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One-pot synthesis of multisubstituted quaterphenyls and cyclopropanes

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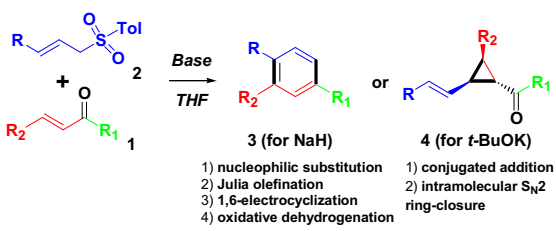
ABSTRACT

An efficient one-step synthetic route toward multifunctionalized quaterphenyls **3** or cyclopropanes **4** is developed from substituted chalcones **1** and sulfones **2** in good yields via a regioselective [3C+3C] or [1C+2C] annulation. The reaction features mild conditions, multisubstitution, and functional groups tolerance and is transition metal catalyst-free. The protocol provides a novel alternative to the conventional methodologies for the synthesis of quaterphenyls or cyclopropanes.

1. Introduction

Polysubstituted phenyls and their analogues have occupied a key position for the aromatic chemistry in the past decades,[1] due to the presence of these diversified frameworks as useful motifs in biological pharmaceuticals and synthetic material sciences.[2,3] Although a huge number of various approaches are known from the literature, new methods for the formation of this type of polyphenyl skeleton attract continuous interest in the organic field.[4] However, transition metal-mediated reaction is the most popular approach among the existing methods, especially Suzuki–Miyaura cross-coupling[5] or transition metal catalyzed Reppe alkynes [2+2+2] cyclotrimerization.[6] It should be noted that the regioselective construction of polysubstituted arenes can still be challenging via previous works because it is difficult to control specific site-selectivity during the carbon–carbon bond formation. It usually results in the undesired generation of a mixture of regioisomers. Fewer methods have been utilized to solve the regioselective issues.[7,8] Cyclopropanes and their derivatives are common core structures presented in a large number of biologically active pharmaceutical agents. They could serve as versatile and important building blocks in organic synthesis because of their unique structural properties.[9] Therefore, enormous effort has been invested in synthesis of functionalized cyclopropanes. Simmons–Smith cyclopropanation is the most often used.[9]

In continuation of our investigation into the synthetic applications of substituted chalcones,[10] a transition metal-free synthetic route employed to create the skeleton of functionalized quaterphenyls and cyclopropanes was investigated next.[11] The one-pot domino base-controlled formal [3+3] or [1+2] cycloaddition route for synthesizing a series of quaterphenyls **3** or cyclopropanes **4** includes two steps: (1) 1,2- or 1,4-addition of chalcones **1** with sulfones **2**[12] and (2) intramolecular 1,6-electrocyclization[13,14] or S_N2 ring-closure (see Scheme 1). The expeditious ring-closure forms a six- or three-membered core structure.[15,16]



Scheme 1. One-pot route of quaterphenyls **3** and cyclopropanes **4**.

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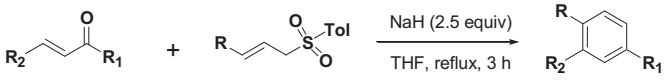
2. Results and discussion

To initiate the synthetic work, several chalcones **1** were prepared in nearly quantitative yields according to our recent literature methods from the NaOH-mediated Claisen–Schmidt condensation of substituted methylketones with benzaldehydes under the methanolic refluxing solution.[10] Next, one-pot synthesis of sulfones **2** was achieved from the allylic chlorination of commercially available cinnamyl alcohols with TsCl and Et_3N in CH_2Cl_2 followed by nucleophilic substitution of the resulting cinnamyl chlorides with RSO_2Na (R=**2a**, 4-MePh; **2b**, 4-MeOPh; **2c**, 4-FPh; **2d**, 3,4-CH_2O_2Ph) in good yields. In an attempt to develop a practical protocol of quaterphenyl with the structure of 1,2,4-triphenylbenzenes, a NaH-mediated one-pot [3C+3C] tandem route of the starting chalcone **1a** with cinnamyl sulfone **2a** in refluxing THF provided a sole quaterphenyl **3a** in a 72% yield. With the result in hand, one-pot preparation of multisubstituted quaterphenyls was examined. Changing R_1 and R_2 substituents of compounds **1a**–**s** or **2a**–**c**, the diversified 1,2,4-triaryl-benzenes **3a**–**v** were isolated in 60–82% yields via the above mentioned protocol.

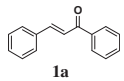
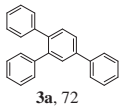
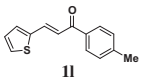
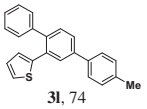
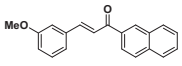
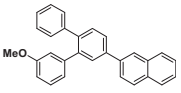
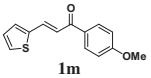
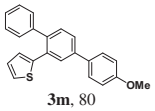
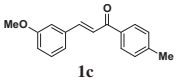
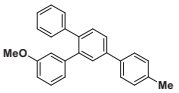
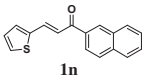
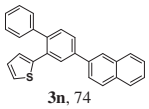
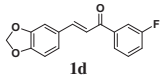
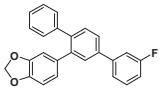
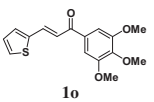
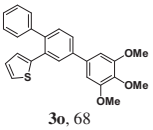
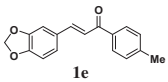
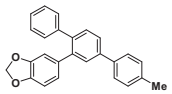
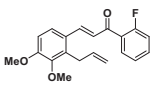
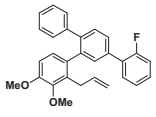
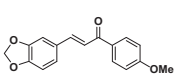
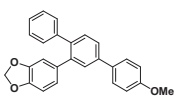
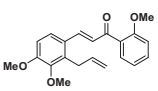
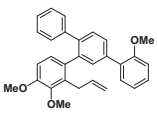
To change the reaction conditions, we found that different yield of quaterphenyl **3a** was obtained via one-pot tandem reaction of model chalcone **1a** with sulfone **2a**, as shown in Table 2. By adjusting the equivalents of NaH (2.5 equiv and 5.0 equiv), reaction concentration (10 mL and 20 mL), reaction temperature (25 °C and 67 °C), and reaction time (3 h and 20 h), different product yield was observed (entries 1–7). When the reaction temperature was elevated to reflux, the yield of quaterphenyl **3a** was increased and the starting materials **1a** and **b** was isolated in trace amounts. After screening base-mediated reaction conditions, we found that NaH provided higher yields than other bases (DBU, Et_3N, DMAP). According to the experimental results, we envision that NaH (2.5 equiv) is an optimal base for increasing the yields of quaterphenyl **3a** under the boiling THF (10 mL) conditions for 3 h (entry 5).

Based on the phenomenon, compounds **3a**–**v** were obtained by one-pot domino methodology; they were summarized in Table 1. The formation of skeleton **3** was confirmed through spectral analysis, including ^1H NMR and HRMS spectrum. The structures of compounds **3g** and **n** were determined by single-crystal X-ray crystallography, as shown in Figs. 1–2.[17] Compared with the isolated yields of products **3a**–**v**, it was found that skeleton **3**, with different aryl substituents (2-thiophene group, electron-withdrawing oxygen-containing group or electron-donating fluoro-containing group), was distributed with moderate ranges. Qinquephenyl **3i** was also prepared from the one-pot domino reaction of chalcone **1i** with sulfone **2a** via a (C3+C3) route.

