Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cooperative NHC and Nickel Catalyzed Asymmetric Reductive Coupling of Nitrobenzyl Bromides and Cyclic Ketimines via SET Process

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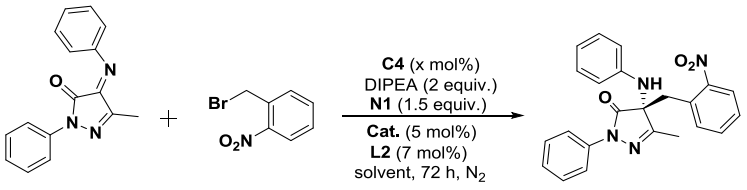
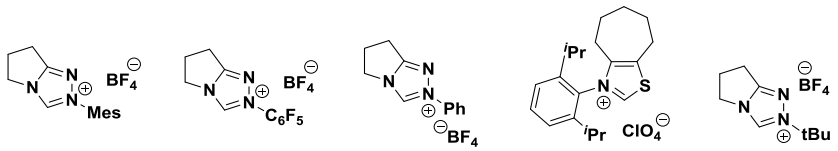
1. General Information

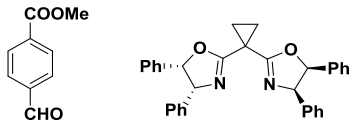
All the commercial reagents were used as such without further purification. All solvents were used as commercial anhydrous grade without further purification. The flash column chromatography was carried out over silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer or Bruker Avance-500 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0 ppm). Chemical shifts in ^{13}C NMR spectra were reported relative to the central line of the chloroform signal (δ = 77.0 ppm). Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were obtained with a Shimadzu LCMS-IT-TOF mass spectrometer. High performance liquid chromatography (HPLC) was conducted on an Agilent 1200 instrument using Daicel Chiralpak column IA, IC or AD-H. Optical rotations were recorded on a Rudolph Autopol I polarimeter. Chemical yields refer to pure isolated substances. Ligands purchased from DAICEL CHIRAL TECHNOLOGIES (CHINA) CO., LTD and used as received. The pyrazolone-derived ketimines, isatin-derived ketimines[1] and nitrobenzyl bromides[2] were prepared according to literature methods.

2. Reaction Optimization

Table S1 Condition optimization for pyrazolone-derived ketamine with nitrobenzyl bromide[a,b]





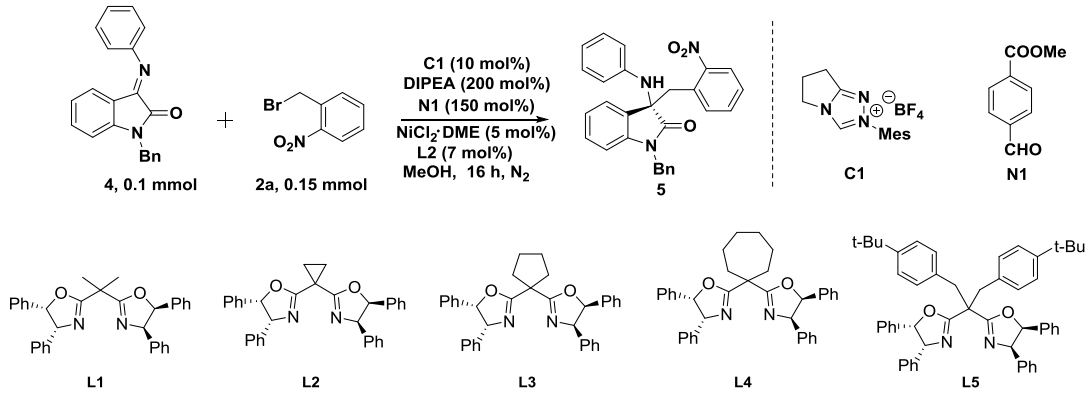


Entry	Precatalyst (x mol%)	**Cat.** (5 mol%)	Solvent	Yield (%)	ee (%)
1[b]	**C1** (5)	--	MeOH	45	--
2[b]	**C2** (5)	--	MeOH	20	--
3[b]	**C3** (5)	--	MeOH	28	--
4[b]	**C4** (5)	--	MeOH	36	--
5[b]	**C5** (5)	--	MeOH	29	--
6[b,c]	**C4** (10)	--	MeOH	60	--
7[d]	**C4** (5)	$NiCl_2$·DME	THF	43	7
8[d]	**C4** (5)	$NiCl_2$·DME	PhMe	27	6
9[d]	**C4** (5)	$NiCl_2$·DME	DCM	62	48
10[d]	**C4** (5)	$NiCl_2$·DME	MeCN	43	75

11	**C4** (5)	$NiCl_2$·DME	EtOH	33	39
12[e]	**C4** (5)	$NiCl_2$·DME	MeOH	ND	--
13[f]	**C4** (5)	$Ni(OTf)_2$	MeOH	21	78
14[f]	**C4** (5)	$Ni(ClO_4)_2·6H_2O$	MeOH	36	86
15[f]	**C4** (5)	$NiBr_2$·DME	MeOH	35	86
16[f]	**C4** (5)	$Ni(OAc)_2·4H_2O$	MeOH	31	38
17[f]	**C4** (5)	$Ni(acac)_2$	MeOH	46	84
18[f]	**C4** (5)	$Ni(hfac)_2$	MeOH	35	47
19[f]	**C4** (5)	$Ni(PPh_3)_2Cl_2$	MeOH	20	84
20[f]	**C4** (5)	$Ni(cod)_2$	MeOH	34	69
21[f]	**C4** (5)	$Nd(OTf)_3$	MeOH	24	4
22[f]	**C4** (5)	$Bi(OTf)_3$	MeOH	21	0

[a] Unless otherwise specified, all reactions were carried out with **1a** (0.1 mmol) and **2a** (0.15 mmol), precatalyst (x mol%), catalyst (5 mol%), **L2** (7 mol%), DIPEA (0.2 mmol), ArCHO (0.15 mmol) and solvent (2.0 mL) under a nitrogen atmosphere at room temperature for 72 h. [b] The reactions was carried out with **1a** (0.1 mmol) and **2a** (0.15 mmol), DIPEA (0.2 mmol) and ArCHO (0.15 mol) and MeOH (2.0 mL) at room temperature for 24 h. [c] 60 h. [d] 10 equiv. of MeOH was used additionally. [e] 0℃. [f] 50℃.

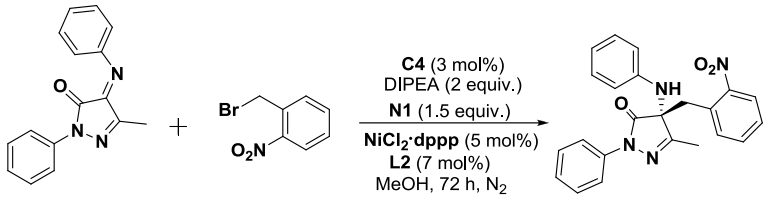
Table S2 Condition optimization for isatin-derived ketamine with nitrobenzyl bromide[a,b]



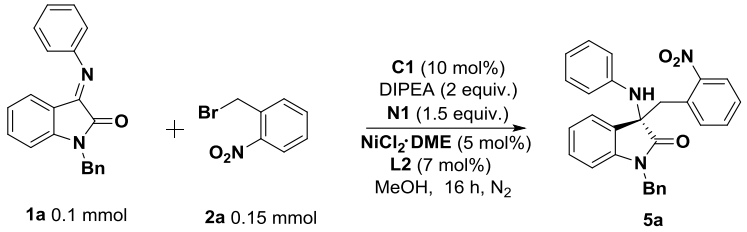
Entry	Cat (5%)	Ligand (7%)	Base	Solvent	Yield (%)	ee (%)
1	$NiCl_2$·DME	**L1**	DIPEA	MeOH	55	5
2	$NiCl_2$·DME	**L2**	DIPEA	MeOH	70	82
3	$NiCl_2$·DME	**L3**	DIPEA	MeOH	56	70
4	$NiCl_2$·DME	**L4**	DIPEA	MeOH	35	41
5	$NiCl_2$·DME	**L5**	DIPEA	MeOH	43	4
6	$NiCl_2$·DPPP	**L2**	DIPEA	MeOH	54	72
7	$NiCl_2$	**L2**	DIPEA	MeOH	60	56
8	$Ni(acac)_2$	**L2**	DIPEA	MeOH	57	0
9	$Ni(OTf)_2$	**L2**	DIPEA	MeOH	55	54

[a] Reaction conditions: **4a** (0.1 mmol), **2a** (0.15 mmol), ArCHO (0.15 mmol), DIPEA (0.2 mmol), **C1** (0.01 mmol), **L2** (0.007 mmol), $NiCl_2$·DME (0.005 mmol), MeOH (2 mL) under a nitrogen atmosphere at room temperature for 16 h. [b] Isolated yield.

3. General Procedure for the Synthesis of 3 and 5

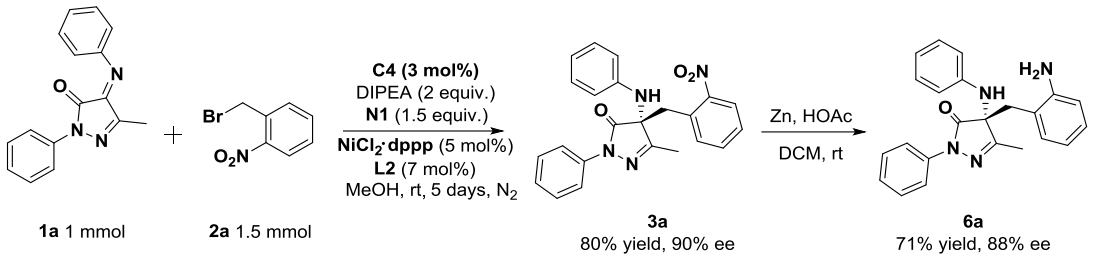


In a dry and nitrogen filled tube, a mixture of $NiCl_2$·dppp (0.005 mmol), **L2** (0.007 mmol) in MeOH (1 mL) was stirred at room temperature under nitrogen for 30 mins. Pyrazolone-derived ketimine **1a** (0.1 mmol), nitrobenzyl bromide **2a** (0.15 mmol), aldehyde **N1** (0.15 mmol), **C4** (0.003 mmol) and DIPEA (0.2 mmol) were added to the above catalyst solution under nitrogen. The reaction mixture was stirred at room temperature for 72 h, then the resulting mixture was concentrated under reduced pressure, and the residue was purified via column chromatography on silica gel to afford product **3a**.



In a dry and nitrogen filled tube, a mixture of $NiCl_2$·DME (0.005 mmol), **L2** (0.007 mmol) in MeOH (2 mL) was stirred at room temperature under nitrogen for 30 mins. Isatin-derived ketimine **1a** (0.1 mmol), nitrobenzyl bromide **2a** (0.15 mmol), aldehyde **N1** (0.15 mmol), **C1** (0.01 mmol) and DIPEA (0.2 mmol) were added to the above catalyst solution under nitrogen. The reaction mixture was stirred at room temperature for 16 h. then the resulting mixture was concentrated under reduced pressure, and the residue was purified *via* column chromatography on silica gel to afford product **5a**.

4. Synthetic Transformations

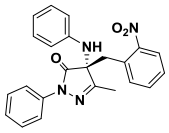


In a dry and nitrogen filled tube, a mixture of $NiCl_2$·dppp (0.05 mmol), **L2** (0.07 mmol) in MeOH (5 mL) was stirred at room temperature under nitrogen for 30 mins. Pyrazolone-derived ketimine **1a** (1 mmol), nitrobenzyl bromide **2a** (1.5 mmol), aldehyde **N1** (1.5 mmol) and **C4** (0.1 mmol) in MeOH (5 mL) were added sequentially. Finally, DIPEA (2 mmol) were added to the above solution through a syringe, then the reaction mixture was stirred at room temperature for 5 days, the resulting mixture was concentrated under reduced pressure, and the residue was purified via column chromatography on silica gel to afford product **3a** (320 mg, 80% yield, 90% ee).

To a stirred solution of compound **3a** (0.17 mmol) in CH_2Cl_2 (5 mL) was added Zn powder (3.4 mmol), followed by the addition of HOAc (1 mL). The resulting mixture was allowed to stir at room temperature after the reaction was completed (determined by TLC analysis). The solvent of the filtrate was poured into water and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure. The residue was purified via column chromatography on silica gel to afford product 6**a** (26.3 mg, 71% yield, 88% ee).

5. Characterization of Compounds

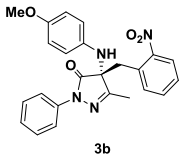
(*R*)-5-Methyl-4-(2-nitrobenzyl)-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3a)**



3a

Yellow solid, 30.8 mg, 77% yield, 90% ee, m.p. 144-146 °C, $[\alpha]_D^{20}$ = 225.1 (c = 0.26, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.46-7.34 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 2H), 4.64 (brs, 1H), 3.96 (d, *J* = 13.2 Hz, 1H), 3.48 (d, *J* = 13.3 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.4, 162.4, 150.1, 144.2, 137.5, 133.8, 132.8, 129.6, 129.6, 129.2, 128.9, 128.9, 126.6, 125.5, 125.2, 120.0, 119.0, 119.0, 114.0, 113.9, 69.4, 38.3, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{21}N_4O_3$ $[M+H]^+$: 401.1608, found: 401.1599; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 9.1 min, t_{minor} = 6.6 min.

(*R*)-4-((4-Methoxyphenyl)amino)-5-methyl-4-(2-nitrobenzyl)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **(3b)**

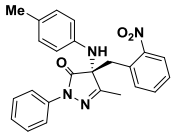


3b

Light yellow oil, 30.1 mg, 70% yield, 83% ee, $[\alpha]_D^{20}$ = 173.3 (c = 0.44, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67-7.64 (m, 2H), 7.47-7.32 (m, 5H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.67-6.64 (m, 2H), 6.41-6.37 (m, 2H), 4.27 (brs, 1H), 3.93 (d, *J* = 13.4 Hz, 1H), 3.66 (s, 3H), 3.46 (d, *J* = 13.4 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.8, 162.3, 154.0, 150.1, 137.8, 137.5, 133.7, 132.8, 129.1, 128.8, 128.8,

126.9, 125.4, 125.2, 118.9, 118.9, 116.6, 116.6, 114.9, 114.9, 70.1, 55.5, 38.1, 13.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}N_4O_4$ $[M+H]^+$: 431.1714, found: 431.1730; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 17.7 min, t_{minor} = 11.0 min.

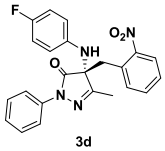
(*R*)-5-Methyl-4-(2-nitrobenzyl)-2-phenyl-4-(p-tolylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3c)**



3c

Light yellow oil, 26.5 mg, 64% yield, 88% ee, $[\alpha]_D^{20}$ = 188.0 (c = 0.26, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.48-7.30 (m, 5H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.29 (d, *J* = 8.5 Hz, 2H), 4.41 (brs, 1H), 3.96 (d, *J* = 13.3 Hz, 1H), 3.46 (d, *J* = 13.2 Hz, 1H), 2.16 (s, 3H), 2.05 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.2, 162.2, 150.2, 144.2, 135.3, 135.1, 133.8, 132.8, 129.6, 129.6, 129.4, 129.4, 129.2, 126.6, 125.2, 119.9, 119.1, 119.1, 113.9, 113.9, 69.3, 38.2, 21.0, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}N_4O_3$ $[M+H]^+$: 415.1765, found: 415.1776; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 12.9 min, t_{minor} = 8.4 min.

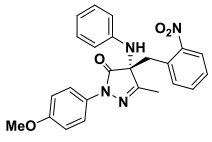
(*R*)-4-((4-Fluorophenyl)amino)-5-methyl-4-(2-nitrobenzyl)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **(3d)**



3d

Yellow solid, 28.0 mg, 67% yield, 80% ee, m.p. 143-145 °C, $[\alpha]_D^{20}$ = 186.1 (c = 0.34, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.94-7.92 (m, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.48-7.34 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.79 (t, *J* = 8.7 Hz, 2H), 6.33 (dd, *J* = 8.9, 4.3 Hz, 2H), 4.51 (brs, 1H), 3.92 (d, *J* = 13.3 Hz, 1H), 3.48 (d, *J* = 13.4 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.3, 162.1, 158.2, 156.3, 150.2, 140.4, 137.4, 133.8, 132.8, 129.3, 128.9, 128.9, 126.6, 125.6, 125.3, 118.9, 118.9, 116.2, 116.1, 115.7, 69.7, 38.2, 13.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -124.18 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}FN_4O_3$ $[M+H]^+$: 450.1812, found: 450.1792; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 7.5 min, t_{minor} = 5.3 min.

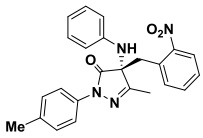
(*R*)-2-(4-Methoxyphenyl)-5-methyl-4-(2-nitrobenzyl)-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3e)**



3e

Yellow solid, 27.1 mg, 63% yield, 88% ee, m.p. 104-106 °C, $[\alpha]_D^{20}$ = 211.9 (c = 0.31, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 7.9 Hz, 1H), 7.52-7.38 (m, 5H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 2H), 4.55 (brs, 1H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.81 (s, 3H), 3.47 (d, *J* = 13.2 Hz, 1H), 2.04 (s, 3H) ppm; **^{13}C NMR** (101MHz, $CDCl_3$) δ: 172.0, 162.2, 157.4, 150.2, 144.2, 133.8, 132.8, 130.8, 129.6, 129.6, 129.2, 126.6, 125.2, 120.9, 120.9, 119.9, 114.0, 114.0, 113.9, 113.9, 69.3, 55.5, 38.2, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}N_4O_4$ $[M+H]^+$: 431.1714, found: 431.1712; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 14.3 min, t_{minor} = 9.1 min.

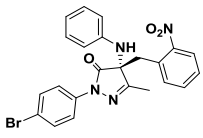
(*R*)-5-Methyl-4-(2-nitrobenzyl)-4-(phenylamino)-2-(p-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one **(3f)**



3f

Light yellow oil, 31.5 mg, 76% yield, 90% ee, $[\alpha]_D^{20}$ = 225.7 (c = 0.25, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.47-7.38 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 2H), 4.57 (brs, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 2.34 (s, 3H), 2.04 (s, 3H) ppm; **^{13}C NMR** (101MHz, $CDCl_3$) δ: 172.6, 162.5, 150.1, 141.8, 137.5, 133.8, 132.7, 130.0, 130.1, 129.5, 129.2, 128.8, 128.8, 126.7, 125.4, 125.2, 119.0, 119.0, 114.3, 114.3, 69.7, 38.3, 20.4, 13.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}N_4O_3$ $[M+H]^+$: 415.1772, found: 415.1765; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH =80/20, 1.0 mL/min, 245 nm): t_{major} = 10.6 min, t_{minor} = 7.0 min.

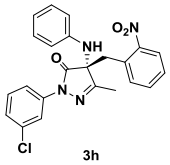
(*R*)-2-(4-Bromophenyl)-5-methyl-4-(2-nitrobenzyl)-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3g)**



3g

Light yellow oil, 26.8 mg, 56% yield, 86% ee, $[\alpha]_D^{20}$ = 192.2 (c = 0.41, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.7 Hz, 1H), 7.62-7.59 (m, 2H), 7.47-7.37 (m, 5H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 2H), 4.55 (brs, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.47 (d, *J* = 13.1 Hz, 1H), 2.06 (s, 3H) ppm; **^{13}C NMR** (101MHz, $CDCl_3$) δ: 172.4, 162.8, 150.1, 144.1, 136.5, 133.7, 132.8, 131.9, 131.9, 129.6, 129.6, 129.4, 126.4, 125.3, 120.1, 120.1, 120.1, 118.3, 113.9, 113.9, 69.4, 38.4, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}N_4O_3Br$ $[M+H]^+$: 479.0713, found: 479.0713; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 7.8 min, t_{minor} = 5.9 min.

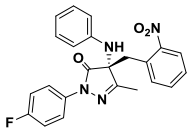
(*R*)-2-(3-Chlorophenyl)-5-methyl-4-(2-nitrobenzyl)-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3h)**



3h

Light yellow oil, 30.5 mg, 70% yield, 86% ee, $[\alpha]_D^{20}$ = 210.4 (c = 0.36, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.94-7.92 (m, 1H), 7.73-7.64 (m, 2H), 7.54-7.37 (m, 3H), 7.29-7.25 (m, 1H), 7.16-7.06 (m, 3H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.34-6.32 (m, 2H), 4.57 (brs, 1H), 3.96 (d, *J* = 13.3 Hz, 1H), 3.47 (d, *J* = 13.3 Hz, 1H), 2.06 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.5, 162.9, 150.1, 144.0, 138.5, 134.6, 133.7, 132.8, 129.9, 129.7, 129.7, 129.3, 126.4, 125.2, 125.3, 120.2, 118.6, 116.5, 113.9, 113.9, 69.5, 38.4, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{20}ClN_4O_3$ $[M+H]^+$: 435.1218, found: 435.1227; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 8.0 min, t_{minor} = 5.4 min.

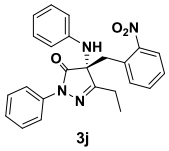
(*R*)-2-(4-Fluorophenyl)-5-methyl-4-(2-nitrobenzyl)-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3i)**



3i

Light yellow oil, 28.0 mg, 67% yield, 70% ee, $[\alpha]_D^{20}$ = 156.39 (c = 0.21, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.94-7.91 (m, 1H), 7.64-7.61 (m, 2H), 7.48-7.37 (m, 3H), 7.10-7.01 (m, 4H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 2H), 4.55 (brs, 1H), 3.98 (d, *J* = 13.1 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.2, 162.6, 161.3, 158.9, 150.1, 144.1, 133.8, 133.6, 132.8, 129.6, 129.6, 129.3, 126.5, 125.2, 120.7, 120.1, 115.7, 115.5, 113.9, 113.9, 69.3, 38.3, 13.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -116.52 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}N_4O_3F$ $[M+H]^+$: 419.1506, found: 419.1514; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 8.1 min, t_{minor} = 5.9 min.

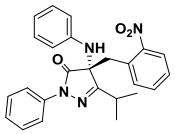
(*R*)-5-Ethyl-4-(2-nitrobenzyl)-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3j)**



3j

Yellow solid, 25.2 mg, 61% yield, 86% ee, m.p. 143-145 °C, $[\alpha]_D^{20}$ = 210.7 (c = 0.26, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.48-7.35 (m, 5H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 2H), 4.61 (brs, 1H), 3.92 (d, *J* = 13.3 Hz, 1H), 3.51 (d, *J* = 13.4 Hz, 1H), 2.48-2.28 (m, 2H), 1.19 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.6, 166.1, 150.1, 144.3, 137.7, 133.9, 132.8, 129.5, 129.5, 129.2, 128.8, 128.8, 126.7, 125.4, 125.3, 119.8, 119.0, 119.0, 113.9, 113.9, 69.3, 38.4, 21.2, 9.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}N_4O_3$ $[M+H]^+$: 415.1765, found: 415.1764; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 9.3 min, t_{minor} = 6.3 min.

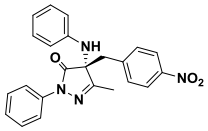
(*R*)-5-Isopropyl-4-(2-nitrobenzyl)-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3k)**



3k

Yellow solid, 28.2 mg, 66% yield, 94% ee, m.p. 133-135 °C, $[\alpha]_D^{20}$ = 151.4 (c = 0.19, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.01 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.86-7.84 (m, 2H), 7.55-7.39 (m, 5H), 7.24-7.20 (m, 1H), 7.04 (dd, *J* = 8.6, 7.4 Hz, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.28 (d, *J* = 7.7 Hz, 2H), 4.82 (brs, 1H), 3.68 (s, 2H), 2.79 (m *J* = 6.8 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.1, 169.3, 150.2, 144.6, 138.0, 133.9, 132.9, 129.3, 129.3, 129.2, 128.9, 128.9, 127.0, 125.5, 125.4, 119.6, 119.0, 119.0, 114.0, 114.0, 68.8, 38.1, 28.1, 21.4, 20.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{25}H_{25}N_4O_3$ $[M+H]^+$: 429.1921, found: 429.1911; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 11.2 min, t_{minor} = 6.2 min.

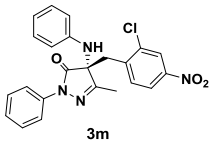
(*R*)-5-Methyl-4-(4-nitrobenzyl)-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3l)**



3l

Yellow solid, 20.0 mg, 50% yield, 94% ee, m.p. 163-166 °C, $[\alpha]_D^{20}$ = 26.75 (c = 0.16, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.3 Hz, 1H), 7.53-7.51(m, 2H), 7.34-7.30 (m, 4H), 7.19-7.09 (m, 3H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.43 (d, *J* = 8.3 Hz, 2H), 4.38 (brs, 1H), 3.39 (d, *J* = 12.3 Hz, 1H), 3.25 (d, *J* = 12.2 Hz, 1H), 2.20 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.2, 161.2, 147.7, 144.2, 138.9, 137.1, 130.8, 130.8, 129.7, 129.7, 128.9, 128.9, 125.8, 123.5, 123.5, 120.3, 119.0, 119.0, 113.9, 113.9, 70.0, 42.6, 14.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{21}N_4O_3$ $[M+H]^+$: 401.1599, found: 401.1608; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm): t_{major} = 26.9 min, t_{minor} = 10.2 min.

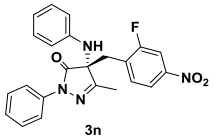
(R)-4-(2-Chloro-4-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3m)**



3m

Yellow solid, 17.8 mg, 41% yield, 94% ee, m.p. 110-114 °C, $[\alpha]_D^{20}$=43.56 (c = 0.29, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.27 (d, *J* = 2.3 Hz, 1H), 7.92 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.72-7.69 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 8.6, 7.3 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 2H), 4.47 (brs, 1H), 3.60 (d, *J* = 13.1 Hz, 1H), 3.46 (d, *J* = 13.1 Hz, 1H), 2.19 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.2, 162.2, 147.8, 144.4, 137.4, 137.3, 135.7, 132.9, 129.7, 129.7, 129.0, 129.0, 125.8, 124.9, 121.5, 120.3, 118.8, 118.8, 114.0, 114.0, 69.4, 39.1, 14.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}N_4O_3Cl$ $[M+H]^+$: 435.1218, found: 435.1230; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm): t_{major} = 14.6 min, t_{minor} = 17.9 min.

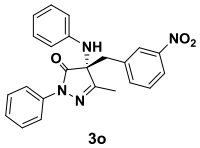
(*R*)-4-(2-Fluoro-4-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3n)**



3n

Light yellow oil, 28.0 mg, 67% yield, 92% ee, $[\alpha]_D^{20}$=32.26 (c = 0.40, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92 (dd, *J* = 9.6, 2.3 Hz, 1H), 7.81 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.41-7.32 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 2H), 4.47 (brs, 1H), 3.51 (d, *J* = 12.6 Hz, 1H), 3.27 (d, *J* = 12.7 Hz, 1H), 2.17 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.1, 162.1, 160.8 (d, *J* = 250.6 Hz), 148.5, 144.0, 137.2, 133.1 (d, *J* = 4.1 Hz), 129.7, 129.7, 129.0, 129.0, 126.7 (d, *J* = 16.0 Hz), 125.8, 120.3, 119.0 (d, *J* = 3.7 Hz), 118.9, 118.9, 113.9, 113.9, 111.3 (d, *J* = 28.3 Hz), 69.6, 35.6, 13.7 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -110.94 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}FN_4O_3$ $[M+H]^+$: 419.1514, found: 419.1514; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 17.9 min, t_{minor} = 21.0 min.

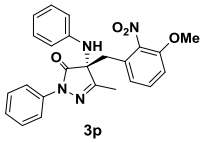
(*R*)-5-Methyl-4-(3-nitrobenzyl)-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3o)**



3o

Light yellow oil, 11.2 mg, 28% yield, 0% ee. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.08-8.02 (m, 2H), 7.50 (dd, *J* = 20.8, 7.8 Hz, 3H), 7.33 (dt, *J* = 16.1, 8.1 Hz, 3H), 7.14 (dt, *J* = 15.7, 7.7 Hz, 3H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 2H), 4.39 (brs, 1H), 3.40 (d, *J* = 12.4 Hz, 1H), 3.26 (d, *J* = 12.4 Hz, 1H), 2.22 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 172.2, 161.2, 147.9, 144.2, 137.1, 135.9, 133.5, 129.7, 129.7, 129.4, 128.9, 128.9, 125.7, 124.6, 123.2, 120.2, 118.9, 118.9, 113.9, 113.9, 70.0, 42.6, 14.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{21}N_4O_3$ $[M+H]^+$: 401.1608, found: 401.1624; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 7.0 min, t_{minor} = 8.8 min.

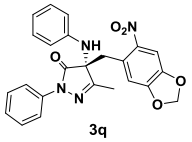
(*R*)-4-(3-Methoxy-2-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3p)**



3p

Yellow solid, 20.2 mg, 47% yield, 72% ee, m.p. 161-163 °C, $[\alpha]_D^{20}$=1.80 (c = 0.33, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.45-7.39 (m, 3H), 7.19 (dd, *J* = 12.8, 7.7 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 2H), 5.62 (brs, 1H), 3.90 (s, 3 H), 3.74 (d, *J* = 14.1 Hz, 1H), 3.61 (d, *J* = 14.1 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 171.9, 162.8, 158.6, 151.2, 144.6, 138.3, 129.5, 129.5, 129.3, 128.9, 128.9, 125.1, 119.1, 118.8, 118.8, 117.8, 117.3, 115.1, 113.4, 113.4, 68.7, 56.5, 31.4, 13.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}N_4O_4$ $[M+H]^+$: 431.1714, found: 431.1701; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm): t_{major} = 17.1 min, t_{minor} = 10.0 min.

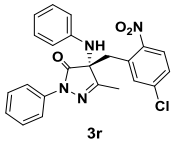
(*R*)-5-Methyl-4-((6-nitrobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-on e **(3q)**



3q

Light yellow oil, 39.9 mg, 83% yield, 90% ee, $[\alpha]_D^{20}$=110.48 (c = 0.53, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 7.7 Hz, 2H), 7.45 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 2H), 6.04 (d, *J* = 1.3 Hz, 1H), 5.92 (d, *J* = 1.3 Hz, 1H), 4.68 (brs, 1H), 3.85 (d, *J* = 13.4 Hz, 1H), 3.43 (d, *J* = 13.5 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.5, 162.6, 151.4, 147.9, 144.4, 144.1, 137.7, 129.6, 129.6, 128.9, 128.9, 125.4, 123.2, 119.9, 118.8, 118.8, 113.9, 113.9, 112.2, 106.1, 103.1, 69.3, 38.5, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{21}N_4O_5$ $[M+H]^+$:445.1506, found: 445.1520; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm): t_{major} = 12.5 min, t_{minor} = 9.4 min.

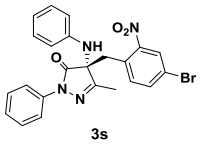
(*R*)-4-(5-Chloro-2-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3r)**



3r

Yellow solid, 37.1 mg, 91% yield, 86% ee, m.p. 138-140 °C, $[\alpha]_D^{20}$=138.99 (c = 0.55, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.42-7.33 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 2H), 4.54 (brs, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 3.42 (d, *J* = 13.3 Hz, 1H), 2.05 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.2, 162.1, 148.3, 144.0, 139.3, 137.4, 133.6, 129.6, 129.6, 129.3, 128.9, 128.9, 128.7, 126.7, 125.6, 120.2, 118.8, 118.8, 114.1, 114.1, 69.2, 38.1, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}ClN_4O_3$ $[M+H]^+$: 435.1218, found: 435.1212; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm): t_{major} = 7.1 min, t_{minor} = 5.7 min.

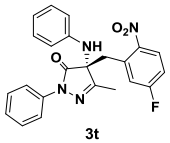
(*R*)-4-(4-Bromo-2-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3s)**



3s

Light yellow oil, 39.8 mg, 83% yield, 90% ee, $[\alpha]_D^{20}$=151.75 (c = 0.65, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 2.1 Hz, 1H), 7.68-7.66 (m, 2H), 7.55 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.39 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.29-7.27 (m, 1H), 7.23-7.19 (m, 1H), 7.09 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.77 (t, *J* = 7.4 Hz, 2H), 6.36 (dt, *J* = 7.7, 1.1 Hz, 2H), 4.52 (brs, 1H), 3.86 (d, *J* = 13.3 Hz, 1H), 3.43 (d, *J* = 13.4 Hz, 1H), 2.06 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.2, 162.2, 150.4, 144.0, 137.4, 135.8, 135.1, 129.6, 129.6, 128.9, 128.9, 128.1, 125.7, 125.5, 122.6, 120.2, 118.9, 118.9, 114.0, 114.0, 69.1, 37.8, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}BrN_4O_4$ $[M+H]^+$: 431.1714, found: 431.1701; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm): t_{major} = 7.2 min, t_{minor} = 5.8 min.

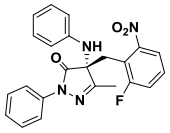
(*R*)-4-(5-Fluoro-2-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3t)**



3t

Light yellow oil, 28.8 mg, 69% yield, 84% ee, $[\alpha]_D^{20}$=174.41 (c = 0.11, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.01 (dd, *J* = 9.1, 5.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.22-7.14 (m, 2H), 7.11-7.05 (m, 3H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 2H), 4.57 (brs, 1H), 3.94 (d, *J* = 13.3 Hz, 1H), 3.49 (d, *J* = 13.3 Hz, 1H), 2.07 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 172.2, 164.0 (d, *J* = 258.4 Hz), 162.2, 146.2, 144.0, 137.4, 130.3 (d, *J* = 9.1 Hz), 129.6, 129.6, 129.9, 128.9, 128.0 (d, *J* = 9.8 Hz), 125.6, 120.7 (d, *J* = 24.1 Hz), 120.2, 118.8, 118.8, 116.2(d, *J* = 22.9 Hz), 114.1, 114.1, 69.1, 38.2, 13.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -103.01 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}N_4O_3F$ $[M+H]^+$: 419.1514, found: 419.1510; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 7.0 min, t_{minor} = 5.5 min.

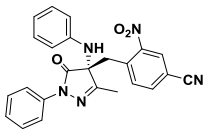
(*R*)-4-(2-Fluoro-6-nitrobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(3u)**



3u

Light yellow oil, 25.9 mg, 62% yield, 82% ee, $[\alpha]_D^{20}$=11.84 (c = 0.37, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.50-7.39 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 2H), 4.90 (brs, 1H), 3.80 (dd, *J* = 14.1, 2.1 Hz, 1H), 3.70 (dd, *J* = 14.1, 2.4 Hz, 1H), 2.10 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 171.5, 162.3, 161.7 (d, *J* = 247.8 Hz), 150.5 (d, *J* = 4,3 Hz), 144.2, 137.8, 129.8 (d, *J* = 10.0 Hz), 129.5, 129.5, 128.9, 128.9, 125.4, 121.7 (d, *J* = 3.1 Hz), 120.7 (d, *J* = 25.0 Hz), 119.9, 119.0, 119.0, 116.5 (d, *J* = 19.1 Hz), 114.0, 114.0, 68.2, 30.9, 13.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -108.08 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}N_4O_3F$ $[M+H]^+$: 419.1514, found: 419.1508; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 16.5 min, t_{minor} = 8.9 min.

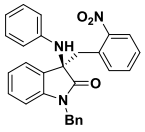
(*R*)-4-((3-Methyl-5-oxo-1-phenyl-4-(phenylamino)-4,5-dihydro-1H-pyrazol-4-yl)methyl)-3-nitrobenzonitrile **(3w)**



3v

Yellow solid, 19.1 mg, 45% yield, 76% ee, m.p. 118-120 °C, $[\alpha]_D^{20}$=144.07 (c = 0.21, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 1.7 Hz, 1H), 7.66 (ddd, *J* = 19.5, 8.4, 1.5 Hz, 3H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.38 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.9 Hz, 2H), 4.49 (brs, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 3.53 (d, *J* = 13.2 Hz, 1H), 2.08 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 171.8, 162.0, 150.1, 143.7, 137.2, 135.3, 135.1, 131.8, 129.7, 129.7, 129.0, 129.0, 128.6, 125.9, 120.5, 118.7, 118.7, 116.0, 114.2, 114.2, 113.6, 69.3, 38.1, 13.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{24}H_{20}N_5O_3$ $[M+H]^+$: 426.1561, found: 426.1562; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm): t_{major} = 22.1 min, t_{minor} = 11.1 min.

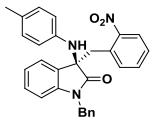
(*R*)-1-Benzyl-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5a)**



5a

Yellow oil, 31.5 mg, 70% yield, 82% ee, $[\alpha]_D^{20}$ = 222.7 (c = 0.36, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.73 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.41-7.28 (m, 3H), 7.24-7.20 (m, 3H), 7.17-7.10 (m, 2H), 7.03-6.90 (m, 5H), 6.71-6.68 (m, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.23 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.96-4.93 (m, 1H), 4.60 (brs, 1H),4.43 (d, *J* = 15.5 Hz, 1H), 4.29 (d, *J* = 13.0 Hz, 1H), 3.48 (d, *J* = 13.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 177.2, 150.2, 144.9, 141.9, 135.3, 134.0, 132.3, 129.4, 129.0, 129.0, 128.7, 128.7, 128.6, 128.4, 127.6, 127.6, 127.5, 127.5, 124.9, 124.8, 123.4, 120.0, 116.6, 116.6, 109.5, 66.2, 44.0, 41.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{28}H_{24}N_3O_3$ $[M+H]^+$: 450.1812, found: 450.1792; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 33.1 min, t_{minor} = 40.8 min.

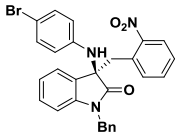
(*R*)-1-Benzyl-3-(2-nitrobenzyl)-3-(p-tolylamino)indolin-2-one **(5b).**



5b

Yellow solid, 29.6 mg, 64% yield, 74% ee, m.p. 143-149 °C, $[\alpha]_D^{20}$=205.6 (c = 0.27, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 7.8 Hz, 1H), 7.40-7.29 (m, 3H), 7.23-7.11 (m, 5H), 6.99-6.93 (m, 3H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 2H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.44-4.40 (m, 2H), 4.28 (d, *J* = 13.0 Hz, 1H), 3.47 (d, *J* = 13.0 Hz, 1H), 2.15 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 177.3, 150.2, 142.3, 142.1, 135.2, 133.9, 132.2, 129.8, 129.4, 129.4, 129.3, 128.8, 128.6, 128.6, 128.3, 127.7, 127.5, 127.4, 127.4, 124.9, 124.8, 123.3, 117.8, 117.8, 109.4, 66.7, 43.9, 40.8, 20.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{29}H_{26}N_3O_3$ $[M+H]^+$: 464.1969, found: 464.1964; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 36.9 min, t_{minor} = 24.6 min.

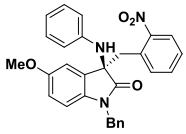
(*R*)-1-Benzyl-3-((4-bromophenyl)amino)-3-(2-nitrobenzyl)indolin-2-one **(5c)**



5c

Yellow oil, 39.6 mg, 75% yield, 86% ee, $[\alpha]_D^{20}$=280.9 (c = 0.23, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.74 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.41-7.33 (m, 2H), 7.27-7.23 (m, 4H), 7.18-7.14 (m, 1H), 7.09-7.07 (m, 1H), 7.01-6.96 (m, 5H), 6.55 (dd, *J* = 20.3, 8.4 Hz, 1H), 6.11-6.07 (m, 2H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.64 (brs, 1H), 4.42 (d, *J* = 15.5 Hz, 1H), 4.26 (d, *J* = 13.0 Hz, 1H), 3.45 (d, *J* = 13.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 176.9, 150.2, 143.9, 141.9, 135.1, 134.0, 132.3, 131.8, 131.8, 129.6, 128.7, 128.7, 128.5, 128.4, 127.8, 127.6, 127.6, 127.1, 124.9, 124.8, 123.5, 118.4, 118.4, 112.3, 109.6, 66.2, 44.1, 40.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{23}N_3O_3Br$ $[M+H]^+$: 528.0917, found: 528.0914; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 245 nm): t_{major} = 87.4 min, t_{minor} = 32.3 min.

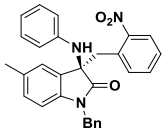
(*R*)-1-Benzyl-5-methoxy-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5d)**



5d

Yellow solid, 41.7 mg, 87% yield, 92% ee, m.p. 200-203 °C, $[\alpha]_D^{20}$=201.9 (c = 0.26, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 7.9 Hz, 1H), 7.41-7.31 (m, 3H), 7.22-7.21 (m, 3H), 7.00-6.99 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.73-6.66 (m, 3H), 6.42 (d, *J* = 8.5 Hz, 1H), 6.25 (d, *J* = 7.9 Hz, 2H), 4.92 (d, *J* = 15.5 Hz, 1H), 4.56 (brs, 1H), 4.34 (dd, *J* = 28.5, 14.2 Hz, 2H), 3.72 (s, 3H), 3.45 (d, *J* = 12.9 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 176.9, 156.5, 150.2, 144.9, 135.3, 135.1, 133.9, 132.2, 129.0, 129.0, 128.6, 128.6, 128.6, 128.4, 128.4, 127.6, 127.5, 127.5, 124.8, 120.0, 116.4, 116.4, 115.1, 110.8, 110.2, 66.6, 55.7, 44.1, 41.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{29}H_{26}N_3O_4$ $[M+H]^+$: 480.1918, found: 480.1925; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 245 nm): t_{major} = 57.3 min, t_{minor} = 63.9 min.

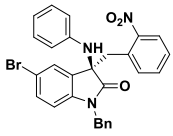
(*R*)-1-Benzyl-5-methyl-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5e)**



5e

Yellow oil, 32.4 mg, 70% yield, 72% ee, $[\alpha]_D^{20}$=184.2 (c = 0.26, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.34-7.29 (m, 2H), 7.22-7.21 (m, 3H), 7.03-7.02 (m, 2H), 6.94-6.91 (m, 4H), 6.71-6.67 (m, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.23 (d, *J* = 7.9 Hz, 2H), 4.94 (d, *J* = 15.5 Hz, 1H), 4.56 (brs, 1H), 4.38 (d, *J* = 15.5 Hz, 1H), 4.28 (d, *J* = 12.9 Hz, 1H), 3.46 (d, *J* = 12.9 Hz, 1H), 2.23 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 177.0, 150.3, 145.0, 139.3, 135.4, 133.9, 133.3, 132.1, 129.6, 129.0, 129.0, 128.6, 128.6, 128.5, 128.3, 127.6, 127.6, 127.6, 127.4, 125.4, 124.7, 119.8, 116.3, 116.3, 109.2, 66.2, 44.0, 41.0, 21.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{29}H_{26}N_3O_3$ $[M+H]^+$: 464.1969, found: 464.1963; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 245 nm): t_{major} = 38.7 min, t_{minor} = 43.3 min.

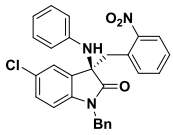
(*R*)-1-Benzyl-5-bromo-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5f)**



5f

Yellow solid, 39.6 mg, 75% yield, 83% ee, m.p. 175-177 °C, $[\alpha]_D^{20}$=200.9 (c = 0.45, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.81-7.79 (m, 1H), 7.46-7.37 (m, 2H), 7.29-7.21 (m, 5H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.03-7.00 (m, 2H), 6.97-6.92 (m, 2H), 6.75-6.71 (m, 1H), 6.45 (d, *J* = 8.3 Hz, 1H), 6.23-6.21 (m, 2H), 4.98 (d, *J* = 15.5 Hz, 1H), 4.60 (s, 1H), 4.41 (d, *J* = 15.5 Hz, 1H), 4.21 (d, *J* = 13.2 Hz, 1H), 3.45 (d, *J* = 13.2 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 176.7, 150.2, 144.5, 140.8, 134.8, 133.9, 132.4, 132.3, 130.0, 129.1, 129.1, 128.8, 128.8, 128.7, 128.2, 127.9, 127.9, 127.6, 127.6, 125.1, 120.3, 116.6, 116.6, 116.3, 111.0, 66.0, 44.1, 41.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{23}N_3O_3Br$ $[M+H]^+$: 528.0917, found: 528.0897; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 245 nm): t_{major} = 49.2 min, t_{minor} = 44.7 min.

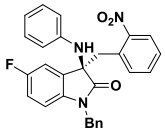
(*R*)-1-Benzyl-5-chloro-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5g)**



5g

Yellow solid, 29.0 mg, 60% yield, 92% ee, m.p. 160-163 °C, $[\alpha]_D^{20}$=210.9 (c = 0.51, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46-7.36 (m, 2H), 7.28-7.20 (m, 4H), 7.12 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.03-7.00 (m, 3H), 6.97-6.92 (m, 2H), 6.75-6.71 (m, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 6.23-6.21 (m, 2H), 4.98 (d, *J* = 15.5 Hz, 1H), 4.60 (s, 1H), 4.41 (d, *J* = 15.5 Hz, 1H), 4.21 (d, *J* = 13.2 Hz, 1H), 3.46 (d, *J* = 13.2 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 176.8, 150.2, 144.5, 140.3, 134.8, 133.9, 132.4, 129.6, 129.4, 129.1, 129.1, 129.0, 128.8, 128.8, 128.7, 128.2, 127.9, 127.6, 127.6, 125.2, 125.0, 120.3, 116.6, 116.6, 110.5, 66.1, 44.2, 41.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{23}N_3O_3Cl$ $[M+H]^+$: 484.1422, found: 484.1405; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 31.7 min, t_{minor} = 25.9 min.

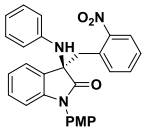
(*R*)-1-Benzyl-5-fluoro-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5h)**



5h

Yellow oil, 42.5 mg, 91% yield, 92% ee, $[\alpha]_D^{20}$=212.7 (c = 0.70, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.77 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46-7.36 (m, 2H), 7.31-7.29 (m, 1H), 7.24-7.21 (m, 3H), 7.02-7.00 (m, 2H), 6.96-6.92 (m, 2H), 6.87-6.82 (m, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.48 (dd, *J* = 8.2, 3.9 Hz, 1H), 6.23 (dd, *J* = 8.6, 0.9 Hz, 2H), 4.97 (d, *J* = 15.5 Hz, 1H), 4.59 (brs, 1H), 4.41 (d, *J* = 15.6 Hz, 1H), 4.22 (d, *J* = 13.1 Hz, 1H), 3.48-3.45 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 177.0, 159.6 (d, *J* = 243.3 Hz), 150.3, 144.6, 137.8, 135.0, 133.9, 132.4, 129.6 (d, *J* = 7.7 Hz), 129.0, 129.0, 128.8, 128.8, 128.7, 128.2, 127.8, 127.5, 127.5, 125.0, 120.3, 116.6, 116.6, 115.8 (d, *J* = 23.6 Hz), 112.9 (d, *J* = 24.9 Hz), 110.3 (d, *J* = 8.0 Hz), 66.3, 44.2, 41.0 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -118.99 (td, *J* = 8.3, 4.0 Hz) ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{23}N_3O_3F$ $[M+H]^+$: 468.1718, found: 468.1701; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 33.9 min, t_{minor} = 27.6 min.

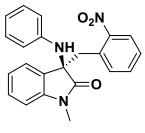
(*R*)-1-(4-Methoxyphenyl)-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5i)**



5i

Yellow solid, 31.6 mg, 68% yield, 83% ee, m.p. 115-118 °C, $[\alpha]_D^{20}$=96.8 (c = 0.56, MeOH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.73-7.71 (m, 1H), 7.46-7.35 (m, 3H), 7.24-7.15 (m, 2H), 7.06-6.92 (m, 5H), 6.85-6.83 (m, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.34-6.32 (m, 2H), 4.64 (brs, 1H), 4.45 (d, *J* = 12.7 Hz, 1H), 3.82 (s, 3H), 3.51 (d, *J* = 12.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 176.6, 159.3, 150.1, 145.0, 143.1, 134.1, 132.4, 129.4, 129.0, 129.0, 128.5, 128.4, 127.5, 127.5, 126.9, 126.5, 124.9, 124.8, 124.0, 119.7, 115.7, 115.7, 114.9, 114.9, 109.4, 66.3, 55.5, 41.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{24}N_3O_4$ $[M+H]^+$: 466.1761, found: 466.1751; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 32.5 min, t_{minor} = 18.4 min.

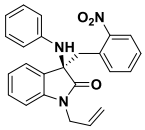
(*R*)-1-Methyl-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5j)**



5j

Yellow solid, 18.7 mg, 50% yield, 76% ee, m.p. 138-142 °C, $[\alpha]_D^{20}$=149.1 (c = 0.11, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.46-7.42 (m, 1H), 7.34-7.24 (m, 3H), 7.08-6.92 (m, 4H), 6.67-6.63 (m, 2H), 6.18 (dd, *J* = 8.6, 0.9 Hz, 2H), 4.60 (brs, 1H), 4.25 (d, *J* = 12.9 Hz, 1H), 3.41 (d, *J* = 12.9 Hz, 1H), 3.01 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 177.1, 150.1, 144.9, 142.5, 133.8, 132.0, 129.5, 129.0, 129.0, 128.5, 128.4, 127.4, 124.8, 124.5, 123.5, 119.5, 115.4, 115.4, 108.2, 66.0, 41.2, 26.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{22}H_{20}N_3O_3$ $[M+H]^+$: 374.1499, found: 374.1491; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (*n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 245 nm): t_{major} = 67.3 min, t_{minor} = 88.2 min.

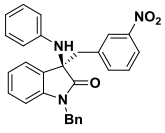
(*R*)-1-Allyl-3-(2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5k)**



5k

Yellow oil, 13.2 mg, 33% yield, 97% ee, $[\alpha]_D^{20}$=133.9 (c = 0.16, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.71 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35-7.29 (m, 2H), 7.25-7.21 (m, 1H), 7.12-7.11 (m, 1H), 7.02-6.99 (m, 1H), 6.95-6.92 (m, 2H), 6.68-6.65 (m, 2H), 6.22 (d, *J* = 7.8 Hz, 2H), 5.53-5.46 (m, 1H), 5.08 (dd, *J* = 10.3, 1.0 Hz, 1H), 4.98-4.94 (m, 1H), 4.55 (brs, 1H), 4.26 (d, *J* = 12.9 Hz, 1H), 4.14 (d, *J* = 5.5 Hz, 2H), 3.45 (d, *J* = 12.9 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 176.8, 150.2, 144.8, 142.0, 134.0, 132.3, 131.0, 129.4, 128.9, 128.9, 128.5, 128.4, 127.4, 124.8, 124.7, 123.4, 119.8, 118.0, 116.1, 116.1, 109.3, 66.1, 42.5, 41.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{24}H_{22}N_3O_3$ $[M+H]^+$: 400.1656, found: 400.1655; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 245 nm): t_{major} = 38.6 min, t_{minor} = 42.0 min.

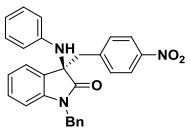
(*R*)-1-Benzyl-3-(3-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5l)**



5l

Yellow oil, 21.6 mg, 48% yield, 78% ee, $[\alpha]_D^{20}$=78.6 (c = 0.17, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.00-7.97 (m, 1H), 7.59-7.58 (m, 1H), 7.43 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.24-7.09 (m, 7H), 6.99-6.95 (m, 2H), 6.89-6.87 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.2 Hz, 1H), 6.33-6.31 (m, 2H), 4.82 (d, *J* = 15.5 Hz, 1H), 4.46 (brs, 1H), 4.34 (d, *J* = 15.5 Hz, 1H), 3.42 (s, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 176.6, 147.6, 144.8, 142.2, 136.5, 135.3, 135.0, 129.7, 129.1, 129.1, 128.6, 128.6, 128.6, 128.1, 127.7, 127.4, 127.4, 125.0, 124.3, 123.3, 122.3, 120.2, 116.6, 116.6, 109.7, 66.2, 45.6, 43.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{24}N_3O_3$ $[M+H]^+$: 450.1812, found: 450.1822; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 25.5 min, t_{minor} = 10.1 min.

