Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cooperative Photocatalysis and *L*-/*D*-Proline Catalysis Enables Enantioselective Oxidative Cross-Dehydrogenative Coupling of Acyclic Benzylic Secondary Amines with Ketones

Chao-Jiu Long,[a] Hong-Ping Pu,[a] Ya-Nan Zhao,[b] Yan-Hong He*[a] and Zhi Guan*[a]

[a] Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

Emails: heyh@swu.edu.cn (for Y.-H. He); guanzhi@swu.edu.cn (for Z. Guan)

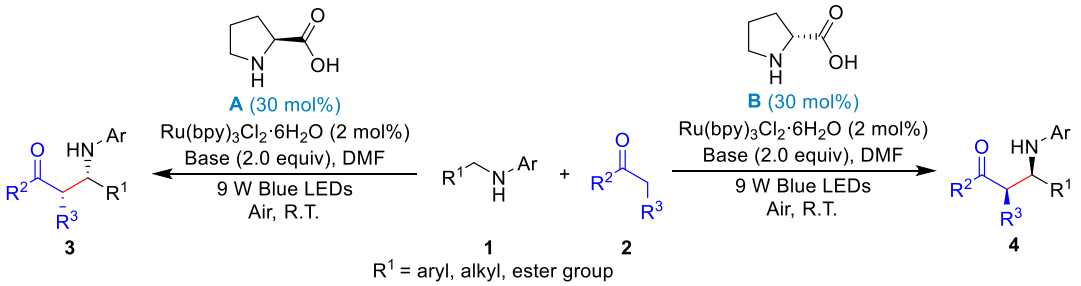
[b] Analytical and Testing Center, Southwest University, Chongqing 400715, China

Table of Contents

1. General considerations

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 °C. 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. Optical rotations were measured on a Perkin Elmer 341 Polarimeter at λ = 589 nm. 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, Chiralpak IC 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.). Single-crystal X-ray diffraction measurements were carried out on an Agilent SuperNova, Dual, Cu at home/near EosS2 diffractometer.

2. General procedure for the visible-light-induced enantioselective oxidative cross-dehydrogenative coupling of acyclic benzylic secondary 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 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. **2** (1.5–6.0 mmol, 5.0–20.0 equiv, as indicated), the chiral catalyst (0.009 mmol, 30 mol% **A** or **B**, as indicated) and the base (0.6 mmol, 2.0 equiv $KHCO_3$ or KOH, as indicated) 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 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, 25:1 to 5:1) as eluent to obtain the corresponding product **3** or **4**.

3. Preparation and characterization of substrates 1

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

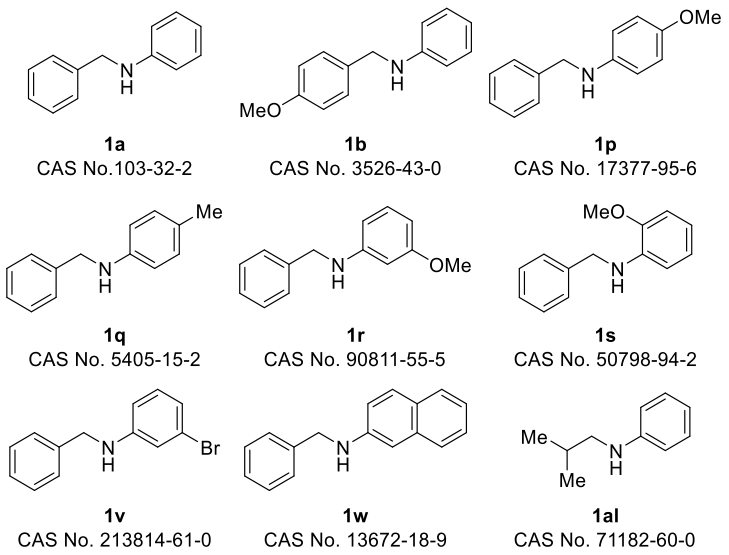
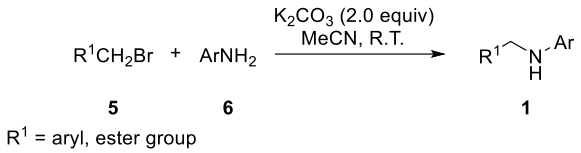


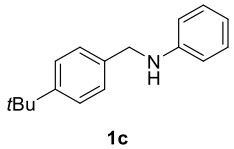
Figure S1. Substrates **1** purchased from commercial sources.

The other substrates **1** were synthesized according to literature:

General procedure[1]



A 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with **5** (5.0 mmol, 1.0 equiv), **6** (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**.

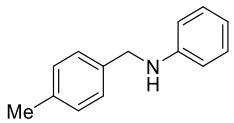


***N*-(4-(*tert*-butyl)benzyl)aniline (1c)[1]**

White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.28 (s, 2H), 4.10 (br s, 1H), 1.32 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 150.3, 148.2, 136.3, 129.3, 127.4, 125.6, 117.6, 113.0, 34.5, 31.4.



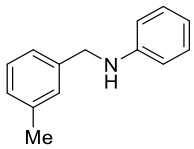
1d

***N*-(4-methylbenzyl)aniline (1d)[2]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.6 Hz, 2H), 7.14 (q, *J* = 7.6 Hz, 4H), 6.69 (t, *J* = 7.1 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 4.25 (s, 2H), 3.92 (br s, 1H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.3, 136.9, 136.5, 129.4, 129.3, 127.6, 117.6, 113.0, 48.2, 21.1.



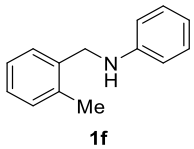
1e

***N*-(3-methylbenzyl)aniline (1e)[3]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.19 (m, 1H), 7.19 – 7.11 (m, 4H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 4.26 (s, 2H), 3.99 (br s, 1H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.3, 139.4, 138.3, 129.2, 128.5, 128.3, 128.0, 124.6, 117.6, 112.9, 48.4, 21.4.



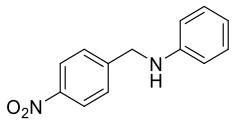
1f

***N*-(2-methylbenzyl)aniline (1f)[4]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.1 Hz, 1H), 7.20 – 7.16 (m, 5H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 4.25 (s, 2H), 3.82 (br s, 1H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.4, 137.1, 136.3, 130.4, 129.3, 128.3, 127.4, 126.2, 117.6, 112.8, 46.5, 18.9.



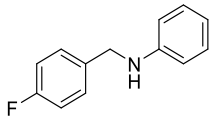
1g

***N*-(4-nitrobenzyl)aniline (1g)[4]**

Red oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 2H), 4.01 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.6, 147.4, 147.3, 129.4, 127.7, 123.9, 118.2, 113.0, 47.7.



1h

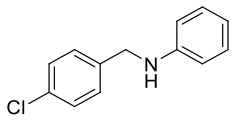
***N*-(4-fluorobenzyl)aniline (1h)[1]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.31 (m, 2H), 7.16 (t, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.29 (s, 2H), 4.04 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.1 (d, *J* = 245.2 Hz), 147.9, 135.1 (d, *J* = 3.0 Hz), 129.3, 129.0 (d, *J* = 8.0 Hz), 117.9, 115.4 (d, *J* = 21.4 Hz), 113.0, 47.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.6.



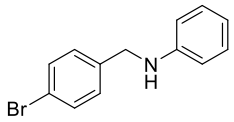
1i

***N*-(4-chlorobenzyl)aniline (1i)[4]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 4H), 7.16 – 7.14 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 2H), 4.28 (s, 2H), 4.02 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.9, 138.1, 132.9, 129.3, 128.8, 128.7, 117.9, 113.0, 47.7.



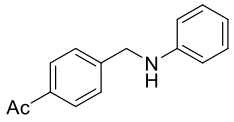
1j

***N*-(4-bromobenzyl)aniline (1j)[4]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.72 (t, *J* = 7.1 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 4.27 (s, 2H), 4.04 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.8, 138.6, 131.7, 129.3, 129.1, 121.0, 117.9, 113.0, 47.8.



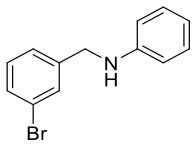
1k

1-(4-((Phenylamino)methyl)phenyl)ethan-1-one (1k)[1]

White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 2H), 4.41 (s, 2H), 4.30 (br s, 1H), 2.58 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 197.6, 147.7, 145.1, 136.3, 129.3, 128.7, 127.3, 118.0, 113.0, 48.1, 26.5.



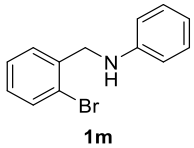
1l

***N*-(3-bromobenzyl)aniline (1l)[3]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.16 (q, *J* = 8.2 Hz, 3H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 4.27 (s, 2H), 4.01 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.8, 142.1, 130.4, 130.3, 130.2, 129.4, 125.9, 122.8, 117.9, 113.0, 47.8.



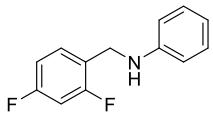
1m

***N*-(2-bromobenzyl)aniline (1m)[1]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.19 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.40 (s, 2H), 4.06 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.6, 138.2, 132.8, 129.3 × 2 (129.29, 129.26), 128.7, 127.6, 123.3, 117.9, 113.1, 48.5.



1n

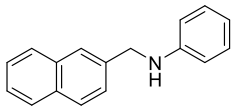
***N*-(2,4-difluorobenzyl)aniline (1n)[1]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.31 (m, 1H), 7.18 – 7.15 (m, 2H), 6.82 – 6.79 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 4.35 (s, 2H), 4.02 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.3 (dd, *J* = 248.2, 12.0 Hz), 160.8 (dd, *J* = 248.8, 11.9 Hz), 147.6, 130.2 (dd, *J* = 9.6, 6.1 Hz), 129.3, 122.3 (dd, *J* = 14.8, 3.5 Hz), 118.0, 113.0, 111.2 (dd, *J* = 21.0, 3.7 Hz), 103.8 (t, *J* = 25.4 Hz), 41.5 (d, *J* = 3.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$): δ -115.2 (d, *J* = 7.1 Hz), -114.9 (d, *J* = 7.1 Hz).



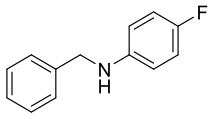
1o

***N*-(naphthalen-2-ylmethyl)aniline (1o)[1]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 – 7.75 (m, 4H), 7.49 – 7.41 (m, 3H), 7.20 – 7.12 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.46 (s, 2H), 4.08 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.2, 137.0, 133.6, 132.8, 129.3, 128.4, 127.8, 127.7, 126.2, 126.0, 125.8 × 2 (125.78, 125.76), 117.7, 113.0, 48.6.



1t

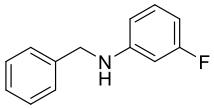
***N*-benzyl-4-fluoroaniline (1t)[4]**

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 6.86 (t, *J* = 8.6 Hz, 2H), 6.59 – 6.51 (m, 2H), 4.26 (s, 2H), 3.76 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.9 (d, *J* = 235.9 Hz), 144.5 (d, *J* = 1.6 Hz), 139.3, 128.7, 127.5, 127.3, 115.7 (d, *J* = 22.4 Hz), 113.7 (d, *J* = 7.4 Hz), 49.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -127.8.



1u

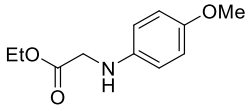
***N*-benzyl-3-fluoroaniline (1u)[5]**

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 4.1 Hz, 4H), 7.30 – 7.24 (m, 1H), 7.10 – 7.03 (m, 1H), 6.42 – 6.34 (m, 2H), 6.33 – 6.28 (m, 1H), 4.28 (s, 2H), 4.13 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 164.2 (d, *J* = 243.0 Hz), 150.0 (d, *J* = 10.7 Hz), 138.9, 130.3 (d, *J* = 10.2 Hz), 128.7, 127.5, 127.4, 108.8, 104.0 (d, *J* = 21.7 Hz), 99.6 (d, *J* = 25.4 Hz), 48.3.

^{19}F NMR (565 MHz, $CDCl_3$): δ -112.8.



1am

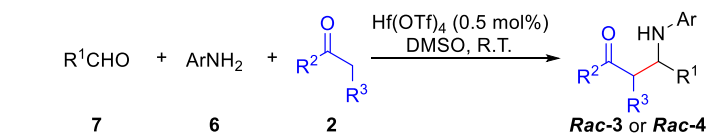
Ethyl (4-methoxyphenyl)glycinate (1am)[6]

Yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.05 (br s, 1H), 3.83 (s, 2H), 3.72 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.4, 152.7, 141.4, 114.9, 114.4, 61.2, 55.7, 46.8, 14.2.

4. General procedure for preparing racemic products as chiral HPLC controls[7]



7 **6** **2** ***Rac*-3** or ***Rac*-4**

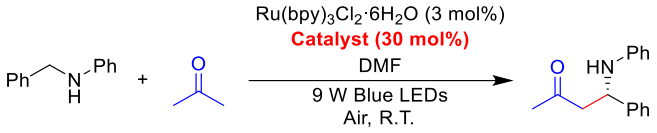
R^1 = aryl, alkyl, ester group

A round-bottomed flask equipped with a magnetic stirring bar was charged with **7** (0.3 mmol, 1.0 equiv), **6** (0.3 mmol, 1.0 equiv), **2** (6.0 mmol, 20.0 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 material 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*-4**).

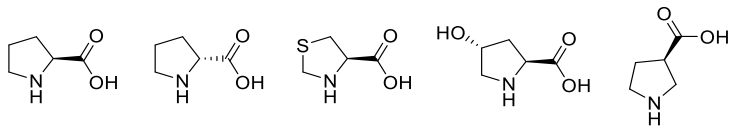
5. Optimization details

Table S1. Screening of catalysts.[a]



1a 2a 3a

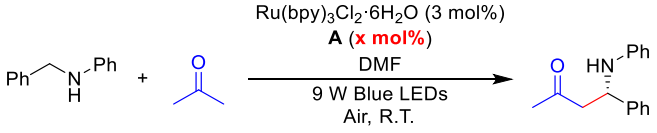
Entry	Catalyst	Yield [%][b]	ee [%][c]
1	**A**	50	90
2	**B**	49	–90
3	**C**	47	56
4	**D**	45	90
5	**E**	20	22



A B C D E

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (6 mg, 0.009 mmol, 3 mol%) and Catalyst (0.09 mmol, 30 mol%) in DMF (dried over 3Å molecular sieves, 3.0 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column.

Table S2. Screening of the amounts of **A**.[a]

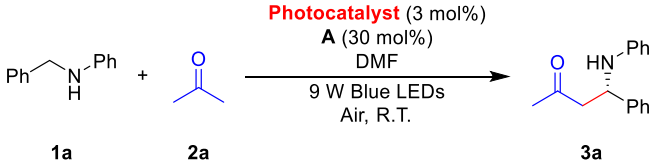


1a 2a 3a

Entry	**A** [mol%]	Yield [%][b]	ee [%][c]
1	10	38	90
2	20	46	90
3	30	50	90
4	40	50	90
5	50	50	90

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (6 mg, 0.009 mmol, 3 mol%) and **A** in DMF (dried over 3Å molecular sieves, 3.0 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column.

Table S3. Screening of photocatalysts.[a]



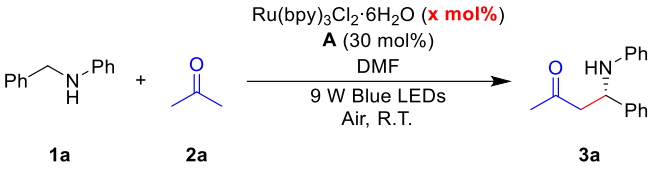
1a **2a** **3a**

Entry	Photocatalyst	Yield [%][b]	ee [%][c]
1	$Ru(bpy)_3Cl_2$ $6H_2O$	50	90
2	Eosin Y	Trace	——
3	Rose Bengal	Trace	——
4	Rhodamine 6G	38	90
5	Mes-Acr-$Me^+ClO_4^-$	43	76
6	*fac*-$Ir(ppy)_3$	35	89
7	$Ru(bpy)_3PF_6$	26	82
8	Methyene blue	18	90
9	Fluorescein	7	88
10	$[Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	35	88
11	$Ir(ppy)_2(dtbbpy)PF_6$	49	87
12	None	N.R.[d]	——

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666

μL, 9.0 mmol, 30.0 equiv), Photocatalyst (0.009 mmol, 3 mol%) and **A** (11 mg, 0.09 mmol, 30 mol%) in DMF (dried over 3Å molecular sieves, 3.0 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column. [d] No reaction.

Table S4. Screening of the amounts of $Ru(bpy)_3Cl_2$ $6H_2O$.[a]

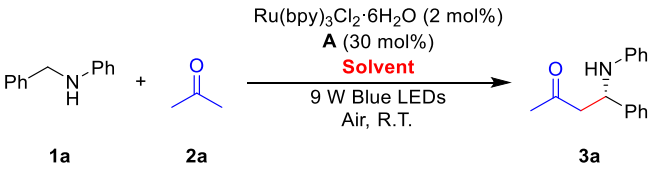


1a 2a 3a

Entry	$Ru(bpy)_3Cl_2$ $6H_2O$ (mol%)	Yield [%][b]	ee [%][c]
1	1	31	90
2	2	50	90
3	3	50	90
4	4	47	91
5	5	46	88

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ and **A** (11 mg, 0.09 mmol, 30 mol%) in DMF (dried over 3Å molecular sieves, 3.0 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column.

Table S5. Screening of solvents.[a]



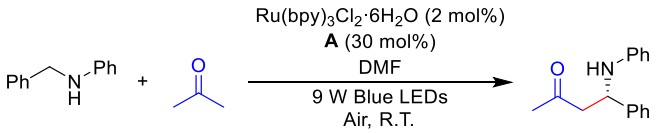
1a 2a 3a

Entry	Solvent	Yield [%][b]	ee [%][c]
1	DMF	50	90
2	MeCN	N.D.[d]	——
3	MeOH	14	90
4	EtOH	15	88

5	THF	N.R.[e]	——
6	DMSO	48	54
7	DCE	Trace	——

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) and **A** (11 mg, 0.09 mmol, 30 mol%) in solvent (dried over molecular sieves, 3.0 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column. [d] Not detected. [e] No reaction.

Table S6. Screening of the amounts of DMF.[a]

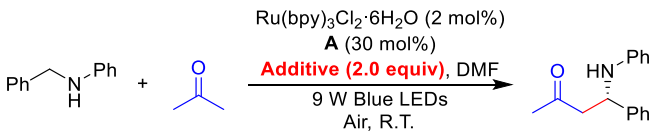


1a **2a** **3a**

Entry	DMF [mL]	Yield [%][b]	ee [%][c]
1	1.0	46	89
2	2.0	50	90
3	3.0	50	90
4	4.0	49	88

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%) and **A** (11 mg, 0.09 mmol, 30 mol%) in DMF (dried over 3Å molecular sieves) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column.

Table S7. Screening of additives.[a]



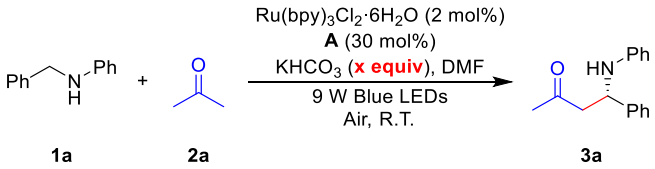
1a **2a** **3a**

Entry	Additive	Yield [%][b]	ee [%][c]

1	None	50	90
2	CH_3COOH	44	89
3	PhCOOH	Trace	——
4	$Cu(OAc)_2·H_2O$	N.R.[d]	——
5	CuI	N.R.[d]	——
6	2,6-Lutidine	50	91
7	K_2CO_3	55	97
8[e]	K_2CO_3	60	96
9[e]	Na_2CO_3	42	97
10[e]	Cs_2CO_3	Trace	——
11[e]	$KHCO_3$	65	97
12[e]	KOH	Trace	——

[a] Reaction conditions: **1a** (55 mg, 0.3 mmol, 1.0 equiv), **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (4 mg, 0.006 mmol, 2 mol%), **A** (11 mg, 0.09 mmol, 30 mol%) and additive (0.6 mmol, 2.0 equiv) in DMF (dried over 3Å molecular sieves, 2.0 mL) irradiated with 9 W blue LEDs under air at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column. [d] No reaction. [e] **2a**, **A** and additive were added after the photo-oxidation process was completed, and then the mixture was stirred without light.

Table S8. Screening of the amounts of $KHCO_3$.[a]



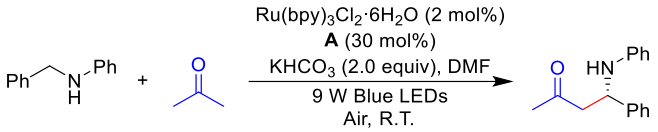
1a **2a** **3a**

Entry	$KHCO_3$ (x equiv)	Yield [%][b]	ee [%][c]
1	0.5	50	91
2	1.0	54	94
3	1.5	56	94
4	2.0	65	97
5	2.5	65	97

6	3.0	61	95

[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, 2.0 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2a** (dried over 3Å molecular sieves, 666 μL, 9.0 mmol, 30.0 equiv), **A** (11 mg, 0.09 mmol, 30 mol%) and $KHCO_3$ were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column.

Table S9. Screening of the amounts of **2a**.[a]

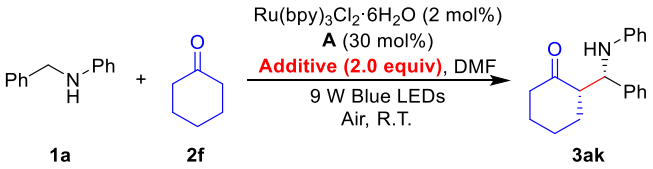


1a **2a** **3a**

Entry	**2a** [equiv]	Yield [%][b]	ee [%][c]
1	5.0	50	96
2	10.0	56	95
3	15.0	60	97
4	20.0	65	97
5[d]	20.0	57	97
6	25.0	65	97
7	30.0	65	97
8	40.0	61	97
9	50.0	56	94

[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, 2.0 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2a** (dried over 3Å molecular sieves), **A** (11 mg, 0.09 mmol, 30 mol%) and $KHCO_3$ (60 mg, 0.6 mmol, 2.0 equiv) were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak AD-H column. [d] All components were added at one time and irradiation.

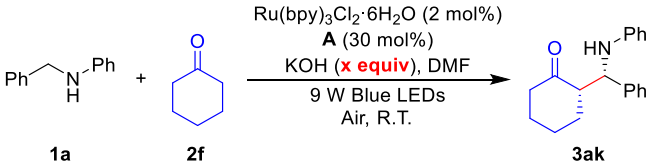
Table S10. Screening of additives (for the reaction using cyclohexanone).[a]



Entry	Additive	Yield [%][b]	dr [*syn*/*anti*][c]	ee [%[*syn*]/%[*anti*]][c]
1	None	45	37/63	50/19
2	K_2CO_3	63	58/42	75/35
3	Na_2CO_3	69	51/49	72/29
4	Cs_2CO_3	51	54/46	85/79
5	$KHCO_3$	74	55/45	80/43
6	KOH	74	62/38	87/58

[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, 2.0 mL) irradiated with 9 W blue LEDs under air at room temperature. After full conversion of **1a**, the light was turned off. **2f** (156 µL, 1.5 mmol, 5.0 equiv), **A** (11 mg, 0.09 mmol, 30 mol%) and additive (0.6 mmol, 2.0 equiv) were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column.

Table S11. Screening of the amounts of KOH (for the reaction using cyclohexanone).[a]



Entry	KOH (equiv)	Yield [%][b]	dr [*syn*/*anti*][c]	ee [%[*syn*]/%[*anti*]][c]
1	0.3	68	48/52	60/27
2	0.6	73	56/44	60/27
3	0.9	72	42/58	65/33
4	1.5	73	56/44	76/26
5	2.0	74	62/38	87/58
6	2.5	73	54/46	81/48

[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, 2.0 mL) irradiated with 9 W blue LEDs

under air at room temperature. After full conversion of **1a**, the light was turned off. **2f** (156 μL, 1.5 mmol, 5.0 equiv), **A** (11 mg, 0.09 mmol, 30 mol%) and KOH were added. [b] Isolated yield. [c] Determined by HPLC analysis using a chiralpak OJ-H column.

6. Scale-up experiments

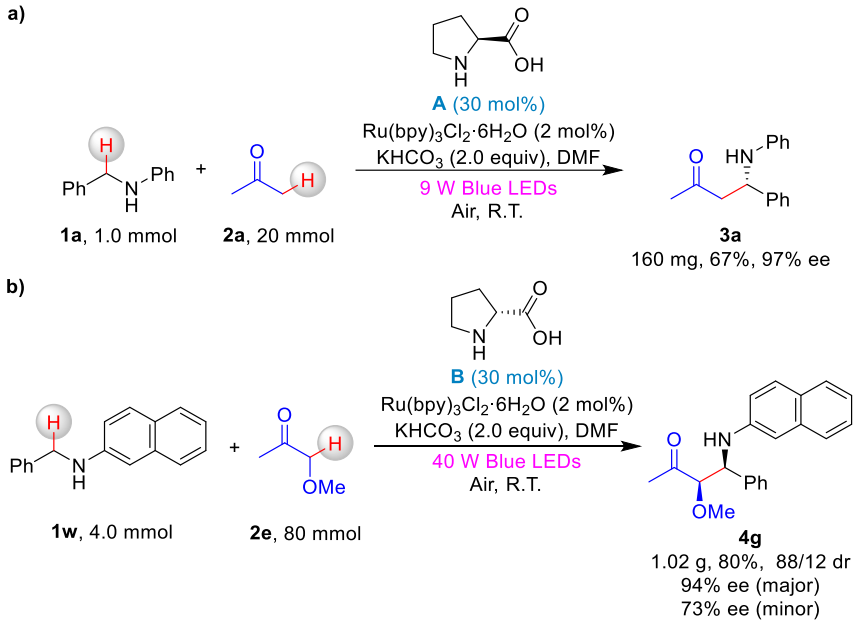


Figure S2. Scale-up experiments.

Reaction conditions:

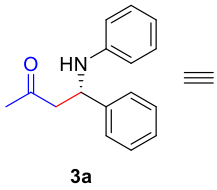
a) **1a** (183 mg, 1.0 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (13 mg, 0.02 mmol, 2 mol%) in DMF (dried over 3Å molecular sieves, 7 mL) irradiated with 9 W blue LEDs under air at room temperature for 17 h. Then, the light was turned off. **2a** (1.5 mL, 20 mmol, 20.0 equiv), **A** (34 mg, 0.3 mmol, 30 mol%) and $KHCO_3$ (200 mg, 2.0 mmol, 2.0 equiv) were added at room temperature for 24 h.

b) **1w** (933 mg, 4.0 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2·6H_2O$ (51 mg, 0.08 mmol, 2 mol%) in DMF (dried over 3Å molecular sieves, 27 mL) irradiated with 40 W blue LEDs under air at room temperature for 16 h. Then, the light was turned off. **2e** (7.4 mL, 80 mmol, 20.0 equiv), **B** (138 mg, 1.2 mmol, 30 mol%) and $KHCO_3$ (801 mg, 8.0 mmol, 2.0 equiv) were added at room temperature for 19 h.

Isolated yield. ee and dr of products were determined by chiral HPLC analysis

7. Crystallographic data of compound 3a

Crystallographic data (excluding structure factors) for the structure reported in this work has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC 2217984**. Copy of the data can be obtained free of charge on application to The director, CCDC, 12 Union Road, Cambridge DB21EZ, UK (fax: + 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).



3a

≡

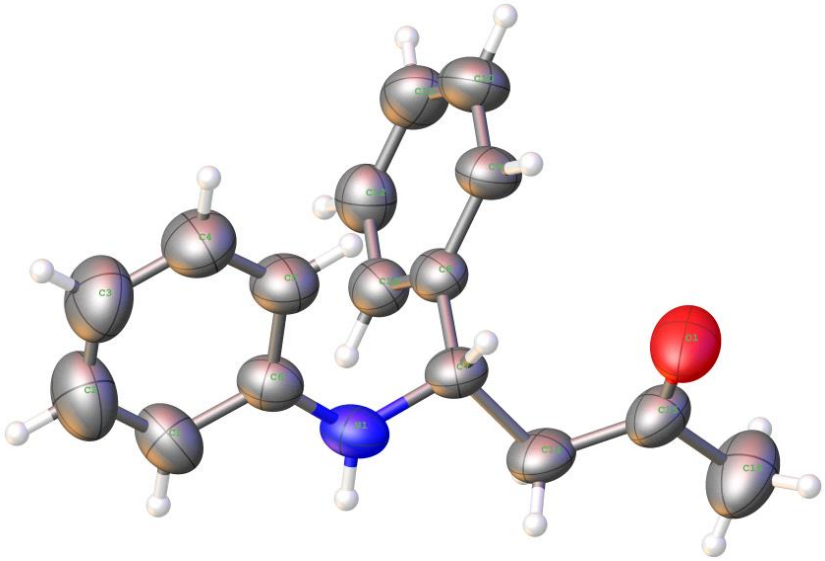


Table S12. Crystal data and structure refinement for **3a**.

Identification code	gz-6-14
Empirical formula	$C_{16}H_{17}NO$
Formula weight	239.30
Temperature/K	289 (1)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.1534 (5)
b/Å	14.2426 (10)
c/Å	7.9499 (6)
α/°	90
β/°	93.172 (7)

γ/°	90
Volume/Å^3	695.66 (9)
Z	2
ρ_{calc}g/cm^3	1.142
μ/mm^{-1}	0.554
F(000)	256.0
Crystal size/mm^3	0.44 × 0.43 × 0.21
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.146 to 143.44
Index ranges	-7 ≤ h ≤ 6, -17 ≤ k ≤ 16, -9 ≤ l ≤ 9
Reflections collected	6709
Independent reflections	2605 [R_{int} = 0.0768, R_{sigma} = 0.0578]
Data/restraints/parameters	2605/1/164
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0763, wR_2 = 0.2125
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.2356
Largest diff. peak/hole / e Å^{-3}	0.21/-0.35
Flack parameter	-0.1 (8)

Table S13. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for **3a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U (eq)
O1	-1010 (7)	-2981 (3)	-1991 (8)	95.1 (15)
N1	-7142 (7)	-4154 (3)	-2719 (5)	60.3 (10)
C1	-9761 (9)	-5344 (5)	-3497 (7)	72.8 (14)
C2	-10316 (12)	-6277 (6)	-3778 (11)	96 (2)
C3	-8797 (12)	-6974 (6)	-3494 (11)	100 (2)
C4	-6702 (12)	-6745 (4)	-2916 (9)	86.0 (17)

C5	-6121 (10)	-5815 (4)	-2610 (7)	70.4 (12)
C6	-7655 (8)	-5099 (4)	-2905 (5)	57.1 (10)
C7	-5111 (7)	-3834 (3)	-1881 (5)	54.1 (9)
C8	-4952 (7)	-4052 (3)	-1 (5)	52.5 (9)
C9	-3038 (8)	-4443 (4)	723 (6)	61.8 (11)
C10	-2878 (9)	-4626 (4)	2440 (7)	74.6 (14)
C11	-4539 (9)	-4407 (4)	3437 (6)	72.1 (13)
C12	-6432 (8)	-4014 (4)	2733 (6)	65.9 (12)
C13	-6622 (8)	-3834 (3)	1012 (6)	58.6 (10)
C14	-4818 (9)	-2788 (3)	-2235 (7)	65.2 (12)
C15	-2525 (9)	-2452 (4)	-1968 (7)	66.9 (12)
C16	-2157 (14)	-1411 (5)	-1775 (13)	104 (2)

Table S14. Anisotropic displacement parameters ($Å^2×10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	69 (2)	61 (2)	156 (4)	11 (3)	20 (3)	15.5 (18)
N1	61 (2)	54 (2)	64.0 (18)	-0.3 (17)	-7.1 (16)	16.0 (17)
C1	59 (2)	81 (3)	77 (3)	-15 (3)	-6 (2)	5 (2)
C2	78 (4)	93 (5)	116 (5)	-25 (4)	2 (3)	-16 (3)
C3	98 (5)	72 (4)	129 (6)	-13 (4)	4 (4)	-17 (4)
C4	89 (4)	59 (3)	109 (4)	2 (3)	-4 (3)	9 (3)
C5	69 (3)	57 (3)	84 (3)	3 (2)	-3 (2)	11 (2)
C6	61 (2)	56 (2)	53.6 (18)	-4.3 (18)	-2.9 (17)	10.0 (19)
C7	59 (2)	43.9 (19)	58.8 (19)	6.6 (17)	0.4 (16)	9.4 (17)
C8	57 (2)	40.0 (18)	60.1 (19)	1.2 (17)	-4.6 (16)	1.9 (16)
C9	57 (2)	61 (3)	67 (2)	10 (2)	-3.0 (17)	12.2 (19)
C10	75 (3)	75 (3)	72 (3)	13 (3)	-17 (2)	5 (3)

C11	83 (3)	74 (3)	58 (2)	5 (2)	-5 (2)	-5 (3)
C12	66 (2)	66 (3)	65 (2)	-6 (2)	4.7 (19)	-7 (2)
C13	59 (2)	48 (2)	68 (2)	0 (2)	-2.9 (18)	1.9 (19)
C14	69 (3)	46 (2)	81 (3)	11 (2)	4 (2)	16 (2)
C15	72 (3)	48 (2)	81 (3)	10 (2)	14 (2)	5 (2)
C16	104 (5)	58 (3)	152 (7)	-2 (4)	30 (5)	0 (3)

Table S15. Bond lengths for **3a**.

Atom	Atom	Length/Å
O1	C15	1.200 (6)
N1	C6	1.388 (7)
N1	C7	1.456 (6)
C1	C2	1.387 (10)
C1	C6	1.399 (7)
C2	C3	1.374 (12)
C3	C4	1.384 (10)
C4	C5	1.389 (9)
C5	C6	1.401 (7)
C7	C8	1.524 (6)
C7	C14	1.529 (6)
C8	C9	1.398 (6)
C8	C13	1.376 (7)
C9	C10	1.388 (7)
C10	C11	1.364 (9)
C11	C12	1.383 (8)
C12	C13	1.391 (7)
C14	C15	1.494 (8)
C15	C16	1.506 (8)

Table S16. Bond angles for **3a**.

Atom	Atom	Atom	Angle/°
C6	N1	C7	122.4 (3)
C2	C1	C6	120.6 (6)
C3	C2	C1	120.5 (6)
C2	C3	C4	119.8 (7)
C3	C4	C5	120.7 (6)
C4	C5	C6	120.0 (6)
N1	C6	C1	118.6 (4)
N1	C6	C5	122.8 (5)
C1	C6	C5	118.5 (5)
N1	C7	C8	113.1 (4)
N1	C7	C14	109.1 (4)
C8	C7	C14	112.1 (4)
C9	C8	C7	119.5 (4)
C13	C8	C7	121.2 (4)
C13	C8	C9	119.3 (4)
C10	C9	C8	119.5 (5)
C11	C10	C9	120.9 (5)
C10	C11	C12	119.9 (5)
C11	C12	C13	119.7 (5)
C8	C13	C12	120.6 (4)
C15	C14	C7	114.0 (4)
O1	C15	C14	121.7 (5)
O1	C15	C16	120.5 (6)
C14	C15	C16	117.8 (5)

Table S17. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a**.

Atom	*x*	*y*	*z*	U (eq)
H1	-8057	-3742	-3112	72
H1A	-10799	-4877	-3705	87
H2	-11725	-6432	-4162	115
H3	-9176	-7599	-3688	120
H4	-5673	-7217	-2731	103
H5	-4713	-5669	-2209	84
H7	-3923	-4169	-2393	65
H9	-1880	-4579	59	74
H10	-1621	-4903	2917	90
H11	-4398	-4521	4590	87
H12	-7574	-3871	3408	79
H13	-7890	-3563	541	70
H14A	-5317	-2661	-3391	78
H14B	-5731	-2432	-1509	78
H16A	-1848	-1264	-608	155
H16B	-3439	-1080	-2182	155
H16C	-948	-1226	-2413	155

Experimental

Single crystals of $C_{16}H_{17}NO$ **[3a]** were obtained by slow evaporation of the solvent from a petroleum ether and EtOAc (v/v, 25/1) solution of **3a**. A suitable crystal was selected and **[]** on a SuperNova, Dual, Cu at home/near, EosS2 diffractometer. The crystal was kept at 289 (1) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst., 40, 786-790; Palatinus, L. & van der Lee, A. (2008). J. Appl. Cryst. 41, 975-984; Palatinus, L., Prathapa, S. J. & van Smaalen, S. (2012). J. Appl. Cryst. 45, 575-580.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 3a

Crystal Data for $C_{16}H_{17}NO$ (M =239.30 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 6.1534 (5) Å, b = 14.2426 (10) Å, c = 7.9499 (6) Å, β = 93.172 (7)°, V = 695.66 (9) Å^3, Z = 2, T = 289 (1) K, μ (CuKα) = 0.554 mm^{-1}, *Dcalc* = 1.142 g/cm^3, 6709 reflections measured (11.146° ≤ 2Θ ≤ 143.44°), 2605 unique (R_{int} = 0.0768, R_{sigma} = 0.0578) which were used in all calculations. The final R_1 was 0.0763 (I > 2σ(I)) and wR_2 was 0.2356 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C (H) groups, All C (H, H) groups, All N (H) groups

At 1.5 times of:

All C (H, H, H) groups

2.a Ternary CH refined with riding coordinates:

C7 (H7)

2.b Secondary CH2 refined with riding coordinates:

C14 (H14A, H14B)

2.c Aromatic/amide H refined with riding coordinates:

N1 (H1), C1 (H1A), C2 (H2), C3 (H3), C4 (H4), C5 (H5), C9 (H9), C10 (H10), C11 (H11), C12 (H12), C13 (H13)

2.d Idealised Me refined as rotating group:

C16 (H16A, H16B, H16C)

8. Stern-Volmer luminescence quenching experiments

The measurements were performed using a 0.05 mM solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ 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 revealed that **1a** could significantly quench $Ru(bpy)_3^{2+}$ (Figure S3, Figure S4).

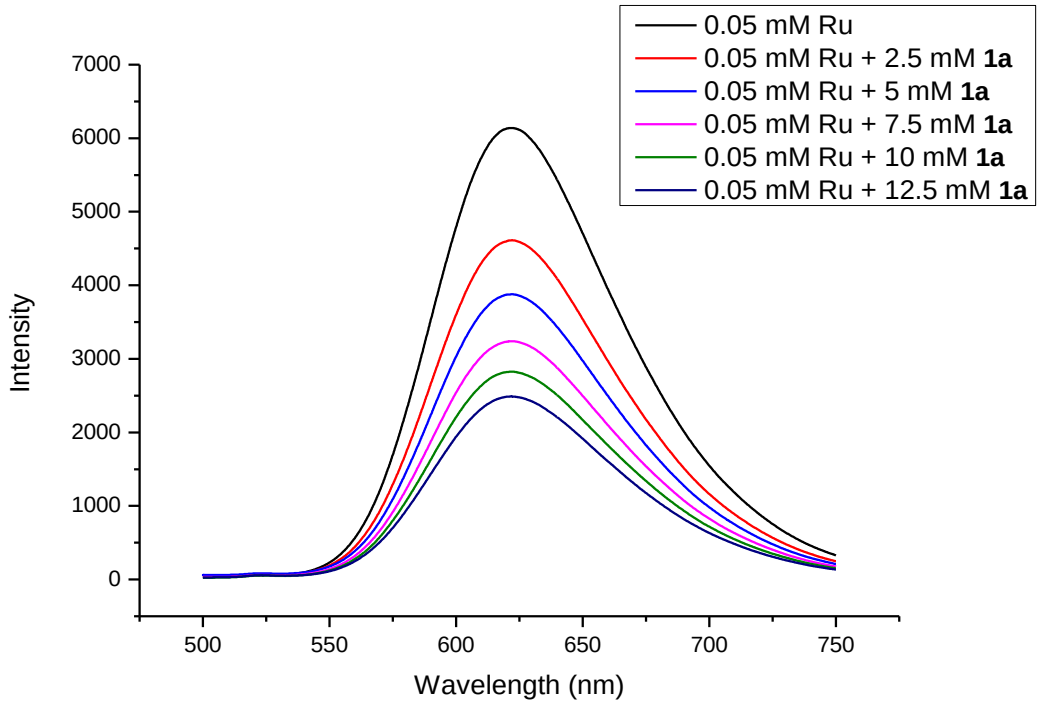


Figure S3. Fluorescence quenching of 0.05 mM $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (in DMF) by increasing concentration of **1a**.

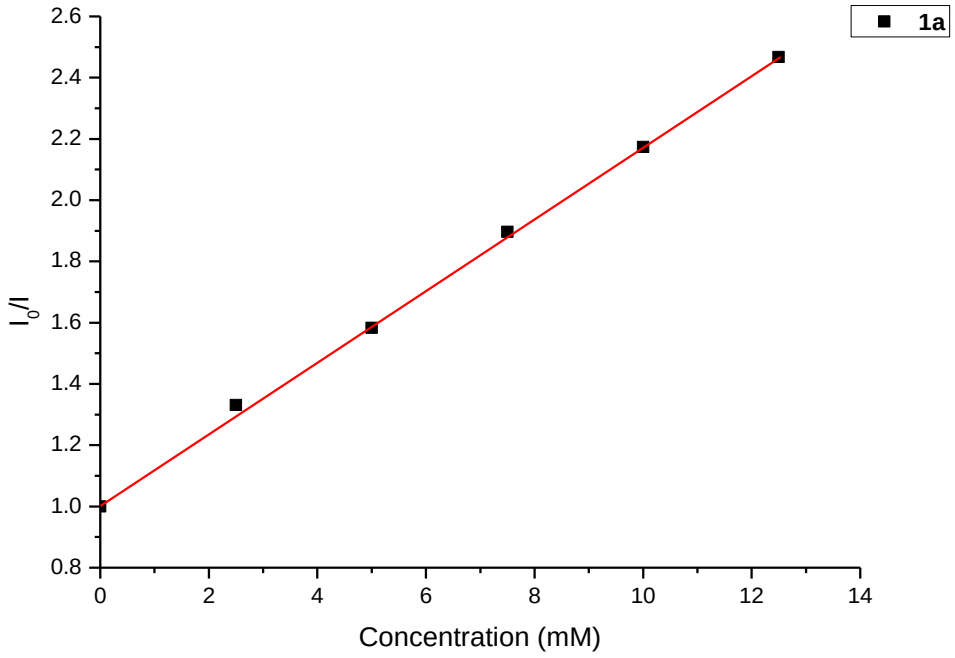


Figure S4. Stern-Volmer plots of fluorescence quenching 0.05 mM $Ru(bpy)_3Cl_2·6H_2O$ (in DMF) by **1a**.

9. 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 DMF or 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 +4.5 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.

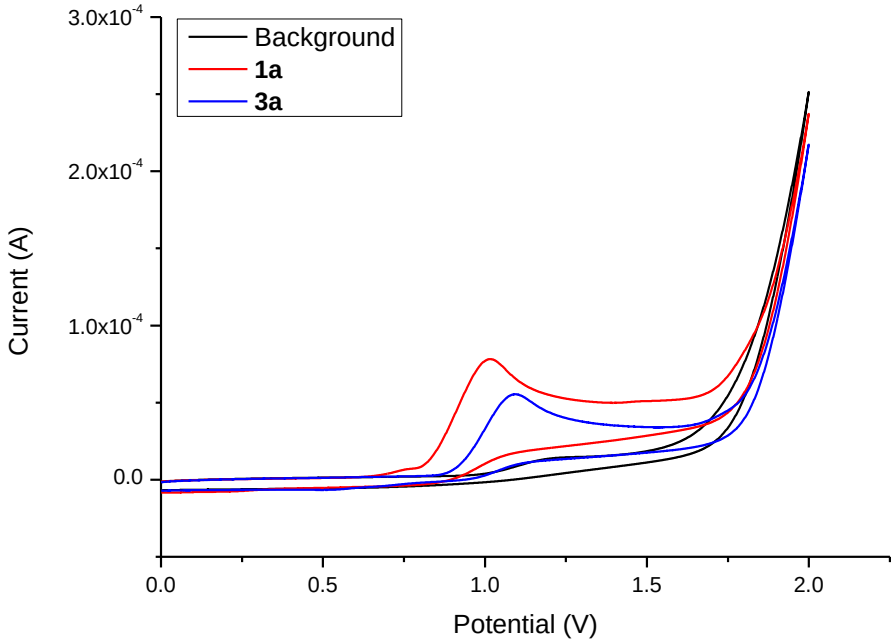


Figure S5. Cyclic voltammograms of background, **1a** (2 mM) and **3a** (2 mM) in an electrolyte of *n*-Bu_4NPF_6 (0.05 mM) in DMF from 0 to +2.0 V. The onset potential for the oxidation of **1a** is around +0.70 V and the E_{ox} is approximately +1.02 V. The onset potential for the oxidation of **3a** is around +0.86 V and the E_{ox} is approximately +1.09 V.

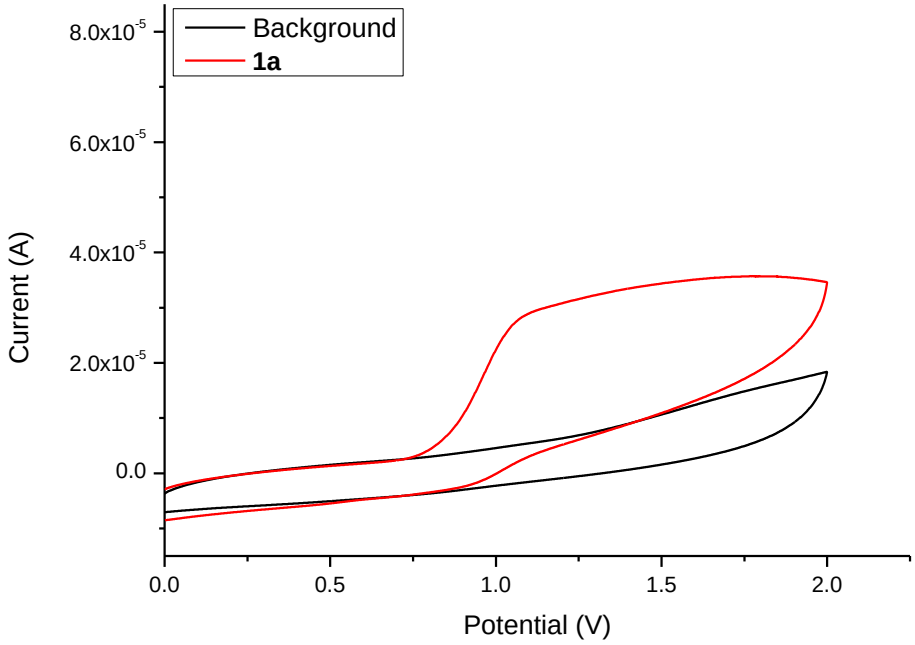


Figure S6. Cyclic voltammograms of background and **1a** (2 mM) in an electrolyte of *n*-Bu_4NPF_6 (0.05 mM) in MeCN from 0 to +2.0 V. The onset potential for the oxidation of **1a** is around +0.72 V and the E_{ox} is approximately +1.07 V.

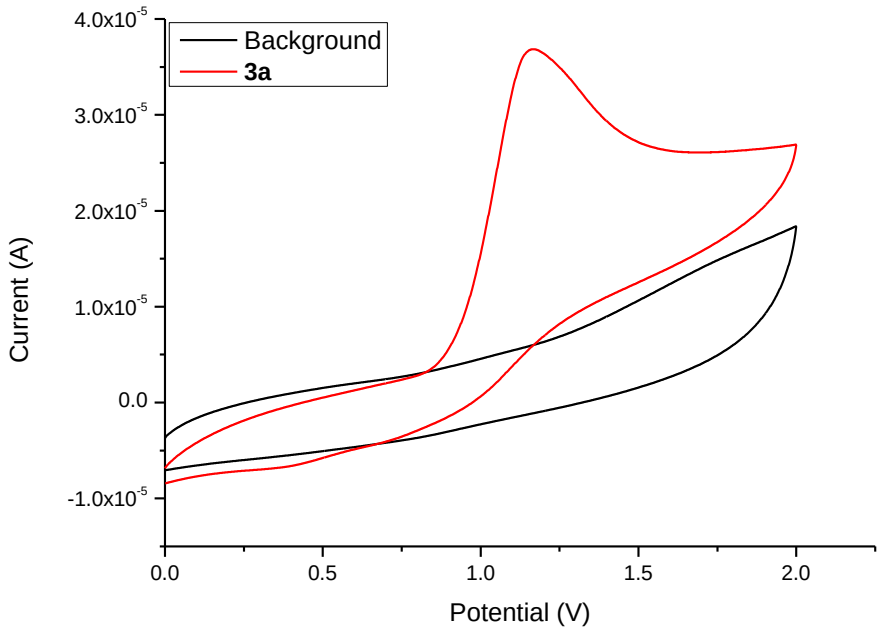


Figure S7. Cyclic voltammograms of background and **3a** (2 mM) in an electrolyte of *n*-Bu_4NPF_6 (0.05 mM) in MeCN from 0 to +2.0 V. The onset potential for the oxidation of **3a** is around +0.86 V and the E_{ox} is approximately +1.15 V.

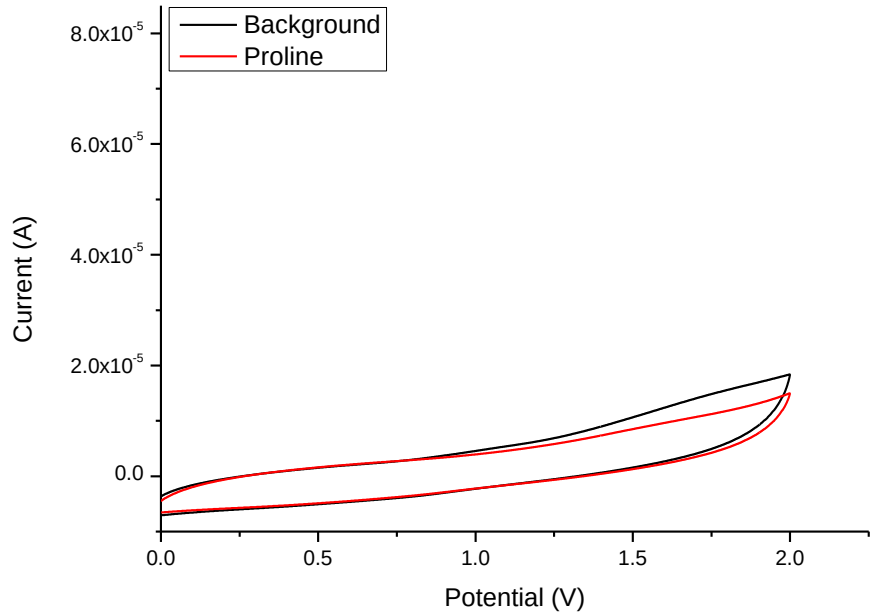


Figure S8. Cyclic voltammograms of background and proline (2 mM) in an electrolyte of *n*-Bu_4NPF_6 (0.05 mM) in MeCN from 0 to +2.0 V. Proline has no oxidation peak in this range.

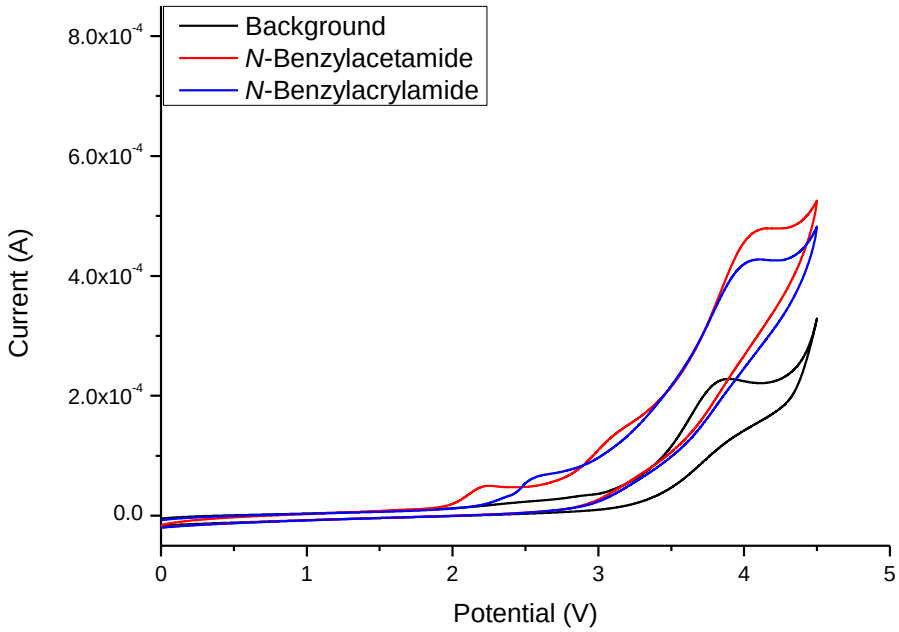


Figure S9. Cyclic voltammograms of background, *N*-benzylacetamide (2 mM) and *N*-benzylacrylamide (2 mM) in an electrolyte of *n*-Bu_4NPF_6 (0.05 mM) in MeCN from 0 to +4.5 V. The onset potential for the oxidation of *N*-benzylacetamide is around +1.89 V and the E_{ox} is

approximately +2.20 V. The onset potential for the oxidation of *N*-benzylacrylamide is around +2.23 V and the E_{ox} is approximately +2.56 V.

10. Unsuccessful substrates

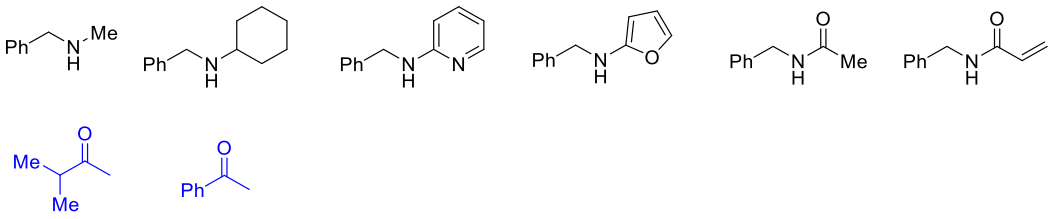


Figure S10. Unsuccessful substrates.

