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One-pot synthesis of multifunctionalized *m*-terphenyls

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ABSTRACT

A facile one-step synthetic protocol toward multifunctionalized *m*-terphenyls **5** and sulfonyl *m*-terphenyls **6** is developed from substituted chalcones **1** and allyl sulfone **2** in good yields via a [3C+3C] annulation. The NaH-mediated annulation features transition metal catalyst-free condition. Chalcones **1** with the functional groups tolerance are easily prepared via Claisen–Schmidt condensation of substituted benzaldehydes **3** with acetophenone **4** in a qualitative yield under an aqueous alkaline methanolic solution.

1. Introduction

Functionalized phenyls are attractive scaffolds for synthetic material sciences and drug discovery.[1] To achieve these diversified frameworks bearing different substituted groups, various kinds of approaches have been established in the past decades.[2] Some functional profiles clearly indicate that polyaryl phenyl is a privileged core for synthetic design.[3] Among those methods, transition metal mediated reactions have been proven to be one of the most popular tools to construct the skeleton, especially Suzuki–Miyaura cross-coupling[4] or Reppe cyclotrimerization.[5] Efficient synthesis of terphenyls is an important issue for organic chemists.[6,7] Some *m*-terphenyls are found in natural products, such as dictyoterphenyl A,[3j] trifucol,[8a] macranthol,[8b] dunnialol,[8c] and mulberrofuran R (Fig. 1).[8d]

We previously reported the one-pot method for synthesizing various carbon-skeletons with different aryl substituents based on chalcones **1**, such as monocyclic oxetanes and cyclohexanes, tricyclic benzo[*g*]indazoles, and tetracyclic azahomoisotwistanes.[9] To explore the synthetic applications of substituted chalcones **1**, a transition metal-free route is employed to create the skeleton of *m*-terphenyls **5** and **6** via a one-pot NaH-mediated tandem annulation of chalcones **1** and allyl sulfone **2**. Substituted chalcones **1** are easily prepared via Claisen–Schmidt condensation of substituted aldehydes **3** (R_2 group) with methyl ketones **4** (R_1 group) (Scheme 1).

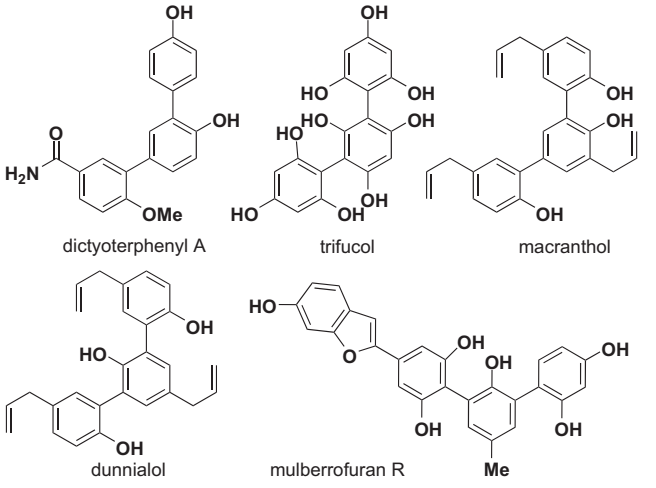
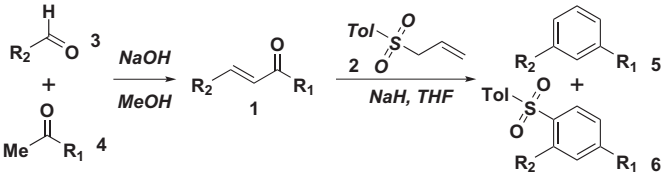


Fig. 1. Structural frameworks of natural *m*-terphenyls.



Scheme 1. One-pot route of *m*-terphenyls **5** and **6**.

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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 methyl ketones **4** with aldehydes **3** under the methanolic refluxing solution.[9] Next, synthesis of allyl sulfone **2** was achieved from nucleophilic substitution of allyl bromide with $TolSO_2Na$ in quantitative good yields. In an attempt to develop a practical protocol of *m*-terphenyl with the structure of 1,3-disubstituted benzene, NaH-mediated one-pot [3C+3C] route of the starting chalcone **1b** (R_1=3-MeOPh; R_2=2-naphthalene) with allyl sulfone **2** in refluxing THF provided *m*-terphenyl **5b** (52%) and sulfonyl *m*-terphenyl **6b** (30%) in a ratio of 6:4. This is a short and efficient route to achieve the structural skeleton of *m*-terphenyl. For the regioselective introduction of a sulfonyl group on the *m*-terphenyl skeleton, only one isomer **6b** with specific site-selectivity was isolated.

To change the bases with different equivalents in various solvents from 25 °C to refluxing temperature, we found that different product ratios of *m*-terphenyl **5b** and sulfonyl *m*-terphenyl **6b** were obtained between 6:4 and 5:5 with the lower total yields via one-pot tandem reaction of model chalcone **1b** with allyl sulfone **2** (see Table 2). By adjusting the equivalents of NaH, reaction time, temperature, and concentration (for entries 1–6), the isolated total yield of *m*-terphenyl **5b** and **6b** was noticeably enhanced (see entry 3). After screening the base-mediated reaction conditions (entries 7–11), we found that NaH provided higher yields than other bases (DBU, Et_3N, DMAP, MeONa, LiHMDS). Furthermore, when the base and solvent were replaced with Et_3N/CH_2Cl_2 or MeONa/MeOH, the isolated total yield of *m*-terphenyl **5b** and **6b** was decreased to 22% or 31% (for entry 8, the starting material **1b** was isolated in 65% yield; for entry 10, unknown mixture was isolated in 46% yield as the major product). According to the experimental results, we envisioned that NaH (4 equiv) is an optimal base for elevating the total yields of *m*-terphenyl **5b** and **6b** (82%) under boiling THF conditions for 3 h (entry 3).[10]

With the result in hand, one-pot preparation of substituted *m*-terphenyl **5** and **6** was further examined. Changing the R_1 and R_2 substituent of chalcones **3**, major 1,3-disubstituted benzenes **5a**–**v** and minor 1,3-disubstituted benzenes **6a**–**v** with sulfonyl group were isolated with good total yields in different ratios by one-pot domino methodology; they are summarized in Table 1. The formation of skeletons **5** and **6** was confirmed through spectral analysis, including ^1H and ^{13}C NMR and HRMS spectra. For example, the ^1H NMR spectra of compound **6u** exhibited three singles at δ 8.32, 7.56 and 7.32 for core benzene ring protons. Three CH protons appeared as one doublet of H-1 (J=8.4 Hz), one doublet of H-3 (J=2.4 Hz), and one doublets of doublets of H-2 (J=2.4 and 8.4 Hz). The structure of compound **6u** was confirmed by HRMS, which showed a peak at m/z 371.1145 [M^++1]. The structural frameworks of compounds **5f**, **6i**, and **6s** were determined by single-crystal X-ray crystallography, as shown in Figs. 2–4.[11] Compared with the isolated yields of products **5a**–**v** and **6a**–**v**, it was found that different kinds of substituents (e.g., electron-withdrawing oxygen-containing groups, electron-donating fluoro-containing groups, heterocyclic 2-thiophene group, aliphatic *tert*-butyl group) did not obviously interfere with the product yields and ratios distribution of skeletons **5** and **6**. Quaterphenyls **5j** and **6j** were also prepared from the one-pot domino reaction of chalcone **1j** with sulfone **2** via a (C3+C3) route.

As shown in Scheme 2, a plausible explanation for the one-pot synthesis of compounds **5a** and **6a** via the reaction of **1a** and **2** should be that intermediate **A** of sodium α-carbanion was first generated via NaH-mediated deprotonation of allyl sulfone **2** in refluxing THF. Initially, intermediate **A** was formed by deprotonation of allyl sulfone **2** with NaH. Under thermodynamic conditions, both possible intermediates **B1** and **B2** should be generated from the 1,2- or 1,4-addition of intermediate **A** with chalcone **1a**. After the removal of toluenesulfonic sodium salt ($TolSO_3Na$), intermediate **C1**, with the (*E*,*E*)-conjugated configuration, should be afforded. Because $TolSO_3Na$ could be isolated by the extraction process (from the aqueous layer), the reaction pathway from intermediate **B1** to **C1** was proposed. Next, the formation of *m*-terphenyl **5a** was observed via the 1,6-6π-electrocyclic disrotatory ring closure followed by the sequential aromatization (oxidative dehydrogenation process) of the resulting intermediate of cyclohexadiene. At another stage, the proton exchange provided the equilibrium process between intermediate **B2** and **C2**. The corresponding carbanion of intermediate **C2** was delocalized to establish intermediate **D** with cyclohexene ring. By the similar pathway above, after dehydration and oxidative dehydrogenation, (an aromatization process), the formation of *m*-terphenyl **6a** with sulfonyl group was provided. 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.[12]

3. Conclusion

In summary, we have successfully presented a novel and one-pot cascade [C3+C3] methodology for synthesizing a series of *m*-terphenyls **5a**–**v** and sulfonyl *m*-terphenyls **6a**–**v** via two important steps: (1) 1,2- addition or 1,4-addition of chalcones **1a**–**v** with the α-carbanion intermediate **A** of allyl sulfone **2** and (2) removal of $TolSO_3Na$/1,6-electrocyclization/aromatization of possible intermediates (for skeleton **5**) or proton exchange/six-membered ring formation/dehydration/aromatization of several possible intermediates (for skeleton **6**). The structural skeletons 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 protocol for the synthetic research and biological activities of *m*-terphenyls. Further investigation regarding one-pot cascade synthesis of multifunctionalized arenes will be conducted and published in due course.

