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Synthesis of polyphenyls

Meng-Yang Chang *, Tein-Wei Lee, Shin-Ying Lin

Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan

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ABSTRACT

A facile synthetic route toward functionalized 3-aryl-, 3,3′-diaryl-, 3,3′,5-triaryl-4,4′-dimethoxybiphenyls (polyphenyls) **3**–**5** with the terphenyl, quaterphenyl, quinquephenyl, and sexiphenyl skeleton starting from biphenyl-4,4′-diol (**1**) in modest total yield is described. The route has been carried by the two transformations of the regioselective NBS (*N*-bromosuccinimide)-mediated bromination of **2** in MeCN at reflux and Suzuki–Miyaura cross-coupling reaction of the resulting bromides with arylboronic acids **6** in DME at reflux.

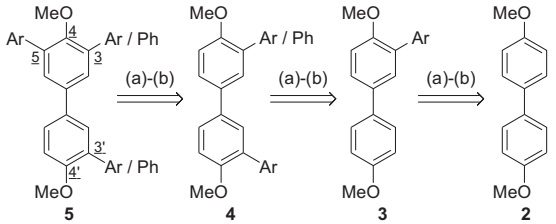
1. Introduction

A number of cross-coupling reactions of polyhalogenated benzofused heterocycles have been reported over the last few years.[1,2] Due to the particular electronic reasons and steric parameters concerning the specific site-selective pattern, some synthetic methods for preparing site-selective aryl-functionalized heterocycles have been developed.[2] For the site-selective Suzuki–Miyaura cross-coupling reactions, the adopted polyhalogenated substrates include benzenes,[2a] benzoquinones,[2b] benzofurans,[2c] thiophenes,[2d] pyrroles,[2e] indenes,[2f] pyrazoles,[2g] naphthalenes,[2h] xanthones,[2i] pyrene,[2j] and coumarins.[2k] In continuation of our investigation into the synthetic applications of biphenyl-4,4′-diol (**1**),[3] a synthetic route is employed to create the skeletons of 3-aryl-, 3,3′-diaryl- and 3,3′,5-triaryl-4,4′-dimethoxy-biphenyls (polyphenyls) **3**–**5**, via two transformations of NBS-mediated bromination of **2** in MeCN at reflux and Suzuki–Miyaura cross-coupling reaction of the resulting bromide with arylboronic acids **6** in DME at reflux (Fig. 1).

Polyphenyls have received considerable attention in the past decades due to their presence as the structural motifs in natural products, biological pharmaceuticals, and functionalized materials.[4] Synthetic polyphenyls are often exploited in the synthetic material fields, such as organic electronics, chemical biosensors, and photovoltaic batteries because of their excellent photo-physical applications.[5] For the related biological activities, substituted polyphenyls also possess potential therapeutic values.[6] There are many approaches that have been reported for the construction of polyphenyls, including the transition-metal mediated coupling reactions or cycloadditions.[7,8] Although some useful routes are valuable protocols for the synthesis of polyphenyls derivatives,[9] it is still of great importance to develop a simple and efficient route for the construction of functionalized polyphenyls, especially those with flexible substitution patterns.

2. Results and discussion

The starting material, 4,4′-dimethoxy-biphenyl (**2**), was provided by the double O-methylation of the commercially available biphenyl-4,4′-diol (**1**) with K_2CO_3 and MeI in the quantitative yield. Next, the synthesis of functionalized polyphenyls **3**–**5** was examined. Treatment of **2** reacted with 1.2 equiv of NBS in MeCN at reflux for 5 h to yield 3-bromo-4,4′-dimethoxybiphenyl (**7**, 84%) and 3,3′-dibromo-



(a) NBS, MeCN, reflux; (b) $Pd(PPh_3)_4$, arylB$(OH)_2$ **6**, Na_2CO_3, DME, reflux
Ar = **a**, Ph; **b**, 4-CF_3-Ph; **c**, 4-MeO-Ph; **d**, 4-pyridinyl; **e**, 3,4-$(MeO)_2$-Ph; **f**, 4-CHO-Ph; **g**, 2-Ph-Ph

Fig. 1. Retrosynthetic route toward skeletons **3**–**5**.

* Corresponding author. Tel.: +886 7 3121101x2220; e-mail addresses: mychang@kmu.edu.tw, mychang624@yahoo.com.tw (M.-Y. Chang).

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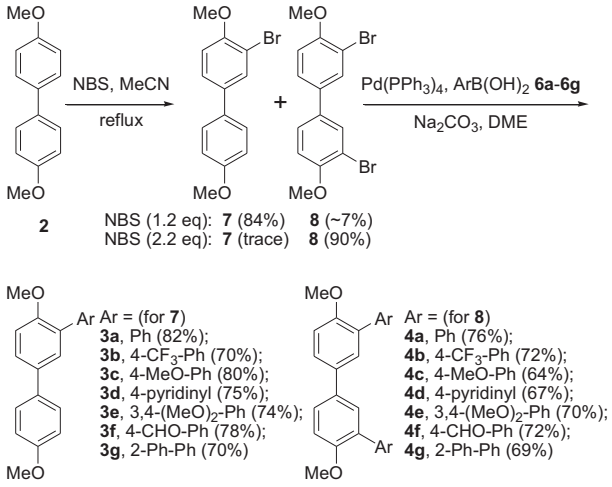
4,4′-dimethoxybiphenyl (**8**, ~7%). To examine the Suzuki–Miyaura cross-coupling reaction conditions, we found that $Pd(PPh_3)_4$-mediated coupling reaction of substrate **7** provided a yield of 82%, which was better than $Pd(MeCN)_2Cl_2$ (65%) or $Pd(OAc)_2$ (55%). Adjusting the solvent for the DMF or 1,4-dioxane, the isolated yield (75% or 80%) was not noticeably enhanced. Furthermore, after screening seven arylboronic acids **6a**–**g** with different electron-donating or electron-withdrawing groups (Ar=**a**, Ph; **b**, 4-CF_3–Ph; **c**, 4-MeO–Ph; **d**, 4-pyridinyl; **e**, 3,4-$(MeO)_2$–Ph; **f**, 4-CHO–Ph; **g**, 2-Ph–Ph), seven terphenyls **3a**–**g** were isolated with 70%–82% yields via the $Pd(PPh_3)_4$-mediated cross-coupling of mono-bromide **7** as shown in Scheme 1. Changing the equivalent of NBS (2.2 equiv), major 3,3′-dibromide **8** was isolated with a 90% yield.[10] Then, by the double Suzuki–Miyaura cross-coupling reaction of **8** with seven arylboronic acids **6a**–**g**, seven quaterphenyls **4a**–**g** were isolated with 64–76% yields. The structural frameworks of **4e** and **4g** were determined using single-crystal X-ray analysis (Figs. 2 and 3).[11]



