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Silver- and Gold-Catalyzed Intramolecular Rearrangement of Propargylic Alcohols Tethered with Methylenecyclopropanes: Stereoselective Synthesis of Allenylcyclobutanols and 1-Vinyl-3-oxabicyclo[3.2.1]octan-8-one Derivatives

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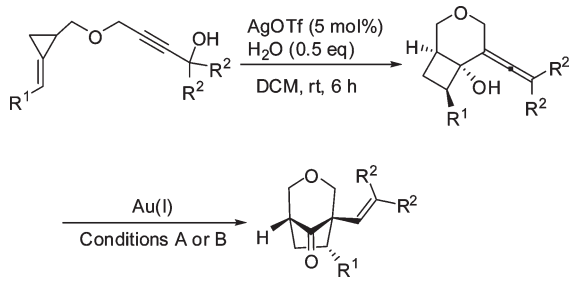

Ag(I)-catalyzed intramolecular reaction of monoarylmethylenecyclopropanes (MCPs) tethered with 1,1,3-triarylprop-2-yn-1-ols provides diastereoselective access to polysubstituted allenylcyclobutanols and the obtained allenylcyclobutanols catalyzed by Au(I) furnish a wide range of bridged bicyclic compounds with a vinyl-substituted quaternary stereogenic center stereoselectively.

Introduction

The use of gold compounds as homogeneous catalysts for the conversion of many organic substrates is one of the fastest growing areas in organic chemistry today.[1] Among these transformations, the cyclization of 2,3-allenols is playing a major role because 2,3-allenols[2] are versatile building blocks for the synthesis of 2,5-dihydrofurans,[3] vinylic epoxides,[4] unsaturated ketones,[5] and numerous other valuable compounds.[6] However, only a few examples of ring expansion of allenylcyclopropanols or allenylcyclobutanols catalyzed by gold or palladium via a Wagner−Meerwein shift have been reported.[7] Hence, a much more appealing strategy for examining the reaction of allenylcyclopropanols or allenylcyclobutanols is, therefore, highly desirable.

Results and Discussion

We have previously reported that the intermolecular reaction of monoarylmethylenecyclopropanes (MCPs) with

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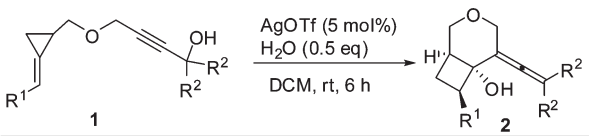
1,1,3-triarylprop-2-yn-1-ols in the presence of $BF_3 \cdot OEt_2$ afforded allenylcyclobutanols in good yields. We have proposed this reaction to proceed via a BF_3-induced Meyer−Schuster rearrangement generating an allene-cationic intermediate that then reacts with MCPs.[8] We anticipated that the allene-cationic intermediate, readily generated from propargylic alcohol in the presence of Lewis acid, might undergo similar Lewis acid-catalyzed intramolecular rearrangement, leading to polysubstituted allenylcyclobutanols. On the basis of this hypothesis, treatment of **1a** with 5 mol % of $Sc(OTf)_3$ produced the desired polysubstituted allenylcyclobutanol **2a** in 26% yield as a single stereoisomer. Next, we screened a wide array of Lewis acids and solvents to determine the optimal reaction conditions. The results of these experiments are summarized in Table SI-1 (see the Supporting Information). The examination of Lewis acids revealed that AgOTf was the best catalyst for this transformation among all tested Lewis acids including $Sc(OTf)_3$, $Zn(NTf_2)_2$, $Nd(NTf_2)_3$, $Bi(OTf)_2Cl$, $La(OTf)_3$, $Cu(OTf)_2$, $Yb(OTf)_3$, $Sn(OTf)_2$, and TMSOTf as well as Brønsted acid trifluoromethanesulfonic acid CF_3SO_3H (TfOH) and transition metal $PtCl_2$. Meanwhile, we also found that dichloromethane (DCM) was the most suitable solvent in this reaction. Moreover, the yield of the rearrangement was improved by employing 50 mol % of H_2O as the additive (see Table SI-2 in the Supporting Information). Therefore, the optimized reaction conditions were determined to be the following: 1.0 equiv of **1a** as the substrate in the presence of 0.5 equiv of H_2O with AgOTf (5 mol %) in DCM at room temperature.

