

Supporting Information

Novel Photochromism of Differently-Linked Bis-Benzopyrans

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EXPERIMENTAL SECTION

General Aspects

All the other solvents were distilled before use. 1,2-Dichloroethane was distilled over calcium hydride under nitrogen prior to use. Anhyd tetrahydrofuran (THF) and toluene were freshly distilled over sodium prior to use and purged with nitrogen gas. The progress of reaction in each case was monitored by analytical thin layer chromatography (TLC) using aluminum sheets pre-coated with silica gel (Merck). Column chromatography was conducted with silica gel (Acme, Mumbai, 60–120 mesh). Melting points are uncorrected. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL-Lambda (400 MHz) spectrometer using CDCl_3 as a solvent. UV-vis absorption spectra were recorded using a JASCO V-550 spectrophotometer.

The commercially-available starting materials such as 4,4'-dihydroxybiphenyl, 1,1-diphenylprop-2-yn-1-ol, pyridinium-*p*-toluene sulfonate, etc. were used as received. Bis-phenols such as 3,3'-dihydroxybiphenyl, 3,4'-dihydroxybiphenyl, etc. were readily prepared from their respective dimethoxy-substituted biaryls, which were in turn prepared by the standard Suzuki coupling protocol. The 4-(4-methoxyphenyl)phenol and 3-(3-methoxyphenyl)phenol were obtained by Suzuki coupling of 4-methoxy- and 3-methoxyphenylboronic acids with the corresponding *p*- and *m*-bromophenols, respectively.

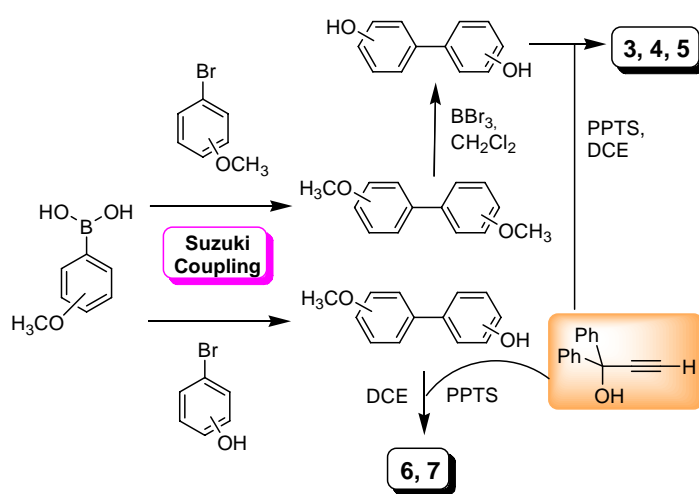
General Procedure for the Synthesis of Bisphenols by Suzuki Coupling¹

A representative procedure for the synthesis of 3,3'-dihydroxybiphenyl is described below. A similar procedure was adopted for the synthesis of other phenols, viz., 3,3'-dihydroxybiphenyl, 3,4'-dihydroxybiphenyl, 4-(4-methoxyphenyl)phenol and 3-(3-methoxyphenyl)phenol.

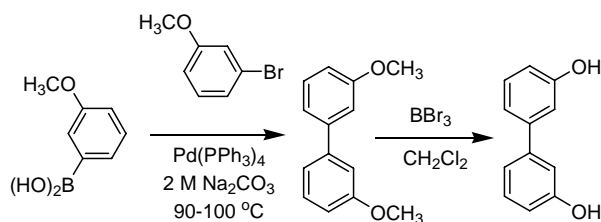
To a oven-dried pressure tube were added 3-methoxyphenylboronic acid (0.484 g, 3.2 mmol), 3-bromoanisole (0.500 g, 2.6 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.075 g, 0.065 mmol), 2.0 mL of Na_2CO_3 solution (2 M) and 4.0 mL of dry toluene, and sealed under nitrogen. The contents were heated at 90–100 °C for 16 h. Subsequently, the tube was cooled and the organic matter was extracted with CHCl_3 (50 mL \times 3). The combined extract was washed thoroughly with brine, dried over anhyd Na_2SO_4 , filtered and evaporated to yield the crude product, which was further purified by silica-gel column chromatography to yield pure 3,3'-dimethoxybiphenyl (0.512 g, 92%).

The 3,3'-dimethoxybiphenyl (0.250 g, 1.2 mmol) thus obtained was treated with BBr_3 (0.25 mL, 2.6 mmol) in dry dichloromethane (10 mL) under ice-cold conditions. The reaction was slowly allowed to attain room temperature over a period of 3–4 h. Subsequently, the reaction mixture was poured into crushed ice and the organic contents were extracted with ethyl acetate. The combined extract was washed thoroughly with brine, dried over anhyd Na_2SO_4 , filtered, and evaporated to yield the crude product. Further purification by silica-gel column chromatography yielded pure 3,3'-dihydroxybiphenyl (0.210 g, 94%). A similar procedure was adopted for the synthesis of other bisphenols.

Scheme S1



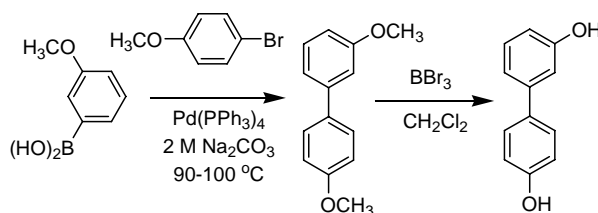
Synthesis of 3,3'-dihydroxybiphenyl



3,3'-Dimethoxybiphenyl:² Colorless solid. Yield: 92%; mp 38–40 °C; IR (KBr) cm^{-1} 2955, 2833, 1845, 1598, 1574, 1476, 1411, 1234; ^1H NMR (CDCl_3 , 400 MHz) δ 3.91 (s, 6H), 6.92–6.98 (m, 2H), 7.18 (s, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.40 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.3, 112.8, 112.9, 119.7, 129.7, 142.6, 159.8.

3,3'-Dihydroxybiphenyl:³ Colorless solid. Yield: 97%; mp 123–125 °C; IR (KBr) cm^{-1} 3322, 2925, 1582, 1478, 1433, 1223, 1185; ^1H NMR (CDCl_3 , 400 MHz) δ 6.73–6.79 (m, 2H), 6.97–7.02 (m, 4H), 7.17 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (Acetone- d_6 + CDCl_3 , 100 MHz) δ 113.1, 113.6, 117.6, 129.1, 141.9, 157.0.

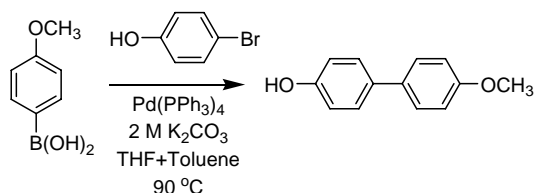
Synthesis of 3, 4'-dihydroxybiphenyl



3,4'-Dimethoxybiphenyl:⁴ Colorless solid. Yield: 91%; mp 59–61 °C; IR (KBr) cm^{-1} 2955, 2834, 1890, 1606, 1517, 1482, 1247, 1215; ^1H NMR (CDCl_3 , 400 MHz) δ 3.78 (s, 3H), 3.79 (s, 3H), 6.78 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.4$ Hz, 1H), 6.90 (d, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 1.8$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.2, 55.3, 112.0, 112.5, 114.1, 119.3, 128.2, 129.7, 133.6, 142.3, 159.2, 159.9.

3,4'-Dihydroxybiphenyl:⁵ Colorless solid. Yield: 96%; mp 180–181 °C; IR (KBr) cm^{-1} 3280, 1602, 1423, 1257, 1202; ^1H NMR (Acetone- d_6 + CDCl_3 , 400 MHz) δ 6.68 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 8.5$ Hz, 2H), 6.90–7.00 (m, 2H), 7.11 (t, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (Acetone- d_6 + CDCl_3 , 100 MHz) δ 114.2, 116.4, 118.6, 128.8, 130.5, 133.3, 143.3, 157.6, 158.3.

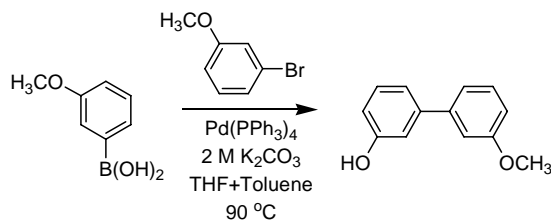
Synthesis of 4-(4-methoxyphenyl)phenol



4-(4-Methoxyphenyl)phenol:⁵ Colorless solid. Yield: 80%; mp 170–172 °C; IR (KBr) cm^{-1} 3404, 2950, 1886, 1605, 1497, 1449, 1376, 1244; ^1H NMR (CDCl_3 , 400 MHz) δ 3.73 (s, 3H), 6.82 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H); ^{13}C

NMR (Acetone- d_6 +CDCl₃, 100 MHz) δ 55.2, 114.4, 115.8, 127.6, 127.8, 132.5, 133.8, 156.6, 158.9.

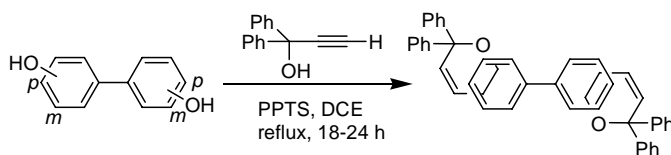
Synthesis of 3-(3-methoxyphenyl)phenol



3-(3-Methoxyphenyl)phenol: Colorless liquid. Yield: 92%; IR (Neat) cm⁻¹ 3396, 2940, 1600, 1578, 1479, 1419, 1306, 1231; ¹H NMR (CDCl₃, 400 MHz) δ 3.80 (s, 3H), 6.79 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.4$ Hz, 1H), 6.86 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.4$ Hz, 1H), 7.01 (t, $J = 2.0$ Hz, 1H), 7.05 (t, $J = 2.0$ Hz, 1H), 7.07–7.15 (m, 2H), 7.20–7.35 (m, 2H); ¹³C NMR (Acetone- d_6 +CDCl₃, 100 MHz) δ 55.3, 112.8, 112.9, 114.1, 114.4, 119.7, 129.7, 129.9, 142.2, 142.7, 155.8, 159.7.

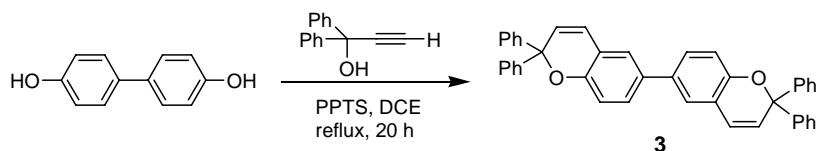
General Procedure for the Synthesis of Chromenes 3–7.

All chromenes **3–7** were prepared by following an analogous literature-reported procedures.⁶ A representative procedure for the synthesis of 4,4'-bischromenes is described below.

