Regiospesific Synthesis of Polysubstituted Phenols via the Palladium-Catalyzed Enyne−Diyne [4 + 2] *Cross*-Benzannulation Pathway

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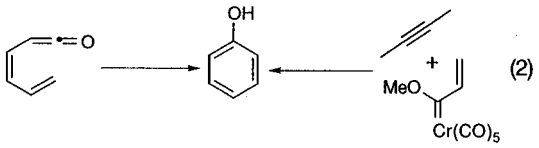
An efficient method for the synthesis of polysubstituted phenols via the consecutive palladium-catalyzed enyne−diyne [4 + 2] *cross*-benzannulation reaction and subsequent deprotection step was developed. In all cases, the reactions proceeded in a regiospecific manner affording the corresponding polysubstituted phenols in good overall yields. It was shown that a more useful one-pot methodology could be applied to the synthesis of polysubstituted phenols **4a**−**e**. The synthetically useful *p*-methoxyphenylacetylene **13** and its monosilylated derivative **12** were smoothly prepared via exhaustive or partial desilylation of bis-silylated aromatic adduct **8c**, respectively.

Phenol derivatives are omnipresent structural constituents in pharmacologically important molecules, and consequently, much attention has been focused on their syntheses. Most of the methods for preparation of substituted phenols involve various kinds of modification of aromatic precursors (eq 1).[1] Furthermore, a number

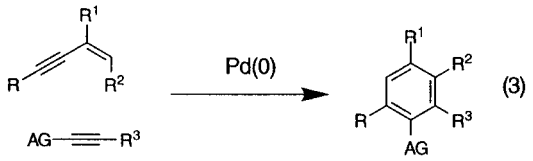
(1)

of reports on the synthesis of phenols via construction of the benzene skeleton from different acyclic units have appeared in the literature during the past three decades. Among them, perhaps two the following reactions could be considered as the most general and synthetically important procedures: ring closure of dienylketenes and cycloaddition of Fisher carbenes with alkynes (eq 2).[2]



(2)

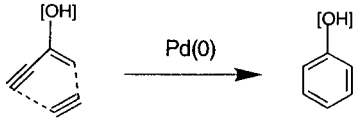
To the best of our knowledge, there is no precedent for the preparation of phenol derivatives through a [4 + 2] benzannulation pathway. We have recently reported an efficient approach to polysubstituted benzenes via the novel palladium-catalyzed homodimerization of conjugated enynes[3] and the enyne−diyne *cross*-benzannulation[4] reactions (eq 3).[5] This methodology allowed us to



(3)

AG= activating group (alkynyl or alkenyl)

construct a benzene ring with several alkyl, aryl, or silyl substituents in a *regio*- and in some cases[4b] *chemospecific* manner. Encouraged by successful benzannulation of carbon- and silyl-substituted enynes and diynes, we intended to apply this technique to the synthesis of synthetically useful heteroatom-substituted aromatics, particularly phenol and its derivatives. Herein we wish to report a novel efficient method for the synthesis of polysubstituted phenols via the palladium-catalyzed enyne−yne [4 + 2] cycloaddition protocol (eq 4).



(4)

Results and Discussion

Synthesis of Polysubstituted Phenols. The obvious impossibility of introduction of unprotected hydroxy group into either of the partners (enynes or diynes) of the [4 + 2] cycloaddition reaction prompted us to search for more suitable precursors for phenol synthesis, bearing a hydroxy group equivalent. After some work on the design of reactants,[8] we found that readily available and

(1) For a general review, see: (a) Whiting, D. A. In *Comprehensive Organic Chemistry*; Stoddart, J. F., Ed.; Pergamon Press: Oxford, 1979; Vol. 1, Chapter 4.2. For a review on aryl C−O bond-forming reactions, see: (b) Chiu, C. K.-F. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon Press: New York, 1995; Vol. 2, Chapter 2.13. For a review on electrophilic hydroxylation, see: (c) Jacquesy, J. C.; Gesson, J. P.; Jonannetand, M. P. *Rev. Chem. Intermed.* **1988**, *9*, 1−26, 5. For a review on OH^- and OR^- as nucleophiles in aromatic substitution, see: (d) *The Chemistry of the Hydroxyl Group*; Patai, S.; Ed.; Wiley Interscience: New York, 1971; Vol. 1; p 83. For most recent works on the preparation of phenols from aryl halides and aryl ethers, see: (e) Mann, G.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 5413. (f) Pews, R. G.; Lysenko, Z.; Vosejpka, P. C. *J. Org. Chem.* **1997**, *62*, 8255. (g) Nayak, M. K.; Chakraborti, A. K. *Tetrahedron Lett.* **1997**, *38*, 8749.

