

Supporting Information

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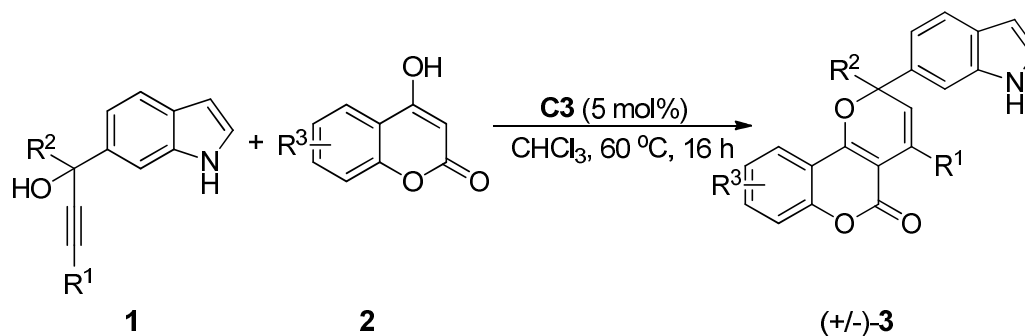
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A: General Information and Starting Materials

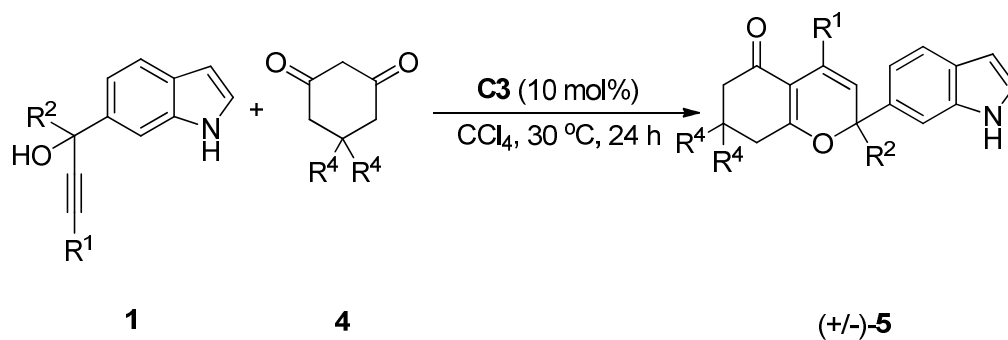
General Information. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 126 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl_3 : δ 7.26, $(\text{CD}_3)_2\text{SO}$: δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl_3 : δ 77.16, $(\text{CD}_3)_2\text{SO}$: δ 39.50). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. Optical Rotation was measured on a Rudolph Autopol I polarimeter. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Starting Materials. All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted. The propargylic alcohol and was prepared following the literature procedures.¹⁻²

B: General Procedure

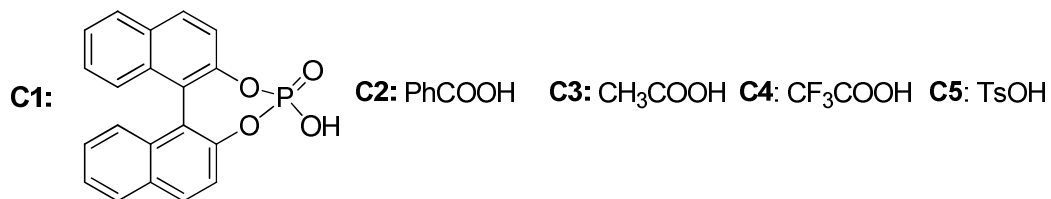
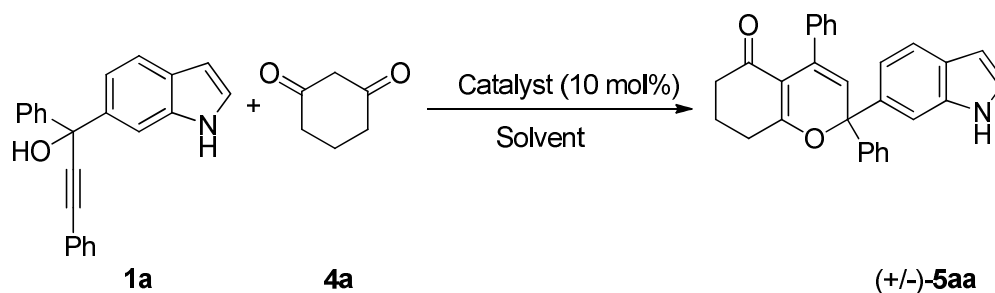


To a solution of CHCl_3 (0.5 mL) were added α -indolyl propargylic alcohols **1** (0.05 mmol), coumarins **2** (0.06 mmol) and **C3** (0.0025 mmol). The reaction mixture was stirred at 60°C for 16 h, then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product (+/-)-**3**.



To a solution of CCl_4 (0.3 mL) were added α -indolyl propargylic alcohols **1** (0.05 mmol), 1,3-cyclohexanediones **4** (0.06 mmol) and **C3** (0.005 mmol). The reaction mixture was stirred at 30 °C for 24 h, then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **(+/-)-5**.

C: The optimization of **1a** and **4a**^a

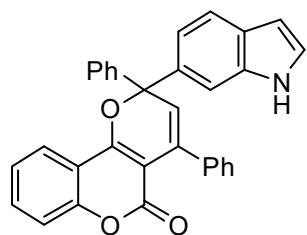


Entry	Cat.	Solvent	Yield[%] ^b
1	C1	DCM	39
2	C2	DCM	37
3	C3	DCM	57
4	C4	DCM	<5
5	C5	DCM	<5
6	C3	toluene	60
7	C3	PhCF ₃	78
8	C3	PhCl	36
9	C3	xylene	55
10	C3	CHCl ₃	60
11	C3	CCl ₄	82
12	C3	DCE	47
13	C3	THF	<5
14 ^c	C3	CCl ₄	91
15 ^d	C3	CCl ₄	77
18 ^e	C3	CHCl ₃	71

^a Reaction conditions: a mixture of **1a** (0.05 mmol), **4a** (0.06 mmol) and catalyst (10 mol%) in the solvent (0.3 mL) was stirred at room temperature for 24 h. ^b Isolated yield. ^c The reaction was stirred at 30 °C for 24 h. ^d The reaction was stirred at 50 °C for 6 h. ^e 5 mol% of **C3** was used at 60 °C for 16 h.

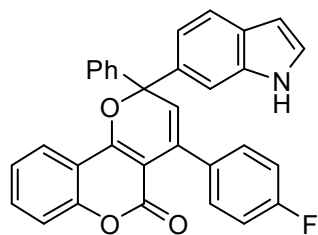
D: Characterization Data

2-(1*H*-indol-6-yl)-2,4-diphenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3aa)



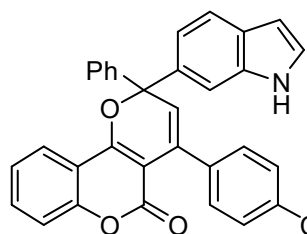
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 22.8 mg, 98% yield. Mp 188.6-191.6 °C. ¹H NMR ((CD₃)₂SO, 500 MHz): □ (ppm) 11.23 (s, 1H), 8.22-8.20 (m, 1H), 7.76 (t, *J* = 10.0 Hz, 1H), 7.66-7.64 (m, 3H), 7.58-7.52 (m, 4H), 7.46-7.38 (m, 8H), 7.20-7.18 (d, *J* = 10.0 Hz, 1H), 6.44 (s, 1H), 6.35 (s, 1H). ¹³C NMR ((CD₃)₂SO, 126 MHz): □ (ppm) 160.1, 158.0, 153.4, 144.2, 138.2, 136.0, 135.7, 133.7, 133.3, 128.9, 128.4, 128.1, 128.0, 127.8, 127.3, 127.1, 126.6, 125.2, 123.7, 120.7, 118.3, 116.9, 115.3, 110.4, 102.9, 101.4, 86.4. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₂NO₃) requires *m/z* 468.1594, found *m/z* 468.1596.

4-(4-Fluorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ba)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.0 mg, 95% yield. Mp 179.4-181.3 °C. ¹H NMR ((CD₃)₂SO, 500 MHz): □ (ppm) 11.17 (s, 1H), 8.15-8.13 (m, 1H), 7.69 (m, 1H), 7.60-7.58 (m, 3H), 7.54-7.50 (m, 3H), 7.47-7.44 (m, 1H), 7.41-7.36 (m, 4H), 7.33-7.30 (m, 1H), 7.20-7.16 (m, 2H), 7.14-7.12 (m, 1H), 6.39 (s, 1H), 6.32 (s, 1H). ¹³C NMR ((CD₃)₂SO, 126 MHz): □ (ppm) 162.3 (d, *J* = 244.4 Hz), 160.1, 158.1, 153.4, 144.1, 135.8 (d, *J* = 40.0 Hz), 134.5, 133.7, 132.3, 130.3 (d, *J* = 8.8 Hz), 128.9, 128.3, 127.8, 127.3, 127.1, 126.6, 125.2, 123.7, 120.6, 118.3, 116.9, 115.3, 114.9 (d, *J* = 21.3 Hz), 110.4, 102.7, 101.4, 86.3. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁FNO₃) requires *m/z* 486.1500, found *m/z* 486.1499.

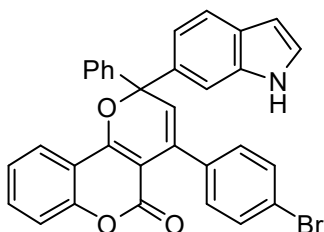
4-(4-Chlorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ca)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.7 mg, 95% yield. Mp 179.3-181.4 °C. ¹H NMR ((CD₃)₂SO, 500 MHz): □ (ppm) 11.16 (s, 1H), 8.15-8.14 (m, 1H), 7.72-7.68 (m, 1H), 7.59-7.57 (m, 3H), 7.52-7.50 (m, 3H), 7.48-7.45 (m, 1H), 7.42-7.36 (m, 6H), 7.32-7.30 (m, 1H), 7.13-7.11 (m, 1H), 6.39-6.38 (m, 1H), 6.36 (s, 1H). ¹³C NMR ((CD₃)₂SO, 126 MHz): □ (ppm) 160.2, 158.1, 153.4, 144.0, 137.0, 135.9, 135.6, 133.8, 132.7, 132.1, 130.0, 128.9, 128.4, 128.0, 127.8, 127.7, 127.1, 126.6, 125.2, 123.7, 120.7, 118.3, 116.9, 115.3, 110.3, 102.6, 101.4, 86.4. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁ClNO₃)

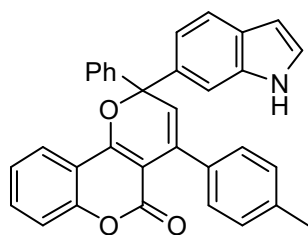
requires m/z 502.1204, found m/z 502.1205.

4-(4-Bromophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3da)



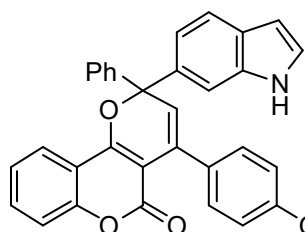
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 25.8 mg, 95% yield. Mp 170.1-172.9 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.29 (s, 1H), 8.05-8.03 (m, 1H), 7.60 (d, $J = 10.0$ Hz, 1H), 7.55-7.54 (m, 1H), 7.52-7.47 (m, 5H), 7.38-7.29 (m, 6H), 7.25 (d, $J = 10.0$ Hz, 1H), 7.21-7.18 (m, 2H), 6.52 (s, 1H), 6.02 (s, 1H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 160.6, 158.8, 153.6, 143.7, 137.0, 136.3, 135.2, 132.8, 132.7, 131.0, 129.3, 128.4, 128.1, 127.8, 126.8, 126.4, 125.6, 124.1, 123.3, 121.9, 120.9, 119.4, 116.7, 115.5, 110.4, 102.5, 102.2, 86.7. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{32}\text{H}_{21}\text{BrNO}_3$) requires m/z 546.0699, found m/z 546.0703.

2-(1*H*-indol-6-yl)-2-phenyl-4-(*p*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ea)



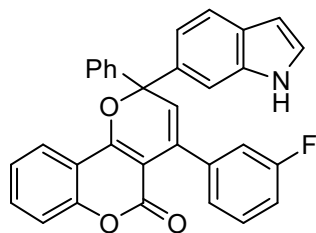
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.8 mg, 91% yield. Mp 176.8-178.1 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.26 (s, 1H), 8.04-8.03 (m, 1H), 7.59-7.50 (m, 5H), 7.36-7.27 (m, 5H), 7.26-7.15 (m, 6H), 6.51 (s, 1H), 6.01 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 160.4, 158.8, 153.6, 144.0, 137.6, 136.6, 135.1, 135.0, 133.6, 132.4, 128.7, 128.3, 128.0, 127.7, 127.4, 126.9, 125.7, 125.5, 124.0, 123.3, 120.8, 119.5, 116.6, 115.7, 110.5, 102.7, 102.5, 86.7, 21.3. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{33}\text{H}_{24}\text{NO}_3$) requires m/z 482.1751, found m/z 482.1753.

2-(1*H*-indol-6-yl)-4-(4-methoxyphenyl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3fa)



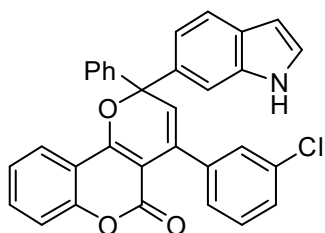
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12:1. White solid, 21.3 mg, 86% yield. Mp 198.1-201.9 °C. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 500 MHz): \square (ppm) 11.21 (s, 1H), 8.14 (d, $J = 10.0$ Hz, 1H), 7.70-7.67 (m, 1H), 7.58-7.56 (m, 3H), 7.50 (d, $J = 10.0$ Hz, 1H), 7.47-7.44 (m, 1H), 7.40-7.35 (m, 6H), 7.32-7.29 (m, 1H), 7.12 (d, $J = 10.0$ Hz, 1H), 6.91-6.90 (m, 2H), 6.38 (s, 1H), 6.21 (s, 1H), 3.77 (s, 3H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 126 MHz): \square (ppm) 160.1, 159.3, 158.0, 153.4, 144.3, 136.0, 135.6, 133.6, 132.9, 130.3, 129.3, 128.8, 128.3, 127.8, 127.0, 126.5, 126.2, 125.1, 123.6, 120.6, 118.3, 116.8, 115.5, 113.5, 110.3, 103.0, 101.4, 86.3, 55.6. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{33}\text{H}_{24}\text{NO}_4$) requires m/z 498.1700, found m/z 498.1704.

4-(3-Fluorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ga)



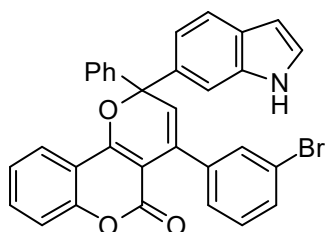
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.3 mg, 88% yield. Mp 164.1-167.6 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.27 (s, 1H), 8.06-8.04 (m, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.57 (s, 1H), 7.56-7.53 (m, 1H), 7.51-7.50 (m, 2H), 7.39-7.28 (m, 6H), 7.25-7.24 (m, 1H), 7.22-7.18 (m, 2H), 7.17-7.15 (m, 1H), 7.06-7.02 (m, 1H), 6.54 (s, 1H), 6.05 (s, 1H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 162.4 (d, *J* = 244.4 Hz), 160.5, 158.7, 153.6, 143.7, 140.2 (d, *J* = 8.8 Hz), 136.3, 135.1, 132.8, 132.7, 129.3 (d, *J* = 8.8 Hz), 128.4, 128.1, 127.8, 126.8, 126.7, 125.5, 124.1, 123.4, 123.3, 120.9, 119.4, 116.7, 115.5, 114.8 (d, *J* = 7.5 Hz), 114.6 (d, *J* = 6.3 Hz), 110.3, 102.6, 102.3, 86.7. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁FNO₃) requires *m/z* 486.1500, found *m/z* 486.1501.

4-(3-Chlorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ha)



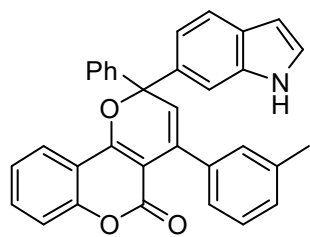
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.8 mg, 87% yield. Mp 166.6-167.9 °C. ¹H NMR ((CD₃)₂SO, 500 MHz): □ (ppm) 11.17 (s, 1H), 8.16-8.14 (m, 1H), 7.71-7.68 (m, 1H), 7.60-7.59 (m, 4H), 7.51 (d, *J* = 10.0 Hz, 1H), 7.48-7.47 (m, 1H), 7.45-7.43 (m, 2H), 7.40-7.36 (m, 5H), 7.33-7.30 (m, 1H), 7.14-7.12 (m, 1H), 6.40 (s, 1H), 6.39-6.38 (m, 1H). ¹³C NMR ((CD₃)₂SO, 126 MHz): □ (ppm) 160.2, 158.1, 153.4, 143.9, 140.3, 135.8, 135.6, 133.8, 132.9, 131.9, 129.9, 128.9, 128.8, 128.4, 128.2, 127.9, 127.8, 127.1, 126.9, 126.6, 125.2, 123.7, 120.7, 118.3, 116.9, 115.3, 110.3, 102.6, 101.4, 86.4. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁ClNO₃) requires *m/z* 502.1024, found *m/z* 502.1026.

4-(3-Bromophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ia)



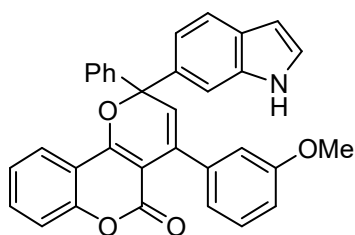
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.3 mg, 85% yield. Mp 131.4-134.3 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.30 (s, 1H), 8.07-8.05 (m, 1H), 7.63-7.61 (m, 2H), 7.58-7.54 (m, 2H), 7.52-7.48 (m, 3H), 7.40-7.33 (m, 5H), 7.32-7.28 (m, 2H), 7.25-7.23 (m, 1H), 7.21-7.19 (m, 1H), 6.55 (s, 1H), 6.04 (s, 1H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 160.6, 158.7, 153.6, 143.6, 140.1, 136.2, 135.1, 132.7, 132.5, 130.8, 130.4, 129.3, 128.4, 128.1, 127.8, 126.9, 126.8, 126.4, 125.6, 124.1, 123.3, 122.0, 120.9, 119.4, 116.7, 115.5, 110.4, 102.5, 102.2, 86.7. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁BrNO₃) requires *m/z* 546.0699, found *m/z* 546.0701.

2-(1*H*-indol-6-yl)-2-phenyl-4-(*m*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ja)



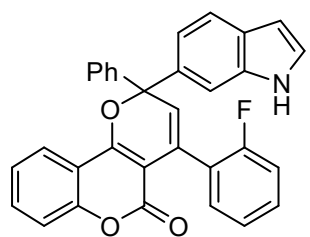
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 20.4 mg, 85% yield. Mp 186.2-191.0 °C. ¹H NMR ((CD₃)₂SO, 500 MHz): □ (ppm) 11.17 (s, 1H), 8.14 (d, *J* = 10.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.59-7.57 (m, 3H), 7.51 (d, *J* = 10.0 Hz, 1H), 7.47-7.44 (m, 1H), 7.41-7.36 (m, 4H), 7.32-7.30 (m, 2H), 7.23-7.22 (m, 2H), 7.13-7.12 (m, 2H), 6.38 (s, 1H), 6.25 (s, 1H), 2.33 (s, 3H). ¹³C NMR ((CD₃)₂SO, 126 MHz): □ (ppm) 160.1, 158.0, 153.4, 144.2, 138.1, 137.2, 135.9, 135.6, 133.7, 133.4, 128.9, 128.7, 128.5, 128.3, 128.0, 127.8, 127.1, 127.0, 126.6, 125.2, 125.1, 123.6, 120.6, 118.3, 116.8, 115.3, 110.4, 103.0, 101.4, 86.4, 21.4. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₃H₂₄NO₃) requires *m/z* 482.1751, found *m/z* 482.1751.

2-(1*H*-indol-6-yl)-4-(3-methoxyphenyl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ka)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12:1. White solid, 21.6 mg, 87% yield. Mp 139.1-141.9 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.28 (s, 1H), 8.04 (d, *J* = 10.0 Hz, 1H), 7.59-7.57 (m, 2H), 7.53-7.49 (m, 3H), 7.36-7.33 (m, 2H), 7.32-7.28 (m, 3H), 7.25 (s, 1H), 7.22-7.21 (m, 1H), 7.19-7.18 (m, 1H), 7.03-7.01 (m, 1H), 6.98 (s, 1H), 6.88-6.86 (m, 1H), 6.51 (s, 1H), 6.04 (s, 1H), 3.80 (s, 3H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 160.4, 159.1, 158.7, 153.6, 143.9, 139.5, 136.4, 135.1, 133.6, 132.5, 128.9, 128.3, 128.0, 127.7, 126.8, 126.2, 125.5, 124.0, 123.3, 120.8, 120.2, 119.4, 116.6, 115.6, 113.6, 113.1, 110.5, 102.7, 102.4, 86.7, 55.3. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₃H₂₄NO₄) requires *m/z* 498.1700, found *m/z* 498.1700.

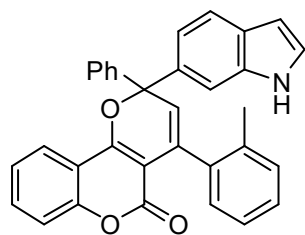
4-(2-Fluorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3la)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 20.6 mg, 85% yield. Mp 171.8-173.5 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.39 (s, 1H), 8.06-8.05 (m, 1H), 7.66-7.64 (m, 2H), 7.57-7.49 (m, 4H), 7.41-7.28 (m, 7H), 7.23-7.18 (m, 2H), 7.12-7.10 (m, 1H), 6.56 (s, 1H), 6.11 (s, 1H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 160.1 (d, *J* = 234.4 Hz), 159.1, 153.4, 143.8, 136.4, 135.2, 132.4, 129.9, 129.8, 129.6 (d, *J* = 8.8 Hz), 128.4, 128.2, 128.1, 127.7, 127.4, 126.9, 126.3 (d, *J* = 15.0 Hz), 125.6, 124.0, 123.9 (d, *J* = 3.8 Hz), 123.3, 120.8, 119.3, 116.6, 115.6, 115.1 (d, *J* = 21.4 Hz), 110.5, 102.7, 102.4, 86.4. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁FNO₃) requires *m/z* 486.1500, found *m/z*

486.1501.

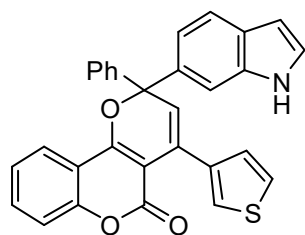
2-(1*H*-indol-6-yl)-2-phenyl-4-(*o*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ma)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 20.9 mg, 87% yield.

Mp 196.8-199.1 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.29 (s, 1H), 8.04 (d, *J* = 10.0 Hz, 1H), 7.63-7.48 (m, 5H), 7.39-7.28 (m, 5H), 7.23-7.16 (m, 6H), 6.53 (s, 1H), 5.95 (s, 1H), 2.25 (s, 3H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 159.0, 158.8, 153.5, 138.6, 137.6, 135.9, 135.2, 132.9, 132.4, 129.5, 128.4, 128.3, 128.2, 127.9, 127.7, 126.7, 126.0, 125.5, 124.0, 123.3, 120.8, 119.3, 116.6, 115.6, 110.4, 110.0, 102.9, 102.4, 86.5, 20.1. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₃H₂₄NO₃) requires *m/z* 482.1751, found *m/z* 482.1753.

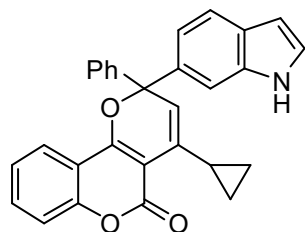
2-(1*H*-indol-6-yl)-2-phenyl-4-(thiophen-3-yl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3na)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.5 mg, 91% yield.

Mp 164.1-169.2 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.24 (s, 1H), 7.99 (d, *J* = 10.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.50-7.45 (m, 3H), 7.37 (s, 1H), 7.33-7.27 (m, 4H), 7.24-7.21 (m, 2H), 7.19-7.18 (m, 1H), 7.15 (d, *J* = 10.0 Hz, 1H), 7.11-7.10 (m, 1H), 6.48 (s, 1H), 6.06 (s, 1H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 160.3, 158.8, 153.5, 143.8, 138.3, 136.4, 135.1, 132.5, 128.7, 128.3, 128.0, 127.9, 127.7, 126.9, 125.5, 124.6, 124.0, 123.3, 122.5, 120.8, 119.5, 116.6, 115.6, 110.5, 102.6, 102.5, 86.5. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₀H₂₀NO₃S) requires *m/z* 474.1158, found *m/z* 474.1161.

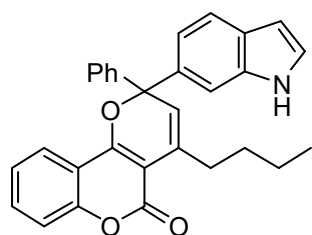
4-Cyclopropyl-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3oa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10:1. White solid, 15.3 mg, 71% yield.

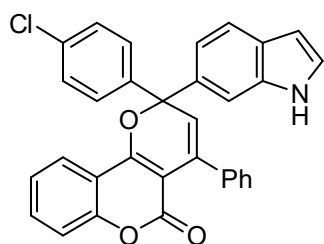
Mp 126.5-129.8 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.27 (s, 1H), 7.96 (d, *J* = 10.0 Hz, 1H), 7.57-7.56 (m, 1H), 7.50-7.47 (m, 1H), 7.45 (s, 1H), 7.41-7.39 (m, 2H), 7.35-7.29 (m, 3H), 7.25-7.22 (m, 3H), 7.09-7.07 (m, 1H), 6.52 (s, 1H), 5.64 (s, 1H), 2.52-2.50 (m, 1H), 0.91-0.87 (m, 2H), 0.64-0.57 (m, 2H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 159.7, 159.1, 153.4, 144.4, 137.4, 135.1, 134.6, 132.2, 128.2, 127.8, 127.5, 126.8, 125.3, 123.9, 123.3, 120.7, 119.7, 119.4, 116.4, 115.5, 110.2, 103.6, 102.5, 86.3, 13.1, 7.3, 7.1. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₂₉H₂₂NO₃) requires *m/z* 432.1594, found *m/z* 432.1594.

