Supporting Information

Palladium-catalyzed Intramolecular Coupling of 2-[(2-Pyrrolyl)silyl]aryl Triflates through 1,2-Silicon Migration

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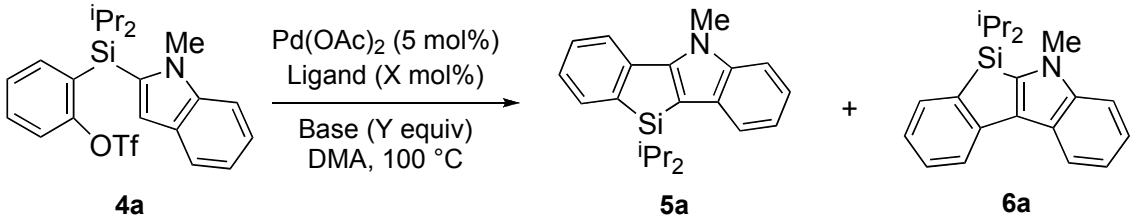
General Information

Melting points were determined using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm), chloroform (δ = 7.26 ppm), or benzene (δ = 7.16 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; hep, heptet; m, multiplet; brs: broad singlet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm), chloroform-*d* (δ = 77.0 ppm), or benzene-d_6 (δ = 128.4 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standards. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. EI-MS analyses were performed with a JEOL JMS–700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL–HX110A spectrometer. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254}. Column chromatography was carried out using silica gel of Merck Kieselgel 60 (230–400 mesh) or aminopropyl-functionalized sphere silica gel (N–H silica gel) of FUJI SILYSIA CHEMICAL Ltd. NH-DM2035 (200–350 mesh). Alumina column chromatography was carried out using Merck Aluminium oxide 90 active neutral. Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC–908 chromatograph using COSMOSIL 5C_{18}–MS–II column. Dichlorodiisopropylsilane was purchased from Tokyo Chemical Industry Co., Ltd. Dimethylacetamide (DMA) was purchased from Wako, Inc. Reagent-grade dichloromethane, diethyl ether, and tetrahydrofuran (THF) were passed through two packed columns of neutral alumina and copper oxide, respectively, under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere.

Screening of Conditions for Intramolecular Coupling of 2-[(2-Pyrrolyl)silyl]aryl Triflates

Representative results on screening of the conditions for the reaction of 2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (**4a**) were summarized in Table 1.

Table 1. Ligand and base screening of the reaction of **4a**.



4a **5a** **6a**

Ligand Screening

Entry	Ligand (X mol%)	Base (Y equiv)	Yields (%)[a]		Ratio (**5a**/**6a**)
			5a	**6a**	
1	PCy_3 (10)	Et_2NH (2.0)	67	8	8
2	PCy_3 (10)	Et_2NH (14.0)	74	12	6
3	dppm (5.0)	Et_2NH (14.0)	54	27	2
4	**dppe (5.0)**	**Et_2NH (14.0)**	**91**	**7**	**13**
5	dppp (5.0)	Et_2NH (14.0)	82	7	12
6	P(*t*Bu)$_3$ (10)	Et_2NH (14.0)	68	23	3
7	P(Bu)$_3$ (10)	Et_2NH (14.0)	75	11	7
8	P(Cyp)$_3$ (10)	Et_2NH (14.0)	78	14	6
9	PPh_3 (10)	Et_2NH (14.0)	50	6	8
10	none	Et_2NH (14.0)	52	3	17
11	No Pd/dppe (5.0)	Et_2NH (14.0)	0	0	–

a) Determined by GC using $C_{12}H_{26}$ as an internal standard.

Base Screening

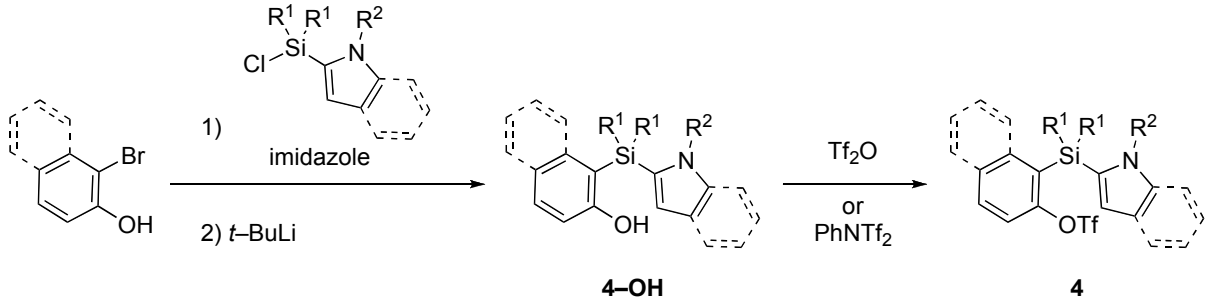
Entry	Ligand (X mol%)	Base (Y eq)	Yields (%)[a]		Ratio (**5a**/**6a**)
			5a	**6a**	
1	dppe (5)	Et_2NH (2.0)	49	45	1
2	dppe (5)	Et_2NH (5.0)	62	33	2
3	dppe (5)	Et_2NH (10.0)	67	12	6
4	**dppe (5)**	**Et_2NH (14.0)**	**91**	**7**	**13**
5	dppe (5)	Et_2NH (19.0)	36	6	6
6	dppe (5)	Et_2NH (19.0) [b]	0	0	-
7	dppe (5)	Et_3N (14.0)	76	4	19
8	dppe (5)	NMP (14.0)	0	0	-
9	dppe (5)	K_2CO_3 (2.0)	0	0	-
10	dppe (5)	Cs_2CO_3 (2.0)	0	0	-
11	dppe (5)	NaOAc (2.0)	0	0	-
12	dppe (5)	KOAc (2.0)	0	0	-
13	PPh_3 (10)	CsOAc (2.0)	9	4	2

a) Determined by GC using $C_{12}H_{26}$ as an internal standard.
b) Reaction was conducted without DMA.

General Procedure for Preparation of 2-Silylindoles and -pyrroles 4

Silylindoles and -pyrroles **4** were prepared according to the following scheme.

Scheme



Synthesis of 2-silylphenols:

2-Silylphenols **4-OH** were prepared by silylation of the corresponding 2-bromophenols with chloro(2-indolyl)silane, followed by retro-Brook rearrangement of the silyl ethers in a manner similar to those reported in the following reference.

Shimizu, M.; Mochida, K.; Hiyama, T. *Angew*. *Chem*. *Int*. *Ed*. **2008**, *47*, 9760.

Synthesis of 2-silylindoles and -pyrroles 4:

Triflation of **4**–**OH** was effected by either Method A or B.

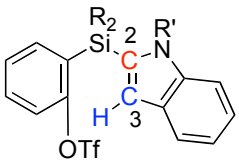
<Method A> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-(2-pyrrolylsilyl)phenol **4-OH** (3.0 mmol) and Et_2O (10 mL), and the solution was cooled to 0 °C. To the solution was added *n*-butyllithium (1.59 M in hexane, 1.9 mL, 3.0 mmol) dropwise via syringe over 10 min. The solution was stirred at 0 °C for 1 h before adding Tf_2O (0.75 mL, 3 mmol). The resulting solution was allowed to warm to room temperature and then stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **4** as a colorless solid or oil.

<Method B> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with NaH (72 mg, 3.0 mmol) and DMF (5 mL). A DMF solution (5 mL) of 2-(2-pyrrolylsilyl)phenol **4-OH** (3.0 mmol) was added to the suspension dropwise at room temperature. The resulting solution was stirred at room temperature for 1 h and then $PhNTf_2$ (1.07 g, 3.0 mmol) was added to the solution. The mixture was stirred for 12 h at room temperature before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **4** as a colorless solid or oil.

The structure of **4n** was confirmed unambiguously by X-ray analysis. The structures of other **4** were confirmed by characteristic ^1H and ^{13}C NMR data regarding 2- and 3-positions of the indole moieties in **4** on the basis of comparison of **4a** and the reported regioisomeric congener as shown in the following Figure.

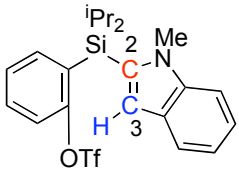
Figure

Characteristic NMR data of **4**



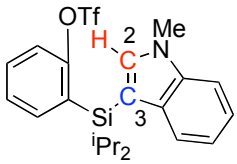
^{1}H NMR H(3) δ 6.81~6.90 ppm
^{13}C NMR C(2) δ 131.5~135.9 ppm
C(3) δ 112.7~117.3 ppm

NMR data of **4a**



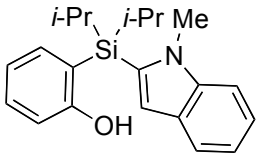
^{1}H NMR H(3) δ 6.90 ppm
^{13}C NMR C(2) δ 133.4 ppm
C(3) δ 115.0 ppm

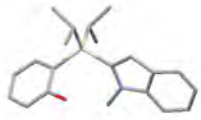
Previously reported data
(*Angew. Chem. Int. Ed.* **2008**, *47*, 9760)



^{1}H NMR H(2) δ 7.17 ppm
^{13}C NMR C(2) δ 137.6 ppm
C(3) δ 100.4 ppm

2-[Diisopropyl(1-methylindol-2-yl)silyl]phenol (4a-OH)

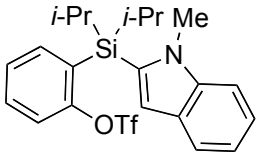




Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 57%, a colorless solid. Mp: 109.0–110.0 °C. TLC: R_f 0.15 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.72 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.69 (s, 3H), 5.20 (s, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.96–7.00 (m, 2H), 7.14 (dd, *J* = 7.9, 7.8 Hz, 1H), 7.25–7.29 (m, 1H), 7.33–7.36 (m, 2H), 7.41 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 33.7, 109.5, 115.3, 115.8, 117.3, 119.4, 120.2, 120.8, 122.5, 128.4, 131.5, 133.4, 136.2, 140.8, 161.3. IR (KBr): ν = 3158, 2949, 2832, 2943, 1591, 1574, 1485, 1462, 1435, 1277, 1174, 1072, 993, 879, 781, 752, 659, 630 cm^{-1}. MS (FAB) *m/z*: 337 (28, M^+), 294 (28), 250 (5), 236 (6), 206 (4). Anal. Calcd for $C_{21}H_{27}NOSi$: C, 74.73; H, 8.06. Found: C, 74.84; H, 7.99.

CCDC–722329 contains the crystallographic data for **4a-OH**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

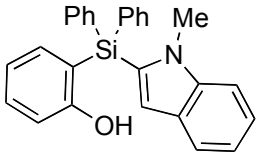
2-[Diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4a)



Prepared by Method A. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 85%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.80 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.54 (s, 3H), 6.90 (s, 1H), 7.13 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.24–7.33 (m, 3H), 7.45–7.53 (m, 3H), 7.68 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.3, 34.5, 109.2, 115.0, 118.2 (q, *J* = 318.0 Hz), 118.9, 119.2, 120.6, 122.2, 125.8, 126.8, 128.4, 131.7, 133.4, 138.9, 140.4, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2949, 2985, 1595, 1464, 1417, 1356,

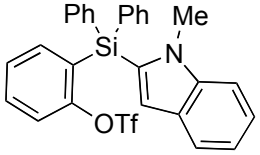
1248, 1213, 1142, 1055, 897, 797, 746, 737, 661, 631 cm^{-1}. MS (FAB) *m/z*: 469 (100, M^+), 426 (21), 250 (13), 154 (19). Anal. Calcd for $C_{21}H_{23}F_3O_4SSi$: C, 56.27; H, 5.58. Found: C, 56.02; H, 5.60.

2-[(1-Methylindol-2-yl)diphenylsilyl]phenol (4b-OH)



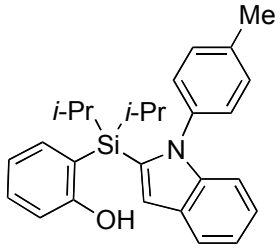
Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 51%, a colorless solid. Mp: 170.5–171.4 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 3.57 (s, 3H), 5.08 (s, 1H), 6.69 (d, *J* = 0.7 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.94 (ddd, *J* = 7.3, 7.3, 0.9 Hz, 1H), 7.11 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 7.25–7.30 (m, 1H), 7.29–7.42 (m, 7H), 7.45–7.49 (m, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.67–7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.9, 109.3, 116.1, 116.8, 118.5, 119.4, 120.8, 121.1, 122.7, 128.1, 128.3, 130.0, 132.3, 132.9, 134.8, 135.9, 137.4, 140.9, 160.8. IR (KBr): ν = 3545, 3061, 3045, 2935, 1591, 1570, 1483, 1435, 1354, 1278, 1234, 1167, 1103, 1068, 831, 798, 744, 704, 630 cm^{-1}. MS (FAB) *m/z*: 405 (6, M^+), 330 (1), 274 (3). Anal. Calcd for $C_{27}H_{23}NOSi$: C, 79.96; H, 5.72. Found: C, 79.73; H, 5.66.

2-[(1-Methylindol-2-yl)diphenylsilyl]phenyl trifluoromethanesulfonate (4b)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 52%, a colorless solid. Mp: 166.8–167.6 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 3.49 (s, 3H), 6.65 (d, *J* = 0.8 Hz, 1H), 7.10 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 7.25–7.29 (m, 1H), 7.32–7.35 (m, 2H), 7.38–7.42 (m, 4H), 7.45–7.52 (m, 4H), 7.56–7.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.9, 109.2, 117.1, 117.9 (q, *J* = 318.0 Hz), 119.1, 119.3, 121.1, 122.6, 126.4, 127.3, 128.0, 128.3, 130.1, 131.9, 132.5, 134.0, 135.8, 139.1, 140.8, 155.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (KBr): ν = 3061, 2934, 2854, 1595, 1562, 1492, 1465, 1415, 1354, 1228, 1139, 1057, 997, 900, 798, 744, 700, 626 cm^{-1}. MS (FAB) *m/z*: 597 (100, M^+), 460 (3), 404 (6), 386 (2). Anal. Calcd for Calcd for $C_{28}H_{22}F_3NO_3SSi$: C, 62.55; H, 4.12. Found: C, 62.57; H, 4.26.

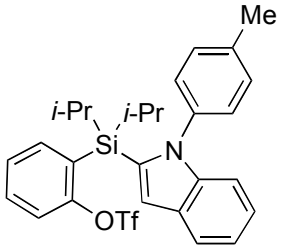
2-[Diisopropyl[1-(4-methylphenyl)indol-2-yl]silyl]phenol (4c-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 51%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.03 (d, *J* = 7.6 Hz, 6H), 1.33 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.39 (s, 3H), 5.46 (s, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.87 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.00–7.08 (m, 5H), 7.11–7.17 (m, 4H), 7.26–7.30 (m, 1H),

7.67–7.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 18.6, 18.8, 21.3, 110.7, 116.0, 116.2, 119.9, 120.0, 120.6, 122.9, 128.1, 128.4, 129.2 (2C), 131.1, 135.6, 136.1, 136.7, 137.9, 142.1, 160.8. IR (neat): ν = 3445, 2947, 2926, 2866, 1593, 1514, 1464, 1435, 1361, 1276, 1211, 1120, 1012, 906, 837, 752, 678 cm^{-1}. MS (FAB) *m/z*: 413 (35, M^+), 370 (50), 326 (10), 312 (2). Anal. Calcd for $C_{27}H_{31}NOSi$: C, 78.40; H, 7.55. Found: C, 78.29; H, 7.83.

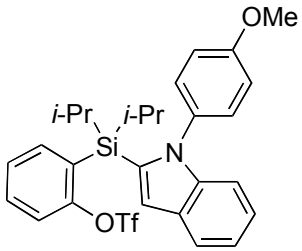
2-[Diisopropyl[1-(4-methylphenyl)indol-2-yl]silyl]phenyl trifluoromethanesulfonate (4c)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 40:1). Yield: 77%, a colorless solid. Mp: 122.1–122.8 °C. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.6 Hz, 6H), 1.13 (d, *J* = 7.6 Hz, 6H), 1.56 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.38 (s, 3H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.93–6.96 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 7.07–7.11 (m, 3H), 7.17 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.21 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.41 (ddd, *J* = 7.6, 7.4, 2.0 Hz, 1H), 7.67–7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 18.9, 19.0, 21.3, 110.3, 116.1, 118.2 (q, *J* = 317.9 Hz), 118.5, 119.5, 120.5, 122.4, 126.5, 128.06, 128.12, 128.3, 129.2, 131.0, 135.8, 137.0, 137.66, 137.68, 141.4, 155.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6. IR (KBr): ν = 2949, 2924, 2862, 1597, 1514, 1466, 1417, 1247, 1203, 1140, 1122, 1053, 902, 840, 743, 660cm^{-1}. MS (FAB) *m/z*: 545 (100, M^+), 502 (35), 412 (18), 368 (8). Anal. Calcd for $C_{28}H_{30}F_3NO_3SSi$: C, 61.63; H, 5.54. Found: C, 61.43; H, 5.55.

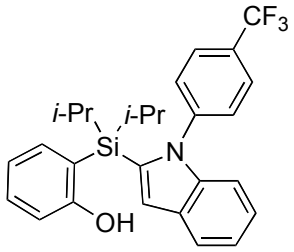
2-[Diisopropyl[1-(4-methoxylphenyl)indol-2-yl)silyl]phenol was prepared according to the general procedures and used for triflation without isolation.

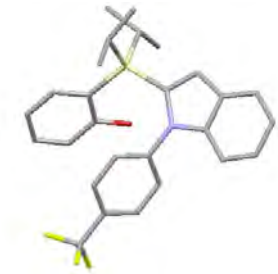
2-[Diisopropyl[1-(4-methoxylphenyl)indol-2-yl]silyl]phenyl trifluoromethanesulfonate (4d)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 13%, a colorless solid. Mp: 111.2–112.2 °C. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.6 Hz, 6H), 1.14 (d, *J* = 7.6 Hz, 6H), 1.56 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.84 (s, 3H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.89–8.93 (m, 3H), 7.07 (s, 1H), 7.10–7.12 (m, 2H), 7.18 (dd, *J* = 7.4, 7.9 Hz, 1H), 7.22 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.41 (ddd, *J* = 8.8, 8.2, 2.0 Hz, 1H), 7.67–7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 18.9, 19.0, 55.5, 110.3, 113.7, 116.0, 118.2 (q, *J* = 317.9 Hz), 118.6, 119.5, 120.5, 122.4, 126.6, 128.06, 128.13, 129.7, 131.1, 1324, 136.0, 137.7, 141.7, 155.4, 158.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6. IR (KBr): ν = 3064, 2949, 2906, 2868, 1593, 1514, 1466, 1410, 1300, 1246, 1219, 1138, 1120, 1051, 889, 842, 767, 682, 826 cm^{-1}. MS (FAB) *m/z*: 561 (100, M^+), 518 (29), 428 (6), 384 (6). Anal. Calcd for $C_{28}H_{30}F_3NO_4SSi$: C, 59.87; H, 5.38. Found: C, 59.93; H, 5.40.

2-[Diisopropyl[1-(4-trifluoromethylphenyl)indol-2-yl]silyl]phenol (4e-OH)

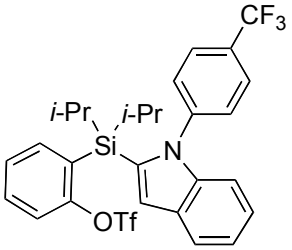




Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 21%, a colorless solid. Mp: 126.9–127.6 °C. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, J = 7.6 Hz, 6H), 1.09 (d, J = 7.6 Hz, 6H), 1.43 (qq, J = 7.6, 7.6 Hz, 2H), 5.12 (s, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.83 (ddd, J = 7.8, 7.0, 0.8 Hz, 1H), 7.00–7.02 (m, 1H), 7.07 (dd, J = 7.3, 1.7 Hz, 1H), 7.16–7.18 (m, 2H), 7.21–7.27 (m, 4H), 7.47 (d, J = 7.4 Hz, 2H), 7.67–7.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 18.82, 18.85, 110.3, 115.7, 116.85, 116.89, 119.9, 120.4, 120.8, 123.3, 123.7 (q, J = 269.9 Hz), 125.7, 128.4, 128.9, 130.0 (q, J = 32.8 Hz), 131.3, 135.5, 136.6, 141.4, 142.6, 160.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9. IR (KBr): ν = 3500, 2967, 2947, 2866, 1614, 1595, 1520, 1466, 1438, 1323, 1165, 1124, 1066, 852, 800, 746, 688 cm^{-1}. MS (FAB) *m/z*: 467 (28, M^+), 424 (57), 380 (13), 330 (14). Anal. Calcd for $C_{27}H_{28}F_3NOSi$: C, 69.35; H, 6.04. Found: C, 69.36; H, 6.12.

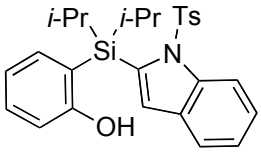
CCDC–722330 contains the crystallographic data for **4e-OH**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-[Diisopropyl[1-(4-trifluoromethylphenyl)indol-2-yl]silyl]phenyl trifluoromethanesulfonate (4e)



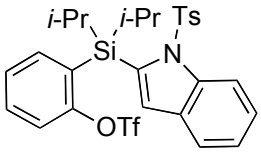
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 47%, a colorless solid. Mp: 115.3–116.3 °C. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J = 7.6 Hz, 6H), 1.19 (d, J = 7.6 Hz, 6H), 1.61 (qq, J = 7.6, 7.6 Hz, 2H), 6.91–6.95 (m, 1H), 7.08–7.17 (m 7H), 7.26–7.28 (m, 1H), 7.39–7.43 (m, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.70–7.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.7, 18.8, 19.1, 109.9, 117.3, 118.2 (q, J = 318.0 Hz), 118.9, 120.1, 120.8, 123.0, 123.7 (q, J = 269.9 Hz), 125.8 (q, J = 3.9 Hz),126.9, 127.8, 128.4, 128.9, 129.8 (q, J = 32.0 Hz), 131.4, 135.5, 137.0, 141.1, 143.0, 155.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9, –74.6. IR (KBr): ν = 3063, 2957, 2935, 2858, 1616, 1597, 1521, 1467, 1413, 1327, 1246, 1165, 1068, 999, 898, 744, 678 cm^{-1}. MS (FAB) *m/z*: 599 (100, M^+), 556 (67), 466 (8), 422 (9). Anal. Calcd for $C_{28}H_{27}F_6NO_3SSi$: C, 56.08; H, 4.54. Found: C, 55.93; H, 4.61.

