Supporting Information

Copper(II) perchlorate-promoted tandem reaction of internal alkynol and salicyl *N*-tosylhydrazone: direct access to isochromeno[3,4-*b*]chromene

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1. General Information

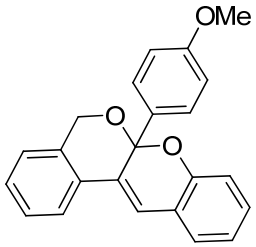
All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (THF, toluene, dioxane) or calcium hydride (CH_3CN, CH_3NO_2, DCE). Chemical shifts (δ, ppm) in the ^1H NMR spectra were recorded using TMS as internal standard. Chemical shifts in $^{13}C\{^1H\}$ NMR spectra were internally referenced to $CDCl_3$ (δ = 77.1 ppm).

2. Experimental procedures

Typical procedure for the tandem reaction of substituted internal alkynol **1** with various salicyl tosylhydrazone **2** catalyzed by $Cu(ClO_4)_2{\cdot}6H_2O$.

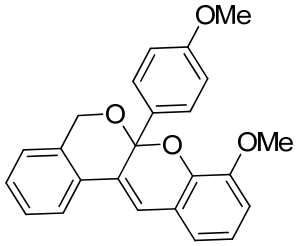
Procedure: To a mixture of internal alkynol **1** (0.6 mmol) and salicyl *N*-tosylhydrazone **2** (0.3 mmol) in a mixture solvent (toluene:dioxane= 1:4, v/v, 2 ml) was added the copper(II) perchlorate (0.09 mmol, 30 mol%) under Ar. The reaction mixture was stirred at 60 ^oC for 11 hours and the progress was monitored using TLC detection. After completion of present reaction, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the desired products **3**.

3. Analytical data for products.

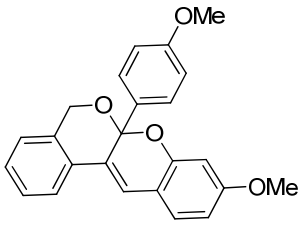


6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3a). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.096 g (94% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v)as white solid, mp 137.3-139.1 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 7.84 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.23-7.26 (m, 1H), 7.14-7.17 (m, 3H), 7.02 (d, J = 7.5 Hz, 1H), 6.87-6.94 (m, 2H), 6.74 (d, J = 8.8 Hz, 2H), 4.94 (d, J = 14.8 Hz, 1H), 4.61

(d, J = 14.8 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 151.6, 133.9, 131.2, 130.9, 129.5, 128.2, 127.9, 127.8, 127.4, 127.1, 124.6, 123.3, 122.6, 121.9, 119.2, 116.5, 113.6, 102.0, 65.0, 55.2; HRMS (ESI, TOF) calcd for $C_{23}H_{19}O_3$ $[M+H]^+$ 343.1334, found 343.1331.

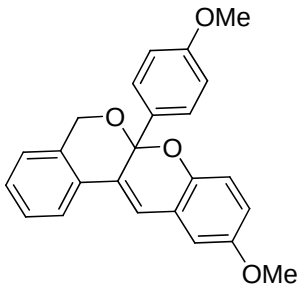


8-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3b). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2b** (0.096 g, 0.3 mmol) following typical procedure: 0.078 g (70% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 20:1 v/v) as white solid, mp 191.9-193.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.81 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.24-7.28 (m, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.05 (s, 1H), 6.82-6.86 (m, 1H), 6.75-6.79 (m, 2H), 6.73 (d, J = 8.9 Hz, 2H), 4.96 (d, J = 14.3 Hz, 1H), 4.64 (d, J = 14.3 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 159.9, 148.3, 140.9, 134.4, 132.0, 131.7, 128.2, 127.9, 127.8, 127.8, 124.6, 123.5, 123.3, 121.5, 120.0, 119.2, 113.4, 112.6, 102.4, 65.1, 56.3, 55.2; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_4$ $[M+H]^+$ 373.1440, found 373.1443.

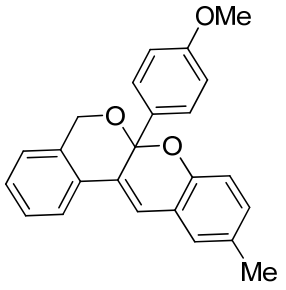


9-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3c). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2c** (0.096 g, 0.3 mmol) following typical procedure: 0.079 g (71% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 25:1 v/v) as white solid, mp 169.8-171.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.80 (d, J = 7.8 Hz, 1H), 7.43 (d, J

= 8.8 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.50-6.51 (m, 1H), 6.46 (dd, J_1= 2.4 Hz, J_2= 8.4 Hz, 1H), 4.92 (d, *J* = 14.6 Hz, 1H), 4.61 (d, *J* = 14.6 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 161.0, 160.0, 152.9, 133.6, 131.5, 131.2, 128.2, 127.9, 127.7, 127.4, 124.6, 124.5, 123.0, 119.1, 115.8, 113.6, 108.1, 102.2, 102.1, 65.1, 55.4, 55.2; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_4$ $[M+H]^+$ 373.1440, found 373.1440.

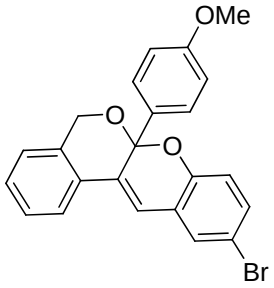


10-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3d). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2d** (0.096 g, 0.3 mmol) following typical procedure: 0.072 g (64% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v) as white solid, mp 172.2-173.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.84 (d, *J* = 7.4 Hz, 1H), 7.36-7.43 (m, 4H), 7.12 (s, 1H), 7.03 (d, *J* = 6.1 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.66-6.76 (m, 4H), 4.93 (d, *J* = 14.9 Hz, 1H), 4.59 (d, *J* = 14.3 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 154.4, 145.6, 134.0, 131.0, 130.8, 128.2, 128.2, 128.0, 127.7, 124.6, 123.2, 123.1, 119.1, 117.1, 115.0, 113.5, 111.6, 102.0, 64.9, 55.7, 55.2; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_4$ $[M+H]^+$ 373.1440, found 373.1432.

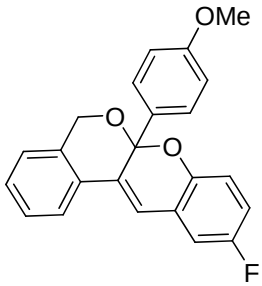


6a-(4-methoxyphenyl)-10-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene (3e).

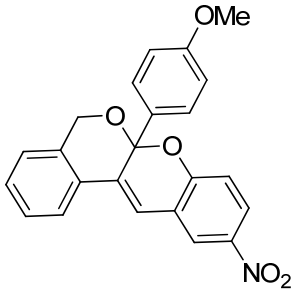
The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2e** (0.091 g, 0.3 mmol) following typical procedure: 0.078 g (73% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v) as white solid, mp 139.7-141.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.84 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 8.9 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.22-7.24 (m, 1H), 7.11 (s, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.95-6.96 (m, 1H), 6.89-6.92 (m, 1H), 6.82-6.84 (m, 1H), 6.74 (d, J = 8.9 Hz, 2H), 4.93 (d, J = 14.8 Hz, 1H), 4.59 (d, J = 14.8 Hz, 1H), 3.70 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 159.9, 149.4, 133.8, 131.1, 131.0, 130.9, 130.1, 128.2, 127.8, 127.7, 127.4, 127.3, 124.5, 123.1, 122.3, 119.2, 116.1, 113.5, 101.9, 64.9, 55.1, 20.6; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1491, found 357.1492.



10-bromo-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3f). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2f** (0.110 g, 0.3 mmol) following typical procedure: 0.094 g (75% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 25:1 v/v) as white solid, mp 173.5-175.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.83 (d, J = 7.8 Hz, 1H), 7.35-7.41 (m, 3H), 7.26-7.29 (m, 2H), 7.18 (d, J = 8.6 Hz, 1H), 7.08 (s, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 8.5 Hz, 1H), 6.76 (d, J = 8.4 Hz, 2H), 4.94 (d, J = 14.8 Hz, 1H), 4.60 (d, J = 14.8 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.2, 150.5, 134.0, 131.9, 130.5, 130.2, 129.3, 128.6, 128.4, 128.2, 127.9, 124.6, 124.5, 123.3, 118.3, 117.7, 114.0, 113.7, 102.1, 65.0, 55.2; HRMS (ESI, TOF) calcd for $C_{23}H_{18}O_3Br$ $[M+H]^+$ 421.0439, found 421.0428.

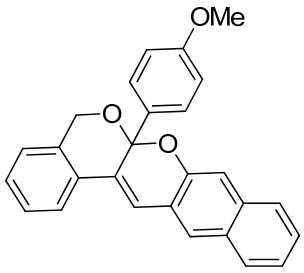


10-fluoro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3g). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2g** (0.092 g, 0.3 mmol) following typical procedure: 0.087 g (81% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 25:1 v/v) as white solid, mp 174.0-176.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.84 (d, J = 7.8 Hz, 1H), 7.35-7.42 (m, 3H), 7.27 (t, J = 7.5 Hz, 1H), 7.10 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.85-6.88 (m, 2H), 6.75-6.80 (m, 3H), 4.94 (d, J = 14.8 Hz, 1H), 4.59 (d, J = 14.8 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.1, 157.7 (J_{CF} = 238.4 Hz), 147.5 (J_{CF} = 2.1 Hz), 134.0, 130.5, 130.3, 128.7, 128.3, 128.2, 127.8, 124.6, 123.5 (J_{CF} = 8.7 Hz), 123.3, 118.2 (J_{CF} = 2.3 Hz), 117.4 (J_{CF} = 8.2 Hz), 115.7 (J_{CF} = 23.6 Hz), 113.6, 112.9 (J_{CF} = 23.9 Hz), 102.1, 65.0, 55.2; HRMS (ESI, TOF) calcd for $C_{23}H_{18}FO_3$ $[M+H]^+$ 361.1240, found 361.1242.

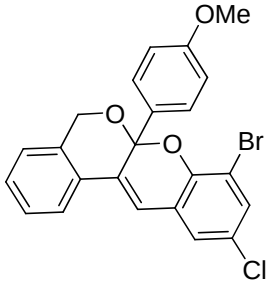


6a-(4-methoxyphenyl)-10-nitro-5,6a-dihydroisochromeno[3,4-*b*]chromene (3h). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2h** (0.101 g, 0.3 mmol) following typical procedure: 0.047 g (41% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 20:1 v/v) as bright yellow solid, mp 207.9-209.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 8.11 (d, J = 2.6 Hz, 1H), 8.01 (dd, J_1= 2.6 Hz, J_2= 8.9 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.38-7.42 (m, 3H), 7.29-7.33

(m, 1H), 7.20 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 4.98 (d, *J* = 15.0 Hz, 1H), 4.64 (d, *J* = 14.9 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.4, 156.4, 142.4, 133.9, 129.9, 129.6, 129.4, 128.9, 128.1, 128.0, 125.1, 124.6, 123.5, 122.6, 122.5, 117.1, 116.9, 113.9, 102.8, 65.2, 55.3; HRMS (ESI, TOF) calcd for $C_{23}H_{18}NO_5$ $[M+H]^+$ 388.1185, found 388.1185.

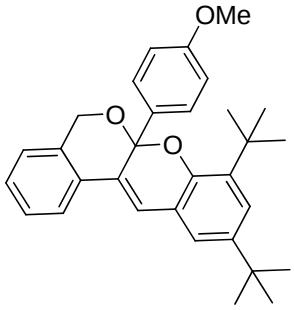


6a-(4-methoxyphenyl)-5,6a-dihydrobenzo[g]isochromeno[3,4-*b*]chromene (3i). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2i** (0.102 g, 0.3 mmol) following typical procedure: 0.061 g (52% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v) as bright yellow solid, mp 190.3-192.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.78 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.53-7.55 (m, 1H), 7.34-7.45 (m, 4H), 7.28-7.30 (m, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 2H), 4.98 (d, *J* = 14.4 Hz, 1H), 4.68 (d, *J* = 14.4 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 149.9, 133.9, 131.8, 131.2, 130.1, 129.6, 128.8, 128.0, 127.9, 127.7, 126.9, 126.0, 124.6, 124.1, 123.4, 121.7, 117.9, 115.8, 115.6, 113.5, 102.5, 65.1, 55.2; HRMS (ESI, TOF) calcd for $C_{27}H_{21}O_3$ $[M+H]^+$ 393.1491, found 393.1490.

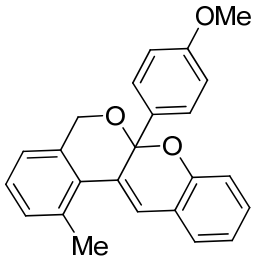


8-bromo-10-chloro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3j). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2j** (0.121 g, 0.3 mmol)

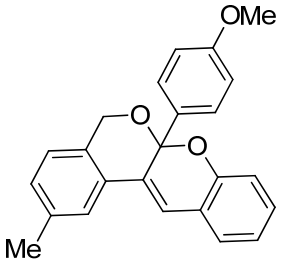
following typical procedure: 0.061 g (45% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 139.7-141.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.83 (d, J = 6.2 Hz, 1H), 7.29-7.45 (m, 5H), 7.03-7.07 (m, 3H), 6.76 (d, J = 6.2 Hz, 2H), 4.95 (d, J = 14.4 Hz, 1H), 4.59 (d, J = 13.8 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.3, 147.3, 134.2, 131.8, 130.3, 130.0, 129.9, 128.7, 128.2, 128.0, 127.0, 125.6, 125.1, 124.7, 123.4, 117.6, 113.6, 111.0, 103.3, 65.1, 55.3; HRMS (ESI, TOF) calcd for $C_{23}H_{17}BrClO_3$ $[M+H]^+$ 455.0050, found 455.0059.



8,10-di-tert-butyl-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3k). The compound was prepared from **1a** (0.143 g, 0.6 mmol) and **2k** (0.121 g, 0.3 mmol) following typical procedure: 0.048 g (35% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 260.6-262.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.82 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.14-7.20 (m, 2H), 7.05-7.06 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.76 (d, J = 8.8 Hz, 2H), 4.97 (d, J = 15.2 Hz, 1H), 4.67 (d, J = 15.2 Hz, 1H), 3.71 (s, 3H), 1.33 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 159.9, 147.5, 143.2, 136.2, 133.5, 130.6, 129.9, 128.9, 127.5, 127.4, 124.8, 124.5, 124.3, 123.2, 122.3, 121.4, 120.0, 113.5, 102.1, 65.1, 55.2, 34.8, 34.3, 31.6, 30.1; HRMS (ESI, TOF) calcd for $C_{31}H_{35}O_3$ $[M+H]^+$ 455.2586, found 455.2584.

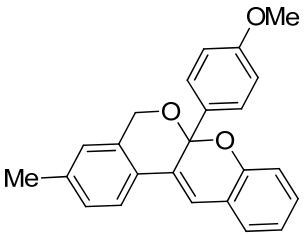


6a-(4-methoxyphenyl)-1-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene (3l). The compound was prepared from corresponding internal alkynol **1** (0.151 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.071 g (66% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 113.2-115.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.29-7.31 (m, 3H), 7.18-7.23 (m, 2H), 7.15 (d, J = 7.1 Hz, 1H), 7.07-7.09 (m, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.83 (s, 1H), 6.71 (d, J = 8.8 Hz, 2H), 4.98 (d, J = 12.8 Hz, 1H), 4.72 (d, J = 12.8 Hz, 1H), 3.69 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 159.6, 151.8, 136.7, 134.5, 134.0, 132.6, 130.8, 130.1, 127.9, 127.4, 127.1, 126.8, 124.3, 122.4, 122.3, 121.7, 116.4, 113.4, 103.1, 65.8, 55.2, 20.2; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1491, found 357.1477.

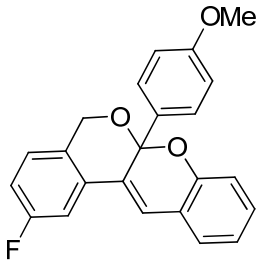


6a-(4-methoxyphenyl)-2-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene (3m). The compound was prepared from corresponding internal alkynol **1** (0.151 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.064 g (60% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 144.2-146.4; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.65 (s, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.06-7.17 (m, 4H), 6.87-6.93 (m, 3H), 6.75 (d, J = 8.8 Hz, 2H), 4.91 (d, J = 14.6 Hz, 1H), 4.57 (d, J = 14.6 Hz, 1H), 3.71 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 151.5, 137.3, 131.1, 131.0, 130.9, 129.4, 128.9, 128.2, 127.5, 127.0, 124.4, 123.6, 122.6, 121.8, 118.8, 116.5, 113.5, 102.0, 64.9, 55.2,

21.5; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1491, found 357.1491.

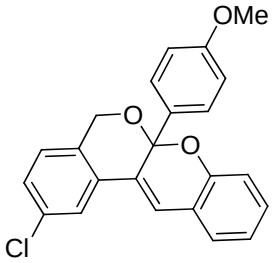


6a-(4-methoxyphenyl)-3-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene (3n). The compound was prepared from corresponding internal alkynol **1** (0.151 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.065 g (61% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 138.4-140.1 ^oC;^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 7.74 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.8 Hz, 2H), 7.06-7.17 (m, 4H), 6.86-6.92 (m, 2H), 6.82 (s, 1H), 6.75 (d, J = 8.8 Hz, 2H), 4.89 (d, J = 14.8 Hz, 1H), 4.55 (d, J = 14.8 Hz, 1H), 3.71 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^oC) δ 160.0, 151.4, 138.0, 133.7, 130.7, 129.2, 128.6, 128.3, 128.1, 127.3, 126.8, 125.0, 123.1, 122.7, 121.8, 117.9, 116.4, 113.5, 102.0, 65.0, 55.2, 21.4; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1491, found 357.1485.

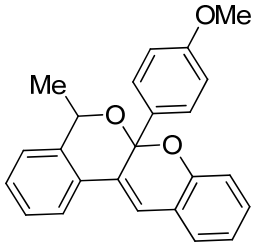


2-fluoro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3o). The compound was prepared from corresponding internal alkynol **1** (0.154 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.098 g (91% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 118.2-120.5 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 7.51 (dd, J_1 = 2.2 Hz, J_2 = 9.7 Hz, 1H), 7.41 (d, J = 8.9 Hz, 2H), 7.10-7.18 (m, 3H), 6.88-7.01 (m, 4H), 6.76 (d, J = 8.8 Hz, 2H), 4.90 (d, J = 14.6 Hz, 1H), 4.56 (d, J = 14.6 Hz, 1H), 3.71 (s, 3H);

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 162 (J_{CF} = 245.1 Hz), 160.1, 151.6, 133.1, 133.0 (J_{CF} = 7.8 Hz), 130.5, 129.9, 129.6 (J_{CF} = 2.8 Hz), 128.1, 127.2, 126.4 (J_{CF} = 2.5 Hz), 126.3 (J_{CF} = 8.6 Hz), 122.1, 122.0, 120.2, 116.5, 115.1 (J_{CF} = 22.4 Hz), 114.1, 113.6, 109.6 (J_{CF} = 22.7 Hz), 101.7, 64.5, 55.2; HRMS (ESI, TOF) calcd for $C_{23}H_{18}O_3F$ $[M+H]^+$ 361.1240, found 361.1249.

