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Palladium Acetate Catalyzed Oxidative Aromatization of Methylenecyclopropanes

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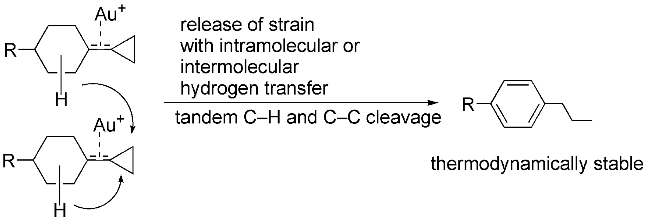
Isopropenylbiaryl derivatives were produced in moderate to good yields at high temperature from the reaction of methylenecyclopropanes (MCPs) **1** in the presence of palladium acetate under ambient atmosphere by tandem intramolecular C–H and C–C bond activation and aromatization through dehydrogenated rearrangement of MCPs **1**. A plausible mechanism has been proposed on the basis of deuterium labeling and control experiments.

Introduction

Direct functionalization of organic compounds by metal-catalyzed C–H bond activation[1] and utilization of O_2 as a terminal oxidant in oxidative transformations[2] are highly attractive strategies in current organic synthesis, but there still remains many challenges. The development of practical methods in these two cases could have a significant environmental and economic impact in a number of different areas. The pioneering report by Trost and Metzner in 1980 has shown an example of facile C–H bond activation, wherein cyclohexene is catalytically disproportionated into 1 equivalent of benzene and 2 equivalents of cyclohexane or dehydrogenated to benzene by using dimethyl fumarate or maleic acid as sacrificial hydrogen acceptors in the presence of palladium trifluoroacetate.[3] Recently, several groups have established similarities between the reactions of O_2 and olefins with palladium hydrides.[4] For example, Bercaw and Labinger have demonstrated that molecular oxygen can replace sacrificial olefins as the hydrogen acceptor in the palladium trifluoroacetate catalyzed dehydrogenation of cyclohexene and related cyclic olefins into aromatics.[5] Methylenecyclopropanes (MCPs) as highly strained but readily accessible molecules can undergo a variety of ring-opening reactions in the presence of transition metals or Lewis acids because the relief of ring strain provides a potent thermodynamic driving force. It should be also noted that release of such strain energy (27 kcal mol^{-1}) is not sufficient for high reactivity.[6,7] The π character of the ring bonds of a cyclopropane provides the kinetic opportunity to initiate the unleashing of the strain. We have recently reported that (cyclopropylidenecyclohexyl)benzene derivatives **1** undergo the dehydrogenated rearrangement in the presence of $AuPPh_3Cl/AgOTf$ at high temperature in toluene or xylene to give the corresponding biaryl derivatives in moderate to good yields. Experimental and theoretical DFT studies agree with a mechanism involving tandem intramolecular/intermolecular C–H and C–C activation (Scheme 1).[8] It is anticipated that the same type of substrates catalyzed by other transition metal complexes of palladium or rhodium would give different biaryl products. In this paper, we wish to report such an interesting C–H and C–C bond activation as well as oxidative aromatization through the dehydrogenated rearrangement of **1** under ambient atmosphere in the presence of palladium acetate at high temperature in toluene to give the corresponding isopropenylbiaryl derivatives in moderate to good yields.



Scheme 1. Au^{I}-catalyzed rearrangement of MCPs.

Results and Discussion

We initially examined the oxidative aromatization reaction by using (cyclopropylidenecyclohexyl)benzene (**1a**) as the substrate to determine the optimal reaction conditions, and the results of these experiments are summarized in Table 1. The results revealed that $Pd(OAc)_2$ (10 mol-%, 0.1 equiv.) could catalyze this reaction in toluene at 100 °C to afford propenylbiphenyl (**2a**) in 27% yield (Table 1, En-

