Steric-Hindrance Triggered Remote Lithiations of Bulky Silyl-Substituted Arenes

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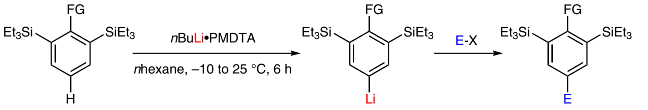

16 examples, up to 59% yield

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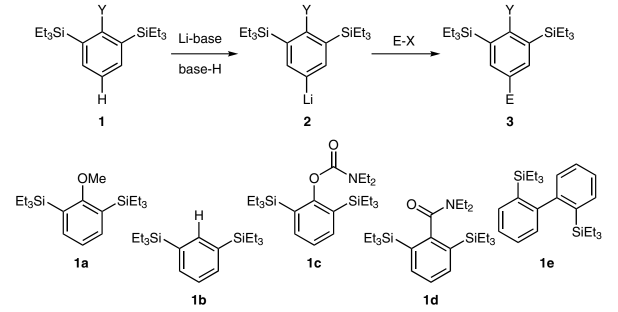
Abstract Functionalized arenes bearing two bulky triethylsilyl substituents were regioselectively lithiated at the 4-position (*para* position) by using a mixture of *n*BuLi and PMDTA (*N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine). The resulting aryllithium species, bearing sensitive functional groups such as amides or carbamates, reacted with a range of electrophiles leading to tri- and tetrasubstituted remote-functionalized products. This lithiation could be extended to 2,2′-bis(triethylsilyl)biphenyl, for which the favored metalation site was the one where steric interference of the silyl group could be avoided.

Key words arylsilanes, arene functionalization, lithiation, remote metalation, steric hindrance

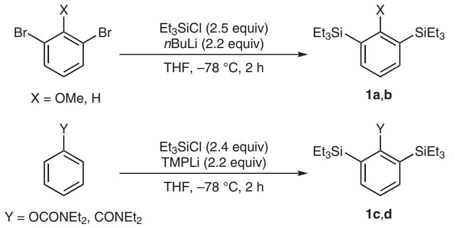
The directed functionalization of arenes via organometallic intermediates is an essential method to prepare a range of substituted aromatic target molecules.[1] Especially the directed lithiation of arenes via a precoordination by a directing group pioneered by Snieckus has found widespread applications.[2] This proximity-induced metalation has been especially useful for the *ortho* lithation of various aromatic compounds. Schlosser has reported an alternative approach for directed metalations, i.e. the steric hindrance of substituents utilizing a buttress effect.[3] Recently, we have shown that 1,3-bis-silylated arenes were especially well suited for remote lithiations at the 5-position.[4] Herein, we wish to report additional lithiations of 4-bis-silylated substrates **1a**–**d**, as well as a remote lithiation of bis-silylated biphenyl **1e** (Scheme 1).

Due to the two bulky triethylsilyl groups of the arenes of type **1**, lithiation occurred only at the less sterically hindered 5-position, leading to aryllithiums of type **2** which, after quenching with electrophiles, led to functionalized arenes of type **3**.



Scheme 1 Substrates of type **1** for remote lithiations leading to 5-lithiated arenes **2** and subsequent quenching with electrophiles leading to products of type **3**

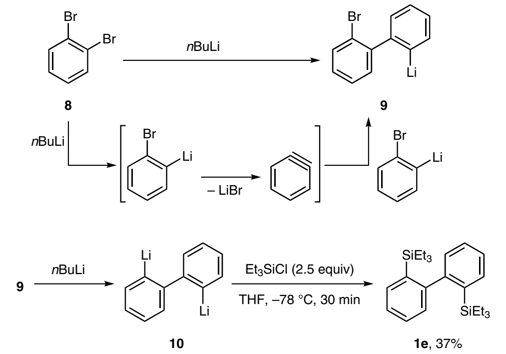
Bis-silylated arenes **1a**–**e** were easily prepared by various complementary methods. Thus, a mixture of 2,6-dibromoanisole (**4**) or 1,3-dibromobenzene (**5**) and Et_3SiCl (2.5 equiv) was treated with *n*BuLi (2.2 equiv) at −78 °C in THF, furnishing **1a** and **1b** in 80 and 97% yield, respectively (Scheme 2). Bis-silylated carbamate (**1c**) and benzamide (**1d**) were prepared by treating either phenyl diethylcarbamate (**6**) or *N*,*N*-diethylbenzamide (**7**) in the presence of Et_3SiCl (2.4 equiv) with TMPLi (2.2 equiv, TMP = 2,2,6,6-te-



Scheme 2 Preparation of bis(triethylsilyl)arenes **1a–d** via in situ silyl chloride trapping reactions

tramethylpiperidyl)[5] at −78 °C in THF furnishing the desired carbamate **1c** and amide **1d** in 78% and 85% yield, respectively.

Additionally, biphenyl **1e** was prepared by the reaction of 1,2-dibromobenzene (**8**) with *n*BuLi (2.1 equiv) in the presence of an excess of Et_3SiCl (2.5 equiv) in THF (−78 °C, 30 min), leading first to biphenyllithium **9**, which, after a second Br/Li exchange, furnished the bis(lithio)biphenyl **10**. An in situ quenching reaction with Et_3SiCl furnished the desired bis(silyl)biphenyl **1e** in 37% yield (Scheme 3).

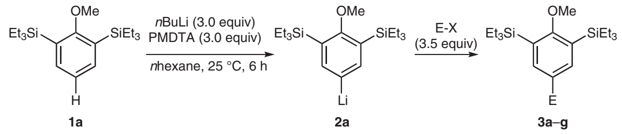


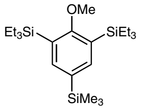
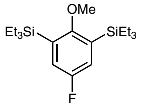
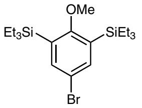
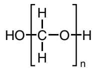
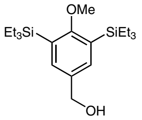
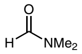
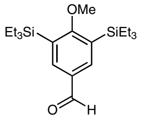
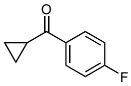
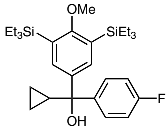
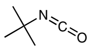
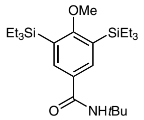
Scheme 3 Proposed mechanism for the formation of the bis(silyl)biphenyl **1e** from arene **8**

With the bis-silylated arenes **1a–e** in hand, we examined the lithiation of **1a** with various bases and found that an excess of *n*BuLi (3.0 equiv) in combination with PMDTA (*N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine; 3.0 equiv) in hexanes at 25 °C for 6 hours gave the best results.[4] Longer reaction times led to a partial decomposition of the aryllithium intermediates **2**. The large excess of *n*BuLi may be necessary due to a competitive lithiation of the ligand PMDTA by *n*BuLi.[6]

