DOI: 10.1002/ejoc.200800888

Platinum-Catalyzed Cyclization of *o*-Alkynyl(oxo)benzenes with Alkenes by 1,2-Migration of Benzene: Synthesis of 8-Oxabicyclo[3.2.1]octane Derivatives

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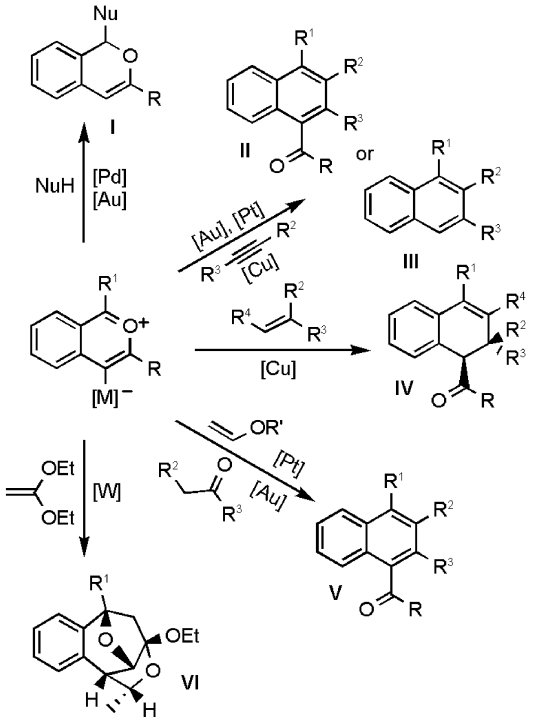
Keywords: Platinum / 1,2-Migration / Homogeneous catalysis / Alkenes

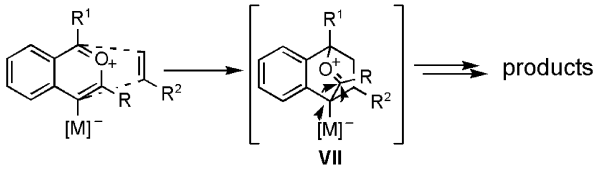
An interesting migration of the rigid structure of benzene was observed when propargylic esters were introduced to the cyclization chemistry of *o*-alkynyl(oxo)benzene. Various 8-oxabicyclo[3.2.1]octane derivatives with many functional groups could be synthesized from this efficient approach catalyzed by platinum. The high stereo- and regioselectivity involved in this transformation was also attractive.

Introduction

As a result of its synthetic potential, the transition-metal-catalyzed cyclization of *o*-alkynyl(oxo)benzenes is currently a popular research topic.[1–7] The formation of metal-containing benzopyrylium-type intermediates is considered a common process, which upon further treatment with various reaction partners, such as, nucleophiles,[2] alkynes,[3] alkenes,[4] vinyl ethers,[5] carbonyl compounds,[6] and ketene acetals,[7] result in diverse products (Scheme 1). However, to our surprise there was no skeletal rearrangement observed, although oxonium ions and metal carbenes are presumed to exist in almost all reactions.[8] We envisioned that intermediate **VII**, formed from the Diels–Alder reaction of benzopyrylium with olefin, might undergo 1,2-aryl or alkyl migration driven by both the oxonium ion and the negative metal (Scheme 2). Herein, we report a platinum[9]-catalyzed cyclization of *o*-alkynyl(oxo)benzenes with conventional alkenes to afford synthetically useful 8-oxabicyclo[3.2.1]octane derivatives in good yield, where the 1,2-migration of the rigid benzene groups was the key step.[10]



Scheme 1.



Scheme 2.

Results and Discussion

We started by using *o*-(phenylethynyl)benzaldehyde (**1a**) with styrene (3 equiv.) in the presence of $PtCl_2$ (5 mol-%) under CO (1 atm) in toluene at 80 °C, and desired product **2a** was obtained in 25% yield after 2.5 h (Table 1, entry 1). To improve this result, we examined different types of alkynes, among which the exciting result was just obtained when propargylic ester[11] was used (Table 1, entries 2–4). A

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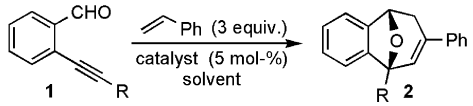
similar result was also observed with a lower temperature, whereas the changes in solvent and catalyst systems could not improve the yield (Table 1, entries 5–7). In contrast, gold catalysis gave either a low yield or no desired product (Table 1, entries 8–11). Thus, the use of $PtCl_2$ (5 mol-%) and CO (1 atm) in toluene (3 mL) at 60 °C was found to be the most efficient system, and it was used as the standard conditions.

Table 1. Optimization of the reaction conditions.[a]



Entry	R	Conditions	Product (% Yield)[b]
1	Ph (**1a**)	$PtCl_2$, CO, toluene, 80 °C, 2.5 h	**2a** (25)
2	C_5H_{11} (**1b**)	$PtCl_2$, CO, toluene, 80 °C, 3 h	**2b** (61)
3	CH_2OH (**1c**)	$PtCl_2$, CO, toluene, 80 °C, 1 h	**2c** (23)
4	CH_2OAc (**1d**)	$PtCl_2$, CO, toluene, 80 °C, 1 h	**2d** (80)
5	CH_2OAc (**1d**)	$PtCl_2$, CO, toluene, 60 °C, 1.5 h	**2d** (83)
6	CH_2OAc (**1d**)	$PtCl_2$, CO, DCE, 60 °C, 1 h	**2d** (76)
7	CH_2OAc (**1d**)	$PtCl_2$, toluene, 60 °C, 10 h	**2d** (65)
8	CH_2OAc (**1d**)	$AuCl_3$, DCM, room temp., 3 h	**2d** (7)
9	CH_2OAc (**1d**)	AuCl, DCM, room temp., 4 h	**2d** (11)
10	CH_2OAc (**1d**)	$Au(PPh_3)BF_4$, DCM, room temp., 4 h	–[c]
11	CH_2OAc (**1d**)	$Au(PPh_3)OTf$, DCM, room temp., 4 h	–[c]

