Enhanced Reactivity of Electron-Deficient Enynes in the Palladium-Catalyzed *homo*-Benzannulation of Conjugated Enynes

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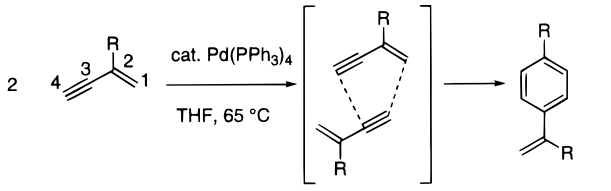
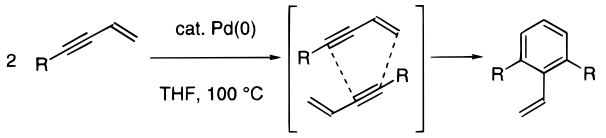
We report the high reactivity of electron-deficient enynes in the *homo*-benzannulation of conjugated enynes in the presence of $Pd(PPh_3)_4$. The introduction of electron-withdrawing groups enabled us to carry out the benzannulation of 1-substituted enynes as well as 1,2- and 2,4-disubstituted enynes. Polysubstituted benzenes were prepared in a highly regioselective manner in good to excellent yields.

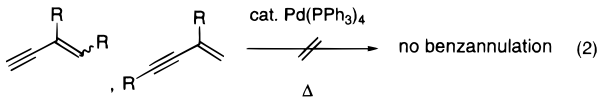
Polysubstituted benzenes are useful synthetic intermediates in organic synthesis, and the development of efficient synthetic methods for such compounds is very important. The preparation of polysubstituted benzenes has been mainly carried out by stepwise introduction of functional groups into the benzene ring via electrophilic[1] or nucleophilic[2] substitution. Careful choice of parameters such as synthetic route and reaction condition is necessary to achieve highly regioselective syntheses of polysubstituted benzenes. Recently, we reported the palladium-catalyzed *homo*-benzannulation reaction (cyclodimerization) of 2-substituted enynes (eq 1).[3] The



(1)

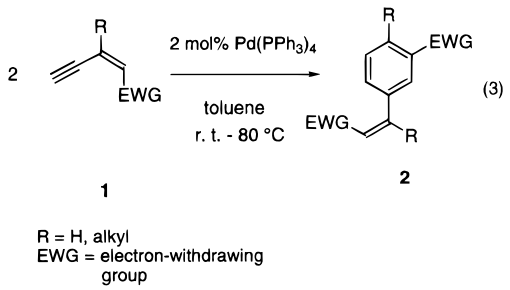


homo-benzannulation of 4-substituted enynes also proceeded to yield 2,6-disubstituted styrenes (eq 1).[4] These reactions have been applied to the synthesis of many functionalized benzenes such as paracyclophanes and phenols.[5] A common and useful feature of these reactions is the highly regioselective formation of substituted benzenes. For example, 2-substituted enynes always cyclodimerize to give the corresponding 1,4-disubstituted benzenes, and no isomeric 1,3-disubstituted benzenes are isolated. While di- or trisubstituted enynes were used as the substrates for the *cross*-benzannulation reaction,[5,6] only monosubstituted enynes cyclodimerized in the *homo*-benzannulation reaction: the reaction did not proceed when a 1,2- or 2,4-dialkyl enyne was employed as the substrate (eq 2).



(2)

Our recent study of the substituent effects on the reactivity of substituted enynes revealed that the reactivity of electron-deficient enynes was much higher compared to that of alkyl enynes. The introduction of an electron-withdrawing group into the conjugated enynes enabled the *homo*-benzannulation of polysubstituted enynes to proceed.[7] In this paper we report details of the palladium-catalyzed *homo*-benzannulation of electron-deficient enynes (eq 3).[8]



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(4) Gevorgyan, V.; Tando, K.; Uchiyama, N.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 7022−7025.
(5) Reviews: (a) Saito, S.; Yamamoto, Y. *Chem. Rev.* in press. (b) Gevorgyan, V.; Yamamoto, Y. *J. Organomet. Chem.* **1999**, *576*, 232−247.

