Supporting Information for

Rhodium-Catalyzed Enantioselective Silylation of Arene C-H bonds: Desymmetrization of Diarylmethanols

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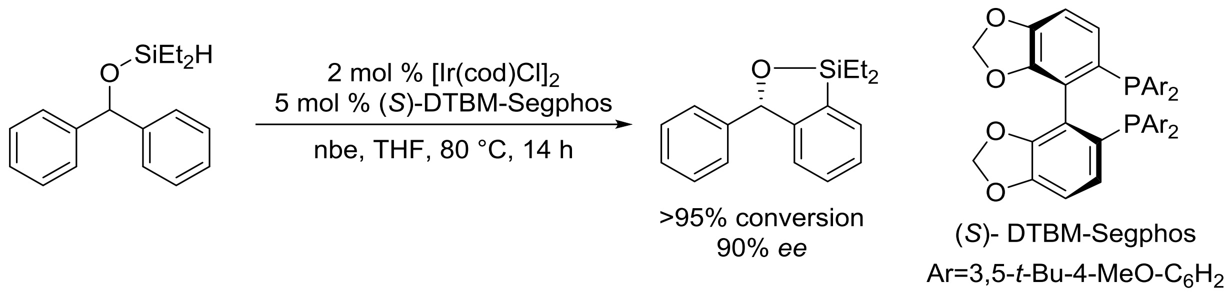
Materials and Methods

The silylation reactions were assembled in an N_2-filled glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. $[Ir(cod)OMe]_2$ was obtained as a gift from Johnson Matthey or purchased from Strem and was used as received. $[Rh(cod)Cl]_2$ was either obtained as a gift from Johnson Matthey, purchased from Strem, or prepared from $[RhCl_3 \cdot xH_2O]$ according to the standard procedure.[1] CatASium® and Walphos ligands were purchased from Strem and were used as received. Diethylsilane (Et_2SiH_2) was purchased from Gelest and was used as received. Norbornene (nbe) was purchased from Aldrich and was used as received. Compounds **1h**, **1k**, **1l** and **S1** were prepared according to the literature procedures.[2,3,4,5] Tetrahydrofuran (THF) was degassed by purging with nitrogen and then dried with a solvent purification system containing activated alumina. All other solvents and reagents were used as received.

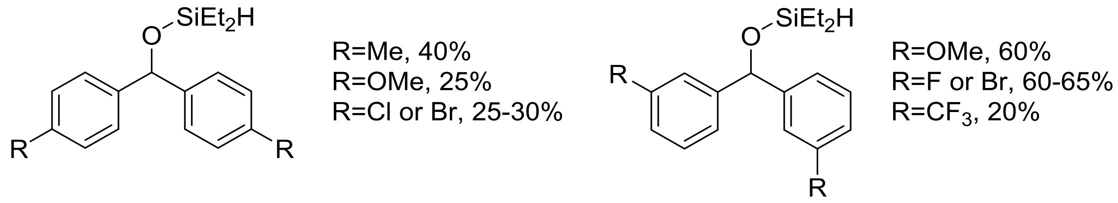
Reaction temperatures above 23 °C refer to temperatures of an aluminum heating block, which were controlled by an electronic temperature modulator. Silica gel chromatography was performed using a Teledyne Isco CombiFlash® R_f system with Redi*Sep* R_f Gold™ columns. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVB-400, AV-500 and AV-600 with ^{13}C operating frequencies of 101 MHz, 125 MHz and 150 MHz, respectively. ^{19}F NMR spectra were recorded on a Bruker AVQ-400 spectrometer with a ^{19}F operating frequency of 376 MHz. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal ($\delta = 7.26$ for ^{1}H NMR and $\delta = 77.0$ for ^{13}C NMR). High-resolution mass spectral data were obtained from the QB3/Chemistry Mass Spectrometry Facility, University of California, Berkeley. Chiral HPLC analysis was conducted on Waters or Shimadzu chromatography system. Racemic samples were obtained following the procedure reported by our group.[6]

Summary of Ir-catalyzed, Enantioselective C-H Silylation

1) Optimized condition



2) Limited substrate scope



Procedure for high throughput ligand evaluation of Rh-catalyzed, enantioselective C-H silylation

Catalyst stock solutions (0.00075 M) were prepared by adding 1.00 mL of a solution of $[Rh(cod)Cl]_2$ in THF (0.000375 M) to vials containing 0.000770 mmol of ligands **L1-L58** followed by agitation for 15 minutes (See Figure S1 for the structures). Stock solutions of substrates (**2a** or **2j**, 0.68 M), dodecane (1.0 M, internal standard) and norbornene (1.36 M) were prepared in THF. To 2 mL GC vials were added stock solutions of substrate, dodecane, and norbornene (25 µL each). Then, 100 µL of catalyst stock solution was added. The vials were capped and heated to 50 °C for 10 hours. The reaction mixtures were diluted with THF (600 µL). The conversions were determined by GC analysis according to the following formula:

conversion (%) = 100 x (1 - (reactant area/dodecane area)$_{\text{after reaction}}$/(reactant area/dodecane area)$_{\text{before reaction}}$).

The enantiomeric excesses were determined by chiral HPLC.

Figure S1. Structures of the ligands used for the Rh-catalyzed, enantioselective C-H silylation

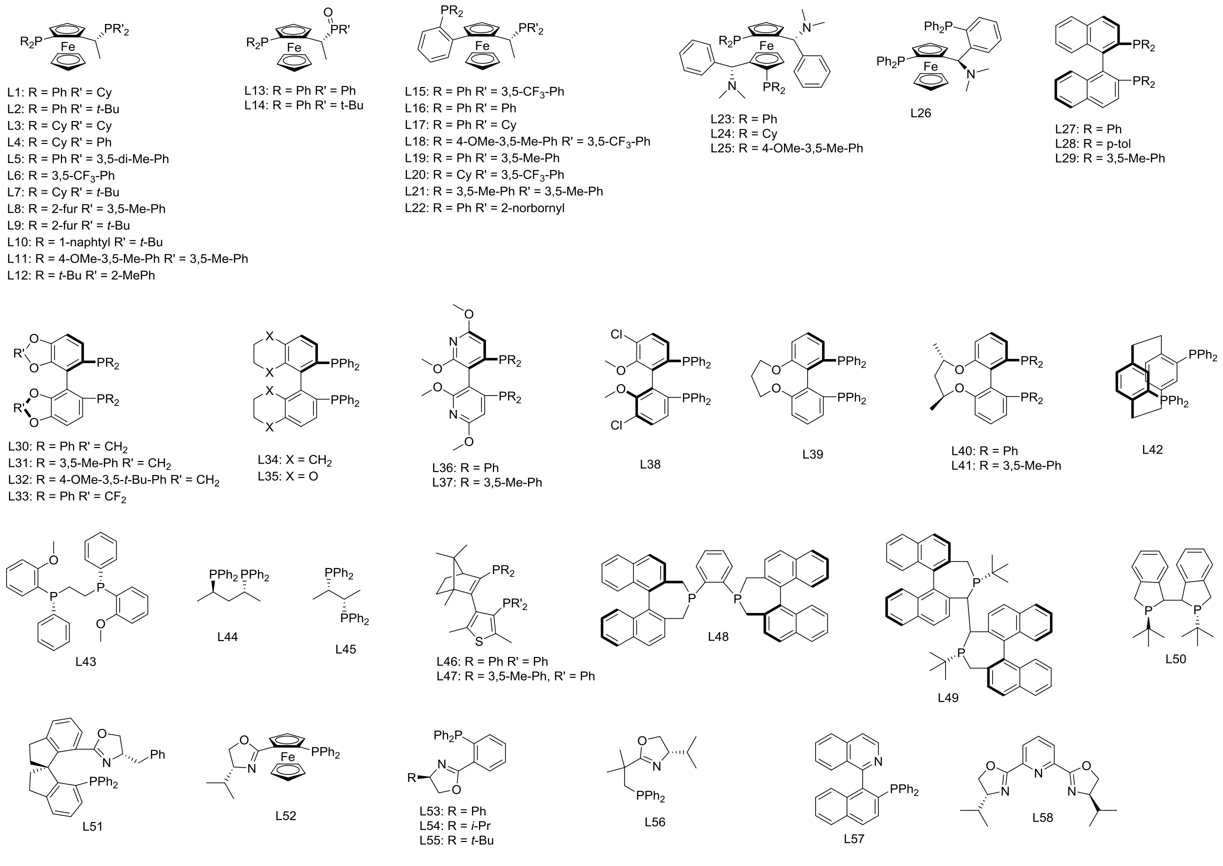
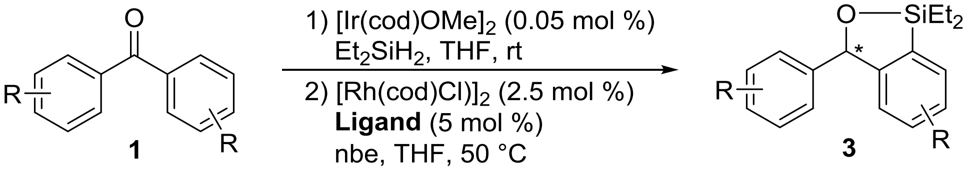


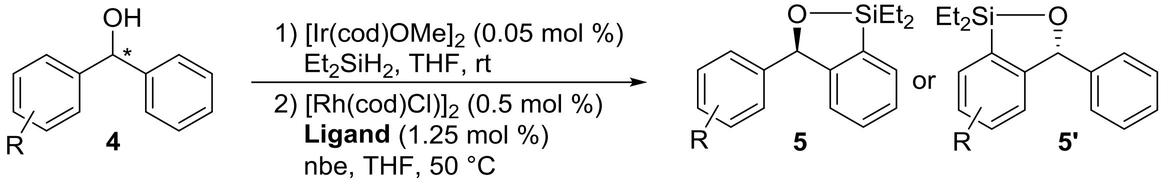
Table S1. Ligand evaluation for substrates in Table 1



entry	R	%*ee*				
		L17	**L18**	**L22**	**L46**	**L47**
1a	H	15	87	44	-99	-99
1b	4-Me	60	88	56	-97	-96
1d	3-Me	-10	88	40	-99	-99
1e	2,4-Me	77	5	77	nd[c]	nd[c]
1f[a]	4-Ph	70	nd[c]	nd[c]	-96	nd[b]
1g	4-MeO	57	84	63	-87	-89
1h[a]	3-MeO	-32	90	nd[c]	-94	-99
1i	3-CF$_3$	88	95	94	-88	-82
1j	4-Cl	94	84	88	-80	-82
1k	4-F	67	22	73	-22	-61
1l	3-Cl	46	90	67	-97	-95
1m[a]	4-TBSO	51	96	nd[c]	-96	-93
1n[a]	4-PivO	95	nd[b]	nd[c]	nd[b]	nd[b]

[a] 0.5 mol % [Rh(cod)Cl]$_2$ and 1.25 mol % Ligand. [b] less than 50% yield, determined by crude NMR analysis. [c] These ligands were not tested. [d] The ligand for the substrate **2c** (R = 4-*t*-Bu) was chosen based on the results from **2b**. (nd = not determined)

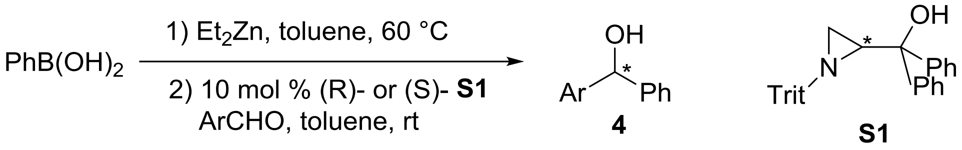
Table S2. Ligand evaluation for substrates in Table 2



entry	**5**:**5'**[a]			
	L17	**L18**	**L46**	**L47**
(*S*)-**4e** 97:3 *er*	16:84	9:91	95:5	90:10
(*R*)-**4e** 97:3 *er*	59:41	93:7	4:96	9:91

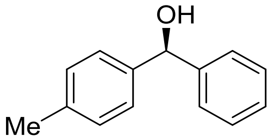
We did not perform ligand evaluation on **4a**-**4d** because the catalyst derived from **L46** provided high *ee* when the substrates with the same substituents as **4a**-**4d** were used in enantioselective C-H silylation (See Table S1).

Synthesis of enantioenriched diarylmethanols

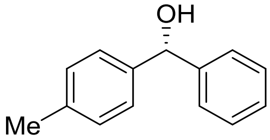


The general conditions developed by Braga and modified by Jarvo were employed.[5,7] To a solution of phenylboronic acid (ca. 4.8 mmol) in toluene (10 mL) was added diethylzinc (14 mL, 15 mmol, 1.1 M in toluene), and the resulting solution was heated at 60 °C for 12 h. After cooling to room temperature, a solution of (*S*)- or (*R*)-(1-tritylaziridin-2-yl)diphenylmethanol **S1**[5] (93.5 g, 0.200 mmol) in toluene (5 mL) was added. The reaction mixture was allowed to stir for 10 minutes before a solution of the corresponding aldehyde (ca. 2.0 mmol) in toluene (5 mL) was added. The reaction was stirred for 12 h at room temperature, at which time it was quenched by careful addition of 1 N HCl (10 mL). The resulting mixture was diluted with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$) and concentrated. The crude product was purified by silica gel chromatography.

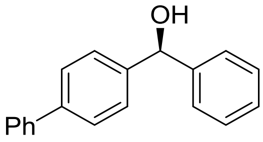
Spectral data of enantioenriched diarylmethanols



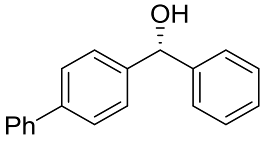
(*S*)-(4-Tolyl)phenylmethanol 4a: Following the general procedure, 4-tolualdehyde (241 mg, 2.01 mmol) was allowed to react with phenyl boronic acid and (*S*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 353 mg (89% yield) of (*S*)-**4a** as a white solid. **HPLC analysis**: 98:2 er, Chiralcel OD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 20.5 min (major), t_R = 21.6 min (minor). $[\alpha]_D^{25}$ = -8.1 (c 1.05, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, J = 7.4 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.15 (d, J = 7.9 Hz, 2H), 5.83 (d, J = 3.3 Hz, 1H), 2.33 (s, 3H), 2.15 (d, J = 3.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 140.9, 137.0, 129.0, 128.3, 127.2, 126.4, 126.4, 75.8, 21.0. (^{1}H and ^{13}C NMR data and $[\alpha]_D^{25}$ value were consistent with previously reported values.[5])



(*R*)-(4-Tolyl)phenylmethanol 4a: Following the general procedure, 4-toluadehyde (242 mg, 2.01 mmol) was allowed to react with phenyl boronic acid and (*R*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 372 mg (94% yield) of (*R*)-**4a** as a white solid, which gave ^{1}H and ^{13}C NMR data data identical to that of (*S*)-**4a**. **HPLC analysis**: 98:2 er, Chiralcel OB-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 10.9min (major), t_R = 13.3 min (minor). $[\alpha]_D^{25}$ = +7.8 (c 0.98, $CHCl_3$).

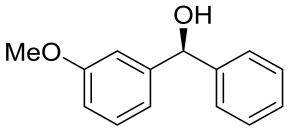


(*S*)-(4-Biphenyl)phenylmethanol 4b: Following the general procedure, biphenyl-4-carboxaldehyde (368 mg, 2.02 mmol) was allowed to react with phenyl boronic acid and (*S*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) and then recrystallized from ethyl acetate and hexanes to give 437 mg (84% yield) of (*S*)-**4b** as a white solid. **HPLC analysis**: 97:3 er, Chiralcel OD-H column, 6% isopropanol in hexane, 0.8 mL/min flow rate, 220 nm UV lamp, t_R = 33.7 min (major), t_R = 36.3 min (minor). $[\alpha]_D^{25}$ = +7.1 (c 1.05, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.50 – 7.39 (m, 6H), 7.39 – 7.33 (m, 3H), 7.33 – 7.26 (m, 1H), 5.91 (d, J = 2.9 Hz, 1H), 2.25 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 142.8, 140.7, 140.4, 128.7, 128.5, 127.6, 127.3, 127.2, 127.0, 126.9, 126.5, 76.0. (^{1}H and ^{13}C NMR data and $[\alpha]_D^{25}$ value were consistent with previously reported values.[7])

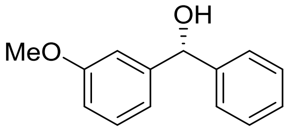


(*R*)-(4-Biphenyl)phenylmethanol 4b: Following the general procedure, biphenyl-4-carboxaldehyde (370 mg, 2.03 mmol) was allowed to react with phenyl boronic acid and (*R*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 455 mg (87% yield) of (*S*)-**4b** as a white solid, which gave ^{1}H and ^{13}C NMR data data identical to that of (*S*)-**4b**. **HPLC analysis**: 97:3 er, Chiralcel OB-H column, 5%

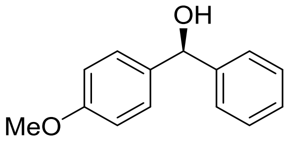
isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 42.4 min (major), t_R = 67.0 min (minor). $[\alpha]_D^{25}$ = -6.8 (c 1.02, $CHCl_3$).



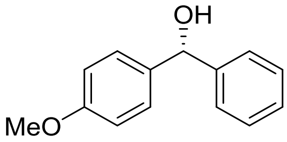
***(S)*-(3-Methoxyphenyl)phenylmethanol 4c**: Following the general procedure, 3-anisaldehyde (272 mg, 2.00 mmol) was allowed to react with phenyl boronic acid and (*S*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 320 mg (75% yield) of (*S*)-**4c** as a pale colorless oil. **HPLC analysis**: 97:3 er, Chiralpak IB column, 5% isopropanol in hexane, 0.8 mL/min flow rate, 220 nm UV lamp, t_R = 17.5 min (minor), t_R = 23.7 min (major). $[\alpha]_D^{25}$ = +15.3 (c 1.01, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.29 – 7.23 (m, 2H), 6.98 – 6.93 (m, 2H), 6.81 (d, J = 8.2 Hz, 1H), 5.82 (s, 1H), 3.79 (s, 3H), 2.19 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5, 145.4, 143.6, 129.4, 128.4, 127.4, 126.4, 118.8, 112.8, 112.0, 75.9, 55.1. (^{1}H and ^{13}C NMR data and $[\alpha]_D^{25}$ value were consistent with previously reported values.[8])



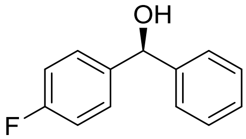
***(R)*-(4-Methoxyphenly)phenylmethanol 4c**: Following the general procedure, 3-anisadehyde (243 mg, 2.01 mmol) was allowed to react with phenyl boronic acid and (*R*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 396 mg (92% yield) of (*R*)-**4c** as a pale colorless oil, which gave ^{1}H and ^{13}C NMR data identical to that of (*S*)-**4c**. **HPLC analysis**: 97:3 er, Chiralpak IB column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 17.8 min (minor), t_R = 24.0 min (major). $[\alpha]_D^{25}$ = -14.9 (c 1.02, CHCl$_3$).



(*S*)-(4-Methoxyphenyl)phenylmethanol 4d: Following the general procedure, 4-anisaldehyde (273 mg, 2.01 mmol) was allowed to react with phenyl boronic acid and (*S*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 321 mg (75% yield) of (*S*)-**4d** as a pale colorless oil. **HPLC analysis**: 97:3 er, Chiralcel AD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 10.9 min (minor), t_R = 11.8 min (major). $[\alpha]_D^{25}$ = -15.1 (c 1.01, CHCl$_3$). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.40 – 7.31 (m, 4H), 7.31 – 7.24 (m, 3H), 6.87 (d, J = 8.7 Hz, 2H), 5.82 (d, J = 2.8 Hz, 1H), 3.79 (s, 3H), 2.14 (d, J = 3.3 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 158.8, 144.0, 136.1, 128.3, 127.8, 127.3, 126.3, 113.7, 75.6, 55.1. (^{1}H and ^{13}C NMR data and $[\alpha]_D^{25}$ value were consistent with previously reported values.[8])

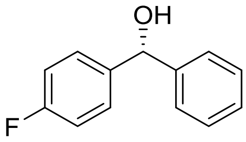


(*R*)-(4-Methoxyphenly)phenylmethanol 4d: Following the general procedure, 4-anisadehyde (242 mg, 2.01 mmol) was allowed to react with phenyl boronic acid and (*R*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 338 mg (79% yield) of (*R*)-**4d** as a pale colorless oil, which gave ^{1}H and ^{13}C NMR data data identical to that of (*S*)-**4d**. **HPLC analysis**: 97:3 er, Chiralcel AD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 11.0 min (major), t_R = 11.8 min (minor). $[\alpha]_D^{25}$ = +14.3 (c 1.04, $CHCl_3$).



(*S*)-(4-Fluorophenyl)phenylmethanol 4e: Following the general procedure, 4-fluorobenzaldehyde (248 mg, 2.00 mmol) was allowed to react with phenyl boronic acid and (*S*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 343 mg (85% yield) of (*S*)-**4e** as a colorless oil, which solidified upon seating. **HPLC analysis**: 97:3 er, Chiralpak IB column, 5% isopropanol in hexane, 0.8 mL/min flow rate, 220 nm UV lamp, t_R = 15.0 min (minor), t_R = 15.6 min (major). $[\alpha]_D^{25}$ = +7.1 (c 1.05, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 6H), 7.31 – 7.26 (m, 1H), 7.02 (t, J = 8.7 Hz, 2H), 5.84 (d, J = 2.7 Hz, 1H), 2.22 (d, J = 3.3 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.1 (d, *J* = 246 Hz), 143.6, 139.5 (d, *J* = 3.0 Hz), 128.5, 128.2 (d, *J* = 8.1

Hz), 127.7, 126.4, 115.2 (d, J = 21.4 Hz), 75.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.23. (^{1}H and ^{13}C NMR data and $[\alpha]_D^{25}$ were consistent with previously reported values.[8])

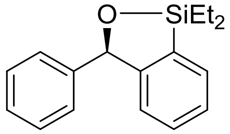


(*R*)-(4-Fluorophenyl)phenylmethanol 4e: Following the general procedure, 4-fluorobenzaldehyde (249 mg, 2.01 mmol) was allowed to react with phenyl boronic acid and (*R*)-**S1**. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 347 mg (86% yield) of (*R*)-**4e** as a colorless oil, which gave ^{1}H and ^{13}C NMR data data identical to that of (*S*)-**4e**. **HPLC analysis**: 97:3 er, Chiralcel OB-H column, 20% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 15.5 min (major), t_R = 21.2 min (minor). $[\alpha]_D^{25}$ = –6.8 (c 1.02, $CHCl_3$).

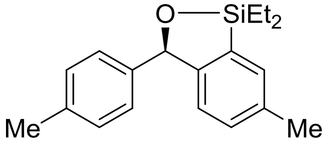
General procedure for enantioselective intramolecular arene silylation

In an N_2-filled glovebox, ca. 1.0 mmol of the benzophenone was weighed into a 1 dram screw-top vial. A stir bar was added, and the substrate was dissolved in THF (0.50 mL). The resulting solution was treated first with a freshly prepared stock solution of $[Ir(cod)OMe]_2$ (0.5 μmol, 0.05 mol %) in THF (0.50 mL) and then neat Et_2SiH_2 (1.20 mmol). The vial was capped with a Teflon-lined screw-cap, and the resulting solution was stirred in the glovebox at rt until complete conversion to the corresponding diethyl(hydrido)silyl ether was observed, as determined by GC-MS analysis (typically 12 h). The volatile materials were then removed by placing the reaction mixture directly under high-vacuum for 1 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated diethyl(hydrido)silyl ether was then sequentially treated with norbornene (1.20 mmol), THF (1.0 mL) and a freshly prepared stock solution of $[Rh(cod)Cl]_2$ (5 μmol, 0.50 mol %) and the corresponding ligand (12.5 μmol, 1.25 mol %) in THF (1.0 mL) . The Teflon-lined screw-cap was replaced, and the resulting solution was stirred in the glovebox for 1 h (to ensure complete formation of the active Rh species). The vial was then removed from the glovebox, placed in a pre-heated aluminum heating block at 50 °C. After the cyclization was complete (as determined by GC-MS analysis), the reaction mixture was allowed to cool to rt, and the solvent was removed via rotary evaporation. The crude product was purified by silica gel chromatography.

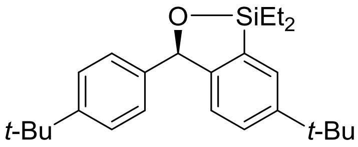
Spectral data for the products of enantiosselective C-H silylation



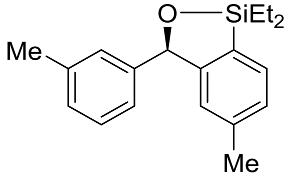
Benzoxasilole 3a: Following the general procedure, benzophenone (182 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L47** (1.0 mol %) at 50 °C for 5 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 229 mg (85%) of **3a** as a colorless oil, which solidified during the storage. Following the general procedure for silylation on 5.0 mmol scale with $[Rh(cod)Cl]_2$/**L47** (1.0 mol %) as catalyst, 917 mg (5.03 mmol) of benzophenone was converted to the corresponding diethyl(hydrido)silyl ether and allowed to cyclize at 50 °C for 9 h. Purification by silica gel chromatography (100:0 →90:10 hexanes/EtOAc) gave 1.13 g (83%) of **3a** as a colorless oil. **HPLC analysis**: 99% *ee*, Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 11.0 min (major), t_R = 17.5 min (minor). $[\alpha]_D^{25}$ = -111 (c 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.61 (dd, *J* = 5.6, 2.6 Hz, 1H), 7.38 – 7.23 (m, 7H), 7.02 (dd, *J* = 5.6, 2.6 Hz, 1H), 6.16 (s, 1H), 1.07 (t, *J* = 7.6 Hz, 3H), 1.03 – 0.82 (m, 7H). **^{13}C NMR** (101 MHz, CDCl3) δ 153.0, 143.7, 133.4, 131.2, 129.7, 128.4, 127.8, 127.3, 126.9, 123.7, 84.2, 7.2, 6.9, 6.8, 6.5. (^{1}H and ^{13}C NMR data were consistent with previously reported values.[6])



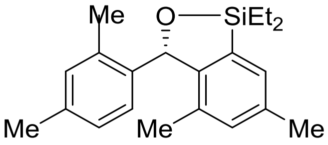
Benzoxasilole 3b: Following the general procedure, 4,4'-dimethylbenzophenone (211 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using [Ir(cod)OMe]$_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with [Rh(cod)Cl]$_2$/**L46** (1.0 mol %) at 50 °C for 6 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 267 mg (90%) of **3b** as an yellow oil. The enantiomeric excess was determined after iodination (96% *ee*, see below). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.43 (s, 1H), 7.21 – 7.13 (m, 5H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.12 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.05 – 0.83 (m, 7H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 150.4, 141.0, 137.2, 136.2, 133.5, 131.4, 130.7, 129.0, 127.2, 123.5, 83.9, 21.0 (*two overlapping resonances*), 7.2, 6.9, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{19}H_{24}OSi]^+$: *m/z* 296.1596, found 296.1598.



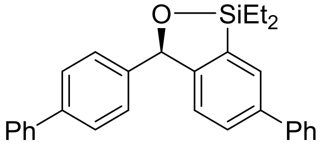
Benzoxasilole 3c: Following the general procedure, 4,4'-di-*tert*-butylbenzophenone (244 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using [Ir(cod)OMe]$_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with [Rh(cod)Cl]$_2$/**L46** (1.0 mol %) at 50 °C for 16 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 300 mg (79%) of **3c** as an yellow oil. The enantiomeric excess was determined after iodination (86% *ee*, see below). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 1.7 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.14 (s, 1H), 1.37 (s, 9H), 1.33 (s, 9H), 1.11 (t, *J* = 7.6 Hz, 3H), 1.07 – 0.86 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 150.3, 149.5, 140.9, 133.3, 127.4, 127.2, 126.9, 125.3, 123.2, 83.8, 34.6, 34.5, 31.5, 31.3, 7.3, 7.0, 6.9, 6.6. **HRMS** (EI+) calcd for $[C_{25}H_{36}OSi]^+$: *m/z* 380.2535, found 380.2526.



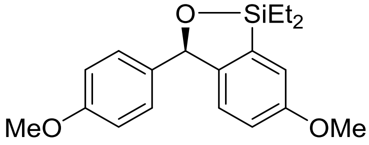
Benzoxasilole 3d: Following the general procedure, 3,3'-dimethylbenzophenone (209 mg, 0.996 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 ˚C for 17 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 251 mg (85%) of **3d** as a clear oil **HPLC analysis**: 99% *ee*, LUX Amylose-2 150 x 2 mm 3µ column, 5mM ammonioum acetate 63% in acetonitrile, 0.3 mL/min flow rate, 220 nm UV lamp, t_R = 22.5 min (minor), t_R = 24.9 min (major). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5Hz, 1H), 7.24 (t, *J* = 7.5Hz, 1H), 7.17-7.05 (m, 4H), 6.85 (m, 1H), 6.09 (s, 1H), 2,35 (s, 3H), 2.31 (s, 3H), 1.12-1.05 (m, 3H), 1.04-0.80 (m, 7H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 153.7, 143.9, 139.9, 138.2, 131.2, 130.2, 128.7, 128.5, 128.3 (*two overlapping resonances*), 124.6, 124.5, 84.4, 21.7, 21.6, 7.5, 7.2, 7.0, 6.7. **HRMS** (EI+) calcd for [$C_{19}H_{22}OSi$]$^+$: *m/z* 296.1596, found 296.1602.



Benzoxasilole 3e: Following the general procedure, 2,2',4,4'-tetramethylbenzophenone (241 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using [Ir(cod)OMe]$_2$ (0.05 mol%) as catalyst. The subsequent cyclization was conducted with [Rh(cod)Cl]$_2$/**L22** (1.0 mol %) at 80 °C for 48 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 255 mg (78%) of **3e** as a clear oil **HPLC analysis**: 72% *ee*, LUX Amylose-2 150 x 2 mm 3μ column, 5mM ammonioum acetate 55% in acetonitrile, 0.3 mL/min flow rate, 220 nm UV lamp, t_R = 27.8 min (major), t_R = 32.2 min (minor). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.35 (s, 1H), 7.07 (s, 1H), 7.04 (s, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.57 (bs, 1H), 6.44 (s, 1H), 2.65 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H), 1.87 (s, 3H), 1.05-0.98 (m, 6H), 0.93-0.82 (m, 4H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 148.4, 138.3, 137.1, 136.8, 136.4, 135.1, 132.7, 132.6, 131.2, 129.1, 126.8 (*two overlapping resonances*), 79.3, 21.2, 21.1, 19.3, 19.1, 7.7, 7.3, 7.1, 6.8. **HRMS** (EI+) calcd for [$C_{21}H_{28}OSi$]$^+$: *m/z* 324.1909, found 324.1915.

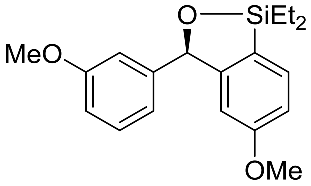


Benzoxasilole 3f: Following the general procedure, 4,4'-diphenylbenzophenone (334 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.1 mol %) as catalyst and 2.80 equiv of Et_2SiH_2 as reagent (otherwise identical condition). The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 60 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 322 mg (77%) of **3f** as a clear foam. **HPLC analysis**: 95% *ee*, Chiralpak IA column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 6.0 min (minor), t_R = 8.2 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.4 Hz, 1H), 7.72 – 7.63 (m, 7H), 7.55 – 7.47 (m, 6H), 7.41 (dt, *J* = 14.6, 7.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 1.22 (t, *J* = 7.7 Hz, 3H), 1.17 – 0.95 (m, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.0, 142.7, 141.1, 140.9, 140.7, 140.1, 134.4, 129.8, 129.0, 128.72, 128.67, 127.8, 127.3, 127.22 (*two overlapping resonances*), 127.19, 127.1, 124.1, 83.8, 7.3, 7.0, 6.9, 6.5. **HRMS** (EI+) calcd for $[C29H28OSi]^+$: *m/z* 420.1909, found 420.1906.



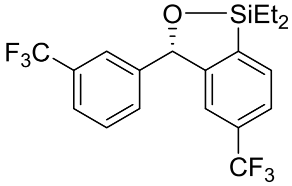
Benzoxasilole 3g: Following the general procedure, 4,4'-dimethoxybenzophenone (243 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using

$[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L47** (1.0 mol %) at 50 °C for 6 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 258 mg (78%) of **3g** as a colorless oil. **HPLC analysis**: 99% *ee*, Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 51.7 min (major), t_R = 79.8 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 2.1 Hz, 1H), 6.97 – 6.84 (m, 4H), 6.11 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.08 (t, *J* = 7.6 Hz, 3H), 1.05 – 0.83 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 158.6, 145.4, 136.3, 135.0, 128.5, 124.7, 116.3, 114.6, 113.6, 83.3, 55.1, 55.0, 7.1, 6.8, 6.7, 6.4. **HRMS** (EI+) calcd for $[C_{19}H_{24}O_3Si]^+$: *m/z* 328.1495, found 328.1493.



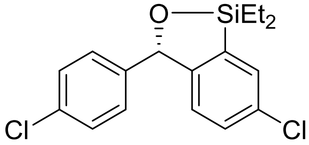
Benzoxasilole 3h: Following the general procedure, bis(3-methoxyphenyl)methanol (244 mg, 0.998 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 19 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 258 mg (78%) of **3h** as a colorless oil. **HPLC analysis**: 99% *ee*, Chiralpak IA column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 21.2 min (major), t_R = 24.3 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* =

8.0 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 6.98 – 6.82 (m, 4H), 6.59 (d, *J* = 1.7 Hz, 1H), 6.11 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 1.11 (t, *J* = 7.7 Hz, 3H), 1.05 – 0.84 (m, 7H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.3, 159.7, 155.1, 145.2, 132.2, 129.4, 124.2, 119.6, 114.1, 113.3, 112.6, 108.6, 83.9, 55.0, 55.0, 7.4, 7.1, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{19}H_{24}O_3Si]^+$: *m/z* 328.1495, found 328.1499.

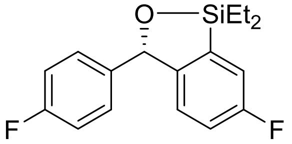


Benzoxasilole 3i: Following the general procedure, 3,3’-bis(trifluoromethyl)benzophenone (319 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.1 mol%) as catalyst (under otherwise identical condition). The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L18** (1.0 mol %) at 50 °C for 18 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 252 mg (62%) of **3i** as a colorless oil. The enantiomeric excess was determined after Tamao-Flemming oxidation (97% *ee*, see below). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.59 (m, 3H), 7.50 (t, J = 7.7 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.23 (s, 1H), 6.23 (s, 1H), 1.11 – 0.85 (m, 10H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 152.9, 143.9, 138.5, 132.3 (q, *J* = 32.1 Hz), 132.1, 131.2 (q, *J* = 32.4 Hz), 130.5, 129.2, 125.1 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 3.3 Hz), 124.1 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.5 Hz, *two overlapping resonances*), 120.2 (q, *J* = 3.8 Hz), 83.4, 7.0, 6.8, 6.6, 6.3. **^{19}F NMR** (376 MHz, CDCl$_3$) δ -62.75, -62.79. **HRMS** (EI+) calcd for

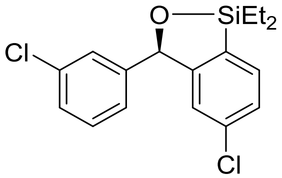
$[C_{19}H_{18}F_6OSi]^+$: *m/z* 404.1031, found 404.1032.



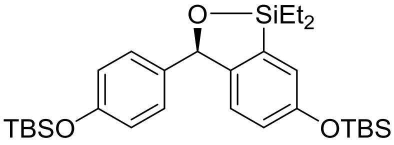
Benzoxasilole 3j: Following the general procedure, 4,4'-dichlorobenzophenone (251 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L17** (1.0 mol %) at 50 °C for 10 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 267 mg (88%) of **3j** as a colorless oil. **HPLC analysis**: 99% *ee,* Chiralcel OD-H column, 1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 8.1 min (major), t_R = 8.9 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.20 (m, 3H), 7.15 (d, *J* = 6.7 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.04 (s, 1H), 1.01 (t, *J* = 7.6 Hz, 3H), 0.97 – 0.77 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 141.8, 136.1, 133.7, 133.5, 130.8, 129.9, 128.7, 128.6, 125.0, 83.0, 7.0, 6.8, 6.7, 6.3. **HRMS** (EI+) calcd for $[C_{17}H_{18}Cl_2OSi]^+$: *m/z* 336.0504, found 336.0502.



