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Rhodium-Catalyzed Reductive Cyclization of 1,6-Diynes and 1,6-Enynes Mediated by Hydrogen: Catalytic C−C Bond Formation via Capture of Hydrogenation Intermediates

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Abstract: Catalytic hydrogenation of carbon-, nitrogen- and oxygen-tethered 1,6-diynes **1a**−**9a** and 1,6-enynes **10a**−**18a** using cationic Rh(I) precatalysts at ambient temperature and pressure enables reductive carbocyclization to afford 1,2-dialkylidene cyclopentanes **1b**−**9b** and monoalkylidene cyclopentanes **10b**−**18b**, respectively, in good to excellent yields and as single alkene stereoisomers. Notably, the 1,3-diene and alkene containing cyclization products **1b**−**9b** and **10b**−**18b** are not subject to over-reduction under the conditions of catalytic hydrogenation in which they are formed. Reductive cyclization 1,6-diyne **1a** and 1,6-enyne **10a** performed under an atmosphere of D_2 provides the carbocyclization products *deuterio*-**1b** and *deuterio*-**10b**, respectively, which incorporate two deuterium atoms. The collective data are consistent with a catalytic mechanism involving heterolytic activation of elemental hydrogen ($H_2 + Rh^+X^- \rightarrow Rh{-}H + HX$) followed by Rh(I)-mediated oxidative cyclization of the 1,6-diyne or 1,6-enyne substrates to afford (hydrido)Rh(III)-based metallocyclopentadiene and metallocyclopentene intermediates, respectively. These transformations represent the first examples of metal-catalyzed reductive carbocyclization mediated by hydrogen.

Introduction

From the seminal studies of Sabatier[1] and Adams[2] to the more recent studies of Knowles[3] and Noyori,[4] catalytic hydrogenation is uniformly regarded as a method of reduction. Recent studies from our lab involving the capture of hydrogenation intermediates establish catalytic hydrogenation as a powerful and mechanistically novel strategy for catalytic C−C bond formation.[5] Specifically, under the neutral conditions of catalytic hydrogenation, the reductive coupling of conjugated enones,[5a−d] dienes,[5e] enynes,[5f] and diynes[5g] to carbonyl partners has been realized, including an enantioselective variant of the latter transformation. A key mechanistic feature of these transformations appears to involve the heterolytic activation of elemental hydrogen ($H_2 + M{-}X \rightarrow M{-}H + H{-}X$),[6,7] which enables monohydride-based catalytic cycles for which direct alkyl-hydrogen reductive elimination manifolds are disabled. Prior to our work, hydrogen-mediated catalytic reductive C−C bond formation was restricted to processes involving migratory insertion of carbon monoxide, such as alkene hydroformylation[8] and the Fischer−Tropsch reaction.[9]

Thus far, the "C−C bond forming hydrogenations" we have developed operate through the addition or insertion of C−O π-bonds.[5] As such, it became of interest to develop related transformations based on the capture of hydrogenation intermediates through migratory insertion of C−C π-bonds. Here, we disclose that catalytic hydrogenation of 1,6-diynes **1a**−**9a** and 1,6-enynes **10a**−**18a** using cationic rhodium(I) precatalysts at ambient temperature and pressure results in efficient cyclization to afford the corresponding 1,2-dialkylidenecyclopentane products **1b**−**9b** and monoalkylidene cyclopentanes **10b**−**18b**, respectively. *These results represent the first examples of the use of elemental hydrogen as a terminal reductant in metal-catalyzed reductive carbocyclization.*[10−13]

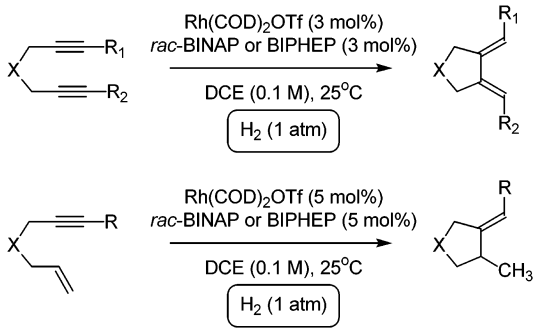

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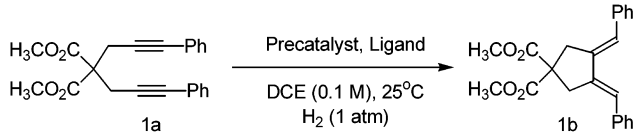
Table 1. Optimization of the Catalytic Reductive Cyclization of Diyne **1a** under Hydrogenation Conditions[a]



entry	catalyst (mol %)	ligand (mol %)	yield **1b** (recovered **1a**)[b,c]
1	$Rh(COD)_2OTf$ (10%)	BIPHEP (10%)	69%
2	$Rh(COD)_2OTf$ (5%)	BIPHEP (5%)	67%
3	$Rh(COD)_2OTf$ (3%)	BIPHEP (3%)	77%
4	$Rh(COD)_2OTf$ (1%)	BIPHEP (1%)	41% (41%)
5	$[Rh(COD)Cl]_2$ (1.5%)	BIPHEP (3%)	− (91%)
6	$Rh(COD)_2OTf$ (3%)	PPh_3 (6%)	− (91%)
7	$Rh(COD)_2BF_4$ (3%)	BIPHEP (3%)	81%
8	$Rh(COD)_2OTf$ (3%)	*rac*-BINAP (3%)	85%

