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Synthesis of 2,3-diiodoindenes and their applications in construction of 13*H*-indeno[1,2-*l*]phenanthrenes

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ABSTRACT

A series of 2,3-diiodoindene were synthesized at first, and 13*H*-indeno[1,2-*l*]phenanthrenes were then constructed via a Suzuki coupling reaction and subsequently a Scholl reaction. Structures of synthesized compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. Their photophysical properties, such as UV–vis and FL spectra were investigated, and electronic properties were theoretically calculated by the software of Gaussian 03. The results suggested that these modified indene and indenophenanthrene compounds might have potential applications as light emitting materials.

1. Introduction

Polysubstituted indene has played an important role in chemical and pharmaceutical industries.[1] Recently, efficient methods for the synthesis of various carbo- and heterocyclic compounds through electrophilic cyclization of appropriate *ortho*-functionalized aromatic acetylenes have been developed.[2–11] Due to the excellent alkynophilicity of molecular iodine, much attention has been paid to iodine-based alkyne activation as an attractive protocol for developing new and efficient iodocyclizations. Many important carbo- and heterocyclic compounds, such as furans,[2] benzofurans,[3] pyrones,[4] isocoumarins,[5] pyrroles,[6] indoles,[7] quinolines, isoquinolines,[8] isoxazoles,[9] benzo[*b*]thiophenes,[10] naphthalenes, and naphthols[11] have been synthesized based on this strategy. Thus, iodine-mediated electrophilic cyclizations continue to be an area of active research in the field of synthetic chemistry.

However, almost all of these iodine-mediated electrophilic cyclizations could only construct monoiodonated compounds, and rare works were reported about the synthesis of diiodonated compounds. Recently, Liang's group has reported an iodine-mediated construction of diiodinated carbocycles and oxygen heterocycles via electrophilic carbocyclization of aryl propargylic alcohols, and mentioned that the diiodinated products can be used to prepare more complex products by using known organopalladium chemistry.[12] Herein, we are pleased to report a similar proposal of the synthesis of diiodonated carbocyclic compounds in good to excellent yields under normal reaction condition, the application of the construction of 13*H*-indeno[1,2-l]phenanthrenes, which could be used as potential light emitting materials.

2. Results and discussion

2.1. Iodine-mediated construction of 2,3-diiodoindenes

Firstly we examined the reaction between 2-methyl-4-phenylbut-3-yn-2-ol (**1a**) and molecular iodine, it led to the formation of 2,3-diiodo-1,1-dimethyl-1*H*-indene (**2a**) in methylene chloride solution at 25 °C as expected.[12] The skeleton of 2,3-diiodo-1*H*-indene was comparatively established by the single crystal analysis of **2e** (Fig. 1). So, we tried to optimize the reaction conditions for this transformation, and the result was listed in Table 1. Initially, we tested the molar ratio of iodine to **1a**. The suitable ratio of iodine to **1a** was found to be 3:1 (Table 1, entries 1–3). The dehydration product, enyne (**3a**) was observed as a by-product. When the reaction was conducted in dry dichloromethane (DCM), trace amount of **2a** could be detected while most of **1a** was remained (Table 1, entry 4). It meant that trace of water was necessary for this reaction to be proceeded. Subsequently, the reaction was tested in other solvents (Table 1, entries 5–10). It was indicated that dichloroethane (DCE) and acetonitrile (MeCN) were also benefited to this reaction as DCM did. Both the reaction temperature and the reaction time played key roles in this transformation (Table 1, entries 11–15). By lowering the temperature of the reaction to

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−20 °C and extending the reaction time to 12 h, the yield of **2a** increased up to 95% (Table 1, entry 15). In this case, the formation of **3a** was effectively inhibited. Finally, the optimized reaction condition was established as **1** (0.30 mmol) and iodine (0.90 mmol, 3 equiv) were mixed in DCM at −20 °C for a certain period of time.

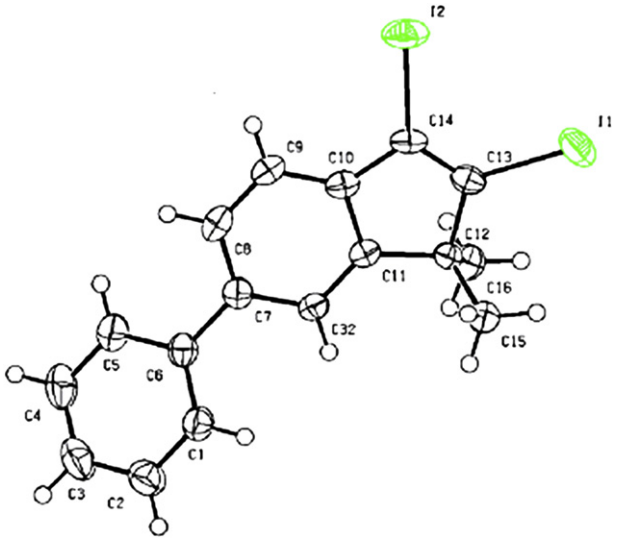
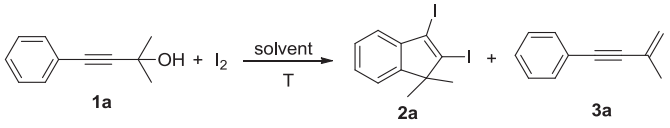


Fig. 1. ORTEP image of **2e**.

