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Synthesis and photoluminescence study of benz[*f*]indene derivatives

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Abstract—The synthesis and optical properties of a series of benz[*f*]indenes as new building blocks for electronic and optoelectronic materials are described.

Anthracene derivatives are key compounds in the design of luminescent materials.[1] For example, 9,10-diphenylanthracene (DPA) has been widely used in chemiluminescene[2] and many functionalized anthracenes have been reported to yield efficient blue organic light-emitting diodes.[3] Moreover, light-emitting polymers containing DPA have been widely studied.[4]

Fluorene has aromatic benzene rings fused to both cyclopentadiene double bonds. Recently, polyfluorenes (PF) have especially attracted much attention as good candidates for light-emitting diode applications because of their high solid-state photoluminescence (PL) quantum efficiencies, excellent solubility, and film-forming capability, and the ease in controlling their properties via facile substitution in the 9-position.[5] Moreover, the liquid-crystalline order of some PFs has opened the way to fabricate blue polarized electroluminescent devices.[6]

In contrast, benz[*f*]indenes, the isomer of fluorenes, having quite a similar structure to anthracenes, have hitherto never attracted attention in relation to the study of luminescent materials, presumably due to the lack of available synthetic methods. However, we recently developed a synthetic method for benz[*f*]indenes using the Diels–Alder reaction and Pauson–Khand reaction.[7] Interestingly, our methodology easily introduces substituents to the 4,9-positions of benz[*f*]indenes. Here we report the synthesis and optical properties of a series of benz[*f*]indenes and a time-dependent DFT calculation of their excited states.

Scheme 1 shows the synthesis of benz[*f*]indenes. Unsubstituted benz[*f*]indene (**1**) was prepared by the procedure reported by Becker and McLaughlin.[9] Compounds **2**–**6** were synthesized by a method previously reported by the authors.[7] As described in Scheme 1, compound **b**, synthesized by an intermolecular Pauson–Khand reaction of substituted oxabenzonorbornadienes and alkynes, was transformed into **c** by dehydration under an acidic condition. Treatment of **c** with a hydrogen balloon in the presence of Pd/C, followed by reduction by LAH and dehydration (refluxing with anhydrous $MgSO_4$ in hexane or toluene) afforded **2**–**6** in high yields. In the dehydration step, compounds **3e**, **4e**, and **5e** were refluxed with anhydrous $MgSO_4$ in hexane because they have a good solubility in hexane at high temperature. However, compounds **2e** and **6e** have a poor solubility in hexane. Thus, they were refluxed with anhydrous $MgSO_4$ in toluene. After dehydration, two isomeric compounds were obtained for **5e** due to a double bond migration. However, a chromatographic separation gave a pure **5**. All compounds except **2** and **6** were quite soluble in dichloromethane and THF. To confirm the structure of this family of compounds, a single-crystal X-ray analysis of **4** (formed in Et_2O by slow cooling) was performed (Fig. 1).[10]

Figure 2 displays the UV–vis and photoluminescent (PL) spectra of **1**–**6** in solution. In the cases of **2**–**4** and **6**, the λ_{max} values were red-shifted compared to those of **1** and **5** presumably due to the longer conjugation by the presence of phenyl group. The absorption spectra of **2**–**4** and **6** display two groups of bands around

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Keywords: Fluorescence; Photoluminescence; Benzindene.