Table 1
Synthesis of multisubstituted quaterphenyls **3**[a,b]

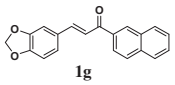
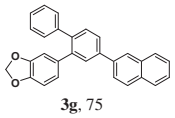
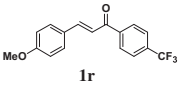
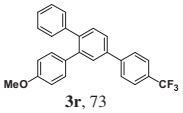
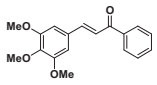
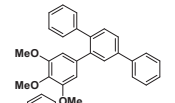
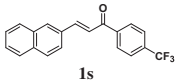
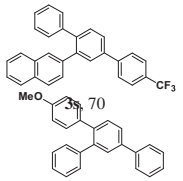
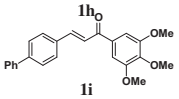
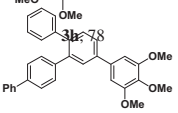
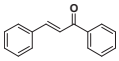
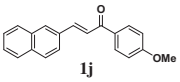
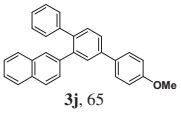
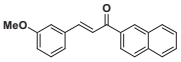
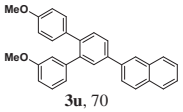
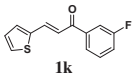
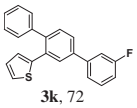
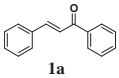
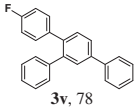


1a-s R =, **2a**, Ph; **2b**, 4-MeOPh; **2c**, 4-FPh **3a-v**

Entry	Chalcones **1**	Sulfones **2**	Quaterphenyls **3** yield (%)	Entry	Chalcones **1**	Sulfones **2**	Quaterphenyls **3** yield (%)
1	 **1a**	**2a**	 **3a**, 72	12	 **1l**	**2a**	 **3l**, 74
2	 **1b**	**2a**	 **3b**, 68	13	 **1m**	**2a**	 **3m**, 80
3	 **1c**	**2a**	 **3c**, 78	14	 **1n**	**2a**	 **3n**, 74
4	 **1d**	**2a**	 **3d**, 76	15	 **1o**	**2a**	 **3o**, 68
5	 **1e**	**2a**	 **3e**, 80	16	 **1p**	**2a**	 **3p**, 60
6	 **1f**	**2a**	 **3f**, 72	17	 **1q**	**2a**	 **3q**, 68

(*continued on next page*)

Table 1 (*continued*)

Entry	Chalcones **1**	Sulfones **2**	Quaterphenyls **3** yield (%)	Entry	Chalcones **1**	Sulfones **2**	Quaterphenyls **3** yield (%)
7	 **1g**	**2a**	 **3g**, 75	18	 **1r**	**2a**	 **3r**, 73
8	 **1h**	**2a**	 **3h**, 78	19	 **1s**	**2a**	 **3s**, 70
9	 **1i**	**2a**	 **3i**, 66	20	 **1a**	**2b**	**3t**, 82
10	 **1j**	**2a**	 **3j**, 65	21	 **1b**	**2b**	 **3u**, 70
11	 **1k**	**2a**	 **3k**, 72	22	 **1a**	**2c**	 **3v**, 78

[a] For the best one-pot reaction conditions: (i) substituted chalcones **1a**–**s** (0.5 mmol), sulfones **2a**–**c** (0.5 mmol), NaH (60%, 50 mg, 1.25 mmol), THF (10 mL), reflux, 3 h.
[b] The isolated quaterphenyl products **3a**–**v** were >95% pure as determined by ^{1}H NMR analysis.

Table 2
NaH-mediated reaction of compounds **1a** and **2a**[a]

Entry	Equiv, THF (mL), temp (°C), time (h)	**3a**, yield[b]
1	2.5, 10, 25, 3	30%
2	2.5, 10, 25, 20	50%
3	5.0, 10, 25, 20	48%
4	5.0, 20, 25, 20	44%
5	2.5, 10, 67, 3	72%
6	2.5, 10, 67, 20	67%
7	5.0, 10, 67, 20	66%

[a] The reactions were run on a 0.5 mmol scale with chalcone **1a** and sulfone **2a**.
[b] The starting materials **1a** and **2a** were recovery (for entry 1, 50%; entry 2, 32%; entry 3, 38%; entry 4, 35%; entries 5–7,<5%).

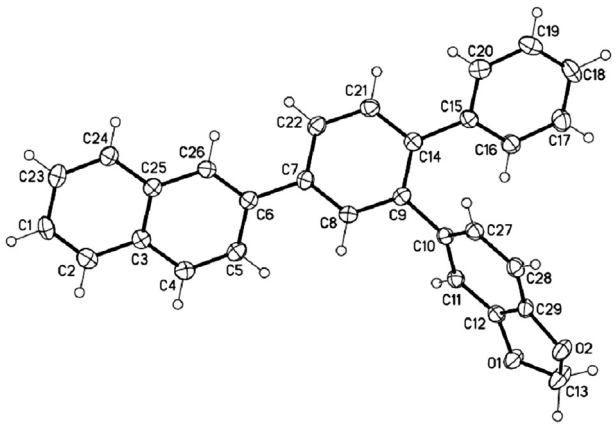


Fig. 1. X-ray structure of compound **3g**.

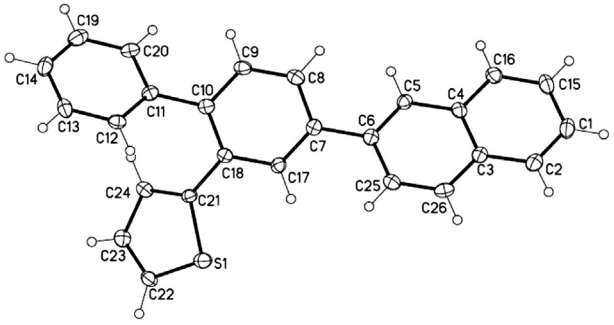
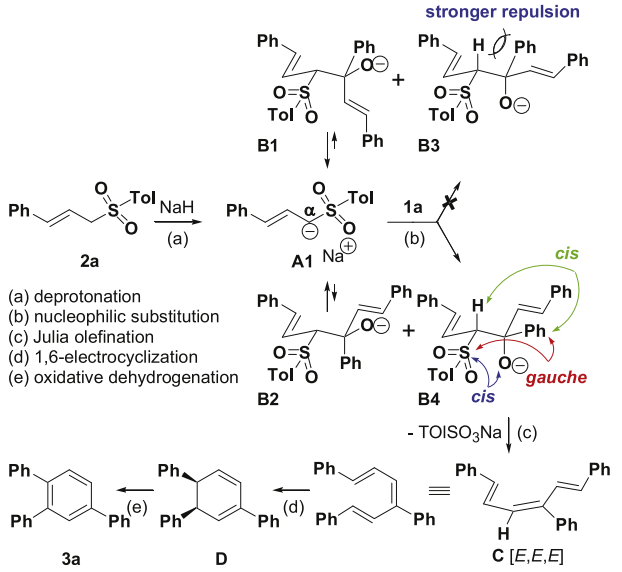


Fig. 2. X-ray structure of compound **3n**.

