JOC The Journal of Organic Chemistry

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Reactivity Insight into Reductive Coupling and Aldol Cyclization of Chalcones by Visible Light Photocatalysis

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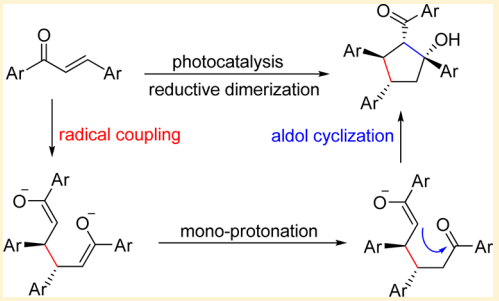
Supporting Information

ABSTRACT: The reductive coupling and cyclization of chalcones to generate cyclopentanol derivatives in up to 84% yield by visible light photoredox catalysis is described. This reaction involves radical anion homocoupling, monoprotonation, and intramolecular cyclization cascade.

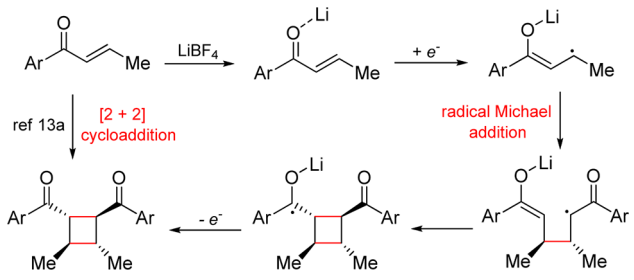


Chalcones are widely distributed in plants and have been associated with various of pharmacological activities.[1] Moreover, they have attracted widespread research interests from organic chemists to investigate their chemical reactivities in a variety of reactions, e.g., classical Claisen–Schmidt condensation,[2] Suzuki coupling,[3] and Heck reaction.[4] Due to the unique structure feature, chalcones have also emerged as a reliable class of reactants and important precursors in synthetic chemisry.[5] Among them, reductive dimerization of chalcones is an available approach for establishing C–C bonds by means of a single-electron-transfer process. In general, the initial step is the single-electron reduction of enone to the corresponding radical anion, which is achieved by electrochemical reduction[6] or a single-electron-transfer reagent such as $^{n}Bu_3SnH$,[7] SmI_2,[8] Yb,[9] Sm,[10] Zn,[11] etc. In such cases, however, specialized equipment or strong stoichiometric reductant is generally required.

Recently, an intriguing and promising strategy for the application of photoredox catalyst to initiate a single-electron-transfer process has been developed in the realm of organic chemistry[12] and well demonstrated by some valuble work that explored the reactions of aryl enone and its derivatives, such as intra- and intermolecular [2 + 2] cycloaddition,[13] intramolecular reductive cyclization,[14] hetero-Diels–Alder reaction,[15] [3 + 2] cycloaddition of aryl cyclopropyl ketone,[16] reduction, as well as reductive allylation of epoxide and aziridine.[17]

In particular, Yoon and co-workers disclosed an elegant strategy access to cyclobutane skeleton under visible light photoredox catalysis.[13a] The mechanism of reaction involved the generation of radical anion from the corresponding enone, subsequent addition to Michael acceptor, and then cyclization to afford [2 + 2] adduct (Scheme 1). However, variation of the substituent at the β-position of enone is limited to the alkyl groups, and the extension of this strategy to chalcones still remains unexploited.

Scheme 1. Reaction Mechanism of [2 + 2] Cycloaddition



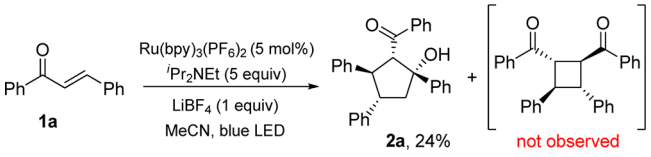
Because of our continuous interest in photochemical reactions,[18] we endeavored to investigate the chemical behavior of chalcones through the application of visible light photocatalysis and found that it preferentially undergoes a reductive dimerization reaction rather than the typical [2 + 2] cycloaddition. Based upon a series of control experiments, the reaction process was suggested to involve both electron and proton transfers, and the intermolecular C–C bond formation was generated from a biradical coupling reaction instead of radical Michael addition, which was comparatively different from an overall redox-neutral [2 + 2] cycloaddition. In this paper, we present a unique and efficient approach to prepare polysubstituted cyclopentanol derivatives by visible-light photoredox catalysis.