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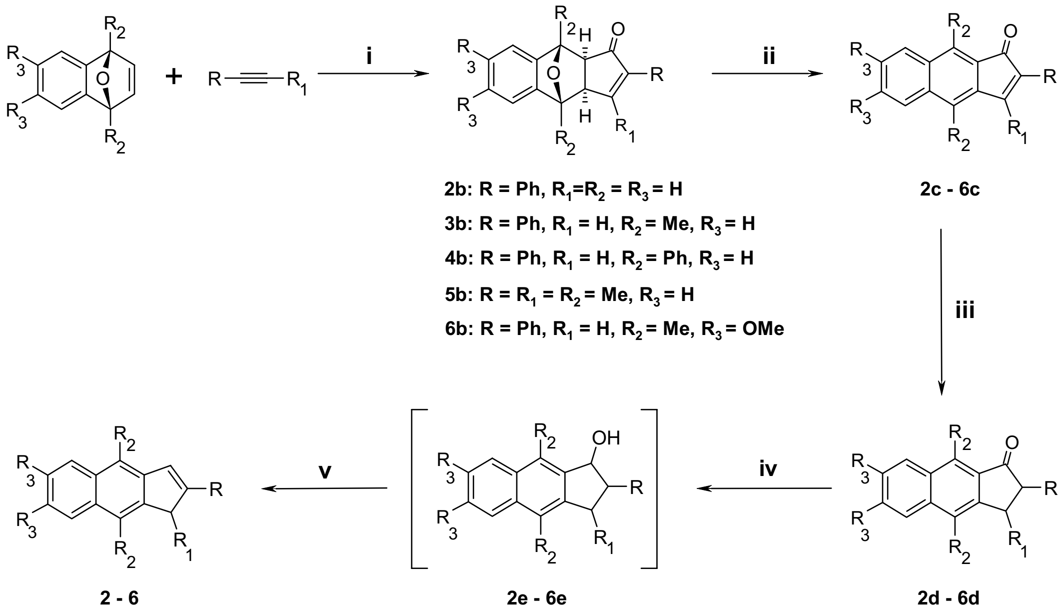

Scheme 1. Synthetic strategy for synthesis of benz[*f*]indenes.[8]

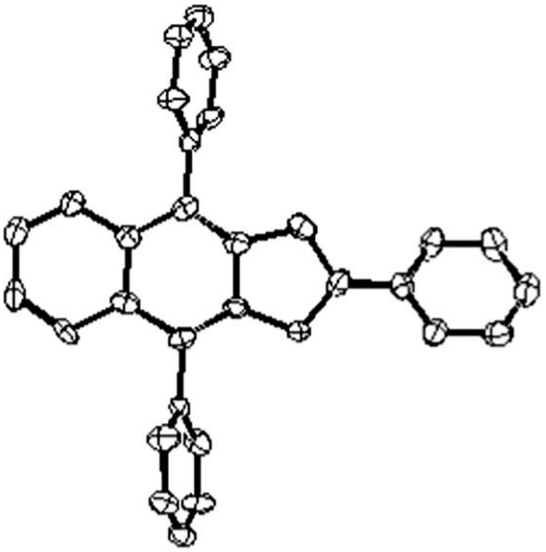

Figure 1. An ORTEP drawing of **4**.

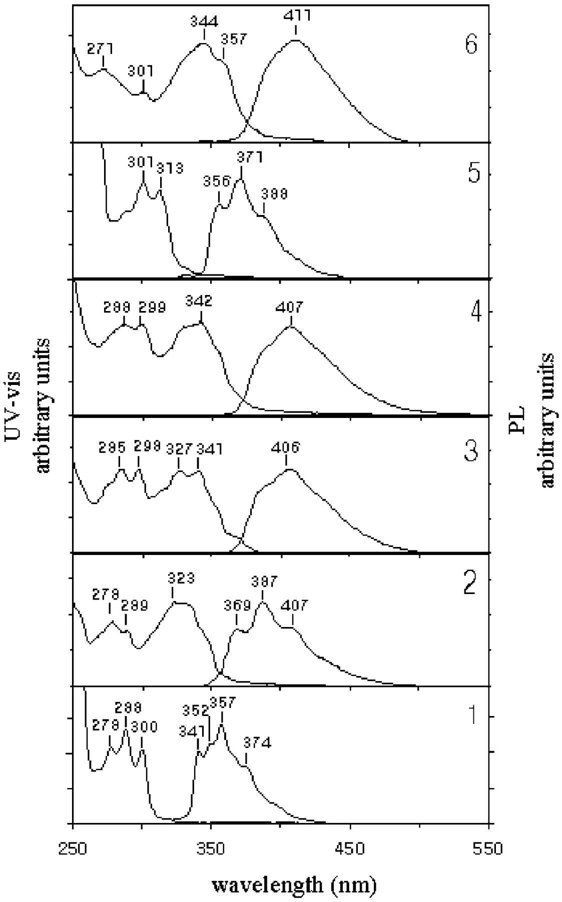

Figure 2. UV–vis absorption (5 μM in dichloromethane) and PL (0.5 μM in dichloromethane).