Benzoxasilole 3k Following the general procedure, 4,4'-difluorobenzophenone (219 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L17** (1.0 mol %) at rt for 72 h (under otherwise identical condition). Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 267 mg (88%) of **3k** as a colorless oil. **HPLC analysis**: 81% *ee*, Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 6.7 min (major), t_R = 8.7 min (minor). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 3H), 7.07 – 7.00 (m, 3H), 6.95 (dd, J = 8.5, 4.5 Hz, 1H), 6.14 (s, 1H), 1.08 (t, J = 7.8 Hz, 3H), 1.03 – 0.84 (m, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.2 Hz), 162.3 (d, *J* = 247.3 Hz), 148.2 (d, *J* = 2.2 Hz), 139.4 (d, *J* = 3.1 Hz), 136.3 (d, *J* = 5.5 Hz), 129.0 (d, *J* = 8.2 Hz), 125.4 (d, *J* = 7.7 Hz), 117.2 (d, *J* = 23.0 Hz), 116.9 (d, *J* = 19.8 Hz), 115.4 (d, *J* = 21.5 Hz), 83.1, 7.1, 6.8, 6.7, 6.3. **^{19}F NMR** (376 MHz, CDCl3) δ -113.46, -115.58. **HRMS** (EI+) calcd for $[C_{17}H_{18}F_2OSi]^+$: *m/z* 304.1095, found 304.1097.

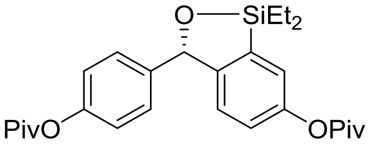


Benzoxasilole 3l: Following the general procedure, 3,3'-dichlorobenzophenone (251 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol%) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 17 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 279 mg (83%) of **3l** as a clear oil **HPLC analysis**: 97% *ee*, LUX Amylose-2 150 x 2 mm 3µ column, 5mM ammonioum acetate 63% in acetonitrile, 0.3 mL/min, 220 nm UV lamp, t_R = 38.3 min (minor), t_R = 39.6 min (major). Alternatively, Chiralcel OD-H column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 12.6 min (minor), t_R = 7.4 min (major). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9Hz, 1H), 7.35-7.25 (m, 4H), 7.20 (m, 1H), 7.03 (m, 1H), 6.09 (s, 1H), 1.14-1.07 (m, 3H), 1.04-0.84 (m, 7H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.4, 145.0, 136.4, 134.6, 132.5, 131.8, 129.9, 128.3, 127.8, 127.4, 125.4, 123.9, 83.1, 7.2, 6.9, 6.7, 6.4. **HRMS** (EI+) calcd for $[C_{17}H_{18}Cl_2OSi]^+$: *m/z* 336.0504, found 336.0514.



Benzoxasilole 3m: Following the general procedure, 4,4’-bis(di-*tert*-butyldimethylsilyloxy)benzophenone (443 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol%) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 ˚C for 25 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 461 mg (87%) of **3m** as a colorless oil. **HPLC analysis**: 97% *ee*, Chiralcel AD-H column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 7.1 min (minor), t_R = 7.4

min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.89 – 6.74 (m, 4H), 6.05 (s, 1H), 1.09 – 0.79 (m, 28H), 0.21 (s, 6H), 0.18 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 154.6, 146.0, 137.0, 135.1, 128.6, 124.8, 122.0, 121.5, 119.9, 83.6, 25.7 (*two overlapping resonances*), 18.2 (*two overlapping resonances*), 7.2, 7.0, 6.8, 6.5, -4.4 (*two overlapping resonances*). **HRMS** (EI+) calcd for $[C_{29}H_{48}O_3Si_3]^+$: *m/z* 528.2911, found 528.2912.

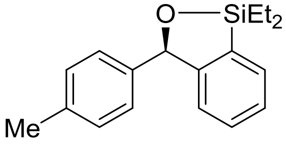


Benzoxasilole 3n: Following the general procedure, 4,4'-bis(trimethylacetoxy)benzophenone (381 mg, 0.996 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol%) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L17** (1.0 mol %) at 50 °C for 17 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 254 mg (54%) of **3n** as a clear foam **HPLC analysis**: 95% *ee*, Chiralpak IC column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 4.9 min (minor), t_R = 5.7 min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 3H), 7.06 – 7.01 (m, 4H), 6.16 (s, 1H), 1.38 (s, 9H), 1.35 (s, 9H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.02 – 0.85 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.0, 176.8, 150.7, 150.3, 149.7, 140.8, 135.3, 128.4, 124.8, 123.3, 123.2, 121.4, 83.3, 39.0, 39.1, 27.1, 27.0, 7.09, 6.81, 6.73, 6.40. **HRMS** (EI+) calcd for $[C_{27}H_{36}O_5Si]^+$: *m/z* 468.2332, found 468.2326.

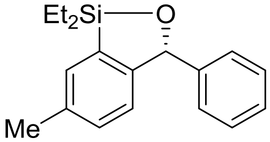
General procedure for site-selective intramolecular arene silylation

In an N_2-filled glovebox, ca. 0.25 mmol of the enantioenriched diarylmethanol substrate was weighed into a 1 dram screw-top vial. A stir bar was added. A freshly prepared stock solution of $[Ir(cod)OMe]_2$ (0.13 µmol, 0.05 mol %) in THF (0.25 mL) and then neat Et_2SiH_2 (0.375 mmol). The vial was capped with a Teflon-lined screw-cap, and the resulting solution was stirred in the glovebox at rt until complete conversion to the corresponding diethyl(hydrido)silyl ether was observed, as determined by GC-MS analysis (typically 12 h). The volatile materials were then removed by placing the reaction mixture directly under high-vacuum for 1 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated diethyl(hydrido)silyl ether was then sequentially treated with norbornene (0.30 mmol), THF (0.25 mL) and a freshly prepared stock solution of $[Rh(cod)Cl]_2$ (1.3 µmol, 0.50 mol %) and the corresponding ligand (3.1 µmol, 1.25 mol %) in THF (0.25 mL) . The Teflon-lined screw-cap was replaced, and the resulting solution was stirred in the glovebox for 1 h (to ensure complete formation of the active Rh species). The vial was then removed from the glovebox, placed in a pre-heated aluminum heating block at 50 ˚C. After the cyclization was complete (as determined by GC-MS analysis), the reaction mixture was allowed to cool to rt, and the solvent was removed via rotary evaporation. The crude product was purified by silica gel chromatography.

Spectral data for the products of site-selective C-H silylation

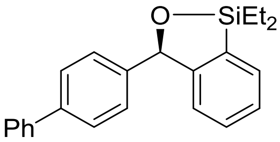


Benzoxasilole 5a: Following the general procedure, (*S*)-(4-tolyl)phenylmethanol **4a** (50.0 mg, 0.252 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 54.5 mg (77%) of a mixture of **5a** and its constitutional isomer **5a'** as a colorless oil. The ratio between **5a** and **5a'** was determined to be 96:4 by GC analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.0 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 6.9 Hz, 1H), 6.19 (s, 1H), 2.38 (s, 3H), 1.12 (t, *J* = 7.8 Hz, 3H), 1.07 – 0.88 (m, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 140.9, 137.4, 133.5, 131.1, 129.6, 129.1, 127.3, 126.8, 123.7, 84.1, 21.1, 7.2, 6.9, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{18}H_{22}OSi]^+$: *m/z* 282.1440, found 282.1434.



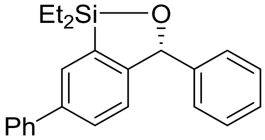
Benzoxasilole 5a': Following the general procedure, (*R*)-(4-tolyl)phenylmethanol **4a** (49.4 mg, 0.250 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with

$[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 51.8 mg (73%) of a mixture of **5a'** and its constitutional isomer **5a** as a colorless oil. The ratio between **5a'** and **5a** was determined to be 96:4 by GC analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.15 (s, 1H), 2.40 (s, 3H), 1.10 (t, *J* = 7.8 Hz, 3H), 1.05 – 0.86 (m, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.3, 143.9, 136.4, 133.6, 131.5, 130.8, 128.4, 127.7, 127.3, 123.5, 84.1, 21.2, 7.3, 6.9, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{18}H_{22}OSi]^+$: *m/z* 282.1440, found 282.1439.

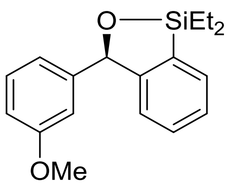


Benzoxasilole 5b: Following the general procedure, (*S*)-(4-biphenyl)phenylmethanol **4b** (65.5 mg, 0.252 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 14 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 72.5 mg (84%) of a mixture of **5b** and its constitutional isomer **5b'** as a colorless oil. The ratio between **5b** and **5b'** was determined to be 96:4 by GC analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.8 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.22 (s, 1H), 1.10 (t, *J* = 7.8 Hz, 3H), 1.05 – 0.97 (m, 5H), 0.96 – 0.86 (m, 2H). **^{13}C NMR** (151

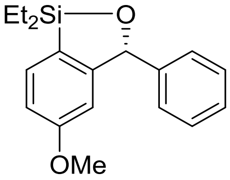
MHz, $CDCl_3$) δ 152.9, 142.8, 140.9, 140.7, 133.6, 131.3, 129.8, 128.7, 127.8, 127.3, 127.2, 127.1, 127.0, 123.8, 84.0, 7.3, 7.0, 6.9, 6.5. **HRMS** (EI+) calcd for $[C_{23}H_{24}OSi]^+$: *m/z* 344.1596, found 344.1602.



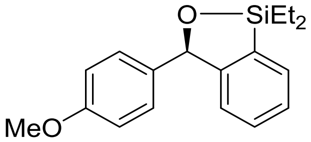
Benzoxasilole 5b': Following the general procedure, (*R*)-(4-biphenyl)phenylmethanol **4b** (65.5 mg, 0.252 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 14 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 67.4 mg (78%) of a mixture of **5b'** and its constitutional isomer **5b** as a colorless oil. The ratio between **5b'** and **5b** was determined to be 93:7 by GC analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.39 – 7.30 (m, 6H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.22 (s, 1H), 1.12 (t, *J* = 7.8 Hz, 3H), 1.07 – 0.99 (m, 5H), 0.99 – 0.88 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.1, 143.7, 141.1, 140.1, 134.3, 129.8, 129.0, 128.7, 128.5, 127.9, 127.3, 127.3, 127.2, 124.1, 84.1, 7.3, 7.0, 6.9, 6.5. **HRMS** (EI+) calcd for $[C_{23}H_{24}OSi]^+$: *m/z* 344.1596, found 344.1594.



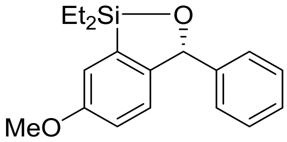
Benzoxasilole 5c: Following the general procedure, (*S*)-(3-methoxyphenyl)phenylmethanol **4c** (54.1 mg, 0.252 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 14 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 52.9 mg (79%) of a mixture of **5c** and its constitutional isomer **5c'** as a colorless oil. The ratio between **5c** and **5c**' was determined to be 97:3 by GC analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.5 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.81 (m, 2H), 6.15 (s, 1H), 3.77 (s, 3H), 1.10 (t, *J* = 7.7 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 5H), 0.95-0.85 (m, 2H).. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 152.8, 145.3, 133.3, 131.2, 129.7, 129.4, 127.0, 123.7, 119.7, 113.4, 112.7, 84.1, 55.1, 7.2, 6.9, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{18}H_{22}O_2Si]^+$: *m/z* 298.1389, found 298.1395.



Benzoxasilole 5c': Following the general procedure, (*R*)-(3-methoxyphenyl)phenylmethanol **4c** (53.9 mg, 0.252 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 14 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 56.1 mg (84%) of a mixture of **5c'** and its constitutional isomer **5c** as a colorless oil. The ratio between **5c'** and **5c** was determined to be 95:5 by GC analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 3H), 6.89 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.53 (d, *J* = 1.9 Hz, 1H), 6.12 (s, 1H), 3.72 (s, 3H), 1.07 (t, *J* = 7.8 Hz, 3H), 1.02 – 0.94 (m, 5H), 0.92 – 0.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.3, 155.3, 143.7, 132.3, 128.5, 127.8, 127.4, 124.4, 114.1, 108.7, 84.1, 55.1, 7.4, 7.1, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{18}H_{22}O_2Si]^+$: *m/z* 298.1389, found 298.1387.

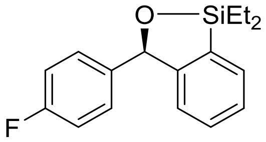


Benzoxasilole 5d: Following the general procedure, (*S*)-(4-methoxyphenyl)phenylmethanol **4d** (53.9 mg, 0.252 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 33 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 45.5 mg (68%) of **5d** as a colorless oil. The ratio between **5d a**nd **5d'** was determined to be 92:8 by GC analysis of the crude mixture. **HPLC analysis**: 99% *ee*, Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 22.1 min (minor), t_R = 36.1 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 7.10 (d, J = 2.4 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.13 (s, 1H), 3.84 (s, 3H), 1.09 (t, *J* = 7.8 Hz, 3H), 1.01 (t, *J* = 7.7 Hz, 3H), 1.00 – 0.86 (m, 4H). **^{13}C NMR** (151 MHz, CDCl3) δ 158.8, 145.2, 144.0, 135.2, 128.4, 127.7, 127.3, 124.8, 116.5, 114.9, 83.9, 55.3, 7.2, 6.9, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{18}H_{22}O_2Si]^+$: *m/z* 298.1389, found 298.1383.

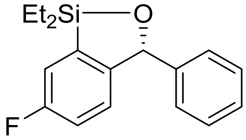


Benzoxasilole 5d': Following the general procedure, (*R*)-(4-methoxyphenyl)phenylmethanol **4d** (53.1 mg, 0.248 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 24 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 36.0 mg (53%) of **5d'** as a colorless oil. The ratio between **5d' a**nd **5d** was determined to be 91:9 by GC analysis of the crude mixture. **HPLC analysis**: 99% *ee*, Chiralpak IA column, 0.1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 7.4 min (major), t_R = 8.6 min (minor). Alternatively, Chiralcel AD-H column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 14.1 min (minor), t_R = 14.9 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (dd, J = 6.2, 1.6 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.15 (s, 1H), 3.81 (s, 3H), 1.08 (t, *J* = 7.8 Hz, 3H), 1.04 – 0.85 (m, 7H). **^{13}C NMR** (151

MHz, CDCl3) δ 159.2, 153.2, 136.2, 133.5, 131.1, 129.6, 128.7, 126.9, 123.8, 113.8, 83.8, 55.2, 7.3, 6.9, 6.8, 6.5. **HRMS** (EI+) calcd for $[C_{18}H_{22}O_2Si]^+$: *m/z* 298.1389, found 298.1387.



Benzoxasilole 5e: Following the general procedure, (*S*)-(4-fluorophenyl)phenylmethanol **4e** (51.4 mg, 0.254 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using $[Ir(cod)OMe]_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with $[Rh(cod)Cl]_2$/**L46** (1.0 mol %) at 50 °C for 14 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 51.7 mg (72%) of a mixture of **5e** and its constitutional isomer **5e'** as a colorless oil. The ratio between **5e a**nd **5e'** was determined to be 95:5 by the NMR analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 7.06 – 7.01 (m, 2H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.16 (s, 1H), 1.08 (t, *J* = 7.7 Hz, 3H), 1.05 – 0.95 (m, 5H), 0.95 – 0.85 (m, 2H). **^{13}C NMR** (151 MHz, CDCl3) δ 162.4 (d, *J* = 246 Hz), 152.7, 139.7, 133.5, 131.3, 129.8, 129.1 (d, *J* = 8.1 Hz), 127.1, 123.7 , 115.3 (d, *J* = 22 Hz), 83.5, 7.2, 6.9, 6.8, 6.5. **^{19}F NMR** (376 MHz, CDCl3) δ -113.86. **HRMS** (EI+) calcd for $[C_{17}H_{19}FOSi]^+$: *m/z* 286.1189, found 286.1190.



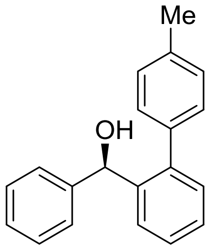
Benzoxasilole 5e': Following the general procedure, (*R*)-(4-fluorophenyl)phenylmethanol **4e**

(49.7 mg, 0.246 mmol) was converted to the corresponding diethyl(hydrido)silyl ether at rt using [Ir(cod)OMe]$_2$ (0.05 mol %) as catalyst. The subsequent cyclization was conducted with [Rh(cod)Cl]$_2$/**L46** (1.0 mol %) at 50 °C for 14 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 57.8 mg (81%) of a mixture of **5e'** and its constitutional isomer **5e** as a colorless oil. The ratio between **5e' a**nd **5e** was determined to be 96:4 by the NMR analysis of the crude mixture. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.04 – 6.96 (m, 2H), 6.13 (s, 1H), 1.08 (t, *J* = 7.8 Hz, 3H), 1.02 – 0.97 (m, 5H), 0.94 – 0.84 (m, 2H). **^{13}C NMR** (151 MHz, CDCl3) δ 162.2 (d, *J* = 247 Hz), 148.4, 143.5 , 136.3 (d, *J* = 5.0 Hz), 128.5 , 128.0, 127.3, 125.4 (d, *J* = 7.7 Hz), 117.2 (d, *J* = 22.9 Hz), 116.8 (d, *J* = 19.7 Hz), 83.9, 7.1, 6.9, 6.7, 6.4. **^{19}F NMR** (376 MHz, CDCl3) δ -116.00 **HRMS** (EI+) calcd for $[C_{17}H_{19}FOSi]^+$: *m/z* 286.1189, found 286.1193.

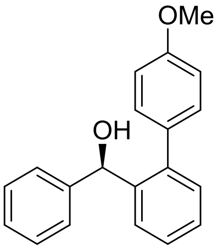
General procedure for Hiyama coupling of benzoxasilole products

In an N_2-filled glovebox, a 1 dram screw-top vial was charged with $Pd(OAc)_2$ (2.3 mg, 10μ mol, 4 mol %), 1,2-bis(dicyclohexylphosphino)ethane (4.7 mg, 11 µmol, 4.5 mol %) and a stir bar. A solution of the benzoxasilole (0.25 mmol) and the aryl iodide (0.30 mmol) in dioxane (1.25 mL) was then added. The vial was capped with a screw cap containing a PTFE-lined septum and removed from the glovebox. After being stirred at rt for 5-10 min, the light yellow/golden solution was treated with 2 M aq NaOH (0.63 mL, 1.25 mmol), and the resulting biphasic mixture was stirred at rt for an additional 30 min. The vial was then placed in a pre-heated aluminum block at 65 °C and stirred for 14 h. The reaction mixture was allowed to cool to rt and then diluted with EtOAc, filtered through SiO_2 and concentrated. The residue was adsorbed onto Celite and purified by silica gel chromatography to provide the biaryl alcohol product.

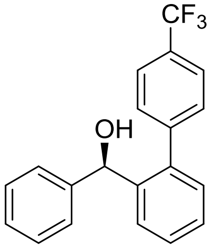
Spectral data for the products of Hiyama coupling:



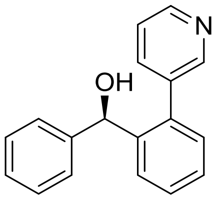
Biarylmethanol 6a: Following the general procedure, benzoxasilole **3a** (67.3 mg, 0.251 mmol) was coupled with 4-iodotoluene (67.5 mg, 0.310 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 47.4 mg (69%) of **3a** as a white oil. **HPLC analysis**: 99% *ee*, Chiralcel OD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 23.4 min (minor), t_R = 26.0 min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 1.6 Hz, 1H), 7.33 (td, *J* = 7.4, 1.6 Hz, 1H), 7.30 – 7.15 (m, 10H), 5.96 (s, 1H), 2.41 (s, 3H), 2.13 (br s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 141.3, 141.1, 137.8, 136.8, 130.1, 129.2, 128.8, 128.2, 127.7, 127.4, 127.3, 127.1, 126.6, 72.3, 21.2. (^{1}H and ^{13}C NMR data were consistent with previously reported values.[9])



Biarylmethanol 6b: Following the general procedure, benzoxasilole **3a** (67.3 mg, 0.251 mmol) was coupled with 4-iodoanisole (74.8 mg, 0.320 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 51.0 mg (70%) of **3b** as a white foam. **HPLC analysis**: 99% *ee*, Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 15.8 min (major), t_R = 18.4 min (minor). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.32 (td, *J* = 7.4, 1.4 Hz, 1H), 7.30 – 7.17 (m, 8H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.96 (s, 1H), 3.85 (s, 3H), 2.14 (br s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.8, 143.9, 141.3, 141.0, 133.1, 130.4, 130.2, 128.2, 127.6, 127.4, 127.2, 127.2, 126.6, 113.6, 72.5, 55.3. **HRMS** (EI+) calcd for $[C_{20}H_{18}O_2]^+$: *m/z* 290.1307, found 290.1307.



Biarylmethanol 6c: Following the general procedure, benzoxasilole **3a** (67.2 mg, 0.250 mmol) was coupled with 4-iodobenzotrifluoride (81.9 mg, 0.301 mmol) with Pd(OAc)$_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 65.3 mg (79%) of **3c** as a colorless foam. **HPLC analysis**: 98% *ee*, Chiralcel OD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t$_R$ = 20.9 min (minor), t$_R$ = 28.6 min (major). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.63 (d, *J* = 7.9 Hz, 3H), 7.44 (td, *J* = 7.6, 1.3 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.30 – 7.19 (m, 4H), 7.15 – 7.10 (m, 2H), 5.84 (s, 1H), 2.16 (br s, 1H) **^{13}C NMR** (101 MHz, CDCl$_3$) δ 144.5, 143.5, 140.8, 139.9, 129.7, 129.4 (q, *J* = 32.6 Hz), 128.5, 128.3, 127.6, 127.5, 127.3, 126.7, 126.5, 125.0 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.1 Hz), 72.6. **^{19}F NMR** (376 MHz, CDCl3) δ -61.62. **HRMS** (EI+) calcd for [$C_{20}H_{15}F_3O$]$^+$: *m/z* 328.1075, found 328.1077.



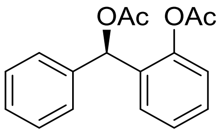
Biarylmethanol 6d: Following the general procedure, benzoxasilole **3a** (67.1 mg, 0.250 mmol) was coupled with 3-iodopyridine (63.7 mg, 0.311 mmol) with Pd(OAc)$_2$/dcpe at 65 °C.

The crude product was purified by silica gel chromatography (100:0→20:80 hexanes/EtOAc) to give 34.4 mg (53%) of **6d** as a white solid. **HPLC analysis**: 99% *ee*, Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 20.6 min (major), t_R = 26.1 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 – 8.35 (br, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.16 (m, 5H), 7.16 – 7.11 (m, 2H), 5.81 (s, 1H), 3.64 (br s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.4, 147.9, 143.7, 141.6, 137.3, 137.0, 130.1 (*two overlapping resonances*), 128.7 (*two overlapping resonances*), 128.3, 127.6, 127.6, 127.3, 126.7, 72.3. **HRMS** (EI+) calcd for $[C_{18}H_{15}NO]^+$: *m/z* 261.1154, found 261.1150.

General procedure for Tamao-Fleming oxidation of benzoxasilole products

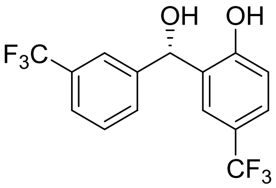
A solution of benzoxasilole (0.25 mmol) in 1:1 THF/MeOH (1.0 mL) was treated sequentially with $KHCO_3$ (0.50 mmol) and H_2O_2 (30% solution in H_2O, 2.0 mmol). The resulting mixture was stirred at rt until complete consumption of the benzoxasilole was observed, as judged by TLC analysis. The reaction was carefully quenched by slow addition of the reaction mixture (via pipette) to a solution of aq $NaHSO_3$ (10 mL), and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed (10 mL water, then 10 mL sat. $NaHCO_3$), dried (Na_2SO_4), and concentrated. The resulting diol was either purified by silica gel chromatography to provide the diol or acetylated to form the corresponding diacetate**.** **Procedure for Diacetylation**: Without further purification, the crude phenol was dissolved in CH_2Cl_2 (0.8 mL) and Et_3N (0.4 mL), and the resulting solution was treated with Ac_2O (3 equiv). After being stirred at rt overnight, the reaction mixture was concentrated. The resulting residue was adsorbed onto Celite and purified by silica gel chromatography to provide the diacetate product.

Spectral data for the products of Tamao-Fleming oxidation:



Diacetate 7: Following the general procedure, benzoxasilole **3a** (67.7 mg, 0.252 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude phenol was acylated with Ac_2O/Et_3N according to the general procedure, and the resulting diactate was purified by silica gel chromatography

(100:0→80:20 hexanes/EtOAc) to give 37.5 mg (53% over 2 steps) of **7** as a colorless oil. **HPLC analysis**: 96% *ee*, Chiralcel OJ-H column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 18.3 min (major), t_R = 34.4 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.22 (m, 7H), 7.14 – 7.06 (m, 2H), 2.21 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 168.9, 148.2, 138.9, 131.9, 129.1, 128.5, 128.4, 128.0, 127.0, 126.0, 123.0, 71.7, 21.0, 20.8. (^{1}H NMR data were consistent with previously reported values. ^{13}C NMR data were not reported. [10])

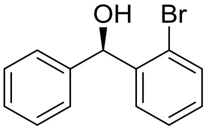


Diol 8: Following the general procedure, benzoxasilole **3i** (67.8 mg, 0.168 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The resulting diol was purified by silica gel chromatography (100:0→65:35 hexanes/EtOAc) to give 45.4 mg (80%) of **8** as a white solid. **HPLC analysis**: 97% *ee*, Chiralcel AD-H column, 10% ethanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 5.6 min (major), t_R = 6.1 min (minor). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.70 (s, 1H), 7.61 (d, J = 6.7 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.22 (s, 1H), 6.97 (d, J = 8.5 Hz, 1H), 6.10 (s, 1H), 3.14 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.0, 142.0, 131.2 (q, *J* = 32.5 Hz), 130.0, 129.4, 127.0 (q, *J* = 3.7 Hz), 126.4, 125.4 (*two overlapping quartets*), 124.1 (q, J = 272.6 Hz), 123.9 (q, J = 271.5 Hz), 123.5 (q, *J* = 3.8 Hz), 122.6 (q, *J* = 32.8 Hz), 117.8, 75.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.68, -61.81. **HRMS** (EI+) calcd for $[C_{15}H_{10}F_6O_2]^+$: *m/z* 336.0585, found 336.0585.

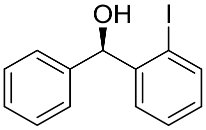
General procedure for halogenation of benzoxasilole products

In an N_2-filled glovebox, a 1 dram screw-top vial was charged with *N*-bromosuccinimide or *N*-iodosuccinimide (1.1 equiv) and AgF (4 equiv). To this vial was added a solution of benzoxasilole in acetonitrile (0.1 M). The vial was capped with a Teflon-lined screw-cap, and the resulting heterogeneous solution was stirred in the glovebox at rt in the dark until complete conversion was observed, as determined by TLC analysis (30 min – 1 h). The reaction mixture was poured onto aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The crude product was adsorbed onto Celite and purified by silica gel chromatography to provide the halogenated biaryl product.

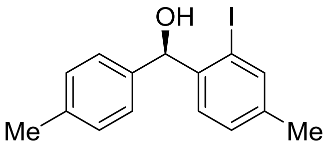
Spectral data for the products of halogenation:



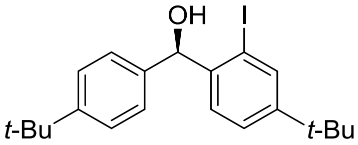
(2-Bromophenyl)phenylmethanol 9: Following the general procedure, benzoxasilole **3a** (67.1 mg, 0.250 mmol) was brominated with NBS/AgF at rt. The resulting product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 44.7 mg (61%) of **9** as a colorless oil. **HPLC analysis**: 98% *ee*, Chiralcel OD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 9.8 min (major), t_R = 13.5 min (minor). $[\alpha]_D^{25}$ = +40.1 (c 1.05, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.26 (m, 4H), 7.16 (td, *J* = 7.8, 1.6 Hz, 1H), 6.19 (s, 1H), 2.49 (br s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 142.1, 132.8, 129.1, 128.4 (*two overlapping resonances*), 127.7, 127.7, 127.0, 122.7, 74.7. (^{1}H and ^{13}C NMR data were consistent with previously reported values.[11])



(2-Iodophenyl)phenylmethanol 10a: Following the general procedure, benzoxasilole **3a** (67.0 mg, 0.250 mmol) was iodinated with NIS/AgF at rt. The resulting product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 67.6 mg (80%) of **7a** as a colorless oil. **HPLC analysis**: 98% *ee*, Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 19.7 min (major), t_R = 27.3 min (minor). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.85 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.45 – 7.28 (m, 6H), 7.00 (td, *J* = 7.7, 1.7 Hz, 1H), 6.05 (s, 1H), 2.64 (br s, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 145.3, 142.0, 139.4, 129.3, 128.5, 128.4, 128.3, 127.7, 127.2, 98.6, 78.9. (^{1}H and ^{13}C NMR data were consistent with previously reported values.[12])



Diarylmethanol 10b: Following the general procedure, benzoxasilole **3b** (29.4 mg, 0.0992 mmol) was iodinated with NIS/AgF at rt. The resulting product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 29.6 mg (80%) of **10b** as a colorless oil. **HPLC analysis**: 96% *ee*, Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 14.3 min (major), t_R = 15.2 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.11 (m, 3H), 5.99 (s, 1H), 2.33 (s, 3H), 2.29 (overlapping s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 139.9, 139.4, 139.36, 137.35, 129.4, 129.1, 127.9, 127.1, 98.5, 78.6, 21.1, 20.4. **HRMS** (EI+) calcd for $[C_{15}H_{15}IO]^+$: *m/z* 338.0168, found 338.0168.



Diarylmethanol 10c: Following the general procedure, benzoxasilole **3c** (38.2 mg, 0.100 mmol) was iodinated with NIS/AgF at rt. The resulting product was purified by silica gel chromatography (100:0→80:20 hexanes/EtOAc) to give 31.0 mg (73%) of **10c** as a colorless foam. **HPLC analysis**: 86% *ee*, Chiralcel OD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 5.6 min (minor), t_R = 6.3 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.36 (s, 4H), 6.02 (d, *J* = 2.5 Hz, 1H), 2.30 (d, *J* = 3.1 Hz, 1H), 1.31 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 150.6, 142.6, 139.4, 136.5, 127.8, 126.8, 125.8, 125.3, 98.9, 78.7, 34.5, 34.4, 31.3, 31.2. **HRMS** (EI+) calcd for $[C_{21}H_{27}IO]^+$: *m/z* 422.1107, found 422.1107.

Assignment of the absolute configuration of the benzoxasilole products

The absolute configuration of the products was assigned based on the following observations. First, the bromination of **3a** yielded (2-bromophenyl)phenylmethanol **9** whose optical rotation value $[\alpha]_D^{25}$ was +40.1 (c 1.05, $CHCl_3$). The (*S*)-enantiomer of **9** was reported to have an $[\alpha]_D^{22}$ value of -41.9 (c 1.19, $CHCl_3$).[13] Therefore, the compounds **3a** and **9** were assigned to have the (*R*) absolute configuration. Because **3a** was prepared using the catalyst derived from a catASium ligand **L47**, the compounds that were formed from the catalyst containing catASium ligands (**L46**, **L47**) were assigned to be (*R*). Second, the silylation of enantioenriched diarylmethanols occurs with site-selectivity that is consistent with the formation of (*R*)-enantiomers. Lastly, the benzoxasiloles formed with the catalyst containing the Walphos ligands (**L17**, **L18**, **L22**) were assigned to be the (*S*)-enantiomers because the absolute configuration of the major enantiomers formed from those catalysts had the opposite configuration to that formed from the catalyst containing **L46** and **L47** in most cases (See Table S1).

