

Supporting Information

Carbon dioxide as a methylene donor: modular synthesis of 3-aminomethyl chromones via a reductive tandem reaction

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List of Contents

A. General methods.....	S2
B. General procedure for the synthesis of 3-aminomethyl chromones 3.....	S2
C. Optimization of the reaction conditions.....	S3
D. Procedure for the synthesis 3aa on a 2 mmol scale	S7
E. Synthetic application of product 3aa.....	S8
F. Deuterium-labeling study	S9
G. X-ray crystal structure and data for product 3ai.....	S11
H. Analytical data	S13
I. References	S24
J. NMR Spectra.....	S25

A. General methods

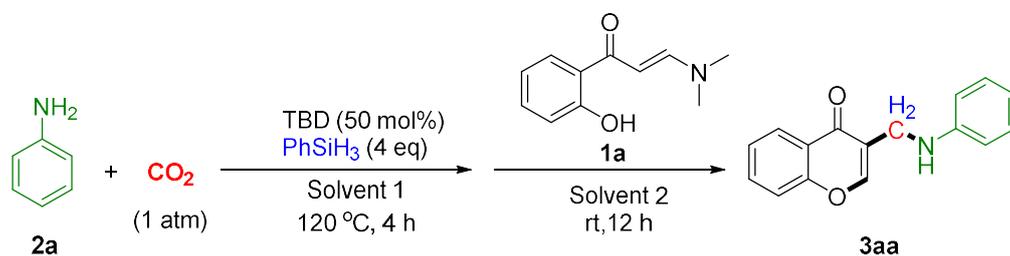
^1H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer using CDCl_3 or $\text{DMSO-}d_6$ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). GC-Mass analyses were conducted on a gas chromatograph-mass spectrometer (Trace 1300 ISQ) at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Melting points were determined with a digital melting point measuring instrument and are uncorrected. All the reaction temperatures reported are oil bath temperatures. Substrates **1a–1s** were synthesized according to the literature procedure.¹ Other reagents were commercially purchased and used without further purification.

B. General procedure for the synthesis of 3-aminomethyl chromones **3**

To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added K_3PO_4 (2.1 mg, 0.01 mmol). The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged with amine (0.3 mmol), acetonitrile (1 mL) and PhSiH_3 (32 mg, 0.3 mmol) successively via a syringe. The mixture was stirred at 110 °C for 4 h. After cooling the reaction mixture to ambient temperature, a solution of *o*-hydroxyphenyl enaminones **1** (0.1 mmol) in hexafluoroisopropanol (1 mL) was added to the vessel via syringe. The mixture was stirred at room temperature for 12 h. After the reaction was completed, the mixture was diluted with saturated brine water (10 mL) and extracted with ethyl acetate (10 mL \times 3). The organic phase was washed with water (10 mL \times 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 20: 1–2: 1) as the eluent to give the desired product **3**.

C. Optimization of the reaction conditions

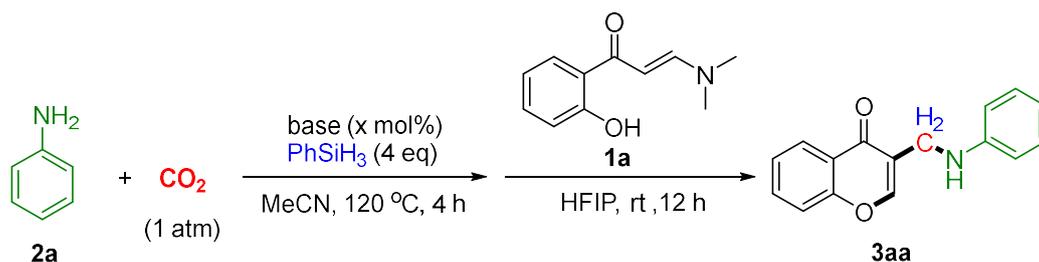
Table S1. The effect of solvent on the reaction^a



Entry	Solvent 1	Solvent 2	Yield (%) ^b
1	MeCN	MeCN	34
2	MeCN	DMF	30
3	MeCN	DCM	27
4	MeCN	THF	16
5	MeCN	toluene	trace
6	MeCN	MeOH	43
7	MeCN	TFE	32
8	MeCN	HFIP	57
9	NMP	HFIP	trace
10	DMF	HFIP	trace
11	THF	HFIP	12
12	DMSO	HFIP	trace
13	1,4-dioxane	HFIP	trace
14	HFIP	HFIP	trace

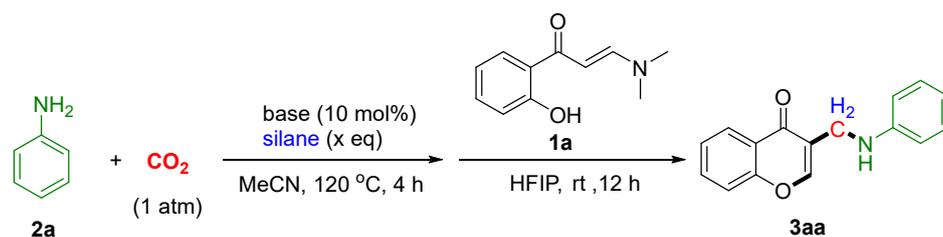
^aReaction conditions: the mixture of **2a** (2.0 eq), CO_2 (1 atm), K_3PO_4 (50 mol%), PhSiH_3 (3.0 eq), solvent 1 (1 mL) was first stirred at 120 °C for 4 h; then a solution of **1a** (0.1 mmol, 1.0 eq) in solvent (1 mL) was added, and the resulting mixture was stirred at room temperature for 12 h. ^bYields based on **1a** were determined by ^1H NMR analysis with CH_2Br_2 as internal standard.

Table S2. The effect of base on the reaction^a



Entry	Base	Amount of Base (x mol%)	Yield (%) ^b
1	TBD	50	57
2	DBU	50	21
3	DBN	50	37
4	NEt_3	50	trace
5	DABCO	50	ND
6	TMG	50	41
7	Cs_2CO_3	50	54
8	CH_3OK	50	59
9	NaHCO_3	50	28
10	K_3PO_4	50	67
11	CH_3COONa	50	13
12	K_2HPO_4	50	59
13	KH_2PO_4	50	23
14	K_2CO_3	50	52
15	K_3PO_4	5	59
16	K_3PO_4	10	68
17	K_3PO_4	20	67
18	K_3PO_4	100	67
19	K_3PO_4	200	65
20	-	-	N. D. ^c

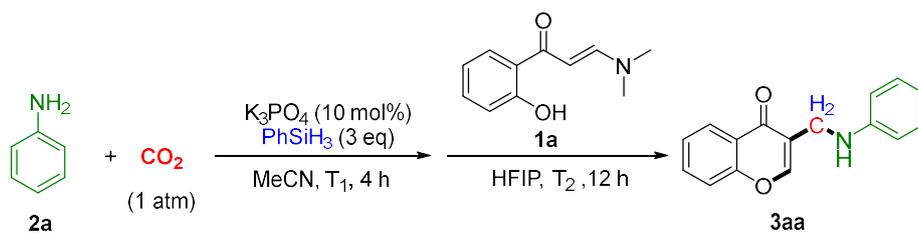
^aReaction conditions: the mixture of **2a** (2.0 eq), CO_2 (1 atm), base (x mol%), PhSiH_3 (3.0 eq), MeCN (1 mL) was first stirred at 120 °C for 4 h; then a solution of **1a** (0.1 mmol, 1.0 eq) in HFIP (1 mL) was added, and the resulting mixture was stirred at room temperature for 12 h. ^bYields based on **1a** were determined by ^1H NMR analysis with CH_2Br_2 as internal standard. ^cN.D. = no detected.

Table S3. The effect of silane on the reaction^a

Entry	Silane	Amount of silane (x eq)	Yield (%) ^b
1	PhSiH ₃	4	68
2	Ph ₂ SiH ₂	4	42
3	Ph ₃ SiH	4	ND
4	Et ₃ SiH	4	ND
5	(MeO) ₃ SiH	4	ND
6	PMHS	4	19
7	PhSiH ₃	2	61
8	PhSiH₃	3	73
9	PhSiH ₃	5	60
10	PhSiH ₃	6	56
11	-	-	N. D. ^c

^aReaction conditions: the mixture of **2a** (2.0 eq), CO_2 (1 atm), K_3PO_4 (10 mol%), silane (x eq), MeCN (1 mL) was first stirred at 120 °C for 4 h; then a solution of **1a** (0.1 mmol, 1.0 eq) in HFIP (1 mL) was added, and the resulting mixture was stirred at room temperature for 12 h. ^bYields based on **1a** were determined by ¹H NMR analysis with CH_2Br_2 as internal standard. ^cN. D. = no detected.

Table S4. The effect of temperature on the reaction^a



Entry	T_1 (°C)	T_2 (°C)	Yield (%) ^b
1	90	rt	69
2	100	rt	72
3	110	rt	78
4	120	rt	73
5	110	50	72
6	110	70	64
7	110	100	57
8	110	0	74

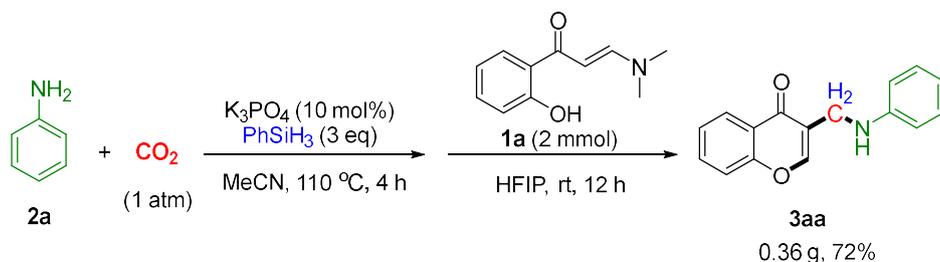
^aReaction conditions: the mixture of **2a** (2.0 eq), CO_2 (1 atm), K_3PO_4 (10 mol%), PhSiH_3 (3 eq), MeCN (1 mL) was first stirred at T_1 for 4 h; then a solution of **1a** (0.1 mmol, 1.0 eq) in HFIP (1 mL) was added, and the resulting mixture was stirred at T_2 for 12 h. ^bYields based on **1a** were determined by ^1H NMR analysis with CH_2Br_2 as internal standard.

Table S5. Optimization of the amount of amine^a

Entry	Amount of 2a (x eq)	Yield (%) ^b
1	1	72
2	1.5	76
3	2	78
4	3	87
5	4	82
6	5	82

^aReaction conditions: the mixture of **2a** (x eq), CO₂ (1 atm), K₃PO₄ (10 mol%), PhSiH₃ (3 eq), MeCN (1 mL) was first stirred at T₁ for 4 h; then a solution of **1a** (0.1 mmol, 1.0 eq) in HFIP (1 mL) was added, and the resulting mixture was stirred at T₂ for 12 h. ^bYields based on **1a** were determined by ¹H NMR analysis with CH₂Br₂ as internal standard.

D. Procedure for the synthesis **3aa** on a 2 mmol scale

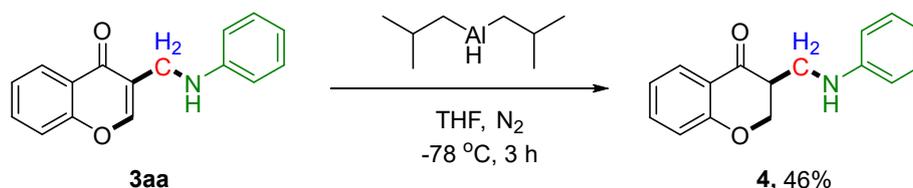


To a 100 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added K₃PO₄ (42 mg, 0.2 mmol). The tube was then evacuated, refilled with CO₂ (1 atm) three times, and charged with aniline (**2a**, 559 mg, 6.0 mmol), acetonitrile (5 mL) and PhSiH₃ (649 mg, 6.0 mmol) successively via a syringe. The mixture was stirred at 110 °C for 4 h. After cooling the reaction mixture to ambient temperature, a solution of *o*-hydroxyphenyl enaminone **1a** (382 mg, 2.0 mmol) in hexafluoroisopropanol (5 mL) was added to the vessel via syringe. The mixture was stirred at room temperature for 12 h. After the reaction was completed, the mixture was diluted with saturated brine water (20 mL) and extracted with ethyl acetate (15 mL × 3). The organic phase was washed with water (15 mL × 3), dried over anhydrous Na₂SO₄ and then filtered. After

removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10: 1) as the eluent to give the desired product **3aa** (0.36 g, 72% yield).

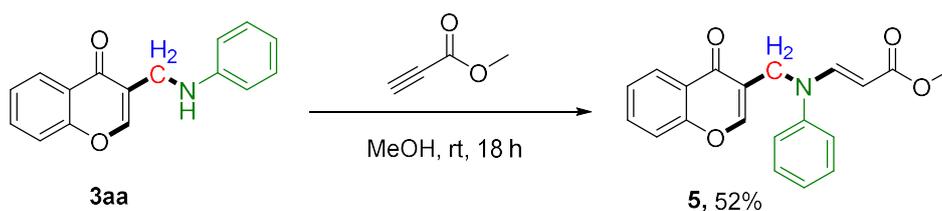
E. Synthetic application of product **3aa**

i) Synthetic procedure for compound **4** ^{ref. 2}



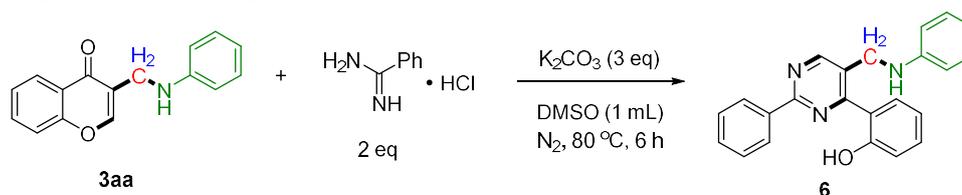
A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **3aa** (0.1 mmol, 25.1 mg, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three cycles), followed by the addition of THF (1 mL) via syringe. The mixture was cooled to $-78\text{ }^\circ\text{C}$, and DIBAL-H (1.0 M in toluene, 0.3 mL, 0.3 mmol, 3.0 equiv) was added dropwise over 5 min using a syringe pump. After stirring at $-78\text{ }^\circ\text{C}$ for an additional 3 h, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature gradually (ca. 20 min) with continued stirring. The reaction was then quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc ($3 \times 10\text{ mL}$). The combined organic layers were washed sequentially with brine and water, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (pentane/EtOAc = 10:1) to afford product **4** as (11.6 mg, 46% yield).

ii) Synthetic procedure for compound **5** ^{ref.3}



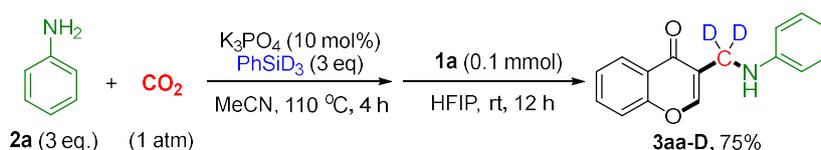
A tube equipped with a magnetic stir bar was charged with **3aa** (0.1 mmol, 25.1 mg, 1.0 equiv), methyl propiolate (0.1 mmol, 8.4 mg, 1.0 equiv), and MeOH (1 mL). The reaction mixture was stirred at room temperature for 18 h. Upon completion as monitored by TLC, the mixture was diluted with EtOAc and washed with brine (three times). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1) to afford product **5** (17.4 mg, 52% yield).

iii) Synthetic procedure for compound **6** ^{ref.4}



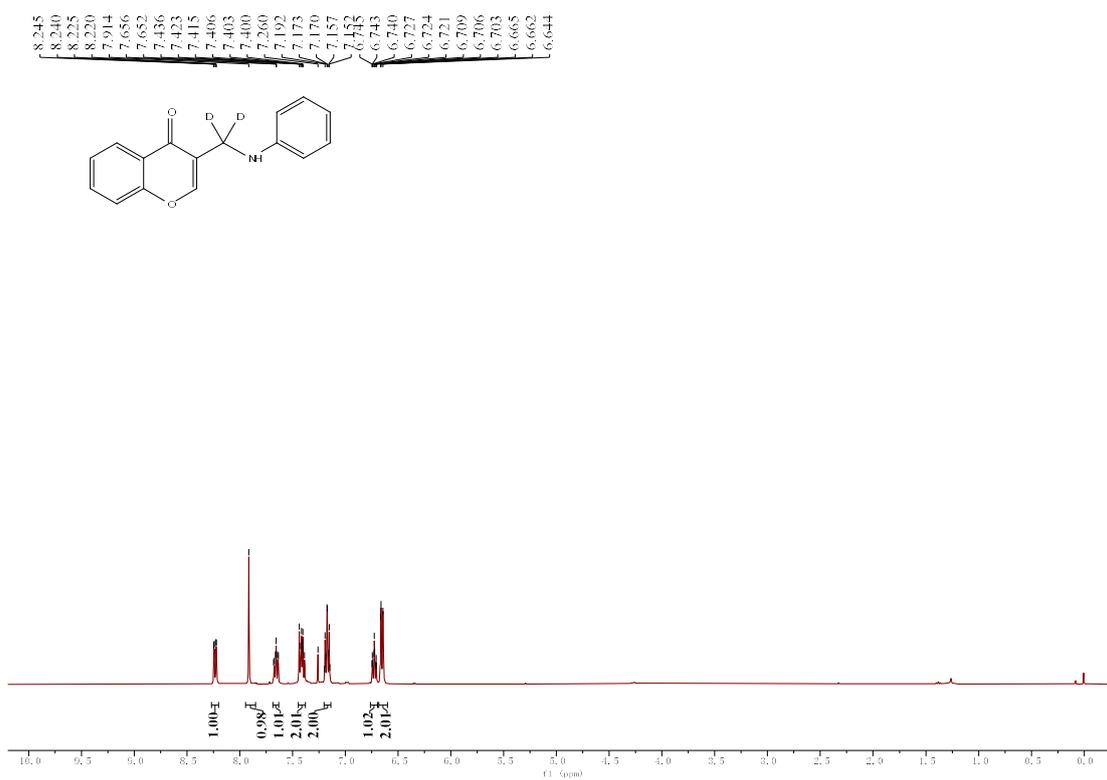
A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **3aa** (0.1 mmol, 25.1 mg, 1.0 equiv), benzimidamide hydrochloride (0.2 mmol, 31.3 mg, 2.0 equiv), and K_2CO_3 (0.3 mmol, 41.4 mg, 3.0 equiv). The tube was evacuated and backfilled with nitrogen (three cycles), followed by the addition of DMSO (1 mL) via syringe. The reaction mixture was stirred at 80 °C for 6 h. Upon completion as monitored by TLC, the mixture was diluted with EtOAc and washed with brine (three times). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1 to 2:1) to afford product **6** (26.5 mg, 75% yield).

F. Deuterium-labeling study

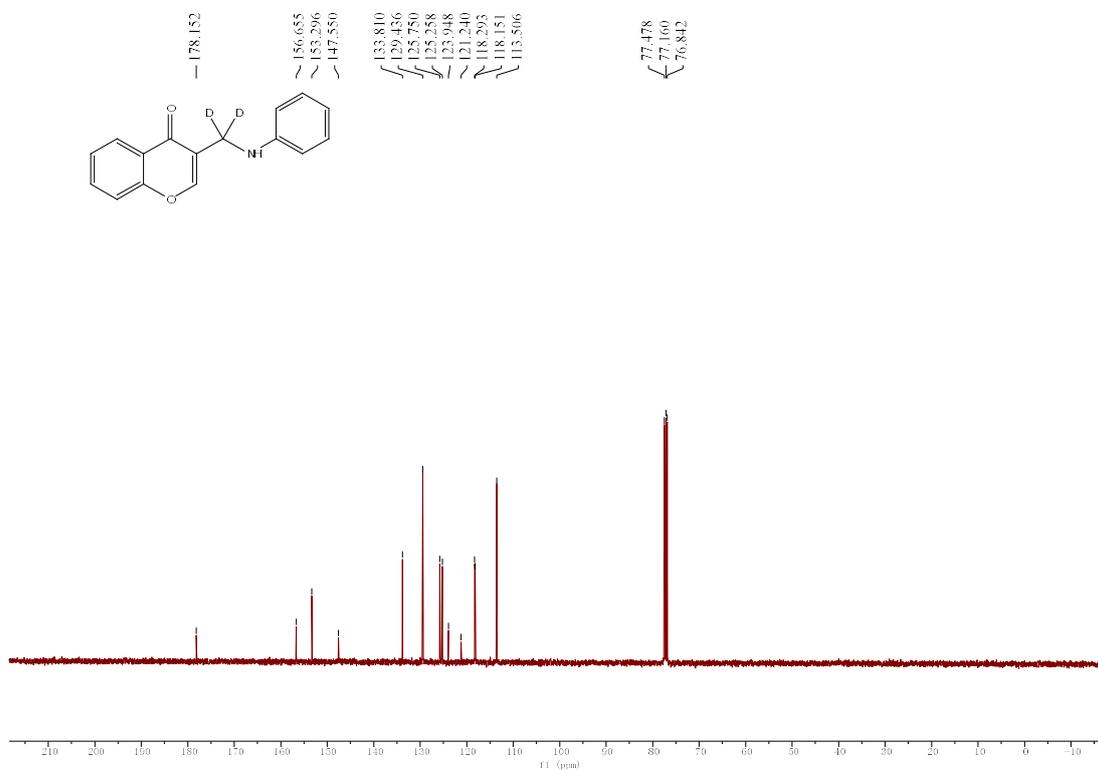


To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added K_3PO_4 (2.1 mg, 0.01 mmol). The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged with aniline (**2a**, 0.3 mmol), acetonitrile (1 mL) and $PhSiD_3$ (32 mg, 0.3 mmol) successively via a syringe. The mixture was stirred at 110 °C for 4 h. After cooling the reaction mixture to ambient temperature, a solution of *o*-hydroxyphenyl enaminone **1a** (0.1 mmol) in hexafluoroisopropanol (1 mL) was added to the vessel via syringe. The mixture was stirred at room temperature for 12 h. After the reaction was completed, the mixture was diluted with saturated brine water (10 mL) and extracted with ethyl acetate (10 mL \times 3). The organic phase was washed with water (10 mL \times 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10: 1) as the eluent to give the desired product **3aa-D** (18.8 mg, 75%). 1H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.0, 1.8 Hz, 1H), 7.91 (s, 1H), 7.66 (ddd, J = 8.6, 7.1, 1.7 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.20 – 7.14 (m, 2H), 6.76 – 6.70 (m, 1H), 6.68 – 6.60 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.2, 156.7, 153.3, 147.5, 133.8, 129.4, 125.8, 125.3, 123.9, 121.2, 118.3, 118.2, 113.5.

400 MHz ^1H NMR Spectrum of 3aa-D in CDCl_3



100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3aa-D in CDCl_3



G. X-ray crystal structure and data for product **3ai**

Single-crystal X-ray diffraction data for **3ai** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of product **3ai** is shown in **Figure S1**, and the crystallographic data for product **3ai** is given in **Table S6**.

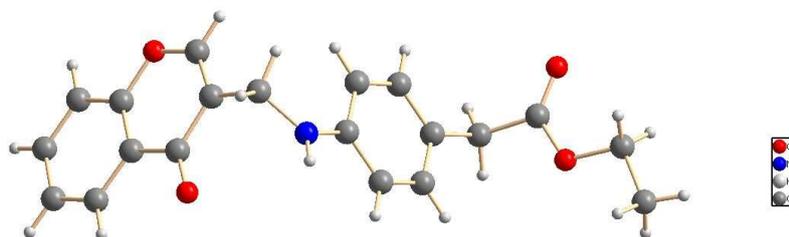


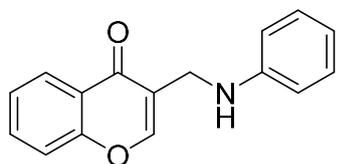
Figure S1. The X-ray crystal structure for product **3ai**

Table S6. Crystal data and structure refinements for **3ai**

Empirical formula	C ₁₉ H ₂₀ NO ₄
Formula weight	337.36
Temperature	170 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 7.2775 (4) Å alpha = 75.036 deg. b = 9.3509 (6) Å beta = 75.370 deg. c = 13.7128 (8) Å gamma = 75.268 deg.
Volume	854.27 (9) Å ³
Z, Calculated density	2, 1312 g/cm ³
Absorption coefficient	0.092 mm ⁻¹
F(000)	356.0
Crystal size	0.15 × 0.08 × 0.05 mm ³
Theta range for data collection	4.604 to 52.726 deg.
Limiting indices	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -16 ≤ l ≤ 17
Reflections collected / unique	9126 / 3459 [R _{int} = 0.0628, R _{sigma} = 0.0739]
Completeness to theta = 26.363	99.3%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3459/19/227
Goodness-of-fit on F ²	1.052
Final R indices [I > 2sigma(I)]	R ₁ = 0.0675, wR ₂ = 0.1624
R indices (all data)	R ₁ = 0.0933, wR ₂ = 0.1916

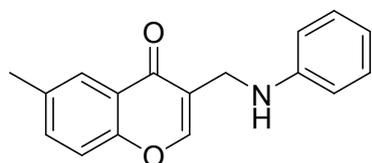
H. Analytical data

3-((Phenylamino)methyl)-4*H*-chromen-4-one (3aa) ^{ref.4}



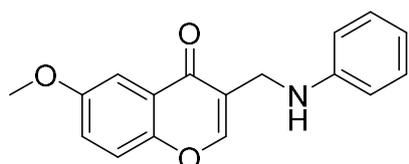
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 20.1 mg, 80% yield, mp: 128 – 129 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.91 (s, 1H), 7.69 – 7.62 (m, 1H), 7.45 – 7.38 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.1, 156.6, 153.3, 147.6, 133.8, 129.4, 125.7, 125.3, 123.9, 121.3, 118.3, 118.1, 113.5, 40.5.

6-Methyl-3-((phenylamino)methyl)-4*H*-chromen-4-one (3ba) ^{ref.4}



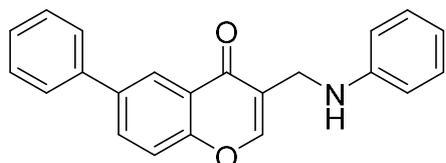
Eluent: 2:1 petroleum ether/ethyl acetate; yellow solid, 17.5 mg, 66% yield, mp: 145 – 146 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.89 (s, 1H), 7.47 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.27 (s, 2H), 2.46 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.2, 155.1, 153.2, 147.7, 135.3, 135.1, 129.4, 125.1, 123.7, 121.2, 118.2, 118.1, 113.6, 40.7, 21.1.

6-Methoxy-3-((phenylamino)methyl)-4*H*-chromen-4-one (3ca) ^{ref.4}



Eluent: 2:1 petroleum ether/ethyl acetate; yellow solid, 19.7 mg, 70% yield, mp: 154 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.58 (d, *J* = 3.1 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.19 – 7.14 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.28 (s, 2H), 3.90 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 177.9, 157.1, 153.1, 151.6, 147.7, 129.5, 124.6, 124.0, 120.6, 119.7, 118.2, 113.6, 104.7, 56.1, 40.7.

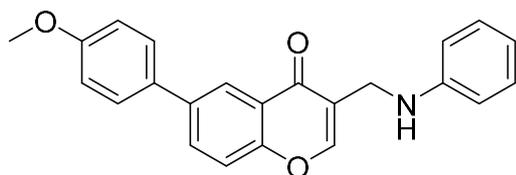
6-Phenyl-3-((phenylamino)methyl)-4*H*-chromen-4-one (3da)



Eluent: 5:1 petroleum ether/ethyl acetate; yellow solid, 15.7 mg, 48% yield, mp: 156 – 158 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, *J* = 2.4 Hz, 1H), 7.94 (t, *J* = 1.1 Hz, 1H), 7.91 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.53 – 7.45 (m, 3H), 7.42 – 7.37 (m, 1H), 7.21 – 7.16 (m, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.67

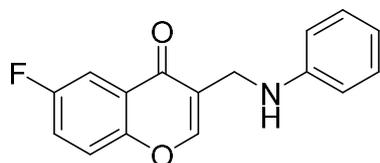
(d, $J = 7.6$ Hz, 2H), 4.32 – 4.28 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.2, 156.1, 153.3, 147.6, 139.5, 138.5, 132.8, 129.5, 129.2, 128.0, 127.3, 124.1, 123.6, 121.4, 118.8, 118.2, 113.6, 40.6. HRMS-ESI (m/z): calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 328.1332; found: 328.1328.

6-(4-Methoxyphenyl)-3-((phenylamino)methyl)-4H-chromen-4-one (3ea)



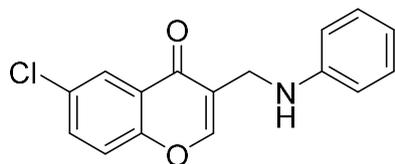
Eluent: 3:1 petroleum ether/ethyl acetate; yellow solid, 16.1 mg, 45% yield, mp: 160-162 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 2.4$ Hz, 1H), 7.93 (s, 1H), 7.86 (dd, $J = 8.7, 2.4$ Hz, 1H), 7.61 – 7.57 (m, 2H), 7.48 (d, $J = 8.7$ Hz, 1H), 7.21 – 7.15 (m, 2H), 7.03 – 6.99 (m, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.69 – 6.64 (m, 2H), 4.30 (d, $J = 1.1$ Hz, 2H), 3.87 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.2, 159.7, 155.7, 153.3, 147.5, 138.1, 132.4, 131.9, 129.5, 128.4, 124.1, 122.8, 121.3, 118.7, 118.2, 114.6, 113.6, 55.5, 40.7. HRMS-ESI (m/z): calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 358.1438; found: 358.1434.

6-Fluoro-3-((phenylamino)methyl)-4H-chromen-4-one (3fa) ^{ref.4}



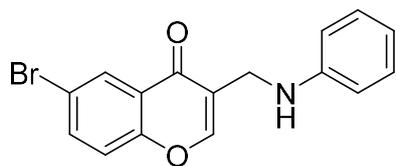
Eluent: 3:1 petroleum ether/ethyl acetate; yellow solid, 20.1 mg, 75% yield, mp: 149 – 150 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.85 (dd, $J = 8.2, 3.1$ Hz, 1H), 7.44 (dd, $J = 9.2, 4.3$ Hz, 1H), 7.41 – 7.35 (m, 1H), 7.17 (t, $J = 7.8$ Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.64 (d, $J = 7.9$ Hz, 2H), 4.27 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 177.4 (d, $J = 2$ Hz), 159.6 (d, $J = 245.5$ Hz), 153.5, 152.9, 147.4, 129.5, 125.0 (d, $J = 7.2$ Hz), 122.2 (d, $J = 25.5$ Hz), 120.8, 120.4 (d, $J = 8.1$ Hz), 118.2, 113.4, 110.5 (d, $J = 23.5$ Hz), 40.4.

6-Chloro-3-((phenylamino)methyl)-4H-chromen-4-one (3ga) ^{ref.4}



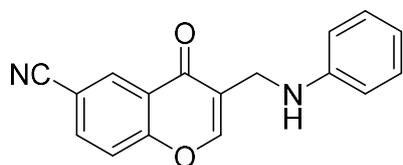
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 21.3mg, 75% yield, mp: 138 – 139 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 2.6$ Hz, 1H), 7.91 (s, 1H), 7.60 (dd, $J = 8.9, 2.6$ Hz, 1H), 7.39 (d, $J = 8.9$ Hz, 1H), 7.20 – 7.15 (m, 2H), 6.76 – 6.72 (m, 1H), 6.67 – 6.63 (m, 2H), 4.28 (d, $J = 1.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 176.9, 155.0, 153.5, 147.2, 134.1, 131.3, 129.5, 125.2, 124.8, 121.5, 120.1, 118.4, 113.6, 40.6.

6-Bromo-3-((phenylamino)methyl)-4H-chromen-4-one (3ha) ^{ref.4}



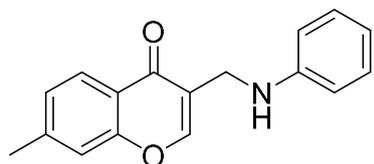
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 24.4mg, 74% yield, mp: 117 – 119 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 2.5 Hz, 1H), 7.90 (s, 1H), 7.72 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.19 – 7.15 (m, 2H), 6.75 – 6.71 (m, 1H), 6.65 – 6.62 (m, 2H), 4.27 (d, *J* = 1.2 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.7, 155.4, 153.4, 147.4, 136.8, 129.5, 128.3, 125.2, 121.6, 120.3, 118.7, 118.3, 113.4, 40.4.

4-Oxo-3-((phenylamino)methyl)-4H-chromene-6-carbonitrile (3ia)



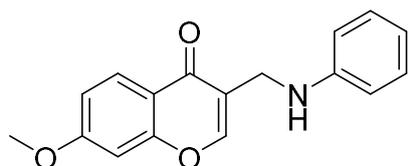
Eluent: 2:1 petroleum ether/ethyl acetate; yellow solid, 17.1 mg, 62% yield, mp: 160-162 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, *J* = 2.1 Hz, 1H), 7.93 (s, 1H), 7.87 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.77 – 6.72 (m, 1H), 6.65 – 6.60 (m, 2H), 4.37 – 4.24 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.3, 158.3, 153.6, 147.1, 136.0, 131.6, 129.5, 124.2, 122.6, 120.1, 118.4, 117.7, 113.4, 109.5, 40.2. HRMS-ESI (*m/z*): calcd for C₁₇H₁₃N₂O₂ [M + H]⁺ : 277.0972; found: 277.0970.

7-Methyl-3-((phenylamino)methyl)-4H-chromen-4-one (3ja)



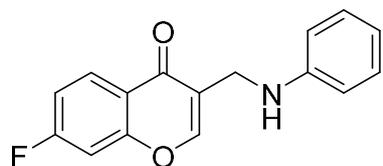
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 18.3 mg, 69% yield, mp: 144 – 146 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.87 (s, 1H), 7.23 – 7.14 (m, 4H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H), 2.47 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.0, 156.8, 153.0, 147.6, 145.2, 129.4, 126.8, 125.5, 121.7, 121.2, 118.1, 118.0, 113.5, 40.6, 21.9. HRMS-ESI (*m/z*): calcd for C₁₇H₁₆NO₂ [M + H]⁺ : 266.1176; found: 266.1170.

7-Methoxy-3-((phenylamino)methyl)-4H-chromen-4-one (3ka)



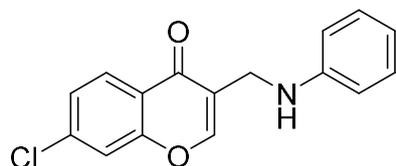
Eluent: 3:1 petroleum ether/ethyl acetate; yellow solid, 19.9 mg, 71% yield, mp: 153 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 1.1 Hz, 1H), 7.19 – 7.14 (m, 2H), 6.97 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.74 – 6.70 (m, 1H), 6.67 – 6.62 (m, 2H), 4.26 – 4.22 (m, 2H), 3.89 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 177.5, 164.3, 158.5, 152.8, 147.7, 129.4, 127.2, 121.2, 118.1, 118.0, 114.8, 113.6, 100.3, 56.0, 40.6. HRMS-ESI (*m/z*): calcd for C₁₇H₁₆NO₃ [M + H]⁺ : 282.1125; found: 282.1120.