270–300 and 320–350 nm, but for **1** and **5** one group of band appears around 280–320 nm. The noticeable difference in the UV–vis spectra between these two groups of compounds is presumably due to the presence of (a) phenyl group(s) in the cyclopentadiene moiety. When we calculated the λ_{max} values for **1**–**6** and compared them with observed values (Table 1), the overall trends were consistent. B3LYP[11] exchange-correlational functions in combination with 6-31G(d) basis sets were adopted to optimize geometries of **1**–**6**. After that, TD-DFT using the same theories were performed to calculate excited states. All calculations were performed using Gaussian98.[12] The λ_{max} values around 288–344 nm for **1**–**6** suggested that benz[*f*]indenes are large band-gap compounds.

In solution, all these neutral compounds exhibit blue emission (maximum of emission around 357–411 nm). The λ_{max} values were slightly dependent upon the

Table 1. Spectroscopic data for **1**–**6**

Compd	Obsd λ_{max}abs (nm)	Calcd λ_{max}abs (nm)	λ_{max}em (nm)	Φ_{rel}[a] (%)
1	278 288 300	295 301	341 352 357 374	5
2	278 289 323	274 292 326	369 387 407	26
3	285 298 327 341	298 331 349	406	38
4	288 299 342	283 305 336	407	78
5	301 313	304 346	356 371 388	5
6	271 301 344 357	258 306 312	344 357	7

[a] Quantum yields were measured by dilute method[14] using 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole as standard.

substituent. Compounds **2**–**4** and **6** having (a) phenyl group(s) have a tendency to be slightly red-shifted and have a similar longest wavelength. Compared with fluorene (λ_{max}abs = 265 nm; λ_{max}em = 313 nm in cyclohexane),[13] λ_{max} values of **1** were red-shifted even though the difference of the solvents were considered. Unfortunately, the quantum yields were poor except for **4** and were highly dependent upon the substituents. In the beginning, we envisioned that the formation of excimers was one of the reasons of poor quantum yields. However, the study on the concentration and solvent effect upon PL spectra showed that the formation of excimers seemed to be difficult for **1**–**6**. For example, the λ_{max}em values of **4** in dichloromethane, chloroform, and ethyl acetate were 407, 406, and 402 nm, respectively. Because **1**–**6** do not have any functional groups to react with solvent molecules, we expect that there is no apparent difference depending upon the solvent. The Stokes shifts were rather insensitive to the substituent. The poor quantum yields might originate from other quenching processes when radiated. Further study will provide some clues for the rationalization of the poor quantum yields. The highest quantum yield (0.78) observed for **4** was presumably due to the barricade of three phenyl groups in the quenching processes. It has been well established[15] that the introduction of long or branched side chains and copolymerization with suitable bulky comonomers in fluorescent planar molecules or polymers suppresses the formation of π-aggregates.

In summary, we have synthesized a series of benz[*f*]indene derivatives by using our newly developed method and studied their photophysical properties. All benz[*f*]indene derivatives investigated in this study have exhibited fluorescence in the blue region (emission maximum around 350–410 nm) and have large band-gaps. Depending upon the substituents, some of them showed potential for application as optoelectronic materials. We are currently exploring the synthesis of benz[*f*]indenes having a polar functional group as well as improvement of the photophysical properties in relation to the substituent.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.04.128.

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8. General procedure for the Pauson–Khand reaction: To a 100 mL high-pressure reactor were added oxabenzonorbornadiene (0.52 g, 3.64 mmol), phenyl acetylene (0.20 mL, 1.82 mmol), 15 mL of CH_2Cl_2, and $Co_2(CO)_8$ (31 mg, 91 μmol). After the solution was flushed with CO gas for several seconds, the reactor was pressurized with 30 atm of CO. The reactor was heated at 130 °C for 18 h. After the reactor was cooled to rt and excess gas was relieved, the solution was transferred into a flask and then evaporated to dryness. The residue was chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 8:1). Compound **2b**. Yield: 98%; ^{1}H NMR ($CDCl_3$): δ 7.81 (d, $J = 2.9$ Hz, 1H), 7.72 (d, $J = 6.9$ Hz, 2H), 7.41–7.33 (m, 5H), 7.21 (m, 2H), 5.52 (s, 1H), 5.23 (s, 1H), 3.10 (dd, $J = 5.2, 2.9$ Hz, 1H), 2.73 (d, $J = 5.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 205.4, 157.0, 147.7, 145.8, 131.6, 129.2, 128.8,

127.7, 127.5, 126.3, 120.2, 119.9, 81.8, 80.4, 54.5, 48.5; IR ν(C=O) 1702 cm^{-1}; HRMS for $C_{19}H_{14}O_2$: calcd 274.0994, obsd 274.0996.

