JOC Note

Highly Efficient Allyl Cross-Coupling Reactions of Allylindiums with Organic Electrophiles

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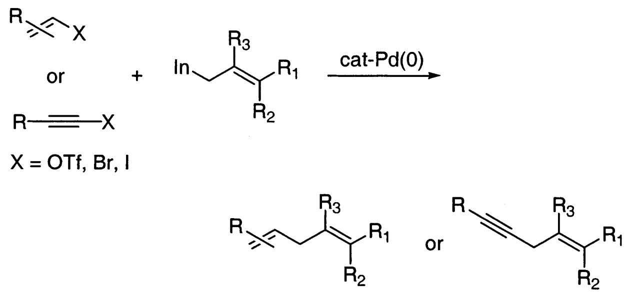
Abstract: This paper describes highly efficient allyl cross-coupling reactions of allylindiums with organic electrophiles such as aryl and vinyl triflates, vinyl halides, dibromoolefin, and alkynyl iodide. The reactions were carried out using 4 mol % Pd(PPh_3)$_4$ in the presence of 3 equiv of LiCl in DMF at 100 °C under a nitrogen atmosphere. Allylindium, generated from the reaction of 1 equiv of indium with 1.5 equiv of allyl halide, gave the best result as a coupling partner. The present method is mild and simple to apply, and it produces a diverse range of allylic compounds in good to excellent yields.

Coupling reactions of organometallic compounds with organic electrophiles catalyzed by transition metals have received much attention in the area of synthetic methods for C−C bond formation.[1] Especially, allyl cross-coupling reactions have been focused on in recent years because the double bond can be further functionalized.[2] One of the most frequently used methods for allyl cross-coupling reactions is the use of allylstannane for coupling partners, which has attracted much attention as a result of its availability as well as its air- and moisture-stability, and its compatibility with a variety of functional groups. Using allylstannanes for nucleophilic coupling partners, however, is faced with several limitations: (1) difficulties associated with the preparation of regiochemically defined allylstannanes, (2) its tendency to undergo allylic isomerization, (3) tin removal from the product, and (4) tin toxicity.[2b,3] On the other hand, the Pd-catalyzed reaction of allylmetals containing Mg, Zn, or Al with aryl and alkenyl halides has not given the desired cross-coupling products in high yields. Inhibition of Pd catalysis by the allylmetal reagents may be suspected, since the charge-affinity-inverted reaction of aryl and alkenylmetals with ally electrophiles is highly satisfactory.[1e] Therefore, overcoming these difficulties is a prerequisite for developing new allylmetals as coupling partners. In connection with our current research interest in the synthetic utility of organoindium,[4] we had previously reported on Pd-catalyzed cross-coupling reactions of allylindiums with aryl halides.[5,6] Here we examine the feasibility and efficiency of Pd-catalyzed allyl cross-coupling reactions of in situ generated allylindiums with a variety of organic electrophiles such as aryl and vinyl triflates, vinyl halides, dibromoolefin, and alkynyl iodide (Scheme 1).

SCHEME 1



Of the catalytic systems screened, the best results were obtained with 4 mol % Pd(PPh_3)$_4$ in the presence of 3 equiv of LiCl in DMF at 100 °C under a nitrogen atmosphere. Allylindium, in situ generated from the reaction of 1 equiv of indium with 1.5 equiv of allyl halide, gave the best result as a coupling partner. To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a variety of allyl halides and organic electrophiles such as aryl and vinyl triflates, vinyl halide, dibromoolefin, and alkynyl iodide. The presence of various alkyl substituents at the α and γ position did not diminish the efficiency and selectivity for the allyl halides as coupling partners. The results are summarized in Table 1. Under the optimized conditions,

