SUPPORTING INFORMATION

Lewis-Base Silane Activation: From Reductive Cleavage of Aryl Ethers to Selective Ortho-Silylation

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Spectral data

General Information

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk line techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless specified otherwise. Mesitylene (puriss., ≥99.0% (GC)) was degassed by three freeze-pump-thaw cycles prior to use. All other solvents were purified by passage through solvent purification columns and further degassed with argon.(1) NMR solvents for air-sensitive experiments were dried over CaH_2 and vacuum transferred or distilled into a dry Schlenk flask and subsequently degassed with argon. Triethylsilane (99%) and deuterotriethylsilane (97 atom % D) were purchased from Sigma-Aldrich and degassed by three freeze-pump-thaw cycles prior to use and other commercially available liquid reagents were treated analogously. Di-4-(methyl)phenyl ether, 1-naphthol, 2-naphthol, 4-*tert*-butylanisole, 4-methylanisole, 1,3-diphenoxybenzene, 2-methoxynaphthalene, and 1.0M tetrabutylammonium fluoride THF solution were purchased from Sigma-Aldrich and used as received. Sublimed grade KO*t*-Bu (99.99%) was purchased from Sigma-Aldrich and subjected to vacuum sublimation (30 mTorr, 160 °C) prior to use. 4-(Methoxy)dibenzofuran,(2) di-4-(*tert*-butyl)phenyl ether,(3) naphthyl ethers,(3) 4-(phenyl)phenyl phenyl ether(3), 2-ethoxynaphthalene(4), 2-neopentyloxynaphthalene(4), 2-*tert*-butyloxynaphthalene(5) were synthesized according to the literature procedures. Standard NMR spectroscopy experiments were conducted on a Varian Mercury (^1H, 300 MHz) spectrometer, a Varian Inova 400 MHz spectrometer, a Varian 500 MHz spectrometer equipped with an AutoX probe, or a Varian 600 MHz spectrometer equipped with a Triax Probe. Chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 7.(6) GC-FID analyses were obtained on an Agilent 6890N gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). GC-MS analyses were obtained on an Agilent 6850 gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High-resolution mass spectra (EI and FAB) were acquired by the California Institute of Technology Mass Spectrometry Facility. EPR spectra were recorded on a Bruker EMS spectrometer.

General Procedure

In a glovebox, a 4 mL screw cap vial was loaded with the corresponding substrate (0.1 mmol, 1 equiv.), base (0.5–5 equiv.) and a magnetic stirring bar, followed by syringe addition of the solvent (1 mL) and triethylsilane (1–5 equiv.). The reaction vial was sealed with a Teflon-lined screw cap and heated at a given temperature and time inside the glovebox (Table S2). After cooling to room temperature, dark red to black reaction mixture was diluted with diethyl ether (3 mL) and carefully quenched with 1 ml of 1 N aqueous HCl. Tridecane (internal standard for GC) was added, the organic layer was separated and the aqueous layer was extracted with ether (3 mL) until TLC controls show no UV-active compounds present in the extracts. The combined organic layers were passed through a short pad of Celite and subjected to GC/FID, GC/MS and ^1H-NMR analyses. Unless stated otherwise, in preparative experiments only products with the overall yield exceeding 2% were isolated and characterized.

In the case of naphthyl alkyl ethers, a different workup procedure was used. After cooling, the reaction was diluted with dichloromethane (5 mL) and carefully quenched with 2 mL of 1 N aqueous HCl. Tridecane was added, and the mixture was transferred to a separatory funnel. The organic phase was separated, and the aqueous layer was extracted with dichloromethane (3 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. For all reactions, the products were identified using GC/MS and GC/FID and NMR by comparison with the authentic samples. Trace soluble side products observed in naphthyl alkyl ether reductions included naphthalene, 1,2,3,4-tetrahydronaphthalene, and 5,6,7,8-tetrahydro-2-naphthol.

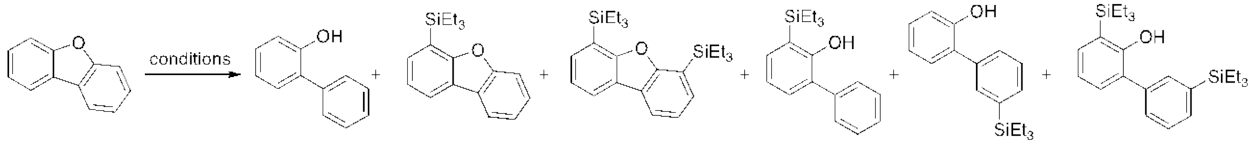
ICP-MS analysis

ICP-MS analysis was conducted using the California Institute of Technology MS facility with 100 mg samples of dibenzofuran, triethylsilane, mesitylene and potassium tert-butoxide, which were added to 50 mL DigiTUBE digestion tubes (SCP Science) followed by addition of 3.0 mL of Plasma Pure nitric acid (SCP Science) to each digestion tube and heating to 75 ^{o}C for 36 hours. After digestion, each sample was diluted using Nanopure/Milli Q water to 50 mL and sample analysis performed on an HP 4500 ICP-MS spectrometer. Semiquantitative analysis was performed using a 10 ppm solution of lithium, yttrium, cerium and thallium for calibration. Each sample was analyzed twice and the average measurements are given.

Table S1. ICP-MS Analysis of Various Metals in Reagents and Reaction Mixture

Element	Reagent (unit: ppm)				
	Dibenzofuran	KO*t*-Bu	Et_3SiH	Mesitylene	Reaction Mixture
Fe	0.15	4.92	0.67	0.11	5.80
Ru	0.00	0.07	0.00	0.01	3.13
Os	0.01	0.01	0.01	0.00	0.20
Co	0.00	0.01	0.00	0.00	0.26
Rh	0.00	0.00	0.00	0.00	1.07
Ir	0.00	0.01	0.00	0.09	0.40
Ni	0.12	0.06	0.06	0.38	0.79
Pd	0.00	0.04	0.00	0.01	0.88
Pt	0.00	0.07	0.00	0.01	1.74
Cu	0.03	10.42	0.04	0.09	7.59

Table S2. Full Optimization Details for the Cleavage of Dibenzofuran



1 2 3 4 5 6 7

Entry	Et_3SiH (equiv)	Base (equiv.)	Solvent	T, °C	Conv. (%)	**2**	**3**	**4**	**5**	**6**	**7**
1	0	KO*t*-Bu (2)	Toluene	100	0	—	—	—	—	—	—
2	5	None	Toluene	100	0	—	—	—	—	—	—
3[a]	5	KO*t*-Bu (2)	Toluene	100	70	34	28	4	—	—	—
4[b]	5	KO*t*-Bu (2)	Toluene	100	98	38	16	10	21	2	7
5	4	KO*t*-Bu (2)	Toluene	100	100	41	17	15	12	1	9
6	3	KO*t*-Bu (2)	Toluene	100	96	42	20	9	13	1	4
7	2	KO*t*-Bu (2)	Toluene	100	87	34	30	10	6	1	3
8	1	KO*t*-Bu (2)	Toluene	100	56	19	29	1	2	—	1
9	5	KO*t*-Bu (0.5)	Toluene	100	89	12	48	20	9	—	1
10	2	KO*t*-Bu (0.5)	Toluene	100	66	9	43	8	2	—	—
11	5	KO*t*-Bu (5)	Toluene	100	97	63	10	1	22	—	2
12	5	KH (1)	Dioxane	100	49	1	43	5	—	—	—
13	5	KO*t*-Bu (2)	Dioxane	100	70	25	28	10	4	1	1
14[c]	—	KO*t*-Bu (2)	Et_3SiH	100	99	26	13	25	11	1	21
15	5	KO*t*-Bu (2)	Toluene	80	98	29	18	26	9	—	7
16	3	KO*t*-Bu (3)	Mesitylene	165	100	85	3	—	5	2	—
17	2	KO*t*-Bu (2)	Mesitylene	165	100	62	8	1	12	1	—
18	3	KOt-Bu (2)	Mesitylene	165	97	52	17	5	16	1	2
19	1	KO*t*-Bu (1)	Mesitylene	165	57	30	21	—	—	—	—
20	3	KO*t*-Bu (0.5)	Mesitylene	165	85	29	35	15	4	—	2
21	5	KO*t*-Bu (5)	Mesitylene	165	100	77	3	0	3	8	—
22	3	KH (3)	Mesitylene	165	100	66	3	0	5	11	—
23	3	KOEt (3)	Mesitylene	165	95	77	10	0	6	1	—
24	3	KOEt (3)	Toluene	100	40	19	19	2	—	—	—
25	3	KOMe (3)	Mesitylene	165	64	31	27	2	3	1	—
26	3	NaO*t*-Bu (3)	Mesitylene	165	0	—	—	—	—	—	—
27	3	LiO*t*-Bu (3)	Mesitylene	165	0	—	—	—	—	—	—

28	3	NaOEt (3)	Mesitylene	165	0	—	—	—	—	—	—
29	5	CsOR[d] (2)	Toluene	100	89	75	3	11	—	—	—
30	3	KO*t*-Bu (3)	Benzene	85	96	37	20	13	12	—	9
31	5	KO*t*-Bu (2)	DMF	100	0	—	—	—	—	—	—
32	5	KO*t*-Bu (2)	DMA	100	0	—	—	—	—	—	—
33	5	KO*t*-Bu (2)	Diglyme	100	0	—	—	—	—	—	—
34	5	KO*t*-Bu (2)	*t*-BuOH	100	0	—	—	—	—	—	—
35	5	KO*t*-Bu (2)	Diisopropyl carbinol	100	0	—	—	—	—	—	—

[a] Yields were reproducible within ±2% when performed in another laboratory at the Center for Catalysis and Chemical Synthesis (California Institute of Technology); [b] Reaction performed in 0.05M solution; [c] Reaction performed in neat Et_3SiH; [d] R = 2-ethylhexyl.

Table S3. Cleavage of Dibenzofuran in the Presence of Additives[a]

Entry	Et_3SiH (equiv.)	Base (equiv.)	Additive	Solvent	T, °C	Convers (%)	**2**	**3**	**4**	**5**	**6**	**7**
1	5	KO*t*-Bu (2)	1,10-phen[b] (2)	Toluene	100	5	—	—	—	—	—	—
2	5	KO*t*-Bu (2)	18-crown-6 (2.5)	Toluene	100	0	—	—	—	—	—	—
3	3	—	KBH_4 (3)	Mesitylene	165	0	—	—	—	—	—	—
4	3	—	KCN (3)	Mesitylene	165	0	—	—	—	—	—	—
5	3	—	DIBAL (3)	Mesitylene	165	0	—	—	—	—	—	—
6	3	—	$LiAlH_4$ (3)	Mesitylene	165	0	—	—	—	—	—	—
7	3	—	Bu_3SnH (3)	Mesitylene	165	0	—	—	—	—	—	—
8	5	—	Me_4NF (2)	Toluene	100	0	—	—	—	—	—	—
9	5	—	TBAF (2)	Toluene	100	0	—	—	—	—	—	—
10	—	KO*t*-Bu (2)	KH (2)	Dioxane	100	0	—	—	—	—	—	—

[a] General Procedure was followed (100 °C, 20 hours); [b] 1,10-phen = 1,10-phenanthroline.

4-(Triethylsilyl)dibenzofuran (**3**)

The title compound was prepared by analogy to the protocol for the synthesis of 4-(trimethylsilyl)dibenzofuran by Kelly and co-workers.(7) Data for (**3**): Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.99-7.96 (m, $2H_{ar}$), 7.59 (d-like, *J* = 10 Hz, $1H_{ar}$), 7.54 (dd, *J* = 2, 5 Hz, $1H_{ar}$), 7.48-7.44 (m, $1H_{ar}$), 7.37-7.33 (m, $2H_{ar}$), 1.03 (m, 15H, $3CH_2CH_3$). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 161.30, 156.05, 133.57, 126.92, 122.52, 122.48, 121.58, 120.68, 111.75, 7.63, 3.59. HRMS: [$C_{18}H_{22}OSi$] calculated 282.1440; measured 282.1444.

4,6-Bis(triethylsilyl)dibenzofuran (**4**)

To a solution of dibenzofuran (2.00 g, 11.9 mmol, 1 equiv.) and tetramethylethylenediamine (11.1 mL, 29.7 mmol, 2.5 equiv.) in tetrahydrofuran (50 ml) *t*-butyllithium (17.5 mL of 1.7 M solution in pentane, 29.8 mmol, 2.5 equiv.) was slowly added at -78 °C under argon. The mixture was allowed to reach ambient temperature and stirring was continued for 4 h prior to addition of chlorotriethylsilane (10.1 mL, 60 mmol, 5 equiv.). The resulting mixture was stirred at ambient temperature for another 16 h. After quenching the reaction with the saturated ammonium chloride solution (40 mL) and extraction with diethyl ether (3x30 mL), the combined organic layers were dried over anhydrous sodium sulfate, filtered and the filtrate concentrated in vacuo. Crude reaction mixture was purified by chromatography on silica (hexanes) and product obtained was recrystallized from a mixture of methanol and isopropanol (1:1) to afford 4,6-bis(triethylsilyl)dibenzofuran (1.28 g, 2.45 mmol, 28%) as colorless needles. Data for (**4**): Colorless needles. M.p. = 59-61 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 3, 9 Hz, $2H_{ar}$), 7.54 (dd, *J* = 3, 9 Hz, $2H_{ar}$), 7.33 (t, *J* = 9 Hz, $2H_{ar}$), 1.07-0.95 (m, 30H, $6CH_2CH_3$). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 160.90, 133.48, 122.87, 122.34, 121.57, 120.03, 7.66, 3.52. HRMS: [$C_{24}H_{36}OSi_2$] calculated 396.2305; measured 396.2321.

3-(Triethylsilyl)biphenyl-2-ol (**5**)

The title compound was prepared via cleavage of **3** (*vide infra*).

Data for (**5**): White solid. M.p. = 44-46 °C ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52-7.40 (m, $5H_{ar}$), 7.36 (dd, *J* = 3, 9 Hz, $1H_{ar}$), 7.23 (dd, *J* = 3, 6 Hz, $1H_{ar}$), 6.98 (t, *J* = 9 Hz, $1H_{ar}$), 5.41 (s, 1H, OH), 1.02-0.96 (m, 9H, CH_3), 0.91-0.83 (m, 6H, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.25, 137.51, 135.97, 131.30, 129.58, 129.39, 128.01, 127.17, 123.04, 120.40, 7.79, 3.69. HRMS: [$C_{18}H_{24}OSi$] calculated 284.1596; measured 284.1583.