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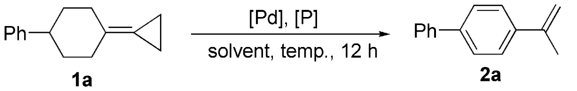
try 1). Adding phosphorus compounds such as PPh_3, P(2-furyl)$_3$, and binap (0.2 equiv.) as the additives did not improve the yields and in fact lower them (Table 1, Entries 2–4). When the reaction was carried out under argon atmosphere, **2a** was produced in 11% yield (Table 1, Entry 5). Next, we tried other palladium compounds as catalysts; however, no reactions occurred when $Pd(PPh_3)_2Cl_2$ and $Pd(CH_3CN)_2(OTs)_2$ (0.1 equiv.) were used (Table 1, Entries 6–8). Using $Pd(OAc)_2(PPh_3)_2$, $Pd(OAc)_2(Py)_2$, and $Pd(OOCCF_3)_2$ as catalysts, we obtained complex product mixtures, as the reaction system became disordered (Table 1, Entries 9–11). Product **2a** could be detected; however, it was hard to isolate when $Pd(OTf)_2(CH_3CN)_2$ or HOTf was used as the catalyst (Table 1, Entries 12 and 13). Gratifyingly, we found that increasing the amount of $Pd(OAc)_2$ to 0.2 equivalent produced **2a** in 38% yield (Table 1, Entry 14). Increasing the amount of $Pd(OAc)_2$ to 0.5 equivalent provided compound **2a** in 67% yield (Table 1, Entry 15). Continuing to increase the amount of $Pd(OAc)_2$ did not further improve the yield of **2a**. If the reaction was conducted under an oxygen atmosphere (a balloon filled with oxygen gas), the reaction system became disordered and complex product mixtures were formed, suggesting that ambient atmosphere is essential in this reaction to give **2a** in high yield (Table 1, Entry 16). Further examination of solvent effects revealed that the use of CH_3CN, tetrahydrofuran (THF), or *N*,*N*-dimethylforamide (DMF) as the solvent did not afford expected product **2a**, and only 25% yield of **2a** was afforded in 1,2-dichloroethane (DCE) (Table 1, Entries 17–20).

Having identified the optimal reaction conditions, we next carried out oxidative aromatization reactions of a variety of MCPs **1** to evaluate the scope of this reaction. The results are summarized in Table 2. For substrates **1b–i** in which R^1 = aryl and $R^2 = R^3$ = H, the corresponding aromatization products **2b–i** could be obtained in moderate yields (65–75%) within 12 h as the sole products (Table 2, Entries 1–8). The substrate with an electron-withdrawing substituent on the benzene rings afforded the corresponding product in lower yield (54%; Table 2, Entry 9). As for MCP **1k** in which R^1 = H, R^2 = Ph, and R^3 = H, and **1l** in which R^1 = H, R^2 = H, and R^3 = Ph, the reaction did not proceed to give the corresponding diaryl derivatives **2k** and **2l**, but complex product mixtures were formed presumably due to steric effects (Table 2, Entries 10 and 11).

Deuterium labeling experiments with MCPs **3**-*d* (C_α and $C_{\alpha'}$, D content = 64 and 69%) and **5**-*d* (C_β and C_γ, D content = 60 and 59%, respectively) were carried out under the standard conditions to clarify the reaction mechanism (Scheme 2). Products **4**-*d* with 32% D content at C_1 or ($C_{1'}$) and **6**-*d* without D content at C_1 and $C_{1'}$ were obtained in 65 and 66% yield, respectively, within 12 h on the basis of the corresponding ^{1}H NMR spectroscopic data (Supporting Information), suggesting that the hydrogen atoms at C_α or $C_{\alpha'}$ are transferred to C_1 or $C_{1'}$ in the presence of $Pd(OAc)_2$.