Received: April 20, 2012
Published: June 25, 2012

dx.doi.org/10.1021/jo300796j | J. Org. Chem. 2012, 77, 6302–6306

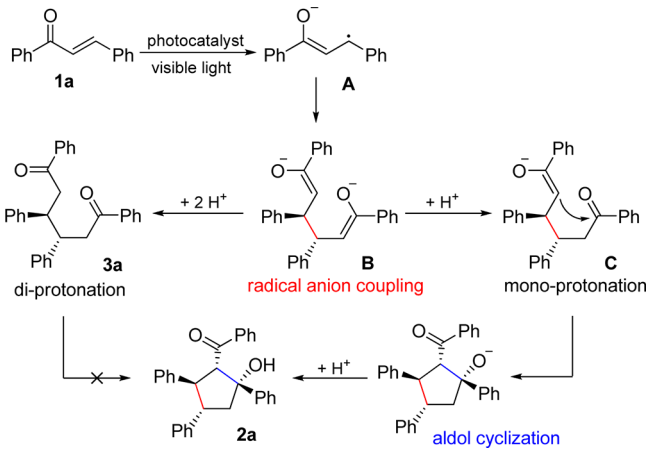
Our initial investigation focused on the reaction of chalcone **1a** with 5 mol % of $Ru(bpy)_3(PF_6)_2$, $LiBF_4$ (1 equiv), and $^iPr_2NEt$ (5 equiv) in MeCN without deoxygenization (Scheme 2).[19] After irradiation for 2 h with a blue LED (1 W, λ_{max} = 470 nm) as a light source,[20] complete consumption of **1a** was observed by TLC analysis, and a complex mixture of reductive dimer was afforded, including linear dimer, cyclic dimer, and pinacol coupling products instead of the [2 + 2] cycloadduct. After recrystallization, cyclic dimer **2a** was obtained in 24% isolated yield as the preliminary result.

Scheme 2. Preliminary Reaction Result



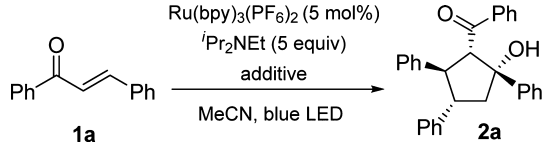
To our knowledge, chalcones can produce radical anion **A** in a single-electron-transfer process (Scheme 3), however, a detailed reaction pathway for the formation of **2a** still remains ambiguous and impedes our efforts to optimize the reaction conditions. Therefore, a series of control experiments needed to be performed before we started to optimize the reaction conditions. Initially, we envisioned that the generated reactive radical anion **A** from chalcone could be intercepted by the better Michael acceptor, methyl vinyl ketone (MVK), leading to the cross coupling product. Nevertheless, treatment of **1a** with 10 equiv of MVK under the same photocatalytic conditions preferentially formed the homocoupling products from **1a**. Such a result shows the likelihood of generation of linear dianion species **B** from two radical anions coupling rather than a radical anion addition to Michael acceptor.

Scheme 3. Reaction Pathways of Reductive Dimerization



It is well-known that $^iPr_2NEt$ is a competent electron and hydrogen atom donor, which has been demonstrated in previous work.[21] Given the observed reactivity, we speculated that the reaction pathway for the conversion of **1a** to **2a** was dominated by the proton transfer from tertiary amine,[22] and consequently, cyclic dimer **2a** resulted from the monoprotonation of dianion **B** followed by the intramolecular Aldol cyclization of **C**. To add credence to our hypothesis, a control experiment was conducted by preparation and sequential treatment of **3a** under the same photocatalytic conditions for 24 h. As expected, no formation of **2a** was observed. Such a result is in good agreement with the designed experiment in which **1a** was subjected to the photocatalytic conditions except $LiBF_4$ was replaced by CH_3CO_2H leading to **3a** as the major product (Table 1, entry 2). These experiments indicate the critical role of the proton transfer.