4. Experimental section

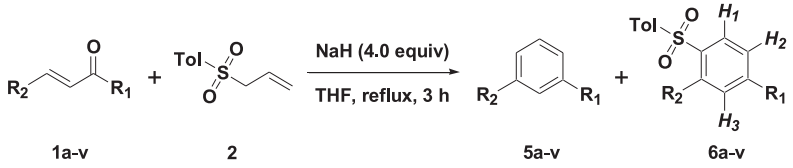
4.1. General

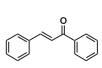
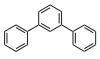
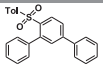
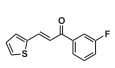
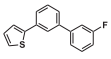
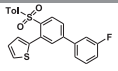
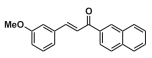
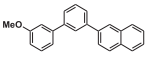
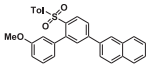
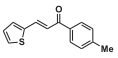
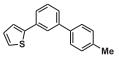
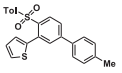
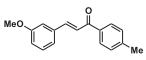
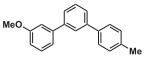
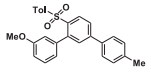
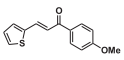
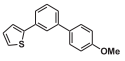
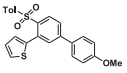
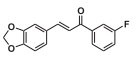
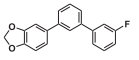
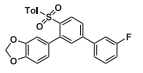
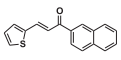
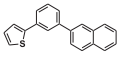
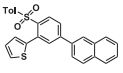
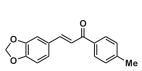
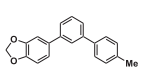
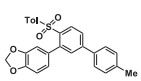
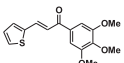
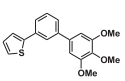
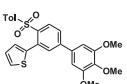
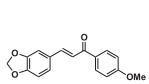
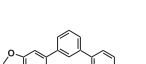
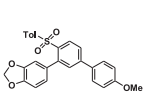
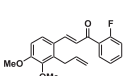
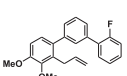
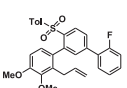
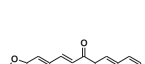
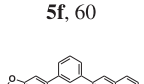
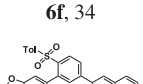
All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous $MgSO_4$ before concentration in vacuo. Melting 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.

4.2. A representative synthetic procedure of compounds 5a–v and 6a–v is as follows

Sodium hydride (NaH, 60% in oil, 80 mg, 2.0 mmol) was added to a solution of allyl sulfone **2** (98 mg, 0.5 mmol) in THF (8 mL). A

Table 1
Synthesis of multisubstituted *m*-terphenyls **5** and **6**[a]



entry	chalcones **1a-x**	**5a-v** Yield (%)	**6a-v** Yield (%)	entry	chalcones **1a-x**	**5a-v** Yield (%)	**6a-v** Yield (%)
1	 **1a**	 **5a**, 50	 **6a**, 36	12	 **1l**	 **5l**, 40	 **6l**, 43
2	 **1b**	 **5b**, 52	 **6b**, 30	13	 **1m**	 **5m**, 42	 **6m**, 38
3	 **1c**	 **5c**, 50	 **6c**, 36	14	 **1n**	 **5n**, 50	 **6n**, 36
4	 **1d**	 **5d**, 48	 **6d**, 40	15	 **1o**	 **5o**, 48	 **6o**, 40
5	 **1e**	 **5e**, 54	 **6e**, 32	16	 **1p**	 **5p**, 62	 **6p**, 30
6	 **1f**	 **5f**, 60	 **6f**, 34	17	 **1q**	 **5q**, 54	 **6q**, 33
7	 **1g**	 **5g**, 62	 **6g**, 26	18	**1r**	**5r**, 43	**6r**, 35
8	**1h**	**5h**, 60	**6h**, 24	19	**1s**	**5s**, 40	**6s**, 38
9	**1i**	**5i**, 56	**6i**, 23	20	**1t**	**5t**, 40	**6t**, 30
10	**1j**	**5j**, 54	**6j**, 20	21	**1u**	**5u**, 43	**6u**, 40
11	**1k**	**5k**, 50	**6k**, 32	22	**1v**	**5v**, 50	**6v**, 33

[a] For the best one-pot reaction conditions: substituted chalcones **1a**–**v** (0.5 mmol), allyl sulfone **2** (0.5 mmol), NaH (60%, 80 mg, 2.0 mmol), THF (15 mL), reflux, 3 h.

Table 2
Reactions of compounds **1b** and **2**[a]

Entry	Base (equiv), solvent (mL), temp (°C), time (h)	Yield (%) **5b**/**6b**
1	NaH (4), THF (15), 25, 3	26/18[b]
2	NaH (4), THF (15), reflux, 1	36/25[b]
3	NaH (4), THF (15), reflux, 3	52/30[c]
4	NaH (4), THF (30), reflux, 3	43/30[c]
5	NaH (10), THF (15), reflux, 3	48/27[c]
6	NaH (4), THF (15), reflux, 10	50/28[c]
7	DBU (4), THF (15), reflux, 3	40/36[b]
8	Et_3N (4), CH_2Cl_2 (15), reflux, 10	12/10[b]
9	DMAP (4), THF (15), reflux, 10	28/27[b]
10	MeONa (4), MeOH (15), reflux, 3	14/17[c,d]
11	LiHMDS (1.0 M, 4), THF (15), reflux, 6	30/27[b]

[a] The reactions were run on a 0.5 mmol scale with chalcone **1b** and allyl sulfone **2**.
[b] The starting material **1b** (for entry 1, 40%; entry 2, 25%; entry 7, 8%; entry 8, 65%; entry 9, 30%; entry 11, 20%) was recovered.
[c] No starting material **1b** was recovered.
[d] Unknown mixture was isolated (for entry 9, 46%).

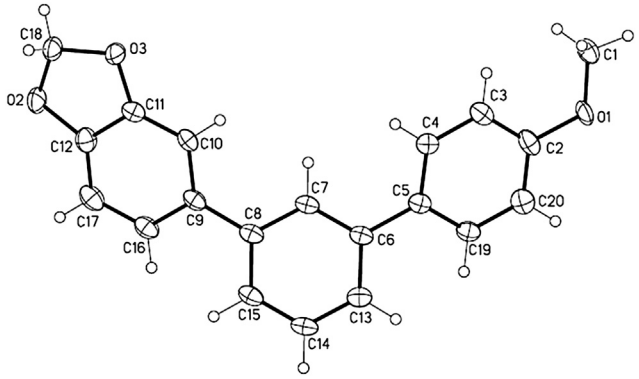


Fig. 2. X-ray structure of compound **5f**.

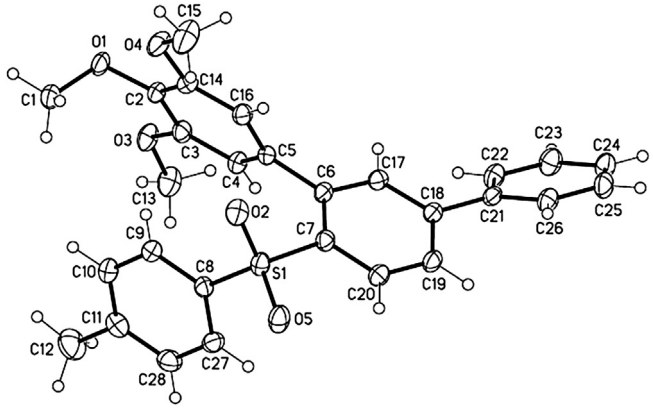


Fig. 3. X-ray structure of compound **6i**.

solution of chalcones **1** (0.5 mmol) in the THF (7 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=50/1–10/1) afforded compounds **5a**–**v** and **6a**–**v**.