11. Possible mechanism for the reaction without $KHCO_3$

A possible mechanism for the reaction without $KHCO_3$ was proposed, as illustrated in Figure S11. Initially, the visible light irradiation of Ru(II) generates the excited state *Ru(II). A subsequent SET between *Ru(II) and **1a** produces Ru(I) and the N-centered radical cation **I**. Ru(I) is oxidized by O_2 to regenerate Ru(II), and the active species superoxide anion $O_2^{\cdot-}$ is produced at the same time. Next, $O_2^{\cdot-}$ abstracts a hydrogen atom from **I** to generate the iminium ion **II**, which deprotonates to afford the imine **III**. Meanwhile, in the *L*-proline catalysis cycle, **2a** is converted to enamine **VII** in the presence of catalyst **A**. The acidic proton of *L*-proline can activate intermediate **III** through a hydrogen bond.[8] Subsequently, the nucleophilic attack of **VII** to the imine **III** *via* **VIII-a** from the *Si* face may be more favorable due to the more suitable position for the C-C bond formation (**VIII-a**),[9,10] thus leading to the target product **3a** with the *S*-configuration in good stereoselectivity.

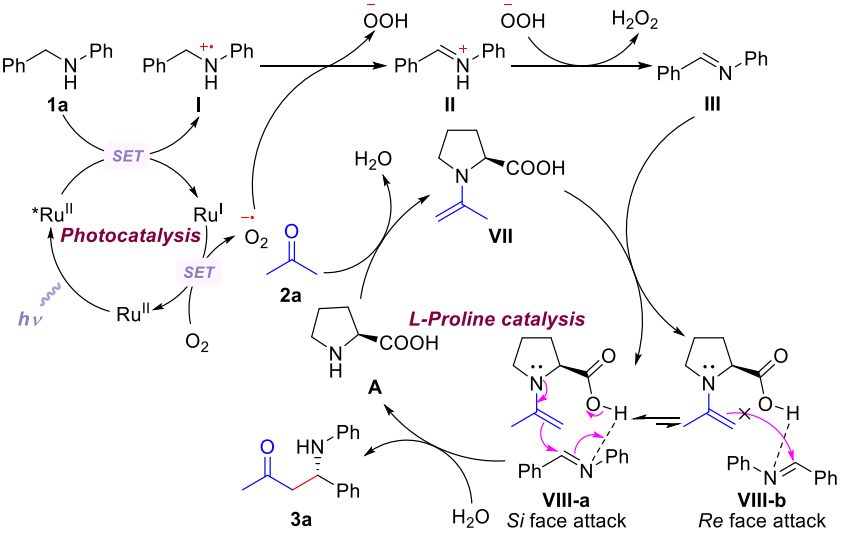
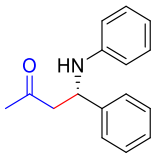


Figure S11 Possible mechanism for the reaction without $KHCO_3$.

12. Characterization data of the products 3 and 4



3a

(*S*)-4-phenyl-4-(phenylamino)butan-2-one (3a)[1]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

47 mg, 65% yield, white solid.

Enantiomeric excess (ee): 97%.

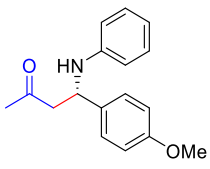
$[\alpha]_D^{20}$ = +20.0 °(*c* = 0.20, $CHCl_3$).

R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 2H), 4.84 (t, *J* = 6.5 Hz, 1H), 4.43 (br s, 1H), 2.92 (d, *J* = 6.5 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.1, 146.8, 142.5, 129.1, 128.8, 127.4, 126.3, 117.9, 113.8, 54.4, 51.2, 30.7.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), retention time: 20.194 min (major), 14.566 min (minor).



3b

(*S*)-4-(4-methoxyphenyl)-4-(phenylamino)butan-2-one (3b)[1]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

58 mg, 72% yield, yellow oil.

Enantiomeric excess (ee): 90%.

$[\alpha]_D^{20}$ = +11.2 °(*c* = 0.80, $CHCl_3$).

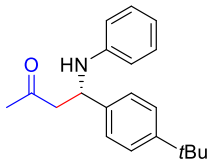
R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 4.79 (t, *J* = 6.3 Hz, 1H), 4.43 (br s, 1H), 3.77 (s, 3H), 2.90 (d, *J* = 5.4 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.1, 158.9, 146.8, 134.5, 129.1, 127.4, 117.9, 114.2, 113.9, 55.2, 54.0, 51.2, 30.7.

HRMS (ESI): Calculated for $C_{17}H_{20}NO_2$ ($[M+H]^+$): 270.1489. Found: 270.1488; Calculated for $C_{17}H_{19}NNaO_2$ ($[M+Na]^+$): 292.1308, Found: 292.1308; Calculated for $C_{17}H_{19}KNO_2$ ($[M+K]^+$): 308.1047, Found: 308.1046.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 28.909 min (major), 23.131 min (minor).



3c

(*S*)-4-(4-(*tert*-butyl)phenyl)-4-(phenylamino)butan-2-one (3c)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

51 mg, 58% yield, yellow oil.

Enantiomeric excess (ee): 84%.

$[\alpha]_D^{20}$ = +25.2 °(*c* = 0.33, $CHCl_3$).

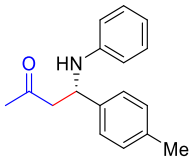
R_f = 0.60 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.66 (t, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 2H), 4.83 (t, *J* = 6.4 Hz, 1H), 4.41 (br s, 1H), 2.92 (d, *J* = 6.4 Hz, 2H), 2.09 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (151 MHz, CDCl3): δ 207.1, 150.2, 146.9, 139.4, 129.1, 125.9, 125.6, 117.8, 113.8, 54.0, 51.1, 34.4, 31.3, 30.6.

HRMS (ESI): Calculated for $C_{20}H_{26}NO$ ($[M+H]^+$): 296.2009. Found: 296.2009; Calculated for $C_{20}H_{25}NNaO$ ($[M+Na]^+$): 318.1828, Found: 318.1829; Calculated for $C_{20}H_{25}KNO$ ($[M+K]^+$): 334.1568, Found: 334.1569.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, λ = 254 nm, retention time: 44.807 min (major), 20.985 min (minor).



3d

(*S*)-4-(phenylamino)-4-(*p*-tolyl)butan-2-one (3d)[11]

Followed the general procedure (Irradiation was conducted for 19 h, followed by the asymmetric catalytic reaction for 25 h).

41 mg, 54% yield, yellow oil.

Enantiomeric excess (ee): 84%.

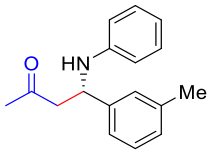
$[\alpha]_D^{20}$ = +12.0 °(*c* = 0.50, $CHCl_3$).

R_f = 0.50 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.09 – 7.06 (m, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 4.80 (t, *J* = 6.5 Hz, 1H), 4.35 (br s, 1H), 2.89 (d, *J* = 6.5 Hz, 2H), 2.30 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.1, 146.9, 139.5, 137.0, 129.5, 129.1, 126.2, 117.8, 113.8, 54.2, 51.3, 30.7, 21.0.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 16.794 min (major), 13.114 min (minor).



3e

(*S*)-4-(phenylamino)-4-(*m*-tolyl)butan-2-one (3e)

Followed the general procedure (Irradiation was conducted for 19 h, followed by the asymmetric catalytic reaction for 25 h).

38 mg, 54% yield, yellow oil.

Enantiomeric excess (ee): 86%.

$[\alpha]_D^{20}$ = -6.0 °(*c* = 0.50, $CHCl_3$).

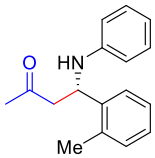
R_f = 0.50 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.13 (m, 2H), 7.10 – 7.06 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 4.79 (t, *J* = 6.5 Hz, 1H), 4.36 (br s, 1H), 2.89 (d, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.1, 147.0, 142.6, 138.4, 129.2, 128.7, 128.2, 127.0, 123.3, 117.8, 113.8, 54.5, 51.3, 30.7, 21.5.

HRMS (ESI): Calculated for $C_{17}H_{20}NO$ ($[M+H]^+$): 254.1538. Found: 254.1538; Calculated for $C_{17}H_{19}NNaO$ ($[M+Na]^+$): 276.1359, Found: 276.1358; Calculated for $C_{17}H_{19}KNO$ ($[M+K]^+$): 292.1098, Found: 292.1097.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 13.454 min (major), 11.026 min (minor).



3f

(*S*)-4-(phenylamino)-4-(*o*-tolyl)butan-2-one (3f)

Followed the general procedure (Irradiation was conducted for 19 h, followed by the asymmetric catalytic reaction for 25 h).

46 mg, 61% yield, yellow oil.

Enantiomeric excess (ee): 90%.

$[\alpha]_D^{20}$ = +14.0 °(*c* = 0.50, $CHCl_3$).

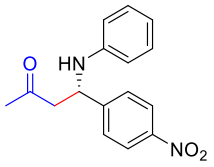
R_f = 0.50 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.34 (m, 1H), 7.18 – 7.13 (m, 3H), 7.10 – 7.06 (m, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 2H), 5.03 (dd, *J* = 7.9, 5.2 Hz, 1H), 4.34 (br s, 1H), 2.90 – 2.80 (m, 2H), 2.45 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.1, 146.8, 140.2, 134.8, 130. 9, 129.2, 127.2, 126.7, 125.6, 117.9, 113.6, 50.9, 49.6, 30.5, 19.1.

HRMS (ESI): Calculated for $C_{17}H_{20}NO$ ($[M+H]^+$): 254.1539. Found: 254.1538; Calculated for $C_{17}H_{19}NNaO$ ($[M+Na]^+$): 276.1359, Found: 276.1358; Calculated for $C_{17}H_{19}KNO$ ($[M+K]^+$): 292.1098, Found: 292.1100.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.990 min (major), 11.345 min (minor).



3g

(*S*)-4-(4-nitrophenyl)-4-(phenylamino)butan-2-one (3g)[12]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 23 h).

33 mg, 39% yield, yellow oil.

Enantiomeric excess (ee): 84%.

$[\alpha]_D^{20}$ = +13.3 °(*c* = 0.50, $CHCl_3$).

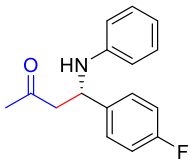
R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.12 – 7.07 (m, 2H), 6.70 (t, *J* = 7.1 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.93 (t, *J* = 6.1 Hz, 1H), 4.47 (s, 1H), 2.97 (d, *J* = 6.1 Hz, 2H), 2.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 205.8, 150.4, 146.1, 129.3, 127.4, 124.2, 124.0, 118.6, 113.9, 53.9, 50.6, 30.6.

HRMS (ESI): Calculated for $C_{16}H_{17}N_2O_3$ ($[M+H]^+$): 285.1234. Found: 285.1232; Calculated for $C_{16}H_{16}N_2NaO_3$ ($[M+Na]^+$): 307.1053, Found: 307.1052.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 24.755 min (major), 19.082 min (minor).



3h

(*S*)-4-(4-fluorophenyl)-4-(phenylamino)butan-2-one (3h)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

55 mg, 71% yield, yellow oil.

Enantiomeric excess (ee): 66%.

$[\alpha]_D^{20}$ = +14.0 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.50 (Petroleum ether/EtOAc, v/v, 5:1).

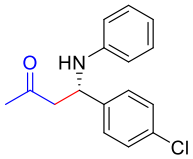
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.3 Hz, 2H), 4.82 (t, *J* = 6.4 Hz, 1H), 4.40 (br s, 1H), 2.90 (d, *J* = 6.4 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 206.9, 162.0 (d, *J* = 246.5 Hz), 146.6, 138.3 (d, *J* = 3.1 Hz), 129.2, 127.9 (d, *J* = 8.1 Hz), 118.1, 115.6 (d, *J* = 21.5 Hz), 113.8, 53.7, 51.2, 30.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.3.

HRMS (ESI): Calculated for $C_{16}H_{17}FNO$ ($[M+H]^+$): 258.1289, Found: 258.1287; Calculated for $C_{16}H_{16}FNNaO$ ($[M+Na]^+$): 280.1108, Found: 280.1107.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 21.894 min (major), 15.443 min (minor).



3i

(*S*)-4-(4-chlorophenyl)-4-(phenylamino)butan-2-one (3i)[12]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

56 mg, 68% yield, yellow oil.

Enantiomeric excess (ee): 96%.

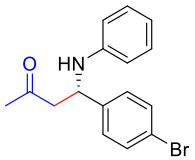
$[\alpha]_D^{20}$ = +13.3 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.30 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 4H), 7.04 – 6.98 (m, 2H), 6.62 – 6.58 (m, 1H), 6.43 (d, *J* = 8.4 Hz, 2H), 4.73 (t, *J* = 6.4 Hz, 1H), 4.36 (br s, 1H), 2.81 (d, *J* = 6.4 Hz, 2H), 2.02 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.6, 146.6, 141.2, 133.0, 129.2, 129.0, 127.8, 118.2, 113.9, 53.8, 51.0, 30.7.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.484 min (major), 19.843 min (minor).



3j

(*S*)-4-(4-bromophenyl)-4-(phenylamino)butan-2-one (3j)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

67 mg, 70% yield, yellow oil.

Enantiomeric excess (ee): 36%.

$[\alpha]_D^{20}$ = +9.3 °(*c* = 0.50, $CHCl_3$).

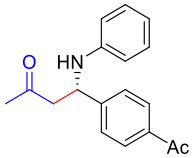
***R*$_f$** = 0.30 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.79 (t, *J* = 6.4 Hz, 1H), 4.41 (br s, 1H), 2.88 (d, *J* = 6.4 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.6, 146.6, 141.8, 131.9, 129.2, 128.2, 121.1, 118.2, 113.9, 53.9, 51.0, 30.7.

HRMS (ESI): Calculated for $C_{16}H_{17}BrNO$ ($[M+H]^+$): 318.0488, Found: 318.0487; Calculated for $C_{16}H_{16}BrNNaO$ ($[M+Na]^+$): 340.0307, Found: 340.0306.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 23.849 min (major), 17.741 min (minor).



3k

(*S*)-4-(4-acetylphenyl)-4-(phenylamino)butan-2-one (3k)

Followed the general procedure (Irradiation was conducted for 19 h, followed by the asymmetric catalytic reaction for 25 h).

38 mg, 45% yield, yellow oil.

Enantiomeric excess (ee): 82%.

$[\alpha]_D^{20}$ = +14.0 °(*c* = 0.50, $CHCl_3$).

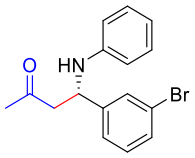
***R*$_f$** = 0.15 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.3 Hz, 2H), 4.89 (t, *J* = 6.3 Hz, 1H), 4.58 (br s, 1H), 2.94 (d, *J* = 6.3 Hz, 2H), 2.56 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 206.5, 197.6, 148.2, 146.5, 136.4, 129.2, 128.9, 126.6, 118.2, 113.8, 54.1, 50.8, 30.7, 26.6.

HRMS (ESI): Calculated for $C_{18}H_{20}NO_2$ ($[M+H]^+$): 282.1489, Found: 282.1487; Calculated for $C_{18}H_{19}NNaO_2$ ($[M+Na]^+$): 304.1308, Found: 304.1307; Calculated for $C_{18}H_{19}KNO_2$ ($[M+K]^+$): 320.1047, Found: 320.1047.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 80.081 min (major), 73.352 min (minor).



3l

(*S*)-4-(3-bromophenyl)-4-(phenylamino)butan-2-one (3l)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

45 mg, 47% yield, yellow oil.

Enantiomeric excess (ee): 54%.

$[\alpha]_D^{20}$ = +11.7 °(*c* = 0.50, $CHCl_3$).

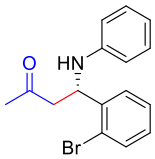
R_f = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 2H), 4.79 (t, *J* = 6.4 Hz, 1H), 4.48 (br s, 1H), 2.90 (d, *J* = 6.3 Hz, 2H), 2.11 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.4, 146.5, 145.2, 130.5, 130.4, 129.4, 129.2, 125.0, 123.0, 118.2, 113.9, 54.0, 51.0, 30.6.

HRMS (ESI): Calculated for $C_{16}H_{17}BrNO$ ($[M+H]^+$): 318.0488, Found: 318.0486; Calculated for $C_{16}H_{16}BrNNaO$ ($[M+Na]^+$): 340.0307, Found: 340.0306.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.909 min (major), 14.631 min (minor).



3m

(*S*)-4-(2-bromophenyl)-4-(phenylamino)butan-2-one (3m)[1]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

41 mg, 43% yield, yellow oil.

Enantiomeric excess (ee): 84%.

$[\alpha]_D^{20}$ = +10.7 °(*c* = 0.50, $CHCl_3$).

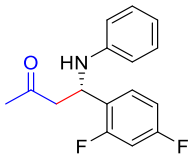
R_f = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.12 – 7.05 (m, 3H), 6.68 – 6.64 (m, 1H), 6.45 (d, *J* = 7.8 Hz, 2H), 5.13 (dd, *J* = 9.1, 3.4 Hz, 1H), 4.64 (br s, 1H), 3.01 (dd, *J* = 15.5, 3.5 Hz, 1H), 2.72 (dd, *J* = 15.5, 9.1 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.2, 146.3, 140.6, 133.2, 129.2, 128.9, 128.1, 128.0, 122.6, 118.1, 113.6, 54.0, 49.2, 30.1.

HRMS (ESI): Calculated for $C_{16}H_{17}BrNO$ ($[M+H]^+$): 318.0488, Found: 318.0486; Calculated for $C_{16}H_{16}BrNNaO$ ($[M+Na]^+$): 340.0307, Found: 340.0306.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, λ = 254 nm, retention time: 30.511 min (major), 26.070 min (minor).



3n

(*S*)-4-(2,4-difluorophenyl)-4-(phenylamino)butan-2-one (3n)

Followed the general procedure (Irradiation was conducted for 19 h, followed by the asymmetric catalytic reaction for 25 h).

45 mg, 54% yield, yellow solid.

Enantiomeric excess (ee): 84%.

$[\alpha]_D^{20}$ = +14.6 °(*c* = 0.50, $CHCl_3$).

R_f = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

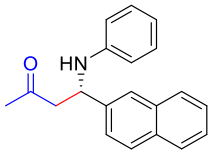
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 1H), 7.12 – 7.07 (m, 2H), 6.83 - 6.73 (m, 2H), 6.70 – 6.65 (m, 1H), 6.54 (d, *J* = 8.3 Hz, 2H), 5.07 (t, *J* = 6.2 Hz, 1H), 4.50 (br s, 1H), 3.00 – 2.88 (m, 2H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 206.8, 162.1 (dd, *J* = 249.3, 12.2 Hz), 160.4 (dd, *J* = 248.2, 11.9 Hz), 146.3, 134.6, 129.3, 124.9 (dd, *J* = 13.4, 3.7 Hz), 118.3, 113.7, 111.5 (dd, *J* = 21.1, 3.5 Hz), 104.0 (t, *J* = 25.8 Hz), 49.2, 48.5, 30.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -111.6 (d, *J* = 6.1 Hz), -115.6 (d, *J* = 6.1 Hz).

HRMS (ESI): Calculated for $C_{16}H_{16}F_2NO$ ($[M+H]^+$): 276.1194, Found: 276.1192; Calculated for $C_{16}H_{15}F_2NNaO$ ($[M+Na]^+$): 298.1014, Found: 298.1013; Calculated for $C_{16}H_{15}F_2KNO$ ($[M+K]^+$): 314.0753, Found: 314.0753.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 15.396min (major), 10.056 min (minor).



3o

(*S*)-4-(naphthalen-2-yl)-4-(phenylamino)butan-2-one (3o)[1]

Followed the general procedure (Irradiation was conducted for 24 h, followed by the asymmetric catalytic reaction for 24 h).

56 mg, 64% yield, yellow oil.

Enantiomeric excess (ee): 90%.

$[\alpha]_D^{20}$ = +7.5 °(*c* = 0.50, $CHCl_3$).

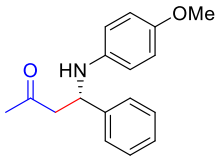
R_f = 0.50 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 – 7.77 (m, 4H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 5.00 (t, *J* = 6.3 Hz, 1H), 4.54 (br s, 1H), 3.02 – 2.97 (m, 2H), 2.10 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.8, 146.9, 140.1, 133.5, 132.9, 129.2, 128.7, 127.9, 127.7, 126.2, 125.8, 125.1, 124.4, 118.0, 113.9, 54.7, 51.2, 30.7.

HRMS (ESI): Calculated for $C_{20}H_{20}NO$ ($[M+H]^+$): 290.1539, Found: 290.1537; Calculated for $C_{20}H_{19}NNaO$ ($[M+Na]^+$): 312.1359, Found: 312.1358; Calculated for $C_{20}H_{19}KNO$ ($[M+K]^+$): 328.1098, Found: 328.1099.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 24.756 min (major), 21.974 min (minor).



3p

(*S*)-4-((4-methoxyphenyl)amino)-4-phenylbutan-2-one (3p)[13]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 31 h).

37 mg, 46% yield, yellow oil.

Enantiomeric excess (ee): 91%.

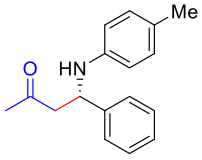
$[\alpha]_D^{20}$ = +55.5 °(*c* = 0.50, $CHCl_3$).

R_f = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 4H), 7.25 – 7.20 (m, 1H), 6.70 – 6.66 (m, 2H), 6.53 – 6.49 (m, 2H), 4.76 (t, *J* = 6.5 Hz, 1H), 3.68 (s, 3H), 2.89 (d, *J* = 6.5 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.2, 152.4, 142.7, 141.0, 128.8, 127.3, 126.3, 115.4, 114.8, 55.7, 55.4, 51.4, 30.7.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 66.631 min (major), 53.004 min (minor).



3q

(*S*)-4-phenyl-4-(p-tolylamino)butan-2-one (3q)[11]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 23 h).

49 mg, 64% yield, white solid.

Enantiomeric excess (ee): 96%.

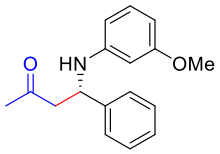
$[\alpha]_D^{20}$ = -15.6 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.30 (Petroleum ether/EtOAc, v/v, 3:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, *J* = 7.1 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.17 – 7.14 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 8.2 Hz, 2H), 4.73 (t, *J* = 6.4 Hz, 1H), 4.15 (br s, 1H), 2.82 (d, *J* = 6.4 Hz, 2H), 2.10 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.1, 144.5, 142.7, 129.6, 128.8, 127.3, 127.1, 126.3, 114.0, 54.8, 51.3, 30.6, 20.3.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 24.049 min (major), 17.663 min (minor).



3r

(*S*)-4-((3-methoxyphenyl)amino)-4-phenylbutan-2-one (3r)

Followed the general procedure (Irradiation was conducted for 13 h, followed by the asymmetric catalytic reaction for 34 h).

62 mg, 77% yield, yellow oil.

Enantiomeric excess (ee): 94%.

$[\alpha]_D^{20}$ = +66.2 °(*c* = 0.50, $CHCl_3$).

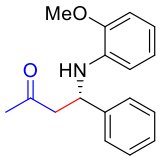
***R*$_f$** = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.99 (t, *J* = 8.1 Hz, 1H), 6.23 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.17 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.10 (s, 1H), 4.82 (t, *J* = 6.5 Hz, 1H), 4.47 (br s, 1H), 3.67 (s, 3H), 2.91 (d, *J* = 6.5 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.1, 160.7, 148.2, 142.5, 129.9, 128.8, 127.4, 126.2, 106.8, 103.2, 99.8, 55.0, 54.4, 51.2, 30.7.

HRMS (ESI): Calculated for $C_{17}H_{20}NO_2$ ($[M+H]^+$): 270.1489, Found: 270.1489.

HPLC: Daicel Chiralpak AS-H, hexane/isopropanol = 88:12, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.470 min (major), 15.769 min (minor).



3s

(*S*)-4-((2-methoxyphenyl)amino)-4-phenylbutan-2-one (3s)[14]

Followed the general procedure (Irradiation was conducted for 13 h, followed by the asymmetric catalytic reaction for 35 h).

50 mg, 62% yield, yellow oil.

Enantiomeric excess (ee): 21%.

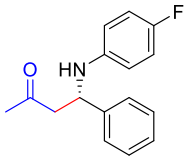
$[\alpha]_D^{20}$ = +43.3 °(*c* = 0.50, $CHCl_3$).

R_f = 0.20 (Petroleum ether/Acetone, v/v, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.18 (m, 5H), 6.76 – 6.68 (m, 2H), 6.65 – 6.59 (m, 1H), 6.43 (d, *J* = 7.7 Hz, 1H), 4.97 – 4.76 (m, 2H), 3.85 (d, *J* = 2.2 Hz, 3H), 3.01 – 2.89 (m, 2H), 2.10 (d, *J* = 2.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 206.7, 147.0, 142.7, 136.6, 128.8, 127.3, 126.3, 121.1, 117.0, 111.4, 109.5, 55.5, 54.2, 51.7, 30.6.

HPLC: Daicel Chiralpak AS-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 13.699 min (major), 10.262 min (minor).



3t

(*S*)-4-((4-fluorophenyl)amino)-4-phenylbutan-2-one (3t)

Followed the general procedure (Irradiation was conducted for 13 h, followed by the asymmetric catalytic reaction for 36 h).

45 mg, 58% yield, yellow solid.

Enantiomeric excess (ee): 95%.

$[\alpha]_D^{20}$ = +16.4 °(*c* = 0.50, $CHCl_3$).

R_f = 0.20 (Petroleum ether/EtOAc, v/v, 10:1).

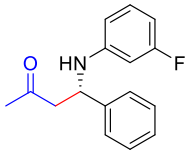
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 4H), 7.27 – 7.20 (m, 1H), 6.82 – 6.65 (m, 2H), 6.50 – 6.44 (m, 2H), 4.75 (t, *J* = 6.5 Hz, 1H), 4.35 (br s, 1H), 2.90 (d, *J* = 6.5 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.1, 156.1 (d, *J* = 236.5 Hz), 143.2 (d, *J* = 1.9 Hz), 142.3, 128.8, 127.5, 126.3, 115.6 (d, *J* = 19.6 Hz), 114.8 (d, *J* = 7.5 Hz), 55.1, 51.2, 30.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -127.4.

HRMS (ESI): Calculated for $C_{16}H_{17}FNO$ ($[M+H]^+$): 258.1289, Found: 258.1287; Calculated for $C_{16}H_{16}FNNaO$ ($[M+Na]^+$): 280.1108, Found: 280.1108.

HPLC: Daicel Chiralpak IC, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.805 min (major), 14.095 min (minor).



3u

(*S*)-4-((3-fluorophenyl)amino)-4-phenylbutan-2-one (3u)[15]

Followed the general procedure (Irradiation was conducted for 18 h, followed by the asymmetric catalytic reaction for 22 h).

47 mg, 61% yield, white solid.

Enantiomeric excess (ee): 81%.

$[\alpha]_D^{20}$ = +23.3 °(*c* = 0.50, $CHCl_3$).

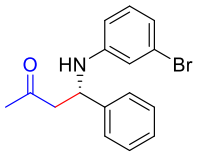
***R*$_f$** = 0.35 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 4H), 7.26 – 7.22 (m, 1H), 7.04 – 6.96 (m, 1H), 6.36 – 6.30 (m, 2H), 6.21 (d, *J* = 11.6 Hz, 1H), 4.79 (t, *J* = 6.3 Hz, 1H), 4.66 (br s, 1H), 2.92 (d, *J* = 6.3 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.0, 163.9 (d, *J* = 243.8 Hz), 148.6 (d, *J* = 10.7 Hz), 142.0, 130.2 (d, *J* = 10.2 Hz), 128.9, 127.5, 126.2, 109.6, 104.3 (d, *J* = 21.6 Hz), 100.5 (d, *J* = 25.5 Hz), 54.4, 50.9, 30.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.8.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.645 min (major), 13.648 min (minor).



3v

(*S*)-4-((3-bromophenyl)amino)-4-phenylbutan-2-one (3v)

Followed the general procedure (Irradiation was conducted for 13 h, followed by the asymmetric catalytic reaction for 35 h).

71 mg, 74% yield, yellow solid.

Enantiomeric excess (ee): 93%.

$[\alpha]_D^{20}$ = +29.5 °(*c* = 0.50, $CHCl_3$).

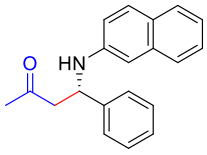
***R*$_f$** = 0.20 (Petroleum ether/EtOAc, v/v, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.68 (t, *J* = 2.0 Hz, 1H), 6.46 – 6.40 (m, 1H), 4.79 (t, *J* = 6.4 Hz, 1H), 4.60 (br s, 1H), 2.90 (d, *J* = 6.4 Hz, 2H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.0, 148.2, 141.9, 130.5, 128.9, 127.6, 126.2, 123.1, 120.6, 116.5, 112.3, 54.2, 50.9, 30.8.

HRMS (ESI): Calculated for $C_{16}H_{17}BrNO$ ($[M+H]^+$): 318.0488, Found: 318.0487; Calculated for $C_{16}H_{16}BrNNaO$ ($[M+Na]^+$): 340.0307, Found: 340.0308.

HPLC: Daicel Chiralpak AS-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.098 min (major), 16.541 min (minor).



3w

(*S*)-4-(naphthalen-2-ylamino)-4-phenylbutan-2-one (3w)

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 19 h).

73 mg, 84% yield, white solid.

Enantiomeric excess (ee): 90%.

$[\alpha]_D^{20}$ = +33.8 °(*c* = 0.50, $CHCl_3$).

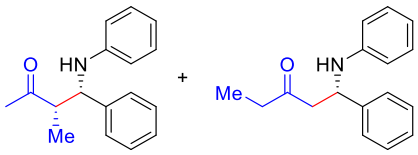
***R*$_f$** = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.24 – 7.20 (m, 1H), 7.17 – 7.12 (m, 1H), 6.91 – 6.87 (m, 1H), 6.68 (s, 1H), 4.97 (t, *J* = 6.4 Hz, 1H), 4.62 (br s, 1H), 2.98 – 2.94 (m, 2H), 2.08 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.0, 144.4, 142.2, 135.0, 128.9, 128.8, 127.8, 127.6, 127.5, 126.3, 126.2, 126.1, 122.2, 118.2, 106.4, 54.5, 51.0, 30.7.

HRMS (ESI): Calculated for $C_{20}H_{20}NO$ ($[M+H]^+$): 290.1539, Found: 290.1535; Calculated for $C_{20}H_{19}NNaO$ ($[M+Na]^+$): 312.1359, Found: 312.1358; Calculated for $C_{20}H_{19}KNO$ ($[M+K]^+$): 328.1098, Found: 328.1098.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 30.621 min (major), 37.347 min (minor).



3x **3y**

(*3S,4S*)-3-methyl-4-phenyl-4-(phenylamino)butan-2-one (3x) and (*S*)-1-phenyl-1-(phenylamino)pentan-3-one (3y)[11] (inseparable mixture of regioisomers, 3x:3y = 63:37)

Followed the general procedure (Irradiation was conducted for 18 h, followed by the asymmetric catalytic reaction for 40 h).

54 mg, 71% yield, white solid.

Diastereomeric ratio (dr): > 99:1 (**3x**).

Enantiomeric excess (ee): 99% (**3x**), 90% (**3y**).

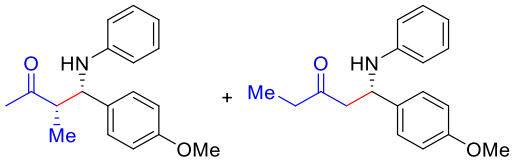
***R*$_f$** = 0.40 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.5 Hz, 1.18H), 7.31 – 7.28 (m, 5.18H), 7.23 – 7.20 (m, 1.59H), 7.09 – 7.04 (m, 3.18H), 6.66 – 6.62 (m, 1.59H), 6.54 (d, *J* = 7.8 Hz, 1.18H), 6.49 (d, *J* = 7.8 Hz, 2H), 4.83 (t, *J* = 6.4 Hz, 0.59H), 4.74 (d, *J* = 5.4 Hz, 1H), 4.27 (br s, 1.59H), 3.01 (p, *J* = 6.8 Hz, 1H), 2.88 (d, *J* = 6.4 Hz, 1.18H), 2.38 – 2.26 (m, 1.18H), 2.07 (s, 3H), 1.08 (d, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 1.77H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.5, 209.8, 147.0, 146.9, 142.7, 141.1, 129.1 × 2 (129.13, 129.10), 128.8, 128.6, 127.3 ×2 (127.325, 127.316), 126.9, 126.3, 117.8 ×2 (117.82, 117.77), 113.8, 113.7, 59.0, 54.6, 53.1, 50.0, 36.9, 29.3, 11.1, 7.4.

HRMS (ESI): Calculated for $C_{17}H_{20}NO$ ($[M+H]^+$): 254.1539, Found: 254.1540; Calculated for $C_{17}H_{19}NNaO$ ($[M+Na]^+$): 276.1359, Found: 276.1359; Calculated for $C_{17}H_{19}KNO$ ($[M+K]^+$): 292.1098, Found: 292.1098.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 99:1, flow rate 1.0 mL/min, λ = 254 nm, retention time of **3x**: 19.735 min (major), 13.867 min (minor); retention time of **3y**: 28.980 min (major), 20.763 min (minor).



3z **3aa**

(*3S*,*4S*)-4-(4-methoxyphenyl)-3-methyl-4-(phenylamino)butan-2-one (3z)[16] and (*S*)-1-(4-methoxyphenyl)-1-(phenylamino)pentan-3-one (3aa)[16] (inseparable mixture of regioisomers, 3z:3aa = 57:43)

Followed the general procedure (Irradiation was conducted for 15 h, followed by the asymmetric catalytic reaction for 26 h).

58 mg, 68% yield, yellow oil.

Diastereomeric ratio (dr): > 99:1 (**3z**).

Enantiomeric excess (ee): 96% (**3z**), 95% (**3aa**).

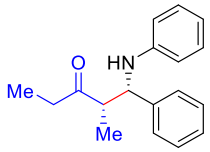
R_f = 0.25 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.18 (m, 3.50H), 7.11 – 7.03 (m, 3.50H), 6.84 (d, *J* = 8.0 Hz, 3.5H), 6.68 – 6.61 (m, 1.50H), 6.54 (d, *J* = 7.8 Hz, 1.50H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.79 (t, *J* = 6.3 Hz, 0.75H), 4.67 (d, *J* = 5.4 Hz, 1H), 4.63 – 3.93 (m, 1.75H), 3.77 (s, 5.25H), 3.02 – 2.95 (m, 1H), 2.92 – 2.83 (m, 1.50H), 2.40 – 2.27 (m, 1.50H), 2.07 (s, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 2.25H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.8, 210.0, 158.8 ×2 (158.80, 158.77), 147.0, 146.8, 134.5, 132.9, 129.1 ×2 (129.12, 129.07), 127.9, 127.4, 117.8, 117.7, 114.2, 114.0, 113.9, 113.6, 58.4, 55.2 ×2 (55.24, 55.22), 54.1, 53.2, 50.0, 36.9, 29.5, 11.3, 7.4.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_2$ ($[M+H]^+$): 284.1645, Found: 284.1644; Calculated for $C_{18}H_{21}NNaO_2$ ($[M+Na]^+$): 306.1464, Found: 306.1463.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time of **3z**: 16.518 min (major), 14.325 min (minor); retention time of **3aa**: 23.656 min (major), 19.386 min (minor).



3ab

(1*S*,2*S*)-2-methyl-1-phenyl-1-(phenylamino)pentan-3-one (3ab)[17]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 32 h).

11 mg, 14% yield, white solid.

Diastereomeric ratio (dr): 56:44.

Enantiomeric excess (ee): 18% (*syn*), 4% (*anti*).

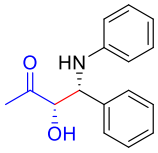
$[\alpha]_D^{20}$ = +5.8 °(*c* = 0.50, $CHCl_3$).

R_f = 0.65 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.65 – 6.57 (m, 1H), 6.54 – 6.46 (m, 2H), 4.66 (d, *J* = 5.8 Hz, 0.56H), 4.49 (d, *J* = 6.3 Hz, 0.44H), 3.07 – 2.94 (m, 1H), 2.40 – 1.93 (m, 2H), 1.15 (d, *J* = 7.0 Hz, 1.32H), 1.09 (d, *J* = 7.0 Hz, 1.68H), 0.91 (t, *J* = 7.2 Hz, 1.68H), 0.87 (t, *J* = 7.2 Hz, 1.32H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.3, 213.3, 147.1, 147.0, 141.7, 141.3, 129.1 × 2 (129.14, 129.11), 128.7, 128.6, 127.4, 127.3, 126.9, 126.6, 117.7, 117.3, 113.7, 113.4, 60.7, 59.3, 52.3, 52.2, 36.3, 35.6, 15.6, 11.7, 7.6, 7.3.

HPLC: Daicel Chiralpak IC, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 7.698 min (*syn* major enantiomer), 5.978 min (*syn* minor enantiomer), 10.406 min (*anti* major enantiomer), 9.114 min (*anti* minor enantiomer).



3ac

(*3S,4R*)-3-hydroxy-4-phenyl-4-(phenylamino)butan-2-one (3ac)[18]

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 24 h).

55 mg, 72% yield, yellow solid.

Diastereomeric ratio (dr): 96:4.

Enantiomeric excess (ee): 76%.

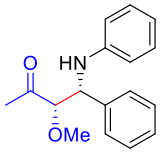
$[\alpha]_D^{20}$ = -13.0 °(*c* = 0.33, $CHCl_3$).

R_f = 0.25 (Petroleum ether/EtOAc, v/v, 3:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.10 – 7.05 (m, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.95 (d, *J* = 1.9 Hz, 1H), 4.42 (d, *J* = 2.3 Hz, 1H), 3.74 (br s, 1H), 2.29 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.3, 146.2, 139.3, 129.2, 128.7, 127.6, 127.0, 118.2, 113.9, 80.8, 58.4, 25.2.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 28.110 min (*syn* major enantiomer), 17.779 min (*syn* minor enantiomer).



3ad

(*3S,4R*)-3-methoxy-4-phenyl-4-(phenylamino)butan-2-one (3ad)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 26 h).

67 mg, 83% yield, yellow oil.

Diastereomeric ratio (dr): 91:9.

Enantiomeric excess (ee): 94% (*syn*), 97% (*anti*).

$[\alpha]_D^{20}$ = +62.6 °(*c* = 0.33, $CHCl_3$).

R_f = 0.30 (Petroleum ether/EtOAc, v/v, 5:1).

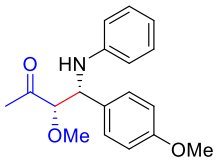
Mixture of two diastereomers:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.11 – 7.03 (m, 2H), 6.68 – 6.66 (m, 0.09H), 6.63 (t, *J* = 7.2 Hz, 0.09H), 6.58 (d, *J* = 8.3 Hz, 0.18H), 6.52 (d, *J* = 8.2 Hz, 1.82H), 4.82 (d, *J* = 2.5 Hz, 0.91H), 4.69 (d, *J* = 5.4 Hz, 0.91H), 3.92 (d, *J* = 5.2 Hz, 0.09H), 3.84 (d, *J* = 2.5 Hz, 0.91H), 3.37 (s, 0.27H), 3.28 (s, 2.73H), 2.16 (s, 2.73H), 1.82 (s, 0.27H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.7, 210.0, 146.4, 146.2, 139.7, 138.5, 129.2 × 2 (129.20, 129.16), 128.6, 128.5, 127.8 × 2 (127.85, 127.77), 127.5, 127.0, 118.1, 117.9, 114.0, 113.8, 90.6, 89.7, 59.7, 59.4, 59.1, 58.7, 27.3, 26.6.

HRMS (ESI): Calculated for $C_{17}H_{20}NO_2$ ($[M+H]^+$): 270.1489, Found: 270.1490; Calculated for $C_{17}H_{19}NNaO_2$ ($[M+Na]^+$): 292.1308, Found: 292.1310; Calculated for $C_{17}H_{19}KNO_2$ ($[M+K]^+$): 308.1047, Found: 308.1049.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 99:1, flow rate 0.7 mL/min, λ = 254 nm, retention time: 23.324 min (*syn* major enantiomer), 20.982 min (*syn* minor enantiomer), 43.307 min (*anti* major enantiomer), 27.774 min (*anti* minor enantiomer).



3ae

(*3S,4R*)-3-methoxy-4-(4-methoxyphenyl)-4-(phenylamino)butan-2-one (3ae)

Followed the general procedure (Irradiation was conducted for 15 h, followed by the asymmetric catalytic reaction for 26 h).

77 mg, 86% yield, yellow oil.

Diastereomeric ratio (dr): 83:17.

Enantiomeric excess (ee): 96% (*syn*), 98% (*anti*).

$[\alpha]_D^{20}$ = -46.0 °(*c* = 0.50, $CHCl_3$).

R_f = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

Mixture of two diastereomers:

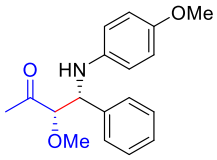
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 2H), 7.09 – 7.03 (m, 2H), 6.86 – 6.80 (m, 2H), 6.63 (t, *J* = 7.3, 1H), 6.58 (d, *J* = 7.8 Hz, 0.34H), 6.52 (d, *J* = 7.8 Hz, 1.66H), 4.83 – 4.69 (m, 1.83H),

4.64 (d, *J* = 5.2 Hz, 0.17H), 3.90 (d, *J* = 5.2 Hz, 0.17H), 3.80 (d, *J* = 3.1 Hz, 0.83H), 3.75 (s, 3H), 3.37 (s, 0.51H), 3.31 (s, 2.49H), 2.14 (s, 2.49H), 1.83 (s, 0.51H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.8, 210.2, 159.2, 159.0, 146.5, 146.2, 131.6, 130.4, 129.2, 129.1, 128.8, 128.1 × 2 (128.11, 128.08), 117.8, 114.1, 114.0, 113.9, 113.8, 90.6, 89.8, 59.6, 59.4, 58.5, 58.2, 55.2, 27.3, 26.6.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_3$ ($[M+H]^+$): 300.1594, Found: 300.1592; Calculated for $C_{18}H_{21}NNaO_3$ ($[M+Na]^+$): 322.1414, Found: 322.1412; Calculated for $C_{18}H_{21}KNO_3$ ($[M+K]^+$): 338.1153, Found: 338.1151.

HPLC: Daicel Chiralpak OJ-H, hexane/isopropanol = 80:20, flow rate 0.75 mL/min, λ = 254 nm, retention time: 12.846 min (*syn* major enantiomer), 20.152 min (*syn* minor enantiomer), 21.892 min (*anti* major enantiomer), 16.583 min (*anti* minor enantiomer).



3af

(*3S*,*4R*)-3-methoxy-4-((4-methoxyphenyl)amino)-4-phenylbutan-2-one (3af)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 27 h).

71 mg, 79% yield, yellow oil.

Diastereomeric ratio (dr): 90:10.

Enantiomeric excess (ee): 98% (*syn*), 83% (*anti*).

$[\alpha]_D^{20}$ = +57.2 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.20 (Petroleum ether/EtOAc, v/v, 10:1).

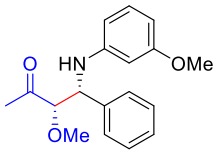
Mixture of two diastereomers:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.32 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 6.65 – 6.62 (m, 2H), 6.49 – 6.45 (m, 2H), 4.74 (d, *J* = 3.1 Hz, 0.90H), 4.68 – 4.47 (m, 1.1H), 3.90 (d, *J* = 5.3 Hz, 1H), 3.80 (d, *J* = 3.2 Hz, 0.90H), 3.64 (s, 0.30H), 3.62 (s, 2.70H), 3.33 (s, 0.30H), 3.25 (s, 2.70H), 2.14 (s, 2.70H), 1.81 (s, 0.30H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.6, 210.1, 152.6, 152.4, 140.6, 140.3, 139.9, 138.7, 128.5, 128.4, 127.8 × 2 (127.83, 127.79), 127.4, 127.1, 115.6, 115.2, 114.8 × 2 (114.84, 114.81), 90.7, 89.8, 60.2, 59.7, 59.6, 59.3, 55.7, 55.6, 27.3, 26.5.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_3$ ($[M+H]^+$): 300.1594, Found: 300.1593; Calculated for $C_{18}H_{21}NNaO_3$ ($[M+Na]^+$): 322.1414, Found: 322.1413; Calculated for $C_{18}H_{21}KNO_3$ ($[M+K]^+$): 338.1153, Found: 338.1154.

HPLC: Daicel Chiralpak OD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.688 min (*syn* major enantiomer), 11.280 min (*syn* minor enantiomer), 14.065 min (*anti* major enantiomer), 16.083 min (*anti* minor enantiomer).



3ag

(*3S*,*4R*)-3-methoxy-4-((3-methoxyphenyl)amino)-4-phenylbutan-2-one (3ag)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 27 h).

72 mg, 80% yield, yellow oil.

Diastereomeric ratio (dr): 87:13.

Enantiomeric excess (ee): 97% (*syn*), 91% (*anti*).

$[\alpha]_D^{20}$ = +34.8 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.30 (Petroleum ether/EtOAc, v/v, 10:1).

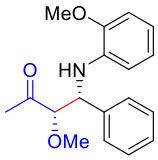
Mixture of two diastereomers:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 7.23 – 7.20 (m, 1H), 6.97 – 6.92 (m, 1H), 6.21 – 6.18 (m, 1H), 6.16 – 6.12 (m, 1H), 6.07 (t, *J* = 2.2 Hz, 1H), 4.86 – 4.77 (m, 1.87H), 4.67 (d, *J* = 5.2 Hz, 0.13H), 3.91 (d, *J* = 4.8 Hz, 0.13H), 3.82 (d, J = 1.4 Hz, 0.87H), 3.65 (s, 0.39H), 3.63 (s, 2.61H), 3.33 (s, 0.39H), 3.26 (s, 2.61H), 2.13 (s, 2.61H), 1.80 (s, 0.39H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.5, 209.8, 160.7 × 2 (160.75, 160.73), 147.9, 147.7, 139.8, 138.5, 130.0, 129.9, 128.6, 128.5, 127.9, 127.8, 127.5, 127.0, 107.0, 106.8, 103.4, 103.2, 100.1, 99.9, 90.4, 89.7, 59.7, 59.4, 59.1, 58.7, 55.0 × 2 (54.99, 54.97), 27.3, 26.6.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_3$ ([M+H]$^+$): 300.1594, Found: 300.1593; Calculated for $C_{18}H_{21}NNaO_3$ ([M+Na]$^+$): 322.1414, Found: 322.1412.

HPLC: Daicel Chiralpak AS-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.080 min (*syn* major enantiomer), 13.843 min (*syn* minor enantiomer), 21.425 min (*anti* major enantiomer), 16.762 min (*anti* minor enantiomer).



3ah

(*3S*,*4R*)-3-methoxy-4-((2-methoxyphenyl)amino)-4-phenylbutan-2-one (3ah)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 27 h).

48 mg, 53% yield, yellow oil.

Diastereomeric ratio (dr): 79:21.

Enantiomeric excess (ee): 70% (*syn*), 51% (*anti*).

$[\alpha]_D^{20}$ = +61.3 °(*c* = 0.50, $CHCl_3$).

R_f = 0.20 (Petroleum ether/EtOAc, v/v, 10:1).

Mixture of two diastereomers:

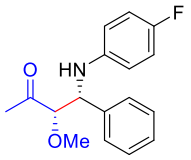
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 6.75 – 6.71 (m, 1H), 6.69 – 6.56 (m, 2H), 6.47 (dd, *J* = 7.7, 1.5 Hz, 0.21H), 6.32 (dd, *J* = 7.7, 1.6 Hz, 0.79H), 5.26 (br s, 1H), 4.82 (d, *J* = 2.9 Hz, 0.79H), 4.70 (d, *J* = 5.4 Hz, 0.21H), 3.92 (d, *J* = 5.4 Hz, 0.21H), 3.86 (s, 2.37H), 3.84 (s, 0.63H), 3.82 (d, *J* = 8.7 Hz, 0.79H), 3.35 (s, 0.21H), 3.26 (s, 2.37H), 2.17 (s, 2.37H), 1.84 (s, 0.63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.7, 210.4, 147.3, 147.2, 139.9, 138.7, 136.4, 136.1, 128.5, 128.4, 127.8, 127.7, 127.4, 127.0, 121.2, 118.5, 117.4, 117.0, 111.6, 111.4, 109.8, 109.7, 90.9, 90.0, 59.8, 59.5, 59.0, 58.8, 55.6 ×2 (55.61, 55.60), 27.4, 26.4.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_3$ ([M+H]$^+$): 300.1594, Found: 300.1594; Calculated for $C_{18}H_{21}NNaO_3$ ([M+Na]$^+$): 322.1414, Found: 322.1412; Calculated for $C_{18}H_{21}KNO_3$ ([M+K]$^+$): 338.1153, Found: 338.1153.

HPLC: Daicel Chiralpak OD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm,

retention time: 11.633 min (*syn* major enantiomer), 12.532 min (*syn* minor enantiomer), 10.623 min (*anti* major enantiomer), 11.217 min (*anti* minor enantiomer).



3ai

(*3S*,*4R*)-4-((4-fluorophenyl)amino)-3-methoxy-4-phenylbutan-2-one (3ai)

Followed the general procedure (Irradiation was conducted for 17 h, followed by the asymmetric catalytic reaction for 27 h).

64 mg, 74% yield, yellow oil.

Diastereomeric ratio (dr): 90:10.

Enantiomeric excess (ee): 99% (*syn*), 83% (*anti*).

$[\alpha]_D^{20}$ = +43.5 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.40 (Petroleum ether/EtOAc, v/v, 5:1).

Mixture of two diastereomers:

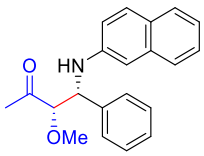
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 4H), 7.23 – 7.19 (m, 1H), 6.77 – 6.71 (m, 2H), 6.52 – 6.48 (m, 0.20H), 6.46 – 6.42 (m, 1.80H), 4.82 – 4.64 (m, 1.90H), 4.61 (d, *J* = 5.3 Hz, 0.20H), 3.91 (d, J = 5.3 Hz, 0.10H), 3.81 (d, *J* = 3.1 Hz, 0.90H), 3.34 (s, 0.30H), 3.25 (s, 2.70H), 2.14 (s, 2.70H), 1.80 (s, 0.30H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.7, 209.9, 156.1 (d, *J* = 236.7 Hz), 156.0 (d, *J* = 236.4 Hz), 142.8 (d, *J* = 1.8 Hz), 142.6 (d, *J* = 1.9 Hz), 139.5, 138.3, 128.8, 128.6, 127.9, 127.8, 127.6, 127.1, 115.6 ×2 [115.63 (d, *J* = 22.4 Hz), 115.57 (d, *J* = 22.4 Hz)], 115.1 (d, *J* = 7.5 Hz), 114.7 (d, *J* = 7.5 Hz), 90.5, 89.6, 59.8, 59.7 59.4, 59.3, 27.3, 26.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -127.0, -127.4.

HRMS (ESI): Calculated for $C_{17}H_{19}FNO_2$ ($[M+H]^+$): 288.1394, Found: 288.1393; Calculated for $C_{17}H_{18}FNNaO_2$ ($[M+Na]^+$): 310.1214, Found: 310.1213.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 89.488 min (*syn* major enantiomer), 9.511 min (*syn* minor enantiomer), 16.912 min (*anti* major enantiomer), 11.515 min (*anti* minor enantiomer).



3aj

(*3S,4R*)-3-methoxy-4-(naphthalen-2-ylamino)-4-phenylbutan-2-one (3aj)

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 19 h).

79 mg, 82% yield, white solid.

Diastereomeric ratio (dr): 85:15.

Enantiomeric excess (ee): 92% (*syn*), 74% (*anti*).

$[\alpha]_D^{20}$ = +63.6 °(*c* = 0.33, $CHCl_3$).

R_f = 0.35 (Petroleum ether/EtOAc, v/v, 5:1).

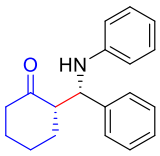
Mixture of two diastereomers:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.54 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.32 – 7.25 (m, 3H), 7.24 – 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 6.93 – 6.88 (m, 1H), 6.73 (d, *J* = 2.2 Hz, 0.15H), 6.64 – 6.61 (m, 0.85H), 5.06 – 4.85 (m, 1.85H), 4.84 – 4.82 (m, 0.15H), 4.01 – 3.98 (m, 0.15H), 3.88 (s, 0.85H), 3.36 (s, 0.45H), 3.29 (s, 2.55H), 2.16 (s, 2.55H), 1.82 (s, 0.45H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.7, 209.91, 144.2, 143.9, 139.50, 138.3, 135.0 × 2 (135.00, 134.95), 129.4, 129.2, 129.1, 129.0, 128.6 ×2 (128.63, 128.59), 128.0 ×2 (128.01, 127.97), 127.8, 127.7, 127.6, 127.0, 126.3, 126.2, 126.0, 125.8, 122.4, 122.2, 118.3, 118.0, 108.6, 106.5, 90.5, 89.5, 59.7, 59.4, 59.1, 58.7, 27.3, 26.7.

HRMS (ESI): Calculated for $C_{21}H_{22}NO_2$ ($[M+H]^+$): 320.1645, Found: 320.1645; Calculated for $C_{21}H_{21}NNaO_2$ ($[M+Na]^+$): 342.1464, Found: 342.1465; Calculated for $C_{21}H_{21}KNO_2$ ($[M+K]^+$): 358.1204, Found: 358.1207.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 15.559 min (*syn* major enantiomer), 14.849 min (*syn* minor enantiomer), 24.594 min (*anti* major enantiomer), 17.174 min (*anti* minor enantiomer).



3ak

(*S*)-2-((*S*)-phenyl(phenylamino)methyl)cyclohexan-1-one (3ak)[19]

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 25 h).

62 mg, 74% yield, white solid.

Diastereomeric ratio (dr): 62:38.

