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Diels−Alder Reactions of Cyclopentadienones with Aryl Alkynes To Form Biaryl Compounds

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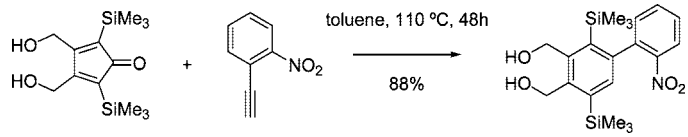

Diels−Alder reactions of cyclopentadienones, to afford substituted biaryls, were studied using an expanded substrate base. Electron-withdrawing groups on the aryl alkyne dienophile facilitated the reaction, and these substrates gave better yields than those with electron-donating substituents. Steric effects were also found to be important, and *o*,*o*′-dimethylphenylacetylene gave much poorer yield of biaryl product.

Introduction

Biaryls are important structural units in many biologically active compounds,[1] as well as ligands used in asymmetric catalysis.[2] Palladium-mediated cross-coupling reactions for the synthesis of biaryl structures, such as Negishi, Stille, and Suzuki reactions, have been extensively used in synthetic chemistry,[1,3] but these methods do have limitations, such as lack of chemoselectivity when using substrates with more than one halogen substituent and steric retardation when using hindered arenes. An alternative approach to these direct couplings is the use of Diels−Alder cycloadditions, which are well documented for their generality and broad applicability, and syntheses of biaryl natural products and ligands using this approach have grown steadily.[4]

Reaction of a cyclopentadienone derivative with a suitably functionalized alkyne is well known to generate aromatic molecules by cycloaddition followed by cheletropic extrusion of carbon monoxide.[5] A previous communication from our laboratory[6] reported preliminary results showing that monocyclic cyclopentadienones, which are obtained from silicon-tethered $Fe(CO)_5$-promoted cyclocarbonylation of alkynes,[7] are good candidates for preparing aromatic and biaryl structures via Diels−Alder-type reactions and in situ thermal decarbonylation. The biaryl structures formed by this methodology could find use as intermediates in the synthesis of complex molecules. This paper reports further optimization of the cycloaddition reaction and expansion of the substrate base.

Results and Discussion

In our previous communication, Diels−Alder reaction of cyclopentadienone **1** with aryl alkyne **2** (eq 1) at 140 °C in mesitylene afforded product **3** in 75% yield after 8 h. In order to further optimize the procedure, this reaction was chosen for a survey of different solvents and temperatures. When the reaction was carried out at higher temperature (140 or 210 °C), two side products were isolated in about 10% yield each. Mass spectrometry indicated that one of the side products likely has the structure **4a** (HRMS (FAB) calcd for MH^+ ($C_{24}H_{29}O_4SSi$) 441.1556, found, 441.1573), the result of partial desilylation. The other product is most likely **4b** (HRMS (FAB) calcd for MH^+ ($C_{21}H_{21}O_4S$) 369.1160, found, 369.1169), corresponding

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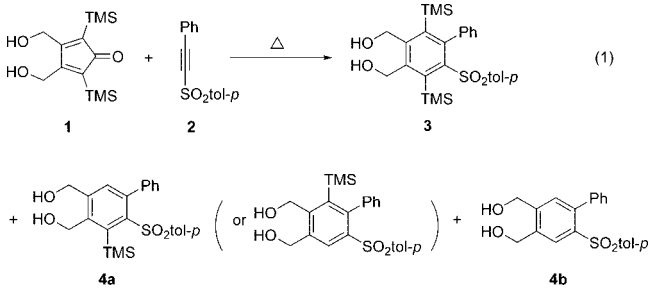
to loss of both trimethylsilyl groups. We have not determined the regiochemistry of compound **4a**, and we do not speculate here on the mechanism of the (thermal) desilylation reaction. In order to avoid desilylation, lower temperature was tested. When the reaction was carried out in toluene at 110 °C, product **3** was obtained in 89% yield without any desilylated product after 24 h. It should be noted that the trimethylsilyl groups are a necessary feature for these cyclopentadienones as they (sterically) prevent Diels−Alder dimerization.