Scheme 1. Synthesis of skeletons **3** and **4**.

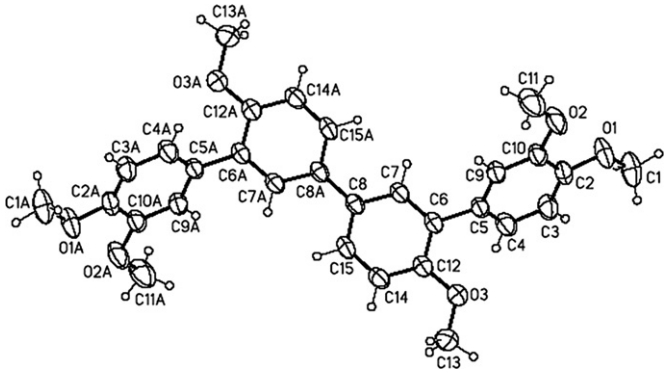


Fig. 2. X-ray structure of **4e**.

The crystal structures of both quaterphenyl **4e** and sexiphenyl **4g** belong to a monoclinic crystal system and $P\,1\,21/c\,1$ space group, and possess the unique serrate helix shape (see Table 1). Single-crystal X-ray diffraction analysis was employed to prove the constitution and relative configuration of the isolated product. The ORTEP plot clearly shows that the configuration of a benzene ring of 3,4-dimethoxyphenyl or 2-biphenyl moiety in the 3,3′-position of the 4,4′-dimethoxy-biphenyl skeletons are parallel to each other.

Furthermore, synthesis of the quinquephenyl skeleton **4** with the unsymmetrical 3,3′-diaryl-4,4′-dimethoxybiphenyl skeleton was

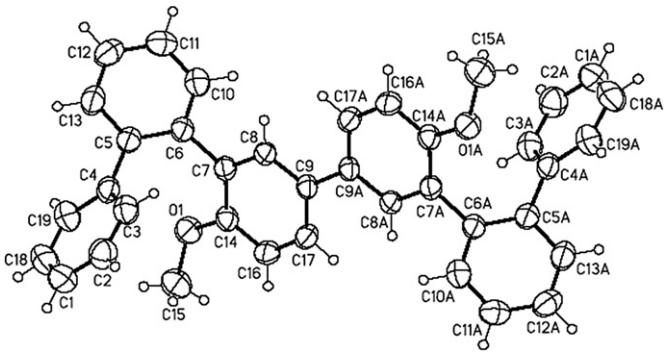


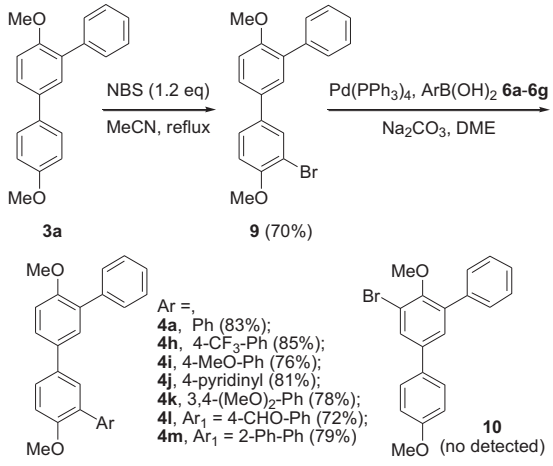
Fig. 3. X-ray structure of **4g**.

Table 1
Crystal data for **4e** and **4g**

CCDC number	887702 (**4e**)	887701 (**4g**)
Crystal system	Monoclinic	Monoclinic
Space group	$P\,1\,21/c\,1$	$P\,1\,21/c\,1$
a (Å)	15.9092(8)	8.6547(3)
b (Å)	6.7774(3)	20.2740(8)
c (Å)	11.7769(6)	8.8027(4)
α (°)	90	90
β (°)	94.4430(10)	117.4240(10)
γ (°)	90	90
Volume (Å^3)/Z	1266.00(11)/4	1370.99(10)/4
Temperature (K)	296(2)	296(2)
D_{calcd} (Mg/m^3)	1.276	1.256
Absorption coefficient (mm^{-1})	0.088	0.076
Crystal size (mm)	0.30×0.30×0.10	0.30×0.20×0.17
θ Range for data collection (°)	1.28–26.44	2.65–26.40
Reflections collected	10,119	10,763
Independent reflections	2603 (R_{int}=0.0207)	2788 (R_{int}=0.0249)
R_F, R_w (F^2) (all data)[a]	0.0558, 0.1212	0.0635, 0.1274
R_F, R_w (F^2) ($I>2\sigma(I)$)[a]	0.0413, 0.1101	0.0461, 0.1170
GOF	1.050	1.040

[a] $R_F=\Sigma|F_o-F_c|/\Sigma|F_o|$; $R_W(F^2)=[\Sigma^W|F_o^2-F_c^2|^2/\Sigma^W F_o^4]^{1/2}$.