Enantiomeric excess (ee): 87% (*syn*), 58% (*anti*).

$[\alpha]_D^{20}$ = -33.0 °(*c* = 0.33, $CHCl_3$). {*Ref.* 18, $[\alpha]_D^{25}$ = -44.2 °(*c* = 0.98, $CHCl_3$, > 99% ee)}.

R_f = 0.35 (Petroleum ether/EtOAc, v/v, 5:1).

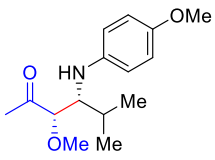
Mixture of two diastereomers:

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.10 – 7.02 (m, 2H), 6.66 – 6.60 (m, 1H), 6.57 – 6.51 (m, 2H), 4.80 (d, *J* = 4.3 Hz, 0.62H), 4.76 – 4.28 (m, 1.38H), 2.82 – 2.77 (m, 0.62H), 2.77 – 2.73 (m, 0.38H), 2.45 – 2.38 (m, 1H), 2.35 – 2.26 (m, 1H), 2.08 – 1.99 (m, 1H), 1.93 – 1.81 (m, 2H), 1.72 – 1.63 (m, 2H), 1.62 – 1.58 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 212.6, 211.2, 147.5, 147.2, 141.7, 141.6, 129.0 × 2 (129.04, 129.00), 128.5, 128.4, 127.5, 127.3, 127.2, 127.0, 117.7, 117.6, 114.1, 113.8, 58.2, 57.4 × 2 (57.45, 57.41), 56.6, 42.4, 41.8, 31.2, 28.8, 27.8, 26.9, 24.8, 23.7.

HRMS (ESI): Calculated for $C_{19}H_{22}NO$ ($[M+H]^+$): 280.1696, Found: 280.1696; Calculated for $C_{19}H_{21}NNaO$ ($[M+Na]^+$): 302.1515, Found: 302.1515; Calculated for $C_{19}H_{21}KNO$ ($[M+K]^+$): 318.1255, Found: 318.1255.

HPLC: Daicel Chiralpak OJ-H, hexane/isopropanol = 80:20, flow rate 0.75 mL/min, λ = 254 nm, retention time: 25.390 min (*syn* major enantiomer), 19.037 min (*syn* minor enantiomer), 16.664 min (*anti* major enantiomer), 12.149 min (*anti* minor enantiomer).



3al

(*3S*,*4R*)-3-methoxy-4-((4-methoxyphenyl)amino)-5-methylhexan-2-one (3al)

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 28 h).

57 mg, 72% yield, yellow oil.

Diastereomeric ratio (dr): > 99:1.

Enantiomeric excess (ee): 83%.

$[\alpha]_D^{20}$ = +14.7 °(*c* = 0.50, $CHCl_3$).

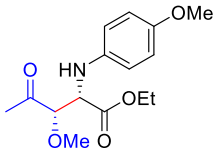
R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 – 6.73 (m, 2H), 6.66 – 6.54 (m, 2H), 3.96 (s, 3H), 3.75 – 3.67 (m, 4H), 3.37 (s, 3H), 2.62 – 2.54 (m, 2H), 1.97 – 1.87 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 203.8, 147.4, 136.9, 110.3, 110.2, 73.3, 54.5, 51.6, 51.0, 35.9, 26.9, 14.0, 13.6.

HRMS (ESI): Calculated for $C_{15}H_{24}NO_3$ ($[M+H]^+$): 266.1751, Found: 266.1751; Calculated for $C_{15}H_{23}NNaO_3$ ($[M+Na]^+$): 288.1570, Found: 288.1572.

HPLC: Daicel Chiralpak AS-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 23.463 min (*syn* major enantiomer), 31.452 min (*syn* minor enantiomer).



3am

Ethyl (*2S,3S*)-3-methoxy-2-((4-methoxyphenyl)amino)-4-oxopentanoate (3am)[20]

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 28 h).

67 mg, 76% yield, yellow oil.

Diastereomeric ratio (dr): 96:4.

Enantiomeric excess (ee): 98%.

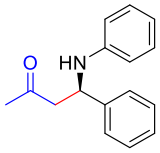
$[\alpha]_D^{20}$ = +65.5 °(*c* = 0.50, $CHCl_3$).

R_f = 0.30 (Petroleum ether/EtOAc, v/v, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 4.40 (s, 1H), 4.28 – 4.12 (m, 3H), 4.10 (d, *J* = 2.6 Hz, 1H), 3.72 (s, 3H), 3.47 (s, 3H), 2.25 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.6, 166.5, 148.6, 136.1, 111.4, 110.0, 82.7, 56.7, 55.9, 55.1, 50.9, 22.4, 9.4.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 214 nm, retention time: 27.804 min (*syn* major enantiomer), 30.092 min (*syn* minor enantiomer).



4a

(*R*)-4-phenyl-4-(phenylamino)butan-2-one (4a)[1]

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 24 h).

46 mg, 64% yield, white solid.

Enantiomeric excess (ee): 95%.

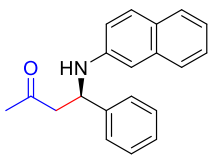
$[\alpha]_D^{20}$ = -18.9 °(*c* = 0.20, $CHCl_3$).

R_f = 0.40 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 4.84 (t, *J* = 6.4 Hz, 1H), 4.41 (br s, 1H), 2.91 (d, *J* = 6.4 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.0, 146.9, 142.6, 129.2, 128.8, 127.4, 126.3, 117.9, 113.8, 54.5, 51.2, 30.7.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), retention time: 12.943 min (major), 16.832 min (minor).



4b

(*R*)-4-(naphthalen-2-ylamino)-4-phenylbutan-2-one (4b)

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 19 h).

69 mg, 79% yield, white solid.

Enantiomeric excess (ee): 90%.

$[\alpha]_D^{20}$ = -30.1 °(*c* = 0.50, $CHCl_3$).

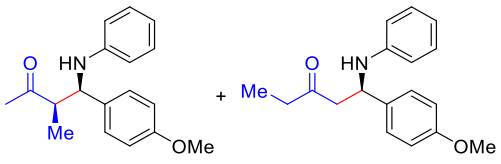
***R*$_f$** = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.20 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.07 (m, 1H), 6.83 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.61 (s, 1H), 4.91 (t, *J* = 6.4 Hz, 1H), 4.62 (br s, 1H), 2.92 (d, *J* = 6.9 Hz, 2H), 2.04 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.0, 143.4, 141.2, 133.9, 127.9, 127.8, 126.7, 126.5, 126.4, 125.3, 125.2, 125.1, 121.2, 117.2, 105.3, 53.4, 50.0, 29.7.

HRMS (ESI): Calculated for $C_{20}H_{20}NO$ ($[M+H]^+$): 290.1539, Found: 290.1536; Calculated for $C_{20}H_{19}NNaO$ ($[M+Na]^+$): 312.1359, Found: 312.1357; Calculated for $C_{20}H_{19}KNO$ ($[M+K]^+$): 328.1098, Found: 328.1097.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 37.366 min (major), 30.320 min (minor).



4c **4d**

(*3R*,*4R*)-4-(4-methoxyphenyl)-3-methyl-4-(phenylamino)butan-2-one (4c)[16] and (*S*)-1-(4-methoxyphenyl)-1-(phenylamino)pentan-3-one (4d)[16] (inseparable mixture of regioisomers, 4c:4d = 52:48)

Followed the general procedure (Irradiation was conducted for 15 h, followed by the asymmetric catalytic reaction for 26 h).

55 mg, 65% yield, yellow oil.

Diastereomeric ratio (dr): > 99:1 (**4c**).

Enantiomeric excess (ee): 89% (**4c**), 94% (**4d**).

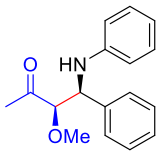
***R*$_f$** = 0.25 (Petroleum ether/EtOAc, v/v, 5:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.24 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1.84H), 7.10 – 7.04 (m, 3.84H), 6.84 (d, *J* = 7.9 Hz, 3.84H), 6.67 – 6.62 (m, 1.84H), 6.54 (d, *J* = 7.9 Hz, 1.84H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.79 (t, *J* = 6.4 Hz, 0.92H), 4.67 (d, *J* = 5.6 Hz, 1H), 4.59 – 4.12 (m, 1.92H), 3.76 (s, 5.76H), 3.00 – 2.96 (m, 1H), 2.90 – 2.86 (m, 1.84H), 2.36 – 2.29 (m, 1.84H), 2.06 (s, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 2.76H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.6, 209.9, 158.8 × 2 (158.86, 158.83), 147.0, 146.9, 134.6, 133.0, 129.1 ×2 (129.10, 129.06), 127.9, 127.4, 117.8, 117.7, 114.2, 114.1, 113.9, 113.7, 58.5, 55.2 ×2 (55.23, 55.21), 54.1, 53.2, 49.9, 36.9, 29.4, 11.4, 7.4.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_2$ ($[M+H]^+$): 284.1645, Found: 284.1644; Calculated for $C_{18}H_{21}NNaO_2$ ($[M+Na]^+$): 306.1464, Found: 306.1463; Calculated for $C_{18}H_{21}KNO_2$ ($[M+K]^+$): 322.1204, Found: 322.1205.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time of **4c**: 14.038 min (major), 16.241 min (minor); retention time of **4d**: 19.007 min (major), 23.184 min (minor).



4e

(*3R,4S*)-3-methoxy-4-phenyl-4-(phenylamino)butan-2-one (4e)

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 24 h).

66 mg, 82% yield, yellow oil.

Diastereomeric ratio (dr): 86:14.

Enantiomeric excess (ee): 98% (*syn*), 91% (*anti*).

$[\alpha]_D^{20}$ = -62.4 °(*c* = 0.33, $CHCl_3$).

***R*$_f$** = 0.30 (Petroleum ether/EtOAc, v/v, 5:1).

Mixture of two diastereomers:

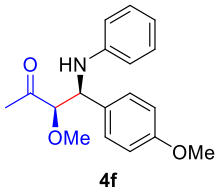
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.08 – 7.03 (m, 2H), 6.66 – 6.61 (m, 1H), 6.60 – 6.56 (m, 0.28H), 6.54 – 6.50 (m, 1.72H), 4.85

– 4.74 (m, 1.86H), 4.69 (d, *J* = 5.4 Hz, 0.14H), 3.92 (d, *J* = 5.3 Hz, 0.14H), 3.83 (d, *J* = 2.8 Hz, 0.86H), 3.36 (s, 0.42H), 3.28 (s, 2.58H), 2.15 (s, 2.58H), 1.82 (s, 0.42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.6, 210.0, 146.4, 146.2, 139.7, 138.5, 129.2 × 2 (129.21, 129.16), 128.6, 128.5, 127.8 × 2 (127.86, 127.78), 127.5, 127.0, 118.2, 117.9, 114.1, 113.8, 90.6, 89.7, 59.7, 59.4, 59.1, 58.7, 27.3, 26.6.

HRMS (ESI): Calculated for $C_{17}H_{20}NO_2$ ($[M+H]^+$): 270.1489, Found: 270.1488; 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: 308.1048.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 99:1, flow rate 0.7 mL/min, λ = 254 nm, retention time: 21.007 min (*syn* major enantiomer), 22.543 min (*syn* minor enantiomer), 26.512 min (*anti* major enantiomer), 42.136 min (*anti* minor enantiomer).



4f

(*3R,4S*)-3-methoxy-4-(4-methoxyphenyl)-4-(phenylamino)butan-2-one (4f)

Followed the general procedure (Irradiation was conducted for 15 h, followed by the asymmetric catalytic reaction for 26 h).

74 mg, 82% yield, yellow oil.

Diastereomeric ratio (dr): 85:15.

Enantiomeric excess (ee): 96% (*syn*), 86% (*anti*).

$[\alpha]_D^{20}$ = +49.7 °(*c* = 0.50, $CHCl_3$).

***R*$_f$** = 0.20 (Petroleum ether/EtOAc, v/v, 5:1).

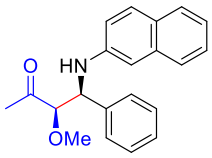
Mixture of two diastereomers:

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2H), 7.10 – 7.03 (m, 2H), 6.85 – 6.80 (m, 2H), 6.67 – 6.61 (m, 1H), 6.58 (d, *J* = 7.7 Hz, 0.30H), 6.51 (d, *J* = 7.8 Hz, 1.70H), 4.84 – 4.55 (m, 2H), 3.90 (d, *J* = 5.2 Hz, 0.15H), 3.79 (d, *J* = 2.9 Hz, 0.85H), 3.75 (s, 3H), 3.36 (s, 0.45H), 3.30 (s, 2.55H), 2.13 (s, 2.55H), 1.83 (s, 0.45H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.6, 210.0, 159.2, 159.0, 146.6, 146.3, 131.6, 130.5, 129.2, 129.1, 128.9, 128.1 × 2 (128.12, 128.08), 118.1, 117.8, 114.1, 114.0, 113.9, 90.6, 89.8, 59.6, 59.4, 58.6, 58.2, 55.2 × 2 (55.19, 55.18), 27.3, 26.6.

HRMS (ESI): Calculated for $C_{18}H_{22}NO_3$ ($[M+H]^+$): 300.1594, Found: 300.1592; Calculated for $C_{18}H_{21}NNaO_3$ ($[M+Na]^+$): 322.1414, Found: 322.1412; Calculated for $C_{18}H_{21}KNO_3$ ($[M+K]^+$): 338.1153, Found: 338.1152.

HPLC: Daicel Chiralpak OJ-H, hexane/isopropanol = 80:20, flow rate 0.75 mL/min, λ = 254 nm, retention time: 19.951 min (*syn* major enantiomer), 13.448 min (*syn* minor enantiomer), 16.756 min (*anti* major enantiomer), 22.922 min (*anti* minor enantiomer).



4g

(*3R,4S*)-3-methoxy-4-(naphthalen-2-ylamino)-4-phenylbutan-2-one (4g)

Followed the general procedure (Irradiation was conducted for 16 h, followed by the asymmetric catalytic reaction for 19 h).

74 mg, 77% yield, white solid.

Diastereomeric ratio (dr): 89:11.

Enantiomeric excess (ee): 94% (*syn*), 79% (*anti*).

$[\alpha]_D^{20}$ = -67.6 °(*c* = 0.33, $CHCl_3$).

R_f = 0.35 (Petroleum ether/EtOAc, v/v, 5:1).

Mixture of two diastereomers:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.54 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.31 – 7.25 (m, 3H), 7.24 – 7.20 (m, 1H), 7.15 – 7.10 (m, 1H), 6.90 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.73 (d, *J* = 1.8 Hz, 0.11H), 6.62 (d, *J* = 2.1 Hz, 0.89H), 5.02 – 4.89 (m, 1.89H), 4.82 (d, *J* = 5.4 Hz, 0.11H), 3.99 (d, *J* = 5.2 Hz, 0.11H), 3.88 (d, *J* = 2.4 Hz, 0.89H), 3.36 (s, 0.33H), 3.29 (s, 2.67H), 2.16 (s, 2.67H), 1.82 (s, 0.33H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.7, 209.9, 144.1, 143.9, 139.5, 138.3, 135.0 × 2 (135.02, 134.95), 129.0 × 2 (129.06, 129.00), 128.6 × 2 (128.62, 128.58), 128.0, 127.8 × 2 (127.84, 127.81),

127.7, 127.6, 127.0, 126.3, 126.2, 126.1, 126.0, 122.4, 122.2, 118.3, 118.0, 106.7, 106.5, 90.5, 89.5, 59.7, 59.4, 59.1, 58.7, 27.3, 26.7.

HRMS (ESI): Calculated for $C_{21}H_{22}NO_2$ ($[M+H]^+$): 320.1645, Found: 320.1643; Calculated for $C_{21}H_{21}NNaO_2$ ($[M+Na]^+$): 342.1464, Found: 342.1463; Calculated for $C_{21}H_{21}KNO_2$ ($[M+K]^+$): 358.1204, Found: 358.1200.

HPLC: Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.000 min (*syn* major enantiomer), 14.438 min (*syn* minor enantiomer), 16.069 min (*anti* major enantiomer), 23.398 min (*anti* minor enantiomer).

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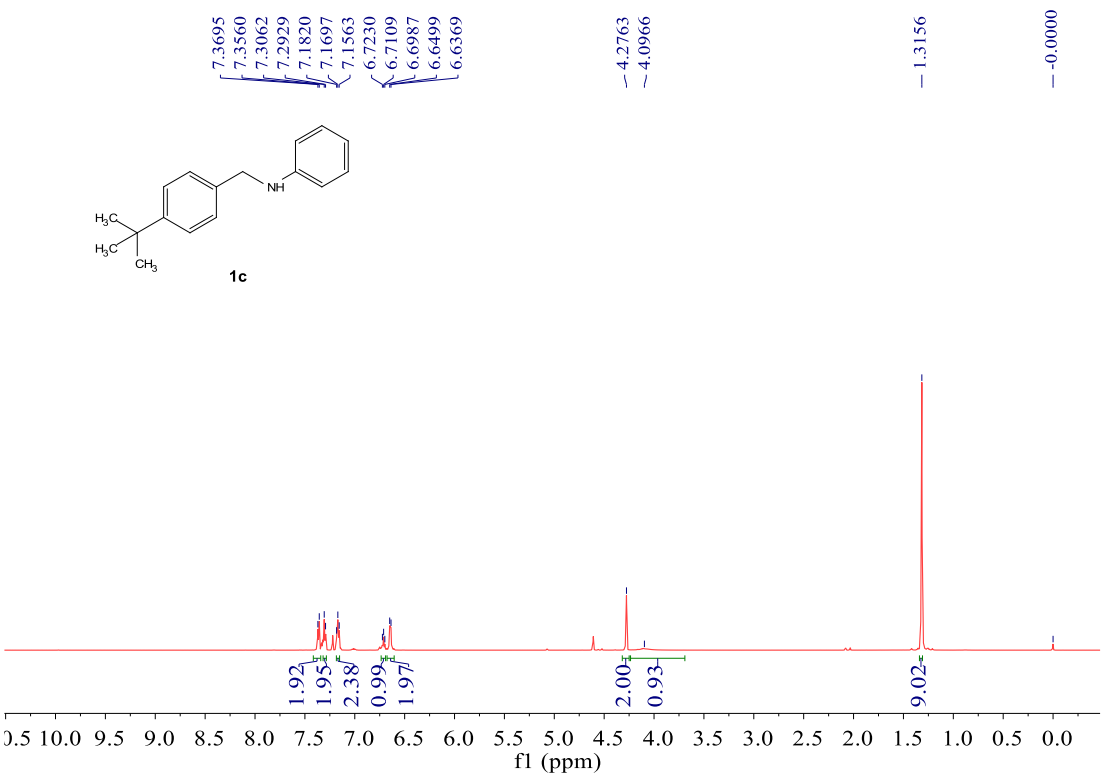
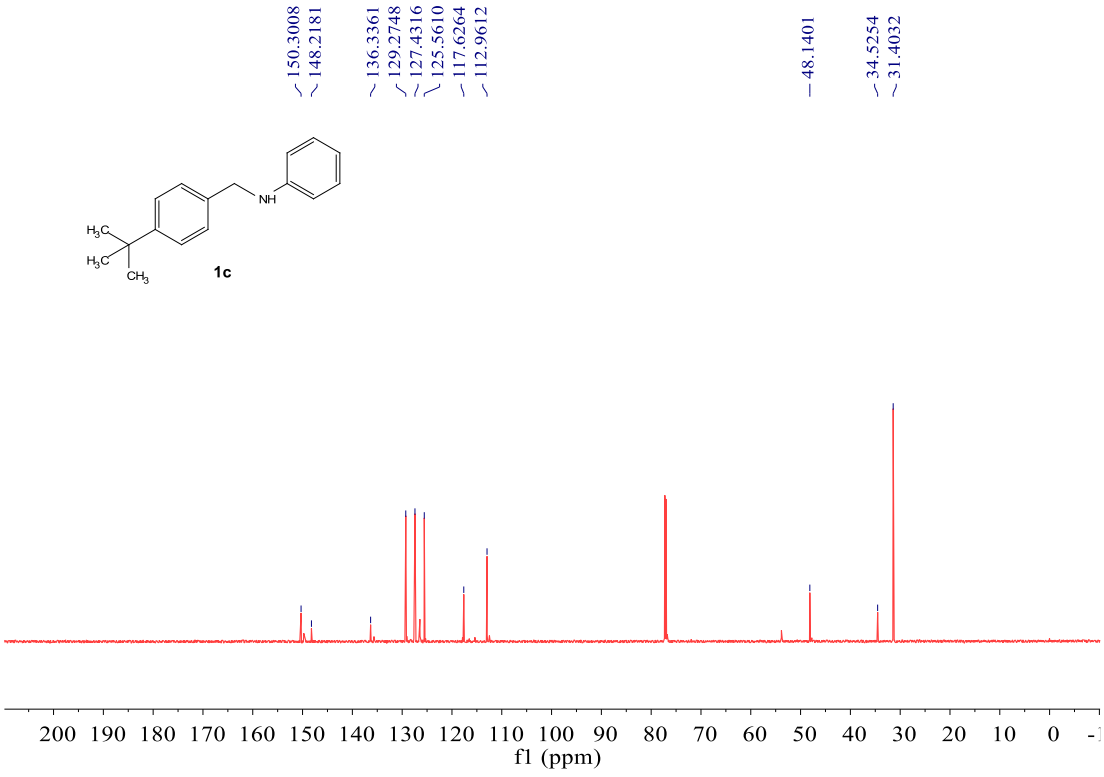
14. NMR spectra

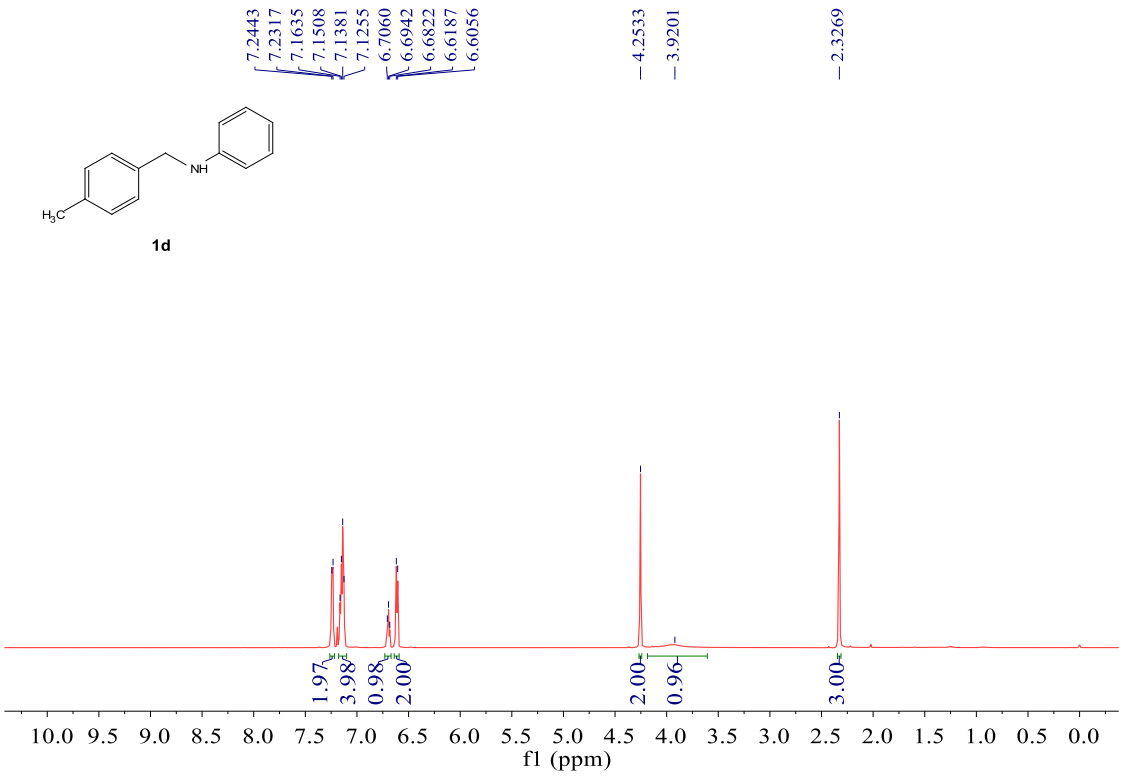
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1c



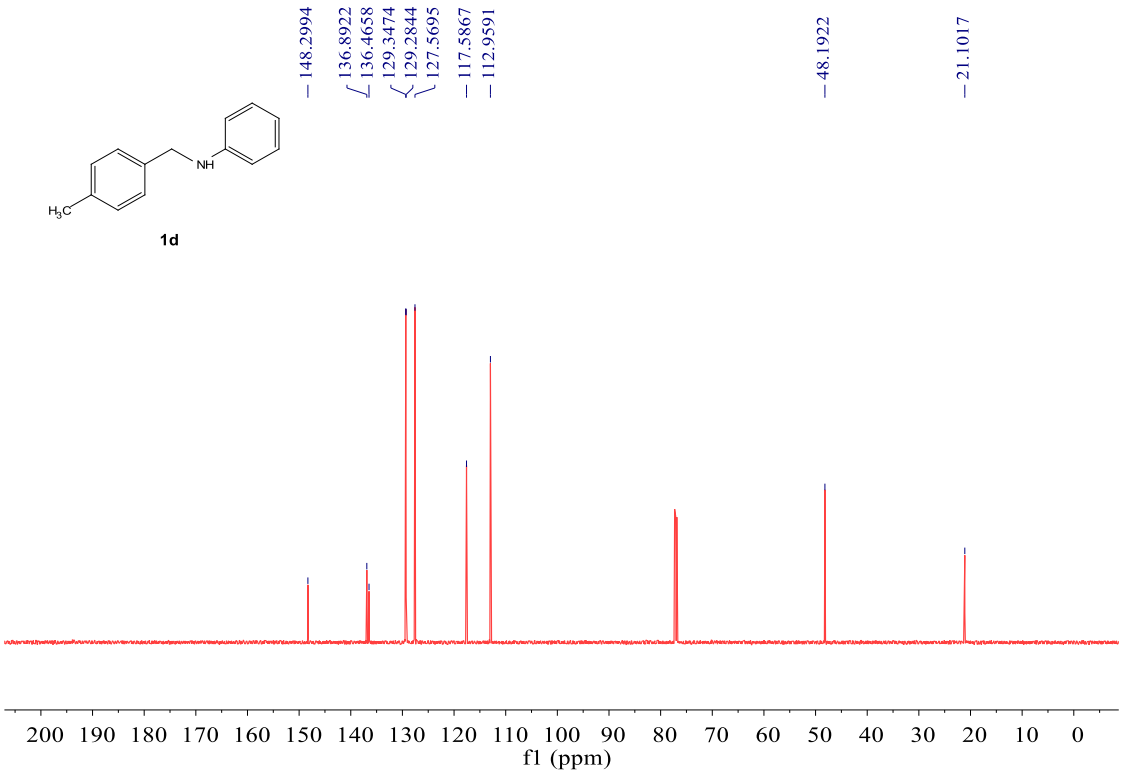
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1c



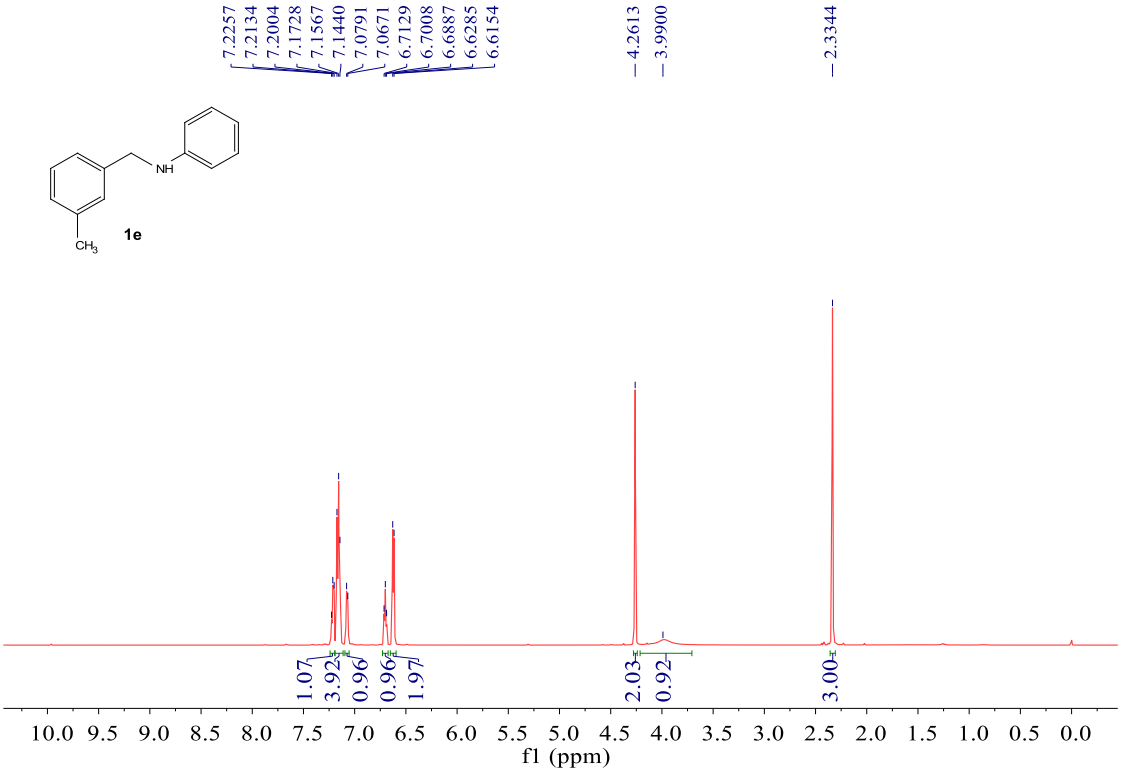
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1d



^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1d



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



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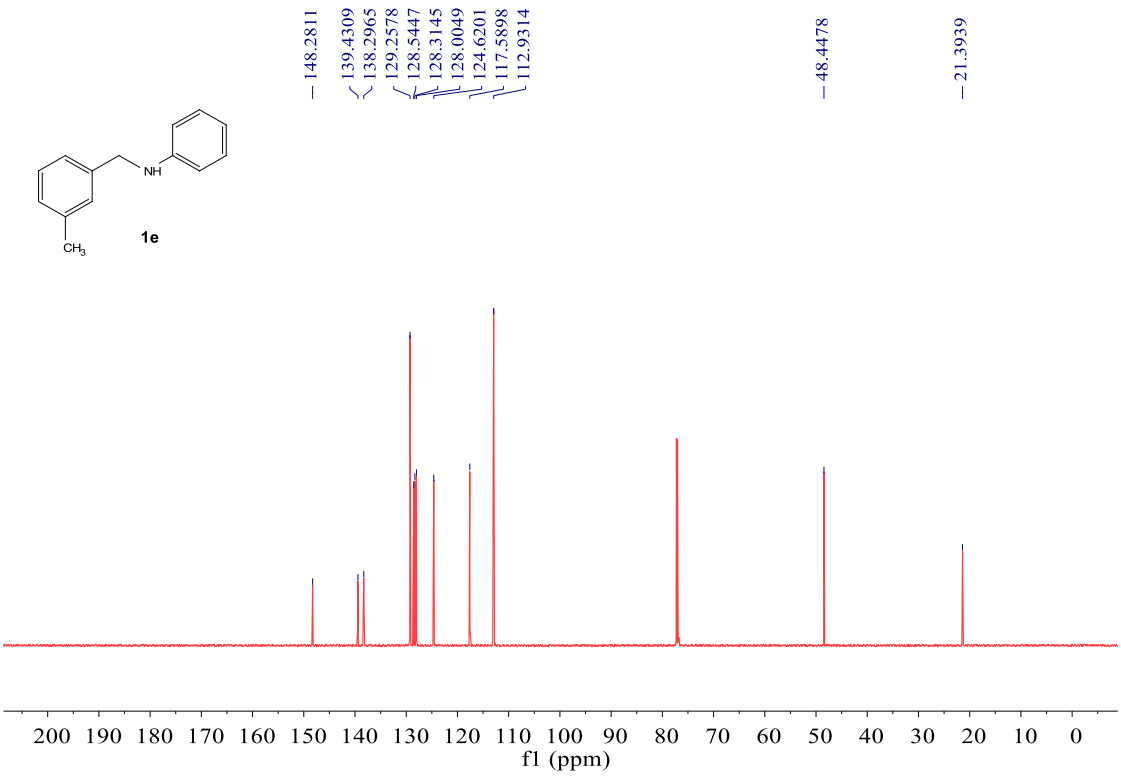
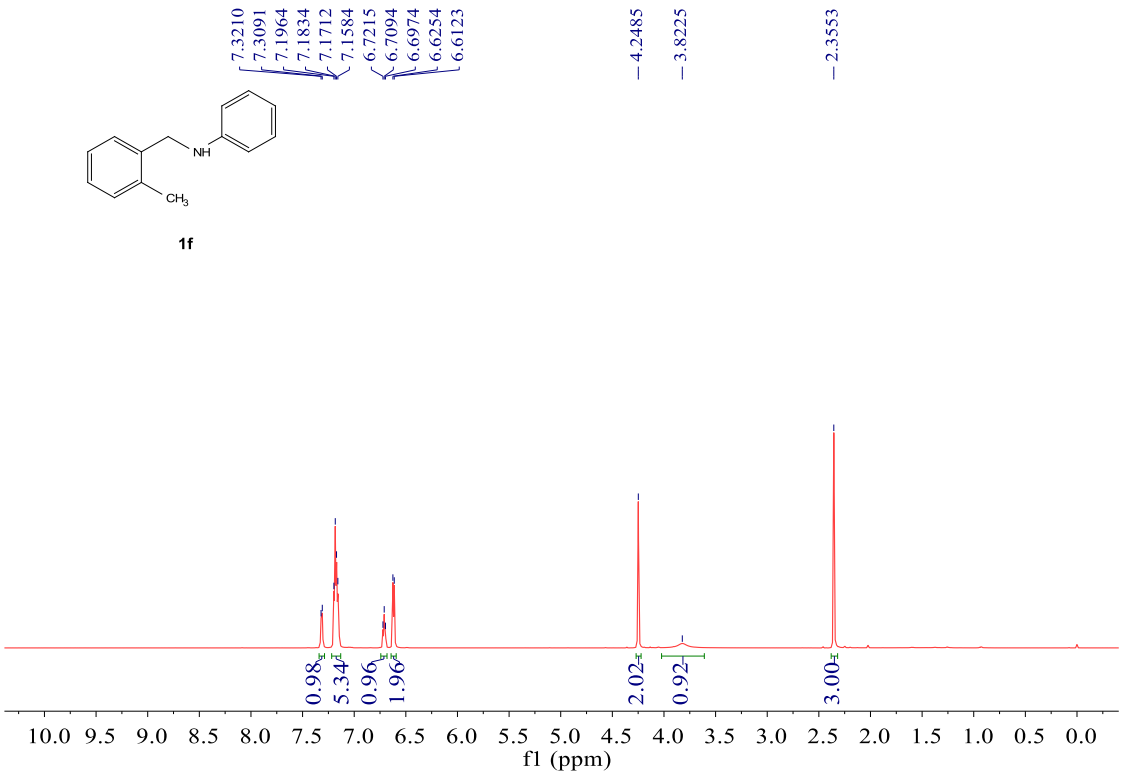
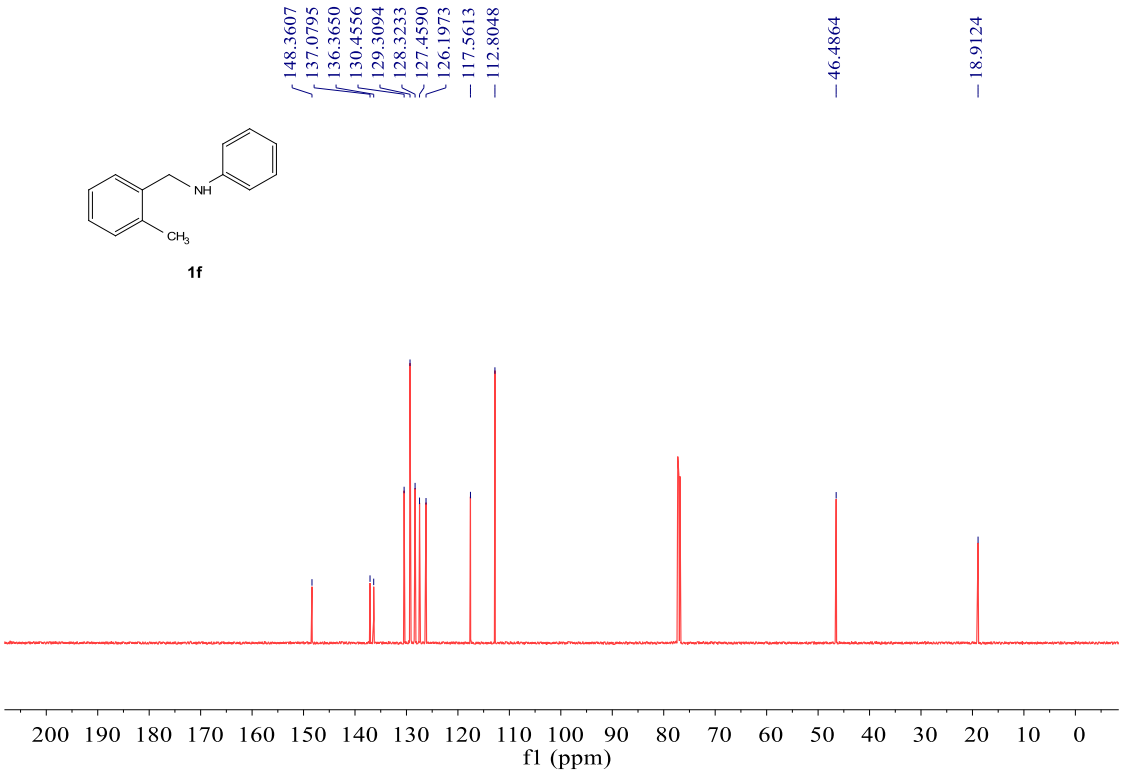


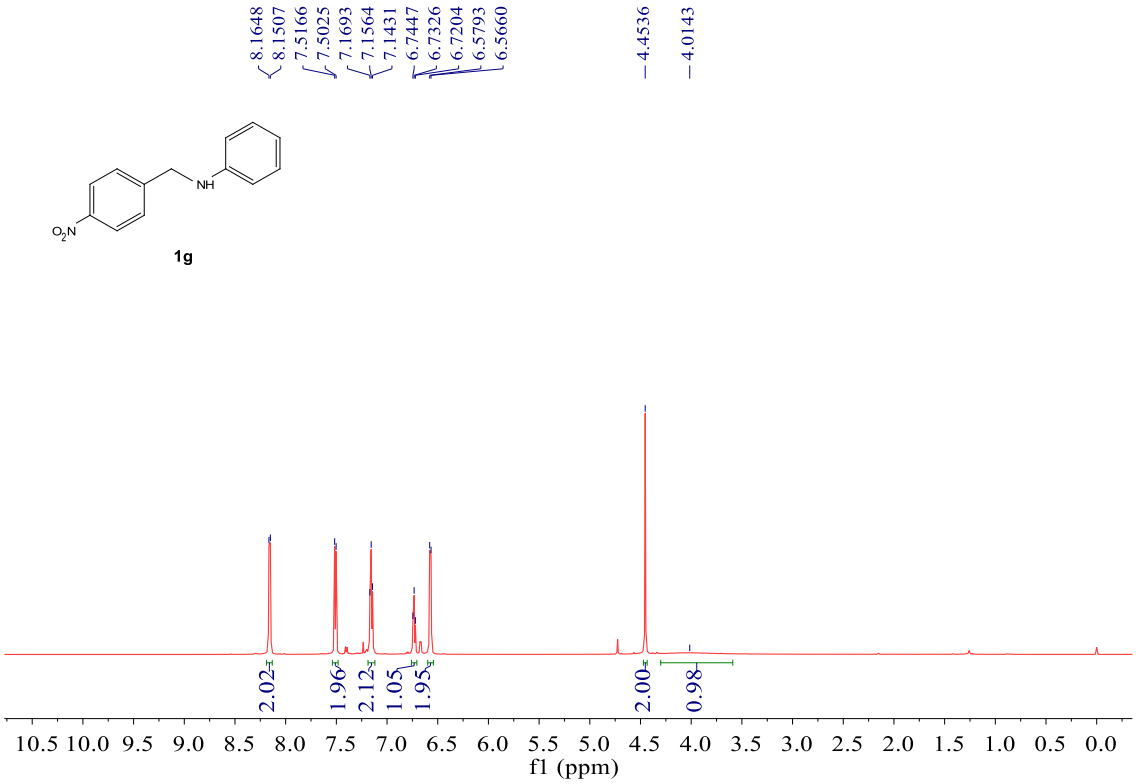
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1f



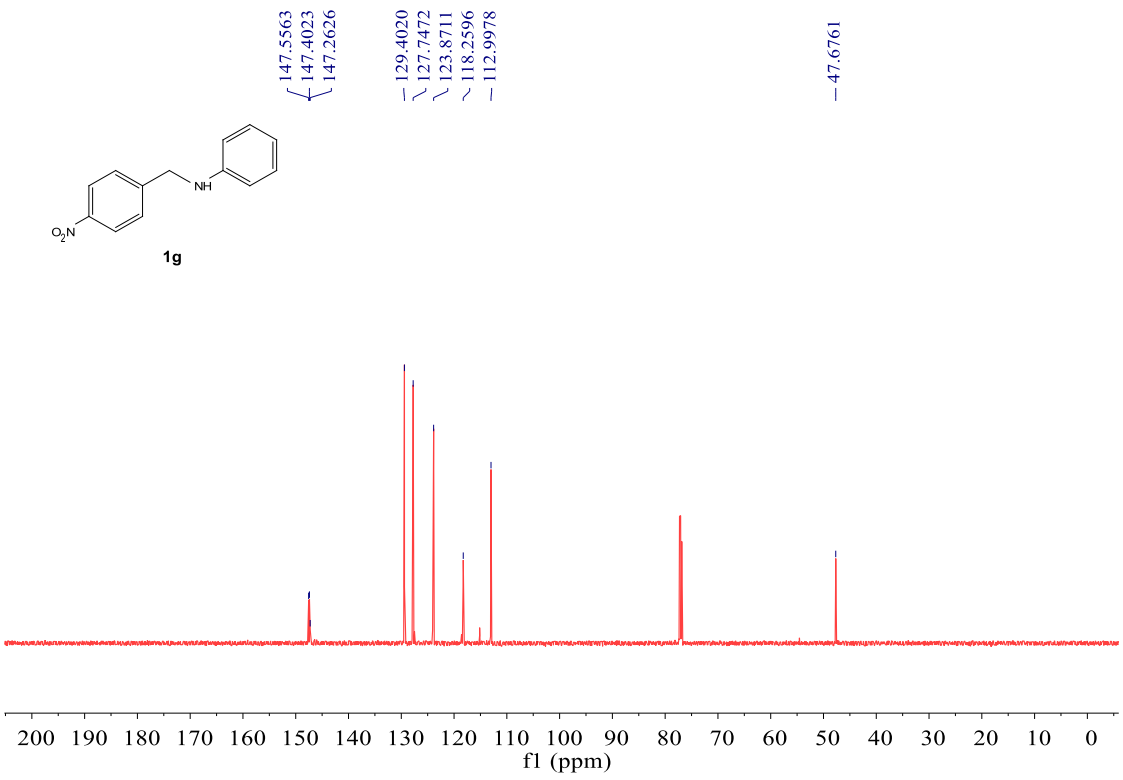
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1f



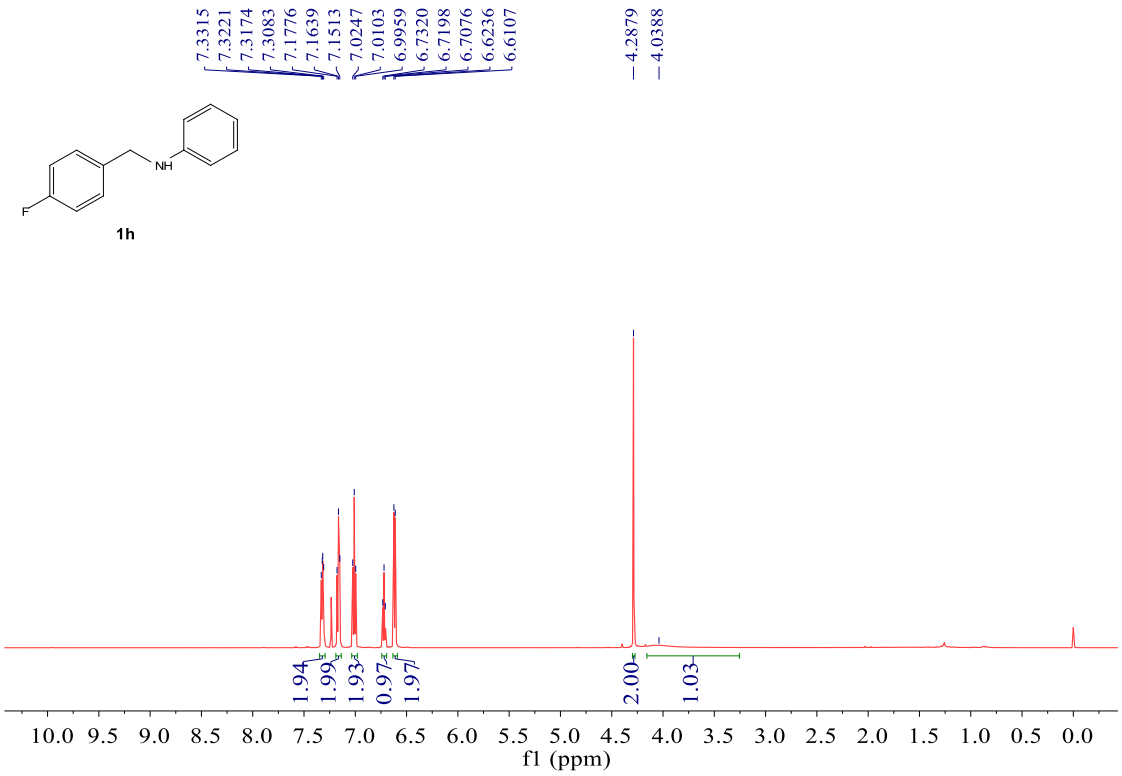
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1g



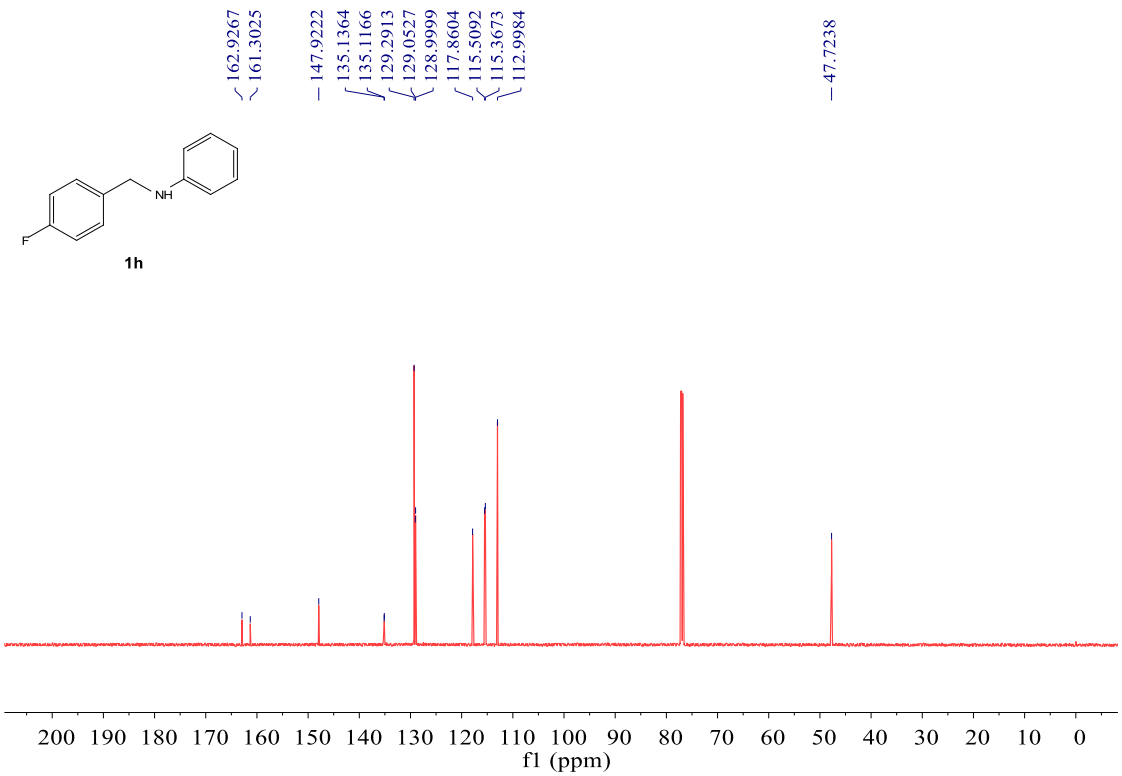
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1g



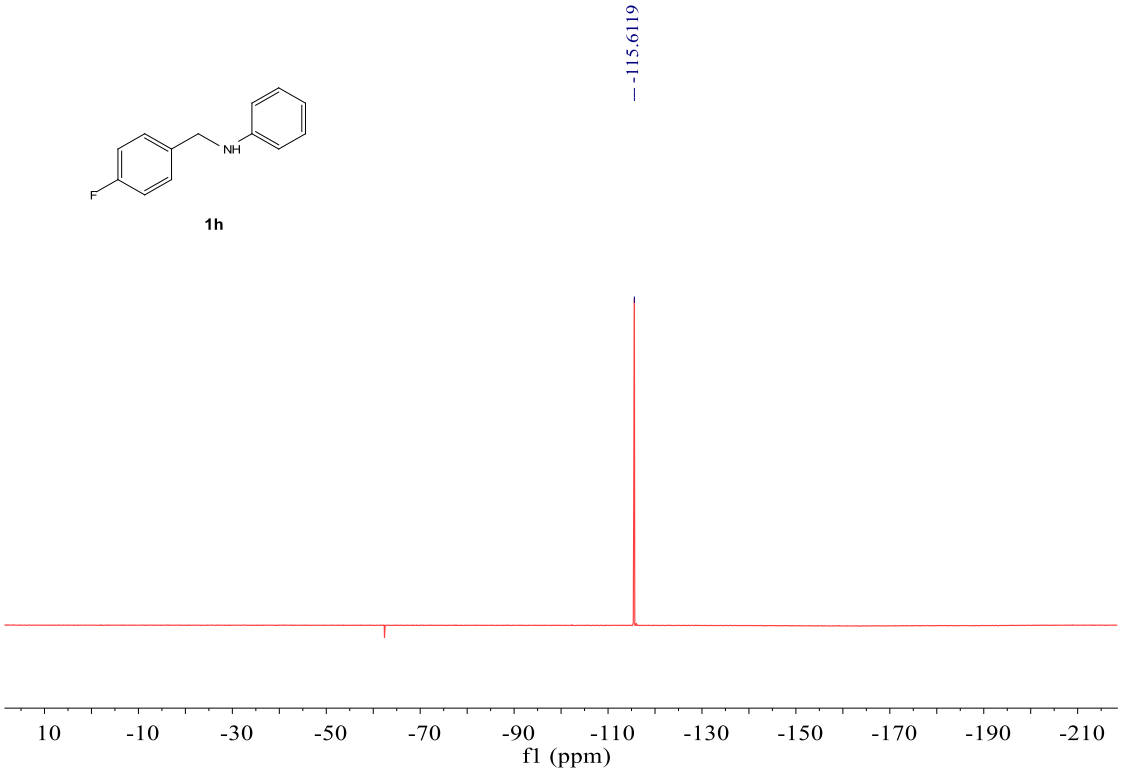
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1h



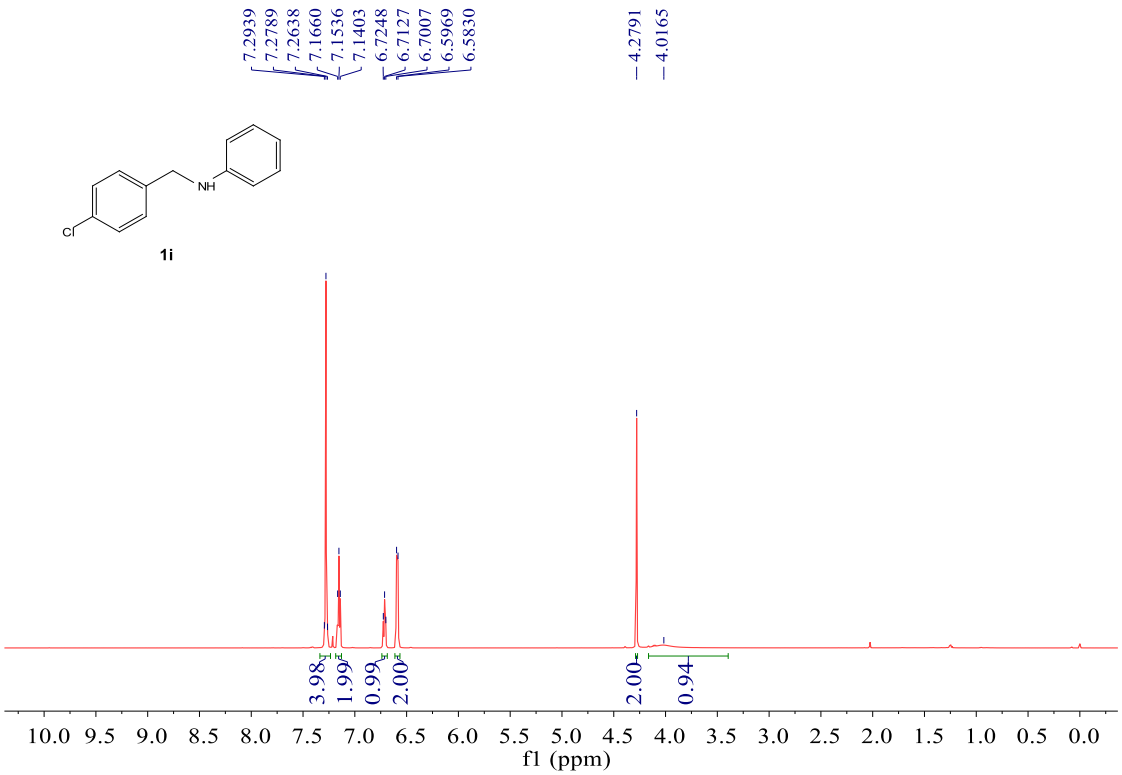
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1h