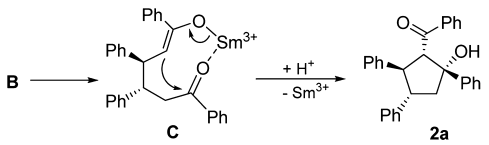
Table 1. Investigation of Lewis Acid Additives[a]



entry	additive (equiv)	time[b] (h)	yield[c] (%)
1	$LiBF_4$ (1)	2.0	24
2	CH_3CO_2H (3)	0.5	0[d]
3	None	1.0	7
4	$La(OTf)_3$ (1)	3.5	53
5	$Mg(ClO_4)_2$ (1)	2.0	19
6	**$Sm(OTf)_3$ (1)**	**3.0**	62
7	$Yb(OTf)_3$ (1)	4.0	45

[a]Reaction conditions: **1a** (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.05 mmol), $^iPr_2NEt$ (5 mmol) in CH_3CN (10 mL), irradiation with a blue LED (1 W). [b]Complete consumption for substrate **1a**. [c]Isolated yield. [d]The mixture of linear dimer **3a** and pinacol products were obtained in 94% yield.

It should be pointed out that Lewis acid or Brønsted acid was not necessary for activating the chalcones toward one-electron reduction in this process (Table 1, entry 3), but the presence of $LiBF_4$ undoubtedly resulted in a higher yield of **2a**. Therefore, several Lewis acid additives were subjected to the reaction, including $La(OTf)_3$, $Mg(ClO_4)_2$, $Sm(OTf)_3$, and $Yb(OTf)_3$, and the results are listed in Table 1 (entries 4–7). As can be seen, the best yield was obtained by using $Sm(OTf)_3$ as an additive (Table 1, entry 6). Therefore, we reasoned that the presence of $Sm(OTf)_3$ was in coordination with the carbonyl and enol groups in a stable transition state responsible for the high yield and chemical selectivity (eq 1).

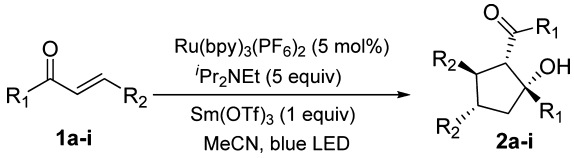


(1)

Having developed conditions for this unique reaction, our next work focused on the investigation of structure–reactivity relationships. Thus, a variety of chalcones were synthesized and subjected to the reaction conditions. As shown in Table 2, the reactions led to the desired products in moderate to high yields. The substituent group had significant effect on the reaction efficiency and reactivity of aldol cyclization. For example, the carbonyl substituent R_1 bearing electron-withdrawing groups on aromatic rings led to the products in good yields (entries 2 and 4). In contrast, substituent R_1 bearing electron-donating groups resulted in the relatively lower yields (entries 3, 5, 6, and 9). When the alkene substituent R_2 bearing a electron-donating group, it took longer reaction time and gave rise to the cyclization product in moderate yields (entry 7). The stereochemistry of **2a–i** was assigned based upon the previous work[23] as well as NMR spectra. However, the reaction is

dx.doi.org/10.1021/jo300796j | J. Org. Chem. 2012, 77, 6302–6306

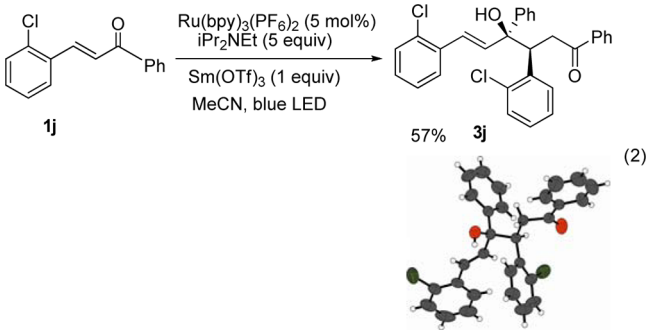
Table 2. Investigation of Structure−Reactivity Relationships[a]



entry	substrate	time (h)	yield[b] (%)
1	**1a**, R_1 = C_6H_4, R_2 = C_6H_5	3	**2a**, 62
2	**1b**, R_1 = 4-ClC_6H_5, R_2 = C_6H_5	3	**2b**, 84
3	**1c**, R_1 = 4-$MeOC_6H_4$, R_2 = C_6H_5	4	**2c**, 47
4	**1d**, R_1 = 4-ClC_6H_4, R_2 = 4-FC_6H_4	3	**2d**, 78
5	**1e**, R_1 = 4-$MeOC_6H_4$, R_2 = 4-FC_6H_4	3	**2e**, 51
6	**1f**, R_1 = 4-$MeOC_6H_4$, R_2 = 4-$MeOC_6H_4$	7	**2f**, 40
7	**1g**, R_1 = C_6H_5, R_2 = 4-$MeOC_6H_4$	6	**2g**, 54
8	**1h**, R_1 = C_6H_5, R_2 = 4-FC_6H_4	3	**2h**, 59
9	**1i**, R_1 = 3,5-$(MeO)_2C_6H_3$, R_2 = C_6H_5	7	**2i**, 65

[a]Reaction conditions: substrate (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.05 mmol), iPr_2NEt (5 mmol), $Sm(OTf)_3$ (1 mmol) in CH_3CN (10 mL), irradiation with a blue LED (1 W). [b]Isolated yield.