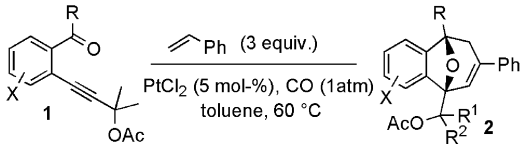
[a] Unless noted, all reactions were carried out by using **1** (0.5 mmol) with styrene (3 equiv.) under catalyst (5 mol-%) in solvent (3 mL). [b] Isolated yield. [c] The substrate disappeared after 4 h; however, no desired product was observed.

Under the optimal conditions, we studied the scope of this cyclization, as shown in Table 2. Various substituents at the propargylic position were tolerated (Table 2, entries 1–9), where aryl groups, such as phenyl and electron-withdrawing and electron-rich aromatics, all led to good yields of the desired products (Table 2, entries 2–5). The 2-furyl substituent gave a moderate yield of **2i** (Table 2, entry 6). The reaction efficiency was consistent with the steric hindrance. The less-hindered methyl group gave a better result than a benzyl group on the propargyl acetate or dimethyl substituents (Table 2, entry 7 vs. entries 8 and 9).

When the substrate with a ketone function was used, the reaction also proceeded smoothly to afford **2m** in slightly lower yield (Table 2, entry 10). Furthermore, substituents on the benzene ring did not affect the reaction, and always good-to-excellent results were always achieved (Table 2, entries 11 and 12).

We tested this cyclization with different alkenes (Table 3). Among these, styrene gave the best result, especially the electron-rich one (Table 3, entries 1 and 2). Hexene was also applied in this transformation and a moderate yield was obtained (Table 3, entry 3). However, alkenes with functional groups always led to a poor yield of the desired product or decomposition of the substrate (Table 3, entries 4 and 5). Internal alkenes, such as cyclohexene and *trans*-stilbene, reacted smoothly to give corresponding *trans* and *cis* products in moderate yield (Table 3, entry 6 vs. 7).

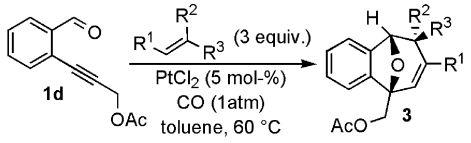
Table 2. Scope study of the cyclization of *o*-alkynyl(oxo)benzenes.[a]



Entry	Substrate	Time [h]	Product (% Yield)[b]
1	X = R = R^1 = R^2 = H (**1d**)	1.5	**2d** (83)
2	X = R = R^1 = H, R^2 = Ph (**1e**)	4	**2e** (82)
3	X = R = R^1 = H, R^2 = 4-ClC_6H_4 (**1f**)	4	**2f** (76)
4	X = R = R^1 = H, R^2 = 4-$CH_3C_6H_4$ (**1g**)	1	**2g** (86)
5	X = R = R^1 = H, R^2 = 2,3-methylenedioxy (**1h**)	3	**2h** (73)
6	X = R = R^1 = H, R^2 = 2-furanyl (**1i**)	3	**2i** (48)
7	X = R = R^1 = H, R^2 = CH_3 (**1j**)	1	**1j** (72)
8	X = R = R^1 = H, R^2 = $C_6H_5CH_2$ (**1k**)	6	**2k** (73)
9	X = R = H, R^1 = R^2 = CH_3 (**1l**)	1.5	**2l** (25)
10	X = H, R = CH_3, R^1 = R^2 = H (**1m**)	8	**2m** (41)
11	X = 4-Cl, R = R^1 = R^2 = H (**1n**)	4	**2n** (89)
12	X = 3-CH_3[c], R^1 = R^2 = H (**1o**)	2	**2o** (98)

[a] Unless noted, all reactions were carried out by using **1** (0.5 mmol) with styrene (3 equiv.) under $PtCl_2$/CO (5 mol-%/1 atm) in toluene (3 mL) at 60 °C. [b] Isolated yield. [c] The methyl substituent is *ortho* to the alkyne.

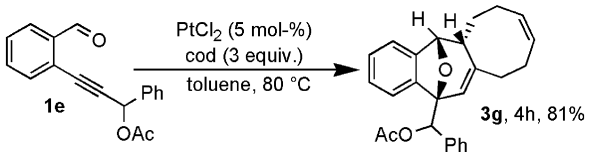
Table 3. Scope of the platinum-catalyzed cyclization of **1d** with different alkenes.[a]



Entry	R^1	R^2	R^3	Time [h]	Product (% Yield)[b]
1	4-ClC_6H_4	H	H	4	**3a** (53)
2	4-$CH_3C_6H_4$	H	H	1	**3b** (82)
3	C_4H_9	H	H	3	**3c** (51)
4	CH_2OTBS	H	H	4	**3d** (21)
5[c]	OEt	H	H	1	–[d]
6	–$(CH_2)_4$–		H	6	**3e** (37)
7	Ph	H	Ph	5	**3f** (46)

[a] Unless noted, all reactions were carried out by using **1d** (0.5 mmol) with the alkenes (3 equiv.) under $PtCl_2$/CO (5 mol-%/1 atm) in toluene (3 mL) at 60 °C. [b] Isolated yield. [c] Run at room temp. [d] Decomposed.