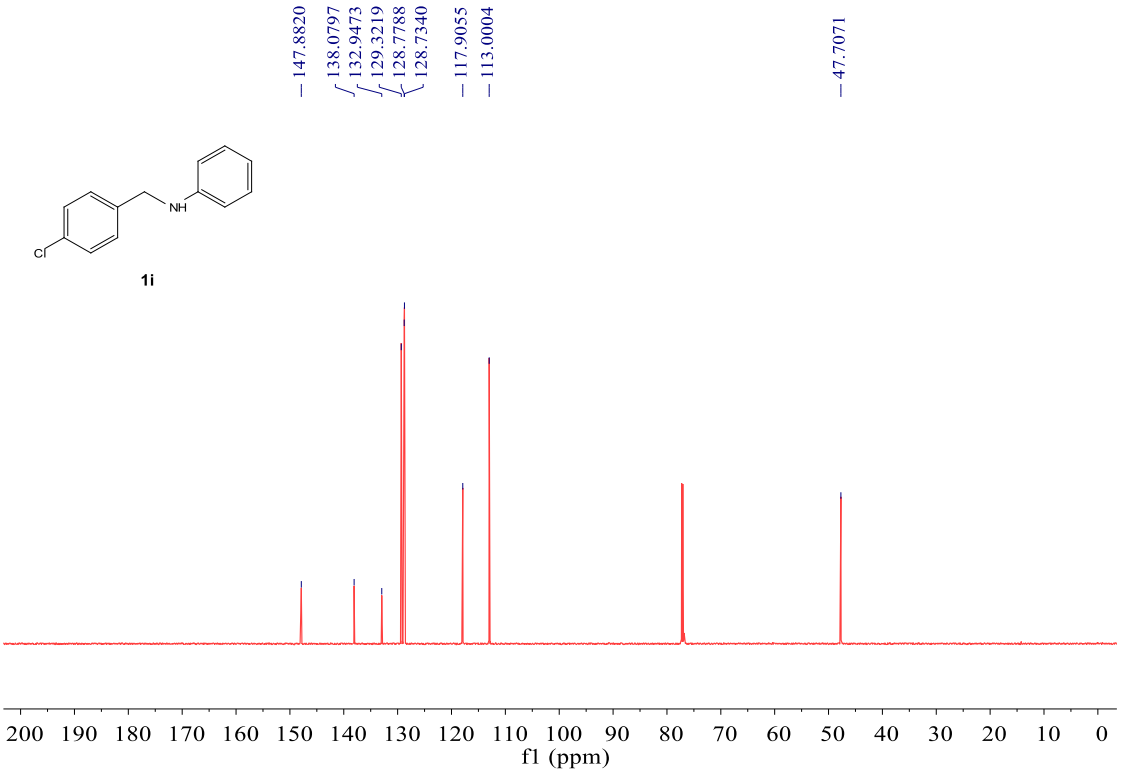
^{19}F NMR Spectrum (376 MHz, $CDCl_3$) of 1h



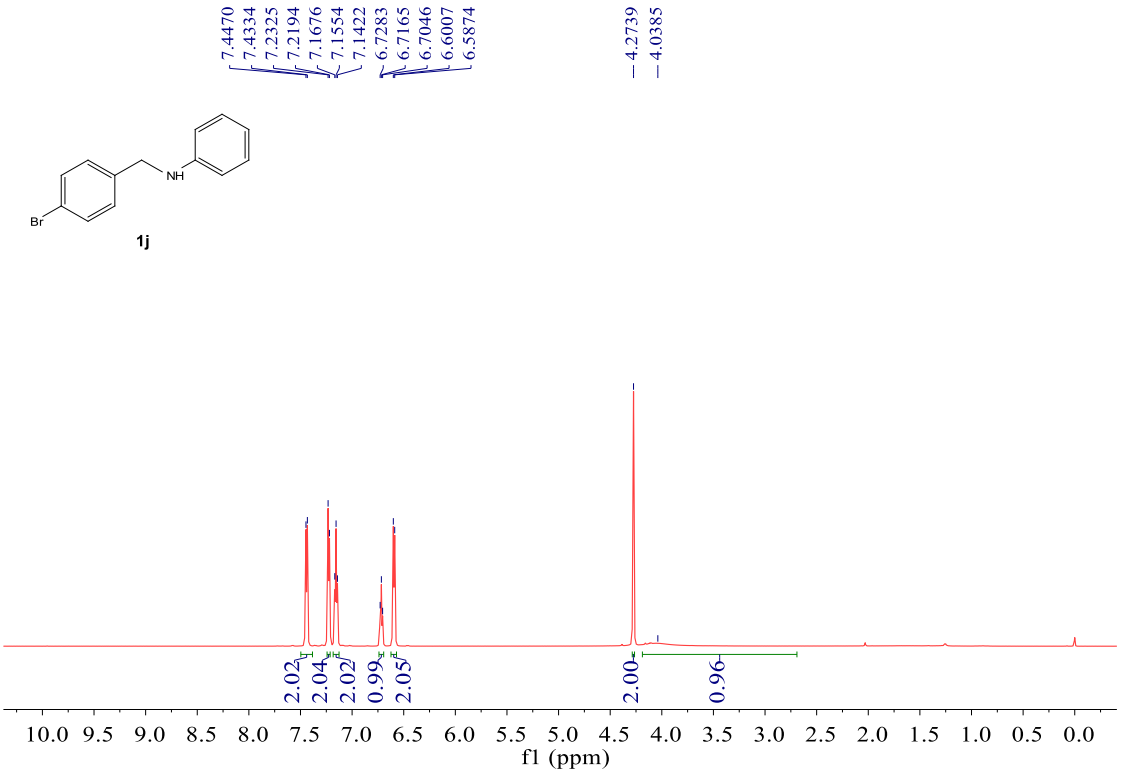
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1i



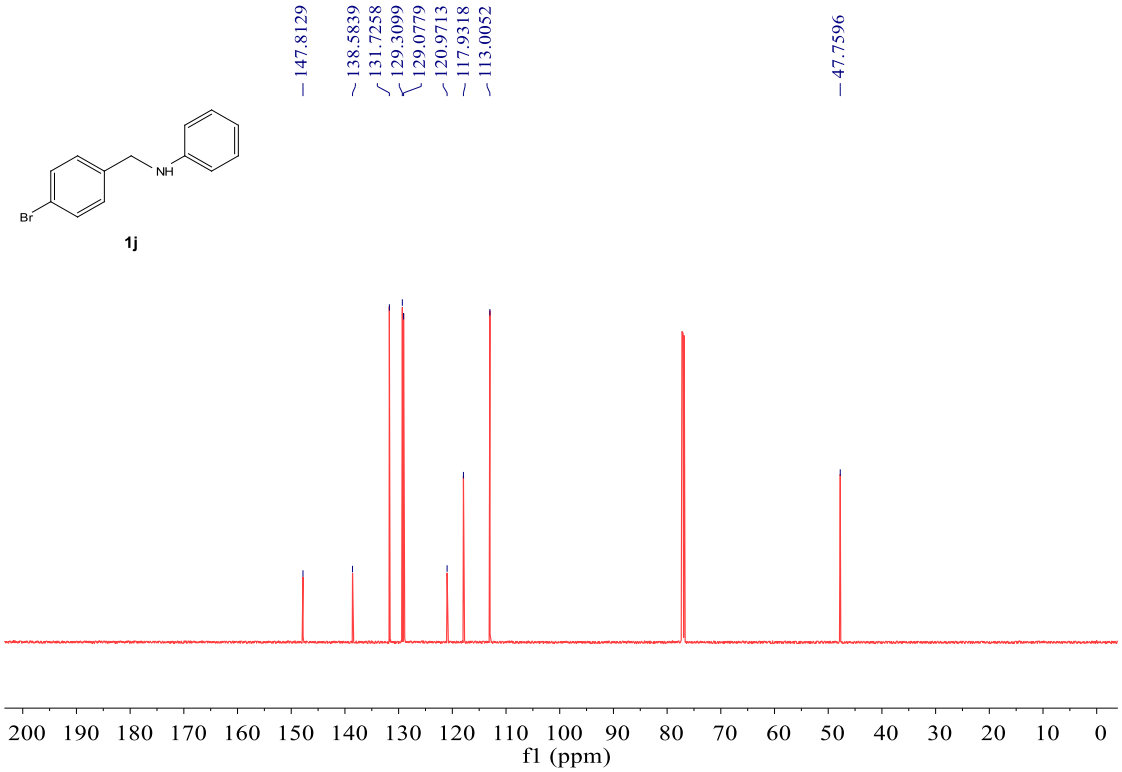
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1i



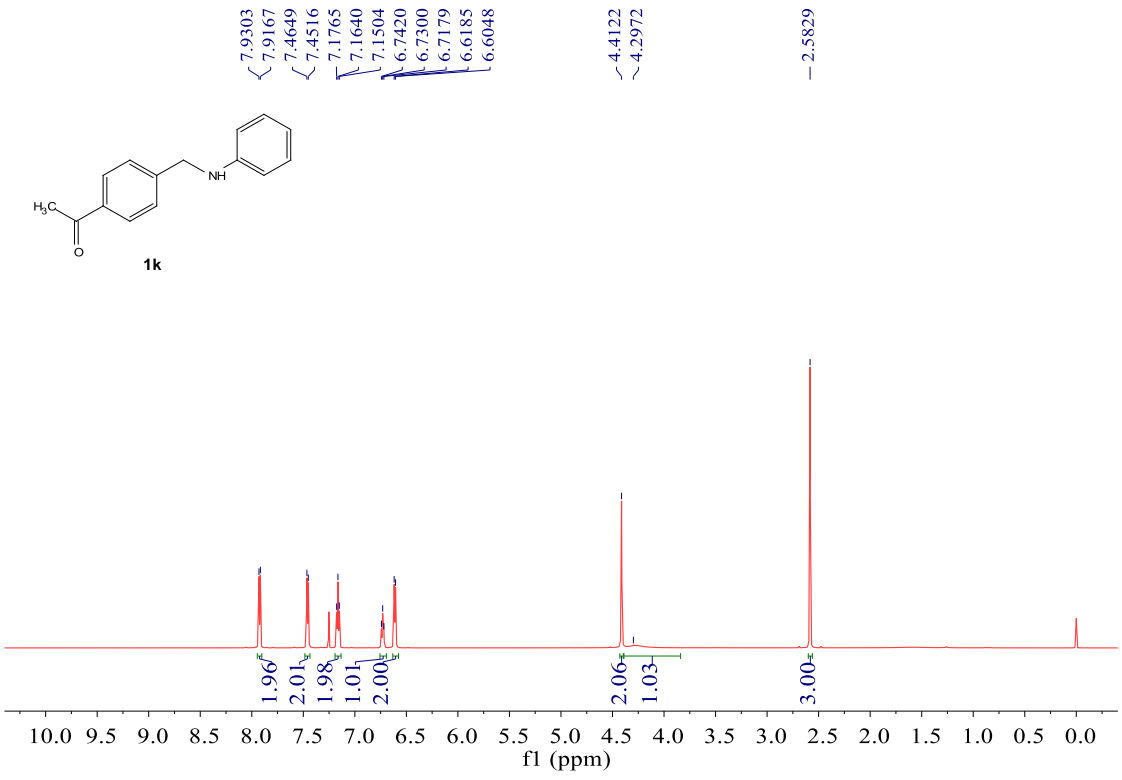
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1j



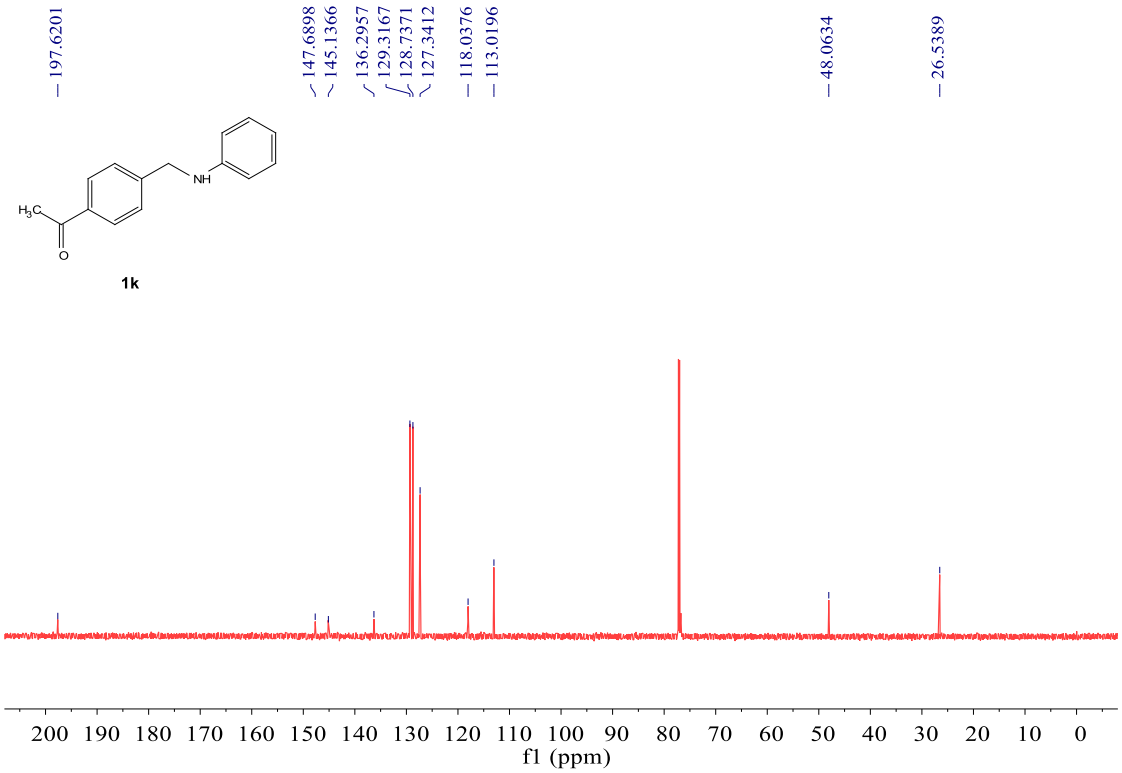
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1j



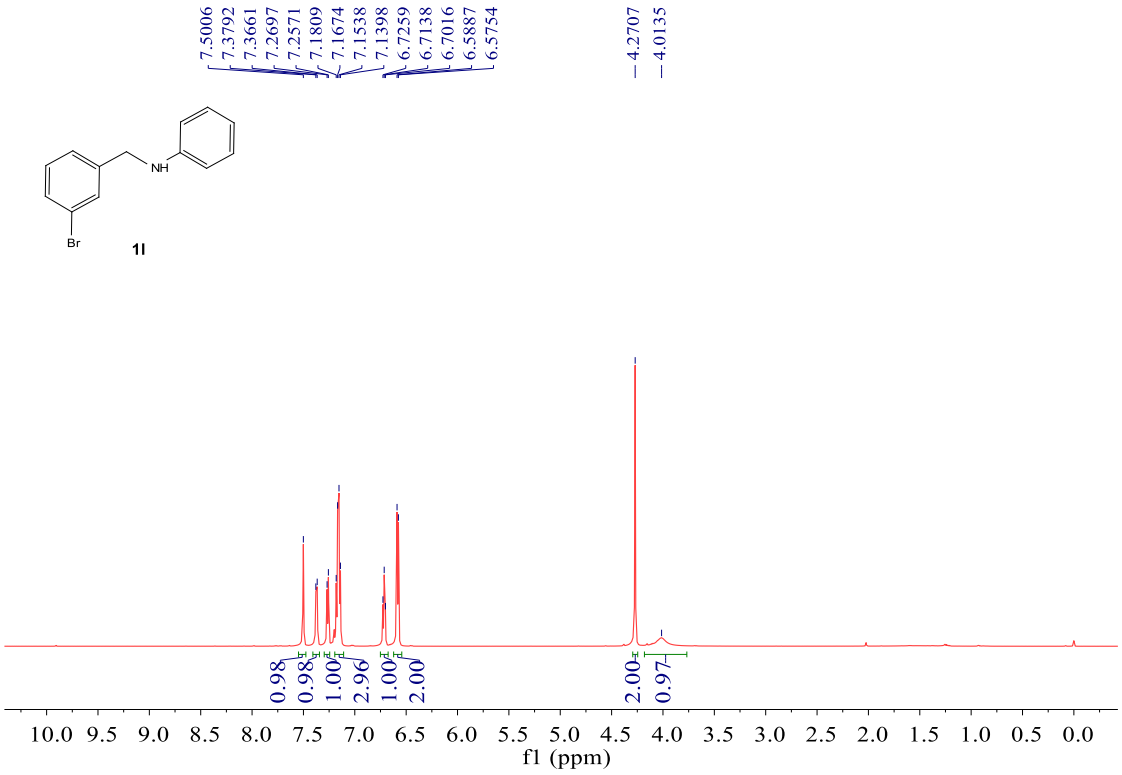
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1k



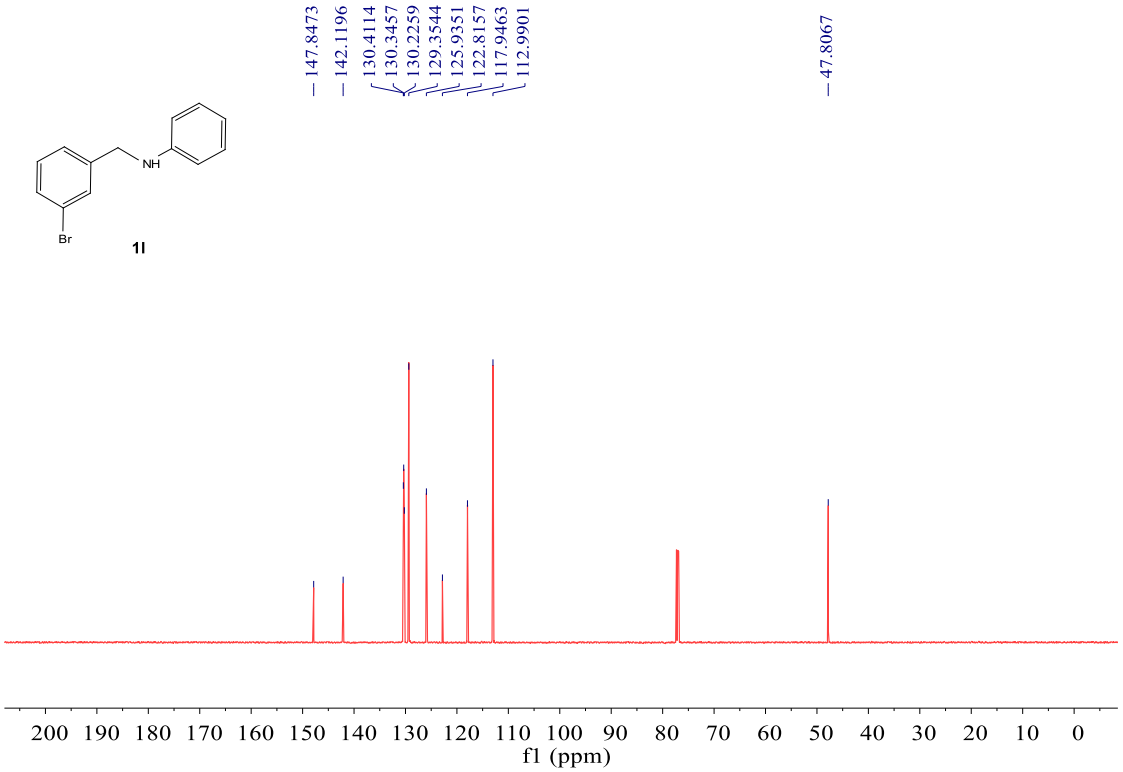
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1k



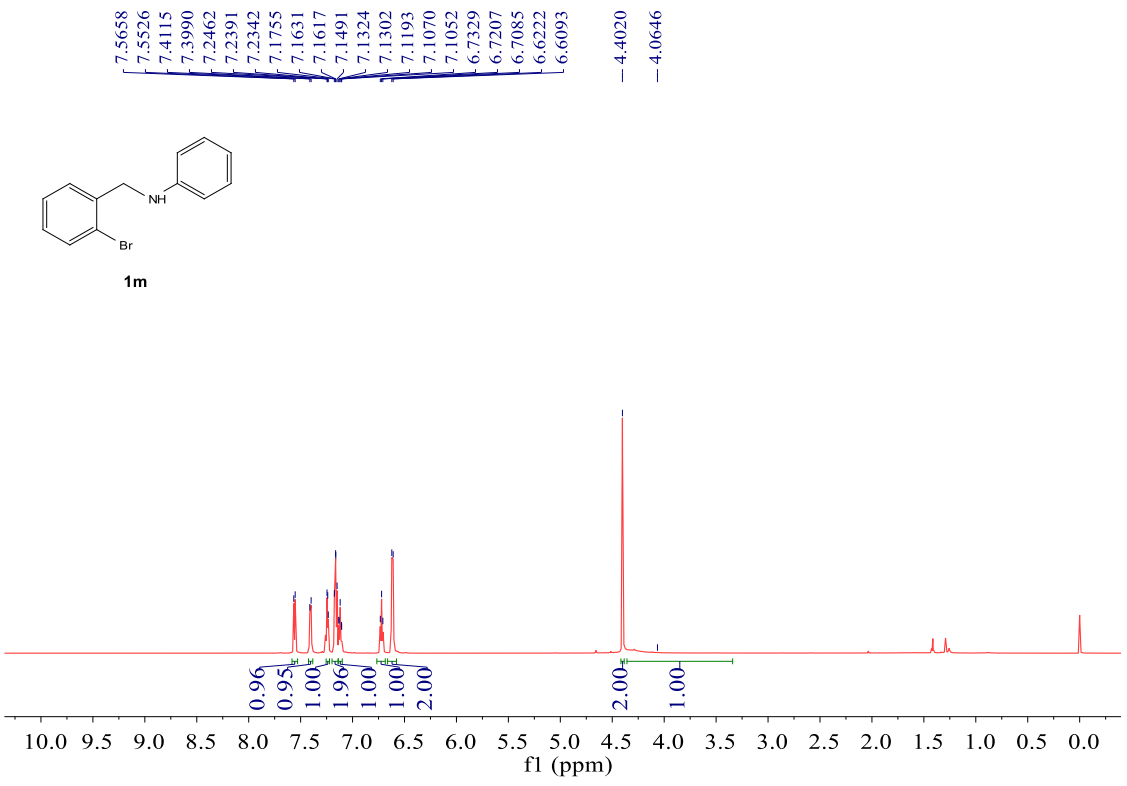
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1l



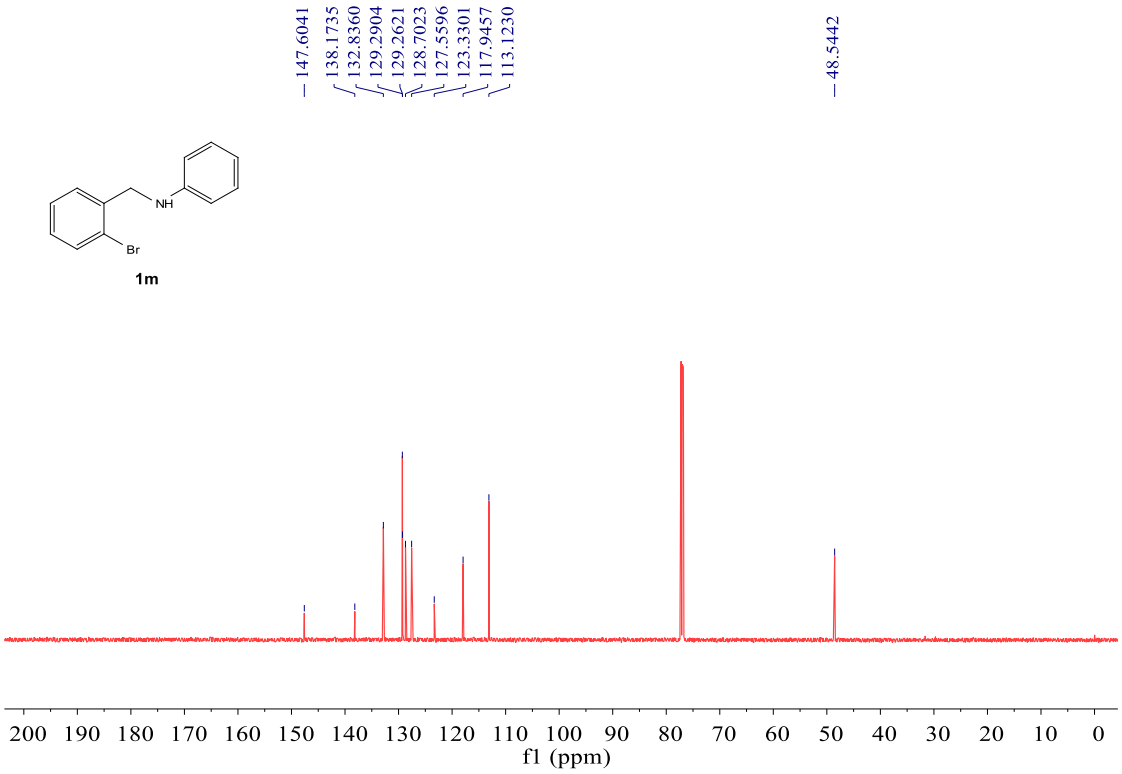
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1l



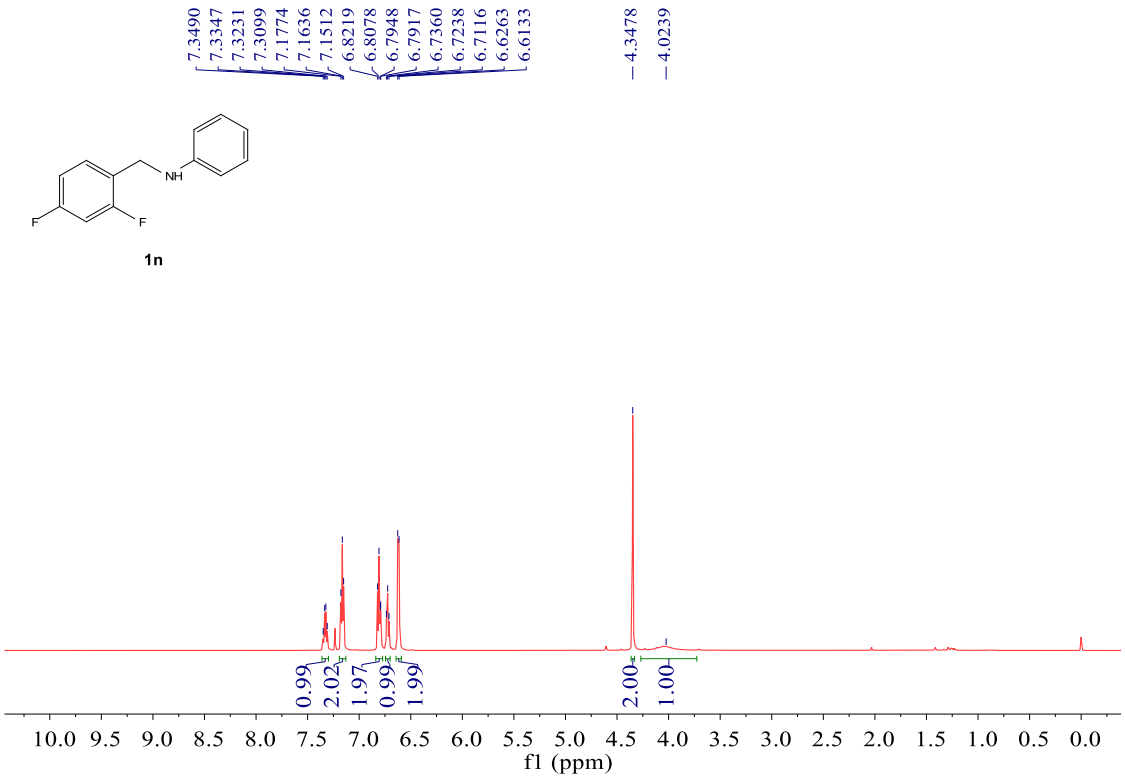
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1m



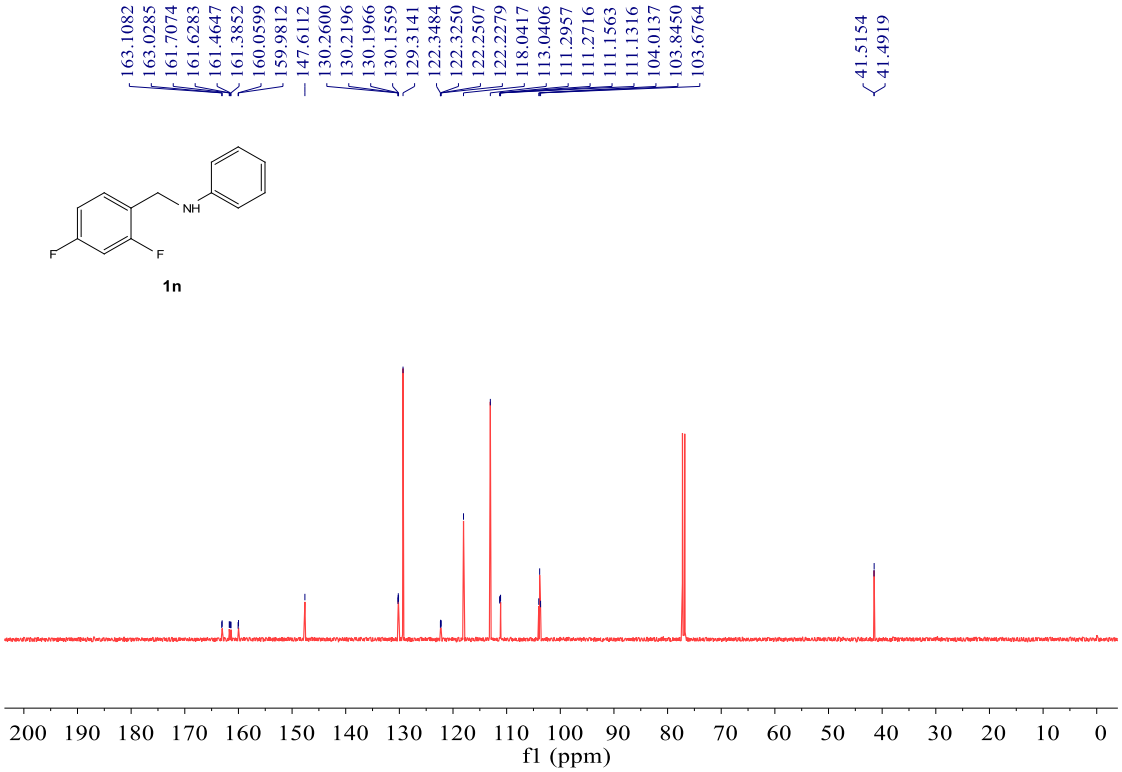
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1m



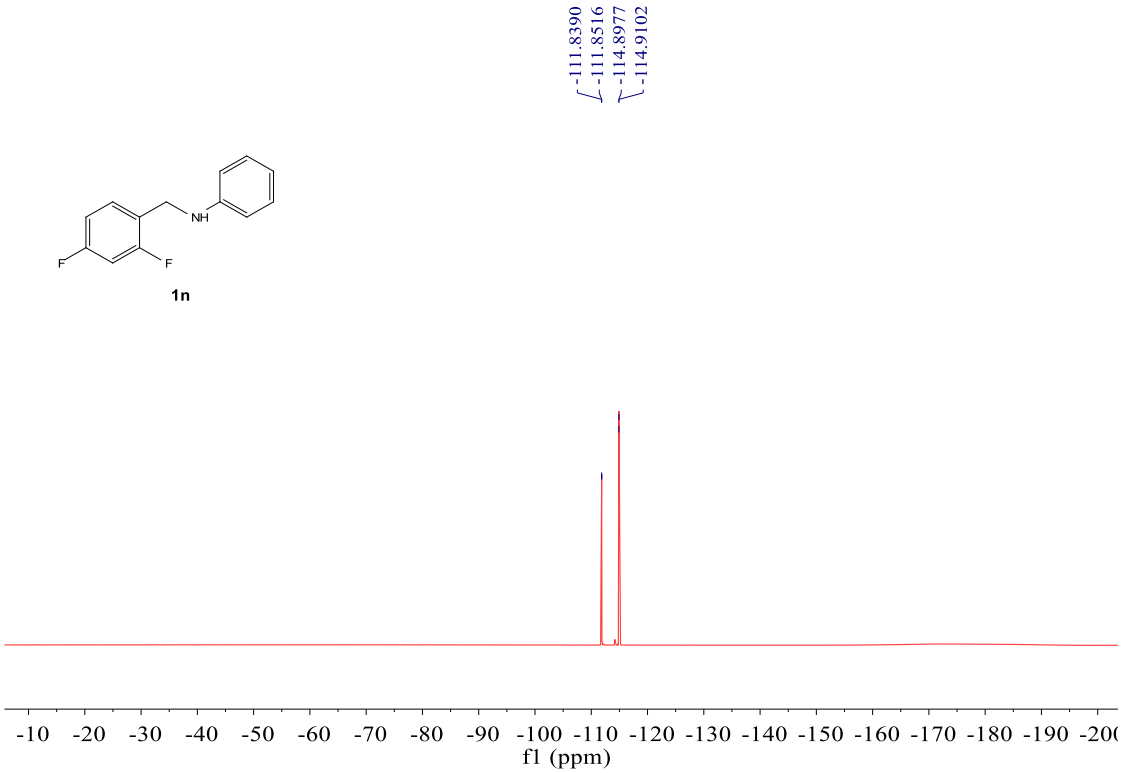
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1n



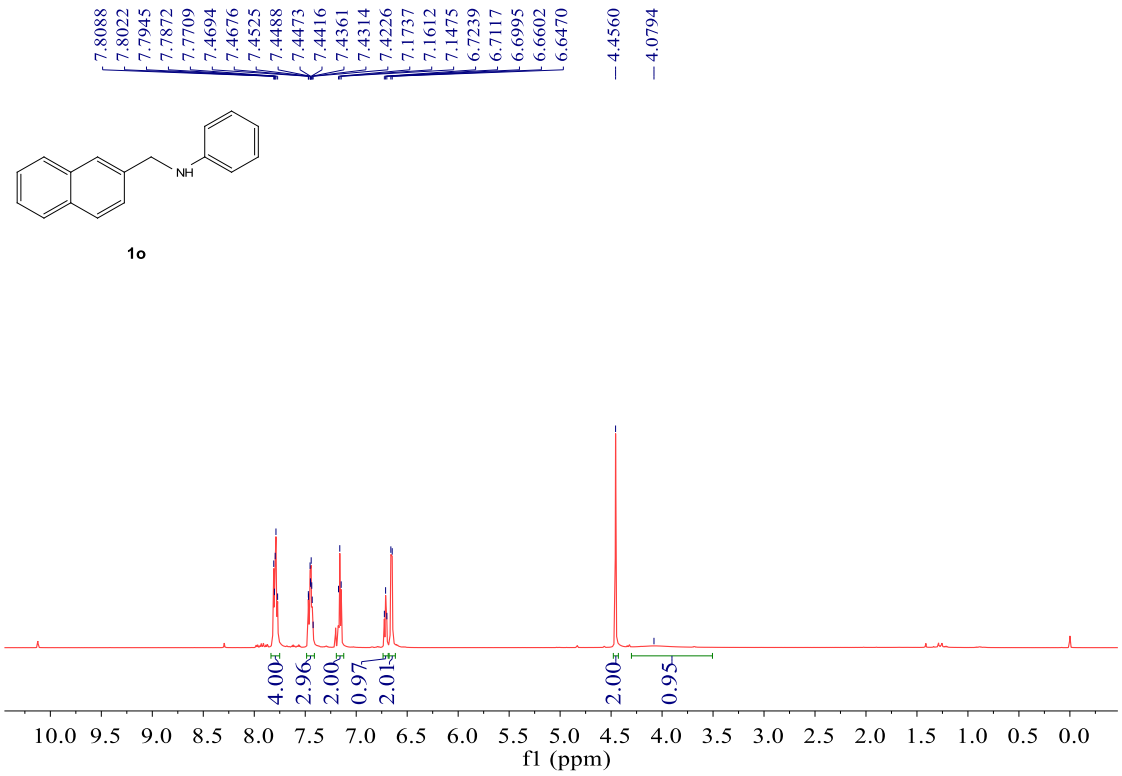
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1n



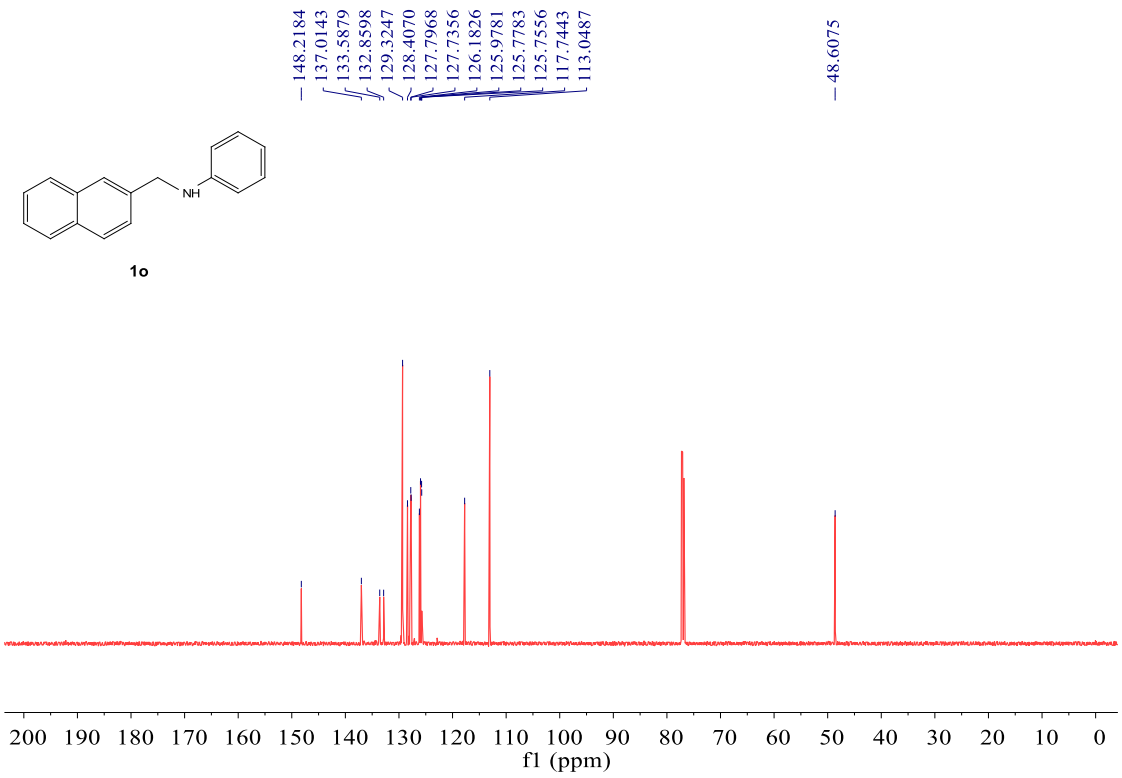
^{19}F NMR Spectrum (565 MHz, $CDCl_3$) of 1n



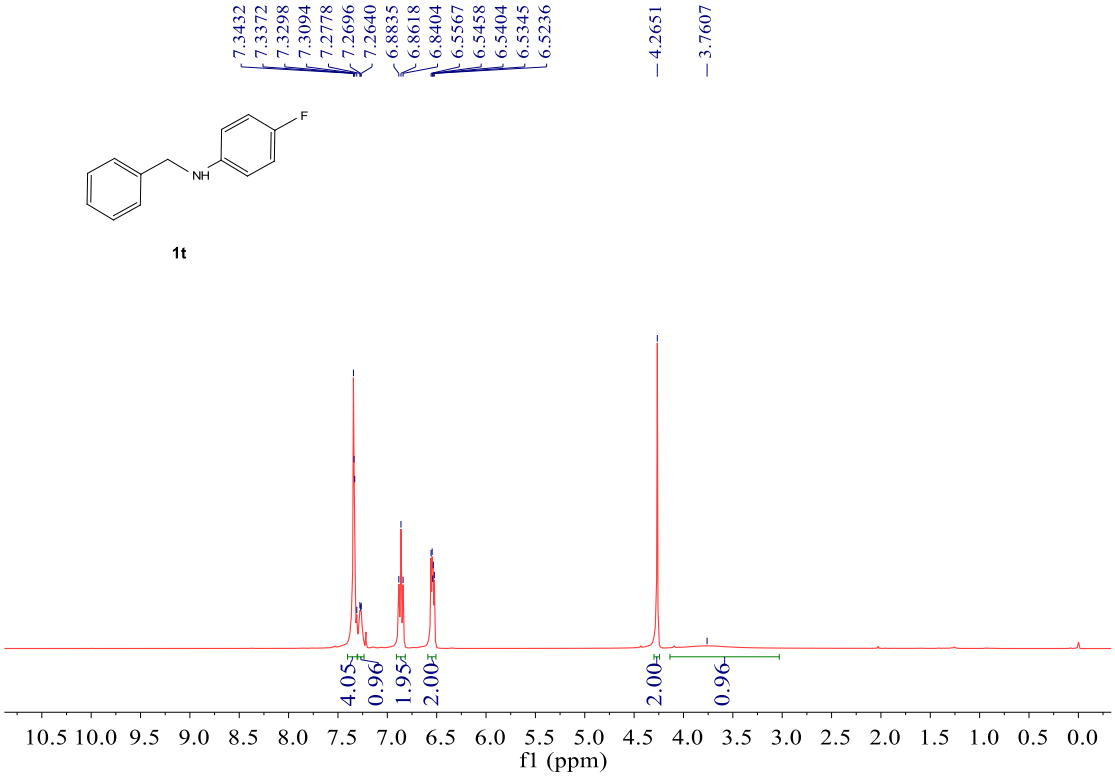
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1o



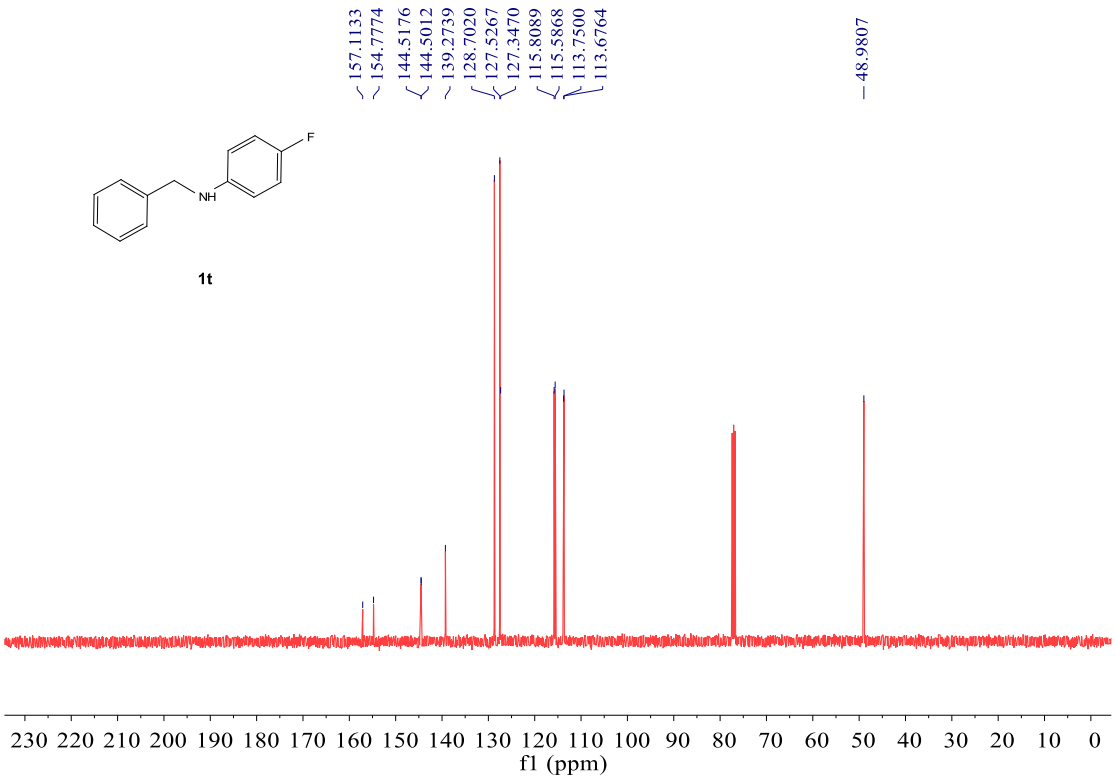
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1o



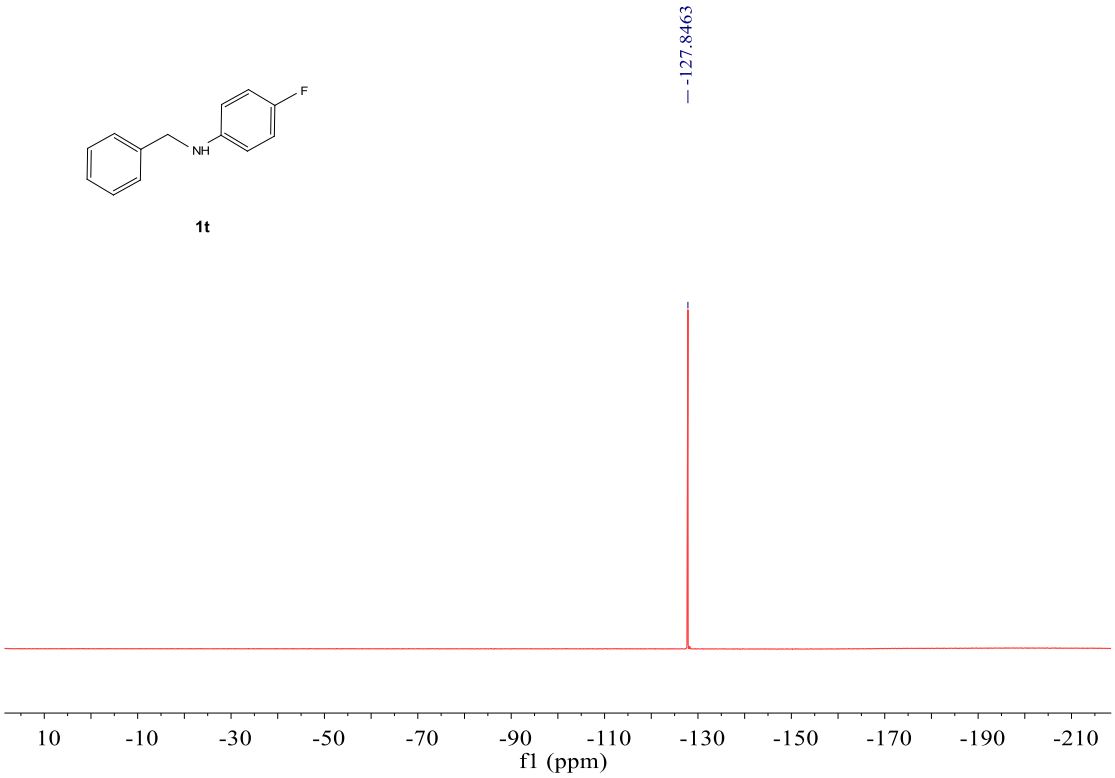
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1t



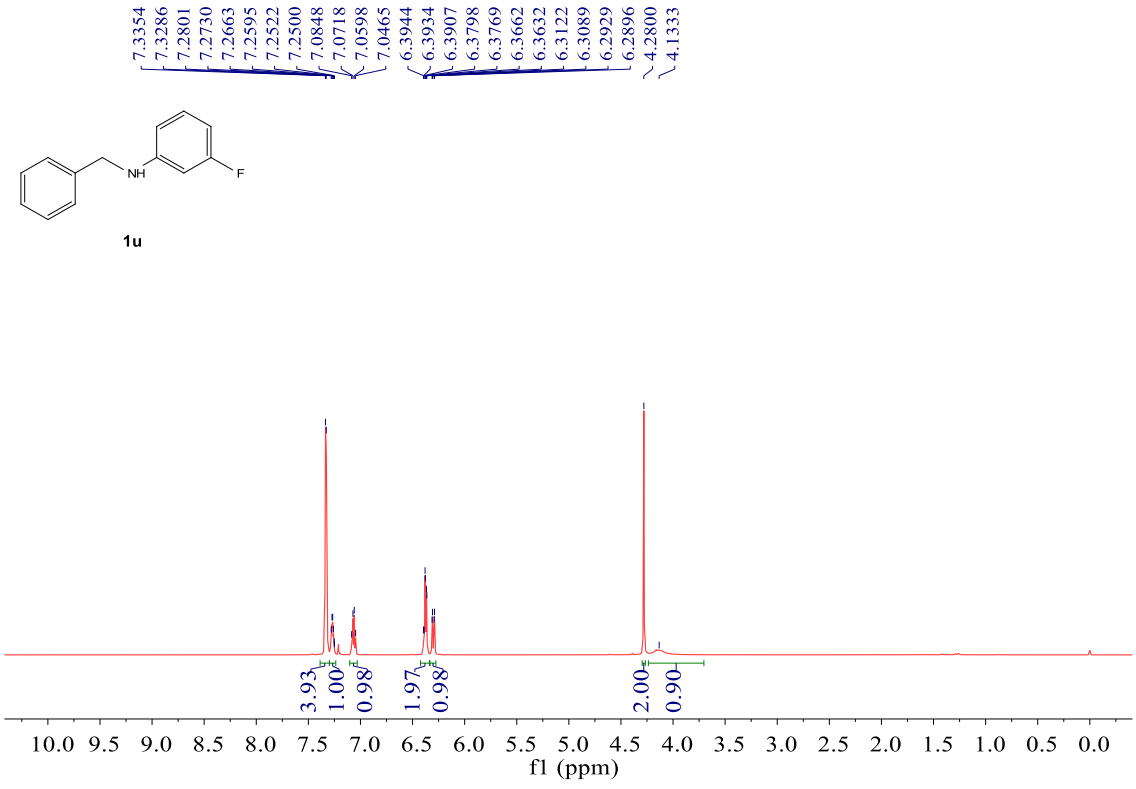
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1t



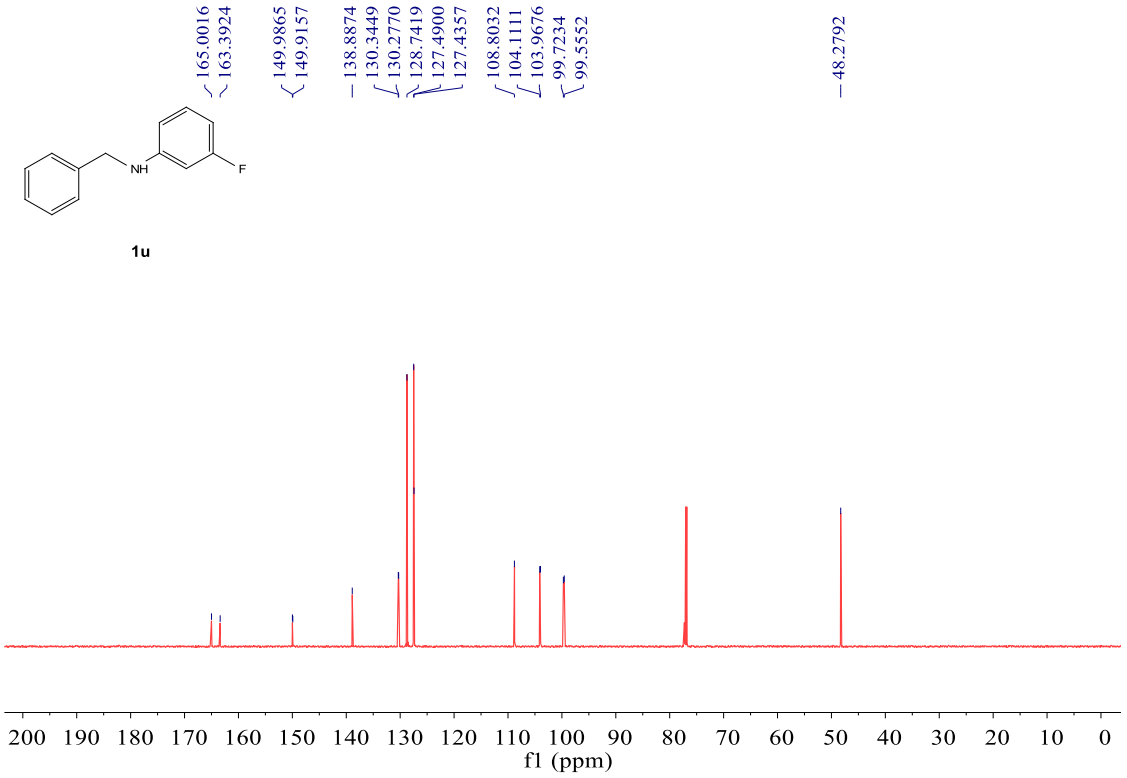
^{19}F NMR Spectrum (376 MHz, $CDCl_3$) of 1t