Compound **3b**. Yield: 92%; ^{1}H NMR (CDCl$_3$): δ 7.76 (d, J = 3.0 Hz, 1H), 7.72 (m, 2H), 7.40–6.90 (m, 7H), 3.06 (dd, J = 5.1, 2.9 Hz, 1H), 2.57 (d, J = 5.1 Hz, 1H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 204.2, 155.5, 148.5, 147.6, 131.3, 128.7, 128.4, 127.3, 127.2, 126.9, 125.8, 118.2, 118.1, 85.8, 85.1, 57.5, 52.6, 14.7, 14.4; IR ν(C=O) 1698 cm^{-1}; HRMS for $C_{21}H_{18}O_2$: calcd 302.1307, obsd 302.1306.

Compound **4b**. Yield: 96%; ^{1}H NMR (CDCl$_3$): δ 8.06 (d, J = 7.1 Hz, 2H), 7.74 (d, J = 7.0 Hz, 2H), 7.51–6.86 (m, 15H), 4.19 (m, 1H), 3.86 (d, J = 5.9 Hz, 1H); ^{13}C NMR (CDCl$_3$): δ 203.3, 154.9, 145.4, 144.9, 143.7, 137.6, 130.9, 128.7, 128.4, 128.2, 128.1, 127.6, 127.5, 127.3, 127.1, 126.7, 126.3, 125.9, 120.9, 119.5, 90.4, 89.8, 58.6, 53.3; IR ν(C=O) 1699 cm^{-1}; HRMS for $C_{31}H_{22}O_2$: calcd 426.1620, obsd 426.1622.

Compound **5b**. Yield: 85%; ^{1}H NMR (CDCl$_3$): δ 7.18 (m, 4H), 2.79 (d, J = 4.6 Hz, 1H), 2.36 (d, J = 5.1 Hz, 1H), 2.15 (s, 3H), 1.84 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 204.9, 166.4, 148.8, 148.3, 141.7, 126.8, 126.6, 117.8, 117.7, 84.9, 84.8, 57.0, 56.7, 17.5, 15.9, 14.0, 8.17; IR ν(C=O) 1689 cm^{-1}; HRMS for $C_{17}H_{18}O_2$: calcd 254.1307, obsd 254.1311.

Compound **6b**. Yield: 82%; ^{1}H NMR (CDCl$_3$): δ 7.76 (d, J = 2.9 Hz, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.40 (m, 3H), 6.84 (s, 1H), 6.81 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.06 (dd, J = 2.9, 5.0 Hz, 1H), 2.56 (d, J = 5.3 Hz, 1H), 1.88 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 204.6, 155.8, 148.4, 148.2, 147.6, 141.1, 140.8, 131.5, 128.9, 128.6, 127.5, 102.9, 86.2, 85.5, 58.3, 56.6, 56.5, 53.4, 15.0, 14.8; IR ν(C=O) 1704 cm^{-1}; HRMS for $C_{23}H_{22}O_4$: calcd 362.1518, obsd 362.1514.

General procedure for the synthesis of benz[*f*]indenone: To a 100 mL of round-bottom flask was added **b**. To the solution was added MeOH and hydrochloric acid (2 mL of HCl in 30 mL of MeOH). After the resulting solution was refluxed for 6 h, the solution was cooled to rt. The solution was filtered and the precipitant was washed with methanol. Dichloromethane was added to extract organic compounds. The dichloromethane extract was dried over anhydrous MgSO$_4$, filtered, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 9:1).