(3'-Triethylsilyl)biphenyl-2-ol (**6**)

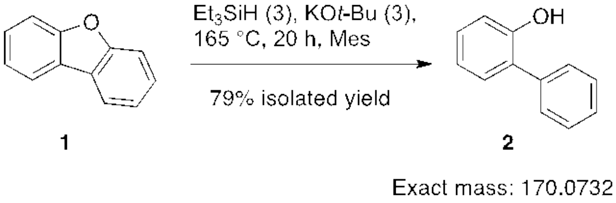
The title compound was prepared via cleavage of **3** (*vide infra*).

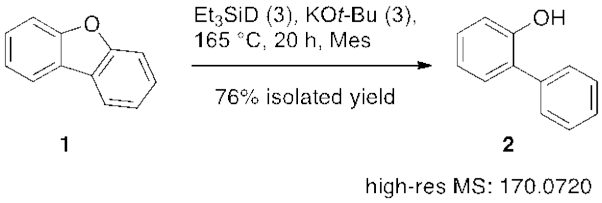
Data for (**6**): Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.57-7.56 (m, $1H_{ar}$), 7.54-7.52 (m, $1H_{ar}$), 7.49-7.44 (m, $2H_{ar}$), 7.28-7.24 (m, $2H_{ar}$), 7.02-6.99 (m, $2H_{ar}$), 5.24 (s, 1H, OH), 0.98 (t, *J* = 10 Hz, 9H, CH_3), 0.82 (q, *J* = 15 Hz, 6H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.44, 139.07, 136.12, 134.71, 133.76, 130.23, 129.36, 129.08, 128.53, 128.44, 120.80, 115.72, 7.43, 3.31. HRMS: [$C_{18}H_{24}OSi$] calculated 284.1596; measured 284.1585.

3,3'-Bis(triethylsilyl)biphenyl-2-ol (**7**)

The title compound was prepared according to General Procedure by heating dibenzofuran (**1**, 840 mg, 5.0 mmol, 1 equiv.) with KO*t*-Bu (1.12 g, 10 mmol, 2 equiv.) and Et_3SiH (4.0 ml, 25 mmol, 5 equiv.) in 20 ml of toluene for 20 hours at 100 ^{o}C. After acidic aqueous work up, the crude reaction mixture was purified by chromatography on silica using hexanes and hexanes-ether (10:1) to give, among other isolated products, 20 mg (0.05 mmol, 1%) of **7**. Data for (**7**): oily solid ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.53-7.44 (m, 2H_{ar}), 7.46-7.44 (m, 2H_{ar}), 7.36 (dd, *J* = 1.5, 7.5 Hz, 1H_{ar}), 7.23 (dd, *J* = 1.5, 7.5 Hz, 1H_{ar}), 6.98 (t, *J* = 7 Hz, 1H_{ar}), 5.42 (s, 1H, OH), 1.01-0.96 (m, 18H, 6CH_3) 0.91-0.77 (m, 15H, 6CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.37, 139.45, 136.61, 135.87, 135.09, 133.86, 131.38, 129.57, 128.71, 127.55, 122.97, 120.36, 7.80, 7.57, 3.69, 3.46. HRMS: [$C_{24}H_{38}OSi_2$] calculated 398.2461; measured 396.2470.

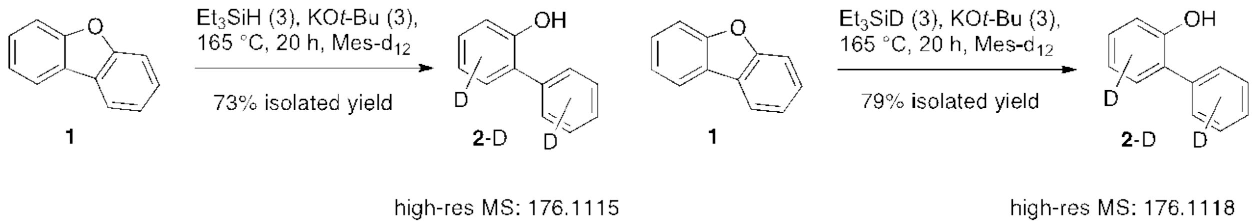
Preparative Scale Cleavage of Dibenzofuran and Deuteration Experiments





The reaction was conducted according to the General Procedure by heating dibenzofuran (**1**, 250 mg, 1.49 mmol, 1 equiv.), KO*t*-Bu (500 mg, 4.46 mmol, 3 equiv.) and Et_3SiH (713 μl, 4.46 mmol, 3 equiv.) in 4.4 mL of mesitylene for 20 hours at 165 ^{o}C. After dilution with diethyl ether (5 mL), the organic phase was first washed with water (1 mL), and then with 2.5N KOH solution (3 x 20 mL). The basic aqueous fractions were collected and washed through once with CH_2Cl_2 (25 ml) to remove any undesired organics. The resulting basic aqueous fractions were then acidified with concentrated HCl until a pH of 1 and then subsequently extracted with CH_2Cl_2 (3 x 25 mL). The organic fractions were collected and concentrated under reduced pressure to give pale yellow crystals. Purification by chromatography on silica gel with hexanes/ethyl acetate (gradient elution: 0% to 5% ethyl acetate) afforded biphenyl-2-ol (**2**, 198 mg, 1.16 mmol, 79 %) as a colorless solid. ^{1}H and ^{13}C NMR spectral assignments of **1** were consistent with those of the authentic sample.

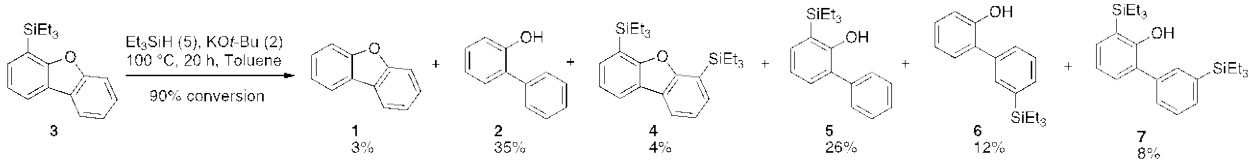
The identical procedure applied to the reductive cleavage of dibenzofuran but now with Et_3SiD gave undeuterated biphenyl-2-ol with 76% isolated yield. HRMS: [$C_{12}H_{10}O$] calculated 170.0732; measured 170.0720.



Repeating the aforementioned experiment with Et_3SiH and Mes-d_{12} gave deuterated biphenyl-2-ol in 73% isolated yield. HRMS: [$C_{12}H_4D_6O$] calculated 176.1108; measured 176.1115; FWHM ~ 4 Da.

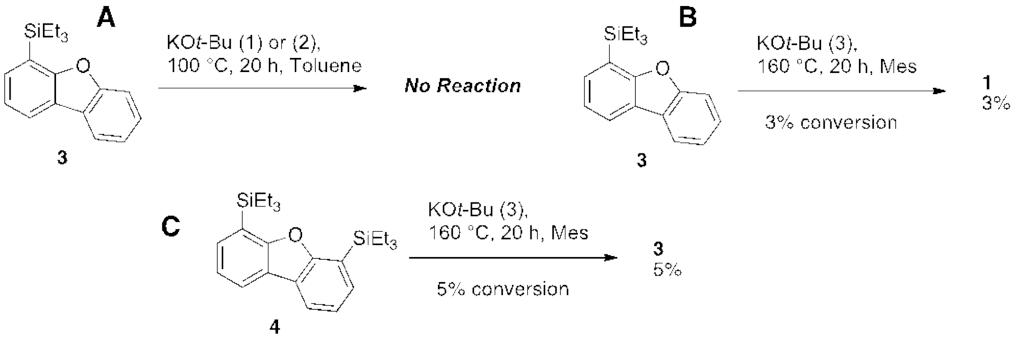
The identical procedure applied to the reductive cleavage of dibenzofuran but now with Et_3SiD and Mes-d_{12} gave deuterated biphenyl-2-ol with 79% isolated yield. HRMS: [$C_{12}H_4D_6O$] calculated 176.1108; measured 176.1108; FWHM ~ 4 Da.

Cleavage of 4-(Triethylsilyl)dibenzofuran



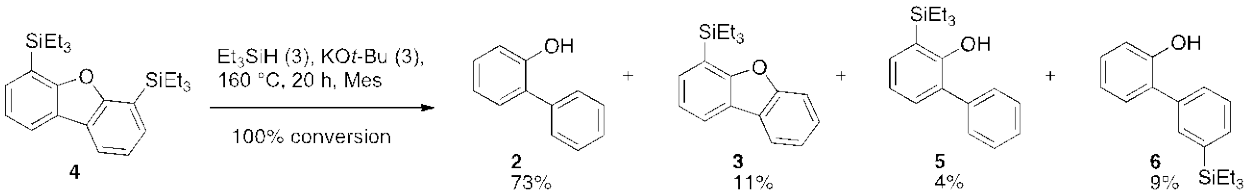
The reaction was conducted according to the General Procedure by heating 4-Et_3Si-dibenzofuran (**3**, 141 mg, 0.5 mmol, 1 equiv.), KO*t*-Bu (112 mg, 1 mmol, 2 equiv.) and Et_3SiH (401 μl, 2.5 mmol, 5 equiv.) in 2 ml of toluene for 20 hours at 100 ^{o}C. After acidic aqueous work up, the crude reaction mixture was purified by chromatography on silica using hexanes and hexanes-ether (10:1) to isolate 2-phenylphenol (**2**, 30 mg, 0.177 mmol, 35%), 2-triethylsilyl-6-phenylphenol (**5**, 37 mg, 0.134 mmol, 26%), 2-(3-triethylsilylphenyl)phenol (**6**, 17 mg, 0.063 mmol, 12%). Quantities of unconsumed **3** as well as products **1**, **4** and **7** were obtained using post-chromatography GC-FID analysis of the corresponding mixed fractions.

Investigation of Silylated Dibenzofurans as Intermediates Towards C-O Bond Cleavage: Cleavage Attempts with KO*t*-Bu



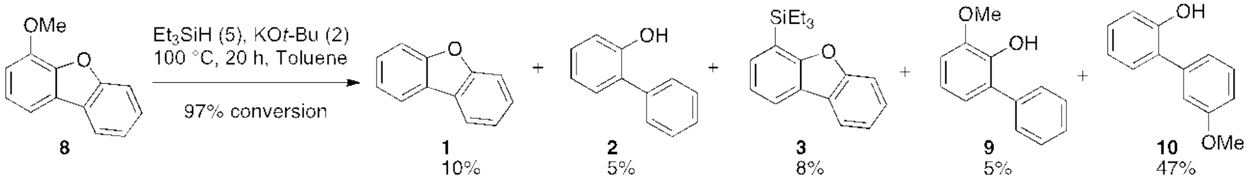
Starting material **3** (14.1 mg, 0.05 mmol, 1 equiv.) was heated with KO*t*-Bu (5.6 mg or 11.2 mg, 1 or 2 equiv., respectively) in 0.8 ml d-toluene at 100 ^{o}C for 20 hours in a J. Young tube under nitrogen. Monitoring the reaction progress by ^{1}H NMR showed no conversion of **3** in both cases. Likewise, starting materials **3** (28.2 mg, 0.1 mmol, 1 equiv.) or **4** (39.6 mg 0.1 mmol, 1 equiv.) were heated with KO*t*-Bu (36.6 mg) in 0.3 mL of mesitylene at 160 ^{o}C for 20 hours. Subsequent analysis of the crude reaction mixtures by GC-FID or ^{1}H NMR revealed 3% conversion to **1** in case of **3** and 5% conversion to **3** from **4**.

Cleavage of 4,6-Bis(triethylsilyl)dibenzofuran



The reaction was conducted according to the General Procedure by heating 2-(3'-triethylsilylphenyl)phenol (**4**, 39.6 mg, 0.1 mmol, 1 equiv.), KO*t*-Bu (33.6 mg, 0.3 mmol, 3 equiv.) and Et$_3$SiH (48 μl, 0.3 mmol, 3 equiv.) in 0.2 ml of mesitylene for 20 hours at 160 ^{o}C. After acidic aqueous work up, internal standard was added and the crude reaction mixture was analyzed by GC-FID.

Cleavage of 4-(Methoxy)dibenzofuran



The reaction was conducted according to the General Procedure by heating 4-MeO-dibenzofuran (**8**, 89 mg, 0.5 mmol, 1 equiv.), KO*t*-Bu (112 mg, 1 mmol, 2 equiv.) and Et$_3$SiH (401 μl, 2.5 mmol, 5 equiv.) in 2 ml of toluene for 20 hours at 100 ^{o}C. After aqueous work up, the crude reaction mixture was purified by chromatography on silica using hexanes and hexanes-ether to recover unconsumed starting material **8** (3 mg, 0.015 mmol, 3%) and isolate dibenzofuran (**1**, 8.4 mg, 0.05 mmol, 10%; since fractions of **1** contained small amounts of starting **8**, quantification was done by ^{1}H-NMR with CH_2Br_2 as an internal standard), 1,1′-biphenyl-2-ol (**2**, 4.3 mg, 0.025 mmol, 5%), 4-Et$_3$Si-dibenzofuran (**3**, 11 mg, 0.039 mmol, 8%), 2-methoxy-6-phenyl-phenol (**9**, mg, 0.025 mmol, 5%), 2-(3'-methoxyphenyl)phenol (**10**, 47 mg, 0.235 mmol, 47%). Note: only compounds with the yield exceeding 2% were characterized. ^{1}H and ^{13}C NMR spectral assignments of **9**(8) and **10**(9) were consistent with literature reports.