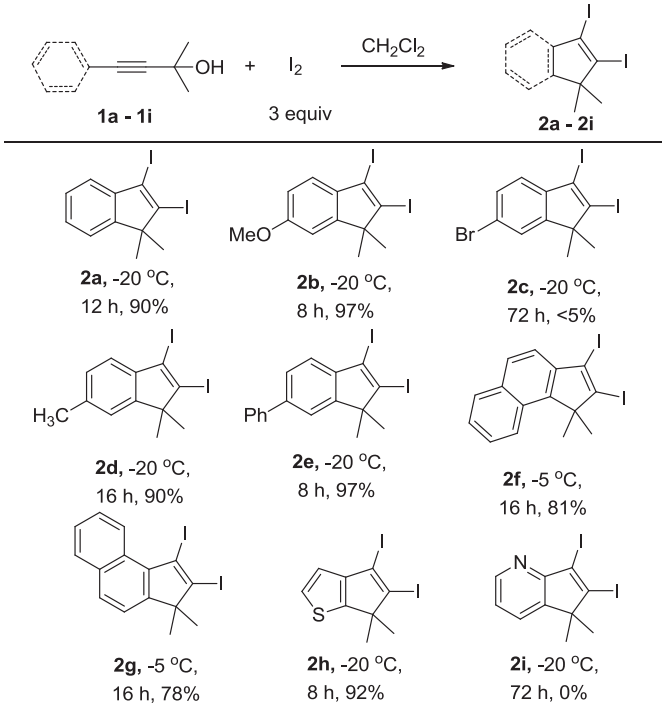
Table 1
Optimization of the reaction conditions for the iodine-mediated electrophilic cyclizations of **1a**[a]



Entry	Solvent	Time (h)	Temp (°C)	**2a** (%)[b]	**3a** (%)[b]
1[c]	DCM	4	25	30	8
2[d]	DCM	1	25	32	15
3	DCM	0.75	25	73	12
4	DCM (dry)	36	25	Trace	—
5	MeCN	0.75	25	72	9
6	DCE	0.75	25	71	18
7	$CHCl_3$	0.75	25	20	46
8	CCl_4	18	25	19	39
9	Hexane	16	25	45	<5
10	Ethyl acetate	5	25	21	21
11	DCM	1	20	73	12
12	DCM	5	10	83	<5
13	DCM	8	0	92	<5
14	DCM	10	−10	94	<5
15	DCM	12	−20	95	<5

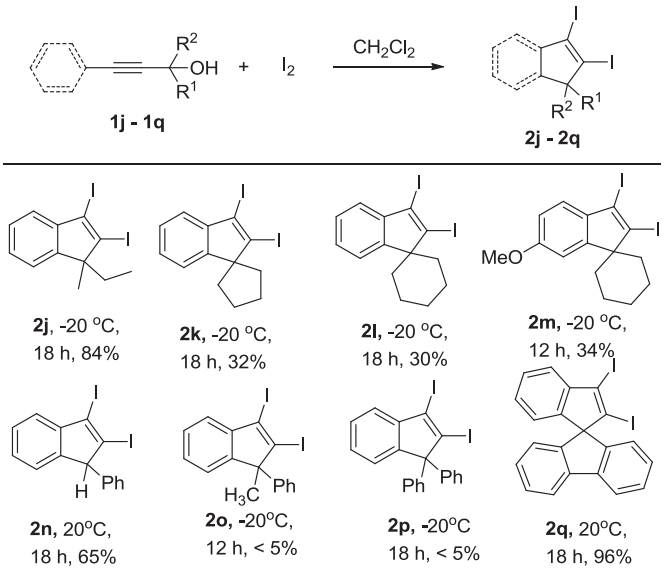
[a] All reactions were run under the following condition, unless otherwise indicated: **1a** (0.30 mmol) and I_2 (0.90 mmol, 3.0 equiv) in relevant solvent (3 mL).
[b] Isolated yield.
[c] I_2 (1.0 equiv, 0.30 mmol).
[d] I_2 (1.5 equiv, 0.75 mmol).

Under the optimized reaction condition in hand, we tested the substrate diversity. Firstly, we tested the aromatic part of the propargylic alcohol of **1** (Scheme 1). Electronic effect was significant. When the *para*-substituent of the aryl of **1** was electron donating, it was benefited to this cyclization. Yields of **2b**, **2d**, and **2e** were determined to be 97%, 90%, and 97%, respectively. As a comparison, the bromo-substituted propargylic alcohol **1c** only afforded **2c** in a trace amount even though the reaction time was extended to 72 h. In addition, cyclization to the thiophene ring worked completely, while the reaction did not work for the pyridine ring because of the electron deficient.



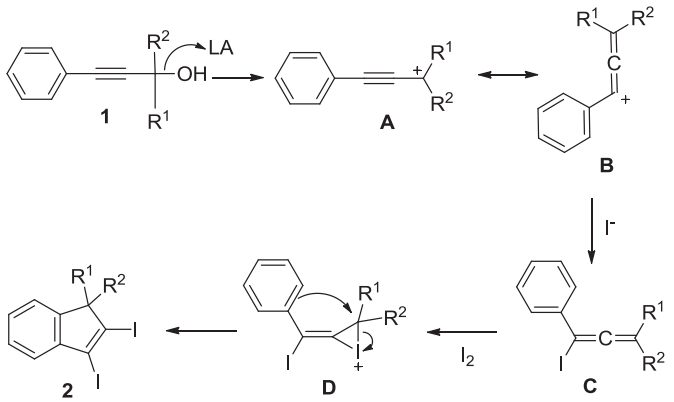
Scheme 1. Effect of aromatic part of propargylic alcohols (**1a**–**i**) on the cyclization.

Secondly, we investigated the effect of R^1 and R^2 of propargylic alcohols (**1j**–**q**) (Scheme 2). Compound **1j** could be transferred into **2j** in 84% yield under optimized reaction condition. With cycloalkyl substituents, **1k**–**m** afforded the desired spiro products **2k**–**m**, but in relatively lower yield. Interestingly, when R^1 was phenyl and R^2 was H, the corresponding 2,3-diiodoindene **2n** could be isolated in yield of 65%. When R^1 was phenyl, R^2 was methyl or phenyl, only trace of corresponding 2,3-diiodoindene (**2o** and **2p**, respectively) could be detected by TLC. It was also noticeable that **2q** could be isolated in 96% yield. In this case, the two aryl groups were fixed.