Compound **2c**. Yield: 84%; ^{1}H NMR (CDCl$_3$): δ 7.94 (s, 1H), 7.89 (d, J = 6.9 Hz, 2H), 7.83 (s, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.1 Hz, 1H), 7.46 (t, J = 6.9 Hz, 1H), 7.46–7.39 (m, 3H), 7.40 (s, 1H); ^{13}C NMR (CDCl$_3$): δ 195.2, 143.6, 140.1, 138.6, 131.6, 130.9, 128.9, 128.7, 128.6, 127.3, 127.0, 125.9, 124.6, 121.2; IR ν(C=O) 1698 cm^{-1}; HRMS for $C_{19}H_{12}O$: calcd 256.0888, obsd 256.0883.

Compound **3c**. Yield: 90%; ^{1}H NMR (CDCl$_3$): δ 8.07 (d, J = 6.8 Hz, 1H), 7.98 (s, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.49 (t, J = 7.1 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 2.92 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 197.2, 141.7, 141.6, 139.1, 136.1, 135.9, 135.8, 134.7, 132.2, 128.7, 128.6, 128.5, 127.5, 126.9, 126.7, 126.3, 125.5, 13.8, 12.0; IR ν(C=O) 1694 cm^{-1}; HRMS for $C_{21}H_{16}O$: calcd 284.1201, obsd 284.1201.

Compound **4c**. Yield: 99%; ^{1}H NMR (CDCl$_3$): δ 7.69–7.17 (m, 20H); ^{13}C NMR (CDCl$_3$): δ 194.8, 142.6, 139.7, 139.3, 136.4, 136.1, 135.5, 135.3, 134.4, 131.6, 130.6, 129.4, 128.6, 128.5, 128.3, 128.2, 128.1, 127.4, 127.3, 126.7, 126.0, 125.9; IR ν(C=O) 1698 cm^{-1}; HRMS for $C_{31}H_{20}O$: calcd 408.1514, obsd 408.1516.

Compound **5c**. Yield: 92%; ^{1}H NMR (CDCl$_3$): δ 7.99 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 2.85 (s, 3H), 2.61 (s, 3H), 2.34 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 197.8, 155.2, 137.3, 136.8, 134.2, 133.6, 127.9, 126.6, 126.2, 126.1, 125.3, 124.9, 16.17, 14.4, 11.8, 7.98; IR ν(C=O) 1679 cm^{-1}; HRMS for $C_{17}H_{16}O$: calcd 236.1201, obsd 236.1203.

Compound **6c**. Yield: 86%; ^{1}H NMR (CDCl$_3$): δ 7.90 (s, 1H), 7.85 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.32 (s, 1H), 7.16 (s, 1H), 4.04 (s, 3H), 4.02 (s, 3H), 2.85 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 197.6, 150.6, 149.1, 141.7, 137.9, 135.5, 134.6, 132.4, 131.3, 129.6, 128.6, 128.3, 127.4, 126.0, 125.4, 125.2, 106.6, 105.3, 56.0, 14.1, 12.3; IR ν(C=O) 1685 cm^{-1}; HRMS for $C_{23}H_{20}O_3$: calcd 344.1412, obsd 344.1417.

General procedure for the synthesis of benz[*f*]indanone: To a 50 mL schlenk flask filled with nitrogen were added a solution of **3c** (0.30 g, 1.06 mmol) in 25 mL of THF and Pd/C (0.30 g, Pd 10%, dry wt. basis Water ~50%). The solution was flushed with a balloon of H$_2$ gas. The resulting solution was stirred for 10 min. When the yellow color of the solution disappeared, the reaction was completed. Pd/C was recovered by filtration and reused for other reactions. Filtrate was concentrated and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 9:1).

Compound **2d**. Yield: 87%; ^{1}H NMR (CDCl$_3$): δ 8.39 (s, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.95 (s, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.62 (t, J = 8.1 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.36–7.21 (m, 5H), 4.02 (dd, J = 4.6, 8.9 Hz, 1H), 3.87 (dd, J = 8.9, 17 Hz, 1H), 3.46 (dd, J = 4.2, 17 Hz, 1H); ^{13}C NMR (CDCl$_3$): δ 206.5, 146.5, 140.0, 137.5, 134.1, 132.8, 130.6, 129.1, 129.0, 128.1, 128.0, 127.3, 126.4, 126.0, 125.6, 124.8, 54.4, 35.5; IR ν(C=O) 1716 cm^{-1}; HRMS for $C_{19}H_{14}O_1$: calcd 258.1045, obsd 258.1046.

