J. Org. Chem. **2001,** *66,* 2743−2746

Synthesis of Cyclophanes via an Intermolecular Pd-Catalyzed Enyne−Diyne Cross-Benzannulation Approach

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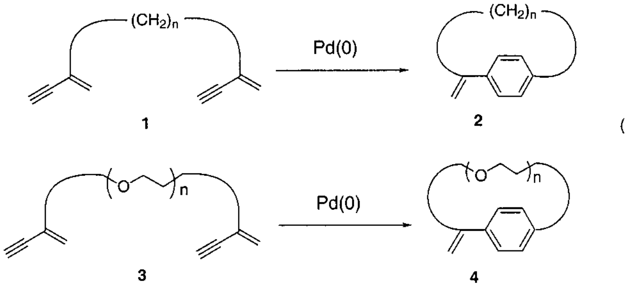
Received November 22, 2000

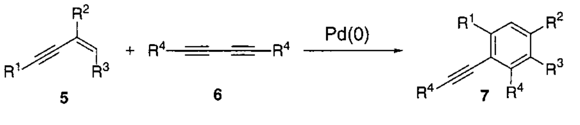
Several novel types of cyclophanes were efficiently synthesized via an intermolecular palladium-catalyzed cross-benzannulation of cyclic enynes and diynes. These types of cyclophanes are not accessible through an intramolecular mode of the homo-benzannulation protocol, reported previously. Cyclic reactants (enynes and diynes) were readily prepared in reasonable yields from commercially available materials using known procedures. The fact that the cyclic *Z*-enyne **29**, in contrast to its *E*-counterpart, underwent benzannulation to produce the cyclophane **28** brought additional support for the necessity of having an *E*-hydrogen atom at the terminal olefin moiety of nonactivated enynes, which was found previously in the benzannulation of the acyclic susbstrates.

Cyclophanes are attractive synthetic targets due to their intriguing chemical, physicochemical, and biological properties.[1] We have recently reported an efficient synthetic route for constructing a variety of carbon-tethered exomethylene cyclophanes **2**[2] and crown ether-like cyclophanes **4**[3] via the palladium-catalyzed homodimerization of bis-enynes **1** and **2**, respectively (eq 1). An efficient cyclization of **1** proceeded in the presence of 5−40 mol % of palladium catalyst and only under high dilution conditions (to avoid formation of dimers and oligomers).[2] In contrast, polyether bis-enyne **3** cyclized in the presence of 4−5 mol % of Pd catalyst and under relatively concentrated conditions to produce the corresponding polyether cyclophanes **4**. In some cases, the yield of polyether cyclophanes was quantitative.[3] It was proposed that, in the latter case, a host/guest relationship between **3** and palladium could be responsible for the observed remarkable intramolecular control of benzannulation.[3]



(1)

We have also recently developed an intermolecular palladium-catalyzed cross-benzannulation reaction of conjugated enynes **5** with diynes **6** to give the multisubstituted benzenes **7** in good to excellent yields (eq 2).[4]



(2)

Naturally, we attempted to apply the high yielding intermolecular cross-benzannulation method for the synthesis of cyclophanes. Obviously, the accessibility of the cyclic substrates, which are needed for this type of benzannulation, is lower compared to that of acyclic substrates. This method, however, can give access to several types of cyclophanes which are not available through the previously reported intramolecular benzannulation protocol.[2,3]

Herein, we wish to report a synthesis of the several different types of cyclophanes via an intermolecular palladium-catalyzed cross-benzannulation reaction of cyclic enynes and diynes.

Results and Discussion

Benzannulation of Cylic Enynes and Diynes. It was found that the cyclic 2,4-disubstituted enyne **8**, possessing a tether of 12 methylene units, reacted smoothly with dodecadiyne **9** and diphenyldiyne **11** in the presence of Pd(PPh_3)$_4$ catalyst (5 mol %) in THF (1 M) at 100 °C (overnight) to produce *meta*-cyclophanes **10** and **12** in good yields (Table 1, entries 1 and 2). The reaction of **8** with bis-silyl diyne **13** was much more sluggish and gave the *meta*-cyclophane **14** in 48% only (entry 3). Interestingly, cyclic enyne **8** readily reacted with the 12 carbon-tethered cyclic diyne **15** to produce the benzene **16**, a cyclophane having both 15- and 16-membered cycles, in 72% yield (entry 4). It was earlier reported that acyclic 1,4-disubstituted enynes undergo the benzannulation reaction much slower than the analogous 2,4-disubstituted enynes.[4c] Not surprisingly, the cyclic 1,4-disubstituted enyne **17** reacted rather

