Effective Synthesis of Aryl Ethers and Coumaranones Employing the Palladium-Catalyzed Enyne−Diyne [4 + 2] Cycloaddition Protocol

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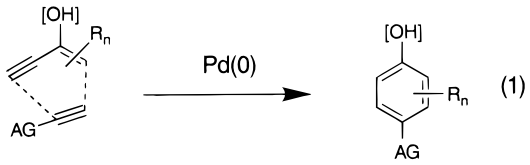
Alkyl-, alkoxy-, and aryloxy-substituted conjugated enynes **1** in the presence of $Pd(PPh_3)_4$ catalyst smoothly underwent the regiospecific [4 + 2] cycloaddition reaction with conjugated alkyl- and alkoxy-substituted symmetric diynes **2** to give multisubstituted aryl ethers **3** in good to high yields. Benzannulation of enynes **1d**−**g** with unsymmetric diyne **6**, possessing alkyl and alkoxy groups at acetylenic terminii, in most cases produced an aromatic product **8** with an alkoxy group of diyne attached to the ethynyl moiety of the aromatic product. Remarkably, alkoxy-substituted diynes **2c** and **6** underwent the benzannulation reaction with **1** at an unusually low temperature of 0 °C! One-pot consecutive benzannulation of alkyl-substituted enynes **1d**,**e** and alkoxy-substituted enynes **1f**,**g** with alkoxy-substituted diynes **2c** and **6** followed by protonolysis with TsOH afforded coumaranones **9a**−**c** and **10** in reasonable to high overall yields.

Aryl ethers are ubiquitous structural units in biologically important molecules and thus are of great importance for synthetic organic chemistry. Generally, aryl ethers (aryl−OR) are prepared either through aryl carbon−OR or through aryl oxygen−R bond-forming reactions: aromatic compounds are used as precursors in both methods.[1] Accordingly, development of complementary methods for the preparation of aryl ethers from aliphatic precursors should be highly desired. We have recently developed an effective methodology for the synthesis of polysubstituted benzenes[2] and phenols[3] via the palladium-catalyzed enyne−diyne [4 + 2] benzannulation motif (eq 1).[4] Herein we report an extension of this



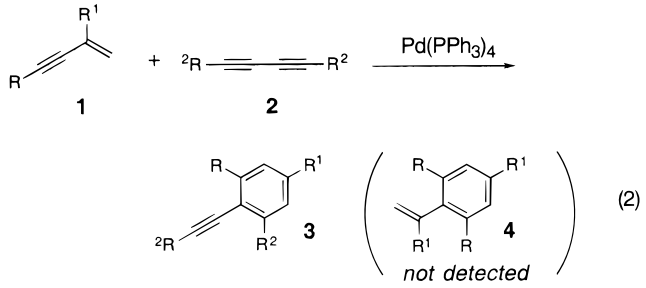
(1)

AG= activating group (alkynyl or alkenyl)

cycloaddition methodology to the regiospecific synthesis of polysubstituted aryl ethers,[5] and to the one-pot preparation of coumaranones via the benzannulation−cyclization sequence.

Results and Discussion

Synthesis of Aryl Ethers. To apply the aforementioned cycloaddition methodology (eq 1)[2,3] for the preparation of aryl ethers, we tested the palladium-catalyzed benzannulation of the alkoxy-substituted enynes **1a**−**c** with dodecadiyne **2a** and diphenyldiyne **2b** (eq 2, Table



(2)

1). We found that the standard conditions for our benzannulation reaction ($Pd(PPh_3)_4$ (5 mol %), 0.5M in THF)[2,3] were effective for the preparation of the aryl ethers **3**. Thus, the monosubstituted enyne **1a** smoothly reacted at 65 °C with **2a** and **2b** to give the trisubstituted diaryl ethers **3a** and **3b** in 56 and 65% isolated yields, respectively (eq 2, Table 1, entries 1 and 2). As expected,[2b] the cycloaddition of the disubstituted enynes **1b** and **1c** with diynes **2a**,**b** required more drastic reaction conditions in comparison with the reaction of monosubstituted