(2) For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, 1065. (b) Schore, N. E. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 1081−1119. See also: (c) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (d) Turnbull, P.; Heilman, M. J.; Moore, H. W. *J. Org. Chem.* **1996**, *61*, 2584. (e) Koo, S. H.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 3389. (f) Covarrubias-Zúñiga, A.; Ríos-Barrios, E. *J. Org. Chem.* **1997**, *62*, 5688. (g) Collomb, D.; Doutheau, A. *Tetrahedron Lett.* **1997**, 1397. (h) Barluenga, J.; Refnández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591.

(3) Saito, S.; Salter, M. M.; Gevorgyan, V.; Tsuboya, N.; Tando, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970.

(4) (a) Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11313. (b) Gevorgyan, V.; Sadayori, N.; Yamamoto, Y. *Tetrahedron Lett.* **1997**, *38*, 8603.

(5) Some data on related processes such as thermal[6,7] or Lewis acid mediated[6] *intramolecular* enyne−yne [4 + 2] cycloaddition reactions were recently reported.

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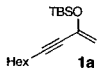
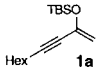
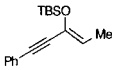
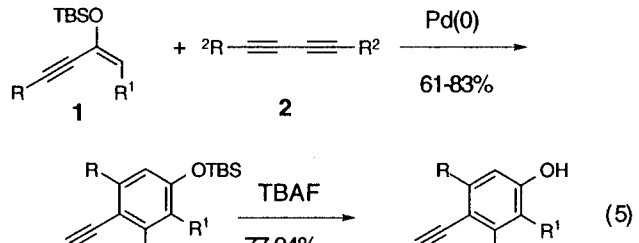
Table 1. Synthesis of Phenols via the Palladium-Catalyzed Enyne−Diyne Benzannulation Protocol

entry	enyne **1**	diyne **2** R^2	method	product **3** [a,b]	product **4** [c,b] (overall yield)
1	 **1a**	Bu **2a**	A	**3a**, 83%	**4a** 94% (78%)
2	 **1a**	Ph **2b**	A	**3b**, 70%	**4b** 77% (54%)
3	 **1b**	Bu **2a**	A	**3c**, 79%	**4c** 86% (68%)
4	**1b**	**2a**	B		**4c** (73%)
5	 **1b**	Ph **2b**	A	**3d**, 61%	**4d** 89% (54%)
6	**1b**	**2b**	B		**4d** (57%)
7	 **1c**	Bu **2a**	A	**3e**, 66%[d]	**4e** 92% (61%)[d]
8	 **1d**	**2a**		**3e**, 0%	

[a] The benzannulation reactions were carried out in the Wheaton microreactors with 0.5 mmol of **1** and **2** in THF (1 mL) at 100 °C in the presence of $Pd(PPh_3)_4$ (2 mol %) and $(o\text{-Tol})_3P$ (20 mol %) except where otherwise noted. [b] Isolated yield. [c] All deprotection reactions of **3** were conducted with TBAF (2 equiv) in THF (1 mL) at room temperature. [d] The reaction was carried ut in the presence of $Pd(PPh_3)_4$ (5 mol %).

easily handled 2-siloxy-substituted enyne **1** could perfectly serve for this purpose (eq 5, Table 1). Two methods



(5)