Thus, treatment of **2a** with an excess of electrophile (E-X; 3.5 equiv) regioselectively provides a range of 5-functionalized products of type **3** (Table 1). As an example, the addition of Me_3SiCl furnished 2,4,6-trisilylated anisole **3a** in 39% yield (entry 1). Electrophilic aryl fluorination at the 5-position was possible by treating **2a** with NFSI (*N*-fluorobenzenesulfonimide), affording fluoroarene **3b** in 40% yield (entry 2). The bromination of **2a** was readily achieved after a transmetalation to the corresponding zinc reagent by using $ZnCl_2$ (3.0 equiv) and adding bromine in THF, leading to bromoarene **3c** in 51% yield (entry 3). A *para*-hydroxymethylation was performed by treating **2a** with an excess of paraformaldehyde and acidic workup, which furnished benzylic alcohol **3d** in 39% yield (entry 4). Formylation of **2a** was done by treating the aryllithium reagent with dimethylformamide, leading to benzaldehyde **3e** in 38% yield (entry 5). The reaction of the *para*-lithiated anisole **2a** with a ketone proceeded smoothly and afforded the tertiary alcohol **3f** in 44% yield (entry 6). Finally, reaction of **2a** with *tert*-butyl isocyanate gave amide **3g** in 38% yield (entry 7).

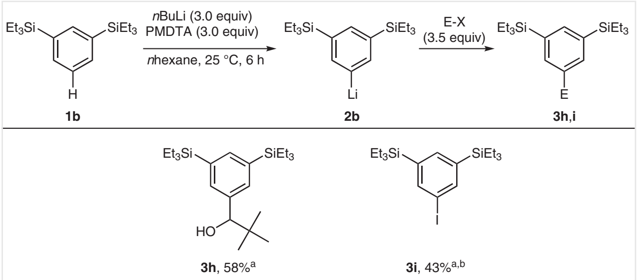
Table 1 Remote Lithiation of Anisole **1a**, Leading to the Functionalized Anisoles **3a–g**



Entry	Electrophile	Product	3	Yield (%)[a]
1	Me_3SiCl		**3a**	39
2	NFSI		**3b**	40
3	Br_2		**3c**	51[b]
4			**3d**	39
5			**3e**	38
6			**3f**	44
7			**3g**	38

[a] Yields of isolated, analytically pure products.
[b] $ZnCl_2$ (3.0 equiv) was added.

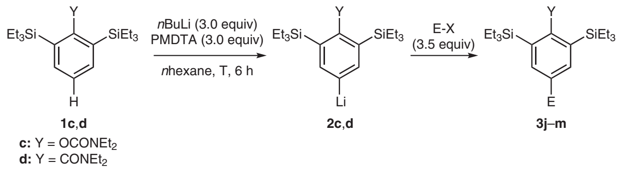
Interestingly, even the non-functionalized bis-silane **1b** was lithiated under our reaction conditions, regioselectively affording *meta*-aryllithium **2b** in ca. 60% yield. Quenching with electrophiles such as pivaldehyde or iodine (after transmetalation to the corresponding zinc reagent) gave the expected products **3h** and **3i** in 58 and 43% yield, respectively (Scheme 4).

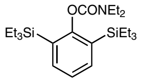
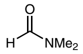
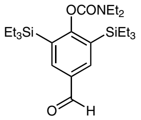
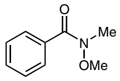
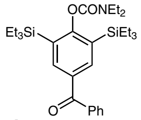
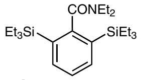
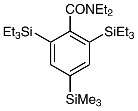
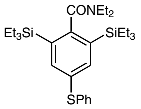


Scheme 4 Trifunctionalized benzenes **3h**,**i** obtained after regioselective lithiation of benzene **1b** and reaction with electrophiles. [a] Yield of analytically pure, isolated product. [b] $ZnCl_2$ (3.0 equiv) was added.

We noticed that the introduction of a good coordination function such as a carbamate ($OCONEt_2$) or an amide ($CONEt_2$) gave the expected aryllithium species (**2c** and **2d**) in similar yields. The lithiated carbamate **2c** displayed moderate thermal stability and decomposed at 25 °C. Therefore, the lithiation was performed at −10 °C instead of 25 °C as usual (Table 2). Quenching of **2c** and **2d** with various electrophiles provided the desired tetrasubstituted arenes **3j**–**m** in 34–46% yield (entries 1–4).

Table 2 Remote Lithiation of the Functionalized Arenes **1c**,**d**, Leading to the Tetrasubstituted Silylated Arenes **3j**–**m**

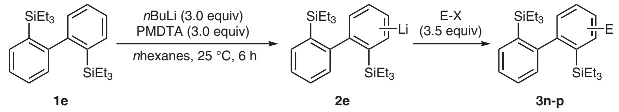


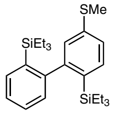
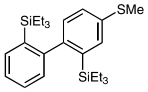
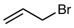
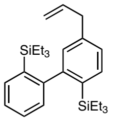
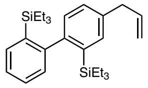
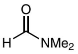
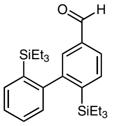
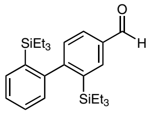
Entry	Substrate	Electrophile	Product	Temp (°C)	Yield (%)[a]
1	 **1c**		 **3j**	−10	34
2	**1c**		 **3k**	−10	44
3	 **1d**	Me_3SiCl	 **3l**	25	46
4	**1d**	PhSSPh	 **3m**	25	44

[a] Yields of isolated, analytically pure products.

The lithiation of bis(silyl)biphenyl **1e** was only partially regioselective and produced an 86:14 mixture of two regioisomers. The major biphenyllithium species was metalated at the *para* position relative to the bulky triethylsilyl group, showing the steric hindrance of this silyl group compared to the 2-(triethylsilyl)phenyl substituent. Reaction with electrophiles such as dimethyl disulfide, allyl bromide, or dimethylformamide provided the expected product mixtures **3n**,**3n′**, **3o**,**3o′**, and **3p**,**3p′** in good yields (Table 3, entries 1–3).

Table 3 Remote Lithiation of Biphenyl **1e**, Leading to Product Mixtures of Type **3n**,**n′**–**p**,**p′**



Entry	Electrophile	Product, yield (%)	
1	MeSSMe	 **3n**, 53[a]	 **3n′**, 9[a]
2		 **3o**, 59[a,b]	 **3o′**, 10[b,c]
3		 **3p**, 57[a]	 **3p′**, 9[c]

[a] Yield of isolated, analytically pure product.
[b] $ZnCl_2$ (3.0 equiv) and $CuCN{\cdot}2LiCl$ (11 mol%) were added.
[c] Yield determined by GC and NMR analysis of crude mixtures.

