Supporting Information

Palladium-Catalyzed Coupling of N-Tosylhydrazones and β-Bromostyrene Derivatives: New Approach to 2H-Chromenes

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1. General

All the palladium-catalyzed reactions were performed under argon atmosphere in a flame-dried reaction flask. All solvents were distilled under nitrogen atmosphere prior to use. 1,4-Dioxane and toluene were dried over Na with benzophenone-ketyl intermediate as indicator, and acetonitrile was dried over CaH₂. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. LRMS were obtained on an Agilent 5975C inert 350 EI mass spectrometer. HRMS were obtained on a Bruker Apex IV FTMS by ESI or GCT CA127 Micronass UK by EI.

2. Preparation of N-Tosylhydrazones

Typical procedure for converting salicylaldehydes to the corresponding N-tosylhydrazones: salicylaldehyde (4.88 g, 40 mmol) was dissolved in methanol (30 mL), then TsNHNH₂ (7.44 g, 40 mmol) was added to the reaction mixture. The resulting mixture was heated to 60 °C, and stirring was continued for 5 h. After the reaction was cooled to room temperature, the precipitates were filtered and washed by petroleum ether, and then kept in desiccator under vacuum to afford pure product 1a (9.98 g, 86%). The yields for other tosylhydrazones were about 73-88%. The reactions were usually carried out overnight and were monitored by TLC.

3. Preparation of (E)-2-(Bromovinyl)styrenes¹²

Compounds 2a-2e, 2g-2i, 2m were prepared according to the procedure described in ref. 1. The yields were about 53-67%.

Compounds 2f, 2j-l were prepared according to the procedure described in ref. 2. The yields were about 58-86%.

4. General Procedure of Palladium-Catalyzed Reductive Coupling

Under an argon atmosphere, Pd₂(dba)₃·CHCl₃ (5.2 mg, 0.005 mmol, 2.5 mol%), PCy₃·HBF₄ (11.1 mg, 0.03 mmol, 15 mol%), N-tosylhydrazones (0.4 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol) are successively added to a flame-dried 25 mL Schlenk flask. The reaction flask was degassed three times with argon and dry dioxane (2.0 mL) was added using a syringe. Then (E)-2-(bromovinyl)styrenes (0.2 mmol) were added by syringe. Note that (E)-2-(bromovinyl)styrene in a solid form was added to the reaction flask prior to K₂CO₃. The reaction was heated at 100 °C with stirring for about 12 h, then cooled to room temperature and filtered through a short path of neutral alumina with petroleum ether/ethyl acetate (5:1, 30 mL) as eluents. Solvent was then removed in vacuo to leave a crude mixture, which was purified by silica gel column chromatography to afford the pure product.
5. Characterization data

2-phenyl-2H-chromene (3a)\(^3,6\)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (petroleum ether, PE), the product was isolated as a colorless oil (38 mg, 91%). \(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.45-7.43 (m, 2H), 7.37-7.30 (m, 3H), 7.11-7.07 (m, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.87-6.83 (m, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 10.0 Hz, 1H), 5.90-5.89 (m, 1H), 5.78 (dd, J = 10.0 Hz, 3.6 Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 153.1, 140.8, 129.4, 128.6, 128.3, 126.9, 126.5, 124.8, 123.9, 121.2, 121.1, 115.9, 77.1.

2-(p-tolyl)-2H-chromene (3b)\(^3,6\)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (39 mg, 88%). \(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.34-7.32 (m, 2H), 7.19-7.15 (m, 2H), 7.10-7.06 (m, 1H), 6.98 (d, J = 8.0 Hz, 1.6 Hz, 1H), 6.86-6.82 (m, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.51 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 5.87-5.86 (m, 1H), 5.77 (dd, J = 10.0 Hz, 3.6 Hz, 1H), 2.33 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 153.1, 138.1, 137.8, 129.3, 129.2, 127.0, 126.5, 124.9, 123.9, 121.3, 121.0, 115.9, 77.0, 21.1.