Table 1. Optimized conditions for the reaction of MCP **1a** with $Pd(OAc)_2$.[a]

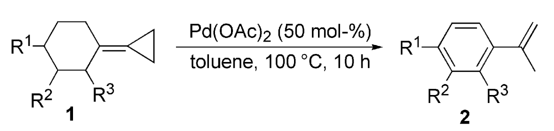


1a **2a**

Entry	[Pd] (equiv.)	[P] (equiv.)	Solvent	Temp. [°C]	% Yield[b] of **2a**
1	$Pd(OAc)_2$ (0.1)	–	toluene	100	27
2	$Pd(OAc)_2$ (0.1)	PPh_3 (0.2)	toluene	100	12
3	$Pd(OAc)_2$ (0.1)	P(2-furyl)$_3$ (0.2)	toluene	100	8
4	$Pd(OAc)_2$ (0.1)	binap (0.2)	toluene	100	NR
5	$Pd(OAc)_2$ (0.1)	–	toluene	100	11[c]
6	$PdCl_2(PPh)_3$ (0.1)	–	toluene	100	NR
7	$Pd(MeCN)_2(OTs)_2$ (0.1)	–	toluene	100	NR
8	$Pd(OOCPh)_2$ (0.1)	–	toluene	100	NR
9	$Pd(OAc)_2(Py)_2$ (0.1)	–	toluene	100	complex mixtures
10	$Pd(OAc)_2(PPh_3)_2$ (0.1)	–	toluene	100	complex mixtures
11	$Pd(OOCCF_3)_2$ (0.1)	–	toluene	100	complex mixtures
12	$Pd(MeCN)_2(OTf)_2$ (0.1)	–	toluene	100	–
13	HOTf (0.1)	–	toluene	100	complex mixtures
14	Pd(OAc)2 (0.2)	–	toluene	100	38
15	$Pd(OAc)_2$ (0.5)	–	toluene	100	67
16	$Pd(OAc)_2$ (0.5)	–	toluene	100	complex mixtures[d]
17	$Pd(OAc)_2$ (0.5)	–	CH_3CN	80	complex mixtures
18	$Pd(OAc)_2$ (0.5)	–	DCE	80	25
19	$Pd(OAc)_2$ (0.5)	–	THF	80	complex mixtures
20	$Pd(OAc)_2$ (0.5)	–	DMF	80	NR

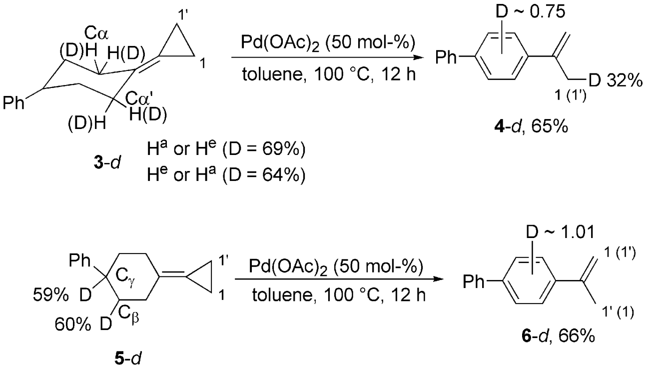
[a] Reaction conditions: **1a** (0.2 mmol), [Pd], [P] (0.04 mmol), and solvent (2.0 mL), and the reactions were carried out at various temperatures under ambient atmosphere unless otherwise specified. [b] Isolated yields. [c] Under an argon atmosphere. [d] Under an oxygen atmosphere.

Table 2. Pd(OAc)$_2$-catalyzed rearrangement of **1** under the optimal conditions.[a]



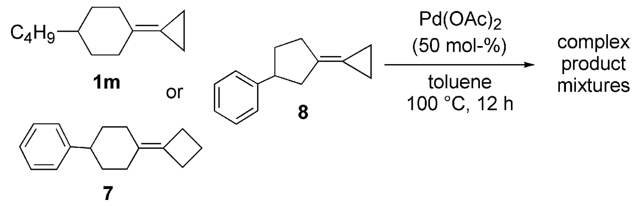
Entry	**1** (R^1, R^2, R^3)	Product, % Yield[b]
1	**1b** (*p*-MeC$_6$H$_4$, H, H)	**2b**, 75
2	**1c** (*m*-MeC$_6$H$_4$, H, H)	**2c**, 64
3	**1d** (*o,p*-MeC$_6$H$_3$, H, H)	**2d**, 67
4	**1e** (*o,m*-Me$_2$C$_6$H$_3$, H, H)	**2e**, 71
5	**1f** (*m,m*-Me$_2$C$_6$H$_3$, H, H)	**2f**, 65
6	**1g** (*m*-MeOC$_6$H$_4$, H, H)	**2g**, 65
7	**1h** (*p*-MeOC$_6$H$_4$, H, H)	**2h**, 62
8	**1i** (*p*-C$_6$H$_5$C$_6$H$_4$, H, H)	**2i**, 61
9	**1j** (*p*-ClC$_6$H$_4$, H, H)	**2j**, 54
10	**1k** (H, C$_6$H$_5$, H)	**2k**, complex mixtures
11	**1l** (H, H, C$_6$H$_5$)	**2l**, complex mixtures

