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Electronic Supporting Information

Rhodium-Catalyzed Coupling of Arenes and Fluorinated α-Diazo Diketones: Synthesis of Chromones

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Table of Contents

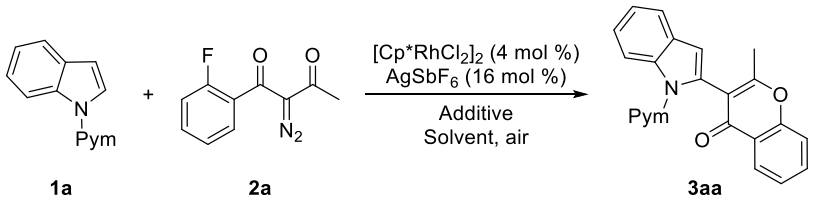
I. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. *N*-pyrimidylindoles,[1] diazos,[2] *N*-pyrimidylisoquinolinone[3] and 2-pyridone[4] were synthesized according to literature reports. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm precoated silica gel plates. Visualization was carried out with UV light or aqueous potassium permanganate stain. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ^{o}C on a Bruker 600 MHz and 151 MHz NMR spectrometers, respectively. And ^{19}F NMR were recorded at 25 ^{o}C on a JEOL 376 MHz NMR spectrometers. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts were converted to the TMS scale (TMS: δ H = 0.00 ppm, $CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm, CD_2Cl_2: δ H = 5.32 ppm, δ C = 53.84 ppm). Coupling constants (*J*) are given in Hertz (Hz). Letters m, s, d, t and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. High resolution mass spectra were recorded on Bruck Microtof. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

II. Experiment Details and Analytical Data of 3, 6 and 7a

1) Optimization of the Reaction Conditions

2) Table S1. Optimization of the Reaction Conditions[a,b]

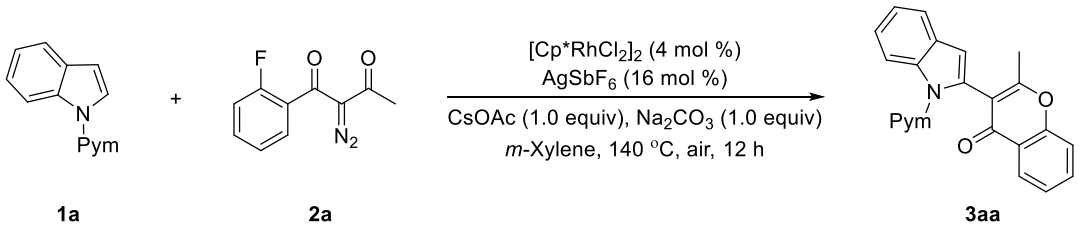


1a **2a** **3aa**

Entry	Additive (equiv.)	Solvent	*T* (°C)	Yield(%)
1	Na_2CO_3 (2.0)	*m*-Xylene	140	45
2	K_3PO_4 (2.0)	*m*-Xylene	140	55
3	Cs_2CO_3 (2.0)	*m*-Xylene	140	20
4	CsOAc (2.0)	*m*-Xylene	140	67
5	CsOAc (2.0)	PhCl	140	45
6	CsOAc (2.0)	PhMe	140	40
7	CsOAc (1.0) + Na_2CO_3 (1.0)	*m*-Xylene	140	88
8	Cs_2CO_3 (1.0) + Na_2CO_3 (1.0)	*m*-Xylene	140	58
9	Cs_2CO_3 (1.0) + CsOAc (1.0)	*m*-Xylene	140	50
10	Cs_2CO_3 (0.75) + Na_2CO_3 (0.75)	*m*-Xylene	140	59
11	Cs_2CO_3 (0.5) + CsOAc (0.5)	*m*-Xylene	140	23
12	CsOAc (0.5) + Na_2CO_3 (1.0)	*m*-Xylene	140	46
13	CsOAc (1.0) + Na_2CO_3 (0.5)	*m*-Xylene	140	48
14	CsOAc (1.25) + Na_2CO_3 (0.75)	*m*-Xylene	140	70
15	CsOAc (0.75) + Na_2CO_3 (1.25)	*m*-Xylene	140	68
16	CsOAc (1.0) + Na_2CO_3 (1.0)	*m*-Xylene	135	62
17[c]	CsOAc (1.0) + Na_2CO_3 (1.0)	*m*-Xylene	140	nd

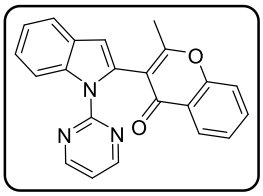
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv.), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), solvent (1.5 mL) under air for 12 h. [b]Isolated yield after column chromatography. [c]No $[Cp^*RhCl_2]_2$ was used.

2) General procedure for preparation of 3



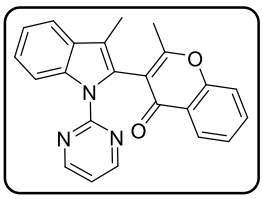
1a **2a** **3aa**

Representative Synthesis of Product 3: A pressure tube was charged with **1a** (39.0 mg, 0.2 mmol), **2a** (82.5 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (5.0 mg, 4 mol %), $AgSbF_6$ (11.0 mg, 16 mol %), CsOAc (38.4 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol) and anhydrous *m*-Xylene (2.0 mL). The reaction mixture was stirred at 140 °C for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 5:1 (v/v) to give the corresponding product **3aa** (62.2 mg, 88%).



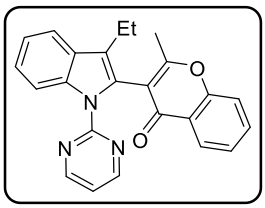
2-Methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3aa)

yellow solid (62.2 mg, 88%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 4.8 Hz, 2H), 8.51 (d, J = 8.4 Hz, 1H), 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 6.97 (t, J = 4.8 Hz, 1H), 6.66 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.0, 158.1, 157.9, 156.1, 137.0, 133.4, 131.7, 129.2, 126.4, 124.9, 123.7, 123.1, 122.0, 120.6, 118.9, 117.8, 117.0, 115.0, 110.2, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{15}N_3NaO_2$, ($[M + Na]^+$), 376.1056, found 376.1055.



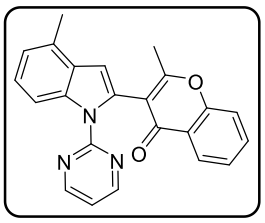
2-Methyl-3-(3-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ba)

brown solid (35.2 mg, 48%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 4.8 Hz, 2H), 8.17 (dd, J = 7.9, 1.5 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.26 (m, 1H), 6.91 (t, J = 4.8 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 164.2, 158.1, 157.9, 156.2, 136.8, 133.4, 130.4, 128.1, 126.5, 124.9, 124.0, 123.2, 121.7, 118.9, 117.8, 117.1, 116.5, 115.1, 19.5, 9.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$, ($[M + Na]^+$), 390.1213, found 390.1211.



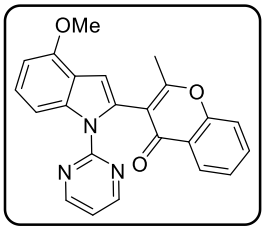
3-(3-Ethyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ca)

yellow solid (29.7 mg, 39%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 4.7 Hz, 2H), 8.21 (dd, J = 7.9, 1.4 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.27 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 4.7 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.25 (s, 3H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 164.5, 158.0, 157.9, 156.1, 137.1, 133.4, 129.5, 127.3, 126.6, 124.9, 123.8, 123.2, 123.16, 121.7, 119.1, 117.8, 117.7, 116.4, 115.2, 19.6, 18.2, 14.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{19}N_3NaO_2$, ($[M + Na]^+$), 404.1369, found 404.1371.



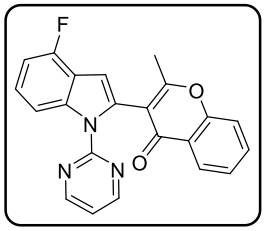
2-Methyl-3-(4-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3da)

yellow solid (61.7 mg, 84%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 2H), 8.35 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 7.2 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.25 (t, J = 7.3 Hz,1H), 7.06 (d, J = 7.2 Hz, 1H), 6.96 (t, J = 4.7 Hz, 1H), 6.72 (s, 1H), 2.59 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.0, 158.0, 157.9, 156.0, 136.7, 133.3, 131.0, 129.9, 128.9, 126.3, 124.8, 123.7, 123.0, 122.3, 118.9, 117.7, 116.9, 112.5, 108.6, 19.9, 18.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$, ([M + Na]$^+$), 390.1213, found 390.1214.



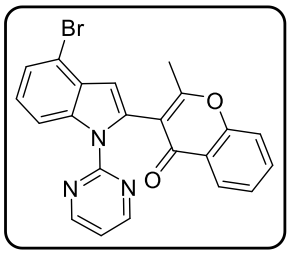
3-(4-Methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ea)

brown solid (69.0 mg, 90%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 4.8 Hz, 2H), 8.14 – 8.09 (m, 2H), 7.67 – 7.64 (m, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.28 (t, J = 4.1 Hz, 1H), 6.98 (t, J = 4.8 Hz, 1H), 6.81 (s, 1H), 6.70 (d, J = 7.9 Hz, 1H), 3.99 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 164.0, 158.1, 157.9, 155.9, 152.9, 138.2, 133.3, 130.1, 126.3, 124.7, 124.4, 123.0, 119.7, 118.8, 117.7, 117.1, 108.1, 107.1, 102.0, 55.5, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_3$, ([M + Na]$^+$), 406.1162, found 406.1164.



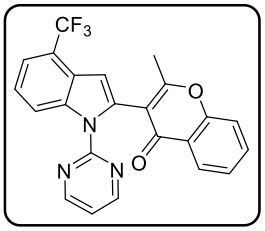
3-(4-Fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3fa)

yellow solid (60.9 mg, 82%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 4.2 Hz, 2H), 8.27 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.65 (t, J = 7.3 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.00 (t, J = 4.4 Hz, 1H), 6.92 (t, J = 8.7 Hz, 1H), 6.77 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 164.3, 158.0, 157.9, 156.0, 155.9 (J = 246.5 Hz), 139.2 (J = 15.5 Hz), 133.5, 131.8, 126.2, 124.9, 124.1 (J = 7.4 Hz), 122.9, 118.4, 118.2 (J = 22.1 Hz), 117.7, 117.4, 111.0 (J = 3.1 Hz), 106.9 (J = 18.5 Hz), 105.4, 100.0, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}FN_3NaO_2$, ([M + Na]$^+$), 394.0962, found 394.0969.



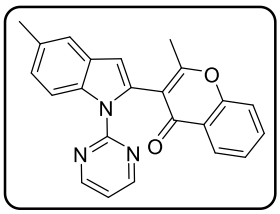
3-(4-Bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ga)

yellow solid (66.4 mg, 77%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 4.6 Hz, 2H), 8.45 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.00 (t, J = 4.5 Hz, 1H), 6.76 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 164.3, 158.0, 157.8, 155.9, 137.2, 133.5, 132.5, 129.7, 126.2, 124.9, 124.8, 124.5, 122.9, 118.3, 117.8, 117.5, 114.4, 114.0, 109.7, 20.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}BrN_3NaO_2$, ([M + Na]$^+$), 454.0162, found 454.0172.



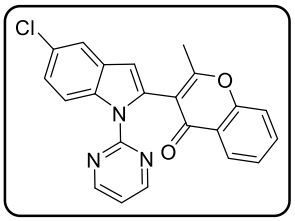
2-Methyl-3-(1-(pyrimidin-2-yl)-4-(trifluoromethyl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ha)

brown solid (67.4 mg, 80%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 4.8 Hz, 2H), 8.08 (d, J = 7.8 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.03 (t, J = 4.7 Hz, 1H), 6.87 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 164.5, 158.1, 157.7, 156.0, 137.4, 133.7, 133.6, 126.2, 125.5, 125.0 (J = 272.8 Hz), 124.99, 122.9, 122.86, 121.7 (J = 32.7 Hz), 119.3 (J = 4.7 Hz), 118.4, 118.2, 117.8 (J = 10.66 Hz), 108.1, 20.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{14}F_3N_3NaO_2$, ([M + Na]$^+$), 444.0930, found 444.0942.



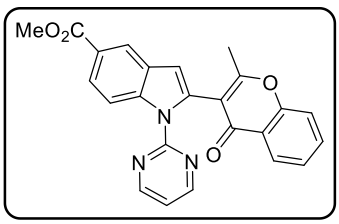
2-Methyl-3-(5-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ia)

brown solid (67.6 mg, 92%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, J = 4.7 Hz, 2H), 8.42 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.42 (s, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 6.93 (t, J = 4.7 Hz, 1H), 6.60 (s, 1H), 2.49 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 163.8, 158.1, 157.8, 156.0, 135.3, 133.4, 131.6, 131.3, 129.4, 126.3, 125.2, 124.8, 123.1, 120.3, 119.0, 117.7, 116.7, 114.8, 110.0, 21.4, 19.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$, ([M + Na]$^+$), 390.1213, found 390.1224.



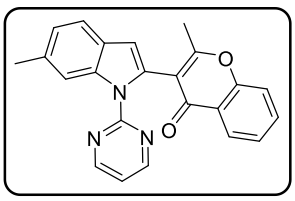
3-(5-Chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ja)

brown solid (60.4 mg, 78%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 3.2 Hz, 2H), 8.45 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.58 (s, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 7.3 Hz, 1H), 6.98 (t, J = 4.9 Hz, 1H), 6.60 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 164.0, 158.0, 157.8, 156.0, 135.4, 133.5, 133.1, 130.3, 127.5, 126.3, 124.9, 123.8, 123.0, 119.9, 118.6, 117.8, 117.3, 116.2, 109.4, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}ClN_3NaO_2$, ([M + Na]$^+$), 410.0667, found 410.0663.



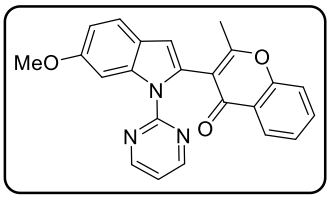
Methyl 2-(2-methyl-4-oxo-4*H*-chromen-3-yl)-1-(pyrimidin-2-yl)-1*H*-indole-5-carboxylate (3ka)

yellow solid (69.1 mg, 84%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 4.8 Hz, 2H), 8.48 (d, J = 8.8 Hz, 1H), 8.37 (s, 1H), 8.07 (dd, J = 7.8, 1.0 Hz, 1H), 8.01 (dd, J = 8.8, 1.4 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 4.8 Hz, 1H), 6.74 (s, 1H), 3.94 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 167.9, 164.2, 158.1, 157.7, 156.0, 139.5, 133.6, 133.3, 128.7, 126.3, 124.9, 124.9, 123.8, 123.1, 123.0, 118.3, 117.8, 117.6, 114.5, 110.6, 52.0, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{17}N_3NaO_4$, ([M + Na]$^+$), 434.1111, found 434.1110.



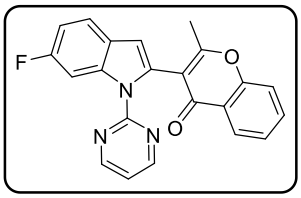
2-Methyl-3-(6-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3la)

yellow solid (44.1 mg, 60%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 4.8 Hz, 2H), 8.31 (s, 1H), 8.11 (dd, J = 7.9, 1.3 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.96 (t, J = 4.8 Hz, 1H), 6.61 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.0, 158.1, 158.0, 156.0, 137.4, 133.7, 133.4, 131.0, 127.0, 126.4, 124.8, 123.6, 123.1, 120.2, 119.0, 117.8, 116.9, 114.8, 110.1, 22.3, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$, ([M + Na]$^+$), 390.1213, found 390.1211.



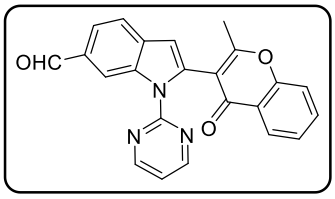
3-(6-Methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ma)

brown solid (47.5 mg, 62%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, J = 4.7 Hz, 2H), 8.14 (d, J = 1.7 Hz, 1H), 8.11 (dd, J = 7.9, 1.0 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 4.7 Hz, 1H), 6.91 (dd, J = 8.5, 2.2 Hz, 1H), 6.59 (s, 1H), 3.91 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 163.7, 158.1, 157.8, 157.4, 155.9, 137.8, 133.3, 130.5, 126.3, 124.7, 123.3, 123.0, 120.9, 119.0, 117.7, 116.8, 111.2, 110.1, 99.4, 55.8, 19.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_3$, ([M + Na]$^+$), 406.1162, found 406.1161.



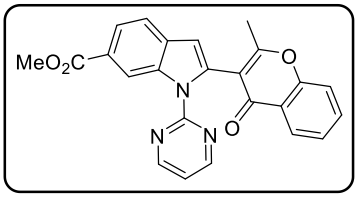
3-(6-Fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3na)

brown solid (52.0 mg, 70%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, J = 4.7 Hz, 2H), 8.31 (dd, J = 11.0, 1.6 Hz, 1H), 8.11 (d, J = 7.1 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.53 (dd, J = 8.5, 5.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.63 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 163.9, 160.8 (J = 238.1 Hz), 156.0, 157.94, 157.91, 156.0, 137.1 (J = 12.9 Hz), 133.5, 132.2, 126.3, 125.6, 124.9, 123.0, 121.1 (J = 9.9 Hz), 118.8, 117.8, 117.2, 110.4 (J = 24.4 Hz), 102.3 (J = 28.8 Hz), 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.43. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}FN_3NaO_2$, ([M + Na]$^+$), 394.0962, found 394.0964.



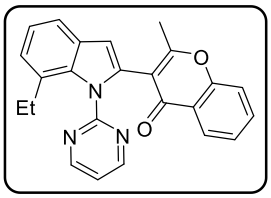
2-(2-Methyl-4-oxo-4*H*-chromen-3-yl)-1-(pyrimidin-2-yl)-1*H*-indole-6-carbaldehyde (3oa)

yellow solid (55.6 mg, 73%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.10 (s, 1H), 9.00 (s, 1H), 8.59 (d, J = 4.6 Hz, 2H), 8.08 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.05 (t, J = 4.6 Hz, 1H), 6.73 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 176.3, 164.2, 158.2, 157.7, 156.0, 136.6, 136.1, 134.1, 133.7, 132.6, 126.3, 125.1, 122.9, 122.4, 121.0, 118.9, 118.3, 117.8, 117.8, 110.2, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{15}N_3NaO_3$, ([M + Na]$^+$), 404.1006, found 404.1005.



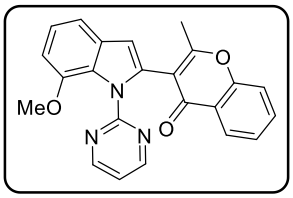
Methyl 2-(2-methyl-4-oxo-4*H*-chromen-3-yl)-1-(pyrimidin-2-yl)-1*H*-indole-6-carboxylate (3pa)

yellow solid (69.9 mg, 85%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.58 (d, J = 4.7 Hz, 2H), 8.09 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 4.7 Hz, 1H), 6.70 (s, 1H), 3.95 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 168.2, 164.2, 158.2, 157.6, 156.0, 136.3, 134.9, 133.6, 132.7, 126.3, 125.2, 125.0, 123.1, 122.9, 120.2, 118.3, 117.8, 117.6, 117.0, 109.9, 52.1, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{17}N_3NaO_4$, ([M + Na]$^+$), 434.1111, found 434.1116.



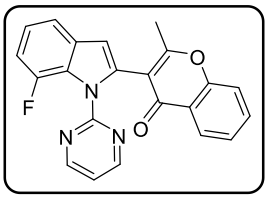
3-(7-Ethyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3qa)

brown solid (40.4 mg, 53%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, J = 4.8 Hz, 2H), 8.06 (d, J = 7.1 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 4.8 Hz, 1H), 6.66 (s, 1H), 2.49 (q, J = 7.4 Hz, 2H), 2.38 (s, 3H), 1.01 (t, J = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 166.4, 158.7, 158.0, 155.9, 136.1, 133.4, 133.2, 129.9, 129.1, 126.3, 124.9, 123.9, 122.9, 121.8, 118.7, 117.7, 116.8, 108.5, 26.3, 19.9, 13.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{19}N_3NaO_2$, ([M + Na]$^+$), 404,1369, found 404,1368.



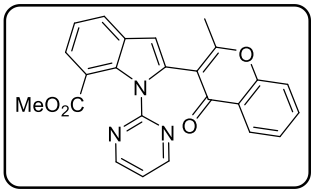
3-(7-Methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ra)

yellow solid (29.9 mg, 39%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, J = 4.7 Hz, 2H), 8.06 (d, J = 7.7 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.08 (t, J = 4.7 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.62 (s, 1H), 3.71 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 166.6, 158.3, 157.5, 155.9, 147.6, 133.4, 132.8, 131.1, 127.4, 126.4, 125.0, 123.1, 122.0, 118.5, 117.7, 116.4, 113.7, 108.0, 105.5, 55.8, 20.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_3$, ([M + Na]$^+$), 406.1162, found 406.1163.



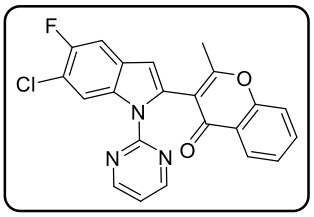
3-(7-Fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3sa)

yellow solid (54.2 mg, 73%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, J = 4.8 Hz, 2H), 8.05 (d, J = 7.2 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.43 (dd, J = 7.9, 5.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.08 (t, J = 4.8 Hz, 1H), 7.00 (dd, J = 12.1, 8.0 Hz, 1H), 6.68 (d, J = 1.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 166.1, 158.0, 157.4, 155.1 (J = 248.4 Hz), 149.3, 133.6, 133.5, 132.6 (J = 4.2 Hz), 126.3, 125.0, 124.8 (J = 9.5 Hz), 123.0, 121.9 (J = 6.8 Hz), 118.5, 117.8, 116.6 (J = 3.4 Hz), 116.5, 109.8 (J = 19.3 Hz), 108.9 (J = 1.4 Hz), 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}FN_3NaO_2$, ([M + Na]$^+$), 394.0962, found 394.0964.



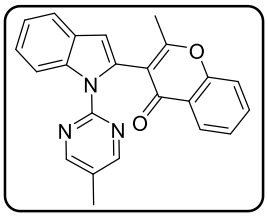
Methyl 2-(2-methyl-4-oxo-4*H*-chromen-3-yl)-1-(pyrimidin-2-yl)-1*H*-indole-7-carboxylate (3ta)

brown solid (47.7 mg, 58%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 2H), 8.01 (dd, J = 7.9, 1.3 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.66 – 7.61 (m, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.26 (s, 1H), 7.03 (t, J = 4.8 Hz, 1H), 6.71 (s, 1H), 3.38 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 168.1, 166.0, 158.8, 157.8, 155.9, 134.0, 133.6, 130.6, 126.2, 125.6, 125.0, 124.8, 122.9, 121.1, 118.6, 118.2, 117.8, 117.0, 108.7, 51.7, 20.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{17}N_3NaO_4$, ([M + Na]$^+$), 434.1111, found 434.1115.



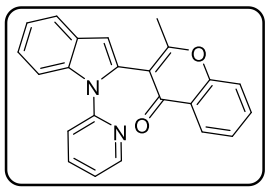
3-(6-Chloro-5-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-methyl-4*H*-chromen-4-one (3ua)

yellow solid (55.9 mg, 69%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, J = 6.6 Hz, 1H), 8.54 (d, J = 3.1 Hz, 2H), 8.09 (d, J = 7.9 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.00 (t, J = 4.7 Hz, 1H), 6.59 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 164.0, 158.0, 157.6, 156.0, 154.2 (J = 240.9 Hz), 133.8 (J = 3.5 Hz), 133.6, 133.1, 128.2 (J = 9.0 Hz), 126.3, 125.0, 123.0, 118.5, 117.8, 117.4, 117.0 (J = 20.2 Hz), 116.9, 109.7 (J = 3.9 Hz), 106.5 (J = 23.4 Hz), 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{13}ClFN_3NaO_2$, ([M + Na]$^+$), 428.0573, found 428.0578.



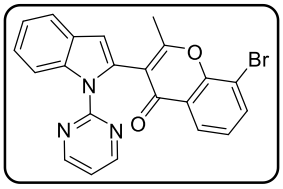
2-Methyl-3-(1-(5-methylpyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3va)

yellow solid (25.7 mg, 35%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 8.3 Hz, 1H), 8.37 (s, 2H), 8.11 (dd, J = 7.9, 1.2 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.64 (s, 1H), 2.45 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.2, 158.1, 156.3, 156.1, 137.0, 133.4, 131.6, 129.1, 126.5, 126.2, 124.8, 123.6, 123.1, 121.8, 120.6, 118.8, 117.8, 114.6, 109.6, 20.0, 15.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$, ([M + Na]$^+$), 390.1213, found 390.1220.



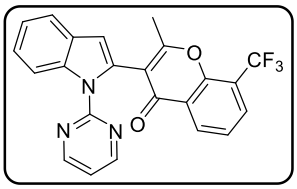
2-Methyl-3-(1-(pyridin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3wa)

brown solid (37.3 mg, 53%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (dd, J = 4.7, 1.1 Hz, 1H), 8.14 (dd, J = 7.9, 1.4 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.40 (dd, J = 16.1, 8.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.18 (m, 1H), 7.17 – 7.14 (m, 1H), 6.68 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 166.9, 156.0, 151.7, 149.2, 138.3, 137.4, 133.6, 131.2, 128.7, 126.4, 125.2, 123.1, 123.0, 121.8, 121.1, 120.9, 120.5, 117.8, 116.4, 111.3, 107.4, 20.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{16}N_2NaO_2$, ([M + Na]$^+$), 375.1104, found 375.1110.



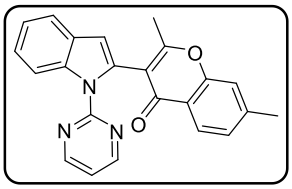
8-Bromo-2-methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ab)

yellow solid (71.6 mg, 83%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 4.9 Hz, 3H), 8.06 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.97 (t, J = 4.2 Hz, 1H), 6.68 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 164.1, 158.0, 157.9, 152.7, 137.1, 136.9, 131.1, 129.2, 125.8, 125.5, 124.4, 123.9, 122.1, 120.7, 119.2 117.0, 115.1, 111.3, 110.4, 19.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}BrN_3NaO_2$, ([M + Na]$^+$), 454.0162, found 454.0170.



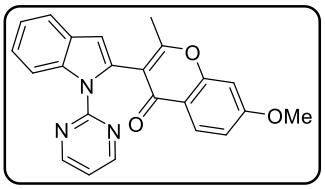
2-Methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-8-(trifluoromethyl)-4*H*-chromen-4-one (3ac)

brown solid (28.6 mg, 34%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 – 8.53 (m, 3H), 8.31 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 4.7 Hz, 1H), 6.69 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 163.9, 158.1, 158.0, 152.8, 137.1, 131.0 (J = 4.8 Hz), 130.8, 130.7, 129.2, 124.1 (J = 5.0 Hz), 124.0, 122.9 (J = 275.1 Hz), 122.2, 120.7, 120.0 (J = 32.1 Hz), 119.7, 117.1, 115.2, 110.6, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{14}F_3N_3NaO_2$, ([M + Na]$^+$), 444.0930, found 444.0935.



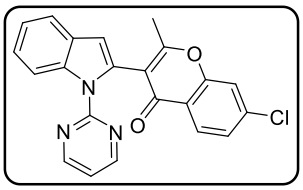
2,7-Dimethyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ad)

black solid (43.3 mg, 59%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 4.3 Hz, 2H), 8.50 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.16 (d, J = 7.8 Hz, 1H), 6.97 (t, J = 4.6 Hz, 1H), 6.67 (s, 1H), 2.49 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 163.8, 157.9, 156.2, 144.7, 137.0, 131.8, 129.2, 126.4, 126.2, 123.7, 122.0, 120.9, 120.8, 120.6, 117.54, 117.51, 117.0, 114.9, 110.1, 21.9, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$, ([M + Na]$^+$), 390.1213, found 390.1221.



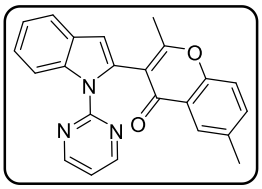
7-Methoxy-2-methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ae)

black solid (36.8 mg, 48%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 4.7 Hz, 2H), 8.49 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 6.98 (t, J = 4.7 Hz, 1H), 6.91 (dd, J = 8.8, 2.2 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 6.65 (s, 1H), 3.91 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 163.4, 158.1, 157.9, 157.7, 137.0, 131.9, 129.3, 127.8, 123.7, 122.0, 120.6, 118.6, 117.0, 114.9, 114.0, 110.2, 100.1, 55.9, 19.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_3$ ([M + Na]$^+$), 406.1162, found 406.1170.



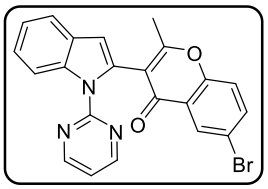
7-Chloro-2-methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3af)

brown solid (31.7 mg, 41%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 – 8.49 (m, 3H), 8.04 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.49 (s, 1H), 7.33 (dd, J = 16.6, 8.2 Hz, 2H), 7.24 (t, J = 8.0 Hz, 1H), 6.97 (t, J = 4.7 Hz, 1H), 6.66 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 164.0, 158.1, 157.9, 156.2, 139.4, 137.1, 131.2, 129.2, 127.8, 125.7, 123.9, 122.1, 121.7, 120.7, 119.3, 117.9, 117.0, 115.1, 110.4, 19.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}ClN_3NaO_2$ ([M + Na]$^+$), 410.0667, found 410.0671.



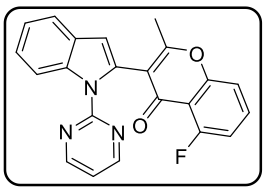
2,6-Dimethyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ag)

yellow solid (50.7 mg, 69%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 3.3 Hz, 2H), 8.40 (d, J = 8.6 Hz, 1H), 7.80 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.15 (t, J = 6.9 Hz, 1H), 6.88 (t, J = 4.3 Hz, 1H), 6.57 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 163.9, 158.0, 157.9, 154.3, 137.0, 134.7, 131.9, 129.2, 125.7, 123.7, 122.7, 121.9, 120.6, 118.6, 117.5, 117.0, 114.9, 110.1, 21.0, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$ ([M + Na]$^+$), 390.1213, found 390.1221.



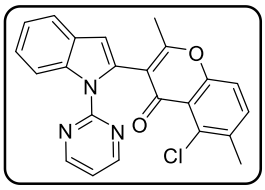
6-Bromo-2-methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ah)

yellow solid (67.2 mg, 78%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 4.7 Hz, 2H), 8.52 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 2.1 Hz, 1H), 7.73 (dd, J = 8.8, 2.1 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 6.99 (t, J = 4.7 Hz, 1H), 6.67 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 164.2, 158.0, 157.9, 154.8, 137.0, 136.4, 131.1, 129.1, 128.9, 124.4, 123.9, 122.1, 120.7, 119.8, 119.1, 118.2, 117.1, 115.0, 110.4, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}BrN_3NaO_2$ ([M + Na]$^+$), 454.0162, found 454.0160.



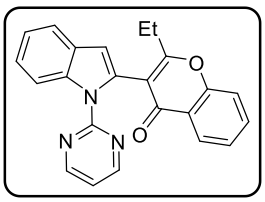
5-Fluoro-2-methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ai)

brown solid (25.2 mg, 34%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 – 8.53 (m, 3H), 7.62 (d, J = 7.7 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.35 – 7.31 (m, 1H), 7.26 – 7.22 (m, 2H), 7.00 – 6.97 (m, 2H), 6.65 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 162.9, 161.0 (J = 264.95 Hz), 158.1, 157.9, 157.1 (J = 3.8 Hz), 137.1, 133.4 (J = 10.6 Hz), 131.2, 129.2, 123.8, 122.1, 120.6, 120.1, 117.0, 115.3, 113.7 (J = 4.3 Hz), 113.6 (J = 10.1 Hz), 111.8 (J = 20.8 Hz), 110.5, 19.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}FN_3NaO_2$ ([M + Na]$^+$), 394.0962, found 394.0969.



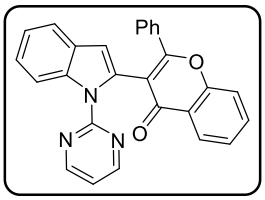
5-Chloro-2,6-dimethyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3aj)

brown solid (44.1 mg, 55%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 – 8.53 (m, 3H), 7.62 (d, J = 7.1 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 6.9 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 4.0 Hz, 1H), 6.65 (s, 1H), 2.43 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 161.9, 158.1, 157.9, 156.0, 137.1, 134.5, 132.9, 131.6, 129.3, 123.7, 122.0, 120.6, 120.2, 120.0, 116.9, 116.2, 115.3, 110.5, 20.5, 19.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{16}ClN_3NaO_2$ ([M + Na]$^+$), 424.0823, found 424.0833.



2-Ethyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3ak)

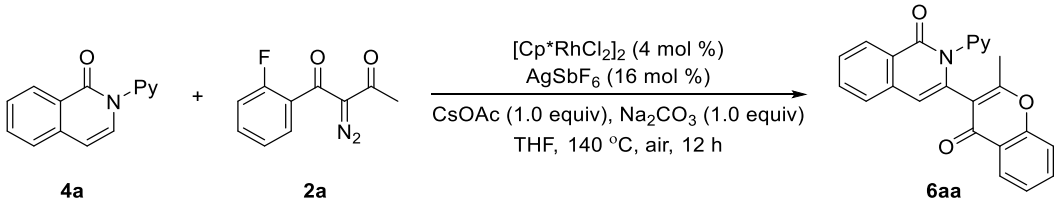
yellow solid (58.0 mg, 79%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (t, J = 6.6 Hz, 3H), 8.15 (dd, J = 7.9, 1.4 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.26 (t, J = 7.4 Hz, 1H), 6.95 (t, J = 4.8 Hz, 1H), 6.68 (s, 1H), 2.77 (dd, J = 7.5, 4.8 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.0, 167.7, 158.0, 157.8, 156.1, 137.0, 133.4, 131.6, 129.2, 126.3, 124.8, 123.6, 123.0, 122.0, 120.6, 118.1, 117.8, 117.0, 115.0, 110.0, 26.5, 11.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}N_3NaO_2$ ([M + Na]$^+$), 390.1213, found 390.1220.



2-Ethyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-4-one (3al)

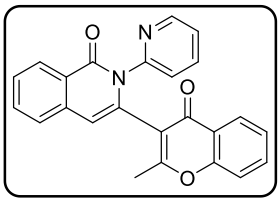
yellow solid (45.7 mg, 55%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, J = 4.8 Hz, 2H), 8.51 (d, J = 8.4 Hz, 1H), 8.15 (dd, J = 7.9, 1.3 Hz, 1H), 7.70 (ddd, J = 8.6, 7.1, 1.5 Hz, 1H), 7.62 (dd, J = 8.4, 1.1 Hz, 2H), 7.56 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.39 (td, J = 7.1, 3.5 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.25 (s, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.00 (t, J = 4.8 Hz, 1H), 6.38 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 158.0, 158.0, 156.3, 137.0, 133.8, 133.6, 132.1, 130.4, 129.4, 129.0, 128.3, 128.3, 126.5, 125.1, 123.6, 123.1, 121.9, 120.8, 118.3, 118.1, 117.0, 114.9, 110.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{17}N_3NaO_2$ ([M + Na]$^+$), 438.1213, found 438.1214.

General procedure for preparation of 6



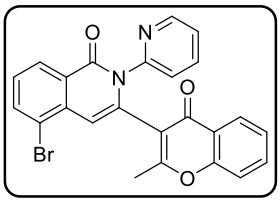
4a **2a** **6aa**

Representative Synthesis of Product 6: A pressure tube was charged with **4a** (44.4 mg, 0.2 mmol), **2a** (82.5 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (5.0 mg, 4 mol %), $AgSbF_6$ (11.0 mg, 16 mol %), CsOAc (38.4 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol) and anhydrous THF (2.0 mL). The reaction mixture was stirred at 140 °C for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 2:1 (v/v) to give the corresponding product **6aa** (67.7 mg, 89%).



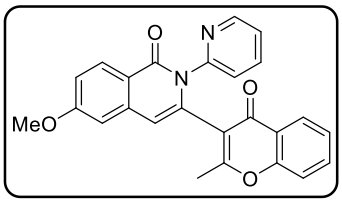
3-(2-Methyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6aa)

yellow solid (67.7 mg, 89%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, J = 7.9 Hz, 1H), 8.40 (d, J = 3.6 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.61 – 7.58 (m, 1H), 7.53 (t, J = 7.7 Hz, 3H), 7.32 (dd, J = 15.0, 7.8 Hz, 2H), 7.13 (dd, J = 7.0, 5.2 Hz, 1H), 6.52 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 167.4, 163.4, 155.7, 152.4, 148.8, 137.9, 137.0, 135.2, 133.8, 132.9, 128.4, 127.4, 126.4, 126.3, 126.0, 125.3, 124.4, 123.8, 122.7, 119.1, 117.8, 109.0, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{16}N_2NaO_3$ ([M + Na]$^+$), 403.1053, found 403.1063.



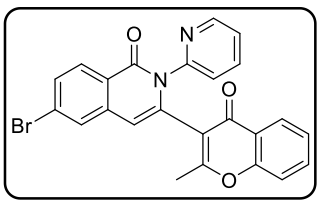
5-Bromo-3-(2-methyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6ba)

yellow solid (49.5 mg, 54%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 3.0 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.15 (t, J = 5.7 Hz, 1H), 6.87 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 167.4, 162.7, 155.8, 152.1, 148.9, 138.0, 136.7, 136.6, 136.3, 133.9, 128.0, 127.9, 127.88, 126.0, 125.4, 124.3, 124.0, 122.7, 121.1, 119.1, 117.9, 107.6, 20.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{15}BrN_2NaO_3$ ([M + Na]$^+$), 481.0158, found 481.0159.



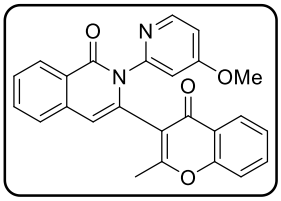
6-Methoxy-3-(2-methyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6ca)

yellow solid (43.5 mg, 53%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (t, J = 6.1 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.60 – 7.56 (m, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.31 (dd, J = 12.9, 7.9 Hz, 2H), 7.12 – 7.10 (m, 1H), 7.08 (dd, J = 8.9, 2.3 Hz, 1H), 6.88 (d, J = 2.2 Hz, 1H), 6.43 (s, 1H), 3.90 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 167.2, 163.3, 163.0, 155.7, 152.4, 148.8, 139.1, 137.8, 135.8, 133.7, 130.4, 126.0, 125.3, 124.4, 123.7, 122.7, 120.0, 119.1, 117.8, 116.6, 108.8, 107.4, 55.6, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{18}N_2NaO_4$ ([M + Na]$^+$), 433.1159, found 433.1159.



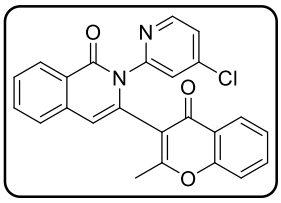
6-Bromo-3-(2-methyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6da)

yellow solid (42.1 mg, 46%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 3.9 Hz, 1H), 8.30 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.69 (s, 1H), 7.66 – 7.63 (m, 1H), 7.62 – 7.58 (m, 2H), 7.51 (d, J = 7.9 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.14 (dd, J = 6.9, 5.3 Hz, 1H), 6.43 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 167.3, 162.9, 155.7, 152.1, 148.9, 138.4, 138.0, 136.8, 133.9, 130.7, 130.2, 128.8, 128.1, 126.0, 125.4, 124.9, 124.3, 124.0, 122.7, 118.9, 117.9, 107.8, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{15}BrN_2NaO_3$ ([M + Na]$^+$), 481.0158, found 481.0157.



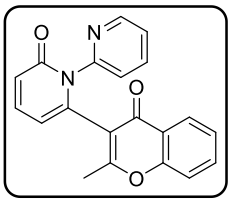
2-(4-Methoxypyridin-2-yl)-3-(2-methyl-4-oxo-4*H*-chromen-3-yl)isoquinolin-1(2*H*)-one (6ea)

brown solid (36.1 mg, 44%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 5.6 Hz, 1H), 8.07 (d, J = 7.5 Hz, 1H), 7.67 (t, J = 7.3 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.04 (s, 1H), 6.66 (dd, J = 5.7, 2.0 Hz, 1H), 6.51 (s, 1H), 3.73 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 167.4, 167.0, 163.3, 155.8, 154.0, 149.5, 137.0, 135.1, 133.8, 132.8, 128.3, 127.4, 126.3, 126.28, 125.9, 125.4, 122.9, 119.0, 117.9, 111.8, 109.0, 108.9, 55.6, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{18}N_2NaO_4$ ([M + Na]$^+$), 433.1159, found 433.1154.



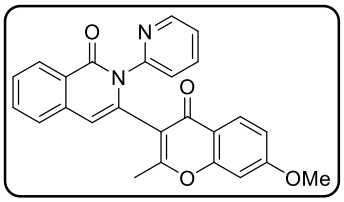
2-(4-Chloropyridin-2-yl)-3-(2-methyl-4-oxo-4*H*-chromen-3-yl)isoquinolin-1(2*H*)-one (6fa)

yellow solid (25.7 mg, 31%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 8.1 Hz, 1H), 8.28 (d, J = 5.3 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.70 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.59 (d, J = 1.1 Hz, 1H), 7.54 (t, J = 6.8 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.15 (dd, J = 5.3, 1.5 Hz, 1H), 6.53 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 167.3, 163.2, 155.8, 153.2, 149.2, 145.1, 136.9, 134.9, 133.9, 133.1, 128.4, 127.6, 126.4, 126.1, 125.5, 125.2, 124.4, 122.8, 119.0, 117.8, 109.4, 100.1, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{15}ClN_2NaO_3$ ([M + Na]$^+$), 437.0663, found 437.0672.



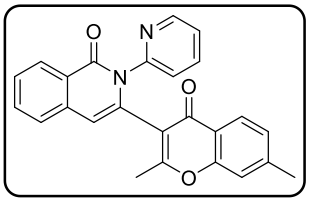
6-(2-Methyl-4-oxo-4*H*-chromen-3-yl)-2*H*-[1,2'-bipyridin]-2-one (6ga)

black solid (26.4 mg, 40%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (dd, J = 4.8, 1.1 Hz, 1H), 8.02 (dd, J = 8.3, 1.6 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.62 – 7.58 (m, 1H), 7.47 (dd, J = 9.3, 6.8 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.15 – 7.13 (m, 1H), 6.73 (dd, J = 9.4, 1.1 Hz, 1H), 6.17 (dd, J = 6.7, 1.1 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 167.0, 163.7, 155.7, 152.0, 148.9, 141.5, 140.1, 138.1, 133.9, 126.0, 125.4, 124.1, 123.9, 122.6, 121.7, 118.7, 117.9, 108.7, 20.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{14}N_2NaO_3$ ([M + Na]$^+$), 353.0897, found 353.0904.



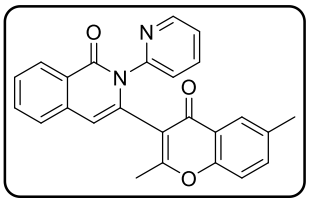
3-(7-Methoxy-2-methyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6ab)

yellow solid (49.2 mg, 60%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 7.9 Hz, 1H), 8.39 (d, J = 3.9 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.53 – 7.49 (m, 3H), 7.13 (dd, J = 6.9, 5.3 Hz, 1H), 6.87 (dd, J = 8.9, 2.1 Hz, 1H), 6.72 (d, J = 2.0 Hz, 1H), 6.51 (s, 1H), 3.84 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 166.7, 164.1, 163.3, 157.4, 152.4, 148.8, 137.9, 137.0, 135.3, 132.8, 128.3, 127.3, 127.3, 126.3, 126.2, 124.4, 123.8, 118.8, 116.5, 114.5, 108.9, 100.2, 55.9, 20.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{18}N_2NaO_4$ ([M + Na]$^+$), 433.1159, found 433.1170.



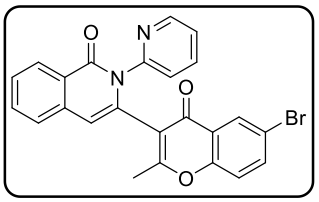
3-(2,7-Dimethyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6ac)

yellow solid (63.8 mg, 81%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 7.8 Hz, 1H), 8.39 (d, J = 3.2 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.53 – 7.49 (m, 3H), 7.13 – 7.10 (m, 3H), 6.52 (s, 1H), 2.48 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 167.0, 163.3, 155.8, 152.4, 148.8, 145.2, 137.9, 137.0, 135.3, 132.8, 128.3, 127.3, 126.8, 126.3, 126.2, 125.7, 124.4, 123.8, 120.4, 118.9, 117.6, 109.0, 21.8, 20.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{18}N_2NaO_3$ ([M + Na]$^+$), 417.1210, found 417.1221.