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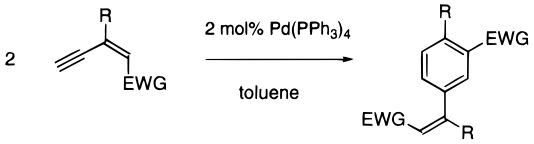
Table 1. *homo*-Benzannulation of Electron-Deficient Enynes (1)



1 2

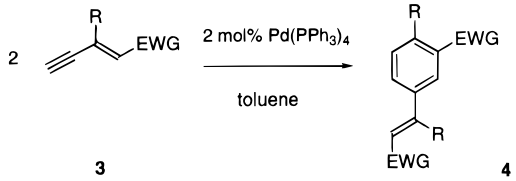
entry	enyne	EWG	R^1	temp (°C)	time (h)	product	yield (%)
1	**1a**	COOEt	H	rt	2	**2a**	88
2	**1b**	COOEt	n-C_6H_{13}	80	2	**2b**	73
3	**1c**	CN	n-C_5H_{11}	80	1.5	**2c**	84
4	**1d**	$CONMe_2$	H	45	4	**2d**	62
5	**1d**	$CONMe_2$	H	80	1	**2d**	53

Results

Benzannulation of Conjugated (*Z*)-Enynes. (*Z*)-1-Ethoxycarbonyl-1-butene-3-yne (**1a**) cyclodimerized in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give the 1,3-disubstituted benzene (**2a**) in good yield (Table 1, entry 1). It is noteworthy that the reactivity of this enyne was significantly higher compared to that of other alkyl enynes,[3,4] and the reaction proceeded smoothly at room temperature. The stereochemistry of the olefinic moiety was unaffected during the reaction, and we did not isolate the regioisomeric (*E*)-styrene derivative from the reaction mixture. The enhanced reactivity of enynes in the benzannulation in the presence of an alkoxycarbonyl group was also demonstrated in the reaction of 1,2-disubstituted enynes. Thus, the *homo*-benzannulation of (*Z*)-1-ethoxycarbonyl-2-hexyl-1-butene-3-yne **1b** also proceeded smoothly in the presence of $Pd(PPh_3)_4$ at 80 °C to give the 1,2,4-trisubstituted benzene **2b** in 73% yield (Table 1, entry 2). When a cyano group was introduced in the C-1 position of the enyne, a similar rate acceleration of the reaction was observed, and the reaction of **1c** proceeded at 80 °C to give the 1,2,4-trisubstituted benzene **2c** (Table 1, entry 3). The *homo*-benzannulation of enyne **1d** bearing a dimethylaminocarbonyl group, which is a less electron-withdrawing group, at the C-1 position proceeded smoothly (Table 1, entries 4 and 5). However, the reactivity of the enyne **1d** was much lower compared to that of **1a**, and it was necessary to carry out the reaction at higher temperature for the complete conversion in a short period.[9]

Benzannulation of Conjugated (*E*)-Enynes and 2,4-Disubstituted Enynes. The reactivity of (*E*)-enynes was lower compared to that of (*Z*)-enynes in the *homo*-benzannulation reaction. Thus, the *homo*-benzannulation of the (*E*)-ethoxycarbonylenyne **3a** proceeded in the presence of Pd catalyst (Table 2, entry 1), though the yield of the product **4a** was lower (43%) and a higher

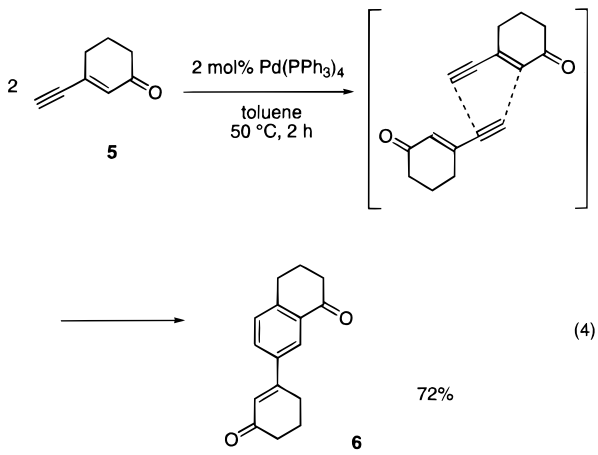
Table 2. *homo*-Benzannulation of Electron-Deficient Enynes (2)



