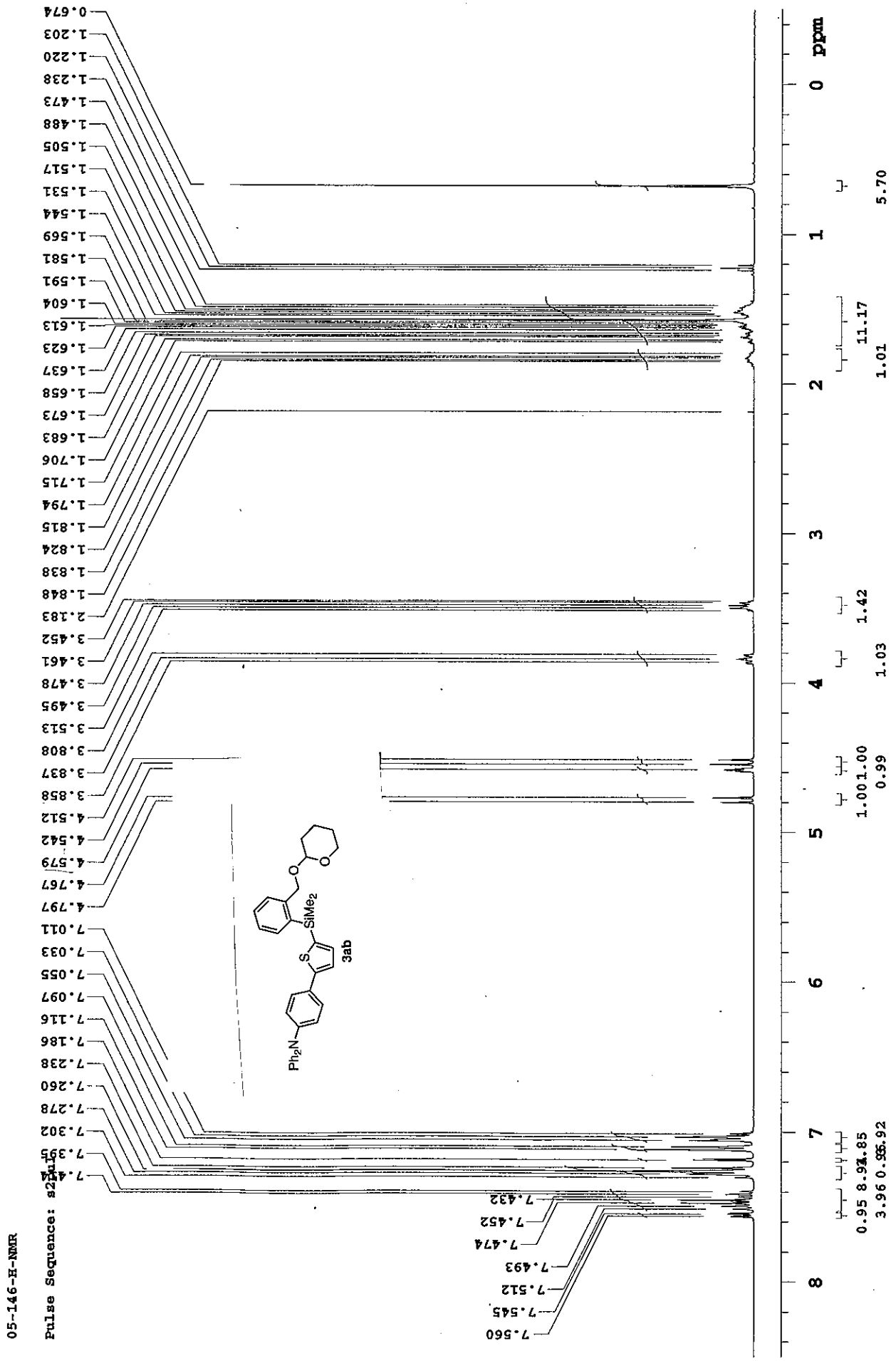
140
160
180
SiMe2
HO
N
Et
Br


05-146-H-NMR
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1.604
1.613
1.623
1.637
1.658
1.673
1.683
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1.848
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4.542
4.579
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4.797
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7.238
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7.432