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[1] For reviews, see: (a) *Topics in Current Chemistry 172*; Weber, E., Ed.; Springer-Verlag: Berlin, 1994. (b) *Cyclophane Chemistry*; Vögtle, F., Ed.; Willey: Chichester, 1993. (c) Diederich, F. *Cyclophanes*; Royal Society of Chemistry: Cambridge, 1991.

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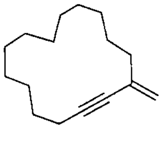
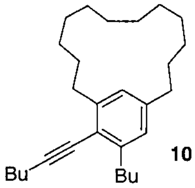
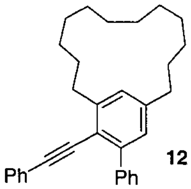
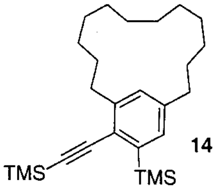
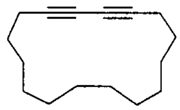
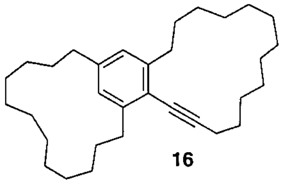
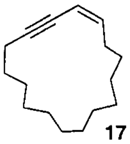
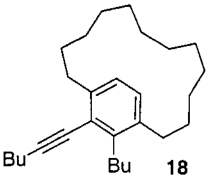
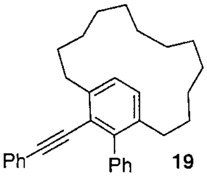
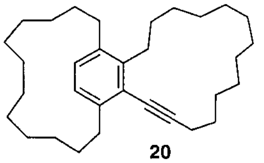
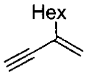
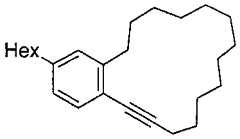
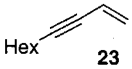
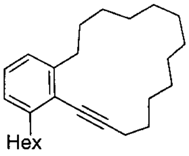
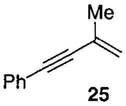
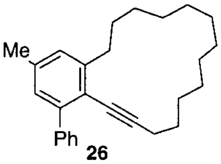
[4] (a) Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11313. (b) Gevorgyan, V.; Sadayori, N.; Yamamoto, Y. *Tetrahedron Lett.* **1997**, *38*, 8603. (c) Gevorgyan, V.; Takeda, A.; Homma, M.; Sadayori, N.; Radhakrishnan, U.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 6391.

10.1021/jo0016531 CCC: $20.00

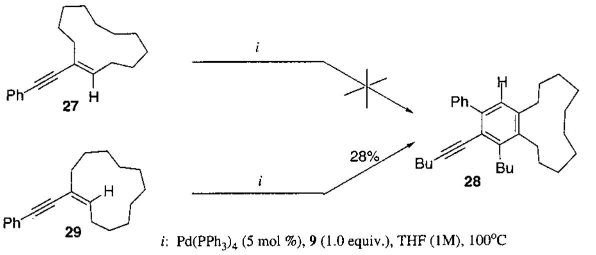
Table 1. Pd-Catalyzed Benzannulation of Cyclic Enynes and Diynes

Entry	Enyne	Diyne	Product	Yield (%)[a]
1	 **8**	Bu—≡—≡—Bu **9**	 **10**	78
2	**8**	Ph—≡—≡—Ph **11**	 **12**	68
3	**8**	TMS—≡—≡—TMS **13**	 **14**	48
4	**8**	 **15**	 **16**	72
5	 **17**	**9**	 **18**	20[b]
6	**17**	**11**	 **19**	44[b]
7	**17**	**15**	 **20**	25[b]
8	 **21**	**15**	 **22**	80
9	 **23**	**15**	 **24**	85
10	 **25**	**15**	 **26**	76

[a] Isolated yield. [b] NMR yield.

sluggishly with the diynes **9**, **11**, and **15** (4 days at 120 °C) to afford the corresponding *para*-cyclophanes **18**−**20** in low to fair yields (entries 5−7).[5] The cyclic diyne **15** smoothly reacted with the acyclic 2-substituted enyne **21** (at 65 °C), with the 4-substituted enyne **23** (at 80 °C), and with the 2,4-disubstituted enyne **25** (at 100 °C) to give the corresponding benzenes **22**, **24**, and **26** in good yields (entries 8−10).