*4.2.1. Compound (**5a**).* Yield=50% (58 mg); mp=86–88 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{15}$ 231.1174, found 231.1180; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (t, J=2.0 Hz, 1H), 6.67–6.64 (m, 4H), 7.60–7.58 (m, 3H), 7.54–7.45 (m, 4H), 7.38 (dt, J=2.0, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.78 (2×), 141.18, 129.17 (2×), 128.79 (4×), 127.39 (2×), 127.26 (4×), 126.16, 126.11 (2×); Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.67; H, 6.02.

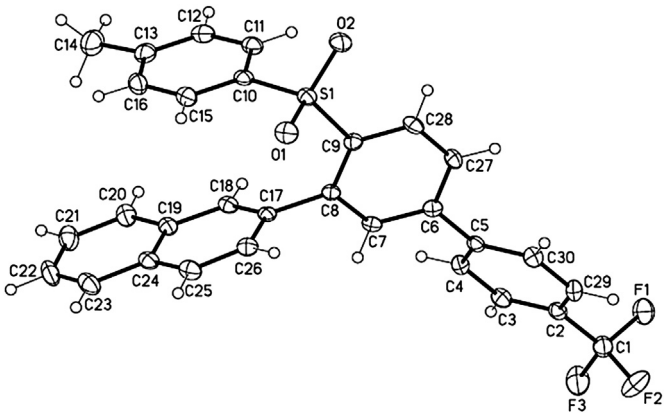
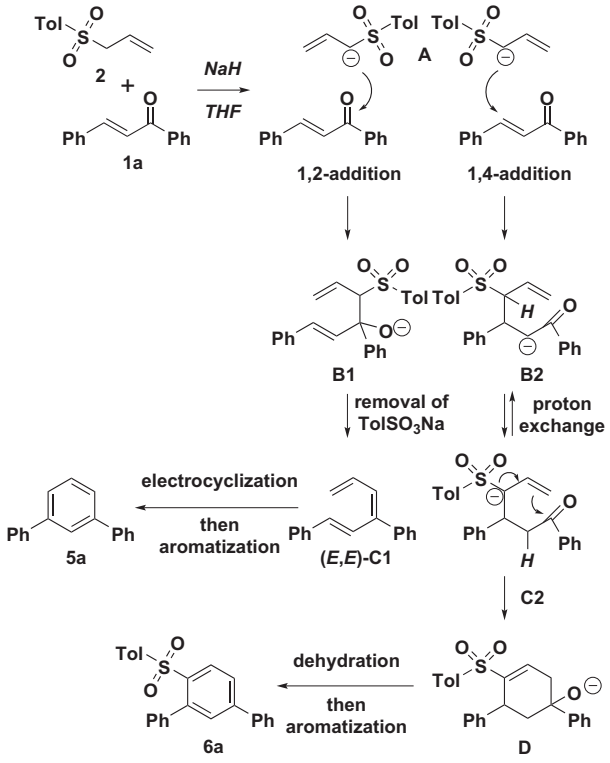


Fig. 4. X-ray structure of compound **6s**.



Scheme 2. A possible mechanism to compounds **5a** and **6a**.

*4.2.2. Compound (**5b**).* Yield=52% (81 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O$ 311.1436, found 311.1441; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J=0.8 Hz, 1H), 8.01–7.92 (m, 4H), 7.85 (dd, J=2.0, 8.4 Hz, 1H), 7.76 (dt, J=1.6, 7.6 Hz, 1H), 7.66 (dt, J=1.6, 7.6 Hz, 1H), 7.61 (d, J=7.6 Hz, 1H), 7.59–7.52 (m, 2H), 7.45 (t, J=8.0 Hz, 1H), 7.35–7.32 (m, 1H), 7.29–7.28 (m, 1H), 7.49 (ddd, J=0.8, 2.4, 8.4 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.97, 142.69, 141.74, 141.61, 138.40, 133.65, 132.66, 129.80,

129.23, 128.45, 128.18, 127.62, 126.49, 126.38, 126.30, 126.21, 125.97, 125.89, 125.57, 119.78, 113.07, 112.75, 55.28.

*4.2.3. Compound (**5c**).* Yield=50% (69 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{19}O$ 275.1436, found 275.1435; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (t, J=2.0 Hz, 1H), 7.61–7.57 (m, 2H), 7.58 (d, J=8.0 Hz, 2H), 7.52 (t, J=7.6 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.29 (d, J=8.0 Hz, 2H), 7.28–7.25 (m, 1H), 7.21 (t, J=2.4 Hz, 1H), 6.95 (ddd, J=0.8, 2.4, 8.4 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.94, 142.79, 141.66, 141.60, 138.24, 137.19, 129.76, 129.51 (2×), 129.09, 127.07 (2×), 126.07, 125.97, 125.86, 119.75, 112.98, 112.76, 55.29, 21.09.

*4.2.4. Compound (**5d**).* Yield=48% (70 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{19}H_{14}FO_2$ 293.0978, found 293.0982; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (t, J=2.4 Hz, 1H), 7.55–7.47 (m, 3H), 7.44–7.42 (m, 2H), 7.37–7.34 (m, 1H), 7.14 (s, 1H), 7.12 (dd, J=1.6, 8.4 Hz, 1H), 7.11–7.06 (m, 1H), 6.92 (dd, J=1.6, 8.4 Hz, 1H), 6.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.17 (d, J=244.1 Hz), 148.17, 147.25, 143.40 (d, J=7.6 Hz), 141.58, 140.43 (d, J=2.3 Hz), 135.23, 130.21 (d, J=8.4 Hz), 129.24, 126.36, 125.73, 125.67, 122.81 (d, J=3.0 Hz), 120.72, 114.14 (d, J=21.3 Hz), 114.07 (d, J=21.9 Hz), 108.60, 107.69, 101.17.

*4.2.5. Compound (**5e**).* Yield=54% (78 mg); mp=89–90 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{17}O_2$ 289.1229, found 289.1232; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.75 (m, 1H), 7.57 (d, J=8.0 Hz, 2H), 7.56–7.54 (m, 1H), 7.52–7.48 (m, 2H), 7.30 (dd, J=0.8, 8.4 Hz, 2H), 7.16 (s, 1H), 7.15 (dd, J=2.0, 8.8 Hz, 1H), 6.93 (dd, J=0.8, 8.0 Hz, 1H), 6.02 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.10, 147.12, 141.65, 141.39, 138.23, 137.16, 135.59, 129.49 (2×), 129.08, 127.04 (2×), 125.64, 125.59, 125.54, 120.70, 108.56, 107.74, 101.12, 21.08; Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.52; H, 5.80.

*4.2.6. Compound (**5f**).* Yield=60% (91 mg); mp=165–166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{17}O_3$ 305.1178, found 305.1182; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.70 (m, 1H), 7.59 (d, J=8.8 Hz, 2H), 7.53–7.46 (m, 3H), 7.14 (s, 1H), 7.13 (dd, J=2.0, 8.8 Hz, 1H), 7.01 (d, J=9.2 Hz, 2H), 6.91 (dd, J=0.8, 8.0 Hz, 1H), 6.02 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.24, 148.11, 147.12, 141.41, 141.33, 135.62, 133.65, 129.10, 128.21 (2×), 125.42, 125.37, 125.25, 120.70, 114.22 (2×), 108.56, 107.74, 101.14, 55.32; Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 79.12; H, 5.45. Single-crystal X-ray diagram: crystal of compound **5f** was grown by slow diffusion of EtOAc into a solution of compound **5f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 1 21/c 1, a=15.2923(13) Å, b=7.2462(6) Å, c=13.8147(11) Å, V=1468.1(2) Å^3, Z=4, d_{calcd}=1.377 g/cm^3, F(000)=640, 2θ range 1.39–26.43°, R indices (all data) R1=0.0516, wR2=0.0966.

*4.2.7. Compound (**5g**).* Yield=62% (100 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{23}H_{17}O_2$ 325.1229, found 325.1236; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J=1.2 Hz, 1H), 7.96–7.87 (m, 4H), 7.80 (dd, J=2.0, 8.4 Hz, 1H), 7.70–7.67 (m, 1H), 7.56–7.48 (m, 4H), 7.18 (s, 1H), 7.17 (dd, J=2.4, 8.8 Hz, 1H), 6.94 (dd, J=0.8, 8.8 Hz, 1H), 6.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.16, 147.21, 141.65, 141.58, 138.46, 135.54, 133.67, 132.69, 129.24, 128.46, 128.20, 127.64, 126.33, 126.11, 126.05, 125.98, 125.92, 125.90, 125.59, 120.78, 108.62, 107.78, 101.18.