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(4) (a) Lee, P. H.; Bang, K.; Lee, K.; Lee, C.-H.; Chang, S. *Tetrahedron Lett.* **2000**, *41*, 7521. (b) Lee, P. H.; Ahn, H.; Lee, K.; Sung, S.-Y.; Kim, S. *Tetrahedron Lett.* **2001**, *42*, 37. (c) Lee, P. H.; Lee, K.; Kim, S. *Org. Lett.* **2001**, *3*, 3205. (d) Lee, P. H.; Bang, K.; Ahn, H.; Lee, K. *Bull. Korean Chem. Soc.* **2001**, *22*, 1385. (e) Lee, P. H.; Seomoon, S.; Lee, K. *Bull. Korean Chem. Soc.* **2001**, *22*, 1380. (f) Lee, P. H.; Lee, K.; Sung, S.-Y.; Chang, S. *J. Org. Chem.* **2001**, *66*, 8646. (g) Lee, P. H.; Lee, K.; Chang, S. *Synth. Commun.* **2001**, *31*, 3189. (h) Lee, P. H.; Bang, K.; Lee, K.; Sung, S.-Y.; Chang, S. *Synth. Commun.* **2001**, *31*, 3781. (i) Lee, P. H.; Sung, S.-Y.; Lee, K.; Chang, S. *Synlett* **2002**, 146.

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(6) For some previously reported examples of indium-mediated cross-coupling reactions, see: (a) Nomura, R.; Miyazaki, S.-I.; Matsuda, H. *J. Am. Chem. Soc.* **1992**, *114*, 2738. (b) Perez, I.; Sestelo, J. P.; Sarandeses, L. A. *Org. Lett.* **1999**, *1*, 1267. (c) Gelman, D.; Schumann, H.; Blum, J. *Tetrahedron Lett.* **2000**, *41*, 7555. (d) Perez, I.; Sestelo, J. P.; Sarandeses, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 4155. (e) Hirashita, T.; Yamamura, H.; Kawai, M.; Araki, S. *Chem. Commun.* **2001**, 387. (f) Takami, K.; Yorimitsu, H.; Shnokubo, H.; Matsubara, S.; Oshima, K. *Org. Lett.* **2001**, 3, 1997. (g) Lee, P. H.; Sung, S.-Y.; Lee, K. *Org. Lett.* **2001**, *3*, 3201.

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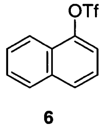
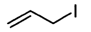
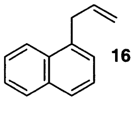
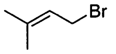
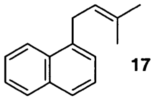
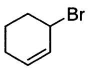
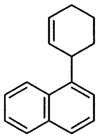
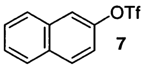
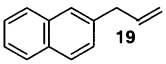
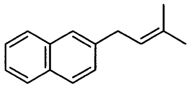
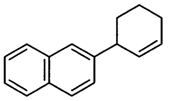
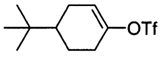
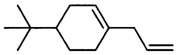
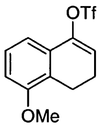
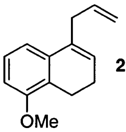
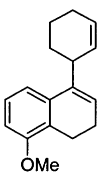
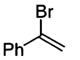
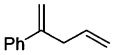
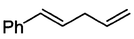
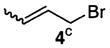
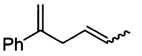
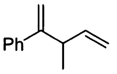
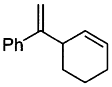
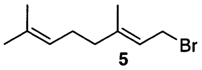
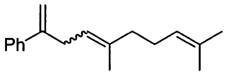
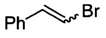
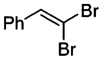
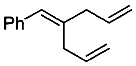
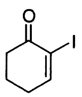
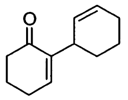
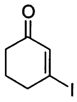
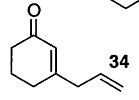
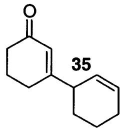
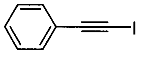
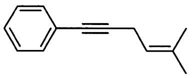
TABLE 1. Pd-Catalyzed Allyl Cross-Coupling Reactions of Allylindiums with Organic Electrophiles

Entry	Organic Electrophiles	Allyl Halides	Product	Isolated Yield (%)
1	 **6**	 **1**	 **16**	92
2	**6**	 **2**	 **17**	87
3	**6**	 **3**	 **18**	87
4	 **7**	**1**	 **19**	92[a]
5	**7**	**2**	 **20**	87[a]
6	**7**	**3**	 **21**	87[a]
7	 **8**	**1**	 **22**	93
8	 **9**	**1**	 **23**	84[a]
9	**9**	**3**	 **24**	73[a]
10	 **10**	**1**	 **25**  **26**	97(2:1)[b]
11	**10**	 **4**[c]	 **27**  **28**	89(1.9[d]:1)[e]
12	**10**	**3**	 **29**	91
13	**10**	 **5**	 **30**	97(1:1)[f]
14	 **11**[g]	**1**	 **31**	96(1:4)[f]
15	 **12**	**1**	 **32**	92[a,h]
16	 **13**	**3**	 **33**	89
17	 **14**	**1**	 **34**	88 77[i]
18	**14**	**3**	 **35**	96
19	 **15**	**2**	 **36**	82[a]