[a] Reaction conditions: **1** (0.2 mmol), Pd(OAc)$_2$ (0.1 mmol), and toluene (2.0 mL), and the reactions were carried out at 100 °C. [b] Isolate yield.



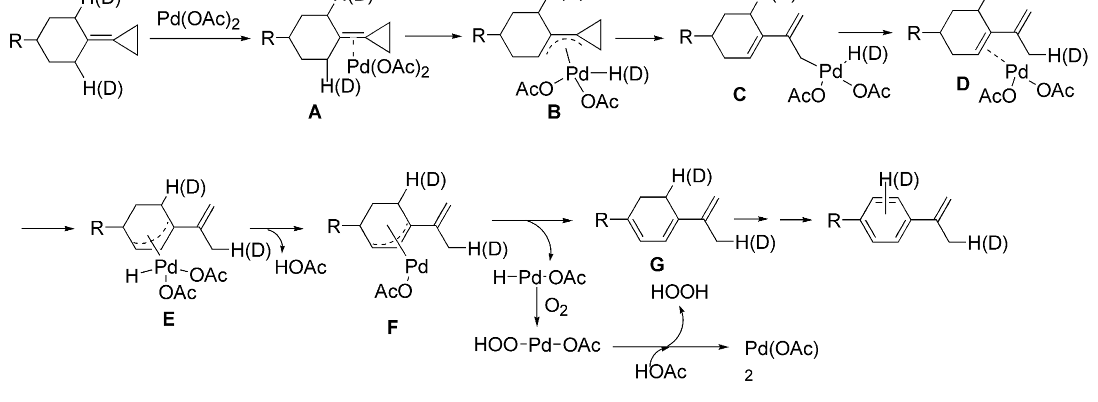
Scheme 2. Deuterium labeling experiment for the rearrangement of MCPs **3** and **5**.

The control experiments shown in Scheme 3 indicated that a cyclopropane ring, a cyclohexane ring, and an aryl group in MCPs **1** are crucial in this palladium-catalyzed aromatization, as complex product mixtures were obtained by using aliphatic MCP **1m**, **7**, and **8** as the substrates under the standard conditions (Scheme 3).



Scheme 3. Control experiment.

A plausible mechanism for the formation of 4-isopropenylbiaryl derivatives **2** is outlined in Scheme 4, and it is based on the above deuterium labeling and control experiments and the propositions of Trost and Labinger for the heterogeneous case.[3,4] Initially, MCP **1** reacts with the palladium catalyst to form complex **A**. The C$_\alpha$–H or C$_{\alpha'}$–H bond of MCP **1** is activated by Pd^{II} to generate allylic intermediate **B** (a Pd^{IV} species),[5] followed by ring opening and rearrangement to afford intermediate **C**. Then, through reductive elimination intermediate **D** is obtained. Notably, one of the hydrogen atoms at the methyl group is derived from the C$_\alpha$–H or C$_{\alpha'}$–H bond, which is consistent with the results of the deuterium labeling experiment shown in Scheme 2. The following process is similar to that suggested by the group of Labinger.[4] Palladium(II) inserts into the allylic C–H bond of cyclohexene to give intermediate **E**, which is followed by elimination of acetic acid to subsequently give intermediate **F**, which undergoes dehydrogenated elimination to give 1,3-cyclohexadiene (**G**) and a palladium hydride species. Insertion of O$_2$ into the Pd–H bond then produces a peroxy intermediate that reacts with acetic acid to regenerate the catalyst. The further dehydrogenated elimination of **G** produces the final 4-isopropenylbiaryl product. In a similar cycle (not shown) 1,3-cyclohexadiene would react analogously to give benzene.[5,9]



Scheme 4. Proposed reaction mechanism.

