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A Synthetic Strategy for Polyfunctionalized Bicyclo-[3.3.1]nonanes Based on a Tandem Three-Component [3 + 2] Cycloaddition of α-Cinnamoyl Ketene-*S*,*S*-acetals with Oxalyl Chloride

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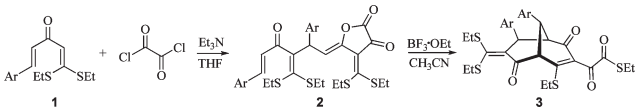
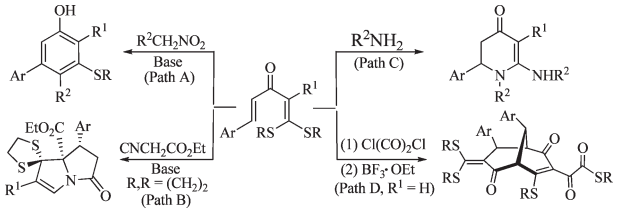


A simple and highly efficient three-component reaction of the readily available α-cinnamoyl ketene-*S*,*S*-acetals **1** with oxalyl chloride has been developed and the corresponding γ-alkylidenebutenolides **2** were obtained stereospecifically in excellent yields under very mild conditions. On the basis of this reaction, a series of highly functionalized bicyclo[3.3.1]nonanes **3** were constructed in good to high yields in an atom-economic manner with good diastereoselectivity via a $BF_3 \cdot OEt_2$-mediated novel tandem double cyclization of γ-alkylidenebutenolides **2** under very mild conditions.

Functionalized ketene-*S*,*S*-acetals are versatile intermediates in organic synthesis.[1,2] Among them, the easily available α-cinnamoyl ketene-*S*,*S*-acetals **1** have proven to be promising structural features as novel organic intermediates because of their (a) five-carbon 1,5-bielectrophilic nature,[3,4] for example, in the regiospecific [5C + 1C] annulations for the construction of substituted phenolic ring (Scheme 1, path A),[3a] (b) dense and flexible substitution patterns, for example, applicable to the stereoselective construction of polysubstituted pyrrolizidines (Scheme 1, path B),[5] and (c) good leaving group (alkylthio) that can be subjected to a nucleophilic vinylic substitution (S_NV) reaction,[1,2a−2d,2g] for instance, the subsequent displacement of the remaining alkylthio by an amino group in the [5C + 1N] annulations (Scheme 1, path C).[4a,4b] In this paper, it is shown that the easily available α-cinnamoyl ketene-*S*,*S*-acetals **1** can be regarded as either a 1,3- binucleophile (α-carbon and carbonyl oxygen)[6] or a C4 1,4-dipole (α- and β′-carbon atoms) in the reaction of α-cinnamoyl ketene-*S*,*S*-acetals **1** with oxalyl chloride.[7] Therefore, the efficient use of the reactive sites[5] of **1** provides rapid access to γ-alkylidenebutenolides **2** and polyfunctionalized bicyclo[3.3.1]nonanes **3** (Scheme 1, path D) in good to high selective manner under mild conditions.

SCHEME 1. Reaction of α-Cinnamoyl Ketene-*S*,*S*-acetals



In our experiment, at first, a model reaction of α-cinnamoyl ketene-*S*,*S*-acetal **1a** with oxalyl chloride was examined under various reaction conditions (Table 1).[8] It was found that after treatment of **1a** (1.0 mmol) with oxalyl chloride (0.5 mmol) in THF (10 mL) at room temperature for 1 h, γ-alkylidenebutenolide **2a** was produced in 50% yield (Table 1, entry 1). Whereas when the reaction was performed at 0 °C for 1.5 h, product **2a** was obtained in 70% yield (Table 1, entry 2). To our satisfaction, the yield of **2a** was increased to 91% when the reaction was carried out at 0 °C in the presence of triethylamine (1.0 mmol) for 1 h (Table 1, entry 3). Among the solvents tested, THF seemed to be the best choice although comparable results were obtained with dichloromethane as the solvent (Table 1, entry 4). Other solvents examined, such as DMF and diethyl ether, gave lower yields (Table 1, entries 5 and 6). In addition, the reaction of α-cinnamoyl ketene-*S*,*S*-acetal **1a** with malonyl chloride was also investigated at 0−25 °C for 8 h under