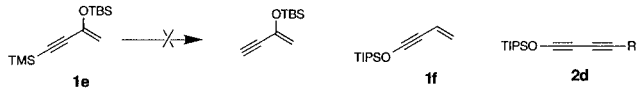
were utilized for the preparation of phenols **4**: the stepwise method A and one-pot method B. According to method A the aromatic silyl ethers **3** were isolated and then converted into the phenols **4** by treatment with Bu_4NF, whereas in method B the benzannulation reaction and the deprotection step **3** → **4** were accomplished in one-pot sequence (for details, see the Experimental Section). Thus, 2,4-disubstituted enynes **1a**,**b** in the presence of $Pd(PPh_3)_4$ (2 mol %) and $(o\text{-Tol})_3P$ (20 mol %)[10] in THF smoothly reacted with diynes **2**, producing siloxybenzenes **3a**−**d** in 61−83% isolated yields (method A, entries 1, 2, 3, and 5, Table 1). Trisubstituted *E*-enyne **1c** (with a methyl group *cis*-oriented toward an alkynyl moiety) easily reacted with diyne **2b**, affording pentasubstituted aromatic silyl ether **4e** in 66% isolated yield (entry 7), whereas its *Z* counterpart **1d** did not undergo the benzannulation reaction at all (entry 8, Table 1).[12] Subsequent deprotection of **3** with TBAF afforded the desired phenols **4** in good overall yields (eq 5, Table 1). Practically, the simpler and more convenient one-pot procedure **B** gave phenols **4c**,**d** in even slightly higher isolated yields, as compared to the overall yields obtained via method A (entries 4 and 6 vs entries 3 and 5 correspondingly, Table 1). It was found that in all cases the enyne−diyne [4 + 2] cycloaddition reaction proceeded not only in *regiospecific* but also in *chemospecific* fashion, affording tetra- and pentasubstituted *cross*-benzannulation products **3**, exclusively.[13] No detectable amounts of enyne dimer[13] or any other regioisomers of **3** were detected by ^1H NMR and GC−MS analyses of the crude reaction mixtures.

Synthesis of Alkoxybenzenes. We next attempted to apply the palladium-catalyzed enyne−diyne benzannulation method for the synthesis of polysubstituted benzenes bearing an alkoxy group.[14,15] At first, we tried to introduce an alkoxy group in the diyne component. However, the mono- and dialkoxy-substituted diynes **2e**,**f**[9] appeared to be unstable under the various reaction conditions tested, and in all cases only the rapid total decomposition of the diynes was observed. The introduction of a methoxy susbstituent at the terminal olefinic moiety of enyne turned out to be unsuccessful, as well. Thus, mono- and dimethoxy-substituted enynes **5** and **6** did not undergo the [4 + 2] benzannulation reaction with

(6) Danheiser, R. L.; Gould, A. E.; Fernandez de la Predilla, R.; Helgason, A. L. *J. Org. Chem.* **1994**, *59*, 5514.

(7) Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218.

(8) The bis-silylated enyne **1e** did not undergo the benzannulation reaction. Moreover, all attempts to carry out selective deprotection of the alkynyl-TMS group of **1e** failed, perhaps due to similar reactivity of both silyl groups toward nucleophilic reagents (e.g., MeO^- and F^-).[9] Furthermore, we did not succeed in isolating the siloxy-substituted enyne **1f** and diyne **2d** due to their low stability.



(9) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988.

(10) In the absence of additional phosphine ligand all benzannulation reactions (even in the presence of 5 mol % of $Pd(PPh_3)_4$) proceeded somewhat slower than in the presence of 2 mol % of $Pd(PPh_3)_4$−20 mol % of $(o\text{-Tol})_3P$ catalyst system.[11]

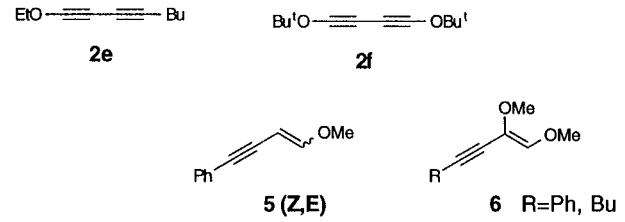
(11) Gevorgyan, V.; Tando, K.; Uchiyama, N.; Yamamoto, Y. Unpublished results.