[a] 2 mol % $Pd_2dba_3CHCl_3$/16 mol % PPh_3 was used as catalyst. [b] Isomeric ratio of **25** and **26**. [c] Isomeric ratio of crotyl bromide: cis:trans = 1:5. [d] Isomeric ratio of **27**: cis:trans = 1:1. [e] **27**(α):**28**(γ) ratio. [f] Cis:trans ratio. [g] Isomeric ratio of β-bromostyrene: cis:trans = 1:4. [h] 2 equiv of In and 3 equiv of allyl iodide were used. [i] Pd(0) catalyst was not used. Yield of 1-allyl-3-iodo-2-cyclohexenol.

6 was treated with allyl iodide and indium to produce **16** in 92% yield (entry 1). Whereas addition of prenylindium to carbonyl groups usually yielded the product resulting from γ-attack,[7] we found that the reaction of **6** with prenylindium regioselectively produced **17** resulting from α-attack due to the steric effect in 87% yield (entry 2). The reaction of **7** with 3-bromocyclohexene in the presence of indium afforded 2-(2′-cyclohexenyl)naphthalene in 87% yield (entry 6). Vinyl triflates worked equally well with allylindiums (entries 7−9), producing allylic compounds in good to excellent yield. α-Bromostyrene was treated with allylindium to give 2-phenyl-1,4-pentadiene and *trans*-1-phenyl-1,4-pentadiene in 65% and 32% yields, respectively. Although mechanism of formation of *trans*-1-phenyl-1,4-pentadiene is not clear at the present time, we believe that 1,4-diene **26** was produced via oxidative addition of Pd(0) to α-bromostyrene, dehydropalladation due to steric effect to produce phenylacetylene, hydropalladation to phenylacetylene, followed by the allyl cross-coupling reaction (entry 10).[8] The reaction of α-bromostyrene with crotyl bromide (cis:trans = 1:5) in the presence of indium produced a 1.9:1 mixture of α (cis:trans = 1:1, **27**) and γ products (**28**), but the product resulting from α attack predominated (entry 11). Treatment of **10** with geranylindium produced the desired product **30** in 97% yield (entry 13). The reaction of β-bromostyrene (cis:trans = 1:4) with allylindium gave cross-coupling product 1-phenyl-1,4-pentadiene (cis:trans = 1:4, **31**) in 96% yield (entry 14). In the case of β,β-dibromostyrene (**12**),[9] double cross-coupling product **32** was obtained in 92% yield with 2 equiv of allylindium (entry 15). It should be noted that 2-iodo or 3-iodo-2-cyclohexen-1-one having a labile ketone group toward allylindium provided the desired products **33** and **34** in good yields (entries 16 and 17), respectively. The reaction of **14** with allylindium in the absence of Pd(0) produced 1-allyl-3-iodo-2-cyclohexenol in 77% yield. These results mean that 3-allyl-2-cyclohexen-1-one was produced not via 1,4-addition of allylindium followed by an elimination reaction, but through a Pd-catalyzed cross-coupling reaction. Treatment of iodophenylacetylene[10] with prenylindium regioselectively produced 5-methyl-1-phenyl-4-hexen-1-yne in 82% yield (entry 19).

In conclusion, we have shown here several noteworthy features (availability, ease of preparation and handling, high reactivity as well as selectivity, and operational simplicity) of allylindium reagents for the cross-coupling reaction. The present method is mild and simple to apply, and it produces a diverse range of allylic compounds in good to excellent yields. This protocol can be readily applied to cross-coupling reactions with aryl and vinyl triflates, vinyl halides, dibromoolefin, and alkynyl iodide.