It was shown earlier that nonactivated acyclic *Z*-enynes enabled the benzannulation reaction, whereas the analogous *E*-isomers remained inert.[4c] Furthermore, deuterium labeling studies confirmed that only the *E*-hydrogen atom of the terminal olefin moiety in the nonactivated enyne undergoes a sigmatropic shift.[4c] Accordingly, we were anxious to learn if the above-mentioned requirement for acyclic enynes is also crucial for the cyclic substrates. To clarify this question, we tested the benzannulation reaction of the diyne **9** with cyclic 1,2-disubstituted *E*-enyne **27** and Z-enyne **29** (eq 3). It was found that the cyclic enynes **27** and **29** follow the above-mentioned trend for acyclic systems: the *Z*-enyne **29** underwent the benzannulation reaction to produce the benzene **28** (although with low yield), whereas its *E*-isomer **27** did not produce any detectable amount of **28** under the same reaction conditions (eq 3).



i: Pd(PPh$_3$)$_4$ (5 mol %), **9** (1.0 equiv.), THF (1M), 100°C

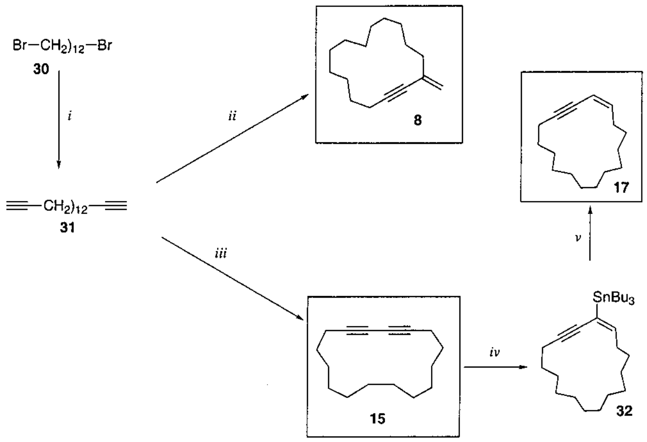
In conclusion, a method for the synthesis of several novel types of cyclophanes via an intermolecular palladium-catalyzed cross-benzannulation of cyclic enynes and diynes was developed. These types of cyclophanes are not accessible through an intramolecular mode of the homo-benzannulation protocol and not easily available using other methods. Cyclic enynes and diynes were readily prepared in reasonable yields from commercially available materials using standard procedures.

Experimental Section

Instrumentation. NMR spectra were recorded on JEOL JNM LA-300 (300 MHz) and JEOL JNM α-500 (500 MHz) instruments. IR spectra were recorded on a Shimadzu FTIR-8200A spectrometer. High-resolution mass spectra were recorded on a Hitachi M-2500S spectrometer. GC−MS analyses were performed on a Hewlett-Packard Model 6890 GC interfaced to a Hewlett-Packard Model 5973 mass selective detector (30 m × 0.25 mm capillary column, HP-5MS). Capillary GLC analysis was performed on SHIMADZU GC-18A (30 m × 0.25 mm capillary column, DB-5). Column chromatography was carried out employing Merck silica gel (Kieselgel 70−230 mesh), and analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated silica gel plates (Kieselgel 60 F$_{254}$).

Chemicals. Anhydrous solvents were purchased from Kanto Chemicals. All other compounds used were commercially available and purchased from Aldrich.