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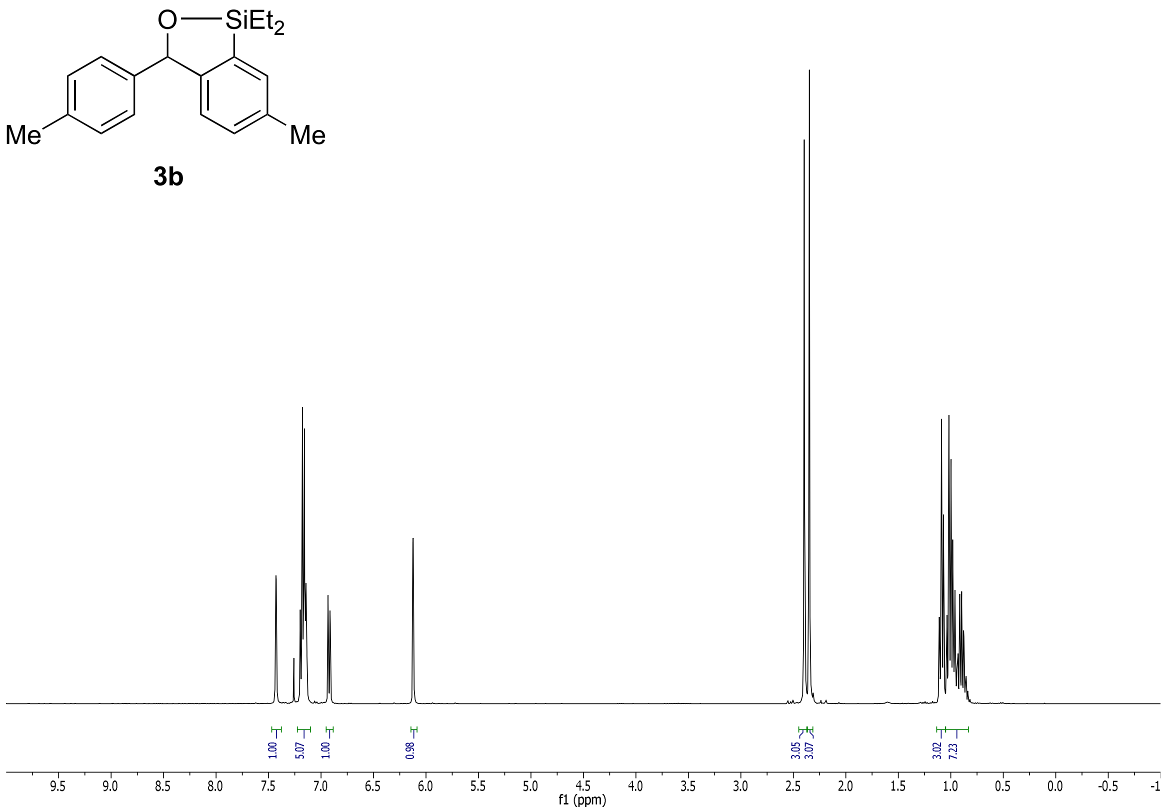

3b

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1.00
0.98
3.05
3.07
3.02
7.23
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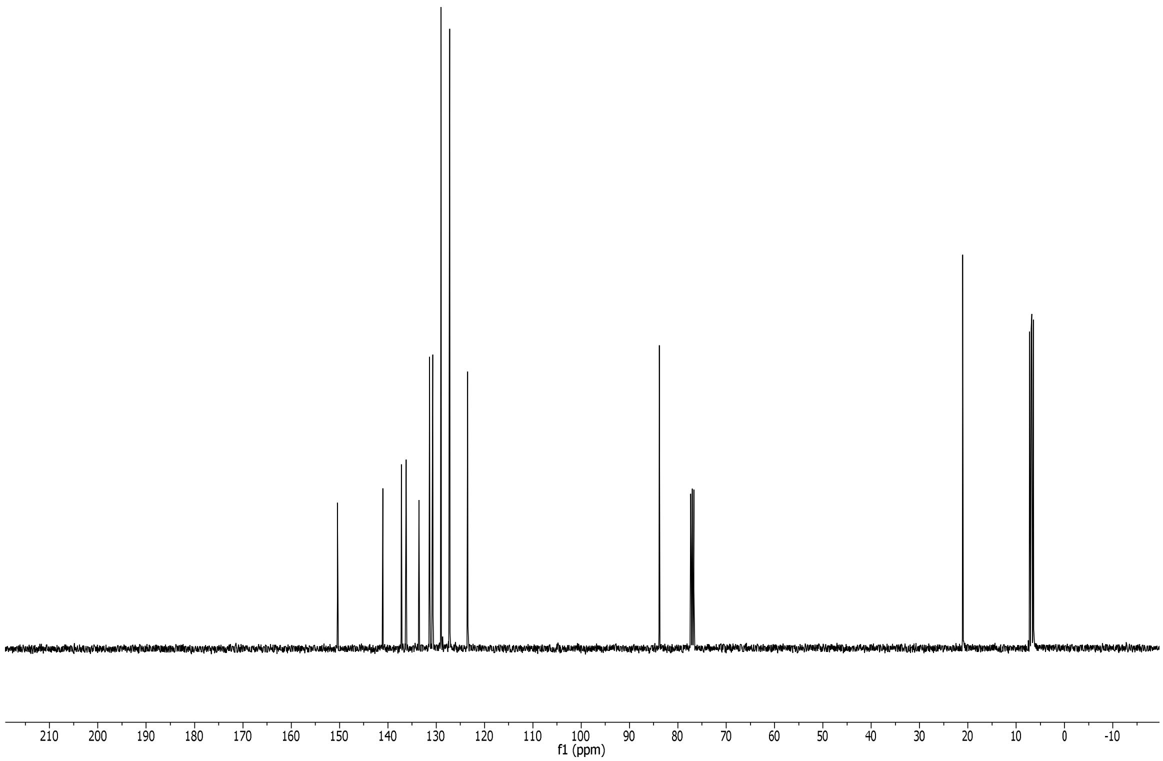

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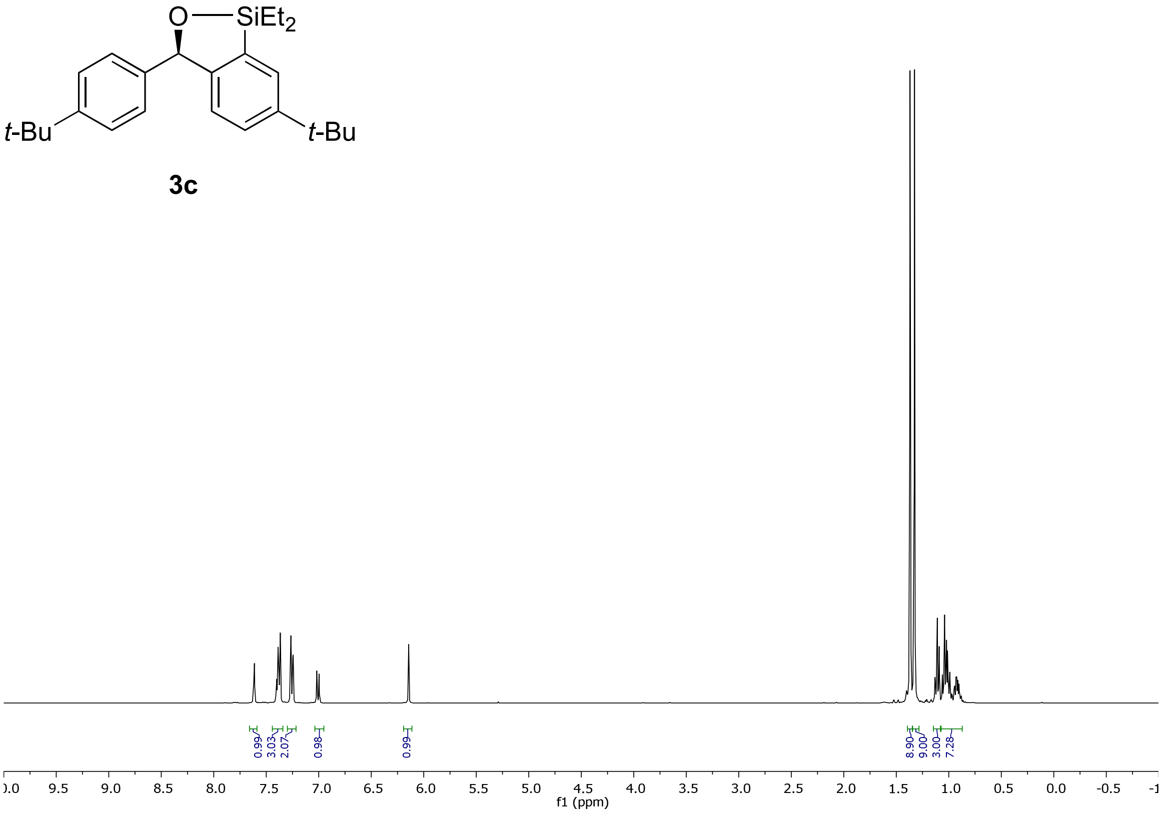
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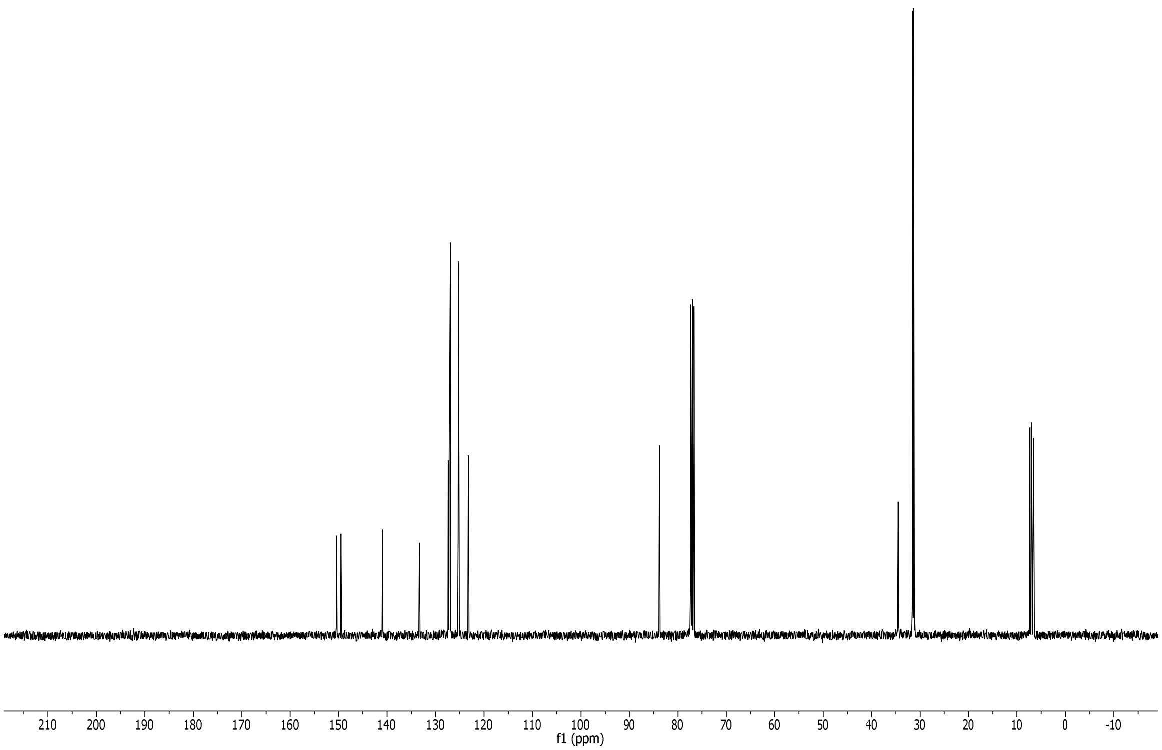
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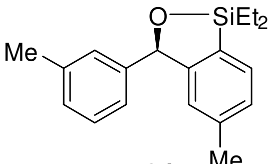
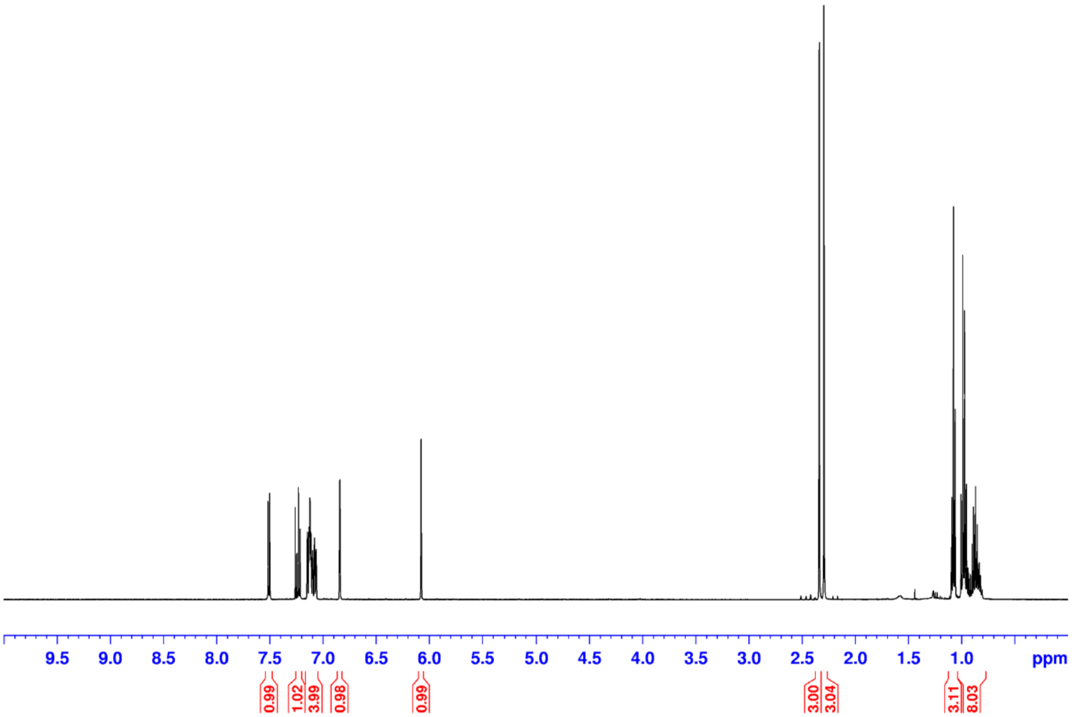


3d



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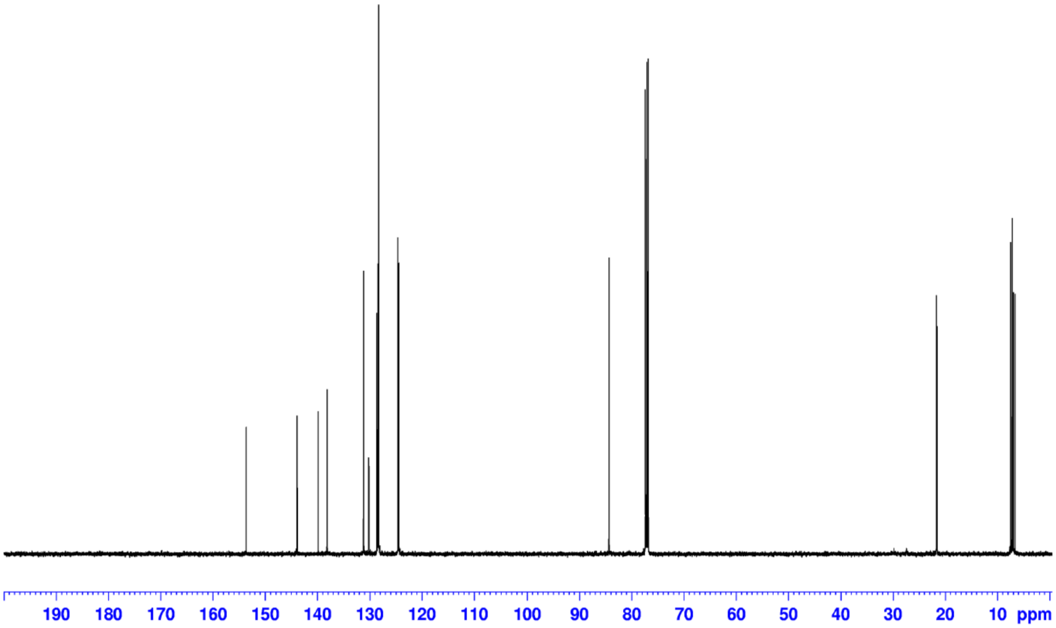

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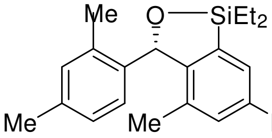
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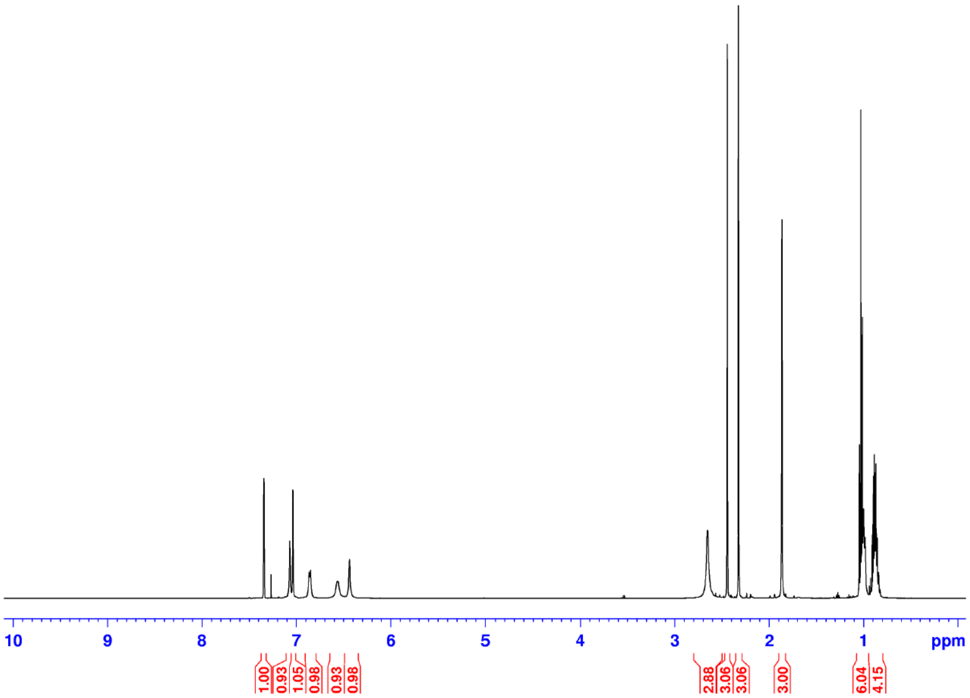
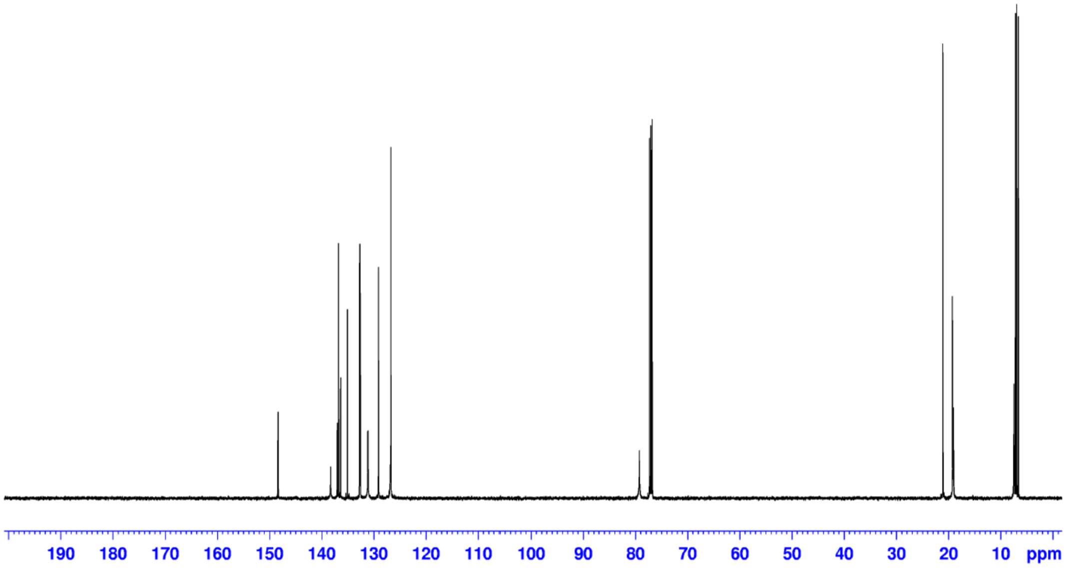
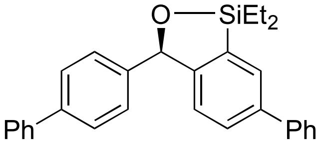
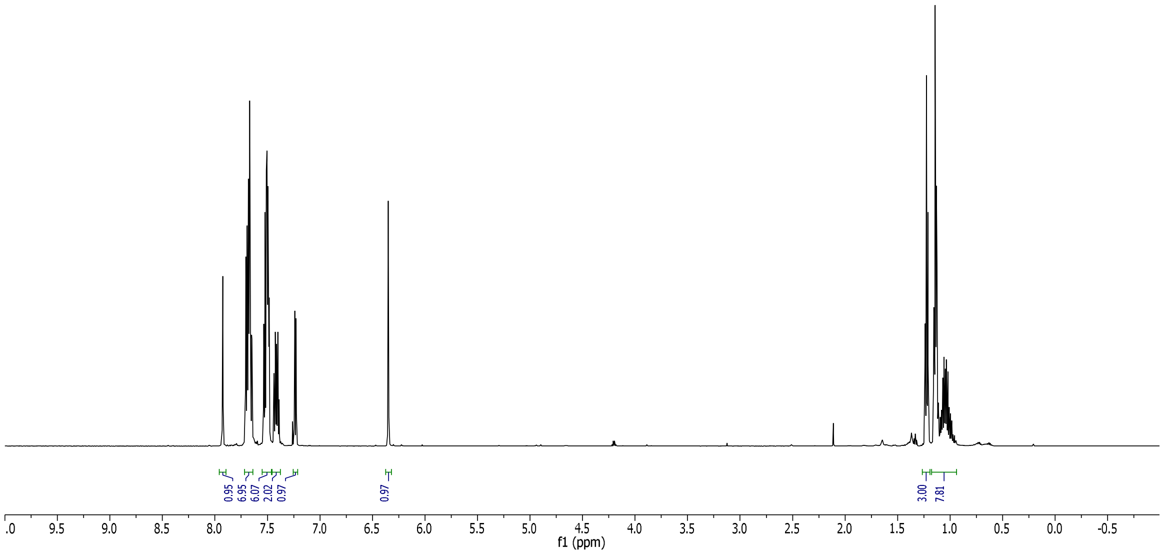
3e

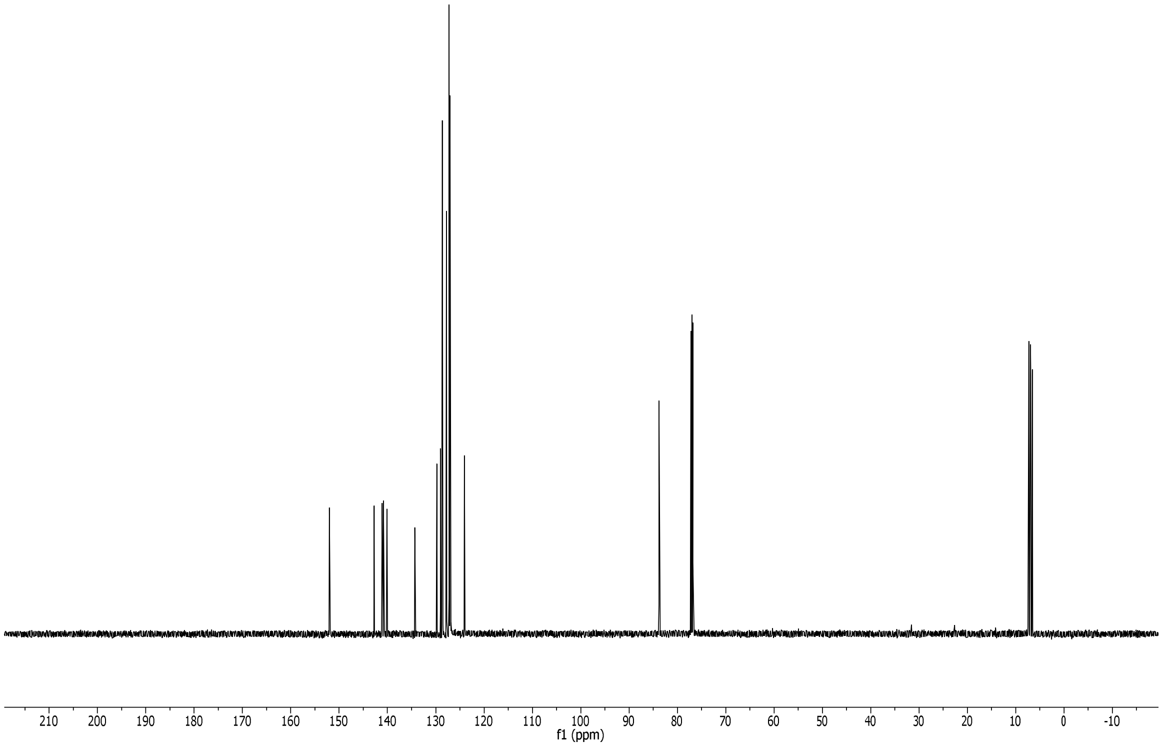

10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.93
1.05
0.98
0.93
0.98
2.88
3.06
3.06
3.00
6.04
4.15

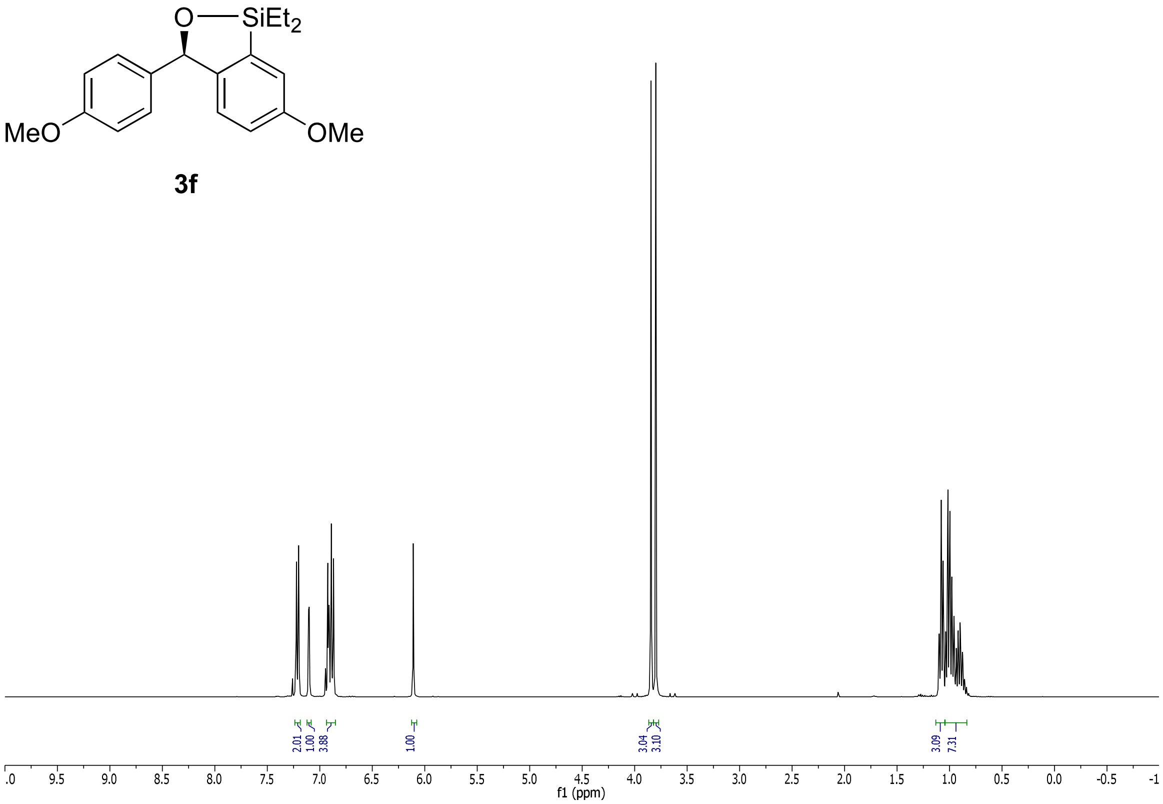

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
SiEt2
Ph
Ph

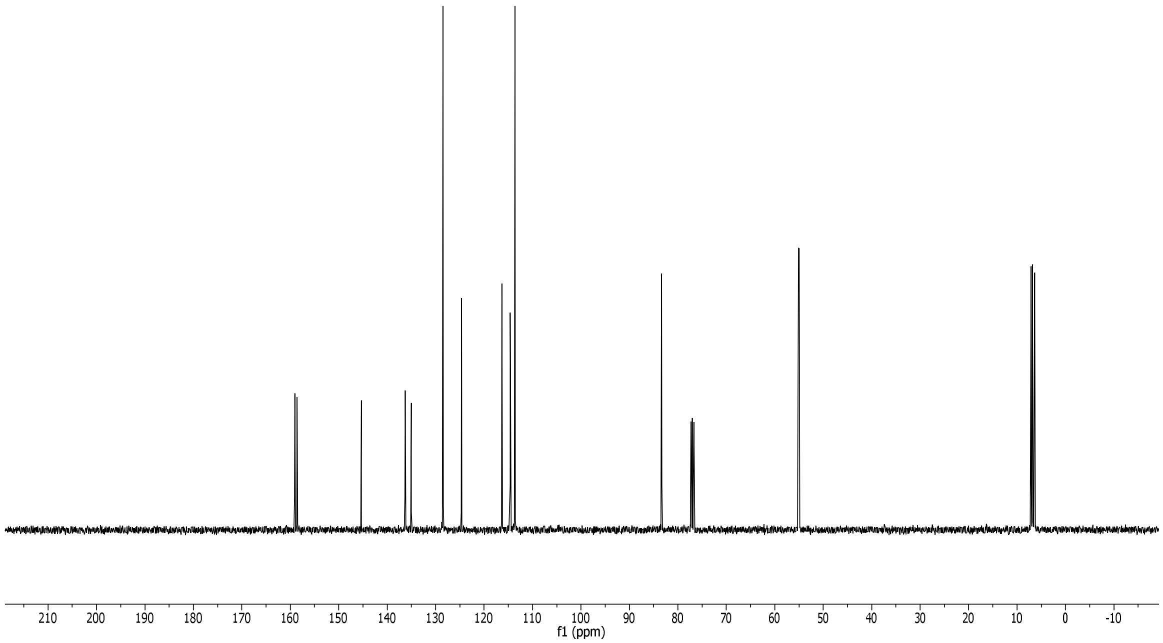
3f

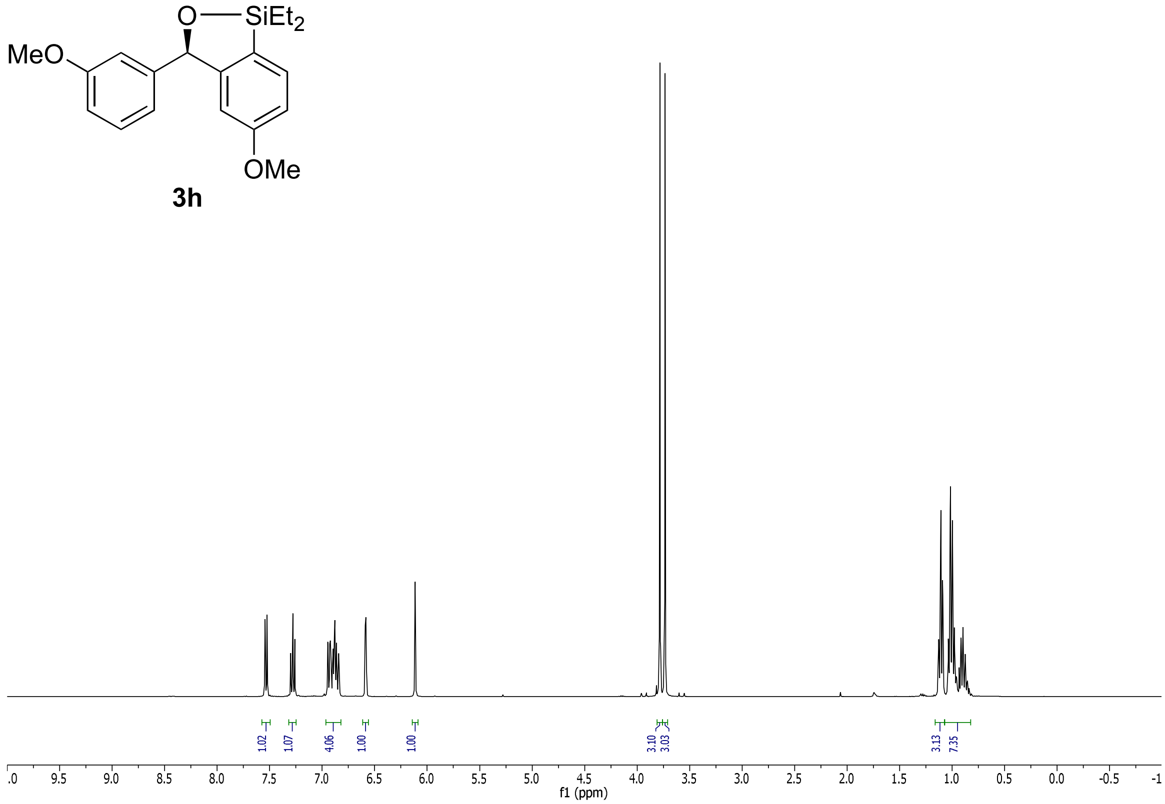

0.95
6.95
6.07
2.02
0.97
0.97
3.00
7.81
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

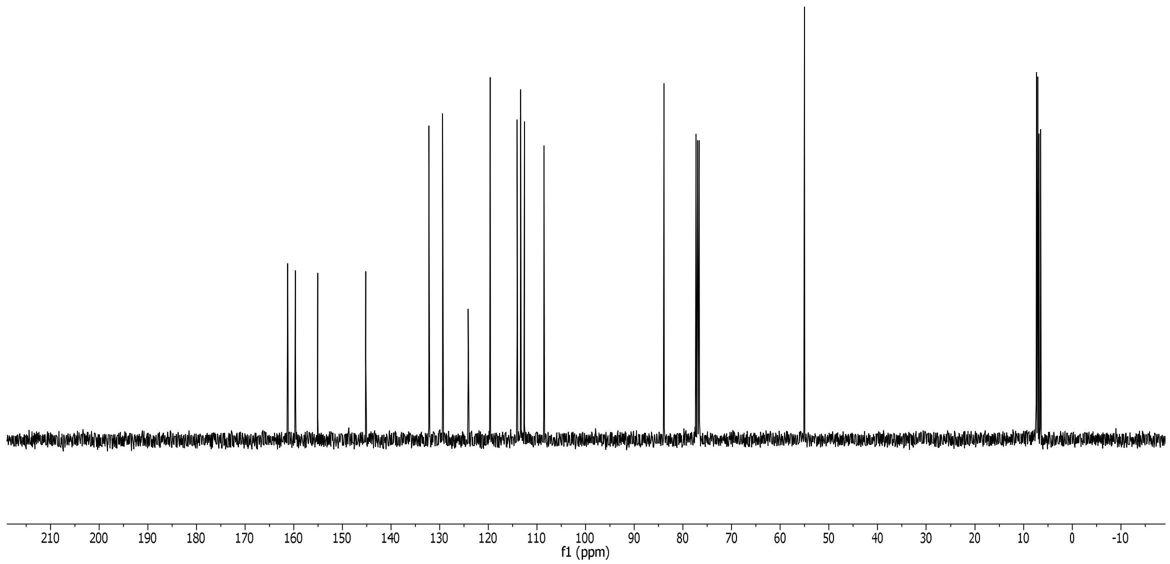

O
SiEt2
MeO
OMe
2.01
1.00
3.88
1.00
3.04
3.10
3.09
7.31
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

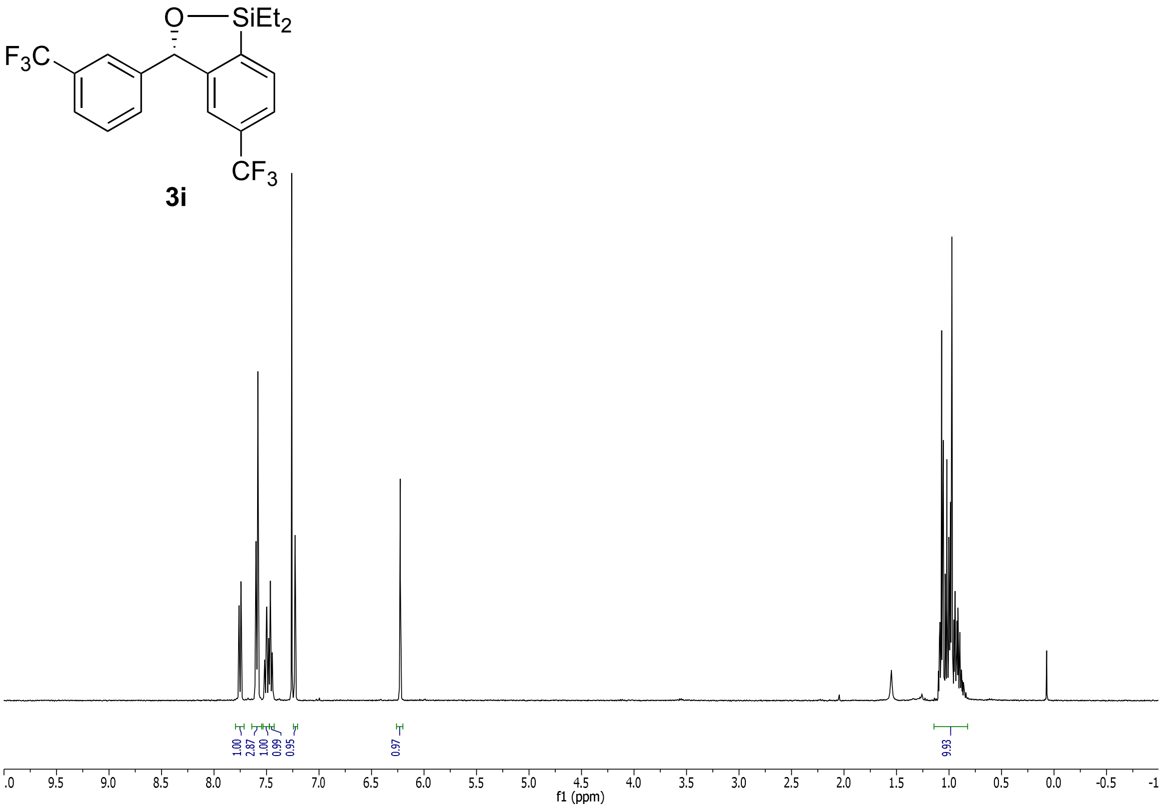
3f


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

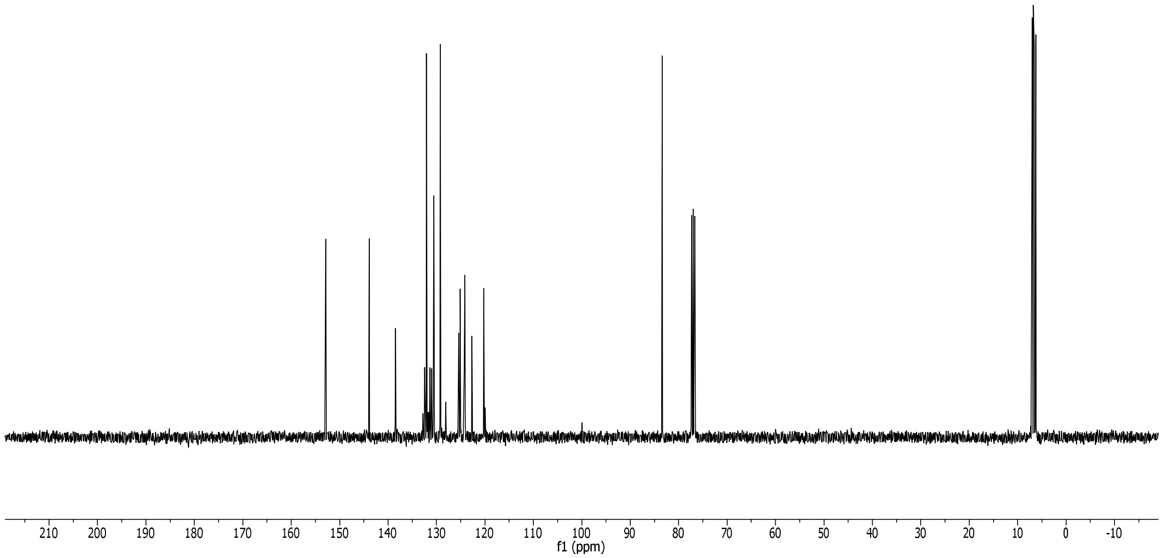

O
SiEt2
MeO
OMe
1.02
1.07
4.06
1.00
1.00
3.10
3.03
3.13
7.35
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