*4.2.8. Compound (**5h**).* Yield=60% (109 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{22}H_{21}O_5$ 365.1389, found 365.1392; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (br s, 1H), 7.52–7.46 (m, 3H), 7.12 (s, 1H), 7.11 (dd, J=2.0, 8.4 Hz, 1H), 6.91 (dd, J=0.8, 8.4 Hz, 1H), 6.81 (s, 2H), 6.02 (s, 2H), 3.94 (s, 6H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.48 (2×), 148.16, 147.22, 141.95, 141.50, 137.17, 135.45, 129.99, 129.12, 128.76, 125.90, 125.77 (2×), 120.75, 108.61, 107.76, 104.57, 101.19, 60.95, 56.22 (2×).

*4.2.9. Compound (**5i**).* Yield=56% (90 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{21}H_{21}O_3$ 321.1491, found 321.1496; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, J=1.6 Hz, 1H), 7.67–7.65 (m, 2H), 7.60–7.47 (m, 5H), 7.41–7.37 (m, 1H), 6.84 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.47 (2×), 141.94, 141.82, 141.12, 137.73, 137.18, 129.12, 128.80 (2×), 127.45, 127.26 (2×), 126.17, 126.07 (2×), 104.46 (2×), 60.94, 56.21 (2×).

*4.2.10. Compound (**5j**).* Yield=54% (107 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{27}H_{25}O_3$ 397.1804, found 397.1812; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (t, J=1.6 Hz, 1H), 7.77–7.63 (m, 7H), 7.59–7.47 (m, 4H), 7.41–7.37 (m, 1H), 6.87 (s, 2H), 3.96 (s, 6H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.48 (2×), 142.02, 141.28, 140.57, 140.33, 139.96, 137.75, 137.16, 129.18, 128.80 (2×), 127.59 (2×), 127.52 (2×), 127.38, 127.00 (2×), 126.15, 126.04, 125.92, 104.57 (2×), 60.93, 56.20 (2×).

*4.2.11. Compound (**5k**).* Yield=50% (78 mg); mp=135–136 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O$ 311.1436, found 311.1435; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.12 (m, 1H), 7.97–7.89 (m, 4H), 7.83 (dd, J=1.6, 8.4 Hz, 1H), 7.70–7.50 (m, 7H), 7.04 (d, J=8.4 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.28, 141.61, 141.46, 138.58, 133.69, 133.66, 132.66, 129.22, 128.43, 128.27 (2×), 128.18, 127.64, 126.30, 125.95 (2×), 125.88, 125.79 (2×), 125.63, 114.25 (2×), 55.33; Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.31; H, 6.01.

*4.2.12. Compound (**5l**).* Yield=40% (51 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{16}H_{12}FS$ 255.0644, found 255.0646; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (t, J=1.6 Hz, 1H), 7.62 (dt, J=1.6, 6.8 Hz, 1H), 7.50–7.31 (m, 7H), 7.11 (dd, J=3.6, 5.2 Hz, 1H), 7.10–7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.19 (d, J=244.8 Hz), 144.03, 143.16 (d, J=7.6 Hz), 135.06, 130.28 (d, J=9.1 Hz), 129.43, 128.07, 126.23, 125.44, 125.12, 125.12, 124.76, 123.45, 122.84 (d, J=3.0 Hz), 114.31 (d, J=21.2 Hz), 114.11 (d, J=21.9 Hz).

*4.2.13. Compound (**5m**).* Yield=42% (53 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{15}S$ 251.0895, found 251.0902; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dt, J=0.4, 1.6 Hz, 1H), 7.63 (ddd, J=1.2, 1.6, 7.6 Hz, 1H), 7.59 (d, J=8.0 Hz, 2H), 7.56–7.53 (m, 1H), 7.49 (dt, J=0.4, 7.6 Hz, 1H), 7.42 (dd, J=0.4, 3.6 Hz, 1H), 7.35–7.31 (m, 3H), 7.15 (dd, J=3.6, 5.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.37, 141.85, 137.96, 137.28, 134.80, 129.50 (2×), 129.22, 127.98, 127.01 (2×), 126.14, 124.86, 124.64, 124.60, 123.24, 21.80.

*4.2.14. Compound (**5n**).* Yield=50% (67 mg); mp=110–111 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{15}OS$ 267.0844, found 267.0841; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (t, J=1.6 Hz, 1H), 7.58 (d, J=8.8 Hz, 2H), 7.58–7.56 (m, 1H), 7.48 (dt, J=1.6, 8.0 Hz, 1H), 7.44 (t, J=7.6 Hz, 1H), 7.38 (dd, J=1.2, 3.6 Hz, 1H), 7.31 (dd, J=1.2, 5.2 Hz, 1H), 7.11 (dd, J=3.6, 5.2 Hz, 1H), 7.02 (d, J=8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.32, 144.41, 141.52, 134.82, 133.38, 129.24, 128.21 (2×), 127.99, 125.92, 124.86, 124.43, 124.31, 123.23, 114.24 (2×), 55.34; Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.85; H, 5.13.

*4.2.15. Compound (**5o**).* Yield=48% (69 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{15}S$ 287.0895, found 287.0899; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J=1.2 Hz, 1H), 7.98–7.89 (m, 4H), 7.80 (dd, J=1.6, 8.4 Hz, 1H), 7.65 (J=8.0 Hz, 1H), 7.65 (d, J=7.6 Hz, 1H), 7.56–7.49 (m, 3H), 7.43 (dd, J=0.8, 3.6 Hz, 1H), 7.34 (dd, J=1.2,

5.2 Hz, 1H), 7.14 (dd, *J*=3.6, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.30, 141.56, 138.19, 134.99, 133.63, 132.72, 129.38, 128.49, 128.21, 128.05, 127.65, 126.59, 126.36, 126.05, 125.92, 125.51, 125.09, 124.99 (2×), 123.38.

*4.2.16. Compound (**5p**).* Yield=62% (101 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_3S$ 327.1055, found 327.1056; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J*=1.2 Hz, 1H), 7.60 (dt, *J*=2.0, 6.8 Hz, 1H), 7.48–7.42 (m, 2H), 7.38 (dd, *J*=0.8, 3.6 Hz, 1H), 7.32 (dd, *J*=1.2, 5.2 Hz, 1H), 7.11 (dd, *J*=3.6, 5.2 Hz, 1H), 6.81 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.46 (2×), 144.15, 142.14, 137.79, 136.90, 134.86, 129.24, 128.02, 136.30, 125.02, 124.95, 124.78, 123.38, 104.55 (2×), 60.93, 56.22 (2×).

*4.2.17. Compound (**5q**).* Yield=54% (94 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{23}H_{22}FO_2$ 349.1604, found 349.1612; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.43 (m, 4H), 7.35–7.29 (m, 2H), 7.21 (dt, *J*=1.2, 7.6 Hz, 1H), 7.16 (ddd, *J*=1.2, 8.4, 10.8 Hz, 1H), 7.02 (d, *J*=8.4 Hz, 1H), 6.88 (d, *J*=8.4 Hz, 1H), 5.98–5.89 (m, 1H), 4.96 (dq, *J*=1.6, 10.4 Hz, 1H), 4.82 (dq, *J*=1.6, 17.2 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.42 (dt, *J*=1.6, 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.80 (d, *J*=246.4 Hz), 152.02, 147.38, 141.58, 137.64, 135.58, 135.36, 131.61, 130.78 (d, *J*=3.7 Hz), 130.06, 128.97, 128.89, 128.73, 127.93, 127.39 (d, *J*=3.1 Hz), 125.41, 124.30 (d, *J*=3.0 Hz), 116.08 (d, *J*=22.7 Hz), 114.94, 110.24, 60.67, 55.71, 21.83.

*4.2.18. Compound (**5r**).* Yield=43% (71 mg); mp=140–142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{16}F_3O$ 329.1153, found 329.1160; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.70 (m, 5H), 7.61–7.57 (m, 3H), 7.55–7.52 (m, 2H), 7.02 (d, *J*=8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.41, 144.78, 141.66 (2×), 140.29, 133.32, 129.37, 128.25 (2×), 127.52 (2×), 126.59 (2×), 125.77, 125.72 (q, *J*=3.8 Hz), 125.60, 114.32 (2×), 114.27, 55.37; Anal. Calcd for $C_{20}H_{15}F_3O$: C, 73.16; H, 4.60. Found: C, 73.32; H, 4.35.

*4.2.19. Compound (**5s**).* Yield=40% (70 mg); mp=84–86 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{16}F_3$ 349.1204, found 349.1200; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.98–7.89 (m, 4H), 7.82–7.74 (m, 6H), 7.63–7.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.68, 141.97, 140.43, 138.11 (2×), 133.65, 132.75, 129.50, 128.58, 128.21, 127.67, 127.55 (4×), 127.26, 126.45, 126.43, 126.26, 126.14, 125.98, 125.76 (q, *J*=3.8 Hz), 125.48; Anal. Calcd for $C_{23}H_{15}F_3$: C, 79.30; H, 4.34. Found: C, 79.62; H, 4.26.