Compound **3d**. Yield: 93%; ^{1}H NMR (CDCl$_3$): δ 8.27 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 8.4 Hz, 1H), 7.56 (t, J = 8.4 Hz, 1H), 7.32–7.20 (m, 5H), 3.95 (dd, J = 4.8, 9.1 Hz, 1H), 3.73 (dd, J = 9.1, 17 Hz, 1H), 3.28 (dd, J = 4.7, 17 Hz, 1H), 3.07 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 208.2, 144.5, 140.6, 136.6, 135.6, 132.8, 130.1, 128.9, 128.4, 128.1, 127.1, 126.7, 126.0, 125.6, 124.4, 54.7, 34.2, 14.2, 12.7; IR ν(C=O) 1705 cm^{-1}; HRMS for $C_{21}H_{18}O$: calcd 286.1358, obsd 286.1363.

Compound **4d**. Yield: 88%; ^{1}H NMR (CDCl$_3$): δ 7.80 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.55–7.35 (m, 12H), 7.19 (m, 5H), 3.87 (dd, J = 5.4, 8.9 Hz, 1H), 3.52 (dd, J = 9.0, 17 Hz, 1H), 3.22 (dd, J = 5.4, 17 Hz, 1H); ^{13}C NMR (CDCl$_3$): δ 205.1, 144.3, 139.7, 137.6, 136.6, 136.2, 135.7, 132.8, 130.2, 130.1, 129.9, 129.7, 129.0, 128.9, 128.8, 128.6, 128.2, 128.1, 127.9, 127.0, 126.2, 126.0, 54.6, 34.3; IR ν(C=O) 1711 cm^{-1}; HRMS for $C_{31}H_{22}O$: calcd 410.1671, obsd 410.1676.

Compound **5d**. Yield: 63%; ^{1}H NMR (CDCl$_3$): δ 8.22 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.59 (t, J = 8.2 Hz, 1H), 7.50 (t, J = 8.2 Hz, 1H), 3.66 (q, J = 7.4 Hz, 1H), 3.03 (s, 3H), 2.85 (q, J = 7.3 Hz, 1H), 2.65 (s, 3H), 1.23 (d, J = 7.2 Hz, 3H), 1.09 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$): δ 210.2, 149.9, 135.7, 135.3, 132.7, 129.6, 127.9, 127.2, 126.6, 125.5, 124.4, 49.0, 36.1, 18.0, 13.9, 12.7, 10.1; IR ν(C=O) 1707 cm^{-1}; HRMS for $C_{17}H_{18}O$: calcd 238.1358, obsd 238.1360.

Compound **6d**. Yield: 85%; ^{1}H NMR (CDCl$_3$): δ 7.43 (s, 1H), 7.32–7.20 (m, 5H), 7.26 (s, 1H), 4.09 (s, 3H), 4.06 (s, 3H), 3.94 (dd, J = 4.5, 9.0 Hz, 1H), 3.69 (dd, J = 9.0, 17 Hz, 1H), 3.27 (dd, J = 4.5, 17 Hz, 1H), 3.01 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 208.4, 151.7, 149.3, 144.4, 141.2, 134.7, 132.6, 129.2, 128.7, 128.3, 127.3, 126.6, 104.9, 103.1, 56.3, 54.9, 34.5, 14.7, 13.2; IR ν(C=O) 1709 cm^{-1}; HRMS for $C_{23}H_{22}O_3$: calcd 346.1569, obsd 346.1569.

General procedure for the synthesis of benz[*f*]indene: To a 50 mL schlenk flask filled with nitrogen in an ice-bath were added a solution of **3d** (0.28 g, 0.98 mmol) in 15 mL of THF and $LiAlH_4$ (23 mg, 0.59 mmol). The resulting solution was allowed to warm to rt. After the solution was stirred for 4 h, several drops of satd aqueous NH_4Cl solution were added. As the NH_4Cl solution was added, fluorescence disappeared. The resulting solution was filtered over a $MgSO_4$ pad and the filtrate was evaporated to dryness. The residue was used for further reactions without further purification. To a 100 mL round-bottom flask were added the residue, $MgSO_4$ (5.0 g), and 60 mL of hexane. After the resulting solution was refluxed, the solution was filtered, evaporated, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 24:1).