Scheme 1[a]



[a] Key: (i) HCCLi·H$_2$NCH$_2$CH$_2$NH$_2$ (2.2 equiv), DMSO (0.5 M), 72%;[7] (ii) Pd(OAc)$_2$ (20 mol %), TDMPP (40 mol %), C$_6$H$_6$, (0.02 M), reflux, 32%;[8] (iii) Pd(PPh$_3$)$_2$Cl$_2$ (20 mol %), CuI (65 mol %), I$_2$ (5 equiv), *i*-Pr$_2$NH (0.02 M), rt, 56%;[9] (iv) *n*-Bu$_3$SnH (1.1 equiv), Pd(PPh$_3$)$_2$Cl$_2$ (2 mol %), THF (0.33M), rt, 77%;[10] (v) HCl (1.0 M in Et$_2$O), rt, quant.

Synthesis of Substrates. Cyclic *Z*-enyne **27** and *E*-enyne **29** were prepared via the modified Sonogashira coupling[6] of phenylacetylene with *E*-1-bromocyclododecene[7] and *Z*-1-bromocyclododecene[7] in 46% and 70% yield, respectively. Diacetylene **31**, which was readily prepared from the corresponding dibromide, was used as a common substrate for the preparation of **8**, **15**, and **17** (Scheme 1). Cyclic enyne **8** was prepared via intramolecular Trost reductive coupling of **31**.[8] Intramolecular modified Glaser oxidative coupling of **31** produced **15** in 56% yield.[9] Cyclic enyne **17** was prepared via the Pd-catalyzed hydrostannation of **15** (77% yield),[10] followed by quantitative protiodestanylation of the forming vinylstannane **32** (Scheme 1).

Enynes **21**, **23**, and **25** were prepared according to known procedures.[7] Diynes **9**, **11**, and **13** were commercially available and purchased from Aldrich.

General Procedures. All manipulations were conducted in oven-dried Wheaton microreactors under an argon atmosphere.

Pd-Catalyzed Enyne−Diyne [4 + 2] Cross-Benzannulation (General Procedure). A 1:1 mixture of enyne and diyne and Pd(PPh$_3$)$_4$ (5 mol %) in THF (1.0M) was stirred at the temperature described in the text above. The reaction course was monitored by capillary GLC analysis. After completion of the reaction, the mixture was filtered through a short column (silica gel) and concentrated. Benzannulation products were purified by column chromatography (silica gel; eluent, hexane).

8: ^{1}H NMR (270 MHz, CDCl$_3$) δ 5.19 (d, J = 2.2 Hz, 1H), 5.12 (d, J = 2.2 Hz, 1H), 2.37 (t, J = 5.6 Hz, 2H), 2.14 (t, J = 6.9 Hz, 2H), 1.74−1.33 (m, 20H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 132.4, 119.8, 90.1, 81.1, 37.9, 27.9, 27.4, 26.9, 26.84, 26.81, 26.80, 26.7. 26.44, 26.41, 24.9, 18.8; IR (neat) 3092, 2930, 2856, 2222, 1611, 1458, 1350, 1292, 891, 721 cm^{-1}; HRMS calcd for C$_{16}$H$_{26}$ 218.2033, found 218.2043. Anal. Calcd for C$_{16}$H$_{26}$: C, 88.00; H, 12.00. Found: C, 88.00; H, 11.66.

10: ^{1}H NMR (300.5 MHz, CDCl$_3$) δ 6.83 (s, 1H), 6.80 (s, 1H), 2.81−2.71 (m, 4H), 2.58 (t, J = 6.0 Hz, 2H), 2.47 (t, J = 6.8 Hz, 2H), 1.67−1.13 (m, 28H), 0.97−0.91 (m, 6H); ^{13}C NMR

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[5] Tris(2,6-dimethoxyphenyl)phosphine (TDMPP) (20 mol %) was added to all reaction mixtures, which were stirred at 120 °C in order to avoid the formation of Pd−black.

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(67.9 MHz, $CDCl_3$) δ 144.9, 143.8, 140.7, 127.1, 126.7, 120.2, 96.8, 78.0, 34.84, 34.78, 33.9, 33.0, 31.2, 29.8, 29.0, 27.3, 27.23, 27.20, 26.9, 26.04, 26.00, 25.8, 25.7, 22.7, 22.0, 19.4, 14.1, 13.7; IR (neat) 2928, 2856, 1605, 1560, 1458, 1377, 1352, 1327, 1300, 1103, 897, 745, 727 cm^{-1}; HRMS calcd for $C_{28}H_{44}$ 380.3443, found 380.3439. Anal. Calcd for $C_{28}H_{44}$: C, 88.35; H, 11.65. Found: C, 88.20; H, 11.89.