*4.2.20. Compound (**5t**).* Yield=40% (51 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{16}H_{18}NO_2$ 256.1338, found 256.1339; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J*=9.2 Hz, 2H), 7.74 (d, *J*=8.8 Hz, 2H), 7.62 (br s, 1H), 7.51–7.46 (m, 1H), 7.44–7.43 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.18, 148.30, 138.60, 128.89, 127.91 (2×), 126.01, 125.51, 124.62, 124.42, 124.04 (2×), 34.88, 31.34 (3×).

*4.2.21. Compound (**5u**).* Yield=43% (46 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{14}H_{17}S$ 217.1051, found 217.1055; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J*=1.2, 2.4 Hz, 1H), 7.45–7.43 (m, 1H), 7.35–7.30 (m, 3H), 7.28 (dd, *J*=1.2, 5.2 Hz, 1H), 7.11 (dd, *J*=3.6, 5.2 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.77, 145.05, 134.10, 128.58, 127.89, 124.64, 124.56, 123.32, 123.14, 122.96, 34.73, 31.31 (3×).

*4.2.22. Compound (**5v**).* Yield=50% (60 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{17}H_{21}O$ 241.1592, found 241.1596; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.56 (m, 1H), 7.53 (d, *J*=8.8 Hz, 2H), 7.37–7.34 (m, 3H), 6.99 (d, *J*=8.4 Hz, 2H), 3.86 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.03, 151.53, 134.44, 130.06, 128.40, 128.28 (2×), 124.02, 123.95, 123.72, 114.13 (2×), 55.34, 34.78, 31.40 (3×).

*4.2.23. Compound (**6a**).* Yield=36% (69 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{25}H_{21}O_2S$ 385.1262, found 385.1263; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J*=8.4 Hz, 1H), 7.77 (dd, *J*=2.0, 8.4 Hz, 1H), 7.62–7.59 (m, 2H), 7.47–7.31 (m, 5H), 7.25–7.21 (m, 2H), 7.16 (d, *J*=8.0 Hz, 2H), 7.07–7.04 (m, 2H), 7.01 (d, *J*=8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.50, 143.32, 142.58, 138.86, 138.56, 138.22, 138.09, 131.20, 130.00 (2×), 129.21, 128.98 (2×), 128.93 (2×), 128.53, 127.77 (2×), 127.63, 127.30 (2×), 127.24 (2×), 125.92, 21.47.

*4.2.24. Compound (**6b**).* Yield=30% (70 mg); mp=151–152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{30}H_{25}O_3S$ 465.1524, found 465.1533; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J*=8.4 Hz, 1H), 8.08 (d, *J*=1.2 Hz, 1H), 7.93–7.84 (m, 4H), 7.74 (dd, *J*=1.6, 8.4 Hz, 1H), 7.59 (d, *J*=2.0 Hz, 1H), 7.54–7.51 (m, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 7.19 (t, *J*=3.6 Hz, 1H), 7.04 (d, *J*=8.4 Hz, 2H), 6.91 (dd, *J*=2.4, 7.6 Hz, 1H), 6.75 (dd, *J*=2.4, 7.6 Hz, 1H), 6.51 (t, *J*=2.4 Hz, 1H), 3.71 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.49, 145.30, 143.27, 142.34, 139.27, 138.62, 138.01, 135.99, 133.40, 133.04, 131.04, 129.11, 128.87 (2×), 128.75, 128.27 (2×), 127.81 (2×), 127.59, 126.59, 126.58, 126.53, 126.11, 124.88, 122.63, 114.83, 113.99, 54.93, 21.37; Anal. Calcd for $C_{30}H_{24}O_3S$: C, 77.56; H, 5.21. Found: C, 77.92; H, 4.87.

*4.2.25. Compound (**6c**).* Yield=36% (77 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{27}H_{25}O_3S$ 429.1524, found 429.1530; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J*=8.4 Hz, 1H), 7.76 (dd, *J*=2.0, 8.4 Hz, 1H), 7.51 (d, *J*=8.4 Hz, 2H), 7.43 (d, *J*=2.0 Hz, 1H), 7.27–7.25 (m, 2H), 7.19 (d, *J*=8.4 Hz, 2H), 7.15 (t, *J*=8.0 Hz, 1H), 7.02 (d, *J*=8.0 Hz, 2H), 6.87 (ddd, *J*=0.8, 2.4, 8.4 Hz, 1H), 6.69 (dt, *J*=0.8, 7.6 Hz, 1H), 6.46 (t, *J*=2.0 Hz, 1H), 3.69 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.49, 145.40, 143.23, 142.26, 139.39, 138.61, 138.29, 138.14, 135.91, 130.62, 129.71 (2×), 129.06, 128.87 (2×), 128.25, 127.83 (2×), 127.11 (2×), 125.66, 122.65, 114.81, 114.01, 54.96, 21.41, 21.12.

*4.2.26. Compound (**6d**).* Yield=40% (89 mg); mp=170–171 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{20}FO_4S$ 447.1066, found 447.1068; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J*=8.4 Hz, 1H), 7.72 (dd, *J*=2.0, 8.4 Hz, 1H), 7.43–7.36 (m, 3H), 7.30–7.27 (m, 1H), 7.26 (d, *J*=8.4 Hz, 2H), 7.11–7.06 (m, 1H), 7.08 (d, *J*=8.0 Hz, 2H), 6.68 (d, *J*=8.0 Hz, 1H), 6.51 (dd, *J*=1.6, 8.0 Hz, 1H), 6.42 (d, *J*=1.6 Hz, 1H), 5.97 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.10 (d, *J*=245.6 Hz), 147.21, 146.69, 144.09 (d, *J*=3.1 Hz), 143.56, 141.07, 141.00, 139.55, 137.97, 131.51, 131.26, 130.53 (d, *J*=8.3 Hz), 129.23 (2×), 127.79 (2×), 125.91, 123.76, 122.94, 122.92, 115.35 (d, *J*=21.2 Hz), 114.19 (d, *J*=22.0 Hz), 110.46, 107.20, 101.01, 21.44; Anal. Calcd for $C_{26}H_{19}FO_4S$: C, 69.94; H, 4.29. Found: C, 70.18; H, 4.02.

*4.2.27. Compound (**6e**).* Yield=32% (71 mg); mp=161––162 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{27}H_{23}O_4S$ 443.1317, found 443.1320; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J*=8.4 Hz, 1H), 7.73 (dd, *J*=2.0, 8.4 Hz, 1H), 7.50 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=2.0 Hz, 1H), 7.28–7.24 (m, 4H), 7.07 (d, *J*=8.0 Hz, 2H), 6.68 (d, *J*=8.0 Hz, 1H), 6.53 (dd, *J*=1.6, 8.0 Hz, 1H), 6.43 (d, *J*=2.0 Hz, 1H), 5.97 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.10, 146.63, 145.42, 143.40, 141.95, 138.59, 138.57, 138.23, 135.88, 131.87, 130.98, 129.70 (2×), 129.13, 128.85 (2×), 127.77 (2×), 127.08 (2×), 125.63, 123.79, 110.54, 107.16, 100.98, 21.44, 21.10; Anal. Calcd for $C_{27}H_{22}O_4S$: C, 73.28; H, 5.01. Found: C, 73.60; H, 5.38.

*4.2.28. Compound (**6f**).* Yield=34% (78 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{27}H_{23}O_5S$ 459.1266, found 459.1262; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 8.40 (d, J=8.4 Hz, 1H), 7.70 (dd, J=2.0, 8.4 Hz, 1H), 7.54 (d, J=9.2 Hz, 2H), 7.36 (d, J=2.0 Hz, 1H), 7.26 (d, J=8.4 Hz, 2H), 7.07 (d, J=8.0 Hz, 2H), 6.97 (d, J=8.8 Hz, 2H), 6.68 (d, J=8.0 Hz, 1H), 6.52 (dd, J=1.6, 8.0 Hz, 1H), 6.42 (d, J=1.6 Hz, 1H), 5.97 (s, 2H), 3.84 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.13, 147.10, 146.63, 145.06, 143.38, 141.96, 138.29, 138.18, 131.92, 131.14, 130.65, 129.18, 128.85 (2×), 128.40 (2×), 127.77 (2×), 125.28, 123.78, 114.42 (2×), 110.54, 107.16, 100.98, 55.33, 21.44.