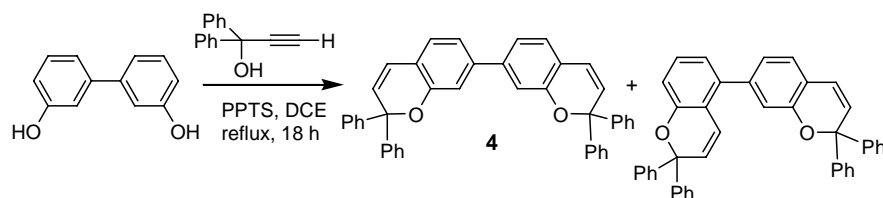


To a solution of 4,4'-bisphenol (0.075 g, 0.4 mmol), 1,1-diphenylprop-2-yn-1-ol (0.201 g, 1.0 mmol) in dry 1,2-dichloroethane (6 mL) was added a catalytic amount of PPTS (0.010 g, 10 mol%). The contents were refluxed under a nitrogen gas atmosphere for 18–24 h. After this period, the contents were cooled, washed with saturated Na₂CO₃ solution, and the organic contents were extracted with chloroform (15 mL \times 3). The combined extract was dried over anhyd Na₂SO₄, filtered, and evaporated to yield the crude product. Further purification with silica-gel column chromatography yielded pure 6,6'-bischromenes in ca. 60% isolated yield.

The 4,4'-dihydroxybiphenyl yielded exclusively 6,6'-bischromenes, while 3,4'- and 3,3'-dihydroxybiphenyl led to a regioisomeric mixture of 5,6'-, 6,7'- and 7,7'-, 5,7'-bischromenes respectively. The regioisomers in each case were separated by a radial chromatography technique using chromatotron, and the pure regioisomers (24–64%) thus isolated were thoroughly characterized by IR, ^1H and ^{13}C NMR spectroscopic techniques.



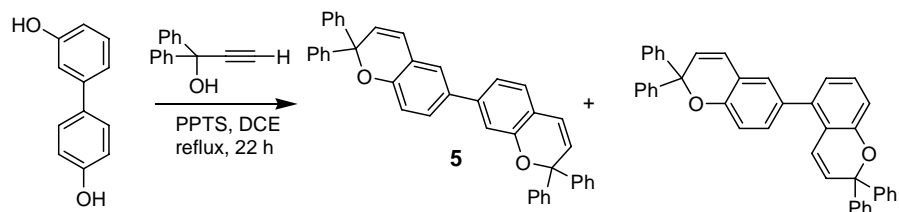
6,6'-Bis-chromene, 3. Colorless solid. Yield 60%; mp 216–218 °C; IR (KBr) cm^{-1} 3020, 1623, 1478, 1446, 1240, 1214, 1126, 1055; ^1H NMR (CDCl_3 , 400 MHz) δ 6.17 (d, $J = 10.0$ Hz, 2H), 6.62 (d, $J = 10.0$ Hz, 2H), 6.92 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 2.2$ Hz, 2H), 7.24 (t, $J = 7.5$ Hz, 6H), 7.31 (t, $J = 8.0$ Hz, 8H), 7.42 (d, $J = 7.1$ Hz, 8H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 82.8, 116.7, 121.1, 123.4, 124.8, 127.0, 127.5, 127.8, 128.1, 129.1, 133.9, 144.8, 151.7; ESI- MS^+ 567 [M+H].



7,7'-Bis(chromene), 4: Colorless solid. Yield: 32%; mp 143–145 °C; IR (KBr) cm^{-1} 3056, 3026, 2923, 1950, 1879, 1613, 1487, 1443, 1305, 1219, 1176, 1054, 1030; ^1H NMR (CDCl_3 , 400 MHz) δ 6.09 (d, $J = 9.9$ Hz, 2H), 6.55 (d, $J = 9.9$ Hz, 2H), 6.93–7.00 (m, 4H), 7.08 (s, 2H), 7.10–7.17 (m, 4H), 7.18–7.28 (m, 8H), 7.30–7.40 (m, 8H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 82.8, 114.8, 119.7, 123.0, 123.1, 126.9, 127.5, 128.1, 128.6, 129.8, 141.9, 144.9, 152.7; ESI- MS^+ 567 [M+H].

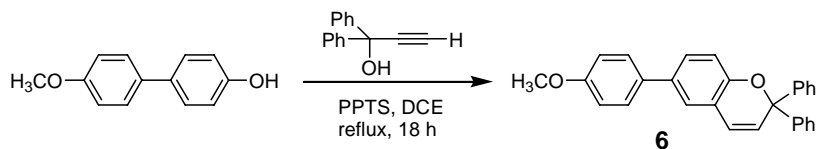
5,7'-Bis(chromene): Colorless solid. Yield: 21%; mp 174–176 °C; IR (KBr) cm^{-1} 3058, 3029, 2923, 2854, 2370, 2341, 1596, 1490, 1447, 1250, 1181, 1216, 1099, 1054; ^1H NMR (CDCl_3 , 400 MHz) δ 6.03 (d, $J = 10.0$ Hz, 1H), 6.15 (d, $J = 10.0$ Hz, 1H), 6.59 (t, $J = 8.8$ Hz, 2H), 6.73 (t, $J = 8.0$ Hz, 2H), 6.85 (d, $J = 12.0$ Hz, 2H), 6.95 (d, $J = 7.3$ Hz, 1H), 7.05 (t, $J = 7.8$ Hz, 1H), 7.14–7.21 (m, 4H), 7.22–7.29 (m, 8H), 7.32–7.52 (m, 8H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 81.7,

82.7, 115.9, 117.7, 118.9, 120.1, 122.0, 122.3, 122.8, 123.0, 126.3, 127.1, 127.5, 127.6, 128.1, 128.2, 128.6, 128.9, 129.1, 139.2, 141.0, 144.8, 144.9, 152.2, 152.9; ESI-MS⁺ 567 [M+H].

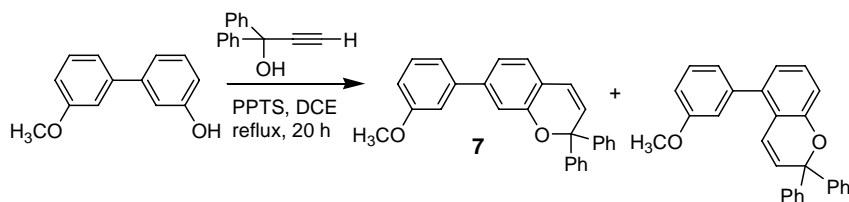


6,7'-Bis-chromene, 5. Viscous liquid. Yield 57%; IR (KBr) cm⁻¹ 3057, 3028, 2923, 2854, 1611, 1483, 1444, 1245, 1219, 1183, 1130, 1087. ¹H NMR (CDCl₃, 400 MHz) δ 6.08 (d, *J* = 9.8 Hz, 1H), 6.12 (d, *J* = 9.8 Hz, 1H), 6.56 (t, *J* = 9.0 Hz, 2H), 6.85–7.0 (m, 3H), 7.02 (s, 1H), 7.12–7.21 (m, 6H), 7.22–7.28 (m, 8H), 7.34–7.38 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ 82.7, 114.5, 116.7, 119.4, 119.6, 121.1, 123.0, 123.3, 125.0, 126.8, 127.0, 127.4, 127.5, 127.9, 128.1, 128.4, 129.1, 133.6, 142.0, 144.8, 144.9, 152.2, 152.7; ESI-MS⁺ 567 [M+H].

5,6'-Bis-chromene. Viscous liquid. Yield 20%; IR (KBr) cm⁻¹ 3058, 3027, 2923, 1632, 1599, 1491, 1447, 1243, 1182, 1103, 1055. ¹H NMR (CDCl₃, 400 MHz) δ 6.02 (d, *J* = 10.0 Hz, 1H), 6.13 (d, *J* = 10.0 Hz, 1H), 6.56 (AB_q, *J*_{AB} = 10.0 Hz, 2H), 6.57 (AB_q, *J*_{AB} = 10.0 Hz, 2H), 6.70 (d, *J* = 6.8 Hz, 1H), 6.81 (m, 3H), 6.97 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 7.13–7.30 (m, 12 H), 7.34–7.45 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ 81.7, 82.8, 115.5, 116.1, 119.0, 120.6, 122.1, 122.4, 123.1, 127.00, 127.03, 127.4, 127.6, 127.7, 128.1, 128.2, 128.5, 128.9, 129.0, 130.9, 132.5, 139.3, 144.9, 145.0, 151.9, 152.9; ESI-MS⁺ 567 [M+H].



6-(4-Methoxyphenyl)chromene, 6. Colorless solid. Yield 64%; mp 148–150 °C; IR (KBr) cm⁻¹ 3059, 3029, 2955, 2833, 1886, 1603, 1518, 1485, 1444, 1271, 1238, 1184, 1131, 1085, 1032; ¹H NMR (CDCl₃, 400 MHz) δ 3.74 (s, 3H), 6.12 (d, *J* = 10.0 Hz, 1H), 6.58 (d, *J* = 10.0 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 7.10 (s, 1H), 7.12–7.28 (m, 7H), 7.33–7.38 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 55.3, 82.7, 114.1, 116.7, 121.2, 123.4, 124.8, 127.0, 127.5, 127.6, 127.8, 128.1, 129.1, 133.3, 134.0, 144.9, 151.6, 158.7; ESI-MS⁺ 391 [M+H].



7-(3-Methoxyphenyl)chromene, 7. Viscous liquid. Yield 47%; IR (KBr) cm^{-1} 3058, 3029, 3001, 2956, 2936, 2833, 1809, 1606, 1552, 1483, 1447, 1406, 1230, 1131, 1032; ^1H NMR (CDCl_3 , 400 MHz) δ 3.75 (s, 3H), 6.10 (d, $J = 10.0$ Hz, 1H), 6.56 (d, $J = 10.0$ Hz, 1H), 6.79 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.4$ Hz, 1H), 6.94–7.03 (m, 2H), 7.07 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.0$ Hz, 1H), 7.11 (s, 1H), 7.13–7.20 (m, 2H), 7.21–7.28 (m, 5H), 7.34–7.38 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.3, 82.8, 112.4, 113.0, 115.1, 119.4, 120.0, 120.2, 123.0, 126.8, 127.0, 127.5, 128.1, 128.8, 129.7, 142.1, 142.4, 144.9, 152.7, 159.9; ESI-MS⁺ 391 [M+H].

5-(3-Methoxyphenyl)chromene. Viscous liquid. Yield 44%; IR (KBr) cm^{-1} 3058, 3027, 2956, 2933, 1632, 1491, 1448, 1420, 1250, 1224, 1108, 1047; ^1H NMR (CDCl_3 , 400 MHz) δ 3.84 (s, 3H), 6.12 (d, $J = 10.0$ Hz, 1H), 6.67 (d, $J = 10.0$ Hz, 1H), 6.83–6.94 (m, 4H), 6.97 (d, $J = 8.0$ Hz, 1H), 7.17 (t, $J = 8.0$ Hz, 1H), 7.23–7.29 (m, 2H), 7.30–7.36 (m, 5H), 7.46–7.48 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.2, 81.8, 112.6, 115.3, 115.9, 119.1, 122.0, 122.2, 122.4, 127.0, 127.4, 128.1, 128.7, 128.9, 129.1, 139.6, 141.0, 144.9, 152.9, 159.3; ESI-MS⁺ 391 [M+H].