2-[(1,1'-biphenyl)-4-yl]-2H-chromene (3c)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless solid (41 mg, 71%); mp 103-104 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.60-7.56 (m, 4H), 7.53-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.36-7.31 (m, 1H), 7.14-7.09 (m, 1H), 7.02 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 6.89-6.85 (m, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.56 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 5.97-5.95 (m, 1H), 5.83 (dd, J = 10.0 Hz, 3.2 Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 153.1, 141.3, 140.7, 139.7, 129.4, 128.7, 127.5, 127.4, 127.3, 127.1, 126.6, 124.6, 124.1, 121.3, 121.2, 116.0, 76.8; HRMS (ESI, m/z): calcd for C\(_{21}\)H\(_{17}\)O [M+H]\(^+\) 285.1274, found 285.1271; LRMS (EI, m/z): 284 (M\(^+\), 93), 283 (100), 252 (19), 207 (46), 152 (61); IR (film): 1486, 1209, 1108, 954, 748 cm\(^{-1}\).

2-(3,4-dimethoxyphenyl)-2H-chromene (3d)\(^7\)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 60:1), the product was isolated as a colorless oil (23 mg, 42%). \(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.13-7.08 (m, 1H), 7.03-6.97 (m, 3H), 7.01-6.96 (m, 1H), 6.99 (d, J = 10.0 Hz, 1H), 6.92-6.89 (m, 1H), 6.63-6.59 (m, 1H), 6.57 (d, J = 10.0 Hz, 1H), 5.99 (dd, J = 10.0 Hz, 3.6 Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 153.1, 140.8, 129.4, 128.6, 128.3, 126.9, 126.5, 124.8, 123.9, 121.2, 121.1, 115.9, 77.1.
6.89-6.83 (m, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.54 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 5.87-5.85 (m, 1H), 5.78 (dd, J = 10.0 Hz, 3.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 149.2, 149.1, 133.2, 129.4, 126.5, 124.9, 124.1, 121.3, 121.1, 119.7, 116.0, 110.9, 110.4, 77.1, 55.9, 55.8.

2-[4-(3,4-methenedioxy)phenyl]-2H-chromene (3e)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 60:1), the product was isolated as a colorless oil (27 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.09 (m, 1H), 7.00 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 6.95 (d, J = 1.6 Hz, 1H), 6.90 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.87-6.83 (m, 1H), 6.79-6.74 (m, 2H), 6.53 (dd, J = 10.0 Hz, 1.2 Hz, 1H), 5.93 (d, J = 1.6 Hz, 2H), 5.81 (dd, J = 3.2 Hz, 2.0 Hz, 1H), 5.75 (dd, J = 10.0 Hz, 3.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 147.9, 147.7, 134.6, 129.4, 126.5, 124.6, 124.1, 121.2, 121.1, 120.8, 116.0, 108.1, 107.8, 101.1, 76.9; HRMS (ESI, m/z): calcd for C₁₆H₁₃O₃ [M+H]+ 253.0859, found 253.0860; LRMS (EI, m/z): 252 (M+, 100), 221 (28), 205 (21), 165 (92); IR (film): 1502, 1484, 1249, 1226, 1038, 794 cm⁻¹.

2-[4-(trifluoromethoxy)phenyl]-2H-chromene (3f)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1, EA = ethyl acetate), the product was isolated as a colorless oil (39 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.45 (m, 2H), 7.21-7.18 (m, 2H), 7.13-7.09 (m, 1H), 7.01 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.89-6.85 (m, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.54 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 5.91-5.89 (m, 1H), 5.76 (dd, J = 10.0 Hz, 3.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 149.0, 139.4, 129.6, 128.4, 126.6, 124.3, 124.1, 121.4, 121.1, 121.0, 120.4 (q, J = 257.0 Hz), 116.0, 76.1.