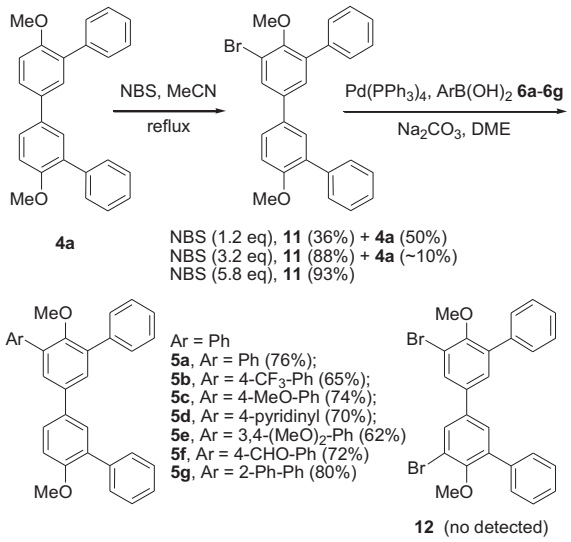
studied, as shown in Scheme 2, by the above-mentioned protocol; treatment of model substrate **3a** with 1.2 equiv of NBS in MeCN at reflux yielded 3-phenyl-5-bromo-4,4′-dimethoxybiphenyl **9** with 70% yield via a regioselective bromination reaction. However, by controlling the equivalent of NBS, 3-phenyl-3′-bromo-4,4′-dimethoxybiphenyl **10** had been not detected due to the steric hindrance of the 3-phenyl group affecting the bromination. $Pd(PPh_3)_4$-mediated Suzuki–Miyaura cross-coupling of **9** with seven arylboronic acids **6a**–**g** were isolated **4a** and **4h**–**m** with 72–85% yields. For the formation of compounds **3a**–**g** and **4a**–**m** with different electron-



Scheme 2. Synthesis of unsymmetrical skeleton **4**.

donating aryl groups and electron-withdrawing aryl groups, the useful combination of the NBS-mediated bromination of **2** or **3a** followed by Suzuki–Miyaura cross-coupling of the resulting bromide **7**, **8** or **9** with arylboronic acids **6a**–**g** provided different angular and curved skeletons of six terphenyls (**3a**–**f**), twelve quaterphenyls (**3g**, **4a**–**f**, **4h**–**l**), one quinquephenyl (**4m**) and one sexiphenyl (**4g**) with good to acceptable yields.

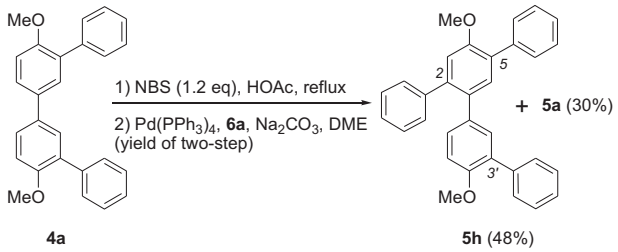
Based on the results, the skeleton of dendritic quinquephenyls **5** was examined next, as shown in Scheme 3. First, treatment of the starting material **4a** with NBS (1.2 equiv) provided **11** (36%) and **4a** (50%). To increase the equivalent of NBS, the yield of **11** provided 88% (3.2 equiv) and 93% (5.8 equiv). However, dibromide **12** was observed by the treatment of **4a** with excess NBS. Screening the conditions (equivalent, reaction time and temperature) in an attempt to provide **12** were unsuccessful. From the phenomenon, we envisioned that 5-bromo and 3,3′-diphenyl group of **11** should produce the more bulky steric hindrance to decrease the possibility of a second bromination on the 5′-position for the formation of **12**. For the excess NBS-mediated reaction of **4b** or **4c** in MeCN at reflux for 5 h, several bromide isomers were isolated from the complex reaction products in a different product ratio. Then, Suzuki–Miyaura cross-coupling of the resulting bromide **11** with arylboronic acids **6a**–**g** afforded six quinquephenyls **5a**–**f** and one sexiphenyl **5g** with 65–80% yields.



Scheme 3. Synthesis of skeleton **5**.

From the synthetic route of **5a**, the combination of the regioselective bromination and coupling reaction provided an ordinal sequence to introduce a bromo atom into the C3 (**7**)→C3′ (**9**)→C5 (**11**) position followed by the involvement of phenyl group at the same C3 (**3a**)→C3′ (**4a**)→C5 (**5a**) position for the construction of the skeleton of polyphenyls from the compound **2**. We have successfully presented an easy and efficient synthetic methodology for the preparation of polyphenyls. To the best of our knowledge, there are no reports in the literature considering the preparation of skeleton **5**, with a novel dendritic polyphenyls structural framework (Scheme 4).

It deserves to be mentioned that when the reaction solvent was changed to acetic acid for the two steps of **4a** via the bromination reaction/Suzuki–Miyaura cross-coupling reaction, **5h** with 2,3′,5-triphenyl groups was formed as the major isomer and another 3,3′,5-triphenyl isomer **5a** was isolated in a 30% yield. And, quinquephenyl **5h** was determined by single-crystal X-ray crystallography. Structure **5h** was shown in Fig. 4.[11]



Scheme 4. Synthesis of **5h**.

