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Relative carbanion basicities as driving force for an intramolecular silyl migration of lithiated biphenyls

Laurence Bonnafoux,[a] Rosario Scopelliti,[b] Frédéric R. Leroux[a,*] and Françoise Colobert[a]

[a]*Laboratoire de Stéréochimie, Université Louis Pasteur (ECPM), CNRS, 25 rue Becquerel, F-67087 Strasbourg Cedex 2, France*
[b]*Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

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Abstract—A solvent-dependent silyl migration of lithiated biphenyls is described, involving the intermediate formation of a penta-coordinated silicate complex. Differences in the relative basicities of the aryllithium intermediates are the possible driving force for this migration.

Halogen/metal permutations, independently and almost simultaneously discovered by Wittig[1] and Gilman,[2] have been considered for a long while as a mature method lacking both appeal and surprise. However, the last years marked a revival. Owing to new insight and techniques, the halogen/metal exchange has recaptured its former role as one of the most important and versatile methods in organic synthesis.[3–5]

Due to the importance of the biaryl motif as the backbone of ligands in asymmetric catalysis, highly functionalized biaryl derivatives are very desirable targets. Recently, we reported on the first modular synthesis of atropisomeric C_1-symmetric biaryl ligands by means of highly regioselective bromine/lithium interconversions[6] on polybrominated precursors.[7,8] In the framework of these studies we prepared a dissymmetrically substituted biphenyl, 2,2′-dibromo-6-methoxy-6′-(trimethylsilyl)-biphenyl (**1**),[9] which allows a racemate resolution on an early stage of the synthesis.

When dibromobiaryl **1** was subjected to two consecutive halogen–metal permutations followed by trapping with 2 equiv of chlorodiphenylphosphine, not 2,2′-bis(diphenylphosphino)-substituted diphosphine **2a** but its regioisomer **2b** was obtained, as confirmed by single-crystal X-ray analysis (Fig. 1).[10,11] Apparently, the trimethylsilyl group migrated from one phenyl ring to the methoxy-bearing phenyl ring (Scheme 1).

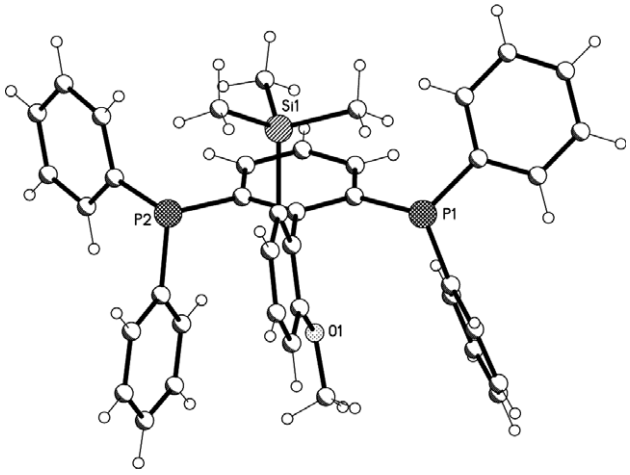

Figure 1. X-ray structure of compound **2b**.

In order to find out at which moment the silyl migration occurred, we treated **1** with just 1 equiv of butyllithium. Due to our previous investigations,[6–8] we expected the bromine–lithium exchange to occur on the anisyl rather than on the silylated ring. After trapping with chlorodiphenylphosphine, we did not obtain monophosphine **3a** but its regioisomer **3b** (Scheme 2).[12] Its structure could be confirmed by single-crystal X-ray analysis (Fig. 2).[13] This result indicates that the silyl migration occurred after the first bromine/lithium exchange on the OMe-substituted phenyl ring.

* Corresponding author. Tel.: +33 3 90 24 26 40; fax: +33 3 90 24 27 42; e-mail: frederic.leroux@ecpm.u-strasbg.fr