2-(2-methoxyphenyl)-2H-chromene (3g)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (29 mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.30-7.22 (m, 1H), 7.12-7.07 (m, 1H), 6.99-6.88 (m, 3H), 6.86-6.79 (m, 2H), 6.46 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 6.35-6.33 (m, 1H), 5.78 (dd, J = 10.0 Hz, 3.2 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 153.5, 129.3, 129.2, 129.1, 127.6, 126.4, 124.9, 123.2, 121.2, 120.9, 120.7, 115.8, 110.5, 71.5, 55.4.
2-(3-methoxyphenyl)-2H-chromene (3h)\(^6\)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (28 mg, 59%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.24 (m, 1H), 7.13-7.08 (m, 1H), 7.04-6.99 (m, 3H), 6.88-6.84 (m, 2H), 6.79 (d, \(J = 8.0\) Hz, 1H), 6.52 (dd, \(J = 9.6\) Hz, 1.6 Hz, 1H), 5.90-5.87 (m, 1H), 5.79 (dd, \(J = 9.6\) Hz, 3.2 Hz, 1H), 3.78 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.8, 153.1, 142.4, 129.7, 129.4, 126.6, 124.8, 124.0, 121.3, 121.2, 119.2, 116.0, 113.8, 112.561, 77.0, 55.2.

2-(4-methoxyphenyl)-2H-chromene (3i)\(^3,6\)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (35 mg, 74%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38-7.36 (m, 2H), 7.10-7.06 (m, 1H), 7.00 (dd, \(J = 7.6\) Hz, 1.6 Hz, 1H), 6.90-6.82 (m, 3H), 6.75 (d, \(J = 8.0\) Hz, 1H), 6.53 (dd, \(J = 10.0\) Hz, 1.6 Hz, 1H), 5.85 (dd, \(J = 3.2\) Hz, 2.0 Hz, 1H), 5.77 (dd, \(J = 10.0\) Hz, 3.2 Hz, 1H), 3.78 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.7, 153.0, 132.8, 129.3, 128.6, 126.4, 124.8, 123.9, 121.3, 121.0, 116.0, 113.9, 76.7, 55.2.

2-(4-fluorophenyl)-2H-chromene (3j)\(^3,5\)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (31 mg, 67%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.40 (m, 2H), 7.13-7.09 (m, 1H), 7.07-6.99 (m, 3H), 6.89-6.84 (m, 1H), 6.77 (d, \(J = 8.0\) Hz, 1H), 6.55 (dd, \(J = 10.0\) Hz, 1.6 Hz, 1H), 5.89-6.88 (m, 1H), 5.77 (dd, \(J = 10.0\) Hz, 3.6 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.6 (d, \(J = 245.3\) Hz), 152.8, 136.6 (d, \(J = 3.3\) Hz), 129.5 128.9 (d, \(J = 8.3\) Hz), 126.6, 124.4, 124.2, 121.3, 121.2, 116.0, 115.5 (d, \(J = 21.5\) Hz), 76.3.

2-(2-fluorophenyl)-2H-chromene (3k)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (39 mg, 87%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53-7.48 (m, 1H), 7.31-7.25 (m, 1H), 7.14-7.04 (m, 3H), 7.00 (dd, \(J = 7.2\) Hz, 1.6 Hz, 1H), 6.89-6.84 (m, 1H), 6.80 (d, \(J = 8.0\) Hz, 1H), 6.52 (dd, \(J = 10.0\) Hz, 1.6 Hz, 1H), 6.27 (dd, \(J = 3.2\) Hz, 1.6 Hz, 1H), 5.77 (dd, \(J = 10.0\) Hz, 3.6 Hz, 0.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.5 (d, \(J = 245.9\) Hz), 153.1, 129.9 (d, \(J = 8.3\) Hz), 129.5, 128.6.
(d, J = 2.7 Hz), 128.0 (d, J = 13.5 Hz), 126.7, 124.3 (d, J = 3.6 Hz), 124.2, 123.6, 121.3, 121.0, 115.9, 115.6 (d, J = 21.3 Hz), 70.8 (d, J = 3.5 Hz); HRMS (ESI, m/z): calcd for C_{15}H_{12}FO [M+H]^+ 227.0867, found 227.0863; LRMS (EI, m/z): 226 (M^+, 80), 225 (100), 207 (10), 196 (32), 131 (74); IR (film): 1485, 1455, 1226, 1045, 752 cm\(^{-1}\).