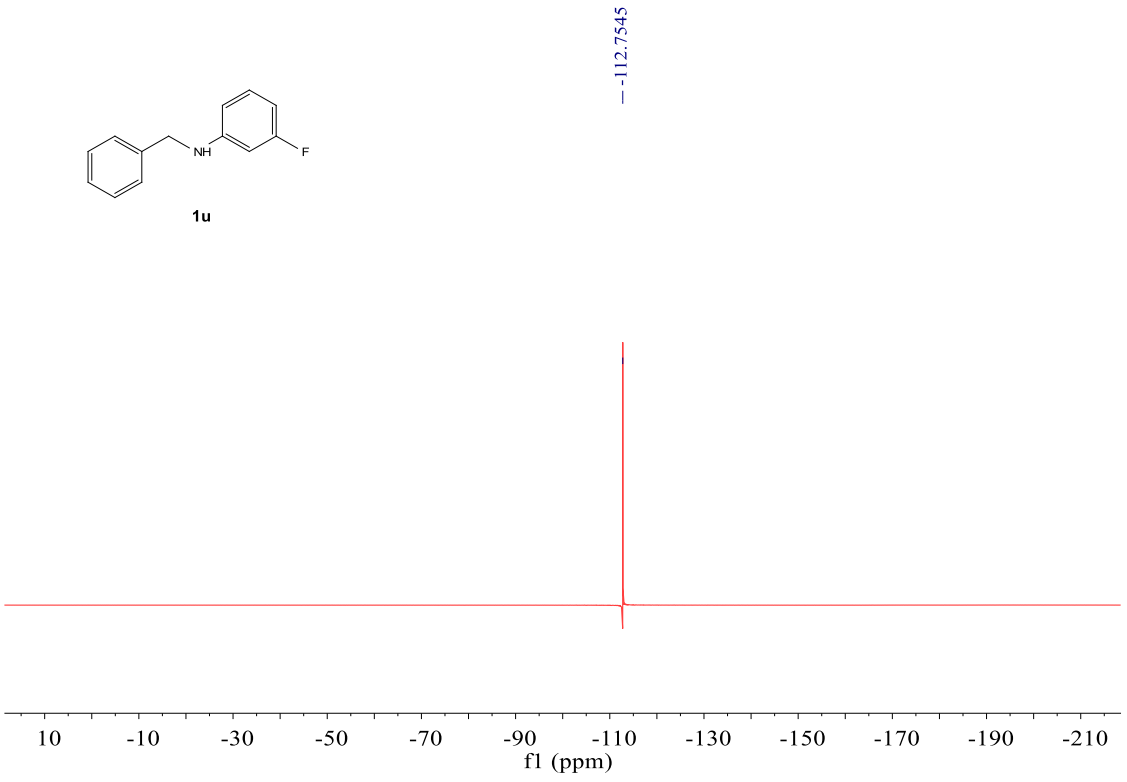
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1u



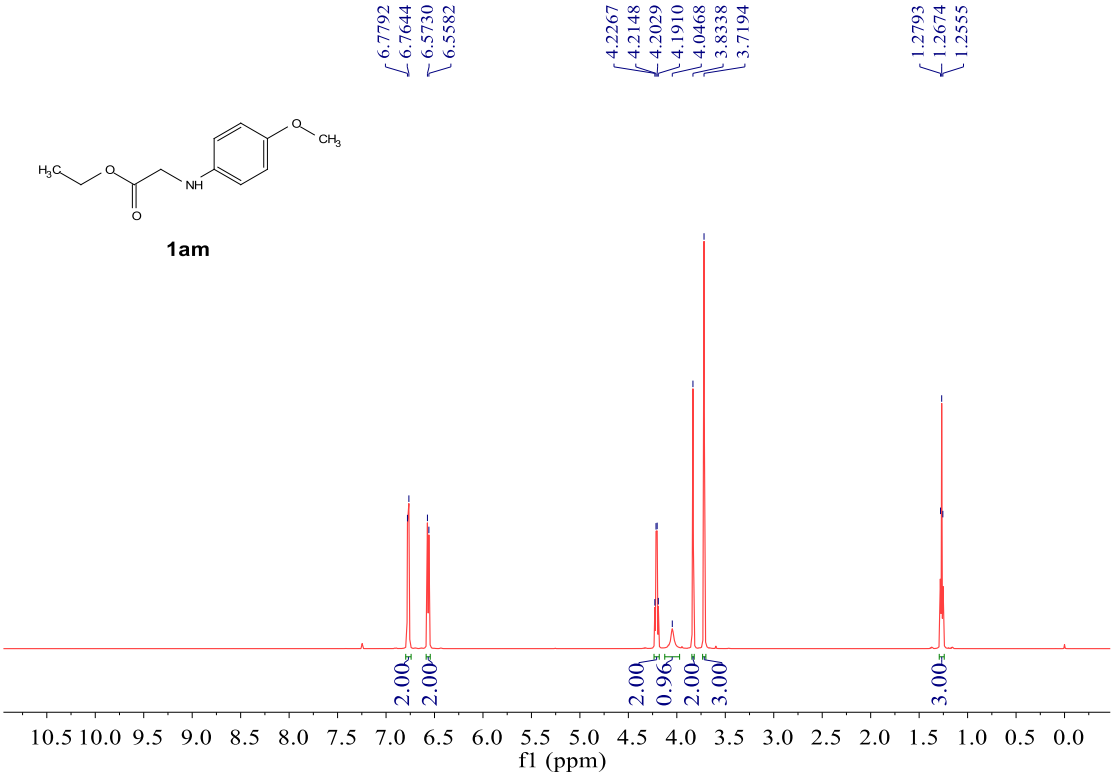
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1u



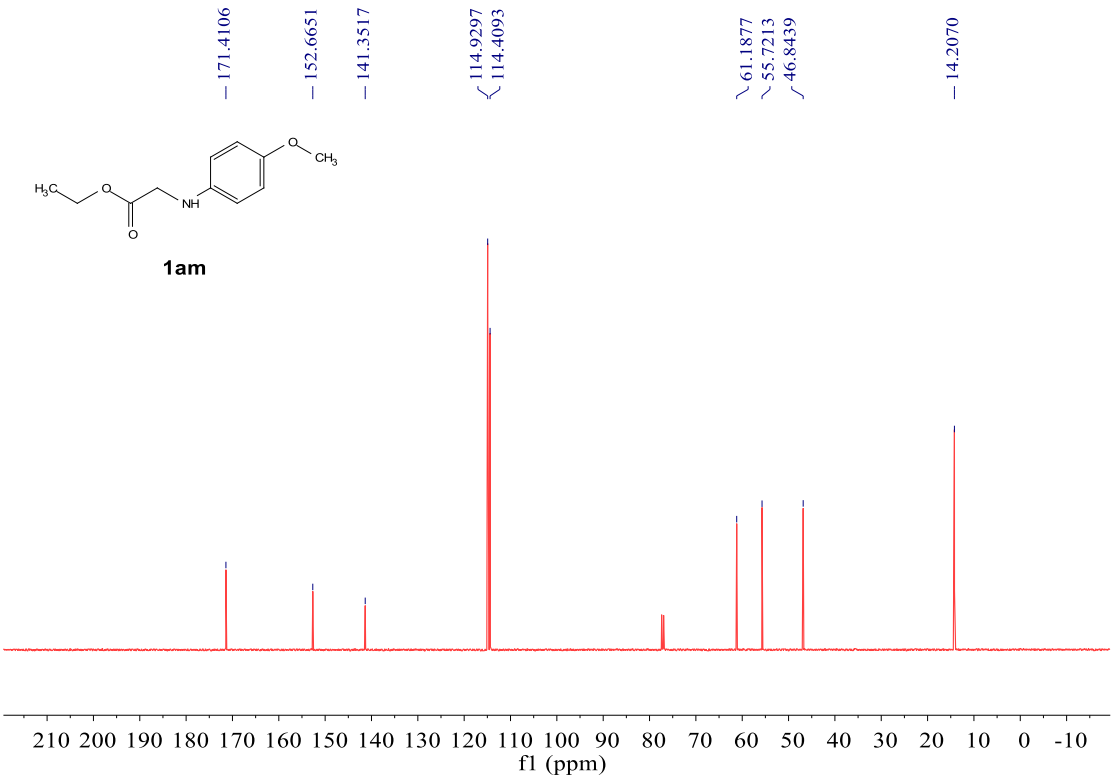
^{19}F NMR Spectrum (565 MHz, $CDCl_3$) of 1u



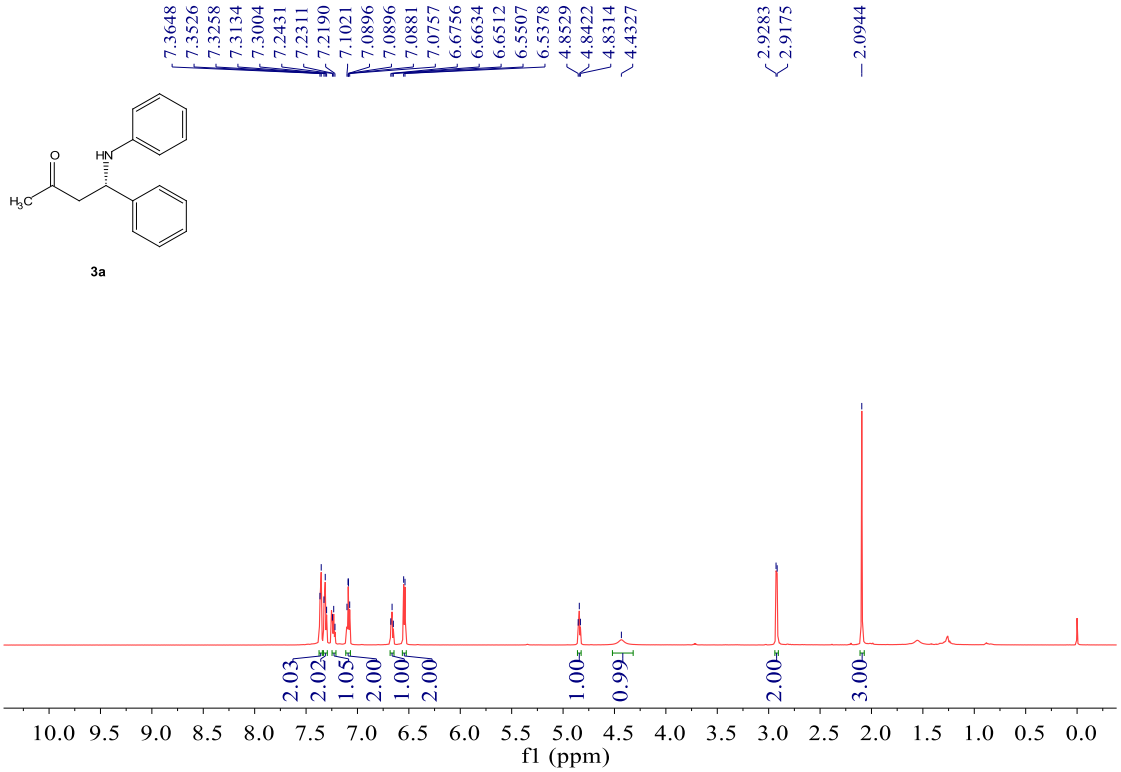
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1am



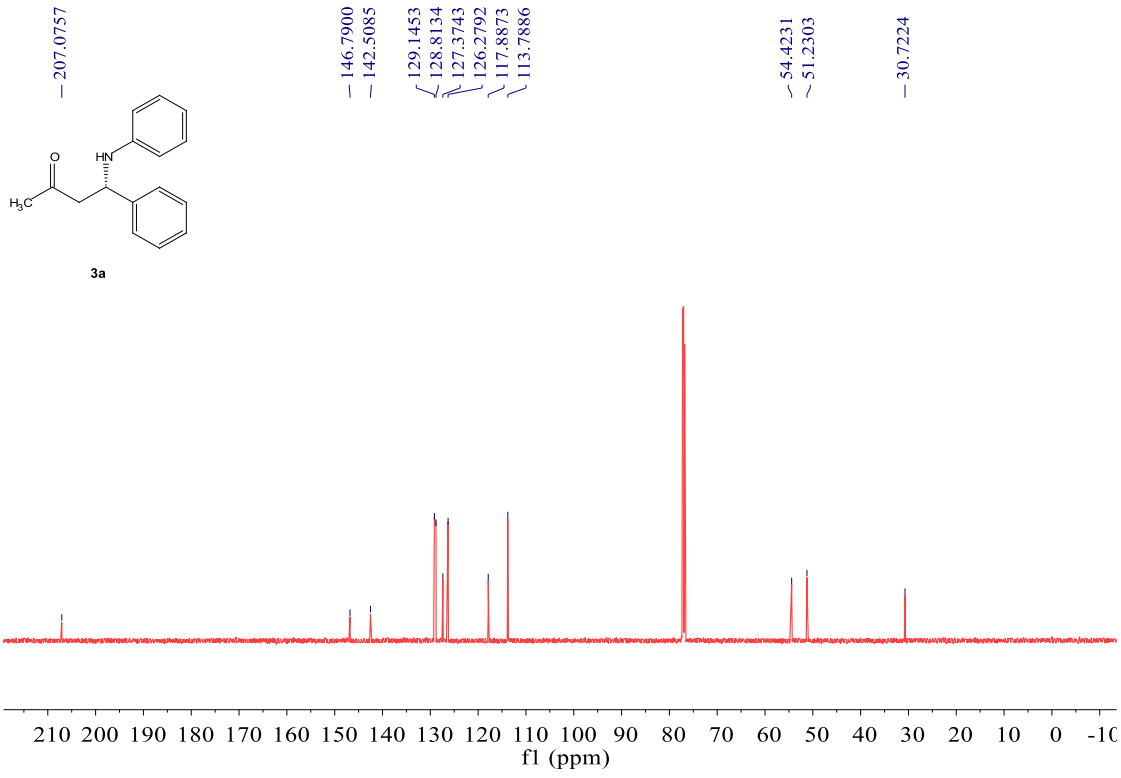
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 1am



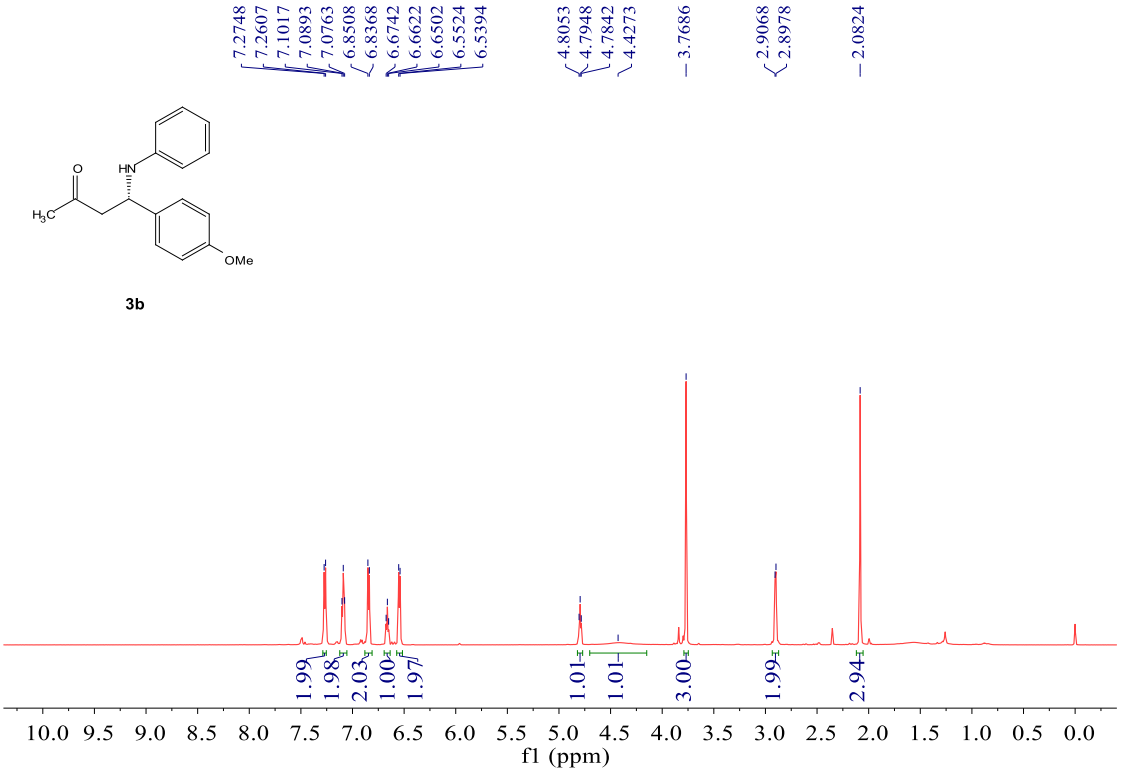
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3a



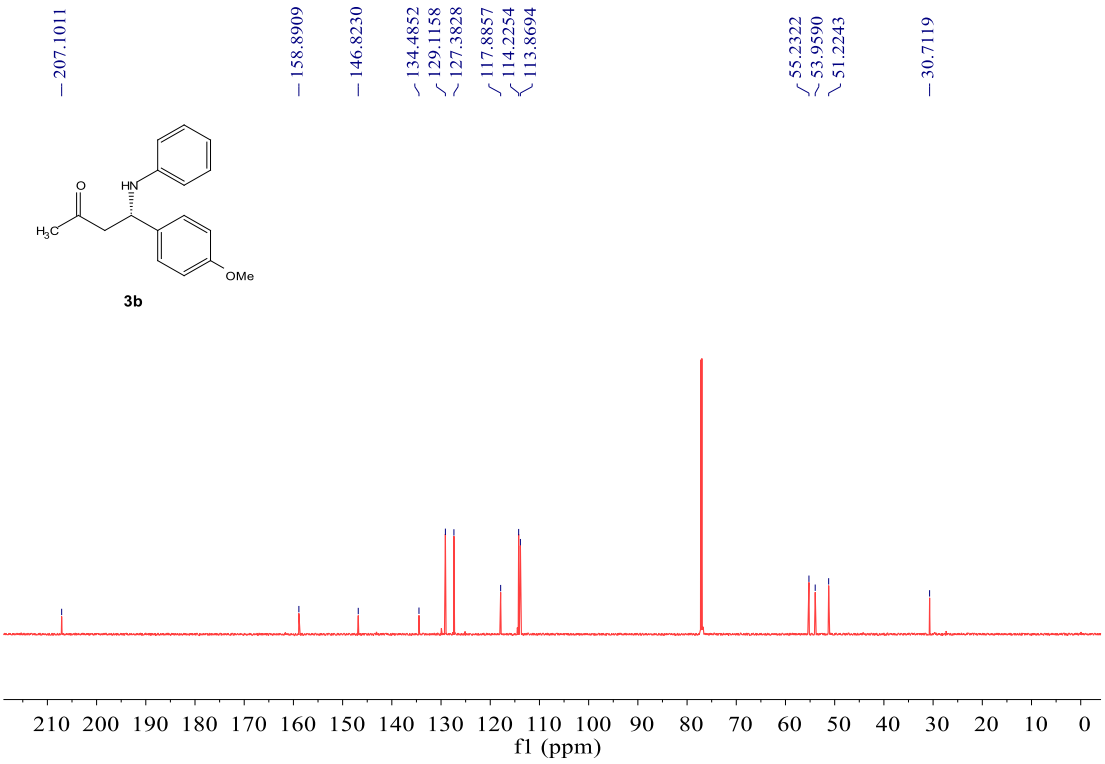
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3a



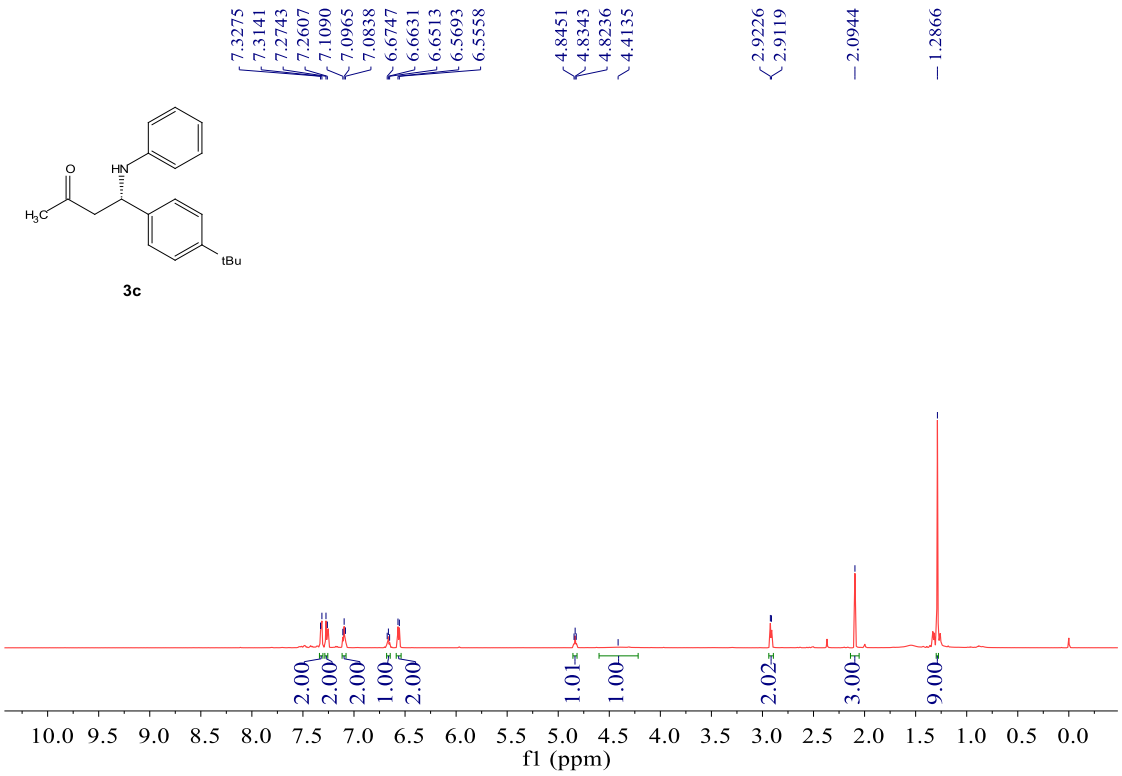
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3b



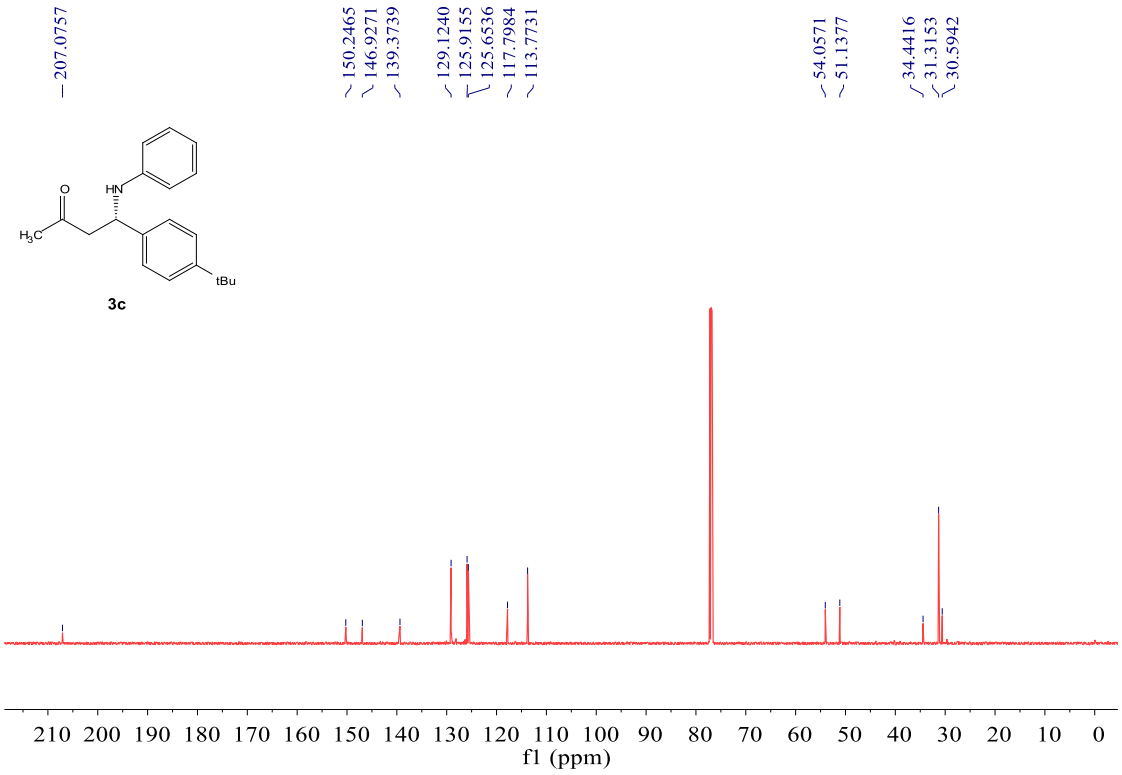
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3b



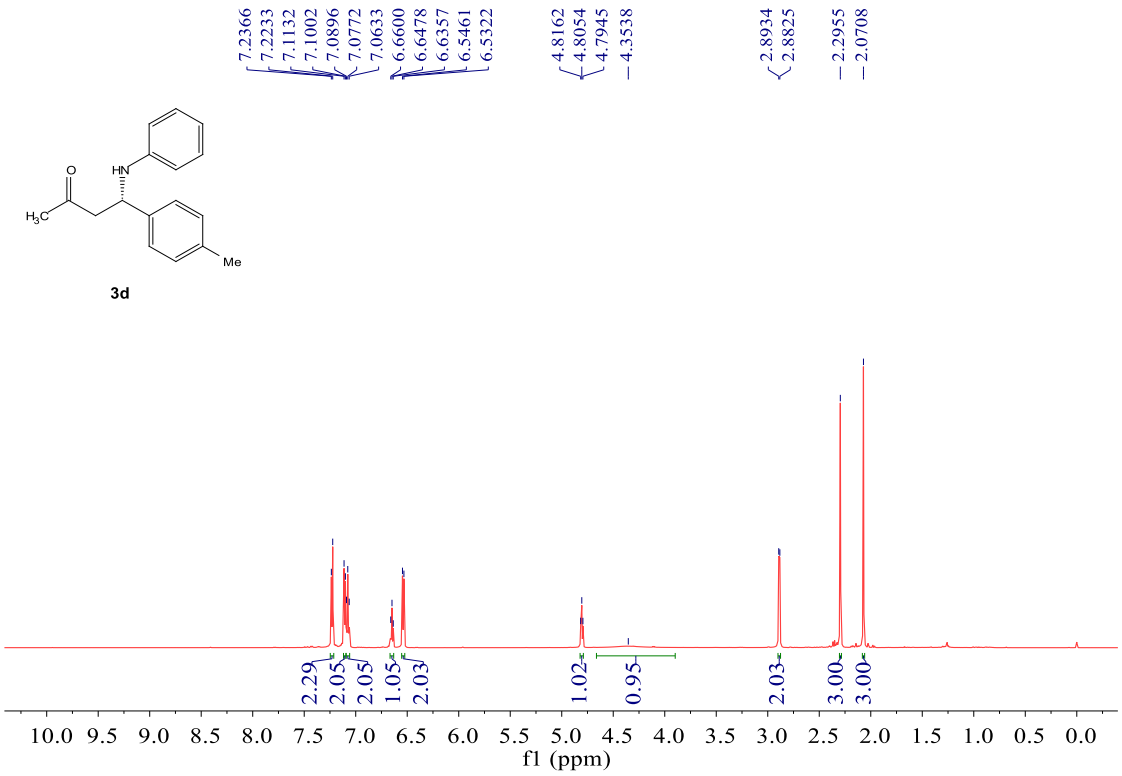
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3c



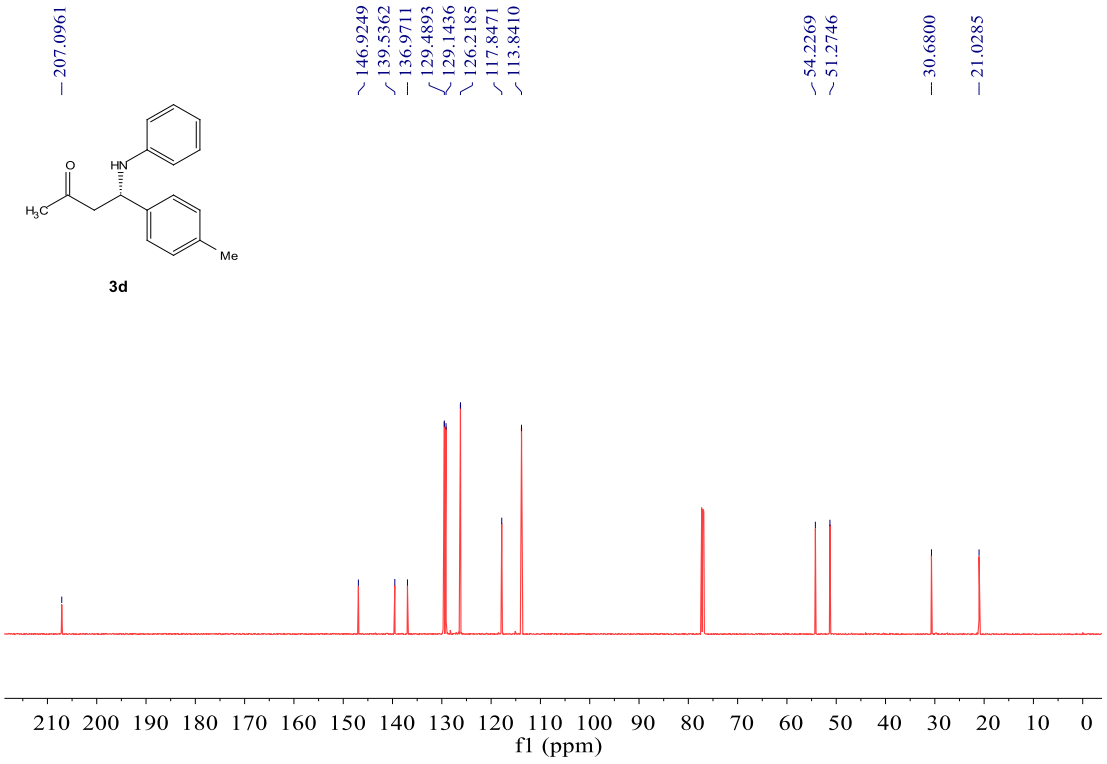
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3c



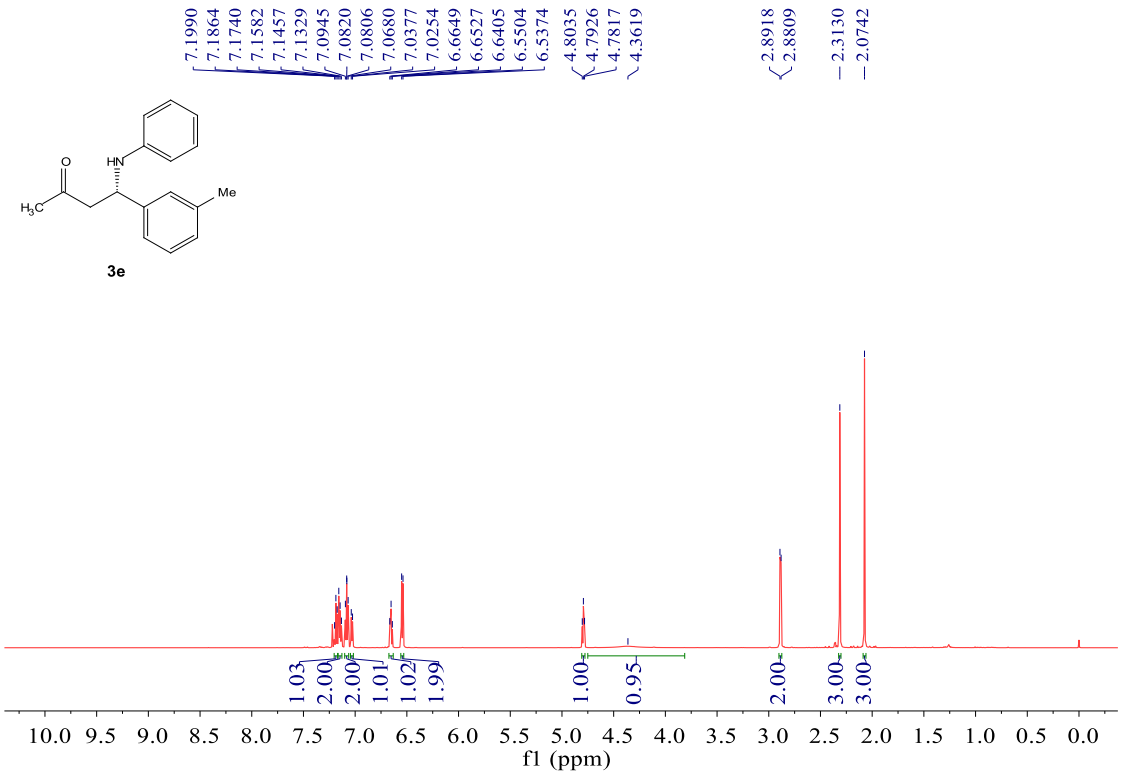
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3d



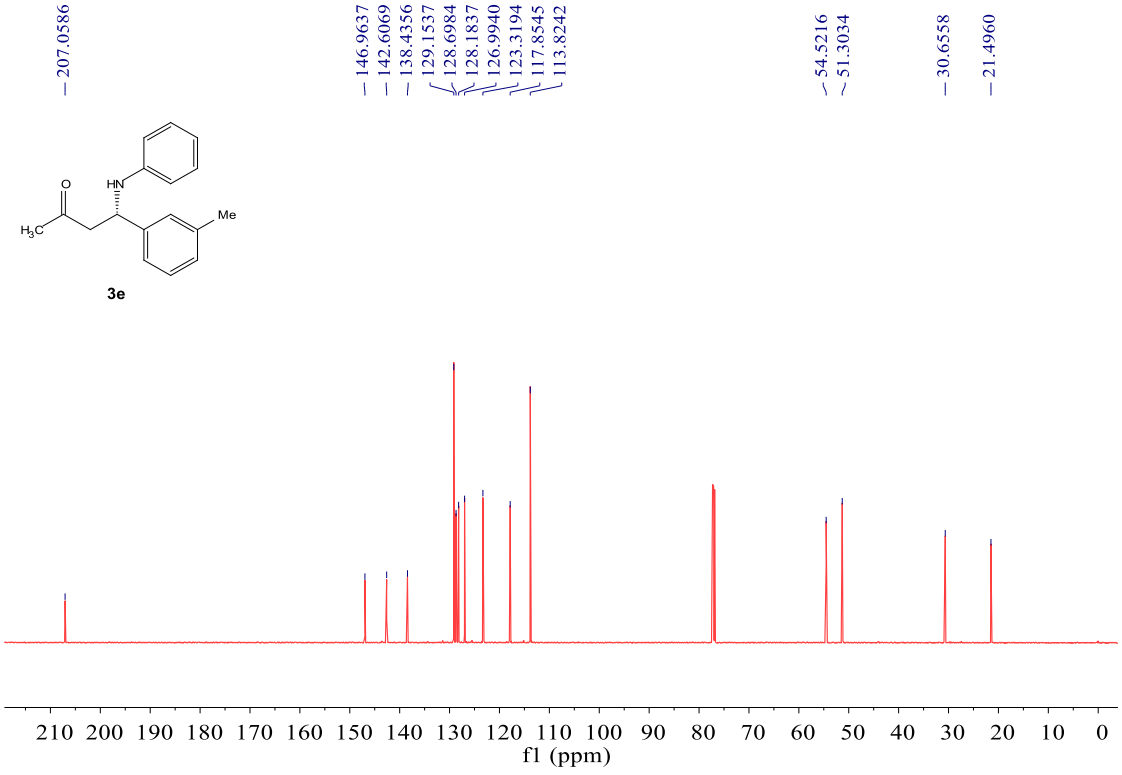
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3d



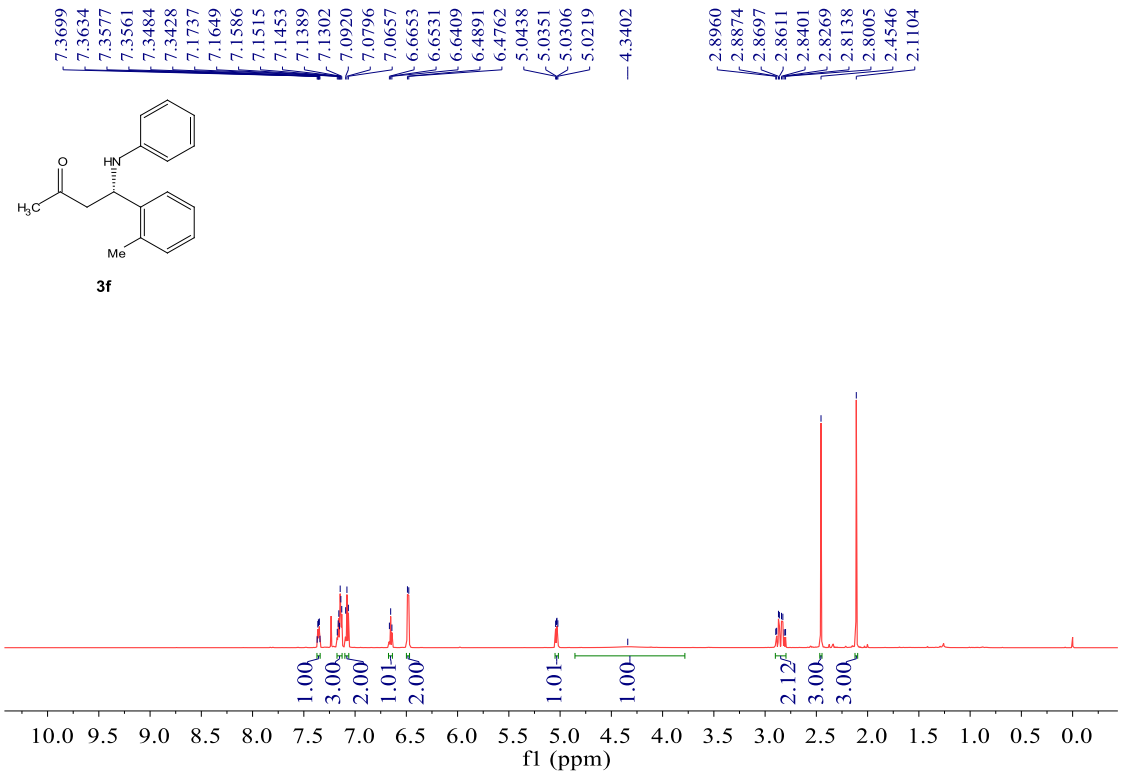
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3e



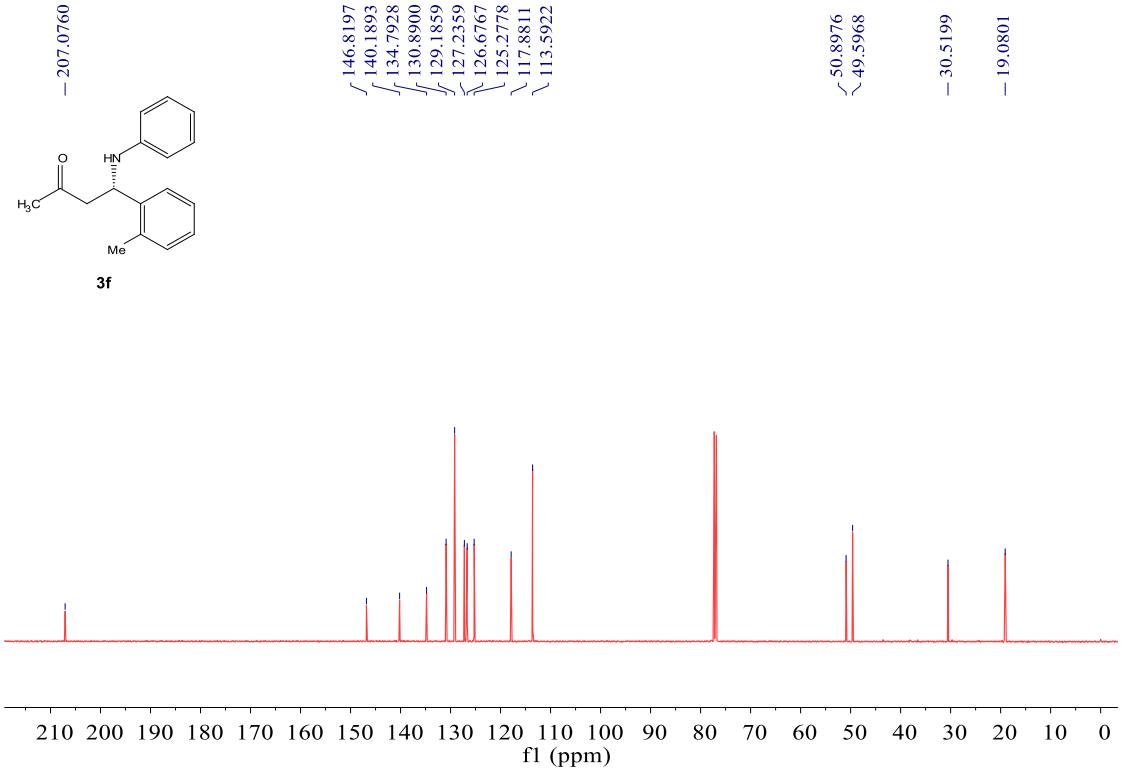
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3e



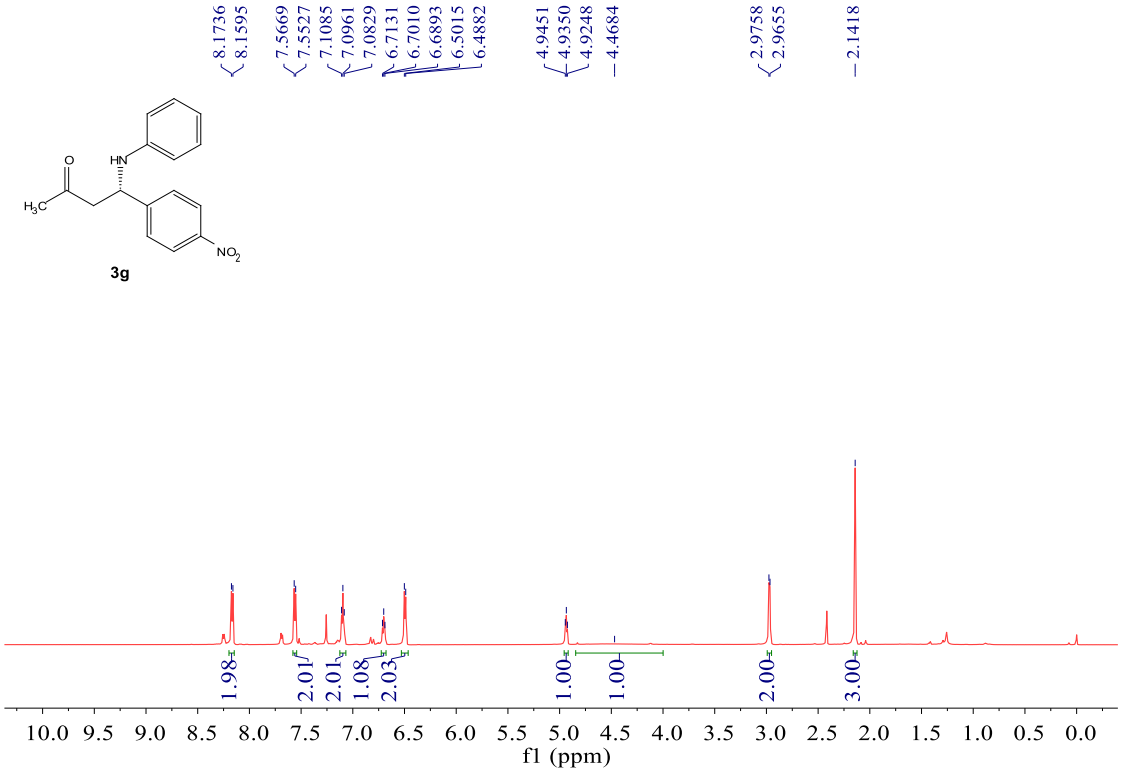
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3f



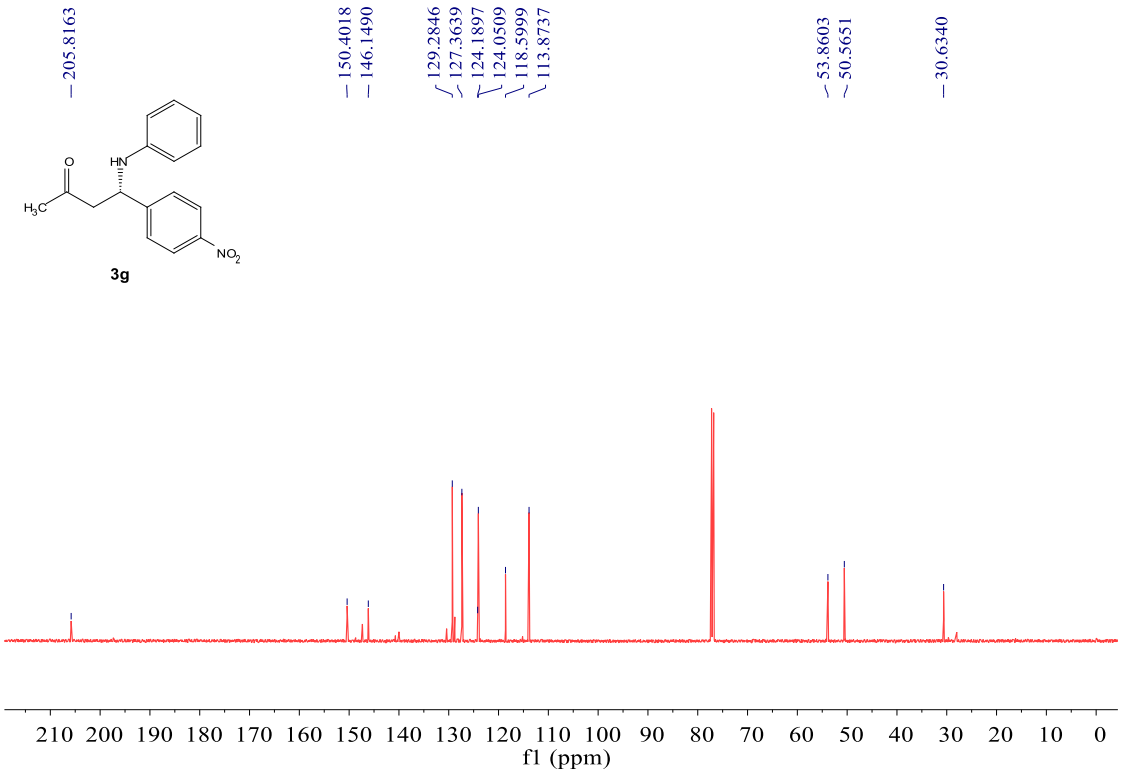
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3f



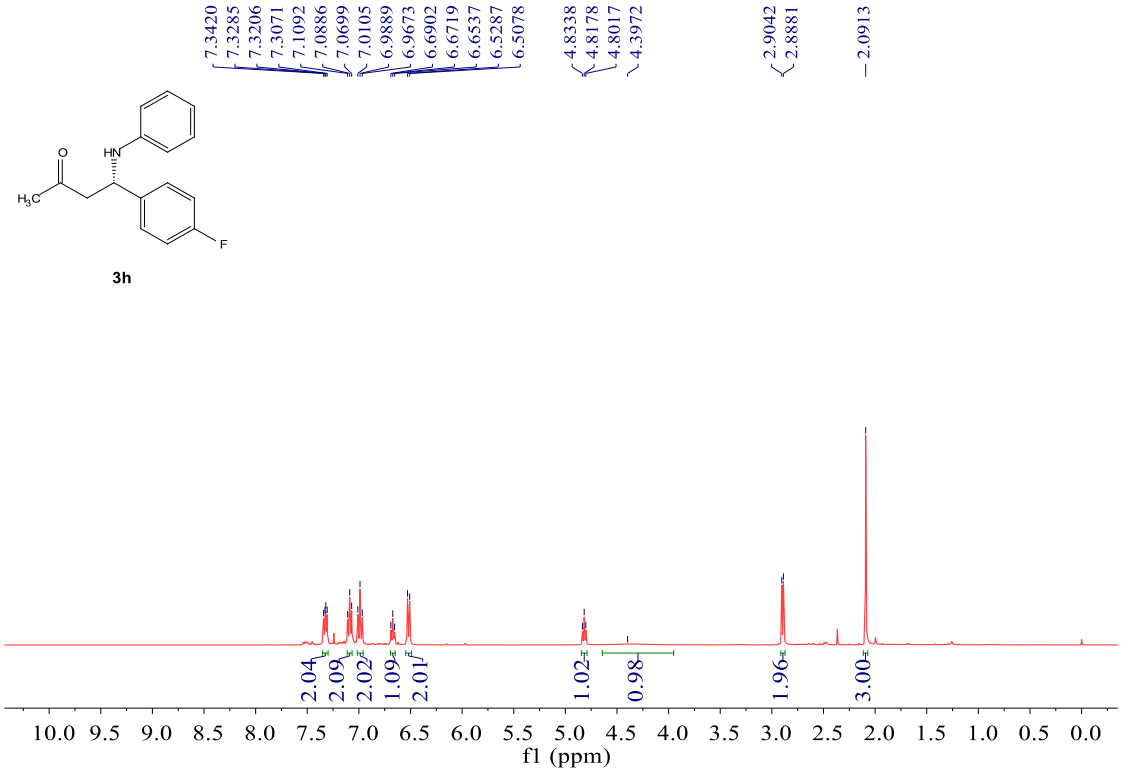
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3g



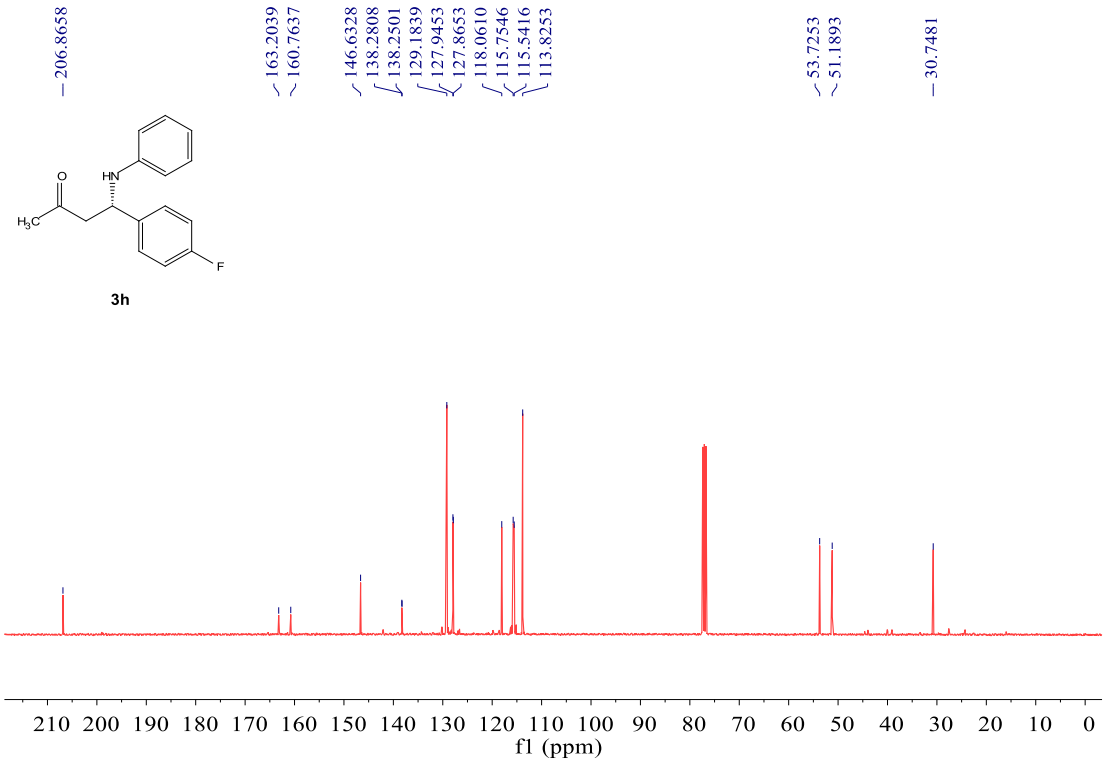
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3g



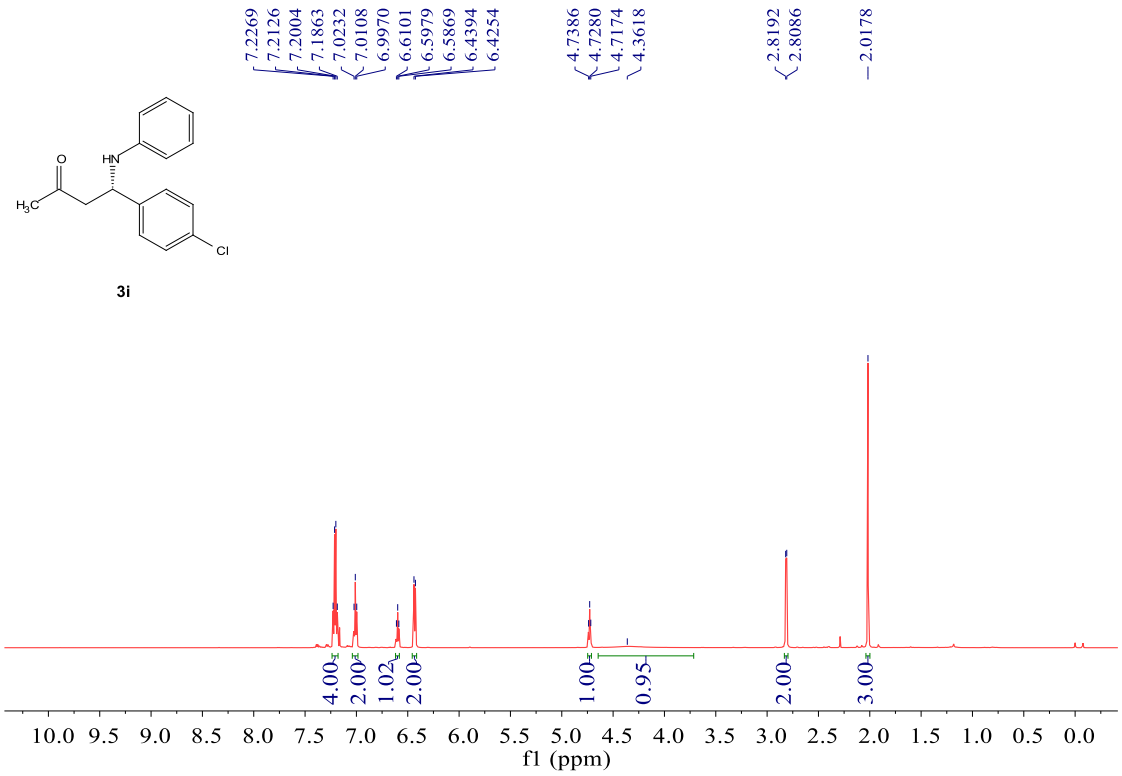
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3h