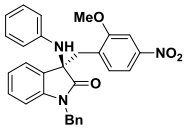
(*R*)-1-Benzyl-3-(4-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5m)**



5m

Yellow oil, 30.1 mg, 67% yield, 70% ee, $[\alpha]_D^{20}$=16.1 (c = 0.34, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.86-7.84 (m, 2H), 7.43 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.22-7.08 (m, 5H), 6.99-6.94 (m, 4H), 6.89-6.87 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.33-6.30 (m, 2H), 4.76 (d, *J* = 15.5 Hz, 1H), 4.48-4.41 (m, 2H), 3.42 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 176.6, 147.1, 144.8, 142.3, 140.9, 135.0, 131.1, 131.1, 129.7, 129.1, 129.1, 128.6, 128.6, 128.2, 127.8, 127.5, 127.5, 124.2, 123.2, 122.8, 122.8, 120.2, 116.6, 116.6, 109.7, 66.2, 45.8, 43.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{24}N_3O_3$ $[M+H]^+$: 450.1812, found: 450.1807; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 17.4 min, t_{minor} = 10.6 min.

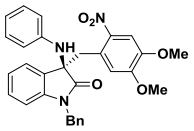
(*R*)-1-Benzyl-3-(2-methoxy-4-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5n)**



5n

Yellow solid, 25.8 mg, 54% yield, 60% ee, m.p. 158-162 °C, $[\alpha]_D^{20}$=64.6 (c = 0.22, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.64-7.62 (m, 2H), 7.27-7.25 (m, 3H), 7.19-7.15 (m, 3H), 6.99-6.90 (m, 5H), 6.71-6.64 (m, 2H), 6.15 (d, *J* = 7.8 Hz, 2H), 5.09 (brs, 1H), 5.00 (d, *J* = 15.4 Hz, 1H), 4.70 (d, *J* = 15.4 Hz, 1H), 3.86 (s, 3H), 3.76 (d, *J* = 12.8 Hz, 1H), 2.99 (d, *J* = 12.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 177.6, 158.2, 148.2, 145.0, 141.8, 135.5, 132.8, 130.6, 129.2, 129.2, 129.0, 128.7, 128.7, 128.3, 127.8, 127.7, 127.7, 125.2, 122.3, 119.3, 115.5, 115.5, 115.2, 109.5, 105.4, 65.9, 55.86, 44.1, 39.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{29}H_{26}N_3O_4$ $[M+H]^+$: 480.1918, found: 480.1909; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 19.5 min, t_{minor} = 13.6 min.

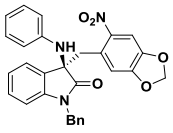
(*R*)-1-Benzyl-3-(4,5-dimethoxy-2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5o)**



5o

Yellow oil, 21.9 mg, 43% yield, 76% ee, $[\alpha]_D^{20}$=97.9 (c = 0.29, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.37 (s, 1H), 7.26-7.15 (m, 5H), 7.00-6.99 (m, 3H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.60-6.59 (m, 2H), 6.24 (d, *J* = 7.9 Hz, 2H), 4.93 (d, *J* = 15.5 Hz, 1H), 4.73 (brs, 1H), 4.54 (d, *J* = 15.6 Hz, 1H), 4.35 (d, *J* = 13.0 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.43 (d, *J* = 13.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 177.4, 151.9, 147.9, 144.9, 142.6, 142.1, 135.3, 129.4, 129.0, 129.0, 128.7, 128.7, 128.7, 128.0, 127.3, 127.3, 125.0, 123.2, 123.0, 119.9, 116.6, 116.6, 115.1, 109.5, 108.2, 66.5, 56.3, 56.2, 44.0, 40.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{30}H_{28}N_3O_5$ $[M+H]^+$: 510.2023, found: 510.2016; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 86.0 min, t_{minor} = 20.0 min.

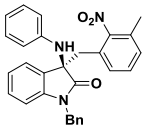
(*R*)-1-Benzyl-3-((6-nitrobenzo[*d*][1,3]dioxol-5-yl)methyl)-3-(phenylamino)indolin-2-one **(5p)**



5p

Yellow oil, 10.8 mg, 22% yield, 72% ee, $[\alpha]_D^{20}$= 101.8 (c = 0.11, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.29 (s, 1H), 7.24-7.23 (m, 3H), 7.19-7.14 (m, 2H), 7.05-6.90 (m, 5H), 6.71-6.68 (m, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.23 (d, *J* = 8.2 Hz, 2H), 6.05 (d, *J* = 3.6 Hz, 2H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.64-4.60 (m, 2H), 4.22 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 177.3, 150.9, 147.2, 144.8, 144.3, 142.1, 135.4, 129.4, 129.0, 129.0, 128.7, 128.7, 127.8, 127.6, 127.5, 127.5, 125.1, 124.8, 123.4, 120.0, 116.7, 116.7, 112.3, 109.6, 105.9, 102.9, 66.2, 44.1, 41.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{29}H_{24}N_3O_5$ $[M+H]^+$: 494.1710, found: 494.1684; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 40.6 min, t_{minor} = 62.5 min.

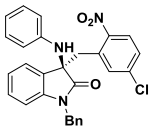
(*R*)-1-Benzyl-3-(3-methyl-2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5q)**



5q

Yellow oil, 31.4 mg, 68% yield, 88% ee, $[\alpha]_D^{20}$ = 129.1 (c = 0.35, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.24-7.17 (m, 6H), 7.11-6.97 (m, 5H), 6.94-6.90 (m, 2H), 6.71-6.64 (m, 2H), 6.23 (d, *J* = 8.0 Hz, 2H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.69-4.65 (m, 2H), 3.52 (d, *J* = 13.9 Hz, 1H), 3.22 (d, *J* = 13.9 Hz, 1H), 2.25 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 177.4, 152.3, 144.8, 142.0, 135.4, 130.7, 130.4, 130.1, 129.6, 129.4, 128.9, 128.9, 128.7, 128.7, 128.1, 127.6, 127.5, 127.5, 126.1, 125.0, 123.2, 119.9, 116.5, 116.5, 109.6, 65.5, 44.1, 40.6, 18.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{29}H_{26}N_3O_3$ $[M+H]^+$: 464.1969, found: 464.1975; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 61.4 min, t_{minor} = 21.8 min.

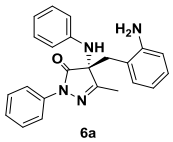
(*R*)-1-Benzyl-3-(5-chloro-2-nitrobenzyl)-3-(phenylamino)indolin-2-one **(5r)**



5r

Yellow oil, 10.1 mg, 21% yield, 68% ee, $[\alpha]_D^{20}$ = 57.5 (c = 0.16, MeOH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.7 Hz, 1H), 7.33-7.27 (m, 2H), 7.23-7.22 (m, 3H), 7.18-7.09 (m, 2H), 7.04-6.90 (m, 5H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 8.1 Hz, 2H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.54 (brs, 1H), 4.45 (d, *J* = 15.5 Hz, 1H), 4.24 (d, *J* = 13.0 Hz, 1H), 3.43 (d, *J* = 13.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 177.0, 148.4, 144.6, 141.9, 138.6, 135.2, 133.7, 130.8, 129.6, 129.0, 129.0, 128.7, 128.7, 128.5, 127.7, 127.4, 127.4, 127.3, 126.3, 124.7, 123.4, 120.4, 117.1, 117.1, 109.7, 66.2, 44.0, 40.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{28}H_{23}N_3O_3Cl$ $[M+H]^+$: 484.1422, found: 484.1399; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IA column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 245 nm): t_{major} = 16.5 min, t_{minor} = 21.4 min.

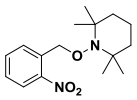
(*R*)-4-(2-Aminobenzyl)-5-methyl-2-phenyl-4-(phenylamino)-2,4-dihydro-3*H*-pyrazol-3-one **(6a)**



6a

Yellow oil, 26.3 mg,71% yield, 88% ee, $[\alpha]_D^{20}$ = 160.9 (c = 0.21, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10-7.05 (m, 3H), 6.97 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.74 (tt, *J* = 7.4, 1.5 Hz, 2H), 6.66 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.36 (d, *J* = 8.1 Hz, 2H), 5.22 (brs, 1H), 3.95 (brs, 2H), 3.20 (s, 2H), 2.08 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 174.2, 163.3, 145.6, 144.7, 137.7, 132.0, 129.6, 129.6, 129.2, 128.9, 128.9, 125.6, 119.6, 119.6, 119.3, 119.3, 118.0, 117.7, 113.4, 113.4, 70.2, 38.8, 14.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{23}H_{23}N_4O$ $[M+H]^+$: 371.1866, found: 317.1868; **HPLC analysis:** The enantiomeric excess was determined by HPLC with a Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm): t_{major} = 7.9 min, t_{minor} = 8.8 min.

2,2,6,6-Tetramethyl-1-((2-nitrobenzyl)oxy)piperidine **(8a)**[3]

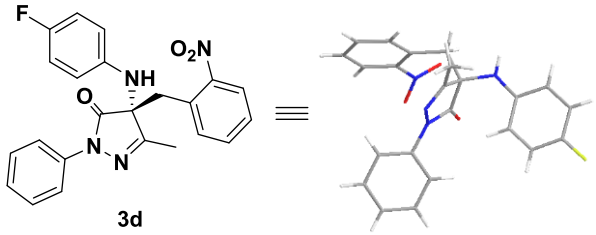


8a

Red oil, 19.9 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.05 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 1H), 7.67-7.63 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 5.20 (s, 2H), 1.58-1.48 (m, 5H), 1.38-1.33 (m, 1H), 1.18 (s, 12H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 146.9, 135.2, 133.5, 128.4, 127.4, 124.5, 75.0, 60.1, 39.7, 39.7, 39.7, 32.9, 32.9, 20.5, 20.5, 17.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{16}H_{25}N_2O_3$ $[M+H]^+$: 293.1860, found: 293.1865.

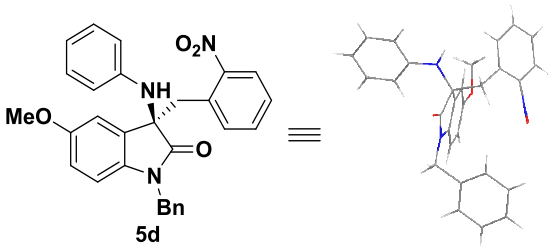
6. Data for X-Ray Crystal Structures of 3d and 5d

Table 1 Crystal data and structure refinement of **3d**



Empirical formula	$C_{23}H_{19}FN_4O_3$
Formula weight	418.42
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.22990(10)
b/Å	7.59620(10)
c/Å	11.50980(10)
α/°	90
β/°	91.8060(10)
γ/°	90
Volume/Å^3	981.351(18)
Z	2
ρ_{calc}mg/mm^3	1.416
μ/mm^{-1}	0.852
F(000)	436.0
2Θ range for data collection/°	7.684 to 156.392°
Index ranges	$-14 \le h \le 13$, $-9 \le k \le 8$, $-14 \le l \le 14$
Reflections collected	19231
Independent reflections	3917[R(int) = 0.0467]
Data/restraints/parameters	3917/1/282
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1= 0.0311, wR_2= 0.0812
Final R indexes [all data]	R_1= 0.0316, wR_2= 0.0817
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15

Table 2 Crystal data and structure refinement of **5d**



Empirical formula	$C_{29}H_{25}N_3O_4$
Formula weight	479.52
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.0511(4)
b/Å	19.4219(8)
c/Å	12.2312(4)
α/°	90
β/°	100.502(3)
γ/°	90
Volume/Å^3	2347.68(15)
Z	4
ρ_{calc}mg/mm^3	1.357
μ/mm^{-1}	0.743
F(000)	1008.0
Crystal size/mm^3	0.1 × 0.05 × 0.05
2Θ range for data collection/°	8.648 to 152.398
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 24$, $-14 \le l \le 15$
Reflections collected	17966
Independent reflections	4692[R(int) = 0.1039]
Data/restraints/parameters	4692/0/327
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.1841
Final R indexes [all data]	R_1 = 0.0885, wR_2 = 0.1957
Largest diff. peak/hole / e Å^{-3}	0.53/-0.67

7. References

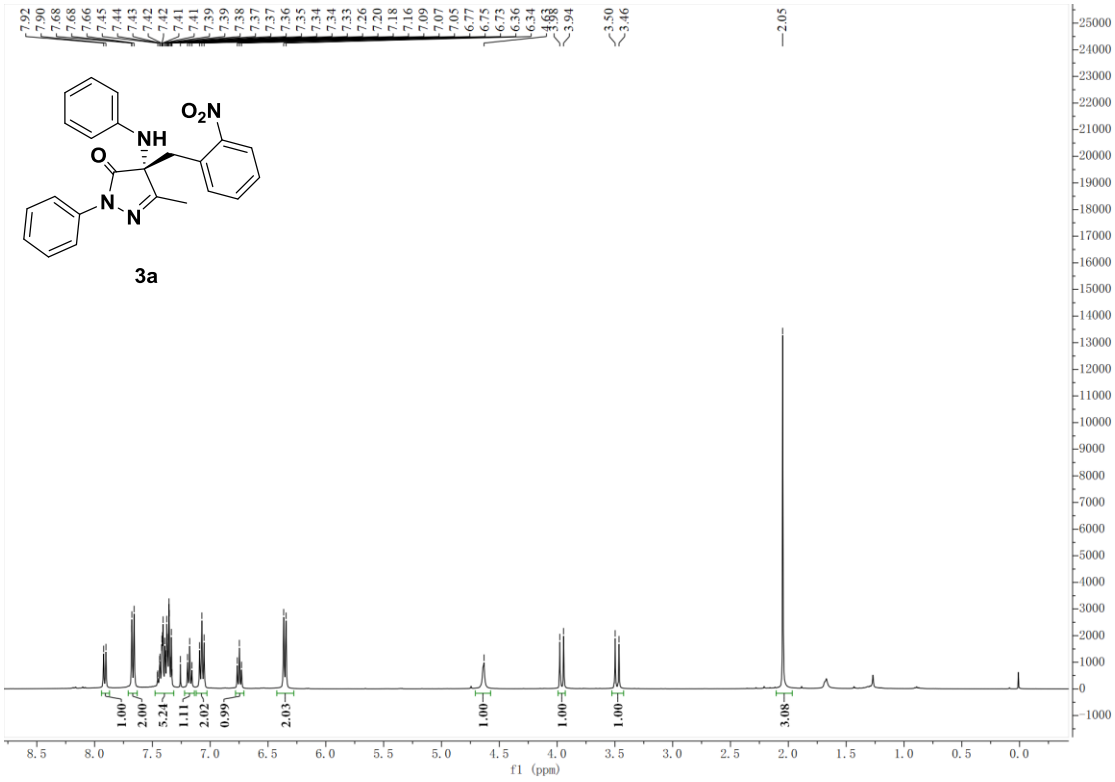
[1] (*a*) Y.-H. Shi, Z. Wang, Y. Shi, W.-P. Deng, *Tetrahedron* **2012**, *68*, 3649-3653; (*b*) S. Mahajan, P. Chauhan, U. Kaya, K. Deckers, K. Rissanen, D. Enders, *Chem. Commun.* **2017**, *53*, 6633-6636.

[2] (*a*) B.-S. Li, Y. Wang, R. S. J. Proctor, Y. Zhang, R. D. Webster, S. Yang, B. Song, Y. R. Chi, *Nat. Commun*. **2016**, *7*, 12933-12940; (*b*) Y. Wang, Y. Du, X. Huang, X. Wu, Y. Zhang, S. Yang, Y. R Chi, *Org. Lett*. **2017**, *19*, 632-635.

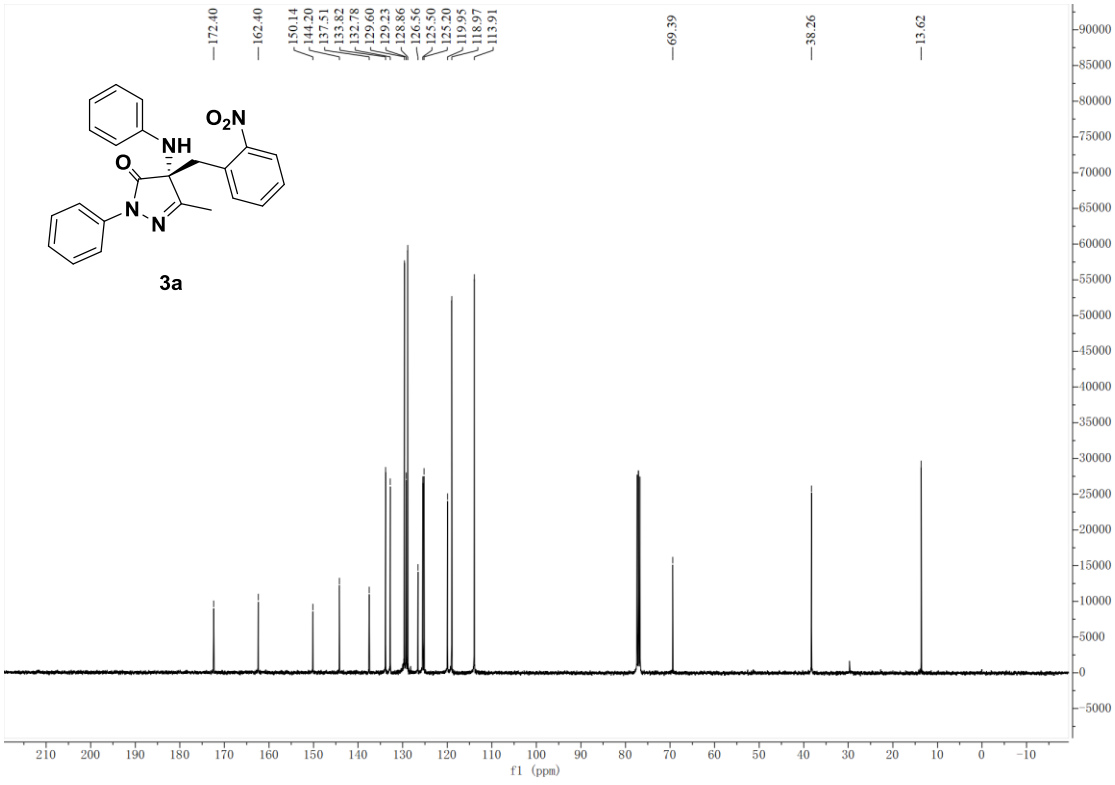
[3] R. Ding, B. Yu, *Asian Journal of Organic Chemistry*, **2018**, 7, 2427-2430.

8. Copies of NMR Spectra

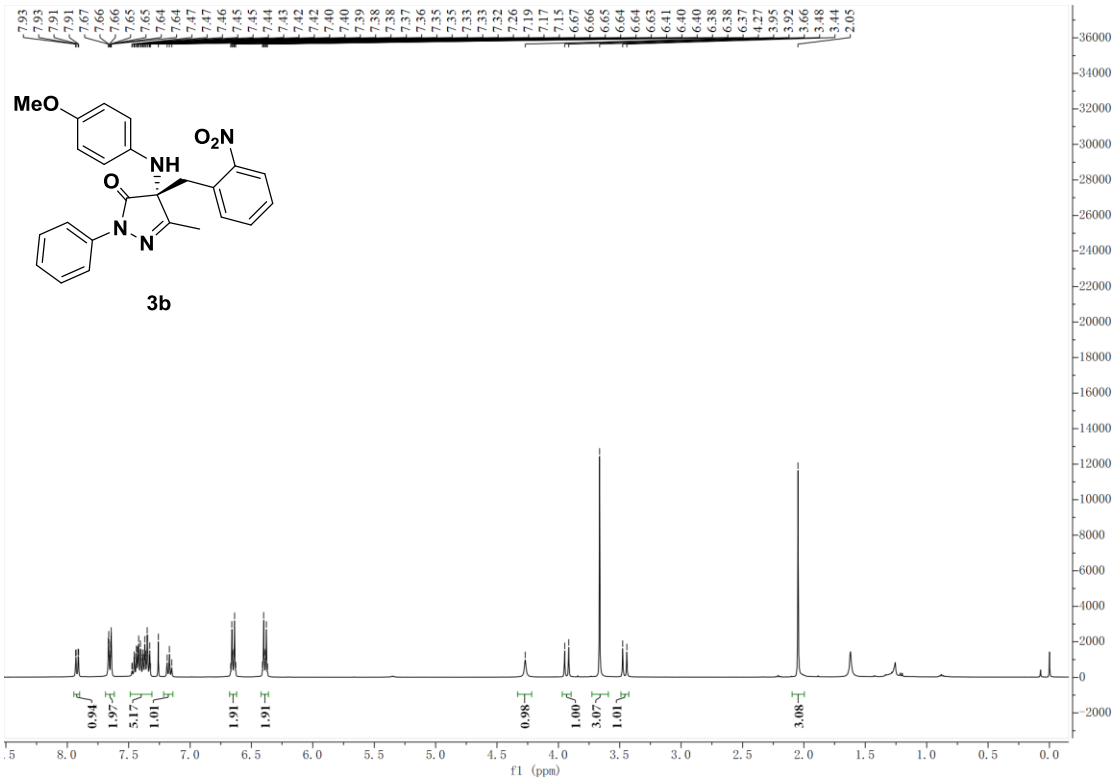
^{1}H NMR spectrum of compound 3a (in $CDCl_3$)



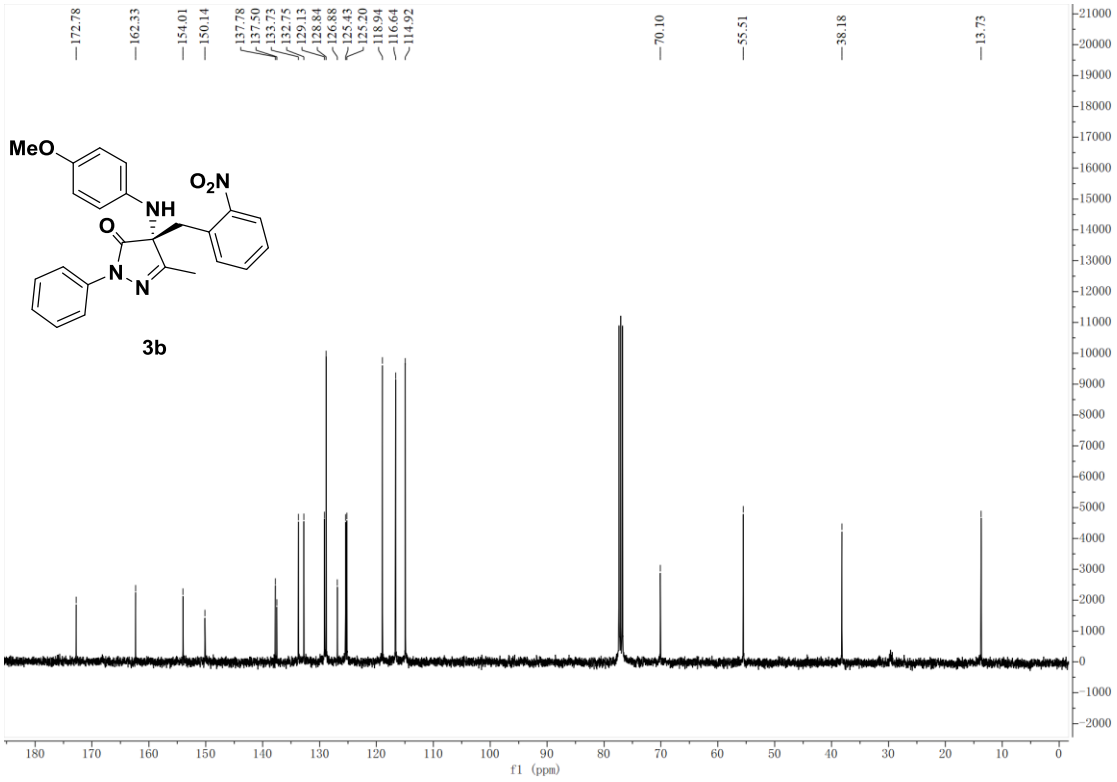
^{13}C NMR spectrum of compound 3a (in $CDCl_3$)



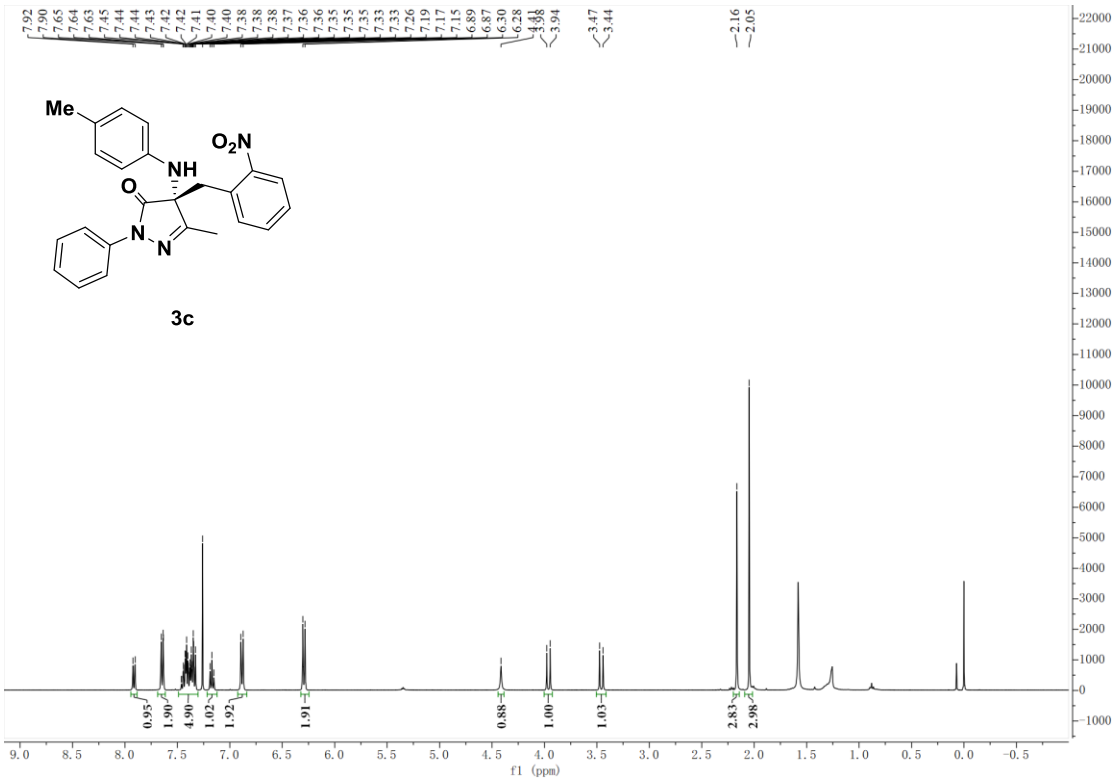
^{1}H NMR spectrum of compound 3b (in $CDCl_3$)



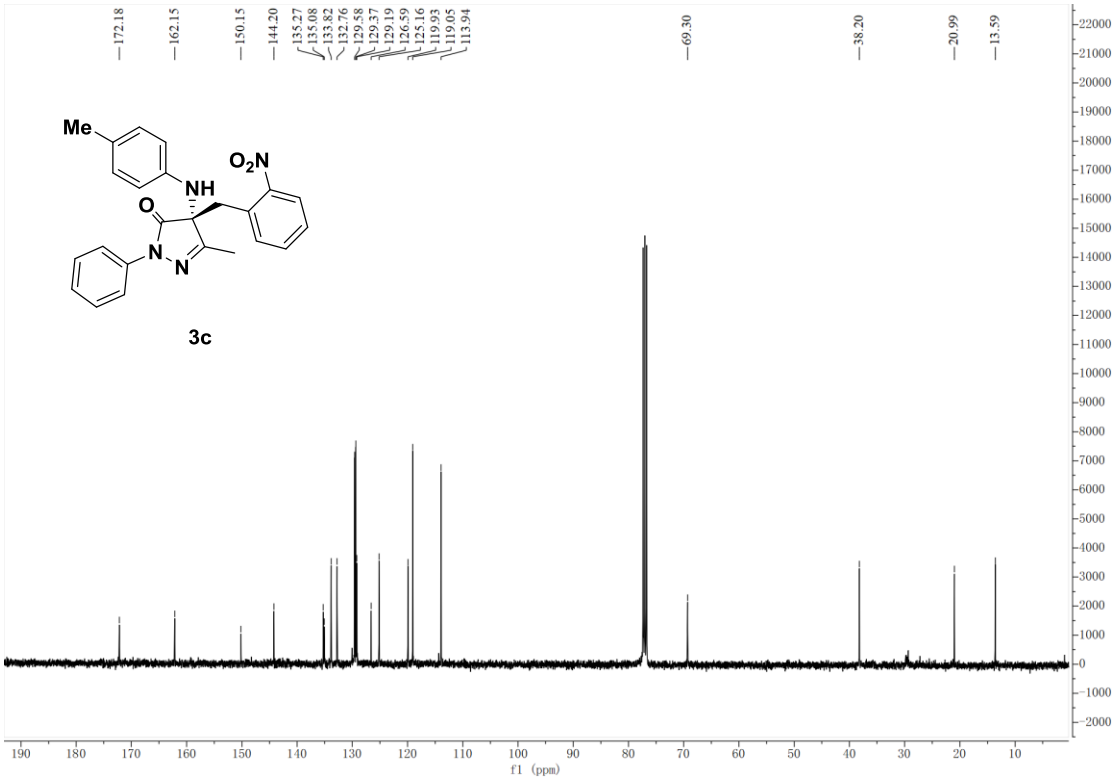
^{13}C NMR spectrum of compound 3b (in $CDCl_3$)



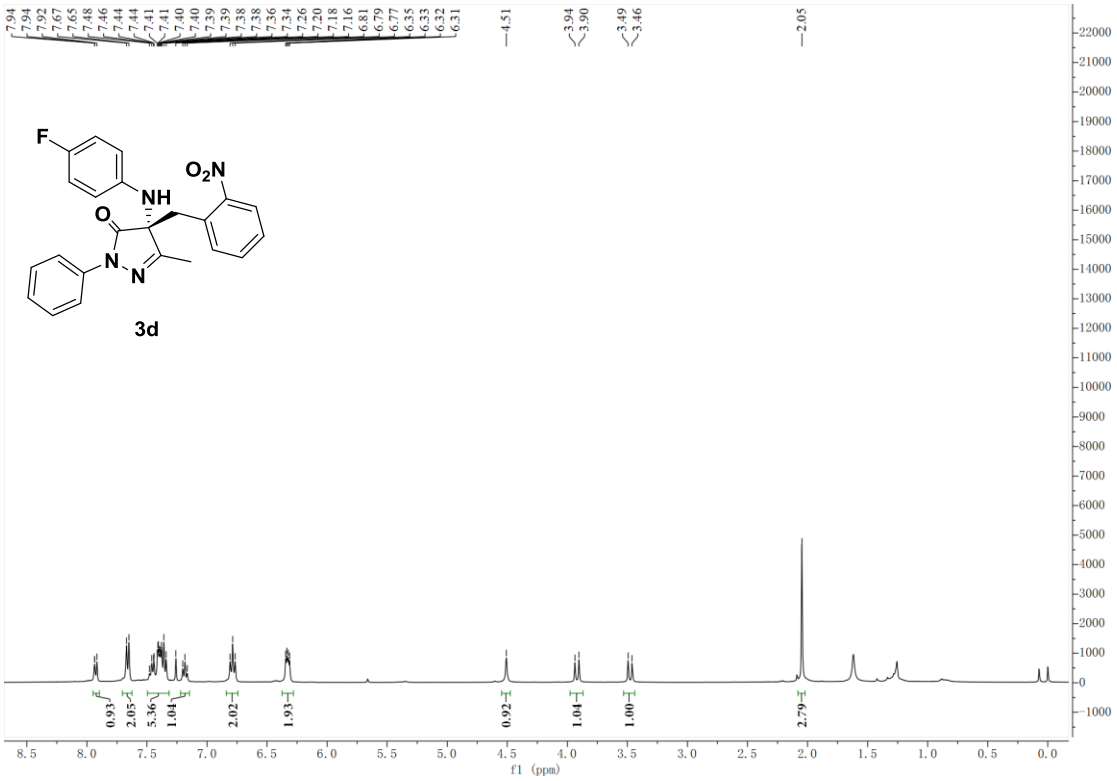
^{1}H NMR spectrum of compound 3c (in $CDCl_3$)



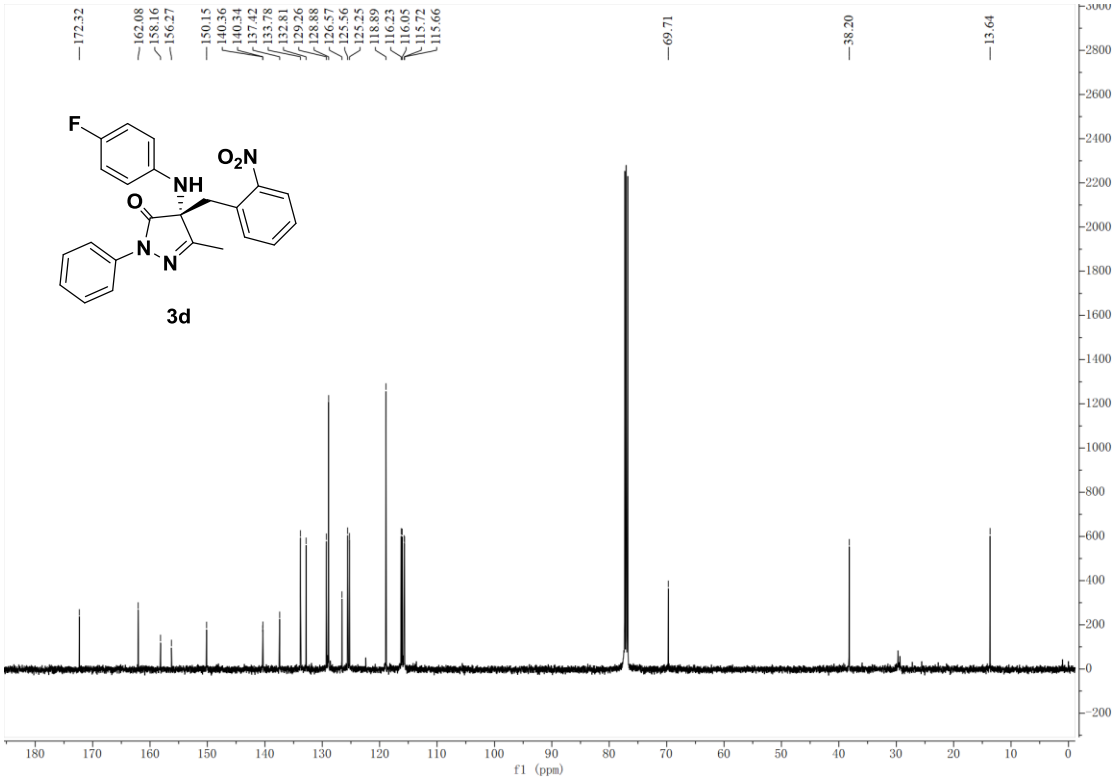
^{13}C NMR spectrum of compound 3c (in $CDCl_3$)



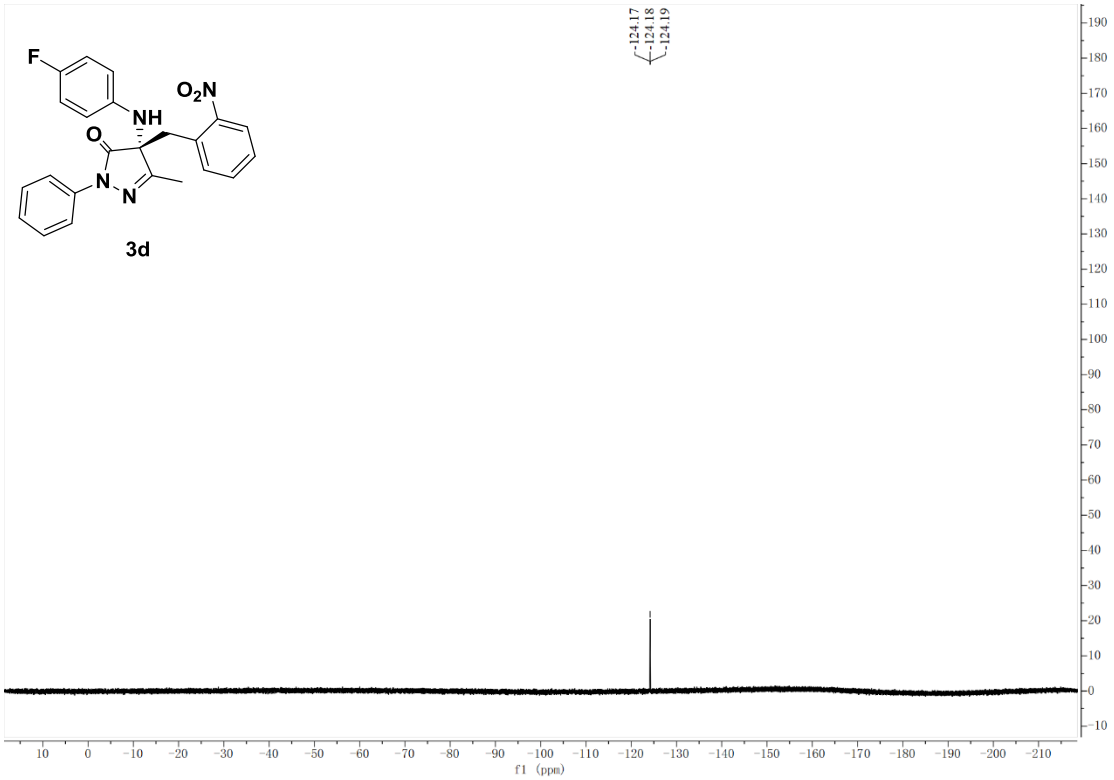
^{1}H NMR spectrum of compound 3d (in $CDCl_3$)



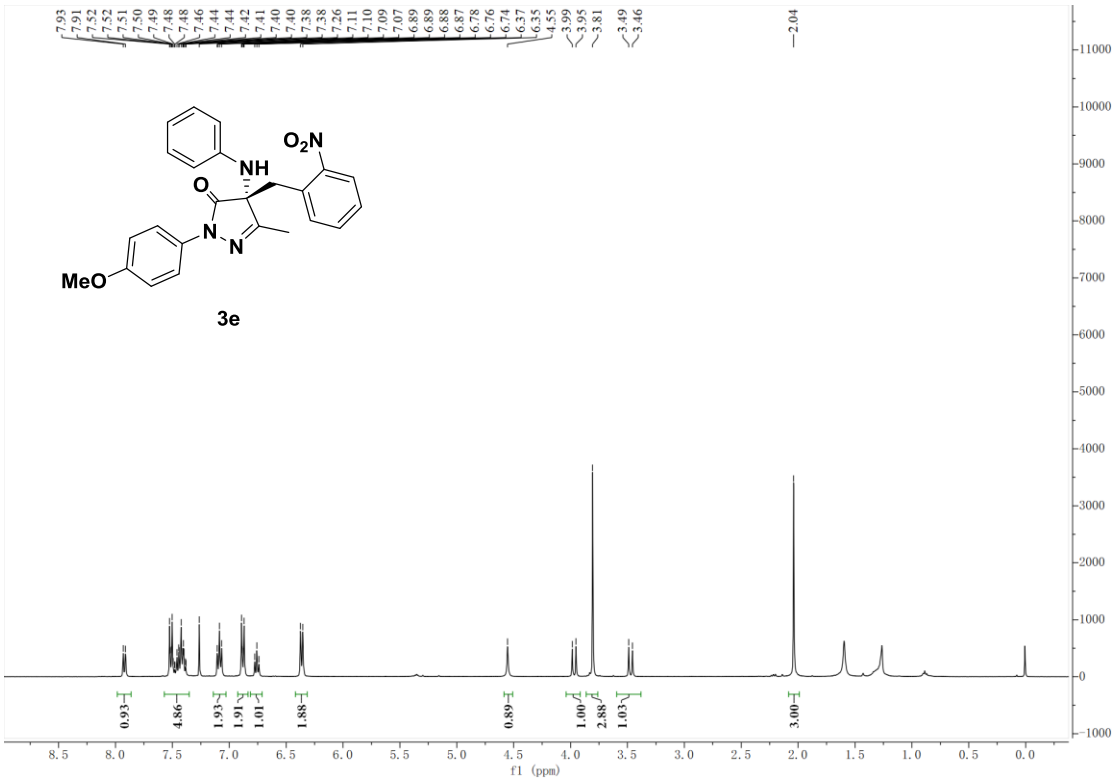
^{13}C NMR spectrum of compound 3d (in $CDCl_3$)



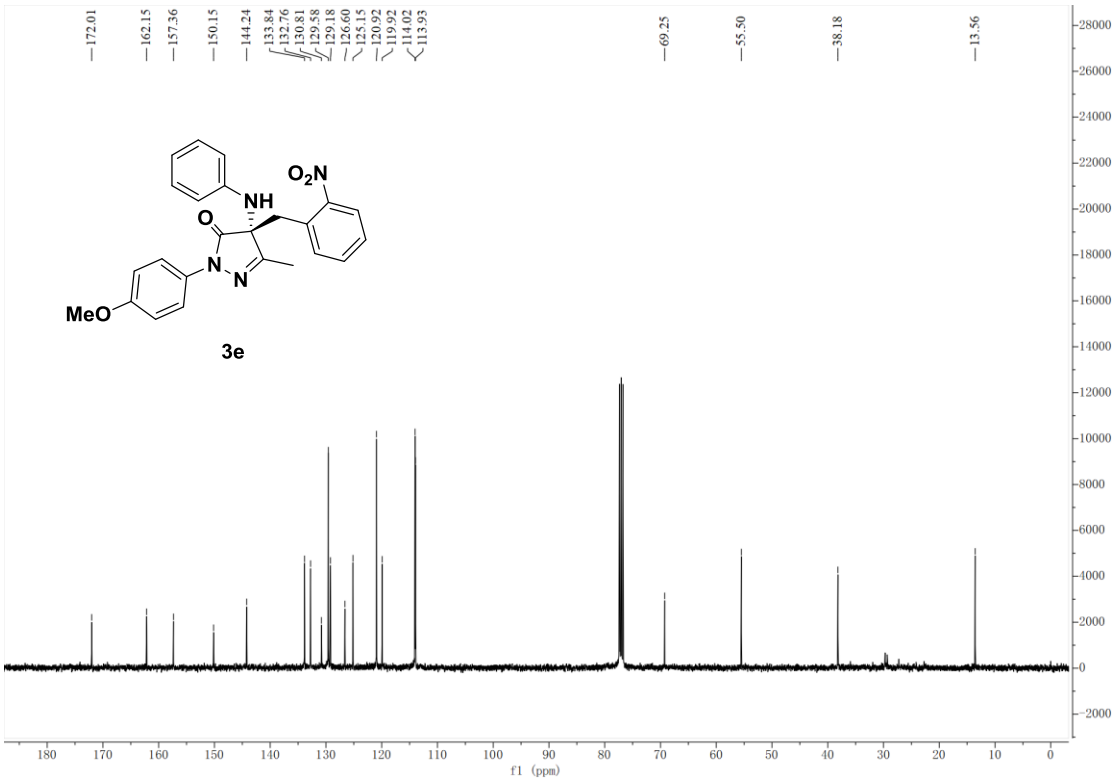
^{19}F NMR spectrum of compound 3d (in $CDCl_3$)



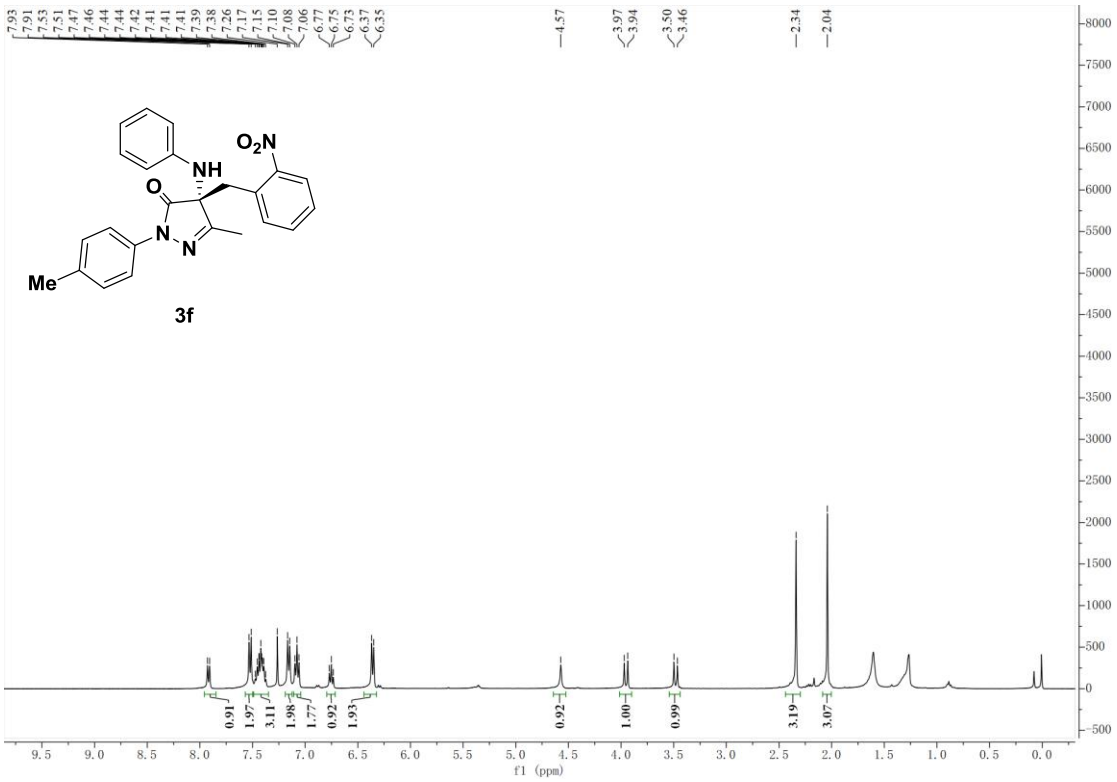
^{1}H NMR spectrum of compound 3e (in $CDCl_3$)



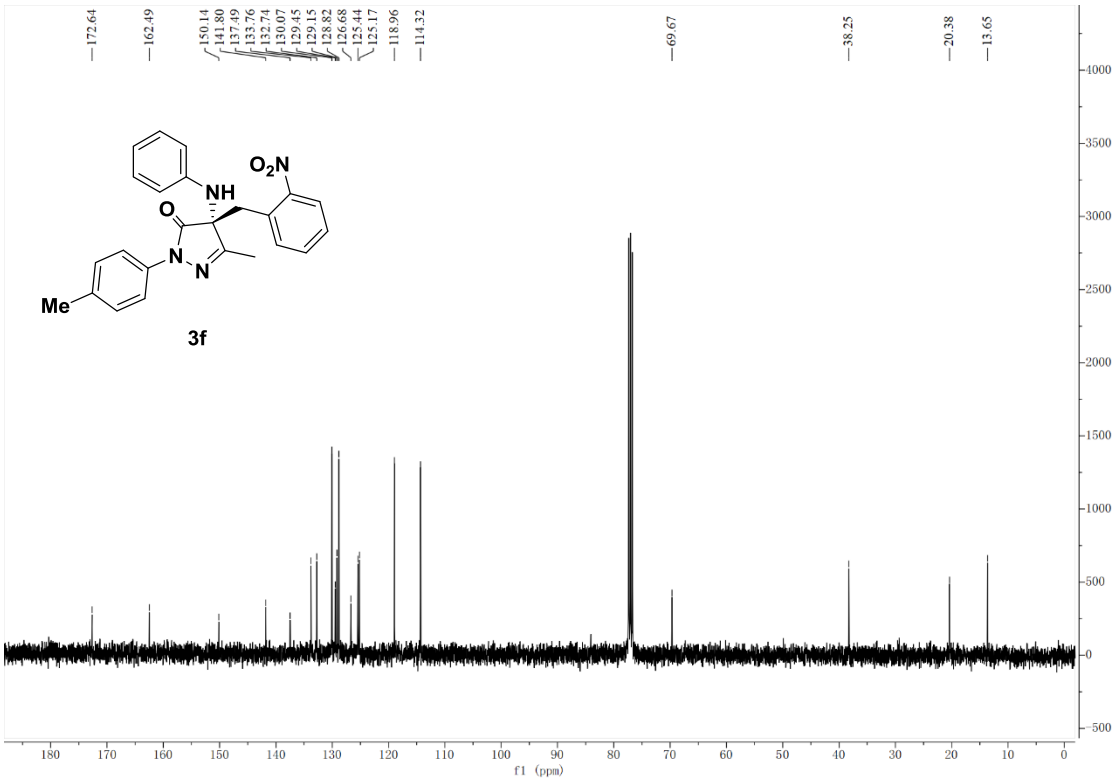
^{13}C NMR spectrum of compound 3e (in $CDCl_3$)



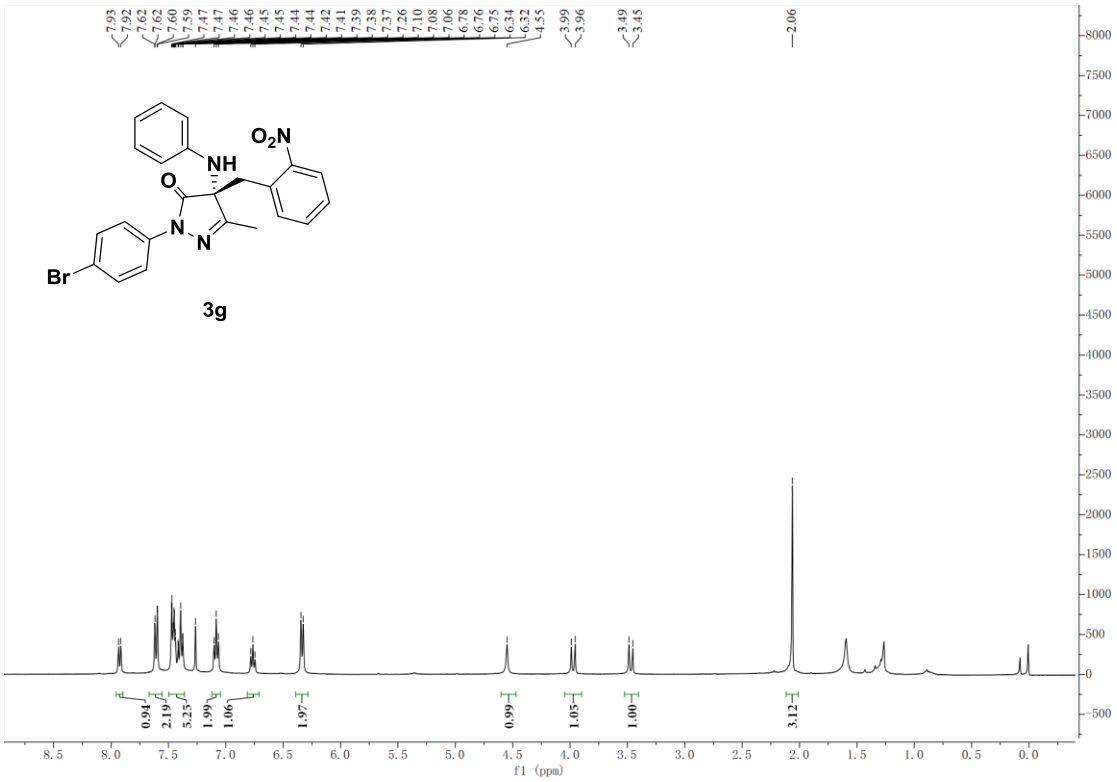
^{1}H NMR spectrum of compound 3f (in $CDCl_3$)