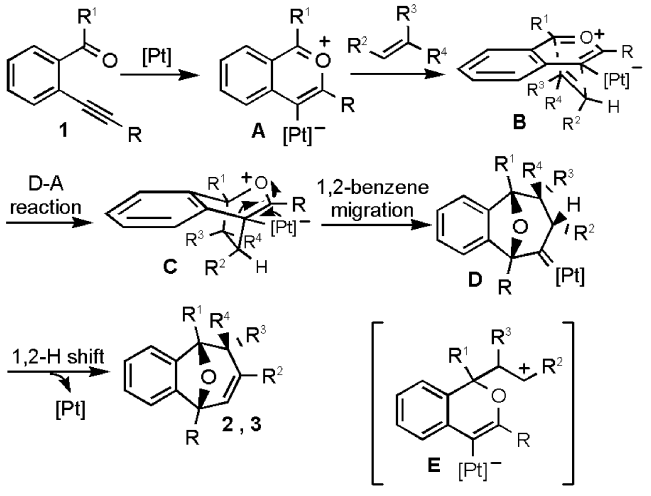
Interestingly, when *o*-alkynyl(oxo)benzene (**1e**; Scheme 3) was exposed to the conditions containing $PtCl_2$ (5 mol-%) and 1,5-cyclooctadiene (3 equiv.) in toluene at 80 °C, polycyclic product **3g** was obtained in 81% yield after 4 h. In this reaction, one of the double bonds in the 1,5-cyclooctadiene



Scheme 3. Cyclization of **1e** with 1,5-cyclooctadiene.

was saved, what could be used for constructing more complex structures.

A plausible mechanism for this transformation is shown in Scheme 4. As previously reported, benzopyrylium-type intermediate **A** is formed after coordination of the alkynes to the platinum catalyst.[1–7] Subsequently, a high stereo- and regiospecific Diels–Alder reaction of **A** with alkenes leads to the formation of complex **C**, where the oxonium ion might trigger the 1,2-migration of an adjacent group when assisted with a metal to give compound **D**.[8] Further, a 1,2-hydrogen-atom shift of nonstabilized carbene intermediate **D** afforded the desired products **2** and **3**.[12] The excellent stereoselectivity might be due to the steric hindrance of the R group, which orients R^2 away from it in steps **A** to **B**. In contrast, the regioselectivity of this reaction might be accounted for by considering carbocation intermediate **E** on the way from **B** to **C**.[4] When R^2 is an aryl group or an electron-donating substituent, carbocation **E** could be well stabilized. The two factors directly lead to the formation of favored intermediate **C**, which further transforms into desired products **2** and **3**.



Scheme 4. Proposed mechanism with stereo- and regiospecific study.

Conclusions

We reported an efficient approach to 8-oxabicyclo[3.2.1]-octane derivatives by platinum-catalyzed cyclization of *o*-alkynyl(oxo)benzenes with alkenes. In this transformation, a 1,2-migration of the rigid structure of benzene was observed. The high stereo- and regioselectivity was also disclosed. In comparison with conventional alkynes, propargylic esters gave the best result. The detailed mechanism of the influence of the ester group is worthy of further study.

Experimental Section

General Remarks: Column chromatography was carried out on silica gel. Unless noted, ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ by using TMS as an internal standard. IR spectra were recorded with an FTIR spectrometer and only major peaks are reported. Melting points were determined with a microscopic apparatus and are uncorrected. All new compounds were further characterized by element analysis. X-ray crystallography of **2e-1** is also provided. Diastereomeric ratio was determined by ^{1}H NMR spectroscopy. Commercially available reagents and solvents were used without further purification.

General Produce for the Platinum-Catalyzed Cyclization of *o*-Alkynyl(oxo)benzenes with Alkenes: To a stirred solution of *o*-alkynyl(oxo)benzene **1** (0.50 mmol) in toluene (3.0 mL) was added $PtCl_2$ (6.7 mg, 5 mol-%) under a CO atmosphere (1 atm) at 60 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was diluted with ethyl acetate (30 mL), and the solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding products.

2a: Yield: 38.7 mg (25%). Solid. M.p. 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.72 (m, 2 H), 7.49–7.14 (m, 11 H), 7.00–6.94 (m, 1 H), 6.93 (s, 1 H), 5.74–5.72 (d, J = 6.0 Hz, 1 H), 3.32–3.26 (m, 1 H), 2.43–2.39 (dd, J = 17.3, 0.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 142.5, 139.8, 139.4, 132.6, 130.1, 128.6, 128.3, 128.1, 127.6, 126.9, 126.8, 126.6, 124.9, 121.0, 118.6, 84.3, 77.3, 31.4 ppm. IR (KBr): $\tilde{\nu}$ = 3380, 3058, 3028, 2952, 2923, 2855, 2246, 1952, 1809 cm^{-1}. $C_{23}H_{18}O$ (310.39): calcd. C 89.00, H 5.85; found C 88.86, H 5.92.