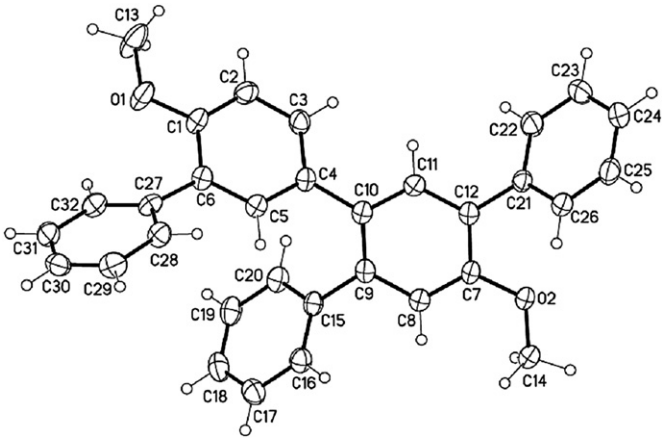


Fig. 4. X-ray structure of **5h**.

3. Conclusion

In summary, we have successfully presented a synthetic route for the synthesis of polyphenyls (terphenyl, quaterphenyl, quinquephenyl, sexiphenyl) with good to acceptable yields via the ordinal sequence combination of the regioselective bromination and Suzuki–Miyaura coupling reaction. This synthesis starts from simple starting material and reagents, and provides a potential methodology for chemical biology or material science research. The Scholl oxidative annulation of **3g**, **4g**, **5g** and **5h** will be investigated.

4. Experimental section

4.1. General

THF was distilled prior to use. 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 nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 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 7 and 8 is as follows

NBS (for **7**, 428 mg, 2.4 mmol; for **8**, 783 mg, 4.4 mmol) was added to a solution of compound **2** (430 mg, 2.0 mmol) in MeCN (10 mL) at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with EtOAc (3×30 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 compound **7** or **8**.

*4.2.1. Compound (**7**).* Yield 84% (491 mg); colorless solid; mp=116–118 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{14}Br_2O_2$ 293.0177, found 293.0182; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J=2.0 Hz, 1H), 7.47–7.43 (m, 3H), 6.98–6.93 (m, 3H), 3.93 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.05, 154.80, 134.88, 132.00, 131.46, 127.74 (2×), 126.55, 114.24 (2×), 112.09, 111.96, 56.31, 55.33; Anal. Calcd for $C_{14}H_{13}Br_2O_2$: C, 57.36; H, 4.47. Found: C, 57.55; H, 4.80.

*4.2.2. Compound (**8**).* Yield 90% (664 mg); colorless solid; mp=164–166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{13}Br_2O_2$ 370.9282, found 370.9287; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J=2.4 Hz, 2H), 7.42 (dd, J=2.4, 8.8 Hz, 2H), 6.95 (d, J=8.8 Hz, 2H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.22 (2×), 133.43 (4×), 131.50 (2×), 126.64 (2×), 112.11 (2×), 56.35 (2×). Compound **8** is a known compound and the analytical data are consistent with those in the literature.[10a,b]

4.3. A representative synthetic procedure of compounds 3a–g is as follows

$Pd(PPh_3)_4$ (100 mg) and Na_2CO_3 (106 mg, 1.0 mmol) were added to a solution of compound **7** (150 mg, 0.5 mmol) in DME (10 mL) at rt. Then, $ArB(OH)_2$ **6a–g** (1.0 mmol) was added to the stirred reaction mixture at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with CH_2Cl_2 (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–g**.

*4.3.1. Compound (**3a**).* Yield 82% (119 mg); colorless solid; mp=100–102 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{19}O_2$ 291.1385, found 291.1395; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.62 (m, 2H), 7.59–7.54 (m, 4H), 7.51–7.46 (m, 2H), 7.42–7.37 (m, 1H), 7.08 (d, J=8.4 Hz, 1H), 7.03–7.00 (m, 2H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.74, 155.56, 138.49, 133.53, 133.25, 130.90, 129.53 (2×), 129.28, 127.99 (2×), 127.73 (2×), 126.99, 126.61, 114.17, 114.15, 111.54, 55.68, 55.27.

*4.3.2. Compound (**3b**).* Yield 70% (125 mg); colorless solid; mp=88–90 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{18}F_3O_2$ 359.1259, found 359.1264; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (br s, 4H), 7.57–7.44 (m, 4H), 7.06 (d, J=8.8 Hz, 1H), 7.00–6.94 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.92, 155.50, 142.20, 133.82, 133.00, 131.50, 129.87 (2×), 129.17, 127.77 (2×), 127.71, 127.49, 126.57, 124.94, 124.90, 114.27 (2×), 111.69, 55.75, 55.34.

*4.3.3. Compound (**3c**).* Yield 80% (128 mg); colorless solid; mp=110–112 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{21}O_3$ 321.1491, found 321.1492; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.48 (m, 6H), 7.04 (d, J=8.4 Hz, 1H), 7.01–6.97 (m, 4H), 3.87 (s, 3H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.73, 158.72, 155.59, 133.55, 133.37, 130.85, 130.60 (2×), 129.12, 127.75 (2×), 126.20, 114.23, 114.15 (2×), 113.51 (2×), 111.51, 55.71, 55.31, 55.25; Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.91; H, 6.51.