2-[Diisopropyl(1-tosylindol-2-yl)silyl]phenol



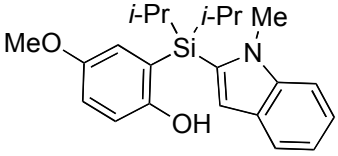
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 46%, a colorless solid. Mp: 165.0–165.9 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (d, *J* = 7.6 Hz, 6H), 1.26 (d, *J* = 7.6 Hz, 6H), 2.17–2.27 (m, 5H), 4.99 (s, 1H), 6.71 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 2H), 7.00–7.05 (m, 3H), 7.22 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 7.24 (d, *J* = 0.7 Hz, 1H), 7.27–7.34 (m, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 7.4, 1.7 Hz, 1H), 8.01 (dd, *J* = 8.4, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 19.15, 19.17, 21.5, 114.4, 115.4, 120.6, 121.0, 121.1, 123.1, 123.8, 125.0, 126.7, 129.1, 130.7, 130.9, 135.1, 136.7, 138.3, 138.6, 144.0, 160.4. IR (KBr): ν = 3487, 3059, 2948, 2946, 2868, 1595, 1435, 1359, 1220, 1168, 1128, 1090, 1022, 810, 750, 687, 648 cm^{-1}. MS (FAB) *m/z*: 477 (1, M^+), 434 (100), 384 (23), 342 (1). HRMS Calcd for $C_{24}H_{24}NO_3SSi$ (M^+–^{i}Pr): 434.1246 Found: 434.1264.

2-[Diisopropyl(1-tosylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4f)



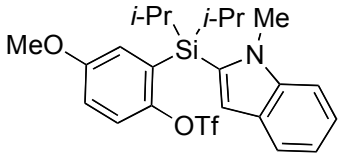
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 79%, a colorless solid. Mp: 152.0–152.7 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, *J* = 7.6 Hz, 6H), 1.25 (d, *J* = 7.6 Hz, 6H), 2.22 (s, 3H), 2.29 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 7.24 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 7.26–7.31 (m, 3H), 7.40 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 7.48 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.58 (m, 1H), 7.86 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.97 (dd, *J* = 8.4, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 19.00, 19.01, 21.5, 114.3, 118.0, 118.1 (q, *J* = 318.0 Hz), 121.2, 123.2, 125.1, 129.1, 129.8, 130.8, 131.0, 135.3, 136.3, 138.3, 138.8, 143.9, 155.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –75.0. IR (KBr): ν = 3068, 2970, 2943, 2866, 1593, 1467, 1413, 1363, 1230, 1197, 1105, 1031, 922, 882, 810, 760, 680, 648 cm^{-1}. MS (FAB) *m/z*: 609 (1, M^+), 566 (100), 434 (2), 384 (28). HRMS Calcd for $C_{28}H_{30}F_3NO_5S_2Si$: 609.1287. Found: 609.1313.

2-[Diisopropyl(1-methylindol-2-yl)silyl]-4-methoxyphenol (4g-OH)



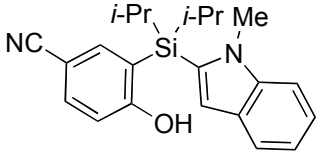
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 35%, a colorless solid. Mp: 95.4–96.2 °C. TLC: R_f 0.12 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.70 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.70 (s, 3H), 3.79 (s, 3H), 4.87 (s, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.90 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.96 (d, *J* = 3.1 Hz, 1H), 6.97 (s, 1H), 7.13 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.27 (dd, *J* = 8.2, 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.01, 18.03, 33.7, 55.8, 109.5, 115.3, 116.5, 116.6, 118.5, 119.4, 120.8, 121.1, 122.6, 128.4, 133.3, 140.8, 153.0, 155.3. IR (KBr): ν = 3460, 2957, 2938, 2899, 2860, 1583, 1489, 1462, 1400, 1269, 1201, 1138, 1069, 1034, 995, 879, 808, 796, 752, 723, 692, 659, 638 cm^{-1}. MS (FAB) *m/z*: 366 (14, M^+), 323 (4), 281 (2), 253 (4). Anal. Calcd for $C_{22}H_{29}NO_2Si$: C, 71.89; H, 7.95. Found: C, 71.59; H, 8.13.

2-[Diisopropyl(1-methylindol-3-yl)silyl]-4-methoxyphenyl trifluoromethanesulfonate (4g)



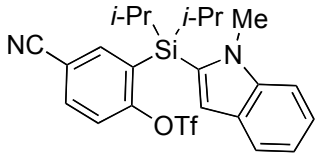
Prepared by Method A. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 10:1). Yield: 73%, a colorless solid. Mp: 92.5–93.5 °C. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.78 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.57 (s, 3H), 3.72 (s, 3H), 6.89 (s, 1H), 6.95–6.99 (m, 2H), 7.13 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.24–7.27 (m, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.3, 34.5, 55.7, 109.2, 115.1, 115.8, 118.3 (q, *J* = 317.2 Hz), 119.1, 120.2, 120.7, 122.2, 123.7, 127.6, 128.4, 133.3, 140.4, 148.9, 157.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (KBr): ν = 2949, 2935, 2870, 1585, 1483, 1464, 1393, 1377, 1304, 1229, 1207, 1139, 1125, 1031, 898, 866, 796, 756, 740, 678, 665 cm^{-1}. MS (FAB) *m/z*: 499 (100, M^+), 456 (11), 366 (11), 350 (13), 322 (47). Anal. Calcd for $C_{23}H_{28}F_3NO_4SSi$: C, 55.29; H, 5.65. Found: C, 55.51; H, 5.65.

4-Cyano-2-[diisopropyl(1-methylindol-2-yl)silyl]phenol (4h-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 50%, a colorless solid. Mp: 167.6–168.5 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.73 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.69 (s, 3H), 5.95 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 0.7 Hz, 1H), 7.16 (dd, *J* = 8.2, 7.8 Hz, 1H), 7.31 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.36 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 17.87, 17.89, 33.8, 104.1, 109.6, 116.1, 116.9, 119.3, 119.8, 119.9, 121.0, 123.2, 128.3, 131.6, 135.5, 140.5, 141.0, 164.8. IR (KBr): ν = 3289, 2945, 2928, 2864, 2228, 1583, 1491, 1464, 1385, 1356, 1329, 1286, 1211, 1070, 997, 883, 833, 796, 748, 731, 636 cm^{-1}. MS (FAB) *m/z*: 362 (42, M^+), 319 (21), 277 (4), 261 (2). HRMS Calcd for $C_{22}H_{26}N_2OSi$: 362.1814. Found: 362.1815.

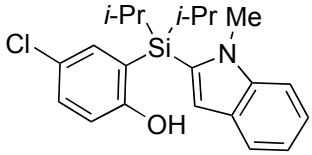
4-Cyano-2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4h)



Prepared by Method B. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 10:1). Yield: 70%, a colorless solid. Mp: 59.2–60.2 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.81 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.57 (s, 3H), 6.89 (s, 1H), 7.15 (dd, *J* = 7.6, 6.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.83–7.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.0, 18.2, 34.4, 109.3, 115.5, 115.7, 117.2, 118.1(q, *J* = 318.0 Hz), 119.5, 119.7, 120.8, 122.7, 128.3, 129.1, 131.5, 135.4, 140.5, 142.2, 157.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 3061, 2951, 2895, 2808, 2233, 1583, 1446, 1408, 1357, 1249, 1215, 1139, 1058, 996, 896, 844, 796, 752, 736, 690, 632, 617 cm^{-1}. MS

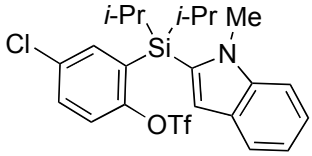
(FAB) *m/z*: 494 (100, M^+), 451 (15), 318 (18), 275 (12), 231 (4). Anal. Calcd for $C_{23}H_{25}F_3N_2O_3SSi$: C, 55.85; H, 5.09. Found: C, 55.62; H, 5.04.

4-Chloro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenol (4i-OH)



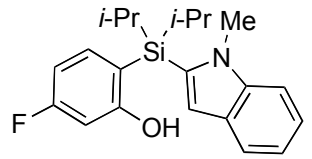
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 36%, a colorless solid. Mp: 107.0–108.0 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 12H), 1.71 (hep, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 5.26 (s, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.99 (s, 1H), 7.14 (dd, *J* = 7.9, 7.5 Hz, 1H), 7.27–7.31 (m, 2H), 7.34 (d, *J* = 2.8 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.9, 18.0, 33.8, 109.5, 115.7, 117.5, 119.6, 119.9, 120.9, 122.8, 125.5, 128.4, 131.4, 132.4, 135.0, 140.9, 159.8. IR (KBr): ν = 3549, 2943, 2902, 2864, 1589, 1460, 1375, 1267, 1234, 1134, 1109, 1064, 997, 878, 815, 750, 734, 651, 638 cm^{-1}. MS (FAB) *m/z*: 372 (30, M^+ + H), 328 (19), 240 (11), 198 (3). Anal. Calcd for $C_{21}H_{26}ClNOSi$: C, 67.81; H, 7.05. Found: C, 67.66; H, 7.05.

4-Chloro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4i)



Prepared by Method A. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 30:1). Yield: 76%, a colorless oil. TLC: R_f 0.51 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.79 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.58 (s, 3H), 6.90 (s, 1H), 7.15 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.26–7.30 (m, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.7 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.2, 34.5, 109.3, 115.3, 118.2 (q, *J* = 317.2 Hz), 119.3, 120.4, 120.7, 122.4, 128.3, 131.5, 132.4, 133.0, 137.9, 140.4, 153.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 3061, 2951, 2931, 2868, 1585, 1492, 1446, 1402, 1359, 1329, 1247, 1207, 1138, 1105, 1072, 1055, 995, 883, 798, 752, 665, 613 cm^{-1}. MS (FAB) *m/z*: 503 (100, M^+), 460 (51), 370 (9), 354 (4), 328 (10). Anal. Calcd for $C_{22}H_{25}ClF_3NO_3SSi$: C, 52.42; H, 5.00. Found: C, 52.52; H, 5.12.

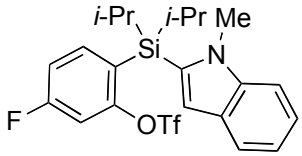
5-Fluoro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenol (4j-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 43%, a colorless solid. Mp: 119.4–120.4 °C. TLC: R_f 0.19 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.69 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.70 (s, 3H), 5.41 (s, 1H), 6.56 (dd, *J* = 10.6, 2.5 Hz, 1H), 6.73 (ddd, *J* = 8.4, 8.4, 2.5 Hz, 1H), 6.99 (d, *J* = 0.7 Hz, 1H), 7.15 (ddd, *J* = 7.5, 7.3, 1.1 Hz, 1H), 7.29 (ddd, *J* = 7.8, 7.5, 1.1 Hz, 1H), 7.34–7.38 (m, 2H), 7.68 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.91, 17.92, 33.7, 103.6 (d, *J*

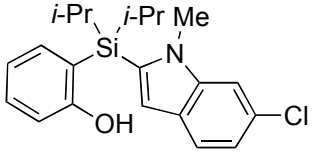
= 22.9 Hz), 197.8 (d, *J* = 19.8 Hz), 109.5, 112.8 (d, *J* = 3.0 Hz), 115.7, 119.5, 120.9, 122.8, 128.4, 132.7, 137.3 (d, *J* = 9.9 Hz), 141.0, 163.0 (d, *J* = 11.4 Hz), 165.2 (d, *J* = 266.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –109.7. IR (KBr): ν = 3466, 2945, 2862, 1585, 1464, 1402, 1282, 1190, 1147, 1070, 976, 881, 835, 783, 740, 655 cm^{-1}. MS (FAB) *m/z*: 355 (100, M^+), 312 (74), 270 (8). Anal. Calcd for $C_{21}H_{26}FNOSi$: C, 70.95; H, 7.37. Found: C, 70.87; H, 7.30.

5-Fluoro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4j)



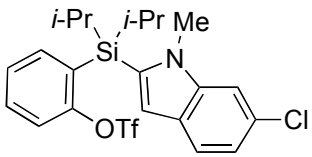
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 83%, a colorless oil. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.78 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.56 (s, 3H), 6.89 (s, 1H), 7.05 (ddd, *J* = 8.5, 7.9, 2.2 Hz, 1H), 7.14 (dd, *J* = 7.6, 7.0 Hz, 1H), 7.23–7.28 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 7.2, 7.0 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.1, 18.3, 34.5 107.6 (d, *J* = 25.9 Hz), 109.2, 114.4 (d, *J* = 19.1 Hz), 115.2, 118.2 (q, *J* = 318.0 Hz), 119.3, 120.7, 121.4 (d, *J* = 3.8 Hz), 122.3, 128.4, 133.0, 139.9 (d, *J* = 7.6 Hz), 140.4, 155.4 (d, *J* = 9.9 Hz), 163.8 (d, *J* = 251.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6, –106.2. IR (neat): ν = 2951, 2906, 2868, 1599, 1487, 1386, 1356, 1246, 1141, 1070, 968, 854, 796, 752, 736, 657 cm^{-1}. MS (FAB) *m/z*: 487 (100, M^+), 444 (33), 354 (8), 266 (10). Anal. Calcd for $C_{22}H_{25}NO_3SSi$: C, 54.19; H, 5.17. Found: C, 54.39; H, 5.11.

2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl]phenol (4k-OH)



Purification: silica gel column chromatography (hexane/AcOEt: 10:1). Yield: 46%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.6 Hz, 6H), 1.07 (d, *J* = 7.6 Hz, 6H), 1.70 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.63 (s, 3H), 5.04 (s, 1H), 6.81 (dd, *J* = 8.0, 0.7 Hz, 1H), 6.92 (d, *J* = 0.7 Hz, 1H), 6.98 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1H), 7.09 (d, *J* = 8.4, 1.8 Hz, 1H), 7.33–7.36 (m, 2H), 7.39 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 33.9, 109.5, 115.0, 115.7, 117.2, 120.1, 120.4, 121.5, 126.9, 128.7, 131.6, 135.0, 136.3, 141.1, 161.1. IR (neat): ν = 3445, 3068, 2945, 2867, 1593, 1566, 1435, 1383, 1359, 1329, 1278, 1192, 1120, 1053, 997, 916, 884, 829, 760, 682, 667 cm^{-1}. MS (FAB) *m/z*: 371 (70, M^+), 328 (62), 300 (6), 284 (11), 250 (10). Anal. Calcd for $C_{21}H_{26}ClNOSi$: C, 67.81; H, 7.05. Found: C, 67.52; H, 6.90.

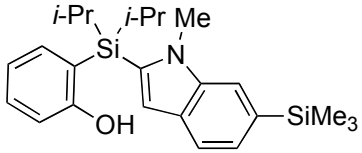
2-[Diisopropyl(6-chloro-1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4k)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt: 40:1). Yield: 78%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.11 (d, *J* = 7.6 Hz, 6H), 1.78 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.50 (s, 3H), 6.85

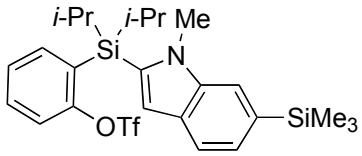
(s, 1H), 7.09 (dd, J = 8.4, 1.8 Hz, 1H), 7.30–7.34 (m, 2H), 7.45–7.49 (m, 2H), 7.51 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.3, 34.5, 109.2, 114.9, 118.2 (q, J = 317.2 Hz), 119.0, 119.9, 121.4, 125.6, 126.9 (2C), 128.3, 131.9, 134.6, 138.6, 140.8, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2951, 2895, 2868, 1607, 1595, 1444, 1402, 1360, 1329, 1287, 1240, 1138, 1053, 997, 918, 816, 766, 667, 651 cm^{-1}. MS (FAB) *m/z*: 503 (100, M^+), 460 (29), 370 (5), 268 (5). HRMS Calcd for $C_{22}H_{25}ClF_3NO_3SSi$: 503.0965. Found: 503.0942.

2-[Diisopropyl(1-methyl-6-trimethylsilylindol-2-yl)silyl]phenol (4l-OH)



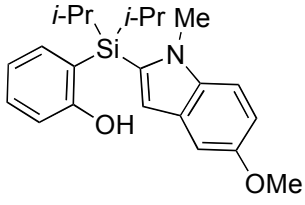
Purification: silica gel column chromatography (hexane/AcOEt 13:1). Yield: 41%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.34 (s, 9H), 1.06 (d, J = 7.2 Hz, 12H), 1.71 (hep, J = 7.2 Hz, 2H), 3.72 (s, 3H), 5.14 (s, 1H), 6.82 (dd, J = 8.0, 0.7 Hz, 1H), 6.96–7.00 (m, 2H), 7.29 (dd, J = 7.9, 0.7 Hz, 1H), 7.34 (ddd, J = 8.0, 7.5, 1.8 Hz, 1H), 7.41 (dd, J = 7.5, 1.8 Hz, 1H), 7.49 (d, J = 0.7 Hz, 1H), 7.68 (dd, J = 7.9, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.4, 18.0, 33.7, 114.3, 115.1, 115.8, 117.2, 120.2, 120.3, 123.9, 129.0, 131.6, 133.6, 133.8, 136.2, 140.6, 161.3. IR (neat): ν = 3443, 3050, 3014, 2965, 2891, 1599, 1568, 1469, 1435, 1314, 1360, 1277, 1192, 1148, 1121, 1076, 997, 881, 835, 810, 756, 692 cm^{-1}. MS (FAB) *m/z*: 409 (89, M^+), 394 (20), 366 (24), 350 (9), 338 (4). HRMS Calcd for $C_{24}H_{25}NOSi_2$: 409.2257. Found: 409.2257.

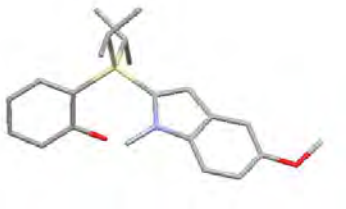
2-[Diisopropyl(1-methyl-6-trimethysilylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4l)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 26%, a colorless solid. Mp: 88.9–89.7 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H), 1.01 (d, J = 7.6 Hz, 6H), 1.12 (d, J = 7.6 Hz, 6H), 1.80 (qq, J = 7.6, 7.6 Hz, 2H), 3.57 (s, 3H), 6.88 (s, 1H), 7.25–7.30 (m, 2H), 7.41 (m, 4H), 7.68 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.6, 18.2, 18.3, 34.6, 114.0, 115.0, 118.3 (q, J = 318.0 Hz), 119.0, 120.2, 123.8, 125.8, 126.8, 128.9, 131.7, 133.2, 133.8, 139.1, 140.1, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 2953, 2935, 2866, 1468, 1423, 1357, 1247, 1219, 1142, 1122, 1055, 995, 897, 841, 813, 766, 744, 628 cm^{-1}. MS (FAB) *m/z*: 541 (100, M^+), 498 (11), 430 (3), 350 (13). Anal. Calcd for $C_{25}H_{34}F_3NO_3SSi_2$: C, 55.42; H, 6.33. Found: C, 55.33; H, 6.38.

2-[Diisopropyl(5-methoxy-1-methylindol-2-yl)silyl]phenol (4m-OH)

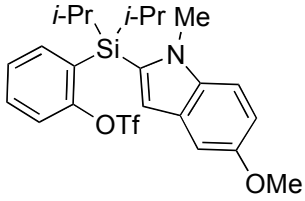




Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 46%, a colorless solid. Mp: 122.0–123.0 °C. TLC: R_f 0.15 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.70 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.66 (s, 3H), 3.87 (s, 3H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.89 (s, 1H), 6.94 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.98 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 7.34 (ddd, *J* = 8.1, 8.1, 1.7 Hz, 1H), 7.41 (dd, *J* = 7.3, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.0, 33.9, 55.9, 101.8, 110.2, 113.5, 114.6, 115.8, 117.3, 120.2, 128.6, 131.5, 133.8, 136.1, 136.5, 153.9, 161.3. IR (KBr): ν = 3377, 2949, 2928, 1616, 1587, 1570, 1500, 1456, 1433, 1344, 1276, 1209, 1177, 1074, 1033, 995, 883, 835, 787, 758, 689, 658, 646, 605 cm^{-1}. MS (FAB) *m/z*: 367 (100, M^+), 324 (44), 266 (14), 176 (13). Anal. Calcd for $C_{22}H_{29}NO_2Si$: C, 71.89; H, 7.95. Found: C, 71.64; H, 7.91.

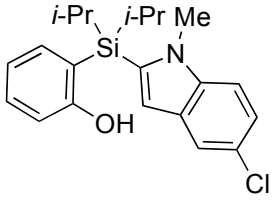
CCDC–722331 contains the crystallographic data for **4m-OH**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

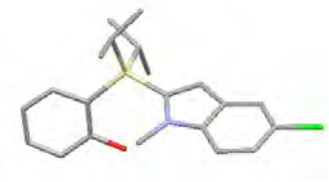
2-[Diisopropyl(5-methoxy-1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4m)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 81%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.79 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.52 (s, 3H), 3.88 (s, 3H), 6.81 (s, 1H), 6.94 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.45–7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.3, 34.6, 55.9, 101.8, 109.9, 112.9, 114.3, 118.2 (q, *J* = 317.2 Hz), 118.9, 125.9, 126.8, 128.6, 131.7, 133.9, 135.9, 138.9, 153.8, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2949, 2868, 2539, 1620, 1595, 1504, 1454, 1415, 1336, 1288, 1246, 1207, 1139, 1122, 1055, 997, 885, 835, 777, 765, 745, 655, 597 cm^{-1}. MS (FAB) *m/z*: 499 (100, M^+), 456 (9), 366 (7), 350 (3), 308 (5). Anal. Calcd for $C_{23}H_{28}F_3NO_4SSi$: C, 55.29; H, 5.65. Found: C, 55.29; H, 5.71.

2-[(5-Chloro-1-methylindol-2-yl)diisopropylsilyl]phenol (4n-OH)

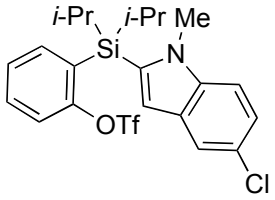


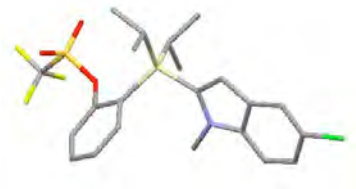


Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 46%, a colorless solid. Mp: 100.0–100.5 °C. TLC: R_f 0.17 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.71 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.65 (s, 3H), 5.05 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 1H), 6.98 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.34 (ddd, *J* = 8.8, 7.5, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 34.0, 110.4, 114.2, 115.7, 117.2, 120.0, 120.4, 122.6, 125.2, 129.3, 131.6, 135.8, 136.3, 139.1, 161.1. IR (KBr): ν = 3507, 2949, 2926, 2862, 1591, 1572, 1481, 1435, 1360, 1317, 1274, 1057, 993, 880, 794, 760, 684, 653 cm^{-1}. MS (FAB) *m/z*: 371 (48, M^+), 328 (61), 284 (12), 270 (7), 250 (11). Anal. Calcd for $C_{21}H_{26}ClNOSi$: C, 67.81; H, 7.05. Found: C, 67.73; H, 7.08.