3-(2,6-Dimethyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6ad)

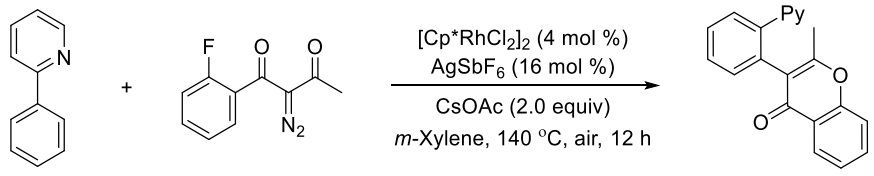
yellow solid (51.2 mg, 65%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 8.0 Hz, 1H), 8.38 (dd, J = 4.7, 0.9 Hz, 1H), 7.80 (s, 1H), 7.68 – 7.62 (m, 2H), 7.54 – 7.48 (m, 3H), 7.38 (dd, J = 8.5, 1.6 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.14 – 7.10 (m, 1H), 2.49 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 167.1, 163.3, 154.0, 152.4, 148.8, 137.9, 137.0, 135.3, 135.3, 135.0, 132.8, 128.3, 127.3, 126.3, 126.2, 125.2, 124.3, 123.8, 122.3, 118.9, 117.5, 109.0, 20.9, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{18}N_2NaO_3$ ([M + Na]$^+$), 417.1210, found 417.1211.



3-(6-Bromo-2-methyl-4-oxo-4*H*-chromen-3-yl)-2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (6ae)

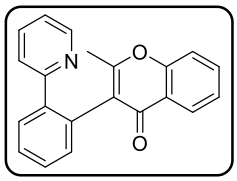
yellow solid (38.5 mg, 42%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, J = 7.8 Hz, 1H), 8.38 (dd, J = 4.8, 1.1 Hz, 1H), 8.14 (d, J = 2.3 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.52 (dd, J = 16.2, 7.9 Hz, 3H), 7.23 (d, J = 8.9 Hz, 1H), 7.15 (dd, J = 7.0, 5.2 Hz, 1H), 6.51 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 167.7, 163.3, 154.5, 152.3, 148.8, 138.0, 136.9, 136.8, 134.7, 132.9, 128.6, 128.4, 127.5, 126.4, 126.3, 124.4, 124.1, 123.9, 119.8, 119.3, 118.8, 109.1, 20.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{15}BrN_2NaO_3$ ([M + Na]$^+$), 481.0158, found 481.0169.

Procedure for preparation of 7a



5 **2a** **7a**

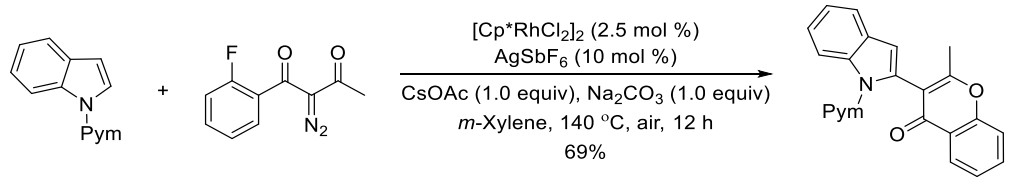
Synthesis of Product 7a: A pressure tube was charged with **5** (31.0 mg, 0.2 mmol), **2a** (82.5 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (5.0 mg, 4 mol %), $AgSbF_6$ (11.0 mg, 16 mol %), CsOAc (76.8 mg, 0.4 mmol) and anhydrous *m*-Xylene (2.0 mL). The reaction mixture was stirred at 140 °C for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 1:1 (v/v) to give the corresponding product **7a** (28.2 mg, 45%).



2-Methyl-3-(2-(pyridin-2-yl)phenyl)-4*H*-chromen-4-one (7a)

yellow solid (28.2 mg, 45%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, J = 4.8 Hz, 1H), 8.22 (dd, J = 8.0, 1.4 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.64 – 7.61 (m, 1H), 7.53 – 7.50 (m, 1H), 7.49 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 7.29 (t, J = 8.4 Hz, 2H), 7.10 (dd, J = 7.4, 5.0 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 164.1, 159.1, 156.1, 149.5, 141.5, 136.1, 133.4, 131.8, 131.5, 130.18, 128.8, 128.7, 126.4, 124.9, 123.9, 123.3, 121.9, 117.8, 19.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{15}NNaO_2$ ($[M + Na]^+$), 336.0995, found 336.0999.

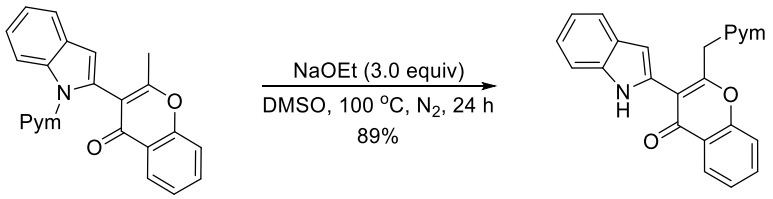
III. Preparation of 3aa in Gram Scale



1a (5.12 mmol 1.0 g) **2a** **3aa** (1.24 g)

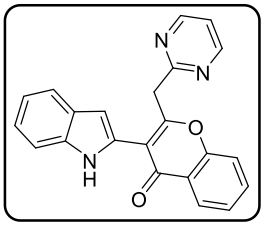
A pressure tube was charged with **1a** (1.0 g, 5.12 mmol), **2a** (2.1 g, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (79.2 mg, 2.5 mol %), $AgSbF_6$ (176.0 mg, 10 mol %), CsOAc (983.4 mg, 1.0 equiv.), Na_2CO_3 (543.0 mg, 1.0 equiv.) and anhydrous *m*-Xylene (30.0 mL). The reaction mixture was stirred at 140 °C for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 5:1 (v/v) to give the corresponding product **3aa** (1.24 g, 69%).

IV. Derivatization of 3aa



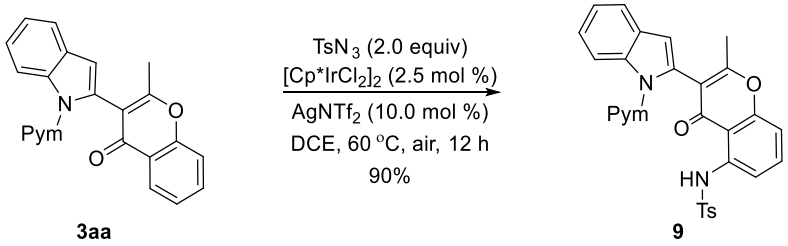
3aa **8**

A pressure tube was charged with **3aa** (70.7 mg, 0.2 mmol), NaOAc (40.8 mg) and anhydrous DMSO (2 mL). The reaction mixture was stirred at 100 °C for 24 h under N_2. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 1:1 (v/v) to give the corresponding product **8** (62.9 mg, 89%).



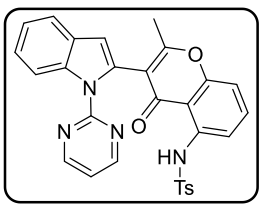
3-(1*H*-indol-2-yl)-2-(pyrimidin-2-ylmethyl)-4*H*-chromen-4-one (8)

yellow solid (62.9 mg, 89%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.78 (d, J = 4.9 Hz, 2H), 8.27 (d, J = 7.4 Hz, 1H), 7.63 (t, J = 9.0 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.27 (t, J = 5.1 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.82 (s, 1H), 4.68 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 166.7, 162.7, 157.8, 155.7, 136.2, 133.8, 129.3, 128.2, 126.3, 125.3, 123.3, 122.2, 120.7, 119.79, 119.7, 117.9, 116.9, 111.3, 104.5, 43.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{15}N_3NaO_2$ ([M + Na]$^+$), 376.1056, found 376.1062.



3aa **9**

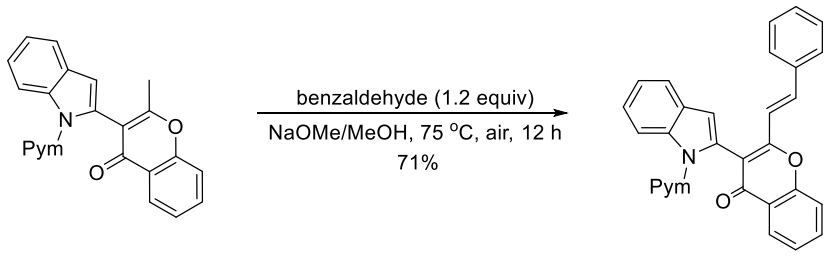
To a solution of **3aa** (70.7 mg, 0.2 mmol) in DCE (2 mL) was added TsN_3 (78.9 mg, 0.4 mmol), $[Cp^*IrCl_2]_2$ (4 mg, 2.5 mol %), $AgNTf_2$ (7.8 mg, 10.0 mol %) and the mixture was stirred at 60 °C for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 2:1 (v/v) to give the corresponding product **9** (94.0 mg, 90 %).



4-Methyl-*N*-(2-methyl-4-oxo-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-4*H*-chromen-5-yl)benzenesulfonamide (9)

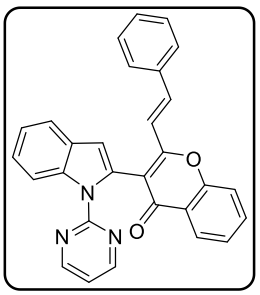
yellow solid (94.0 mg, 90%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.52 (d, J = 4.8 Hz, 2H), 7.93 (dd, J = 7.9, 1.3 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.45 (dd, J = 14.8, 8.1 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.05 (t, J = 4.8 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.57 (s, 1H), 2.39 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 164.9, 157.9, 156.6, 155.9, 142.9, 136.9, 133.6, 133.5, 131.2, 129.3, 129.2, 126.3, 126.1, 125.0,

123.3, 122.7, 122.6, 122.1, 119.2, 118.2, 117.8, 117.76, 110.7, 21.5, 19.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{22}N_4NaO_4S$ ([M + Na]$^+$), 545.1254, found 545.1255.



3aa **10**

Sodium (27.6 mg, 1.2 mmol) was gradually added to dry methanol (2 mL) and the mixture was stirred until the solution reached room temperature. **3aa** (70.7 mg, 0.2 mmol) and benzaldehyde (25.6 mg, 0.24 mmol) were added and the resulting mixture was allowed to stir at reflux for 12 h. After this period, the solution was poured into iced water and the pH was adjusted to 4 with aqueous HCl. The solid was removed by filtration, taken up in DCM, and purified with silica gel chromatography (petroleum ether/ethyl acetate = 1:1) to give **10** (62.6 mg, 71%) as a yellow solid.

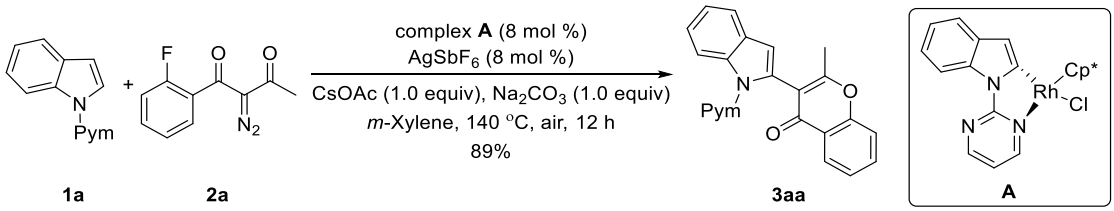


4(*E*)-3-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)-2-styryl-4*H*-chromen-4-one (10)

yellow solid (62.6 mg, 71%), ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.56 (d, J = 4.4 Hz, 2H), 8.52 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 6.6 Hz, 2H), 7.39 – 7.26 (m, 7H), 7.02 (t, J = 4.3 Hz, 1H), 6.77 (s, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 177.0, 158.8, 158.3, 156.0, 137.5, 136.9, 136.0, 134.2, 131.5, 130.0, 129.4, 129.3, 128.2, 126.3, 125.1, 124.2, 123.5, 122.3, 121.3, 120.0, 118.7, 118.2, 117.6, 115.1, 111.8, 100.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}N_3NaO_2$ ([M + Na]$^+$), 464.1369, found 464.1374.

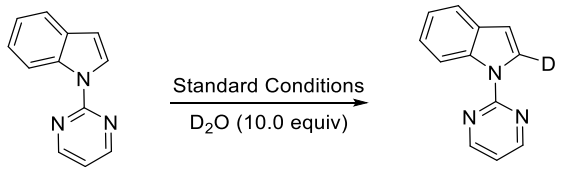
V. Mechanistic Studies

(1) Complex A



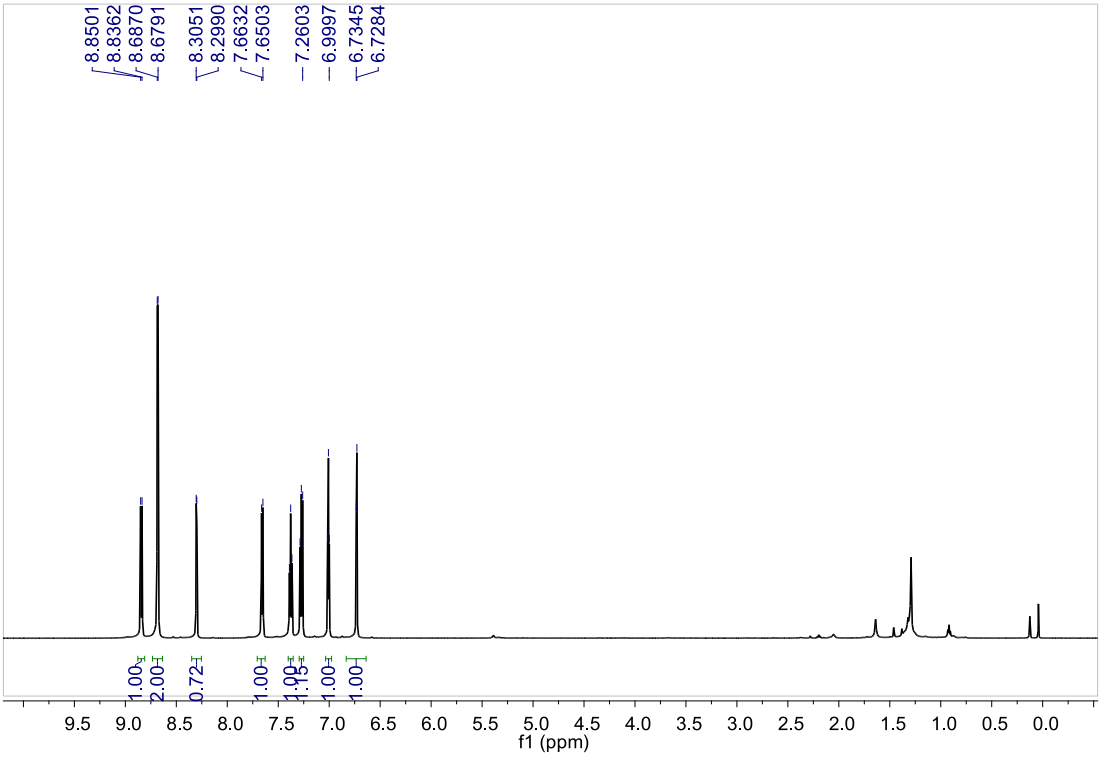
Rhodium Complex **A** was synthesized according to literature report.[5] **1a** (70.7 mg, 0.2 mmol), **2a** (82.5, 0.4 mmol), complex **A** (7.1 mg, 8 mol %), $AgSbF_6$ (5.5 mg, 8 mol %), CsOAc (38.4 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol), and *m*-Xylene (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 140 ºC for 12 h under air. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to yield product **3aa** (63.1 mg, 89%).

(2) H/D Exchange Experiments

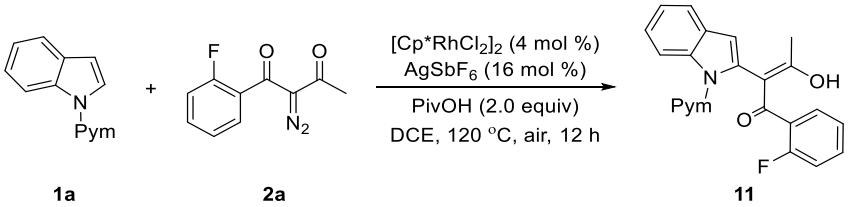


1a **1a**-d_1 (28%)

A pressure tube was charged with **1a** (70.7 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (5.0 mg, 2.5 mol %), $AgSbF_6$ (10.0 mg, 16 mol %), CsOAc (38.4 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol), D_2O (36 uL, 10.0 equiv.) and *m*-Xylene (2.0 mL). The reaction mixture was stirred at 140 °C for 12 h under air. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 5:1 (v/v) to give the corresponding product, and the extent of deuteration was obtained by ^1H NMR analysis.

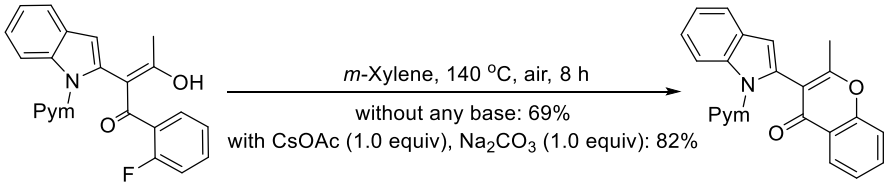


(3) Control Experiments



1a **2a** **11**

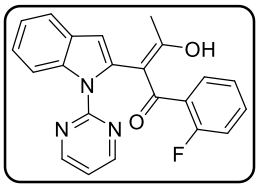
A pressure tube was charged with **1a** (39.0 mg, 0.2 mmol), **2a** (82.5 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (5.0 mg, 4 mol %), $AgSbF_6$ (11.0 mg, 16 mol %), PivOH (40.8 mg, 0.2 mmol), and anhydrous DCE (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 5:1 (v/v) to give the corresponding product **11** (52.2 mg, 70%).



11 **3aa**

11 (79.2 mg, 0.2 mmol) and anhydrous *m*-Xylene (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 140 °C for 8 h under air. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 5:1 (v/v) to give product **3aa** (48.7 mg, 69%).

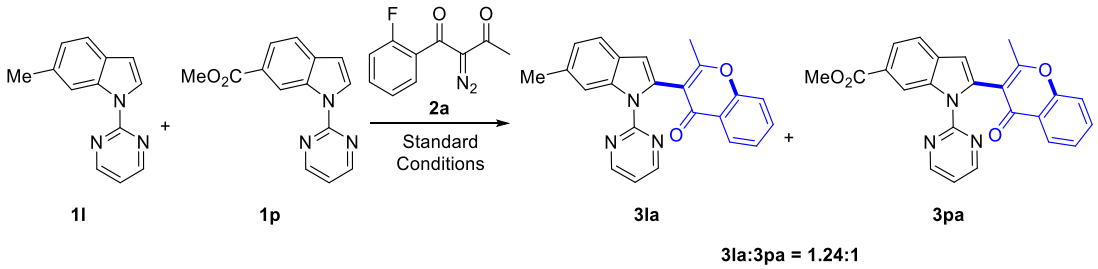
11 (79.2 mg, 0.2 mmol), CsOAc (38.4 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol) and anhydrous *m*-Xylene (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 140 °C for 8 h under air. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 5:1 (v/v) to give product **3aa** (57.9 mg, 82%).



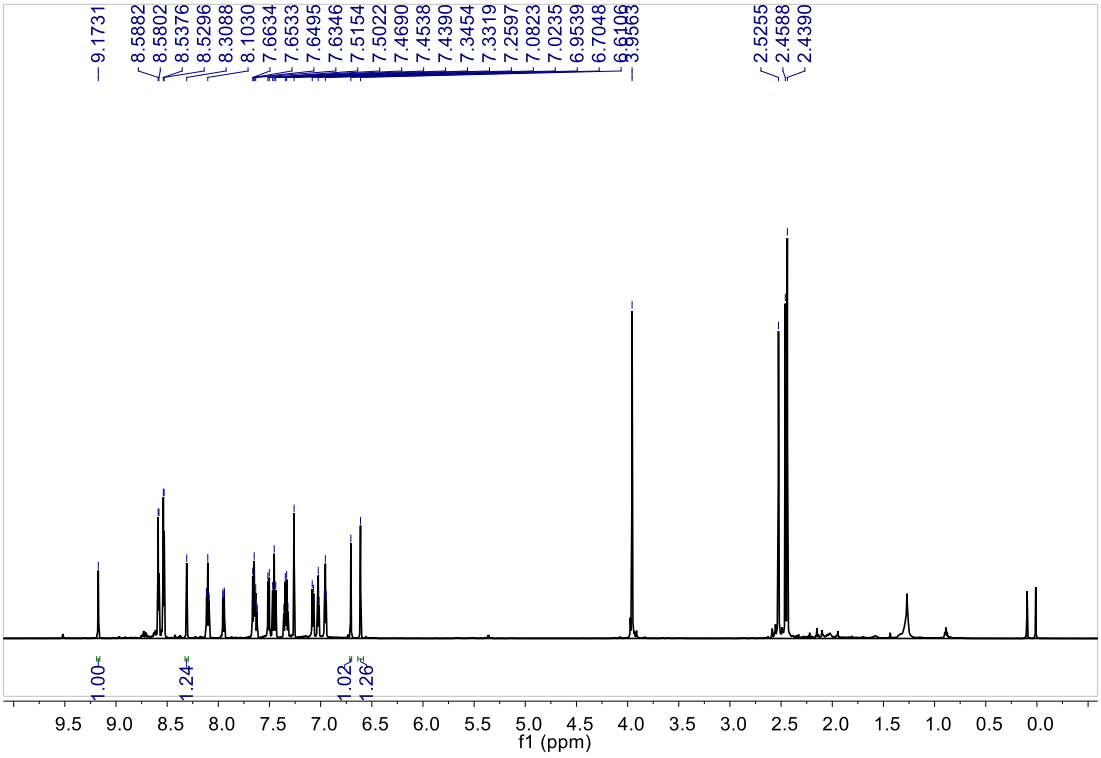
(*Z*)-1-(2-Fluorophenyl)-3-hydroxy-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)but-2-en-1-one (11)

brown solid (52.2 mg, 70%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, J = 4.7 Hz, 2H), 8.25 (d, J = 8.3 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.14 – 7.11 (m, 2H), 7.07 – 7.04 (m, 1H), 6.85 – 6.78 (m, 2H), 6.51 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.5, 177.9, 159.0 (J = 251.8 Hz), 158.0, 157.5, 136.3, 133.9, 131.5 (J = 8.2 Hz), 129.1 (J = 2.6 Hz), 128.8, 123.6, 123.5 (J = 3.3 Hz), 122.0, 120.5, 117.2, 115.7 (J = 21.5 Hz), 114.5, 111.0, 109.5, 27.1, 26.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{16}FN_3NaO_2$ ([M + Na]$^+$), 396.1119, found 396.1124.

(4) Competition experiment



A pressure tube was charged with **1l** (20.9 mg, 0.1 mmol), **1p** (25.4 mg, 0.1 mmol), **2a** (49.5 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (5.0 mg, 4 mol %), $AgSbF_6$ (11.0 mg, 16 mol %), CsOAc (38.4 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol) and anhydrous *m*-Xylene (2.0 mL). The reaction mixture was stirred at 140 ^oC for 12 h under air. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 2:1 (v/v) to afford product **3la** and **3pa**. The ratio of **3la**:**3pa** = 1.24:1 was determined on the basis of ^1H NMR analysis.



VI. References

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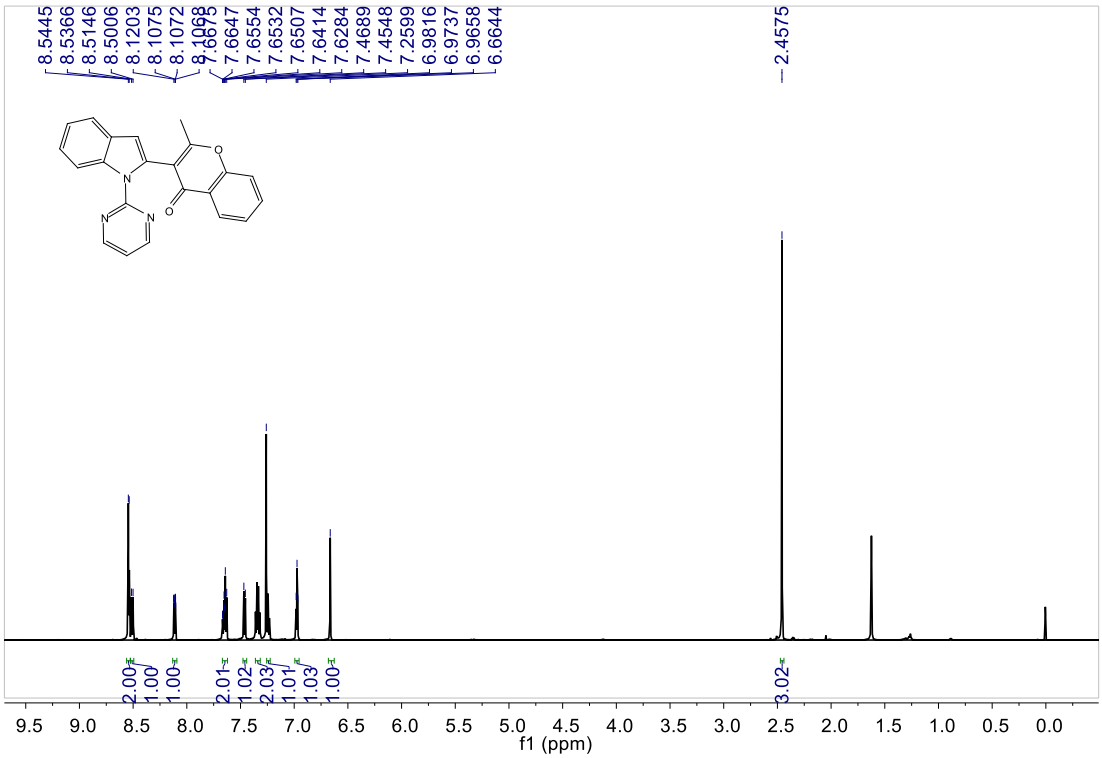
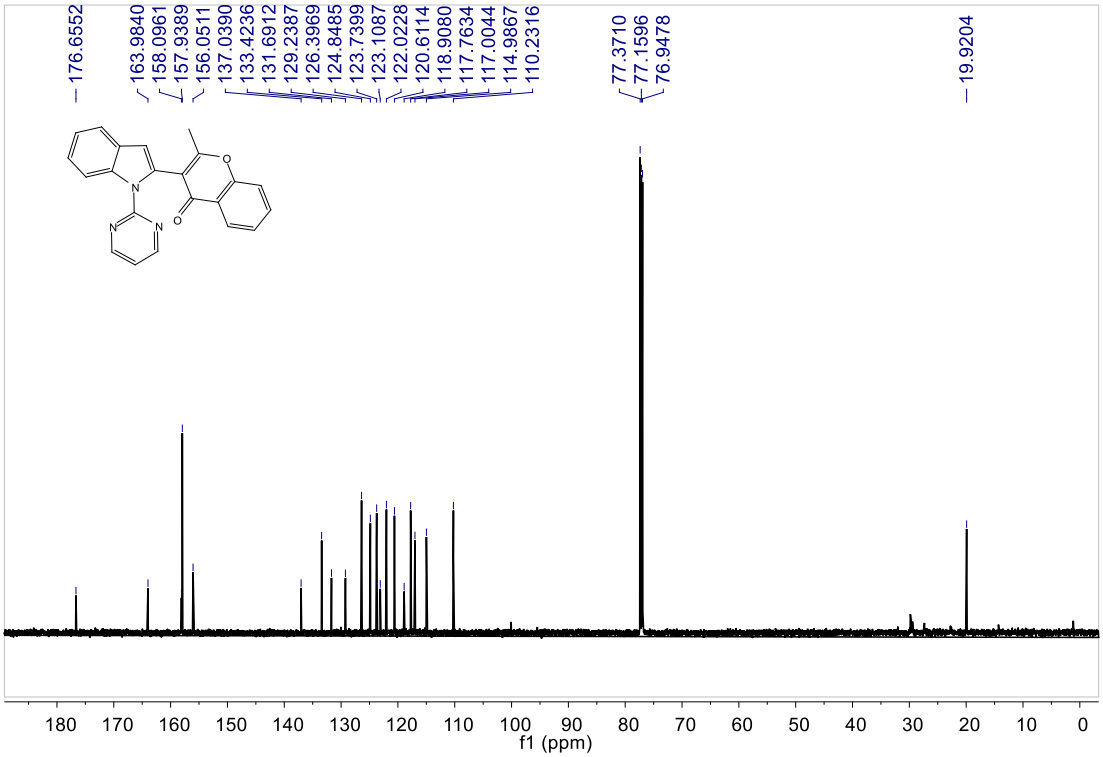
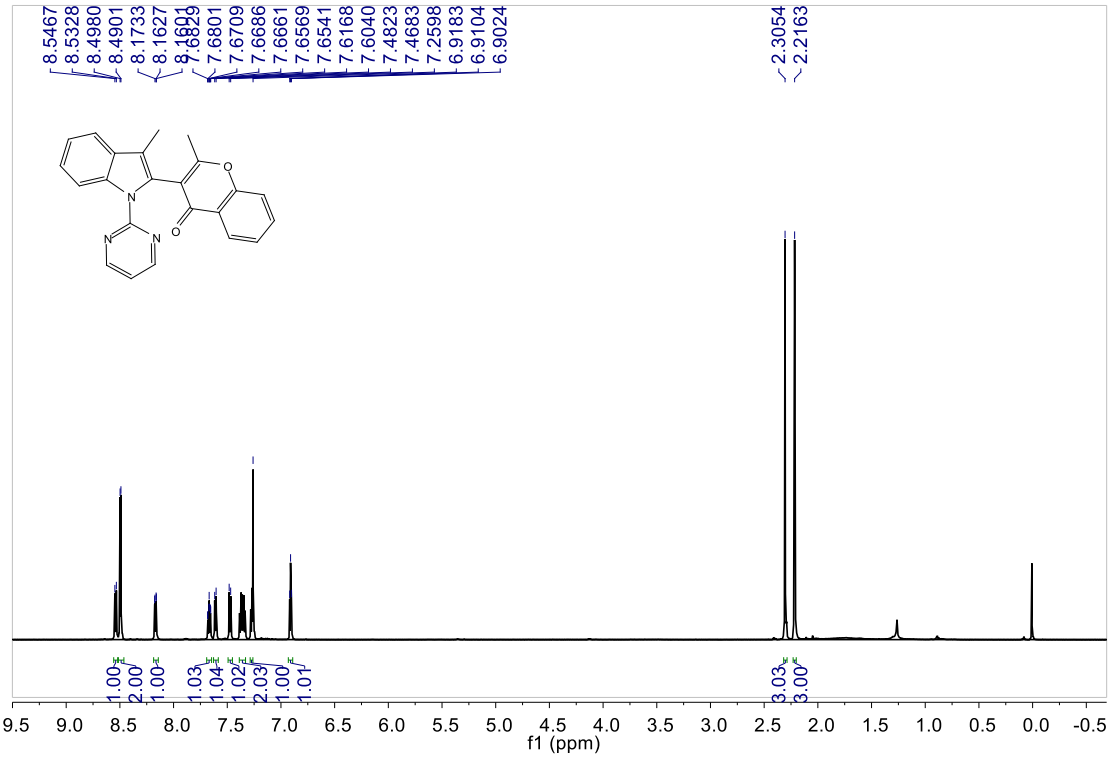
VII. ^{1}H, ^{13}C NMR Spectra of New Compounds



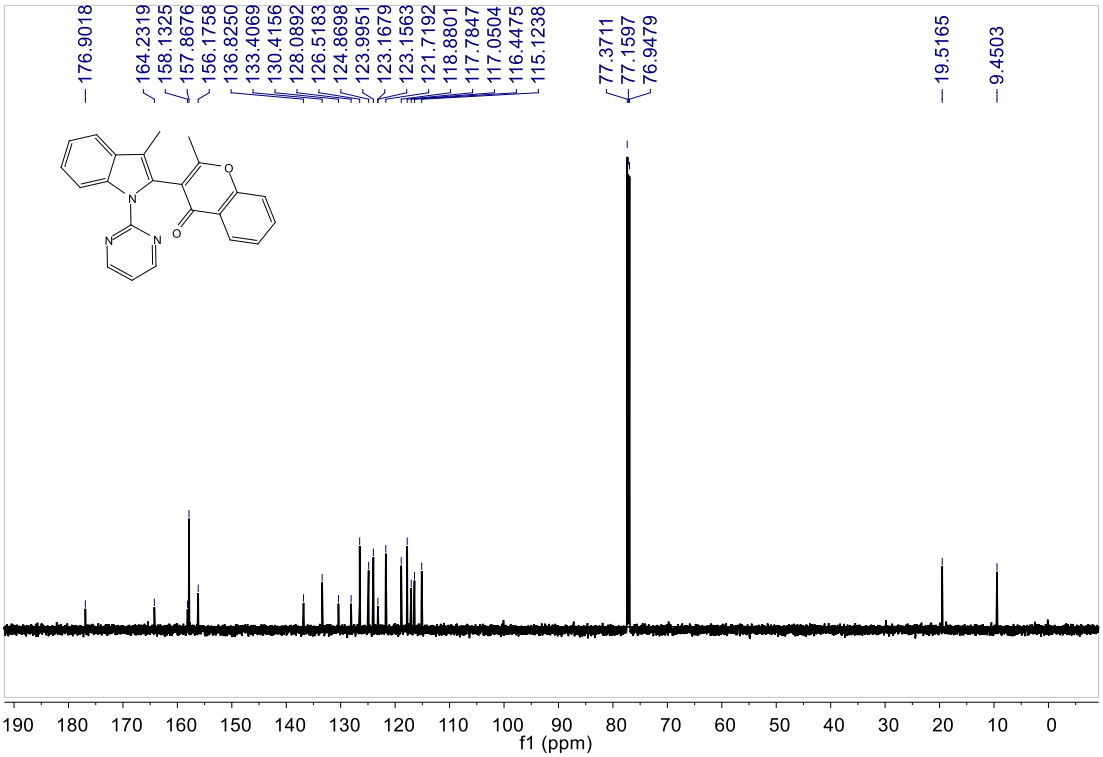
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3aa



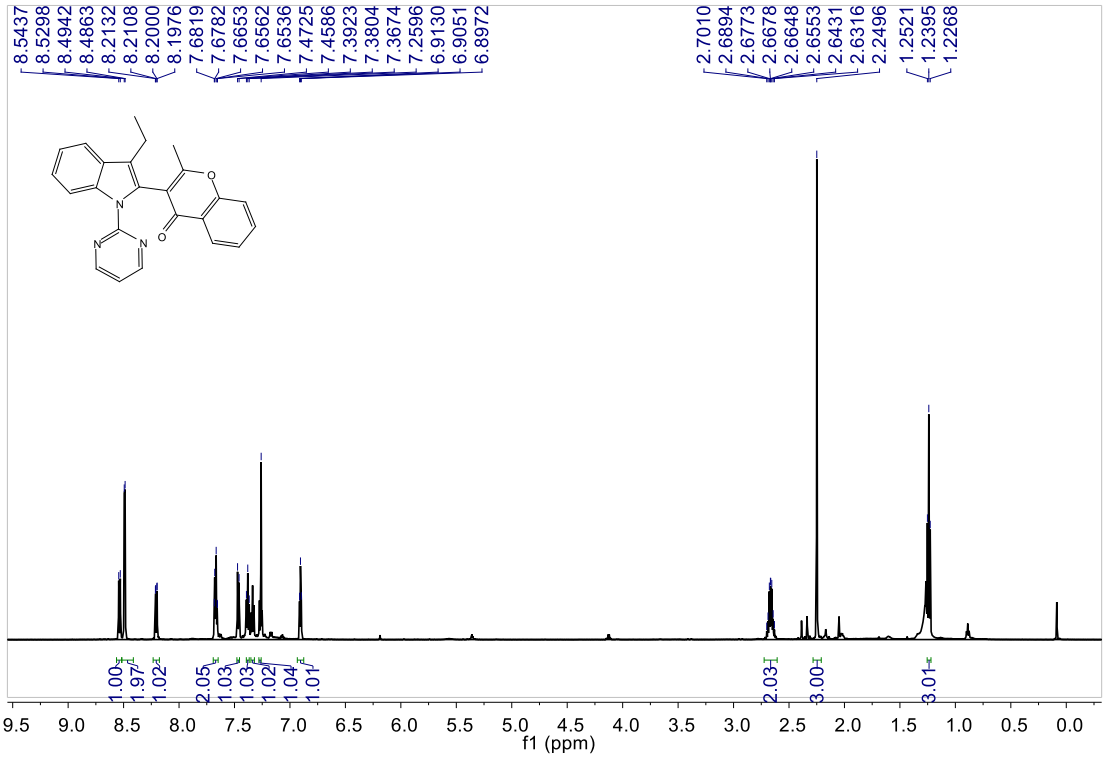
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3aa



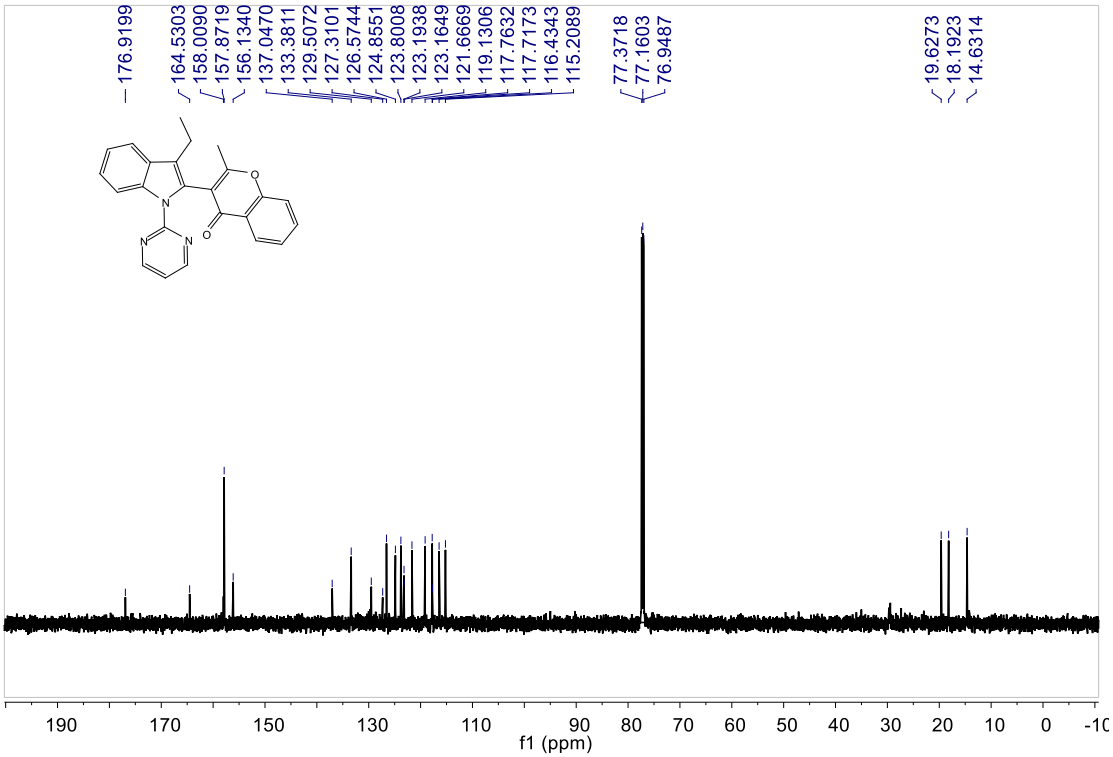
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ba



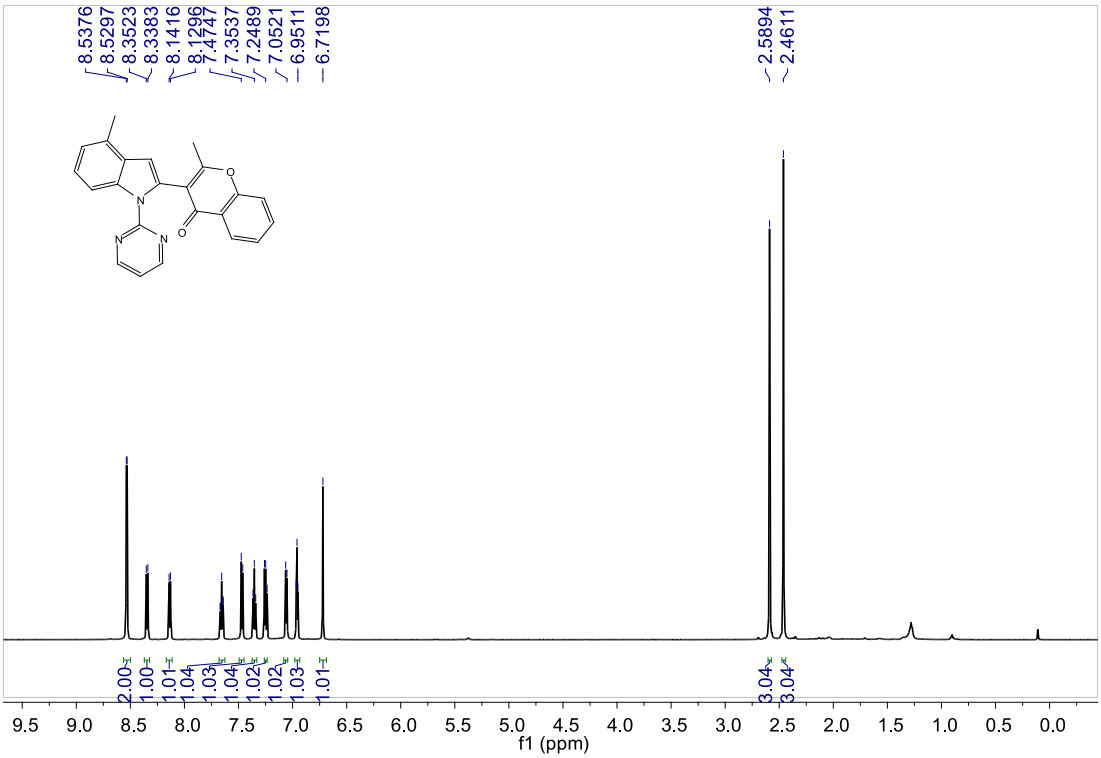
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ba



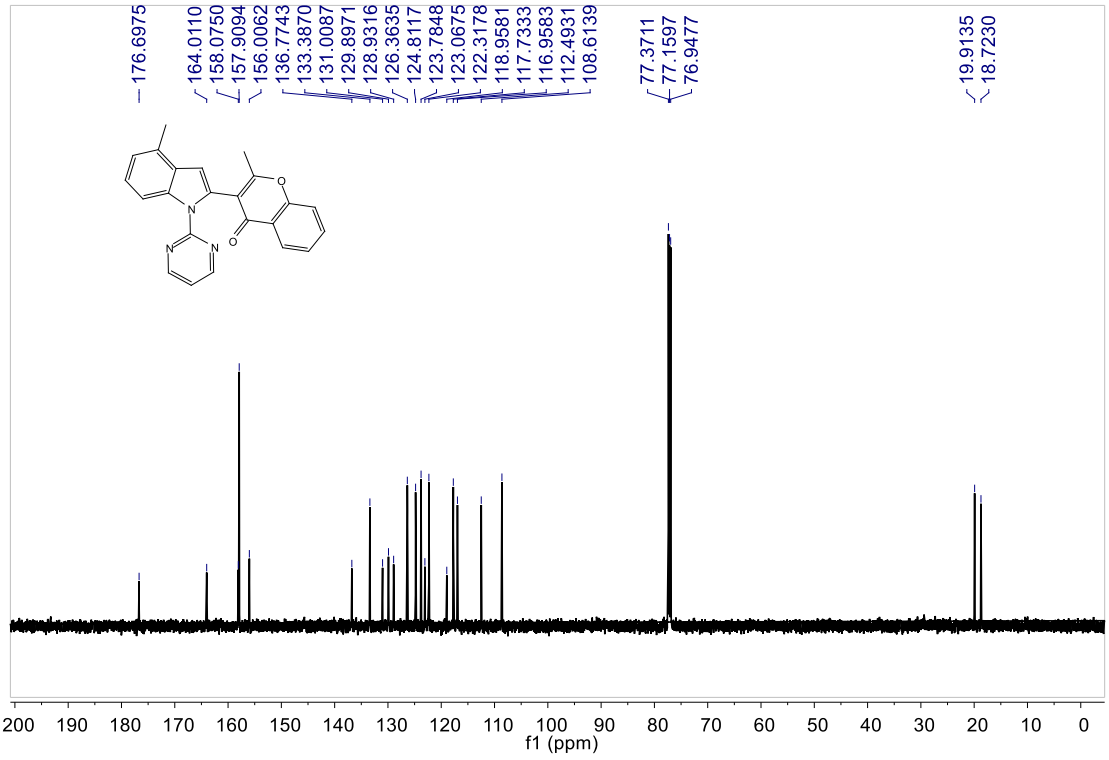
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ca