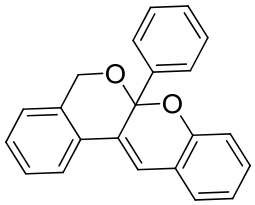


2-chloro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3p). The compound was prepared from corresponding internal alkynol **1** (0.162 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.059 g (52% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 25:1 v/v) as white solid, mp 133.8-135.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.81-7.82 (m, 1H), 7.40 (d, J = 8.8 Hz, 2H), 7.10-7.21 (m, 4H), 6.88-6.96 (m, 3H), 6.76 (d, J = 8.8 Hz, 2H), 4.89 (d, J = 14.9 Hz, 1H), 4.55 (d, J = 14.9 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.1, 151.6, 133.6, 132.8, 132.2, 130.4, 129.9, 128.1, 127.9, 127.3, 126.0, 123.2, 122.1, 122.0, 120.2, 116.5, 113.7, 101.7, 64.5, 55.2; HRMS (ESI, TOF) calcd for $C_{23}H_{18}O_3Cl$ $[M+H]^+$ 377.0944, found 377.0944.

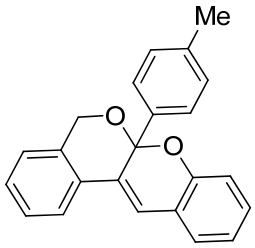


6a-(4-methoxyphenyl)-5-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene (3q). The compound was prepared from corresponding internal alkynol **1** (0.150 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.074 g (69% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v)

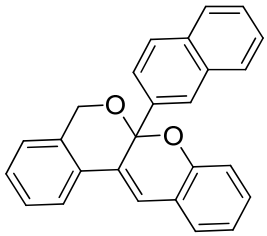
as white solid, mp 150.1-152.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.87 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.30-7.35 (m, 1H), 7.25-7.26 (m, 1H), 7.23 (s, 1H), 7.15-7.17 (m, 1H), 7.03-7.07 (m, 2H), 6.87-6.89 (m, 2H), 6.75 (d, J = 8.8 Hz, 2H), 4.66 (q, J = 6.5 Hz, 1H), 3.70 (s, 3H), 1.66 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 151.4, 138.1, 130.6, 130.0, 129.3, 128.4, 128.2, 127.4, 127.4, 127.1, 126.9, 124.7, 123.1, 122.4, 121.8, 117.7, 116.5, 113.6, 101.2, 55.2, 21.4; HRMS (ESI, TOF) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1491, found 357.1491.



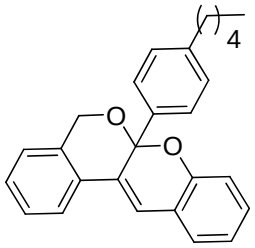
6a-phenyl-5,6a-dihydroisochromeno[3,4-*b*]chromene (3r). To a mixture of corresponding internal alkynol **1** (0.6 mmol) and salicyl *N*-tosylhydrazone **2a** (0.3 mmol) in a mixture solvent (toluene:dioxane= 1:4, v/v, 2 ml) was added the copper(II) perchlorate (0.09 mmol, 30 mol%) under Ar. The reaction mixture was stirred at 80 ^{o}C for 20 hours. 0.048 g (51% yield) of product **3r** was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v) as white solid, mp 109.8-112.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.84 (d, J = 7.8 Hz, 1H), 7.48-7.51 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.22-7.27 (m, 4H), 7.09-7.17 (m, 3H), 7.03 (d, J = 7.5 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 4.96 (d, J = 14.6 Hz, 1H), 4.62 (d, J = 14.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 151.5, 139.0, 133.9, 131.3, 129.5, 129.0, 128.2, 127.9, 127.8, 127.2, 127.1, 126.7, 124.5, 123.3, 122.4, 121.9, 119.5, 116.5, 102.0, 65.1; HRMS (ESI, TOF) calcd for $C_{22}H_{17}O_2$ $[M+H]^+$ 313.1229, found 313.1231.



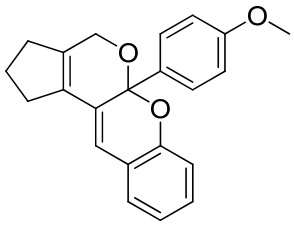
6a-(*p*-tolyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3s). The compound was prepared from corresponding internal alkynol **1** (0.133 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.071 g (73% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 113.4-115.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.85 (d, J = 7.8 Hz, 1H), 7.34-7.39 (m, 3H), 7.23-7.25 (m, 1H), 7.09-7.17 (m, 3H), 7.01-7.05 (m, 3H), 6.94 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 4.95 (d, J = 14.7 Hz, 1H), 4.62 (d, J = 14.7 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 151.5, 138.9, 135.9, 133.9, 131.2, 129.5, 129.0, 127.9, 127.8, 127.3, 127.0, 126.7, 124.5, 123.3, 122.5, 121.9, 119.2, 116.5, 102.0, 65.0, 21.2; HRMS (ESI, TOF) calcd for $C_{23}H_{19}O_2$ $[M+H]^+$ 327.1385, found 327.1379.



6a-(naphthalen-2-yl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3t). The compound was prepared from corresponding internal alkynol **1** (0.155 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.048 g (44% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v) as white solid, mp 163.6-166.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.94 (d, J = 7.8 Hz, 1H), 7.74-7.81 (m, 4H), 7.67 (d, J = 7.6 Hz, 1H), 7.36-7.44 (m, 3H), 7.23-7.26 (m, 2H), 7.18 (dd, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 7.05-7.10 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.85-6.89 (m, 1H), 4.98 (d, J = 14.8 Hz, 1H), 4.61 (d, J = 14.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 151.5, 135.9, 133.8, 133.6, 132.5, 131.0, 129.6, 128.6, 128.6, 128.0, 127.8, 127.6, 127.1, 126.9, 126.7, 126.1, 124.6, 124.0, 123.3, 122.5, 122.0, 119.5, 116.5, 102.2, 65.1; HRMS (ESI, TOF) calcd for $C_{26}H_{19}O_2$ $[M+H]^+$ 363.1385, found 363.1371.

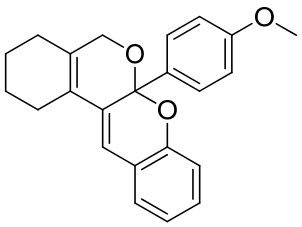


6a-(4-pentylphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3u). The compound was prepared from corresponding internal alkynol **1** (0.167 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.051 g (45% yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 77.3-79.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.84 (d, J = 7.8 Hz, 1H), 7.33-7.40 (m, 3H), 7.24 (t, J = 6.9 Hz, 1H), 7.08-7.16 (m, 3H), 7.01-7.04 (m, 3H), 6.94 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 4.94 (d, J = 14.7 Hz, 1H), 4.62 (d, J = 14.6 Hz, 1H), 2.48 (t, J = 7.6 Hz, 2H), 1.48-1.56 (m, 2H), 1.25-1.26 (m, 4H), 0.84 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 151.6, 143.9, 136.2, 134.0, 131.4, 129.5, 128.3, 127.8, 127.8, 127.3, 127.1, 126.6, 124.5, 123.3, 122.5, 121.8, 119.4, 116.5, 102.1, 65.1, 35.7, 31.6, 30.9, 22.6, 14.1; HRMS (ESI, TOF) calcd for $C_{27}H_{27}O_2$ $[M+H]^+$ 383.2011, found 383.2003.

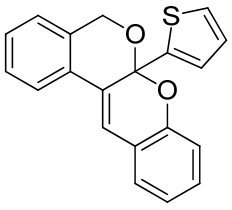


5a-(4-methoxyphenyl)-2,3,4,5a-tetrahydro-1H-cyclopenta[4,5]pyrano[2,3-*b*]chromene (3v). To a mixture of corresponding internal alkynol **1** (0.137g, 0.6 mmol) and salicyl *N*-tosylhydrazone **2a** (0.087g, 0.3 mmol) in toluene (2 ml) was added the copper(II) perchlorate (0.09 mmol, 30 mol%) under Ar. The reaction mixture was stirred at 80 ^{o}C for 4 hours. 0.036 g (36% yield) of product **3v** was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 207.6-209.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.42 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 7.4 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.79-6.85 (m, 4H), 6.43 (s, 1H), 4.41 (d, J = 16.8 Hz, 1H), 4.00 (d, J = 16.8 Hz, 1H), 3.75 (s, 3H), 2.61-2.75 (m, 2H), 2.26-2.44 (m, 2H), 1.96-2.11 (m, 2H);

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 151.6, 140.7, 132.8, 130.1, 128.5, 128.4, 127.3, 126.6, 123.1, 121.8, 116.8, 116.7, 113.5, 101.4, 64.4, 55.2, 33.3, 30.2, 22.8; HRMS (EI, TOF) calcd for $C_{22}H_{20}O_3$ $[M]^+$ 332.1412, found 332.1410.



6a-(4-methoxyphenyl)-1,2,3,4,5,6a-hexahydroisochromeno[3,4-*b*]chromene (3w). To a mixture of corresponding internal alkynol **1** (0.145g, 0.6 mmol) and salicyl *N*-tosylhydrazone **2a** (0.087g, 0.3 mmol) in a mixture solvent (toluene:dioxane= 1:4, v/v, 2 ml) was added the copper(II) perchlorate (0.09 mmol, 30 mol%) under Ar. The reaction mixture was stirred at 80 ^{o}C for 8 hours. 0.043 g (41% yield) of product **3w** was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 182.2-183.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.40 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 7.4 Hz, 1H), 6.99 (t, J = 7.7 Hz, 1H), 6.78-6.84 (m, 4H), 6.55 (s, 1H), 4.16 (d, J = 16.6 Hz, 1H), 3.81 (d, J = 16.6 Hz, 1H), 3.75 (s, 3H), 2.52-2.56 (m, 1H), 2.22-2.26 (m, 1H), 1.92-1.98 (m, 1H), 1.64-1.84 (m, 4H), 1.50-1.53 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 160.0, 151.3, 134.5, 130.2, 128.9, 128.4, 126.6, 124.9, 123.2, 121.7, 116.4, 115.6, 113.5, 101.4, 66.4, 55.2, 25.9, 23.2, 22.4, 21.9; HRMS (EI, TOF) calcd for $C_{23}H_{22}O_3$ $[M]^+$ 346.1569, found 346.1567.



6a-(thiophen-2-yl)-5,6a-dihydroisochromeno[3,4-*b*]chromene (3x). The compound was prepared from corresponding internal alkynol **1** (0.128 g, 0.6 mmol) and **2a** (0.087 g, 0.3 mmol) following typical procedure: 0.072 g (75 % yield) of product was obtained after column chromatography (eluent = petroleum ether/ ethyl acetate 100:1 v/v) as white solid, mp 127.8-129.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.82 (d, J = 7.8 Hz, 1H),

7.35 (t, *J* = 7.6 Hz, 1H), 7.25-7.28 (m, 2H), 7.13-7.20 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.91-6.98 (m, 3H), 6.76 (t, *J* = 4.3 Hz, 1H), 5.00 (d, *J* = 14.8 Hz, 1H), 4.78 (d, J = 14.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 151.4, 143.0, 133.5, 130.2, 129.6, 128.1, 127.8, 127.6, 127.4, 127.3, 127.1, 126.1, 124.6, 123.3, 122.3, 122.2, 119.0, 116.6, 100.1, 65.3; HRMS (EI, TOF) calcd for $C_{20}H_{14}O_2S$ $[M]^+$ 318.0715, found 318.0716.

4. Crystal data and structure refinement of product 3a.

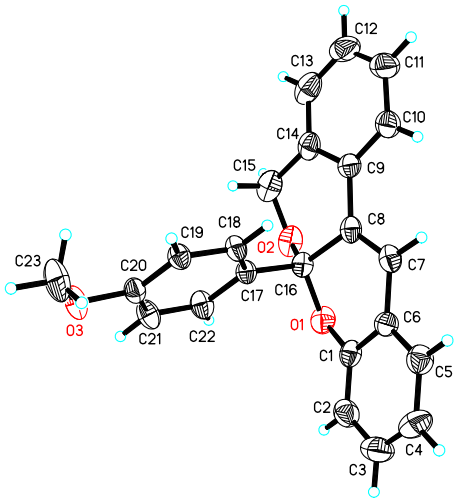


Table 1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	C_{23} H_{18} O_3
Formula weight	342.37
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 25.754(2) A alpha = 90 deg. b = 6.0366(5) A beta = 106.637(2) deg. c = 23.164(2) A gamma = 90 deg.
Volume	3450.5(5) A^3
Z, Calculated density	8, 1.318 Mg/m^3
Absorption coefficient	0.087 mm^-1
F(000)	1440
Crystal size	0.231 x 0.147 x 0.123 mm
Theta range for data collection	1.65 to 26.00 deg.
Limiting indices	-31<=h<=30, -7<=k<=7, -21<=l<=28
Reflections collected / unique	19832 / 6780 [R(int) = 0.0424]
Completeness to theta = 26.00	99.8 %
Absorption correction	Empriical
Max. and min. transmission	1.00000 and 0.21493
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6780 / 13 / 471
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1464
R indices (all data)	R1 = 0.0815, wR2 = 0.1589
Largest diff. peak and hole	0.437 and -0.193 e.A^-3

Table 2. Bond lengths [A] and angles [deg] for **3a**.

O(1)-C(1)	1.406(2)
O(1)-C(16)	1.428(2)
O(2)-C(16)	1.411(2)
O(2)-C(15)	1.411(3)
O(3)-C(20)	1.366(2)
O(3)-C(23)	1.401(3)
O(4)-C(24)	1.374(2)
O(4)-C(39)	1.426(2)
O(5)-C(39)	1.417(2)
O(5)-C(38)	1.421(2)
O(6)-C(43)	1.372(2)
O(6)-C(46)	1.400(3)
C(1)-C(2)	1.348(3)
C(1)-C(6)	1.386(3)
C(2)-C(3)	1.375(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.376(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.380(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.382(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.452(3)
C(7)-C(8)	1.321(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.475(3)
C(8)-C(16)	1.517(3)
C(9)-C(10)	1.394(3)
C(9)-C(14)	1.397(3)
C(10)-C(11)	1.360(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.359(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.368(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.394(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.487(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.521(2)
C(17)-C(18)	1.361(2)
C(17)-C(22)	1.390(3)
C(18)-C(19)	1.393(2)

C(18)-H(18)	0.9300
C(19)-C(20)	1.373(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.386(3)
C(21)-C(22)	1.365(3)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-C(25)	1.374(3)
C(24)-C(29)	1.395(3)
C(25)-C(26)	1.374(3)
C(25)-H(25)	0.9300
C(26)-C(27)	1.368(3)
C(26)-H(26)	0.9300
C(27)-C(28)	1.389(3)
C(27)-H(27)	0.9300
C(28)-C(29)	1.385(3)
C(28)-H(28)	0.9300
C(29)-C(30)	1.452(3)
C(30)-C(31)	1.332(3)
C(30)-H(30)	0.9300
C(31)-C(32)	1.470(3)
C(31)-C(39)	1.508(3)
C(32)-C(37)	1.393(3)
C(32)-C(33)	1.395(3)
C(33)-C(34)	1.374(3)
C(33)-H(33)	0.9300
C(34)-C(35)	1.373(4)
C(34)-H(34)	0.9300
C(35)-C(36)	1.371(3)
C(35)-H(35)	0.9300
C(36)-C(37)	1.394(3)
C(36)-H(36)	0.9300
C(37)-C(38)	1.494(3)
C(38)-H(38A)	0.9700
C(38)-H(38B)	0.9700
C(39)-C(40)	1.516(3)
C(40)-C(41)	1.371(3)
C(40)-C(45)	1.399(3)
C(41)-C(42)	1.393(3)
C(41)-H(41)	0.9300
C(42)-C(43)	1.375(3)
C(42)-H(42)	0.9300
C(43)-C(44)	1.372(3)

C(44)-C(45)	1.363(3)
C(44)-H(44)	0.9300
C(45)-H(45)	0.9300
C(46)-H(46A)	0.9600
C(46)-H(46B)	0.9600
C(46)-H(46C)	0.9600

C(1)-O(1)-C(16)	114.32(14)
C(16)-O(2)-C(15)	112.09(15)
C(20)-O(3)-C(23)	118.08(16)
C(24)-O(4)-C(39)	115.96(15)
C(39)-O(5)-C(38)	111.96(15)
C(43)-O(6)-C(46)	118.53(18)
C(2)-C(1)-C(6)	122.6(2)
C(2)-C(1)-O(1)	119.42(19)
C(6)-C(1)-O(1)	117.79(18)
C(1)-C(2)-C(3)	119.1(2)
C(1)-C(2)-H(2)	120.5
C(3)-C(2)-H(2)	120.5
C(2)-C(3)-C(4)	120.5(2)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	119.5(2)
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	120.7(2)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	117.55(19)
C(5)-C(6)-C(7)	123.21(19)
C(1)-C(6)-C(7)	119.20(18)
C(8)-C(7)-C(6)	120.23(19)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	126.18(19)
C(7)-C(8)-C(16)	117.62(18)
C(9)-C(8)-C(16)	116.12(17)
C(10)-C(9)-C(14)	118.17(19)
C(10)-C(9)-C(8)	123.37(19)
C(14)-C(9)-C(8)	118.46(19)
C(11)-C(10)-C(9)	121.3(2)
C(11)-C(10)-H(10)	119.3
C(9)-C(10)-H(10)	119.3
C(12)-C(11)-C(10)	120.5(3)
C(12)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7

C(11)-C(12)-C(13)	120.0(2)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.8(2)
C(12)-C(13)-H(13)	119.6
C(14)-C(13)-H(13)	119.6
C(13)-C(14)-C(9)	119.2(2)
C(13)-C(14)-C(15)	120.6(2)
C(9)-C(14)-C(15)	120.2(2)
O(2)-C(15)-C(14)	112.06(18)
O(2)-C(15)-H(15A)	109.2
C(14)-C(15)-H(15A)	109.2
O(2)-C(15)-H(15B)	109.2
C(14)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
O(2)-C(16)-O(1)	100.70(14)
O(2)-C(16)-C(8)	110.10(16)
O(1)-C(16)-C(8)	110.70(14)
O(2)-C(16)-C(17)	111.19(14)
O(1)-C(16)-C(17)	109.09(15)
C(8)-C(16)-C(17)	114.23(15)
C(18)-C(17)-C(22)	117.95(17)
C(18)-C(17)-C(16)	124.38(16)
C(22)-C(17)-C(16)	117.65(16)
C(17)-C(18)-C(19)	121.84(17)
C(17)-C(18)-H(18)	119.1
C(19)-C(18)-H(18)	119.1
C(20)-C(19)-C(18)	119.33(17)
C(20)-C(19)-H(19)	120.3
C(18)-C(19)-H(19)	120.3
O(3)-C(20)-C(19)	124.93(18)
O(3)-C(20)-C(21)	115.72(17)
C(19)-C(20)-C(21)	119.36(17)
C(22)-C(21)-C(20)	120.35(18)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(21)-C(22)-C(17)	121.15(19)
C(21)-C(22)-H(22)	119.4
C(17)-C(22)-H(22)	119.4
O(3)-C(23)-H(23A)	109.5
O(3)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
O(3)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(4)-C(24)-C(25)	118.51(19)