Solution-State Photolyses

The toluene solutions (5×10^{-5} M) of bischromenes **3–5** and model chromenes **6** and **7** were taken in a 3 cm³ quartz cuvettes equipped with an extended arm, through which the solution was thoroughly purged with nitrogen gas for 15–20 min. The cuvette containing a chromene solution was cooled (15 °C) and was subjected to UV radiation using $\lambda \approx 350/300$ nm lamps for a brief period of time (ca. 2 min). All the bischromenes turned color upon UV irradiation. The cuvette in each case was removed from the cold bath and the UV-vis absorption spectra of the colored species were recorded immediately. The solutions became colorless when kept in dark (ca. 2–5 min).

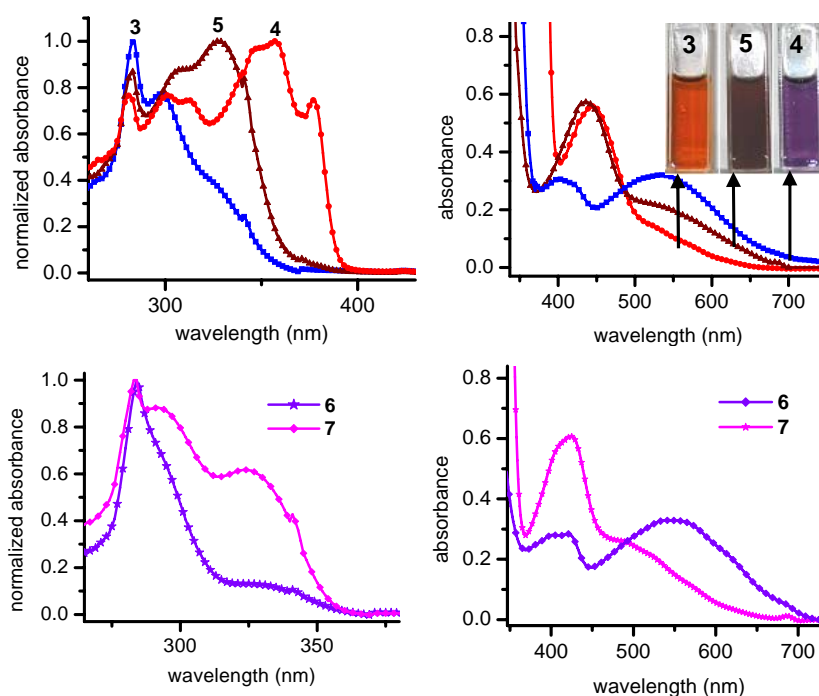


Figure S1. UV-vis absorption spectra of bis-chromenes **3–5** (top) and model anisylchromenes **6** and **7** (bottom) before (left) and after (right) irradiation.

Wavelength- and Temperature-Dependent UV-vis Absorption Studies

The wavelength and temperature dependent UV-vis absorption measurements were carried out at various temperatures, viz., 5, 10, 15, 20 °C by following the similar above set-up procedure. For wavelength-dependent studies, monochromatic light from a high-pressure Hg lamp was isolated at a given wavelength by using spectral energy GM 252 monochromator. For comparison, the typical spectral profiles obtained at two different excitation wavelengths (300 and 350 nm) with variation in temperatures are presented.

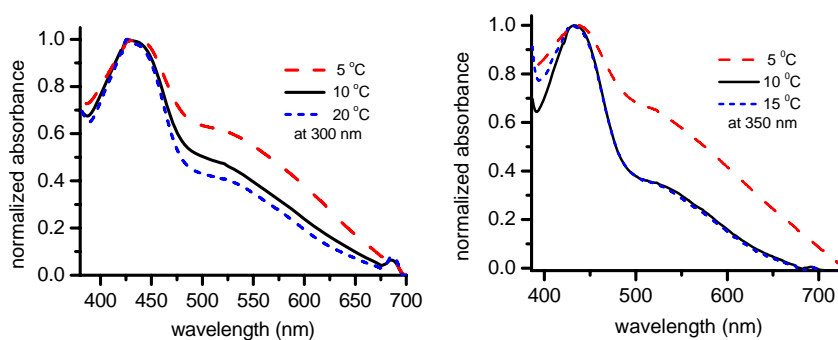


Figure S2. Normalized UV-vis absorption spectra of **5** at different temperatures at two different wavelengths of excitation.

Coloration Curves

The toluene solutions of chromenes **3–5** (5×10^{-4} M) were thoroughly purged with a nitrogen gas for 15–20 min and were irradiated at their λ_{\max} using a 200-Watts high-pressure mercury vapor lamp equipped with a monochromatic filter. The optical densities at various time intervals were recorded at 288 K. The coloration curves were obtained by plotting the absorbance with irradiation time (s).

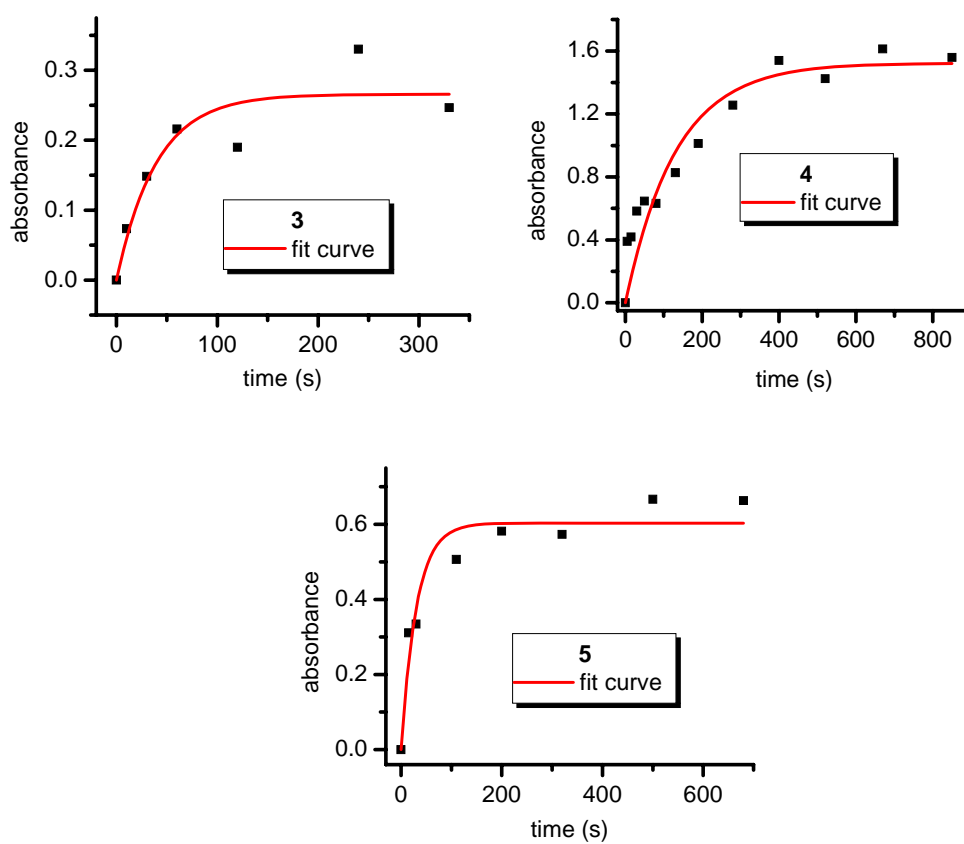


Figure S3. The coloration curves for bischromenes **3–5**.

Thermal Decay Kinetics of *o*-Quinonoid Intermediates

The solutions (5×10^{-4} M) of bischromenes **3**–**5** in toluene were irradiated for 3–6 min (3 min in the case of **3**, and for 6 min in the cases of **4** and **5**) with a monochromatic light from 200-Watts high-pressure mercury lamp. The decays of the colored species were monitored at 288 K by recording the change in absorbance at their λ_{\max} with time (s). The decays for **5** were monitored at two the absorption maxima 450 and 550 nm. The decay plots in the case of **3** turned out to follow a mono-exponential function and the lifetime of the short-lived colored *o*-quinonoid species generated via the photolysis of bischromenes was extracted. In the case of **4** and **5**, the decays were fitted to a bi-exponential function (Levenberg-Marquardt equation) and the lifetimes of both the short- and long-lived components responsible for color were extracted.

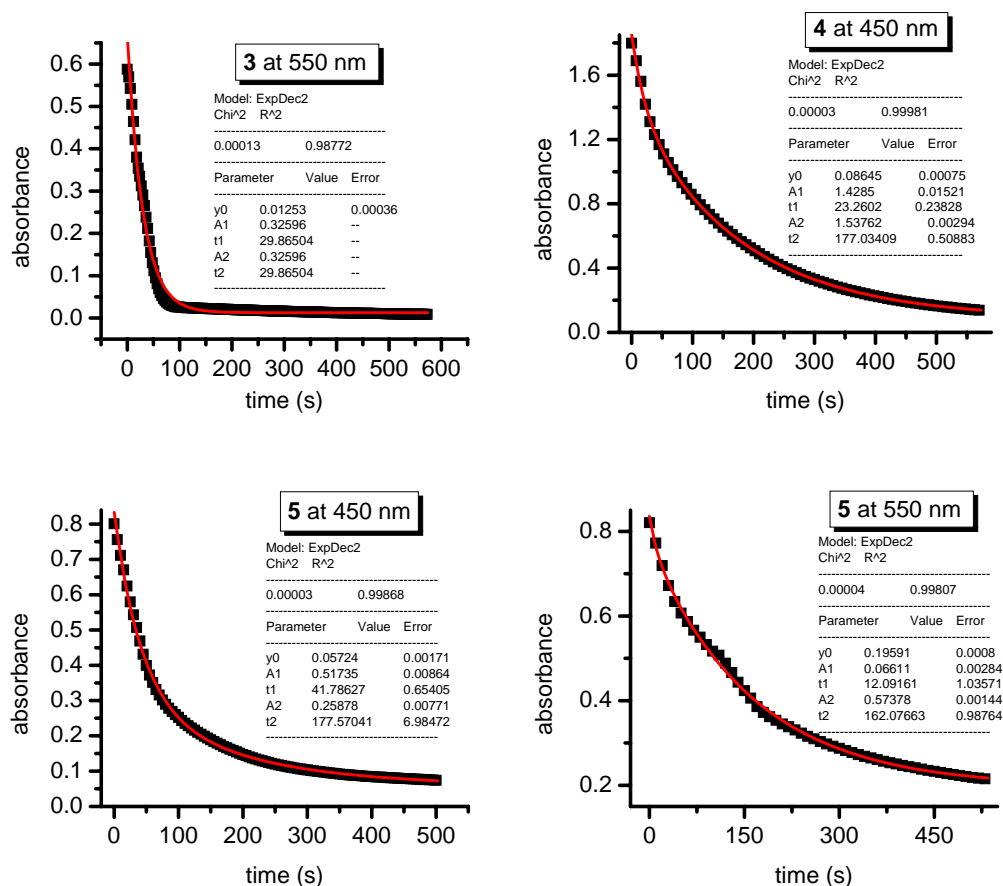


Figure S4. Thermal decay kinetics for the colored *o*-quinonoids derived from the photolyses of **3**–**5**. The red line indicates the best fit curve for the obtained data.