3 4

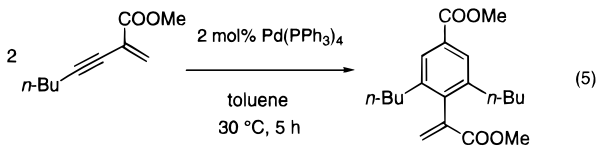
entry	enyne	EWG	R^1	temp (°C)	time (h)	product	yield (%)
1	**3a**	COOEt	H	80	2	**4a**	43
2	**3b**	COOEt	n-C_6H_{13}	80	3	**4b**	38
3	**3c**	CN	n-C_5H_{11}	80	5	**4c**	53

reaction temperature (80 °C) was required (compare Table 1, entry 1 and Table 2, entry 1). A similar tendency was observed in the reaction of other enynes such as **3b** and **3c** (Table 2, entries 2 and 3). The stereochemistry of the olefinic moiety was again unaffected in these reactions. We applied the reaction of (*E*)-enynes to the synthesis of a naphthalenone derivative. Thus, the cyclic carbonyl enyne **5** cyclodimerized efficiently in the presence of $Pd(PPh_3)_4$ to give **6** in 72% yield (eq 4).



5 6 (4)

While 2,4-dialkylenynes did not undergo *homo*-benzannulation, the reaction of an electron-deficient 2,4-disubstituted enyne proceeded rapidly under very mild conditions. Thus, the palladium-catalyzed cyclodimerization of the methoxycarbonylenyne **7** proceeded at 30 °C to give the 1,2,3,5-tetrasubstituted benzene **8** in good yield (eq 5). On the other hand, we previously reported



7 8 68% (5)

that the benzannulation of the cyanoenyne **9a** and perfluorohexylenyne **9b** gave the expected polysubstituted benzenes **10a** and **10b**, respectively, together with

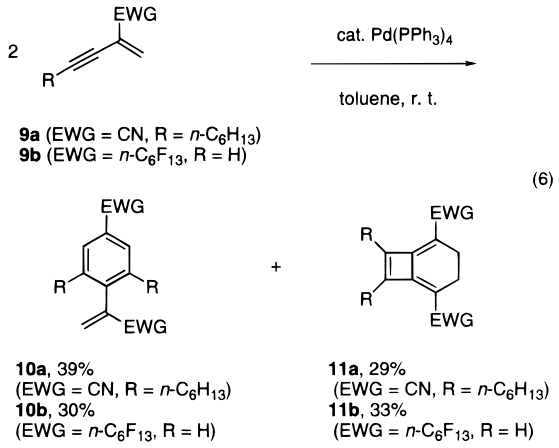
(6) (a) Gevorgyan, V.; Takeda, A.; Homma, M.; Sadayori, N.; Radhakrishnan, U.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 6391−6402. (b) Gevorgyan, V.; Sadayori, N.; Yamamoto, Y. *Tetrahedron Lett.* **1997**, *38*, 8603−8604.

(7) The enhanced reactivity of alkoxycarbonylenynes in the *cross*-benzannulation was reported. See: ref 6.

(8) Preliminary results of this study have been communicated. See: Saito, S.; Tsuboya, N.; Chounan, Y.; Nogami, T.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7529−7532.