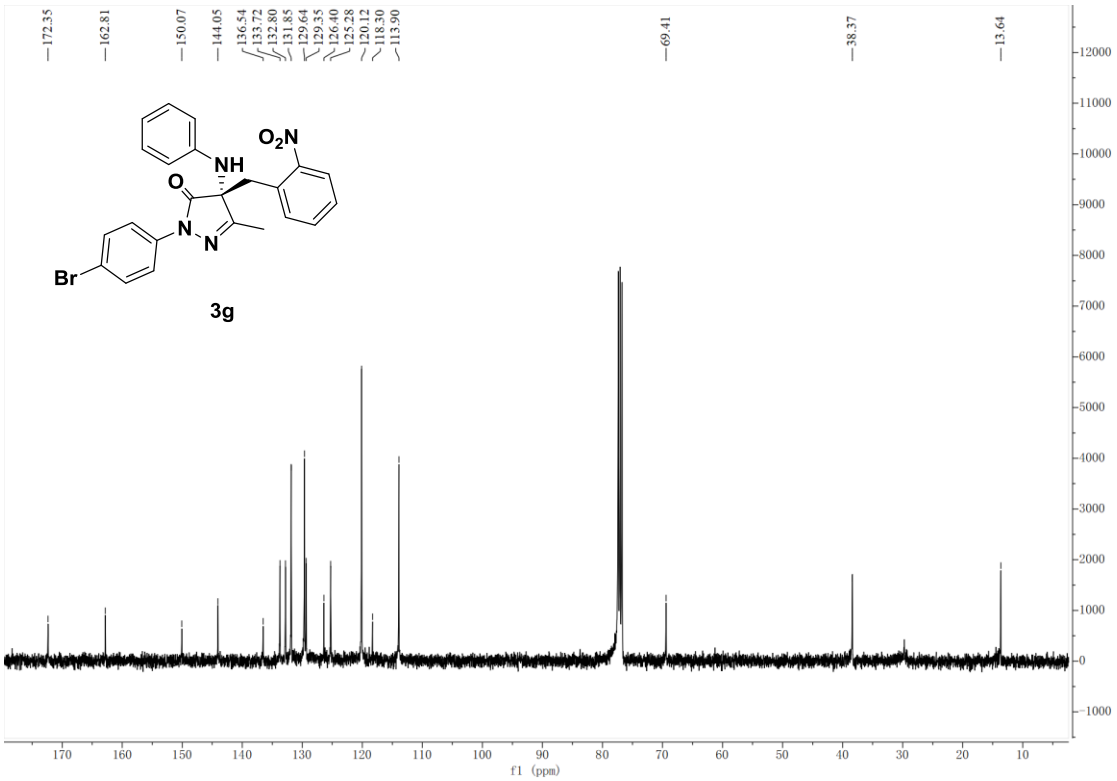
^{13}C NMR spectrum of compound 3f (in $CDCl_3$)



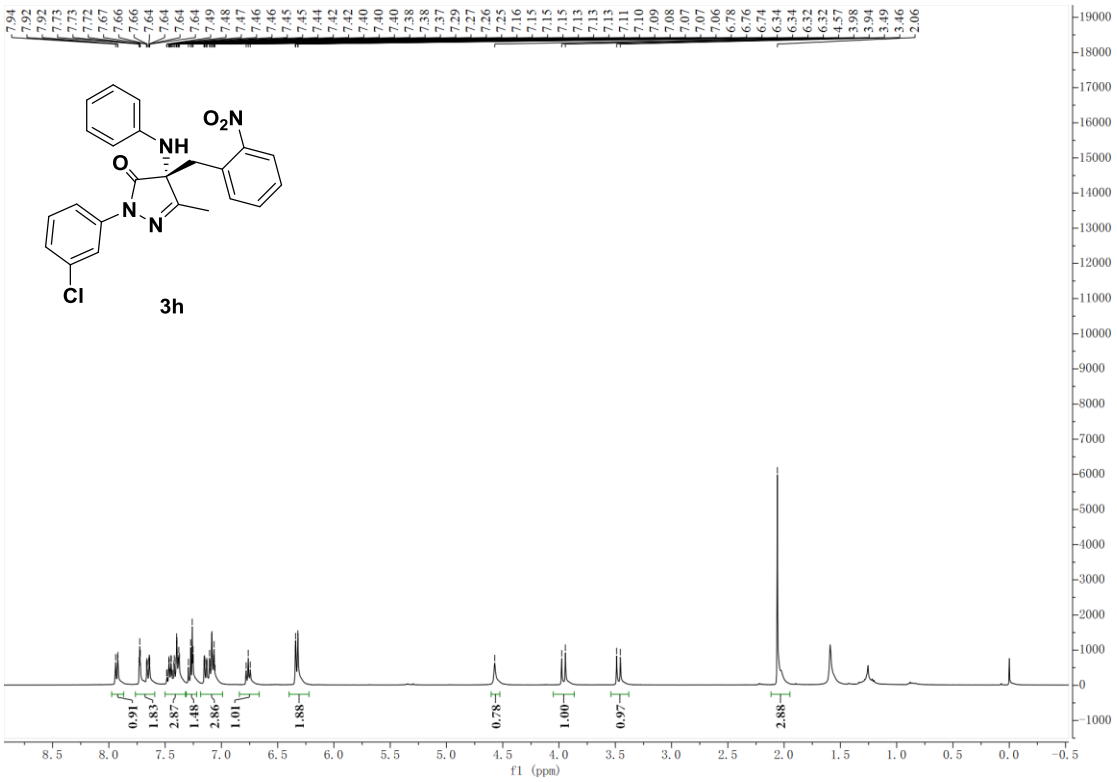
^{1}H NMR spectrum of compound 3g (in $CDCl_3$)



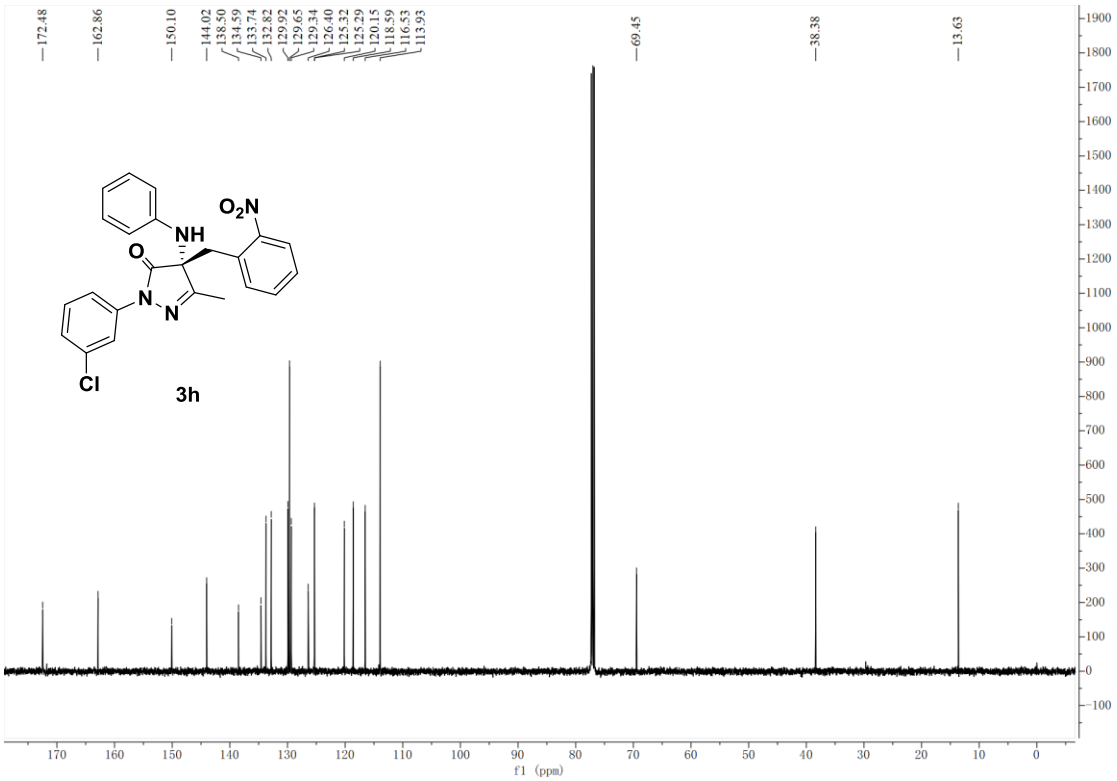
^{13}C NMR spectrum of compound 3g (in $CDCl_3$)



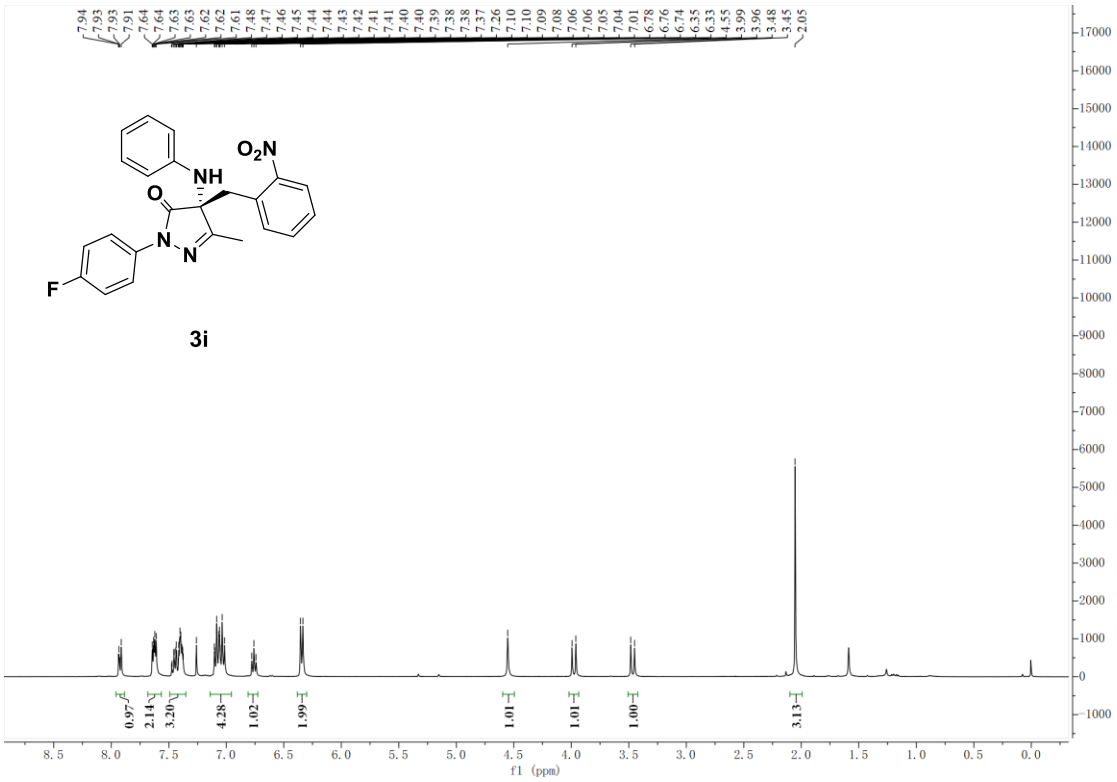
^{1}H NMR spectrum of compound 3h (in $CDCl_3$)



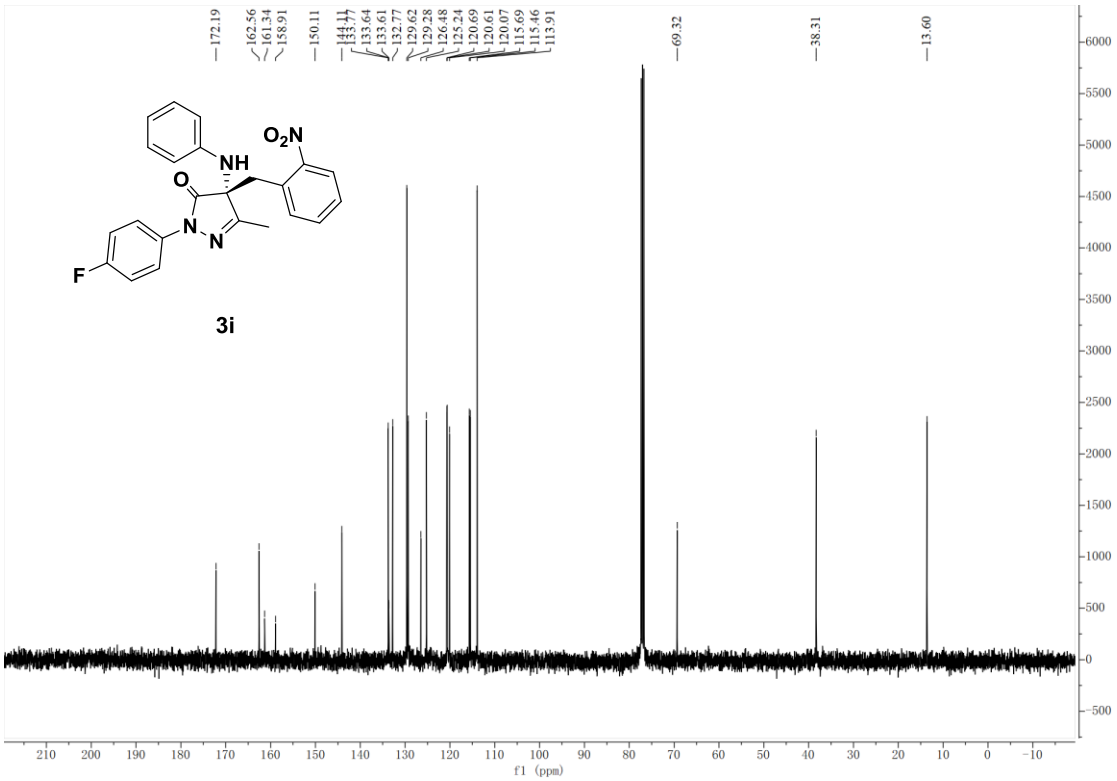
^{13}C NMR spectrum of compound 3h (in $CDCl_3$)



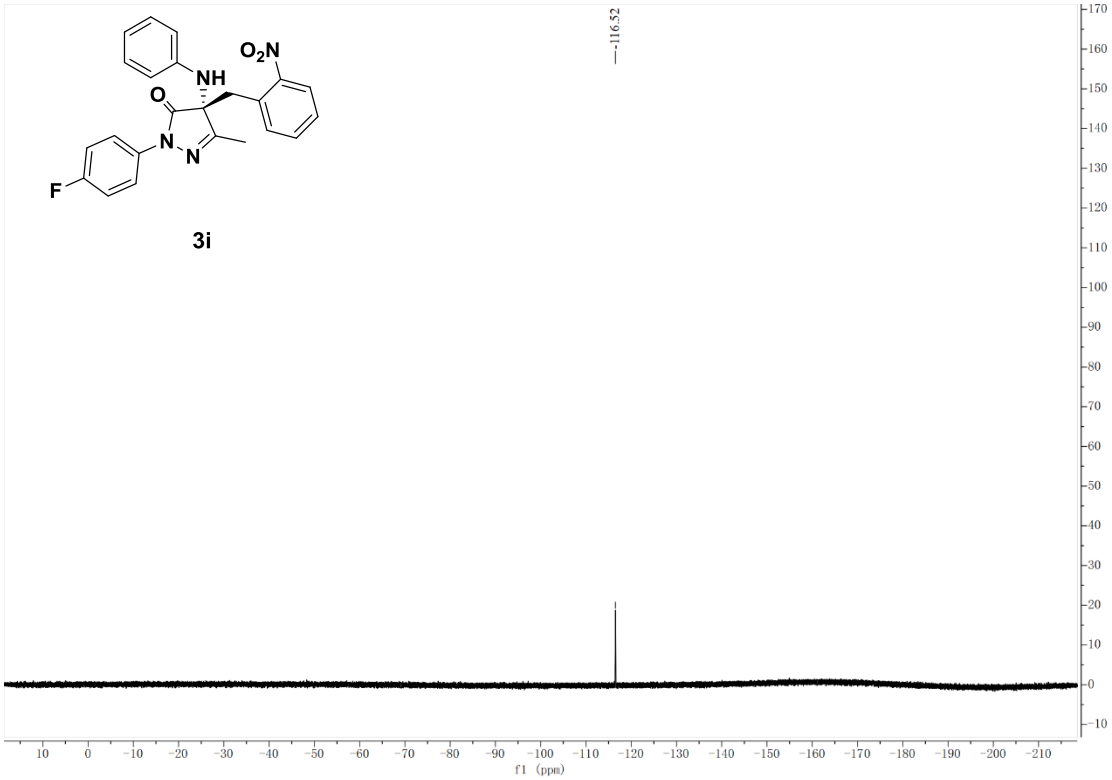
^{1}H NMR spectrum of compound 3i (in $CDCl_3$)



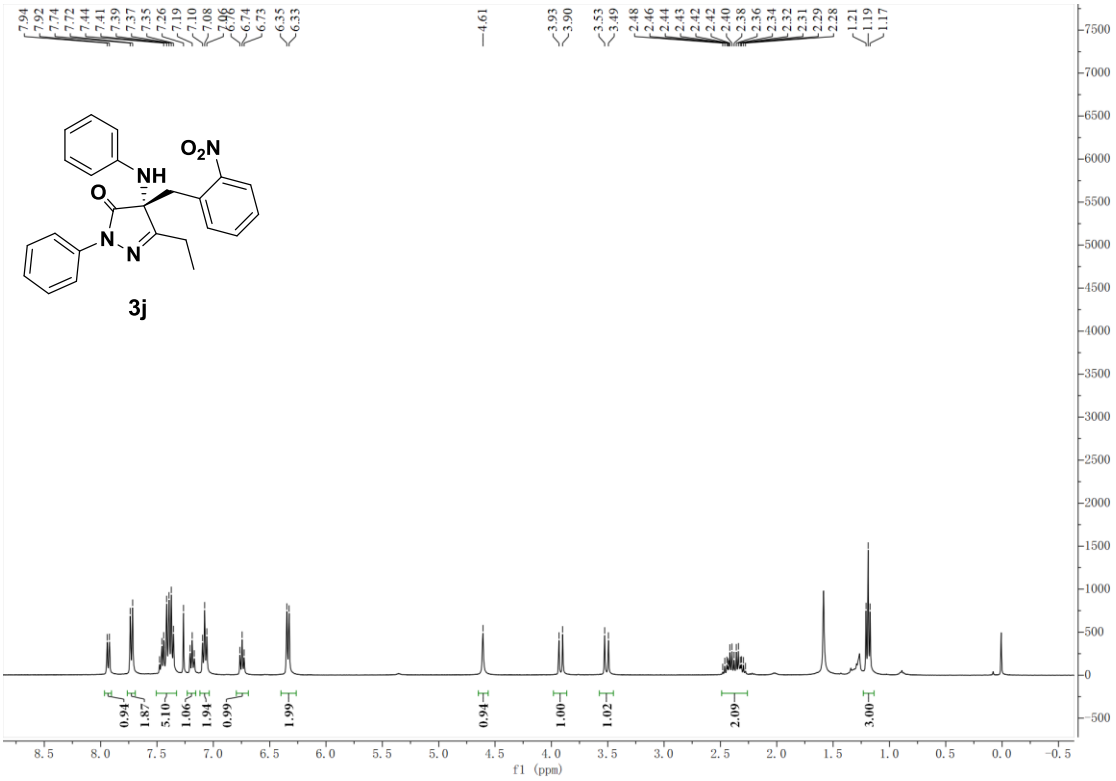
^{13}C NMR spectrum of compound 3i (in $CDCl_3$)



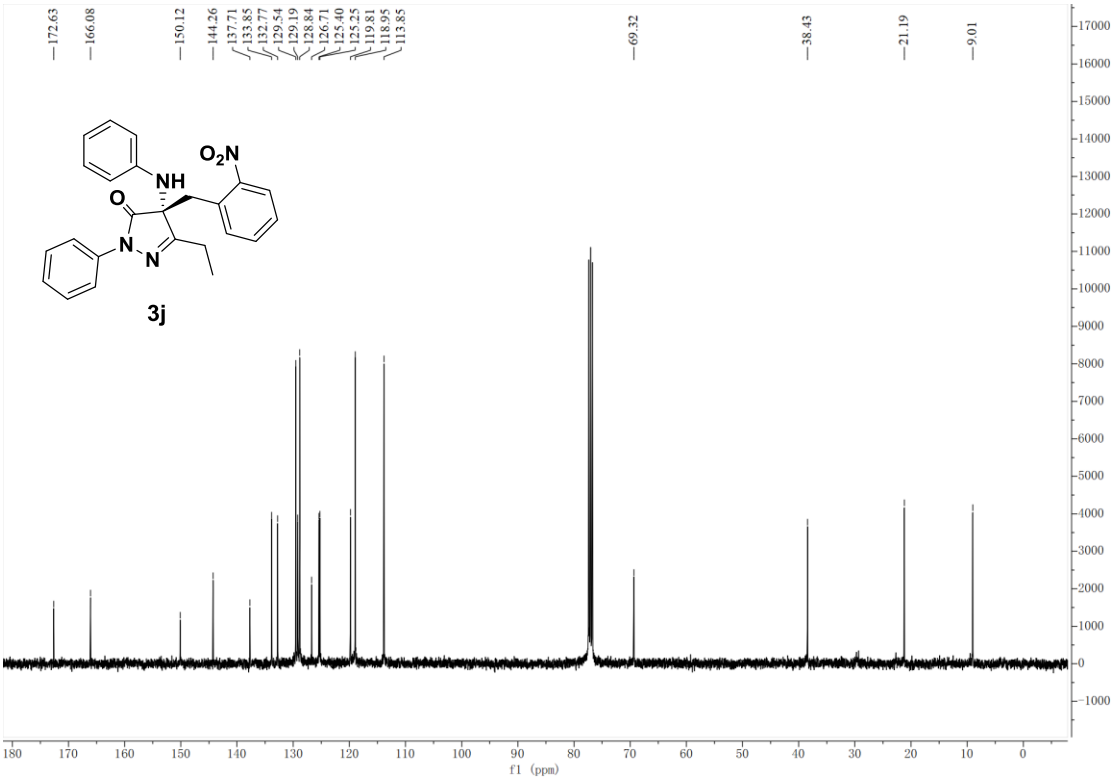
^{19}F NMR spectrum of compound 3i (in $CDCl_3$)



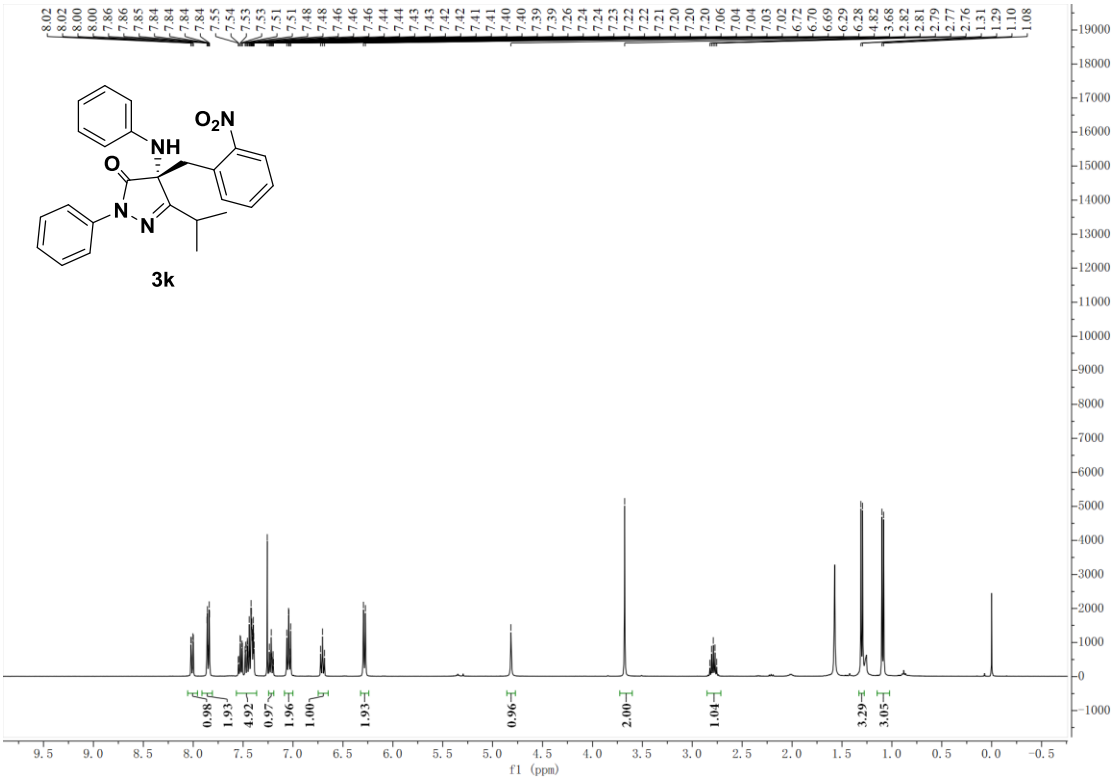
^{1}H NMR spectrum of compound 3j (in $CDCl_3$)



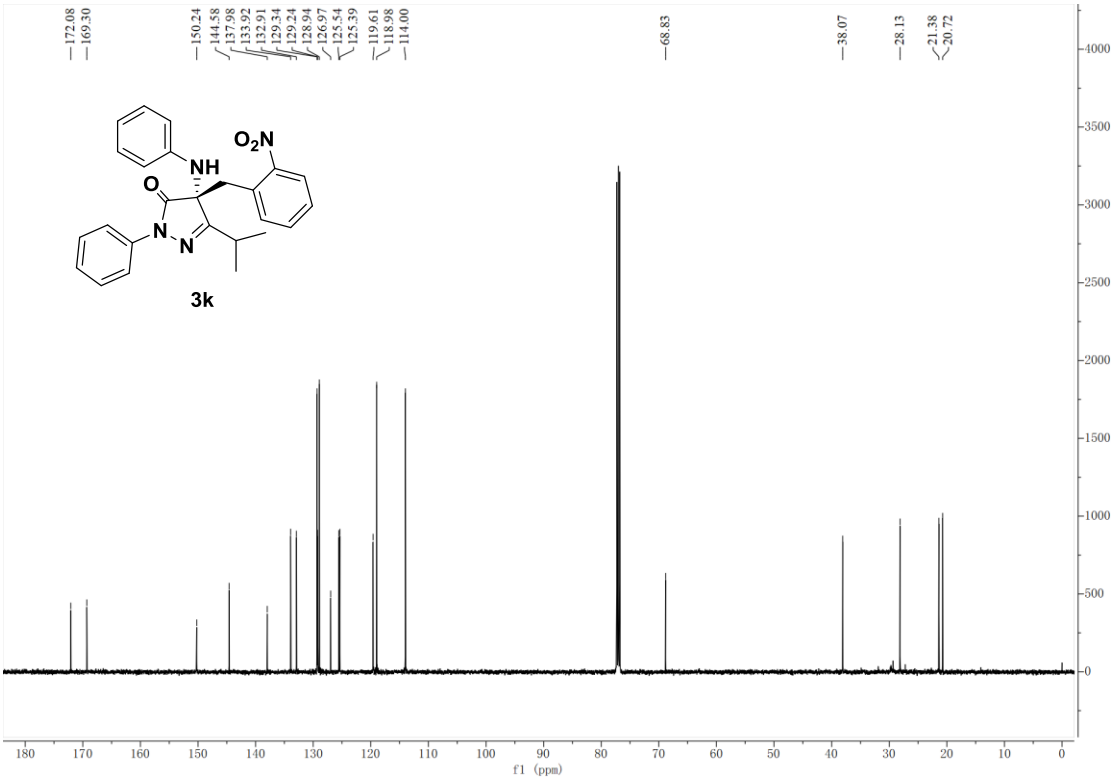
^{13}C NMR spectrum of compound 3j (in $CDCl_3$)



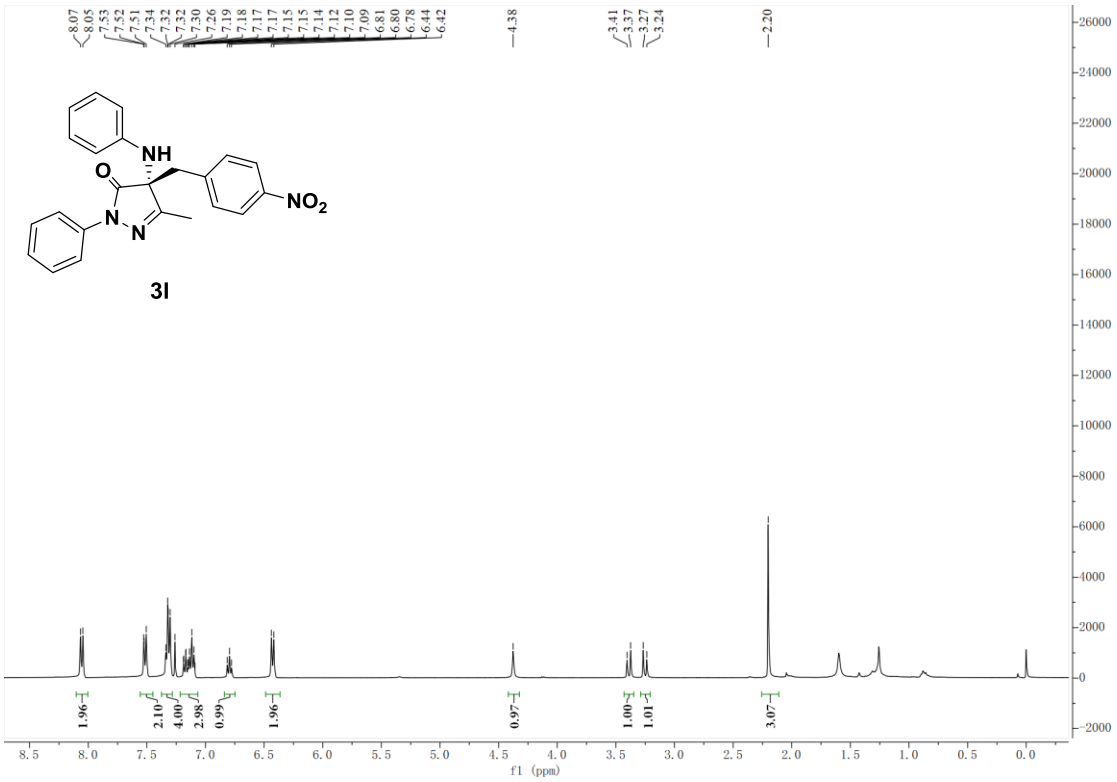
^{1}H NMR spectrum of compound 3k (in $CDCl_3$)



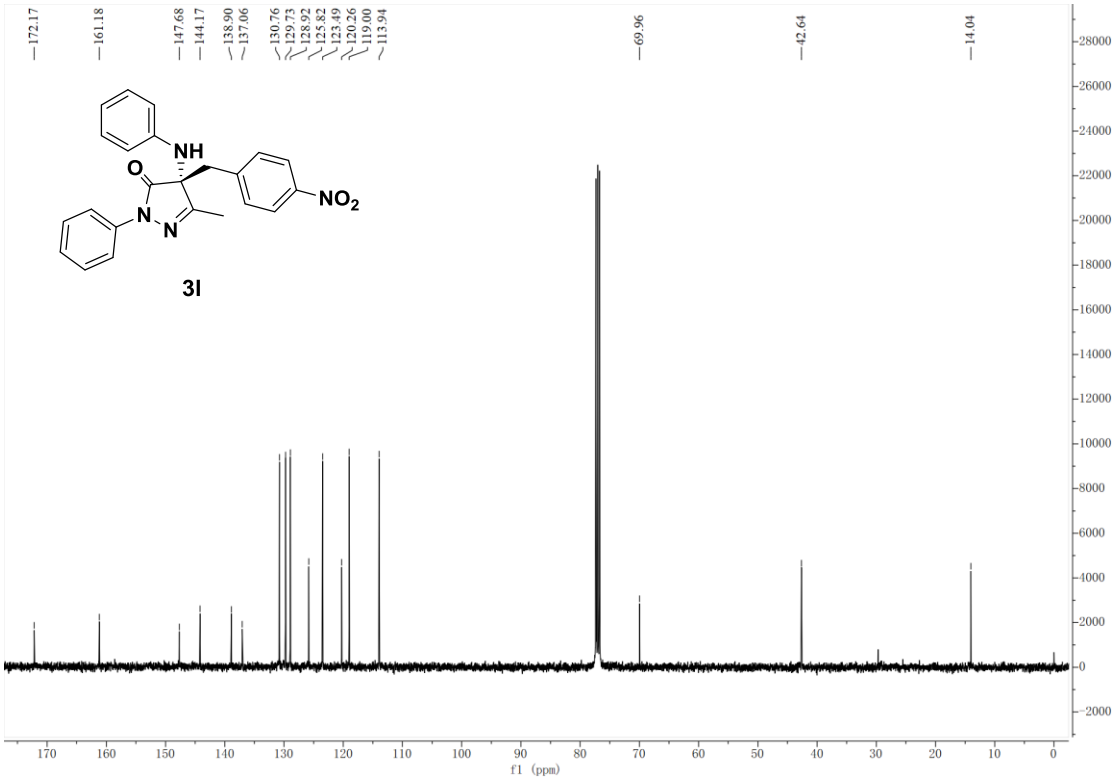
^{13}C NMR spectrum of compound 3k (in $CDCl_3$)



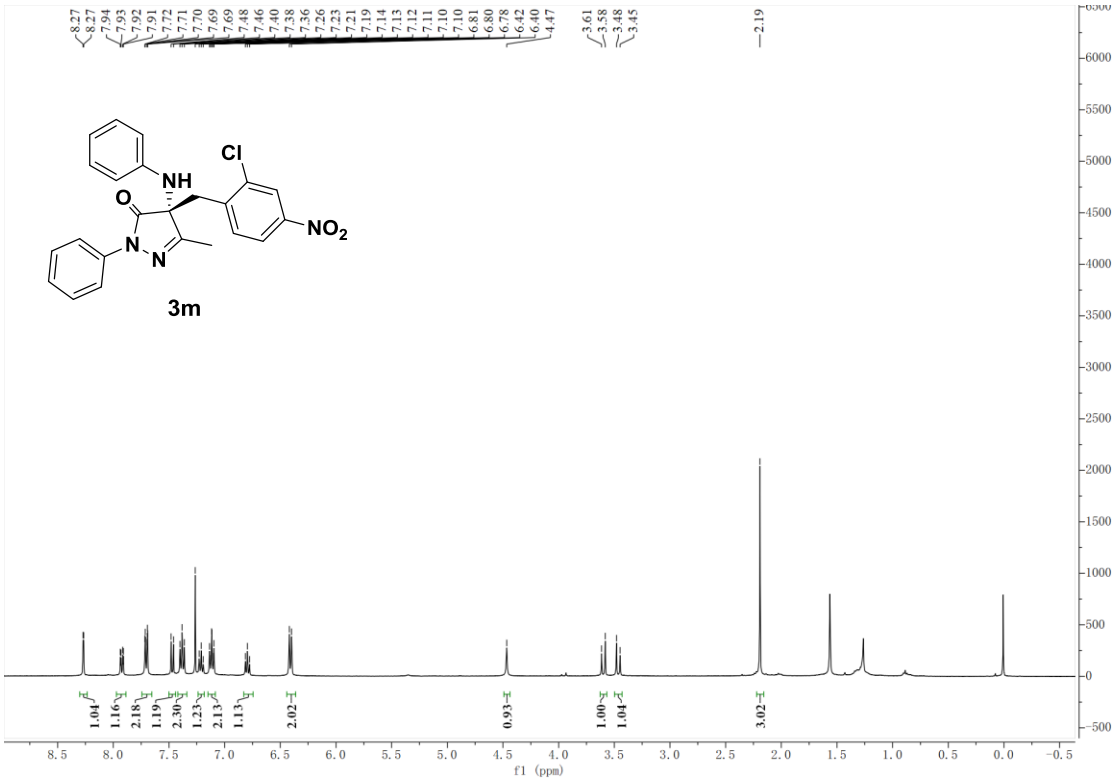
^{1}H NMR spectrum of compound 3l (in $CDCl_3$)



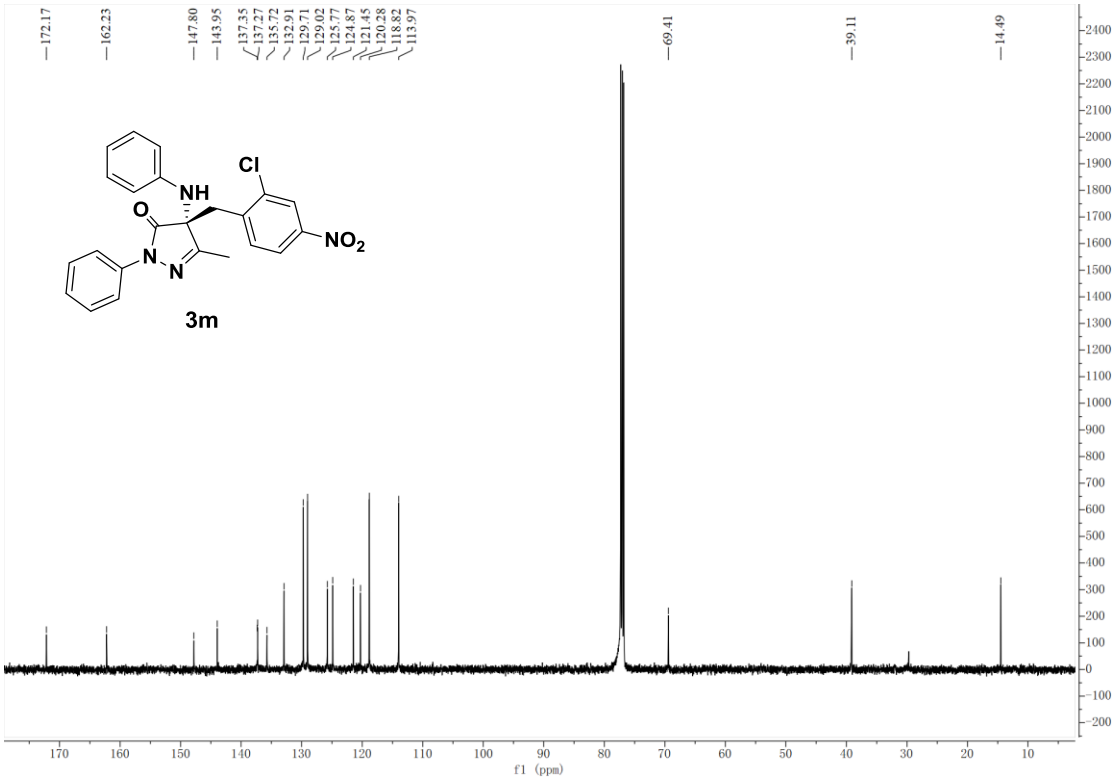
^{13}C NMR spectrum of compound 3l (in $CDCl_3$)



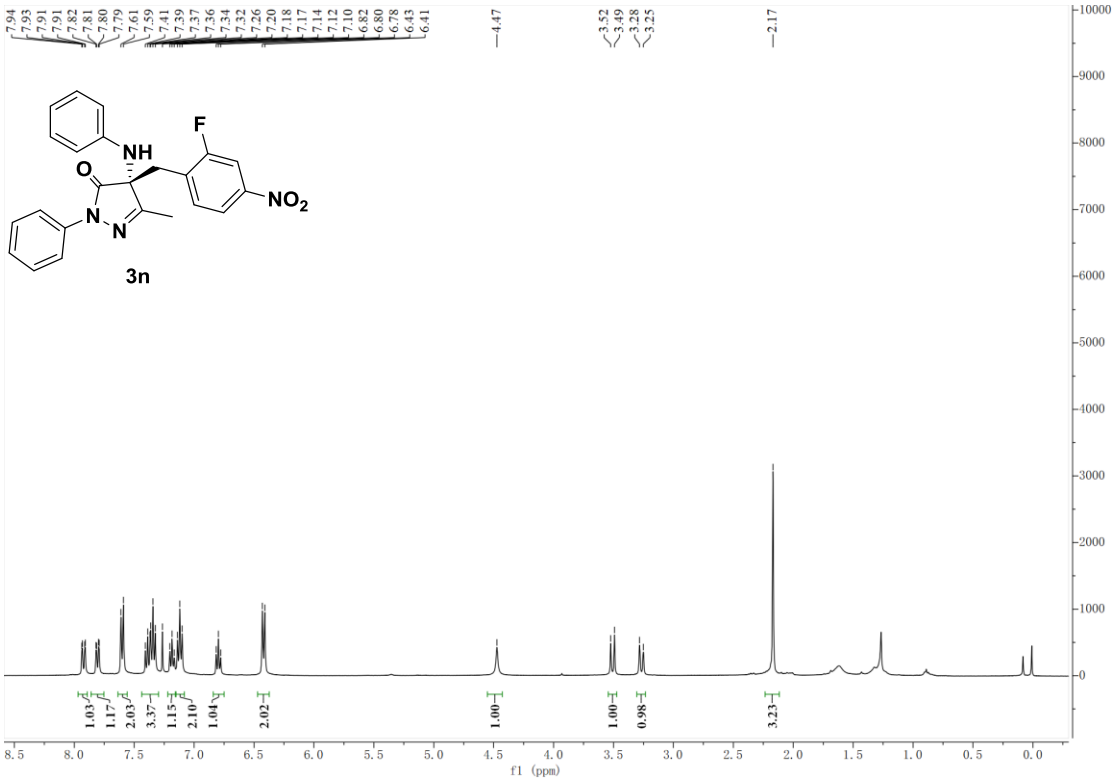
^{1}H NMR spectrum of compound 3m (in $CDCl_3$)



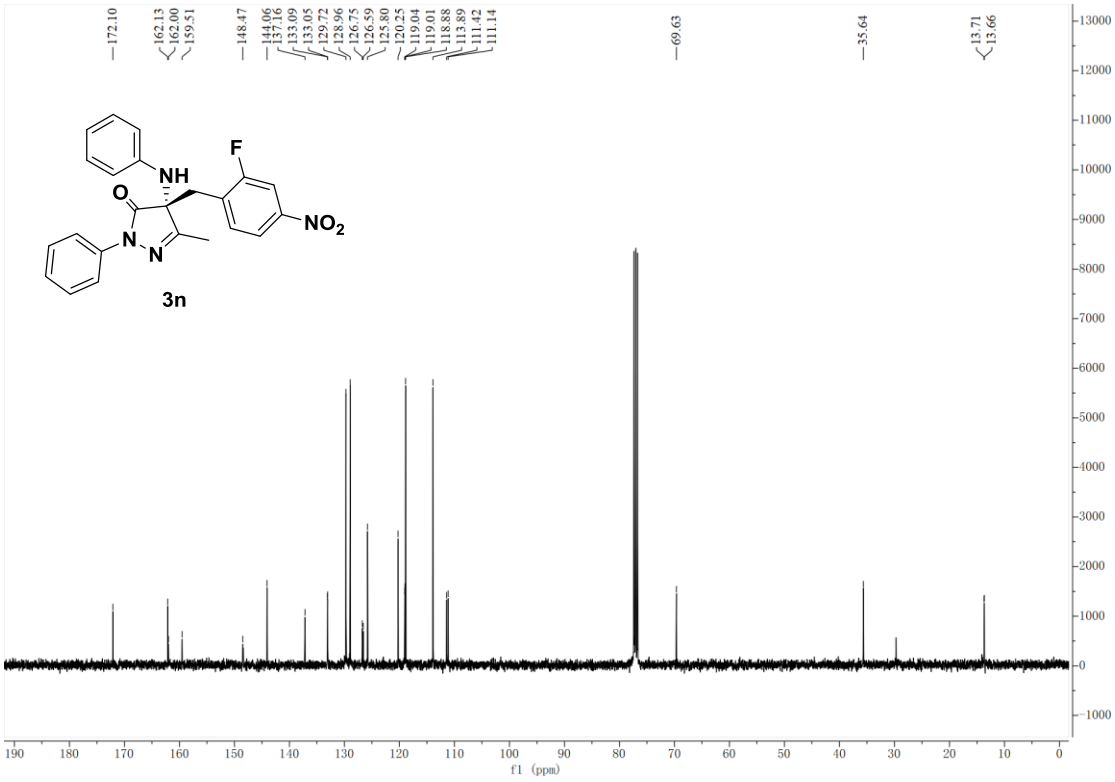
^{13}C NMR spectrum of compound 3m (in $CDCl_3$)



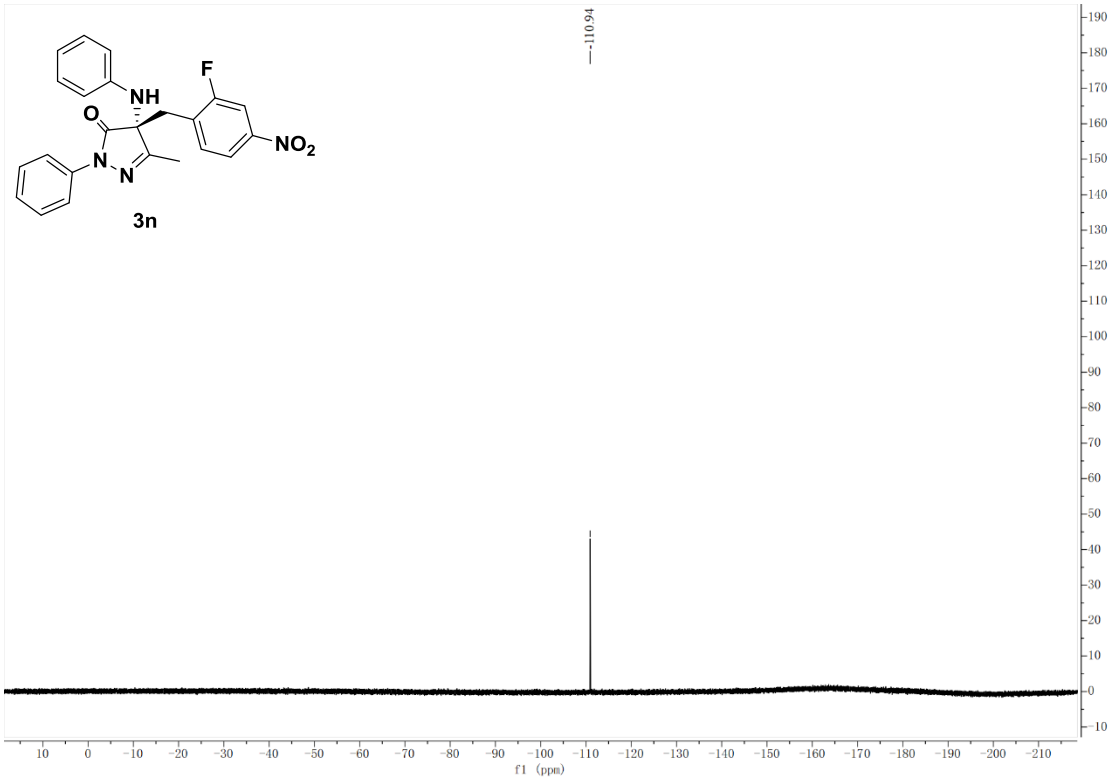
^{1}H NMR spectrum of compound 3n (in $CDCl_3$)



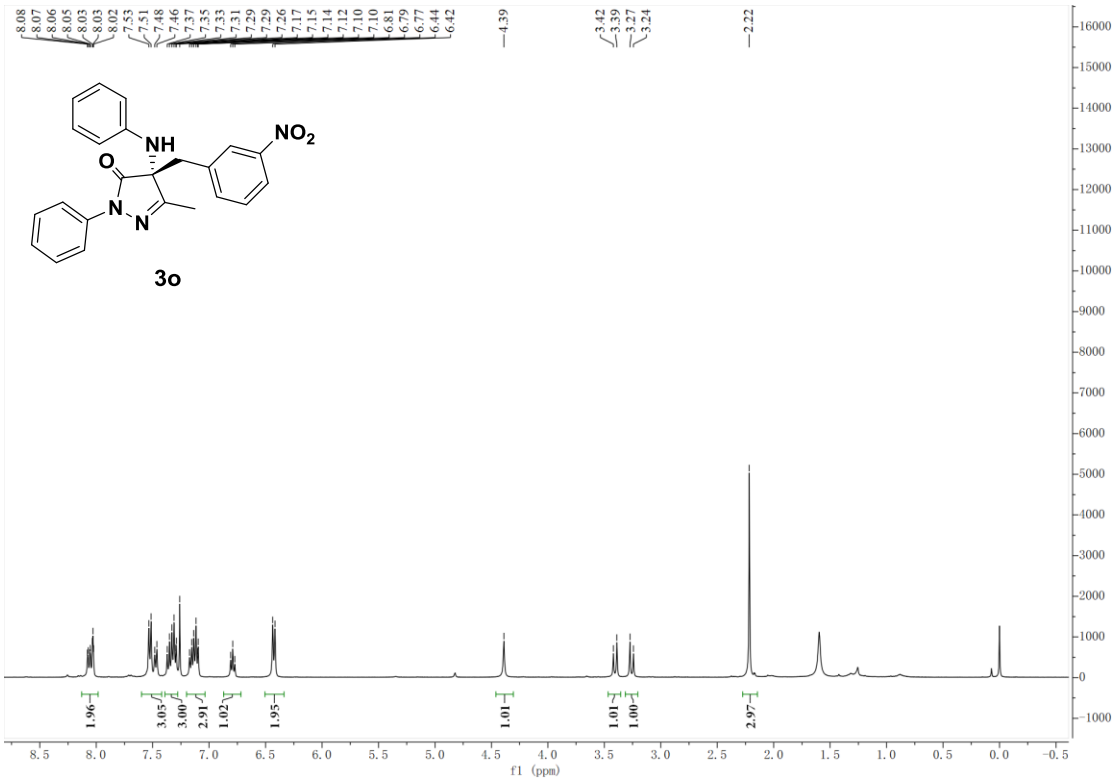
^{13}C NMR spectrum of compound 3n (in $CDCl_3$)



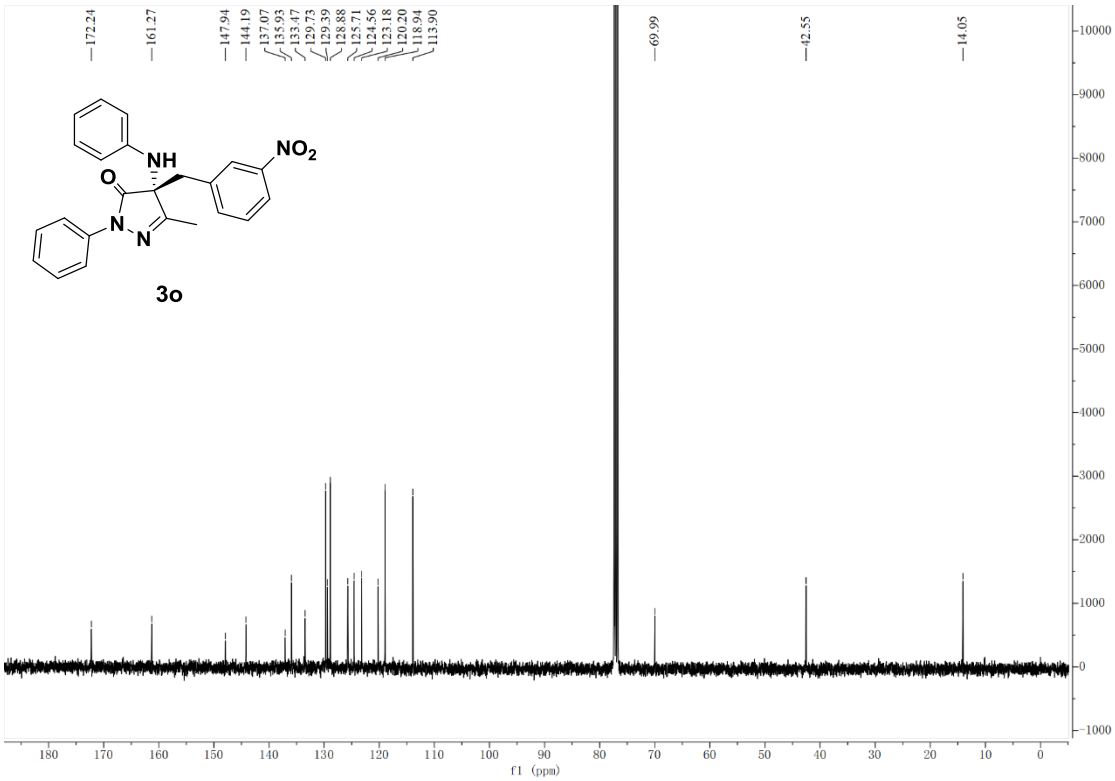
^{19}F NMR spectrum of compound 3n (in $CDCl_3$)