7-Fluoro-3-((phenylamino)methyl)-4H-chromen-4-one (3la)



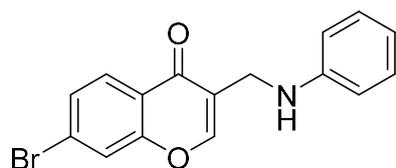
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 21.8mg, 81% yield, mp: 156 – 158 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (dd, $J = 8.8, 6.3$ Hz, 1H), 7.88 (s, 1H), 7.20 – 7.09 (m, 4H), 6.75 – 6.71 (m, 1H), 6.66 – 6.62 (m, 2H), 4.26 (d, $J = 1.2$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 177.2, 165.7 (d, $J = 253.7$ Hz), 157.6 (d, $J = 13.4$ Hz), 153.4, 147.4, 129.5, 128.3 (d, $J = 10.7$ Hz), 121.6, 120.8 (d, $J = 2.3$ Hz), 118.2, 114.2 (d, $J = 22.8$ Hz), 113.4, 104.9 (d, $J = 25.0$ Hz), 40.4. HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{13}\text{FNO}_2$ [$\text{M} + \text{H}$] $^+$: 270.0925; found: 270.0919.

7-Chloro-3-((phenylamino)methyl)-4H-chromen-4-one (3ma)



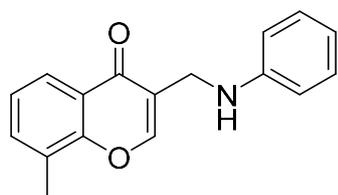
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 19.1 mg, 67% yield, mp: 150 – 152 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.6$ Hz, 1H), 7.87 (d, $J = 1.2$ Hz, 1H), 7.45 (d, $J = 1.9$ Hz, 1H), 7.37 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.20 – 7.15 (m, 2H), 6.76 – 6.71 (m, 1H), 6.65 – 6.61 (m, 2H), 4.26 (d, $J = 1.2$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 177.3, 156.7, 153.3, 147.4, 139.9, 129.5, 127.2, 126.2, 122.5, 121.8, 118.3, 118.3, 113.5, 40.4. HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{13}\text{ClNO}_2$ [$\text{M} + \text{H}$] $^+$: 286.0629; found: 286.0624.

7-Bromo-3-((phenylamino)methyl)-4H-chromen-4-one (3na)



Eluent: 8:1 petroleum ether/ethyl acetate; white solid, 21.1 mg, 64% yield, mp: 161 – 163 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.5$ Hz, 1H), 7.87 (s, 1H), 7.63 (d, $J = 1.8$ Hz, 1H), 7.52 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.20 – 7.14 (m, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 7.9$ Hz, 2H), 4.26 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 177.4, 156.7, 153.2, 147.4, 129.5, 129.0, 128.2, 127.2, 122.8, 121.8, 121.4, 118.3, 113.5, 40.4. HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{13}\text{BrNO}_2$ [$\text{M} + \text{H}$] $^+$: 330.0124; found: 330.0117.

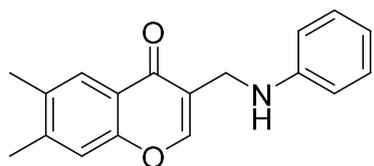
8-Methyl-3-((phenylamino)methyl)-4H-chromen-4-one (3oa)



Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 19.3 mg, 73% yield, mp: 135 – 138 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.96 (s, 1H), 7.49 (d, $J = 7.2$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.17 (dd, $J = 8.5, 7.2$ Hz, 2H), 6.72 (t, $J = 7.4$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 2H), 4.30 – 4.26 (m, 2H),

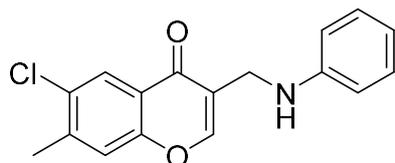
2.44 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.5, 155.3, 153.0, 147.7, 134.7, 129.5, 127.8, 124.8, 123.9, 123.4, 121.1, 118.2, 113.6, 40.6, 15.6. HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 266.1176; found: 266.1169.

6,7-Dimethyl-3-((phenylamino)methyl)-4H-chromen-4-one (3pa) ^{ref.4}



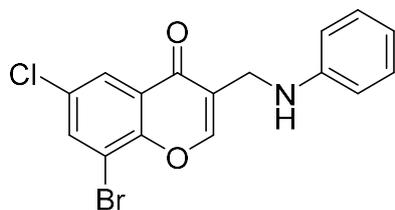
Eluent: 2:1 petroleum ether/ethyl acetate; black solid, 22.0 mg, 79% yield, mp: 104 – 105 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 3.9$ Hz, 1H), 7.84 (d, $J = 3.9$ Hz, 1H), 7.19 – 7.13 (m, 3H), 6.71 (t, $J = 7.2$ Hz, 1H), 6.65 (d, $J = 7.9$ Hz, 2H), 4.24 (d, $J = 4.0$ Hz, 2H), 2.35 (d, $J = 5.9$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.0, 155.2, 152.9, 147.7, 144.3, 134.5, 129.4, 125.2, 121.8, 121.0, 118.3, 118.0, 113.5, 40.6, 20.5, 19.4.

6-Chloro-7-methyl-3-((phenylamino)methyl)-4H-chromen-4-one (3qa)



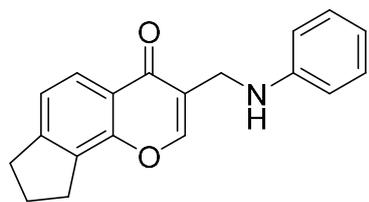
Eluent: 10:1 petroleum ether/ethyl acetate; yellow solid, 11.7 mg, 39% yield, mp: 161 – 163 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 7.87 (s, 1H), 7.31 (d, $J = 1.0$ Hz, 1H), 7.19 – 7.14 (m, 2H), 6.73 (tt, $J = 7.4, 1.1$ Hz, 1H), 6.65 – 6.62 (m, 2H), 4.26 (d, $J = 1.2$ Hz, 2H), 2.48 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 177.0, 155.0, 153.2, 147.5, 143.2, 132.0, 129.5, 125.4, 123.0, 121.3, 120.1, 118.3, 113.5, 40.5, 21.0. HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{15}\text{ClNO}_2$ $[\text{M} + \text{H}]^+$: 300.0786; found: 300.0781.

8-Bromo-6-chloro-3-((phenylamino)methyl)-4H-chromen-4-one (3ra)



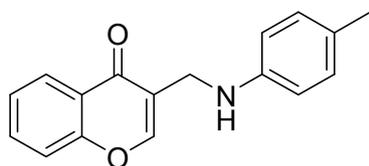
Eluent: 10:1 petroleum ether/ethyl acetate; yellow solid, 22.9 mg, 63% yield, mp: 132 – 134 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 2.5$ Hz, 1H), 7.98 (s, 1H), 7.87 (d, $J = 2.5$ Hz, 1H), 7.18 (t, $J = 7.8$ Hz, 2H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.62 (d, $J = 7.9$ Hz, 2H), 4.29 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 176.4, 153.5, 151.9, 147.2, 137.0, 131.4, 129.5, 125.5, 124.7, 121.8, 118.4, 113.4, 112.9, 40.3. HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{12}\text{BrClNO}_2$ $[\text{M} + \text{H}]^+$: 365.9714; found: 365.9705.

3-((Phenylamino)methyl)-8,9-dihydrocyclopenta[*h*]chromen-4(7*H*)-one (3sa)



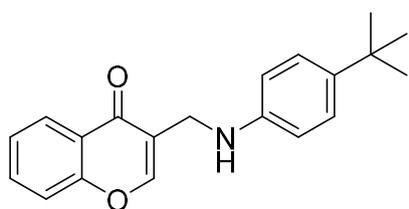
Eluent: 5:1 petroleum ether/ethyl acetate; yellow solid, 19.2 mg, 66% yield, mp: 163-164 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 1.2$ Hz, 1H), 7.28 – 7.25 (m, 2H), 7.19 – 7.14 (m, 2H), 6.74 – 6.69 (m, 1H), 6.67 – 6.63 (m, 2H), 4.26 (d, $J = 1.1$ Hz, 2H), 3.05 (td, $J = 7.5, 3.4$ Hz, 4H), 2.20 (p, $J = 7.5$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.4, 153.5, 152.7, 152.0, 147.6, 132.3, 129.4, 124.3, 122.4, 121.8, 120.9, 118.1, 113.6, 40.6, 33.8, 29.1, 25.1. HRMS-ESI (m/z): calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 292.1332; found: 292.1330.

3-((*p*-Tolylamino)methyl)-4*H*-chromen-4-one (3ab) ^{ref.4}



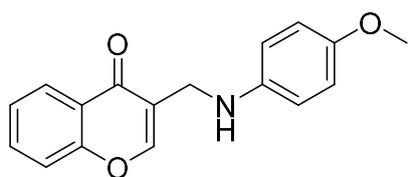
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 19.3 mg, 73% yield, mp: 154 – 155 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.90 (s, 1H), 7.68 – 7.62 (m, 1H), 7.45 – 7.37 (m, 2H), 6.98 (d, $J = 8.4$ Hz, 2H), 6.62 – 6.54 (m, 2H), 4.25 (s, 2H), 2.22 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.2, 156.7, 153.3, 145.3, 133.8, 129.9, 127.5, 125.8, 125.2, 124.0, 121.6, 118.3, 113.8, 41.0, 20.5.

3-(((4-(*tert*-Butyl)phenyl)amino)methyl)-4*H*-chromen-4-one (3ac) ^{ref.5}



Eluent: 3:1 petroleum ether/ethyl acetate; brown solid, 21.7 mg, 71% yield, mp: 127 – 128 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.92 (d, $J = 1.1$ Hz, 1H), 7.68 – 7.63 (m, 1H), 7.44 – 7.38 (m, 2H), 7.22 – 7.18 (m, 2H), 6.63 – 6.59 (m, 2H), 4.26 (s, 2H), 1.27 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.1, 156.6, 153.3, 145.2, 140.9, 133.7, 126.2, 125.8, 125.2, 124.0, 121.6, 118.3, 113.2, 40.7, 34.0, 31.6.

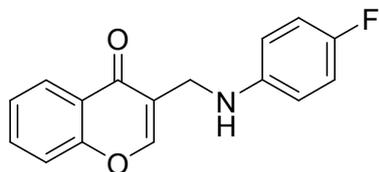
3-(((4-Methoxyphenyl)amino)methyl)-4*H*-chromen-4-one (3ad) ^{ref.4}



Eluent: 2:1 petroleum ether/ethyl acetate; brown solid, 16.5 mg, 59% yield, mp: 152 – 153 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.90 (s, 1H), 7.68 – 7.63 (m, 1H), 7.45 – 7.38 (m, 2H), 6.79 – 6.74 (m, 2H), 6.65 – 6.59 (m, 2H), 4.21 (s, 2H), 3.73 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$

NMR (100 MHz, CDCl₃) δ 178.2, 156.7, 153.3, 152.8, 141.7, 133.8, 125.8, 125.3, 124.0, 121.6, 118.3, 115.2, 115.1, 55.9, 41.8.

3-(((4-Fluorophenyl)amino)methyl)-4H-chromen-4-one (3ae) ^{ref.4}



Eluent: 8:1 petroleum ether/ethyl acetate; black solid, 16.7 mg, 62% yield, mp: 140 – 143 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.90 (s, 1H), 7.70 – 7.63 (m, 1H), 7.46 – 7.38 (m, 2H), 6.91 – 6.81 (m, 2H), 6.62 – 6.54 (m, 2H), 4.22 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ

178.1, 156.7, 156.3 (d, *J* = 234.4 Hz), 153.3, 143.9, 133.9, 125.8, 125.3, 124.0, 121.3, 118.3, 115.9 (d, *J* = 22.2 Hz), 114.6 (d, *J* = 7.5 Hz), 41.4.

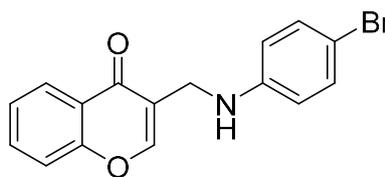
3-(((4-Chlorophenyl)amino)methyl)-4H-chromen-4-one (3af) ^{ref.4}



Eluent: 8:1 petroleum ether/ethyl acetate; brown solid, 12.5 mg, 44% yield, mp: 144 – 145 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.89 (s, 1H), 7.69 – 7.64 (m, 1H), 7.46 – 7.39 (m, 2H), 7.13 – 7.06 (m, 2H), 6.60 – 6.53 (m, 2H), 4.23 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃)

δ 178.1, 156.7, 153.2, 146.2, 133.9, 129.3, 125.8, 125.4, 124.0, 122.9, 121.1, 118.3, 114.7, 40.8.

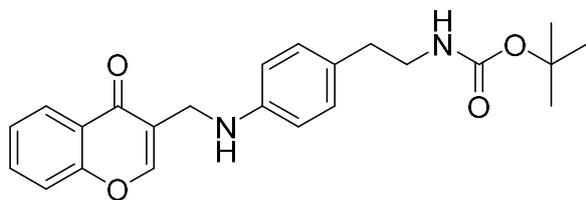
3-(((4-Bromophenyl)amino)methyl)-4H-chromen-4-one (3ag) ^{ref.4}



Eluent: 3:1 petroleum ether/ethyl acetate; yellow solid, 12.5 mg, 38% yield, mp: 185 – 187 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.89 (s, 1H), 7.70 – 7.64 (m, 1H), 7.46 – 7.39 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 4.43 (s, 1H), 4.23 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ

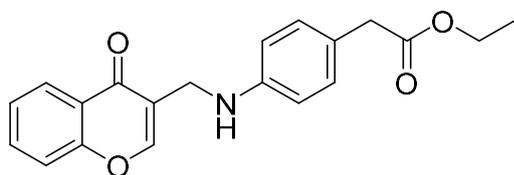
178.1, 156.7, 153.2, 146.6, 134.0, 132.2, 125.8, 125.4, 123.9, 121.0, 118.4, 115.2, 109.9, 40.7.

tert-Butyl (4-(((4-oxo-4H-chromen-3-yl)methyl)amino)phenethyl)carbamate (3ah)



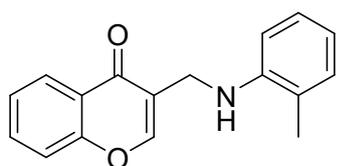
Eluent: 1:1 petroleum ether/ethyl acetate; yellow solid, 21.7 mg, 55% yield, mp: 122 – 124 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.91 (s, 1H), 7.68 – 7.63 (m, 1H), 7.45 – 7.38 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.25 (s, 2H), 3.30 (d, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 1.42 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.1, 156.7, 156.1, 153.3, 146.1, 133.8, 129.8, 125.8, 125.3, 124.0, 121.5, 118.3, 113.8, 40.8, 28.6. HRMS-ESI (*m/z*): calcd for C₂₃H₂₇N₂O₄ [M + H]⁺ : 395.1965; found: 395.1956.

Ethyl 2-(4-(((4-oxo-4H-chromen-3-yl)methyl)amino)phenyl)acetate (3ai)



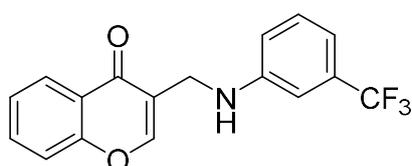
Eluent: 2:1 petroleum ether/ethyl acetate; yellow solid, 18.5 mg, 55% yield, mp: 124 – 125 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.90 (s, 1H), 7.68 – 7.62 (m, 1H), 7.44 – 7.37 (m, 2H), 7.10 – 7.05 (m, 2H), 6.62 – 6.58 (m, 2H), 4.25 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.47 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.1, 172.3, 156.7, 153.3, 146.6, 133.8, 130.2, 125.8, 125.3, 124.0, 123.6, 121.4, 118.3, 113.6, 60.8, 40.6, 14.3. HRMS-ESI (*m/z*): calcd for C₂₀H₂₀NO₄ [M + H]⁺ : 338.1387; found: 338.1380.

3-((*o*-Tolylamino)methyl)-4H-chromen-4-one (3aj) ^{ref.4}



Eluent: 3:1 petroleum ether/ethyl acetate; yellow solid, 15.1 mg, 57% yield, mp: 139 – 140 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.90 (s, 1H), 7.69 – 7.63 (m, 1H), 7.45 – 7.39 (m, 2H), 7.13 – 7.05 (m, 2H), 6.70 – 6.60 (m, 2H), 4.34 (s, 2H), 2.19 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.2, 156.7, 153.3, 145.6, 133.8, 130.5, 127.2, 125.8, 125.3, 124.0, 123.0, 121.4, 118.3, 117.8, 110.4, 40.5, 17.6.

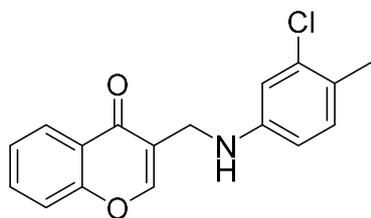
3-(((3-(Trifluoromethyl)phenyl)amino)methyl)-4H-chromen-4-one (3ak) ^{ref.6}



Eluent: 8:1 petroleum ether/ethyl acetate; brown solid, 12.8 mg, 40% yield, mp: 154 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.92 (s, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.27 – 7.20 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.85 (s, 1H), 6.77 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.64 (s, 1H), 4.28 (s, 2H).

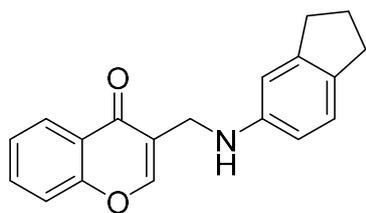
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.1, 156.7, 153.3, 147.9, 134.0, 131.8 (q, $J = 31.6$ Hz), 129.9, 125.8, 125.4, 123.9, 123.0, 124.4 (q, $J = 275.1$ Hz), 118.4, 116.4, 114.6 (q, $J = 3.9$ Hz), 109.6 (q, $J = 4.0$ Hz), 40.5.

3-(((3-Chloro-4-methylphenyl)amino)methyl)-4H-chromen-4-one (3al)



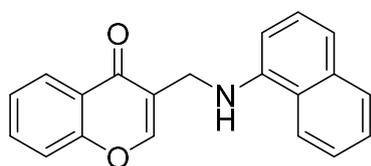
Eluent: 8:1 petroleum ether/ethyl acetate; yellow solid, 18.3 mg, 61% yield, mp: 142 – 144 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.90 (s, 1H), 7.69 – 7.63 (m, 1H), 7.46 – 7.38 (m, 2H), 6.98 (d, $J = 8.2$ Hz, 1H), 6.66 (d, $J = 2.5$ Hz, 1H), 6.46 (dd, $J = 8.2, 2.5$ Hz, 1H), 4.22 (s, 2H), 2.23 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.1, 156.7, 153.2, 146.7, 135.0, 133.9, 131.5, 125.8, 125.3, 125.1, 124.0, 121.1, 118.3, 113.9, 112.4, 40.8, 19.0. HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{15}\text{ClNO}_2$ [$\text{M} + \text{H}$] $^+$: 300.0786; found: 300.0780.

3-(((2,3-Dihydro-1H-inden-5-yl)amino)methyl)-4H-chromen-4-one (3am)



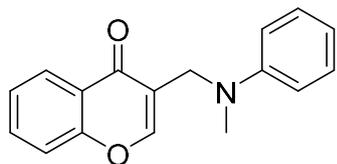
Eluent: 8:1 petroleum ether/ethyl acetate; brown solid, 14.2 mg, 49% yield, mp: 137 – 139 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.91 (s, 1H), 7.67 – 7.63 (m, 1H), 7.44 – 7.38 (m, 2H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.56 (d, $J = 2.3$ Hz, 1H), 6.47 (dd, $J = 8.1, 2.3$ Hz, 1H), 4.26 (s, 2H), 2.80 (q, $J = 7.8$ Hz, 4H), 2.05 – 1.99 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.1, 156.7, 153.3, 146.3, 145.7, 133.9, 133.7, 125.8, 125.2, 124.9, 124.0, 121.6, 118.3, 111.9, 109.8, 41.1, 33.2, 32.0, 25.8. HRMS-ESI (m/z): calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 292.1332; found: 292.1327.

3-((Naphthalen-1-ylamino)methyl)-4H-chromen-4-one (3an)



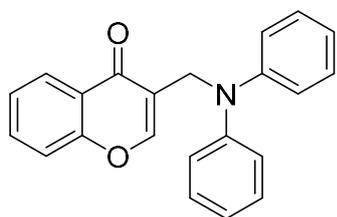
Eluent: 8:1 petroleum ether/ethyl acetate; black solid, 20.2 mg, 67% yield, mp: 149 – 151 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.94 (s, 1H), 7.90 – 7.86 (m, 1H), 7.81 – 7.77 (m, 1H), 7.68 – 7.63 (m, 1H), 7.47 – 7.39 (m, 4H), 7.32 (t, $J = 7.8$ Hz, 1H), 7.28 – 7.25 (m, 1H), 6.64 (dd, $J = 7.4, 1.2$ Hz, 1H), 4.47 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 178.3, 156.7, 153.4, 142.8, 134.5, 133.8, 128.8, 126.5, 126.0, 125.8, 125.3, 125.1, 124.0, 121.0, 120.2, 118.3, 118.2, 105.3, 40.8. HRMS-ESI (m/z): calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 302.1176; found: 302.1170.

3-((Methyl(phenyl)amino)methyl)-4H-chromen-4-one (3ao) ^{ref.4}



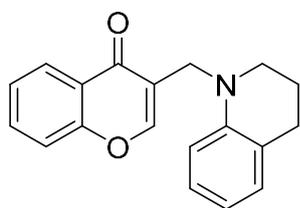
Eluent: 10:1 petroleum ether/ethyl acetate; yellow solid, 13.2mg, 50% yield, mp: 111 – 112 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.45 – 7.39 (m, 2H), 7.25 – 7.22 (m, 1H), 6.74 (dd, *J* = 8.1, 5.8 Hz, 3H), 4.47 (d, *J* = 1.4 Hz, 2H), 3.08 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.2, 156.7, 152.9, 149.1, 133.7, 129.4, 125.7, 125.2, 123.8, 120.3, 118.3, 117.1, 112.4, 49.3, 39.0.

3-((Diphenylamino)methyl)-4H-chromen-4-one (3ap)



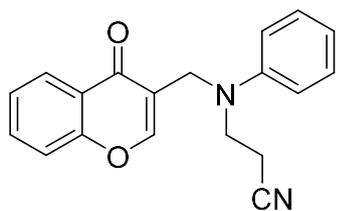
Eluent: 15:1 petroleum ether/ethyl acetate; black solid, 17.0mg, 52% yield, mp: 155 – 157 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.28 – 8.22 (m, 1H), 7.87 (q, *J* = 1.8 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.44 – 7.39 (m, 2H), 7.30 – 7.24 (m, 4H), 7.13 – 7.06 (m, 4H), 6.97 (tt, *J* = 7.3, 1.1 Hz, 2H), 4.95 (d, *J* = 1.6 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 177.9, 156.6, 153.2, 147.5, 133.8, 129.6, 125.7, 125.2, 123.7, 121.9, 120.7, 120.4, 118.3, 48.7. HRMS-ESI (*m/z*): calcd for C₂₂H₁₈NO₂ [M + H]⁺ : 328.1332; found: 328.1325.

3-((3,4-Dihydroquinolin-1(2H)-yl)methyl)-4H-chromen-4-one (3aq)



Eluent: 15:1 petroleum ether/ethyl acetate; yellow solid, 14.6 mg, 50% yield, mp: 144 – 145 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.69 – 7.64 (m, 1H), 7.46 – 7.39 (m, 2H), 7.04 – 6.97 (m, 2H), 6.61 (td, *J* = 7.3, 1.1 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 4.40 (d, *J* = 1.5 Hz, 2H), 3.45 – 3.38 (m, 2H), 2.83 (t, *J* = 6.3 Hz, 2H), 2.07 – 2.00 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.3, 156.8, 152.8, 145.1, 133.7, 129.3, 127.5, 125.7, 125.2, 123.8, 122.6, 119.8, 118.3, 116.5, 111.1, 50.4, 48.2, 28.2, 22.6. HRMS-ESI (*m/z*): calcd for C₁₉H₁₈NO₂ [M + H]⁺ : 292.1332; found: 292.1327.

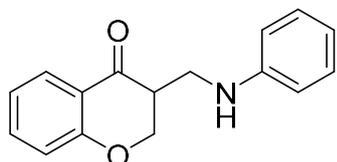
3-(((4-Oxo-4H-chromen-3-yl)methyl)(phenyl)amino)propanenitrile (3ar)



Eluent: 2:1 petroleum ether/ethyl acetate; white solid, 14.6 mg, 48% yield, mp: 128 – 130 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.73 (s, 1H), 7.67 (td, *J* = 7.7, 7.0, 1.7 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.79 (dd, *J* = 28.0, 7.8 Hz, 3H), 4.52 – 4.42 (m, 2H), 3.82 (t, *J* = 7.0 Hz, 2H), 2.69 (t, *J* = 7.0 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 177.9, 156.6, 153.4, 146.5, 133.9, 129.9,

125.8, 125.4, 123.8, 119.8, 118.9, 118.3, 118.2, 113.6, 48.0, 47.4, 16.1. HRMS-ESI (m/z): calcd for C₁₉H₁₇N₂O₂ [M + H]⁺: 305.1285; found: 305.1278.

3-((Phenylamino)methyl)chroman-4-one (4)

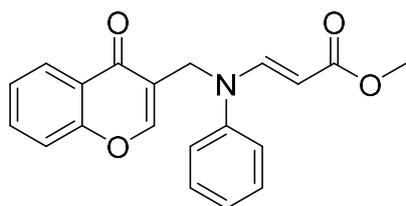


Eluent: 15:1 petroleum ether/ethyl acetate; yellow liquid, 11.6 mg, 46% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.71

(dd, *J* = 30.0, 7.6 Hz, 3H), 4.58 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.43 (dd, *J* = 11.5, 8.4 Hz, 1H), 3.59 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.45 (dd, *J* = 13.7, 6.9 Hz, 1H), 3.05 (dd, *J* = 12.6, 7.2 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.9, 161.7, 147.5, 136.3, 129.5, 127.4, 121.7, 120.8, 118.2, 118.0, 113.2, 69.3, 45.7, 41.3. HRMS-ESI (m/z): calcd for C₁₆H₁₆NO₂ [M + H]⁺: 254.1176; found: 254.1171.

3-((Phenylamino)methyl)chroman-4-one (5)

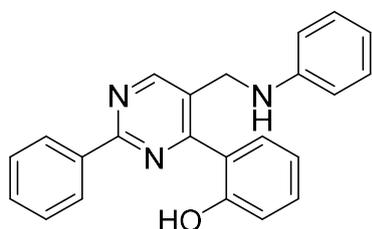


Eluent: 3:1 petroleum ether/ethyl acetate; yellow liquid, 17.4 mg, 52%

yield. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.07 (d, *J* = 13.4 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 – 7.31 (m, 2H), 7.20 – 7.11 (m, 3H), 4.97 (d, *J* =

13.3 Hz, 1H), 4.80 (d, *J* = 1.5 Hz, 2H), 3.67 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 177.3, 169.4, 156.6, 152.7, 147.1, 145.3, 134.1, 129.9, 125.7, 125.5, 124.8, 123.6, 119.7, 118.3, 117.6, 92.0, 51.1, 46.2. HRMS-ESI (m/z): calcd for C₂₀H₁₈NO₄ [M + H]⁺: 336.1230; found: 336.1225.

2-(2-Phenyl-5-((phenylamino)methyl)pyrimidin-4-yl)phenol (6) ^{ref.4}



Eluent: 8:1 petroleum ether/ethyl acetate; white solid, 26.5 mg, 75% yield,

mp: 172 – 173 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.17 (s, 1H), 8.97 (s, 1H), 8.42 – 8.33 (m, 2H), 7.72 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.53 (dd, *J* = 5.3, 2.0 Hz, 3H), 7.43 – 7.38 (m, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 1H),

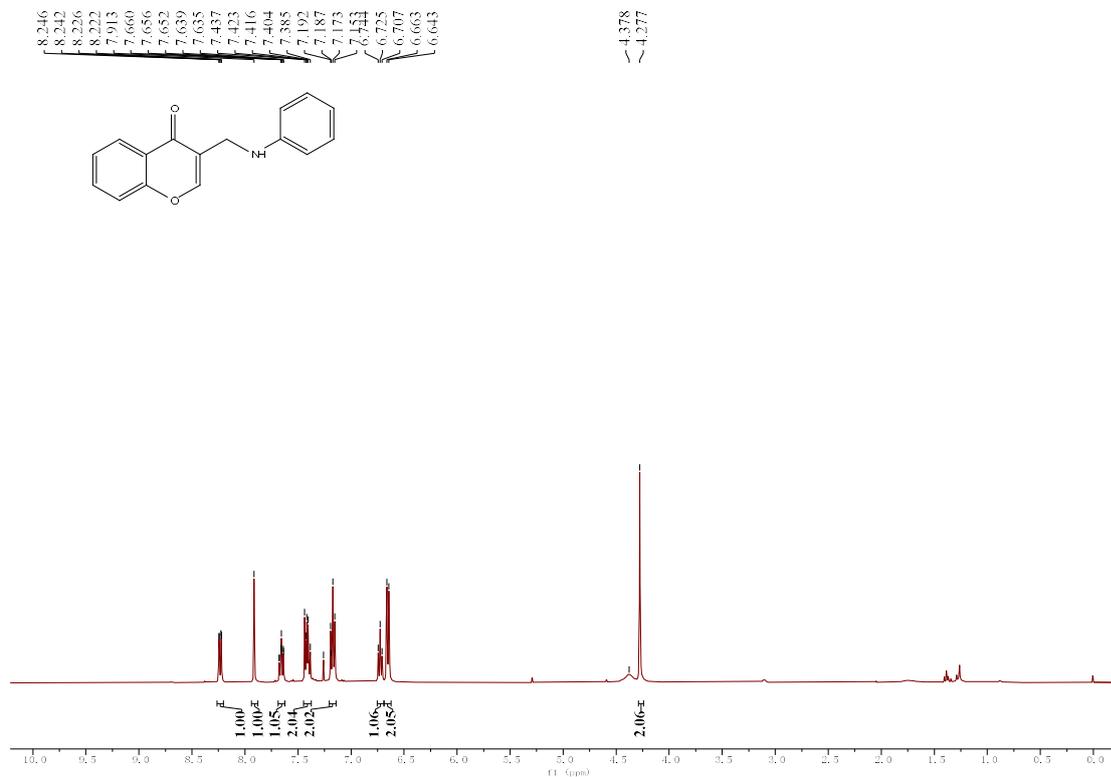
6.93 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 2H), 4.50 (s, 2H), 4.13 (d, *J* = 7.1 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.8, 162.0, 161.1, 158.7, 147.1, 136.3, 132.9, 131.5, 130.4, 129.6, 129.1, 128.2, 126.8, 119.6, 119.1, 118.8, 118.6, 113.3, 44.7.