Compound **2**. Yield: 35%; ^{1}H NMR (CDCl$_3$): δ 7.92 (s, 1H), 7.89 (m, 1H), 7.83 (s, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.47–7.42 (m, 4H), 7.46 (s, 1H), 7.35 (t, J = 7.2 Hz, 1H), 3.99 (s, 2H); Anal. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.09; H, 5.77; HRMS for $C_{19}H_{14}$: calcd 242.1096, obsd 242.1100; decomposed at 262 °C.

Compound **3**. Yield: 70%; ^{1}H NMR (CDCl$_3$): δ 8.03 (m, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.49 (s, 1H), 7.47 (m, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 3.81 (s, 2H), 2.73 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 146.1, 141.9, 138.9, 136.2, 132.8, 131.5, 128.8, 127.8, 125.9, 125.8, 124.9, 124.6, 124.3, 123.1, 38.4, 15.3, 15.0; HRMS for $C_{21}H_{18}$: calcd 270.1409, obsd 270.1405; mp 198 °C.

Compound **4**. Yield: 68%; ^{1}H NMR (CDCl$_3$): δ 7.71 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 8.6 Hz, 1H), 7.51–7.39 (m, 12H), 7.33–7.10 (m, 5H), 7.05 (s, 1H), 3.67 (s, 2H); ^{13}C NMR (CDCl$_3$): δ 147.8, 142.2, 139.3, 139.2, 138.8, 135.7, 134.3, 132.3, 131.2, 131.0, 130.1, 128.8, 128.7, 128.6, 128.0, 127.6, 127.4, 126.2, 126.1, 126.0, 125.3, 124.9, 38.8; HRMS for $C_{31}H_{22}$: calcd 394.1722, obsd 394.1725; mp 180 °C.

Compound **5**. Yield: 58%; ^{1}H NMR (CDCl$_3$): δ 7.98 (m, 2H), 7.43 (m, 2H), 6.63 (s, 1H), 3.46 (q, J = 7.2 Hz, 1H), 2.65 (s, 3H), 2.63 (s, 3H), 2.09 (s, 3H), 1.33 (q, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl$_3$): δ 151.7, 144.9, 141.4, 131.4, 124.8, 124.6, 124.3, 124.2, 47.2, 16.4, 15.5, 15.2, 14.7; HRMS for $C_{17}H_{18}$: calcd 222.1409, obsd 222.1408; mp 66 °C.

Compound **6**. Yield: 49%; ^{1}H NMR (CDCl$_3$): δ 7.62 (d, J = 7.7 Hz, 2H), 7.41 (s, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.21 (s, 2H), 7.20 (t, J = 7.7 Hz, 1H), 3.96 (s, 6H), 3.75 (s, 2H), 2.64 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (CDCl$_3$): δ 148.6, 145.2, 140.8, 137.8, 136.5, 128.8, 128.3, 127.6, 126.1, 126.0, 125.8, 124.7, 121.9, 103.9, 103.8, 55.9, 38.5, 15.6, 15.3; HRMS for $C_{23}H_{22}O_2$: calcd 330.1620, obsd 330.1624; decomposed at 230 °C.

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10. CCDC reference numbers 245437. Crystallographic data for $C_{31}H_{22}$: $M = 394.49$, orthorhombic, $P212121$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $a = 5.9770(10)$ Å, $b = 10.8310(10)$ Å, $c = 32.496(2)$ Å, $V = 2103.7(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.246$ Mg/m^3, $\mu = 0.070$ mm^{-1}, $F(000) = 832$, crystal size $0.19 \times 0.20 \times 0.20$ mm, θ range for data collection 1.98–26.97°, index range $-7 \leqslant h \leqslant 6$, $-13 \leqslant k \leqslant 13$, $-36 \leqslant l \leqslant 34$, 2722 reflections collected, 2722 unique data (R(int) = 0.0000), refinement method full-matrix least-squares on F^2, data/restraints/parameters 2722/0/280, goodness-of-fit on F^2 0.829, final R indices ($I > 2\sigma(I)$) $R1 = 0.0495$, $wR2 = 0.1167$, largest difference peak and hole 0.258 and −0.264 e Å^{-3}.

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