(12) During our study on the benzannulation of carba-substituted enynes we found that enynes having a methyl group *trans*-oriented toward the alkynyl moiety reacted much slower than the corresponding cis-isomers.[4b]

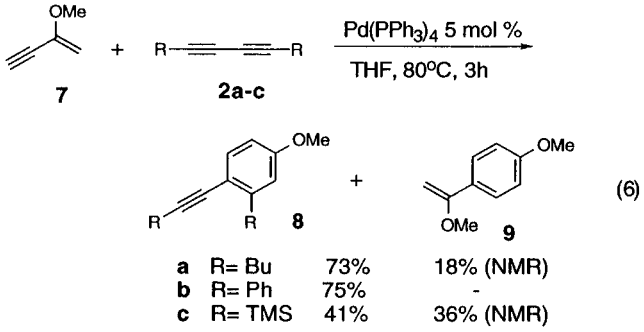
(13) We have recently shown that some of palladium-catalyzed *cross*-benzannulation reactions between diynes and monosubstituted enynes were not completely *chemoselective*,[4a] accordingly, trace to notable amounts of [4 + 2] enyne−enyne homodimer[3] together with major *cross*-benzannulation product were produced. For some examples on *chemospecific* benzannulation of the alkyl- and aryl-substituted enynes, see ref 4b.

(14) Alkoxy-substituted aromatics are ubiquitous structural units in biologically important molecules and thus are of great importance for synthetic organic chemistry. See, for example, ref 1b.

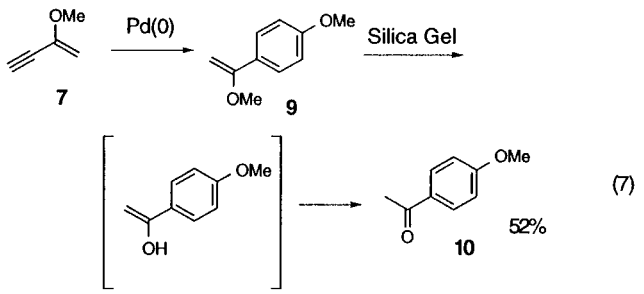
(15) Recently, Merlic and co-worker have demonstrated an example of the construction of alkoxybenzene derivative via ruthenium-catalyzed intramolecular cyclization of dienylalkynes; see: Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319.



diynes **2a**,**b**. In contrast, the introduction of a methoxy group into the internal olefinic position of enyne was much more fruitful. Thus, 2-methoxy-1-buten-3-yne (**7**) in the presence of $Pd(PPh_3)_4$ (5 mol %) smoothly reacted with diyne **2**, producing methoxybenzene **8** in reasonable to good chemical yields (eq 6). The reaction of **7** with

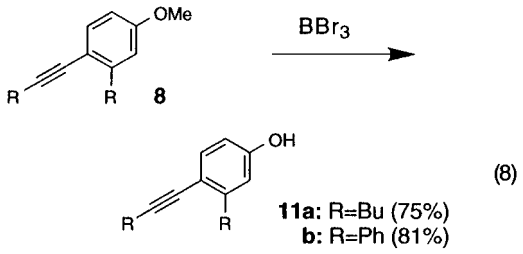


diphenyldiyne **2b** was *chemospecific*, affording the *cross*-benzannulation product **8** exclusively. Unlike benzannulation of **2b**, the reactions of dodecadiyne **2a** and bis-silyldiyne **2c** with **7** were less *chemoselective*.[13] In later cases, the enyne homodimer **9**[3] was detected by ^{1}H NMR analyses of the crude reaction mixtures in 18 and 36% yields, respectively, together with the major *cross*-benzannulation products **8a**,**c** (eq 6). The test experiments indicated that, in the absence of diyne **2**, the methoxy-substituted enyne **7** smoothly underwent the [4 + 2] homodimerization reaction (eq 7).[3]

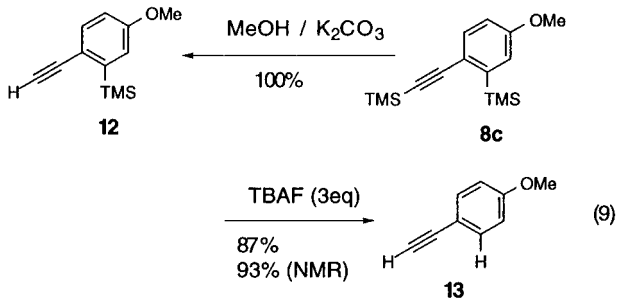


Though the dimer **9** was detected by GLC and ^{1}H NMR analyses of the crude reaction mixtures, its enol ether moiety was not hydrolytically stable under the conditions of column chromatography, and *p*-methoxyacetophenone (**10**) was isolated in 52% overall yield (eq 7).