As shown in Scheme 2, a plausible explanation for the one-pot synthesis of compound **3a** via the reaction of **1a** and **2a** should be that sodium α-carbanion **A1** was first generated via NaH-mediated deprotonation of cinnamyl sulfone **2a** in refluxing THF. Under thermodynamic conditions, four possible intermediates **B1**–**B4** should be formed by the nucleophilic substitution of intermediate **A1** with chalcone **1a**. For intermediates **B1** and **B2**, the orientation of the oxygen anion and the sulfonyl group on the equatorial position was *gauche*-configured. At the stages, the oxygen anion promoted the retro-aldol type reaction via an anti-periplanar conformation and the equilibrium process could be generated. To trigger Julia olefination, the orientation of the oxygen anion and the sulfonyl group was arranged to *cis*-configuration. Intermediate **B3** exhibited a stronger repulsion with steric hindrance than did intermediate **B4**. The *gauche*-configuration between the phenyl group and the sulfonyl group (on the equatorial position) with less steric hindrance was preferred when choosing to provide a more stable intermediate **B4**. After the removal of toluenesulfonate, the

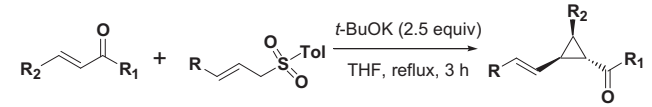
preferred intermediate **C** with a fully (*E*,*E*,*E*)-conjugated configuration was formed. Next, quaterphenyl **3a** was generated by the 1,6-6π-electrocyclic disrotatory ring closure followed by sequential oxidative dehydrogenation of the resulting intermediate **D**. From the above mentioned reaction mechanism, we believe that air (molecular oxygen) plays an important oxidant role to activate the aromatization step during the one-pot direct transformation.[11]



Scheme 2. A possible mechanism to compound **3a**.

With the successful results in hand, when the base was further changed from NaH to *t*-BuOK under boiling THF conditions, six substituted cycolpropanes **4a**–**h** with a three-membered ring skeleton were provided in 56%–80% yields via the one-pot domino reaction of chalcones **1a**, **b**, **f**, **j**, **l**, **t** or **u** with sulfone **2a**, **b** or **2d**, **e** (see Table 3). This is a high-yield and one-pot cascade route to the framework of functionalized cyclopropanes. The structural skeleton of compound **4d** was determined by single-crystal X-ray crystallography (Fig. 3).[17]

Table 3
Synthesis of Cyclopropanes **4a**–**h**[a,b]



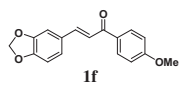
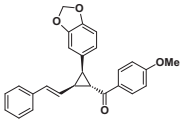
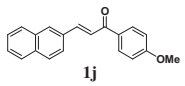
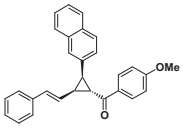
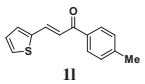
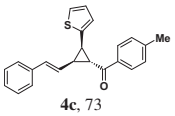
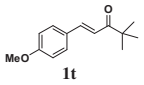
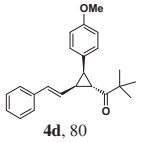
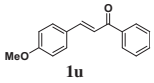
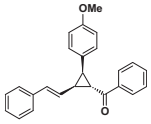
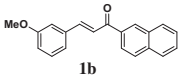
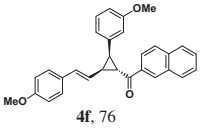
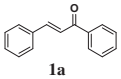
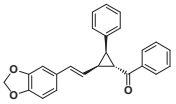
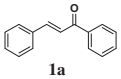
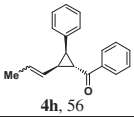
Entry	Chalcones **1**	Sulfones **2**	Cyclopropanes **4** yield (%)
1	 **1f**	**2a**	 **4a**, 70
2	 **1j**	**2a**	 **4b**, 65
3	 **1l**	**2a**	 **4c**, 73

Table 3 (*continued*)

Entry	Chalcones **1**	Sulfones **2**	Cyclopropanes **4** yield (%)
4	 **1t**	**2a**	 **4d**, 80
5	 **1u**	**2a**	 **4e**, 62
6	 **1b**	**2b**	 **4f**, 76
7	 **1a**	**2d**	 **4g**, 71
8	 **1a**	**2e**	 **4h**, 56

[a] For the best one-pot reaction conditions: (i) chalcones **1a**, **b**, **1f**, **1j**, **1l**, **1t**, **1u** (0.5 mmol), sulfones **2a**, **b** or **2d**, **e** (0.5 mmol), *t*-BuOK (140 mg, 1.25 mmol), THF (10 mL), reflux, 3 h.
[b] The isolated quaterphenyls **4a**–**h** were >95% pure as determined by ^{1}H NMR analysis.

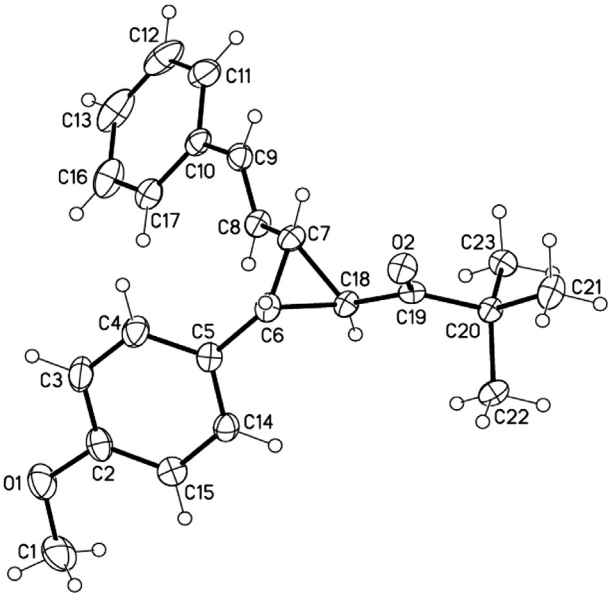
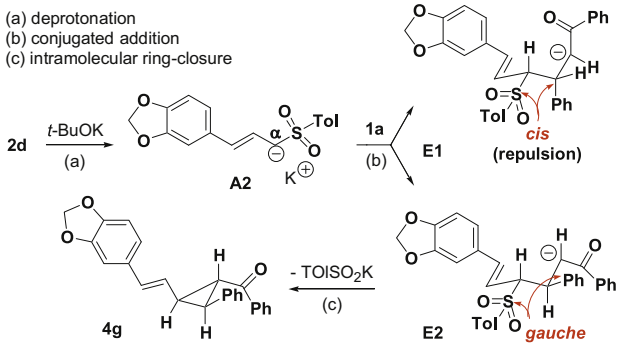


Fig. 3. X-ray structure of compound **4d**.