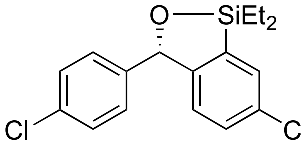
3h


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3i

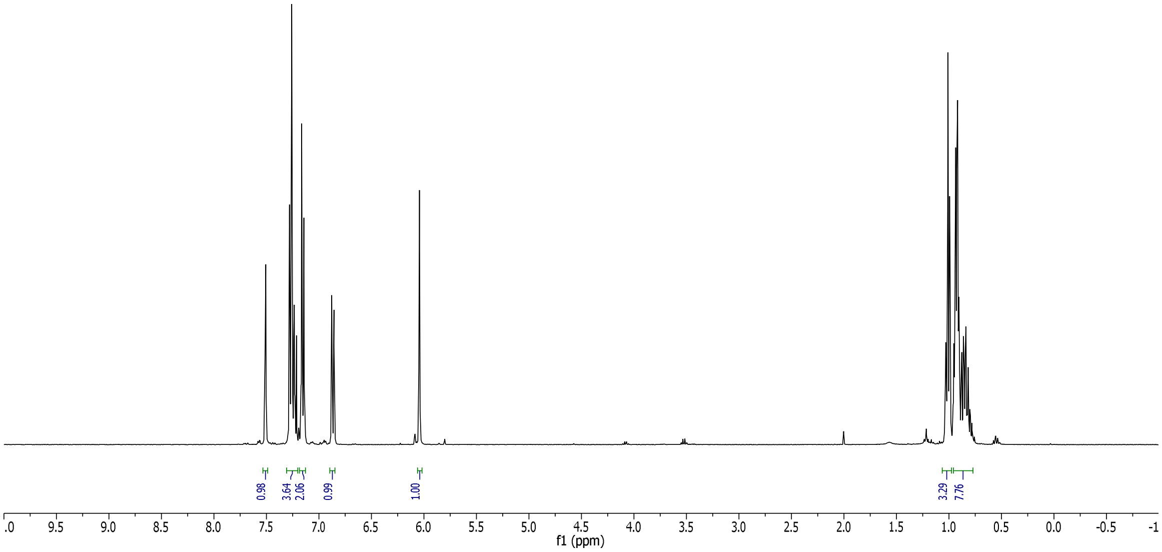
O
SiEt$_2$
F$_3$C
CF$_3$
1.00
2.87
1.00
0.99
0.95
0.97
9.93
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

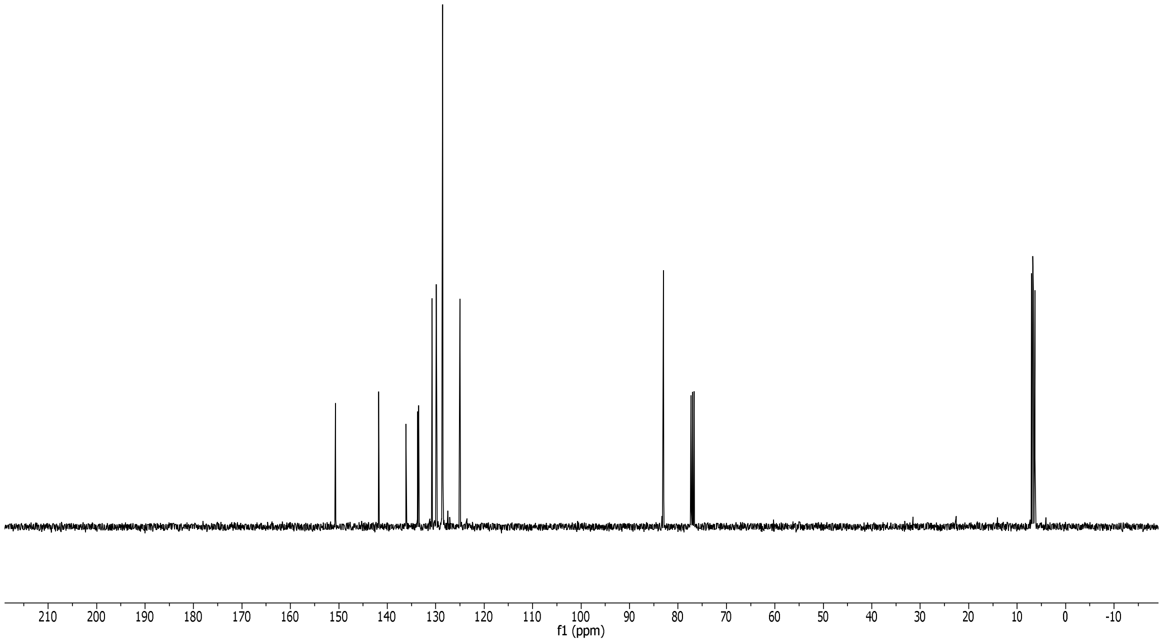


O
SiEt2
Cl
Cl

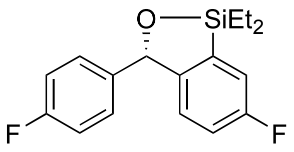
3j



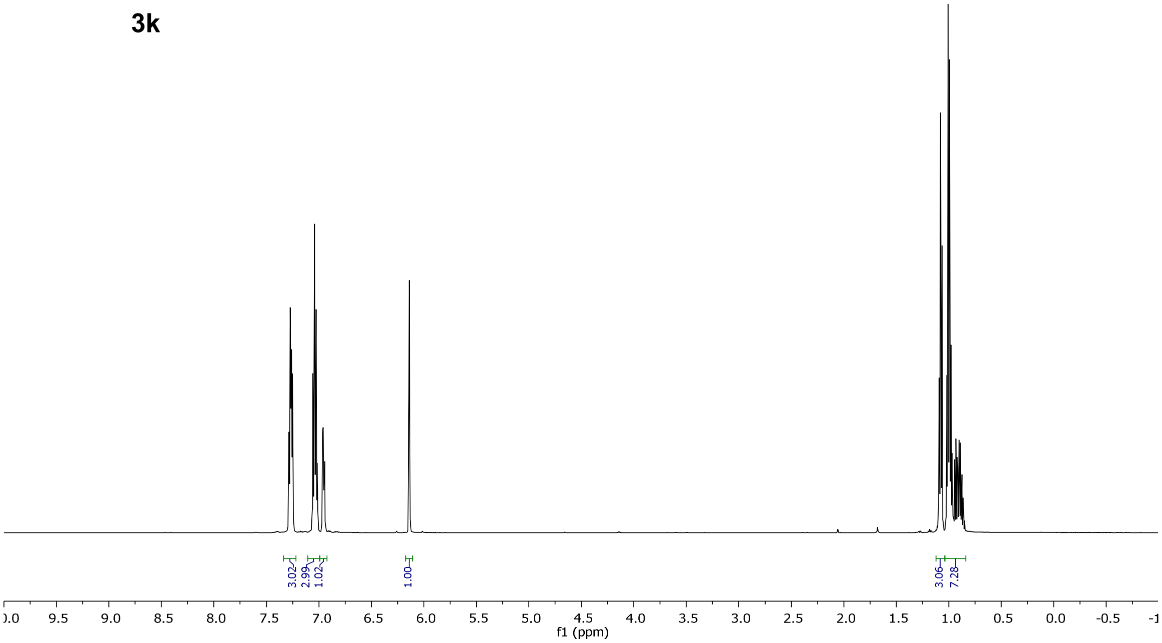
0.98
3.64
2.06
0.99
1.00
3.29
7.76
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

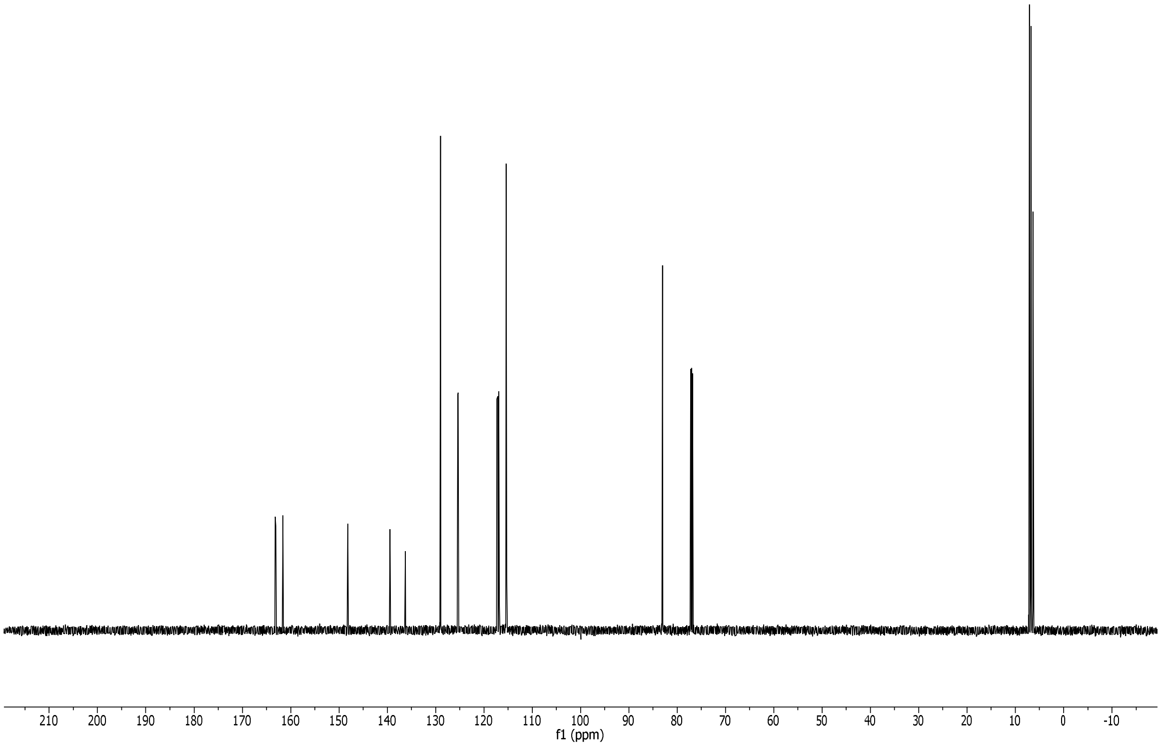


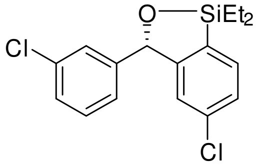
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
SiEt2
F
F

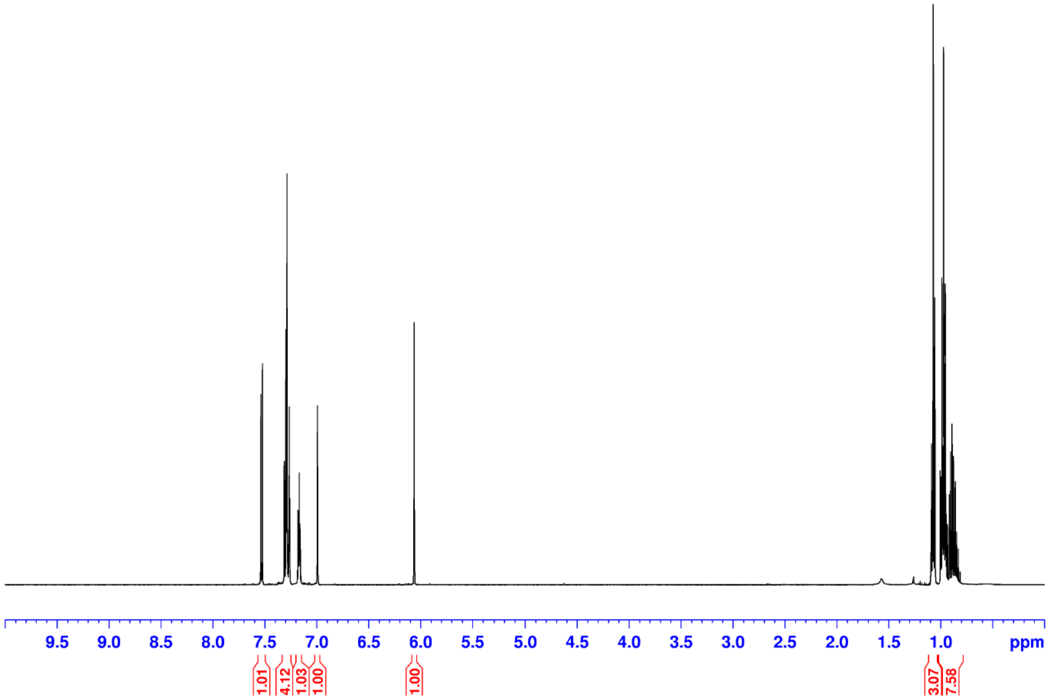
3k

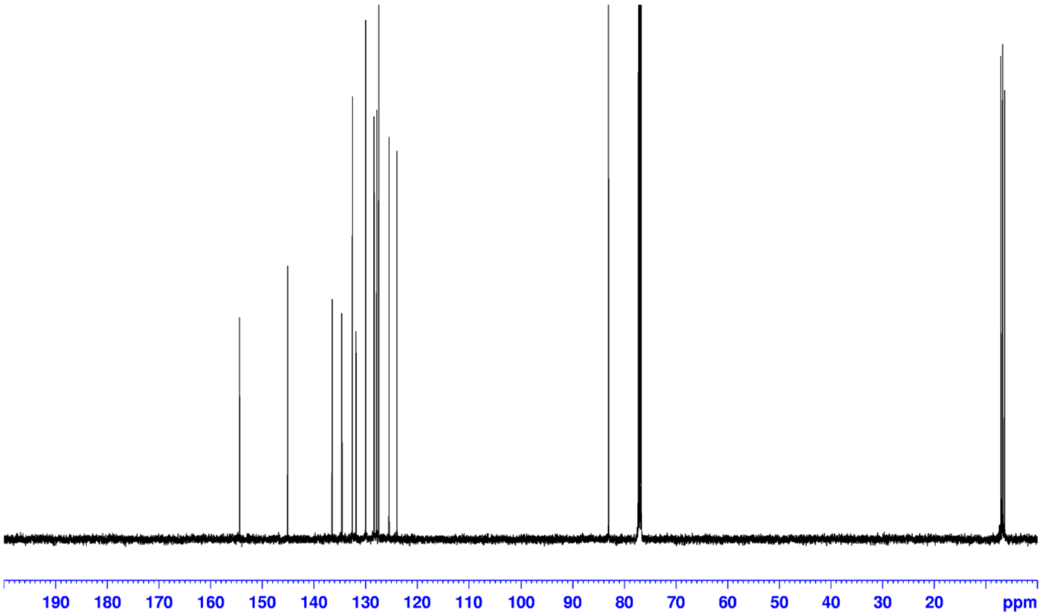

3.02
2.99
1.02
1.00
3.06
7.28
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

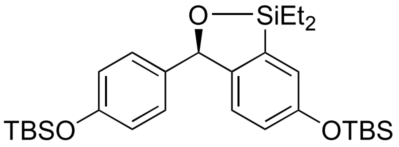

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
SiEt2
Cl
Cl

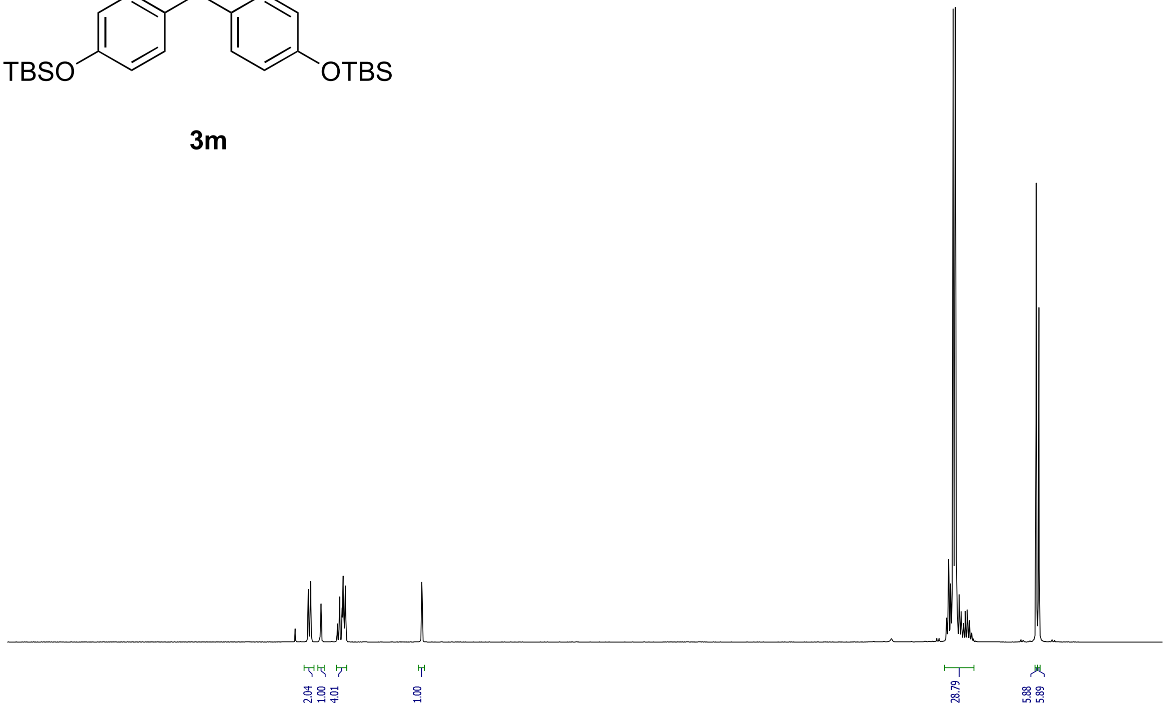
3l

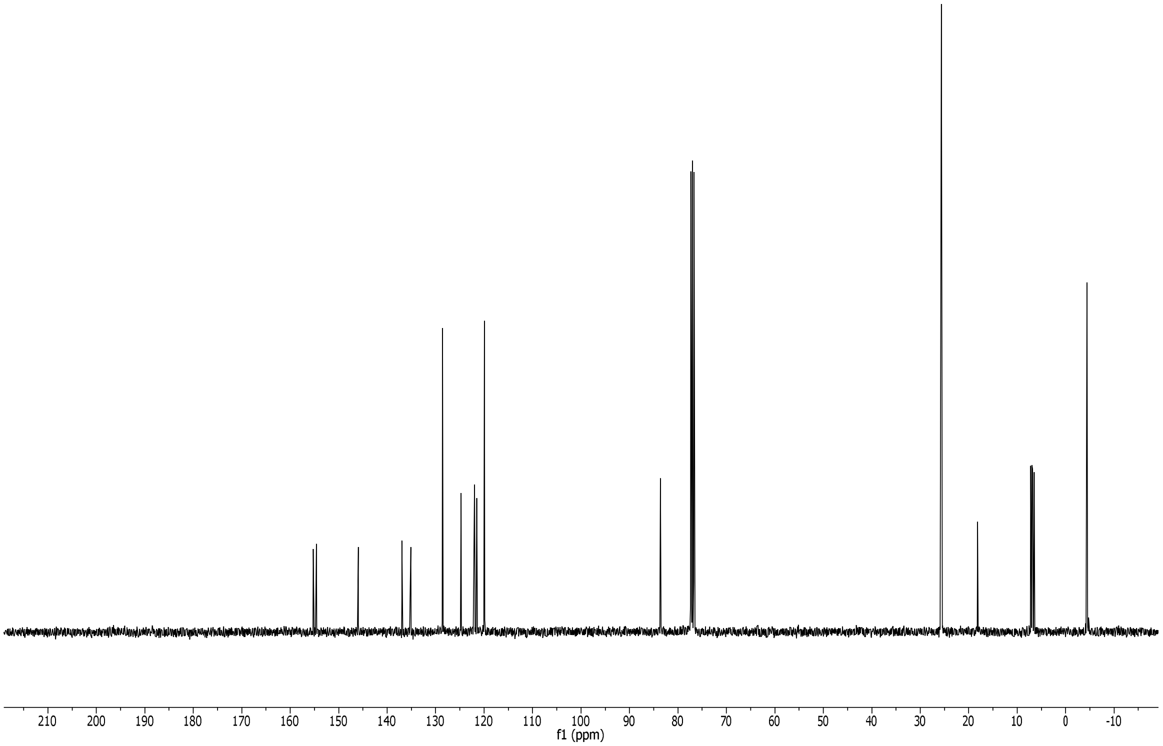

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.01
4.12
1.03
1.00
1.00
3.07
7.58

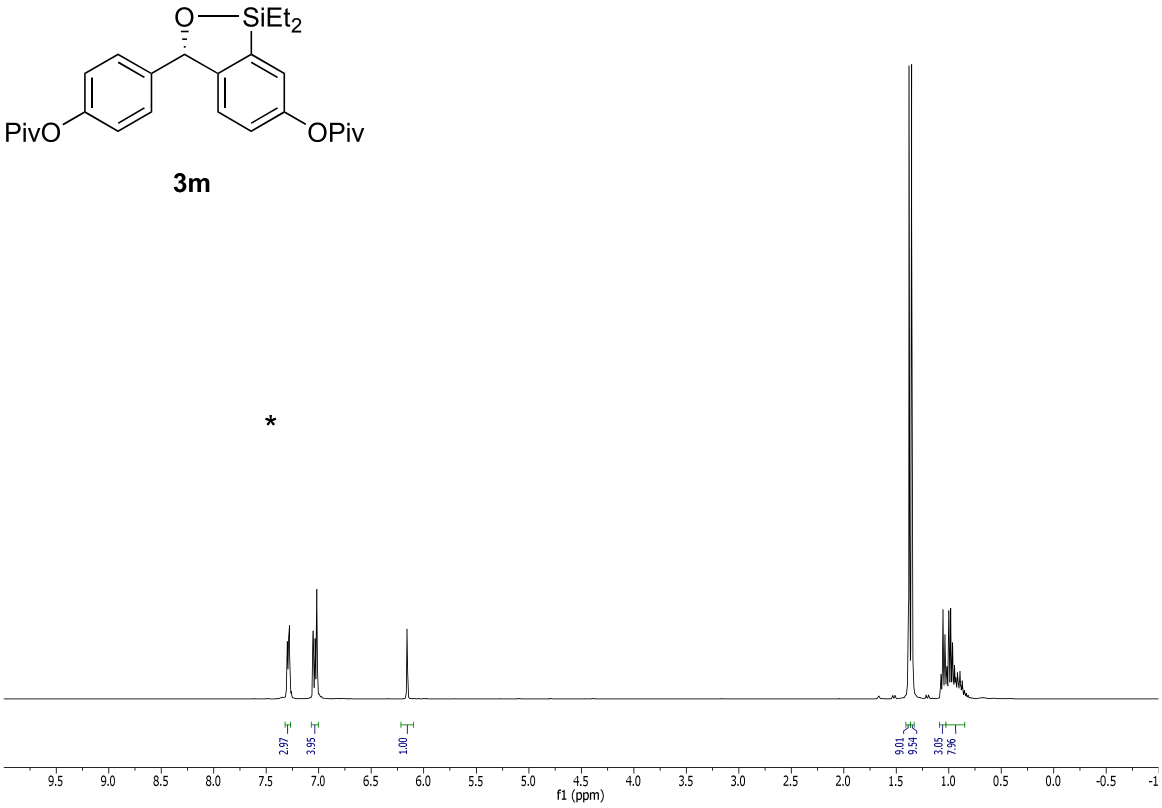

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


O
SiEt$_2$
TBSO
OTBS

3m

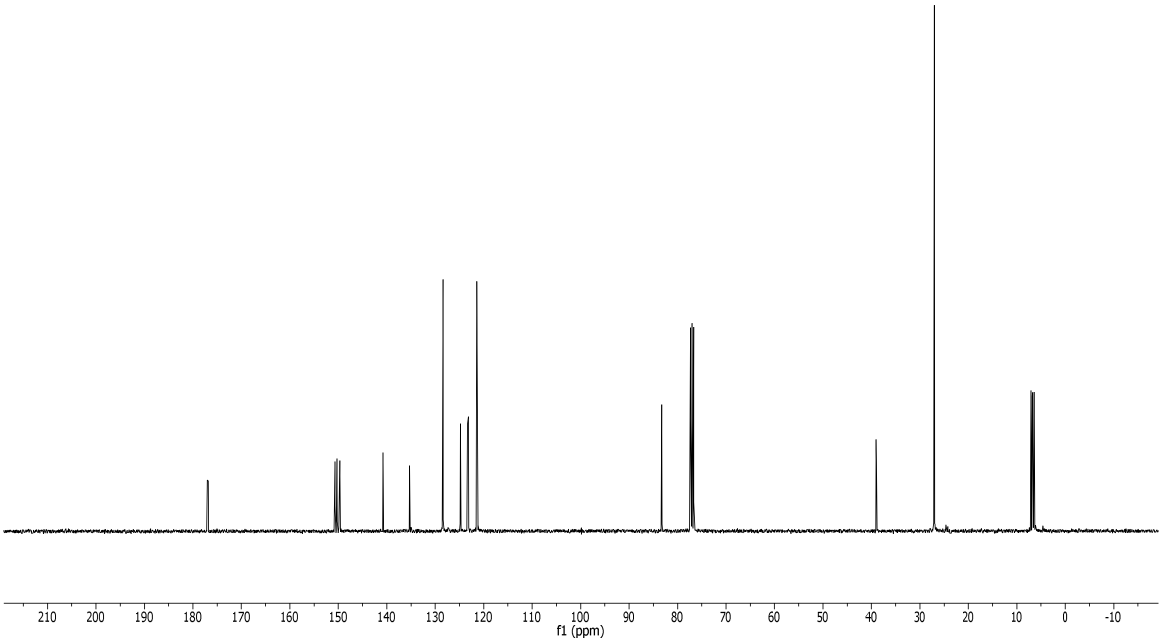

2.04
1.00
4.01
1.00
28.79
5.88
5.89
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

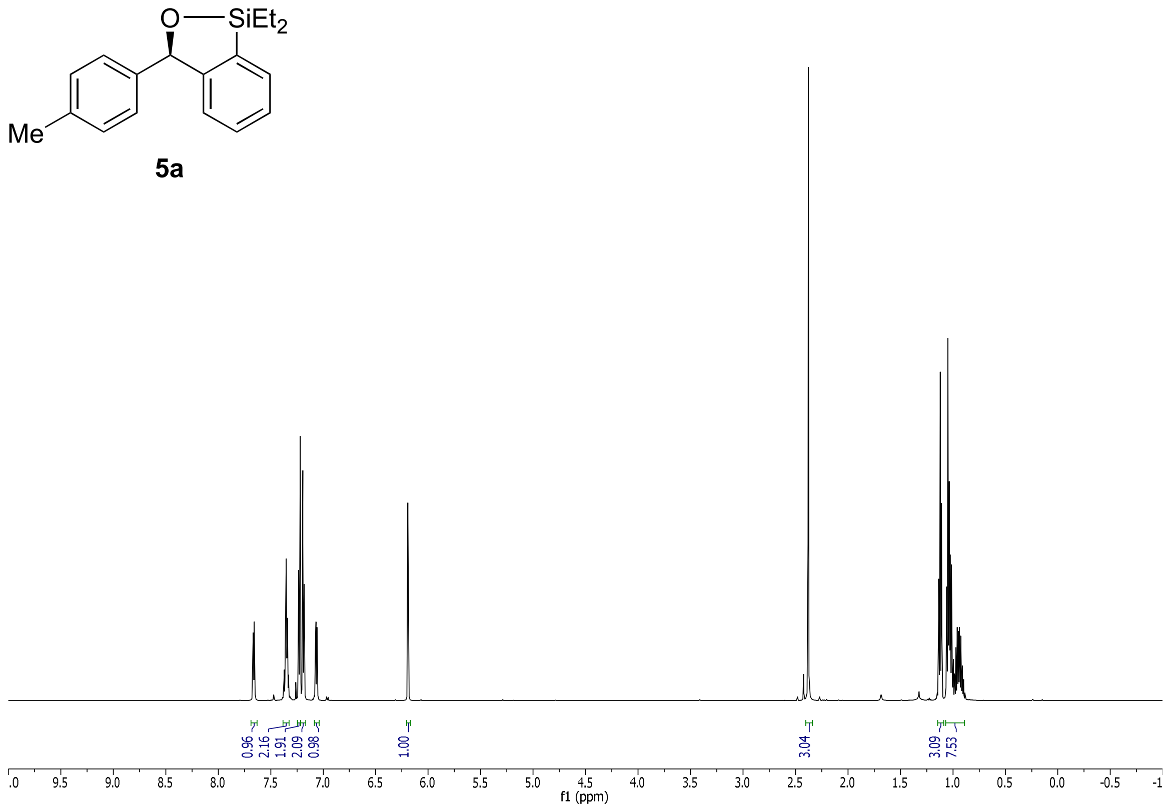


3m

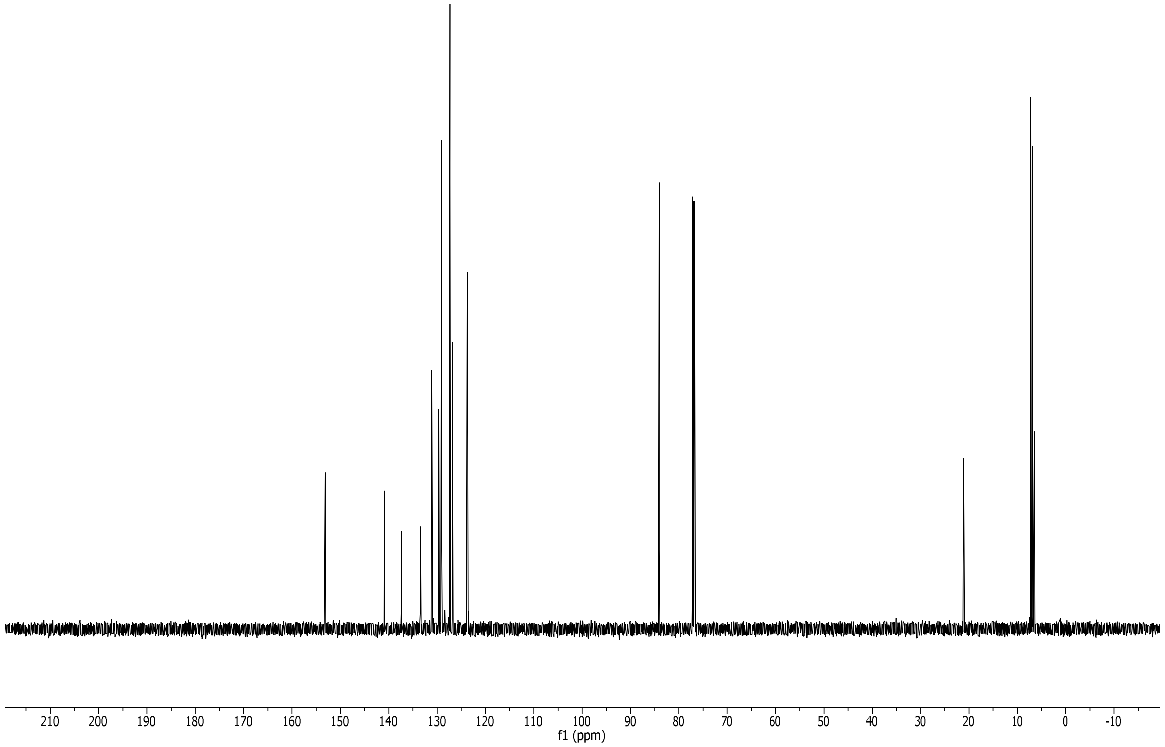
O
SiEt2
PivO
OPiv
*
2.97
3.95
1.00
9.01
9.54
3.05
7.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

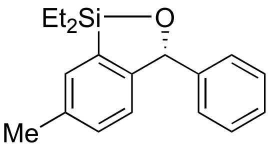


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

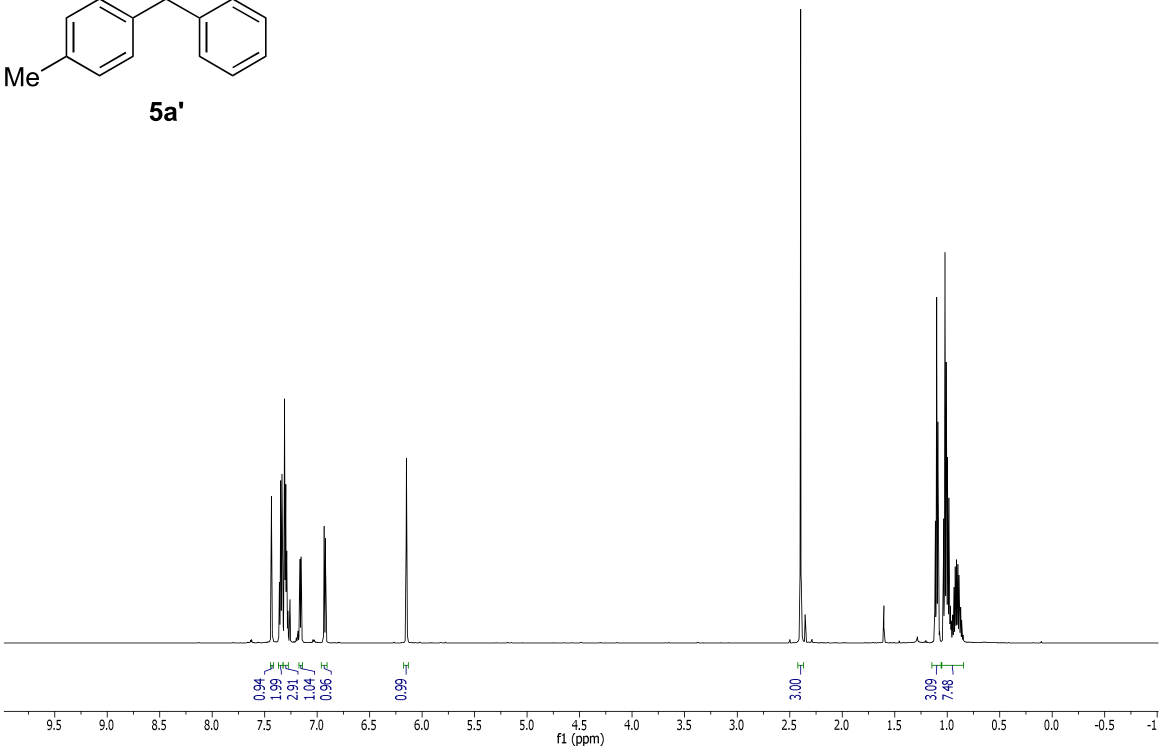

O
SiEt2
Me
0.96
2.16
1.91
2.09
0.98
1.00
3.04
3.09
7.53
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