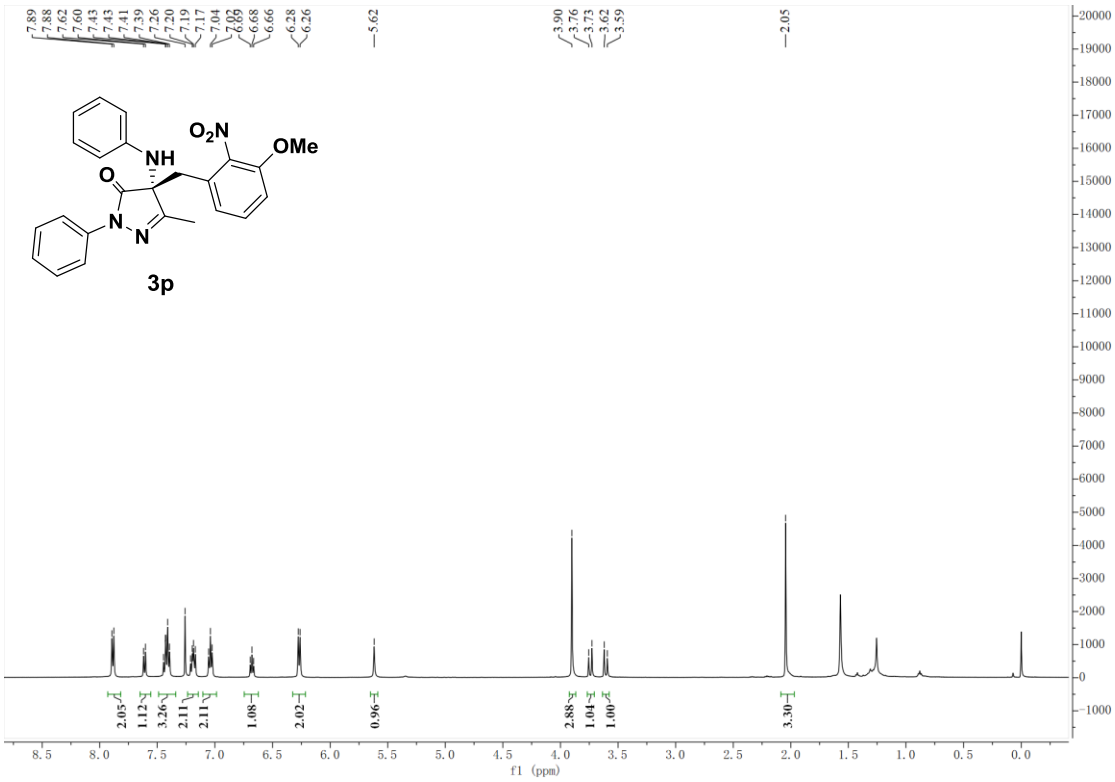
^{1}H NMR spectrum of compound 3o (in $CDCl_3$)



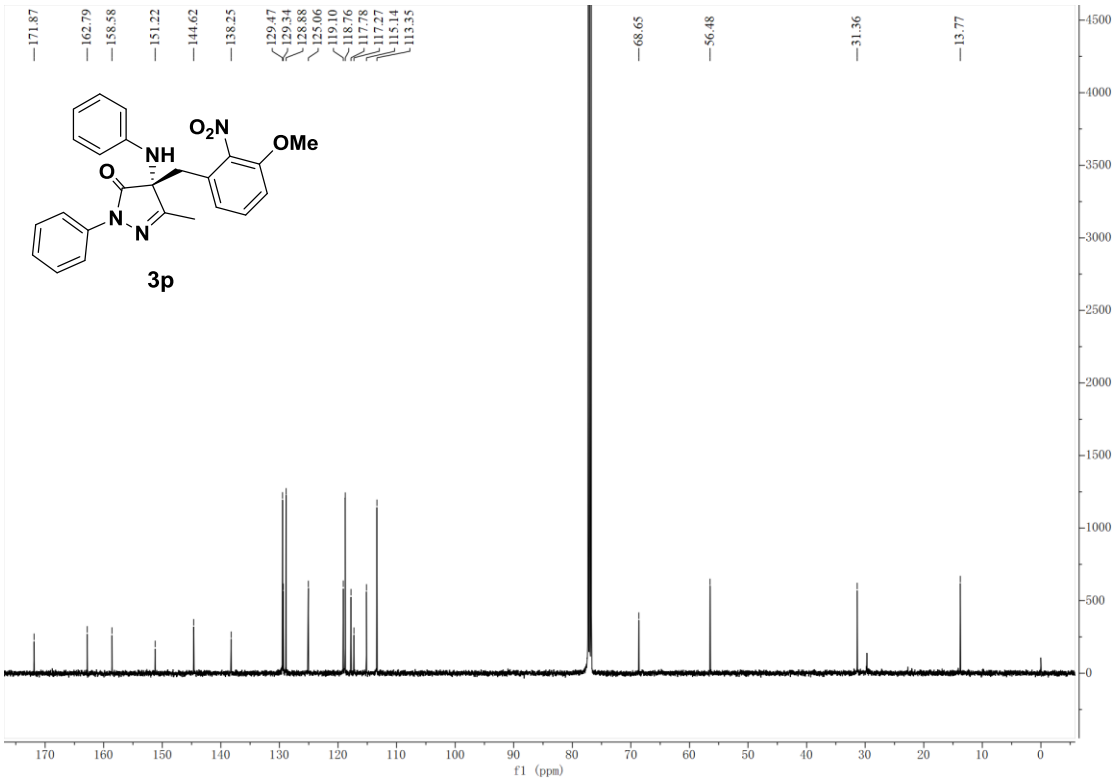
^{13}C NMR spectrum of compound 3o (in $CDCl_3$)



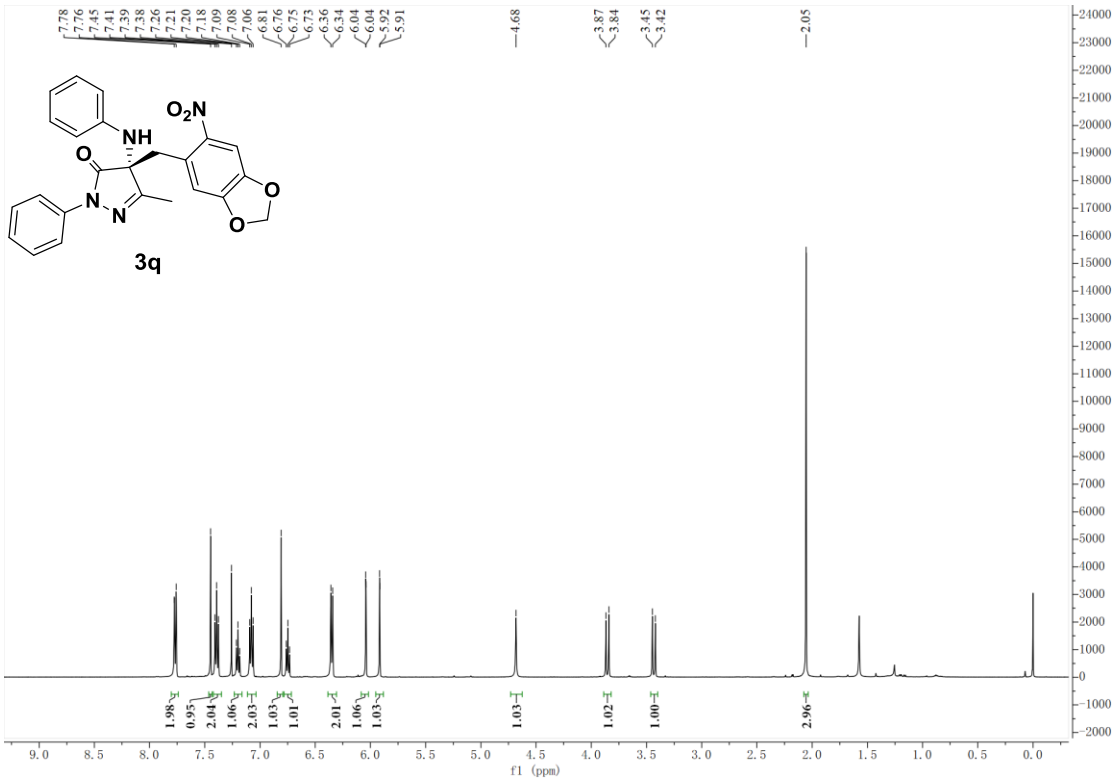
^{1}H NMR spectrum of compound 3p (in $CDCl_3$)



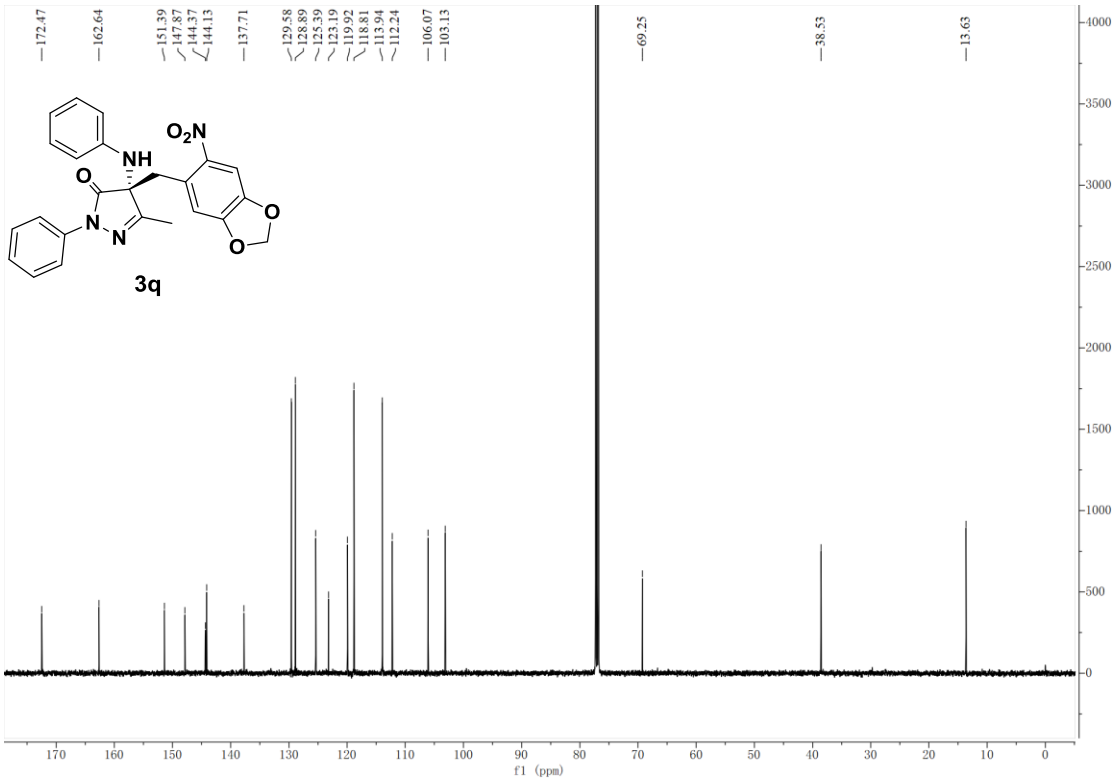
^{13}C NMR spectrum of compound 3p (in $CDCl_3$)



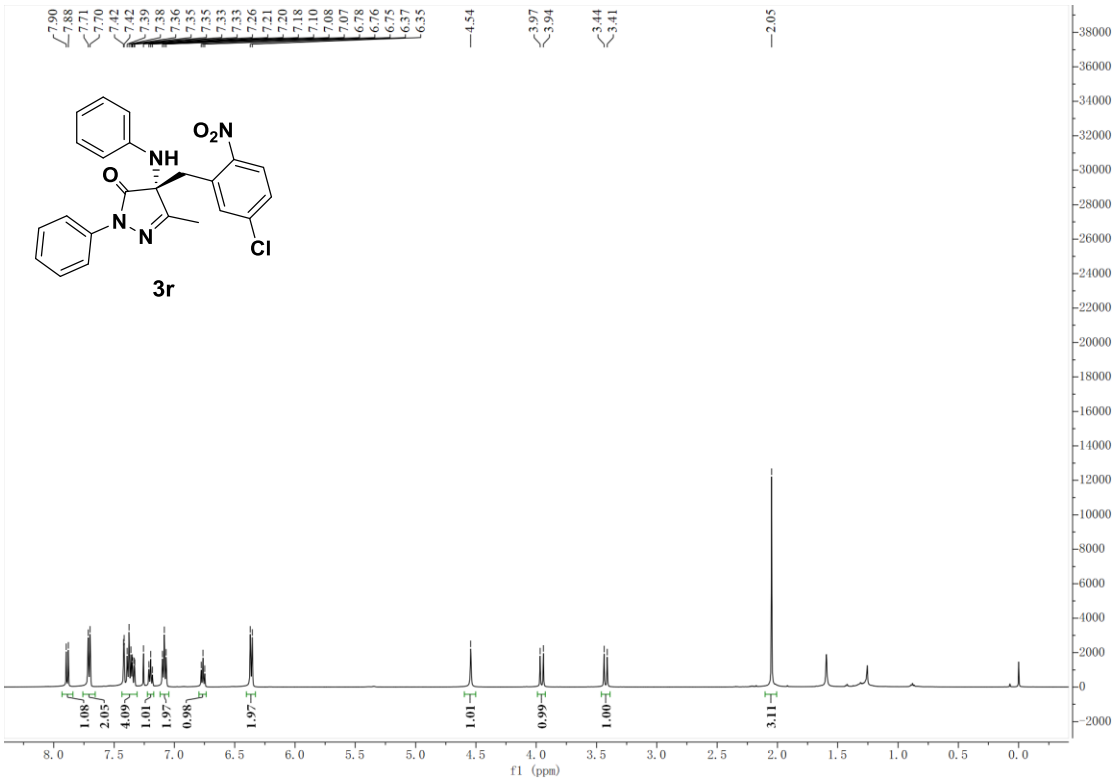
^{1}H NMR spectrum of compound 3q (in $CDCl_3$)



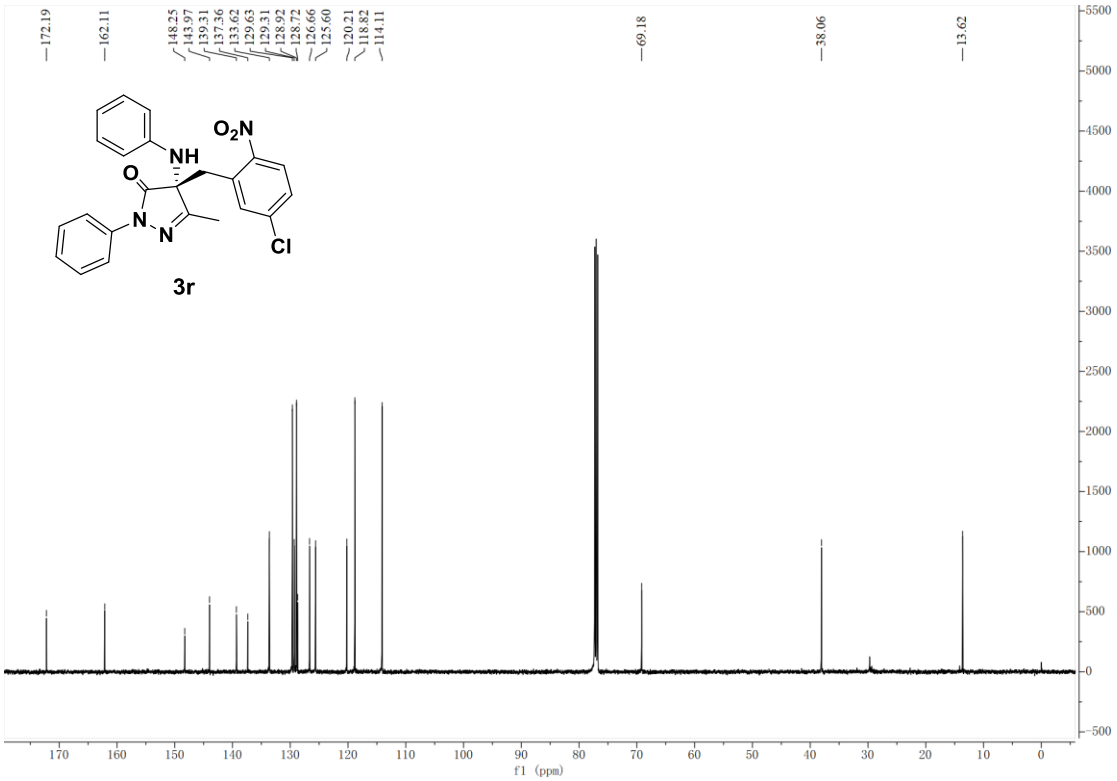
^{13}C NMR spectrum of compound 3q (in $CDCl_3$)



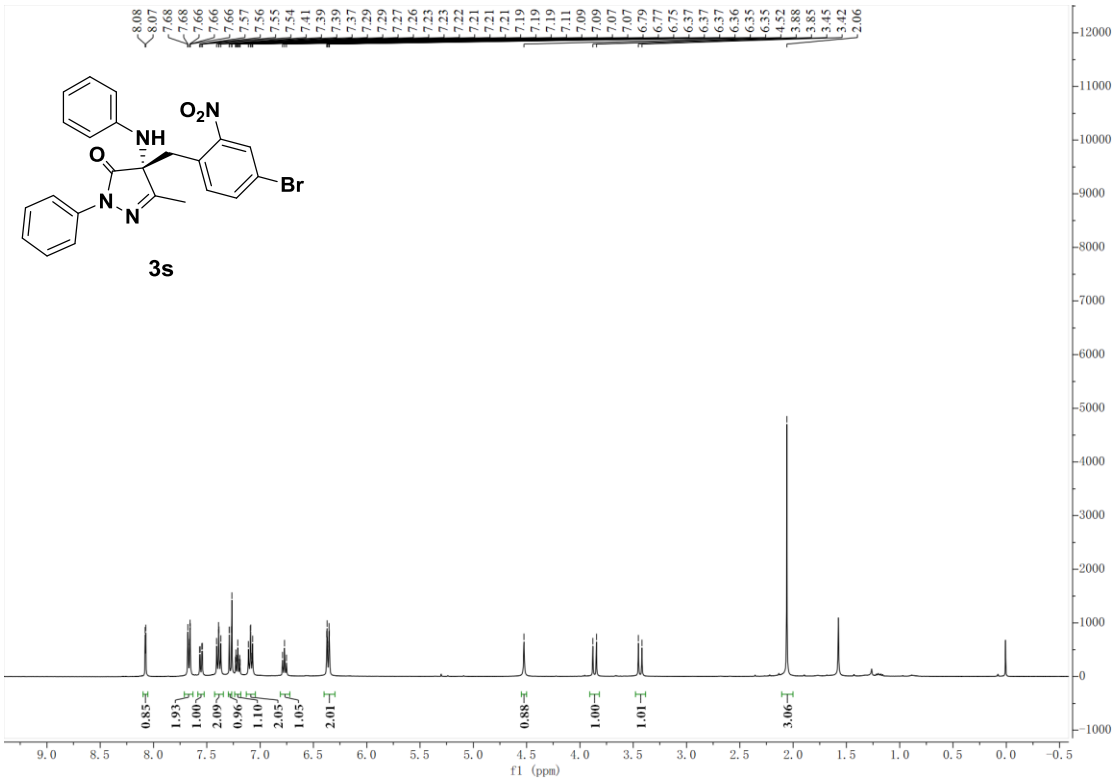
^{1}H NMR spectrum of compound 3r (in $CDCl_3$)



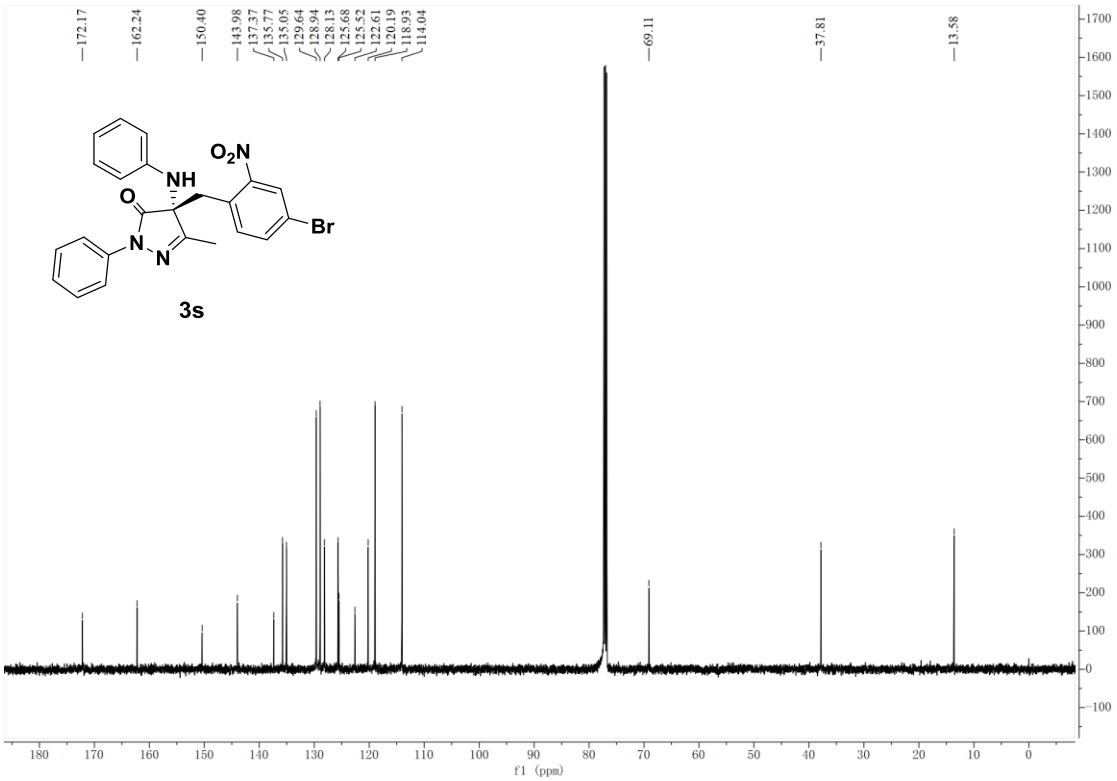
^{13}C NMR spectrum of compound 3r (in $CDCl_3$)



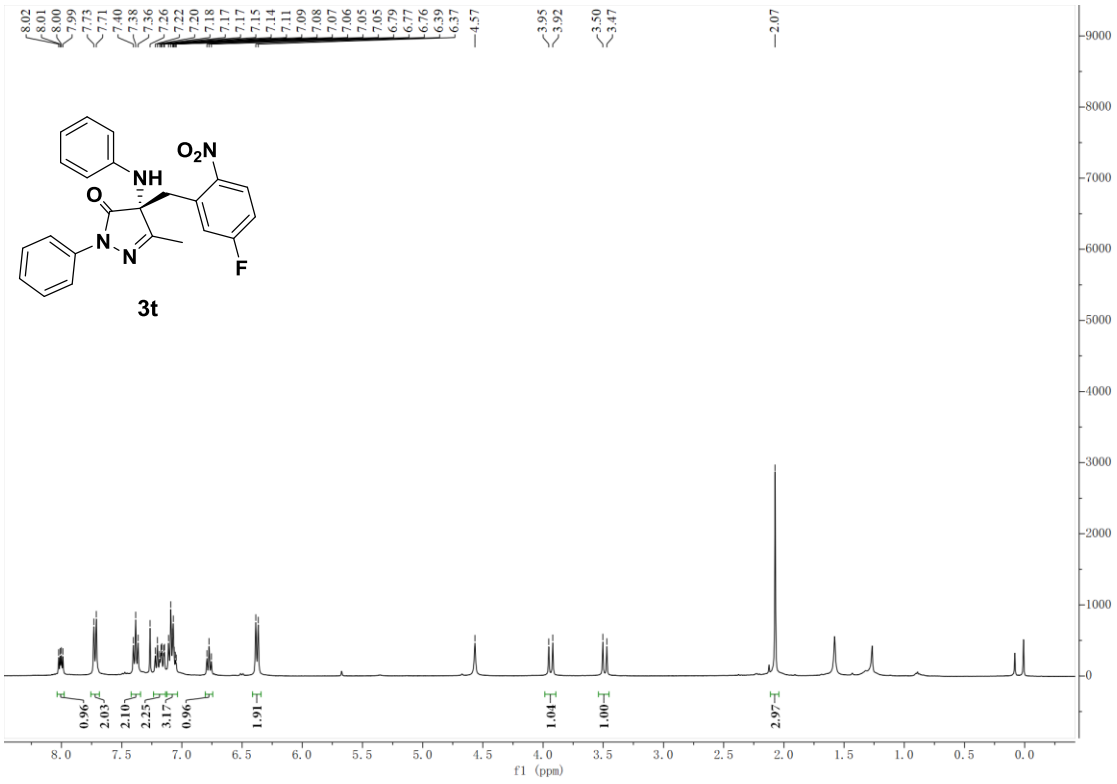
^{1}H NMR spectrum of compound 3s (in $CDCl_3$)



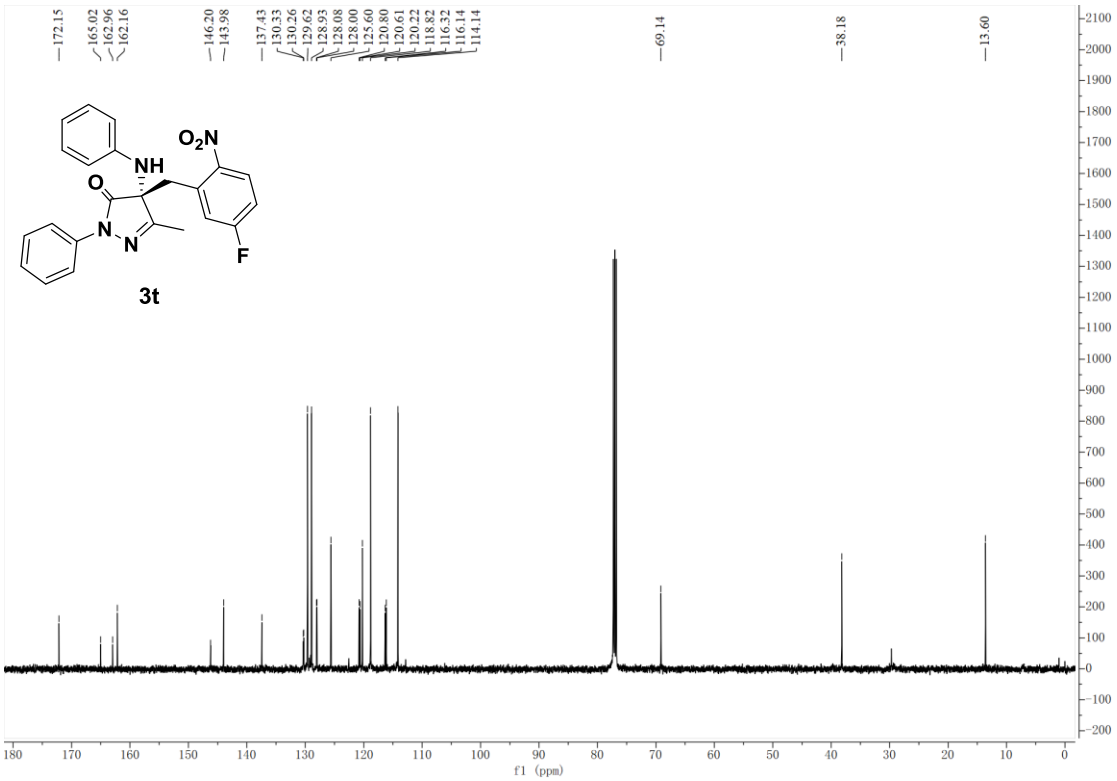
^{13}C NMR spectrum of compound 3s (in $CDCl_3$)



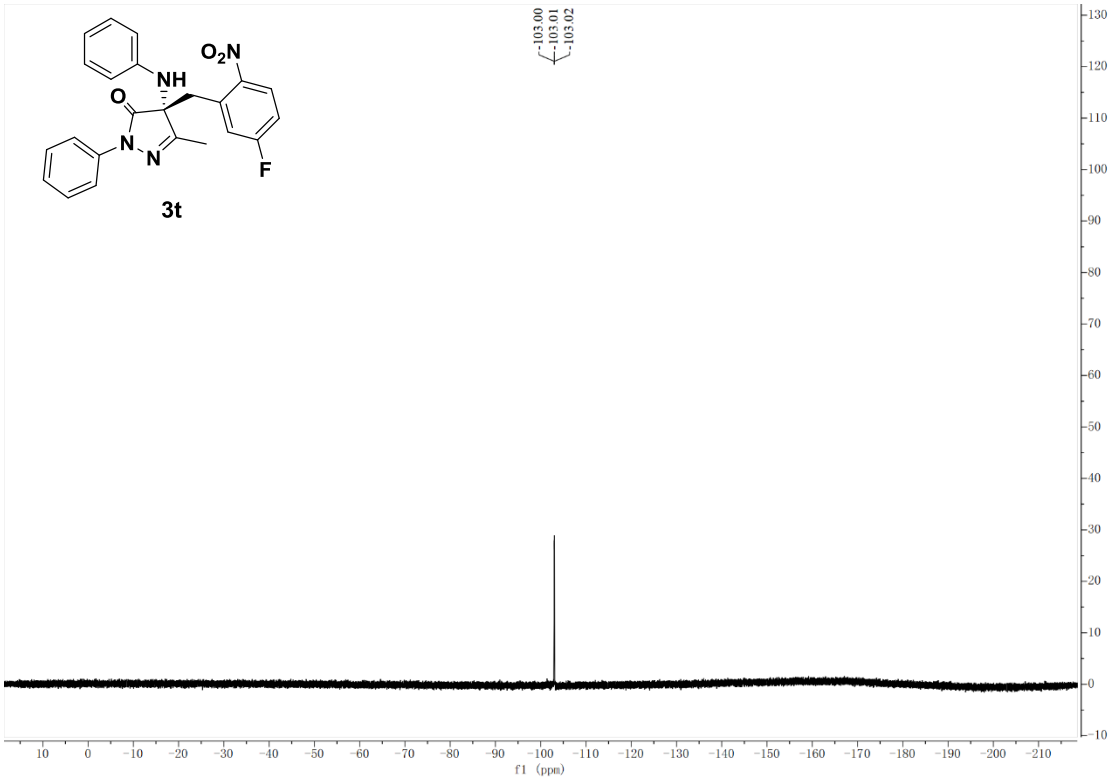
^{1}H NMR spectrum of compound 3t (in $CDCl_3$)



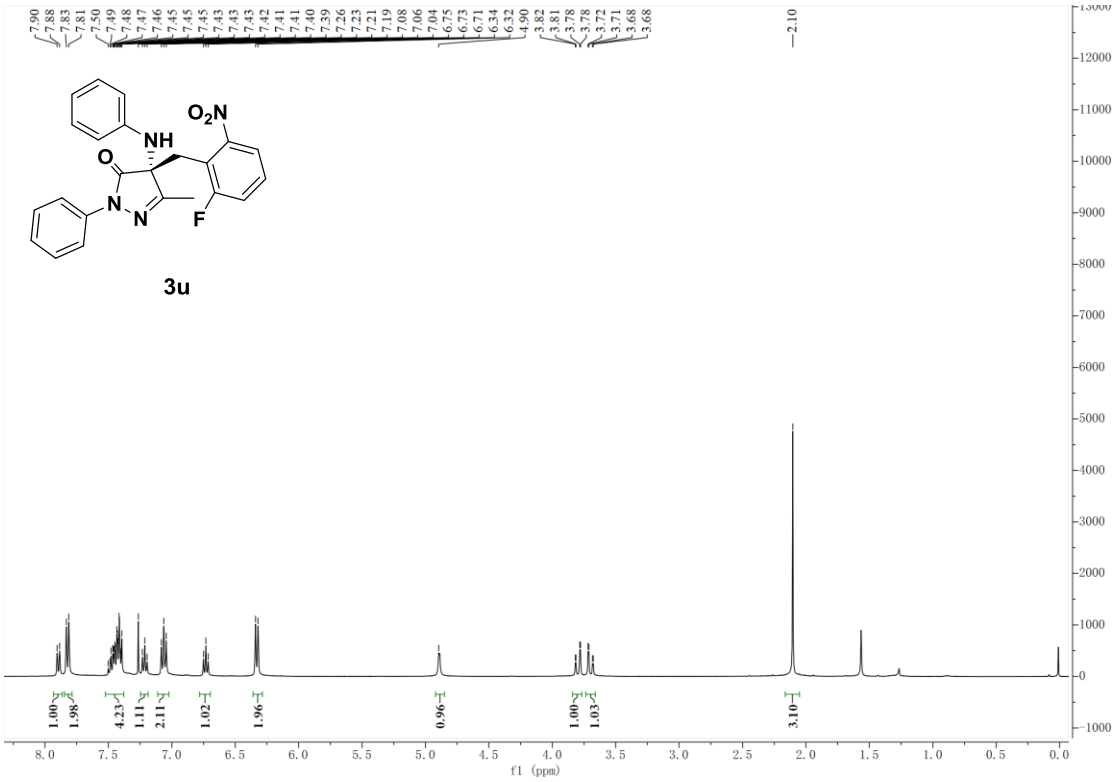
^{13}C NMR spectrum of compound 3t (in $CDCl_3$)



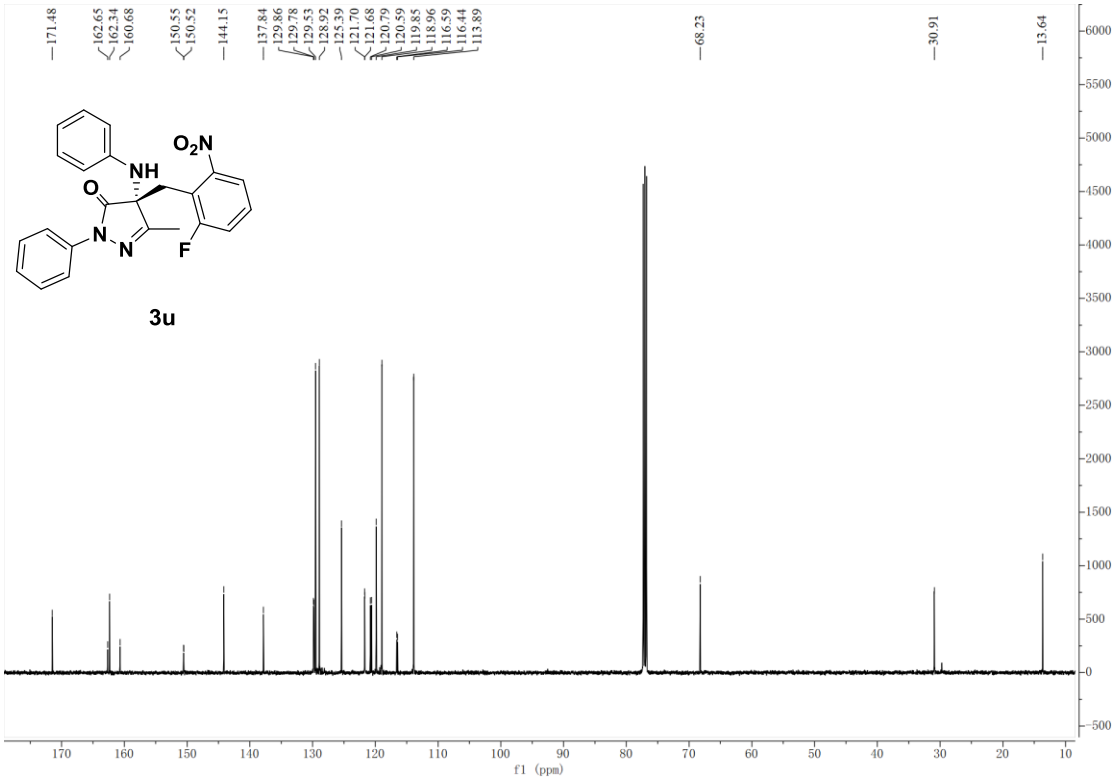
^{19}F NMR spectrum of compound 3t (in $CDCl_3$)



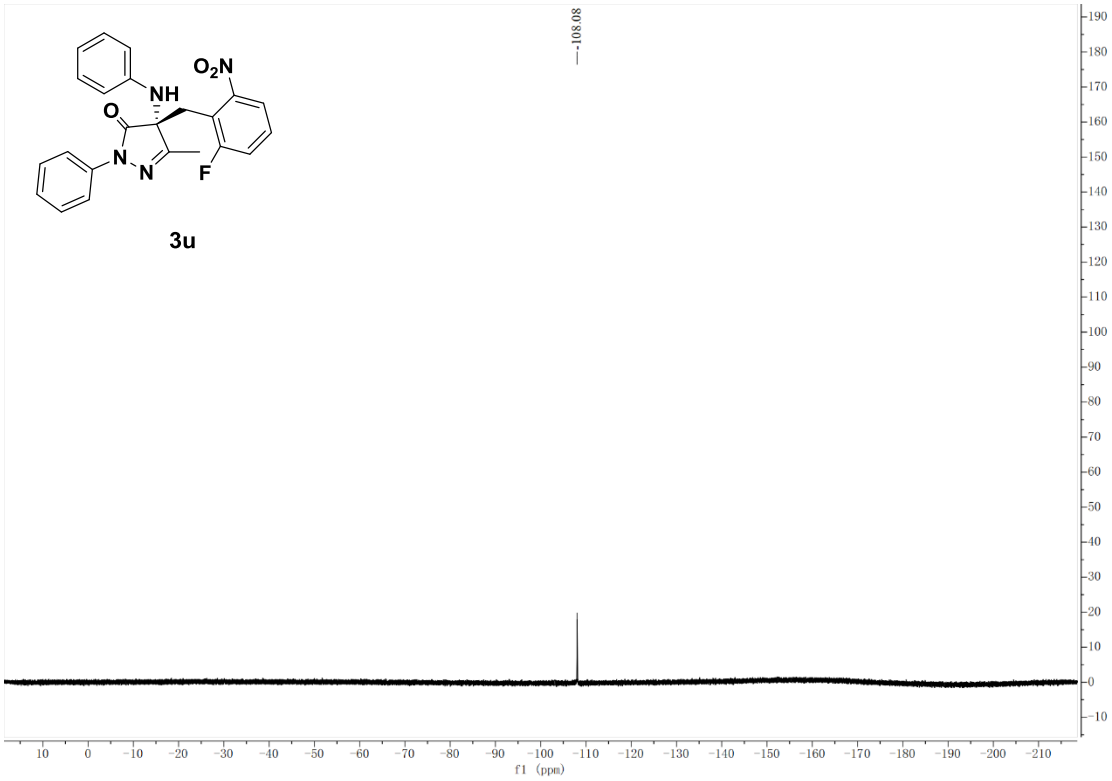
^{1}H NMR spectrum of compound 3u (in $CDCl_3$)



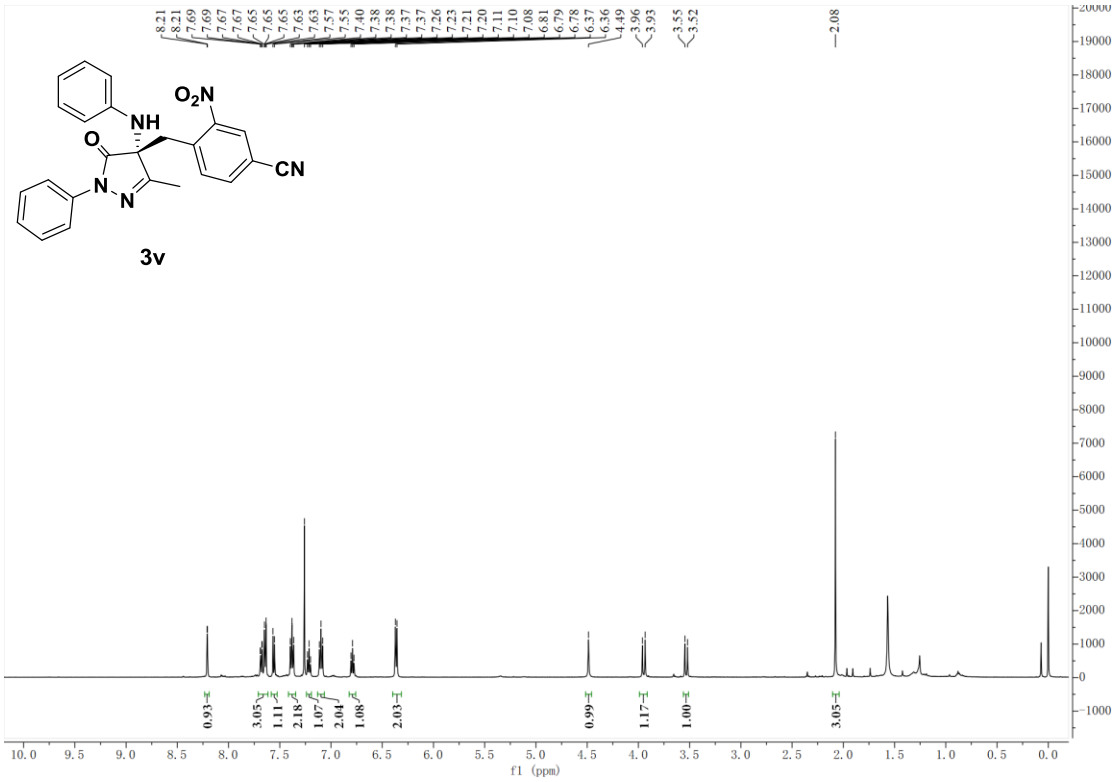
^{13}C NMR spectrum of compound 3u (in $CDCl_3$)



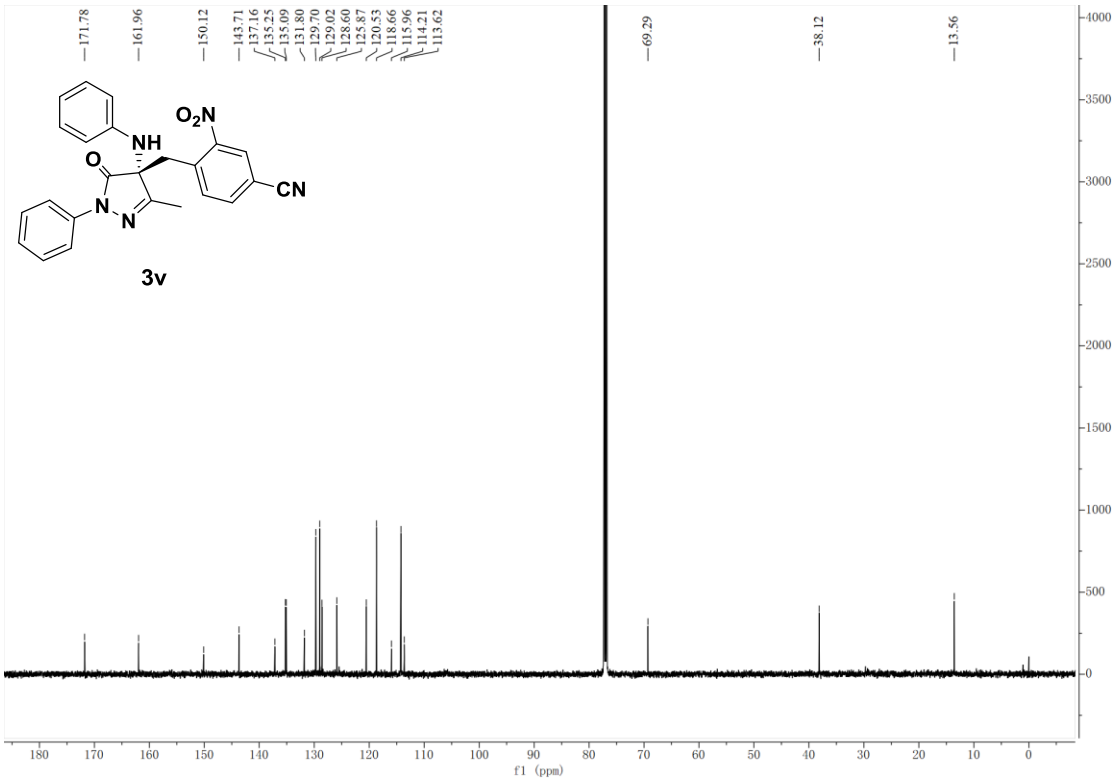
^{19}F NMR spectrum of compound 3u (in $CDCl_3$)



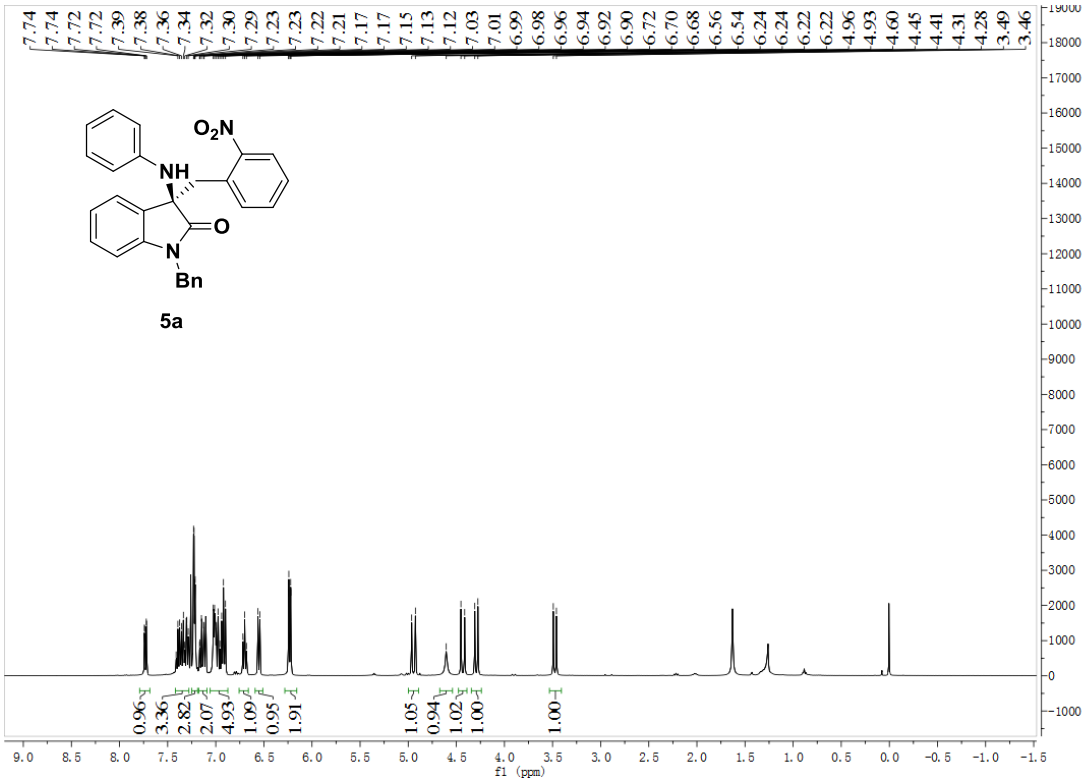
^{1}H NMR spectrum of compound 3v (in $CDCl_3$)



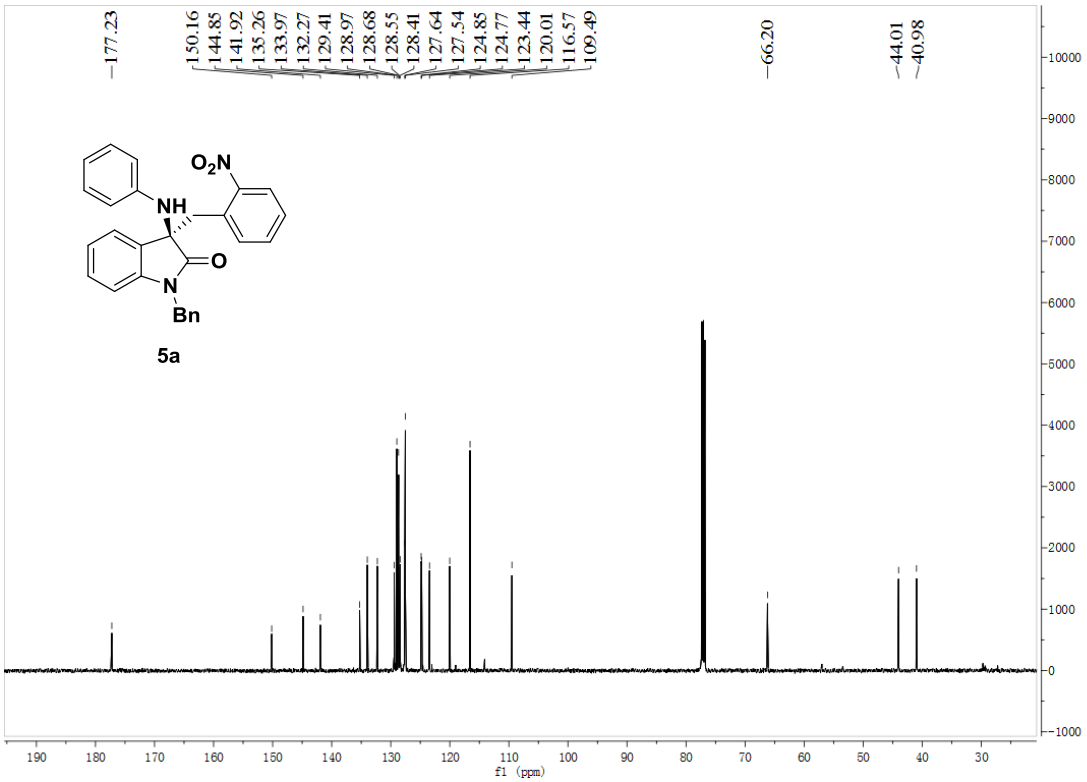
^{13}C NMR spectrum of compound 3v (in $CDCl_3$)



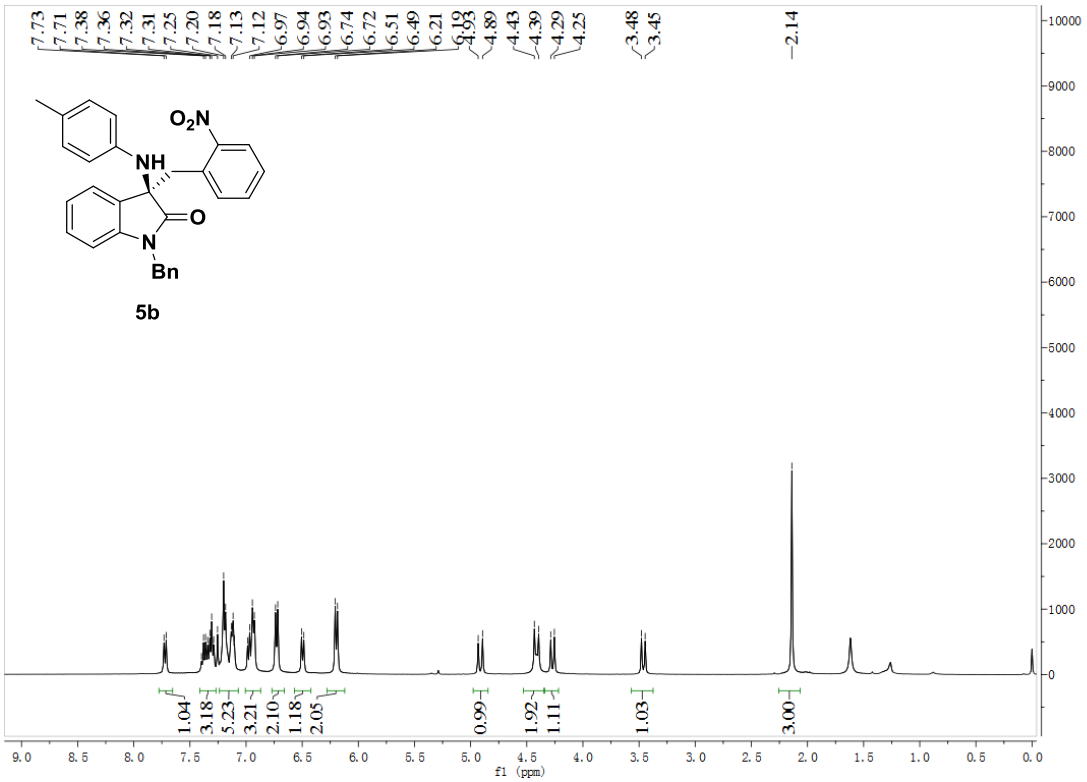
^{1}H NMR spectrum of compound 5a (in $CDCl_3$)