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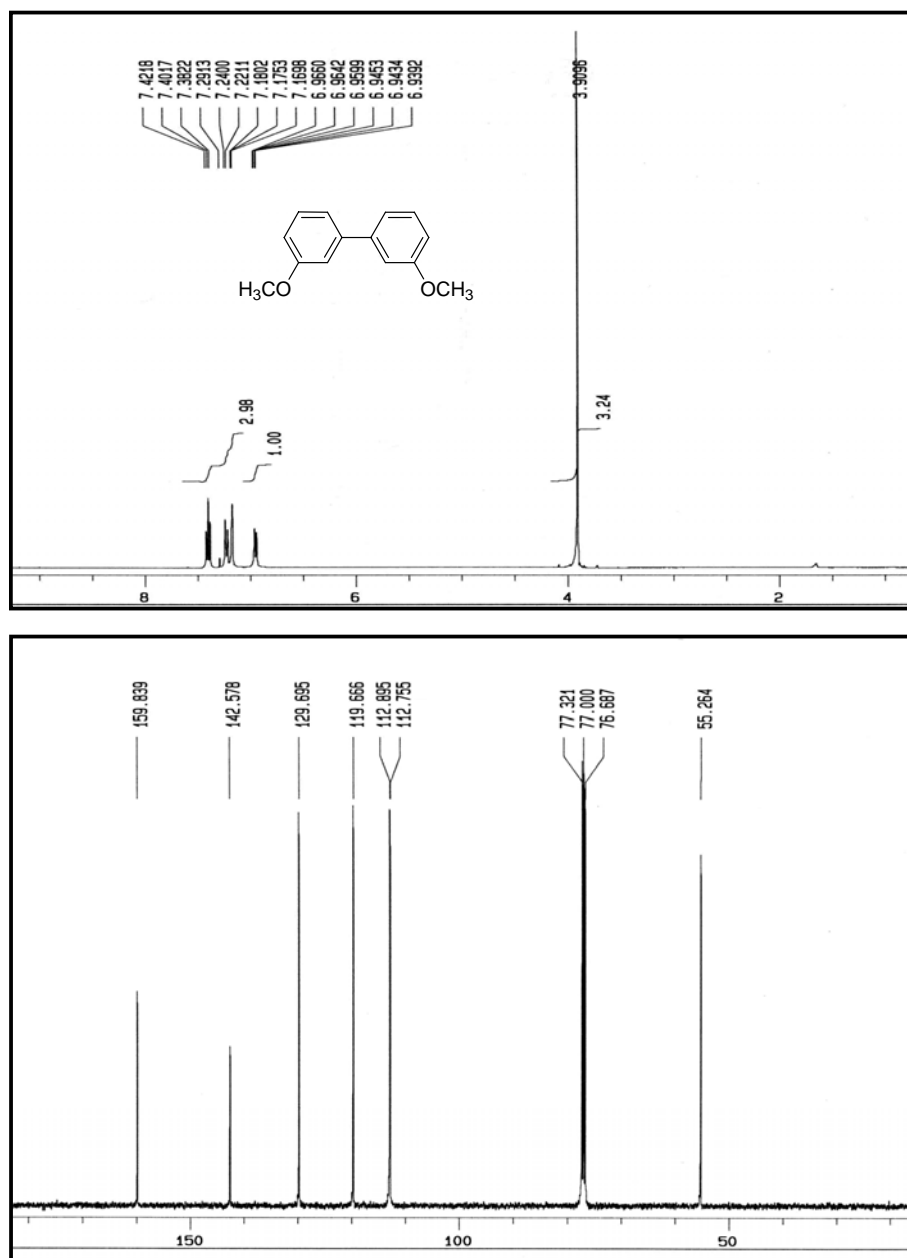


Figure S5. ^1H and ^{13}C NMR spectra of 3,3'-dimethoxybiphenyl.

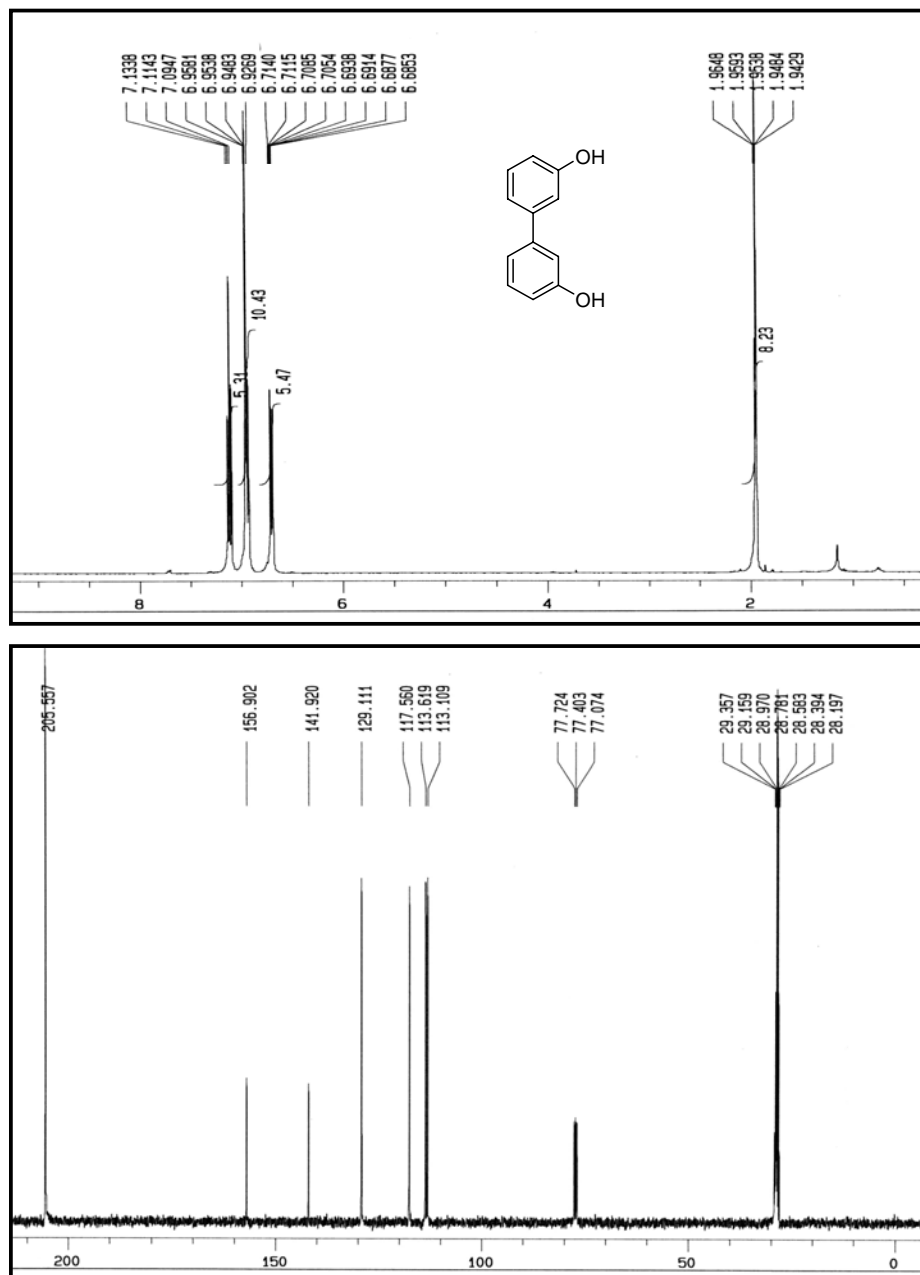


Figure S6. ¹H and ¹³C NMR spectra of 3,3'-dihydroxybiphenyl.

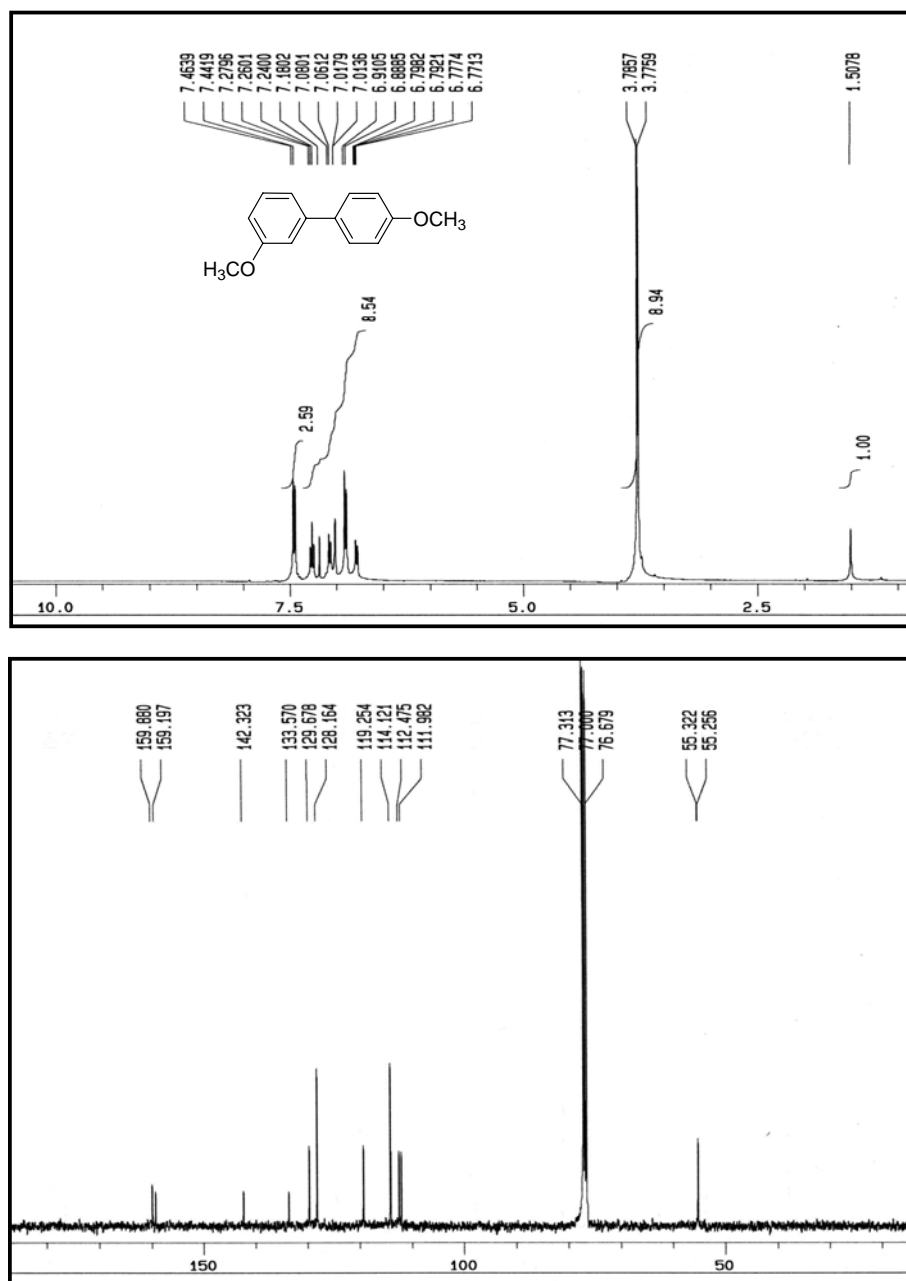


Figure S7. ¹H and ¹³C NMR spectra of 3,4'-dimethoxybiphenyl.