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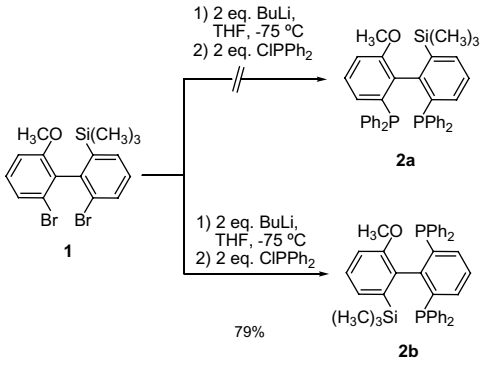
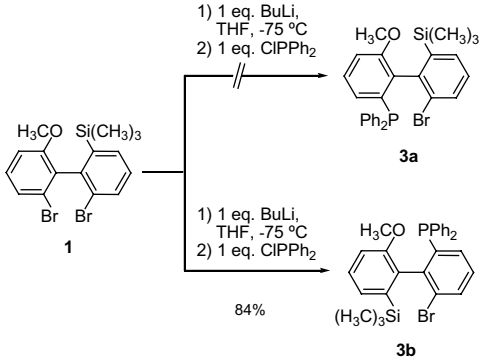


Scheme 1.



Scheme 2.

The striking migration of the silyl group can be explained by the intermediate formation of a silicate-complex **4** (Scheme 3). In fact, generally pentacoordinated organosilicates are unstable, especially silicates carrying only carbon[14] or carbon and hydrogen[14c,15] as ligating atoms at silicon and have, with a few exceptions, been described only recently.[16] For this reason, the silicate complex **4** is formed via an intramolecular attack of the highly polar lithium–carbon bond of intermediate **5** (obtained after Br/Li-exchange on the OMe-substituted phenyl ring) on the trimethylsilyl group. The silicate

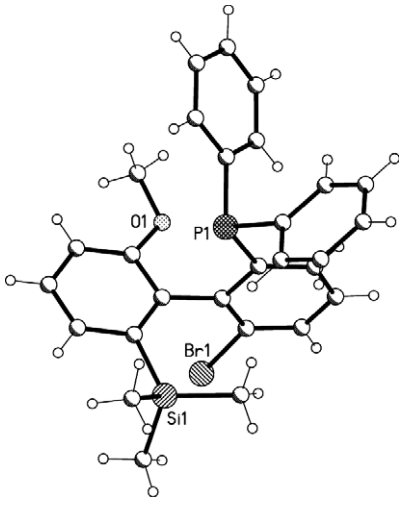
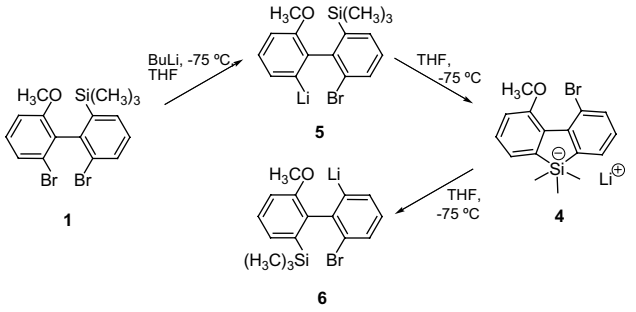


Figure 2. X-ray structure of compound **3b**.



Scheme 3.

complex **4** stabilizes then by migration of the silyl-group affording intermediate **6**.

We wondered about the driving force for the selective formation of intermediate **6**. As we could show by intramolecular competition experiments, bromine stabilizes an aryllithium carbanion in its *meta*-position more effectively than a methoxy group. While the inductive and mesomeric effects of the methoxy group can be neglected (Hammett parameter $\sigma_m = -0.12$),[17] all halogens have not only the same sign but also virtually the same values for the Hammett parameter σ_m ($\sigma_m = +0.34$ (F), +0.37 (Cl) and +0.39 (Br))[17] and would thus favor a negative partial charge at the *meta*-position. The influence of various substituents at the *ortho*-, *meta*-, and *para*-positions of aryllithiums on their stability was shown by means of competition and equilibration studies. Schlosser and Maggi showed that a methoxy group located in the *para*-position destabilizes an organometallic species.[18] In contrast, when the methoxy group is moved from the *para*- to the *ortho*-position it stabilizes an aryllithium carbanion. However, in the *meta*-position its basicity lowering effect was found to be almost invariant. Halogen atoms have a different behavior as they are stabilizing in all three positions.[19] Therefore, the aryllithium intermediate **5** undergoes an intramolecular isomerization toward its regioisomer **6**, via the intermediate formation of the silicate complex **4**. Intermediate **6** is thermodynamically more stable, that is, less basic, than its counterpart **5** due to the better stabilization of the aryllithium carbanion in the *meta*-position to the bromine atom (**6**) relative to an aryllithium carbanion in the *meta*-position to the methoxy group (**5**).