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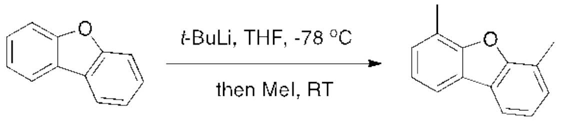
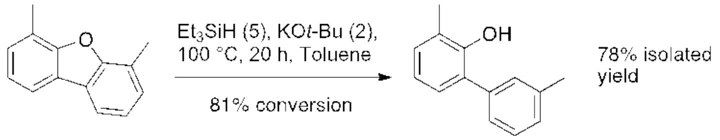
Synthesis of 4,6-Di(methyl)dibenzofuran



1 **15**

To a solution of dibenzofuran (2.00 g, 11.9 mmol, 1 equiv.) and tetramethylethylenediamine (11.1 mL, 29.7 mmol, 2.5 equiv.) in diethyl ether (50 ml) *t*-butyllithium (17.5 mL of 1.7 M solution in pentane, 29.8 mmol, 2.5 equiv.) was slowly added at −78 ^{o}C under argon. The mixture was allowed to reach ambient temperature and stirring was continued for 4 h prior to addition of methyl iodide (3.7 mL, 60 mmol, 5 equiv.). The resulting mixture was stirred at ambient temperature for another 16 h. After quenching the reaction with the saturated ammonium chloride solution (40 mL) and extraction with diethyl ether (3x30 mL), the combined organic layers were dried over anhydrous sodium sulfate, filtered and the filtrate concentrated in vacuo. Crude reaction mixture was purified by chromatography on silica (hexanes) and product obtained was recrystallized from methanol to afford 4,6-dimethyldibenzofuran (480 mg, 2.45 mmol, 21%) as a colorless solid. Data for (**15**): ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.0, 6.0 Hz, $2H_{ar}$), 7.24-7.20 (m, $4H_{ar}$), 2.61 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.07, 128.00, 124.17, 122.60, 122.02, 118.2, 15.41. HRMS: [$C_{14}H_{12}O$] calculated 196.0888; measured 196.0884.

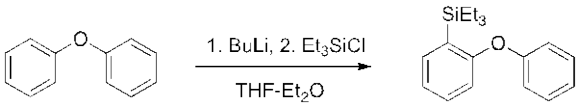
Cleavage of 4,6-Di(methyl)dibenzofuran



15 **16**

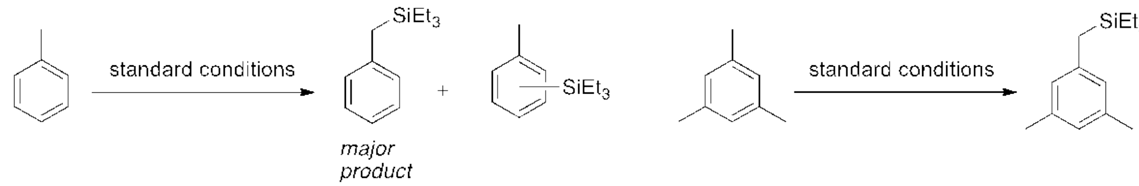
The reaction was conducted according to the General Procedure by heating 4,6-di(methyl)dibenzofuran (**15**, 98 mg, 0.5 mmol, 1 equiv.), KO*t*-Bu (112 mg, 1 mmol, 2 equiv.) and Et_3SiH (401 μl, 2.5 mmol, 5 equiv.) in 2 ml of toluene for 20 hours at 100 ^{o}C. After aqueous work up, the crude reaction mixture was purified by chromatography on silica using hexanes-ether 4:1 to obtain 77 mg of product **16** as yellow oil. Data for (**16**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.5 Hz, $1H_{ar}$), 7.25-7.22 (m, $2H_{ar}$), 7.20-7.18 (m, $1H_{ar}$), 7.11 (d-like, *J* = 10 Hz, $1H_{ar}$), 7.05 (d-like, *J* = 7.5 Hz, $1H_{ar}$), 6.87 (t, *J* = 7.5 Hz $1H_{ar}$), 5.31 (s, 1H, OH), 2.39 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 150.68, 139.26, 137.36, 130.51, 129.93, 129.39, 128.73, 127.83, 127.76, 126.20, 124.70, 120.25, 21.60, 16.33. HRMS: [$C_{14}H_{14}O$] calculated 198.1045, measured 198.1046.

o-Triethylsilyldiphenyl ether



o-Triethylsilyldiphenyl ether was prepared using the modified procedure by Fink[10] on a 30 mmol scale based on diphenyl ether. After addition of Et_3SiCl, the reaction mixture was stirred at 40 °C for 4 hours followed by aqueous work up and vacuum distillation to obtain the title compound as colorless oil in 88% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, J = 7.0, 1.5 Hz, $1H_{ar}$), 7.35-7.31 (m, $2H_{ar}$), 7.30-7.25 (m, $1H_{ar}$), 7.10-7.06 (m, $1H_{ar}$), 7.02-6.97 (m, $2H_{ar}$), 6.79 (d, J = 8.0, $1H_{ar}$), 0.95 (t-like, J = 8.5 Hz, 9H), 0.83 (q-like, J = 8.0 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 162.33, 157.39, 136.57, 130.58, 129.86, 129.82, 127.76, 123.34, 123.08, 122.86, 119.04, 117.22, 7.71, 3.55. HRMS: [$C_{18}H_{24}SiO$] calculated 284.1596, measured 284.1587.

Triethylsilylation of Toluene and Mesitylene



In many instances we have observed the formation of the solvent-derived silylated products when using toluene or mesitylene for our ether reductive cleavage reactions. Since it was not possible to separate the resulting products from their respective parent solvents by column chromatography or distillation, at this point we cannot assess their yields, but tentatively estimate them to be in 5-10% range based on Et_3SiH. In case of toluene, the identity of products was confirmed by comparison of the NMR spectra obtained with the literature data.(11) Thus, we can conclude that the major product is benzyl triethylsilane (**17**), which is also consistent with the GC-MS analysis of fragmentation patterns of isomeric products. Likewise, it appears that silylation of mesitylene proceeds predominantly into the benzylic position. HRMS [$C_{15}H_{26}Si$] calculated 234.1804, measured 234.1804). Full characterization details for those compounds will be reported in due course.

EPR experiments

Dibenzofuran (**1**, 16.8 mg, 0.1 mmol, 1 equiv.), KO*t*-Bu (22.5 mg, 0.2 mmol, 2 equiv.) and Et_3SiH (80 μl, 0.5 mmol, 5 equiv.) were heated in 0.4 ml of toluene for 1 hour at 100 °C inside the glovebox. After this time reaction mixture was diluted with 0.8 ml of toluene and filtered into an EPR tube. The spectrum was recorded within 20 min after filtration. In a control experiment recorded without dibenzofuran, the same signal was observed albeit with lower intensity.

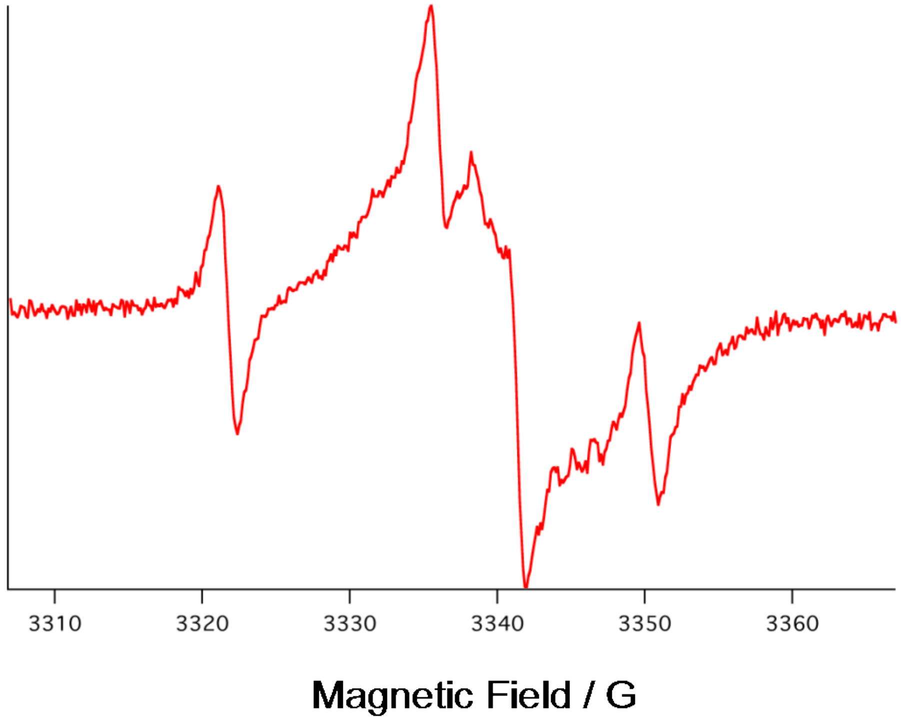


Figure S1. EPR spectrum of dibenzofuran, Et_3SiH and KO*t*-Bu reaction mixture in toluene. The same signal is observed without dibenzofuran added.

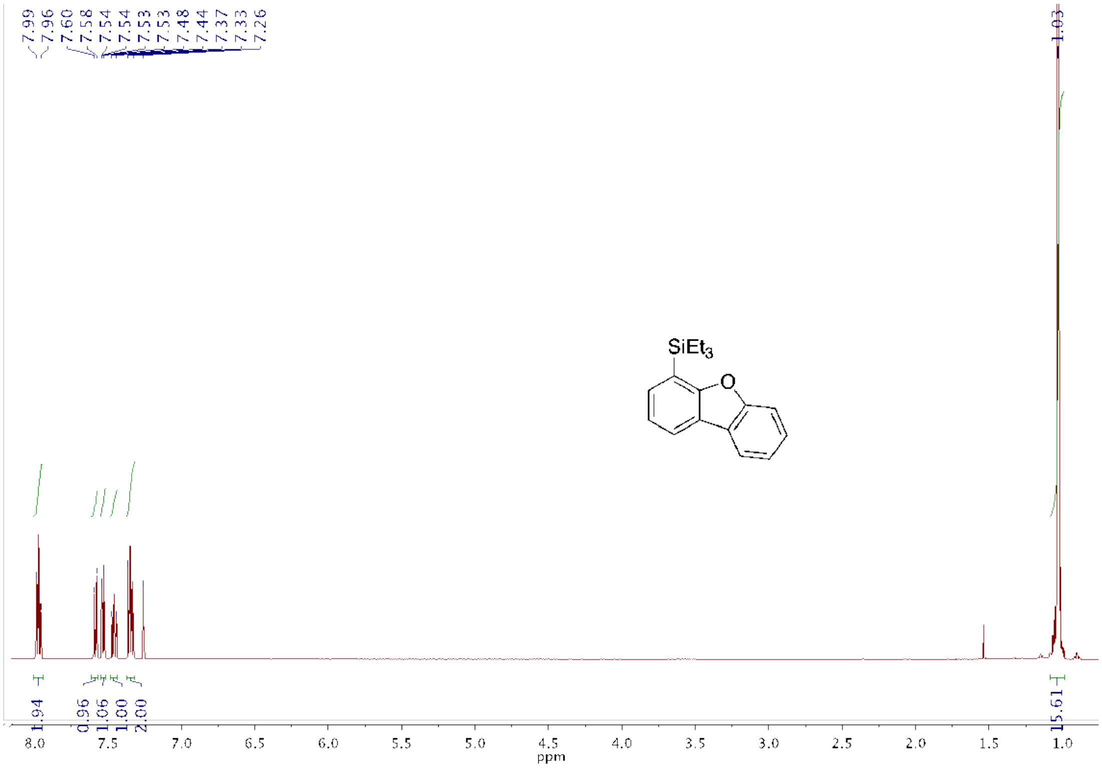


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-(triethylsilyl)dibenzofuran (**3**)

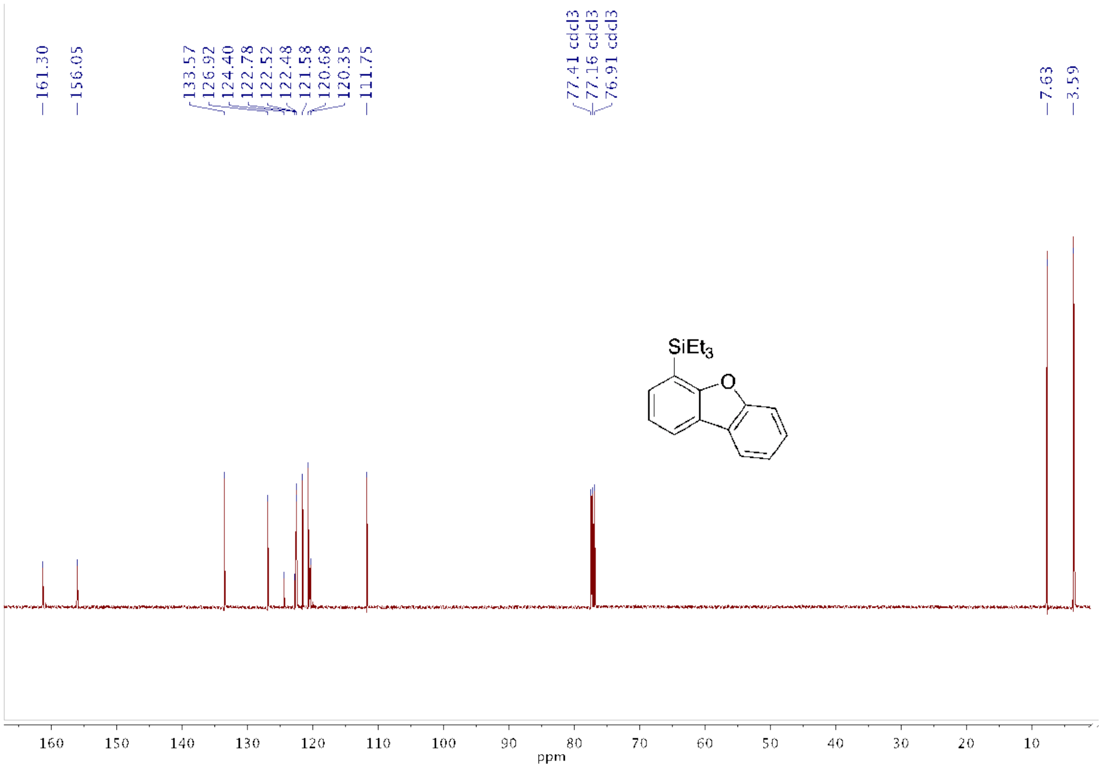


Figure S3. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-(triethylsilyl)dibenzofuran (**3**)

