Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct enantioselective *α*-alkylation of secondary acyclic amines with ketones by combining photocatalysis and lipase catalytic promiscuity

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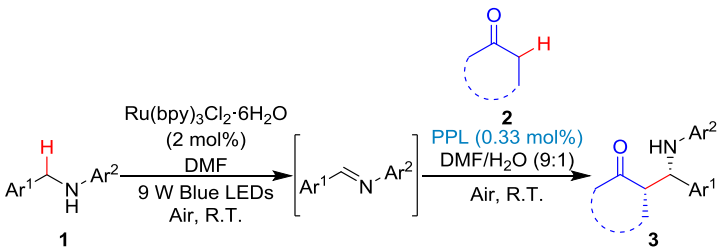
1. General information

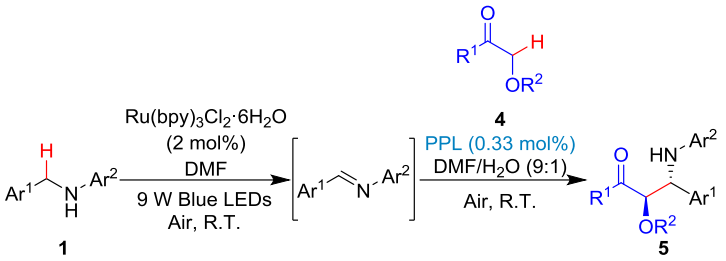
Lipase from porcine pancreas (PPL) – Type II [lyophilized powder, L3126-25G, Lot # SLCJ9303, 33% protein (Biuret), 39 units/mg protein (one unit will hydrolyze 1.0 microequivalent of fatty acid from Triacetin in 1 h at pH 7.4 at 37 °C), with a molecular weight of 50 – 52 kDa],[1] protease from *Streptomyces griseus* (SGP) – Type XIV [lyophilized powder, P5147-1G, Lot # SLBD9380V, 5.2 units/mg solid (one unit will hydrolyze casein to produce color equivalent to 1.0 μmol of Tyrosine per minute at pH 7.5 at 37 °C)], lipase from wheat germ (WGL) – Type I [lyophilized powder, L3001-5G, Lot # SLCF4529, 8 units/mg solid (one unit will hydrolyze 1.0 microequivalent of fatty acid from a triglyceride in 1 h at pH 7.4 at 37 °C), with a molecular weight of 141 – 145kDa (determined by gel chromatography)],[2] acylase I from *Aspergillus melleus* (AMA) [lyophilized powder, 01818-25G, Lot # 1348941V, 0.58 units/mg solid (one unit corresponds to the amount of enzyme which hydrolyzes 1.0 μmol *N*-acetyl-*L*-methionine per minute at pH 8.0 at 37 °C)], lysozyme chicken egg white (CEWL) (lyophilized powder, 6971-10G-F, Lot # BCBJ2814V, 102375 units/mg solid), papain carica papaya (CPP) [lyophilized powder, 76220-25G, Lot # BCBD3116V, 3.6 units/mg solid (one unit corresponds to the amount of enzyme which hydrolyzes 1.0 μmol *N*-benzoyl-*L*-arginine ethyl ester (BAEE, fluka No. 12880) per minute at pH 6.2 at 25 °C)], lipase A Candida antarctica immobilized on immobead 150, recombinant *Aspergillus oryzae* (CALA) [lyophilized powder, 41658-10G, Lot # BCBC1259V, 1624 units/g (one unit corresponds to the amount of enzyme which liberates 1.0 μmol butyric acid per minute at pH 10.0 at 40 °C, tributyrin, fluka No. 91010, as substrate)], lipase B Candida antarctica immobilized on immobead 150, recombinant yeast (CALB) [lyophilized powder, 52583-10G, Lot # BCBB5644, 3766 units/g solid (one unit corresponds to the amount of enzyme which liberates 1.0 μmol butyric acid per minute at pH 7.5 at 40 °C, tributyrin, fluka No. 91010, as substrate)], and amyloglucosidase *aspergillus niger* (ANA) [lyophilized powder, 10115-1G-F, Lot # BCBF3497V, 62.4 units/g solid (one unit corresponds to the amount of enzyme which liberates 1.0 μmol of glucose per minute at pH 4.8 at 60 °C, starch acc. to Zulkowsky, cat. No. 85642, as substrate)] were purchased from Sigma-Aldrich, Shanghai, China. Nuclease P1 from *Penicillium citrinum* (EC 3.1.30.1, lyophilized powder, 5 units/mg solid. The activity was measured in terms of the amount of acid-soluble nucleotides produced by RNA hydrolysis which is catalyzed by nuclease P1. One unit of enzyme activity was

defined as the amount of enzyme that produced an increase in the optical density of 1.0 in 1 min at 260 nm) was purchased from Nanning Pangbo Biological Engineering Co. Ltd., Nanning, China.

Unless otherwise noted, all chemicals and reagents were purchased from commercial suppliers and were used without further purification. All glassware was oven-dried at 120 ℃. All photoreactions were conducted in single neck round bottom flask unless otherwise noted. The light source was a 9 W blue LED lamp (450 nm, placed approximately 5 cm from the reaction flask) without any filters. All reactions were monitored by thin-layer chromatography (TLC) with GF 254 silica gel pre-coated plates (0.25 mm, Qingdao Haiyang chemical industry Co. Ltd., Qingdao, China) using UV light and vanillic aldehyde as visualizing agents. Flash chromatography was performed using silica gel (200-300 mesh) at increased pressure. NMR spectra were recorded on Bruker AVANCE III (400 MHz) and Bruker AVANCE DMX600 (600 MHz) spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR were referenced to TMS (0.00 ppm) or residual undeuterated solvent signals (7.26 ppm for ^{1}H NMR in $CDCl_3$, 77.16 ppm for ^{13}C NMR in $CDCl_3$) respectively. ^{19}F NMR data were calibrated using $CFCl_3$ as an external reference (0.0 ppm). Data for NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, br = broad and m = multiplet), and coupling constant (Hz). High-resolution mass spectra (HRMS) were acquired on Bruker Impact II TOF mass spectrometer using ESI ionization sources. The diastereomeric ratio (dr) and enantiomeric excess (ee) of products were determined by chiral HPLC analysis carried out on a Shimadzu LC-20A instrument using Chiralpak AD-H, Chiralpak OD-H, Chiralpak AS-H and Chiralpak OJ-H (0.46 cm Φ × 25 cm, 5 μm, Daicel Chiral Technologies CO., LTD.). Cyclic voltammograms were obtained on a CHI 700E potentiostat (CH Instruments, Inc.).

2. General procedure for the photoenzyme-catalyzed enantioselective *α*-alkylation of secondary acyclic amines with ketones





To a 10 mL round-bottom flask equipped with a magnetic stirring bar was added **1** (0.3 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%), and DMF (dried over 3Å molecular sieves, 2.7 mL). The mixture was irradiated with a 9 W blue LED lamp under the air atmosphere at room temperature. After full conversion of **1** as monitored by TLC, the light was turned off. Ketone [**2** (1.5 mmol, 5.0 equiv) or **4** (3.0 mmol, 10.0 equiv), as indicated], PPL (150 mg, 1930 U, 0.33 mol%) and deionized water (0.3 mL) were added, then the mixture was stirred without light. The reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with 20 mL EtOAc and filtered. The filtrate was washed with brine (10 mL × 2). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was collected and concentrated in vacuum to remove the solvent. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (v/v, 20:1 to 5:1) as eluent to obtain the corresponding product **3** or **5**.

3. Preparation of substrates 1

The following substrates **1** were purchased from commercial sources (Figure S1).

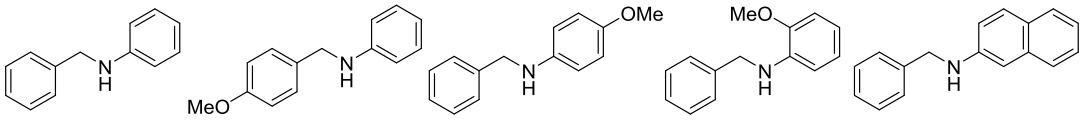


Figure S1. Substrates **1** purchased from commercial sources.

The other substrates **1** were synthesized according to literature (Figure S2).

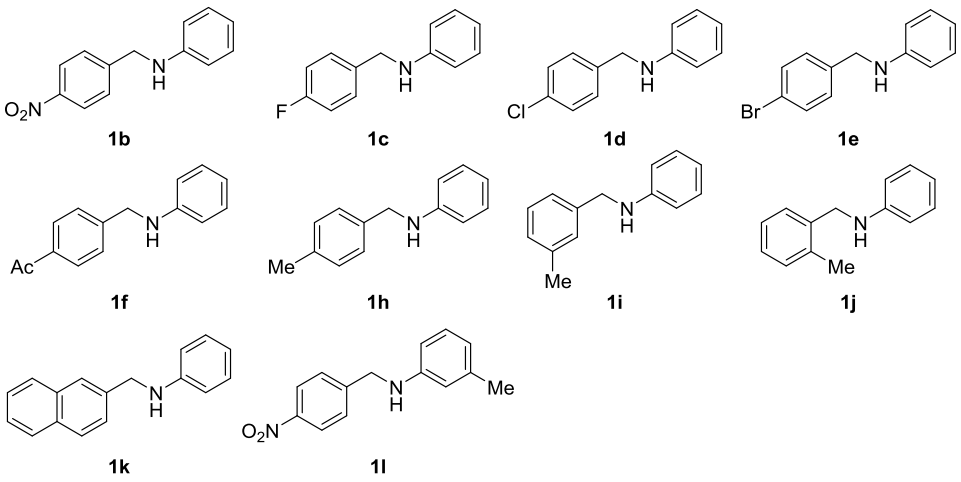
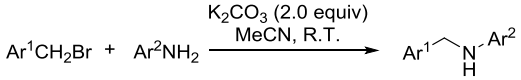


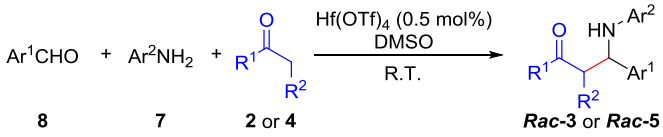
Figure S2. Substrates **1** synthesized according to the literature.

General procedure[3]



A 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with **6** (5.0 mmol, 1.0 equiv), **7** (7.5 mmol, 1.5 equiv), K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv) and MeCN (70 mL). The reaction mixture was vigorously stirred at room temperature. The reaction was monitored by TLC. Upon completion, the reaction mixture was filtered by Celite and washed with EtOAc. The filtrate was collected and concentrated in vacuum to remove the solvent. The residue was directly submitted to flash column chromatography on silica gel using petroleum ether/EtOAc (300:1 to 20:1) to obtain the corresponding compound **1**.

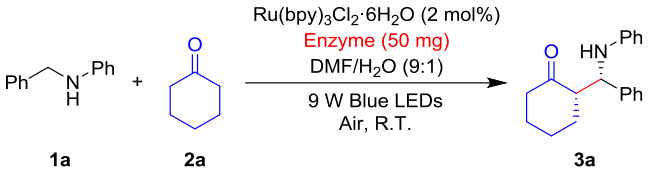
4. General procedure for preparing racemic products as chiral HPLC controls[3]



A round-bottomed flask equipped with a magnetic stirring bar was charged with **8** (0.3 mmol, 1.0 equiv), **7** (0.3 mmol, 1.0 equiv), **2** or **4** (1.5 mmol, 5.0 equiv), $Hf(OTf)_4$ (1.2 mg, 0.0015 mmol, 0.5 mol%) and DMSO (3.0 mL). The reaction mixture was stirred at room temperature and monitored by TLC. After completion of the reaction, CH_2Cl_2 (5 mL) was added to the reaction to dissolve the residue. The crude product was purified by preparative thin layer chromatography (silica gel, petroleum ether/EtOAc = 5:1 to 1:1) to give the desired racemic product (***Rac*-3** or ***Rac*-5)**.

5. Optimization details

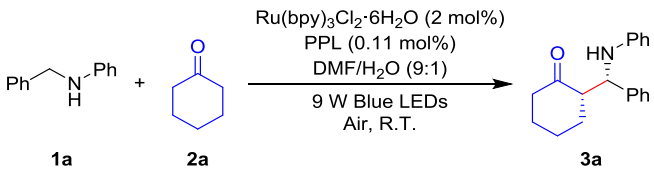
Table S1. Screening of enzymes.[a]



Entry	Enzyme	Yield [%][b]	dr [*syn*/*anti*][c]	er [*syn* (*anti*)][c]
1	Lipase from porcine pancreas	21	73/27	78/22 (56/44)
2	Protease from *streptomyces griseus*	18	82/18	78/22 (56/44)
3	Lipase from wheat germ	6	44/56	53/47 (52/48)
4	Acylase I from *aspergillus melleus*	10	53/47	67/33 (50/50)
5	Lysozyme chicken egg white	22	32/68	50/50 (50/50)
6	Papain carica papaya	12	54/46	58/42 (50/50)
7	Lipase A candida Antarctica	10	38/62	51/49 (51/49)
8	Lipase B candida Antarctica	10	36/64	50/50 (50/50)
9	Nuclease P1	15	38/62	54/46 (51/49)
10	Amyloglucosidase *aspergillus niger*	8	47/53	59/41 (50/50)

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (467 µL, 4.5 mmol, 15.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%), enzyme (50 mg) and deionized water (0.3 mL) in DMF (dried over 3Å molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column.

Table S2. Screening of addition procedures.[a]

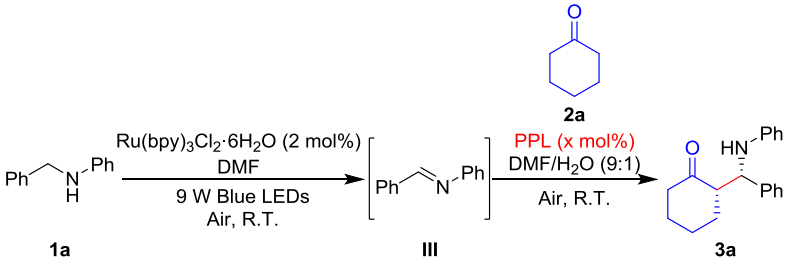


Entry	Method[b]	Yield [%][c]	dr [*syn*/*anti*][d]	er [*syn* (*anti*)][d]
1	A	21	73/27	78/22 (56/44)
2	B	14	71/29	77/23 (53/47)

3	C	59	74/26	78/22 (59/41)

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (467 μL, 4.5 mmol, 15.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%), PPL (50 mg, 644 U, 0.11 mol%) and deionized water (0.3 mL) in DMF (dried over 3Å molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Method A: all components were added at one time and irradiation; Method B: **2a** and PPL were added after the photo-oxidation process was completed, and then the mixture was stirred without light; Method C: **2a**, PPL and deionized water were added after the photo-oxidation process was completed, and then the mixture was stirred without light. [c] Isolated yield. [d] Determined by HPLC analysis using a chiralpak OJ-H column.

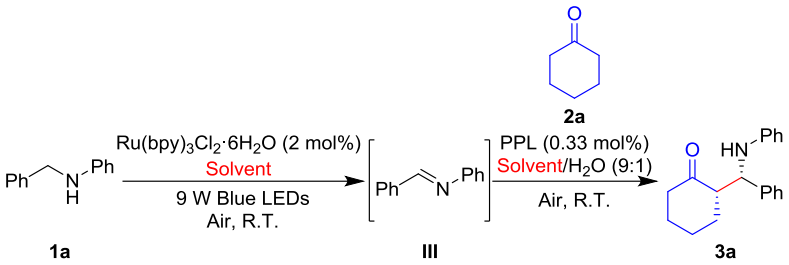
Table S3. Screening the amount of PPL.[a]



Entry	PPL		Yield [%][b]	dr [*syn*/*anti*][c]	er [*syn* (*anti*)][c]
	[mg]	[mol%]			
1	25	0.06	45	60/40	70/30 (55/45)
2	50	0.11	59	74/26	78/22 (59/41)
3	100	0.22	67	76/24	77/23 (59/41)
4	150	0.33	78	77/23	79/21 (57/43)
5	200	0.44	76	75/25	77/23 (58/42)
6	300	0.66	73	75/25	76/24 (59/41)

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) in DMF (dried over 3Å molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2a** (467 μL, 4.5 mmol, 15.0 equiv), PPL and deionized water (0.3 mL) were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column.

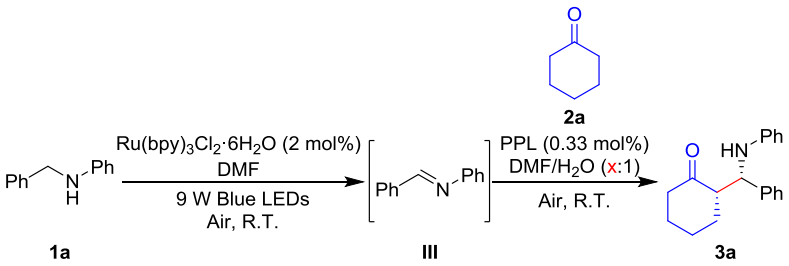
Table S4. Screening of solvents.[a]



Entry	Solvent	Yield [%][b]	dr [*syn*/*anti*][c]	er [*syn* (*anti*)][c]
1	DMF	78	77/23	79/21 (57/43)
2	MeCN	ND[d]	——	——
3	EtOH	27	75/25	76/24 (58/42)
4	IPA	20	78/22	77/23 (56/44)
5	DCM	NR[e]	——	——
6	THF	NR[e]	——	——

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) in solvent (dried over molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2a** (467 µL, 4.5 mmol, 15.0 equiv), PPL (150 mg, 1930 U, 0.33 mol%) and deionized water (0.3 mL) were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column. [d] Not detected. [e] No reaction.

Table S5. Water content screening.[a]

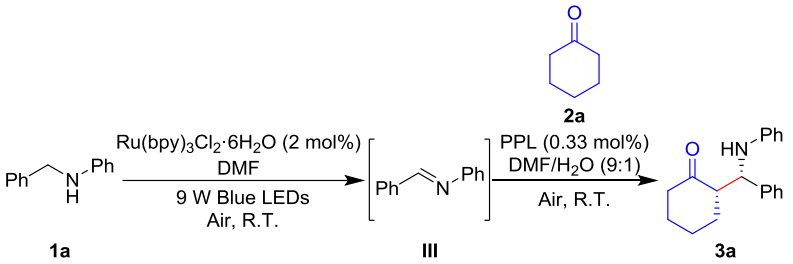


Entry	Water [mL]	DMF/H_2O [v/v]	Water content [%]	Yield [%][b]	dr [*syn*/*anti*][c]	er [*syn* (*anti*)][c]
1	0	——	0	Trace	——	——
2	0.15	18/1	5.26	59	68/32	70/30 (50/50)
3	0.30	9/1	10.00	78	77/23	79/21 (57/43)

4	0.45	6/1	14.28	67	75/25	76/24 (55/45)
5	0.90	3/1	25.00	69	71/29	73/27 (53/47)

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) in DMF (dried over 3Å molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2a** (467 µL, 4.5 mmol, 15.0 equiv), PPL (150 mg, 1930 U, 0.33 mol%) and deionized water were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column.

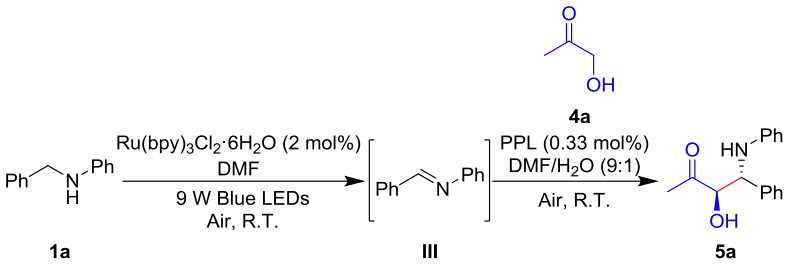
Table S6. Screening the amount of cyclohexanone (**2a**).[a]



Entry	**2a** [equiv]	Yield [%][b]	dr [*syn*/*anti*][c]	er [*syn* (*anti*)][c]
1	2.5	65	73/27	77/23 (58/42)
2	5.0	78	75/25	79/21 (59/41)
3	10.0	75	75/25	78/22 (53/47)
4	15.0	78	77/23	79/21 (57/43)
5	20.0	71	77/23	78/22 (59/41)
6	25.0	67	75/25	77/23 (55/45)

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) in DMF (dried over 3Å molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2a**, PPL (150 mg, 1930 U, 0.33 mol%) and deionized water (0.3 mL) were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column.

Table S7. Screening the amount of hydroxyacetone (**4a**).[a]



Entry	**4a** [equiv]	Yield [%][b]	dr [*anti*/*syn*][c]	er [*anti* (*syn*)][c]
1	5.0	66	73/27	85/15 (59/41)
2	10.0	81	76/24	88/12 (62/38)
3	15.0	81	75/25	88/12 (60/40)
4	20.0	79	76/24	88/12 (60/40)
5	25.0	75	78/22	87/13 (63/37)

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) in DMF (dried over 3Å molecular sieves, 2.7 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **4a**, PPL (150 mg, 1930 U, 0.33 mol%) and deionized water (0.3 mL) were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column.

6. Enzymatic assay of natural activity of PPL

The natural activity of PPL was determined according to the procedure described in literature.[3] The results showed that the native activity of PPL was significantly decreased after denatured and inhibitor pretreatment. Therefore, the natural active center of PPL might be essential for the catalytic activity.

Table S8. The natural activity of denatured and inhibitor-pretreated PPL.

Entry	Pretreatment of PPL	Natural activity of PPL [U/mg protein][a]
1	PPL	39
2	High-temperature-pretreated PPL[b]	5
3	GuHCl-pretreated PPL[c]	6
4	PMSF-pretreated PPL[d]	6
5	DEPC-pretreated PPL[e]	8
6	DCC-pretreated PPL[f]	10

[a] One unit will hydrolyze 1.0 microequivalent of fatty acid from Triacetin in 1 h at pH 7.4 at 37 °C. 33% protein (Biuret)。[b] PPL (150 mg, 1930 U) in deionized water (3.0 mL) was stirred at 100 ℃ for 3 days, then the water was removed under reduced pressure. [c] PPL (150 mg, 1930 U) and GuHCl (1.74 g, 18.0 mmol) in deionized water (3.0 mL) was stirred at 30 ℃ for 10 h, the water was removed by lyophilization. [d] PPL (150 mg, 1930 U) and PMSF (314 mg, 1.8 mmol) in THF (3.0 mL) was stirred at 30 ℃ for 10 h, then THF was removed under reduced pressure. [e] PPL (150 mg, 1930 U) and DEPC (145 mg, 0.90 mmol) in phosphate buffer (NaH_2PO_4/Na_2HPO_4, pH = 8.0, 3.0 mL) was stirred at 37 ℃ for 2 h, then water was removed by lyophilization. [f] PPL (150 mg, 1930 U) and DCC (620 mg, 3.0 mmol) in deionized water (3.0 mL) was stirred at 30 ℃ for 2 h, then water was removed by lyophilization.

7. Stern-Volmer luminescence quenching experiments

The measurements were performed using a 0.05 mM solution of $Ru(bpy)_3Cl_2·6H_2O$ in DMF with varying concentration of a quencher. The samples were excited at 450 nm and emission intensity was recorded at 622 nm. The results showed that **1a** could significantly quench the excited state of Ru^{2+} (Figure S3, Figure S4).

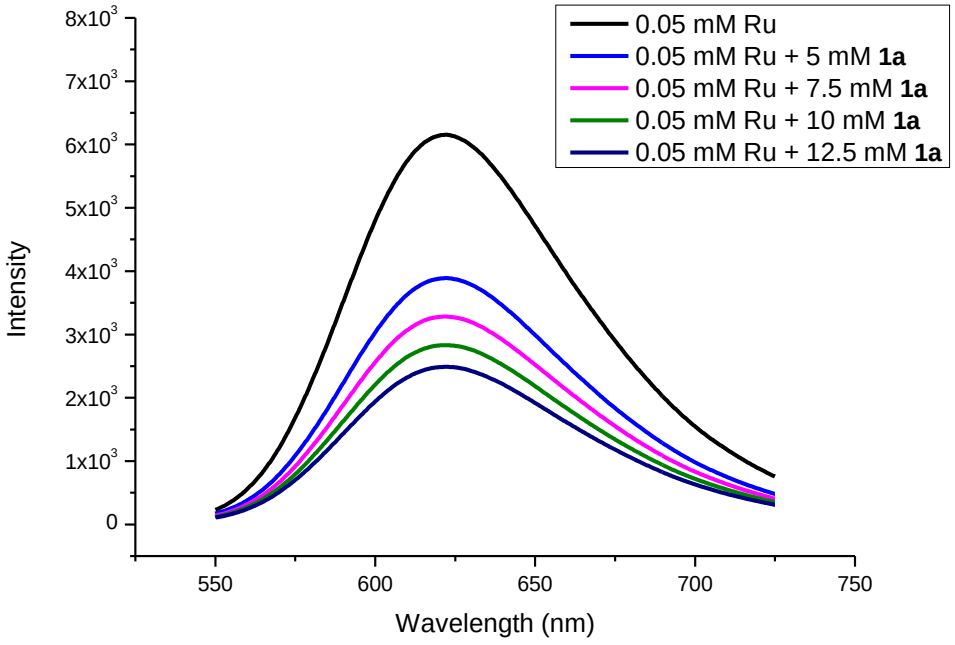


Figure S3. Fluorescence quenching of 0.05 mM $Ru(bpy)_3Cl_2·6H_2O$ (in DMF) by increasing

concentration of **1a**.

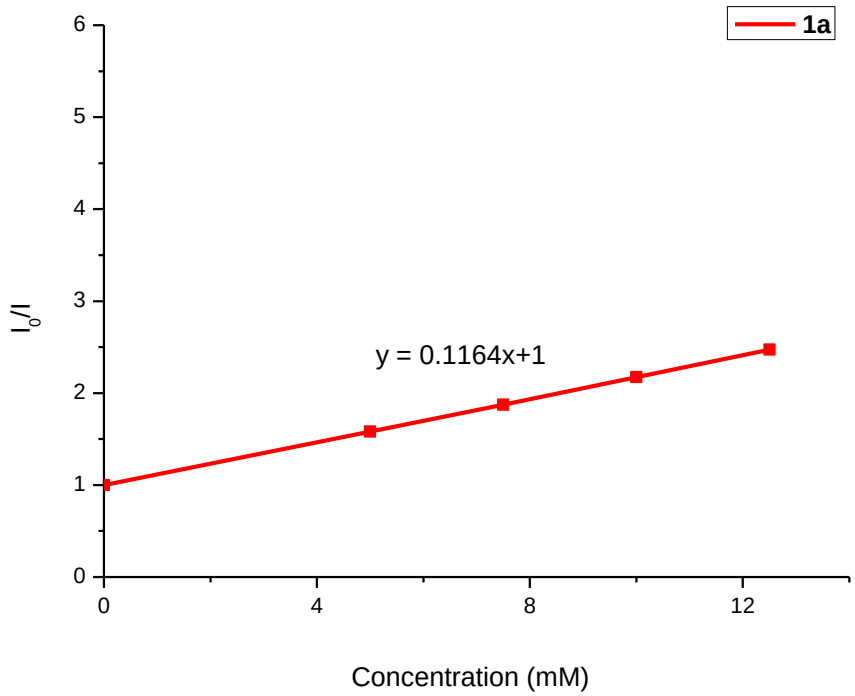


Figure S4. Stern-Volmer plots of fluorescence quenching 0.05 mM $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (in DMF) by **1a**.

8. Cyclic voltammetry studies

The cyclic voltammetry experiments were performed in a three-electrode undivided cell, and were recorded with a CHI 700E potentiostat (CH Instruments, Inc.) at room temperature in MeCN (15 mL). *n*-Bu_4NPF_6 (0.05 M) was used as the supporting electrolyte, and the concentration of the tested compound was 2.0 mM. The scan rate was 100 mV/s. The potential ranges investigated for oxidations were 0 to +2.0 V *vs.* SCE (saturated aqueous KCl). CV plotting convention is IUPAC.

Working electrode: The working electrode is a 3 mm diameter glassy carbon working electrode. Polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

Reference electrode: The reference electrode is SCE (saturated aqueous KCl) that was washed with water and ethanol before measurements.

Counter electrode: The counter electrode is a platinum wire that was polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

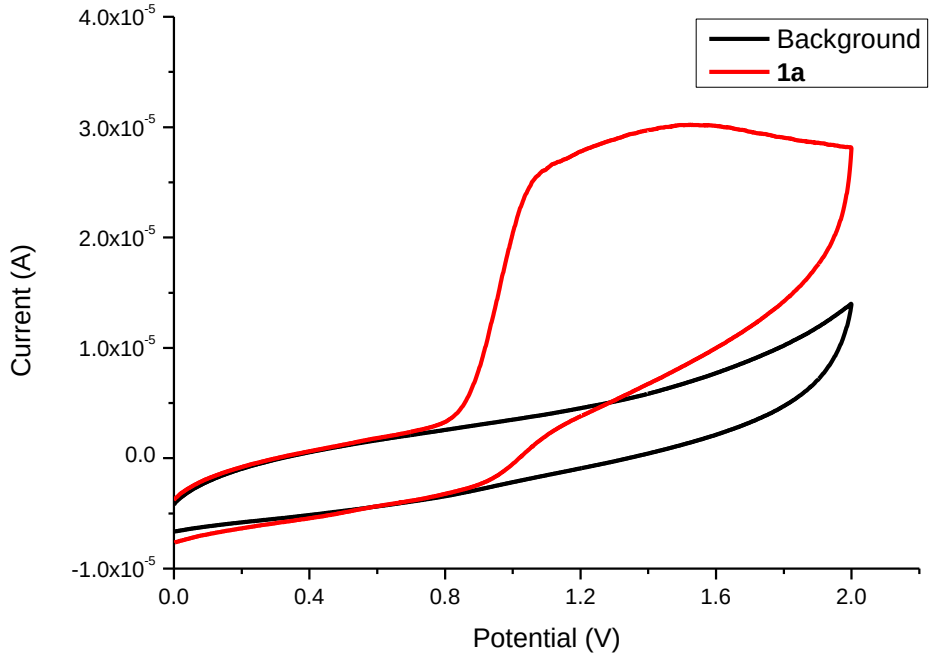


Figure S5. Cyclic voltammograms of background and **1a** (2 mM) in an electrolyte of *n*-Bu_4NPF_6 (0.05 mM) in MeCN from 0 to +2.0 V. The onset potential for the oxidation of **1a** is around +0.69 V and the E_{ox} is approximately +1.08 V.

9. Unsuccessful substrates

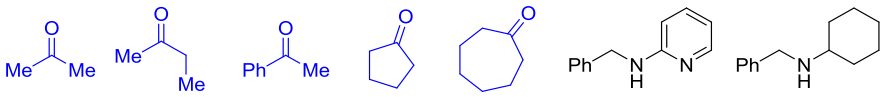
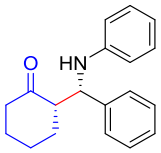


Figure S6. Unsuccessful substrates.

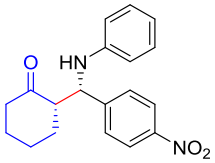
10. Characterization data of the products



(*S*)-2-((*S*)-Phenyl(phenylamino)methyl)cyclohexan-1-one (3a)[3]

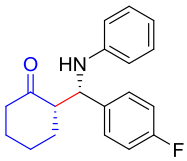
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 38 h). 65 mg, 78% yield, white solid. **Diastereomeric ratio (dr)**: 75:25. **Enantiomeric ratio (er):** 79:21 (*syn*), 59:41 (*anti*). R_f = 0.35 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.37 – 7.32 (m, 2H), 7.31 – 7.25 (m,

2H), 7.22 – 7.18 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.67 – 6.59 (m, 1H), 6.57 – 6.51 (m, 2H), 4.80 (d, *J* = 3.6 Hz, 0.75H), 4.62 (d, *J* = 6.9 Hz, 0.25H), 2.83 – 2.71 (m, 1H), 2.43 – 2.38 (m, 1H), 2.33 – 2.26 (m, 1H), 2.09 – 2.03 (m, 1H), 2.02 – 1.98 (m, 0.75H), 1.92 – 1.84 (m, 1.25H), 1.71 – 1.54 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 212.7, 211.2, 147.5, 147.2, 141.7, 141.6, 129.1, 129.0, 128.5, 128.4, 127.5, 127.3, 127.2, 127.0, 117.7, 117.6, 114.1, 113.7, 58.1, 57.5, 57.4, 56.6, 42.4, 41.8, 31.3, 28.7, 27.8, 27.0, 24.8, 23.7. **HPLC:** Daicel Chiralpak OJ-H, hexane/isopropanol = 80:20, flow rate 0.75 mL/min, λ = 254 nm, retention time: 27.549 min (*syn* major enantiomer), 21.125 min (*syn* minor enantiomer), 18.291 min (*anti* major enantiomer), 12.999 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(4-Nitrophenyl)(phenylamino)methyl)cyclohexan-1-one (3b)[4]

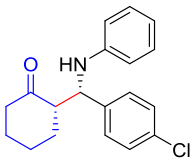
Followed the general procedure (Irradiation was conducted for 14 h, followed by the enzyme-catalyzed reaction for 36 h). 68 mg, 70% yield, yellow oil. **Diastereomeric ratio (dr)**: 82:18. **Enantiomeric ratio (er):** 79:21 (*syn*), 63:37 (*anti*). R_f = 0.40 (Petroleum ether/EtOAc, v/v, 3:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 8.6 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.70 – 6.64 (m, 1H), 6.50 (d, *J* = 7.9 Hz, 2H), 4.85 (d, *J* = 4.5 Hz, 0.82H), 4.84 – 4.43 (m, 1.18H), 2.89 – 2.80 (m, 1H), 2.46 – 2.38 (m, 1H), 2.36 – 2.29 (m, 1H), 2.11 – 2.01 (m, 2H), 1.96 – 1.88 (m, 1H), 1.68 – 1.56 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 211.6, 210.5, 149.9, 149.6, 147.2, 147.1, 146.7 × 2 (146.74, 146.69), 129.3, 129.2, 128.6, 128.3, 123.6 × 2 (123.64, 123.60), 118.4, 118.2, 114.1, 113.6, 57.9, 57.3, 57.0, 56.2, 42.4 × 2 (42.42, 42.37), 32.0, 29.2, 27.7, 27.0, 24.9, 24.5. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 16.266 min (*syn* major enantiomer), 12.402 min (*syn* minor enantiomer), 14.366 min (*anti* major enantiomer), 10.040 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(4-Fluorophenyl)(phenylamino)methyl)cyclohexan-1-one (3c)[5]

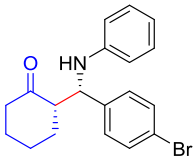
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 36 h). 71 mg, 80% yield, yellow oil. **Diastereomeric ratio (dr)**: 59:41.

Enantiomeric ratio (er): 74:26 (*syn*), 54:46 (*anti*). R_f = 0.40 (Petroleum ether/EtOAc, v/v, 3:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.36 – 7.29 (m, 2H), 7.10 – 7.04 (m, 2H), 7.00 – 6.93 (m, 2H), 6.67 – 6.61 (m, 1H), 6.54 – 6.49 (m, 2H), 4.74 (d, *J* = 4.4 Hz, 0.59H), 4.60 (d, *J* = 6.7 Hz, 0.41H), 2.83 – 2.69 (m, 1H), 2.44 – 2.36 (m, 1H), 2.35 – 2.25 (m, 1H), 2.08 – 1.91 (m, 2H), 1.90 – 1.86 (m, 1H), 1.70 – 1.55 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 212.2, 211.2, 161.9 ×2 [161.91 (d, *J* = 245.5 Hz), 161.86 (d, *J* = 245.2 Hz)], 147.2, 147.0, 137.4, 137.2 (d, *J* = 2.8 Hz), 129.2 (d, *J* = 7.9 Hz), 129.1, 129.0, 128.8 (d, *J* = 7.9 Hz), 117.9, 117.8, 115.3 (d, *J* = 21.3 Hz), 115.2 (d, *J* = 21.3 Hz), 114.1, 113.8, 57.6, 57.4, 57.0, 56.5, 42.4, 41.9, 31.4, 29.0, 27.8, 27.0, 24.8, 23.9. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -115.61, -115.9. **HRMS (ESI):** Calculated for $C_{19}H_{21}FNO$ ($[M+H]^+$): 298.1602, Found: 298.1599; Calculated for $C_{19}H_{20}FNNaO$ ($[M+H]^+$): 320.1421, Found: 320.1421. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.195 min (*syn* major enantiomer), 9.106 min (*syn* minor enantiomer), 10.032 min (*anti* major enantiomer), 7.802 min (*anti* minor enantiomer).



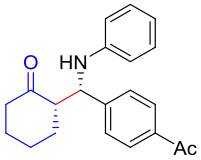
(*S*)-2-((*S*)-(4-Chlorophenyl)(phenylamino)methyl)cyclohexan-1-one (3d)[5]

Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 36 h). 67 mg, 71% yield, yellow oil. **Diastereomeric ratio (dr)**: 68:32. **Enantiomeric ratio (er):** 77:23 (*syn*), 56:44 (*anti*). R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 7.09 – 7.04 (m, 2H), 6.68 – 6.63 (m, 1H), 6.54 – 6.48 (m, 2H), 4.73 (d, *J* = 4.4 Hz, 0.68H), 4.59 (d, J = 6.4 Hz, 0.32H), 4.44 (br s, 1H), 2.80 – 2.75 (m, 0.68H), 2.75 – 2.70 (m, 0.32H), 2.44 – 2.38 (m, 1H), 2.34 – 2.27 (m, 1H), 2.06 – 2.01 (m, 1H), 1.91 – 1.88 (m, 1H), 1.70 – 1.55 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 212.1, 211.0, 147.1, 147.0, 140.4, 140.0, 132.8, 132.7, 129.1 ×2 (129.11, 129.06), 129.0, 128.7, 128.6, 128.5, 118.0, 117.8, 114.1, 113.7, 57.6, 57.3, 57.1, 56.4, 42.4, 42.0, 31.4, 29.0, 27.8, 27.0, 24.9, 24.0. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 16.850 min (*syn* major enantiomer), 12.786 min (*syn* minor enantiomer), 13.784 min (*anti* major enantiomer), 10.609 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(4-Bromophenyl)(phenylamino)methyl)cyclohexan-1-one (3e)[5]

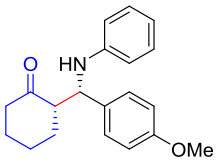
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 36 h). 79 mg, 74% yield, yellow oil. **Diastereomeric ratio (dr)**: 77:23. **Enantiomeric ratio (er):** 79:21 (*syn*), 59:41 (*anti*). R_f = 0.35 (Petroleum ether/EtOAc, v/v, 3:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.46 – 7.42 (m, 1.77H), 7.36 – 7.32 (m, 0.23H), 7.31 – 7.25 (m, 2H), 7.11 (t, *J* = 7.7 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 4.75 (d, *J* = 4.3 Hz, 0.77H), 4.61 (d, *J* = 6.5 Hz, 0.23H), 2.87 – 2.76 (m, 1H), 2.47 – 2.42 (m, 1H), 2.39 – 2.30 (m, 1H), 2.16 – 1.98 (m, 2H), 1.95 – 1.91 (m, 1H), 1.73 – 1.57 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 212.2, 211.0, 147.1, 147.0, 140.6, 140.1, 131.6, 131.5, 129.4, 129.1 × 3 (129.14, 129.12, 129.07), 121.0, 120.8, 118.0 ×2 (118.02, 117.98), 114.1, 113.8, 57.2, 57.1, 56.4, 56.3, 42.4, 42.0, 31.5, 29.0, 27.8, 27.0, 24.9, 24.0. **HRMS (ESI):** Calculated for $C_{19}H_{21}BrNO$ ($[M+H]^+$): 358.0801, Found: 358.0800. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.493 min (*syn* major enantiomer), 14.385 min (*syn* minor enantiomer), 15.282 min (*anti* major enantiomer), 12.267 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(4-Acetylphenyl)(phenylamino)methyl)cyclohexan-1-one (3f)

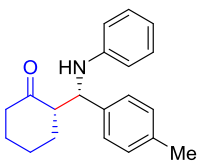
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 36 h). 64 mg, 66% yield, yellow oil. **Diastereomeric ratio (dr)**: 82:18. **Enantiomeric ratio (er):** 81:19 (*syn*), 55:45 (*anti*). R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.37 (m, 2H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.58 (t, *J* = 7.4 Hz, 1H), 6.47 – 6.42 (m, 2H), 4.76 (d, *J* = 4.4 Hz, 0.88H), 4.70 – 4.35 (m, 1.12H), 2.77 – 2.72 (m, 1H), 2.48 (s, 3H), 2.37 – 2.32 (m, 1H), 2.27 – 2.20 (m, 1H), 2.02 – 1.94 (m, 2H), 1.86 – 1.80 (m, 1H), 1.60 – 1.50 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 211.0, 209.8, 146.6, 146.4, 146.1, 146.0, 135.2 × 2 (135.24, 135.20), 128.2, 128.1, 127.6, 127.5, 126.9, 126.6, 117.1, 116.9, 113.1, 112.6, 57.0, 56.4, 56.2, 55.3, 41.4, 41.1, 30.7, 28.0, 26.8,

26.0, 25.5, 25.0, 23.9, 23.1. **HRMS (ESI):** Calculated for $C_{21}H_{24}NO_2$ ([M+H]$^+$): 322.1802, Found: 322.1801; Calculated for $C_{21}H_{23}NNaO_2$ ([M+Na]$^+$): 344.1621, Found: 344.1622. **HPLC:** Daicel Chiralpak OD-H, hexane/isopropanol = 80:20, flow rate 0.3 mL/min, λ = 254 nm, retention time: 41.069 min (*syn* major enantiomer), 69.795 min (*syn* minor enantiomer), 44.412 min (*anti* major enantiomer), 39.701 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(4-Methoxyphenyl)(phenylamino)methyl)cyclohexan-1-one (3g)[6]

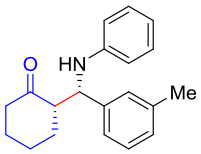
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 38 h). 62 mg, 67% yield, yellow oil. **Diastereomeric ratio (dr)**: 70:30. **Enantiomeric ratio (er):** 76:24 (*syn*), 61:39 (*anti*). R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.30 – 7.22 (m, 3H), 7.09 – 7.02 (m, 2H), 6.82 (t, *J* = 8.6 Hz, 2H), 6.66 – 6.60 (m, 1H), 6.58 – 6.51 (m, 2H), 4.71 (d, *J* = 4.4 Hz, 0.70H), 4.58 (d, *J* = 7.1 Hz, 0.30H), 3.75 (s, 3H), 2.81 – 2.68 (m, 1H), 2.45 – 2.36 (m, 1H), 2.34 – 2.25 (m, 1H), 2.07 – 1.98 (m, 1H), 1.93 – 1.80 (m, 2H), 1.70 – 1.55 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 212.8, 211.5, 158.8, 158.6, 147.5, 147.2, 133.6, 133.5, 129.0 × 2 (129.03, 128.99), 128.6, 128.3, 117.6, 114.4, 114.1, 113.9 × 2 (113.93, 113.87), 113.8, 57.6 × 2 (57.61, 57.56), 57.0, 56.6, 55.2 × 2 (55.20, 55.18), 42.4, 41.7, 31.1, 29.0, 27.8, 27.0, 24.8, 23.6. **HPLC:** Daicel Chiralpak AS-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 20.391 min (*syn* major enantiomer), 14.239 min (*syn* minor enantiomer), 10.020 min (*anti* major enantiomer), 16.801 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(Phenylamino)(*p*-tolyl)methyl)cyclohexan-1-one (3h)[6]

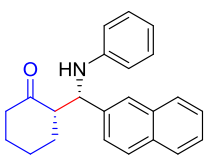
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 35 h). 56 mg, 64% yield, yellow oil. **Diastereomeric ratio (dr)**: 63:37. **Enantiomeric ratio (er):** 79:21 (*syn*), 63:37 (*anti*). R_f = 0.50 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26 – 7.19 (m, 2H), 7.11 – 7.01 (m,

4H), 6.66 – 6.57 (m, 1H), 6.53 (t, *J* = 7.4 Hz, 2H), 4.75 (d, *J* = 4.5 Hz, 0.63H), 4.59 (d, *J* = 7.2 Hz, 0.37H), 2.80 – 2.69 (m, 1H), 2.43 – 2.33 (m, 2H), 2.28 (s, 3H), 2.03 – 1.95 (m, 1H), 1.90 – 1.82 (m, 2H), 1.71 – 1.56 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 212.9, 211.4, 147.6, 147.3, 138.6, 138.5, 136.7, 136.5, 129.2, 129.1 × 2 (129.08, 129.05), 129.0, 127.4, 127.2, 117.6 × 2 (117.63, 117.55), 114.1, 113.8, 57.8, 57.5, 57.1, 56.6, 42.4, 41.7, 31.2, 28.8, 27.9, 27.0, 24.8, 23.6, 21.4, 21.0. **HPLC:** Daicel Chiralpak OJ-H, hexane/isopropanol = 97:03, flow rate 1.0 mL/min, λ = 254 nm, retention time: 37.645 min (*syn* major enantiomer), 33.056 min (*syn* minor enantiomer), 27.180 min (*anti* major enantiomer), 20.670 min (*anti* minor enantiomer).