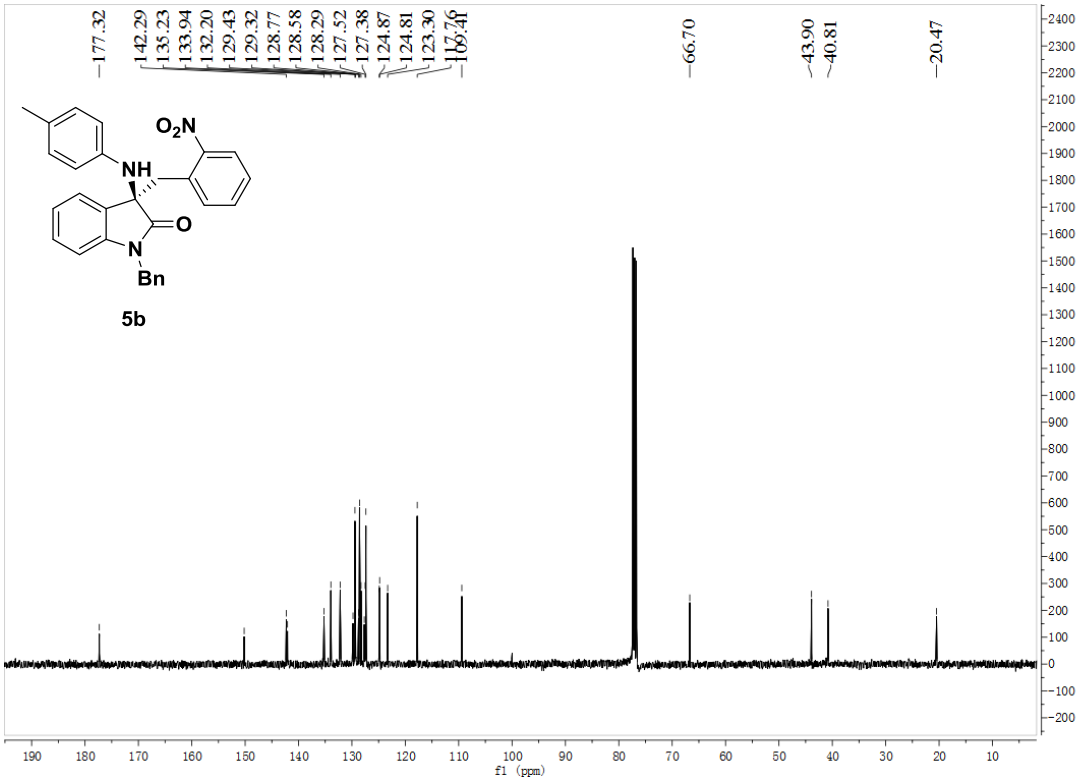
^{13}C NMR spectrum of compound 5a (in $CDCl_3$)



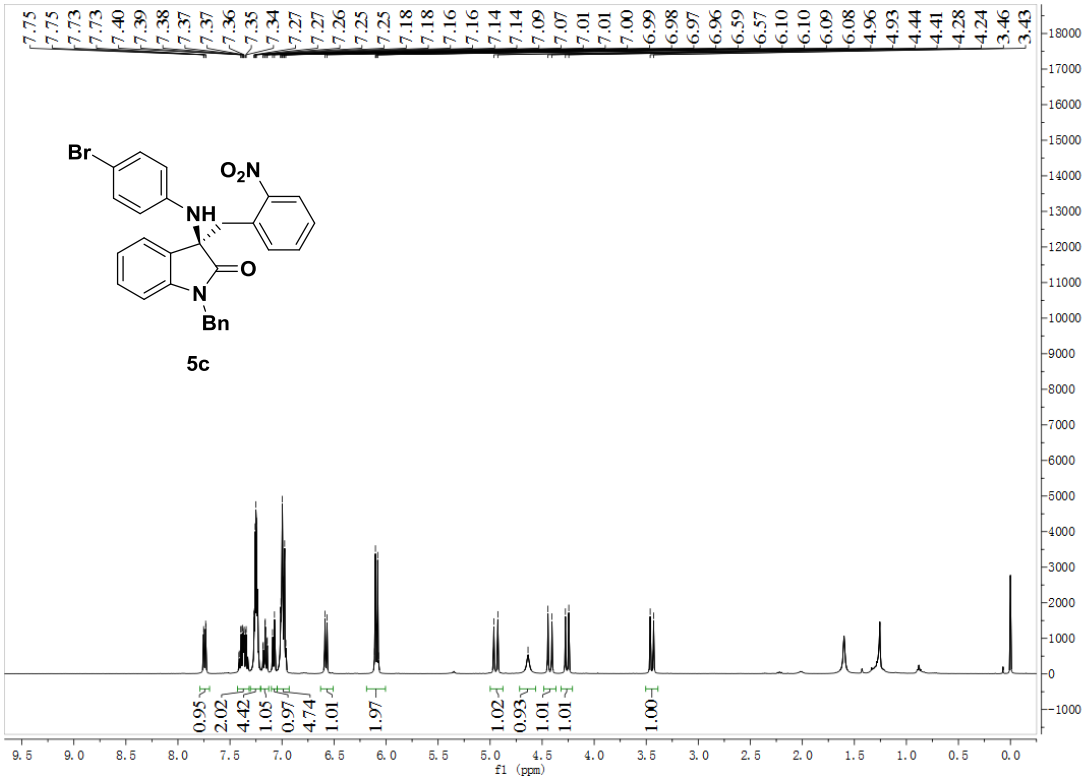
^{1}H NMR spectrum of compound 5b (in $CDCl_3$)



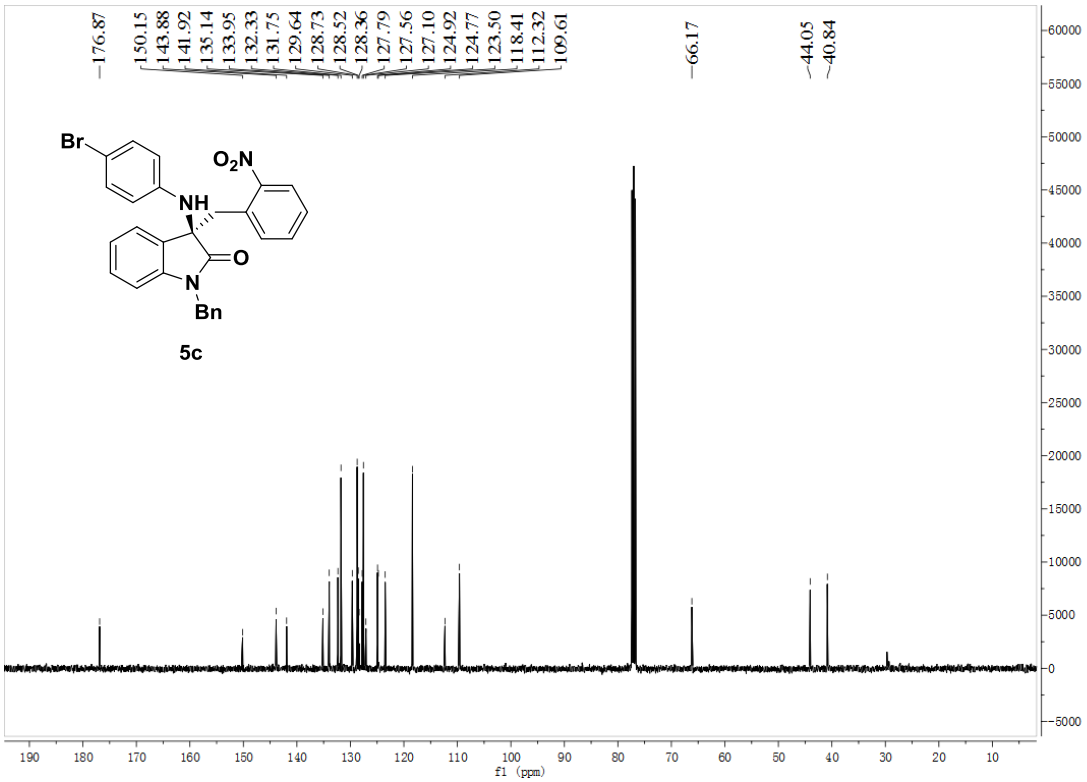
^{13}C NMR spectrum of compound 5b (in $CDCl_3$)



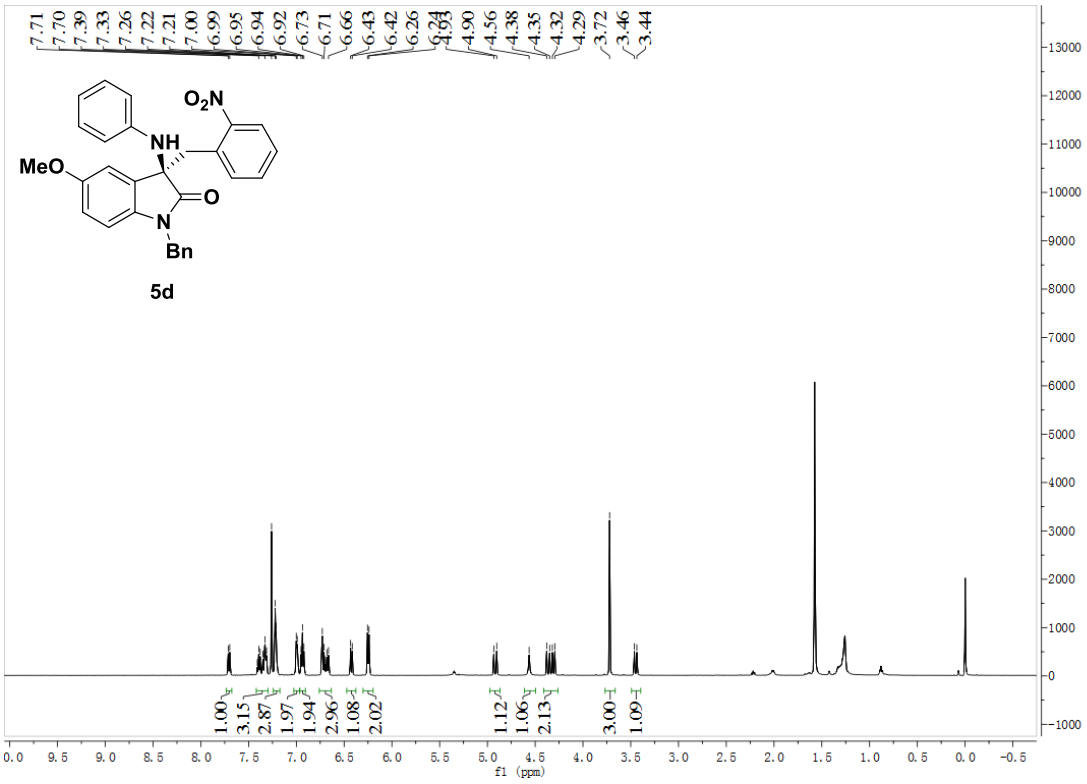
^{1}H NMR spectrum of compound 5c (in $CDCl_3$)



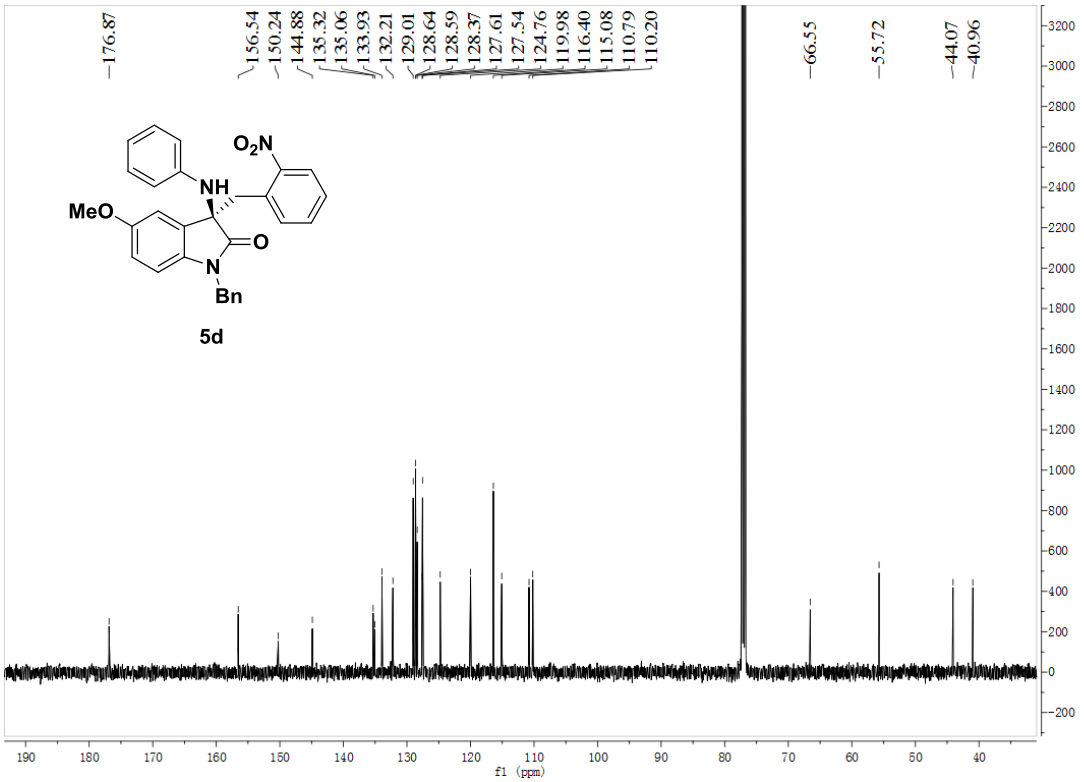
^{13}C NMR spectrum of compound 5c (in $CDCl_3$)



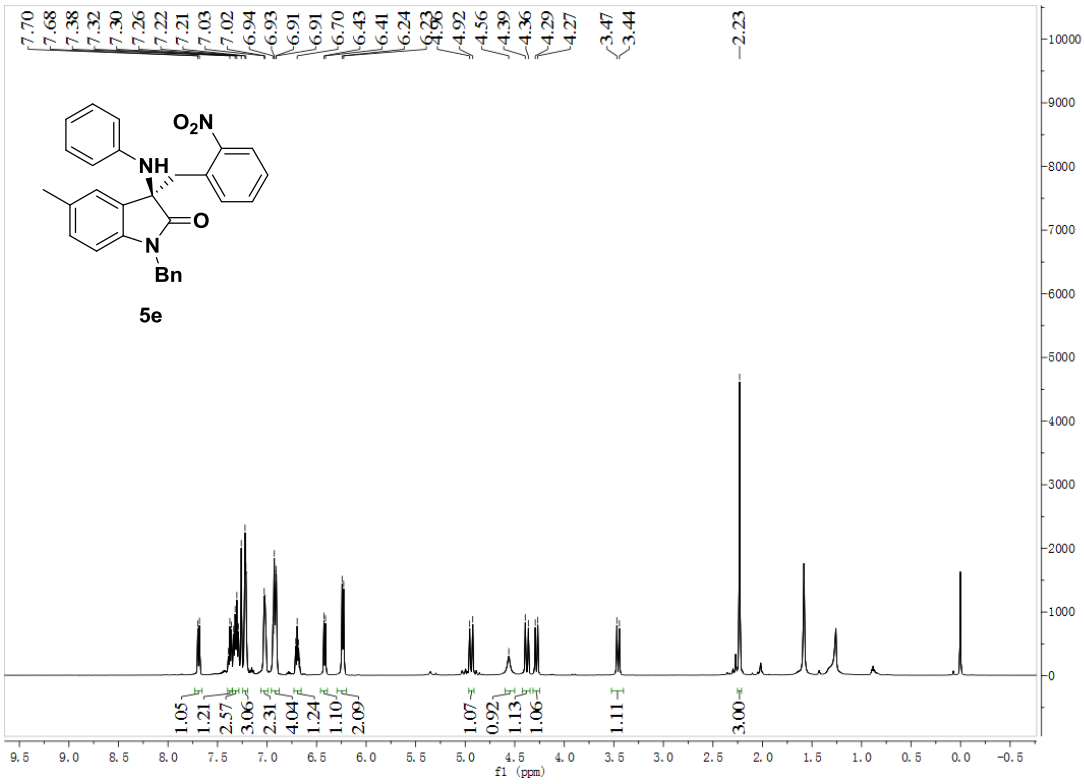
^{1}H NMR spectrum of compound 5d (in $CDCl_3$)



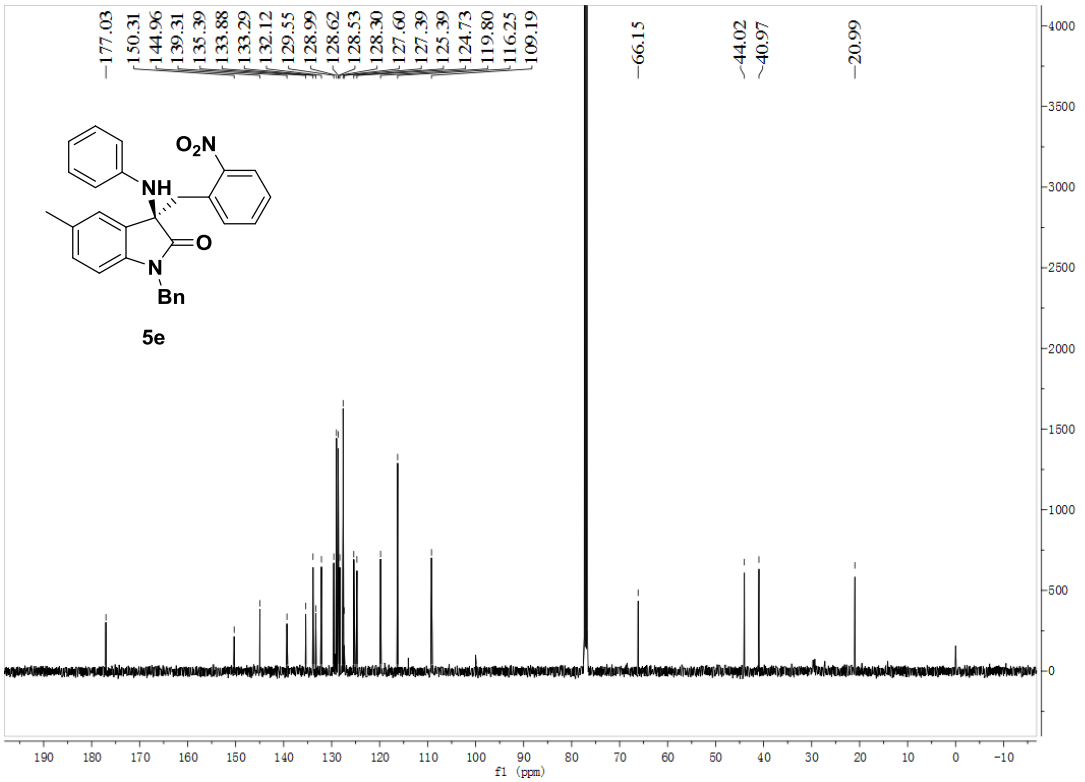
^{13}C NMR spectrum of compound 5d (in $CDCl_3$)



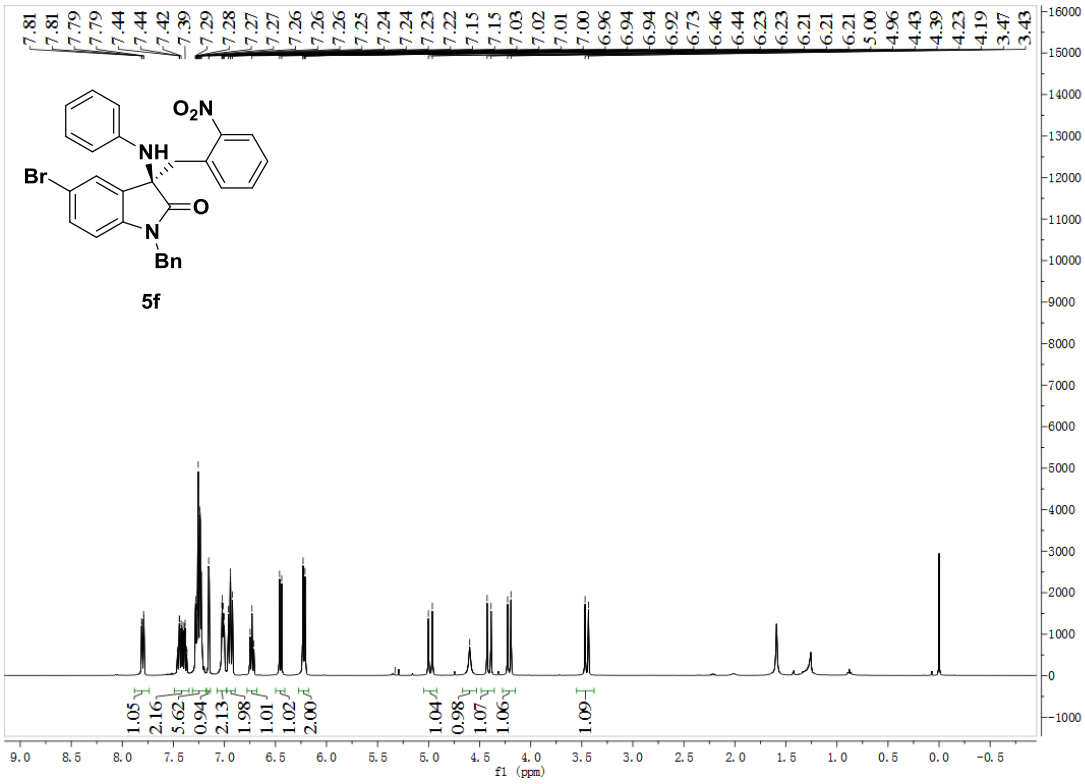
^{1}H NMR spectrum of compound 5e (in $CDCl_3$)



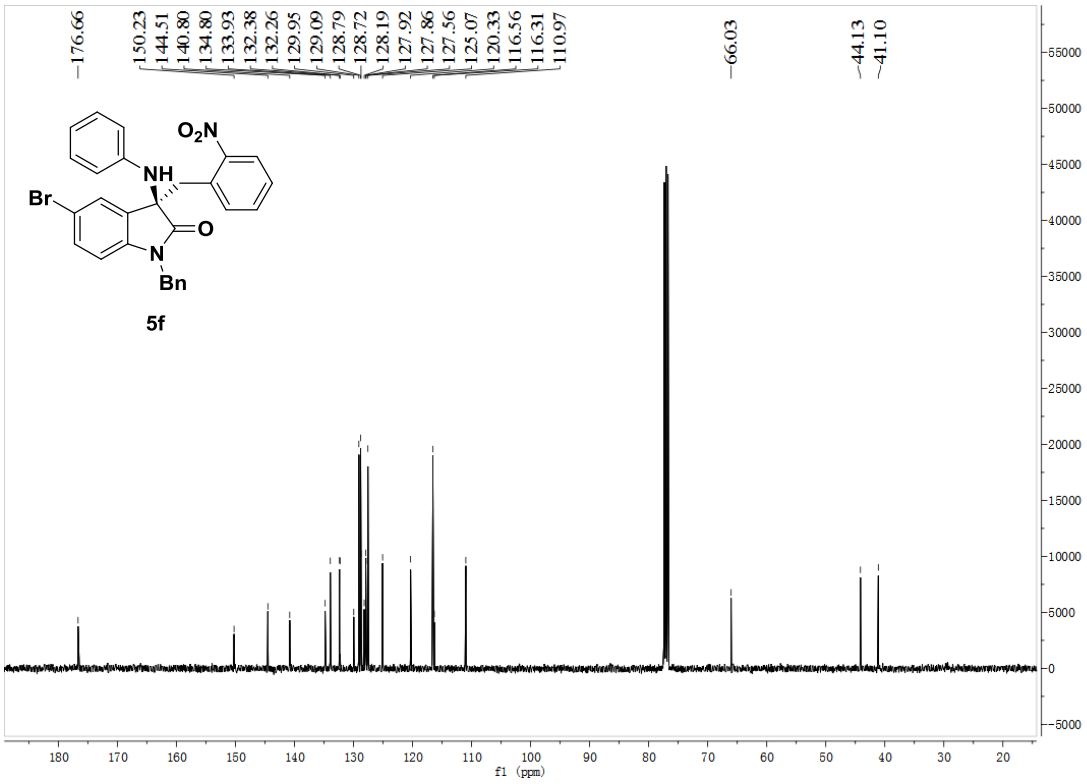
^{13}C NMR spectrum of compound 5e (in $CDCl_3$)



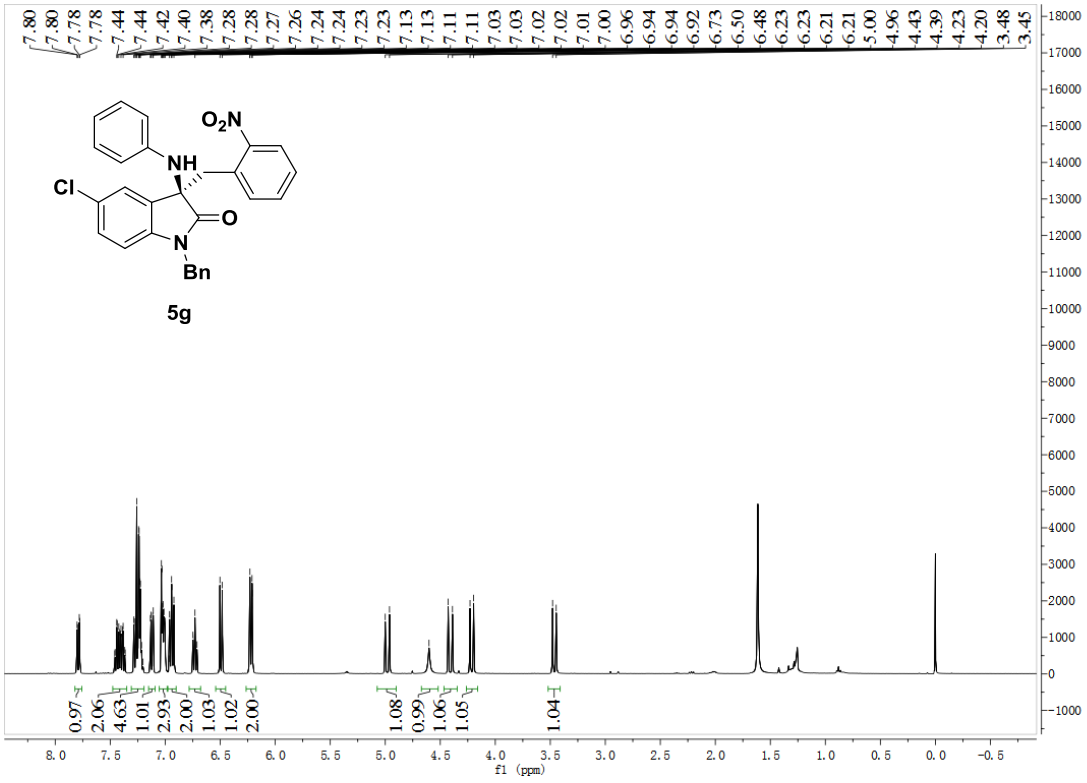
^{1}H NMR spectrum of compound 5f (in $CDCl_3$)



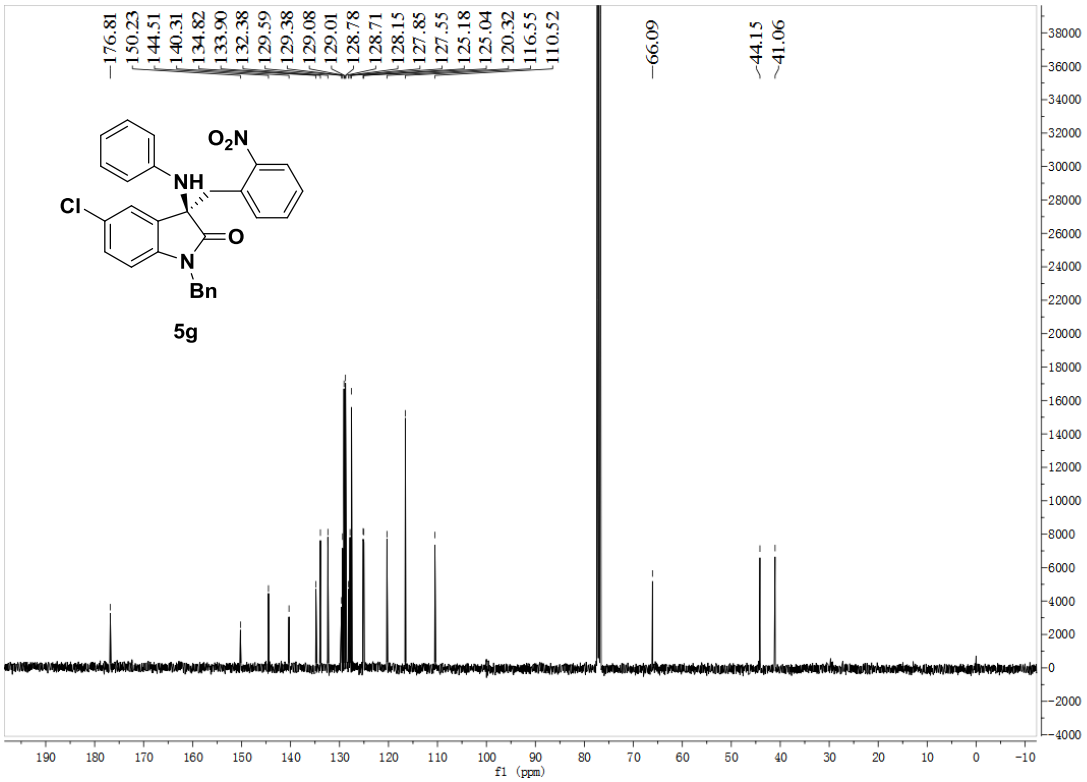
^{13}C NMR spectrum of compound 5f (in $CDCl_3$)



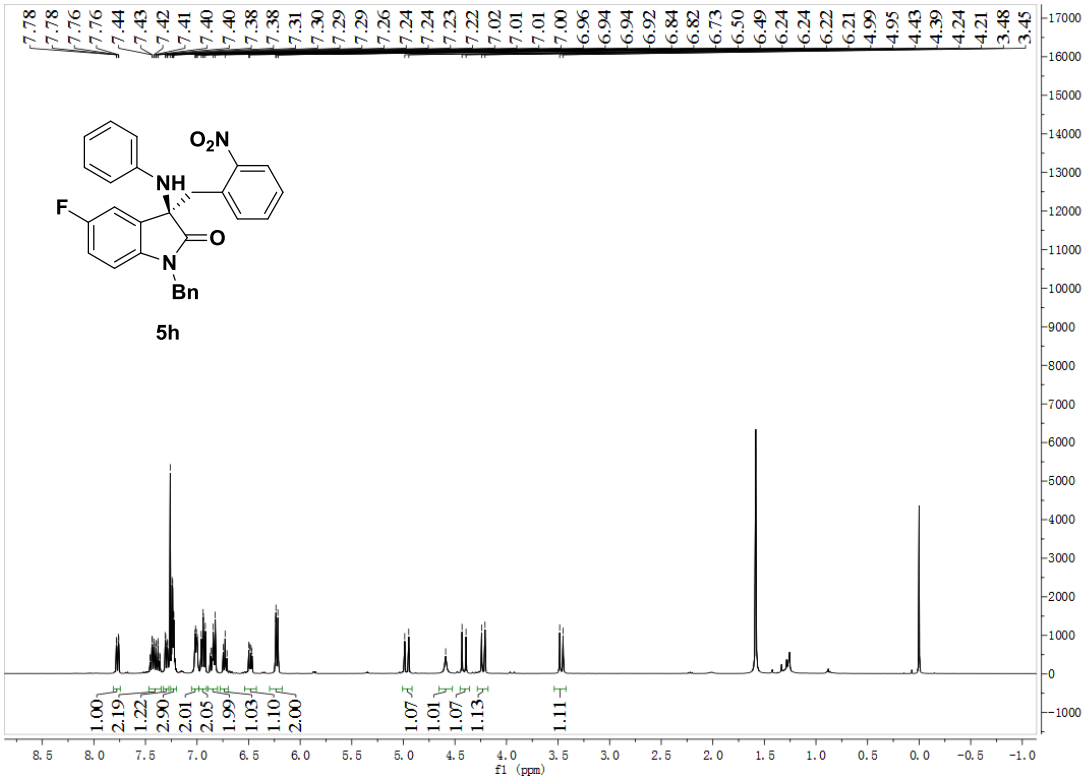
^{1}H NMR spectrum of compound 5g (in $CDCl_3$)



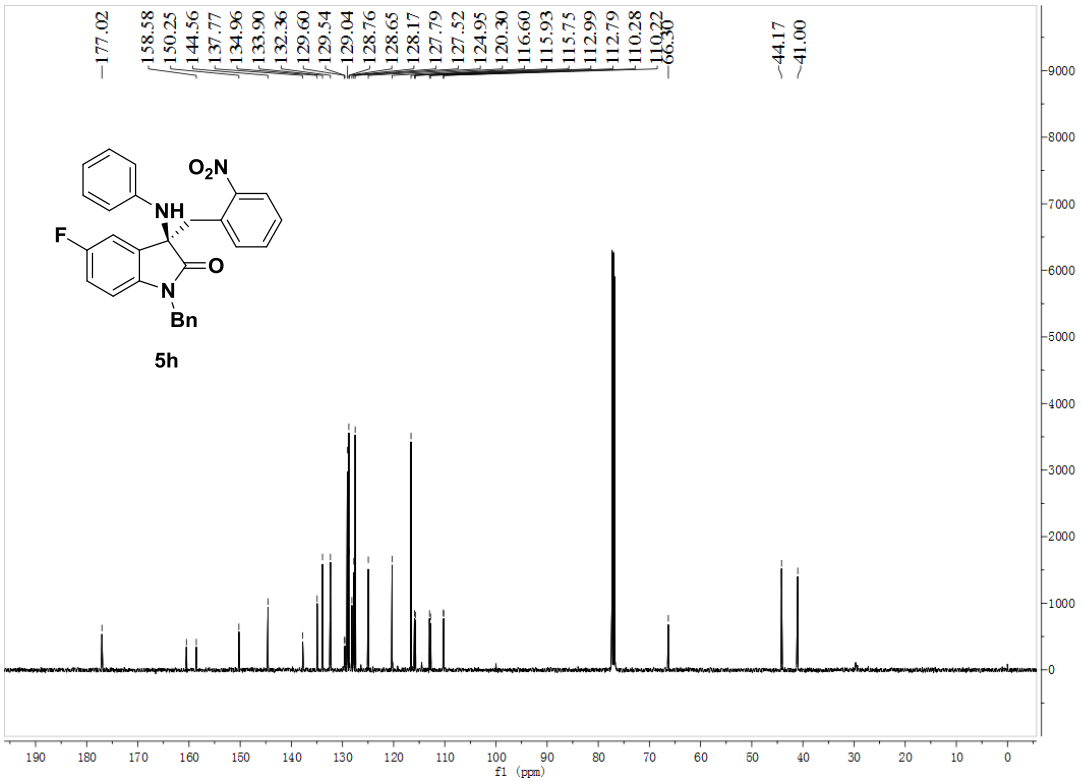
^{13}C NMR spectrum of compound 5g (in $CDCl_3$)



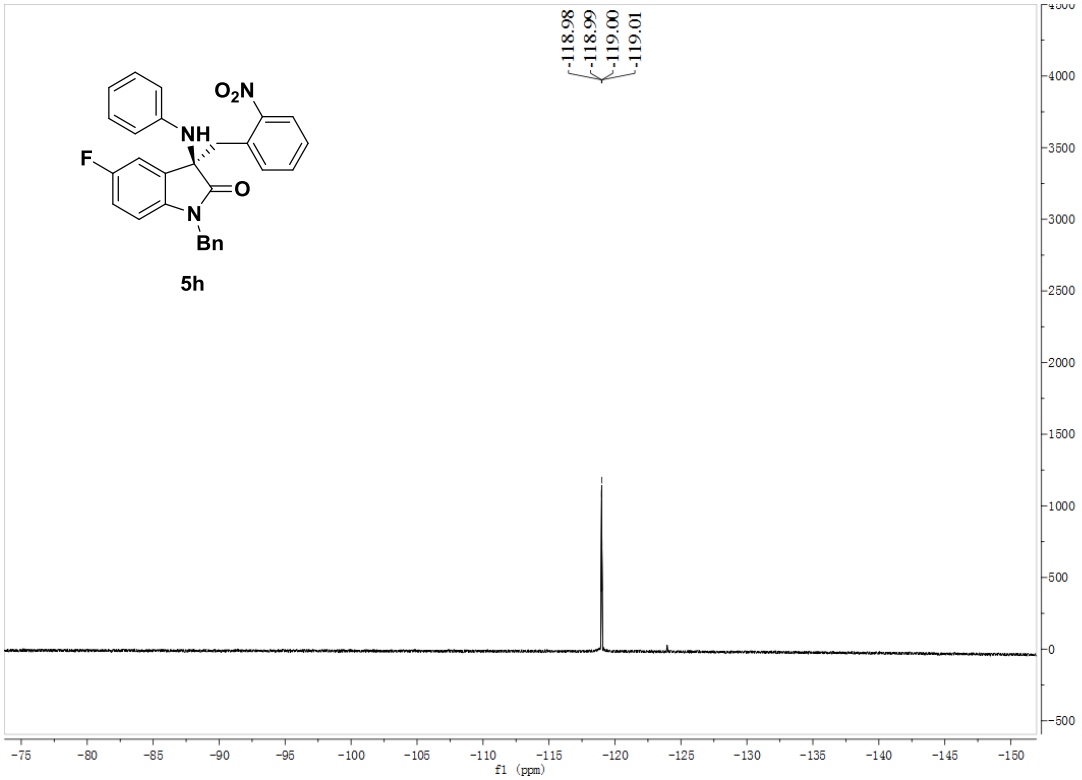
^{1}H NMR spectrum of compound 5h (in $CDCl_3$)



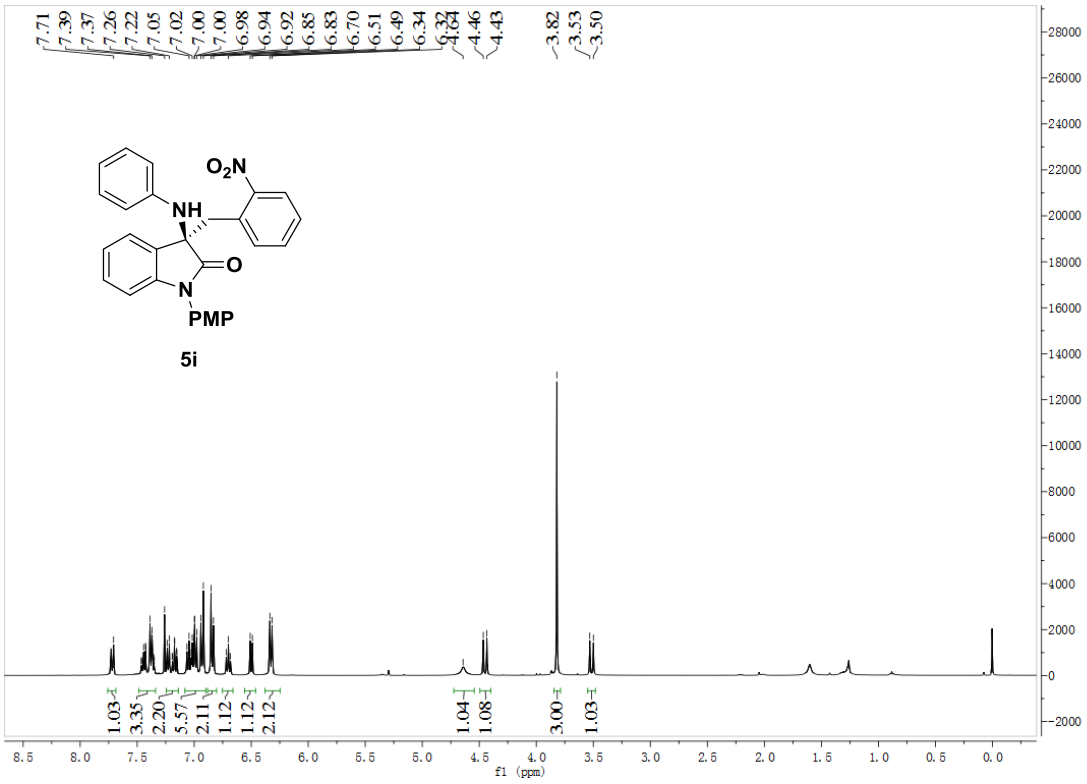
^{13}C NMR spectrum of compound 5h (in $CDCl_3$)



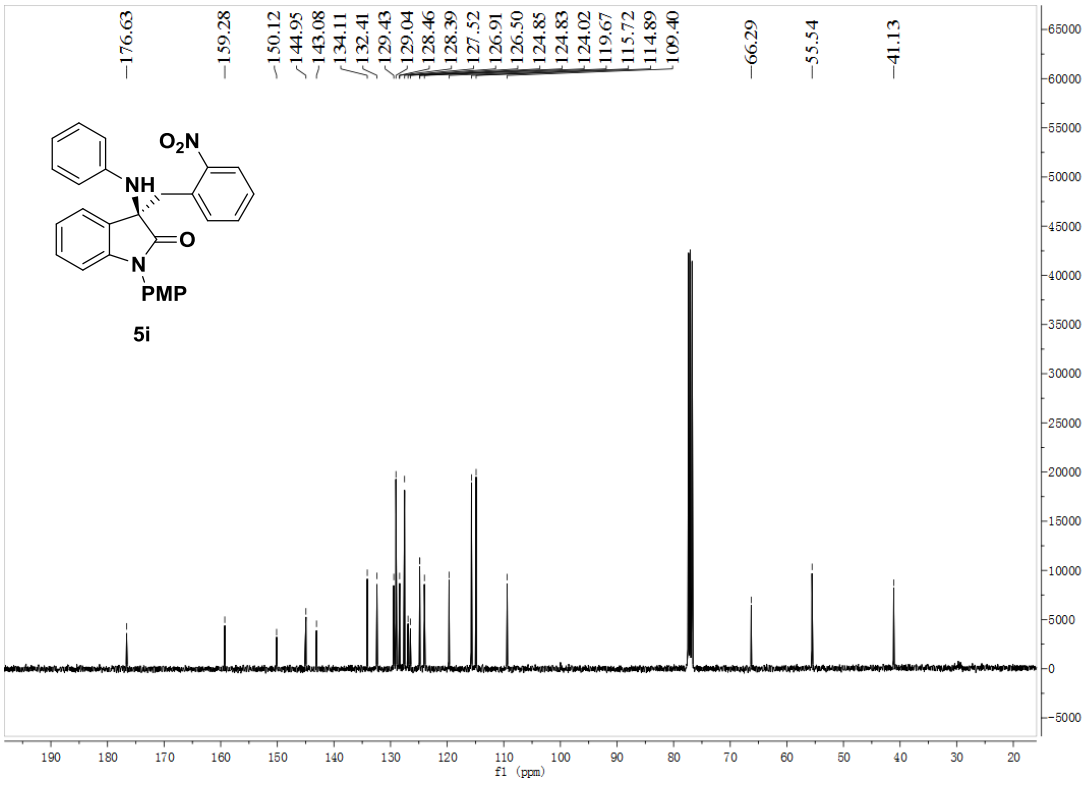
^{19}F NMR spectrum of compound 5h (in $CDCl_3$)



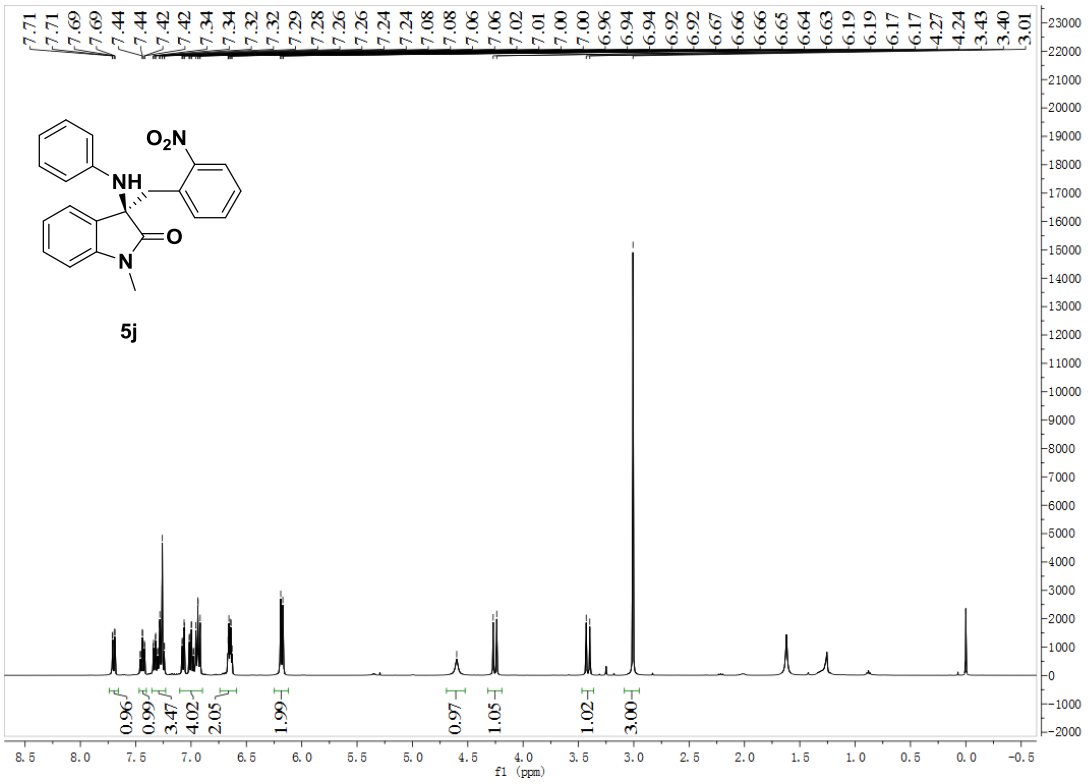
^{1}H NMR spectrum of compound 5i (in $CDCl_3$)



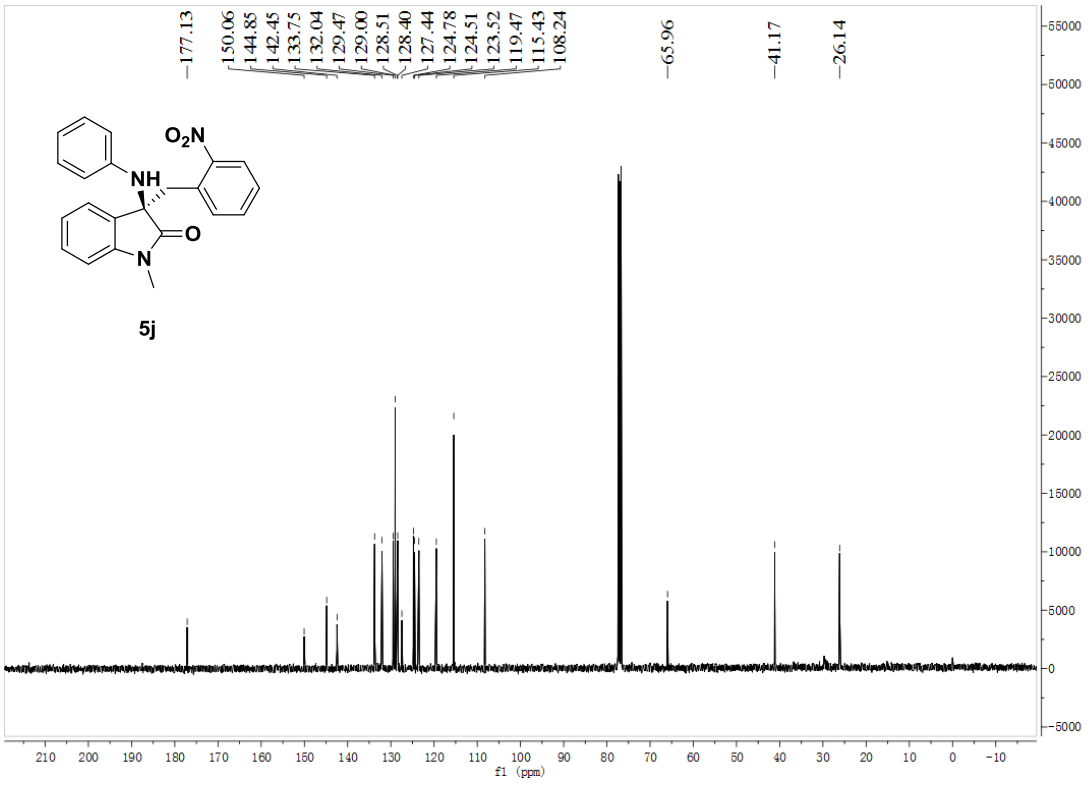
^{13}C NMR spectrum of compound 5i (in $CDCl_3$)



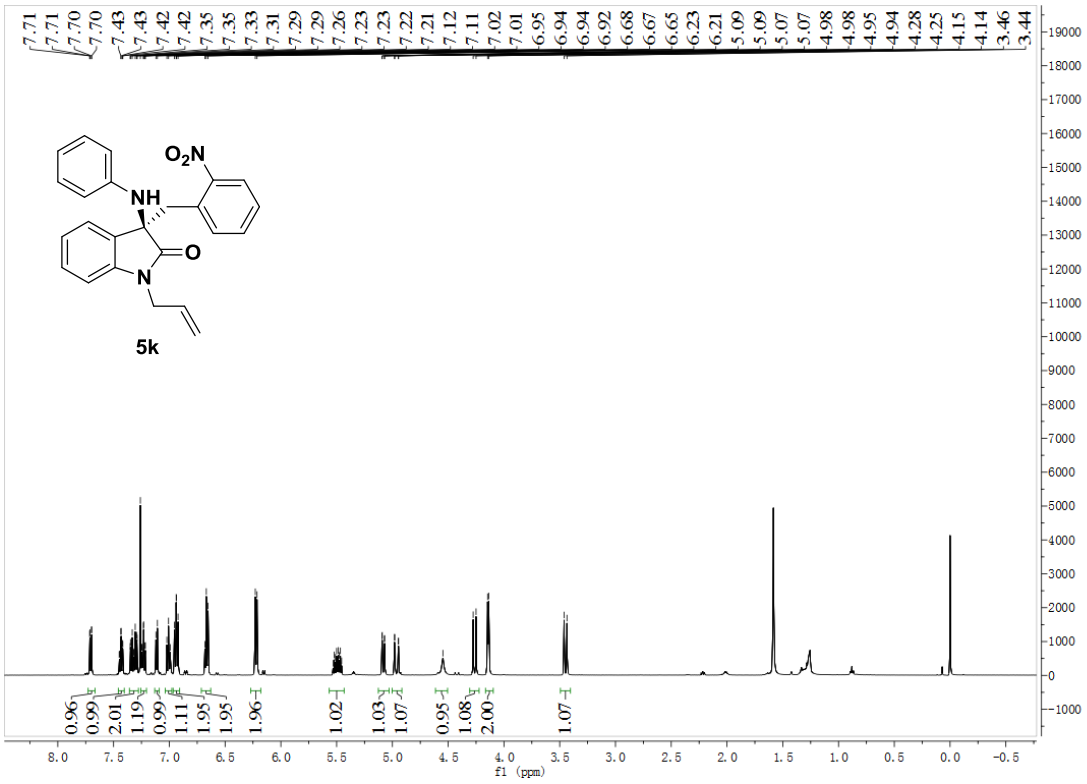
^{1}H NMR spectrum of compound 5j (in $CDCl_3$)