Based on the results, a possible reaction mechanism for model substrate **4g** is shown in Scheme 3. Initially, intermediate **A2** was formed by deprotonation of sulfone **2d** with *t*-BuOK. Intermediate **E1** or **E2** should be afforded via the conjugated addition of chalcone **1a** with the resulting potassium α-carbanion **A2**. Generating the intermediate **E1** should not be preferred since the relative orientation between the phenyl group and the sulfonyl group was *cis*-configured with stronger repulsion. At another intermediate **E2** stage, *gauche*-configuration between the phenyl group and the sulfonyl group easily triggered the occurrence of an intramolecular S_N2 ring-closure, and the three-membered ring could be cyclized for the formation of cyclopropane skeleton. After removal of toluenesulfinic potassium salt ($TolSO_2K$), compound **4g** was provided. During the tandem reaction procedure, the regio- and stereoselective formation of three contiguous chiral centers was well-developed. So far, there are a few of literature reports to describe the base-promoted straightforward synthesis of skeleton **4** via an interrupted Julia reaction.[18] Under thermal conditions, skeleton **4**, with contiguous stereogenic centers advanced an intramolecular cascade stereospecific ring closure to three adjacent stereocenters with the *cis*–*trans* configuration. For possible differences between NaH-mediated 1,2-addition and *t*-BuOK-mediated 1,4-addition, it should be envisioned as the nature of sodium α-carbanion **A1** or potassium α-carbanion **A2** with specific electronic effects affecting the addition position of chalcone **1** in the formation of skeleton **3** or **4**. To further investigate the origin of this regioselectivity, chalcone **1f** and sulfone **2a** were chosen as the model materials in the reaction of KH-mediated formal [3+3] benzannulation or *t*-BuONa-mediated formal [1+2] cyclopropanation. We found that the corresponding quaterphenyl **3f** (70%) or cyclopropanes **4a** (65%) was isolated as the major product, respectively. The results demonstrated sodium α-carbanion **A1** or potassium α-carbanion **A2** control the shift of regioselectivity. In the other way, LDA-mediated reaction of chalcone **1f** and sulfone **2a** was also examined. Quaterphenyl **3f** (58%) along with the recovery starting materials **1f** and **4a** (~15%) was observed.



Scheme 3. A possible mechanism to compound **4g**.

3. Conclusion

In summary, we have successfully presented a synthetic methodology for multi-functionalized quaterphenyls **3** and cyclopropanes **4**, which involves the tandem site-selective nucleophilic substitution of substituted chalcones **1** with the carbanion of sulfones **2** and intramolecular 1,6-electrocyclic disrotatory annulation or S_N2 ring closure. The one-pot synthesis of quaterphenyls and cyclopropanes via base-controlled reaction conditions was investigated thoroughly. The structures of key products were confirmed by X-ray crystal analysis. The one-pot transition metal-free synthetic approach begins with simple starting materials and reagents, and provides a potential methodology for the synthetic research and biological activities of quaterphenyls and cyclopropanes. Further investigation regarding one-pot cascade synthesis of multi-functionalized carbocycles will be conducted and published in due course.

4. Experimental section

4.1. General

All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous $MgSO_4$ before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 200/400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD). Elemental analyses were carried out with Heraeus Vario III-NCSH, Heraeus CHN-OS-Rapid Analyzer or Elementar Vario EL III.

A representative synthetic procedure of compounds **3a**–**v** *is as follows*: Sodium hydride (NaH, 60%, 50 mg, 1.25 mmol) was added to a solution of sulfones **2a**–**c** (0.5 mmol) in THF (8 mL). A solution of chalcones **1a**–**s** (0.5 mmol) in the THF (2 mL) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt. Water (1 mL) was added to the reaction mixture at 0 °C. The solvent was concentrated under reduced pressure. The residue was diluted with water (10 mL) and the mixture was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc=10/1–6/1) afforded compounds **3a**–**v**.

*4.1.1. Compound (**3a**).* Yield=72% (110 mg); mp=103–105 °C, (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3054, 3032, 1475, 1255, 1078, 795 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{24}H_{19}$ 307.1487, found 307.1489; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.65 (m, 4H), 7.52 (d, J=8.4 Hz, 1H), 7.49–7.44 (m, 2H), 7.39–7.36 (m, 1H), 7.25–7.17 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.49, 141.11, 140.99, 140.59, 140.36, 139.55, 131.09, 129.90 (2×), 129.87 (2×), 129.41, 128.82 (2×), 127.92 (2×), 127.89 (2×), 127.42, 127.13 (2×), 126.58, 126.52, 126.11.

*4.1.2. Compound (**3b**).* Yield=68% (131 mg); mp=100–101 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2962, 2922, 1615, 1483, 1176, 1020, 750 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{29}H_{23}O$ 387.1749, found 387.1755; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=1.2 Hz, 1H), 7.96–7.78 (m, 6H), 7.56 (d, J=7.6 Hz, 1H), 7.54–7.48 (m, 2H), 7.29–7.13 (m, 6H), 6.85 (dt, J=1.2, 7.6 Hz, 1H), 6.80 (dd, J=0.8, 2.8 Hz, 1H), 6.78–6.75 (m, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.10, 142.81, 141.15, 140.93, 140.22, 139.66, 137.83, 133.69, 132.72, 131.15, 129.78 (2×), 129.45, 128.96, 128.51, 128.21, 127.96 (2×), 127.65, 126.58, 126.42, 126.35, 126.01, 125.81, 125.44, 122.39, 115.28, 112.76, 55.09.

*4.1.3. Compound (**3c**).* Yield=78% (137 mg); colorless gum; IR ($CHCl_3$): 2930, 2360, 1524, 1488, 1142, 1028, 807 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{26}H_{23}O$ 351.1749, found 351.1758; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69–7.63 (m, 2H), 7.59 (d, J=8.0 Hz, 2H), 7.50 (d, J=8.4 Hz, 1H), 7.28 (d, J=8.0 Hz, 2H), 7.25–7.14 (m, 6H), 6.82 (ddd, J=0.8, 1.6, 7.6 Hz, 1H), 6.77 (ddd, J=0.8, 2.4, 8.4 Hz, 1H), 6.72 (dd, J=1.6, 2.4 Hz, 1H), 3.62 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.06, 142.56, 141.23, 140.77, 140.30, 139.28, 137.66,

137.26, 131.02, 129.77 (2×), 129.55 (2×), 129.01, 128.90, 127.91 (2×), 126.96 (2×), 126.48, 125.99, 122.37, 115.22, 112.76, 55.06, 21.12.

*4.1.4. Compound (**3d**).* Yield=76% (140 mg); colorless gum; IR ($CHCl_3$): 2896, 1604, 1473, 1158, 836 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{25}H_{18}FO_2S$ 369.1291, found 369.1298; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, J=2.0, 6.8 Hz, 1H), 7.60 (s, 1H), 7.50–7.35 (m, 4H), 7.29–7.15 (m, 5H), 7.09–7.04 (m, 1H), 6.70 (d, J=8.4 Hz, 1H), 6.67–6.65 (m, 2H), 5.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.23 (d, J=244.1 Hz), 147.26, 146.44, 142.81 (d, J=7.6 Hz), 140.93, 140.74, 140.09, 139.01 (d, J=2.3 Hz), 135.26, 131.24, 130.28 (d, J=8.3 Hz), 129.70 (2×), 129.27, 128.03 (2×), 126.70, 125.89, 123.44, 122.71 (d, J=3.0 Hz), 114.22 (d, J=21.2 Hz), 113.96 (d, J=21.3 Hz), 110.36, 107.99, 100.93.