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(1) For a review on the aryl C−O bond-forming reactions, see: (a) 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 the aryl ether forming reactions using OH^- and OR^- as nucleophiles in aromatic substitution, see: (b) In *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 aryl ethers and phenols from aryl halides, see: (c) Mann, G.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 5413. (d) Pews, R. G.; Lysenko, Z.; Vosejpka, P. C. *J. Org. Chem.* **1997**, *62*, 8255. (e) Nayak, M. K.; Chakraborti, A. K. *Tetrahedron Lett.* **1997**, *38*, 8749.

(2) (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. (c) Gevorgyan, V.; Takeda, A.; Homma, M.; Sadayori, N.; Radhakrishnan, U.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 6391.

(3) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 1244.

(4) For the construction of alkoxybenzene derivatives via the ruthenium-catalyzed intramolecular cyclization of dienylalkynes, see: Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319.

(5) For the synthesis of several aryl ethers as precoursors for the preparation of phenols via the palladium-catalyzed enyne−diyne [4 + 2] cycloaddition pathway, see: ref 3.

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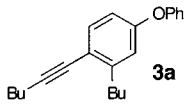
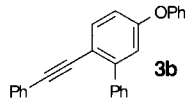
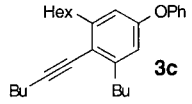
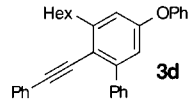
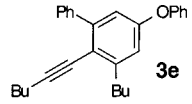
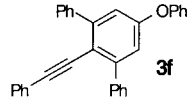
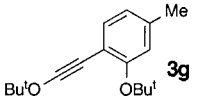
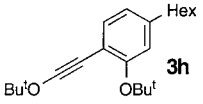
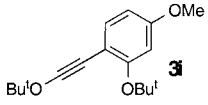
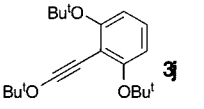
Table 1. Synthesis of Aryl Ethers 3 via Palladium-Catalyzed [4 + 2] Cycloaddition of Conjugated Enynes 1 with Symmetric Diynes 2

entry	enyne 1 R	enyne 1 R^1	diyne 2 R^2	time/temp (h/°C)	product 3	isolated yield (%)
1	H	OPh (**1a**)	Bu (**2a**)	8/65	 **3a**	56
2	H	OPh (**1a**)	Ph (**2b**)	24/65	 **3b**	65
3	Hex	OPh (**1b**)	Bu (**2a**)	24/100	 **3c**	83
4	Hex	OPh (**1b**)	Ph (**2b**)	48/100	 **3d**	73
5	Ph	OPh (**1c**)	Bu (**2a**)	24/100	 **3e**	82
6	Ph	OPh (**1c**)	Ph (**2b**)	48/100	 **3f**	61
7	H	Me (**1d**)	^{t}BuO (**2c**)	48/0	 **3g**	91
8	H	Hex (**1e**)	^{t}BuO (**2c**)	48/0	 **3h**	81
9	H	OMe (**1f**)	^{t}BuO (**2c**)	48/0	 **3i**	78
10	^{t}BuO	H (**1g**)	^{t}BuO (**2c**)	48/0	 **3j**	66

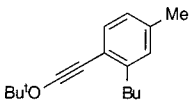
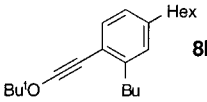
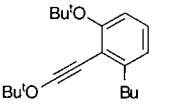
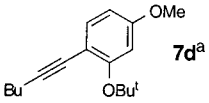
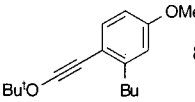
enyne **1a** with **2a**,**b**. Hence, heating the reaction mixtures for 1−2 days at 100 °C was effective for the synthesis of the tetrasubstituted diaryl ethers **3c**−**f** in rather high yields (entries 3−6).