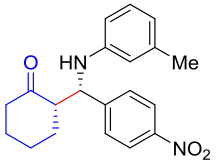
(*S*)-2-((*S*)-(Phenylamino)(*m*-tolyl)methyl)cyclohexan-1-one (3i)[7]

Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 35 h). 55 mg, 62% yield, yellow oil. **Diastereomeric ratio (dr)**: 71:29. **Enantiomeric ratio (er):** 77:23 (*syn*), 57:43 (*anti*). R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18 – 7.11 (m, 3H), 7.10 – 7.03 (m, 2H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.66 – 6.59 (m, 1H), 6.58 – 6.51 (m, 2H), 4.77 (d, *J* = 4.4 Hz, 0.71H), 4.57 (d, *J* = 7.2 Hz, 0.29H), 2.81 – 2.70 (m, 1H), 2.44 – 2.33 (m, 2H), 2.31 (s, 3H), 2.03 – 1.96 (m, 1H), 1.91 – 1.80 (m, 2H), 1.71 – 1.56 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 212.9, 211.3, 147.6, 147.2, 141.7 × 2 (141.74, 141.66), 138.1, 138.0, 129.1, 129.0, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 124.6, 124.5, 117.6 × 2 (117.64, 117.59), 114.1, 113.7, 58.2, 57.5, 57.2, 56.7, 42.4, 41.7, 31.3, 28.6, 27.9, 27.0, 25.0, 24.8, 23.6, 21.6. **HPLC:** Daicel Chiralpak OJ-H, hexane/isopropanol = 97:03, flow rate 1.0 mL/min, λ = 254 nm, retention time: 36.776 min (*syn* major enantiomer), 32.200 min (*syn* minor enantiomer), 23.964 min (*anti* major enantiomer), 19.814 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-Naphthalen-2-yl(phenylamino)methyl)cyclohexan-1-one (3j)[8]

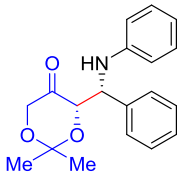
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 38 h). 63 mg, 64% yield, yellow oil. **Diastereomeric ratio (dr)**: 78:22. **Enantiomeric ratio (er):** 83:17 (*syn*), 59:41 (*anti*). R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.83 – 7.75 (m, 4H), 7.51 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.10 – 7.00 (m, 2H), 6.65 – 6.55 (m, 3H), 4.96 (d, *J* = 4.1 Hz, 0.78H), 4.79 (d, *J* = 7.1 Hz, 0.22H), 2.91 – 2.79 (m, 1H), 2.46 – 2.38 (m, 1H), 2.34 – 2.26 (m, 1H), 2.10 – 1.83 (m, 3H), 1.69 – 1.59 (m, 2H), 1.59 – 1.51 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 212.6, 211.2, 147.6, 147.3, 139.3, 139.2, 133.4, 133.3, 132.9, 132.8, 129.1, 129.0, 128.4, 128.1, 128.0 ×2 (128.00, 127.91), 127.7, 127.6, 126.4 ×2 (126.42, 126.35), 126.1, 126.0, 125.8, 125.7, 125.6, 125.2, 117.8, 117.7, 114.2, 113.8, 58.4, 57.6, 57.5, 56.6, 42.4, 41.8, 31.3, 28.8, 27.8, 27.0, 24.8, 23.7. **HPLC:** Daicel Chiralpak AS-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 19.775 min (*syn* major enantiomer), 12.736 min (*syn* minor enantiomer), 7.440 min (*anti* major enantiomer), 14.469 min (*anti* minor enantiomer).



(*S*)-2-((*S*)-(4-Nitrophenyl)(*m*-tolylamino)methyl)cyclohexan-1-one (3k)[9]

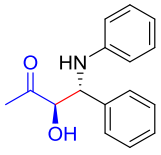
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 38 h). 71 mg, 70% yield, white solid. **Diastereomeric ratio (dr)**: 87:13. **Enantiomeric ratio (er):** 82:18 (*syn*), 64:36 (*anti*). R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.4 Hz, 0.26H), 8.14 (d, *J* = 8.4 Hz, 1.74H), 7.55 (d, *J* = 8.5 Hz, 1.74H), 7.48 (d, J = 8.5 Hz, 0.26H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.53 – 6.47 (m, 1H), 6.36 (s, 1H), 6.28 (d, *J* = 7.9 Hz, 1H), 4.85 (d, *J* = 4.4 Hz, 0.87H), 4.71 (d, *J* = 5.2 Hz, 0.13H), 4.56 (s, 1H), 2.87 – 2.80 (m, 1H), 2.43 (d, *J* = 14.2 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.19 (s, 3H), 2.10 – 2.03 (m, 2H), 1.93 (d, *J* = 6.9 Hz, 1H), 1.67 – 1.56 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 211.6, 210.5, 150.0, 149.7, 147.1, 146.7, 139.1, 139.0, 129.1, 129.0, 128.6, 128.2, 126.6, 123.6 ×2 (123.63, 123.58), 123.4, 119.4, 119.1, 115.0, 114.5, 111.0, 110.5, 57.8, 57.3, 56.8, 56.2, 42.4, 42.3, 31.9, 29.2, 27.0, 25.9, 24.9, 24.8, 24.5, 21.5. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm, retention time: 20.875 min (*syn*

major enantiomer), 16.896 min (*syn* minor enantiomer), 15.288 min (*anti* major enantiomer), 13.003 min (*anti* minor enantiomer).



(*S*)-2,2-Dimethyl-4-((*R*)-phenyl(phenylamino)methyl)-1,3-dioxan-5-one (3l)

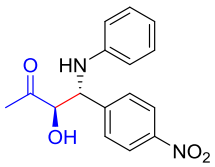
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 40 h). 73 mg, 78% yield, white solid. **Diastereomeric ratio (dr)**: 93:7. **Enantiomeric ratio (er):** 79:21 (*syn*), 74:26 (*anti*). $\boldsymbol{R_f}$ = 0.20 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.12 – 7.05 (m, 2H), 6.69 – 6.62 (m, 1H), 6.59 (d, *J* = 8.3 Hz, 2H), 5.10 (s, 0.93H), 5.0 (d, *J* = 3.2 Hz, 0.07H), 4.98 – 4.60 (m, 1.07H), 4.49 (s, 0.93H), 4.41 (d, *J* = 23.0 Hz, 0.07H), 4.26 (d, *J* = 17.0 Hz, 0.93H), 4.05 (d, *J* = 17.0 Hz, 0.93H), 3.82 (d, *J* = 8.6 Hz, 0.07H), 1.52 (s, 2.79H), 1.45 (s, 0.21H), 1.42 (s, 0.21H), 1.32 (s, 2.79H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 206.9 × 2 (206.91, 206.86), 146.9, 146.4, 139.74, 137.9, 129.2 × 2 (129.21, 129.15), 128.8, 128.4, 128.0, 127.6, 127.4, 127.1, 118.3, 118.0, 114.3, 114.1, 100.8, 100.7, 79.4, 77.8, 67.4, 67.1, 57.1, 56.3, 24.9, 24.6, 23.4, 22.9. **HRMS (ESI):** Calculated for $C_{19}H_{22}NO_3$ ($[M+H]^+$): 312.1594, Found: 312.1593; Calculated for $C_{19}H_{21}NNaO_3$ ($[M+Na]^+$): 334.1414, Found: 334.1412; Calculated for $C_{19}H_{21}KNO_3$ ($[M+K]^+$): 350.1153, Found: 350.1151. **HPLC:** Daicel Chiralpak OJ-H, hexane/isopropanol = 80:20, flow rate 0.75 mL/min, λ = 254 nm, retention time: 11.489 min (*syn* major enantiomer), 15.486 min (*syn* minor enantiomer), 13.604 min (*anti* major enantiomer), 7.094 min (*anti* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-phenyl-4-(phenylamino)butan-2-one (5a)[10]

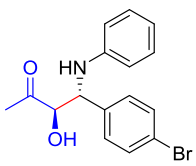
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 40 h). 62 mg, 81% yield, yellow oil. **Diastereomeric ratio (dr)**: 76:24. **Enantiomeric ratio (er):** 88:12 (*anti*), 62:38 (*syn*). $\boldsymbol{R_f}$ = 0.25 (Petroleum ether/EtOAc, v/v, 5:1). **^{1}H**

NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.30 (m, 1H), 7.30 – 7.21 (m, 4H), 7.12 – 7.05 (m, 2H), 6.70 – 6.64 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1.52H), 6.53 (d, *J* = 7.9 Hz, 0.48H), 4.95 (s, 0.24H), 4.85 (d, *J* = 3.0 Hz, 0.76H), 4.66 (d, *J* = 2.9 Hz, 0.76H), 4.42 (s, 0.24H), 3.47 (br s, 1H), 2.28 (s, 0.72H), 2.13 (s, 2.28H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 207.4, 207.3, 146.4, 146.2, 139.3, 137.3, 129.3, 129.2, 128.7, 128.6, 128.1, 127.6, 127,4, 127.0, 118.3, 118.2, 114.1, 113.9, 80.8, 79.9, 59.6, 58.4, 26.8, 25.2. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 0.5 mL/min, λ = 254 nm, retention time: 15.333 min (*anti* major enantiomer), 15.046 min (*anti* minor enantiomer), 19.149 min (*syn* major enantiomer), 12.700 min (*syn* minor enantiomer).



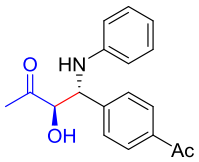
(3*R*,4*R*)-3-Hydroxy-4-(4-nitrophenyl)-4-(phenylamino)butan-2-one (5b)[11]

Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 28 h). 62 mg, 69% yield, yellow oil. **Diastereomeric ratio (dr)**: 86:14. **Enantiomeric ratio (er):** 87:13 (*anti*), 65:35 (*syn*). R_f = 0.20 (Petroleum ether/EtOAc, v/v, 5:1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 9.0 Hz, 0.28H), 8.13 (d, *J* = 8.6 Hz, 1.72H), 7.56 (d, *J* = 8.5 Hz, 0.28H), 7.48 (d, *J* = 8.6 Hz, 1.72H), 7.14 – 7.07 (m, 2H), 6.71 (t, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1.72H), 6.50 (d, *J* = 7.9 Hz, 0.28H), 5.08 (s, 0.14H), 4.96 (d, *J* = 2.7 Hz, 0.86H), 4.84 (br s, 0.86H), 4.73 (s, 0.86H), 4.55 (br s, 0.14H), 4.45 (s, 0.14H), 3.53 (s, 0.86H), 2.36 (s, 0.42H), 2.25 (s, 2.58H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 206.3, 206.2, 147.8, 147.6, 147.1, 145.5, 145.3, 145.0, 129.4 × 2 (129.45, 129.40), 128.5, 128.0, 123.9, 123.7, 118.9 × 2 (118.92, 118.90), 114.0, 113.8, 80.0, 79.6, 59.2, 58.0, 26.6, 24.9. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 34.336 min (*anti* major enantiomer), 23.332 min (*anti* minor enantiomer), 42.833 min (*syn* major enantiomer), 36.393 min (*syn* minor enantiomer).



(3*R*,4*R*)-4-(4-Bromophenyl)-3-hydroxy-4-(phenylamino)butan-2-one (5c)

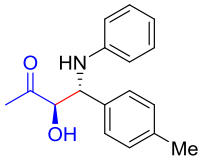
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 28 h). 73 mg, 73% yield, yellow oil. **Diastereomeric ratio (dr)**: 82:18. **Enantiomeric ratio (er):** 88:12 (*anti*), 61:39 (*syn*). $\boldsymbol{R_f}$ = 0.25 (Petroleum ether/EtOAc, v/v, 5:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.44 (m, 0.36H), 7.42 – 7.38 (m, 1.64H), 7.26 – 7.23 (m, 0.36H), 7.16 (d, *J* = 8.4 Hz, 1.64H), 7.13 – 7.06 (m, 2H), 6.72 – 6.65 (m, 1H), 6.58 – 6.54 (m, 1.64H), 6.52 – 6.48 (m, 0.36H), 4.92 (d, *J* = 2.1 Hz, 0.18H), 4.81 (d, *J* = 3.3 Hz, 0.82H), 4.64 (d, *J* = 3.3 Hz, 0.82H), 4.38 (d, *J* = 2.0 Hz, 0.18H), 2.30 (s, 0.54H), 2.17 (s, 2.46H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 207.0, 206.9, 146.0, 145.7, 138.4, 136.4, 131.8 × 2 (131.84, 131.77), 129.3 × 2 (129.33, 129.30), 129.2, 128.8, 122.1, 121.6, 118.5 × 2 (118.51, 118.47), 114.0, 113.8, 80.4, 79.7, 59.0, 57.8, 26.7, 25.1. **HRMS (ESI):** Calculated for $C_{16}H_{17}BrNO_2$ ($[M+H]^+$): 334.0437, Found: 334.0436. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 16.871 min (*anti* major enantiomer), 11.811 min (*anti* minor enantiomer), 17.868 min (*syn* major enantiomer), 11.988 min (*syn* minor enantiomer).



(3*R*,4*R*)-4-(4-Acetylphenyl)-3-hydroxy-4-(phenylamino)butan-2-one (5d)

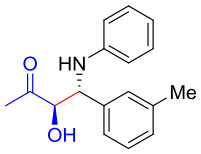
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 28 h). 66 mg, 74% yield, yellow oil. **Diastereomeric ratio (dr)**: 85:15. **Enantiomeric ratio (er):** 88:12 (*anti*), 60:40 (*syn*). $\boldsymbol{R_f}$ = 0.20 (Petroleum ether/EtOAc, v/v, 5:1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 8.2 Hz, 0.30H), 7.86 (d, *J* = 8.2 Hz, 1.70H), 7.47 (d, *J* = 8.1 Hz, 0.30H), 7.40 (d, *J* = 8.1 Hz, 1.70H), 7.12 – 7.06 (m, 2H), 6.71 – 6.66 (m, 1H), 6.57 (d, *J* = 8.3 Hz, 1.70H), 6.52 (d, *J* = 8.0 Hz, 0.30H), 5.03 (s, 0.15H), 4.91 (d, *J* = 2.8 Hz, 0.85H), 4.70 (s, 0.85H), 4.45 (s, 0.15H), 3.90 (s, 0.15H), 3.59 (s, 0.85H), 2.55 – 2.51 (m, 3H), 2.34 (s, 0.45H), 2.19 (s, 2.55H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 207.0, 206.8, 197.6, 197.5, 146.0, 145.8, 145.0, 142.9, 136.9, 136.6, 129.3 × 2 (129.33, 129.29), 128.8, 128.6, 127.8, 127.3, 118.6, 118.5, 114.0, 113.8, 80.3, 79.7, 59.4, 58.2, 26.7, 26.5 × 2 (26.51, 26.48), 25.1. **HRMS (ESI):** Calculated for $C_{18}H_{20}NO_3$ ($[M+H]^+$): 298.1438, Found: 298.1437. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 32.234 min (*anti* major enantiomer),

27.494 min (*anti* minor enantiomer), 44.333 min (*syn* major enantiomer), 29.170 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-(phenylamino)-4-(p-tolyl)butan-2-one (5e)

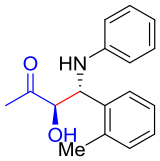
Followed the general procedure (Irradiation was conducted for 18 h, followed by the enzyme-catalyzed reaction for 30 h). 67 mg, 83% yield, yellow oil. **Diastereomeric ratio (dr)**: 77:23. **Enantiomeric ratio (er):** 82:18 (*anti*), 57:43 (*syn*). R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.23 (d, *J* = 7.7 Hz, 0.46H), 7.15 (d, *J* = 7.7 Hz, 1.54H), 7.13 – 7.03 (m, 4H), 6.68 – 6.62 (m, 1H), 6.60 – 6.50 (m, 2H), 4.91 (s, 0.23H), 4.80 (d, *J* = 2.5 Hz, 0.77H), 4.61 (d, *J* = 2.7 Hz, 0.77H), 4.37 (s, 0.23H), 3.52 (br s, 1H), 2.28 (s, 0.69H), 2.27 - 2.23 (m, 3H), 2.10 (s, 2.31H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 207.6, 207.5, 146.5, 146.4, 137.8, 137.3, 136.3, 134.2, 129.5, 129.4, 129.3, 129.2, 127.3, 126.9, 118.2, 118.1, 114.1, 113.9, 80.9, 79.9, 59.3, 58.2, 26.8, 25.3, 21.1, 21.1. **HRMS (ESI):** Calculated for $C_{17}H_{20}NO_2$ ($[M+H]^+$): 270.1489, Found: 270.1492; Calculated for $C_{17}H_{19}NNaO_2$ ($[M+Na]^+$): 292.1308, Found: 292.1312. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.132 min (*anti* major enantiomer), 11.548 min (*anti* minor enantiomer), 16.947 min (*syn* major enantiomer), 10.399 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-(phenylamino)-4-(*m*-tolyl)butan-2-one (5f)

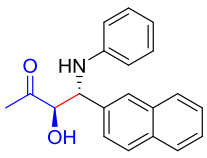
Followed the general procedure (Irradiation was conducted for 18 h, followed by the enzyme-catalyzed reaction for 30 h). 57 mg, 71% yield, yellow oil. **Diastereomeric ratio (dr)**: 73:27. **Enantiomeric ratio (er):** 82:18 (*anti*), 52:48 (*syn*). R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24 – 6.98 (m, 6H), 6.77 – 6.64 (m, 1H), 6.64 – 6.48 (m, 2H), 4.90 (d, *J* = 2.4 Hz, 0.27H), 4.79 (d, *J* = 3.6 Hz, 0.73H), 4.62 (d, *J* = 3.6 Hz, 0.73H), 4.39 (d, *J* = 2.4 Hz, 0.27H), 4.30 – 3.46 (m, 2H), 2.33 – 2.25 (m, 3.81H), 2.10 (s, 2.19H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 207.6, 207.2, 146.5, 146.3, 139.3, 138.3 × 2 (138.34, 138.28), 137.3, 129.3, 129.2, 129.0, 128.6,

128.5, 128.0, 127.6, 124.5, 124.0, 120.9, 118.2, 118.1, 114.0, 113.8, 80.9, 79.9, 59.6, 58.3, 26.8, 25.3, 21.6, 21.5. **HRMS (ESI):** Calculated for $C_{17}H_{20}NO_2$ ([M+H]$^+$): 270.1489, Found: 270.1487; Calculated for $C_{17}H_{19}NNaO_2$ ([M+Na]$^+$): 292.1308, Found: 292.1314. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.920 min (*anti* major enantiomer), 12.158 min (*anti* minor enantiomer), 13.166 min (*syn* major enantiomer), 8.649 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-(phenylamino)-4-(*o*-tolyl)butan-2-one (5g)

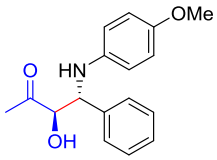
Followed the general procedure (Irradiation was conducted for 18 h, followed by the enzyme-catalyzed reaction for 31 h). 72 mg, 89% yield, yellow oil. **Diastereomeric ratio (dr)**: 89:11. **Enantiomeric ratio (er):** 89:11 (*anti*), 57:43 (*syn*). R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 7.0 Hz, 0.89H), 7.26 (d, *J* = 7.0 Hz, 0.11H), 7.20 – 7.01 (m, 5H), 6.72 – 6.59 (m, 1H), 6.56 – 6.50 (m, 1.78H), 6.45 – 6.41 (m, 0.22H), 5.14 (s, 0.11H), 4.98 (dd, *J* = 4.6, 2.1 Hz, 0.89H), 4.55 (dd, *J* = 4.5, 2.2 Hz, 0.89H), 4.28 (d, *J* = 2.0 Hz, 0.11H), 3.77 (br s, 1H), 2.52 (d, *J* = 2.2 Hz, 0.33H), 2.45 (d, *J* = 2.1 Hz, 2.67H), 2.27 (d, *J* = 2.0 Hz, 0.33H), 1.92 (d, *J* = 2.2 Hz, 2.67H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 209.6, 207.7, 146.6, 146.1, 136.9, 136.2, 135.8, 134.5, 131.1, 130.8, 129.3 × 2 (129.33, 129.29), 127.9, 127.6, 126.9, 126.8, 126.6, 126.5, 118.5, 118.1, 114.0, 113.8, 78.6, 78.3, 56.6, 54.5, 27.7, 25.3, 19.5, 19.3. **HRMS (ESI):** Calculated for $C_{17}H_{20}NO_2$ ([M+H]$^+$): 270.1489, Found: 270.1486; Calculated for $C_{17}H_{19}NNaO_2$ ([M+Na]$^+$): 292.1308, Found: 292.1308. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 26.786 min (*anti* major enantiomer), 29.598 min (*anti* minor enantiomer), 52.100 min (*syn* major enantiomer), 20.597 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-(naphthalen-2-yl)-4-(phenylamino)butan-2-one (5h)

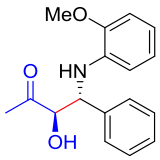
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 28 h). 63 mg, 69% yield, yellow oil. **Diastereomeric ratio (dr)**: 81:19.

Enantiomeric ratio (er): 87:13 (*anti*), 59:41 (*syn*). R_f = 0.65 (Petroleum ether/EtOAc, v/v, 5:1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.83 – 7.74 (m, 4H), 7.52 – 7.49 (m, 0.19H), 7.46 – 7.42 (m, 2.81H), 7.11 – 7.04 (m, 2H), 6.68 – 6.65 (m, 1H), 6.65 – 6.62 (m, 1.62H), 6.58 (d, *J* = 8.4 Hz, 0.38H), 5.11 (s, 0.19H), 5.01 (d, *J* = 3.4 Hz, 0.81H), 4.73 (d, *J* = 3.1 Hz, 0.81H), 4.51 (s, 0.19H), 2.32 (s, 0.57H), 2.15 (s, 2.43H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 207.2 × 2 (207.22, 207.20), 146.4, 146.2, 136.9, 134.9, 133.4, 133.2 × 2 (133.21, 133.20), 133.1, 129.3, 129.2, 128.6 × 2 (128.63, 128.56), 128.0, 127.9, 127.7 × 2 (127.709, 127.707), 126.6, 126.3, 126.2 × 2 (126.23, 126.16), 126.0 × 2 (126.04, 125.98), 125.1, 124.8, 118.4, 118.3, 114.1, 114.0, 80.8, 80.0, 59.9, 58.6, 26.8, 25.3. **HRMS (ESI):** Calculated for $C_{20}H_{20}NO_2$ ($[M+H]^+$): 306.1489, Found: 306.1493; Calculated for $C_{20}H_{19}NNaO_2$ ($[M+Na]^+$): 328.1308, Found: 328.1309. **HPLC:** Daicel Chiralpak OD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.516 min (*anti* major enantiomer), 65.165 min (*anti* minor enantiomer), 29.210 min (*syn* major enantiomer), 32.480 min (*syn* minor enantiomer).



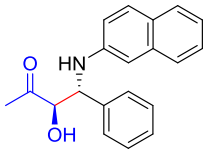
(3*R*,4*R*)-3-Hydroxy-4-((4-methoxyphenyl)amino)-4-phenylbutan-2-one (5i)[12]

Followed the general procedure (Irradiation was conducted for 18 h, followed by the enzyme-catalyzed reaction for 30 h). 47 mg, 55% yield, yellow oil. **Diastereomeric ratio (dr)**: 75:25. **Enantiomeric ratio (er):** 83:17 (*anti*), 58:42 (*syn*). R_f = 0.25 (Petroleum ether/EtOAc, v/v, 3:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 – 7.21 (m, 5H), 6.73 – 6.65 (m, 2H), 6.59 – 6.47 (m, 2H), 4.87 (d, *J* = 2.6 Hz, 0.25H), 4.77 (d, *J* = 3.5 Hz, 0.75H), 4.64 (d, *J* = 3.5 Hz, 0.75H), 4.40 (d, *J* = 2.6 Hz, 0.25H), 4.29 – 3.74 (m, 2H), 3.67 (s, 2.25H), 3.66 (s, 0.75H), 2.14 (s, 0.75H) 2.10 (s, 2.25H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 207.6, 207.5, 158.5, 152.7, 140.4, 140.2, 137.4, 136.5, 128.7 × 2 (128.74, 128.68), 128.6, 128.1, 127.4, 127.0, 122.2, 115.7, 114.8, 114.4, 80.8, 79.8, 60.6, 59.3, 55.6, 55.5, 26.8, 25.3. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 23.893 min (*anti* major enantiomer), 20.623 min (*anti* minor enantiomer), 30.311 min (*syn* major enantiomer), 18.439 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-((2-methoxyphenyl)amino)-4-phenylbutan-2-one (5j)

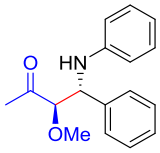
Followed the general procedure (Irradiation was conducted for 18 h, followed by the enzyme-catalyzed reaction for 40 h). 40 mg, 47% yield, yellow oil. **Diastereomeric ratio (dr)**: 75:25. **Enantiomeric ratio (er):** 80:20 (*anti*), 53:47 (*syn*). $\boldsymbol{R_f}$ = 0.25 (Petroleum ether/EtOAc, v/v, 3:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 – 7.22 (m, 5H), 6.78 – 6.60 (m, 3H), 6.45 (dd, *J* = 7.7, 1.3 Hz, 0.75H), 6.40 (dd, *J* = 7.7, 1.5 Hz, 0.25H), 5.21 (br s, 1H), 4.99 (d, *J* = 1.7 Hz, 0.25H), 4.87 (d, *J* = 3.4 Hz, 0.75H), 4.71 (s, 0.75H), 4.46 (s, 0.25H), 3.88 (s, 2.25H), 3.86 (s, 0.75H), 2.32 (s, 0.75H), 2.16 (s, 2.25H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 207.4, 207.3, 147.3, 147.2, 139.3, 137.3, 136.2, 136.0, 128.7, 128.6, 128.1, 127.6, 127.4, 126.9, 121.0 × 2 (121.05, 121.02), 117.5, 117.4, 111.4 × 2 (111.41, 111.38), 109.7 × 2 (109.74, 109.67), 80.9, 80.0, 59.5, 58.3, 55.5 × 2 (55.54, 55.53), 26.9, 25.3. **HRMS (ESI):** Calculated for $C_{17}H_{20}NO_3$ ($[M+H]^+$): 286.1438, Found: 286.1435; Calculated for $C_{17}H_{19}NNaO_3$ ($[M+Na]^+$): 308.1257, Found: 308.1256. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 24.265 min (*anti* major enantiomer), 21.883 min (*anti* minor enantiomer), 20.269 min (*syn* major enantiomer), 16.807 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Hydroxy-4-(naphthalen-2-ylamino)-4-phenylbutan-2-one (5k)

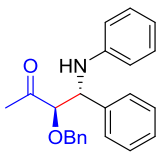
Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 28 h). 63 mg, 69% yield, yellow oil. **Diastereomeric ratio (dr)**: 74:26. **Enantiomeric ratio (er):** 86:14 (*anti*), 51:49 (*syn*). $\boldsymbol{R_f}$ = 0.70 (Petroleum ether/EtOAc, v/v, 5:1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.64 – 7.57 (m, 2H), 7.51 – 7.45 (m, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.23 (t, *J* = 2.3 Hz, 1H), 7.18 – 7.06 (m, 1H), 6.96 – 6.87 (m, 1H), 6.74 – 6.66 (m, 1H), 5.10 – 4.46 (m, 3H), 3.83 - 3.42 (m, 1H), 2.32 – 2.16 (m, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 207.1 × 2 (207.14, 207.12), 144.0, 143.8, 137.0, 134.9, 129.1 × 2 (129.13, 129.09), 128.8, 128.7, 128.6, 128.2, 127.9, 127.7, 127.6, 127.4, 126.9, 126.8, 126.3 × 2 (126.33, 126.30), 126.0 × 2

(126.04, 126.00), 122.4, 122.0, 118.3, 118.0, 114.1, 113.8, 106.7, 106.5, 80.7, 79.8, 59.6, 58.4, 26.8, 25.2. **HRMS (ESI):** Calculated for $C_{20}H_{19}NNaO_2$ ([M+Na]$^+$): 328.1308, Found: 328.1309. **HPLC:** Daicel Chiralpak AS-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 36.680 min (*anti* major enantiomer), 24.209 min (*anti* minor enantiomer), 33.739 min (*syn* major enantiomer), 38.521 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-Methoxy-4-phenyl-4-(phenylamino)butan-2-one (5l)

Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 36 h). 66 mg, 82% yield, white solid. **Diastereomeric ratio (dr)**: 83:17. **Enantiomeric ratio (er):** 84:16 (*anti*), 69:31 (*syn*). R_f = 0.30 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.36 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.11 – 7.03 (m, 2H), 6.68 – 6.61 (m, 1H), 6.58 (d, *J* = 7.9 Hz, 1.68H), 6.52 (d, *J* = 5.3 Hz, 0.32H), 4.82 (d, *J* = 1.2 Hz, 0.32H), 4.68 (d, *J* = 5.2 Hz, 0.84H), 4.59 (br s, 1H), 3.92 (d, *J* = 5.2 Hz, 0.84H), 3.83 (d, *J* = 1.4 Hz, 0.32H), 3.36 (s, 2.52H), 3.28 (s, 0.48H), 2.15 (s, 0.48H), 1.82 (s, 2.52H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 210.5, 209.9, 146.5, 146.2, 139.8, 138.6, 129.2, 129.1, 128.5 × 2 (128.53, 128.48), 127.8 × 2 (127.83, 127.78), 127.5, 127.0, 118.2, 117.9, 114.1, 113.8, 90.6, 89.8, 59.6, 59.4, 59.2, 58.7, 27.2, 26.5. **HRMS (ESI):** Calculated for $C_{17}H_{20}NO_2$ ([M+H]$^+$): 270.1489, Found: 270.1489; Calculated for $C_{17}H_{19}NNaO_2$ ([M+Na]$^+$): 292.1308, Found: 292.1307; Calculated for $C_{17}H_{19}KNO_2$ ([M+K]$^+$): 308.1047, Found: 308.1047. **HPLC:** Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 0.7 mL/min, λ = 254 nm, retention time: 41.968 min (*anti* major enantiomer), 27.972 min (*anti* minor enantiomer), 26.171 min (*syn* major enantiomer), 20.844 min (*syn* minor enantiomer).



(3*R*,4*R*)-3-(Benzyloxy)-4-phenyl-4-(phenylamino)butan-2-one (5m)

Followed the general procedure (Irradiation was conducted for 12 h, followed by the enzyme-catalyzed reaction for 40 h). 66 mg, 64% yield, yellow oil. **Diastereomeric ratio (dr)**: 85:15.

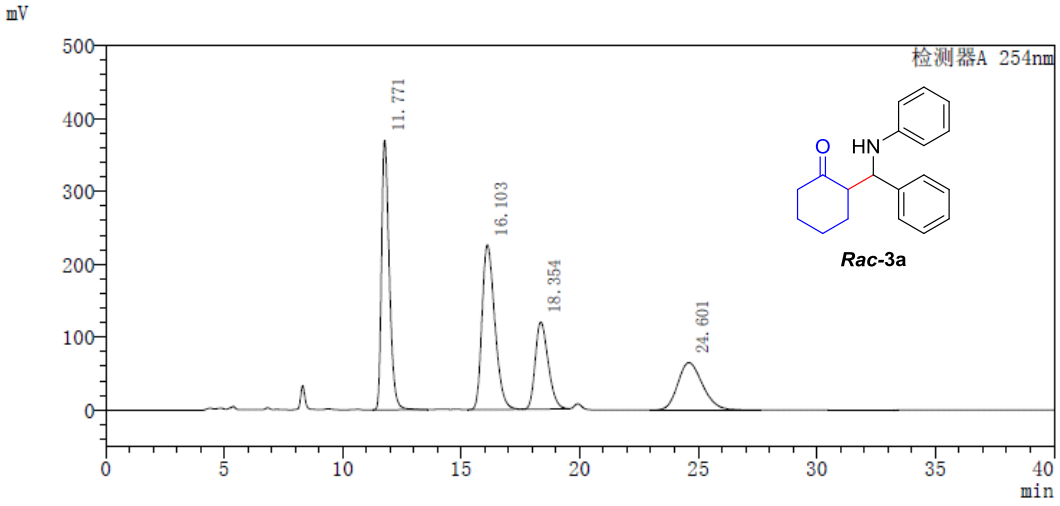
Enantiomeric ratio (er): 83:17 (*anti*), 65:35 (*syn*). R_f = 0.45 (Petroleum ether/EtOAc, v/v, 5:1). Mixture of two diastereomers: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.36 – 7.27 (m, 7H), 7.26 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 7.08 – 7.03 (m, 2H), 6.67 – 6.61 (m, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.69 (d, *J* = 5.6 Hz, 0.85H), 4.63 – 4.36 (m, 2.15H), 4.34 (d, *J* = 11.8 Hz, 0.85H), 4.26 (d, *J* = 5.6 Hz, 0.15H), 4.09 (d, *J* = 5.6 Hz, 0.85H), 4.06 (d, *J* = 2.0 Hz, 0,15H), 2.18 (s, 0.45H), 1.87 (s, 2.55H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 210.5, 209.5, 146.4, 146.2, 139.7, 138.7, 137.0, 136.8, 129.3, 129.2, 128.8, 128.6 × 2 (128.62, 128.55), 128.5, 128.2, 128.1, 128.0 × 2 (128.02, 127.95), 127.9, 127.8, 127.5, 127.1, 118.1, 117.9, 114.0, 113.8, 88.0, 87.3, 73.8, 73.6, 59.3, 58.9, 27.5, 26.6. **HRMS (ESI):** Calculated for $C_{23}H_{24}NO_2$ ($[M+H]^+$): 346.1802, Found: 346.1799; Calculated for $C_{23}H_{23}NNaO_2$ ($[M+Na]^+$): 368.1621, Found: 368.1619; Calculated for $C_{23}H_{23}KNO_2$ ($[M+K]^+$): 384,1360, Found: 384.1359. **HPLC:** Daicel Chiralpak OD-H, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, λ = 254 nm, retention time: 26.702 min (*anti* major enantiomer), 43.411 min (*anti* minor enantiomer), 22.056 min (*syn* major enantiomer), 37.099 min (*syn* minor enantiomer).

11. Comparison of dr determined by HPLC and ^{1}HNMR analysis of mixture.

Table S9. Comparison of dr determined by HPLC and ^{1}HNMR analysis of the mixture.

Entry	Product	dr of isolated products determined by HPLC analysis	dr of crude reaction mixtures determined by ^{1}HNMR analysis
1	**3a**	75/25 (*syn*/*anti*)	75/25 (*syn*/*anti*)
2	**3j**	78/22 (*syn*/*anti*)	79/21 (*syn*/*anti*)
3	**3l**	93/7 (*syn*/*anti*)	90/10 (*syn*/*anti*)
4	**5a**	76/24 (*anti*/*syn*)	76/24 (*anti*/*syn*)
5	**5l**	83/17 (*anti*/*syn*)	83/17 (*anti*/*syn*)
6	**5m**	85/15 (*anti*/*syn*)	85/15 (*anti*/*syn*)

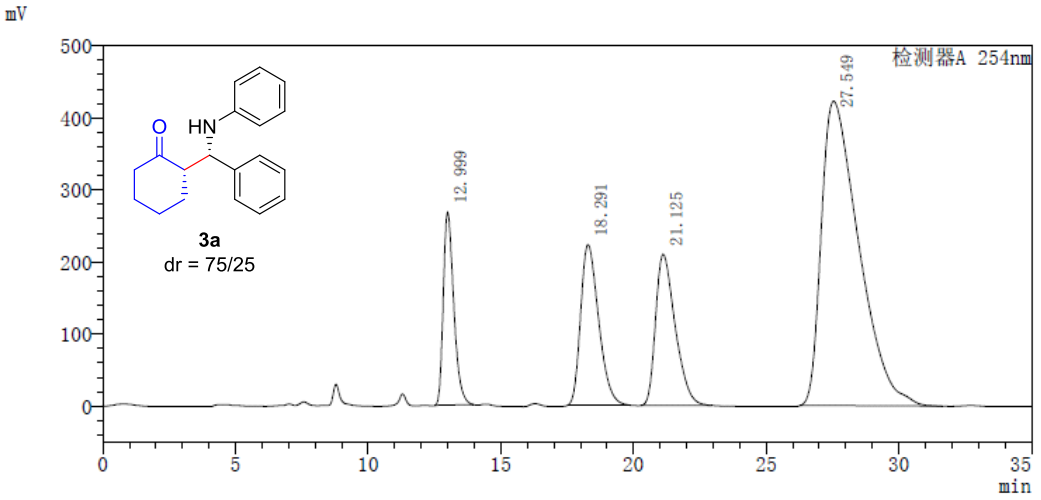
HPLC spectrum of ***Rac*-3a**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.771	8401948	369500	32.159
2	16.103	8477829	225903	32.450
3	18.354	4537721	119703	17.369
4	24.601	4708447	64951	18.022
总计		26125945	780058	

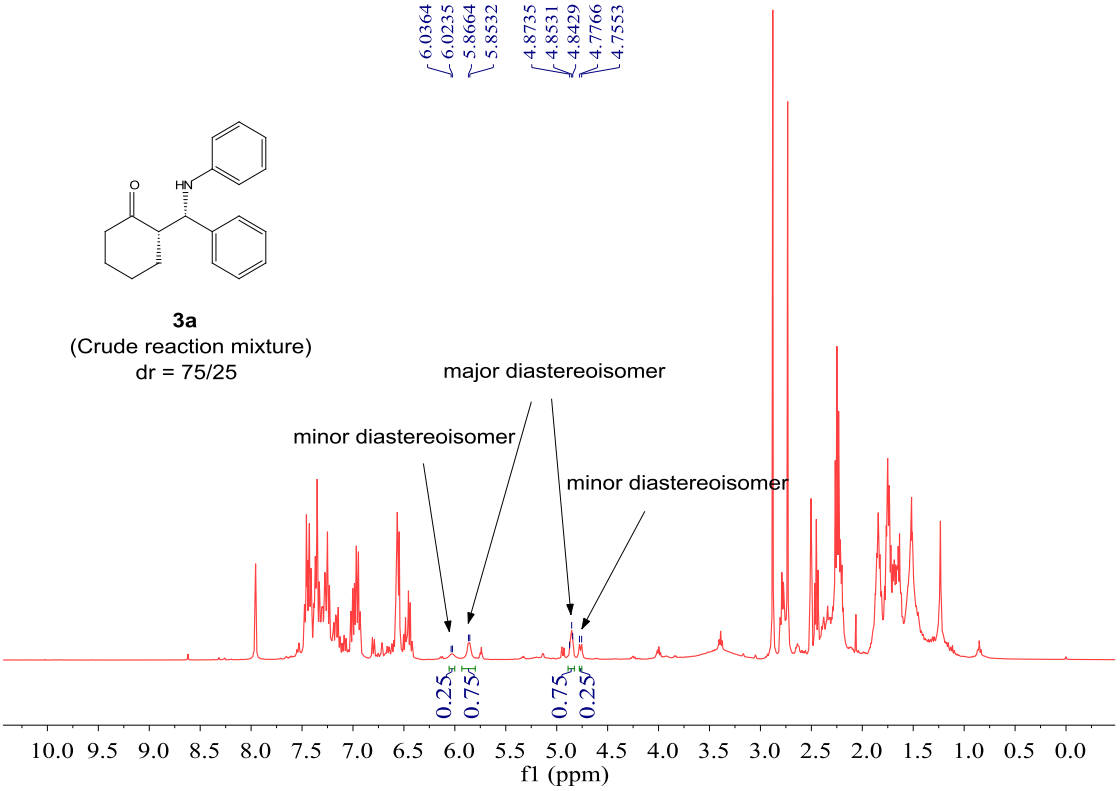
HPLC spectrum of **3a**



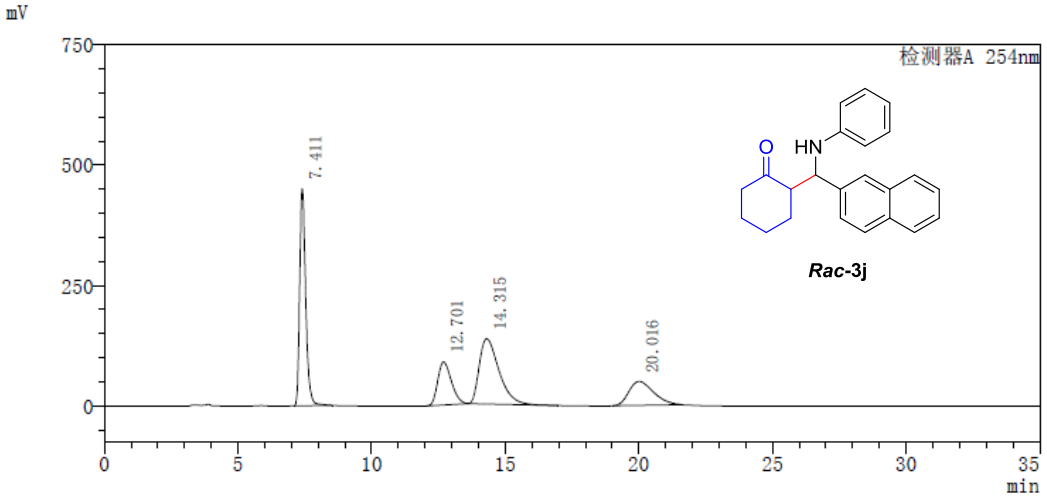
检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.999	7337657	267309	10.459
2	18.291	10543487	222899	15.029
3	21.125	10767896	209409	15.349
4	27.549	41505024	422224	59.163
总计		70154064	1121840	

^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of **3a** (Crude reaction mixture)



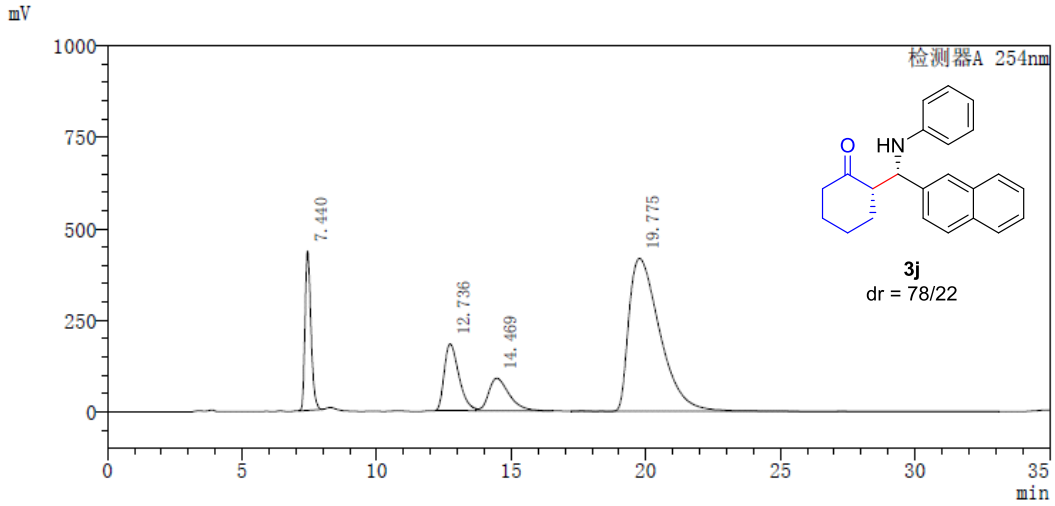
HPLC spectrum of ***Rac*-3j**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.411	7041227	451410	34.538
2	12.701	3174983	89458	15.574
3	14.315	6962883	135562	34.154
4	20.016	3207544	49717	15.734
总计		20386636	726147	

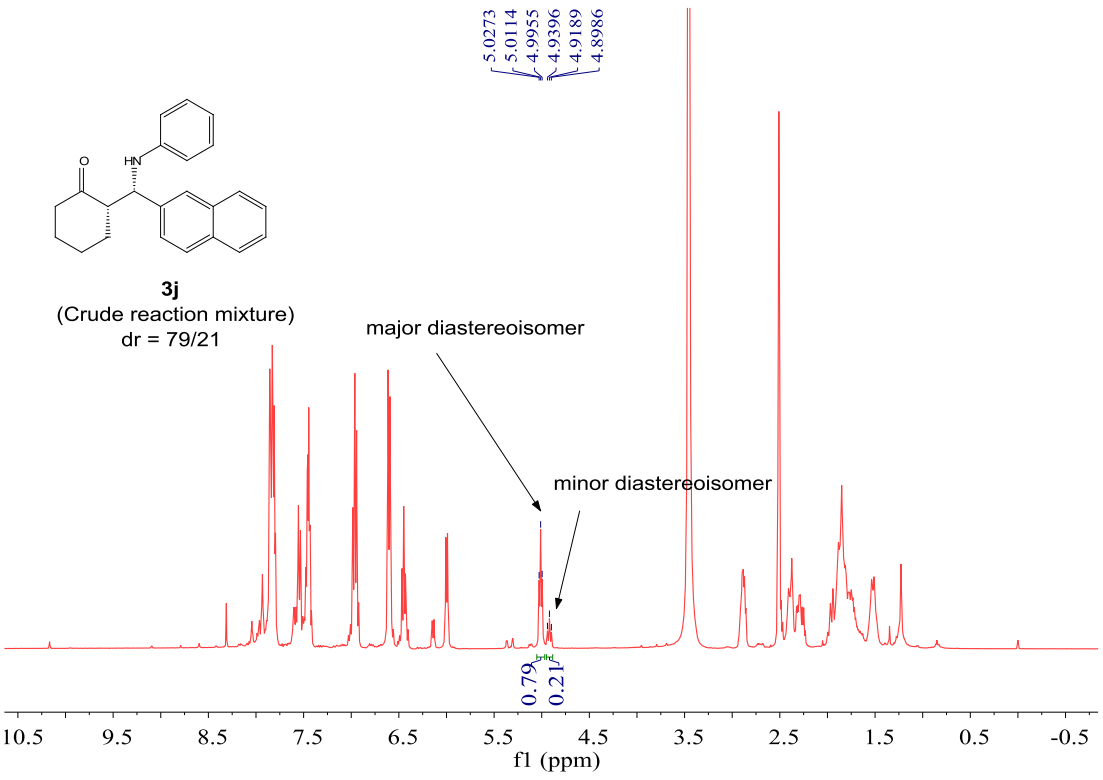
HPLC spectrum of **3j**



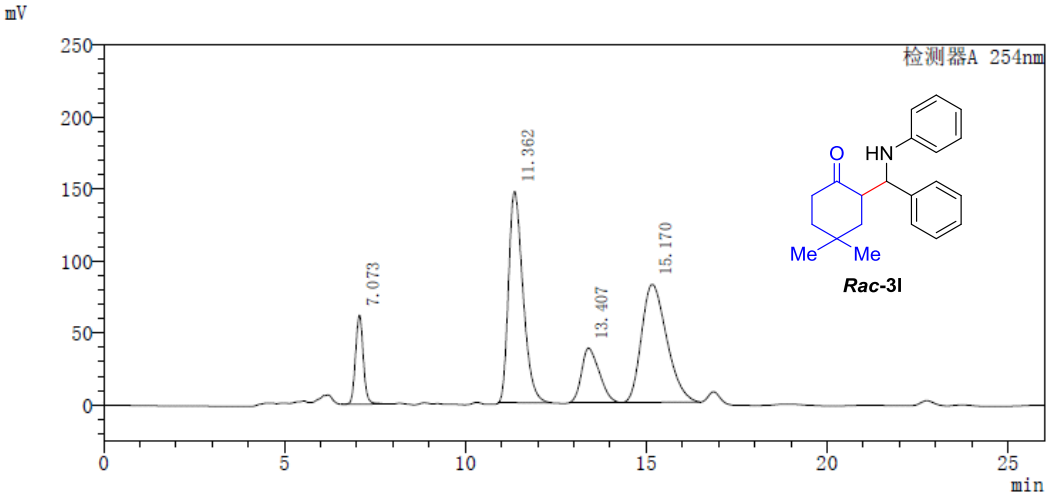
检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.440	6673589	435276	12.860
2	12.736	6873230	182312	13.244
3	14.469	4709979	88754	9.076
4	19.775	33639277	417749	64.820
总计		51896075	1124091	