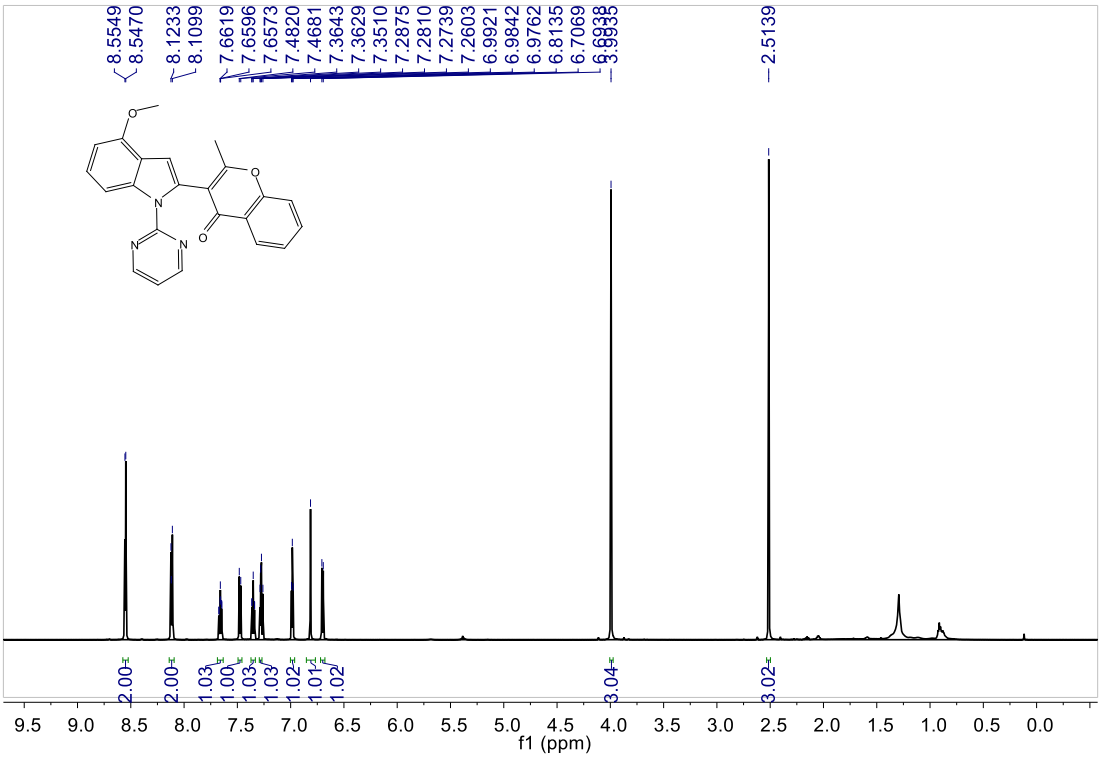
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ca



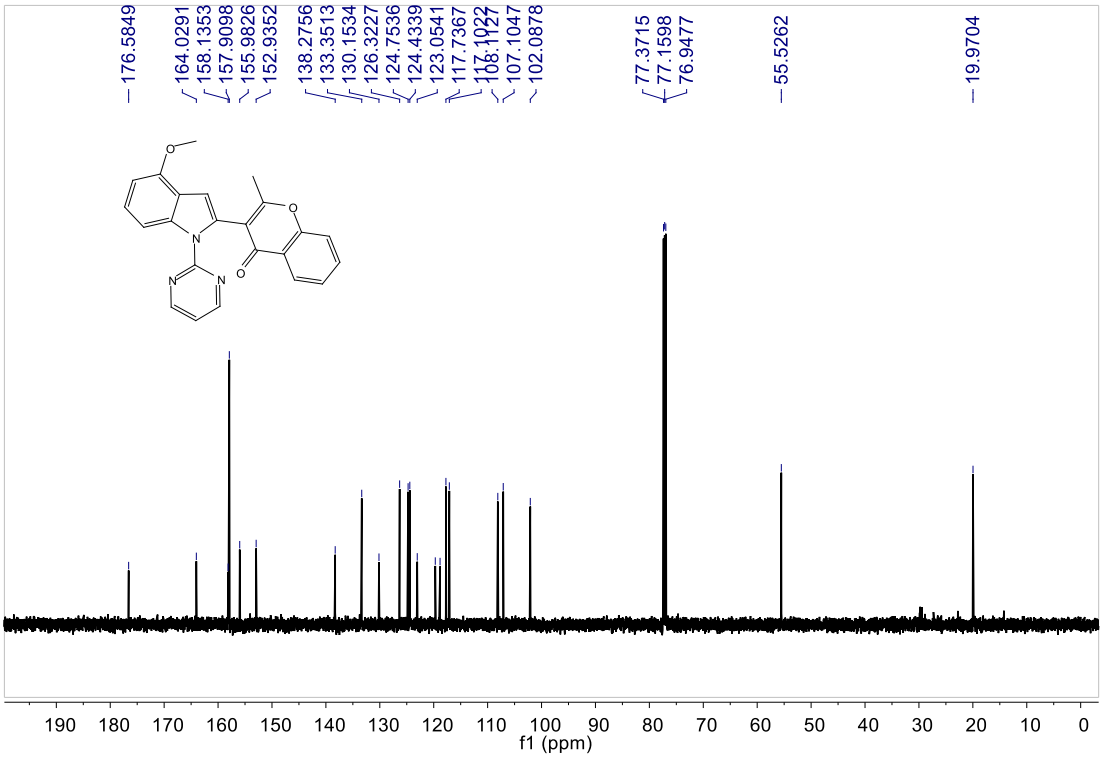
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3da



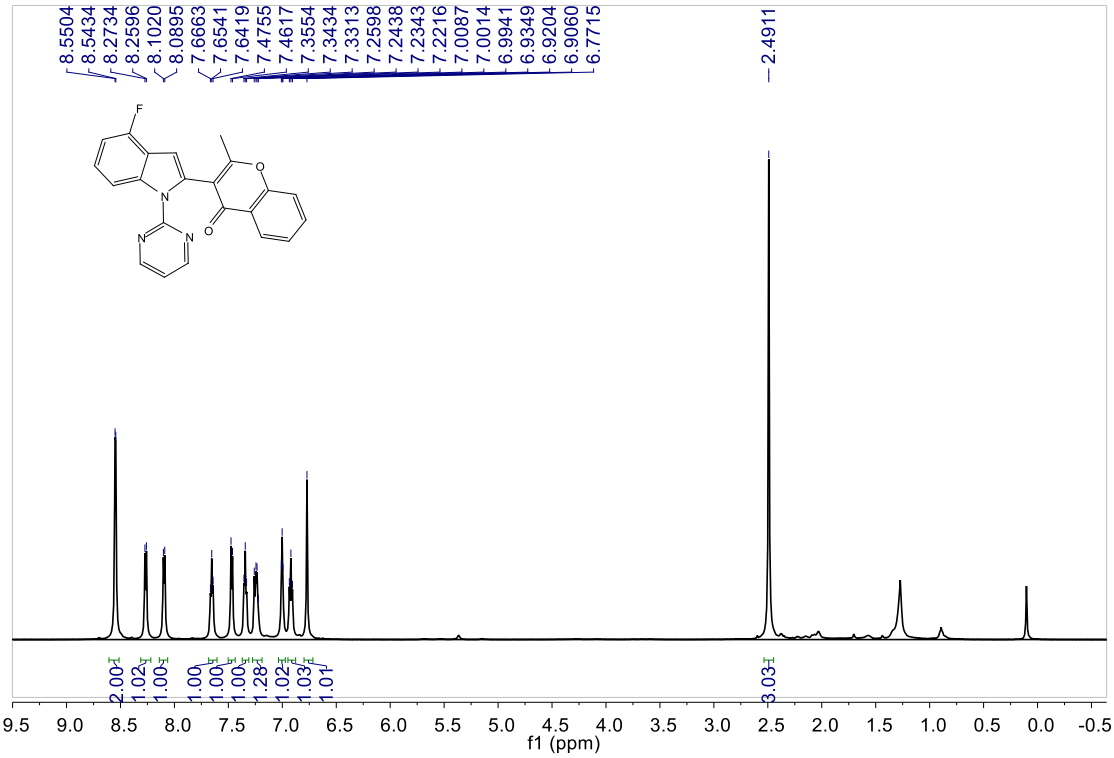
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3da



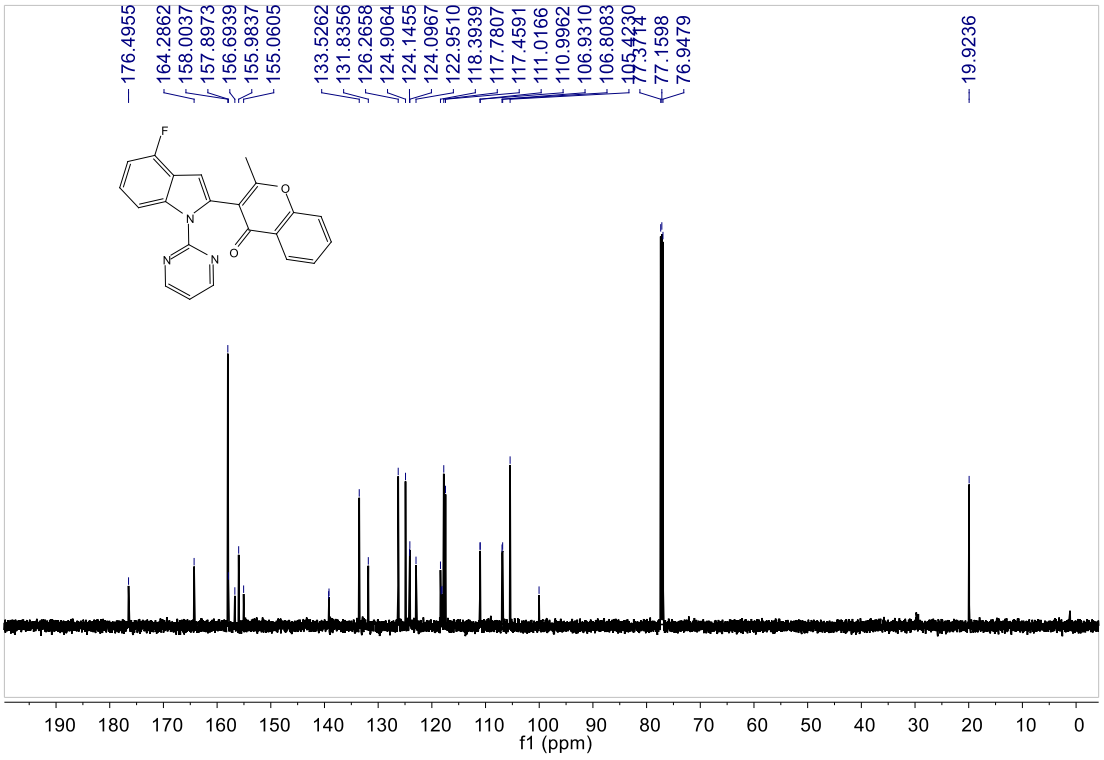
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ea



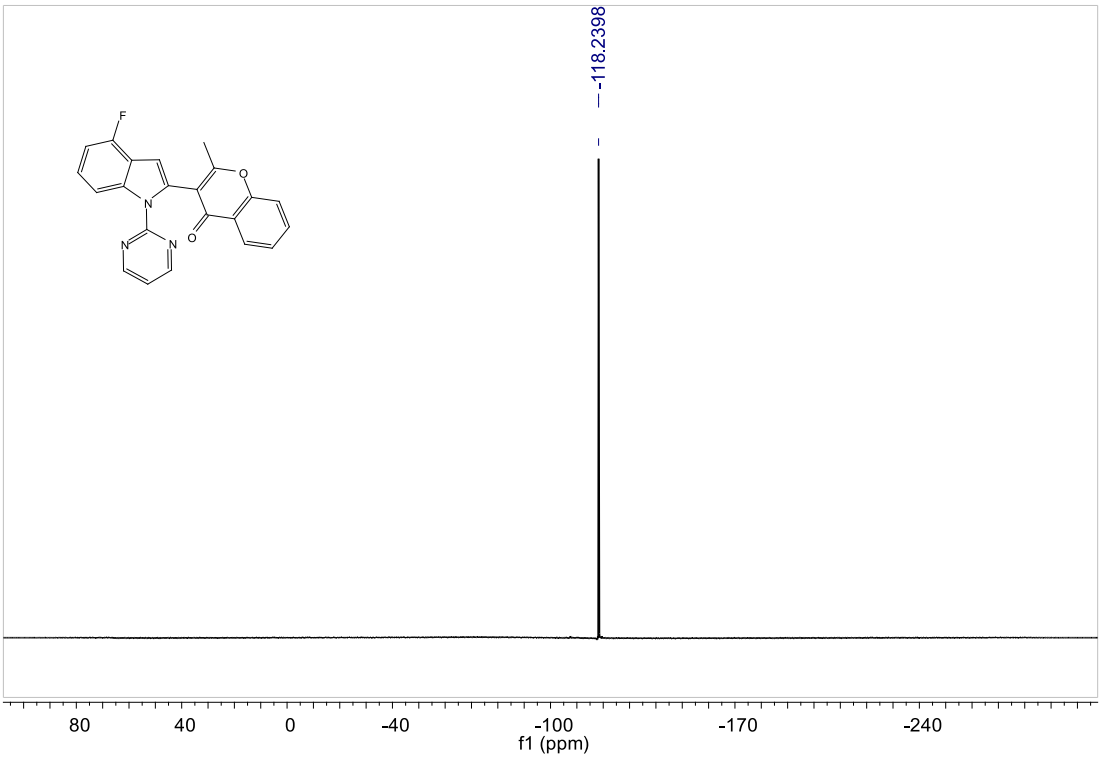
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ea



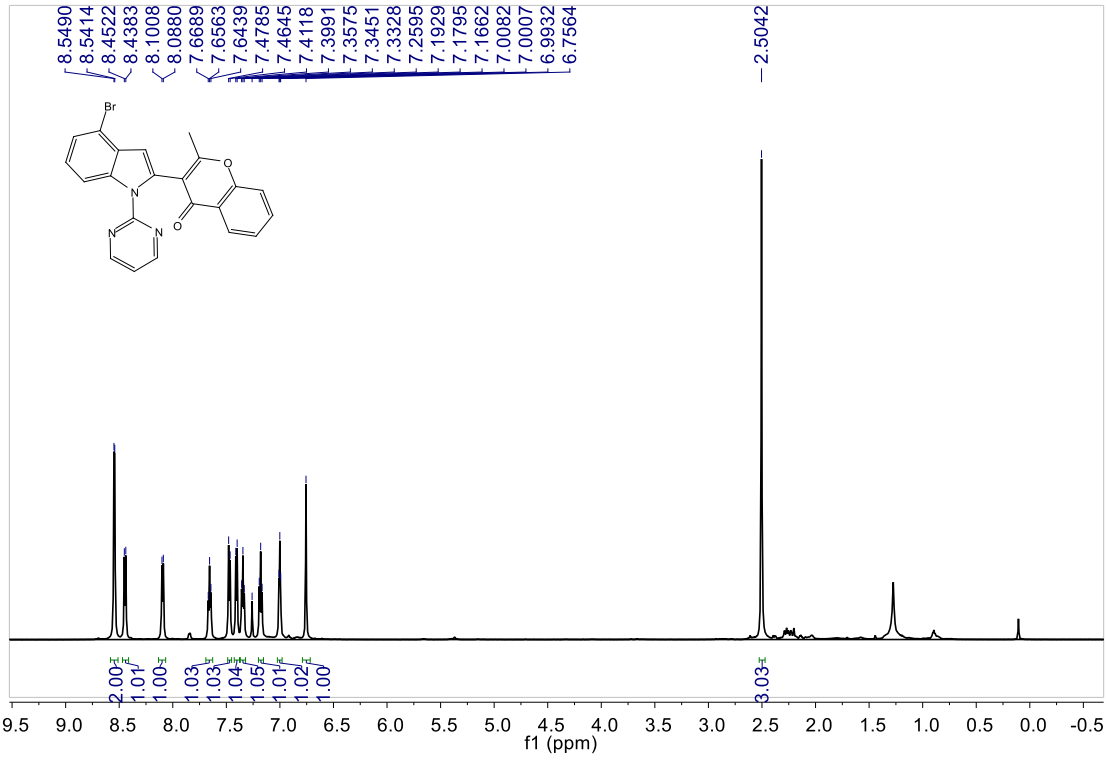
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3fa



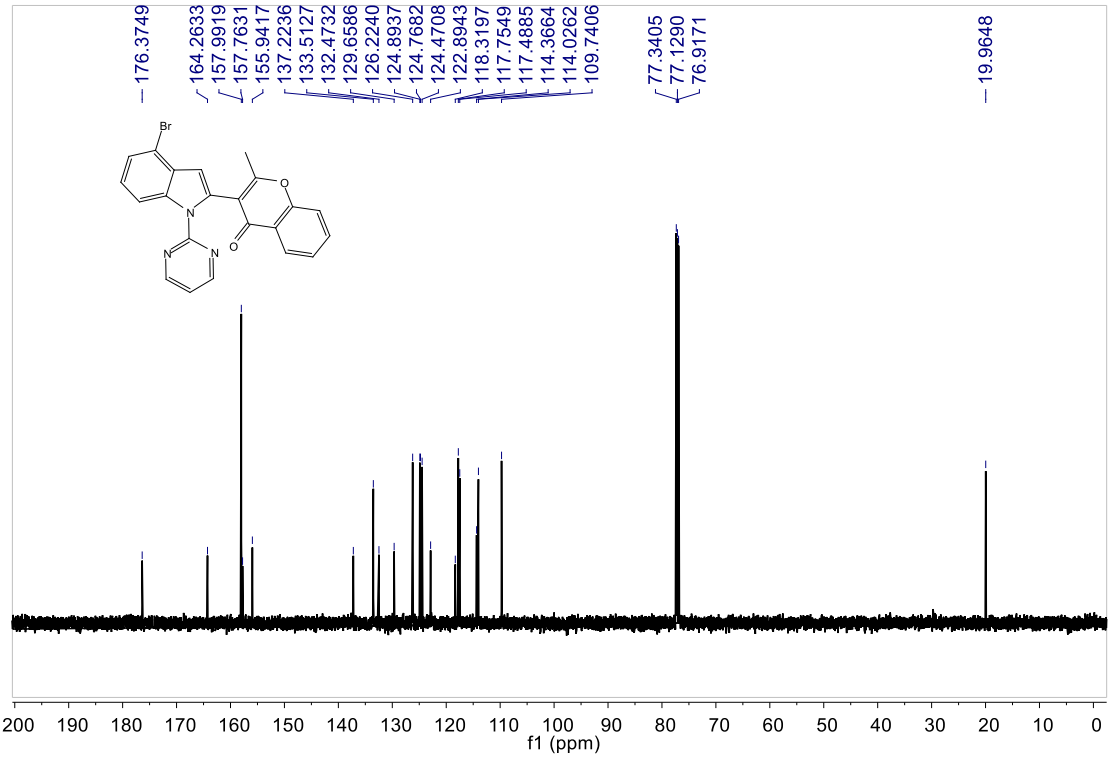
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3fa



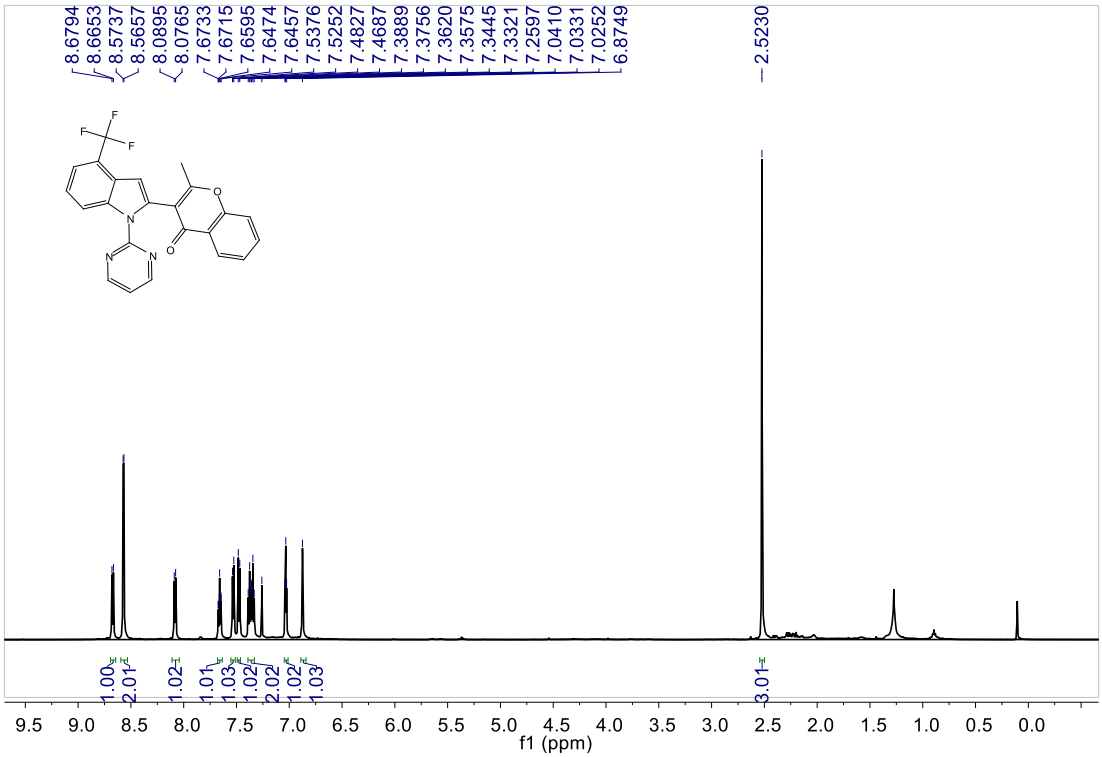
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3fa



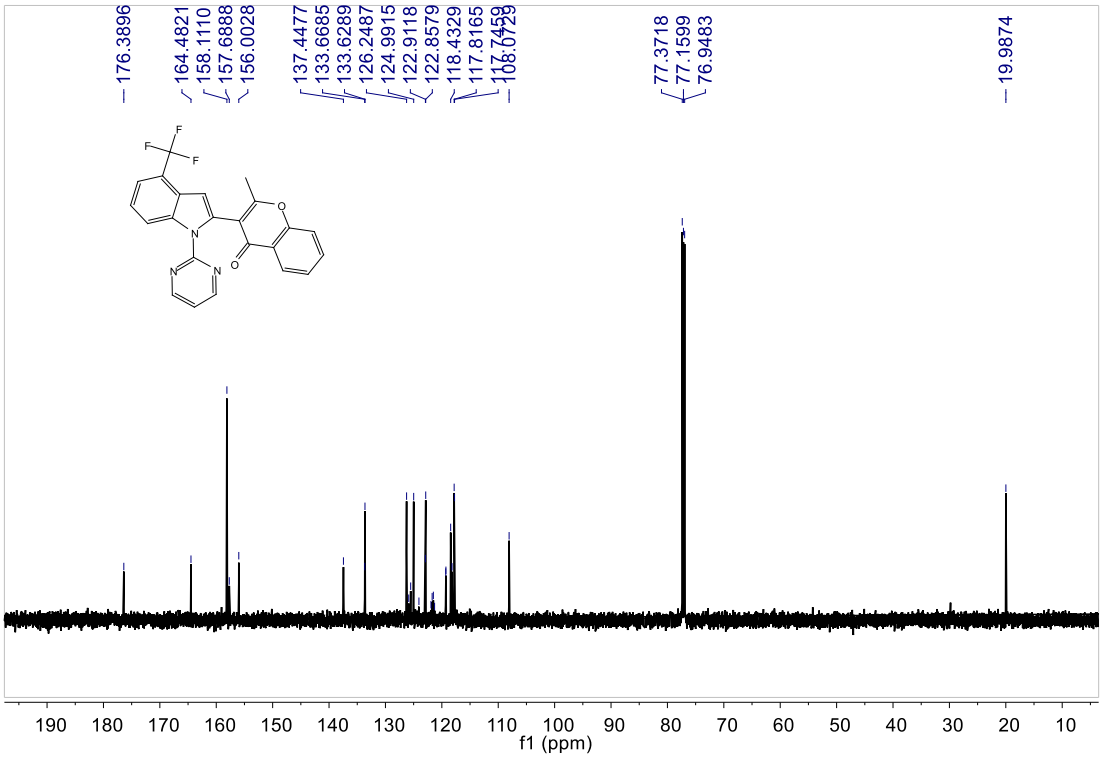
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ga



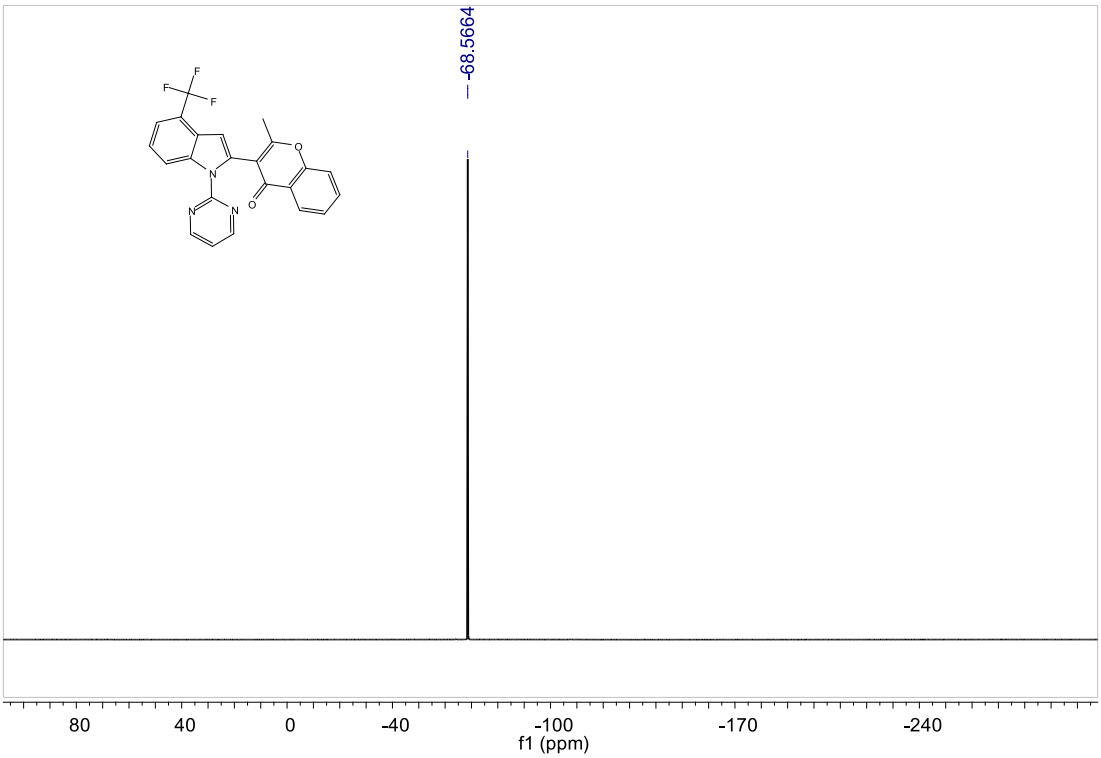
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ga



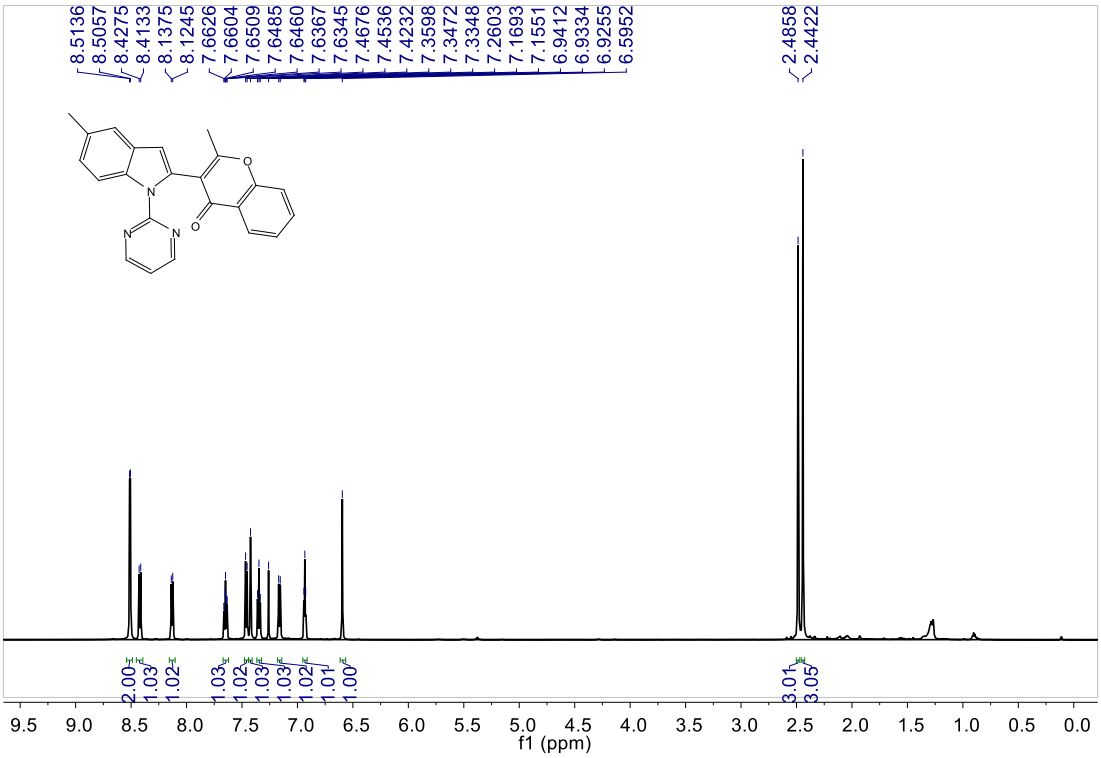
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ha



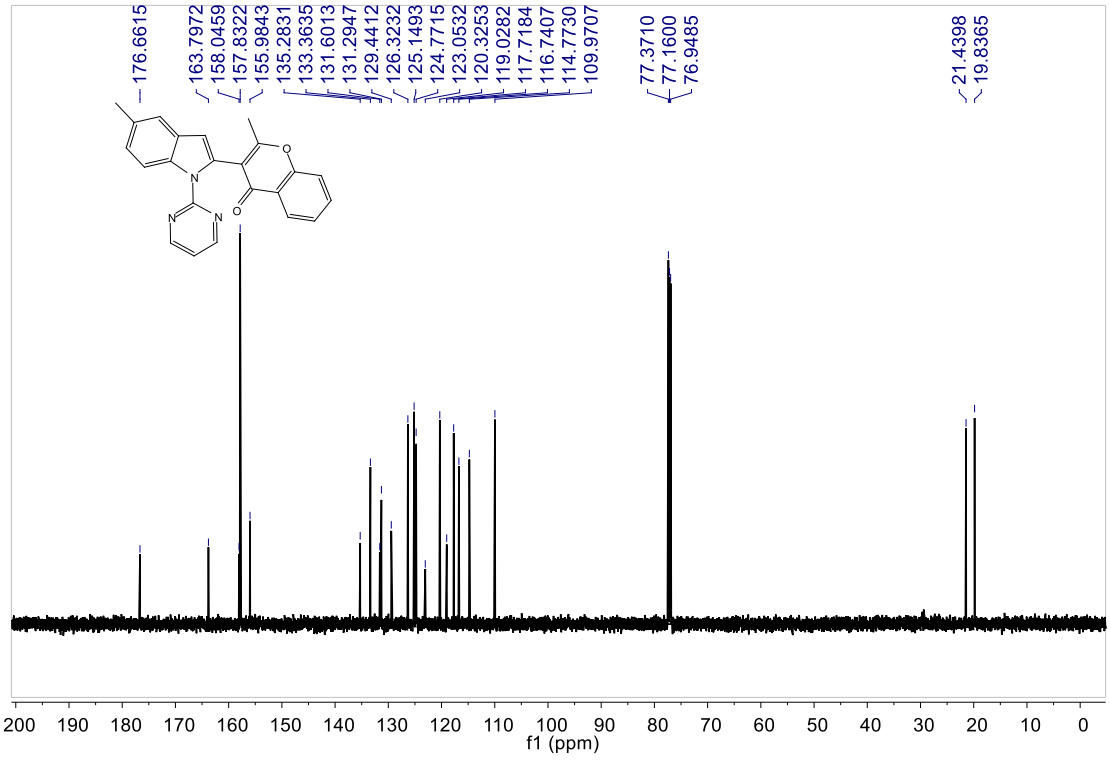
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ha



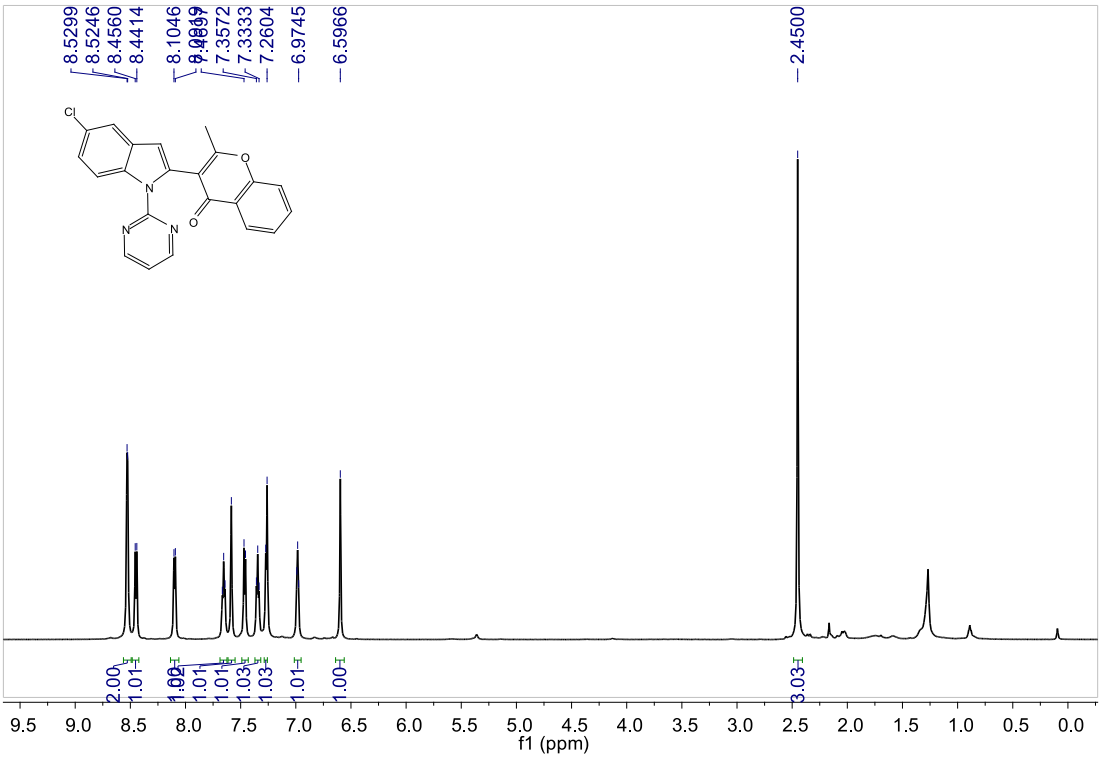
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ha



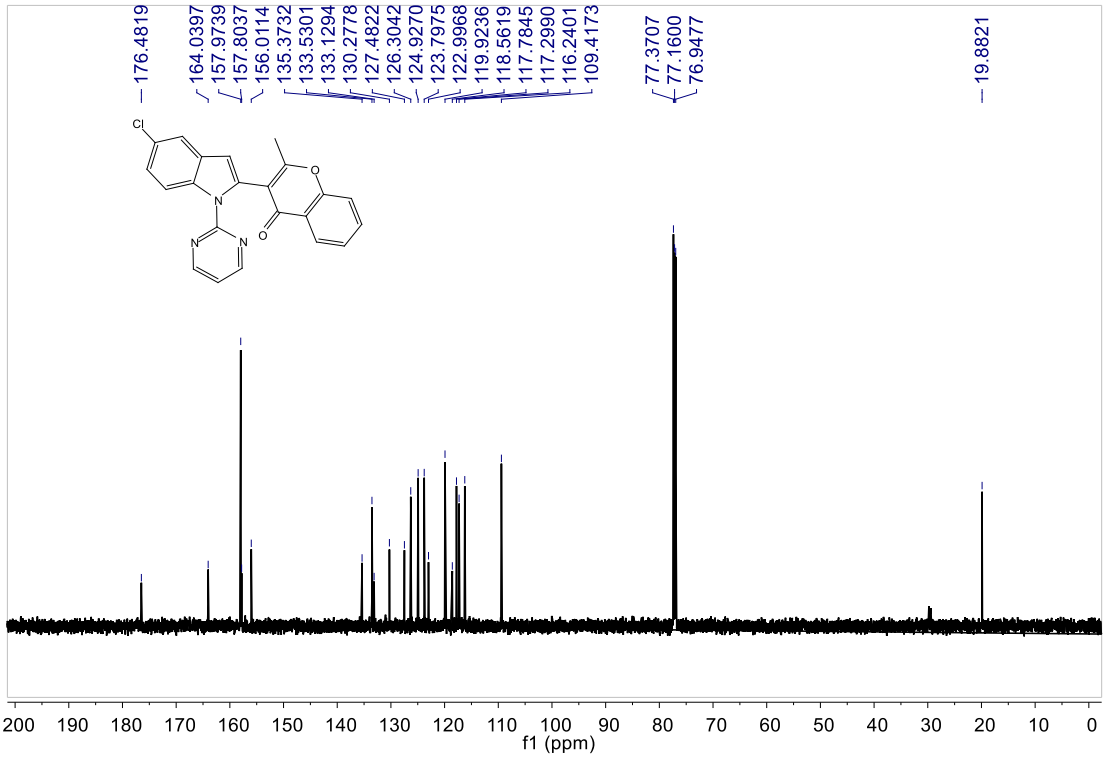
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ia



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ia



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ja



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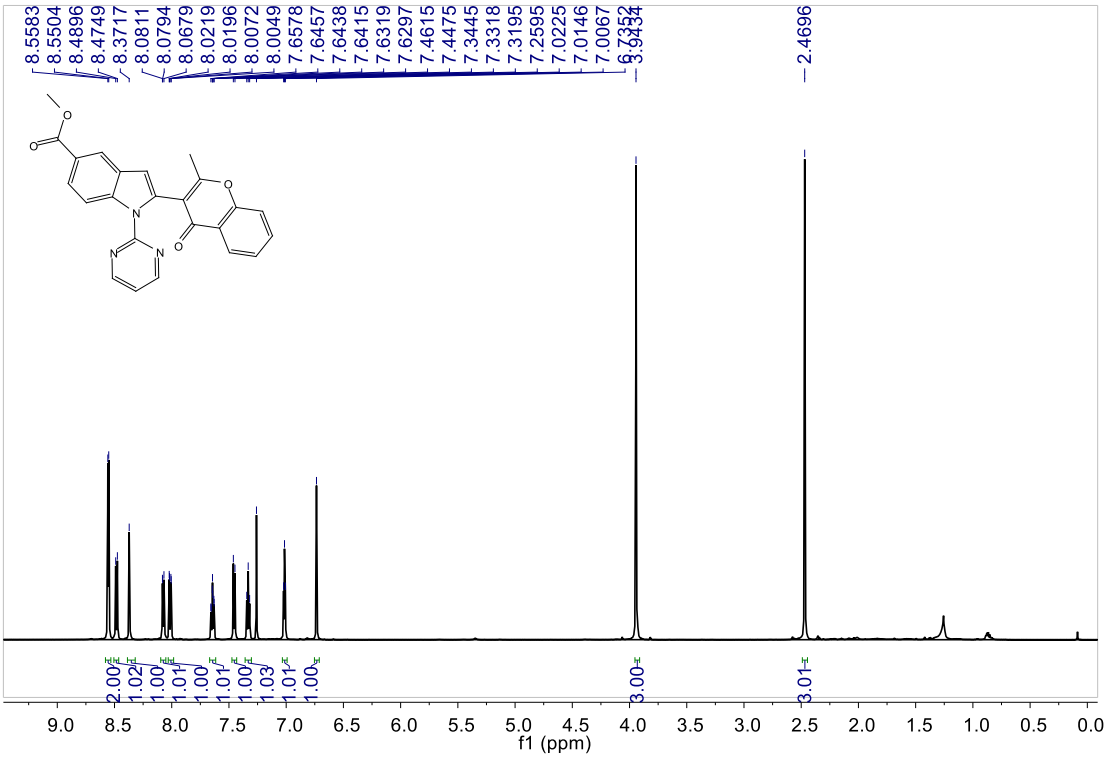
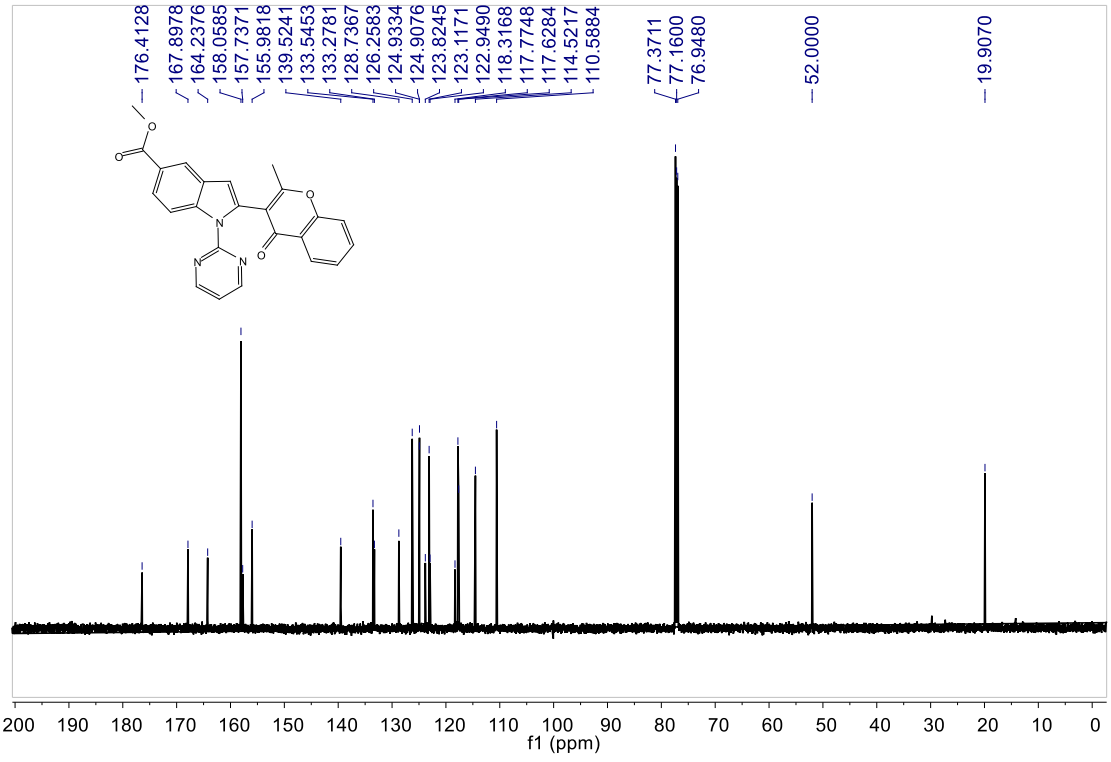
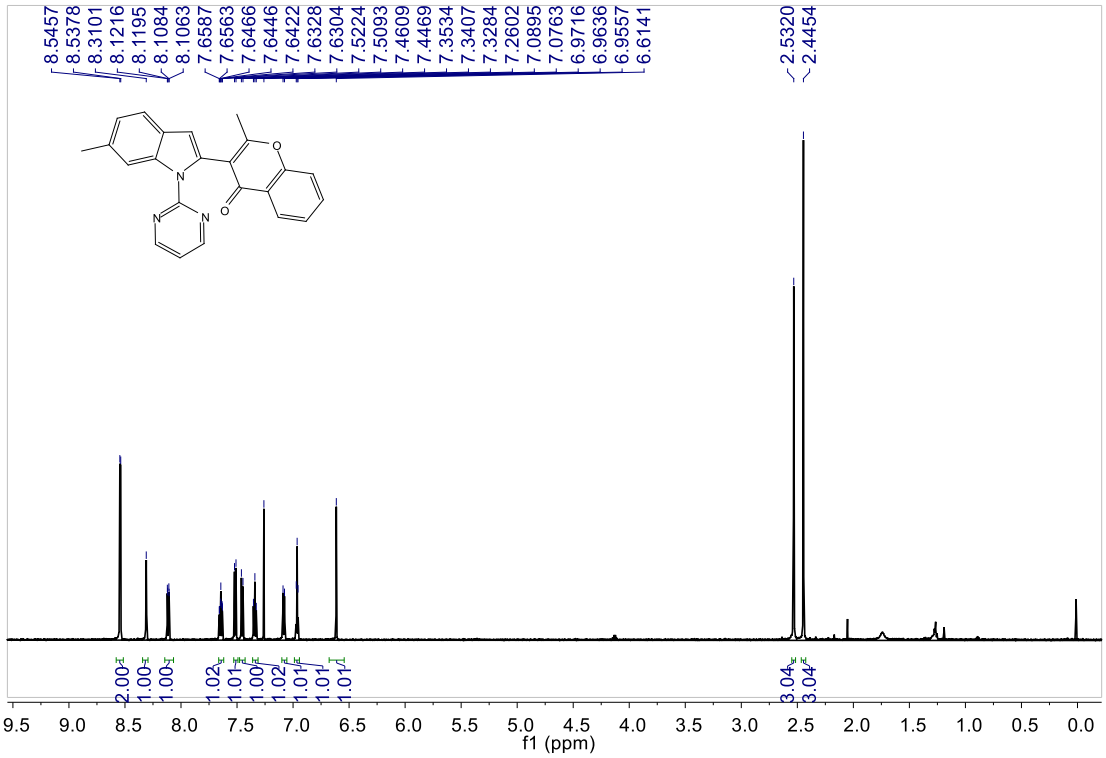