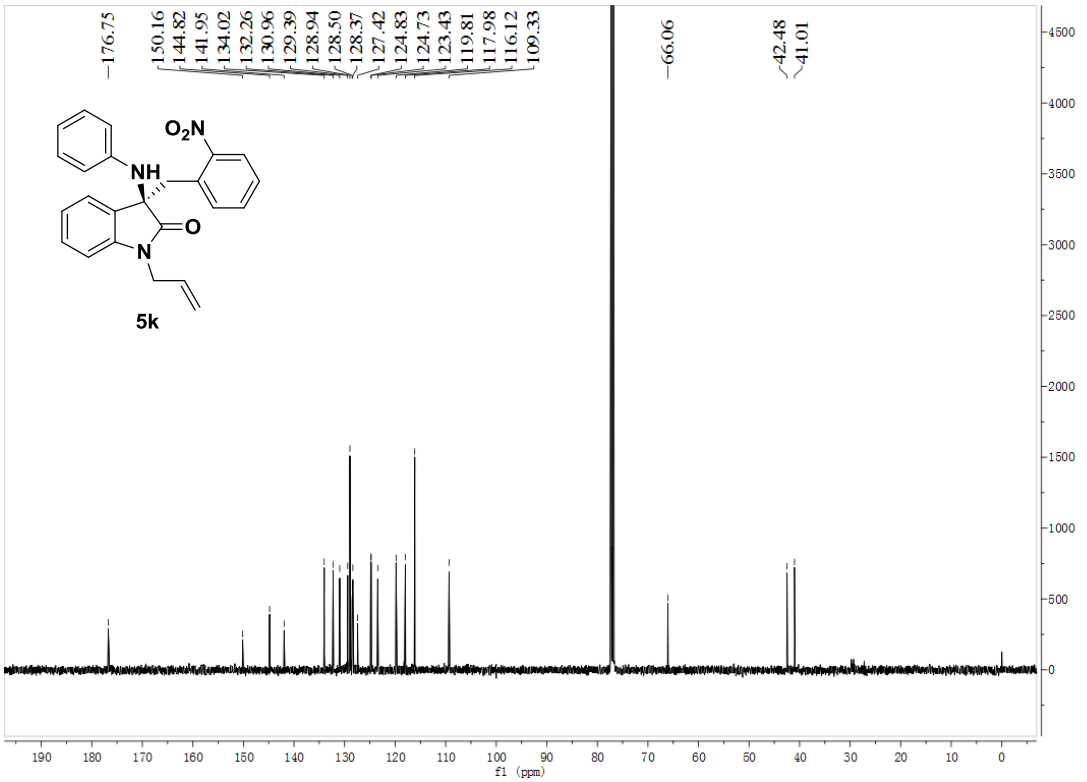
^{13}C NMR spectrum of compound 5j (in $CDCl_3$)



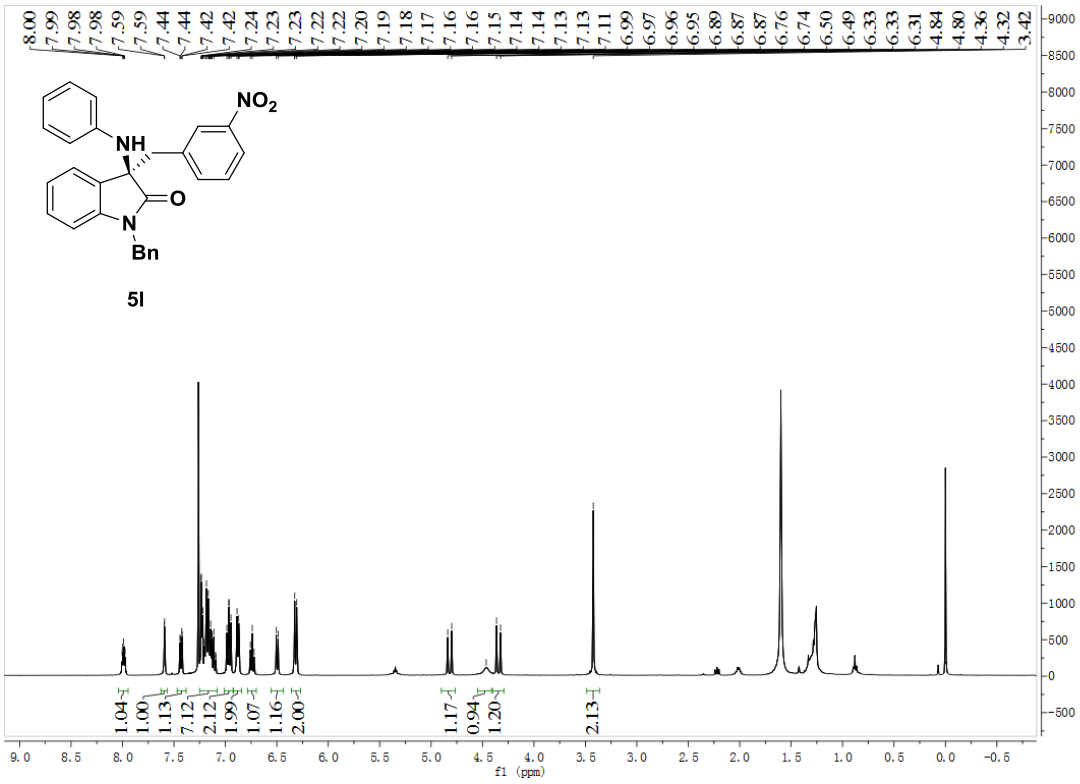
^{1}H NMR spectrum of compound 5k (in $CDCl_3$)



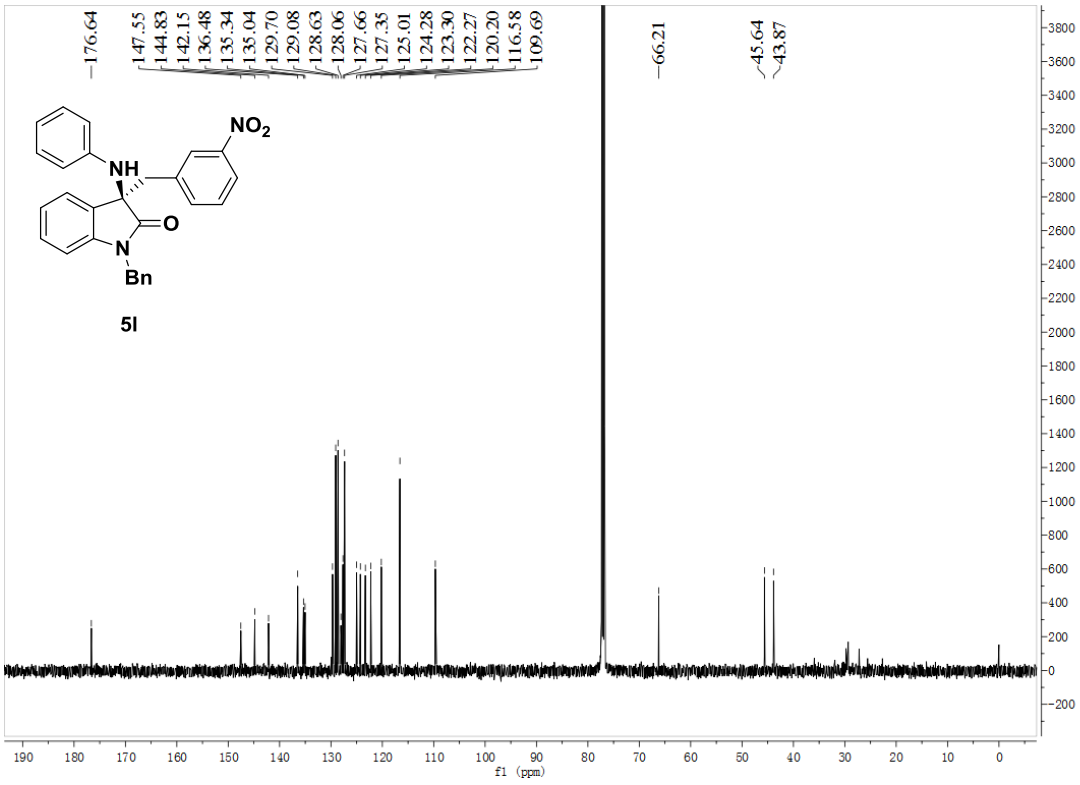
^{13}C NMR spectrum of compound 5k (in $CDCl_3$)



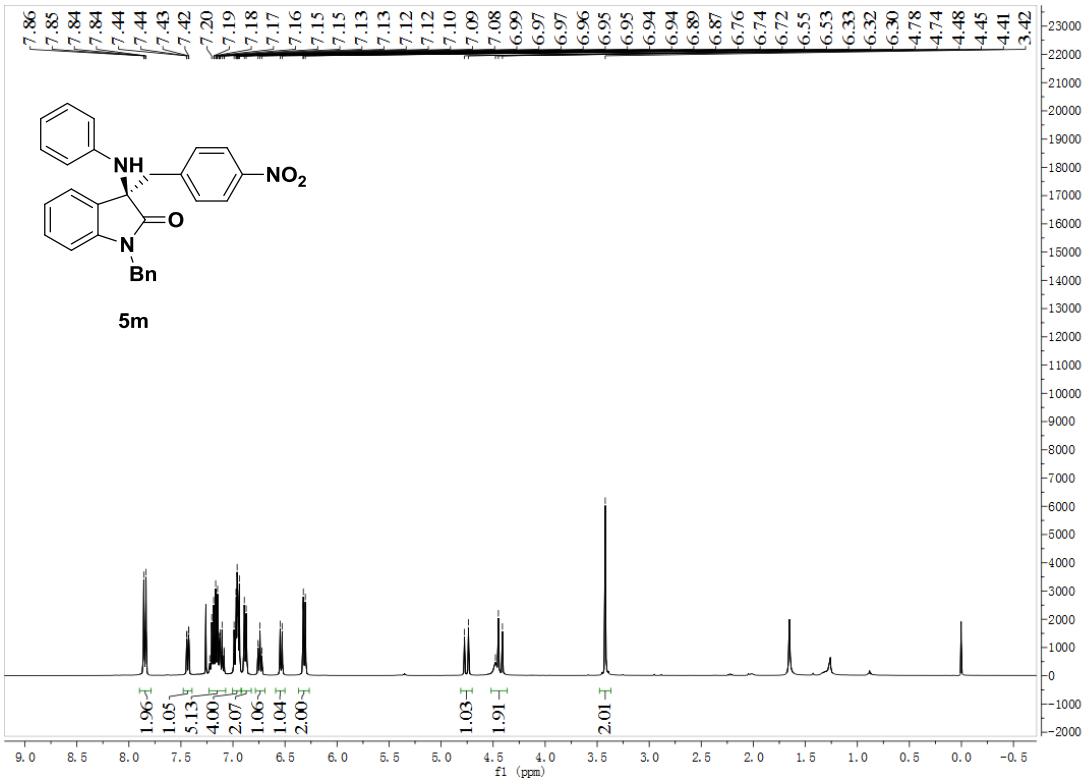
^{1}H NMR spectrum of compound 5i (in $CDCl_3$)



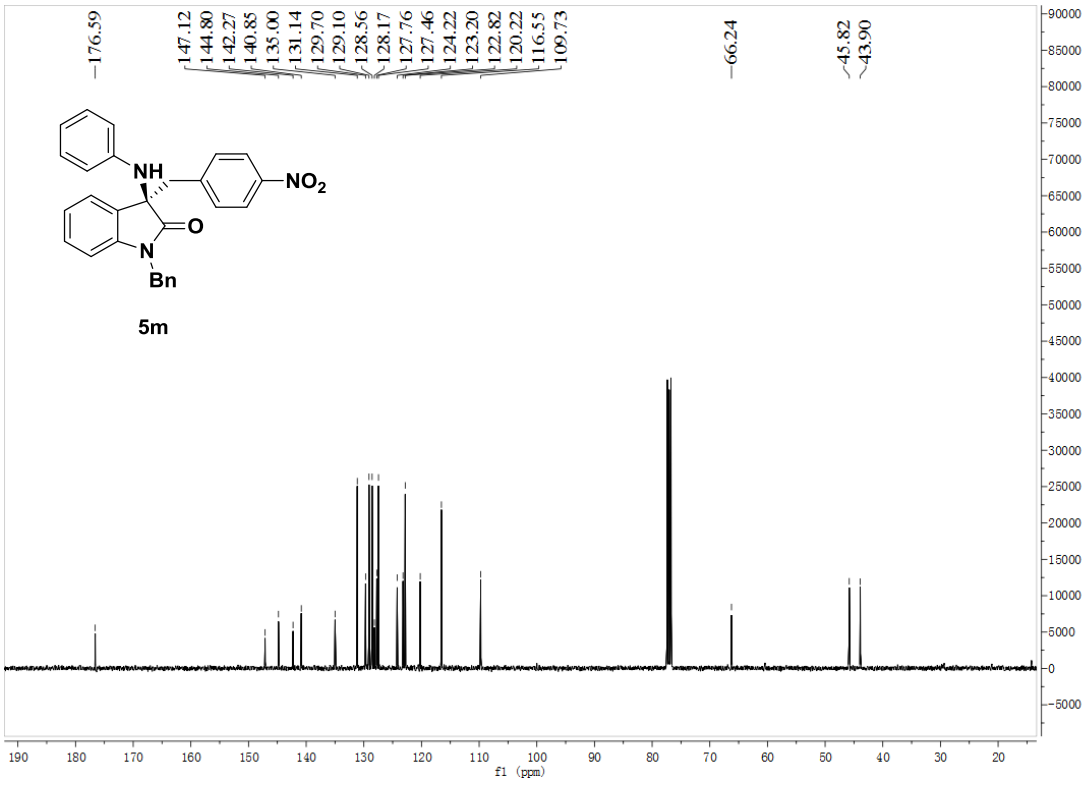
^{13}C NMR spectrum of compound 5l (in $CDCl_3$)



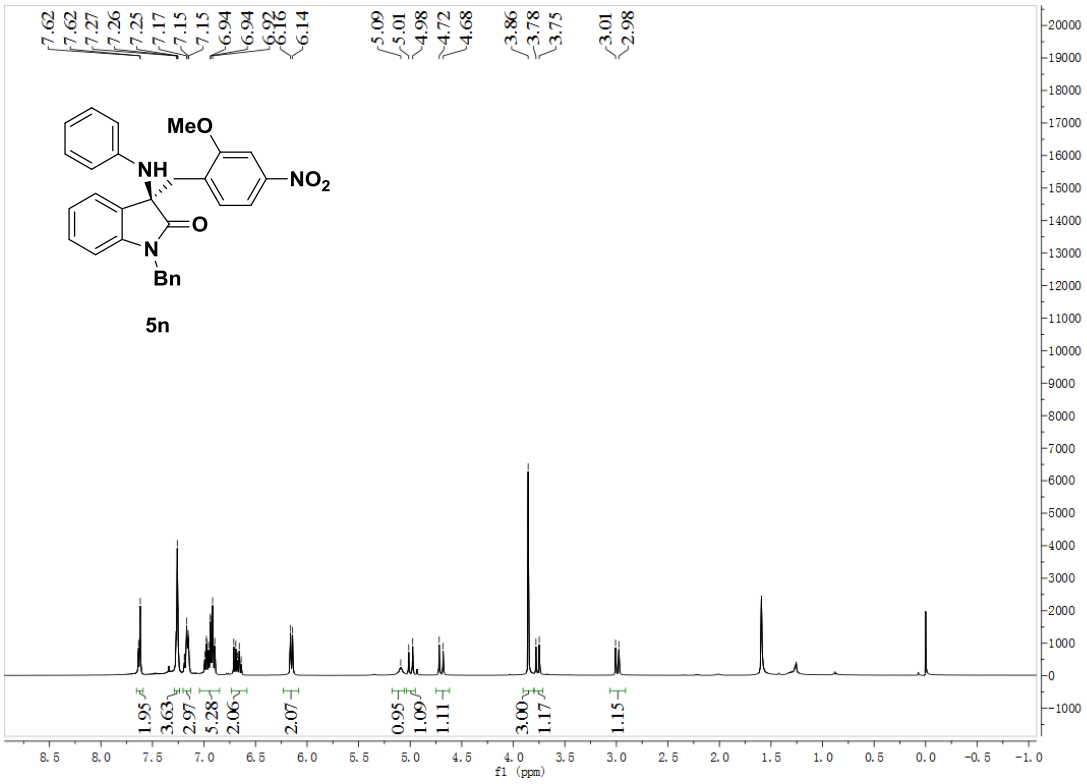
^{1}H NMR spectrum of compound 5m (in $CDCl_3$)



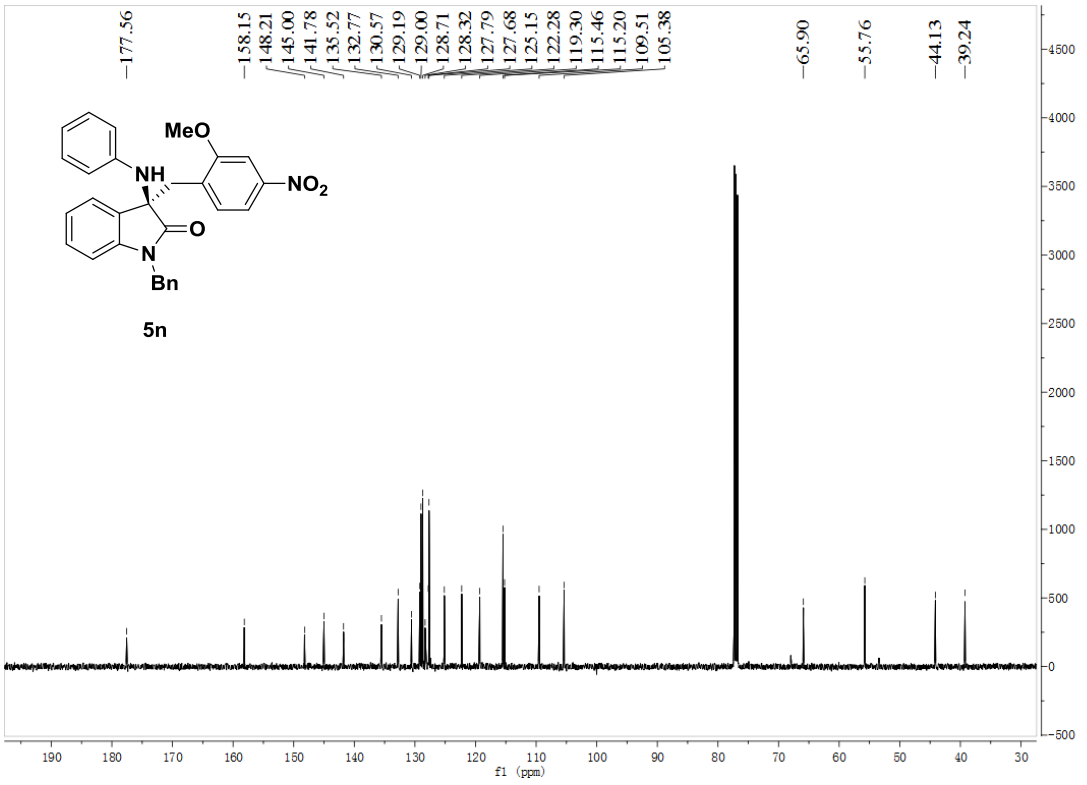
^{13}C NMR spectrum of compound 5m (in $CDCl_3$)



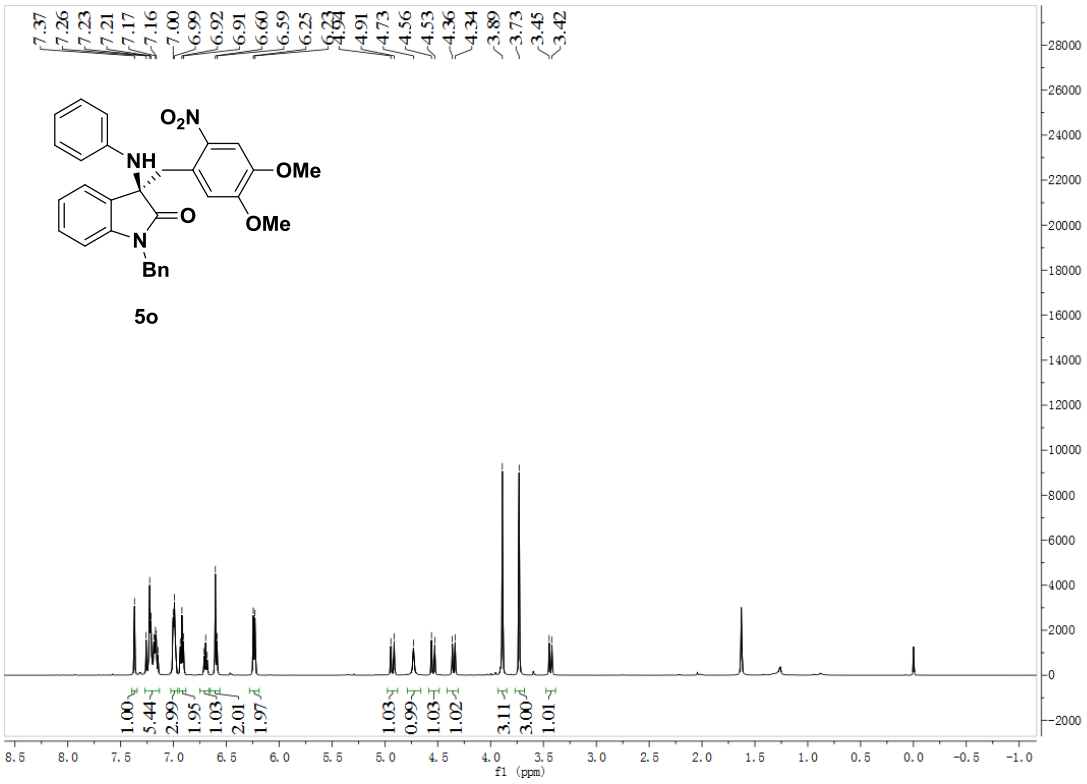
^{1}H NMR spectrum of compound 5n (in $CDCl_3$)



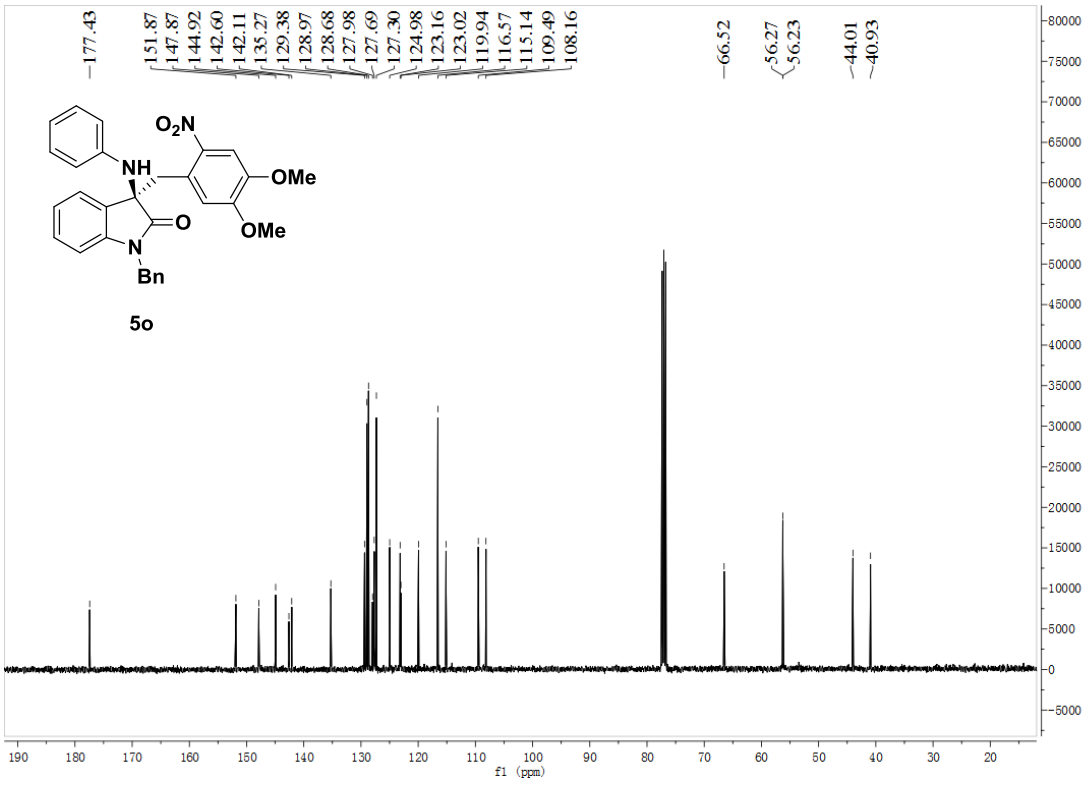
^{13}C NMR spectrum of compound 5n (in $CDCl_3$)



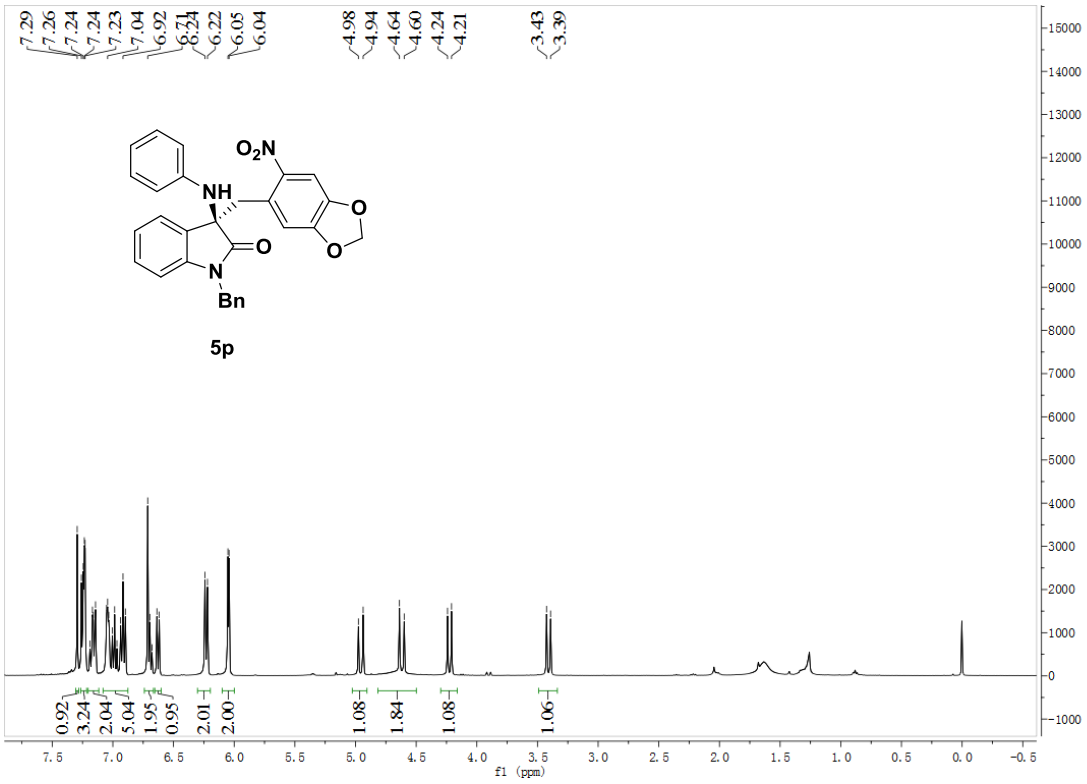
^{1}H NMR spectrum of compound 5o (in $CDCl_3$)



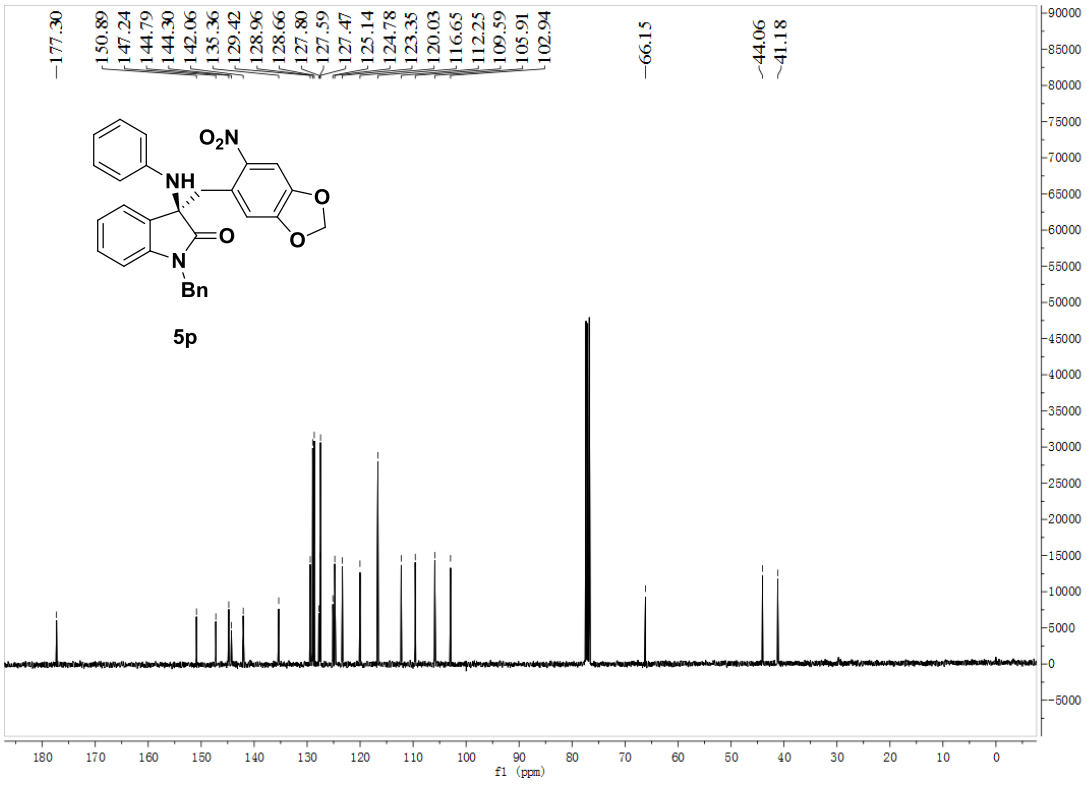
^{13}C NMR spectrum of compound 5o (in $CDCl_3$)



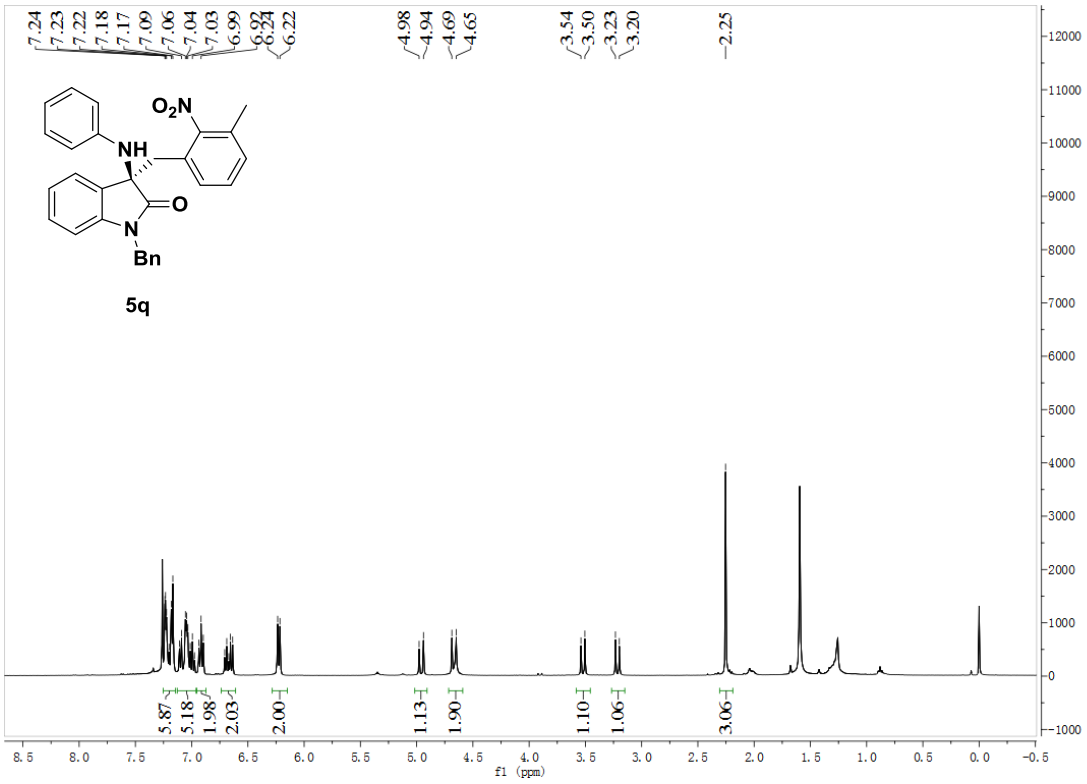
^{1}H NMR spectrum of compound 5p (in $CDCl_3$)



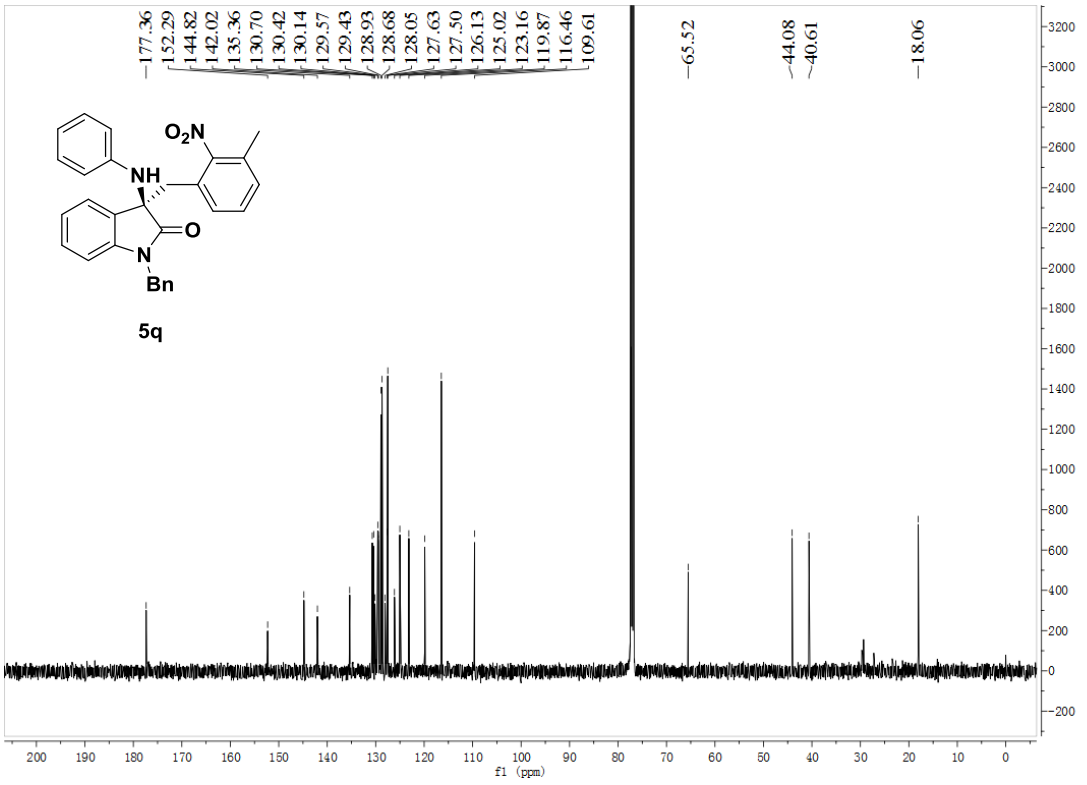
^{13}C NMR spectrum of compound 5p (in $CDCl_3$)



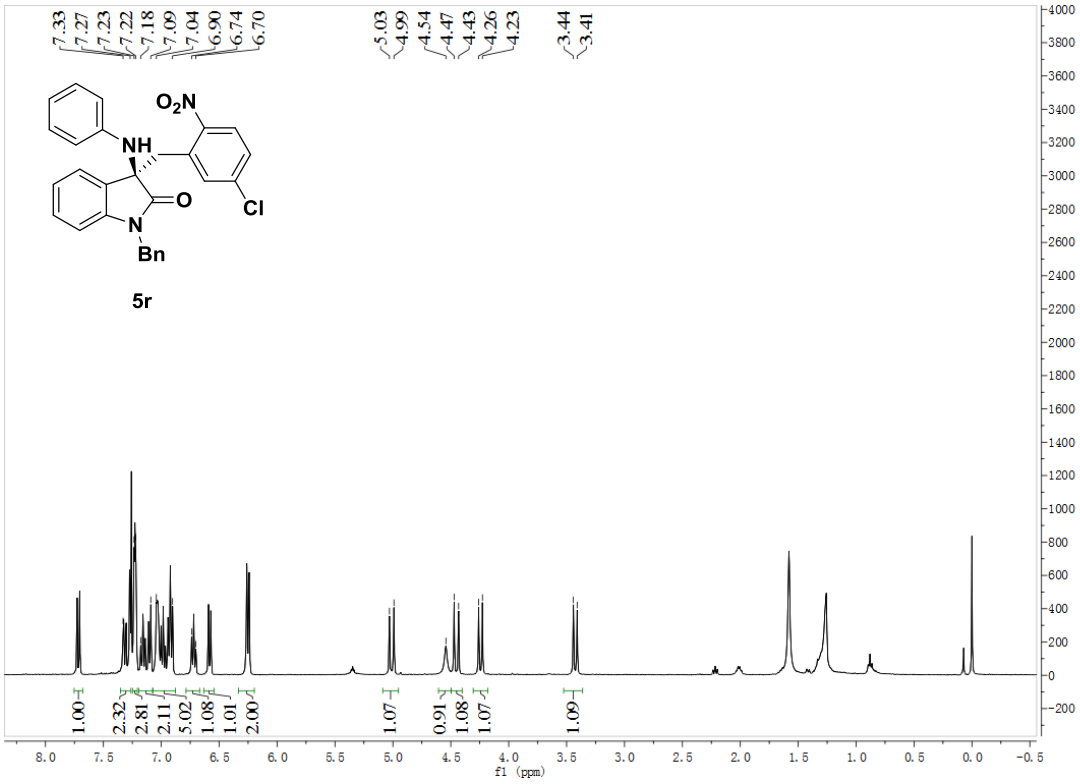
^{1}H NMR spectrum of compound 5q (in $CDCl_3$)



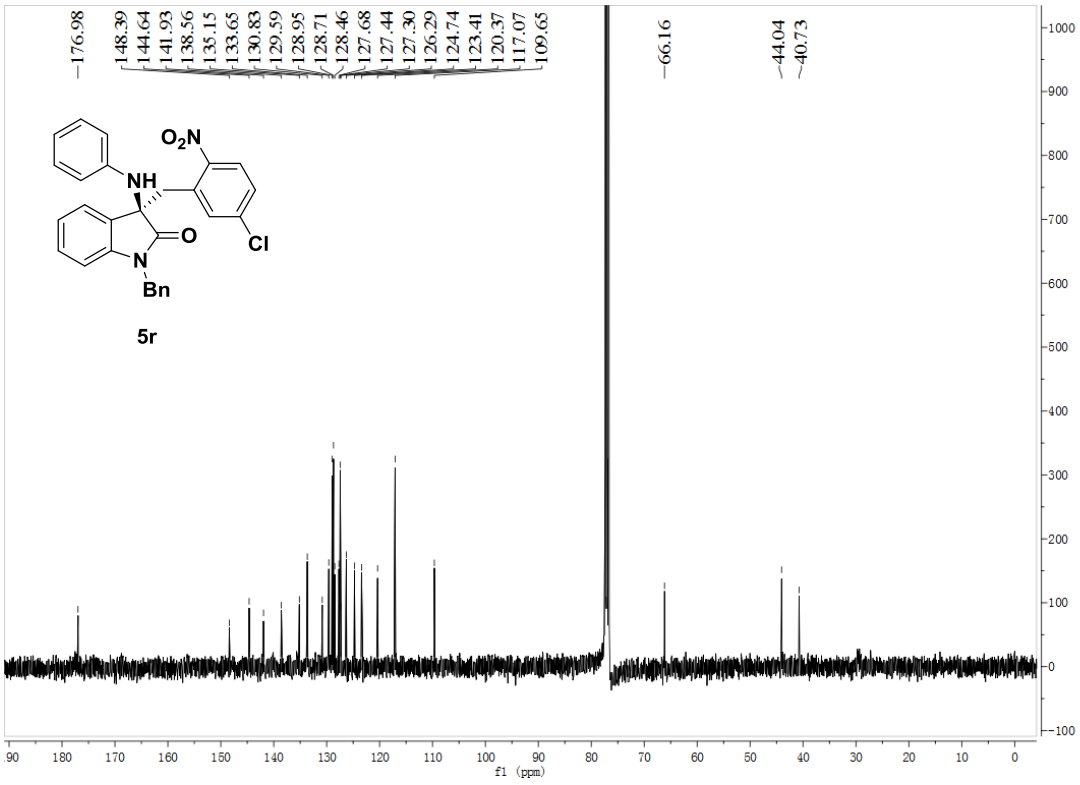
^{13}C NMR spectrum of compound 5q (in $CDCl_3$)



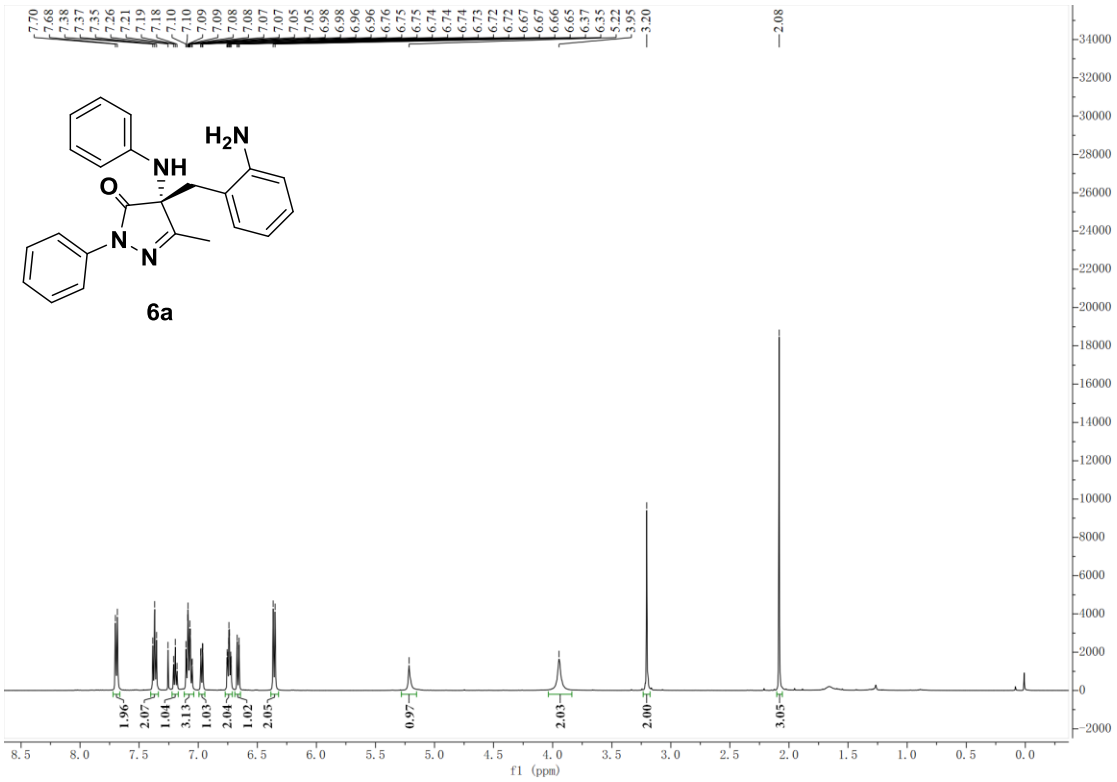
^{1}H NMR spectrum of compound 5r (in $CDCl_3$)



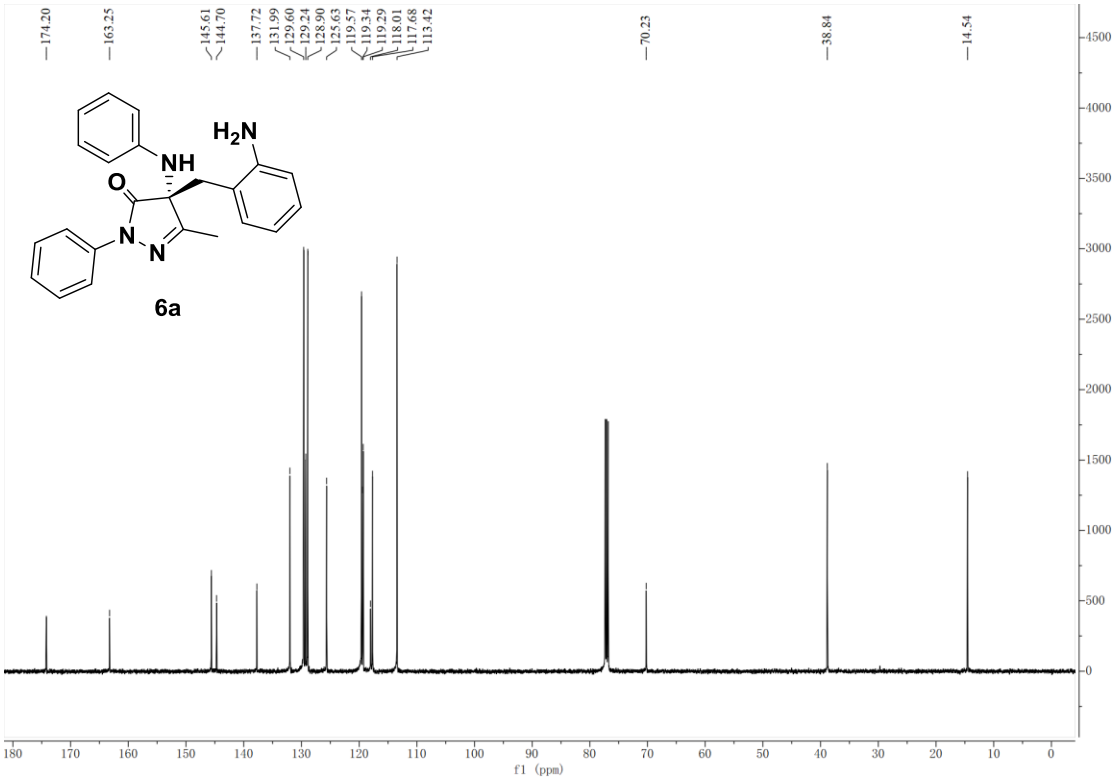
^{13}C NMR spectrum of compound 5r (in $CDCl_3$)



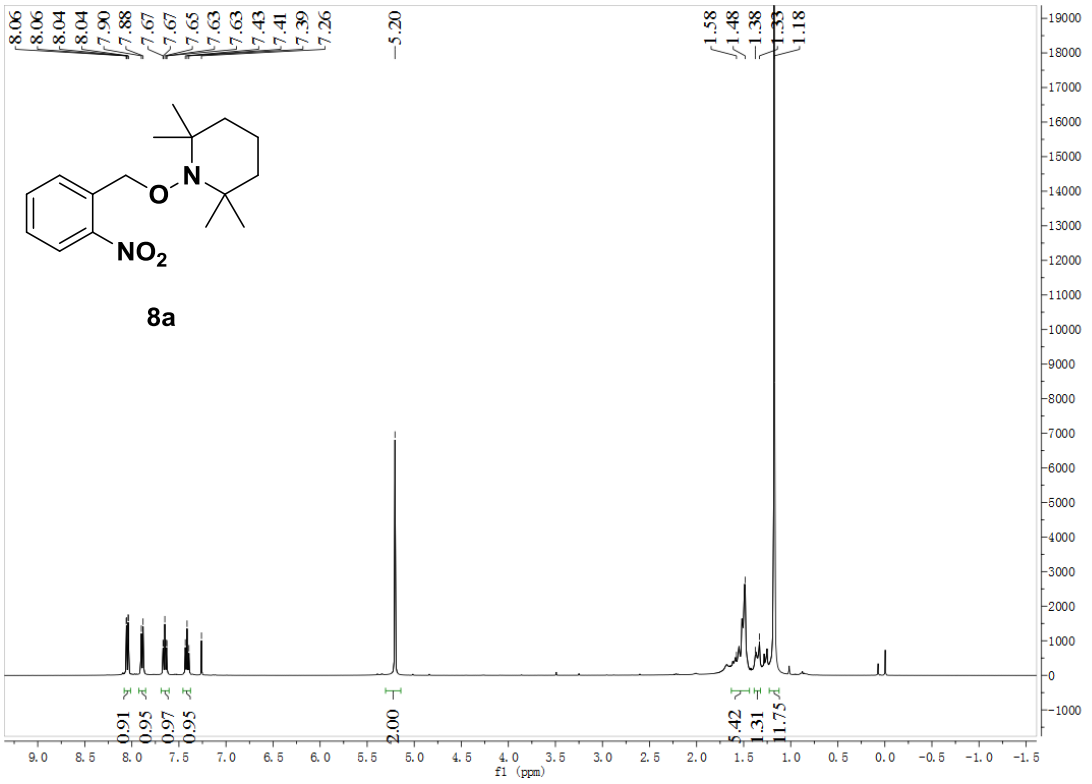
^{1}H NMR spectrum of compound 6a (in $CDCl_3$)



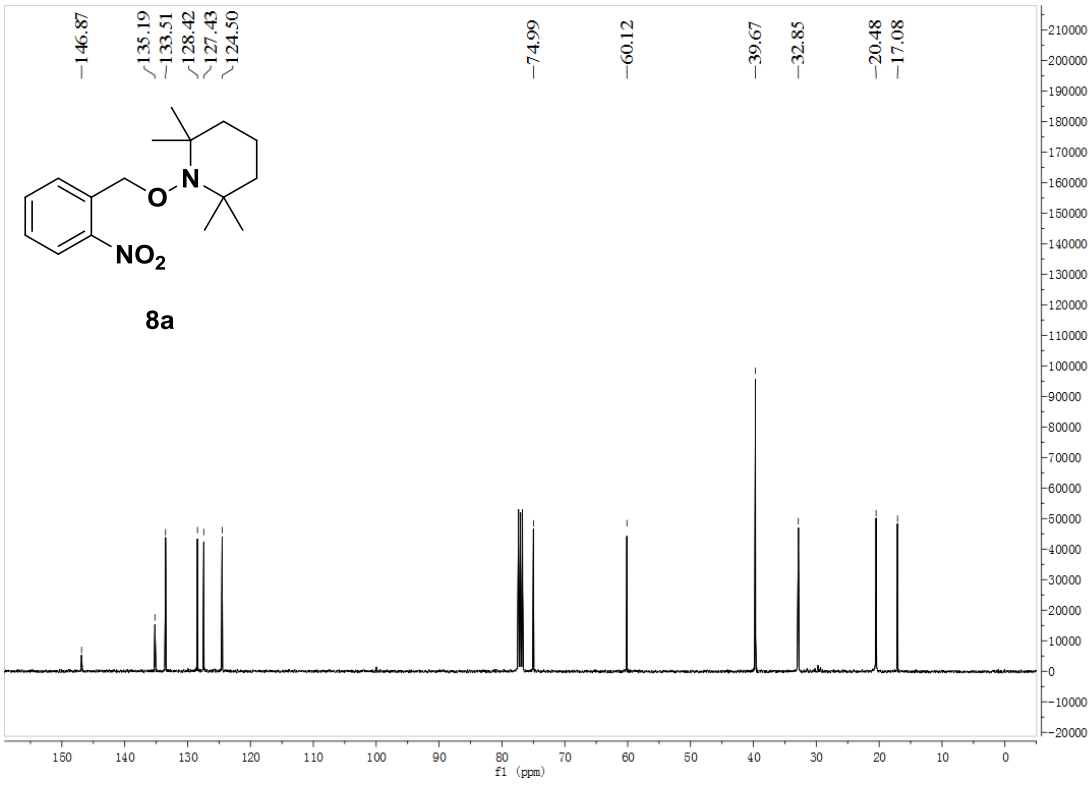
^{13}C NMR spectrum of compound 6a (in $CDCl_3$)