Experimental Section

Typical Experimental Procedure. To a suspension of $Pd(PPh_3)_4$ (23.0 mg, 4 mol %) and lithium chloride (63.5 mg, 1.5 mmol) in DMF (1 mL) was added trifluoromethanesulfonic acid naphthalen-1-yl ester (138.1 mg, 0.5 mmol) at room temperature under a nitrogen atmosphere. After 15 min, allyl indium, which is generated from allyl iodide (126.0 mg, 0.75 mmol) and indium (57.0 mg, 0.5 mmol) in DMF (1 mL), was added and the mixture was stirred at 100 °C for 1 h. The reaction mixture was quenched with $NaHCO_3$ (saturated aqueous). The aqueous layer was extracted with ether (3 × 20 mL), and the combined organics were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane to give 1-allylnaphthalene (77.3 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.08 Hz, 1H), 7.83 (t, J = 7.76 Hz, 1H), 7.72 (d, J = 6.89 Hz, 1H), 7.50−7.42 (m, 2H), 7.39 (d, J = 7.25 Hz, 1H), 7.32 (d, J = 6.89 Hz, 1H), 6.16−6.65 (m, 1H), 5.11−5.06 (m, 2H), 3.82 (d, J = 6.30 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.13, 133.27, 132.01, 130.15, 126.84, 125.13, 124.44, 123.96, 123.77, 123.68, 122.19, 114.33, 35.43; IR (film) 3003, 2916, 1684, 1606, 1414, 1358 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}$ M^+ 168.0939, found 168.0934.

1-Prenylnaphthalene (17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.04 Hz, 1H), 7.85 (d, J = 9.05 Hz, 1H), 7.71 (d, J = 8.11 Hz, 1H), 7.49 (m, 2H), 7.40 (dd, J = 7.91, 7.25 Hz, 1H), 7.33 (d, J = 6.83 Hz, 1H), 5.40 (t, J = 6.92 Hz, 1H), 3.77 (d, J = 6.92 Hz, 2H), 1.80 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.78, 133.85, 132.69, 132.04, 128.30, 126.56, 125.71, 125.64, 125.58, 125.44, 124.00, 122.88, 31.78, 25.74, 17.95; IR (film) 3053, 2986, 2305, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}$ M^+ 196.1252, found 196.1251.

1-(2′-Cyclohexenyl)naphthalene (18): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.27 Hz, 1H), 7.87 (d, J = 8.07 Hz, 1H), 7.72 (d, J = 7.76 Hz, 1H), 7.53−7.38 (m, 4H), 6.04−5.99 (m, 1H), 5.83 (dd, J = 9.98, 1.80 Hz, 1H), 4.24−4.22 (m, 3H), 2.21−2.11 (m, 3H), 1.76−1.66 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.78, 133.85, 132.69, 132.04, 128.30, 126.56, 125.71, 125.64, 125.58, 125.44, 124.00, 122.88, 31.78, 25.74, 17.95; IR (film) 3053, 2978, 2870, 2305, 1422 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{16}$ M^+ 208.1252, found 208.1256.

2-Allylnaphthalene (19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.77 (m, 3H), 7.63 (s, 1H), 7.49−7.40 (m, 3H), 7.33 (dd, J = 8.46, 1.42 Hz, 1H), 6.05 (ddt, J = 16.98, 10.09, 6.77 Hz, 1H), 5.16−5.11 (m, 2H), 3.55 (d, J = 6.66 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.55, 137.32, 133.65, 132.12, 128.04, 127.62, 127.48, 127.39, 126.66, 125.93, 125.27, 40.36; IR (film) 3003, 2916, 1684, 1606, 1414, 1358 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}$ M^+ 168.0939, found 168.0934.

2-Prenylnaphthalene (20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.78 (m, 3H), 7.64 (s, 1H), 7.49−7.35 (m, 2H), 7.36 (d, J = 8.33 Hz, 1H), 5.45 (t, J = 10.24 Hz, 1H), 3.54 (d, J = 7.31 Hz, 2H), 1.82 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.76, 134.13, 133.26, 128.29, 128.01, 127.86, 127.80, 126.51, 126.26, 125.47, 123.46, 34.97, 26.22, 18.33; IR (film) 3691, 3054, 2986, 2305, 1422, 1270 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}$ M^+ 196.1252, found 196.1258.