2b: Yield: 92.7 mg (61%). Solid. M.p. 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.14 (m, 8 H), 7.04–7.03 (m, 1 H), 6.39 (s, 1 H), 5.54–5.53 (d, J = 6 Hz, 1 H), 3.21–3.15 (m, 1 H), 2.29–2.24 (d, J = 17.2 Hz, 1 H), 2.16–2.12 (m, 1 H), 2.07–2.03 (m, 1 H), 1.57–1.54 (m, 2 H), 1.42–1.35 (m, 4 H), 0.92–0.89 (t, J = 14 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 143.0, 139.8, 131.9, 131.0, 128.2, 127.4, 126.8, 126.5, 124.7, 120.9, 117.3, 83.3, 76.9, 34.2, 32.4, 31.3, 23.3, 22.6, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 3025, 2952, 2931, 2863, 2729, 1944, 1896, 1795, 1708 cm^{-1}. $C_{22}H_{24}O$ (304.43): calcd. C 86.80, H 7.95; found C 86.69, H 8.02.

2c: Yield: 30.4 mg (23%). Solid. M.p. 121–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.11 (m, 9 H), 6.43–6.42 (m, 1 H), 5.60–5.59 (d, J = 6.0 Hz, 1 H), 4.22–4.19 (m, 2 H), 3.27–3.21 (m, 1 H), 2.37–2.32 (m, 1 H); 2.06 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 143.2, 139.3, 133.4, 128.3, 127.7, 127.1, 127.1, 127.0, 124.8, 121.1, 117.7, 84.1, 77.2, 63.6, 31.5 ppm. IR (KBr): $\tilde{\nu}$ = 3430, 3051, 3027, 2923, 2857, 2246, 1951, 1791, 1692 cm^{-1}. $C_{18}H_{16}O_2$ (264.32): calcd. C 81.79, H 6.10; found C 81.90, H 6.07.

2d: Yield: 127.0 mg (83%). Solid. M.p. 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.08 (m, 9 H), 6.45 (s, 1 H), 5.62–5.60 (d, J = 6.0 Hz, 1 H), 4.82–4.79 (d, J = 12.4 Hz, 1 H), 4.63–4.60 (d, J = 12.0 Hz, 1 H), 3.28–3.22 (m, 1 H), 2.32–2.28 (m, 1 H), 2.10 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 147.1, 142.7, 139.2, 133.3, 128.2, 127.7, 127.1, 127.0, 126.6, 124.7, 121.1, 117.4, 82.1, 77.3, 64.5, 31.2, 20.8 ppm. IR (KBr): $\tilde{\nu}$ = 3465, 3051, 3026, 2950, 2899, 2251, 1953, 1741 cm^{-1}. $C_{20}H_{18}O_3$ (306.36): calcd. C 78.41, H 5.92; found C 78.46, H 5.77.

(*R*,*S*/*S*,*R*)-2e-1: Yield: 82.1 mg (43%). Solid. M.p. 166–167 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.54 (d, J = 7.2 Hz, 2 H), 7.30–7.08 (m, 12 H), 6.70 (s, 1 H), 6.50 (s, 1 H), 5.55–5.53 (d, J = 5.7 Hz, 1 H), 3.23–3.15 (m, 1 H), 2.24–2.18 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1, 147.7, 142.3, 139.5, 136.1, 132.8, 128.7, 128.2, 128.2, 127.8, 127.6, 126.9, 126.8, 124.7, 120.9, 118.1, 84.6, 77.2, 76.3, 31.2, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 3405, 3034, 2954, 2922, 2853, 2527, 1952, 1733 cm^{-1}. $C_{26}H_{22}O_3$ (382.46): calcd. C 81.65, H 5.80; found C 81.82, H 5.73.

(*R*,*R*/*S*,*S*)-2e-2: Yield: 74.5 mg (39%). Solid. M.p. 129–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.61 (d, J = 6.6 Hz, 2 H), 7.37–7.10 (m, 12 H), 6.55 (s, 1 H), 6.45 (s, 1 H), 5.65–5.63 (d, J = 6.0 Hz, 1 H), 3.17–3.10 (m, 1 H), 2.27–2.21 (m, 1 H), 2.02 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 147.6, 142.4, 139.3, 136.2, 132.5, 128.7, 128.4, 128.2, 128.1, 127.6, 127.1, 127.0, 124.8, 121.1, 117.8, 85.2, 77.1, 74.5, 31.3, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 3632, 3457, 3407, 3062, 3032, 2954, 2925, 1955, 1737 cm^{-1}. $C_{26}H_{22}O_3$ (382.46): calcd. C 81.65, H 5.80; found C 81.87, H 5.74.

2f (10:7 *dr*): Yield: 158.1 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$, main isomer): δ = 7.49–7.47 (d, J = 8.4 Hz, 2 H), 7.30–7.12 (m, 11 H), 6.66 (s, 1 H), 6.45 (s, 1 H), 5.56–5.54 (d, J = 6.0 Hz, 1 H), 3.24–3.18 (m, 1 H), 2.27–2.21 (m, 1 H), 2.19 (s, 3 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.57–7.55 (d, J = 8.4 Hz, 2 H), 7.30–7.12 (m, 11 H), 6.50 (s, 1 H), 6.40 (s, 1 H), 5.63–5.61 (d, J = 6.0 Hz, 1 H), 3.16–3.09 (m, 1 H), 2.27–2.21 (m, 1 H), 2.01 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 170.1, 170.0, 147.6, 147.3, 142.4, 142.3, 139.4, 139.2, 134.7, 134.7, 134.3, 134.1, 133.1, 132.8, 130.2, 130.2, 128.3, 128.3, 128.1, 127.7, 127.7, 127.3, 127.1, 127.1, 127.0, 127.0, 126.8, 124.8, 124.7, 121.1, 121.0, 118.1, 117.7, 85.0, 84.5, 77.4, 77.1, 75.6, 73.8, 31.3, 21.2, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 3664, 3462, 3054, 3029, 2953, 2924, 2855, 2250, 1948, 1901, 1739 cm^{-1}. $C_{26}H_{21}ClO_3$ (416.90): calcd. C 74.91, H 5.08; found C 74.77, H 5.21.