In summary, we have reported a remote lithiation of 1,3-disilylsilanes and a related biphenyl by using two bulky triethylsilyl groups, which hampered *ortho* and *meta* lithiations. Further extensions of this type of steric-hindrance-based regioselective metalations of arenes are currently investigated in our laboratories.

Unless stated otherwise, all reactions were carried out with magnetic stirring and in flame-dried glassware under argon. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. Reactions were monitored by gas chromatography or by thin-layer chromatography. TLC was performed using aluminum plates coated with SiO_2 (Merck 60, F-254) and visualized by UV radiation. Purification by column chromatography was performed using silica gel 60 (40–63 mm, 230–400 mesh, ASTM from Merck). For purification, an Agilent Technologies 1260 Infinity HPLC-System was used, consisting of two prep-pumps ($MeCN/H_2O$, no additives), a

MWD-detector (210 nm wavelength, 40 nm bandwidth, reference wavelength 400 nm, reference bandwidth 100 nm) and a fraction collector. Three different columns were used: (a) Kinetix EVO C18, 5 µm column (length: 150 mm, diameter: 10 mm), (b) Kinetix EVO C18, 5 µm column (length: 150 mm, diameter: 21.2 mm), and (c) Waters XBridge Prep C8, 5 µm column (length: 150 mm, diameter: 30 mm). Commercially available starting materials were used without further purification unless stated otherwise. THF was continuously refluxed and freshly distilled from sodium benzophenone. Commercially available Grignard reagents were titrated against iodine in THF prior to use. Other Grignard reagents were prepared from the corresponding bromides by insertion of magnesium in the presence of lithium chloride, and were titrated against iodine in THF prior to use. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H NMR (25 °C) and capillary GC analysis. Melting points were measured with a Büchi B-540 apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer spectrum BX-59343 instrument. For detection, a Smiths Detection DuraSamplIR II Diamond ATR sensor was used. NMR spectra of samples in $CDCl_3$ were recorded on a Bruker Avance III HD 400 spectrometer. Mass spectra and high-resolution mass spectra were recorded on Finnigan MAT 90 or Finnigan MAT 95 instruments using electron ionization (EI).

o,o′-Bis-silylated Arenes 1 via In Situ Silylation of Dibromoarenes; General Procedure 1 (GP1)

A dry and argon-flushed Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with the appropriate dibromoarene (1.0 equiv) and Et_3SiCl (2.5 equiv) in anhyd THF (0.5–1.0 M solution). The resulting solution was cooled to −78 °C and *n*BuLi (2.2 equiv) was added dropwise. The mixture was slowly warmed to 25 °C and subsequently quenched with sat. aq NH_4Cl. The aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo.

o,o′-Bis-silylated Arenes 1 via In Situ Lithiation and Silylation Sequence; General Procedure 2 (GP2)

A dry and argon-flushed Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with the appropriate arene (1.0 equiv) and Et_3SiCl (2.4 equiv) in anhyd THF (0.5–1.0 M solution). The resulting solution was cooled to −78 °C and TMPLi (2.2 equiv) was added dropwise. The mixture was allowed to warm to 25 °C and was subsequently quenched with sat. aq NH_4Cl. The aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo.

p-Substituted Arenes 3 from *p*-Lithiated Arenes 2, Obtained by Using *n*BuLi·PMDTA, Followed by Reaction with an Electrophile ; General Procedure 3 (GP3)

A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with the appropriate bis-silylated arene **1** (1.0 equiv) in anhyd *n*-hexane (0.5 M solution), and PMDTA (3.0 equiv) was added. The solution was stirred at 25 °C and *n*BuLi (3.0 equiv) was added in one portion. After 6 h, the reaction mixture was cooled to −20 °C and THF (1 mL) or a metal salt solution (3.0 equiv) was added, immediately followed by the appropriate electrophile (3.5 equiv). The reaction mixture was allowed to warm to 25 °C, quenched with a sat. aq NH_4Cl solution (or sat. aq $Na_2S_2O_3$ for halogenolysis) and extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo.

(2-Methoxy-1,3-phenylene)bis(triethylsilane) (1a)

According to GP1, 1,3-dibromo-2-methoxybenzene (5.04 g, 19 mmol) and Et_3SiCl (8.0 mL, 47.5 mmol) were dissolved in THF (40 mL). A 2.55 M solution of *n*BuLi in hexane (16.4 mL, 41.8 mmol) was slowly added to the mixture at −78 °C. Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded the title compound as a colorless oil.

Yield: 5.1 g (15 mmol, 80%).

IR (diamond-ATR, neat): 2951 (m), 2909 (w), 2874 (m), 1562 (w), 1457 (w), 1416 (w), 1370 (s), 1236 (w), 1209 (m), 1170 (vw), 1148 (vw), 1120 (w), 1076 (vw), 1014 (s), 1003 (s), 973 (w), 960 (w), 809 (w), 769 (vs), 717 (vs), 682 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.2 Hz, 2 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 3.67 (s, 3 H), 1.03–0.76 (m, 30 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.33, 138.24, 128.64, 123.18, 63.65, 7.74, 4.27.

MS (EI, 70 eV): *m*/*z* (%) = 307 (5), 297 (25), 280 (14), 279 (100), 269 (12), 251 (89), 223 (71), 221 (17), 195 (47), 193 (23), 191 (12), 179 (14), 167 (27), 165 (24), 163 (17), 161 (30), 151 (22), 137 (19), 135 (13), 133 (46), 131 (18), 117 (65), 115 (12), 111 (11), 107 (14), 105 (15), 97 (12), 91 (13), 89 (84), 87 (27), 61 (26), 59 (13).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{31}O^{28}Si_2$: 307.1913 $[M - Et]^{•+}$; found: 307.1910.

1,3-Bis(triethylsilyl)benzene (1b)

According to GP1, 1,3-dibromobenzene (11.8 g, 50 mmol) and Et_3SiCl (21 mL, 125 mmol) were dissolved in THF (100 mL). A 2.55 M solution of *n*BuLi in hexane (43.1mL, 110 mmol) was slowly added to the mixture at −78 °C. Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded the title compound as a colorless oil.

Yield: 14.9 g (48.6 mmol, 97%).