2-(2′-Cyclohexenyl)naphthalene (21): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.77 (m, 3H), 7.64 (s, 1H), 7.46−7.36 (m, 3H), 5.97−5.94 (m, 1H), 5.81 (dd, J = 10.04, 1.42 Hz, 1H), 3.56 (s, 1H), 2.12−2.05 (m, 3H), 1.81−1.70 (m, 1H), 1.67−1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.05, 133.54, 132.15, 130.05, 128.64, 127.84, 127.58, 127.55, 126.71, 125.81, 125.79, 125.14, 41.90, 32.41, 25.09, 21.12; IR (film) 3053, 2978, 2870, 2305, 1422 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{16}$ M^+ 208.1252, found 208.1256.

1-Allyl-4-(*tert*-butyl)-1-cyclohexene (22): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, J = 16.1, 9.96, 6.89 Hz, 1H), 5.43 (d, J = 3.61 Hz, 1H), 5.02 (d, J = 15.33 Hz, 1H), 4.99 (d, J = 8.31 Hz, 1H), 2.68 (d, J = 6.66 Hz, 2H), 2.05−1.74 (m, 5H), 1.26−1.12 (m, 2H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.99, 136.14, 122.08, 115.41, 44.15, 42.01, 32.20, 29.83, 27.25, 26.87, 24.26; IR (film) 3054, 2862, 2305, 1637, 1423, 1267 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{22}$ M^+ 178.1721, found 178.1717.

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4-Allyl-8-methoxy-1,2-dihydronaphthalene (23): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (d, J = 7.86 Hz, 1H), 6.92 (d, J = 7.86 Hz, 1H), 6.79 (d, J = 8.20 Hz, 1H), 5.95 (ddt, J = 16.70, 10.17, 6.35 Hz, 1H), 5.90−5.88 (m, 1H), 5.11 (dd, J = 17.16, 1.58 Hz, 1H), 5.06 (dd, J = 10.07, 1.58 Hz, 1H), 3.83 (s, 3H), 3.18 (dd, J = 6.36, 1.28 Hz, 2H), 2.76 (t, J = 8.07 Hz, 2H), 2.27−2.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.02, 136.79, 135.91, 134.47, 126.17, 124.40, 115.96, 115.89, 109.46, 55.48, 37.37, 22.53, 19.89; IR (film) 3054, 2986, 1573, 1422, 1263 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{16}O$ M$^+$ 200.1201, found 200.1202.

4-(2′-Cyclohexenyl)-8-methoxy-1,2-dihydronaphthalene (24): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (t, J = 8.03 Hz, 1H), 7.00 (d, J = 9.82 Hz, 1H), 6.78 (d, J = 8.19 Hz, 1H), 5.89−5.82 (m, 2H), 5.68−5.64 (m, 1H), 3.83 (s, 3H), 3.43 (s, 1H), 2.83−2.62 (m, 2H), 2.25−2.19 (m, 2H), 2.04−1.86 (m, 3H), 1.70−1.53 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.59, 139.78, 136.19, 130.48, 128.45, 126.61, 126.22, 125.44, 115.94, 109.66, 55.96, 37.05, 31.78, 29.10, 25.74, 22.94, 20.64, 20.40; IR (film) 3054, 2986, 2305, 1422, 1265 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{20}O$ M$^+$ 240.1514, found 240.1510.

2-Phenyl-1,4-pentadiene (25): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, J = 7.15 Hz, 2H), 7.36−7.42 (m, 3H), 5.94−5.86 (m, 1H), 5.39 (s, 1H), 5.12 (d, J = 13.69 Hz, 1H), 5.10 (s, 1H), 5.07 (d, J = 8.60 Hz, 1H), 3.25 (d, J = 6.49 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.33, 140.94, 136.20, 128.25, 127.44, 125.99, 116.46, 113.15, 39.51; IR (film) 3053, 2986, 2305, 1422, 1265 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}$ M$^+$ 144.0939, found 144.0935.

***trans*-1-Phenyl-1,4-pentadiene (26):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36−7.19 (m, 5H), 6.41 (d, J = 15.90 Hz, 1H), 6.23 (dt, J = 15.77, 6.66 Hz, 1H), 5.96−5.86 (m, 1H), 5.11 (d, J = 17.13 Hz, 1H), 5.07 (d, J = 10.12 Hz, 1H), 2.96 (t, J = 7.04 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.62, 136.47, 130.85, 128.49, 128.18, 127.02, 126.04, 115.67, 37.00; IR (film) 3053, 2986, 2395, 1421, 1270 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}$ M$^+$ 144.0939, found 144.0935.