2g (10:9 *dr*): Yield: 170.3 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$, main isomer): δ = 7.46–7.44 (d, J = 8.0 Hz, 2 H), 7.25–7.04 (m, 11 H), 6.71 (s, 1 H), 6.48 (s, 1 H), 5.54–5.52 (d, J = 6.0 Hz, 1 H), 3.21–3.15 (m, 1 H), 2.22–2.18 (m, 1 H), 2.21 (s, 3 H), 2.15 (s, 3 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.53–7.51 (d, J = 8.0 Hz, 2 H), 7.25–7.04 (m, 11 H), 6.54 (s, 1 H), 6.46 (s, 1 H), 5.62–5.60 (d, J = 6.0 Hz, 1 H), 3.13–3.07 (m, 1 H), 2.26 (s, 3 H), 2.22–2.18 (m, 1 H), 1.96 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 170.1, 170.0, 147.8, 147.6, 142.4, 142.3, 139.5, 139.3, 138.0, 137.8, 133.2, 133.1, 132.7, 132.3, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1, 127.7, 127.5, 127.2, 126.9, 126.8, 124.7, 124.6, 120.9, 120.8, 118.1, 117.7, 85.2, 84.6, 77.2, 76.2, 74.3, 31.2, 31.2, 21.1, 21.1, 21.0, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 3459, 3051, 3028, 2952, 2923, 2858, 2248, 1948, 1904, 1739 cm^{-1}. $C_{27}H_{24}O_3$ (396.48): calcd. C 81.79, H 6.10; found C 81.73, H 6.21.

2h (10:8 *dr*): Yield: 170.3 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$, main isomer): δ = 7.29–7.00 (m, 11 H), 6.68–6.66 (d, J = 8.4 Hz, 1 H), 6.66 (s, 1 H), 6.42 (s, 1 H), 5.83–5.81 (m, 2 H), 5.58–5.56 (d, J = 6.0 Hz, 1 H), 3.25–3.19 (m, 1 H), 2.25–2.21 (m, 1 H), 2.18 (s, 3 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.29–7.00 (m, 11 H), 6.75–6.73 (d, J = 8.0 Hz, 1 H), 6.47 (s, 1 H), 6.40 (s, 1 H), 5.87–5.85 (m, 2 H), 5.64–5.63 (d, J = 6.0 Hz, 1 H), 3.17–3.11 (m, 1 H), 2.25–2.21 (m, 1 H), 1.98 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 170.2, 170.1, 147.8, 147.6, 147.6, 147.4, 147.2, 142.4, 142.3, 139.5, 139.2, 132.9, 132.3, 129.9, 128.3, 128.2, 127.6, 127.6, 127.1, 126.9, 126.9, 124.7, 124.7, 122.8, 122.7, 121.0, 120.9, 118.2, 117.7, 109.4, 109.3, 107.7, 107.5, 100.9, 100.9, 85.2, 84.6, 77.3, 77.1, 76.1, 74.1, 31.3, 31.2, 21.2, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3457, 3050, 3026, 2954, 2924, 2901, 2856, 2778, 2249, 1743 cm^{-1}. $C_{27}H_{22}O_5$ (426.47): calcd. C 76.04, H 5.20; found C 76.32, H 5.09.

(*R*,*S*/*S*,*R*)-2i-1: Yield: 50.2 mg (27%). Solid. M.p. 148–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.36 (m, 1 H), 7.30–7.21 (m, 6 H), 7.18–7.15 (m, 3 H), 6.64 (s, 1 H), 6.62–6.61 (m, 1 H), 6.45 (m, 1 H), 6.29–6.27 (m, 1 H), 5.64–5.63 (d, J = 6.0 Hz, 1 H), 3.29–3.23 (m, 1 H), 2.32–2.27 (m, 1 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 149.5, 147.6, 142.5, 142.2, 139.5, 133.0, 128.3, 127.7, 127.2, 127.1, 127.0, 124.9, 121.0, 118.2, 110.7, 110.4, 84.2, 77.5, 69.4, 31.3, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 3432, 3054, 2954, 2924, 2854, 2252, 1748 cm^{-1}. $C_{24}H_{20}O_4$ (372.42): calcd. C 77.40, H 5.41; found C 77.34, H 5.42.