CCDC–722332 contains the crystallographic data for **4n-OH**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-[(5-Chloro-1-methylindol-2-yl)diisopropylsilyl]phenyl trifluoromethanesulfonate (4n)

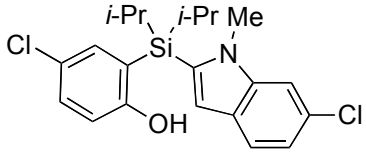




Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 81%, a colorless solid. Mp: 77.5–78.5 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, J = 7.2 Hz, 6H), 1.17 (d, J = 7.2 Hz, 6H), 1.78 (qq, J = 7.2, 7.2 Hz, 2H), 3.52 (s, 3H), 6.81 (s, 1H), 7.18 (dd, J = 8.8, 1.8 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.33 (ddd, J = 7.4, 7.3, 0.8 Hz, 1H), 7.45–7.49 (m, 2H), 7.53 (ddd, J = 7.9, 7.4, 1.9 Hz, 1H), 7.62 (dd, J = 1.8, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.2, 34.6, 110.1, 114.2, 118.2 (q, J = 317.2 Hz), 119.1, 119.9, 122.4, 125.0, 125.5, 126.9, 129.3, 131.9, 135.3, 138.5, 138.6, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 2965, 2951, 2868, 1485, 1467, 1417, 1244, 1217, 1203, 1140, 1053, 891, 814, 748, 667, 640 cm^{-1}. MS (FAB) *m/z*: 503 (100, M^+), 460 (21), 370 (9), 328 (11), 312 (4). Anal. Calcd for $C_{22}H_{25}ClF_3NO_3SSi$: C, 52.42; H, 5.00. Found: C, 52.14; H, 4.92.

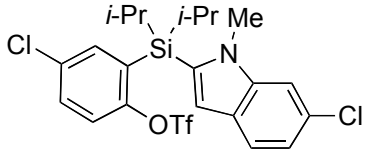
CCDC–722333 contains the crystallographic data for **4n**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4-Chloro-2-[(6-chloro-1-methylindol-2-yl)diisopropylsilyl]phenol (4o-OH)



Purification: silica gel column chromatography (hexane/AcOEt: 10:1). Yield: 59%, a colorless oil. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, J = 7.6 Hz, 6H), 1.76 (hep, J = 7.6, Hz, 2H), 3.64 (s, 3H), 5.10 (s, 1H), 6.76 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 0.7 Hz, 1H), 7.10 (dd, J = 8.4, 1.8 Hz, 1H), 7.28 (dd, J = 8.6, 1.6 Hz, 1H), 7.32 (d, J = 1.6 Hz, 1H), 7.33 (dd, J = 1.8, 0.7 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.95, 17.98, 33.9, 109.5, 115.4, 117.4, 119.9, 120.3, 121.6, 125.6, 126.8, 129.0, 131.4, 134.0, 135.1, 141.2, 159.6. IR (neat): ν = 3548, 3063, 2960, 2889, 1874, 1606, 1444, 1384, 1327, 1286, 1224, 1182, 1134, 1107, 1053, 997, 918, 882, 825, 752, 740, 665, 632 cm^{-1}. MS (FAB) *m/z*: 405 (22, M^+), 362 (18), 318 (4), 318 (4), 290 (3). Anal. Calcd for $C_{21}H_{25}Cl_2NOSi$: C, 62.06; H, 6.20. Found: C, 62.20; H, 6.39.

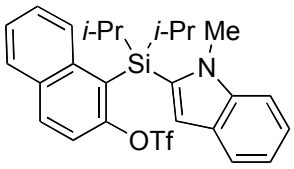
4-Chloro-2-[(6-chloro-1-methylindol-2-yl)diisopropylsilyl]phenyl trifluoromethanesulfonate (4o)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt: 20:1). Yield: 84%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 6H), 1.11 (d, *J* = 7.6 Hz, 6H), 1.78 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.53 (s, 1H), 6.85 (d, *J* = 0.7 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.32 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.48 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.2, 34.5, 115.2, 109.3, 118.1 (q, *J* = 317.2 Hz), 120.1, 120.5, 121.4, 126.9, 128.59, 128.64, 131.7, 133.1, 133.7, 137.6, 140.8, 153.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (neat): ν = 2953, 2930, 2868, 1608, 1447, 1427, 1417, 1368, 1248, 1138, 1056, 996, 919, 816, 767, 667, 613 cm^{-1}. MS (FAB) *m/z*: 537 (100, M^+), 494 (20), 404 (7), 362 (13), 318 (12). Anal. Calcd for $C_{22}H_{24}Cl_2F_3NO_3SSi$: C, 49.07; H, 4.49. Found: C, 49.00; H, 4.68.

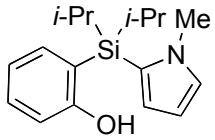
2-[Diisopropyl(1-methylindol-2-yl)silyl]naphthalen-2-ol was prepared according to the general procedures and used for triflation without isolation.

2-[Diisopropyl(1-methylindol-2-yl)silyl]naphthalen-1-yl trifluoromethanesulfonate (4p)



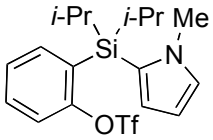
Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 36%, a colorless solid. Mp: 66.8–67.7 °C. TLC: R_f 0.35 (hexane/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.15 (d, *J* = 7.2 Hz, 6H), 2.03 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.09 (s, 3H), 6.99 (d, *J* = 0.8 Hz, 1H), 7.08 (ddd, *J* = 7.9, 7.7, 1.4 Hz, 1H), 7.14–7.23 (m, 3H), 7.40 (ddd, *J* = 7.8, 7.4, 1.1 Hz, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.73 (dm, *J* = 7.8 Hz, 1H), 7.84 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.89 (dd, *J* = 8.8, 0.7 Hz, 1H), 8.02 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9, 18.5, 18.9, 33.8, 109.3, 112.7, 117.4, 118.5 (q, *J* = 317.2 Hz), 119.2, 120.6, 121.9, 122.0, 126.2, 127.0, 128.5, 128.6, 129.0, 131.9, 133.5, 136.0, 138.6, 140.1, 154.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 3057, 2949, 2868, 1620, 1587, 1566, 1508, 1464, 1421, 1354, 1327, 1300, 1246, 1215, 1159, 1070, 1003, 984, 925, 883, 829, 810, 797, 750, 699, 615 cm^{-1}. MS (FAB) *m/z*: 519 (100, M^+), 476 (34), 386 (64), 370 (27), 342 (23). HRMS Calcd for $C_{26}H_{28}F_3NO_3SSi$: 519.1511. Found: 519.1487.

2-[Diisopropyl(1-methylpyrrol-2-yl)silyl]phenol (4q-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 23%, a colorless solid. Mp: 46.4–47.4 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.04 (d, *J* = 7.2 Hz, 6H), 1.59 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.59 (s, 1H), 5.56 (s, 1H), 6.28 (dd, *J* = 3.3, 1.3 Hz, 1H), 6.67 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.93-6.98 (m, 2H), 7.32 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.38 (dd, *J* = 7.3, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.9, 18.0, 37.3, 109.3, 115.8, 117.4, 119.9, 123.5 (2C), 129.3, 131.4, 135.7, 161.7. IR (KBr): ν = 3418, 2943, 2862, 1599, 1564, 1512, 1471, 1438, 1278, 1203, 1118, 997, 882, 829, 760, 731, 677, 628 cm^{-1}. MS (FAB) *m/z*: 288 (13, M^+ + H), 244 (28), 202 (7), 164 (6). Anal. Calcd for $C_{17}H_{25}NOSi$: C, 71.03; H, 8.77. Found: C, 70.80; H, 8.56.

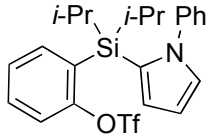
2-[Diisopropyl(1-methylpyrrol-2-yl)silyl]phenyl trifluoromethanesulfonate (4q)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 40:1). Yield: 73%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.58 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.72 (s, 3H), 6.21 (dd, *J* = 3.9, 1.8 Hz, 1H), 6.70 (dd, *J* = 1.8, 1.7 Hz, 1H), 6.75 (dd, *J* = 2.2, 2.2 Hz, 1H), 7.22–7.26 (m, 1H), 7.36–7.44 (m, 2H), 7.56 (dd, *J* = 7.3, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.3, 18.4, 36.0, 108.2, 115.5, 118.3, 118.4 (q, *J* = 318.0 Hz), 122.7, 126.3, 128.2, 129.7, 130.8, 139.7, 155.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2947, 2866, 2359, 2341, 1595, 1514, 1468, 1417, 1246, 1211, 1130, 1051, 891, 779, 765, 746, 684 cm^{-1}. MS (FAB) *m/z*: 420 (6, M^+ + H), 376 (100), 340 (9), 242 (6). Anal. Calcd for $C_{18}H_{24}F_3NO_3SSi$: C, 51.53; H, 5.77. Found: C, 51.62; H, 5.67.

2-[Diisopropyl(1-phenylpyrrol-2-yl)silyl]phenol was prepared according to the general procedures and used for triflation without isolation.

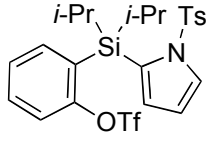
2-[Diisopropyl(1-phenylpyrrol-2-yl)silyl]phenyl trifluoromethanesulfonate (4r)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 25%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.08 (d, *J* = 7.6 Hz, 6H), 1.64 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.40 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.17 (dd, *J* = 1.7, 1.4 Hz, 1H), 7.22 (dd, *J* = 2.6, 2.2 Hz, 1H), 7.25–7.30 (m, 2H), 7.39–7.46 (m, 6H), 7.62 (dd, *J* = 7.5, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.3, 18.4, 110.9, 117.3, 118.4 (q, *J* = 317.1 Hz), 118.5, 120.4, 120.5, 125.6, 126.6, 126.8, 127.7, 129.4, 131.0, 139.5, 140.3, 155.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2947, 2866, 2359, 1600, 1508, 1417, 1246, 1216, 1142, 1053, 893, 758, 688 cm^{-1}. MS (FAB) *m/z*: 482 (7, M^+ + H), 438 (100), 288 (7), 262 (20). Anal. Calcd for $C_{23}H_{26}F_3NO_3SSi$: C, 57.36; H, 5.44. Found: C, 57.34; H, 5.42.

2-[Diisopropyl(1-tosylpyrrol-2-yl)silyl]phenol was prepared according to the general procedures and used for triflation without isolation.

2-[Diisopropyl(1-tosylpyrrol-2-yl)silyl]phenyl trifluoromethanesulfonate (4s)



Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 11%, a colorless solid. Mp: 91.8–92.8 °C. TLC: R_f 0.27 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, *J* = 7.6 Hz, 6H), 1.19 (d, *J* = 7.6 Hz, 6H), 2.11 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.23 (s, 3H), 6.45 (dd, *J* = 3.3, 3.1 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.86 (dd, *J* = 3.3, 1.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.44 (ddd, *J* = 8.1, 7.3, 2.0 Hz, 1H), 7.50 (dd, *J* = 3.1, 1.4 Hz, 1H), 7.78 (dd, *J* = 7.3, 2.0 Hz, 1H); ^{13}C NMR

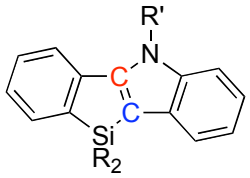
(100 MHz, $CDCl_3$): δ 13.2, 19.3, 19.4, 21.8, 113.9, 118.37, 118.40 (q, J = 318.0 Hz), 125.9, 127.0, 128.0, 128.1, 128.8, 129.6, 129.9, 131.2, 136.4, 138.4, 144.0, 155.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –75.2. IR (KBr): ν = 2963, 2951, 2872, 1595, 1421, 1362, 1244, 1213, 1175, 1146, 1088, 1049, 891, 806, 781, 745, 675 cm^{-1}. MS (FAB) *m/z*: 560 (8, M^+ + H), 516 (100), 384 (2), 334 (30). Anal. Calcd for $C_{24}H_{28}FNO_5S_2Si$: C, 51.50; H, 5.04. Found: C, 51.71; H, 5.08.

General Procedure for Pd-catalyzed Intramolecular Coupling Reaction of 4

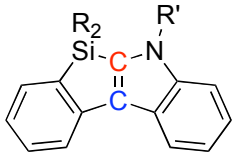
An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with 2-(2-pyrrolylsilyl)aryl triflate **4** (0.30 mmol), dppe (6.0 mg, 0.015 mmol), Et_2NH (0.45 ml, 4.2 mmol), and DMA (1.0 mL). Then, the vial was stirred for 3 min at room temperature. To the solution was added a solution of $Pd(OAc)_2$ (3.4 mg, 0.015 mmol) in DMA (0.5 mL). The vial was stirred at 100 °C on a hot plate for 12 h. The resulting mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with H_2O (15 mL x 3) and then with saturated aq. NaCl (15 mL). Drying the organic solvent over anhydrous $MgSO_4$ followed by concentration under reduced pressure gave the crude product, which was purified by column chromatography on N–H silica gel to give **5** solely or **5** and **6**.

The structures of **5a**, **5e**, **5f**, **5h**, **5k**, **5n** were unambiguously determined by X-ray analysis. The structures of other **5**/**6** were assigned by the similarity of the characteristic ^{13}C NMR data of the indole moieties as shown in the Figure below.

Figure

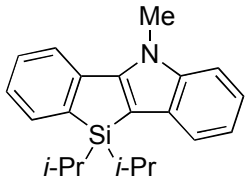


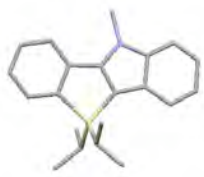
^{13}C NMR C(2) δ 151.2~154.4 ppm
C(3) δ 106.5~110.4 ppm



^{13}C NMR C(2) δ 146.3~150.9 ppm
C(3) δ 124.1~124.9 ppm

10,10-Diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5a)



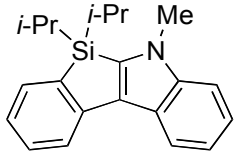


Purification: N–H silica gel column chromatography (hexane/AcOEt 40:1). Yield: 89%, a colorless solid. Mp: 122.6–123.7 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, J = 7.2 Hz, 6 H), 1.14 (d, J = 7.2 Hz, 6H), 1.40 (qq, J = 7.2, 7.2 Hz, 2H), 4.13 (s, 3H), 7.13 (ddd, J = 7.6, 7.2, 0.8 Hz, 1H), 7.18–7.24 (m, 2H), 7.35–7.39 (m, 2H), 7.56–7.60 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.8, 32.3, 108.4, 109.4, 120.0, 120.1, 121.3, 122.1, 126.0, 129.1, 130.5, 133.7, 142.1, 142.28, 142.32, 153.3. IR (KBr): ν = 2937, 2887, 2860, 1583, 1462, 1398, 1329, 1282, 1130, 1068, 974, 879, 821, 773, 680, 634 cm^{-1}. MS (FAB) *m/z*: 319 (100, M^+), 276 (13), 248 (11), 234 (10), 218 (6). Anal. Calcd for $C_{21}H_{25}NSi$: C,

78.94; H, 7.89. Found: C, 78.89; H, 8.16.

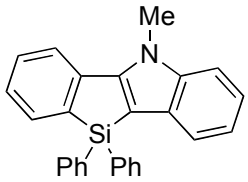
CCDC–697662 contains the crystallographic data for **5a**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6,6-Diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-*b*][1]indole (6a)



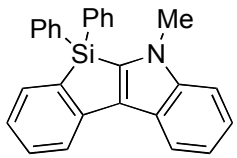
Purification: N–H silica gel column chromatography (hexane/AcOEt 40:1). Yield: 3%, a colorless oil. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6 H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.89 (s, 3H), 7.06 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.19 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.23–7.26 (m, 1H), 7.34–7.40 (m, 2H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.8, 34.8, 109.9, 119.6, 119.9, 120.1, 121.8, 123.7, 124.2, 129.9, 132.6, 133.3, 134.9, 142.8, 143.1, 146.6. IR (neat): ν = 2942, 2862, 1587, 1479, 1456, 1373, 1337, 1182, 1090, 991, 882, 814, 772, 750, 673 cm^{-1}. MS (FAB) *m/z*: 319 (100, M^+), 276 (13), 234 (9) 218 (4). HRMS Calcd for $C_{21}H_{25}NSi$: 319.1756. Found: 319.1763.

5-Methyl-10,10-diphenyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5b)



Purification: N–H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 59%, a colorless solid. Mp: 205.5–206.5 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (s, 3H), 7.16 (dd, *J* = 7.6, 7.1 Hz, 1H), 7.23–7.28 (m, 2H), 7.31–7.35 (m, 4H), 7.37–7.44 (m, 4H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.72–7.75 (m, 4H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.3, 108.2, 109.7, 120.5, 120.6, 121.7, 121.8, 126.8, 127.9, 129.8, 129.9, 130.1, 133.3, 134.2, 135.3, 141.8, 141.9, 142.5. 153.6. IR (KBr): ν = 3064, 3050, 2995, 2359, 2341, 1471, 1427, 1392, 1352, 1111, 1014, 977, 819, 773, 742, 692 cm^{-1}. MS (FAB) *m/z*: 387 (100, M^+), 310 (21), 240 (2). Anal. Calcd for $C_{27}H_{21}Si$: C, 83.68; H, 5.46. Found: C, 83.52; H, 5.61.

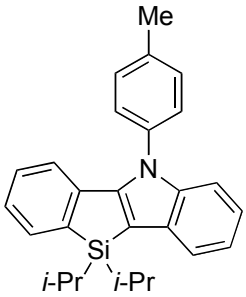
5-Methyl-6,6-diphenyl-6*H*-[1]benzosilolo[2,3-*b*][1]indole (6b)



Purification: N–H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 17%, a colorless solid. Mp: 192.0–193.0 °C. TLC: R_f 0.15 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 7.10 (dd, *J* = 7.3, 7.0 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.26–7.34 (m, 1H), 7.34–7.41 (m, 5H), 7.43–7.47 (m, 3H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.70–7.72 (m, 4H), 7.81 (d, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.3, 110.1, 119.9, 120.1, 120.6, 122.4, 124.2, 124.5, 128.2, 130.3, 130.7, 131.3, 132.8, 133.7, 135.46, 135.50, 142.4, 143.0, 146.3. IR (KBr): ν = 3063, 3016, 2359, 2341, 1585, 1479, 1427, 1375, 1338, 1255, 1112, 943,

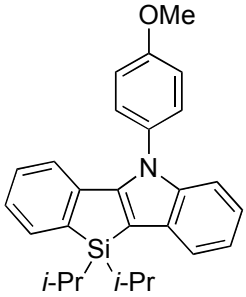
815, 767, 750, 698, 660 cm^{-1}. MS (FAB) *m/z*: 387 (27, M^+), 310 (7), 232 (1). HRMS Calcd for $C_{27}H_{21}Si$: 387.1443. Found: 387.1453.

10,10-Diisopropyl-5-(4-methylphenyl)-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5c)



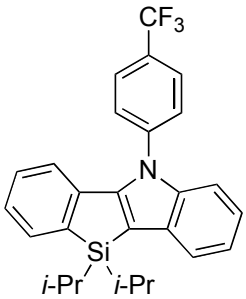
Purification: N–H silica gel column chromatography (hexane/AcOEt 30:1), followed by recrystallization from hexane. Yield: 74%, a colorless solid. Mp: 111.5–112.5 °C. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.44 (qq, *J* = 7.2, 7.2 Hz, 2H), 2.53 (s, 3H), 6.61 (d, *J* = 7.5 Hz, 1H), 7.00–7.06 (m, 2H), 7.08–7.18 (m, 3H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 19.0, 19.2, 21.9, 109.6, 111.1, 120.8 (2C), 121.0, 120.0, 122.2, 126.3, 128.6, 129.1, 130.5, 130.9, 133.7, 136.1, 138.7, 142.0, 144.1, 153.3. IR (KBr): ν = 2940, 2861, 1585, 1514, 1458,1388, 1334, 1008, 881, 854, 736, 686, 665 cm^{-1}. MS (FAB) *m/z*: 395 (100, M^+), 352 (41), 324 (13), 310 (13). Anal. Calcd for $C_{27}H_{29}NSi$: C, 81.97; H, 7.39. Found: C, 82.03; H, 7.55.

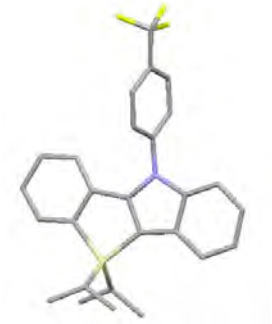
10,10-Diisopropyl-5-(4-methoxylphenyl)-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5d)



Purification: N–H silica gel column chromatography (hexane), followed by recrystallization from hexane. Yield: 73%, a colorless solid. Mp: 159.4–160.4 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.44 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.95 (s, 3H), 6.61 (d, *J* = 8.0 Hz, 1H), 7.02–7.16 (m, 7H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.7, 18.9, 55.6, 109.1, 110.7, 114.6, 120.4, 120.6, 121.7, 121.9, 126.0, 128.8, 129.6, 130.5, 131.2, 133.4, 141.6, 141.7, 143.9, 153.2, 159.4. IR (KBr): ν = 3005, 2939, 2860, 2835, 1583, 1512, 1460, 1393, 1246, 1166, 1031, 989, 854, 745, 713, 689 cm^{-1}. MS (FAB) *m/z*: 411 (100, M^+), 368 (24), 326 (8). Anal. Calcd for $C_{27}H_{29}NOSi$: C, 78.79; H, 7.10. Found: C, 78.50; H, 7.32.

10,10-Diisopropyl-5-(4-trifluoromethylphenyl)-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5e)

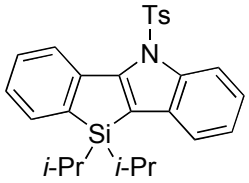


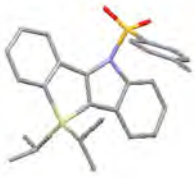


Purification: N–H silica gel column chromatography (hexane), followed by recrystallization from hexane. Yield: 80%, a colorless solid. Mp: 176.0–177.0 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (d, J = 7.2 Hz, 6H), 1.20 (d, J = 7.2 Hz, 6H), 1.47 (qq, J = 7.2, 7.2 Hz, 2H), 6.56 (d, J = 7.5 Hz, 1H), 7.04–7.09 (m, 2H), 7.11–7.17 (m 2H), 7.20 (ddd, J = 7.6, 7.1, 1.3 Hz, 1H), 7.55 (d, J = 6.2 Hz, 1H), 7.62–7.66 (m, 3H), 7.87 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.7, 18.9, 110.4, 111.1, 120.4, 121.3, 122.2, 122.3, 123.8 (q, J = 270.7 Hz), 126.6, 126.7 (q, J = 3.8 Hz), 128.89, 128.91, 130.5 (q, J = 32.8 Hz), 130.8, 133.6, 141.1, 141.5, 141.9, 142.3, 152.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.7. IR (KBr): ν = 3072, 2938, 2860, 1616, 1518, 1458, 1388, 1323, 1132, 1067, 1014, 868, 744, 684 cm^{-1}. MS (FAB) *m/z*: 449 (100, M^+), 406 (25), 378 (11), 364 (10). Anal. Calcd for $C_{27}H_{26}F_3NSi$: C, 72.13; H, 5.83. Found: C, 71.86; H, 5.96.