^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of **3j** (Crude reaction mixture)



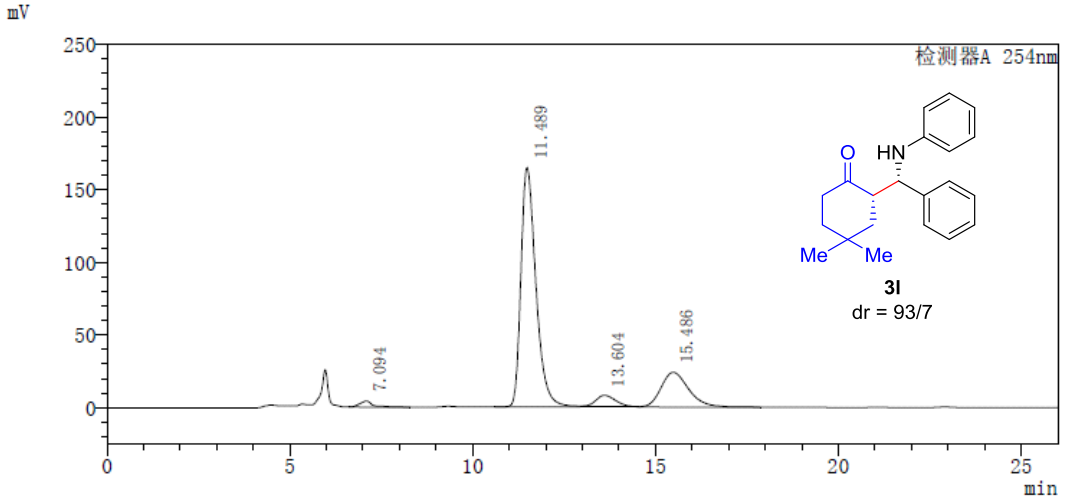
HPLC spectrum of ***Rac*-3l**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.073	930394	61685	9.062
2	11.362	4075009	146518	39.689
3	13.407	1282763	37804	12.494
4	15.170	3979225	81840	38.756
总计		10267391	327846	

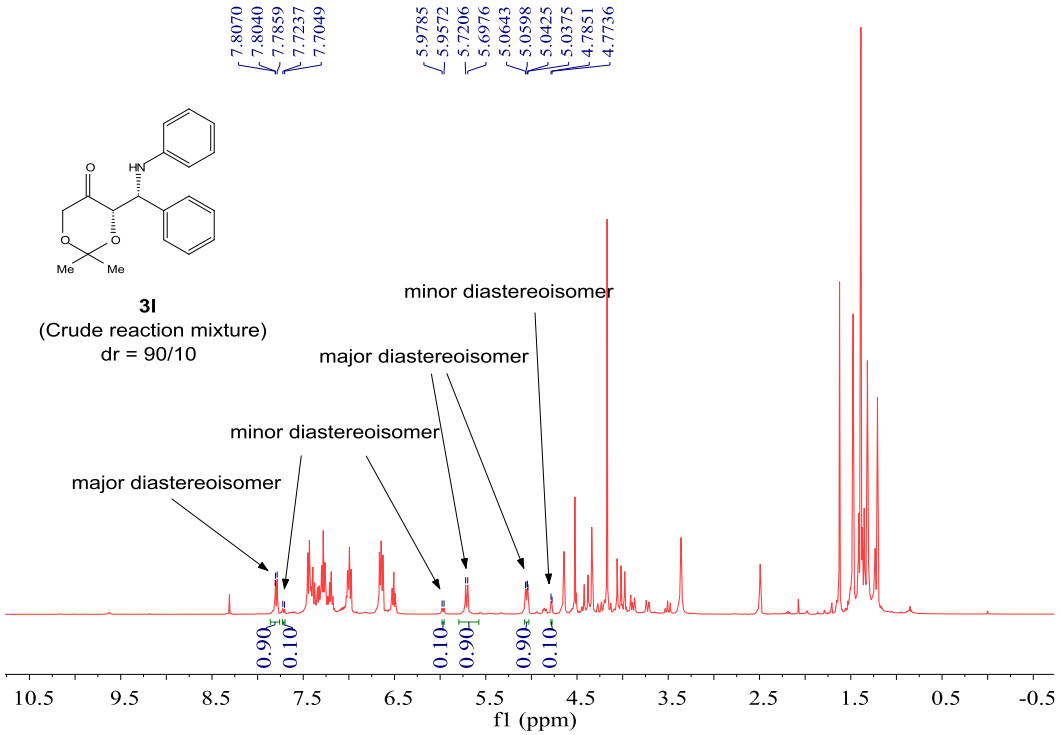
HPLC spectrum of **3l**



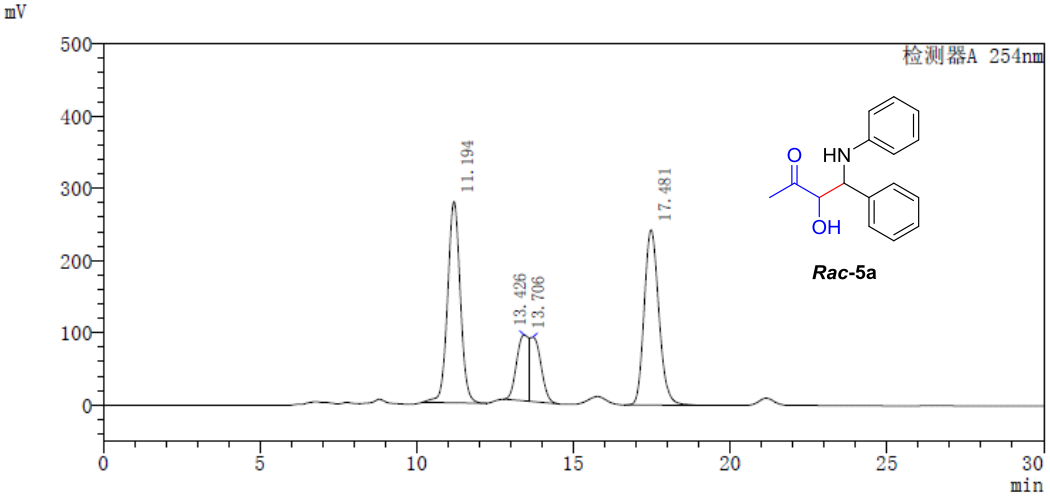
检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.094	107527	4310	1.688
2	11.489	4688244	164680	73.578
3	13.604	314134	8025	4.930
4	15.486	1261912	23912	19.805
总计		6371818	200927	

^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of **3l** (Crude reaction mixture)



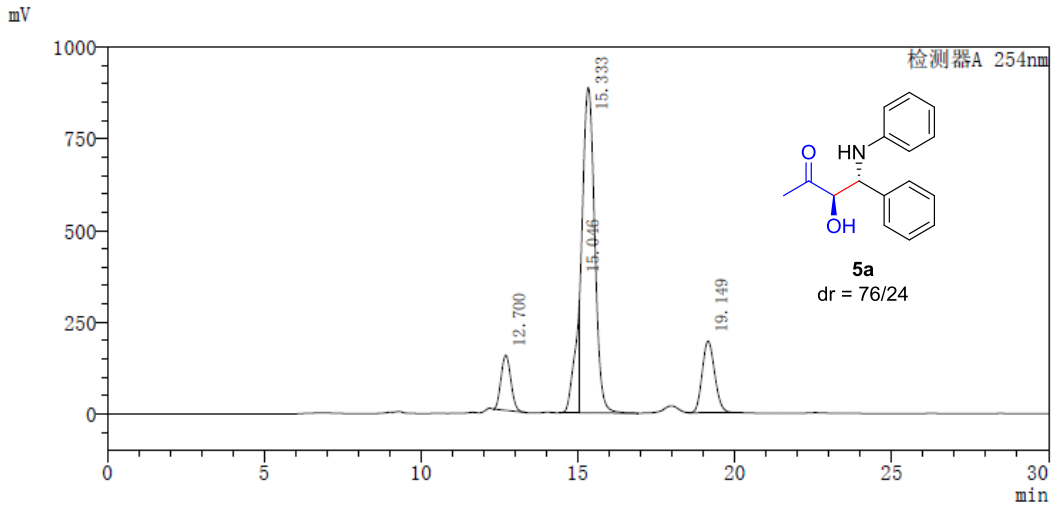
HPLC spectrum of ***Rac*-5a**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.194	7862006	278694	38.609
2	13.426	2306976	91127	11.329
3	13.706	2297040	88878	11.280
4	17.481	7897257	242491	38.782
总计		20363280	701189	

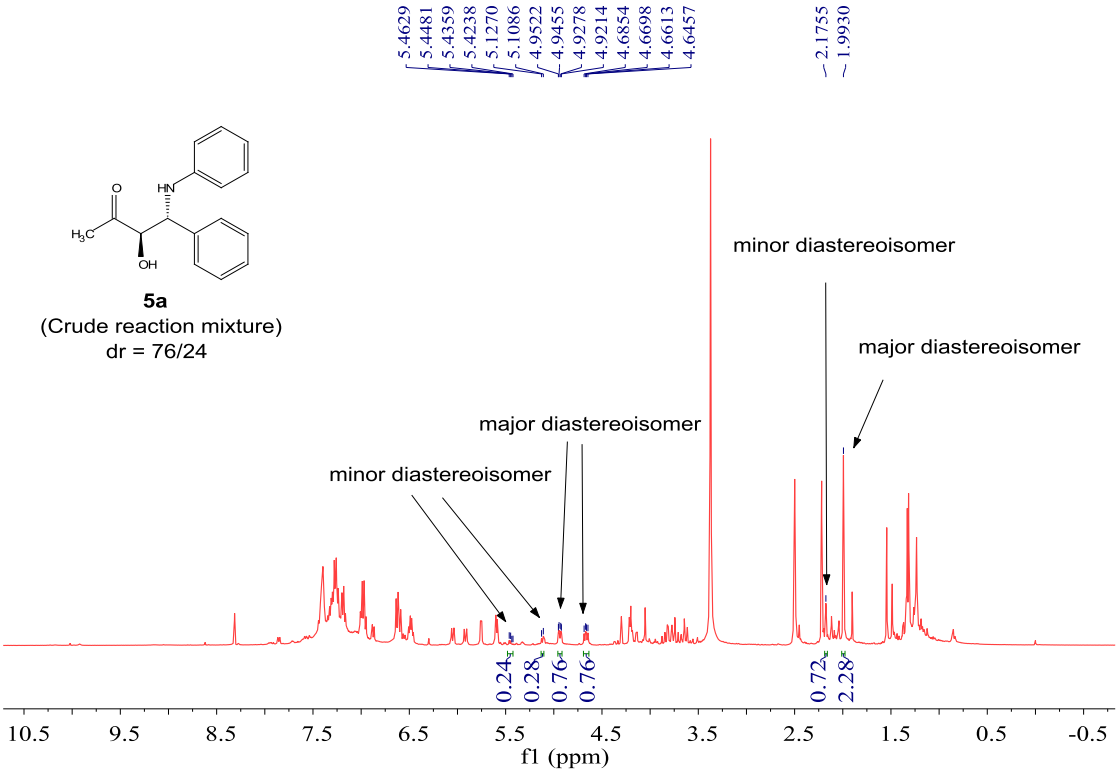
HPLC spectrum of **5a**



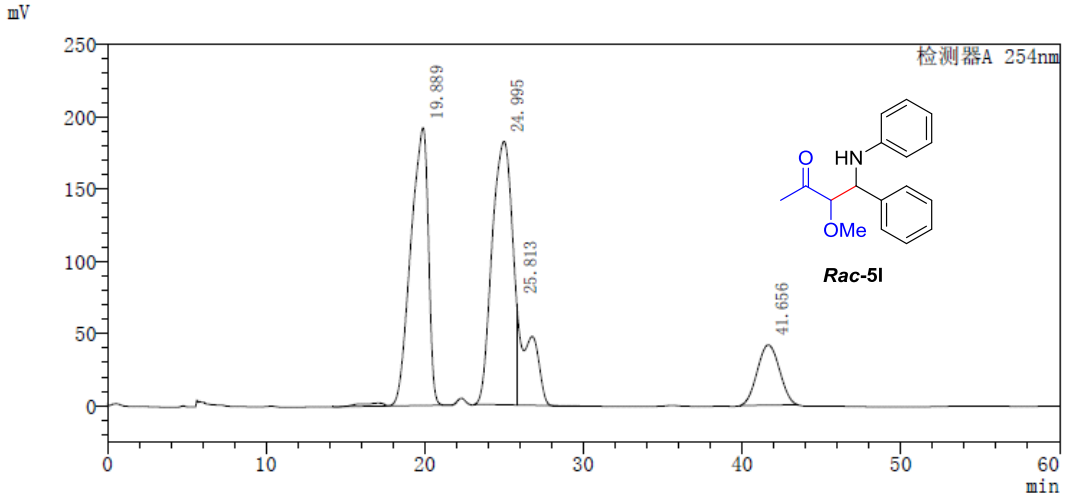
检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.700	3286250	150384	9.168
2	15.046	3321781	292288	9.267
3	15.333	23804952	887767	66.410
4	19.149	5432206	194962	15.155
总计		35845189	1525401	

^{1}H NMR Spectrum (400 MHz, DMSO-*d6*) of **5a** (Crude reaction mixture)



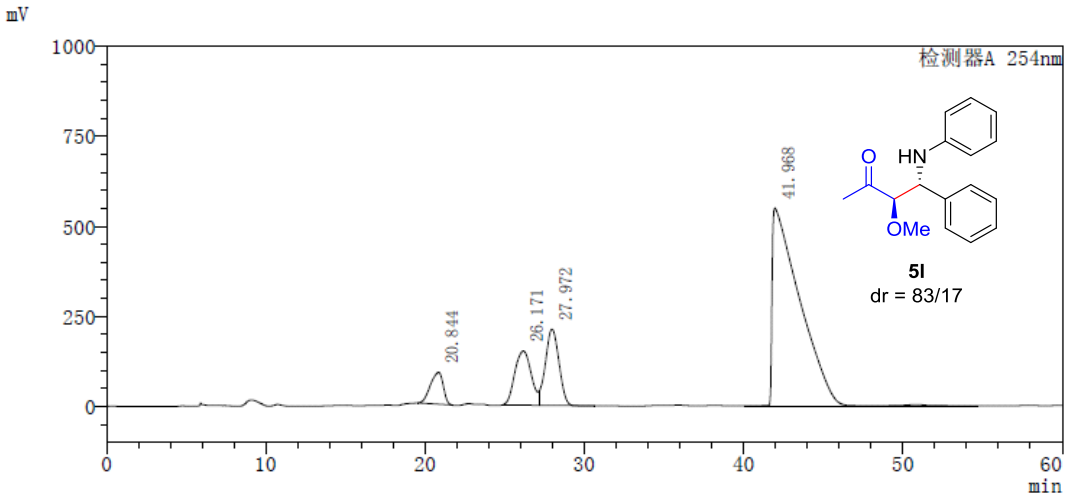
HPLC spectrum of ***Rac*-5l**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.889	14964440	192101	38.343
2	24.995	15951513	182189	40.872
3	25.813	4056313	68333	10.393
4	41.656	4055674	41684	10.392
总计		39027940	484306	

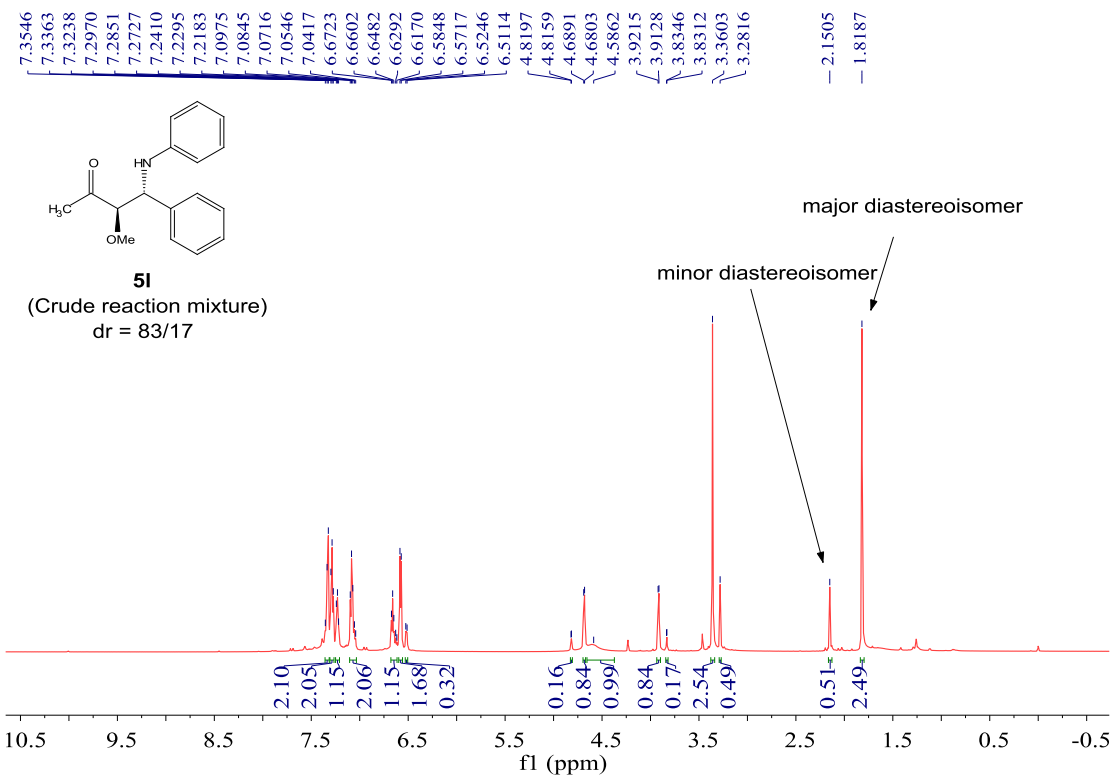
HPLC spectrum of **5l**



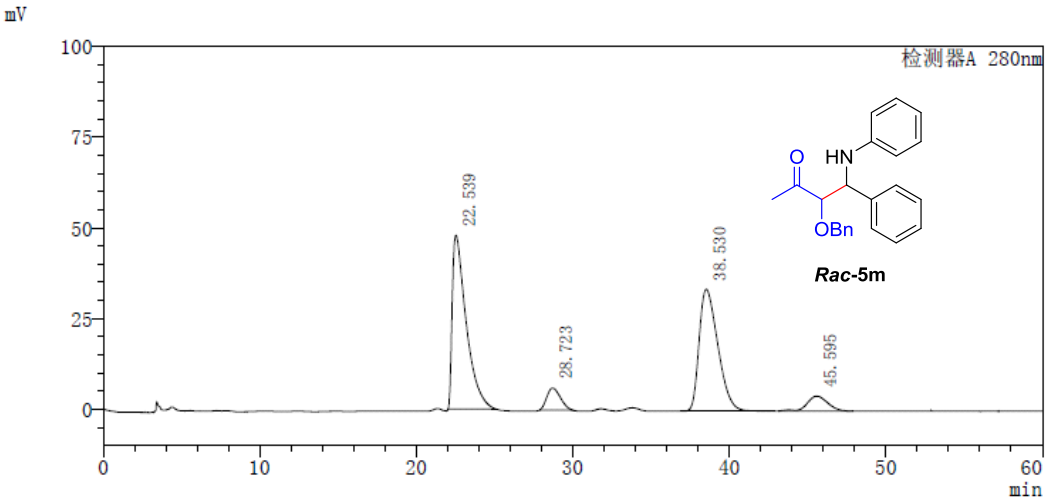
检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.844	4933836	88521	5.228
2	26.171	10902284	150815	11.552
3	27.972	12578698	212517	13.328
4	41.968	65962502	548951	69.892
总计		94377320	1000804	

^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of **5l** (Crude reaction mixture)



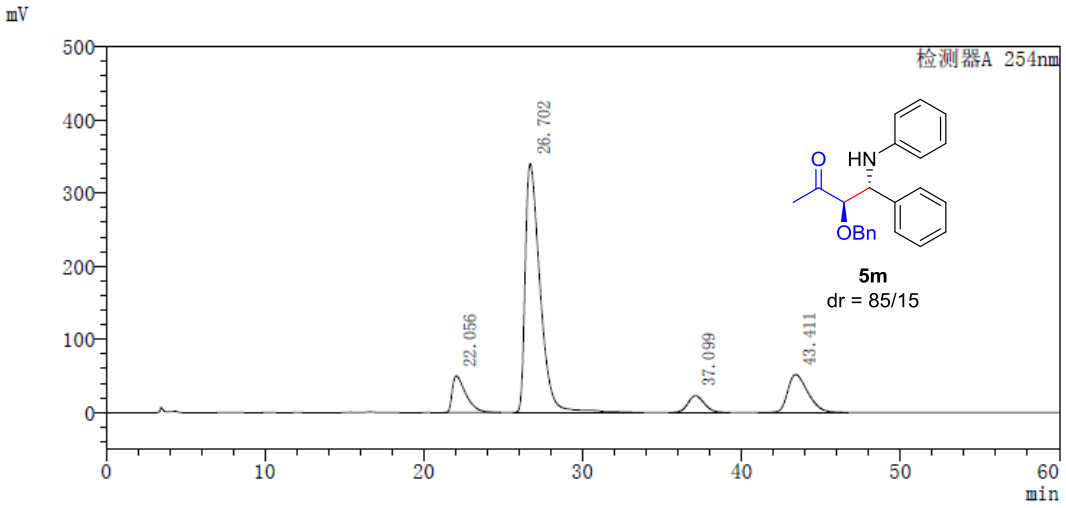
HPLC spectrum of ***Rac*-5m**



检测器A 280nm

No.	Retention Time	Area	Height	Concentration
1	22.539	2978868	47938	45.566
2	28.723	368617	6082	5.638
3	38.530	2804840	33615	42.904
4	45.595	385221	4148	5.892
总计		6537546	91782	

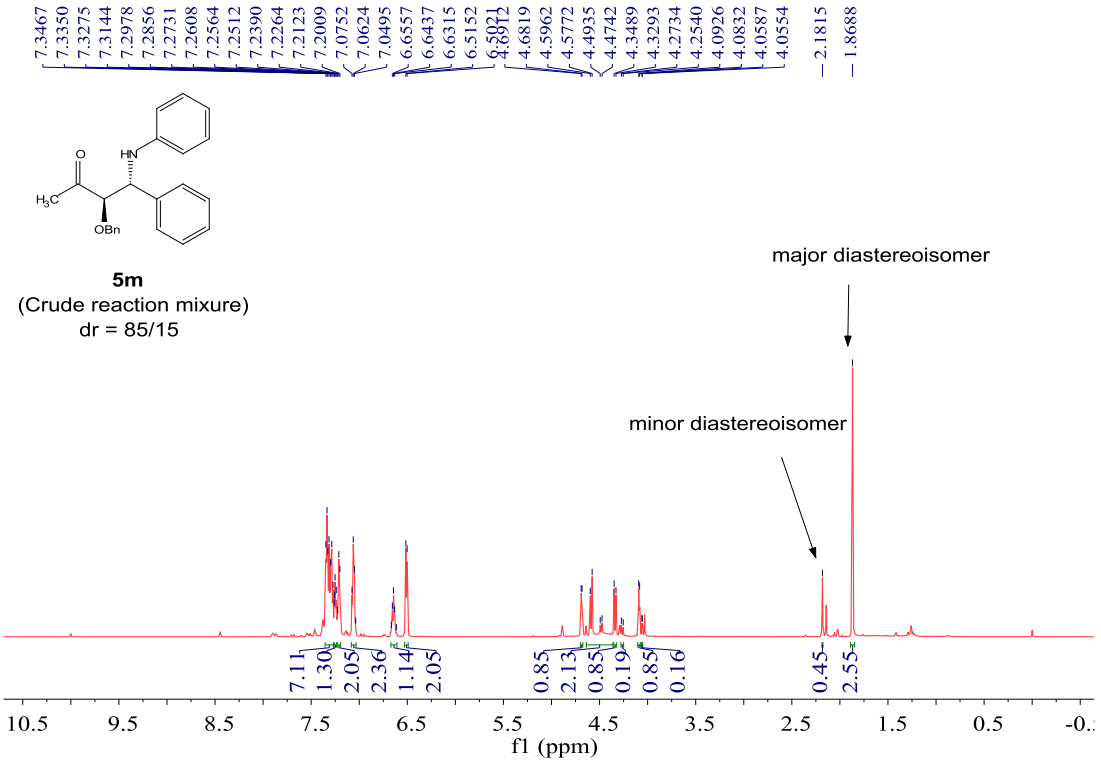
HPLC spectrum of **5m**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	22.056	2977804	50010	9.545
2	26.702	22084297	339942	70.792
3	37.099	1617680	22730	5.186
4	43.411	4516347	51753	14.477
总计		31196128	464435	

^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of **5m** (Crude reaction mixture)



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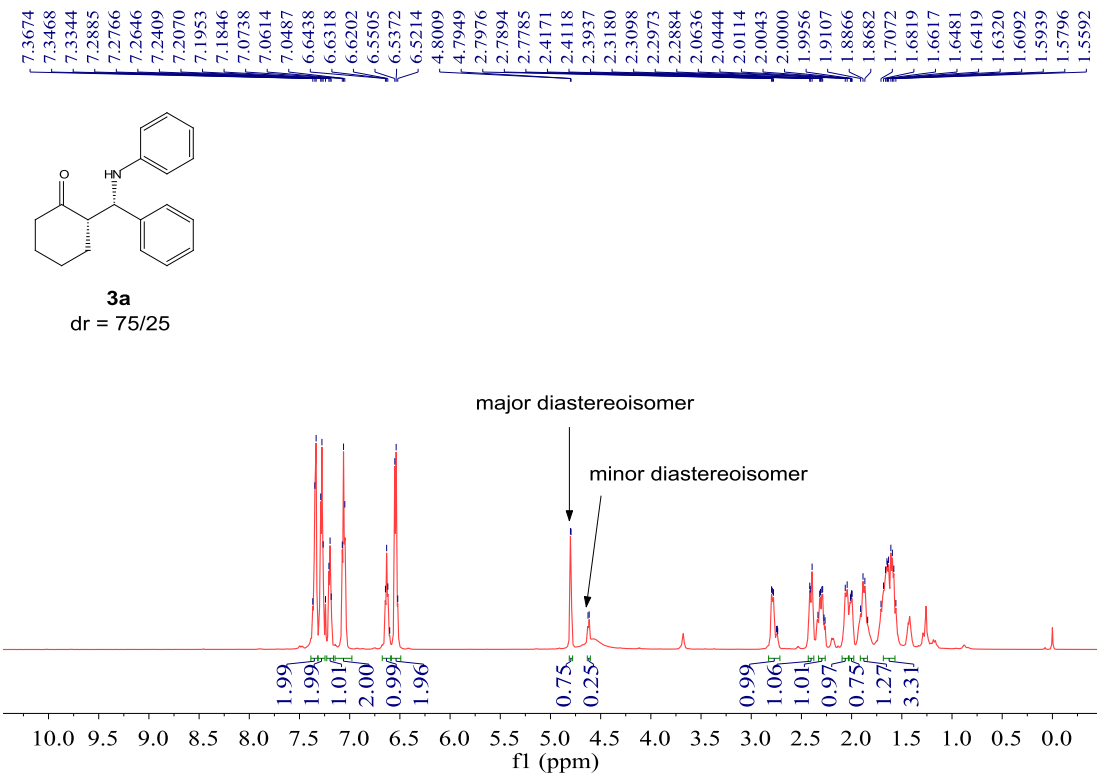
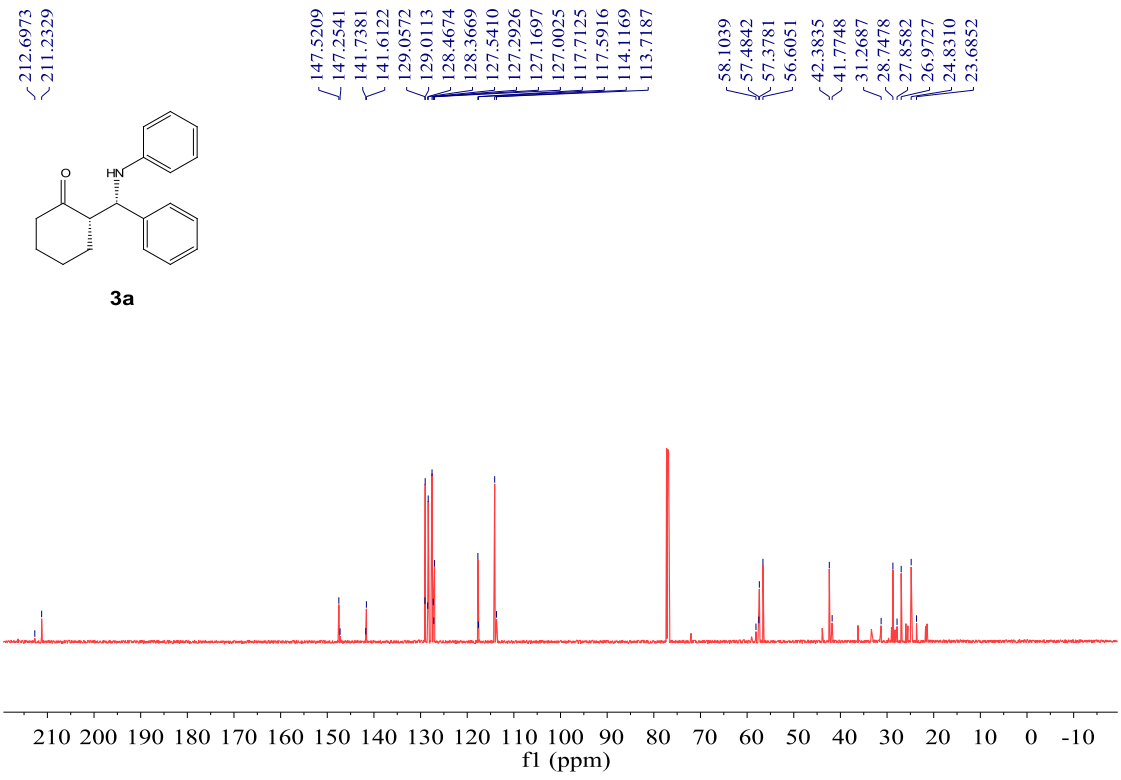
13. NMR spectra

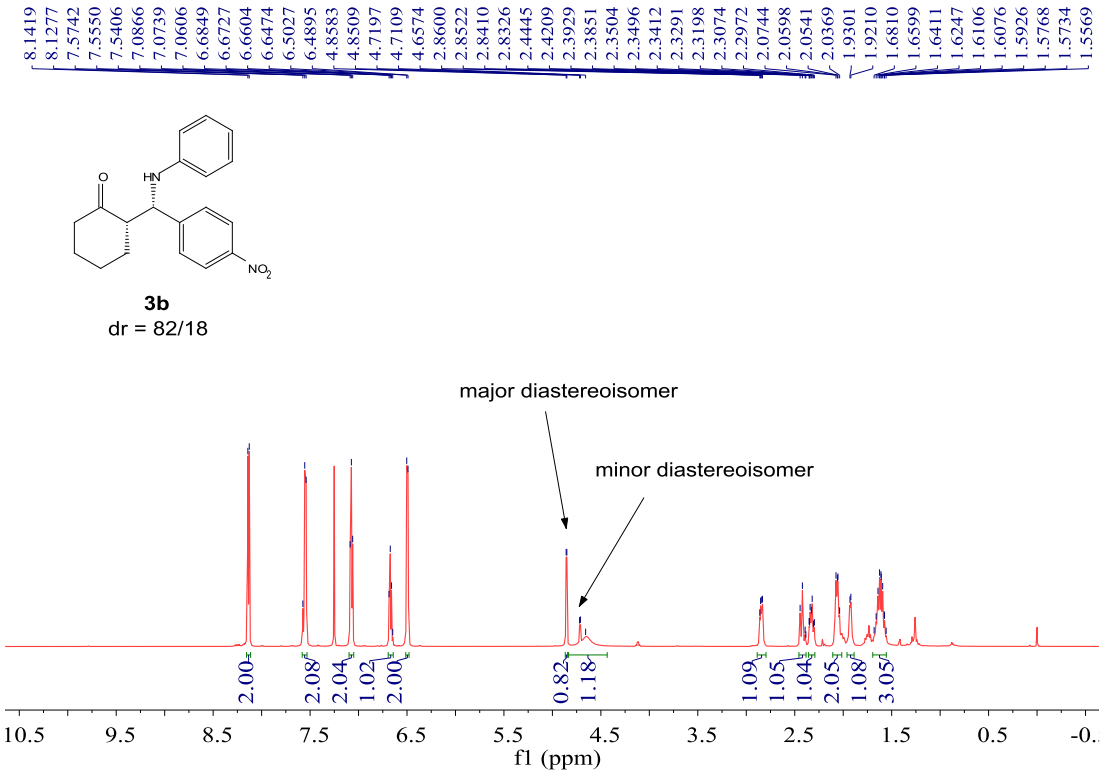
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3a**



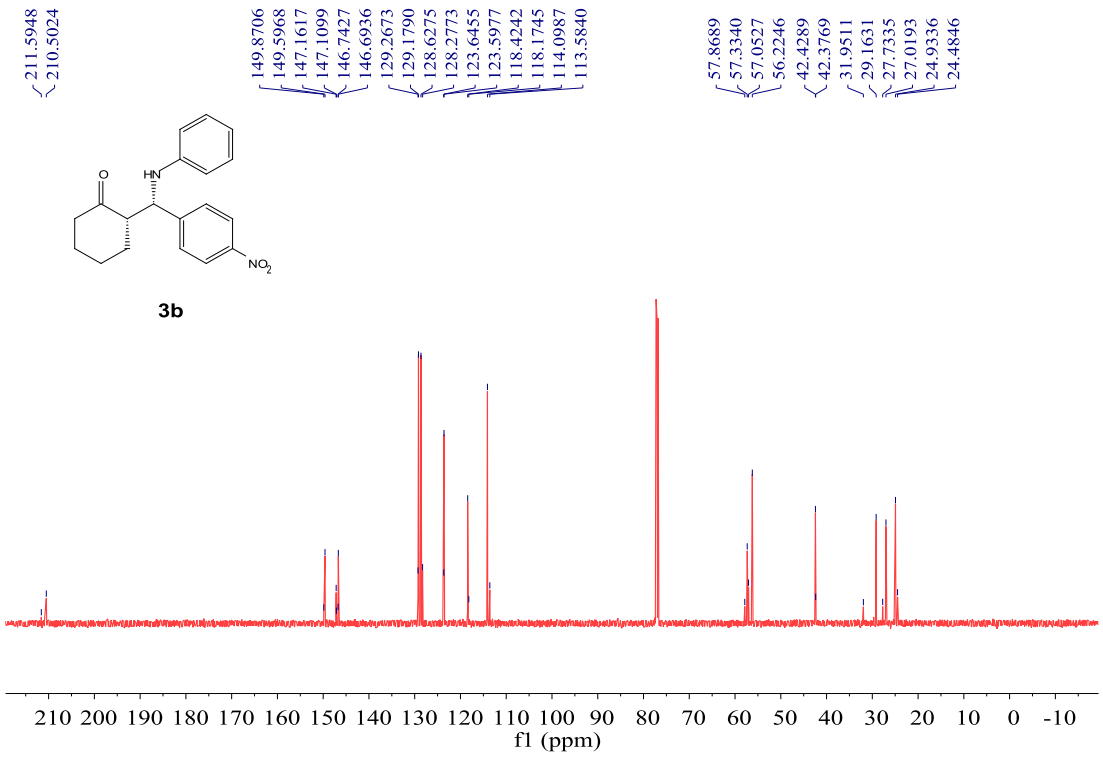
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3a**



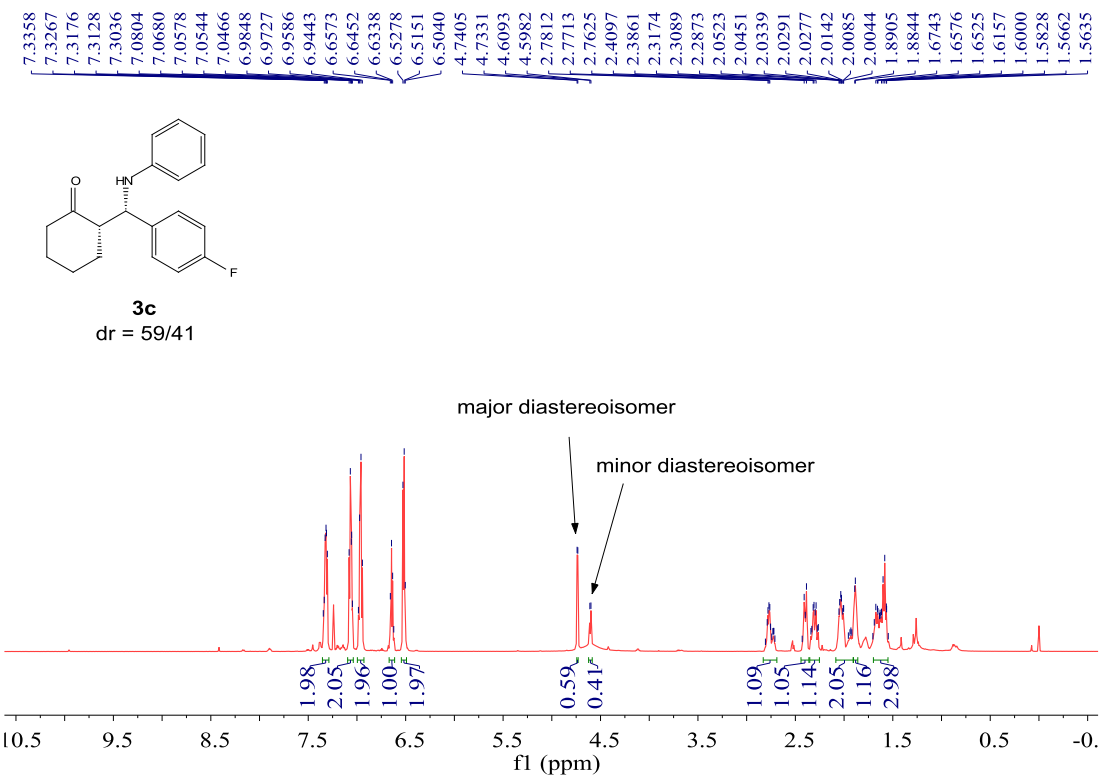
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3b**



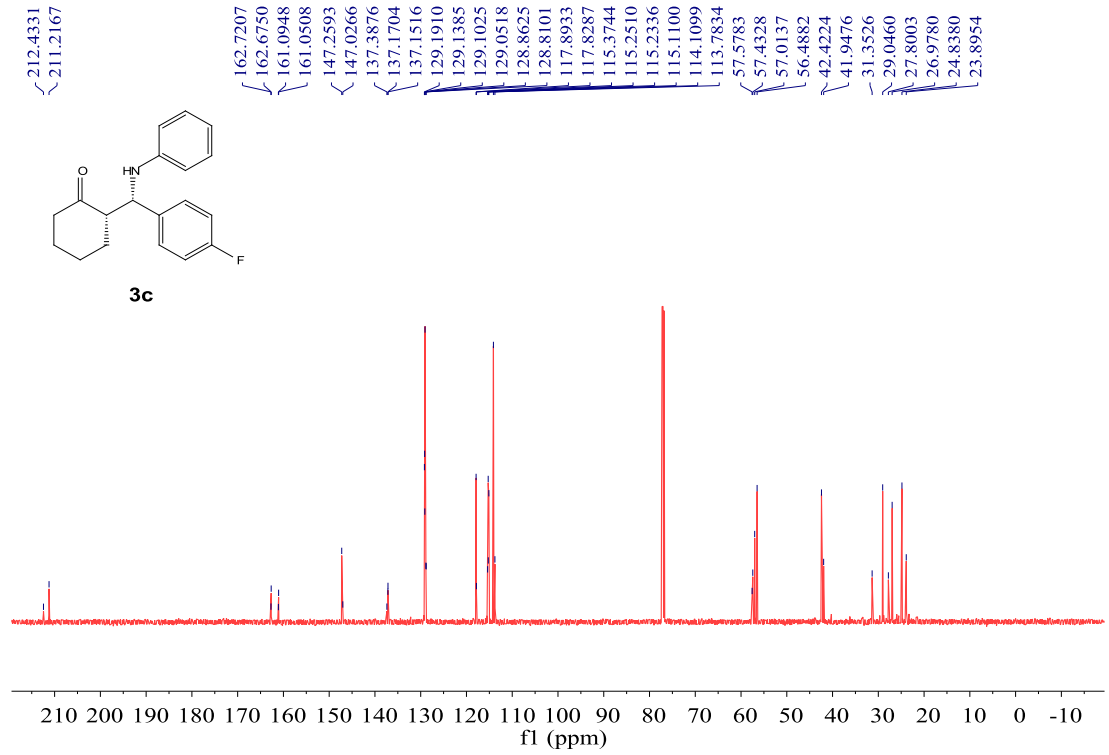
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3b**



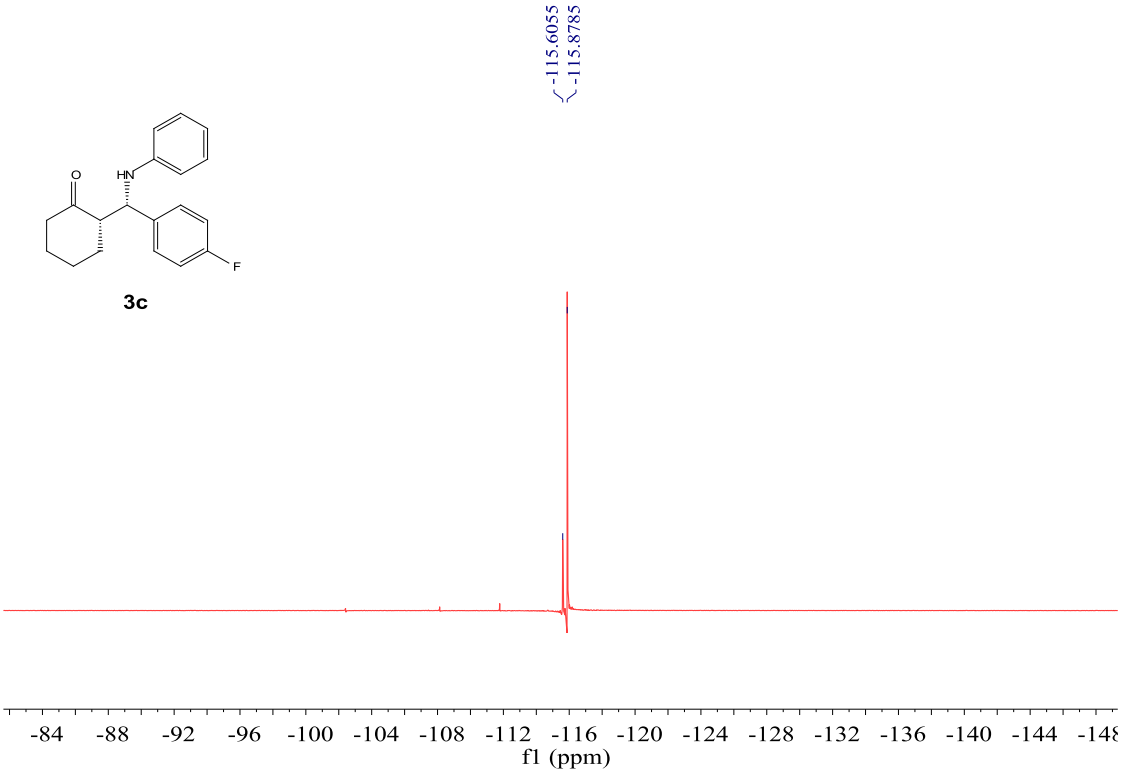
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3c**



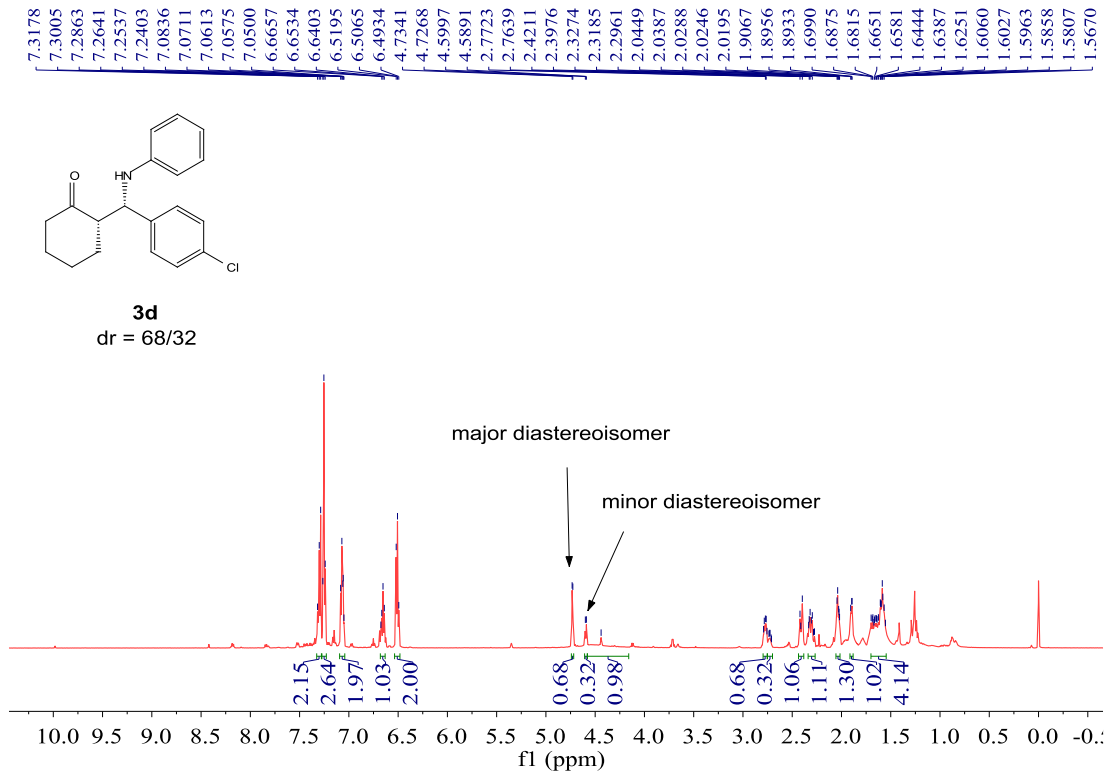
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3c**