With these results in hand, we probed the scope of this reaction using the optimized conditions. As shown in Table 1, a wide range of polysubstituted allenylcyclobutanols were accessible in synthetic modest yields ranging from 20% to 56%. Substrates possessing electron-rich aromatic substituents were generally tolerated (Table 1, entries 4−7); however, substrates **1b** and **1c** with the electron-poor substituents afforded slightly lower yields (Table 1, entries 2 and 3). The geometric isomer *Z*-**1a** furnished the corresponding **2a** in 38% yield, which presumably results from the sterically hindered factor (Table 1, entry 8). In the case of **1i**, **1j**, and **1k**, the corresponding **2i**, **2j**, and **2k** were obtained in moderate yields and the substituents on the aromatic R^2 of **1** did not significantly affect the reaction outcomes (Table 1, entries 10−12). Using **1h** as the substrate led to **2h** in 20% yield along with a novel compound **3h** in 18% yield (Table 1, entry 9). Alkyl-substituent compound ***1l*** was also a suitable substrate for this reaction, giving ***2l*** in 32% yield (Table 1, entry 13). The structure of **2e** has been further confirmed by X-ray diffraction and its ORTEP drawing is indicated in Figure 1 and the CIF data have been presented in the Supporting Information.[9] It should be emphasized here that when R^1 = alkenyl or alkynyl group, the corresponding substrate **1** cannot be prepared under the previously reported conditions.

TABLE 1. AgOTf-Promoted Intramolecular Rearrangement of 1 to 2

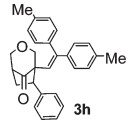


entry[a]	R^1/R^2	yield of **2** [%][b]
1	C_6H_5/C_6H_5, **1a**	**2a**, 50
2	4-ClC_6H_4/C_6H_5, **1b**	**2b**, 44
3	4-FC_6H_4/C_6H_5, **1c**	**2c**, 44
4	4-MeC_6H_4/C_6H_5, **1d**	**2d**, 53
5	4-$MeOC_6H_4/C_6H_5$, **1e**	**2e**, 56 X-ray
6	3,4,5-$(MeO)_3C_6H_2/C_6H_5$, **1f**	**2f**, 53
7	3-$BnOC_6H_4/C_6H_5$, **1g**	**2g**, 40
8	C_6H_5/C_6H_5, ***Z*-1a**	**2a**, 38
9	C_6H_5/4-MeC_6H_4, **1h**	**2h**, 20[c]
10	C_6H_5/4-ClC_6H_4, **1i**	**2i**, 34
11	C_6H_5/4-FC_6H_4, **1j**	**2j**, 44
12	C_6H_5/4-$MeOC_6H_4$, **1k**	**2k**, 40
13	C_7H_{15}/C_6H_5, ***E*** and ***Z*-1l**	***2l***, 32

[a]Reaction conditions: using **1** (0.2 mmol), H_2O (0.1 mmol) and AgOTf (5 mol%) in DCM (2 mL) at rt. [b]Isolated yield. [c]Another product **3h** was formed in 18% yield.

entry[a]	R^1/R^2	yield of **2** [%][b]
1	C_6H_5/C_6H_5, **1a**	**2a**, 50
2	4-ClC_6H_4/C_6H_5, **1b**	**2b**, 44
3	4-FC_6H_4/C_6H_5, **1c**	**2c**, 44
4	4-MeC_6H_4/C_6H_5, **1d**	**2d**, 53
5	4-$MeOC_6H_4/C_6H_5$, **1e**	**2e**, 56 X-ray
6	3,4,5-$(MeO)_3C_6H_2/C_6H_5$, **1f**	**2f**, 53
7	3-$BnOC_6H_4/C_6H_5$, **1g**	**2g**, 40
8	C_6H_5/C_6H_5, ***Z*-1a**	**2a**, 38
9	C_6H_5/4-MeC_6H_4, **1h**	**2h**, 20[c]
10	C_6H_5/4-ClC_6H_4, **1i**	**2i**, 34
11	C_6H_5/4-FC_6H_4, **1j**	**2j**, 44
12	C_6H_5/4-$MeOC_6H_4$, **1k**	**2k**, 40
13	C_7H_{15}/C_6H_5, ***E*** and ***Z*-1l**	***2l***, 32

[a]Reaction conditions: **1** (0.2 mmol), H_2O (0.1 mmol), and AgOTf (5 mol %) in DCM (2 mL) at rt. [b]Isolated yield. [c]Another product **3h** was formed in 18% yield.