12: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.38−7.16 (m, 8H), 6.99 (s, 2H), 2.93−2.89 (m, 2H), 2.63−2.90 (m, 2H), 1.74−1.61 (m, 4H) 1.23−1.10 (m, 16H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ144.8, 144.4, 142.2, 141.4, 131.0, 129.6, 128.9, 128.2, 127.7, 127.6, 127.1, 124.0, 118.4, 95.6, 88.4, 34.9, 34.1, 29.6, 29.0, 27.3, 27.2, 27.1, 26.8, 26.1, 26.0, 25.80, 25.75; IR (KBr) 3080, 3057, 2928, 2856, 2210, 1944, 1801, 1597, 1558, 1493, 1458, 1443, 1420, 1367, 1350, 1294, 1177, 1155, 1097, 1069, 1026, 910, 889, 772, 754, 698, 691 cm^{-1}; HRMS calcd for $C_{32}H_{36}$ 420.2817, found 420.2804.

14: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.06 (d, J = 1.7 Hz, 1H), 7.01 (d, J = 1.7 Hz, 1H), 2.85−2.80 (m, 2H), 2.63−2.59 (m, 2H), 1.69−1.64 (m, 4H) 1.29−1.11 (m, 16H), 0.36 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ144.6, 142.7, 141.2, 132.1, 130.3, 124.9, 105.7, 100.4, 34.9, 33.5, 29.7, 28.7, 27.4, 27.2, 27.1, 26.8, 26.1, 26.0, 25.9, 25.8, −0.1, −0.8; IR (KBr) 2926, 2856, 2149, 1749, 1734, 1684, 1647, 1558, 1541, 1508, 1489, 1474, 1458, 1340, 1248, 1219, 1142, 1113, 868, 839, 746, 556, 517 cm^{-1}; HRMS calcd for $C_{26}H_{44}Si_2$ 412.2981, found 412.2983.

15: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.25 (t, J = 5.8 Hz, 4H), 1.58−1.35 (m, 20H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 78.7, 66.7, 28.4, 28.0, 27.13, 27.08, 26.5, 19.0; IR (neat) 2928, 2856, 2255, 2164, 1460, 1429, 1369, 1346, 1315, 723 cm^{-1}; HRMS calcd for $C_{16}H_{24}$ 216.1876, found 216.1871.

16: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 6.83−6.81 (m, 2H), 2.81−2.74 (m, 4H), 2.60−2.51 (m, 4H), 1.60−1.12 (m, 40H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 144.8, 144.0, 140.8, 127.1, 126.3, 120.3, 96.7, 78.2, 35.0, 34.9, 33.9, 30.6, 29.8, 29.0, 28.7, 27.6, 27.31, 27.27, 27.23, 27.17, 27.14, 27.08, 26.9, 26.5, 26.1, 25.9, 25.8, 25.7, 25.1, 19.4; IR (KBr) 2939, 2855, 1684, 1638, 1605, 1460, 1352, 1335, 1294 cm^{-1}; HRMS calcd for $C_{32}H_{50}$ 434.3913, found 434.3893. Anal. Calcd for $C_{32}H_{50}$: C, 88.41; H, 11.59. Found: C, 88.34; H, 11.47.

17: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.81 (dt, J = 10.5, 7.7 Hz, 1H), 5.45 (d, J = 10.5 Hz, 1H), 2.40 (brs, 2H), 2.36−2.28 (m, 2H), 1.57−1.35 (m, 20H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ142.7, 109.5, 94.2, 77.8, 30.0, 28.1, 27.6, 27.2, 27.1, 26.9, 26.6, 26.50, 26.48, 25.9, 25.8, 25.8, 19.2; IR (neat) 3018, 2928, 2856, 2683, 2210, 1616, 1460, 1443, 1396, 1367, 1348, 1327, 1292, 1101, 737 cm^{-1}; HRMS calcd for $C_{16}H_{26}$ 218.2033, found 218.2041. Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.92; H, 12.18.