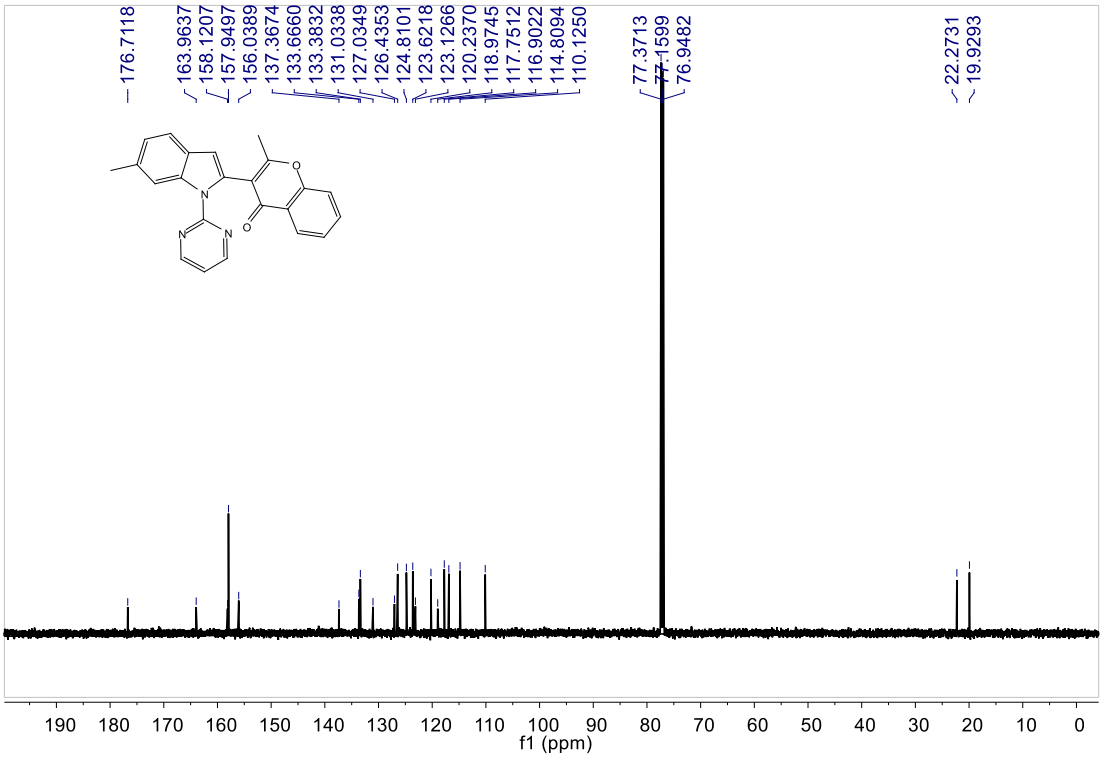
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ka



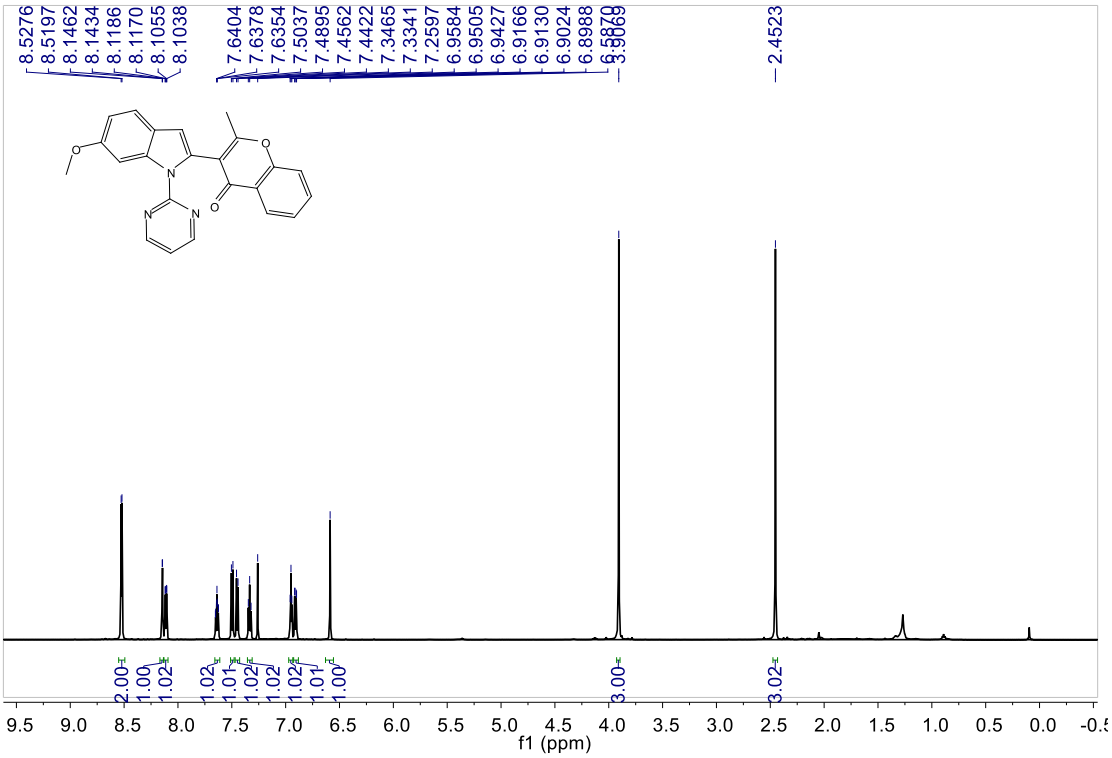
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ka



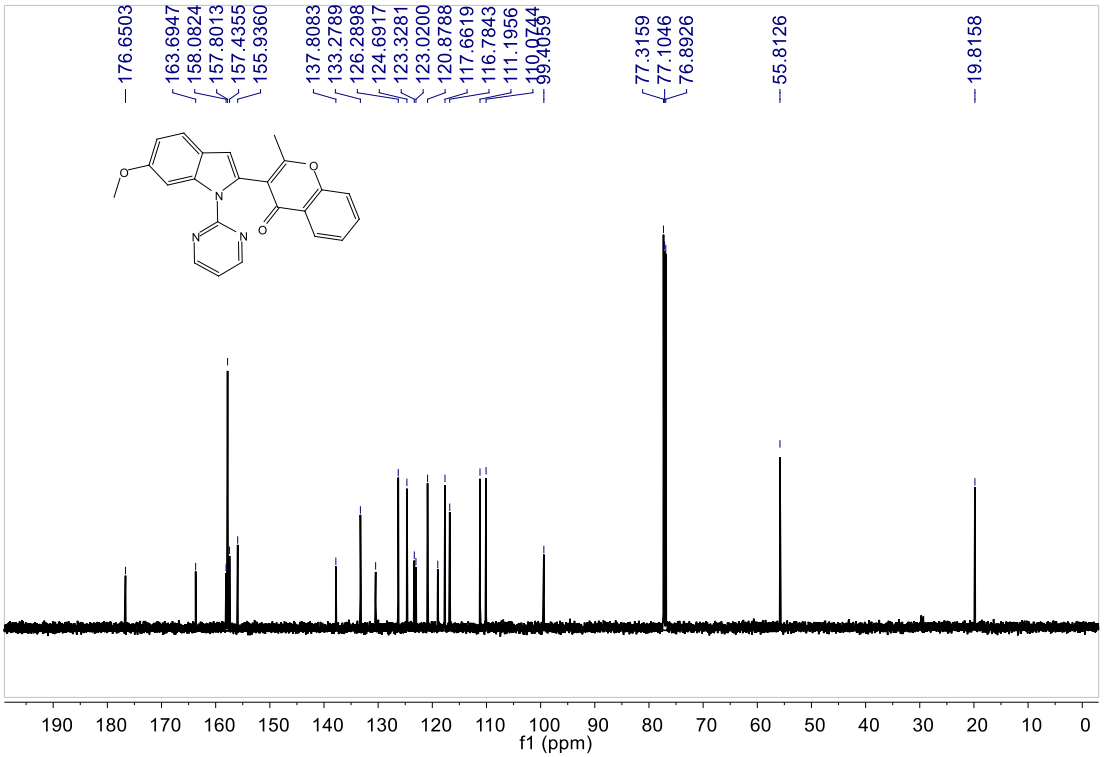
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3la



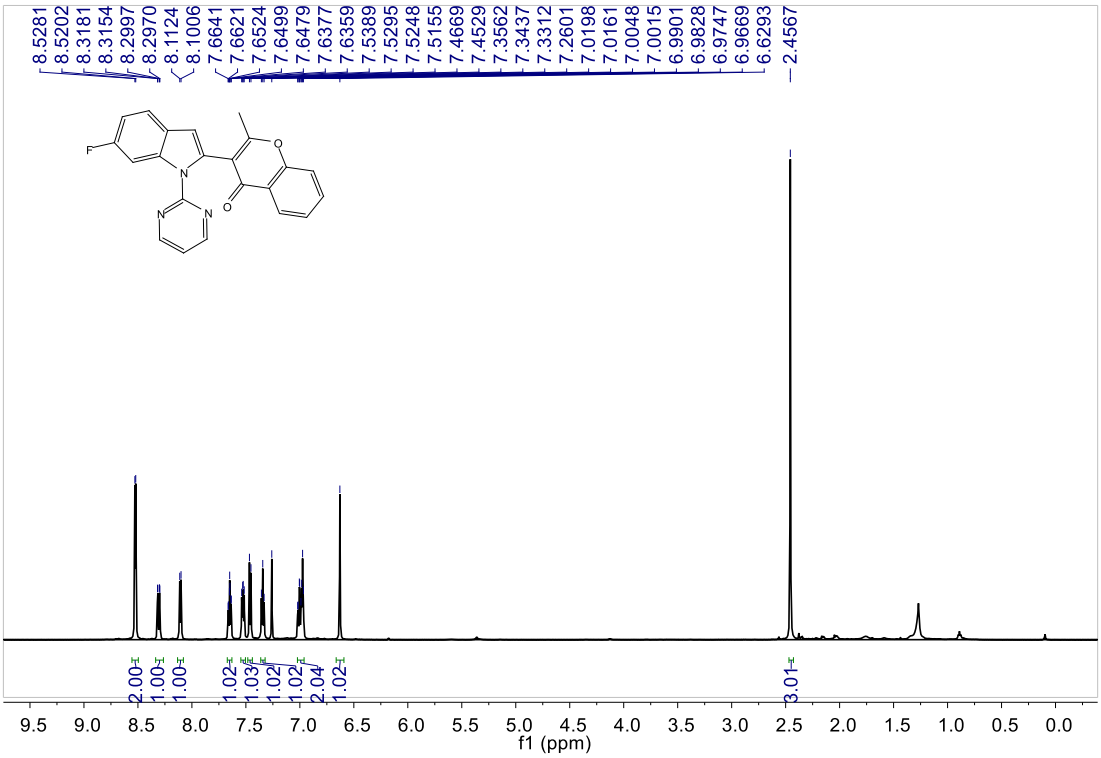
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3la



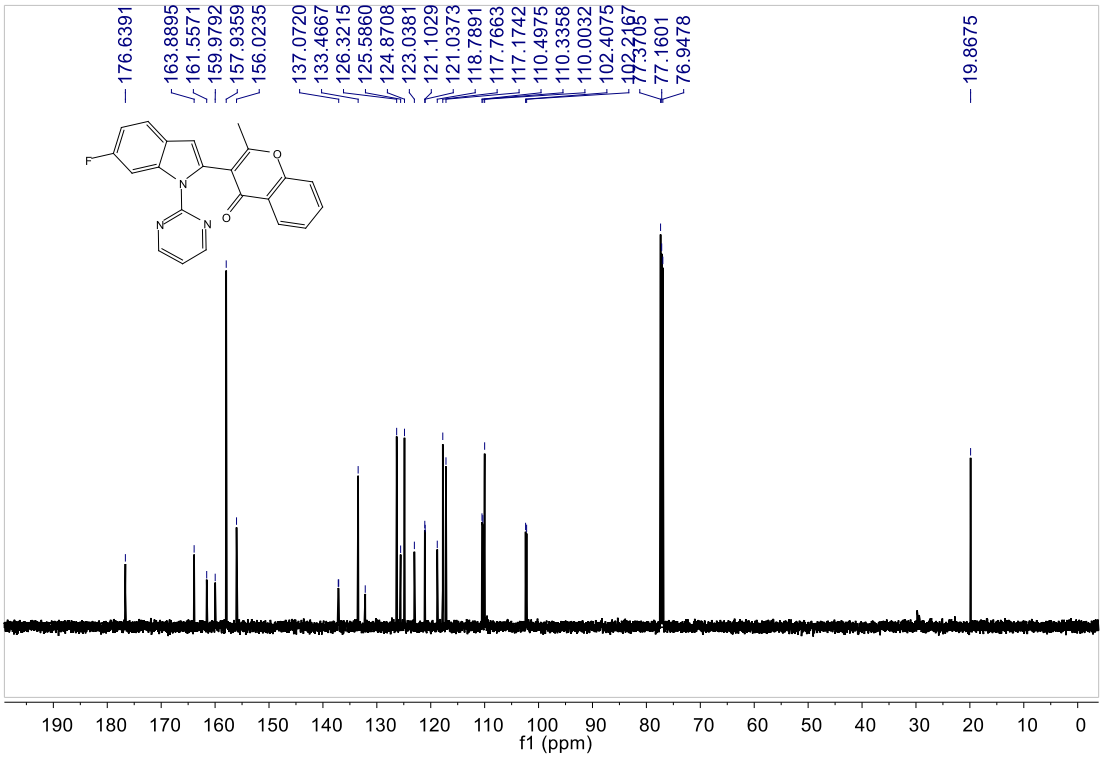
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ma



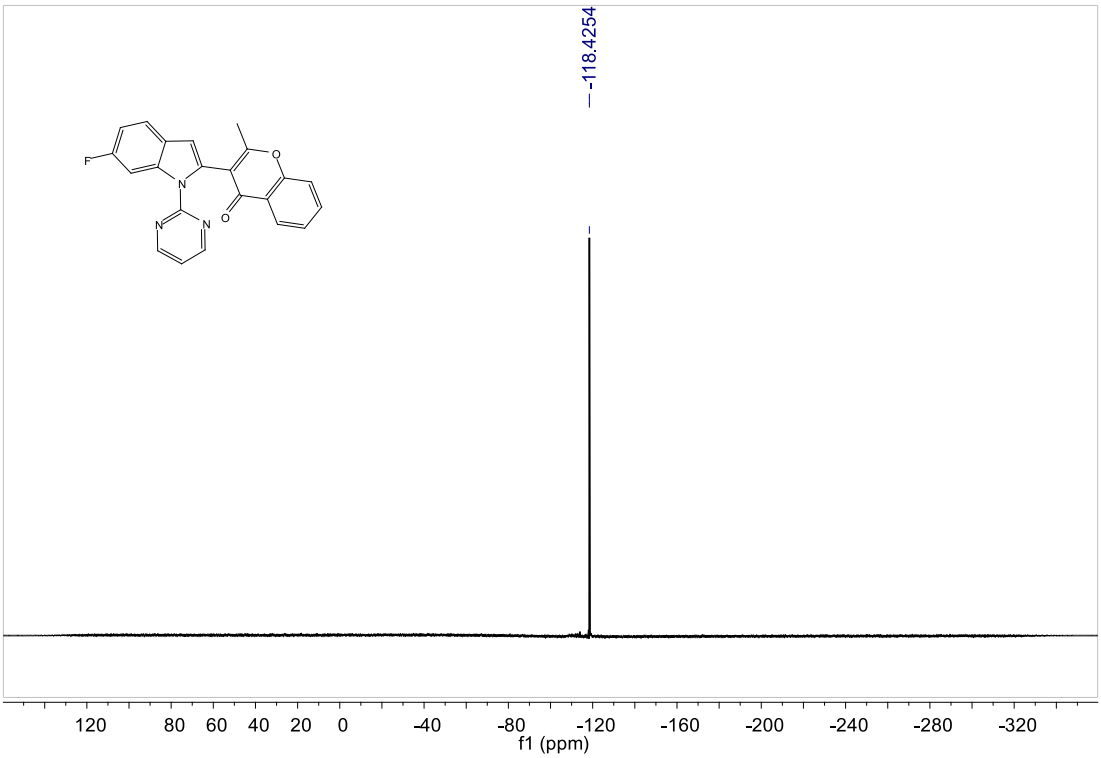
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ma



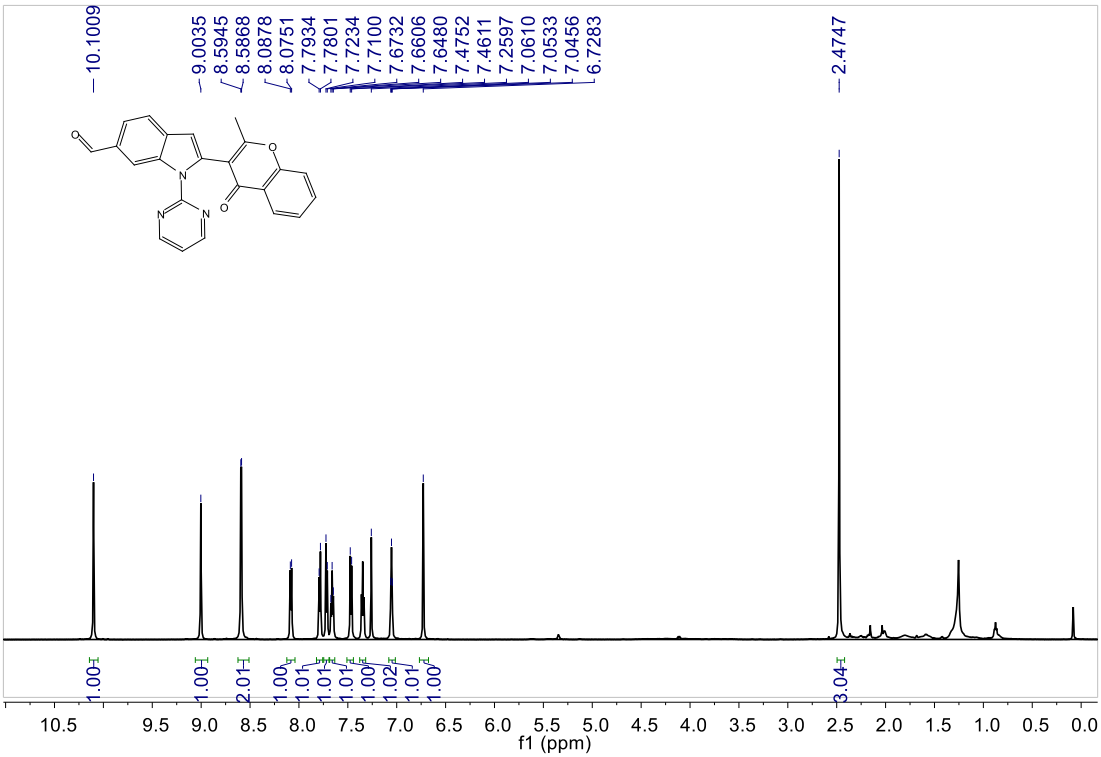
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3na



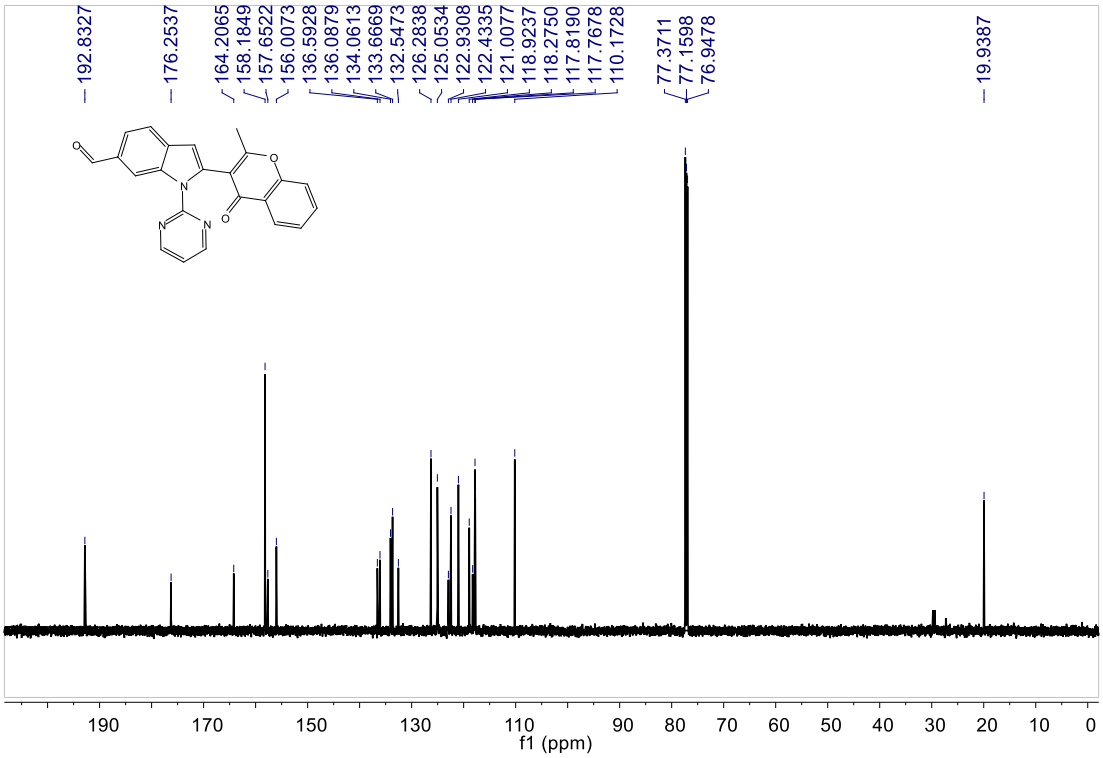
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3na



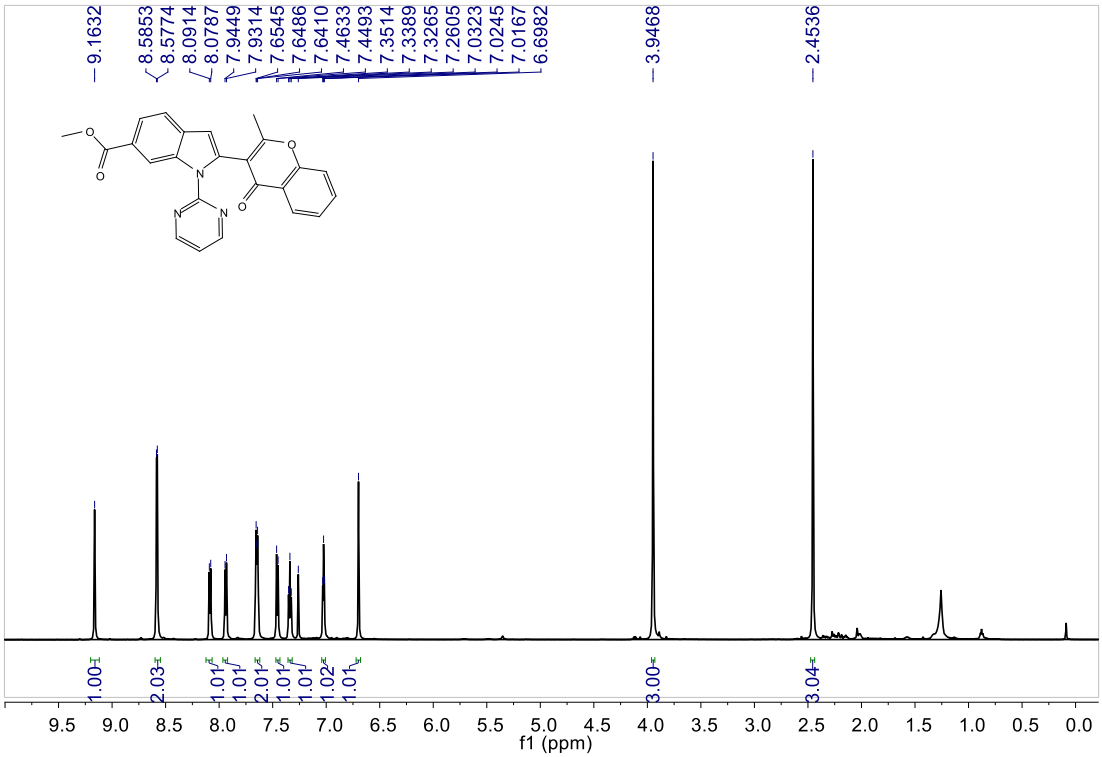
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3na



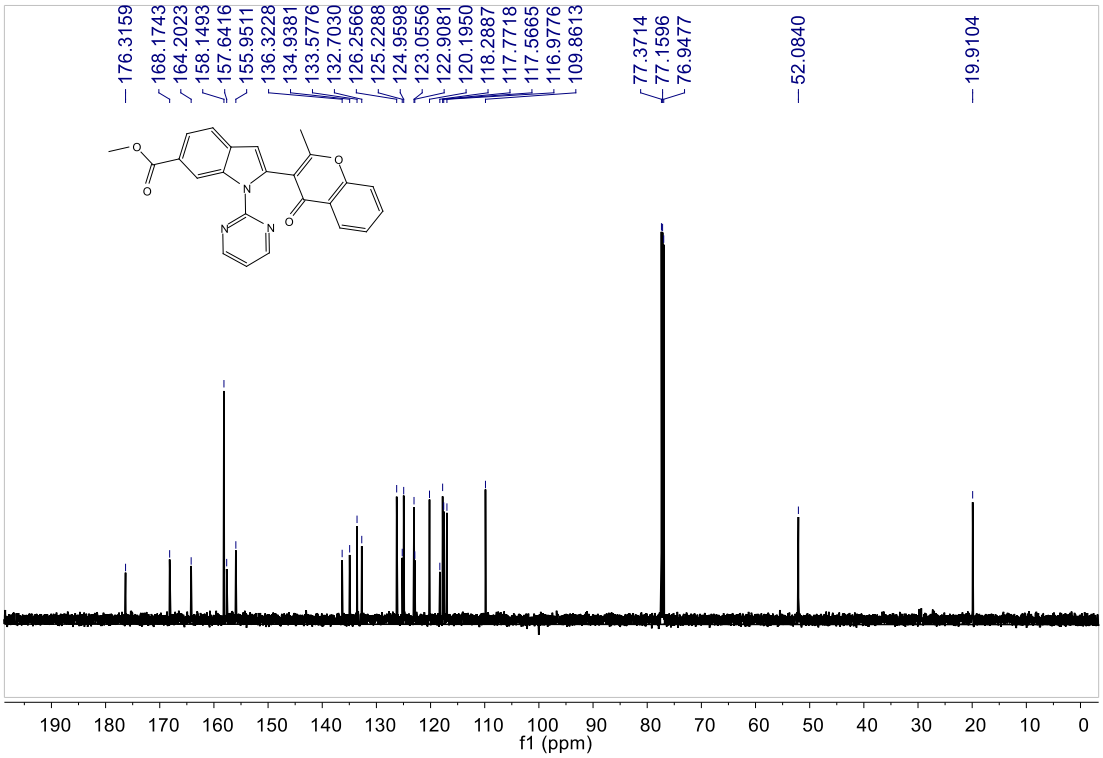
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3oa



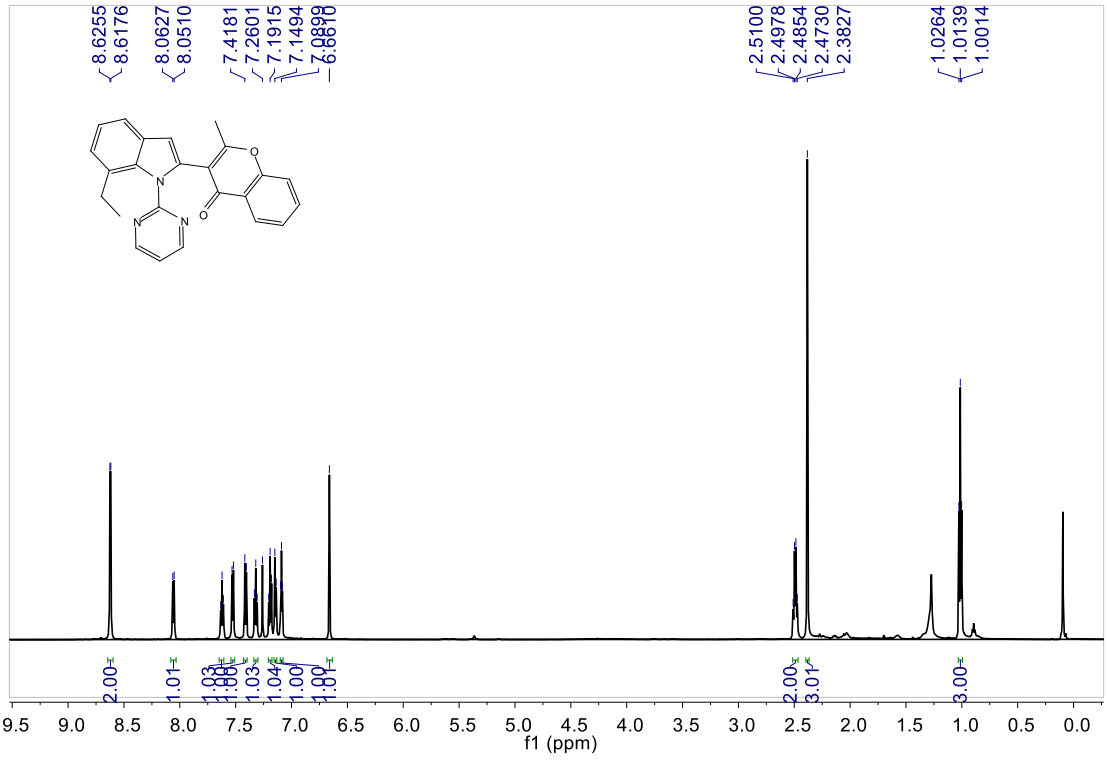
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3oa



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3pa



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3pa



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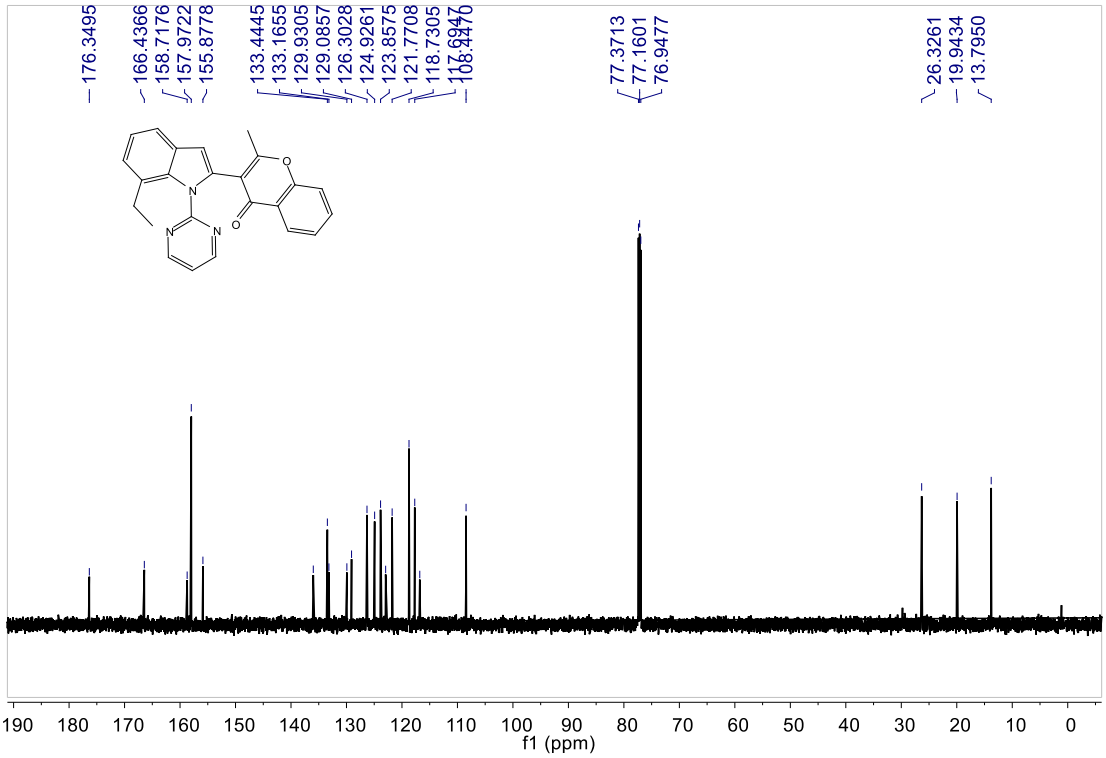
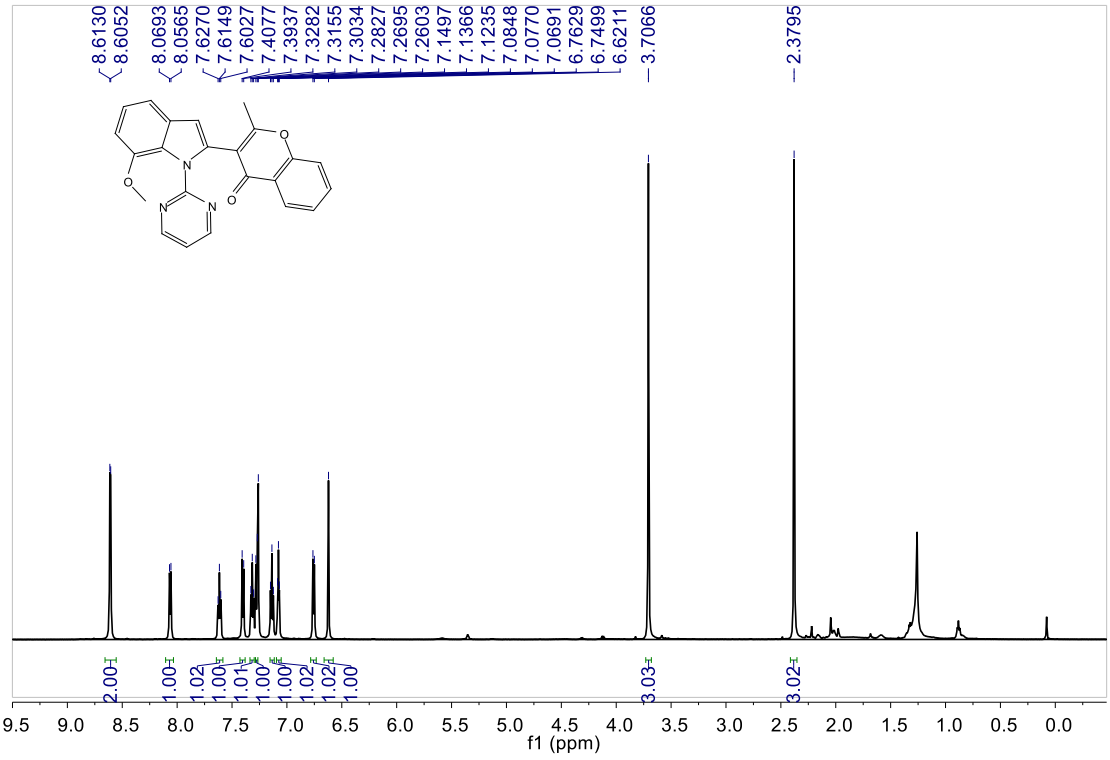


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3qa



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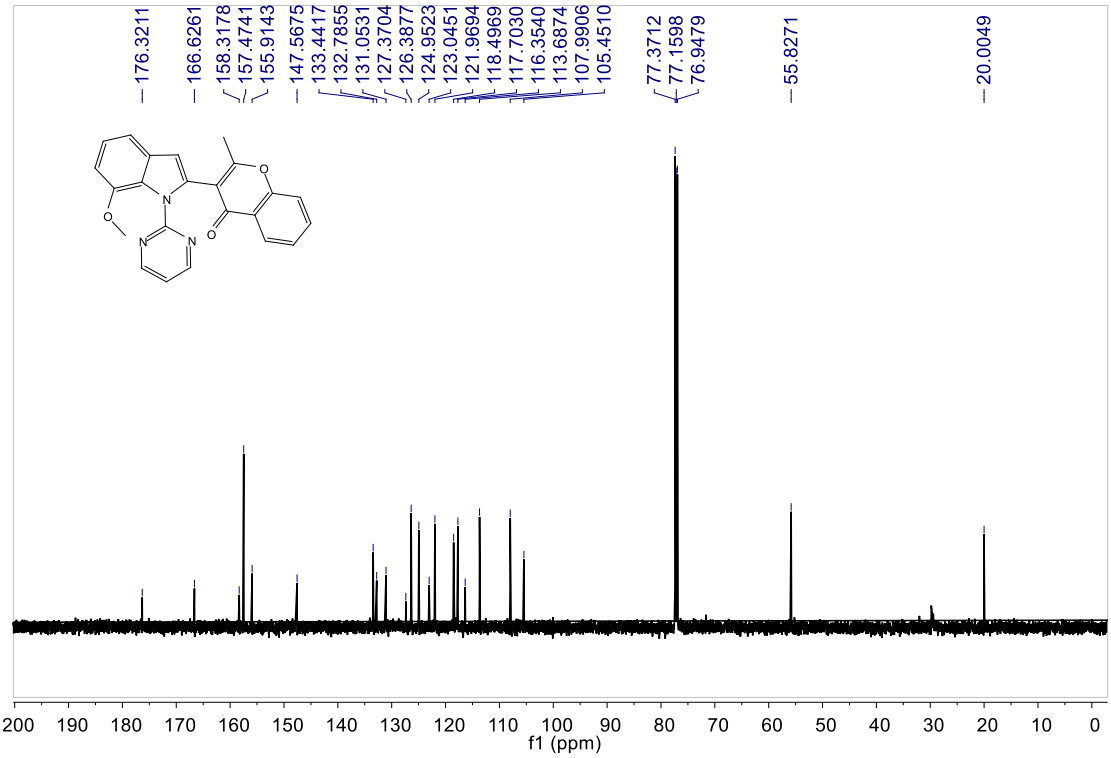
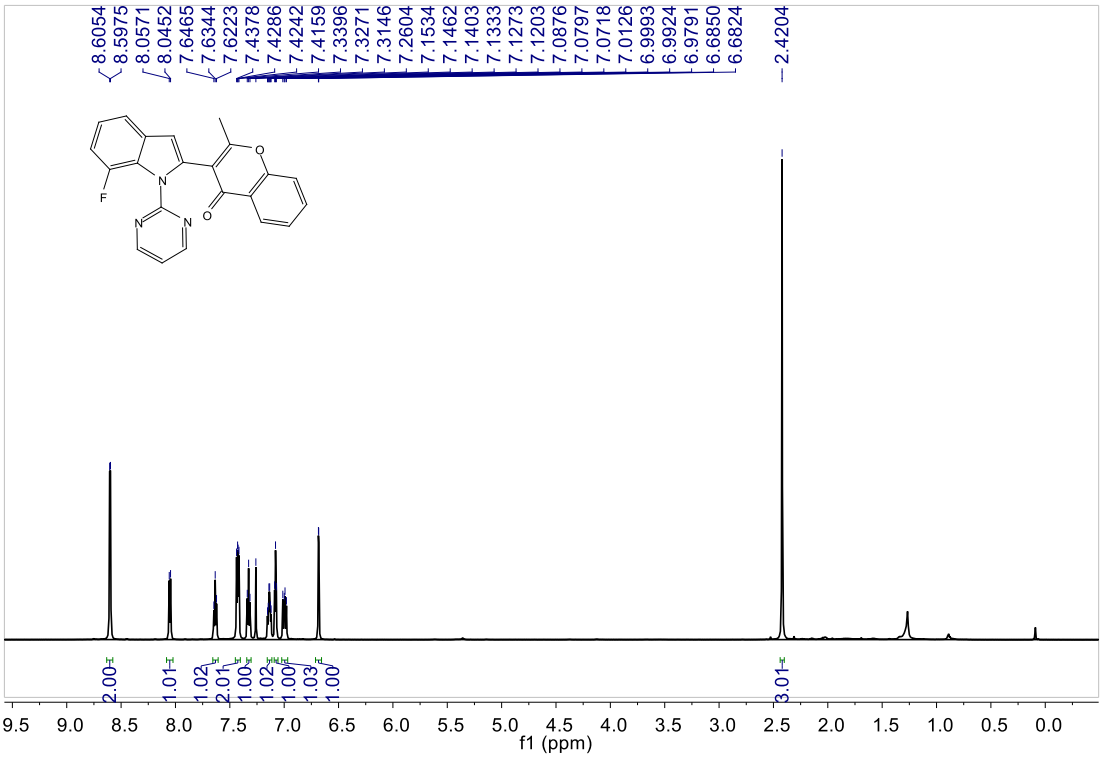
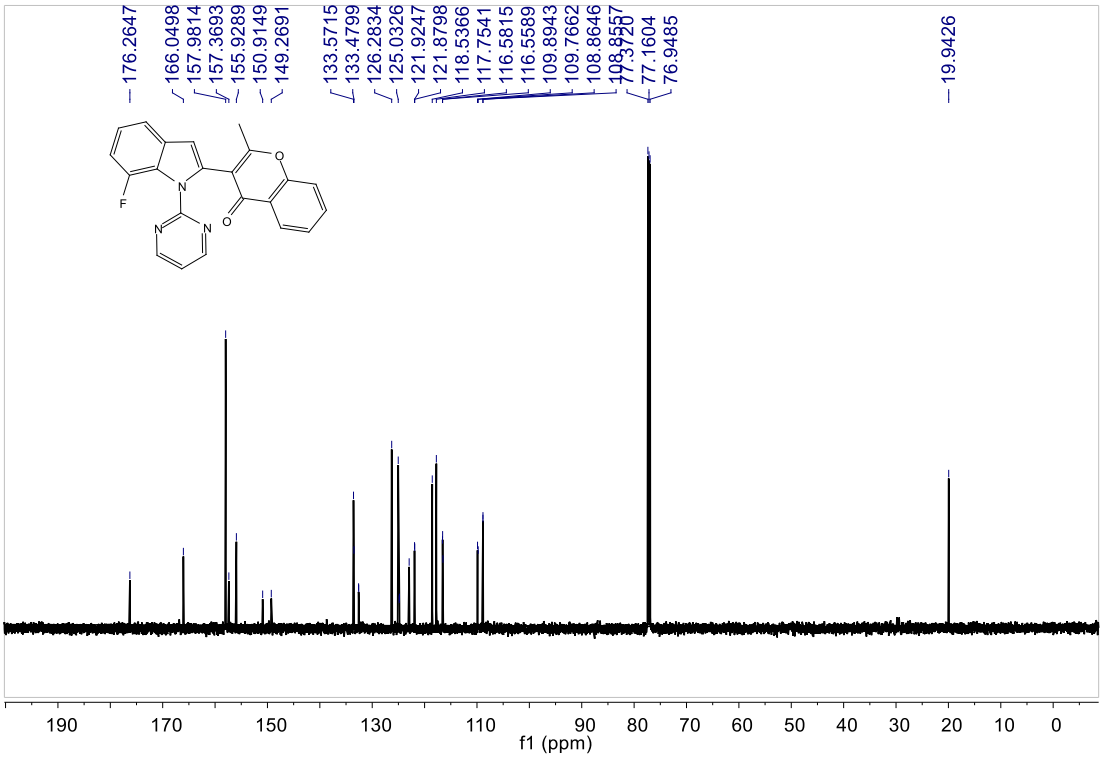