Although the alkoxy-substituted aromatics by themselves are synthetically useful compounds,[14] they could be also easily transformed into the corresponding phenols using standard deprotection techniques. As an example, the treatment of methoxybenzenes **8a** and **8b** with BBr_3[16] afforded the phenols **11a** and **11b** in 75 and 81% isolated yields, respectively (eq 8).[9] Furthermore, the bis-silyl substituted benzene **8c** could be effectively transformed



via the partial desilylation into the monosilylated benzene **12** or via the exhaustive desilylation into the *p*-methoxyethynylbenzene (**13**) (eq 9).



Conclusion

A synthetically useful and effective method for the preparation of polysubstituted siloxybenzenes (**3**), alkoxybenzenes (**8**), and phenols (**4**, **11**) via the palladium-catalyzed enyne−diyne [4 + 2] *cross*-benzannulation reaction was developed. It was shown that conjugated enynes bearing a hydroxy group equivalent at internal olefinic moiety, in contrast to enynes bearing ones at any other positions, or correspondingly substituted diynes, are the best substrates for the preparation of phenols and aryl ethers. The efficient conversion of bis-silyl substituted methoxybenzene **8c** into the corresponding phenylacetylenes **12** and **13** was demonstrated.

Experimental Section

General Information. All solvents were purified and dried before use according to standard procedures. Reactions were performed under an argon atmosphere in oven-dried glassware. The diynes **2a**−**c** were purchased from Aldrich. Silylated enynes **1a**−**d** were obtained from the corresponding alkynyl ketones via the standard procedures for the preparation of silyl ethers.[17] All other starting materials were prepared according to the described methods.[9]

Synthesis of Phenols 4a−e. General Procedure. Stepwise Method A. Diyne **2** (1.0 mmol) and enyne **1** (1.0 mmol) were consecutively added at room temperature to a solution of $Pd(PPh_3)_4$ (2 mol %) and $(o\text{-Tol})_3P$ (20 mol %) in THF (1.0 mL) in a 5 mL Wheaton microreactor under an argon atmosphere. After being stirred for 12 h at 100 °C, THF was evaporated off, hexane was added, and the resulting mixture was filtered through silica gel. Purification by silica gel column chromatography using hexanes−ethyl acetate as an eluent gave siloxybenzenes **3** in 61−83% yields. TBAF (1 M solution in THF, 1 mmol) was added at room temperature to a solution of **3** (0.5 mmol) in THF (2.5 mL). After being stirred for 1 h, THF was evaporated off and the mixture was extracted with ether−water. Purification by column chromatography (silica gel, hexanes−ethyl acetate as an eluent) gave phenols **4** in 77−94% yields.

One-Pot Method B. After completion of the first benzannulation step, which was carried out as described in method

(16) Felix, A. M. *J. Org. Chem.* **1974**, *39*, 1427.

(17) For a review, see: Brownbridge, P. *Synthesis* **1983**, 1.

A, TBAF (1M solution in THF, 1 mmol) was directly added to the reaction mixture at room temperature, and the mixture was stirred for 1 h at room temperature. The workup similar to that for the second step of method A gave the phenols **4c**,**d** in 73 and 57% overall yields, respectively.

3a: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.49 (s, 2H), 2.73−2.66 (m, 4H), 2.47 (t, J = 6.6 Hz, 2H), 1.61−1.31(m, 16H), 0.97−0.86 (m, 18H), 0.18 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 154.5, 146.5, 146.4, 117.8, 115.9, 95.9, 77.7, 35.1, 34.7, 32.7, 31.8, 31.2, 30.5, 29.3, 25.7, 22.6, 22.0, 19.3, 18.2, 14.1, 13.9, 13.6, −4.3; IR (neat) 2956, 2929, 2858, 1599, 1466, 1308, 0.1253, 1157, 862, 839, 665 cm^{-1}; MS (EI) m/z 428 (M$^+$, 100); HRMS calcd for $C_{28}H_{48}OSi$ 428.3474, found 428.3473. Anal. Calcd for $C_{28}H_{48}OSi$: C, 78,43; H, 11.28. Found: C, 78.34; H, 11.07.