*4.2.29. Compound (**6g**).* Yield=26% (62 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{30}H_{23}O_4S$ 479.1317, found 479.1321; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J=8.0 Hz, 1H), 8.07 (d, J=1.2 Hz, 1H), 7.93–7.85 (m, 4H), 7.72 (dd, J=2.0, 8.4 Hz, 1H), 7.55–7.51 (m, 3H), 7.30 (d, J=8.0 Hz, 2H), 7.09 (d, J=8.0 Hz, 2H), 6.71 (d, J=8.4 Hz, 1H), 6.58 (dd, J=1.6, 8.4 Hz, 1H), 6.48 (d, J=1.6 Hz, 1H), 5.99 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.17, 146.68, 145.38, 143.47, 142.08, 138.95, 138.18, 136.04, 133.43, 133.08, 131.47, 129.24, 128.88 (2×), 128.77, 128.30, 127.80 (2×), 127.73, 127.63, 127.61 (2×), 126.55, 126.13, 124.92, 123.83, 110.56, 107.21, 101.01, 21.45.

*4.2.30. Compound (**6h**).* Yield=24% (62 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{29}H_{27}O_7S$ 519.1478, found 519.1482; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J=8.4 Hz, 1H), 7.71 (dd, J=2.0, 8.4 Hz, 1H), 7.34 (d, J=2.0 Hz, 1H), 7.25 (d, J=8.4 Hz, 2H), 7.07 (d, J=8.0 Hz, 2H), 6.76 (s, 2H), 6.68 (d, J=8.0 Hz, 1H), 6.52 (dd, J=1.6, 8.0 Hz, 1H), 6.42 (d, J=1.6 Hz, 1H), 5.97 (s, 2H), 3.90 (s, 6H), 3.88 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.59 (2×), 147.16, 146.65, 145.56, 143.48, 141.95, 138.88, 138.10, 134.63, 131.68, 131.06, 129.87, 129.12, 128.86 (2×), 127.74 (2×), 125.86, 123.79, 110.51, 107.17, 104.59 (2×), 101.01, 60.88, 56.22 (2×), 21.43.

*4.2.31. Compound (**6i**).* Yield=23% (55 mg); mp=202–204 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{28}H_{27}O_5S$ 475.1579, found 475.1574; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J=8.4 Hz, 1H), 7.78 (dd, J=2.0, 8.4 Hz, 1H), 7.63–7.61 (m, 2H), 7.48–7.38 (m, 4H), 7.20 (d, J=8.4 Hz, 2H), 7.04 (d, J=8.0 Hz, 2H), 6.20 (s, 2H), 3.91 (s, 3H), 3.69 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.04 (2×), 145.53, 143.18, 142.22, 138.85, 138.79, 138.03, 137.43, 133.18, 130.74, 129.00 (2×), 128.94, 128.81 (2×), 128.59, 127.88 (2×), 127.27 (2×), 125.91, 107.43 (2×), 60.90, 55.77 (2×), 21.35; Anal. Calcd for $C_{28}H_{26}O_5S$: C, 70.86; H, 5.52. Found: C, 70.96; H, 5.74. Single-crystal X-ray diagram: crystal of compound **6i** was grown by slow diffusion of EtOAc into a solution of compound **6i** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, a=9.918(3) Å, b=11.088(3) Å, c=11.599(3) Å, V=1166.7(5) Å^3, Z=2, d_{calcd}=1.351 g/cm^3, $F(000)$=500, 2θ range 1.91–26.39°, R indices (all data) $R1$=0.0544, $wR2$=0.1623.

*4.2.32. Compound (**6j**).* Yield=20% (55 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{34}H_{31}O_5S$ 551.1892, found 551.1899; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J=8.4 Hz, 1H), 7.75 (dd, J=2.0, 8.4 Hz, 1H), 7.65–7.62 (m, 2H), 7.52–7.41 (m, 6H), 7.19 (d, J=8.4 Hz, 2H), 7.13 (d, J=8.4 Hz, 2H), 6.99 (d, J=8.0 Hz, 2H), 6.79 (s, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.67 (2×), 153.02, 145.67, 143.42, 142.20, 140.68, 140.60, 138.79, 138.72, 137.18, 134.69, 130.93, 130.51 (2×), 129.22, 128.90 (2×), 127.83 (2×), 127.57, 127.05 (2×), 125.96 (2×), 125.94 (2×), 105.85, 104.67 (2×), 60.95, 56.29 (2×), 21.53.

*4.2.33. Compound (**6k**).* Yield=32% (74 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{30}H_{25}O_3S$ 465.1524, found 465.1532; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J=8.1 Hz, 1H), 7.87 (d, J=7.6 Hz, 1H), 7.78–7.73 (m, 2H), 7.61–7.47 (m, 6H), 7.30–7.27 (m, 2H), 7.06 (d, J=8.4 Hz, 2H), 6.97 (d, J=8.8 Hz, 2H), 6.77 (d, J=8.4 Hz, 2H), 3.84 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.13, 145.09, 143.26, 142.44, 138.17, 138.11, 135.85, 132.47, 132.34, 131.16, 130.56, 129.18, 128.84, 128.73 (2×), 128.43 (2×), 128.00, 127.95, 127.68 (2×), 127.58, 126.64, 126.26, 126.06, 125.40, 114.45 (2×), 55.32, 21.32.

*4.2.34. Compound (**6l**).* Yield=43% (88 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{23}H_{18}FO_2S_2$ 409.0732, found 409.0736; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J=8.0 Hz, 1H), 7.75 (dd, J=2.0, 8.4 Hz, 1H), 7.53 (d, J=2.0 Hz, 1H), 7.45–7.36 (m, 2H), 7.31–7.25 (m, 4H), 7.21 (dd, J=1.2, 3.6 Hz, 1H), 7.12–7.08 (m, 1H), 7.06 (d, J=8.0 Hz, 2H), 7.02 (dd, J=3.6, 5.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.15 (d, J=245.6 Hz), 144.11, 143.56, 140.85 (d, J=7.6 Hz), 140.17, 137.41, 137.36, 135.01, 132.52, 130.96, 130.60 (d, J=8.3 Hz), 129.79, 129.02 (2×), 127.74 (2×), 127.11, 126.67, 126.58, 123.01 (d, J=3.0 Hz), 115.51 (d, J=21.2 Hz), 114.28 (d, J=21.8 Hz), 21.53.

*4.2.35. Compound (**6m**).* Yield=38% (77 mg); mp=138–139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_2S_2$ 405.0983, found 405.0986; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J=8.4 Hz, 1H), 7.75 (dd, J=1.6, 8.0 Hz, 1H), 7.55 (d, J=1.6 Hz, 1H), 7.50 (d, J=8.0 Hz, 2H), 7.29–7.25 (m, 5H), 7.21 (dd, J=1.6, 8.0 Hz, 1H), 7.06 (d, J=8.4 Hz, 2H), 7.02 (dd, J=3.6, 5.2 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.42, 143.39, 139.17, 138.73, 137.74, 137.64, 135.69, 134.75, 132.26, 130.78, 129.75 (2×), 129.68, 128.97 (2×), 127.70 (2×), 127.13 (2×), 126.91, 126.58, 126.30, 21.51, 21.14; Anal. Calcd for $C_{24}H_{20}O_2S_2$: C, 71.25; H, 4.98. Found: C, 71.52; H, 5.27.

*4.2.36. Compound (**6n**).* Yield=36% (76 mg); mp=115–116 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_3S_2$ 421.0932, found 421.0938; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J=8.4 Hz, 1H), 7.72 (dd, J=2.0, 8.4 Hz, 1H), 7.54 (d, J=8.8 Hz, 2H), 7.52 (d, J=2.0 Hz, 1H), 7.29–7.27 (m, 1H), 7.26 (d, J=8.4 Hz, 2H), 7.58 (dd, J=1.2, 3.6 Hz, 1H), 7.05 (d, J=8.0 Hz, 2H), 7.01 (dd, J=3.6, 5.2 Hz, 1H), 6.97 (d, J=8.4 Hz, 2H), 3.84 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.20, 145.03, 143.36, 138.76, 137.77, 137.67, 134.74, 131.90, 130.90, 130.74, 129.69, 128.96 (2×), 128.43 (2×), 127.66 (2×), 126.87, 126.57, 125.91, 114.46 (2×), 55.34, 21.49; Anal. Calcd for $C_{24}H_{20}O_3S_2$: C, 68.54; H, 4.79. Found: C, 68.85; H, 4.58.

*4.2.37. Compound (**6o**).* Yield=40% (88 mg); mp=169–170 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{27}H_{21}O_2S_2$ 441.0983, found 441.0982; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J=8.4 Hz, 1H), 8.07 (d, J=2.0 Hz, 1H), 7.94–7.84 (m, 4H), 7.72 (dd, J=1.6, 8.4 Hz, 1H), 7.69 (d, J=2.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.30 (dd, J=0.8, 3.6 Hz, 1H), 7.28 (d, J=8.4 Hz, 2H), 7.24 (dd, J=1.2, 5.2 Hz, 1H), 7.07 (d, J=8.0 Hz, 2H), 7.04 (dd, J=3.6, 5.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.44, 143.48, 139.60, 137.70, 137.62, 135.90, 134.93, 133.47, 133.17, 132.75, 130.92, 129.80, 129.03 (2×), 128.87, 128.37, 127.76 (2×), 127.69, 127.01, 126.82, 126.73 (2×), 126.67 (2×), 124.95, 21.54; Anal. Calcd for $C_{27}H_{20}O_2S_2$: C, 73.61; H, 4.58. Found: C, 73.75; H, 4.67.