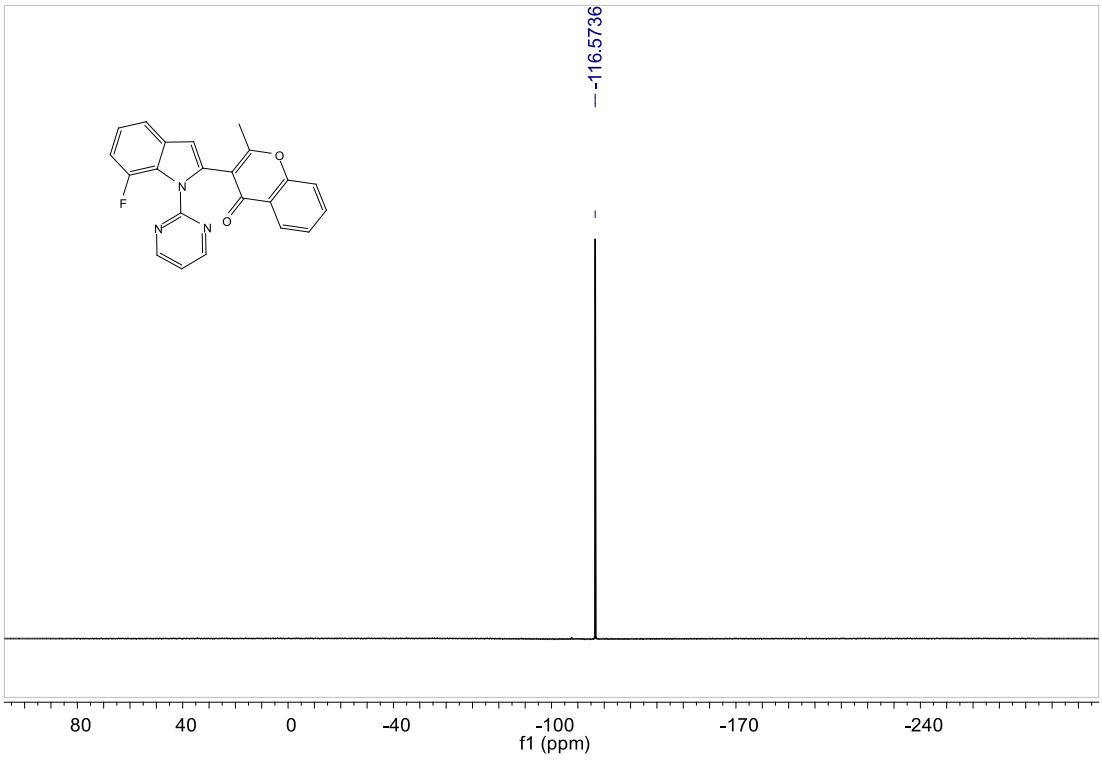
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ra



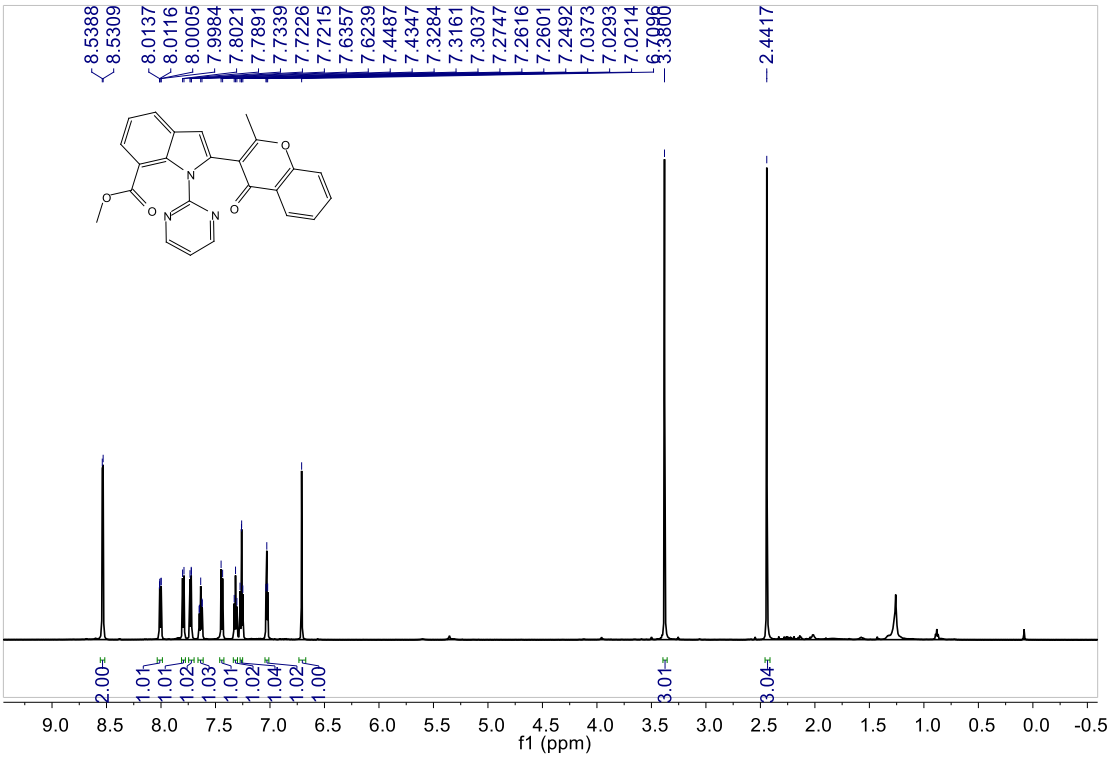
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3sa



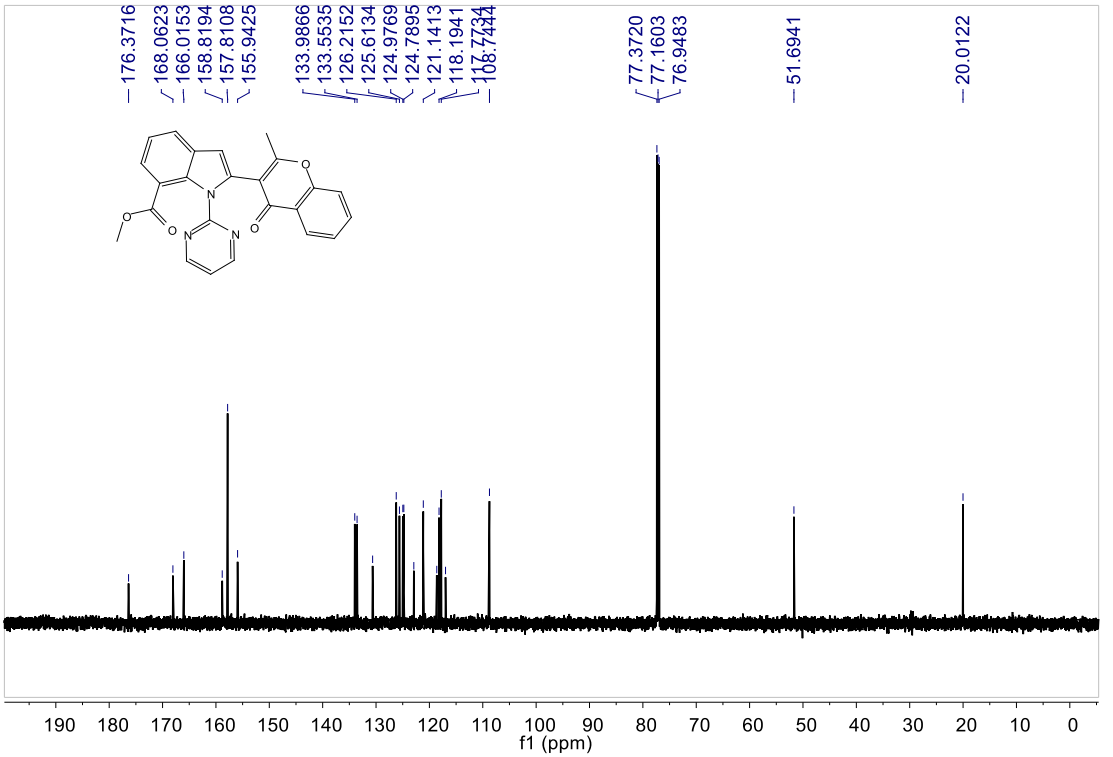
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3sa



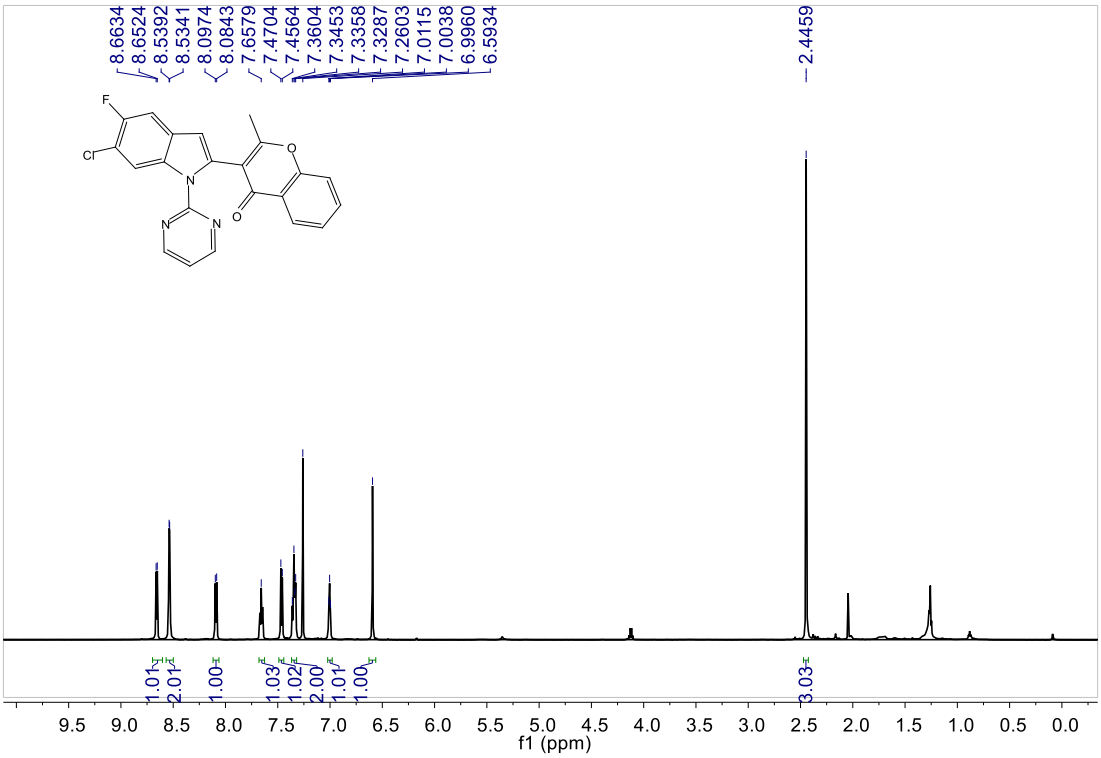
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3sa



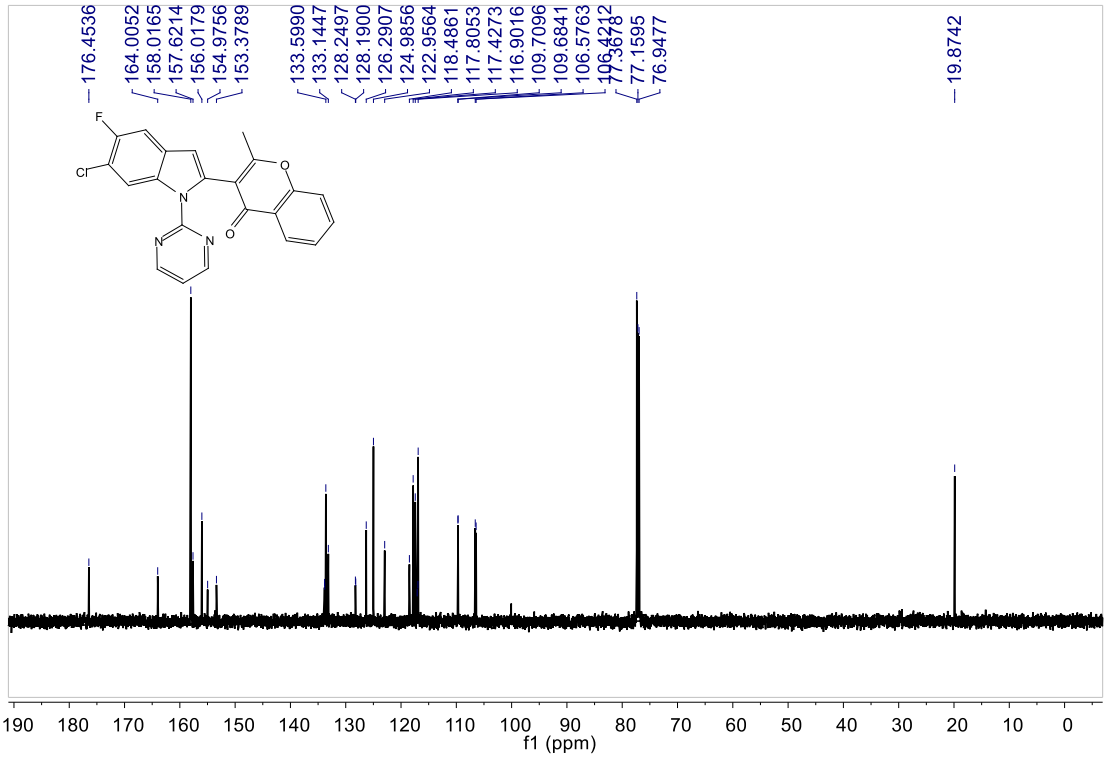
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ta



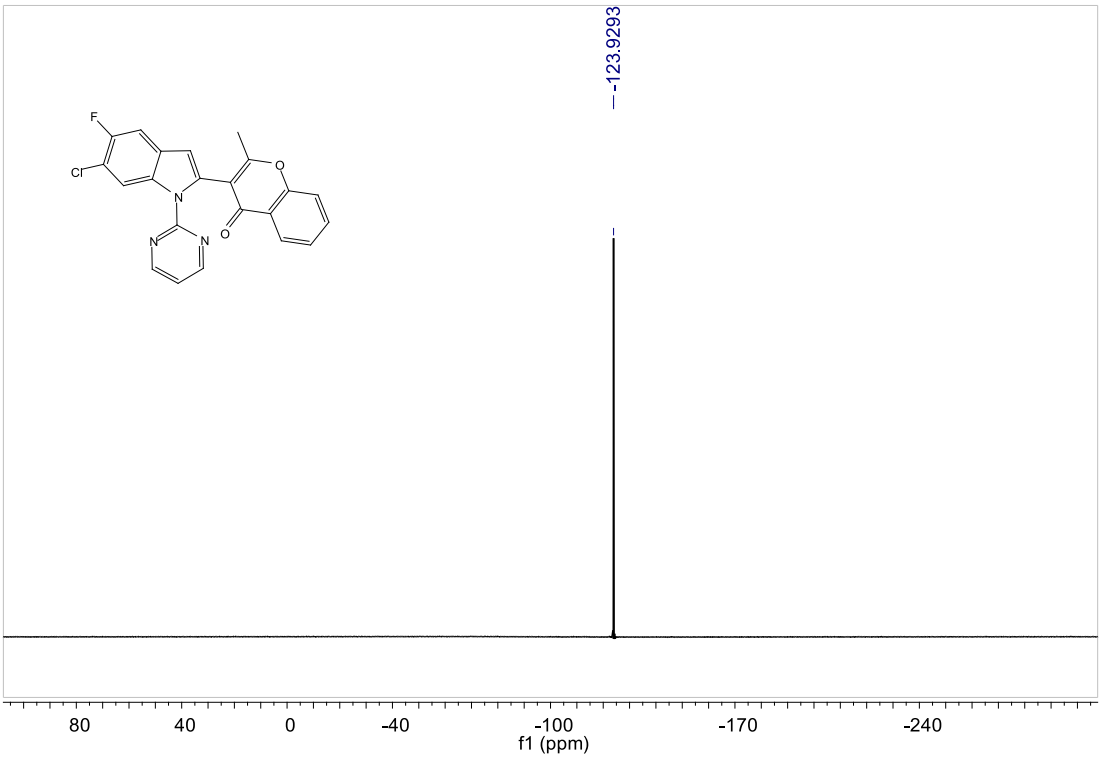
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ta



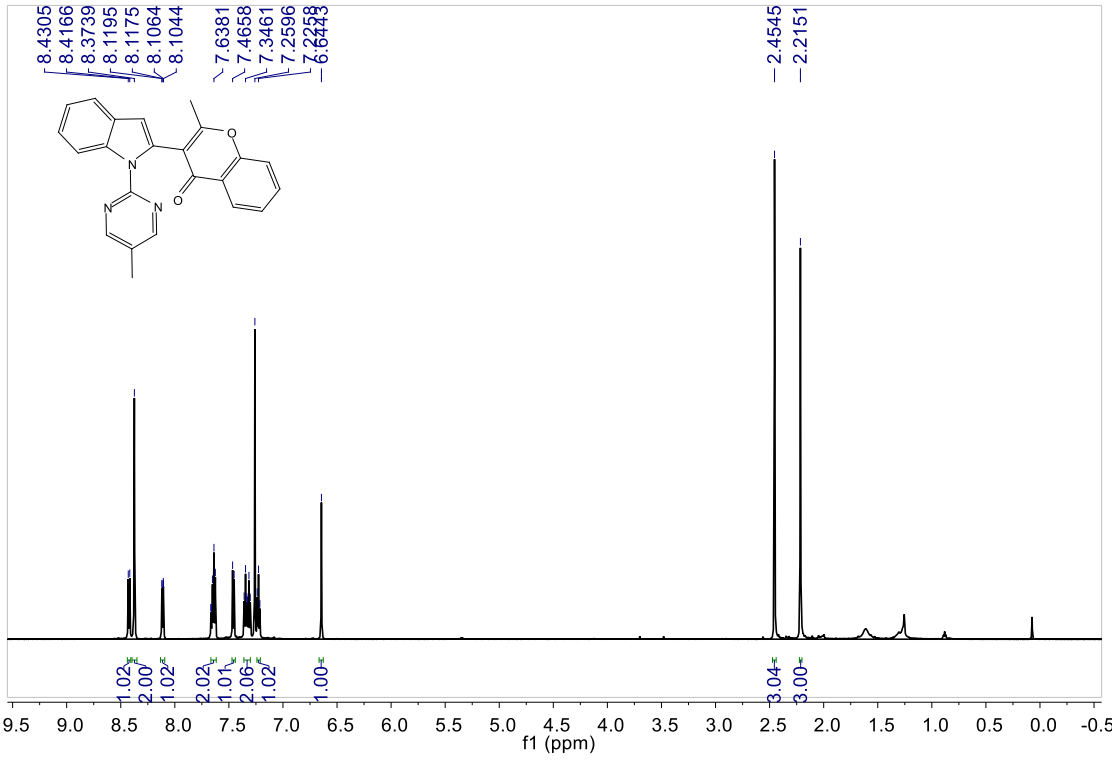
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ua



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ua



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ua



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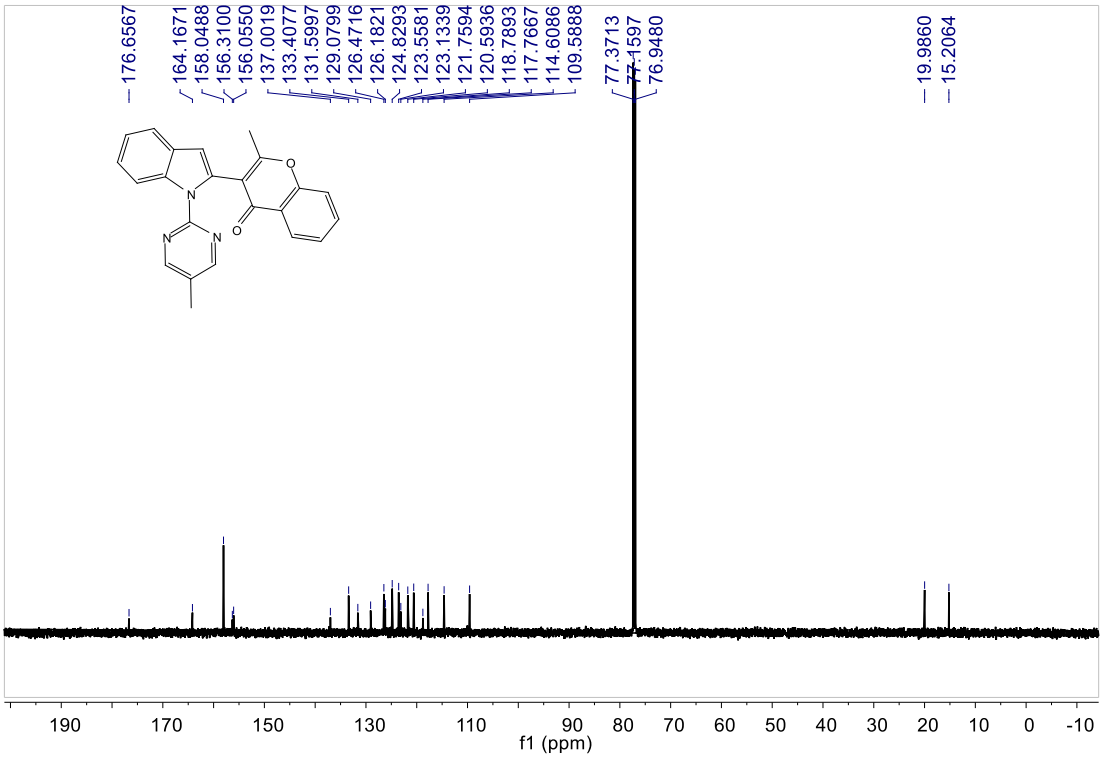
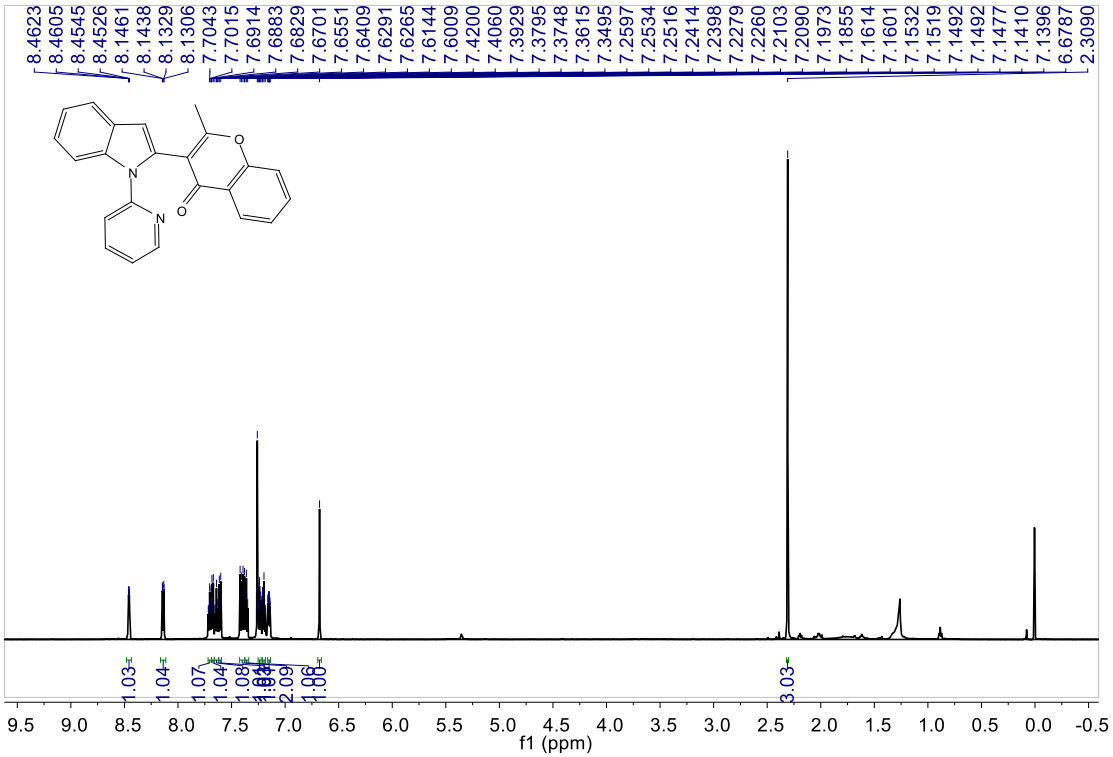
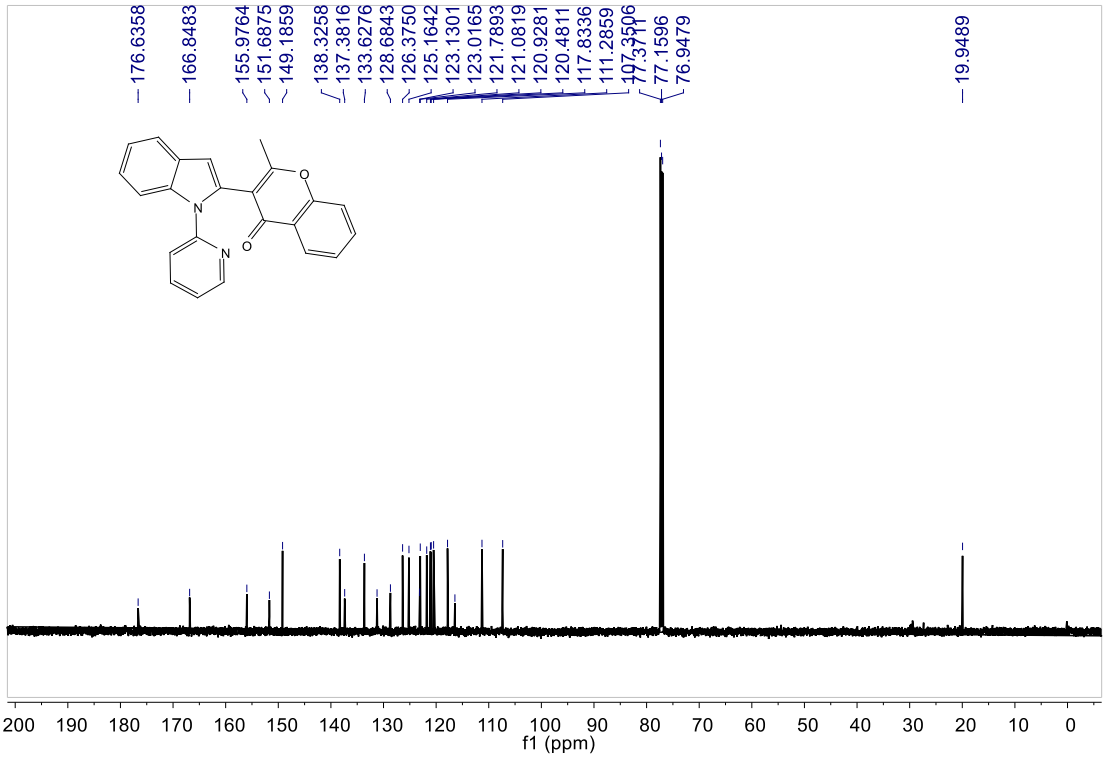


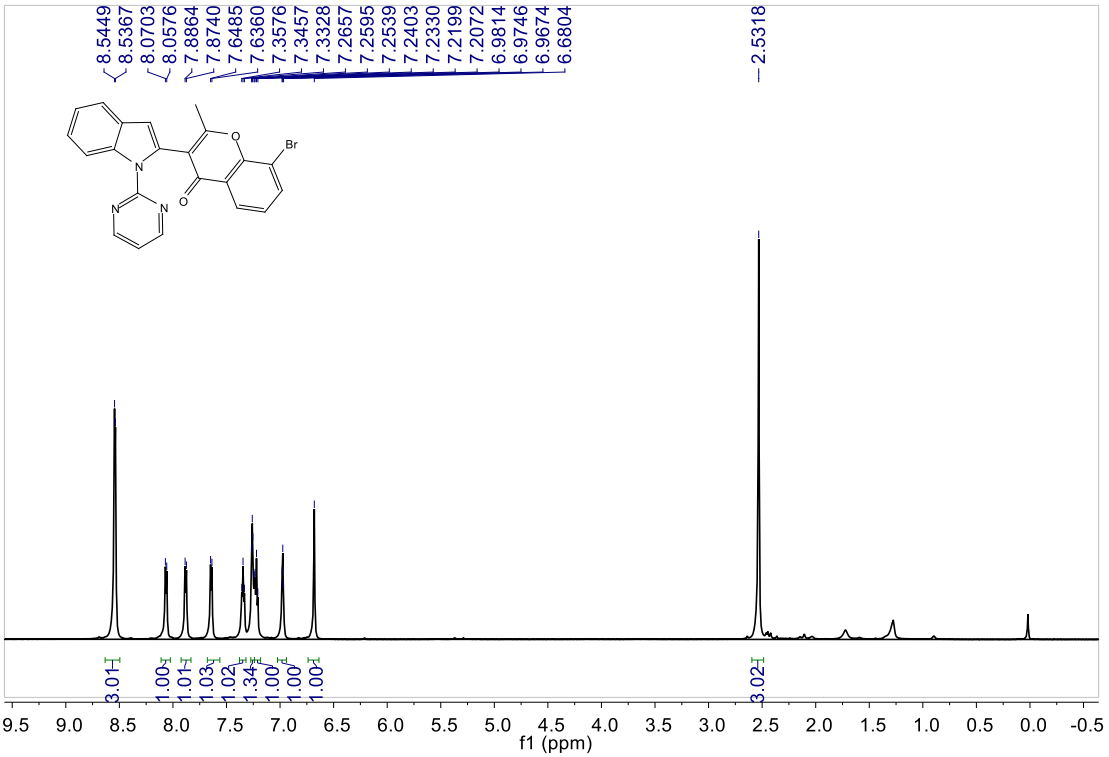
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3va



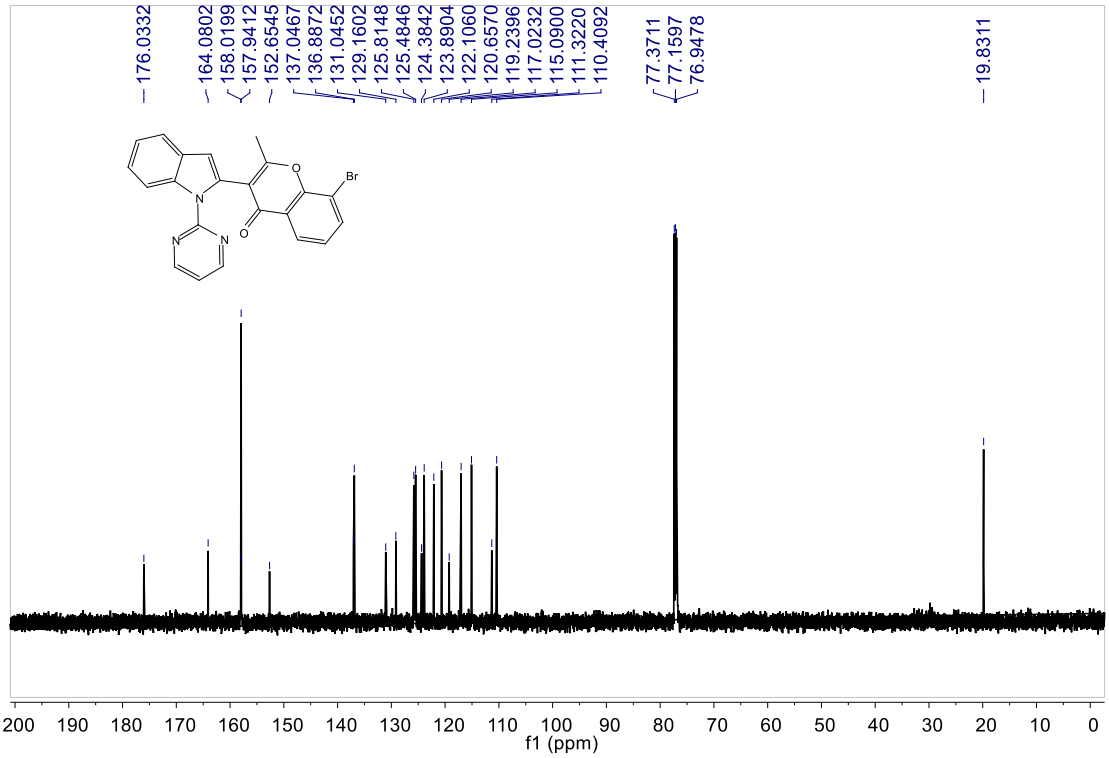
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3wa



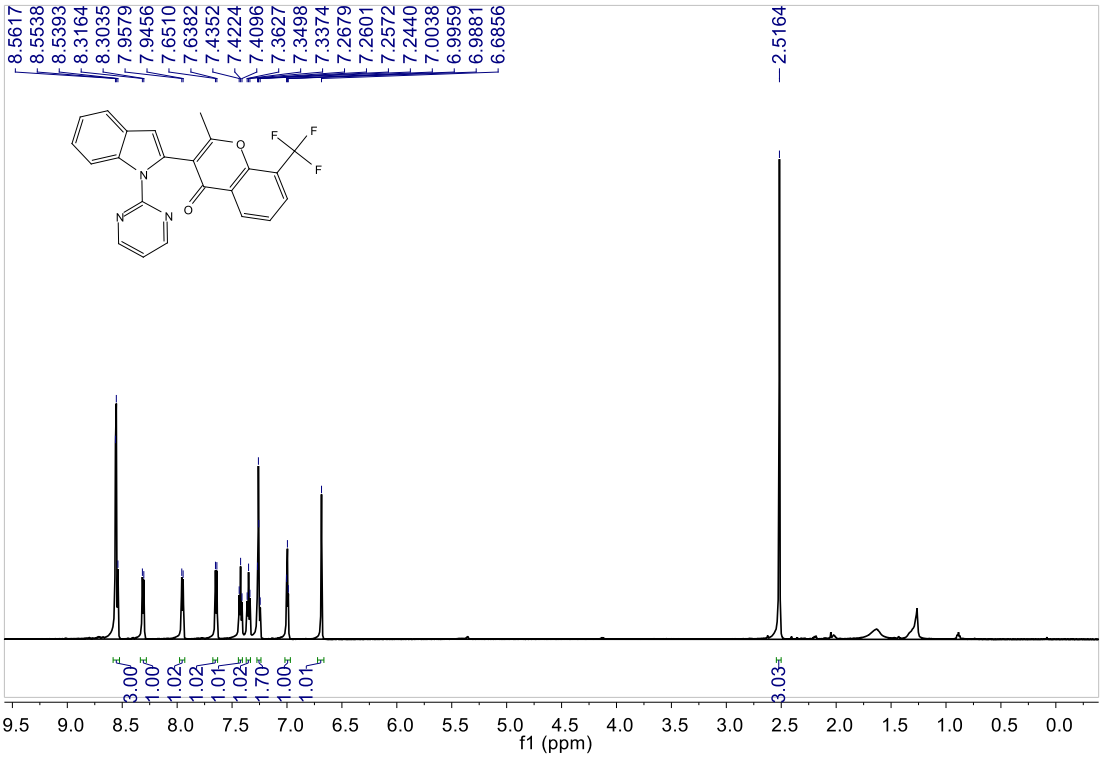
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3wa



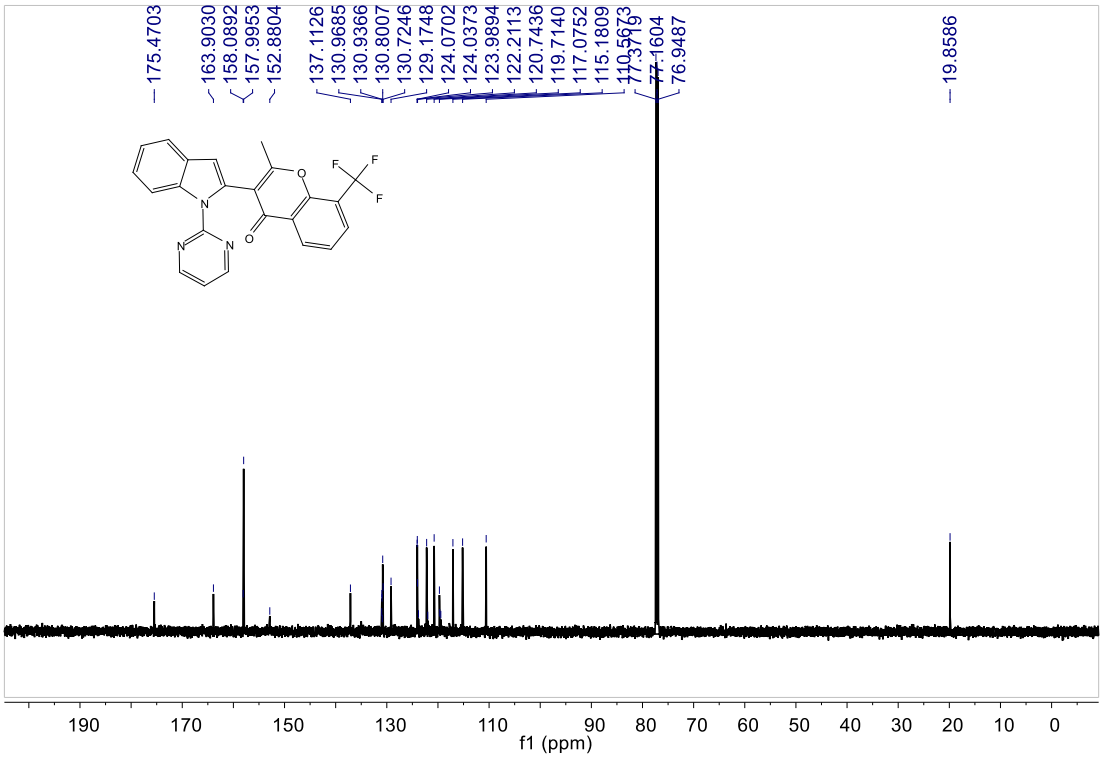
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ab



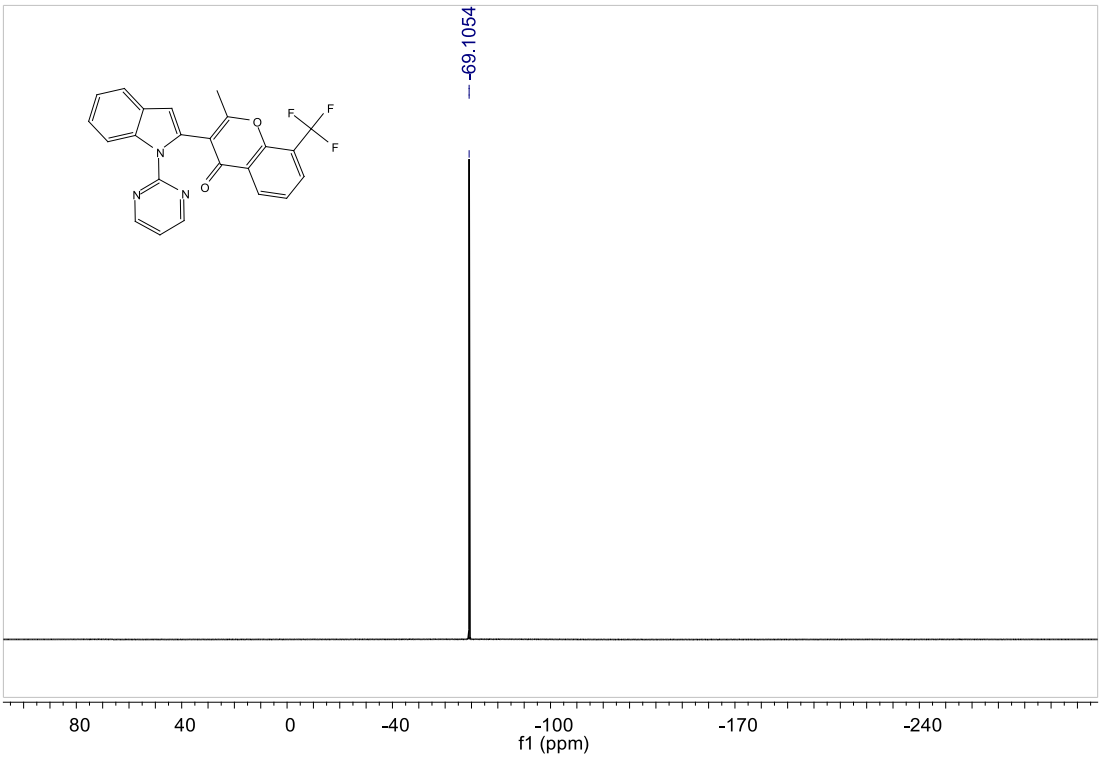
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ab



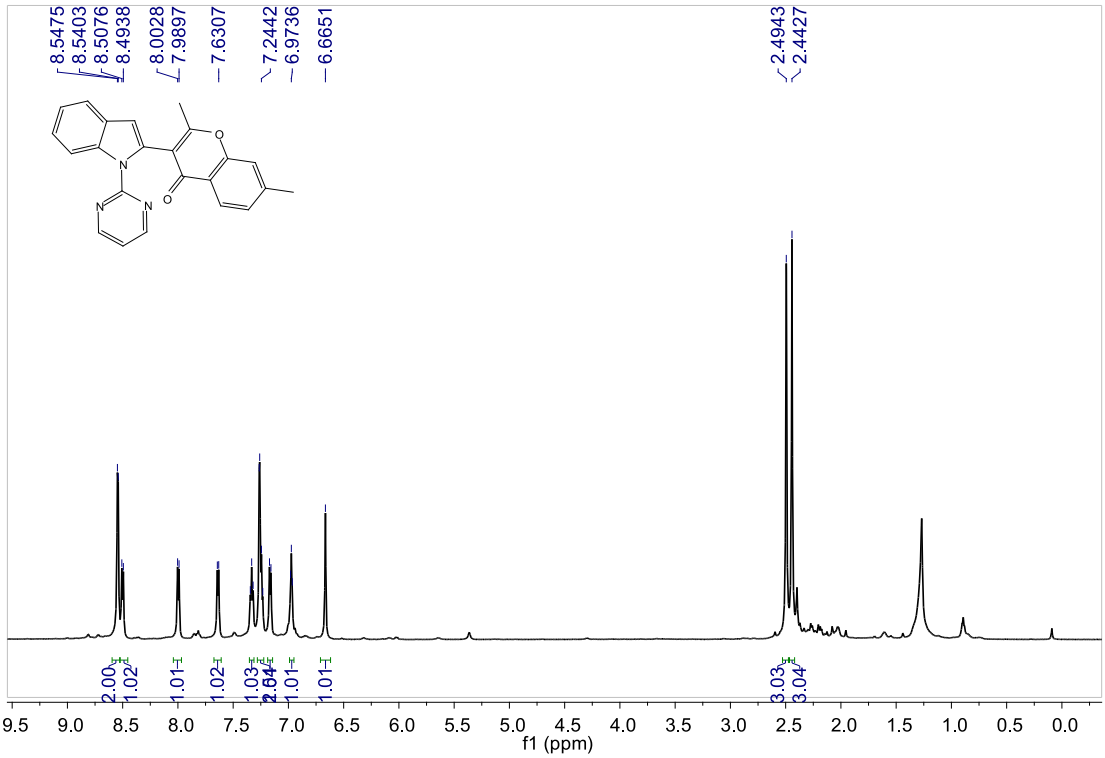
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ac



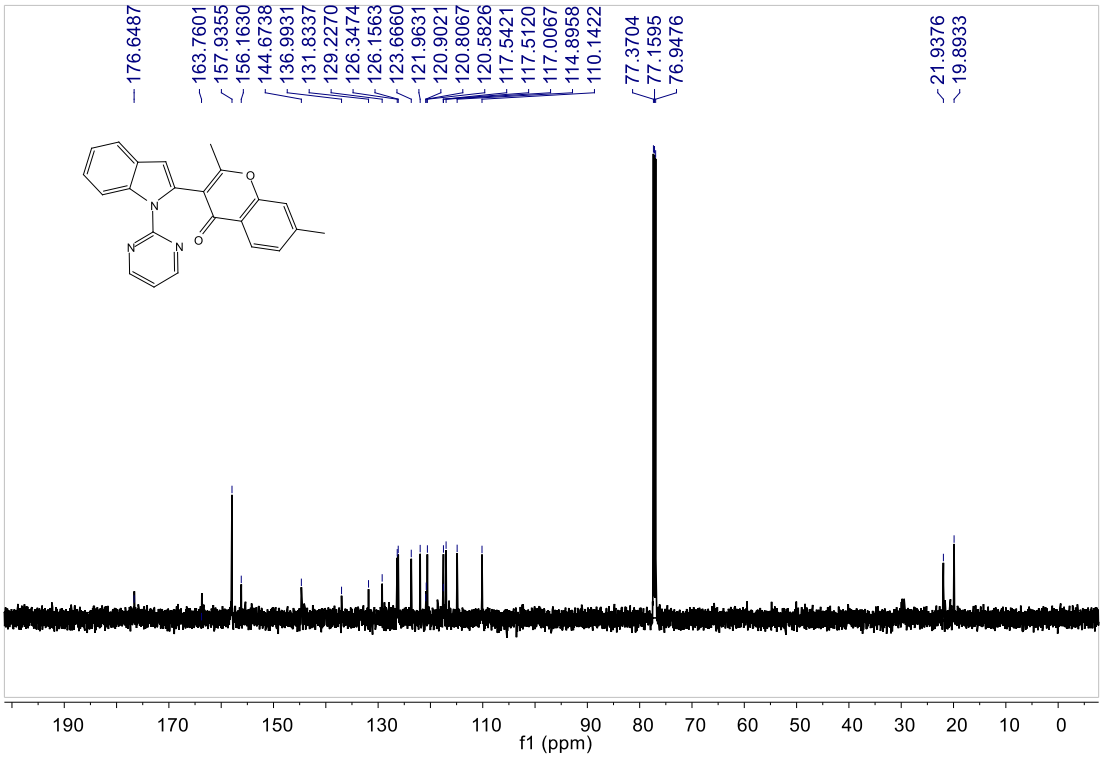
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ac