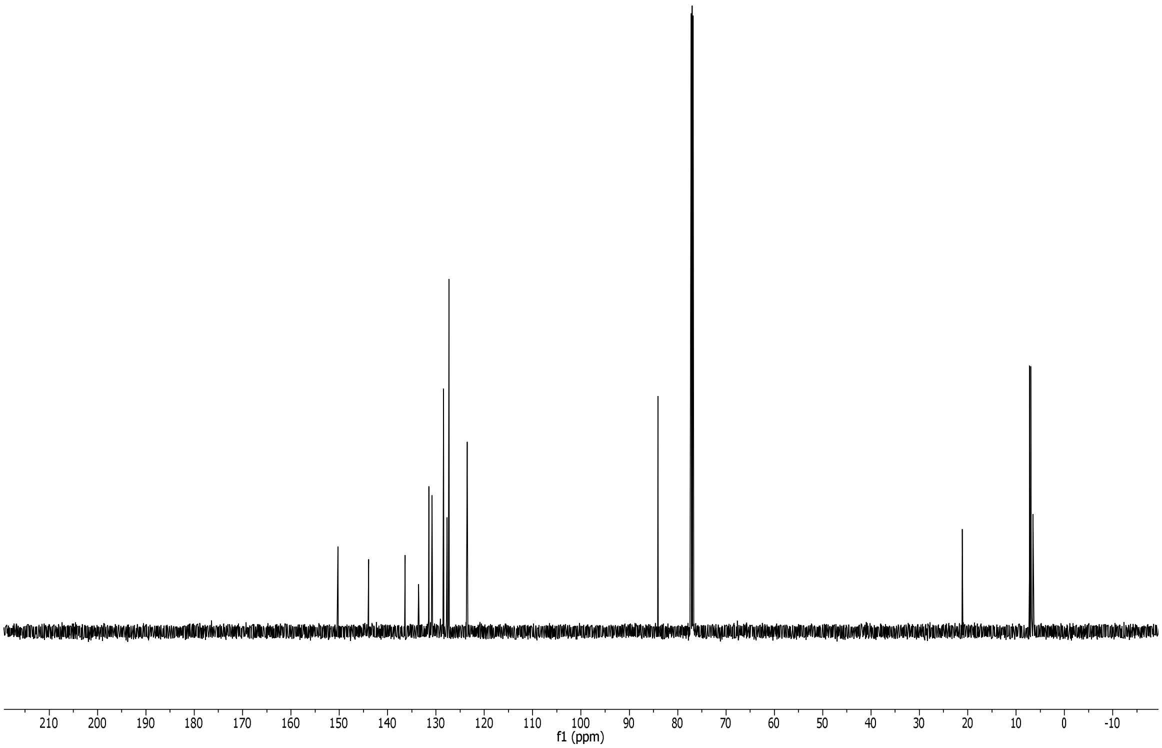
5a

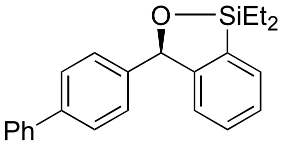

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Et2Si
O
Me

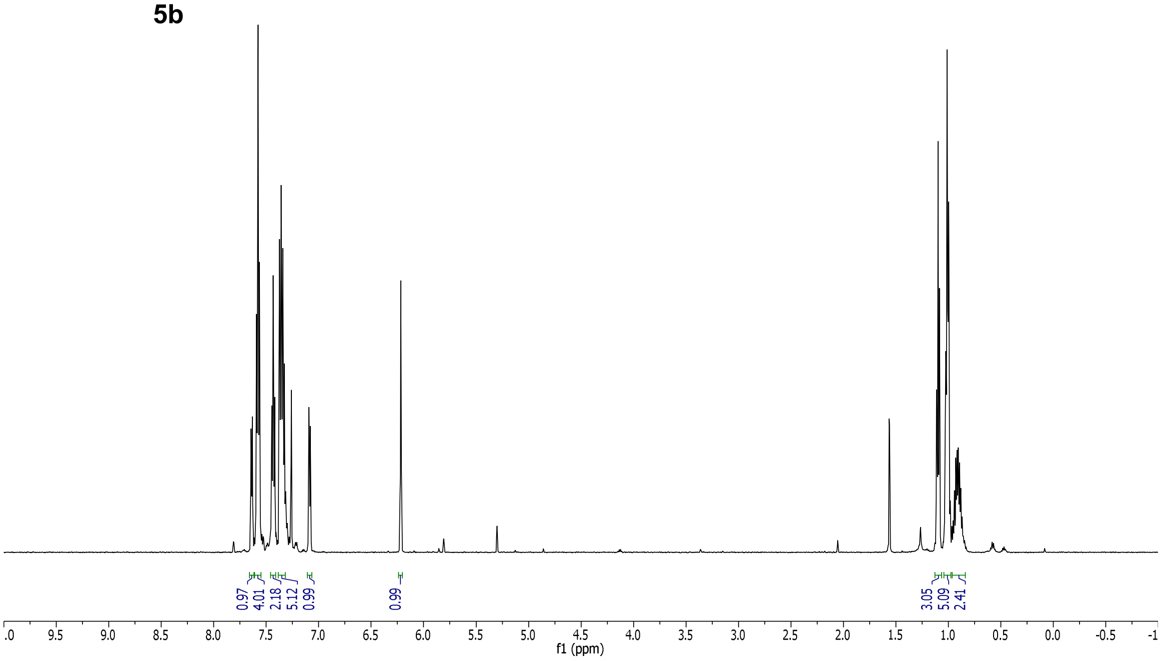
5a'

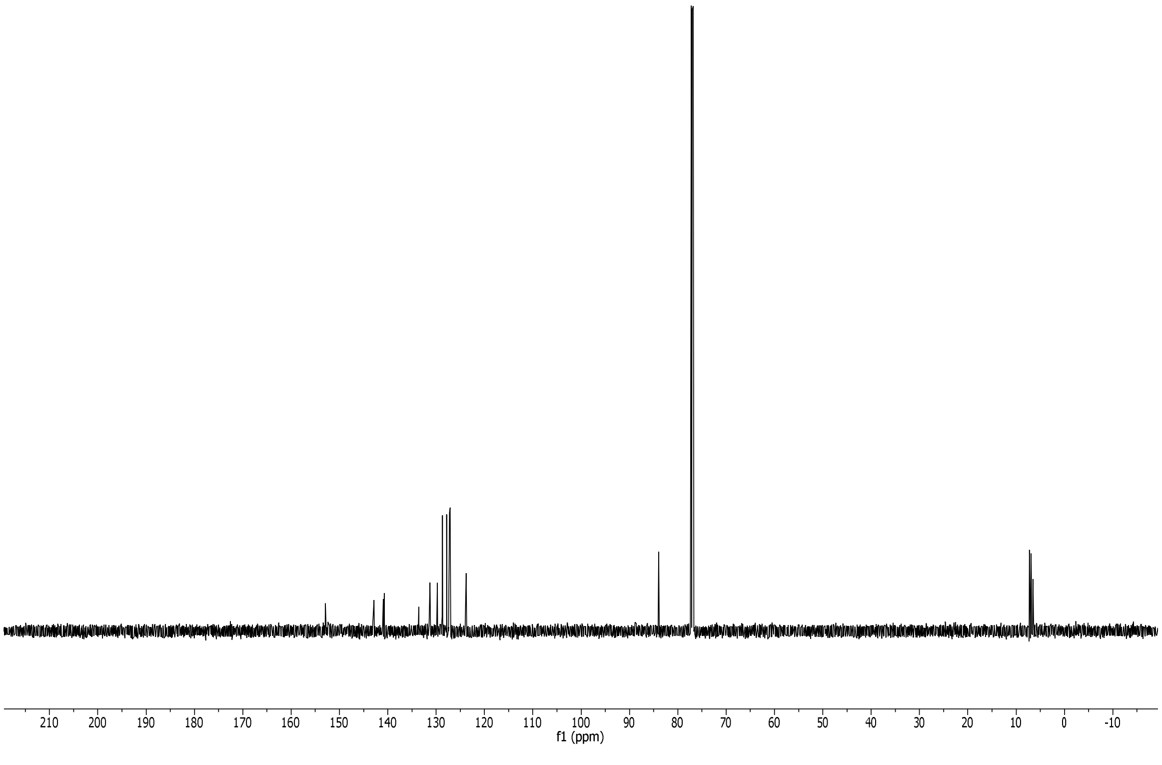

0.94
1.99
2.91
1.04
0.96
0.99
3.00
3.09
7.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

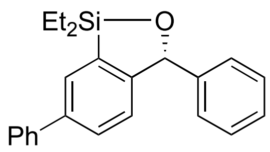

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
SiEt2
Ph

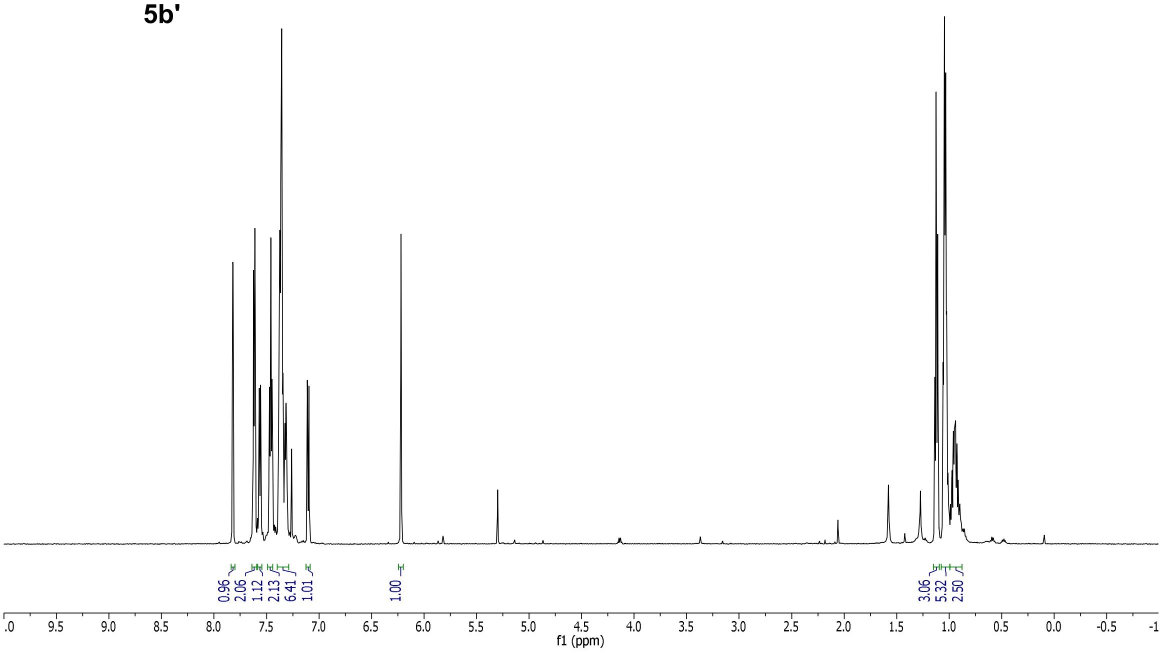
5b

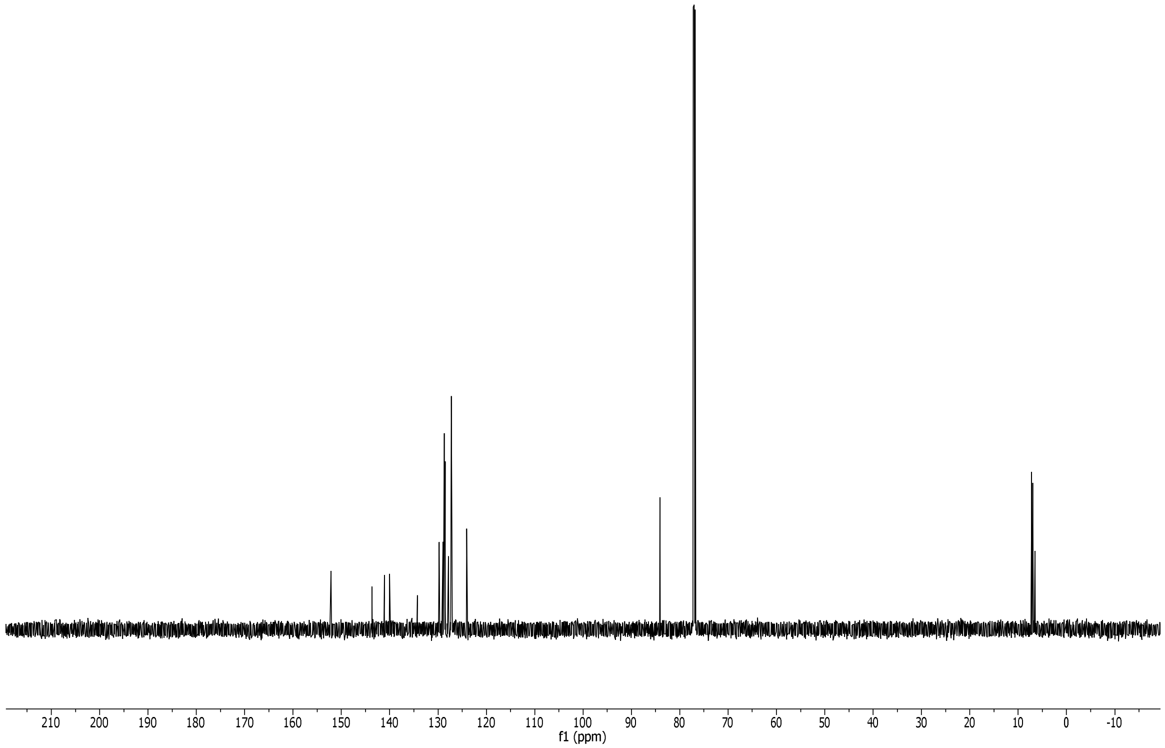

0.97
4.01
2.18
5.12
0.99
0.99
3.05
5.09
2.41
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

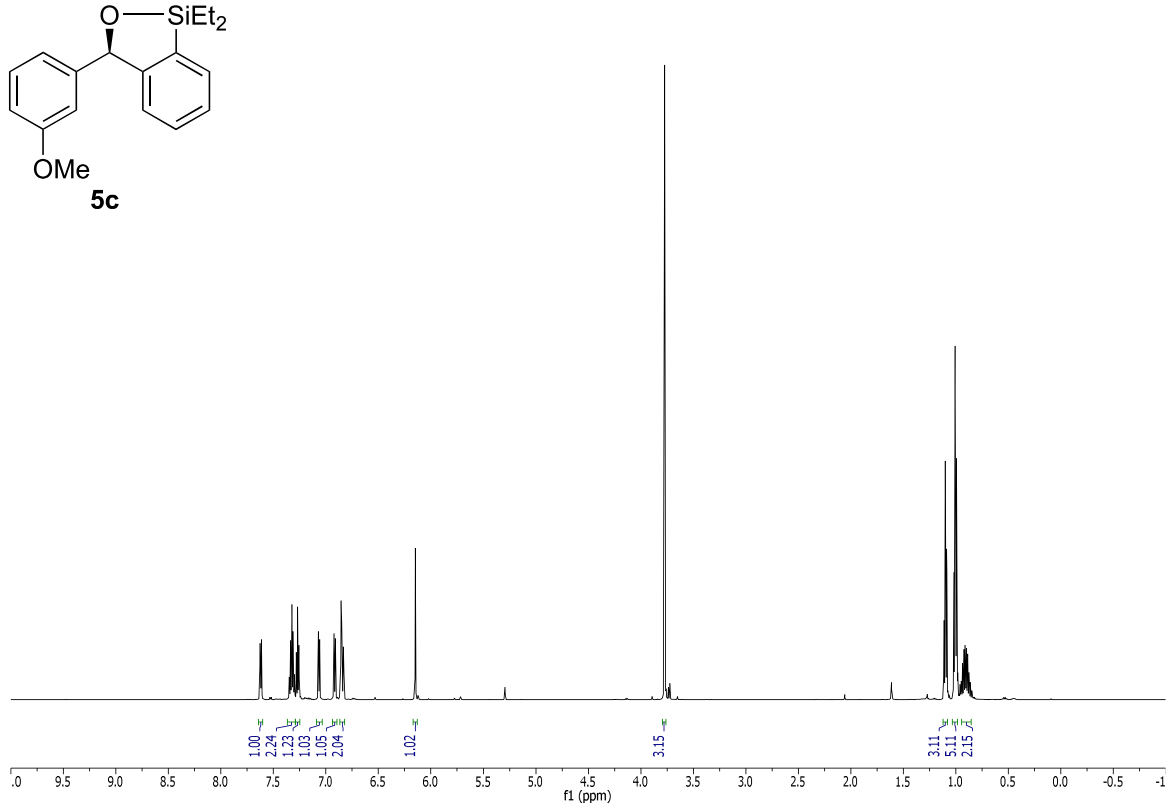

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Et2Si
O
Ph

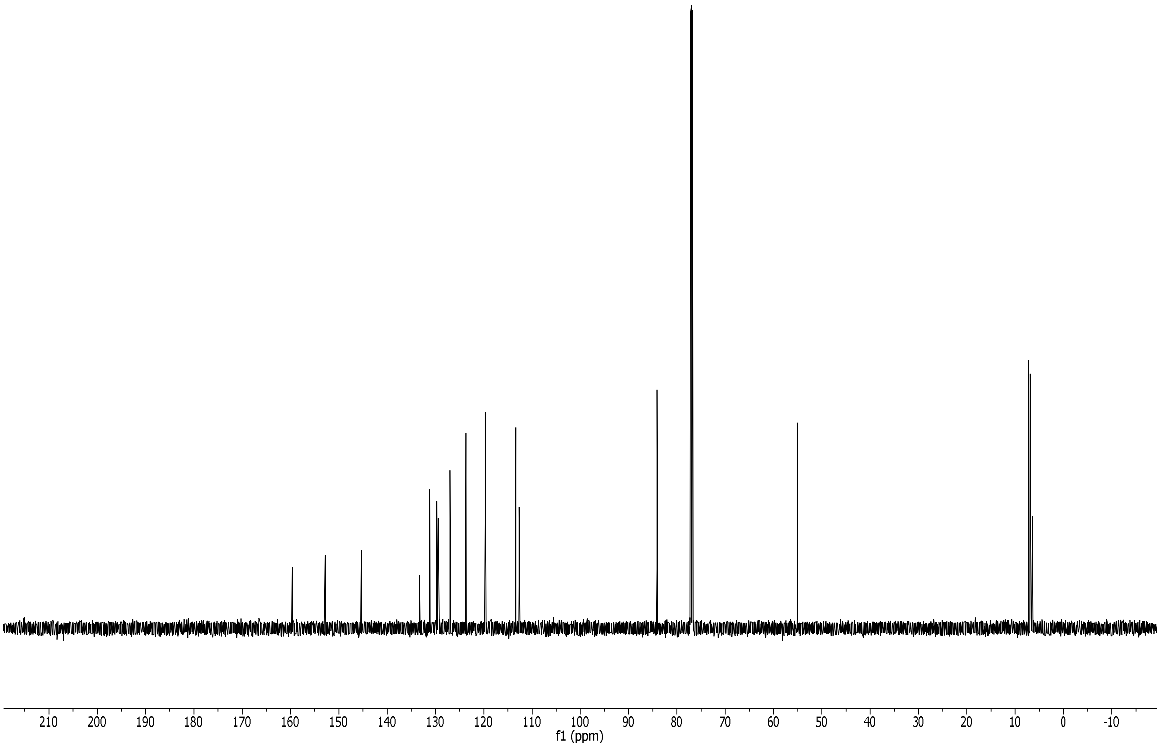
5b'


0.96
2.06
1.12
2.13
6.41
1.01
1.00
3.06
5.32
2.50
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

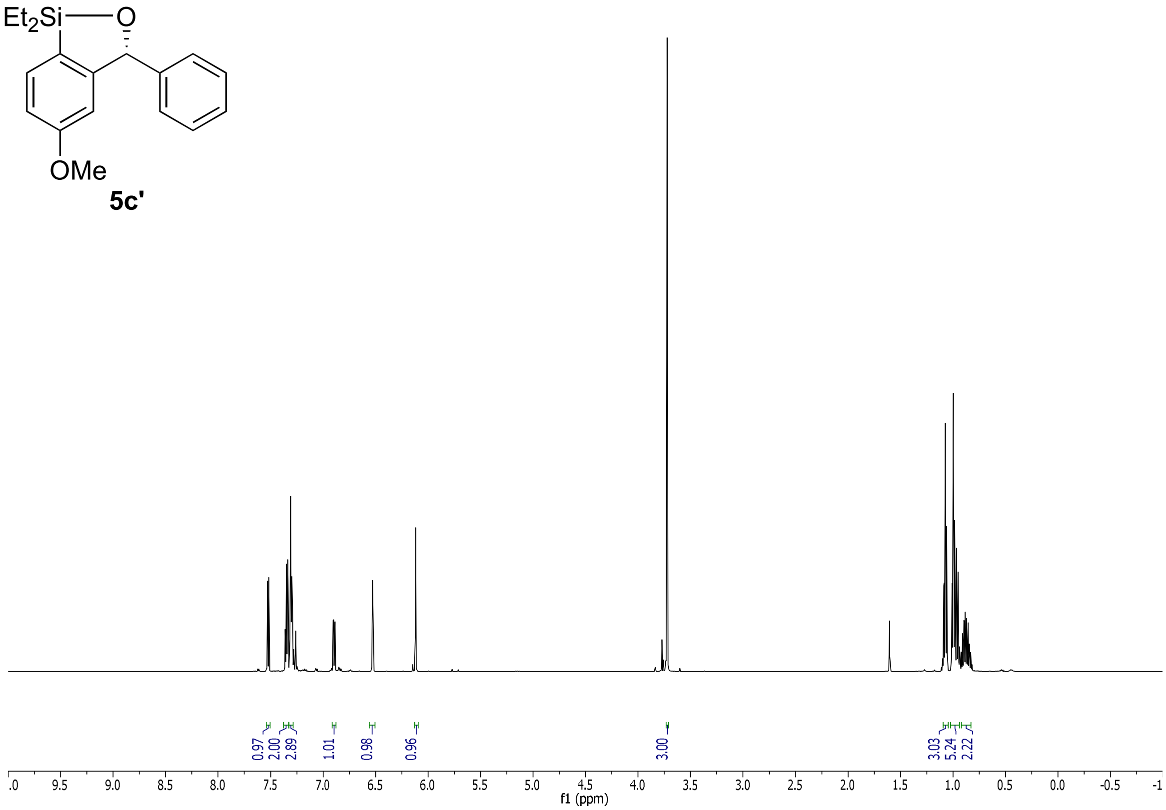

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5c

O
SiEt$_2$
OMe
1.00
2.24
1.23
1.03
1.05
2.04
1.02
3.15
3.11
5.11
2.15
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

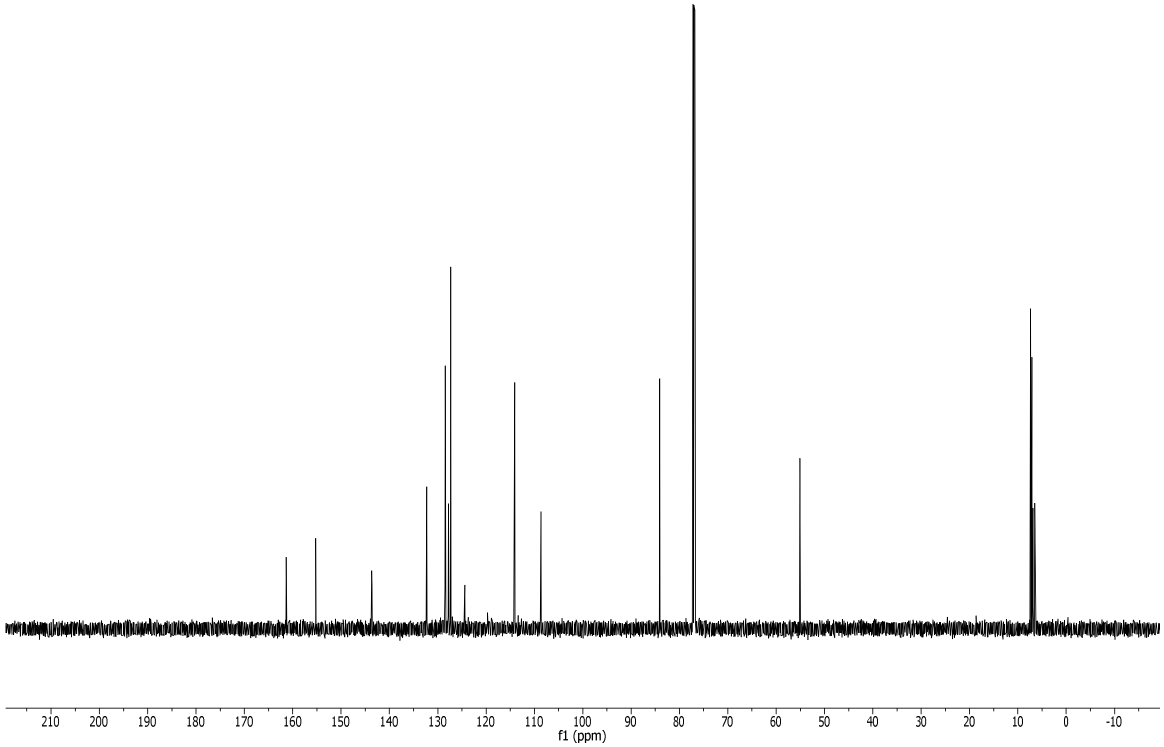


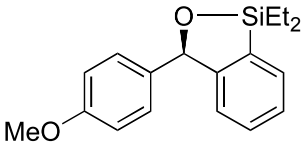
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Et2Si
O
OMe

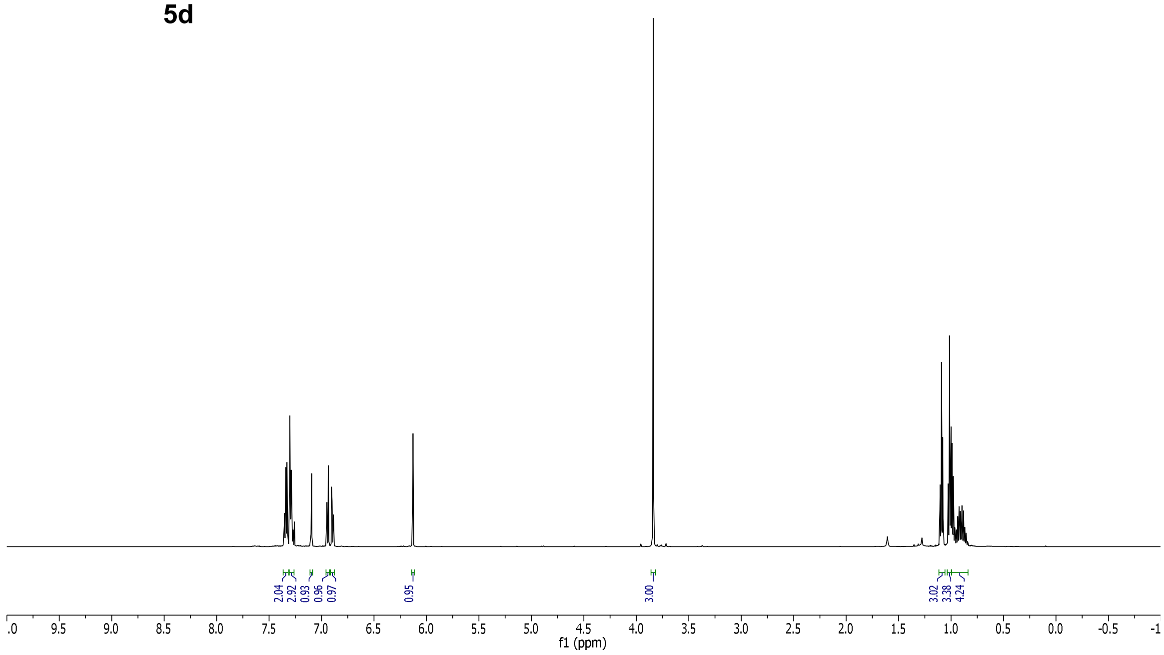
5c'

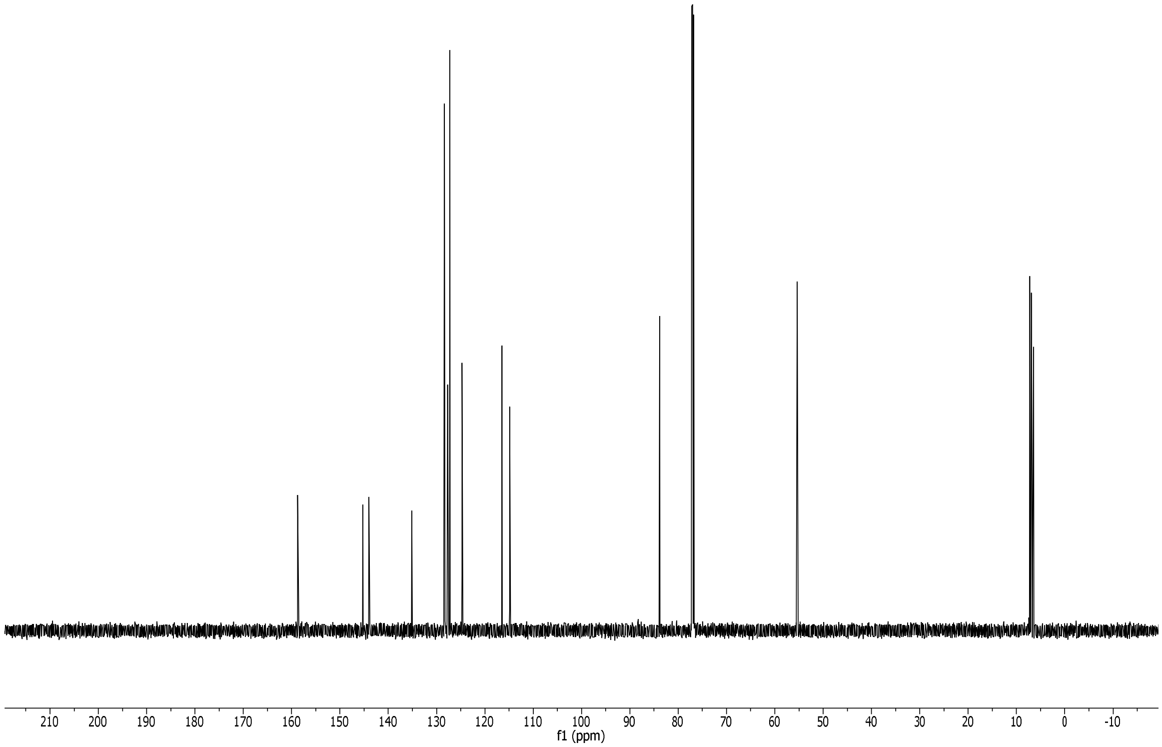
0.97
2.00
2.89
1.01
0.98
0.96
3.00
3.03
5.24
2.22
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

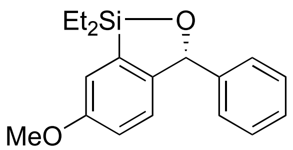

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
SiEt2
MeO

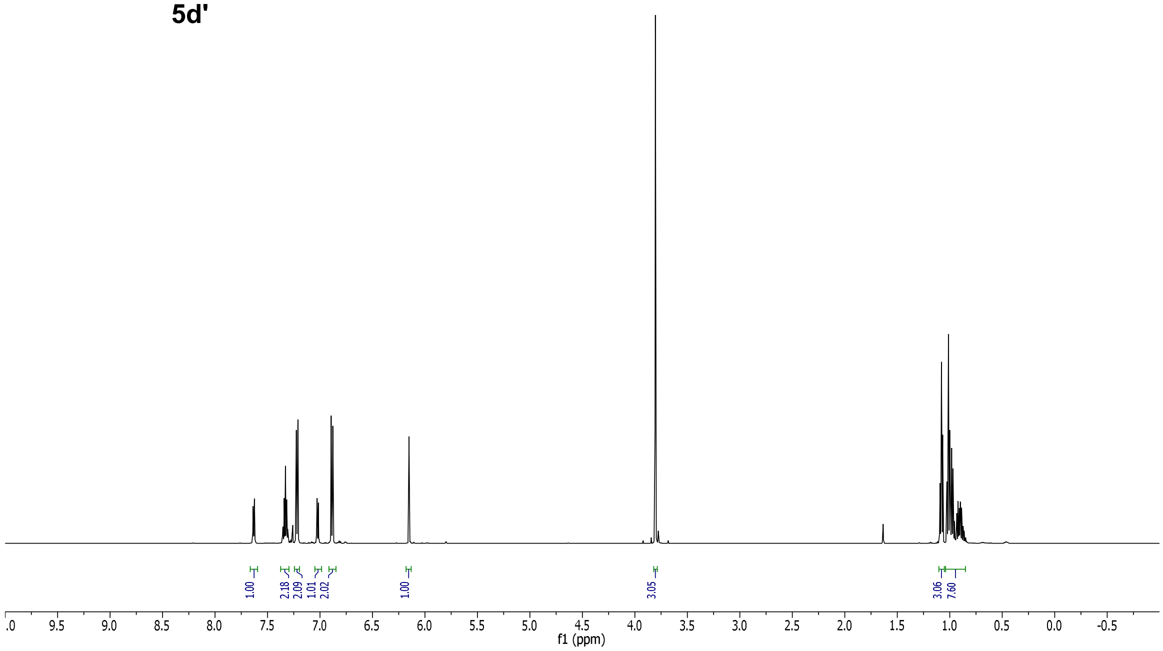
5d

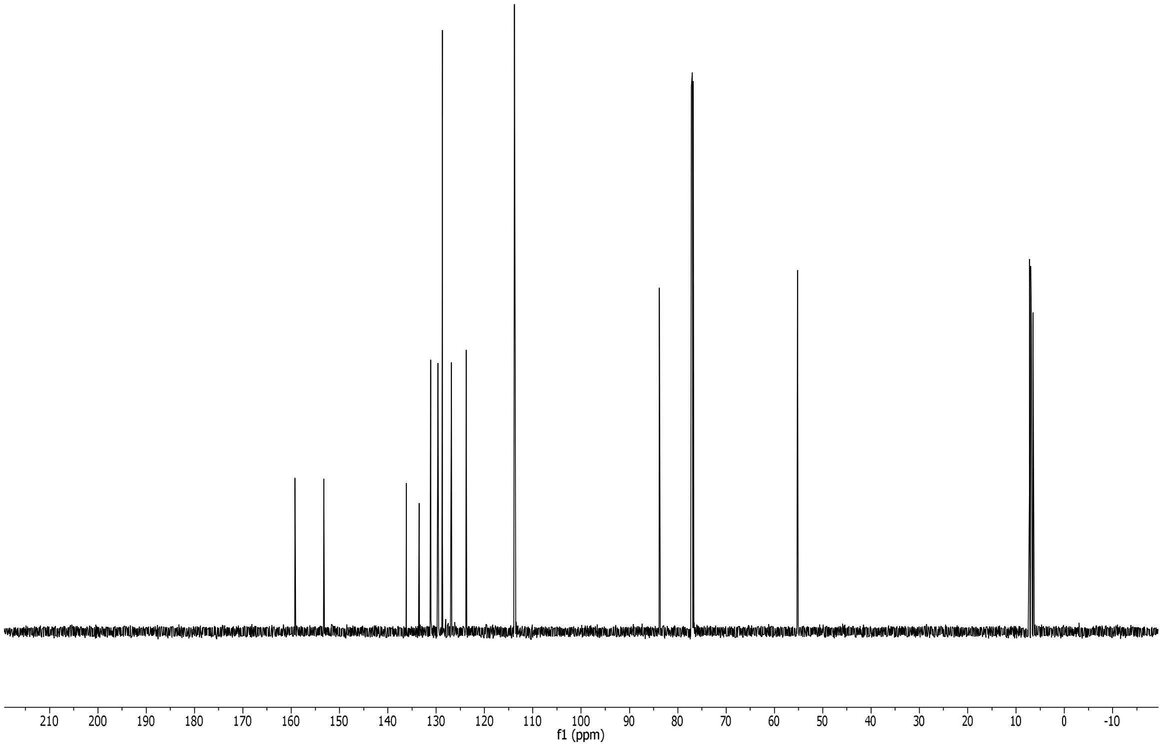

2.04
2.92
0.93
0.96
0.97
0.95
3.00
3.02
3.38
4.24
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