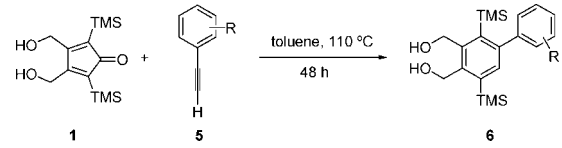
During this study, we also observed that a number of internal alkynes afforded very poor yield of biaryl products, even at higher temperature (not reported here), except for alkyne **2**. Consequently, we have investigated Diels−Alder reactions of cyclopentadienone **1** with terminal aryl alkynes, and electronic and steric effects of a substituted aryl group on this reaction were examined. The results are collected in Table 1.

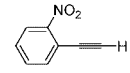
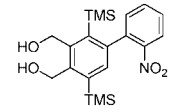
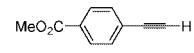
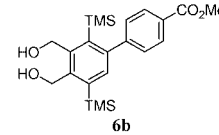
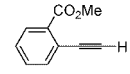
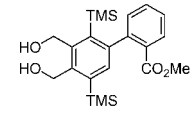
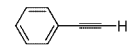
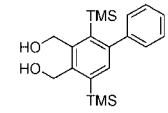
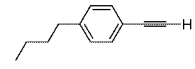
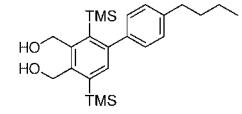
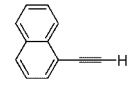
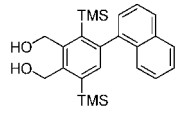
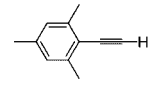
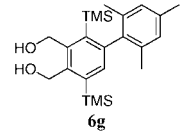
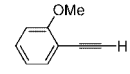
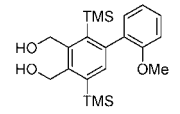
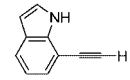
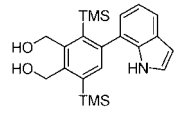
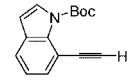
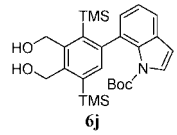
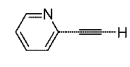
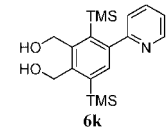
Reaction time is also important for this Diels−Alder reaction. It was found that long reaction time (72 h) caused desilylation for some products, while most reactions were not complete after 24 h. After 48 h, most substrates gave highest yields, and cyclopentadienone **1** was consumed completely. However, 2-ethynyl pyridine (entry 11) gave best results after 36 h (40% yield), wherein after 48 h, 20% desilylated Diels−Alder product was obtained in addition to 28% expected product **6k**.

Substrates with strong electron-withdrawing groups on the aryl ring afforded biaryl products in better yields (entries 1−3). The best result was obtained for 1-ethynyl-2-nitrobenzene (entry 1), which gives good yield despite the possibility of steric hindrance from the nitro group. When the substrate has a weaker or no electron-withdrawing group on the aryl ring, such as phenyl (entries 4−7), the yields are from low to moderate. 2-Ethynylanisole has an electron-donating group on the aryl ring and afforded the biaryl product in low yield (entry 8). These results indicate that electron-withdrawing groups on the aromatic ring do have a significant effect on the dienophile and promote the Diels−Alder reaction. Of great interest is the construction of biaryls containing substituents at *ortho* and *ortho′* positions, for which purpose the reaction between **1** and **5g** was studied (entry 7). The biaryl product was obtained in only 25% yield, appreciably lower than for the unsubstituted ethynylbenzene (entry 4), as a result of steric hindrance. However, we have not investigated the use of substrates having electron-withdrawing groups at the *ortho* and *ortho′* positions.

Heterocyclic substrates are of interest, which is one of the reasons substrates **5i**, **5j**, and **5k** were examined. Biaryl products related to **6i** and **6j** may be useful for synthesis of more complex natural products, such as hippadine (**11**).[8] It should be noted that an approach to **11** using this cycloaddition chemistry would require an appropriate 3,4-dialkoxycyclopentadienone as the Diels−Alder diene, and a dienophile related to **5** with, e.g., a nitrile attached to the alkyne. Alternatively, use of cyclopen-