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(3) For selected examples, see: [5C + 1C] annulations and related reactions: (a) Bi, X.; Dong, D.; Liu, Q.; Pan, W.; Zhao, L.; Li, B. *J. Am. Chem. Soc.* **2005**, *127*, 4578–4579. (b) Zhang, L.; Liang, F.; Cheng, X.; Liu, Q. *J. Org. Chem.* **2009**, *74*, 899–902. (c) Zhang, Q.; Sun, S.; Hu, J.; Liu, Q.; Tan, J. *J. Org. Chem.* **2007**, *72*, 139–143.

(4) For selected examples, see: [5C + 1N] annulations: (a) Dong, D.; Bi, X.; Liu, Q.; Cong, F. *Chem. Commun.* **2005**, 3580–3582. (b) Zhao, L.; Liang, F.; Bi, X.; Sun, S.; Liu, Q. *J. Org. Chem.* **2006**, *71*, 1094–1098. (c) Hu, J.; Zhang, Q.; Yuan, H.; Liu, Q. *J. Org. Chem.* **2008**, *73*, 2442−2445. [5C + 1S] annulations: (d) Bi, X.; Dong, D.; Li, Y.; Liu, Q. *J. Org. Chem.* **2005**, *70*, 10886–10889.

(5) Tan, J.; Xu, X.; Zhang, L.; Li, Y.; Liu, Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 2868–2872.

(6) For a review on the synthesis of butenolides by one-pot cyclization reactions of silyl enol ethers with oxalyl chloride, see: Langer, P. *Synlett* **2006**, 3369–3381.

(7) Zhang, G.; Huang, X.; Li, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 1814–1815.

(8) For C−C bond-forming reactions at the α-position of functionalized ketene-*S*,*S*-acetals with aldehydes, ketones, or unsaturated ketones, see: (a) Yuan, H.-J.; Wang, M.; Liu, Y.-J.; Liu, Q. *Adv. Synth. Catal.* **2009**, *351*, 112–116. (b) Fu, Z.; Wang, M.; Ma, Y.; Liu, Q.; Liu, J. *J. Org. Chem.* **2008**, *73*, 7625–7630. (c) Yin, Y.-B.; Wang, M.; Liu, Q.; Hu, J.-L.; Sun, S.-G.; Kang, J. *Tetrahedron Lett.* **2005**, *46*, 4399–4402. (d) Zhang, Q.; Liu, Y.; Wang, M.; Liu, Q.; Hu, J.; Yin, Y. *Synthesis* **2006**, 3009–3014.

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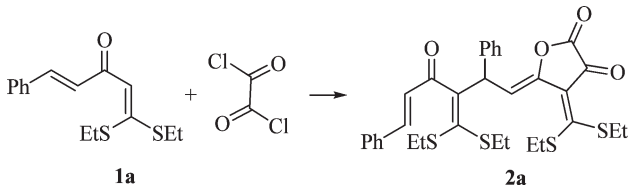
TABLE 1. Optimization of Reaction Conditions of 1a with Oxalyl Chloride



entry	Et_3N (equiv)	solvent	T (°C)	time (h)	**2a** yield (%)
1	Et_3N (0)	THF	25	1.0	50
2	Et_3N (0)	THF	0	1.5	70
3	Et_3N (1.0)	THF	0	1.0	91
4	Et_3N (1.0)	CH_2Cl_2	0	1.0	88
5	Et_3N (1.0)	DMF	0	6.0	20
6	Et_3N (1.0)	$(C_2H_5)_2O$	0	6.0	35