[a] Procedure: See Experimental Section. [b] Isolated yields after purification by silica gel chromatography. [c] The structural assignment of **1b** is corroborated by single-crystal X-ray diffraction analysis.

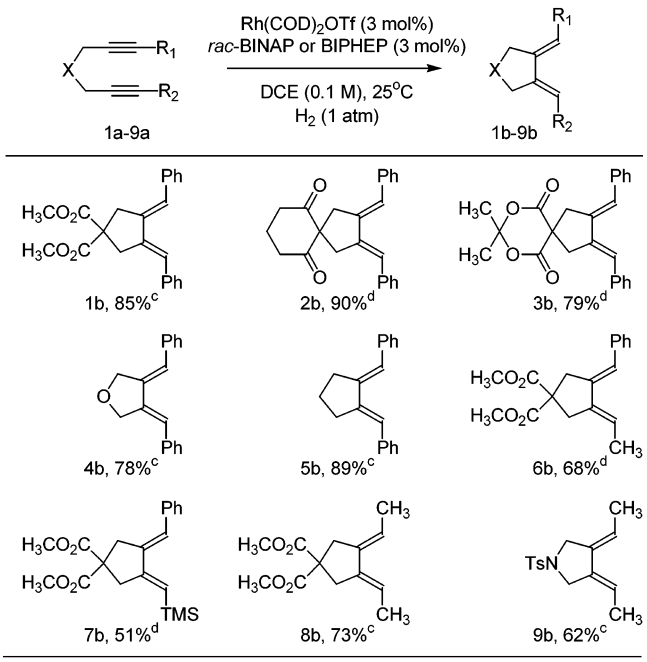
Results

To assess the feasibility of using hydrogen as a terminal reductant in carbocyclization, the reductive cyclization of 1,6-diyne **1a** was explored under the conditions of catalytic hydrogenation. Gratifyingly, upon exposure of **1a** to conditions identical to those employed for related 1,3-enyne−aldehyde couplings,[5f] the reductive cyclization product **1b** is produced in 67% isolated yield (Table 1, entry 2). While increased catalyst loading (10 mol %) does not enhance the yield of cyclization product (Table 1, entry 1), reactions performed at lower catalyst loadings (3 mol %) provide **1b** in 77% isolated yield (Table 1, entry 3). A further decrease in catalyst loading (1 mol %) results in incomplete consumption of **1a** (Table 1, entry 4). Consistent with the hypothesis that cationic rhodium catalysts are required for heterolytic activation of hydrogenation due to the enhanced acidity of the resulting hydrides,[14] the use of $[Rh(COD)Cl]_2$ under otherwise optimal conditions fails to produce reductive cyclization product **1b** (Table 1, entry 5). In contrast, use of $Rh(COD)_2BF_4$, an alternative cationic rhodium source, under otherwise optimal conditions, provides **1b** in 81% isolated chemical yield. As observed for the corresponding 1,3-enyne−aldehyde couplings,[5f] the catalyst is rendered inoperative upon use of monodentate phosphine ligands (Table 1, entry 6). Finally, upon screening diverse bidentate phosphine ligands, *rac*-BINAP was found to provide **1b** in higher yields than BIPHEP under otherwise identical conditions (Table 1, entry 8).

Under the conditions established for the reductive cyclization of 1,6-diyne **1a**, the cyclization of assorted 1,6-diynes was explored. Whereas certain substrates cyclize with greater efficiency using *rac*-BINAP as ligand, BIPHEP was preferable in other cases. As demonstrated by the reductive cyclization of substrates **1a**−**3a**, substrates that possess geminal substitution in the tether cyclize with great facility. However, as revelaed by the cyclization of substrates **4a** and **5a**, preorganization induced through Thorpe−Ingold effect[15] is not a prerequisite for high-yielding cyclization. Finally, substrates **6a**−**9a** establish applicability of this method to alkyl- and silyl-substituted alkynes. In the case of 1,6-diyne substrates, unsubstituted alkynes provide poor yields of cyclization product (Table 2).