4-Butyl-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3pa)



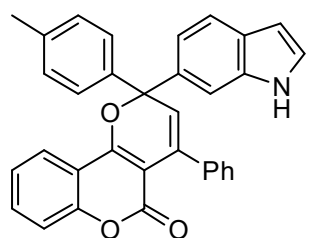
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 16:1. White solid, 16.3 mg, 73% yield. Mp 63.2-65.0 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.27 (s, 1H), 7.98 (d, *J* = 10.0 Hz, 1H), 7.59 (d, *J* = 10.0 Hz, 1H), 7.51-7.248(m, 2H), 7.46-7.44 (m, 2H), 7.37-7.31 (m, 3H), 7.28-7.27 (s, 1H), 7.25-7.23 (m, 2H), 7.15-7.13 (m, 1H), 6.53 (s, 1H), 5.81 (s, 1H), 2.90-2.76 (m, 2H), 1.56-1.52 (m, 2H), 1.46-1.40 (m, 2H), 0.94 (t, *J* = 10.0 Hz, 3H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 159.7, 153.3, 144.5, 137.4, 135.1, 133.1, 132.1, 128.6, 128.2, 127.8, 127.5, 126.8, 125.3, 123.9, 123.2, 122.6, 120.7, 119.4, 116.4, 115.6, 110.3, 102.9, 102.5, 86.3, 32.8, 31.4, 22.6, 14.1. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₀H₂₆NO₃) requires *m/z* 448.1907, found *m/z* 448.1904.

2-(4-Chlorophenyl)-2-(1*H*-indol-6-yl)-4-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3qa)



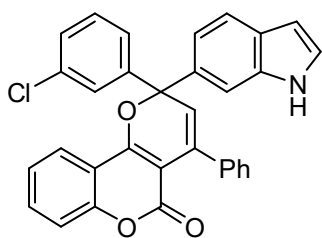
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.8 mg, 95% yield. Mp 175.1-179.4 °C. ¹H NMR ((CD₃)₂SO, 500 MHz): □ (ppm) 11.18 (s, 1H), 8.15-8.13 (m, 1H), 7.71-7.68 (m, 1H), 7.61-7.59 (m, 3H), 7.52 (d, *J* = 10.0 Hz, 1H), 7.48-7.44 (m, 5H), 7.40-7.34 (m, 5H), 7.12-7.10 (m, 1H), 6.39-6.38 (m, 1H), 6.25 (s, 1H). ¹³C NMR ((CD₃)₂SO, 126 MHz): □ (ppm) 159.9, 157.9, 153.4, 143.1, 138.0, 135.6, 135.5, 133.8, 133.6, 133.1, 128.9, 128.6, 128.1, 128.0, 127.9, 127.2, 126.8, 125.2, 123.7, 120.8, 118.2, 116.9, 115.2, 110.4, 102.9, 101.5, 85.9. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₂H₂₁ClNO₃) requires *m/z* 502.1204, found *m/z* 502.1205.

2-(1*H*-indol-6-yl)-4-phenyl-2-(*p*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ra)



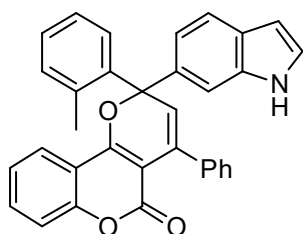
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.1 mg, 96% yield. Mp 185.2-189.9 °C. ¹H NMR (CDCl₃, 500 MHz): □ (ppm) 8.26 (s, 1H), 8.03 (d, *J* = 10.0 Hz, 1H), 7.60-7.58 (m, 2H), 7.53-7.50 (m, 1H), 7.44-7.33 (m, 8H), 7.30-7.27 (m, 1H), 7.22-7.15 (m, 4H), 6.52 (s, 1H), 6.01 (s, 1H), 2.34 (s, 3H). ¹³C NMR (CDCl₃, 126 MHz): □ (ppm) 160.5, 158.9, 153.6, 140.9, 138.4, 137.9, 136.7, 135.2, 133.6, 132.4, 129.0, 127.9, 127.8, 127.6, 127.5, 126.9, 126.3, 125.4, 124.0, 123.3, 120.8, 119.4, 116.6, 115.7, 110.4, 102.6, 102.4, 86.7, 21.1. HRMS (ESI): exact mass calculated for [M+H]⁺ (C₃₃H₂₄NO₃) requires *m/z* 482.1751, found *m/z* 482.1752.

2-(3-Chlorophenyl)-2-(1*H*-indol-6-yl)-4-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3sa)



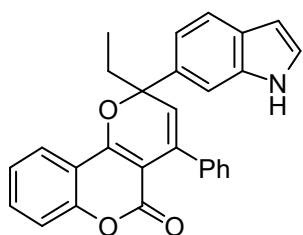
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.3 mg, 85% yield. Mp 170.1-172.2 °C. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 500 MHz): \square (ppm) 11.20 (s, 1H), 8.18-8.17 (m, 1H), 7.71-7.67 (m, 1H), 7.64 (s, 1H), 7.61-7.60 (m, 1H), 7.58-7.56 (m, 1H), 7.53-7.52 (m, 1H), 7.50-7.42 (m, 4H), 7.40-7.33 (m, 6H), 7.15-7.13 (m, 1H), 6.40-6.39 (m, 1H), 6.34 (s, 1H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 126 MHz): \square (ppm) 159.9, 157.9, 153.4, 146.7, 137.9, 135.6, 135.2, 133.8, 133.7, 133.7, 130.9, 128.4, 128.2, 128.1, 128.0, 127.9, 127.3, 126.7, 126.4, 125.3, 125.2, 123.7, 120.8, 118.2, 116.9, 115.2, 110.4, 102.9, 101.5, 85.8. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{32}\text{H}_{21}\text{ClNO}_3$) requires m/z 502.1204, found m/z 502.1204.

2-(1H-indol-6-yl)-4-phenyl-2-(*o*-tolyl)pyrano[3,2-*c*]chromen-5(2H)-one (3ta)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.6 mg, 90% yield. Mp 199.4-200.6 °C. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 500 MHz): \square (ppm) 11.14 (s, 1H), 8.09 (d, $J = 10.0$ Hz, 1H), 7.69-7.65 (m, 1H), 7.57-7.53 (m, 2H), 7.50 (s, 1H), 7.45-7.33 (m, 8H), 7.28-7.26 (m, 2H), 7.21-7.19 (m, 1H), 7.06-7.04 (m, 1H), 6.41 (s, 1H), 6.00 (s, 1H), 2.16 (s, 3H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 126 MHz): \square (ppm) 160.2, 158.0, 153.4, 140.5, 138.1, 136.9, 135.8, 135.4, 133.7, 133.0, 129.0, 128.2, 128.1, 127.9, 127.8, 127.1, 126.2, 126.0, 125.1, 123.4, 120.7, 118.2, 117.0, 115.2, 110.4, 102.4, 101.5, 87.6, 21.6. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{33}\text{H}_{24}\text{NO}_3$) requires m/z 482.1751, found m/z 482.1751.

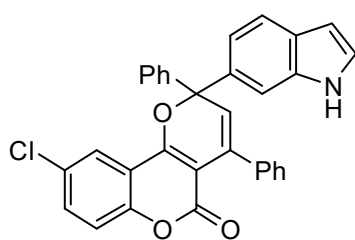
2-Ethyl-2-(1H-indol-6-yl)-4-phenylpyrano[3,2-*c*]chromen-5(2H)-one (3ua)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 14:1. White solid, 14.6 mg, 70% yield. Mp 82.4-86.3 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.21 (s, 1H), 8.07 (d, $J = 12.0$ Hz, 1H), 7.61 (d, $J = 12.0$ Hz, 1H), 7.56-7.52 (m, 2H), 7.40-7.33 (m, 6H), 7.31-7.27 (m, 2H), 7.21-7.20 (m, 1H), 6.52 (s, 1H), 5.96 (s, 1H), 2.41-2.27 (m, 2H), 1.02 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 161.2, 158.8, 153.5, 138.4, 136.4, 135.2, 134.3, 132.3, 127.8, 127.7, 127.6, 125.1, 125.0, 123.9, 123.1, 120.8, 117.3, 116.6, 115.7, 108.6, 102.7, 102.4, 85.9, 35.5, 8.7. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{28}\text{H}_{22}\text{NO}_3$) requires m/z 420.1594, found m/z 420.1594.

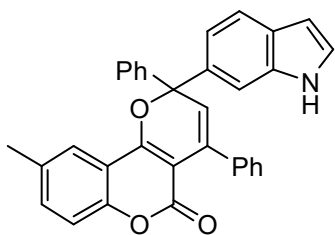
9-Chloro-2-(1H-indol-6-yl)-2,4-diphenylpyrano[3,2-*c*]chromen-5(2H)-one (3ab)

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.1 mg, 92% yield. Mp 144.0-150.5 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.27 (s, 1H), 7.97 (s, 1H), 7.61 (d, $J = 10.0$ Hz, 1H), 7.56 (s, 1H), 7.50-7.49 (m, 1H),



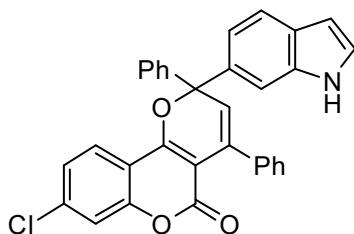
7.48-7.47 (m, 1H), 7.45-7.41 (m, 3H), 7.39-7.32 (m, 6H), 7.24-7.23 (m, 1H), 7.21-7.18 (m, 2H), 6.53 (s, 1H), 6.05 (s, 1H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 159.2, 158.3, 151.9, 143.6, 137.7, 136.1, 135.1, 133.5, 132.4, 129.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 126.9, 126.7, 125.6, 122.6, 120.9, 119.5, 118.1, 116.8, 110.5, 103.3, 102.5, 87.1. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{32}\text{H}_{21}\text{ClNO}_3$) requires m/z 502.1204, found m/z 502.1206.

2-(1H-indol-6-yl)-9-methyl-2,4-diphenylpyrano[3,2-c]chromen-5(2H)-one (3ac)



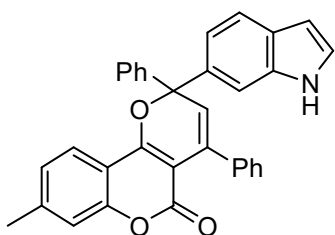
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.8 mg, 91% yield. Mp 122.6-127.6 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.28 (s, 1H), 7.80 (s, 1H), 7.60-7.58 (m, 2H), 7.51 (d, $J = 10.0$ Hz, 2H), 7.44-7.43 (m, 2H), 7.38-7.31 (m, 7H), 7.22-7.20 (m, 2H), 7.16-7.14 (d, $J = 10.0$ Hz, 1H), 6.52 (s, 1H), 6.01 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 160.4, 159.0, 151.8, 143.9, 138.1, 136.5, 135.1, 133.9, 133.8, 133.6, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 126.9, 126.0, 125.5, 122.8, 120.8, 119.5, 116.4, 115.3, 110.6, 102.5, 102.4, 86.7, 21.0. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{33}\text{H}_{24}\text{NO}_3$) requires m/z 482.1751, found m/z 482.1752.

8-Chloro-2-(1H-indol-6-yl)-2,4-diphenylpyrano[3,2-c]chromen-5(2H)-one (3ad)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 21.7 mg, 87% yield. Mp 150.2-156.9 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.25 (s, 1H), 7.95 (d, $J = 10.0$ Hz, 1H), 7.59 (d, $J = 10.0$ Hz, 1H), 7.55 (s, 1H), 7.49-7.48 (m, 2H), 7.44-7.42 (m, 2H), 7.39-7.27 (m, 8H), 7.21 (t, $J = 10.0$ Hz, 1H), 7.19-7.17 (m, 1H), 6.52 (s, 1H), 6.04 (s, 1H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 159.9, 158.3, 153.8, 143.7, 138.4, 137.7, 136.2, 135.1, 133.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 126.8, 126.4, 125.6, 124.7, 124.3, 120.9, 119.4, 116.9, 114.3, 110.5, 102.6, 102.5, 87.0. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{32}\text{H}_{21}\text{ClNO}_3$) requires m/z 502.1204, found m/z 502.1206.

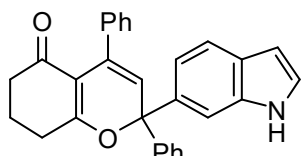
2-(1H-indol-6-yl)-8-methyl-2,4-diphenylpyrano[3,2-c]chromen-5(2H)-one (3ae)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15:1. White solid, 23.0 mg, 96% yield. Mp 163.5-168.6 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.25 (s, 1H), 7.92 (d, $J = 5.0$ Hz, 1H), 7.59-7.57 (m, 2H), 7.51 (d, $J = 5.0$ Hz, 2H), 7.44-7.43 (m, 2H), 7.38-7.30 (m, 6H), 7.20-7.18 (m, 2H), 7.11 (d, $J = 10.0$

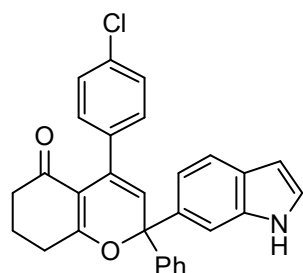
Hz, 1H), 7.06 (s, 1H), 6.51 (s, 1H), 6.00 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 160.7, 159.1, 153.8, 144.0, 143.9, 138.1, 136.5, 135.1, 133.9, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 126.8, 125.8, 125.5, 125.3, 123.1, 120.8, 119.5, 116.8, 113.1, 110.5, 102.4, 101.8, 86.6, 21.9. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{33}\text{H}_{24}\text{NO}_3$) requires m/z 482.1751, found m/z 482.1753.

2-(1*H*-indol-6-yl)-2,4-diphenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5aa)



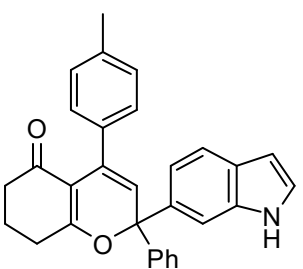
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 18.9 mg, 91% yield. Mp 192.3-194.4 °C. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 500 MHz): \square (ppm) 11.11 (s, 1H), 7.50 (d, $J = 10.0$ Hz, 1H), 7.46-7.44 (m, 3H), 7.38-7.35 (m, 3H), 7.31-7.25 (m, 6H), 7.02-7.00 (m, 1H), 6.39 (s, 1H), 5.94 (s, 1H), 2.70-2.54 (m, 2H), 2.18-2.15 (m, 2H), 1.95-1.93 (m, 2H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 126 MHz): \square (ppm) 193.0, 173.3, 145.0, 139.7, 136.9, 135.7, 133.9, 128.6, 128.0, 127.9, 127.6, 127.4, 126.8, 126.5, 124.0, 120.4, 118.4, 113.6, 110.3, 101.4, 85.4, 37.5, 29.2, 19.9. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{29}\text{H}_{24}\text{NO}_2$) requires m/z 418.1802, found m/z 418.1801.

4-(4-Chlorophenyl)-2-(1*H*-indol-6-yl)-2-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ca)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 20.2 mg, 90% yield. Mp 205.7-207.5 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.25 (s, 1H), 7.60 (d, $J = 5.0$ Hz, 1H), 7.47 (s, 1H), 7.42-7.40 (m, 2H), 7.35-7.27 (m, 6H), 7.23-7.22 (m, 1H), 7.12-7.10 (m, 1H), 6.54 (s, 1H), 5.74 (s, 1H), 2.65-2.46 (m, 2H), 2.33-2.19 (m, 2H), 2.04-1.97 (m, 2H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 193.7, 173.4, 144.3, 137.9, 136.9, 135.2, 133.3, 132.9, 128.5, 128.2, 127.9, 127.7, 127.5, 126.7, 125.3, 123.5, 120.7, 119.5, 113.6, 110.3, 102.4, 86.0, 37.3, 29.4, 19.9. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{29}\text{H}_{23}\text{ClNO}_2$) requires m/z 452.1412, found m/z 452.1414.

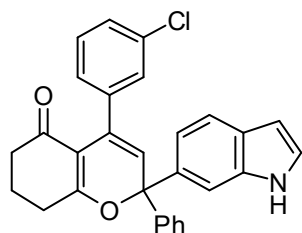
2-(1*H*-indol-6-yl)-2-phenyl-4-(*p*-tolyl)-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ea)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 20.3 mg, 94% yield. Mp 135.1-137.5 °C. ^1H NMR (CDCl_3 , 500 MHz): \square (ppm) 8.22 (s, 1H), 7.57 (d, $J = 5.0$ Hz, 1H), 7.48 (s, 1H), 7.42-7.40 (m, 2H), 7.33-7.27 (m, 3H), 7.22-7.19 (m, 3H), 7.13-7.10 (m, 3H), 6.52 (s, 1H), 5.72 (s, 1H), 2.63-2.44 (m, 2H), 2.34 (s, 3H), 2.27-2.18 (m, 2H), 2.03-1.96 (m, 2H). ^{13}C NMR (CDCl_3 , 126 MHz): \square (ppm) 193.8, 173.0, 144.6, 137.2, 136.9, 136.5, 135.1, 134.2, 128.5, 128.1, 127.6, 127.4, 126.9, 126.8, 125.2, 122.7, 120.6, 119.7, 114.1,

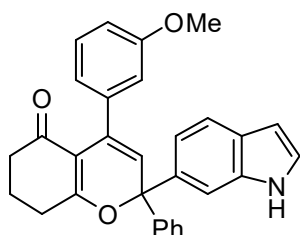
110.5, 102.3, 86.0, 37.4, 29.4, 21.3, 20.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{30}H_{26}NO_2$) requires m/z 432.1958, found m/z 432.1963.

4-(3-Chlorophenyl)-2-(1*H*-indol-6-yl)-2-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ha)



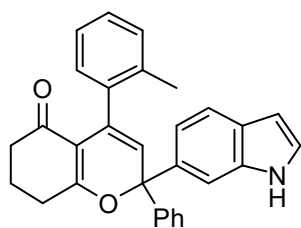
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 18.9 mg, 84% yield. Mp 98.8-100.7 °C. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.25 (s, 1H), 7.59 (d, $J = 5.0$ Hz, 1H), 7.46 (s, 1H), 7.41-7.39 (m, 2H), 7.34-7.27 (m, 4H), 7.24-7.21 (m, 3H), 7.17-7.15 (m, 1H), 7.10-7.09 (m, 1H), 6.53 (s, 1H), 5.74 (s, 1H), 2.63-2.45 (m, 2H), 2.33-2.18 (m, 2H), 2.05-1.97 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) 193.6, 173.4, 144.2, 141.4, 136.8, 135.2, 133.6, 133.2, 128.8, 128.2, 127.7, 127.6, 127.3, 127.2, 126.7, 125.5, 125.3, 124.0, 120.7, 119.5, 113.6, 110.4, 102.4, 86.0, 37.3, 29.4, 19.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{29}H_{23}ClNO_2$) requires m/z 452.1412, found m/z 452.1416.

2-(1*H*-indol-6-yl)-4-(3-methoxyphenyl)-2-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ka)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 19.4 mg, 87% yield. Mp 71.1-73.8 °C. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.23 (s, 1H), 7.57 (d, $J = 10.0$ Hz, 1H), 7.50 (s, 1H), 7.41-7.40 (m, 2H), 7.33-7.27 (m, 3H), 7.23-7.21 (m, 2H), 7.11-7.09 (m, 1H), 6.90-6.88 (m, 2H), 6.83-6.82 (m, 1H), 6.52 (s, 1H), 5.76 (s, 1H), 3.81 (s, 3H), 2.62-2.45 (m, 2H), 2.31-2.19 (m, 2H), 2.03-1.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) 193.5, 172.9, 159.1, 144.4, 140.9, 137.1, 135.2, 134.2, 128.6, 128.1, 127.6, 127.5, 126.7, 125.2, 123.3, 120.6, 119.9, 119.6, 114.1, 113.4, 112.2, 110.4, 102.4, 86.0, 55.2, 37.3, 29.4, 19.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{30}H_{26}NO_3$) requires m/z 448.1907, found m/z 448.1911.

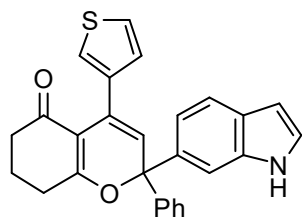
2-(1*H*-indol-6-yl)-2-phenyl-4-(*o*-tolyl)-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ma)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 20.0 mg, 93% yield. Mp 114.0-117.3 °C. 1H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 11.15 (s, 1H), 7.53 (d, $J = 10.0$ Hz, 1H), 7.44-7.37 (m, 6H), 7.32-7.29 (m, 1H), 7.15-7.08 (m, 4H), 7.05-7.03 (m, 1H), 6.41 (s, 1H), 5.75 (s, 1H), 2.71-2.60 (m, 2H), 2.13 (s, 5H), 1.92-1.87 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) 193.2, 171.8, 140.7, 135.8, 135.2, 133.2, 129.6, 128.7, 128.4, 127.9, 127.5, 126.9, 126.8, 126.5, 125.6, 123.7, 120.4, 118.4, 113.6, 110.2, 109.9, 101.4, 85.2, 37.4, 29.1, 20.4, 20.3. HRMS (ESI):

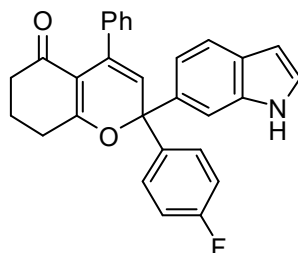
exact mass calculated for $[M+H]^+$ ($C_{30}H_{26}NO_2$) requires m/z 432.1958, found m/z 432.1964.

2-(1*H*-indol-6-yl)-2-phenyl-4-(thiophen-3-yl)-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5na)



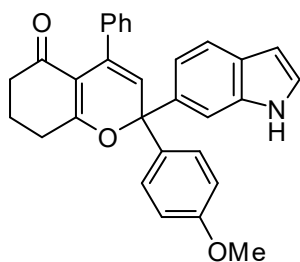
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 17.3 mg, 82% yield. Mp 208.6-212.0 °C. 1H NMR ($(CD_3)_2SO$, 500 MHz): \square (ppm) 11.11 (s, 1H), 7.50 (d, $J = 10.0$ Hz, 1H), 7.46-7.43 (m, 4H), 7.39-7.35 (m, 4H), 7.31-7.28 (m, 1H), 7.04-7.00 (m, 2H), 6.40 (s, 1H), 6.06 (s, 1H), 2.68-2.53 (m, 2H), 2.19-2.16 (m, 2H), 1.94-1.92 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): \square (ppm) 193.2, 173.0, 144.9, 140.0, 136.9, 135.7, 128.7, 128.6, 128.5, 128.0, 127.6, 126.8, 126.6, 124.6, 123.1, 122.1, 120.3, 118.4, 113.9, 110.3, 101.4, 85.3, 37.5, 29.2, 19.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}NO_2S$) requires m/z 424.1366, found m/z 424.1371.

2-(4-Fluorophenyl)-2-(1*H*-indol-6-yl)-4-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5va)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 19.3 mg, 89% yield. Mp 155.5-158.7 °C. 1H NMR ($CDCl_3$, 500 MHz): \square (ppm) 8.28 (s, 1H), 7.59 (d, $J = 10.0$ Hz, 1H), 7.46 (s, 1H), 7.39-7.36 (m, 2H), 7.32-7.31 (m, 4H), 7.29-7.28 (m, 1H), 7.21-7.19 (m, 1H), 7.08 (d, $J = 10.0$ Hz, 1H), 7.01-6.98 (m, 2H), 6.52 (s, 1H), 5.70 (s, 1H), 2.60-2.44 (m, 2H), 2.32-2.17 (m, 2H), 2.03-1.98 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): \square (ppm) 193.8, 173.0, 162.1 (d, $J = 246.9$ Hz), 140.31, 139.3, 136.8, 135.2, 134.5, 128.7 (d, $J = 7.6$ Hz), 127.8, 127.5, 127.4, 127.1, 125.4, 122.9, 120.7, 119.4, 114.9 (d, $J = 21.4$ Hz), 114.1, 110.4, 102.3, 85.6, 37.3, 29.4, 19.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{29}H_{23}FNO_2$) requires m/z 436.1707, found m/z 436.1714.

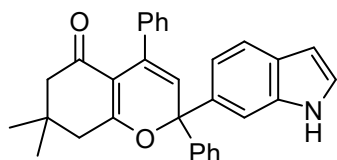
2-(1*H*-indol-6-yl)-2-(4-methoxyphenyl)-4-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5wa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 19.8 mg, 89% yield. Mp 73.5-75.7 °C. 1H NMR ($CDCl_3$, 500 MHz): \square (ppm) 8.26 (s, 1H), 7.58 (d, $J = 10.0$ Hz, 1H), 7.46 (s, 1H), 7.33-7.28 (m, 7H), 7.20-7.19 (m, 1H), 7.12-7.10 (m, 1H), 6.85-6.82 (m, 2H), 6.52 (s, 1H), 5.72 (s, 1H), 3.79 (s, 3H), 2.55-2.50 (m, 2H), 2.28-2.23 (m, 2H), 2.00-1.98 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): \square (ppm) 193.8, 173.2, 159.0, 139.5, 137.4, 136.5, 135.2,

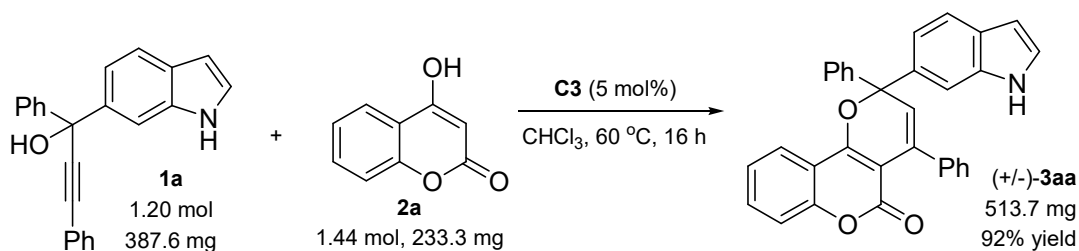
134.1, 128.3, 127.7, 127.4, 127.2, 127.1, 125.2, 123.4, 120.5, 119.5, 113.9, 113.4, 110.3, 102.3, 85.9, 55.3, 37.4, 29.4, 20.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{30}H_{26}NO_3$) requires m/z 448.1907, found m/z 448.14913.