2-Phenyl-1,4-hexadiene (27): ^{1}H NMR (400 MHz, CDCl$_3$) cis/trans mixture δ 7.44−7.24 (m, 5H), 5.60−5.46 (m, 4H), 5.36 (s, 1H), 5.34 (s, 1H), 5.10 (s, 1H), 5.08 (s, 1H), 3.21 (d, J = 6.99 Hz, 2H), 3.17 (s, 2H), 1.67 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) cis isomer δ 147.16, 141.30, 128.13, 127.39, 126.98, 126.00, 125.45, 112.43, 32.77, 12.81, trans isomer δ 146.80, 114.17, 128.22, 127.92, 127.35, 126.66, 125.99, 112.62, 41.85, 19.25; IR (film) 3053, 2986, 2305, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}$ M$^+$ 158.1096, found 158.1091 (cis isomer), 158.1091 (trans isomer).

3-Methyl-2-phenyl-1,4-pentadiene (28): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44−7.24 (m, 5H), 5.91 (ddd, J = 17.06, 10.39, 6.67 Hz, 1H), 5.26 (s, 1H), 5.08 (s, 1H), 5.07 (d, J = 15.06 Hz, 1H), 5.01 (d, J = 10.59 Hz, 1H), 3.40 (quint, J = 6.85 Hz, 1H), 1.21 (d, J = 6.98 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.65, 142.38, 142.20, 128.62, 128.15, 127.20, 113.67, 112.14, 38.31, 17.95; IR (film) 3053, 2986, 2305, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}$ M$^+$ 158.1096, found 158.1094.

α-(2′-Cyclohexenyl)styrene (29): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40−7.23 (m, 5H), 5.86−5.82 (m, 1H), 5.73−5.70 (m, 1H), 5.29 (s, 1H), 5.05 (s, 1H), 2.04−1.99 (m, 2H), 1.83−1.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.44, 141.99, 128.24, 128.18, 128.01, 127.16, 126.56, 113.06, 39.87, 28.39, 25.24, 20.29; IR (film) 3053, 2986, 1531, 1351, 1267 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{16}$ M$^+$ 184.1252, found 184.1251.

5,9-Dimethyl-2-phenyl-1,4,8-decatriene (30): ^{1}H NMR (400 MHz, CDCl$_3$) cis isomer δ 7.45−7.24 (m, 5H), 5.32 (s, 1H), 5.26−5.22 (m, 1H), 5.13−5.11 (m, 1H), 5.07 (t, J = 1.39 Hz, 1H), 2.09−2.10 (m, 4H), 1.72 (s, 3H), 1.69 (s, 3H), 1.66 (s, 3H), trans isomer δ 7.45−7.24 (m, 5H), 5.32 (s, 1H), 5.26−5.22 (m, 1H), 5.09−5.05 (m, 1H), 5.07 (t, J = 1.39 Hz, 1H), 3.18 (d, J = 6.86 Hz, 2H), 1.72 (s, 3H), 1.69 (s, 3H), 5.40 (t, J = 6.92 Hz, 1H), 3.77 (d, J = 6.92 Hz, 2H), 2.09−2.01 (m, 4H), 1.65 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) cis isomer δ 147.46, 141.47, 136.88, 131.67, 128.20, 127.50, 126.01, 124.20, 122.47, 112.28, 33.59, 32.02, 26.50, 25.73, 17.66, 16.03, trans isomer δ 147.19, 141.54, 136.80, 131.42, 128.18, 127.29, 126.23, 124.25, 121.89, 112.12, 39.71, 33.78, 26.59, 25.70, 23.43, 17.69; IR (film) 3054, 2986, 2305, 1674, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{24}$ M$^+$ 240.1878, found 240.1877 (cis isomer), 240.1877 (trans isomer).