(9) We monitored these reactions by TLC and quenched the reaction when the starting material disappeared. Therefore, the results described in Tables 1 and 2 would reflect the difference of the reactivity of the enynes to some extent.

the zipper annulated products **11a** and **11b** (eq 6).[10] It



should be noted that a nearly 1:1 mixture of the ordinary benzannulation product and nonordinary zipper annulation product was obtained in the presence of Pd catalyst, though the use of Ni catalyst resulted in the formation of zipper annulation products in some reactions.[10]

Discussion

On the basis of the results mentioned above, it is now obvious that the reactivity of electron-deficient enynes is much higher compared to that of alkylenynes: the very mild condition (rt, 2 h) required for the cyclodimerization of **1a** is remarkable compared to the reaction conditions required for the reaction of 2-substituted enynes and 4-substituted enynes (65 °C, 1 h[3] or 100 °C, 24 h,[4] respectively). Comparing the reaction conditions of **1a** and **1d** (Table 1), we assume that the rate of the reaction depends on the electron-withdrawing ability of the substituent: the reactivity of the less electron-deficient enyne **1d** was lower compared to that of more electron-deficient **1a**. Currently the precise mechanism of this benzannulation is not clear, and therefore the role of the electron-withdrawing group in the reaction is difficult to understand. Since it has been shown that the interaction of palladium(0) species with electron-deficient alkynes is much stronger than that with electron-rich alkynes,[11] the increased reactivity of the enynes might be explained in terms of stronger interaction of the electron-deficient enynes with the Pd catalyst.

The isomerization of the less reactive (*E*)-enynes to more reactive (*Z*)-enynes has been suggested as a possible pathway for the benzannulation reaction.[6] However, this isomerization process is unlikely to occur during the reaction, since the formation of a single isomer was observed in all of the reactions we carried out. Furthermore, the successful benzannulation of the cyclic enyne **5** clearly shows that the isomerization of (*E*)-enyne to (*Z*)-enyne is not a requirement for the reaction to proceed. The reactions of (*Z*)-enynes proceeded under milder conditions compared to those of (*E*)-enynes, probably because the rate of the formal [1,3]-migration of the hydrogen atom is quite different.[12,13] As is the case for

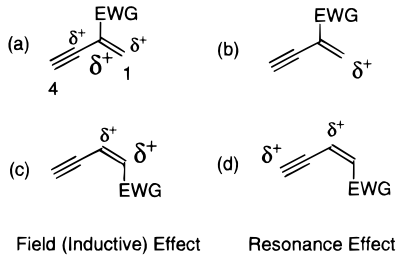


Figure 1. Electronic effects of the substitutents (electron-withdrawing groups) on the enynes.

other benzannulation reactions, the reactivity of polysubstituted enynes was lower compared to that of monosubstituted enynes, probably because of steric effects.

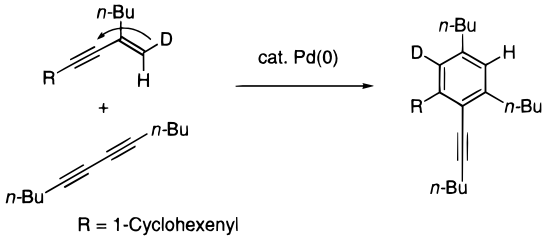
A similar rate-acceleration effect was also observed in the reactions of 1-cyanoenynes, 1-alkoxycarbonylenynes, and 1-ketoenynes, in which only the benzannulation products were obtained, whereas a rate-acceleration effect and the formation of the zipper annulation products (bicyclic compounds) were observed in the reaction of 2-cyanoenyne **9a** and 2-perfluorohexylenyne **9b**.[10] The formation of these bicyclic compounds might be explained in terms of the different electronic properties of the substituents present in the C-2 position. Thus, the ethoxycarbonyl group has the relatively stronger conjugation effect (field value (F) = 0.34, resonance value (R) = 0.11),[14] while the cyano group has the stronger inductive effect (F = 0.51) and a relatively weak resonance effect (R = 0.15).[15] The perfluoroalkyl group also has a similar electronic effect (F = 0.42, R = 0.06).[14,15] The difference of the electronic properties of the substituents should play an important role in the reaction of 2-substituted enynes, and it is likely that the enyne with a substituent that has a stronger field effect cyclodimerizes to give the bicyclic compound in addition to the benzene derivative in the presence of palladium catalysts. Considering the electronic structures of the enynes, the activation of the C-1 and/or C-4 carbon might be important for the benzannulation to proceed (Figure 1 (b)−(d)). On the other hand, the activation of C-3 carbon might be important for the zipper annulation to proceed (compare Figure 1a and b).[16] The nature of the electron-withdrawing substituents had no influence on the reaction pathway of 1-substituted enynes.