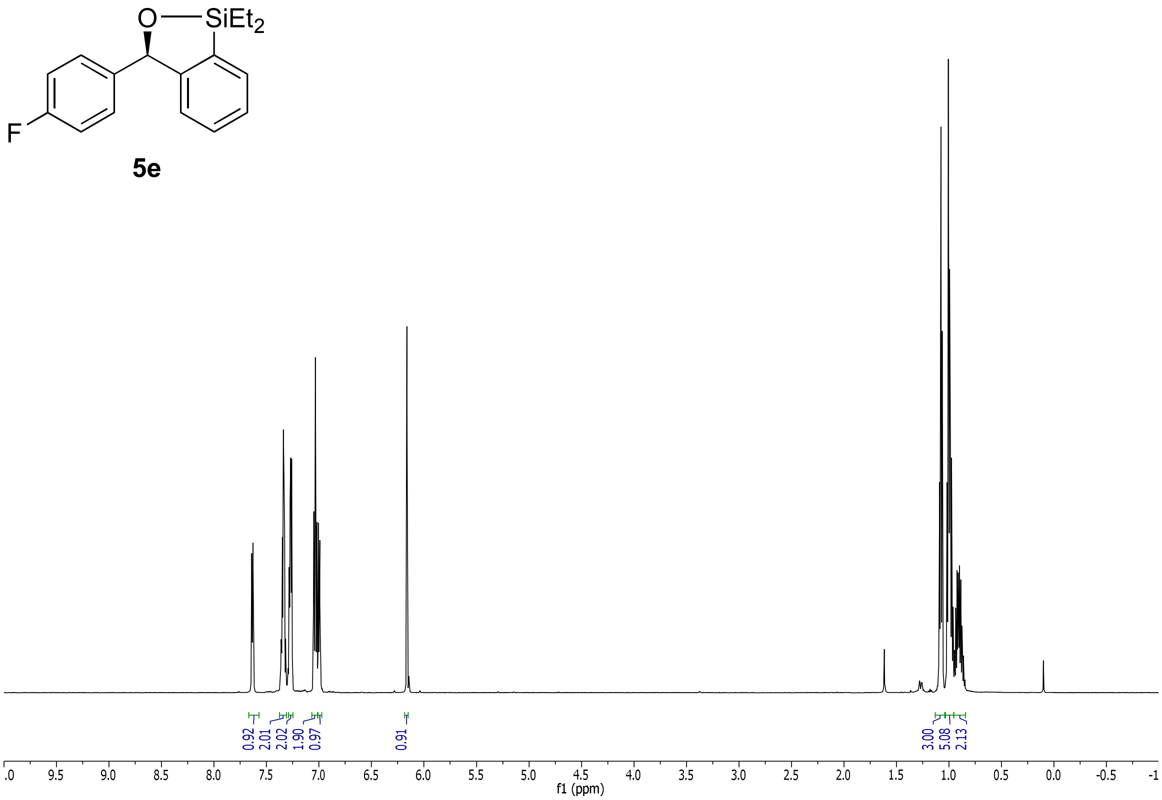

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Et2Si
O
MeO

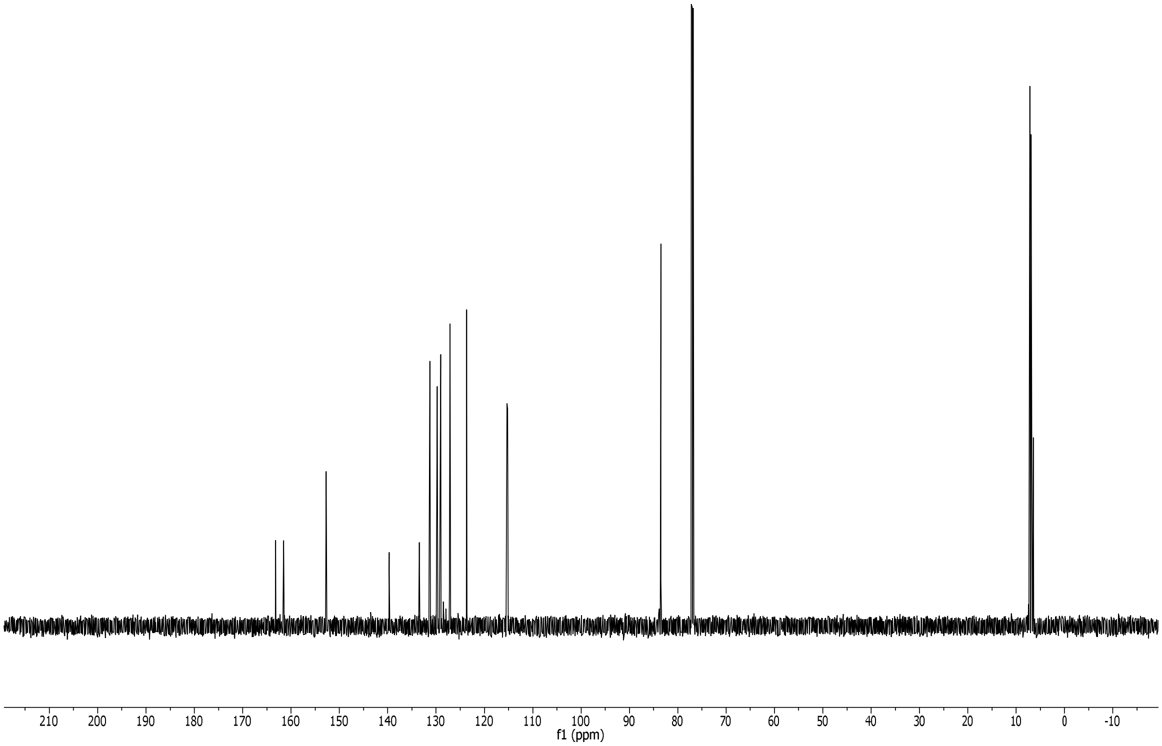
5d'

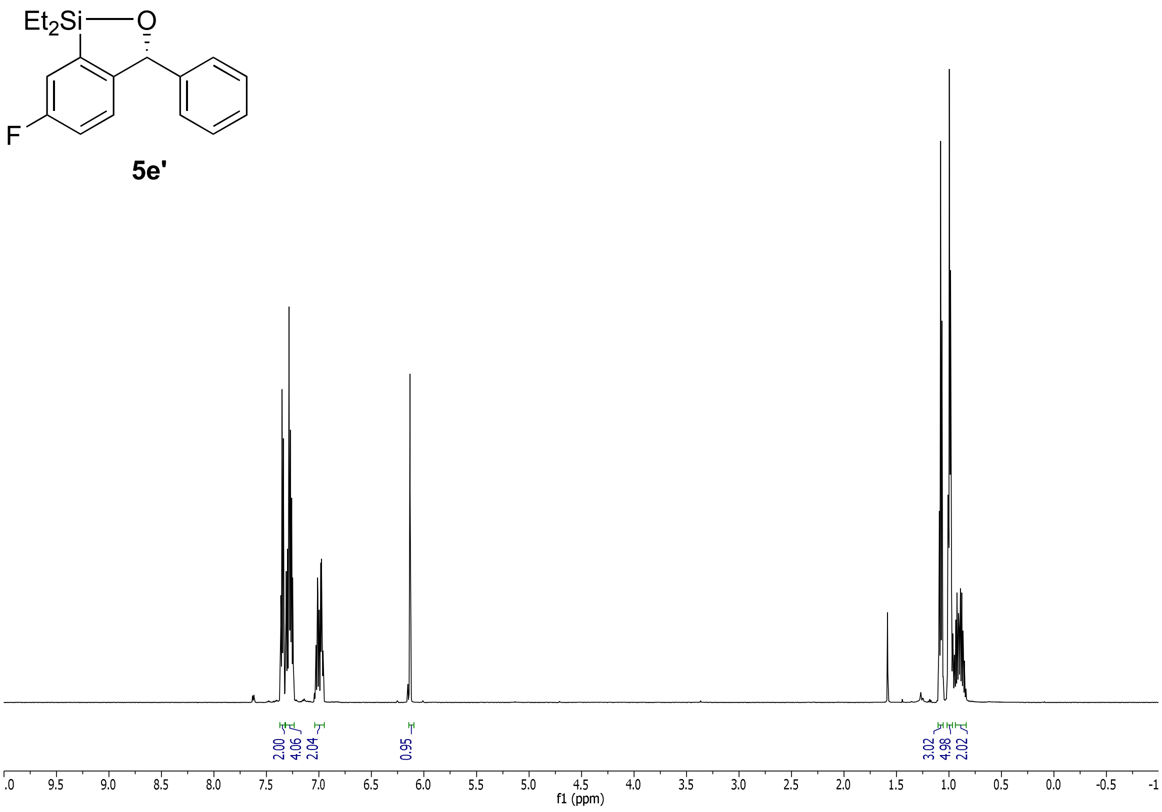

1.00
2.18
2.09
1.01
2.02
1.00
3.05
3.06
7.60
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

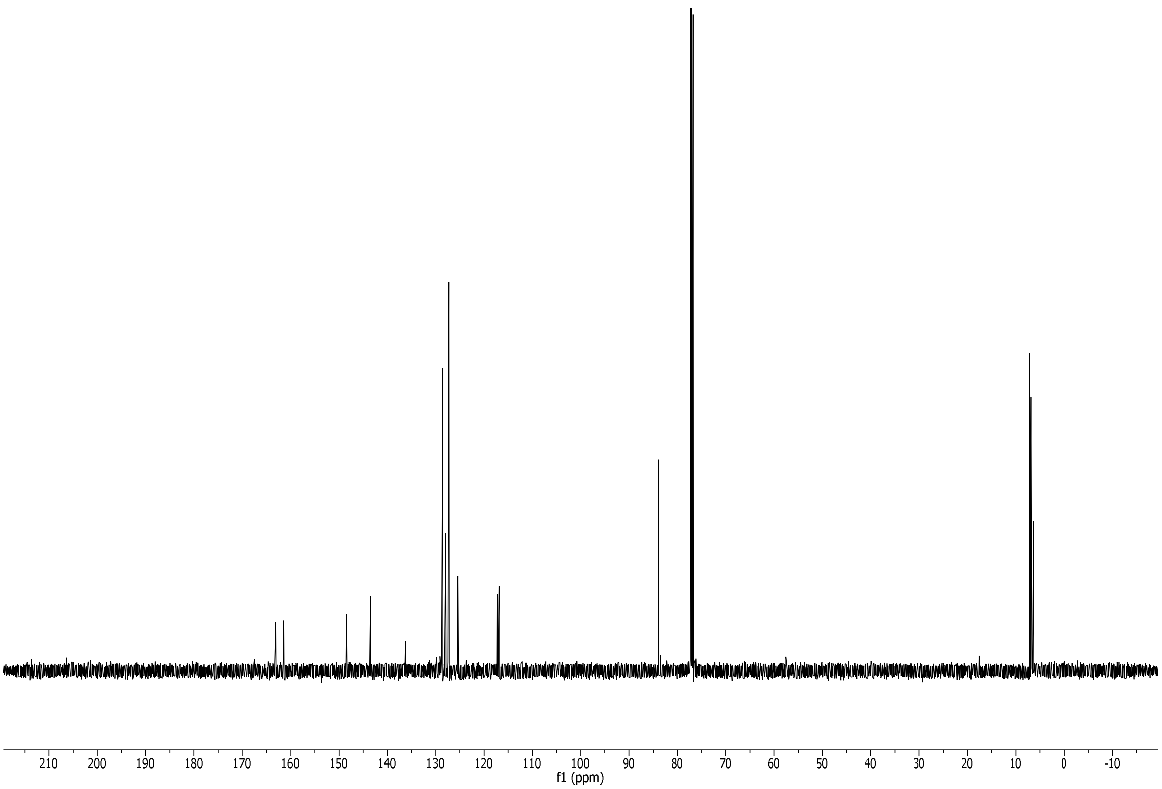

O
SiEt2
F
0.92
2.01
2.02
1.90
0.97
0.91
3.00
5.08
2.13
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

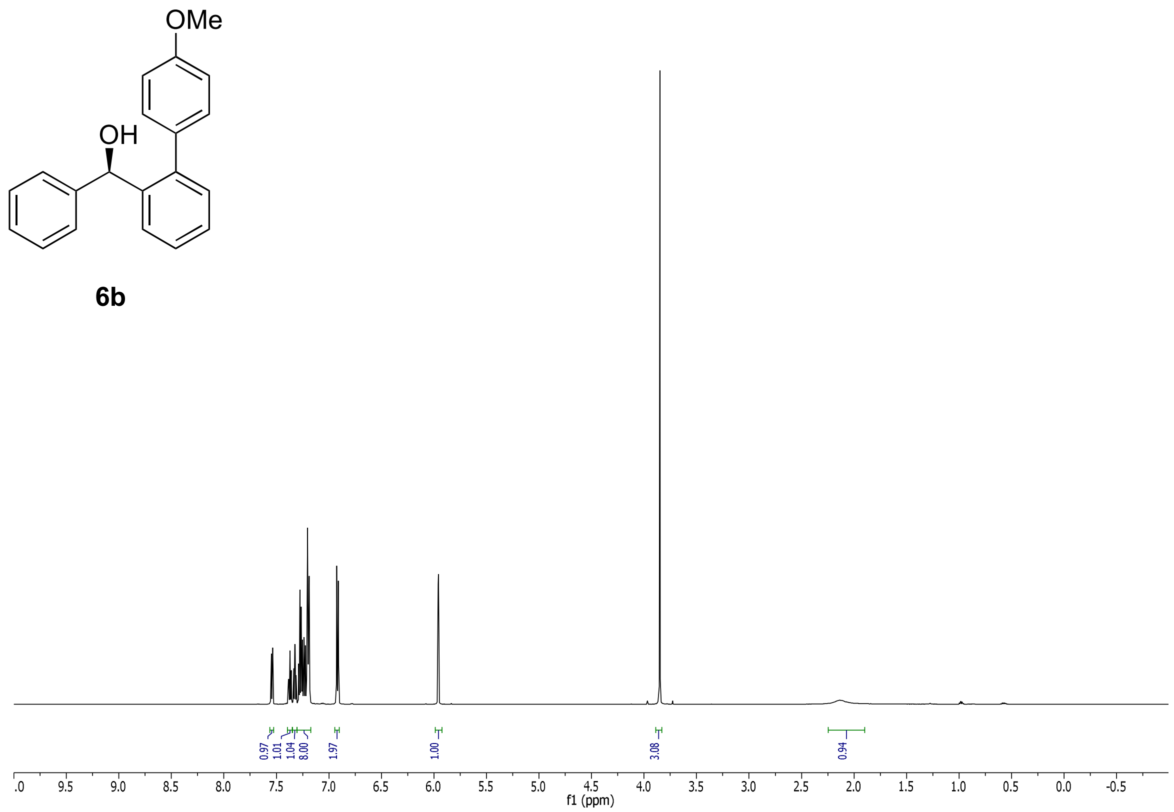
5e


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

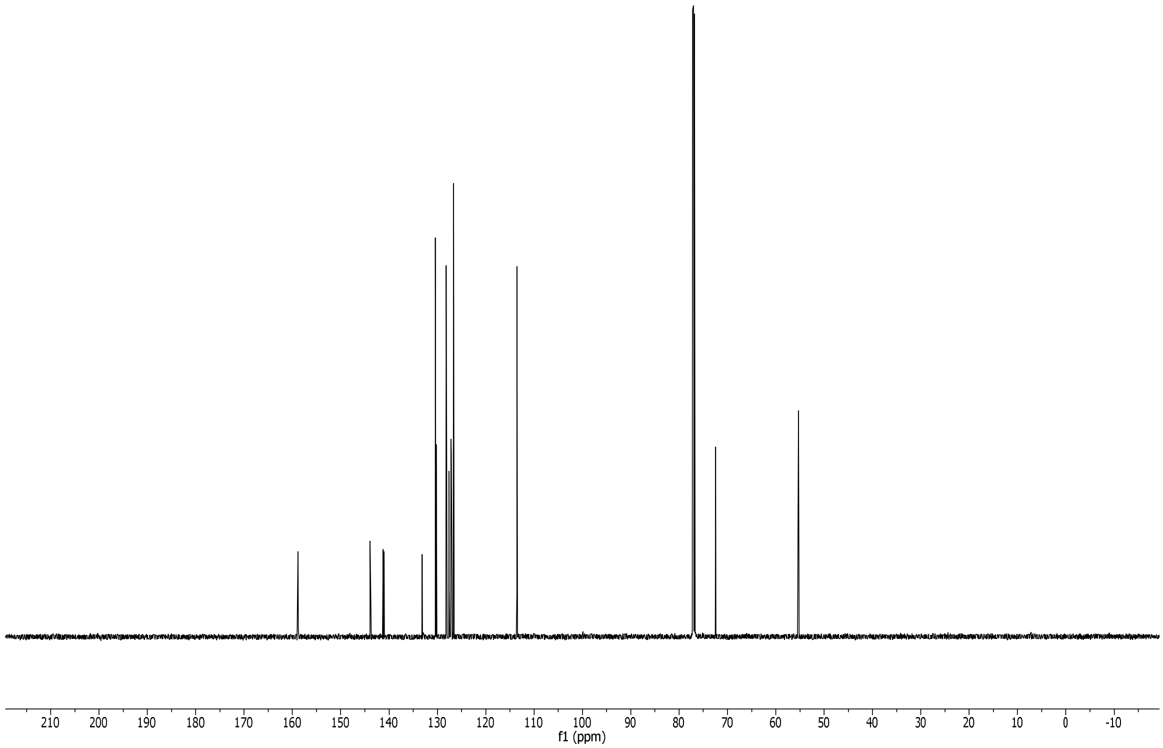

Et2Si
O
F
2.00
4.06
2.04
0.95
3.02
4.98
2.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

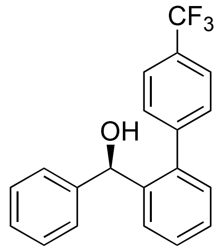
5e'


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

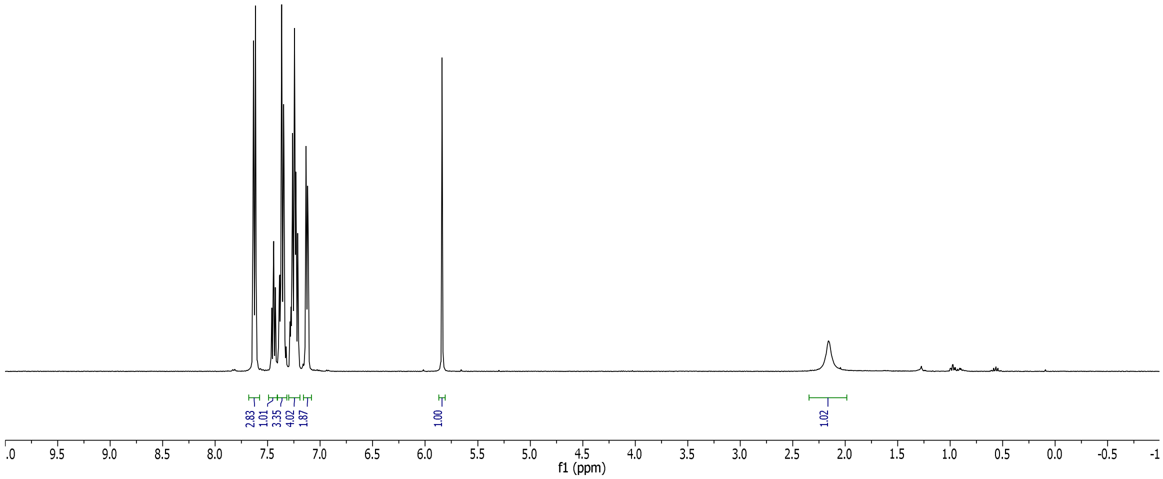

OMe
OH
0.97
1.01
1.04
8.00
1.97
1.00
3.08
0.94
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

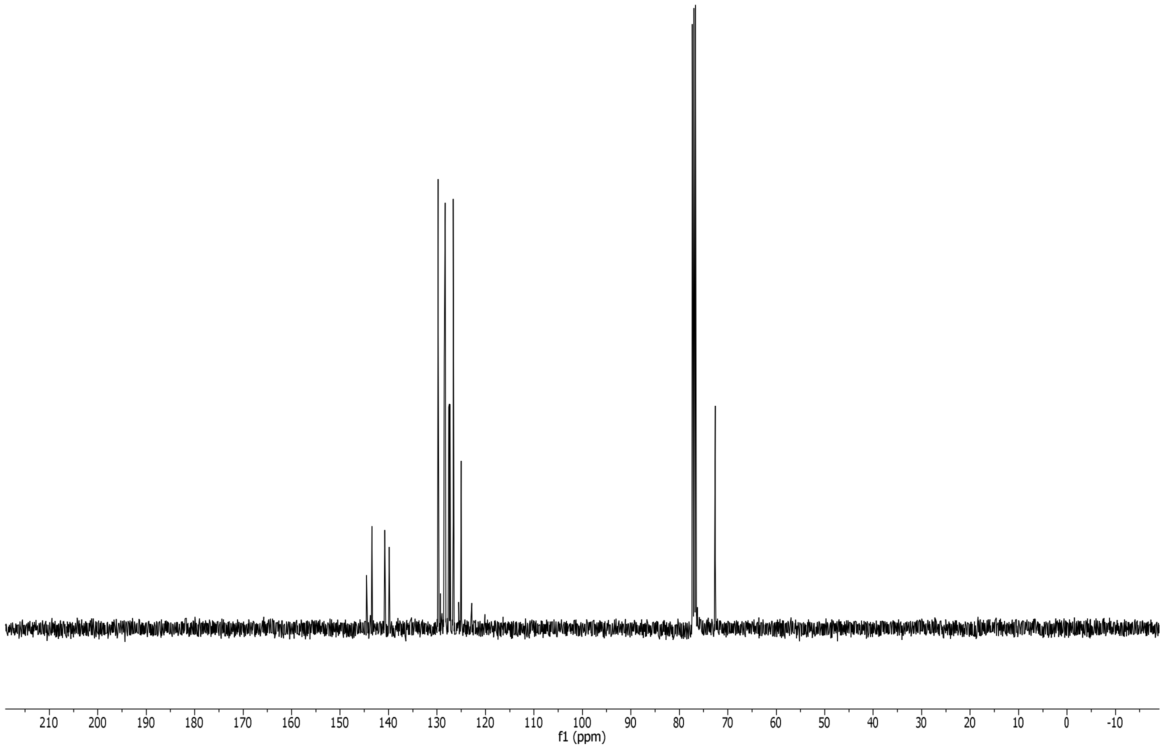
6b

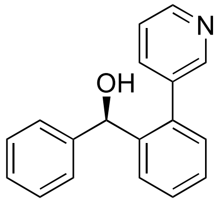

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CF3
OH

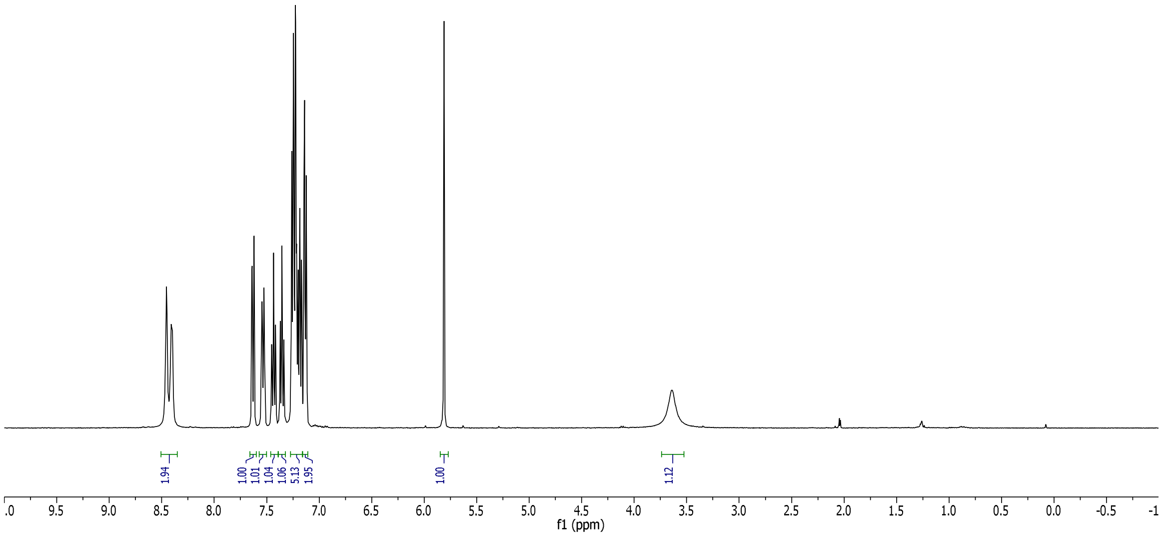
6c

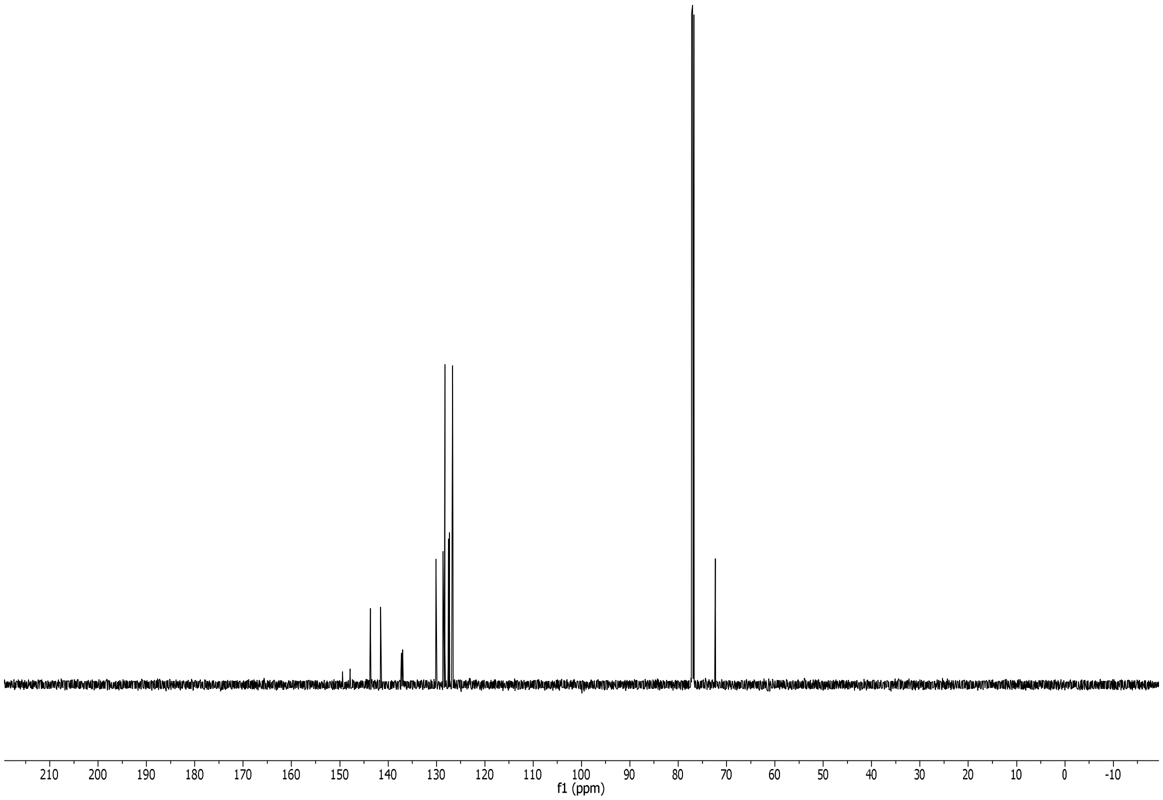

2.83
1.01
3.35
4.02
1.87
1.00
1.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

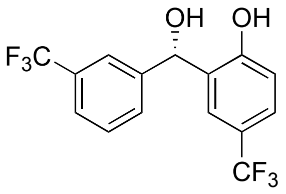

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



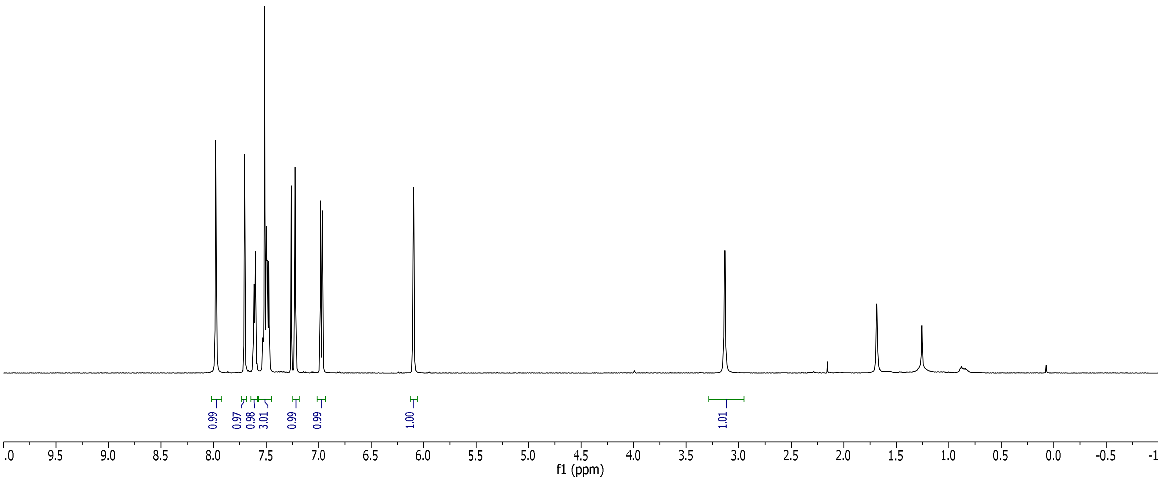
6d

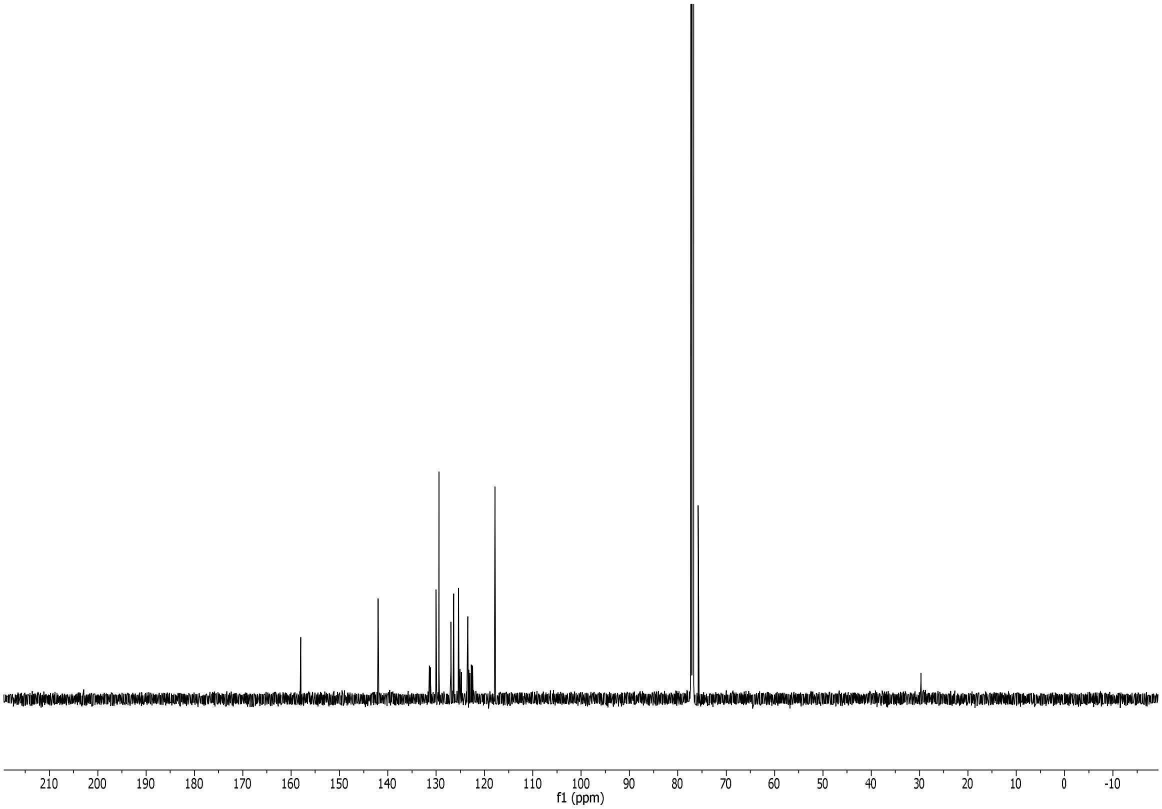

1.94
1.00
1.01
1.04
1.06
5.13
1.95
1.00
1.12
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

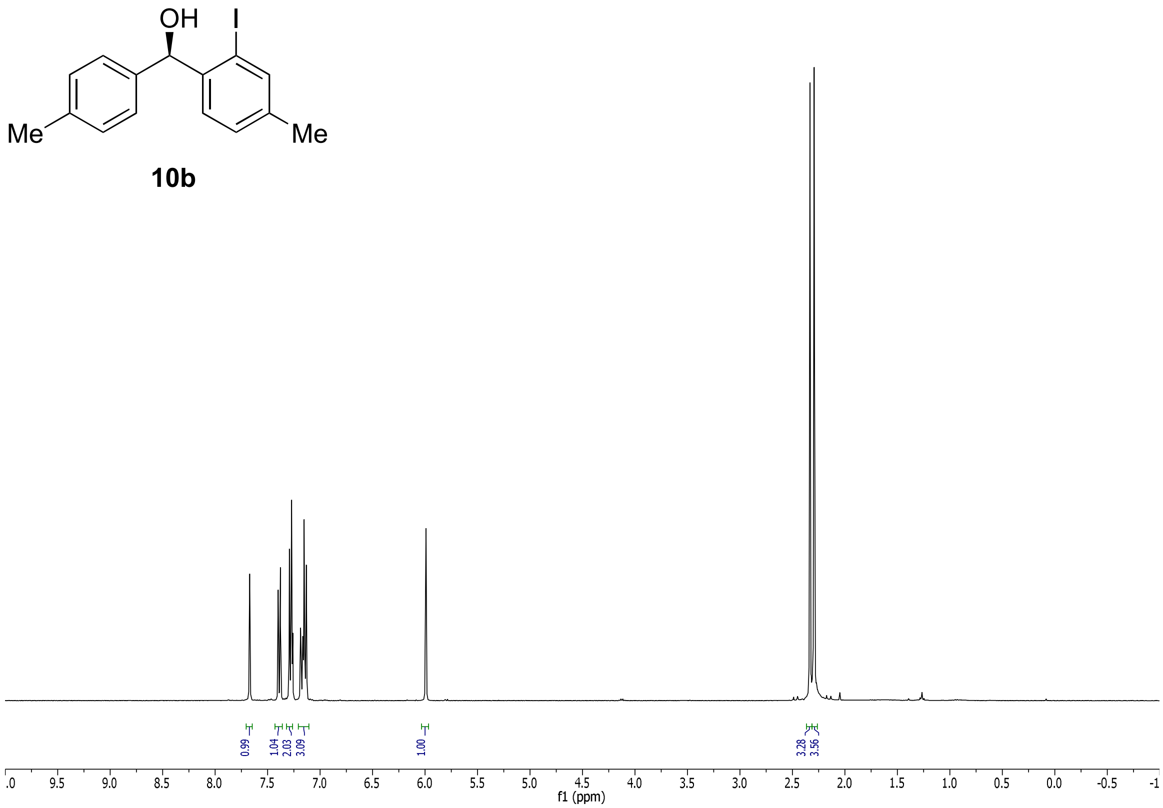

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
OH
F$_3$C
CF$_3$

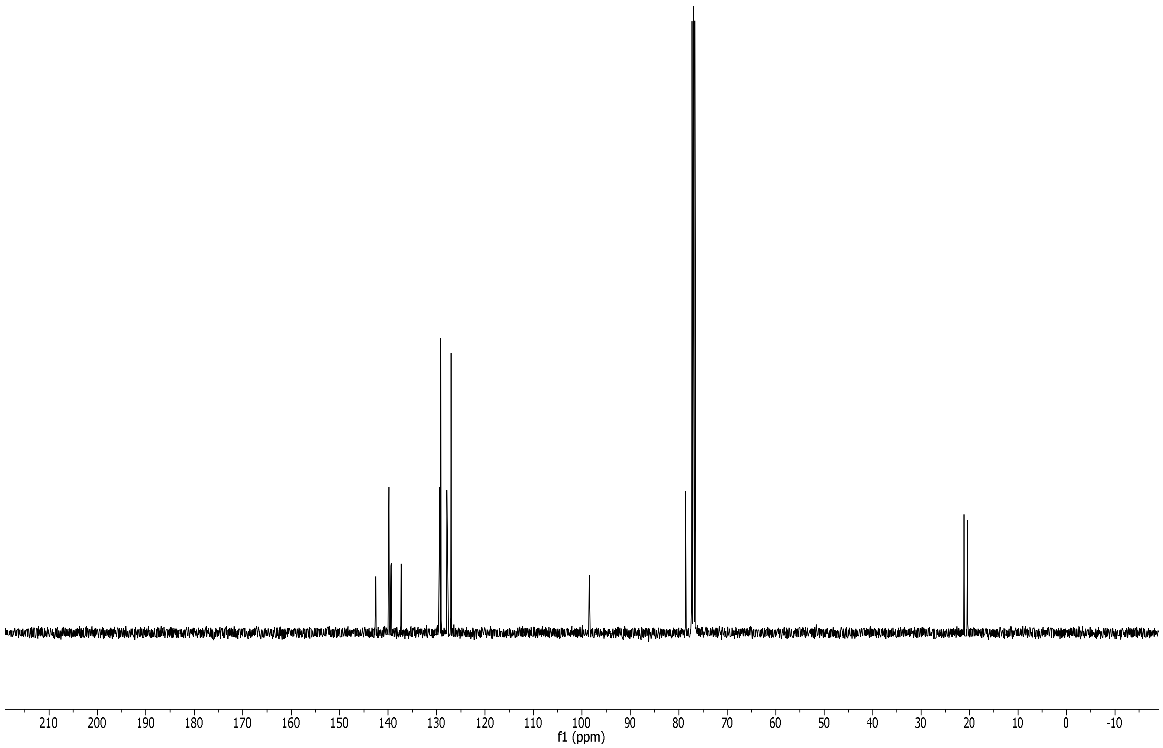
8

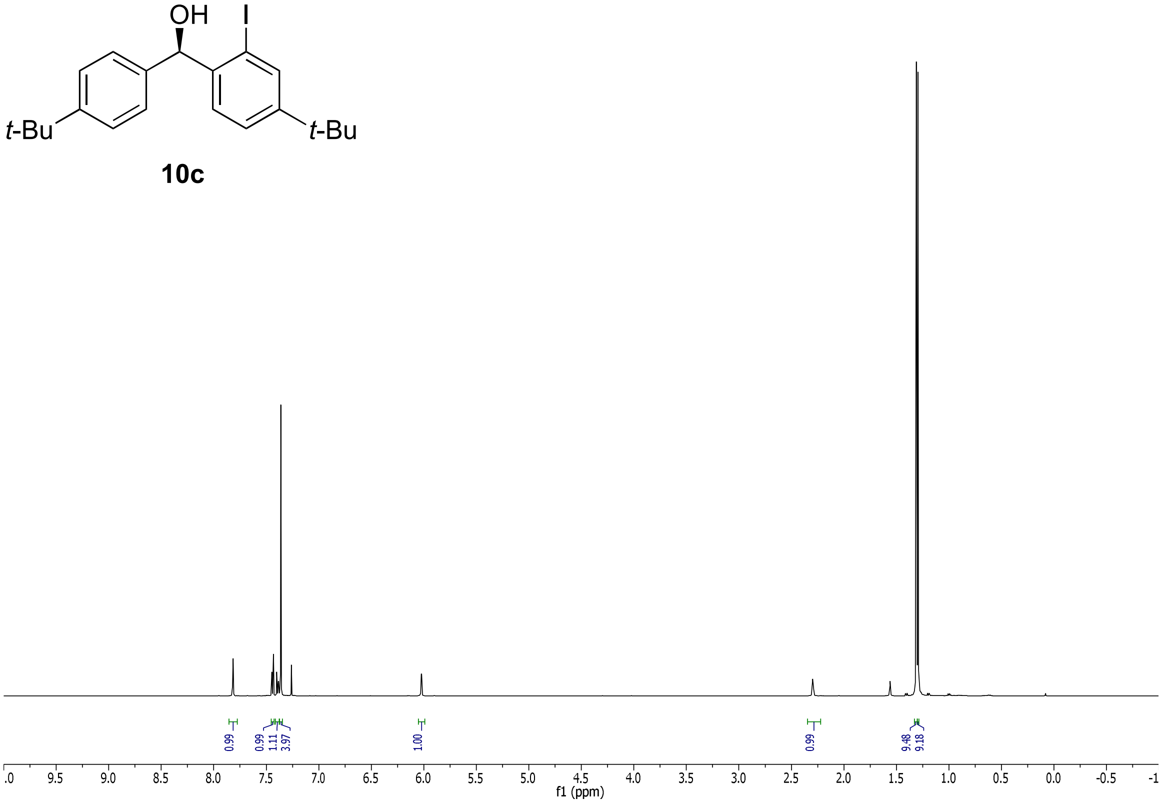

0.99
0.97
0.98
3.01
0.99
0.99
1.00
1.01
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