Conclusions

In conclusion, we have developed an effective palladium-catalyzed tandem C–H and C–C bond activation and oxidative aromatization through intramolecular hydrogen transfer and dehydrogenated rearrangement of methylenecyclopropanes **1** to produce isopropenylbiaryl derivatives **2** in moderate to good yields at high temperature under an ambient atmosphere. The reaction proceeds through transfer of a hydrogen atom from the cyclohexyl ring to the cyclopropane ring in the presence of Pd^{II} followed by dehydrogenation with oxygen. This new palladium(II)-catalyzed process provides an alternative way to attain biaryl products that constitute core structural units for a wide range of functional molecules synthesized primarily by using transition-metal-catalyzed aryl–aryl cross-coupling reactions.[10] Efforts are in progress to elucidate further mechanistic details of this reaction and to understand its scope and limitations.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Low- and high-resolution mass spectra were recorded by EI methods. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out by using silica gel at increased pressure.

Typical Reaction Procedure for the Reactions: Under ambient atmosphere, to a solution of methylenecyclopropane **1a** (40 mg, 0.2 mmol) in toluene (2.0 mL) was added Pd(OAc)$_2$ (22 mg, 0.1 mmol). The reaction mixture was stirred at 100 °C for 10 h (monitored by TLC). Then the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO$_2$) to give corresponding product **2a** (27 mg, 67%) as a colorless oil.

Compound 2a: Yield: 27 mg, 67%. Known compound; colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.20 (s, 3 H, CH$_3$), 5.11 (d, J = 2.0 Hz, 1 H, =CH$_2$), 5.44 (s, 1 H, =CH$_2$), 7.34–7.37 (m, 1 H, ArH), 7.42–7.47 (m, 2 H, ArH), 7.56–7.62 (m, 6 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 21.8, 112.2, 125.1, 126.5, 129.1, 131.1, 135.1, 136.9, 141.0, 142.1 ppm. Spectroscopic data are consistent with those reported in the literature.[11]

Compound 2b: Yield: 32 mg, 75%. Colorless oil. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3078, 2922, 2855, 1903, 1686, 1609, 1492, 1453, 1376, 1265, 1114, 1006, 889, 846, 815, 565 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.19 (s, 3 H, CH$_3$), 2.40 (s, 3 H, CH$_3$), 5.10 (d, J = 0.8 Hz, 1 H, =CH$_2$), 5.42 (s, 1 H, =CH$_2$), 7.25 (d, J = 7.2 Hz, 2 H, ArH), 7.50–7.55 (m, 6 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 21.1, 21.8, 112.3, 125.8, 126.7, 126.8, 126.9, 127.0, 129.5, 137.1 ppm. MS (EI) m/z (%): 208 (100.00) [M]$^+$, 193 (24.78), 178 (21.22), 165 (13.27), 152 (8.32), 115 (7.21), 89 (7.23), 43 (27.19). HRMS (EI): calcd. for C$_{16}$H$_{16}$ [M]$^+$ 208.1252; found 208.1255.

Compound 2c: Yield: 27 mg, 64%. Colorless oil. IR: $\tilde{\nu}$ = 3020, 2925, 2856, 1685, 1606, 1483, 1458, 1377, 1266, 1112, 844, 762, 726 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.20 (d, J = 0.4 Hz, 3 H, CH$_3$), 2.29 (s, 3 H, CH$_3$), 5.11–5.12 (m, 1 H, =CH$_2$), 5.44 (d, J = 0.4 Hz, 1 H, =CH$_2$), 7.24–7.31 (m, 6 H, ArH), 7.52 (d, J = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 20.5, 21.8, 112.3, 125.1, 125.4, 125.8, 127.2, 129.1, 129.7, 130.2, 130.3, 141.0, 142.8 ppm. MS (EI) m/z (%): 208 (100.00) [M]$^+$, 195 (46.87), 178 (32.08), 165 (46.06), 152 (27.65), 118 (36.13), 57 (50.19), 43 (98.53). HRMS (EI): calcd. for C$_{16}$H$_{16}$ [M]$^+$ 208.1252; found 208.1250.