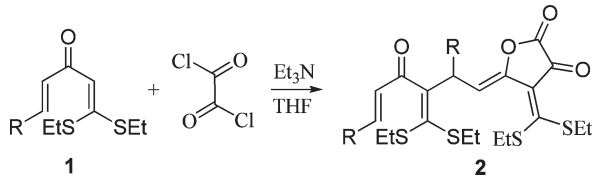
essentially the identical conditions (Table 1, entry 3). However, no reaction was observed and the α-cinnamoyl ketene-*S*,*S*-acetal **1a** was recovered in nearly quantitative yield.

Next, under the optimized conditions (Table 1, entry 3), the scope of the reaction was investigated and the results are summarized in Table 2. This reaction shows wide applicability to various aryl groups in α-cinnamoyl ketene-*S*,*S*-acetals **1**. For instance, the reaction of the substrates **1a**−**g** with either electron-donating or electron-withdrawing aryl groups successfully afforded the corresponding γ-alkylidenebutenolides **2a**−**g** in excellent yields (Table 2, entries 1−7). In the case of **1h** with a heteroaryl group, the reaction also worked well, yielding the desired product **2h** in 90% yield (Table 2, entry 8). However, when the substrate **1i** bearing a aliphatic group was treated with oxalyl chloride under identical conditions, no desired γ-alkylidenebutenolide **2i** was obtained (Table 2, entry 9). The structure of **2** was further confirmed by the X-ray diffraction analysis of **2h**.[9] It should be emphasized that, based on the above experimental results and the NMR spectra of products **2**, the reaction of α-cinnamoyl ketene-*S*,*S*-acetal **1** with oxalyl chloride proceeds in a highly chemo- and stereospecific manner.

The reaction of **1** with oxalyl chloride mentioned above represents a new application of the powerful α-cinnamoyl ketene-*S*,*S*-acetal intermediates.[3−5] On the basis of the above experimental results together with our previous reports[3−5,8] and those of others,[6,10] a possible mechanism for the formation of γ-alkylidenebutenolides **2** is proposed (Scheme 2).

Initially, the nucleophilic attack of the α-carbon atom of **1** on a carbonyl carbon of oxalyl chloride generates the tricarbonyl intermediate **A** under the reaction conditions as described (Table 1, either in the presence or absence of TEA), which is easy to understand because oxalyl chloride is more

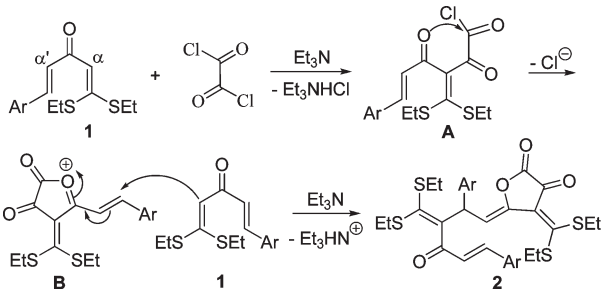
TABLE 2. Reactions of α-Alkenoyl Ketene-*S*,*S*-acetals 1 with Oxalyl Chloride[a]



entry	substrate **1**	R	time (h)	**2** yield (%)
1	**1a**	C_6H_5	1.0	**2a** (91)
2	**1b**	$4\text{-}ClC_6H_4$	1.0	**2b** (96)
3	**1c**	$4\text{-}NO_2C_6H_4$	2.0	**2c** (91)
4	**1d**	$4\text{-}FC_6H_4$	1.5	**2d** (95)
5	**1e**	$4\text{-}MeC_6H_4$	1.0	**2e** (93)
6	**1f**	$4\text{-}MeOC_6H_4$	1.0	**2f** (94)
7	**1g**	$3,4\text{-}CH_2O_2C_6H_3$	1.0	**2g** (89)
8	**1h**	2-furanyl	1.0	**2h** (90)
9	**1i**	$(CH_3)_3$	2.0	**2i** (0)

[a] Reaction conditions: **1** (1.0 mmol), oxalyl chloride (0.5 mmol), Et_3N (1.0 mmol) in THF (10 mL) at 0 °C.