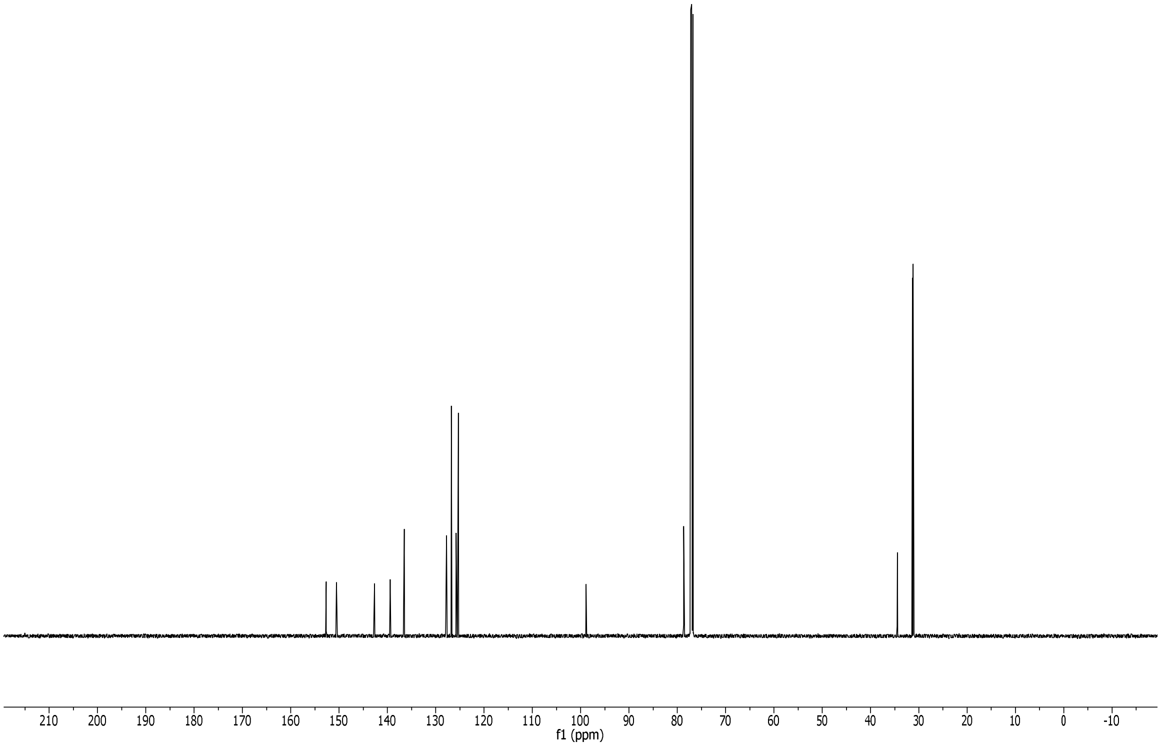

OH
I
Me
Me
0.99
1.04
2.03
3.09
1.00
3.28
3.56
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

10b

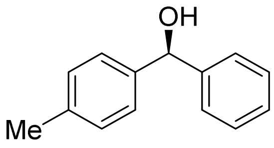

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
I
t-Bu
t-Bu
0.99
0.99
1.11
3.97
1.00
0.99
9.48
9.18
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

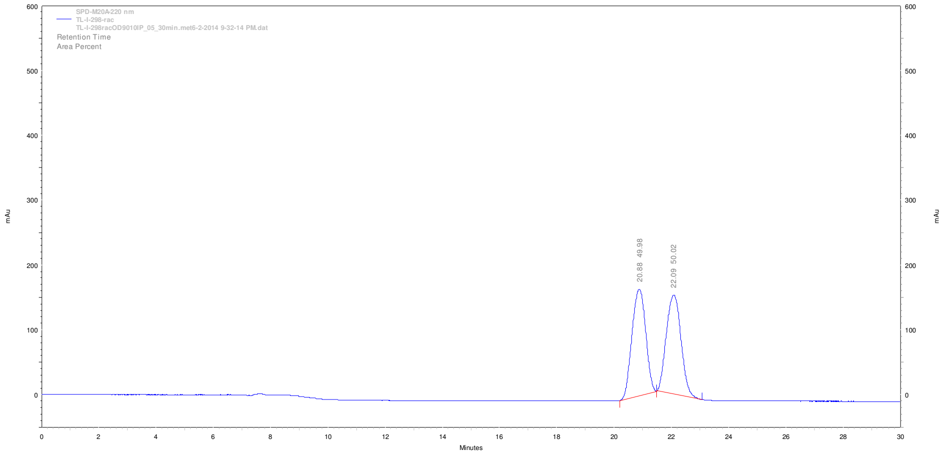
10c

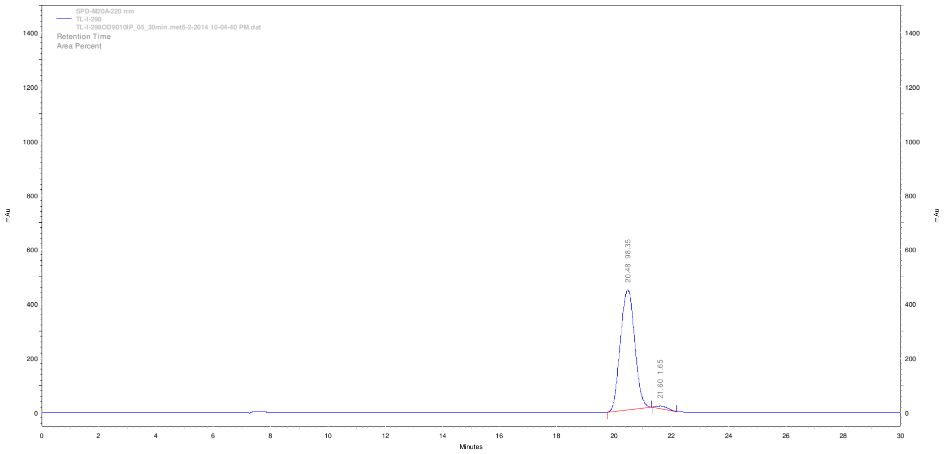

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

HPLC Data

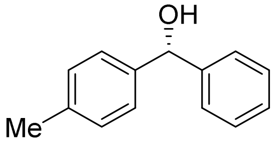


(*S*)-4a

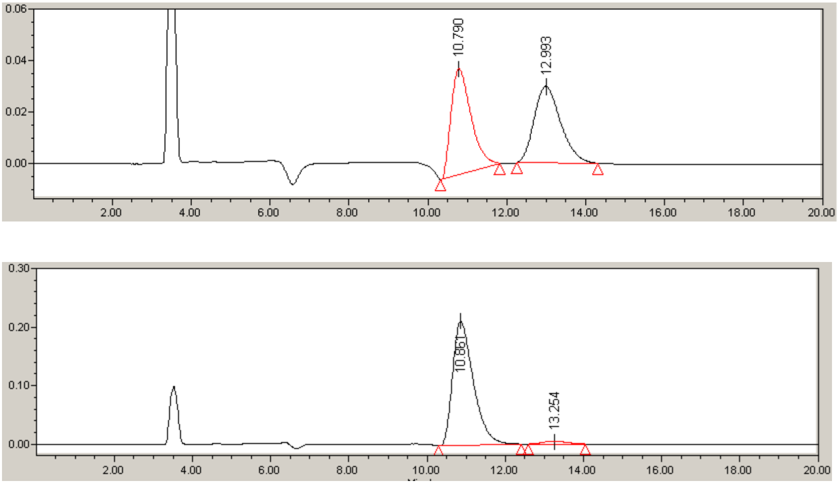




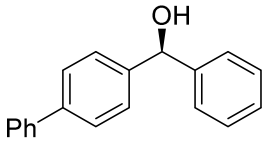
Chiralcel OD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 20.4 min (98.35%), t_R = 21.2 min (1.65%)



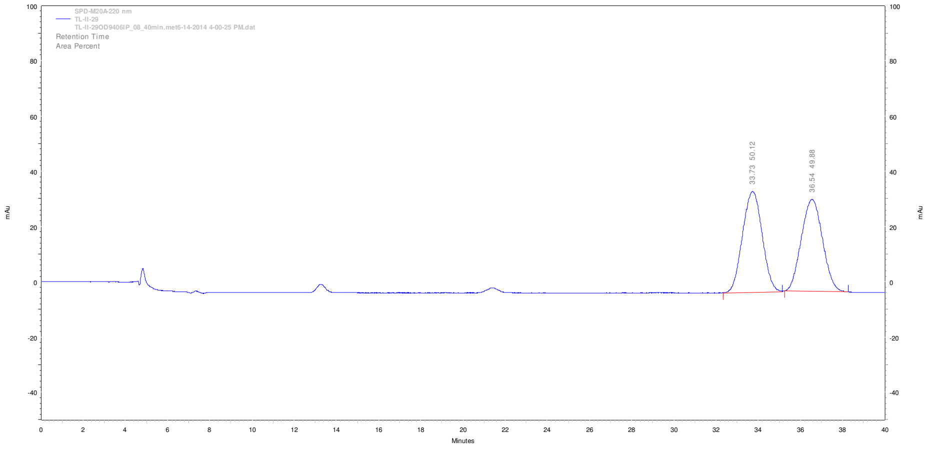
(*R*)-4a

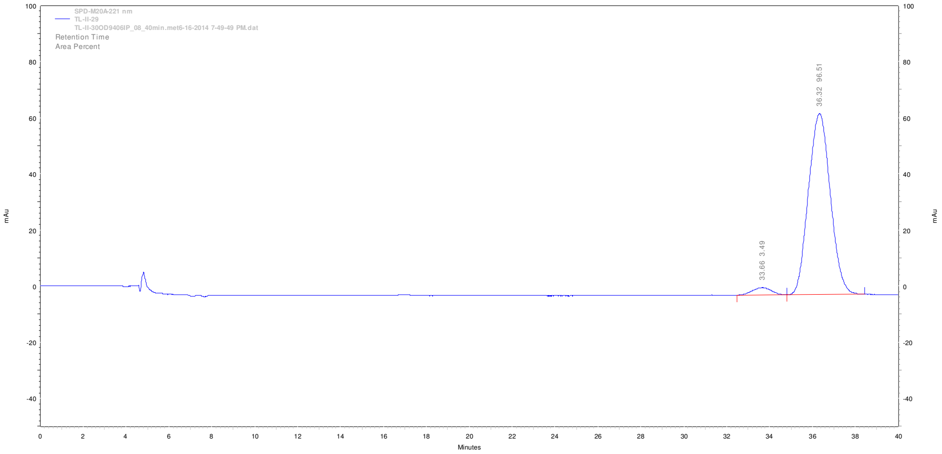


Chiralcel OB-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 10.9 min (97.56%), t_R = 13.2 min (2.44%).

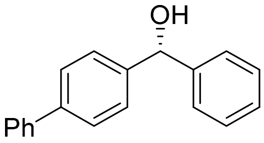


(*S*)-4b

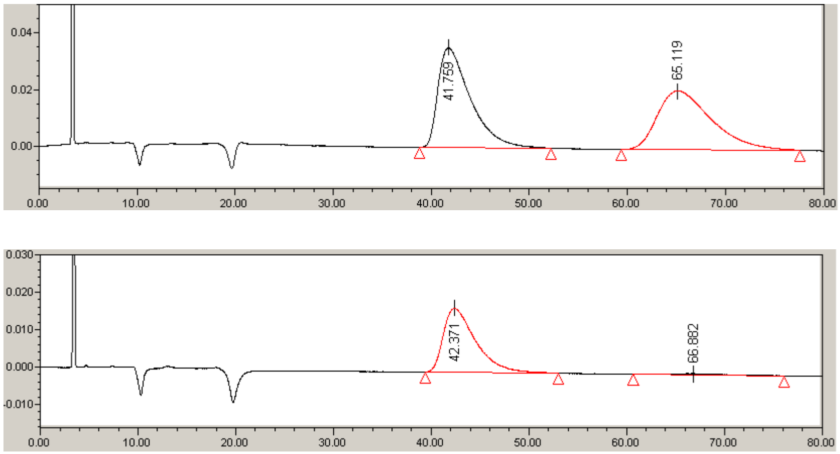




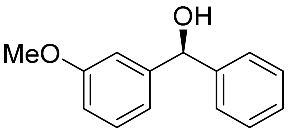
Chiralcel OD-H column, 6% isopropanol in hexane, 0.8 mL/min flow rate, 220 nm UV lamp, t_R = 33.7 min (3.49%), t_R = 36.3 min (96.51%)



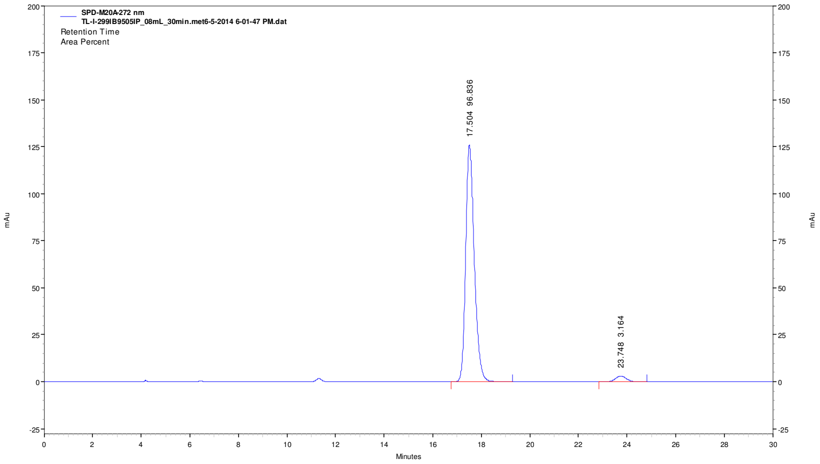
(*R*)-4b



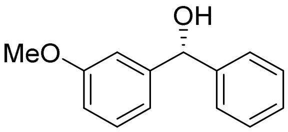
Chiralcel OB-H column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 42.4 min (96.62%), t_R = 66.9 min (3.38%).



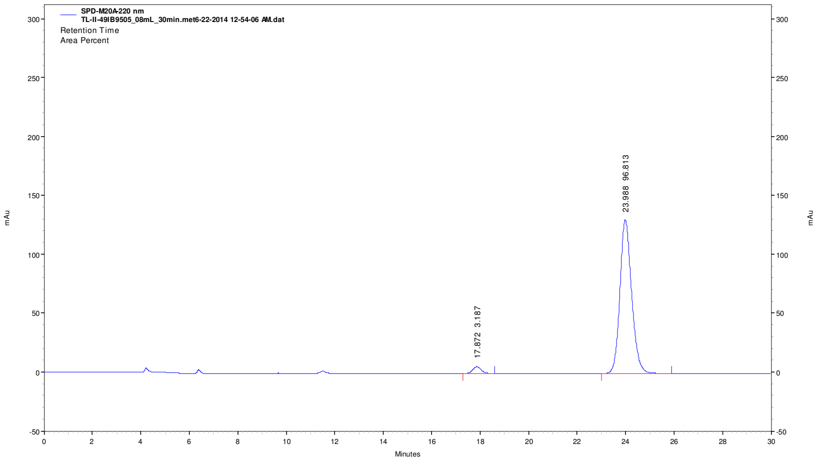
(*S*)-4c



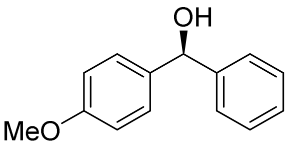
Chiralpak IB column, 5% isopropanol in hexane, 0.8 mL/min flow rate, 220 nm UV lamp, t_R = 17.5 min (96.83%), t_R = 23.7 min (3.16%)



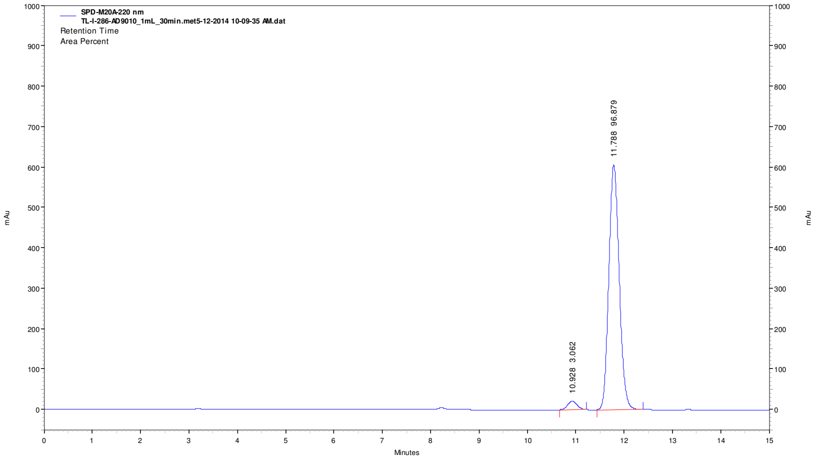
(*R*)-4c



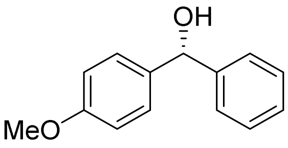
t_R = 17.9 min (3.19%), t_R = 24.0 min (96.81%).



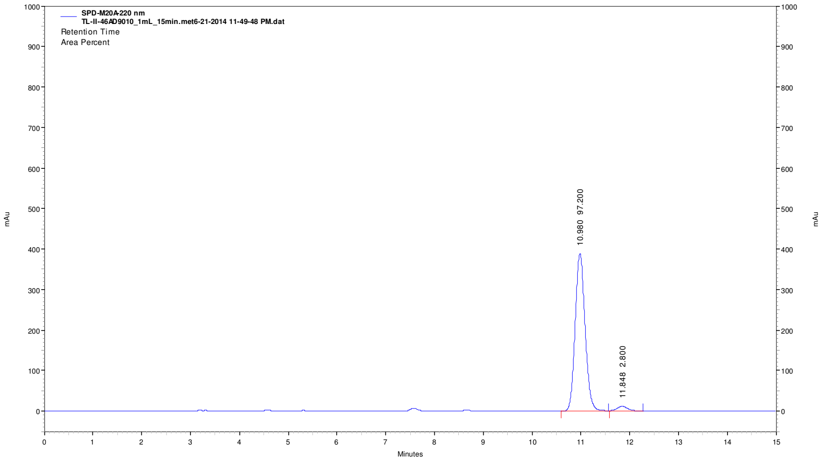
(*S*)-4d



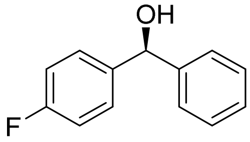
Chiralcel AD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 10.9 min (3.08%), t_R = 11.8 min (96.88%)



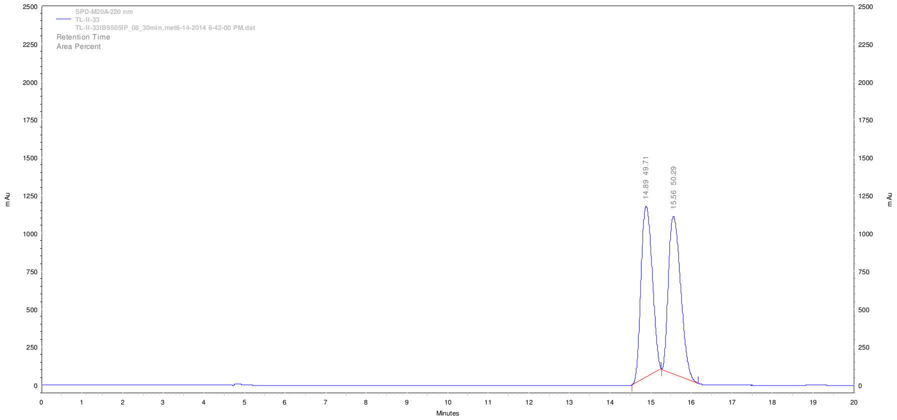
(*R*)-4d

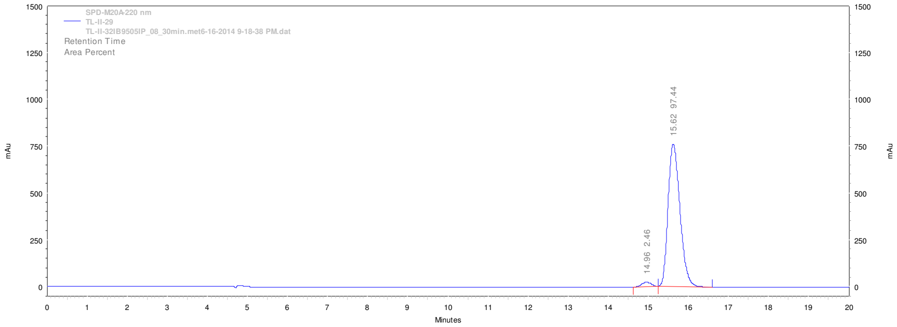


t_R = 11.0 min (97.20%), t_R = 11.9 min (2.80%).

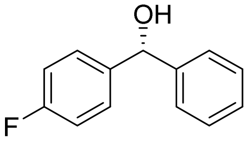


(*S*)-4e

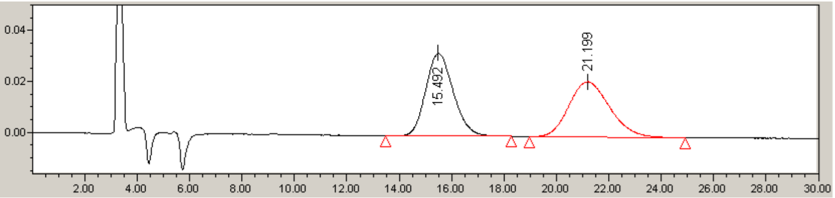


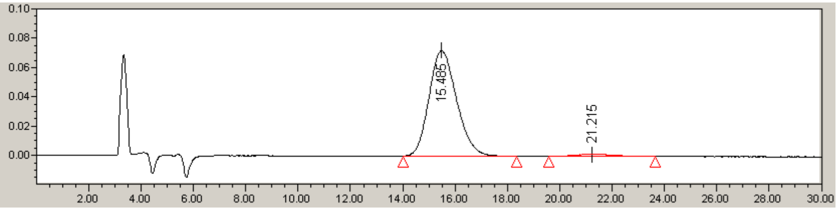


Chiralpak IB column, 5% isopropanol in hexane, 0.8 mL/min flow rate, 220 nm UV lamp, t_R = 15.0 min (2.46%), t_R = 15.6 min (97.44%)

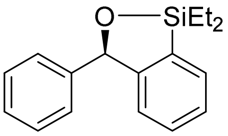


(*R*)-4e





Chiralcel OB-H column, 20% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 15.5 min (97.26%), t_R = 21.2 min (2.74%).



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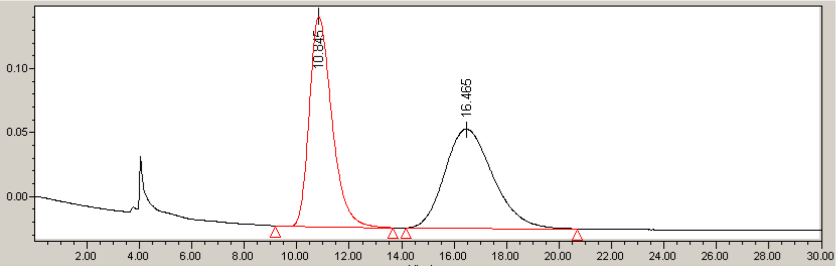
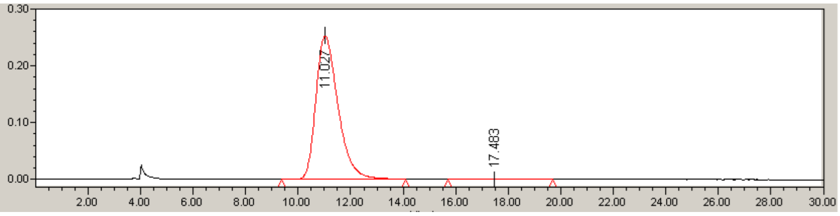
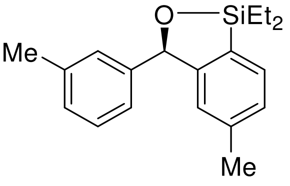




Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 11.0 min (99.4%), t_R = 17.5 min (0.61%).



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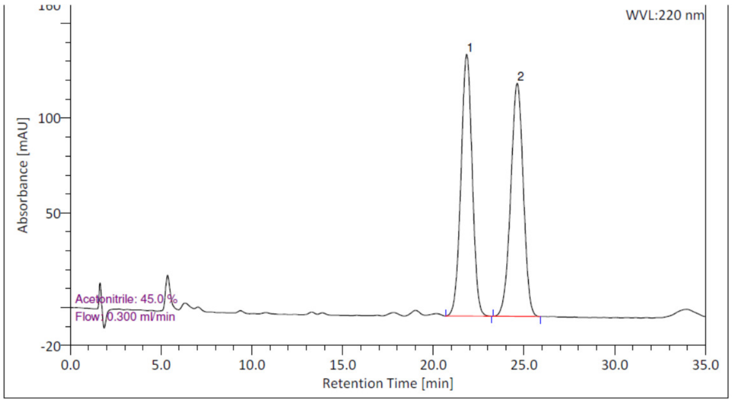
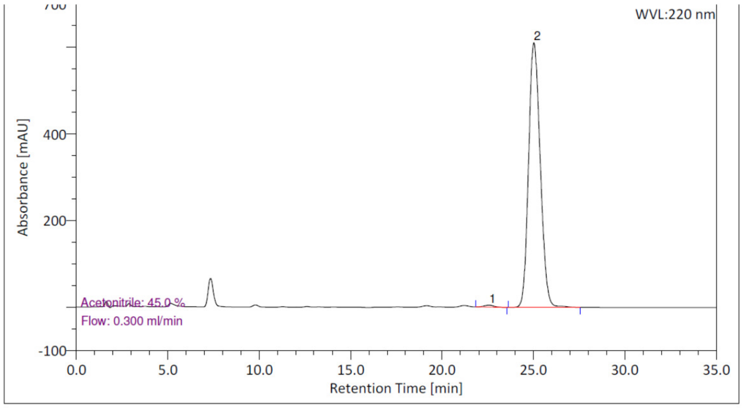
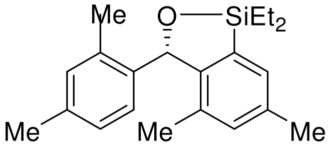


No.	Time min	RRT %	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Rel.Area(ISTD) %	Amount mg/mL	Type
1	21.839	n.a.	n.a.	138.209	99.270	50.06	n.a.	n.a.	BMB
2	24.631	n.a.	n.a.	123.147	99.029	49.94	n.a.	n.a.	BMB
Total:					198.299	100.00			



No.	Time min	RRT %	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Rel.Area(ISTD) %	Amount mg/mL	Type
1	22.569	n.a.	n.a.	4.642	2.767	0.61	n.a.	n.a.	BMB*
2	25.022	n.a.	n.a.	611.773	453.110	99.39	n.a.	n.a.	BMB
Total:					455.878	100.00			

LUX Amylose-2 150 x 2 mm 3µ column, 5mM ammonioum acetate 63% in acetonitrile, 0.3mL/min flow rate, 220 nm UV lamp



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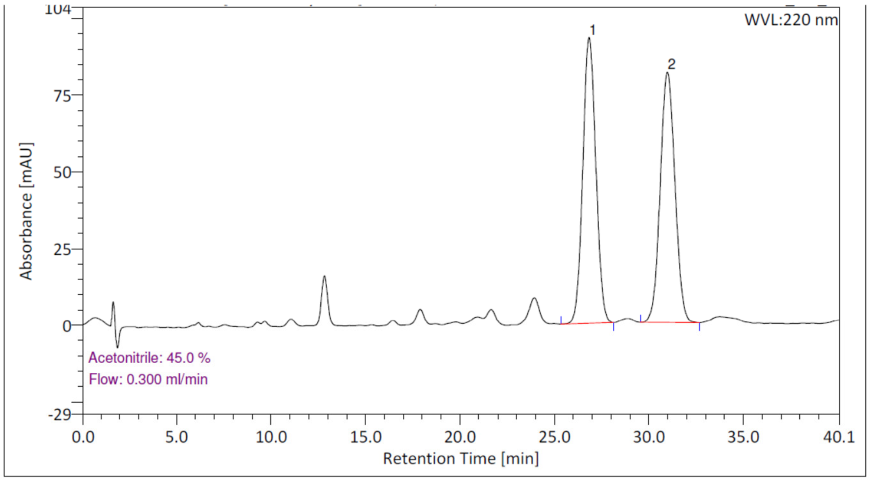
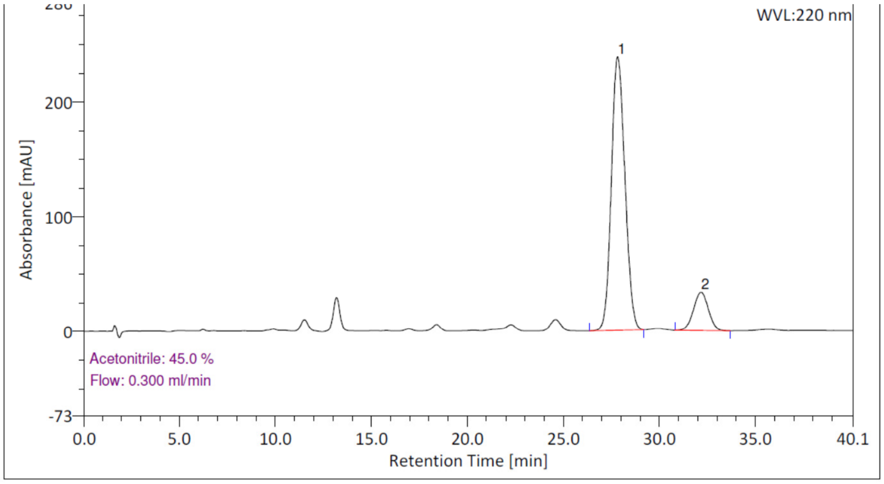
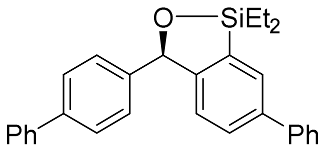


No.	Time min	RRT %	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Rel.Area(ISTD) %	Amount mg/mL	Type
1	26.841	n.a.	n.a.	93.241	74.745	50.24	n.a.	n.a.	BMB
2	30.989	n.a.	n.a.	81.681	74.016	49.76	n.a.	n.a.	BMB
Total:					148.762	100.00			



No.	Time min	RRT %	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Rel.Area(ISTD) %	Amount mg/mL	Type
1	27.829	n.a.	n.a.	238.289	195.408	86.57	n.a.	n.a.	BMB*
2	32.176	n.a.	n.a.	33.513	30.307	13.43	n.a.	n.a.	BMB
Total:					225.715	100.00			

LUX Amylose-2 150 x 2 mm 3μ column, 5mM ammonioum acetate 55% in acetonitrile, 0.3 mL/min flow rate, 220 nm UV lamp



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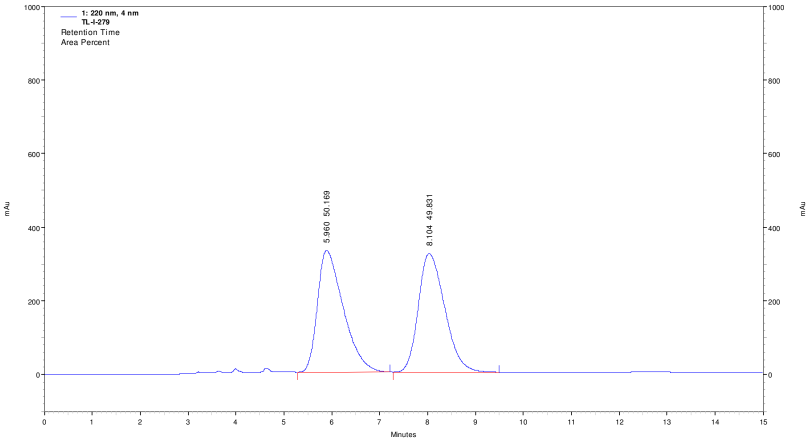
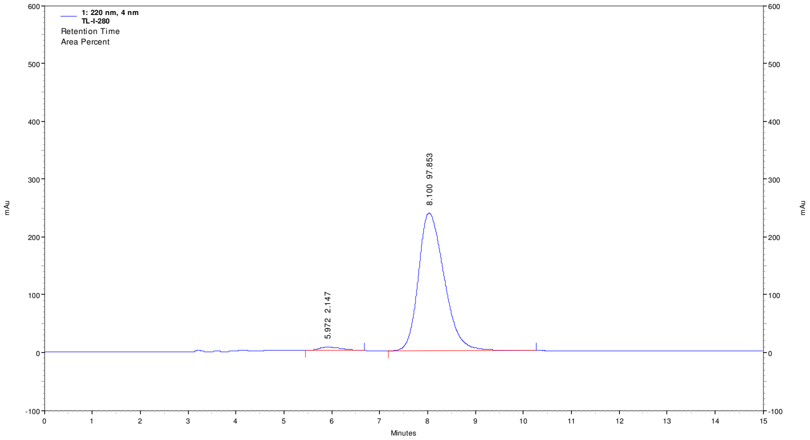
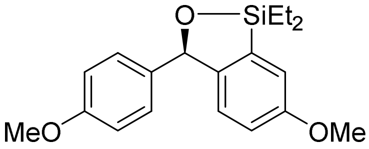




Chiralpak IA column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 6.0 min (2.15%), t_R = 8.1 min (97.85%).