(*R*,*R*/*S*,*S*)-2i-2: Yield: 39.1 mg (21%). Solid. M.p. 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 1 H), 7.33–7.11 (m, 8 H), 6.89–6.88 (m, 1 H), 6.66–6.65 (m, 1 H), 6.62–6.60 (m, 2 H), 6.38–6.36 (m, 1 H), 5.68–5.67 (d, J = 6.0 Hz, 1 H), 3.27–3.21 (m, 1 H), 3.33–3.28 (d, J = 17.2 Hz, 1 H), 2.04 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 149.4, 147.0, 142.9, 142.5, 139.4, 132.4, 128.3, 127.7, 127.1, 127.0, 126.9, 124.8, 121.0, 117.9, 111.2, 110.5, 84.6, 77.4, 68.0, 31.3, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 3450, 3027, 2954, 2924, 2854, 2251, 1746 cm^{-1}. $C_{24}H_{20}O_4$ (372.42): calcd. C 77.40, H 5.41; found C 77.27, H 5.46.

2j (10:5 *dr*): Yield: 115.2 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$, main isomer): δ = 7.30–7.04 (m, 9 H), 6.49 (s, 1 H), 5.76–5.71 (q, J = 6.4, 13.2 Hz, 1 H), 5.62–5.60 (d, J = 5.6 Hz, 1 H), 3.28–3.22 (m, 1 H), 2.29–2.25 (d, J = 17.2 Hz, 1 H), 2.15 (s, 3 H), 1.36–1.34 (d, J = 6.4 Hz, 3 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.30–7.04 (m, 9 H), 6.39 (s, 1 H), 5.70–5.65 (q, J = 6.8, 13.2 Hz, 1 H), 5.62–5.60 (d, J = 5.6 Hz, 1 H), 3.24–3.17 (m, 1 H), 2.30–2.26 (d, J = 17.2 Hz, 1 H), 2.00 (s, 3 H), 1.46–1.44 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 170.6, 170.4, 147.8, 147.2, 142.5, 142.5, 139.3, 139.2, 132.8, 132.7, 128.2, 128.2, 127.7, 127.6, 127.5, 127.0, 127.0, 127.0, 126.8, 124.6, 124.6, 120.9, 117.8, 117.6, 84.9, 84.5, 77.3, 76.8, 71.0, 69.6, 31.2, 21.1, 20.9, 14.8, 14.6 ppm. IR (KBr): $\tilde{\nu}$ = 3452, 3052, 3027, 2987, 2939, 2902, 2251, 1951, 1733 cm^{-1}. $C_{21}H_{20}O_3$ (320.39): calcd. C 78.73, H 6.29; found C 78.92, H 6.13.

2k (10:5 *dr*): Yield: 144.5 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$, main isomer): δ = 7.33–7.13 (m, 14 H), 6.49 (s, 1 H), 6.05–6.01 (m, 1 H), 5.67–5.65 (d, J = 6.0 Hz, 1 H), 3.30–3.19 (m, 1 H), 3.13–2.92 (m, 2 H), 2.31–2.27 (d, J = 17.2 Hz, 1 H), 1.97 (s, 3 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.33–7.13 (m, 14 H), 6.35 (s, 1 H), 5.98–5.94 (m, 1 H), 5.67–5.65 (d, J = 6.0 Hz, 1 H), 3.30–3.19 (m, 1 H), 3.13–2.92 (m, 2 H), 2.33–2.28 (d, J = 17.2 Hz, 1 H), 1.81 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 170.5, 170.2, 147.6, 147.2, 142.3, 142.3, 139.3, 139.2, 137.7, 137.5, 132.8, 132.6, 129.4, 129.3, 128.3, 128.2, 127.7, 127.6, 127.2, 127.1, 127.0, 126.9, 126.5, 126.4, 124.7, 124.7, 121.1, 121.0, 117.9, 117.6, 85.3, 84.9, 77.4, 74.5, 73.3, 36.2, 35.7, 31.3, 31.3, 20.7, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 3652, 3454, 3061, 3028, 2955, 2926, 2901, 2854, 2821, 2250, 1950, 1741 cm^{-1}. $C_{27}H_{24}O_3$ (396.48): calcd. C 81.79, H 6.10; found C 81.53, H 6.29.

2l: Yield: 41.7 mg (25%). Solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.13 (m, 9 H), 6.81 (s, 1 H), 5.57–5.56 (d, J = 6.0 Hz, 1 H), 3.22–3.15 (m, 1 H), 2.30–2.26 (d, J = 17.2 Hz, 1 H), 2.20 (s, 3 H), 1.77 (s, 3 H), 1.63 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 147.9, 143.1, 139.9, 132.3, 128.3, 127.6, 127.5, 126.8, 124.8, 120.8, 119.7, 86.7, 84.0, 76.9, 31.5, 22.6, 21.6, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3456, 3054, 2987, 2924, 2853, 1946, 1739 cm^{-1}. $C_{22}H_{22}O_3$ (334.41): calcd. C 79.02, H 6.63; found C 79.23, H 6.54.

2m: Yield: 65.6 mg (41%). Solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.17 (m, 8 H), 7.09–7.08 (m, 1 H), 6.48 (s, 1 H), 4.89–4.86 (d, J = 12 Hz, 1 H), 4.58–4.54 (d, J = 12.4 Hz, 1 H), 2.98–2.93 (m, 1 H), 2.39–2.34 (m, 1 H), 2.13 (s, 3 H), 1.83 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 147.2, 145.6, 139.2, 135.3, 128.3, 127.7, 127.3, 127.0, 126.5, 124.8, 120.3, 117.4, 82.1, 82.0, 64.9, 38.0, 24.2, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 3462, 3029, 2926, 2249, 1952, 1741 cm^{-1}. $C_{21}H_{20}O_3$ (320.39): calcd. C 78.73, H 6.29; found C 78.57, H 6.32.