3b: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.65−7.26 (m, 10H), 6.74 (d, J = 2.7 Hz, 1H), 6.72 (d, J = 2.7 Hz, 1H), 2.88 (t, J = 7.7 Hz, 2H), 1.76−1.32 (m, 8H), 1.01 (s, 9H), 0.89 (t, J = 7.0 Hz, 3H), 0.24 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.4, 147.5, 146.1, 141.1, 130.9, 129.5, 128.2, 127.7, 127.5, 127.3, 124.2, 119.5, 118.8, 114.2, 94.9, 88.2, 35.4, 31.8, 30.6, 29.3, 25.7, 22.7, 18.3, 14.1, −4.3; IR (neat) 2954, 2927, 2858, 1593, 1492, 1460, 1441, 1340, 1194, 854, 754 cm^{-1}; MS (E1) m/z 468 (M$^+$ 100); HRMS calcd for $C_{32}H_{40}OSi$ 468.2849, found 468.2851. Anal. Calcd for $C_{32}H_{40}OSi$: C, 81.99; H, 8.60. Found: C, 82.10; H, 8.74.

3c: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.56−7.25 (m, 5H), 6.66 (s, 2H), 2.74 (t, J = 7.7 Hz, 2H), 2.88 (t, J = 6.9 Hz, 2H), 1.69−1.32 (m, 8H), 1.04−0.93 (m, 12H), 0.86 (t, J = 7.2 Hz, 3H), 0.2 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 154.5, 147.2, 145.6, 141.4, 129.4, 127.6, 127.0, 119.3, 118.7, 115.0, 95.7, 78.3, 34.9, 32.7, 30.7, 25.7, 22.6, 21.8, 19.3, 18.3, 14.0, 13.6, −4.3; IR (neat) 3033, 2956, 2929, 1595, 1462, 1340, 1255, 1197, 1182, 875, 835, 698 cm^{-1}; MS (E1) m/z 420 (M$^+$ 100); HRMS calcd for $C_{28}H_{40}$-OSi 420.2849, found 420.2856. Anal. Calcd for $C_{28}H_{40}OSi$: C, 79.94; H, 9.58. Found: C, 79.63; H, 9.80.

3d: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.68−6.96 (m, 15H), 6.90 (s, 2H), 1.01 (s, 9H), 0.26 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.4, 146.5, 140.9, 130.7, 129.6, 128.0, 127.7, 127.4, 123.9, 120.2, 120.1, 113.4, 94.3, 89.1, 25.7, 18.3, −4.2; IR (KBr) 2954, 2929, 2854, 1591, 1494, 1425, 1209, 954, 854, 781, 702, 688 cm^{-1}; MS (E1) m/z 460 (M$^+$ 100); HRMS calcd for $C_{32}H_{32}OSi$ 460.2223; found 460.2223. Anal. Calcd for $C_{32}H_{32}OSi$: C, 83.43; H, 7.00. Found: C, 83.52; H, 7.09.

3e: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.59−7.31 (m, 5H), 6.66 (s, 3H), 2.91 (t, J = 7.8 Hz, 2H), 2.3 (t, J = 6.8 Hz, 2H), 2.33 (s, 3H), 1.54−0.99 (m, 20H), 0.88 (t, J = 6.6 Hz, 3H), 0.24 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 152.9, 145.6, 142.4, 141.6, 129.4, 127.5, 126.7, 125.9, 117.2, 115.0, 94.8, 79.0, 32.3, 31.8, 30.8, 25.8, 23.3, 21.9, 19.3, 18.3, 14.1, 13.6, 12.6, −4.01; IR (neat) 2956, 2929, 2858, 1587, 1463, 1400, 1338, 1259, 1168, 1082, 837, 698 cm^{-1}. Anal. Calcd for $C_{29}H_{42}OSi$: C, 80.12; H, 9.74. Found C, 80.44; H, 9.79. Anal. Calcd for $C_{29}H_{42}$-OSi: C, 80.12; H, 9.74. Found: C, 80.44; H, 9.79.