2-(1*H*-indol-6-yl)-7,7-dimethyl-2,4-diphenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ab)



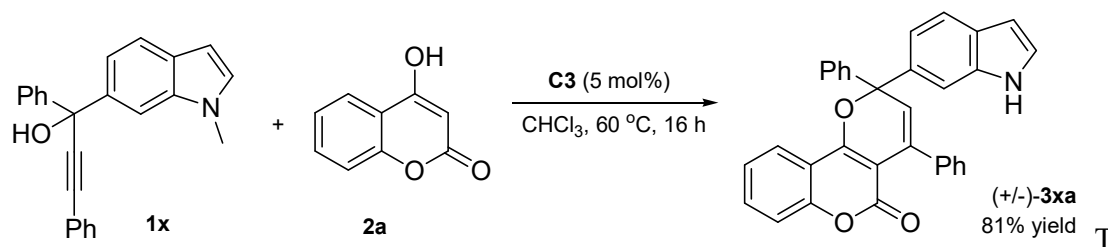
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 8:1. White solid, 11.6 mg, 52% yield. Mp 58.2-60.2 °C. 1H NMR ($CDCl_3$, 500 MHz): \square (ppm) 8.21 (s, 1H), 7.58 (d, $J = 10.0$ Hz, 1H), 7.23 (s, 1H), 7.44-7.43 (m, 2H), 7.35-7.28 (m, 8H), 7.25-7.24 (m, 1H), 7.12 (d, $J = 10.0$ Hz, 1H), 6.54 (s, 1H), 5.75 (s, 1H), 2.51-2.39 (m, 2H), 2.17-2.16 (m, 2H), 1.12 (s, 3H), 1.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): \square (ppm) 193.6, 171.6, 144.5, 139.5, 137.2, 135.1, 134.4, 128.1, 127.7, 127.6, 127.5, 127.3, 127.2, 126.7, 125.2, 123.1, 120.6, 119.6, 110.3, 102.4, 85.9, 51.4, 42.9, 31.7, 28.6, 28.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{31}H_{28}N_2O_2$) requires m/z 446.2115, found m/z 446.2108.

E: Large Scale Reaction



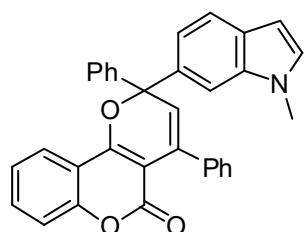
To a solution of CHCl_3 (12.0 mL) were added **1a** (387.6 mg, 1.2 mmol), **2a** (233.3 mg, 1.4 mmol) and **C3** (3.6 mg, 0.06 mmol). The reaction mixture was stirred at $60\text{ }^\circ\text{C}$ for 16 h. The solvent was evaporated to give the crude product, which was purified by silica gel chromatography (PE/EA = 4:1) to provide the desired product (+/-)-**3aa** as a white solid (513.7 mg, 92% yield).

F: Control Experiments

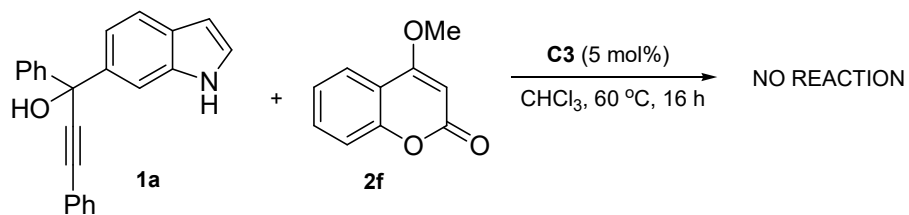


To a solution of CHCl_3 (0.5 mL) were added **1x** (16.85 mg, 0.05 mmol), **2a** (11.58 mg, 0.06 mmol) and **C3** (0.15 mg, 0.0025 mmol). The reaction mixture was stirred at $60\text{ }^\circ\text{C}$ for 16 h. The solvent was evaporated to give the crude product, which was purified by silica gel chromatography (PE/EA = 18:1) to provide the desired product (+/-)-**3xa** as a white solid (19.6 mg, 81% yield).

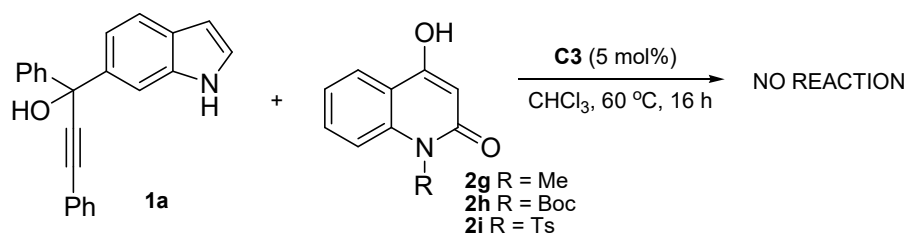
2-(1-Methyl-1H-indol-6-yl)-2,4-diphenylpyrano[3,2-c]chromen-5(2H)-one (**3xa**)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 18:1. White solid, 19.6 mg, 81% yield. Mp $108.7\text{--}110.1\text{ }^\circ\text{C}$. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ (ppm) 8.09 (d, $J = 10.0\text{ Hz}$, 1H), 7.59 (d, $J = 10.0\text{ Hz}$, 1H), 7.55-7.53 (m, 4H), 7.48-7.47 (m, 2H), 7.42-7.31 (m, 7H), 7.27 (d, $J = 10.0\text{ Hz}$, 1H), 7.20 (d, $J = 10.0\text{ Hz}$, 1H), 7.10-7.09 (m, 1H), 6.48-6.47 (m, 1H), 6.09 (s, 1H), 3.77 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ (ppm) 160.4, 158.7, 153.6, 143.9, 138.1, 136.2, 136.0, 133.8, 132.5, 130.1, 128.3, 128.1, 127.9, 127.9, 127.6, 126.9, 126.3, 124.0, 123.3, 120.9, 118.9, 116.7, 115.7, 108.3, 102.8, 100.9, 86.8, 32.9. HRMS (ESI): exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{33}\text{H}_{24}\text{N}_2\text{O}_3$) requires m/z 482.1751, found m/z



To a solution of CHCl_3 (0.5 mL) were added **1a** (16.15 mg, 0.05 mmol), **2f** (10.56 mg, 0.06 mmol) **C3** (0.15 mg, 0.0025 mmol). The reaction mixture was stirred at 60 °C for 16 h. We found the reaction didn't occur.

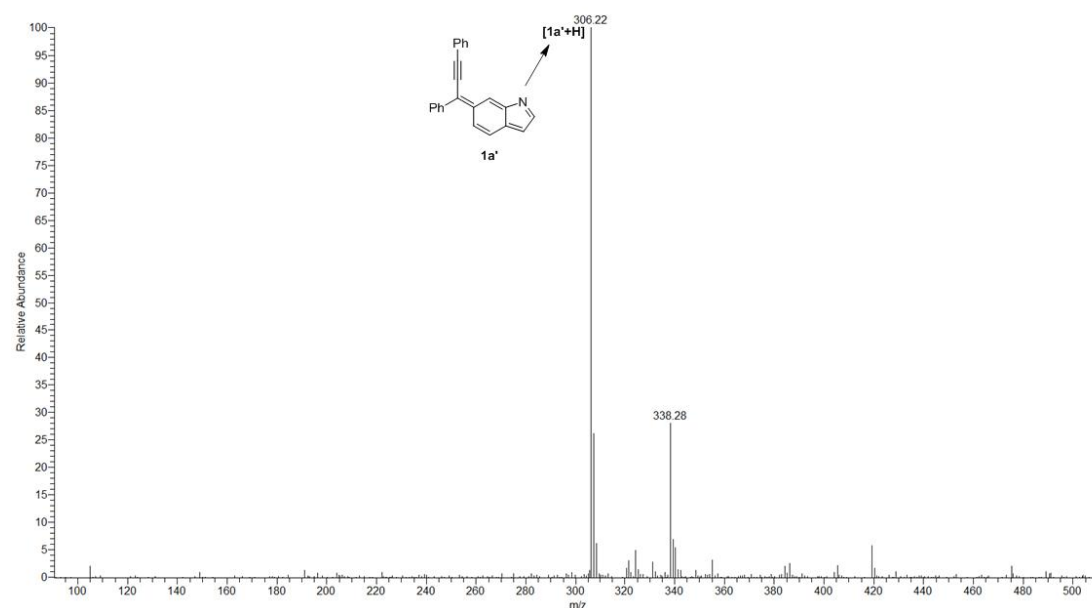


To a solution of CHCl_3 (0.5 mL) were added **1a** (16.15 mg, 0.05 mmol), **2g-i** (0.06 mmol), **C3** (0.15 mg, 0.0025 mmol). The reaction mixture was stirred at 60 °C for 16 h. We found the reaction didn't occur.

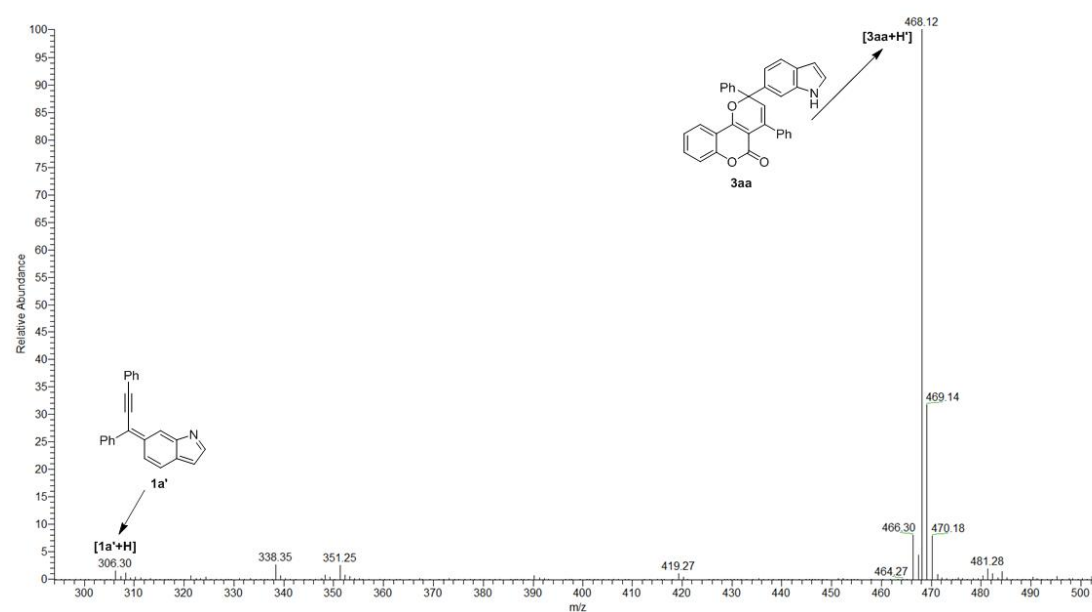
G: ESI-MS Studies

a) ESI(+)-MS spectra for the reaction of catalyst **C3** and propargylic alcohol **1a** for 2 h; b) ESI(+)-MS spectra for the 1,10-conjugate addition of propargylic alcohol **1a** catalyzed by catalyst **C3** for 12 h. Other unidentified ions are likely to correspond to either impurities or side-reaction products.

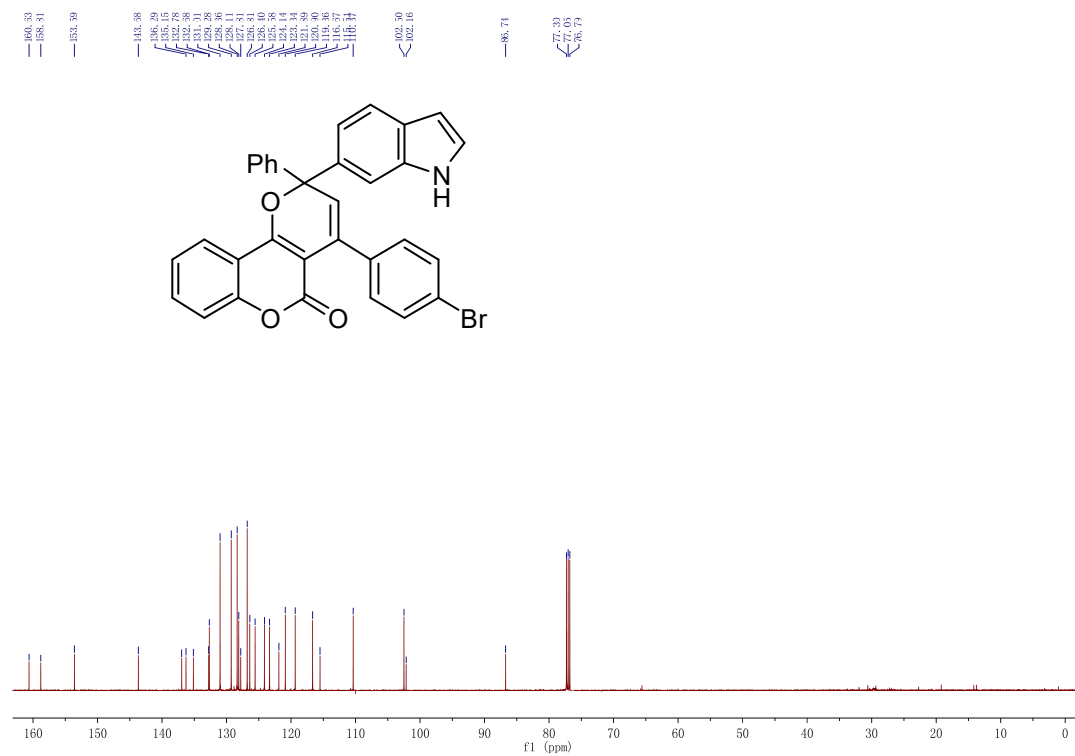
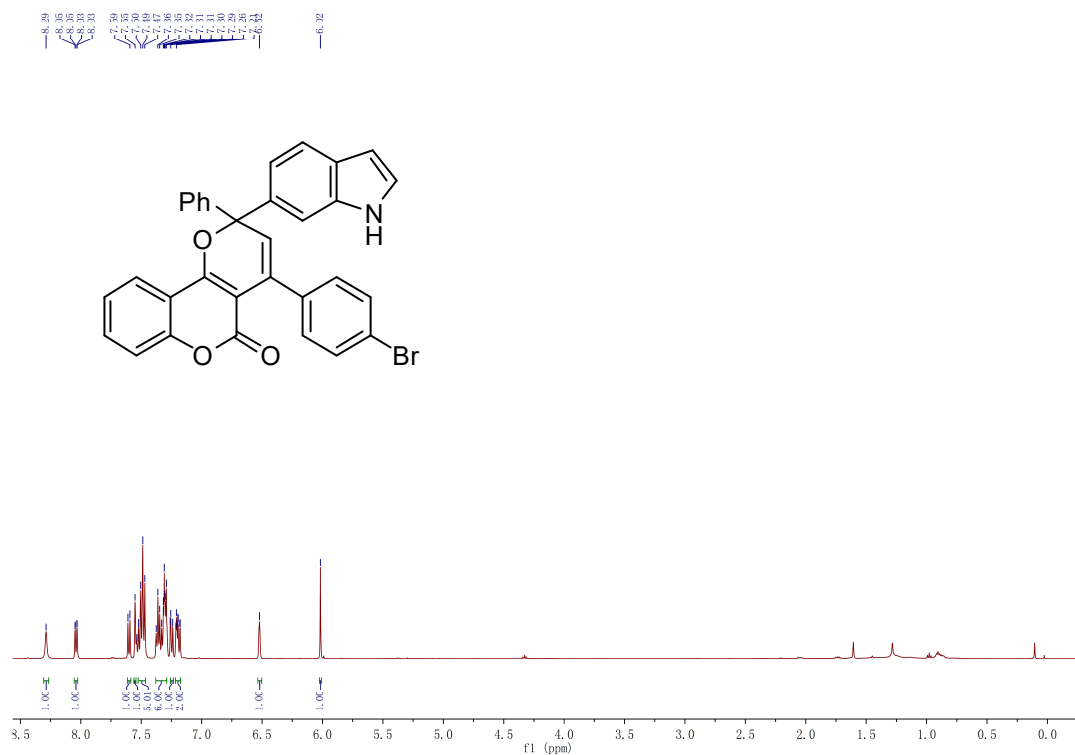
a)



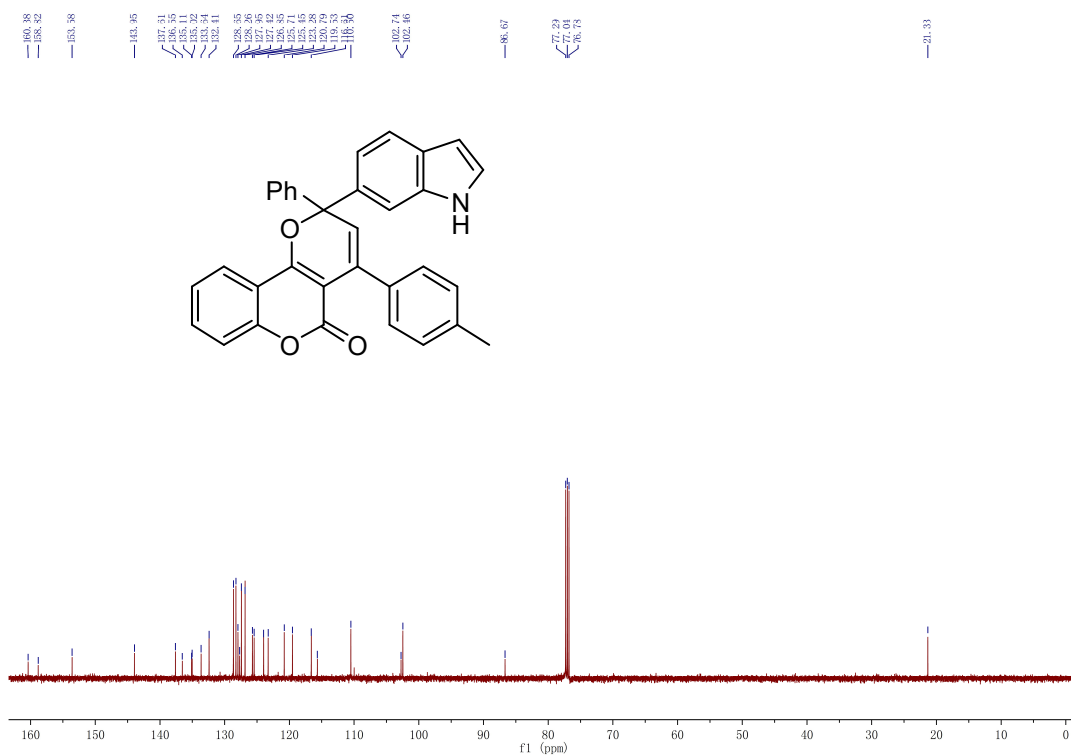
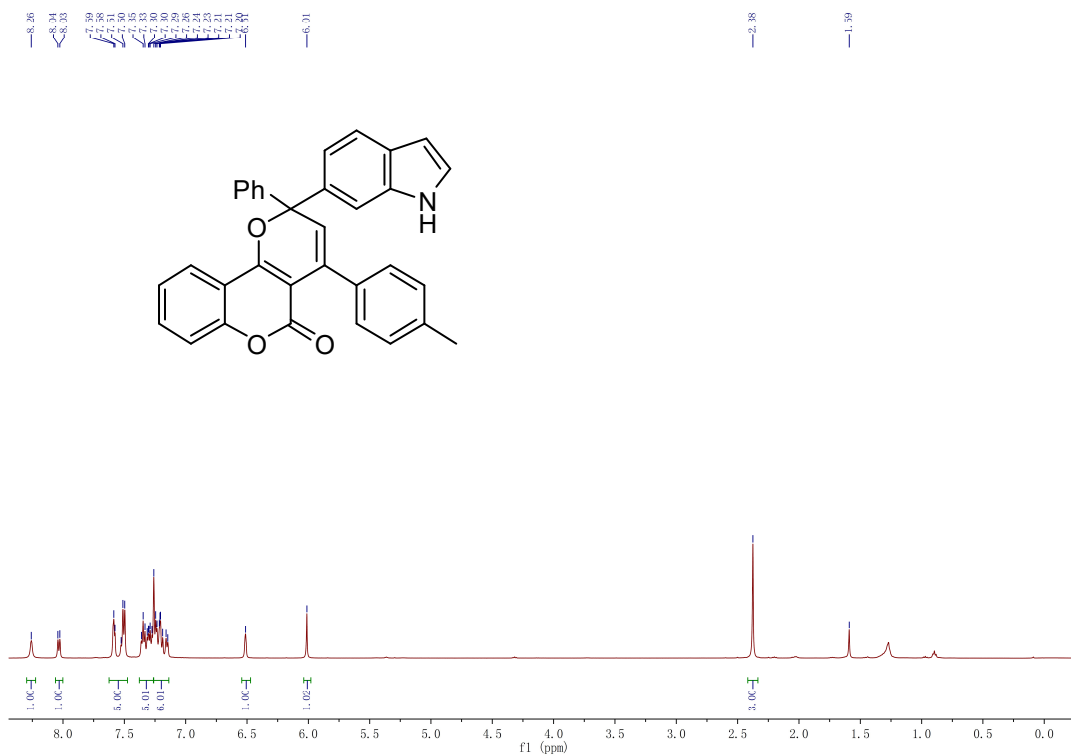
b)



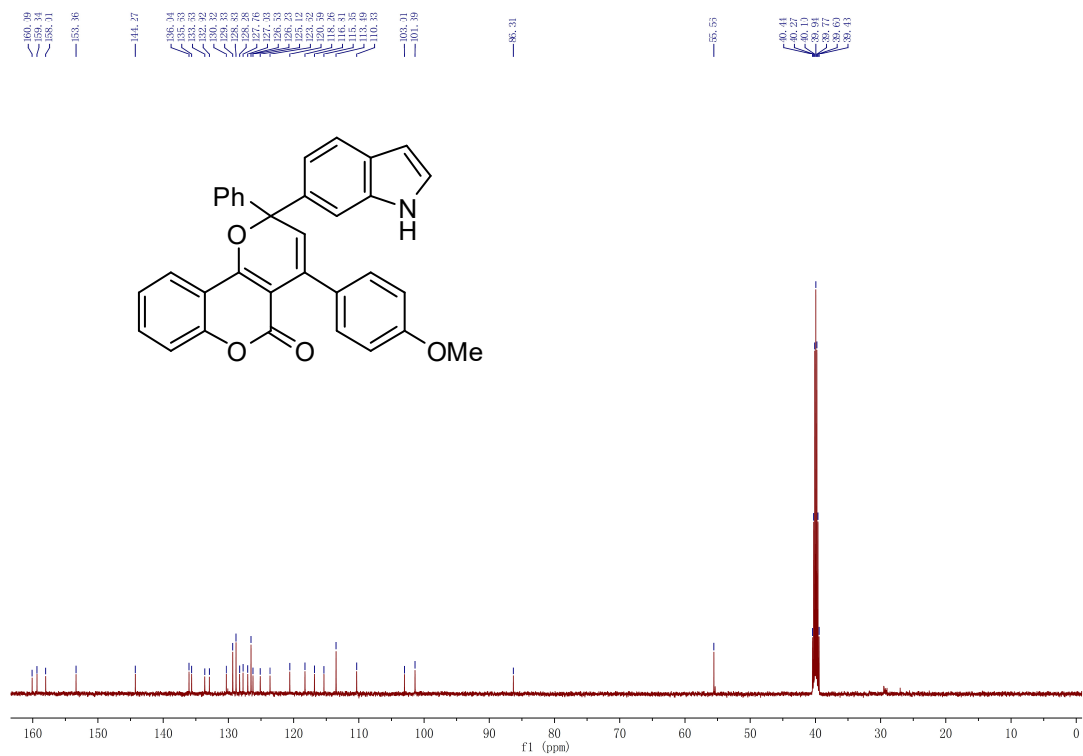
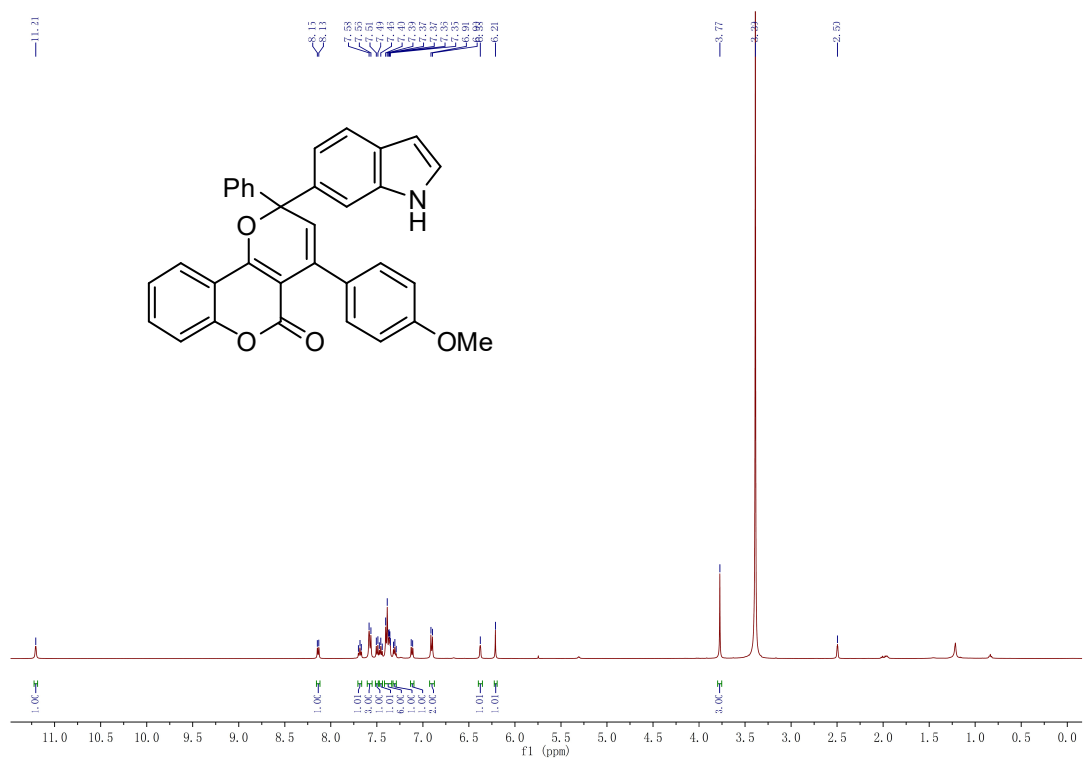
**4-(4-Bromophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one
(3da)**