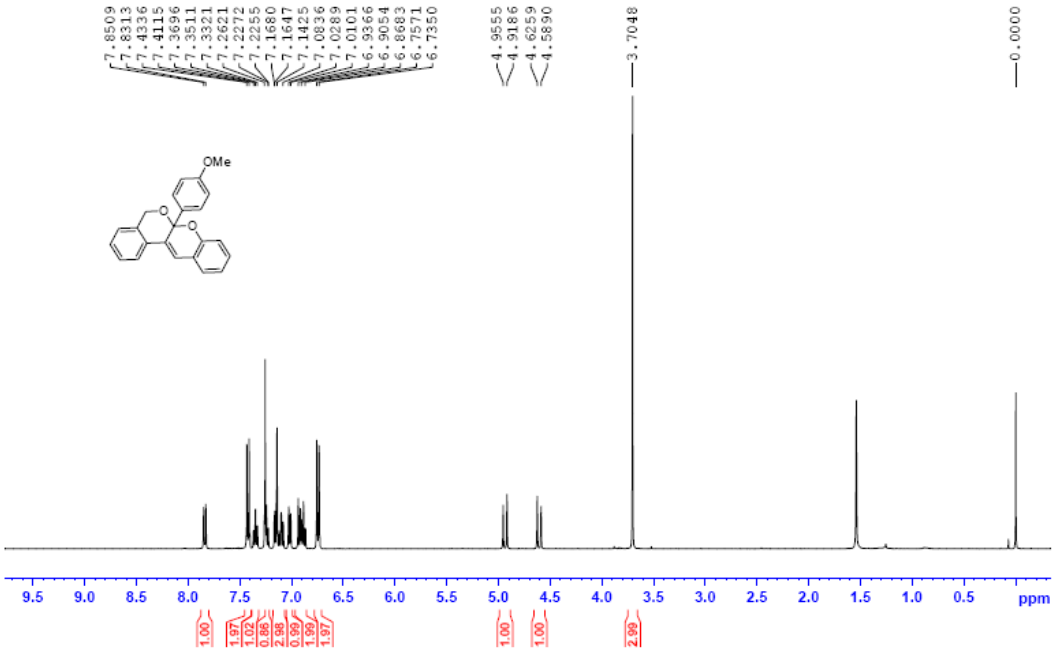
O(4)-C(24)-C(29)	119.95(18)
C(25)-C(24)-C(29)	121.4(2)
C(26)-C(25)-C(24)	119.1(2)
C(26)-C(25)-H(25)	120.5
C(24)-C(25)-H(25)	120.5
C(27)-C(26)-C(25)	121.1(2)
C(27)-C(26)-H(26)	119.4
C(25)-C(26)-H(26)	119.4
C(26)-C(27)-C(28)	119.6(2)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
C(29)-C(28)-C(27)	120.6(2)
C(29)-C(28)-H(28)	119.7
C(27)-C(28)-H(28)	119.7
C(28)-C(29)-C(24)	118.16(19)
C(28)-C(29)-C(30)	123.97(19)
C(24)-C(29)-C(30)	117.83(19)
C(31)-C(30)-C(29)	120.57(18)
C(31)-C(30)-H(30)	119.7
C(29)-C(30)-H(30)	119.7
C(30)-C(31)-C(32)	126.04(18)
C(30)-C(31)-C(39)	118.18(18)
C(32)-C(31)-C(39)	115.73(17)
C(37)-C(32)-C(33)	118.81(19)
C(37)-C(32)-C(31)	118.92(18)
C(33)-C(32)-C(31)	122.24(19)
C(34)-C(33)-C(32)	120.5(2)
C(34)-C(33)-H(33)	119.8
C(32)-C(33)-H(33)	119.8
C(35)-C(34)-C(33)	120.4(2)
C(35)-C(34)-H(34)	119.8
C(33)-C(34)-H(34)	119.8
C(36)-C(35)-C(34)	120.4(2)
C(36)-C(35)-H(35)	119.8
C(34)-C(35)-H(35)	119.8
C(35)-C(36)-C(37)	120.0(2)
C(35)-C(36)-H(36)	120.0
C(37)-C(36)-H(36)	120.0
C(32)-C(37)-C(36)	119.9(2)
C(32)-C(37)-C(38)	120.23(19)
C(36)-C(37)-C(38)	119.8(2)
O(5)-C(38)-C(37)	113.01(18)
O(5)-C(38)-H(38A)	109.0
C(37)-C(38)-H(38A)	109.0
O(5)-C(38)-H(38B)	109.0
C(37)-C(38)-H(38B)	109.0

H(38A)-C(38)-H(38B)	107.8
O(5)-C(39)-O(4)	100.15(14)
O(5)-C(39)-C(31)	110.28(15)
O(4)-C(39)-C(31)	112.03(15)
O(5)-C(39)-C(40)	111.34(15)
O(4)-C(39)-C(40)	108.89(15)
C(31)-C(39)-C(40)	113.39(15)
C(41)-C(40)-C(45)	117.35(18)
C(41)-C(40)-C(39)	123.74(16)
C(45)-C(40)-C(39)	118.91(17)
C(40)-C(41)-C(42)	121.62(18)
C(40)-C(41)-H(41)	119.2
C(42)-C(41)-H(41)	119.2
C(43)-C(42)-C(41)	119.62(19)
C(43)-C(42)-H(42)	120.2
C(41)-C(42)-H(42)	120.2
C(44)-C(43)-O(6)	115.58(18)
C(44)-C(43)-C(42)	119.35(18)
O(6)-C(43)-C(42)	125.0(2)
C(45)-C(44)-C(43)	120.83(18)
C(45)-C(44)-H(44)	119.6
C(43)-C(44)-H(44)	119.6
C(44)-C(45)-C(40)	121.2(2)
C(44)-C(45)-H(45)	119.4
C(40)-C(45)-H(45)	119.4
O(6)-C(46)-H(46A)	109.5
O(6)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
O(6)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5

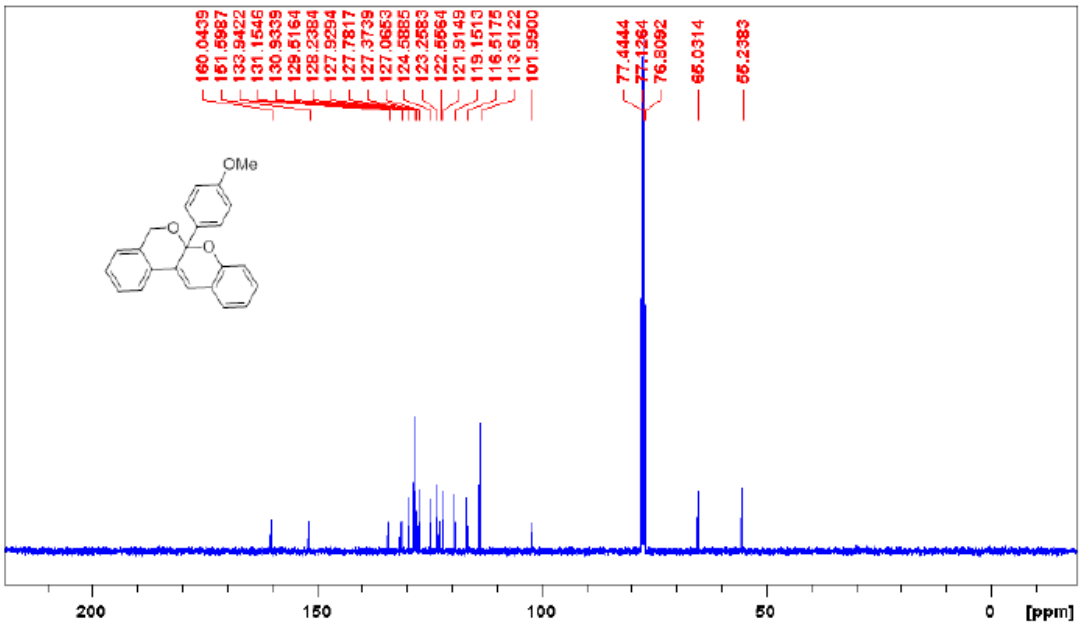
Symmetry transformations used to generate equivalent atoms:

5. Copies of ^{1}H and ^{13}C NMR spectra

^{1}H NMR of 6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3a)**.

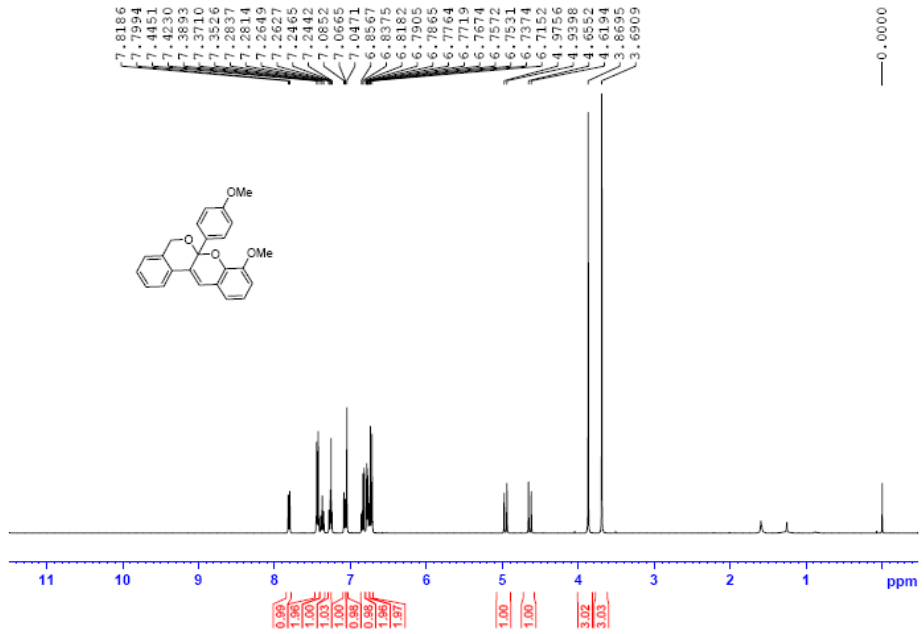


^{13}C NMR of 6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3a)**.



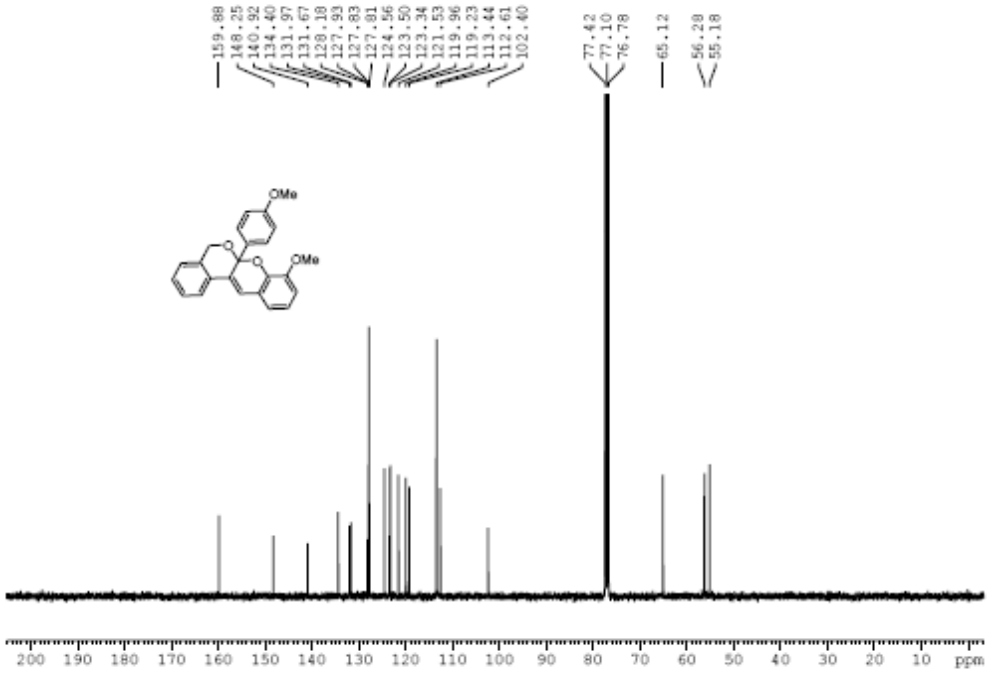
^{1}H NMR of

8-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3b)**.



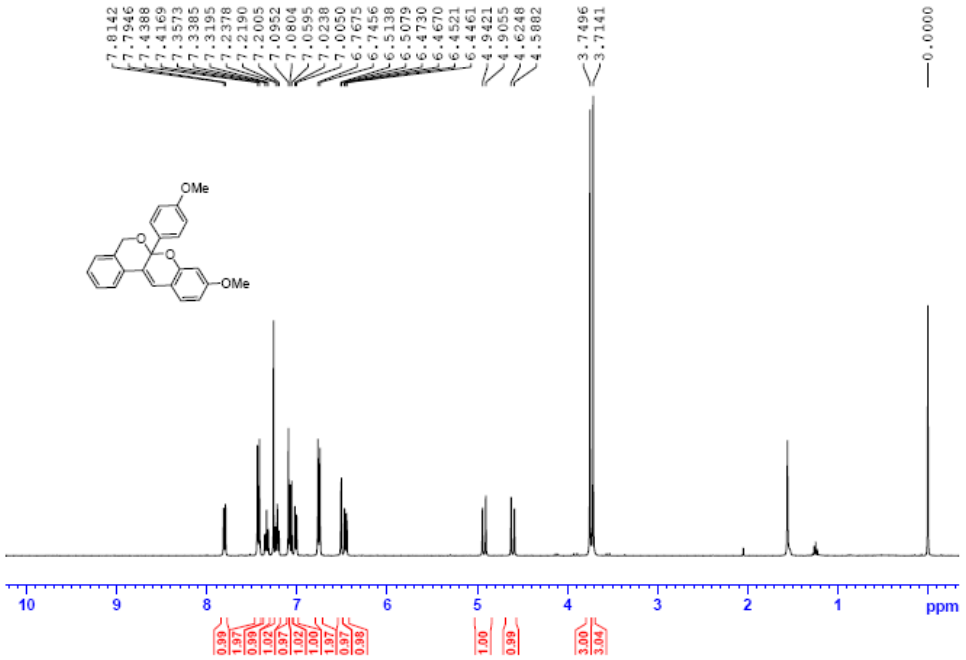
^{13}C NMR of

8-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3b)**.



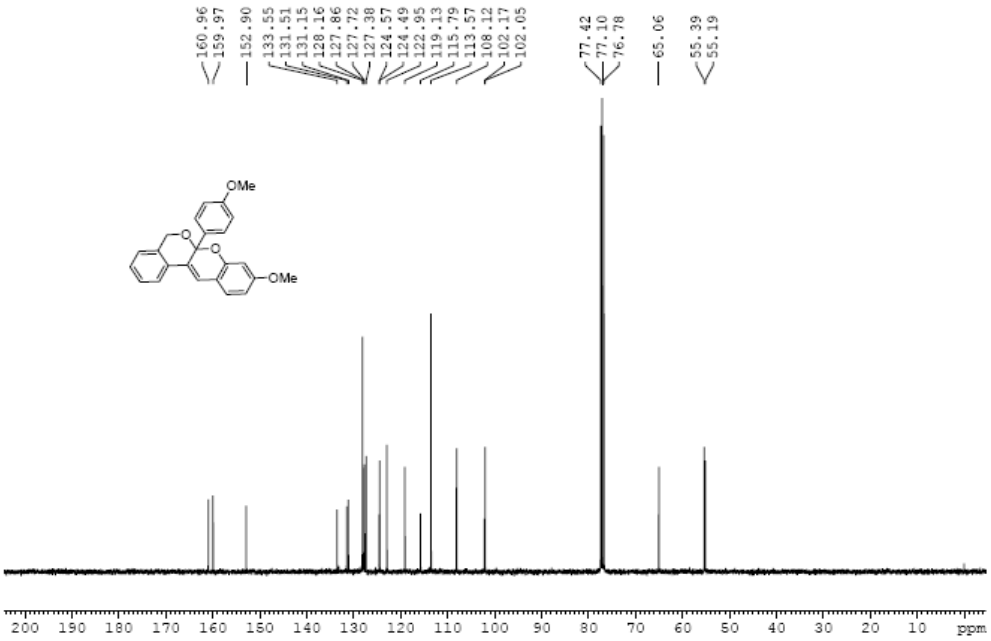
^{1}H NMR of

9-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3c)**.



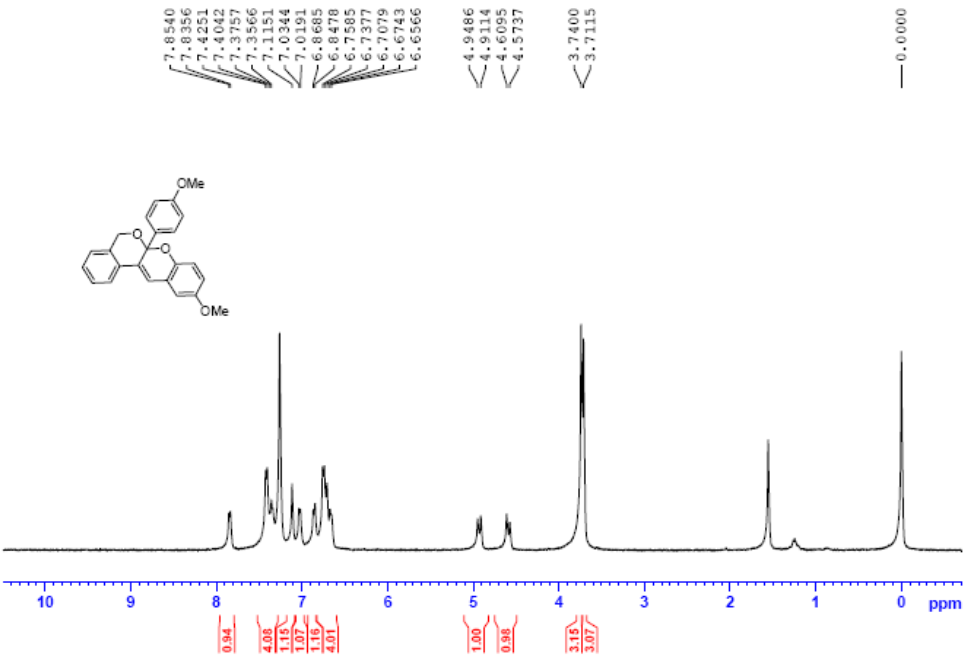
^{13}C NMR of

9-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3c)**.