IR (diamond-ATR, neat): 2952 (m), 2909 (w), 2874 (m), 1457 (w), 1415 (w), 1361 (w), 1236 (w), 1106 (m), 1002 (m), 972 (w), 778 (vs), 729 (s), 714 (vs), 685 (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 2.2, 1.2 Hz, 1 H), 7.48 (dd, *J* = 7.3, 1.3 Hz, 2 H), 7.32 (ddd, *J* = 7.7, 6.8, 0.7 Hz, 1 H), 1.01–0.94 (m, 18 H), 0.83–0.74 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.32, 136.27, 134.68, 127.05, 7.57, 3.56.

MS (EI, 70 eV): *m*/*z* (%) = 306 (1), 278 (11), 277 (71), 249 (76), 221 (100), 217 (14), 189 (23), 165 (18), 163 (12), 161 (20), 137 (31), 135 (17), 135 (11), 133 (31), 131 (12), 115 (36), 107 (19), 105 (16), 96 (10), 87 (16).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{34}{}^{28}Si_2$: 306.2199 $[M]^{•+}$; found: 306.2197.

2,6-Bis(triethylsilyl)phenyl Diethylcarbamate (1c)

According to GP2, phenyl diethylcarbamate (1.93 g, 10 mmol) and Et_3SiCl (4.2 mL, 25 mmol) were dissolved in THF (20 mL). TMPLi (18.6 mL, 22 mmol) was slowly added to the mixture at −78 °C. Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 29:1) afforded the title compound as a colorless oil.

Yield: 3.3 g (7.8 mmol, 78%).

IR (diamond-ATR, neat): 2952 (m), 2936 (w), 2909 (w), 2874 (m), 1714 (vs), 1573 (w), 1458 (w), 1422 (m), 1371 (s), 1350 (w), 1315 (vw), 1270 (vs), 1236 (w), 1211 (vw), 1178 (m), 1148 (vs), 1118 (s), 1070 (w), 1003 (s), 962 (m), 935 (w), 772 (s), 756 (m), 720 (vs), 684 (m) cm^{-1}.

^1H NMR (599 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.2 Hz, 2 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 3.59 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.1 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 0.96–0.90 (m, 18 H), 0.78 (dtd, *J* = 8.5, 7.2, 3.8 Hz, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.68, 154.85, 137.60, 129.75, 124.73, 40.78, 40.69, 13.94, 13.01, 7.59, 3.66.

MS (EI, 70 eV): *m*/*z* (%) = 392 (80), 278 (32), 221 (14), 202 (14), 179 (12), 151 (30), 133 (16), 100 (100), 72 (63).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{38}NO_2{}^{28}Si_2$: 392.2441 $[M - Et]^{\bullet+}$; found: 392.2442.

N,*N*-Diethyl-2,6-bis(triethylsilyl)benzamide (1d)

According to GP2, *N*,*N*-diethylbenzamide (3.36 g, 30 mmol) and Et_3SiCl (12.6 mL, 75 mmol) were dissolved in THF (60 mL). TMPLi (39 mL, 66 mmol) was slowly added to the mixture at −78 °C. Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a colorless solid.

Yield: 10.3 g (25.5 mmol, 85%); mp 77.8–79.3 °C.

IR (diamond-ATR, neat): 2953 (s), 2908 (m), 2872 (s), 1627 (vs), 1456 (m), 1434 (m), 1380 (m), 1363 (m), 1280 (s), 1235 (m), 1219 (m), 1155 (w), 1124 (w), 1094 (m), 1062 (w), 1001 (vs), 962 (m), 872 (w), 795 (vs), 782 (vs), 720 (vs), 682 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.5 Hz, 2 H), 7.28 (t, *J* = 7.4 Hz, 1 H), 3.54 (q, *J* = 7.2 Hz, 2 H), 2.99 (q, *J* = 7.2 Hz, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.00–0.62 (m, 33 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.39, 149.62, 136.05, 133.46, 125.94, 43.29, 38.71, 13.33, 12.89, 7.68, 3.92.

MS (EI, 70 eV): *m*/*z* (%) = 404 (1), 377 (31), 376 (100), 318 (19), 260 (21), 232 (16), 87 (19), 59 (16).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{42}NO^{28}Si_2$: 404.2805 $[M - H]^{\bullet+}$; found: 404.2804.

2,2′-Bis(triethylsilyl)-1,1′-biphenyl (1e)

According to GP1, 1,2-dibromobenzene (**8**; 7.08 g, 30 mmol) and Et_3SiCl (12.6 mL, 75 mmol) were dissolved in THF (60 mL). A 2.55 M solution of *n*BuLi in hexane (25.9 mL, 66 mmol) was slowly added to the mixture at −78 °C. Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded the title compound as a colorless solid.

Yield: 2.1 g (5.5 mmol, 37%); mp 89.9–91.4 °C.

IR (diamond-ATR, neat): 2952 (m), 2910 (w), 2872 (w), 1456 (w), 1416 (w), 1233 (w), 1121 (w), 1007 (w), 995 (m), 970 (w), 710 (vs), 675 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.53 (m, 2 H), 7.35–7.28 (m, 4 H), 7.15–7.10 (m, 2 H), 0.85–0.76 (m, 18 H), 0.59–0.31 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.09, 135.99, 135.40, 130.33, 127.61, 126.13, 7.73, 4.32.

MS (EI, 70 eV): *m*/*z* (%) = 382 (1), 227 (15), 209 (60), 199 (17), 181 (53), 115 (62), 87 (100), 59 (30).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{38}{}^{28}Si_2$: 382.2512 $[M]^{\bullet+}$; found: 382.2511.

[2-Methoxy-5-(trimethylsilyl)-1,3-phenylene]bis(triethylsilane) (3a)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to −20 °C and THF (1 mL) was added, followed by Me_3SiCl (0.22 mL, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 99:1) afforded the title compound as a colorless oil.

Yield: 79 mg (0.19 mmol, 39%).

IR (diamond-ATR, neat): 2951 (m), 2909 (w), 2874 (w), 1537 (w), 1457 (w), 1417 (vw), 1382 (m), 1247 (m), 1215 (w), 1107 (m), 1003 (m), 974 (vw), 869 (vs), 834 (vs), 782 (s), 718 (vs), 686 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 2 H), 3.69 (s, 3 H), 1.02–0.93 (m, 18 H), 0.91–0.81 (m, 12 H), 0.26 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.11, 143.56, 133.46, 127.52, 63.52, 7.79, 4.42, −0.78.

MS (EI, 70 eV): *m*/*z* (%) = 393 (6), 369 (37), 352 (25), 351 (100), 341 (18), 323 (66), 295 (50), 267 (30), 265 (22), 249 (25), 247 (70), 239 (21), 235 (19), 221 (22), 219 (19), 207 (20), 193 (33), 191 (21), 179 (25), 163 (22), 161 (23), 117 (30), 89 (66), 87 (32), 73 (57), 61 (27), 59 (25).