To enrich the diversity of the reaction for allenylcyclobutanols, we initially examined the ring expansion reaction of **2a** in the presence of Au(I) catalyst. When allenylcyclobutanol **2a** was treated with Ph_3PAuCl (5 mol %) and AgOTf (5 mol %) in DCM at 40 °C, a novel bridged compound **3a** was exclusively delivered in 65% yield as a single stereoisomer (Scheme 1, eq 1). Notably, if **1a** was employed as the substrate under identical conditions (5 mol % Ph_3PAuCl and 5 mol % AgOTf) in DCM through a one-pot reaction, **3a** was also obtained in 43% yield (Scheme 1, eq 2). After many attempts, we identified the optimized reaction conditions that were to carry out the reaction using Ph_3PAuCl (5 mol %) and AgOTf (5 mol %) in DCM at 40 °C (conditions A) (see Table SI-3 in the Supporting Information).

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(9) The crystal data of **2e** have been deposited in CCDC with number 732287. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk). Empirical formula $C_{28}H_{26}O_3$; formula weight 410.49; crystal size 0.217 × 0.216 × 0.041; crystal color colorless, crystal habit prismatic; crystal system monoclinic; lattice type primitive; lattice parameters a = 13.5410(18) Å, b = 16.611(2) Å, c = 10.4723(14) Å, α = 90°, β = 108.179(3)°, γ = 90°, V = 2237.9(5) Å^3; space group $P2(1)/c$; Z = 4; D_{calc} = 1.218 g/cm^3; F_{000} = 872; R_1 = 0.0474, wR_2 = 0.0913; diffractometer Rigaku AFC7R.

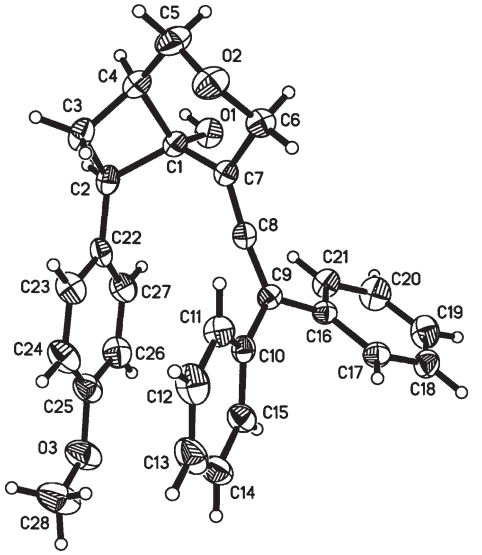
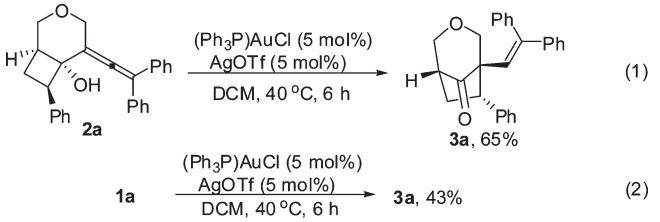


FIGURE 1. ORTEP drawing of **2e**.