The favorable results obtained for the catalytic reductive cyclization of diynes **1a**−**9a** under hydrogenation conditions

Table 2. Catalytic Reductive Cyclization of Diynes **1a**−**9a** under Hydrogenation Conditions[a,b]



[a] Procedure: See Experimental Section. [b] Isolated yields after purification by silica gel chromatography. [c] *rac*-BINAP was used as ligand. [d] BIPHEP was used as ligand.

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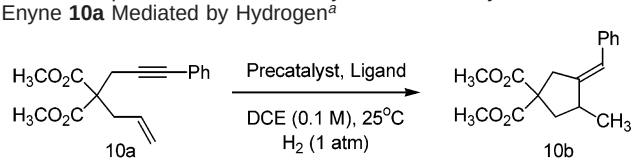
(15) For a review, see: Jung, M. E. *Synlett* **1999**, 843.

Table 3. Optimization of the Catalytic Reductive Cyclization of Enyne **10a** Mediated by Hydrogen[a]



entry	catalyst (mol %)	ligand (mol %)	yield **10b** (recovered **10a**)[b,c]
1	$Rh(COD)_2OTf$ (10%)	BIPHEP (10%)	87%
2	$Rh(COD)_2OTf$ (5%)	BIPHEP (5%)	89%
3	$Rh(COD)_2OTf$ (3%)	BIPHEP (3%)	80%
4	$Rh(COD)_2BF_4$ (3%)	BIPHEP (3%)	91%
5	$[Rh(COD)Cl]_2$ (5%)	BIPHEP (10%)	− (78%)
6	$Rh(COD)_2OTf$ (3%)	PPh_3 (6%)	partial alkyne reduction

[a] Procedure: See Experimental Section. [b] Isolated yields after purification by silica gel chromatography. [c] In certain instances, the formation of **1a** was accompanied by trace quantities of the corresponding 1,2-dialkylidenecyclopentane.

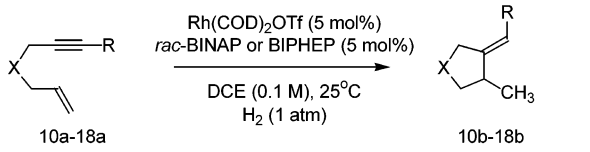
suggest the feasibility of performing related cyclizations using 1,6-enynes.[12,13] To explore this possibility, the hydrogen-mediated reductive cyclization of 1,6-enyne **10a** was examined. Gratifyingly, exposure of **10a** to using BIPHEP as ligand results in clean conversion to reductive cyclization product **10b**, which is isolated in 89% yield (Table 3, entry 2). Again, consistent with the hypothesis that cationic rhodium catalysts are required for heterolytic activation of hydrogen because of enhanced acidity of the resulting hydrides,[14] use of $[Rh(COD)Cl]_2$ under otherwise optimal conditions fails to produce reductive cyclization product **10b** (Table 3, entry 5). However, using $Rh(COD)_2BF_4$ as precatalyst, a 91% isolated yield of **10b** is obtained at only 3 mol % catalyst loading (Table 3, entry 4). As for the corresponding 1,6-diyne cyclization, the catalyst is rendered inoperative upon use of monodentate phosphines (Table 3, entry 6).

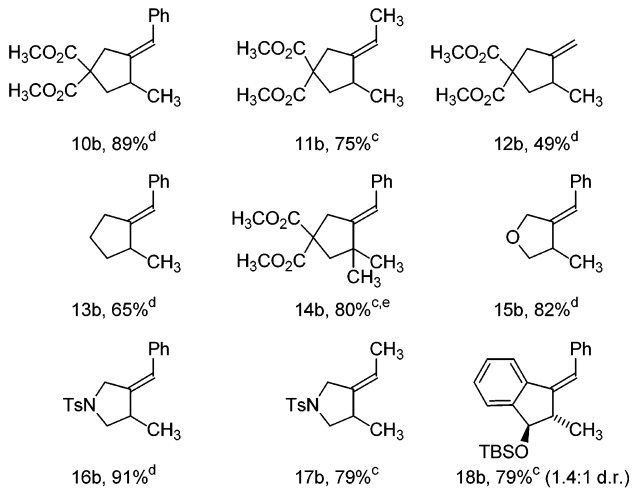
A preliminary assessment of the scope of the 1,6-enyne cyclization was made using the optimum conditions identified for the reductive cyclization diyne **10a** using commercially available $Rh(COD)_2OTf$ as precatalyst. As revealed by substrates **10a**−**18a**, cyclization proceeds efficiently across a range of carbon-, oxygen-, and nitrogen-tethered enynes. Unlike the corresponding 1,6-diynes, geminal substitution in the tether appears to facilitate cyclization and unsubstituted alkynes are tolerated (Table 4).