2-(4-chlorophenyl)-2H-chromene (3l)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (34 mg, 69%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.39-7.36 (m, 2H), 7.33-7.31 (m, 2H), 7.13-7.08 (m, 1H), 7.00 (dd, \(J = \) 7.6 Hz, 1.6 Hz, 1H), 6.89-6.84 (m, 1H), 6.77 (d, \(J = \) 8.0 Hz, 1H), 6.54 (dd, \(J = \) 9.6 Hz, 1.6 Hz, 1H), 5.87 (dd, \(J = \) 3.6 Hz, 1.6 Hz, 1H), 5.75 (dd, \(J = \) 9.6 Hz, 3.6 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 152.8, 139.2, 134.1, 129.5, 128.7, 128.4, 126.6, 124.3, 124.2, 121.3, 121.1, 115.9, 76.2.

2-(thiophen-2-yl)-2H-chromene (3m)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (40 mg, 92%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.26 (dd, \(J = \) 5.2 Hz, 1.2 Hz, 1H), 7.12-7.07 (m, 2H), 7.02 (dd, \(J = \) 7.2 Hz, 1.2 Hz, 1H), 6.97-6.94 (m, 1H), 6.89-6.84 (m, 1H), 6.78 (d, \(J = \) 8.0 Hz, 1H), 6.57 (d, \(J = \) 9.6 Hz, 1H), 6.11-6.09 (m, 1H), 5.90 (dd, \(J = \) 9.6 Hz, 4.0 Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 152.4, 143.6, 129.5, 126.7, 126.6, 126.2, 126.0, 124.5, 123.8, 121.4, 121.3, 116.3, 71.6; HRMS (ESI, m/z): calcd for C\(_{13}\)H\(_{11}\)OS [M+H]^+ 215.0525, found 215.0524; LRMS (EI, m/z): 214 (M^+, 83), 213 (100), 184 (28), 152 (30); IR (film): 1484, 1225, 1197, 1034, 754 cm\(^{-1}\).

6-methyl-2-phenyl-2H-chromene (3n)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (41 mg, 91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.45-7.42 (m, 2H), 7.37-7.27 (m, 3H), 6.90 (dd, \(J = \) 8.0 Hz, 1.6 Hz, 1H), 6.82-6.80 (m, 1H), 6.69 (d, \(J = \) 8.0 Hz, 1H), 6.48 (dd, \(J = \) 10.0 Hz, 3.2 Hz, 1H), 5.87-5.85 (m, 1H), 5.77 (dd, \(J = \) 10.0 Hz, 3.2 Hz, 1H), 2.24 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 150.9, 140.8, 130.3, 129.8, 128.5, 128.2, 127.0, 126.9, 124.9, 124.0, 121.0, 115.6, 77.0, 20.4.

8-methyl-2-phenyl-2H-chromene (3o)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (29 mg, 65%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.45-7.43 (m, 2H), 7.38-7.29 (m,
6-(tert-butyl)-2-phenyl-2H-chromene (3p)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (46 mg, 87%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.43 (m, 2H), 7.37-7.30 (m, 3H), 7.13 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 7.01 (d, $J = 2.0$ Hz, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 6.51 (dd, $J = 9.6$ Hz, 2.0 Hz, 1H), 5.90-5.88 (m, 1H), 5.76 (dd, $J = 9.6$ Hz, 3.2 Hz, 1H), 1.28 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.8, 143.8, 141.0, 128.5, 128.2, 126.9, 126.3, 124.7, 124.4, 123.5, 120.5, 115.2, 77.1, 34.0, 31.4.

5,7-dimethyl-2-phenyl-2H-chromene (3q)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (34 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.43 (m, 2H), 7.37-7.29 (m, 3H), 6.68 (dd, $J = 10.0$ Hz, 0.8 Hz, 1H), 6.53 (s, 1H), 6.50 (s, 1H), 5.82-5.80 (m, 1H), 5.77 (dd, $J = 10.0$ Hz, 3.6 Hz, 1H), 2.27 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.2, 140.9, 139.0, 133.9, 128.5, 128.1, 126.9, 123.7, 123.5, 121.1, 117.3, 114.5, 76.4, 21.3, 18.2. HRMS (ESI, $m/z$): calcd for C$_{17}$H$_{17}$O [M+H]$^+$ 237.1274, found 237.1281; LRMS (El, $m/z$): 236 (M$^+$, 92), 235 (100), 221 (34), 209 (16), 178 (20), 159 (56); IR (film): 1613, 1453, 1282, 1140, 1074, 842, 761, 699 cm$^{-1}$.