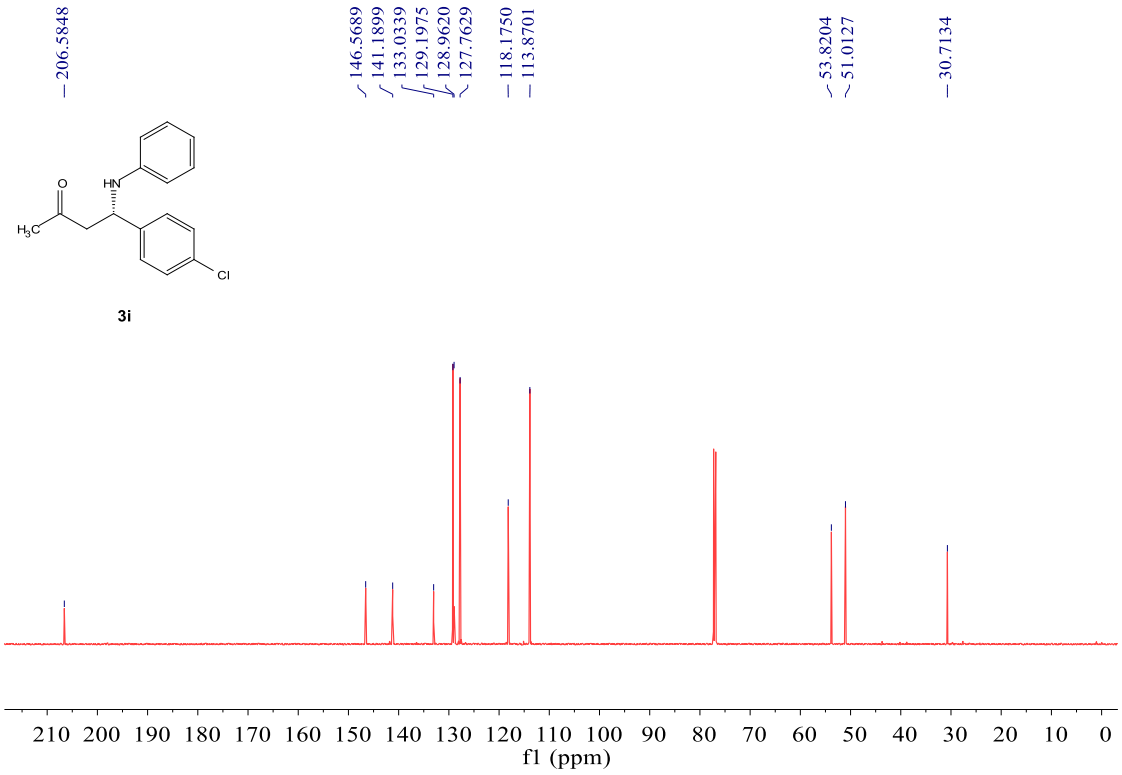
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3h



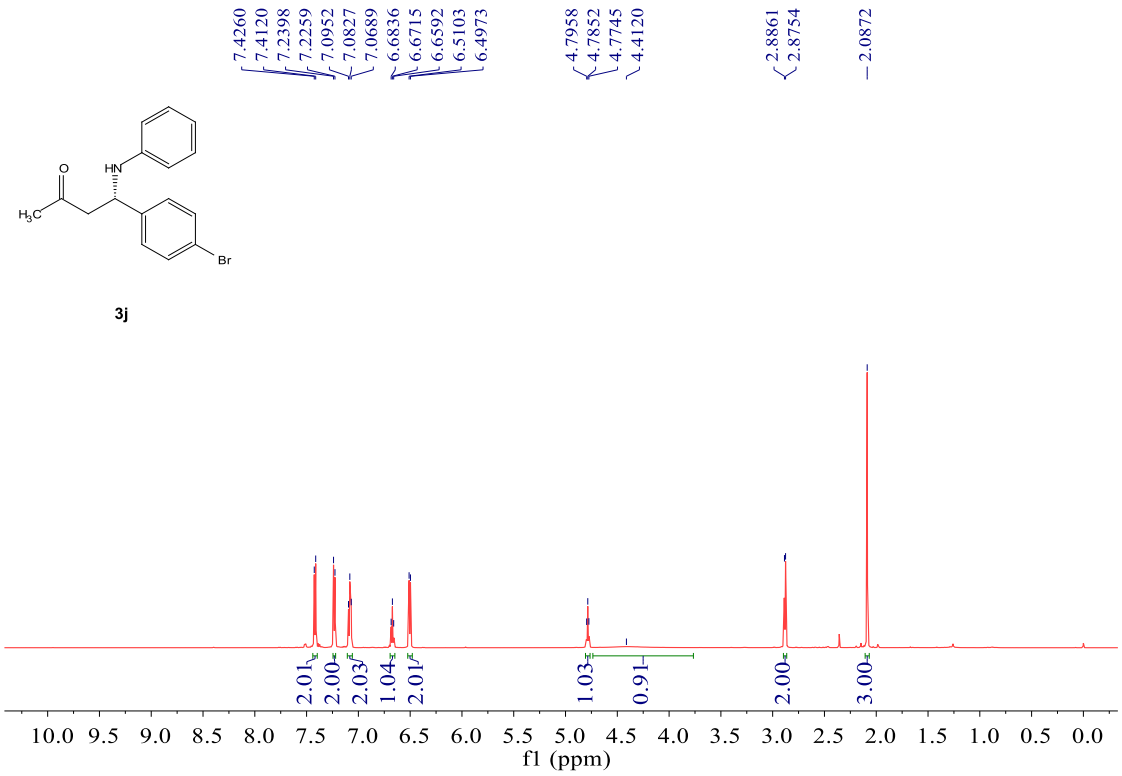
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3i



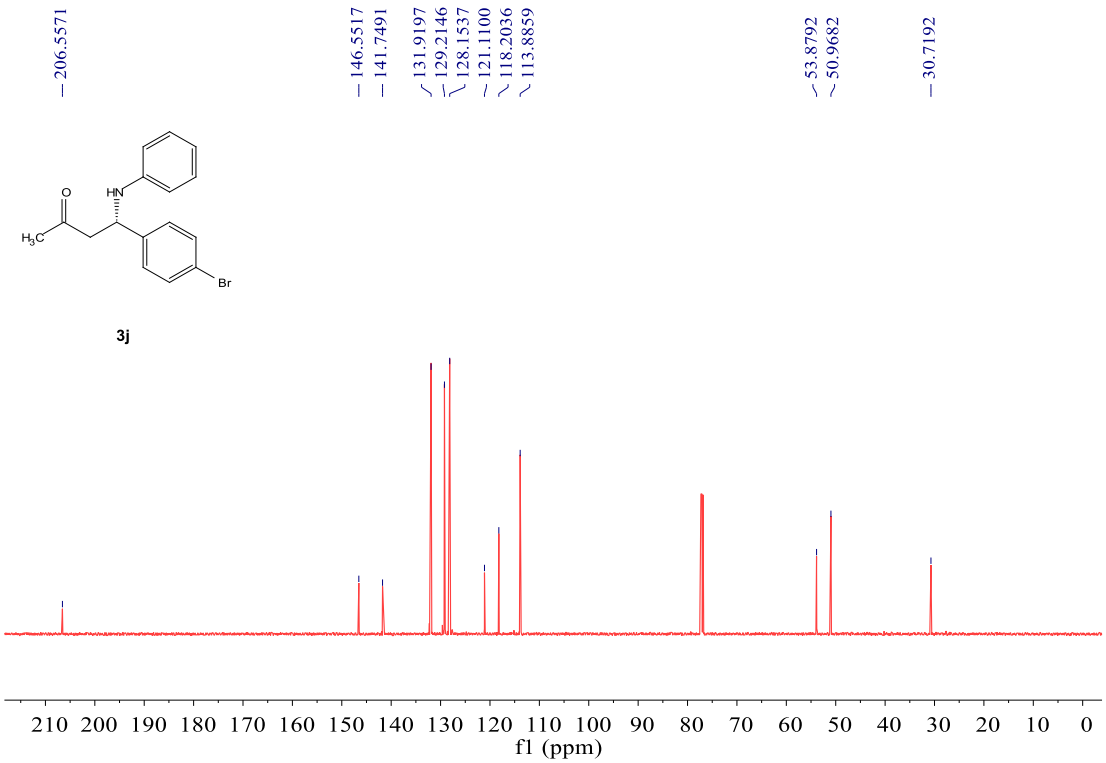
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3i



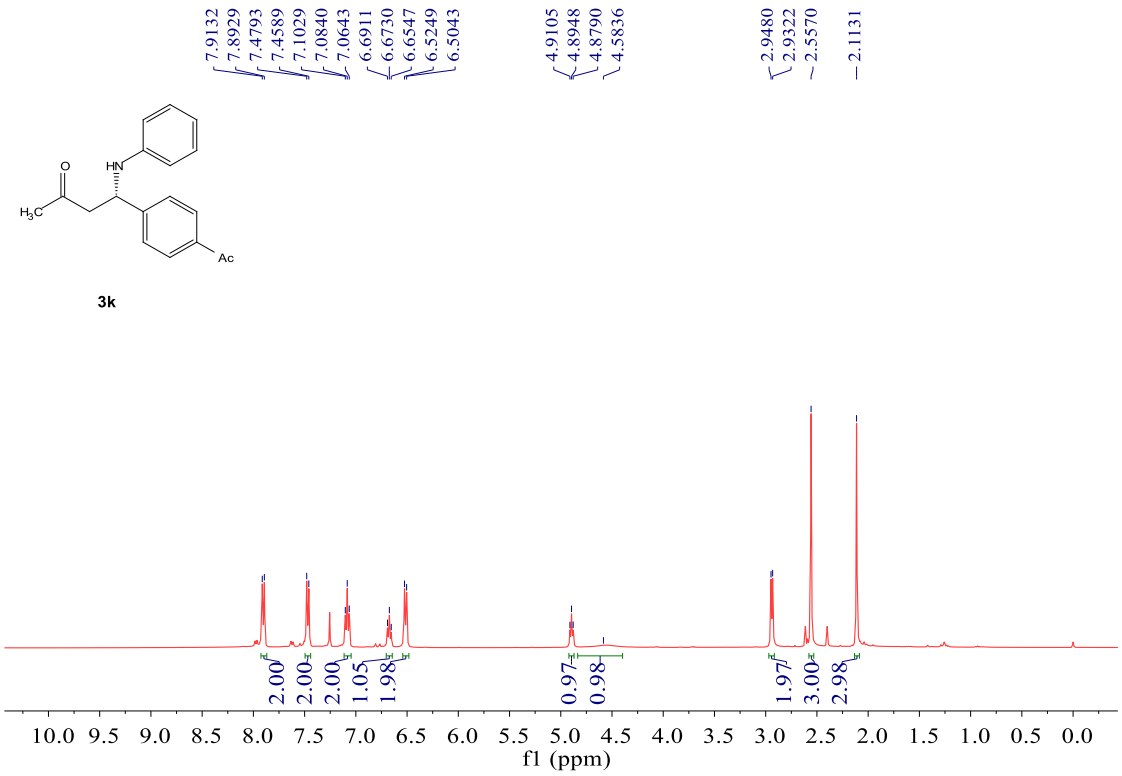
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3j



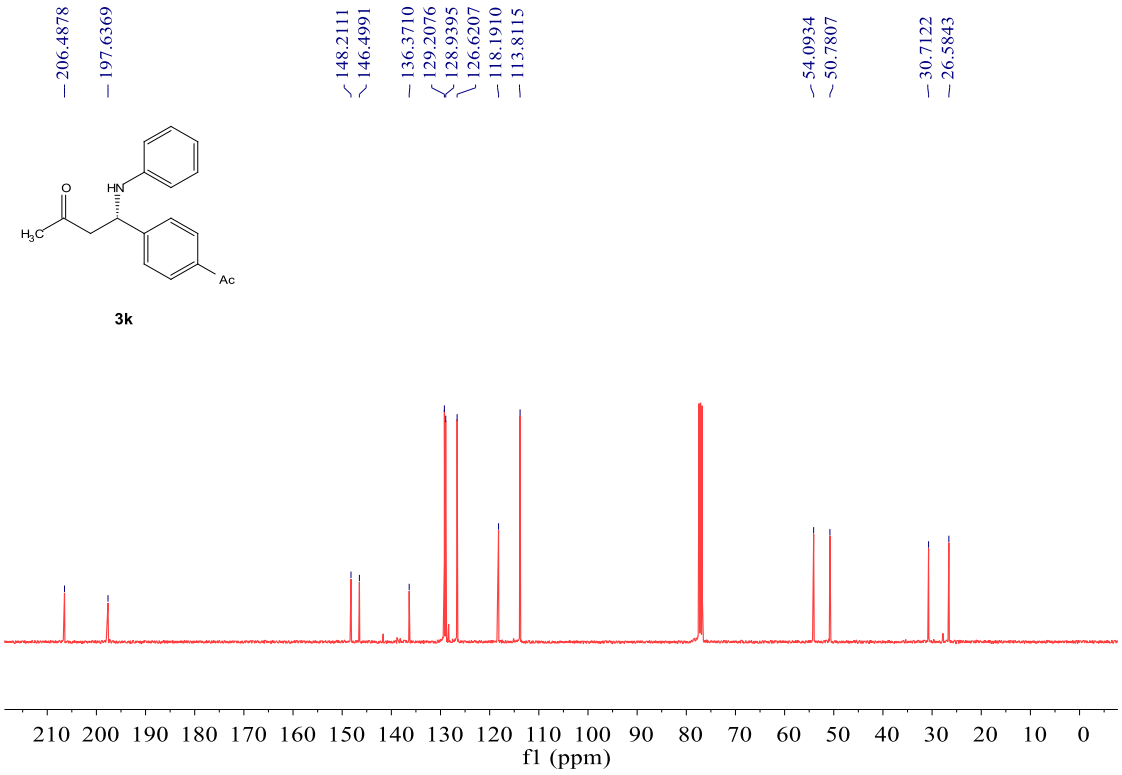
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3j



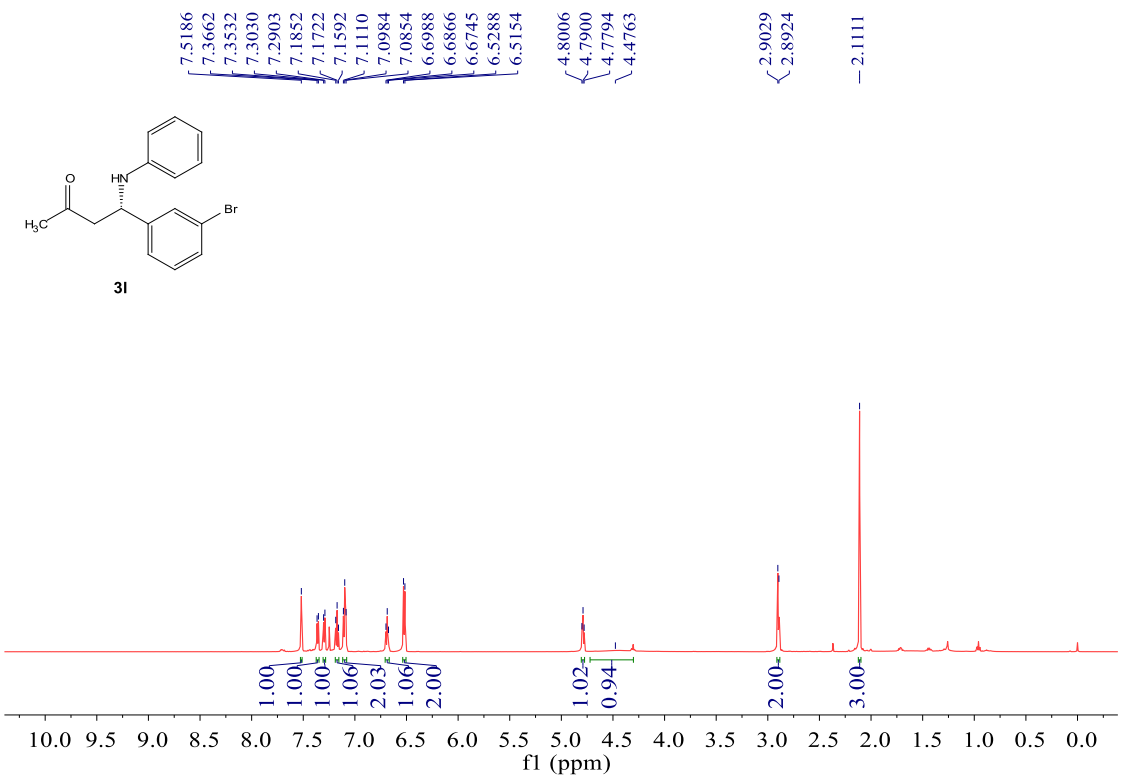
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3k



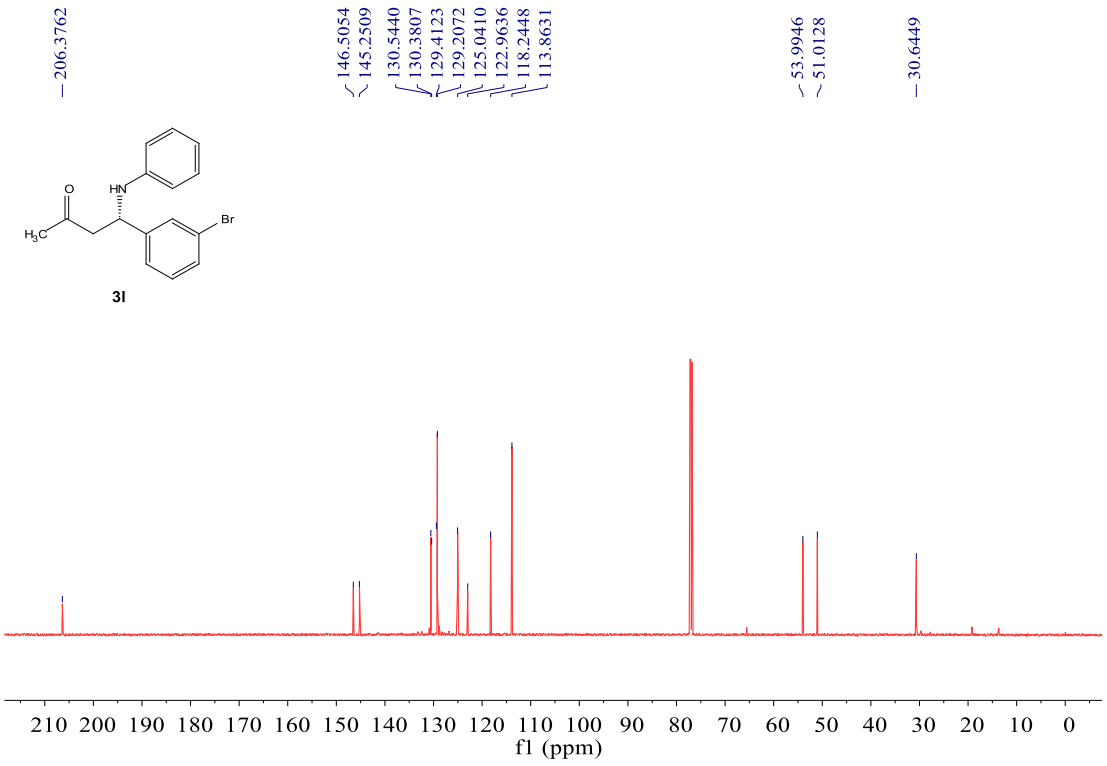
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3k



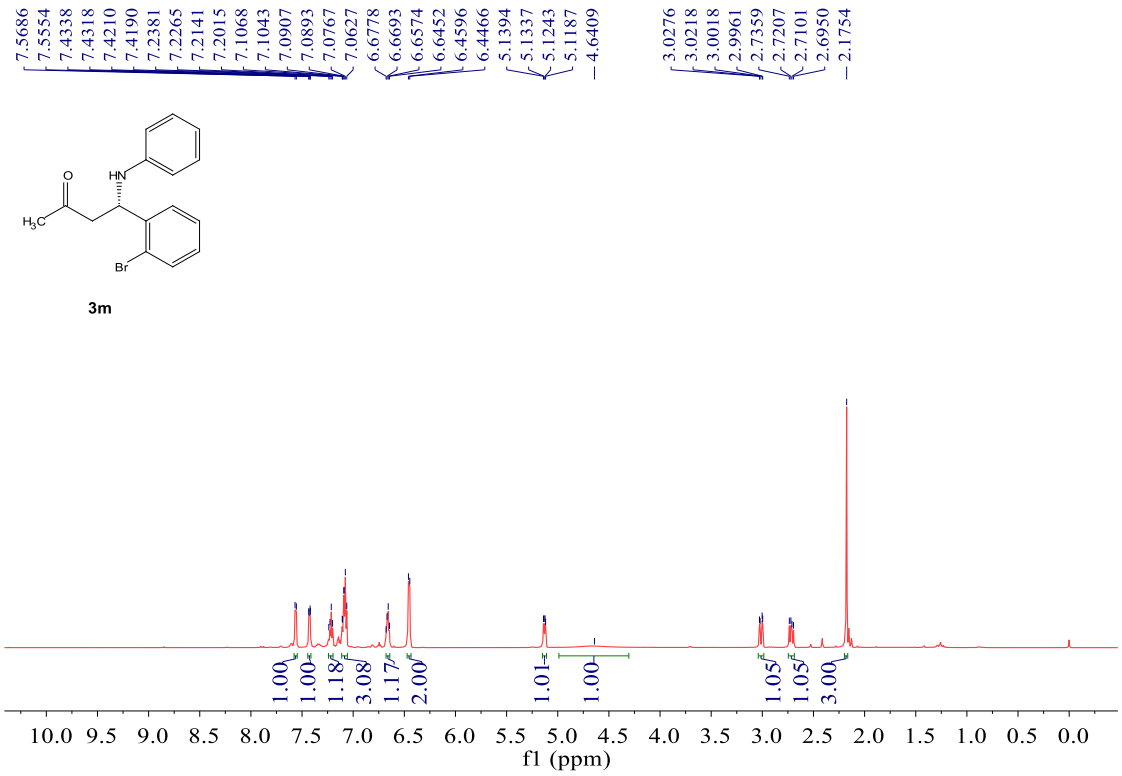
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3l



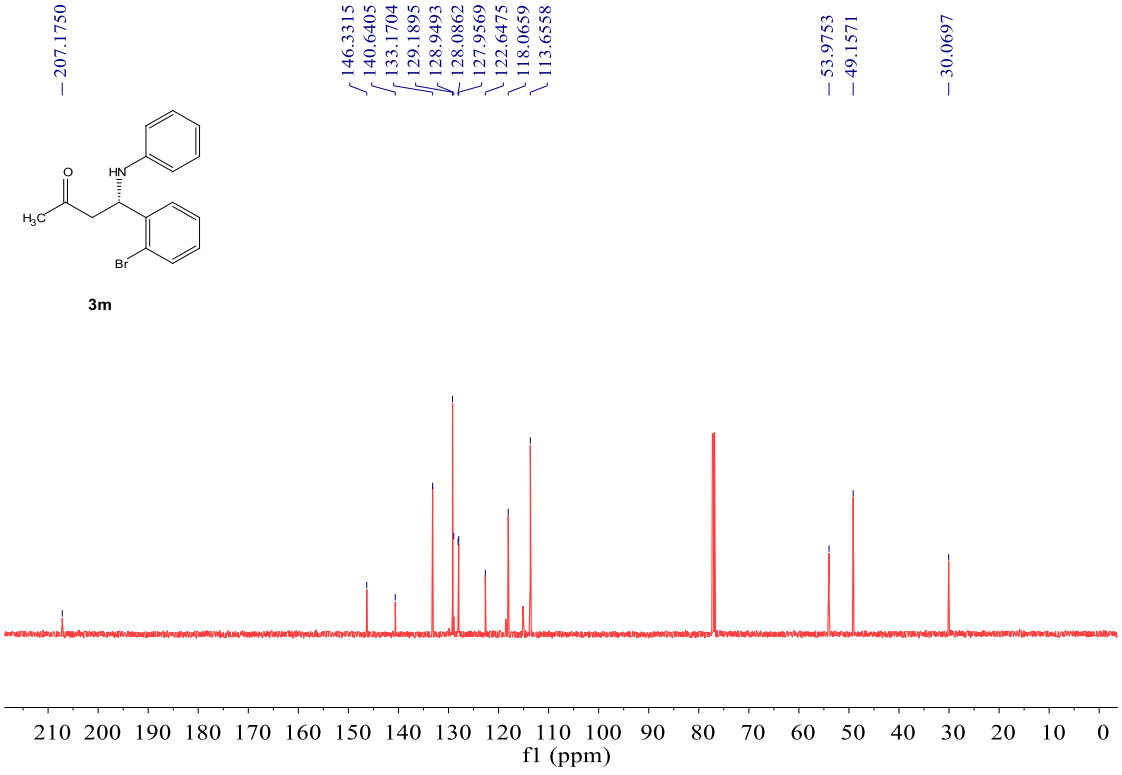
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3l



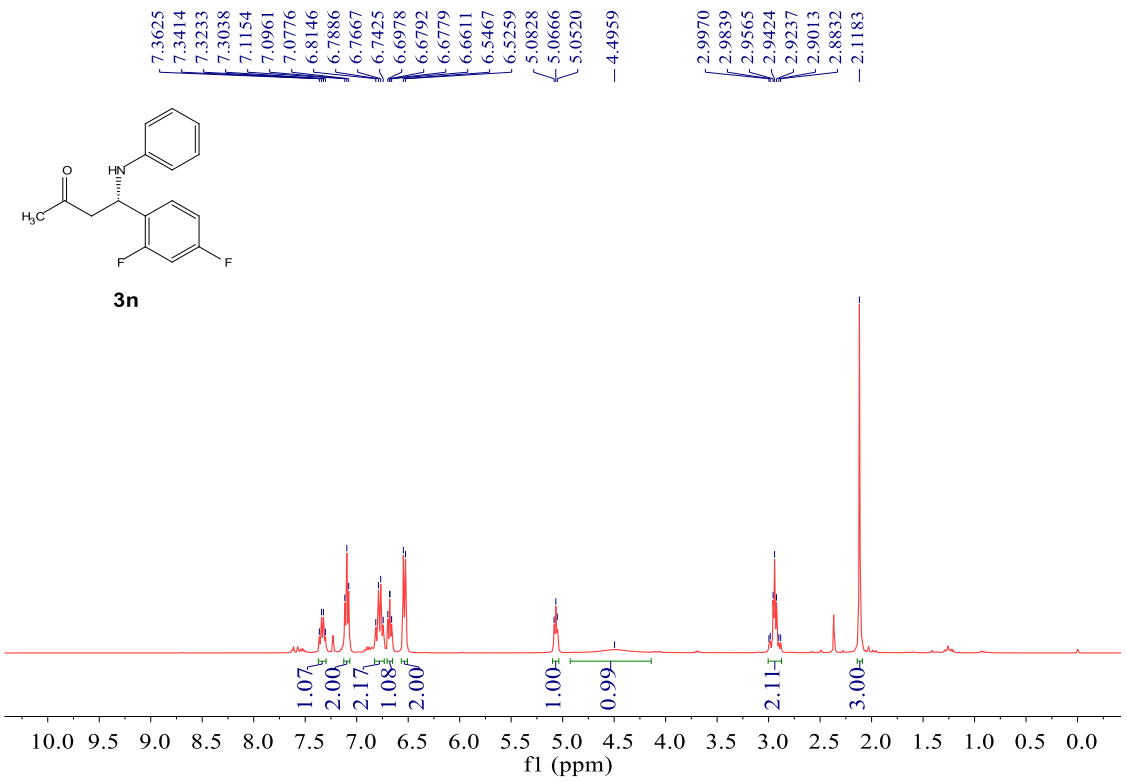
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3m



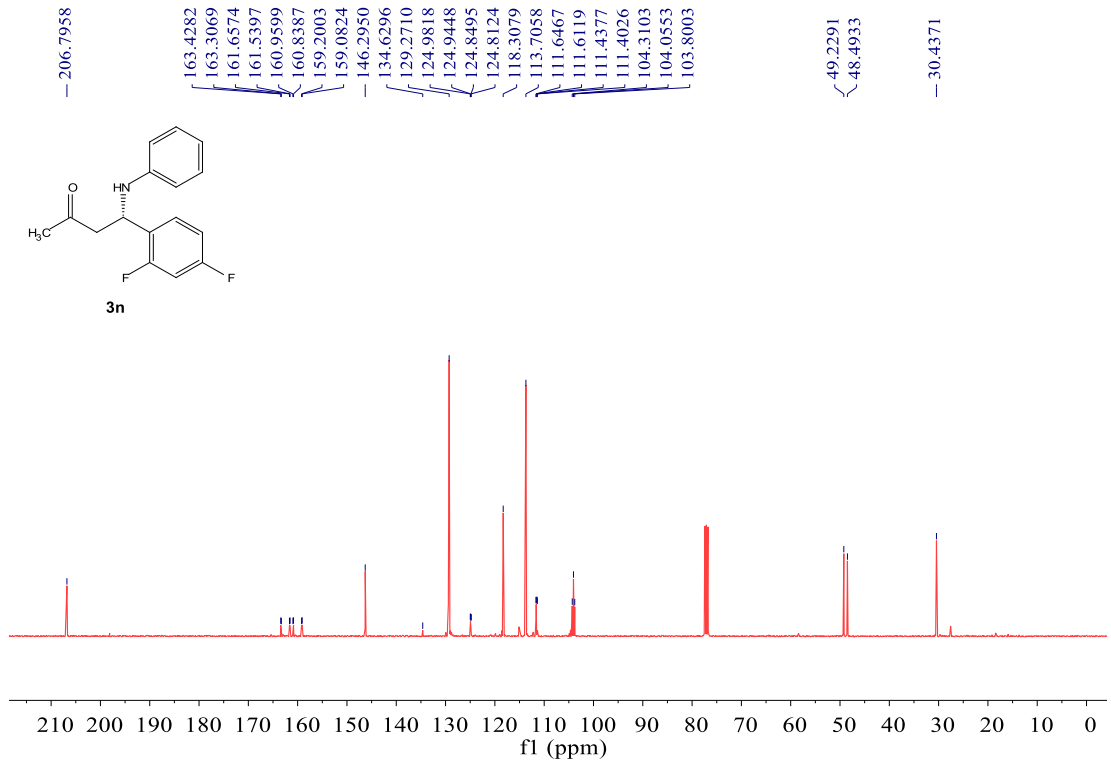
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3m



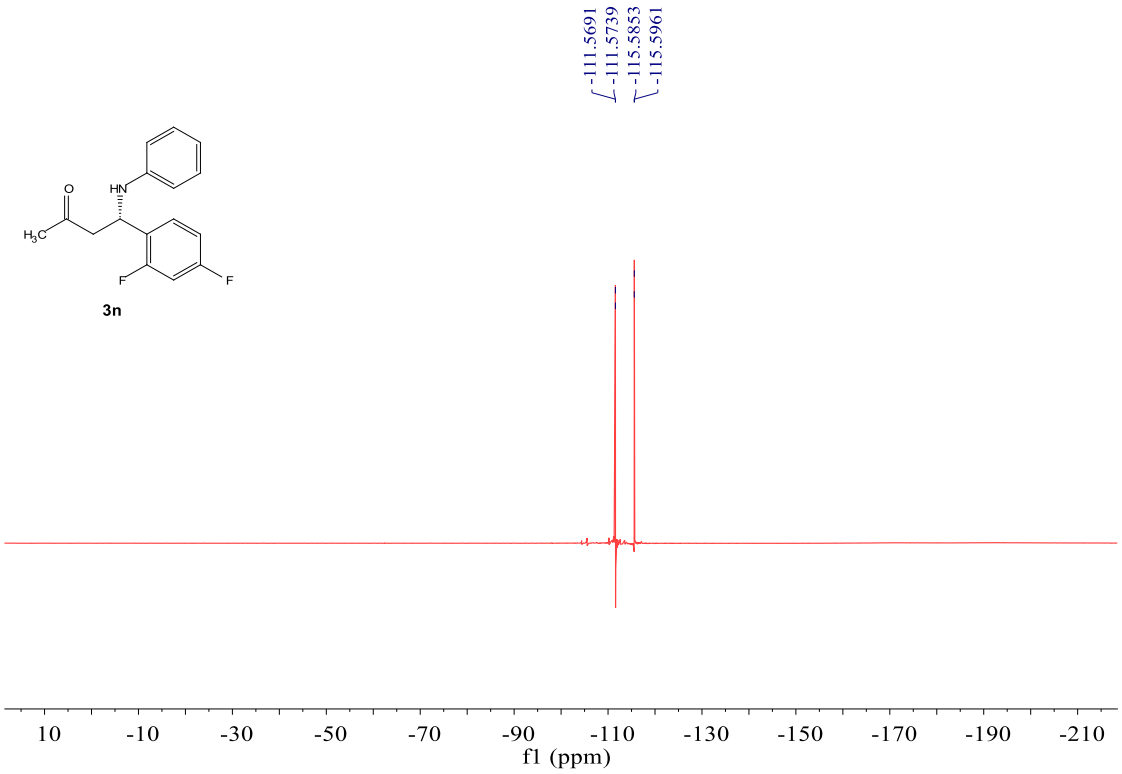
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3n



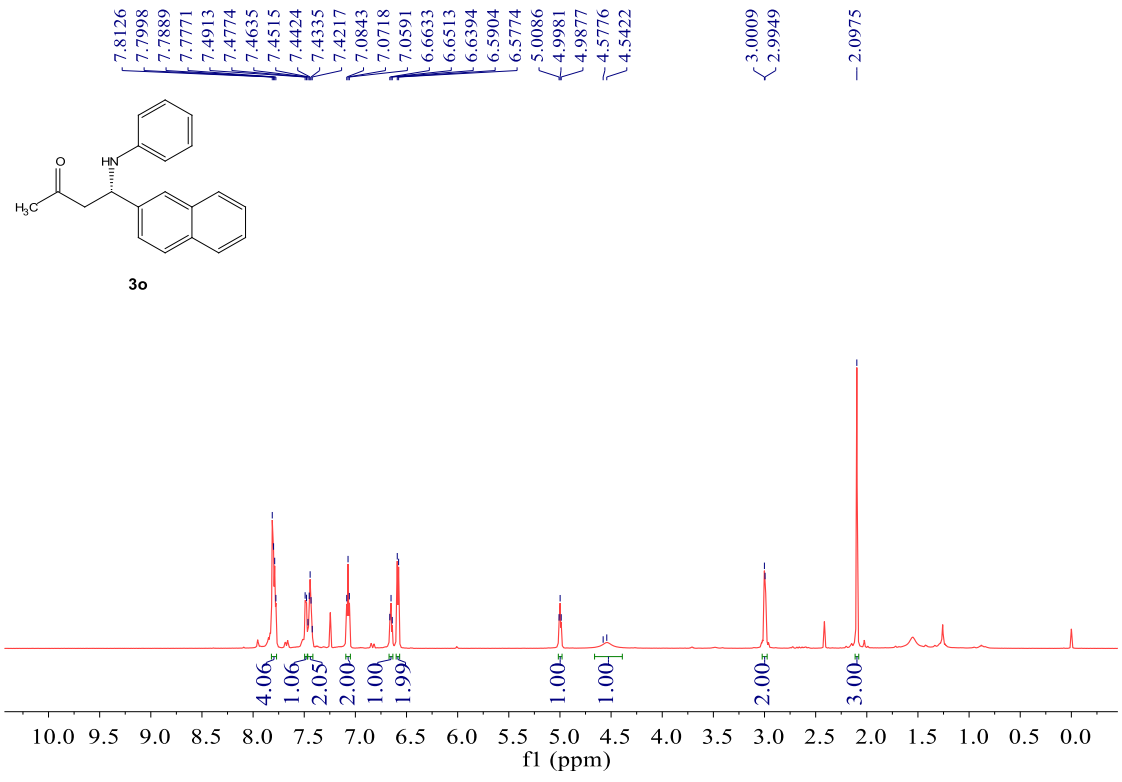
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3n



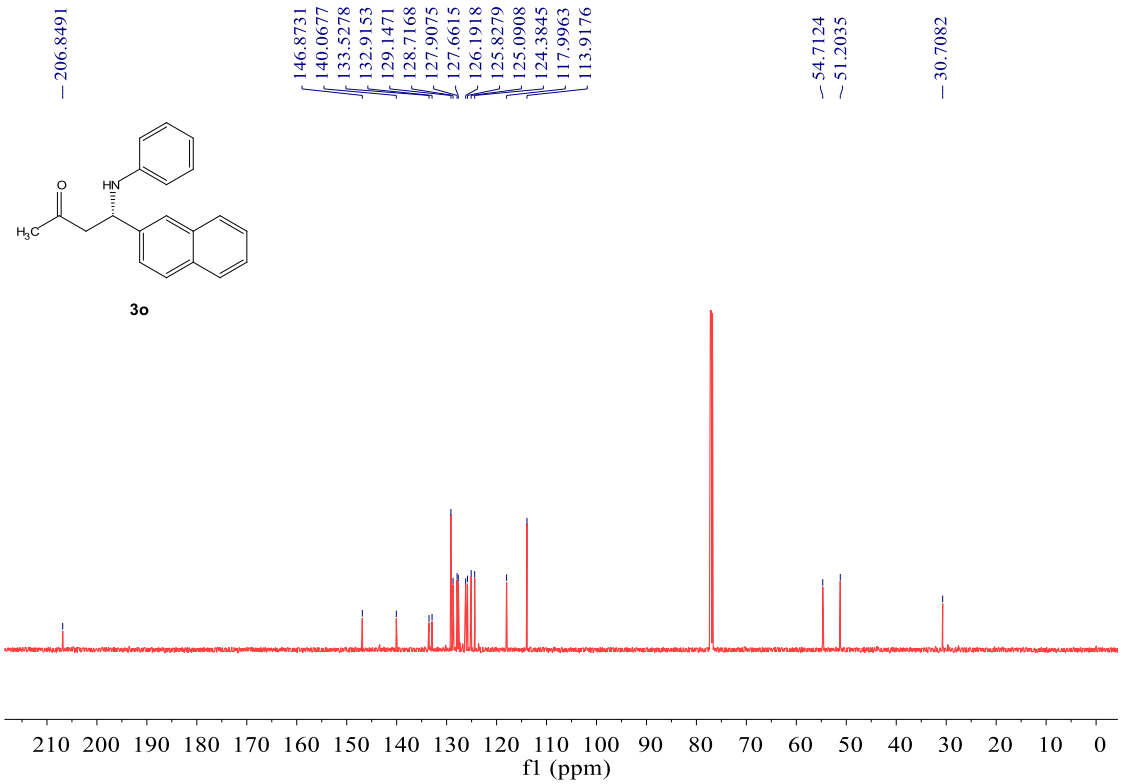
^{19}F NMR Spectrum (565 MHz, $CDCl_3$) of 3n



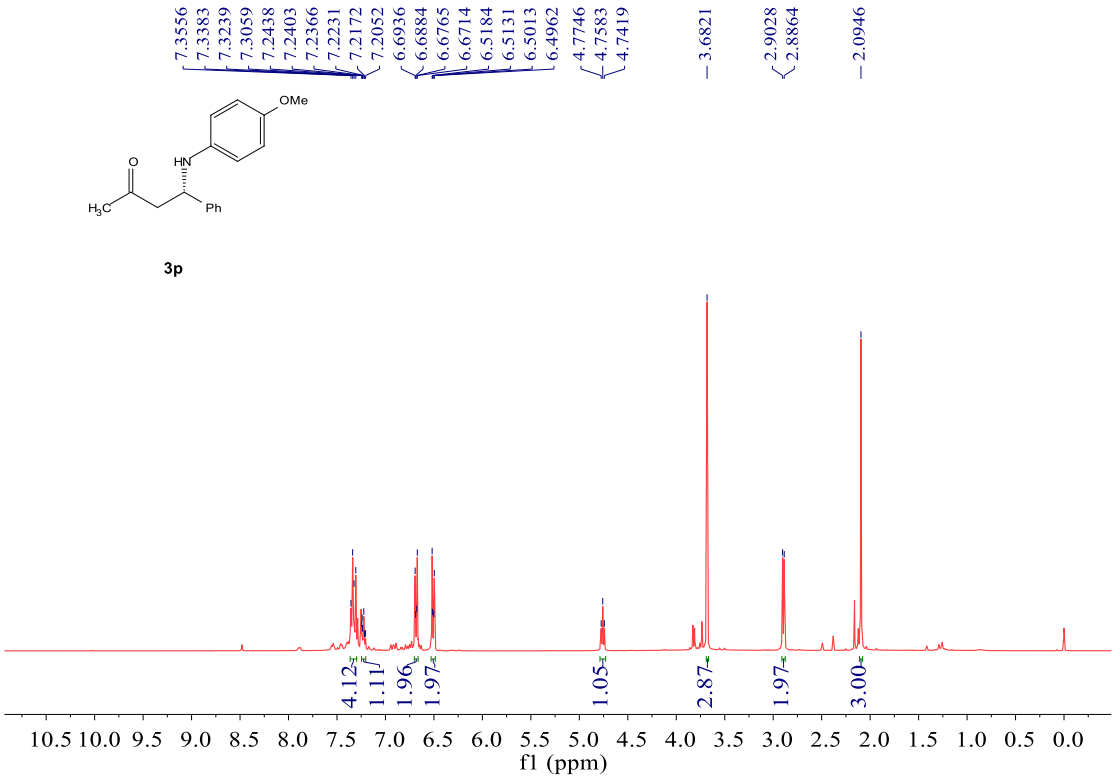
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3o



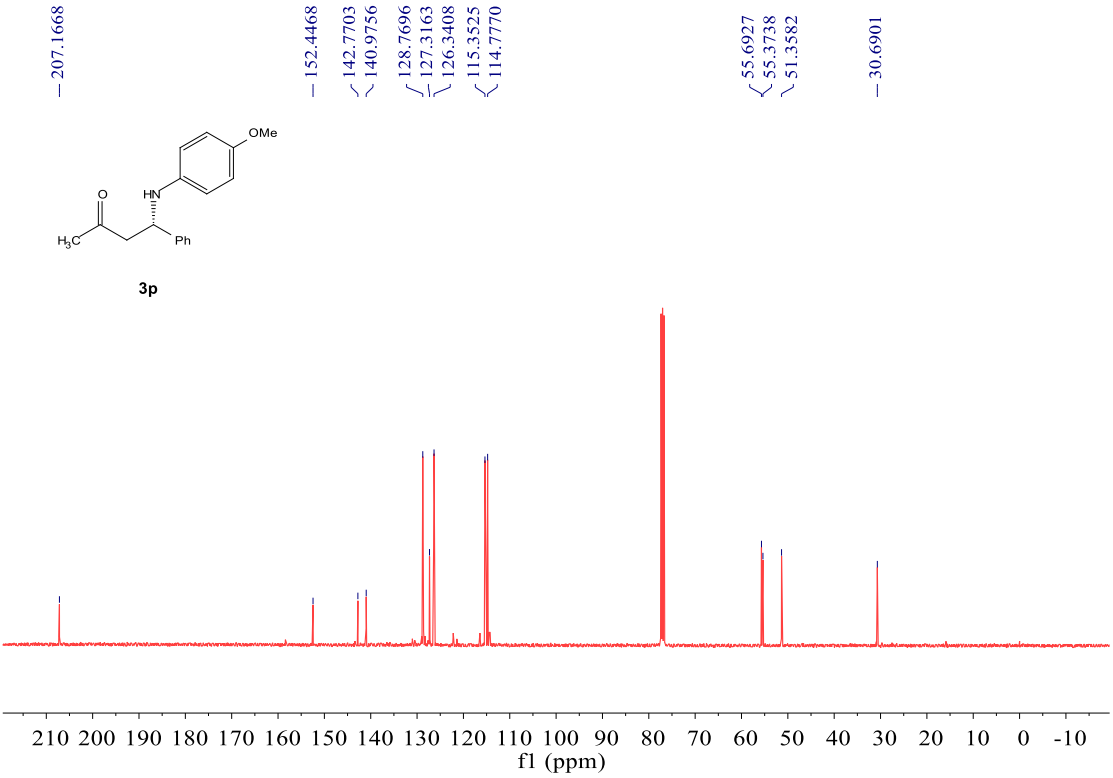
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3o



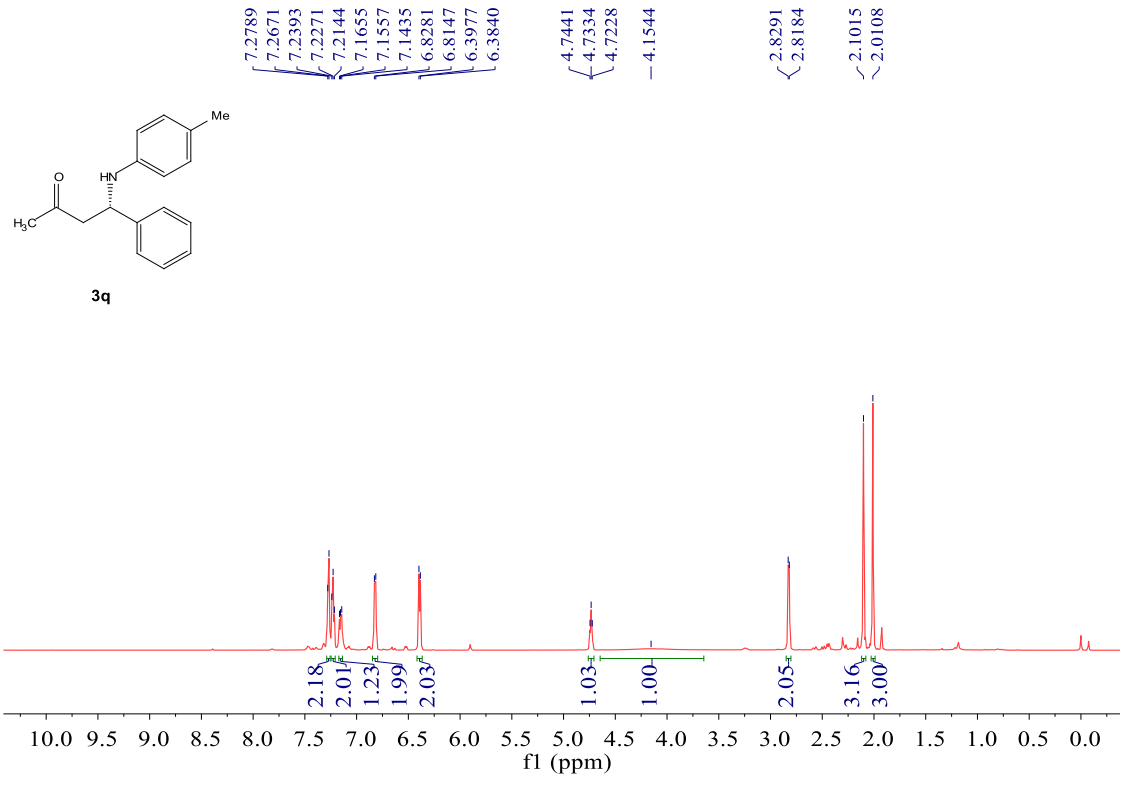
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3p



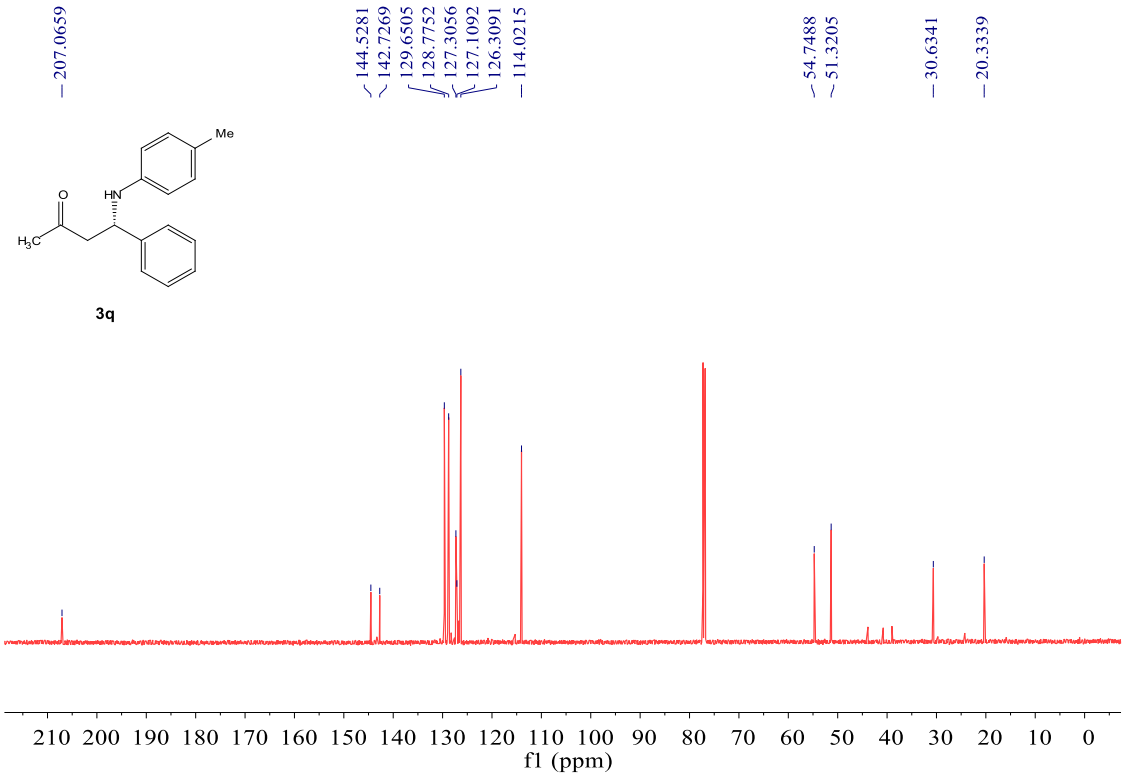
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3p



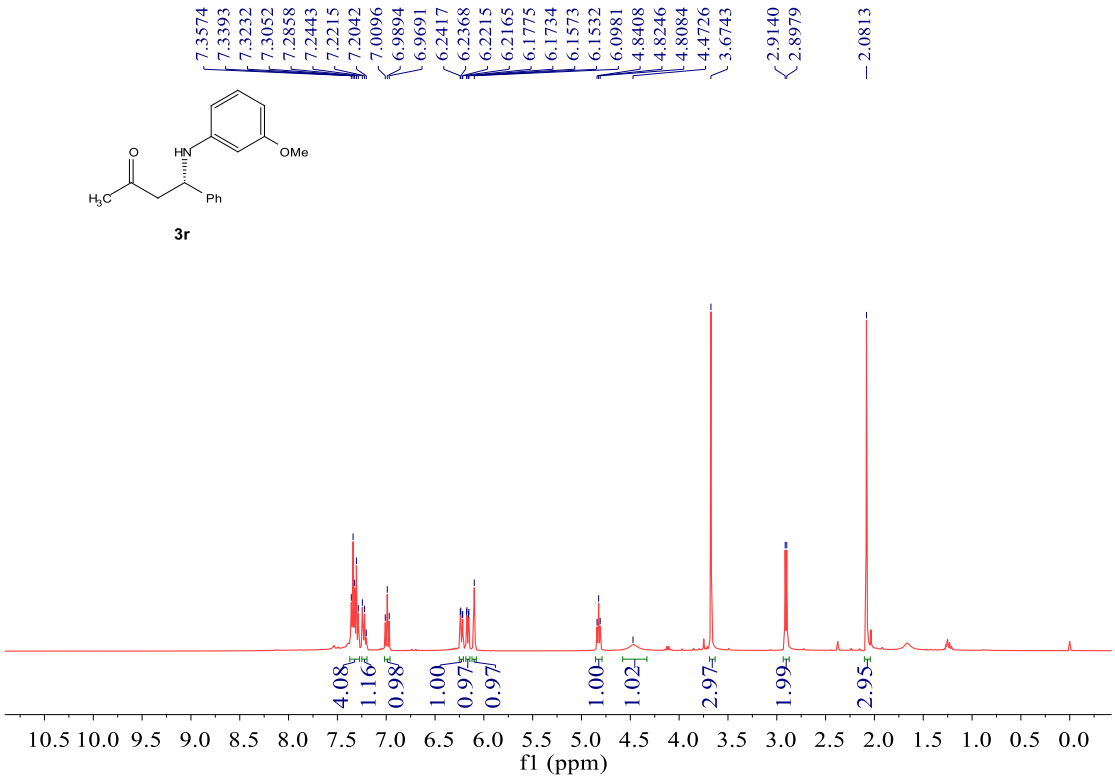
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3q