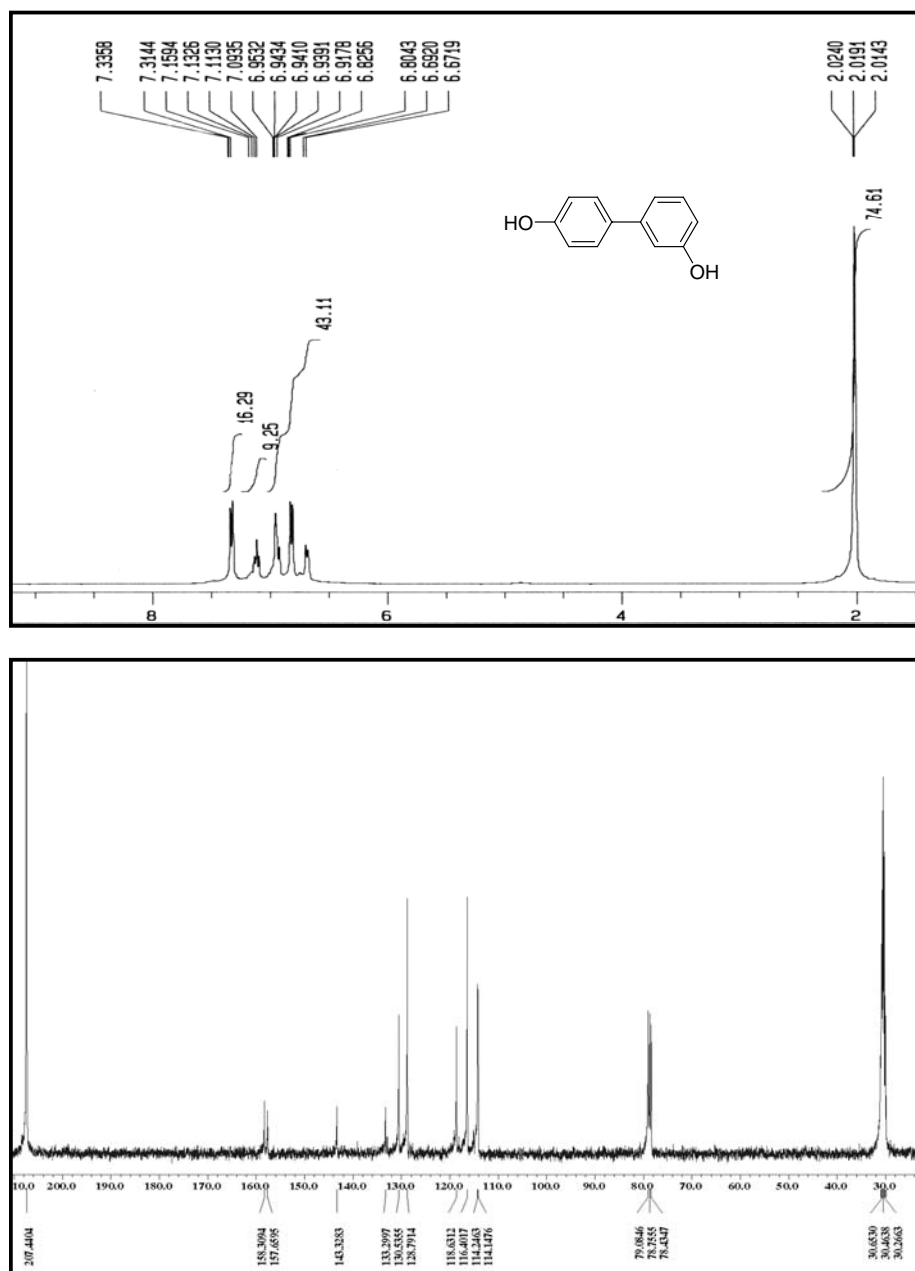


Figure S8. ¹H and ¹³C NMR spectra of 3,4'-dihydroxybiphenyl.

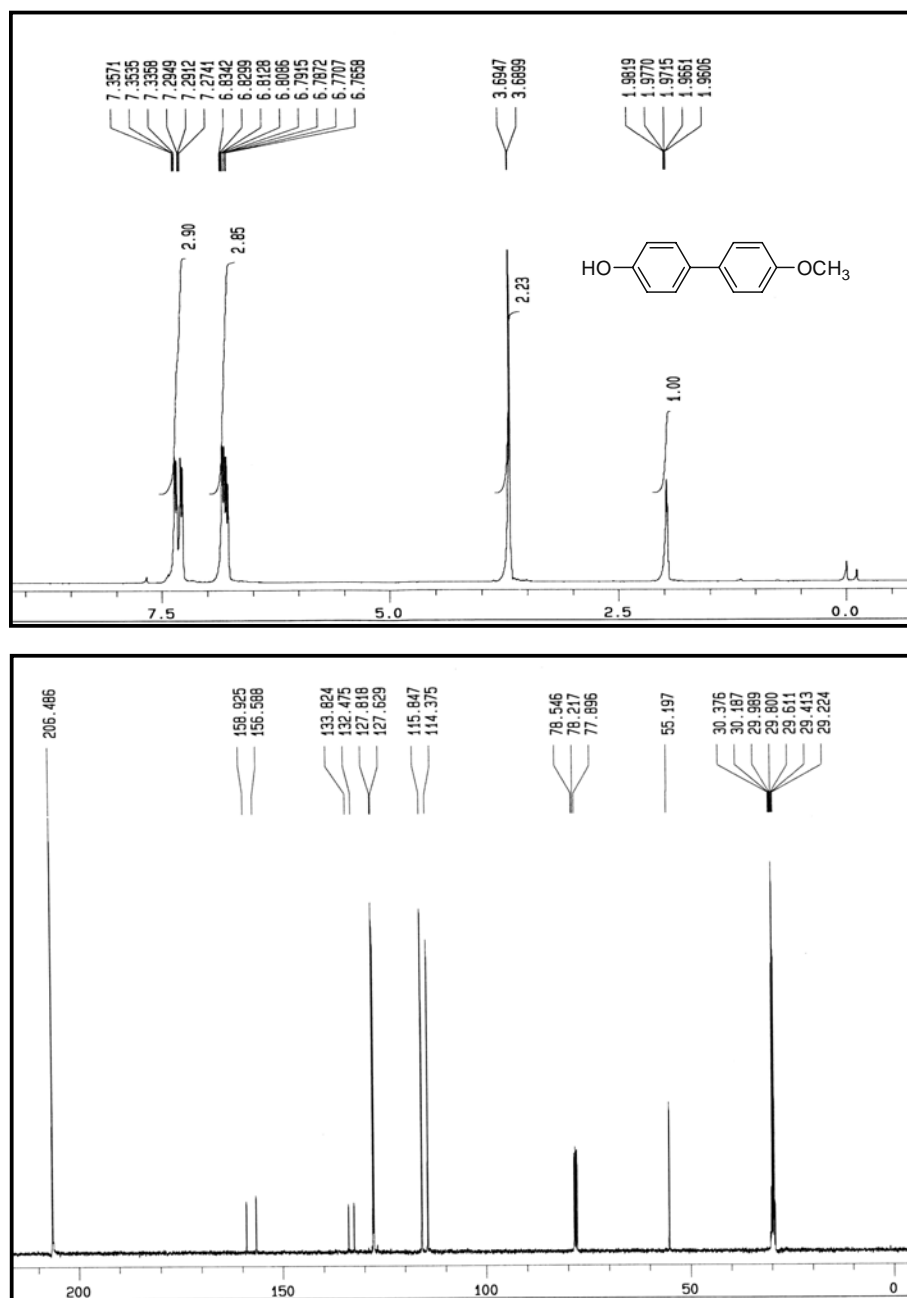


Figure S9. ¹H and ¹³C NMR spectra of 4-methoxy-4'-hydroxybiphenyl.