(10) Saito, S.; Tanaka, T.; Koizumi, T.; Tsuboya, N.; Itagaki, H.; Kawasaki, T.; Endo, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 1810−1811.

(11) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879−3891.

(12) The rate of the reaction may also be controlled by the steric effect. The lower yields of the products in the reaction of (*E*)-enynes may be explained in terms of the formation of polymeric compounds.

(13) Exclusive hydrogen migration from *E*-position of conjugated enynes has been reported in the *cross*-benzannulation reaction. See: ref 6a.



(14) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(15) Values of *n*-perfluoropropyl group.

(16) Though the C-2 carbon is most activated by the field effect of the electron-withdrawing group attached to the C-2 position (Figure 1 (a), no intermolecular C−C bond between C-2 carbons was formed in the zipper annulation.

In summary, we found that some electron-deficient enynes are highly reactive substrates for the palladium-catalyzed *homo*-benzannulation. We succeeded in extending the scope of the benzannulation reaction, and some disubstituted enynes also cyclodimerized in the presence of a Pd catalyst. Useful functional groups such as cyano group and alkoxycarbonyl group were introduced to the benzene ring under mild conditions. This reaction provides another efficient method for the regioselective synthesis of functionalized polysubstituted benzenes.

Experimental Section

Synthesis of the Conjugated Enynes. Monosubstituted enynes **1a**,[17] **1d**, and **3a**[17] were prepared by the Sonogashira reaction[18] of (*Z*)-ethyl 3-bromopropenate,[19] (*E*)-ethyl 3-bromopropenate,[19] or (*Z*)-2-bromopropenoic acid dimethylamide[20] with (trimethylsilyl)acetylene, followed by the removal of the trimethylsilyl group (KF/MeOH). The synthesis of 1,2-disubstituted enynes **1b** and **3b** was carried out by the Horner−Wadsworth−Emmons reaction of the (trimethylsilyl)ethynyl ketones[21] with triethyl phosphonoacetate,[22] isolation of the isomers by column chromatography, and deprotection (KF/MeOH). The synthesis of 1,2-disubstituted enynes **1c** and **3c** was carried out by the Horner−Wadsworth−Emmons reaction of the ethynyl ketones[23] with diethyl (cyanomethyl)phosphonate,[22] and isolation of the isomers by column chromatography. Cyclic ketoenyne **5**[23] was prepared according to the published method. The synthesis of **7** was carried out by the Sonogashira reaction[18] of methyl 1-bromovinylacrylate[25] with 1-hexyne. Compound **7** has limited stability, and the polymerization proceeded easily in the absence of a radical inhibitor such as BHT (2,6-di-*tert*-butyl-4-methylphenol).

(*Z*)-3-Hexyl-pent-2-en-4-ynoic acid ethyl ester (1b): yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.03 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.57 (d, J = 0.7 Hz, 1H), 2.25 (ddd, J = 7.5, 7.5, 1.0 Hz, 2H), 1.56 (quint, J = 7.1 Hz, 2H), 1.2−1.3 (m, 9H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 164.8, 138.6, 125.7, 88.4, 81.2, 60.2, 38.7, 31.5, 28.5, 27.7, 22.5, 14.2, 14.0; IR (neat) 3256, 2957, 2932, 2860, 2095, 1732, 1622, 1456, 1373, 1350, 1283, 1205, 1142, 1099, 1040, 862, 640 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1467. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.64; H, 9.35.