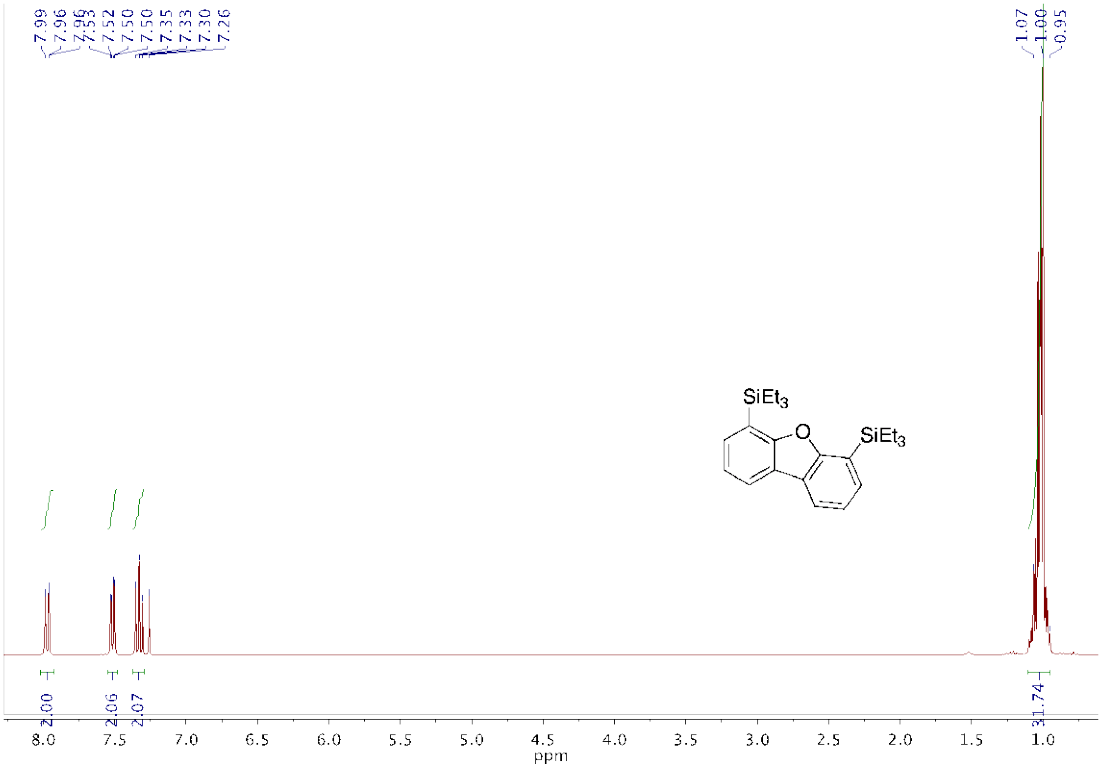


Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4,6-bis(triethylsilyl)dibenzofuran (**4**)

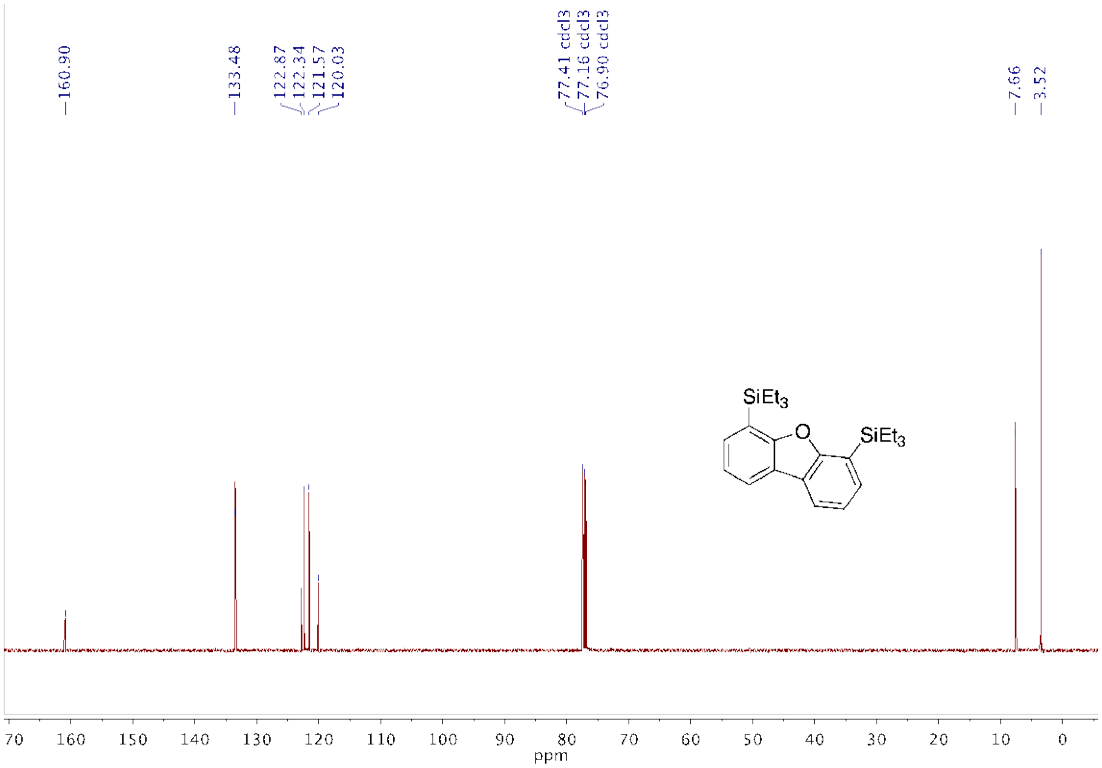


Figure S5. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4,6-bis(triethylsilyl)dibenzofuran (**4**)

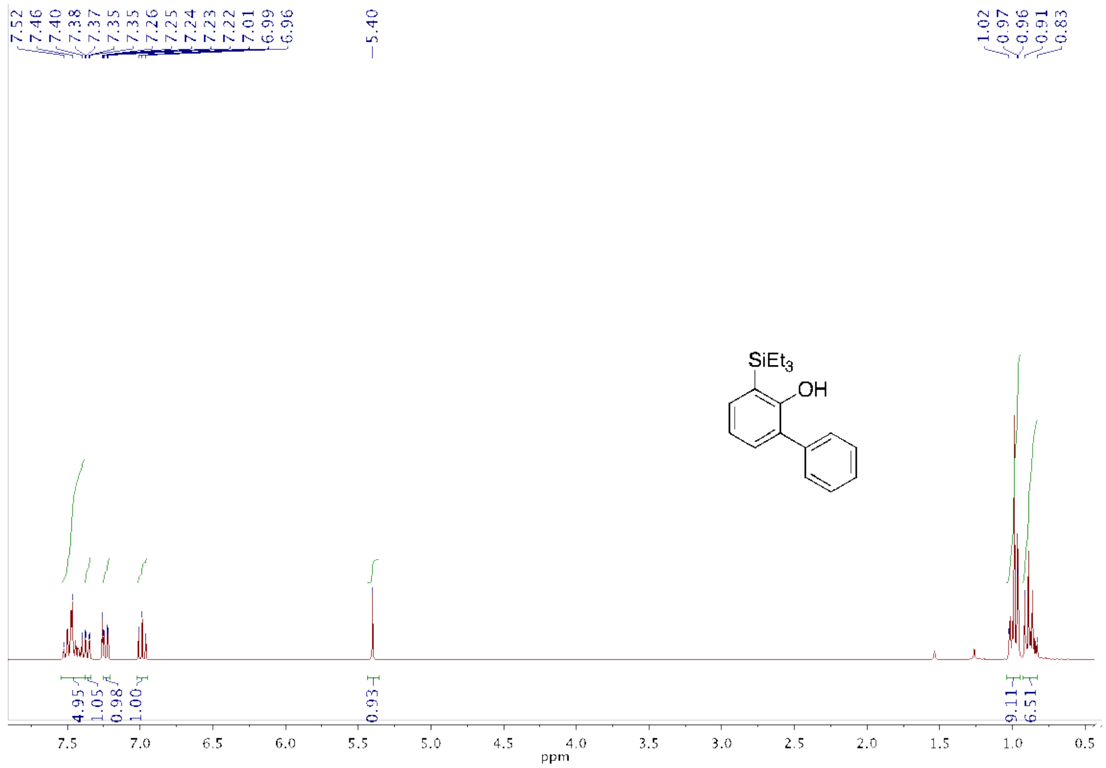


Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 3-(triethylsilyl)biphenyl-2-ol (**5**)

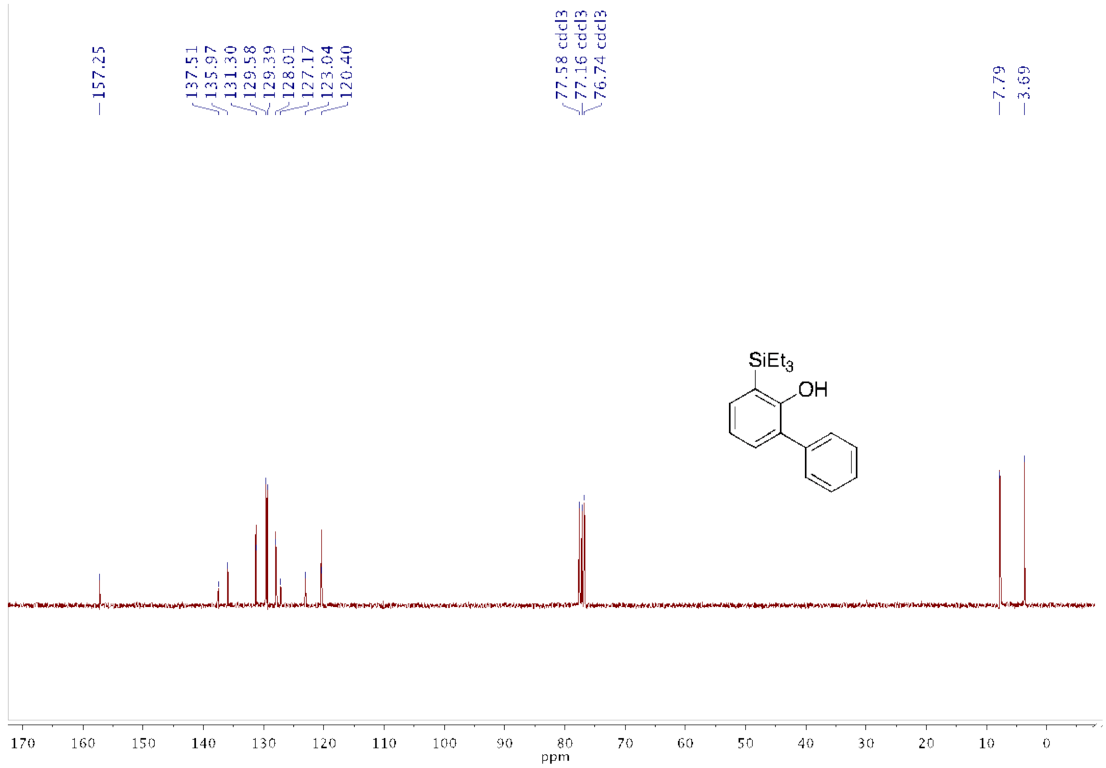


Figure S7. ^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of 3-(triethylsilyl)biphenyl-2-ol (**5**)

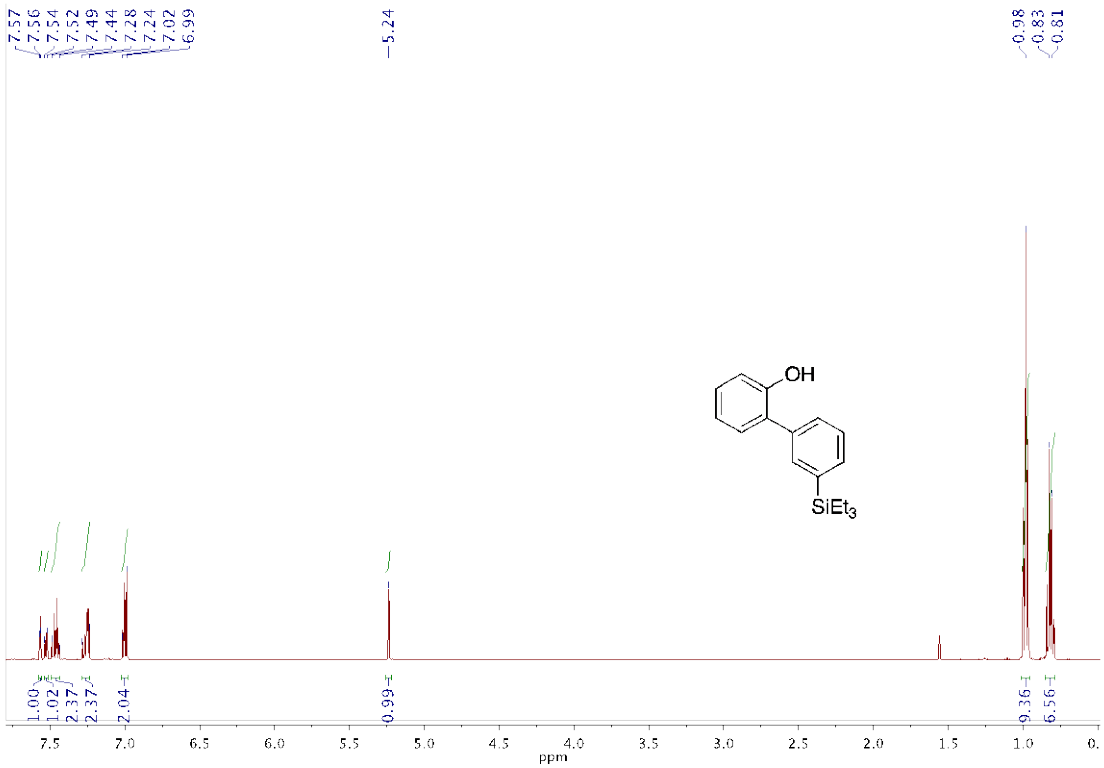


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (3'-triethylsilyl)biphenyl-2-ol (**6**)