*4.3.4. Compound (**3d**).* Yield 75% (109 mg); colorless solid; mp=163–165 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{18}NO_2$ 292.1338, found 292.1346; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J=8.8 Hz, 2H), 7.56 (dd, J=2.0, 8.4 Hz, 1H), 7.52–7.49 (m, 5H), 7.06 (d, J=8.4 Hz, 1H), 6.98 (d, J=8.8 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.93, 155.56, 149.47 (2×), 146.28, 133.88, 132.78, 128.79, 128.08, 127.89, 127.72 (2×), 124.29 (2×), 114.23, 114.21, 111.76, 55.69, 55.30; Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.50; H, 6.12; N, 5.02. Single-crystal X-ray diagram: crystal of compound **3d** was grown by slow diffusion of EtOAc into a solution of compound **3d** in CH_2Cl_2 to yield colorless prism. The compound crystallizes in the orthorhombic crystal system, space group *P b c a*, a=13.8183(12) Å, b=6.7898(6) Å, c=31.286(3) Å, V=2935.4(4) Å^3, Z=8, D_{calcd}=1.318 g/cm^3, F(000)=1232, 2θ range 1.30–26.41°, R indices (all data) $R1$=0.0450, $wR2$=0.0909.

*4.3.5. Compound (**3e**).* Yield 74% (130 mg); colorless solid; mp=156–158 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{23}O_4$ 351.1596, found 351.1600; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.52 (m, 3H), 7.50 (dd, J=2.4, 8.4 Hz, 1H), 7.16–7.14 (m, 2H), 7.04 (d, J=8.4 Hz, 1H), 7.00–6.95 (m, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.75, 155.52, 148.38, 148.20, 133.57, 133.28, 131.16, 130.66, 129.12, 127.74 (2×), 126.32, 121.81, 114.15 (2×), 113.06, 111.58, 110.89, 55.88, 55.86, 55.74, 55.28; Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.60; H, 6.49.

*4.3.6. Compound (**3f**).* Yield 78% (124 mg); colorless solid; mp=118–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{19}O_3$ 319.1334, found 319.1341; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.94 (d, J=8.8 Hz, 2H), 7.76 (d, J=8.0 Hz, 2H), 7.56 (dd, J=2.4, 8.4 Hz, 1H), 7.53 (s, 1H), 7.52 (d, J=8.8 Hz, 2H), 7.07 (d, J=8.4 Hz, 1H), 6.98 (d, J=8.8 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.05, 158.92, 155.55, 145.02, 134.92, 133.84, 132.93, 130.21 (2×), 129.50, 129.46 (2×), 129.12, 127.77 (2×), 127.72, 114.25 (2×), 111.74, 55.75, 55.34.

*4.3.7. Compound (**3g**).* Yield 70% (128 mg); colorless solid; mp=114–115 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{23}O_2$ 367.1698, found 367.1700; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.38 (m, 8H), 7.21–7.16 (m, 5H), 6.96–6.93 (m, 2H), 6.76 (d, J=8.4 Hz, 1H), 3.84 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.67, 155.40, 142.17, 141.74, 137.16, 133.28, 132.96, 130.96, 130.80, 130.07, 129.74, 129.01 (2×), 127.64, 127.61 (2×), 127.49 (2×), 127.17, 126.50, 126.23, 114.11 (2×), 111.04, 55.34, 55.09.

4.4. A representative synthetic procedure of compounds 4a–g is as follows

$Pd(PPh_3)_4$ (100 mg) and Na_2CO_3 (106 mg, 1.0 mmol) were added to a solution of compound **8** (185 mg, 0.5 mmol) in DME (10 mL) at rt. Then, $ArB(OH)_2$ **6a–g** (2.0 mmol) was added to the stirred reaction mixture at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with CH_2Cl_2 (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–g**.

*4.4.1. Compound (**4a**).* Yield 76% (139 mg); colorless solid; mp=112–114 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{23}O_2$ 367.1698, found 367.1703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.51 (m, 8H), 7.45–7.41 (m, 4H), 7.37–7.32 (m, 2H), 7.05 (d, J=9.2 Hz, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.68 (2×), 138.48 (2×), 133.40 (2×), 130.99 (2×), 129.56 (4×), 129.38 (2×), 128.02 (4×), 127.04 (2×), 126.68 (2×), 111.57 (2×), 55.75 (2×). Compound **4a** is a known compound and the analytical data are consistent with those in the literature.[12]

*4.4.2. Compound (**4b**).* Yield 72% (181 mg); colorless solid; mp=177–178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{28}H_{21}F_6O_2$ 504.1524, found 504.1531; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (br s, 8H), 7.52 (dd, J=2.4, 8.4 Hz, 2H), 7.46 (d, J=2.4 Hz, 2H), 7.01 (d, J=8.4 Hz, 2H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.72 (2×), 142.09 (2×), 133.33 (2×), 131.53 (2×), 129.87 (8×), 129.62 (2×), 127.55 (2×), 126.63 (2×), 124.95 (q, J=3.8 Hz, 2×), 111.73 (2×), 55.76 (2×).

*4.4.3. Compound (**4c**).* Yield 64% (136 mg); colorless solid; mp=131–133 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{28}H_{27}O_4$ 427.1909, found 427.1908; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.51 (m, 8H), 7.04 (d, J=8.4 Hz, 2H), 7.01–6.97 (m, 4H), 3.87 (s, 6H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.72 (2×), 155.64 (2×), 133.45 (2×), 130.81 (2×), 130.60 (6×), 130.56 (2×), 126.24 (2×), 113.51 (4×), 111.51 (2×), 55.70 (2×), 55.25 (2×); Anal. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14. Found: C, 79.03; H, 6.31.

*4.4.4. Compound (**4d**).* Yield 67% (123 mg); colorless solid; mp >245 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{21}N_2O_2$ 369.1603, found 369.1611; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (dd, J=2.0, 4.8 Hz, 4H), 7.59 (dd, J=2.0, 8.4 Hz, 2H), 7.54–7.50 (m, 6H), 7.07 (d, J=8.8 Hz, 2H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.83 (2×), 150.64 (2×), 149.50 (2×), 146.13 (2×), 133.27 (2×), 128.81 (2×), 128.16 (2×), 128.08 (2×), 124.28 (2×), 121.35 (2×), 111.82 (2×), 55.73 (2×).