7.452
7.474
7.493
7.512
7.545
7.560
SiMe2
S
O
O
Ph2N
3ab
ppm
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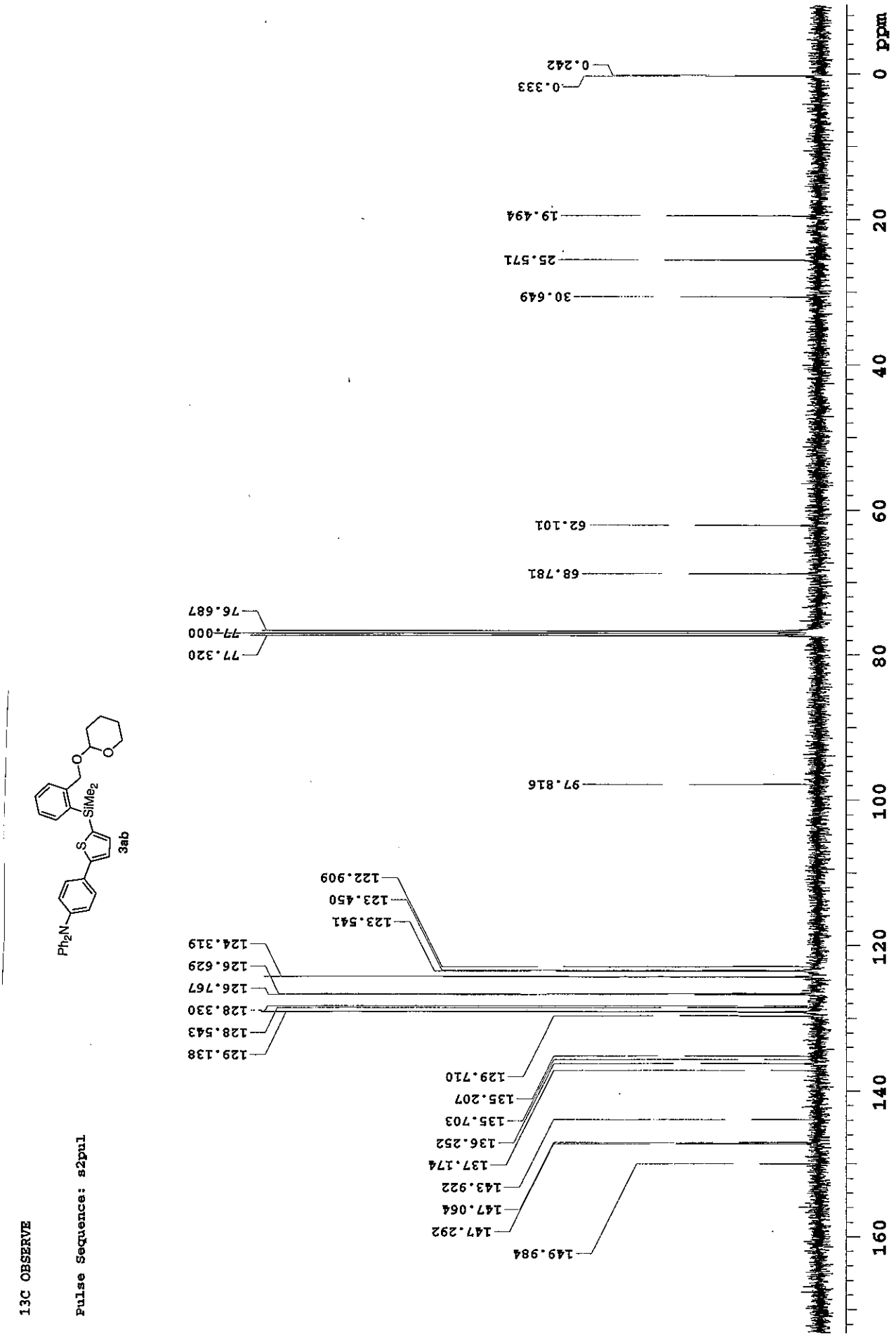
1.01
5.70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128.543
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129.710
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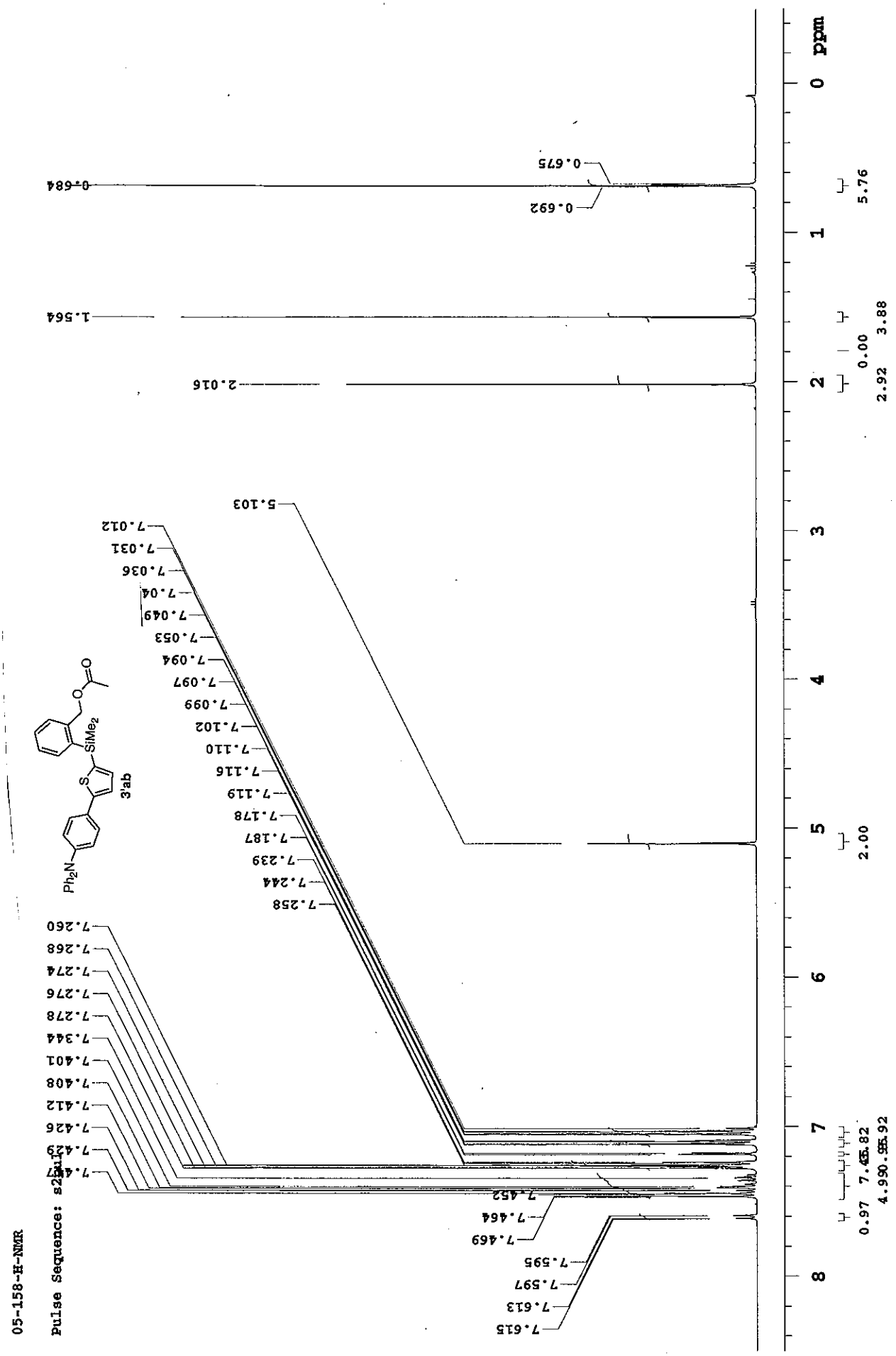

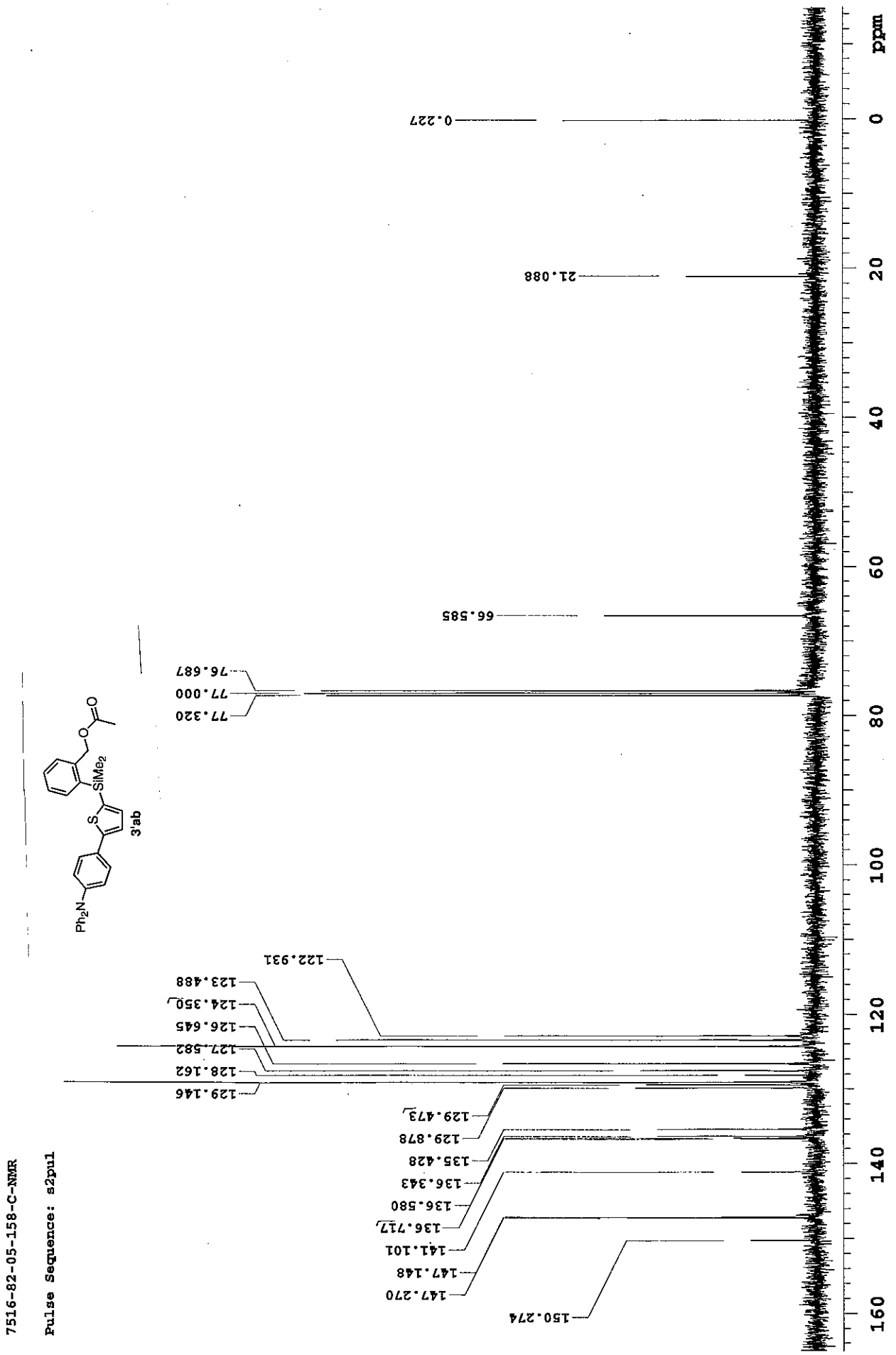
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SiMe2