Although the dialkoxysubstituted diyne **2c** appeared to be unstable under the standard benzannulation conditions,[3] surprisingly it underwent the benzannulation reaction with the conjugated enynes **1d**−**g** under a remarkably low temperature of 0 °C! Thus, the benzannulation of **2c** with the 2-substituted alkyl enynes **1d**,**e** and alkoxy enyne **1f** under these mild conditions produced the 1,2,4-trisubstituted aryl ethers **3g**, **3h**, and **3i** in 91, 81, and 78% yields, respectively (entries 7−9). The cycloaddition of **2c** with the 1-susbstituted enyne **1g** gave the 1,2,3-trisubstituted arene **3j** in 66% isolated yield (entry 10).

It is worth noting that in all cases tested the enyne−diyne [4 + 2] cycloaddition reactions proceeded not only in the *regiospecific* fashion, producing the *single regioisomers* of the aromatic products **3**, but also in a highly *chemoselective* manner, affording exclusively the *cross*-benzannulation products **3**, with no traces of the *homo*dimerization products **4** being produced (eq 2).[6] However, the control experiments revealed that the alkoxy-substituted enyne **1g**, in the absence of diyne component, smoothly underwent the [4 + 2] *homodimerization* reac-

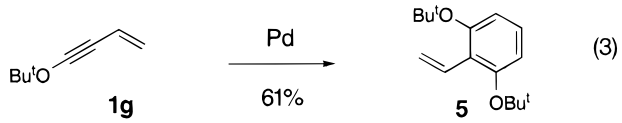
(6) We have reported that the *chemoselectivity* of benzannulation of monosubstituted enynes[2a,c,3] with diynes was not perfect; in most cases the enyne−diyne *cross*-benzannulation products were contaminated with trace to notable amounts of enyne-enyne *homo*-dimerization products.[2a,c,3]

Table 2. Palladium-Catalyzed [4 + 2] Cycloaddition of Conjugated Enynes 1 with Unsymmetric Diyne 6

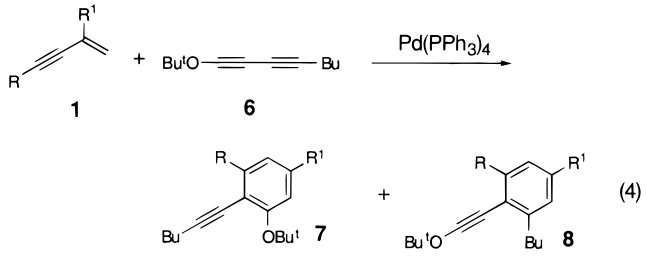
entry	enyne **1** R	R¹	product **7** (yield, %)[a]	product **8** (isolated yield, %)
1	H	Me(**1d**)	**7a** (-)	 **8a** (72)
2	H	Hex(**1e**)	**7b** (-)	 **8b** (70)
3	^{t}BuO	H (**1g**)	**7c** (-)	 **8c** (52)
4	H	OMe (**1f**)	 **7d**[a]	 **8d**[a]

[a] Isolated in 70% combined yield, as 18:82 nonseparable mixture of **7d** and **8d**. The ratio of **7d:8d** was determined by ^{1}H NMR analysis.

tion to afford the vinyl resorcinol derivative **5** in 61% isolated yield (eq 3).[7]

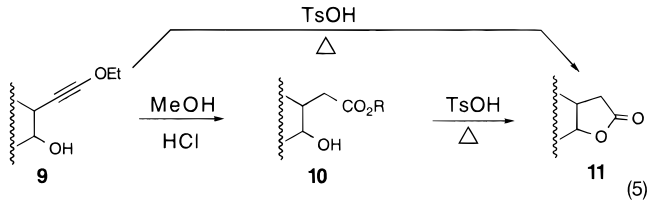


Next, we examined the palladium-catalyzed cycloaddition of **1** with the unsymmetric diyne **6** (eq 4). Two