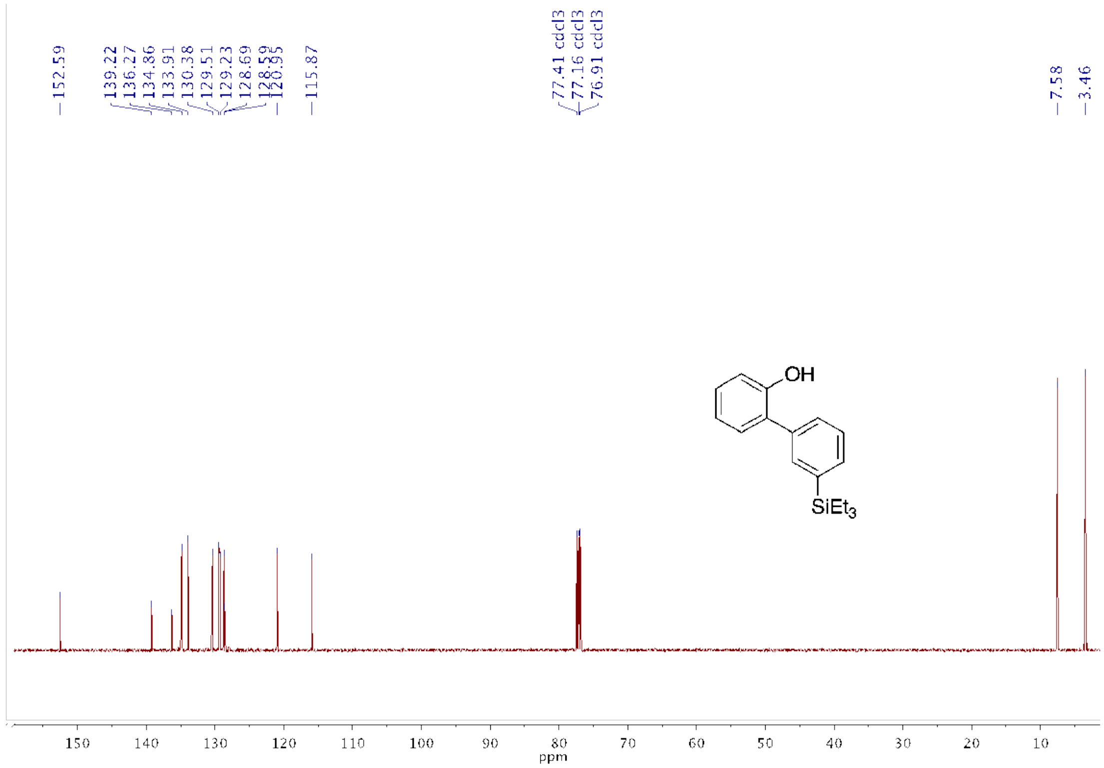


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (3'-triethylsilyl)biphenyl-2-ol (**6**)

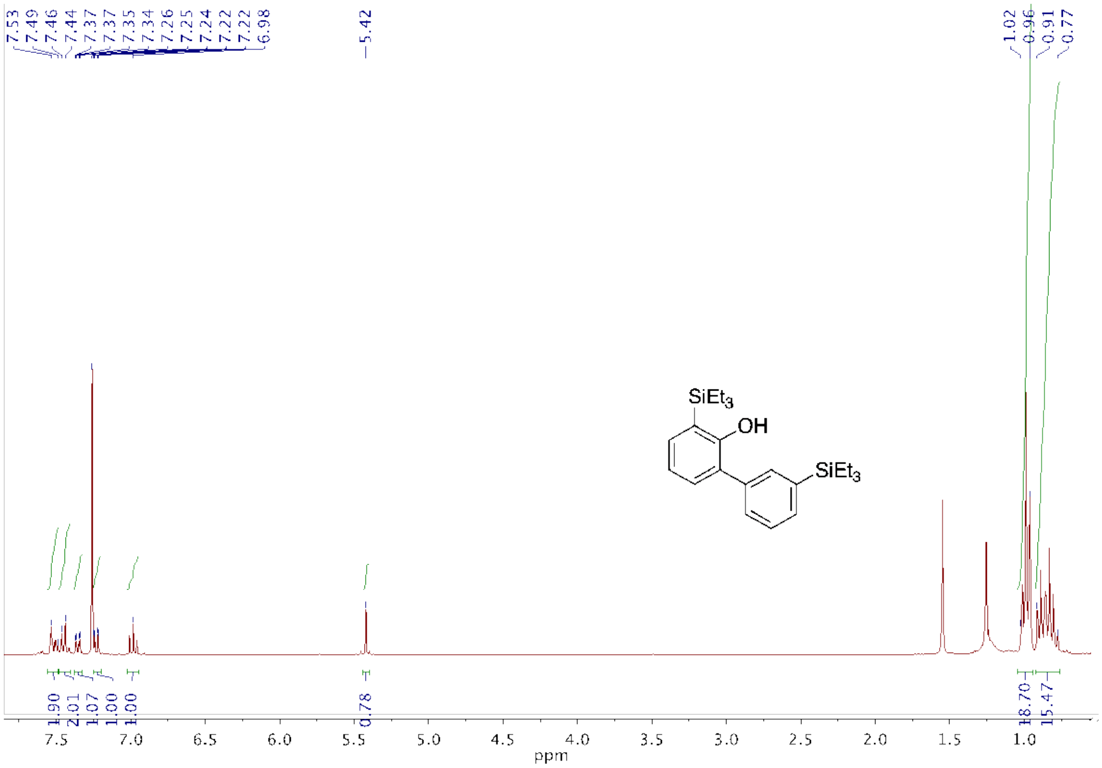


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 3,3'-bis(triethylsilyl)biphenyl-2-ol (**7**)[11]

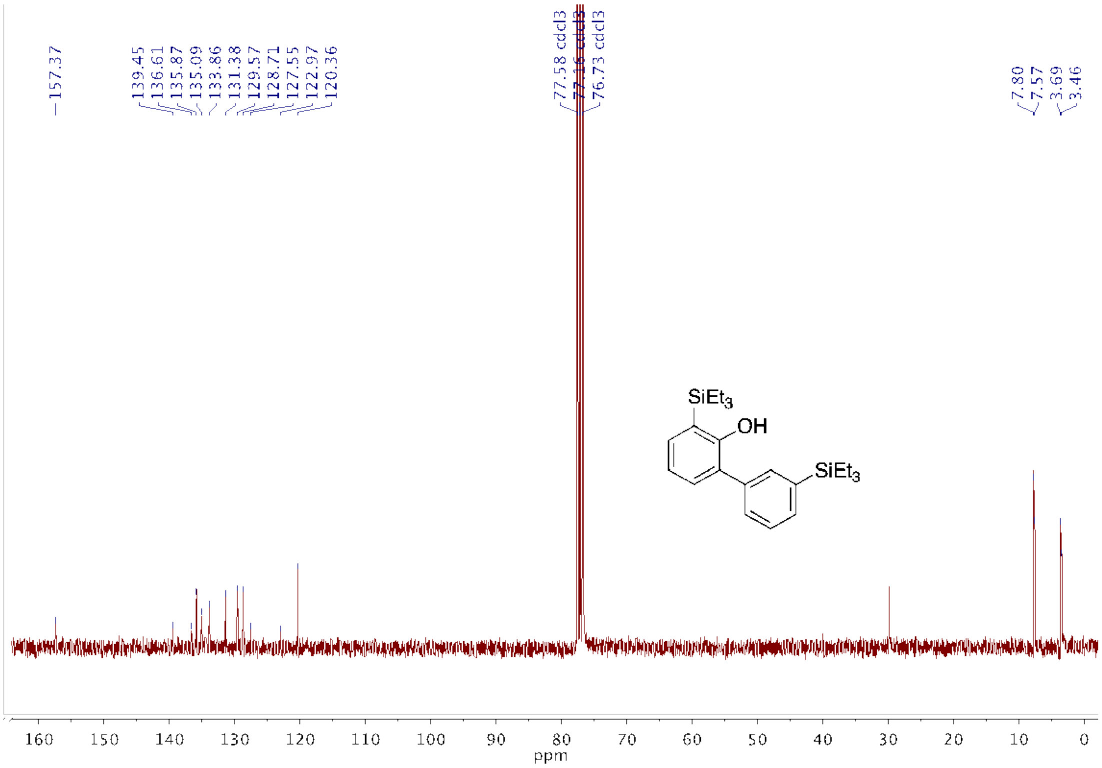


Figure S11. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3,3'-bis(triethylsilyl)biphenyl-2-ol (**7**)[11]

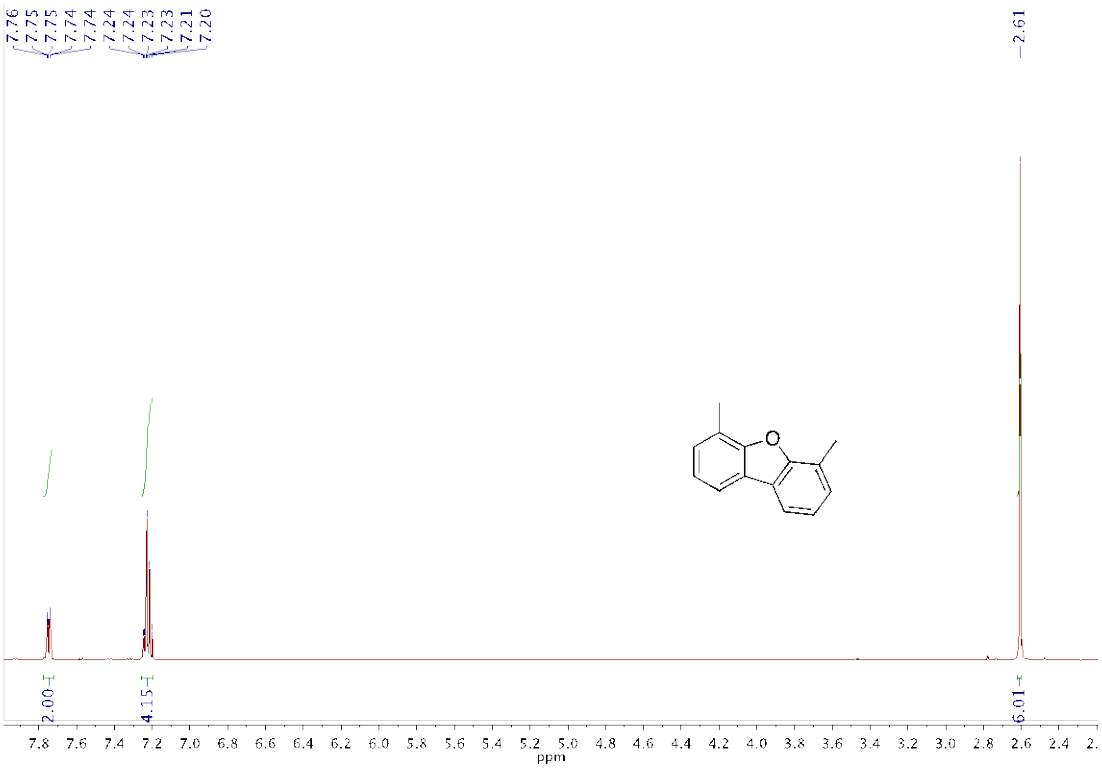


Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4,6-(dimethyl)dibenzofuran (**15**)

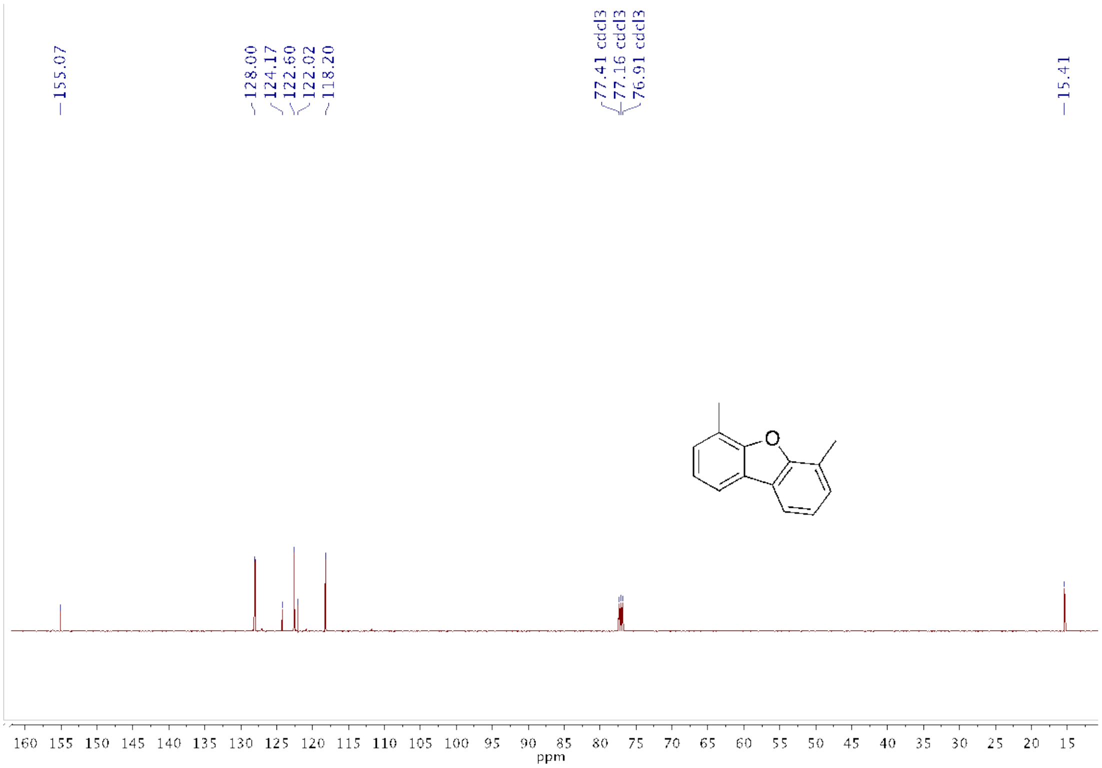


Figure S13. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 4,6-(dimethyl)dibenzofuran (**15**)