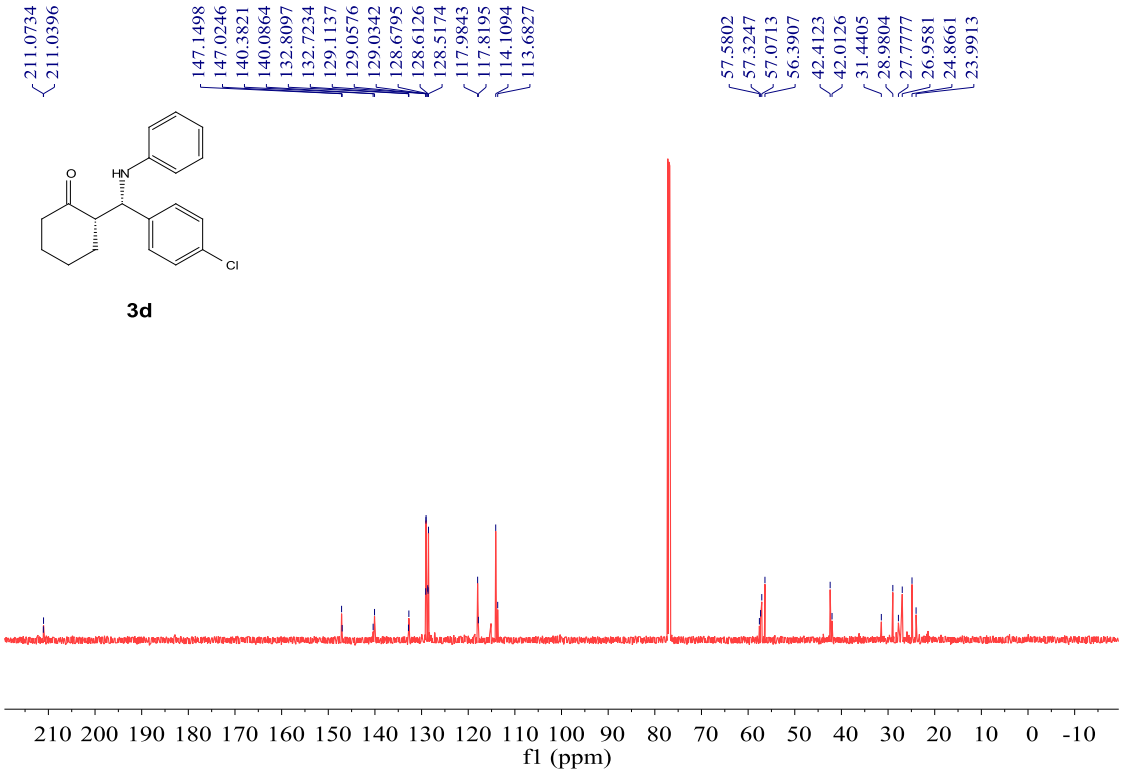
^{19}F NMR Spectrum (565 MHz, $CDCl_3$) of **3c**



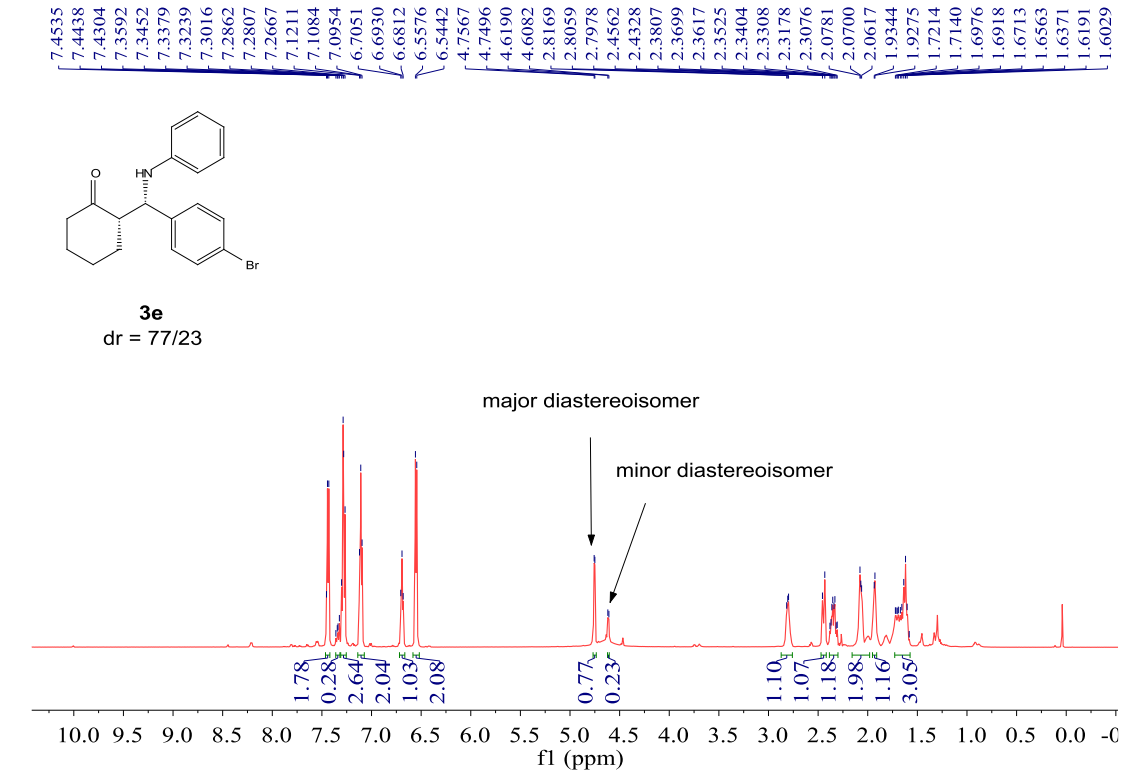
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3d**



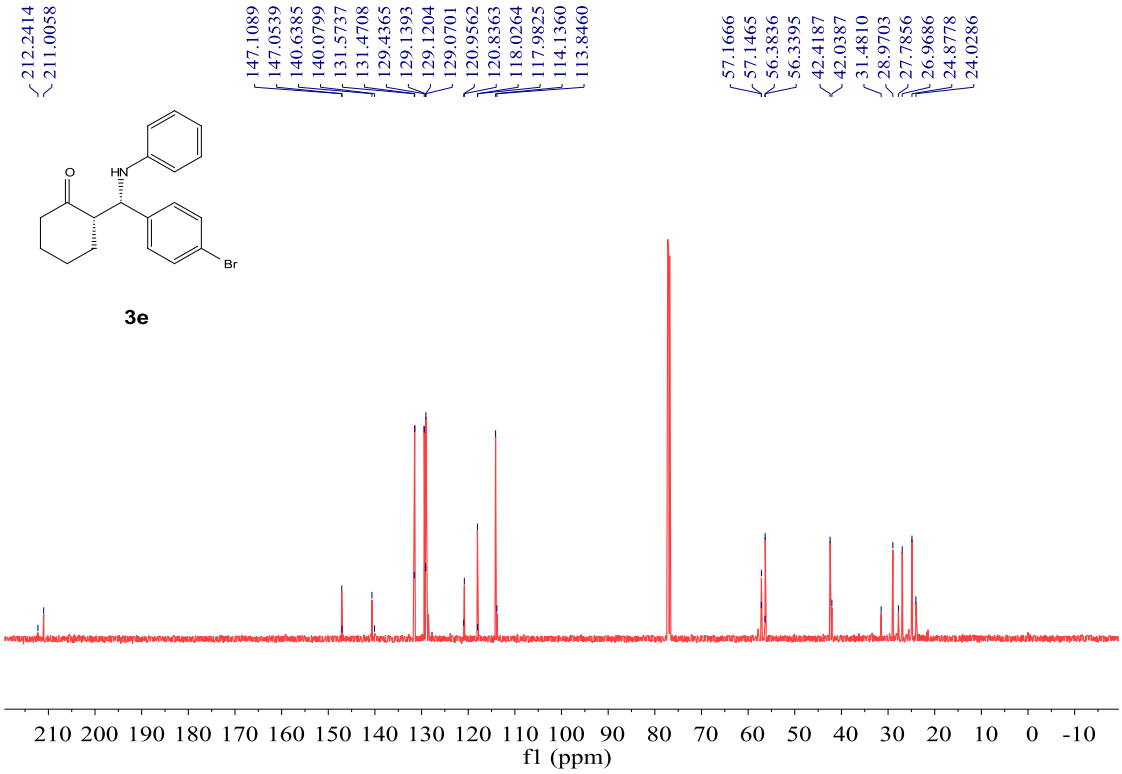
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3d**



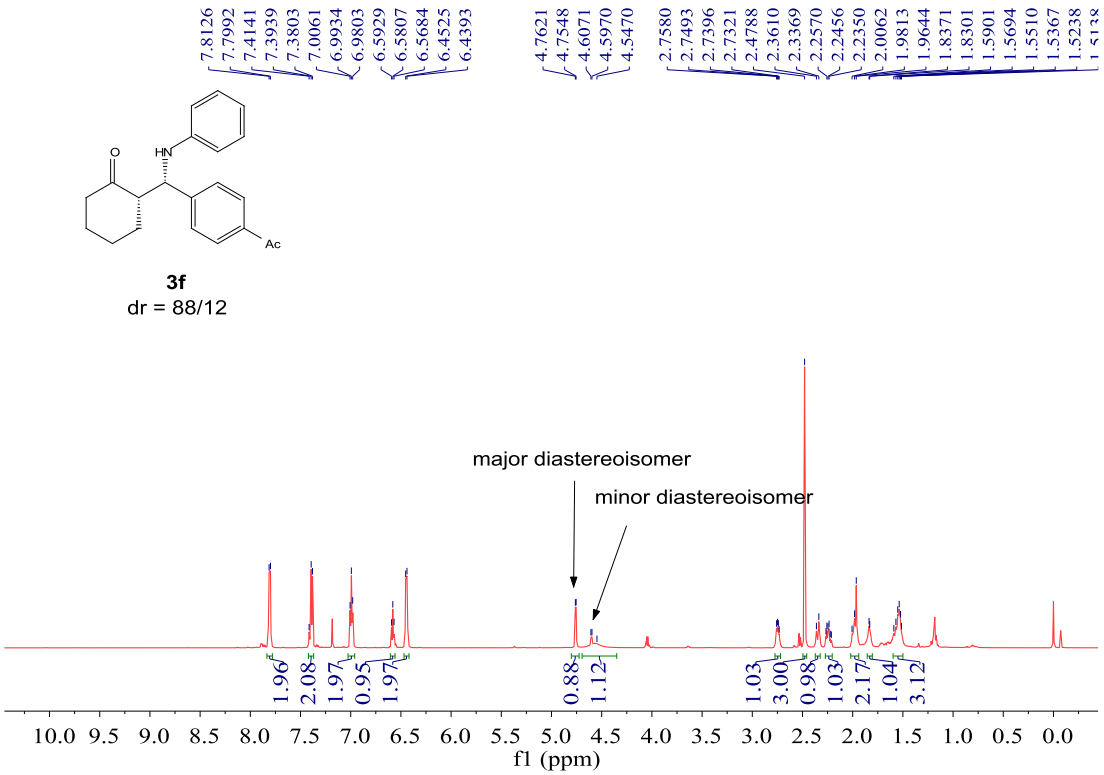
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3e**



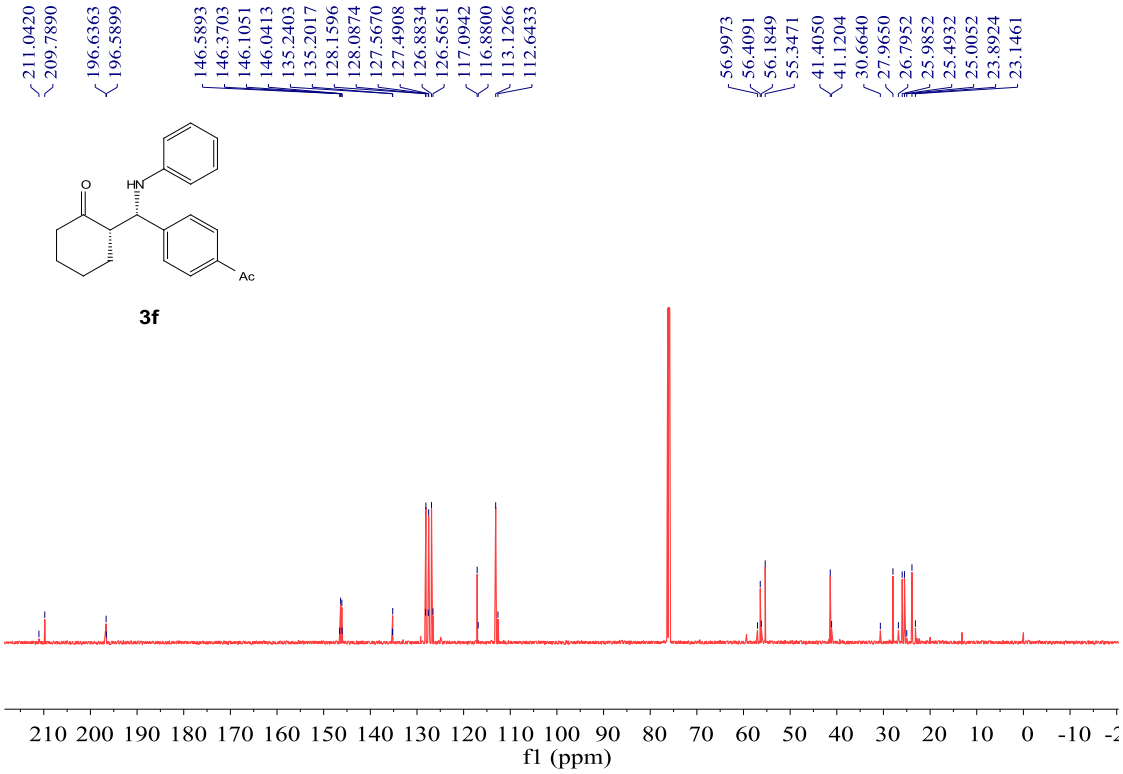
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3e**



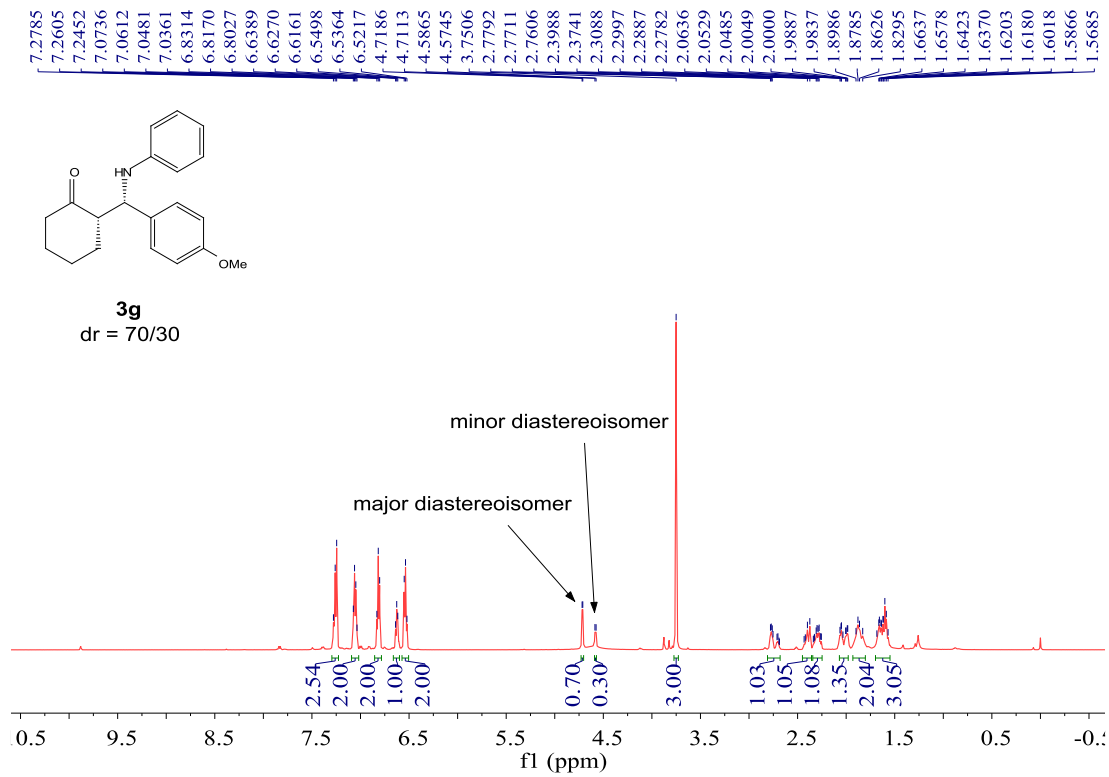
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3f**



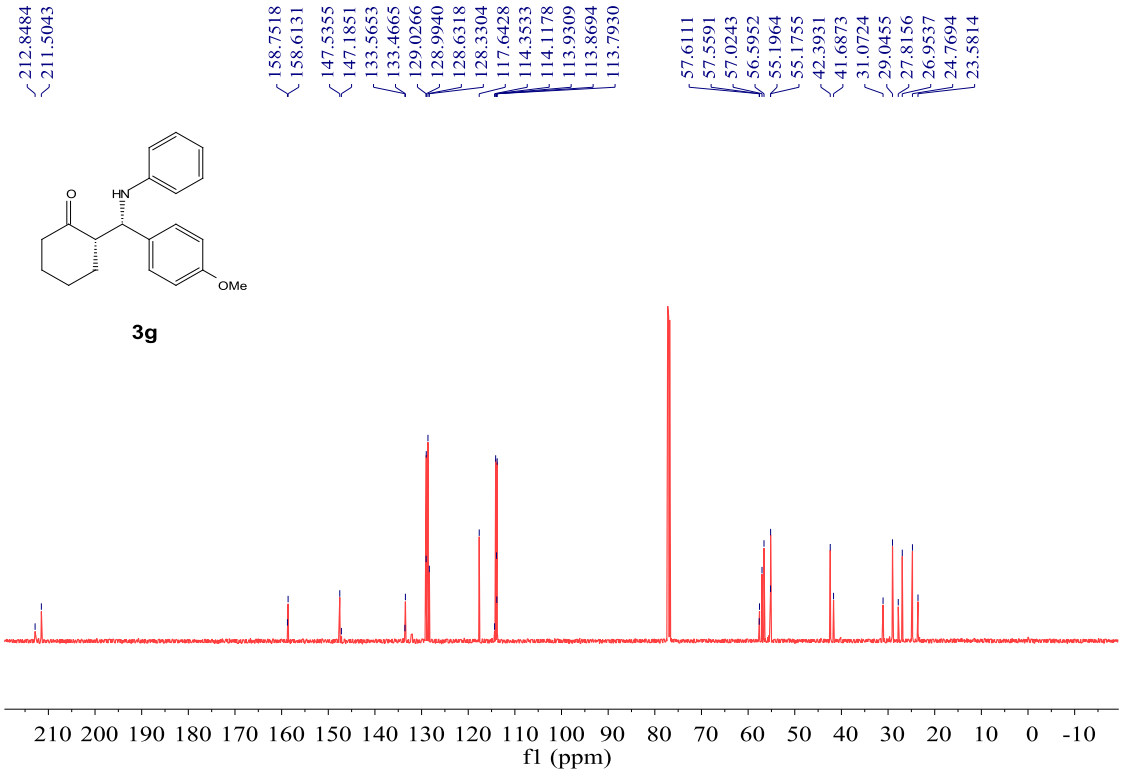
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3f**



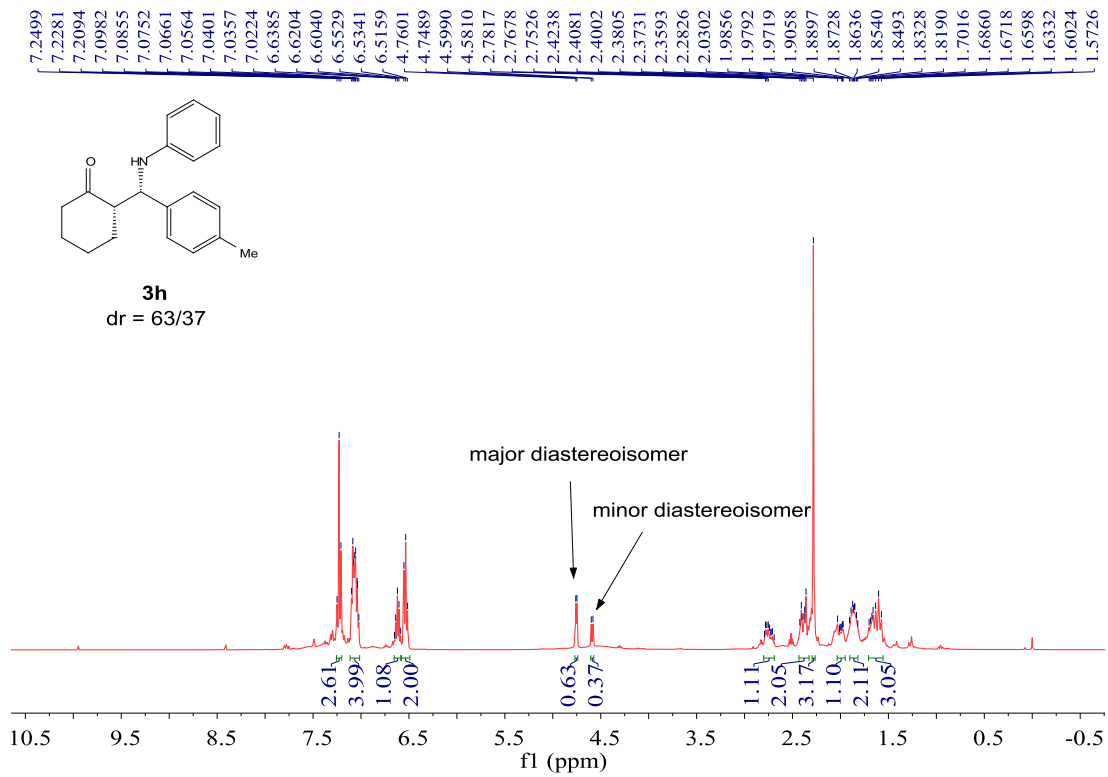
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3g**



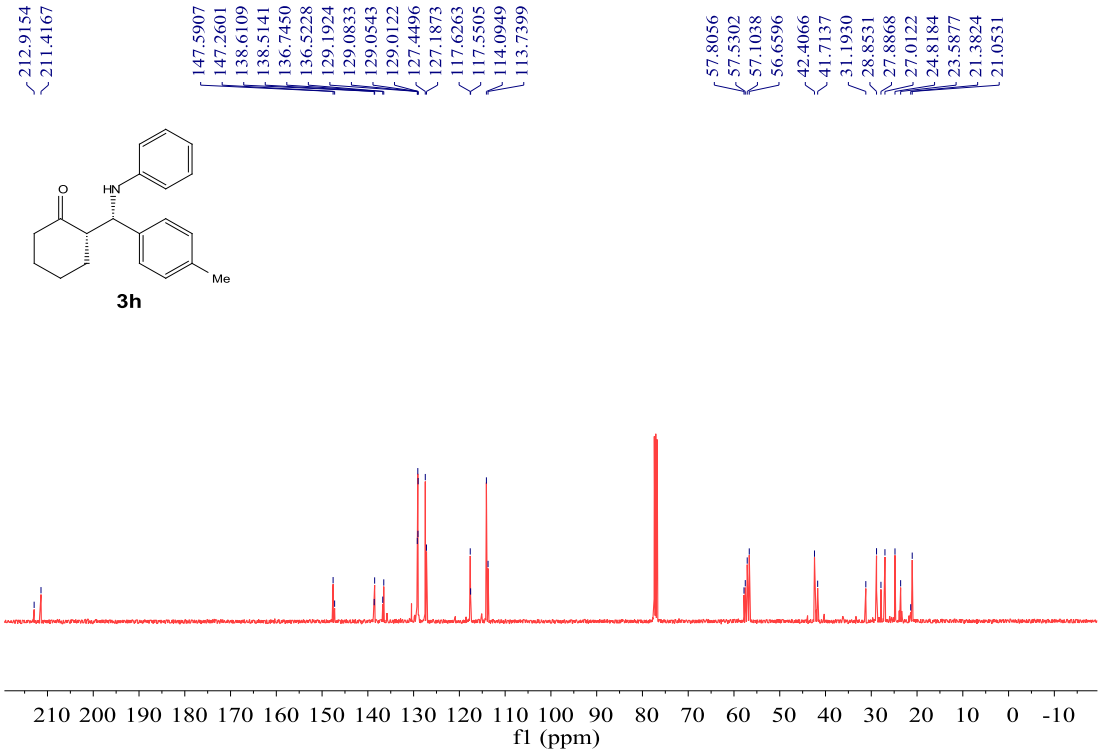
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3g**



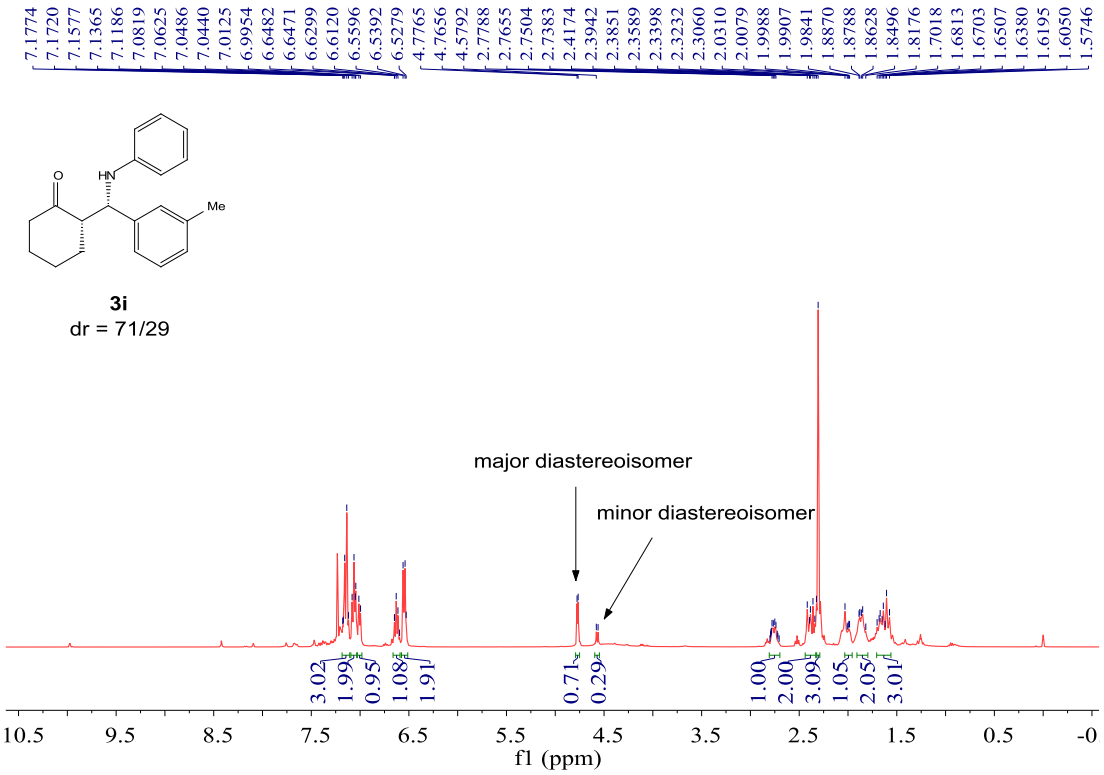
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **3h**



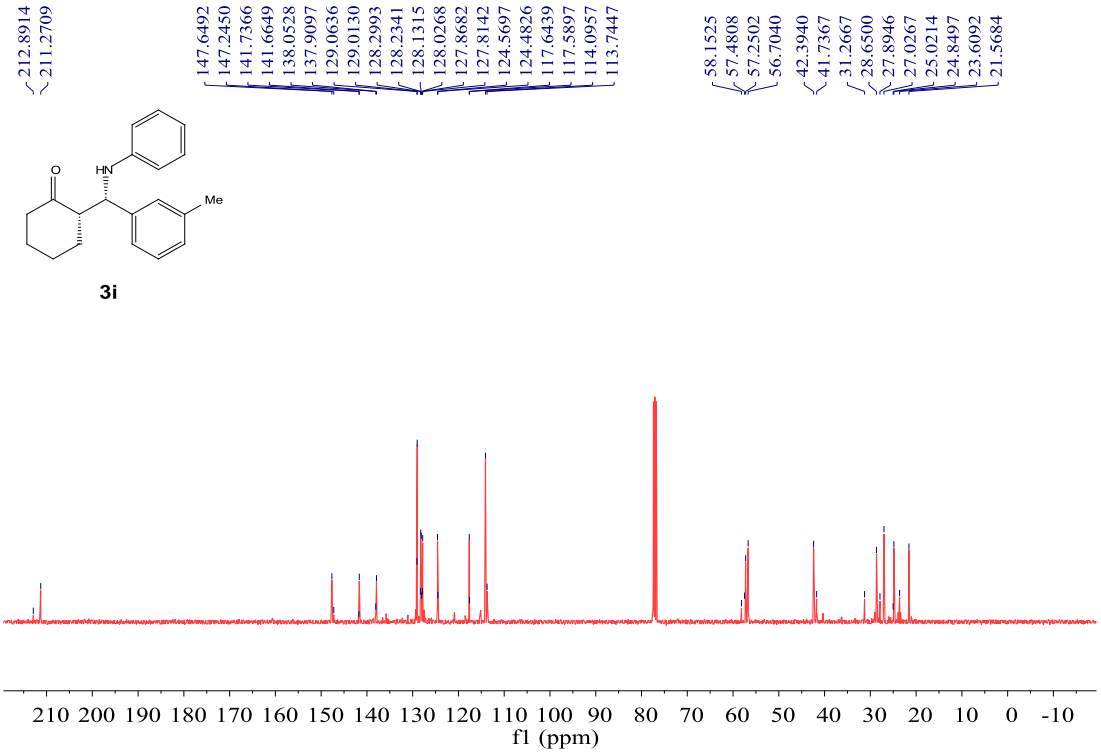
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **3h**



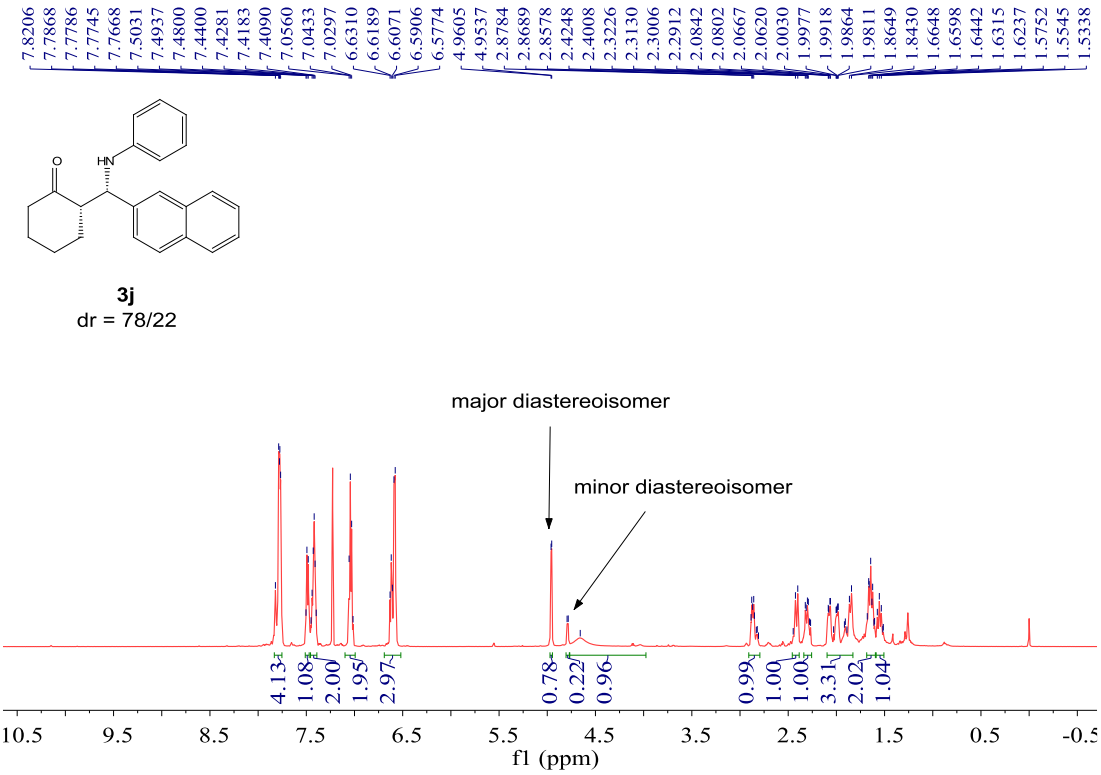
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **3i**



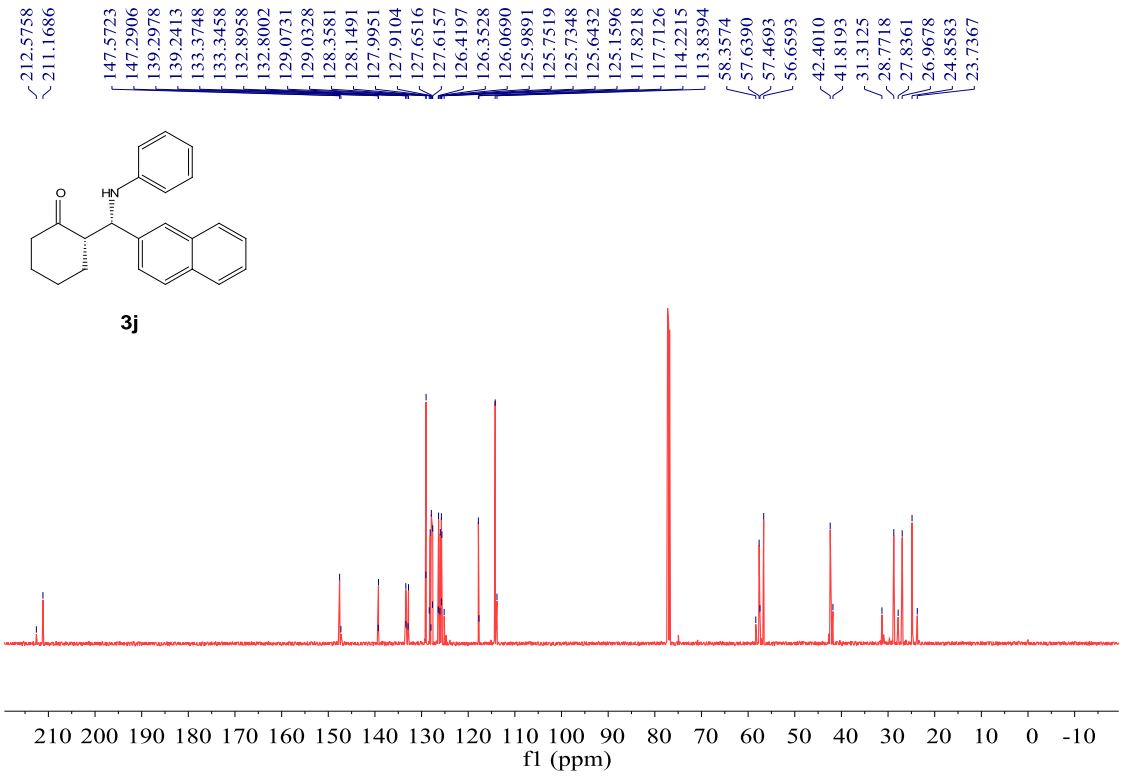
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **3i**



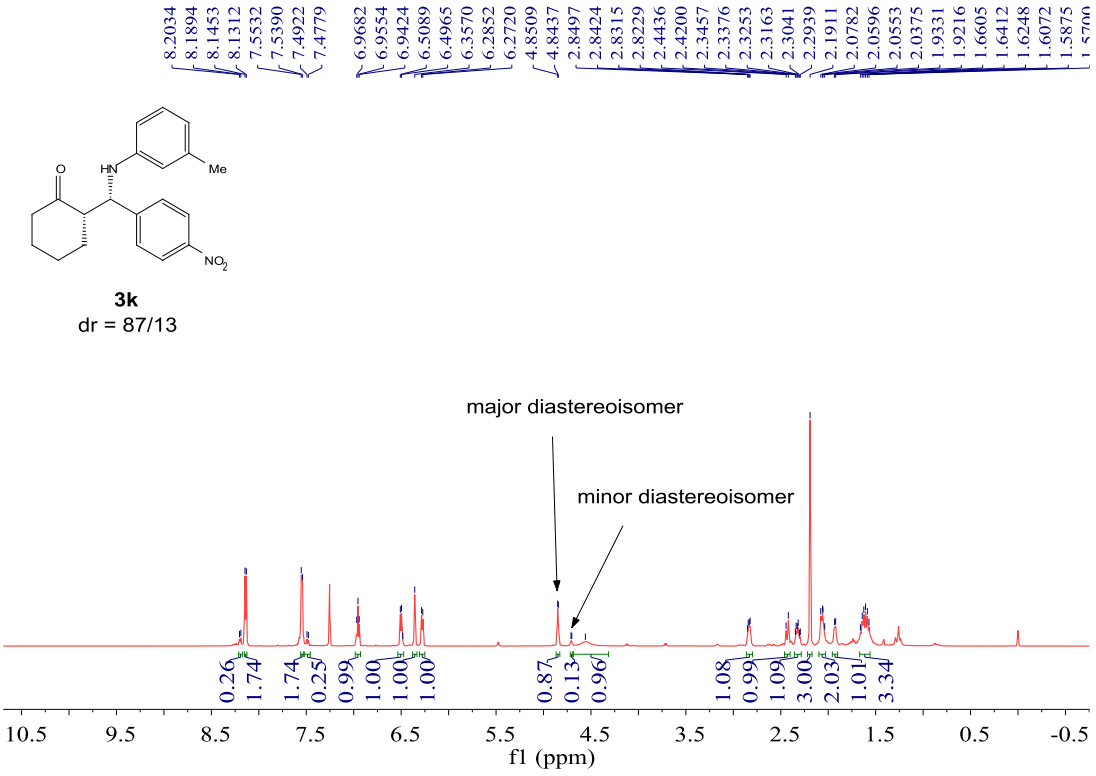
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3j**



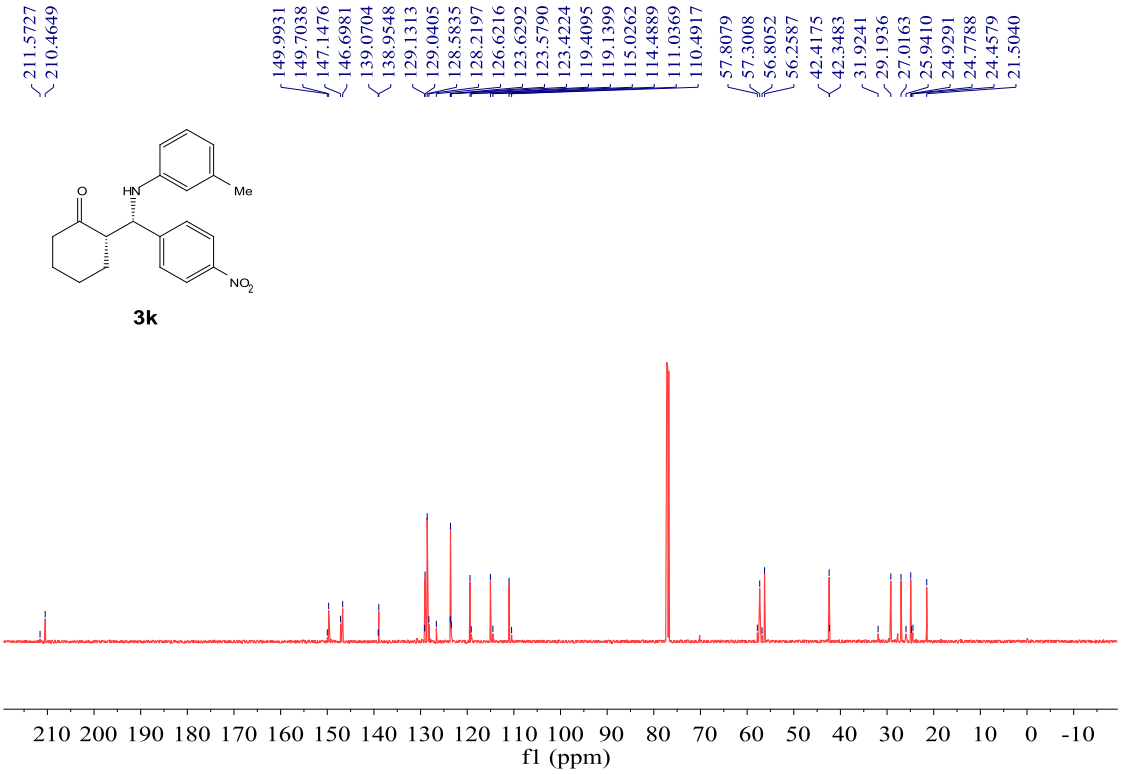
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3j**



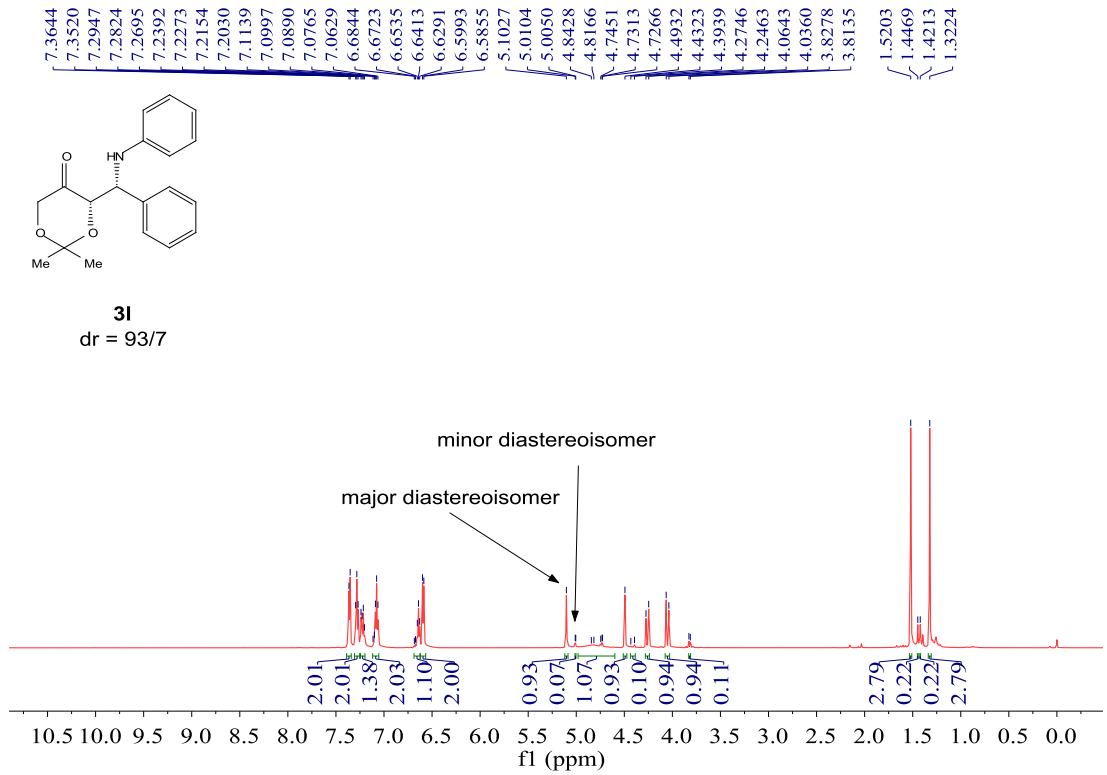
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3k**



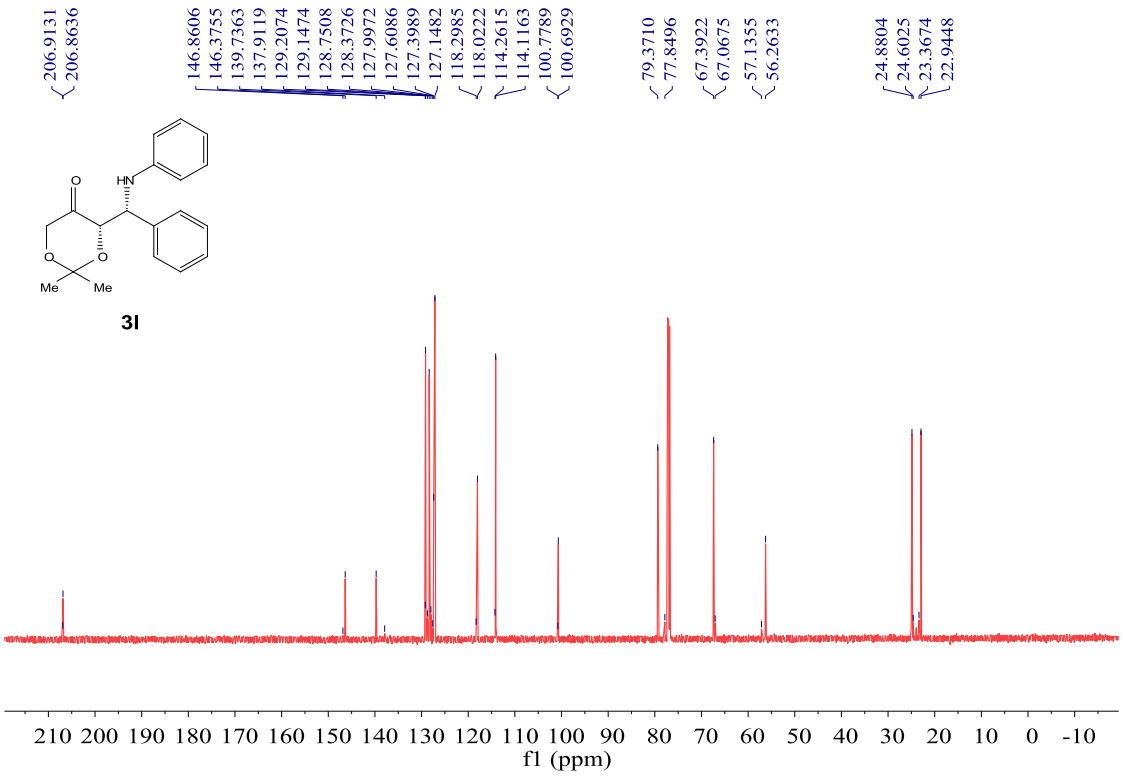
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3k**