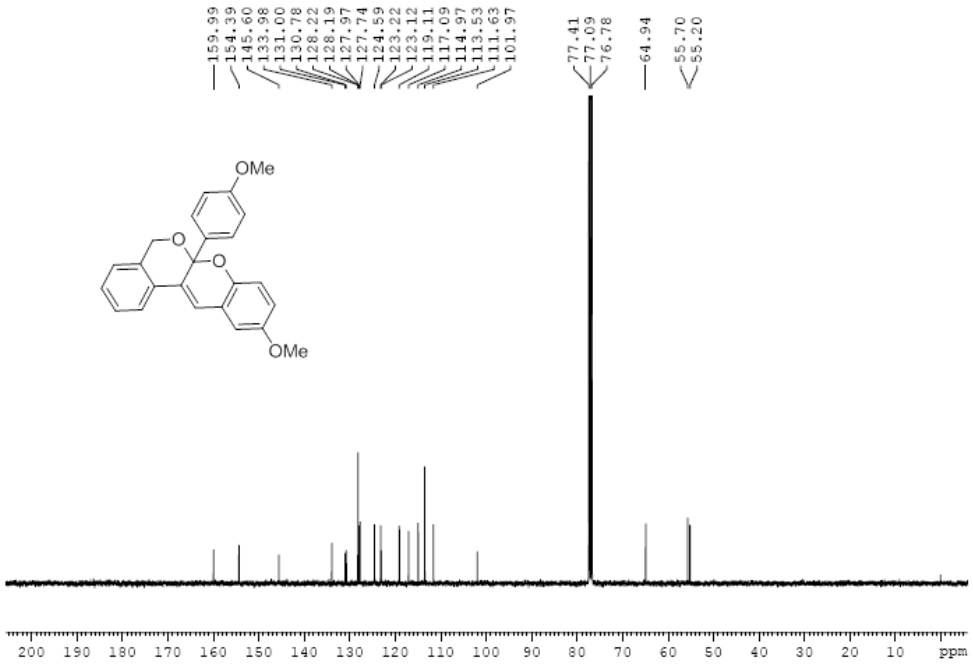
^{1}H NMR of

10-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3d)**.

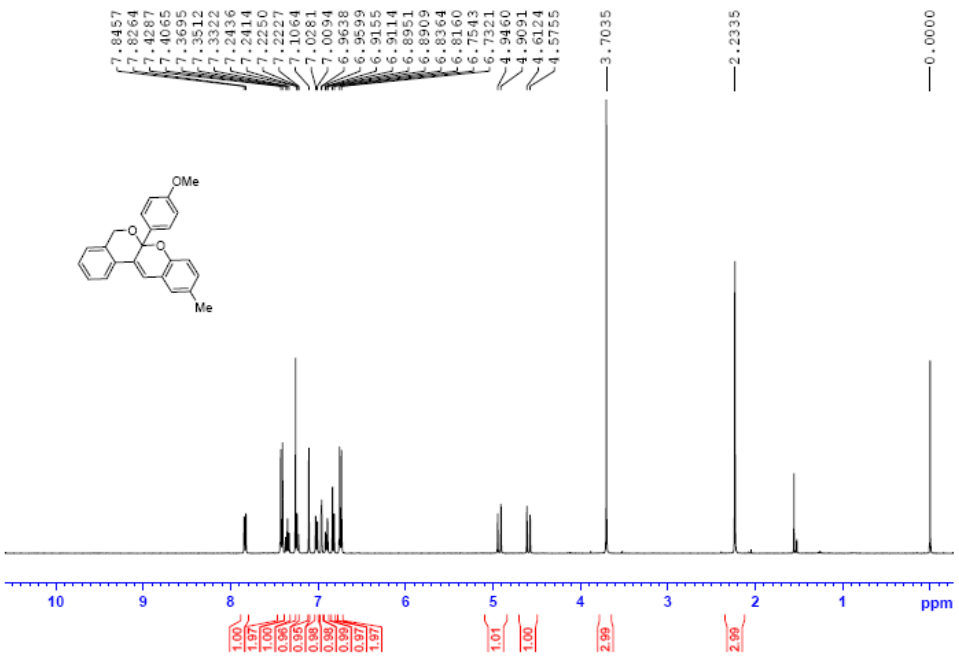


^{13}C NMR of

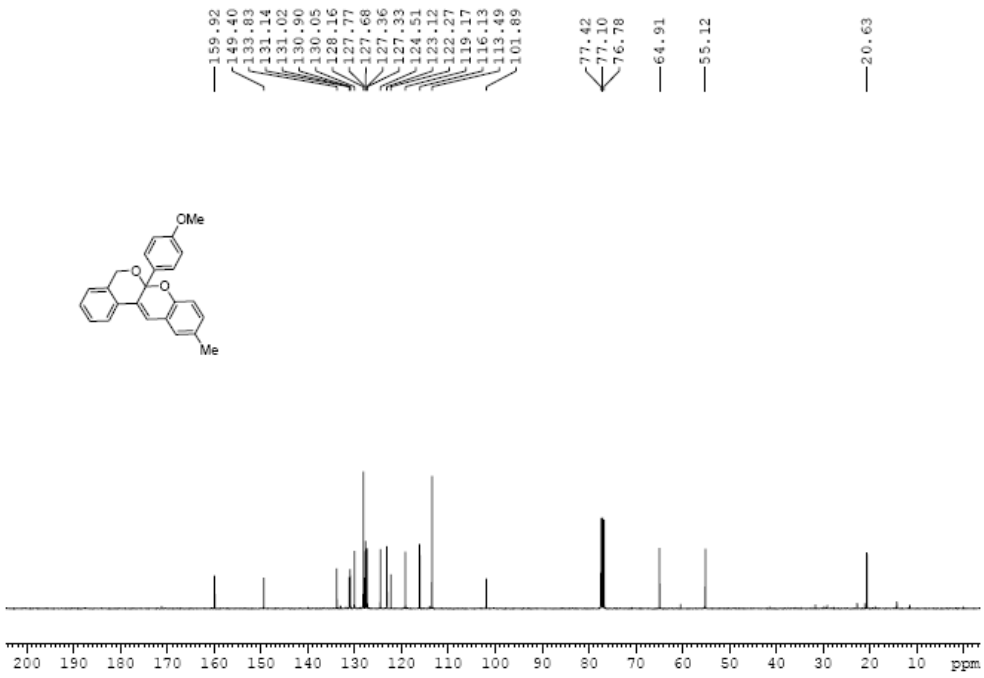
10-methoxy-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3d)**.



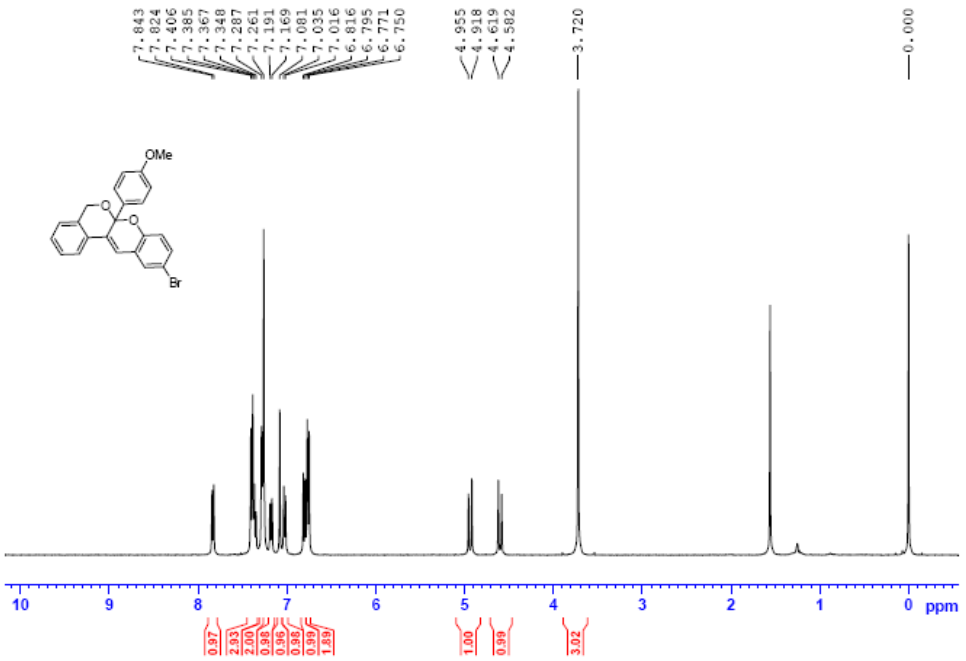
^{1}H NMR of 6a-(4-methoxyphenyl)-10-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3e)**.



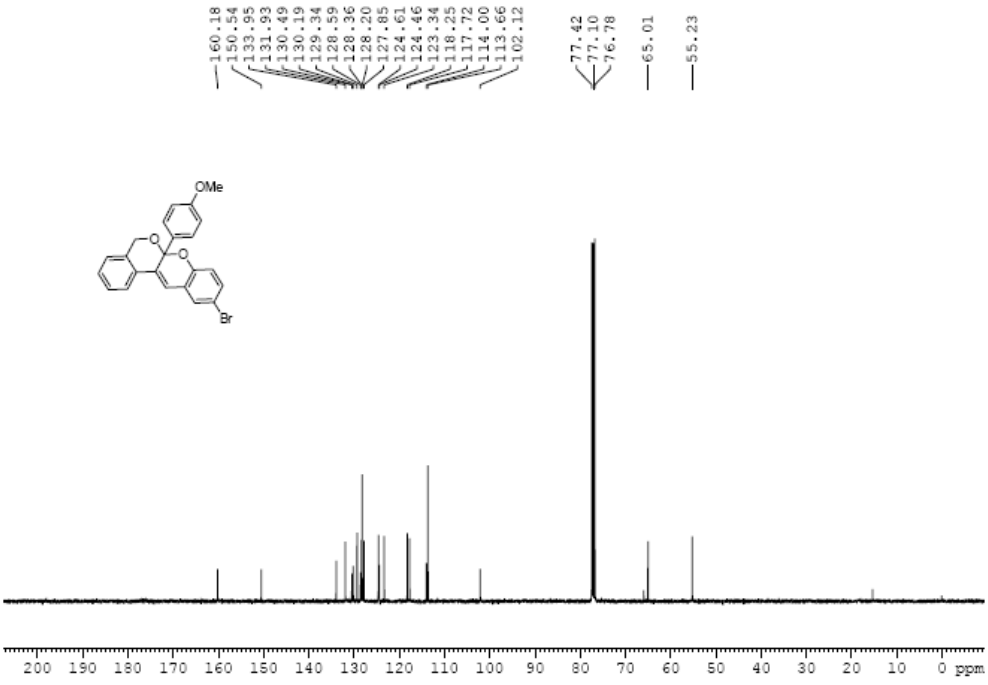
^{13}C NMR of 6a-(4-methoxyphenyl)-10-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3e)**.



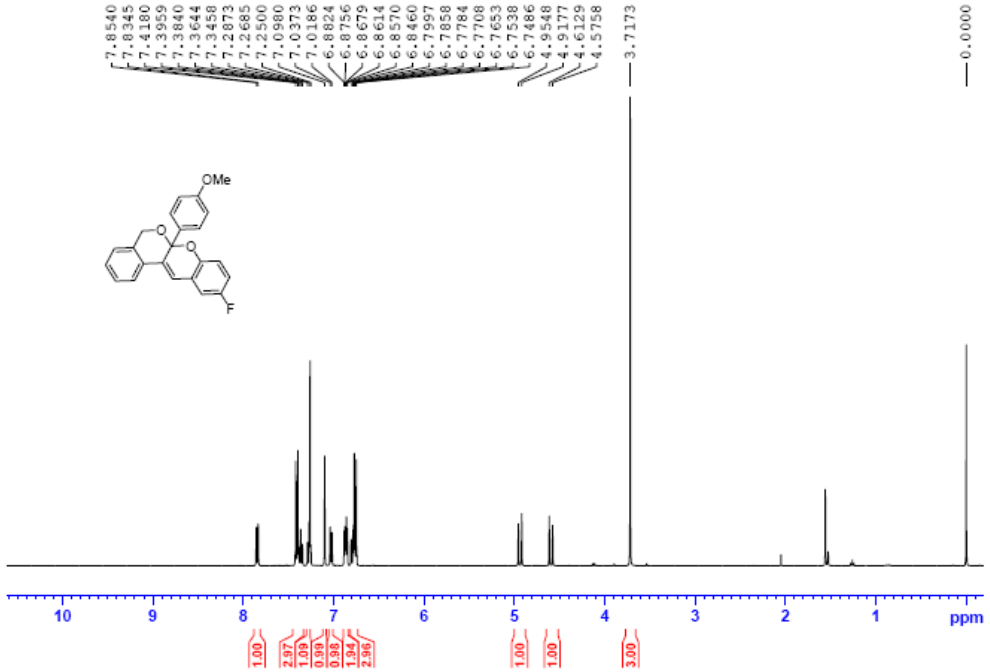
^{1}H NMR of 10-bromo-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3f)**.



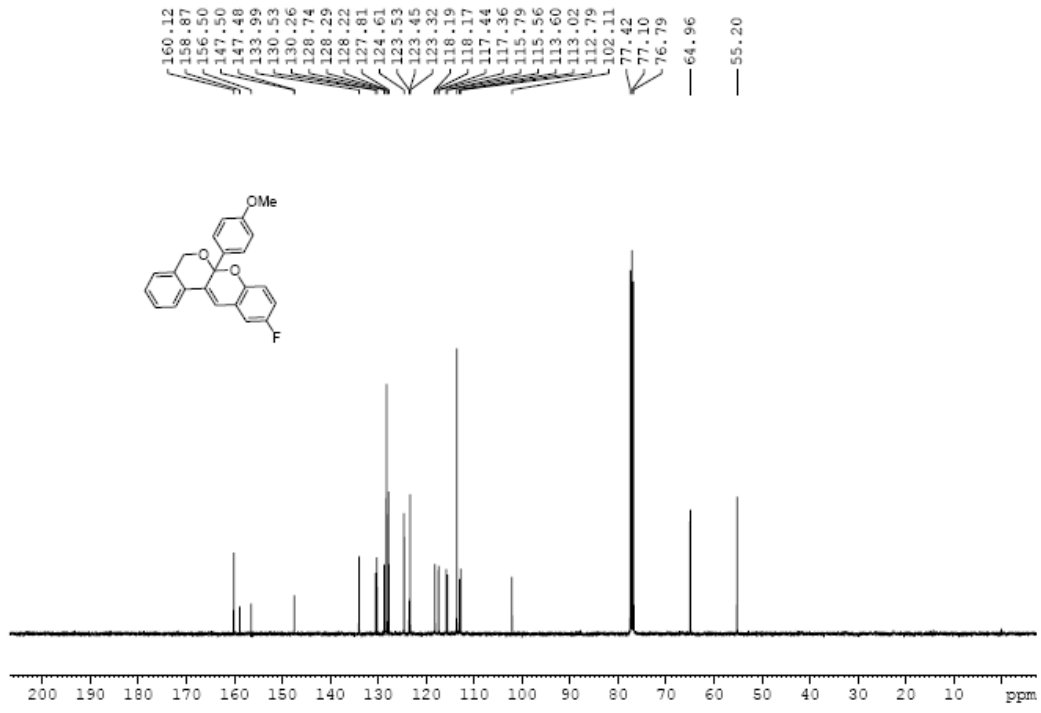
^{13}C NMR of 10-bromo-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3f)**.



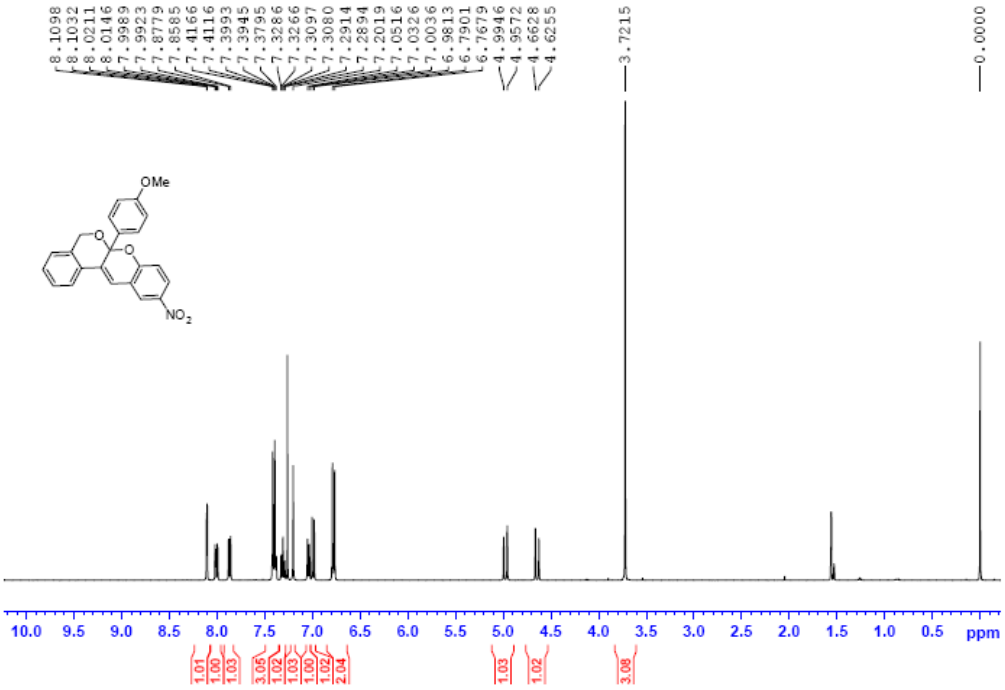
^{1}H NMR of 10-fluoro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3g)**.



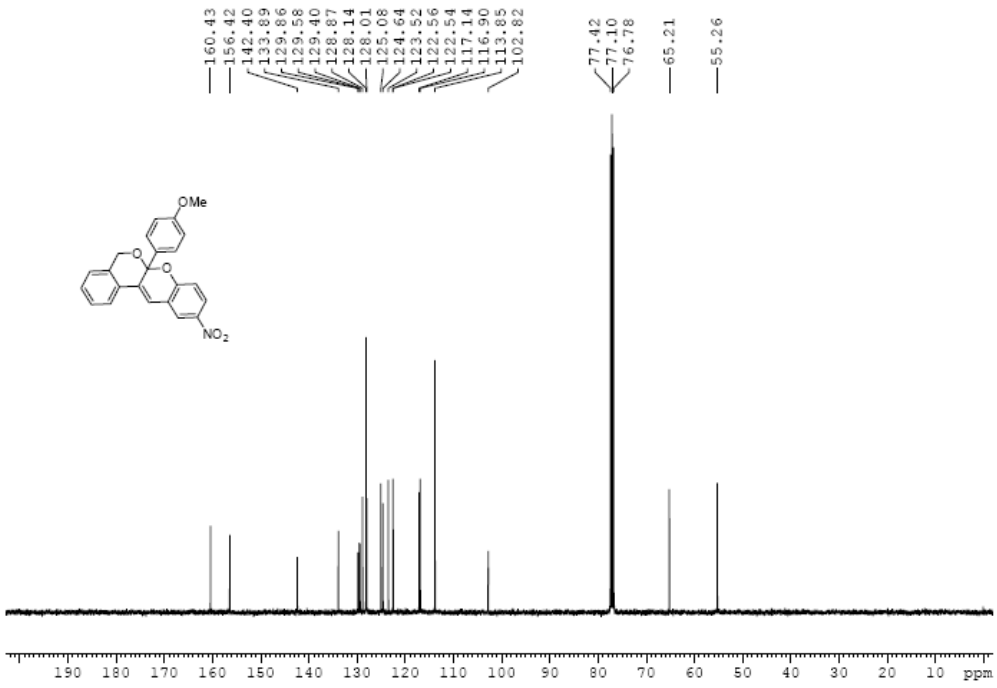
^{13}C NMR of 10-fluoro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3g)**.