Scheme 2. Effect of R^1 and R^2 of propargylic alcohols (**1j**–**q**) on the cyclization.

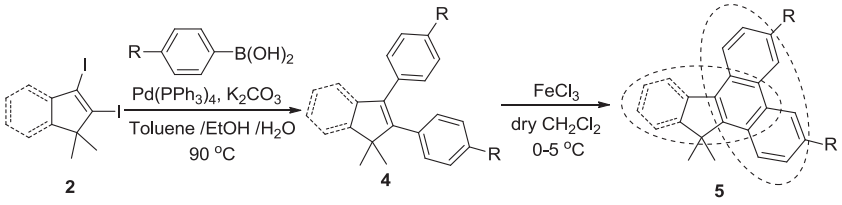
Based on the observation above, we proposed a possible mechanism for this iodine-mediated cyclization (Scheme 3). In the presence of trace amount of water, iodine[13] acted as a Lewis acid to generate the propargylic carbocation **A**, which possessed an allenic carbocation **B** via Meyer–Schuster rearrangement.[14] **B** subsequently abstracted the iodide to form iodoallene **C**. Iodination on the electron richer double bond of **C** created an iodonium intermediate **D**. Finally, intramolecular Friedel–Crafts alkylation of **D** afforded the final product **2**.



Scheme 3. Proposed mechanism for the formation of **2**.

2.2. Extension of indene to construct the skeleton of indenophenanthrenes

As the importance of polycyclic aromatic hydrocarbons (PAHs),[15] in optoelectronic materials, it could be a potential application of **2** for the synthesis of materials for organic solar cells and organic light emitting diodes.[16] Compound **2** could be easily converted into **5** as shown in Scheme 4. Compounds **5** are typical aromatic hydrocarbons (PAHs) that possess both fluorene and phenanthrene skeletons. In this synthetic route, **2** was firstly applied for synthesizing 2,3-diarylindenes **4** via Suzuki coupling.[17] (4-Alkoxyphenyl)boronic acid was used for the Suzuki coupling as the subsequent Scholl reaction could only be conducted with electron-rich aromatic system.[18] Finally, **5** could be obtained in relatively high yield. By this sequential method, 2,3-diarylindenes **4a**–**i** and 13*H*-indeno[1,2-*l*]phenanthrenes **5a**–**i** (Scheme 5) are constructed for photophysical investigation.



Scheme 4. Synthetic strategy of the synthesis of 13*H*-indeno[1,2-*l*]phenanthrenes **5**.

2.3. Photophysical properties of diarylindenes and indenophenanthrenes

Photophysical data of **4** and **5** were summarized in Table 2. The UV–vis absorption wavelengths of **4a**–**h** and **5a**–**h** were shown in Table 2, while the spectra of **4a**–**h** and **5a**–**h** were given in Supplementary data. The absorptive spectra of these compounds were complex with multiple overlapping broad bands. With the similar conjugation lengths, all the absorptive bands of **4** exhibited similar patterns and the maximum absorptive wavelengths were focused around 300 nm, which was attributed to indene skeleton of **4**. The electron-donating group, such as methoxy, had little influence on the absorption spectra of **4**. However, they moved to about 350 nm after the intramolecularly oxidative coupling. Absorption around 350 nm might be assigned to $\pi-\pi^*$ transition of the indenephenanthrene core of **5**.[19] This was also noticeable that there was a relatively tiny shoulder peak at about 380 nm, which might be the contribution of the lone pair electrons of the oxygen via intramolecular charge transfer.[20] These results were matched with the energy gap calculated by the software of Gaussian 03 on the basis set of B3LYP/6-31G(d), which was shown in Table 2.

Emissive spectra of **4a**–**h** and **5a**–**h** were measured in cyclohexane and the results were listed in Table 2. Emission spectra of **4** and **5** were slightly changed even though their skeletons were altered from indene to indenephenanthrene. For example, the emissive spectra of **4a** and **5a** were almost similar with a light emitting at 436 nm. Similar phenomenon was observed in the previous study, which was reported by Hursthouse's group.[20] However, the quantum yield was increased significantly after the oxidative coupling. It might be explained by the decreased non-radiative decay of the excited state in the rigid indenophenanthrene system of **5**.