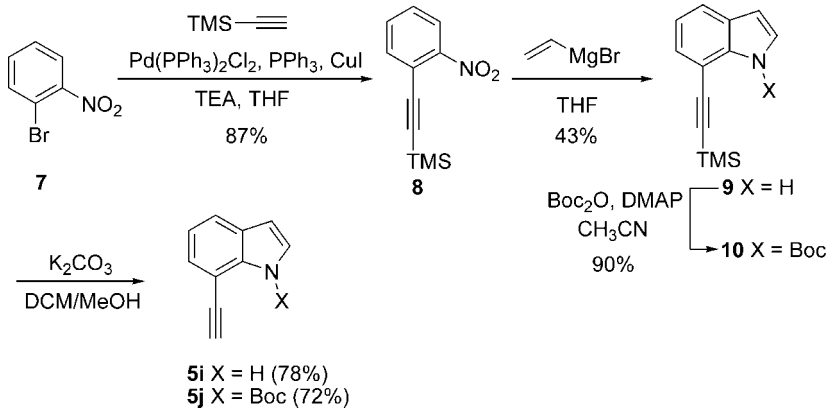
TABLE 1. Diels−Alder Reaction of Cyclopentadienone 1 with Aryl Alkynes To Form Biaryl Compounds



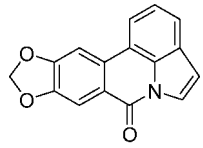
entry	aryl alkyne	product	yield
1	 **5a**	 **6a**	88%
2	 **5b**	 **6b**	62%
3	 **5c**	 **6c**	65%
4	 **5d**	 **6d**	50%
5	 **5e**	 **6e**	32%
6	 **5f**	 **6f**	58%
7	 **5g**	 **6g**	25%
8	 **5h**	 **6h**	35%
9	 **5i**	 **6i**	40%
10	 **5j**	 **6j**	38%
11	 **5k**	 **6k**	28% 40%[a]

[a] Reaction time: 36 h.

SCHEME 1



tadienone **1** would require additional steps to convert the hydroxymethyl side chains in the biaryl product to phenolic hydroxyls. Substrates **5i** and **5j** were made through Sonogashira coupling[9] and Bartoli reaction (Scheme 1).[10] Even though substrate **5j** has bulky a Boc group on the side ring, reactions of cyclopentadienone **1** with **5i** and **5j** afforded similar yields of biaryl products **6i** and **6j**.



Hippadine (**11**)

Conclusions

In summary, we have demonstrated that cyclopentadienones are potentially useful intermediates for the construction of multisubstituted biaryl compounds via Diels−Alder reactions with aryl alkynes. The electronic and steric nature of the dienophile have significant effects on this Diels−Alder reaction, and the use of *o*,*o*′-dialkylphenylacetylenes remains a significant challenge.

Experimental Section

Alkynes **5a**−**h** are known compounds, and their preparation is not described here.

7-(2-(Trimethylsilyl)ethynyl)-1*H*-indole (9). Following the procedure described by Bartoli et al.,[10] trimethyl(2-(2-nitrophenyl)-ethynyl)silane (**8**) (0.40 g, 1.8 mmol) was dissolved in THF (10 mL) and cooled to −42 °C. To this solution was added dropwise vinylmagnesium bromide (1.0 M solution in THF, 5.4 mL, 5.4 mmol). After being stirred at −42 °C for 3 h, the reaction was quenched with 2.5 mL of satd aq NH_4Cl solution. The mixture was extracted with ethyl acetate (10 mL × 3), and the combined ethyl acetate phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residual liquid was purified by flash chromatography (Hex/EA 95:5) to afford **9** as an oil (0.13 g, 35%): TLC R_f = 0.75 (Hex/EA 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, br, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.03 (dd, J = 7.4 Hz, 1H), 6.94 (t, J = 3.0 Hz, 1H), 6.75 (dd, J = 8.0, 7.4 Hz, 1H), 6.27 (dd, J = 3.0, 2.0 Hz, 1H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 127.3, 125.7, 124.3, 121.8, 119.6, 105.9, 103.3, 101.3, 98.4, 0.16; HRMS (FAB) calcd for M^+ ($C_{13}H_{15}NSi$) 213.0974, found, 213.0980.