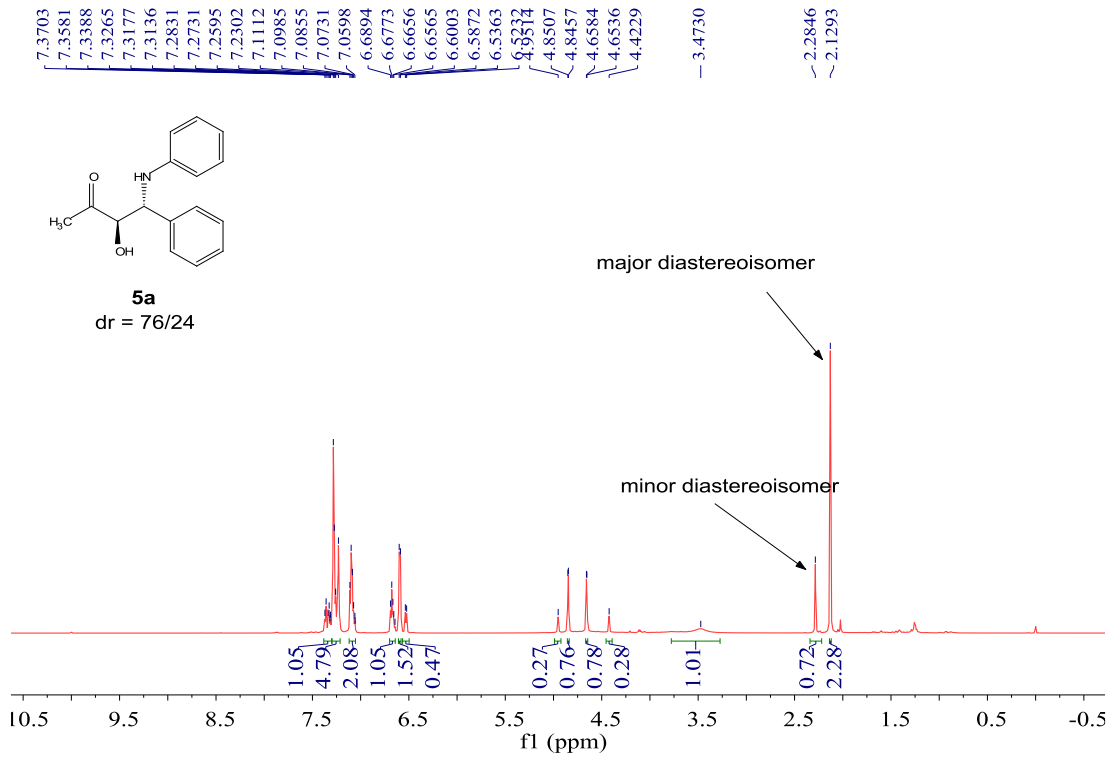
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3l**



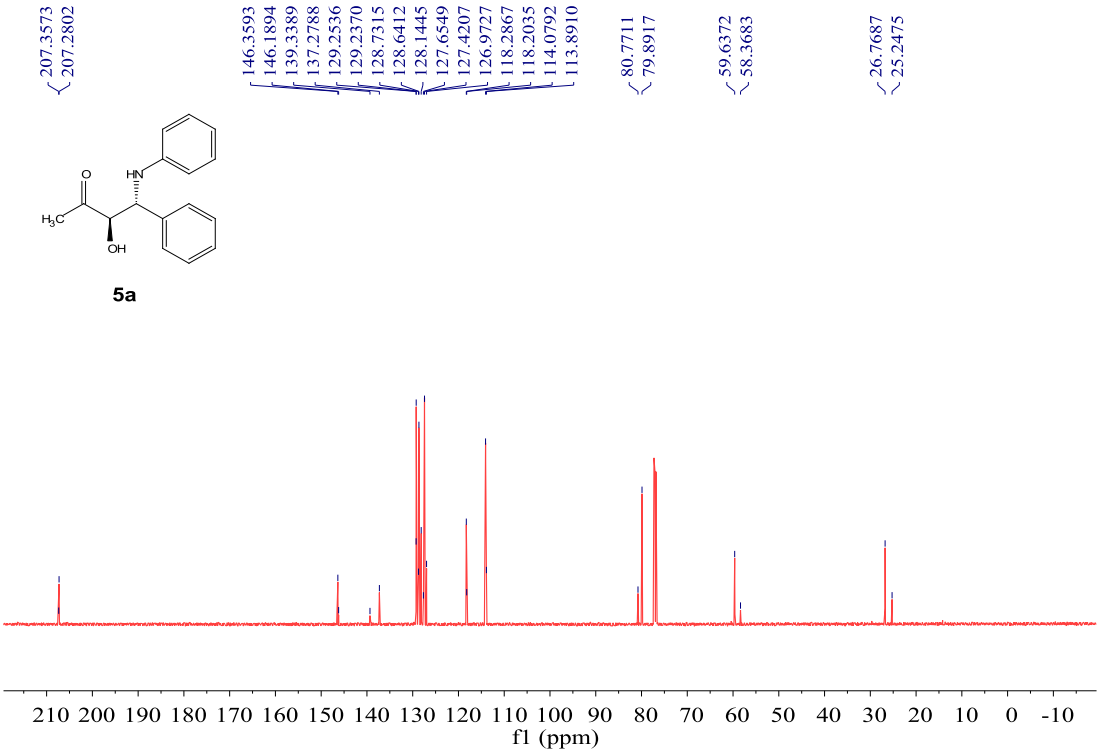
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **3l**



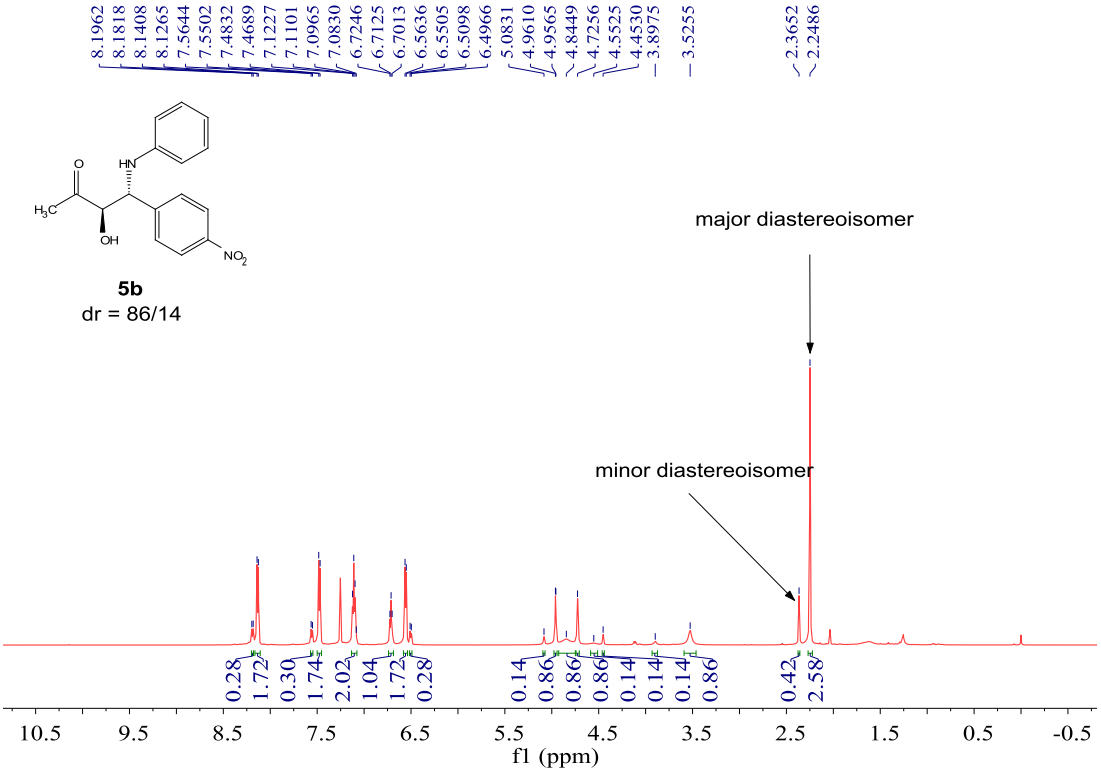
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5a**



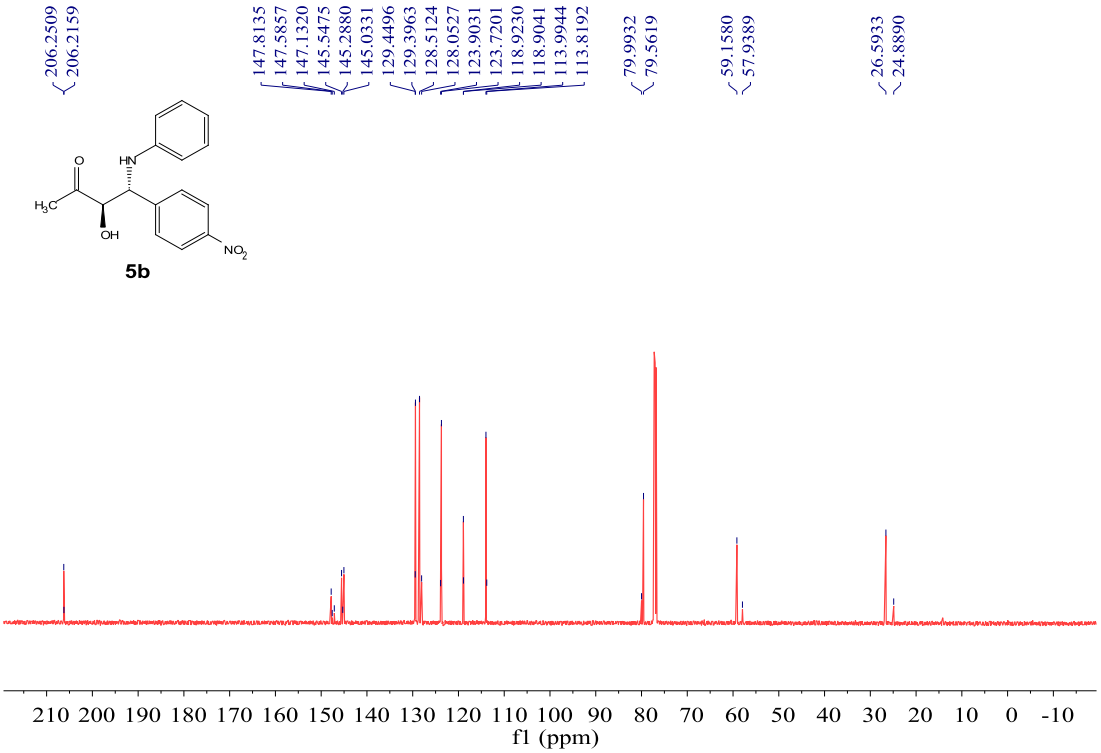
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5a**



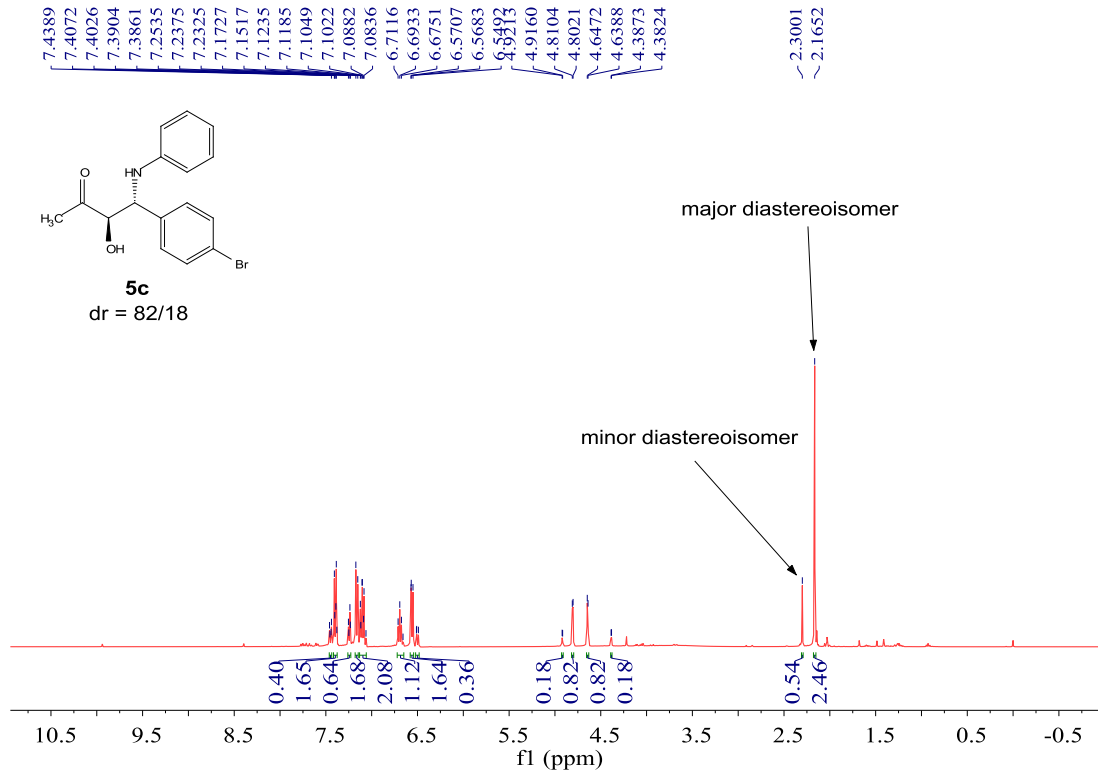
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5b**



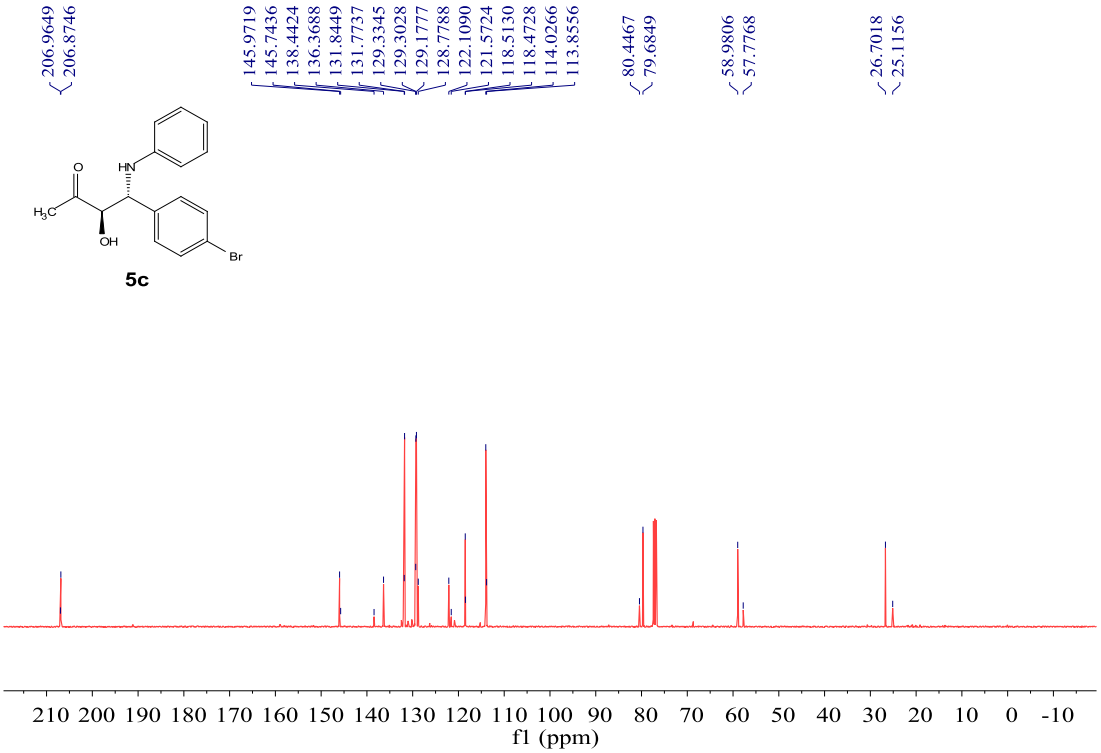
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5b**



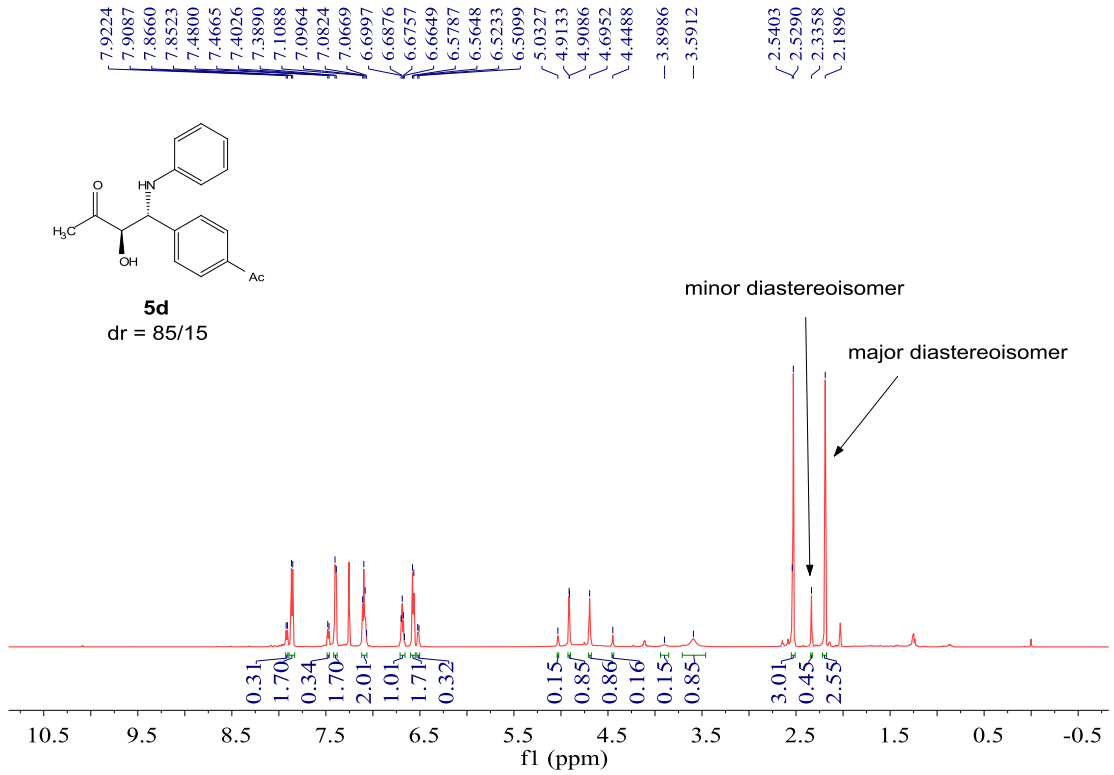
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **5c**



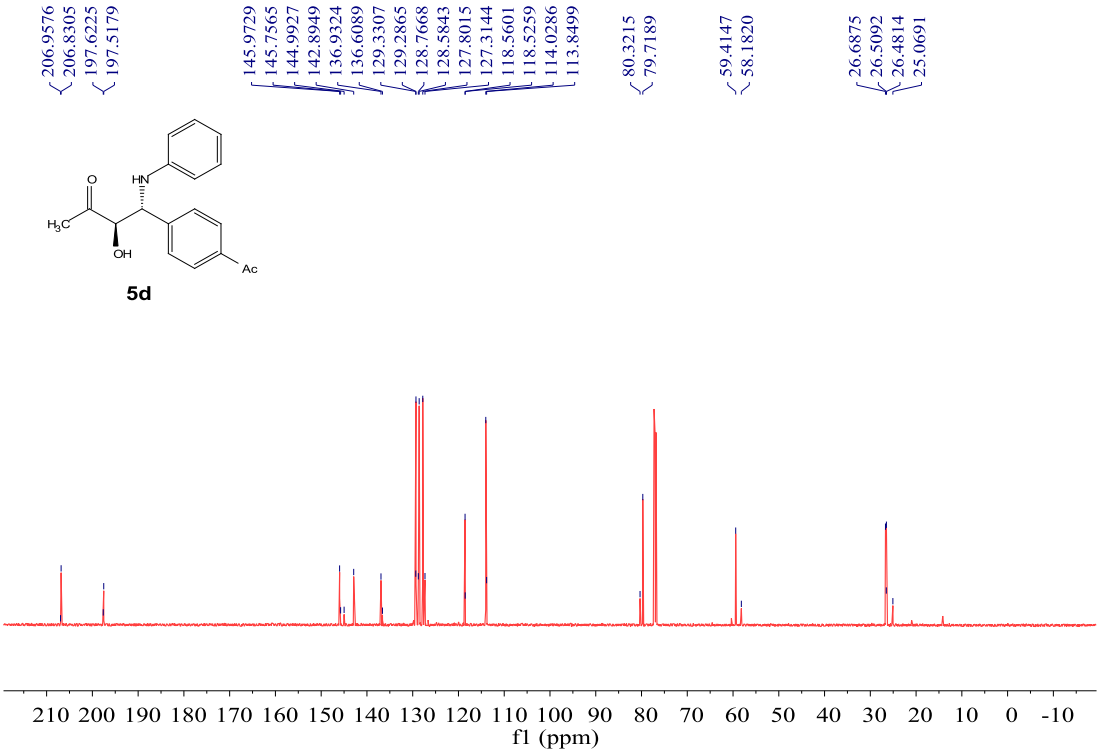
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **5c**



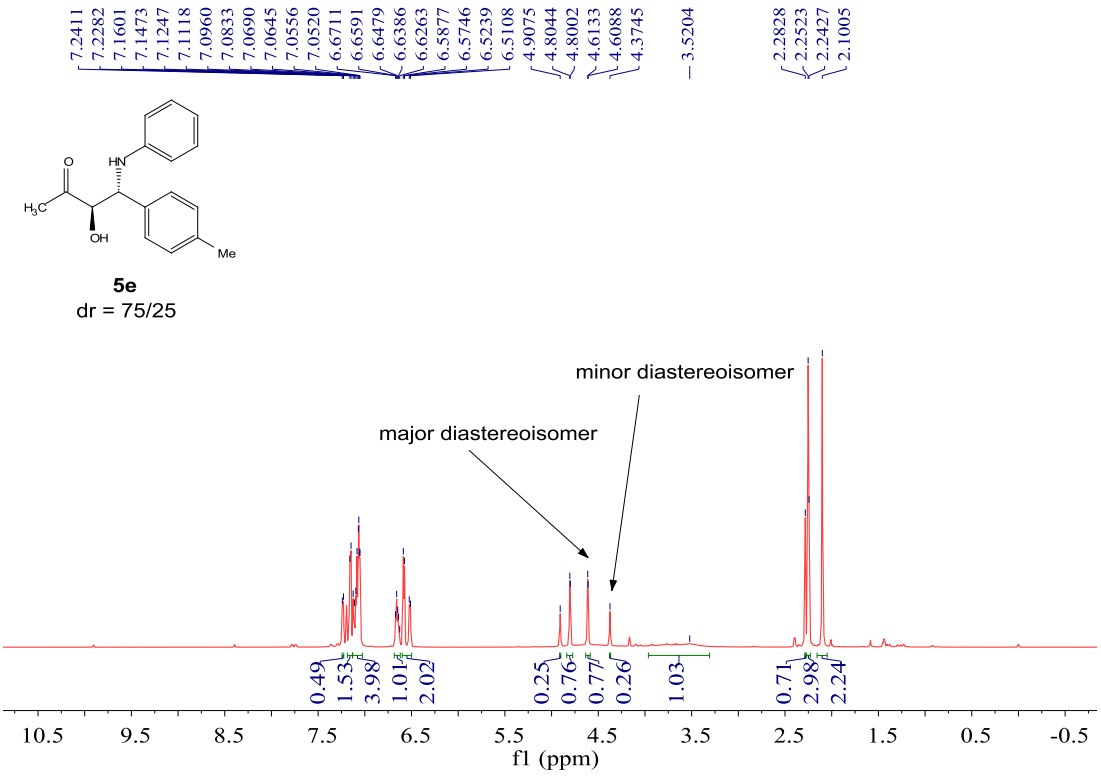
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5d**



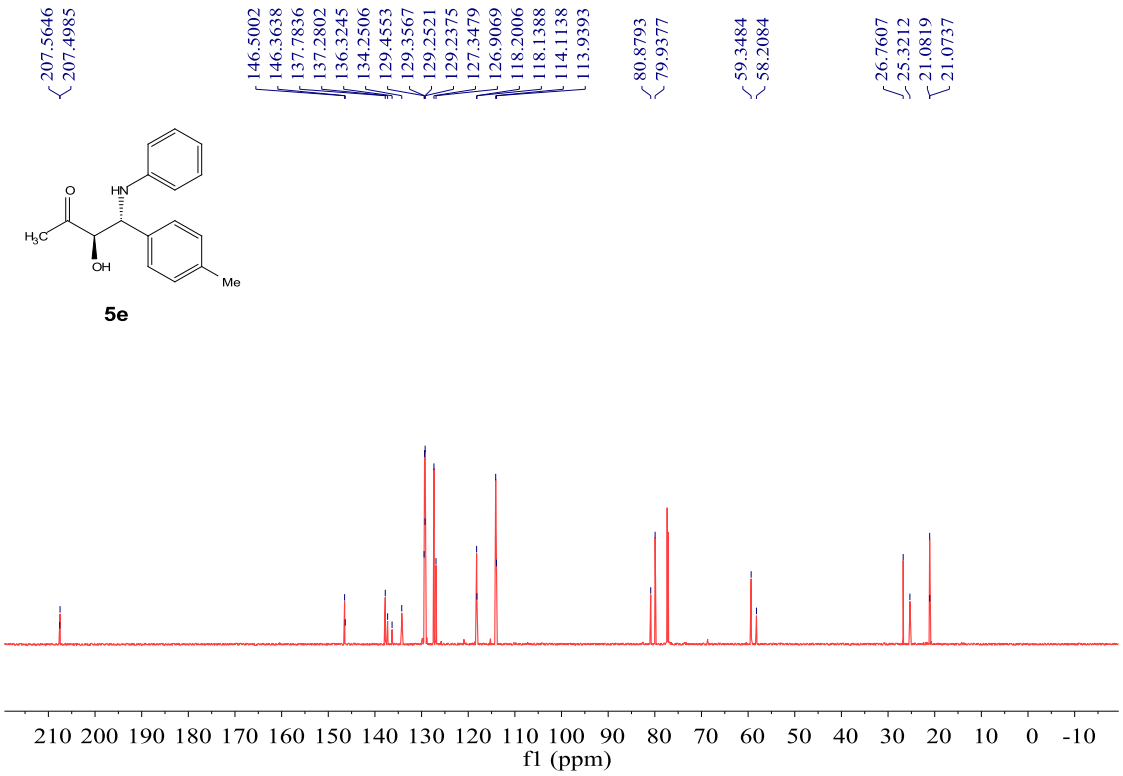
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5d**



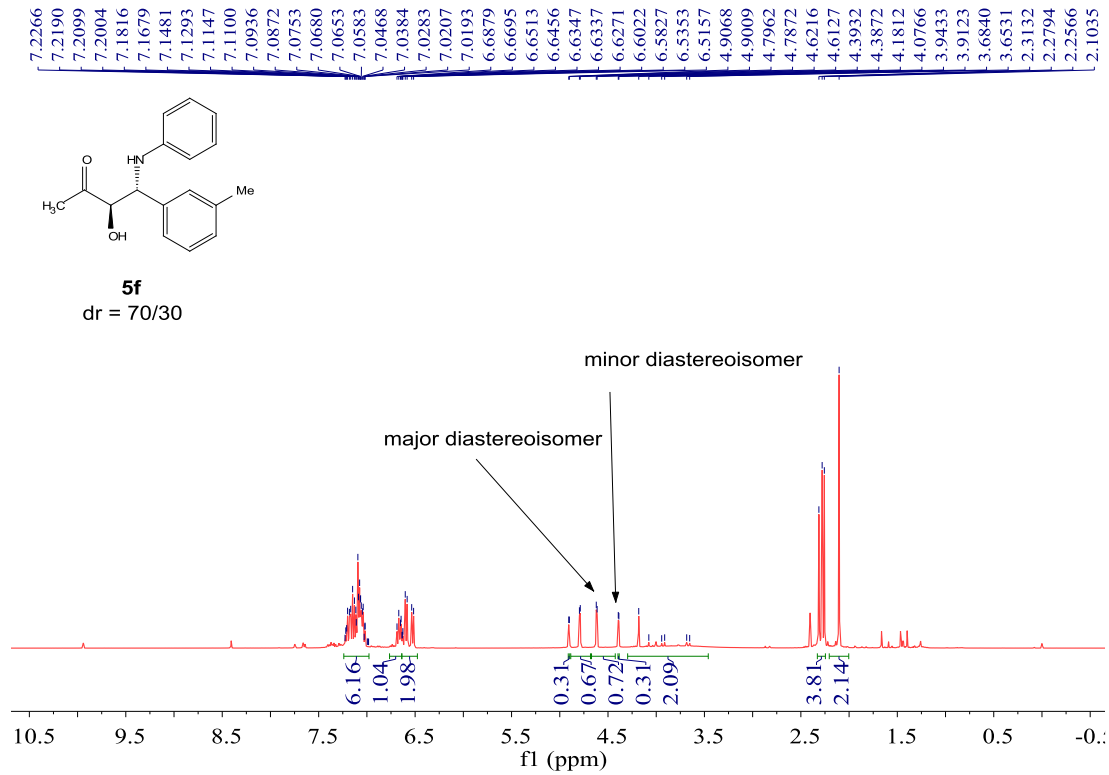
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5e**



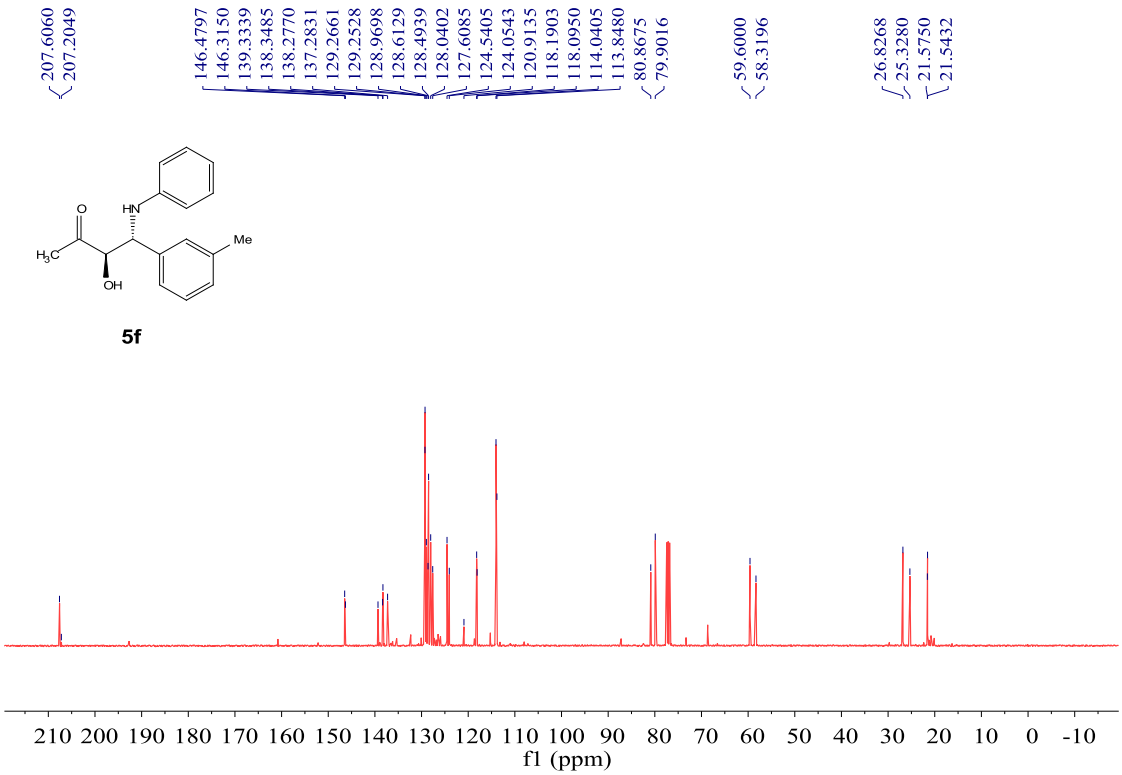
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5e**



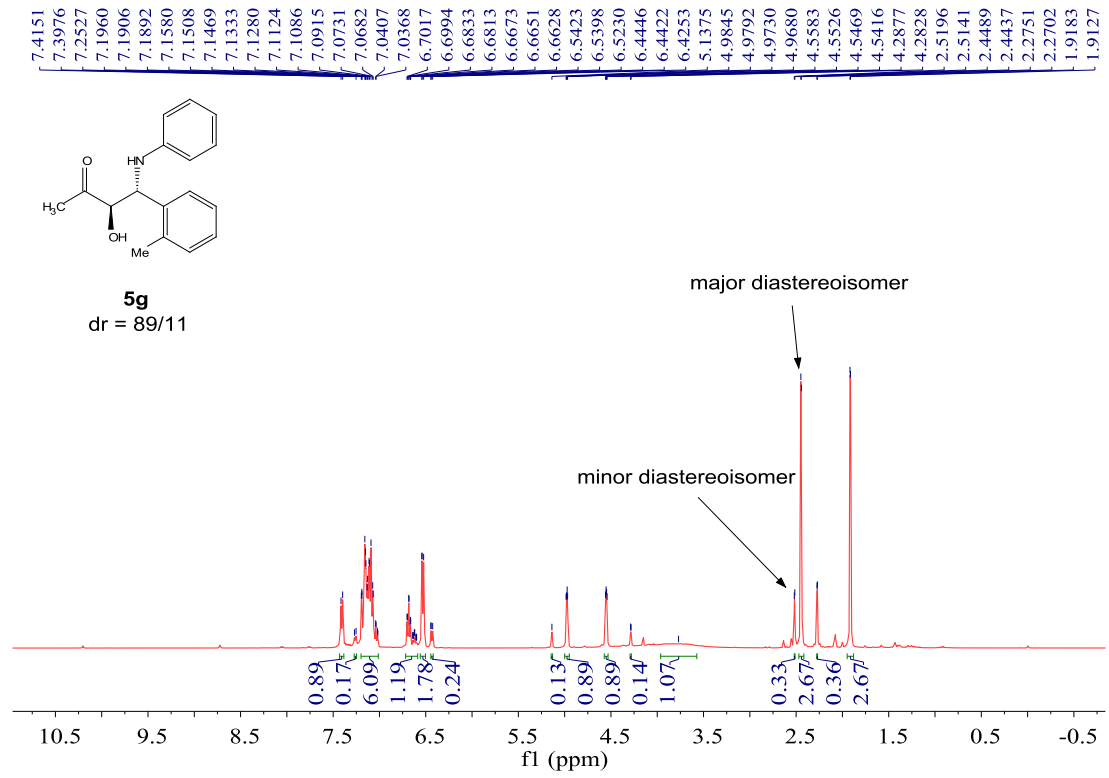
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **5f**



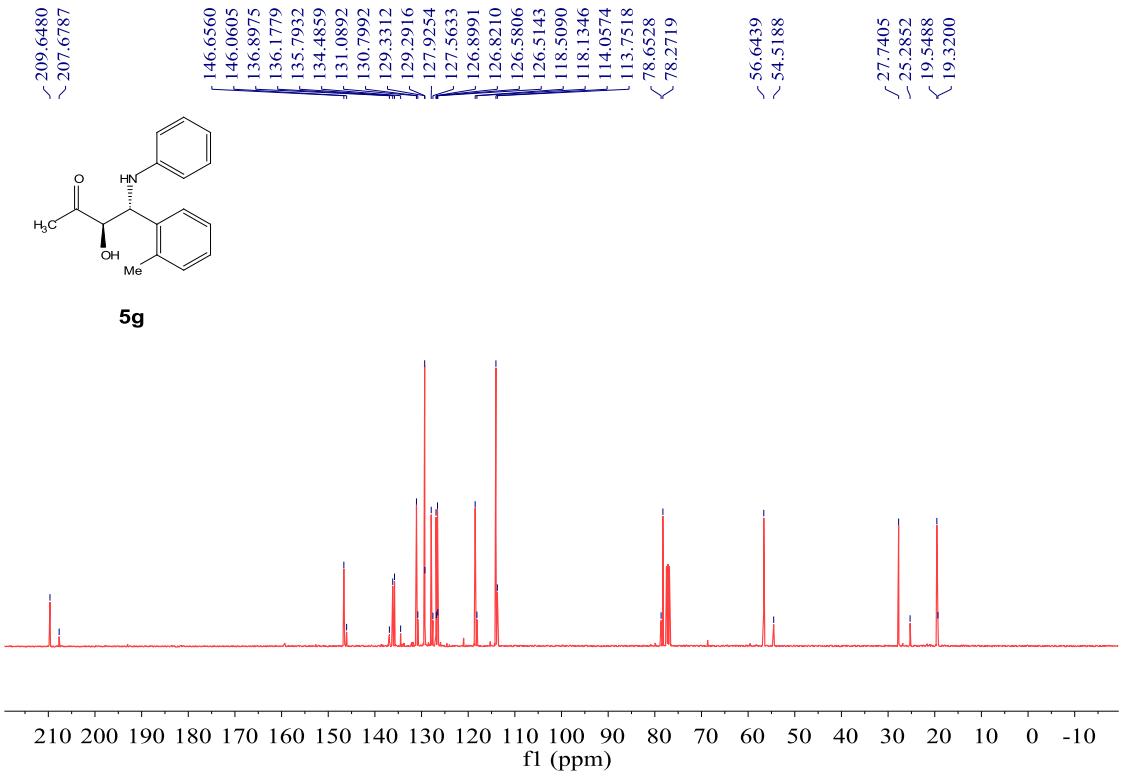
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **5f**



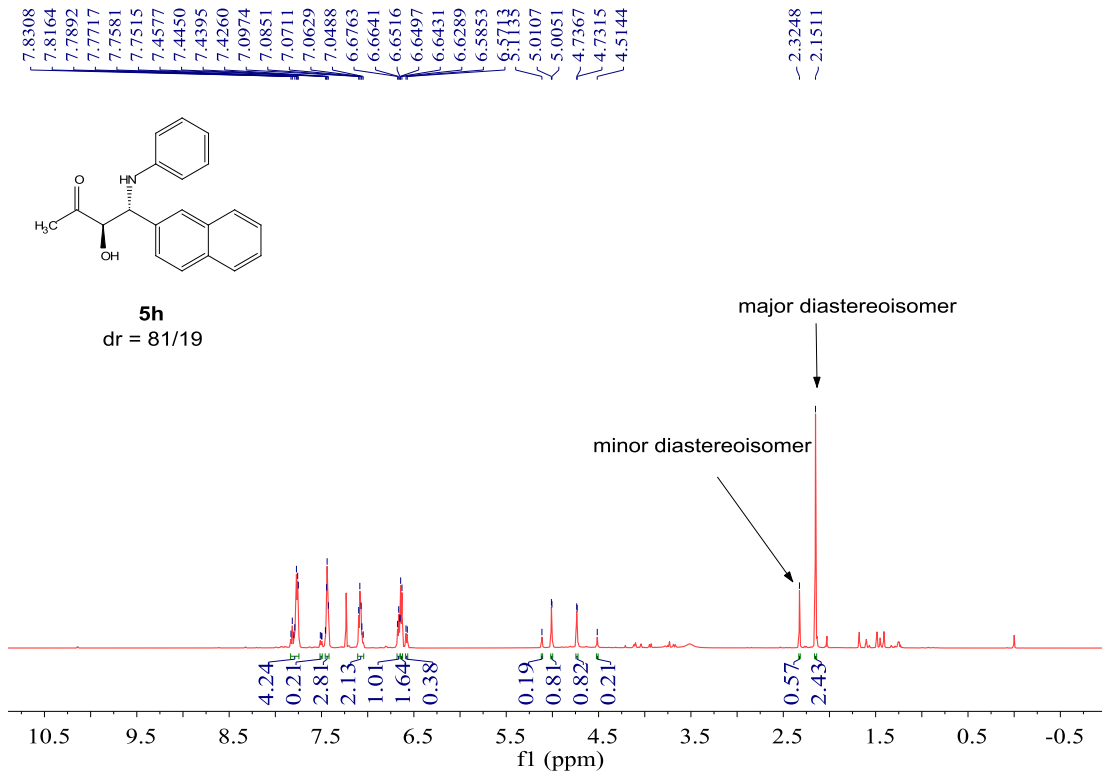
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **5g**



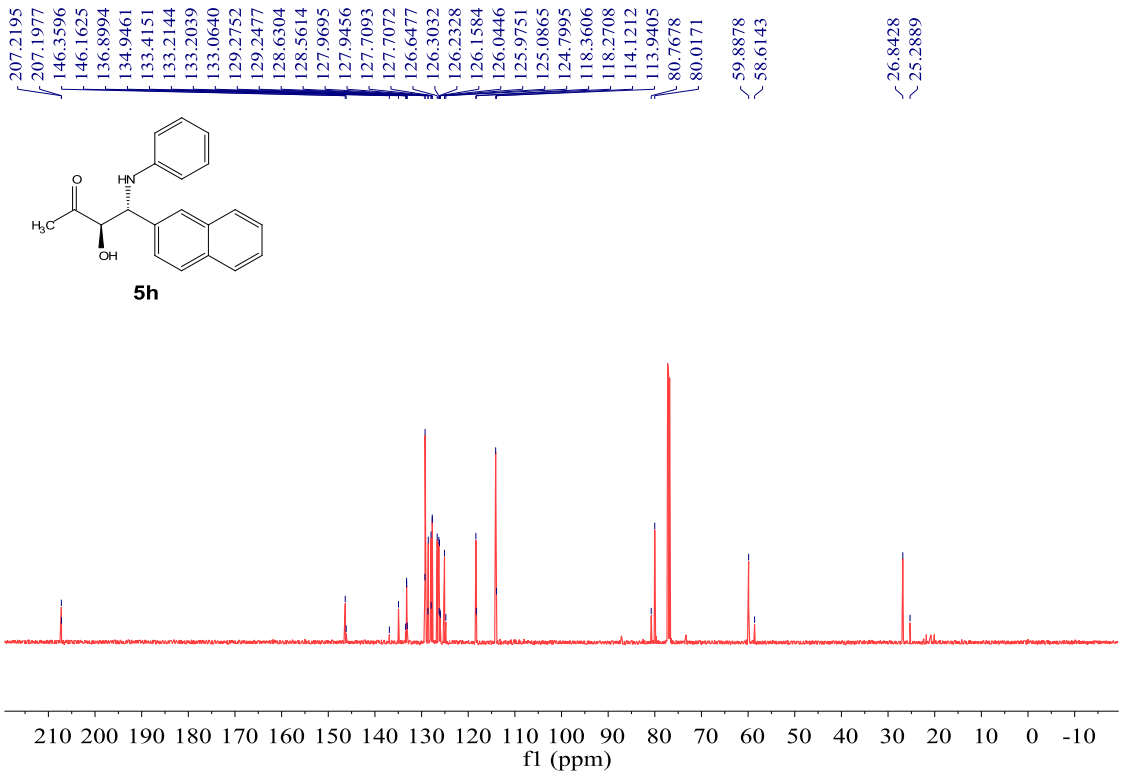
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **5g**



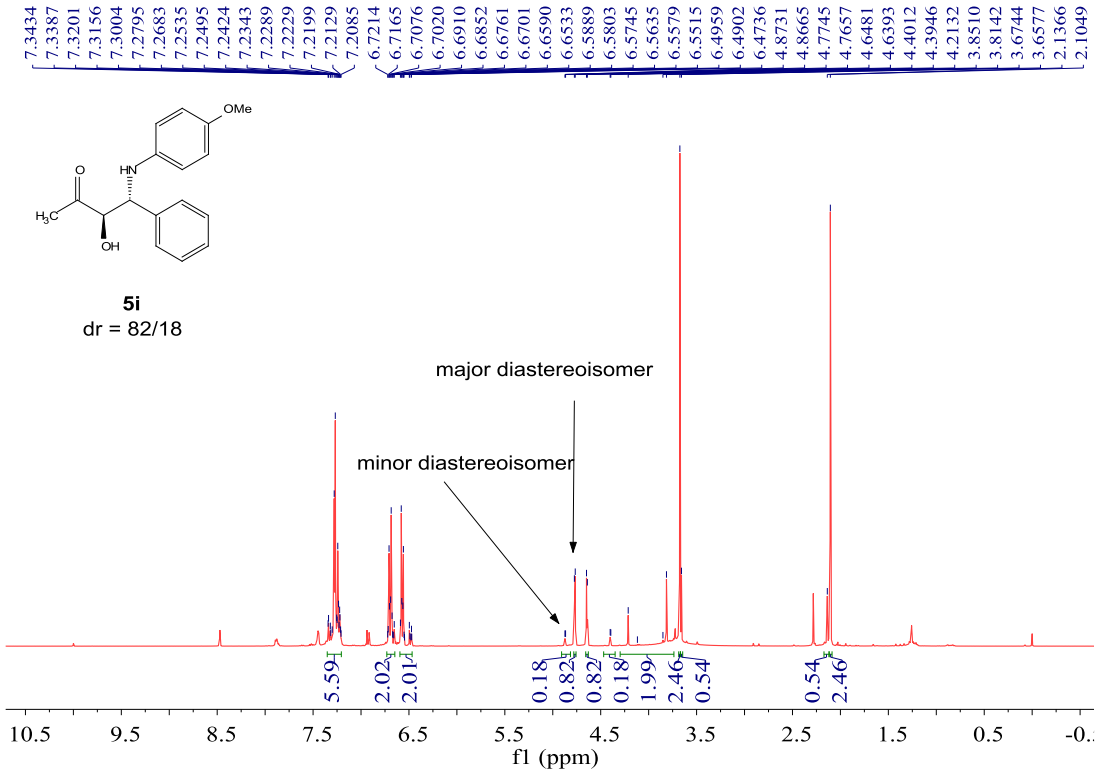
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5h**