SCHEME 2. Proposed Mechanism for the Formation of 2



reactive than an aldehyde or ketone toward nucleophilic attack.[6,8,10] Subsequently, an unstable oxonium intermediate **B** appears to be formed by the attack of the carbonyl oxygen of the cinnamoyl on the carbon atom of the acid chloride site of intermediate **A**. Thus, the β′-position of the cinnamoyl group is more reactive toward a nucleophile and is attacked by the α-carbon atom of another ketene-*S*,*S*-acetal **1** (intermolecular Michael addition) to give γ-alkylidenebutenolides **2** in a stereospecific manner due to steric hindrances. Obviously, the use of triethylamine to remove HCl from the reaction mixture will increase the yield and reduce reaction time.

With the consideration that the γ-alkylidenebutenolides **2** possess the structural features of both vinylogous ketene-*S*,*S*-acetals[11a] and Michael acceptor (β′-carbon atom of the α-cinnamoyl ketene-*S*,*S*-acetal moiety), the cyclization of **2a** as a model reaction in various conditions including catalysts and solvents via intramolecular Michael addition was investigated (Table 3).[11b] As a result, in the presence of $BF_3\cdot OEt_2$ (1.0 equiv) the intramolecular cyclization of **2a** could easily proceed to give the bicyclo[3.3.1]nonane **3a** in 60% yield at room temperature for 6 h (Table 3, entry 1). Meanwhile, it was proved that a catalytic amount of $BF_3\cdot OEt_2$

(9) Crystal data for **2h**: $C_{28}H_{30}O_6S_4$, red crystal, M_r = 590.76, triclinic, $P\bar{1}$, a = 8.7052(10) Å, b = 9.8540(12) Å, c = 18.635(2) Å, α = 99.850(2)°, β = 97.480(2)°, γ = 104.845(2)°, V = 1496.8(3) Å^3, Z = 2, T = 293(2), F_{000} = 620, R_1 = 0.0627, wR_2 = 0.1419. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (deposition number CCDC-722177). Copies of the data can be obtained, free of charge, on application to the director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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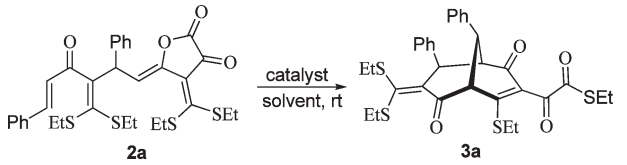
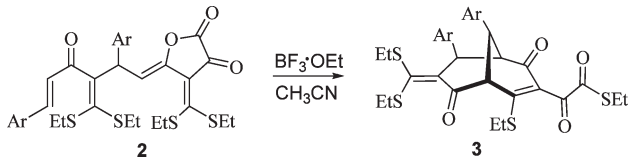
TABLE 3. Acid-Mediated Cyclization of 2a under Different Conditions



entry	catalyst (equiv)	solvent	time (h)	**3a** yield (%)
1	$BF_3 \cdot OEt_2$ (1.0)	CH_3CN	6	60
2	$BF_3 \cdot OEt_2$ (0.5)	CH_3CN	10	21
3	$BF_3 \cdot OEt_2$ (1.0)	benzene	6	27
4	$BF_3 \cdot OEt_2$ (1.0)	THF	6	13
5	$BF_3 \cdot OEt_2$ (1.0)	DMF	12	
6	$TiCl_4$ (1.0)	CH_3CN	6	24
7	$FeCl_3$ (1.0)	CH_3CN	6	15
8	CF_3CO_2H (1.0)	CH_3CN	12	