CCDC–722334 contains the crystallographic data for **5e**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

10,10-Diisopropyl-5-tosyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5f)

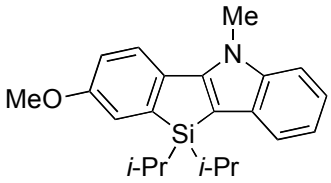




Purification: N-H silica gel column chromatography (hexane/AcOEt 100:1). Yield: 83%, a colorless solid. Mp: 98.0–99.0 °C. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, J = 7.6 Hz, 6H), 0.94 (d, J = 7.6 Hz, 6H), 1.35 (qq, J = 7.6, 7.6 Hz, 2H), 2.22 (s, 3H), 6.94 (d, J = 8.2 Hz, 2H), 7.21–7.31(m, 5H), 7.37 (d, J = 7.0 Hz, 1H), 7.43 (ddd, J = 8.0, 8.0, 1.4 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 18.1, 18.3, 21.5, 117.8, 122.0, 124.5, 124.6, 124.7, 125.1, 126.4, 126.6, 129.0, 129.6, 132.9, 133.0, 133.9, 139.2, 141.6, 142.6, 144.2, 154.7. IR (KBr): ν = 3047, 2936, 2860, 1597, 1464, 1450, 1423, 1373, 1178, 1091, 1076, 947, 748, 721, 692, 658 cm^{-1}. MS (FAB) *m/z*: 459 (100, M^+), 352 (9), 262 (12). HRMS Calcd for $C_{27}H_{29}NO_2SSi$: 459.1688 Found: 459.1686.

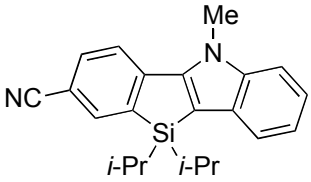
CCDC–731564 contains the crystallographic data for **5f**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

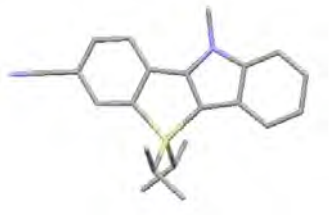
5,5-Diisopropyl-3-methoxy-10-methyl-5*H*-[1]benzosilolo[3,2-*b*][1]indole (5g)



Purification: N–H silica gel column chromatography (hexane/AcOEt 50:1). Yield: 77%, a colorless solid. Mp: 151.6–152.0 °C. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.39 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.87 (s, 3H), 4.09 (s, 3H), 6.86 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.11 (dd, *J* = 7.9, 7.1 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.18 (dd, *J* = 8.2, 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.8, 32.1, 55.4, 106.5, 109.3, 112.5, 120.0, 120.80, 120.83, 120.9, 121.7, 130.7, 135.1, 142.0, 144.7, 152.3, 157.9. IR (KBr): ν = 2935, 2859, 1573, 1458, 1398, 1281, 1234, 1045, 880, 740, 707, 680, 638 cm^{-1}. MS (FAB) *m/z*: 349 (100, M^+), 306 (25), 280 (3), 264 (79), 248 (4). Anal. Calcd for $C_{22}H_{27}NOSi$: C, 75.59; H, 7.79. Found: C, 75.33; H, 7.69.

3-Cyano-5,5-diisopropyl-10-methyl-5*H*-[1]benzosilolo[3,2-*b*][1]indole (5h)

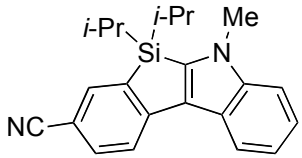




Purification: N–H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 75%, a colorless solid. Mp: 167.7–168.2 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.44 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.13 (s, 3H), 7.17 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.29 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.75 (d, *J* = 1.5 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.5, 18.6, 32.4, 108.9, 109.8, 112.1, 119.6, 119.8, 120.7, 122.7, 122.9, 130.1, 133.8, 136.1, 142.8, 143.3, 146.2, 151.2. IR (KBr): ν = 2941, 2887, 2860, 2220, 1587, 1479, 1458, 1398, 1332, 1188, 1066, 1028, 991, 877, 764, 738, 680, 646 cm^{-1}. MS (FAB) *m/z*: 344 (67, M^+), 301 (25), 273 (10), 259 (9), 243 (4). Anal. Calcd for $C_{22}H_{24}N_2Si$: C, 76.70; H, 7.02. Found: C, 76.53; H, 6.98.

CCDC–722335 contains the crystallographic data for **5h**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

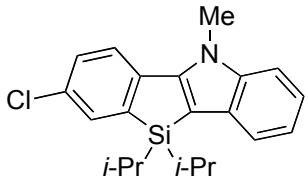
3-Cyano-5,5-diisopropyl-6-methyl-5*H*-[1]benzosilolo[2,3-*b*][1]indole (6h)



Purification: N–H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 15%, a colorless oil. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.52 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.91 (s, 3H), 7.22–7.26 (m, 1H), 7.31 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

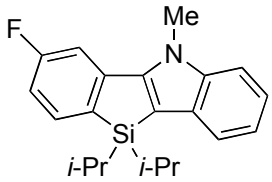
11.1, 18.4, 18.7, 35.0, 106.3, 110.3, 119.7, 119.8, 120.2, 120.6, 122.7, 124.1, 131.4, 134.6, 136.0, 136.2, 143.1, 145.4, 150.9. IR (neat): ν = 2943, 2864, 2216, 1587, 1556, 1454, 1381, 1336, 1193, 1089, 908, 881, 815, 738, 677 cm^{-1}. MS (FAB) *m/z*: 344 (100, M^+), 301 (12) 259 (10). HRMS Calcd for $C_{22}H_{24}N_2Si$: 344.1709. Found: 344.1717.

3-Chloro-5,5-diisopropyl-10-methyl-5*H*-[1]benzosilolo[3,2-*b*][1]indole (5i)



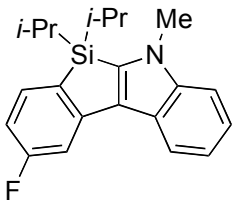
Purification: N–H silica gel column chromatography (hexane/AcOEt 50:1). Yield: 81%, a colorless solid. Mp: 163.1–164.0 °C. TLC: R_f 0.48 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.41 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.10 (s, 3H), 7.14 (dd, *J* = 8.2, 7.4 Hz, 1H), 7.23 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.2, 108.6, 109.5, 120.3, 120.9, 121.7, 122.1, 128.9, 130.4, 132.0, 133.4, 140.6, 142.3, 144.9, 152.2. IR (KBr): ν = 2935, 2922, 2860, 1554, 1458, 1396, 1379, 1097, 879, 815, 775, 736, 680, 638 cm^{-1}. MS (FAB) *m/z*: 354 (67, M^+ + H), 312 (9), 282 (9), 268 (8), 254 (3). Anal. Calcd for $C_{21}H_{24}ClNSi$: C, 71.26; H, 6.83. Found: C, 71.01; H, 6.88.

2-Fluoro-5,5-diisopropyl-10-methyl-5*H*-[1]benzosilolo[3,2-*b*][1]indole (5j)



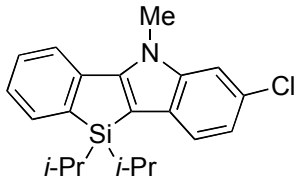
Purification: N–H silica gel column chromatography (hexane/AcOEt 40:1) followed by reverse phase preparative HPLC (CH_3CN). Yield: 74%, a colorless solid. Mp: 111.1–112.1 °C. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.10 (s, 3H), 6.87–6.91 (m, 1H), 7.14 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H), 7.22–7.26 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.45–7.50 (m, 2H), 7.58 (dm, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.1, 108.3 (d, *J* = 23.6 Hz), 109.6, 110.3, 112.2 (d, *J* = 20.6 Hz), 120.3, 121.9, 122.3, 130.3, 134.6 (d, *J* = 8.4 Hz), 136.8 (d, *J* = 3.8 Hz), 142,3, 144.4 (d, *J* = 8.4 Hz), 151.8 (d, *J* = 3.1 Hz), 164.6 (d, *J* = 243.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –122.4. IR (KBr): ν = 2935, 2859, 1589, 1479, 1402, 1330, 1283, 1219, 1170, 1016, 910, 852, 808, 735, 665 cm^{-1}. MS (FAB) *m/z*: 337 (100, M^+), 294 (35), 266 (9), 252 (7). Anal. Calcd for $C_{21}H_{24}FNSi$: C, 74.13; H, 7.17. Found: C, 74.41; H, 7.13.

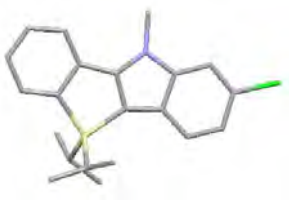
2-Fluoro-5,5-diisopropyl-6-methyl-5*H*-[1]benzosilolo[2,3-*b*][1]indole (6j)



Purification: N–H silica gel column chromatography (hexane/AcOEt 40:1) followed by reverse phase preparative HPLC (CH_3CN). Yield: 6%, a colorless oil. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.47 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.89 (s, 3H), 6.74 (ddd, *J* = 10.5, 7.4, 2.2 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.7, 1.1 Hz, 1H), 7.27 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.35–7.38 (m, 2H), 7.42 (dd, *J* = 10.5, 2.2 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.4, 18.7, 34.8, 108.0 (d, *J* = 11.0 Hz), 109.8, 110.0, 119.6, 120.0, 122.1, 124.0, 129.7 (d, *J* = 3.6 Hz), 131.5 (d, *J* = 3.1 Hz), 134.3 (d, *J* = 8.4 Hz), 142.8, 144.3, 149.0 (d, *J* = 9.2 Hz), 165.0 (d, *J* = 243.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –112.1. IR (neat): ν = 3050, 2942, 2864, 1595, 1576, 1485, 1454, 1394, 1356, 1269, 1134, 1085, 979, 881, 866, 814, 742, 680 cm^{-1}. MS (FAB) *m/z*: 337 (100, M^+), 294 (33), 266 (6), 252 (7). HRMS Calcd for $C_{21}H_{24}FNSi$: 337.1662. Found: 337.1654.

3-Chloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5k)

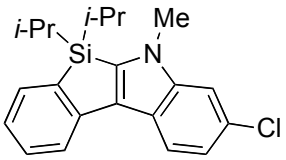




Purification: N–H silica gel column chromatography (hexane). Yield: 70%, a colorless solid. Mp: 144.6–145.2 °C. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.09 (s, 3H), 7.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.37 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.5, 108.6, 109.6, 120.2, 120.7, 122.7, 126.2, 127.2, 129.0, 129.3, 133.8, 141.8, 141.9, 142.7, 154.0. IR (KBr): ν = 2940, 2888, 1587, 1473, 1460, 1417, 1389, 1325, 1281, 1205, 1136, 1063, 987, 974, 880, 842, 797, 765, 682 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (37), 282 (11), 268 (9). Anal. Calcd for $C_{21}H_{24}ClNSi$: C, 71.26; H, 6.83. Found: C, 71.20; H, 6.83.

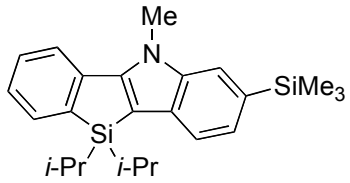
CCDC–722337 contains the crystallographic data for **5k**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-Chloro-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-*b*][1]indole (6k)



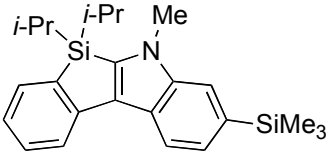
Purification: N–H silica gel column chromatography (hexane). Yield: 10%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.85 (s, 3H), 7.08 (dd, *J* = 7.4, 6.9 Hz, 1H), 7.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.45 (d, *J* = 6.9 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.4, 18.8, 34.9, 109.9, 120.1, 120.2, 120.5, 122.7, 124.1, 128.0, 130.0, 132.7, 133.4, 134.9, 142.8, 143.2, 146.0. IR (neat): ν = 2942, 2887, 1589, 1483, 1456, 1375, 1364, 1332, 1062, 947, 881, 850, 800, 742, 709, 675 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (14), 238 (8), 248 (2). HRMS Calcd for $C_{21}H_{24}ClNSi$: 353.1367. Found: 353.1379.

10,10-Diisopropyl-5-methyl-3-trimethylsilyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5l)



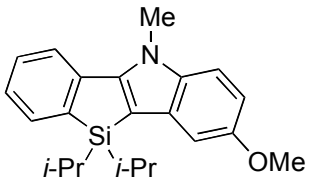
Purification: N–H silica gel column chromatography (hexane). Yield: 82%, a colorless oil. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H), 1.03 (d, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.39 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.15 (s, 3H), 7.20 (dd, *J* = 7.7, 6.9 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.51 (s, 1H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.4, 18.6, 18.8, 32.2, 108.3, 114.2, 120.2 (2C), 121.6, 124.7, 126.1, 129.1, 131.2, 132.0, 133.7, 142.1, 142.3, 153.6. IR (neat): ν = 3048, 2951, 2864, 1599, 1454, 1415, 1325, 1281, 1122, 1080, 881, 748, 731, 682 cm^{-1}. MS (FAB) *m/z*: 391 (100, M^+), 348 (44), 332 (6), 320 (11). Anal. Calcd for $C_{24}H_{33}NSi_2$: C, 73.59; H, 8.49. Found: C, 73.40; H, 8.49.

6,6-Diisopropyl-5-methyl-3-trimethylsilyl-6*H*-[1]benzosilolo[2,3-*b*][1]indole (6l)



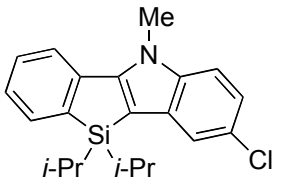
Purification: N–H silica gel column chromatography (hexane). Yield: 5%, a colorless oil. TLC: R_f 0.52 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.36 (s, 9H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.92 (s, 3H), 7.05 (dd, *J* = 7.3, 7.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.49 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.3, 18.5, 18.8, 34.8, 114.6, 119.4, 120.1, 123.7, 124.2, 124.6, 129.9, 132.6, 132.7, 133.3, 134.9, 142.6, 143.6, 146.6. IR (neat): ν = 3046, 2951, 2862, 1589, 1454, 1375, 1335, 1246, 1150, 1112, 866, 829, 748, 675 cm^{-1}. MS (FAB) *m/z*: 391 (100, M^+), 348 (7), 306 (4), 248 (6). HRMS Calcd for $C_{24}H_{33}NSi_2$: 391.2152. Found: 391.2158.

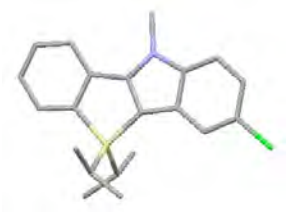
10,10-Diisopropyl-2-methoxy-5-methyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5m)



Purification: N–H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 88%, a colorless solid. Mp: 151.5–151.9 °C. TLC: R_f 0.37 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.88 (s, 3H), 4.09 (s, 3H), 6.87 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 7.4, 7.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.36 (dd, *J* = 8.8, 7.4 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.9, 32.4, 56.0, 104.6, 109.7, 109.9, 110.7, 120.0, 125.9, 129.1, 131.0, 133.7, 137.7, 142.0, 142.3, 153.7, 154.4. IR (KBr): ν = 2953, 2935, 2860, 1614, 1568, 1485, 1460, 1415, 1342, 1221, 1198, 1170, 1036, 984, 883, 870, 832, 769, 690, 661 cm^{-1}. MS (FAB) *m/z*: 349 (100, M^+), 306 (35), 264 (8), 248 (4). Anal. Calcd for $C_{22}H_{27}NOSi$: C, 75.59; H, 7.79. Found: C, 75.59; H, 7.58.

2-Chloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5n)

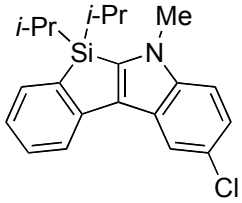




Purification: N–H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 63%, a colorless solid. Mp: 162.7–163.5 °C. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6 H), 1.12 (d, *J* = 7.6 Hz, 6H), 1.40 (qq, *J* = 7.6, 7.6 Hz, 2H), 4.10 (s, 3H), 7.15 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.20–7.26 (m, 2H), 7.38 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.8, 32.5, 108.0, 110.4, 120.3, 121.2, 121.5, 125.8, 126.4, 129.2, 131.5, 133.8, 140.7, 141.8, 142.0, 154.4. IR (KBr): ν = 2922, 2888, 2860, 2359, 1606, 1585, 1471, 1462, 1417, 1398, 1329, 1296, 1063, 989, 980, 880, 837, 790, 769, 713, 685, 655 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (45), 282 (13), 268 (11), 252 (5). Anal. Calcd for $C_{21}H_{24}ClNSi$: C, 71.26; H, 6.83. Found: C, 71.22; H, 6.75.

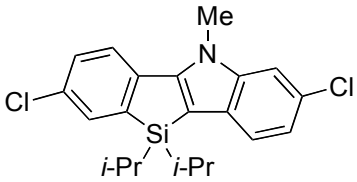
CCDC–722336 contains the crystallographic data for **5n**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-Chloro-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-*b*][1]indole (6n)



Purification: N–H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 22%, a colorless oil. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6 H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.87 (s, 3H), 7.08 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.39 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.4, 18.8, 35.0, 110.7, 119.2, 120.1, 122.0, 124.0, 124.9, 125.5, 130.0, 132.0, 133.4, 134.7, 141.2, 144.8, 145.9. IR (neat): ν = 3068, 2941, 2862, 2360, 2341, 1589, 1479, 1406, 1385, 1307, 1143, 1091, 991, 881, 835, 795, 768, 677 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (15), 268 (7), 234 (2). HRMS Calcd for $C_{21}H_{24}ClNSi$: 353.1367. Found: 353.1379.

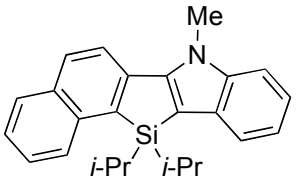
3,8-Dichloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (5o)



Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 84%, a colorless solid. Mp: 148.3–149.3 °C. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.13 (d, *J* = 7.6 Hz, 6H), 1.41 (qq, *J* = 7.6, 7.6 Hz, 2H), 4.05 (s, 3H), 7.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.32–7.35 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H) 7.66 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.5, 18.6,

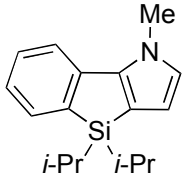
32.4, 108.7, 109.7, 121.0 (2c), 122.7, 127.6, 128.8, 129.1, 132.3, 133.5, 140.2, 142.7, 144.6, 152.9. IR (KBr): ν = 2953, 2940, 2862, 1553, 1460, 1419, 1391, 1327, 1263, 1099, 1060, 974, 882, 845, 808, 797, 680 cm^{-1}. MS (FAB) *m/z*: 387 (100, M^+), 344 (24), 302 (6), 266 (2). Anal. Calcd for $C_{21}H_{23}Cl_2NSi$: C, 64.94; H, 5.97. Found: C, 65.00; H, 6.08.

11,11-Diisopropyl-5-methyl-11*H*-indololo[3,2-*b*]naphtho[1,2-*d*][1]silole (5p)



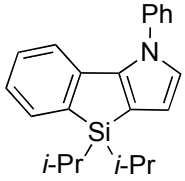
Purification: N–H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 91%, a yellow solid. Mp: 173.8–174.6 °C. TLC: R_f 0.35 (hexane/AcOEt). ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, *J* = 7.2 Hz, 6H), 1.28 (d, *J* = 7.2 Hz, 6H), 1.61 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.23 (s, 3H), 7.15 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.21–7.26 (m, 1H), 7.38–7.43 (m, 2H), 7.49 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 18.6,.19.3, 32.4, 107.1, 109.5, 119.2, 120.2, 121.2, 122.1, 125.1, 126.4, 128.6, 128.7, 129.9, 130.8, 131.9, 137.1, 141.1, 141.3, 142.4, 153.5. IR (KBr): ν = 2939, 2924, 2860, 2831, 1581, 1512, 1462, 1398, 1311, 1213, 1136, 1066, 1014, 974, 881, 814, 746, 699, 623 cm^{-1}. MS (FAB) *m/z*: 369 (100, M^+), 326 (21), 284 (9), 270 (3). Anal. Calcd for $C_{25}H_{27}NSi$: C, 81.25; H, 7.36. Found: C, 81.05; H, 7.29.

8,8-Diisopropyl-3-methyl-8*H*-[1]benzosilolo[3,2-*b*][1]pyrrole (5q)



Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 78%, a colorless solid. Mp: 57.1–58.0 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6 H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.28 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.94 (s, 3H), 6.19 (d, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 7.06 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.26–7.30 (m, 1H), 7.46–7.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.50, 18.54, 36.2, 110.9, 116.1, 117.9, 124.1, 127.7, 129.0, 133.7, 140.2, 142.7, 146.4. IR (KBr): ν = 2940, 2924, 2860, 1583, 1498, 1475, 1448, 1357, 1280, 1198, 1124, 999, 985, 880, 765, 688 cm^{-1}. MS (FAB) *m/z*: 269 (100, M^+), 226 (42), 198 (17), 184 (11), 154.8 (8). Anal. Calcd for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60. Found: C, 75.56; H, 8.42.

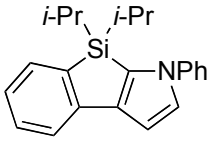
8,8-Diisopropyl-3-phenyl-8*H*-[1]benzosilolo[3,2-*b*][1]pyrrole (5r)



Purification: N–H silica gel column chromatography (hexane). Yield: 73%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.33 (qq, *J* = 7.2, 7.2 Hz, 2H), 6.35 (d, *J* = 2.7 Hz, 1H), 6.54–6.58 (m, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.96–7.00 (m, 2H), 7.44–7.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.57, 18.61, 112.2, 117.0, 118.5, 124.3, 126.7, 127.8, 128.1, 128.6, 129.0, 133.4, 140.1,

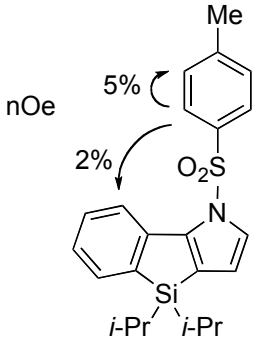
140.5, 142.1, 146.2. IR (neat): ν = 2939, 2889, 2862, 1597, 1587, 1503, 1464, 1423, 1354, 1188, 1070, 991, 881, 766, 687 cm^{-1}. MS (FAB) *m/z*: 331 (100, M^+), 288 (43), 260 (18), 246 (11). Anal. Calcd for $C_{22}H_{25}NSi$: C, 79.70; H, 7.60. Found: C, 79.49; H, 7.56.

4,4-Diisopropyl-3-phenyl-4*H*-[1]benzosilolo[2,3-*b*][1]pyrrole (6r)



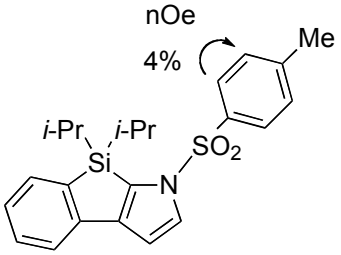
Purification: N–H silica gel column chromatography (hexane). Yield: 23%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.32 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.09–7.13 (m, 2H), 7.22–7.28 (m, 1H), 7.32 (ddd, *J* = 7.5, 7.4, 1.6 Hz, 1H), 7.40 (d, *J* = 1.6 Hz, 1H), 7.41–7.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.4, 18.5, 112.3, 116.9, 120.2, 120.5, 122.8, 124.9, 125.4, 129.36, 129.39, 133.6, 138.9, 139.8, 140.5, 144.7. IR (neat): ν = 2939, 2887, 1707, 1591, 1506, 1460, 1386, 1251, 1124, 1045, 881, 758, 733, 705, 690, 678 cm^{-1}. HRMS Calcd for $C_{22}H_{25}NSi$: 331.1756. Found: 331.1757.