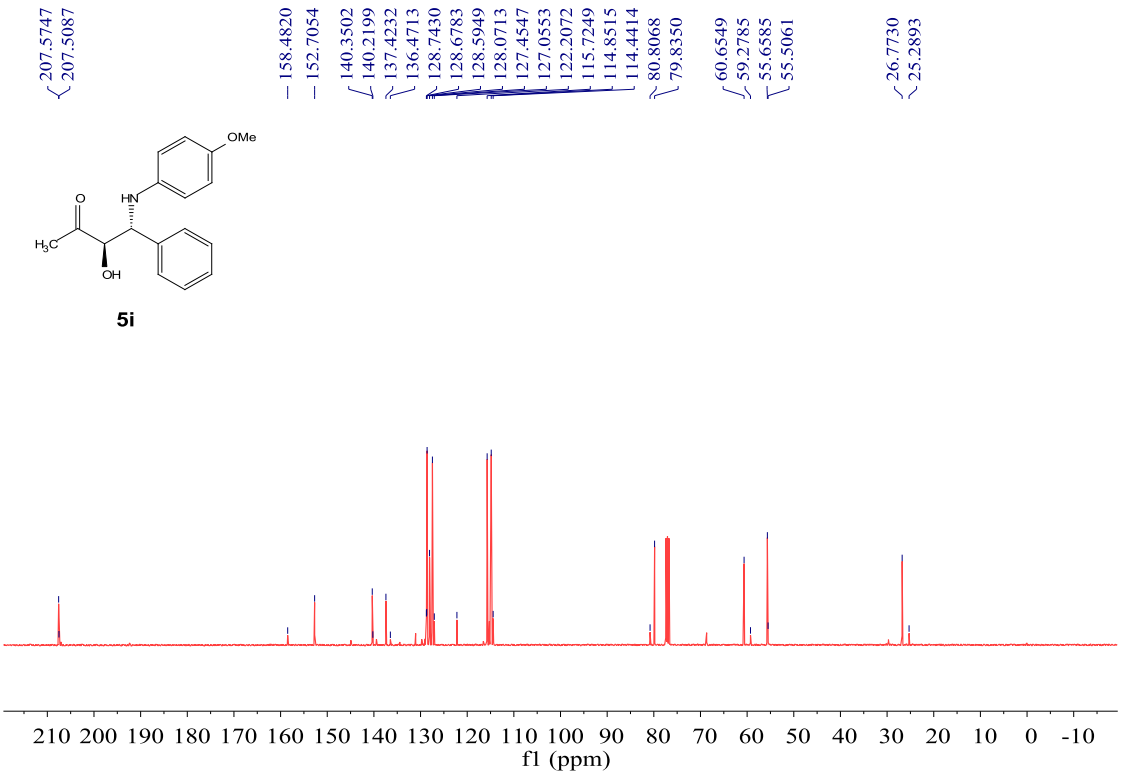
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5h**



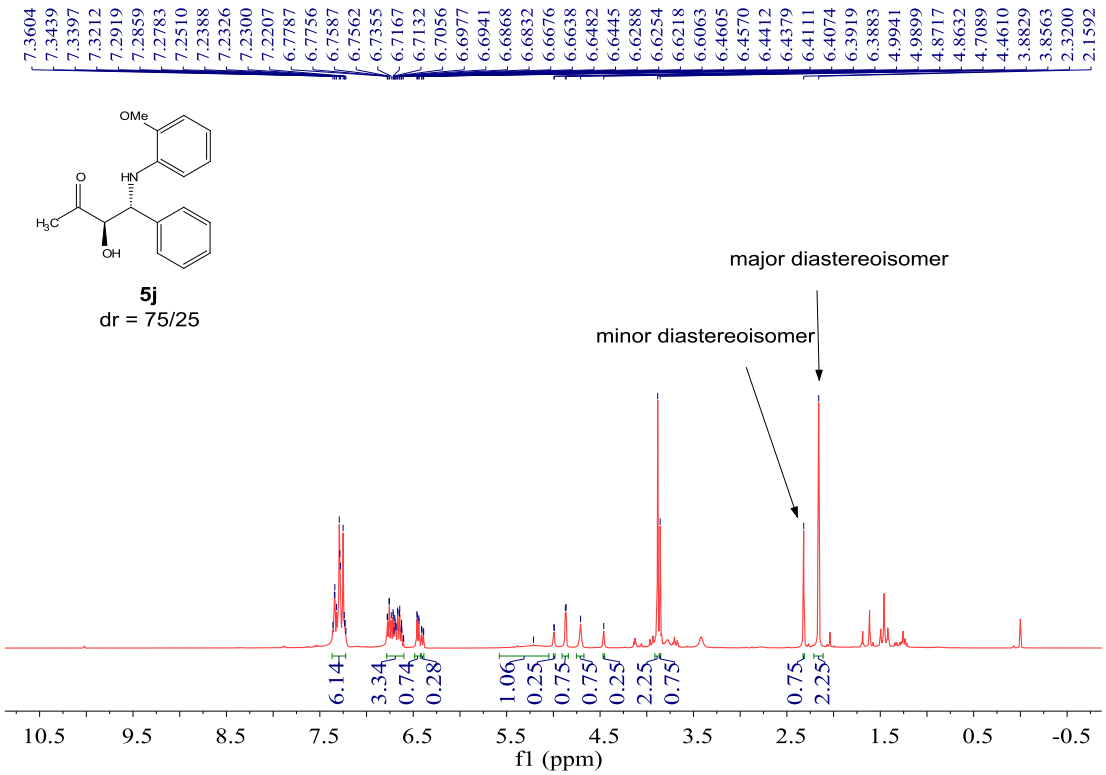
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **5i**



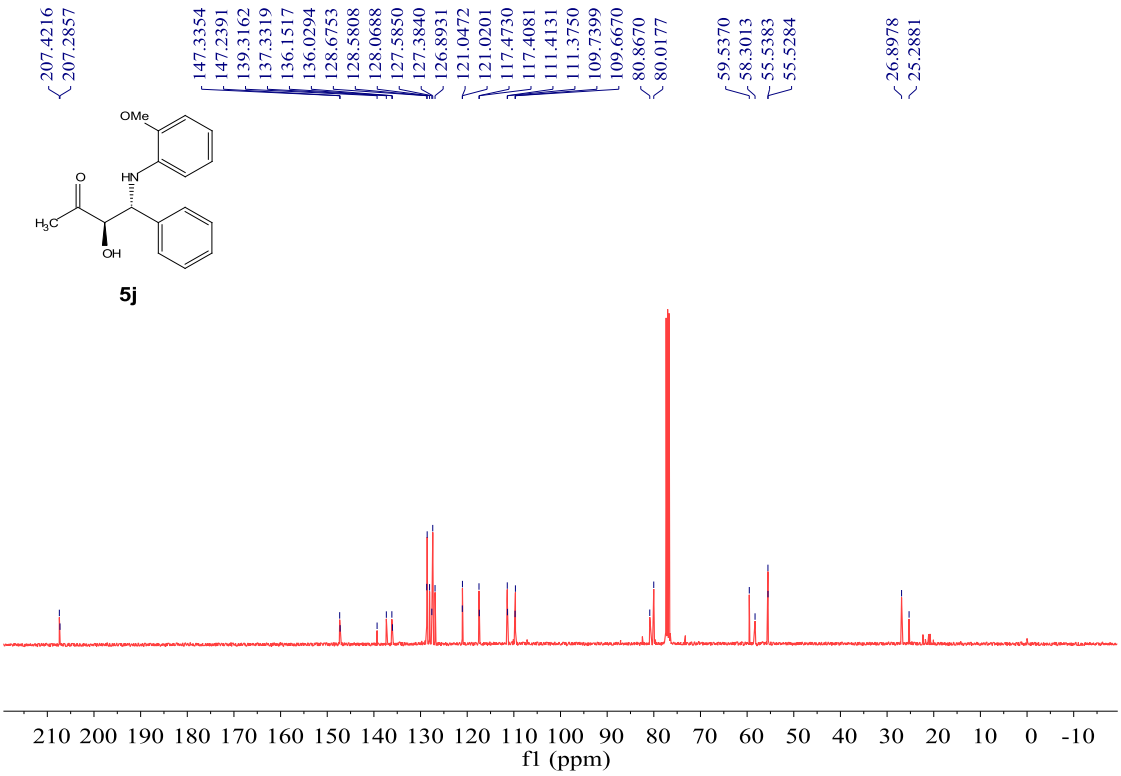
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **5i**



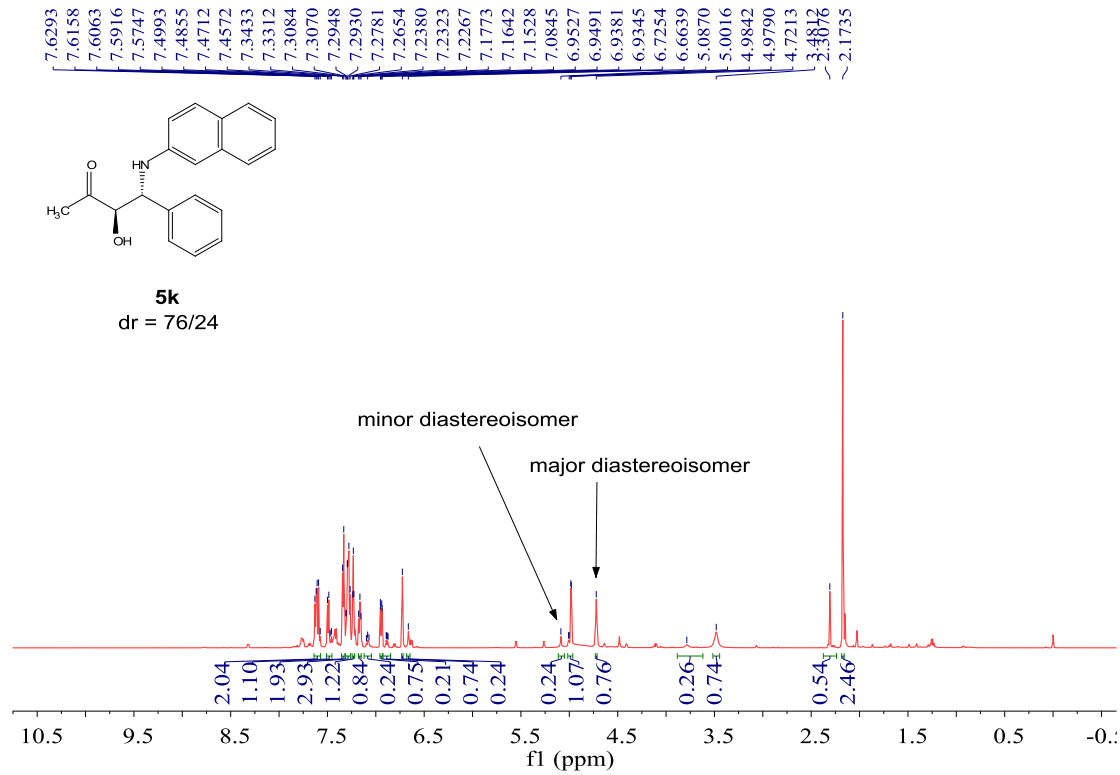
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **5j**



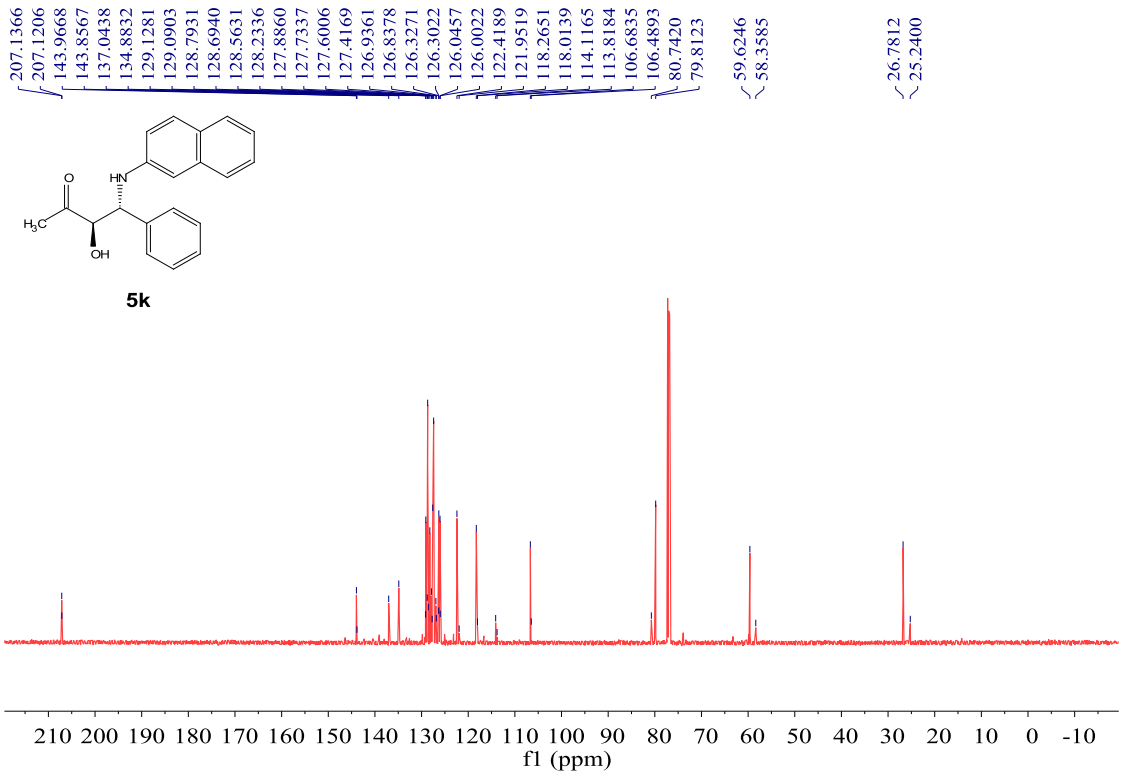
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of **5j**



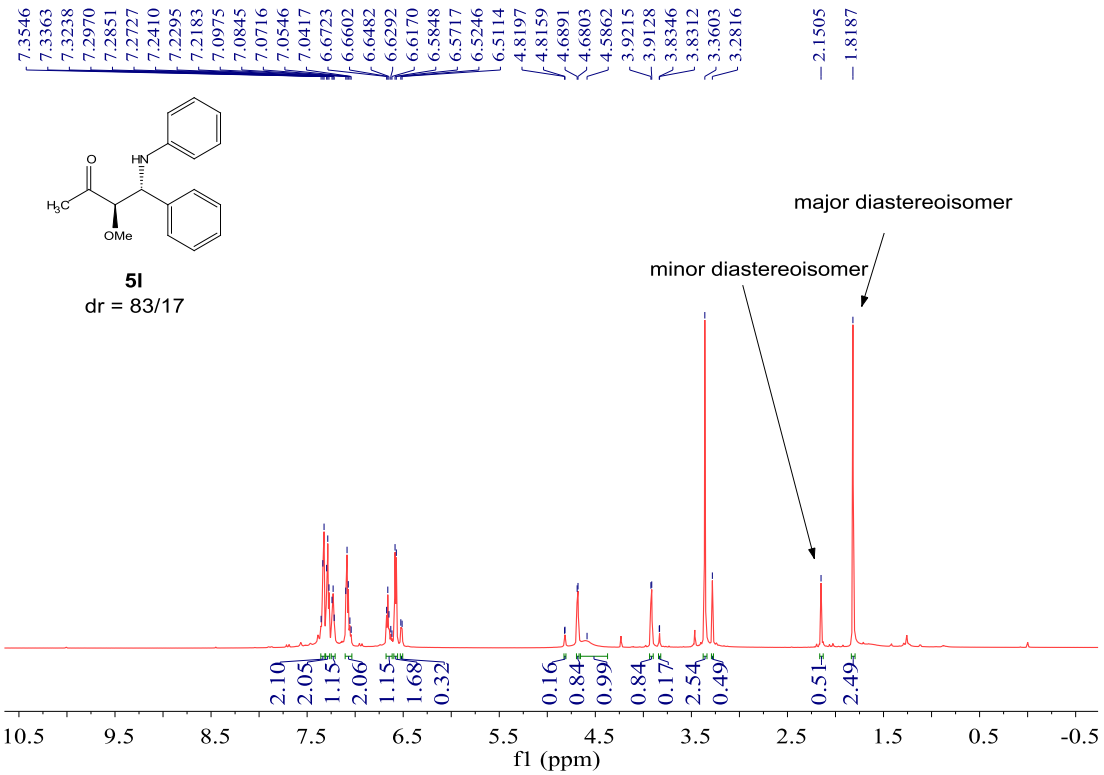
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5k**



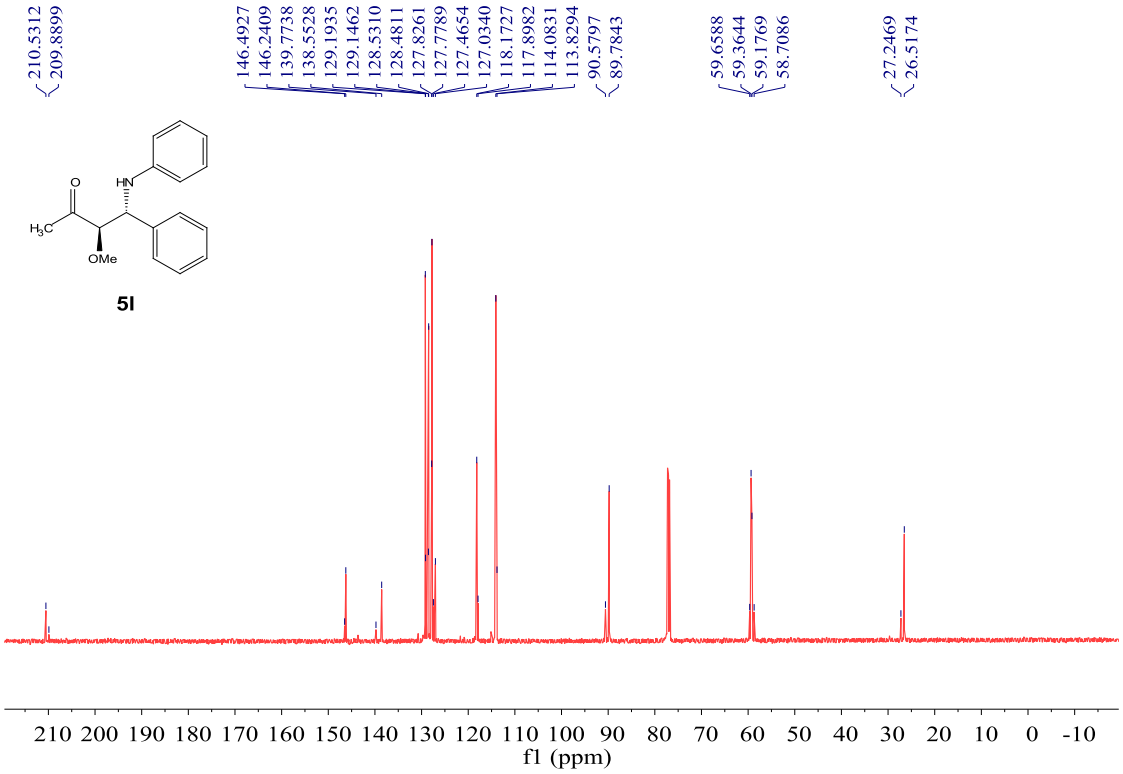
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5k**



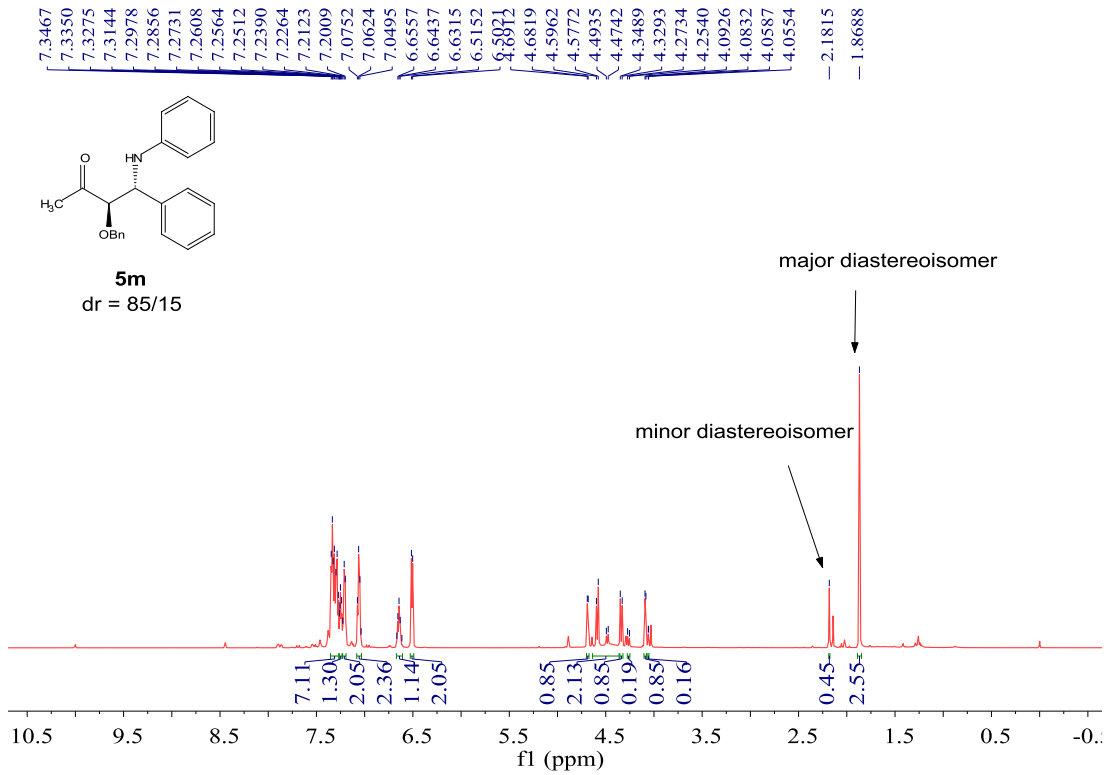
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5l**



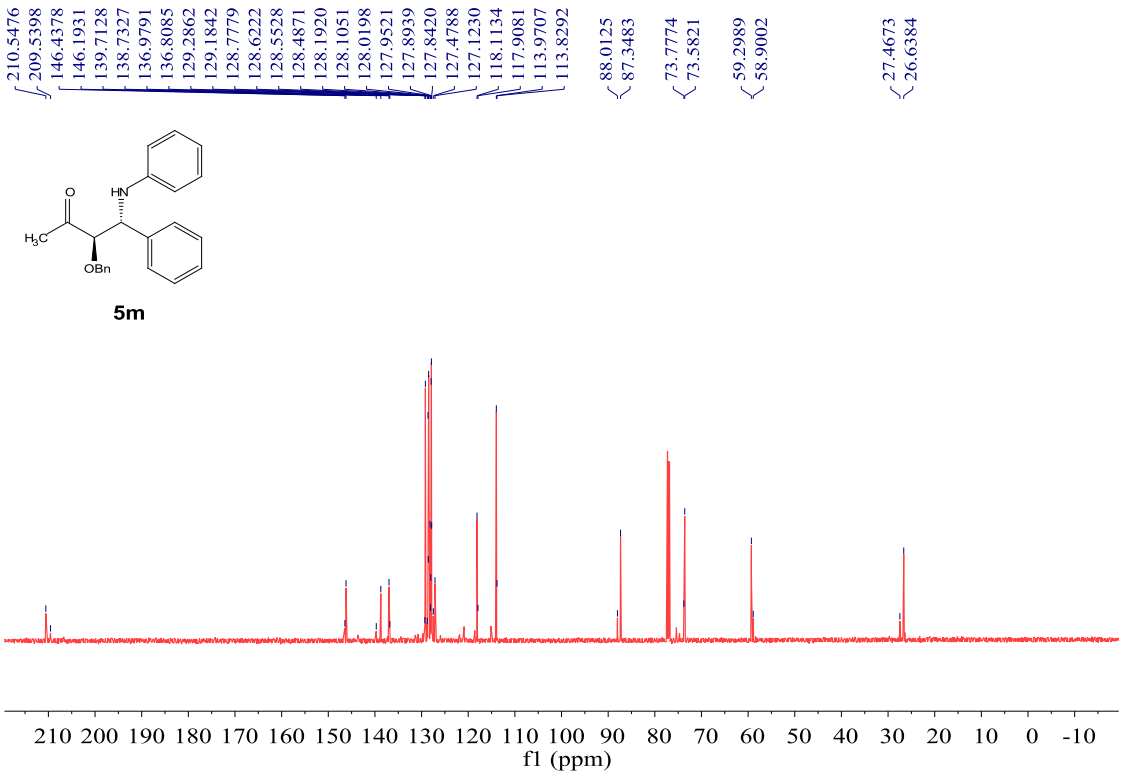
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5l**



^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **5m**

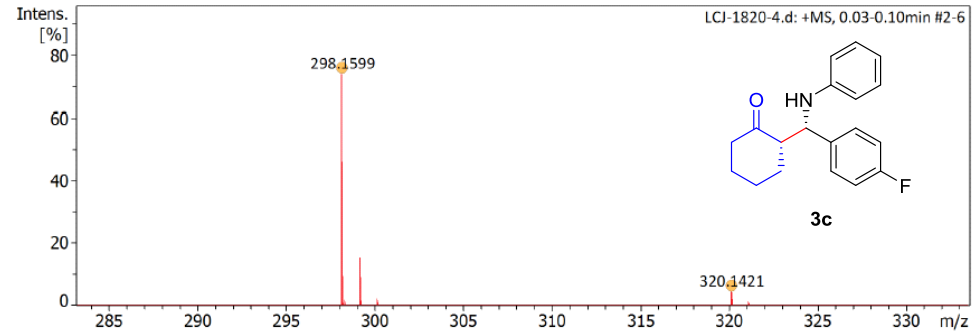


^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of **5m**



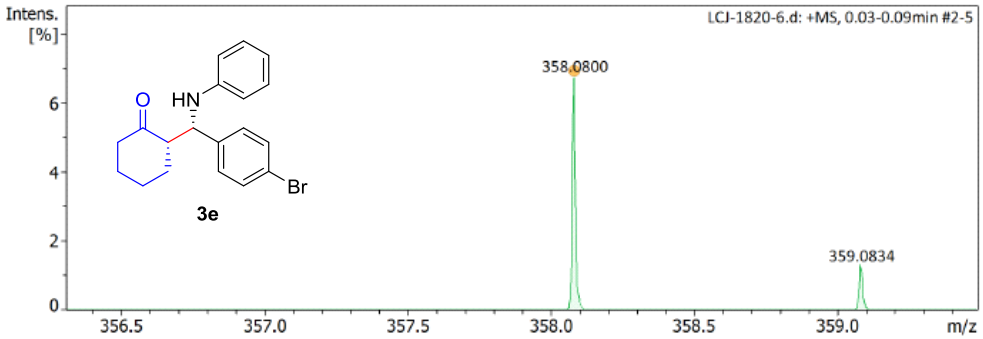
14. HRMS spectra

HRMS spectrum of **3c**



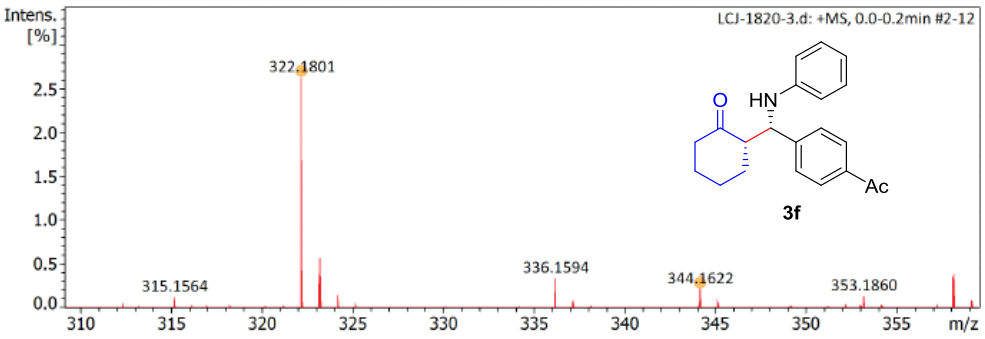
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
298.1599	1	C19H21FNO	298.1602	M+H	0.9	3.7	100.00	10.0	ok
320.1421	1	C19H20FNNaO	320.1421	M+Na	0.0	13.8	100.00	10.0	ok

HRMS spectrum of **3e**



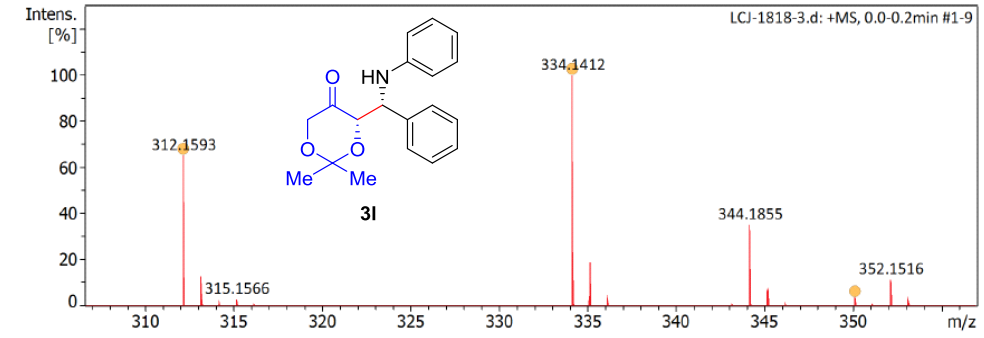
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
358.0800	1	C19H21BrNO	358.0801	M+H	0.3	21.8	100.00	12.0	ok

HRMS spectrum of **3f**



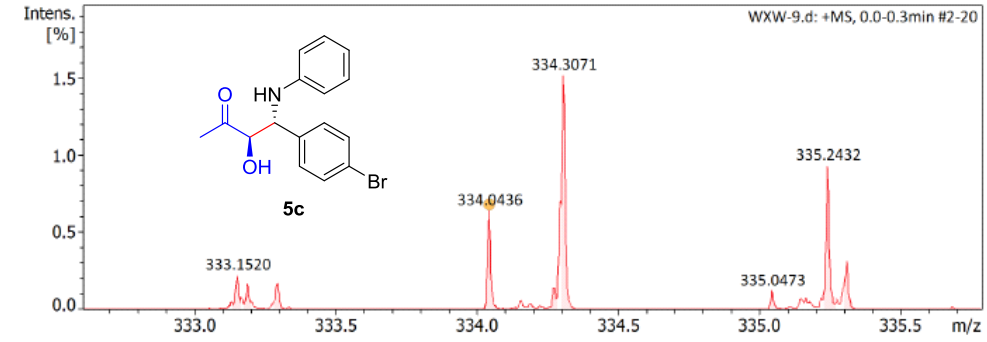
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
322.1801	1	C21H24NO2	322.1802	M+H	0.3	17.2	100.00	11.0	ok
344.1622	1	C21H23NNaO2	344.1621	M+Na	-0.3	n.a.	100.00	11.0	ok

HRMS spectrum of **3l**



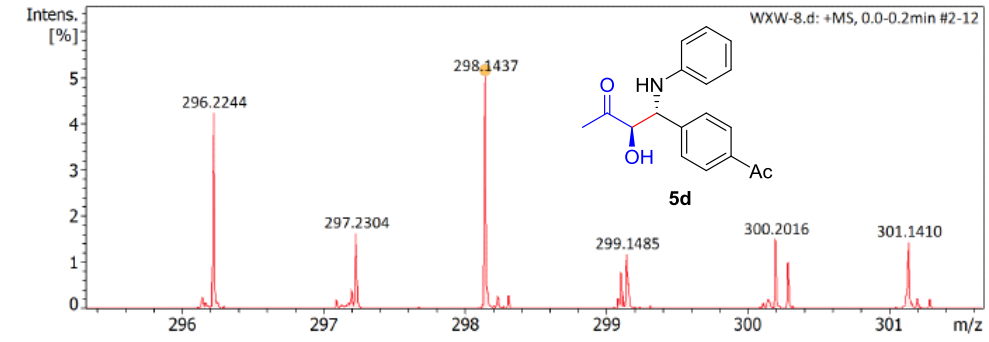
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
312.1593	1	C19H22NO3	312.1594	M+H	0.5	10.7	100.00	10.0	ok
334.1412	1	C19H21NNaO3	334.1414	M+Na	0.6	14.6	100.00	10.0	ok
350.1151	1	C19H21KNO3	350.1153	M+K	0.7	11.8	100.00	10.0	ok

HRMS spectrum of **5c**



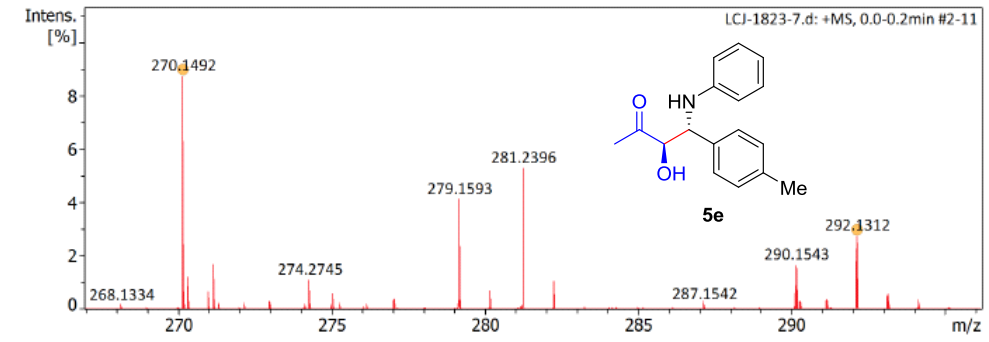
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
334.0436	1	C16H17BrNO2	334.0437	M+H	0.4	21.1	100.00	11.0	ok

HRMS spectrum of **5d**



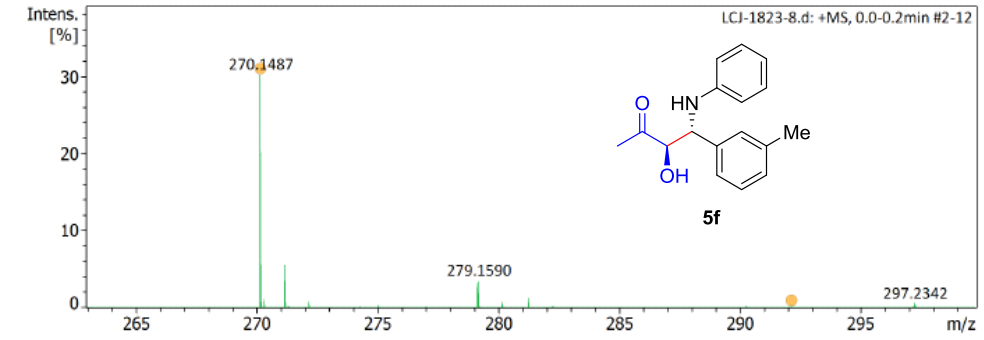
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
298.1437	1	C18H20NO3	298.1438	M+H	0.2	19.9	100.00	10.0	ok

HRMS spectrum of **5e**



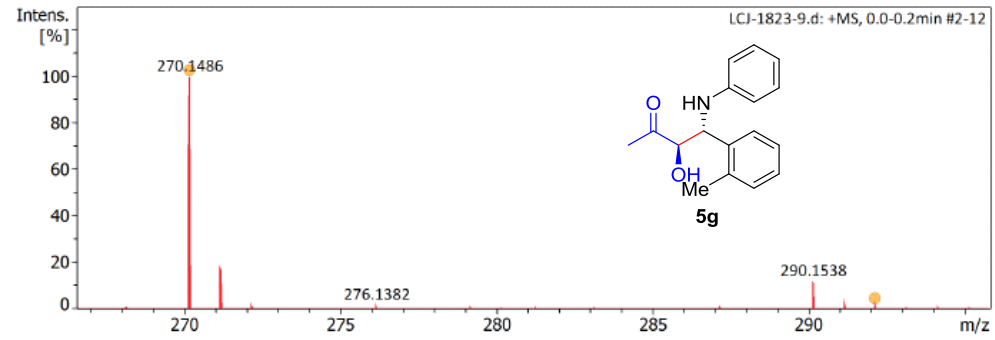
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1492	1	C17H20NO2	270.1489	M+H	-1.3	1.3	100.00	9.0	ok
292.1312	1	C17H19NNaO2	292.1308	M+Na	-1.4	13.2	100.00	9.0	ok

HRMS spectrum of **5f**



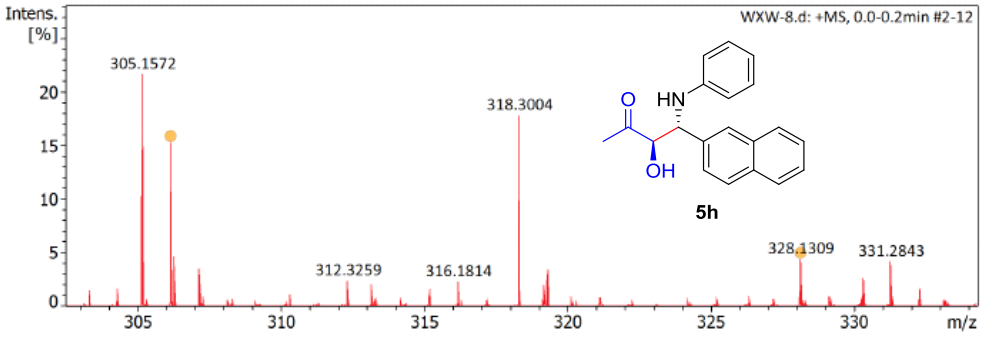
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1487	1	C17H20NO2	270.1489	M+H	0.4	3.8	100.00	9.0	ok
292.1314	1	C17H19NNaO2	292.1308	M+Na	-2.1	n.a.	100.00	9.0	ok

HRMS spectrum of **5g**



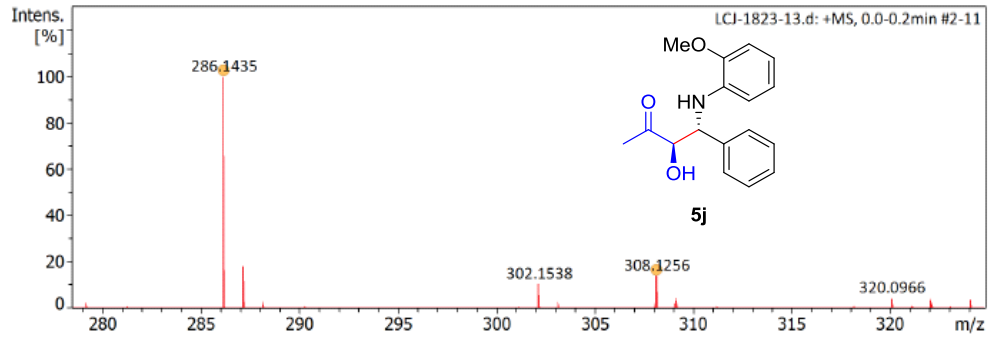
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1486	1	C17H20NO2	270.1489	M+H	1.0	6.9	100.00	9.0	ok
292.1308	1	C17H19NNaO2	292.1308	M+Na	-0.1	27.8	100.00	9.0	ok

HRMS spectrum of **5h**



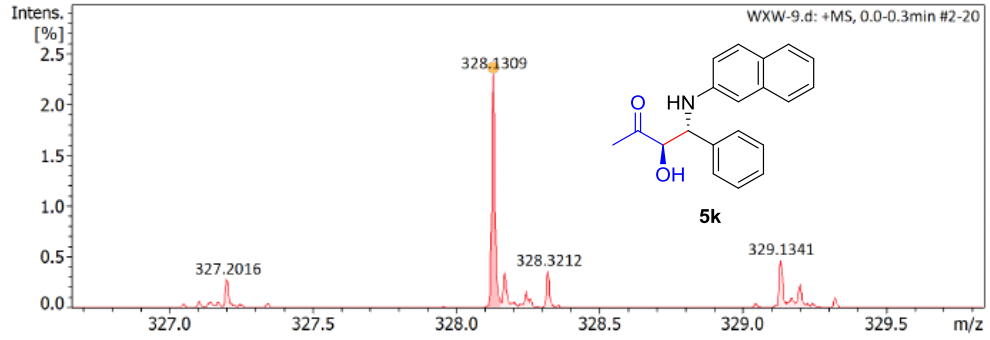
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
306.1493	1	C20H20NO2	306.1489	M+H	-1.4	5.9	100.00	12.0	ok
328.1309	1	C20H19NNaO2	328.1308	M+Na	-0.2	14.5	100.00	12.0	ok

HRMS spectrum of **5j**



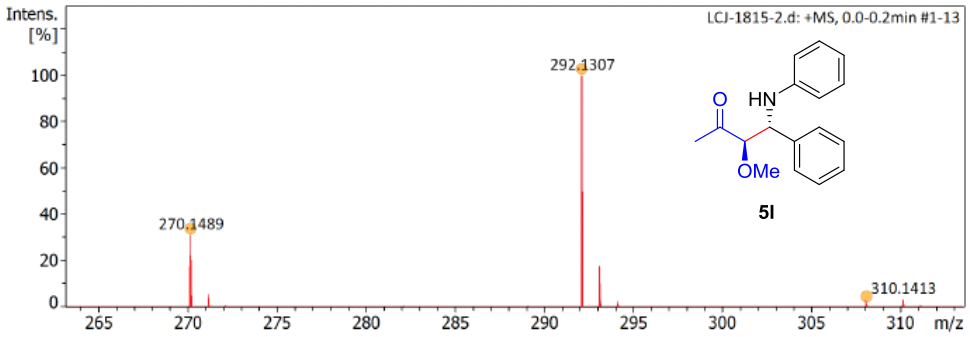
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
286.1435	1	C17H20NO3	286.1438	M+H	1.0	5.0	100.00	9.0	ok
308.1256	1	C17H19NNaO3	308.1257	M+Na	0.4	7.7	100.00	9.0	ok

HRMS spectrum of **5k**



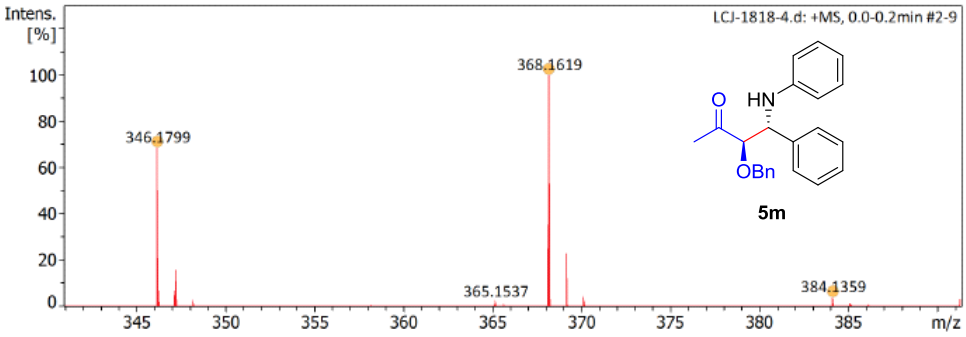
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
328.1309	1	C20H19NNaO2	328.1308	M+Na	-0.4	19.8	100.00	12.0	ok

HRMS spectrum of **5l**



Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1489	1	C17H20NO2	270.1489	M+H	0.0	8.7	100.00	9.0	ok
292.1307	1	C17H19NNaO2	292.1308	M+Na	0.2	8.5	100.00	9.0	ok
308.1047	1	C17H19KNO2	308.1047	M+K	0.2	8.7	100.00	9.0	ok

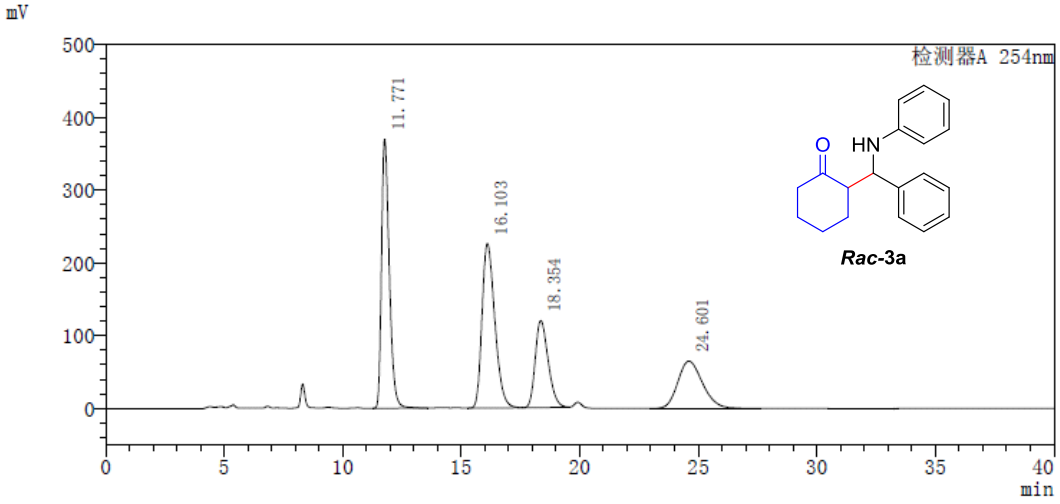
HRMS spectrum of **5m**



Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
346.1799	1	C23H24NO2	346.1802	M+H	0.6	15.0	100.00	13.0	ok
368.1619	1	C23H23NNaO2	368.1621	M+Na	0.6	14.8	100.00	13.0	ok
384.1359	1	C23H23KNO2	384.1360	M+K	0.3	13.9	100.00	13.0	ok