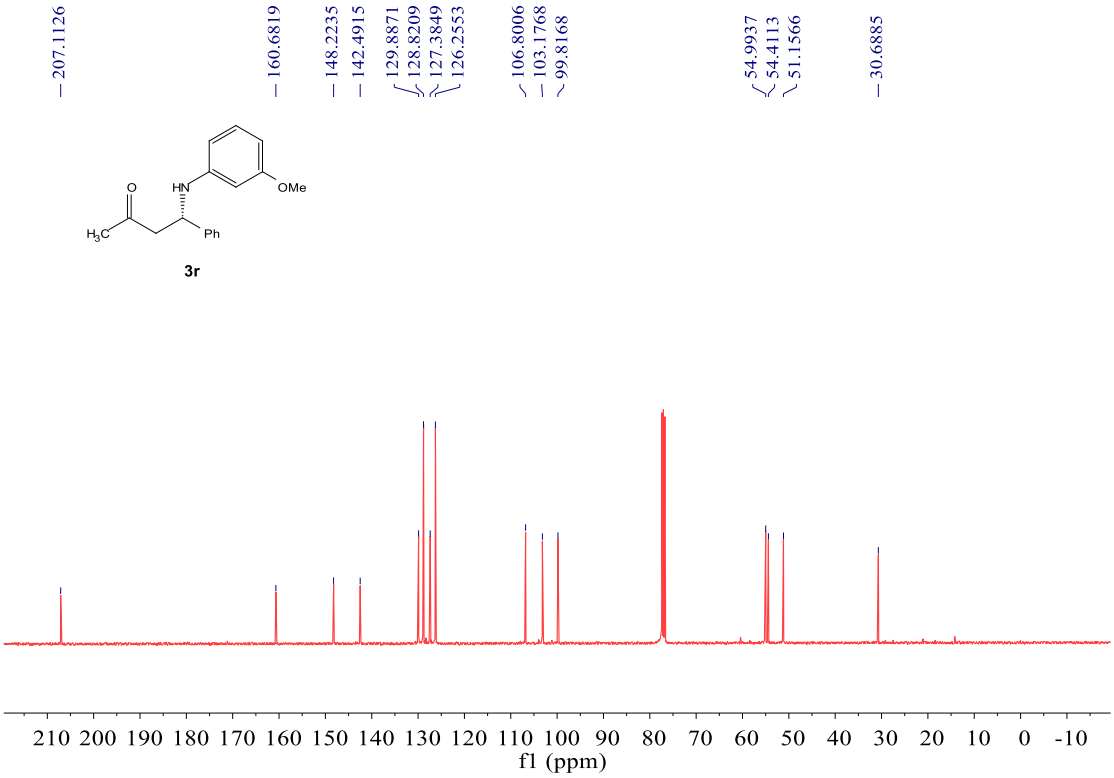
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3q



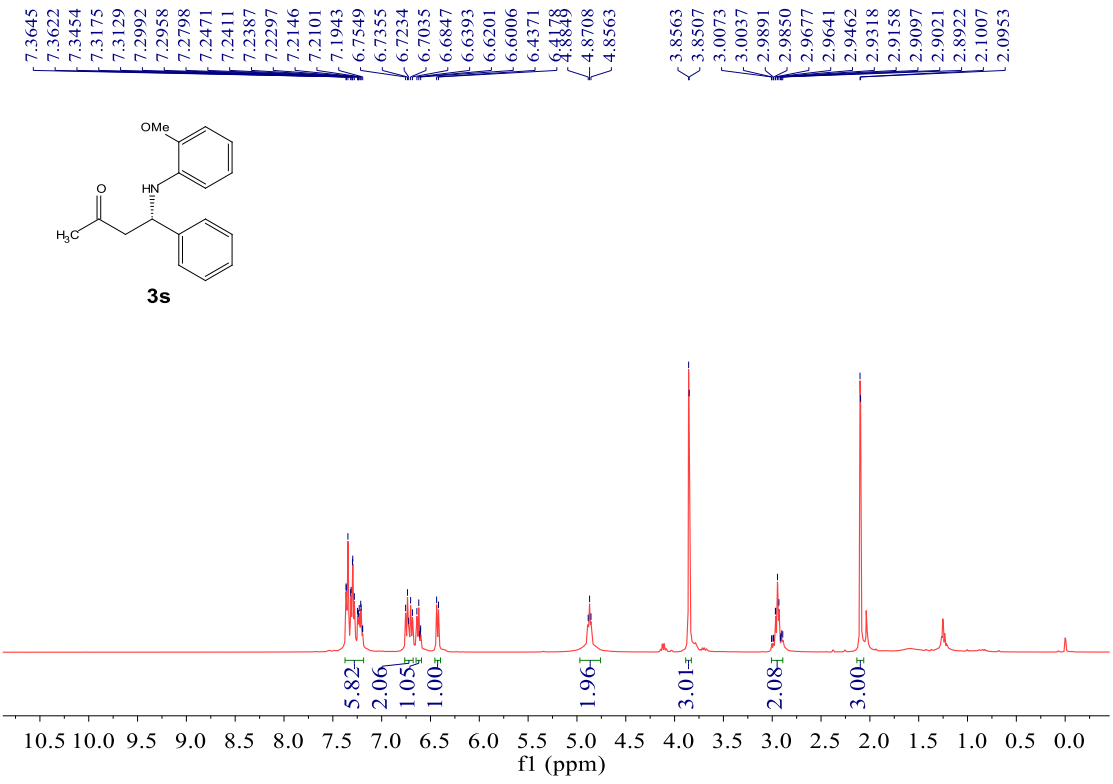
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3r



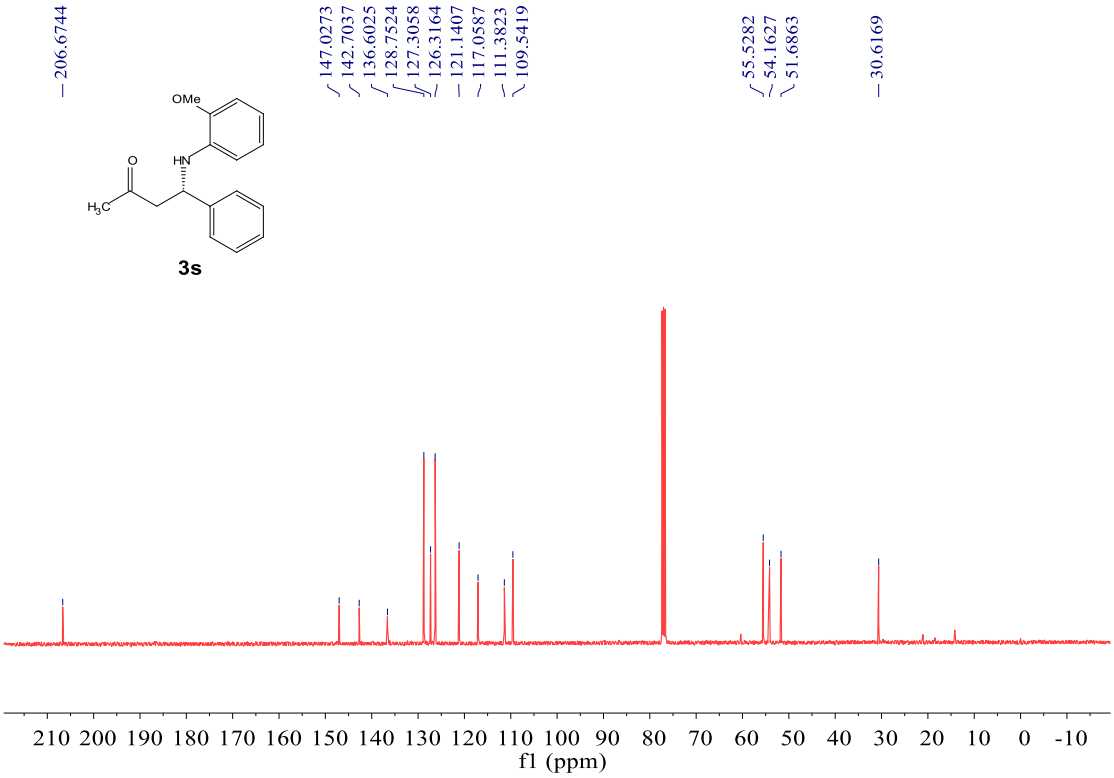
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3r



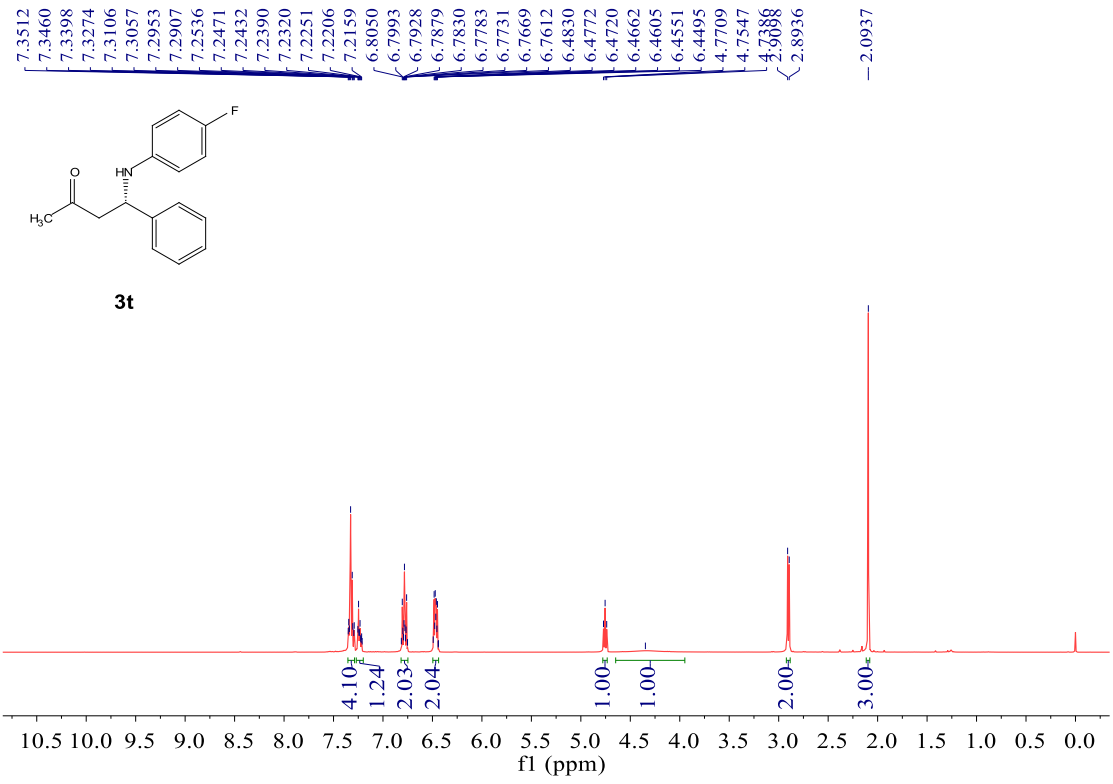
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3s



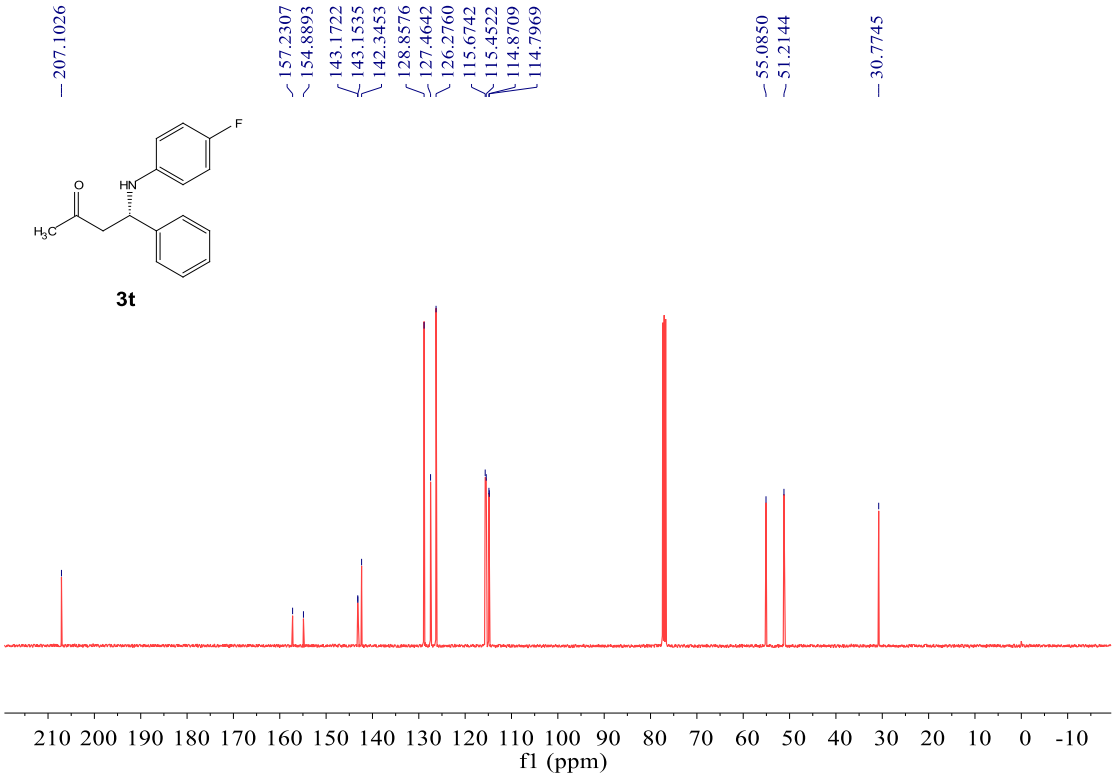
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3s



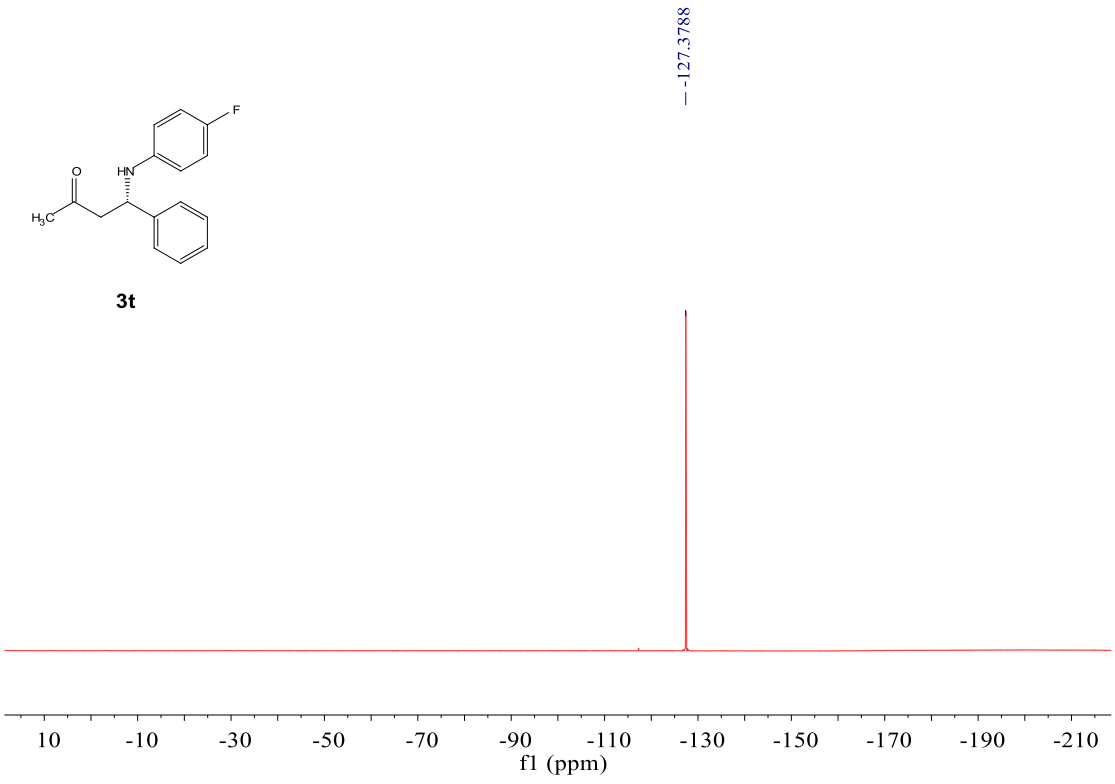
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3t



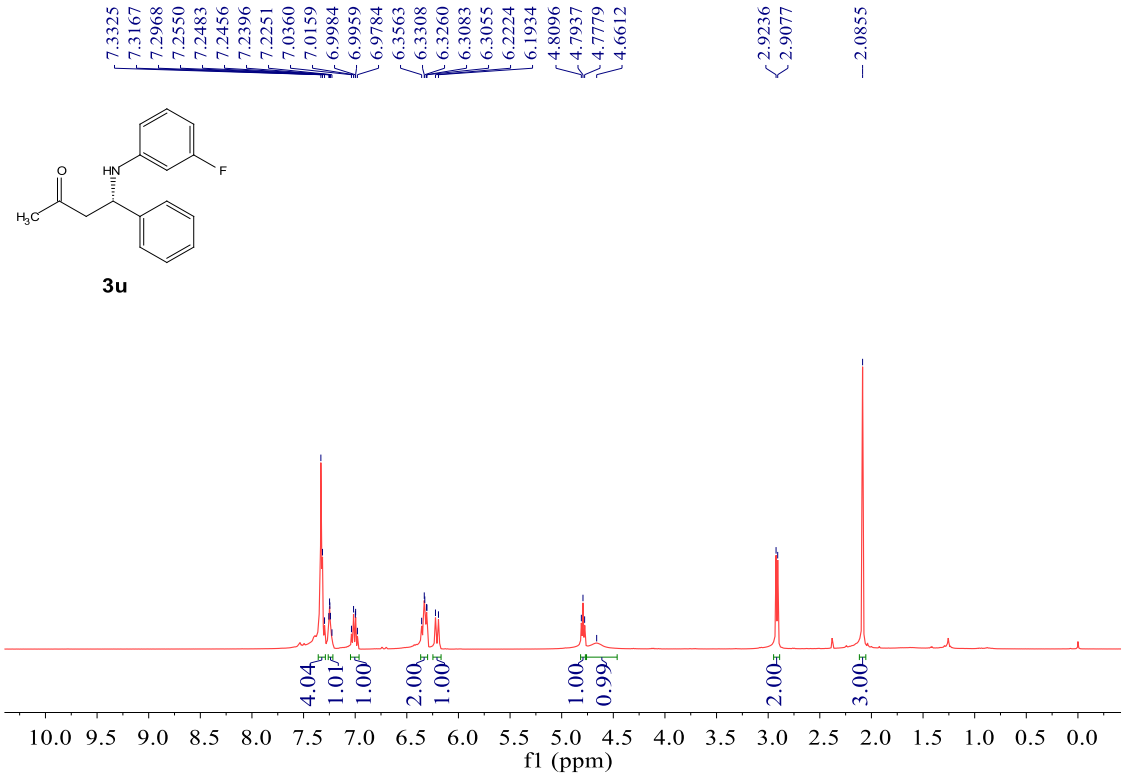
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3t



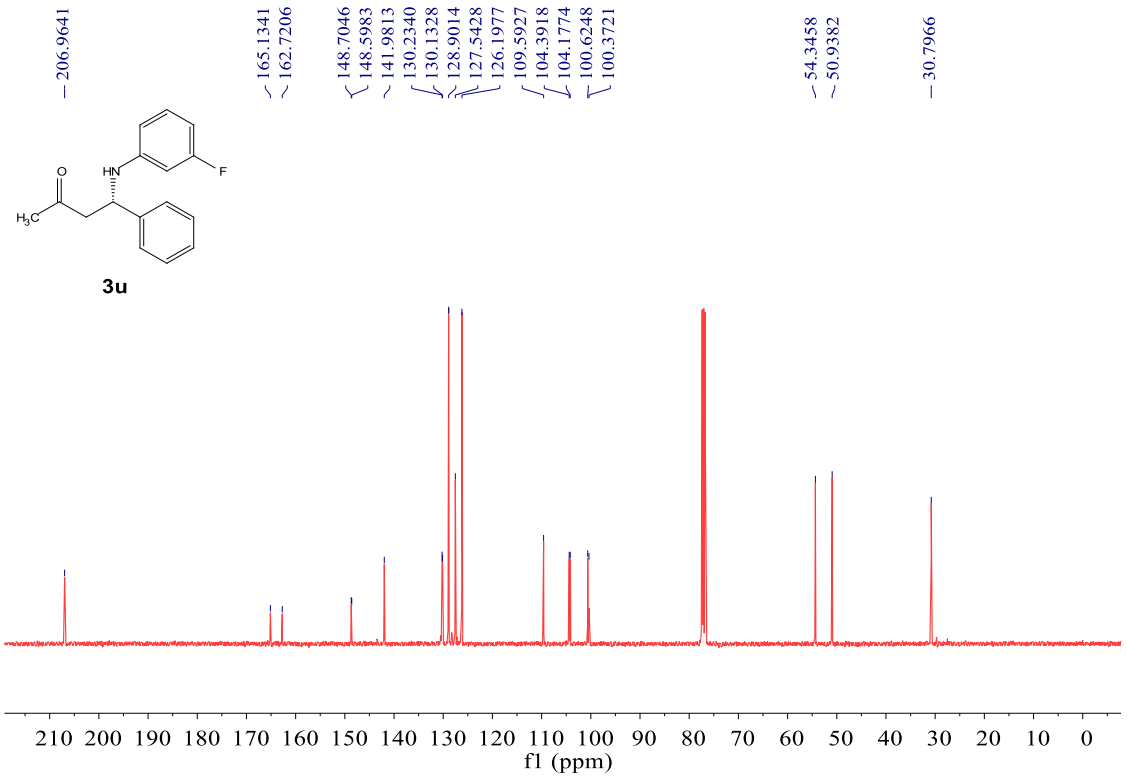
^{19}F NMR Spectrum (376 MHz, $CDCl_3$) of 3t



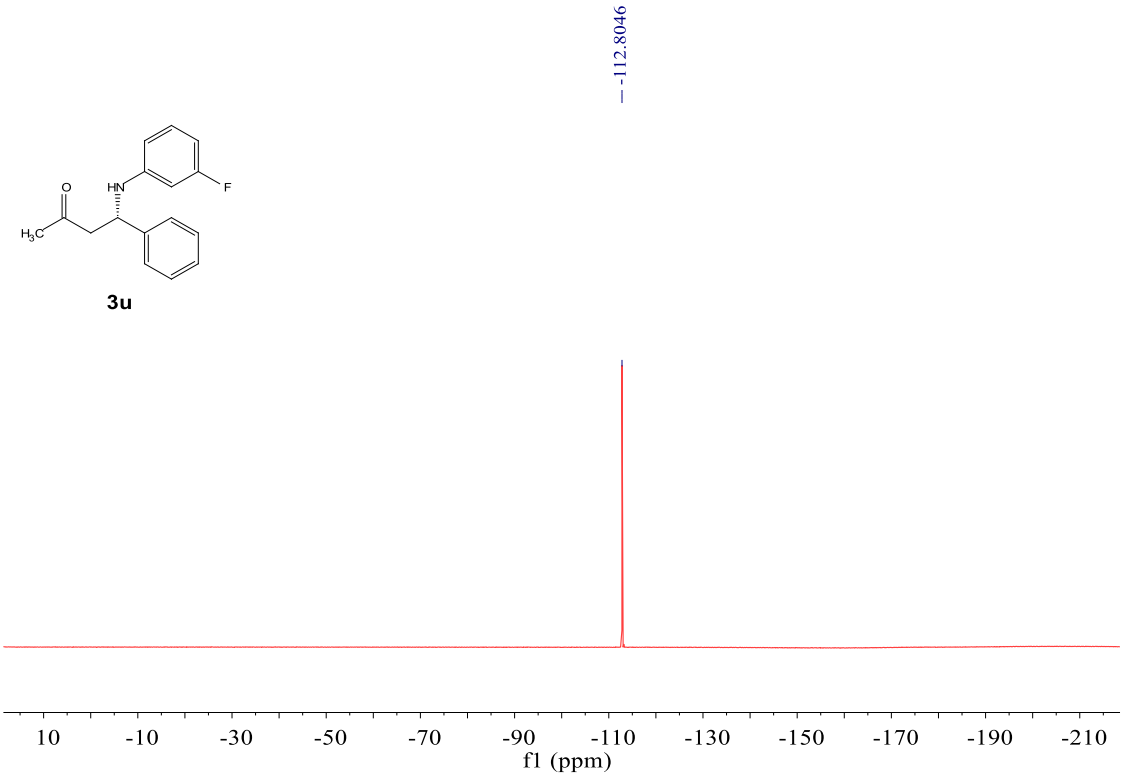
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3u



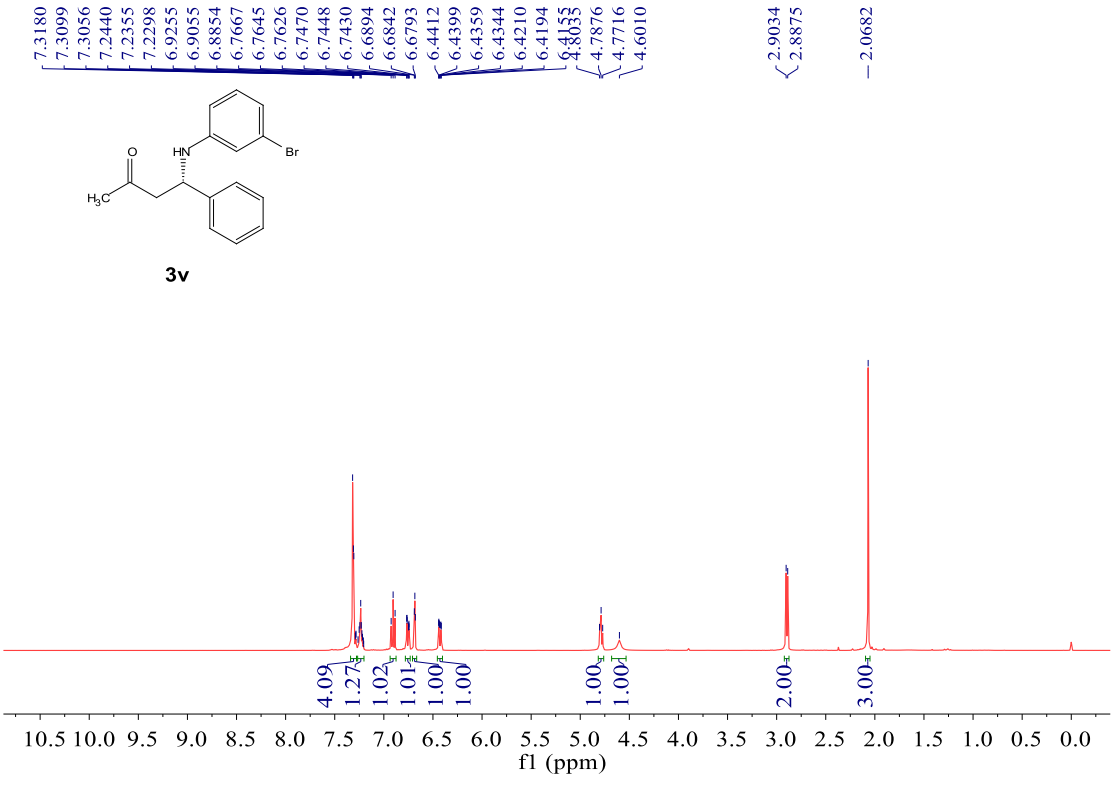
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3u



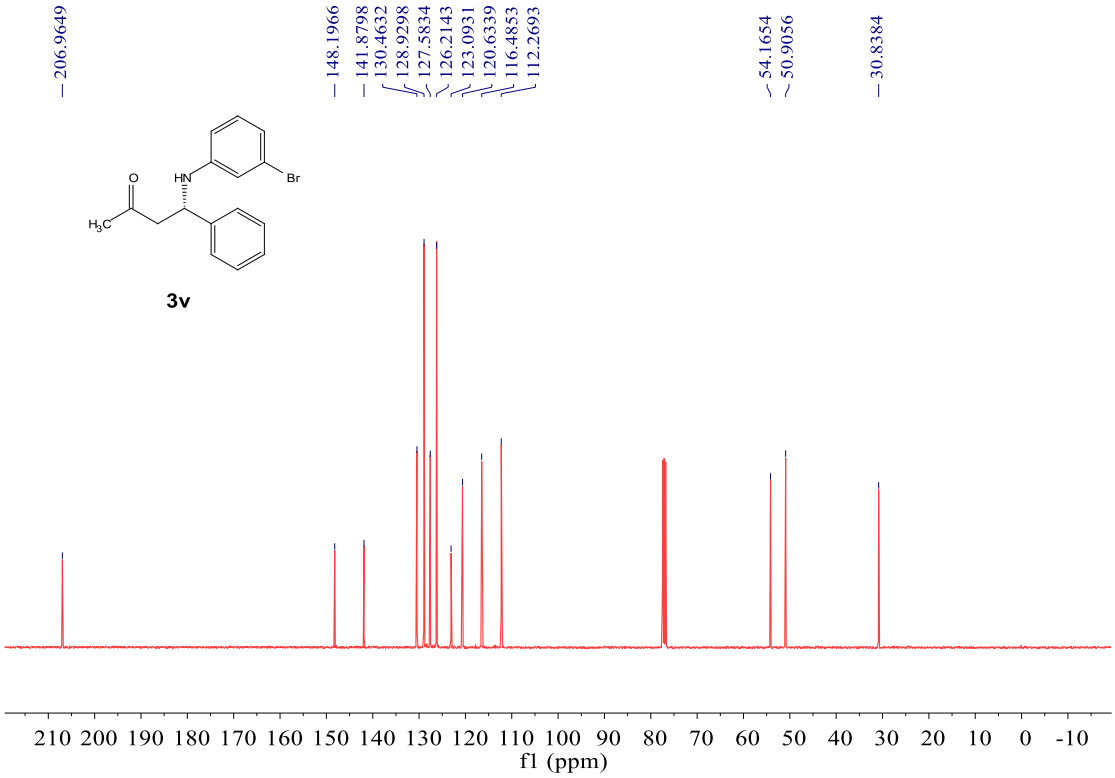
^{19}F NMR Spectrum (376 MHz, $CDCl_3$) of 3u



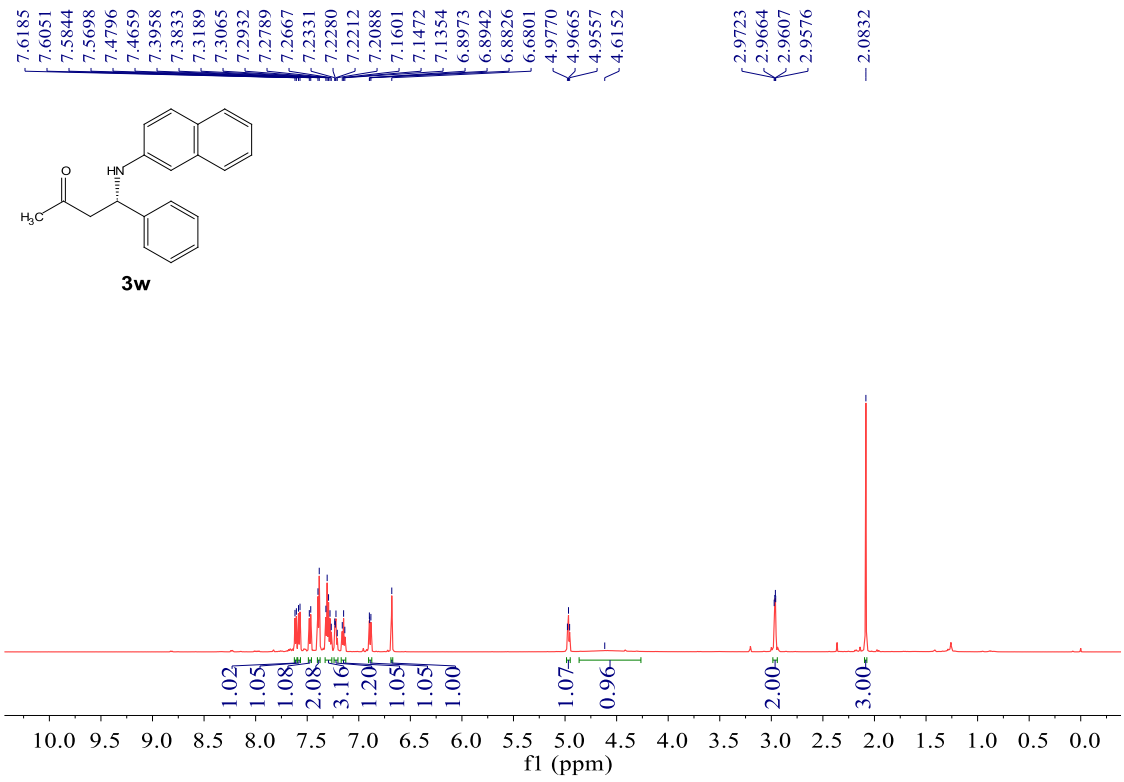
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3v



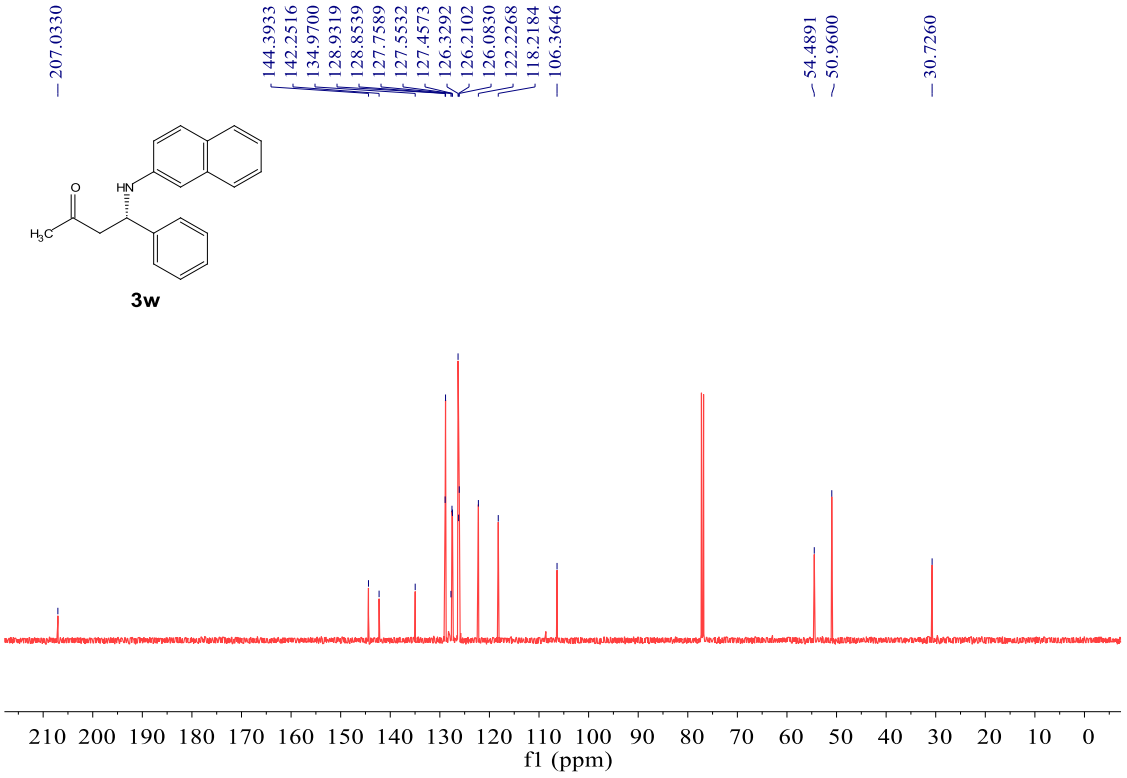
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3v



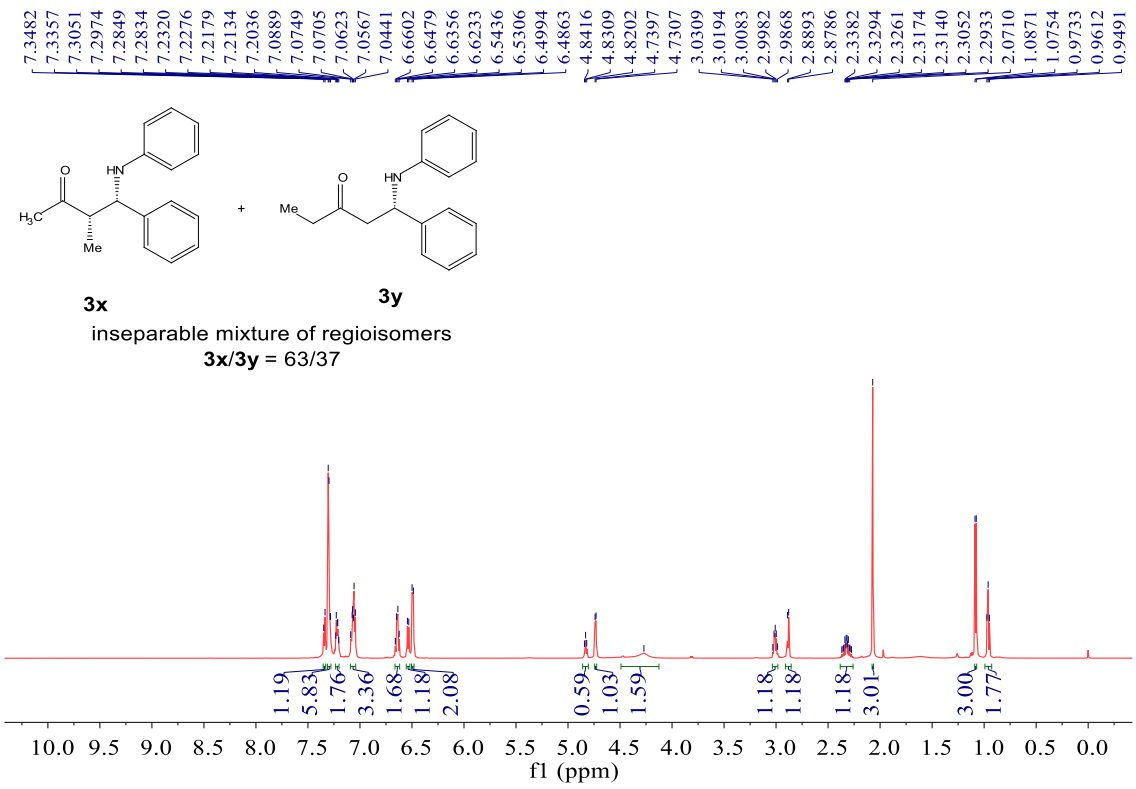
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3w



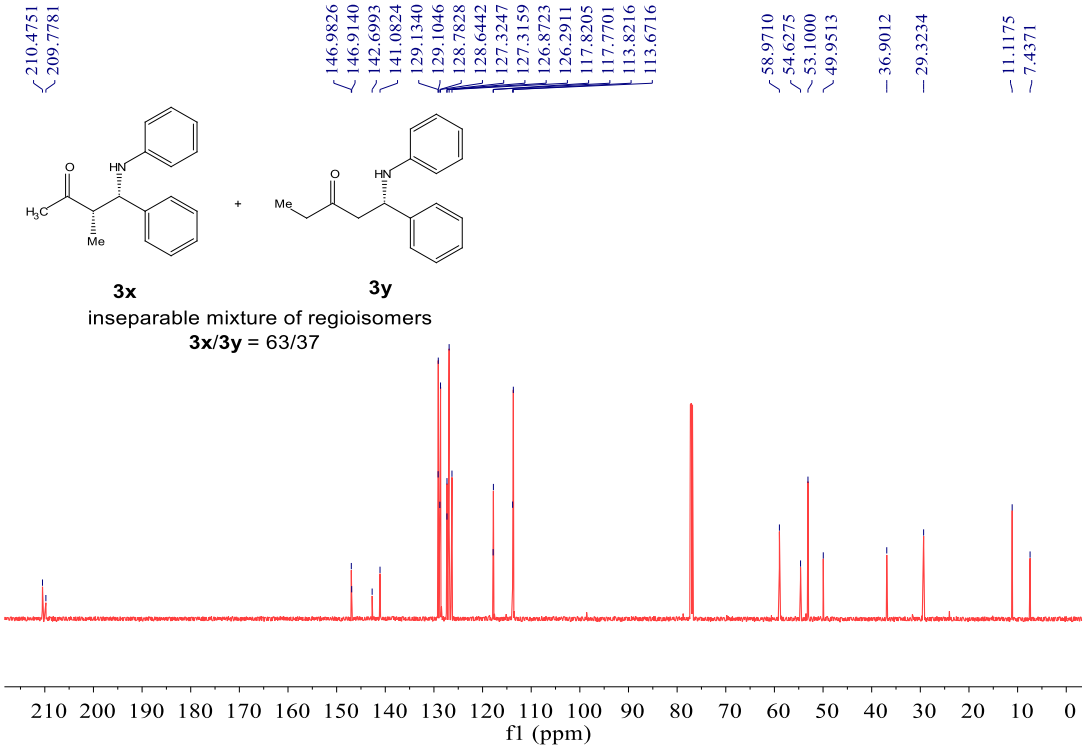
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3w



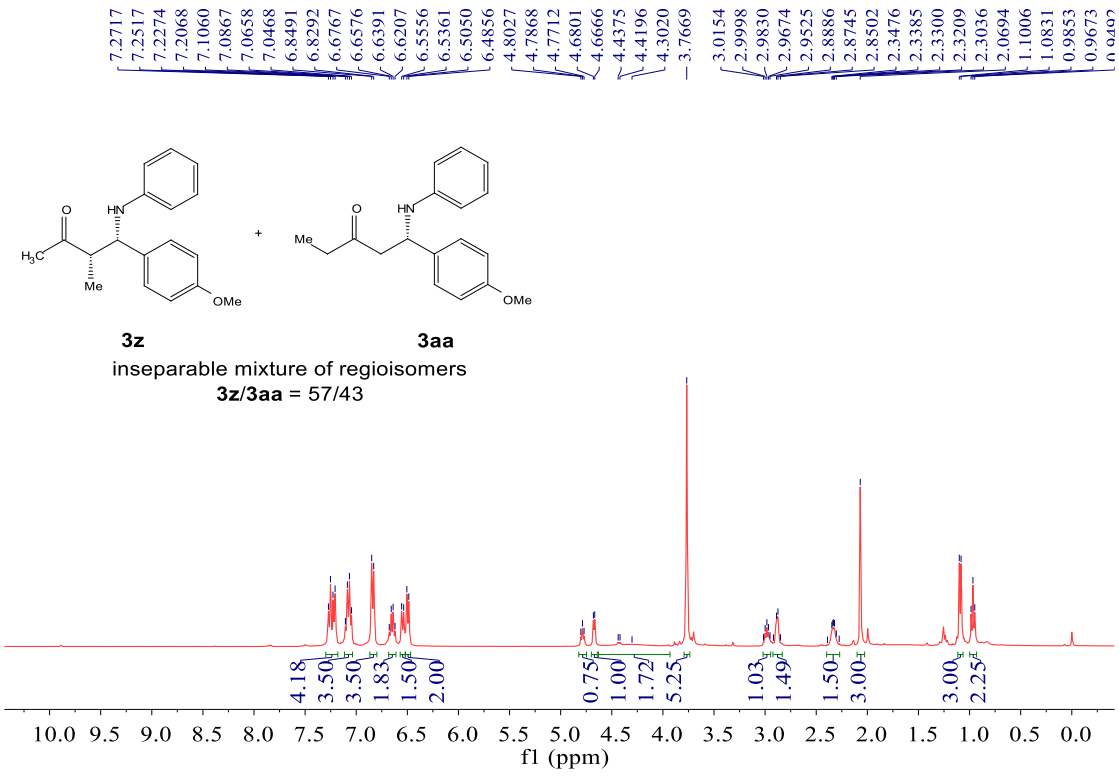
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3x and 3y



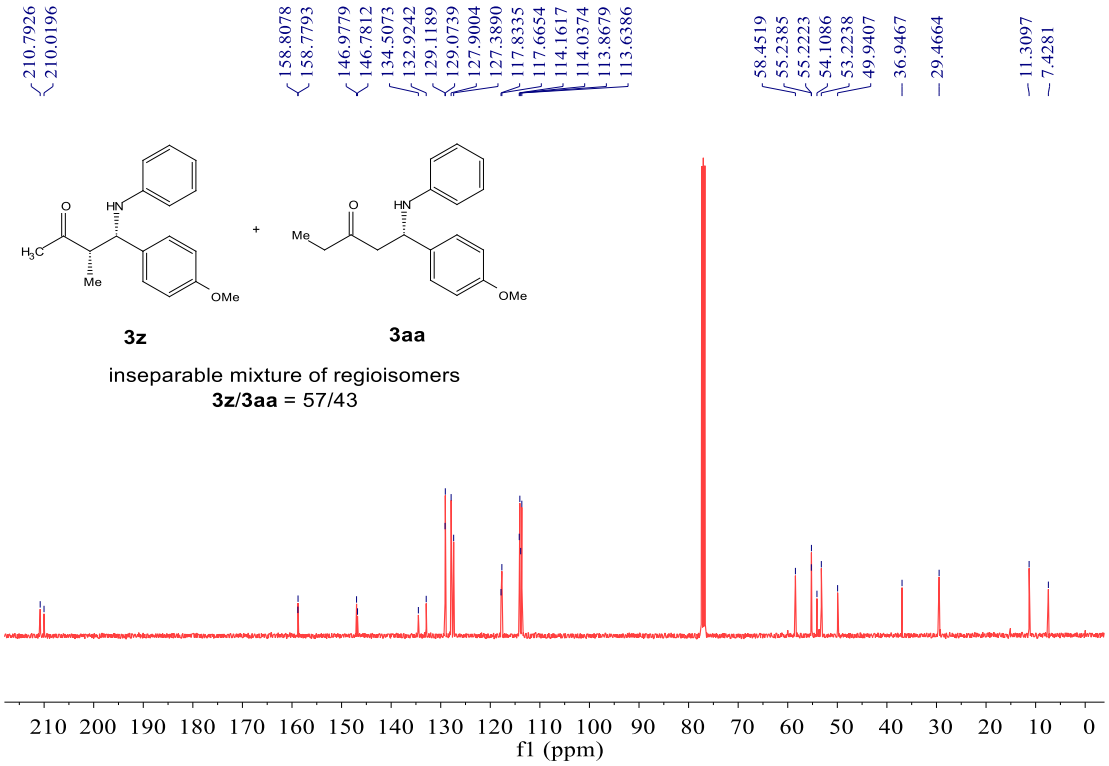
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3x and 3y



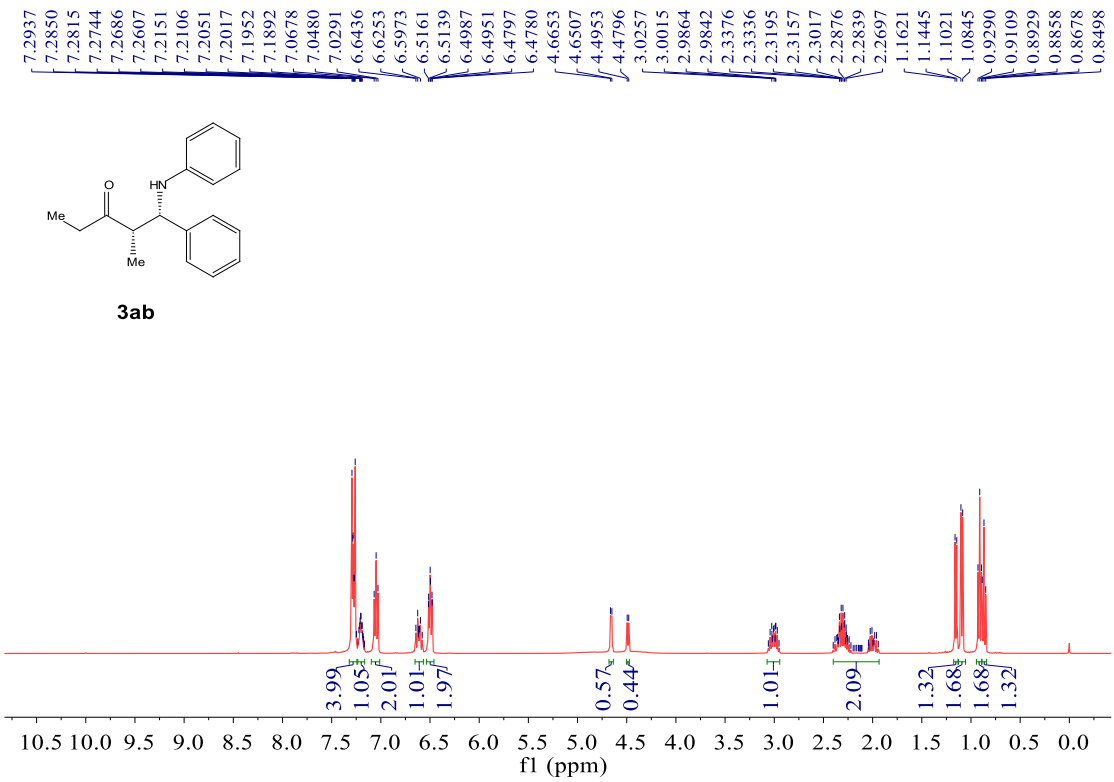
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3z and 3aa



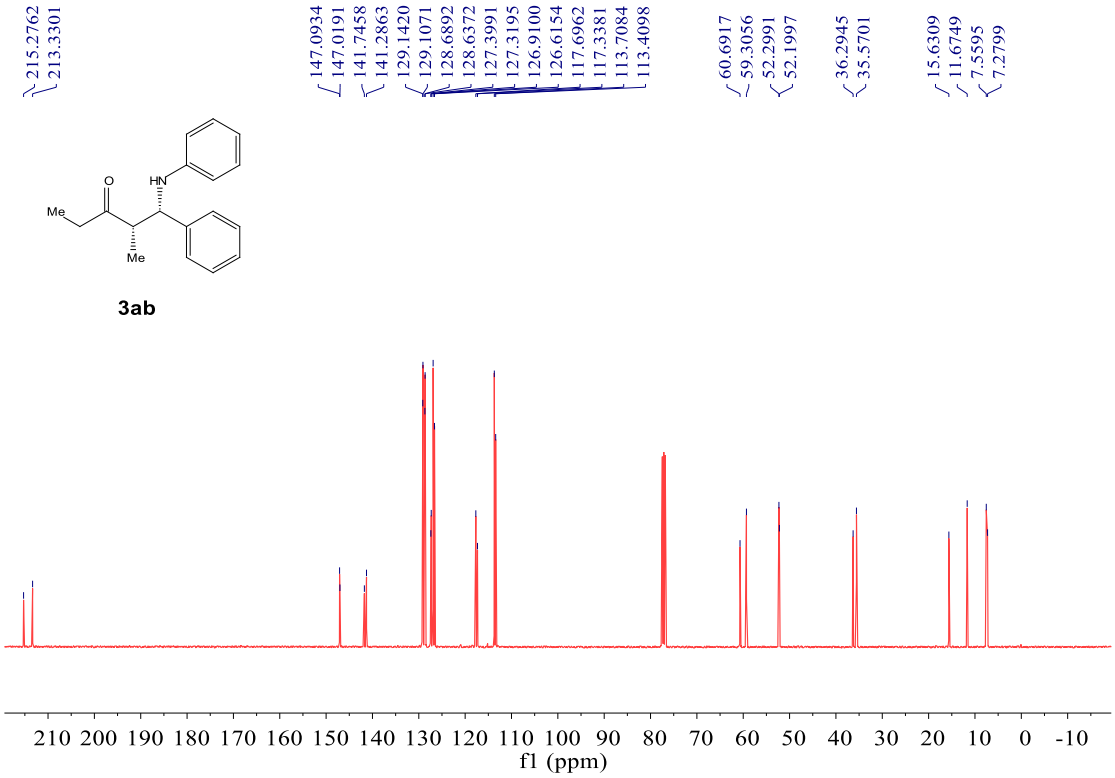
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3z and 3aa



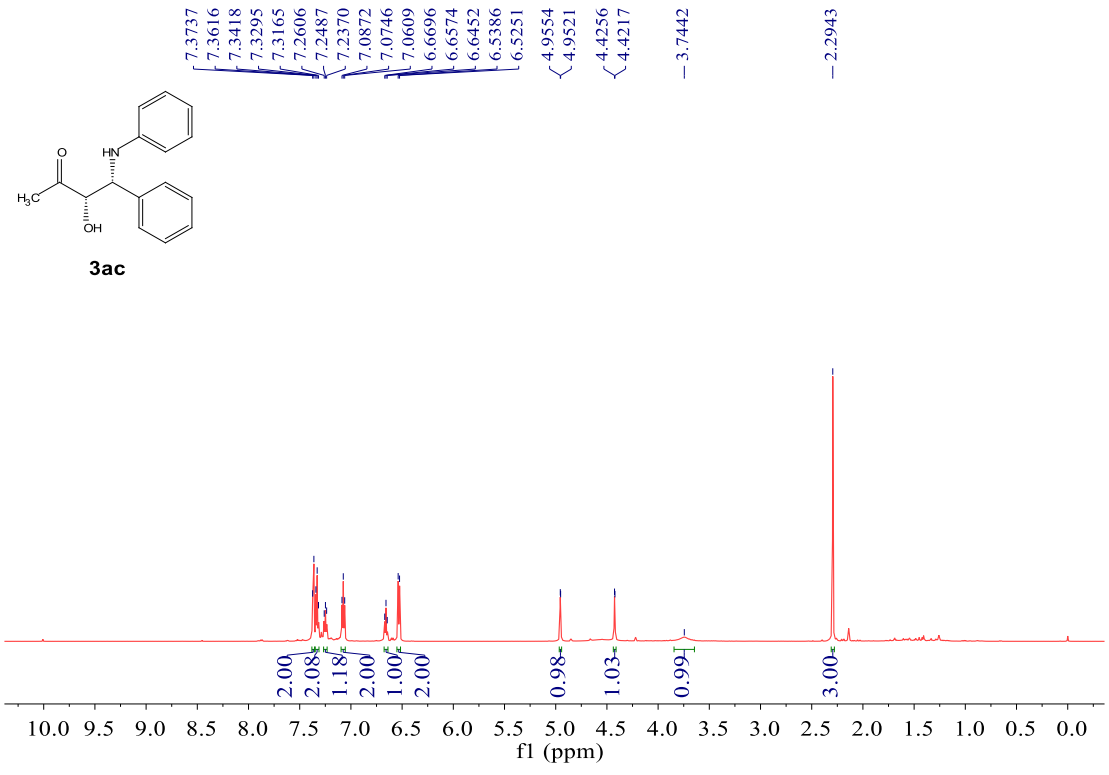
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3ab