8,8-Diisopropyl-3-tosyl-8*H*-[1]benzosilolo[3,2-*b*][1]pyrrole (5s)



Purification: N–H silica gel column chromatography (hexane). Yield: 31%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, **$CDCl_3$**): δ 0.94 (d, *J* = 7.2 Hz, 6H), 0.96 (d, *J* = 7.2 Hz, 6H), 1.14 (qq, *J* = 7.2, 7.2 Hz, 2H), 2.32 (s, 3H), 6.38 (d, *J* = 3.1 Hz, 1H), 7.07 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.26 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 3.1 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, **$CDCl_3$**): δ 10.6, 18.1, 18.2, 21.6, 114.6, 121.8, 125.0, 125.3, 126.3, 128.9, 129.5, 129.6, 133.1, 135.8, 138.8, 140.7, 144.5, 147.2. ^{1}H NMR (400 MHz, **C_6D_6**): δ 0.92 (d, *J* = 7.2 Hz, 6H), 0.94 (d, *J* = 7.2 Hz, 6H), 1.14 (qq, *J* = 7.2, 7.2 Hz, 2H), 1.60 (s, 3H), 6.20 (d, *J* = 3.1 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 2H), 6.92 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.21 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 3.1 Hz, 1H), 8.73 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, **C_6D_6**): δ 11.4, 18.7, 18.8, 21.5, 115.2, 123.0, 125.5, 126.4, 127.0, 127.9, 129.9, 130.0, 130.4, 133.9, 139.5, 141.9, 144.6, 148.3. IR (neat): ν = 2941, 2890, 1587, 1460, 1361, 1180, 1167, 1117, 1072, 767, 690, 667, 642 cm^{-1}. MS (FAB) *m/z*: 409 (100, M^+), 366 (14), 256 (4), 212 (8). Anal. Calcd for $C_{23}H_{27}NO_2SSi$: C, 67.44; H, 6.64. Found: C, 67.50; H, 6.58.

4,4-Diisopropyl-3-tosyl-4*H*-[1]benzosilolo[2,3-*b*][1]pyrrole (6s)

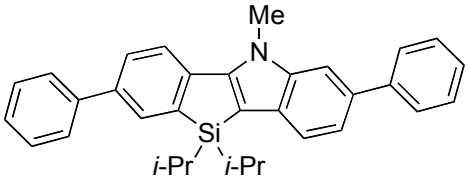


Purification: N–H silica gel column chromatography (hexane). Yield: 42%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, **CDCl$_3$**): δ 0.81 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.52 (qq, *J* = 7.2, 7.2 Hz, 2H), 2.40 (s, 3H), 6.62 (d, *J* = 3.0 Hz, 1H), 7.12 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 7.6, 7.0 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 3.0 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, **CDCl$_3$**): δ 11.5, 18.0, 18.1, 21.7, 108.4, 120.1, 125.6, 126.7, 128.1, 129.5, 129.7, 133.3, 133.8, 136.2, 136.3, 143.5, 144.7, 146.9. ^{1}H NMR (400 MHz, **C$_6$D$_6$**): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.17 (d, *J* = 7.2 Hz, 6H), 1.63 (qq, *J* = 7.2, 7.2 Hz, 2H), 1.78 (s, 3H), 6.42 (d, *J* = 3.0 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.19 (dd, *J* = 7.6, 7.0 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 3.0 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, **C$_6$D$_6$**): δ 12.5, 18.6, 18.9, 21.7, 109.2, 121.2, 126.6, 127.3, 129.1, 130.2, 130.4, 134.2, 134.6, 137.2, 137.7, 144.6, 144.8, 148.1. IR (neat): ν = 2943, 2864, 1595, 1462, 1368, 1173, 1140, 1092, 812, 717, 675, 636 cm^{-1}. MS (FAB) *m/z*: 409 (100, M^+), 366 (16), 324 (3), 212 (5). Anal. Calcd for $C_{23}H_{27}NO_2SSi$: C, 67.44; H, 6.64. Found: C, 67.47; H, 6.61.

Palladium-catalyzed two-fold cross-coupling reaction of 5o with PhB(OH)$_2$

An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with **5o** (39 mg, 0.10 mmol), $PhB(OH)_2$ (43 mg, 0.35 mmol), $Pd(OAc)_2$ (3.4 mg, 15 μmol), 1-dicyclohexylphosphino-2-(1,6-dimethoxyphenyl)benzene (SPhos, 12 mg, 30 μmol), K_3PO_4 (0.11 g, 0.50 mmol), and THF (1 mL). The mixture was heated at 60 °C on a hot plate for 16 h. The resulting mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on N‒H silica gel to give **12** (39 mg, 83%).

10,10-Diisopropyl-5-methyl-3,8-diphenyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (12)



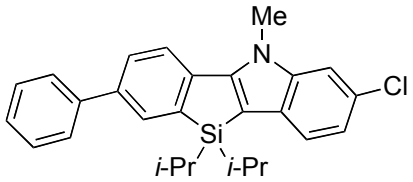
Purification: N–H silica gel column chromatography (hexane). Yield: 83%, a colorless solid. Mp: 143.6–144.8 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.46 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.20 (s, 3H), 7.32–7.45 (m, 3H), 7.45–7.49 (m, 4H), 7.56 (d, *J* = 1.1 Hz, 1H), 7.61 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.64–7.67 (m, 3H), 7.71–7.80 (m, 2H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.7, 18.9, 32.3, 108.1, 108.7, 120.1, 120.3, 122.2, 126.4, 126.8, 127.1, 127.3, 128.0, 128.6, 128.7, 129.9, 132.4, 135.1, 138.6, 140.9, 141.3, 142.4, 142.9, 150.9, 153.7. IR (KBr): ν = 2934, 2858, 1595, 1468, 1396, 1352, 1261, 1203, 1097, 1074, 1030, 879, 810, 760, 694,

682, 640 cm^{-1}. MS (FAB) *m/z*: 471 (100, M^+), 428 (21), 386 (7), 370 (4). Anal. Calcd for $C_{27}H_{28}ClNSi$: C, 84.03; H, 7.05. Found: C, 83.79; H, 7.05.

Palladium-catalyzed site-selective cross-coupling reaction of 5o with $PhB(OH)_2$

An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with **5o** (39 mg, 0.10 mmol), $PhB(OH)_2$ (8.2 mg, 0.070 mmol), $Pd(OAc)_2$ (0.5 mg, 2 μmol), 1-dicyclohexylphosphino-2-(1,6-dimethoxyphenyl)benzene (SPhos, 1.6 mg, 4 μmol), K_3PO_4 (43 mg, 0.20 mmol), and THF (0.5 mL). The mixture was heated at 50 °C on a hot plate for 20 h. The resulting mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on N–H silica gel to give **13** (20 mg, 70%).

3-Chloro-10,10-diisopropyl-5-methyl-8-phenyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (13)



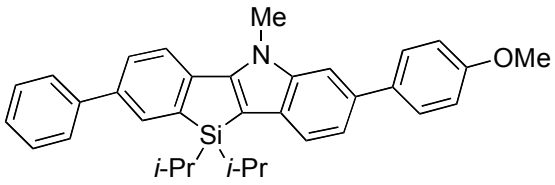
Purification: N–H silica gel column chromatography (hexane). Yield: 70%, a colorless solid. Mp: 157.4–158.2 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.3 Hz, 6 H), 1.15 (d, *J* = 7.2 Hz, 6H), 1.43 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.11 (s, 3H), 7.10 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.35–7.39 (m, 2H), 7.45–7.49 (m, 3H), 7.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.63–7.65 (m, 2H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.8, 32.4, 108.9, 109.6, 120.3, 120.8, 122.7, 126.8, 127.1, 127.3, 128.1, 128.7, 129.0, 132.4, 138.8, 140.8, 141.0, 142.7, 142.8, 153.7. IR (KBr): ν = 2942, 2888, 2860, 1597, 1460, 1442, 1397, 1323, 1296, 1153, 1074, 974, 882, 829, 802, 766, 694 cm^{-1}. MS (FAB) *m/z*: 429 (100, M^+), 386 (27), 344 (8), 252 (2). Anal. Calcd for $C_{27}H_{28}ClNSi$: C, 75.41; H, 6.56. Found: C, 75.54; H, 6.60.

CCDC–722338 contains the crystallographic data for **13**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

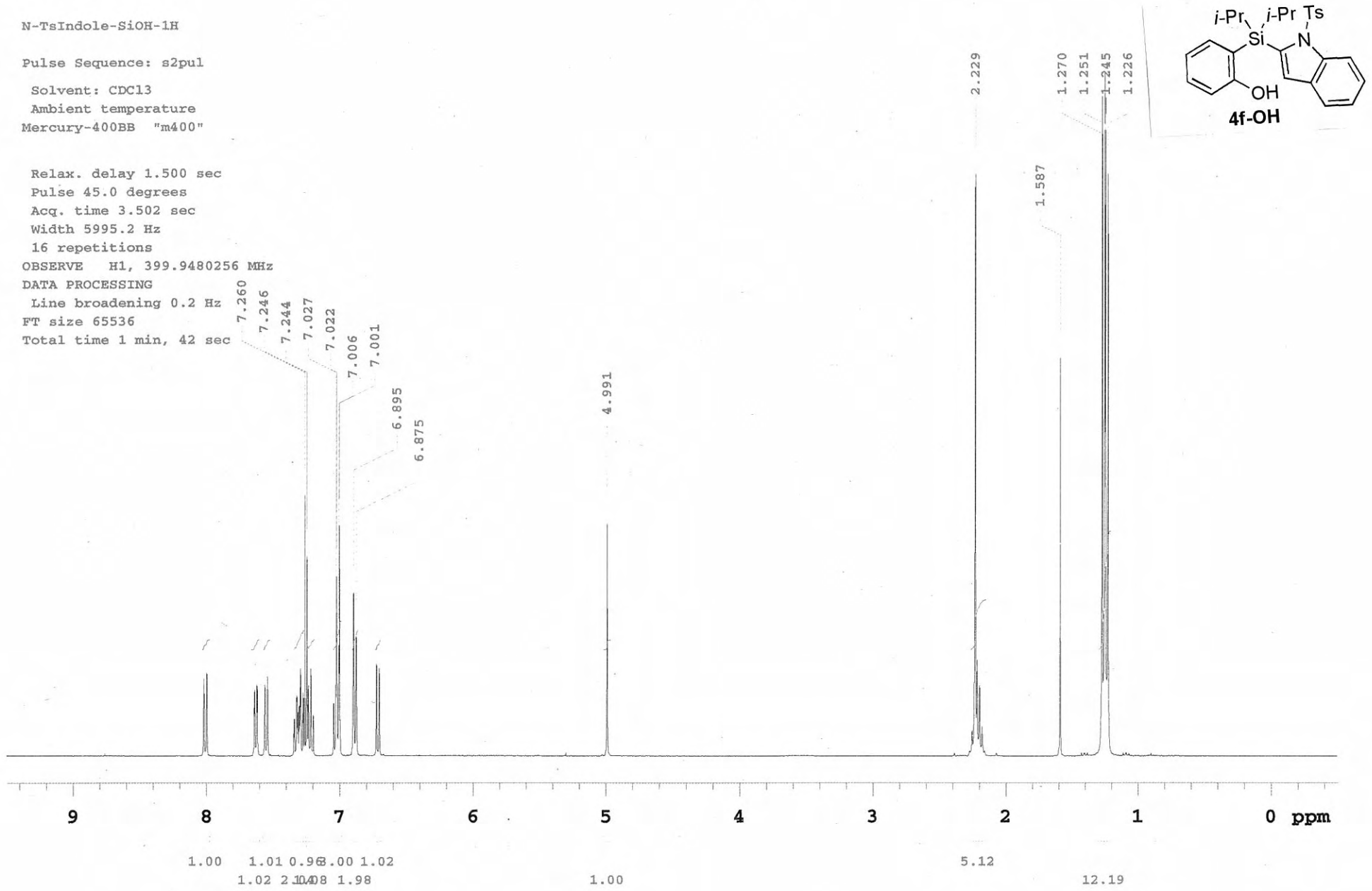
Palladium-catalyzed cross-coupling reaction of 14 with 4-$MeOC_6H_4B(OH)_2$

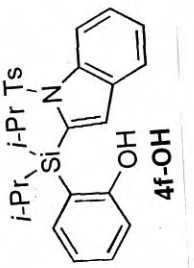
An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with **13** (50 mg, 0.10 mmol), 4–$MeOC_6H_4B(OH)_2$ (50 mg, 0.30 mmol), $Pd(OAc)_2$ (2.5 mg, 10 μmol), 1-dicyclohexyl-phosphino-2-(1,6-dimethoxyphenyl)benzene (SPhos, 9.0 mg, 20 μmol), K_3PO_4 (70 mg, 0.30 mmol), and THF (1.0 mL). The mixture was heated at 50 °C on a hot plate for 20 h. The resulting mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on N–H silica gel to give **14** (50 mg, 91%).

10,10-Diisopropyl-3-(4-methoxyphenyl)-5-methyl-8-phenyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (14)



Purification: N–H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 91%, a colorless solid. Mp: 170.6–171.6 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.19 (d, *J* = 7.2 Hz, 6H), 1.46 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.88 (s, 3H), 4.19 (s, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.35–7.39 (m, 2H), 7.45–7.52 (m, 3H), 7.60–7.67 (m, 6H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.7, 18.9, 32.3, 55.4, 107.7, 108.7, 114.1, 119.9, 120.2, 122.2, 126.8, 127.1, 128.0, 128.2, 128.7, 129.5, 132.4, 134.8, 135.0, 138.5, 140.9, 141.3, 142.9, 143.0, 153.5, 158.5. IR (KBr): ν = 2939, 2922, 2860, 1608, 1518, 1470, 1460, 1394, 1279, 1242, 1180, 1043, 814, 766, 690 cm^{-1}. MS (FAB) *m/z*: 501 (100, M^+), 458 (17), 416 (4). HRMS Calcd for $C_{34}H_{35}NOSi$: 501.2448. Found: 501.2485. Anal Calcd for $C_{34}H_{35}NOSi$: C, 81.39; H, 7.03. Found: C, 81.30; H, 6.94.


N-TsIndole-SiOH-1H
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, 399.9480256 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec
7.260
7.246
7.244
7.027
7.022
7.006
7.001
6.895
6.875
4.991
2.229
1.587
1.270
1.251
1.245
1.226
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
0.96
3.00
1.02
1.02
1.00
1.98
5.12
12.19
i-Pr
i-Pr
Ts
Si
N
OH
4f-OH



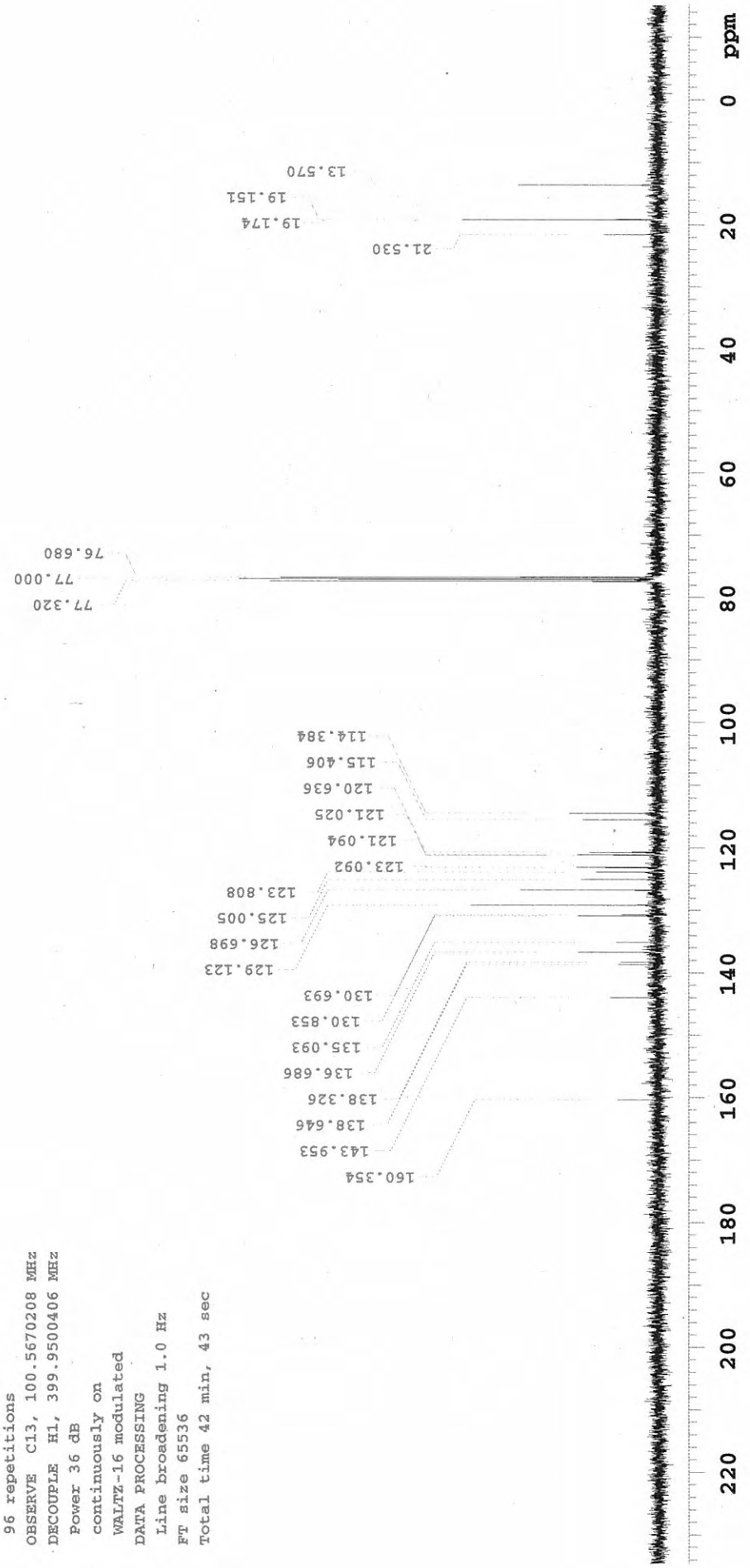
4f-OH

13C OBSERVE

Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
96 repetitions
OBSERVE C13, 100.5670208 MHz
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 42 min, 43 sec

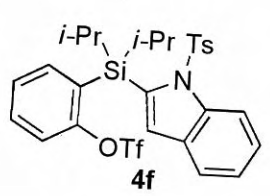


STANDARD 1H OBSERVE

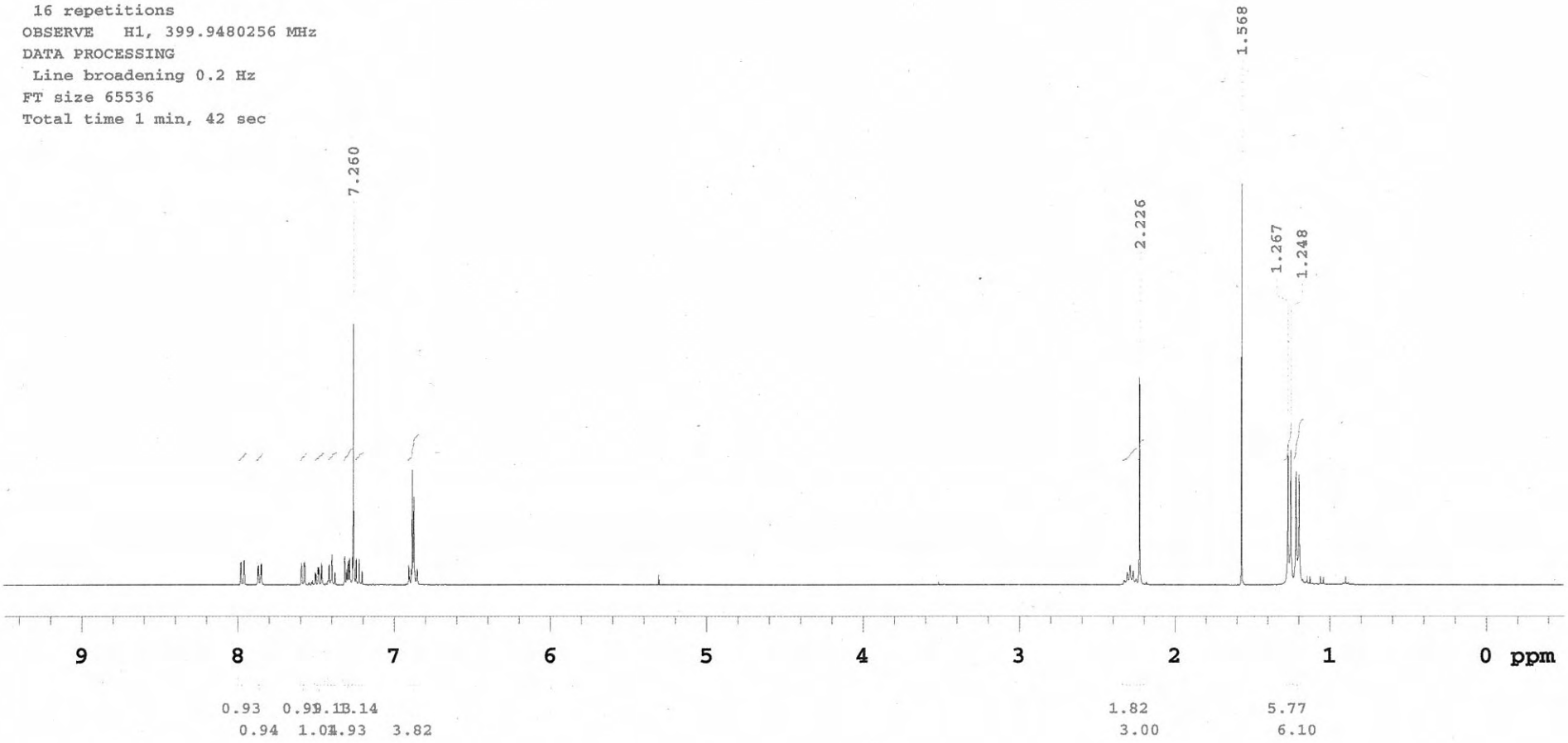
Pulse Sequence: s2pul

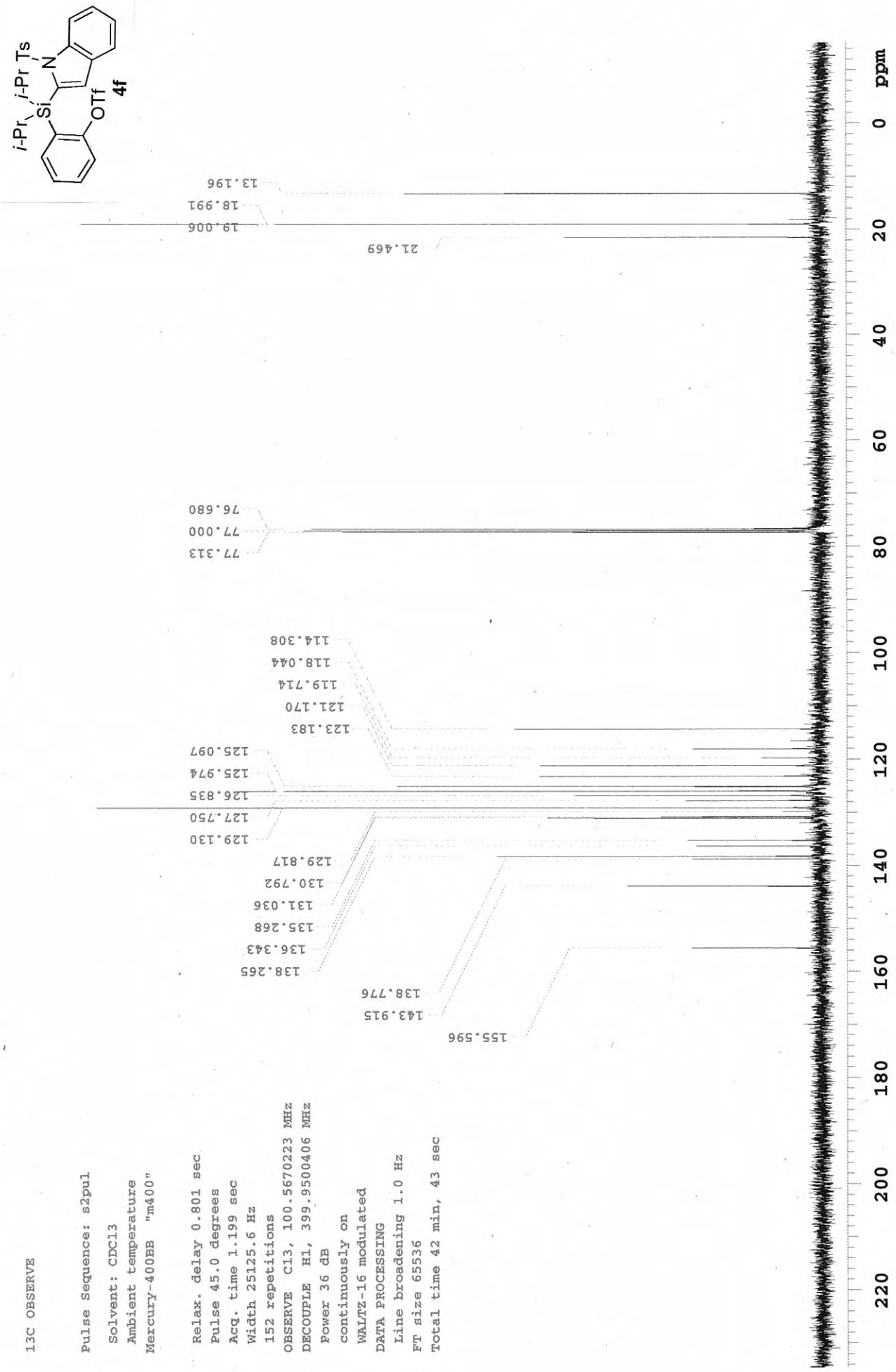
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480256 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