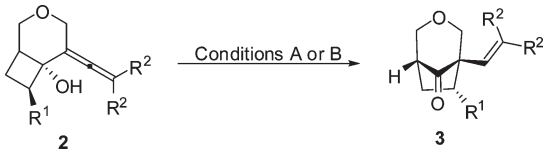
SCHEME 1. The Transformation of 2a



The scope of this reaction was then probed by using the optimal protocol shown in eq 1 (Scheme 1). As can be seen in Table 2, the reaction of substrates **2** proceeded smoothly under the optimal reaction conditions. The electronic nature of the substituents on the aromatic rings of **2** has a small influence on the reaction outcomes. The reaction of **2b**−**g** with either electron-donating or electron-withdrawing substituents on the aromatic rings R^1 gave rise to **3b**−**g** in moderate to excellent yields (as for electron-withdrawing substituents on the aromatic rings R^1, the reaction should be carried out at 60 °C: conditions B) (Table 2, entries 2−7). Similarly, compounds **2h**−**k** possessing various substituents on the R^2 aromatic rings afforded the corresponding products **3h**−**k** in 63−85% yields (Table 2, entries 8−11). To our delight, when R^2 is an aliphatic group, the formation of ***3l*** was observed in 52% yield (Table 2, entry 12). The structure of **3a** has been further confirmed by X-ray diffraction (Figure 2) and its CIF data have been presented in the Supporting Information.[10] It should be noted that when R^2 is an alkyl group such as Me (substrate **1m**), the reaction is sluggish under the standard conditions, affording the hydroxyl group migrated product **4a** in 12% yield along with the recovery of **1m** in 85% yield (Scheme 2).

(10) The crystal data of **3a** have been deposited in CCDC with number 704726. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk). Empirical formula $C_{27}H_{24}O_2$; formula weight 380.46; crystal size 0.412 × 0.201 × 0.075; crystal color colorless, crystal habit prismatic; crystal system orthorhombic; lattice type primitive; lattice parameters a = 11.3164(12) Å, b = 17.6548(19) Å, c = 20.537(2) Å, α = 90°, β = 90°, γ = 90°, V = 4103.0(8) Å^3; space group *Pcab*; Z = 8; D_{calc} = 1.232 g/cm^3; F_{000} = 1616; R_1 = 0.0777, wR_2 = 0.1888; diffractometer Rigaku AFC7R.

TABLE 2. Gold-Catalyzed Reaction of 2 To Construct Bridged Bicyclic Compound 3



entry	R^1/R^2	conditions[a]	yield of **3** [%][b]
1	C_6H_5/C_6H_5, **2a**	A	**3a**, 65, X-ray
2	4-ClC_6H_4/C_6H_5, **2b**	B	**3b**, 64
3	4-FC_6H_4/C_6H_5, **2c**	B	**3c**, 75
4	4-MeC_6H_4/C_6H_5, **2d**	A	**3d**, 74
5	4-$MeOC_6H_4/C_6H_5$, **2e**	A	**3e**, 80
6	3,4,5-$(MeO)_3C_6H_2/C_6H_5$, **2f**	A	**3f**, 70
7	3-$BnOC_6H_4/C_6H_5$, **2g**	A	**3g**, 60
8	C_6H_5/4-MeC_6H_4, **2h**	A	**3h**, 63
9	C_6H_5/4-ClC_6H_4, **2i**	A	**3i**, 77
10	C_6H_5/4-FC_6H_4, **2j**	A	**3j**, 70
11	C_6H_5/4-$MeOC_6H_4$, **2k**	A	**3k**, 85
12	C_7H_{15}/C_6H_5, ***2l***	A	***3l***, 52

[a]Conditions A: The reactions were carried out with **2** (0.2 mmol), $Au(Ph_3P)Cl$ (5 mol %), and AgOTf (5 mol %) in DCM (2 mL) at 40 °C. Conditions B: The reactions were carried out with **2** (0.2 mmol), $Au(Ph_3P)Cl$ (5 mol %), and AgOTf (5 mol %) in DCE (2 mL) at 60 °C. [b]Isolated yield.

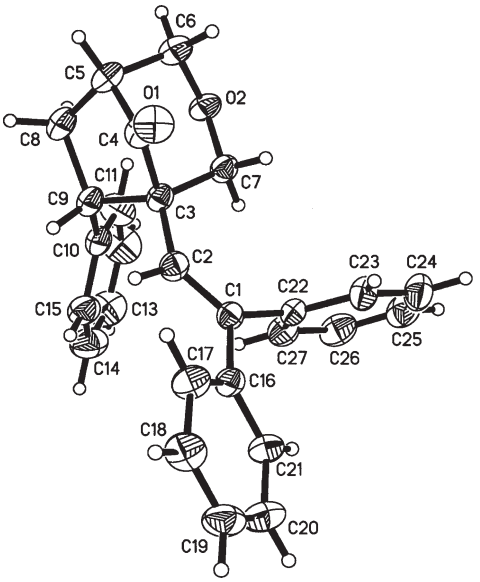
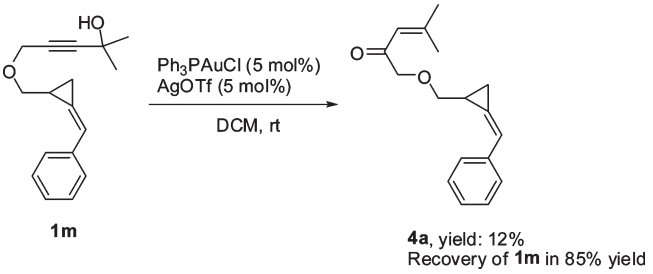