S
O
O
Ph2N
3'ab


05-118-H-NMR
Pulse Sequence: s2pul
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1.484
1.504
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1.527
1.542
1.564
1.582
1.614
1.651
1.663
1.680
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1.842
1.855
1.866
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3.468
3.482
3.496
3.509
3.856
3.885
3.906
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4.645
4.672
4.865
4.895
6.656
6.703
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6.986
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7.532
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Me2
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3af
ppm
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3
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5
6
7
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1.09
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1.08
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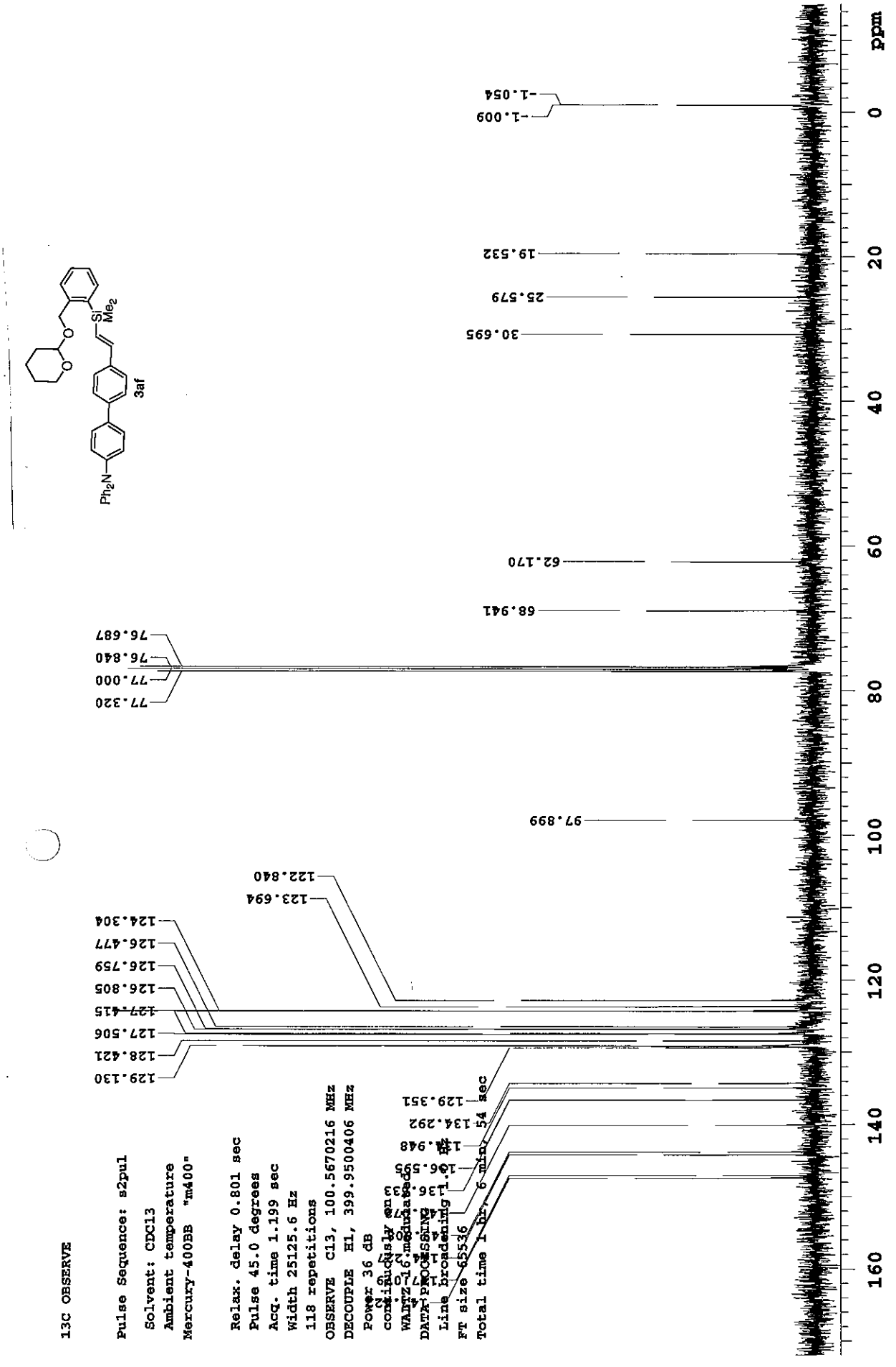
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Acq. time 1.199 sec
Width 25125.6 Hz
118 repetitions
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DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 6 min, 54 sec
3af
Me2
Si
Ph2N
O
ppm
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77.320
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123.694