^{1}H NMR spectrum of compound 8a (in $CDCl_3$)



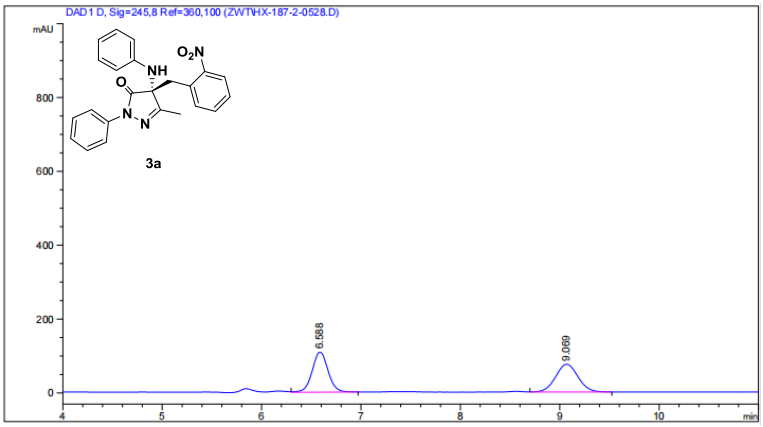
^{13}C NMR spectrum of compound 8a (in $CDCl_3$)



9. Copies of HPLC Data

HPLC spectra of 3a

racemate



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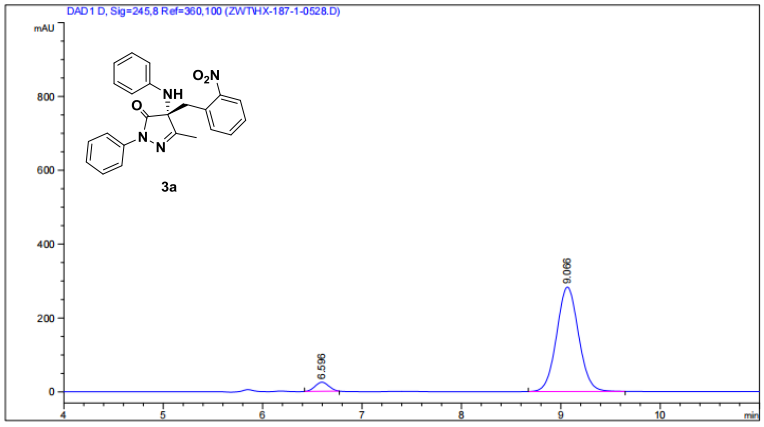
2	9.069	VB	0.2430	1180.79517	75.28924	49.2746

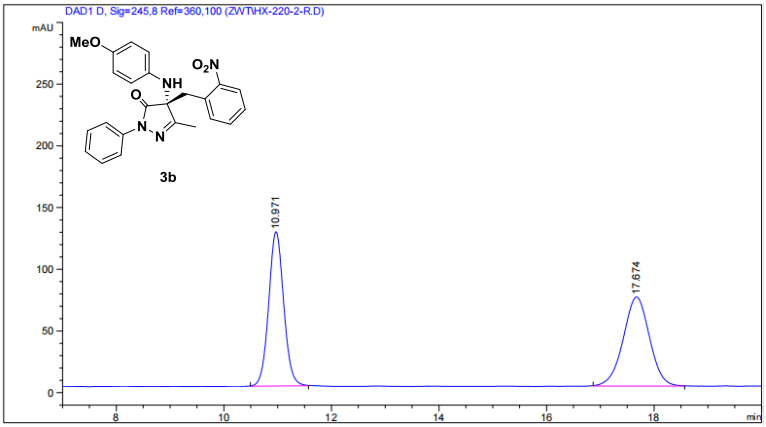
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.596	MM R	0.1592	234.19368	24.51466	5.1027
2	9.066	BB	0.2376	4355.39600	282.92685	94.8973

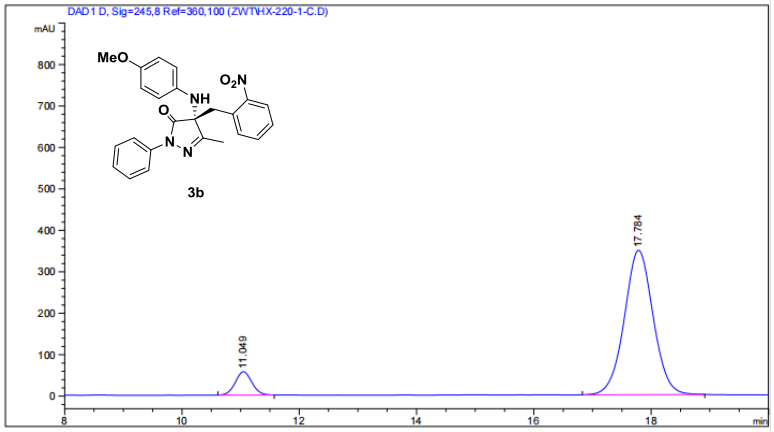
HPLC spectra of 3b

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.971	BB	0.2980	2421.44141	125.01467	49.7195
2	17.674	BB	0.5219	2448.76025	72.16841	50.2805

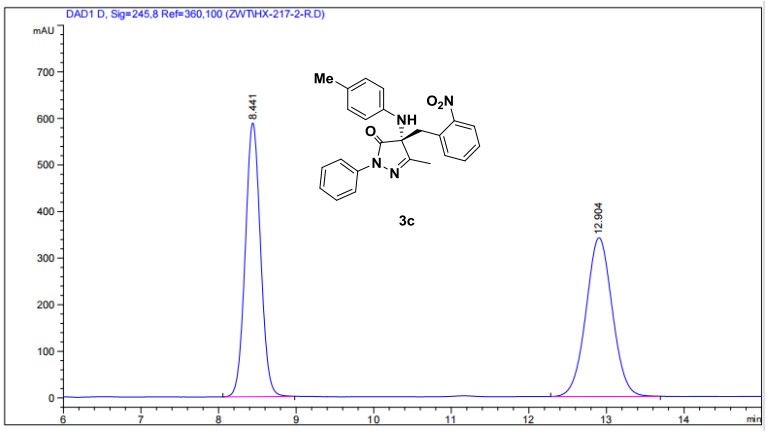
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.049	BB	0.3037	1110.18506	56.39314	8.5070
2	17.784	BB	0.5276	1.19400e4	348.58365	91.4930

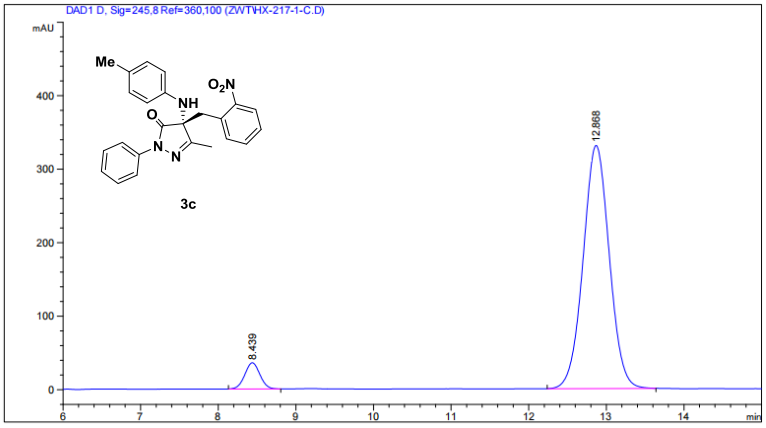
HPLC spectra of 3c

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.441	BB	0.2132	8026.01416	588.28253	49.9370
2	12.904	BB	0.3633	8046.25488	341.00577	50.0630

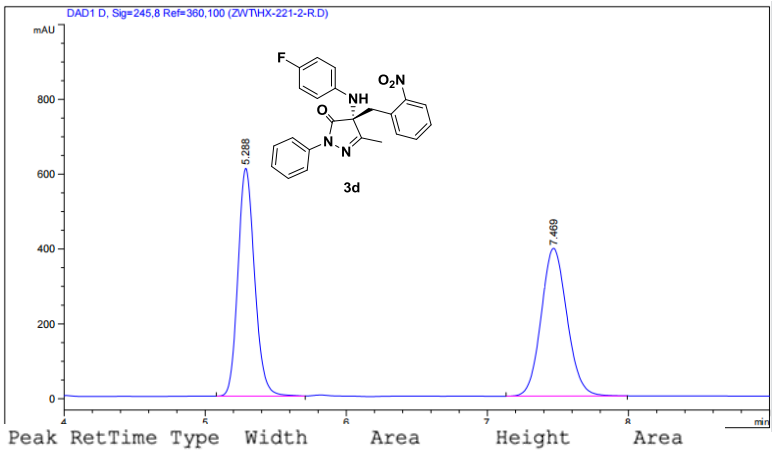
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.439	BB	0.2079	483.05579	35.69959	5.8688
2	12.868	BB	0.3612	7747.91602	330.92142	94.1312

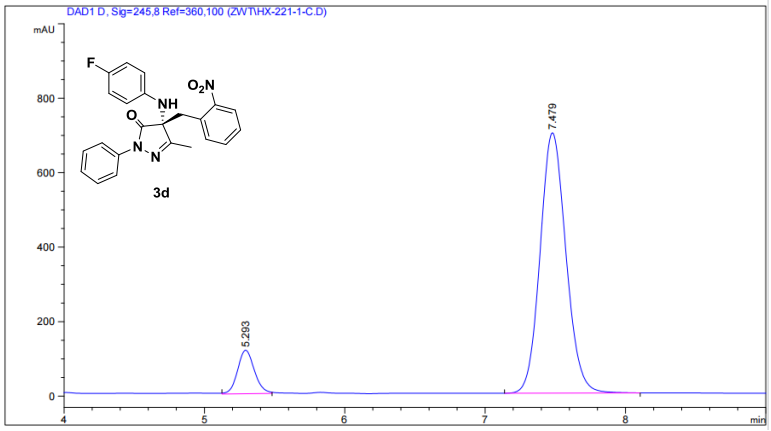
HPLC spectra of 3d

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.288	BV	0.1277	5000.94531	609.60297	49.8609
2	7.469	BB	0.1965	5028.85742	395.16641	50.1391

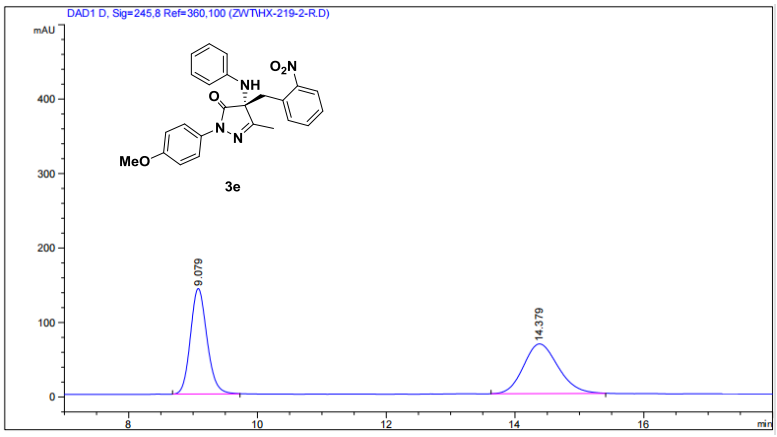
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.293	MM R	0.1385	973.18060	117.14494	9.8194
2	7.479	BB	0.1991	8937.65625	699.39496	90.1806

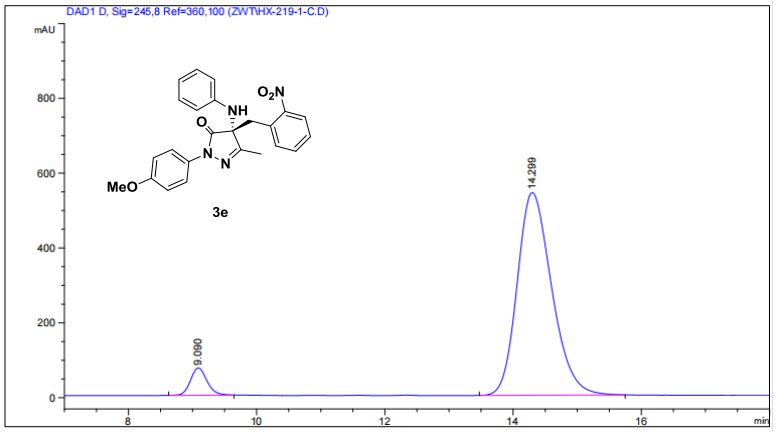
HPLC spectra of 3e

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.079	BB	0.2747	2537.90186	141.86200	50.2392
2	14.379	BB	0.5867	2513.73950	66.84922	49.7608

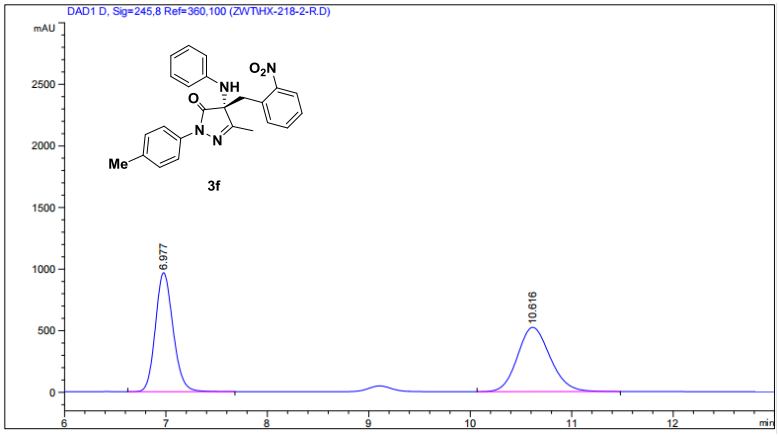
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.090	BB	0.2777	1311.82446	73.00029	6.0835
2	14.299	BB	0.5760	2.02519e4	541.91162	93.9165

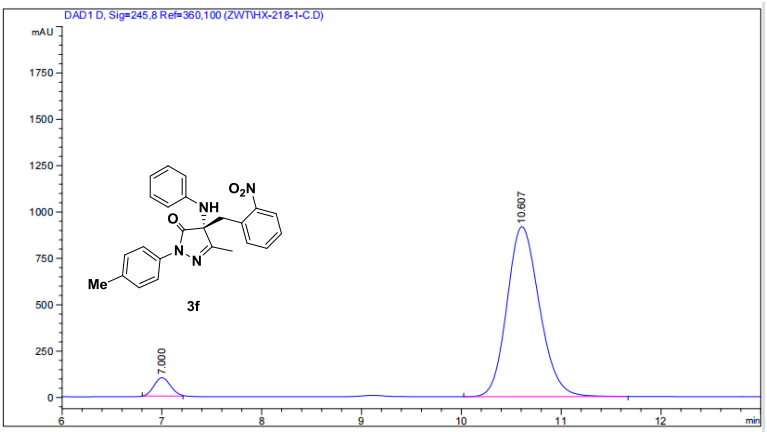
HPLC spectra of 3f

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.977	VB	0.1874	1.17162e4	966.88989	50.0512
2	10.616	BB	0.3454	1.16922e4	521.77979	49.9488

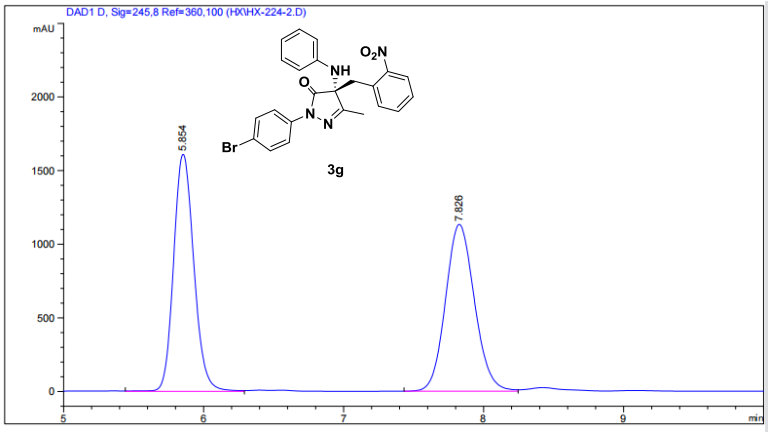
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.000	MM R	0.1900	1129.20422	99.04319	5.1693
2	10.607	BB	0.3498	2.07152e4	916.18219	94.8307

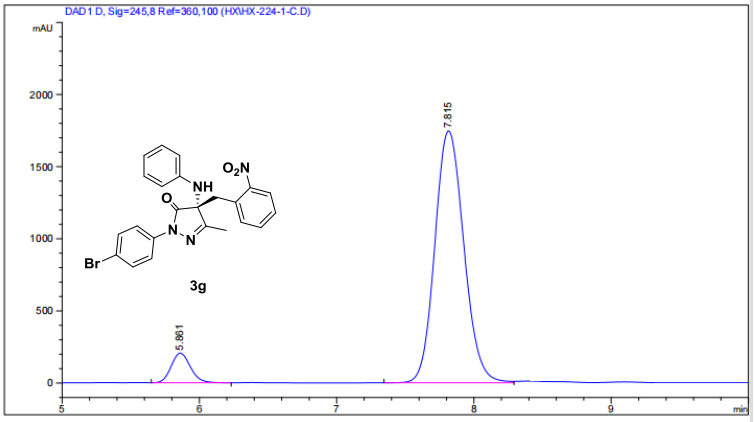
HPLC spectra of 3g

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.854	VV	0.1573	1.61999e4	1611.56738	49.7989
2	7.826	BV	0.2240	1.63308e4	1133.87744	50.2011

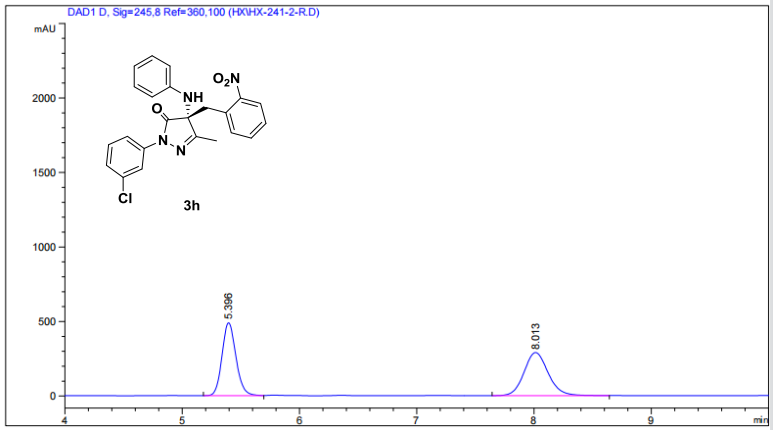
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.861	VB	0.1515	2000.38879	205.59995	7.2297
2	7.815	BV	0.2294	2.56685e4	1747.30322	92.7703

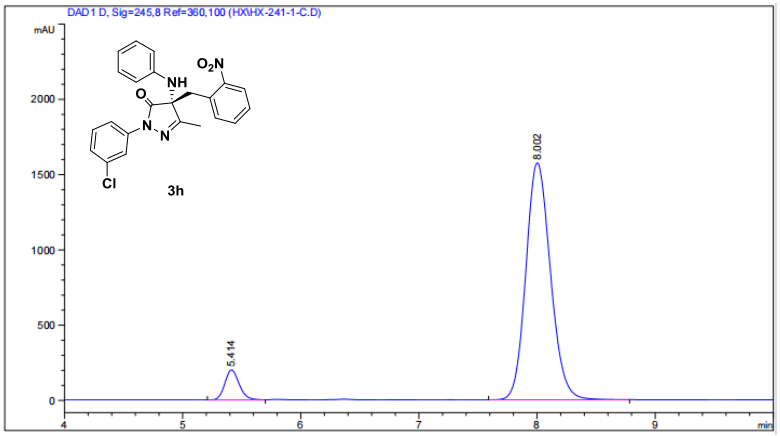
HPLC spectra of 3h

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.396	BV	0.1266	4052.34497	489.59232	49.4626
2	8.013	BB	0.2188	4140.40381	289.51068	50.5374

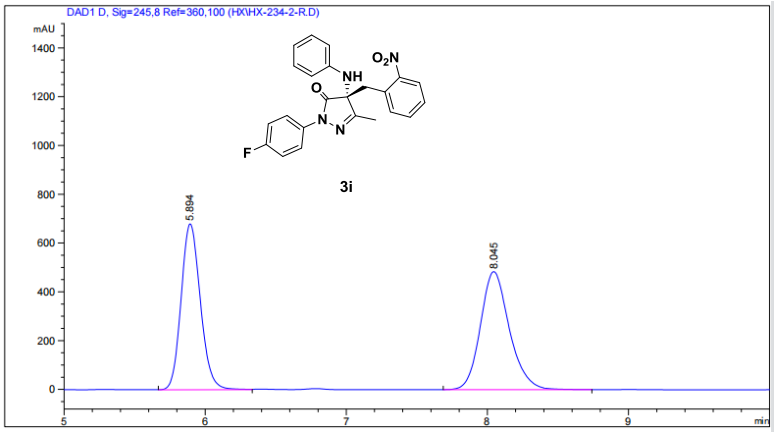
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.414	BV	0.1311	1696.97583	199.69678	6.9372
2	8.002	BB	0.2227	2.27651e4	1573.91846	93.0628

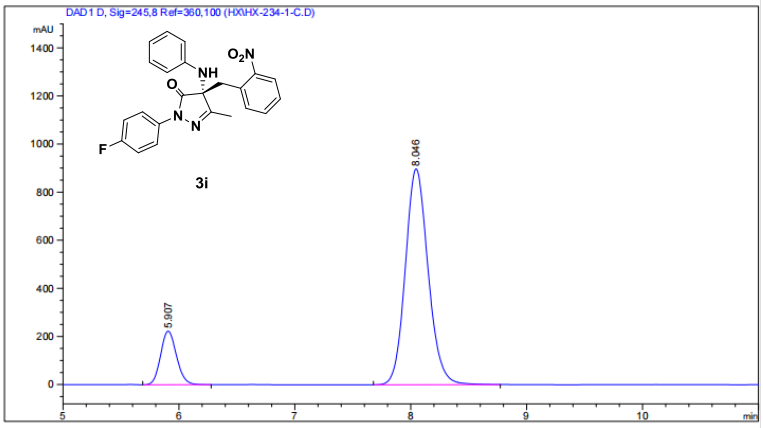
HPLC spectra of 3i

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.894	VB	0.1487	6458.96924	680.54382	48.3370
2	8.045	BB	0.2185	6903.38916	483.67743	51.6630

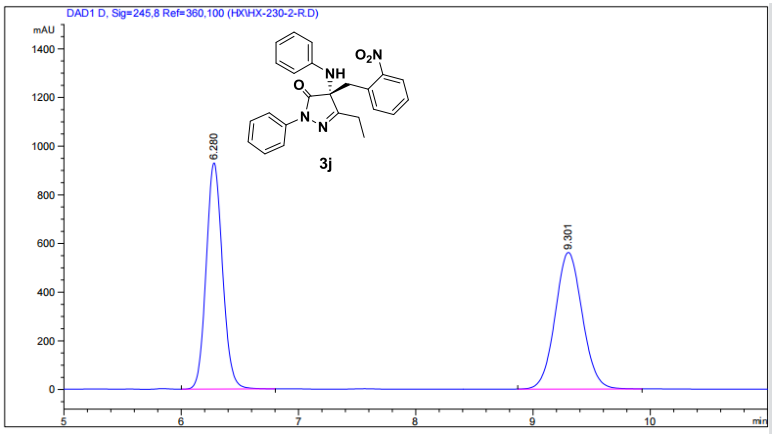
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.907	VB	0.1493	2131.50000	223.44695	14.7848
2	8.046	BB	0.2097	1.22854e4	897.72150	85.2152

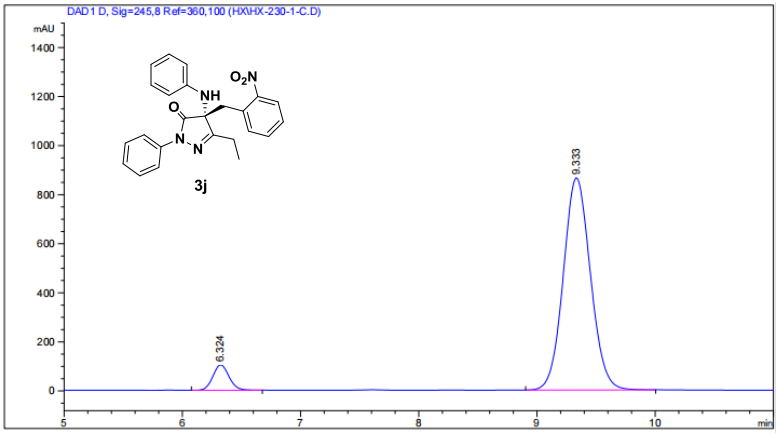
HPLC spectra of 3j

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.280	VB	0.1490	9009.25879	930.17627	49.9275
2	9.301	BB	0.2498	9035.42285	561.21057	50.0725

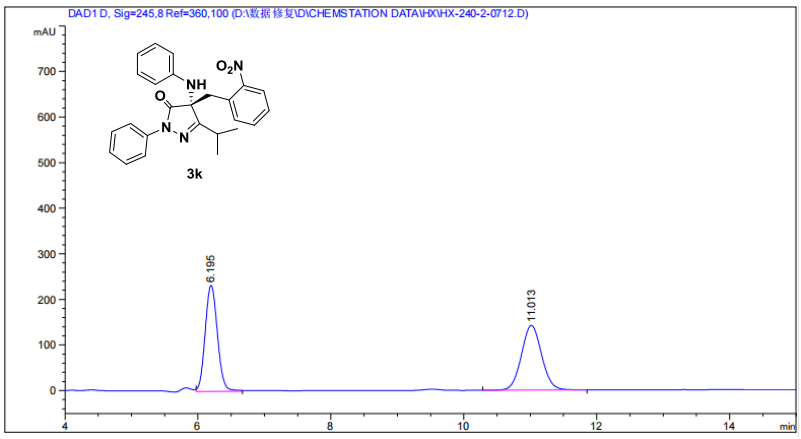
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.324	VB	0.1471	984.69659	103.44350	6.6570
2	9.333	BB	0.2463	1.38073e4	864.87512	93.3430

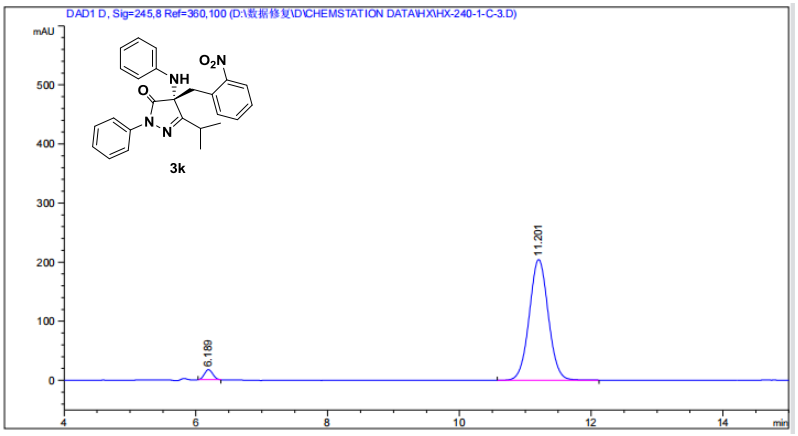
HPLC spectra of 3k

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.195	MM R	0.2135	2977.80054	232.45711	49.8249
2	11.013	BB	0.3284	2998.73291	142.01079	50.1751

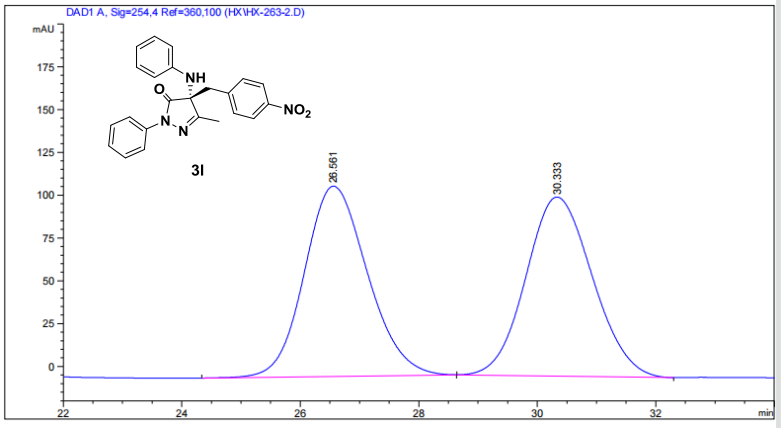
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.189	MM R	0.1420	143.74097	16.87157	3.3831
2	11.201	BB	0.3102	4105.01270	204.44774	96.6169

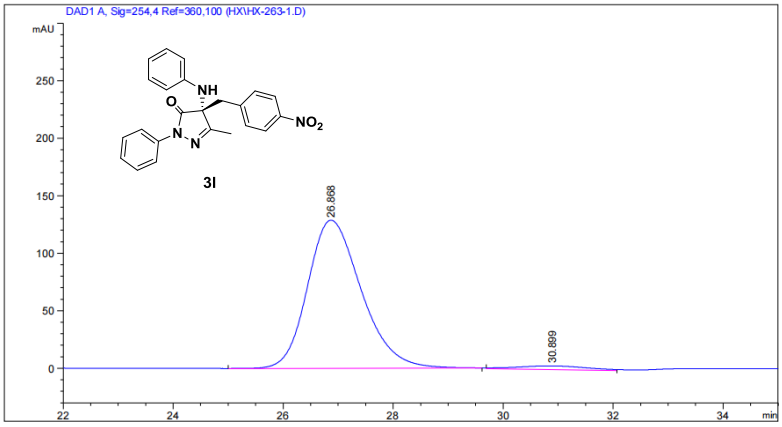
HPLC spectra of 3l

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.561	BB	1.1295	8197.31250	111.01217	50.1382
2	30.333	BB	1.2020	8152.12646	104.51913	49.8618

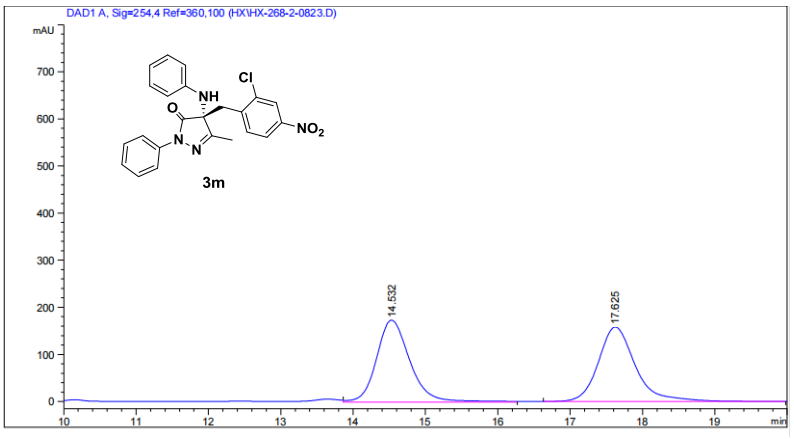
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.868	BB	1.0310	8726.05859	128.69531	96.8502
2	30.899	MM R	1.4619	283.78882	3.23548	3.1498

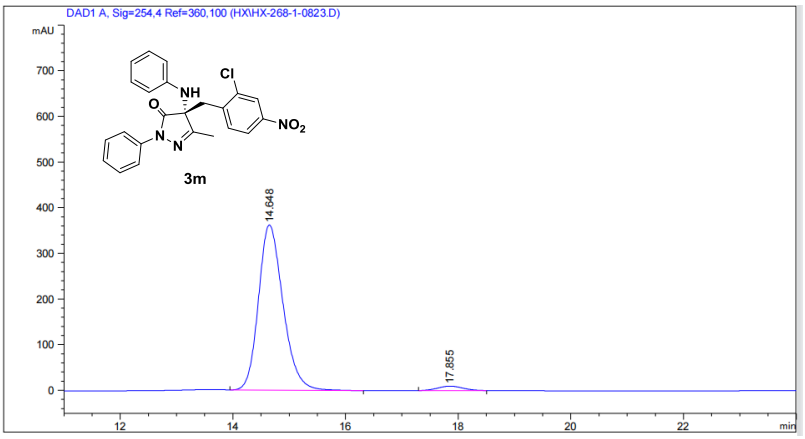
HPLC spectra of 3m

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.532	MM R	0.5366	5597.83691	173.85474	49.9803
2	17.625	BB	0.5362	5602.24512	157.80455	50.0197

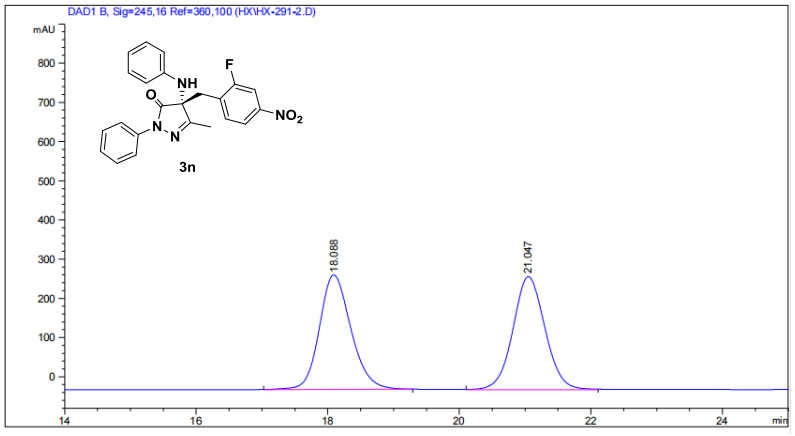
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.648	BB	0.4635	1.09584e4	361.66602	97.1376
2	17.855	MM R	0.5400	322.91187	9.96678	2.8624

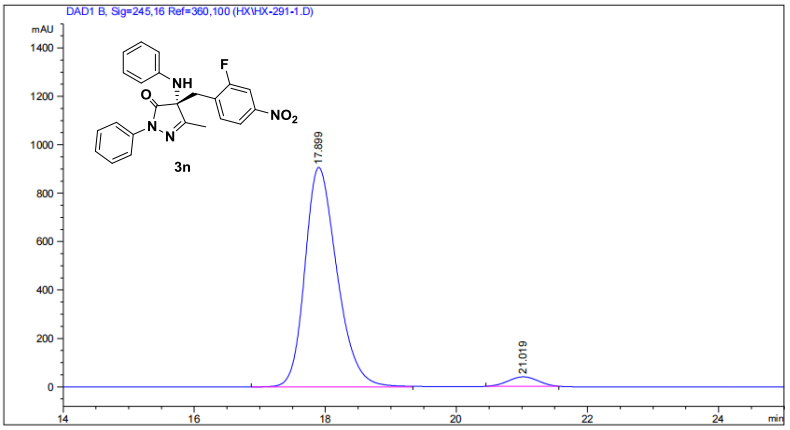
HPLC spectra of 3n

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.088	MM R	0.5569	9762.43164	292.15189	49.9277
2	21.047	MM R	0.5660	9790.69141	288.29462	50.0723

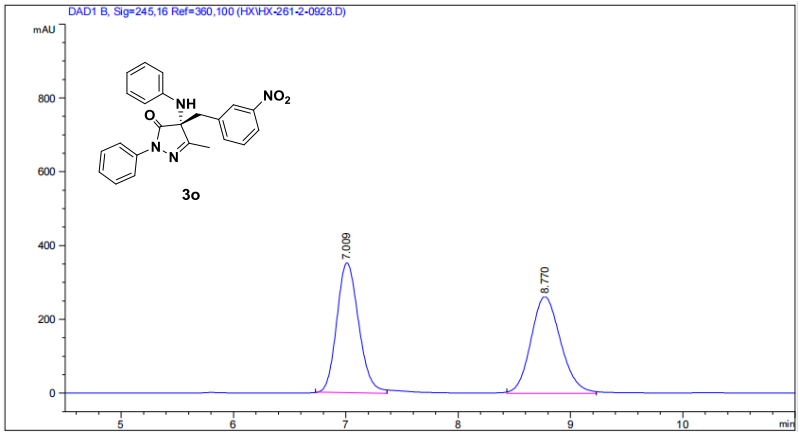
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.899	MM R	0.5686	3.09497e4	907.25391	96.1146
2	21.019	MM R	0.5297	1251.11536	39.36663	3.8854

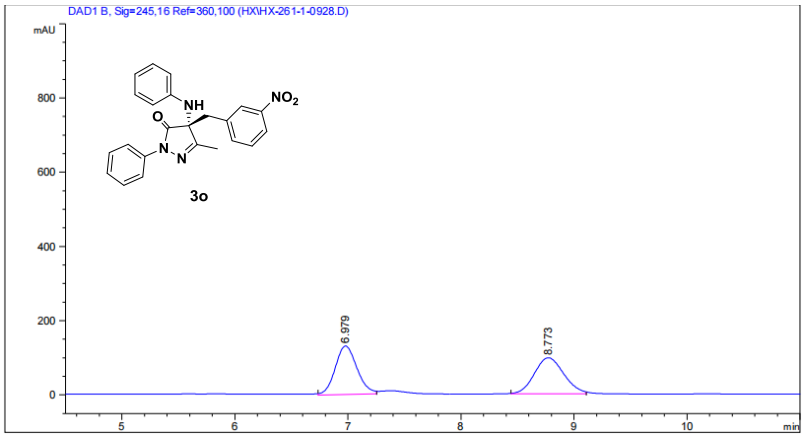
HPLC spectra of 3o

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.009	MM R	0.2262	4778.79541	352.04843	49.6384
2	8.770	MM R	0.3076	4848.41406	262.66681	50.3616

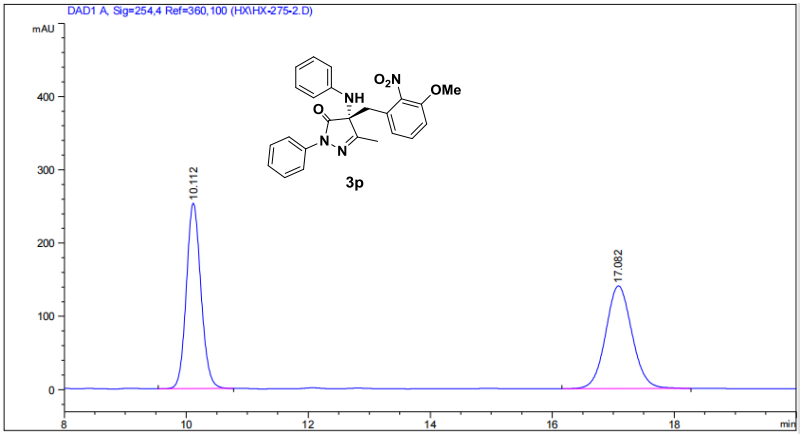
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.979	MM R	0.2239	1759.79102	131.01114	50.0123
2	8.773	MM R	0.3016	1758.92810	97.19313	49.9877

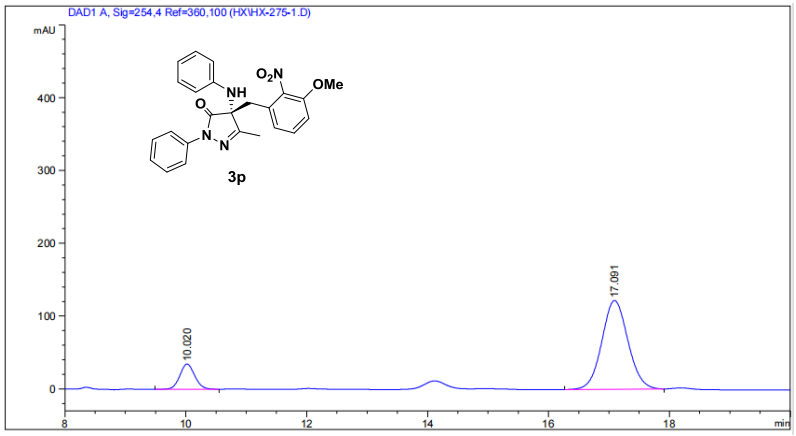
HPLC spectra of 3p

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.112	BB	0.2562	4210.47217	252.98915	50.0349
2	17.082	BB	0.4639	4204.59961	140.18813	49.9651

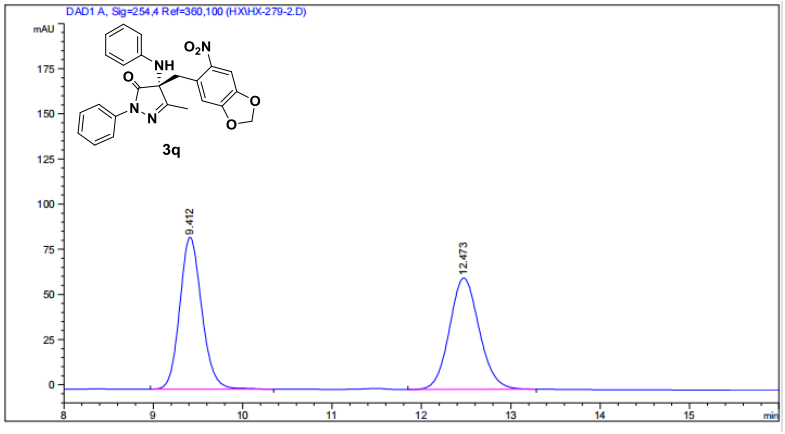
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.020	BB	0.2650	591.05914	34.65162	13.9389
2	17.091	BB	0.4634	3649.30981	121.84766	86.0611

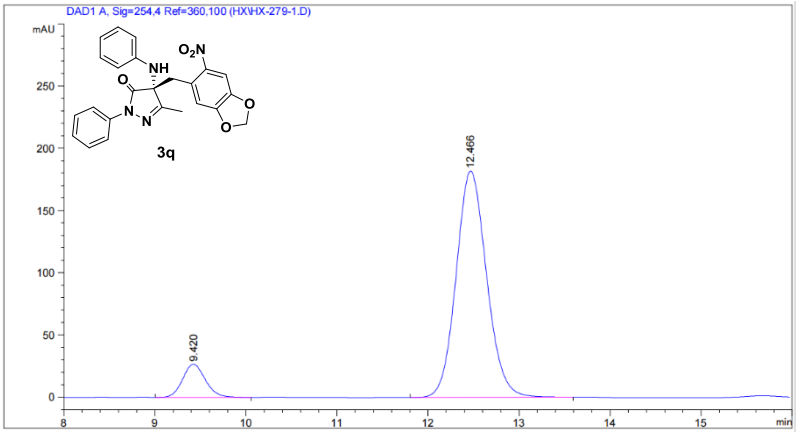
HPLC spectra of 3q

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.412	BB	0.2640	1441.25342	84.06722	50.2201
2	12.473	BB	0.3563	1428.61743	61.65652	49.7799

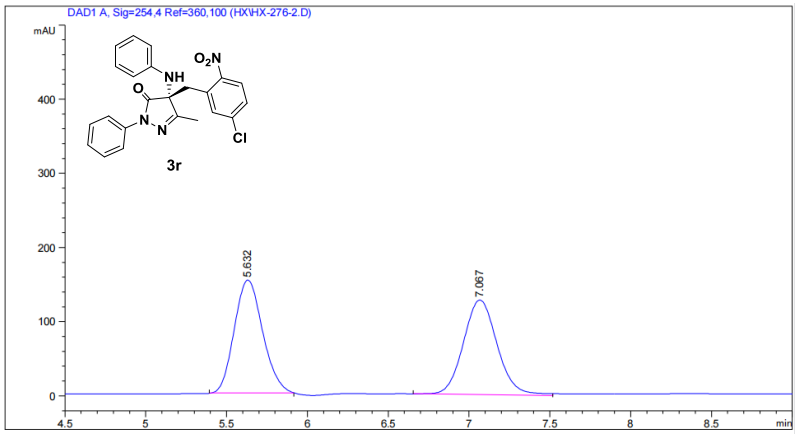
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.420	BB	0.2665	463.33389	26.68783	9.8617
2	12.466	BB	0.3595	4234.98291	181.96730	90.1383

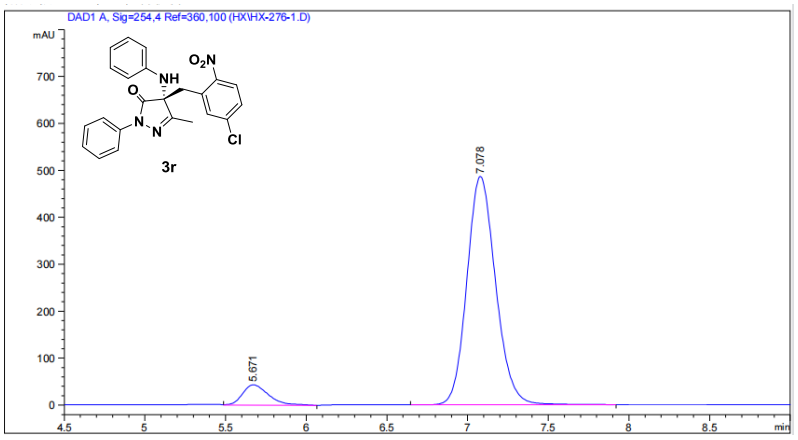
HPLC spectra of 3r

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.632	MM R	0.2033	1858.71509	152.37257	50.0704
2	7.067	MM R	0.2420	1853.48804	127.63619	49.9296

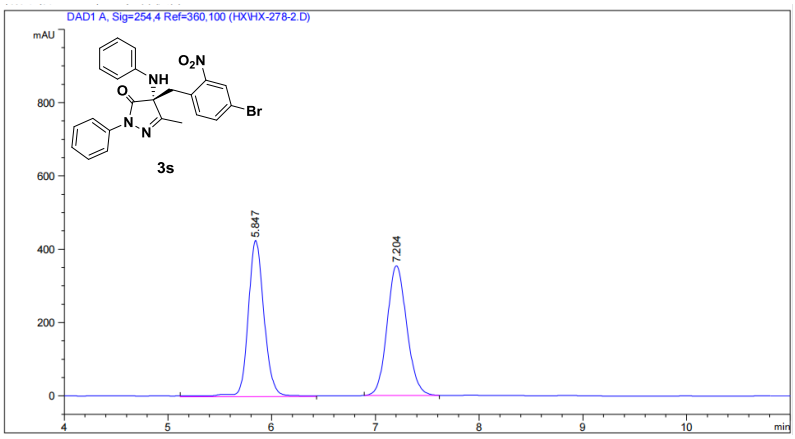
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.671	VB	0.1697	479.75815	43.15161	7.3902
2	7.078	BB	0.1902	6012.01563	486.44424	92.6098

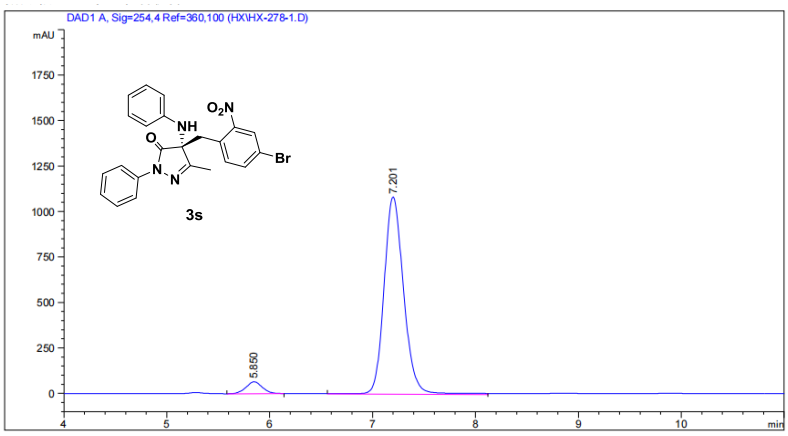
HPLC spectra of 3s

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.847	MM R	0.1785	4562.71436	426.00339	49.4583
2	7.204	MM R	0.2195	4662.66846	354.03357	50.5417

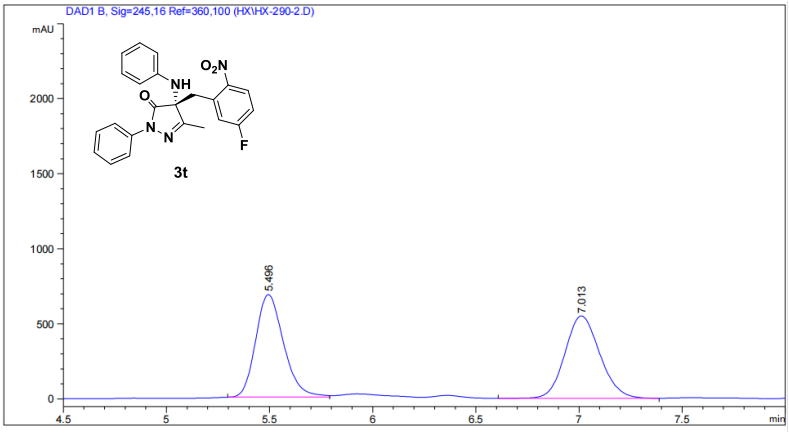
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.850	BB	0.1664	719.48065	65.37186	4.7748
2	7.201	MM R	0.2208	1.43488e4	1082.94897	95.2252

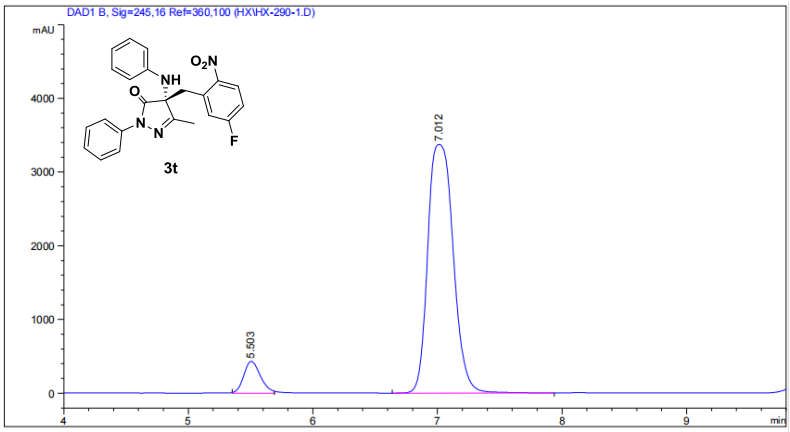
HPLC spectra of 3t

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.496	MM R	0.1572	6458.63379	684.60016	49.9082
2	7.013	BV	0.1815	6482.39404	550.14276	50.0918

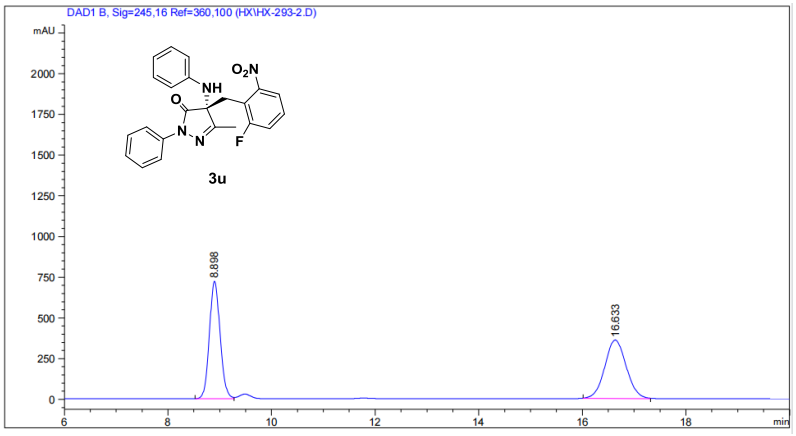
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.503	MM R	0.1554	4049.71533	434.28860	7.7834
2	7.012	BV	0.2239	4.79806e4	3374.14600	92.2166