different alkyne moieties of **6** could act as enynophiles in the reaction with **1**, and accordingly two regioisomeric products could be expected; the desired aryl ether **7** and alkoxy aryl alkyne **8** (eq 4). We found that the alkyl-substituted enynes **1d** and **1e** completely preferred the alkyl-substituted triple bond of **6**, producing the corresponding alkoxy-substituted aryl alkynes **8a** and **8b** in 72 and 70% yields, respectively, with none of the desired aryl ethers **7a** and **7b** being produced (Table 2, entries 1 and 2). The aryl ether **8c**, however, was obtained as a single reaction product in 52% yield by the reaction between **6** and alkoxy-substituted enyne **1g** (entry 3). The benzannulation reaction of **1f** with **6**, in contrast to that of **1d**,**e**,**g**, was not perfectly regioselective. Accordingly, the major aromatic acetylenic ether **8d** (57%) was contaminated with a notable amount of isomeric dialkoxybenzene **7d** (13%) (Table 2, entry 4). It should be pointed out that the all above-mentioned [4 + 2] benzannulation reactions (Tables 1, 2) are truly palladium-catalyzed processes, since the test experiments ruled out any background reaction catalyzed by PPh_3.

One-Pot Synthesis of Coumaranones via the Benzannulation−Lactonization Sequence. Danishefsky and co-workers demonstrated that β-hydroxy alkynyl ethers are suitable precursors for the synthesis of lactones (eq 5).[8a] Thus, lactone **11** could be directly obtained from the alcohol **9** by refluxing it in the presence of TsOH, or by the stepwise alcoholysis−lactonization sequence: **9** → **10** → **11** (eq 5).[8a] Later, Miller and Matthews utilized



thioalkyne precursors in the similar protocol.[8b]

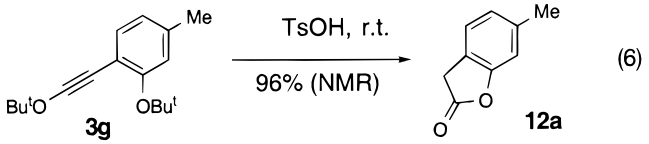
The presence of a masked hydroxyl group at the *ortho*-position to the acetylenic ether moiety of the aromatic products **3g**−**j** (Table 1, entries 7−10) and **8c** (Table 2, entry 3) encouraged us to test the possibility of their transformation into substituted coumaranones, similarly to the transformation **9** → **11** (eq 5).[8] In other words, to complete the sequence, we need to deprotect the *tert*-butoxy group attached to an aromatic ring under relatively mild reaction conditions (e.g., in the presence of TsOH).[9] The experiment surpassed the above expectations; the acetylenic ether **3g** in the presence of TsOH (5 equiv) in 48 h at room temperature (!) was completely converted into the coumaranone **12a** (eq 6).

Inspired by the successful lactonization of **3g** into **12a**, we attempted the one-pot synthesis of the coumaranones

(7) For the palladium-catalyzed [4 + 2] *homo*-dimerization of monosubstituted enynes, see: (a) Saito, S.; Salter, M. M.; Gevorgyan, V.; Tsuboya, N.; Tando, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970. (b) Gevorgyan, V.; Tando, K.; Uchiyama, N.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 7022.

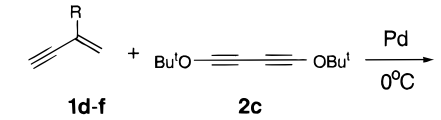
(8) (a) Danishefsky, S.; Kitahara, T.; Tsai, M.; Dynak, J. *J. Org. Chem.* **1976**, *41*, 1669. (b) Miller, A. J.; Matthews, R. S. *J. Org. Chem.* **1992**, *57*, 2516.

(9) Normally, for cleavage of the *tert*-butyl protection of phelols more strong acids, such as TfOH are needed; see for example: Holcombe, J. L.; Livinghouse, T. *J. Org. Chem.* **1986**, *51*, 111.