In order to avoid the undesired silyl migration, we had to avoid the intermediate silicate-complex formation. Klumpp et al. showed[14a] that the stabilities of silicate complexes like **4** depend on a large degree on the strength of complexation of their counter ions by the solvent. These authors were able to detect lithium 2,2′-biphenyldiyltrimethylsilicate in THF solution by ^{29}Si NMR. In THF, the lithium ion has an optimum complexation by tetra-coordination.[20] However, in diethyl ether the thermodynamic stability of silicate complexes is so low that they cannot be detected.

Aggregation plays an important role in organolithium chemistry. Coordinating ligands—such as ethers—can provide an alternative source of electron density for

the electron-deficient lithium atoms. Ethers can stabilize aggregates by coordination to the lithium atoms and then allow organolithiums to shift to an entropically favored lower degree of aggregation.[21] For example, THF is a strong decoordinating solvent producing low aggregation degrees albeit with an increase of basicity and concomitantly an increase of nucleophilicity. The latter could explain the formation of the silicate complex **4**. Thus, in order to avoid the silyl migration, we had to perform the bromine–lithium exchange in a non-coordinating solvent and we have chosen toluene instead of THF. In fact, toluene or generally hydrocarbon solutions of organolithiums are invariably aggregated as hexamers or tetramers. These solvents favor internal stabilization of lithiated species.[22] When **1** was consecutively treated in toluene at −75 °C with butyllithium, chlorodiphenylphosphine, again butyllithium followed by chlorodiphenylphosphine, diphosphine **2a** was selectively obtained via monophosphine **3a** (Scheme 4).[23] The structure of **2a** could be confirmed by single-crystal X-ray analysis (Fig. 3).[24]

In order to confirm our hypothesis, we subjected the methoxy-substituted biphenyl **7**[25] to the silyl migration (Scheme 5). When **7** was treated at −75 °C in THF with 1 equiv of butyllithium and subsequently trapped with iodomethane, gas chromatographic analysis revealed the presence of two isomeric compounds **8a** and **8b** in a ration of 2.3:1.[26] However, in toluene only one regioisomer, compound **8a**, could be detected. The outcome of the reaction in THF is in perfect accordance with the poor stabilization of an aryllithium carbanion in the *meta*-position of a methoxy group.[19] The stabilizing effect was found to be almost the same as an unsubstituted phenyllithium. Thus, no significant extra-stabilization is obtained when the carbanion is located at the methoxy-substituted phenyl ring compared with the unsubstituted phenyl ring and as a corollary, a mixture of the two regioisomers is obtained.

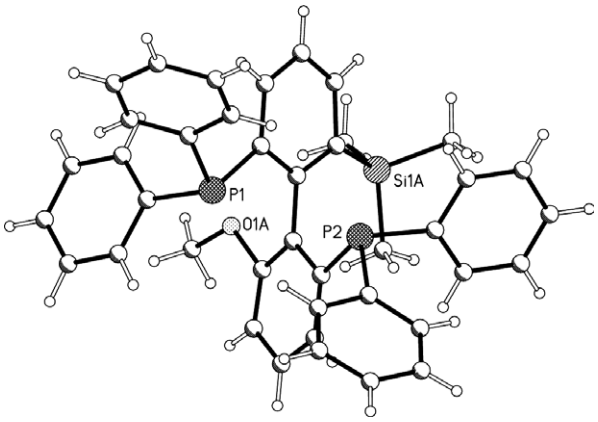
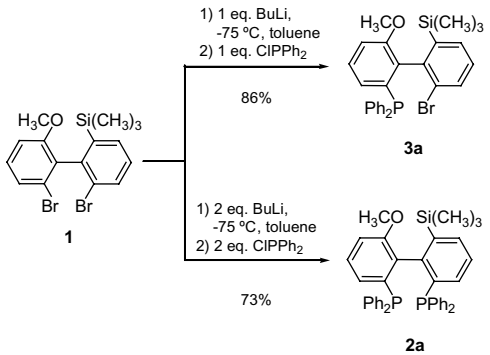
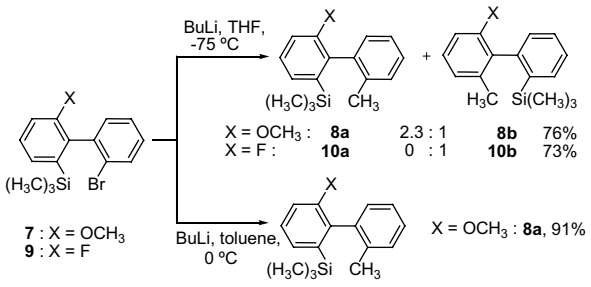


Figure 3. X-ray structure of compound **2a**.