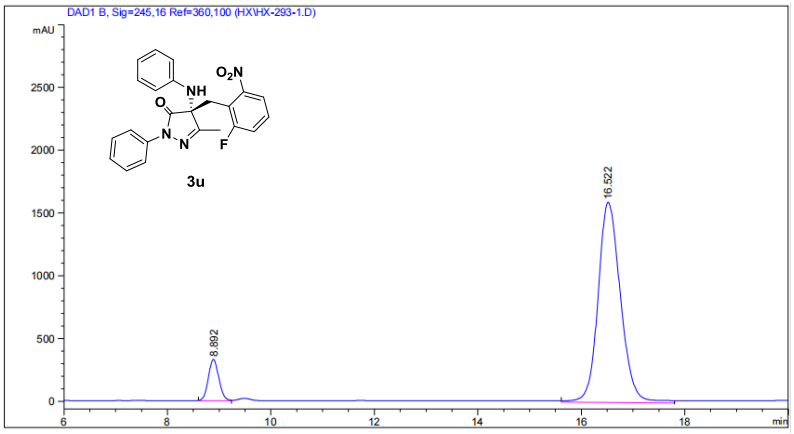
HPLC spectra of 3u

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.898	MM R	0.2411	1.04558e4	722.72736	50.1207
2	16.633	MM R	0.4814	1.04054e4	360.25122	49.8793

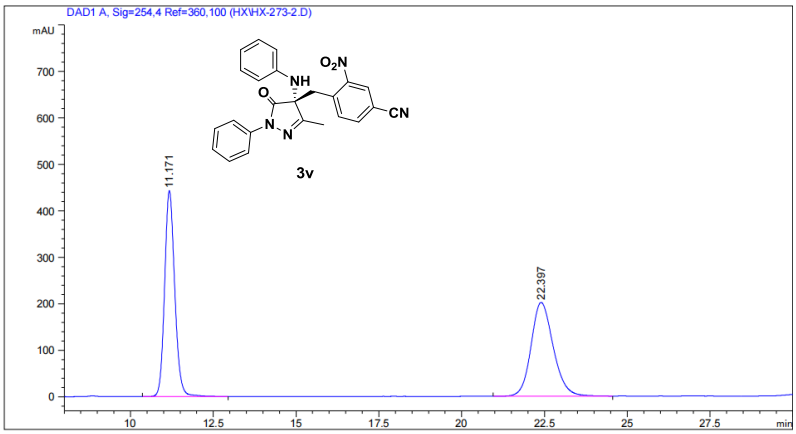
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.892	MM R	0.2360	4680.60986	330.57544	8.8455
2	16.522	MM R	0.5045	4.82344e4	1593.55518	91.1545

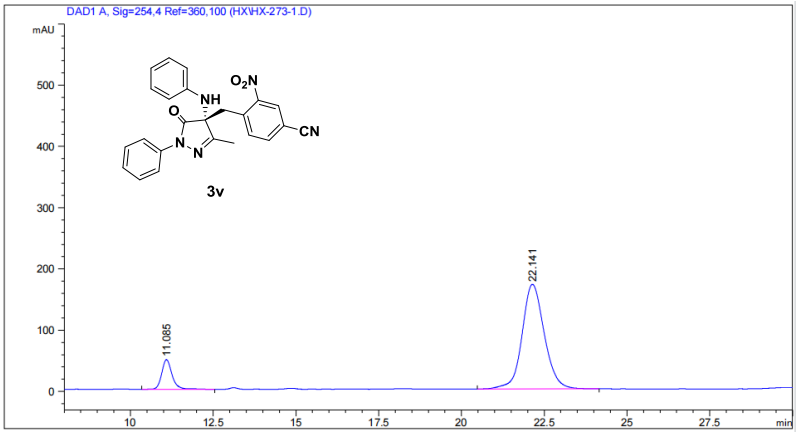
HPLC spectra of 3v

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.171	BB	0.3256	9401.69727	443.04437	50.0224
2	22.397	BB	0.7134	9393.26172	201.67099	49.9776

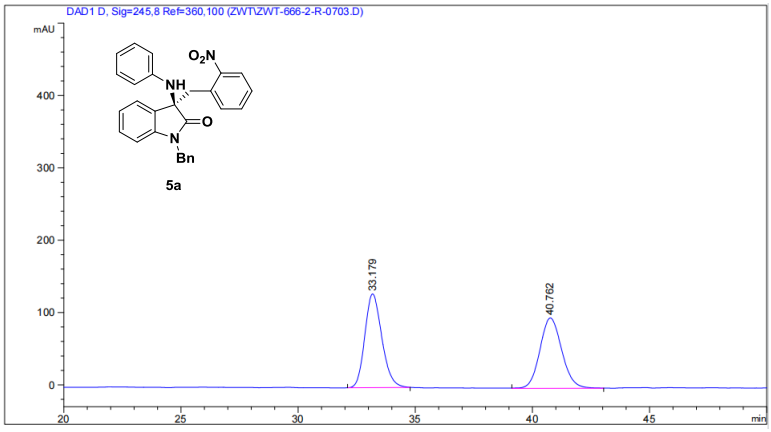
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.085	BB	0.3337	1072.90198	48.57457	11.8751
2	22.141	BB	0.7099	7961.98779	170.77788	88.1249

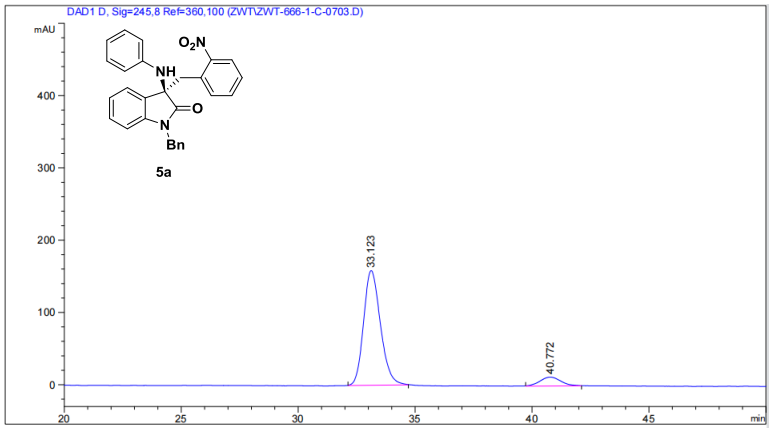
HPLC spectra of 5a

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.179	MM R	0.8435	6555.91992	129.53688	50.8957
2	40.762	MM R	1.0836	6325.16260	97.28752	49.1043

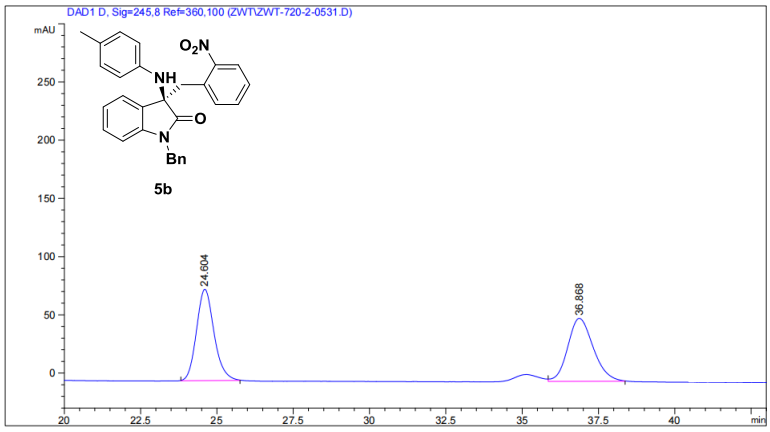
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.123	BB	0.7735	7967.12451	158.76015	91.2581
2	40.772	MM R	1.0325	763.19537	12.31930	8.7419

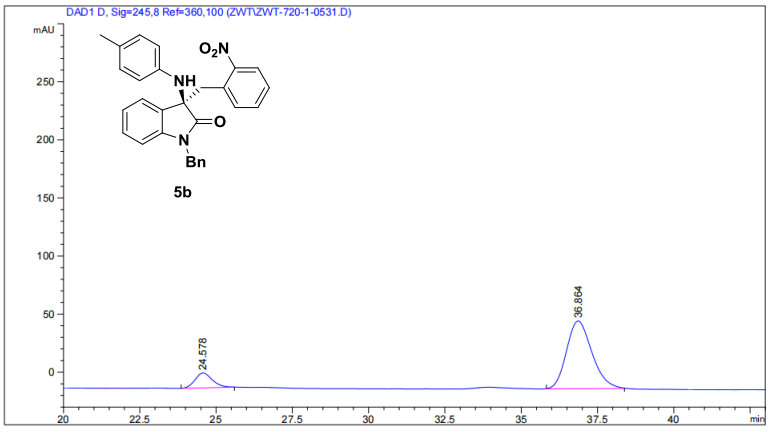
HPLC spectra of 5b

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.604	BB	0.6181	3149.94507	78.50486	50.0397
2	36.868	VB	0.8646	3144.94702	54.06780	49.9603

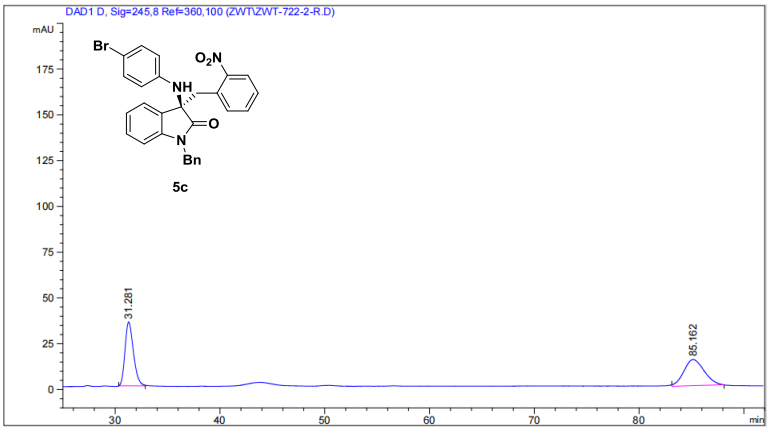
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.578	BB	0.5660	503.97830	12.78151	12.9859
2	36.864	BB	0.8777	3376.99072	58.30880	87.0141

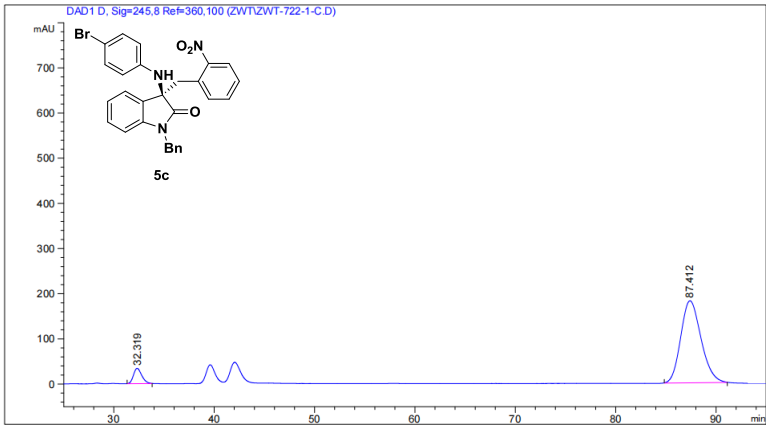
HPLC spectra of 5c

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.281	MM R	0.9329	1955.15674	34.92988	50.4782
2	85.162	MM R	2.2430	1918.11255	14.25281	49.5218

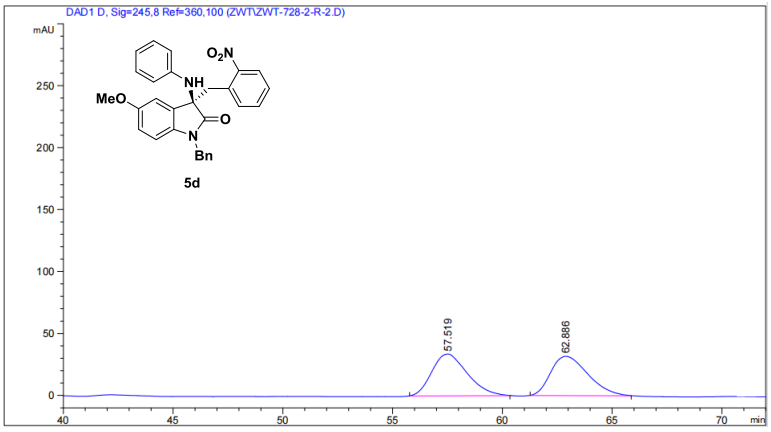
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.319	BB	0.8644	1944.72217	33.94425	7.0662
2	87.412	BB	2.0861	2.55768e4	181.71820	92.9338

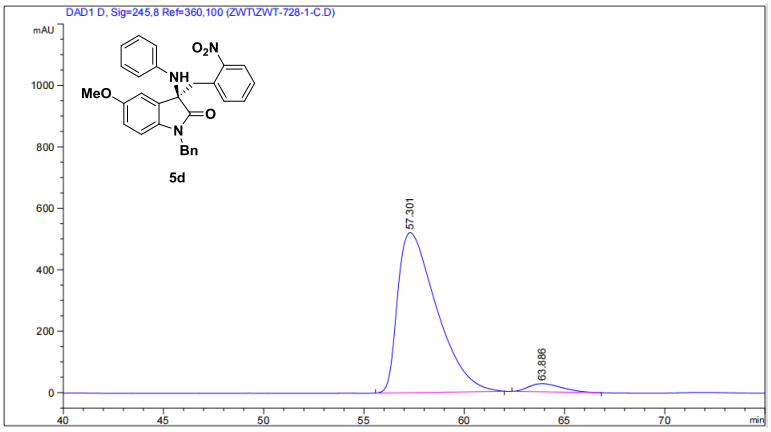
HPLC spectra of 5d

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	57.519	BB	1.3354	3802.58984	33.77673	50.3456
2	62.886	BB	1.4555	3750.37891	31.76430	49.6544

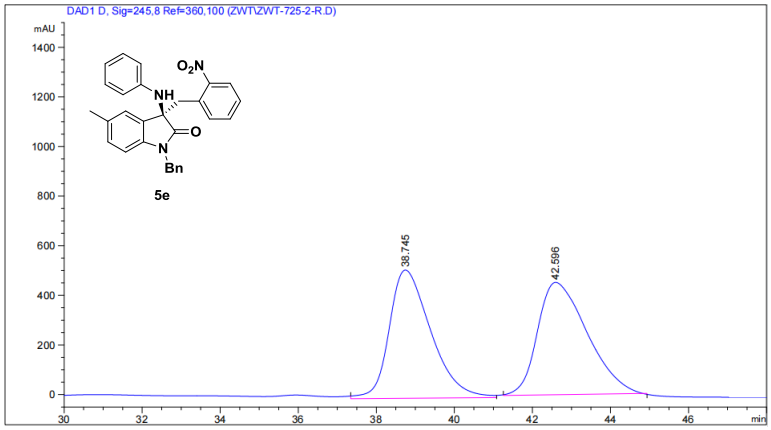
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	57.301	BB	1.9747	7.03149e4	520.94275	95.8357
2	63.886	BB	1.3891	3055.33813	26.38337	4.1643

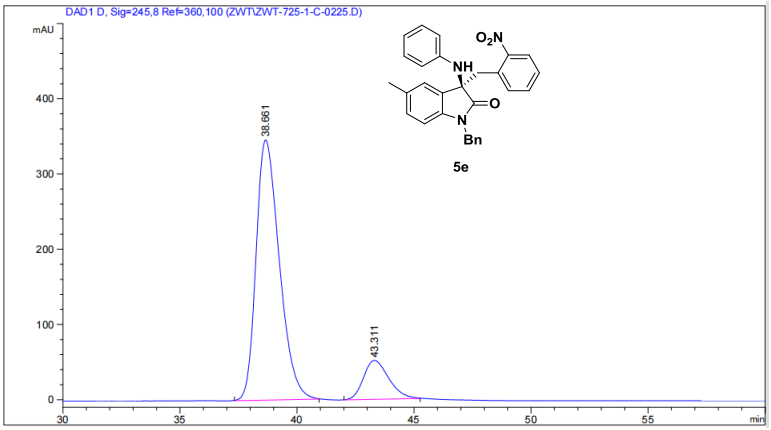
HPLC spectra of 5e

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.745	MM R	1.2360	3.83311e4	516.88690	48.9499
2	42.596	MM R	1.4709	3.99756e4	452.95828	51.0501

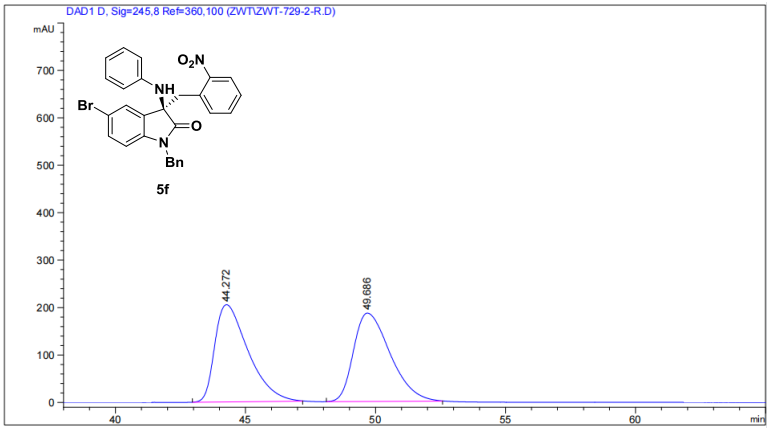
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.661	BB	1.0714	2.38770e4	345.88895	86.0537
2	43.311	BB	1.1290	3869.63794	51.59584	13.9463

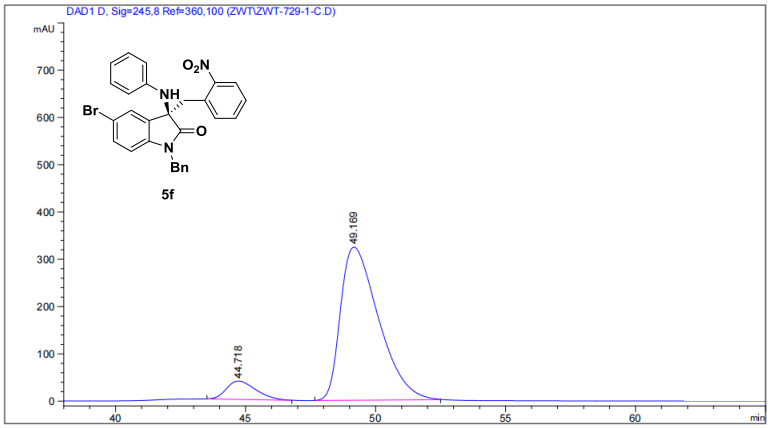
HPLC spectra of 5f

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.272	BB	1.3323	1.83129e4	204.98898	50.0254
2	49.686	BB	1.5138	1.82943e4	186.27048	49.9746

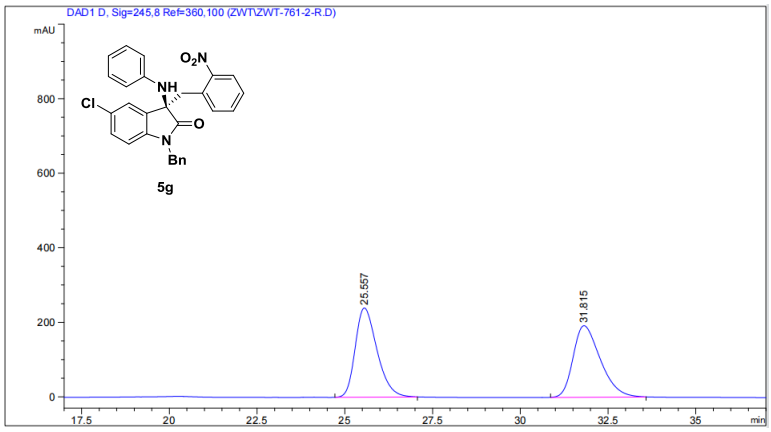
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.718	BB	1.1875	3062.51782	38.85547	8.4836
2	49.169	BB	1.5619	3.30367e4	323.91385	91.5164

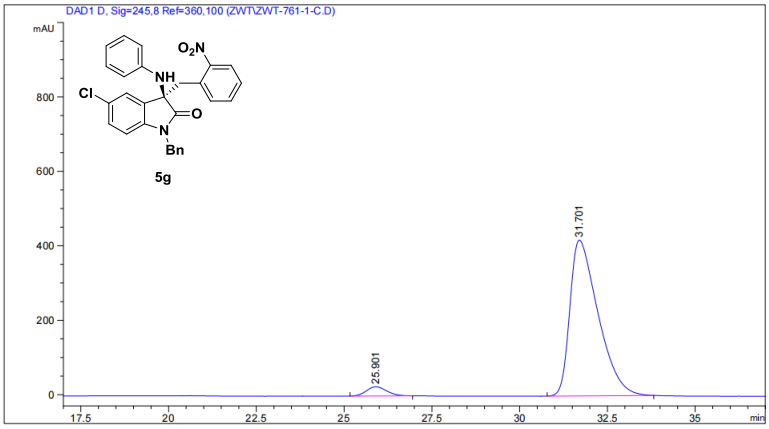
HPLC spectra of 5g

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.557	BB	0.6647	1.03611e4	239.49306	50.0043
2	31.815	BB	0.8213	1.03593e4	192.06451	49.9957

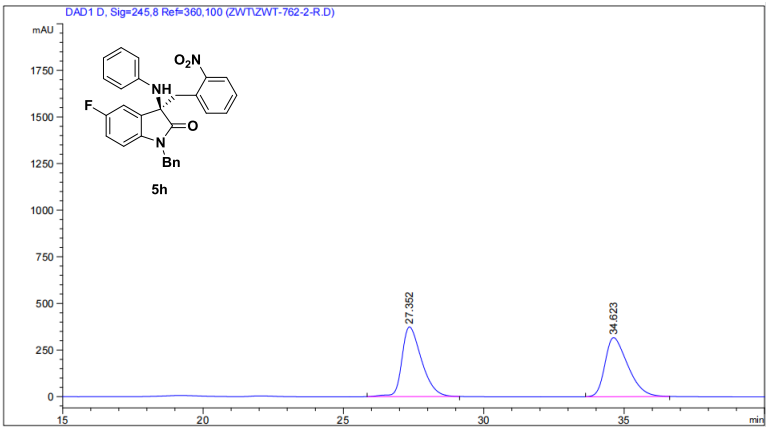
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.901	BB	0.6131	1003.36798	24.74120	4.1070
2	31.701	BB	0.8388	2.34273e4	418.70901	95.8930

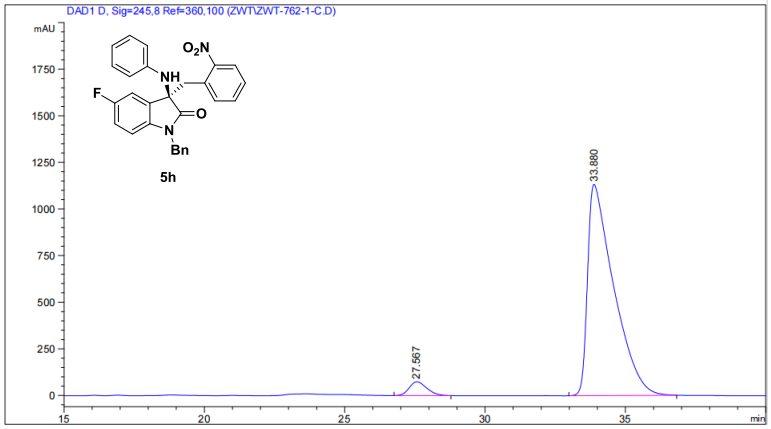
HPLC spectra of 5h

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.352	BB	0.7360	1.82564e4	373.68207	50.4606
2	34.623	BB	0.8618	1.79231e4	316.93573	49.5394

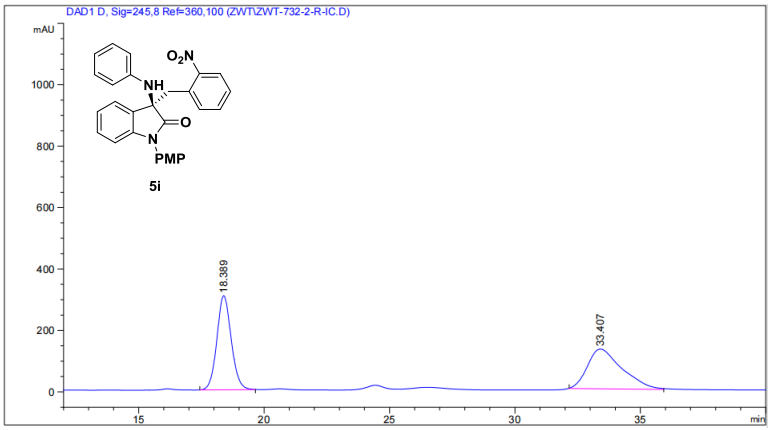
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.567	BB	0.6623	3255.92480	74.14738	4.2500
2	33.880	BB	0.9112	7.33543e4	1133.27600	95.7500

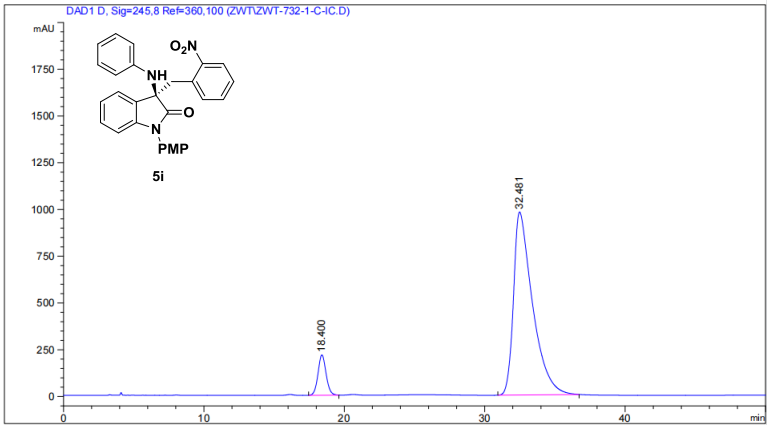
HPLC spectra of 5i

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.389	BB	0.6110	1.22146e4	306.44577	49.6215
2	33.407	MM R	1.5967	1.24009e4	129.44260	50.3785

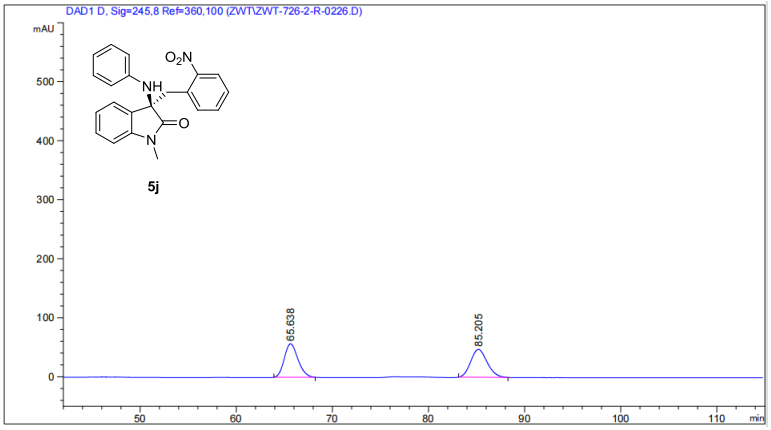
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.400	BB	0.6130	8645.40039	215.95935	8.5697
2	32.481	BB	1.3712	9.22384e4	978.98431	91.4303

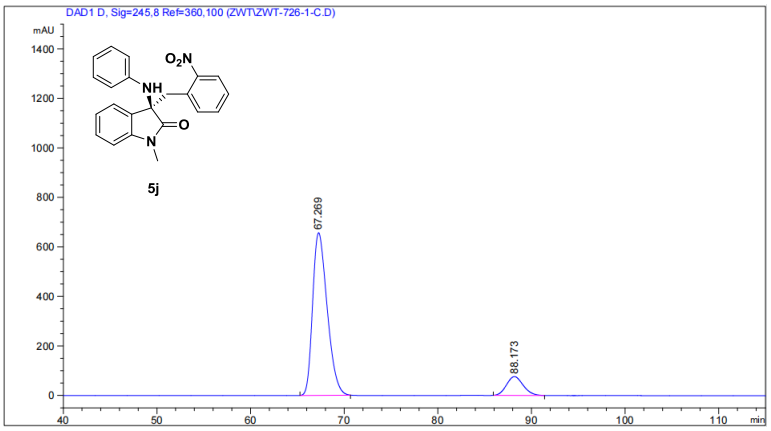
HPLC spectra of 5j

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	65.638	BB	1.4615	5619.28613	56.83198	49.9820
2	85.205	BB	1.5143	5623.33691	47.39162	50.0180

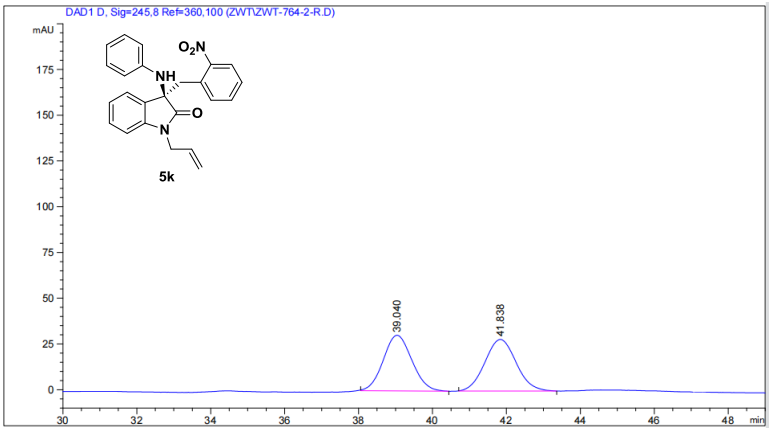
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	67.269	BB	1.6663	7.08282e4	656.70953	88.2834
2	88.173	BB	1.7748	9399.99707	76.11349	11.7166

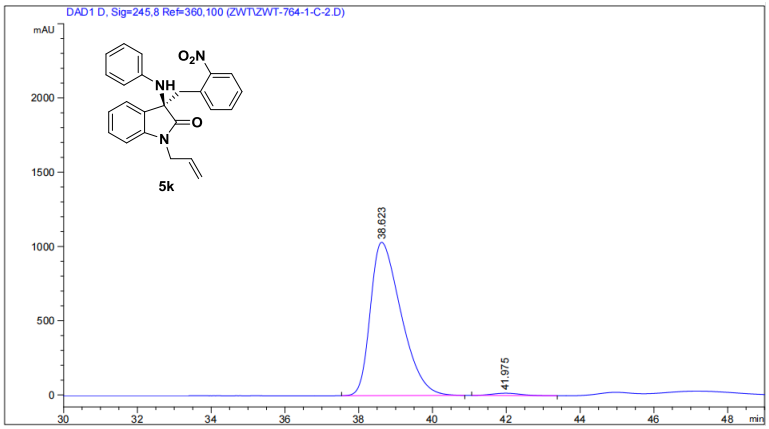
HPLC spectra of 5k

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.040	BB	0.7737	1641.82556	30.41783	49.6752
2	41.838	BB	0.7844	1663.29626	28.18859	50.3248

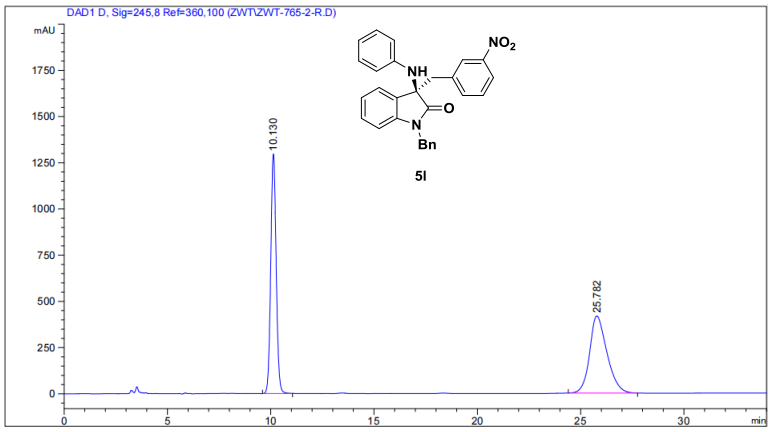
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.623	BB	0.8869	5.98987e4	1032.37012	98.5992
2	41.975	BB	0.6420	850.98523	15.85870	1.4008

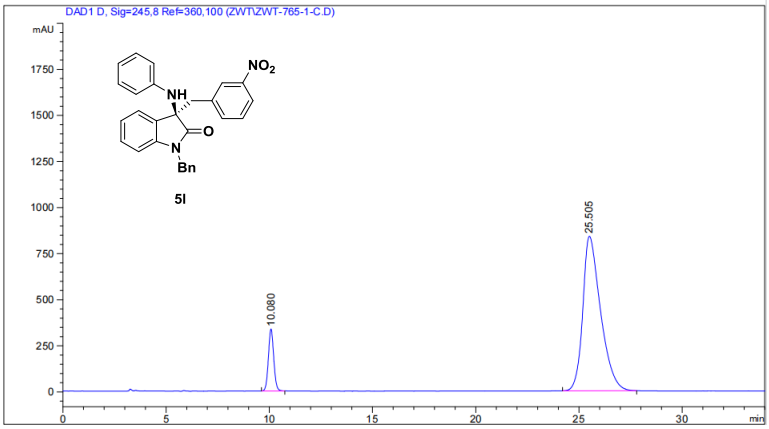
HPLC spectra of 5l

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.130	BB	0.2829	2.36681e4	1296.80359	49.2829
2	25.782	BB	0.8769	2.43569e4	417.34329	50.7171

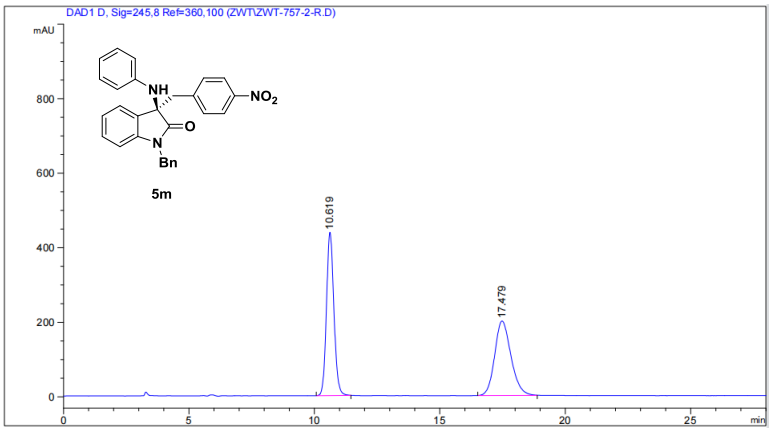
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.080	BB	0.2776	6051.52148	336.78287	10.7588
2	25.505	BB	0.8803	5.01954e4	838.58313	89.2412

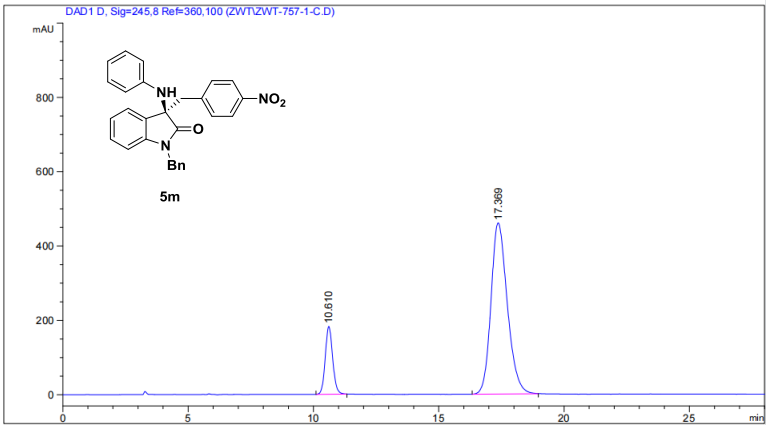
HPLC spectra of 5m

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.619	BB	0.3165	9033.90234	438.19180	50.0372
2	17.479	BB	0.6845	9020.45801	199.88538	49.9628

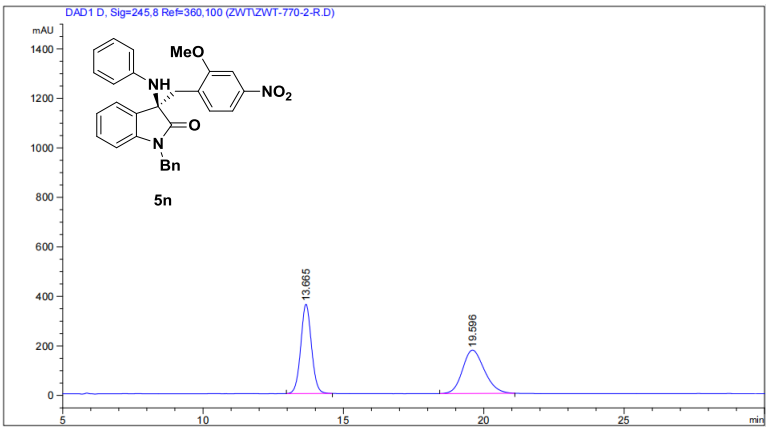
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.610	BB	0.3189	3770.53589	182.61259	15.2881
2	17.369	BB	0.6932	2.08926e4	460.58722	84.7119

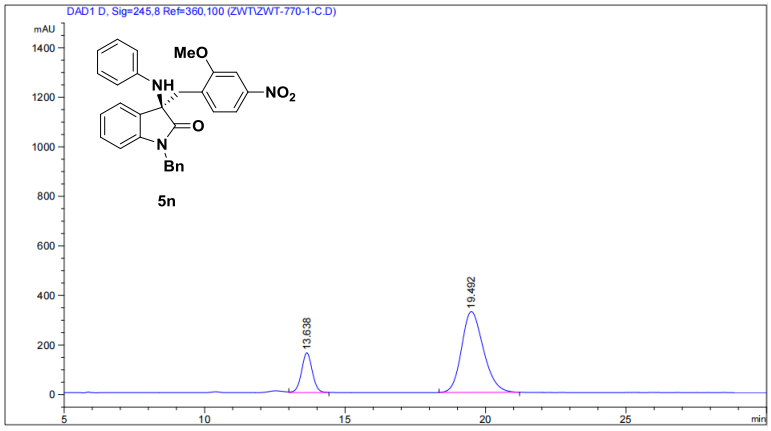
HPLC spectra of 5n

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.665	BB	0.4083	9598.02051	360.85202	50.2002
2	19.596	BB	0.8316	9521.45898	175.32883	49.7998

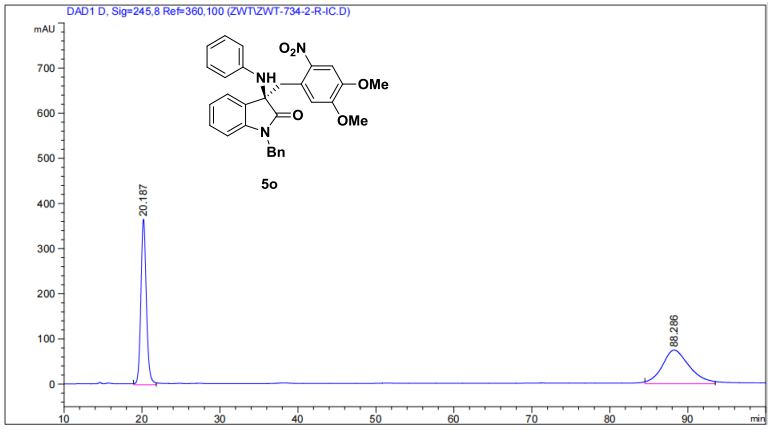
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.638	VB	0.4102	4258.50293	160.18808	19.4005
2	19.492	BB	0.8285	1.76920e4	326.32584	80.5995

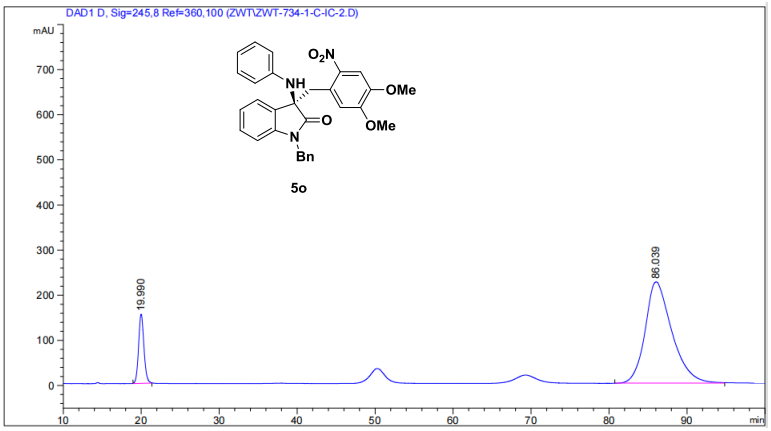
HPLC spectra of 5o

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.187	MM R	0.8144	1.79183e4	366.69794	49.6941
2	88.286	MM R	4.0493	1.81389e4	74.65785	50.3059

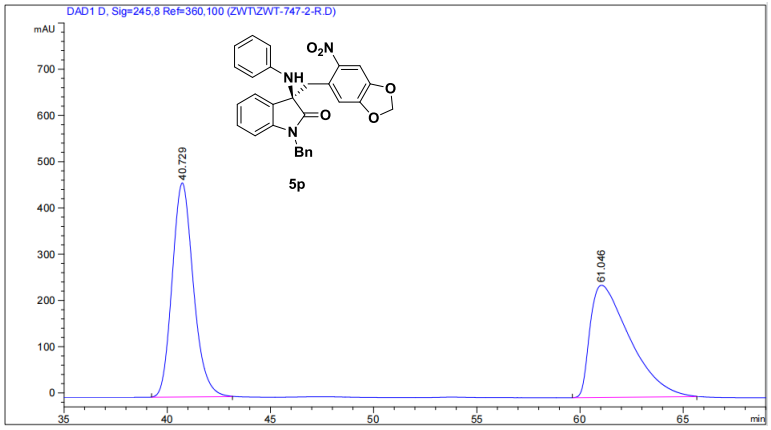
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.990	BB	0.7300	7279.75244	153.30196	11.9996
2	86.039	MM R	3.9652	5.33871e4	224.39896	88.0004

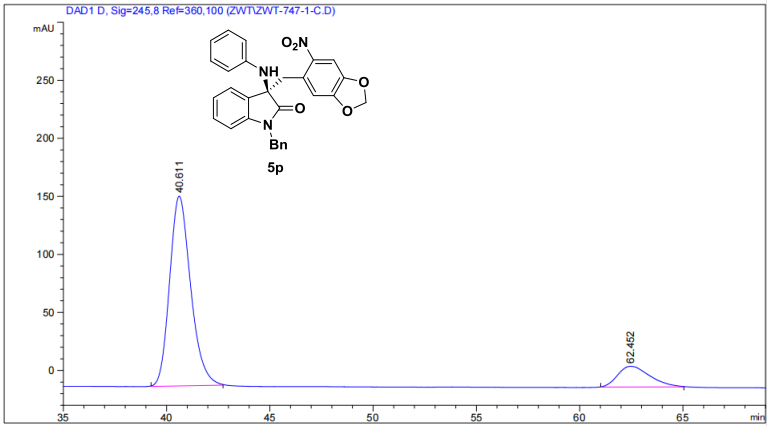
HPLC spectra of 5p

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.729	BB	1.1037	3.30754e4	462.85052	50.3640
2	61.046	BB	1.8543	3.25973e4	242.50082	49.6360

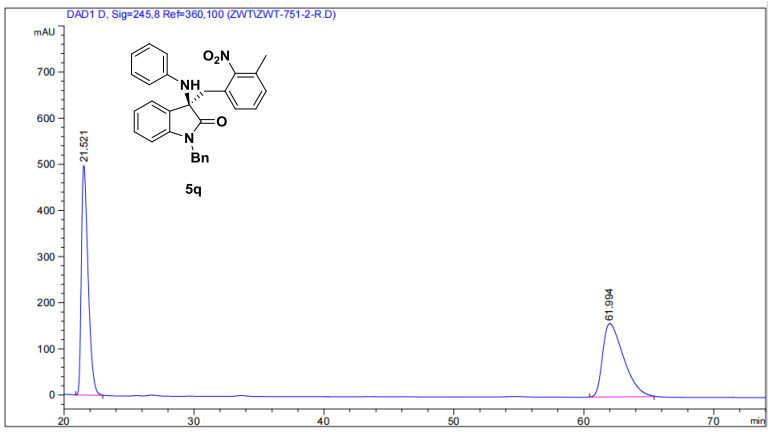
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.611	BB	1.0791	1.15934e4	163.52388	85.7461
2	62.452	BB	1.2744	1927.20801	17.83901	14.2539

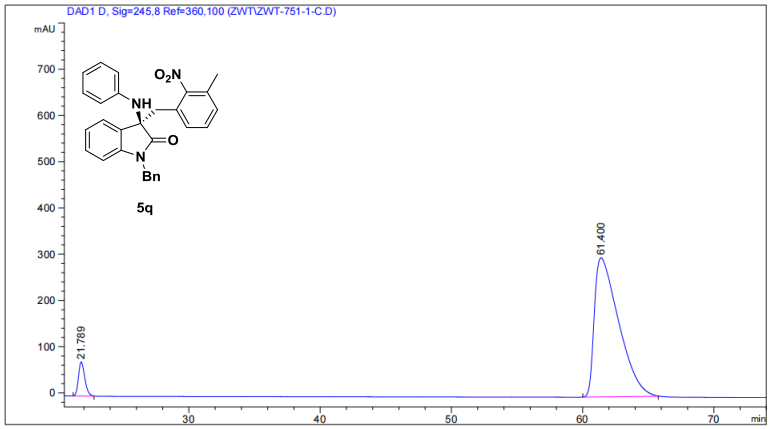
HPLC spectra of 5q

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.521	BB	0.5551	1.79742e4	497.96985	50.1471
2	61.994	BB	1.6156	1.78687e4	158.93817	49.8529

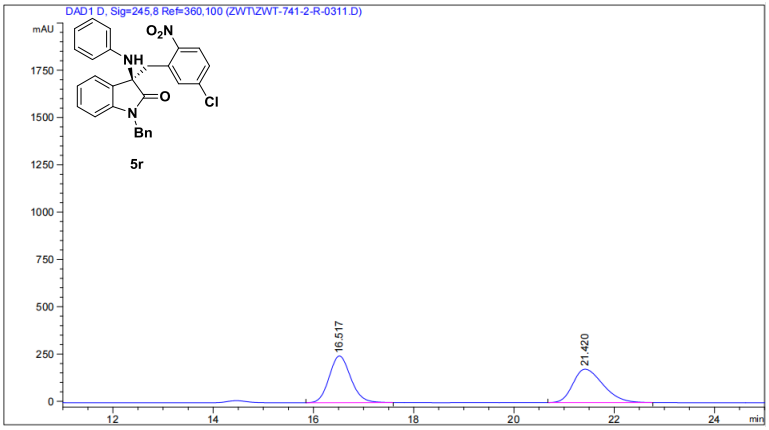
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.789	BB	0.5175	2478.22656	73.84467	6.0096
2	61.400	BB	1.7964	3.87597e4	300.58850	93.9904

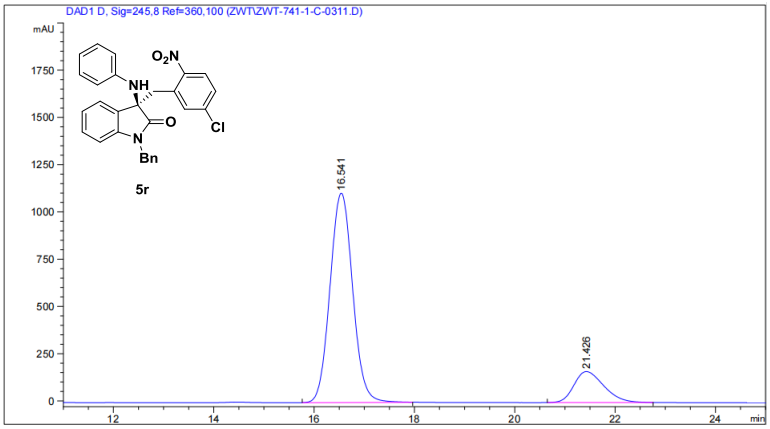
HPLC spectra of 5r

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.517	BB	0.4638	7400.93506	246.85519	50.0258
2	21.420	BB	0.6504	7393.30273	176.62201	49.9742

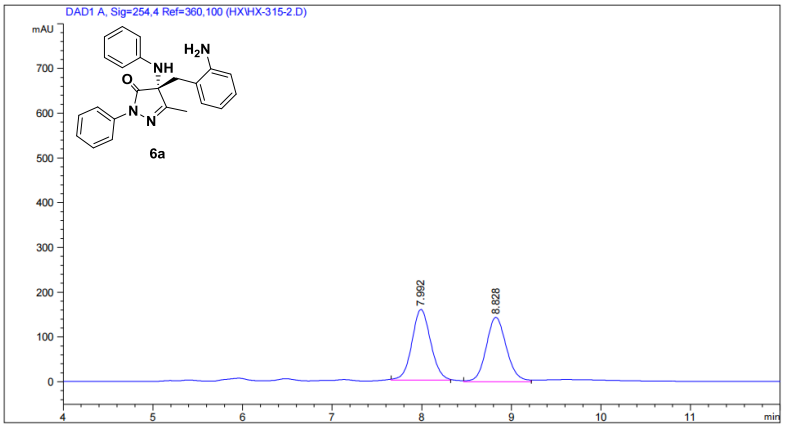
chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.541	BB	0.4904	3.47762e4	1107.23792	83.6137
2	21.426	BB	0.6450	6815.30273	163.95471	16.3863

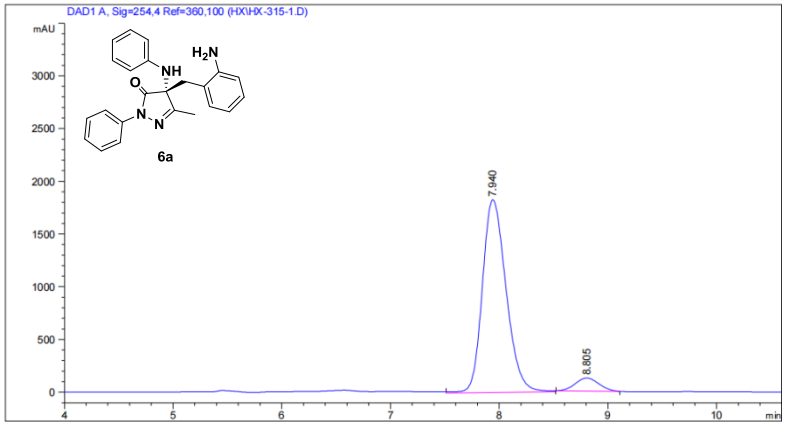
HPLC spectra of 6a

racemate



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.992	MM R	0.2417	2285.12598	157.58295	50.0956
2	8.828	MM R	0.2629	2276.40747	144.29836	49.9044

chiral compound



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.940	MM R	0.2529	2.77238e4	1827.36926	93.7828
2	8.805	MM R	0.2493	1837.92627	122.85209	6.2172