***tert*-Butyl 7-(2-(Trimethylsilyl)ethynyl)-1*H*-indole-1-carboxylate (10).** To a 25 mL round-bottom flask were added 7-(2-(trimethylsilyl)ethynyl)-1*H*-indole **(9)** (0.106 g, 0.5 mmol), DMAP (0.012 g, 0.1 mmol), di-*tert*-butyl dicarbonate (0.11 g, 0.5 mmol), and acetonitrile (5 mL). After being stirred at room temperature for 18 h, the resulting solution was concentrated in vacuo. The product was purified by flash chromatography (Hex/EA 98:2) and obtained as an oil (0.14 g, 92%): TLC R_f = 0.75 (Hex/EA 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.50 (3H), 7.17 (t, J = 7.6 Hz, 1H), 6.54 (dd, J = 3.6 Hz, 1H), 1.66 (s, 9H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 134.2, 131.9, 131.4, 128.1, 122.5, 121.7, 110.5, 106.9, 103.1, 99.7, 83.5, 28.1, 0.1; HRMS (FAB) calcd for M^+ ($C_{18}H_{23}NO_2Si$) 313.1498, found 313.1492.

7-Ethynyl-1*H*-indole (5i). 7-(2-(Trimethylsilyl)ethynyl)-1*H*-indole (**9**) (0.106 g, 0.5 mmol) was dissolved in 6 mL of methanol/dichloromethane 2:1. To this solution was added K_2CO_3 (0.55 g, 4 mmol). After 2 h of stirring at room temperature, the reaction mixture was diluted with dichloromethane (20 mL), washed with water, dried over $MgSO_4$, concentrated in vacuo, and purified by flash chromatography to give **5i** as a brown solid (0.60 g, 85%): mp 68.5−70 °C; TLC R_f = 0.50 (Hex/EA 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (br s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.26 (dd, J = 3.2, 2.2 Hz, 1H), 7.10 (dd, J = 7.8, 7.2 Hz, 1H), 6.60 (dd, J = 3.2, 2.2 Hz, 1H), 3.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 127.4, 125.9, 124.4, 122.0, 119.7, 104.8, 103.3, 81.1, 80.3; HRMS (FAB) calcd for MH^+ ($C_{10}H_8N$) 142.0656, found 142.0662.

***tert*-Butyl 7-Ethynyl-1*H*-indole-1-carboxylate (5j).** *tert*-Butyl 7-(2-(trimethylsilyl)ethynyl)-1*H*-indole-1-carboxylate (**10**) (0.156 g, 0.5 mmol) was dissolved in 6 mL of methanol/dichloromethane 2:1. The same procedure as for the preparation of **5i** was carried out to afford **5j** as a light brown solid (0.096 g, 80%): mp 65.5−68 °C; TLC R_f = 0.65 (Hex/EA 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.52 (3H), 7.19 (tr, J = 7.6 Hz, 1H), 6.56 (d, J = 3.6 Hz, 1H), 3.42 (s, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 134.4, 132.0, 131.4, 128.3, 122.6, 122.1, 109.5, 106.9, 84.0, 82.6, 82.1, 28.0; HRMS (FAB) calcd for M^+ − H ($C_{15}H_{14}NO_2$) 240.1025, found 240.1009.

General Procedures for Diels−Alder Reaction of Cyclopentadienone 1 with Aryl Alkynes (3 and 6a−k Were Made via This Method). Cyclopentadienone **1** (6 mg, 0.021 mmol) and the appropriate aryl alkyne (0.06 mmol) were dissolved in toluene (1 mL). The solution was degassed by bubbling with Ar for 30 min and then stirred at 110 °C under Ar atmosphere for 48 h. The

(8) For syntheses of hippadine and related alkaloids, as well as references to biological activity, see: (a) Miki, Y.; Shirokoshi, H.; Matsushita, K. *Tetrahedron Lett.* **1999**, *40*, 4347. (b) Padwa, A.; Brodney, M. A.; Liu, B.; Satake, K.; Wu, T. *J. Org. Chem.* **1999**, *64*, 3595. (c) Boger, D. L.; Wolkenberg, S. E. *J. Org. Chem.* **2000**, *65*, 9120. (d) Stark, L. M.; Lin, X.-F.; Flippin, L. A. *J. Org. Chem.* **2000**, *65*, 3227. (e) Wolkenberg, S. E.; Boger, D. L. *J. Org. Chem.* **2002**, *67*, 7361. (f) Knölker, H.-J.; Filali, S. *Synlett* **2003**, 1752.