*4.1.5. Compound (**3e**).* Yield=80% (146 mg); colorless gum; IR ($CHCl_3$): 2882, 1477, 1225, 1040, 806, 734 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{26}H_{21}O_2$ 365.1542, found 365.1550; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, J=2.0, 6.8 Hz, 1H), 7.60 (s, 1H), 7.57 (d, J=8.4 Hz, 2H), 7.47 (d, J=8.4 Hz, 1H), 7.28–7.18 (m, 7H), 6.70 (dd, J=0.8, 7.2 Hz, 1H), 6.67 (s, 1H), 6.66 (dd, J=2.0, 7.2 Hz, 1H), 5.93 (s, 2H), 2.41 (s, 3H).

*4.1.6. Compound (**3f**).* Yield=72% (137 mg); mp=130–131 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2921, 1487, 1460, 1022, 912, 870, 841, 736 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{26}H_{21}O_3$ 381.1491, found 381.1502; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J=8.8 Hz, 2H), 7.58 (d, J=8.0 Hz, 2H), 7.46 (dd, J=1.6, 6.8 Hz, 1H), 7.28–7.18 (m, 5H), 7.00 (d, J=8.0 Hz, 2H), 6.70 (dd, J=0.8, 7.2 Hz, 1H), 6.67 (s, 1H), 6.66 (dd, J=2.0, 7.2 Hz, 1H), 5.93 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.30, 147.19, 146.31, 141.20, 140.52, 139.93, 138.89, 135.59, 133.06, 131.09, 129.74 (2×), 128.88, 128.12 (2×), 127.96 (2×), 126.49, 125.54, 123.45, 114.27 (2×), 110.41, 107.93, 100.89, 55.36.

*4.1.7. Compound (**3g**).* Yield=75% (150 mg); mp=110–111 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2902, 1475, 1222, 1041, 812, 739 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{29}H_{21}O_2$ 401.1542, found 401.1552; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.96–7.76 (m, 6H), 7.55–7.48 (m, 3H), 7.34–7.19 (m, 6H), 6.72 (br s, 2H), 5.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.25, 146.40, 141.11, 140.70, 140.18, 139.60, 137.83, 135.51, 133.70, 132.72, 131.23, 129.75 (2×), 129.55, 128.50, 128.21, 128.02 (2×), 127.65, 126.61, 126.35, 126.21, 126.01, 125.79, 125.43, 123.49, 110.43, 107.98, 100.92. Single-crystal X-ray diagram: crystal of compound **3g** was grown by slow diffusion of EtOAc into a solution of compound **3g** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 1 21 1, a=11.2874(12) Å, b=5.9914(6) Å, c=15.6427(16) Å, V=1001.67(18) $Å^3$, Z=2, d_{calcd}=1.328 g/cm^3, $F(000)$=420, 2θ range 1.37–26.37°, R indices (all data) $R1$=0.0470, $wR2$=0.1343.

*4.1.8. Compound (**3h**).* Yield=78% (154 mg); colorless gum; IR ($CHCl_3$): 2939, 1587, 1474, 1245, 1130, 993, 825, 731 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{27}H_{25}O_3$ 397.1804, found 397.1810; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71–7.64 (m, 4H), 7.54–7.47 (m, 3H), 7.29–7.19 (m, 6H), 6.40 (s, 2H), 3.84 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.65 (2×), 141.31, 140.80, 140.60, 140.52, 139.63, 136.82, 136.62, 131.06, 129.67 (2×), 128.86 (2×), 128.82, 127.99 (2×), 127.49, 127.17 (2×), 126.55, 126.18, 107.34 (2×), 60.93, 55.90 (2×).

*4.1.9. Compound (**3i**).* Yield=66% (156 mg); mp=169–170 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2943, 1586, 1480, 1242, 1136, 1003, 830, 734 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{33}H_{29}O_3$ 473.2117, found 473.2120; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67–7.59 (m, 4H), 7.54–7.49 (m, 3H), 7.45–7.41 (m, 2H), 7.36–7.20 (m, 8H), 6.87 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.55 (2×), 141.03, 140.61, 140.57, 140.52, 140.40, 139.65, 139.36, 137.79, 136.60, 131.15, 130.31 (2×), 129.86 (2×), 129.24, 128.75 (2×), 128.02 (2×), 127.29, 126.95 (2×), 126.64 (3×), 126.18, 104.45 (2×), 60.98, 56.26 (2×).

*4.1.10. Compound (**3j**).* Yield=65% (125 mg); mp=137–138 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2970, 2929, 1625, 1488, 1178, 1016, 753 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{29}H_{23}O$ 387.1749, found 387.1752; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J=1.6 Hz, 1H), 7.80–7.77 (m, 2H), 7.74 (d, J=2.0 Hz, 1H), 7.67–7.62 (m, 4H), 5.54 (d, J=7.6 Hz, 1H), 7.48–7.43 (m, 2H), 7.23–7.17 (m, 6H), 7.02 (d, J=8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.32, 141.09, 140.76, 140.08, 139.36, 139.07, 133.39, 133.09, 132.09, 131.17, 129.89 (2×), 129.32, 128.41 (2×), 128.18 (2×), 127.98 (3×), 127.59, 127.09, 126.52, 125.95, 125.84, 125.79, 114.30 (2×), 55.37.

*4.1.11. Compound (**3k**).* Yield=72% (119 mg); colorless gum IR ($CHCl_3$): 2948, 1650, 1533, 1480, 1225, 1162, 847, 764 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{22}H_{16}FS$ 331.0957, found 331.0963; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J=2.0 Hz, 1H), 7.60 (dd, J=2.0, 8.0 Hz, 1H), 7.46 (d, J=8.0 Hz, 1H), 7.45–7.26 (m, 8H), 7.22 (dd, J=1.2, 5.2 Hz, 1H), 7.10–7.05 (m, 1H), 6.90 (dd, J=3.6, 5.2 Hz, 1H), 6.77 (dd, J=1.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.23 (d, J=244.1 Hz), 142.84, 142.59, 140.90, 140.46, 139.18 (d, J=2.3 Hz), 133.75, 131.37, 130.32 (d, J=8.4 Hz), 129.59 (2×), 129.27, 128.07 (2×), 127.15, 127.09, 126.95, 126.33, 125.73, 122.73 (d, J=3.0 Hz), 114.27 (d, J=33.4 Hz), 114.08 (d, J=39.4 Hz).

*4.1.12. Compound (**3l**).* Yield=74% (121 mg); mp=115–116 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3004, 2915, 2011, 1513, 1478, 1253, 1115, 820, 741 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{23}H_{19}S$ 327.1208, found 327.1215; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J=2.0 Hz, 1H), 7.60 (dd, J=2.0, 8.0 Hz, 1H), 7.57 (d, J=8.4 Hz, 2H), 7.44 (d, J=7.6 Hz, 1H), 7.32–7.27 (m, 7H), 7.21 (dd, J=0.8, 5.2 Hz, 1H), 6.89 (dd, J=4.0, 5.2 Hz, 1H), 6.76 (dd, J=0.8, 4.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.21, 141.16, 140.42, 139.59, 137.47, 137.37, 133.52, 131.21, 129.65 (2×), 129.57 (2×), 129.15, 128.02 (2×), 127.03, 126.96 (2×), 126.92, 126.89, 126.25, 125.54, 21.13.