18: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 6.94 (d, J = 13.1 Hz, 2H), 3.23−3.12 (m, 1H), 3.02−2.66 (m, 3H), 2.51−2.43 (m, 4H), 1.75−0.82 (m, 34H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 143.0, 142.4, 137.3, 128.8, 126.6, 123.3, 96.7, 78.8, 34.3, 32.8, 32.0, 31.2, 31.1, 29.4, 28.6, 27.64, 27.58, 27.4, 27.2, 26.6, 26.5, 25.4, 25.1, 23.2, 22.0, 19.4; IR (neat) 2955, 2928, 2856, 1460, 1413, 1377, 1327, 1103, 816, 727 cm^{-1}; HRMS calcd for $C_{28}H_{44}$ 380.3443, found 380.3452. Anal. Calcd for $C_{28}H_{44}$: C, 88.35; H, 11.65. Found: C, 88.21; H, 11.86.

19: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.46−7.35 (m, 4H), 7.23−7.13 (m, 6H), 7.07−7.03 (m, 2H), 3.36−3.29 (m, 1H), 2.70−2.56 (m, 2H), 2.49−2.39 (m, 1H), 1.98−1.82 (m, 1H), 1.74−1.60 (m, 1H), 1.34−0.92 (m, 18H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 144.7, 142.3, 140.9, 137.8, 131.11, 131.05, 129.6, 129.5, 128.4, 128.0, 127.8, 127.6, 127.4, 126.7, 123.9, 122.7, 96.5, 88.8, 34.4, 32.6, 28.8, 28.7, 27.7, 27.6, 27.4, 26.7, 26.6, 25.5, 25.4; IR (KBr) 3051, 2922, 2855, 1595, 1570, 1508, 1491, 1458, 1441, 1412, 1261, 1155, 1069, 1026, 910, 754, 700, 689, 662, 640, 596, 527, 507 cm^{-1}; HRMS calcd for $C_{32}H_{36}$ 420.2817, found 420.2801. Anal. Calcd for $C_{32}H_{36}$: C, 91.37; H, 8.63. Found: C, 91.32; H, 8.70.

20: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 6.96 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 3.24−3.14 (m, 1H), 3.05−2.94 (m, 1H), 2.88−2.70 (m, 2H), 2.57−2.42 (m, 4H), 1.74−0.82 (m, 40H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 142.8, 142.6, 137.3, 128.7, 126.7, 123.3, 96.5, 78.9, 34.5, 32.2, 31.2, 30.7, 29.5, 28.8, 28.6, 27.9, 27.7, 27.5, 27.4, 27.3, 27.1, 27.0, 26.63, 26.57, 26.2, 26.1, 25.8, 25.5, 25.3, 24.6, 19.2; IR (neat) 2928, 2857, 1558, 1541, 1508, 1458, 1418, 1348, 816, 723 cm^{-1}; HRMS calcd for $C_{32}H_{50}$ 434.3912, found 434.3910.

22: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.29−7.25 (m, 1H), 6.98−6.90 (m, 2H), 2.77−2.72 (m, 2H), 2.57−2.48 (m, 4H), 1.58−1.28 (m, 28H), 0.87 (t, J = 6.5 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 144.5, 142.5, 132.1, 128.3, 125.5, 120.5, 92.5, 79.6, 35.9, 34.7, 31.7, 31.3, 30.7, 29.0, 28.5, 27.5, 27.14, 27.10, 26.5, 26.3, 25.7, 25.0, 22.6, 19.3, 14.1; IR (neat) 2928, 2856, 2683, 2226, 1896, 1609, 1560, 1495, 1460, 1445, 1350, 1331, 891, 826, 723 cm^{-1}; HRMS calcd for $C_{26}H_{40}$ 352.3130, found 352.3124. Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.68; H, 11.70.

24: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.23−6.98 (m, 3H), 2.82−2.72 (m, 4H), 2.54 (t, J = 6.0 Hz, 2H), 1.62−1.33 (m, 28H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 145.1, 144.9, 126.9, 125.8, 125.4, 122.7, 97.3, 77.8, 35.13, 35.07, 31.8, 30.7, 30.6, 29.4, 28.6,m 27.6, 27.08, 27.04, 26.6, 26.4, 26.3, 25.8, 25.0, 22.7, 19.3, 14.2; IR (neat) 3061, 2928, 2856, 2683, 2224, 1925, 1574, 1460, 1377, 1350, 1329, 1298, 1165, 1111, 789, 752, 723 cm^{-1}; HRMS calcd for $C_{26}H_{40}$ 352.3129, found 352.3137. Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.73; H, 11.54.