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resulting solution was concentrated in vacuo, and the product was purified by flash chromatography (Hex/EA 80:20).

Compound 6a. The product was obtained as a light yellow solid (0.0074 g, 88%): mp 151−153 °C; TLC R_f = 0.30 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 1H), 7.60−7.49 (2H), 7.27 (d, J = 7.4 Hz, 1H), 7.07 (s, 1H), 5.04 (s, 2H), 4.93 (ABq, J = 12.4 Hz, 2H), 3.14 (br s, 2H), 0.33 (s, 9H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 146.2, 144.8, 143.7, 141.8, 140.1, 139.7, 135.0, 132.9, 131.9, 128.4, 124.0, 63.2, 62.9, 2.5, 0.5; HRMS (FAB) calcd for $M^+ - OH$ ($C_{20}H_{28}O_3NSi_2$) 386.1608, found 386.1572.

Compound 6b. The product was obtained as a pale yellow solid (0.0054 g, 62%): mp 156−158 °C; TLC R_f = 0.30 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.31 (s, 1H), 5.02 (s, 2H), 4.94 (s, 2H), 3,95 (s, 3H), 0.38 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 150.0, 148.3, 146.4, 144.6, 141.9, 140.3, 136.3, 129.6, 129.3, 128.9, 63.3, 63.1, 52.2, 3.0, 0.6; HRMS (FAB) calcd for MH^+($C_{22}H_{33}O_4Si_2$) 417.1917, found 417.1914.

Compound 6c. The product was obtained as a pale yellow solid (0.0056 g, 65%): mp 160−161 °C; TLC R_f = 0.30 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 7.6, 1.6 Hz, 1H), 7.50−7.40 (m, 2H), 7.18 (dd, J = 7.6, 1.6 Hz, 1H), 7.10 (s, 1H), 5.03 (s, 2H), 4.92 (ABq, J = 12.4 Hz, 2H), 3.62 (s, 3H), 0.33 (s, 9H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 147.9, 145.8, 145.7, 143.9, 141.0, 139.6, 135.8, 131.8, 130.8, 130, 6, 129.7, 127.3, 63.3, 63.1, 51.9, 2.5, 0.6; HRMS (FAB) calcd for $M^+ -$ OH ($C_{22}H_{31}O_3Si_2$) 399.1812, found 399.1796.

Compound 6d. The product was obtained as a light yellow solid (0.0037 g, 50%): mp 80−81 °C; TLC R_f = 0.35 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.36 (4H), 7.28−7.26 (2H), 5.02 (s, 2H), 4.94 (s, 2H), 0.38 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 146.2, 145.3, 144.1, 141.7, 140.4, 136.7, 129.5, 128.0, 127.2, 63.4, 63.1, 2.9, 0.6; HRMS (FAB) calcd for $M^+ -$ OH ($C_{20}H_{29}OSi_2$) 341.1757, found 341.1748.

Compound 6e. The product was obtained as a white solid (0.0029 g, 32%): mp 142−145 °C; TLC R_f = 0.40 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H), 7.18−7.17 (4H), 5.01 (s, 2H), 4.93 (s, 2H), 3.14 (br, s, 2H), 2.63 (t, J = 7.6 Hz, 2H), 1.64−1.56 (2H), 1.19−1.14 (2H), 0.95 (t, J = 7.2 Hz, 3H), 0.37 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 146.2, 143.9, 142.6, 142.0, 141.6, 140.5, 136.7, 129.3, 128.0, 63.4, 63.1, 35.3, 33.7, 22.3, 14.0, 2.9. 0.6; HRMS (FAB) calcd for $M^+ - CH_5O$ ($C_{23}H_{33}OSi_2$) 381.2071, found 381.2072.

Compound 6f. The product was obtained as a white solid (0.0047 g, 58%): TLC R_f = 0.45 (Hex/EA 2:1); mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.85 (2H), 7.56 (d, J = 8.4 Hz, 1H), 7.50−7.46 (2H), 7.41−7.37 (2H), 7.28−7.25 (1H), 5.08 (s, 2H), 5.00 (s, 2H), 0.35 (s, 9H), −0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 145.9, 144.4, 142.7, 141.6, 141.5, 137.6, 133.4, 133.2, 128.1, 127.6, 127.3, 126.6, 126.0, 125.8, 125.0, 63.3, 63.1, 2.5, 0.7; HRMS (FAB) calcd for $M^+ -$ OH ($C_{24}H_{31}OSi_2$) 391.1913, found 391.1846.