4a: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.49 (s, 2H), 4.78 (s, 1H), 2.78−2.66 (m, 4H), 2.46 (t, J = 6.7 Hz, 2H), 1.65−1.30 (m, 16H), 0.97−0.87 (m, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 154.3, 147.1, 115.5, 112.9, 95.9, 35.0, 34.7, 32.7, 31.7, 31.2, 30.5, 29.3, 22.6, 22.0, 19.3, 14.1, 14.0, 13.6; IR (neat) 3350, 2956, 2927, 2858, 1106, 1458, 1147, 665 cm^{-1}; MS (E1) m/z 314 (M$^+$ 100); HRMS calcd for $C_{22}H_{34}O$ 314.2609, found 314.2607.

4b: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.56−7.40 (m, 10H), 6.73 (s, 2H), 5.11 (s, 1H), 2.89 (t, J = 6.75 Hz, 2H), 1.79−1.22 (m, 8H), 0.88 (t, J = 6.75 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.2, 148.0, 146.4, 140.8, 130.9, 129.4, 128.2, 127.7, 127.6, 127.5, 124.1, 114.8, 114.1, 113.9, 94.8, 87.9, 35.4, 31.8, 30.6, 29.4, 22.7, 14.1; IR (neat) 3369, 2954, 2927, 2856, 1595, 1493, 1454, 754, 665 cm^{-1}; MS (E1) m/z 354 (M$^+$ 100); HRMS calcd $C_{26}H_{26}O$ 354.1984, found 354.1989.

4c: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.57−7.32 (m, 5H), 6.67 (d, J = 2.5 Hz, 1H), 6.64 (d, J = 2.5 Hz, 1H), 4.68 (s, 1H), 2.78 (t, J = 7.75 Hz, 2H), 2.28 (t, J = 6.75 Hz, 3H); 1.70−1.25 (m, 8H), 0.95 (t, J = 7.25 Hz, 3H), 0.85 (t, J = 7.25 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 154.3, 147.6, 145.9, 141.1, 129.3, 127.5, 127.1, 114.6, 114.5, 113.9, 95.6, 78.0, 34.9, 32.6, 30.6, 22.6, 21.8, 19.2, 14.0, 13.6; IR (neat) 3270, 2956, 2929, 2871, 2860, 1456, 1317, 1174, 771, 665 cm^{-1}; MS (E1) m/z 306 (M$^+$ 100); HRMS calcd for $C_{22}H_{26}O$ 306.1984; found 306.1983.

4d: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.68−6.95 (m, 15H), 6.88 (s, 2H), 5.20 (s, 1H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 155.1, 146.8, 140.7, 130.7, 129.5, 128.0, 127.8, 127.6, 127.5, 123.8, 115.6, 113.1, 94.2, 88.9; IR (KBr) 3340, 1597, 1560, 1490, 1421, 1182, 771, 692 cm^{-1}; MS (E1) m/z 346 (M$^+$ 100); HRMS calcd for $C_{26}H_{18}O$ 346.1358, found 346.1365.

4e: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54−7.30 (m, 5H), 6.61 (s, 1H), 4.78 (s, 1H), 2.90 (t, J = 7.1 Hz, 2H), 2.27 (t, J = 6.8 Hz, 2H), 2.23 (s, 3H), 1.58−1.22 (m, 8H), 0.97 (t, J = 6.8 Hz, 3H), 0.85 (t, J = 7.53 Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 152.8, 145.8, 142.9, 141.2, 129.3, 127.5, 126.9, 121.0, 114.4, 113.6, 94.5, 78.2, 32.0, 31.8, 30.7, 23.2, 21.8, 19.2, 14.0, 13.6, 11.5; IR (KBr) 3468, 2958, 2931, 2872, 2858, 1593, 1475, 1407, 1251, 702 cm^{-1}; MS (E1) m/z 320 (M$^+$ 100); HRMS calcd for $C_{23}H_{28}O$ 320.2140, found 320.2146. Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 85.82; H, 8.72.