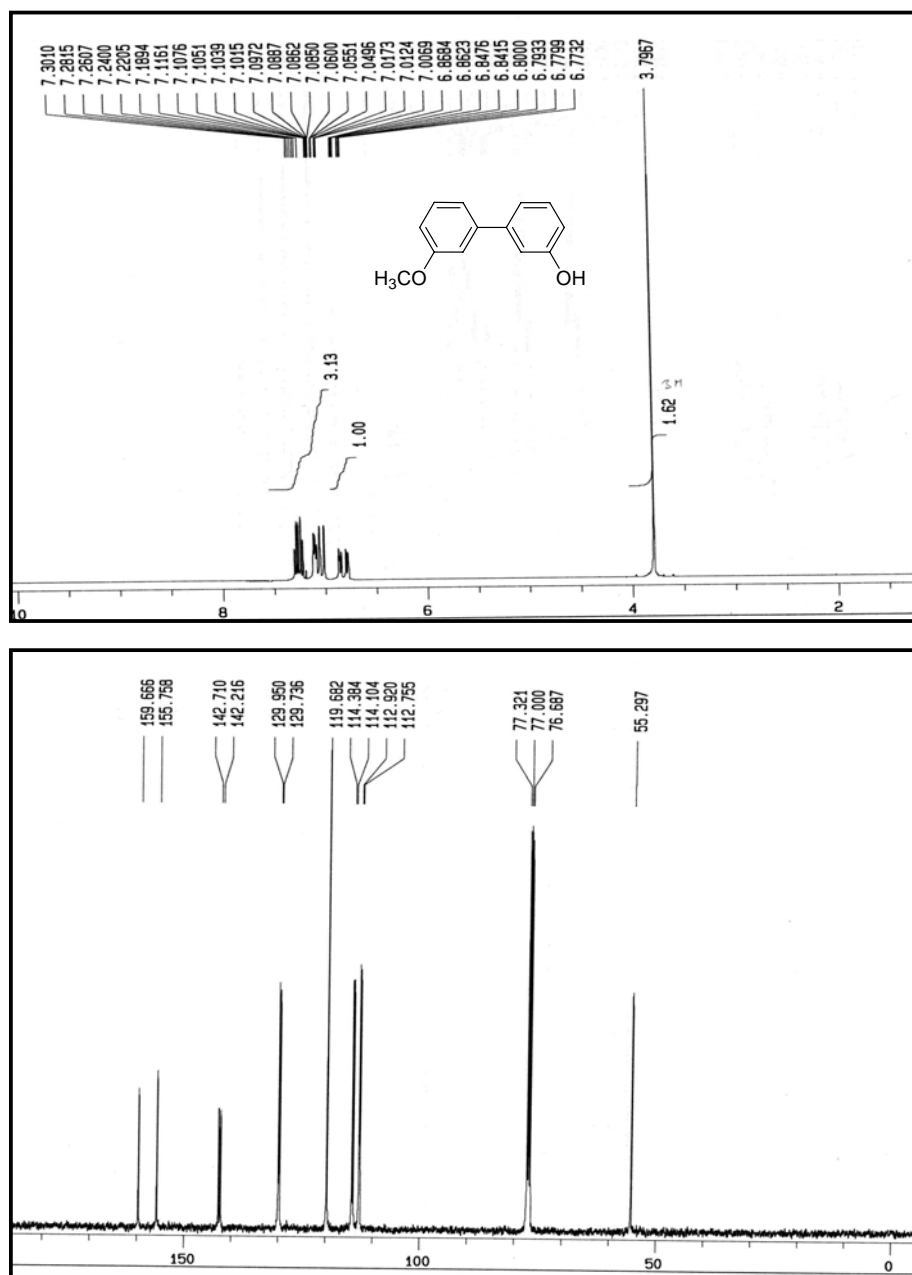


Figure S10. ¹H and ¹³C NMR spectra of 3-methoxy-3'-hydroxybiphenyl.

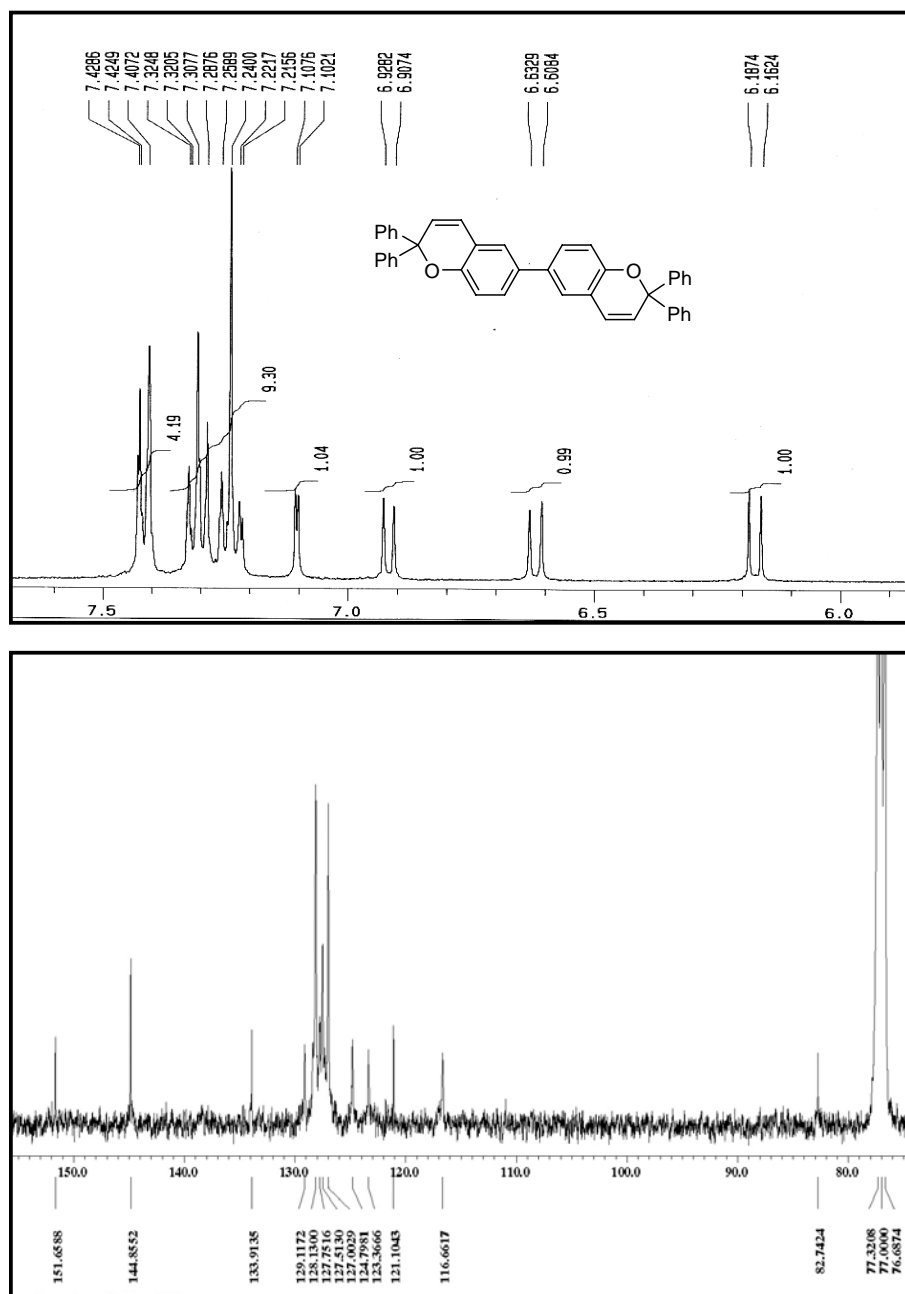


Figure S11. ¹H and ¹³C NMR spectra of 6,6'-bischromene, **3**.

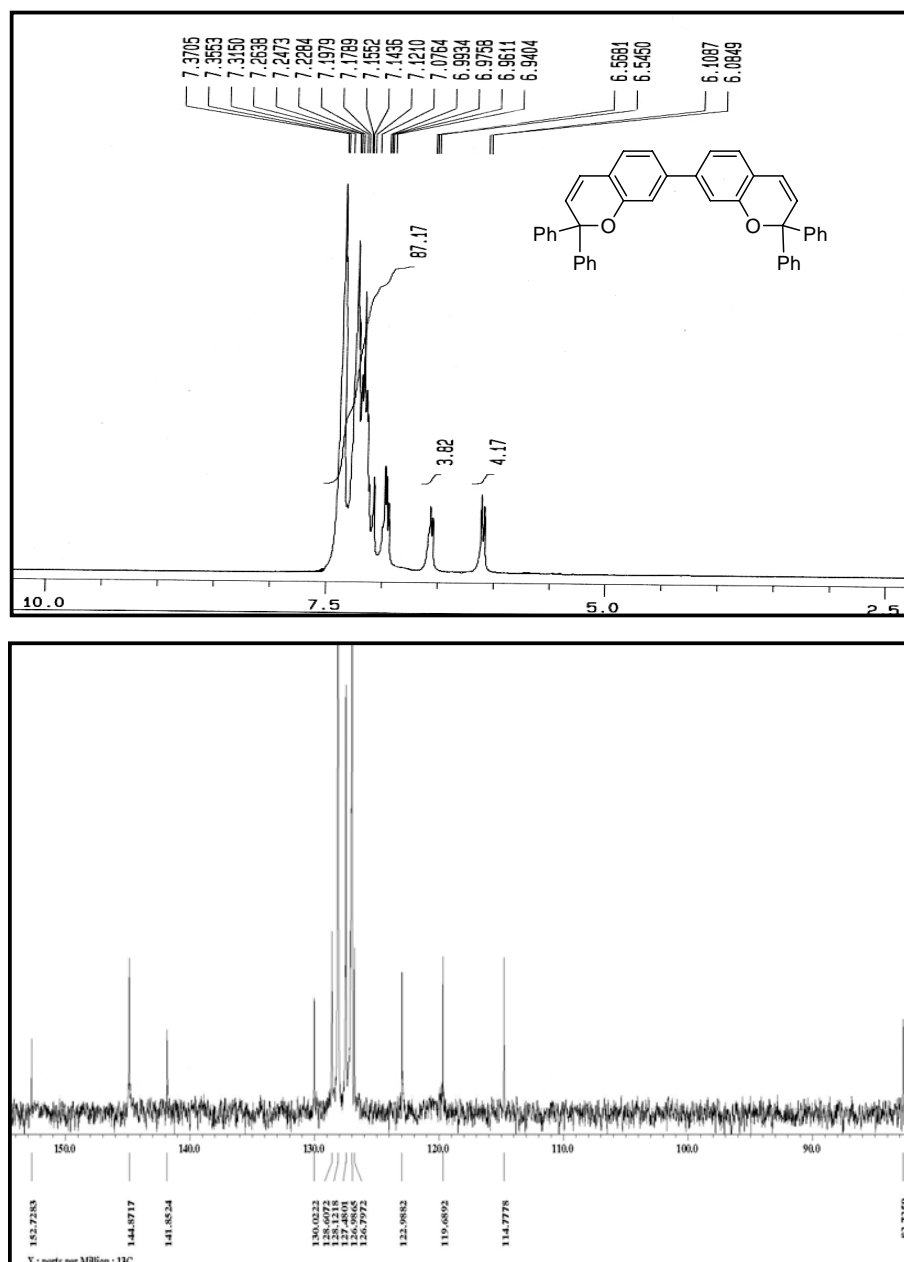


Figure S12. ^1H and ^{13}C NMR spectra of 7,7'-bischromene, **4**.