3g **12a** (6)

12 from the conjugated enynes **1d**−**f** and diynes **2c** and **6** (eqs 7 and 8). Hence, the benzannulation reaction of

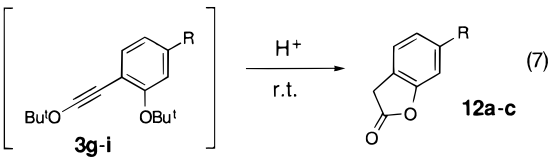


1d-f **2c**

R=Me, **1d**

R=Hex, **1e**

R=OMe, **1f**

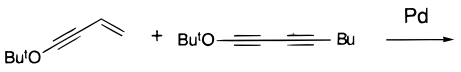


3g-i **12a-c** (7)

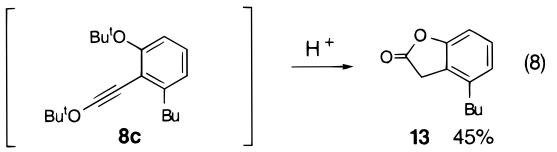
3g **12a** 84%

3h **12b** 83%

3i **12c** 58%



1g **6**



8c **13** 45% (8)

the enynes **1d**, **1e**, and **1f** with the diyne **2c** was performed under the conditions indicated in the Tables 1 and 2. After completion of the first step (formation of the aryl ethers **3g**−**i** was monitored by capillary GLC analysis), TsOH was directly added to the reaction mixtures. Additional stirring of the reaction mixtures for 2 days gave the coumaranones **12a**, **12b**, and **12c** in 84, 83, and 58% isolated yields, respectively (eq 7). Analogous one pot benzannulation−lactonization sequential transformation of **1g** and **6** produced the butyl-substituted coumaranone **13** in 45% yield (eq 8).

Conclusion

A number of differently substituted aryl ethers **3** was synthesized via the [4 + 2] enyne−diyne *cross*-cycloaddition reaction. A remarkably mild condition (0 °C!) for the palladium-catalyzed benzannulation of alkoxy enynes and/or alkoxy diynes was found. A synthetically useful and effective method for the synthesis of substituted coumaranones **12** and **13** from easily available conjugated enynes and diynes via the one-pot benzannulation−cyclization sequence was developed.

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. Enyne **1d** and the diynes **2a**,**b** were purchased from Aldrich. Enyne **1a** was prepared by consecutive Sonogashira coupling[10] of (*E*)-1,2-dibromo-1-phenyloxyethene[11] with TMS acetylene, followed by the reduction of the resulting vinylic bromide[12] and a desilylation step with K_2CO_3/MeOH. Enynes **1b** and **1c** were obtained through a similar protocol for the preparation of **1a**, except for the last desilylation step, employing 1-octyne and phenylacetylene, respectively. Enynes **1e**,[13] **1f**,[14] and **1g**[14] were prepared according to the described methods. Symmetrical diyne **2c** and unsymmetrical diyne **6** were synthesized by Glaser oxidative homocoupling of *tert*-butoxyacetylene[15] and its heterocoupling with 1-hexyne, respectively.[16]

Synthesis of Aryl Ethers 3 (General Procedure). Diyne **2** (1.0 mmol) and enyne **1** (1.0 mmol) were consecutively added at room temperature to a solution of $Pd(PPh_3)_4$ (5 mol %) in THF (1.0 mL) in a 5 mL Wheaton microreactor under an argon atmosphere. After being stirred under the conditions indicated in the Table 1, 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 aryl ethers **3** in 61−91% yields.

One-Pot Synthesis of Coumaranones 12 and 13 (General Procedure). Diyne **2** (1.0 mmol) and enyne **1** (1.0 mmol) were consecutively added at room temperature to a solution of $Pd(PPh_3)_4$ (5 mol %) in CH_2Cl_2 (2.0 mL) in a 20 mL two-neck round-bottom flask under an argon atmosphere. After completion of the first benzannulation step, which was monitored by capillary GLC analysis, TsOH (5 mmol) and toluene (10 mL) were directly added to the reaction mixture at room temperature, and the mixture was stirred for 2 days at room temperature. The mixture was extracted (Et_2O−water), dried (Na_2SO_4), and concentrated. Purification by silica gel column chromatography using hexanes−ethyl acetate as an eluent gave coumaranones **12** and **13** in 45−84% yields.