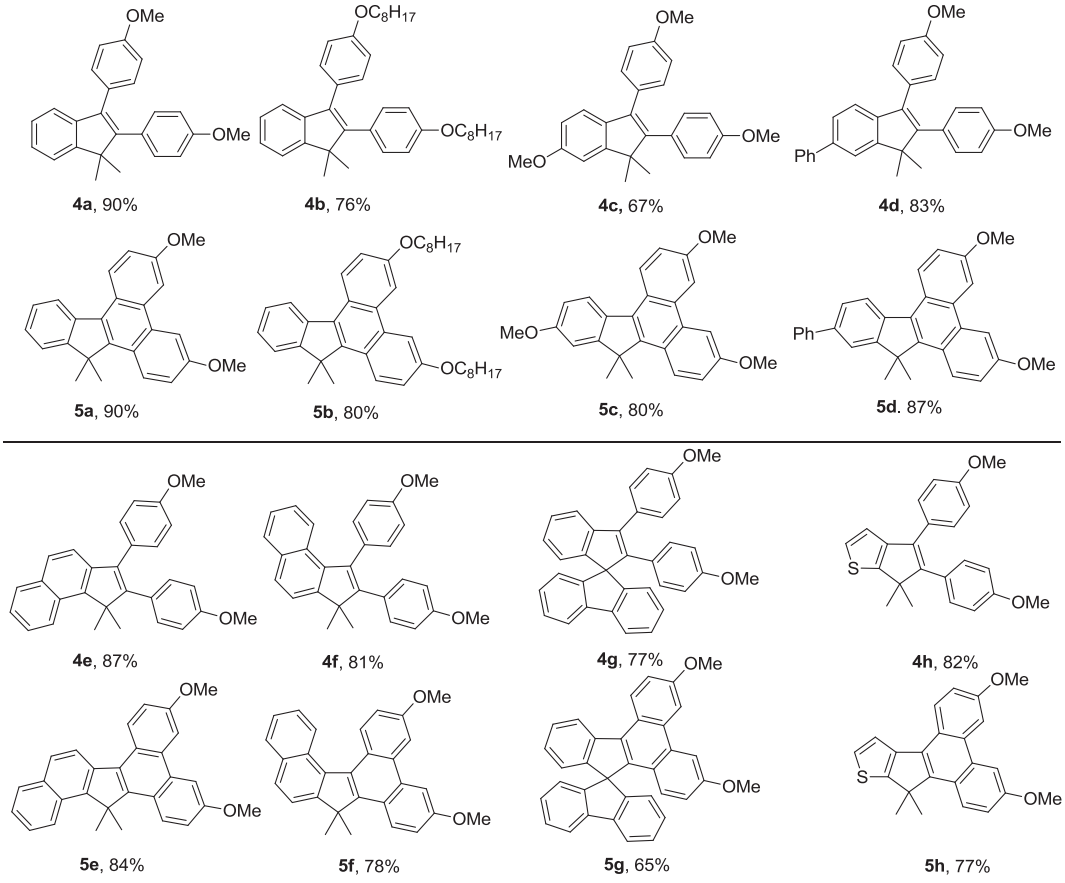
3. Conclusions

In conclusion, an efficient synthesis of highly substituted 2,3-diiodoindenes **2** from substituted propargylic alcohols has been developed. In this reaction, trace amounts of water are necessary and both iodine atoms are used efficiently. Moreover, 13*H*-indeno[1,2-*l*]phenanthrenes **5** could be constructed easily from the substituted 2,3-diiodoindenes **2** via Suzuki coupling reaction and the subsequential Scholl oxidative coupling. By the investigation of their photophysical properties, compounds **4** and **5** show potential applications as light emitting materials.

4. Experimental

4.1. General

Melting points were measured with micro melting point apparatus. NMR spectra were recorded for ^{1}H NMR at 400 or 500 MHz, using TMS as internal standard and ^{13}C NMR at 100 or 125 MHz using $CDCl_3$ as internal standard. The following abbreviations are used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants are reported in Hertz (Hz). All high-resolution mass spectra (HRMS) were obtained using EI ionization. Flash column chromatography was performed employing 300–400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel. Fluorescence measurements were made with an RF-5301pc spectrofluorometer (Shimadzu, Kyoto, Japan) equipped with a xenon lamp. UV–vis absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. The solvents were distilled before used. Commercially available reagents were used without further purification unless otherwise.



Scheme 5. Structures of 2,3-diarylindenes **4a**–**h** and 13*H*-indeno[1,2-*l*]phenanthrenes **5a**–**h**.

Table 2
Absorption and emission data of **4** and **5**, as well as their calculated energy levels

Cpds.	λ_{abs}[a]/nm ($\varepsilon\times10^{-5}$ M^{-1} cm^{-1})	λ_{em}[a]/nm	Φ[b]	HOMO/LUMO[c] (eV)
4a	283 (0.138)	391, 413, 436	0.09	−5.14/−0.73
4b	271 (0.444)	390, 412, 435	0.11	−5.07/−0.70
4c	296 (0.090)	398, 420, 446	0.12	−4.92/−0.59
4d	305 (0.173)	417	0.06	−5.10/−0.96
4e	321 (0.061), 336 (0.059)	419	0.11	−5.07/−1.04
4f	321 (0.060), 336 (0.059)	419	0.11	−5.02/−1.02
4g	314 (0.187)	437	0.06	−5.05/−0.91
4h	296 (0.070)	433	0.02	−5.00/−0.73
5a	328 (0.313), 342 (0.310), 368 (0.065), 388 (0.066)	391, 413, 437	0.19	−4.94/−1.05
5b	330 (0.204), 343 (0.197), 368 (0.045), 388 (0.043)	390, 412, 436	0.24	—
5c	331 (0.156), 345 (0.155), 374 (0.029), 394 (0.028)	398, 421, 443	0.23	−4.76/−0.94
5d	344 (0.075), 389 (0.018)	392, 413, 434	0.37	−4.92/−1.19
5e	331 (0.116), 371 (0.048), 391 (0.047)	396, 419, 442	0.26	−4.89/−1.17
5f	329 (0.118), 348 (0.118), 370 (0.048), 391 (0.047)	396, 418, 442	0.26	−4.80/−1.25
5g	335 (0.097), 348 (0.091), 386 (0.024)	389, 410, 437	0.21	−5.02/−1.88
5h	346 (0.069), 371 (0.018), 391 (0.017)	402, 426, 449	0.12	−4.83/−0.93

[a] Absorption and emission spectra were measured in cyclohexane (1×10^{-5} M).
[b] Fluorescence quantum yields were calculated using DPA as standard.
[c] The results were calculated via the software of Gaussian 03 on the basis set of B3LYP/6-31G(d).

4.2. General procedure for the synthesis of compounds 2

These compounds were obtained following an essentially similar procedure. An illustrative example is provided for **2a**.