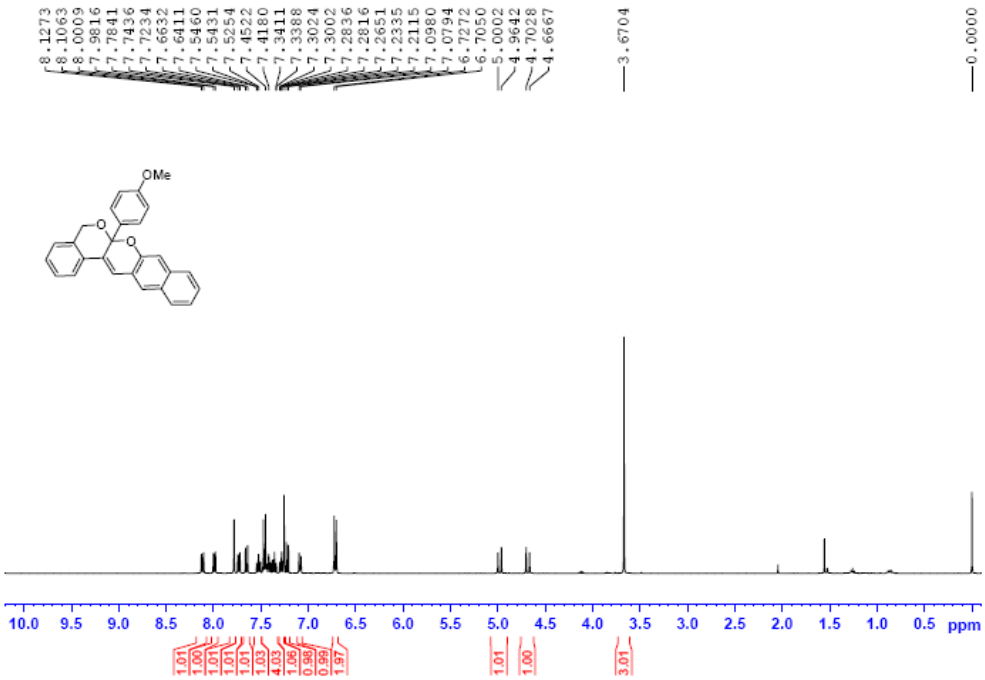
^{1}H NMR of 6a-(4-methoxyphenyl)-10-nitro-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3h)**.



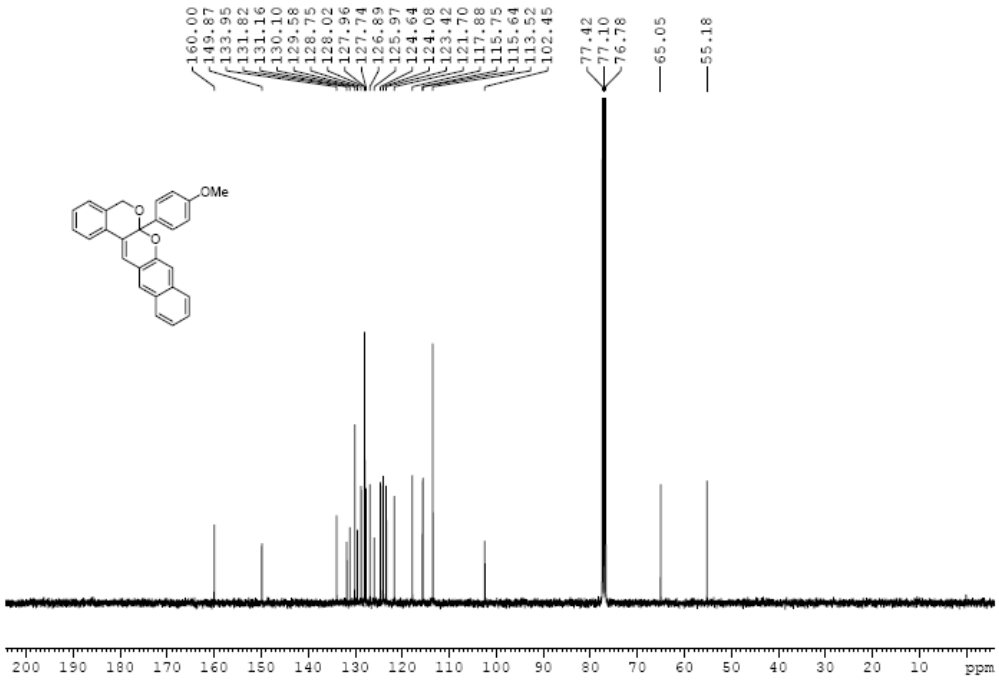
^{13}C NMR of 6a-(4-methoxyphenyl)-10-nitro-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3h)**.



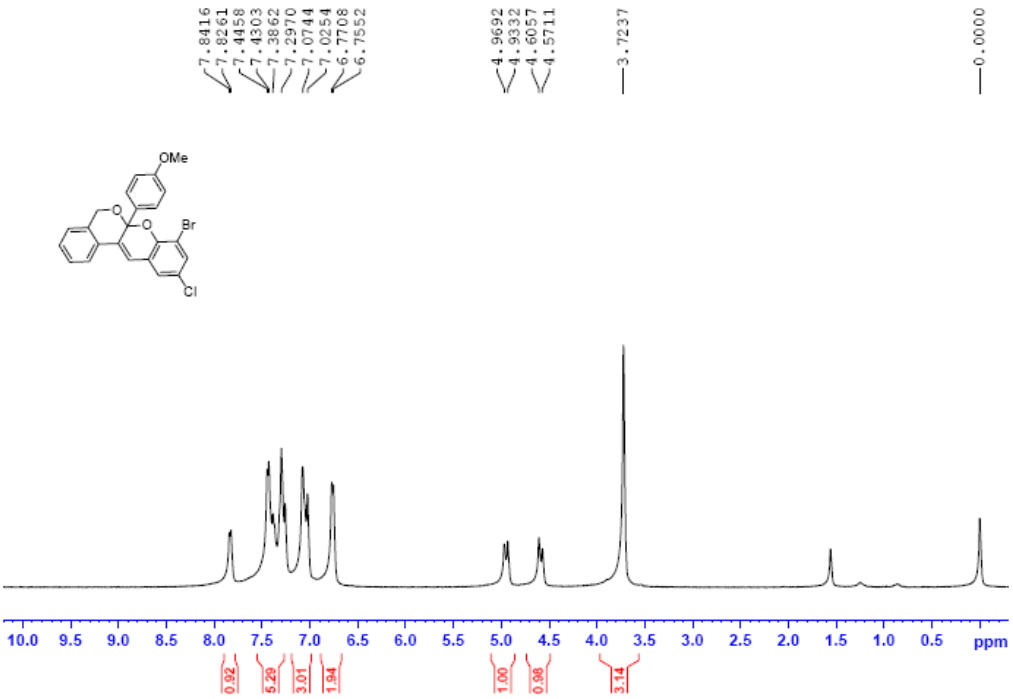
^{1}H NMR of 6a-(4-methoxyphenyl)-5,6a-dihydrobenzo[g]isochromeno[3,4-*b*]chromene **(3i)**.



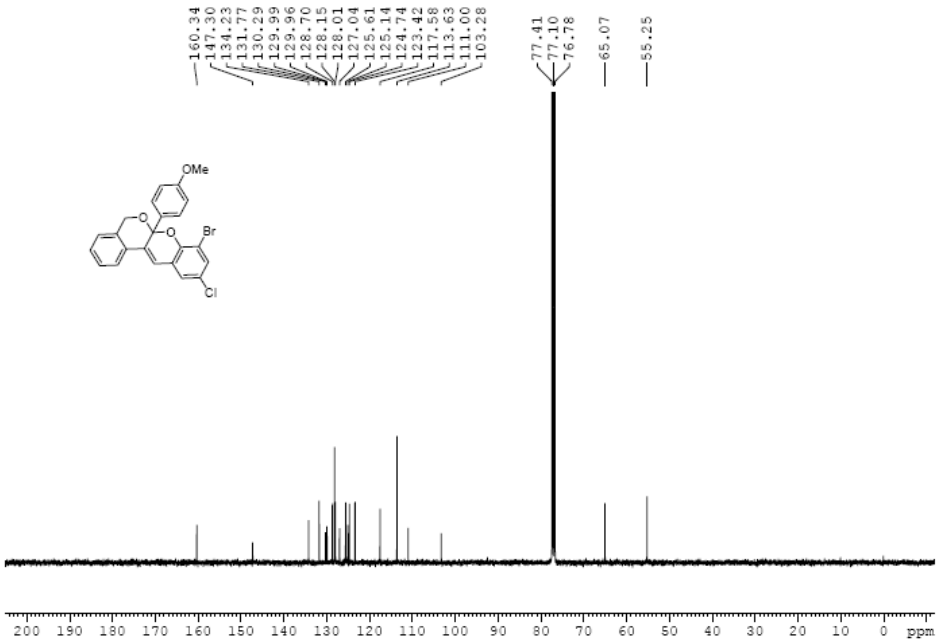
^{13}C NMR of 6a-(4-methoxyphenyl)-5,6a-dihydrobenzo[g]isochromeno[3,4-*b*]chromene **(3i)**.



^{1}H NMR of 8-bromo-10-chloro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*] chromene **(3j)**.

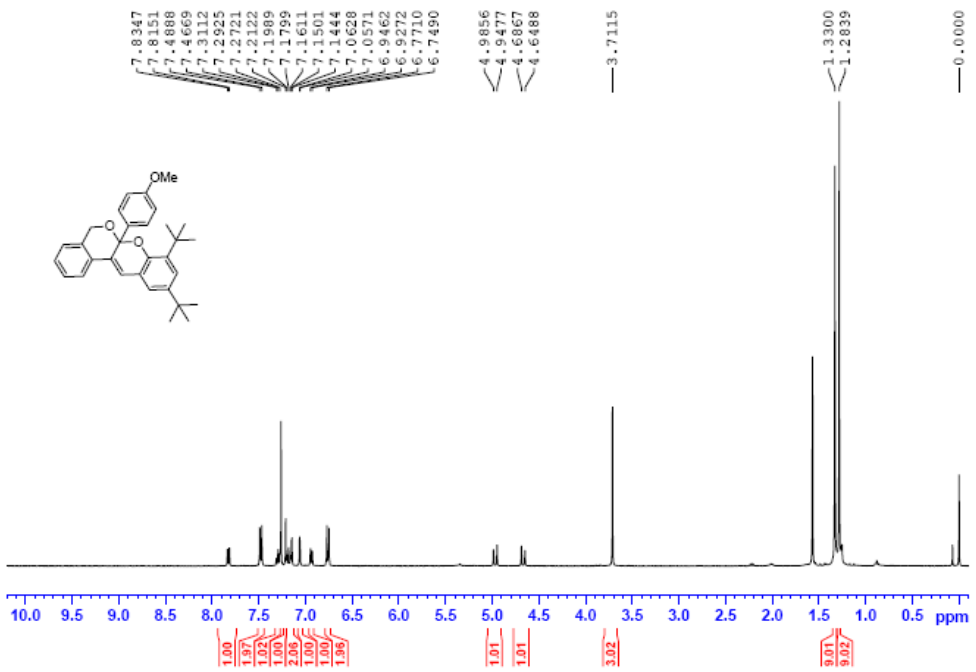


^{13}C NMR of 8-bromo-10-chloro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*] chromene **(3j)**.



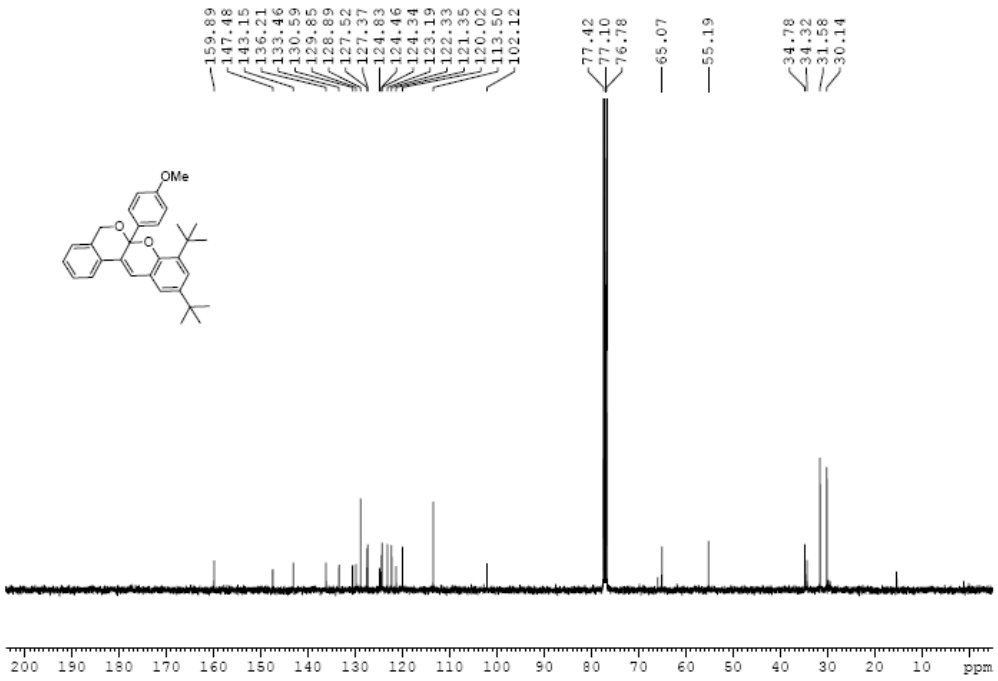
^{1}H NMR of

8,10-di-tert-butyl-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3k)**.

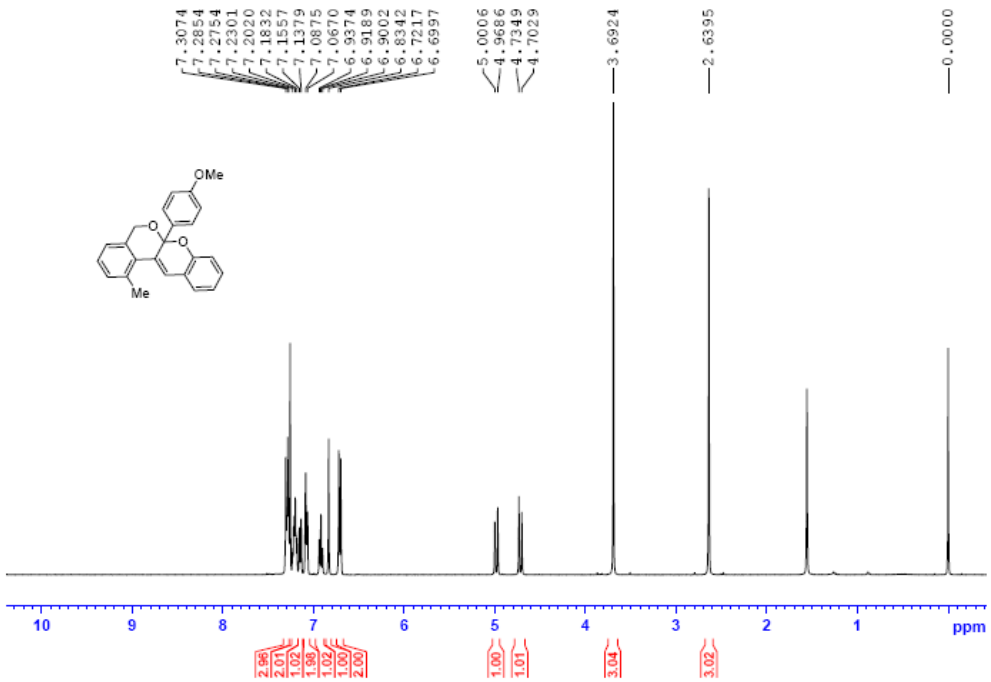


^{13}C NMR of

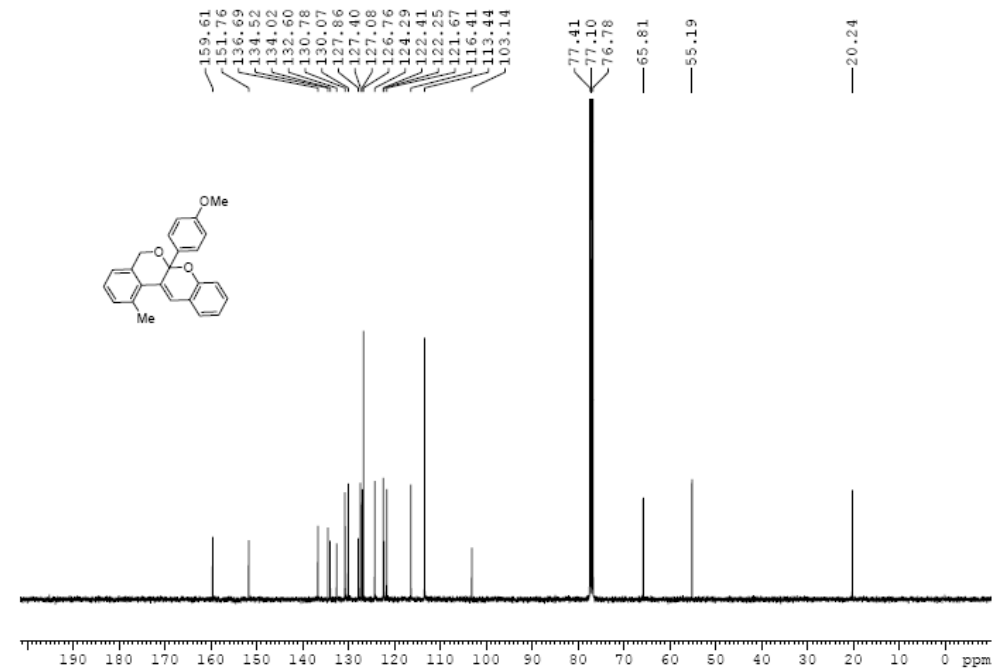
8,10-di-tert-butyl-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3k)**.