Mechanism. To probe the mechanism of these transformations, the reductive cyclization of 1,6-diyne **1a** was performed under an atmosphere of elemental deuterium in the presence of 3 mol % of the $Rh(COD)_2OTf$-BIPHEP catalyst system. The reductive cyclization product *deuterio*-**1b** incorporates two deuterium atoms and is obtained in 79% yield. These data are consistent with a catalytic mechanism involving heterolytic activation of elemental hydrogen ($H_2 + Rh^+X^- \rightarrow Rh-H + HX$) followed by [2 + 2 + 1] oxidative cyclization of LnRh(I)D with the 1,6-diyne **1a** to afford a (hydrido)Rh(III)-based rhodacyclopentadiene intermediate. Carbon−deuterium reductive elimination then provides a vinyl rhodium species, which upon hydrogenolytic cleavage of the vinylic carbon−rhodium bond, liberates the product of reductive cyclization along with LnRh(I)D to close the catalytic cycle (Scheme 1, top left).

Similarly, 1,6-enyne **10a** was exposed to an atmosphere of elemental deuterium in the presence of 5 mol % of the Rh-

Table 4. Catalytic Cyclization of 1,6-Enynes **10a**−**19a**[a,b]





[a] Procedure: See Experimental Section. [b] Isolated yields after purification by silica gel chromatography. [c] *rac*-BINAP was used as ligand. [d] BIPHEP was used as ligand. [e] The product of partial alkyne hydrogenationwas also formed in 10% yield.

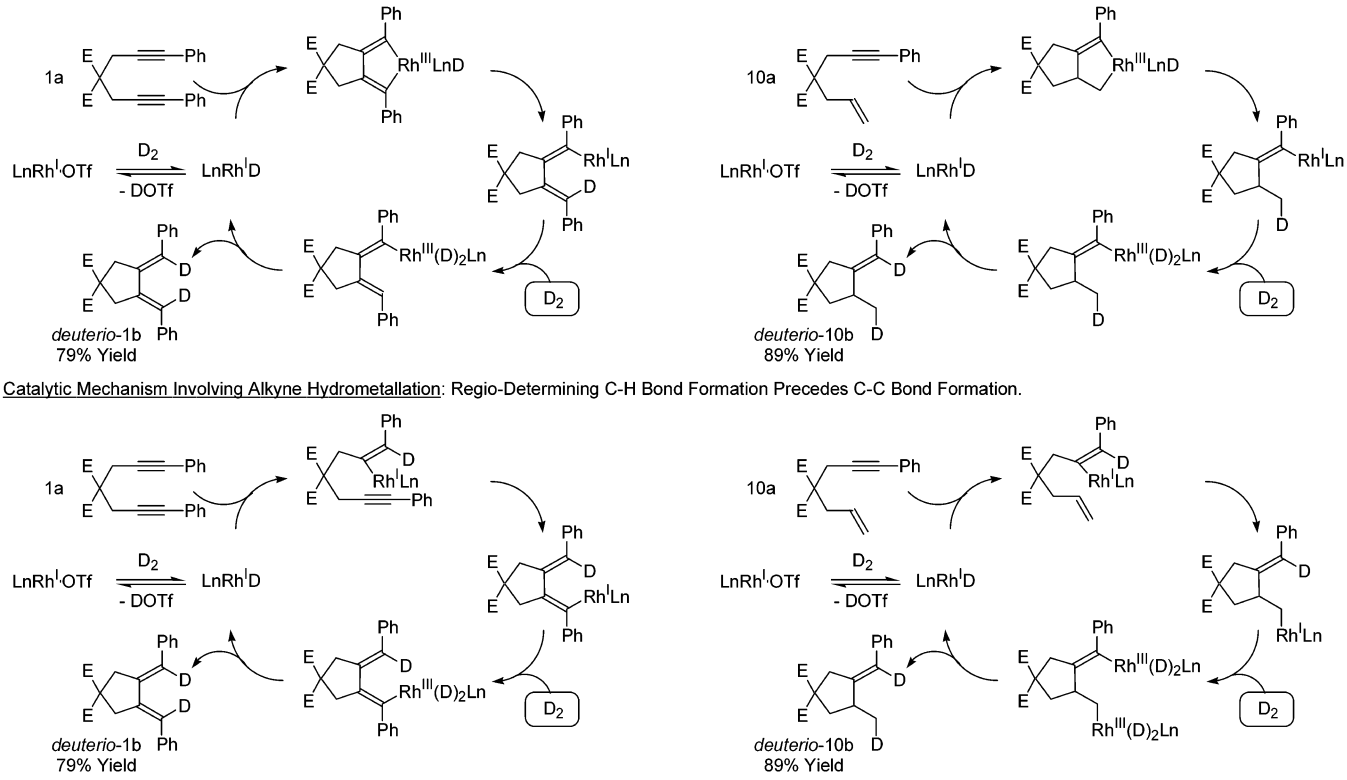
$(COD)_2OTf$-BIPHEP catalyst system. Here, the reductive cyclization product *deuterio*-**10b**, which incorporates two deuterium atoms, is obtained in 89% yield. These data are again consistent with a catalytic mechanism involving oxidative cyclization to form a metallocyclic intermediate, followed by carbon−deuterium reductive elimination to afford a vinyl rhodium intermediate, which upon hydrogenolytic cleavage gives the product of reductive cyclization along with LnRh(I)D to close the catalytic cycle (Scheme 1, top right).