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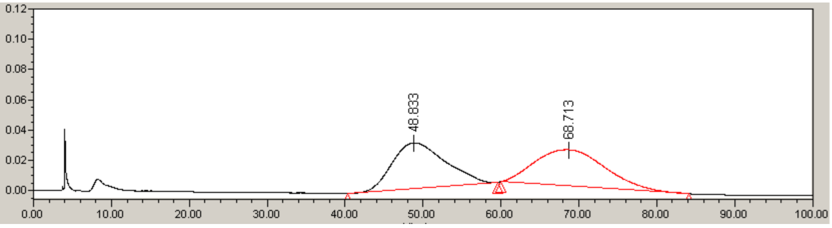
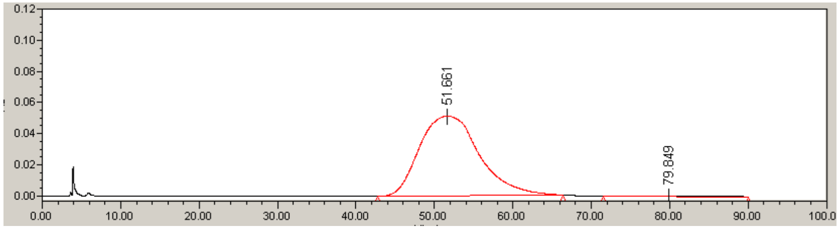
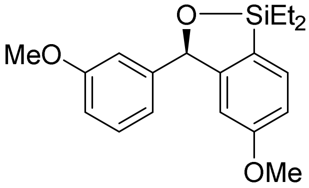




99% *ee*, Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 51.7 min (99.31%), t_R = 79.8 min (0.69%)



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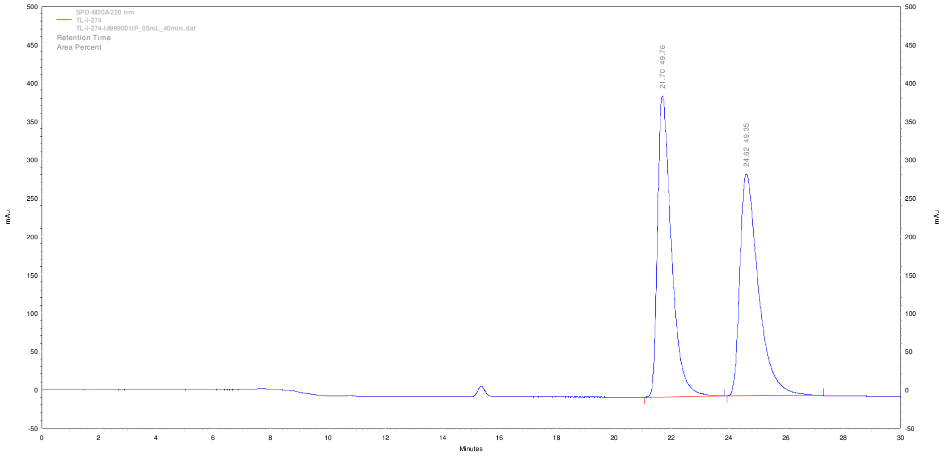
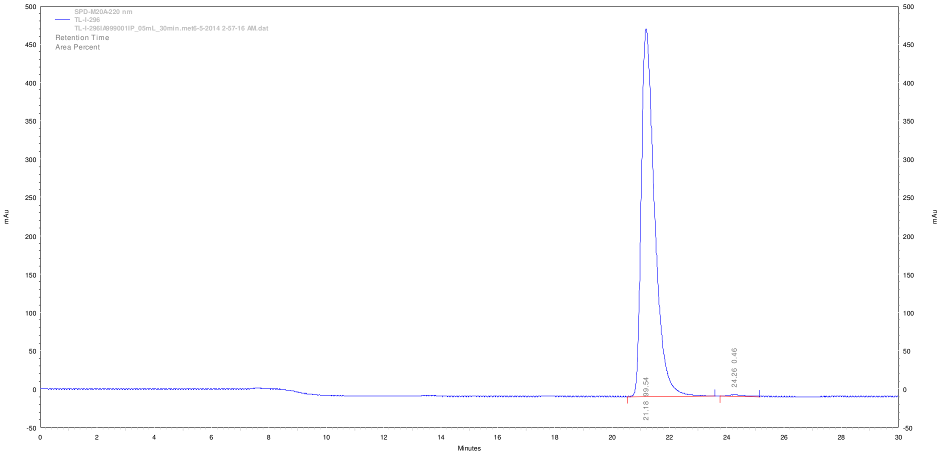
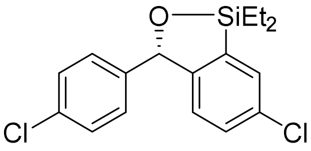




Chiralpak IA column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 21.2 min (99.54%), t_R = 24.3 min (0.46%).



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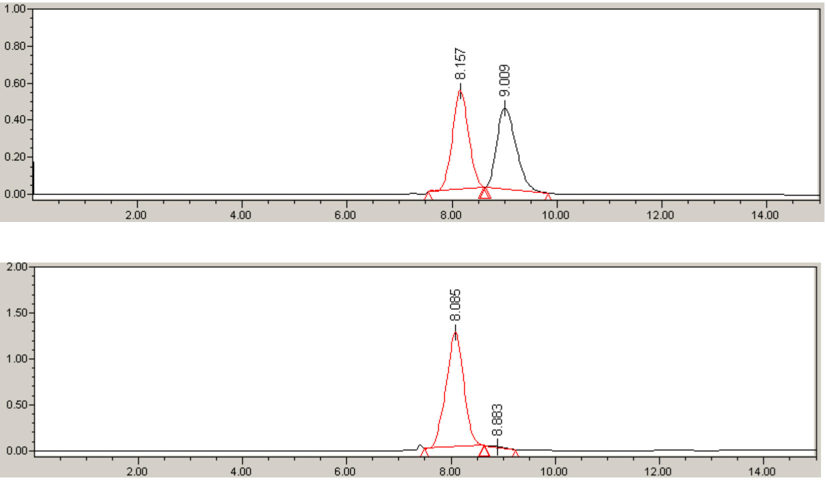
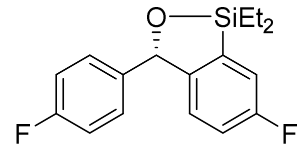


Chiralcel OD-H column, 1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 8.1 min (99.60%), t_R = 8.9 min (0.40%).



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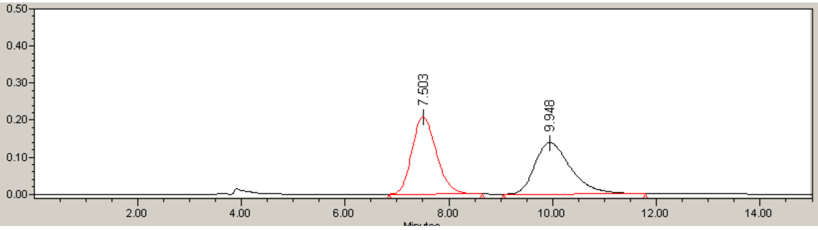
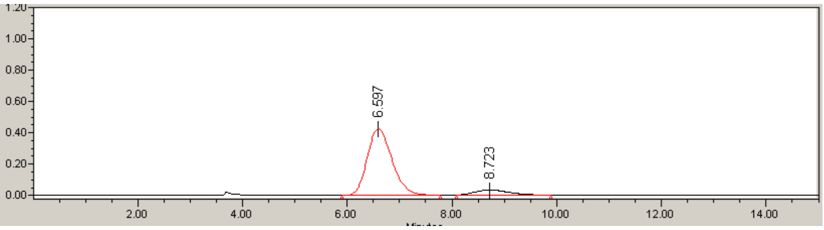
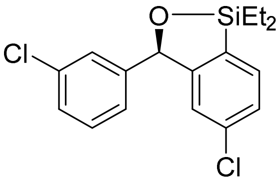




Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 6.7 min (90.27%), t_R = 8.7 min (9.73%).



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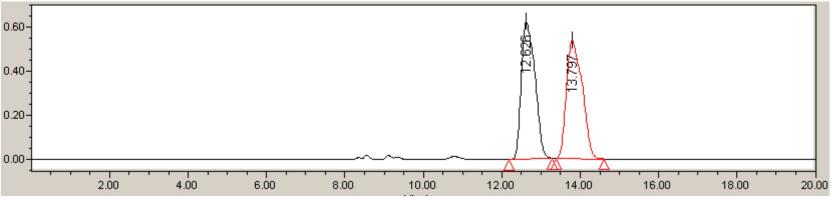
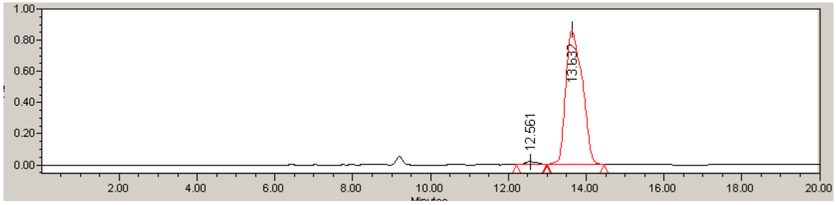
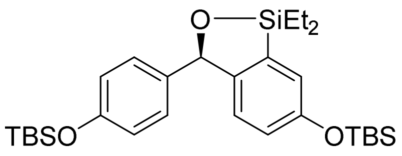




Chiralcel OD-H column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 12.6 min (1.61%), t_R = 7.4 min (98.39%).



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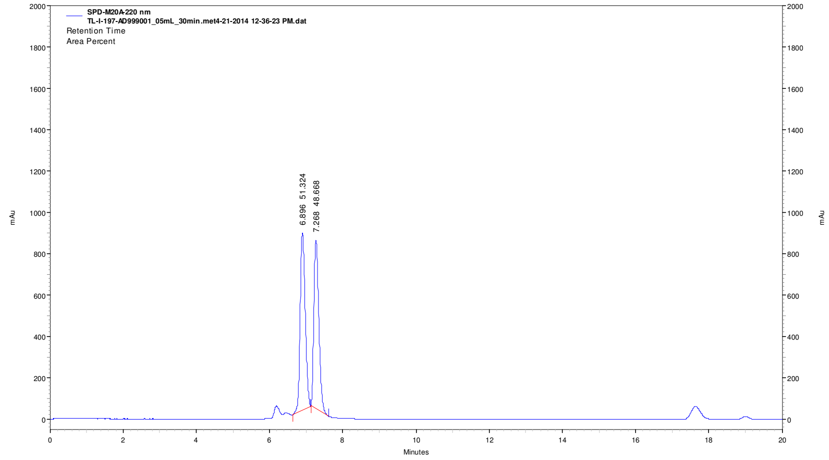
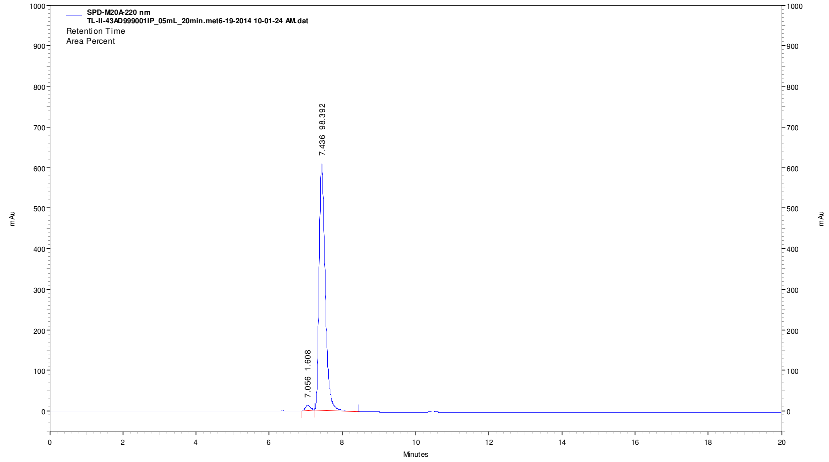
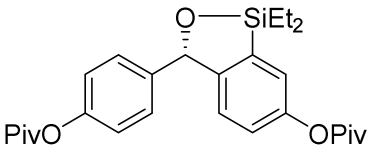




Chiralcel AD-H column, 0.1% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 7.1 min (1.61%), t_R = 7.4 min (98.39%).



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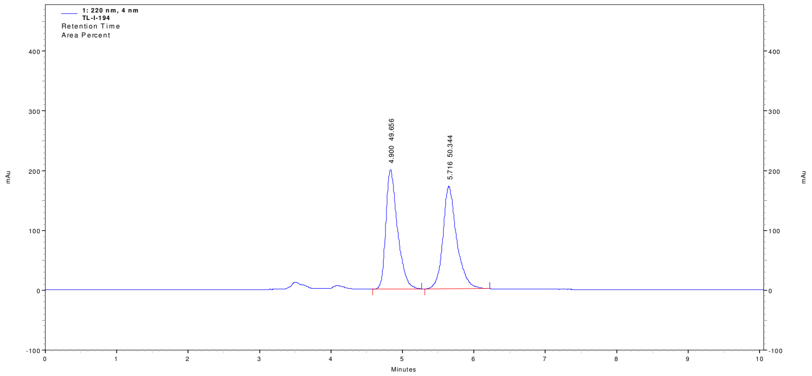
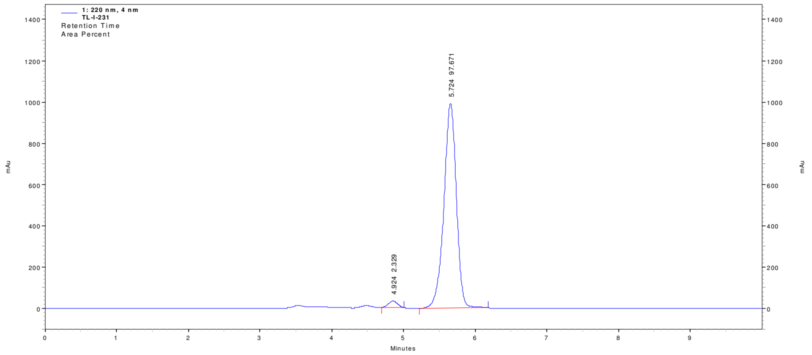
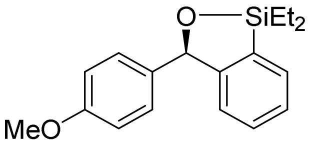




95% *ee*, Chiralpak IC column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 4.9 min (2.33%), t_R = 5.7 min (97.67%).



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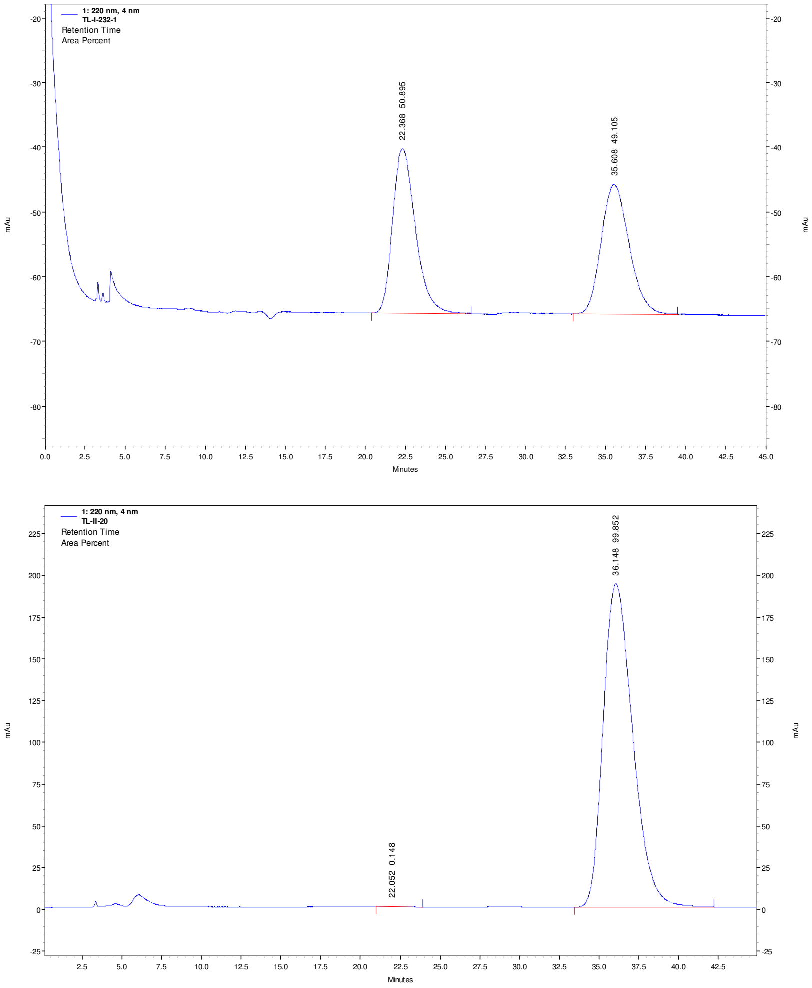
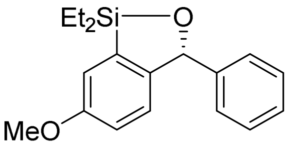
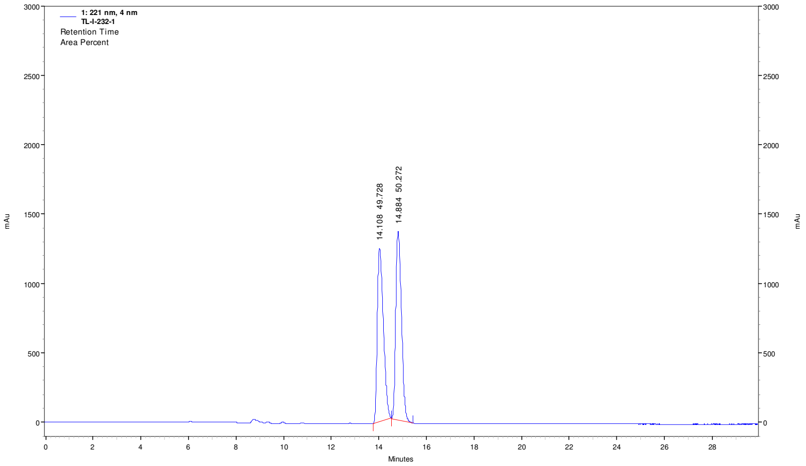
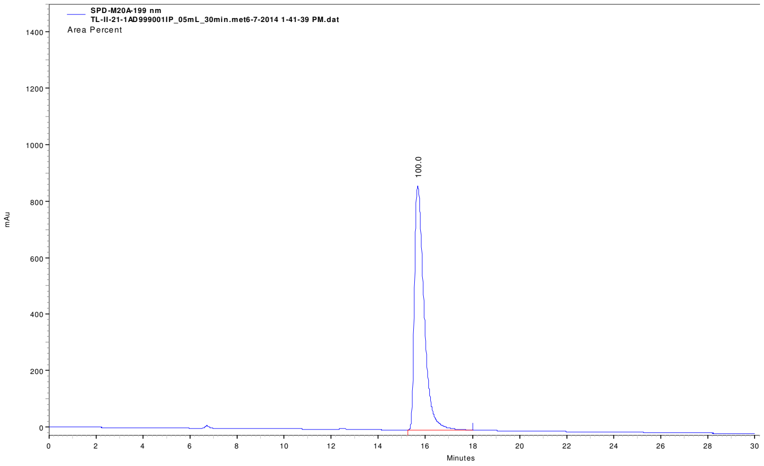


Chiralcel OJ-H column, 1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 22.1 min (0.15%), t_R = 36.1 min (99.85%).

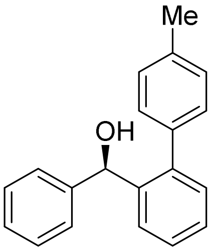


5d’





Chiralpak IA column, 0.1% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 14.1 min (<0.5%), t_R = 14.8 min (>99.5%).



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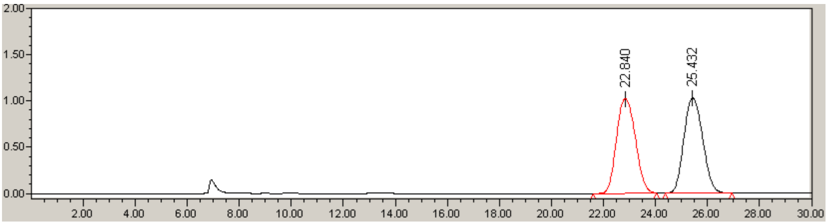
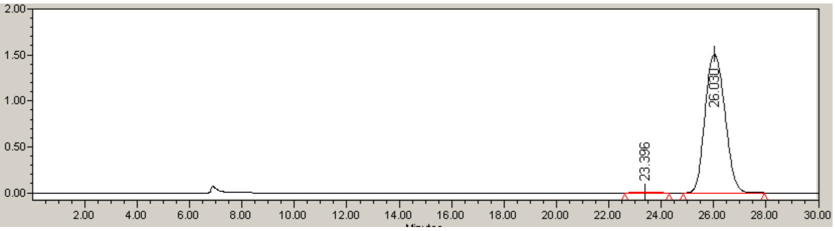
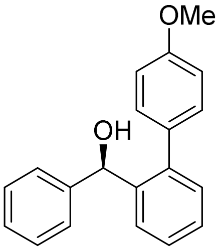




Chiralcel OD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 23.4 min (0.74%), t_R = 26.0 min (99.26%).



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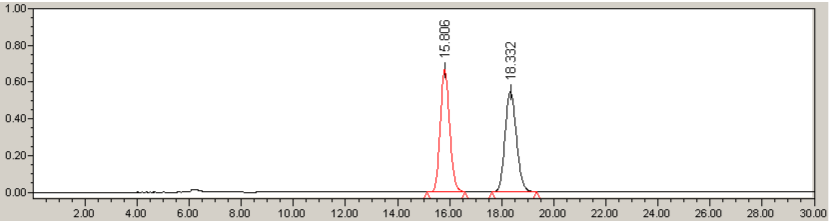
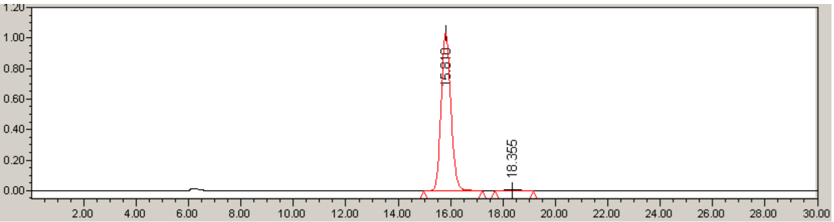
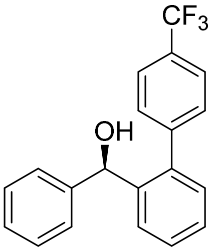




Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 15.8 min (99.35%), t_R = 18.4 min (0.65%).



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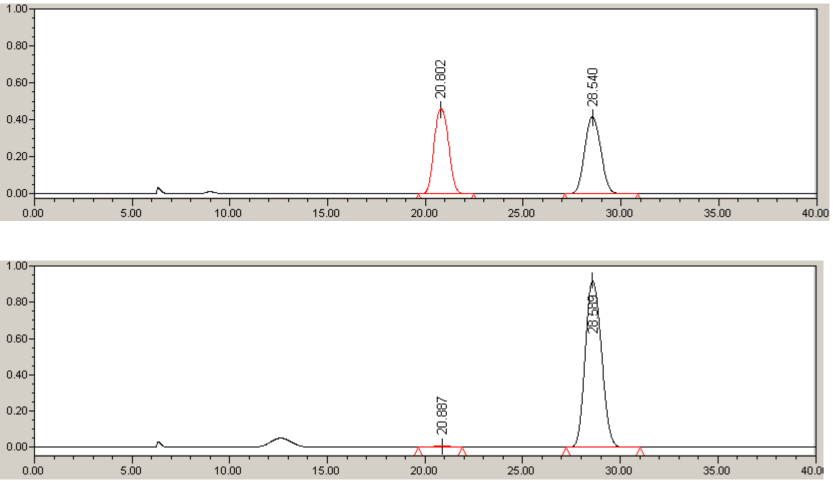
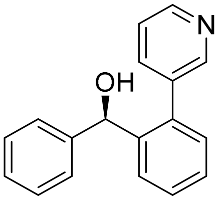


Chiralcel OD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 20.9 min (0.87%), t_R = 28.6 min (99.13%).



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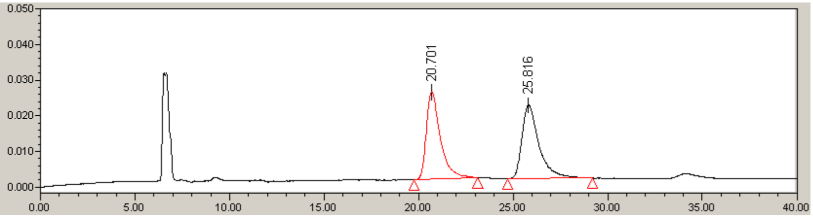
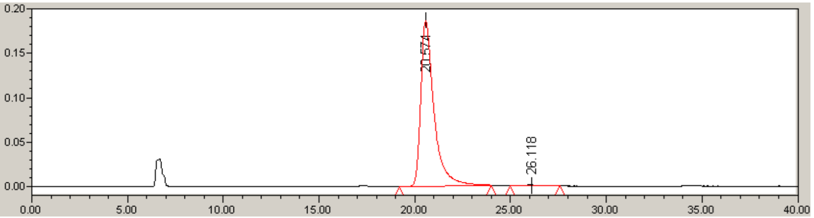
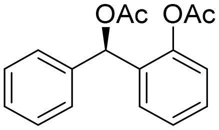
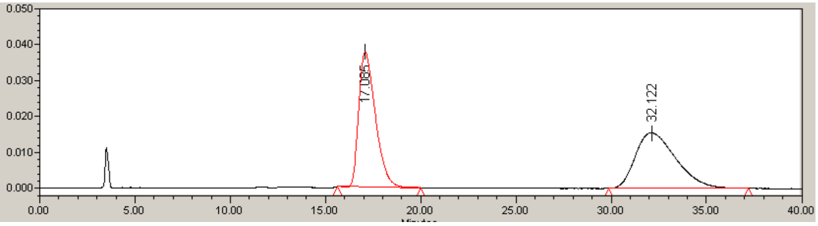


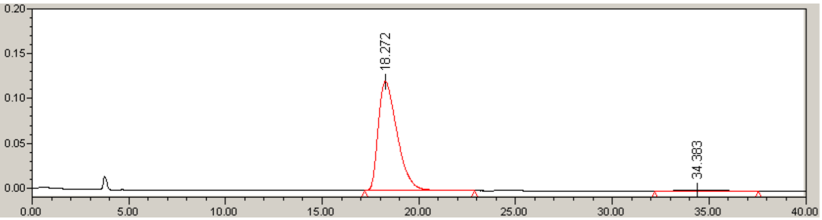


Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 20.6 min (99.46%), t_R = 26.1 min (0.54%).

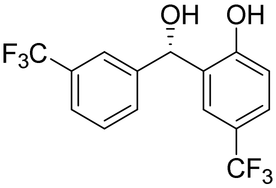


7





Chiralcel OJ-H column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 18.3min (97.77%), t_R = 34.4 min (2.23%).



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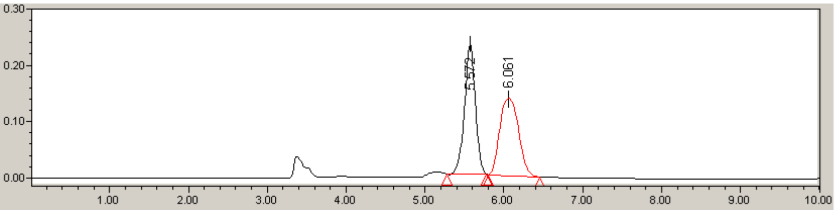
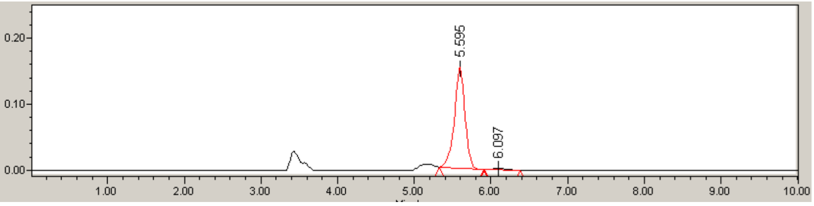
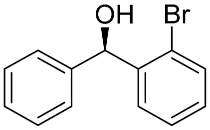




Chiralcel AD-H column, 10% ethanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 5.6 min (98.33%), t_R = 6.1 min (1.67%).



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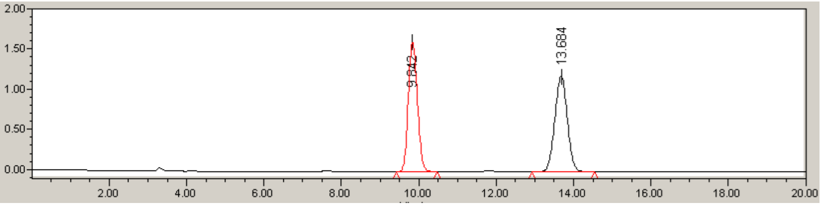
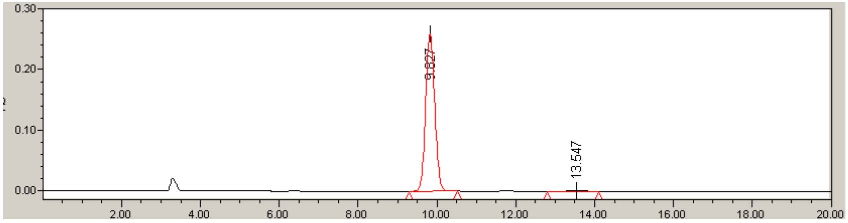
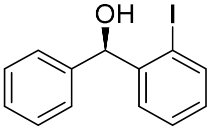




Chiralcel OD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 9.8 min (99.05%), t_R = 13.5 min (0.95%).



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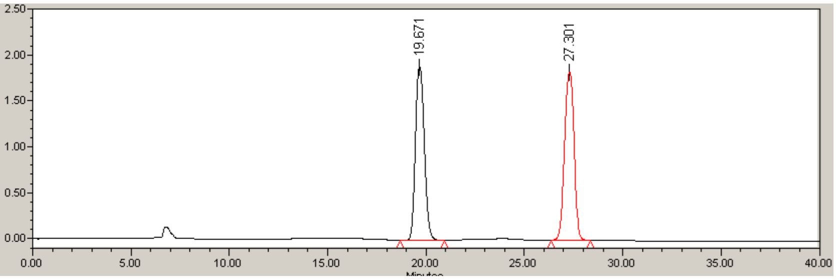
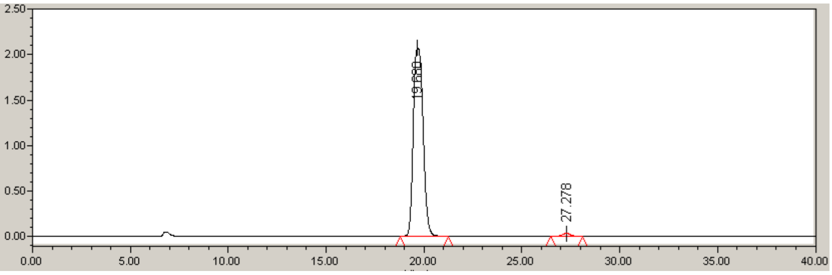
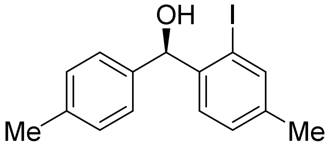




Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 19.7 min (98.79%), t_R = 27.3 min (1.21%).



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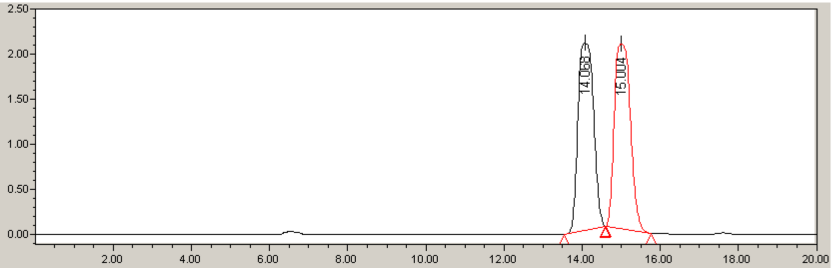
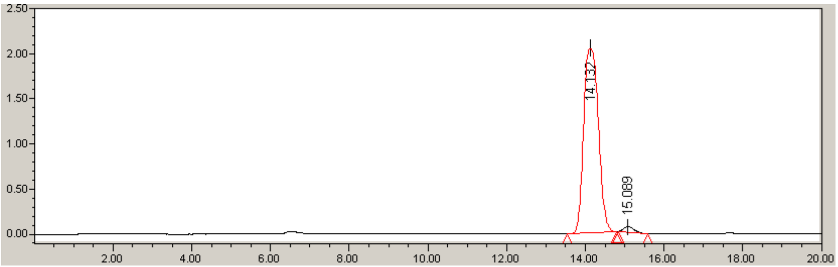
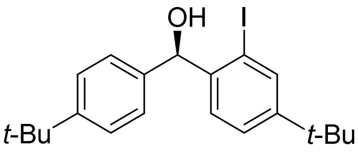




Chiralcel OD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 220 nm UV lamp, t_R = 14.1 min (97.76%), t_R = 15.1 min (2.24%).



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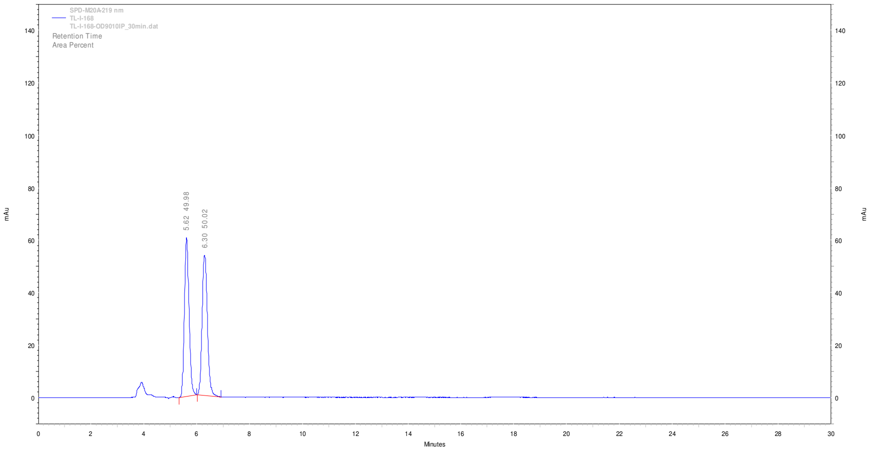

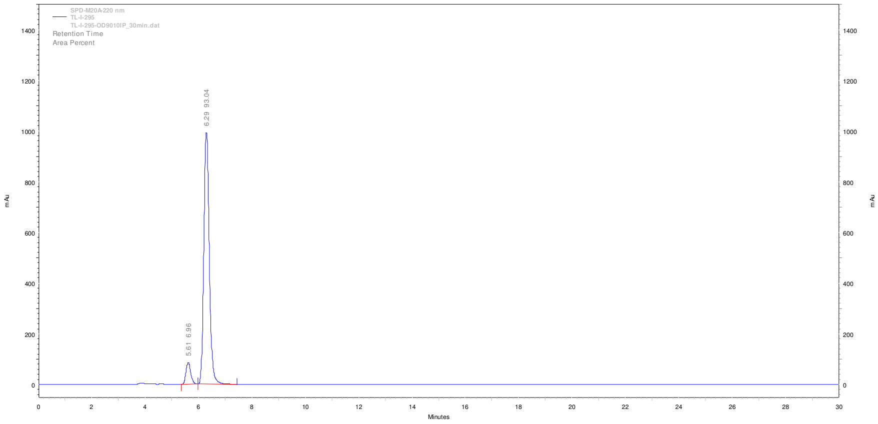

Chiralcel OD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rate, 220 nm UV lamp, t_R = 5.6 min (6.96%), t_R = 6.3 min (93.04%).