4f



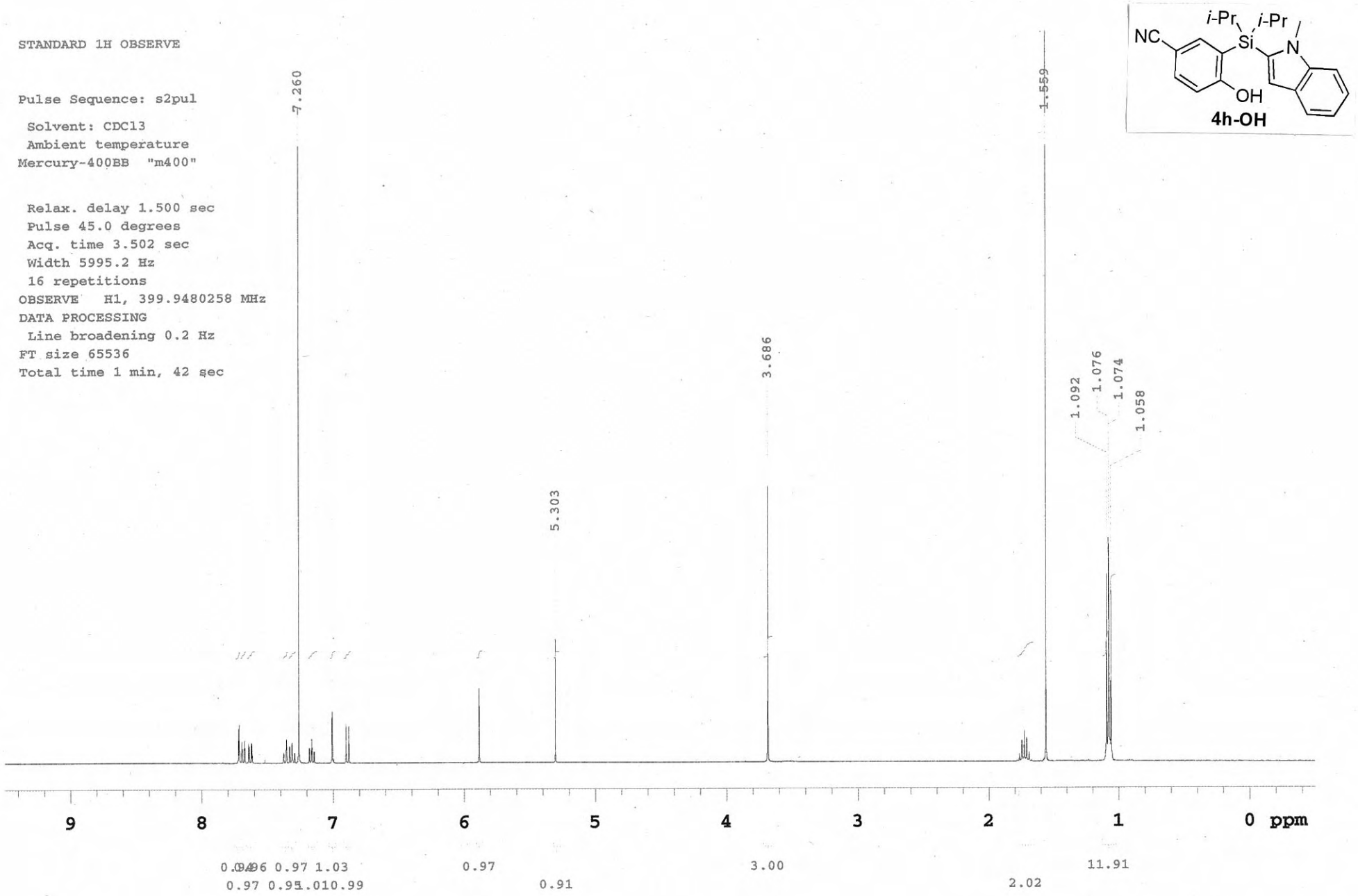


13C OBSERVE

Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
152 repetitions
OBSERVE C13, 100.5670223 MHz
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 42 min, 43 sec

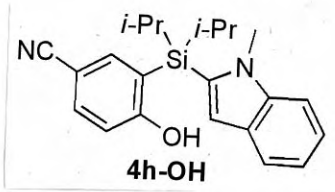

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec
7.260
5.303
3.686
1.559
1.092
1.076
1.074
1.058
9
8
7
6
5
4
3
2
1
0 ppm
0.94 0.97 1.03
0.97 0.95 1.01 0.99
0.97
0.91
3.00
2.02
11.91
i-Pr
i-Pr
Si
N
NC
OH
4h-OH

13C OBSERVE

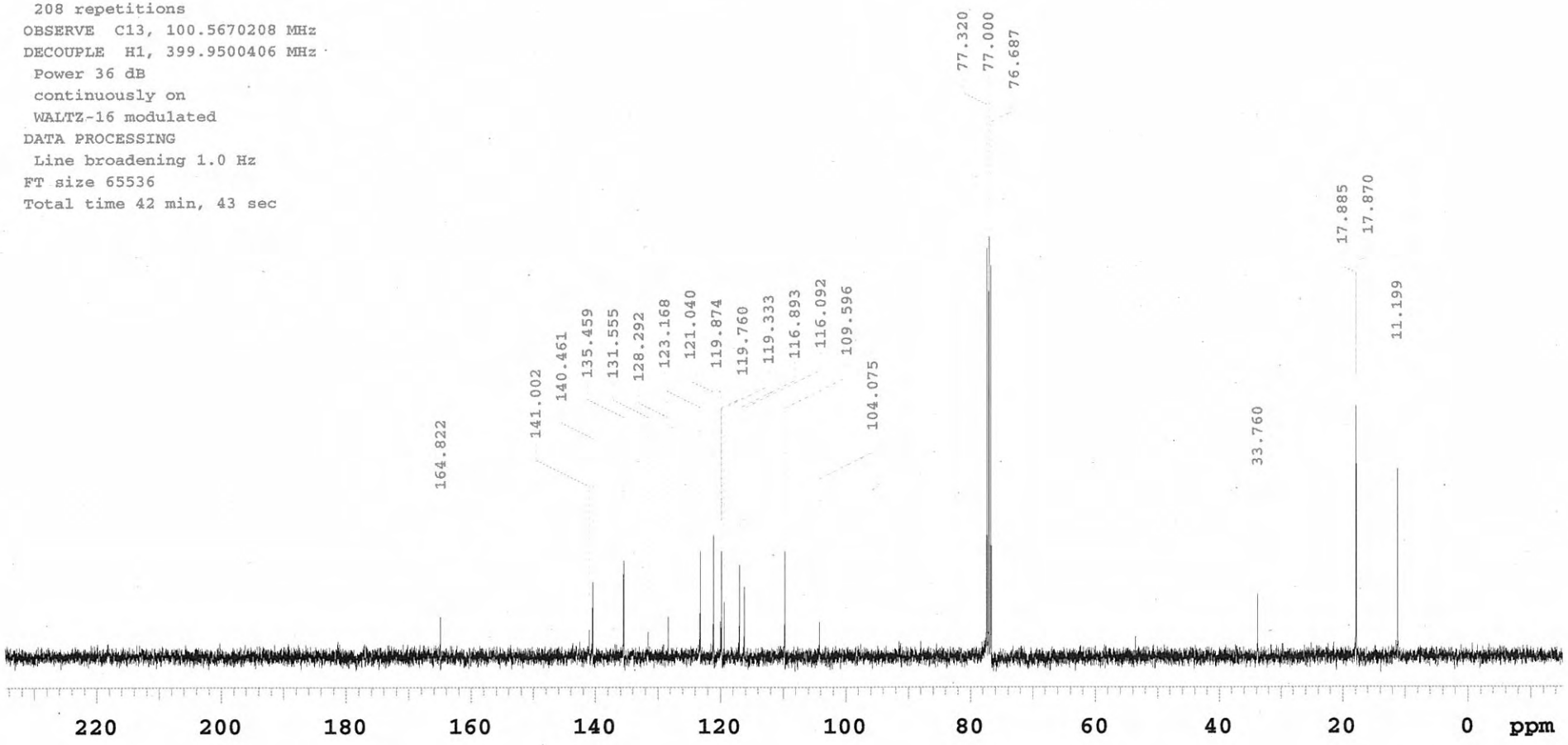
Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
208 repetitions
OBSERVE C13, 100.5670208 MHz
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 42 min, 43 sec



4h-OH



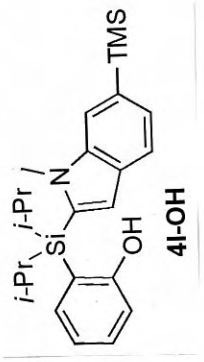
TMSIndole-SiPhOH-1H

Pulse Sequence: s2pul

Solvent: CDC13
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, 399.9480256 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec

4l-OH

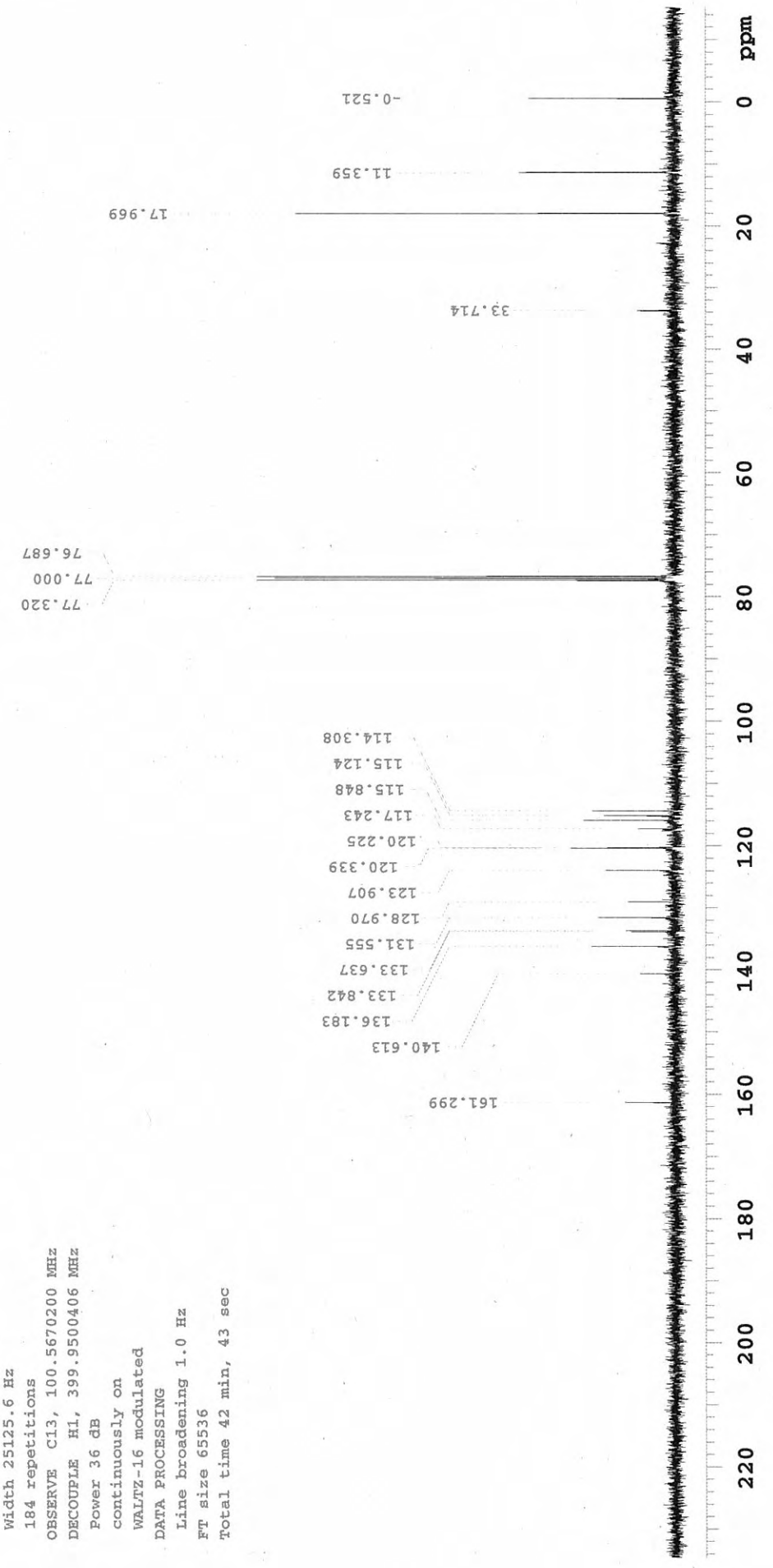


4l-OH

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
184 repetitions
OBSERVE C13, 100.5670200 MHz
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 42 min, 43 sec

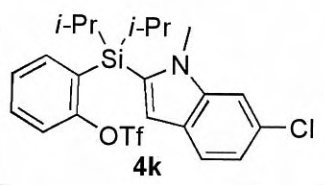


STANDARD 1H OBSERVE

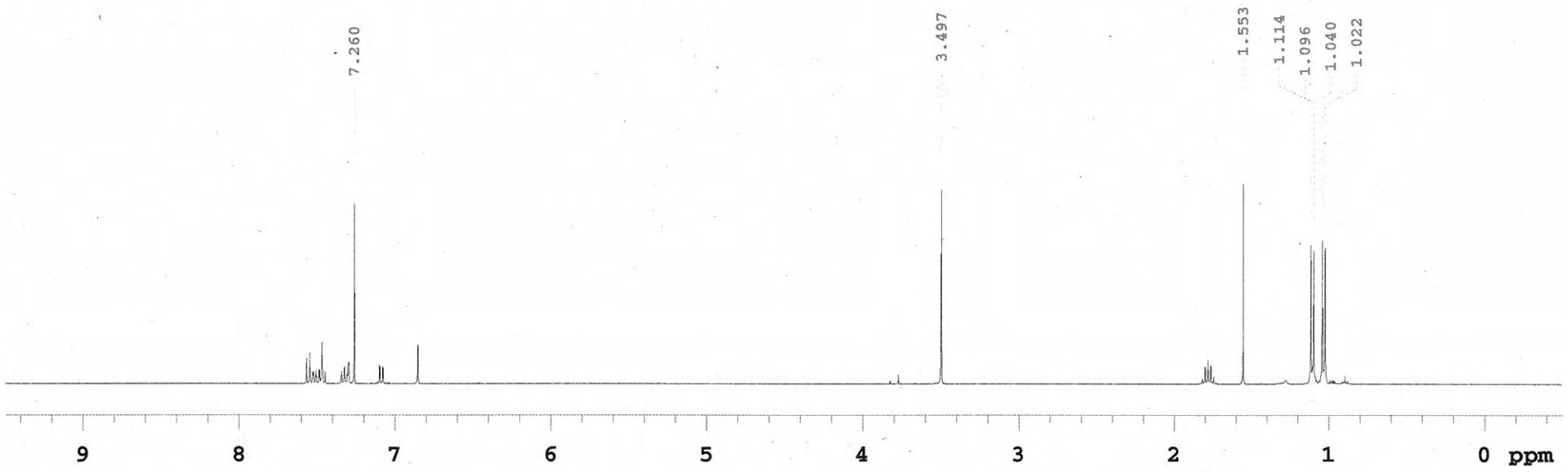
Pulse Sequence: s2pul

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, 399.9480260 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



4k

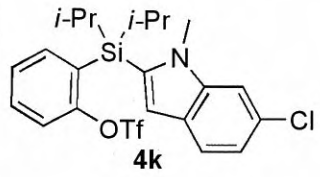


13C OBSERVE

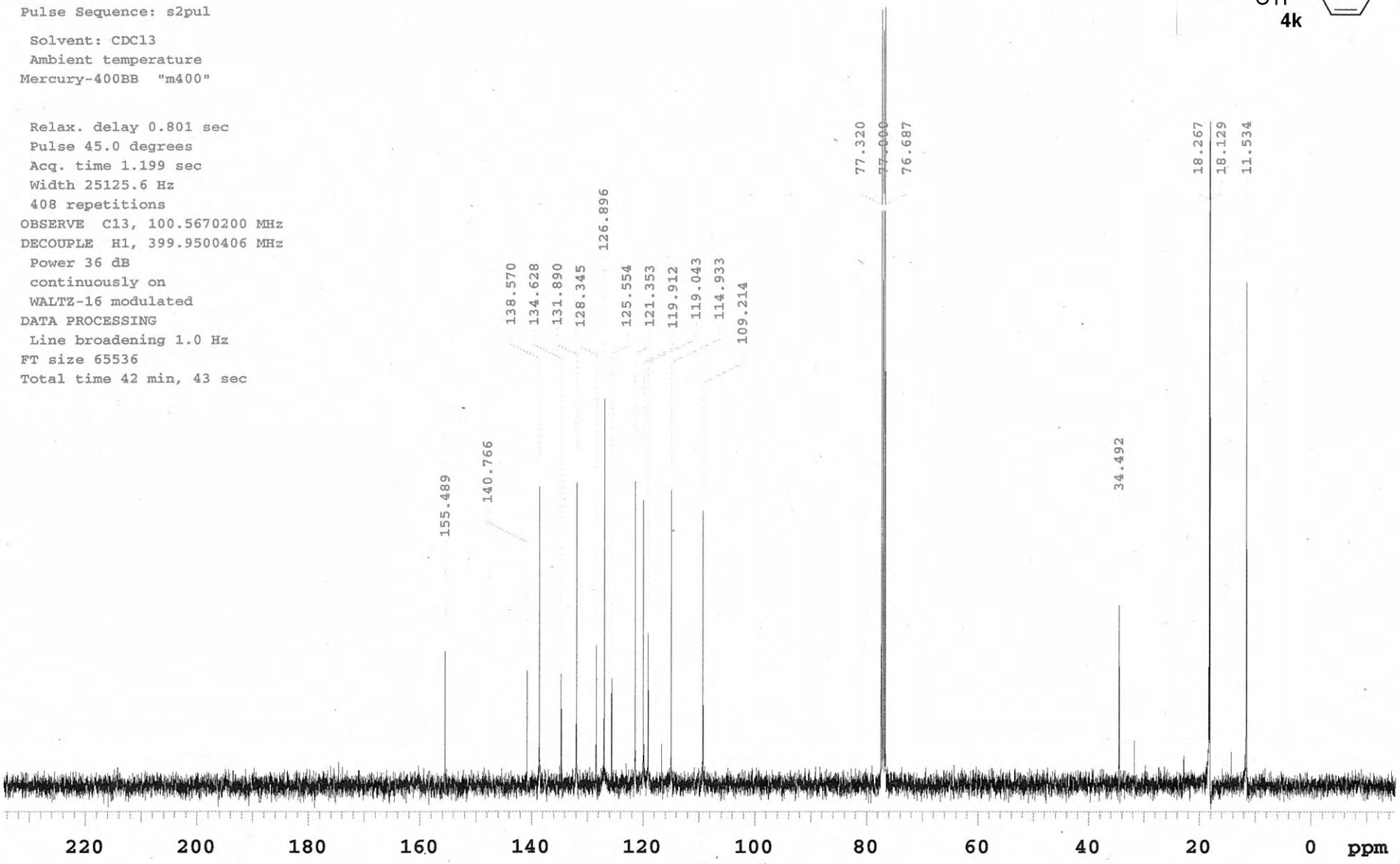
Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
408 repetitions
OBSERVE C13, 100.5670200 MHz
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 42 min, 43 sec