For the proposed catalytic mechanisms involving oxidative cyclization to form metallocyclic intermediates, C−C bond formation precedes C−H bond formation. Additionally, C−C bond formation is regiodetermining with respect to functionalization of the alkyne. For the reductive cyclization of both 1,6-diyne and 1,6-enyne substrates, related hydrometallative mechanisms also may be envisioned (Scheme 1, bottom left and right). For such hydrometallative mechanisms, C−H bond formation precedes C−C bond formation and hydrometalation is regiodetermining. While the available data do not enable unambiguous discrimination between these two catalytic mechanisms, the hydrometallative mechanism is deemed unlikely as it would require a completely regioselective addition of LnRh(I)H across the alkyne.

Conclusion

In summation, we report the first examples of metal-catalyzed carbocyclization mediated by hydrogen. The collective studies establish the interception of hydrogenation intermediates as a new and effective strategy for C−C bond formation and support the feasibility of developing a broad family of catalytic C−C bond-forming hydrogenations. Future research will focus on the development of enantioselective variants of the transformations described herein, as well as the design of second-generation

Scheme 1. Plausible Catalytic Mechanisms for the Cyclization of 1,6-Diyne and 1,6-Enyne Substrates as Corroborated by Deuterium Labeling



catalysts enabling the hydrogen-mediated condensation of basic chemical feedstocks.

Experimental Section

General. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloroethane was distilled from calcium hydride. Substrates **1a**−**9a**[16] and **10a**−**18a**[17] were prepared according to the previously reported procedures. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Krieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still.[18] Solvents for chromatography are listed as volume/volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Micromass ZAB-2E and are reported as *m*/*z* (relative intensity). Accurate masses were reported for the molecular ion (M+1) or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Mercury (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Mercury 400 (100 MHz) spectrometer. Chemical shifts are reported in δ units, in parts per million relative to the center of the triplet at 77.00 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broad-brand decoupling.

Representative Procedure for the Reductive Cyclization of 1,6-Diynes and 1,6-Enynes. To a solution of diyne **1a** or enyne **10a** (100 mol %) in dichloroethane (0.1 M) at ambient temperature were added rhodium catalyst and ligand in the quantities specified. The system was purged with hydrogen gas, and the reaction was stirred under an atmosphere of hydrogen until complete consumption of substrate was observed, at which point the reaction mixture was evaporated onto silica gel and the product was purified by silica gel chromatography.

(3*E*,4*E*)-Dimethyl 3,4-Dibenzylidenecyclopentane-1,1-dicarboxylate (1b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (m, 8H), 7.24 (m, 2H), 6.99 (m, 2H), 3.70 (s, 6H), 3.40 (d, J = 2.4 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 139.3, 137.2, 128.8, 128.3, 126.7, 120.4, 58.7, 52.8, 38.8. IR (NaCl): 3025, 2954, 1734, 1595, 1489, 1444, 1322, 1266, 1203, 1173, 1070, 866 cm^{-1}. HRMS: calcd for $C_{23}H_{22}O_4$ [M], 362.1518; found, 362.1528. mp: ∼130−132 °C.

***deuterio*-(3*E*,4*E*)-Dimethyl 3,4-Dibenzylidenecyclopentane-1,1-dicarboxylate (*deuterio*-1b).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 8H), 7.21 (m, 2H), 3.66 (s, 6H), 3.38 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.5, 139.2, 137.2, 128.8, 128.3, 126.7, 58.7, 52.8, 38.8. IR (NaCl): 2953, 1736, 1493, 1443, 1267, 1231, 1204, 1167, 1077, 768 cm^{-1}. HRMS: calcd for $C_{23}H_{20}D_2O_4$ [M], 364.1644; found, 364.1644. mp: ∼136−138 °C.

2,3-Dibenzylidene-spiro[4.5]decane-6,10-dione (2b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 8H), 7.23 (m, 2H), 6.98 (s, 2H), 3.23 (d, J = 1.2 Hz, 4H), 2.69 (t, J = 6.8 Hz, 4H), 1.96 (qt, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.1, 139.8, 137.5, 129.0, 128.4, 126.8, 120.5, 71.2, 37.7, 37.5, 17.8. IR (NaCl): 1723, 1693, 1639, 741, 632 cm^{-1}. HRMS: calcd for $C_{24}H_{23}O_2$ [M + 1], 343.1698; found, 343.1696. mp: ∼214−216 °C.