2n: Yield: 151.3 mg (89%). Solid. M.p. 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.16 (m, 7 H), 7.09 (m, 1 H), 6.41 (s,

1 H), 5.58–5.56 (d, J = 6.0 Hz, 1 H), 4.76–4.73 (d, J = 12.4 Hz, 1 H), 4.60–4.57 (d, J = 12 Hz, 1 H), 3.27–3.21 (m, 1 H), 2.30–2.25 (d, J = 17.6 Hz, 1 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 149.2, 141.2, 138.9, 133.9, 132.8, 128.3, 127.9, 127.1, 125.9, 124.8, 122.2, 118.3, 82.0, 77.0, 64.1, 31.1, 20.7 ppm. IR (KBr): $\tilde{\nu}$ = 3466, 3058, 3032, 2855, 2924, 2855, 2253, 1883, 1742 cm^{-1}. $C_{20}H_{17}ClO_3$ (340.81): calcd. C 70.49, H 5.03; found C 70.32, H 5.08.

2o: Quantitative yield. Solid. M.p. 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.06 (m, 7 H), 6.93–6.92 (d, J = 7.6 Hz, 1 H), 6.50 (s, 1 H), 5.57–5.55 (d, J = 5.6 Hz, 1 H), 4.98–4.95 (d, J = 12.4 Hz, 1 H), 4.63–4.60 (d, J = 12.4 Hz, 1 H), 3.20–3.15 (m, 1 H), 2.31 (s, 3 H), 2.27–2.23 (d, J = 17.6 Hz, 1 H), 2.04 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 145.1, 142.9, 139.2, 133.9, 129.3, 128.2, 127.9, 127.7, 127.2, 125.2, 124.7, 118.5, 83.1, 76.5, 65.2, 31.2, 20.7, 19.0 ppm. IR (KBr): $\tilde{\nu}$ = 3052, 3026, 2955, 2924, 2857, 2729, 2250, 1951, 1740 cm^{-1}. $C_{21}H_{20}O_3$ (320.39): calcd. C 78.73, H 6.29; found C 78.94, H 6.21.

3a: Yield: 90.1 mg (53%). Solid. M.p. 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.33 (d, J = 6.8 Hz, 1 H), 7.25–7.17 (m, 6 H), 7.11–7.09 (m, 1 H), 6.45 (s, 1 H), 5.62–5.60 (d, J = 6.0 Hz, 1 H), 4.82–4.79 (d, J = 12.4 Hz, 1 H), 4.62–4.59 (d, J = 12.4 Hz, 1 H), 3.25–3.18 (m, 1 H), 2.28–2.24 (m, 1 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 147.0, 142.6, 137.7, 133.5, 132.4, 128.4, 127.3, 127.2, 127.1, 126.1, 121.2, 117.5, 82.1, 77.3, 64.5, 31.2, 20.8 ppm. IR (KBr): $\tilde{\nu}$ = 3466, 3069, 3046, 2952, 2900, 2251, 1900, 1742 cm^{-1}. $C_{20}H_{17}ClO_3$ (340.81): calcd. C 70.49, H 5.03; found C 70.61, H 5.05.

3b: Yield: 131.2 mg (82%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.31 (m, 1 H), 7.19–7.16 (m, 4 H), 7.09–7.04 (m, 3 H), 6.40 (s, 1 H), 5.60–5.59 (d, J = 6.0 Hz, 1 H), 4.81–4.78 (d, J = 12.0 Hz, 1 H), 4.63–4.60 (d, J = 12.4 Hz, 1 H), 3.26–3.20 (m, 1 H), 2.31–2.26 (d, J = 17.2 Hz, 1 H), 2.28 (s, 3 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 147.2, 142.8, 137.5, 136.4, 133.2, 128.9, 127.1, 126.9, 125.7, 124.6, 121.1, 117.4, 82.2, 77.4, 64.5, 31.2, 20.9, 20.8 ppm. IR (neat): $\tilde{\nu}$ = 3651, 3464, 3026, 2950, 2920, 2250, 1903, 1741 cm^{-1}. $C_{21}H_{20}O_3$ (320.39): calcd. C 78.73, H 6.29; found C 78.92, H 6.17.

3c: Yield: 72.9 mg (51%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 1 H), 7.19–7.15 (m, 2 H), 7.03–7.01 (m, 1 H), 5.72 (s, 1 H), 5.45–5.43 (d, J = 6.0 Hz, 1 H), 4.70–4.67 (d, J = 12.0 Hz, 1 H), 4.54–4.51 (d, J = 12.0 Hz, 1 H), 2.85–2.79 (m, 1 H), 2.09 (s, 3 H), 1.84–1.76 (m, 3 H), 1.31–1.23 (m, 2 H), 1.19–1.12 (m, 2 H), 0.83–0.79 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 147.8, 142.9, 135.9, 126.8, 126.7, 124.6, 120.9, 117.1, 82.0, 77.3, 64.5, 36.0, 32.8, 29.0, 22.0, 20.8, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3467, 3069, 3044, 3025, 2955, 2929, 2866, 1743 cm^{-1}. $C_{18}H_{22}O_3$ (286.37): calcd. C 75.50, H 7.74; found C 75.53, H 7.49.