Compound 2d: Yield: 28 mg, 67%. Colorless oil. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3084, 2922, 2857, 1686, 1491, 1452, 1375, 1265, 1231, 1115, 1035, 1006, 846, 816 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.19–2.20 (m, 3 H, CH$_3$), 2.27 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 5.10–5.11 (m, 1 H, =CH$_2$), 5.43–5.44 (m, 1 H, =CH$_2$), 7.07–7.15 (m, 3 H, ArH), 7.28 (d, J = 8.4 Hz, 2 H, ArH), 7.51 (d, J = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 20.4, 21.0, 21.8, 112.2, 125.1, 126.5, 129.1, 129.7, 131.1, 135.1, 136.9, 138.7, 141.0, 142.9 ppm. MS (EI) m/z (%): 222 (100.00) [M]$^+$, 207 (23.92), 192 (18.53), 179 (13.73), 132 (16.12), 96 (7.91), 58 (12.02), 43 (39.50). HRMS (EI): calcd. for C$_{17}$H$_{18}$ [M]$^+$ 222.1409; found 222.1410.

Compound 2e: Yield: 32 mg, 71%. Colorless oil. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3084, 2969, 2921, 2857, 1627, 1491, 1453, 1375, 1300, 1231, 1116, 1006, 889, 846, 817, 580 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.19 (s, 3 H, CH$_3$), 2.27 (s, 3 H, CH$_3$), 2.37 (s, 3 H, CH$_3$), 5.10–5.11 (m, 1 H, =CH$_2$), 5.43 (d, J = 0.8 Hz, 1 H, =CH$_2$), 7.07–7.15 (m, 3 H, ArH), 7.28 (d, J = 8.8 Hz, 2 H, ArH), 7.51 (d, J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 20.4, 21.0, 21.8, 112.2, 125.1, 126.5, 129.1, 129.7, 131.1, 135.2, 136.9, 141.0, 142.9 ppm. MS (EI) m/z (%): 222 (86.22) [M]$^+$, 209 (37.15), 192 (19.63), 179 (16.85), 165 (30.42), 132 (18.80), 115 (9.73), 43 (100.00). HRMS (EI): calcd. for C$_{17}$H$_{18}$ [M]$^+$ 222.1409; found 222.1410.

Compound 2f: Yield: 29 mg, 65%. Colorless oil. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2922, 2851, 1686, 1604, 1512, 1459, 1375, 1265, 1017, 834 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.18–2.19 (m, 3 H, CH$_3$), 2.38 (s, 6 H, CH$_3$), 5.10–5.11 (m, 1 H, =CH$_2$), 5.42–5.43 (m, 1 H, =CH$_2$), 6.85 (s, 1 H, ArH), 6.99 (s, 1 H, ArH), 7.21 (d, J = 0.4 Hz, 2 H, ArH), 7.52–7.54 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 21.4, 21.8, 112.3, 124.9, 125.8, 126.9, 128.9, 138.3, 139.9, 140.4, 140.7, 142.8 ppm. MS (EI) m/z (%): 222 (56.97) [M]$^+$, 209 (14.05), 191 (6.68), 165 (8.49), 132 (17.24), 115 (5.88), 58 (17.35), 43 (100.00). HRMS (EI): calcd. for C$_{17}$H$_{18}$ [M]$^+$ 222.1409; found 222.1411.

Compound 2g: Yield: 29 mg, 65%. Colorless oil. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3081, 3029, 2957, 2854, 1600, 1583, 1481, 1464, 1295, 1213, 1053, 1032, 889, 778, 696 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.19 (s, 3 H, CH$_3$), 3.87 (s, 3 H, OCH$_3$), 5.11–5.12 (m, 1 H, =CH$_2$), 5.43 (d, J = 0.4 Hz, 1 H, =CH$_2$), 7.13–7.21 (m, 2 H, ArH), 7.29–7.38 (m, 3 H, ArH), 7.54–7.57 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 21.8, 55.3, 112.4, 112.5, 112.6, 112.7, 119.5, 125.9, 126.8, 126.9, 127.1, 129.2, 129.6, 129.7 ppm. MS (EI) m/z (%): 224 (100.00) [M]$^+$, 209 (15.30), 178 (8.79), 165 (15.62), 134 (8.14), 71 (8.70), 58 (25.53), 43 (70.64). HRMS (EI): calcd. for C$_{16}$H$_{16}$O [M]$^+$ 224.1201; found 224.1202.