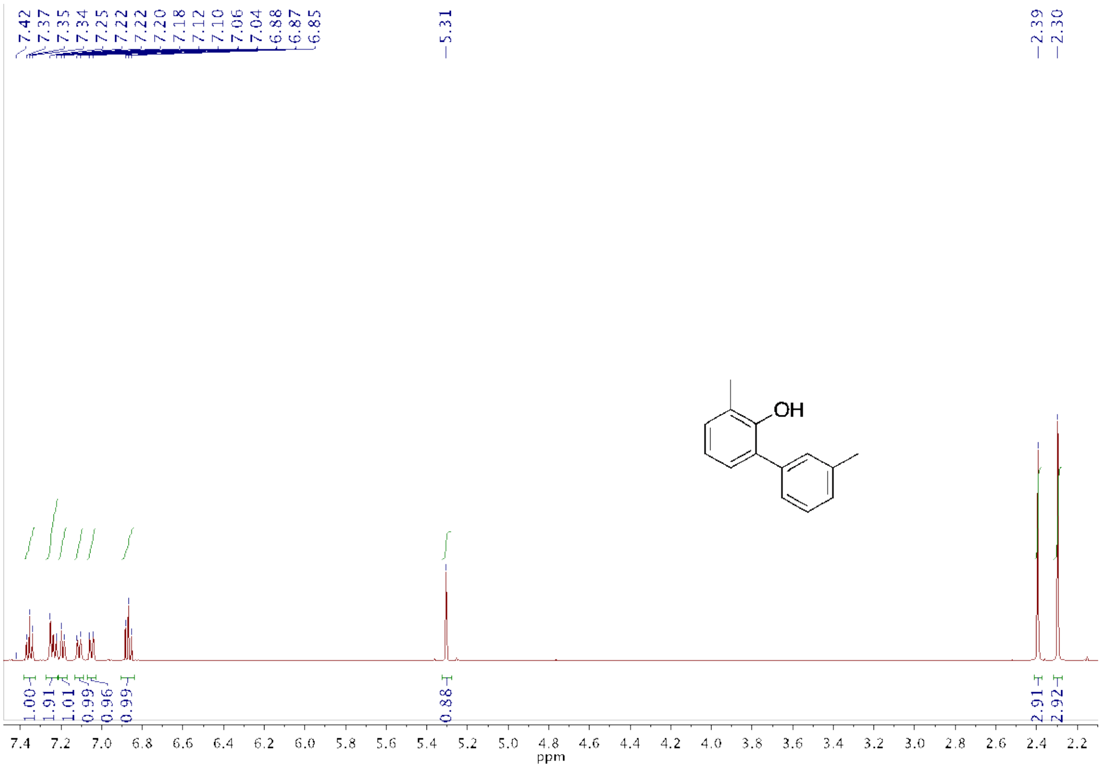


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3,3'-dimethylbiphenyl-2-ol (**16**)

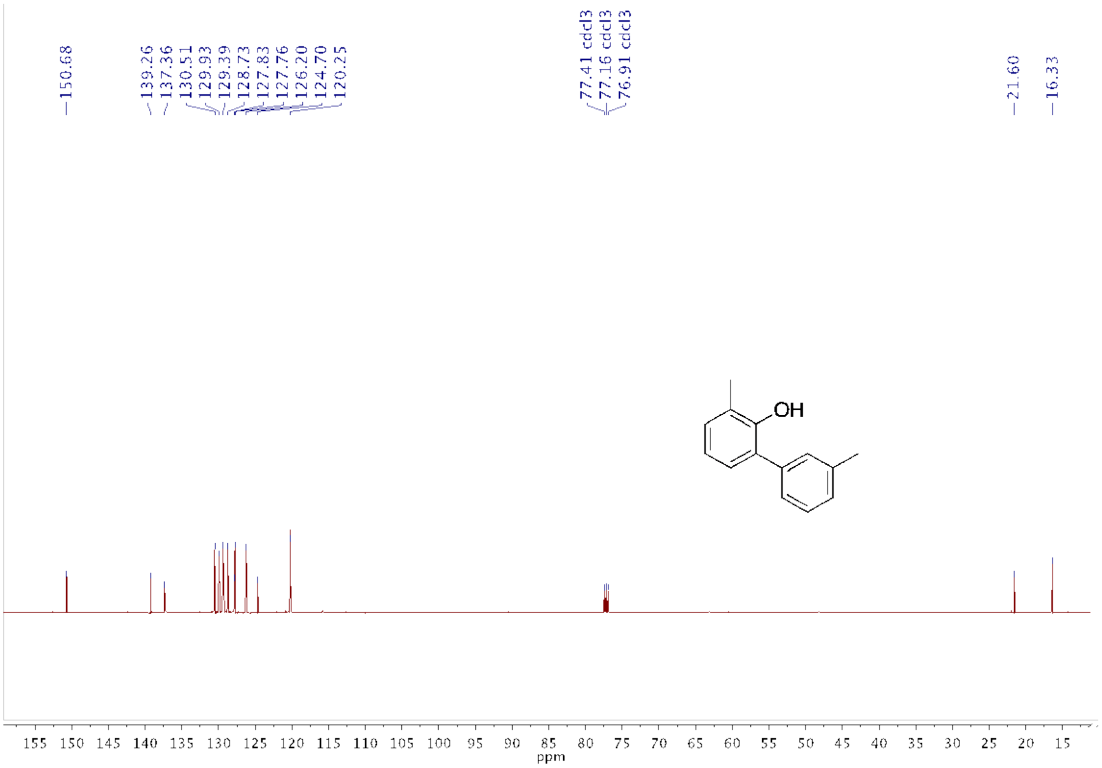


Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3,3'-dimethylbiphenyl-2-ol (**16**)

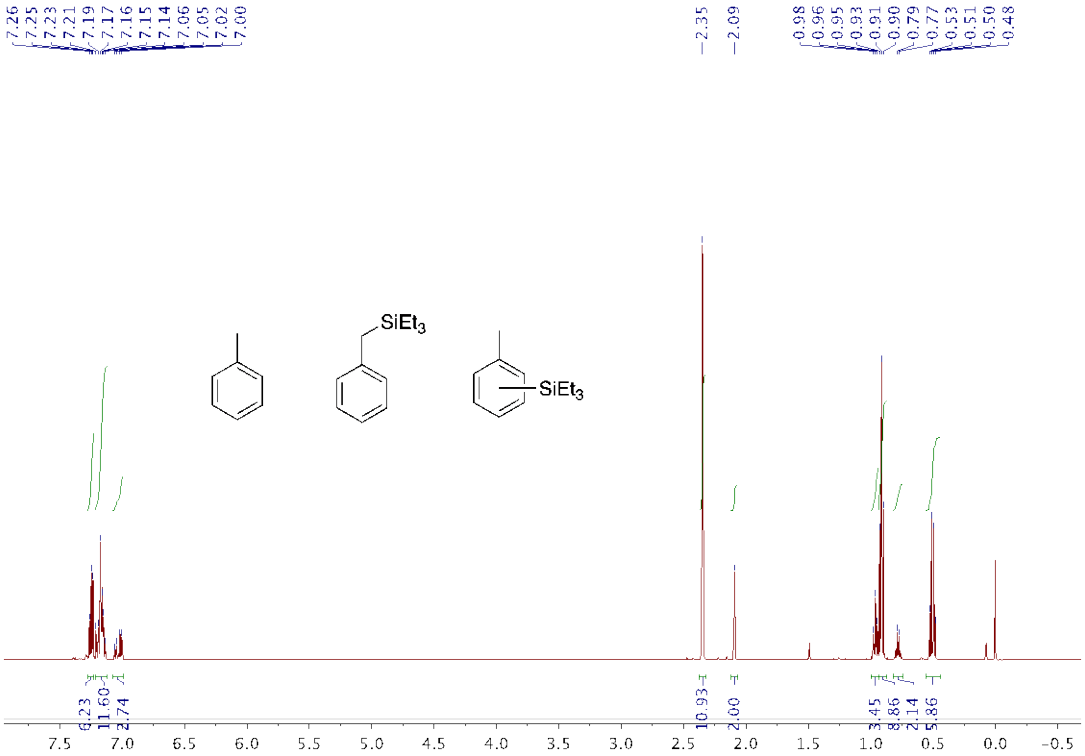


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of toluene and its triethylsilylation products

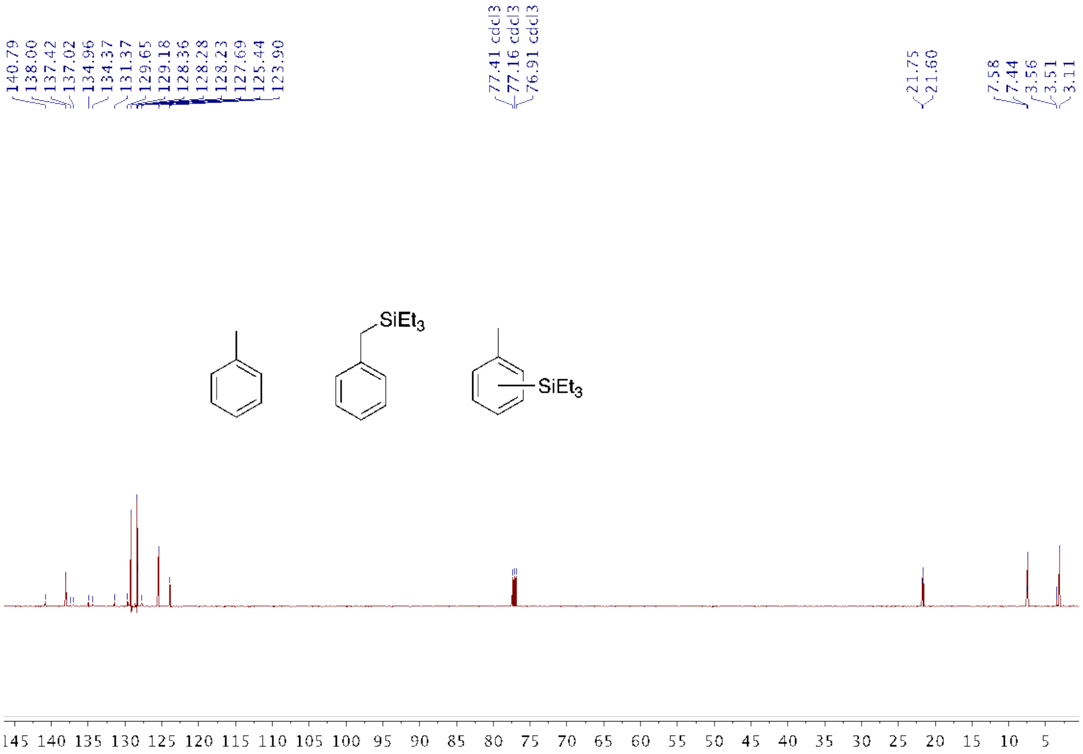


Figure S17. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of toluene and its triethylsilylation products

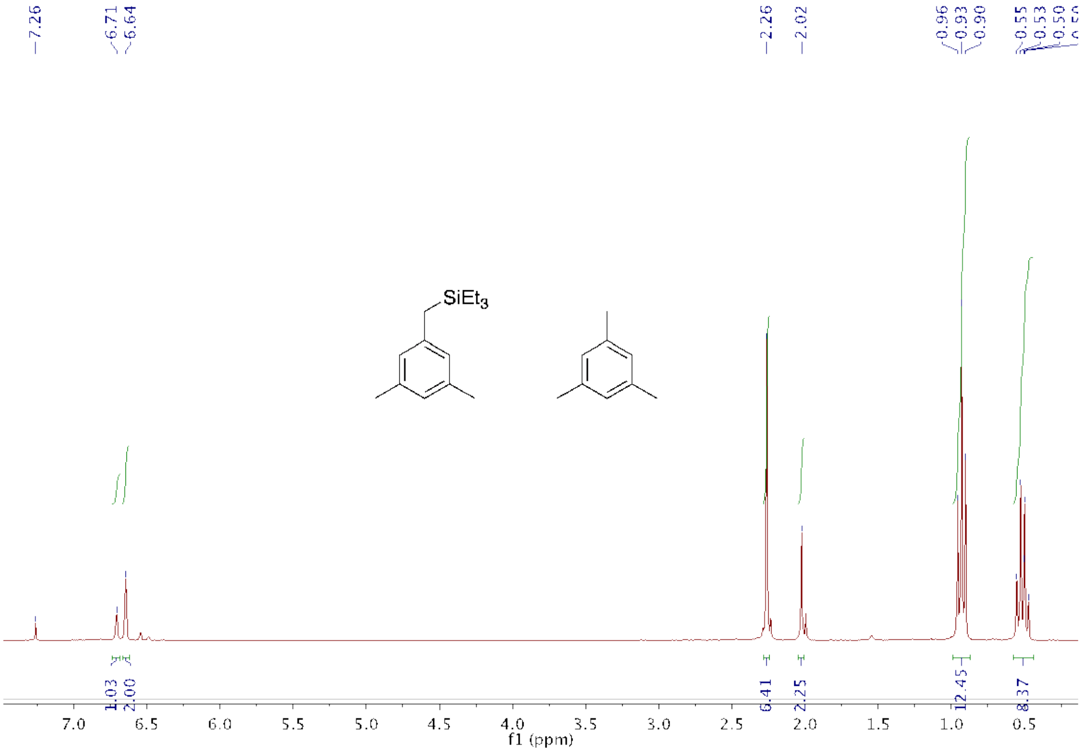


Figure S18. Crude ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of mesitylene and its triethylsilylation product

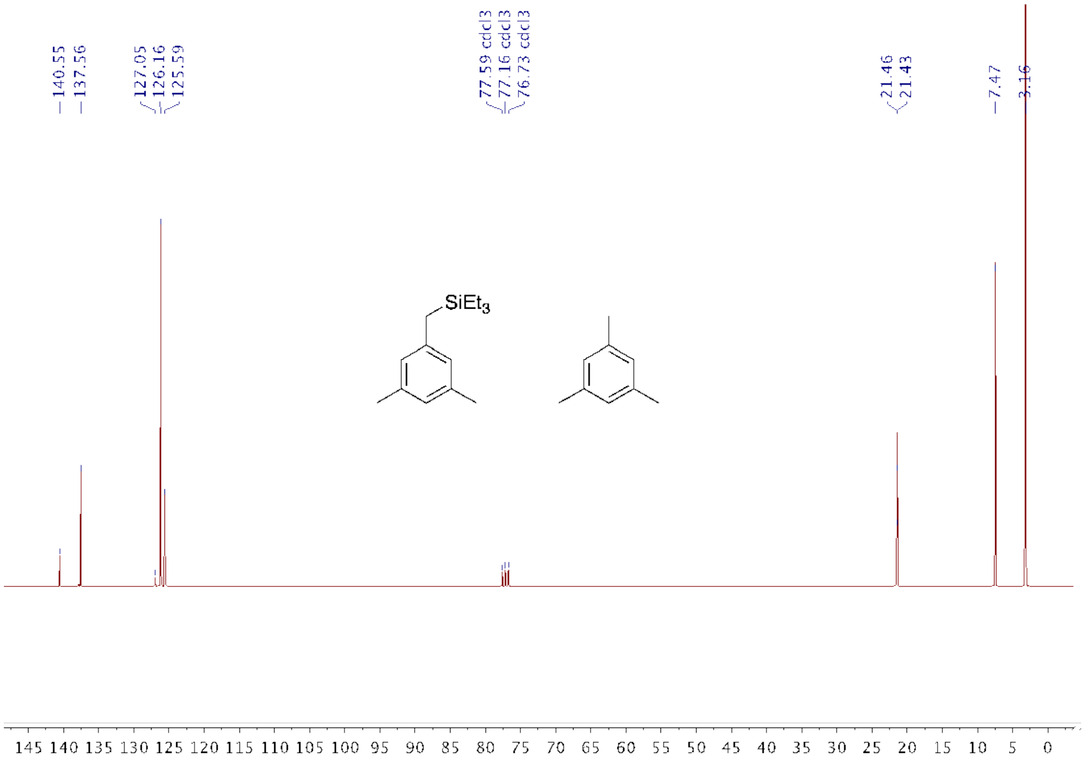


Figure S19. Crude ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of mesitylene and its triethylsilylation product