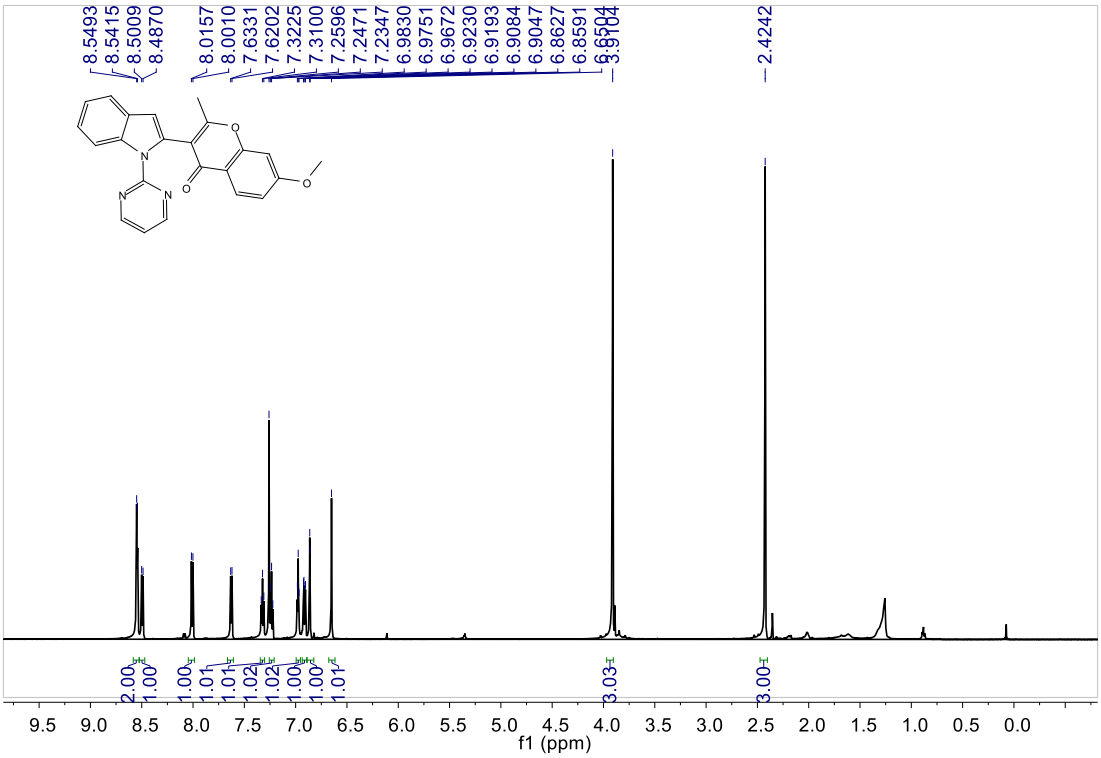
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ac



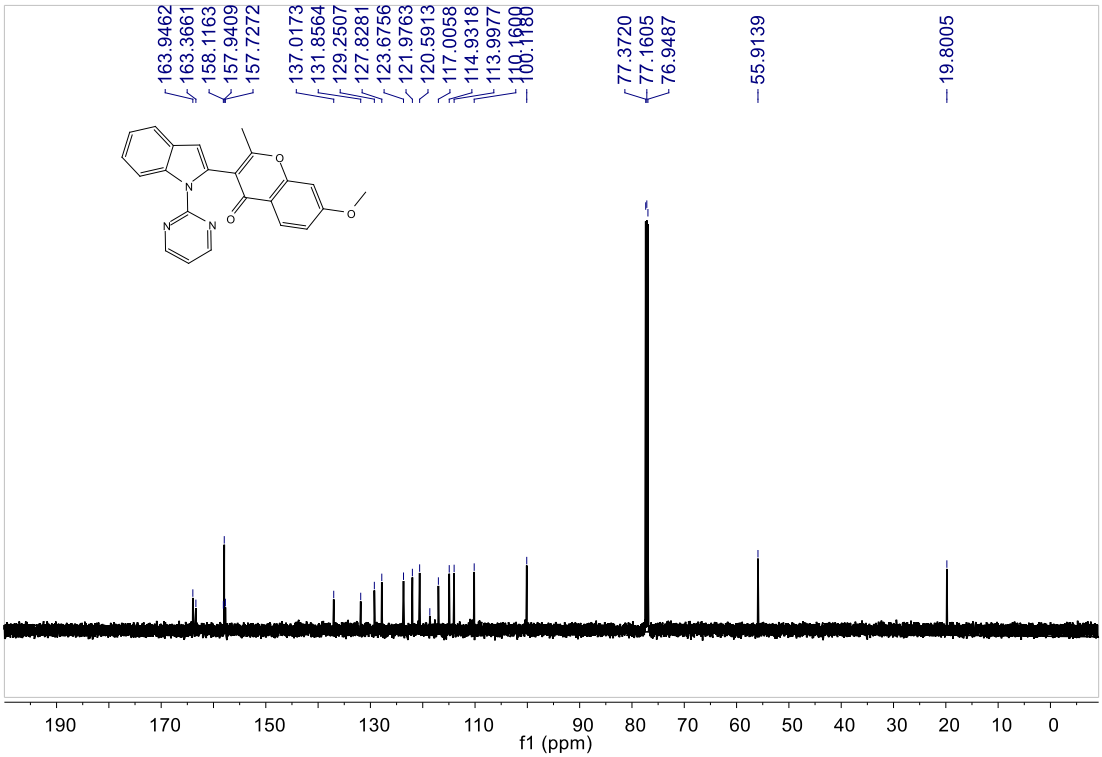
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ad



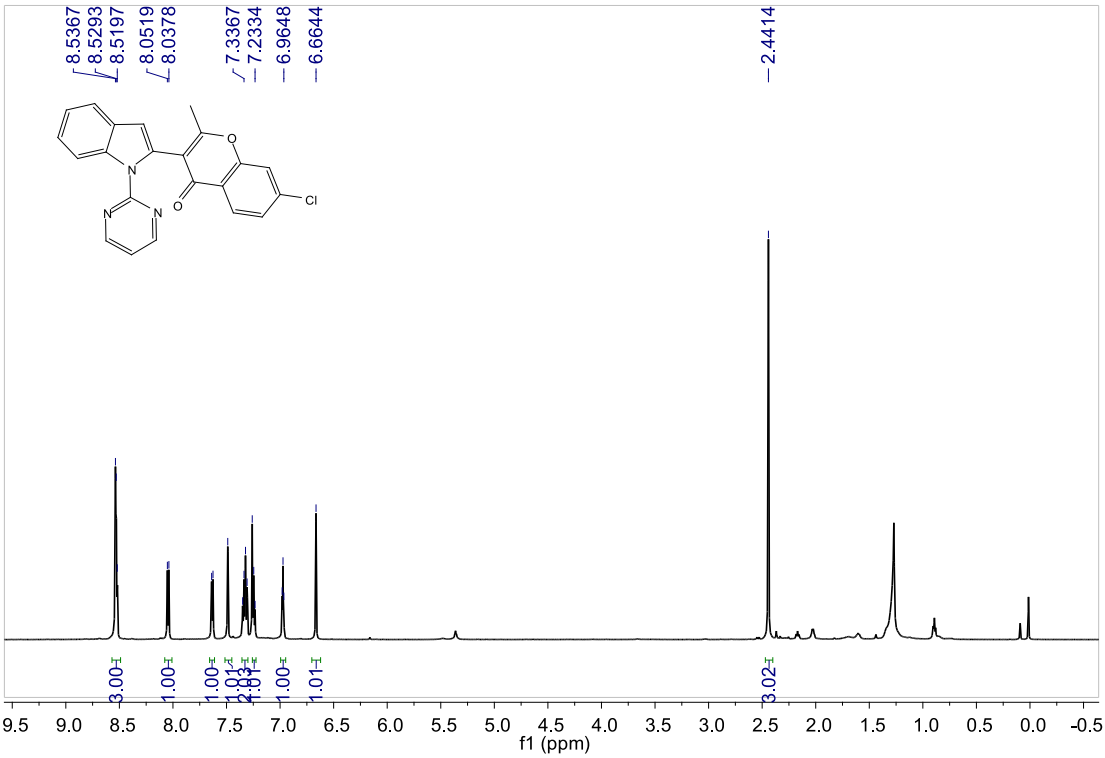
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ad



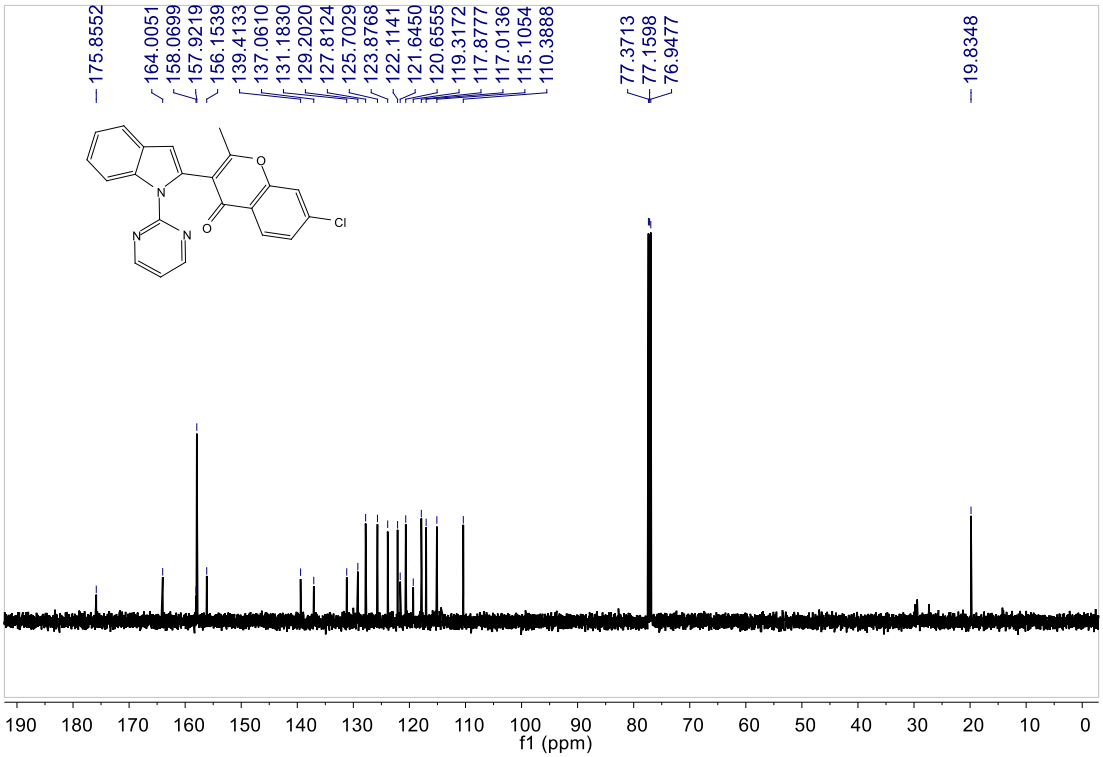
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ae



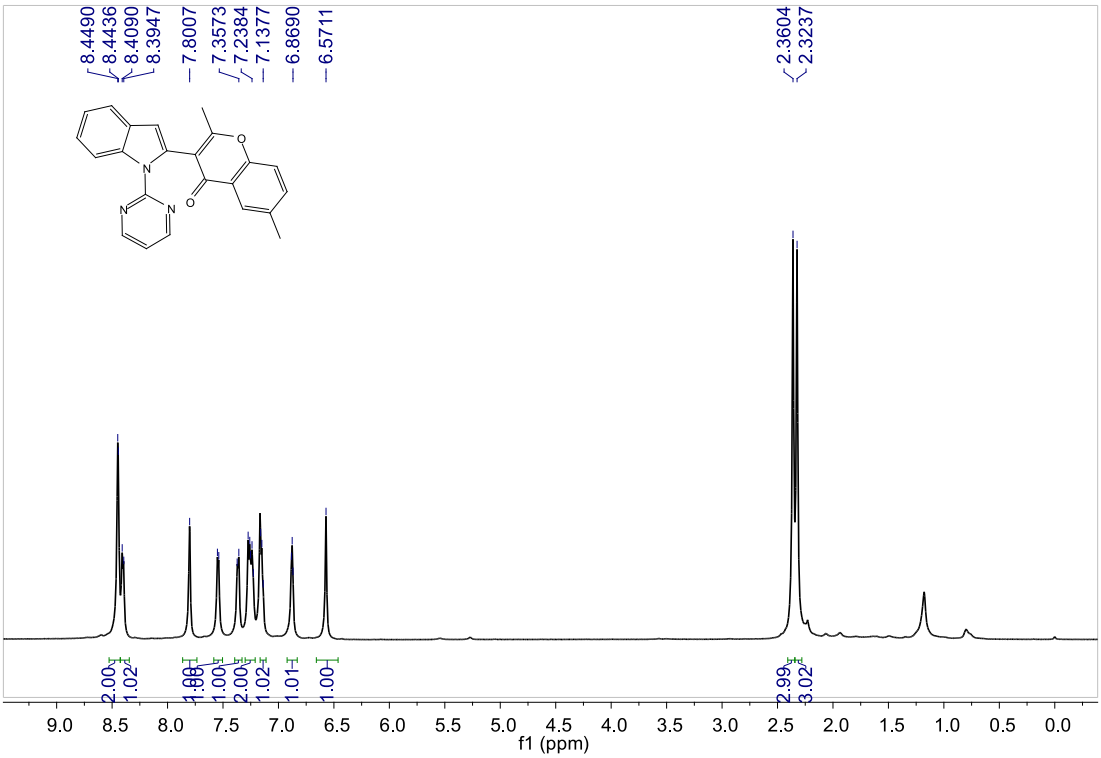
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ae



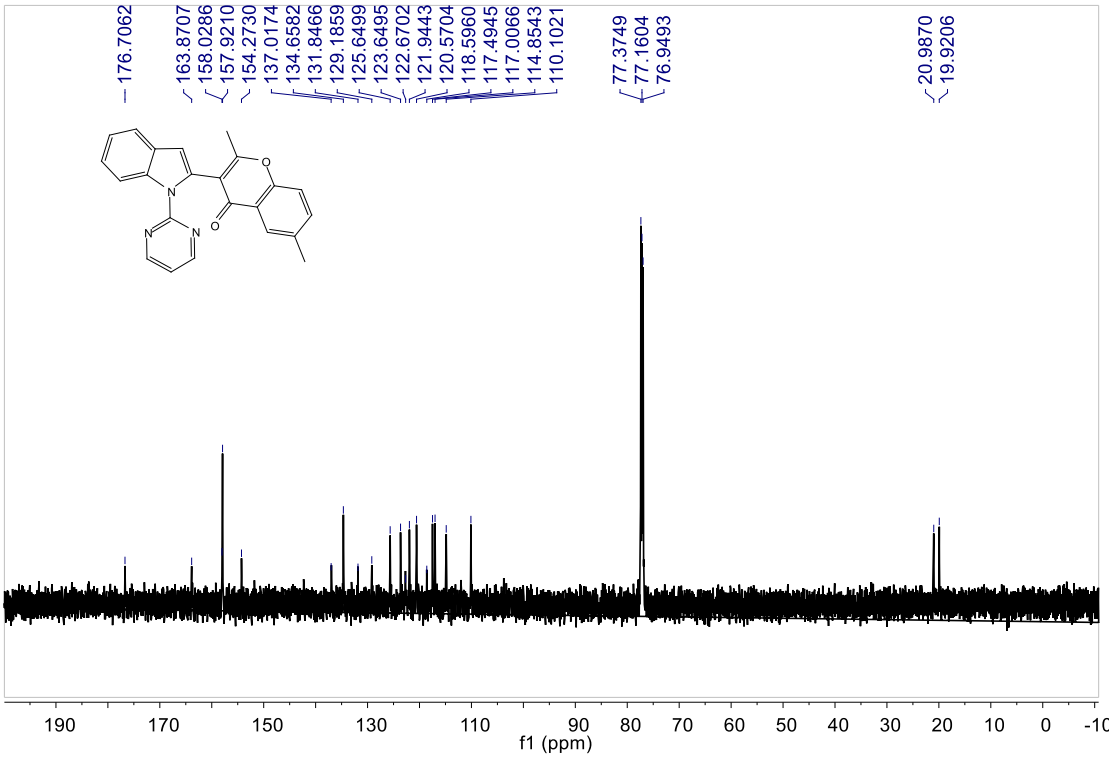
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3af



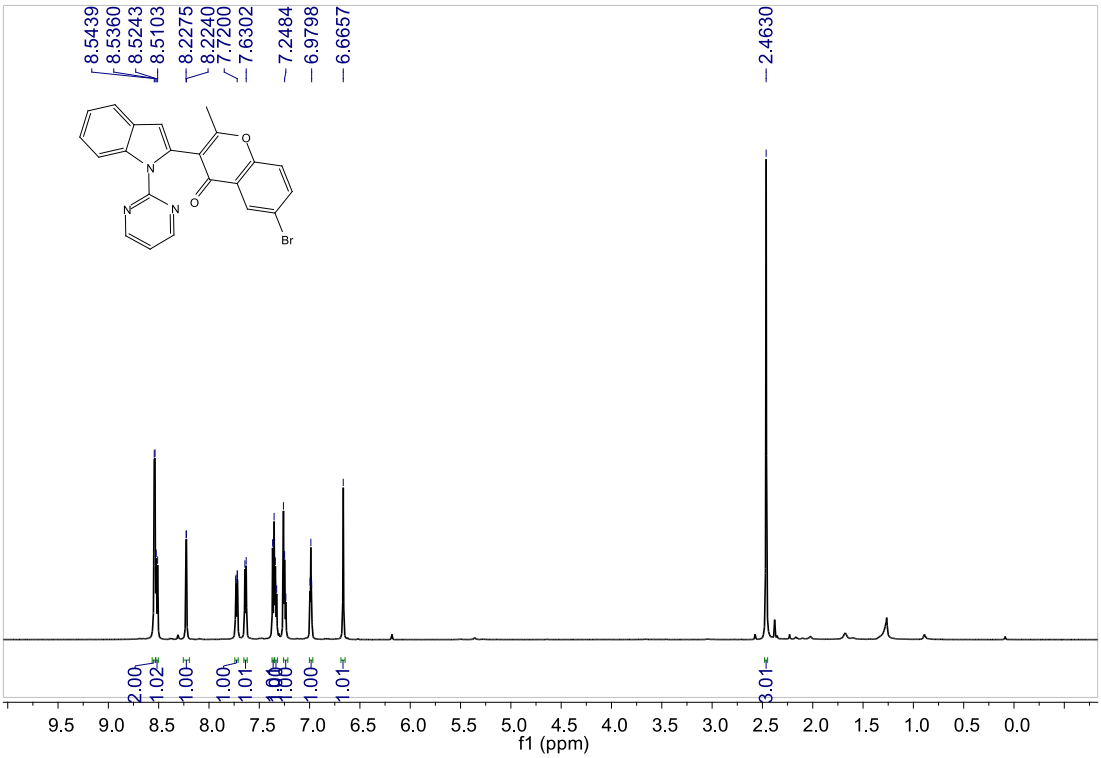
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3af



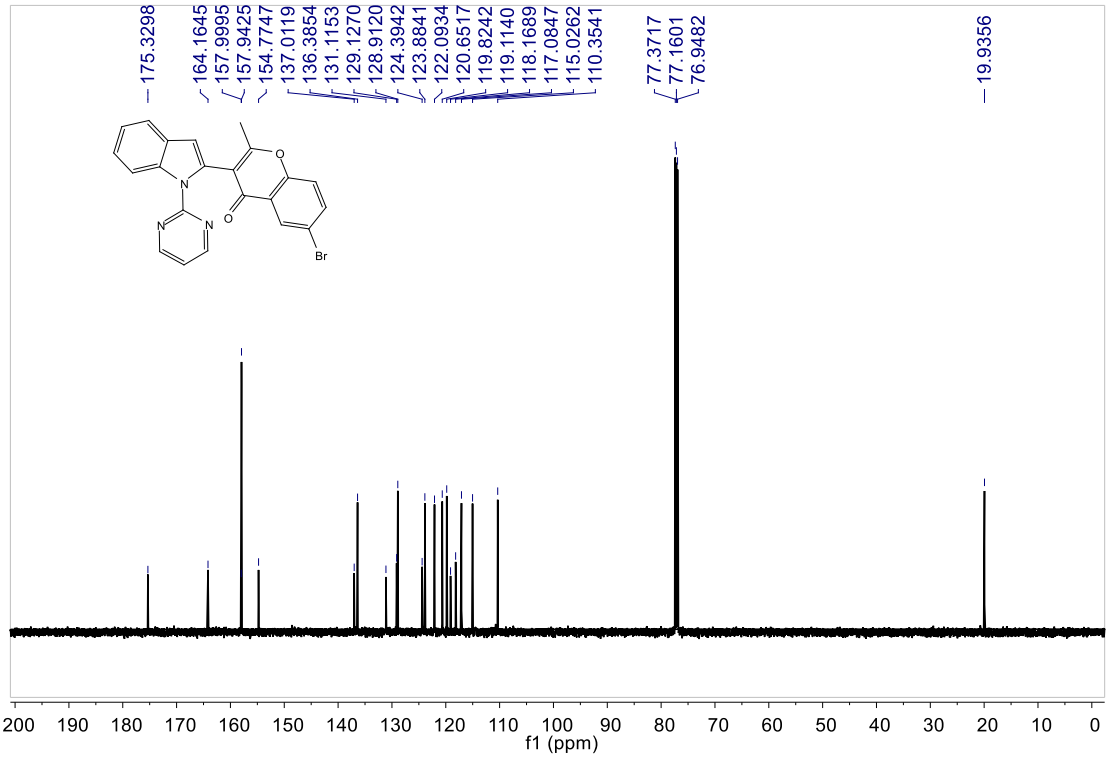
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ag



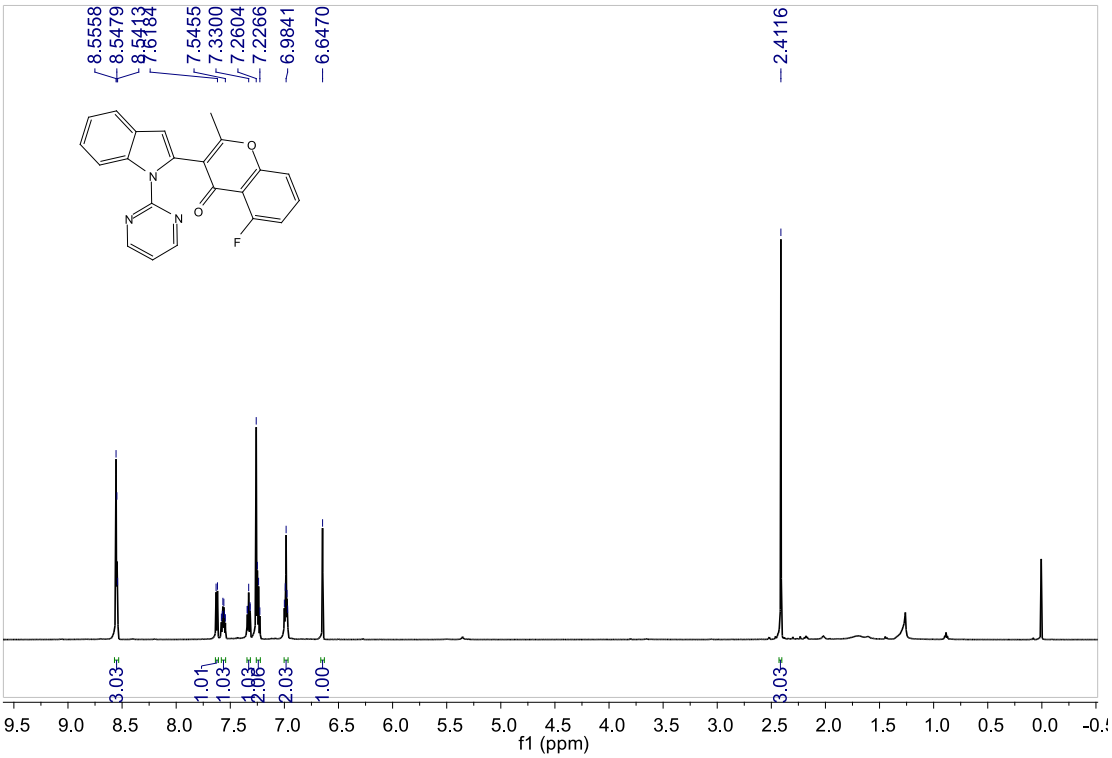
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ag



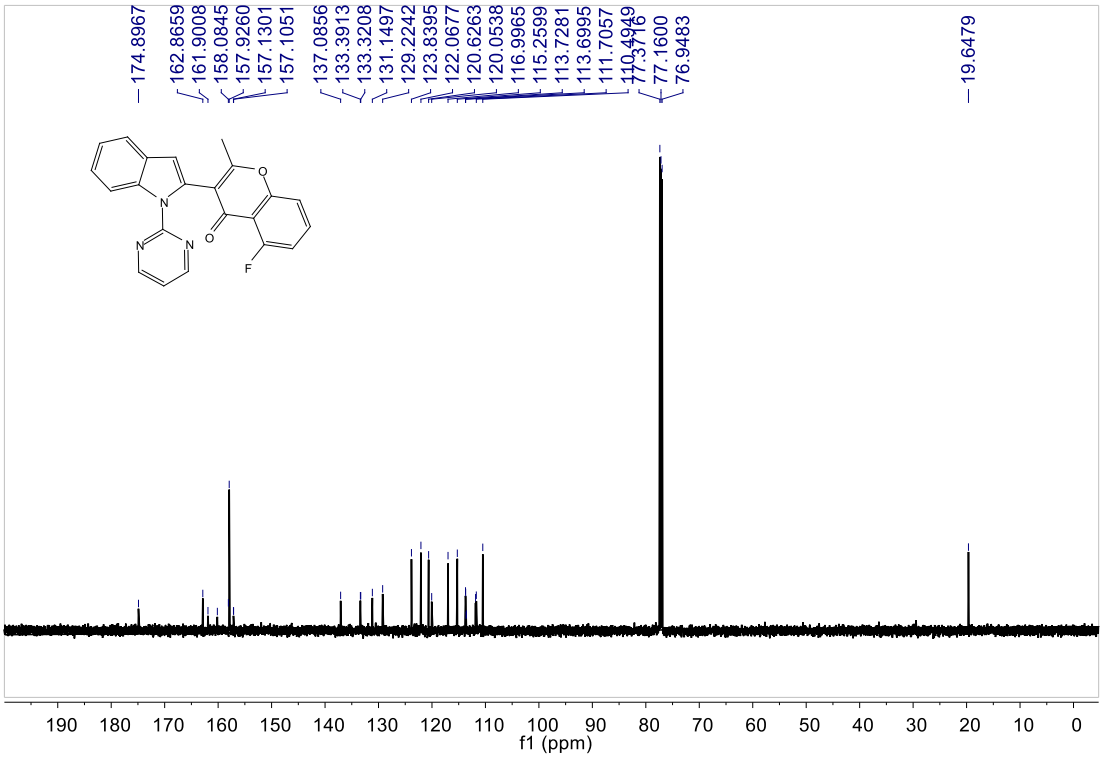
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ah



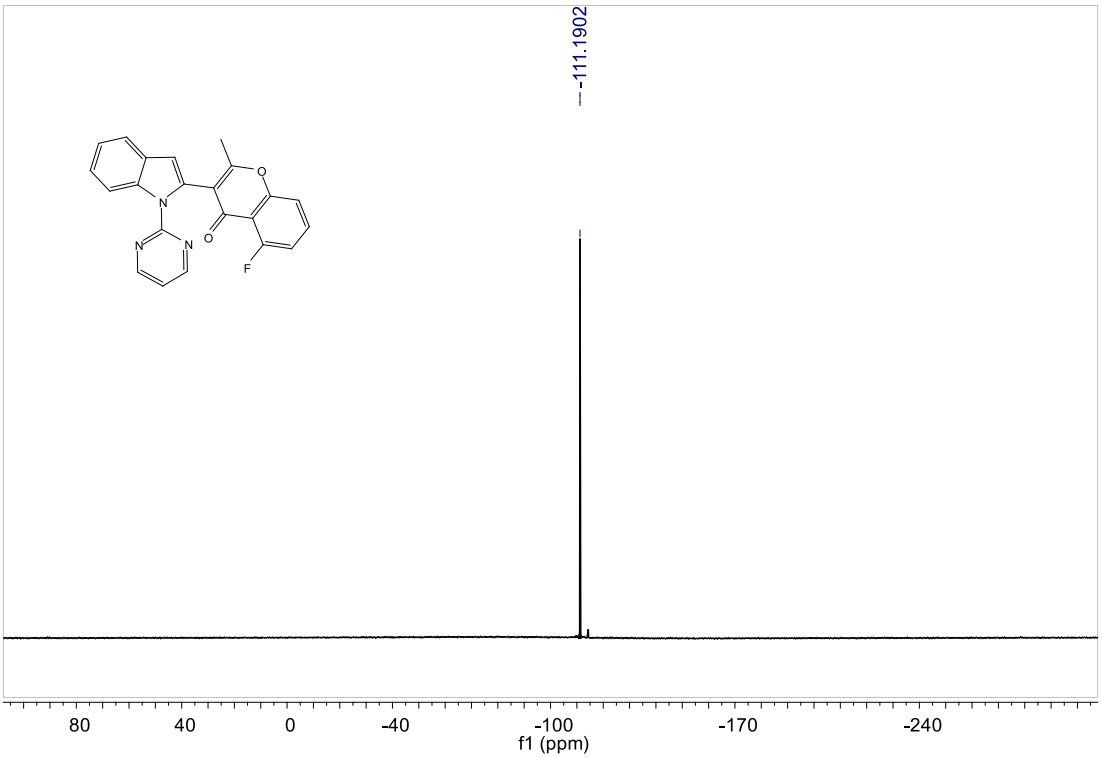
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ah



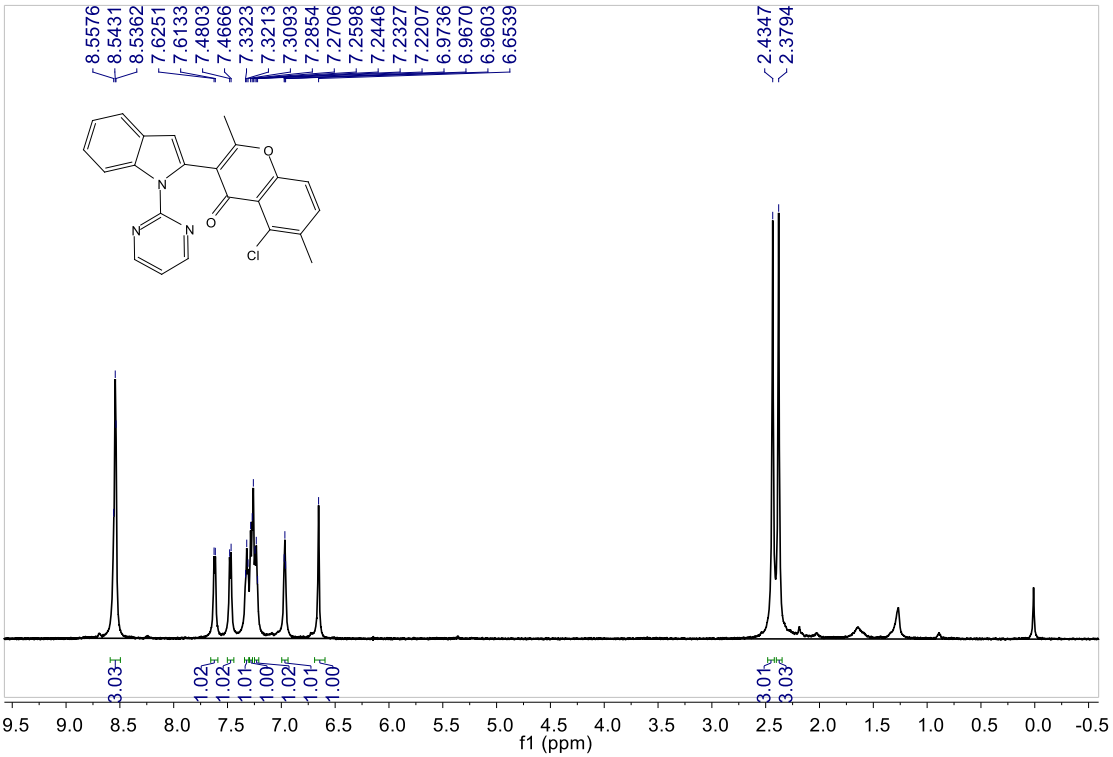
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ai



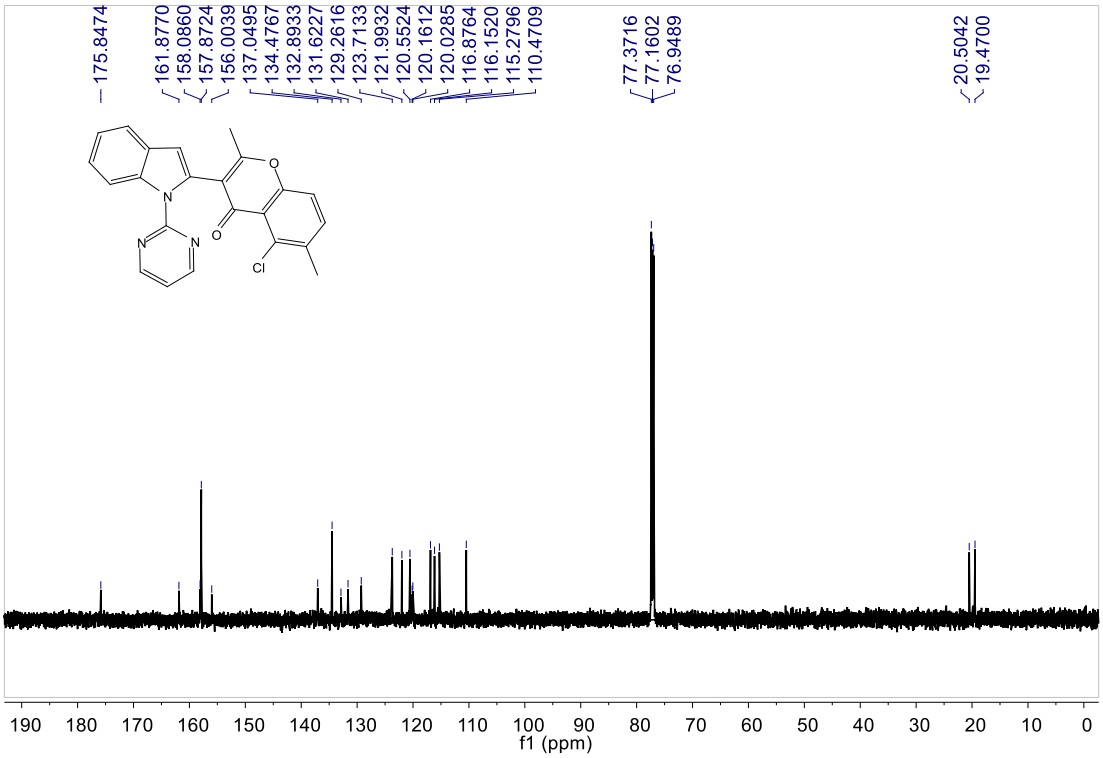
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ai



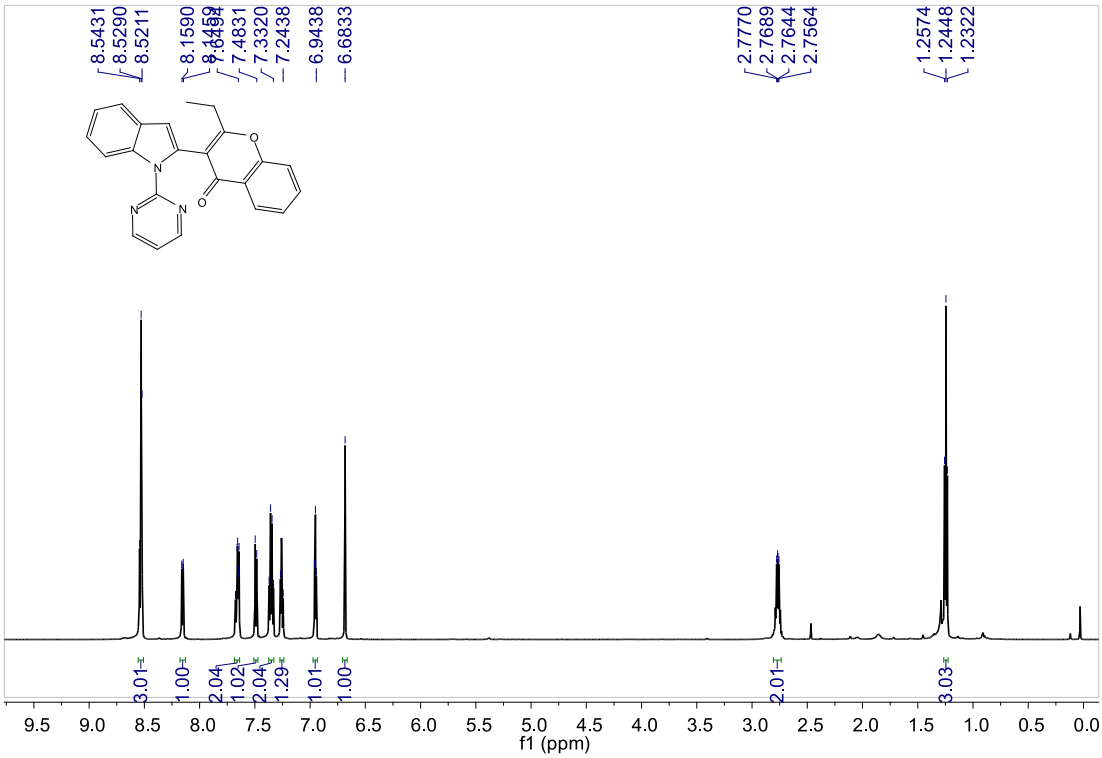
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ai



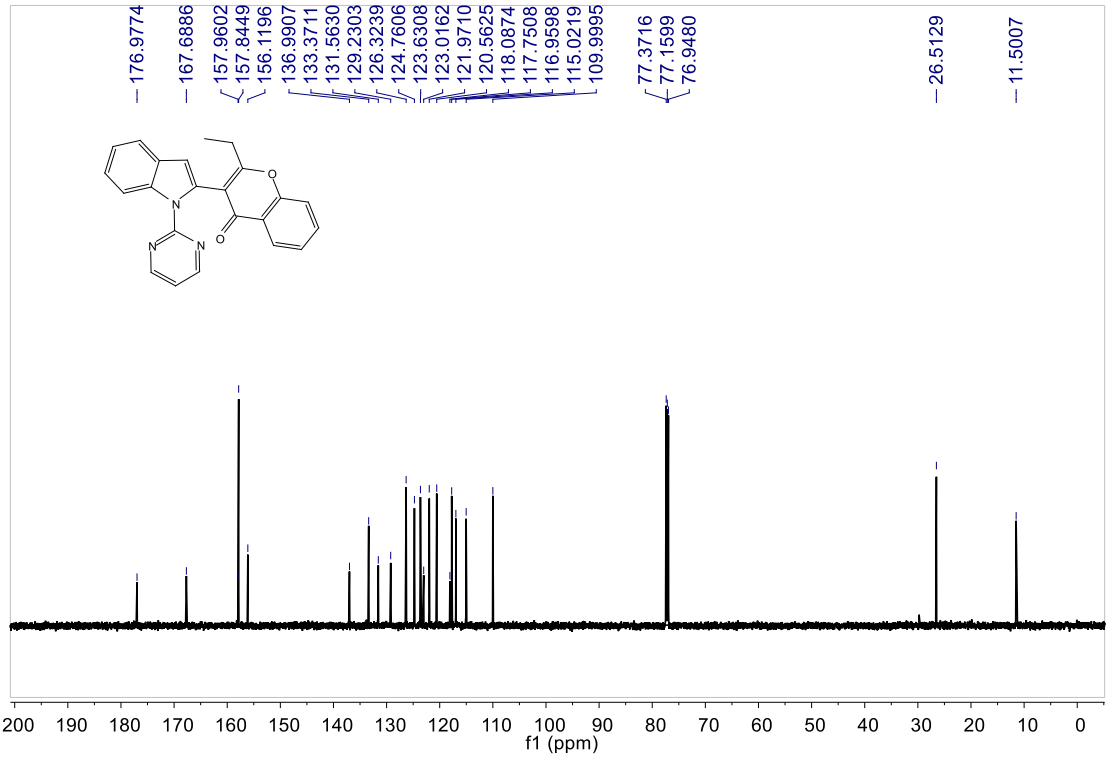
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3aj



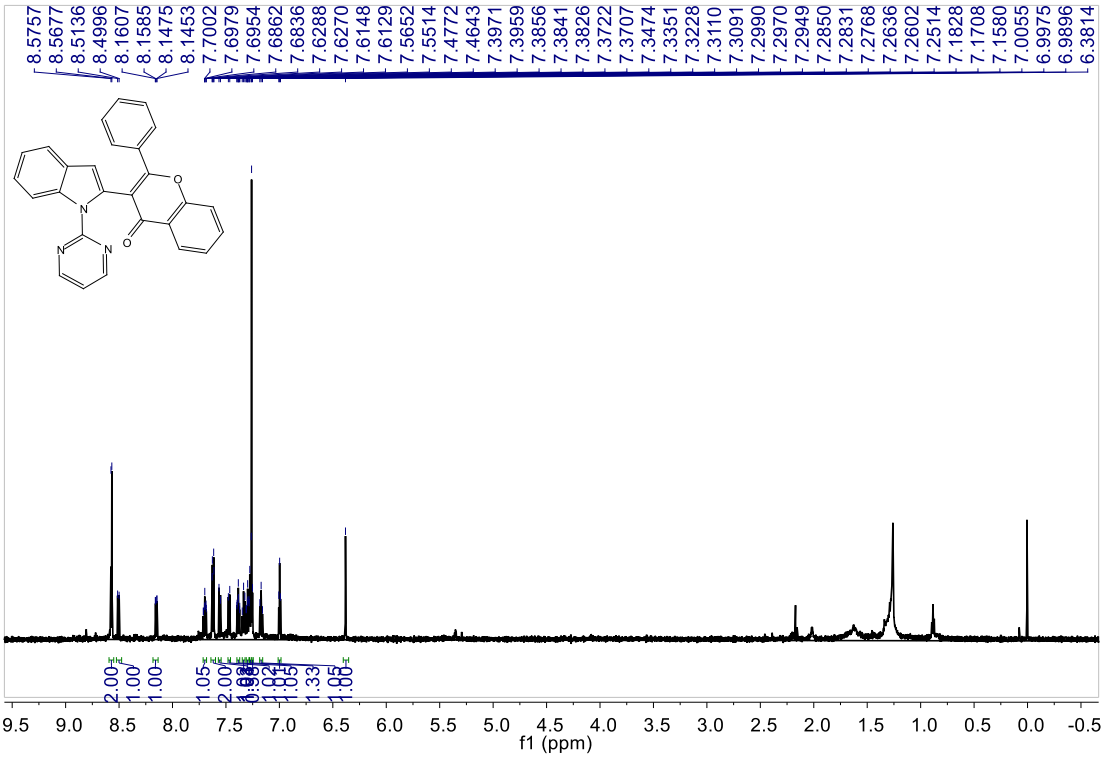
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3aj



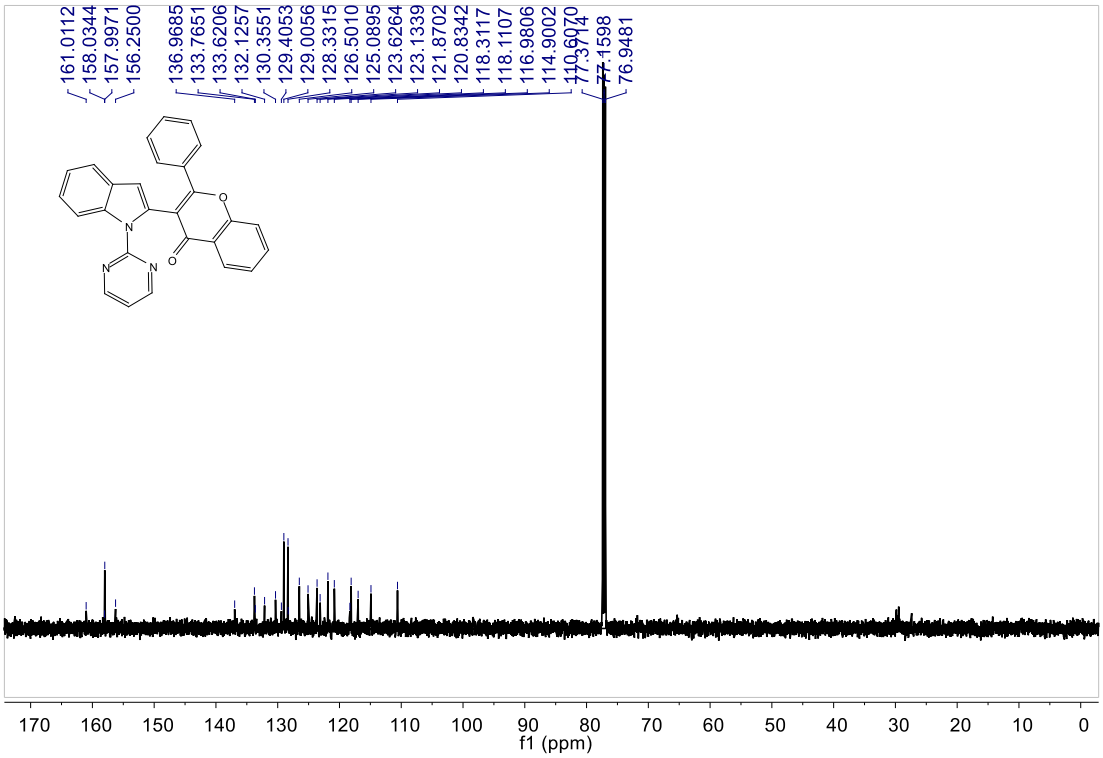
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ak