Compound 2h: Yield: 28 mg, 62%. Colorless oil. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3081, 3029, 2957, 2854, 1600, 1583, 1481, 1464, 1295, 1213, 1053, 1032, 889, 778, 696 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.19 (s, 3 H, CH$_3$), 3.87 (s, 3 H, OCH$_3$), 5.11–5.12 (m, 1 H, =CH$_2$), 5.43 (d, J = 0.4 Hz, 1 H, =CH$_2$), 7.13–7.21 (m, 2 H, ArH), 7.29–7.38 (m, 3 H, ArH), 7.54–7.57 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 21.8, 55.3, 112.4, 112.6, 112.7, 119.5, 125.9, 126.8, 126.9, 127.1, 129.6, 129.7 ppm. MS (EI) m/z (%): 224 (100.00) [M]$^+$, 207 (43.25), 178 (9.78), 165 (15.62), 134 (8.94), 71

(4.70), 58 (32.90), 43 (71.34). HRMS (EI): calcd. for $C_{16}H_{16}O$ $[M]^+$ 224.1201; found 224.1202.

Compound 2i: Yield: 34 mg, 61%. Colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3052, 2962, 2928, 1485, 1265, 1006, 894, 825, 765, 738, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.20 (s, 3 H, CH_3), 5.12 (d, J = 0.4 Hz, 1 H, =CH_2), 5.45 (s, 1 H, =CH_2), 7.31–7.35 (m, 2 H, ArH), 7.43–7.47 (m, 3 H, ArH), 7.56–7.68 (m, 8 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.8, 112.5, 125.9, 126.8, 126.9, 127.0, 127.2, 127.3, 127.4, 127.5, 128.8, 138.2, 139.6, 140.2, 142.7 ppm. MS (EI) m/z (%): 270 (100.00) $[M]^+$, 257 (42.05), 243 (19.88), 226 (11.63), 180 (19.68), 152 (16.32), 115 (17.17), 77 (25.88). HRMS (EI): calcd. for $C_{21}H_{18}$ $[M]^+$ 270.1409; found 270.1412.

Compound 2j: Yield: 25 mg, 54%. Known compound; colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3081, 3029, 2957, 2854, 1600, 1583, 1481, 1464, 1295, 1213, 1053, 1032, 889, 778, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.19 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 5.11 (s, 1 H, =CH_2), 5.43 (s, 1 H, =CH_2), 7.24–7.26 (m, 4 H, ArH), 7.50–7.55 (m, 4 H, ArH), 7.54–7.57 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.8, 112.2, 115.1, 126.0, 126.4, 126.5, 129.1, 129.7, 129.8, 131.0, 131.1 ppm. Spectroscopic data are consistent with those reported in the literature.[11]

Compound (4-*d*): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.19 (s, 2.68 H, CH_3), 5.11 (s, 1 H, =CH_2), 5.43 (s, 1 H, =CH_2), 7.23–7.29 (m, 2 H, ArH), 7.42–7.44 (m, 1.85 H, ArH), 7.54–7.62 (m, 5.40 H, ArH) ppm.

Compound (6-*d*): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.19 (s, 3 H, CH_3), 5.11–5.12 (m, 1 H, =CH_2), 5.43 (s, 1 H, =CH_2), 7.32–7.36 (m, 0.84 H, ArH), 7.42–7.46 (m, 2 H, ArH), 7.55–7.62 (m, 5.10 H, ArH).

Supporting Information (see footnote on the first page of this article): Detailed description of the experimental procedures, NMR spectroscopic charts of the products shown in the tables and schemes.

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