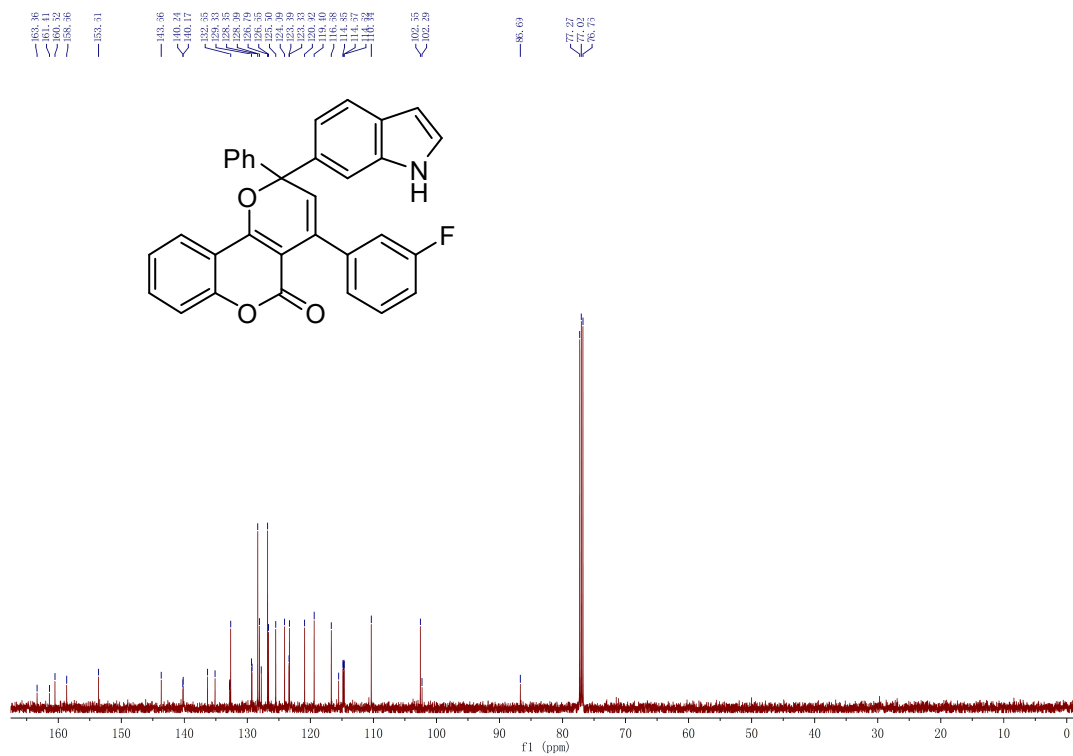
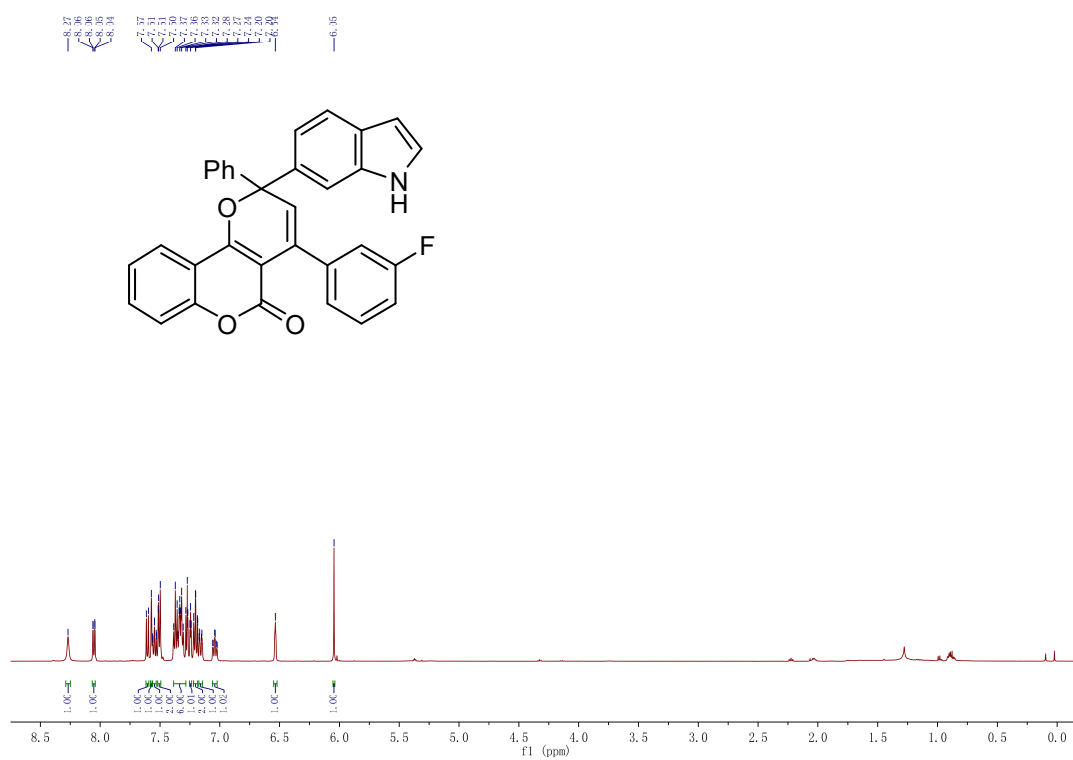
2-(1*H*-indol-6-yl)-2-phenyl-4-(*p*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ea)



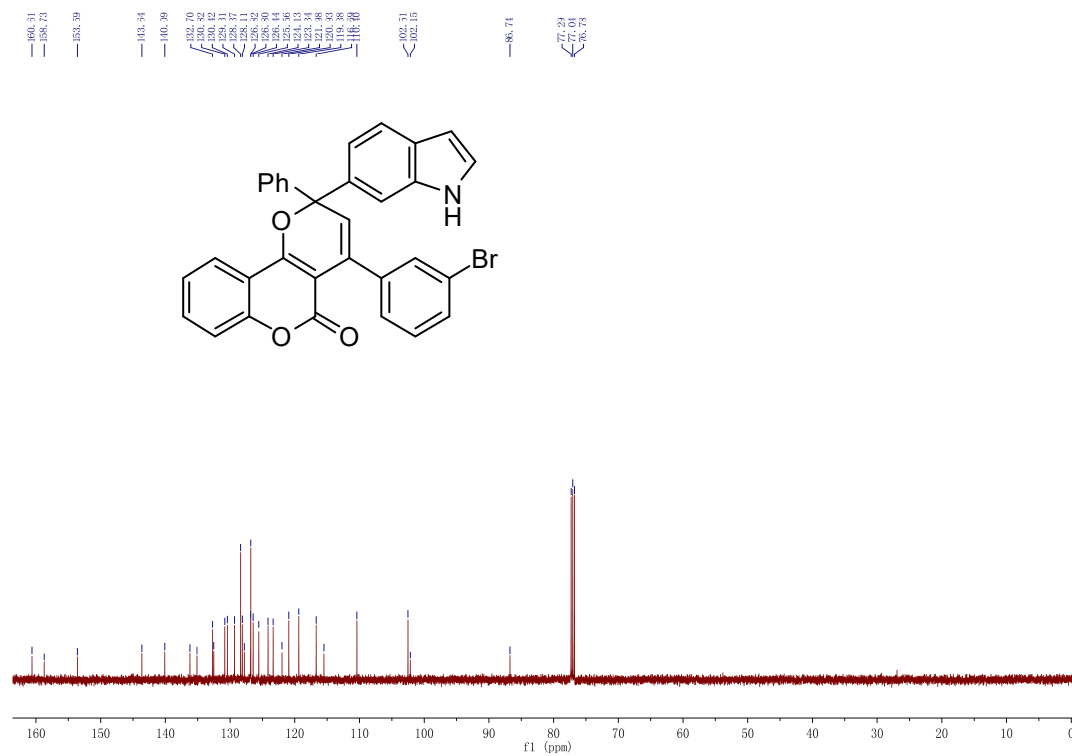
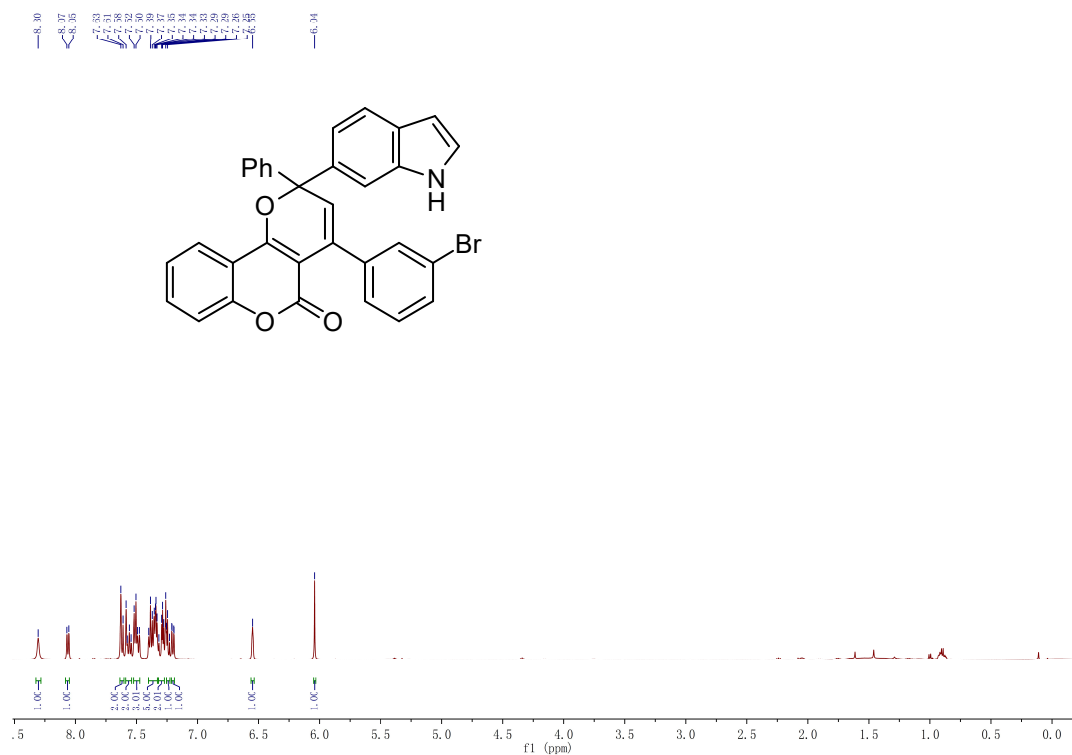
2-(1*H*-indol-6-yl)-4-(4-methoxyphenyl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3fa)



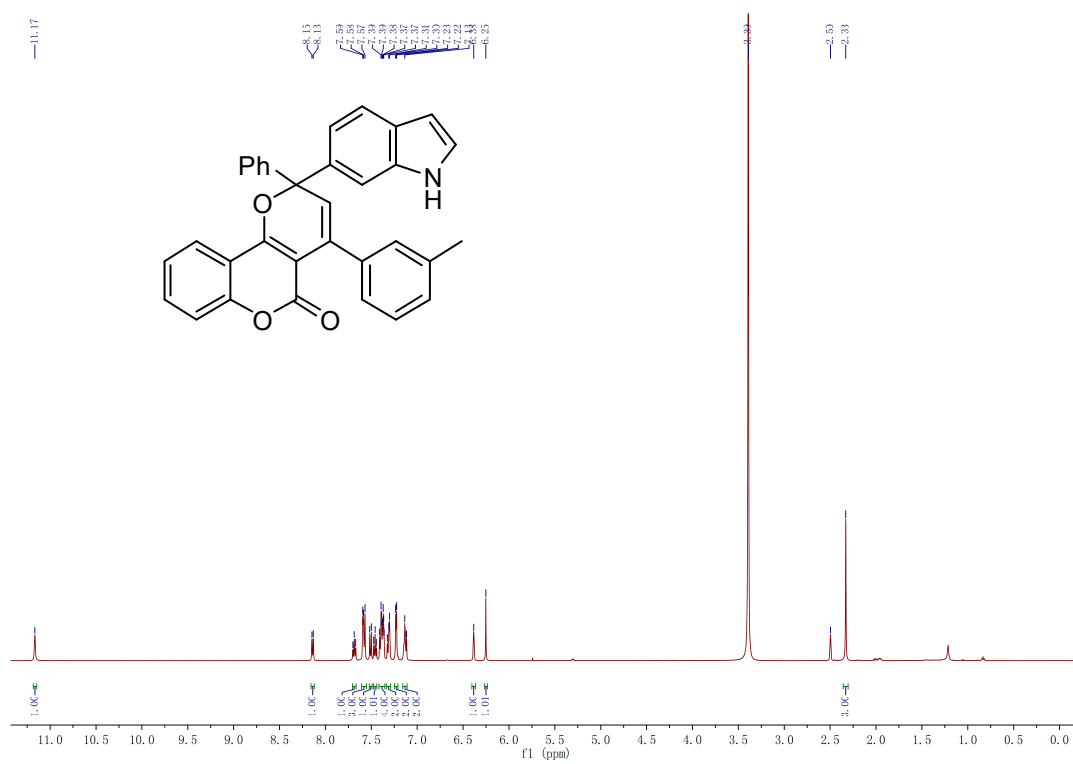
**4-(3-Fluorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one
(3ga)**



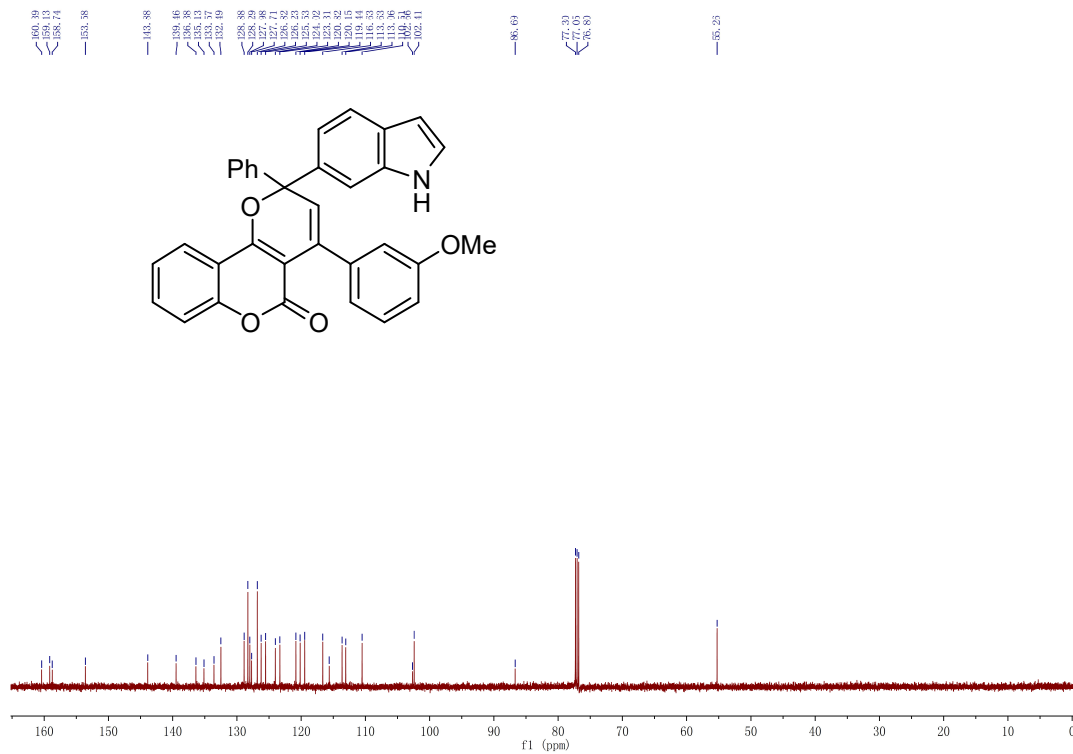
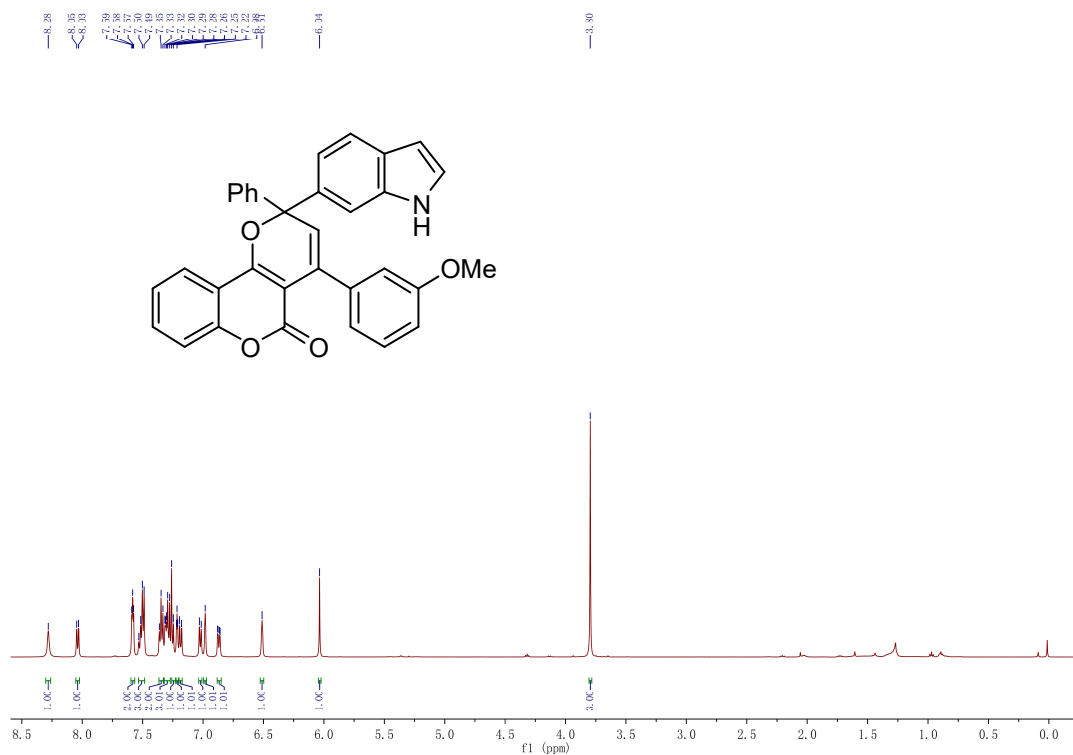
**4-(3-Bromophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one
(3ia)**



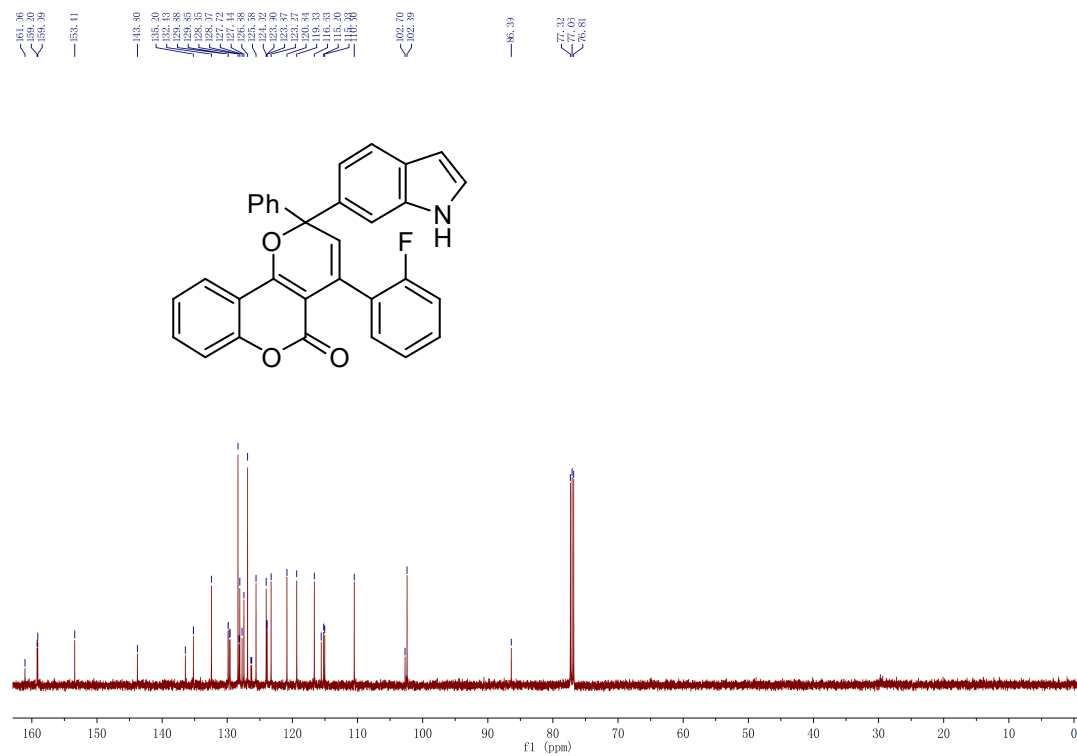
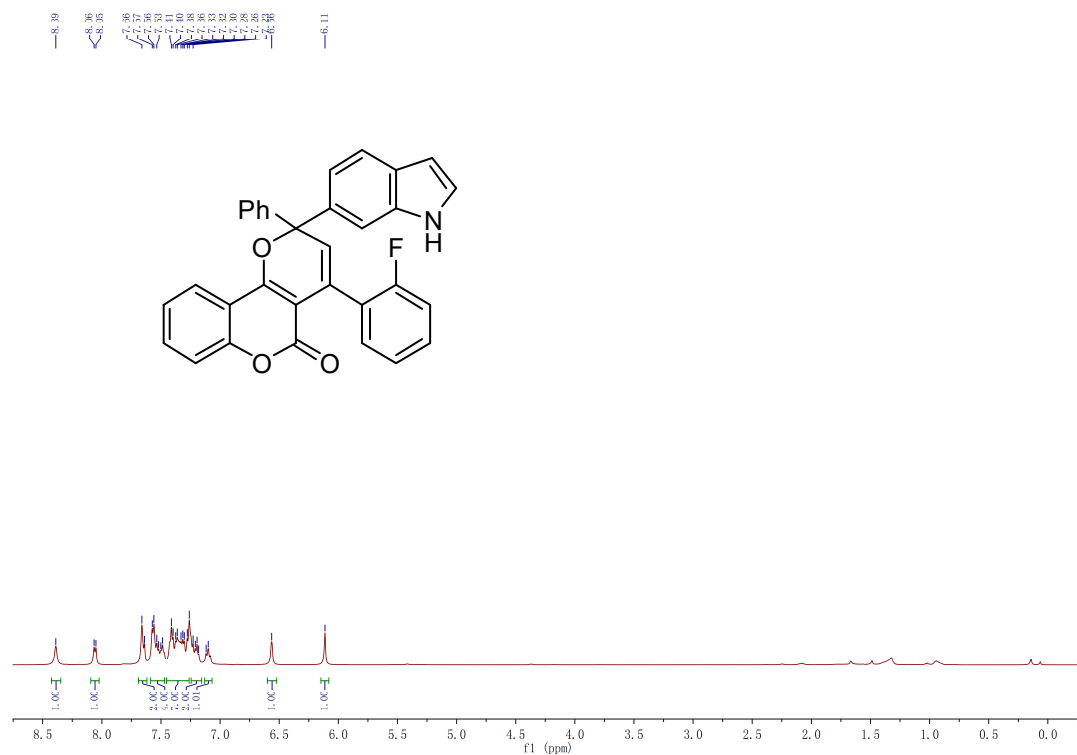
2-(1*H*-indol-6-yl)-2-phenyl-4-(*m*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ja)



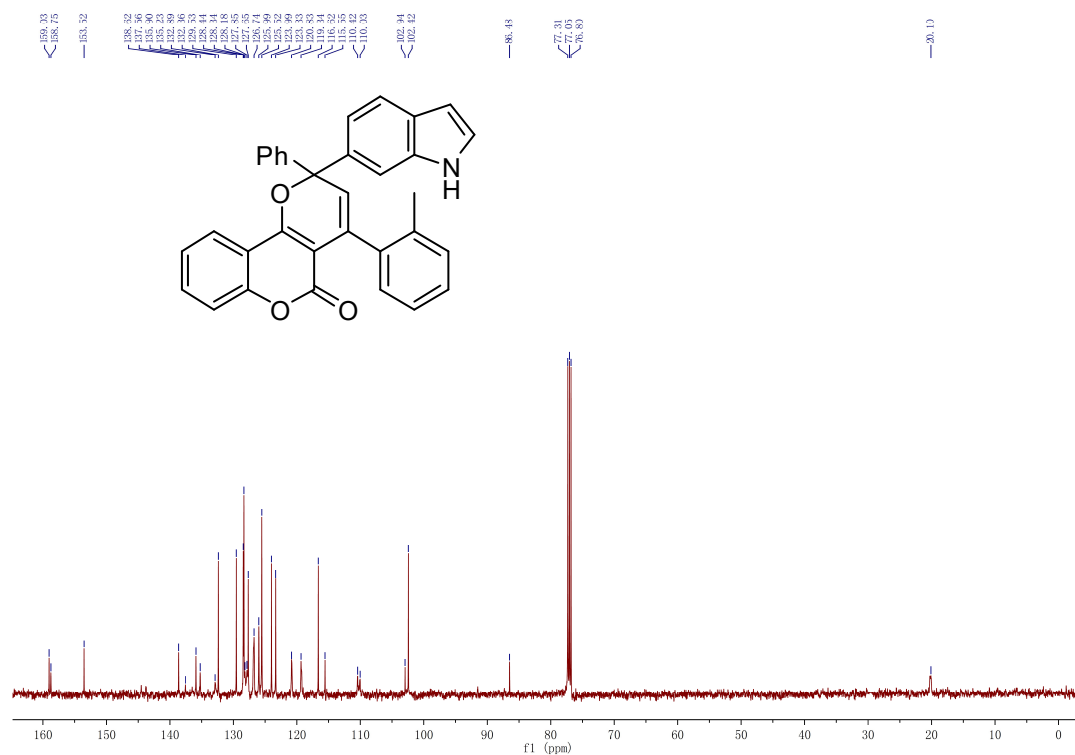
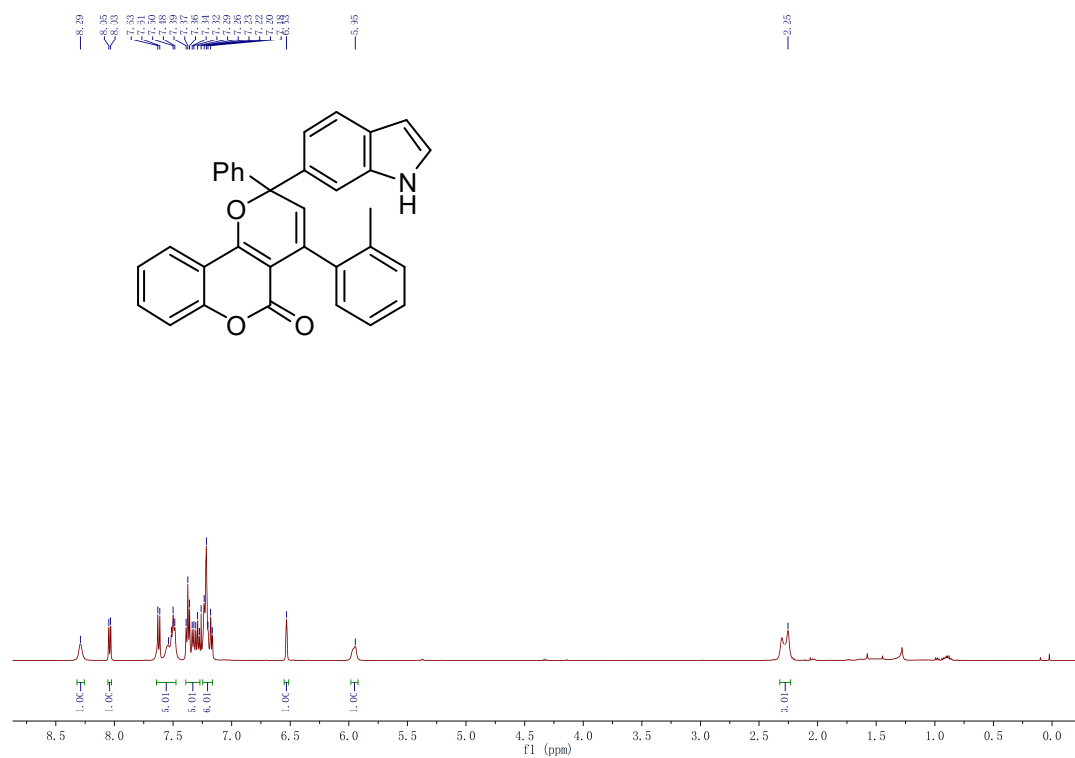
2-(1*H*-indol-6-yl)-4-(3-methoxyphenyl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ka)