3d: Yield: 39.3 mg (21%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.28 (m, 1 H), 7.21–7.14 (m, 2 H), 7.05–7.03 (m, 1 H), 5.98 (s, 1 H), 5.49–5.48 (d, J = 6.0 Hz, 1 H), 4.73–4.70 (d, J = 12.0 Hz, 1 H), 4.56–4.53 (d, J = 12.0 Hz, 1 H), 3.94–3.84 (m, 2 H), 2.84–2.78 (m, 1 H), 2.10 (s, 3 H), 1.87–1.83 (d, J = 17.6 Hz, 1 H), 0.83 (s, 9 H), –0.04 (s, 3 H), –0.09 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 147.5, 142.8, 135.2, 127.0, 126.9, 124.9, 121.1, 117.4, 82.0, 77.2, 65.8, 64.5, 30.1, 25.8, 20.8, 18.2, –5.41, –5.43 ppm. IR (neat): $\tilde{\nu}$ = 3402, 3070, 2953, 2927, 2855, 1942, 1746 cm^{-1}. $C_{21}H_{30}O_4Si$ (374.55): calcd. C 67.34, H 8.07; found C 67.12, H 8.13.

3e: Yield: 52.5 mg (37%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.16 (m, 3 H), 7.06–7.04 (m, 1 H), 5.67 (s, 1 H), 5.20–5.18 (d, J = 6.0 Hz, 1 H), 4.65–4.62 (d, J = 12.4 Hz, 1 H), 4.54–4.49 (d, J = 12.4 Hz, 1 H), 2.77–2.71 (m, 1 H), 2.10–2.06 (m, 4 H), 1.99–1.93 (m, 1 H), 1.78–1.61 (m, 3 H), 1.39–1.28 (m, 1 H), 1.00–0.90 (m, 1 H), 0.79–0.70 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 148.9, 140.4, 138.7, 126.8, 126.2, 123.2, 122.1, 117.4, 82.5, 81.2, 64.5, 39.6, 34.0, 27.6, 26.8, 25.2, 20.9 ppm. IR (neat): $\tilde{\nu}$ = 3467, 3069, 3024, 2929, 2855, 2657, 2249, 1743 cm^{-1}. $C_{18}H_{20}O_3$ (284.35): calcd. C 76.03, H 7.09; found C 76.11, H 7.33.

3f: Yield: 87.9 mg (46%). Solid. M.p. 182–183 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 3 H), 7.30–7.07 (m, 11 H), 6.57 (s, 1 H), 5.35 (s, 1 H), 4.85–4.82 (d, J = 12.4 Hz, 1 H), 4.78–4.75 (d, J = 12.0 Hz, 1 H), 3.71 (s, 1 H), 2.16 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 148.1, 142.4, 142.1, 138.9, 135.7, 128.7, 128.7, 128.6, 128.2, 127.5, 127.2, 126.8, 125.9, 121.6, 117.8, 84.3, 82.7, 64.3, 47.5, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 3449, 3058, 3026, 2949, 2883, 2251, 1952, 1740 cm^{-1}. $C_{26}H_{22}O_3$ (382.46): calcd. C 81.65, H 5.80; found C 81.79, H 5.77.

3g (10:8 *dr*): Yield: 156.3 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$, main isomer): δ = 7.52–7.50 (m, 2 H), 7.32–7.07 (m, 7 H), 6.37 (s, 1 H), 5.98 (s, 1 H), 5.65–5.56 (m, 2 H), 5.12–5.11 (d, J = 5.6 Hz, 1 H), 3.25–3.22 (m, 1 H), 2.78–2.32 (m, 3 H), 2.27 (s, 3 H), 2.16–2.11 (m, 2 H), 2.05–1.88 (m, 1 H), 1.66–1.60 (m, 1 H), 1.27–1.22 (m, 1 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.58–7.55 (m, 2 H), 7.32–7.07 (m, 7 H), 6.39 (s, 1 H), 5.77 (s, 1 H), 5.46–5.42 (m, 2 H), 5.18–5.17 (d, J = 5.6 Hz, 1 H), 3.15–3.11 (m, 1 H), 2.78–2.32 (m, 3 H), 2.16–2.11 (m, 2 H), 2.06 (s, 3 H), 2.05–1.88 (m, 1 H), 1.66–1.60 (m, 1 H), 1.27–1.22 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 170.2, 170.1, 149.4, 149.2, 141.3, 140.8, 140.3, 140.1, 136.2, 136.1, 131.8, 131.7, 129.0, 128.8, 128.1, 128.0, 127.9, 127.7, 126.7, 126.6, 126.1, 126.0, 125.9, 125.6, 125.2, 125.2, 123.0, 122.9, 118.1, 117.8, 85.0, 84.6, 81.8, 81.6, 76.1, 74.5, 37.0, 35.2, 35.0, 31.1, 30.9, 26.8, 26.8, 23.9, 23.9, 21.2, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3655, 3462, 3067, 3010, 2932, 2883, 2827, 2246, 1950, 1738 cm^{-1}. $C_{26}H_{26}O_3$ (386.49): calcd. C 80.80, H 6.78; found C 80.62, H 6.89.

X-ray Crystallography: The molecular structure of product **2e-1** was determined by X-ray crystallography. CCDC-695098 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures; ^{1}H and ^{13}C NMR spectra; crystal data and structure refinement data for **2e-1**.

Acknowledgments

We thank the NSF (NSF-20621091, NSF-20672049) and the "Hundred Scientist Program" from the Chinese Academy of Sciences for financial support.

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Received: September 11, 2008
Published Online: November 12, 2008