*4.1.13. Compound (**3m**).* Yield=80% (137 mg); colorless gum; IR ($CHCl_3$): 2965, 2903, 1606, 1461, 1145, 996, 755 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{23}H_{19}OS$ 343.1157, found 343.1166; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J=2.0 Hz, 1H), 7.61 (d, J=8.8 Hz, 2H), 7.73 (dd, J=2.0, 8.0 Hz, 1H), 7.43 (d, J=8.0 Hz, 1H), 7.34–7.26 (m, 5H), 7.21 (dd, J=1.2, 5.2 Hz, 1H), 7.01 (d, J=8.8 Hz, 2H), 6.89 (dd, J=3.6, 5.2 Hz, 1H), 6.75 (dd, J=1.2, 3.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.37, 143.23, 141.18, 140.09, 139.27, 133.51, 132.86, 131.22, 129.65 (2×), 128.91, 128.15 (2×), 128.02, 127.02, 126.89 (2×), 126.01, 125.53, 114.30 (2×), 114.27, 55.37.

*4.1.14. Compound (**3n**).* Yield=74% (134 mg); mp=155–156 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2920, 1481, 1446, 1026, 908, 868, 731 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{26}H_{19}S$ 363.1208, found 363.1215; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.97–7.88 (m, 4H), 7.83 (dd, J=2.0, 8.4 Hz, 1H), 7.76 (dd, J=2.0, 8.4 Hz, 1H), 7.55–7.49 (m, 3H), 7.34–7.30 (m, 5H), 7.23 (dd, J=1.2, 5.2 Hz, 1H), 6.92 (dd, J=3.6, 5.2 Hz, 1H), 6.81 (dd, J=1.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.12, 141.09, 140.37, 139.99, 137.65, 133.72, 133.69, 132.75, 131.36, 129.66 (2×), 129.59, 128.55, 128.24, 128.07 (2×), 127.67, 127.13, 127.02, 126.95, 126.68, 126.39, 126.08, 125.86, 125.67, 125.41. Single-crystal X-ray diagram: crystal of compound **3n** was grown by slow diffusion of EtOAc into a solution of compound **3n** in CH_2Cl_2 to yield colorless prisms. The

compound crystallizes in the orthorhombic crystal system, space group P *c* a 21, *a*=25.3470(16) Å, *b*=6.0008(3) Å, *c*=12.0246(8) Å, *V*=1828.97(19) Å^3, *Z*=4, d_{calcd}=1.316 g/cm^3, *F*(000)=760, 2θ range 1.61–26.41°, *R* indices (all data) *R*1=0.0593, *wR*2=0.1488.

*4.1.15. Compound (**3o**).* Yield=68% (137 mg); colorless oil; IR ($CHCl_3$): 2937, 1572, 1483, 1145, 1024, 841, 740 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{25}H_{23}O_3S$ 403.1368, found 403.1378; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J*=2.0 Hz, 1H), 7.58 (dd, *J*=2.0, 8.0 Hz, 1H), 7.45 (d, *J*=8.0 Hz, 1H), 7.34–7.26 (m, 5H), 7.22 (dd, *J*=1.2, 5.2 Hz, 1H), 6.91 (dd, *J*=3.6, 5.2 Hz, 1H), 6.85 (s, 2H), 6.77 (dd, *J*=1.2, 3.6 Hz, 1H), 3.95 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.55 (2×), 143.04, 141.02, 140.68, 139.66, 136.38, 133.59, 131.20, 129.61 (2×), 129.27, 128.78, 128.05 (2×), 127.12, 127.02, 126.95, 126.44, 125.70, 104.49 (2×), 60.98, 56.27 (2×).

*4.1.16. Compound (**3p**).* Yield=60% (127 mg); mp=104–105 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3042, 2928, 1621, 1483, 1256, 1168, 937, 873, 755 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{29}H_{26}FO_2$ 425.1917, found 425.1923; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dt, *J*=2.0, 8.4 Hz, 1H), 7.55–7.49 (m, 3H), 7.35–7.30 (m, 1H), 7.25–7.16 (m, 7H), 6.85 (d, *J*=8.4 Hz, 1H), 7.74 (d, *J*=8.4 Hz, 1H), 5.75–5.65 (m, 1H), 4.82 (dq, *J*=1.6, 10.0 Hz, 1H), 4.70 (dq, *J*=1.6, 17.2 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.31 (ddt, *J*=1.6, 6.0, 14.4 Hz, 1H), 2.97 (ddt, *J*=1.2, 6.0, 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.89 (d, *J*=246.4 Hz), 151.77, 147.29, 140.93, 140.33, 139.61, 136.97, 134.35, 134.20, 132.15, 131.87 (d, *J*=3.0 Hz), 130.68 (d, *J*=3.0 Hz), 129.99, 129.48 (2×), 129.28, 129.01, 128.04 (d, *J*=3.8 Hz), 127.70 (2×), 126.43 (d, *J*=3.8 Hz), 124.36, 124.32, 116.13 (d, *J*=22.7 Hz), 114.76, 109.89, 60.60, 55.58, 32.05.

*4.1.17. Compound (**3q**).* Yield=68% (148 mg); colorless gum; IR ($CHCl_3$): 3054, 2937, 1643, 1464, 1262, 1173, 869, 751 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{30}H_{29}O_3$ 437.2117, found 437.2122; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dt, *J*=2.0, 8.0 Hz, 1H), 7.49 (d, *J*=2.0 Hz, 1H), 7.47 (d, *J*=8.0 Hz, 1H), 7.39 (dd, *J*=1.6, 7.6 Hz, 1H), 7.34 (dd, *J*=1.6, 7.6 Hz, 1H), 7.32 (dd, *J*=1.6, 7.6 Hz, 1H), 7.22–7.12 (m, 4H), 7.04 (dt, *J*=1.2, 7.6 Hz, 1H), 7.00 (d, *J*=8.4 Hz, 1H), 6.84 (d, *J*=8.4 Hz, 1H), 6.71 (d, *J*=8.4 Hz, 1H), 5.76–5.67 (m, 1H), 4.82 (dq, *J*=1.6, 10.0 Hz, 1H), 4.72 (dq, *J*=1.6, 17.2 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.73 (s, 3H), 3.33 (ddt, *J*=1.6, 6.0, 14.4 Hz, 1H), 3.01 (ddt, *J*=1.2, 6.0, 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.57, 151.65, 147.25, 141.27, 139.50, 139.02, 137.14, 136.97, 134.70, 132.45, 132.25, 130.85, 130.12, 129.56, 129.53 (2×), 128.64, 128.52, 127.63 (2×), 126.48, 126.23, 120.85, 114.69, 111.22, 109.82, 60.59, 55.57, 55.56, 32.01.