Compound **2a**: To a solution of CH_2Cl_2 (5 mL), was added 2-methyl-4-phenylbut-3-yn-2-ol (0.25 mmol). After the solution was cooled down to −20 °C for 10 min, 3 equiv of I_2 was added. The reaction mixture was allowed to stir at required temperature for the desired time. The excess I_2 was removed by saturated $Na_2S_2O_3$ solution. The aqueous solution was then extracted by dichloromethane (2×10 mL). The combined dichloromethane layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum The residue was purified through column chromatography (silica gel, hexane/ethyl acetate as eluent) to afford a yellow oil.

4.2.1. Compound ***2a***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m, 4H), 1.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.23, 144.02, 129.52, 127.65, 126.53, 123.43, 121.90, 106.79,

56.46, 25.91. HRMS: calcd for $C_{11}H_{10}I_2$ [M^+] (m/z) 395.8872, found 395.8879.

4.2.2. Compound ***2b***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J=8.3 Hz, 1H), 6.89 (d, J=2.3 Hz, 1H), 6.79 (dd, J=8.3, 2.3 Hz, 1H), 3.84 (s, 3H), 1.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.26, 151.60, 137.34, 125.61, 124.01, 112.31, 108.82, 105.91, 56.34, 55.98, 26.12. HRMS: calcd for $C_{12}H_{12}I_2O$ [M^+] (m/z) 425.8978, found 425.8976.

4.2.3. Compound ***2d***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 1H), 7.13–7.09 (m, 1H), 7.08–7.02 (m, 1H), 2.38 (s, 3H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.25, 141.58, 136.48, 128.25, 127.94, 123.06, 122.73, 106.57, 56.17, 25.98, 21.80. HRMS: calcd for $C_{12}H_{12}I_2$ [M^+] (m/z) 409.9028, found 409.9031.

4.2.4. Compound ***2e***. Yellow solid: mp 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J=7.2 Hz, 2H), 7.54–7.48 (m, 2H), 7.45 (t, J=7.5 Hz, 2H), 7.39–7.32 (m, 2H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.75, 143.32, 141.31, 139.80, 129.49, 129.19, 127.71, 127.62, 126.74, 123.62, 120.81, 106.33, 56.62, 26.01. HRMS: calcd for $C_{17}H_{14}I_2$ [M^+] (m/z) 471.9185, found 471.9183.

4.2.5. Compound ***2f***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65–9.58 (m, 1H), 7.85 (d, J=8.2 Hz, 1H), 7.76 (d, J=8.3 Hz, 1H), 7.61–7.55 (m, 1H), 7.50–7.42 (m, 2H), 1.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.25, 135.18, 133.77, 133.69, 129.19, 127.88, 127.72, 126.17, 125.65, 123.27, 120.05, 101.08, 56.28, 25.85. HRMS: calcd for $C_{15}H_{12}I_2$ [M^+] (m/z) 445.9029, found 445.9025.

4.2.6. Compound ***2g***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, J=8.7 Hz, 1H), 7.87 (d, J=8.2 Hz, 1H), 7.78 (d, J=8.3 Hz, 1H), 7.59 (t, J=7.7 Hz, 1H), 7.52–7.43 (m, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.24, 135.17, 133.77, 133.58, 129.19, 127.88, 127.72, 126.17, 125.65, 123.26, 120.04, 101.08, 56.27, 25.85. HRMS: calcd for $C_{15}H_{12}I_2$ [M^+] (m/z) 445.9029, found 445.9023.

4.2.7. Compound ***2h***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J=4.7 Hz, 1H), 6.88–6.81 (m, 1H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.87, 148.54, 126.89, 124.34, 120.34, 98.73, 55.78, 26.84. HRMS: calcd for $C_9H_8I_2S$ [M^+] (m/z) 401.8436, found 401.8428.

4.2.8. Compound ***2j***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.17 (m, 4H), 1.94–1.68 (m, 2H), 1.24 (s, 3H), 0.30 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.14, 145.40, 127.90, 127.62, 126.42, 123.26, 121.92, 107.13, 60.52, 32.21, 25.49, 8.29. HRMS: calcd for $C_{12}H_{12}I_2$ [M^+] (m/z) 409.9028, found 409.9033.

4.2.9. Compound ***2k***. Yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J=7.5 Hz, 1H), 7.29–7.24 (m, 2H), 7.22–7.12 (m, 1H), 2.17–1.96 (m, 6H), 1.83–1.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.90, 143.82, 129.92, 127.38, 126.55, 123.21, 121.45, 106.63, 66.49, 37.52, 27.04. HRMS: calcd for $C_{13}H_{12}I_2$ [M^+] (m/z) 421.9028, found 445.9029.

4.2.10. Compound ***2l***. Yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J=7.6 Hz, 1H), 7.34 (m, J=12.2, 8.2, 3.8 Hz, 2H), 7.17 (m, J=7.5, 1.2 Hz, 1H), 2.12–1.78 (m, 7H), 1.52–1.37 (m, 1H), 1.21 (dd, J=8.3, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.52, 144.93, 132.46, 127.71, 125.27, 123.94, 123.82, 107.81, 58.99, 33.78, 25.25, 22.44. HRMS: calcd for $C_{14}H_{14}I_2$ [M^+] (m/z) 435.9185, found 435.9182.

4.2.11. Compound ***2m***. Yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J=2.1 Hz, 1H), 7.25 (d, J=3.5 Hz, 1H), 6.84 (dd, J=8.3, 2.2 Hz, 1H), 3.85 (s, 3H), 2.07–1.77 (m, 7H), 1.41 (dt, J=12.8, 3.8 Hz, 1H), 1.28–1.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.88, 149.61, 138.30, 128.76, 124.17, 112.06, 111.33, 106.92, 58.76, 56.00, 33.70, 25.17, 22.20. HRMS: calcd for $C_{15}H_{16}I_2O$ [M^+] (m/z) 465.9291, found 465.9286.