15. Chiral HPLC spectra

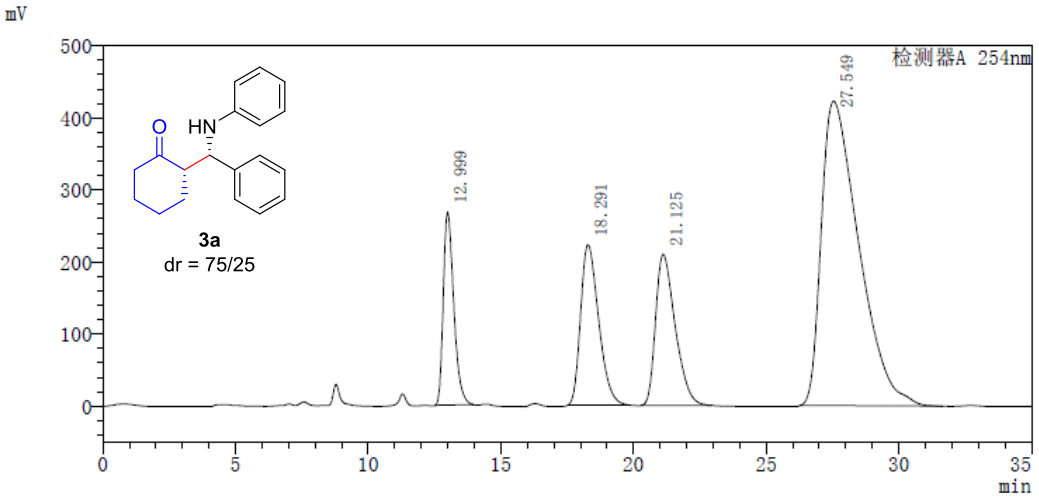
HPLC spectrum of ***Rac*-3a**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.771	8401948	369500	32.159
2	16.103	8477829	225903	32.450
3	18.354	4537721	119703	17.369
4	24.601	4708447	64951	18.022
总计		26125945	780058	

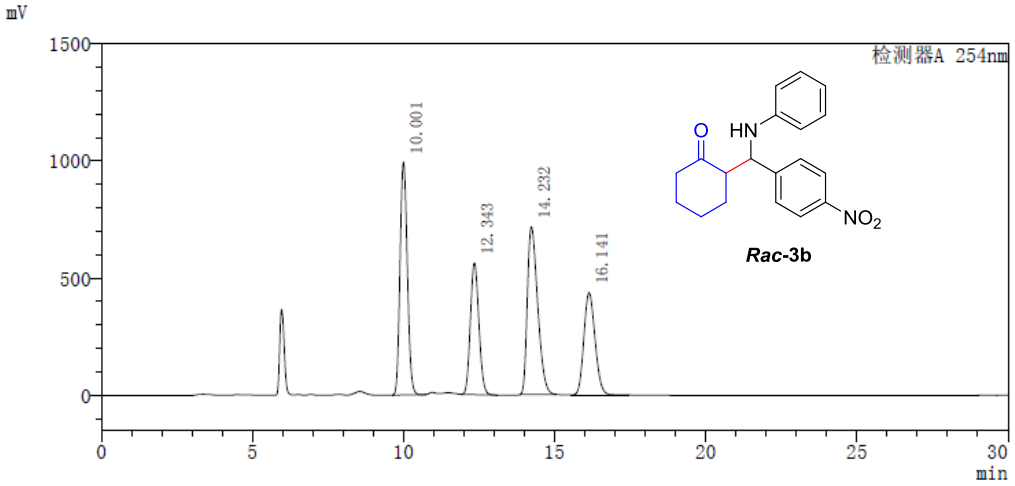
HPLC spectrum of **3a**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.999	7337657	267309	10.459
2	18.291	10543487	222899	15.029
3	21.125	10767896	209409	15.349
4	27.549	41505024	422224	59.163
总计		70154064	1121840	

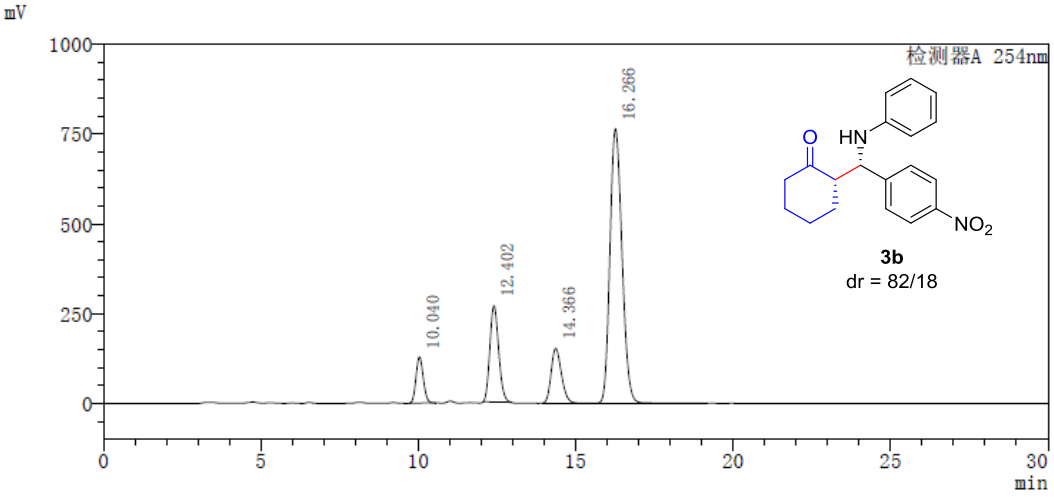
HPLC spectrum of ***Rac*-3b**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.001	16667518	993202	29.763
2	12.343	11040677	561966	19.715
3	14.232	17073650	716308	30.488
4	16.141	11218819	436171	20.033
总计		56000663	2707647	

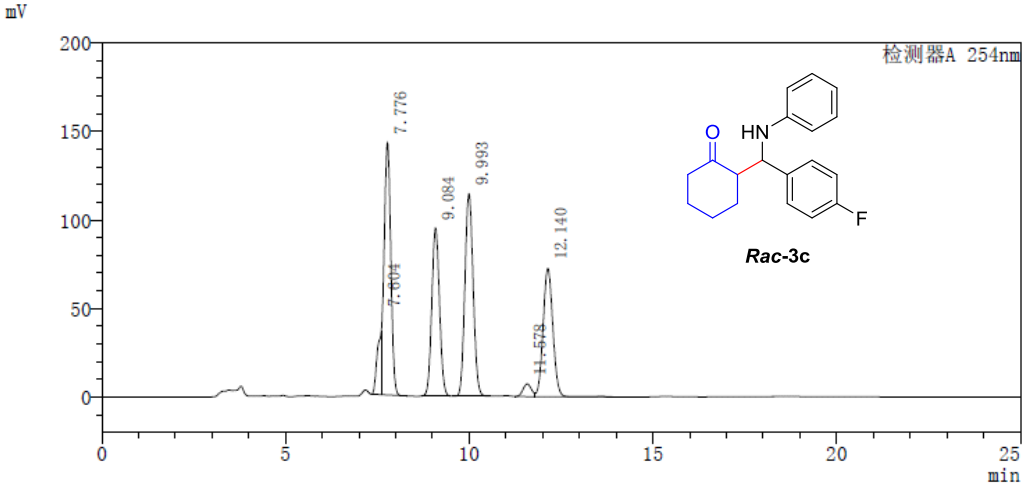
HPLC spectrum of **3b**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.040	2056816	128437	6.619
2	12.402	5241282	268788	16.866
3	14.366	3455178	152264	11.119
4	16.266	20322177	763878	65.396
总计		31075454	1313366	

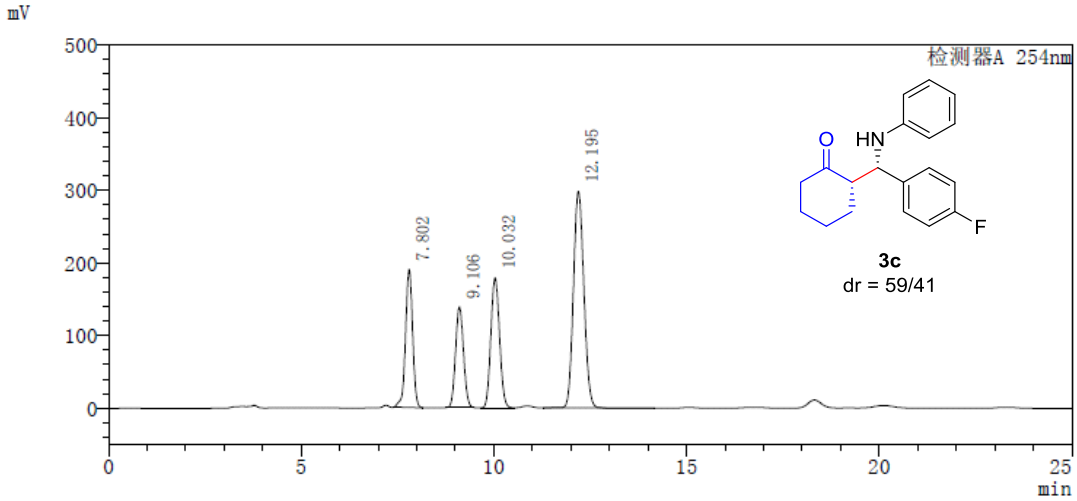
HPLC spectrum of ***Rac*-3c**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.604	280373	34190	4.179
2	7.776	1811267	142502	27.000
3	9.084	1383542	94831	20.624
4	9.993	1784639	114448	26.603
5	11.578	112226	7174	1.673
6	12.140	1336255	72366	19.919
总计		6708302	465511	

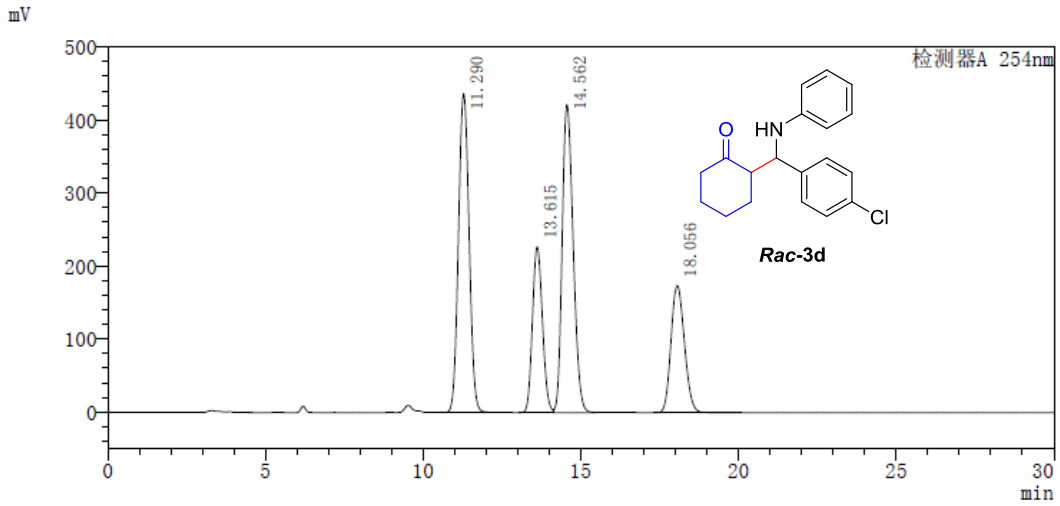
HPLC spectrum of **3c**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.802	2424324	189361	18.868
2	9.106	1995104	138497	15.528
3	10.032	2796311	178809	21.763
4	12.195	5632940	298008	43.841
总计		12848679	804675	

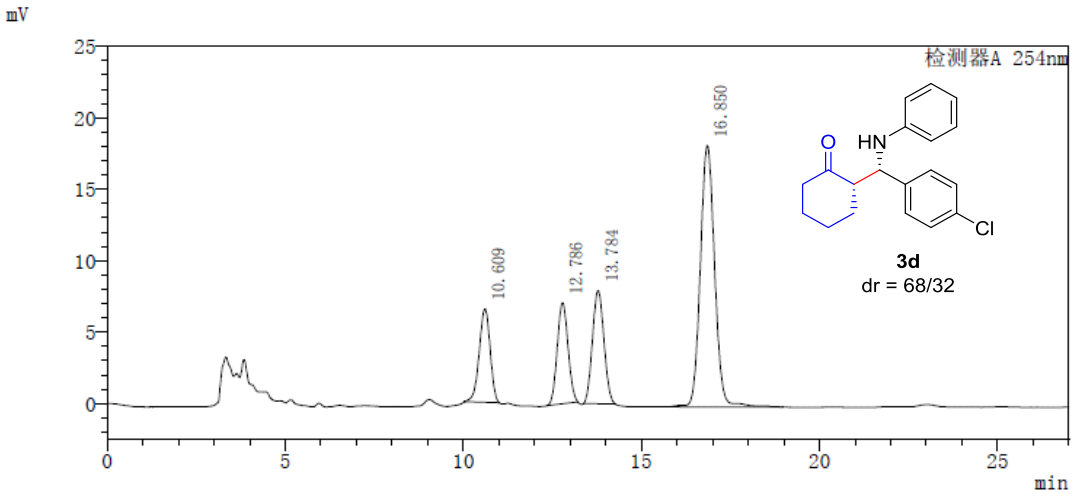
HPLC spectrum of ***Rac*-3d**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.290	10219101	436522	33.419
2	13.615	5021262	226846	16.421
3	14.562	10247714	421225	33.513
4	18.056	5090554	174252	16.647
总计		30578630	1258844	

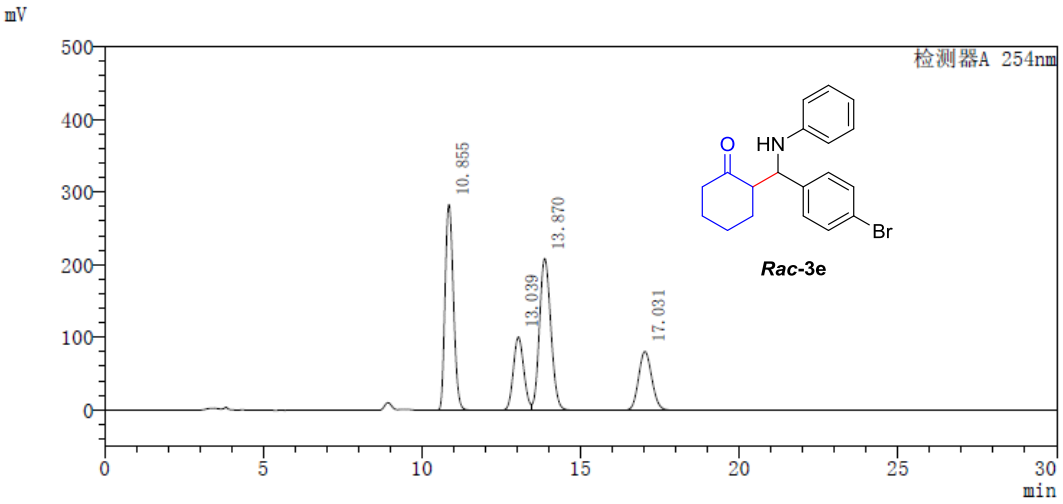
HPLC spectrum of **3d**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.609	139585	6544	14.247
2	12.786	149161	7061	15.224
3	13.784	177710	7917	18.138
4	16.850	513323	18278	52.392
总计		979779	39799	

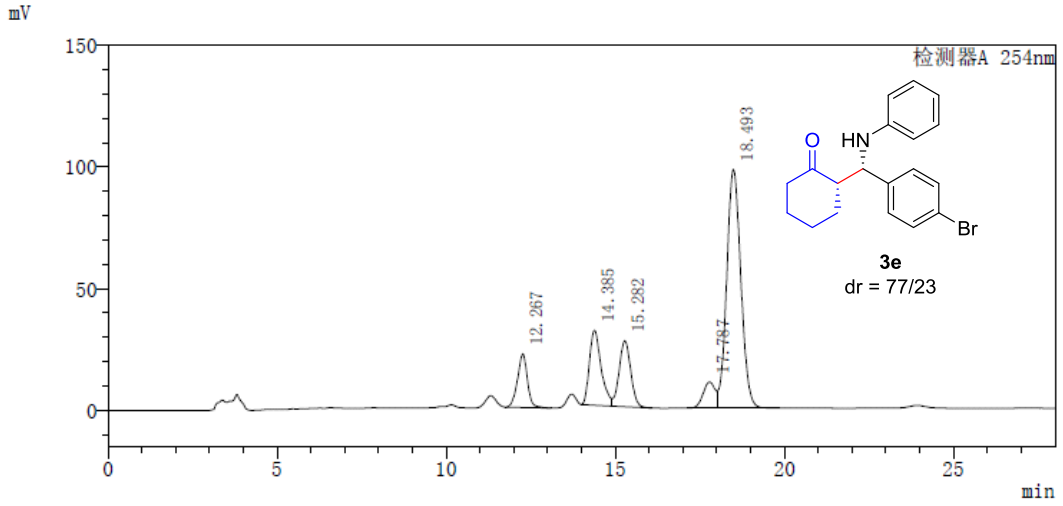
HPLC spectrum of ***Rac*-3e**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.855	5174394	283360	34.348
2	13.039	2311429	100682	15.344
3	13.870	5237335	208840	34.766
4	17.031	2341312	80859	15.542
总计		15064470	673742	

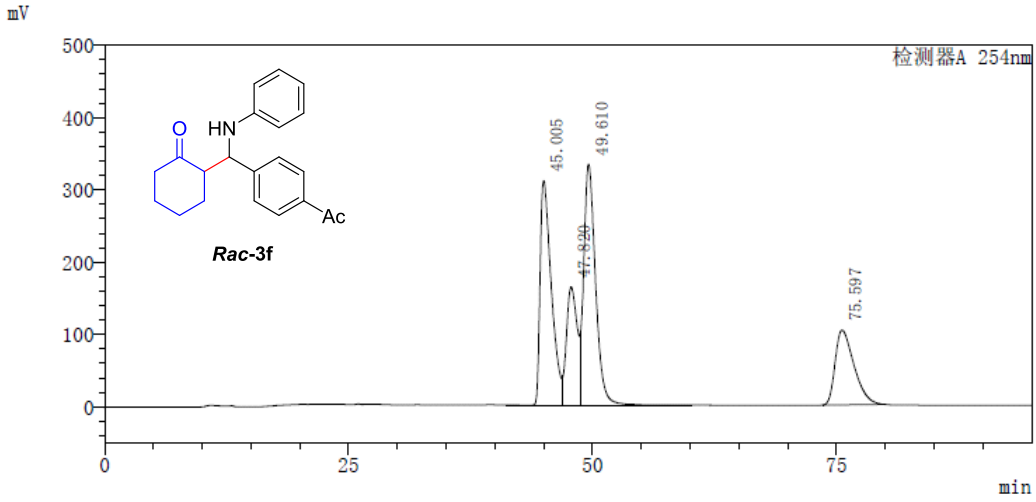
HPLC spectrum of **3e**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.267	448103	22000	9.044
2	14.385	745161	30789	15.039
3	15.282	644081	27057	12.999
4	17.787	261235	10714	5.272
5	18.493	2856139	97955	57.645
总计		4954720	188515	

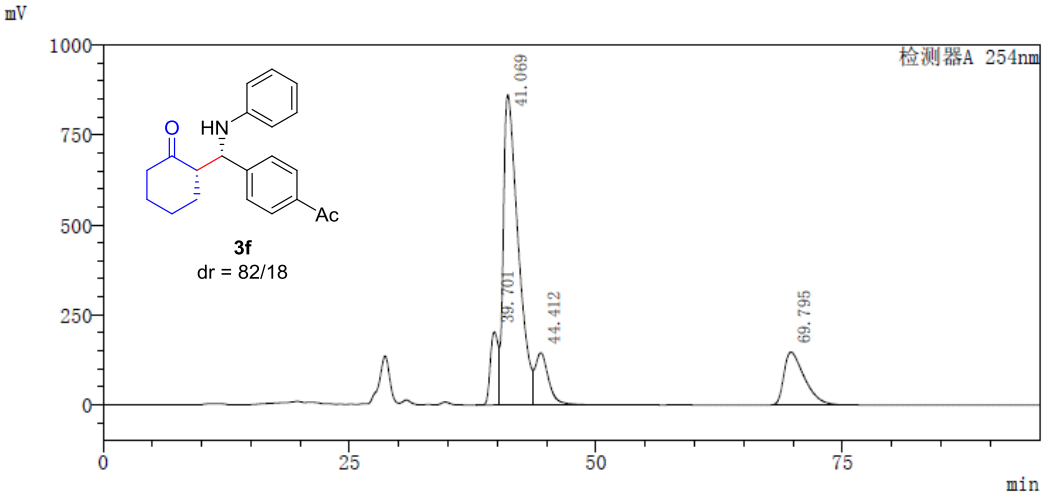
HPLC spectrum of ***Rac*-3f**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	45.005	24943724	310632	31.419
2	47.820	12593381	163332	15.862
3	49.610	27976848	332930	35.239
4	75.597	13877059	103380	17.479
总计		79391012	910274	

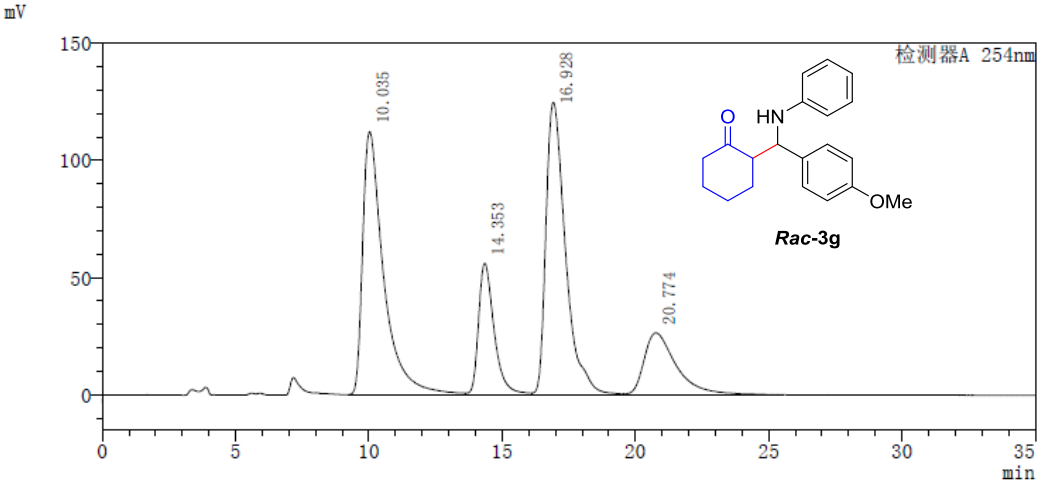
HPLC spectrum of **3f**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	39.701	11283540	203211	8.278
2	41.069	90262111	862853	66.218
3	44.412	13843645	145509	10.156
4	69.795	20920632	146263	15.348
总计		136309928	1357835	

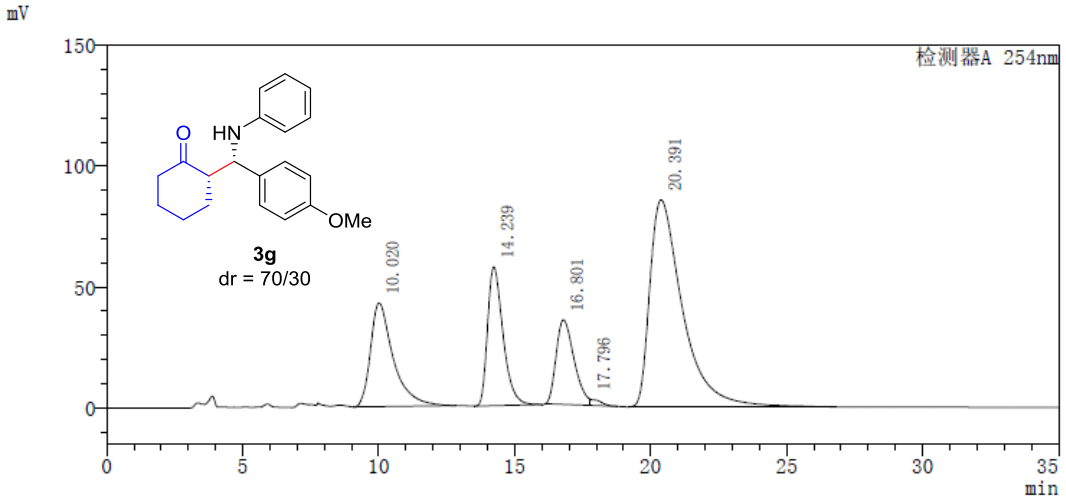
HPLC spectrum of ***Rac*-3g**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.035	6156271	112267	36.147
2	14.353	2286088	56027	13.423
3	16.928	6374914	124744	37.431
4	20.774	2213762	26358	12.998
总计		17031035	319396	

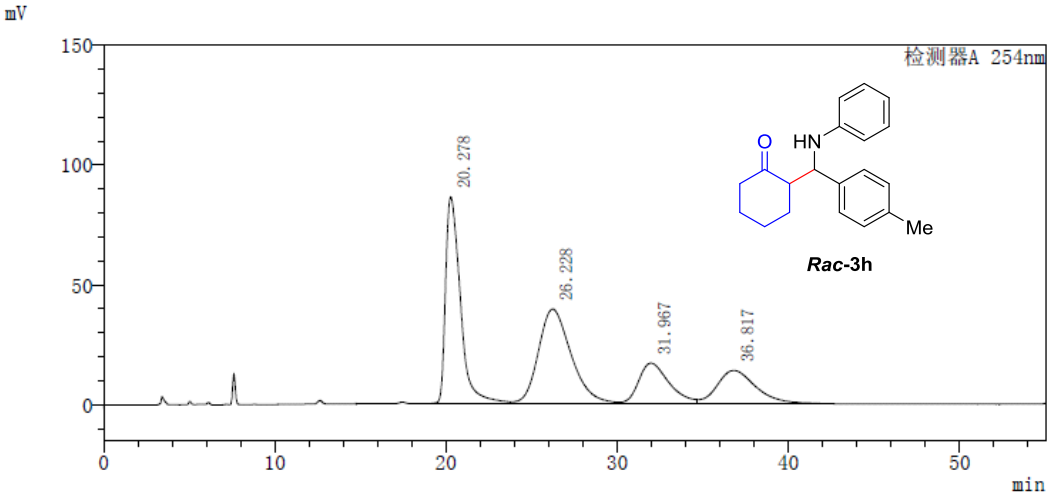
HPLC spectrum of **3g**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.020	2504211	42921	18.354
2	14.239	2282660	57398	16.730
3	16.801	1611812	35055	11.813
4	17.796	67690	2535	0.496
5	20.391	7177755	85651	52.607
总计		13644129	223560	

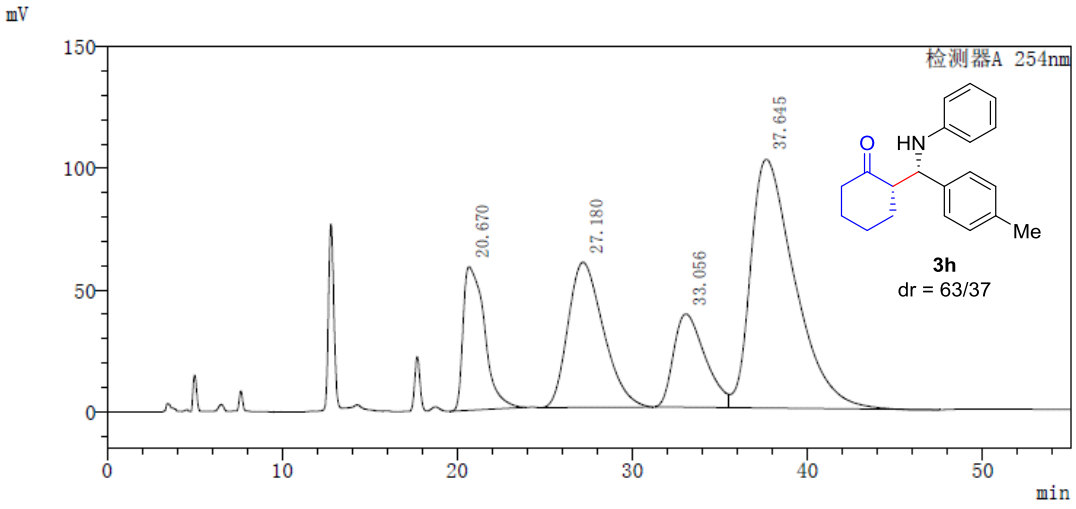
HPLC spectrum of ***Rac*-3h**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.278	5203384	86160	35.523
2	26.228	5223969	39351	35.664
3	31.967	2072592	16818	14.150
4	36.817	2147841	13794	14.663
总计		14647785	156123	

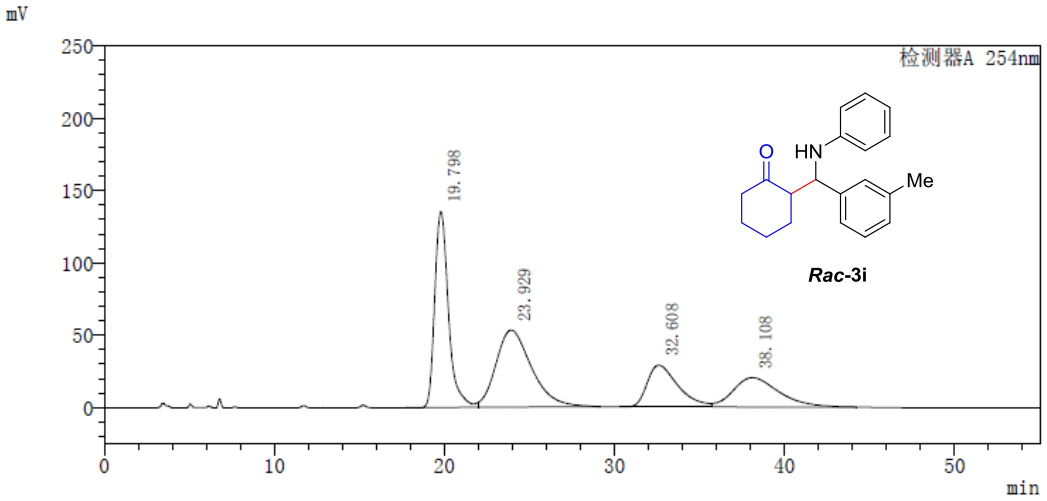
HPLC spectrum of **3h**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.670	5010358	59029	13.844
2	27.180	8389637	59648	23.181
3	33.056	4792032	38279	13.241
4	37.645	17999987	102168	49.735
总计		36192014	259124	

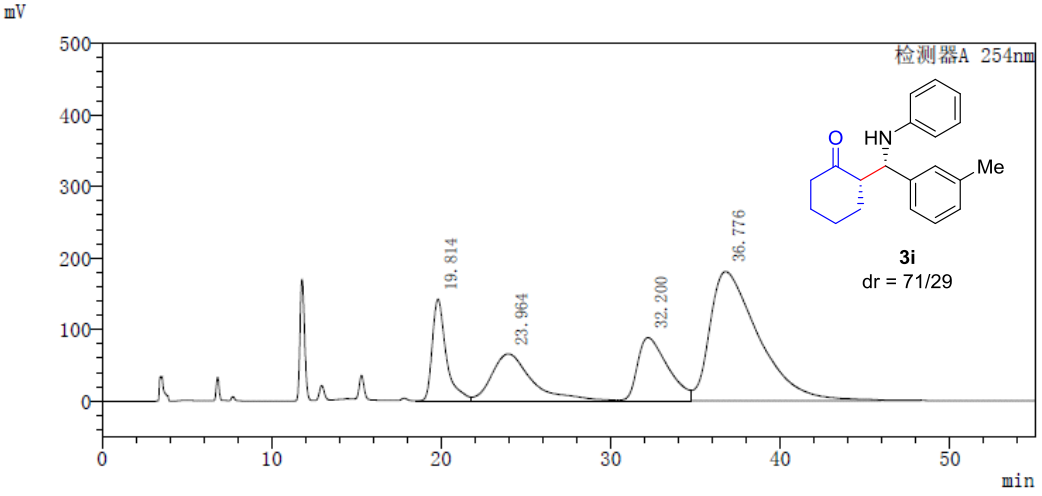
HPLC spectrum of ***Rac*-3i**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.798	7619599	135272	33.378
2	23.929	7719446	53200	33.816
3	32.608	3659992	28943	16.033
4	38.108	3828955	20332	16.773
总计		22827993	237747	

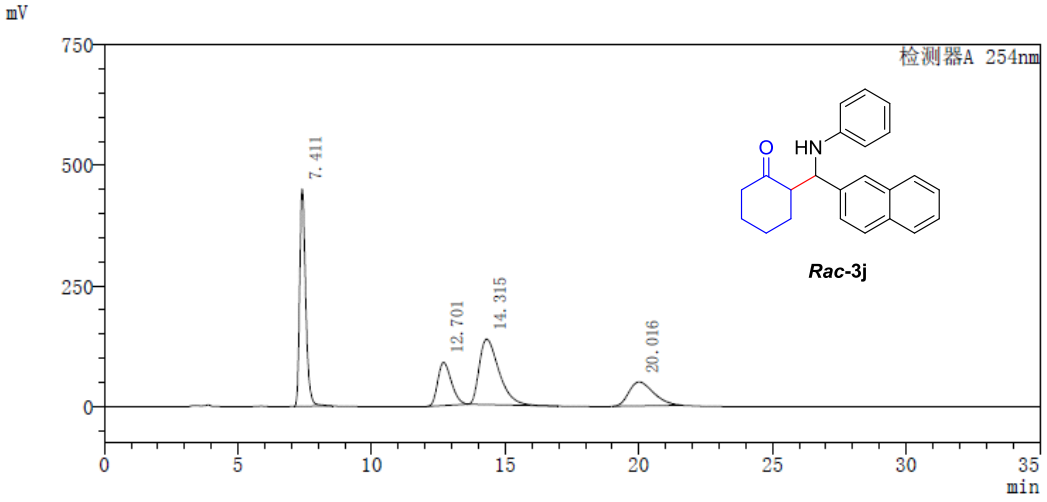
HPLC spectrum of **3i**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.814	8164927	141931	12.399
2	23.964	10776949	65402	16.366
3	32.200	10870028	88142	16.507
4	36.776	36039267	180395	54.728
总计		65851170	475869	

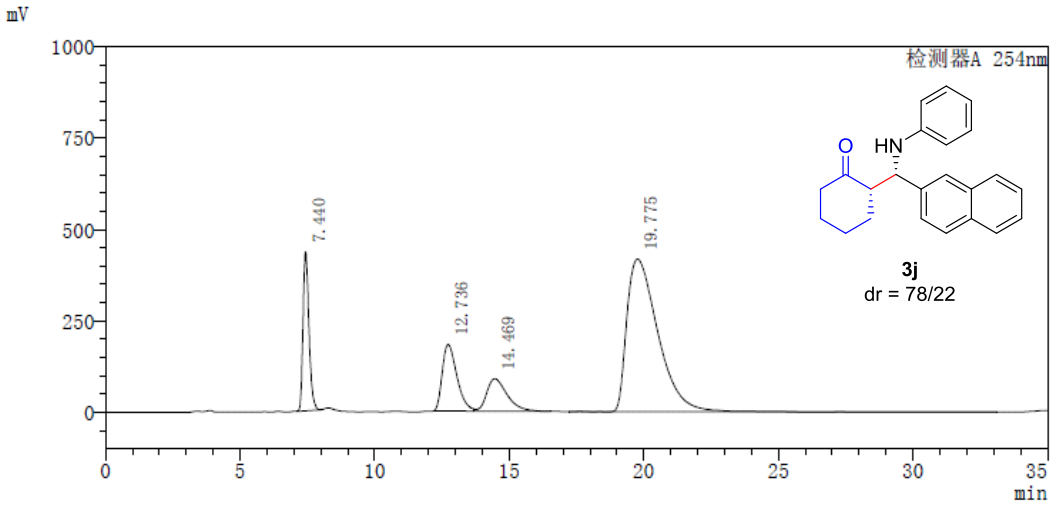
HPLC spectrum of ***Rac*-3j**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.411	7041227	451410	34.538
2	12.701	3174983	89458	15.574
3	14.315	6962883	135562	34.154
4	20.016	3207544	49717	15.734
总计		20386636	726147	

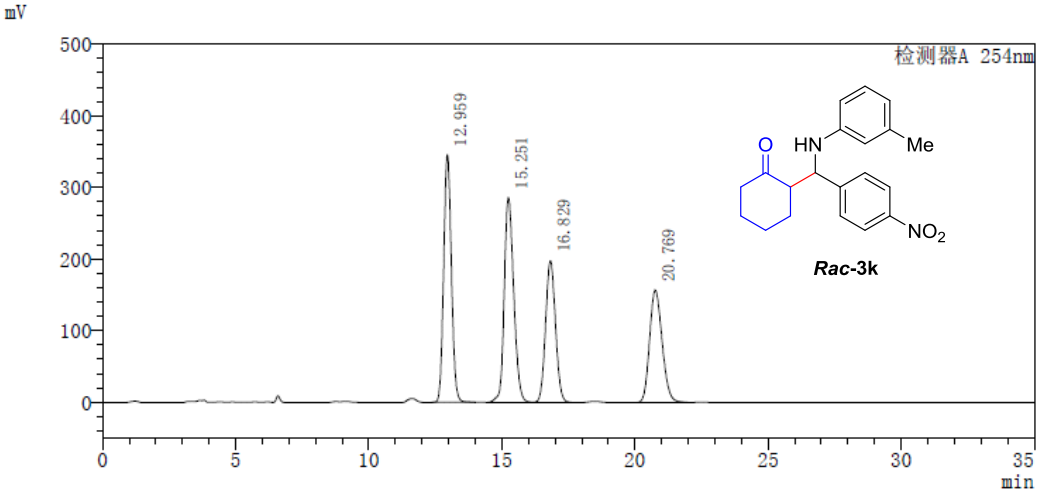
HPLC spectrum of **3j**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.440	6673589	435276	12.860
2	12.736	6873230	182312	13.244
3	14.469	4709979	88754	9.076
4	19.775	33639277	417749	64.820
总计		51896075	1124091	

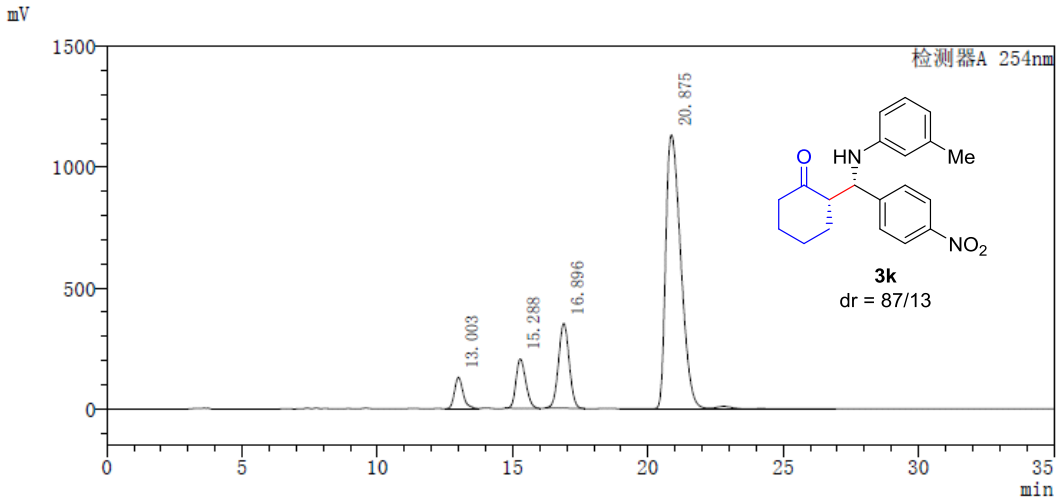
HPLC spectrum of ***Rac*-3k**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.959	6950659	345330	28.600
2	15.251	7104414	285743	29.233
3	16.829	5108399	197532	21.020
4	20.769	5139547	156686	21.148
总计		24303020	985291	

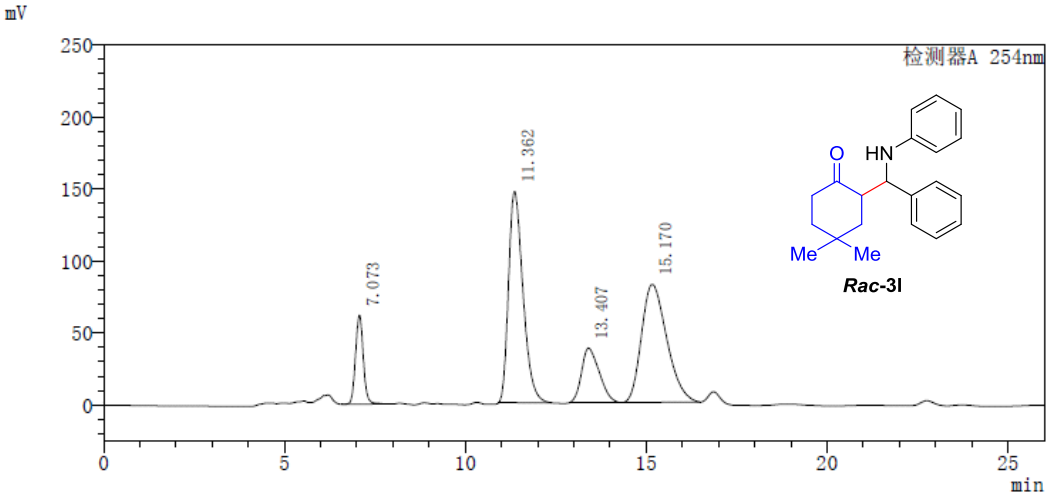
HPLC spectrum of **3k**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.003	2863369	128951	4.651
2	15.288	5133690	203728	8.339
3	16.896	9600775	350388	15.595
4	20.875	43965660	1133141	71.415
总计		61563495	1816209	

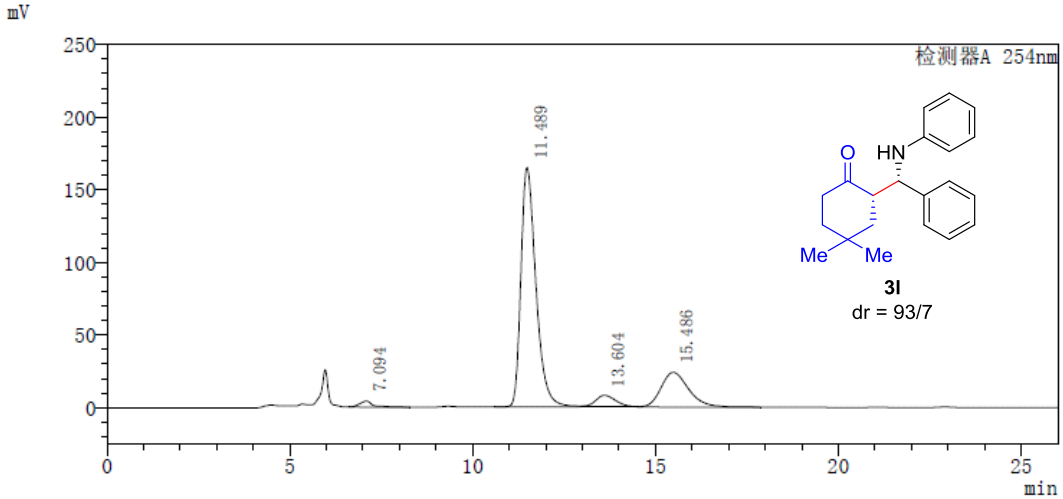
HPLC spectrum of ***Rac*-3l**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.073	930394	61685	9.062
2	11.362	4075009	146518	39.689
3	13.407	1282763	37804	12.494
4	15.170	3979225	81840	38.756
总计		10267391	327846	

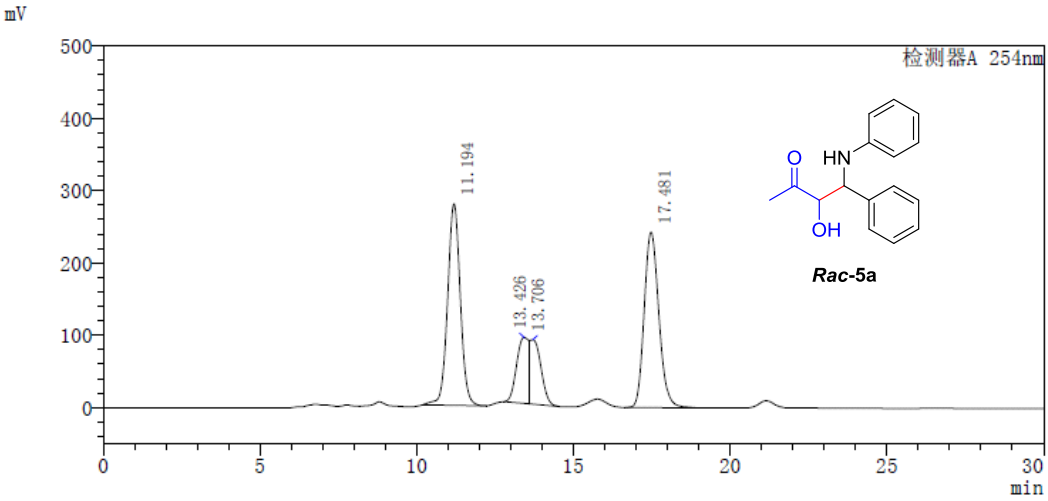
HPLC spectrum of **3l**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.094	107527	4310	1.688
2	11.489	4688244	164680	73.578
3	13.604	314134	8025	4.930
4	15.486	1261912	23912	19.805
总计		6371818	200927	

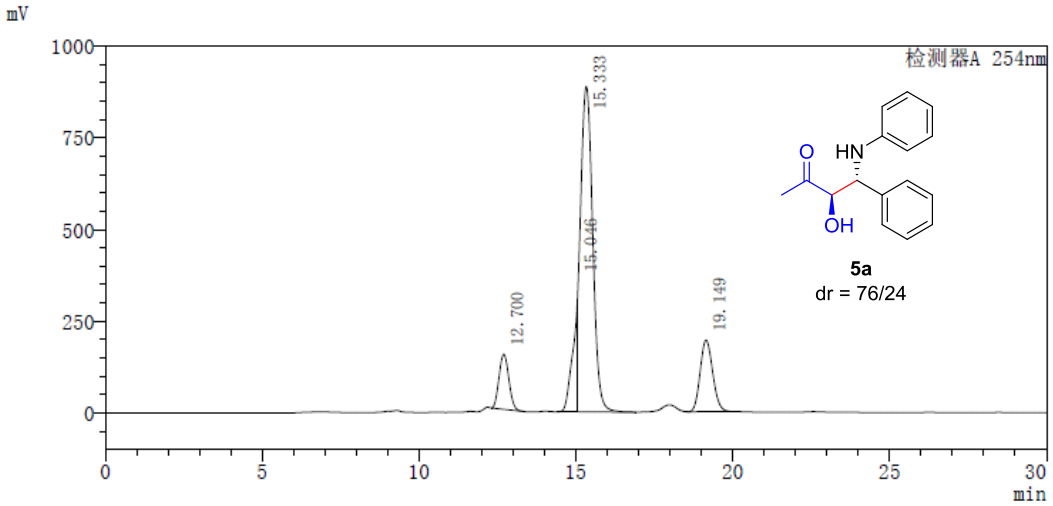
HPLC spectrum of ***Rac*-5a**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.194	7862006	278694	38.609
2	13.426	2306976	91127	11.329
3	13.706	2297040	88878	11.280
4	17.481	7897257	242491	38.782
总计		20363280	701189	