HRMS (EI): *m*/*z* calcd for $C_{26}H_{41}O^{28}Si_3$: 393.2465 $[M - Me]^{\bullet+}$; found: 393.2457.

(5-Fluoro-2-methoxy-1,3-phenylene)bis(triethylsilane) (3b)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to −20 °C and THF (1 mL) was added, followed by NFSI (582 mg, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a colorless oil.

Yield: 71 mg (0.20 mmol, 40%).

IR (diamond-ATR, neat): 2952 (m), 2909 (w), 2874 (m), 1572 (vw), 1457 (w), 1418 (vw), 1372 (vs), 1236 (w), 1200 (m), 1163 (w), 1003 (s), 960 (w), 881 (w), 776 (s), 717 (vs) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 8.4 Hz, 2 H), 3.65 (s, 3 H), 0.95 (td, *J* = 7.1, 1.1 Hz, 18 H), 0.90–0.78 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.98 (d, *J* = 245.0 Hz), 138.24, 131.43 (d, *J* = 3.7 Hz), 123.72 (d, *J* = 20.7 Hz), 63.87, 7.63, 4.07.

^{19}F NMR (377 MHz, $CDCl_3$): δ = −121.97 (t, *J* = 8.4 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 325 (3), 297 (27), 269 (23), 241 (24), 213 (16), 211 (42), 197 (10), 189 (23), 185 (10), 183 (12), 169 (23), 163 (11), 155 (19), 153 (16), 151 (24), 149 (11), 133 (42), 131 (12), 125 (28), 123 (13), 117 (53), 115 (22), 109 (15), 107 (16), 93 (10), 91 (34), 89 (100), 87 (46), 77 (32), 75 (11), 61 (30), 59 (20).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{30}FO^{28}Si_2$: 325.1819 $[M - Et]^{\bullet+}$; found: 325.1820.

(5-Bromo-2-methoxy-1,3-phenylene)bis(triethylsilane) (3c)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to −20 °C and 1.0 M $ZnCl_2$ in THF (1.5 mL, 1.5 mmol) was added, followed by a solution of Br_2 (0.09 mL, 1.75 mmol) in THF (1 mL). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 99:1) afforded the title compound as a colorless oil.

Yield: 106 mg (0.26 mmol, 51%).

IR (diamond-ATR, neat): 2952 (m), 2909 (w), 2874 (m), 1456 (w), 1417 (vw), 1368 (s), 1238 (w), 1207 (m), 1114 (s), 1003 (s), 973 (w), 882 (w), 772 (s), 721 (vs), 683 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 2 H), 3.65 (s, 3 H), 0.99–0.89 (m, 18 H), 0.89–0.78 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.03, 140.33, 132.39, 117.83, 63.73, 7.64, 4.07.

MS (EI, 70 eV): *m*/*z* (%) = 414 (2), 360 (15), 359 (60), 358 (15), 357 (55), 331 (28), 329 (30), 303 (10), 301 (15), 273 (11), 244 (10), 165 (12), 151 (11), 150 (12), 118 (13), 117 (100), 115 (22), 89 (32), 87 (24), 61 (15), 59 (19), 57 (15), 55 (11), 43 (69).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{35}{}^{79}BrO^{28}Si_2$: 414.1410 $[M]^{\bullet+}$; found: 414.1407.

[4-Methoxy-3,5-bis(triethylsilyl)phenyl]methanol (3d)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by paraformaldehyde (53 mg, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a colorless oil.

Yield: 72 mg (0.20 mmol, 39%).

IR (diamond-ATR, neat): 3299 (br vw), 2951 (m), 2909 (w), 2873 (m), 1557 (w), 1456 (w), 1417 (w), 1376 (s), 1210 (s), 1108 (m), 1003 (vs), 917 (vw), 889 (vw), 780 (s), 717 (vs), 685 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 2 H), 4.64 (s, 2 H), 3.67 (s, 3 H), 1.63 (s, 1 H), 0.99–0.92 (m, 18 H), 0.90–0.80 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.06, 137.38, 135.00, 129.01, 65.72, 63.64, 7.74, 4.22.

MS (EI, 70 eV): *m*/*z* (%) = 366 (1), 310 (21), 309 (69), 281 (23), 253 (12), 205 (15), 203 (45), 117 (13), 89 (14), 87 (12), 85 (15), 71 (22), 61 (14), 59 (12), 57 (33), 45 (15), 43 (100).

HRMS (EI): *m*/*z* calcd for $C_{20}H_{38}O_2{}^{28}Si_2$: 366.2410 $[M]^{\bullet+}$; found: 366.2398.

4-Methoxy-3,5-bis(triethylsilyl)benzaldehyde (3e)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by dimethylformamide (0.14 mL, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a colorless oil.

Yield: 69 mg (0.19 mmol, 38%).

IR (diamond-ATR, neat): 2952 (m), 2909 (w), 2874 (m), 1698 (s), 1571 (w), 1554 (w), 1456 (w), 1417 (w), 1380 (w), 1358 (m), 1212 (s), 1101 (s), 1003 (vs), 926 (m), 782 (m), 721 (vs), 684 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 7.94 (s, 2 H), 3.74 (s, 3 H), 0.98–0.83 (m, 30 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.17, 177.39, 140.63, 131.53, 130.08, 63.55, 7.73, 7.65, 4.00.

MS (EI, 70 eV): *m*/*z* (%) = 335 (26), 325 (46), 307 (100), 297 (39), 279 (75), 277 (12), 269 (25), 267 (13), 251 (55), 249 (20), 241 (22), 223 (44), 221 (15), 213 (12), 207 (13), 195 (28), 193 (24), 191 (17), 183 (20), 179 (36), 165 (52), 163 (15), 161 (24), 149 (16), 145 (14), 135 (14), 117 (41), 107 (16), 91 (23), 89 (79), 87 (24), 61 (34), 59 (18).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{31}O_2{}^{28}Si_2$: 335.1863 $[M - Et]^{\bullet+}$; found: 335.1855.

Cyclopropyl(4-fluorophenyl)[4-methoxy-3,5-bis(triethylsilyl)phenyl]methanol (3f)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by cyclopropyl 4-fluorophenyl ketone (0.25 mL, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a slightly yellow oil.

Yield: 110 mg (0.22 mmol, 44%).