*4.1.18. Compound (**3r**).* Yield=73% (147 mg); colorless gum; IR ($CHCl_3$): 2920, 1617, 1325, 1168, 1126, 1095, 850, 835 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{26}H_{20}F_3O$ 405.1466, found 405.1475; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.4 Hz, 2H), 7.72 (d, *J*=8.0 Hz, 2H), 7.62–7.62 (m, 2H), 7.52 (d, *J*=8.0 Hz, 1H), 7.29–7.23 (m, 3H), 7.21–7.18 (m, 2H), 7.11 (d, *J*=8.8 Hz, 2H), 6.79 (d, *J*=8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.54, 144.19, 144.18, 141.01, 140.86, 140.42, 138.84, 133.49, 131.33, 130.90 (2×), 129.78 (2×), 129.45, 128.01 (2×), 127.36 (2×), 126.78 (2×), 126.65, 125.87, 125.76 (q, *J*=3.8 Hz), 113.50 (2×), 55.19.

*4.1.19. Compound (**3s**).* Yield=70% (148 mg); mp=115–116 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 1632, 1475, 1258, 1162, 945, 875, 750 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{29}H_{20}F_3$ 425.1517, found 425.1524; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.79 (m, 8H), 7.74 (d, *J*=8.0 Hz, 2H), 7.71 (dd, *J*=2.4, 8.0 Hz, 1H), 7.65 (d, *J*=8.4 Hz, 1H), 7.60 (d, *J*=8.0 Hz, 1H), 7.49–7.47 (m, 2H), 7.24–7.21 (m, 3H), 7.19 (dd, *J*=2.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.10, 141.10, 140.71, 140.64, 138.95, 138.90, 133.37, 132.16, 131.40, 130.19, 129.87, 129.83 (4×), 128.43, 128.21, 128.08 (2×), 127.98, 127.62, 127.40 (2×), 126.80, 126.36, 126.07, 125.95, 125.85, 125.80 (q, *J*=3.7 Hz).

*4.1.20. Compound (**3t**).* Yield=82% (138 mg); mp=131–133 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2927, 2354, 1531, 1138, 1022, 794 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{25}H_{21}O$ 337.1592, found 337.1597; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.63 (m, 4H), 7.51–7.43 (m, 3H), 7.39–7.34 (m, 1H), 7.29–7.20 (m, 5H), 7.10 (d, *J*=8.8 Hz, 2H), 6.78 (d, *J*=8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.37, 141.70, 140.86, 140.64, 139.99, 139.14, 133.47, 131.00, 130.90 (2×), 129.88 (2×), 129.44, 128.80 (2×), 127.97 (2×), 127.36, 127.10 (2×), 126.52, 126.11, 113.39 (2×), 55.17.

*4.1.21. Compound (**3u**).* Yield=70% (146 mg); mp=108–110 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 2942, 1532, 1452, 1133, 1019, 812 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{30}H_{25}O_2$ 417.1855, found 417.1863; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J*=1.6 Hz, 1H), 7.95–7.76 (m, 6H), 7.56–7.47 (m, 3H), 7.21–7.12 (m, 3H), 6.86–6.79 (m, 5H), 3.80 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.18, 158.44, 143.06, 140.83, 139.83, 139.27, 137.89, 133.71, 133.48, 132.69, 131.09, 130.83 (2×), 129.49, 128.99, 128.49, 128.43, 127.65, 126.77, 126.42, 125.98, 125.73, 125.45, 122.42, 115.30, 113.45 (2×), 112.58, 55.21, 55.12.

*4.1.22. Compound (**3v**).* Yield=78% (126 mg); colorless gum; IR ($CHCl_3$): 2926, 1612, 1512, 1486, 1235, 1145, 837 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{24}H_{18}F$ 325.1393, found 325.1399; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.64 (m, 4H), 7.49–7.45 (m, 3H), 7.39–7.35 (m, 1H), 7.27–7.23 (m, 3H), 7.20–7.17 (m, 2H), 7.15–7.11 (m, 2H), 6.94–6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.77 (d, *J*=244.1 Hz), 141.29, 141.00, 140.52, 140.45, 138.47, 137.06 (d, *J*=3.0 Hz), 131.35 (d, *J*=8.4 Hz, 2×), 130.96, 129.87 (2×), 129.45, 128.84 (2×), 128.04 (2×), 127.49, 127.12 (2×), 126.70, 126.17, 114.85 (d, *J*=21.3 Hz, 2×).

A representative synthetic procedure of compounds **4a**–**h** *is as follows*: Potassium *t*-butoxide (*t*-BuOK, 140 mg, 1.25 mmol) was added to a solution of cinnamy sulfone **2a**, **b**, **d** or crotyl sulfone **2e** (0.5 mmol) in THF (8 mL). A solution of chalcone **1a**, **b**, **f**, **j**, **l**, **t** or **u** (0.5 mmol) in the THF (2 mL) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt. Water (1 mL) was added to the reaction mixture at 0 °C. The solvent was concentrated under reduced pressure. The residue was diluted with water (10 mL) and the mixture was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc=10/1–6/1) afforded compounds **4a**–**h**.

*4.1.23. Compound (**4a**).* Yield=70% (139 mg); colorless gum; IR ($CHCl_3$): 3152, 2989, 1731, 1592, 1485, 1223, 1183, 1148, 1091, 1016, 957, 822; HRMS (ESI, M^++1) calcd for $C_{26}H_{23}O_4$ 399.1596, found 399.1592; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J*=8.8 Hz, 2H), 7.28–7.16 (m, 5H), 6.99 (d, *J*=8.8 Hz, 2H), 6.81–6.76 (m, 3H), 6.63 (d, *J*=15.6 Hz, 1H), 5.96 (d, *J*=1.6 Hz, 1H), 5.95 (d, *J*=1.6 Hz, 1H), 5.72 (dd, *J*=10.0, 15.6 Hz, 1H), 3.89 (s, 3H), 3.24 (dd, *J*=5.2, 9.2 Hz, 1H), 3.16 (dd, *J*=4.4, 5.2 Hz, 1H), 2.73 (dt, *J*=4.4, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.10, 163.54, 147.66, 146.46 (2×), 137.04, 132.02, 130.72, 130.37 (2×), 128.49 (2×), 127.20, 126.89, 125.91 (2×), 122.25, 113.83 (2×), 109.69, 108.16, 101.01, 55.48, 35.51, 34.32, 32.44.

*4.1.24. Compound (**4b**).* Yield=65% (131 mg); colorless gum; IR ($CHCl_3$): 3158, 3004, 1738, 1604, 1457, 1232, 1189, 1123, 1112, 960, 856; HRMS (ESI, M^++1) calcd for $C_{29}H_{25}O_2$ 405.1855, found 405.1862; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J*=8.8 Hz, 2H), 7.86–7.81 (m, 3H), 7.79 (s, 1H), 7.52–7.45 (m, 3H), 7.23–7.12 (m, 5H), 7.02 (d, *J*=8.8 Hz, 2H), 6.68 (d, *J*=16.0 Hz, 1H), 5.74 (dd, *J*=9.6, 16.0 Hz, 1H), 3.90 (s, 3H),

3.50 (dd, J=5.6, 9.2 Hz, 1H), 3.39 (t, J=4.4 Hz, 1H), 2.86 (dt, J=4.4, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.16, 163.58, 136.95, 134.32, 133.32, 132.43, 132.22, 130.78, 130.44 (2×), 128.45 (2×), 128.09, 127.68 (2×), 127.60, 127.49, 127.19, 126.77, 126.19, 125.88 (2×), 125.73, 113.86 (2×), 55.50, 35.69, 34.64, 32.31.