*4.4.5. Compound (**4e**).* Yield 70% (170 mg); colorless solid; mp=176–177 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{30}H_{31}O_6$ 487.2121, found 487.2123; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=2.4 Hz, 2H), 7.53 (dd, J=2.4, 8.4 Hz, 2H), 7.15–7.12 (m, 4H), 7.05 (d, J=8.4 Hz, 2H), 6.95 (d, J=8.4 Hz, 2H), 3.93 (s, 6H), 3.92 (s, 6H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.63 (2×), 148.38 (2×), 148.23 (2×), 133.47 (2×), 131.10 (2×), 130.74 (2×), 129.20 (2×), 126.44 (2×), 121.82 (2×), 113.04 (2×), 111.60 (2×), 110.88 (2×), 55.90 (2×), 55.87 (2×), 55.77 (2×); Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 74.38; H, 6.58. Single-crystal X-ray diagram: crystal of compound **4e** was grown by slow diffusion of EtOAc into a solution of compound **4e** in CH_2Cl_2 to yield colorless prism. The compound crystallizes in the monoclinic crystal system, space group P 1 21/c 1, a=15.9092(8) Å, b=6.7774(3) Å, c=11.7769(6) Å, V=1266.00(11) Å^3, Z=4, D_{calcd}=1.276 g/cm^3, F(000)=516, 2θ range 1.28–26.44°, R indices (all data) R1=0.0558, wR2=0.1212.

*4.4.6. Compound (**4f**).* Yield 72% (152 mg); colorless solid; mp=176–178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{28}H_{23}O_4$ 423.1596, found 423.1602; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 2H), 7.94 (d, J=8.0 Hz, 4H), 7.75 (d, J=8.0 Hz, 4H), 7.59 (dd, J=2.4, 8.8 Hz, 2H), 7.55 (d, J=2.4 Hz, 2H), 7.08 (d, J=8.8 Hz, 2H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.05 (2×), 155.79 (2×), 144.89 (2×), 134.98 (2×), 133.34 (2×), 130.22 (4×), 129.67 (4×), 129.49 (2×), 129.15 (2×), 127.81 (2×), 111.79 (2×), 55.79 (2×).

*4.4.7. Compound (**4g**).* Yield 69% (180 mg); colorless solid; mp=235–236 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{38}H_{31}O_2$ 519.2324, found 519.2326; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.39 (m, 14H), 7.36–7.24 (m, 6H), 6.99 (d, J=8.0 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H), 3.36 (s, 6H). Single-crystal X-ray diagram: crystal of compound **4g** was grown by slow diffusion of EtOAc into a solution of compound **4g** in CH_2Cl_2 to yield colorless prism. The compound crystallizes in the monoclinic crystal system, space group P 1 21/c 1, a=8.6547(3) Å, b=20.2740(8) Å, c=8.8027(4) Å, V=1370.99(10) Å^3, Z=4, D_{calcd}=1.256 g/cm^3, F(000)=548, 2θ range 2.65–26.40°, R indices (all data) R1=0.0635, wR2=0.1274.

4.5. A representative synthetic procedure of compound 9 is as follows

NBS (85 mg, 0.48 mmol) was added to a solution of compound **3a** (115 mg, 0.4 mmol) in MeCN (10 mL) at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with EtOAc (3×30 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 compound **9**.

*4.5.1. Compound (**9**).* Yield 70% (103 mg); colorless oil; HRMS (ESI, M^++1) calcd for $C_{20}H_{18}BrO_2$ 369.0490, found 369.0492; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J=2.4 Hz, 1H), 7.58–7.55 (m, 2H), 7.50–7.41 (m, 5H), 7.37–7.33 (m, 1H), 7.04 (d, J=9.2 Hz, 1H), 6.95 (d, J=8.4 Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.99, 154.92, 138.30, 134.75, 132.13, 131.53, 131.14, 129.53 (2×), 129.31, 128.05 (2×), 127.14, 126.67, 126.61, 112.14, 112.03, 111.61, 56.35, 55.76.

4.6. A representative synthetic procedure of compounds 4h–m is as follows

$Pd(PPh_3)_4$ (100 mg) and Na_2CO_3 (64 mg, 0.6 mmol) were added to a solution of compound **9** (110 mg, 0.3 mmol) in DME (10 mL) at rt. Then, $ArB(OH)_2$ **6b–g** (0.6 mmol) was added to the stirred reaction mixture at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with CH_2Cl_2 (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 **4h–m**.

*4.6.1. Compound (**4h**).* Yield 85% (111 mg); colorless solid; mp=72–74 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{27}H_{22}F_3O_2$ 435.1572, found 435.1576; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (br s, 4H), 7.62–7.58 (m, 2H), 7.58–7.53 (m, 4H), 7.47–7.43 (m, 2H), 7.39–7.34 (m, 1H), 7.10–7.06 (m, 2H), 3.87 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.82, 155.57, 142.17, 138.40, 133.64, 133.32, 133.08, 131.09, 129.87 (2×), 129.54 (2×), 129.50, 129.35, 129.20, 128.84, 128.04 (2×), 127.54, 127.10, 126.69, 124.94, 124.91, 111.68, 111.61, 55.74 (2×).