4k

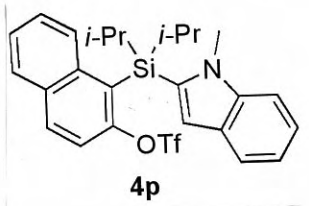


Ind-Si-Np-OTf-1H

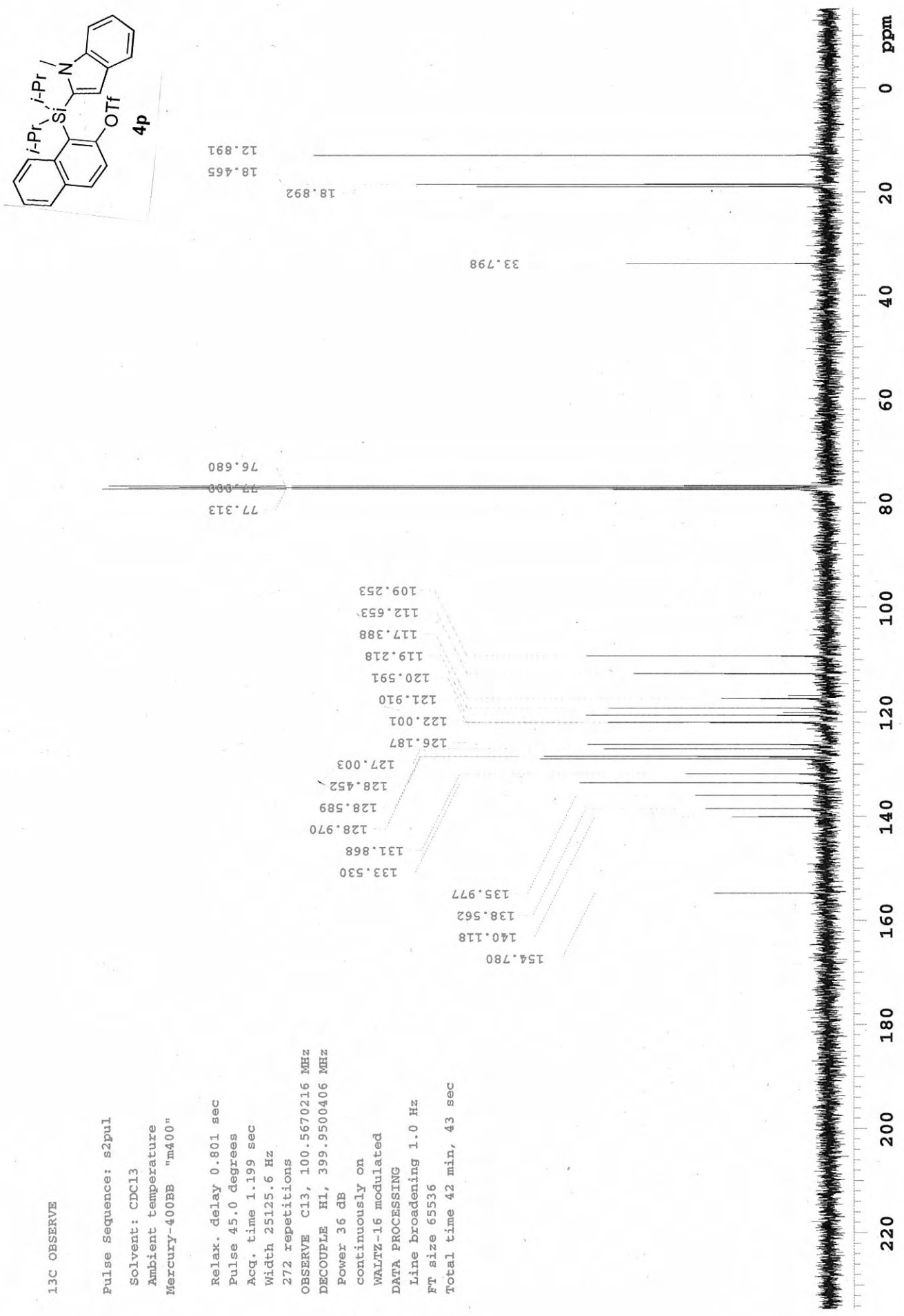
Pulse Sequence: s2pul

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, 399.9480256 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



4p

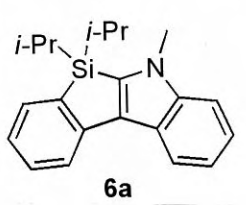

4p
i-Pr
i-Pr
Si
N
OTf
ppm
0
20
40
60
80
100
120
140
160
180
200
220
12.891
18.465
18.892
33.798
76.680
77.000
77.313
109.253
112.653
117.388
119.218
120.591
121.910
122.001
126.187
127.003
128.452
128.589
128.970
131.868
133.530
135.977
138.562
140.118
154.780
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"
Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
272 repetitions
OBSERVE C13, 100.5670216 MHz
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 42 min, 43 sec

9106-75-008-146-column-fr.1

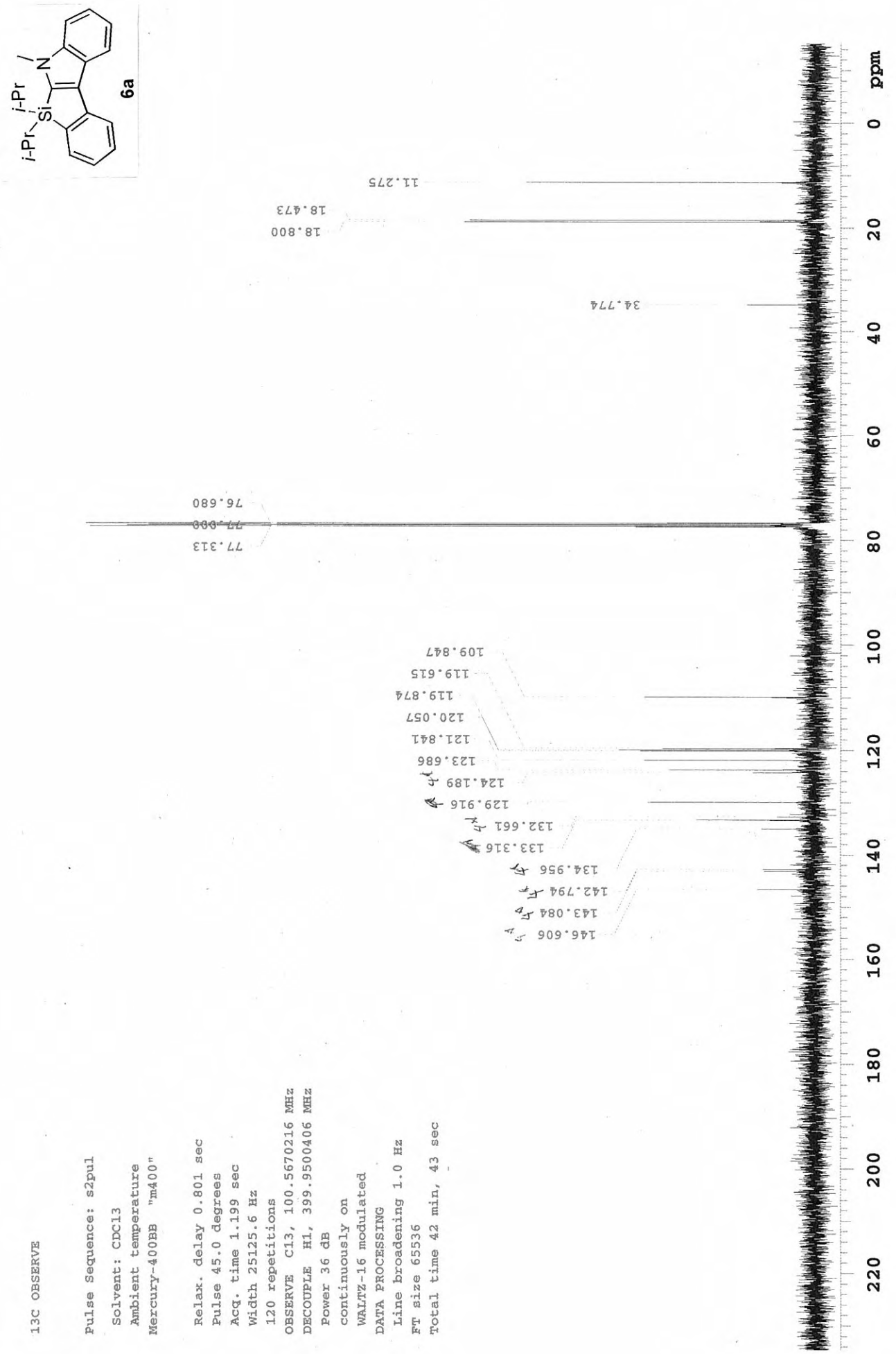
Pulse Sequence: s2pul

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, 399.9480256 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



6a

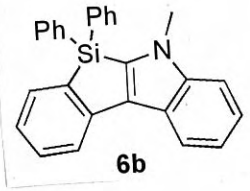

6a
i-Pr
i-Pr
Si
N
11.275
18.473
18.800
34.774
76.680
77.000
77.313
109.847
119.615
119.874
120.057
121.841
123.686
124.189
129.916
132.661
133.316
134.956
142.794
143.084
146.606
ppm
0
20
40
60
80
100
120
140
160
180
200
220
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"
Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
120 repetitions
OBSERVE C13, 100.5670216 MHz
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 42 min, 43 sec

Ind-SiPh2-Stilbene-minor-1H

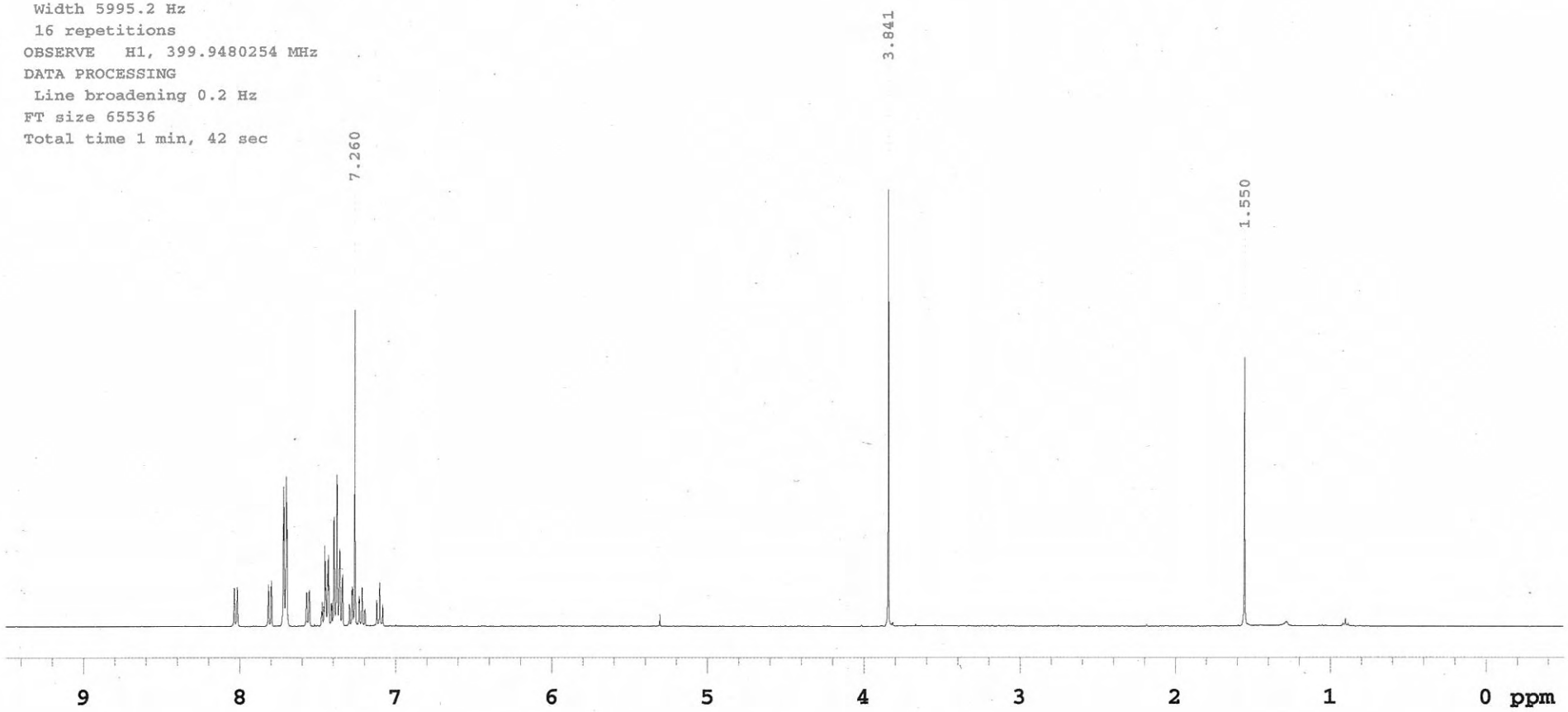
Pulse Sequence: s2pul

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, 399.9480254 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec

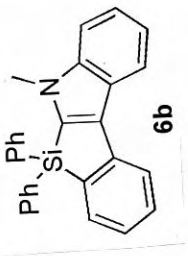


6b



0.99 3.862.93.83.04
0.970.94.91.07

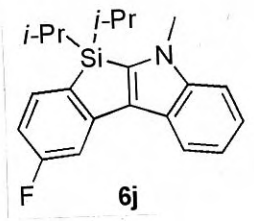
3.00



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
6272 repetitions
OBSERVE C13, 100.5670193 MHz
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 5 hr, 43 min, 27 sec

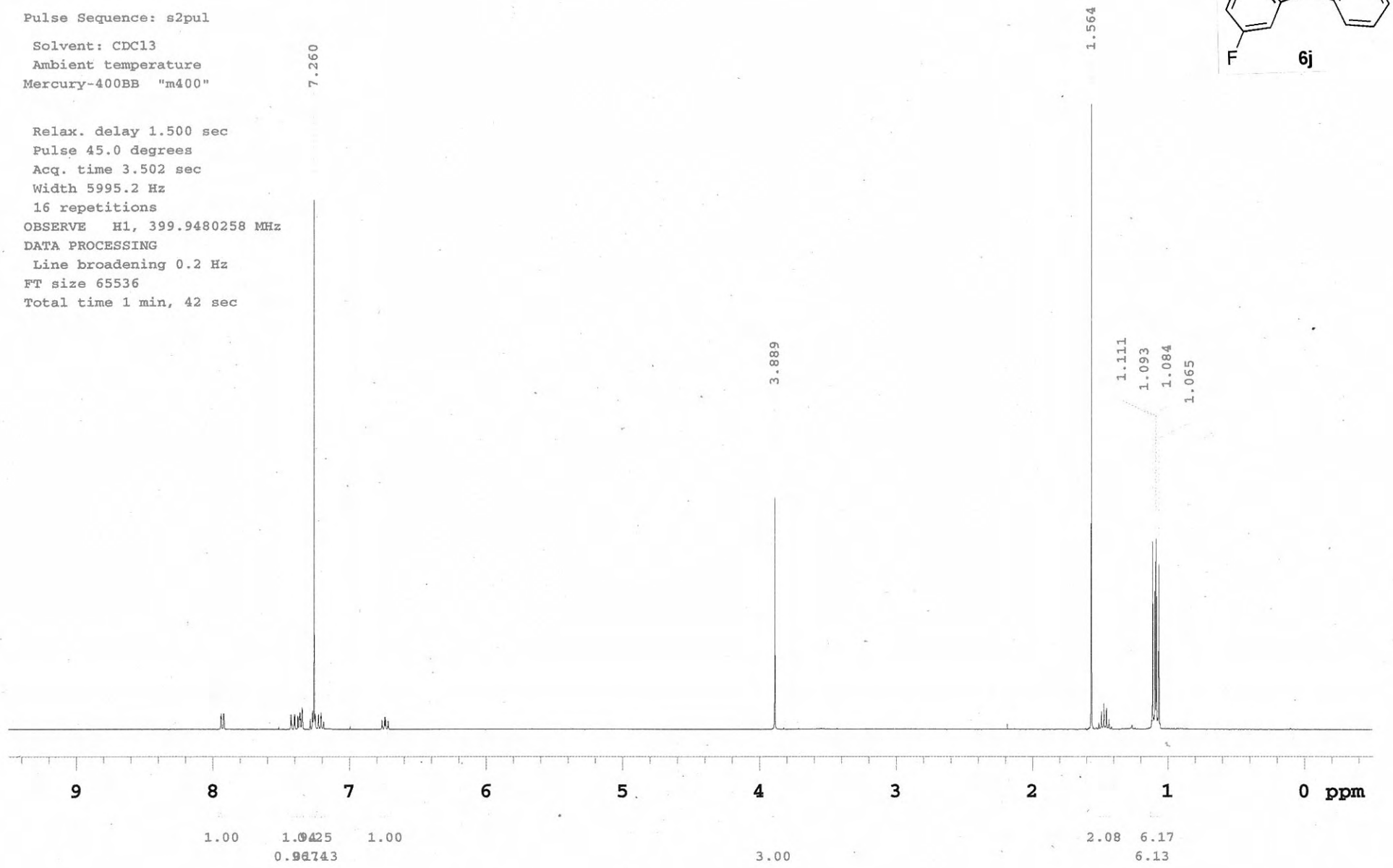


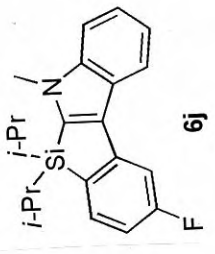
Ind-Si-mF-Stilbene-minor-1H

Pulse Sequence: s2pul

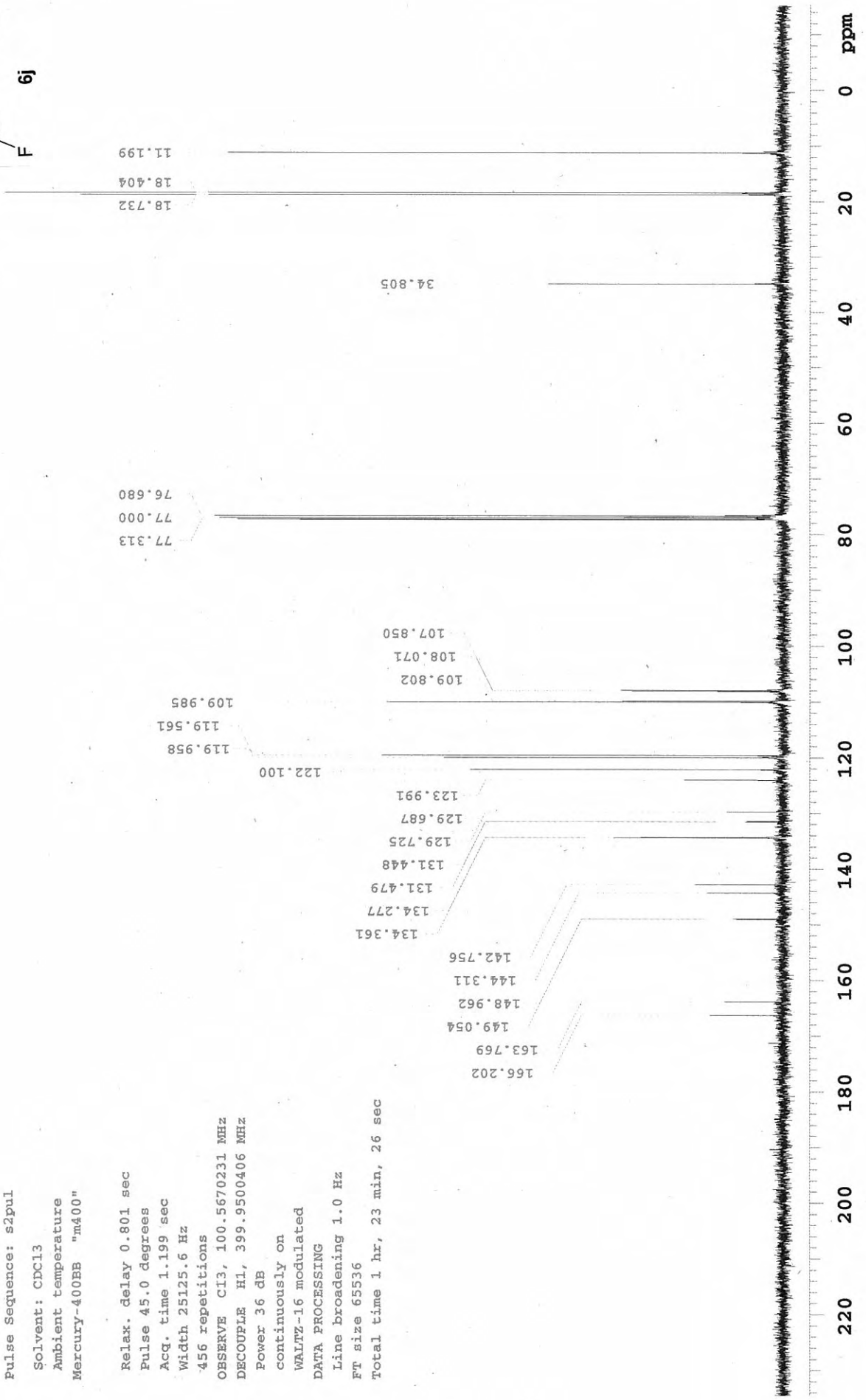
Solvent: CDC13
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec





6j



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

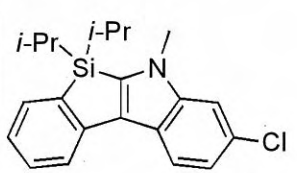
Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
456 repetitions
OBSERVE C13, 100.5670231 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 23 min, 26 sec