8a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28 (d, J = 9.0 Hz, 1H), 6.70 (d, J = 2.58 Hz, 1H), 6.64 (dd, J = 9.0,2.58 Hz, 1H), 3.78 (s, 3H), 2.72 (t, J = 7.77 Hz, 2H), 2.43 (t, J = 6.75 Hz, 2H), 1.65−1.32 (m, 8H), 0.97−0.91 (m, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 158.8, 146.4, 133.2, 115.8, 114.3, 110.9, 91.9, 79.1, 55.1, 34.6, 32.8, 31.1, 22.6, 22.0, 19.2, 14.0, 13.6; IR (neat) 2956, 1604, 1494, 1465, 1298, 1161, 1039, 808 cm^{-1}; MS (E1) m/z 244 (M$^+$ 100); HRMS calcd for $C_{17}H_{24}O$ 244.1827, found 244.1830. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.26; H, 9.88.

8b: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.69−7.65, 7.49−7.23 (m, 10H), 7.58 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 2.6 Hz, 1H), 6.89 (dd, J = 8.5, 2.6 Hz1H), 3.86 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 159.6, 145.5, 140.5, 134.2, 131.0, 129.2, 128.1, 127.8, 127.6, 127.5, 123.7, 114.9, 113.9, 112.9, 90.8, 89.4, 55.3; IR (KBr) 3059, 2964, 2837, 1606, 1595, 1554, 1491, 1479, 1415, 1299, 1213, 1176, 1029, 891, 760, 698 cm^{-1}. Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.36; H, 5.82. Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.36; H, 5.82.

8c: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.45 (d, J = 8.5 Hz, 1H), 7.01 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.5, 2.6 Hz, 1H), 3.79 (s, 3H), 0.38 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 158.9, 144.7, 134.6, 120.2, 113.4, 106.9, 95.3, 55.2, 0.0, −1.0; IR (neat) 2956, 2150, 1589, 1556, 1477, 1463, 1286, 1182, 1139, 893, 840 cm^{-1}; MS (E1) m/z 276 (M$^+$ 100); HRMS calcd for $C_{15}H_{24}OSi_2$ 276.141 06, found 276.1375. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.74. Found: C, 65.29; H, 8.54.

11a: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.24 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 6.57 (dd, J = 8.1, 2.7 Hz, 1H), 4.83 (s, 1H), 2.70 (t, J = 7.5 Hz, 2H), 1.65−1.36 (m, 8H), 0.97−0.91 (m, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.8, 146.7, 133.4, 115.9, 115.5, 112.6, 92.0, 78.9, 34.4, 32.6, 31.1, 22.6, 22.0, 19.2, 14.0, 13.7; IR (neat) 3370, 2956, 2929, 2860, 1654, 1606, 1577, 1286, 1230 cm^{-1}; MS (EI) m/z 230 (M$^+$, 100); HRMS calcd for $C_{16}H_{22}O$ 230.1670, found 230.1675.

11b: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.55−7.24 (m, 11H), 6.89 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.4, 2.6 Hz, 1H), 5.12 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.6, 145.7, 140.1, 134.5, 131.1, 129.2, 128.2, 127.9, 127.7, 127.6, 116.4, 114.4, 114.2, 90.8, 89.3; IR (neat) 3388, 1604, 1595, 1492, 1197, 1114, 908, 732 cm^{-1}; MS (EI) m/z 270 (M$^+$, 100); HRMS calcd for $C_{20}H_{14}O$ 270.1044, found 270.1056.

12: ^{1}H NMR ($CDCl_3$,300 MHz) δ 7.47 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 2.8 Hz, 1H), 6.81 (dd, J = 8.4, 2.8 Hz, 1H), 3.82 (s, 3H), 3.13 (s, 1H), 0.37 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 159.0, 144.8, 134.9, 120.1, 119.2, 113.4, 85.1, 78.7, 55.2, −1.1; IR (neat) 3309, 2956, 2100, 1589, 1463, 1288, 1234, 1037, 883, 839 cm^{-1}; MS (E1) m/z 204 (M$^+$ 100); HRMS calcd for $C_{12}H_{16}$-OSi 204.0971, found 204.0983.

Supporting Information Available: ^{1}H NMR spectra of all new compounds (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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