4.2.12. Compound ***2n***. Yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J=7.3 Hz, 1H), 7.53–7.40 (m, 5H), 7.25–7.15 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.57, 147.94, 140.83, 134.86, 129.06, 129.02, 128.85, 128.42, 127.03, 126.25, 121.09, 104.23, 35.05. HRMS: calcd for $C_{15}H_{10}I_2$ [M^+] (m/z) 443.8872, found. 443.8867.

4.2.13. Compound ***2q***. Yellow solid: mp 155–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J=7.6 Hz, 2H), 7.41 (t, J=7.4 Hz, 3H), 7.30 (t, J=7.6 Hz, 2H), 7.18 (t, J=7.5 Hz, 2H), 7.01 (t, J=7.5 Hz, 1H), 6.80 (d, J=7.6 Hz, 1H), 6.63 (d, J=7.5 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 146.97, 146.18, 144.55, 142.49, 128.92, 128.39, 127.38, 124.13, 123.37, 123.22, 120.65, 120.52, 110.29, 75.01. HRMS: calcd for $C_{21}H_{12}I_2$ [M^+] (m/z) 517.9028, found 517.9022.

4.3. General procedure for the synthesis of compounds 4

These compounds were obtained following an essentially similar procedure. An illustrative example is provided for **4a**.

Compound **4a**: To a well-mixed solution of toluene (9 mL), water (5 mL), and ethanol (1 mL), were added 2,3-diiodo-1,1-dimethyl-1*H*-indene (1 mmol), (4-methoxyphenyl)boronic acid (2.5 mmol), and potassium carbonate (10 mmol) in was added. The reaction mixture was stirred for 2 min. After the solution was purged with nitrogen for half an hour, a catalytic amount of $Pd(PPh_3)_4$ (0.5 mol %) was added and the flask was flushed with N_2, sealed and allowed to stir at 90 °C for 48 h. The resulting reaction mixture was concentrated under vacuum and then was extracted with dichloromethane (3×25 mL). The combined dichloromethane extracts were washed with water, dried over anhydrous $MgSO_4$, and then concentrated under vacuum. The residue was purified through column chromatography (silica gel, hexane/ethyl acetate as eluent) to afford a white solid.

4.3.1. Compound ***4a***. White solid: mp 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.32 (m, 2H), 7.29–7.18 (m, 4H), 7.11–7.05 (m, 2H), 6.85–6.77 (m, 4H), 3.77 (d, J=2.8 Hz, 6H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.71, 158.64, 153.72, 152.51, 143.34, 137.40, 131.23, 130.97, 129.43, 127.97, 126.76, 125.53, 121.78, 120.82, 113.86, 113.80, 55.43, 51.51, 24.95. HRMS: calcd for $C_{25}H_{24}O_2$ [M^+] (m/z) 356.1776, found 356.1771.

4.3.2. Compound ***4b***. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 2H), 7.24 (t, J=4.2 Hz, 2H), 7.19 (d, J=8.5 Hz, 2H), 7.06 (d, J=8.5 Hz, 2H), 6.79 (d, J=8.5 Hz, 4H), 3.91 (t, J=6.5 Hz, 4H), 1.82–1.71 (m, 4H), 1.48–1.27 (m, 26H), 0.88 (t, J=6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.29, 158.22, 153.74, 152.51, 143.41, 137.35, 131.20, 130.94, 129.22, 127.75, 126.74, 125.47, 121.77, 120.82, 114.36, 114.29, 68.16, 51.50, 32.17, 29.73, 29.68, 29.59, 26.44, 24.97, 23.01, 14.46. HRMS: calcd for $C_{39}H_{52}O_2$ [M^+] (m/z) 552.3967, found 552.3973.

4.3.3. Compound ***4c***. Yellow solid: mp 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (q, J=3.8 Hz, 1H), 7.20 (d, J=8.4 Hz, 2H), 7.07 (d, J=8.4 Hz, 2H), 6.98 (d, J=2.1 Hz, 1H), 6.86–6.76 (m, 5H), 3.86 (s, 3H), 3.78 (d, J=2.9 Hz, 6H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.61, 155.64, 150.46, 136.88, 136.37, 131.34, 130.90, 129.62, 128.20, 121.28, 113.84, 113.76, 111.57, 108.75, 55.92, 55.42, 51.40, 25.21. HRMS: calcd for $C_{26}H_{26}O_3$ [M^+] (m/z) 386.1882, found 386.1886.

4.3.4. Compound ***4d***. Yellow solid: mp 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.61 (m, 3H), 7.55–7.40 (m, 4H), 7.34 (t, J=7.3 Hz, 1H), 7.24 (d, J=7.7 Hz, 3H), 7.10 (d, J=8.6 Hz, 2H), 6.83 (d,

J=8.6 Hz, 4H), 3.79 (s, 6H), 1.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.78, 158.72, 154.40, 152.95, 142.72, 142.20, 138.81, 137.20, 131.23, 130.97, 129.40, 129.07, 127.96, 127.57, 127.24, 125.96, 121.06, 120.77, 113.94, 113.84, 55.46, 51.68, 25.07. HRMS: calcd for $C_{31}H_{28}O_2$ [M^+] (m/z) 432.2089, found 432.2092.