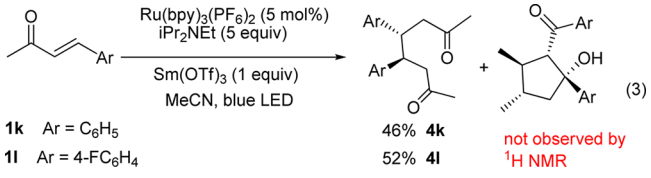
sensitive to steric bulk. No reaction was observed when the chalcones bear methyl substituent at α or β position. In addition, the substituent on *ortho* position of R_1 led to γ-hydroxyl phenyl ketone **3j** instead of the desired cyclopentanol compound (eq 2). The structure and stereochemistry of **3j**



(2)

were determined by NMR spectra and X-ray crystal analysis.[24] However, such a result adds more credence to the intermediate **A** and the radical coupling process (Scheme 3).

The benzylacetones **1k** and **1l** were also investigated under the same photocatalytic conditions (eq 3). The reactions

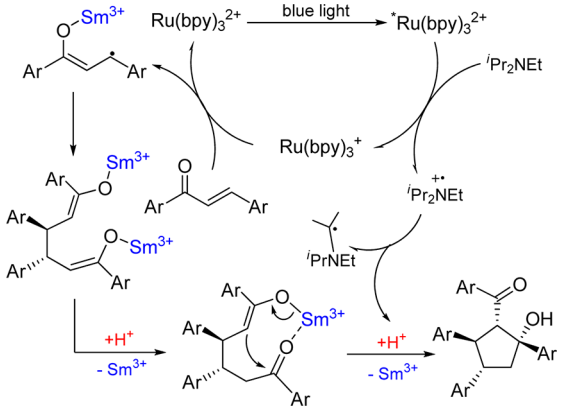


(3)

proceeded smoothly, but the linear dimer products, not the desired cyclopentanol derivatives, were obtained. These results indicated the critical role of the aromatic groups in formation of cyclization products which might stabilize the reactive radical anion formed in the reaction.

Based upon the above investigations and previous work,[25] we propose the reaction mechanism that is outlined in Scheme 4. The reactive radical anion is generated from the corresponding chalcone in the photocatalytic conditions. An initial C−C bond formation process based on two-radical-anion coupling

Scheme 4. Proposed Mechanism



provides a dianion species. Sequential monoprotonation and intramolecular aldol cyclization gave access to polysubstituted cyclopentanol derivatives. An appropriate Lewis acid additive, $Sm(OTf)_3$, is beneficial for the aldol cyclization.

In summary, we have developed a photocatalytic system for the reductive cyclization of chalcones under visible light irradiation. This work indicates an available reactivity of radical anion, which should be helpful to extend the scope of reaction by visible light photocatalysis. Further work to realize this goal is underway in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reagents were purchased from commercial sources unless otherwise noted. Solvents were dried according to standard procedures prior to use. Chemical shifts in ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra are reported in parts per million from tetramethylsilane (TMS) or solvent resonance (e.g., $CDCl_3$) as the internal standard. HR-MS spectra were recorded on an LC mass spectrometer using electrospray ionization (ESI, TOF).

General Procedure for the Synthesis of Cyclopentanols 2. To a solution of chalcone **1** (1 mmol) in dried CH_3CN (10 mL) were added *i*-Pr_2NEt (5 mmol), $Sm(OTf)_3$ (1 mmol), and $Ru(bpy)_3(PF_6)_2$ (0.05 mmol), respectively. The mixtrure was stirred at room temperature under irradiation with a blue LED (1 W) as the light source. Upon consumption of starting material, the solvent was concentrated in vacuo. The residue was purified by flash chromatography and recrystallization to afford the desired product **2**. Spectroscopic data were in accord with those previously published for the known compounds.