Scheme 4.



Scheme 5.

In contrast, the analogous experiment with a fluorinated biphenyl (compound **9**)[27] afforded in THF exclusively the silyl-migrated compound **10b**.[28] The outcome of the reaction was again checked by gas chromatography in comparison with authentic samples. The driving force is the stabilization of the aryllithium carbanion in the *meta*-position of the fluorine atom (Scheme 5).

In conclusion, we could show that trimethylsilyl-substituted biaryls undergo a migration of the silyl group after lithiation involving the intermediate formation of a pentacoordinated silicate complex. The driving force of this silyl migration is the different relative basicity of the aryllithium intermediates. The silyl migration can be successfully avoided by changing the solvent from a strongly coordinating solvent like THF to an apolar non-coordinating solvent like toluene.

This stop-and-go isomerization (stop in toluene and go in THF) can be useful in the synthesis of functionalized biaryl scaffolds. For comparison, the basicity-gradient driven halogen/migration in aromatic and heteroaromatic compounds became one major tool in the regiochemically exhaustive functionalization of these compounds.[3] In the present case, the silyl migration can be exploited to allow the regiochemical synthesis of biaryls. Subsequently, the trimethylsilyl group can be either removed by protodesilylation (with acids, bases, or fluoride ions in the presence of proton sources) or converted into bromine or iodine atoms by halodesilylation (with molecular bromine, iodine, or iodmonochloride) for further functionalization.[29,30]