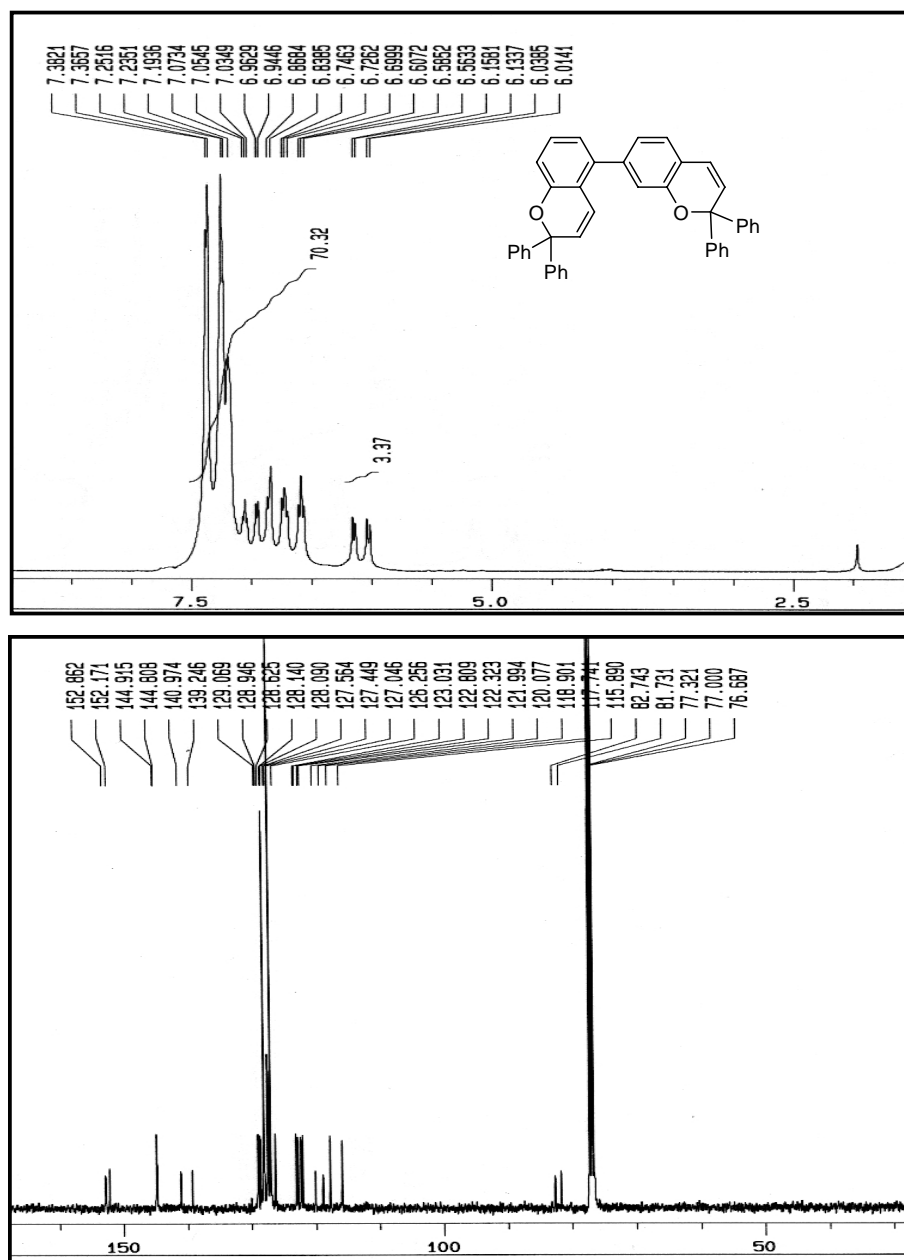


Figure S13. ^1H and ^{13}C NMR spectrum of 5,7'-bischromene.

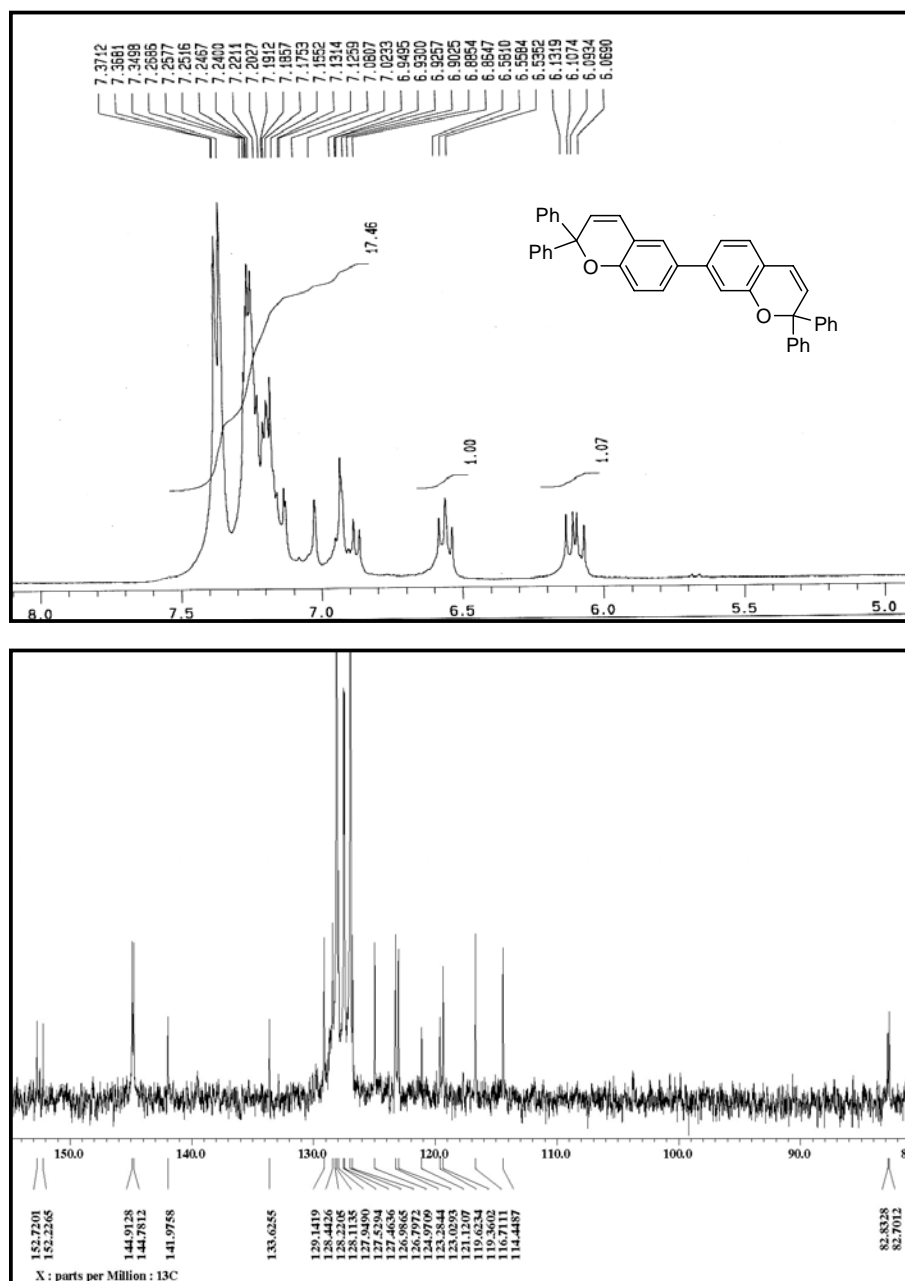


Figure S14. ¹H and ¹³C NMR spectra of 6,7'-bischromene, **5**.

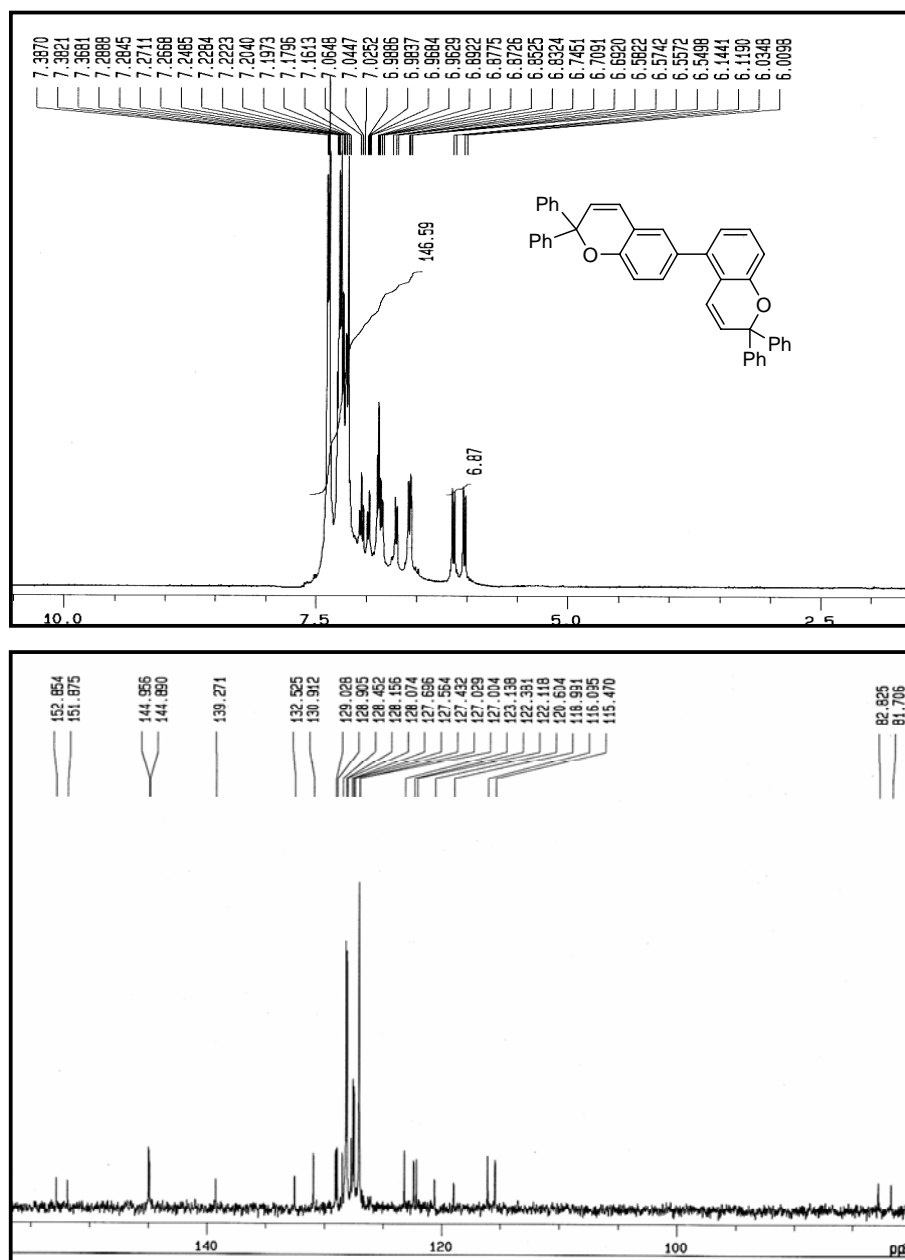


Figure S15. ^1H and ^{13}C NMR spectra of 5,6'-bischromene.