Compound 6g. The product was obtained as a white solid (0.0021 g, 25%): mp 155−156 °C; TLC R_f = 0.40 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.87 (s, 2H), 5.04 (s, 2H), 4.94 (s, 2H), 2.33 (s, 3H), 1.89 (s, 6H), 0.34 (s, 9H), −0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ147.0, 146.0, 143.7, 142.4, 141.3, 140.0, 136.5, 136.4, 136.0, 127.8, 63.4, 62.9, 21.1, 21.0, 2.3, 0.8; HRMS (FAB) calcd for $M^+ -$ OH ($C_{23}H_{35}OSi_2$) 383.2227, found 383.2216.

Compound 6h. The product was obtained as a white solid (0.0029 g, 38%): mp 123−126 °C; TLC R_f = 0.33 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.31 (2H), 7.06 (d, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.01 (s, 2H), 4.93 (s, 2H), 3.76 (s, 3H), 0.38 (s, 9H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 145.7, 145.1, 144.1, 141.2, 137.5, 133.8, 131.6, 128.8, 120.1, 110.4, 109.8, 63.3, 63.2, 55.1, 2.4, 0.7; HRMS (FAB) calcd for $M^+ - CH_3$ ($C_{20}H_{29}O_3Si_2$) 373.1656, found 373.1659.

Compound 6i. The product was obtained as a white solid (0.0033 g, 40%): TLC R_f = 0.30 (Hex/EA 2:1); mp 175−177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (br, 1H), 7.64 (d, J = 8 Hz, 1H), 7.50 (s, 1H), 7.19−7.17 (t, J = 3.0 Hz, 1H), 7.14 (dd, J = 8, 7.0 Hz, 1H), 6.98 (d, J = 7.0 Hz, 1H), 6.61 (dd, J = 3.0, 2 Hz, 1H), 5.03 (s, 2H), 4.97 (q, J = 10.4 Hz, 2H), 0.37 (s, 9H), −0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 145.0, 144.5, 142.3, 141.6, 136.8, 135.4, 128.6, 127.6, 124.2, 122.8, 119.9, 119.7, 103.8, 63.2, 63.1, 2.4, 0.7; HRMS (FAB) calcd for M^+ ($C_{22}H_{31}NO_2Si_2$) 397.1893, found 397.1884.

Compound 6j. The product was obtained as a white solid (0.0040 g, 38%): mp 165−166 °C; TLC R_f = 0.48 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.53 (2H), 7.23−7.19 (2H), 6.99 (dd, J = 7.6, 1.2 Hz, 1H), 6.61 (d, J = 3.6 Hz, 1H), 5.05 (s, 2H), 4.92 (d, J = 1.2 Hz, 2H), 1.30 (s, 9H), 0.30 (s, 9H), −0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 148.2, 145.9, 143.4, 140.5, 139.7, 135.4, 132.2, 131.9, 128.5, 128.1, 122.1, 120.0, 106.7, 99.5, 83.0, 63.4, 63.3, 27.8, 2.8, 0.6; HRMS (FAB) calcd for $M^+ -$ OH ($C_{27}H_{38}NO_3Si_2$) 480.2391, found 480.2371.

Compound 6k. The product was obtained as a white solid (0.0021 g, 28%): mp 159−161 °C; TLC R_f = 0.33 (Hex/EA 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.4 Hz, 1H), 7.76 (dt, J = 8.0, 2.0 Hz, 1H), 7.47−7.45 (m, 2H), 7.30−7.27 (m, 1H), 4.97 (s, 2H), 4.86 (s, 2H), 3.58 (br, 2H), 0.37 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 148.7, 147.9, 146.5, 145.4, 141.8, 141.0, 136.5, 135.9, 123.7, 122.1, 63.4, 63.0, 2.5, 0.5; HRMS (FAB) calcd for MH^+ ($C_{19}H_{29}NO_2Si_2$) 360.1815, found, 360.1824.

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Supporting Information Available: Copies of NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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