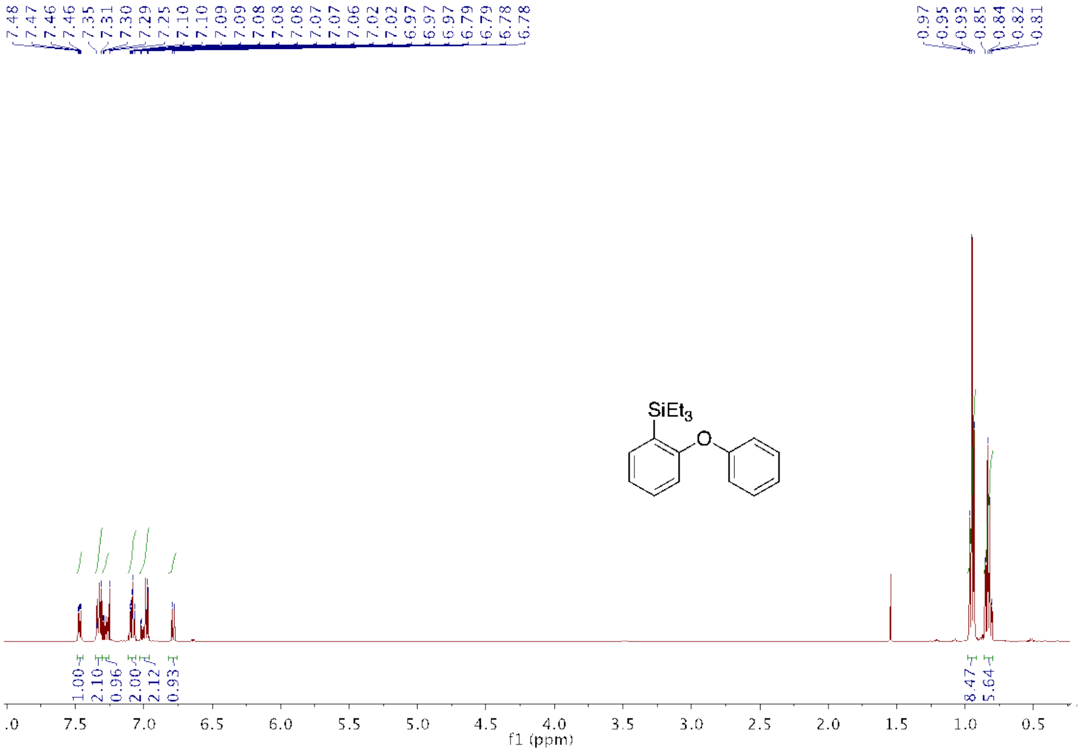


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *o*-triethylsilyldiphenyl ether

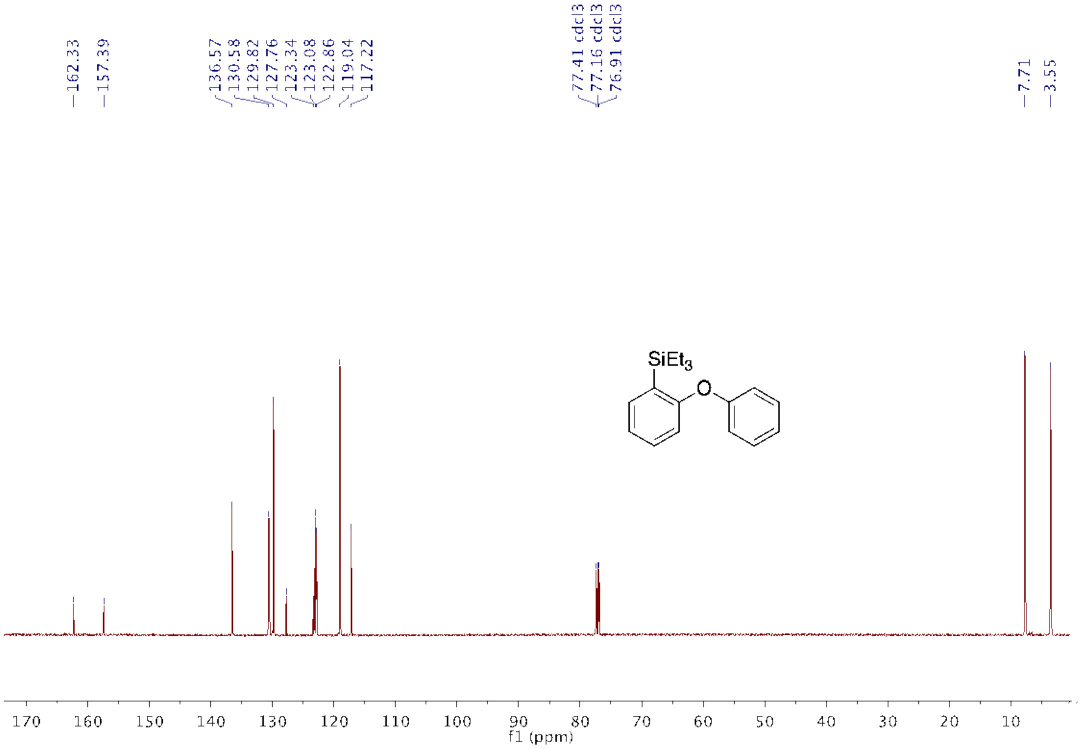


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of *o*-triethylsilyldiphenyl ether

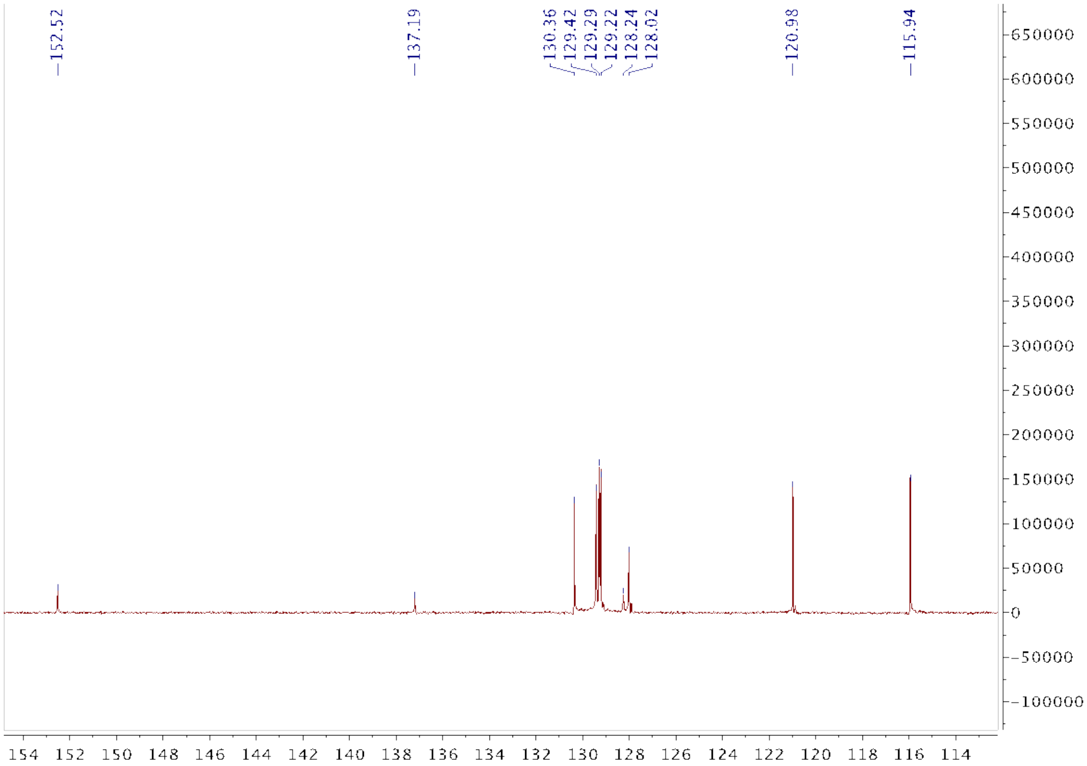


Figure S22. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of biphenyl-2-ol prepared from Et3SiD in Mes-H_{12}

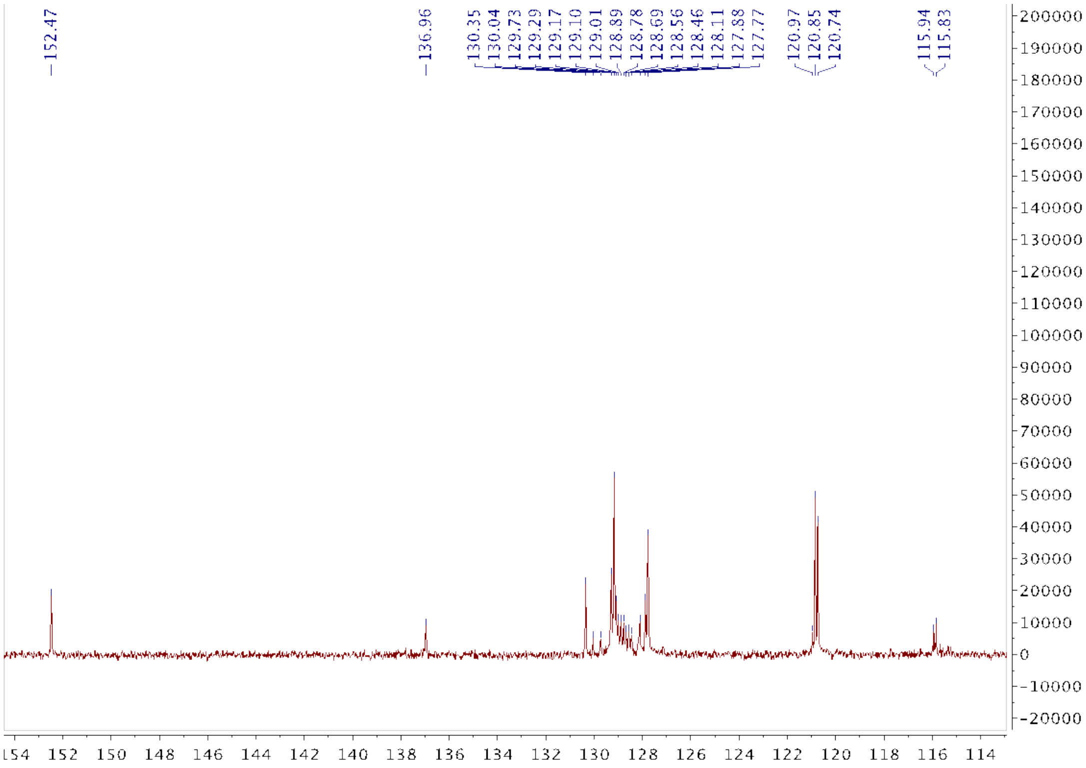


Figure S23. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of biphenyl-2-ol prepared from Et3SiD in Mes-D_{12}

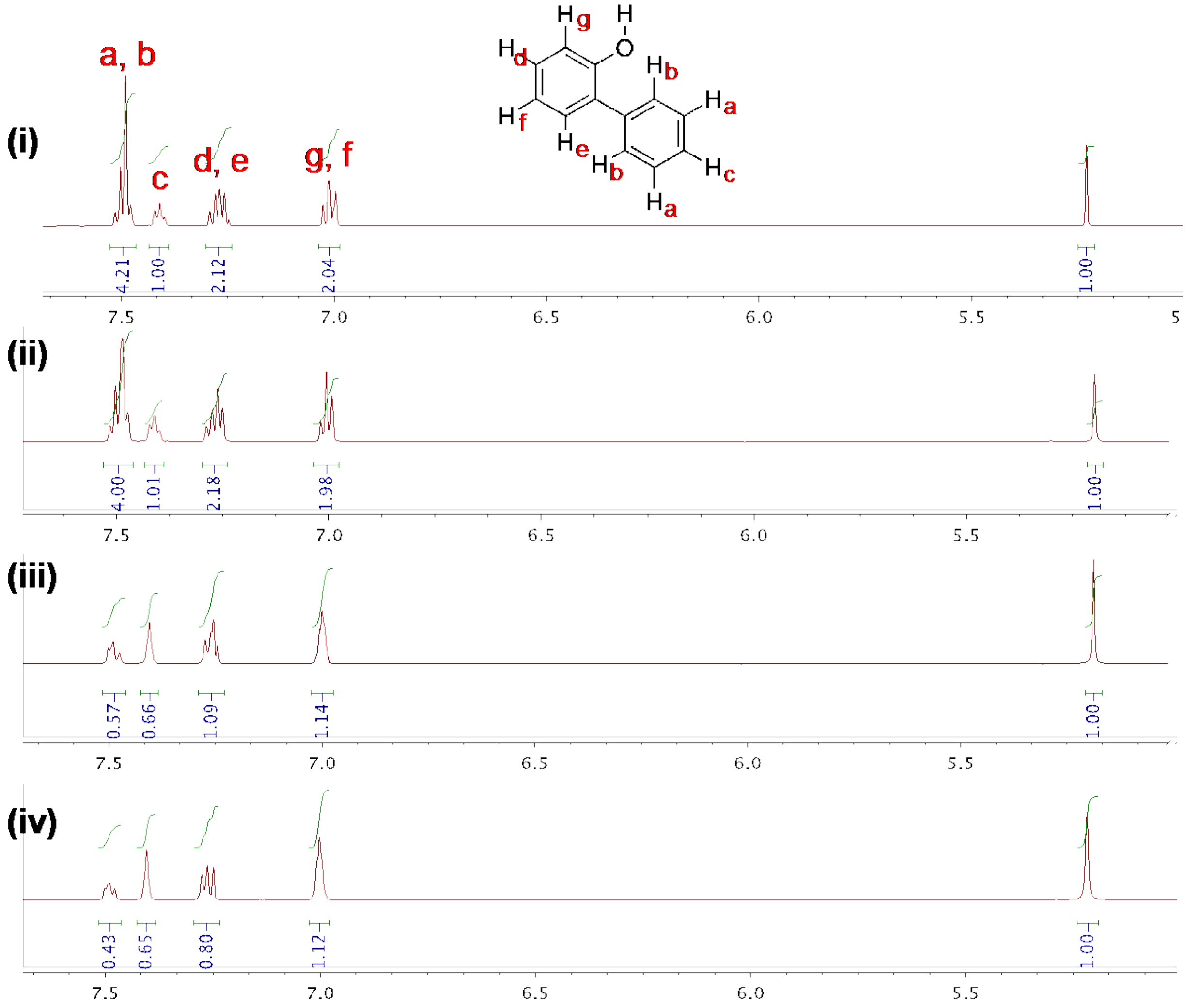


Figure S24. ^{1}H NMR (600 MHz, $CDCl_3$) single-scan overlaid spectra for quantitative comparison of a commercial sample of biphenyl-2-ol (i) with those obtained from dibenzofuran and Et_3SiH in mesitylene (ii); with Et_3SiH in mesitylene-d_{12} (iii); with Et_3SiD in mesitylene-d_{12} (iv)