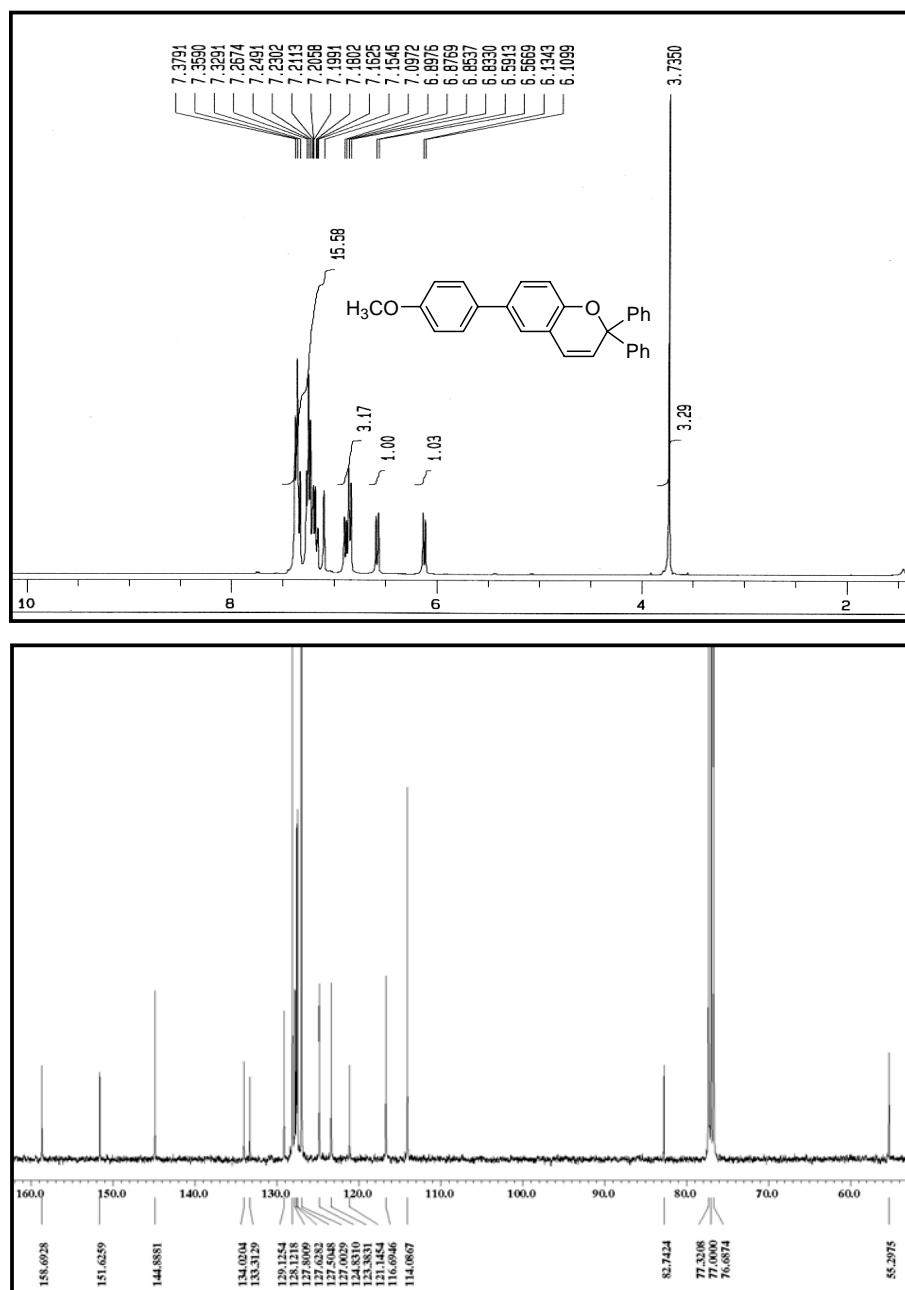


Figure S16. ¹H and ¹³C NMR spectra of 6-(4-methoxyphenyl)chromene, 6.

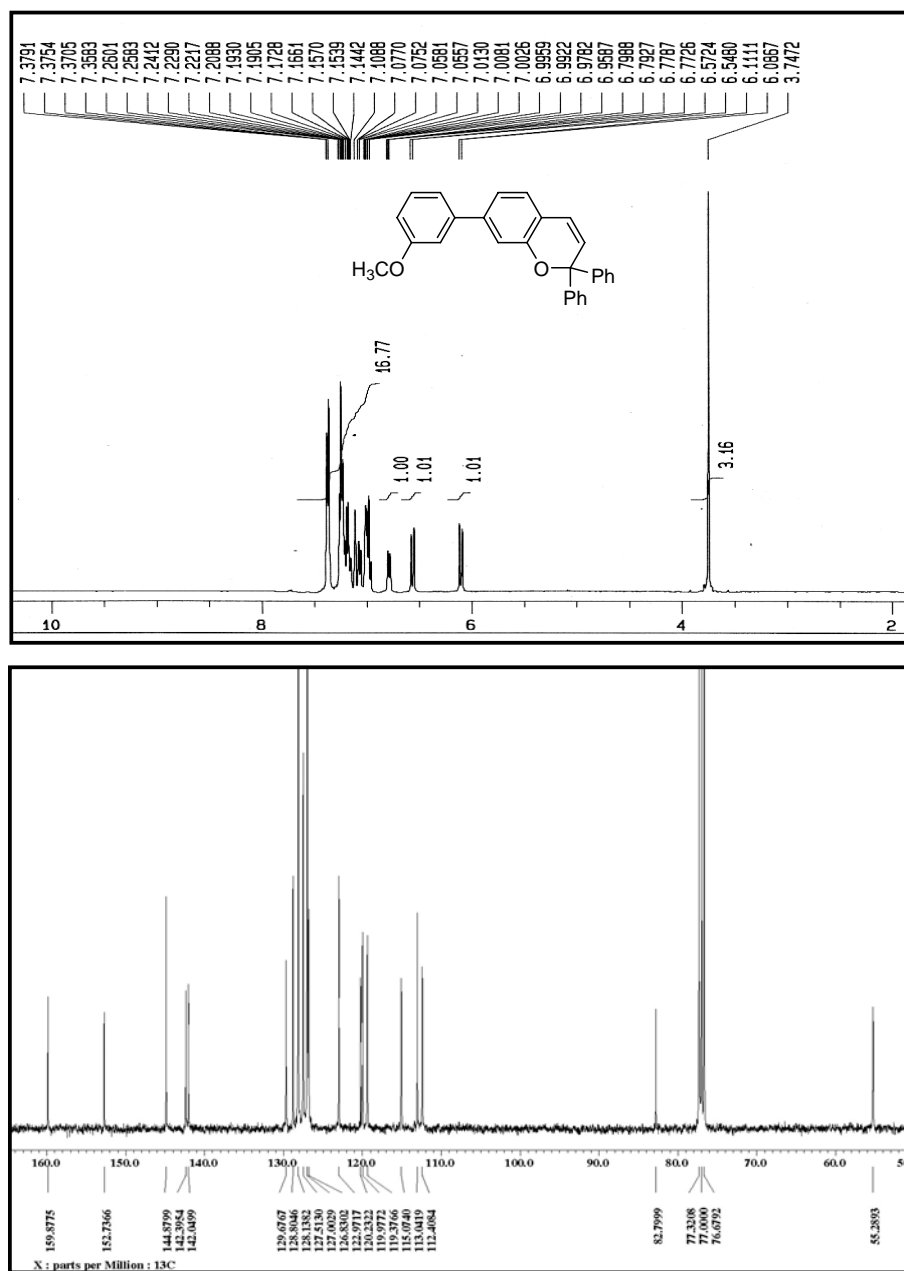


Figure S17. ¹H and ¹³C NMR spectra of 7-(3-methoxyphenyl)chromene, 7.

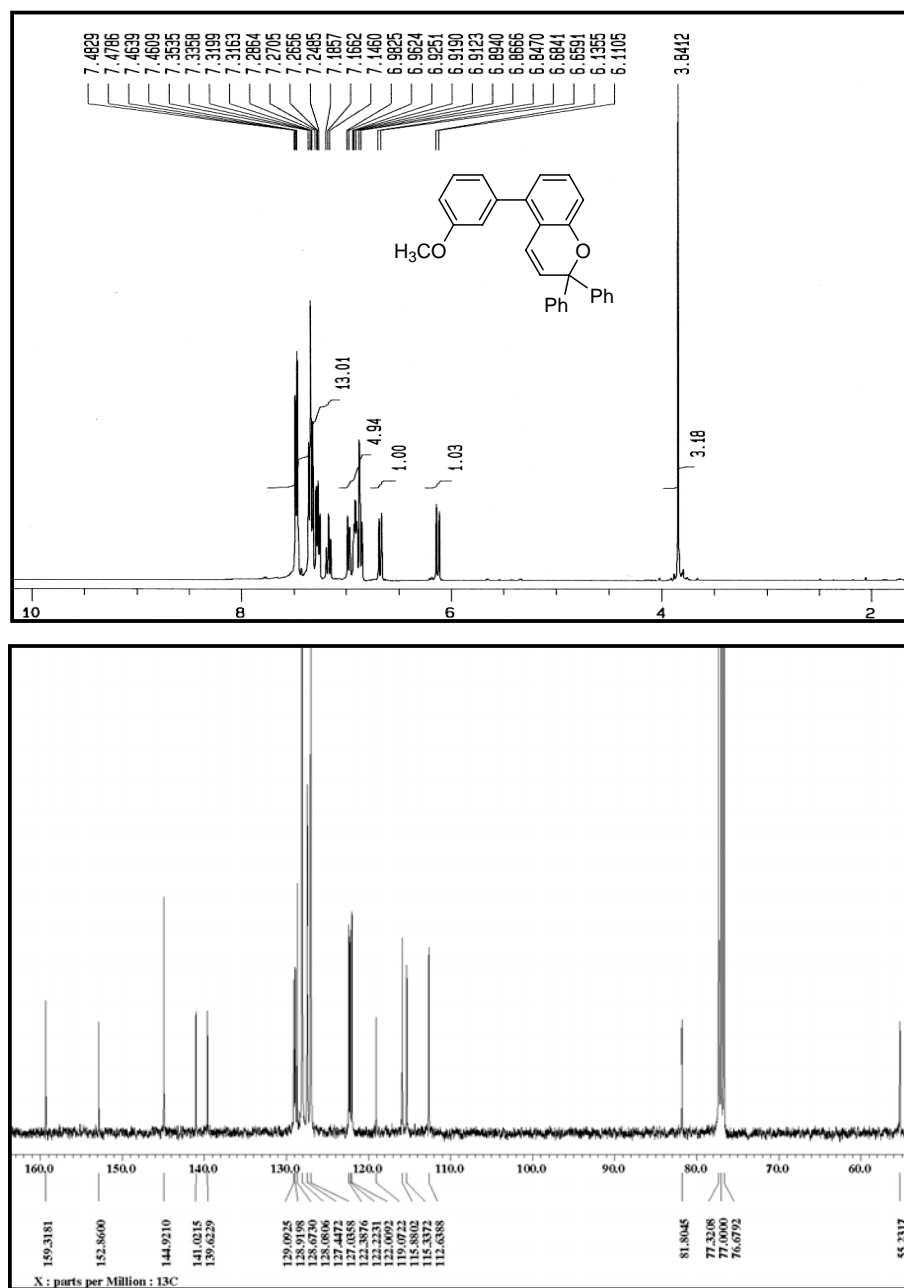


Figure S18. ¹H and ¹³C NMR spectra of 5-(3-methoxyphenyl)chromene.