3a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35−6.98 (m, 6H), 6.83 (d, J = 2.7 Hz, 1H), 6.73 (dd, J = 8.4, 2.4 Hz, 1H), 2.72 (t, J = 7.8 Hz, 2H), 2.44 (t, J = 6.9 Hz, 2H), 1.62−1.34 (m, 8H), 0.98−0.90 (m, 6H).); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 157.0, 156.5, 146.8, 133.4, 129.7, 123.3, 118.93, 118.91, 118.34, 115.9, 92.9, 78.8, 34.4, 32.6, 31.0, 22.5, 21.9, 19.2, 13.9, 13.6; IR (neat) 2956, 1591, 1487 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O$: C, 86.23; H, 8.55. Found: C, 86.17; H, 8.25.

3d: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.06 (m, 15H), 6.88 (s, 2H), 2.90 (t, J = 7.8 Hz, 2H), 1.78−1.26 (m, 8H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 156.9, 147.8, 146.2, 140.6, 130.9, 129.8, 129.4, 128.7, 128.5, 128.4, 128.2, 127.7, 127.5, 123.8, 123.6, 119.3, 117.6, 116.8, 95.3, 87.7, 35.5, 31.8, 30.6, 29.4, 22.7, 14.2; IR (neat) 2927, 2856, 1585, 1488, 1456, cm^{-1}. Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.30; H, 7.18.

3g: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 0.9 Hz, 1H), 6.77 (dd, J = 7.8, 0.9 Hz, 1H), 2.28 (s, 3H), 1.48 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 156.1, 136.7, 132.9, 124.2, 123.7, 117.6, 97.7, 86.2, 79.8, 40.4, 29.0, 27.3, 21.4; IR (neat) 2979, 2250, 1502, 1365, cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H,9.29. Found: C, 78.31; H, 9.25.

3i: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 6.54 (dd, J = 8.4, 2.4 Hz, 1H), 3.77 (s, 3H), 1.47 (s, 9H), 1.42 (s, 9H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 158.5, 157.4, 133.7, 113.0, 109.6, 108.3, 97.0, 86.1, 80.2, 55.3,

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39.9, 29.0, 27.3; IR (neat) 2979, 1604, 1502, 1367, cm^{-1}; MS (EI) *m/z* 276 (M^+ 1.08); HRMS Calcd for $C_{17}H_{24}O_3$ 276.1724, Found 276.1725.

3j: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.97 (t, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 2H), 1.50 (s, 9H), 1.40 (s, 18H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 157.7, 125.3, 118.4, 117.7, 102.1, 86.1, 80.2, 37.9, 29.0, 27.4. Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H,9.49. Found: C, 75.13; H, 9.11.

5: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.01−6.84 (m, 2H), 6.76 (d, $J = 8.4$ Hz, 2H), 6.11 (dd, $J = 18$, 3 Hz, 1H), 5.39 (dd, $J = 12$, 3 Hz, 1H), 1.35 (s, 18H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 155.1, 147.8, 130.4, 126.2, 119.1, 117.7, 80.0, 29.1; IR (neat) 2979, 1569, 1458, 1367, cm^{-1}; MS (EI) *m/z* 248 (M^+ 3.68); HRMS Calcd for $C_{16}H_{24}O_2$ 248.1775, Found 248.1768.

7d:8d (18:82 mixture)**:** ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30−7.25 [m, 1H (1 × 0.82H + 1 × 0.18H)], 6.72−6.54 [m, 2H (2 × 0.82H + 2 × 0.18H)], 3.77 [d, 3H (3 × 0.82H + 3 × 0.18H)], 2.72 (t, $J = 8.0$ Hz, 2 × 0.82H), 2.43 (t, $J = 7.0$ Hz, 2 × 0.18H), 1.54−1.35 [m, 13H (13 × 0.82H + 13 × 0.18H)], 0.98−0.91 (m, 3H (3 × 0.82H + 3 × 0.18H)].