IR (diamond-ATR, neat): 2951 (m), 2909 (w), 2874 (m), 1603 (vw), 1553 (vw), 1506 (m), 1457 (w), 1418 (w), 1379 (m), 1314 (vw), 1221 (s), 1158 (w), 1107 (s), 1002 (vs), 898 (w), 839 (m), 777 (s), 719 (vs), 684 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 2 H), 7.41–7.35 (m, 2 H), 7.02–6.92 (m, 2 H), 3.67 (s, 3 H), 1.87 (d, *J* = 0.8 Hz, 1 H), 1.56 (tt, *J* = 8.2, 5.5 Hz, 1 H), 0.94–0.87 (m, 18 H), 0.84–0.75 (m, 12 H), 0.69–0.61 (m, 1 H), 0.58–0.39 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.46, 161.84 (d, *J* = 245.0 Hz), 143.50 (d, *J* = 3.1 Hz), 140.58, 137.11, 128.57 (d, *J* = 8.3 Hz), 127.89, 114.51 (d, *J* = 21.0 Hz), 63.57, 21.98, 7.70, 4.28, 2.38, 1.40.

^{19}F NMR (377 MHz, $CDCl_3$): δ = –116.49 to –116.64 (m).

MS (EI, 70 eV): *m*/*z* (%) = 482 (1), 443 (15), 254 (13), 252 (14), 249 (12), 225 (17), 209 (12), 207 (39), 203 (14), 202 (19), 196 (13), 189 (10), 183 (12), 165 (11), 123 (100), 117 (30), 115 (12), 109 (25), 107 (20), 105 (11), 103 (24), 89 (78), 87 (76), 77 (12), 75 (37), 61 (39), 59 (54).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{43}FO^{28}Si_2$: 482.2836 $[M - H_2O]^{\bullet+}$; found: 482.2829.

N-tert-Butyl-4-methoxy-3,5-bis(triethylsilyl)benzamide (3g)

According to GP3, anisole derivative **1a** (168 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by *tert*-butyl isocyanate (0.20 mL, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 9:1) afforded the title compound as a colorless solid.

Yield: 83 mg (0.19 mmol, 38%); mp 56.4–58.2 °C.

IR (diamond-ATR, neat): 3318 (vw), 2953 (m), 2909 (w), 2874 (w), 1634 (m), 1573 (w), 1532 (m), 1448 (w), 1365 (m), 1313 (m), 1211 (s), 1165 (vw), 1104 (m), 1003 (s), 908 (m), 785 (w), 729 (vs) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 2 H), 5.82 (s, 1 H), 3.68 (s, 3 H), 1.47 (s, 9 H), 0.98–0.90 (m, 18 H), 0.90–0.80 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.68, 167.57, 136.90, 130.72, 129.16, 63.58, 51.61, 29.06, 7.69, 4.12.

MS (EI, 70 eV): *m*/*z* (%) = 434 (1), 406 (19), 380 (13), 379 (32), 378 (100), 351 (16), 350 (53), 322 (12), 318 (10), 294 (10), 217 (14), 89 (12), 87 (11), 57 (24), 43 (17).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{44}NO_2{}^{28}Si_2$: 434.2911 $[M - H]^{\bullet+}$; found: 434.2899.

1-[3,5-Bis(triethylsilyl)phenyl]-2,2-dimethylpropan-1-ol (3h)

According to GP3, arene **1b** (307 mg, 1.0 mmol) and PMDTA (0.63 mL, 3.0 mmol) were dissolved in *n*-hexane (2 mL). A 2.55 M solution of *n*BuLi in hexane (1.18 mL, 3.0 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (2 mL) was added, followed by trimethylacetaldehyde (0.38 mL, 3.5 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a colorless oil.

Yield: 228 mg (0.58 mmol, 58%).

IR (diamond-ATR, neat): 3455 (vw), 2952 (m), 2908 (w), 2874 (m), 1737 (vw), 1458 (w), 1416 (w), 1363 (w), 1235 (w), 1143 (w), 1055 (w), 1005 (s), 973 (w), 863 (vw), 801 (s), 719 (vs), 678 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (t, *J* = 1.2 Hz, 1 H), 7.44 (d, *J* = 1.2 Hz, 2 H), 4.42 (s, 1 H), 2.00 (s, 1 H), 1.03–0.98 (m, 18 H), 0.94 (s, 9 H), 0.87–0.78 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.08, 139.40, 135.27, 133.98, 82.90, 35.80, 26.08, 7.55, 3.58.

MS (EI, 70 eV): *m*/*z* (%) = 374 (8), 345 (30), 335 (34), 317 (40), 289 (51), 260 (16), 258 (13), 231 (47), 205 (17), 203 (82), 201 (19), 189 (13), 175 (100), 173 (39), 163 (13), 159 (14), 151 (31), 147 (13), 145 (41), 144 (18), 143 (16), 141 (19), 133 (30), 131 (24), 129 (34), 128 (32), 123 (38), 115 (22), 105 (15), 103 (23), 87 (68), 75 (17), 59 (45).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{42}{}^{28}Si_2$: 374.2825 $[M - H_2O]^{\bullet+}$; found: 374.2822.

(5-Iodo-1,3-phenylene)bis(triethylsilane) (3i)

According to GP3, arene **1b** (153 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and 1.0 M $ZnCl_2$ in THF (1.5 mL, 1.5 mmol) was added, followed by a solution of I_2 (444 mg, 1.75 mmol) in THF (1 mL). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 99:1) afforded the title compound as a colorless oil.

Yield: 93 mg (22 mmol, 43%).

IR (diamond-ATR, neat): 2952 (m), 2908 (w), 2873 (m), 1529 (w), 1457 (w), 1414 (w), 1367 (w), 1235 (w), 1135 (s), 1099 (m), 1003 (s), 972 (w), 860 (w), 787 (vs), 716 (vs), 687 (vs) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 1.0 Hz, 2 H), 7.53 (t, *J* = 1.1 Hz, 1 H), 1.01–0.93 (m, 18 H), 0.83–0.74 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.00, 140.27, 138.84, 96.88, 7.46, 3.40.

MS (EI, 70 eV): *m*/*z* (%) = 432 (11), 405 (10), 404 (29), 403 (100), 376 (16), 375 (53), 348 (12), 347 (48), 173 (12), 159 (18), 145 (14), 87 (15), 59 (13), 43 (42).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{33}I^{28}Si_2$: 432.1165 $[M]^{\bullet+}$; found: 432.1165.

4-Formyl-2,6-bis(triethylsilyl)phenyl Diethylcarbamate (3j)

According to GP3, carbamate **1c** (177 mg, 0.42 mmol) and PMDTA (0.26 mL, 1.26 mmol) were dissolved in *n*-hexane (1 mL) and cooled to –10 °C. A 2.55 M solution of *n*BuLi in hexane (0.50 mL, 1.26 mmol) was added and the resulting solution was stirred for 6 h at –10 °C. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by dimethylformamide (0.11 mL, 1.47 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a slight yellow oil.

Yield: 65 mg (0.14 mmol, 34%).