TABLE 4. $BF_3 \cdot OEt_2$-Mediated Cyclization of 2 to Bicycle[3.3.1]nonanes 3[a]



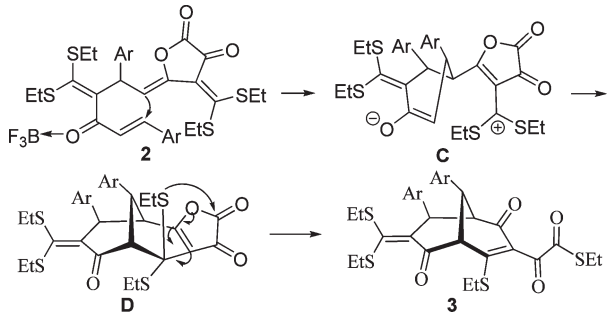
entry	substrate **2**	Ar	time (h)	**3** yield (%)	dr[b]
1	**2a**	C_6H_5	6	**3a** (60)	17:83
2	**2b**	$4\text{-}ClC_6H_4$	7	**3b** (71)	15:85
3	**2d**	$4\text{-}FC_6H_4$	7	**3d** (66)	12:88
4	**2e**	$4\text{-}MeC_6H_4$	6	**3e** (62)	20:80
5	**2f**	$4\text{-}MeOC_6H_4$	6	**3f** (61)	20:80

[a] Reaction conditions: **2** (1.0 mmol), $BF_3 \cdot OEt_2$ (1.0 mmol) in CH_3CN (8.0 mL) at room temperature. [b] Diastereomeric ratios were determined by the ^1H NMR spectra of **3**.

(0.5 equiv) led to lower yield of **3a** (21%) together with the recovery of **2a** in 38% yield (Table 3, entry 2).

Obviously, the above cyclization reaction provides a simple and efficient route to polyfunctionalized bicyclo[3.3.1]nonane derivatives starting from readily available acyclic precursors with perfect atom economy involving an increase in molecular complexity under very mild conditions.[12,13] Encouraged by the above results, the scope of the reaction was examined by selected γ-alkylidenebutenolides **2** under the optimized conditions (Table 3, entry 1); the results are summarized in Table 4. Clearly, compounds **2** with either electron-donating or electron-withdrawing groups on the phenyl ring of the cinnamoyl moiety of **2** could undergo $BF_3 \cdot OEt_2$-mediated intramolecular double cyclization efficiently to give the corresponding polyfunctionalized bicyclo[3.3.1]nonanes **3** in good to high yields (Table 4, entries 1−5). In addition, according to ^1H and ^{13}C NMR spectra of **3**, it was found that the cyclization reaction proceeds in a regio- and diastereoselective manner and the two aryl rings in the main stereoisomer tend to lie coplanar (Table 4, main stereoisomer >80% according to ^1H NMR). The reason for stereoselectivity may be attributed to intramolecular $\pi-\pi$ interaction[14] although the steric hindrances may be responsible.[15] The configuration of the main stereoisomer was finally established by the X-ray diffraction analysis of **3e**.[16]

SCHEME 3. Proposed Mechanism for the Formation of 3



On the basis of the above experimental results and our previous reports,[11] a possible mechanism for the formation of bicyclo[3.3.1]nonanes **3** is proposed and depicted in Scheme 3. In the presence of $BF_3 \cdot OEt_2$, the intramolecular Michael addition of γ-alkylidenebutenolide **2** leads to the formation of intermediate **C** with a negative (enolate anion) and positive charge (carbon cation stabilized by two ethylthio groups), respectively. Then, bicyclo[3.3.1]nonane **3** could be constructed via subsequent processes, including cyclization of intermediate **C** to **D** and followed by nucleophilic attack of the nearby ethylthio sulfur atom at the carbonyl carbon of the lactone followed by C−O bond cleavage, C−S bond breaking, and finally C−C double bond shift.