*4.2.38. Compound (**6p**).* Yield=30% (72 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{25}H_{25}O_5S_2$ 481.1144, found 481.1145; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J=8.4 Hz, 1H), 7.73 (dd, J=2.0, 8.4 Hz, 1H), 7.50 (d, J=2.0 Hz, 1H), 7.29 (dd, J=1.6, 5.2 Hz, 1H), 7.25 (d, J=8.0 Hz, 2H), 7.21 (dd, J=0.8, 3.6 Hz, 1H), 7.05 (d, J=8.0 Hz, 2H), 7.03 (dd, J=3.6, 5.2 Hz, 1H), 6.76 (s, 2H), 3.91 (s, 6H), 3.88 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.65 (2×), 145.58, 143.46, 139.49, 137.57, 135.51, 134.75, 134.44, 132.35, 130.86, 129.65, 128.98 (2×), 127.67 (2×), 127.00, 126.63, 126.54, 104.66 (2×), 60.92, 56.27 (2×), 21.50.

*4.2.39. Compound (**6q**).* Yield=33% (83 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{30}H_{28}FO_4S$ 503.1692, found 503.1695; ^{1}H

NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J=8.4 Hz, 1H), 7.75 (dt, J=1.6, 8.4 Hz, 1H), 7.40–7.29 (m, 3H), 7.24–7.05 (m, 6H), 6.75 (d, J=8.4 Hz, 1H), 6.32 (d, J=8.4 Hz, 1H), 5.69–5.59 (m, 1H), 4.80 (dq, J=1.6, 10.0 Hz, 1H), 4.58 (dq, J=1.6, 17.2 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 2.90–2.84 (m, 1H), 2.37 (s, 3H), 2.16 (ddt, J=1.2, 10.0, 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.74 (d, J=247.8 Hz), 152.53, 146.80, 143.63, 140.30, 139.88, 138.96, 137.79, 137.01, 133.78 (d, J=3.0 Hz), 132.72, 130.58 (d, J=3.0 Hz), 130.15 (d, J=7.6 Hz), 130.08, 129.07 (2×), 128.70, 128.36, 128.31, 128.08 (2×), 126.87, 124.55 (d, J=3.8 Hz), 116.32 (d, J=22.7 Hz), 114.88, 109.34, 60.53, 55.75, 32.50, 21.55.

*4.2.40. Compound (**6r**).* Yield=35% (84 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{27}H_{22}F_3O_3S$ 483.1242, found 483.1250; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J=8.4 Hz, 1H), 7.75 (dd, J=2.0, 8.4 Hz, 1H), 7.70 (s, 4H), 7.41 (d, J=2.0 Hz, 1H), 7.18 (d, J=8.4 Hz, 2H), 7.03 (d, J=8.8 Hz, 2H), 6.97 (d, J=8.8 Hz, 2H), 6.78 (d, J=8.8 Hz, 2H), 3.86 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.43, 143.93, 143.50 (2×), 142.71, 142.50, 139.89, 137.92, 131.72, 131.21 (4×), 130.23, 129.43, 128.94 (2×), 127.81 (2×), 127.68 (2×), 125.98, 125.92 (q, J=3.8 Hz), 112.79 (2×), 55.36, 21.51.

*4.2.41. Compound (**6s**).* Yield=38% (95 mg); mp=216–218 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{30}H_{22}F_3O_2S$ 503.1293, found 503.1289; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J=8.4 Hz, 1H), 7.88 (d, J=8.0 Hz, 1H), 7.82 (dd, J=2.0, 8.4 Hz, 1H), 7.75 (d, J=8.0 Hz, 1H), 7.72 (s, 4H), 7.61 (d, J=8.0 Hz, 1H), 7.56–7.48 (m, 3H), 7.29–7.26 (m, 2H), 7.05 (d, J=8.4 Hz, 2H), 6.78 (d, J=8.0 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.97, 143.55, 142.77, 142.43, 139.94, 137.79, 135.37, 132.56, 132.34, 131.40, 129.34, 128.91, 128.82 (2×), 128.05, 127.96, 127.84, 127.77 (4×), 127.70 (2×), 127.64, 126.81, 126.45, 126.30, 126.22, 125.95 (q, J=3.8 Hz), 21.35; Anal. Calcd for $C_{30}H_{21}F_3O_2S$: C, 71.70; H, 4.21. Found: C, 71.91; H, 4.38. Single-crystal X-ray diagram: crystal of compound **6s** was grown by slow diffusion of EtOAc into a solution of compound **6s** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 1 21/c 1, a=5.8615(4) Å, b=30.118(2) Å, c=13.3762(10) Å, V=2338.5(3) Å^3, Z=4, d_{calcd}=1.427 g/cm^3, F(000)=1040, 2θ range 1.68–26.62°, R indices (all data) $R1$=0.0662, $wR2$=0.1001.

*4.2.42. Compound (**6t**).* Yield=30% (61 mg); mp=197–199 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{24}NO_4S$ 410.1426, found 410.1430; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J=8.4 Hz, 1H), 8.08 (d, J=8.8 Hz, 2H), 7.62 (dd, J=2.0, 8.4 Hz, 1H), 7.20 (d, J=8.4 Hz, 2H), 7.19 (d, J=8.8 Hz, 2H), 7.14 (d, J=2.0 Hz, 1H), 7.06 (d, J=8.4 Hz, 2H), 2.36 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.01, 147.27, 145.61, 143.98, 139.28, 138.16, 136.90, 131.05 (2×), 129.20 (2×), 128.95, 128.90, 127.64 (2×), 125.74, 122.27 (2×), 35.18, 30.98 (3×), 21.51; Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 67.46; H, 5.66; N, 3.42. Found: C, 67.56; H, 5.39; N, 3.65.

*4.2.43. Compound (**6u**).* Yield=40% (74 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{21}H_{23}O_2S_2$ 371.1140, found 371.1145; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J=8.4 Hz, 1H), 7.56 (dd, J=2.4, 8.4 Hz, 1H), 7.32 (d, J=2.4 Hz, 1H), 7.27–7.25 (m, 1H), 7.24 (d, J=8.4 Hz, 2H), 7.15 (dd, J=1.2, 5.2 Hz, 1H), 7.04 (d, J=8.4 Hz, 2H), 7.00 (dd, J=3.6, 5.2 Hz, 1H), 2.33 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.45, 143.24, 138.26, 138.04, 137.79, 133.89, 131.13, 130.61, 128.96, 128.93 (2×), 127.70 (2×), 126.65, 126.53, 125.29, 35.04, 30.97 (3×), 21.50.

*4.2.44. Compound (**6v**).* Yield=33% (65 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{24}H_{27}O_3S$ 395.1681, found 395.1686; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.4 Hz, 1H), 7.53 (dd, J=2.0, 8.4 Hz, 1H), 7.17 (br s, 1H), 7.16 (d, J=8.0 Hz, 2H), 7.01 (d, J=8.0 Hz, 2H), 6.93 (d, J=8.4 Hz, 2H), 6.75 (d, J=8.8 Hz, 2H), 3.85 (s, 3H), 2.32 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.10, 156.43, 143.06, 141.52, 138.35, 137.21, 131.21 (2×), 131.09, 129.98, 128.77 (2×), 128.43, 127.67 (2×), 124.32, 112.56 (2×), 55.28, 34.98, 30.97 (3×), 21.41.

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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.2013.09.036.