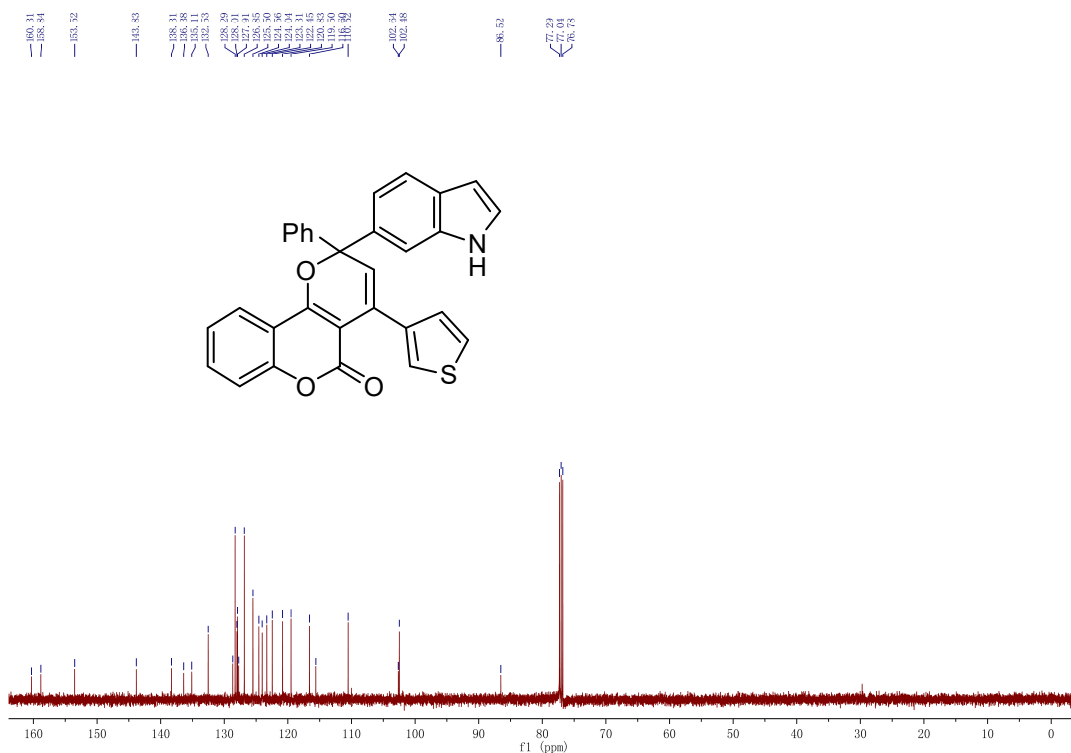
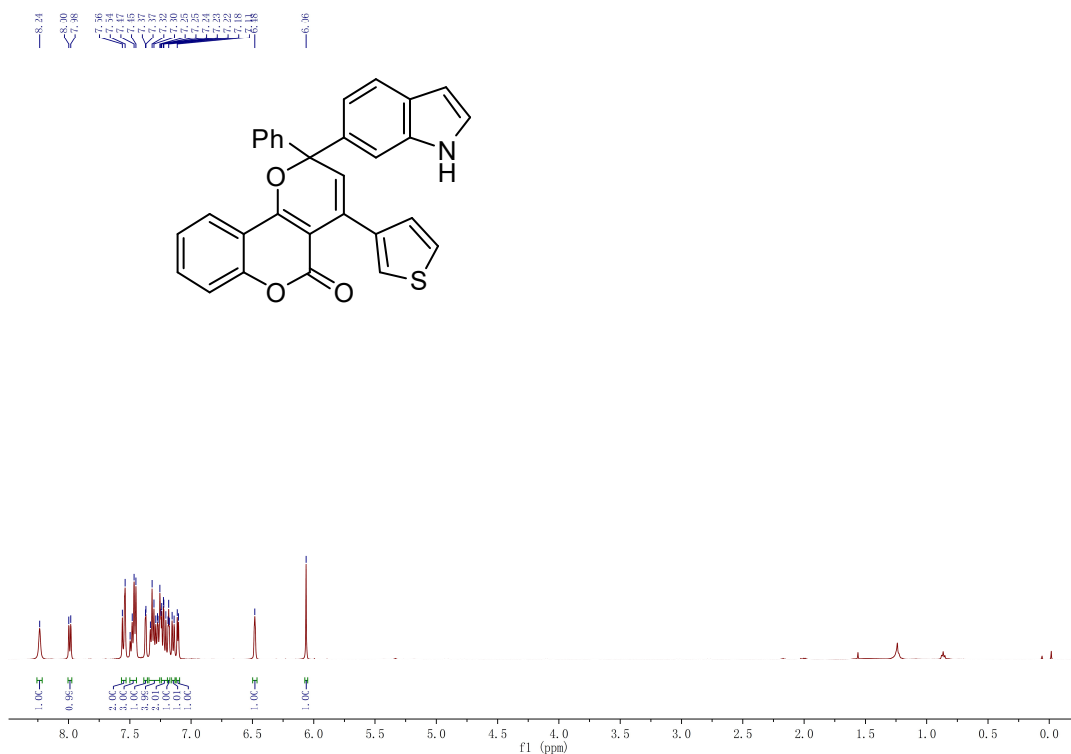
**4-(2-Fluorophenyl)-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one
(3la)**



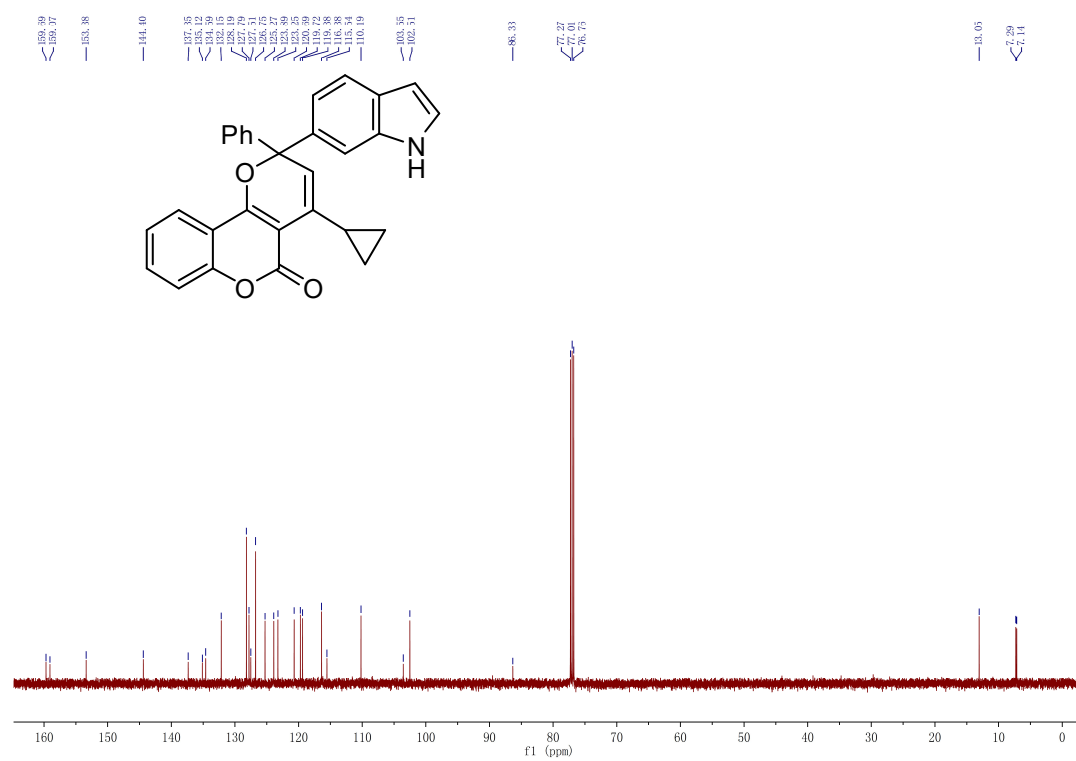
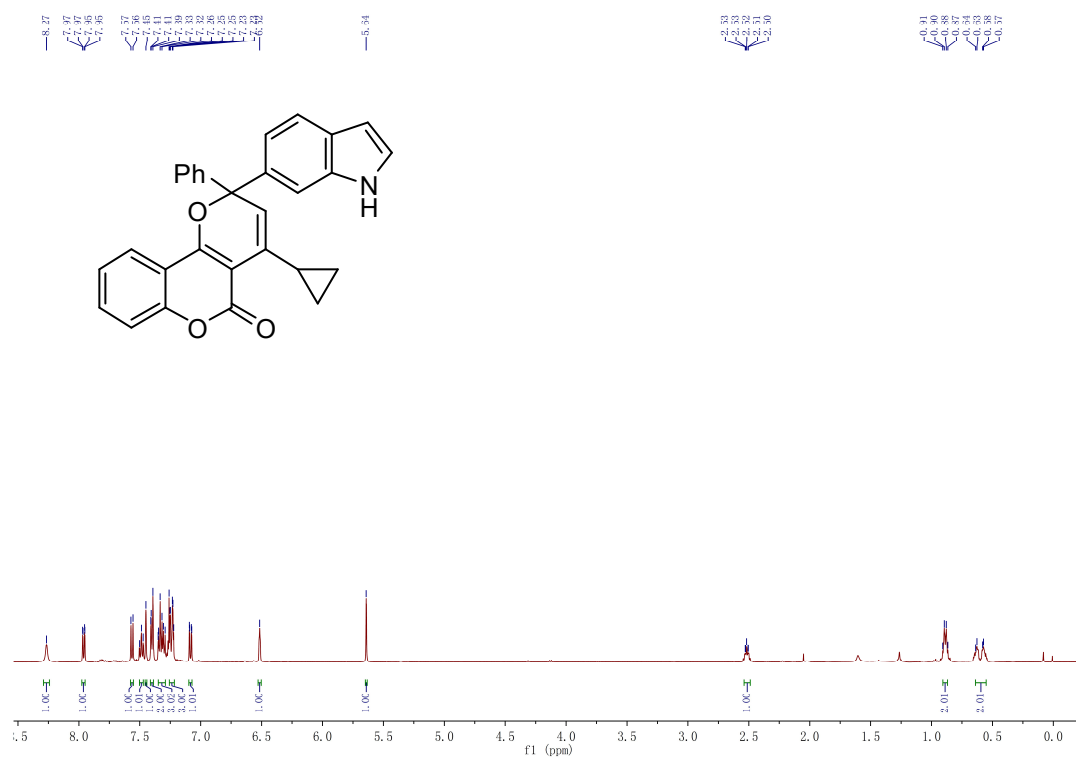
2-(1*H*-indol-6-yl)-2-phenyl-4-(*o*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ma)



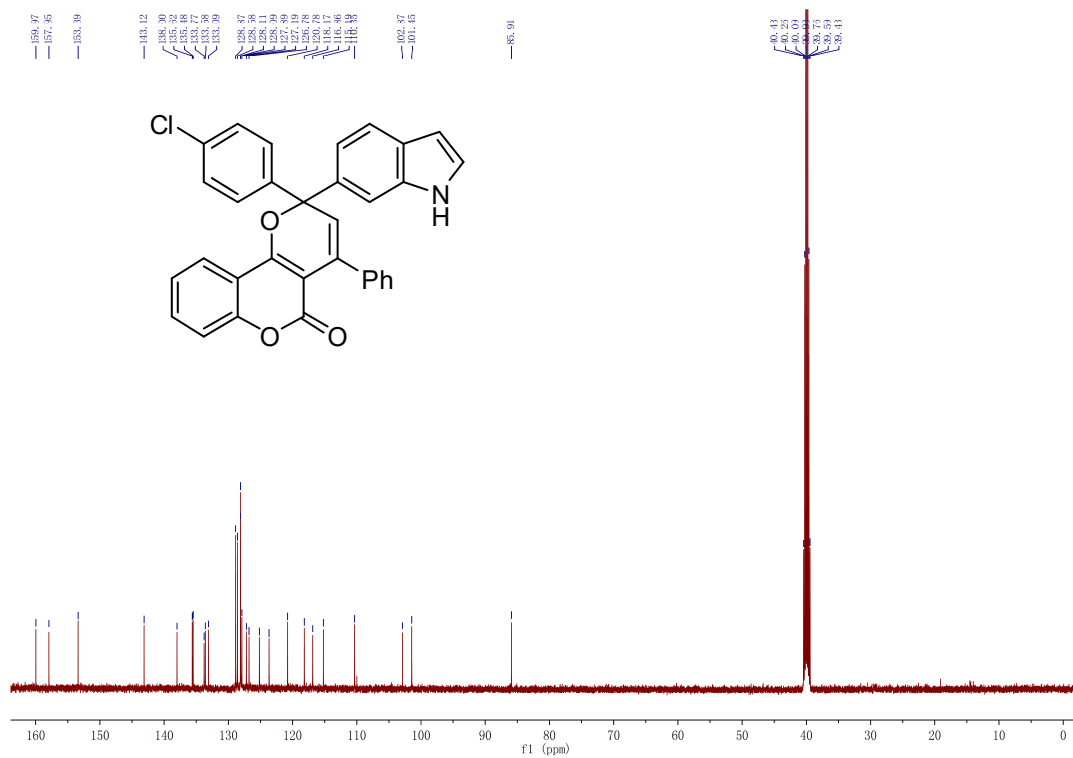
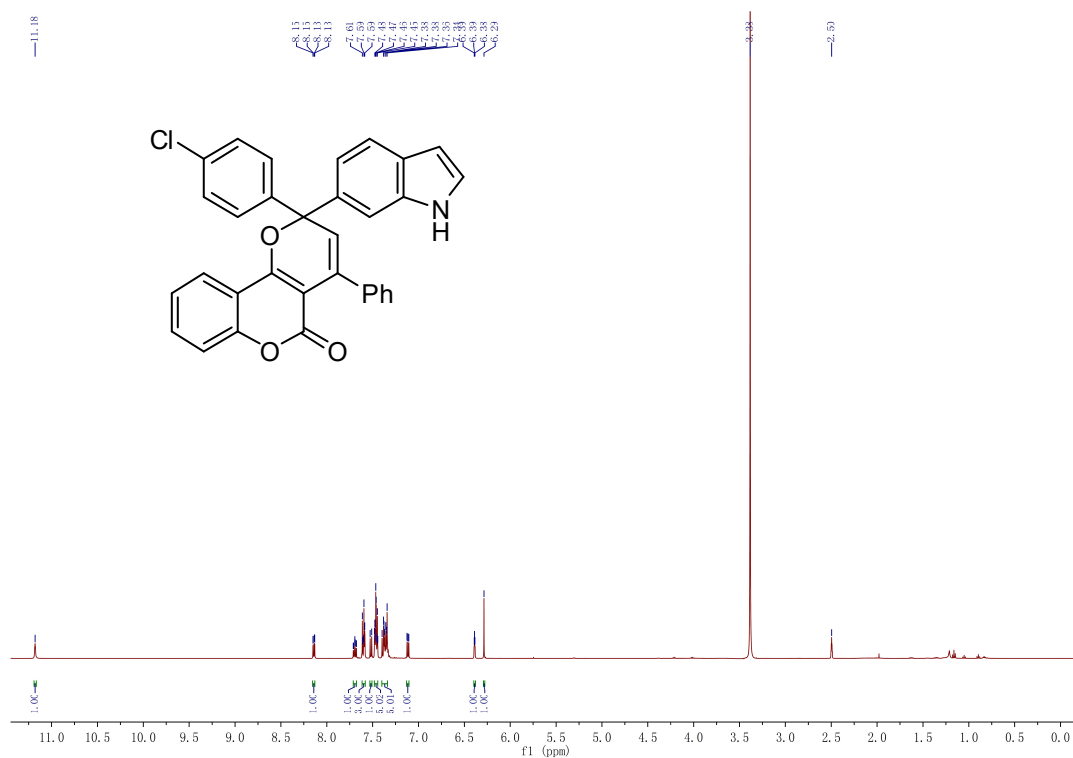
**2-(1*H*-indol-6-yl)-2-phenyl-4-(thiophen-3-yl)pyrano[3,2-*c*]chromen-5(2*H*)-one
(3na)**



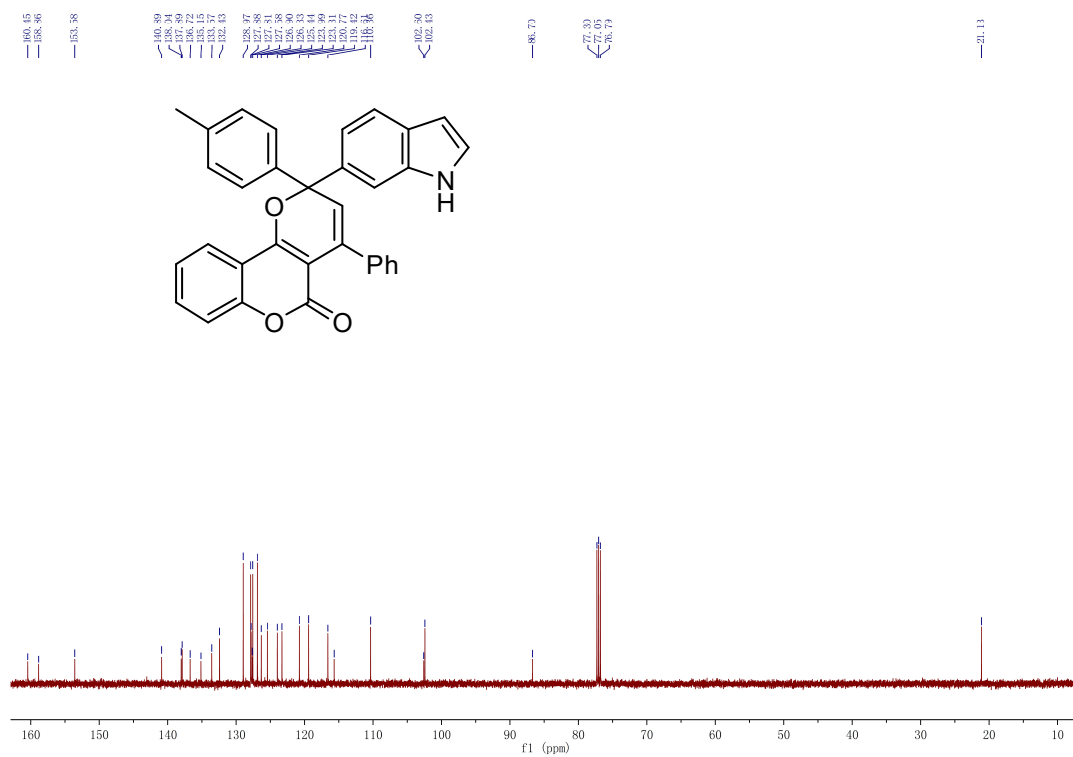
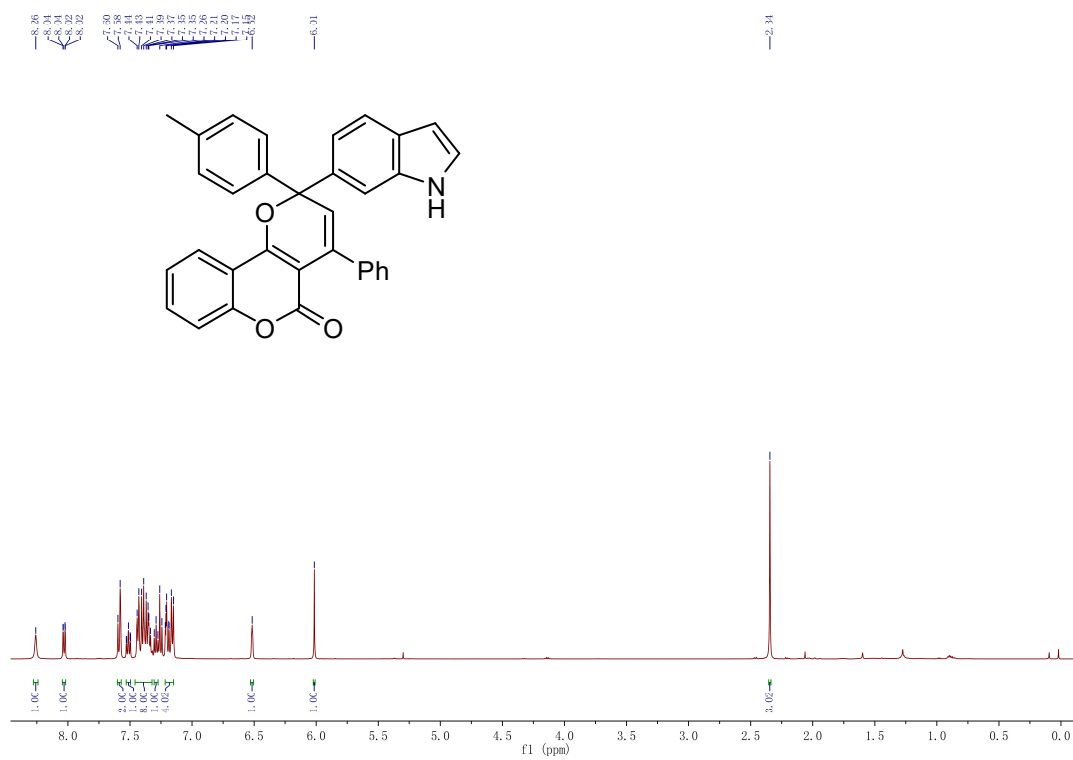
4-Cyclopropyl-2-(1*H*-indol-6-yl)-2-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3oa)



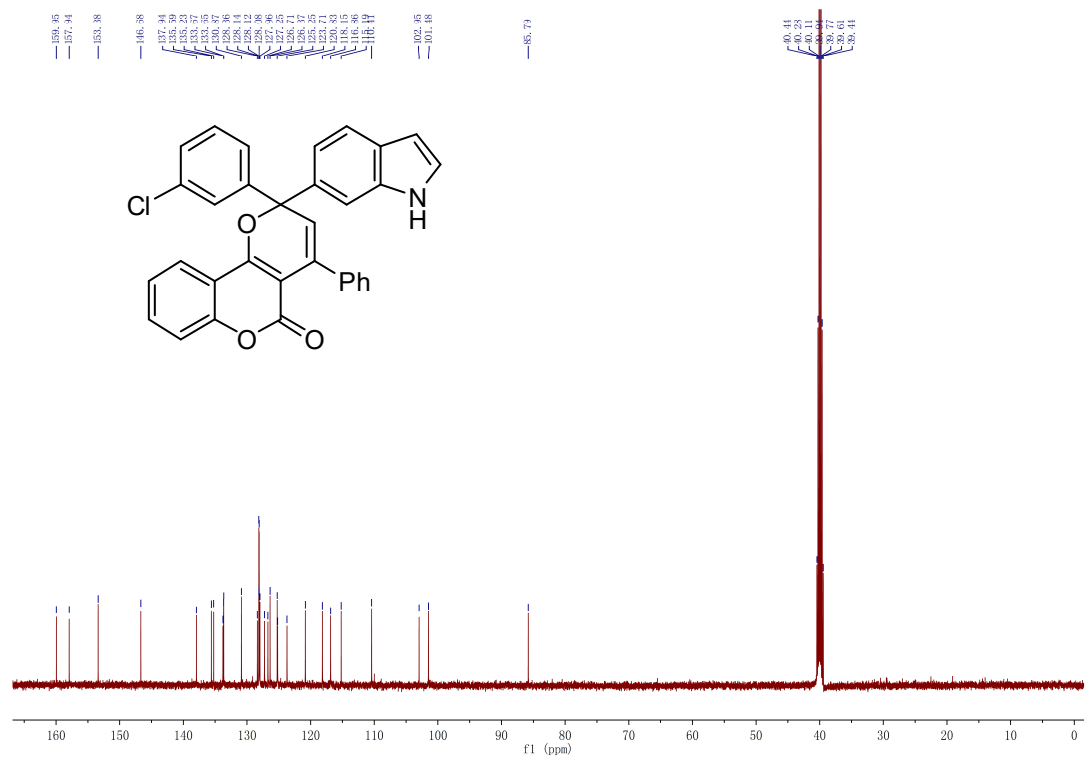
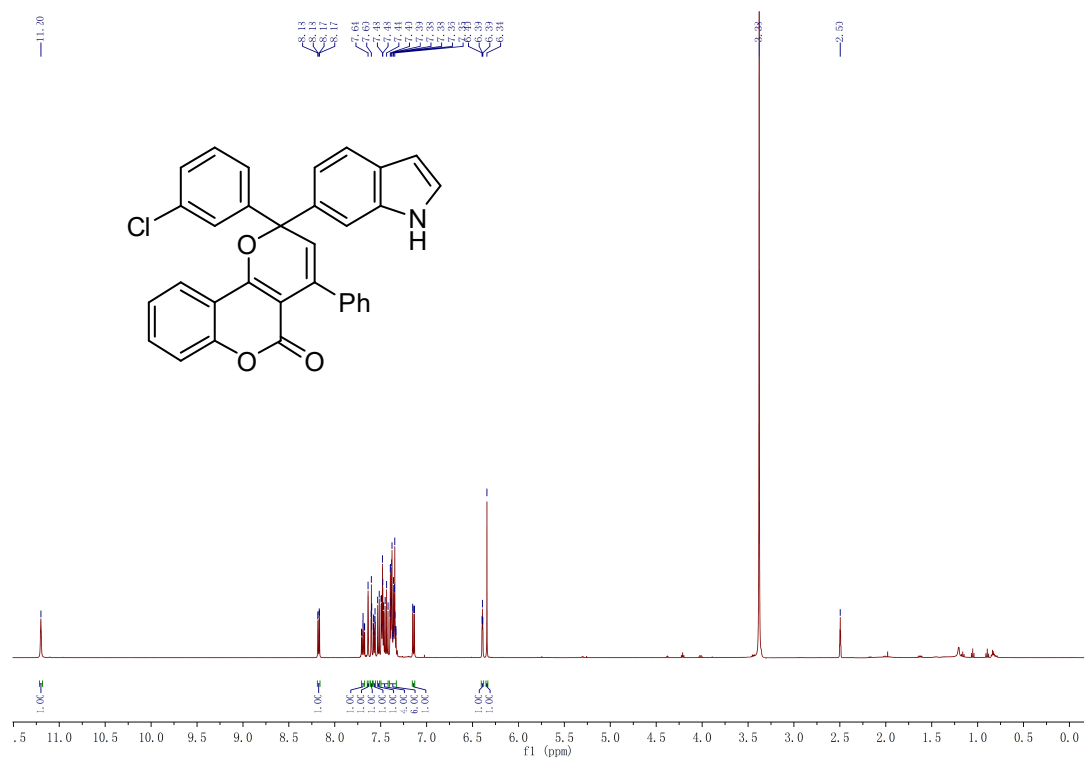
2-(4-Chlorophenyl)-2-(1*H*-indol-6-yl)-4-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3qa)