*4.1.25. Compound (**4c**).* Yield=73% (126 mg); colorless gum; IR ($CHCl_3$): 3147, 2984, 1757, 1450, 1221, 1176, 1115, 943, 823; HRMS (ESI, M^++1) calcd for $C_{23}H_{21}SO$ 345.1313, found 345.1320; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.0 Hz, 2H), 7.28–7.18 (m, 6H), 7.00–6.98 (m, 2H), 6.68 (d, J=16.0 Hz, 1H), 5.94 (dd, J=8.8, 16.0 Hz, 1H), 3.36 (dd, J=5.2, 8.8 Hz, 1H), 3.26 (dd, J=4.8, 5.2 Hz, 1H), 2.82 (dt, J=4.8, 8.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.63, 144.00, 140.23, 136.97, 135.03, 132.66, 129.36 (2×), 128.51 (2×), 128.28 (2×), 127.33, 126.89, 126.32, 126.14, 125.99 (2×), 124.31, 35.75, 34.64, 29.47, 21.64.

*4.1.26. Compound (**4d**).* Yield=80% (134 mg); mp=135–136 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3134, 2965, 1742, 1468, 1245, 943; HRMS (ESI, M^++1) calcd for $C_{23}H_{27}O_2$ 335.2011, found 335.2016; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.15 (m, 7H), 6.87 (d, J=8.8 Hz, 2H), 6.59 (d, J=15.6 Hz, 1H), 5.62 (dd, J=10.0, 15.6 Hz, 1H), 3.82 (s, 3H), 3.00 (dd, J=4.8, 9.2 Hz, 1H), 2.71 (dd, J=4.4, 4.8 Hz, 1H), 2.52 (dt, J=4.4, 9.2 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.70, 158.41, 137.09, 131.55, 130.15 (2×), 128.61, 128.45 (2×), 127.11, 127.12, 125.83 (2×), 113.81 (2×), 55.22, 44.09, 35.03, 33.76, 31.50, 26.22 (3×). Single-crystal X-ray diagram: crystal of compound **4d** was grown by slow diffusion of EtOAc into a solution of compound **4d** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 1 21/c 1, a=10.1827(10) Å, b=55.170(4) Å, c=33.557(3) Å, V=1882.8(3) Å^3, Z=4, d_{calcd}=1.180 g/cm^3, F(000)=720, 2θ range 1.22–26.40°, R indices (all data) R1=0.0754, wR2=0.1749.

*4.1.27. Compound (**4e**).* Yield=62% (110 mg); colorless gum; IR ($CHCl_3$): 2945, 1753, 1632, 1527, 1469, 1212, 1133, 865 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{25}H_{23}O_2$ 355.1698, found 355.1708; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J=8.8 Hz, 2H), 7.63–7.58 (m, 1H), 7.54–7.50 (m, 2H), 7.38–7.34 (m, 4H), 7.31–7.26 (m, 1H), 7.15 (d, J=8.8 Hz, 2H), 6.79 (d, J=8.4 Hz, 2H), 6.60 (d, J=16.0 Hz, 1H), 5.60 (dd, J=9.6, 16.0 Hz, 1H), 3.78 (s, 3H), 3.36 (dd, J=5.2, 9.2 Hz, 1H), 3.30 (dd, J=4.4, 5.2 Hz, 1H), 2.82 (dt, J=4.4, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.95, 158.96, 137.79, 136.57, 132.97, 131.72, 129.85, 129.14 (2×), 128.63 (2×), 128.40 (2×), 128.09 (2×), 127.06 (2×), 126.83, 124.23, 113.90 (2×), 55.21, 36.14, 34.93, 32.67.

*4.1.28. Compound (**4f**).* Yield=76% (165 mg); colorless gum; IR ($CHCl_3$): 3034, 2923, 1749, 1638, 1434, 1221, 1132, 848 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{30}H_{27}O_3$ 435.1960, found 435.1972; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.13 (d, J=8.8 Hz, 1H), 8.01 (d, J=7.6 Hz, 1H), 7.94 (d, J=8.8 Hz, 1H), 7.90 (d, J=8.0 Hz, 1H), 7.64–7.55 (m, 2H), 7.30 (t, J=8.0 Hz, 1H), 7.18 (d, J=8.8 Hz, 2H), 6.99 (d, J=7.6 Hz, 1H), 6.95 (s, 1H), 6.85 (dd, J=2.0, 8.4 Hz, 1H), 6.81 (d, J=8.8 Hz, 2H), 6.63 (d, J=15.6 Hz, 1H), 5.70 (ddd, J=0.8, 9.6, 15.6 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.45 (dd, J=5.2, 9.2 Hz, 1H), 3.41 (dd, J=4.4, 5.2 Hz, 1H), 2.87 (dt, J=4.4, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.72, 159.60, 158.95, 138.23, 135.52, 135.07, 132.53, 131.78, 129.87, 129.68, 129.58, 129.39, 128.50, 128.40, 127.75, 127.08 (2×), 126.77, 124.27, 123.93, 121.42, 115.08, 113.90 (2×), 112.15, 55.20 (2×), 36.33, 34.98, 32.76.

*4.1.29. Compound (**4g**).* Yield=71% (131 mg); colorless gum; IR ($CHCl_3$): 3253, 2945, 1755, 1439, 1236, 1154, 850 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{25}H_{21}O_3$ 369.1491, found 369.1498; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J=8.4 Hz, 2H), 7.62–7.58 (m, 1H), 7.52 (d, J=7.6 Hz, 2H), 7.37–7.25 (m, 5H), 6.70–6.64 (m, 3H), 6.55 (d, J=15.6 Hz, 1H), 5.91 (d, J=1.2 Hz, 1H), 5.89 (d, J=1.2 Hz, 1H), 5.54 (dd, J=9.6, 15.6 Hz, 1H), 3.33 (dd, J=5.2, 9.2 Hz, 1H), 3.27 (dd, J=4.4, 5.2 Hz, 1H), 2.78 (dt, J=4.4, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.91, 147.91, 146.95, 137.79, 136.49, 133.02, 131.88, 131.56, 129.13 (2×), 128.67 (2×), 128.46 (2×), 128.12 (2×), 126.92, 124.76, 120.57, 108.24, 105.23, 100.98, 35.95, 34.98, 32.64.

*4.1.30. Compound (**4h**).* Yield=56% (73 mg); colorless oil; IR ($CHCl_3$): 2943, 1754, 1655, 1428, 1236, 1135, 873 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O$ 263.1436, found 263.1442; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–8.07 (m, 2H), 7.54–7.52 (m, 3H), 7.35–7.31 (m, 5H), 5.79–5.70 (m, 2/3H), 5.62–5.54 (m, 1/3H), 5.06–4.96 (m, 1H), 3.29–2.17 (m, 2H), 2.86 (dt, J=4.4, 9.6 Hz, 1/3H), 2.66 (dt, J=4.8, 9.6 Hz, 2/3H), 1.76 (dd, J=2.0, 6.8 Hz, 1H), 1.63 (dd, J=2.0, 6.8 Hz, 2H).

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Supplementary data

Scanned photocopies of ^{1}H and ^{13}C NMR spectral data were supported. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.09.060.

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