(*Z*)-3-Pentyl-pent-2-en-4-ynenitrile (1c): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (m, 1H), 3.62 (s, 1H), 2.30 (ddd, J = 7.6, 7.6, 1.4 Hz, 2H), 1.63−1.53 (m, 2H), 1.37−1.26 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 116.2, 104.5, 88.4, 79.8, 37.2, 30.8, 27.2, 22.2, 13.8; IR (neat) 3298, 3057, 2959, 2932, 2862, 2222, 2098, 1684, 1593, 1466, 1458, 1379, 1169, 1101, 818, 648 cm^{-1}; HRMS calcd for $C_{10}H_{13}N$ 147.1047, found 147.1058.

(*Z*)-Pent-2-en-4-ynoic acid dimethylamide (1d): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43 (d, J = 11.9 Hz, 1H), 5.84 (dd, J = 11.7, 2.6 Hz, 1H), 3.28 (d, J = 2.6 Hz, 1H), 3.04 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 134.2, 115.0, 85.2, 79.4, 37.5, 34.7; IR (neat) 3217, 2934, 1634, 706 cm^{-1}; HRMS calcd for C_7H_9NO 123.0684, found 123.0687. Anal. Calcd for C_7H_9NO: C, 68.27; H, 7.37; N, 11.37. Found: C, 67.99; H, 7.55; N, 11.18.

(*E*)-3-Hexyl-pent-2-en-4-ynoic acid ethyl ester (3b): pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.10 (s, 1H), 4.15 (q, 2H, J = 7.2 Hz), 3.15 (s, 1H), 2.71 (t, 2H, J = 7.7 Hz), 1.56 (quint, 2H, J = 7.5 Hz), 1.2−1.6 (m, 9H), 0.86 (t, 3H, J = 6.7 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 165.5, 141.8, 125.7, 84.3, 81.6, 60.1, 32.0, 31.6, 28.9, 28.3, 22.6, 14.2, 14.0; IR (neat) 3304, 2959, 2930, 2860, 2097, 1717, 1614, 1466, 1369, 1219, 1178, 1146, 1038, 878, 635 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1476. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.94; H, 9.52.

(*E*)-3-Pentyl-pent-2-en-4-ynenitrile (3c): yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.56 (s, 1H), 3.40 (s, 1H), 2.47 (t, J = 7.6 Hz, 2H), 1.64−1.55 (m, 2H), 1.33−1.28 (m, 4H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 146.7, 115.7, 105.0, 86.3, 81.3, 35.4, 30.8, 27.4, 22.3, 13.8; IR (neat) 3292, 3059, 2959, 2932, 2862, 2220, 2098, 1589, 1466, 1458, 1379, 1339, 827, 650 cm^{-1}; HRMS calcd for $C_{10}H_{13}N$ 147.1047, found 147.1044. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.19; H, 8.82; N, 9.28.

2-Methylene-oct-3-ynoic acid methyl ester (7): colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.50 (d, J = 1.5 Hz, 1H), 5.99 (dt, J = 1.5 Hz, 0.7 Hz, 1H), 3.80 (s, 3H), 2.37 (t, J = 7.0 Hz, 2H), 1.63−1.36 (m, 4H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 165.1, 132.9, 124.2, 93.9, 76.6, 52.6, 30.5, 22.0, 19.1, 13.6; IR (neat) 2957, 2932, 2359, 1736, 1435, 1213 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.0978. Because of the limited stability of **7**, we carried out the benzannulation reaction without completely removing the impurity.

Representative Procedure for the Palladium-Catalyzed Benzannulation of Electron-Deficient Enynes. To a yellow solution of $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in dry toluene (1.0 mL) was added **1c** (73.6 mg, 0.5 mmol) at room temperature, and the mixture was stirred at 80 °C for 1 h under Ar. The mixture was passed through a short alumina column (ether) and evaporated. The residue was further purified by column chromatography (silica gel, hexane/ethyl acetate = 20:1) to give **2c** as a yellow oil (57.4 mg, 0.78 mmol, 78%). The reaction conditions and the isolated yields for the reaction of **1**, **3**, **5**, and **7** are described in Tables 1 and 2 and eqs 5 and 6.