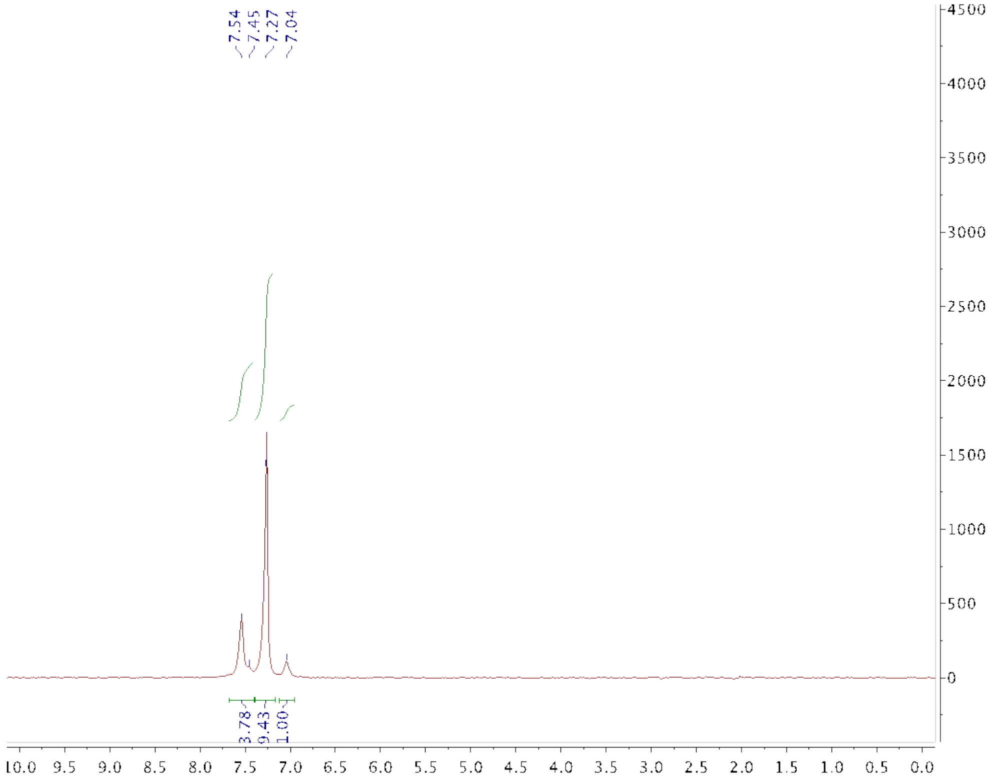


Figure S25. ^{2}D NMR (61.4 MHz, $CHCl_3$) spectrum of partially deuterated biphenyl-2-ol prepared from Et_3SiD in Mes-D_{12}. A drop of deuterated $CDCl_3$ was added for signal locking purposes

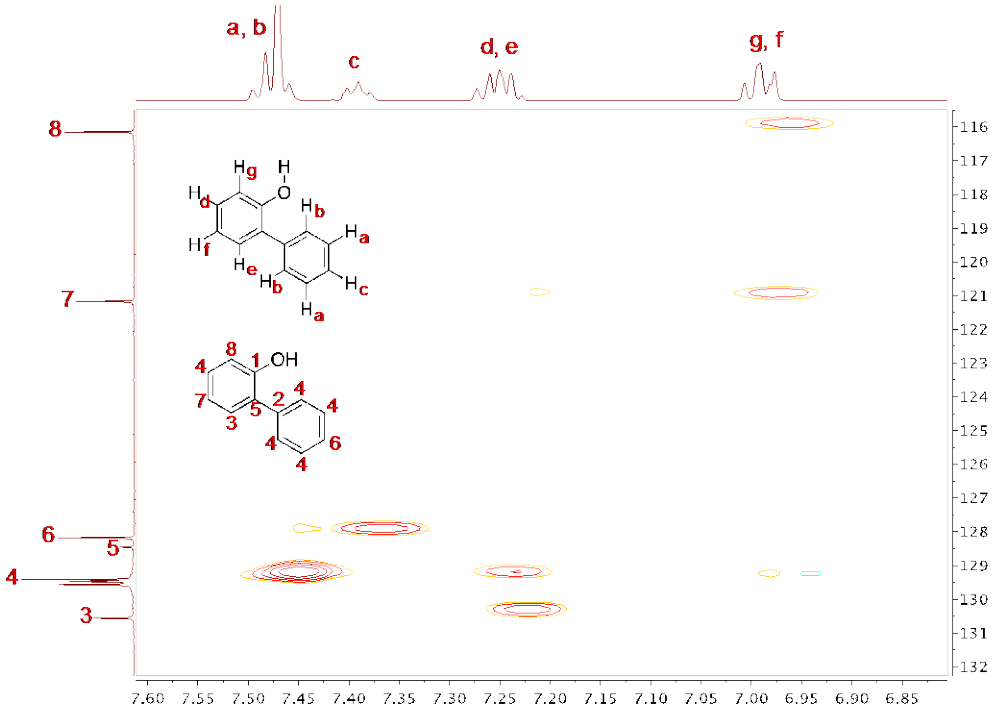


Figure S26. HSCQ ($CDCl_3$) spectrum of a commercial sample of biphenyl-2-ol

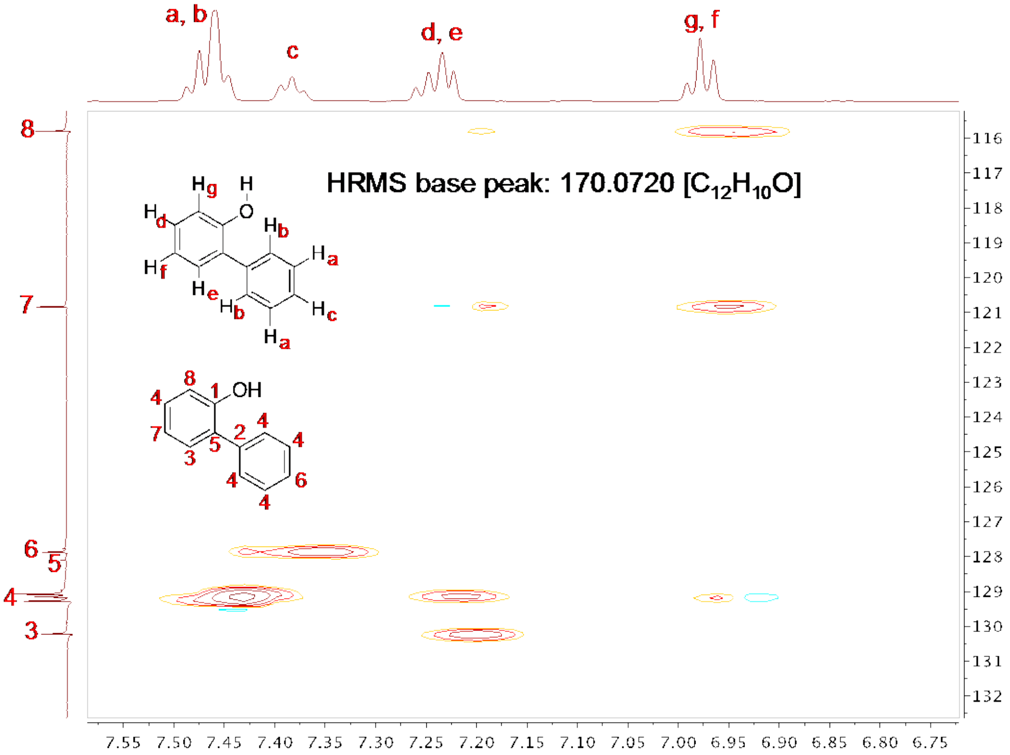


Figure S27. HSCQ ($CDCl_3$) spectrum of biphenyl-2-ol prepared from Et_3SiD in Mes

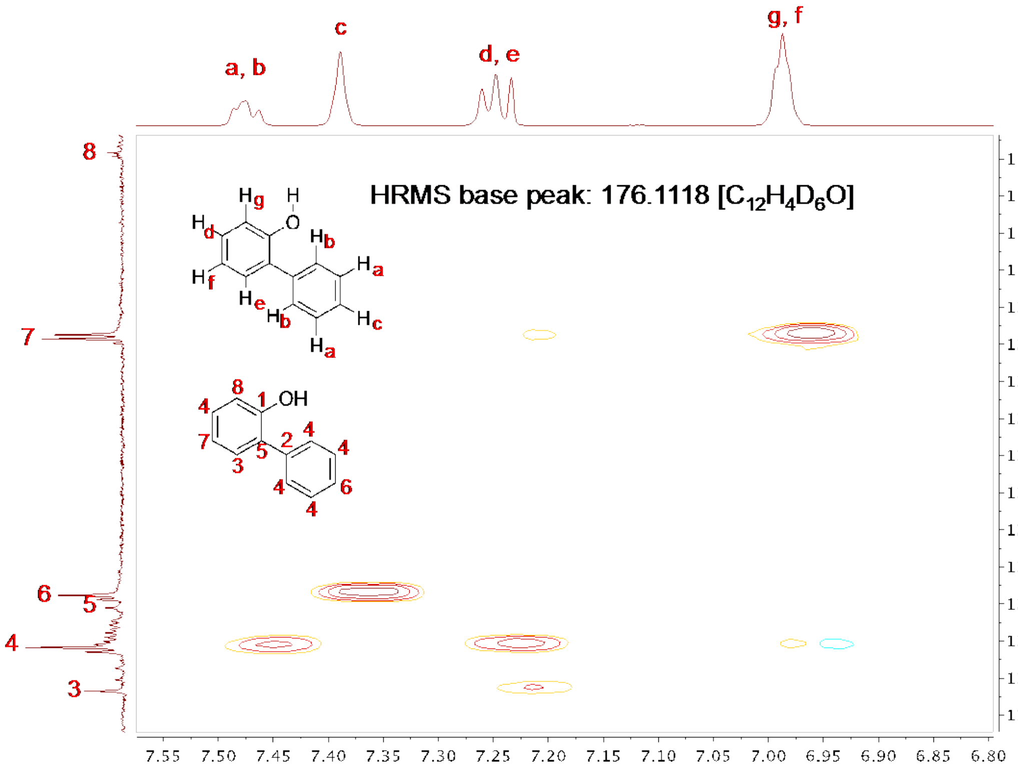


Figure S28. HSCQ ($CDCl_3$) spectrum of biphenyl-2-ol prepared from Et_3SiH in Mes-D_{12}

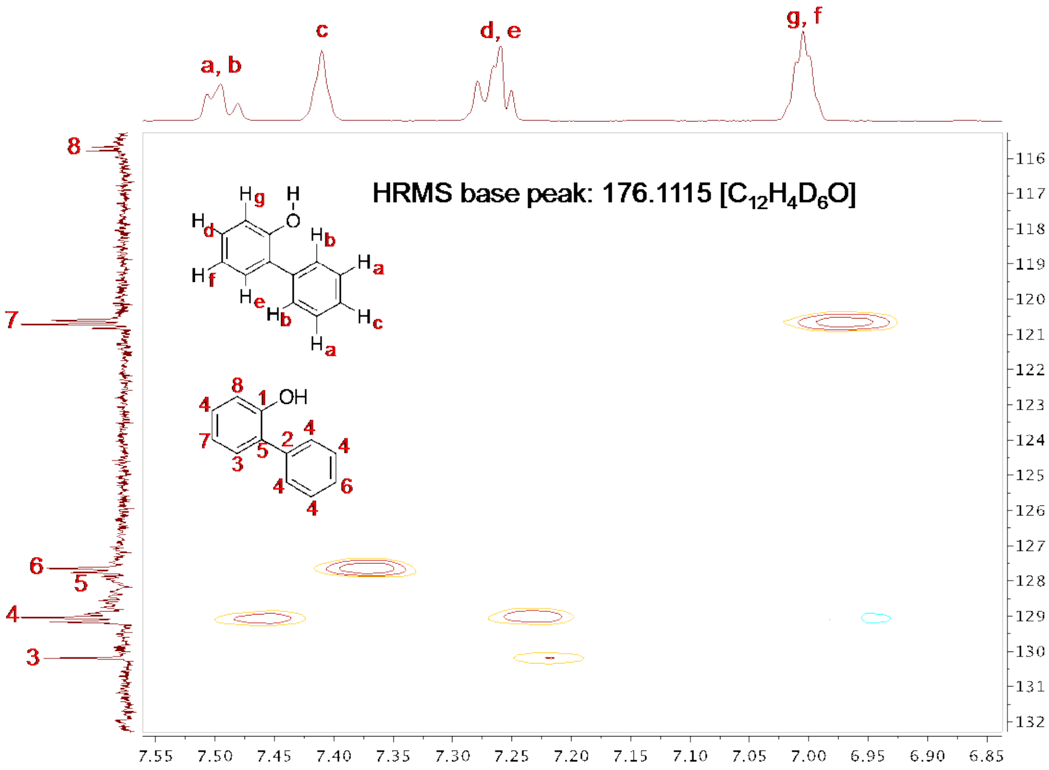


Figure S29. HSCQ ($CDCl_3$) spectrum of biphenyl-2-ol prepared from Et_3SiD in Mes-D_{12}

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(12) A small admixture of grease is present in the sample.