I. References

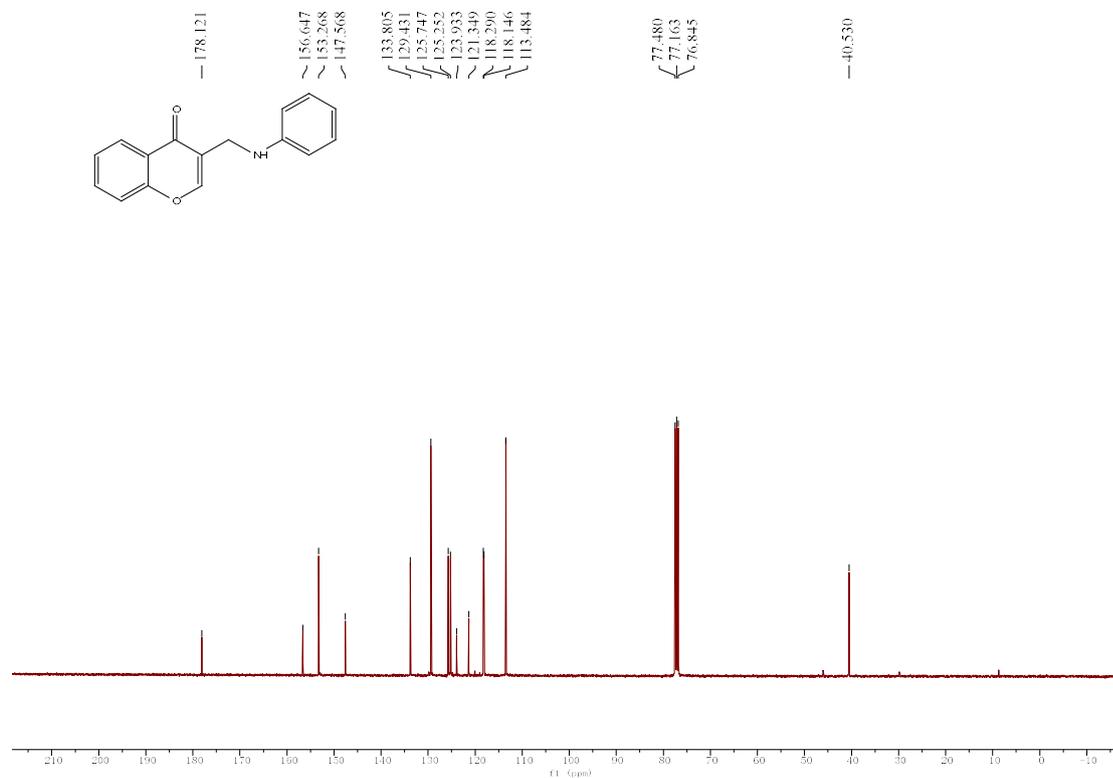
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J. NMR Spectra

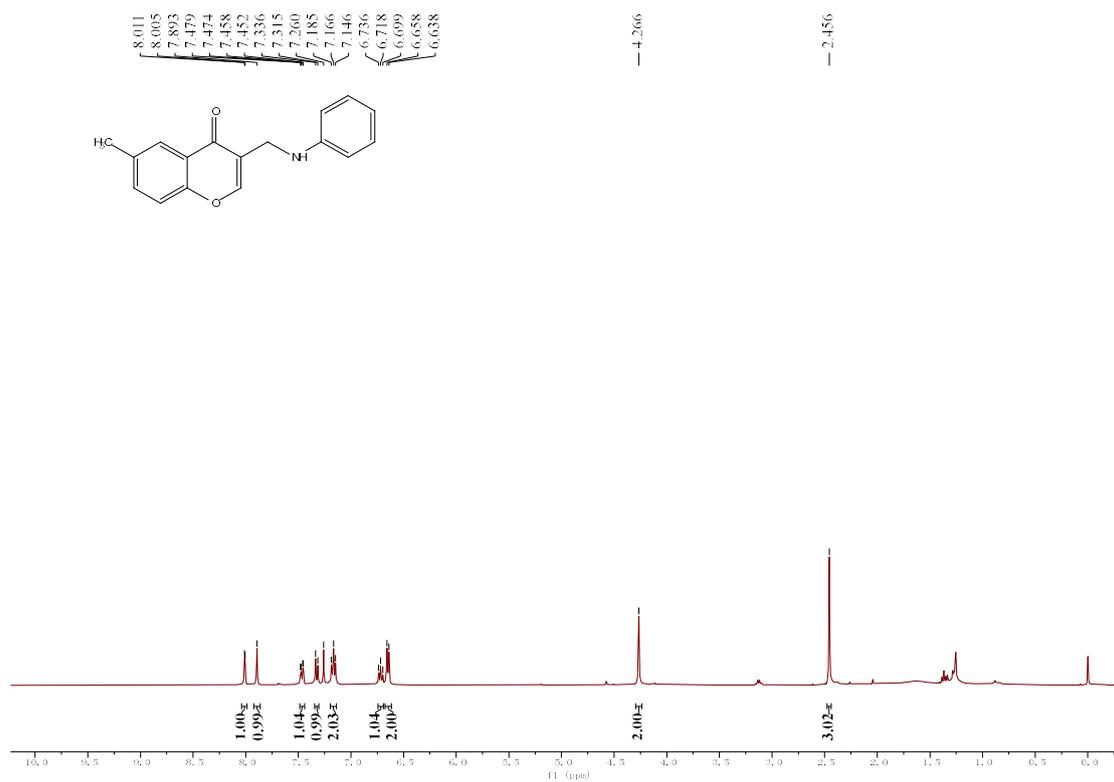
400 MHz ^1H NMR Spectrum of 3aa in CDCl_3



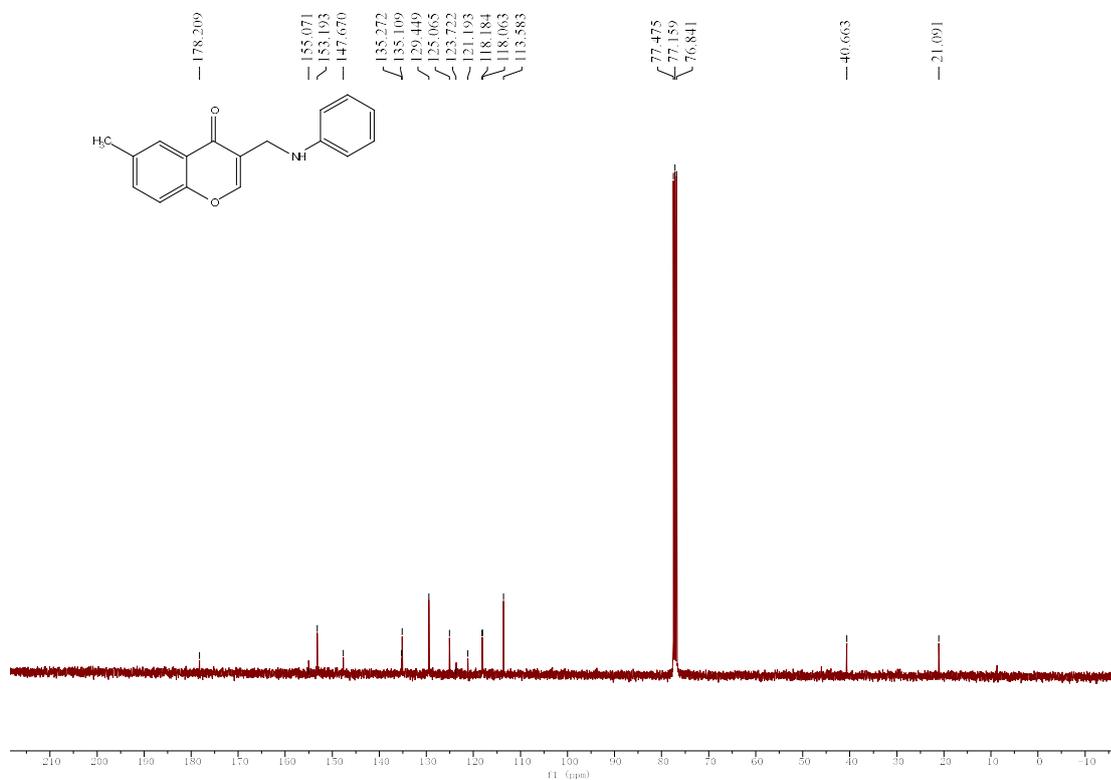
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3aa in CDCl_3



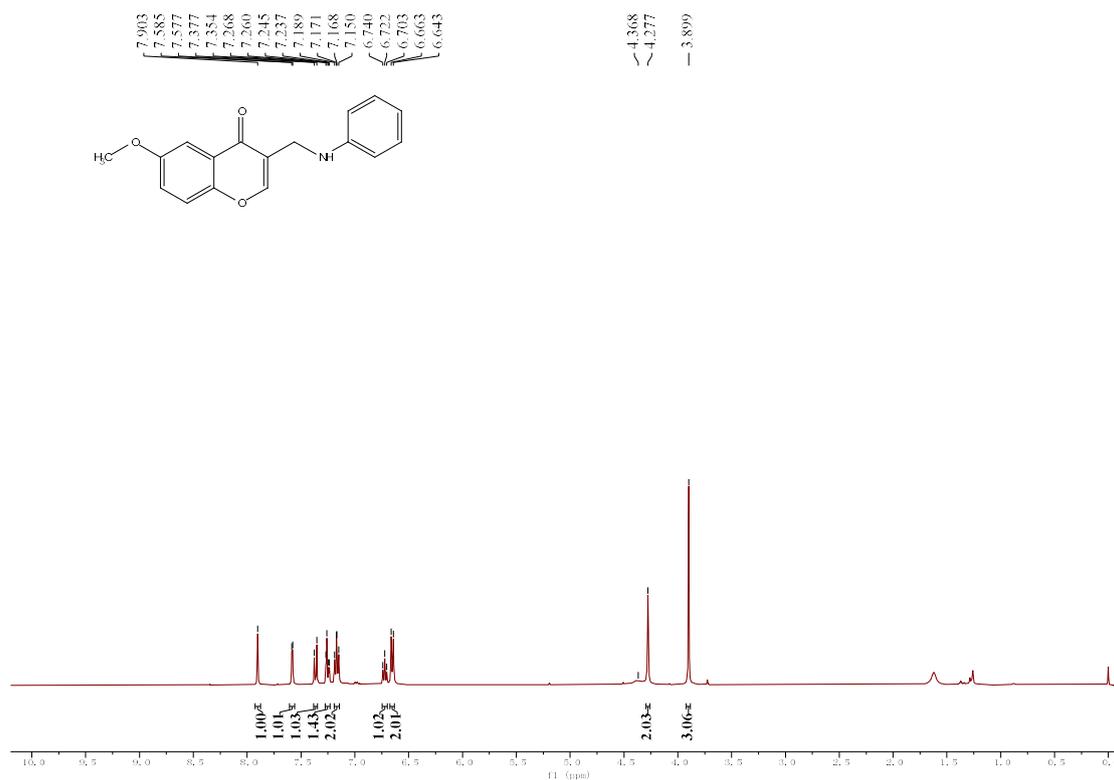
400 MHz ¹H NMR Spectrum of 3ba in CDCl₃



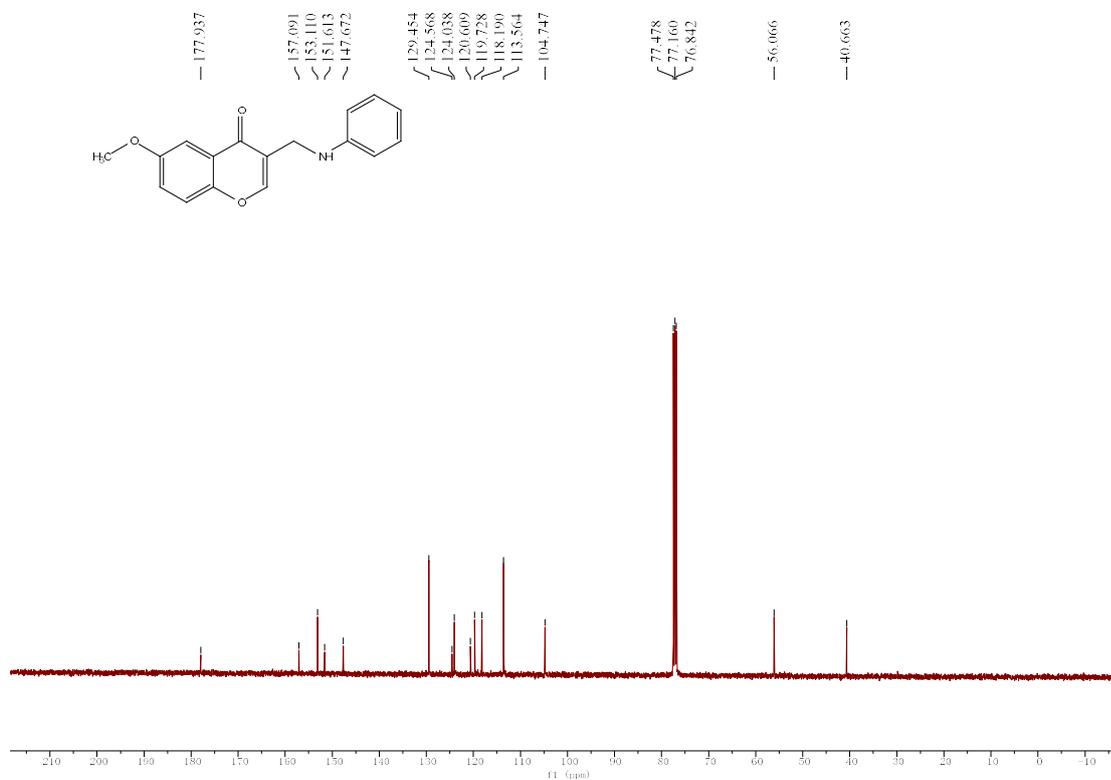
100 MHz ¹³C{¹H} NMR Spectrum of 3ba in CDCl₃



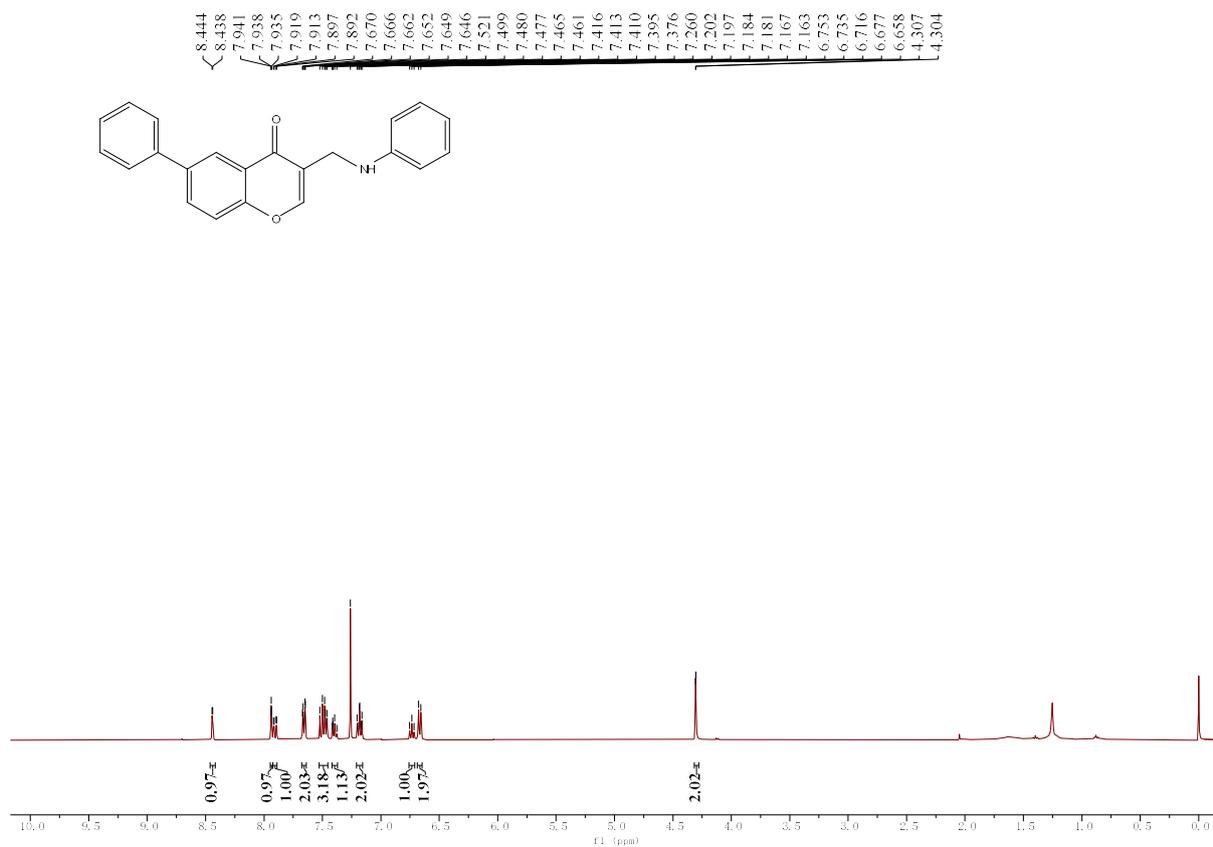
400 MHz ¹H NMR Spectrum of 3ca in CDCl₃



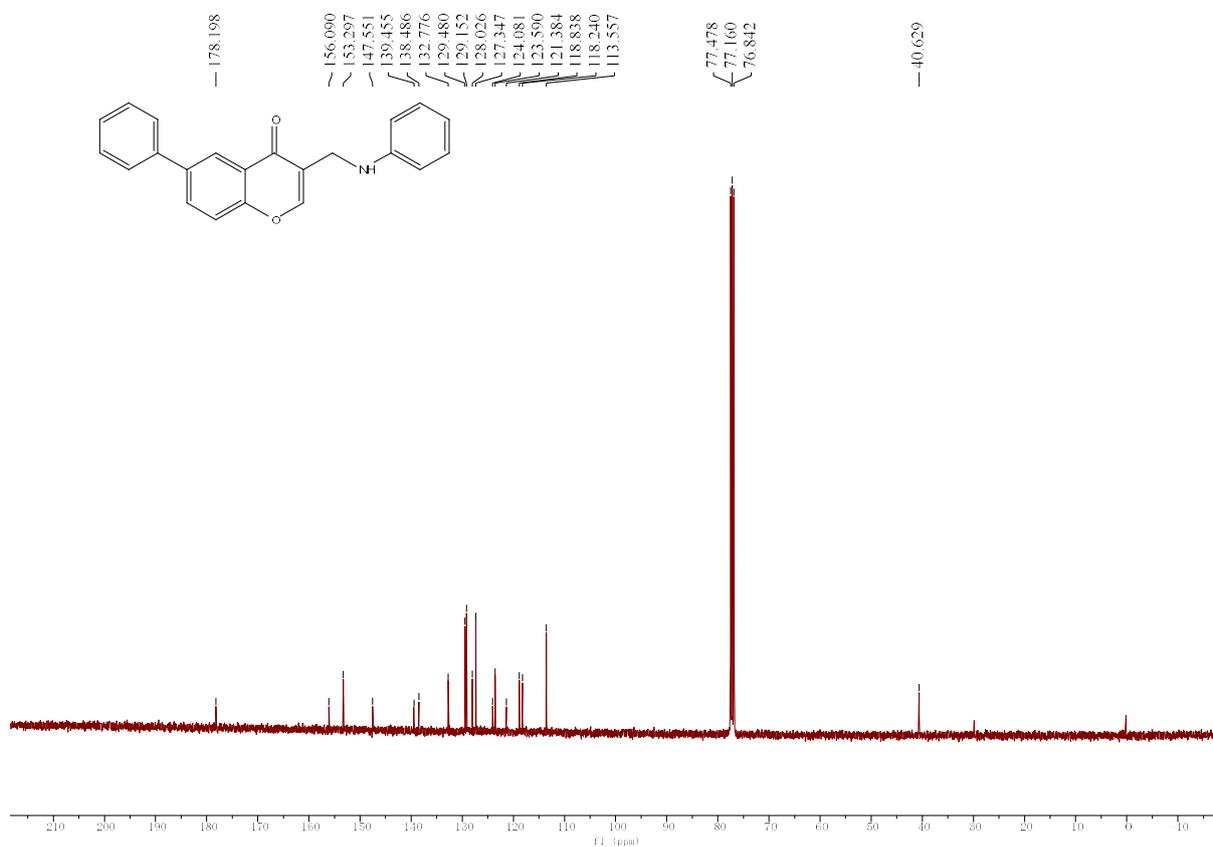
100 MHz ¹³C{¹H} NMR Spectrum of 3ca in CDCl₃



400 MHz ^1H NMR Spectrum of 3da in CDCl_3



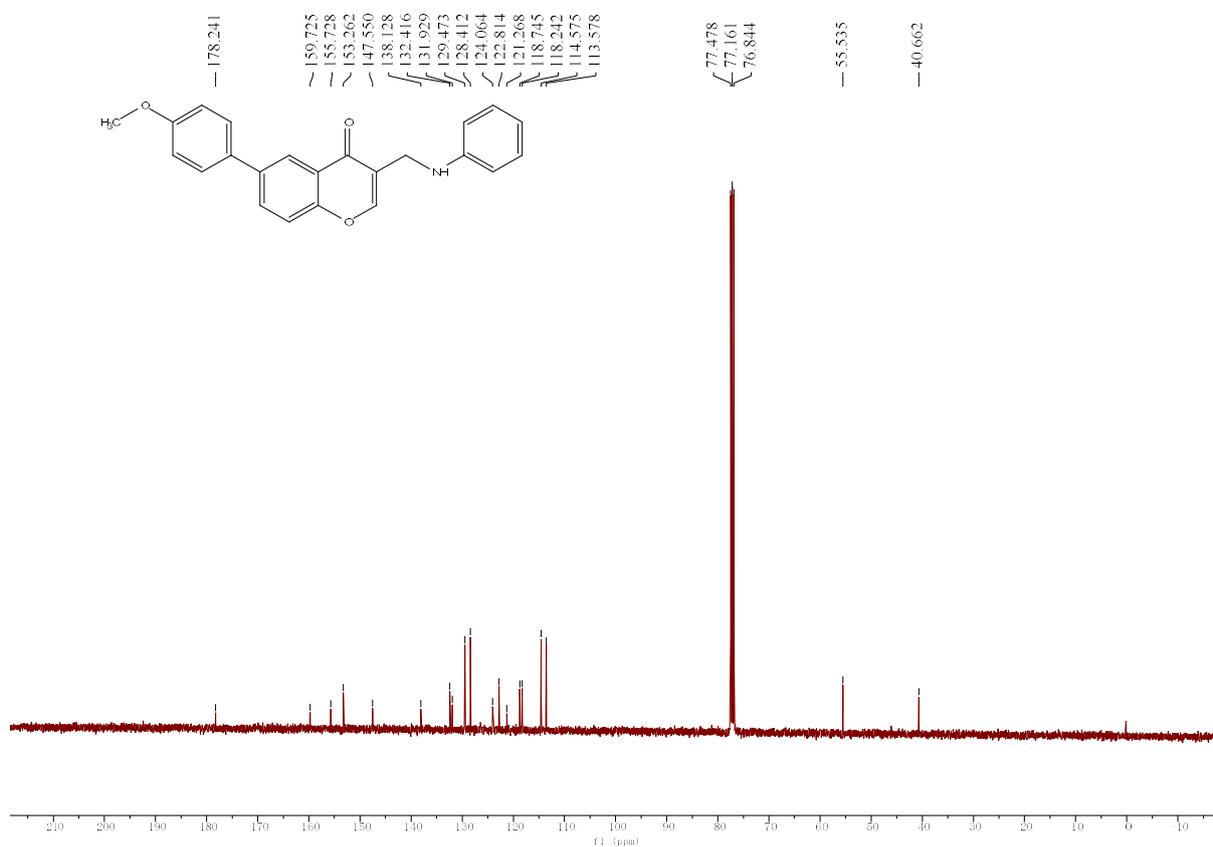
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3da in CDCl_3



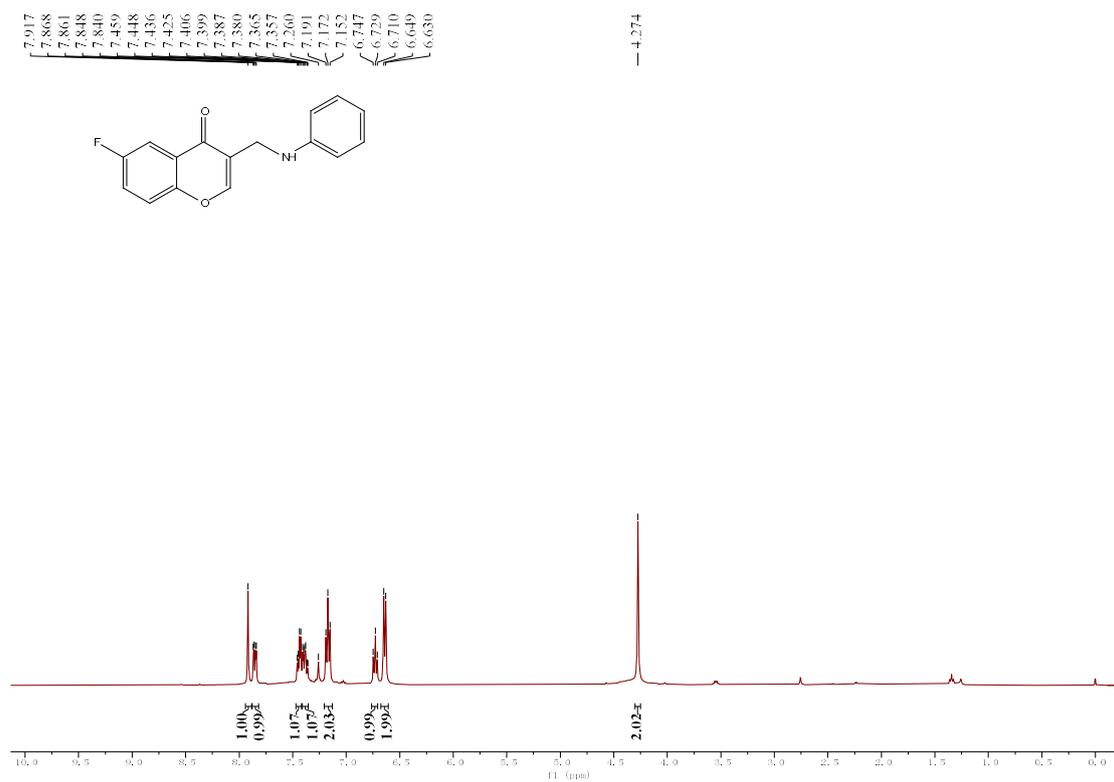
400 MHz ¹H NMR Spectrum of 3ea in CDCl₃



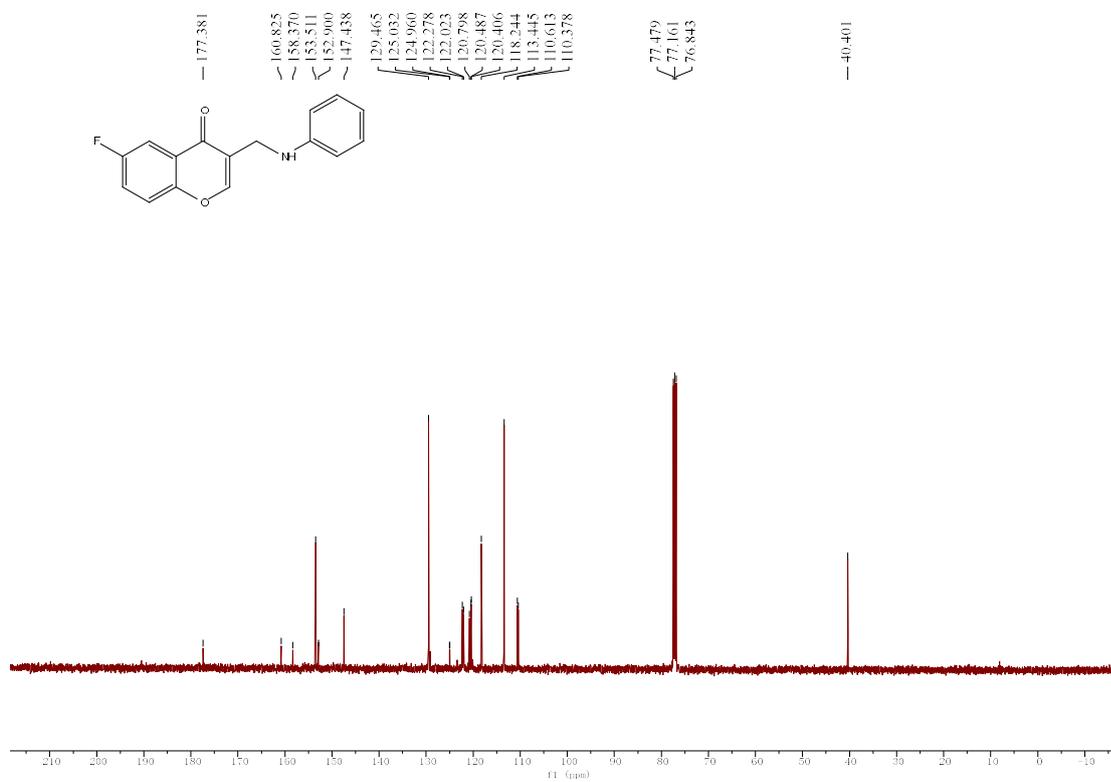
100 MHz ¹³C{¹H} NMR Spectrum of 3ea in CDCl₃



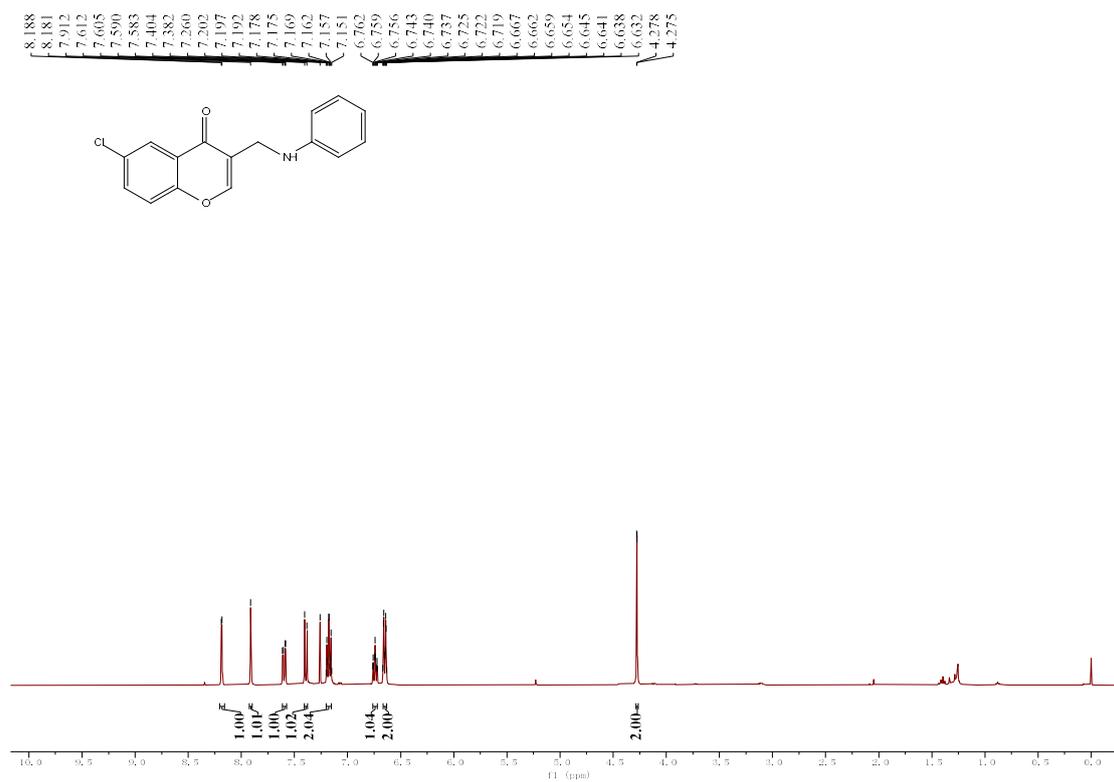
400 MHz ^1H NMR Spectrum of 3fa in CDCl_3



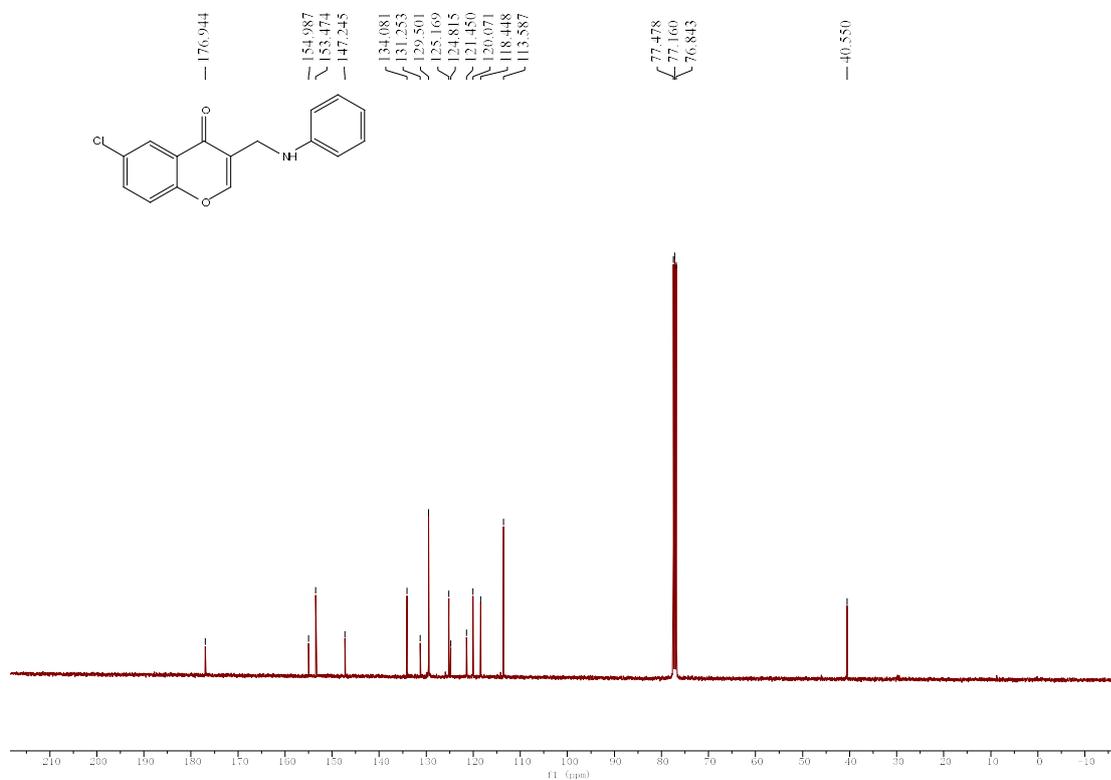
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3fa in CDCl_3



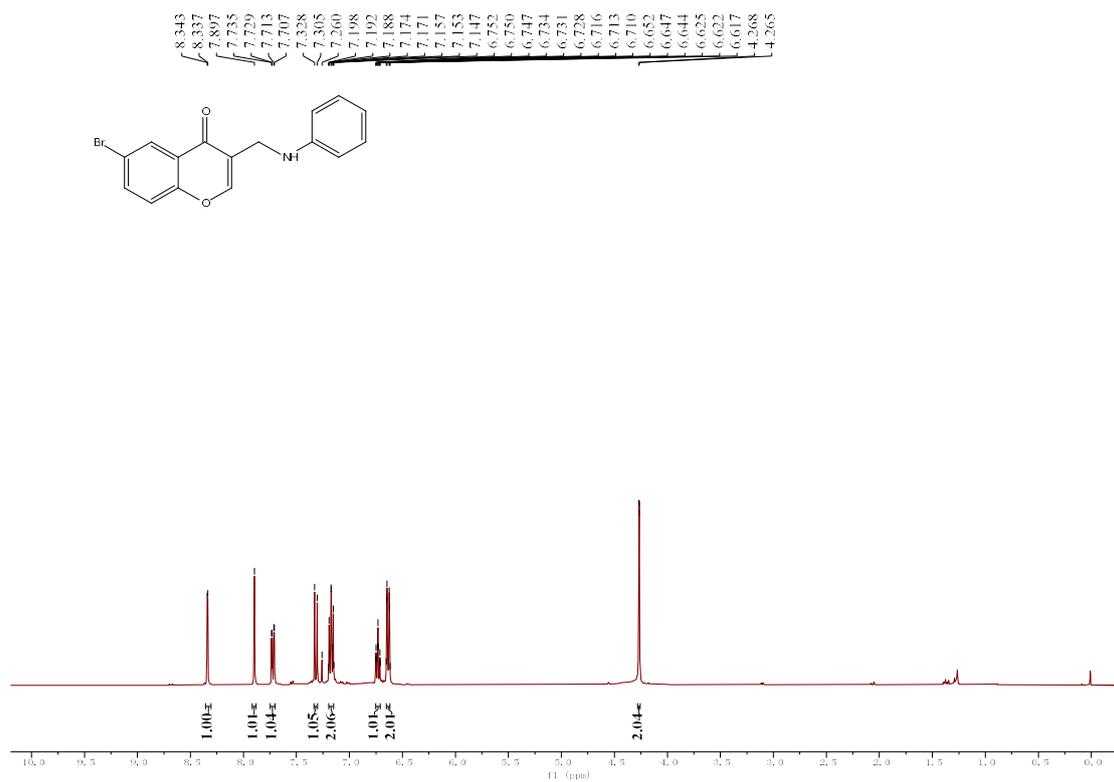
400 MHz ^1H NMR Spectrum of 3ga in CDCl_3