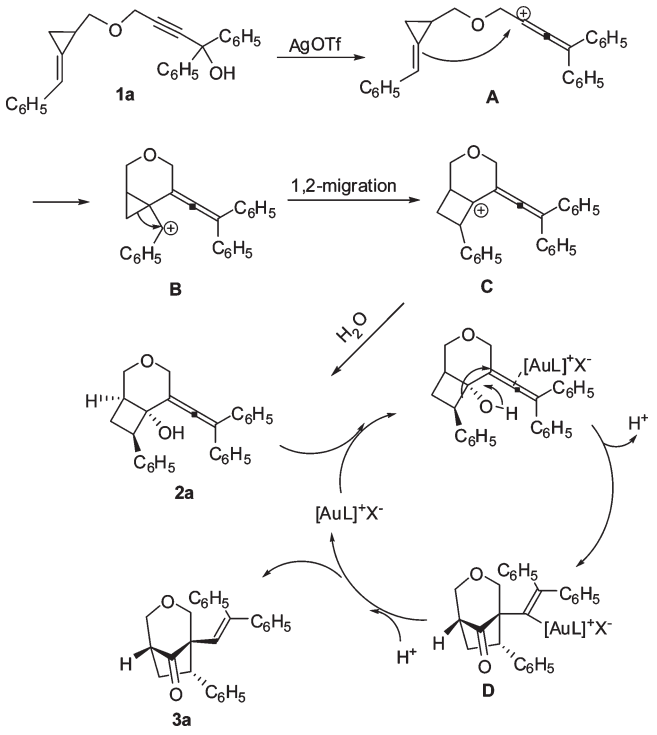
FIGURE 2. ORTEP drawing of **3a**.

SCHEME 2. Gold and Silver Co-catalyzed Reaction of 1m



A proposed mechanism for the formation of allenylcyclobutanols and sequential gold(I)-catalyzed ring expansion of

SCHEME 3. Proposed Reaction Mechanism



allenylcyclobutanols is outlined in Scheme 3. Initially, the reaction of **1a** with AgOTf generates the intermediate **A**, which can undergo intramolecular electrophilic attack to furnish intermediate **B**. Intermediate **B** via 1,2-migration results in ring expansion intermediate **C**. The nucleophilic attack of H_2O to intermediate **C** affords the product **2a**. Subsequently, coordination of the cationic gold(I) catalyst to the internal double bond of the allene moiety in **2a** triggers a ring expansion by a Wagner−Meerwein shift,[7b,11] producing vinylgold intermediate **D**. A subsequent protodemetalation liberates the catalyst and releases the product **3a**.[7c]

In conclusion, a AgOTf-catalyzed intramolecular reaction of monoarylmethylenecyclopropanes (MCPs) tethered with 1,1,3-triarylprop-2-yn-1-ols has been developed, providing diastereoselective access to polysubstituted allenylcyclobutanols. The obtained allenylcyclobutanols catalyzed by gold(I) furnish a wide range of 1-vinyl-3-oxabicyclo[3.2.1]-octan-8-one derivatives with a vinyl-substituted quaternary stereogenic center. Moreover, this method constitutes the first report of synthesizing a polysubstituted bridged bicyclic compound. Further efforts are in progress regarding the scope and mechanistic details.

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Experimental Section

General Procedure for the Reaction of 1a in the Presence of AgOTf and H_2O. (*E*)-4-((2-Benzylidenecyclopropyl)methoxy)-1,1-diphenylbut-2-yn-1-ol (**1a**) (76 mg, 0.2 mmol) and silver triflate (3 mg, 5 mol %) were dissolved in DCM (2.0 mL), then H_2O (1.8 mg, 0.1 mmol) was added to this mixture by a 25 μL microsyringe. The mixture was stirred for 6 h at room temperature (25 °C). The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum ether−EtOAc (4:1) as an eluent to give **2a** as a light yellow oil (38 mg, 50%).