Compound ***2a:*** 129 mg; yield 62%; white solid; mp 194−195 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.2 Hz, 4H), 7.37−7.06 (m, 14H), 5.25 (s, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.13 (dd, J = 11.6, 10.4 Hz, 1H), 3.81 (m,1H), 3.03 (dd, J = 14.4, 12.0 Hz, 1H), 2.61 (dd, J = 14.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 145.3, 144.0, 139.9, 137.6, 133.3, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.0, 126.9, 126.4, 124.9, 84.3, 63.6, 59.6, 51.4; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{30}H_{26}O_2Na$ 441.1830, found 441.1819.

Compound ***2b:*** 204 mg; yield 84%; white solid; mp 175−176 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz, 2H), 7.39−7.07 (m, 16H), 5.27 (s, 1H), 4.39 (d, J = 12.0 Hz), 4.06 (dd, J = 11.6, 10.4 Hz, 1H), 3.78 (m, 1H), 2.91 (dd, J = 14.0, 12.8 Hz, 1H), 2.56 (dd, J = 14.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 143.8, 143.7, 140.2, 140.0, 135.7, 133.0, 129.5, 128.7, 128.6, 128.5, 128.5, 127.8, 127.6, 127.2, 126.5, 126.3, 84.0, 63.5, 60.0, 51.3, 51.1; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{30}H_{24}Cl_2O_2Na$ 509.1051, found 509.1057.

Compound ***2c:*** 112 mg; yield 47%; white solid; mp 146−147 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.48 (m, 4H), 7.43 (d, J = 7.6 Hz, 2H), 7.27−7.07 (m, 8H), 6.84 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8

dx.doi.org/10.1021/jo300796j | J. Org. Chem. 2012, 77, 6302−6306

Hz, 2H), 5.50 (s, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.10 (dd, J = 12.0, 10.0 Hz, 1H), 3.78 (s, 6H), 2.97 (dd, J = 14.0, 12.0 Hz, 1H), 2.57 (dd, J = 14.4, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 163.8, 158.4, 144.3, 140.2, 137.6, 130.7, 130.6, 128.4, 128.4, 127.9, 127.6, 126.8, 126.3, 126.1, 113.6, 113.4, 84.1, 62.7, 59.6, 55.4, 55.2, 51.3, 51.3; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{32}H_{30}O_4Na$, 501.2042, found 501.2037.

Compound ***2d:*** 204 mg; yield 78%; white solid; mp 192−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.34−7.26 (m, 4H), 7.18 (d, J = 8.8 Hz, 2H), 7.12−7.08 (m, 2H), 6.94 (t, J = 8.4 Hz, 2H), 6.84 (t, J = 8.4 Hz, 2H), 5.19 (s, 1H), 4.35 (d, J = 12.0 Hz, 1H), 3.98 (dd, J = 11.6, 10.4 Hz, 1H), 3.66 (m, 1H), 2.90 (dd, J = 14.0, 12.8 Hz, 1H), 2.49 (dd, J = 14.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 143.4, 140.5, 135.5, 133.1, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 126.3, 115.7, 115.5, 115.4, 115.2, 83.9, 63.2, 59.2, 51.2, 50.9; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{30}H_{22}Cl_2F_2O_2Na$ 545.0863, found 545.0871.

Compound ***2e:*** 131 mg; yield 51%; white solid; mp 174−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 8.4 Hz, 4H), 7.34 (dd, J = 8.8, 5.6 Hz, 2H), 7.09 (dd, J = 8.8, 5.6 Hz, 2H), 6.93 (t, J = 8.8 Hz, 2H), 6.84−6.79 (m, 4H), 6.66 (d, J = 8.8 Hz, 2H), 5.43 (s, 1H), 4.39 (d, J = 12.0 Hz, 1H), 3.98 (dd, J = 11.6, 10.4 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.64 (m, 1H), 2.91 (dd, J = 14.0, 12.0 Hz, 1H), 2.47 (dd, J = 14.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 164.0, 158.5, 139.8, 137.2, 135.7, 135.7, 130.7, 130.4, 129.4, 129.3, 129.0, 129.0, 126.0, 115.5, 115.3, 115.1, 113.7, 113.6, 84.0, 62.4, 59.2, 55.4, 55.3, 51.1, 51.0; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{32}H_{28}F_2O_4Na$ 537.1853, found 537.1880.