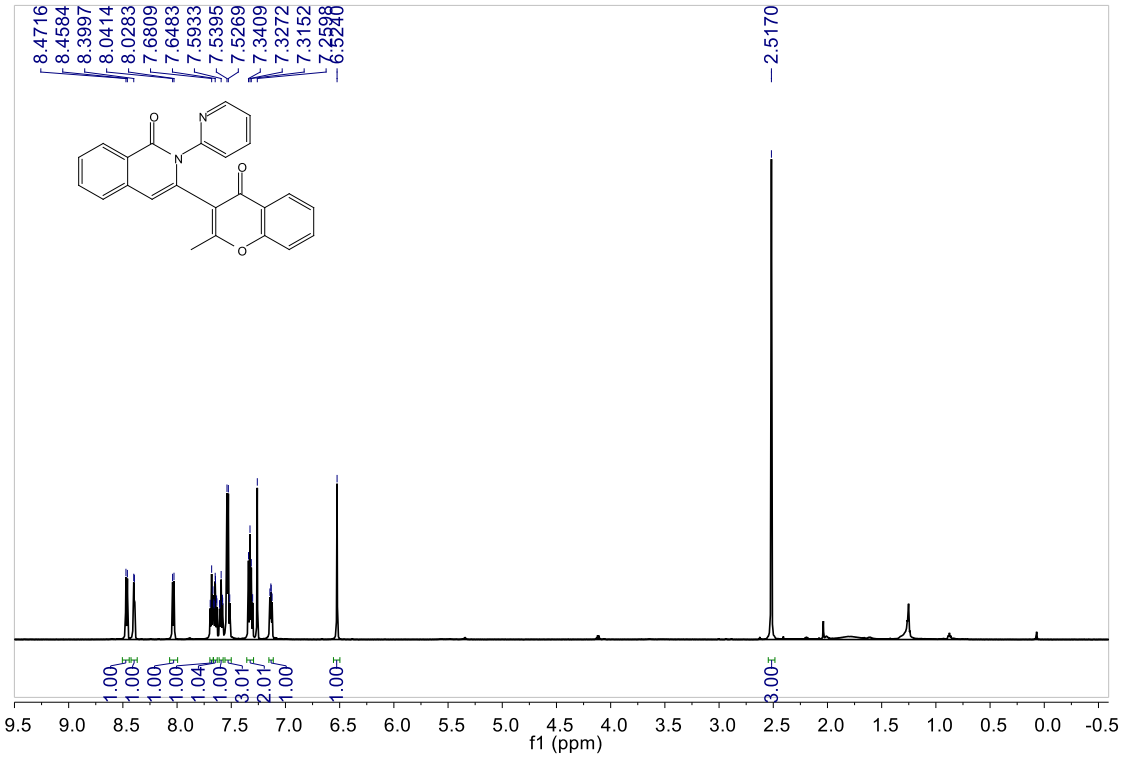
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ak



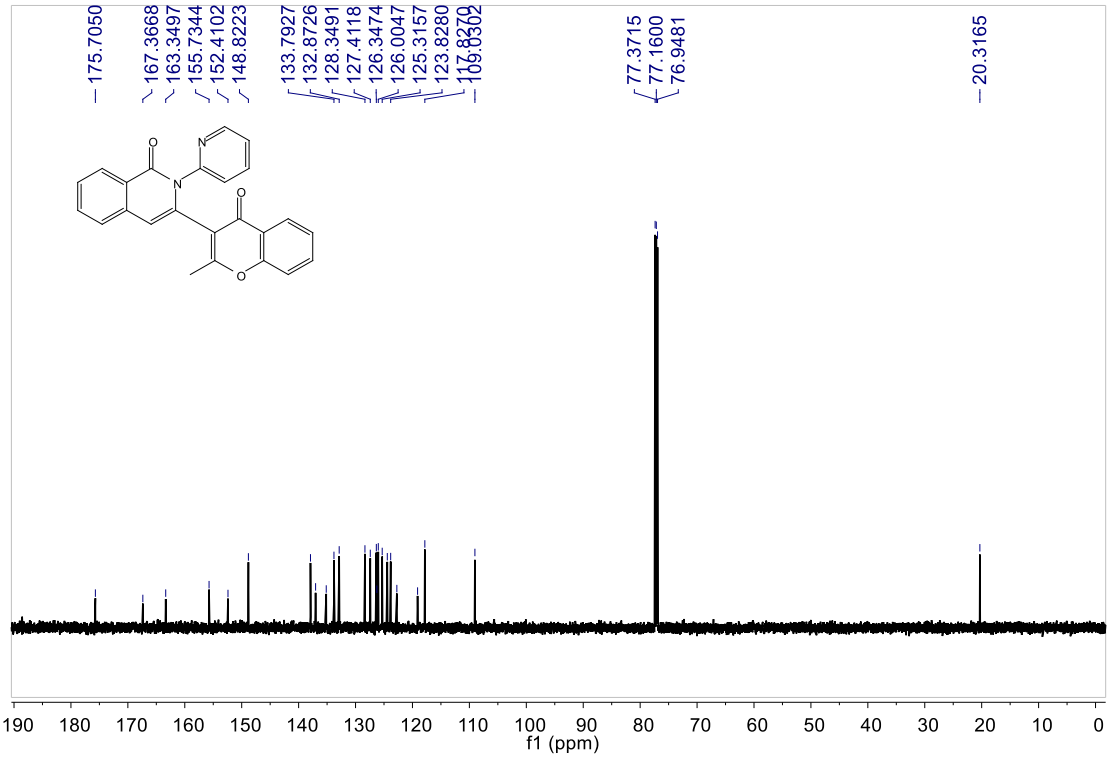
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3al



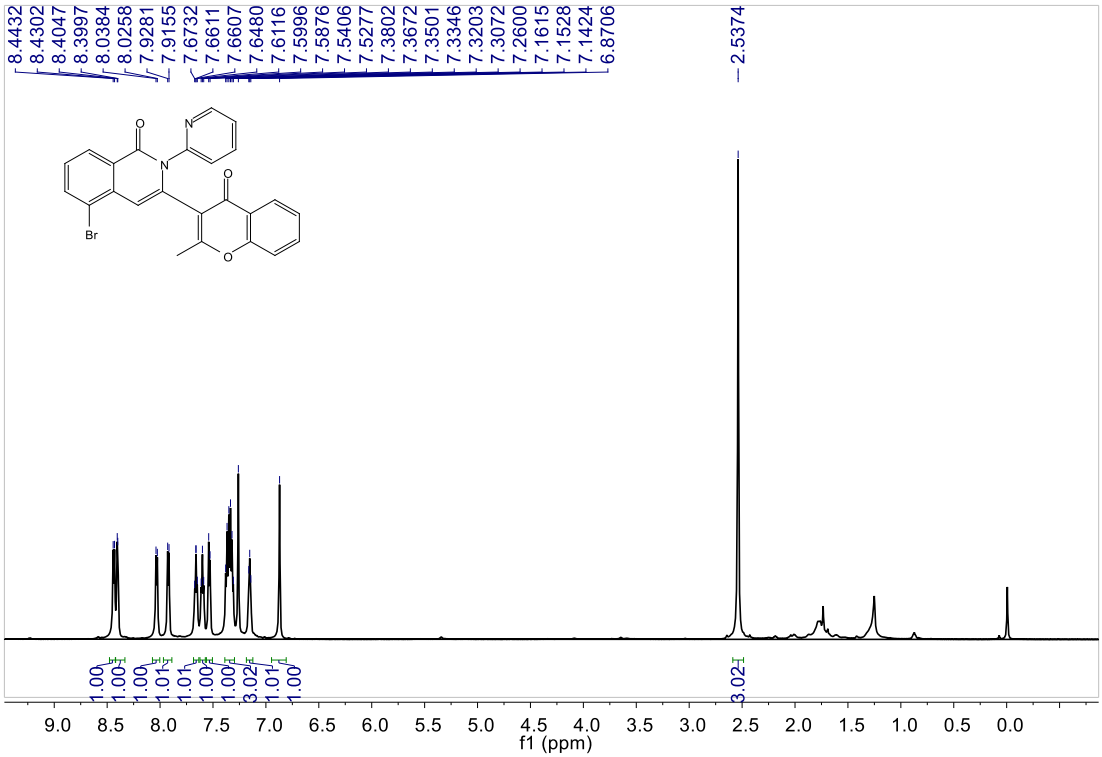
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3al



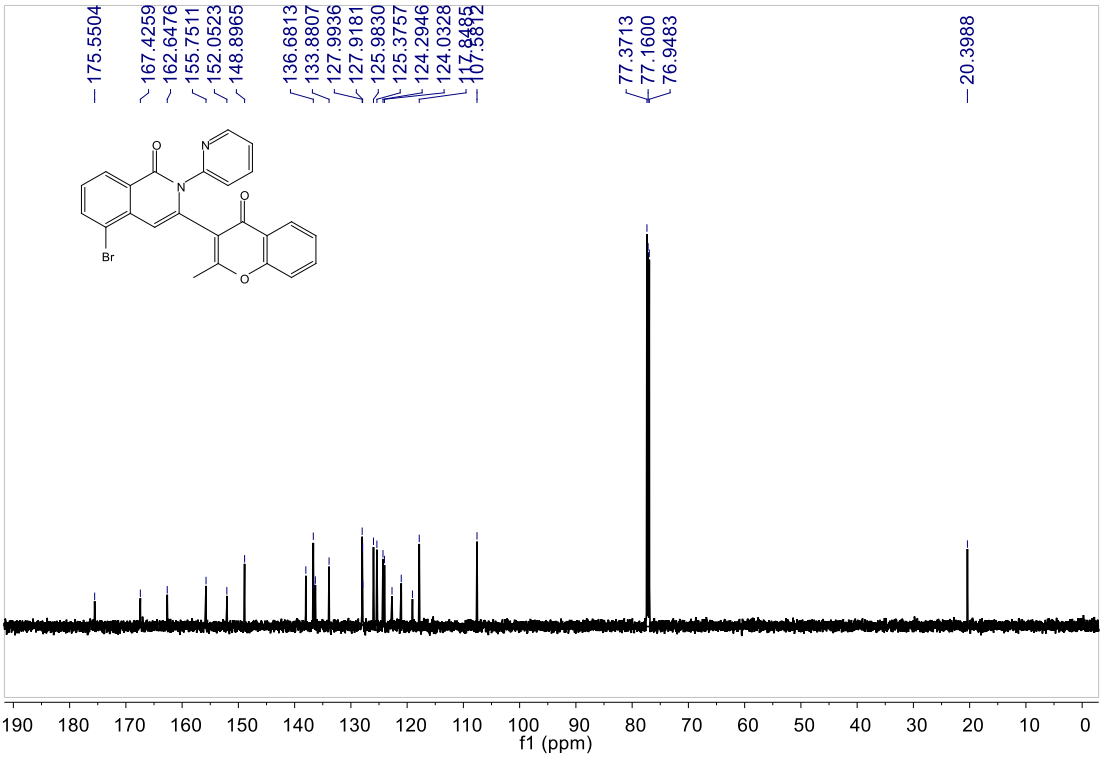
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6aa



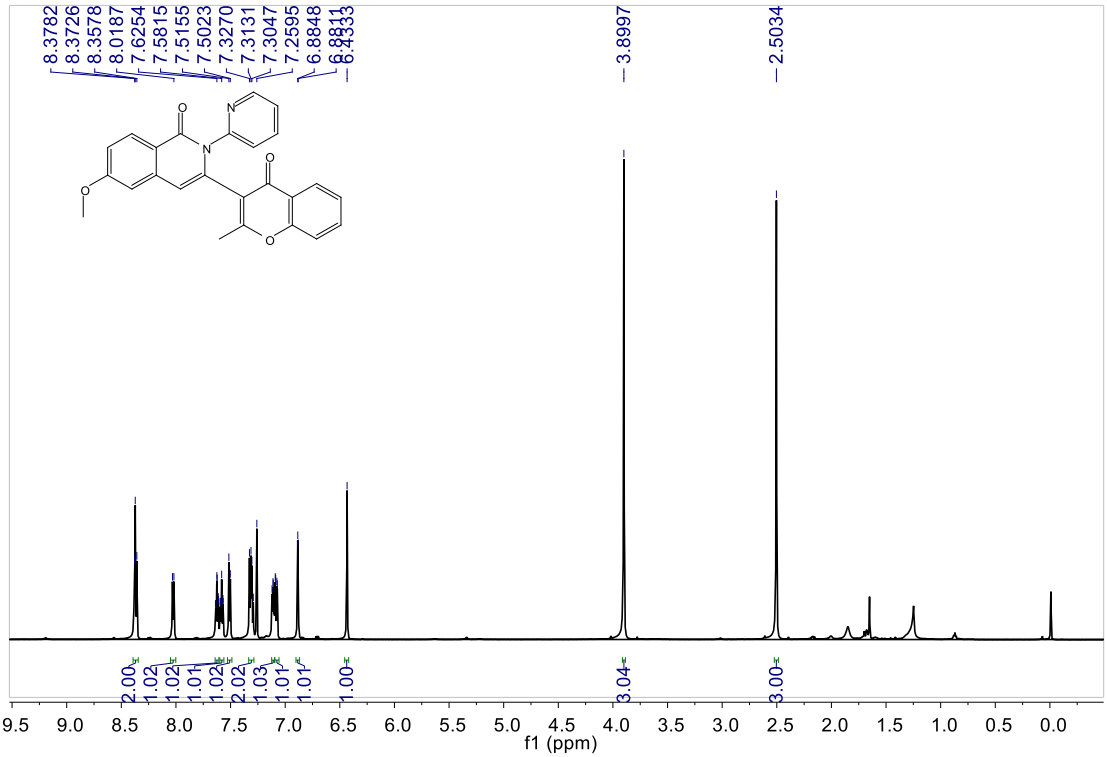
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6aa



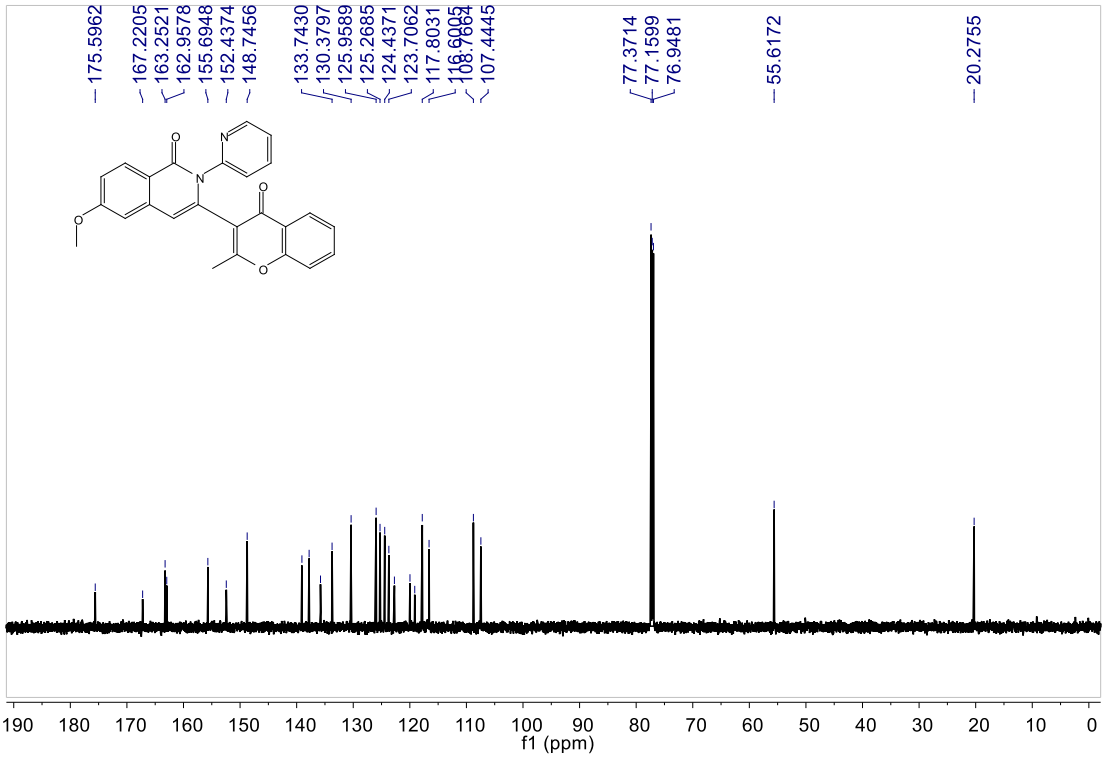
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ba



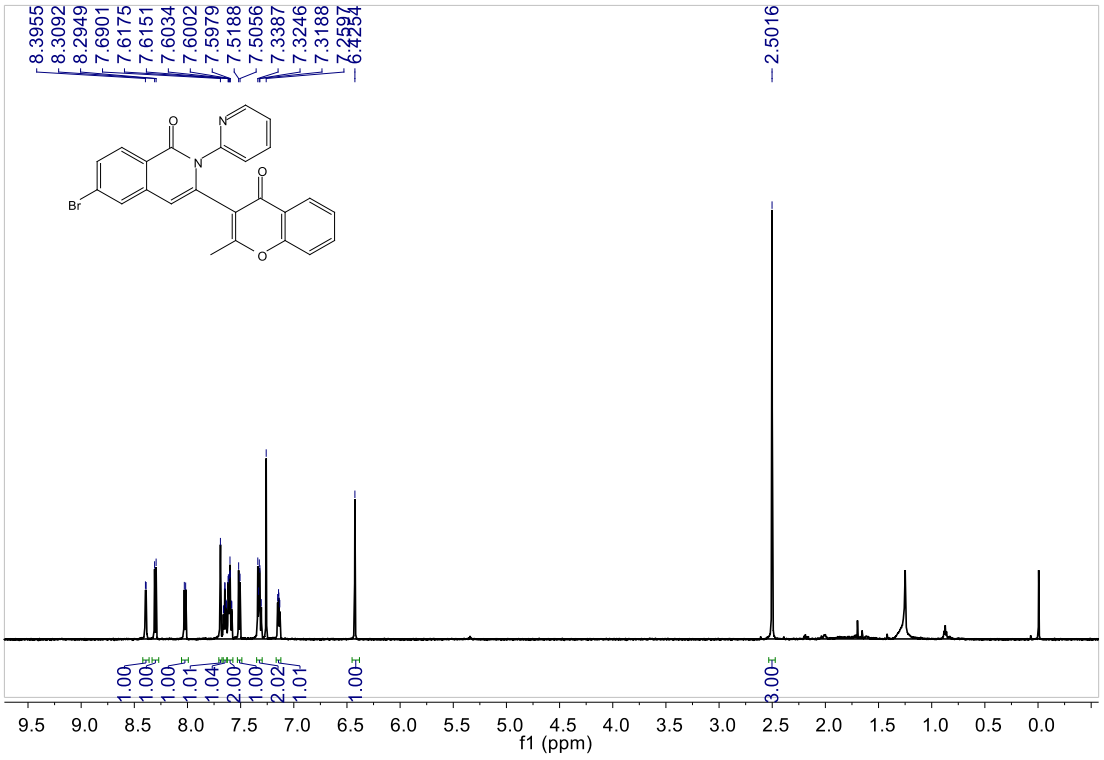
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ba



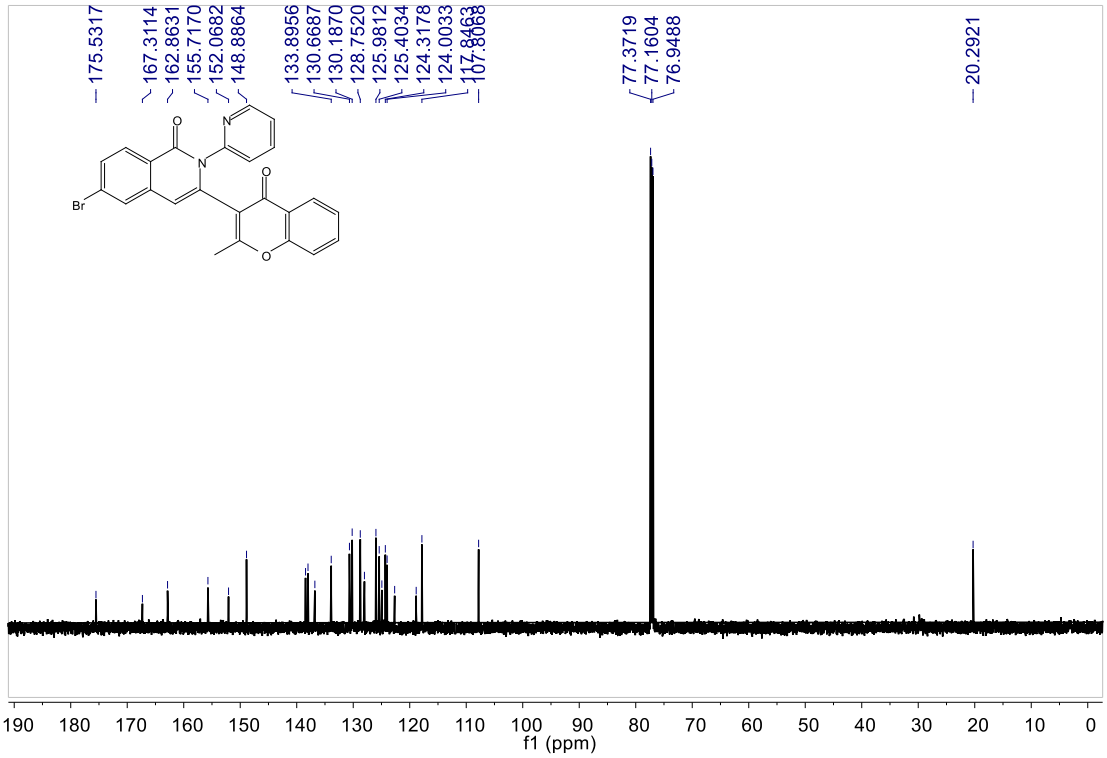
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ca



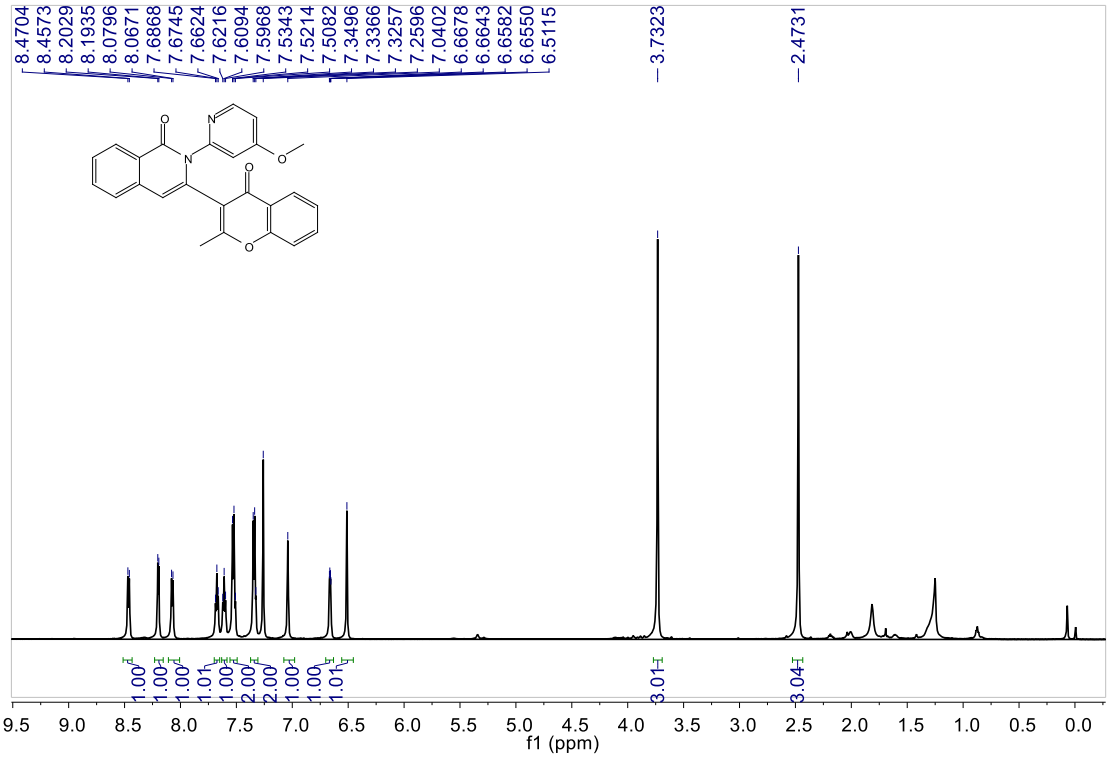
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ca



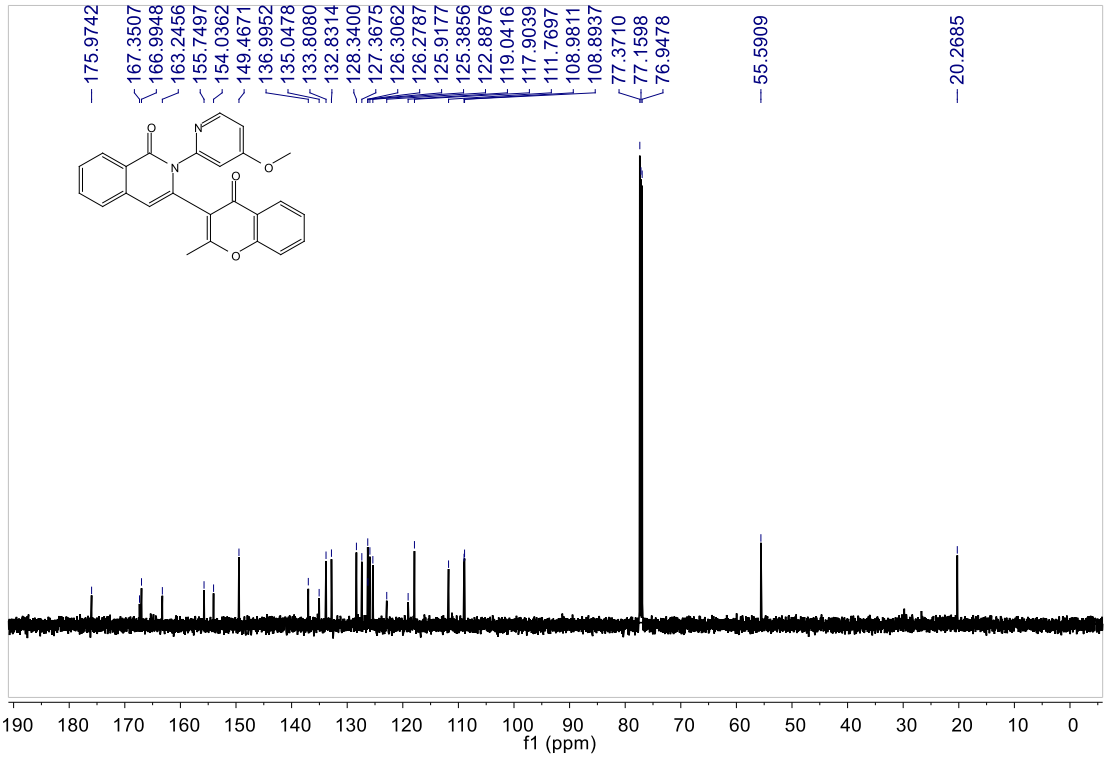
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6da



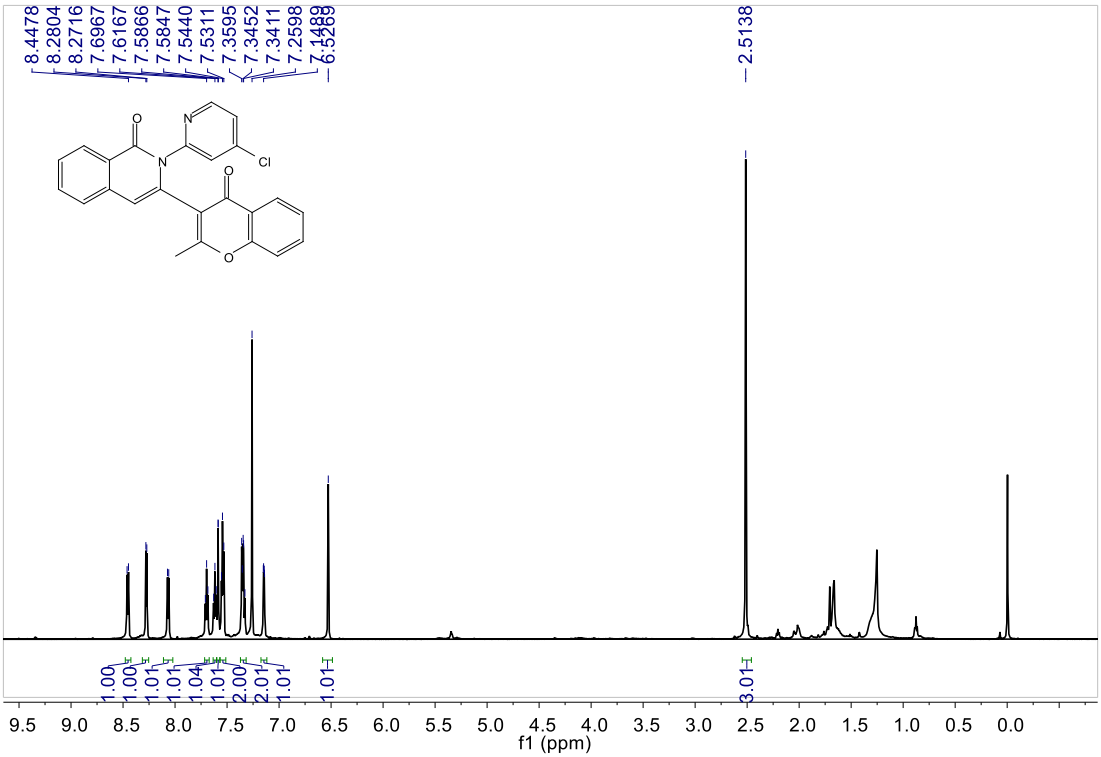
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6da



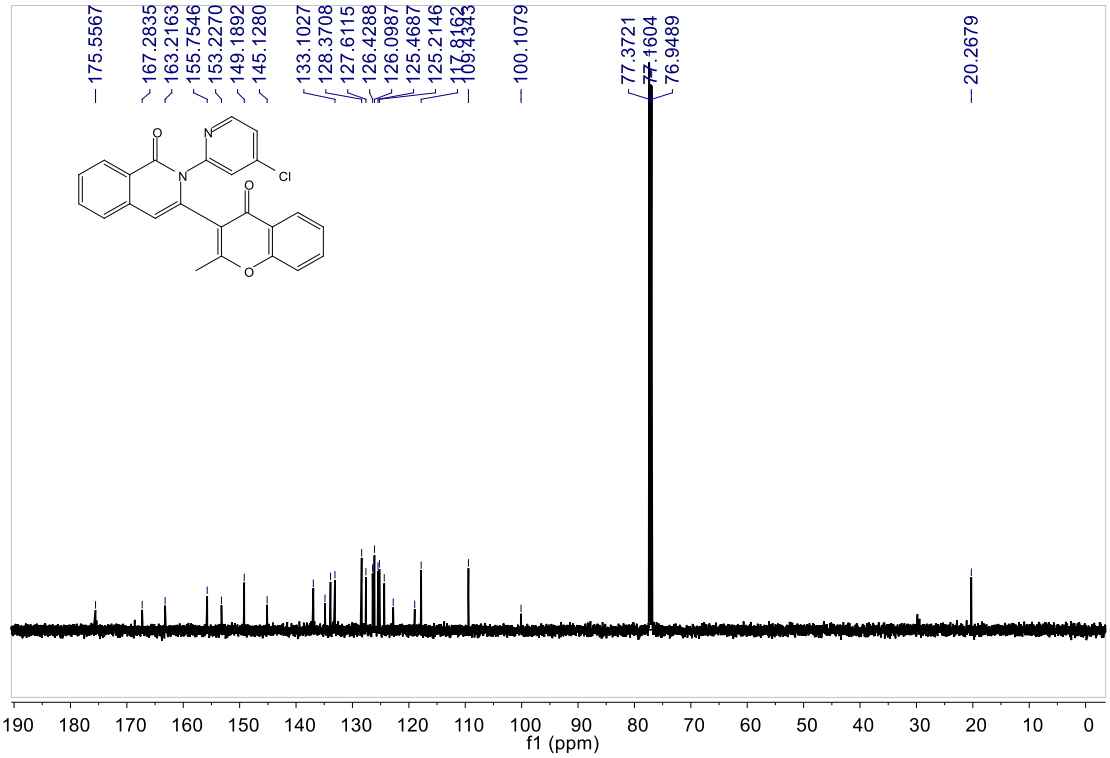
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ea



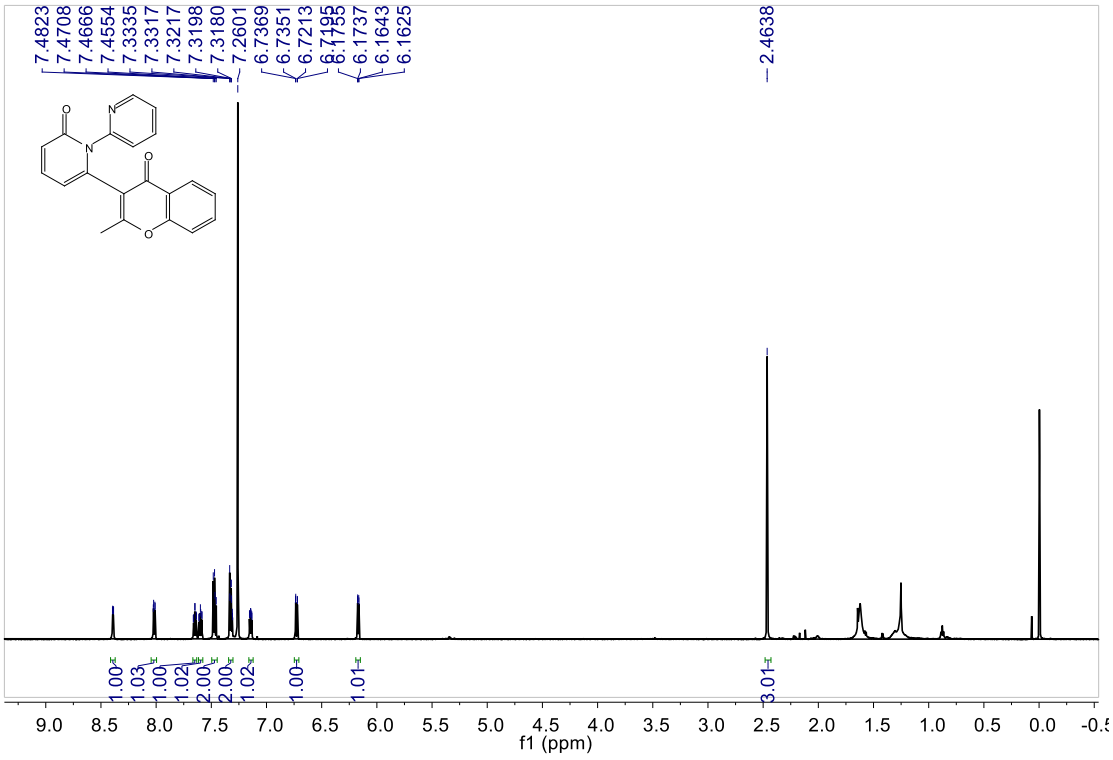
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ea



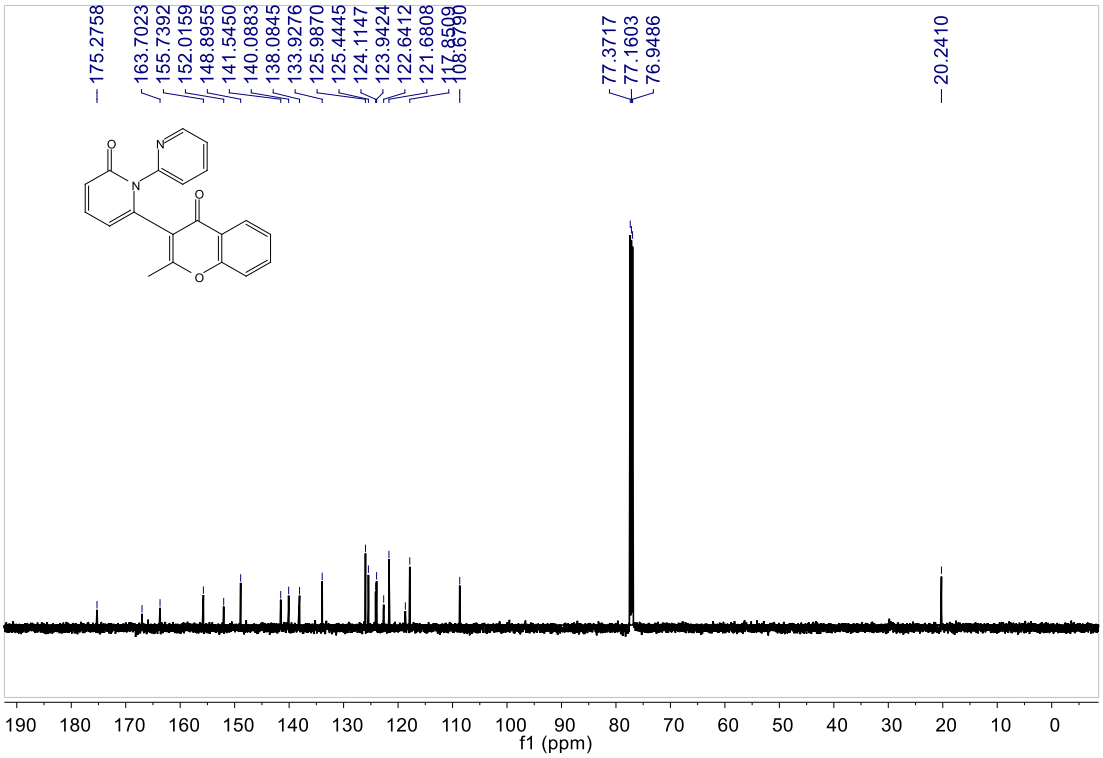
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6fa



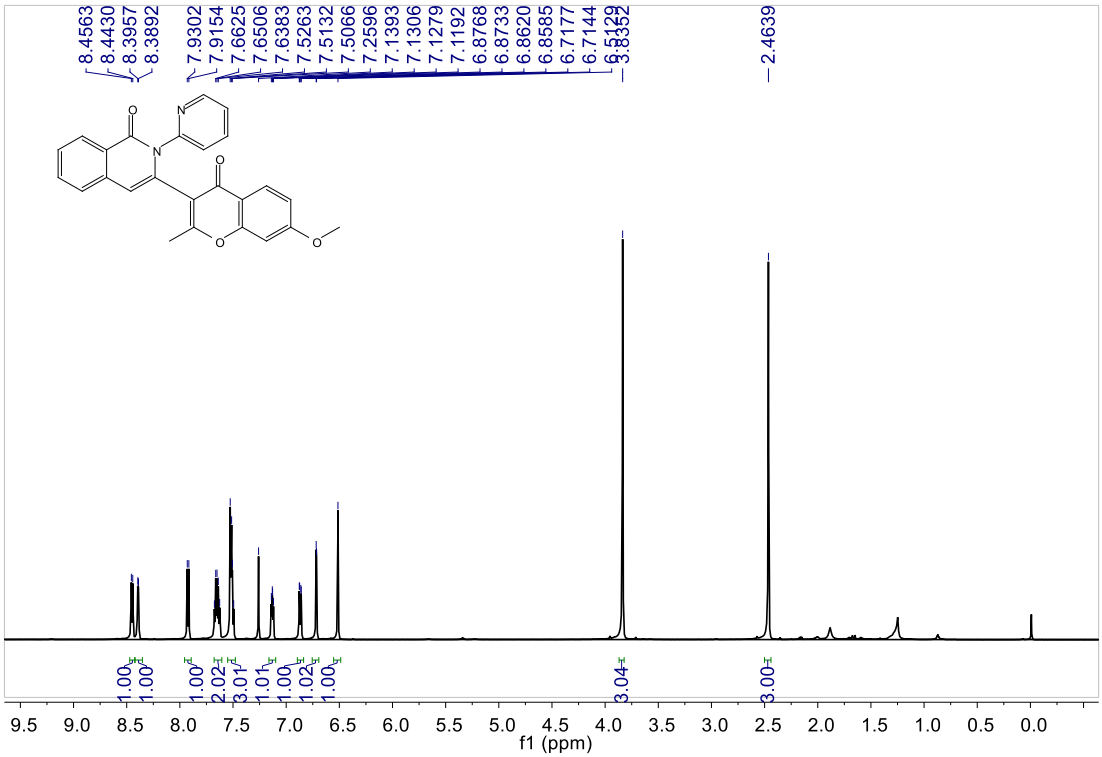
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6fa



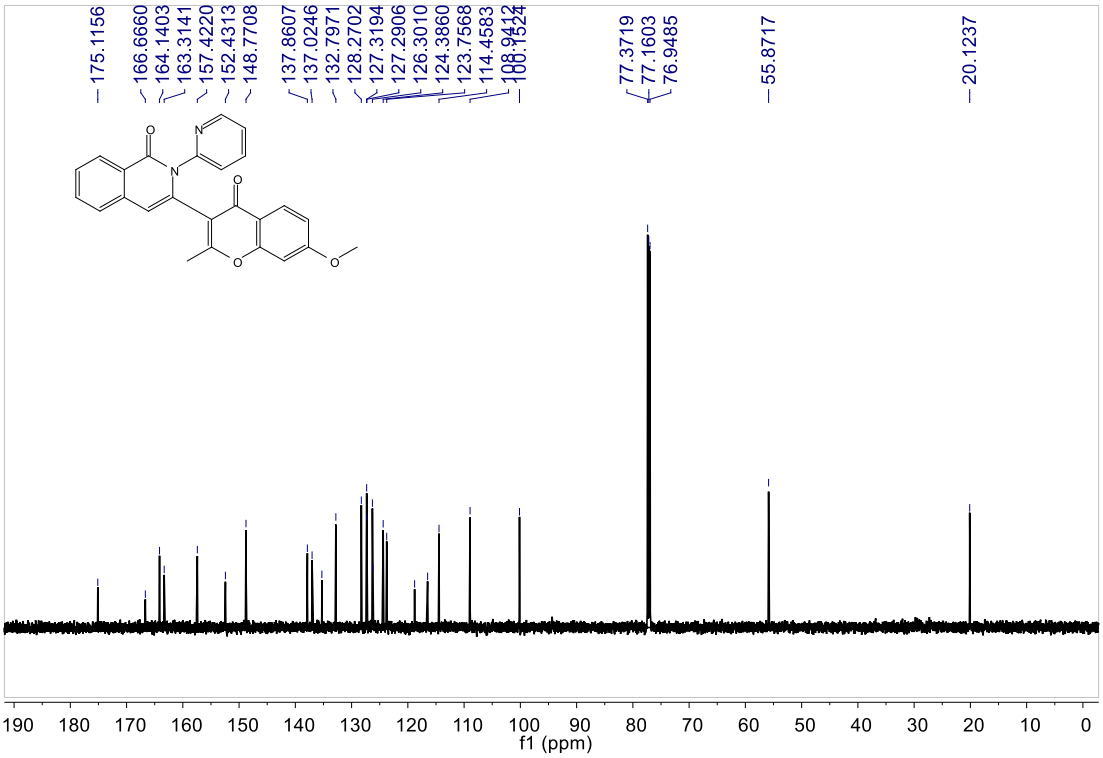
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ga