1-Phenyl-1,4-pentadiene (31): ^{1}H NMR (400 MHz, CDCl$_3$) cis isomer δ 7.36−7.19 (m, 5H), 6.52 (d, J = 11.57 Hz, 1H), 5.96−5.86 (m, 1H), 5.71 (dt, J = 11.54, 7.57 Hz, 1H), 5.11 (d, J = 17.13 Hz, 1H), 5.07 (d, J = 10.12 Hz, 1H), 3.06 (t, J = 9.02 Hz, 2H), trans isomer δ 7.36−7.19 (m, 5H), 6.41 (d, J = 15.90 Hz, 1H), 6.23 (dt, J = 15.77, 6.66 Hz, 1H), 5.96−5.86 (m, 1H), 5.11 (d, J = 17.13 Hz, 1H), 5.07 (d, J = 10.12 Hz, 1H), 2.96 (t, J = 7.04 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) cis isomer δ 137.29, 136.66, 130.05, 129.47, 128.63, 128.17, 126.71, 115.28, 32.70, trans isomer δ 137.62, 136.47, 130.85, 128.49, 128.18, 127.02, 126.04, 115.67, 37.00; IR (film) 3053, 2986, 2305, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}$ M$^+$ 144.0939, found 144.0933 (cis isomer), 144.0935 (trans isomer).

2-Allyl-1-phenyl-1,4-pentadiene (32): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33−7.18 (m, 5H), 6.41 (s, 1H), 5.93−5.83 (m, 2H), 5.12 (d, J = 8.32 Hz, 2H), 5.07 (d, J = 15.97 Hz, 2H), 2.99 (d, J = 5.94 Hz, 2H), 2.92 (d, J = 6.76 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.97, 132.73, 131.16, 128.47, 127.71, 126.23, 121.03, 115.97, 40.91, 34.93; IR (film) 3054, 2987, 1530, 1423, 1267 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{16}$ M$^+$ 184.1252, found 184.1250.

2-(2′-Cyclohexenyl)-2-cyclohexen-1-one (33): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.71 (t, J = 4.22 Hz, 1H), 5.87−5.82 (m, 1H), 5.45−5.41 (m, 1H), 3.44 (s, 1H), 2.44 (t, J = 6.54 Hz, 2H), 2.38 (q, J = 10.32 Hz, 2H), 2.01−1.96 (m, 4H), 1.88−1.81 (m, 1H), 1.59−1.50 (m, 2H), 1.33−1.26 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.81, 145.56, 143.04, 129.17, 128.85, 38.80, 33.36, 28.90, 26.12, 25.12, 23.09, 20.07; IR (film) 3053, 2986, 2305, 1733, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}O$ M$^+$ 176.1201, found 176. 1199.

3-Allyl-2-cyclohexen-1-one (34): ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.77 (s, 1H), 5.80 (ddt, J = 17.01, 10.25, 6.87 Hz, 1H), 5.16 (d, J = 10.25 Hz, 1H), 5.14 (d, J = 17.01 Hz, 1H), 2.95 (d, J = 6.87 Hz, 2H), 2.39 (t, J = 7.59 Hz, 2H), 2.30 (t, J = 6.00 Hz, 2H), 2.00 (quint, J = 6.25 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.91, 164.21, 133.26, 126.28, 118.31, 42.22, 37.32, 29.48, 22.63; IR (film) 3055, 2985, 2305, 1733, 1422, 1265 cm^{-1}; HRMS (EI) calcd for $C_9H_{12}O$ M$^+$ 136.0888, found 136.0885.

3-(2′-Cyclohexenyl)-2-cyclohexen-1-one (35): ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.88 (s, 1H), 5.87−5.85 (m, 1H), 5.52 (dd, J = 10.07, 2.28 Hz, 1H), 2.90−2.94 (m, 1H), 2.41−2.34 (m, 4H), 2.26−2.19 (m, 2H), 2.03−1.96 (m, 4H), 1.91−1.84 (m, 1H), 1.74−1.67 (m, 2H), 1.57−1.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.24, 169.57, 132.34, 129.77, 122.35, 43.28, 37.60, 37.54, 34.67, 31.60, 28.35, 20.64; IR (film) 3055, 2986, 1733, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}O$ M$^+$ 176.1201, found 176.1199.

5-Methyl-1-phenyl-1-hex-4-en-1-yne (36): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, J = 7.87 Hz, 2H), 7.40−7.31 (m, 3H), 5.40 (t, J = 6.82 Hz, 1H), 3.76 (d, J = 6.82 Hz, 1H), 1.80 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.70, 132.52, 129.21, 128.45, 121.80, 117.90, 81.55, 73.90, 42.50, 39.65; IR (film) 3540, 2986, 1422, 1269 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}$ M$^+$ 170.1096, found 170.1091.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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