8a: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.22 (d, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 1.1$ Hz, 1H), 6.89 (dd, $J = 7.8$, 1.1 Hz, 1H), 2.71 (t, $J = 7.5$ Hz, 2H), 2.29 (s, 3H), 1.68−1.53 (m, 2H), 1.48 (s, 9H), 1.44−1.26 (m, 2H), 0.93 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 143.8, 136.0, 132.0, 129.3, 126.2, 120.7, 97.9, 86.3, 41.3, 34.6, 32.9, 27.2, 22.7, 21.3, 14.1; IR (neat) 2979, 2929, 2248, 1610, 1369, cm^{-1}; MS (E1) *m/z* 244 (M^+, 1.8); HRMS Calcd for $C_{17}H_{24}O$ 244.1826, Found 244.1823.

8b: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24 (d, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 1.2$ Hz, 1H), 6.90 (dd, $J = 7.8$, 1.2 Hz, 1H), 2.72 (t, $J = 7.5$ Hz, 2H), 2.54 (t, $J = 7.2$ Hz, 2H), 1.66−1.28 (m, 21H), 0.95−0.88 (m, 6H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 143.8, 141.2, 132.0, 128.7, 125.6, 120.9, 97.9, 86.3, 41.3, 35.8, 34.7, 32.9, 31.7, 31.4, 29.0, 27.2, 22.7, 22.6, 14.1, 14.0; IR (neat) 2929, 2856, 2248, 1610, cm^{-1}. Anal. Calcd for $C_{22}H_{34}O$: C, 84.02; H, 10.90. Found: C, 83.85; H, 10.84.

8c: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.03−6.85 (m, 3H), 2.74 (t, $J = 7.5$ Hz, 2H), 1.63−1.28 (m, 22H), 0.90 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 156.8, 145.9, 125.7, 123.1, 120.2, 120.0, 102.2, 86.2, 79.7, 38.8, 34.9, 32.7, 29.1, 27.3, 22.6, 14.1; IR (neat) 2979, 2248, 1568, 1460, 1390, 1365, 1321 cm^{-1}; MS (EI) *m/z* 302 (M^+, 0.31); HRMS Calcd for $C_{20}H_{30}O_2$ 302.2244, Found 302.2242.

12b: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.16 (dd, $J = 7.5$, 0.9 Hz, 1H), 6.96−6.93 (m, 2H), 3.70 (s, 2H), 2.62 (t, $J = 7.5$ Hz, 2H), 1.61−1.29 (m, 8H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 174.6, 154.8, 144.5, 124.2, 124.1, 120.0, 110.7, 36.0, 32.9, 31.6, 31.4, 28.8, 22.6, 14.1; IR (neat) 2927, 2856, 1809, 1631, 1434, cm^{-1}; MS (EI) *m/z* 218 (M^+, 74.5); HRMS Calcd for $C_{14}H_{18}O_2$ 218.1291, Found 218.1289.

12c: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.14 (dd, $J = 7.8$, 0.9 Hz, 1H), 6.67−6.63 (m, 2H), 3.79 (s, 3H), 3.66 (s, 2H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 174.7, 160.4, 155.6, 124.9, 114.5, 109.7, 97.5, 55.6, 32.6; IR (KBr) 2936, 1803, 1633, 1500 cm^{-1}; MS (EI) *m/z* 164 (M^+, 100); HRMS Calcd for $C_9H_8O_3$ 164.0464, Found 164.0463.

13: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.25−6.92 (m, 3H), 3.66 (s, 2H), 2.56 (t, $J = 7.5$ Hz, 2H), 1.61−1.28 (m, 4H), 0.91 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 174.3, 154.5, 139.6, 128.6, 124.1, 121.7, 108.1, 32.9, 31.9, 31.8, 22.4, 13.9; IR (neat) 2956, 2931, 1809, 1452 cm^{-1}; MS (EI) *m/z* 190 (M^+, 92.8); HRMS Calcd for $C_{12}H_{14}O_2$ 190.0985, Found 190.0984.

Supporting Information Available: ^1H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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