5-((*Z*)-2-Ethoxycarbonyl-1-hexylvinyl)-2-hexylbenzoic acid ethyl ester (2a): pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.15 (bs, 1H), 8.00 (bd, J = 8.1 Hz, 1H), 7.80 (bd, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 6.98 (d, J = 12.5 Hz, 1H), 6.01 (d, J = 12.5 Hz, 1H), 4.38 (q, J = 7.0 Hz, 2H), 4.17 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.2, 165.9, 141.8, 135.2, 133.6, 130.7, 130.3, 129.8, 128.0, 121.1, 61.0, 60.4, 14.3, 14.0. IR (neat) 1717, 1633, cm^{-1}; HRMS calcd for $C_{14}H_{16}O_4$ 248.1048, found 248.1055. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.59; H, 6.51.

5-((*Z*)-2-Ethoxycarbonyl-1-hexylvinyl)-2-hexylbenzoic acid ethyl ester (2b): yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.65 (m, 1 H), 7.21 (m, 2 H), 5.88 (m, 1 H), 4.34 (q, J = 7.3 Hz, 2 H), 3.98 (q, J = 7.3 Hz, 2 H), 2.97−2.91 (m, 2 H), 2.45−2.40 (m, 2 H), 1.62−1.54 (m, 2 H), 1.41−1.25 (m, 15 H), 1.05 (t, J = 7.3 Hz), 0.91 − 0.84 (m, 6 H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 167.7, 166.0, 158.7, 144.0, 137.6, 130.7, 130.3, 129.4, 129.2, 117.6, 60.8, 59.8, 40.3, 34.4, 31.8, 31.78, 31.5, 29.5, 28.7, 27.3, 22.7, 22.5, 14.3, 14.1, 14.0, 13.9; IR (neat) 1722, 1639 cm^{-1}; HRMS calcd for $C_{26}H_{40}O_4$ 416.2926, found 416.2915.

5-((*Z*)-2-Cyano-1-pentylvinyl)-2-pentylbenzonitrile (2c): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.59 (m, 2H), 7.38 (d, J = 7.9 Hz, 1H), 5.43 (s, 1H), 2.85 (t, J = 7.6 Hz, 2H), 2.53 (t, J = 6.9 Hz, 2H), 1.71−1.66 (m, 2H), 1.40−1.26 (m, 10H), 0.92−0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 148.1, 135.8, 131.6, 131.1, 129.9, 117.4, 116.8, 112.9, 96.5, 37.8, 34.4, 31.3, 31.0, 30.3, 27.1, 22.3, 22.2, 13.9, 13.8; IR (neat) 2224, 1612 cm^{-1}; HRMS calcd for $C_{20}H_{26}N_2$ 294.2095, found 294.2097. Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.55; H,8.95; N, 9.38.

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3-((*Z*)-2-Dimethylcarbamoylvinyl)-*N*,*N*-dimethylbenzamide (2d): red purple oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.31 (m, 4H), 6.61 (d, J = 12.6 Hz, 1H), 6.08 (d, J = 12.5 Hz, 1H), 3.08 (s, 3H), 2.96 (s, 3H), 2.94 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.9, 168.4, 136.6, 135.4, 132.4, 129.0, 128.5, 126.9, 126.7, 124.2, 39.4, 37.4, 35.2, 34.3; IR (neat) 2932, 1684, 1393, 750 cm^{-1}; HRMS calcd for $C_{14}H_{18}N_2O_2$ 246.1368, found 246.1370.

3-((*Z*)-2-Ethoxycarbonylvinyl)benzoic acid ethyl ester (4a): pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.21 (bs, 1H), 8.05 (ddd, J = 7.7 Hz, 1.3 Hz, 1.5 Hz, 1H), 7.72 (d, J = 15.8 Hz, 1H), 7.72−7.76 (m, 1H), 7.47 (dd, J = 7.7 Hz, 7.7 Hz, 1H), 6.52 (d, J = 15.8 Hz, 1H), 4.40 (q, J = 7.0 Hz, 2H), 4.28 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.35 (t, J = 7.0 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.7, 166.0, 143.4, 134.8, 132.1, 131.3, 131.0, 128.98, 128.95, 119.6, 61.3, 60.7, 14.34, 14.32; IR (neat) 1717, 1641 cm^{-1}; HRMS calcd for $C_{14}H_{16}O_4$ 248.1048, found 248.1053. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.53; H, 6.59.