Compound ***2f:*** 108 mg; yield 40%; white solid; mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 8.8, 6.4 Hz, 4H), 7.30 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.4, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 8.8 Hz, 4H), 5.42 (s, 1H), 4.38 (d, J = 12.0 Hz, 1H), 3.97 (dd, J = 11.6, 10.4 Hz, 1H), 3.76 (s, 6H), 3.74 (s, 3H), 3.67 (s, 3H), 3.65 (m, 1H), 2.89 (dd, J = 14.0, 12.0 Hz, 1H), 2.48 (dd, J = 14.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 163.8, 158.4,158.3, 158.0, 157.8, 136.4, 132.3, 130.7, 128.9, 128.6, 126.1, 113.8, 113.7, 113.6, 113.5, 83.9, 62.8, 59.1, 55.4, 55.2, 55.1, 51.4, 50.7; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{34}H_{34}O_6Na$ 561.2253, found 561.2262.

Compound ***2g:*** 129 mg; yield 54%; white solid; mp 191−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.34−7.15 (m, 8H), 7.06 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 5.17 (s, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.00 (dd, J = 11.2, 10.8 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 3.64 (m, 1H), 2.95 (dd, J = 14.0, 11.2 Hz, 1H), 2.52 (dd, J = 14.8, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 158.4, 158.1, 145.5, 137.7, 136.2, 133.2, 132.0, 128.9, 128.6, 128.3, 128.2, 128.1, 127.0, 124.9, 113.9, 113.8, 84.1, 63.7, 59.0, 55.2, 55.1, 51.5, 50.8; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{32}H_{30}O_4Na$ 501.2042, found 501.2053.

Compound ***2h:*** 134 mg; yield 59%; white solid; mp 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.37−7.09 (m, 10H), 6.94 (t, J = 8.4 Hz, 2H), 6.81 (t, J = 8.4 Hz, 2H), 5.19 (s, 1H), 4.49 (dd, J = 12.4, 3.2 Hz, 1H), 4.02 (td, J = 12.0, 3.2 Hz, 1H), 3.68 (m, 1H), 2.98 (dd, J = 14.0, 12.0 Hz, 1H), 2.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7, 163.0, 162.9, 160.5, 160.4, 144.9, 139.5, 139.5, 137.5, 135.4, 135.4, 129.4, 129.3, 129.1, 129.0, 128.4, 128.3, 128.1, 127.2, 124.8, 115.5, 115.3, 115.3, 115.1, 84.2, 63.3, 59.2, 51.2, 51.1; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{30}H_{24}F_2O_2Na$ 477.1642, found 477.1646.

Compound ***2i:*** 175 mg; yield 65%; white solid; mp 157−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.19−7.15 (m, 3H), 6.63 (d, J = 2.4 Hz, 2H), 6.30−6.28 (m, 3H), 6.13 (t, J = 2.0 Hz, 1H), 5.10 (s, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.06 (t, J = 10.0 Hz, 1H), 3.76 (s, 6H), 3.69−3.64 (m, 1H), 3.60 (s, 6H), 2.95 (dd, J = 14.0, 11.6 Hz, 1H), 2.54 (dd, J = 14.0, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.0, 160.9, 160.8, 146.7, 145.3, 142.6, 137.8, 133.4, 128.5, 128.3, 128.2, 127.2, 125.0, 106.2, 106.0, 99.0, 98.5, 84.2, 63.4, 59.3, 55.4, 55.3, 51.3, 51.2; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{34}H_{34}O_6Na$ 561.2248, found 561.2248.

Compound ***3j:*** 138 mg; yield 57%; white solid; mp 163−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.54−7.09 (m, 14H), 6.66 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 4.79 (dd, J = 10.4, 3.2 Hz, 1H), 3.74 (m, 1H), 3.09 (dd, J = 17.6, 3.2 Hz, 1H), 2.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.5, 144.5, 138.0, 137.9, 137.0, 136.0, 135.1, 133.2, 133.0, 129.7, 129.5, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.4, 127.2, 127.0, 126.7, 125.5, 124.7, 79.7, 46.2, 39.2; HRMS-ESI (TOF, m/z) $[M + Na]^+$ calcd for $C_{30}H_{24}Cl_2O_2Na$ 509.1046, found 509.1044.

■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from China NSFC (Nos. 21002018 and 21072038) and ZJNSF (No. LY12B02009).

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