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2,3-Dibenzylidene-8,8-dimethyl-7,9-dioxa-spiro[4.5]decane-6,10-dione (3b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 8H), 7.26 (m, 2H), 7.11 (t, J = 2.0 Hz, 2H), 3.47 (d, J = 2.0 Hz, 4H), 1.76 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 138.8, 137.2, 128.9, 128.5, 127.1, 120.9, 105.1, 52.3, 43.1, 29.0. IR (NaCl): 1739, 1642, 1297, 1204, 1096 cm^{-1}. HRMS: calcd for $C_{24}H_{22}O_4$ [M], 374.1518; found, 374.1522. mp: ~216−218 °C.

(3*Z*,4*Z*)-3,4-Dibenzylidene-tetrahydrofuran (4b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (m, 4H), 7.24 (m, 6H), 6.95 (t, J = 2.4 Hz, 2H), 4.82 (d, J = 2.4 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0, 136.9, 128.61, 128.56, 127.1, 118.6, 71.0. IR (NaCl): 1642, 1446, 1075, 1003, 935, 918, 871, 742, 698 cm^{-1}. HRMS: calcd for $C_{18}H_{17}O_1$ [M + 1], 249.1279; found, 249.1276. mp: ~146−148 °C.

(3*E*,4*E*)-3,4-Dibenzylidene-cyclopentane (5b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (m, 8H), 7.21 (m, 2H), 6.98 (s, 2H), 2.76 (dt, J = 7.2, 2.0 Hz, 4H), 1.84 (qt, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 138.3, 128.8, 128.3, 126.4, 119.1, 32.0, 25.1. IR (NaCl): 1641, 1444, 1076, 1035, 741 cm^{-1}. HRMS: calcd for $C_{19}H_{18}$ [M], 246.1409; found, 246.1406. mp: ~150−152 °C.

3-Benzylidene-4-ethylidene-cyclopentane-1,1-dicarboxylic Acid Dimethyl Ester (6b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 4H), 7.20 (m, 1H), 6.74 (t, J = 2.4 Hz, 1H), 6.05 (m, 1H), 3.70 (s, 6H), 3.34 (d, J = 2.4 Hz, 2H), 3.02 (s, 2H), 1.78 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.8, 138.8, 138.1, 137.5, 128.7, 128.2, 126.4, 118.8, 115.8, 58.1, 52.8, 39.6, 36.8, 14.9. IR (NaCl): 3025, 2953, 1738, 1435, 1267, 1231, 1166, 1068, 737, 697 cm^{-1}. HRMS: calcd for $C_{18}H_{20}O_4$ [M], 300.1362; found, 300.1364.

3-Benzylidene-4-trimethylsilanylmethylene-cyclopentane-1,1-dicarboxylic Acid Dimethyl Ester (7b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 4H), 7.24 (m, 1H), 6.88 (t, J = 2.4 Hz, 1H), 6.13 (t, J = 2.0 Hz, 1H), 3.73 (s, 6H), 3.35 (d, J = 2.4 Hz, 2H), 3.11 (d, J = 2.0 Hz, 2H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.6, 153.7, 138.3, 137.2, 129.0, 128.3, 126.9, 121.6, 118.3, 58.3, 52.88, 52.86, 40.5, 38.9, −0.47. IR (NaCl): 2954, 1737, 1638, 1598, 1435, 1259, 1204, 1165, 1068, 865, 840 cm^{-1}. HRMS: calcd for $C_{20}H_{27}O_4Si_1$ [M], 359.1679; found, 359.1665.

3,4-Diethylidene-cyclopentane-1,1-dicarboxylic Acid Dimethyl Ester (8b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.72 (m, 2H), 3.68 (s, 6H), 2.92 (d, J = 0.8 Hz, 4H), 1.64 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.0, 137.3, 113.4, 57.4, 52.7, 37.5, 14.6. IR (NaCl): 2955, 1738, 1667, 1644, 1435, 1264, 1202, 1163, 1064 cm^{-1}. HRMS: calcd for $C_{13}H_{18}O_4$ [M], 238.1205; found, 238.1206.

3,4-Diethylidene-1-(toluene-4-sulfonyl)-pyrrolidine (9b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.73 (m, 2H), 3.94 (d, J = 1.2 Hz, 4H), 2.43 (s, 3H), 1.63 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 134.1, 132.7, 129.6, 127.7, 113.9, 50.9, 21.5, 14.6. IR (NaCl): 3055, 1644, 1265, 1164, 739 cm^{-1}. HRMS: calcd for$C_{15}H_{19}N_1O_2S_1$ [M + 1], 278.1215; found, 278.1214. mp: ~124−126 °C.