5-((*E*)-2-Ethoxycarbonyl-1-hexylvinyl)-2-hexylbenzoic acid ethyl ester (4b): pale yellow oil; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.90 (d, J = 2.0 Hz, 1H), 7.47 (dd, J = 2.0, 8.1 Hz, 1 H), 7.24 (d, J = 8.1 Hz, 1H), 6.03 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.10−3.05 (m, 2H), 3.00−2.90 (m, 2H), 1.64−1.54 (m, 4H), 1.43−1.25 (m, 18H), 0.93−0.82 (m, 6H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 167.71, 166.45, 159.66, 145.12, 138.82, 131.12, 130.28, 129.60, 128.70, 117.29, 61.03, 59.88, 34.29, 31.75, 31.72, 31.56, 30.84, 29.45, 29.40, 29.02, 22.63, 22.58, 14.34, 14.32, 14.09, 14.04. IR (neat) 1717, 1624 cm^{-1}; HRMS calcd for $C_{26}H_{40}O_4$ 416.2926, found 416.2916.

5-((*E*)-2-Cyano-1-pentylvinyl)-2-pentylbenzonitrile (4c): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 2.0 Hz, 1H), 7.52 (dd, J = 8.2, 2.0 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 5.51 (s, 1H), 2.84 (t, J = 7.7 Hz, 4H), 1.70−1.65 (m, 2H), 1.45−1.29 (m, 10H), 0.92−0.84 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 148.6, 136.0, 130.35, 130.28, 130.1, 117.4, 116.7, 113.2, 96.9, 34.3, 33.6, 31.3, 31.2, 30.4, 28.0, 22.3, 22.2, 13.9, 13.8; IR (neat) 2860, 2216, 1603 cm^{-1}; HRMS calcd for $C_{20}H_{26}N_2$ 294.2095, found 294.2096. Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.63; H, 9.20; N, 9.38.

3,5-Dibutyl-4-(1-methoxycarbonylvinyl)benzoic acid methyl ester (8): pale yellow oil; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.74 (s, 2H), 6.71 (d, J = 1.7 Hz, 1H), 5.62 (d, J = 1.7 Hz, 1H), 3.91 (s, 3H), 3.73 (s, 3H), 2.59−2.37 (m, 4H), 1.57−1.21 (m, 8 H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 167.3, 166.9, 141.5, 140.5, 138.6, 129.9, 129.4, 127.4, 52.3, 52.0, 33.4, 33.1, 22.7, 13.9; IR (neat) 1724, 1435 cm^{-1}; HRMS calcd for $C_{20}H_{28}O_4$ 332.1987, found 332.1991.

7-(3-Oxocyclohex-1-enyl)-3,4-dihydro-2*H*-naphthalen-1-one (10): colorless powder, mp 71−74 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.21 (d,J = 2.2 Hz, 1H) 7.66 (dd, J = 2.2, 8.1 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 6.44 (t, J = 1.5 Hz, 1H), 3.01 (t, J = 6.1 Hz, 2H), 2.80 (ddd, J = 1.5, 6.1, 6.1 Hz, 2H), 2.69 (t, J = 6.1 Hz, 2H), 2.50 (t, J = 6.2 Hz, 2H), 2.17 (m, 4 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 199.8, 197.9, 158.6, 146.2, 137.2, 132.7, 130.6, 129.5, 125.6, 124.9, 39.0, 37.2, 29.6, 28.0, 23.0, 22.7; IR(KBr) 1670, 1600, 1409, 1328, 1257, 1203, 1178 cm^{-1}; HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1148. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.96; H, 6.87.

Supporting Information Available: ^{1}H NMR spectra for compounds **1c**, **2b**, **2d**, **4b**, **7**, and **8** (PDF). This material is available free of charge via the Internat at http://pubs.acs.org.

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