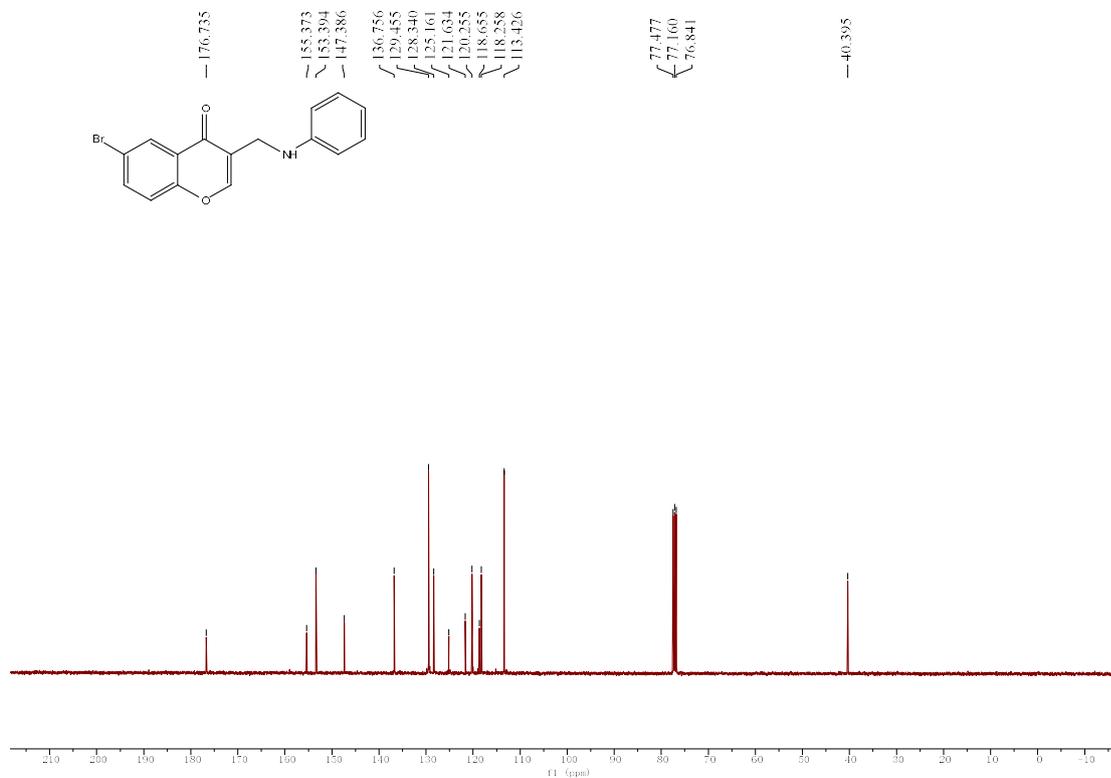
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3ga in CDCl_3



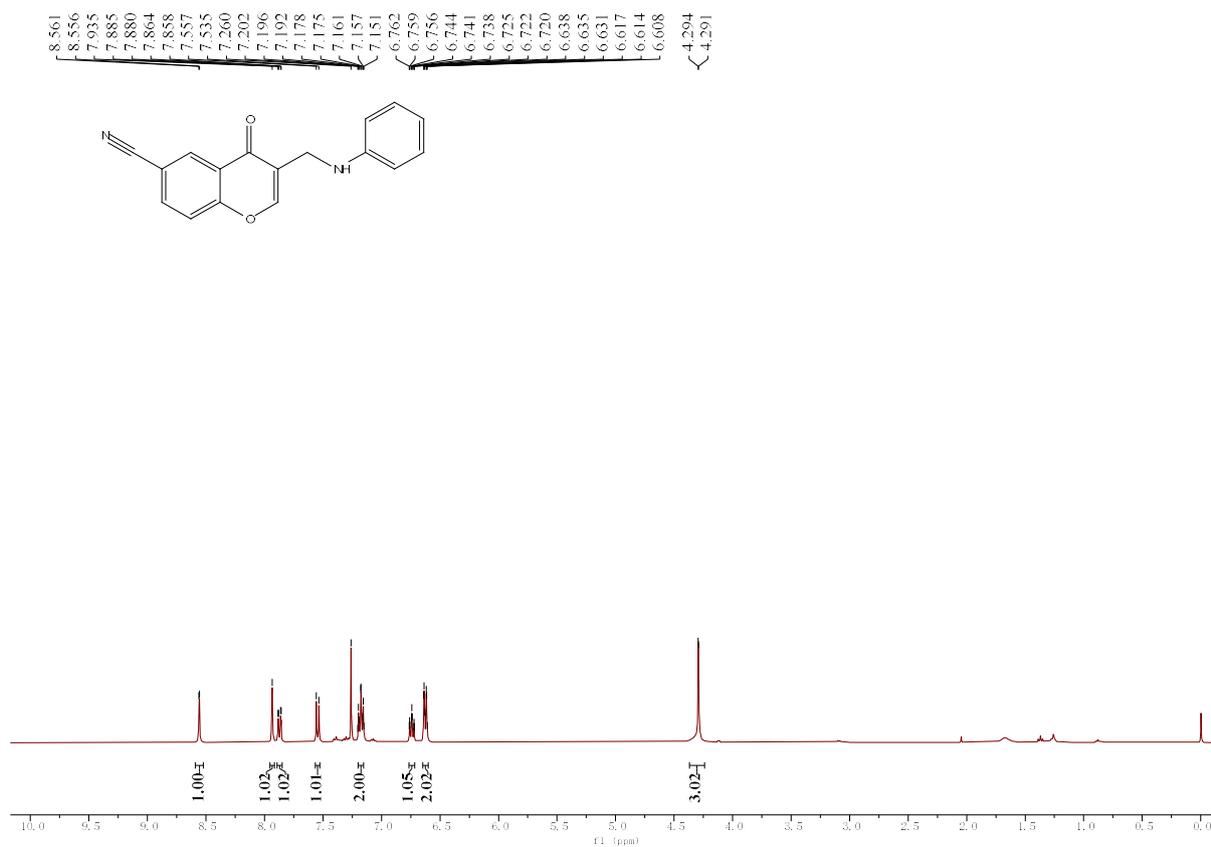
400 MHz ¹H NMR Spectrum of 3ha in CDCl₃



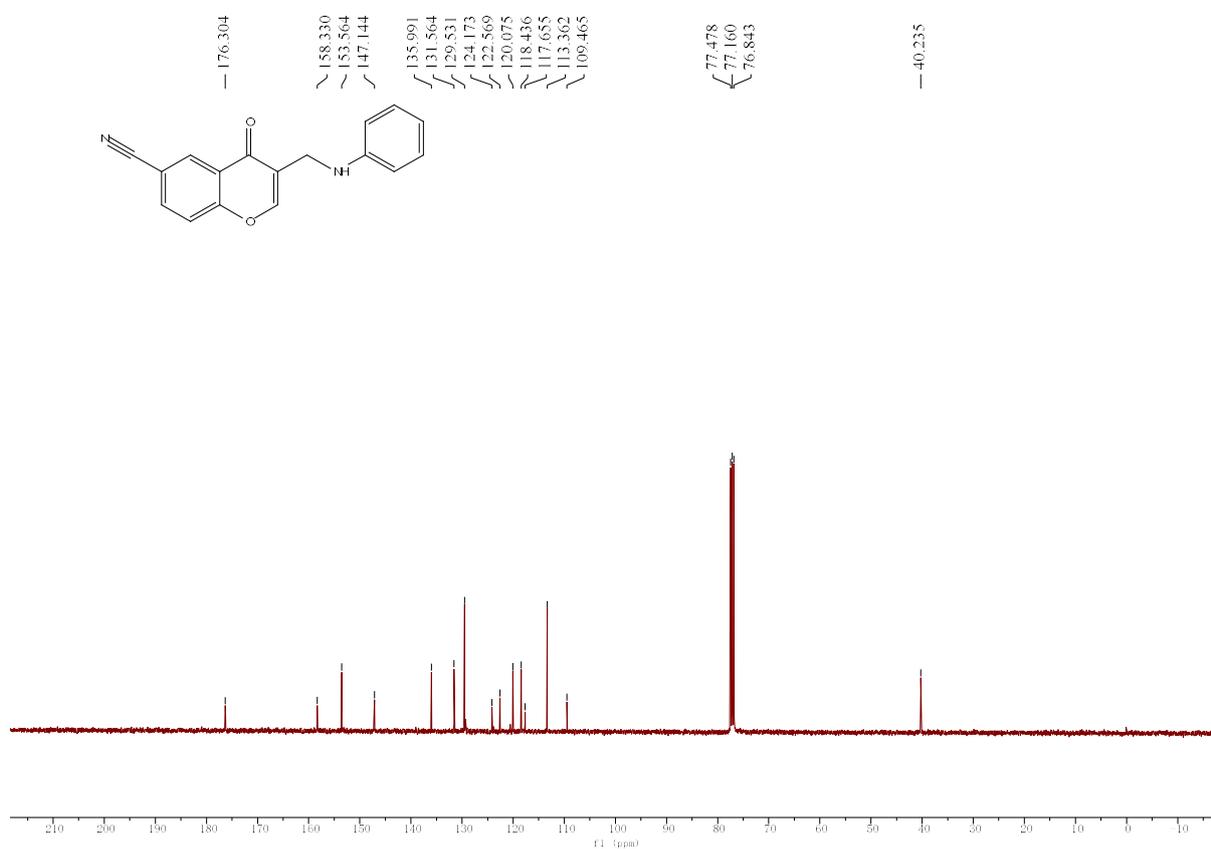
100 MHz ¹³C{¹H} NMR Spectrum of 3ha in CDCl₃



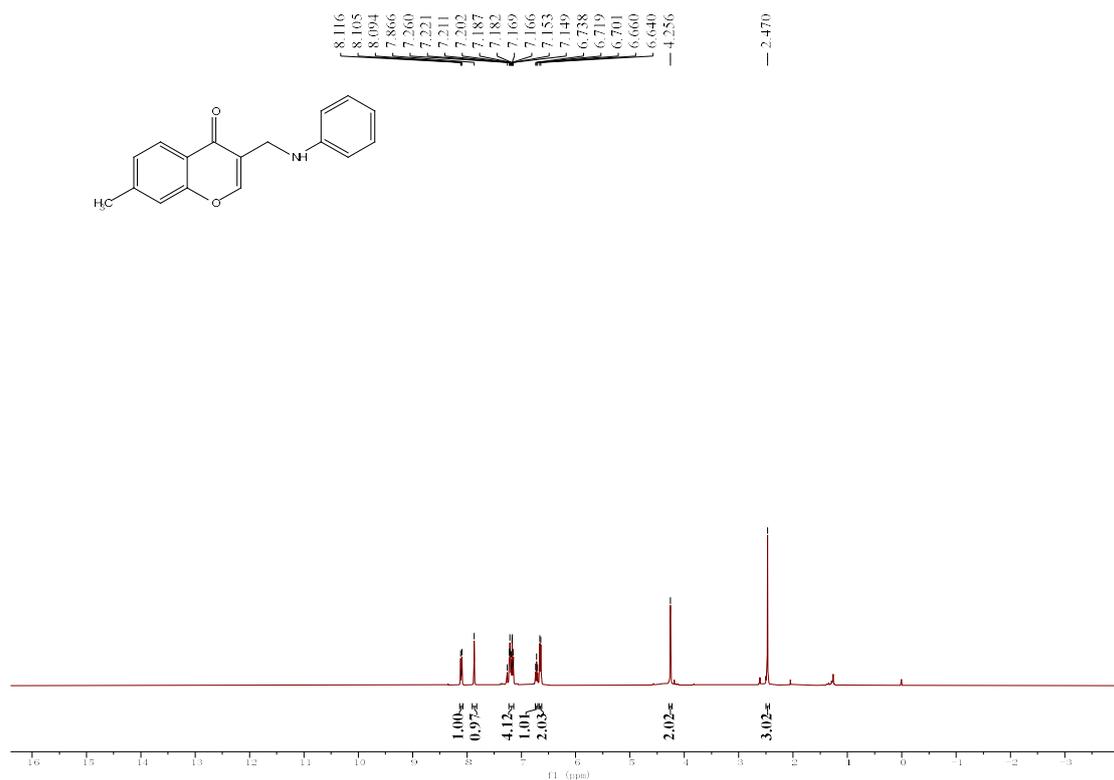
400 MHz ¹H NMR Spectrum of 3ia in CDCl₃



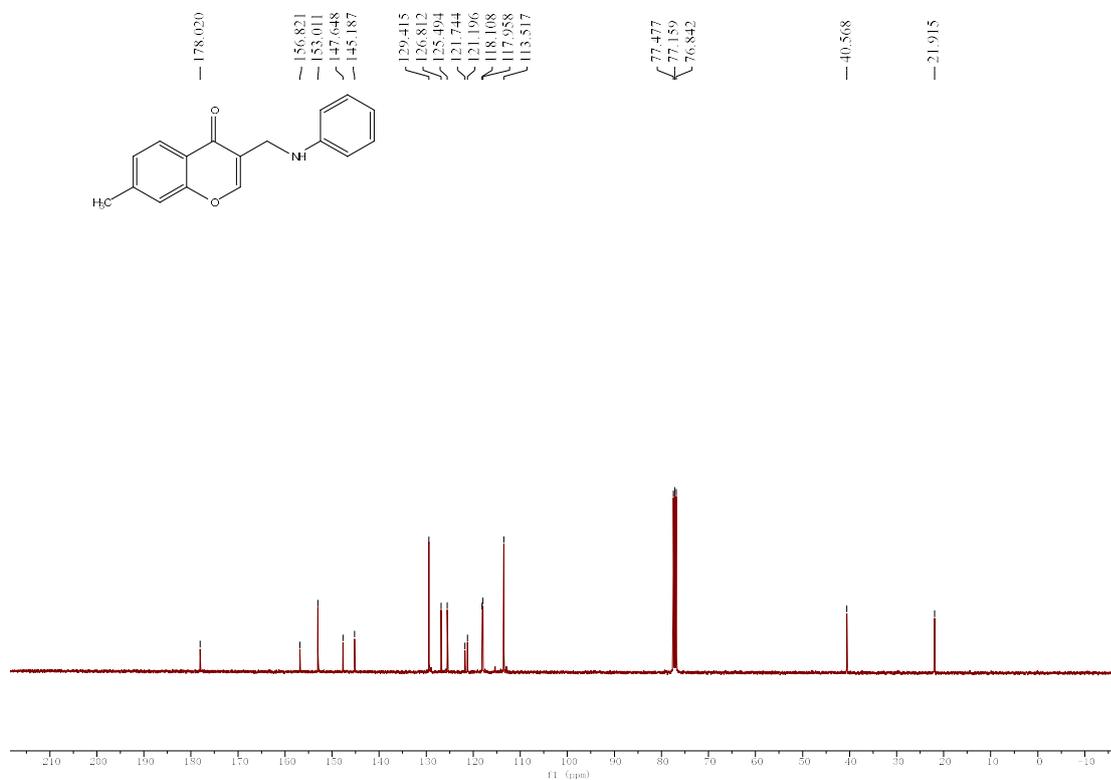
100 MHz ¹³C{¹H} NMR Spectrum of 3ia in CDCl₃



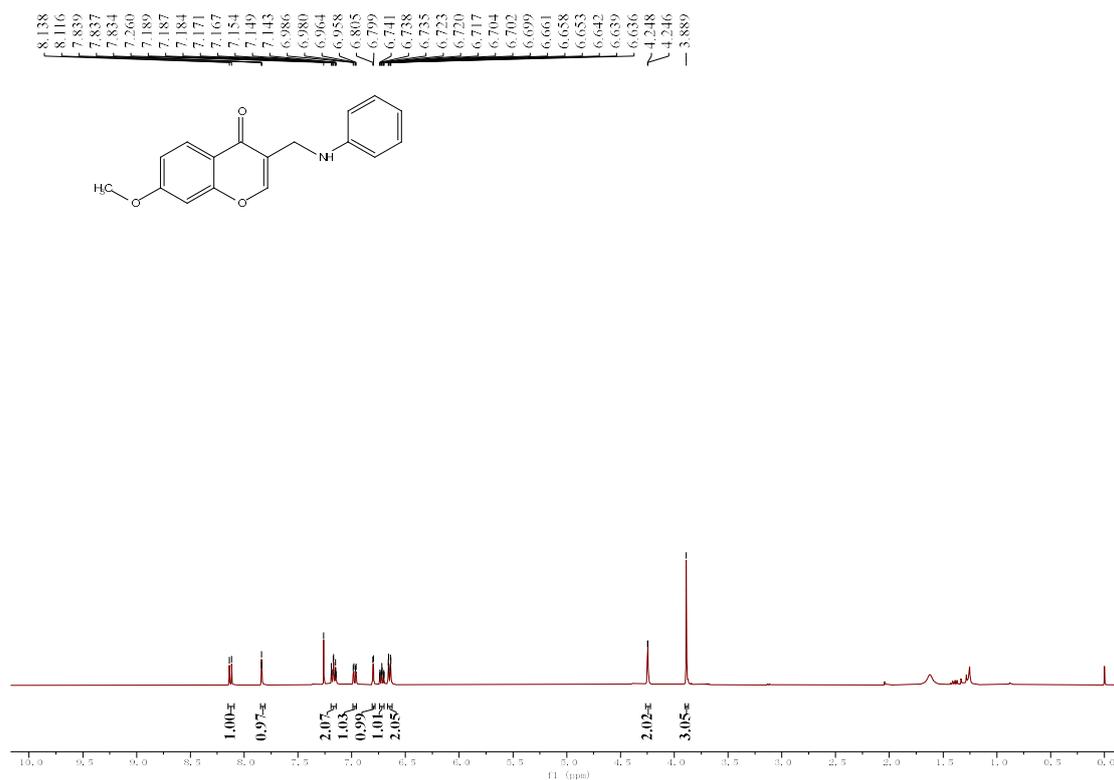
400 MHz ¹H NMR Spectrum of 3ja in CDCl₃



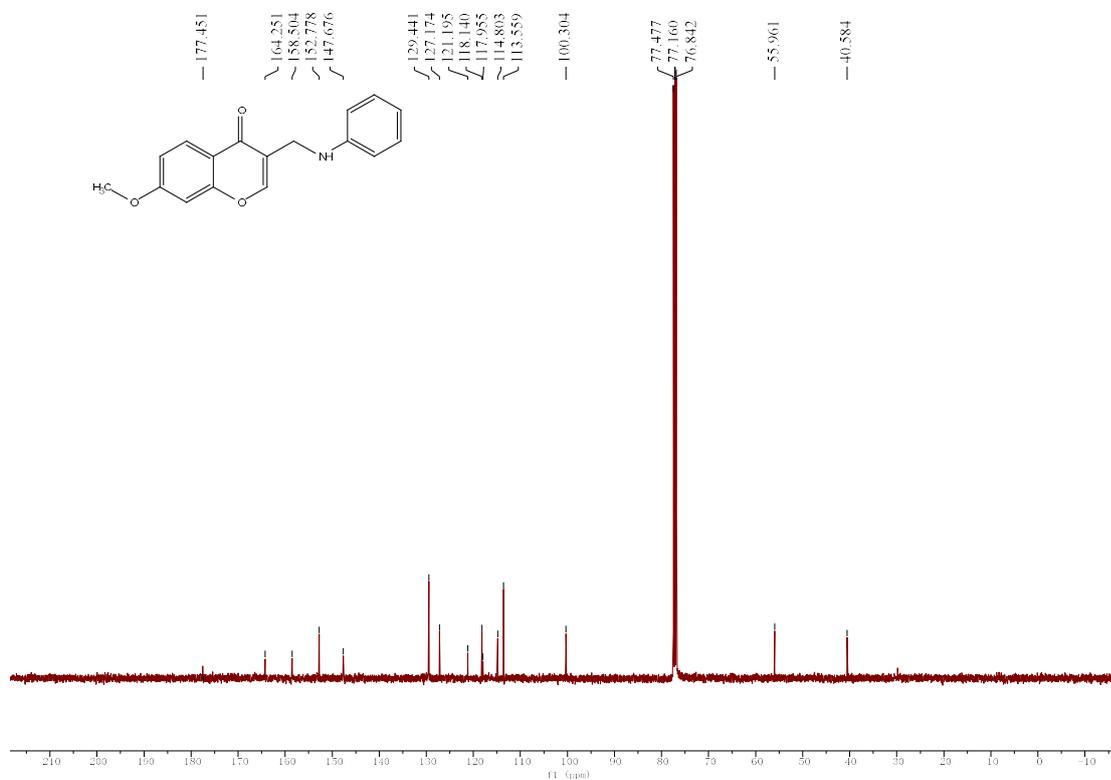
100 MHz ¹³C{¹H} NMR Spectrum of 3ja in CDCl₃



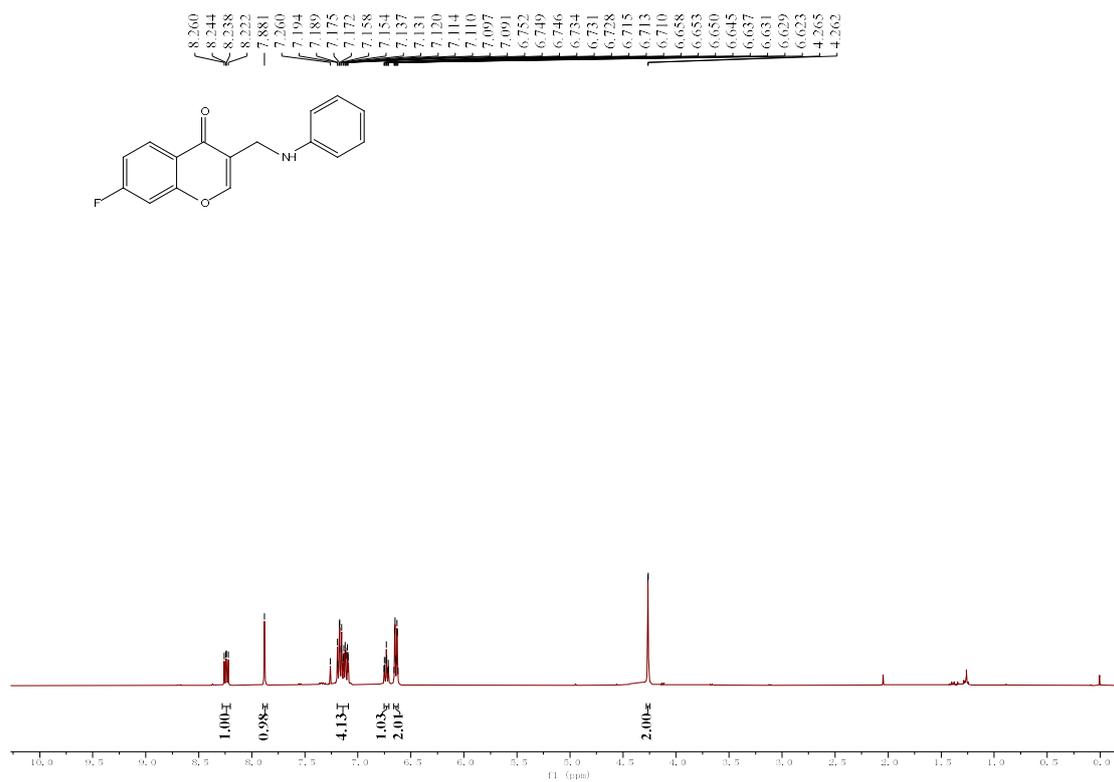
400 MHz ¹H NMR Spectrum of 3ka in CDCl₃



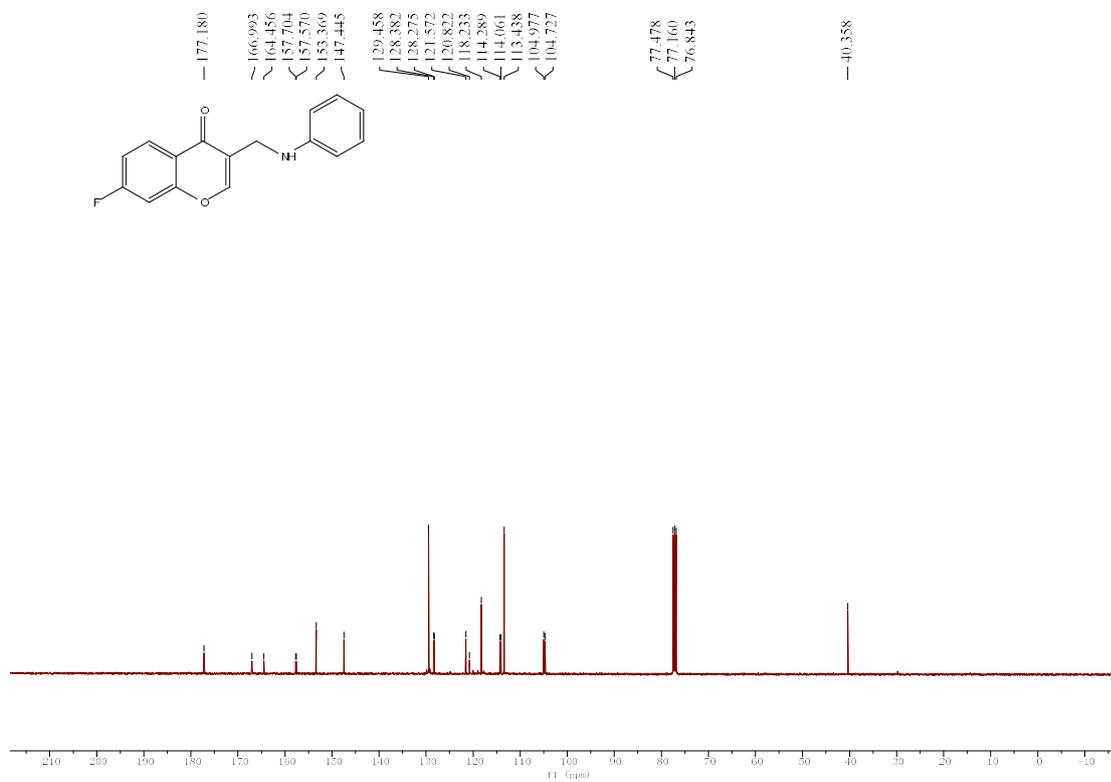
100 MHz ¹³C{¹H} NMR Spectrum of 3ka in CDCl₃



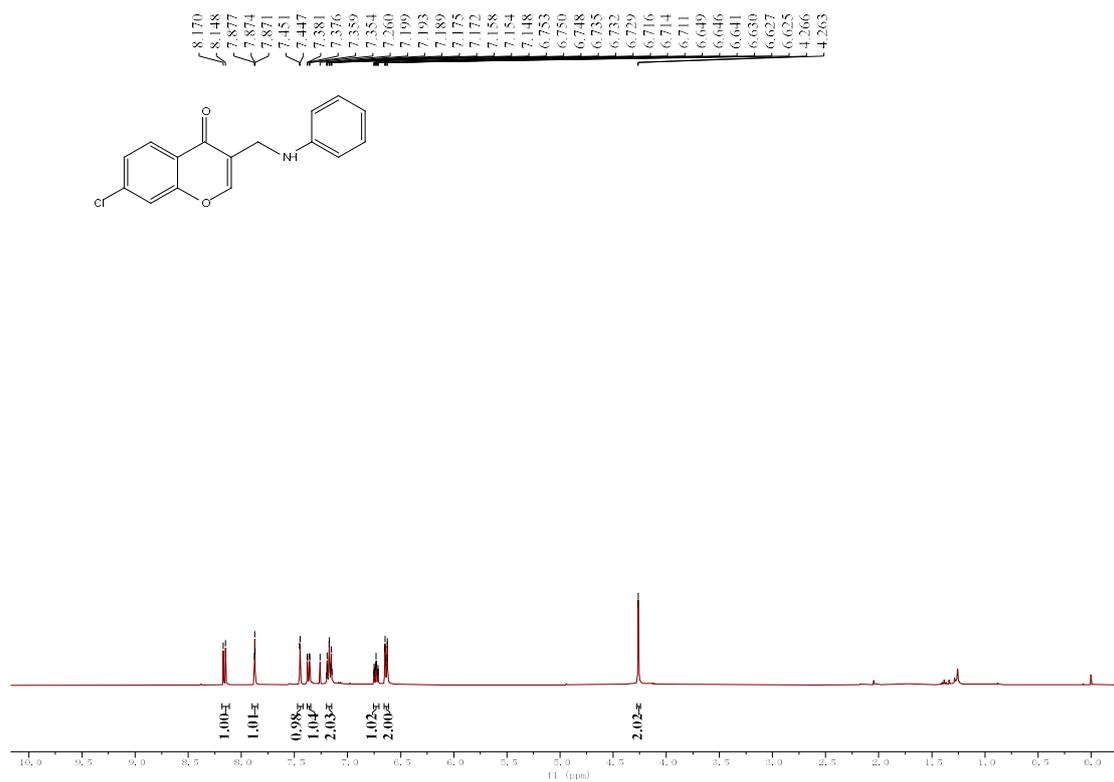
400 MHz ¹H NMR Spectrum of 3a in CDCl₃



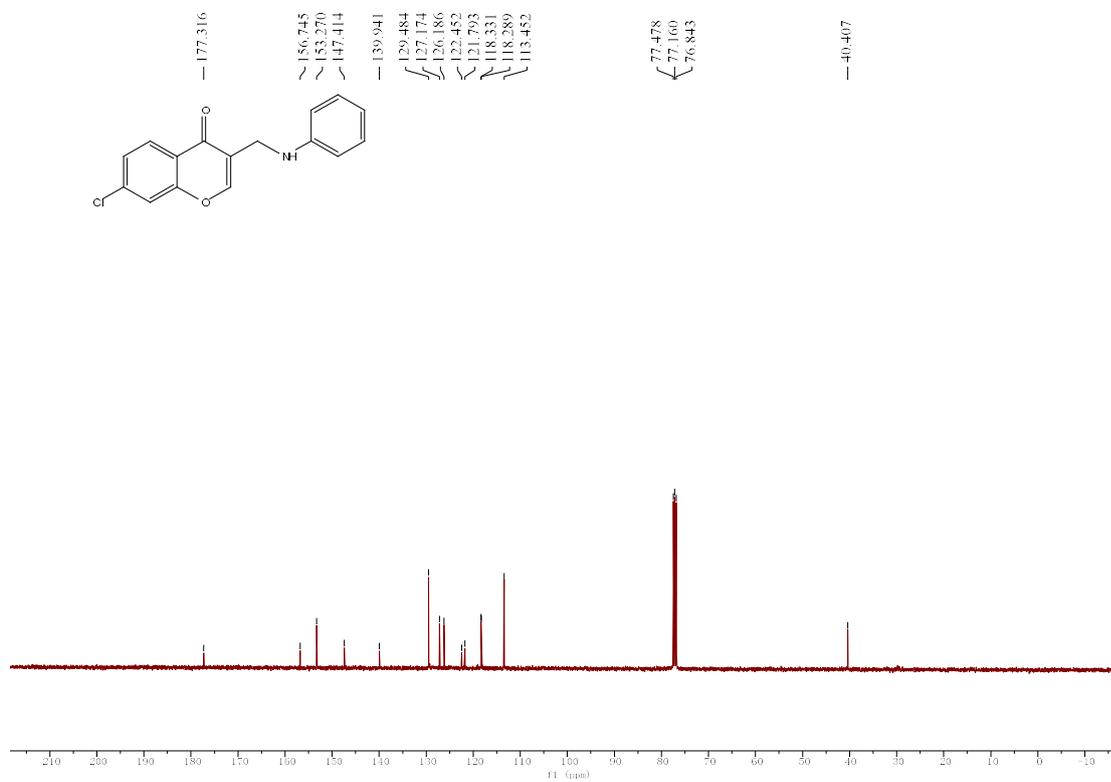
100 MHz ¹³C{¹H} NMR Spectrum of 3a in CDCl₃



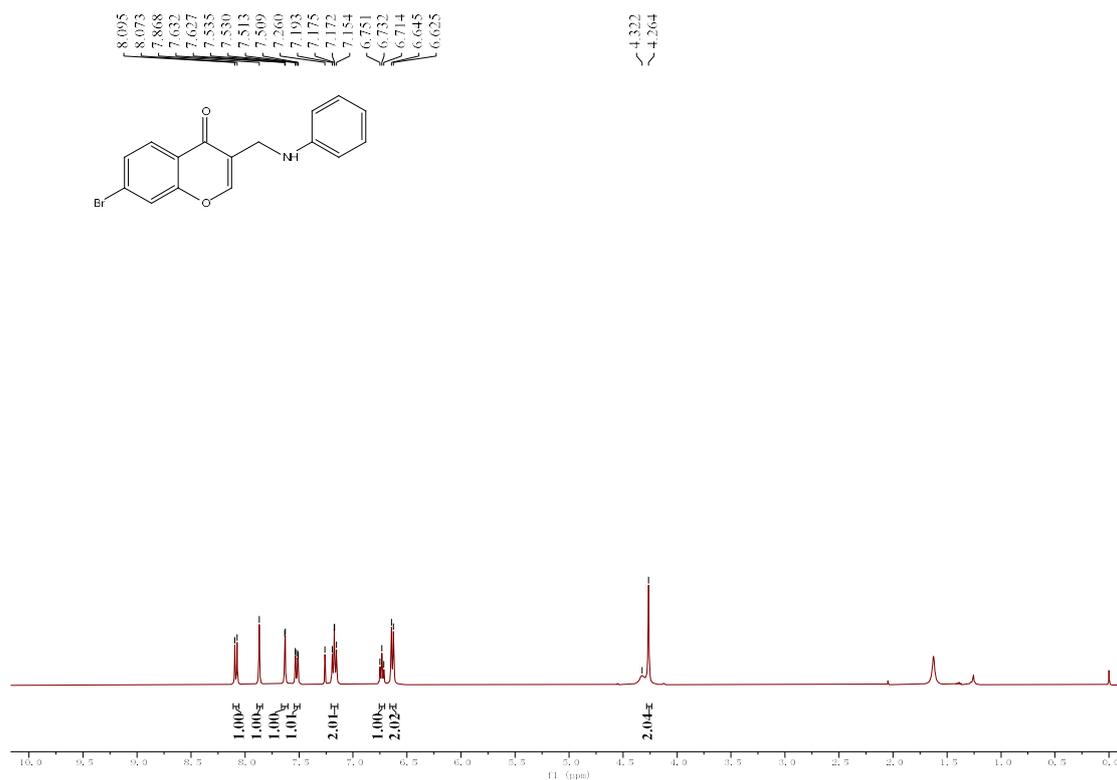
400 MHz ¹H NMR Spectrum of 3ma in CDCl₃



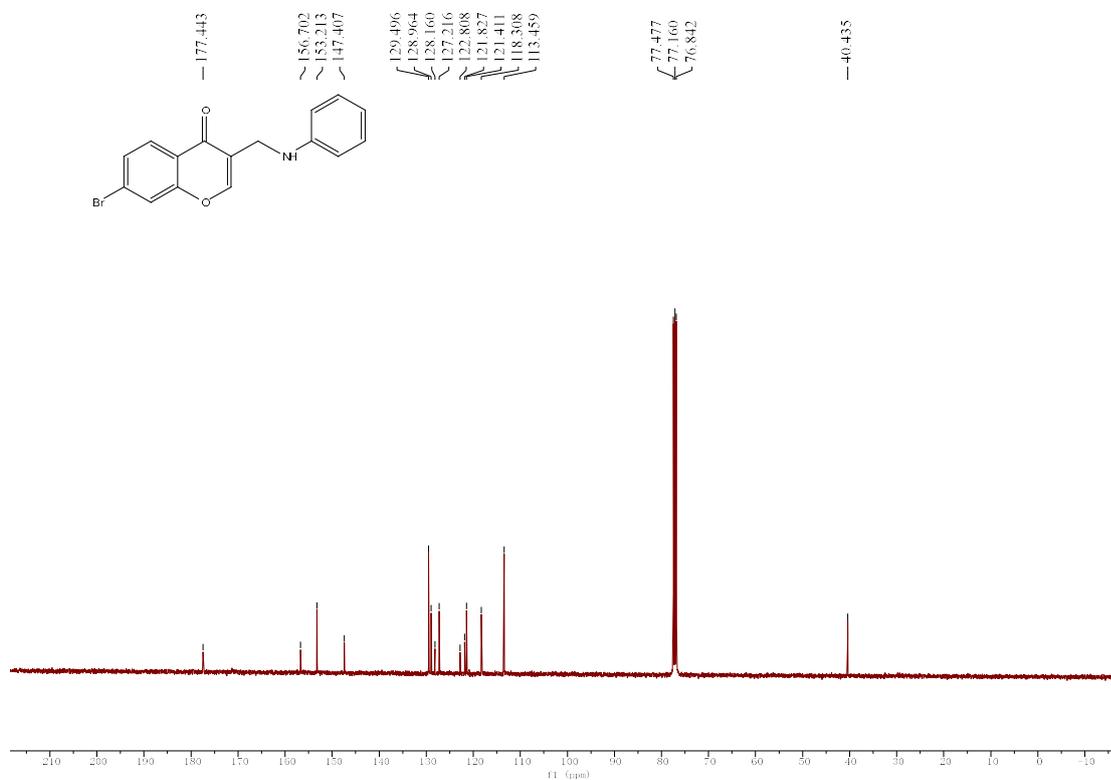
100 MHz ¹³C{¹H} NMR Spectrum of 3ma in CDCl₃