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126.805
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127.506
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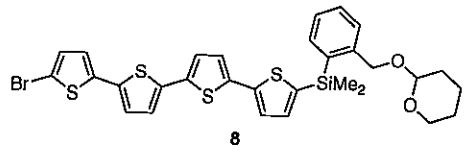
129.130
129.351
134.292
136.595
144.948

STANDARD 1H OBSERVE

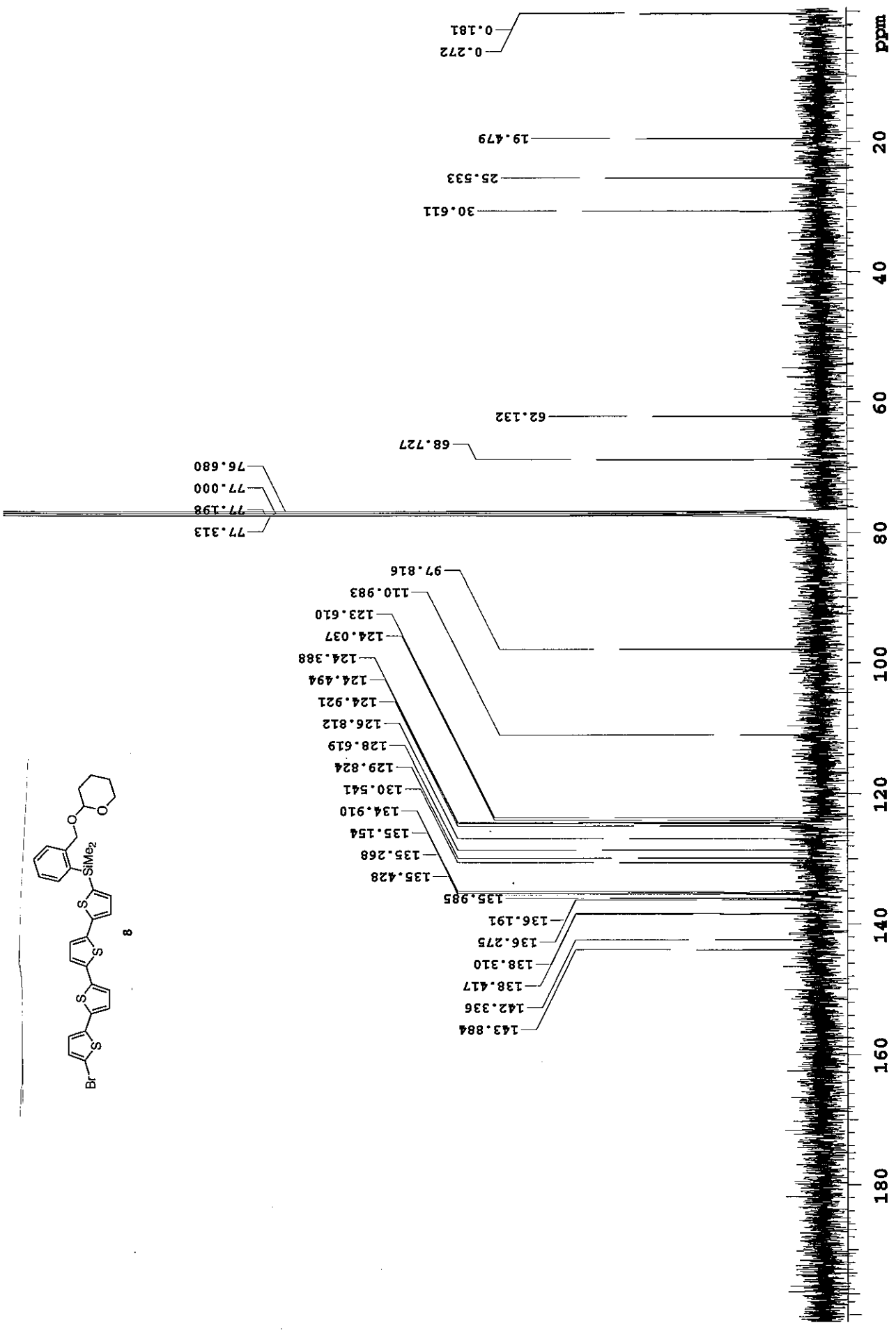
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480302 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



8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