(*E*)-Dimethyl 3-Benzylidene-4-methylcyclopentane-1,1-dicarboxylate (10b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (m, 4H), 7.21 (m, 1H), 6.22 (q, J = 2.4 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.39 (d, J = 17.6 Hz, 1H), 3.21 (dd, J = 17.2, 2.8 Hz, 1H), 2.77 (m, 1H), 2.60 (ddd, J = 12.8, 7.2, 1.6 Hz, 1H), 1.77 (dd, J = 12.4, 11.6 Hz, 1H), 1.22 (d, J = 6.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.3, 172.2, 146.0, 137.9, 128.3, 126.2, 121.5, 109.7, 59.0, 52.8, 41.5, 39.1, 39.0, 18.3. IR (NaCl): 2955, 1735, 1492, 1447, 1279, 1254, 1203, 1174, 1154, 1062, 697 cm^{-1}. HRMS: calcd for $C_{17}H_{20}O_4$ [M], 288.1362; found, 288.1351.

***deuterio*-(*E*)-Dimethyl 3-Benzylidene-4-methylcyclopentane-1,1-dicarboxylate (*deuterio*-10b).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 4H), 7.18 (m, 1H), 3.72 (m, 6H), 3.39 (d, J = 18.0 Hz, 1H), 3.21 (dd, J = 17.6, 2.4 Hz, 1H), 2.76 (m, 1H), 2.60 (ddd, J = 12.4, 7.2, 1.2 Hz, 1H), 1.77 (dd, J = 12.8, 11.6 Hz, 1H), 1.20 (d, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.23, 172.18, 145.9, 137.8, 128.2, 126.1, 59.0, 52.8, 41.4, 39.0, 17.9 (triplet). IR (NaCl): 2953, 1737, 1644, 1435, 1262, 1204, 1167, 1074, 768, 698 cm^{-1}. HRMS: calcd for $C_{17}H_{18}D_2O_4$ [M], 290.1487; found, 290.1491.

(*E*)-Dimethyl 3-Ethylidene-4-methylcyclopentane-1,1-dicarboxylate (11b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.21 (m, 1), 3.73 (m, 6H), 3.01 (dd, J = 17.2, 0.8 Hz, 1H), 2.85 (m, 1H), 2.51 (m, 2H), 1.70 (m, 1H), 1.60 (m, 3H), 1.07 (d, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.5, 143.7, 115.0, 58.2, 52.7, 42.4, 37.1, 37.07, 17.8, 14.4. IR (NaCl): 2955, 1735, 1632, 1435, 1278, 1246, 1202, 1162, 880 cm^{-1}. HRMS: calcd for $C_{12}H_{18}O_4$ [M], 226.1205; found, 226.1204.

Dimethyl 3-Methyl-4-methylenecyclopentane-1,1-dicarboxylate (12b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.87 (q, J = 2.0 Hz, 1H), 4.76 (q, J = 2.0 Hz, 1H), 3.68 (m, 6H), 3.02 (d, J = 16.8 Hz, 1H), 2.91 (dq, J = 15.2, 2.0 Hz, 1H), 2.52 (m, 2H), 1.71 (m, 1H), 1.06 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 172.2, 153.1, 105.5, 58.1, 52.6, 42.2, 40.5, 37.2, 17.9. IR (NaCl): 2957, 1737, 1658, 1435, 1279, 1254, 1202, 1169, 1072, 887 cm^{-1}. HRMS: calcd for $C_{11}H_{16}O_4$ [M + 1], 213.1127; found, 213.1135.

1-((*E*)-(2-Methylcyclopentylidene)methyl)benzene (13b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (m, 4H), 7.15 (m, 1H), 6.23 (q, J = 2.4 Hz, 1H), 2.62 (m, 3H), 1.87 (m, 2H), 1.62 (m, 1H), 1.24 (m, 1H), 1.18 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 138.9, 128.1, 128.0, 125.6, 120.1, 40.9, 34.6, 31.5, 24.7, 19.4. IR (NaCl): 2955, 2868, 1650, 1599, 1495, 1446, 1370, 1290, 694 cm^{-1}. HRMS: calcd for $C_{13}H_{16}$ [M + 1], 173.1330; found, 173.1310.

(*E*)-Dimethyl 4-Benzylidene-3,3-dimethylcyclopentane-1,1-dicarboxylate (14b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27 (m, 5H), 6.22 (t, J = 2.4 Hz, 1H), 3.72 (s, 6H), 3.40 (d, J = 2.4 Hz, 2H), 2.35 (s, 2H), 1.18 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.6, 150.4, 137.9, 128.7, 128.4, 128.2, 126.1, 120.5, 58.5, 52.8, 47.4, 43.6, 38.6, 29.4. IR (NaCl): 2955, 1737, 1435, 1262, 1199, 1135, 1076, 737, 697 cm^{-1}. HRMS: calcd for $C_{18}H_{22}O_4$ [M], 302.1518; found, 302.1524.