4.3.5. Compound ***4e***. Yellow solid: mp 189–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J=8.2 Hz, 1H), 7.78 (d, J=8.2 Hz, 1H), 7.59 (d, J=8.2 Hz, 1H), 7.51 (d, J=8.6 Hz, 1H), 7.33 (t, J=7.5 Hz, 1H), 7.22–7.11 (m, 3H), 7.04 (d, J=8.6 Hz, 2H), 6.84 (d, J=8.6 Hz, 2H), 6.78 (d, J=8.6 Hz, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.71, 158.53, 155.35, 151.49, 139.42, 137.73, 134.01, 131.45, 131.19, 130.63, 129.20, 129.02, 128.97, 126.43, 125.43, 124.78, 124.76, 120.38, 113.85, 113.59, 55.46, 55.40, 51.49, 24.28. HRMS: calcd for $C_{29}H_{26}O_2$ [M^+] (m/z) 406.1933, found 406.1942.

4.3.6. Compound ***4f***. Yellow solid: mp 189–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=8.2 Hz, 1H), 7.78 (d, J=8.3 Hz, 1H), 7.59 (d, J=8.2 Hz, 1H), 7.51 (d, J=8.6 Hz, 1H), 7.33 (t, J=7.2 Hz, 1H), 7.23–7.11 (m, 3H), 7.04 (d, J=8.7 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 6.78 (d, J=8.7 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.72, 158.54, 155.35, 151.49, 139.43, 137.73, 134.02, 131.45, 131.19, 130.64, 129.21, 129.03, 128.98, 126.43, 125.44, 124.79, 124.76, 120.39, 113.85, 113.59, 55.47, 55.41, 51.50, 24.28. HRMS: calcd for $C_{29}H_{26}O_2$ [M^+] (m/z) 406.1933, found 406.1927.

4.3.7. Compound ***4g***. White solid: mp 250–253 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J=7.6 Hz, 2H), 7.40 (t, J=7.8 Hz, 3H), 7.33 (t, J=7.5 Hz, 2H), 7.21 (d, J=7.5 Hz, 1H), 7.14 (t, J=7.5 Hz, 2H), 7.06–6.91 (m, 5H), 6.58 (d, J=7.5 Hz, 1H), 6.52 (d, J=8.2 Hz, 2H), 6.35 (d, J=8.4 Hz, 2H), 3.84 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.18, 158.40, 149.20, 146.99, 145.92, 144.88, 142.53, 141.66, 131.17, 130.12, 128.23, 128.05, 127.95, 127.29, 126.25, 123.98, 122.59, 120.71, 120.52, 114.41, 113.30, 70.35, 55.53, 55.10. HRMS: calcd for $C_{35}H_{26}O_2$ [M^+] (m/z) 478.1993, found 478.1991.

4.3.8. Compound ***4h***. Yellow solid: mp 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, J=11.8, 7.3 Hz, 3H), 7.09 (dd, J=6.1, 4.9 Hz, 3H), 6.84 (d, J=8.4 Hz, 2H), 6.76 (d, J=8.5 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 1.40 (s, 6H); ^{13}C NMR (101 MHz, CD_3Cl) δ 158.75, 158.59, 154.14, 152.33, 146.06, 134.22, 131.37, 130.13, 129.66, 128.47, 126.37, 120.01, 113.97, 113.75, 55.28, 50.92, 25.81. HRMS: calcd for $C_{23}H_{23}O_2S$ [M^+] (m/z) 362.1341, found 362.1343.

4.4. General procedure for the synthesis of the compounds 5

These compounds were obtained following an essentially similar procedure. An illustrative example is provided for **5a**.

Compound **5a**: A solution of 2,3-bis(4-methoxyphenyl)-1,1-dimethyl-1*H*-indene (0.1 mmol) in dichloromethane (10 mL) was cooled to ~0 °C. After the solution was purged with nitrogen for half an hour, $FeCl_3$ (0.5 mol) was added and the flask was flushed with N_2, sealed and allowed to stir at required temperature for the desired time. After completion of the reaction, it was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The dichloromethane layer was separated, washed with water and brine solution, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The residue was purified through column chromatography (silica gel, hexane/ethyl acetate as eluent) to afford a white solid.

4.4.1. Compound ***5a***. Yellow solid: mp 147–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, J=9.0 Hz, 1H), 8.34 (d, J=7.8 Hz, 1H), 8.26 (d, J=9.0 Hz, 1H), 8.10 (t, J=2.2 Hz, 2H), 7.58 (d, J=7.4 Hz, 1H), 7.51–7.42 (m, 1H), 7.36 (m, 3H), 4.03 (s, 6H), 1.75 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.81, 157.74, 156.71, 145.42, 140.35, 132.38, 132.27, 130.48, 127.25, 127.03, 126.41, 126.19, 124.53, 124.18, 122.88, 122.32, 116.62, 116.42, 106.21, 106.01, 55.84, 48.24, 26.88. HRMS: calcd for $C_{25}H_{22}O_2$ [M^+] (m/z) 354.1620, found 354.1629.

4.4.2. Compound ***5b***. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J=9.1 Hz, 1H), 8.34 (d, J=7.7 Hz, 1H), 8.24 (d, J=8.9 Hz, 1H), 8.10 (s, 2H), 7.58 (d, J=7.5 Hz, 1H), 7.49–7.43 (m, 1H), 7.36 (m, 3H), 4.21 (t, J=6.4 Hz, 4H), 1.99–1.84 (m, 4H), 1.75 (s, 5H), 1.56 (dt, J=13.5, 6.7 Hz, 4H), 1.49–1.27 (m, 17H), 0.90 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.38, 156.71, 145.32, 140.44, 132.47, 132.34, 130.35, 127.93, 127.21, 126.89, 126.27, 126.09, 124.40, 124.03, 122.85, 122.27, 116.89, 116.68, 107.16, 106.98, 68.64, 48.20, 32.19, 29.79, 29.64, 26.89, 26.51, 23.03, 14.46. HRMS: calcd for $C_{39}H_{50}O_2$ [M^+] (m/z) 550.3811, found 550.3816.