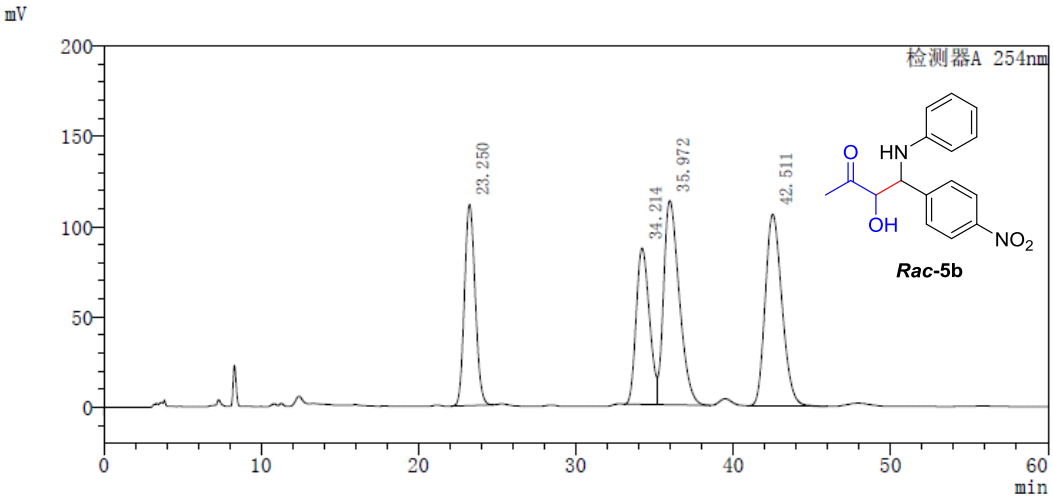
HPLC spectrum of **5a**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.700	3286250	150384	9.168
2	15.046	3321781	292288	9.267
3	15.333	23804952	887767	66.410
4	19.149	5432206	194962	15.155
总计		35845189	1525401	

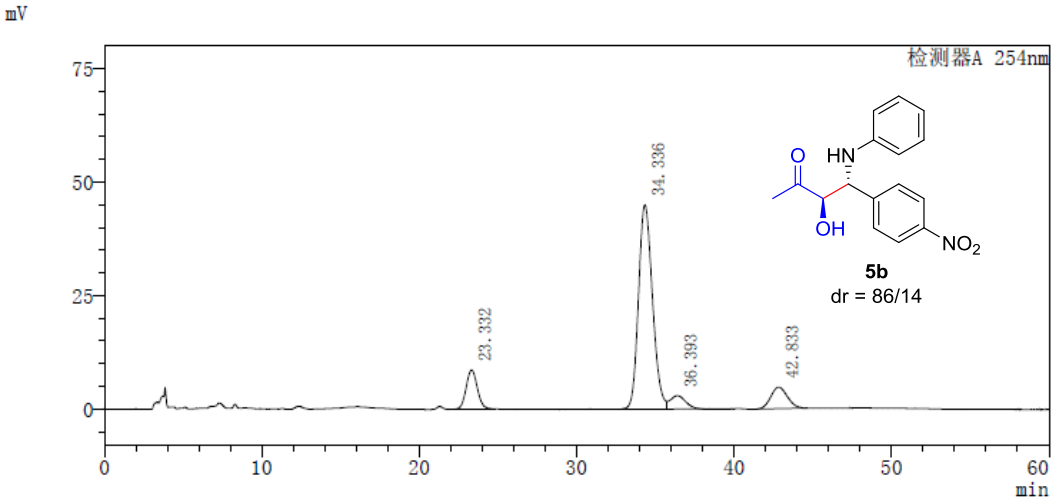
HPLC spectrum of ***Rac*-5b**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	23.250	5267929	111467	20.264
2	34.214	5084154	86527	19.558
3	35.972	7798818	113178	30.000
4	42.511	7845021	106238	30.178
总计		25995922	417410	

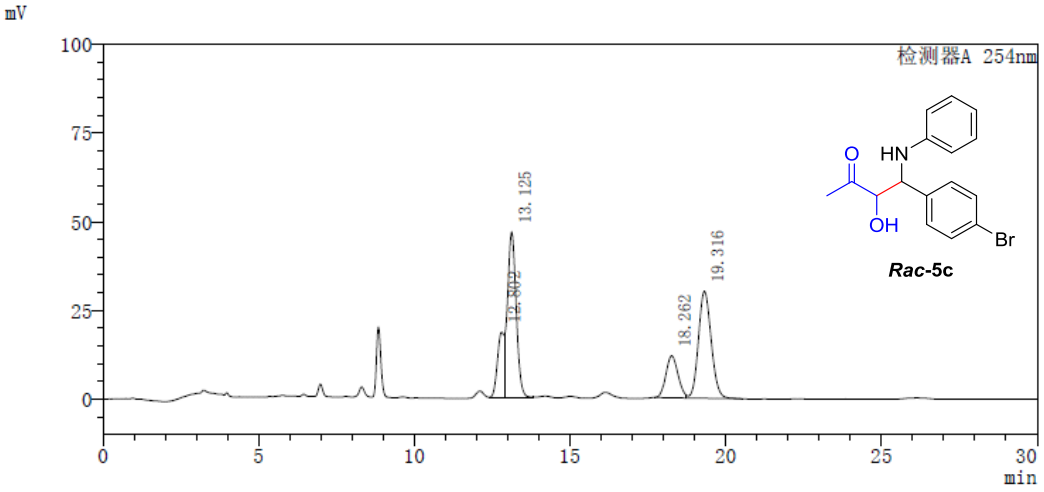
HPLC spectrum of **5b**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	23.332	417157	8578	11.180
2	34.336	2775526	44951	74.388
3	36.393	187890	2930	5.036
4	42.833	350559	4756	9.396
总计		3731133	61216	

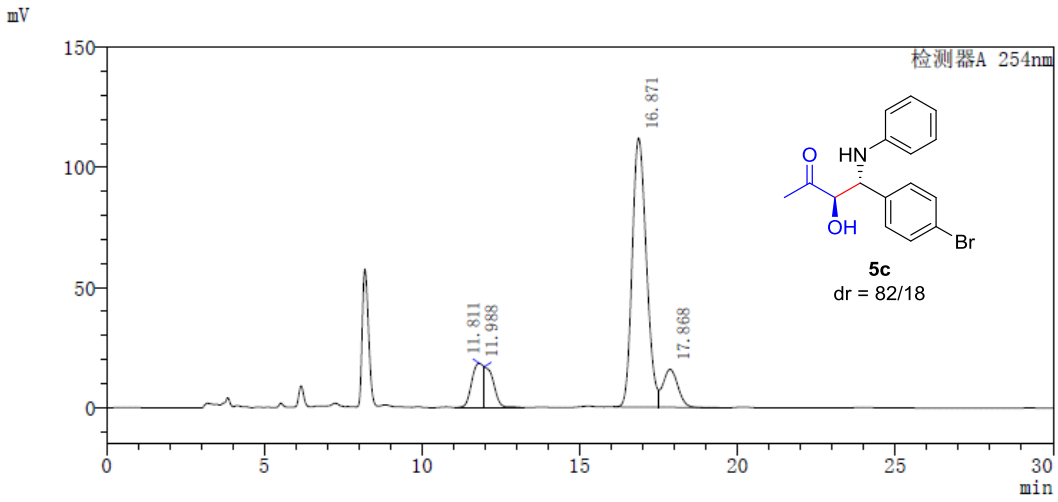
HPLC spectrum of ***Rac*-5c**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.802	280186	18428	11.843
2	13.125	908395	46635	38.397
3	18.262	316875	11799	13.394
4	19.316	860332	30155	36.366
总计		2365789	107016	

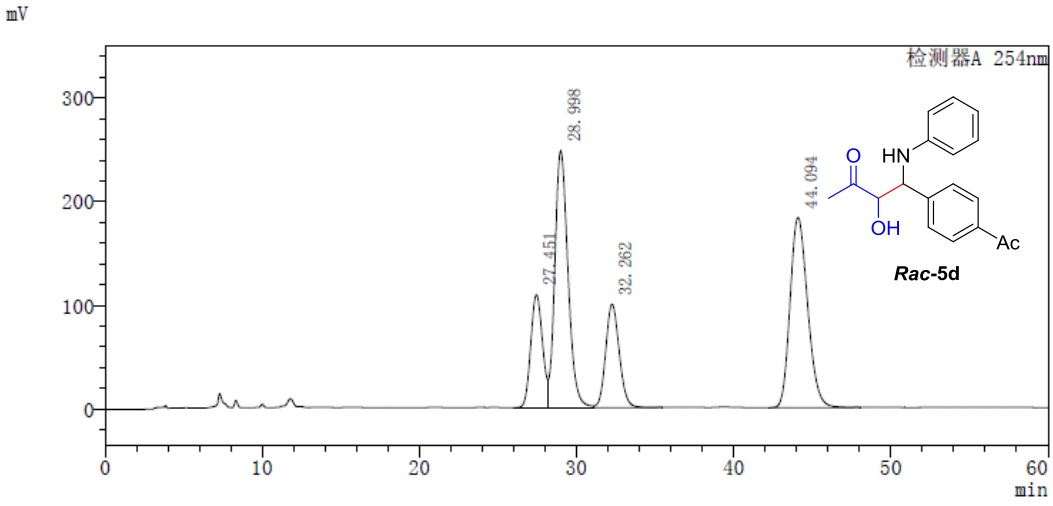
HPLC spectrum of **5c**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.811	467075	18360	9.676
2	11.988	336468	16808	6.971
3	16.871	3509661	111902	72.709
4	17.868	513784	15877	10.644
总计		4826988	162946	

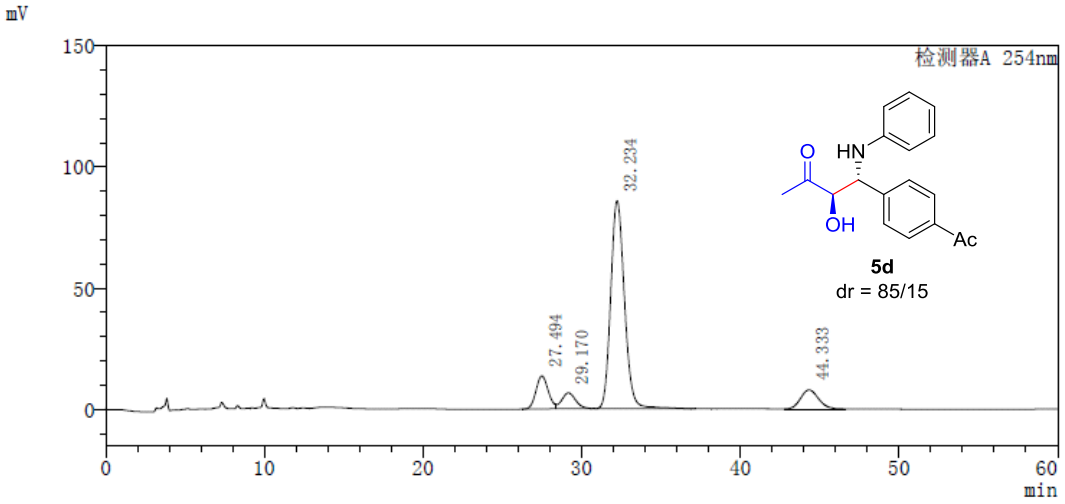
HPLC spectrum of ***Rac*-5d**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	27.451	5700298	108932	14.110
2	28.998	14428942	247659	35.715
3	32.262	5991123	99733	14.830
4	44.094	14279308	183364	35.345
总计		40399671	639688	

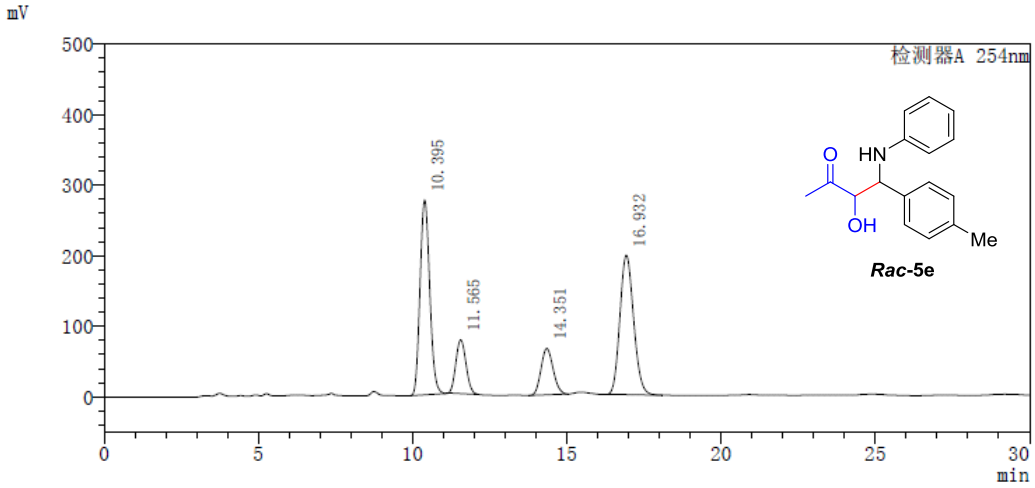
HPLC spectrum of **5d**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	27.494	724939	13640	10.468
2	29.170	400903	6532	5.789
3	32.234	5182683	85781	74.837
4	44.333	616806	7865	8.907
总计		6925331	113818	

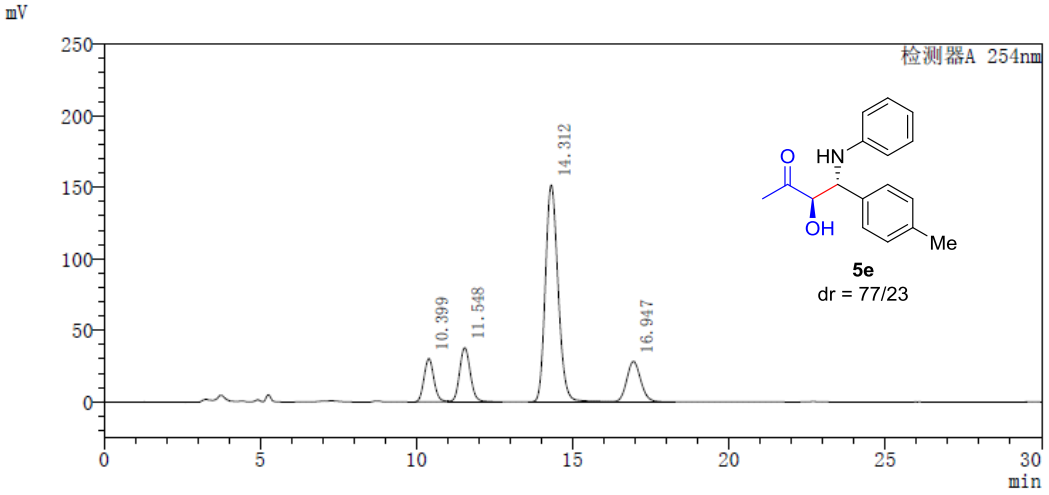
HPLC spectrum of ***Rac*-5e**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.395	6024852	275607	38.392
2	11.565	1752950	76376	11.170
3	14.351	1807648	65745	11.519
4	16.932	6107622	197380	38.919
总计		15693072	615108	

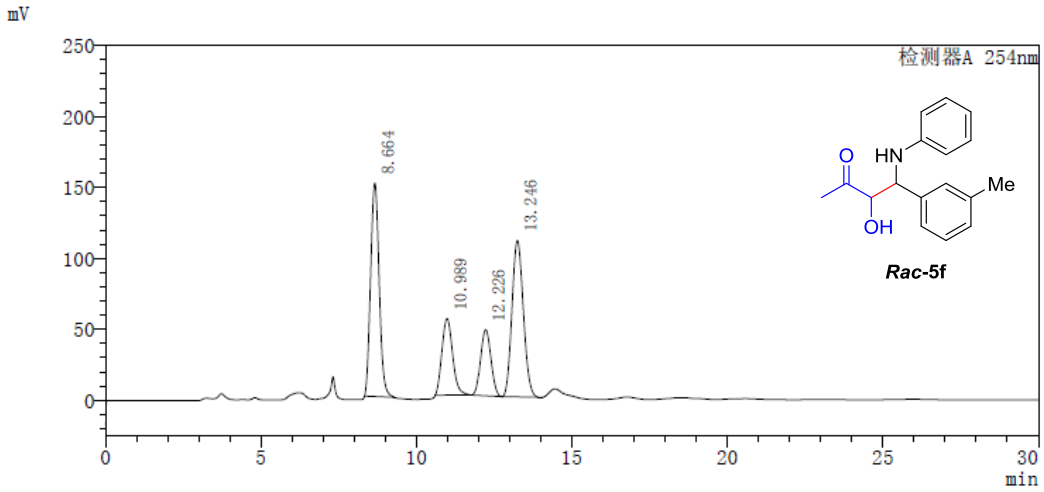
HPLC spectrum of **5e**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.399	668201	30209	9.907
2	11.548	904780	37853	13.415
3	14.312	4292621	151437	63.647
4	16.947	878811	28214	13.030
总计		6744412	247713	

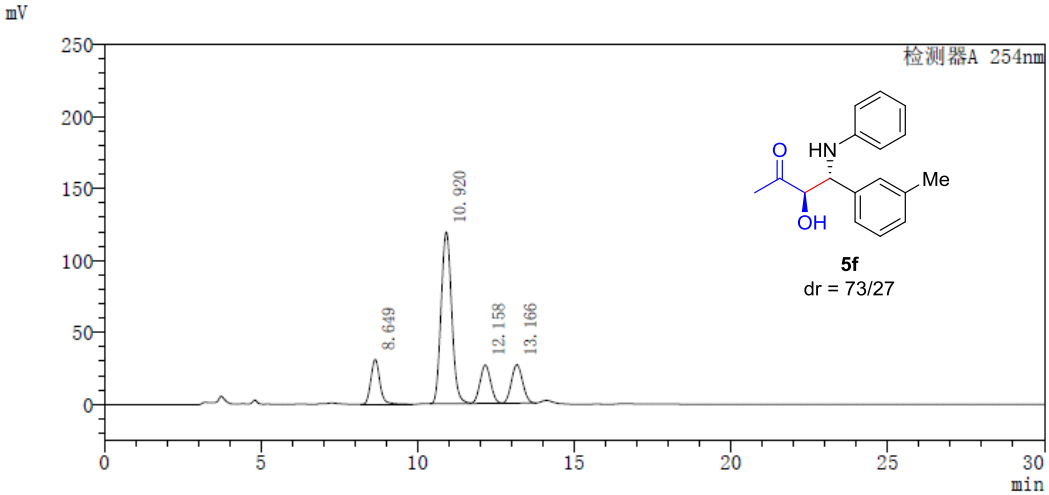
HPLC spectrum of ***Rac*-5f**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	8.664	2883667	150303	35.815
2	10.989	1293166	54041	16.061
3	12.226	1067432	46558	13.257
4	13.246	2807398	110116	34.867
总计		8051663	361017	

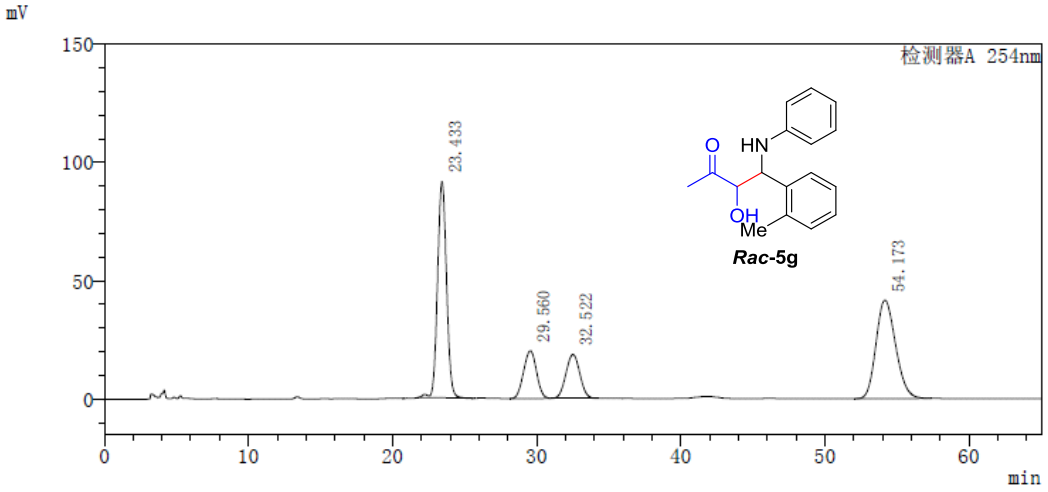
HPLC spectrum of **5f**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	8.649	619022	31186	13.139
2	10.920	2807193	119273	59.584
3	12.158	619659	26658	13.153
4	13.166	665414	26790	14.124
总计		4711288	203906	

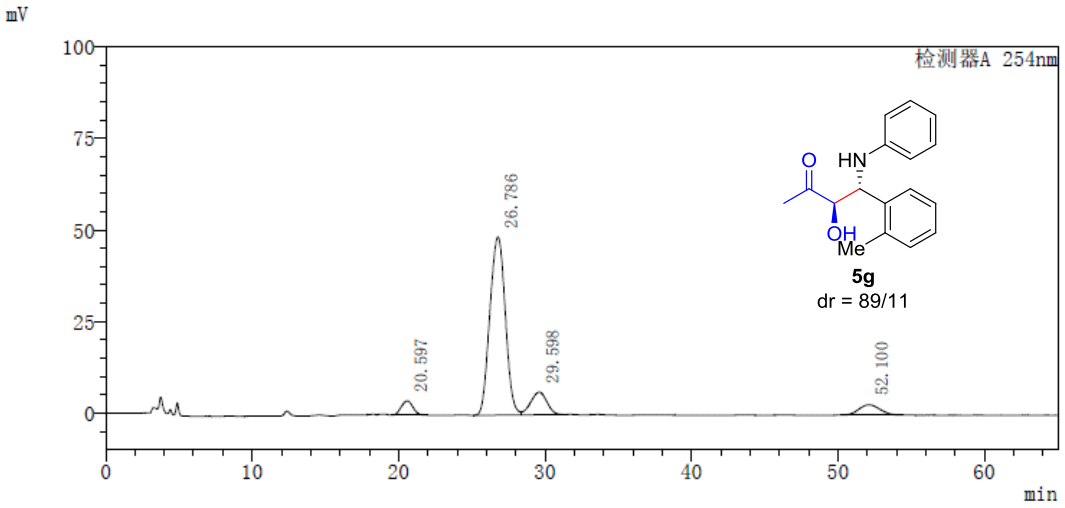
HPLC spectrum of ***Rac*-5g**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	23.433	3954003	91210	38.018
2	29.560	1260561	20162	12.120
3	32.522	1251063	18579	12.029
4	54.173	3934666	41593	37.832
总计		10400293	171544	

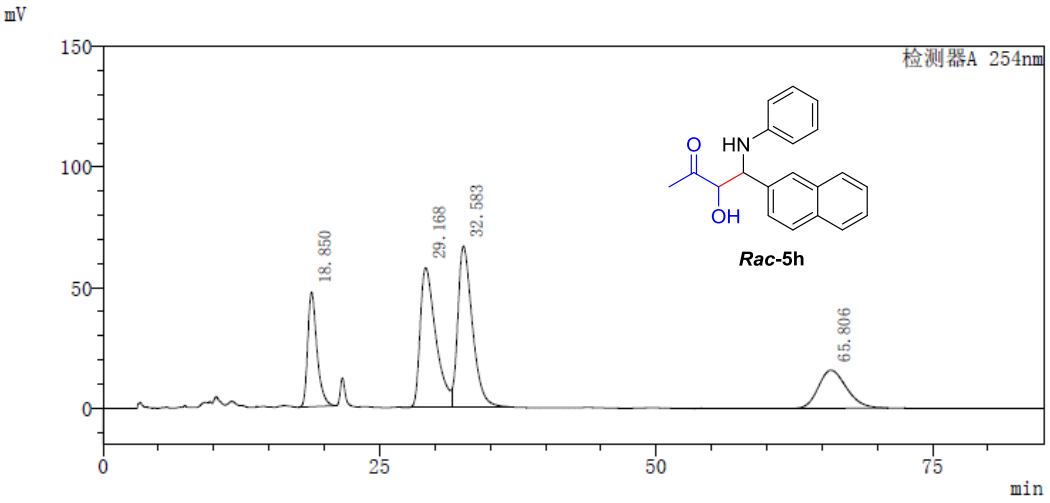
HPLC spectrum of **5g**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.597	218361	3913	4.792
2	26.786	3577902	48665	78.519
3	29.598	474389	6178	10.411
4	52.100	286083	2838	6.278
总计		4556735	61594	

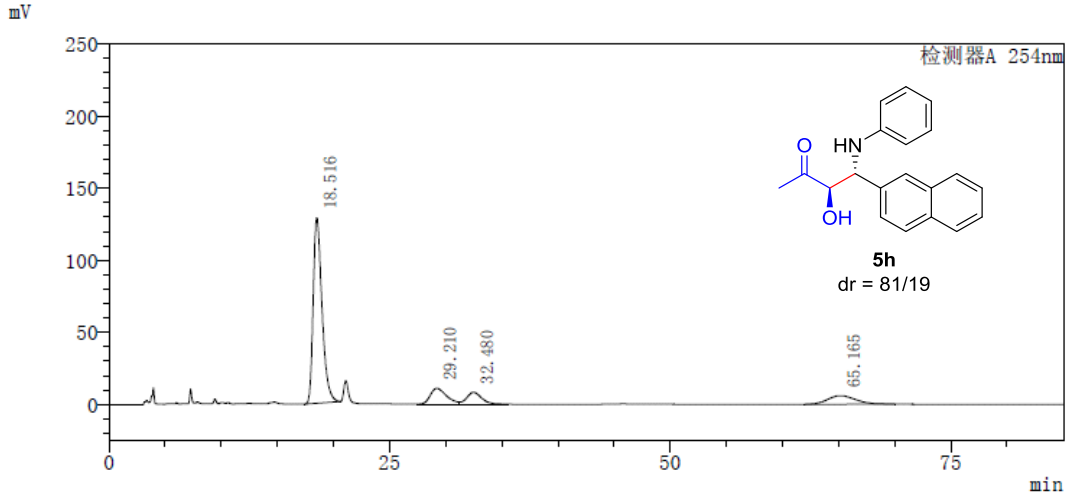
HPLC spectrum of ***Rac*-5h**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	18.850	2763008	47487	15.946
2	29.168	5662053	57853	32.676
3	32.583	6119214	66760	35.314
4	65.806	2783492	15755	16.064
总计		17327767	187855	

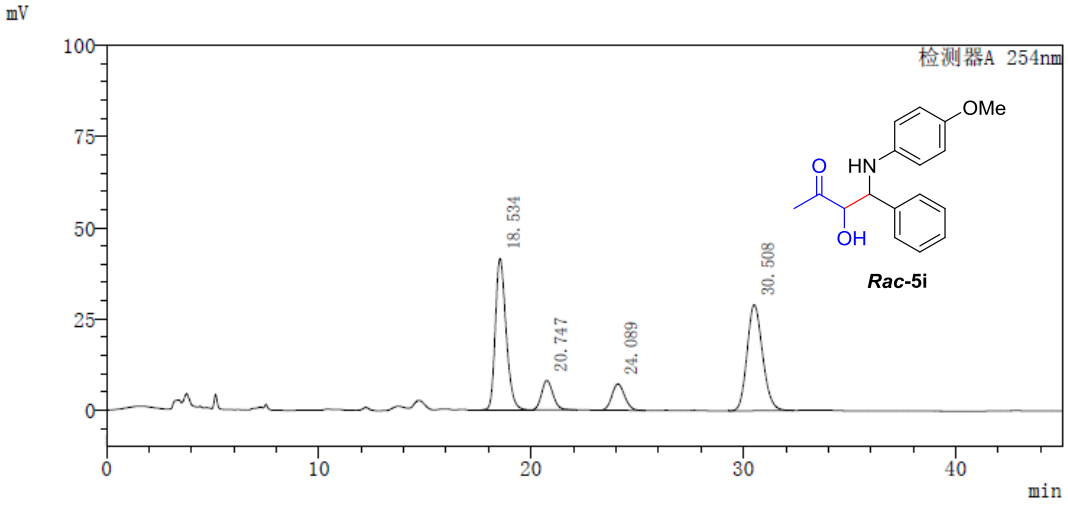
HPLC spectrum of **5h**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	18.516	7026587	128585	70.899
2	29.210	1098278	10980	11.082
3	32.480	759106	8248	7.659
4	65.165	1026764	5942	10.360
总计		9910736	153755	

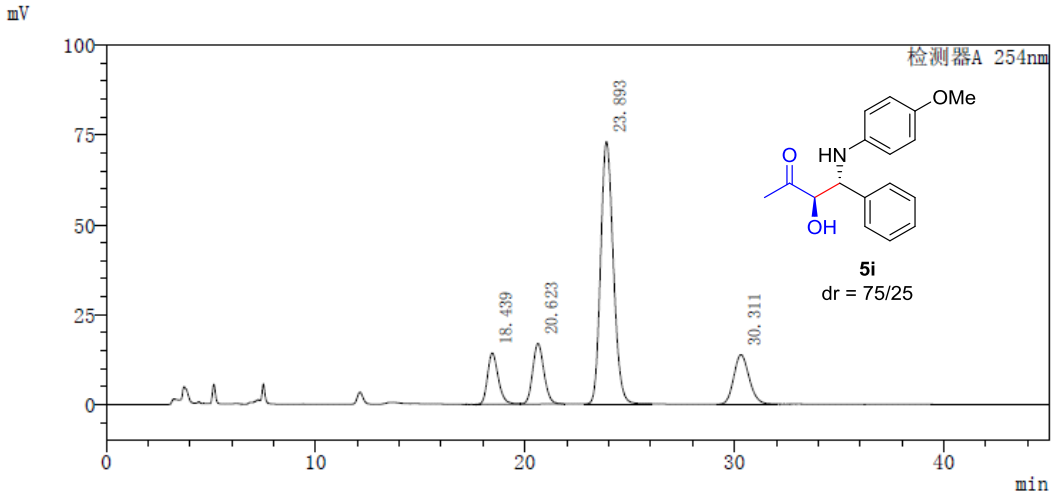
HPLC spectrum of ***Rac*-5i**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	18.534	1481358	41644	41.600
2	20.747	302512	8109	8.495
3	24.089	300793	7249	8.447
4	30.508	1476304	29109	41.458
总计		3560966	86111	

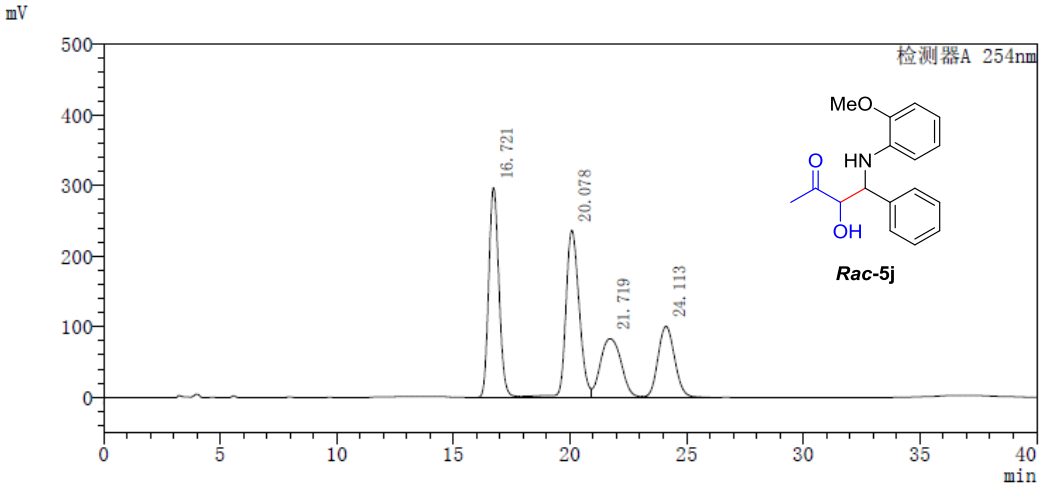
HPLC spectrum of **5i**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	18.439	510187	14251	10.405
2	20.623	629108	16874	12.831
3	23.893	3063393	73071	62.478
4	30.311	700480	13786	14.286
总计		4903167	117982	

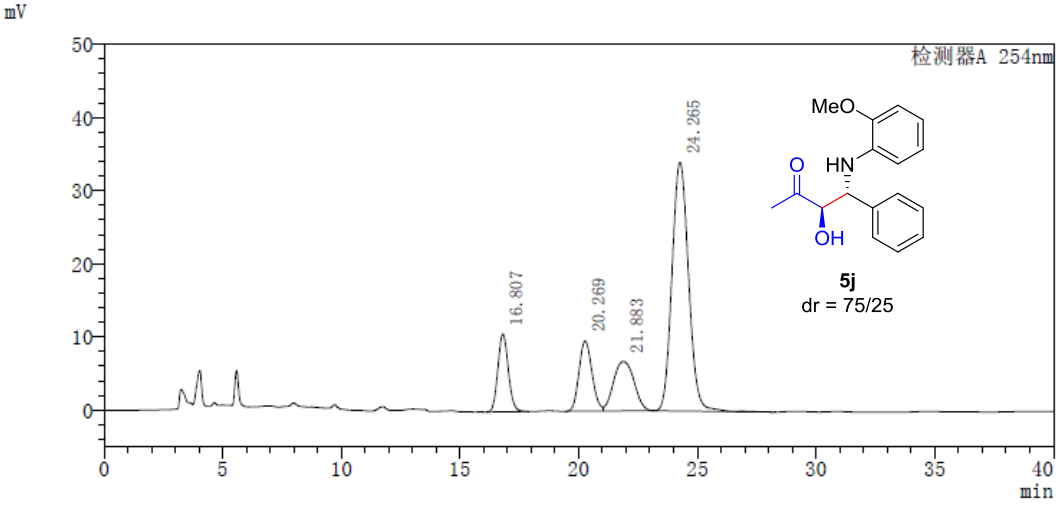
HPLC spectrum of ***Rac*-5j**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	16.721	9027205	297289	31.588
2	20.078	9402798	236550	32.903
3	21.719	5146899	83155	18.010
4	24.113	5000699	100772	17.499
总计		28577600	717765	

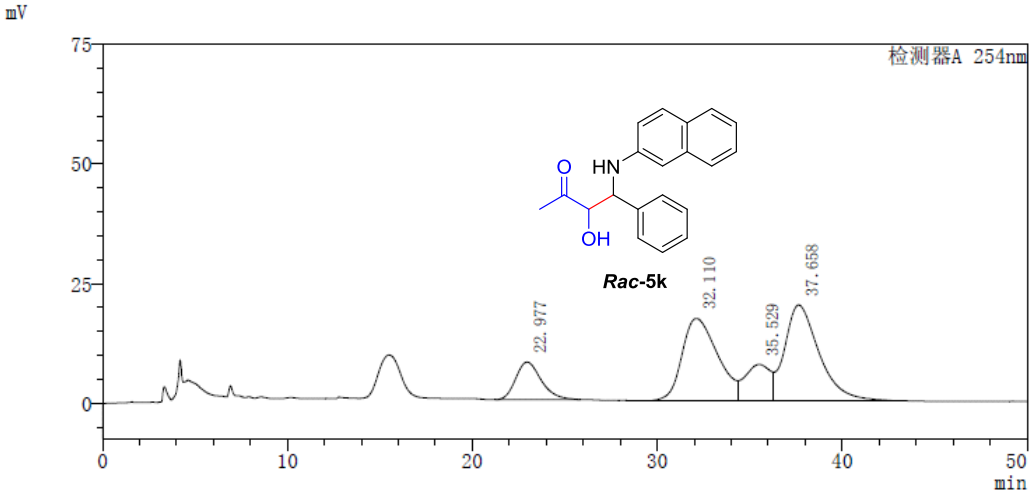
HPLC spectrum of **5j**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	16.807	325903	10623	11.887
2	20.269	365215	9584	13.321
3	21.883	404512	6744	14.754
4	24.265	1646094	33990	60.039
总计		2741724	60942	

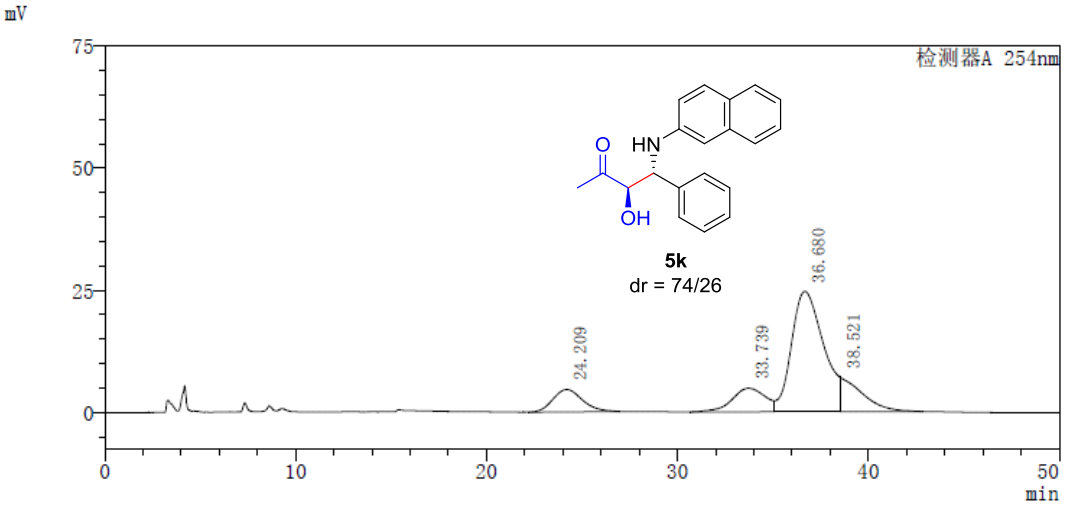
HPLC spectrum of ***Rac*-5k**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	22.977	748920	7842	11.816
2	32.110	2291920	17164	36.162
3	35.529	724891	7542	11.437
4	37.658	2572219	19965	40.584
总计		6337951	52513	

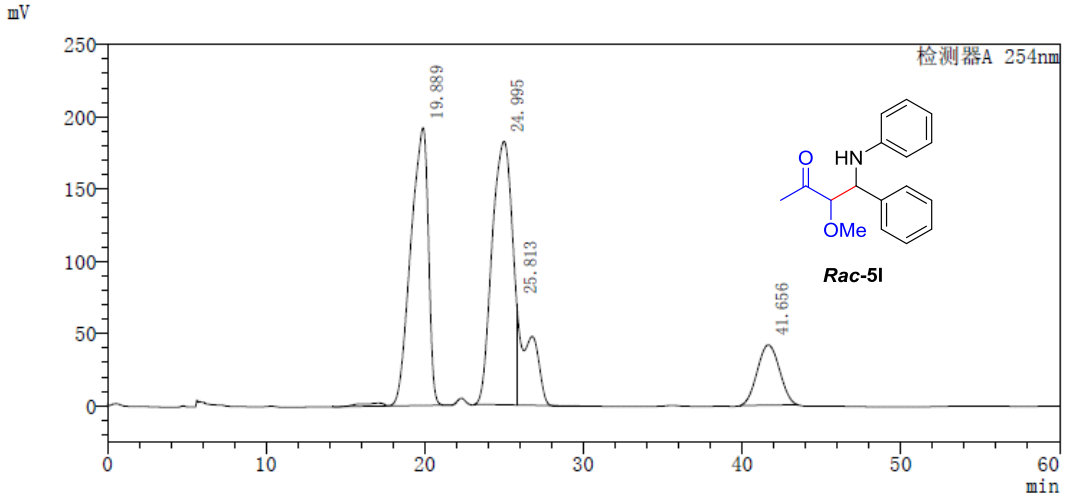
HPLC spectrum of **5k**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	24.209	489971	4577	10.824
2	33.739	590441	4847	13.044
3	36.680	2874182	24634	63.495
4	38.521	572019	7058	12.637
总计		4526614	41116	

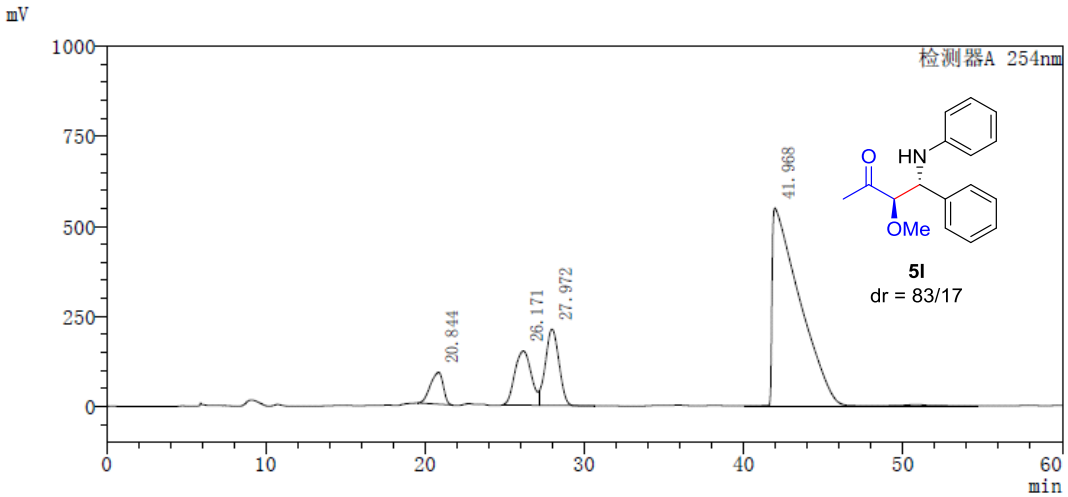
HPLC spectrum of ***Rac*-5l**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.889	14964440	192101	38.343
2	24.995	15951513	182189	40.872
3	25.813	4056313	68333	10.393
4	41.656	4055674	41684	10.392
总计		39027940	484306	

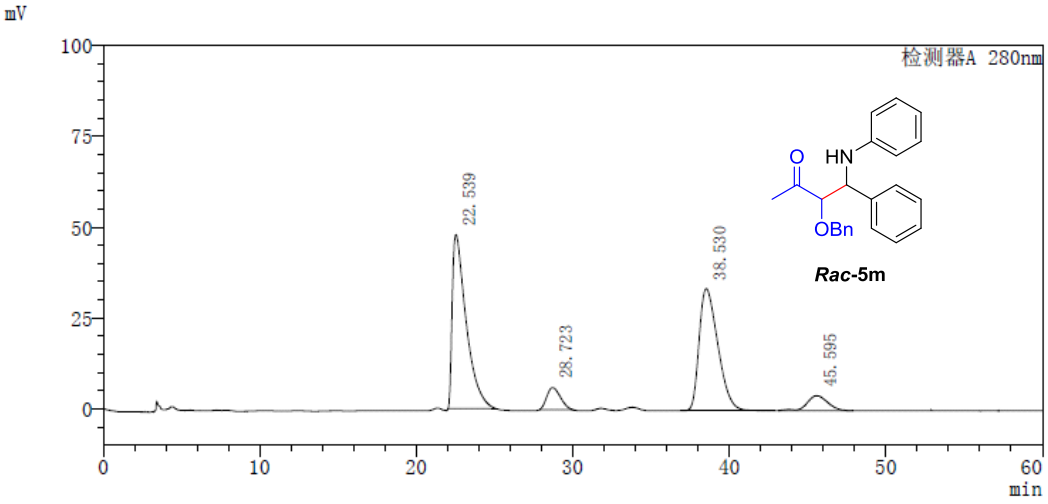
HPLC spectrum of **5l**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.844	4933836	88521	5.228
2	26.171	10902284	150815	11.552
3	27.972	12578698	212517	13.328
4	41.968	65962502	548951	69.892
总计		94377320	1000804	

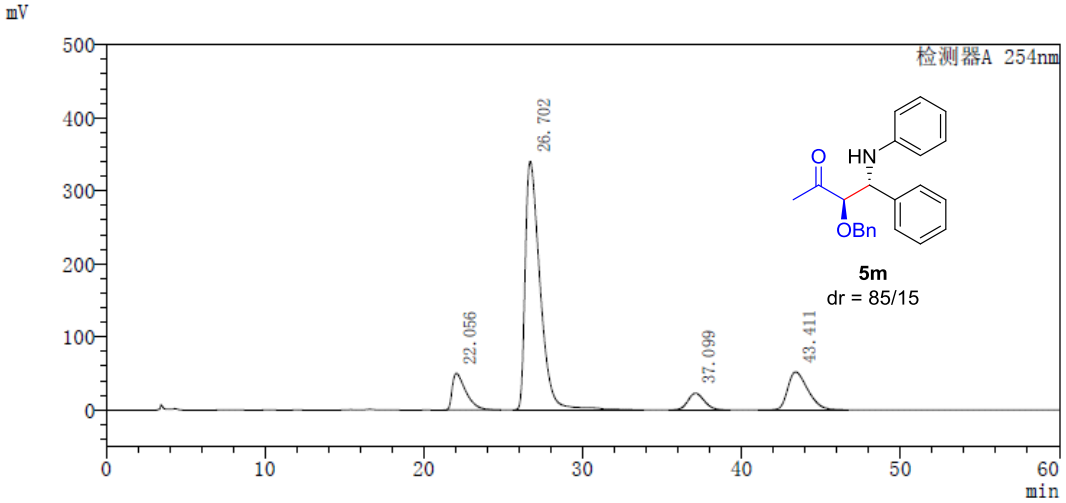
HPLC spectrum of ***Rac*-5m**



检测器A 280nm

No.	Retention Time	Area	Height	Concentration
1	22.539	2978868	47938	45.566
2	28.723	368617	6082	5.638
3	38.530	2804840	33615	42.904
4	45.595	385221	4148	5.892
总计		6537546	91782	

HPLC spectrum of **5m**



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	22.056	2977804	50010	9.545
2	26.702	22084297	339942	70.792
3	37.099	1617680	22730	5.186
4	43.411	4516347	51753	14.477
总计		31196128	464435	