Compound **2a**: brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.99 (dd, 1H, J = 8.7, 18.6 Hz, CH_2), 2.18 (dd, 1H, J = 10.5, 21.3 Hz, CH_2), 2.38−2.44 (m, 1H, CH), 2.47 (s, 1H, OH), 3.61 (dd, 1H, J = 9.0, 11.1 Hz, CH), 3.77 (dd, 1H, J = 3.0, 12.0 Hz, CH_2), 3.86 (d, 1H, J = 12.0 Hz, CH_2), 4.11 (d, 1H, J = 12.6 Hz, CH_2), 4.21 (d, 1H, J = 12.6 Hz, CH_2), 6.73−6.78 (m, 3H, Ar), 6.86−6.88 (m, 2H, Ar), 7.06−7.31 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.8, 40.4, 51.4, 66.1, 67.3, 75.1, 102.1, 112.7, 126.4, 127.07, 127.12, 127.4, 127.5, 127.6, 128.3, 128.7, 129.0, 135.3, 136.6, 138.5, 203.0; IR (CH_2Cl_2) ν 3420, 3081, 3058, 3027, 2975, 2945, 2844, 1941, 1728, 1598, 1493, 1453, 1373, 1334, 1265, 1195, 1160, 1078, 1031, 984, 904, 883, 867, 767, 736, 700, 633, 606, 563 cm^{-1}; MS (%) m/z 380 ($M^{\bullet+}$, 13), 105 (100), 77 (74), 165 (59), 91 (56), 167 (49), 215 (40), 202 (37), 115 (33); HRMS (EI) calcd for $C_{27}H_{24}O_2$ 380.1776, found 380.1773.

Representative Procedure for the Gold(I)-Catalyzed Reaction of 2a. 5-(2,2-Diphenylvinylidene)-7-phenyl-3-oxa-bicyclo[4.2.0]-octan-6-ol (**2a**) (76 mg, 0.2 mmol) was added to a stirring suspension of gold triphenylphosphine chloride (5 mg, 5 mol %) and silver triflate (3 mg, 5 mol %) in dichloromethane (2 mL) then the mixture was stirred for 8 h at 40 °C. After removal of the solvent under reduced pressure, silica gel flash chromatography eluting with 10% ethyl acetate in petroleum ether afforded **3a** as a colorless crystal solid (50 mg, 65%).

Compound **3a**: white solid, mp 120−122 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.37 (dd, 2H, J = 4.2, 9.6 Hz, CH_2), 2.57−2.61 (m, 1H, CH), 3.25−3.40 (m, 3H, CH and CH_2), 3.87 (d, 1H, J = 10.2 Hz, CH_2), 4.09−4.13 (m, 1H, CH_2), 5.82 (s, 1H, =CH), 6.60 (d, 2H, J = 6.9 Hz, Ar), 7.04−7.14 (m, 2H, Ar), 7.15−7.26 (m, 6H, Ar), 7.35−7.40 (m, 3H, Ar), 7.50−7.53 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 28.6, 46.2, 48.6, 61.3, 75.2, 77.1, 124.0, 127.1, 127.21, 127.23, 127.3, 127.7, 128.0, 128.5, 129.4, 129.8, 139.0, 139.6, 143.2, 145.8, 216.0; IR (CH_2Cl_2) ν 3056, 3026, 2959, 2852, 1746, 1598, 1493, 1456, 1445, 1217, 1162, 1068, 967, 809, 761, 737, 700, 616, 506 cm^{-1}; MS (%) m/z 380 ($M^{\bullet+}$, 100), 205 (90), 91 (57), 203 (53), 232 (52), 204 (47), 246 (45), 202 (44); HRMS (EI) calcd for $C_{27}H_{24}O_2$ 380.1776, found 380.1783.

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Supporting Information Available: ^{13}C and ^{1}H NMR spectroscopic and analytic data for **1a**−**1*l***, **2a**−**2*l***, and **3a**−**3*l*** as well as X-ray crystal data of **2e** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.