26: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.58−7.55 (m, 2H), 7.40−7.28 (m, 3H), 7.00−6.99 (m, 2H), 2.85−2.79 (m, 2H), 2.34−2.30 (m, 5H), 1.63−1.34 (m, 20H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 145.4, 144.1, 136.8, 129.4, 127.9, 127.7, 127.4, 126.8, 96.3, 78.5, 35.2, 30.8, 28.2, 27.7, 27.1, 26.32, 26.29, 25.8, 25.0, 21.4, 19.1; IR (neat) 3082, 3057, 3026, 2930, 2856, 2681, 2226, 1942, 1800, 1751, 1603, 1578, 1562, 1497, 1462, 1441, 1350, 1331, 1178, 1155, 1074, 1030, 914, 864, 775, 754, 698, 579 cm^{-1}; HRMS calcd for $C_{27}H_{34}$ 358.2661, found 358.2648. Anal. Calcd for $C_{27}H_{34}$: C, 90.44; H, 9.56. Found: C, 90.09; H, 9.66.

27: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.47−7.43 (m, 2H), 7.35−7.29 (m, 3H), 5.86 (t, J = 7.8 Hz, 1H), 2.44−2.37 (m, 2H), 2.29−2.25 (m, 2H), 1.64−1.31 (m, 16H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 140.22, 140.16, 131.4, 128.2, 127.7, 124.0, 122.2, 93.4, 88.3, 36.2, 30.4, 27.1, 26.3, 25.9, 25.3, 24.8, 24.3, 24.2; IR (neat) 3080, 3055, 3018, 2926, 2856, 2202, 1595, 1572, 1489, 1462, 1443, 1375, 1346, 1327, 1259, 1157,. 1103, 1069, 1026, 910, 862, 754, 732, 691 cm^{-1}; HRMS calcd for $C_{20}H_{26}$ 266.2034, found 266.2044.

28: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.59 (d, J = 6.8 Hz, 2H), 7.41−7.31 (m, 3H), 7.07 (s, 1H), 2.96−2.90 (m, 2H), 2.79−2.66 (m, 4H), 2.34−2.29 (t, J = 6.7 Hz, 2H), 1.72−1.31 (m, 24H), 1.01 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ144.2, 141.77, 141.71, 140.8, 137.5, 129.4, 128.6, 127.4, 126.6, 119.8, 96.0, 79.3, 33.1, 31.9, 31.1, 30.7, 30.0, 29.3, 28.0, 27.8, 27.4, 27.2, 26.6, 23.5, 23.2, 22.5, 21.9, 19.3, 14.0, 13.7; IR (neat) 3084, 3057, 2954, 2927, 2860, 1600, 1544, 1496, 1405, 1458, 1421, 1398, 1377, 1353, 1342, 1328, 1296, 1105, 1074, 1031, 927, 891, 763, 725 cm^{-1}; HRMS calcd for $C_{32}H_{44}$ 428.3443, found 428.3448. Anal. Calcd for $C_{32}H_{44}$: C, 89.66; H, 10.34. Found: C, 89.62; H, 10.59.

29: ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 7.42−7.38 (m, 2H), 7.31−7.21 (m, 3H), 5.94−5.89 (t, J = 8.1 Hz, 1H), 2.30−2.17 (m, 4H), 1.73−1.29 (m, 16H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 138.8, 131.3, 128.0, 127.4, 123.9, 123.2, 91.6, 86.5, 27.0, 26.8, 25.7, 25.3, 24.54, 24.47, 24.3, 24.2, 22.3, 22.2; IR (neat) 3080, 2928, 2855, 2201, 1597, 1570, 1489, 1468, 1443, 1346, 1294, 1069, 1026, 951, 910, 883, 754, 727, 691 cm^{-1}; HRMS calcd for $C_{20}H_{26}$ 266.2035, found 266.2036. Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.79; H, 10.00.

Supporting Information Available: ^{1}H NMR charts for the compounds **12**, **14**, **15**, **20**, and **27** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0016531