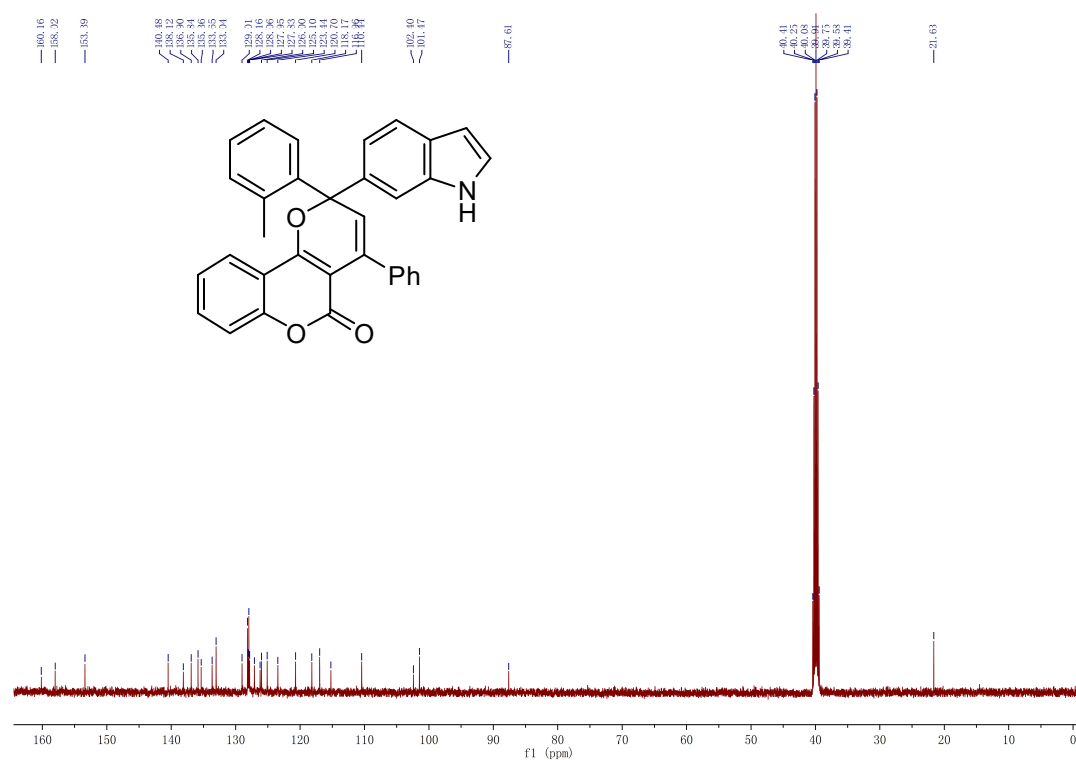
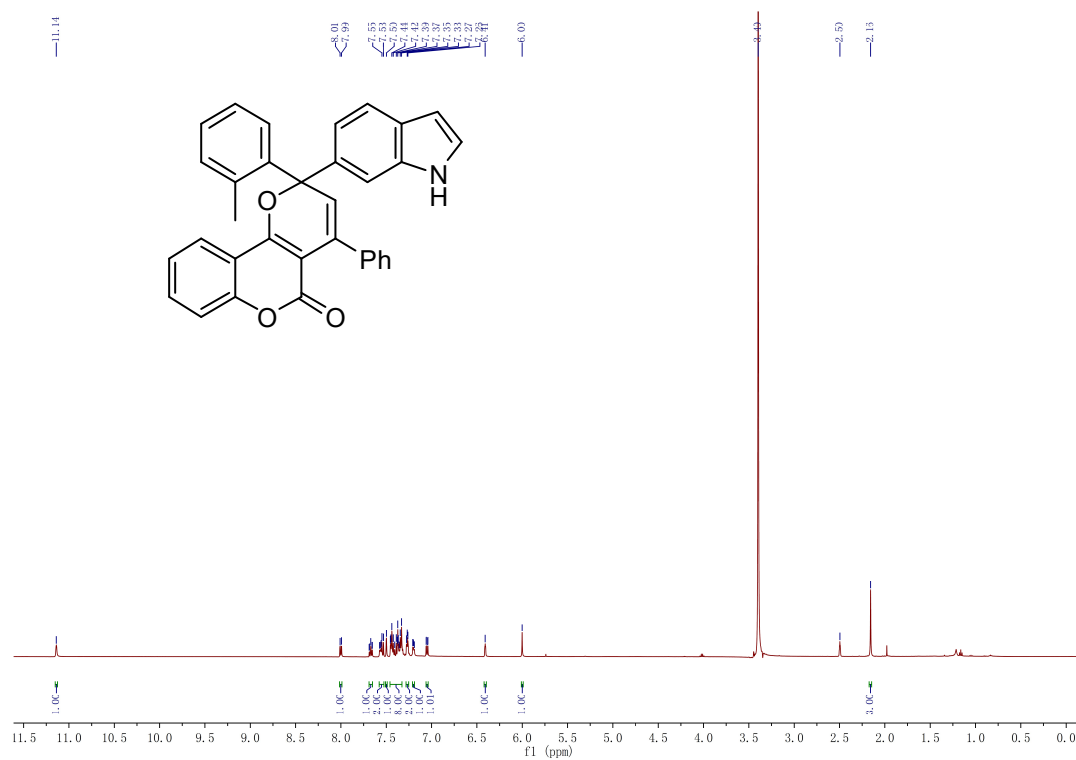
2-(1*H*-indol-6-yl)-4-phenyl-2-(*p*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ra)



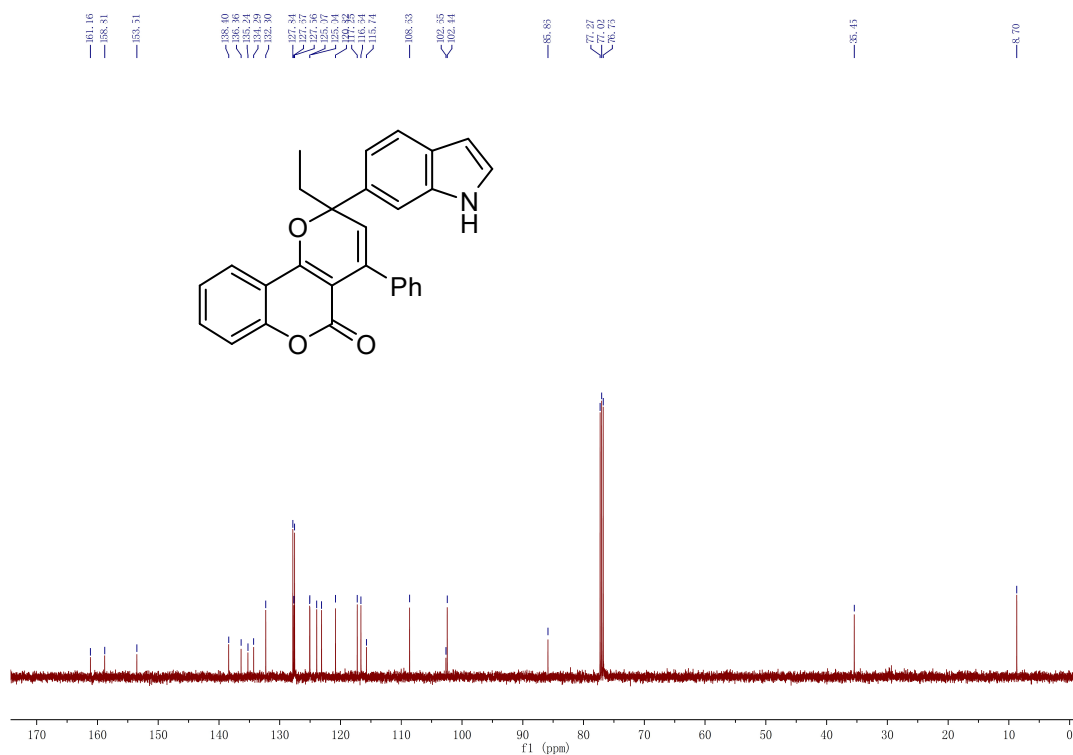
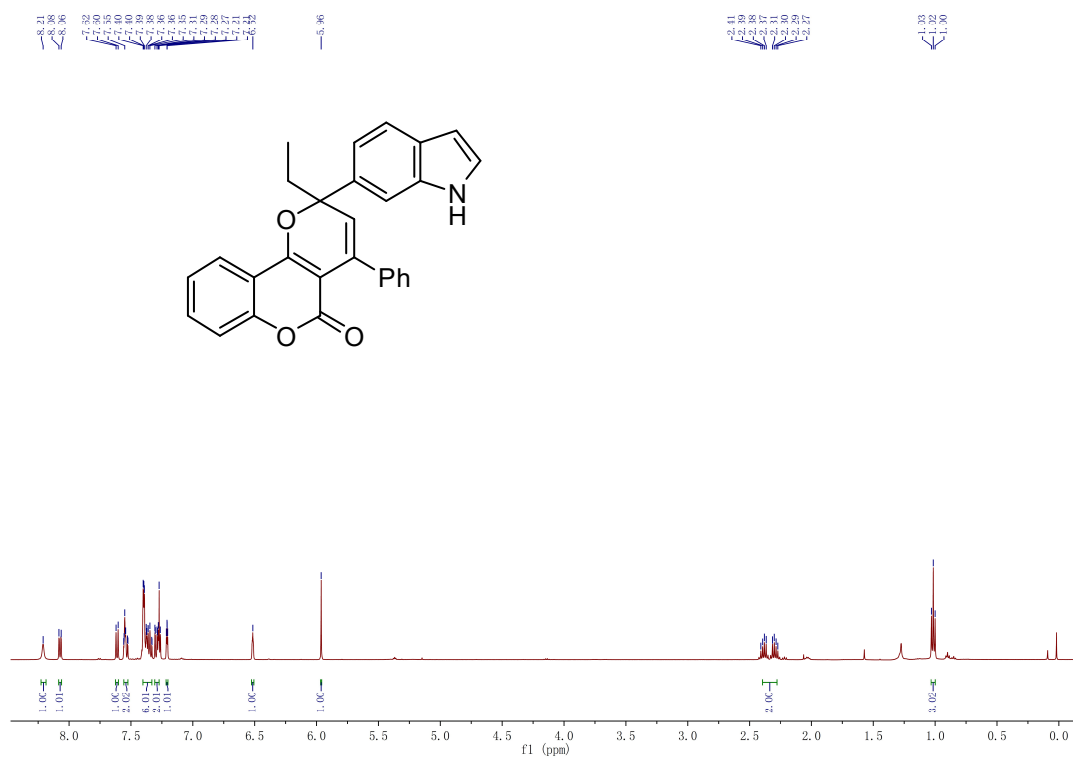
2-(3-Chlorophenyl)-2-(1*H*-indol-6-yl)-4-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3sa)



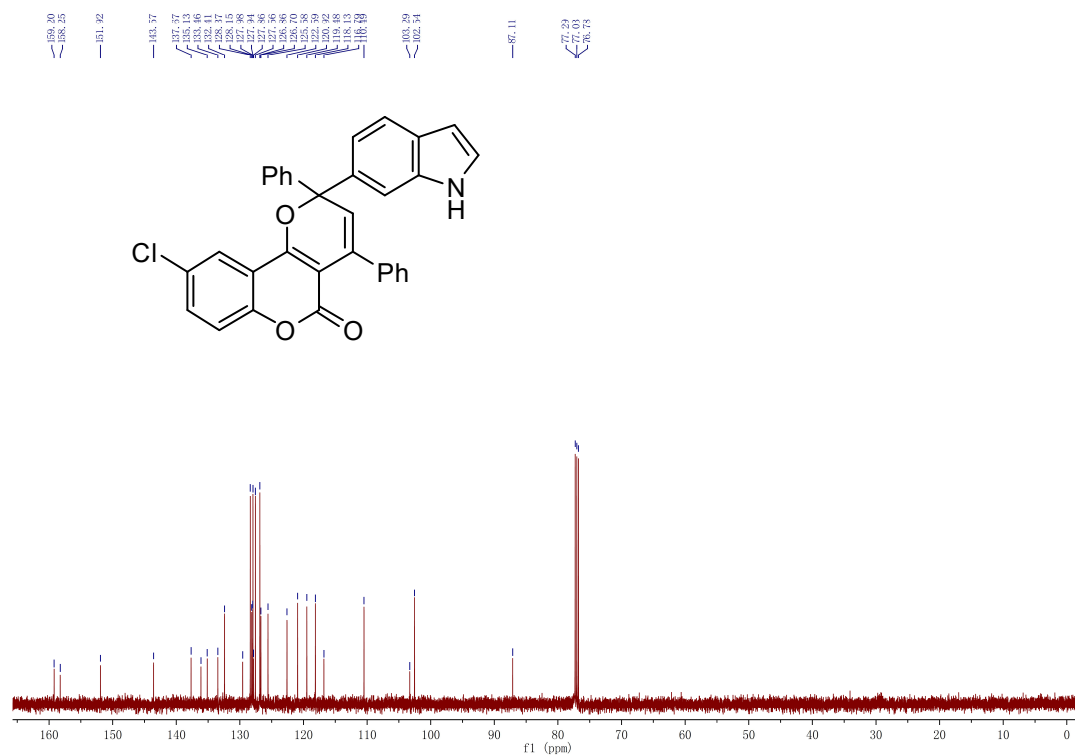
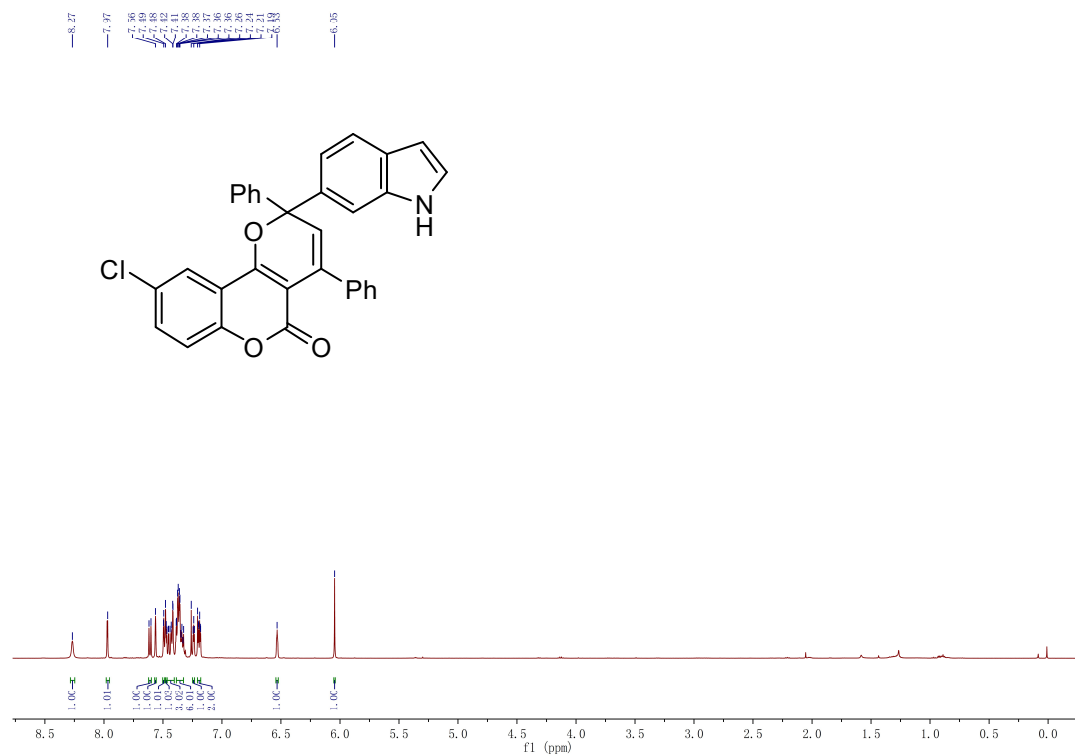
2-(1*H*-indol-6-yl)-4-phenyl-2-(*o*-tolyl)pyrano[3,2-*c*]chromen-5(2*H*)-one (3ta)



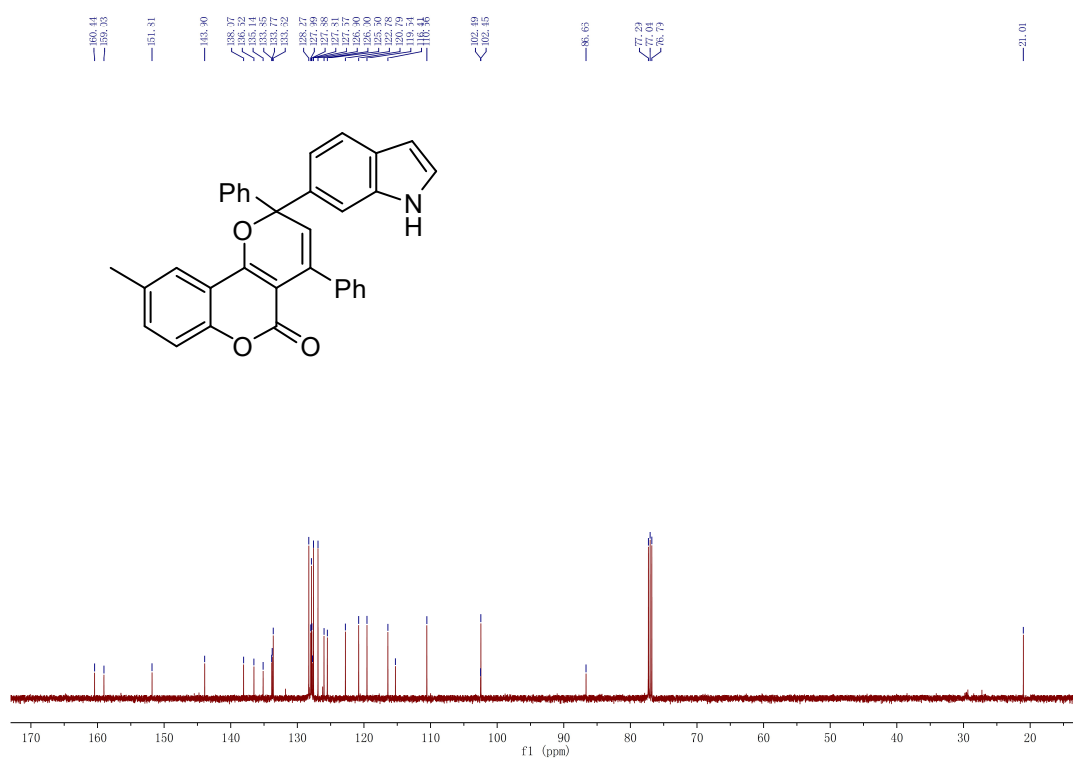
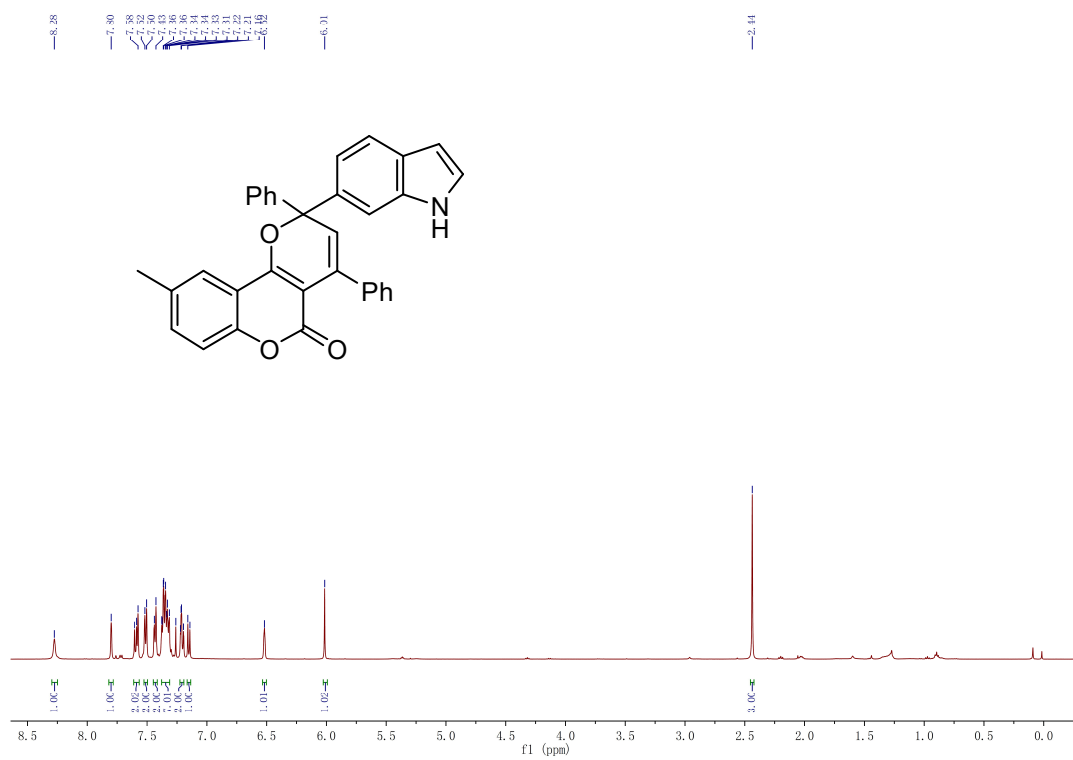
2-Ethyl-2-(1*H*-indol-6-yl)-4-phenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ua)



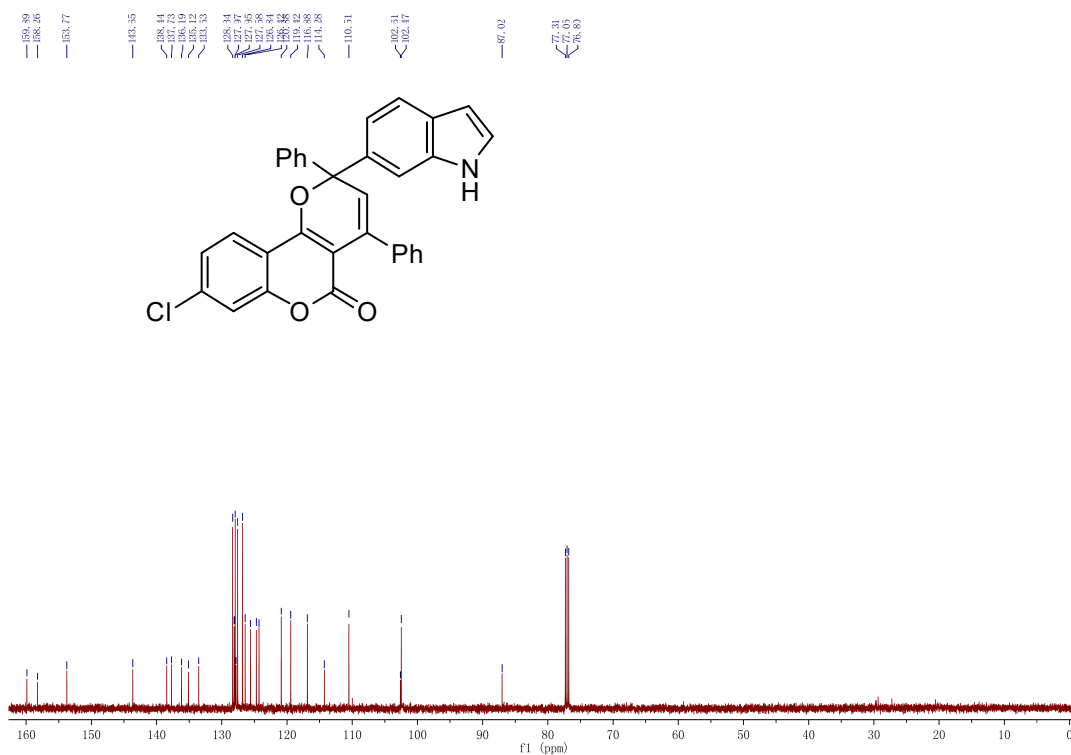
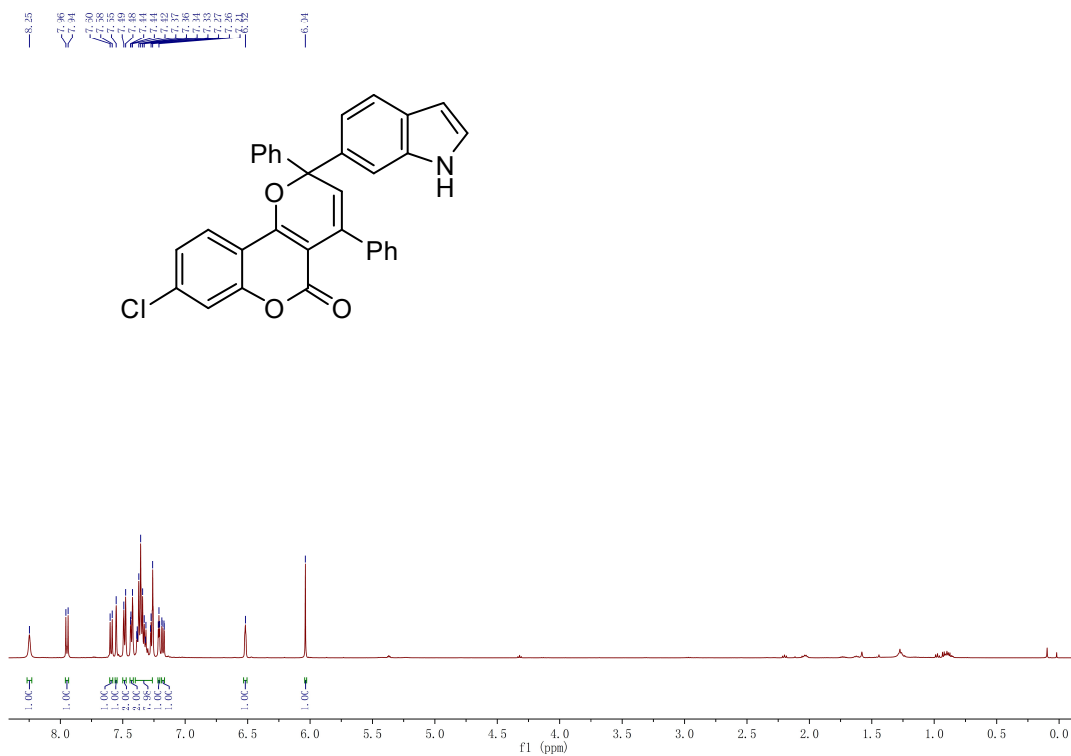
9-Chloro-2-(1*H*-indol-6-yl)-2,4-diphenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ab)