References and notes

1. (a) Liu, J.-K. *Chem. Rev.* **2006**, *106*, 2209; (b) Mullen, K.; Wegner, G. *Electronic Materials: the Oligomer Approach*; Wiley-VCH: Weinhein, Germany, 1988; (c) Cook, T. R.; Zheng, Y. R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734.
2. (a) Ohkanda, J.; Lockman, J. W.; Kothare, M. A.; Qian, Y.; Blaskovich, M. A.; Sebti, S. M.; Hamilton, A. D. *J. Med. Chem.* **2002**, *45*, 177; (b) Roberti, M.; Pizzirani, D.; Recanatini, M.; Simoni, D.; Grimaudo, S.; Di Cristina, A.; Abbadessa, V.; Gebbia, N.; Tolomeo, M. *J. Med. Chem.* **2006**, *49*, 3012; (c) Lin, J. M.; Gowda, A. S. P.; Sharma, A. K.; Amin, S. *Bioorg. Med. Chem.* **2012**, *20*, 3202; (d) Guo, H.; Hu, H.; Liu, S.; Liu, X.; Zhou, Y.; Che, Y. *J. Nat. Prod.* **2007**, *70*, 1519; (e) Zhang, C.; Ondeyka, J. G.; Herath, K. B.; Guan, Z.; Collado, J.; Pelaez, F.; Leavitt, P. S.; Gurnett, A.; Nare, B.; Liberator, P.; Singh, S. B. *J. Nat. Prod.* **2006**, *69*, 710; (f) Simoni, D.; Giannini, G.; Roberti, M.; Rondanin, R.; Baruchello, R.; Rossi, M.; Grisolia, G.; Invidiata, F. P.; Aiello, S.; Marino, S.; Cavallini, S.; Siniscalchi, A.; Gebbia, N.; Crosta, L.; Grimaudo, S.; Abbadessa, V.; Di Cristina, A.; Tolomeo, M. *J. Med. Chem.* **2005**, *48*, 4293; (g) Bugarcic, T.; Novakova, O.; Halamikova, A.; Zerzankova, L.; Vrana, O.; Kasparkova, J.; Habtemariam, A.; Parsons, S.; Sadler, P. J.; Brabec, V. *J. Med. Chem.* **2008**, *51*, 5310; (h) Patrick, D. A.; Ismail, M. A.; Arafa, R. K.; Wenzler, T.; Zhu, X.; Pandharkar, T.; Jones, S. K.; Werbovetz, K. A.; Brun, R.; Boykin, D. W.; Tidwell, R. R. *J. Med. Chem.* **2013**, *56*, 5473; (i) Bakunov, S. A.; Bakunova, S. M.; Wenzler, T.; Ghebru, M.; Werbovetz, K. A.; Brun, R.; Tidwell, R. R. *J. Med. Chem.* **2010**, *53*, 254.
3. (a) Perato, S.; Voisin-Chiret, A. S.; Santos, J. S. O.; Legay, R.; Oulyadi, H.; Rault, S. *Tetrahedron* **2012**, *68*, 1910; (b) Guillen, E.; Hierrezuelo, J.; Martinez-Mallorquin, R.; Lopez-Romero, J. M.; Rico, R. *Tetrahedron* **2011**, *67*, 2555; (c) De Giorgi, M.; Voisin-Chiret, A. S.; Santos, J. S. O.; Corbo, F.; Franchini, C.; Rault, S. *Tetrahedron* **2011**, *67*, 6145; (d) Zhang, X.; Xie, W.; Chen, W. *Tetrahedron* **2010**, *66*, 1188; (e) Voisin-Chiret, A. S.; Muraglia, M.; Burzicki, G.; Perato, S.; Corbo, F.; Santos, J. S. O.; Franchini, C.; Rault, S. *Tetrahedron* **2010**, *66*, 8000; (f) King, B. T.; Kroulik, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279; (g) Goto, H.; Furusho, Y.; Miwa, K.; Yashima, E. *J. Am. Chem. Soc.* **2009**, *131*, 4710; (h) Ormsby, J. L.; Black, T. D.; Hilton, C. L.; Bharat; King, B. T. *Tetrahedron* **2008**, *64*, 11370; (i) Mitchell, P. S. R.; Sengul, I. F.; Kandemir, H.; Nugent, S. J.; Chen, R.; Bowyer, P. K.; Kumar, N.; Black, D. S. *Tetrahedron* **2012**, *68*, 8163; (j) Kikuchi, H.; Matsuo, Y.; Katou, Y.; Kubohara, Y.; Oshima, Y. *Tetrahedron* **2012**, *68*, 8884; (k) Dohi, T.; Kamitanaka, T.; Watanabe, S.; Hu, Y.; Washimi, N.; Kita, Y. *Chem.—Eur. J.* **2012**, *18*, 13614.
4. (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359; (b) Schroter, S.; Stock, C.; Bach, T. *Tetrahedron* **2005**, *61*, 2245; (c) Schnurch, M.; Flasik, R.; Khan, A. F.; Spina, M.; Mihovilovic, M. D.; Stanetty, P. *Eur. J. Org. Chem.* **2006**, 3283; (d) Wang, R.; Manabe, K. *Synthesis* **2009**, 1405; (e) Chang, M.-Y.; Lee, T.-W.; Lin, S.-Y. *Tetrahedron* **2013**, *69*, 228.
5. (a) Varela, J. A.; Saa, C. *Chem. Rev.* **2003**, *103*, 3787; (b) Grotjahn, D. B. Transition Metal Alkyne Complexes: Transition Metal-catalyzed Cyclotrimerization. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Hegedus, L. S., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, p 741; (c) Hilt, G.; Vogler, T.; Hess, W.; Galbiati, F. *Chem. Commun.* **2005**, 1474; (d) Xu, L.; Yu, R.; Wang, Y.; Chen, J.; Yang, Z. *J. Org. Chem.* **2013**, *78*, 5744; (e) Ozelov, O. V.; Patrick, B. O.; Ladipo, F. T. *J. Am. Chem. Soc.* **2000**, *122*, 6423; (f) Cicero, D.; Lembo, A.; Leoni, A.; Tagliatesta, P. *New J. Chem.* **2009**, *33*, 2162; (g) Cadierno, V.; Garcia-Garrido, S. E.; Gimeno, J. *J. Am. Chem. Soc.* **2006**, *128*, 15094; (h) Sugihara, T.; Wakabayashi, A.; Nagai, Y.; Takao, H.; Imagawa, H.; Nishizawa, M. *Chem. Commun.* **2002**, 576; (i) Bu, X.; Zhang, Z.; Zhou, X. *Organometallics* **2010**, *29*, 3530; (j) Liu, Y.; Yan, X.; Yang, N.; Xi, C. *Catal. Commun.* **2011**, *12*, 489.
6. For the one-pot synthesis of *m*-terphenyls, see: (a) Raghukumar, V.; Murugan, P.; Ramakrishnan, V. T. *Synth. Commun.* **2001**, *31*, 3497; (b) Rashidzadeh, B.; Jafarpour, F.; Saednya, A. *Arkivoc* **2008**, *xvii*, 167; (c) Diallo, A.; Zhao, Y.-L.; Wang, H.; Li, S.-S.; Ren, C.-Q.; Liu, Q. *Org. Lett.* **2012**, *14*, 5776 and references cited herein.

7. For the applications with the sulfonyl *m*-terphenyls, see: (a) Sasabe, H.; Seino, Y.; Kimura, M.; Kido, J. *Chem. Mater.* **2012**, *24*, 1404; (b) Wright, R. S.; Vinod, T. K. *Tetrahedron Lett.* **2003**, *44*, 7129; (c) Udayakumar, B. S.; Schuster, G. B. *J. Org. Chem.* **1992**, *57*, 348.
8. For the isolation of *m*-terphenyl natural products, see: (a) Glombitza, K. W.; Rauwald, H. W.; Eckhard, G. *Phytochemistry* **1975**, *14*, 1403; (b) Kouno, I.; Hashimoto, A.; Kawano, N.; Yang, C. S. *Chem. Pharm. Bull.* **1989**, *37*, 1291; (c) Kouno, I.; Morisaki, T.; Hara, Y.; Yang, C. S. *Chem. Pharm. Bull.* **1991**, *39*, 2606; (d) Kohno, H.; Takaba, K.; Fukai, T.; Nomura, T. *Heterocycles* **1987**, *26*, 759.
9. (a) Chang, M.-Y.; Tsai, C.-Y.; Wu, M.-H. *Tetrahedron* **2013**, *69*, 6364; (b) Chang, M.-Y.; Wu, M.-H. *Tetrahedron* **2012**, *68*, 9616; (c) Chang, M.-Y.; Tai, H.-Y.; Chen, Y.-L.; Hsu, R.-T. *Tetrahedron* **2012**, *68*, 7941; (d) Chang, M.-Y.; Wu, M.-H.; Tai, H.-Y. *Org. Lett.* **2012**, *14*, 3936.
10. (a) Chang, M.-Y.; Wu, M.-H.; Chen, Y.-L. *Org. Lett.* **2013**, *15*, 2822; (b) Chang, M.-Y.; Chan, C.-K.; Wu, M.-H. *Tetrahedron* **2013**, *69*, 7916.
11. CCDC 965640 (**5f**), 947193 (**6i**) and 965641 (**6s**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).
12. (a) Shu, Z.-C.; Zhu, J.-B.; Liao, S.; Sun., X.-L.; Tang, Y. *Tetrahedron* **2013**, *69*, 284; (b) Song, Y. Y.; He, H. G.; Li, Y.; Deng, Y. *Tetrahedron Lett.* **2013**, *54*, 2658.