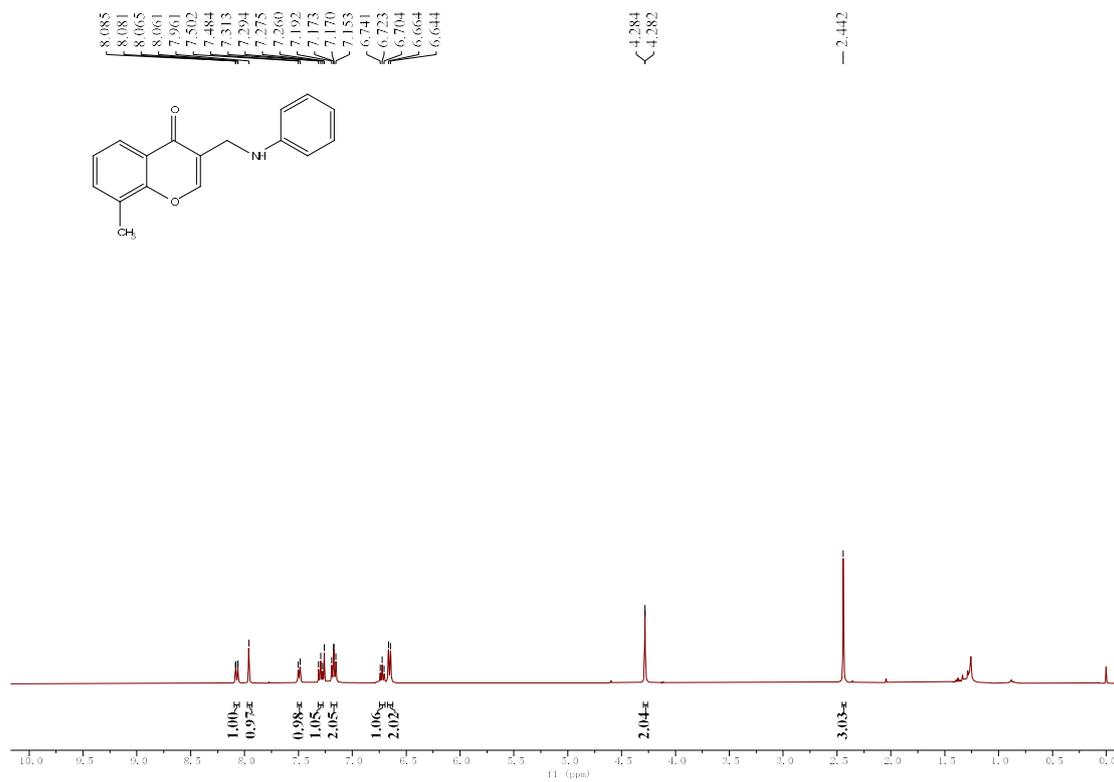
400 MHz ¹H NMR Spectrum of 3na in CDCl₃



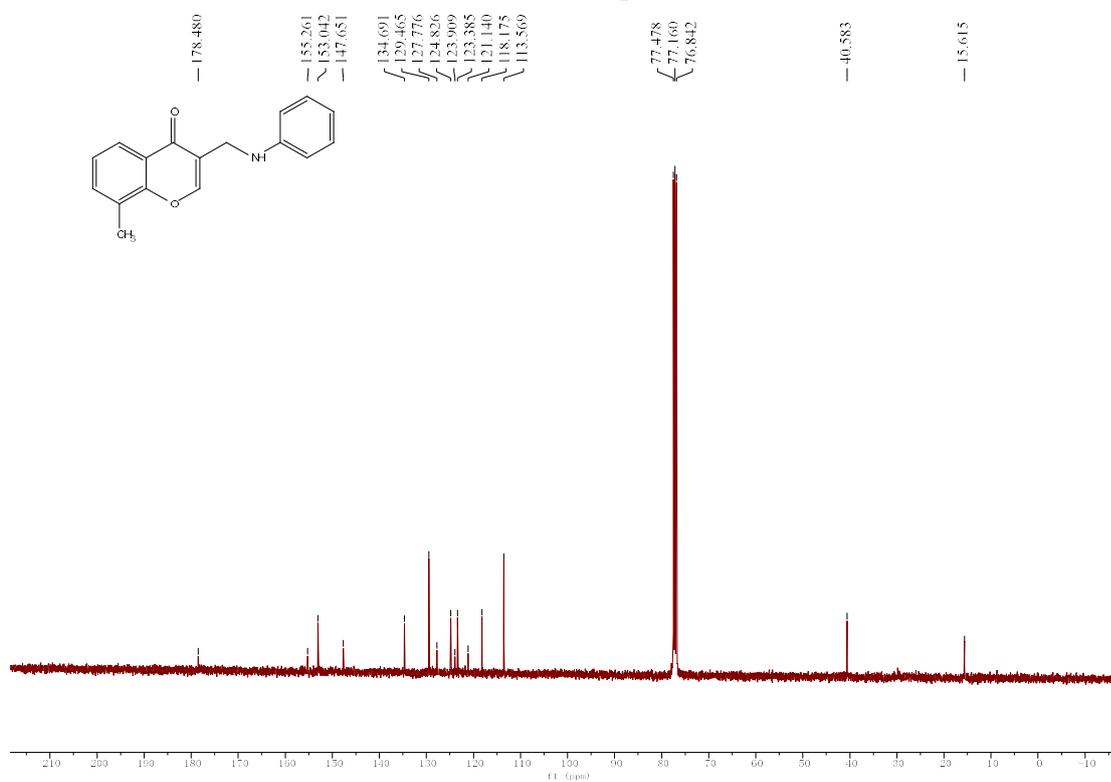
100 MHz ¹³C{¹H} NMR Spectrum of 3na in CDCl₃



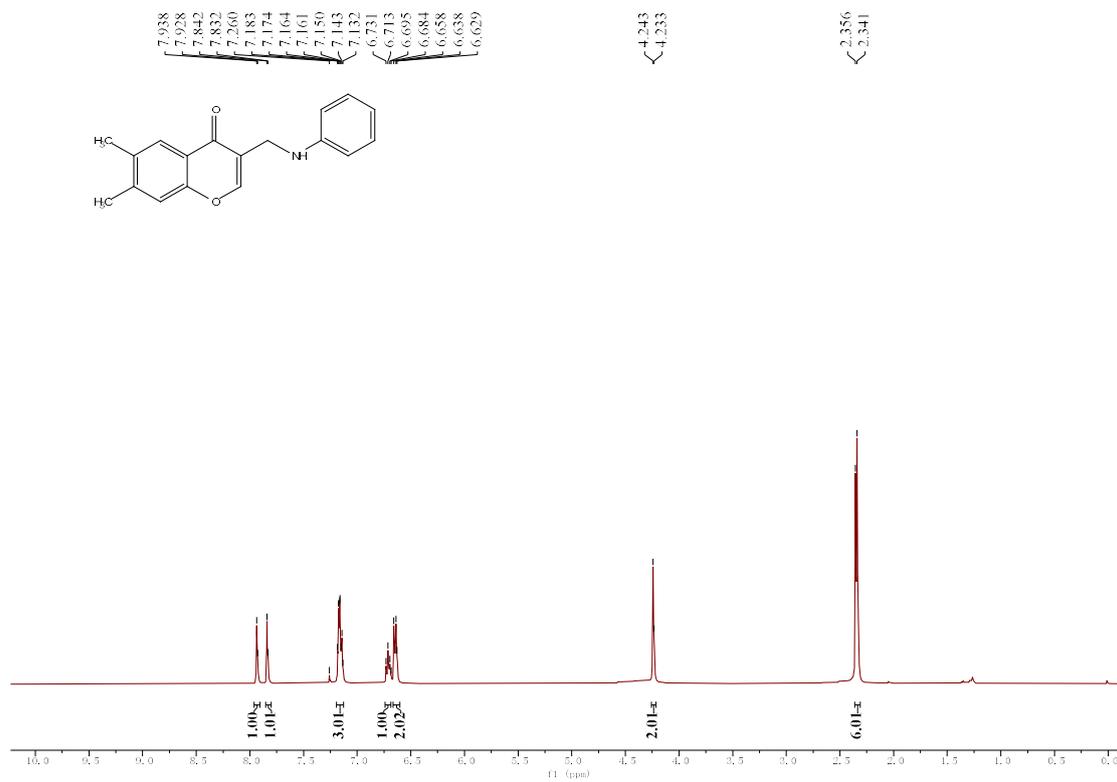
400 MHz ^1H NMR Spectrum of 30a in CDCl_3



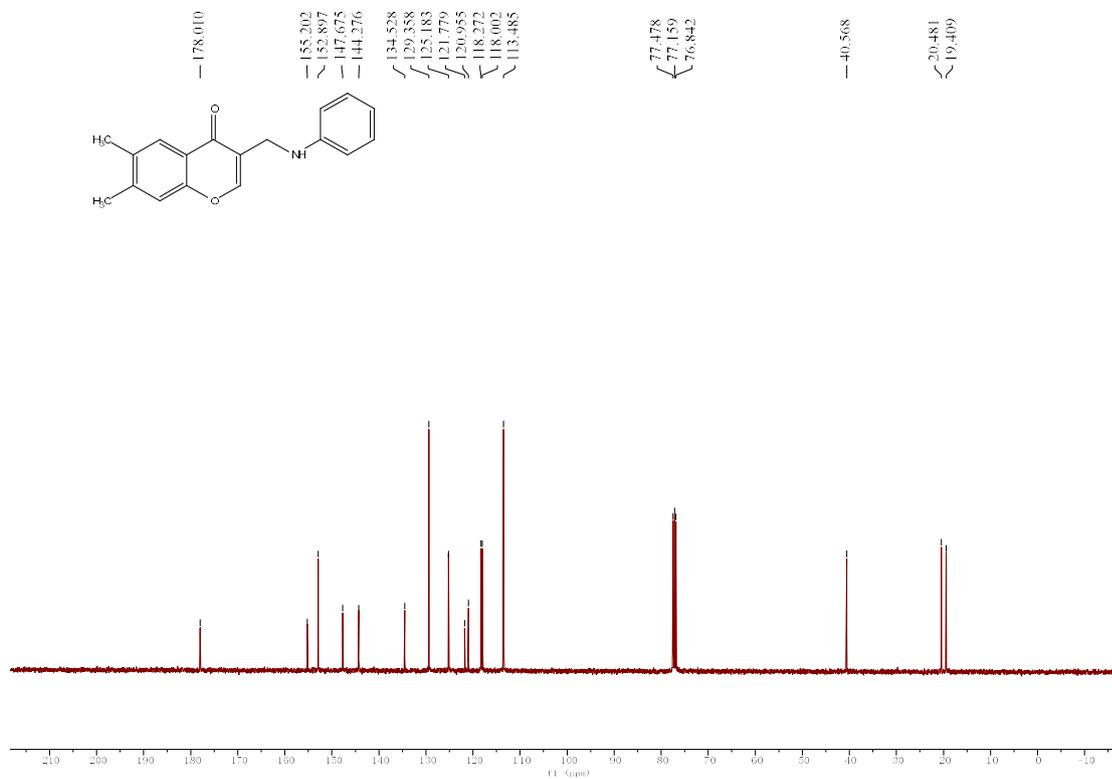
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 30a in CDCl_3



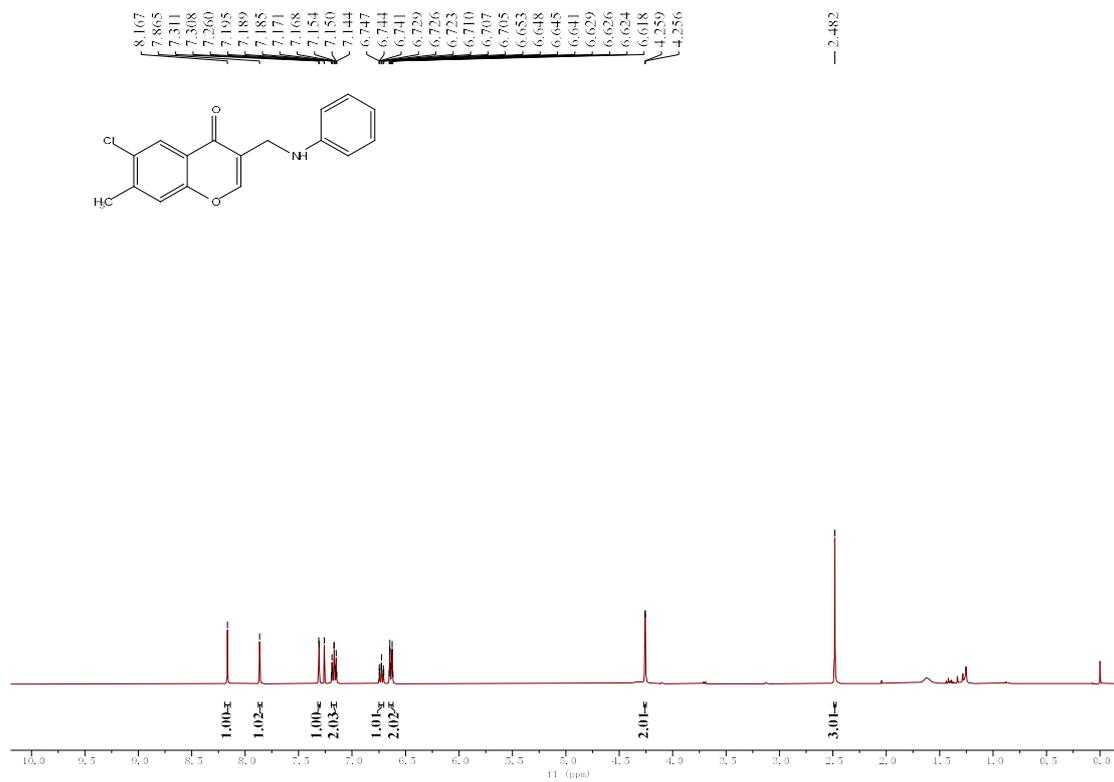
400 MHz ^1H NMR Spectrum of 3pa in CDCl_3



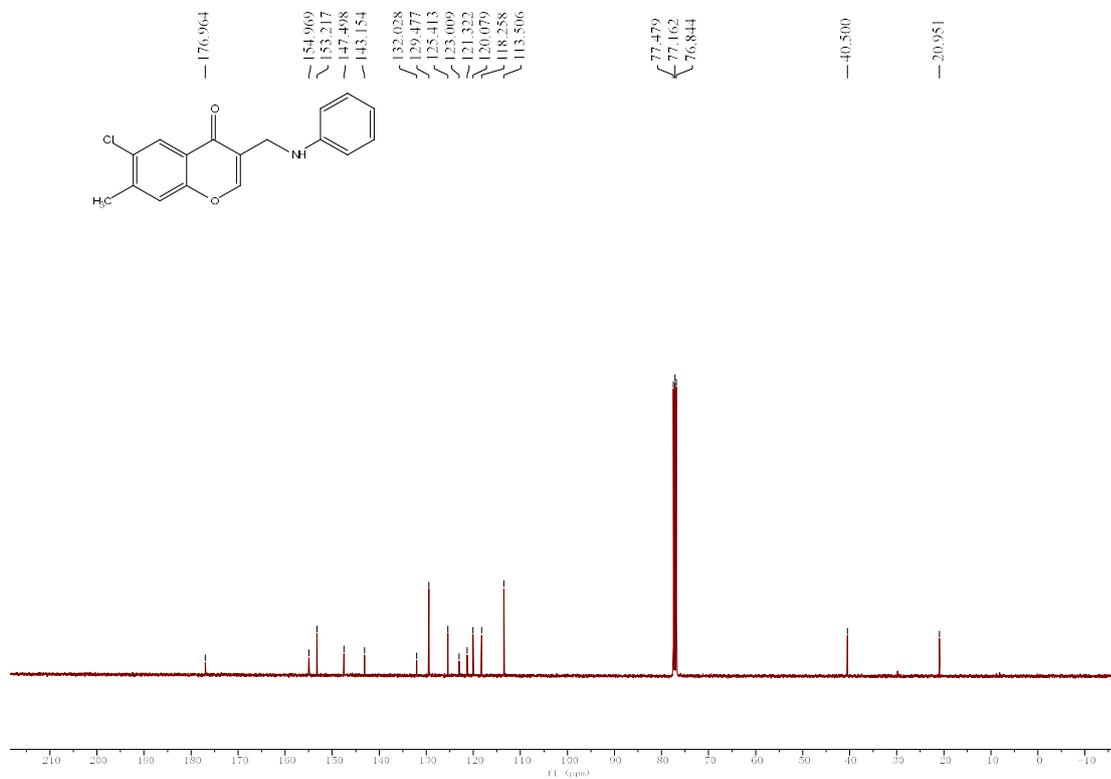
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3pa in CDCl_3



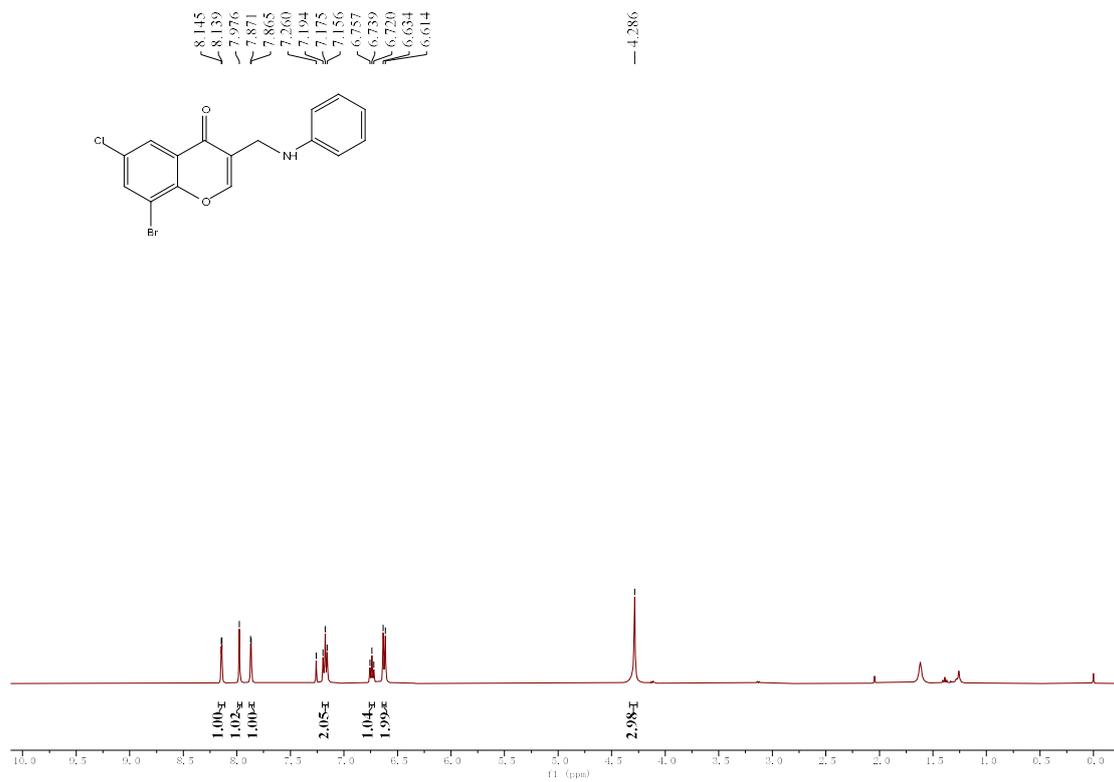
400 MHz ^1H NMR Spectrum of 3qa in CDCl_3



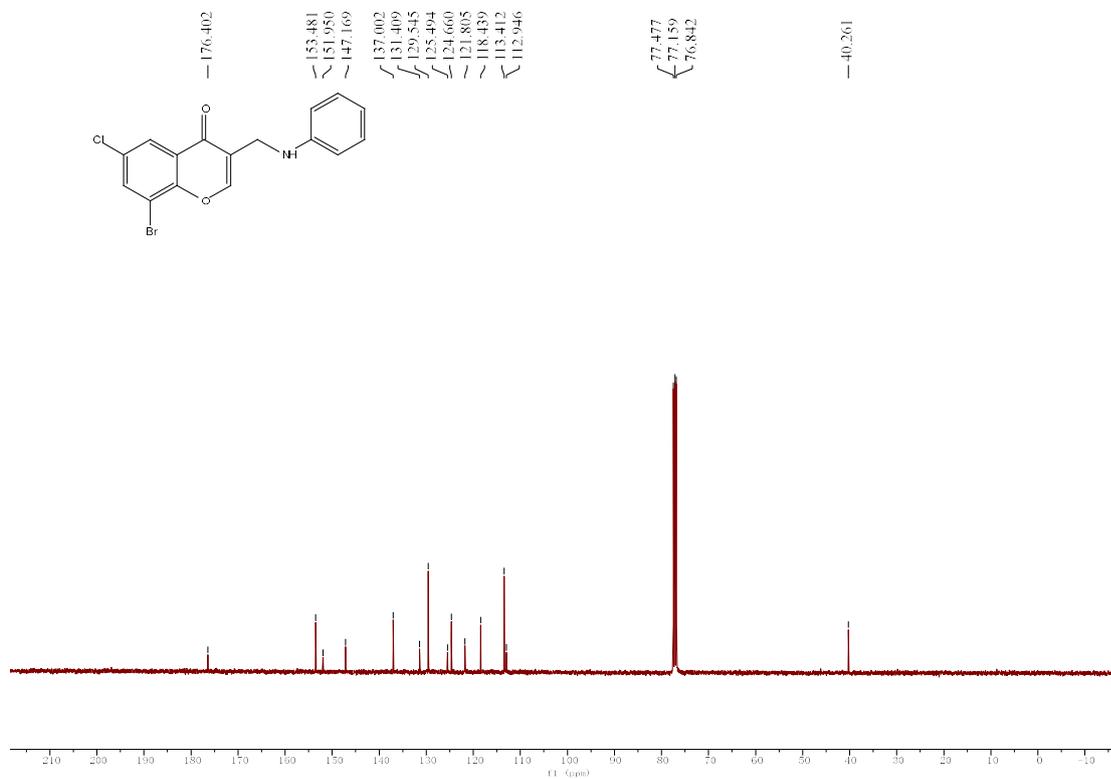
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3qa in CDCl_3



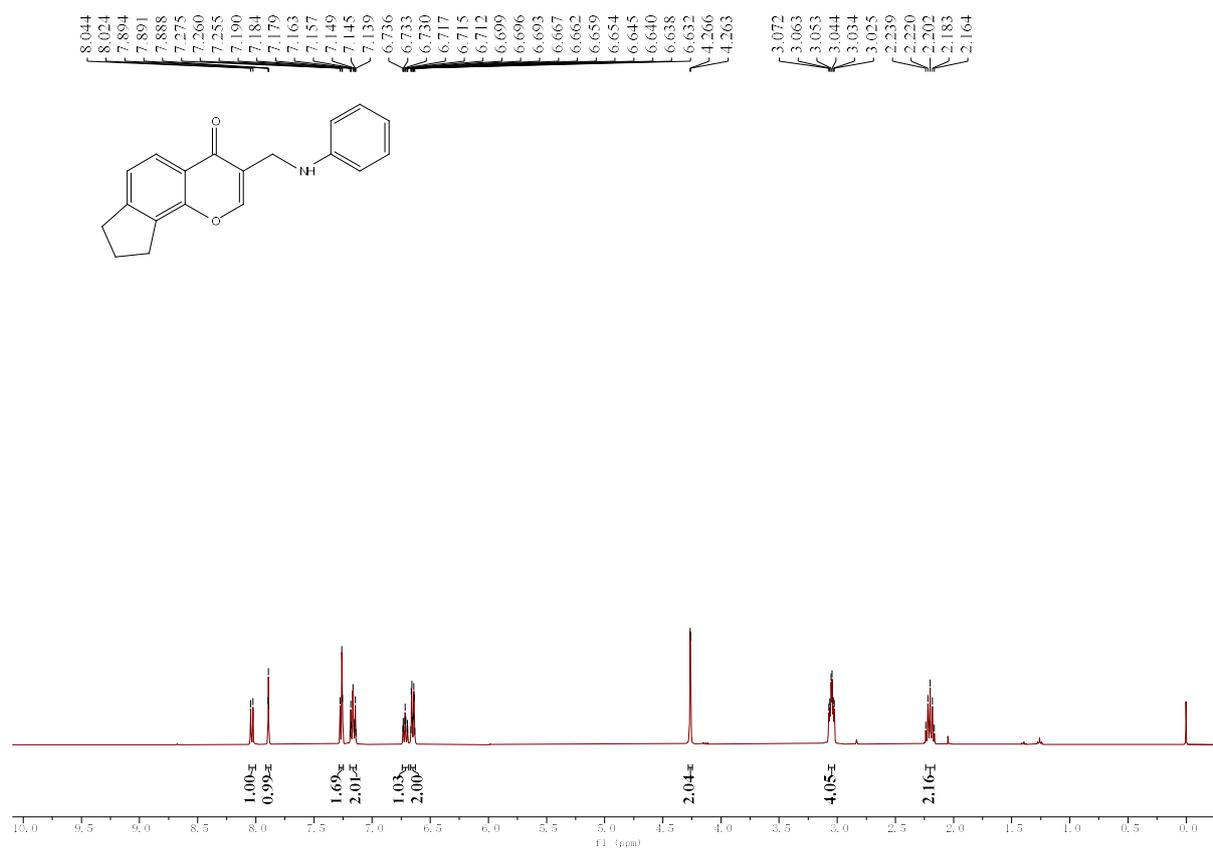
400 MHz ^1H NMR Spectrum of 3ra in CDCl_3



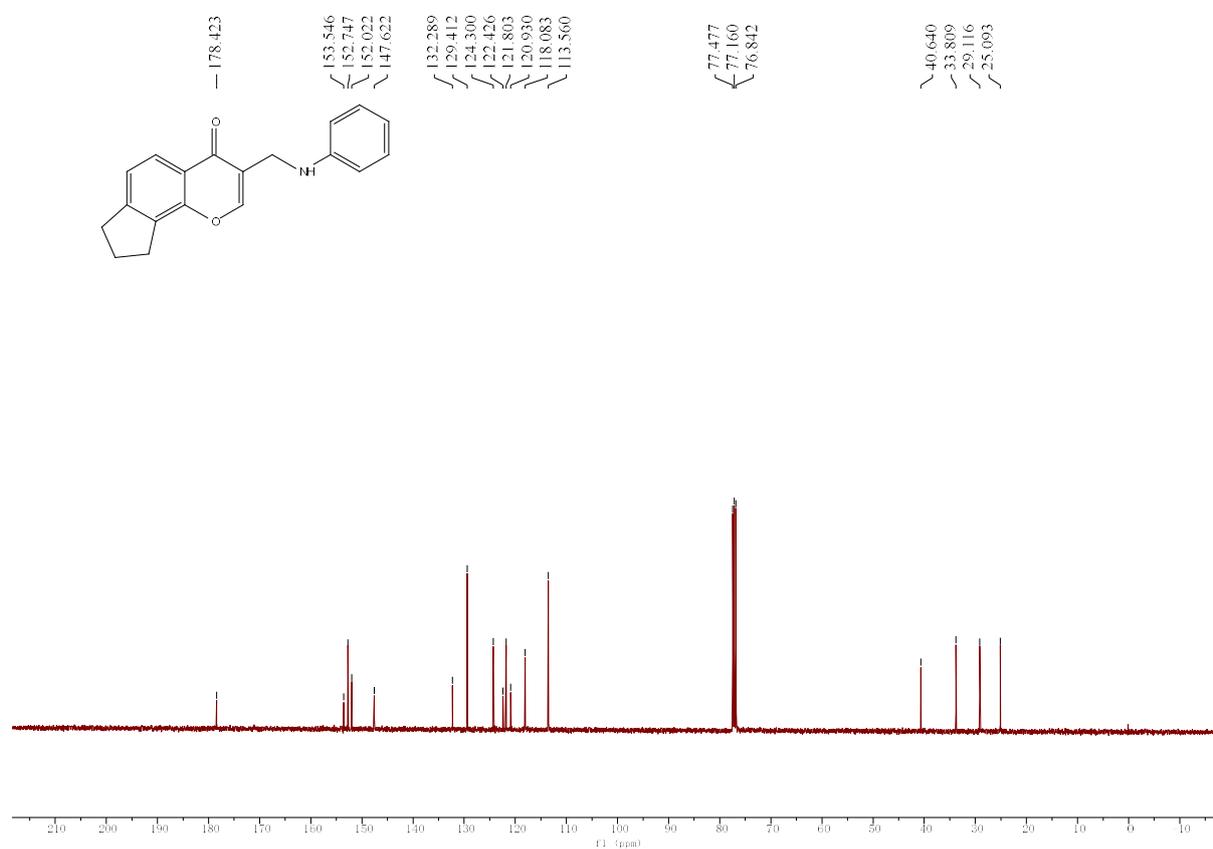
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3ra in CDCl_3



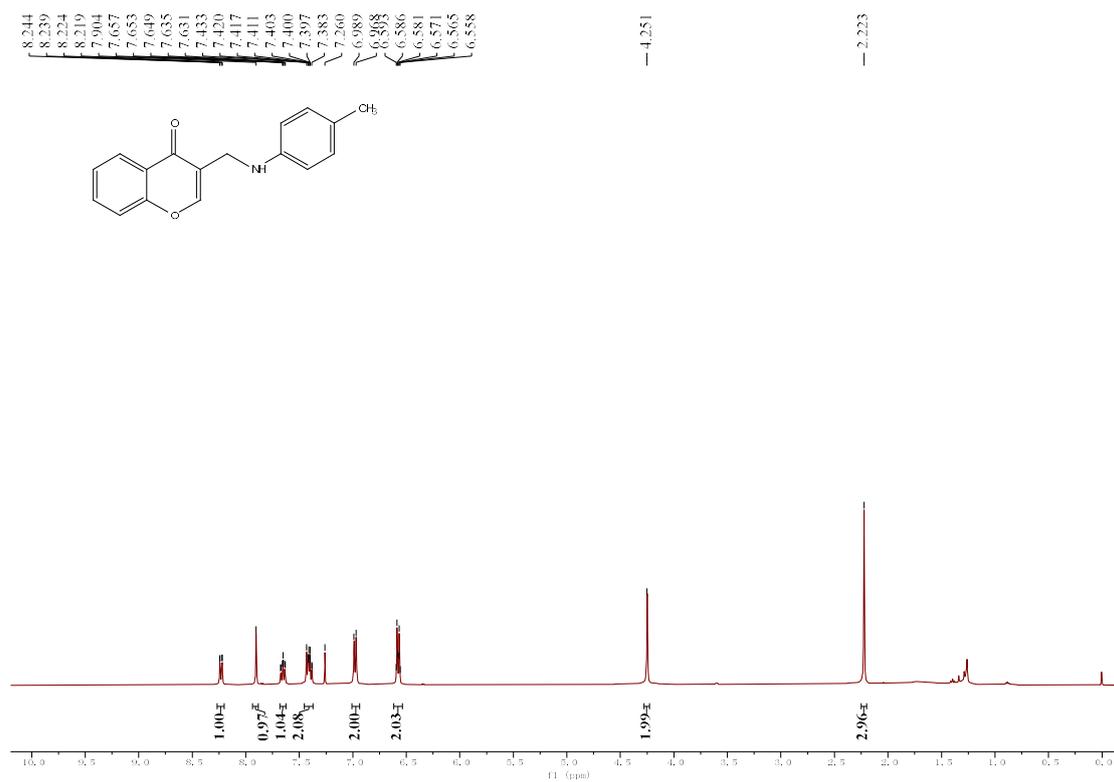
400 MHz ¹H NMR Spectrum of 3sa in CDCl₃



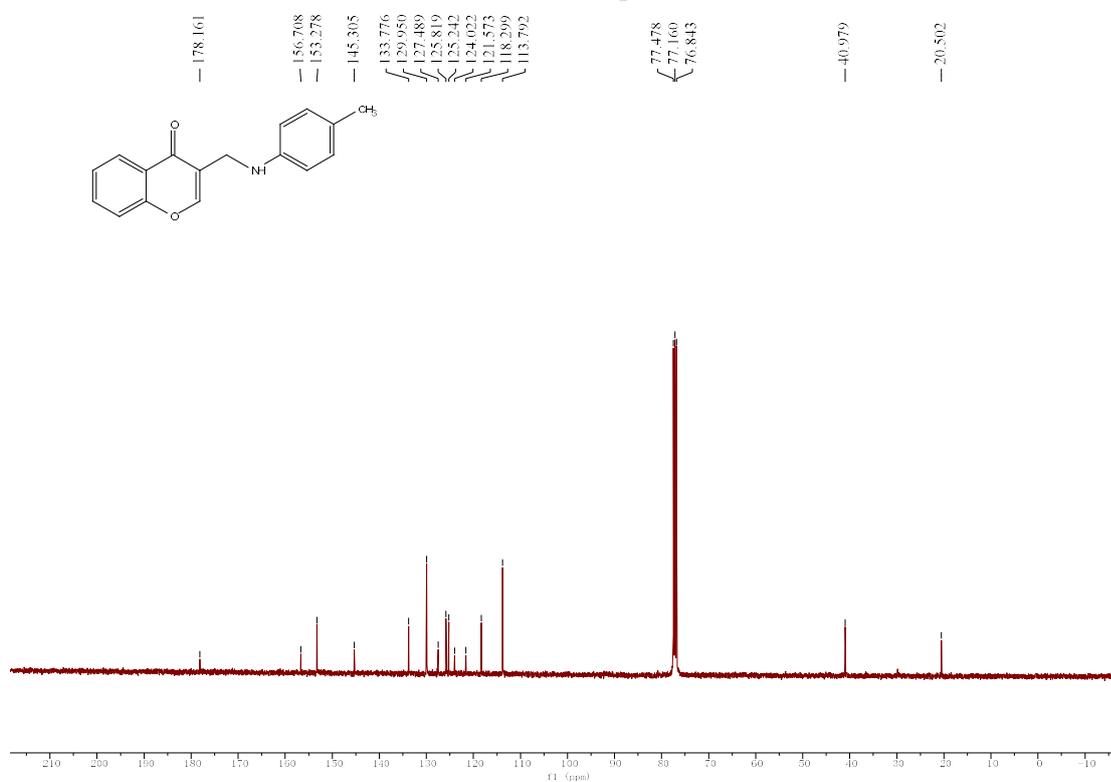
100 MHz ¹³C{¹H} NMR Spectrum of 3sa in CDCl₃