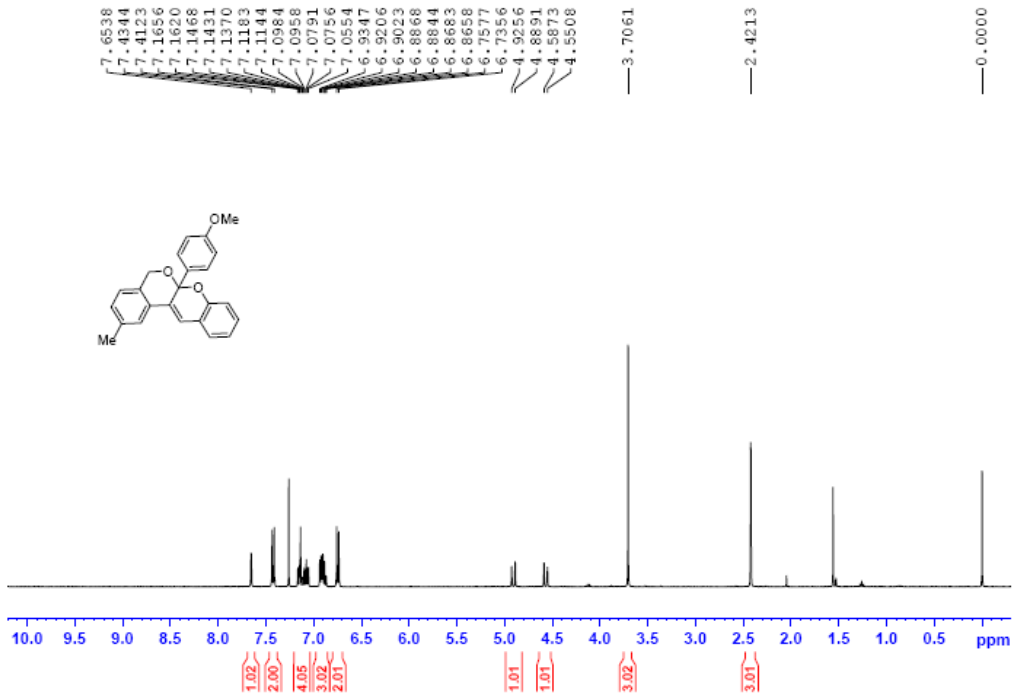
^{1}H NMR of 6a-(4-methoxyphenyl)-1-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3l)**.



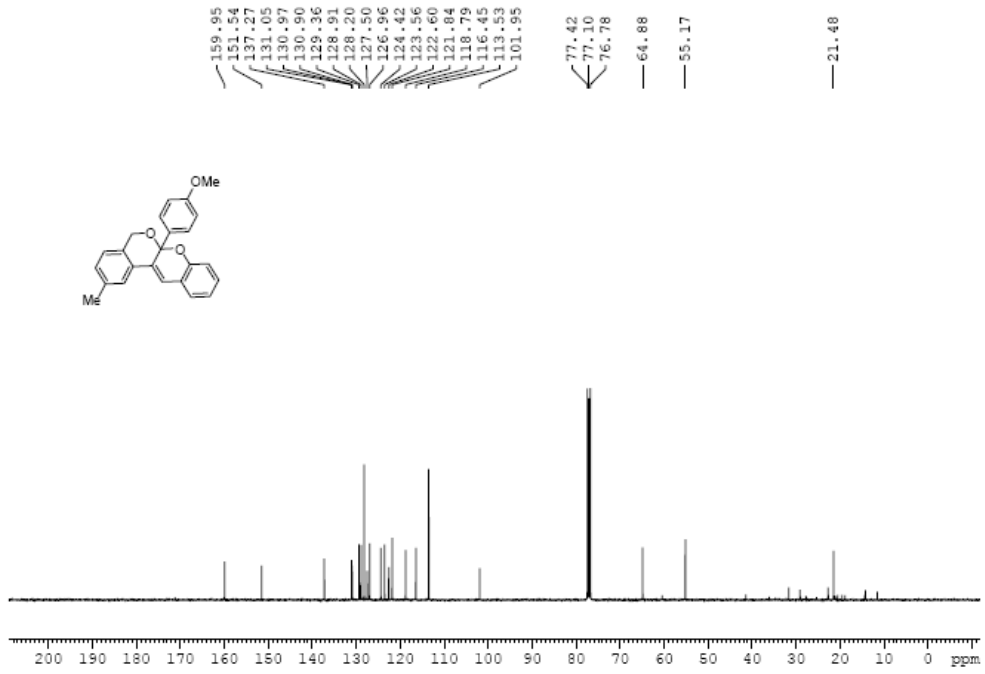
^{13}C NMR of 6a-(4-methoxyphenyl)-1-methyl-5,6a-dihydroisochromeno[3,4-b]chromene **(3l)**.



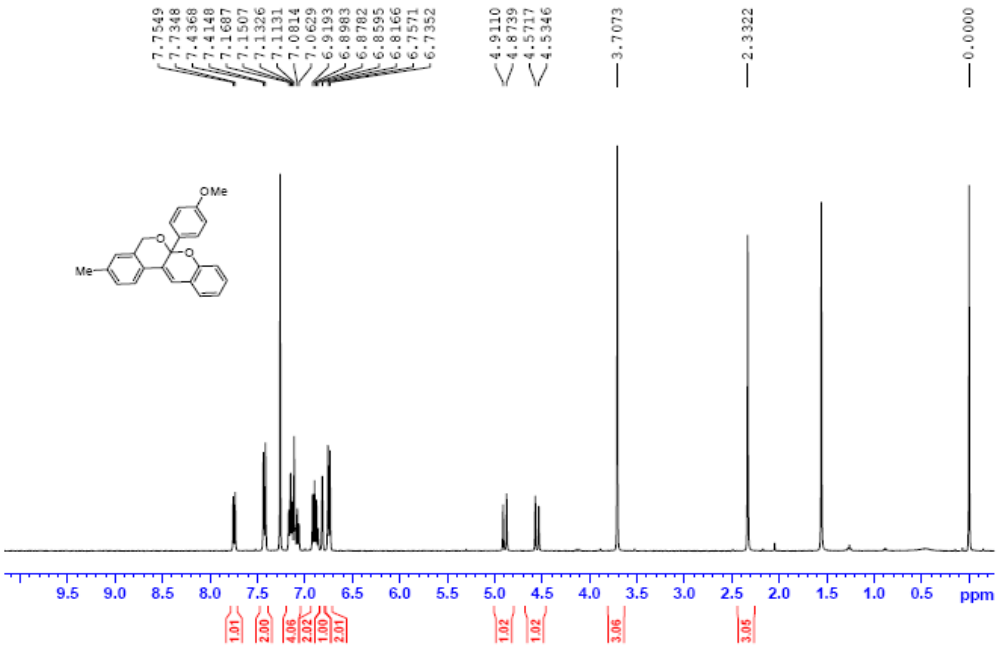
^{1}H NMR of 6a-(4-methoxyphenyl)-2-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3m)**.



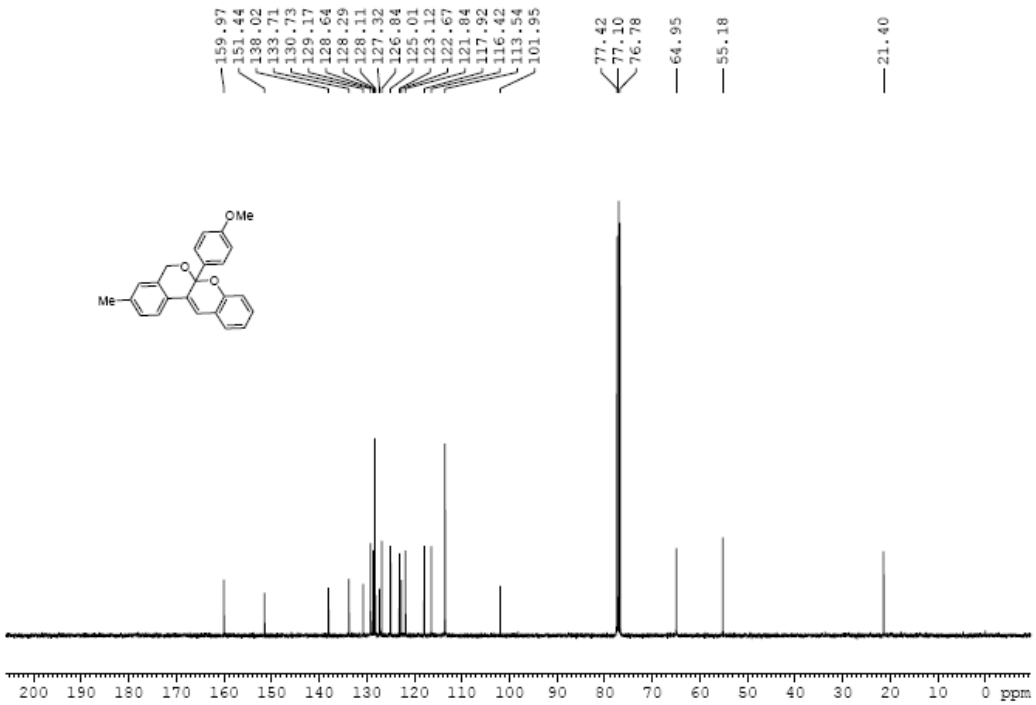
^{13}C NMR of 6a-(4-methoxyphenyl)-2-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3m)**.



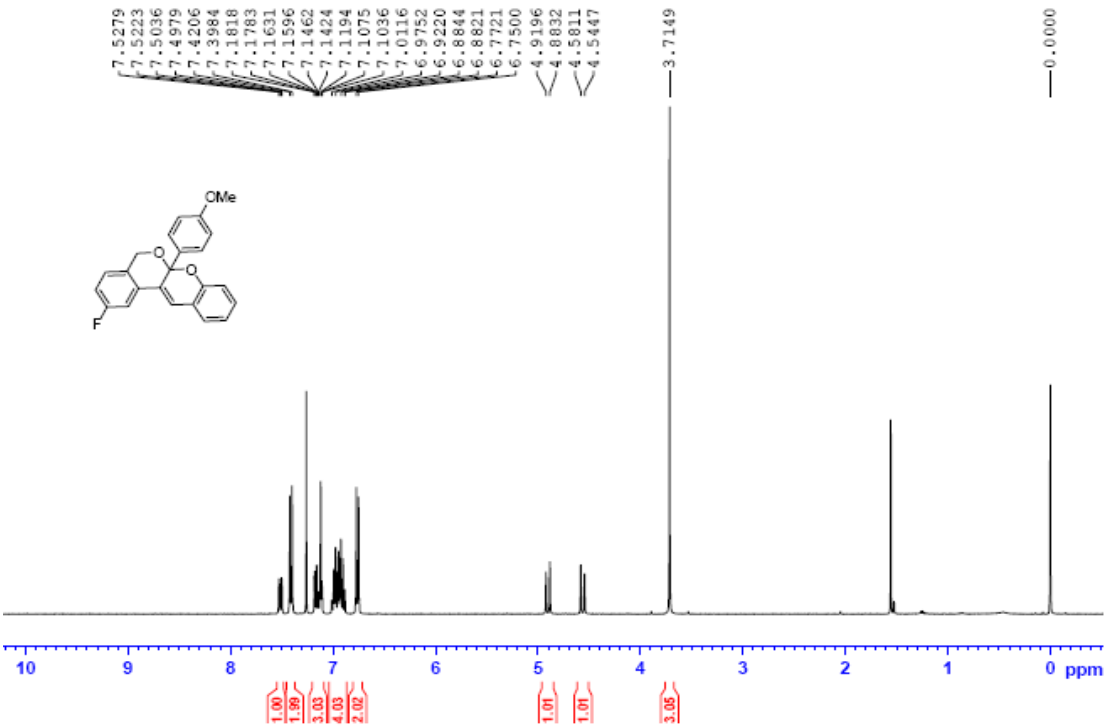
^{1}H NMR of 6a-(4-methoxyphenyl)-3-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3n)**.



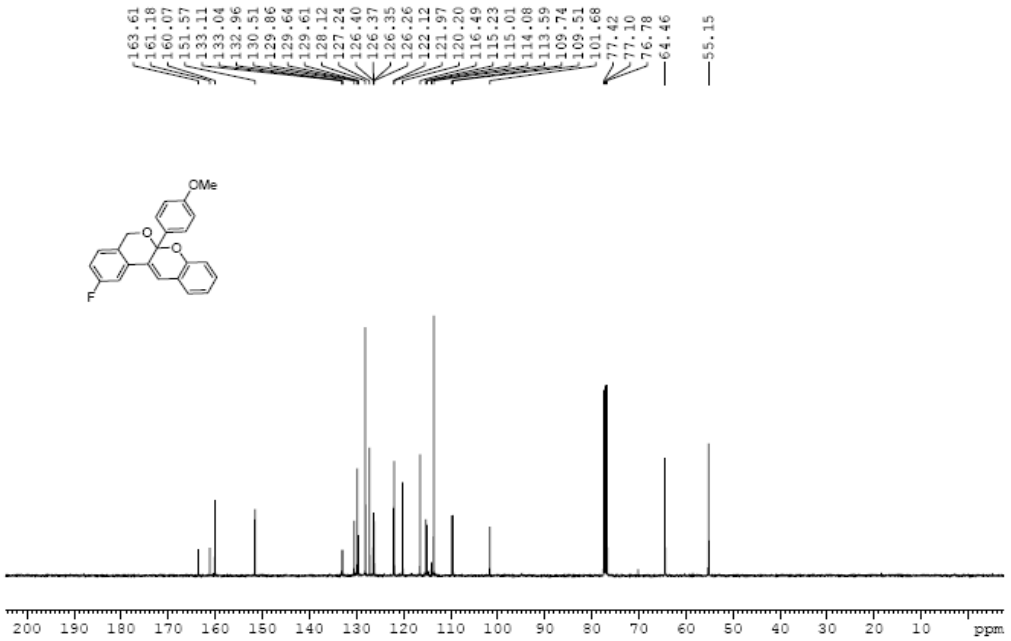
^{13}C NMR of 6a-(4-methoxyphenyl)-3-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3n)**.



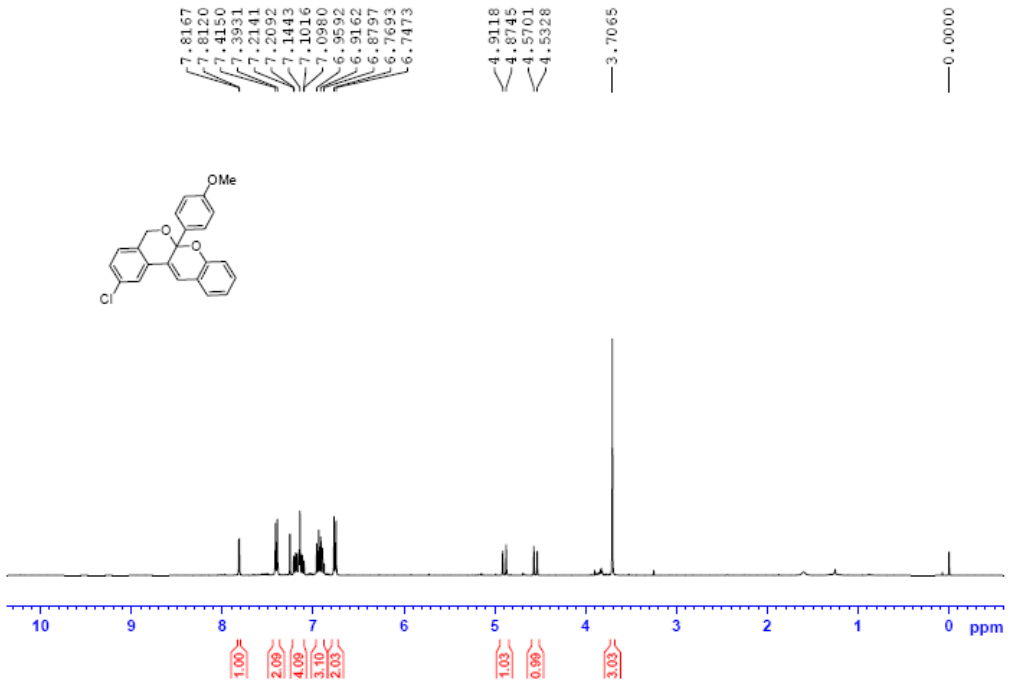
^{1}H NMR of 2-fluoro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3o)**.



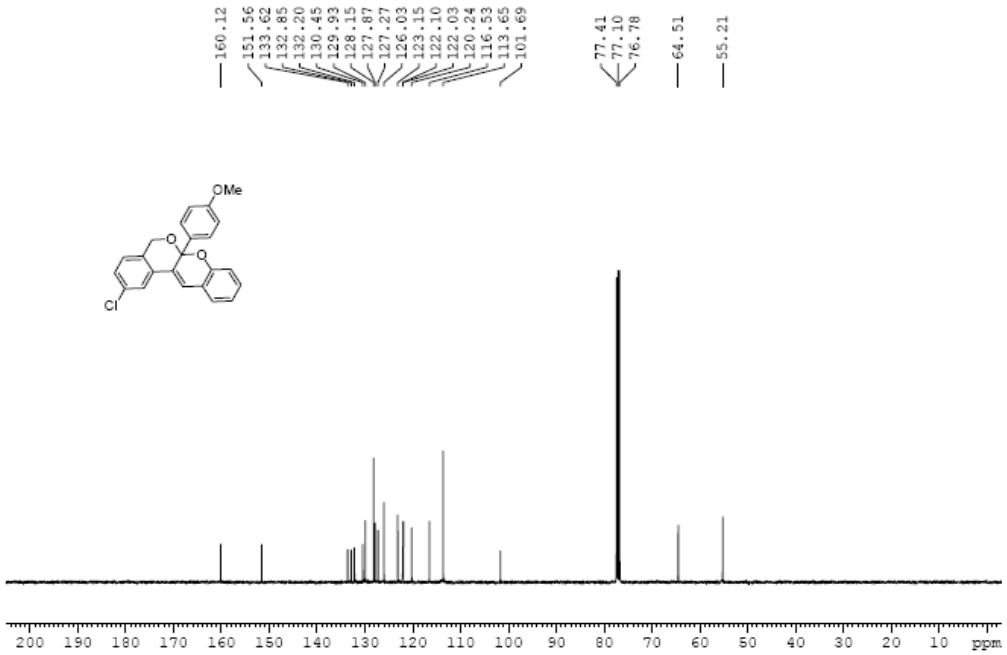
^{13}C NMR of 2-fluoro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3o)**.