6-Cl-Ind-Stilbene-minor-1H

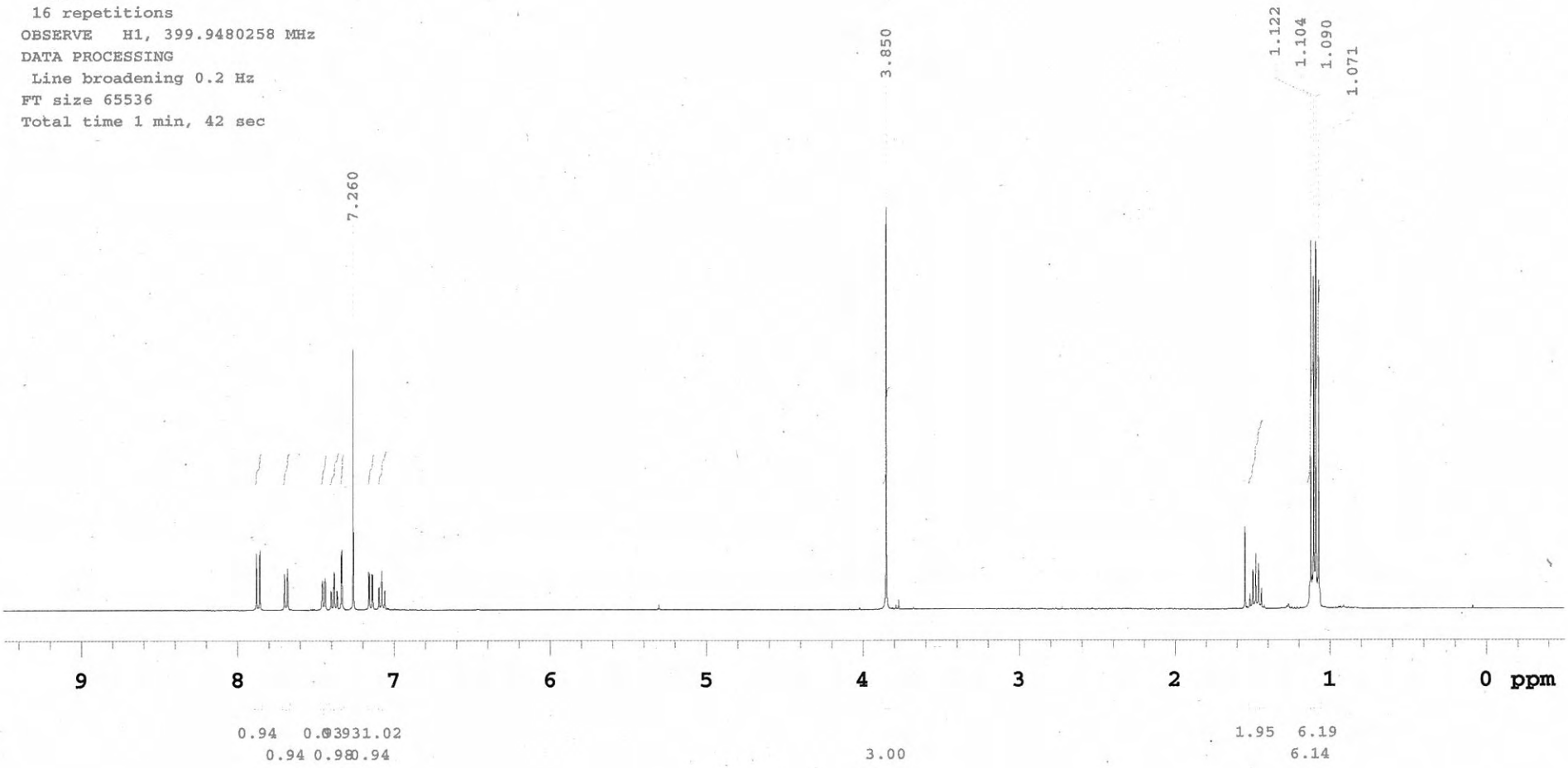
Pulse Sequence: s2pul

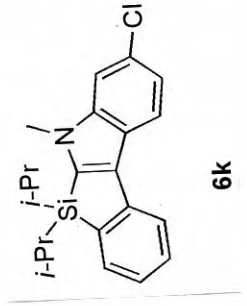
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec

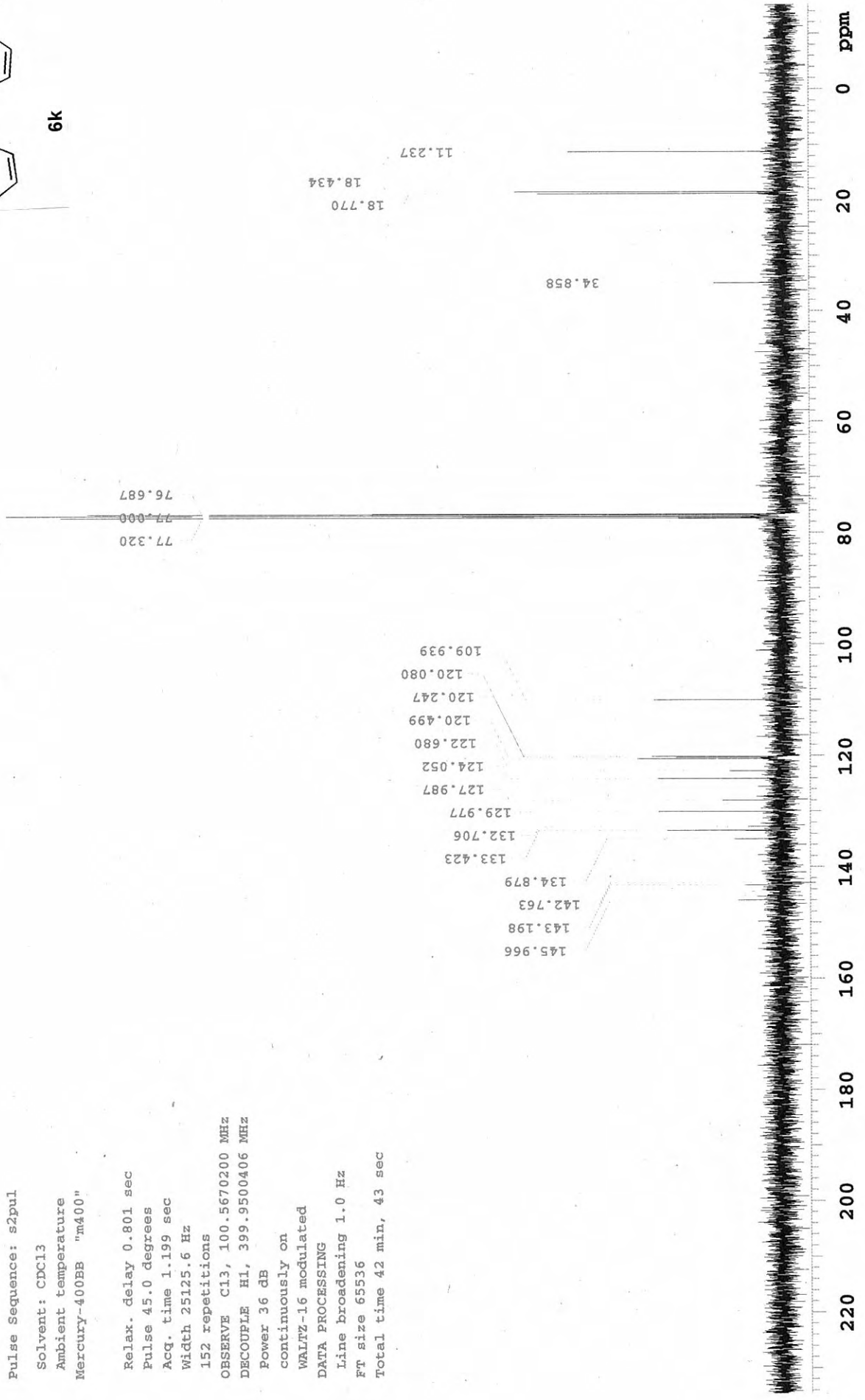


6k





6k

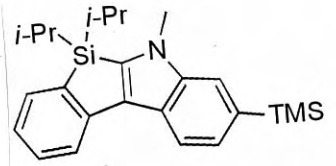


13C OBSERVE

Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
152 repetitions
OBSERVE C13, 100.5670200 MHz
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 42 min, 43 sec



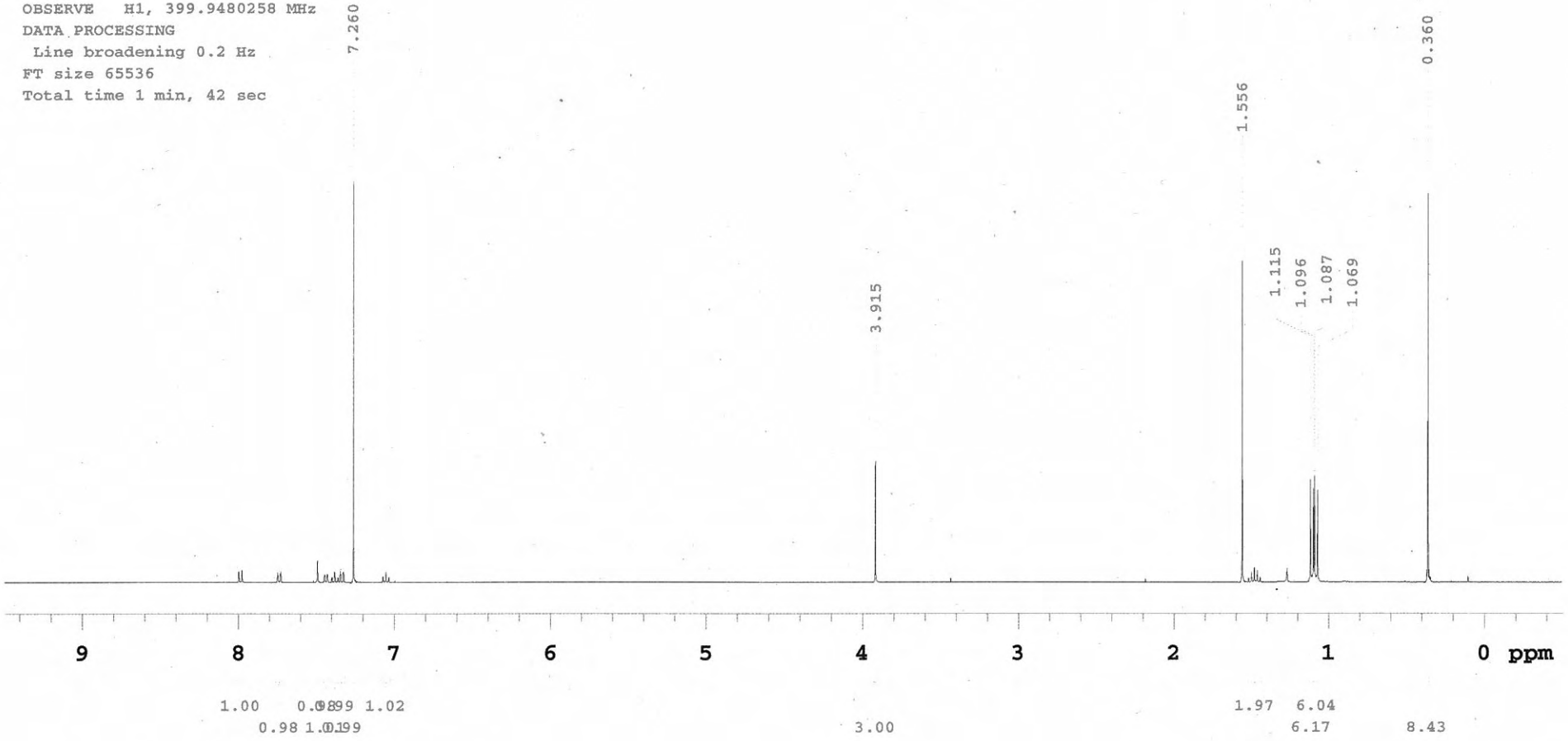
6l

6-TMSInd-Si-Stilbene-minor-1H

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, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec

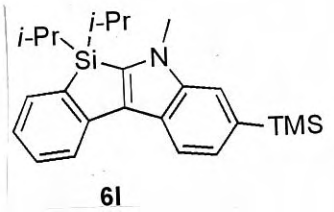


13C OBSERVE

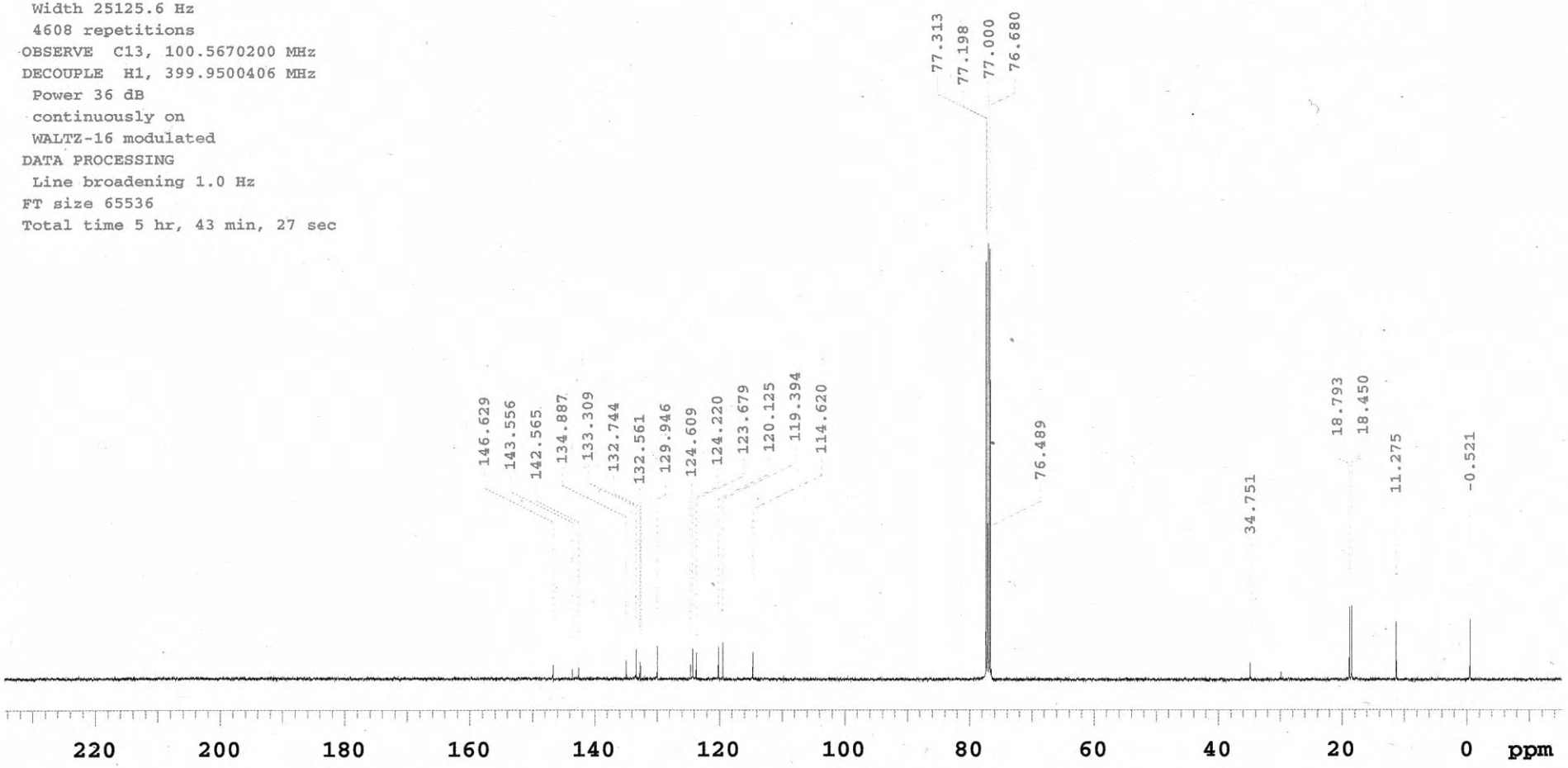
Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
4608 repetitions
OBSERVE C13, 100.5670200 MHz
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 5 hr, 43 min, 27 sec



6l

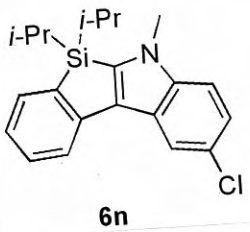


8Z18-75-008-135-column-fr.1

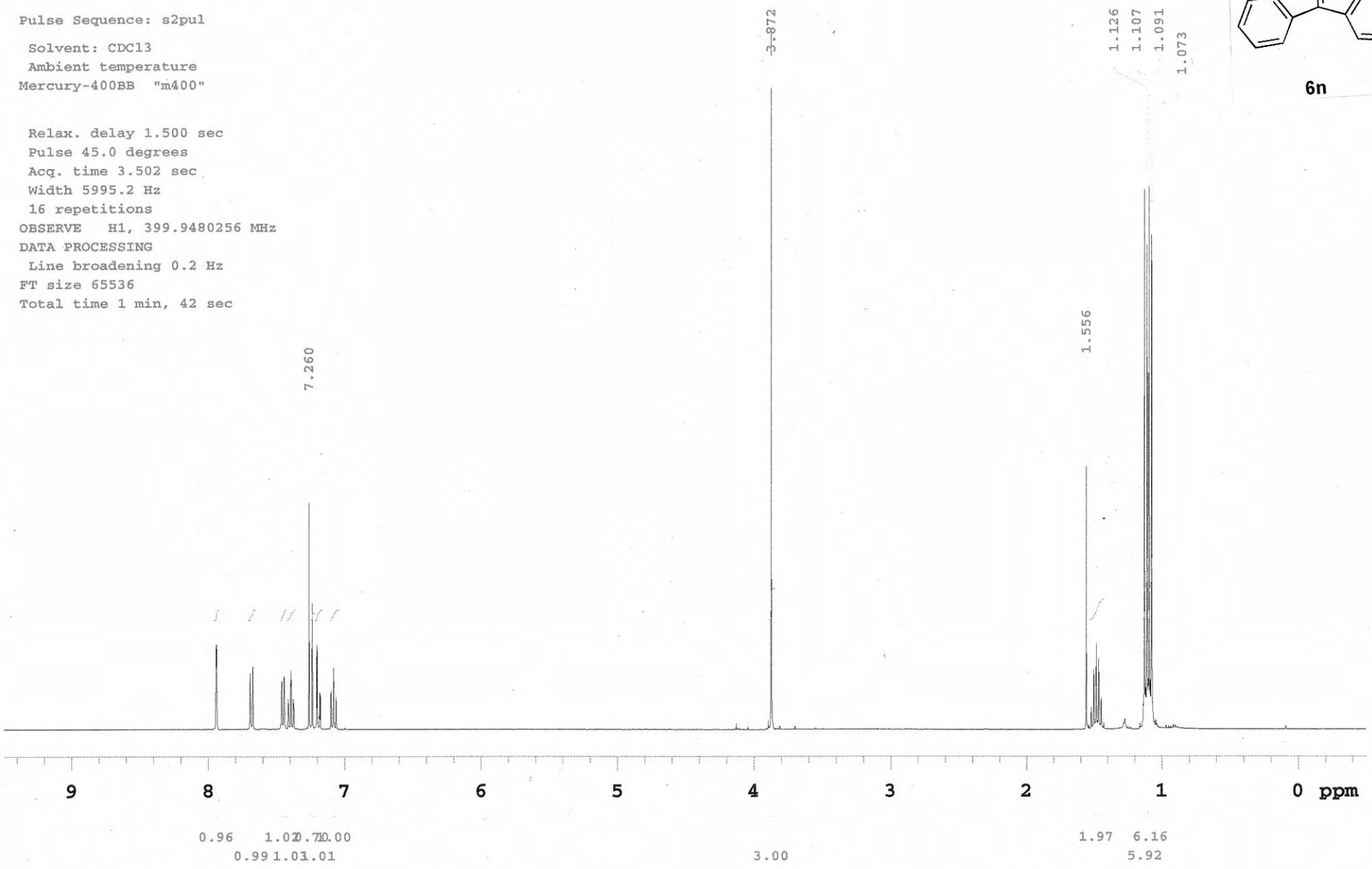
Pulse Sequence: s2pul

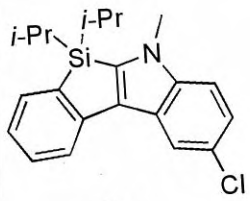
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480256 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



6n





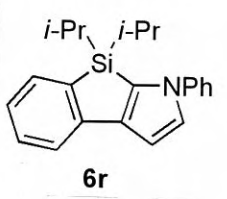
6n

13C OBSERVE

Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
376 repetitions
OBSERVE C13, 100.5670200 MHz
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 42 min, 43 sec



6r

N-PhPyrrole-minor-1H

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, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec

7.260

1.553
1.100
1.081
1.057
1.038

9 8 7 6 5 4 3 2 1 0 ppm

2.D90L.94
4.5116.00

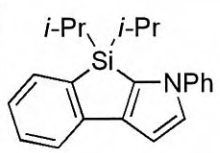
2.336.06
6.31

13C OBSERVE

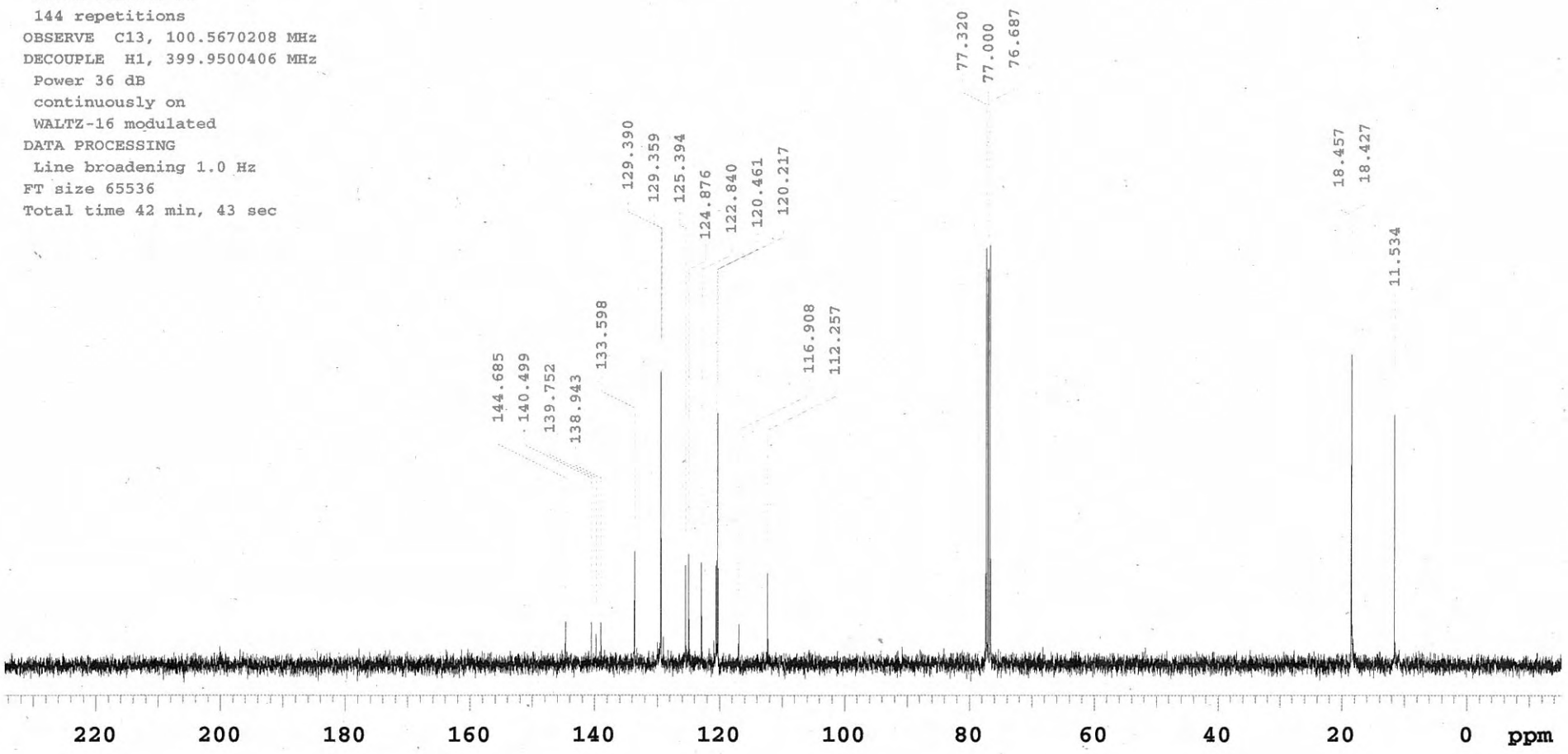
Pulse Sequence: s2pul

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

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
144 repetitions
OBSERVE C13, 100.5670208 MHz
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 42 min, 43 sec



6r



Plausible mechanism