Acknowledgments

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9. *Trimethyl(6,2′-dibromo-6′-methoxy-biphenyl-2-yl)silane* (**1**). Mp 184–185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.69$ (dd, $J = 8.0$, 1.0 Hz, 1H), 7.60 (dd, $J = 7.5$, 1.0 Hz, 1H), 7.26 (m, 3H), 6.92 (dd, $J = 9.0$, 2.5 Hz, 1H), 3.74 (s, 3H), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta = 158.7$, 144.0, 142.7, 134.1, 133.5, 132.5, 130.5, 129.0, 126.6, 125.9, 124.8, 109.9, 56.1, 0.1. Anal. Calcd for $C_{16}H_{18}Br_2OSi$ (414.21): C, 46.39; H, 4.38. Found: C, 46.43; H, 4.41.
10. *(2′-Methoxy-6′-(trimethylsilyl)biphenyl-2,6-diyl)bis(diphenylphosphine)* (**2b**). Mp 170–172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.3$ (m, 7H), 7.2 (m, 18H), 6.25 (dd, $J = 6.7$, 2.2 Hz, 1H), 2.49 (s, 3H), 0.04 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta = 156.3$ (t, $J = 2$ Hz), 151.5 (t, $J = 32$ Hz), 140.9 (t, $J = 2$ Hz), 138.9 (t, $J = 7$ Hz), 138.4 (sym. m), 137.2 (sym. m), 133.7 (sym. m), 134.2 (sym. m), 128.3 (t, $J = 3$ Hz), 128.1, 127.9, 127.6 (sym. m), 127.2, 125.9, 109.1, 52.7, 0.5. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -17.3$ (s). Anal. Calcd for $C_{40}H_{38}OP_2Si$ (624.78): C, 76.90; H, 6.13. Found: C, 76.68; H 5.94.
11. *Crystal data for* **2b**: $C_{40}H_{38}OP_2Si$, $M_r = 624.73$, triclinic, space group $P\bar{1}$, $a = 11.7325(4)$, $b = 15.7258(6)$, $c = 19.6859(7)$ Å, $\alpha = 80.184(3)$, $\beta = 77.447(9)$, $\gamma = 78.813(3)°$, $V = 3446.6(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.204$ g cm^{-3}, $\mu = 0.191$ mm^{-1}, $F(000) = 1320$, crystal dimensions $0.20 \times 0.16 \times 0.12$ mm, $T = 140(2)$ K, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\theta = 2.90$–$25.03°$, $-13 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 18$, $-23 \leqslant l \leqslant 23$, 21,362 reflections collected, 10,694 independent reflections, $R_{int} = 0.0388$, R_1 $[I > 2\sigma(I)] = 0.0507$, wR_2 (all data) $= 0.1480$, largest difference peak 0.577 e Å^{-3}, largest difference minimum -0.391 e Å^{-3}. CCDC 652949.
12. *(6-Bromo-2′-methoxy-6′-(trimethylsilyl)biphenyl-2-yl)diphenylphosphine* **(3b)**. Mp 133–135 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.66$ (dd, $J = 7.7$, 1.4 Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.3 (m, 7H), 7.2 (m, 6H), 6.63 (d, $J = 8.3$ Hz, 1H), 3.03 (s, 3H), 0.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta = 156.0$, 141.3 (d, $J = 14$ Hz), 140.6 (d, $J = 3$ Hz), 137.9 (d, $J = 15$ Hz), 136.4 (d, $J = 12$ Hz), 133.7 (d, $J = 20$ Hz), 132.7, 132.6, 128.6 (d, $J = 4$ Hz), 128.5, 128.4, 127.9 (d, $J = 7$ Hz), 126.8 (d, $J = 6$ Hz), 126.4, 110.2, 54.2, 0.3. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -14.8$ (s). Anal. Calcd for $C_{28}H_{28}BrOPSi$ (521.65): C, 64.88; H 5.41. Found: C, 64.47; H, 5.50.
13. *Crystal data for* **3b**: $C_{28}H_{28}BrOPSi$, $M_r = 519.47$, monoclinic, space group $P2_1/n$, $a = 10.5223(6)$, $b = 8.7751(5)$, $c = 27.669(3)$ Å, $\beta = 90.485(9)°$, $V = 2554.7(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.351$ g cm^{-3}, $\mu = 1.737$ mm^{-1}, $F(000) = 1072$, crystal dimensions $0.28 \times 0.11 \times 0.09$ mm, $T = 140(2)$ K, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\theta = 2.75$–$25.03°$, $-12 \leqslant h \leqslant 12$, $-10 \leqslant k \leqslant 10$, $-31 \leqslant l \leqslant 30$, 14,547 reflections collected, 4288 independent reflections, $R_{int} = 0.0732$, R_1 $[I > 2\sigma(I)] = 0.1210$, wR_2 (all data) $= 0.3100$, largest difference peak 1.629 e Å^{-3}, largest difference minimum -1.437 e Å^{-3}. CCDC 652948.
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23. *2,2′-Bis-diphenylphosphanyl-6-methoxy-6′-trimethylsilanyl-biphenyl* (**2a**). Mp 214–216 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.59$ (dd, $J = 7.4$, 1.6 Hz, 1H), 7.5 (m, 4H), 7.3 (m, 16H), 7.09 (ddd, $J = 7.4$, 3.5, 1.3 Hz, 1H), 7.04 (symm. m, 3H), 6.58 (d, $J = 8.32$ Hz, 1H), 3.08 (s, 3H), −0.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta = 157.1$ (d, $J = 2$ Hz), 144.1 (d, $J = 8$ Hz), 143.8 (d, $J = 8$ Hz), 138.3, 137.4, 136.3 (d, $J = 8$ Hz), 136.1 (d, $J = 7$ Hz), 134.5 (d, $J = 2$ Hz), 133.9 (dd, $J = 20$, 14 Hz), 133.3 (d, $J = 19$ Hz), 131.2 (dd, $J = 6$, 4 Hz), 128.8, 128.4, 128.2, 128.0, 127.9 (d, $J = 2$ Hz), 128.8, 127.6, 125.9 (d, $J = 2$ Hz), 110.6, 54.7. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -12.2$ (d, $J = 38.1$ Hz), −14.9 (d, $J = 38.8$ Hz). Anal.

Calcd for $C_{40}H_{38}OP_2Si$ (624.78): C, 76.90; H, 6.13. Found: C, 76.59; H 6.02.