*4.6.2. Compound (**4i**).* Yield 76% (90 mg); colorless gum; HRMS (ESI, M^++1) calcd for $C_{27}H_{25}O_3$ 397.1804, found 397.1810; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.50 (m, 8H), 7.45–7.41 (m, 2H), 7.37–7.32 (m, 1H), 7.06–7.02 (m, 2H), 6.97 (d, J=8.8 Hz, 2H), 3.85 (s, 3H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.75, 155.70 (2×), 138.51, 133.50, 133.42, 130.99, 130.84 (2×), 130.63 (2×), 129.57 (2×), 129.39, 129.18, 128.02 (2×), 127.03, 126.69, 126.27, 113.55 (2×), 111.60, 111.56, 55.75 (2×), 55.28; Anal. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10. Found: C, 81.98; H, 6.48.

*4.6.3. Compound (**4j**).* Yield 81% (89 mg); colorless solid; mp=150–152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{25}H_{22}NO_2$ 368.1651, found 368.1654; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 8.66 (dd, J=2.0, 4.8 Hz, 2H), 7.63–7.52 (m, 8H), 7.47–7.43 (m, 2H), 7.39–7.34 (m, 1H), 7.08 (d, J=8.8 Hz, 1H), 7.07 (dd, J=0.4, 8.4 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.84, 155.65, 149.48 (2×), 146.24, 138.33, 133.72, 132.89, 131.09, 129.50 (2×), 129.28, 128.83, 128.14, 128.02 (2×), 127.95, 127.08, 126.66, 124.30 (2×), 111.78, 111.60, 55.71 (2×).

*4.6.4. Compound (**4k**).* Yield 78% (100 mg); colorless solid; mp =137–138 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{28}H_{27}O_4$ 427.1909, found 427.1911; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.52 (m, 6H), 7.46–7.41 (m, 2H), 7.37–7.33 (m, 1H), 7.15–7.12 (m, 2H), 7.07–7.04 (m, 2H), 6.95 (d, J=8.8 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.69, 155.64, 148.41, 148.24, 138.45, 133.44 (2×), 131.15, 131.00, 130.76, 129.55 (2×), 129.39, 129.20, 128.02 (2×), 127.05, 126.71, 126.42, 121.84, 113.07, 111.59 (2×), 110.91, 55.92, 55.90, 55.78, 55.75; Anal. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14. Found: C, 79.05; H, 6.29. Single-crystal X-ray diagram: crystal of compound **4k** was grown by slow diffusion of EtOAc into a solution of compound **4k** in CH_2Cl_2 to yield colorless prism. The compound crystallizes in the monoclinic crystal system, space group P 1 21/c 1, a=28.750(3) Å, b=6.7540(7) Å, c=11.4864(12) Å, V=2225.0(4) Å^3, Z=4, D_{calcd}=1.273 g/cm^3, F(000)= 904, 2θ range 0.71–26.44°, R indices (all data) R1=0.0864, wR2=0.1252.

*4.6.5. Compound (**4l**).* Yield 72% (85 mg); colorless solid; mp=104 –106 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{27}H_{23}O_3$ 395.1647, found 395.1655; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.94 (d, J=8.4 Hz, 2H), 7.75 (d, J=8.4 Hz, 2H), 7.61–7.52 (m, 6H), 7.45–7.41 (m, 2H), 7.37–7.33 (m, 1H), 7.07 (dd, J=6.4, 8.4 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.08, 155.84, 155.64, 144.99, 138.40, 134.94, 133.70, 133.06, 131.11, 130.23 (2×), 129.54 (2×), 129.48 (2×), 129.36, 129.17, 128.05 (2×), 127.79, 127.11, 126.70, 113.98, 111.76, 111.63, 55.76 (2×).

*4.6.6. Compound (**4m**).* Yield 79% (105 mg); viscous gum; HRMS (ESI, M^++1) calcd for $C_{32}H_{27}O_2$ 443.2011, found 443.2019; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 2H), 7.50–7.43 (m, 10H), 7.38–7.36 (m, 1H), 7.20–7.16 (m, 5H), 7.02 (d, J=8.4 Hz, 1H), 6.78 (d, J=8.4 Hz, 1H), 3.85 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.58, 155.49, 142.14, 141.73, 138.47, 137.08, 133.35, 132.77, 130.96, 130.92, 130.16, 130.06, 129.74, 129.58 (2×), 129.24, 129.02 (2×), 127.98 (2×), 127.64, 127.51 (2×), 127.15, 127.02, 126.52, 126.49, 126.24, 111.54, 111.07, 55.74, 55.10.

4.7. A representative synthetic procedure of compound 11 is as follows

NBS (206 mg, 1.16 mmol) was added to a solution of compound **4a** (73 mg, 0.2 mmol) in MeCN (10 mL) at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with EtOAc (3×30 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 compound **11**.

*4.7.1. Compound (**11**).* Yield 93% (83 mg); colorless solid; mp= 99–101 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{22}BrO_2$ 445.0803, found 445.0814; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.49 (m, 2H), 7.47–7.42 (m, 3H), 7.35–7.30 (m, 6H), 7.28–7.23 (m, 2H), 7.19 (s, 1H), 6.96–6.94 (m, 1H), 3.78 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.70, 138.24, 134.54, 133.08, 132.20, 131.26, 131.13, 130.09, 129.61, 129.59 (2×), 129.36 (2×), 128.62, 128.13, 128.10 (2×), 127.98 (2×), 127.36, 127.00, 121.80, 115.93, 110.62, 56.00, 55.62.

4.8. A representative synthetic procedure of compounds 5a–g is as follows

$Pd(PPh_3)_4$ (100 mg) and Na_2CO_3 (64 mg, 0.6 mmol) were added to a solution of compound **11** (135 mg, 0.3 mmol) in DME (10 mL) at rt. Then, $ArB(OH)_2$ **6a–g** (0.6 mmol) was added to the stirred reaction mixture at rt. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with CH_2Cl_2 (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 **5a–g**.