4.4.3. Compound ***5c***. Yellow solid: mp 215–217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J=9.0 Hz, 1H), 8.23 (d, J=8.8 Hz, 2H), 8.09 (d, J=2.2 Hz, 2H), 7.35 (m, 2H), 7.13 (d, J=2.3 Hz, 1H), 6.98 (dd, J=8.5, 2.3 Hz, 1H), 4.03 (d, J=2.0 Hz, 6H), 3.92 (s, 3H), 1.74 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.84, 158.81, 157.68, 157.45, 144.24, 133.31, 132.20, 131.81, 130.44, 126.60, 126.30, 124.31, 124.27, 123.46, 116.53, 116.40, 112.19, 108.79, 106.19, 105.94, 55.83, 55.80, 48.19, 27.09. HRMS: calcd for $C_{26}H_{24}O_3$ [M^+] (m/z) 384.1725, found 384.1731.

4.4.4. Compound ***5d***. Yellow solid: mp 249–250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J=9.1 Hz, 1H), 8.39 (d, J=8.1 Hz, 1H), 8.28 (d, J=9.1 Hz, 1H), 8.12 (s, 2H), 7.80 (s, 1H), 7.71 (dd, J=16.5, 8.0 Hz, 3H), 7.49 (t, J=7.6 Hz, 2H), 7.38 (td, J=11.4, 2.3 Hz, 3H), 4.05 (d, J=1.9 Hz, 6H), 1.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.86, 157.82, 157.40, 145.75, 141.80, 139.62, 139.13, 132.42, 132.31, 129.17, 127.53, 127.47, 127.04, 126.45, 126.33, 124.47, 124.21, 123.09, 121.04, 116.69, 116.48, 106.27, 106.05, 55.88, 48.39, 26.99. HRMS: calcd for $C_{31}H_{26}O_2$ [M^+] (m/z) 430.1933, found 430.1938.

4.4.5. Compound ***5e***. Yellow solid: mp 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J=9.1 Hz, 1H), 8.60 (d, J=8.7 Hz, 1H), 8.38 (t, J=8.2 Hz, 2H), 8.13 (d, J=1.9 Hz, 2H), 7.99 (t, J=7.5 Hz, 2H), 7.61 (t, J=7.6 Hz, 1H), 7.49 (t, J=7.4 Hz, 1H), 7.39 (m, 2H), 4.03 (s, 6H), 1.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.71, 150.86, 147.84, 137.87, 133.08, 132.42, 132.29, 130.31, 129.89, 128.87, 128.57, 126.79, 126.37, 126.22, 124.89, 124.39, 124.32, 123.49, 121.81, 116.56, 116.42, 106.39, 106.15, 55.86, 49.73, 26.44. HRMS: calcd for $C_{29}H_{24}O_2$ [M^+] (m/z) 404.1776, found 404.1787.

4.4.6. Compound ***5f***. Yellow solid: mp 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J=9.1 Hz, 1H), 8.62 (d, J=8.7 Hz, 1H), 8.48–8.34 (m, 2H), 8.15 (d, J=2.1 Hz, 2H), 8.01 (dd, J=8.2, 5.1 Hz, 2H), 7.63 (t, J=7.6 Hz, 1H), 7.51 (t, J=7.5 Hz, 1H), 7.41 (m, 2H), 4.07 (d, J=1.6 Hz, 6H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.74, 137.88, 133.10, 132.44, 132.31, 130.35, 129.90, 128.88, 128.58, 126.82, 126.41, 126.23, 124.92, 124.41, 124.35, 123.50, 121.83, 116.59, 116.45, 106.39, 106.17, 55.91, 49.75, 26.47. HRMS: calcd for $C_{25}H_{24}O_2$ [M^+] (m/z) 404.1776, found 404.1780.

4.4.7. Compound ***5g***. Yellow solid: mp 264–266 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J=9.0 Hz, 1H), 8.40 (d, J=7.8 Hz, 1H), 8.11 (d, J=2.5 Hz, 1H), 7.97 (d, J=7.4 Hz, 3H), 7.47 (dd, J=9.0, 2.5 Hz, 1H), 7.39 (td, J=7.5, 3.6 Hz, 3H), 7.05 (dd, J=13.4, 6.8 Hz, 3H), 6.77 (dd, J=9.0, 2.4 Hz, 1H), 6.72–6.67 (m, 3H), 6.64 (d, J=7.5 Hz, 1H), 4.07 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.14, 158.03, 151.11, 149.31, 142.68, 141.89, 139.92, 134.56, 133.08, 132.10, 128.38, 128.19, 128.10, 127.70, 126.67, 126.47, 124.29, 124.13, 123.60, 123.38, 122.79, 120.85, 116.80, 116.65, 106.17, 105.88, 66.65, 55.92, 55.69. HRMS: calcd for $C_{35}H_{24}O_2$ [M^+] (m/z) 476.1776, found 476.1775.

4.4.8. Compound ***5h***. Yellow solid: mp 180–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J=8.9 Hz, 1H), 8.15 (d, J=9.1 Hz, 3H), 8.08

(dd, J=14.5, 2.2 Hz, 2H), 7.68 (d, J=4.9 Hz, 1H), 7.47 (d, J=4.9 Hz, 1H), 7.40–7.31 (m, 2H), 4.04 (d, J=2.4 Hz, 6H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.87, 157.96, 157.05, 146.36, 142.24, 131.65, 130.80, 130.38, 127.45, 126.90, 125.59, 124.57, 123.08, 121.02, 116.80, 116.60, 106.21, 105.53, 55.89, 48.38, 28.05. HRMS: calcd for $C_{23}H_{20}O_2S$ [M^+] (m/z) 360.1184, found 360.1188.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.01.093.

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