24. *Crystal data for* **2a**: $C_{40}H_{38}OP_2Si$, $M_r = 624.73$, monoclinic, space group $P2_1/n$, $a = 12.691(6)$, $b = 17.561(6)$, $c = 15.685(6)$ Å, $\beta = 97.37(3)°$, $V = 3467(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.197$ g cm^{-3}, $\mu = 0.190$ mm^{-1}, $F(000) = 1320$, crystal dimensions $0.18 \times 0.16 \times 0.13$ mm, $T = 140(2)$ K, Mo-K_α radiation, $\lambda = 0.71070$ Å, $\theta = 3.03$–$27.64°$, $-14 \leqslant h \leqslant 16$, $-22 \leqslant k \leqslant 22$, $-20 \leqslant l \leqslant 20$, 27,538 reflections collected, 8029 independent reflections, $R_{int} = 0.0747$, R_1 $[I > 2\sigma(I)] = 0.0940$, wR_2 (all data) $= 0.3398$, largest difference peak 0.329 e Å^{-3}, largest difference minimum -0.284 e Å^{-3}. CCDC 652950.
25. *(2′-Bromo-6-methoxybiphenyl-2-yl)trimethylsilane* (**7**). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.65$ (dd, $J = 8.6$, 1.5 Hz, 1H), 7.5–7.3 (m, 2H), 7.3–7.2 (m, 3H), 7.02 (dd, $J = 8.2$, 0.9 Hz, 1H), 3.77 (s, 3H), 0.01 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 156.4$, 140.7, 140.4, 136.1, 132.1, 132.1, 128.9, 128.6, 126.7, 126.6, 125.9, 111.6, 55.9, 0.14. Anal. Calcd for $C_{16}H_{19}BrOSi$ (335.31): C, 57.31; H, 5.71. Found: C, 57.42; H, 5.53.
26. *(6-Methoxy-2′-methylbiphenyl-2-yl)trimethylsilane* (**8a**). Mp 51–53 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.4$–7.3 (m, 1H), 7.3–7.1 (m, 5H), 6.97 (dd, $J = 8.1$, 1.0 Hz, 1H), 3.61 (s, 3H), 1.96 (s, 3H), -0.13 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 156.42$, 140.6, 139.3, 137.6, 136.8, 130.7, 129.3, 127.9, 127.6, 126.9, 125.1, 111.4, 55.6, 20.0, 0.2. Anal. Calcd for $C_{17}H_{22}OSi$ (270.44): C, 75.50; H, 8.20. Found: C, 75.62; H, 8.19.
27. *(2′-Bromo-6-fluorobiphenyl-2-yl)trimethylsilane* (**9**). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.7$ (d, $J = 7.1$ Hz, 1H), 7.52–7.51 (m, 1H), 7.5–7.3 (m, 3H), 7.26 (td, $J = 7.7$, 2.1 Hz, 1H), 7.17 (t, $J = 9.2$ Hz, 1H), 0.13 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 159.4$ (d, $J = 247$ Hz), 140.0 (d, $J = 310$ Hz), 134.2 (d, $J = 15$ Hz), 132.4, 132.1, 130.1 (d, $J = 4$ Hz), 129.7, 129.2 (d, $J = 7$ Hz), 126.8, 125.4 (d, $J = 1$ Hz), 115.9 (d, $J = 23$ Hz), 0.1. Anal. Calcd for $C_{15}H_{16}BrFSi$ (323.27): C, 55.73; H, 4.99. Found: C, 55.95; H, 5.09.
28. *(6′-Fluoro-2′-methylbiphenyl-2-yl)-trimethylsilane* (**10b**). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.7$ (m, 1H), 7.35 (td, $J = 6.9$, 1.7 Hz, 2H), 7.2–7.1 (m, 1H), 7.05 (dd, $J = 7.3$, 1.6 Hz, 1H), 6.99 (d, $J = 7.6$, 1H), 6.90 (t, $J = 8.8$ Hz, 1H), 1.97 (s, 3H), -0.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 160.3$ (d, $J = 243$ Hz), 140.9 (d, $J = 1.6$ Hz), 139.5 (d, $J = 3$ Hz), 139.3 (d, $J = 0.4$ Hz), 135.0, 131.2 (d, $J = 18$ Hz), 129.8, 129.1, 128.6 (d, $J = 9$ Hz), 127.0, 125.0 (d, $J = 3$ Hz), 112.7 (d, $J = 23$ Hz), 20.3 (d, $J = 3$ Hz), -0.3. Anal. Calcd for $C_{16}H_{19}FSi$ (258.4): C, 74.37; H, 7.41. Found: C, 74.27; H, 7.33.
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