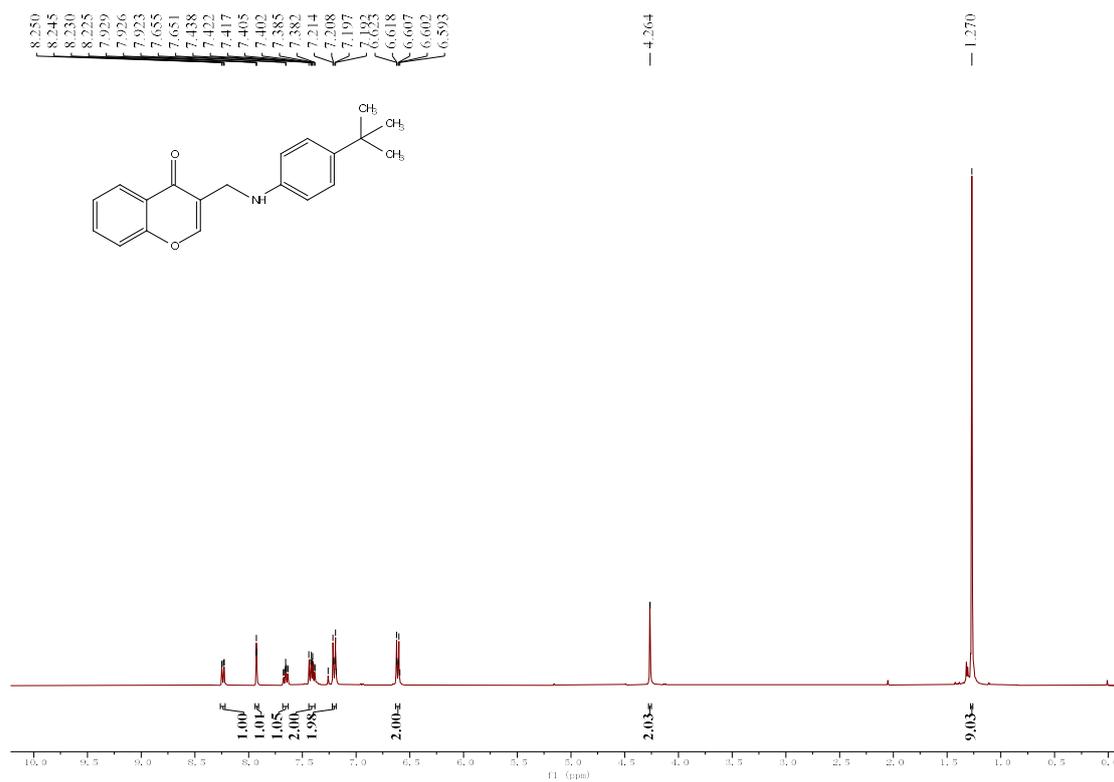
400 MHz ^1H NMR Spectrum of 3ab in CDCl_3



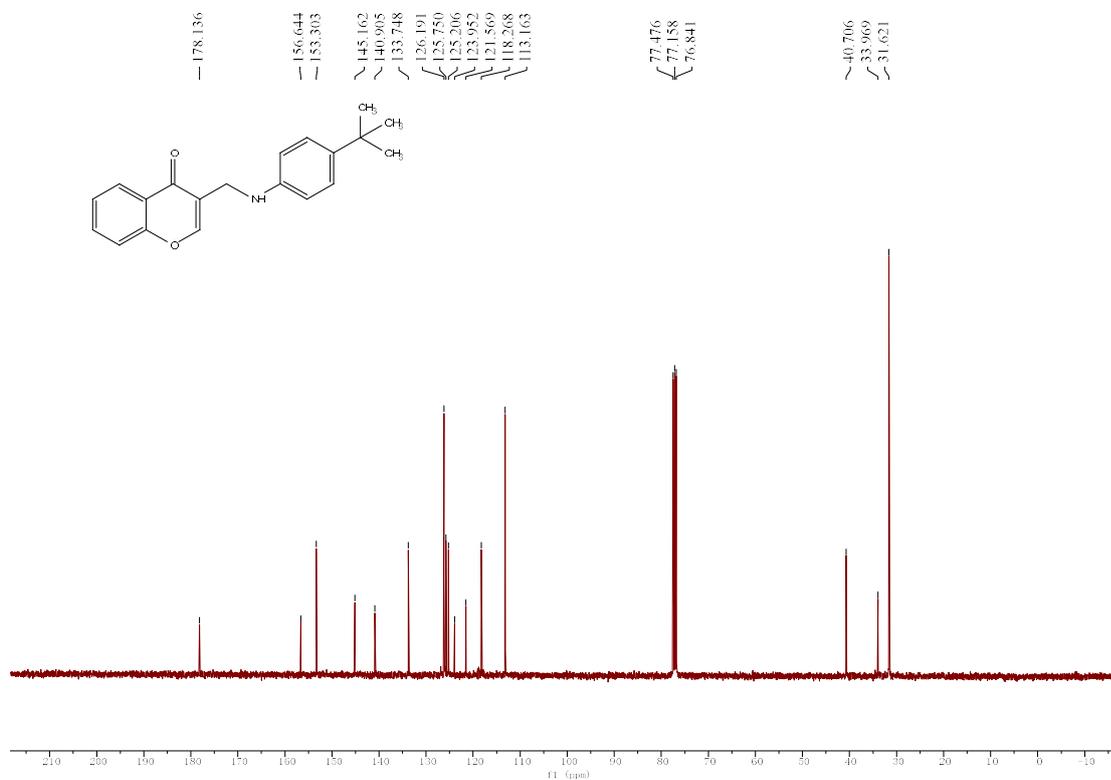
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3ab in CDCl_3



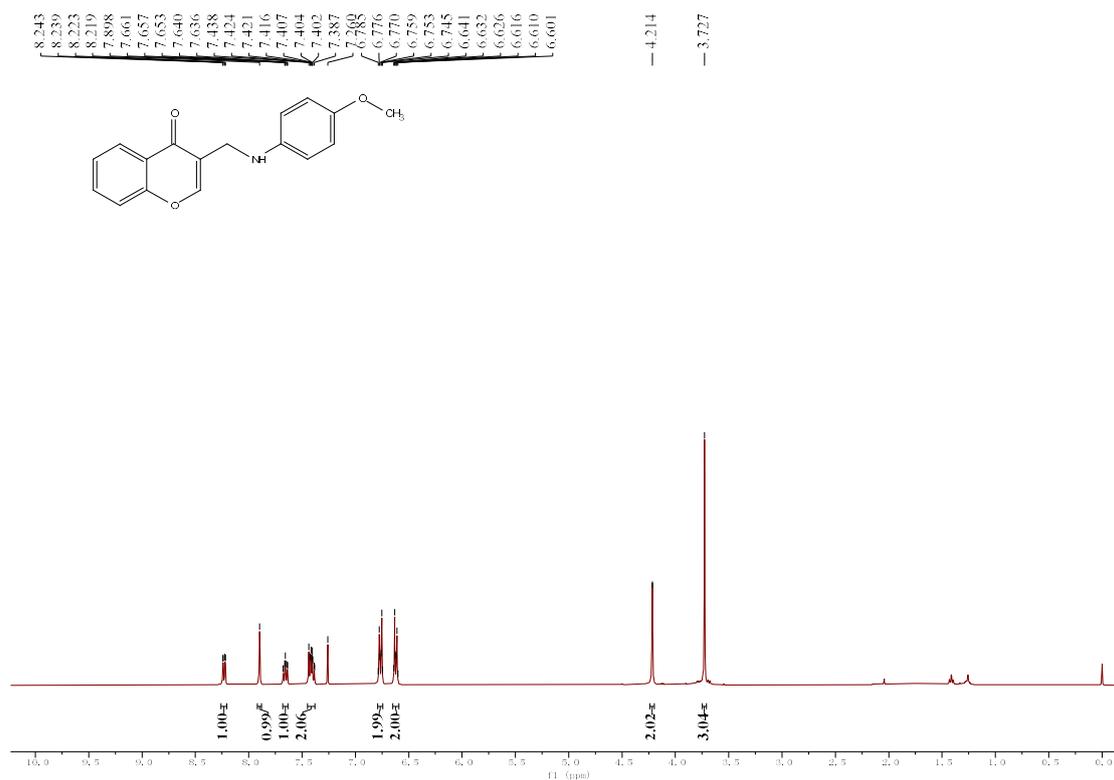
400 MHz ¹H NMR Spectrum of 3ac in CDCl₃



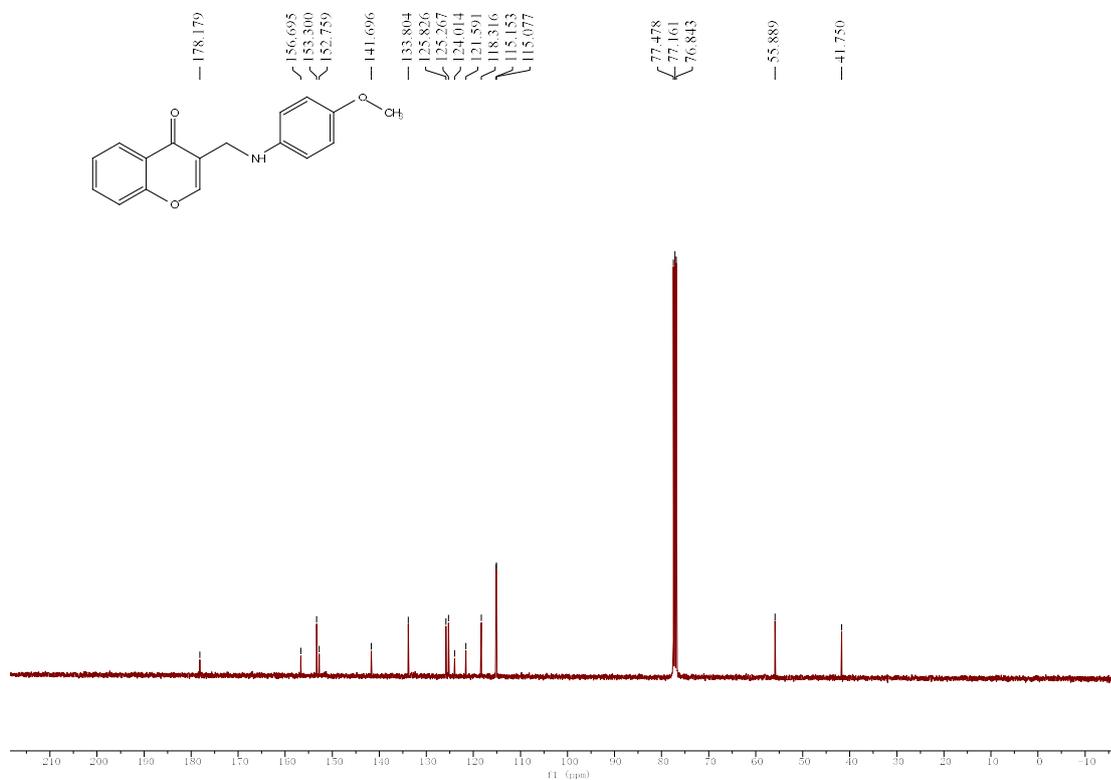
100 MHz ¹³C{¹H} NMR Spectrum of 3ac in CDCl₃



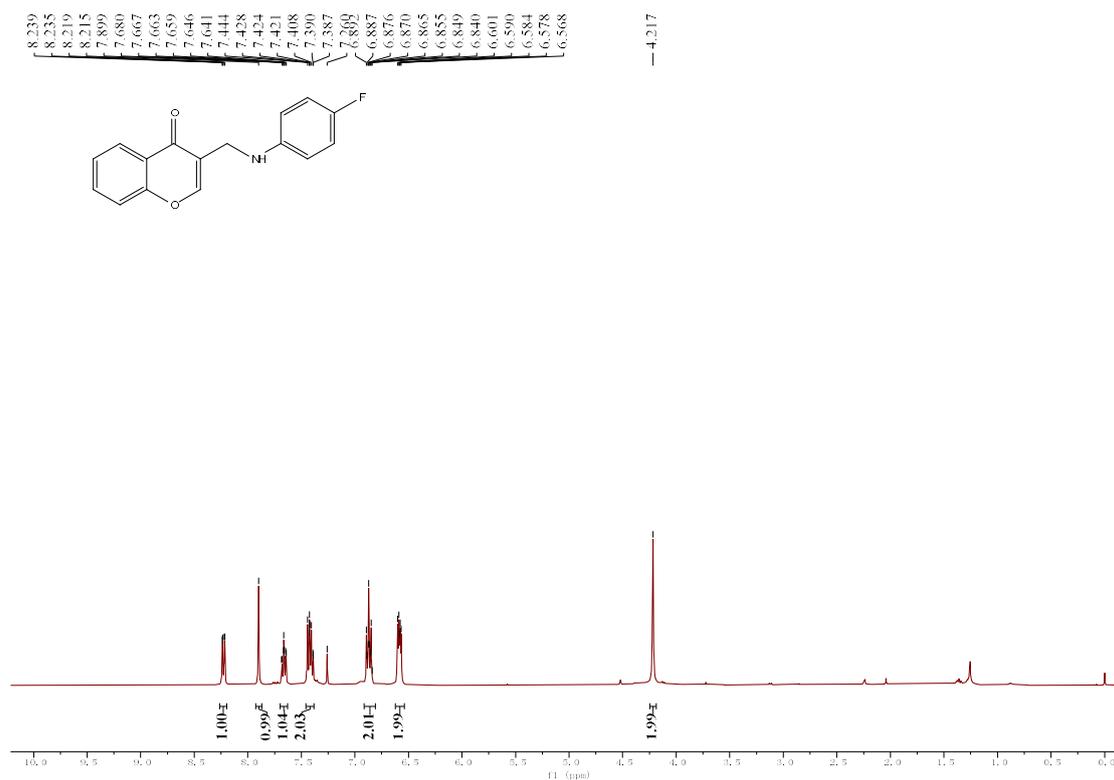
400 MHz ¹H NMR Spectrum of 3ad in CDCl₃



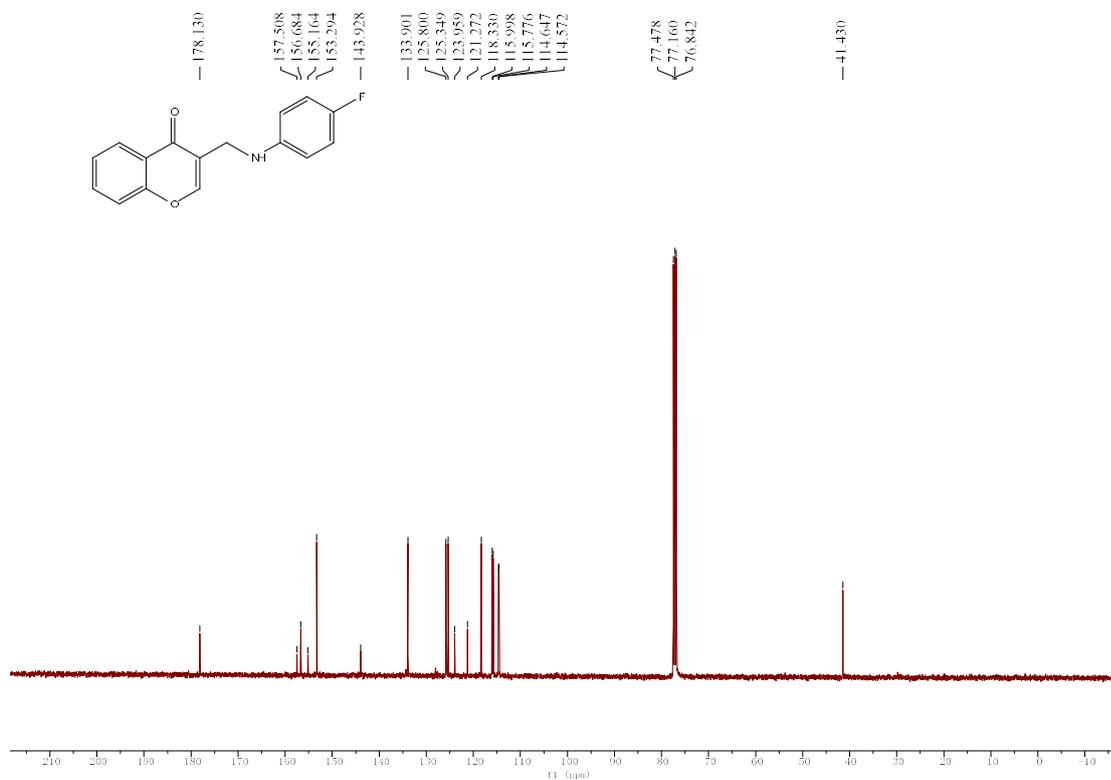
100 MHz ¹³C{¹H} NMR Spectrum of 3ad in CDCl₃



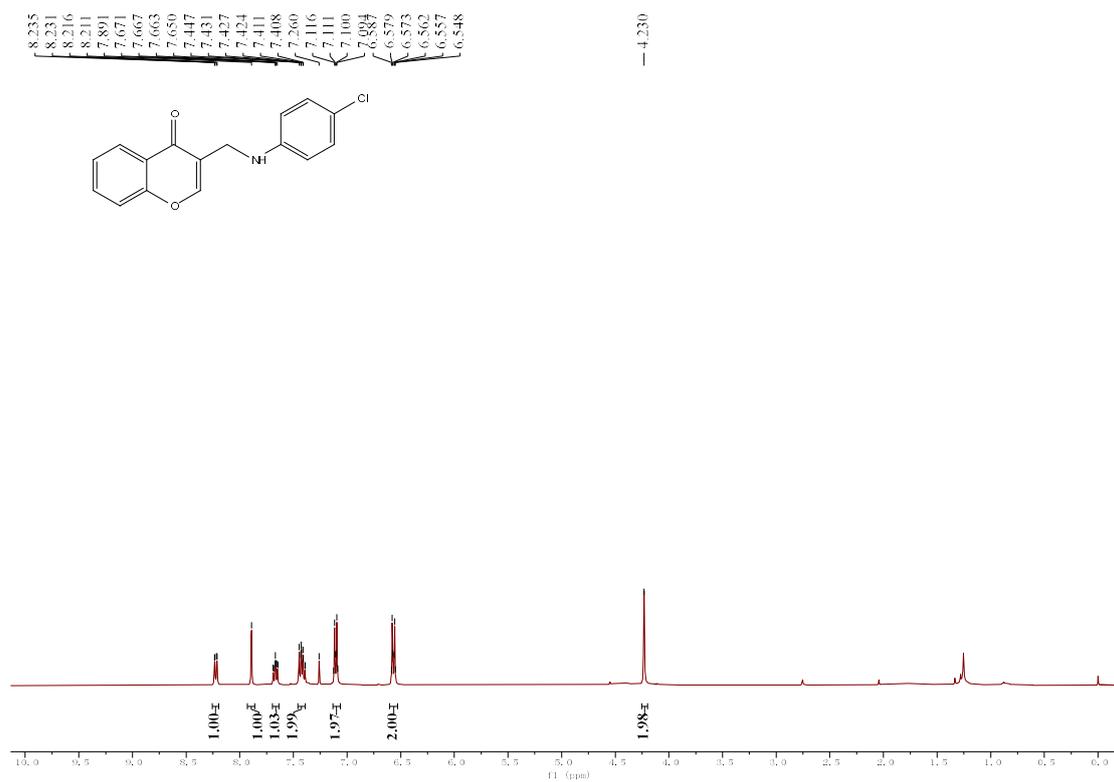
400 MHz ¹H NMR Spectrum of 3ae in CDCl₃



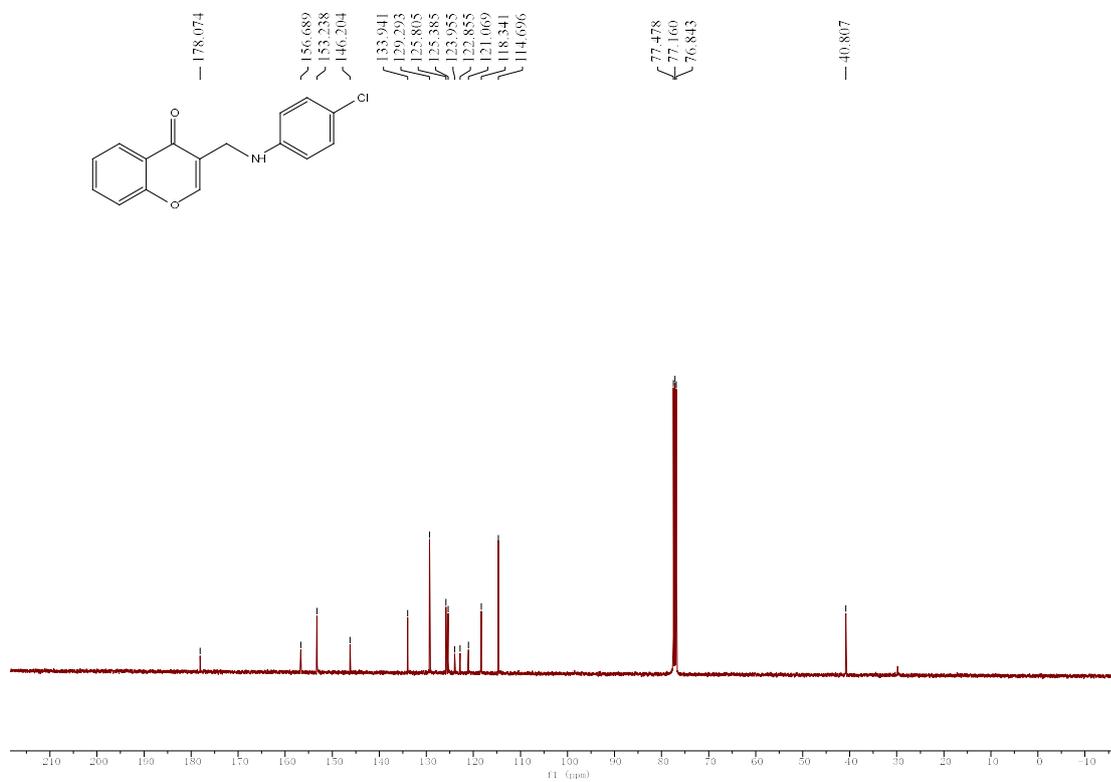
100 MHz ¹³C{¹H} NMR Spectrum of 3ae in CDCl₃



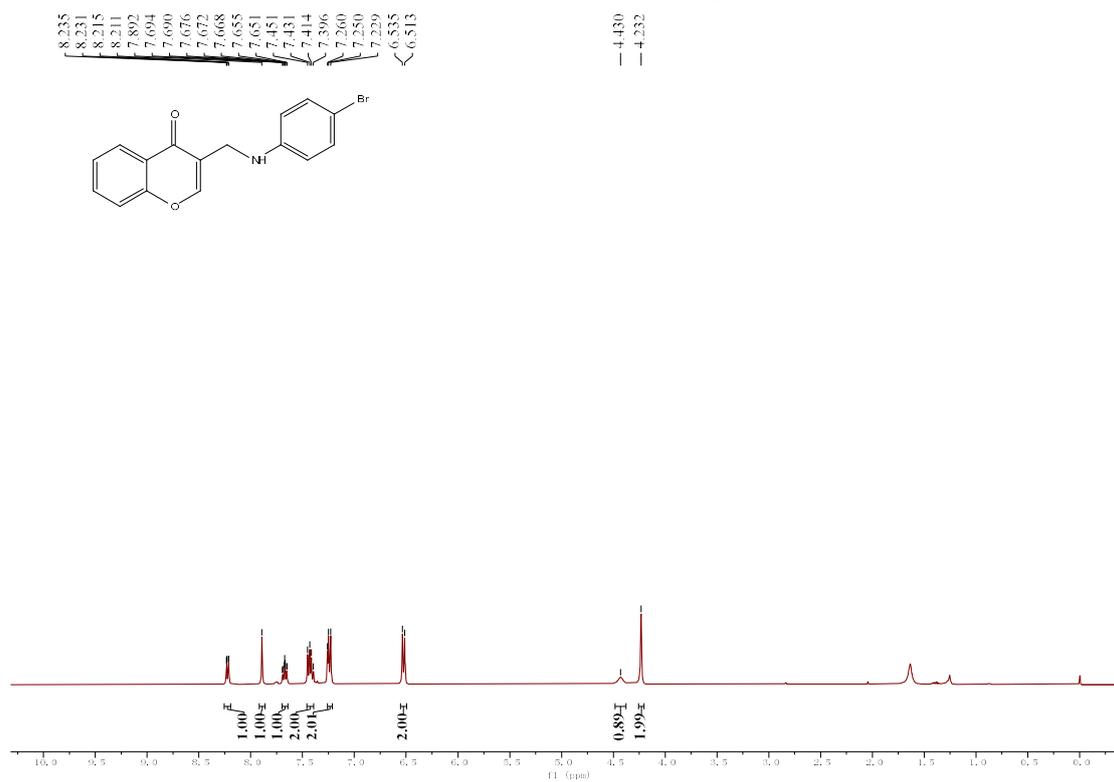
400 MHz ¹H NMR Spectrum of 3af in CDCl₃



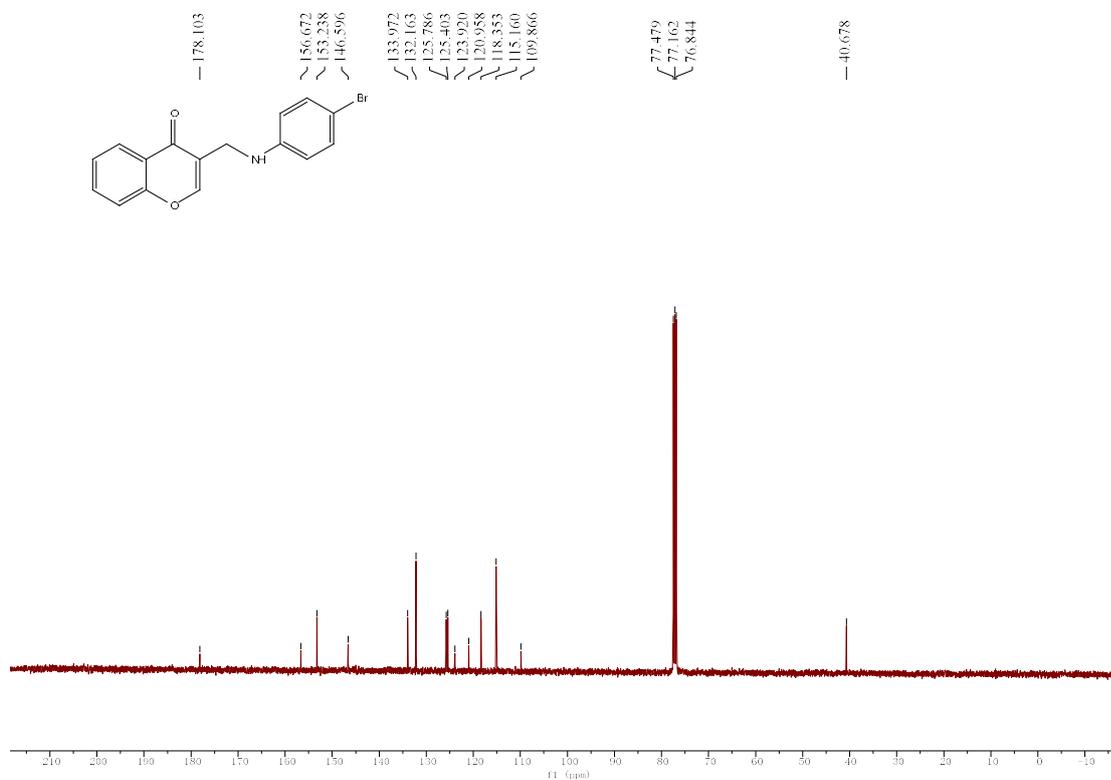
100 MHz ¹³C{¹H} NMR Spectrum of 3af in CDCl₃



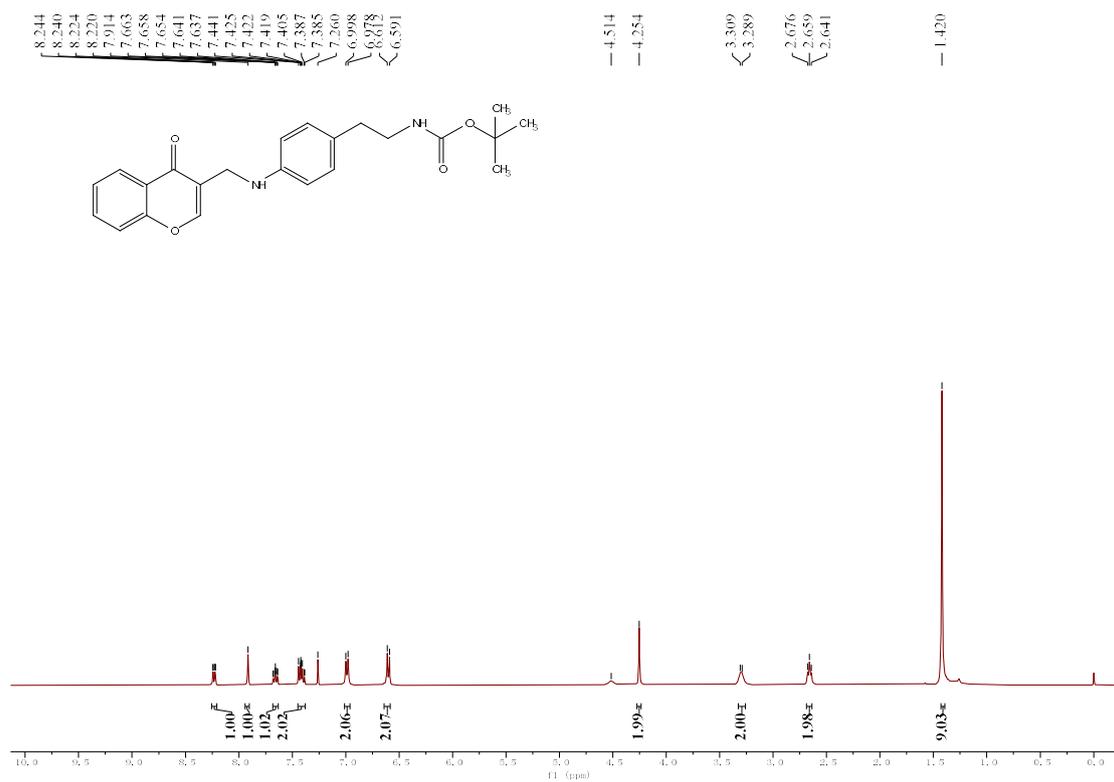
400 MHz ¹H NMR Spectrum of 3ag in CDCl₃



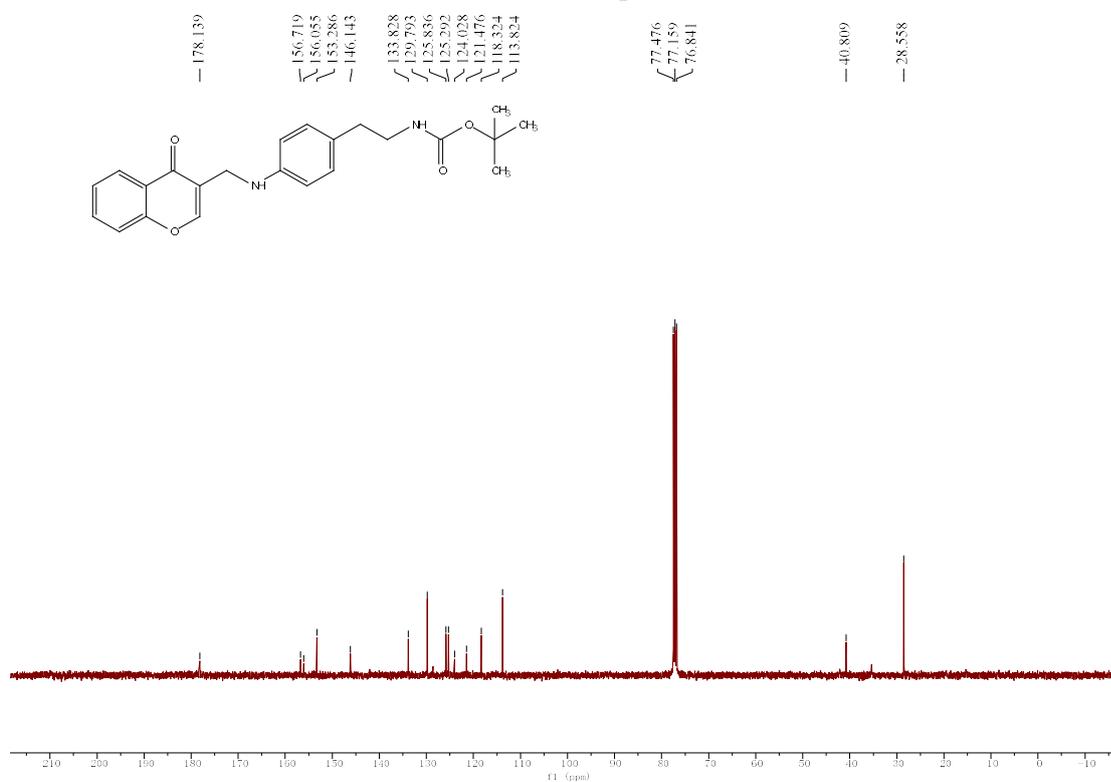
100 MHz ¹³C{¹H} NMR Spectrum of 3ag in CDCl₃