(12) In general, bicyclic [3.3.1] and [3.2.1] frameworks are accomplished by reaction of appropriate C3-synthons with cyclic ketones (α,α'-annulation) or, to a lesser extent, with their enamine derivatives (β,β'-annulation). Designing efficient, short routes for the construction of polycyclic molecules is currently one of the main challenges in synthetic organic chemistry. For synthesis and synthetic application of bicyclo[3.3.1]nonanes, see: (a) Peters, J. A. *Synthesis* **1979**, 321–336. (b) Butkus, E. *Synlett* **2001**, 1827–1835. (c) Ciochina, R.; Grossman, R. B. *Chem. Rev.* **2006**, *106*, 3963–3986.(d) Barboni, L.; Gabrielli, S.; Palmieri, A.; Femoni, C.; Ballini, R. *Chem.—Eur. J.* **2009**, Epub ahead of print, DOI 10.1002/chem.200900366. (e) Bhunia, S.; Wang, K.-C.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5063–5066. (f) Nicolaou, K. C.; Carenzi, G. E. A.; Jeso, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 3895–3899. (g) Nuhant, P.; David, M.; Pouplin, T.; Delpech, B.; Marazano, C. *Org. Lett.* **2007**, *9*, 287–289. (h) Itagaki, N.; Sugahara, T.; Iwabuchi, Y. *Org. Lett.* **2005**, *7*, 4181–4183. (i) Rodeschini, V.; Ahmad, N. M.; Simpkins, N. S. *Org. Lett.* **2006**, *8*, 5283–5285. (j) Muthyala, R. S.; Sheng, S.; Carlson, K. E.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A. *J. Med. Chem.* **2003**, *46*, 1589–1602. (k) Takagi, R.; Miwa, Y.; Nerio, T.; Inoue, Y.; Matsumura, S.; Ohkata, K. *Org. Biomol. Chem.* **2007**, *5*, 286–300. (l) Aoyagi, K.; Nakamura, H.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4148–4151. (m) Nicolaou, K. C.; Pfefferkorn, J. A.; Kim, S.; Wei, H. X. *J. Am. Chem. Soc.* **1999**, *121*, 4724–4725. (n) Geirsson, J. K. F.; Johannesdottir, J. F. *J. Org. Chem.* **1996**, *61*, 7320–7325. (o) Spessard, S. J.; Stoltz, B. M. *Org. Lett.* **2002**, *4*, 1943–1946.

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(15) Yang, J.-D.; Kim, M.-S.; Lee, M.; Baik, W.; Koo, S. *Synthesis* **2000**, 801–804.

(16) Crystal data for **3e**: $C_{34}H_{38}O_4S_4$, yellow crystal, M = 638.88, monoclinic $p2(1)/n$, a = 17.519 (4) Å, b = 9.4020(19) Å, c = 20.893(4) Å, α = 90.00°, β = 97.238(4)°, γ = 90.00°, V = 3414.0(12) Å^3, Z = 4, T = 293 (2), F_{000} = 1352, R_1 = 0.1054, wR_2 = 0.3049. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (deposition number CCDC-722176). Copies of the data can be obtained, free of charge, on application to the director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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In summary, the three-component reaction of the readily available α-cinnamoyl ketene-*S*,*S*-acetals **1** with oxalyl chloride can proceed in a stereospecific manner under very mild conditions to give γ-alkylidenebutenolides **2** in excellent yields. By this reaction, the structural feature that α-cinnamoyl ketene-*S*,*S*-acetals **1** act as either a 1,3-binucleophile or a C4 1,4-dipole has been recognized. In addition, highly functionalized bicyclo[3.3.1]nonanes **3** were prepared in good to high yields in an atom-economic manner with good diastereoselectivity via a $BF_3 \cdot OEt_2$-mediated novel tandem double cyclization of γ-alkylidenebutenolides **2** under very mild conditions. Further studies are in progress.