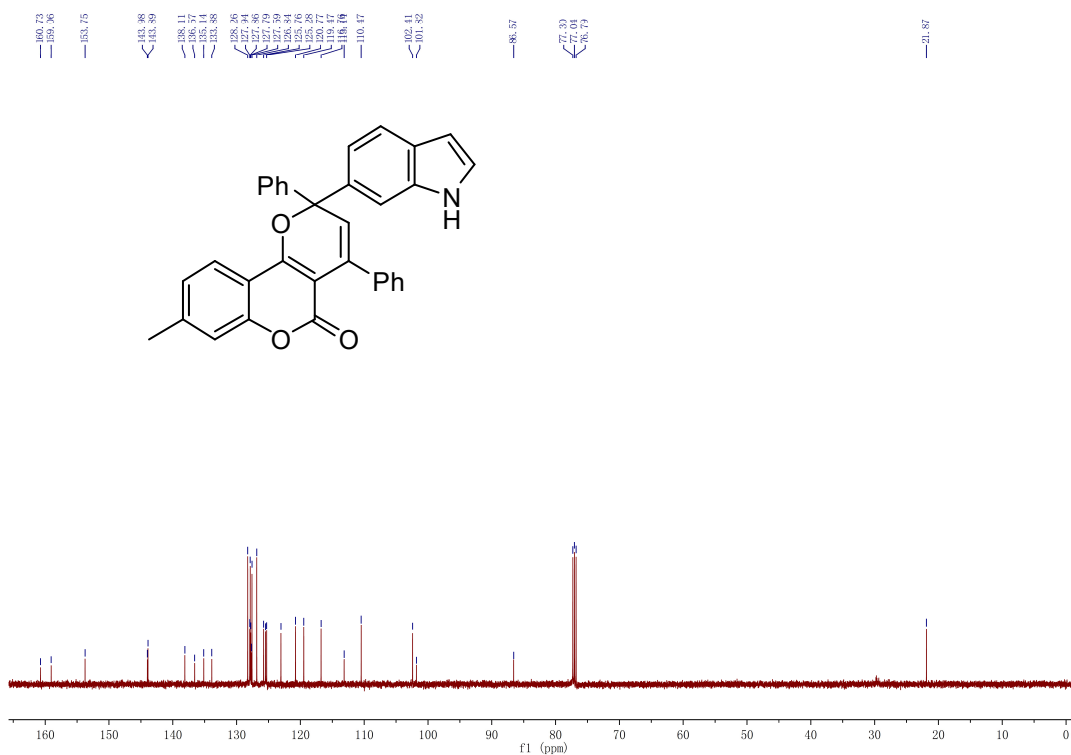
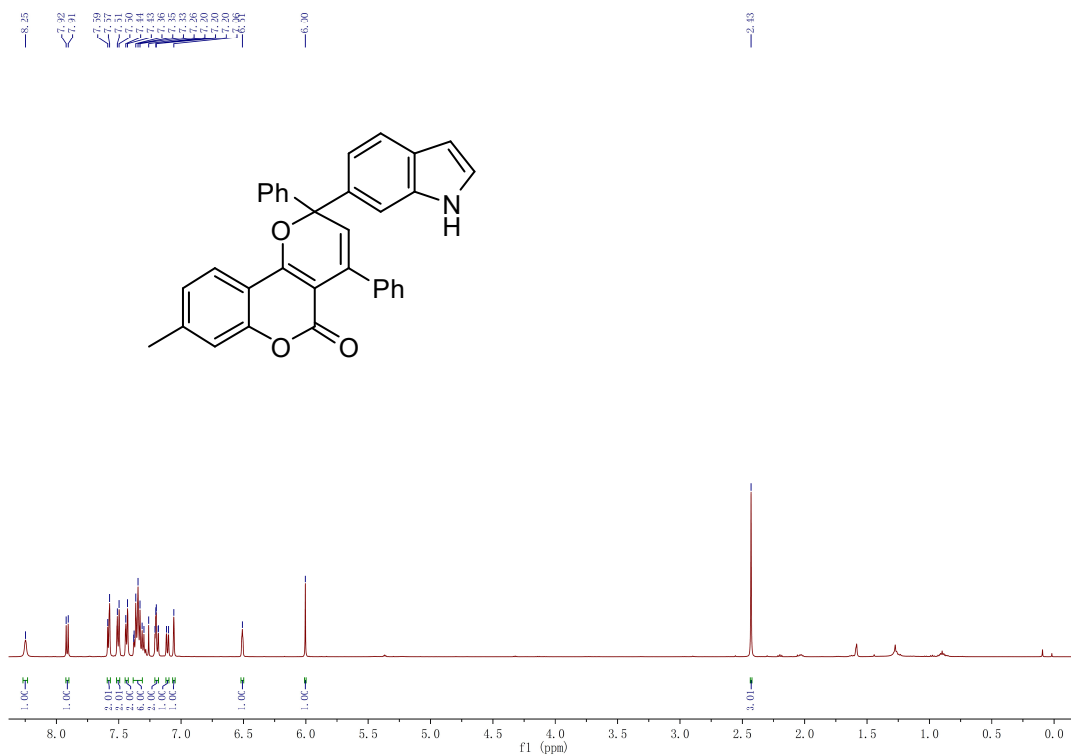
2-(1*H*-indol-6-yl)-9-methyl-2,4-diphenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ac)



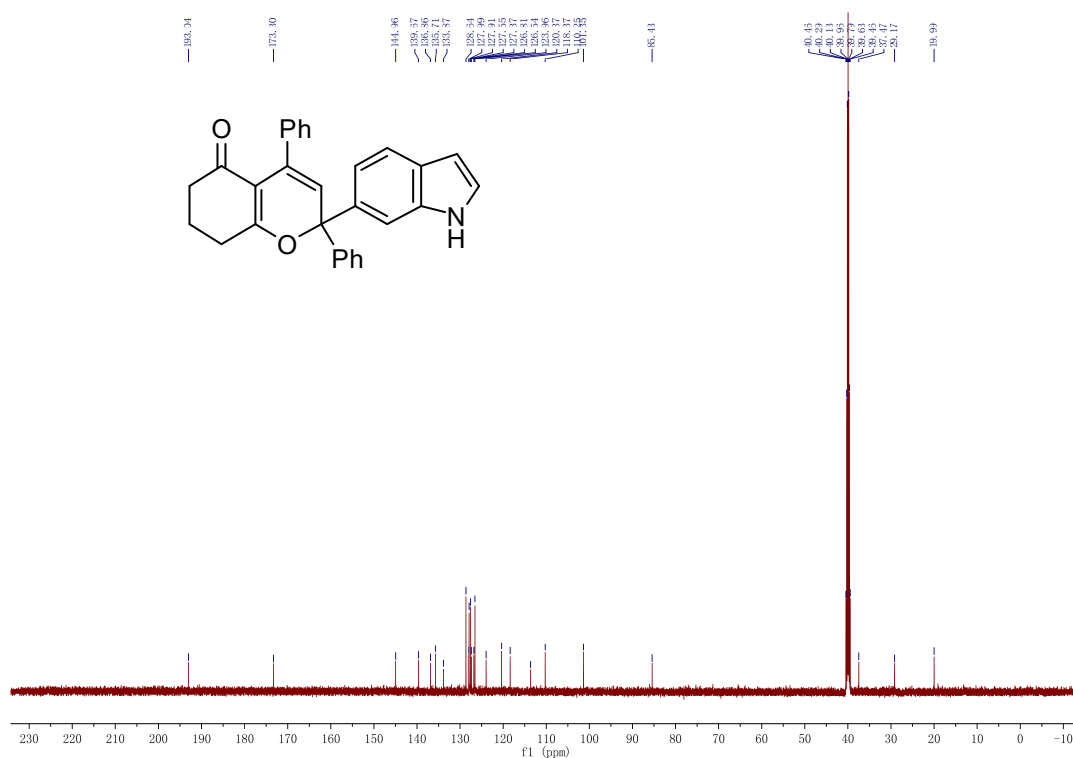
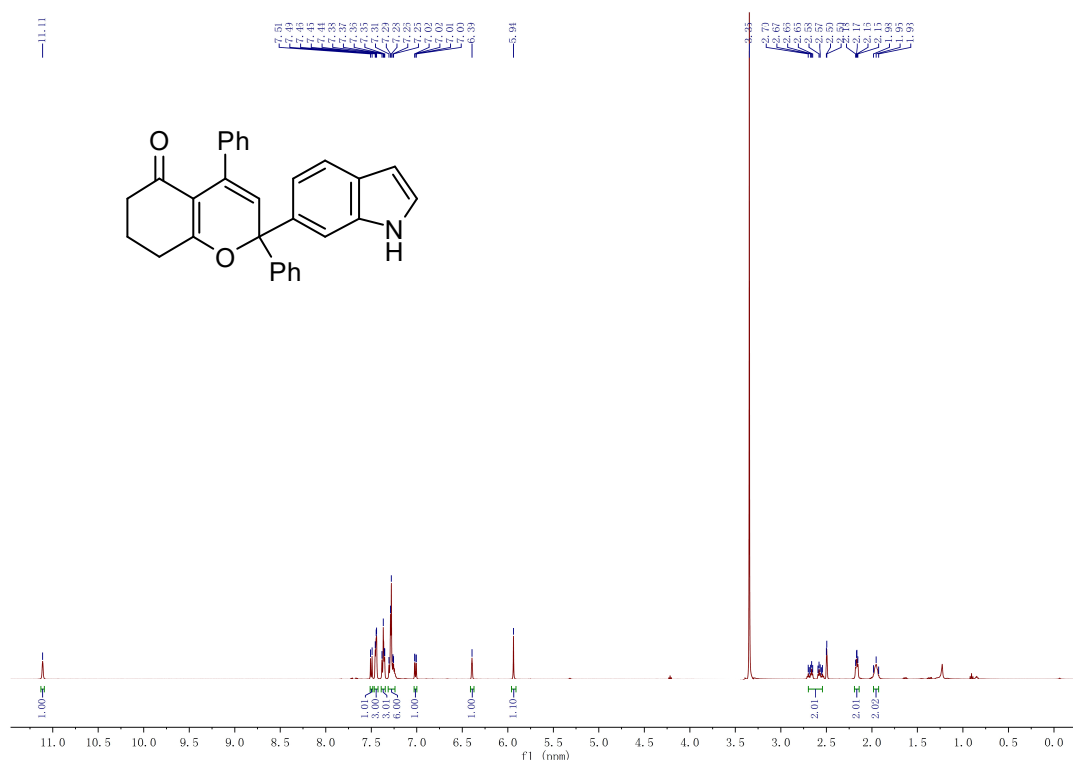
8-Chloro-2-(1*H*-indol-6-yl)-2,4-diphenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ad)



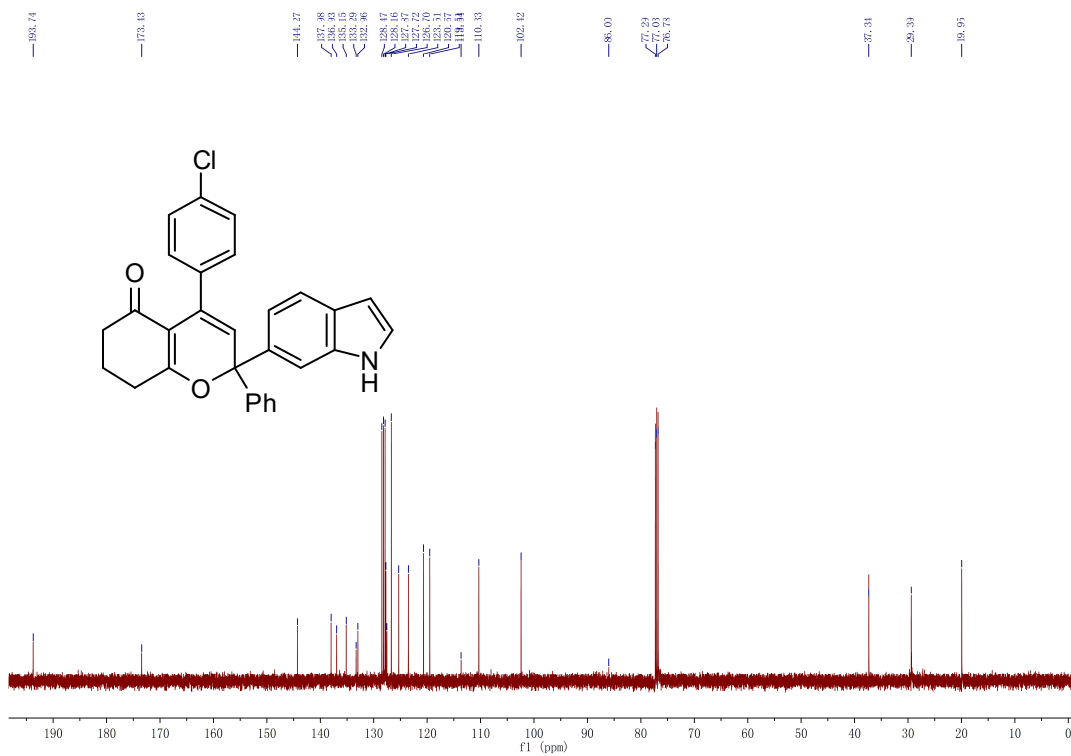
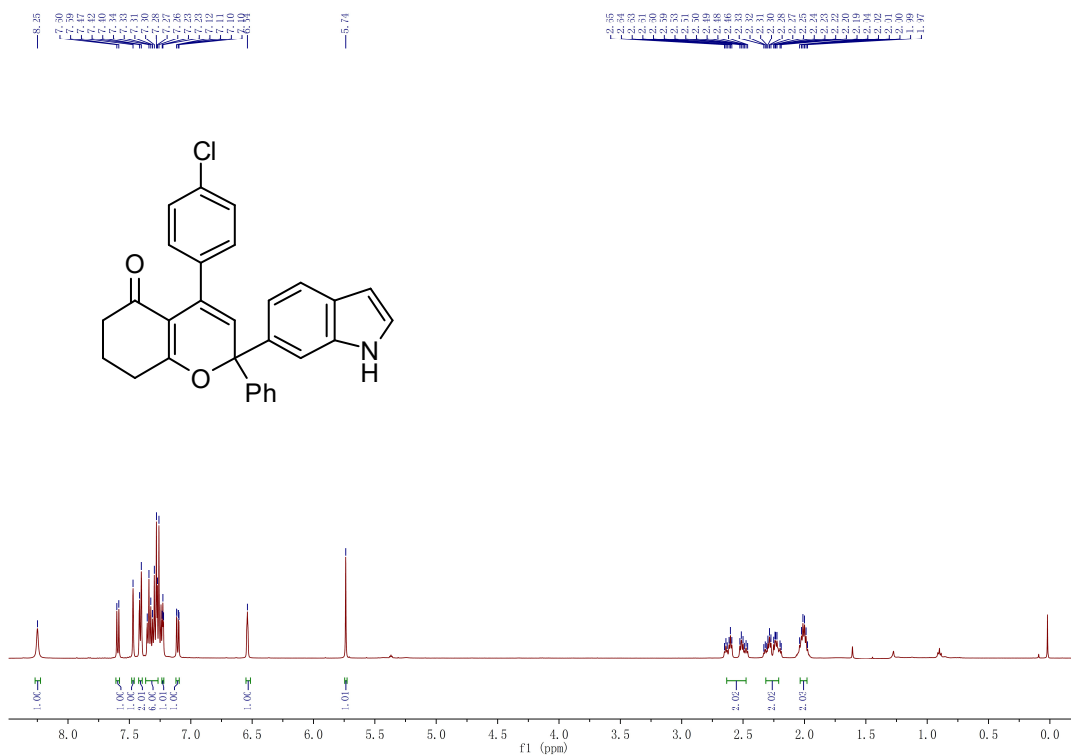
2-(1*H*-indol-6-yl)-8-methyl-2,4-diphenylpyrano[3,2-*c*]chromen-5(2*H*)-one (3ae)



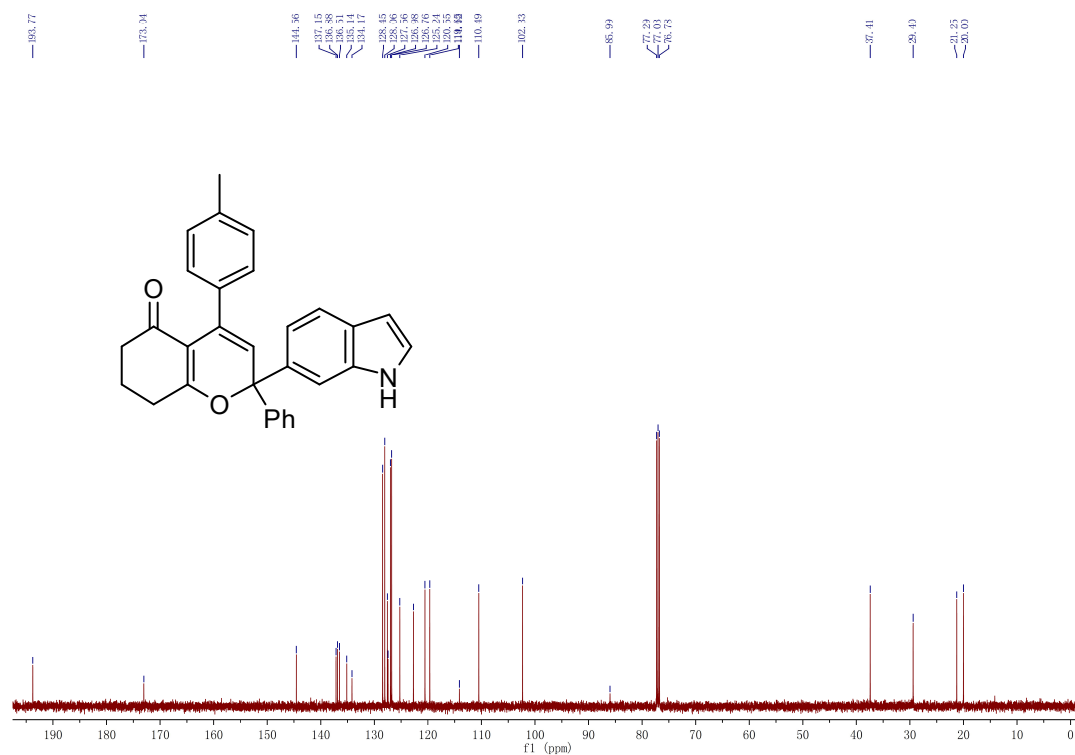
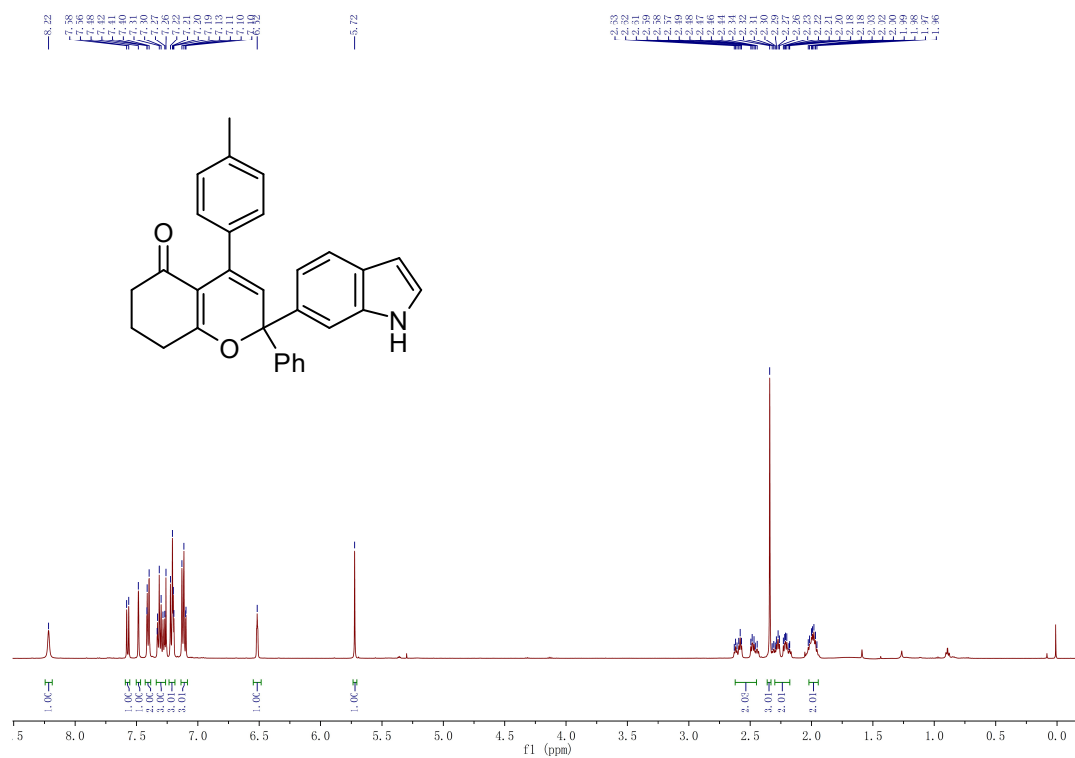
2-(1*H*-indol-6-yl)-2,4-diphenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5aa)



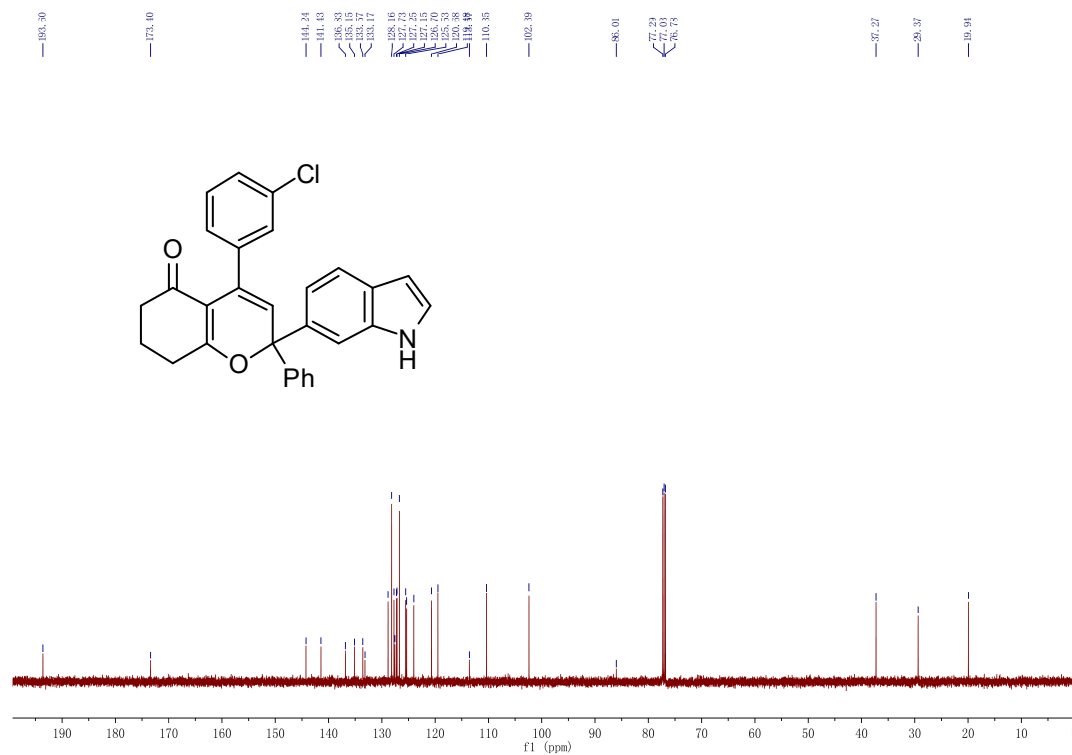
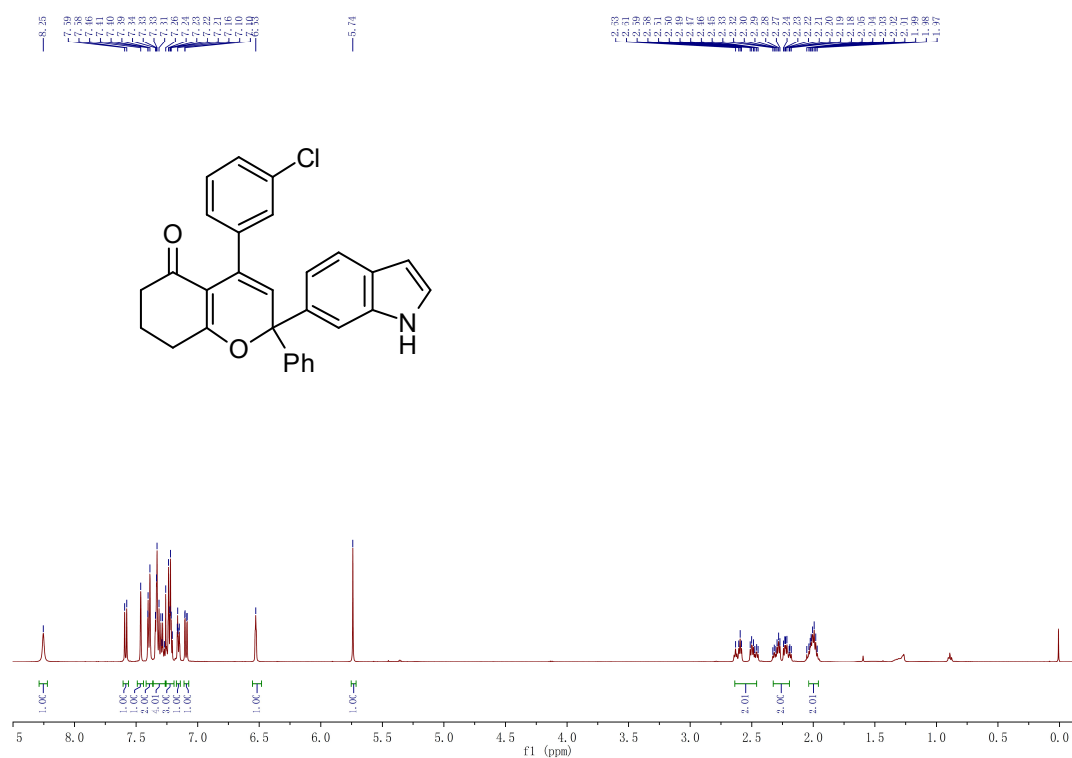
4-(4-Chlorophenyl)-2-(1*H*-indol-6-yl)-2-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ca)