(*Z*)-3-Benzylidene-tetrahydro-4-methylfuran (15b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 2H), 7.20 (m, 1H), 7.13 (m, 2H), 6.28 (q, J = 2.4 Hz, 1H), 4.65 (m, 2H), 4.06 (dd, J = 8.0, 7.6 Hz, 1H), 3.37 (t, J = 8.0 Hz, 1H), 2.89 (m, 1H), 1.21 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.4, 137.3, 128.4, 127.8, 126.4, 119.8, 74.2, 70.2, 39.8, 16.4. IR (NaCl): 2967, 2871, 1660, 1643, 1493, 1448, 1378, 1081, 1059, 990, 920, 735 cm^{-1}. HRMS: calcd for $C_{12}H_{14}O_1$ [M + 1], 175.1123; found, 175.1132.

(*Z*)-3-Benzylidene-4-methyl-1-tosylpyrrolidine (16b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (m, 2H), 7.32 (m, 4H), 7.23 (m, 1H), 7.14 (m, 2H), 6.22 (q, J = 2.4 Hz, 1H), 4.24 (dq, J = 14.8, 1.2 Hz, 1H), 4.05 (dt, J = 15.2, 2.0 Hz, 1H), 3.55 (dd, J = 9.2, 7.6 Hz, 1H), 2.86 (m, 1H), 2.57 (dd, J = 8.8, 8.0 Hz, 1H), 2.40 (s, 3H), 1.16 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 141.7, 136.5, 132.8, 129.7, 128.5, 128.0, 127.7, 126.9, 122.0, 53.8, 50.7, 39.0, 21.5, 16.8. IR (NaCl): 2965, 2925, 2850, 1643, 1494, 1345, 1160, 1093, 1041 cm^{-1}. HRMS: calcd for $C_{19}H_{21}N_1O_2S_1$ [M + 1], 328.1371; found, 328.1365. mp: ~78−80 °C.

(*Z*)-3-Ethylidene-4-methyl-1-tosylpyrrolidine (17b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (m, 2H), 7.34 (m, 2H), 5.22 (m, 1H), 3.87 (m, 1H), 3.71 (m, 1H), 3.51 (m, 1H), 2.64 (m, 2H), 2.43 (s, 3H), 1.53 (dq, J = 6.8, 1.6 Hz, 3H), 1.01 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 140.4, 132.6, 129.6, 127.7, 115.9, 55.0, 49.6, 37.1, 21.4, 16.5, 14.3. IR (NaCl): 2966, 2922, 2859, 1641, 1345, 1163, 1095, 1037, 664 cm^{-1}. HRMS: calcd for $C_{14}H_{19}N_1O_2S_1$ [M + 1], 266.1215; found, 266.1219. mp: ~54−56 °C.

((*Z*,2*S*,3*R*)-1-Benzylidene-2,3-dihydro-2-methyl-1*H*-inden-3-yloxy)-(*tert*-butyl)dimethylsilane (18b). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (m, 8H), 6.99 (q, J = 6.8 Hz, 1H), 6.53 (s, 0.41 × 1H), 6.45 (d, J = 2.0 Hz, 0.59 × 1H), 5.24 (d, J = 6.4 Hz, 0.41 × 1H), 4.80 (d, J = 6.4 Hz, 0.59 × 1H), 3.13 (q, J = 7.2 Hz, 0.41 × 1H), 2.87 (dq, J = 6.4, 2.8 Hz, 0.59 × 1H), 1.38 (d, J = 6.8 Hz, 0.59 × 3H), 1.11 (d, J = 7.2 Hz, 0.41 × 3H), 0.98 (s, 9H), 0.24 (s, 3H), 0.20 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.5, 147.8, 145.4, 143.6, 138.1, 138.0, 137.9, 137.1, 128.4, 128.33, 128.32, 127.1, 127.0, 126.8, 124.6, 124.4, 124.1,

122.3, 121.6, 80.6, 75.1, 51.4, 48.4, 25.9, 18.4, 18.1, 16.1, 15.9, −3.9, −4.5, −4.6. IR (NaCl): 3054, 3027, 2957, 2930, 2886, 2857, 1464, 1264, 1126, 1077, 869, 836, 739 cm^{-1}. HRMS: calcd for $C_{23}H_{30}O_1Si_1$ [M + 1], 351.2144; found, 351.2149.

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Supporting Information Available: Spectral data for all new compounds (^{1}H NMR, ^{13}C NMR, IR, HRMS) and single-crystal X-ray diffraction data for compound **1b** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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