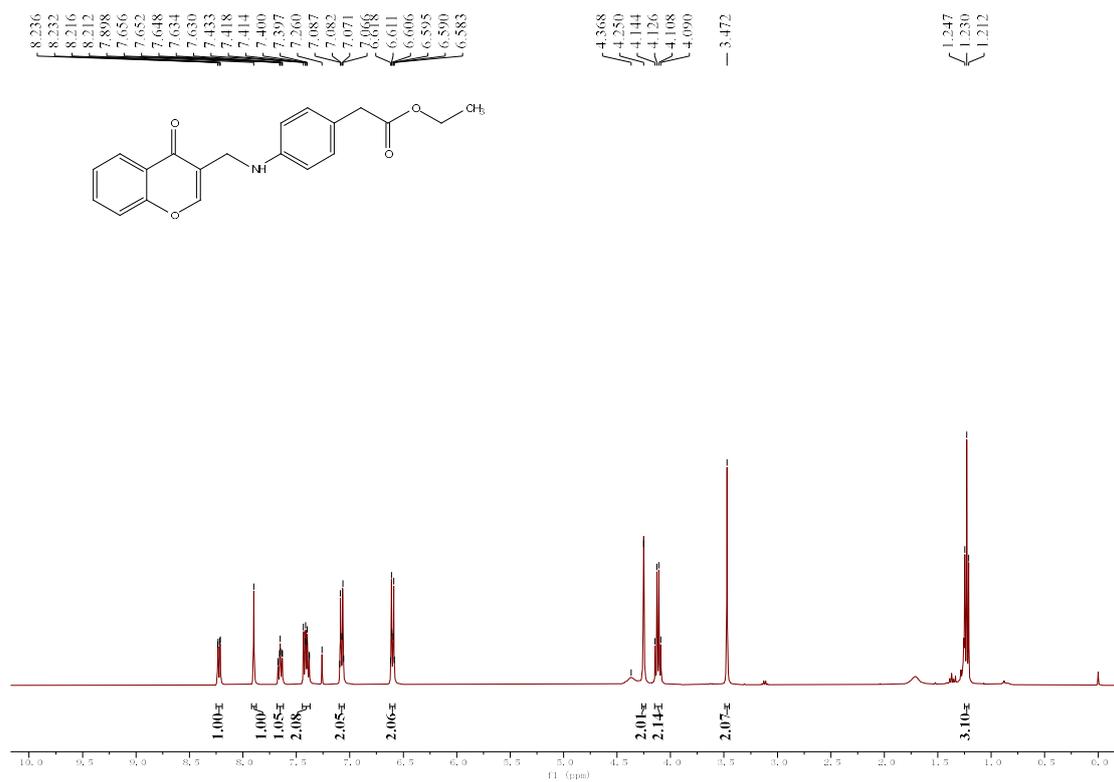
400 MHz ¹H NMR Spectrum of 3ah in CDCl₃



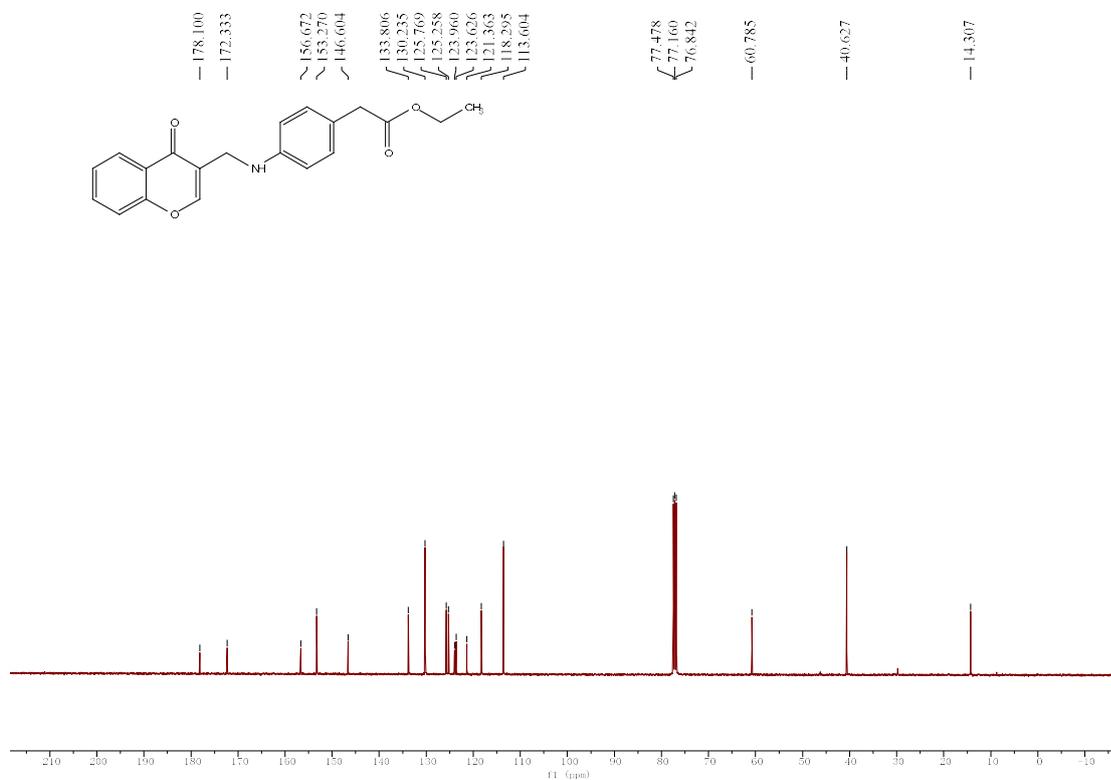
100 MHz ¹³C{¹H} NMR Spectrum of 3ah in CDCl₃



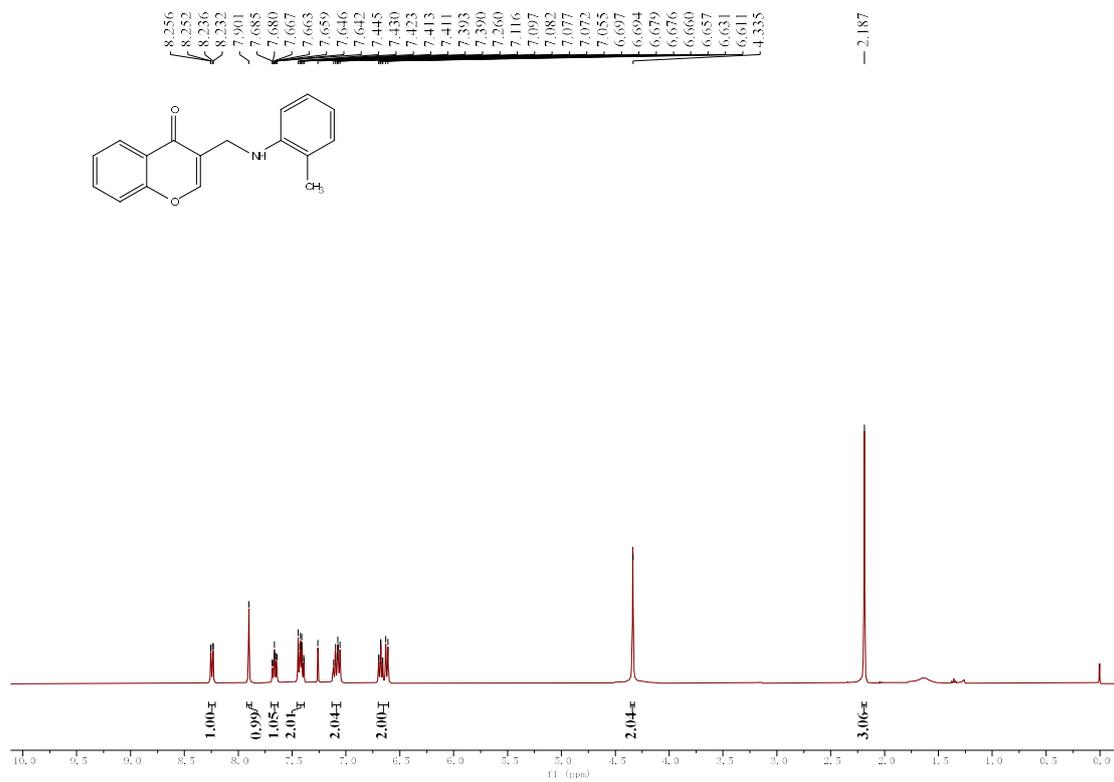
400 MHz ¹H NMR Spectrum of 3ai in CDCl₃



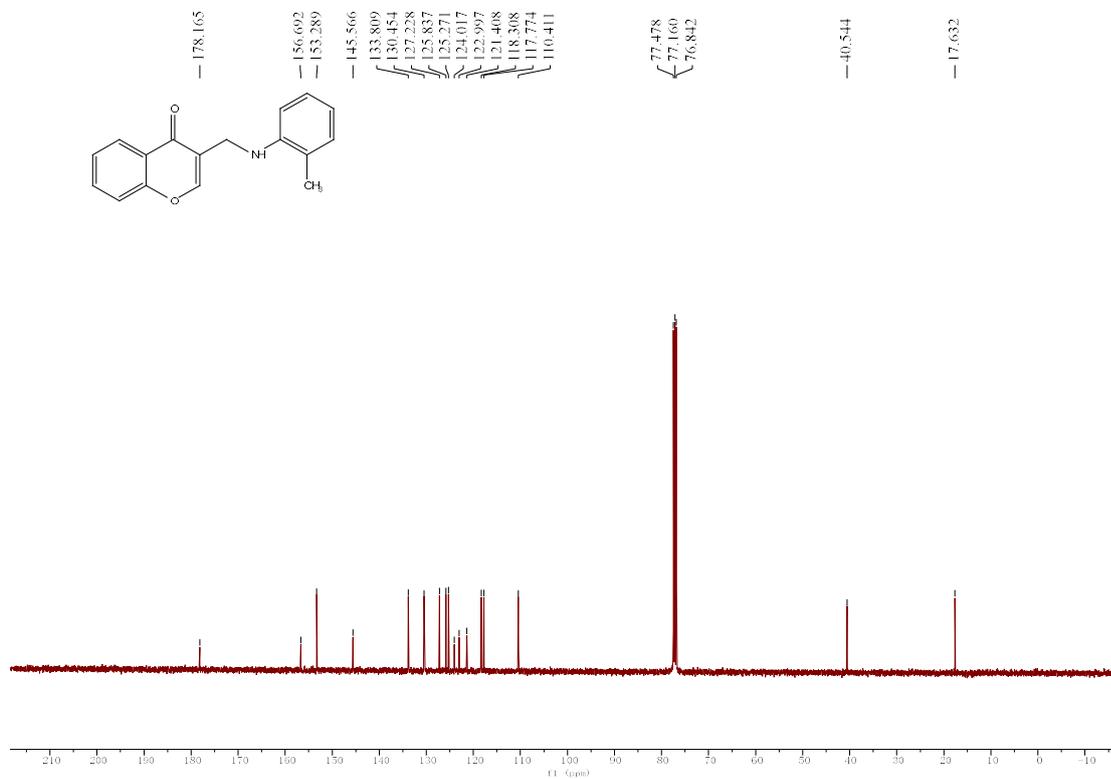
100 MHz ¹³C{¹H} NMR Spectrum of 3ai in CDCl₃



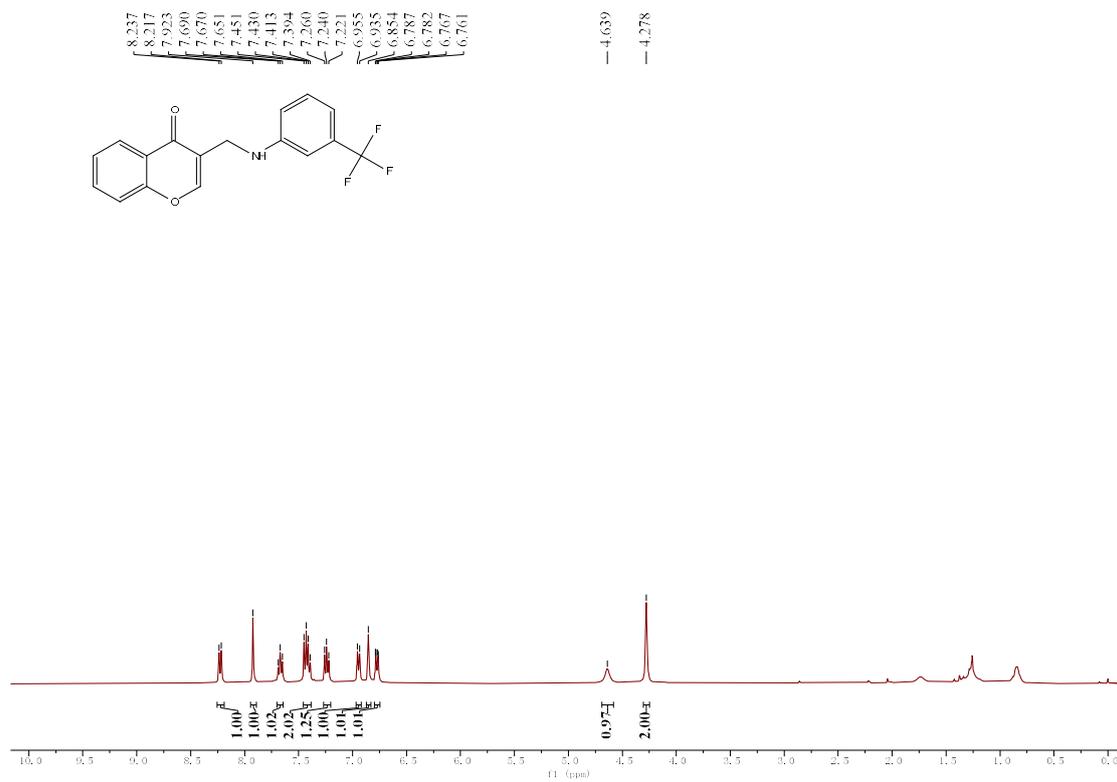
400 MHz ¹H NMR Spectrum of 3aj in CDCl₃



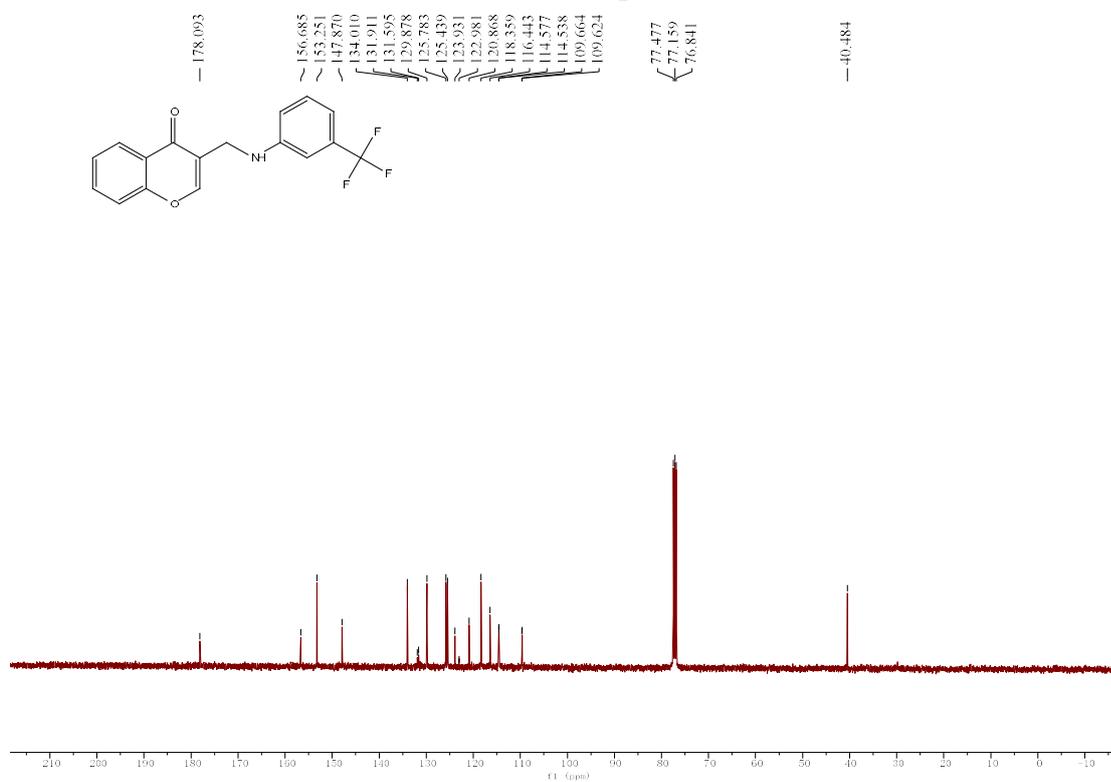
100 MHz ¹³C{¹H} NMR Spectrum of 3aj in CDCl₃



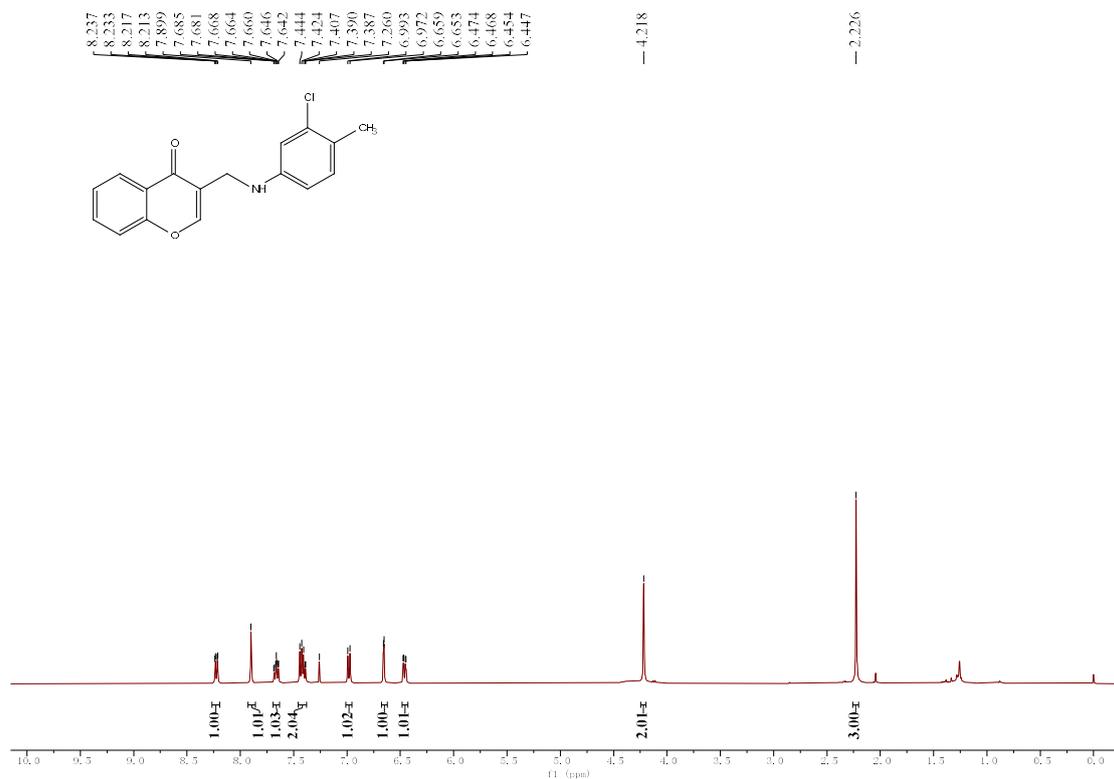
400 MHz ¹H NMR Spectrum of 3ak in CDCl₃



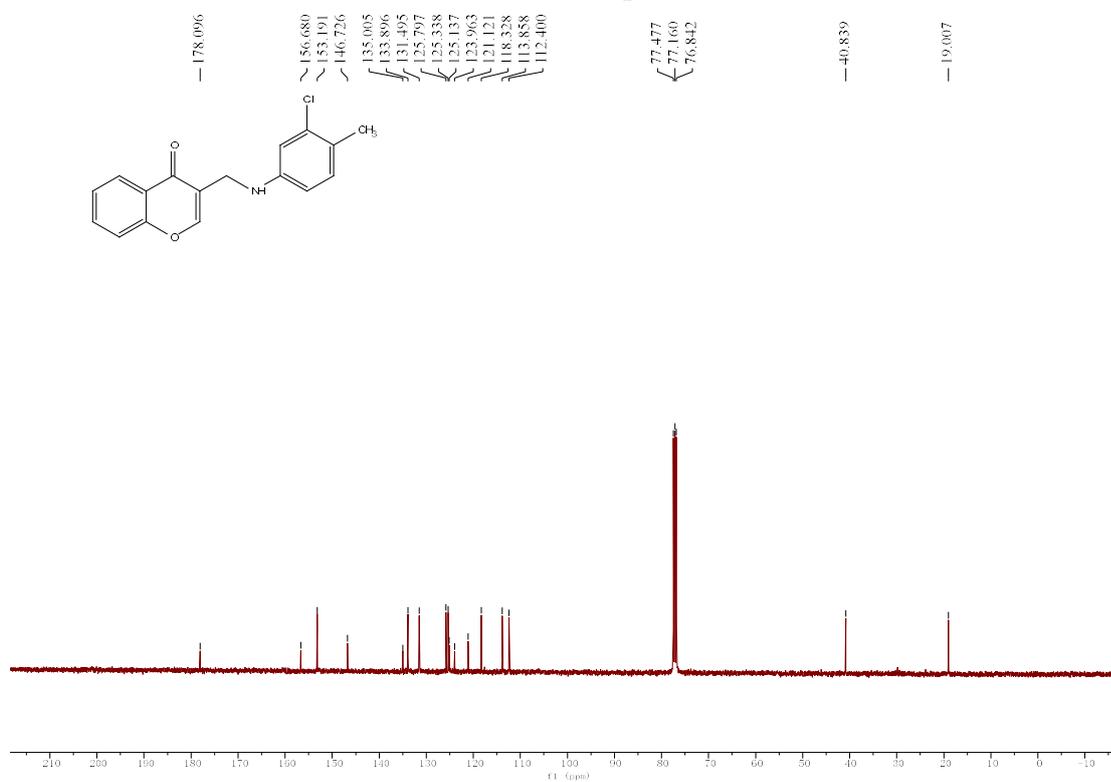
100 MHz ¹³C{¹H} NMR Spectrum of 3ak in CDCl₃



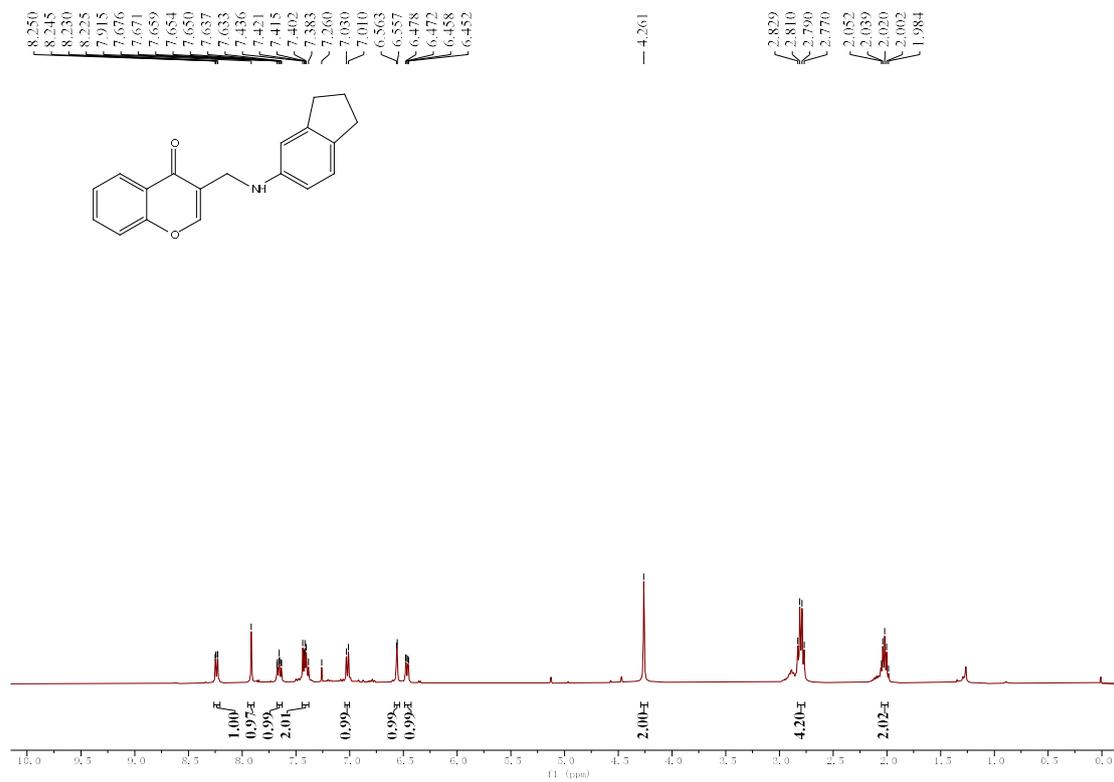
400 MHz ¹H NMR Spectrum of 3al in CDCl₃



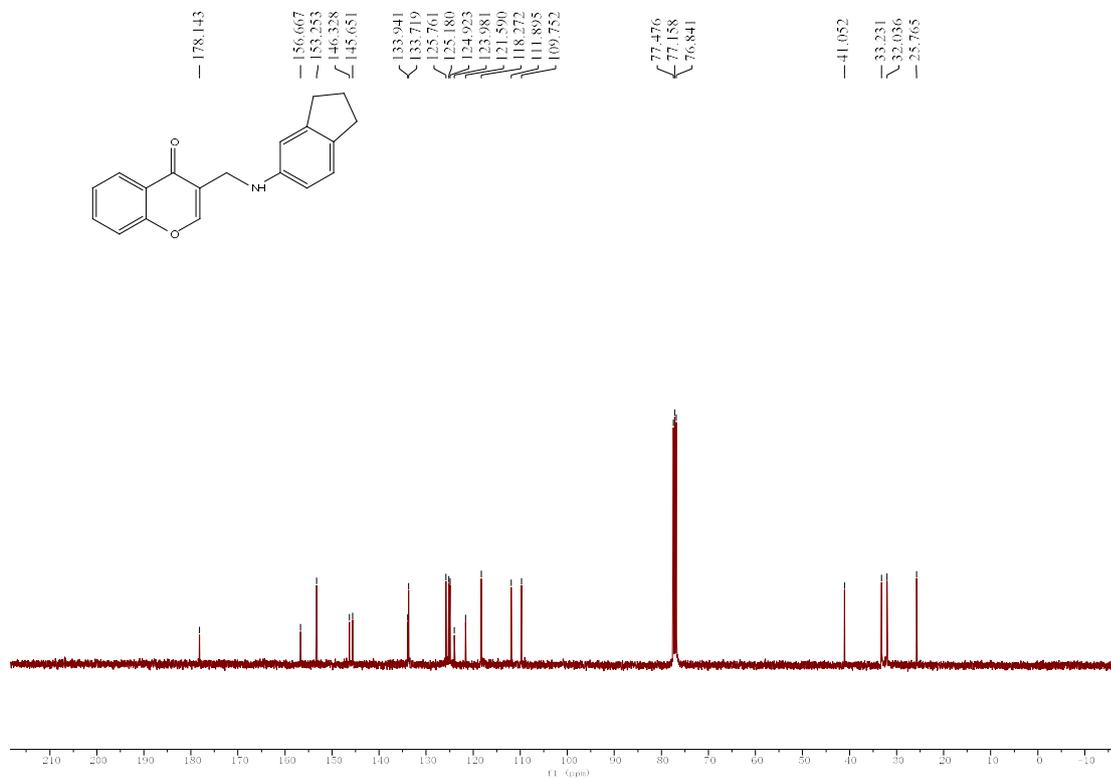
100 MHz ¹³C{¹H} NMR Spectrum of 3al in CDCl₃



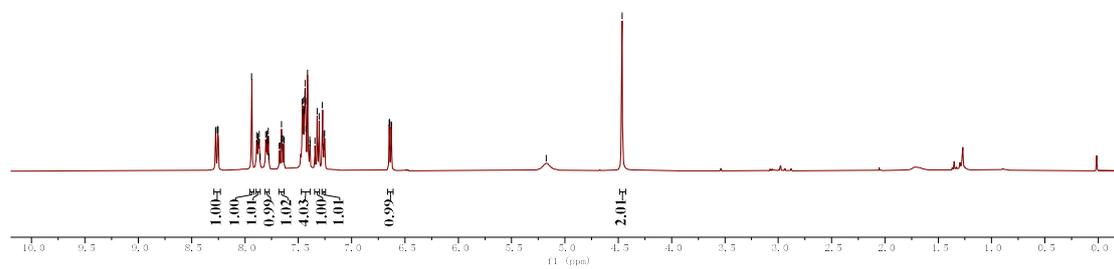
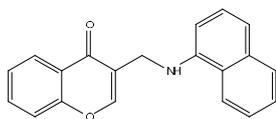
400 MHz ^1H NMR Spectrum of 3am in CDCl_3



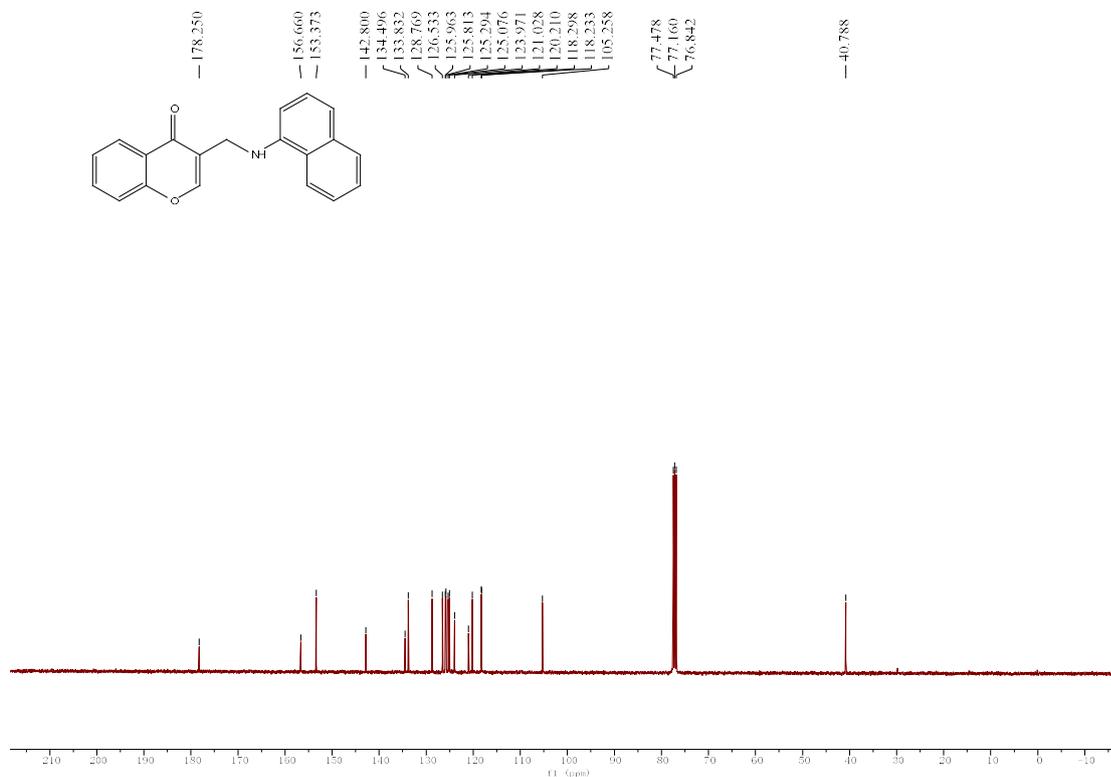
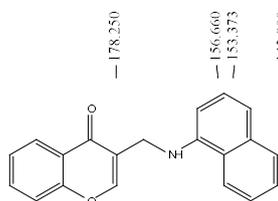
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3am in CDCl_3



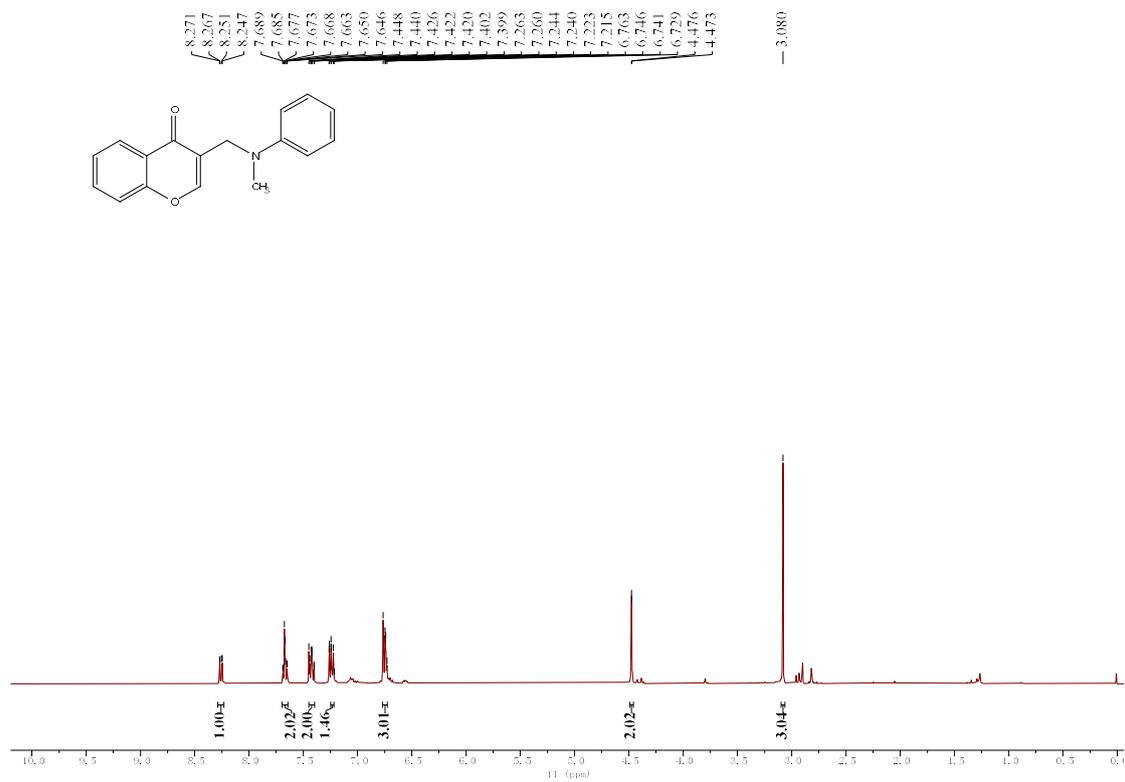
400 MHz ^1H NMR Spectrum of 3an in CDCl_3