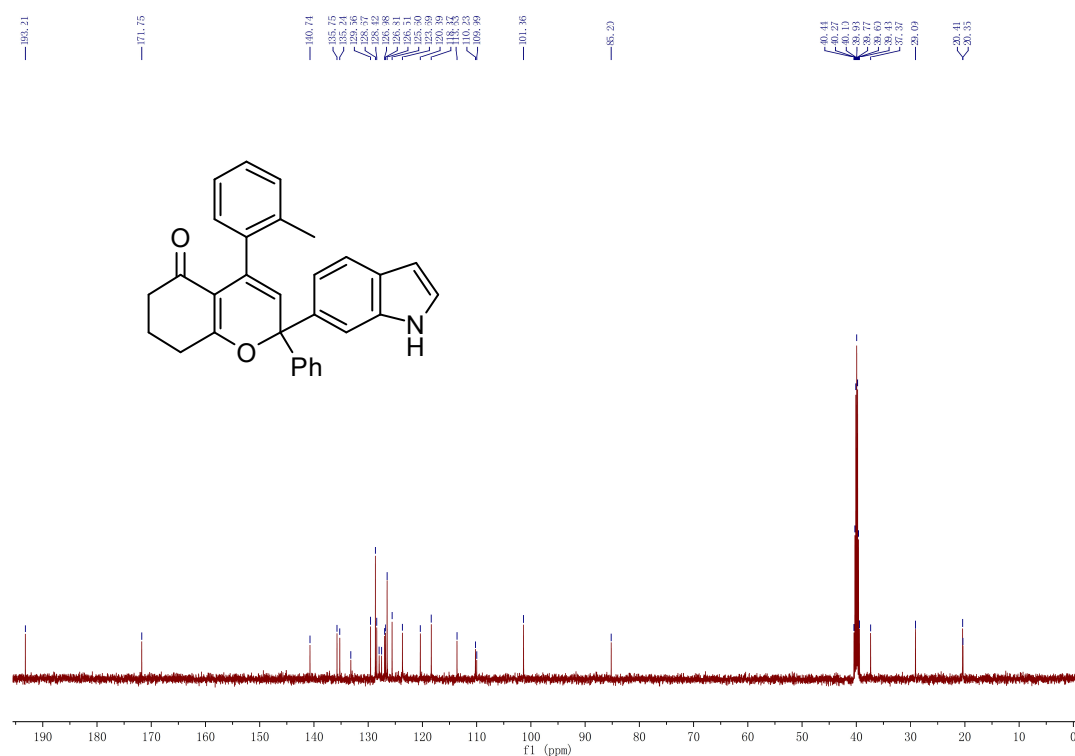
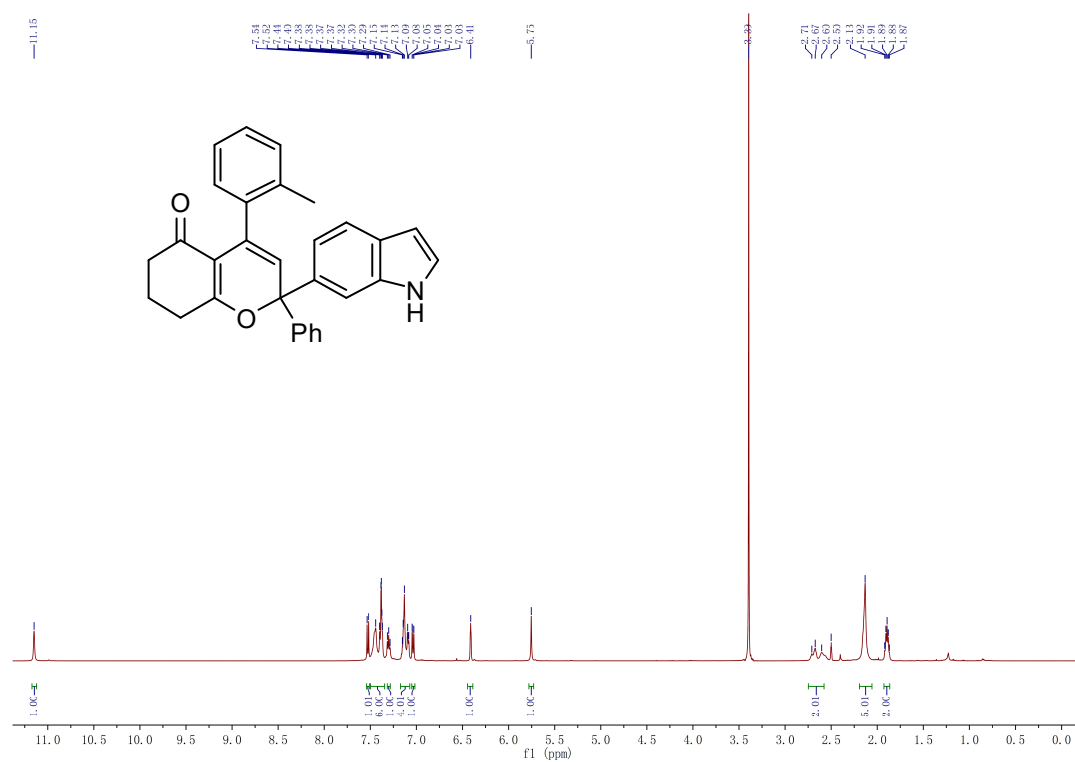
2-(1*H*-indol-6-yl)-2-phenyl-4-(*p*-tolyl)-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ea)



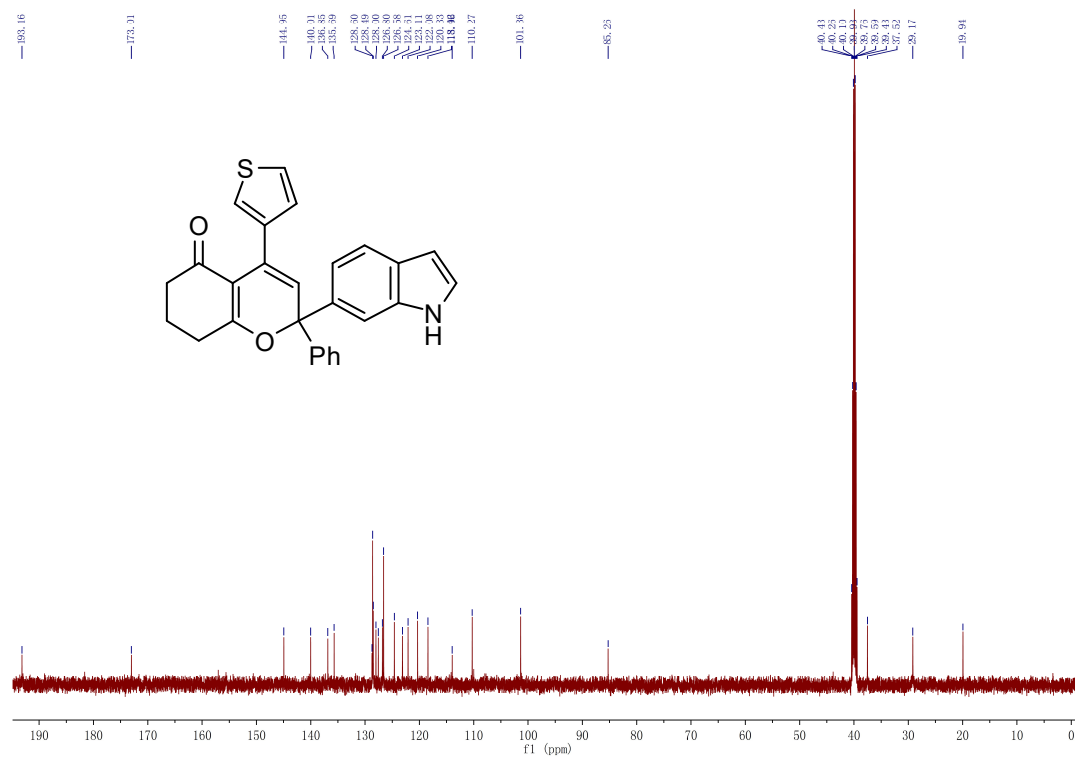
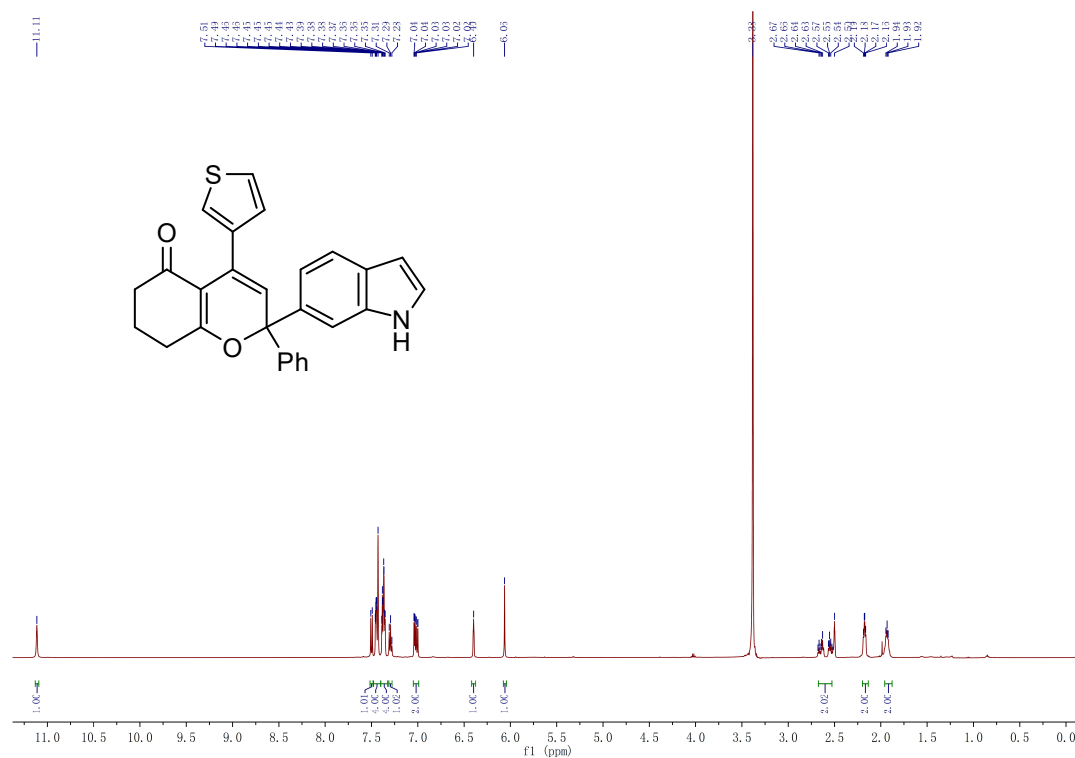
4-(3-Chlorophenyl)-2-(1*H*-indol-6-yl)-2-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (Sha)



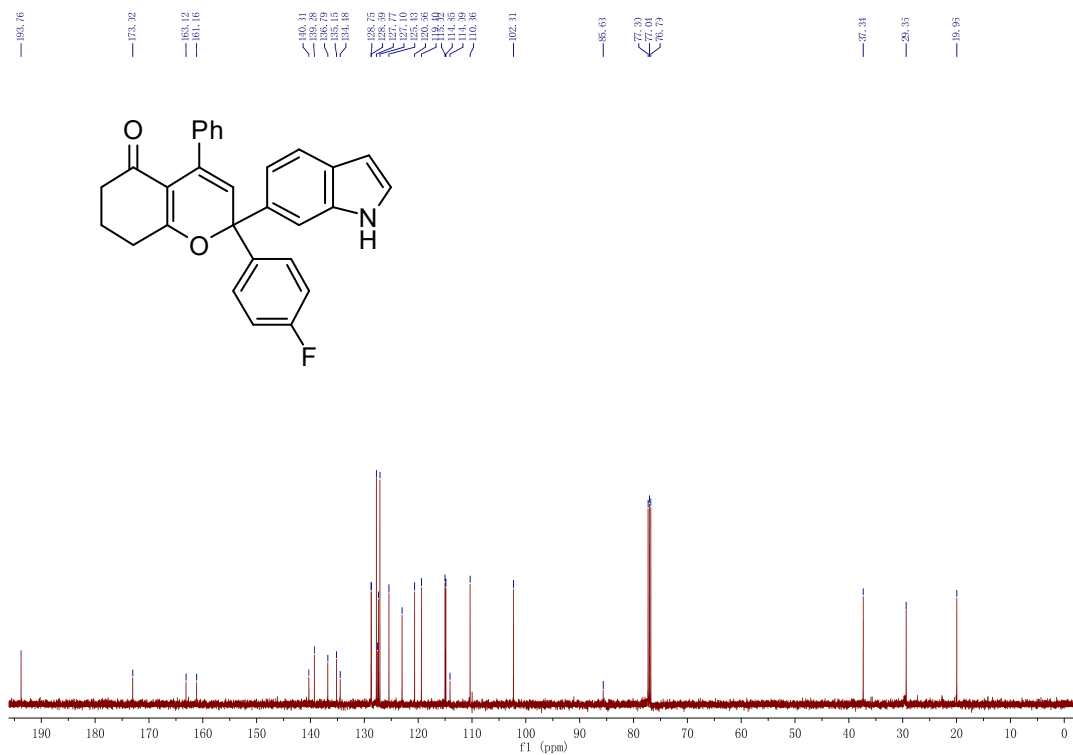
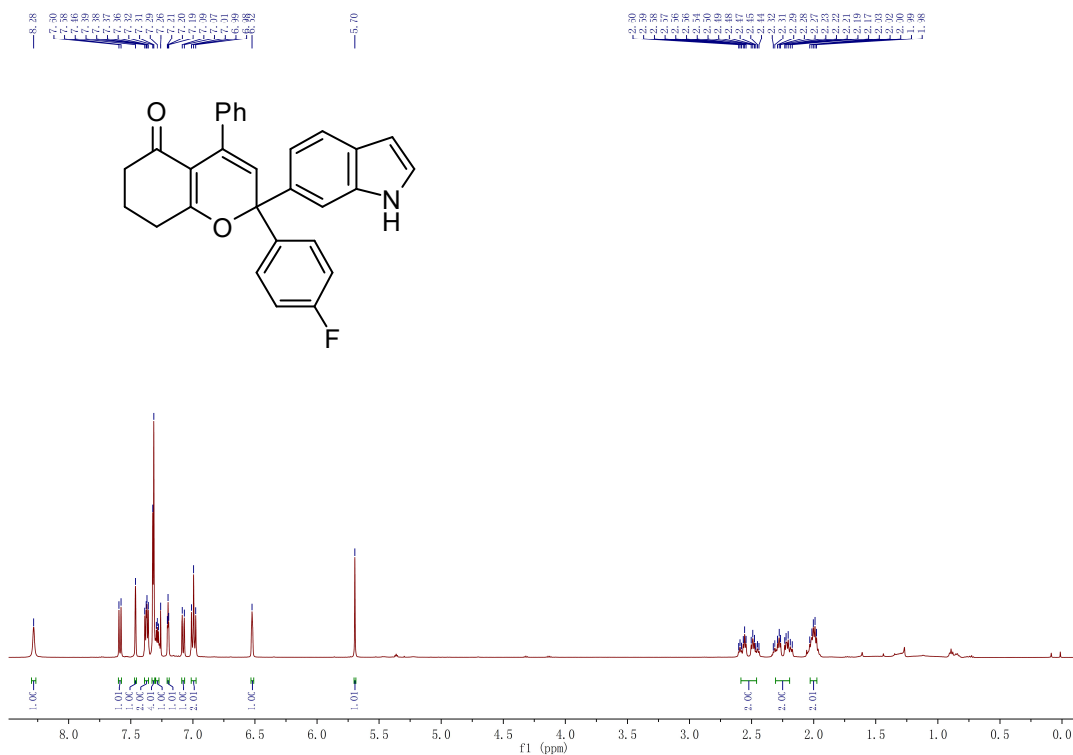
2-(1*H*-indol-6-yl)-2-phenyl-4-(*o*-tolyl)-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5ma)



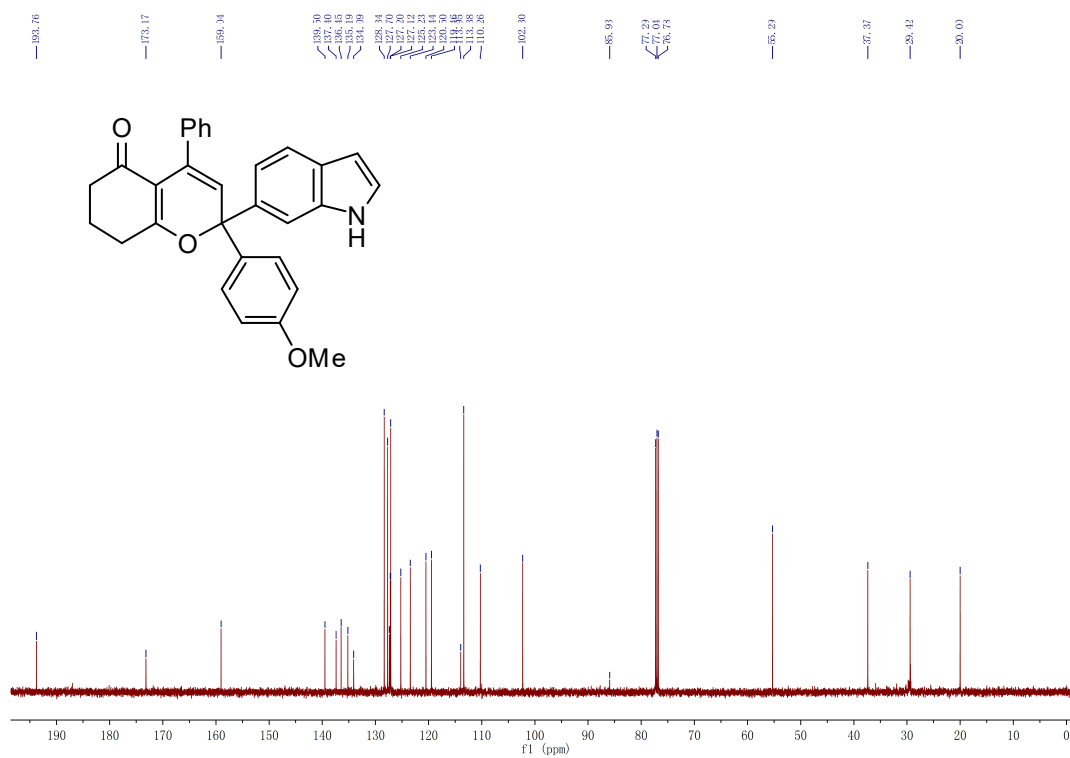
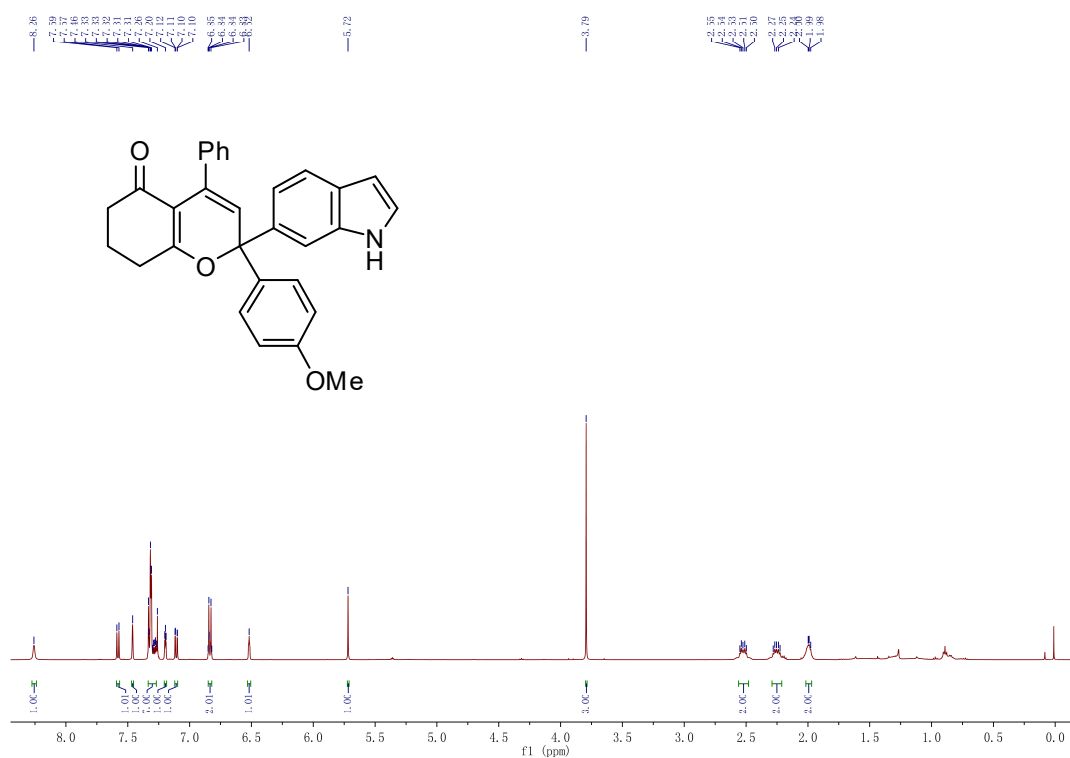
**2-(1*H*-indol-6-yl)-2-phenyl-4-(thiophen-3-yl)-7,8-dihydro-2*H*-chromen-5(6*H*)-one
(5na)**



2-(4-Fluorophenyl)-2-(1*H*-indol-6-yl)-4-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5va)



2-(1*H*-indol-6-yl)-2-(4-methoxyphenyl)-4-phenyl-7,8-dihydro-2*H*-chromen-5(6*H*)-one (5wa)



I: X-Ray Analysis Data

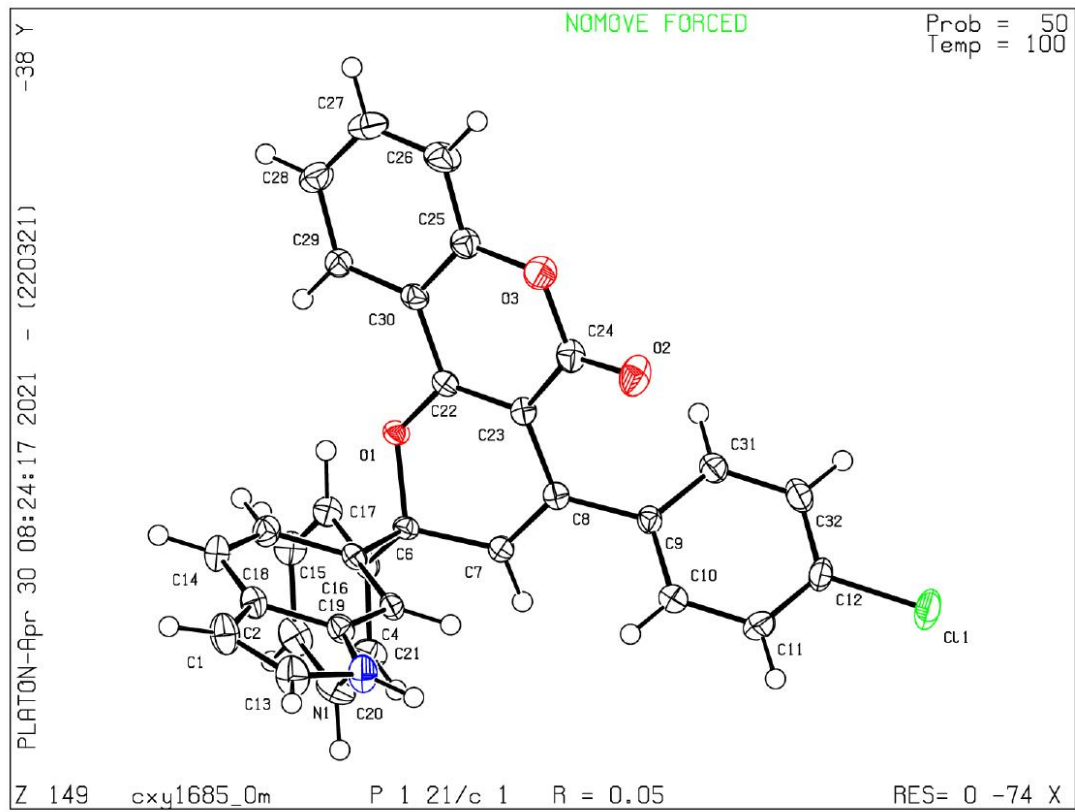


Table Crystal data and structure refinement for 3ca.

Identification code	3ca
Empirical formula	C ₃₂ H ₂₀ ClNO ₃
Formula weight	501.94
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.9392(6)
b/Å	10.0969(4)
c/Å	17.2076(7)
α/°	90
β/°	111.7150(10)
γ/°	90
Volume/Å ³	2411.39(17)
Z	4
ρ _{calc} /cm ³	1.383
μ/mm ⁻¹	0.195
F(000)	1040.0
Crystal size/mm ³	0.35 × 0.31 × 0.24
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.772 to 56.694
Index ranges	-19 ≤ h ≤ 19, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	34701
Independent reflections	6008 [R _{int} = 0.0997, R _{sigma} = 0.0749]
Data/restraints/parameters	6008/0/335
Goodness-of-fit on F ²	1.043
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0484, wR ₂ = 0.1094
Final R indexes [all data]	R ₁ = 0.1033, wR ₂ = 0.1249
Largest diff. peak/hole / e Å ⁻³	0.54/-0.46

J: Reference

1. a) M. Chen, J. Sun, *Angew. Chem. Int. Ed.* **2017**, *56*, 4583. b) D. Qian, L. Wu, Z. Lin, J. Sun, *Nat. Commun.* **2017**, *8*, 567.
2. Z. Chen, L. Tong, Z. Du, Z. Mao, X. Zhang, Y. Zou, M. Yan, *Org. Biomol. Chem.* **2018**, *16*, 2634.