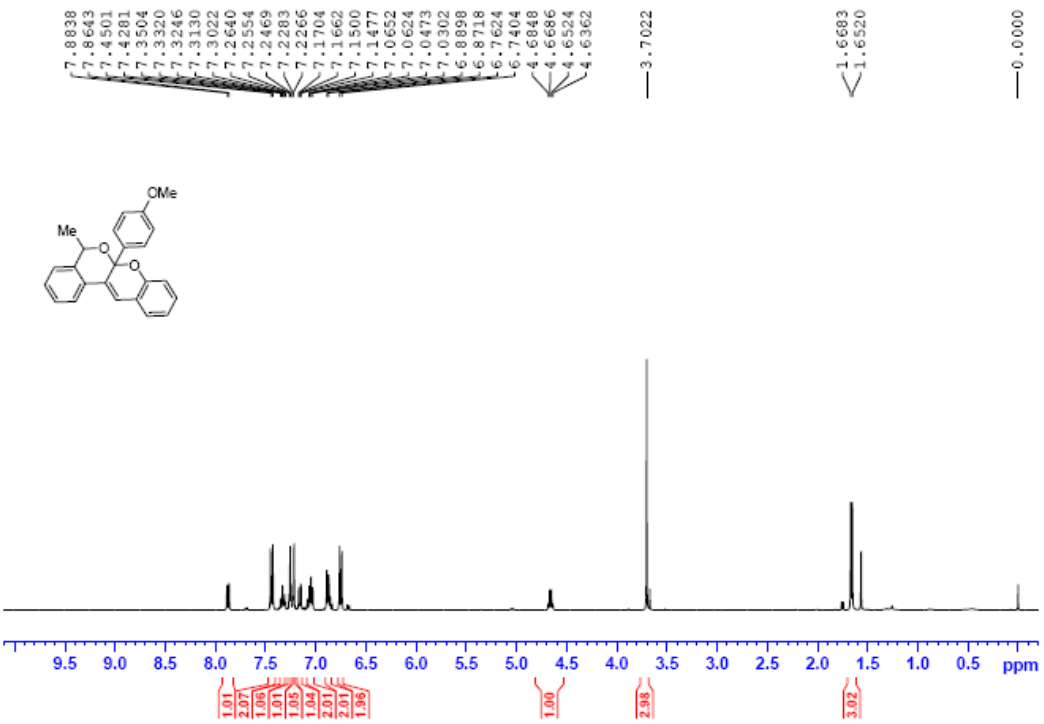
^{1}H NMR of 2-chloro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3p)**.



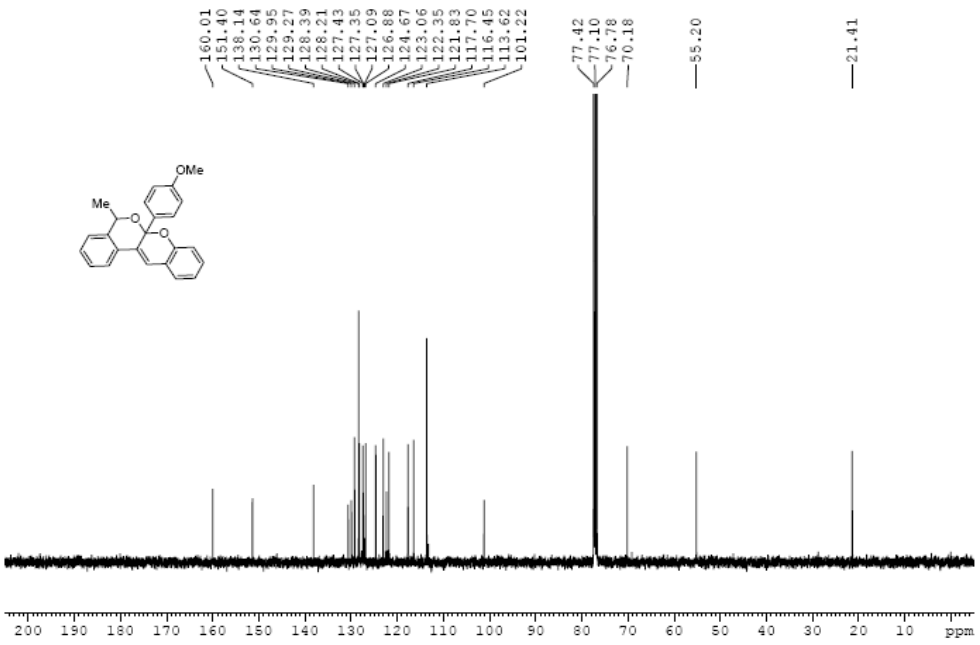
^{13}C NMR of 2-chloro-6a-(4-methoxyphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3p)**.



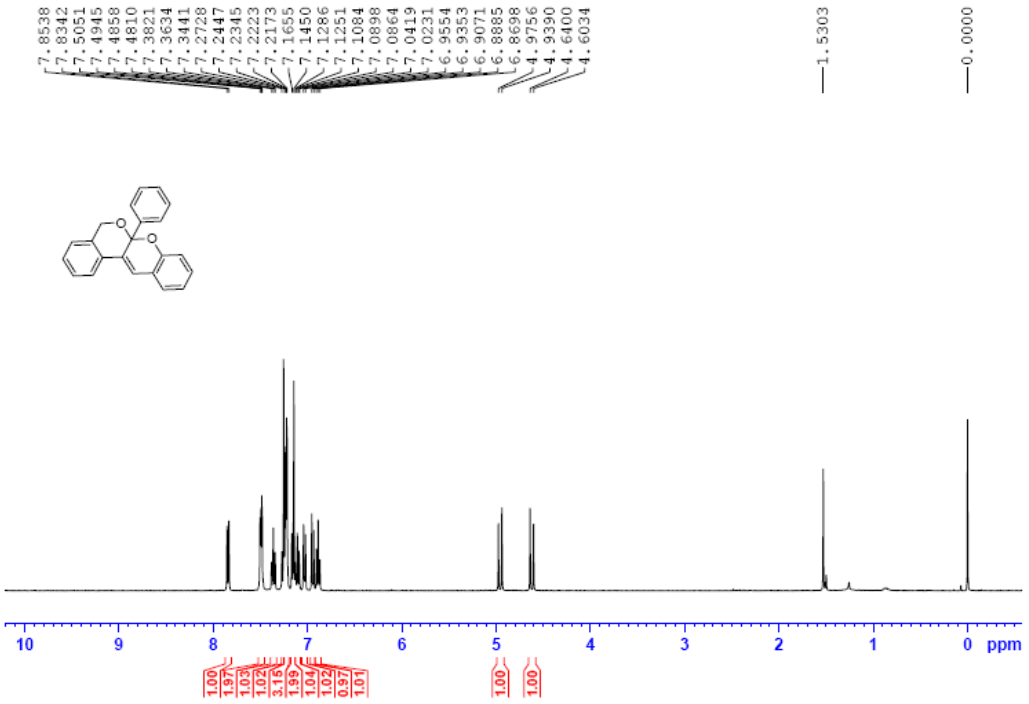
^{1}H NMR of 6a-(4-methoxyphenyl)-5-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3q)**.



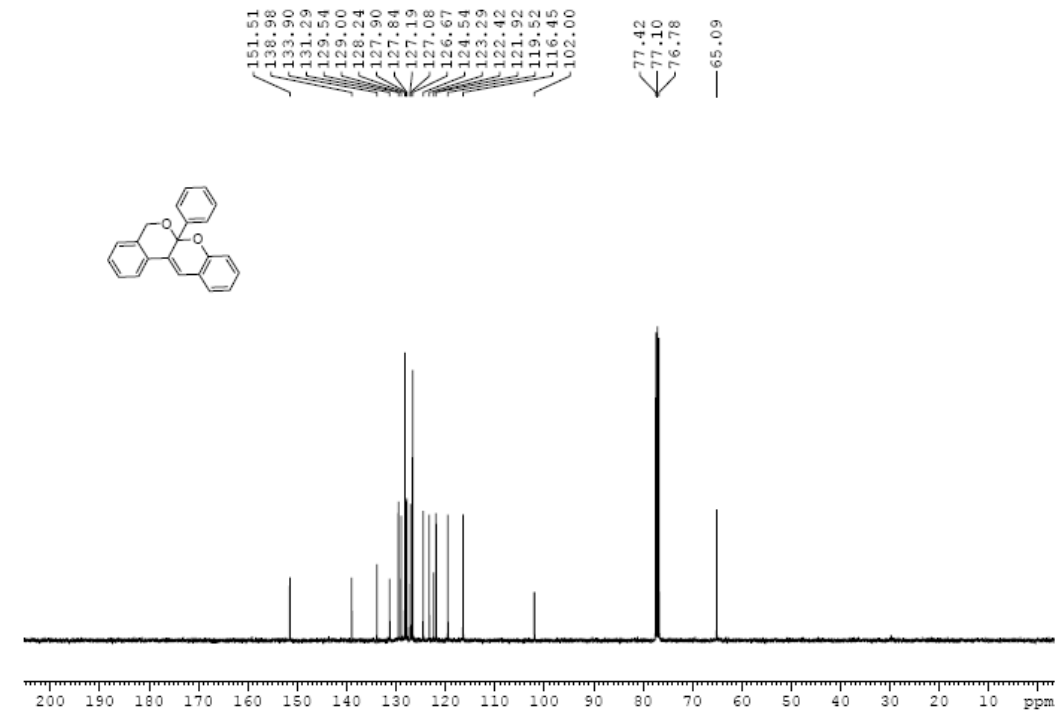
^{13}C NMR of 6a-(4-methoxyphenyl)-5-methyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3q)**.



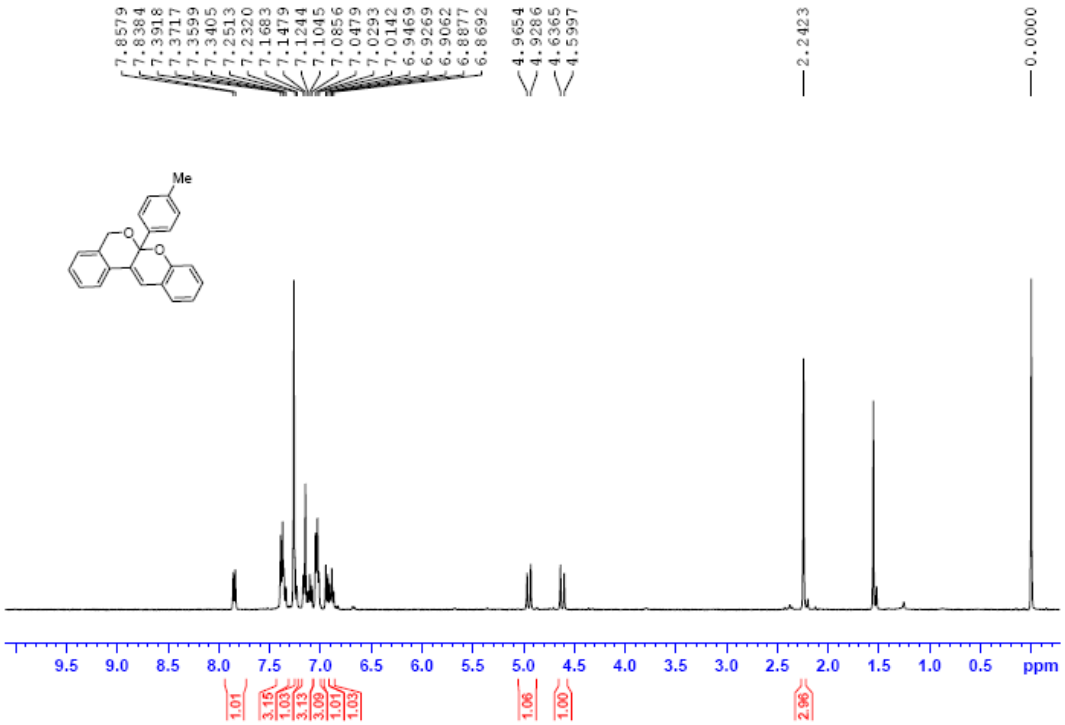
^{1}H NMR of 6a-phenyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3r)**.



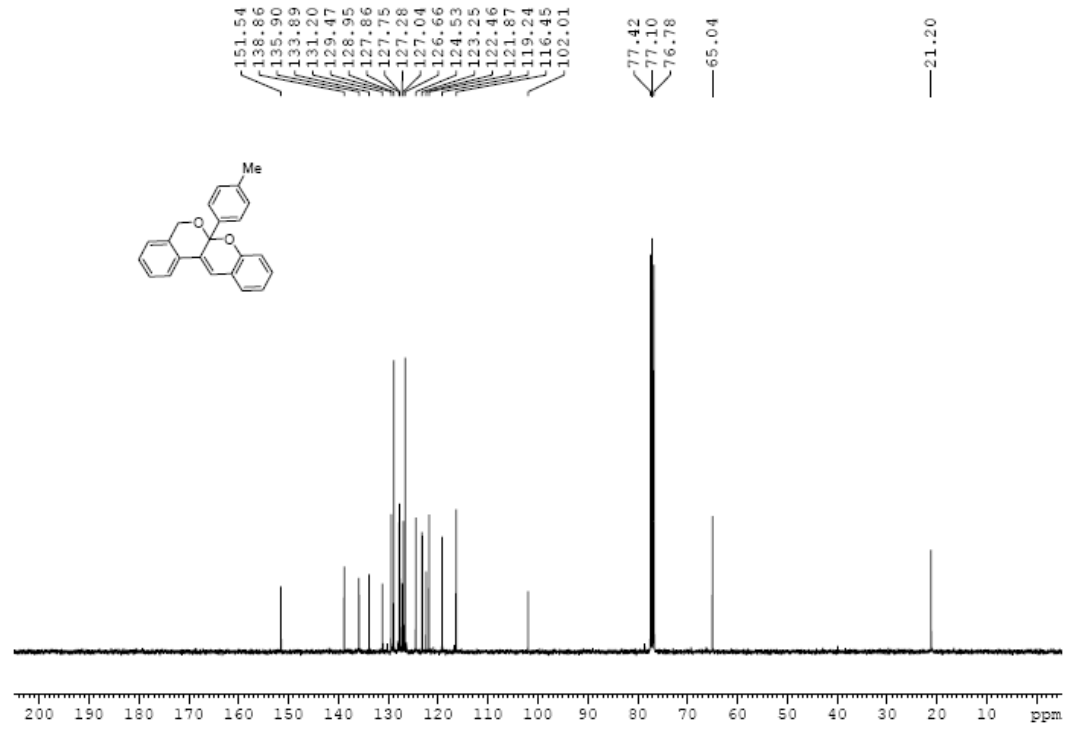
^{13}C NMR of 6a-phenyl-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3r)**.



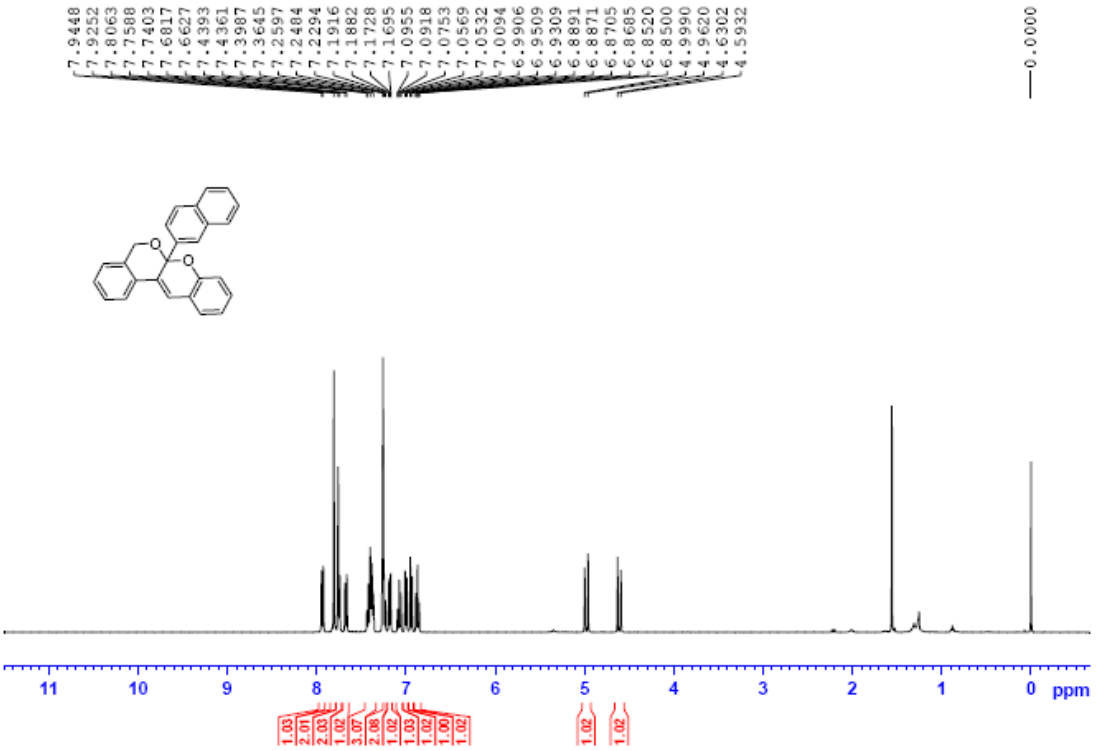
^{1}H NMR of 6a-(*p*-tolyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3s)**.



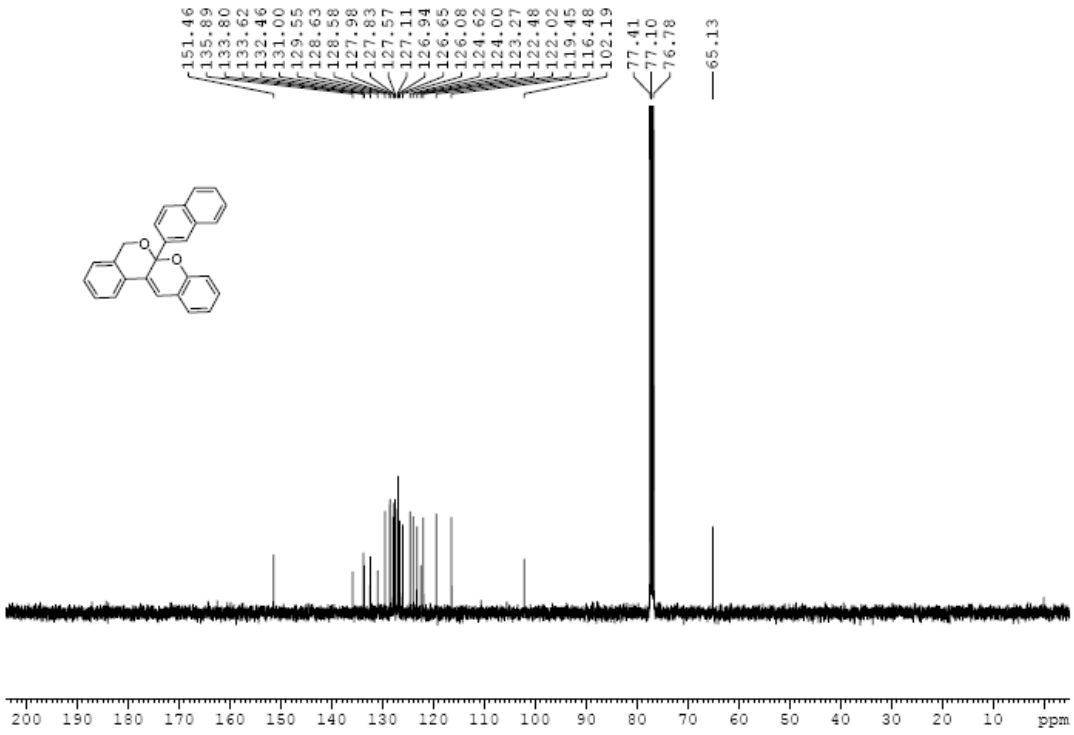
^{13}C NMR of 6a-(*p*-tolyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3s)**.