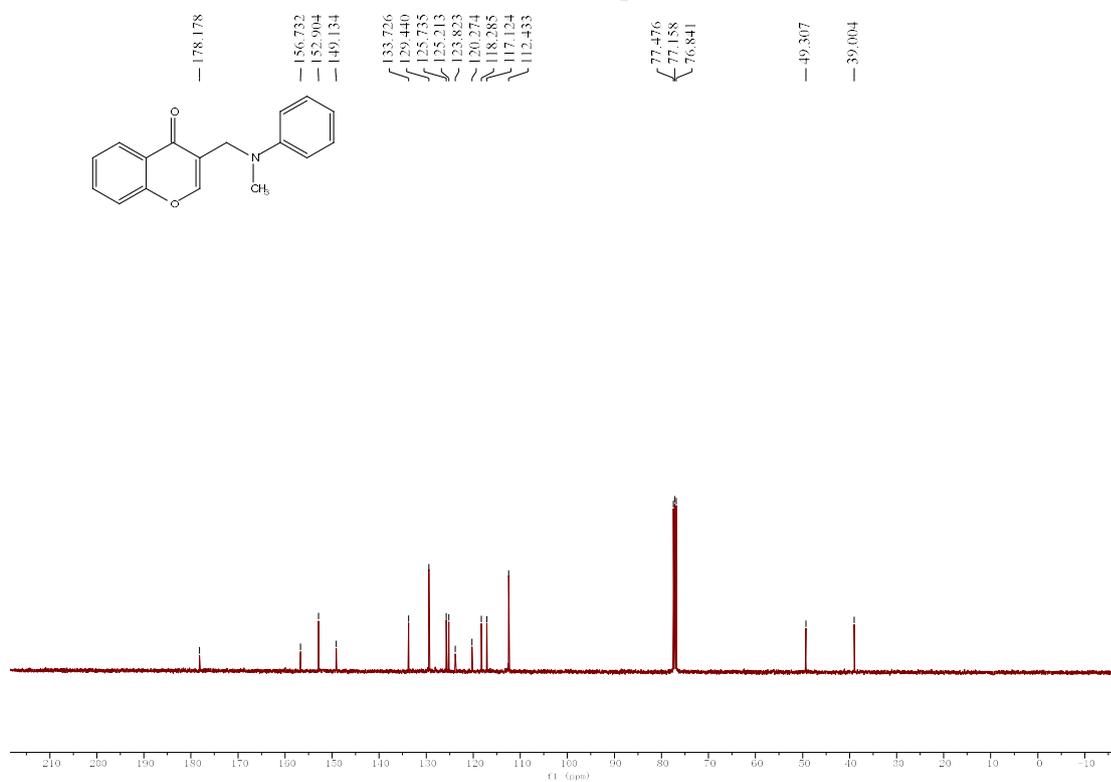
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3an in CDCl_3



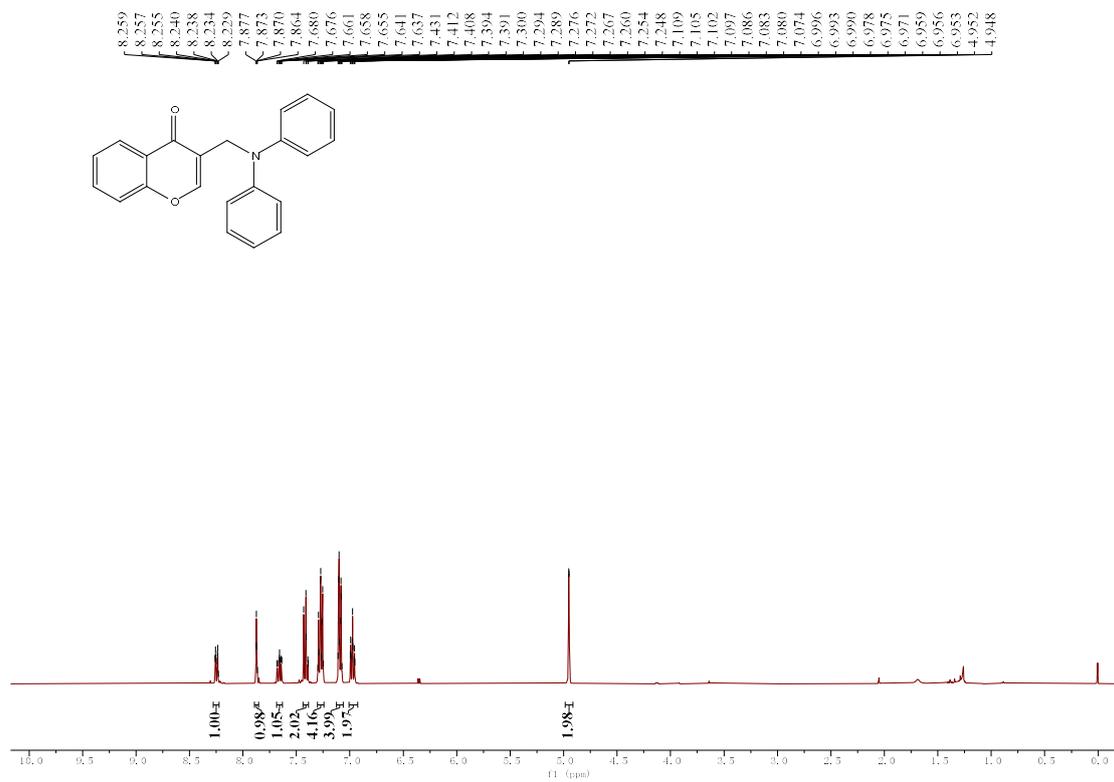
400 MHz ^1H NMR Spectrum of 3ao in CDCl_3



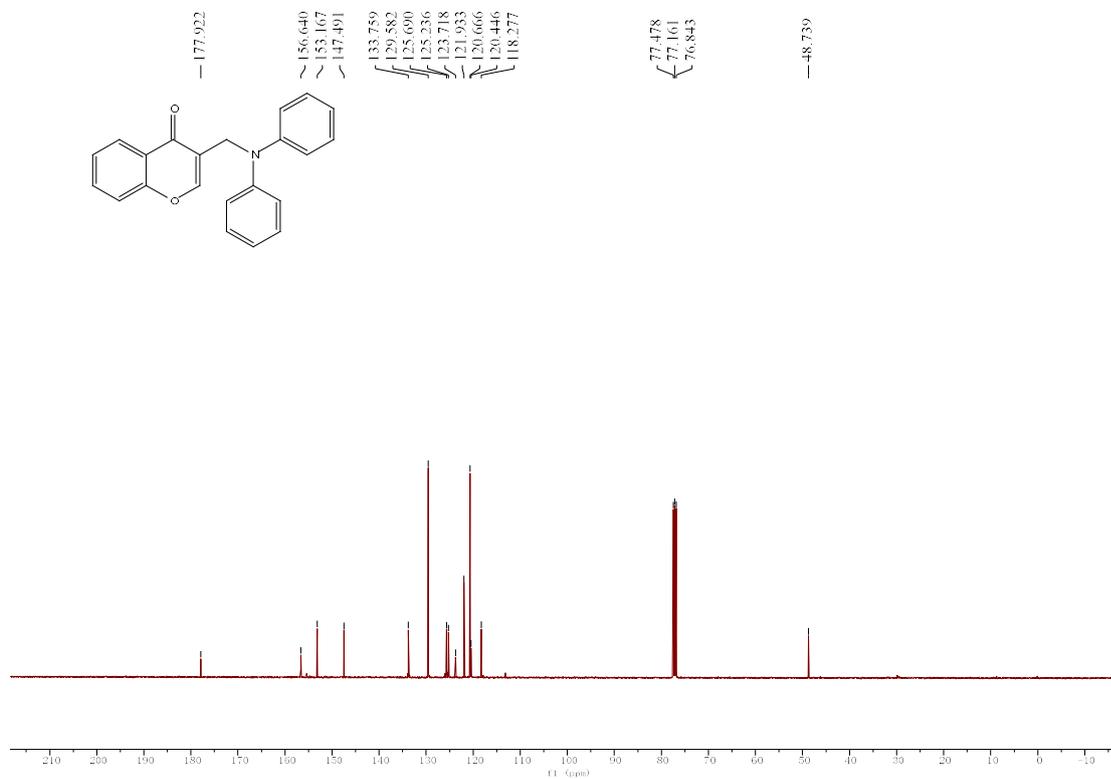
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3ao in CDCl_3



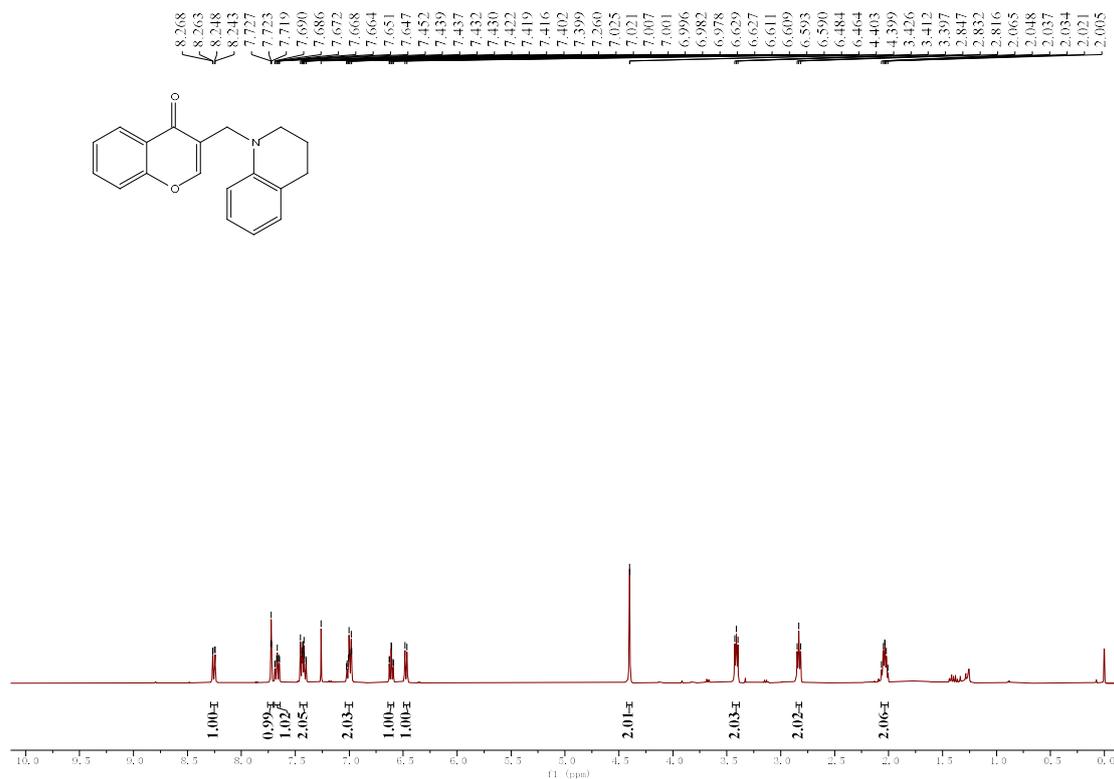
400 MHz ^1H NMR Spectrum of 3ap in CDCl_3



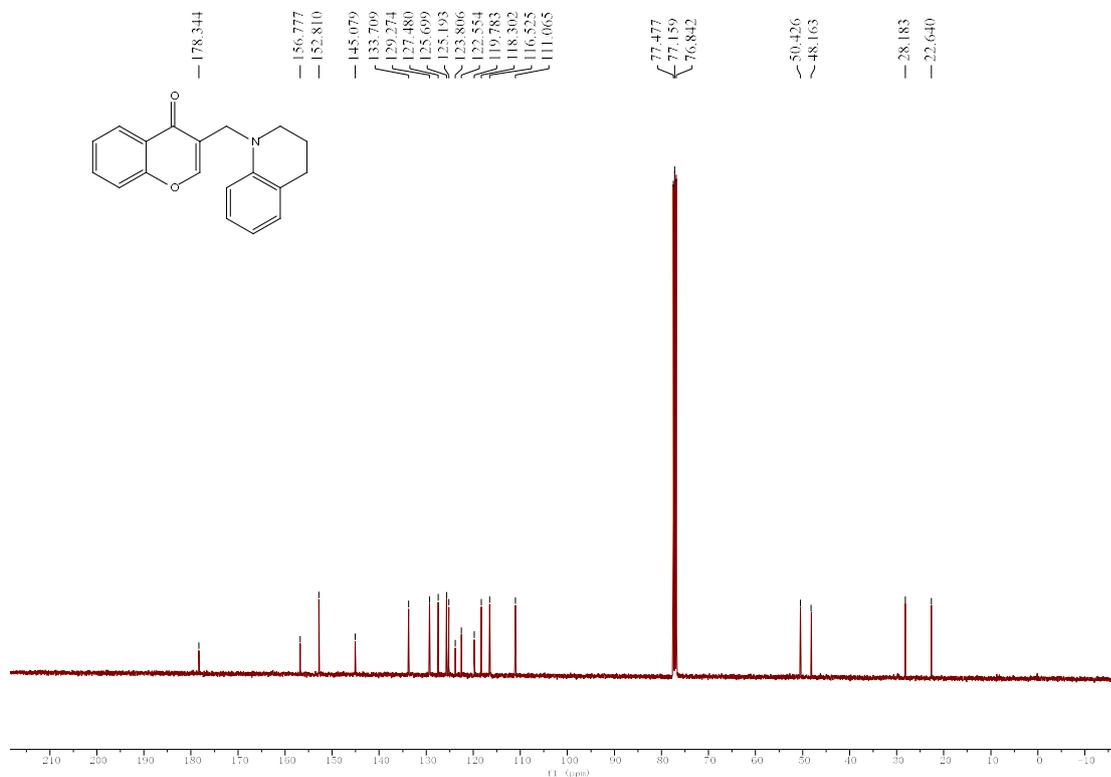
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3ap in CDCl_3



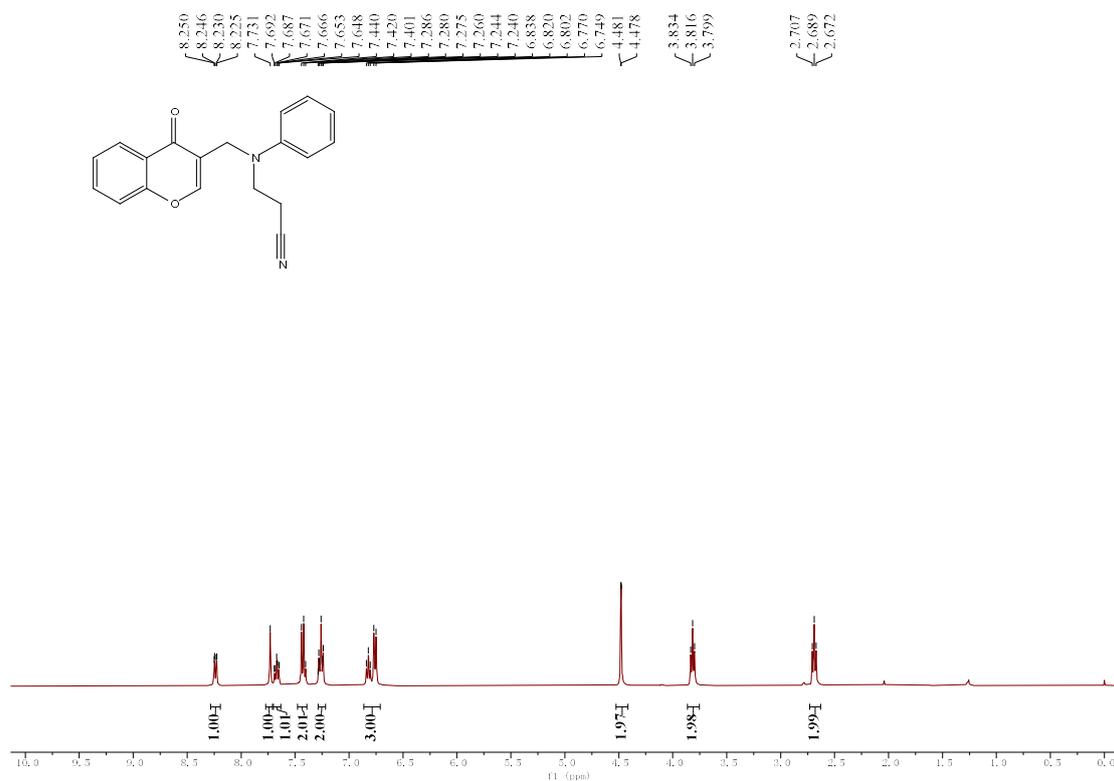
400 MHz ^1H NMR Spectrum of 3aq in CDCl_3



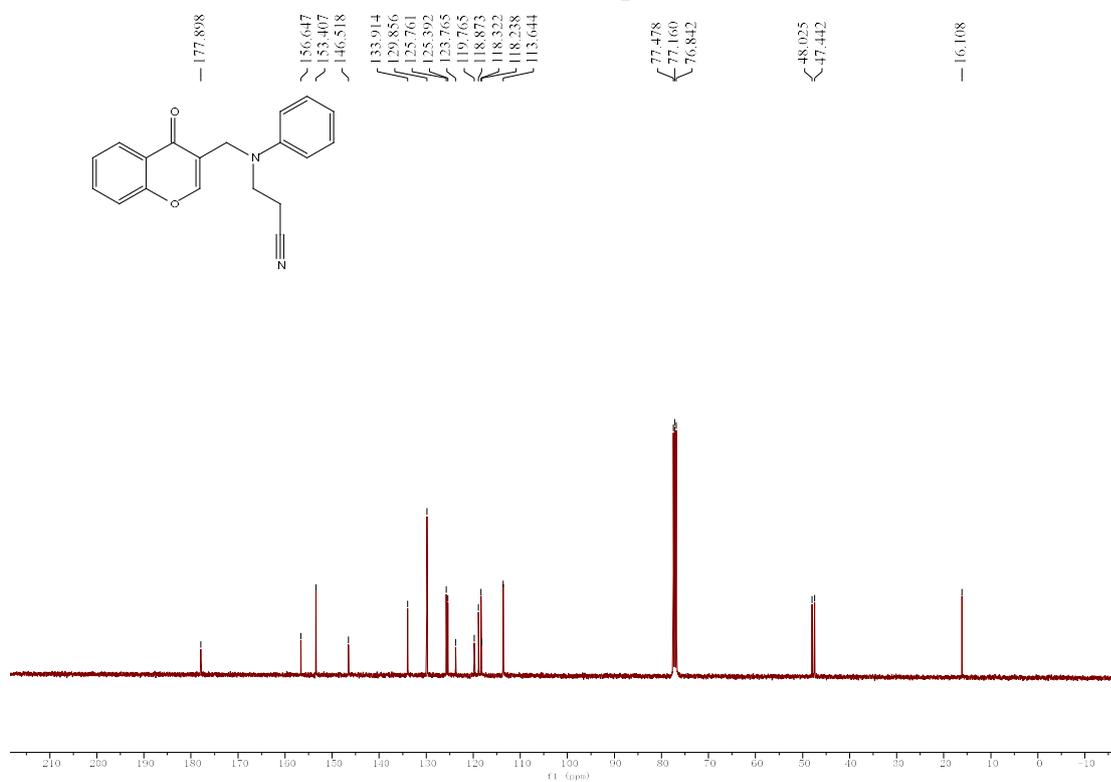
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3aq in CDCl_3



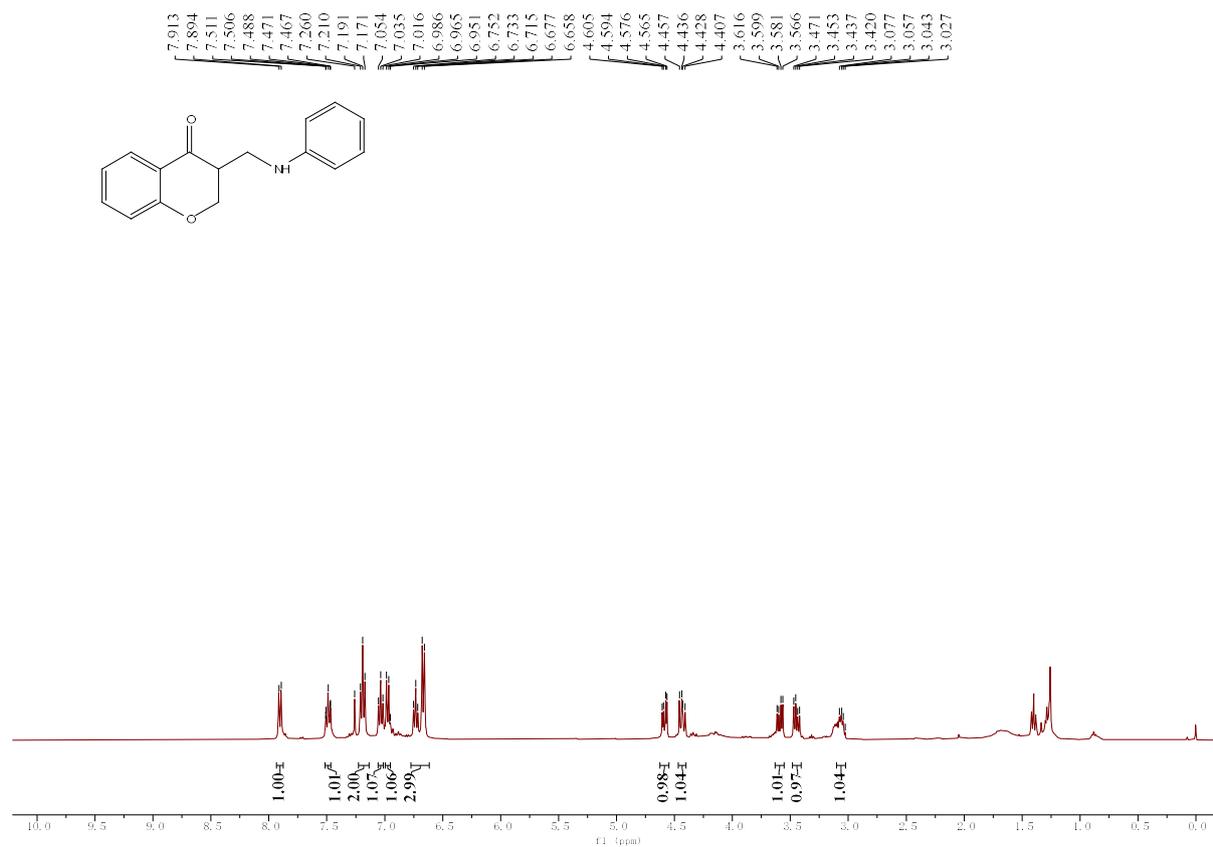
400 MHz ^1H NMR Spectrum of 3ar in CDCl_3



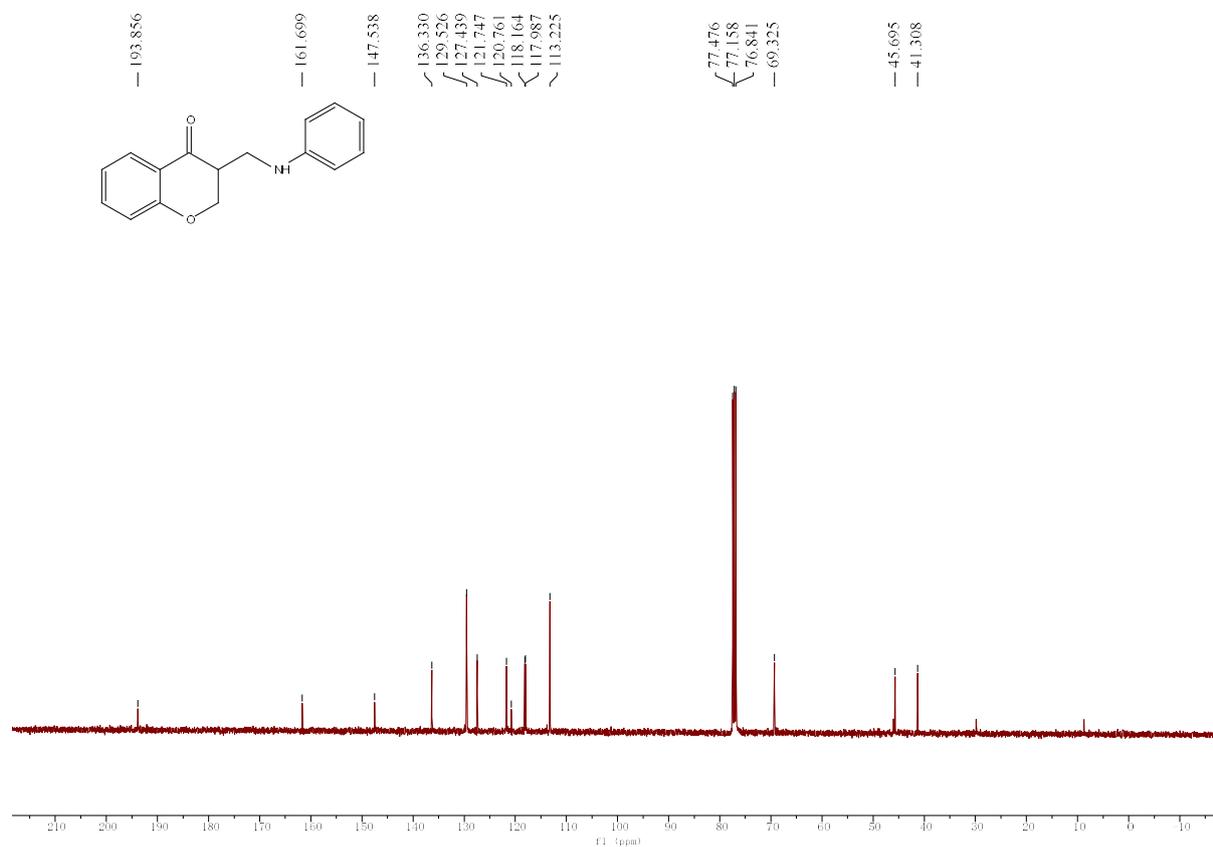
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 3ar in CDCl_3



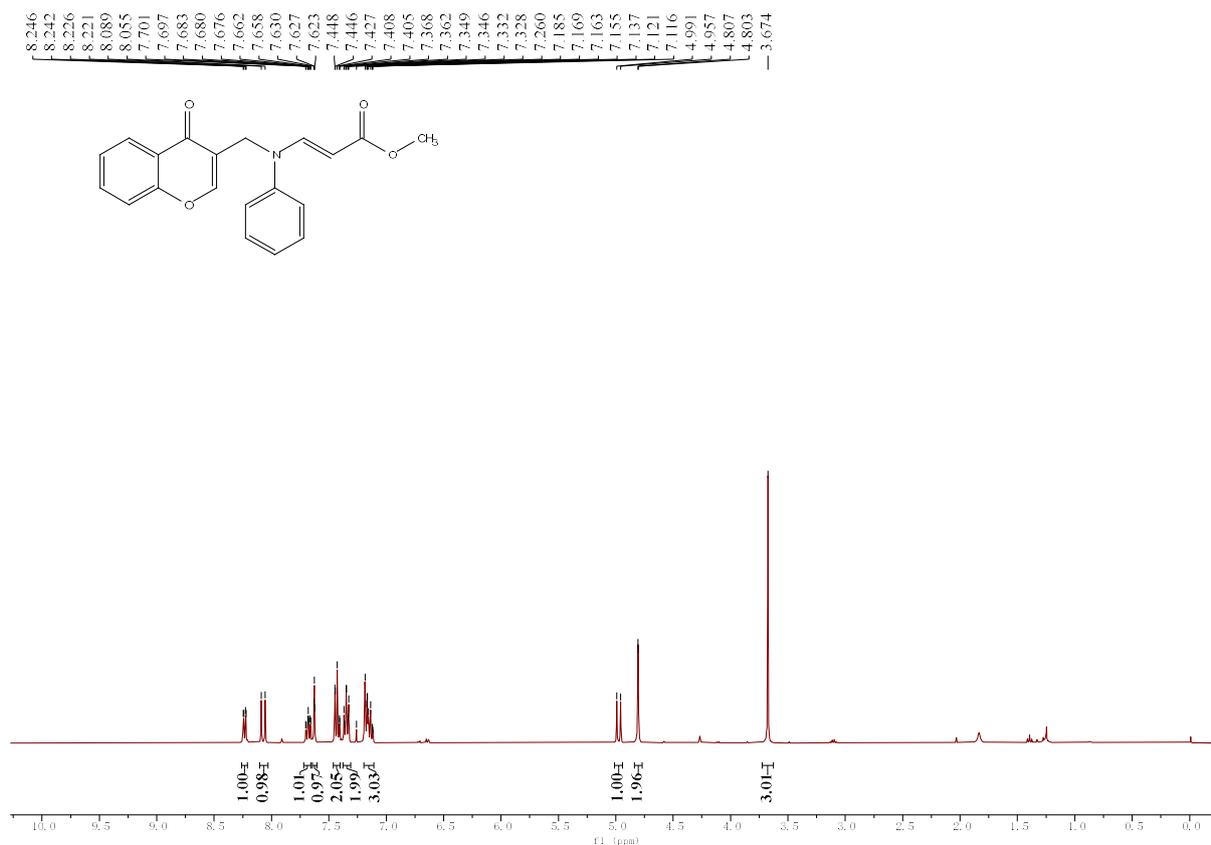
400 MHz ^1H NMR Spectrum of 4 in CDCl_3



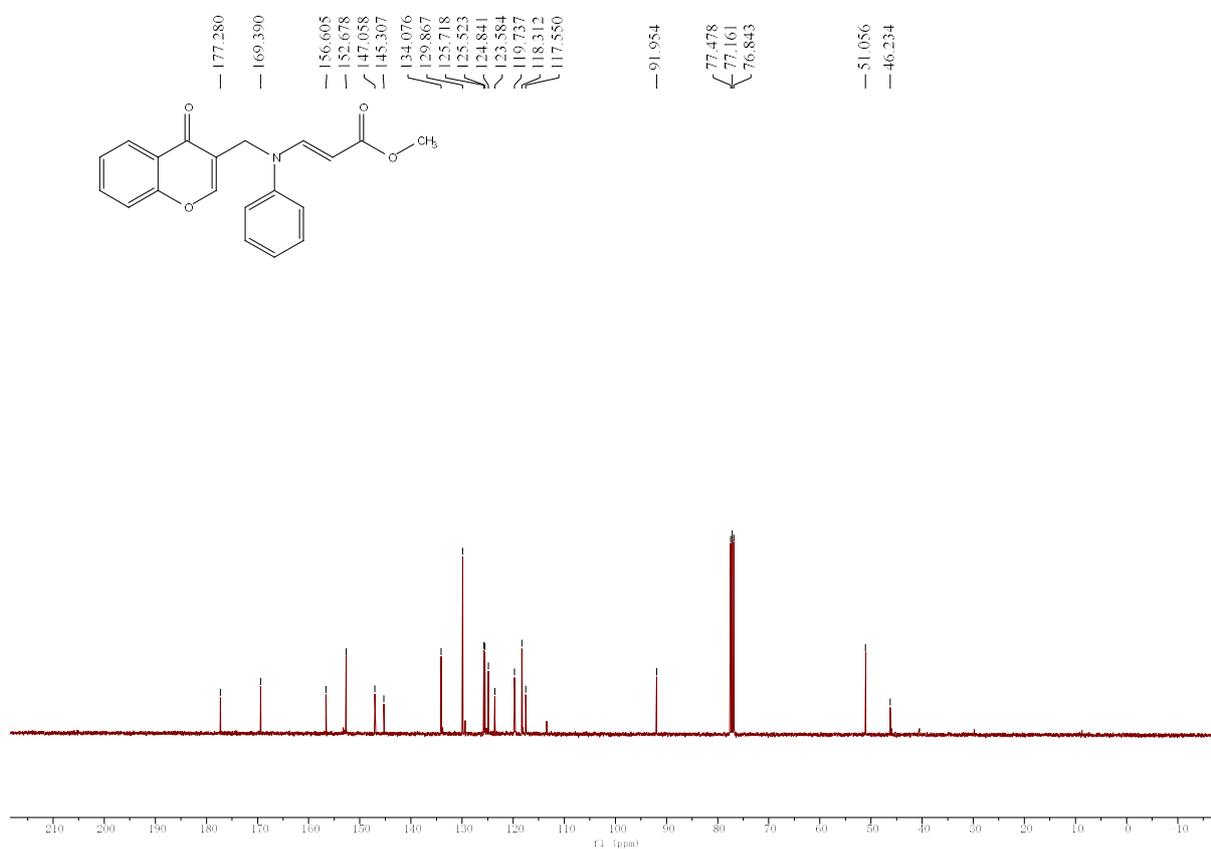
100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 4 in CDCl_3



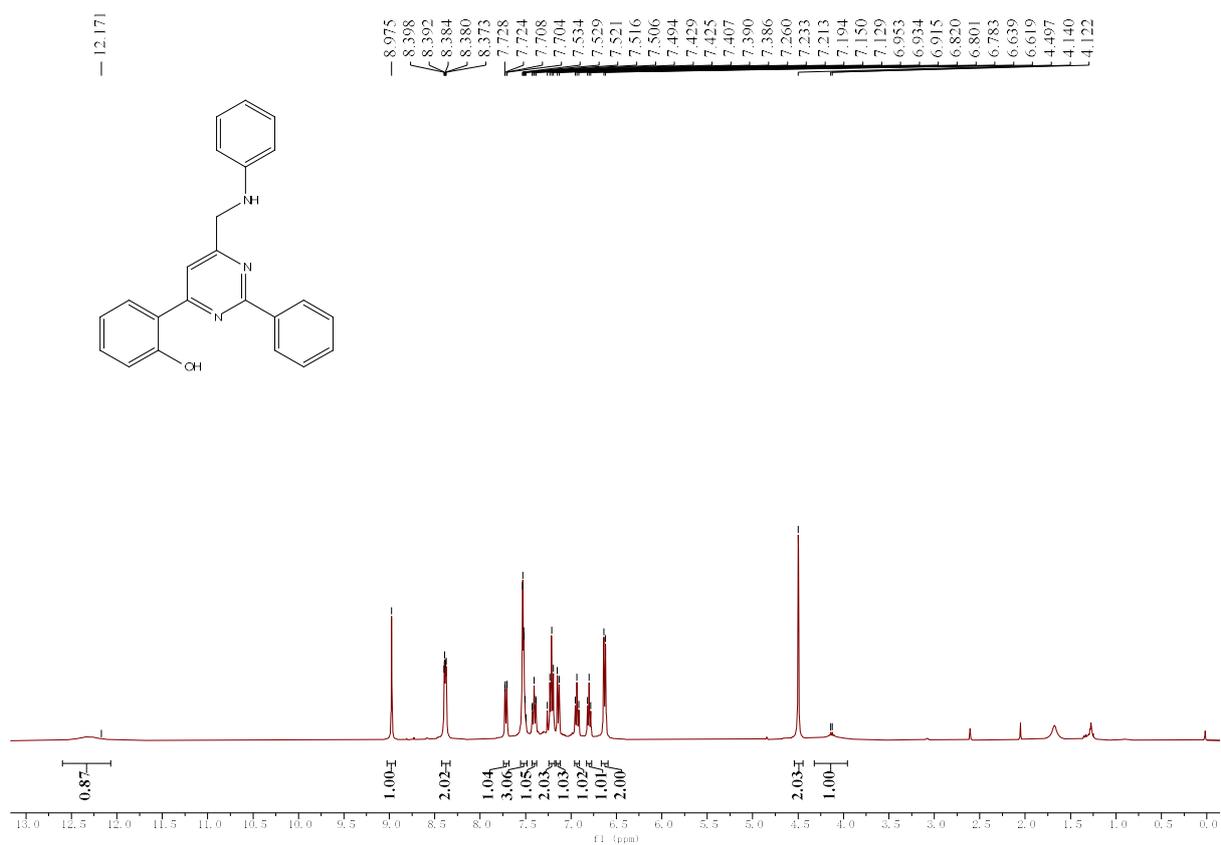
400 MHz ^1H NMR Spectrum of 5 in CDCl_3



100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 5 in CDCl_3



400 MHz ^1H NMR Spectrum of 6 in CDCl_3



100 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 6 in CDCl_3