Experimental Section

General Procedure for Preparation of 2 (2a as an example). To a stirred solution of **1a** (1.0 mmol, 278 mg) and triethylamine (1.0 mmol, 0.14 mL) in THF (10 mL) was added dropwise a solution of oxalyl chloride (0.5 mmol, 0.043 mL) in THF (2.0 mL) via a syringe for 5 min at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into water (30 mL), followed by basification with saturated aqueous $NaHCO_3$ solution to adjust the pH value of the solution to 7, and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (diethyl ether/hexane = 1/12, v/v) to give **2a** (278 mg, 91%) as a red crystal. Mp 60−62 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.17 (t, *J* = 7.0 Hz, 3H), 1.22−1.29 (m, 9H), 2.68−2.80 (m, 3H), 2.90 (q, *J* = 7.0 Hz, 1H), 3.08−3.09 (m, 4H), 6.11 (d, *J* = 10.5 Hz, 1H), 6.27 (d, *J* = 9.5 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 7.12 (d, *J* = 16.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 3H), 7.30 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.7 (2C), 15.1 (2C), 27.6 (2C), 28.1 (2C), 45.3, 108.1, 117.7, 126.8 (2C), 128.1 (2C), 128.3 (2C), 128.5 (2C), 128.9 (2C), 130.3, 133.9, 134.4, 141.1, 143.4, 143.6, 150.0, 159.0, 169.2, 176.4, 196.1; IR (KBr, cm^{-1}) 774, 866, 990, 1084, 1145, 1222, 1271, 1471, 1633, 1659, 1794, 2960; MS (ESI) *m*/*z* 611 [(M + 1)]$^+$. Anal. Calcd for $C_{32}H_{34}O_4S_4$: C, 62.92; H, 5.61. Found: C, 63.10; H, 5.72

General Procedure for Preparation of 3 (3a as an example). To a stirred solution of γ-alkylidenebutenolide **2a** (1.0 mmol, 610 mg) in CH_3CN (8.0 mL) was added $BF_3 \cdot OEt_2$ (1.0 mmol, 0.13 mL) in one portion. Then the reaction mixture was stirred for 6 h at room temperature. After **2a** was consumed (monitored by TLC), the reaction mixture was poured into water (30 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (diethyl ether/hexane = 1/10, v/v) to give **3a** (366 mg, 60%) as a yellow crystal. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84−0.90 (m, 3H), 1.20−1.28 (m, 3H), 1.29−1.40 (m, 6H), 2.56−2.74 (m, 3H), 2.93−3.09 (m, 3H), 3.37−3.54 (m, 2H), 3.71 (s, 1H), 4.09 (s, 1H), 4.71 (s, 1H), 5.00 (s, 1H), 6.68 (d, *J* = 7.5 Hz, 2H), 6.77−6.79 (m, 3H), 6.90 (t, *J* = 7.5 Hz, 2H), 6.93−6.97 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.5, 14.4, 14.8, 15.1, 23.2, 26.7, 29.5, 30.4, 44.4, 50.4, 54.2, 54.9, 125.4, 125.6, 126.5 (2C), 127.5 (2C), 127.7 (2C), 127.9, 128.1 (2C), 134.6, 137.1, 140.9, 156.7, 175.3, 188.3, 191.6, 192.6, 196.0; IR (KBr, cm^{-1}) 695, 753, 817, 854, 889, 1081, 1258, 1314, 1370, 1450, 1472, 1655, 2925, 2962; MS(ESI) *m*/*z* 611 [(M + 1)]$^+$. Anal. Calcd for $C_{32}H_{34}O_4S_4$: C, 62.92; H, 5.61. Found: C, 62.73; H, 5.75.

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Supporting Information Available: Crystallographic data for **2h** (CIF) and **3e** (CIF), experimental procedures, NMR spectra, and characterization data for new compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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