6,8-di-tert-butyl-2-phenyl-2H-chromene (3r)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (60 mg, 93%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49-7.46 (m, 2H), 7.40-7.30 (m, 3H), 7.19 (d, $J = 2.4$ Hz, 1H), 6.92 (d, $J = 2.4$ Hz, 1H), 6.51 (dd, $J = 10.0$ Hz, 2.0 Hz, 1H), 5.86-5.84 (m, 1H), 5.74 (dd, $J = 10.0$ Hz, 3.2 Hz, 1H), 1.31 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.3, 143.0, 140.8, 136.6, 128.5, 128.0, 126.9, 125.4, 124.9, 124.0, 121.7, 121.5, 76.9, 34.6, 34.2, 31.5, 29.7.
7-methoxy-2-phenyl-2H-chromene (3s)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (32 mg, 66%). $^1$H NMR (400 MHz, CDCl₃) δ 7.46-7.43 (m, 2H), 7.39-7.28 (m, 3H), 6.91 (d, $J$ = 8.4 Hz, 1H), 6.48 (dd, $J$ = 10.0 Hz, 1.6 Hz, 1H), 6.42 (dd, $J$ = 8.4 Hz, 2.4 Hz, 1H), 6.38 (d, $J$ = 2.4 Hz, 1H), 5.88 (dd, $J$ = 3.2 Hz, 2.0 Hz, 1H), 5.65 (dd, $J$ = 10.0 Hz, 3.2 Hz, 1H), 3.73 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 160.9, 154.4, 140.9, 128.6, 128.3, 127.2, 127.0, 123.6, 121.8, 114.6, 107.0, 101.8, 77.3, 55.3.

6-methoxy-2-phenyl-2H-chromene (3t)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (32 mg, 68%). $^1$H NMR (400 MHz, CDCl₃) δ 7.45-7.42 (m, 2H), 7.38-7.29 (m, 3H), 6.72 (d, $J$ = 8.8 Hz, 1H), 6.66 (dd, $J$ = 8.8 Hz, 2.8 Hz, 1H), 6.58 (d, $J$ = 3.2 Hz, 1H), 6.49 (dd, $J$ = 10.4 Hz, 2.8 Hz, 1H), 5.86-5.82 (m, 2H), 3.74 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 153.9, 147.0, 140.6, 128.5, 128.2, 126.9, 125.8, 124.1, 121.9, 116.5, 114.4, 111.7, 76.9, 55.6.

8-methoxy-2-phenyl-2H-chromene (3u)

The title compound was prepared via the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (13 mg, 26%). $^1$H NMR (400 MHz, CDCl₃) δ 7.47-7.45 (m, 2H), 7.37-7.29 (m, 3H), 6.84-6.86 (m, 2H), 6.65 (dd, $J$ = 7.2 Hz, 1.6 Hz, 1H), 6.52 (dd, $J$ = 10.0 Hz, 1.6 Hz, 1H), 5.98-5.96 (m, 1H), 5.85 (dd, $J$ = 10.0 Hz, 3.6 Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 147.8, 142.0, 140.7, 128.5, 128.2, 126.8, 124.9, 123.7, 122.0, 120.7, 118.9, 112.7, 76.9, 56.1; HRMS (ESI, m/z): calcd for C₁₆H₁₅O₂ [M+H]+ 239.1067, found 239.1069; LRMS (EI, m/z): 238 (M⁺, 78), 207 (23), 165 (100), 152 (38); IR (film): 1479, 1268, 1211, 1076, 754, 698 cm⁻¹.

6. References

1084-1094.