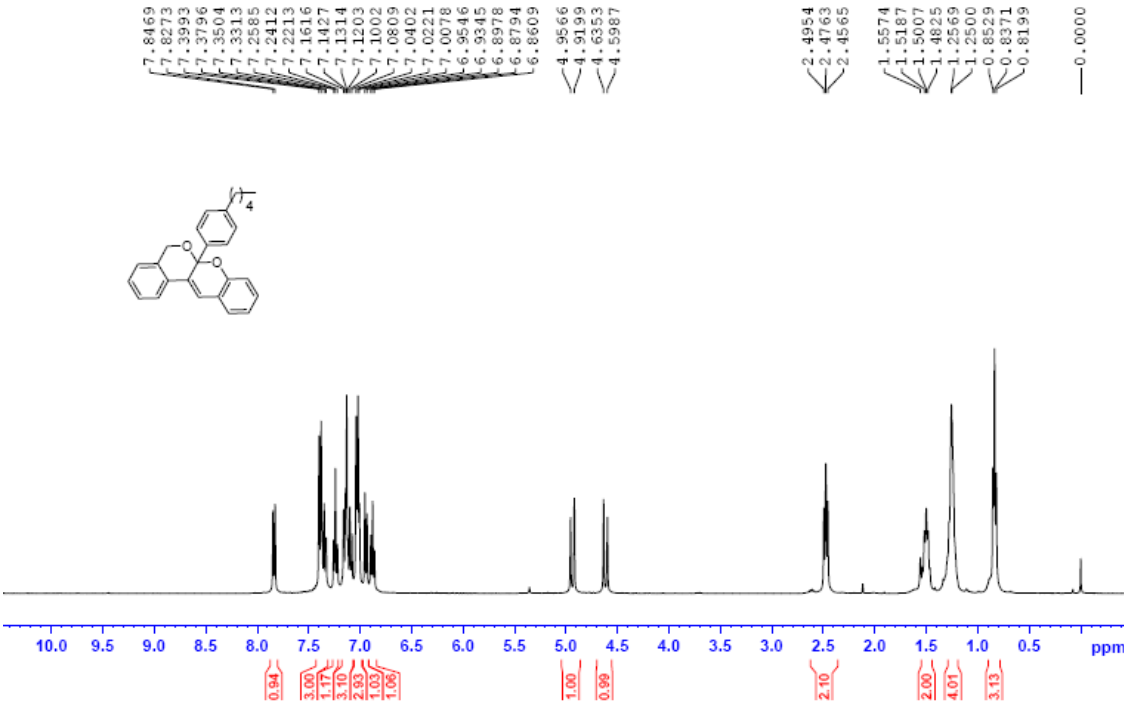
^{1}H NMR of 6a-(naphthalen-2-yl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3t)**.



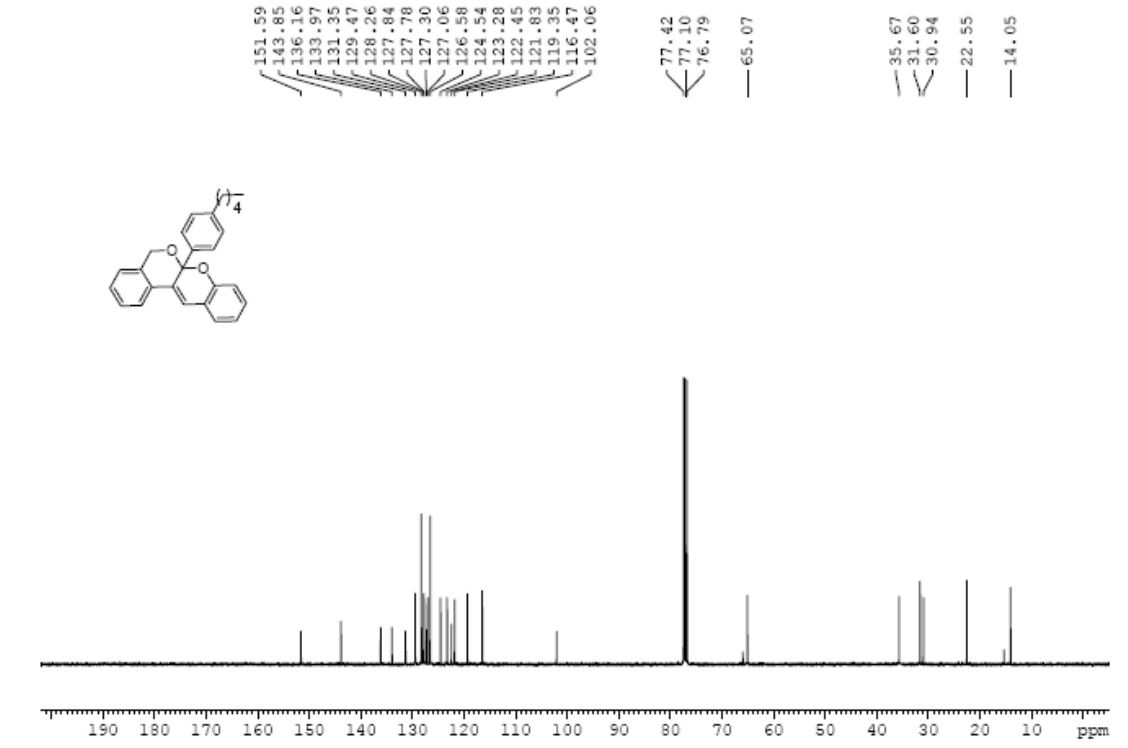
^{13}C NMR of 6a-(naphthalen-2-yl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3t)**.



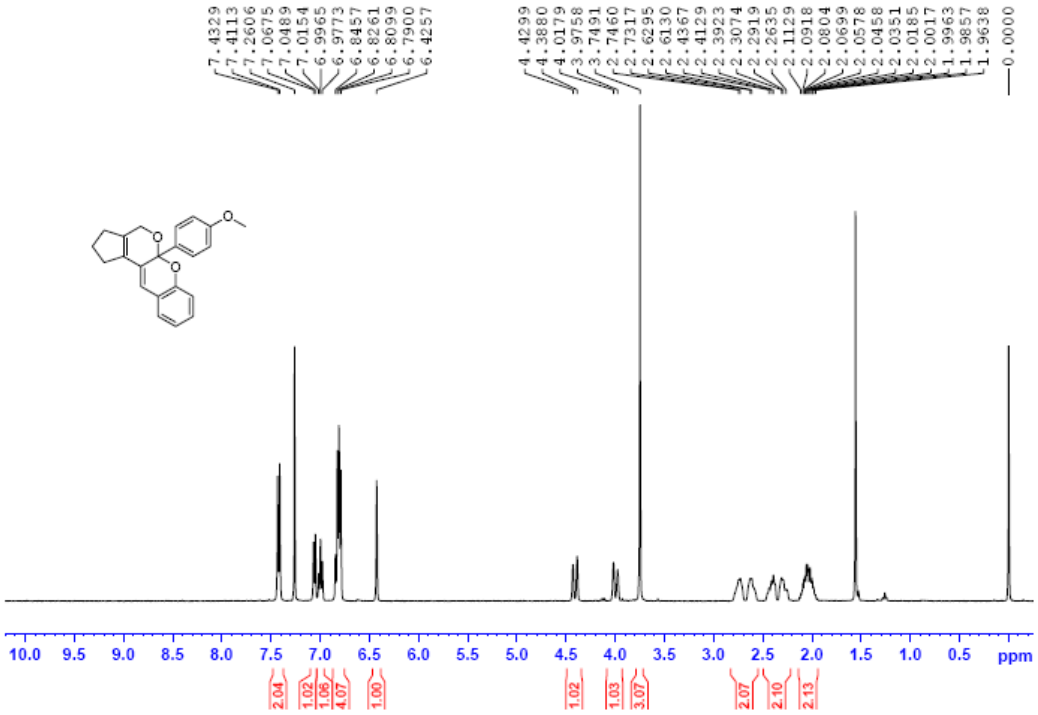
^{1}H NMR of 6a-(4-pentylphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3u)**.



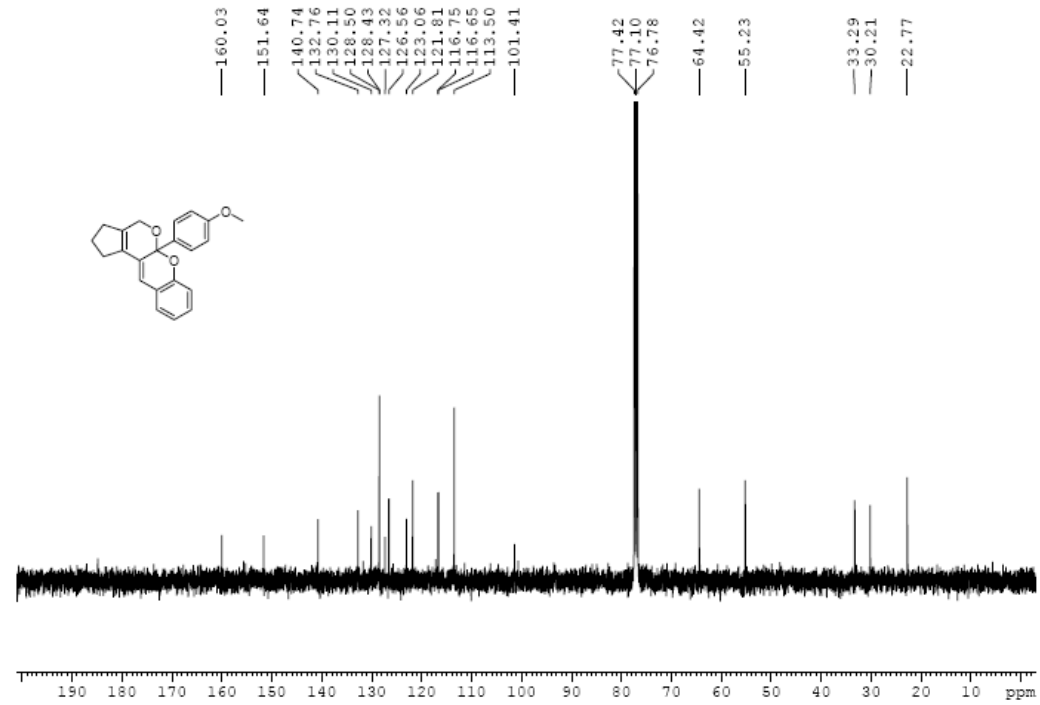
^{13}C NMR of 6a-(4-pentylphenyl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3u)**.



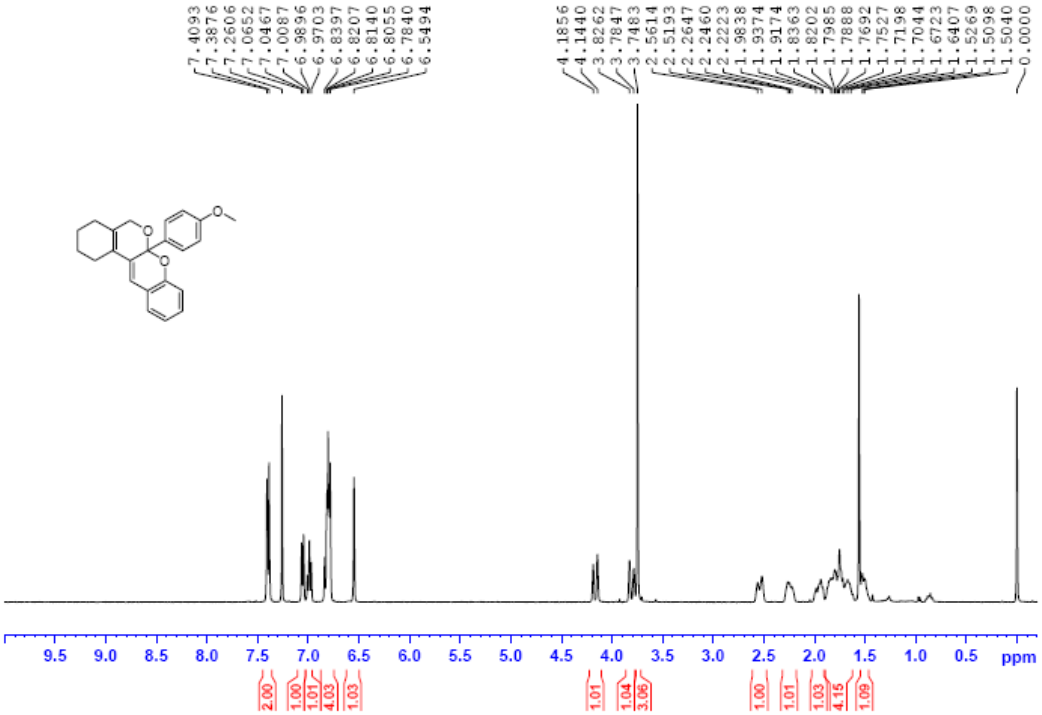
^{1}H NMR of 5a-(4-methoxyphenyl)-2,3,4,5a-tetrahydro-1H-cyclopenta[4,5]pyrano[2,3-*b*] chromene **(3v)**.



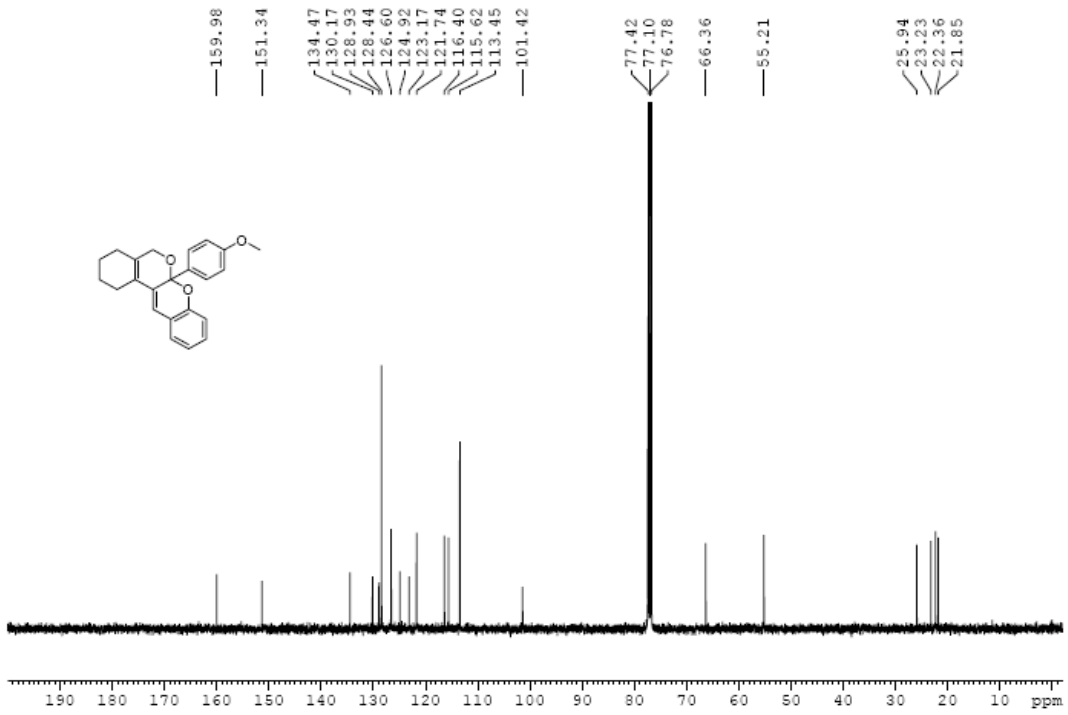
^{13}C NMR of 5a-(4-methoxyphenyl)-2,3,4,5a-tetrahydro-1H-cyclopenta[4,5]pyrano[2,3-*b*]chromene **(3v)**.



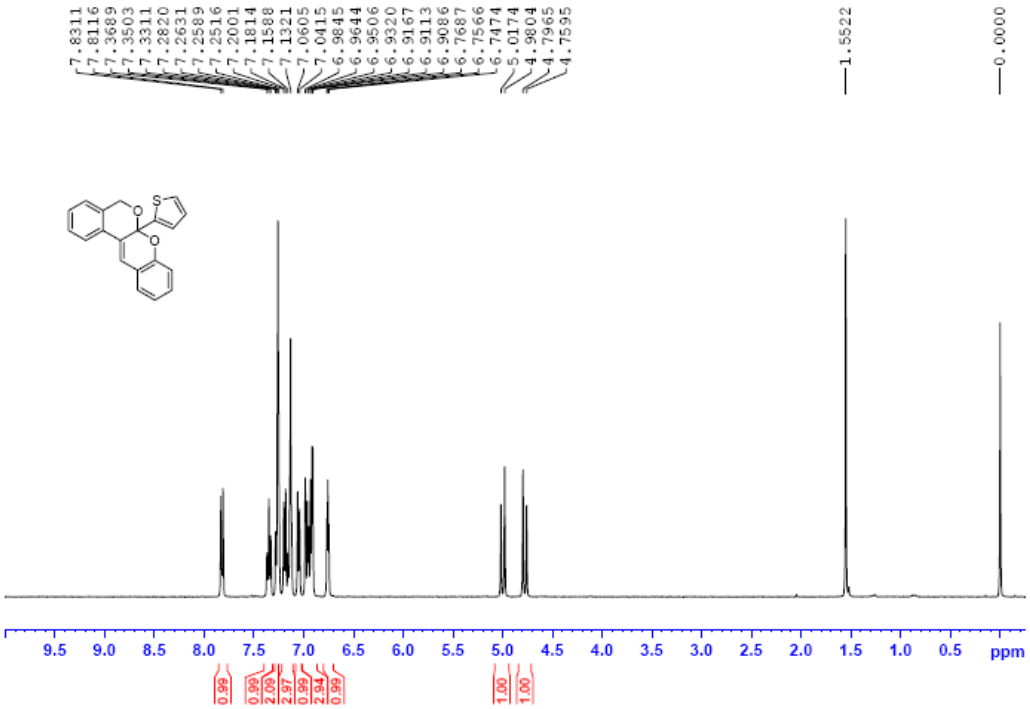
^{1}H NMR of 6a-(4-methoxyphenyl)-1,2,3,4,5,6a-hexahydroisochromeno[3,4-*b*]chromene **(3w)**.



^{13}C NMR of 6a-(4-methoxyphenyl)-1,2,3,4,5,6a-hexahydroisochromeno[3,4-*b*]chromene **(3w)**.



^{1}H NMR of 6a-(thiophen-2-yl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3x).**



^{13}C NMR of 6a-(thiophen-2-yl)-5,6a-dihydroisochromeno[3,4-*b*]chromene **(3x).**