IR (diamond-ATR, neat): 2952 (w), 2909 (w), 2874 (w), 1716 (s), 1696 (s), 1564 (w), 1457 (w), 1424 (m), 1380 (m), 1363 (m), 1272 (s), 1221 (m), 1178 (m), 1145 (vs), 1100 (s), 1003 (s), 961 (m), 936 (m), 807 (w), 784 (m), 726 (vs), 671 (m) cm^{-1}.

^1H NMR (599 MHz, $CDCl_3$): δ = 10.00 (s, 1 H), 7.97 (s, 2 H), 3.58 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.1 Hz, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 0.96–0.90 (m, 18 H), 0.88–0.76 (m, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 192.09, 166.35, 154.02, 139.49, 132.61, 131.55, 40.82, 40.69, 13.73, 12.78, 7.34, 3.35.

MS (EI, 70 eV): *m*/*z* (%) = 448 (1), 422 (18), 421 (55), 420 (40), 179 (11), 168 (12), 100 (100), 72 (23).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{42}NO_3{}^{28}Si_2$: 448.2703 $[M - H]^{\bullet+}$; found: 448.2693.

4-Benzoyl-2,6-bis(triethylsilyl)phenyl Diethylcarbamate (3k)

According to GP3, carbamate **1c** (211 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL) and cooled to –10 °C. A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h at –10 °C. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by *N*-methoxy-*N*-methylbenzamide (0.27 mL, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane/EtOAc = 19:1) afforded the title compound as a slight yellow oil.

Yield: 116 mg (0.22 mmol, 44%).

IR (diamond-ATR, neat): 2952 (w), 2909 (w), 2874 (w), 1715 (s), 1657 (m), 1568 (vw), 1457 (w), 1426 (w), 1375 (m), 1315 (w), 1267 (vs), 1219 (w), 1183 (m), 1146 (vs), 1099 (s), 1002 (s), 967 (s), 852 (vw), 778 (s), 728 (s), 712 (vs), 691 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 2 H), 7.85–7.80 (m, 2 H), 7.61–7.55 (m, 1 H), 7.50–7.44 (m, 2 H), 3.60 (q, *J* = 7.2 Hz, 2 H), 3.39 (q, *J* = 7.1 Hz, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H), 0.98–0.88 (m, 18 H), 0.85–0.75 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.63, 164.95, 154.36, 139.81, 137.95, 133.71, 132.40, 130.47, 130.21, 128.27, 40.93, 40.82, 13.87, 12.94, 7.50, 3.54.

MS (EI, 70 eV): *m*/*z* (%) = 496 (19), 255 (17), 207 (35), 105 (12), 100 (100), 72 (55).

HRMS (EI): *m*/*z* calcd for $C_{28}H_{42}NO_3{}^{28}Si_2$: 496.2703 $[M - Et]^{\bullet+}$; found: 496.2703.

N,*N*-Diethyl-2,6-bis(triethylsilyl)-4-(trimethylsilyl)benzamide (3l)

According to GP3, benzamide **1d** (203 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by Me_3SiCl

(0.22 mL, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded the title compound as a colorless solid.

Yield: 110 mg (0.23 mmol, 46%); mp 67.6–69.2 °C.

IR (diamond-ATR, neat): 2951 (s), 2909 (w), 2872 (m), 1622 (s), 1473 (w), 1456 (w), 1426 (m), 1379 (w), 1286 (m), 1248 (m), 1069 (w), 1002 (m), 881 (w), 851 (vs), 800 (m), 766 (w), 726 (vs), 689 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (s, 2 H), 3.54 (q, *J* = 7.2 Hz, 2 H), 3.00 (q, *J* = 7.2 Hz, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 0.96–0.64 (m, 30 H), 0.27 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.46, 149.82, 141.05, 136.61, 131.84, 43.31, 38.63, 13.36, 12.90, 7.73, 4.05, –1.04.

MS (EI, 70 eV): *m*/*z* (%) = 476 (1), 450 (15), 449 (37), 448 (100), 43 (17).

HRMS (EI): *m*/*z* calcd for $C_{26}H_{50}NO^{28}Si_3$: 476.3200 $[M - H]^{\bullet+}$; found: 476.3202.

N,*N*-Diethyl-4-(phenylthio)-2,6-bis(triethylsilyl)benzamide (3m)

According to GP3, benzamide **1d** (203 mg, 0.5 mmol) and PMDTA (0.31 mL, 1.5 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.59 mL, 1.5 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by diphenyl disulfide (382 mg, 1.75 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded the title compound as an orange oil.

Yield: 112 mg (0.22 mmol, 44%).

IR (diamond-ATR, neat): 2951 (m), 2908 (w), 2873 (m), 1632 (s), 1545 (w), 1473 (w), 1457 (m), 1423 (m), 1378 (w), 1280 (m), 1222 (w), 1124 (m), 1067 (w), 1001 (s), 872 (w), 793 (vs), 722 (vs), 688 (vs) cm^{-1}.

^{1}H NMR (599 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 0.8 Hz, 2 H), 7.35–7.28 (m, 4 H), 7.27–7.23 (m, 1 H), 3.52 (q, *J* = 7.2 Hz, 2 H), 3.00 (q, *J* = 7.2 Hz, 2 H), 1.25 (td, *J* = 7.3, 0.7 Hz, 3 H), 0.96 (t, *J* = 7.3 Hz, 3 H), 0.88–0.60 (m, 30 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.98, 148.03, 137.72, 135.38, 135.08, 133.77, 131.38, 129.32, 127.30, 43.29, 38.75, 13.32, 12.81, 7.58, 3.75.

MS (EI, 70 eV): *m*/*z* (%) = 512 (1), 486 (10), 485 (38), 484 (100), 368 (13), 340 (16), 225 (16), 213 (15), 207 (34), 109 (13), 87 (23), 75 (12), 59 (24).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{46}NOS^{28}Si_2$: 512.2839 $[M - H]^{\bullet+}$; found: 512.2836.

[5-(Methylthio)-1,1′-biphenyl-2,2′-diyl]bis(triethylsilane) (3n) and [4-(Methylthio)-1,1′-biphenyl-2,2′-diyl]bis(triethylsilane) (3n′)

According to GP3, biphenyl **1e** (172 mg, 0.45 mmol) and PMDTA (0.28 mL, 1.35 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.53 mL, 1.35 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by dimethyl disulfide (0.14 mL, 1.58 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded a mixture of the regioisomers as a colorless oil; yield: 120 mg (0.28 mmol, 62%). The mixture of regioisomers was further purified by HPLC yielding **3n** (53%) as a colorless oil and **3n′** (9%) as a colorless solid.

Compound 3n

Yield: 102 mg (0.24 mmol, 53%).