*4.8.1. Compound (**5a**).* Yield 76% (101 mg); colorless solid; mp=72–74 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{32}H_{27}O_2$ 443.2011, found 443.2018; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.60 (m, 2H), 7.45 (s, 1H), 7.45–7.40 (m, 2H), 7.35–7.23 (m, 11H), 7.13 (dd, J=2.4, 8.4 Hz, 1H), 7.06 (d, J=2.4 Hz, 1H), 7.03 (s, 1H), 6.83 (d, J=8.4 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.47, 154.98, 141.83, 140.64, 138.31, 138.02, 133.29, 132.88, 132.78, 132.57, 129.91 (2×), 129.84, 129.83, 129.70, 129.55 (2×), 129.48 (2×), 128.13 (2×), 128.05 (2×), 127.78 (2×), 127.05, 126.74, 126.62, 113.52, 110.75, 55.81, 55.52; Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92. Found: C, 86.98; H, 6.11.

*4.8.2. Compound (**5b**).* Yield 65% (99 mg); colorless solid; mp=150 –152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{33}H_{26}F_3O_2$ 511.1885, found 511.1891; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.57 (m, 5H), 7.49 (s, 1H), 7.47–7.25 (m, 7H), 7.18–7.15 (m, 3H), 7.02 (s, 1H), 6.97 (d, J=2.0 Hz, 1H), 6.87 (d, J=8.4 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.62, 155.19, 145.65, 139.02, 138.08, 137.75, 133.03, 132.80, 132.53, 130.65, 130.27 (2×), 129.65 (2×), 129.56 (2×), 129.52 (2×), 129.39 (2×), 128.11 (2×), 128.02, 127.83 (2×), 127.25, 126.89, 126.68, 125.11, 113.23, 110.91, 55.85, 55.52.

*4.8.3. Compound (**5c**).* Yield 74% (105 mg); colorless solid; mp=144 –146 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{33}H_{29}O_3$ 473.2117, found 473.2122; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.61 (m, 2H), 7.45–7.41 (m, 2H), 7.44 (s, 1H), 7.36–7.27 (m, 6H), 7.20 (d, J=8.8 Hz, 2H), 7.14–7.10 (m, 2H), 7.02 (s, 1H), 6.87 (d, J=8.8 Hz, 2H), 6.85 (d, J=8.4 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.55, 155.47, 154.93, 140.27, 138.35, 138.07, 134.18, 133.49, 132.89, 132.67, 132.53, 130.96 (2×), 129.87, 129.78, 129.55 (2×), 129.52 (2×), 128.03 (2×), 127.80 (2×), 127.00, 126.76 (2×), 113.63 (2×), 113.43, 110.76, 55.80, 55.53, 55.32.

*4.8.4. Compound (**5d**).* Yield 70% (93 mg); viscous gum; HRMS (ESI, M^++1) calcd for $C_{31}H_{26}NO_2$ 444.1964, found 444.1970; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.68–8.65 (m, 2H), 7.65–7.52 (m, 12H), 7.47–7.43 (m, 3H), 7.13 (dd, J=2.4, 8.4 Hz, 1H), 7.06 (d, J=2.4 Hz, 1H), 3.97 (s, 3H), 3.77 (s, 3H).

*4.8.5. Compound (**5e**).* Yield 62% (93 mg); colorless solid; mp=183 –185 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{34}H_{31}O_4$ 503.2222, found 503.2225; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J=7.2 Hz, 2H), 7.45 (s, 1H), 7.43 (d, J=7.6 Hz, 2H), 7.38–7.33 (m, 4H), 7.31–7.27 (m, 1H), 7.19 (d, J=2.4 Hz, 2H), 7.09 (dd, J=2.4, 8.4 Hz, 1H), 7.02 (s, 1H), 6.94 (dd, J=2.0, 8.4 Hz, 1H), 6.88 (d, J=8.0 Hz, 1H), 6.84 (d, J=8.8 Hz, 1H), 6.69 (d, J=1.6 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.79 (s, 3H), 3.62 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.51, 154.98, 148.29, 147.96, 140.31, 138.29, 127.98, 134.31, 133.66, 132.87, 132.61, 132.45, 130.07, 129.86, 129.62, 129.52 (2×), 129.43 (2×), 128.04 (2×), 127.88 (2×), 127.03, 126.83, 121.80, 113.77, 113.15, 110.99, 110.80, 55.93, 55.81, 55.66, 55.59.

*4.8.6. Compound (**5f**).* Yield 72% (102 mg); colorless solid; mp=193–194 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{33}H_{27}O_3$ 471.1960, found 471.1969; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.83 (d, J=8.4 Hz, 2H), 7.62–7.60 (m, 2H), 7.47 (s, 1H), 7.46–7.42 (m, 4H), 7.37–7.24 (m, 6H), 7.08 (s, 1H), 7.07 (dd, J=2.4, 10.0 Hz, 1H), 7.03 (s, 1H), 6.82 (d, J=8.4 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.93, 155.65, 155.26, 148.37, 139.13, 138.08, 137.69, 134.63, 133.16, 132.78, 132.72, 132.56, 130.79, 130.60 (2×), 130.20, 129.83, 129.55 (2×), 129.52 (2×), 129.38 (2×), 128.11 (2×), 127.87 (2×), 127.27, 126.91, 113.17, 110.88, 55.87, 55.53.

*4.8.7. Compound (**5g**).* Yield 80% (124 mg); viscous gum; HRMS (ESI, M^++1) calcd for $C_{38}H_{31}O_2$ 519.2324, found 519.2332; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.58–7.21 (m, 17H), 7.21–7.01 (m, 3H), 6.85–6.77 (m, 2H), 6.64–6.62 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H).

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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.2012.10.039.

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