7. $^1$H NMR and $^{13}$C NMR spectra

$^1$H NMR, 2-phenyl-2$H$-chromene (3a)

$^{13}$C NMR, 2-phenyl-2$H$-chromene (3a)
$^1$H NMR, 2-(p-tolyl)-2H-chromene (3b)

$^{13}$C NMR, 2-(p-tolyl)-2H-chromene (3b)
$^1$H NMR, 2-[(1,1'-biphenyl)-4-yl]-2H-chromene (3c)

$^{13}$C NMR, 2-[(1,1'-biphenyl)-4-yl]-2H-chromene (3c)
$^1$H NMR, 2-(3,4-dimethoxyphenyl)-2$H$-chromene (3d)

$^{13}$C NMR, 2-(3,4-dimethoxyphenyl)-2$H$-chromene (3d)
\[^1\text{H NMR, 2-[4-(3,4-methenedioxy)phenyl]-2H-chromene (3e)}\]

\[^{13}\text{C NMR, 2-[4-(3,4-methenedioxy)phenyl]-2H-chromene (3e)}\]
$^1$H NMR, 2-[4-(trifluoromethoxy)phenyl]-2H-chromene (3f)

$^{13}$C NMR, 2-[4-(trifluoromethoxy)phenyl]-2H-chromene (3f)
$^1$H NMR, 2-(2-methoxyphenyl)-2H-chromene (3g)

$^{13}$C NMR, 2-(2-methoxyphenyl)-2H-chromene (3g)
$^1$H NMR, 2-(3-methoxyphenyl)-2$H$-chromene (3h)

$^{13}$C NMR, 2-(3-methoxyphenyl)-2$H$-chromene (3h)
$^1$H NMR, 2-(4-methoxyphenyl)-2H-chromene (3i)

$^{13}$C NMR, 2-(4-methoxyphenyl)-2H-chromene (3i)
$^1$H NMR, 2-(4-fluorophenyl)-2$H$-chromene (3j)

$^{13}$C NMR, 2-(4-fluorophenyl)-2$H$-chromene (3j)
$^1$H NMR, 2-(2-fluorophenyl)-2$H$-chromene (3k)

$^{13}$C NMR, 2-(2-fluorophenyl)-2$H$-chromene (3k)
$^1$H NMR, 2-(4-chlorophenyl)-2H-chromene (3I)

$^{13}$C NMR, 2-(4-chlorophenyl)-2H-chromene (3I)
$^1$H NMR, 2-(thiophen-2-yl)-2$H$-chromene (3m)

$^{13}$C NMR, 2-(thiophen-2-yl)-2$H$-chromene (3m)
$^1$H NMR, 6-methyl-2-phenyl-$2H$-chromene (3n)

$^{13}$C NMR, 6-methyl-2-phenyl-$2H$-chromene (3n)
$^1$H NMR, 8-methyl-2-phenyl-2$H$-chromene (3o)

$^{13}$C NMR, 8-methyl-2-phenyl-2$H$-chromene (3o)
$^1$H NMR, 6-(tert-butyl)-2-phenyl-2H-chromene (3p)

$^{13}$C NMR, 6-(tert-butyl)-2-phenyl-2H-chromene (3p)
$^1$H NMR, 5,7-dimethyl-2-phenyl-$2H$-chromene (3q)

$^{13}$C NMR, 5,7-dimethyl-2-phenyl-$2H$-chromene (3q)
$^1$H NMR, 6,8-di-tert-butyl-2-phenyl-2H-chromene (3r)

$^{13}$C NMR, 6,8-di-tert-butyl-2-phenyl-2H-chromene (3r)
$^1$H NMR, 7-methoxy-2-phenyl-2$H$-chromene (3s)

$^{13}$C NMR, 7-methoxy-2-phenyl-2$H$-chromene (3s)
$^1$H NMR, 6-methoxy-2-phenyl-$2H$-chromene (3t)

$^{13}$C NMR, 6-methoxy-2-phenyl-$2H$-chromene (3t)
$^1$H NMR, 8-methoxy-2-phenyl-2$H$-chromene (3u)

$^{13}$C NMR, 8-methoxy-2-phenyl-2$H$-chromene (3u)