IR (diamond-ATR, neat): 2951 (w), 2908 (w), 2872 (w), 1573 (w), 1455 (w), 1420 (w), 1239 (w), 1086 (w), 1055 (w), 1003 (m), 966 (w), 821 (w), 769 (m), 715 (vs), 685 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 1 H), 7.45 (d, *J* = 7.9 Hz, 1 H), 7.36–7.27 (m, 2 H), 7.20 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.14–7.10 (m, 1 H), 6.99 (d, *J* = 2.0 Hz, 1 H), 2.47 (s, 3 H), 0.87–0.75 (m, 18 H), 0.61–0.28 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.51, 150.59, 138.10, 135.95, 135.80, 135.49, 132.00, 130.18, 127.71, 127.68, 126.31, 123.70, 15.07, 7.75, 7.69, 4.39, 4.29.

MS (EI, 70 eV): *m*/*z* (%) = 428 (1), 413 (19), 285 (11), 273 (18), 255 (40), 245 (11), 227 (25), 165 (13), 115 (33), 105 (13), 87 (100), 59 (36).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{40}S^{28}Si_2$: 428.2389 $[M]^{\bullet+}$; found: 428.2382.

Compound 3n′

Yield: 17 mg (0.04 mmol, 9%); colorless solid; mp 71.3–73.7 °C.

IR (diamond-ATR, neat): 2949 (m), 2930 (w), 2906 (w), 2870 (w), 1585 (vw), 1453 (w), 1418 (w), 1375 (vw), 1360 (w), 1320 (vw), 1234 (w), 1149 (vw), 1121 (w), 1108 (w), 1091 (w), 1012 (m), 996 (w), 973 (w), 948 (vw), 833 (w), 810 (vw), 769 (w), 751 (w), 728 (vs), 716 (vs), 680 (m), 667 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 1 H), 7.45 (d, *J* = 2.1 Hz, 1 H), 7.34–7.27 (m, 2 H), 7.21 (dd, *J* = 8.0, 2.1 Hz, 1 H), 7.10–7.07 (m, 1 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 2.53 (s, 3 H), 0.80 (td, *J* = 7.9, 1.7 Hz, 18 H), 0.57–0.31 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.43, 148.20, 136.96, 136.11, 135.91, 135.48, 133.96, 130.84, 130.46, 127.68, 126.23, 126.17, 16.57, 7.74, 7.73, 4.40, 4.29.

MS (EI, 70 eV): *m*/*z* (%) = 428 (18), 400 (29), 227 (11), 115 (69), 88 (12), 87 (63), 70 (11), 61 (20), 59 (26), 45 (15), 43 (100).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{40}S^{28}Si_2$: 428.2389 $[M]^{\bullet+}$; found: 428.2380.

[5-Allyl-1,1′-biphenyl-2,2′-diyl]bis(triethylsilane) (3o)

According to GP3, biphenyl **1e** (172 mg, 0.45 mmol) and PMDTA (0.28 mL, 1.35 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.53 mL, 1.35 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and 1.0 M $ZnCl_2$ in THF (1.5 mL, 1.5 mmol) and CuCN•2LiCl (0.05 mL, 0.05 mmol, 0.11 equiv) were added, followed by allyl bromide (0.14 mL, 1.58 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded a mixture of the regioisomers as a colorless oil; yield: 131 mg (0.31 mmol, 69%). The mixture was further purified by HPLC and the major regioisomer was isolated as a colorless oil.

Yield: 112 mg (0.27 mmol, 59%).

IR (diamond-ATR, neat): 2951 (w), 2908 (w), 2873 (w), 1458 (w), 1415 (w), 1235 (vw), 1094 (w), 1003 (m), 973 (vw), 913 (w), 770 (w), 711 (vs), 677 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.55 (m, 1 H), 7.51 (d, *J* = 7.7 Hz, 1 H), 7.36–7.29 (m, 2 H), 7.20–7.12 (m, 2 H), 6.99 (d, *J* = 1.9 Hz, 1 H), 6.14–5.90 (m, 1 H), 5.17–5.04 (m, 2 H), 3.43–3.38 (m, 2 H), 0.82 (td, *J* = 7.9, 1.2 Hz, 18 H), 0.64–0.26 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.24, 151.16, 139.40, 137.20, 135.95, 135.66, 135.44, 133.21, 130.75, 130.29, 127.58, 126.41, 126.08, 116.11, 40.26, 7.74, 7.73, 4.36, 4.32.

MS (EI, 70 eV): *m*/*z* (%) = 422 (1), 306 (10), 267 (45), 250 (16), 249 (100), 239 (14), 221 (38), 217 (12), 115 (40), 105 (14), 87 (98), 59 (36).

HRMS (EI): *m*/*z* calcd for $C_{27}H_{42}{}^{28}Si_2$: 422.2825 $[M]^{\bullet+}$; found: 422.2819.

2′,6-Bis(triethylsilyl)-1,1′-biphenyl-3-carbaldehyde (3p)

According to GP3, biphenyl **1e** (172 mg, 0.45 mmol) and PMDTA (0.28 mL, 1.35 mmol) were dissolved in *n*-hexane (1 mL). A 2.55 M solution of *n*BuLi in hexane (0.53 mL, 1.35 mmol) was added and the resulting solution was stirred for 6 h. Afterwards, the mixture was cooled to –20 °C and THF (1 mL) was added, followed by dimethylformamide (0.12 mL, 1.58 mmol). Purification of the crude product by flash column chromatography (silica gel, isohexane) afforded a mixture of the regioisomers as a yellow oil; yield: 122 mg (0.30 mmol, 67%).The mixture was further purified by HPLC and the major regioisomer was isolated as a yellow oil.

Yield: 106 mg (0.26 mmol, 57%).

IR (diamond-ATR, neat): 2952 (w), 2909 (w), 2873 (w), 1701 (s), 1457 (w), 1416 (vw), 1376 (w), 1237 (w), 1174 (w), 1121 (vw), 1091 (vw), 1003 (m), 962 (vw), 706 (vs) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1 H), 7.82 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.74 (d, *J* = 7.7 Hz, 1 H), 7.62–7.57 (m, 2 H), 7.34 (pd, *J* = 7.4, 1.6 Hz, 2 H), 7.12–7.07 (m, 1 H), 0.80 (td, *J* = 7.9, 3.7 Hz, 18 H), 0.59–0.27 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.70, 151.93, 149.60, 145.16, 136.11, 136.08, 135.70, 135.30, 131.16, 130.16, 127.87, 126.73, 126.67, 7.69, 7.64, 4.46, 4.17.

MS (EI, 70 eV): *m*/*z* (%) = 410 (1), 381 (13), 209 (20), 115 (21), 105 (14), 87 (100), 59 (43).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{38}O^{28}Si$: 410.2461 $[M]^{\bullet+}$; found: 410.2461.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611480.

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