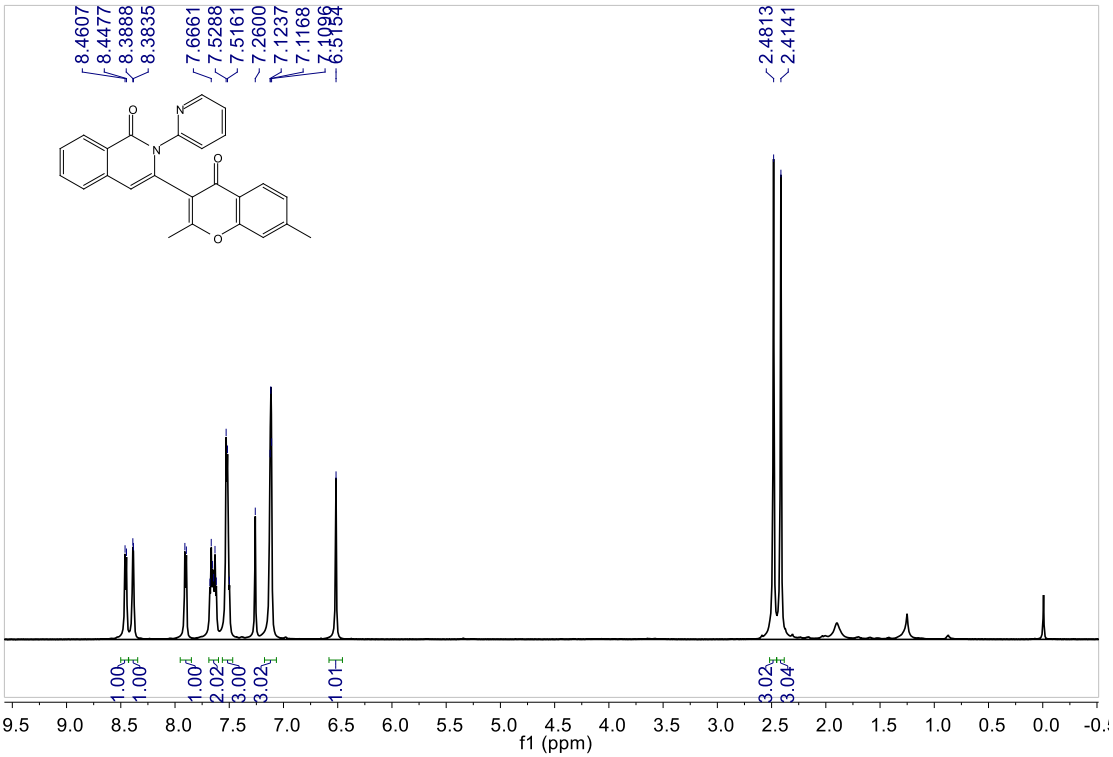
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ga



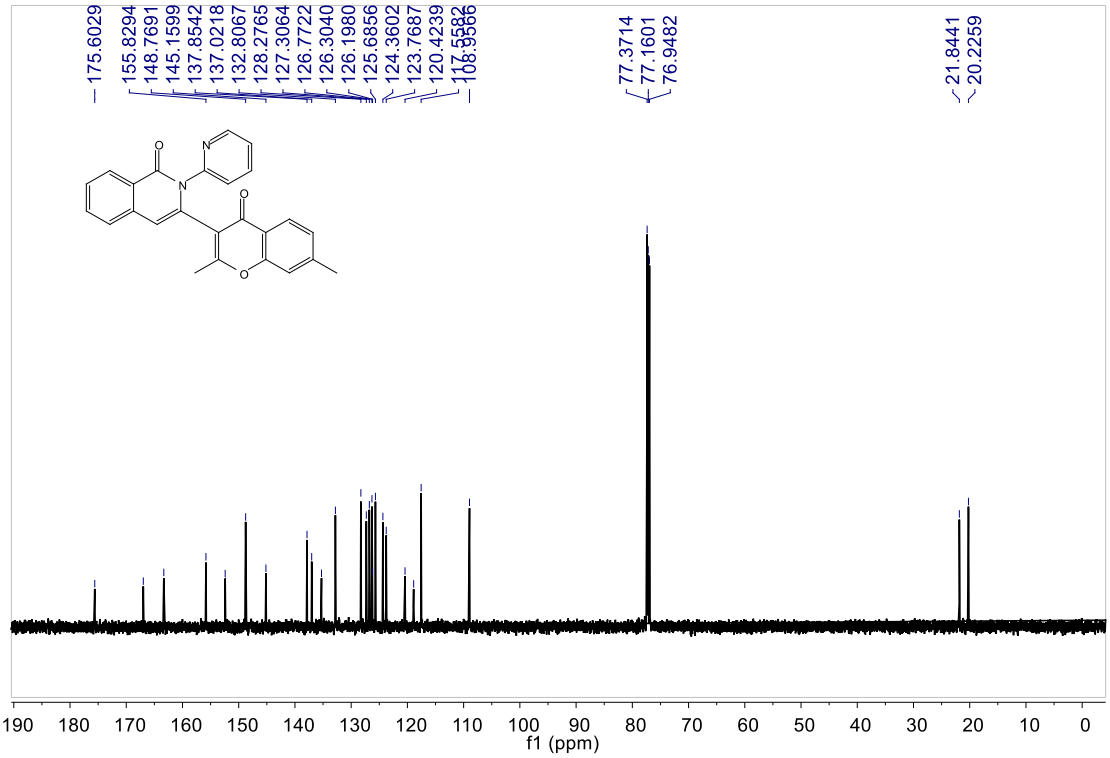
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ab



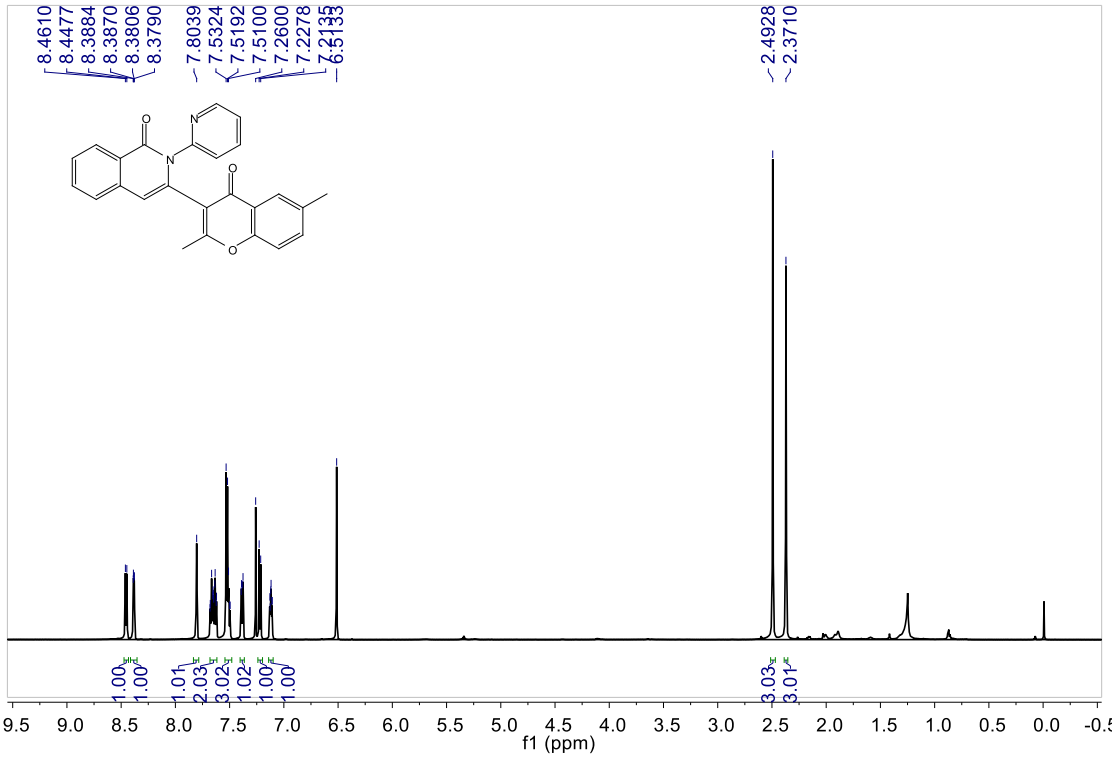
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ab



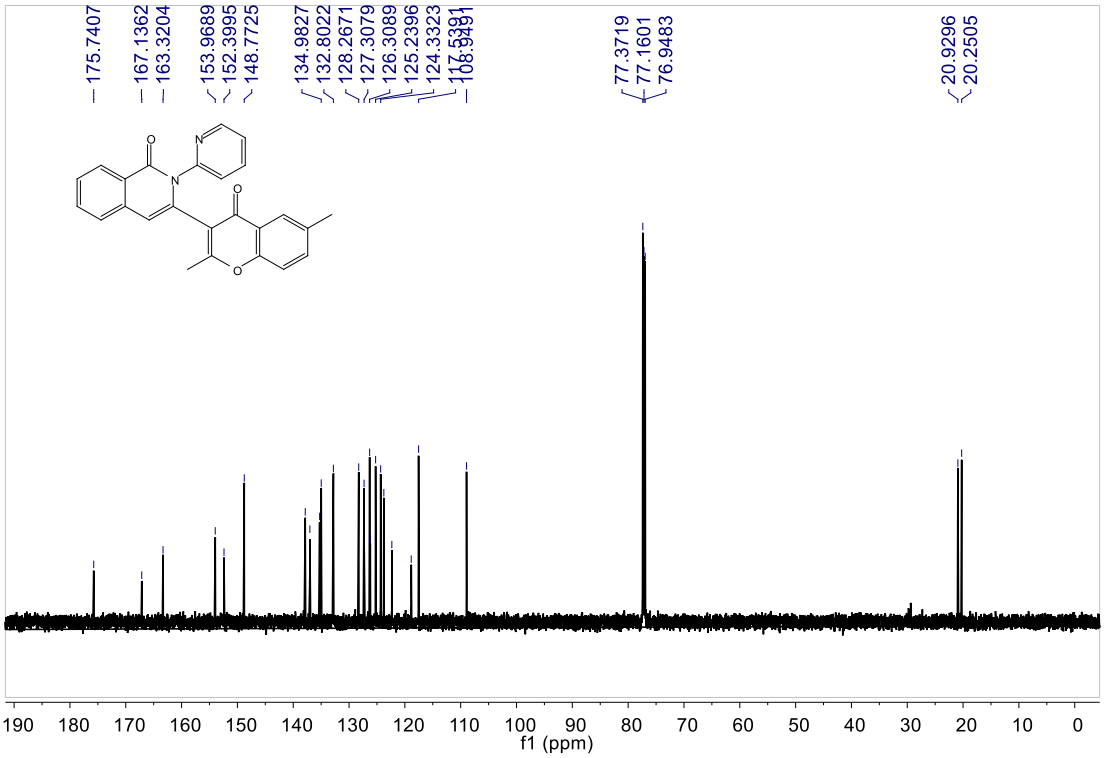
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ac



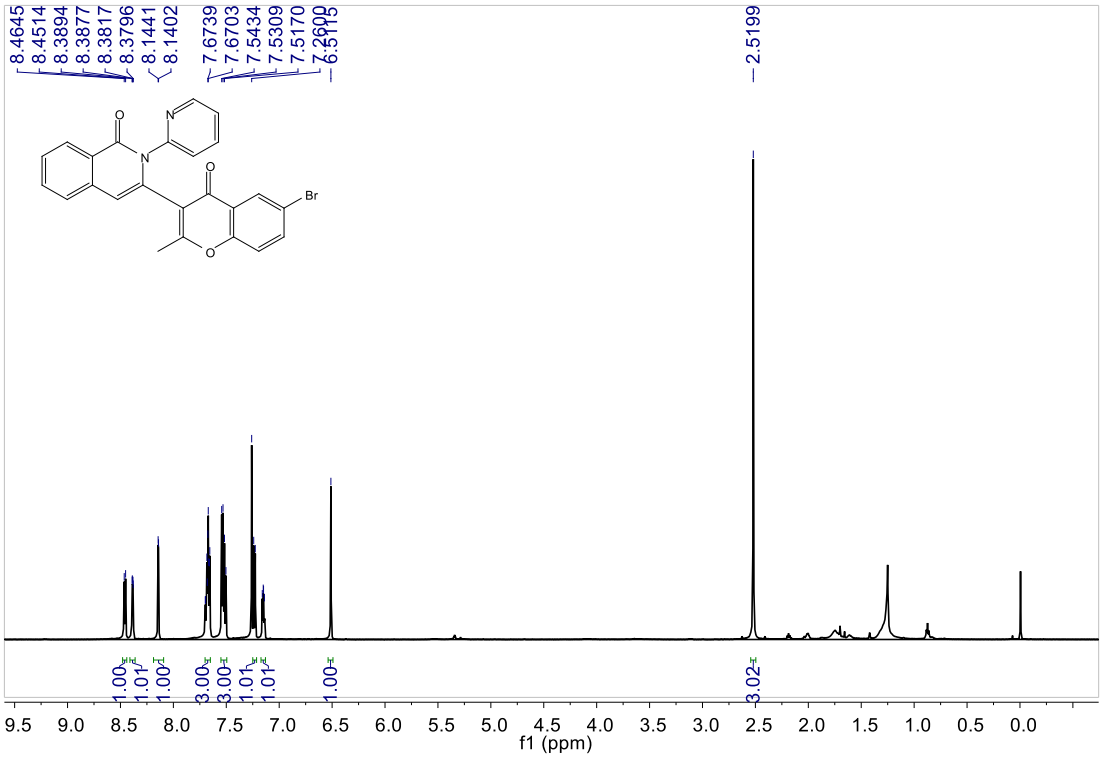
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ac



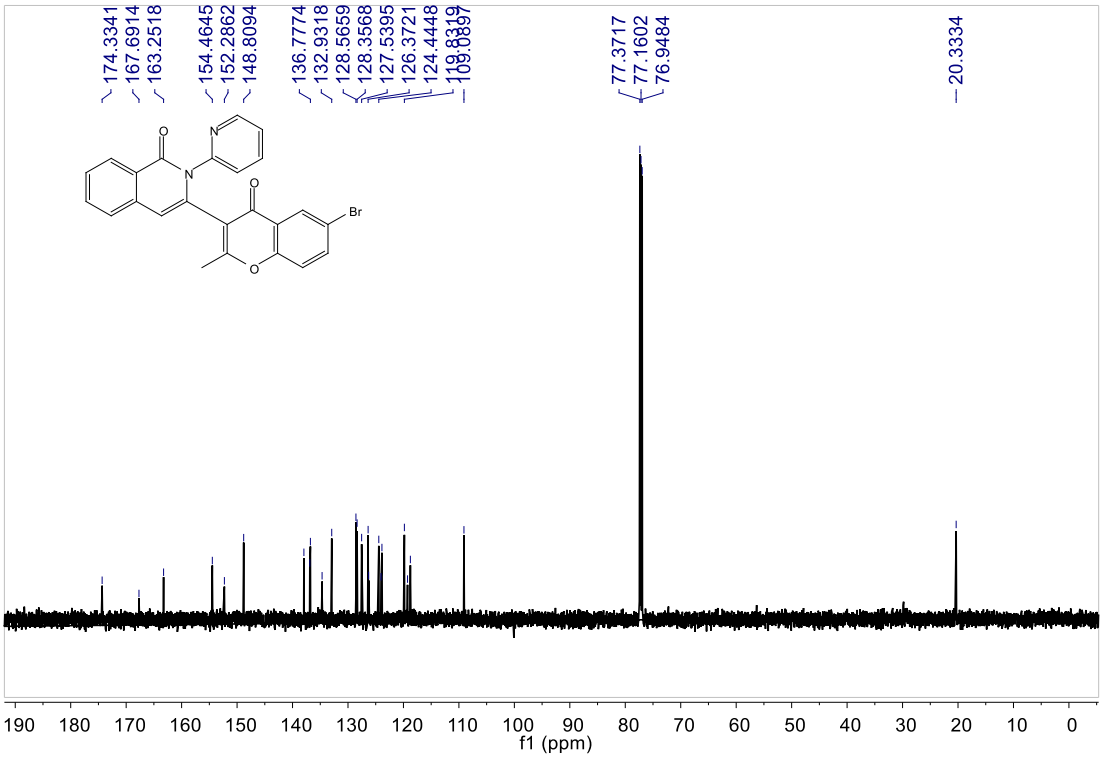
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ad



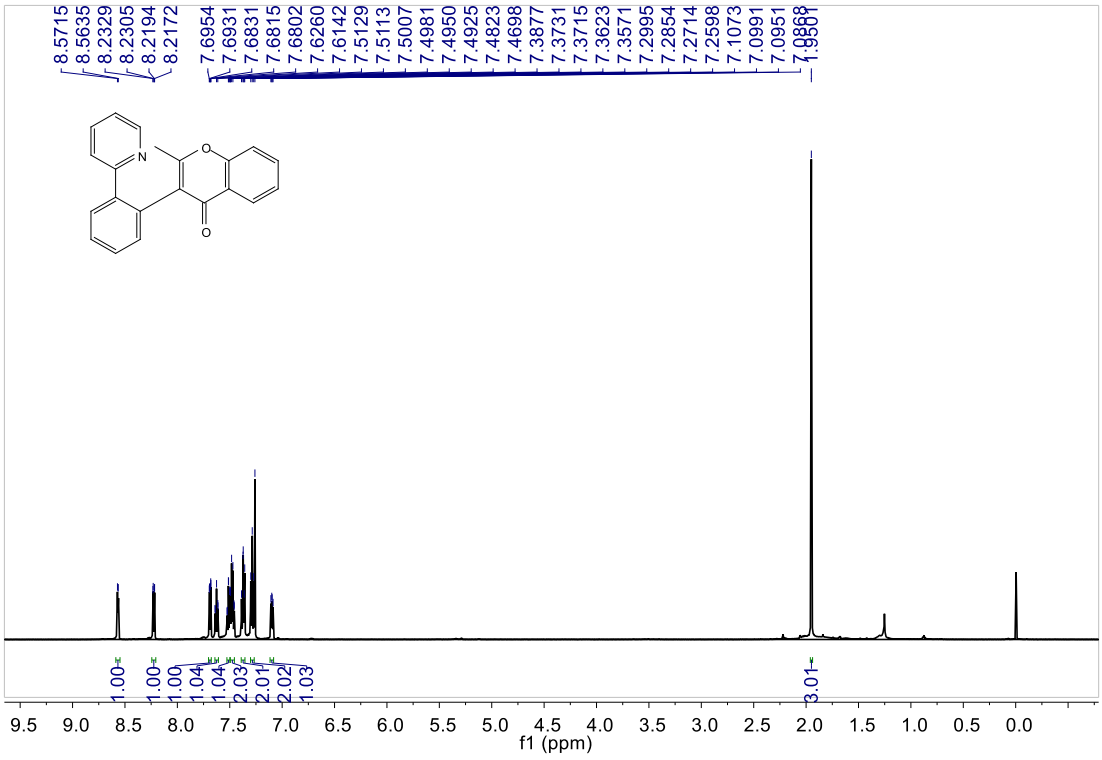
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ad



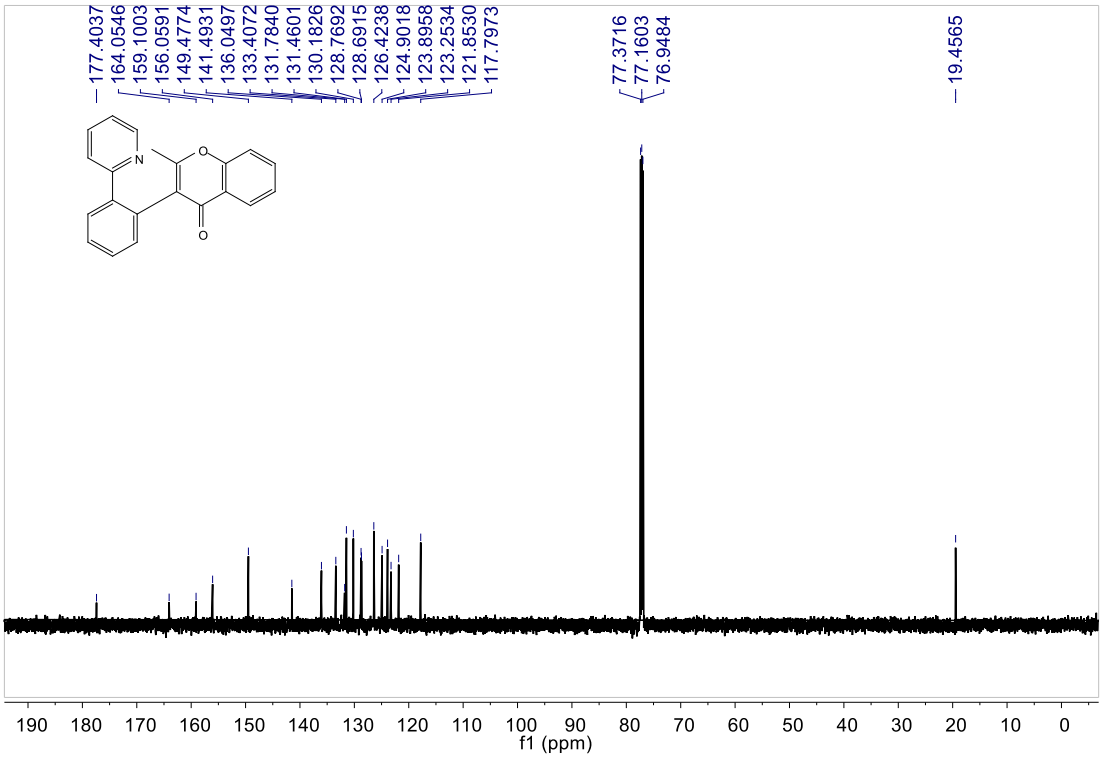
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6ae



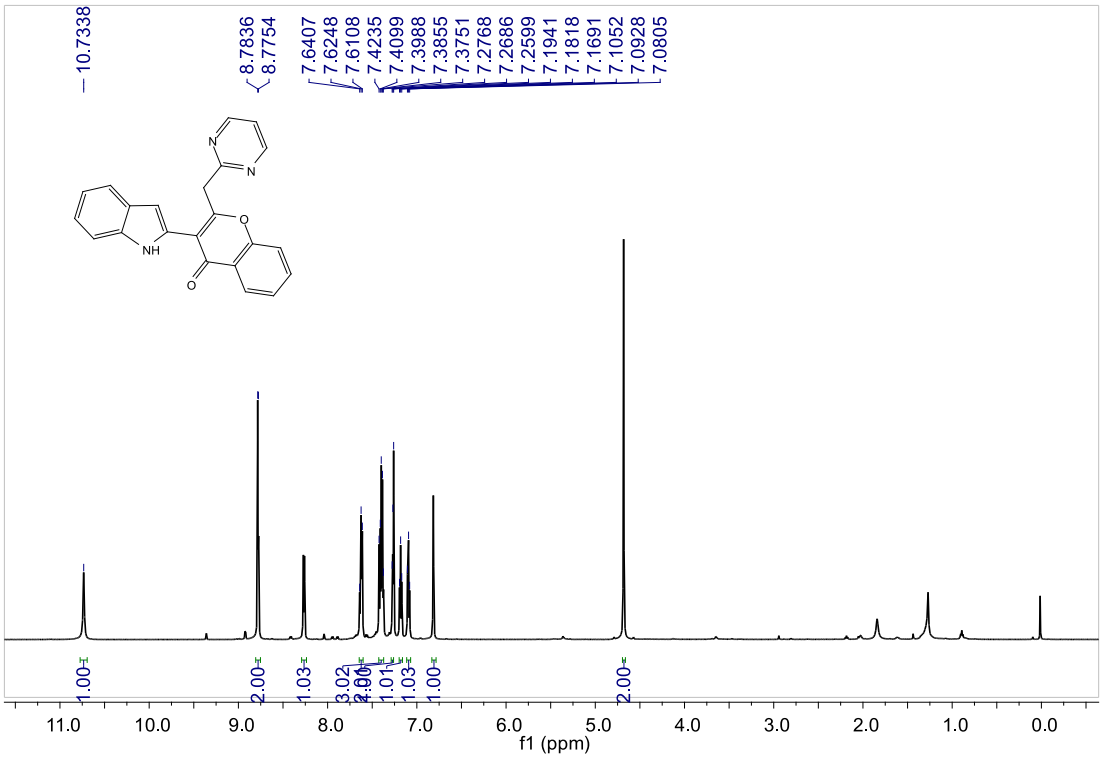
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6ae



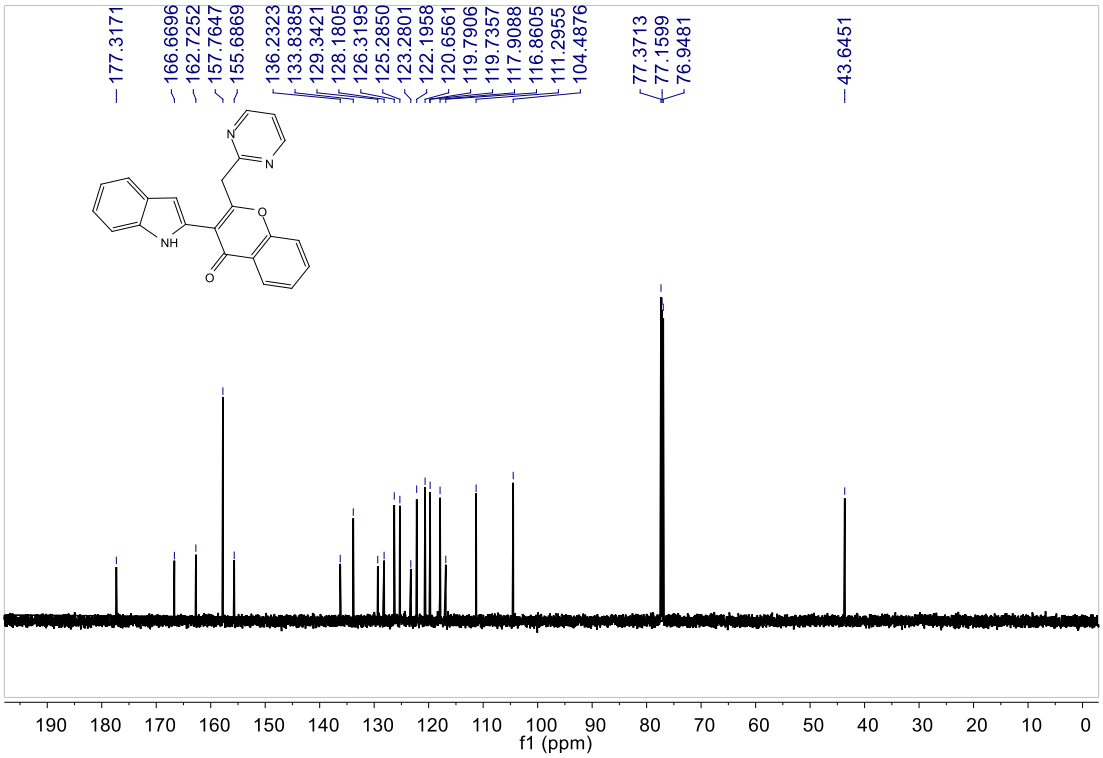
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 7a



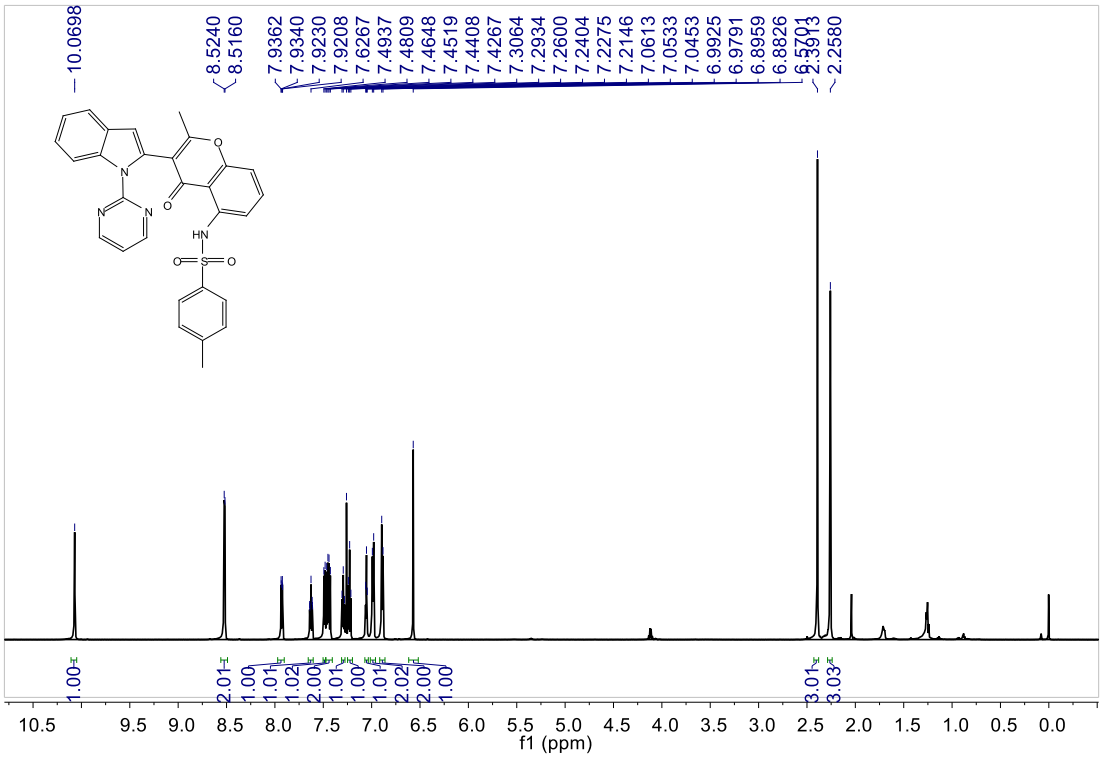
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 7a



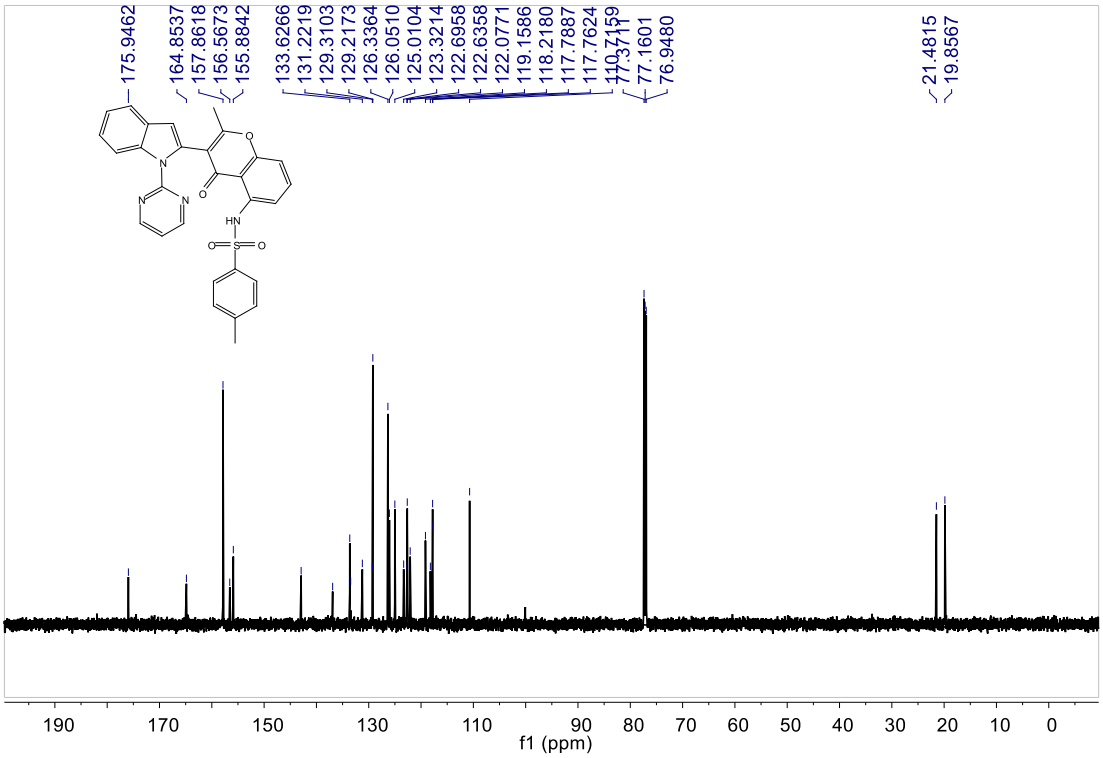
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 8



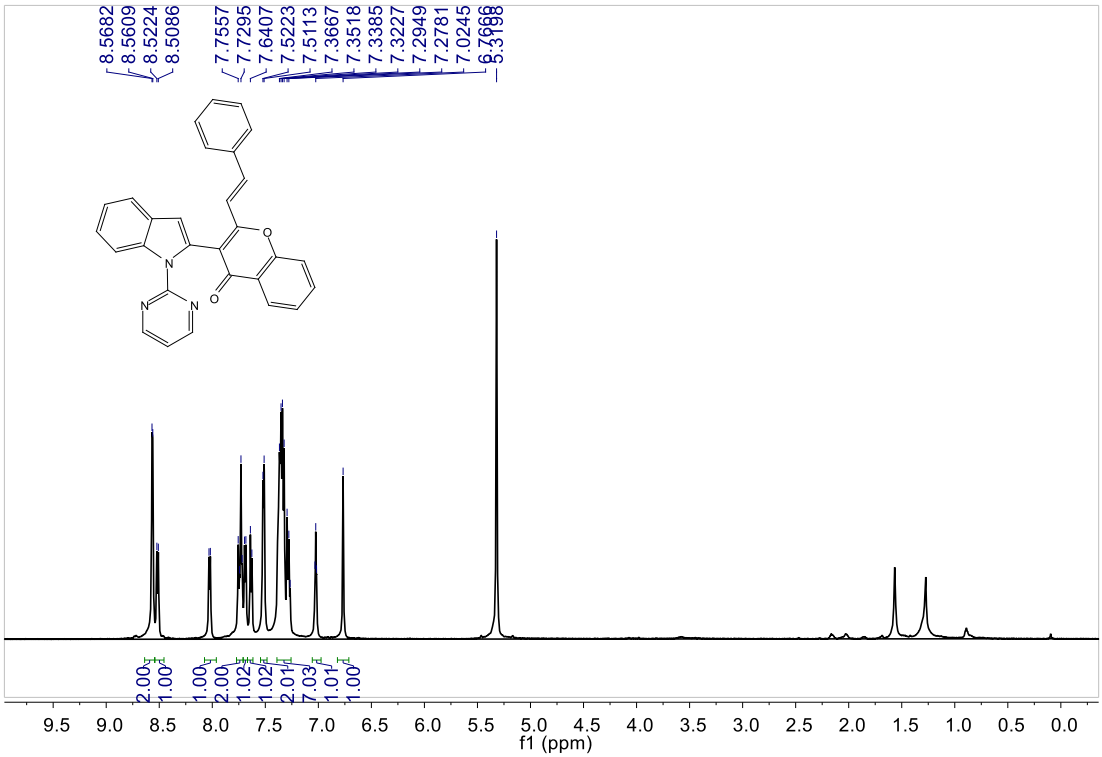
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 8



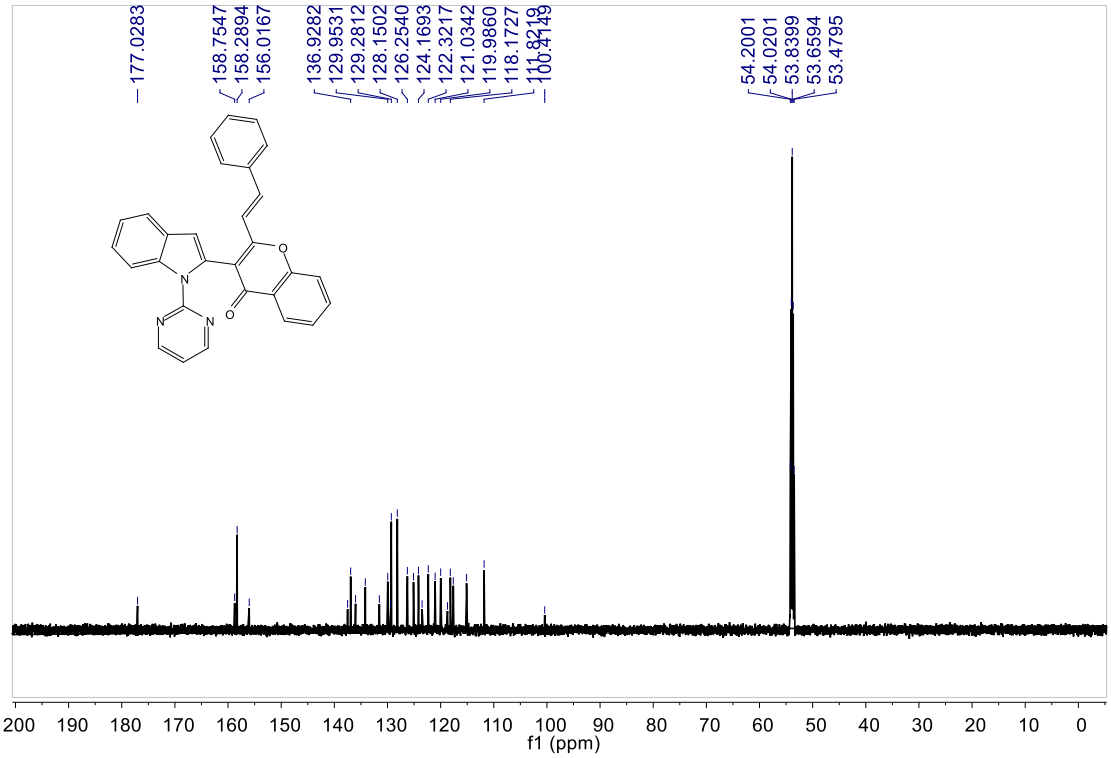
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 9



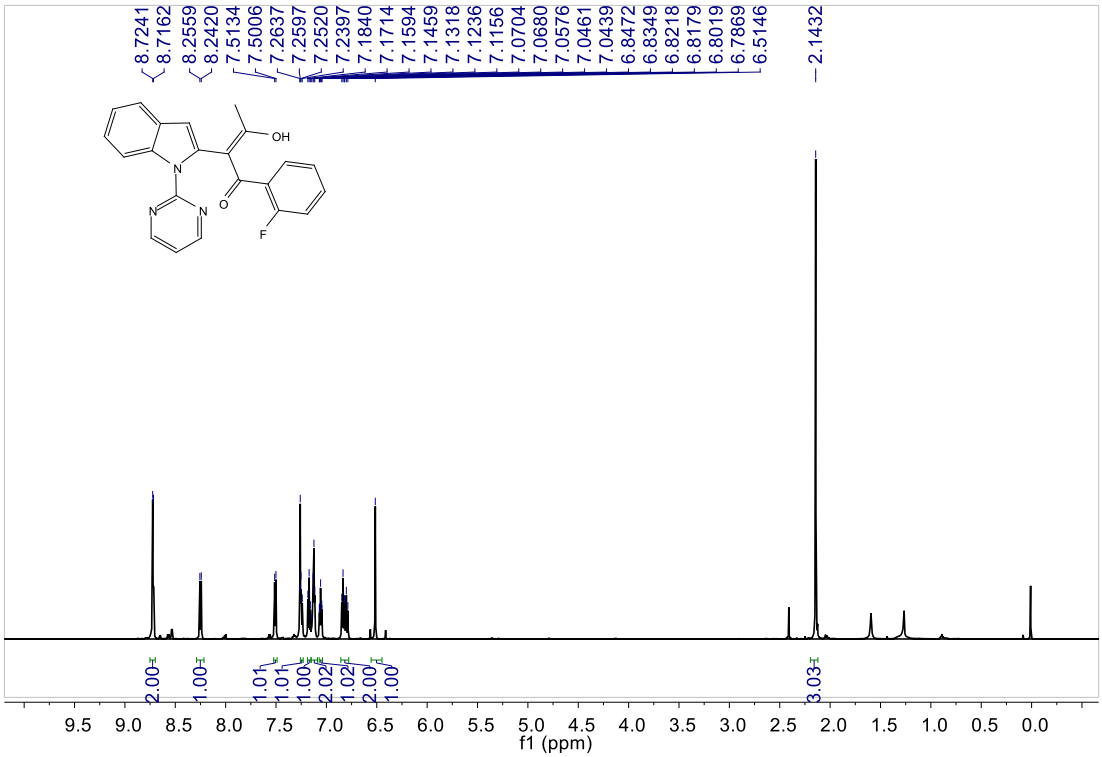
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 9



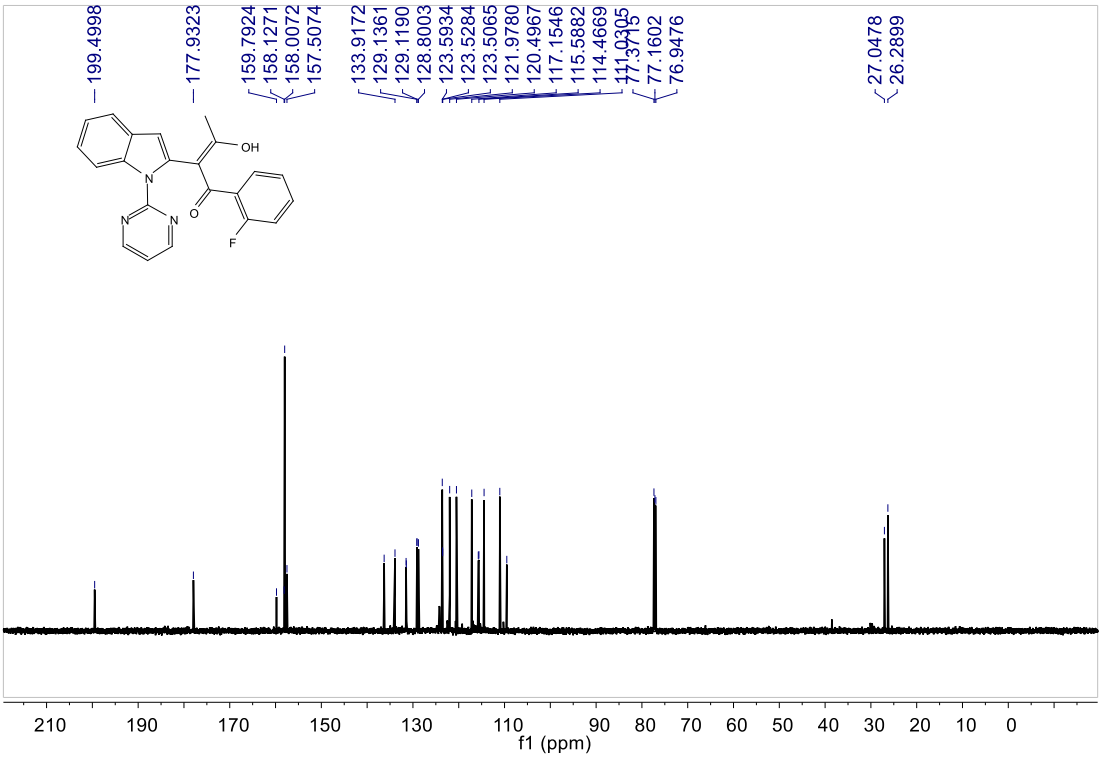
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of 10



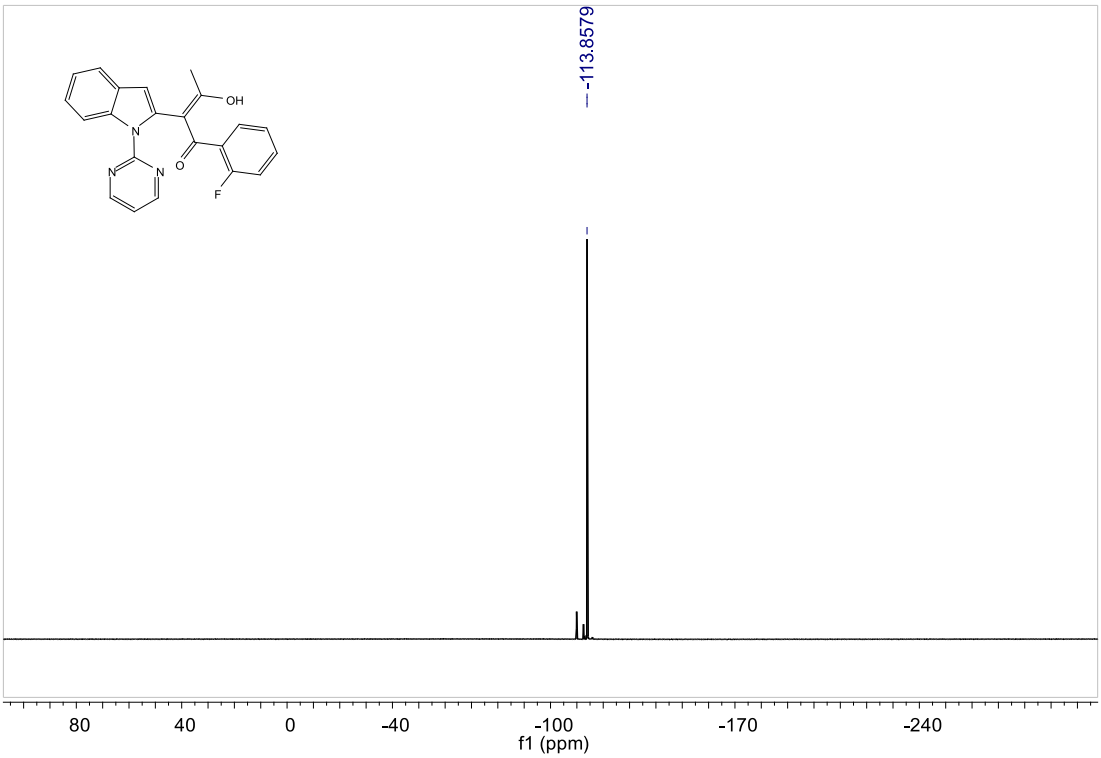
^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of 10



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 11



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 11



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 11