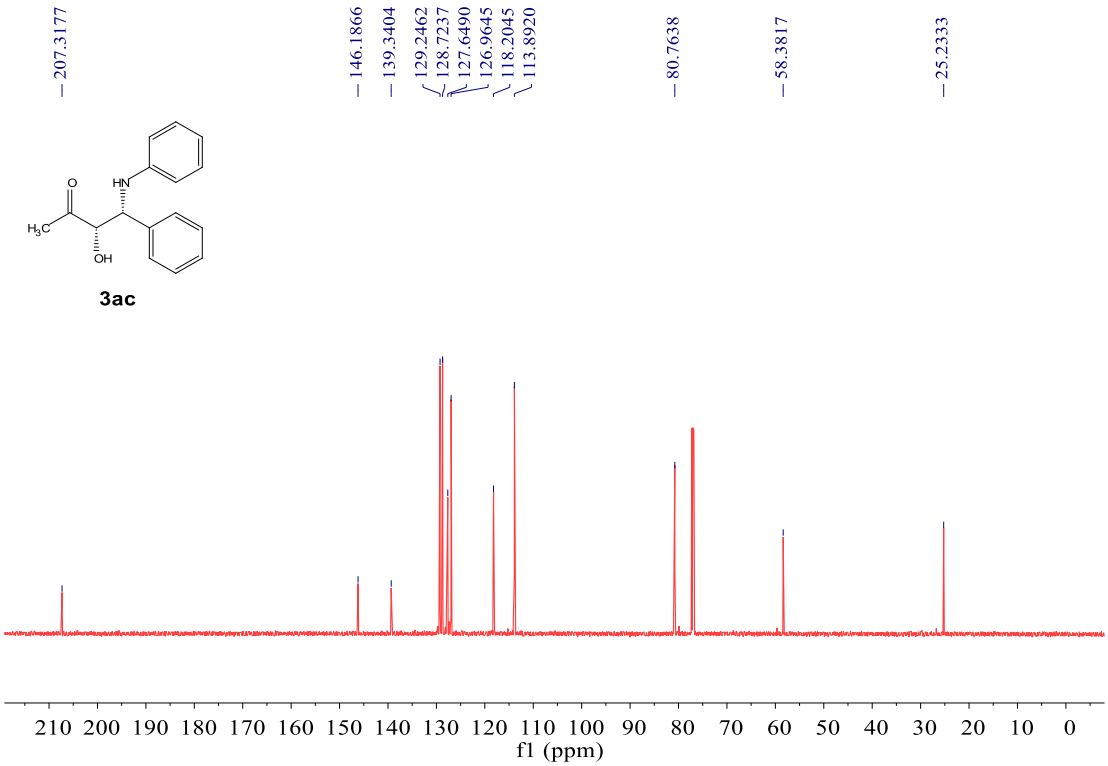
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3ab



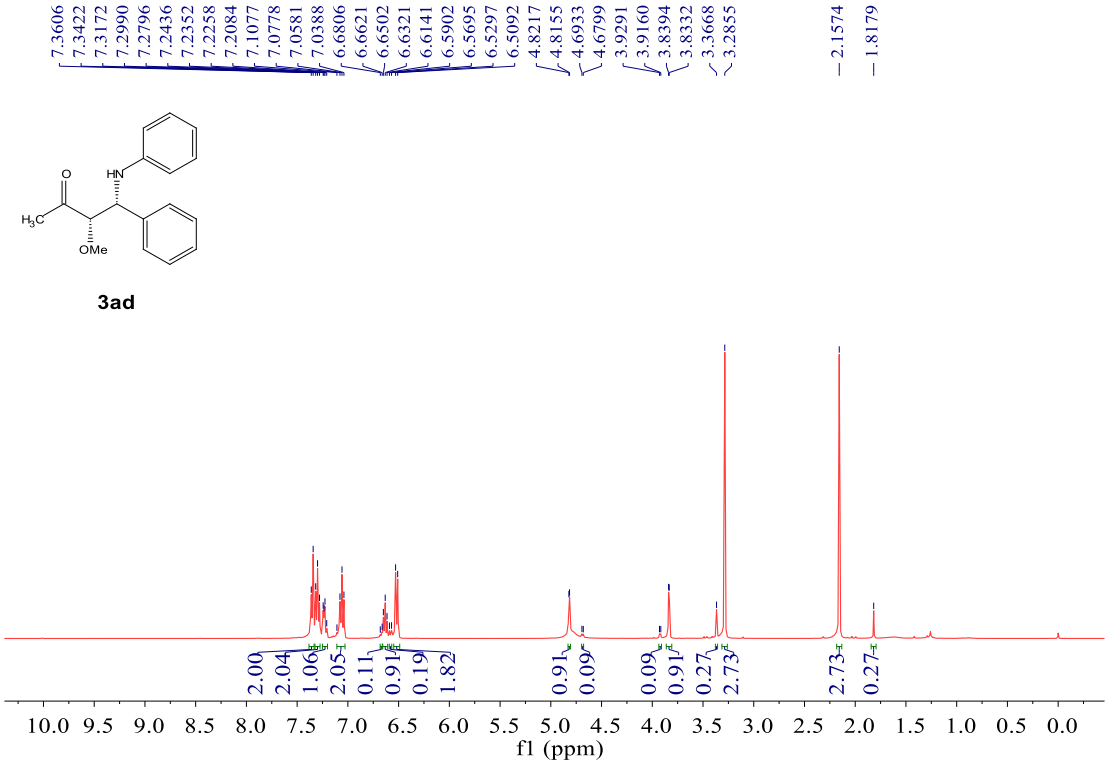
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3ac



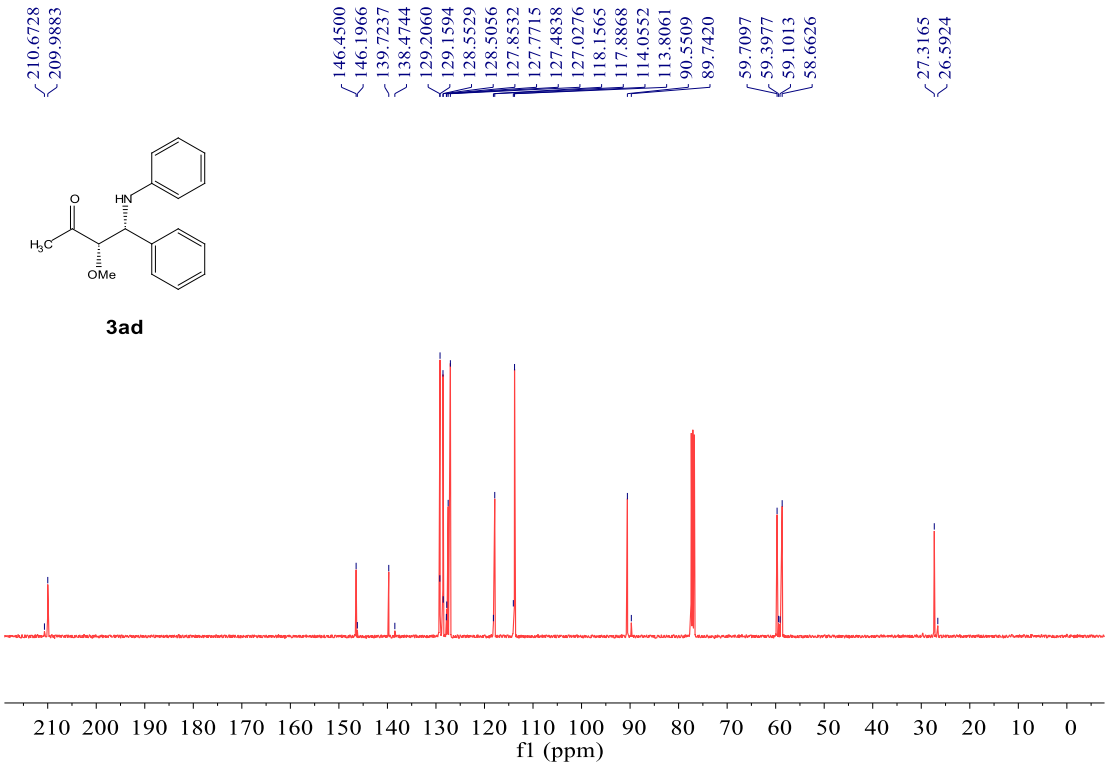
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 3ac



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

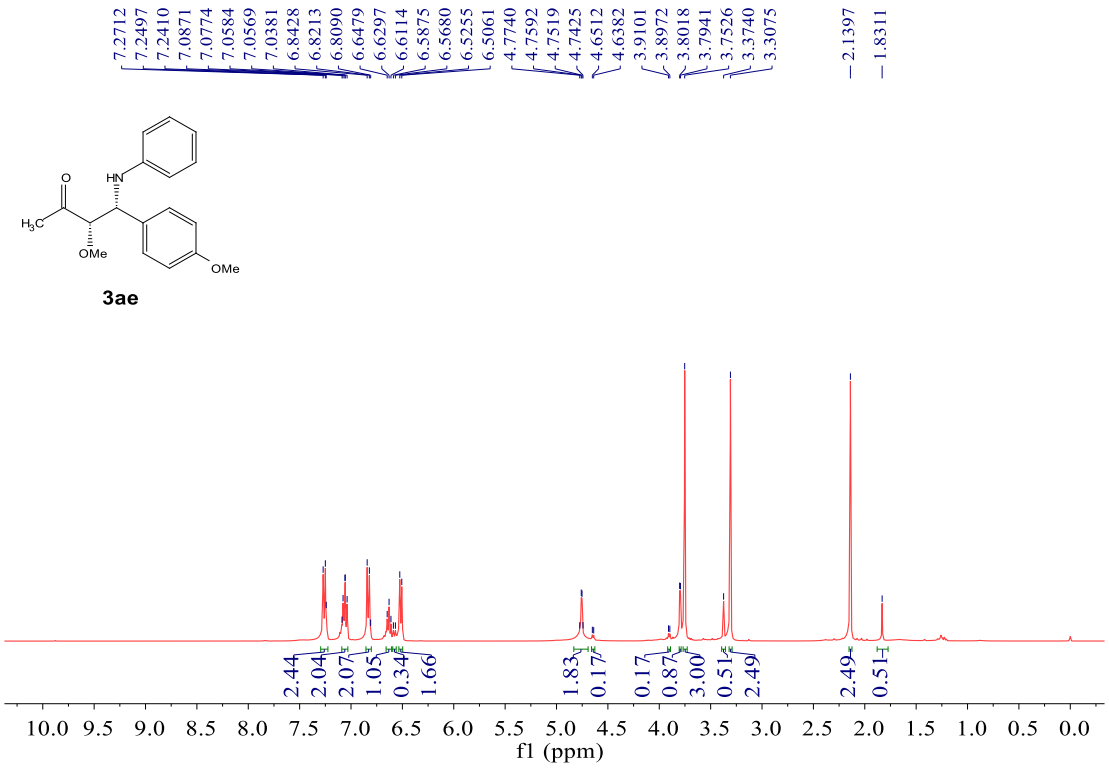


^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3ad



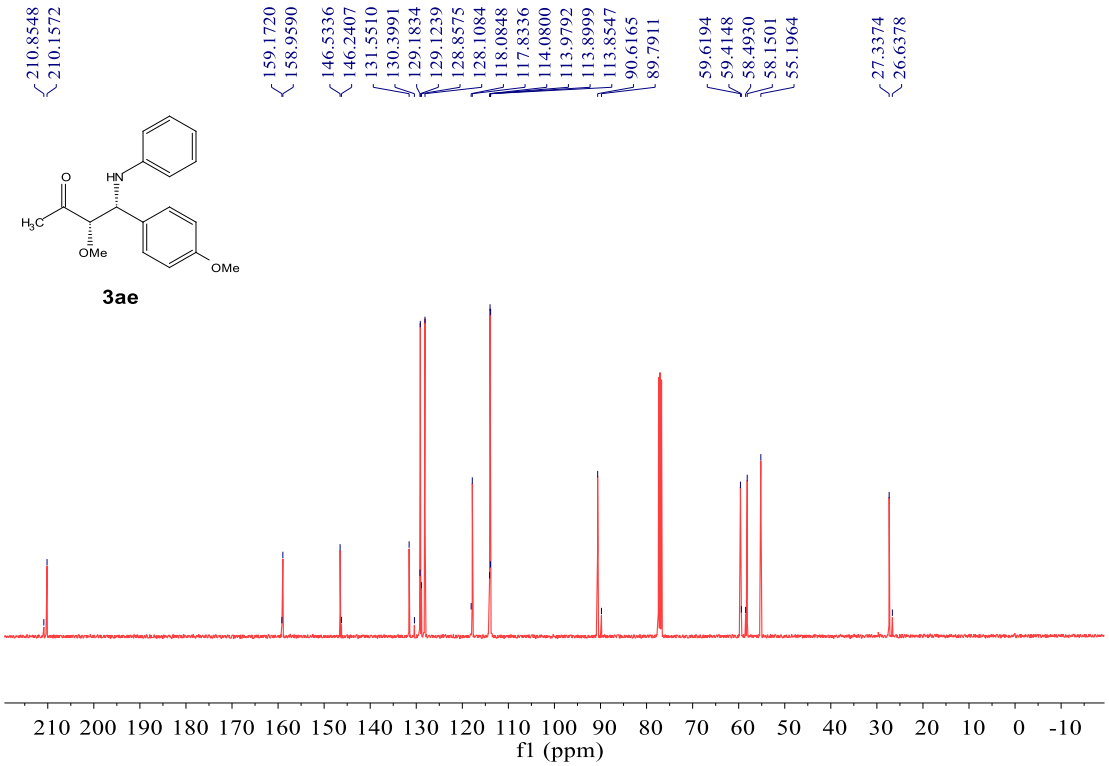
3ad

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

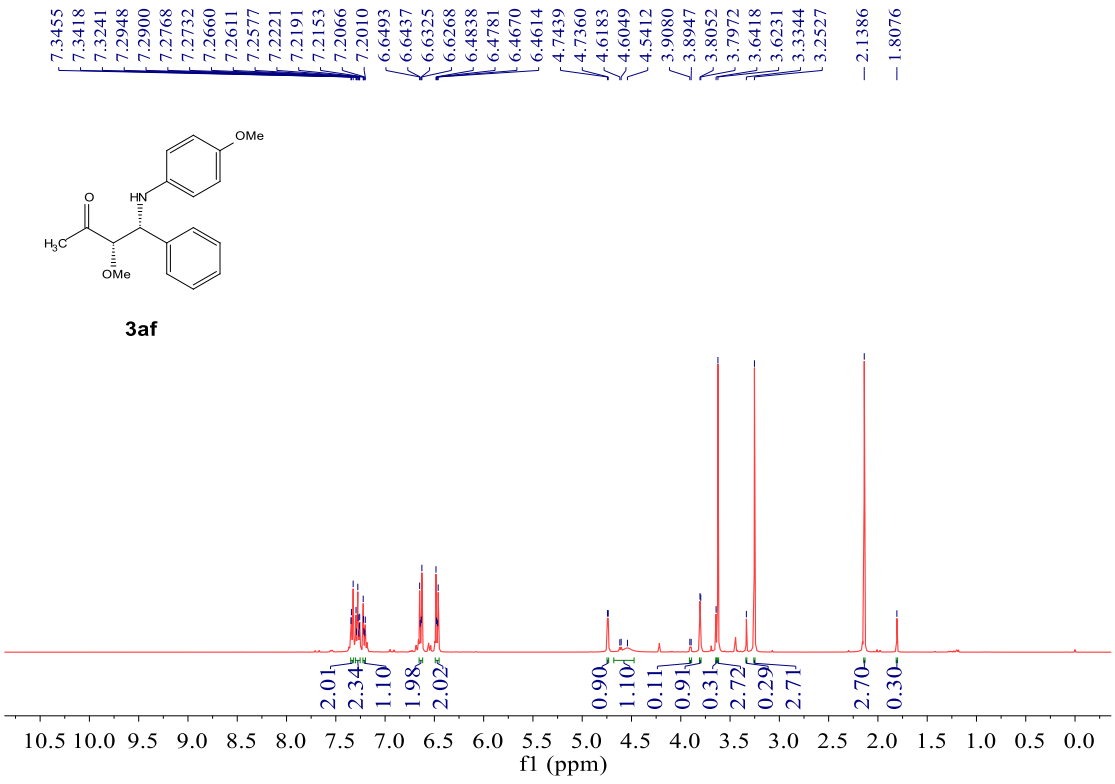


3ae

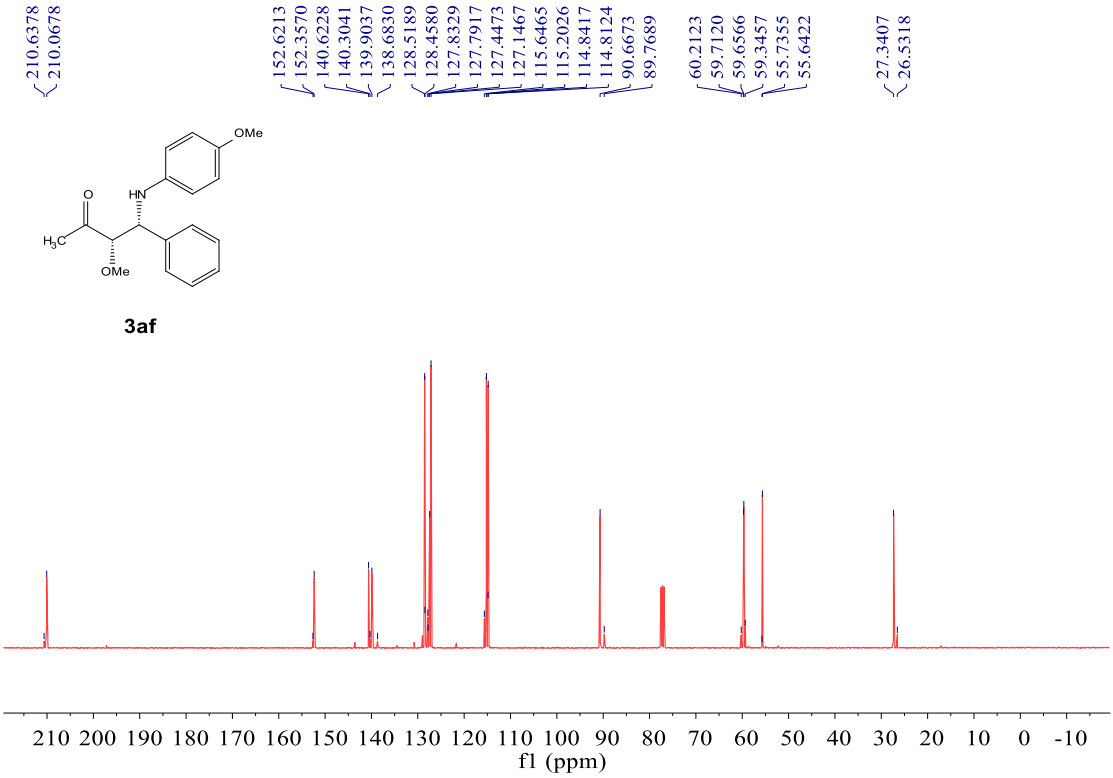
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3ae



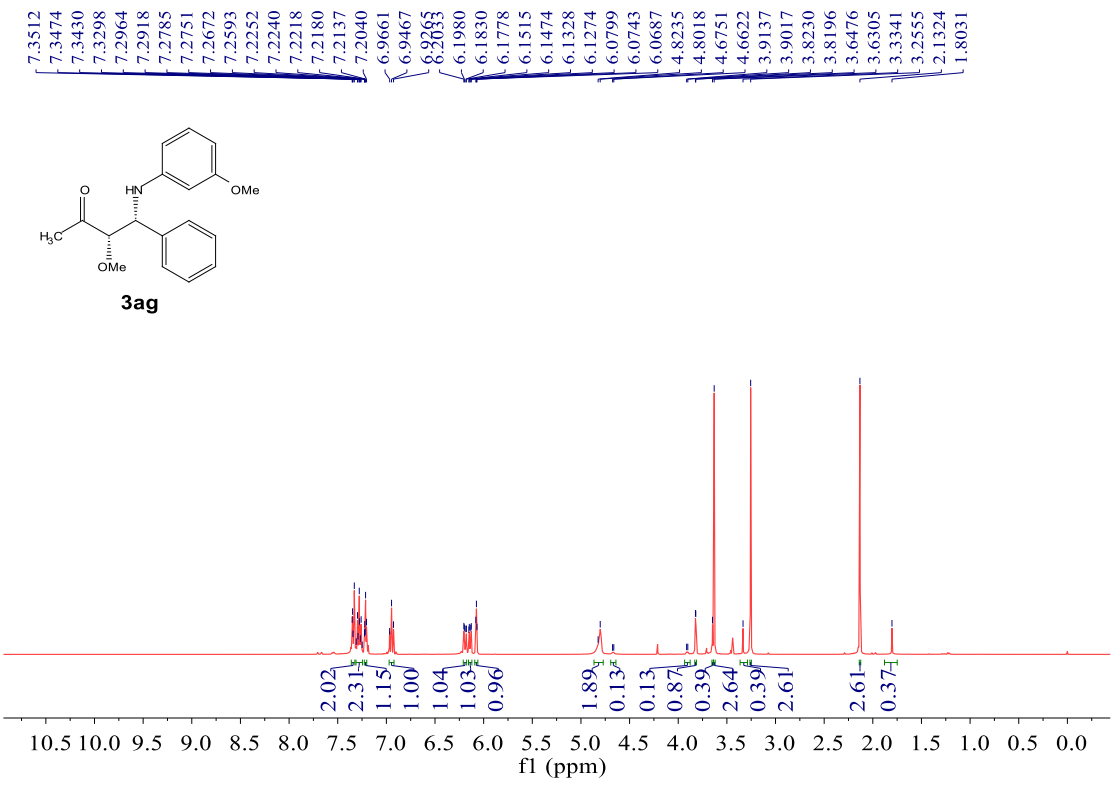
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3af



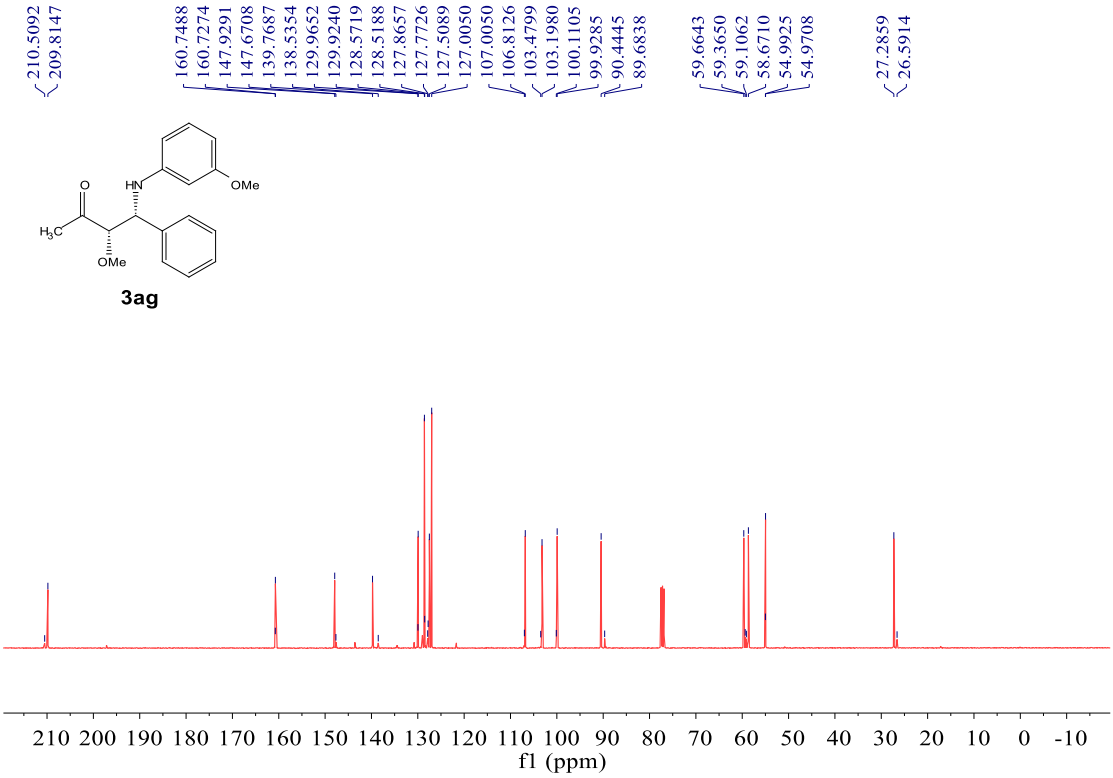
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3af



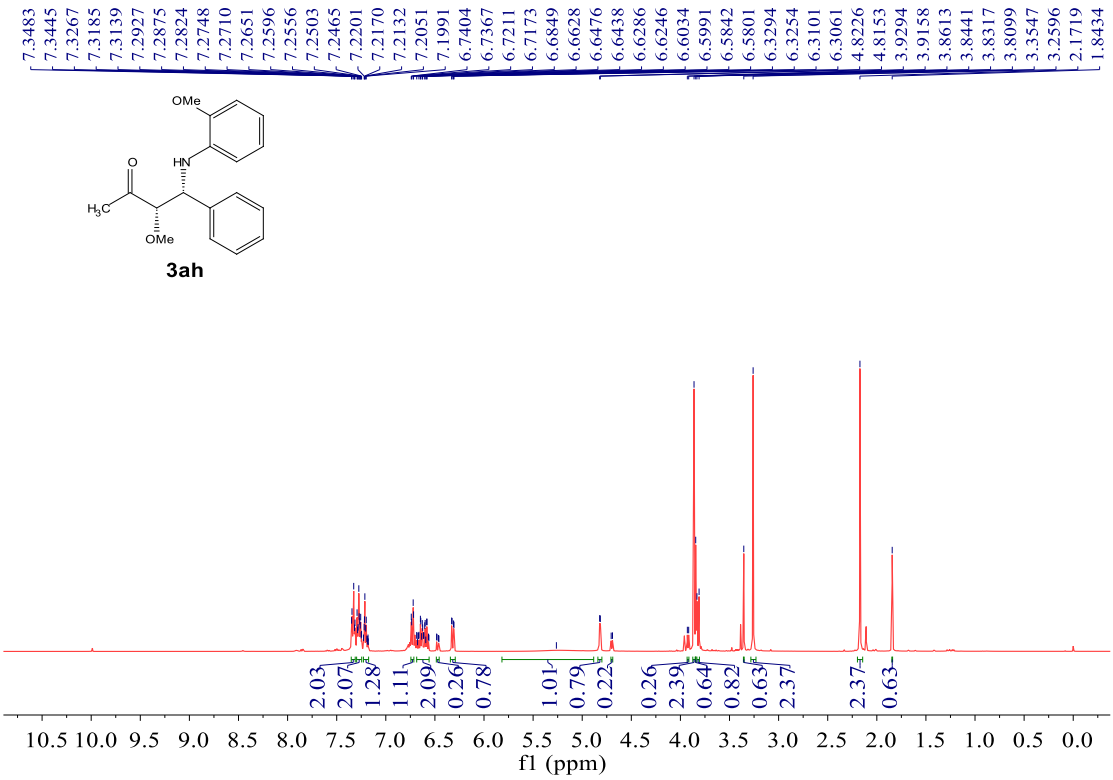
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3ag



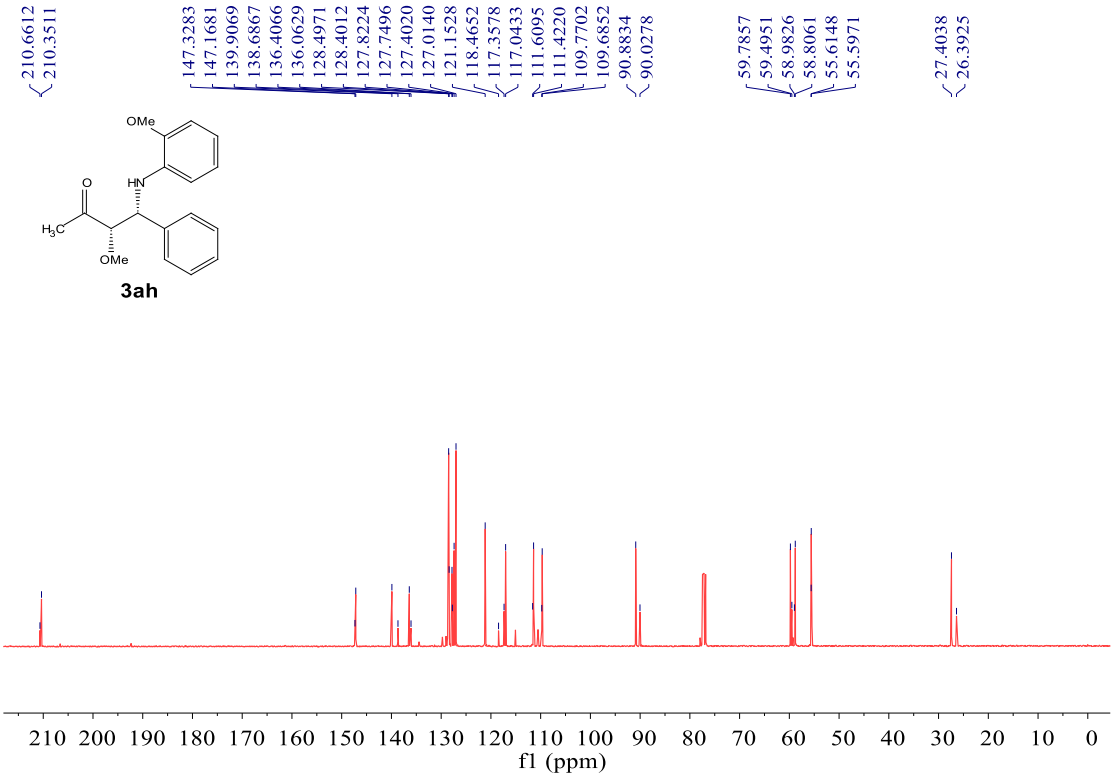
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3ag



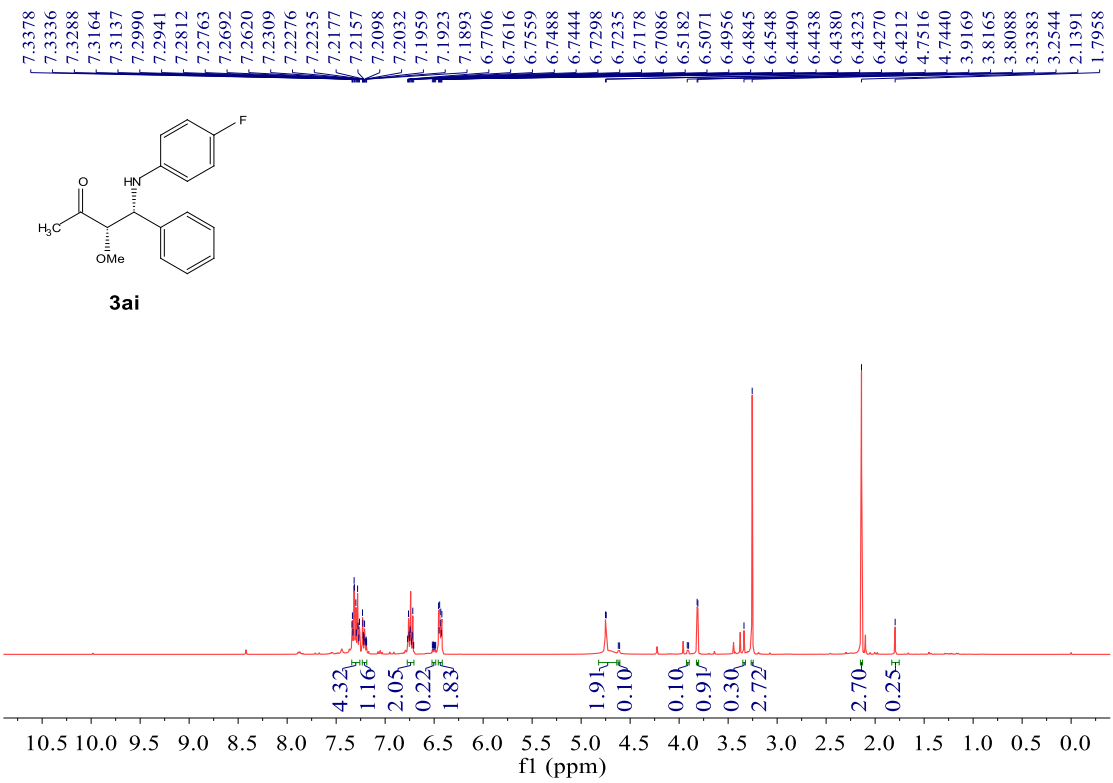
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3ah



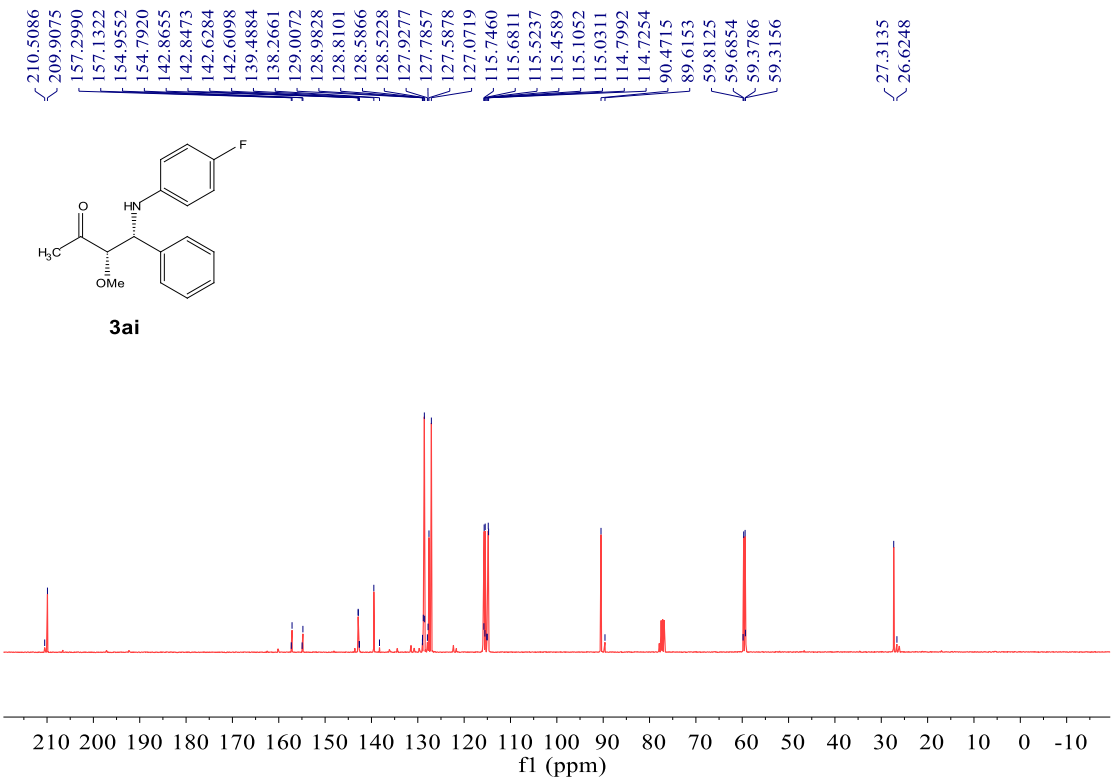
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3ah



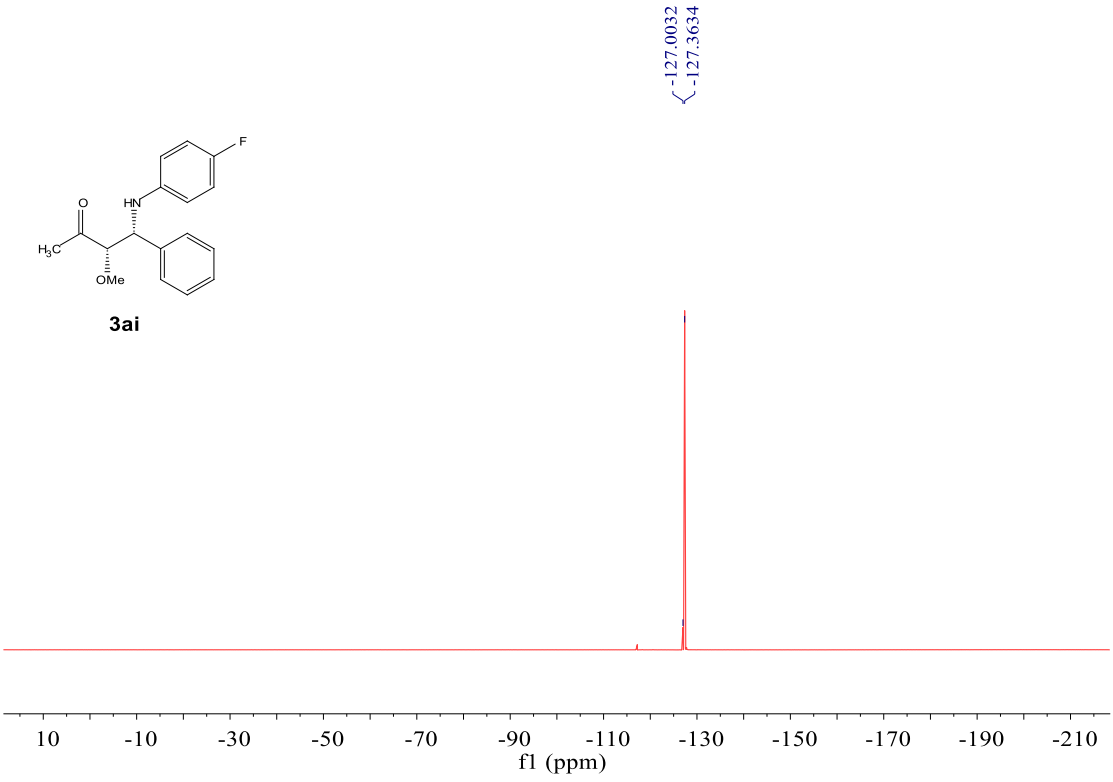
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3ai



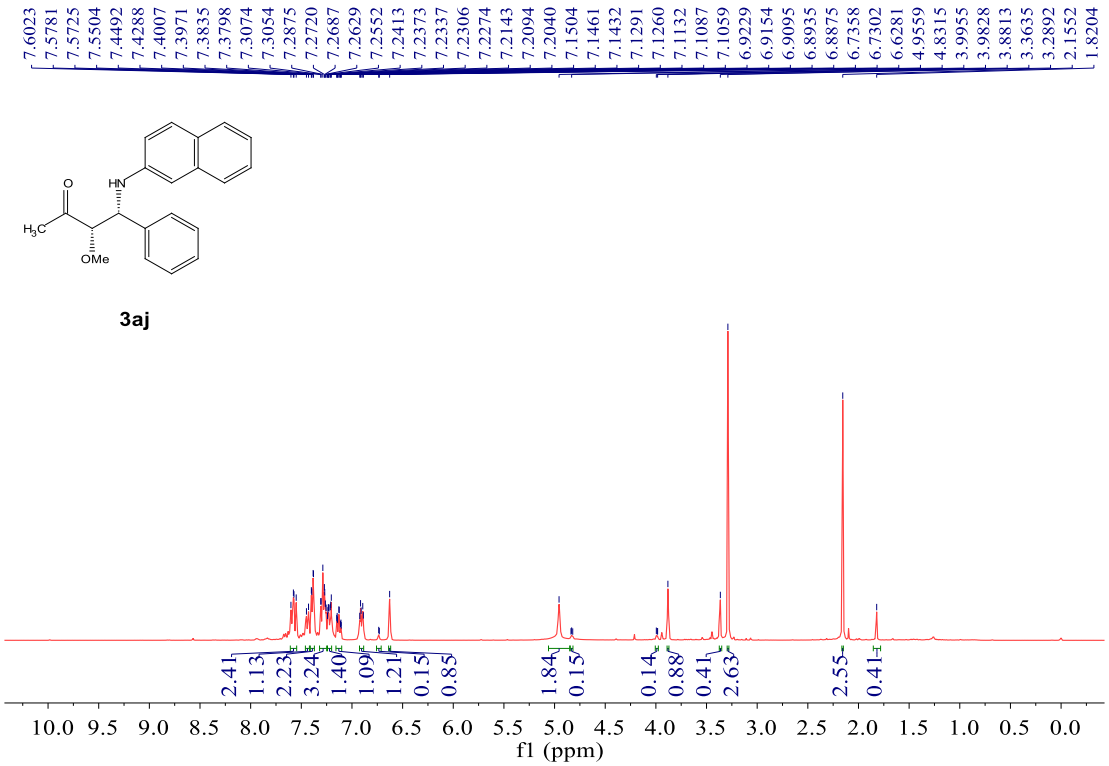
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3ai



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

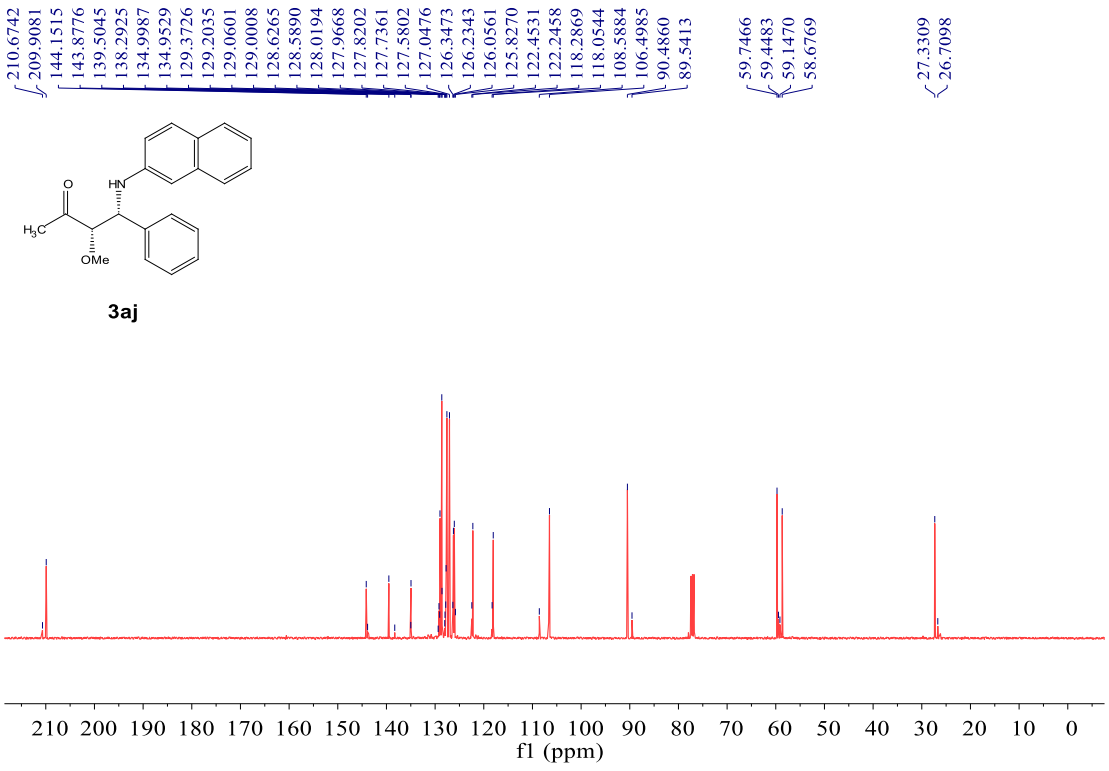


^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3aj



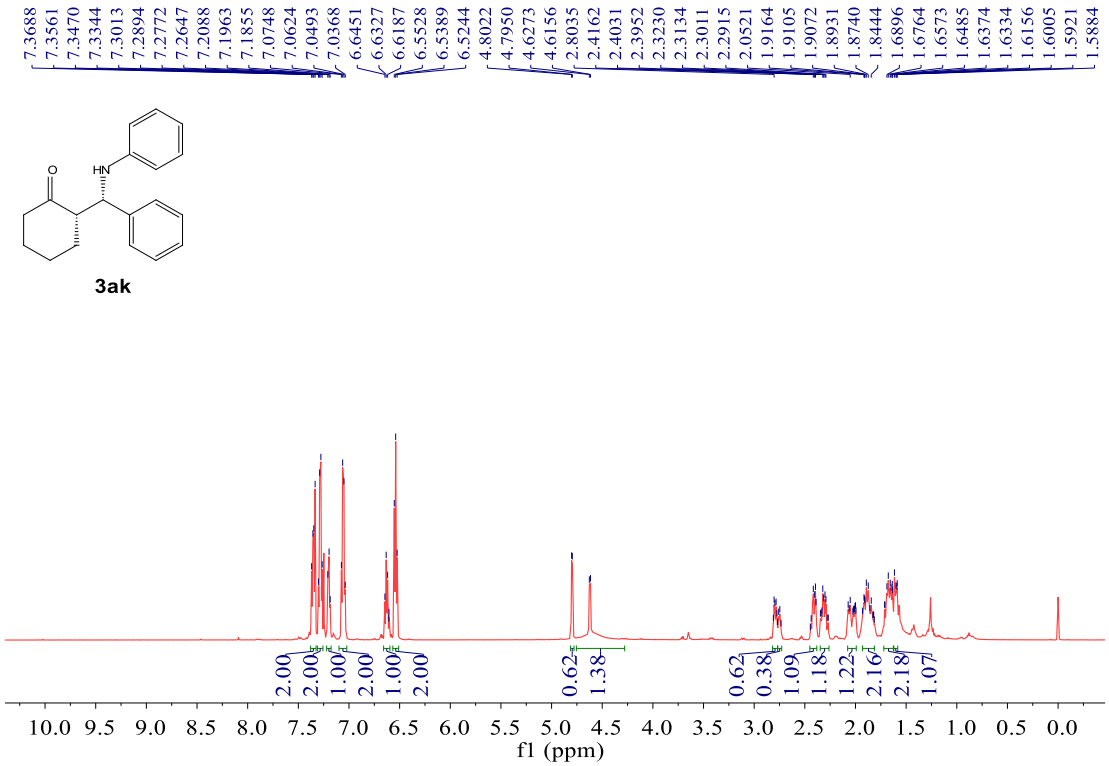
3aj

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

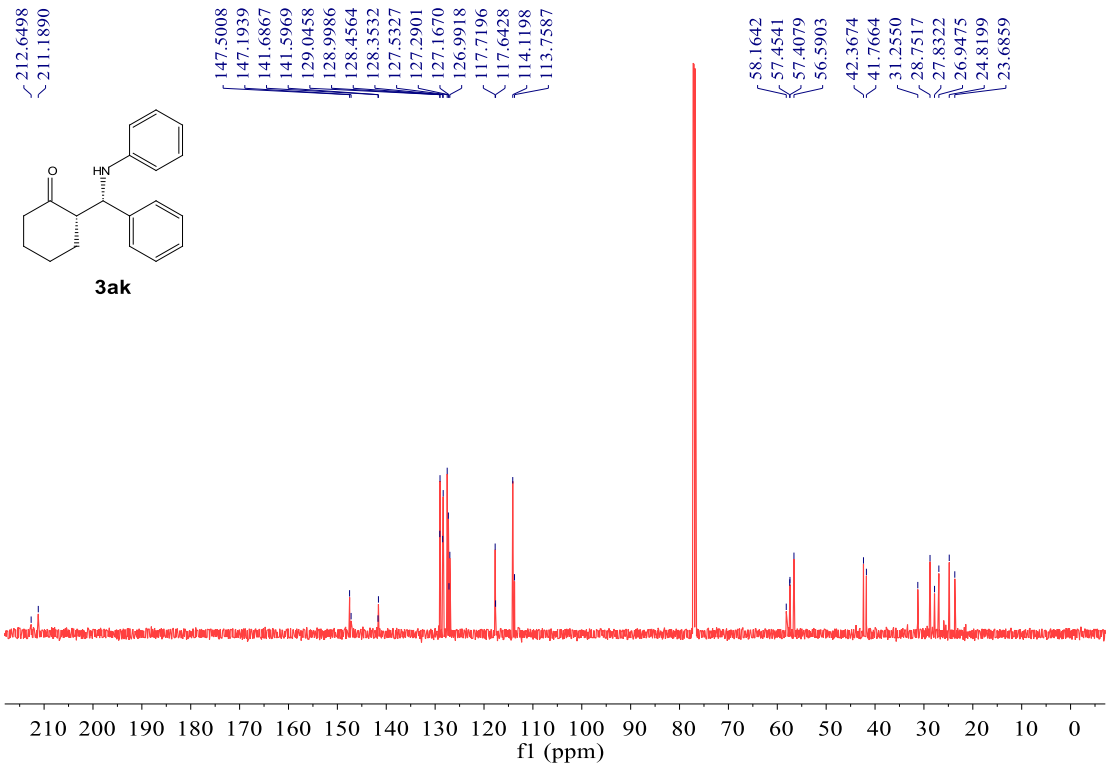


3aj

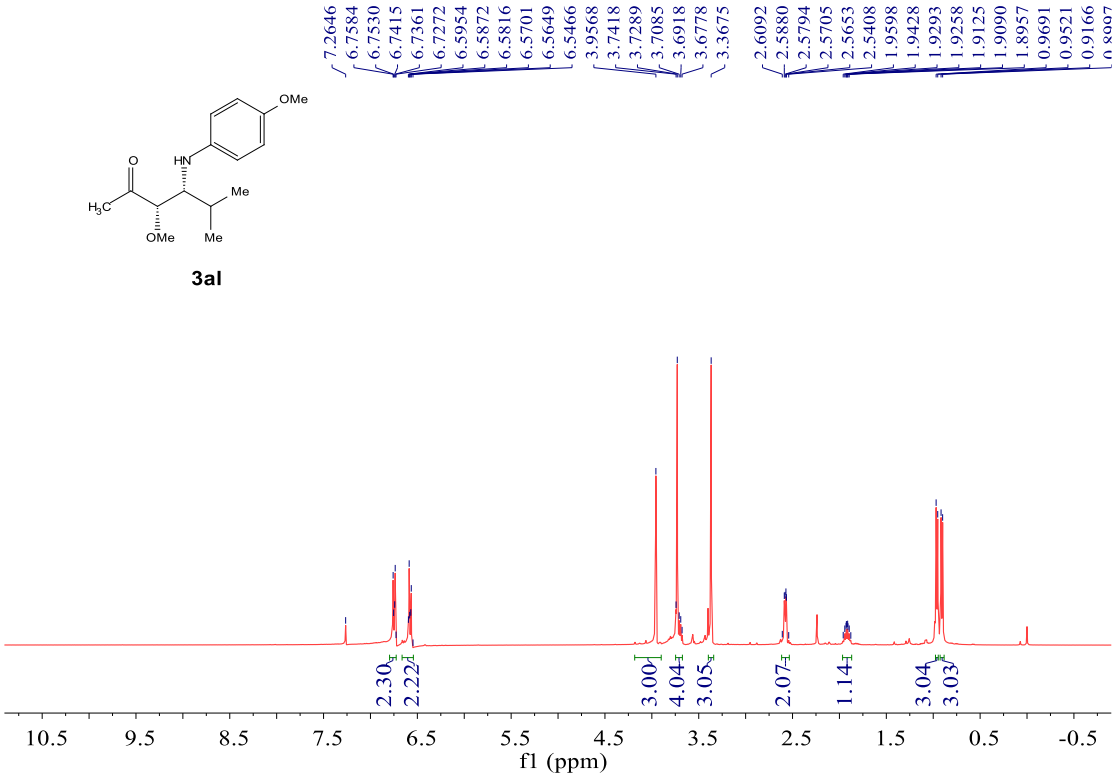
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 3ak



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

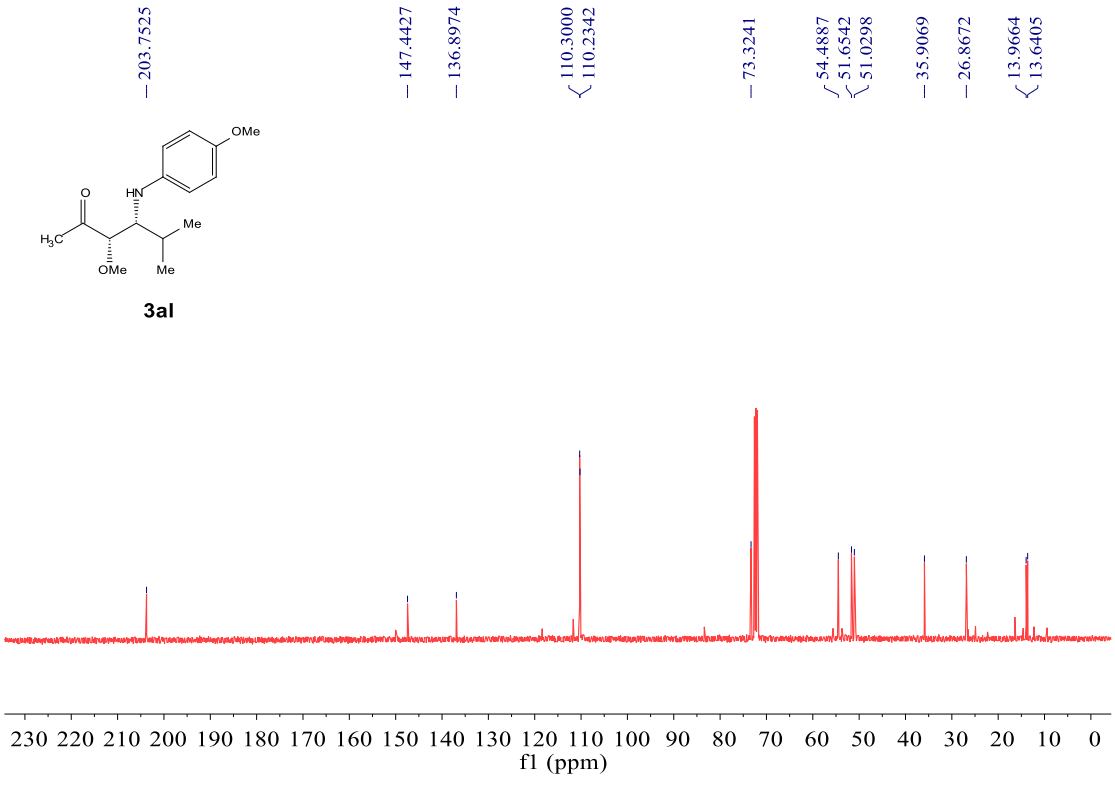


^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3al



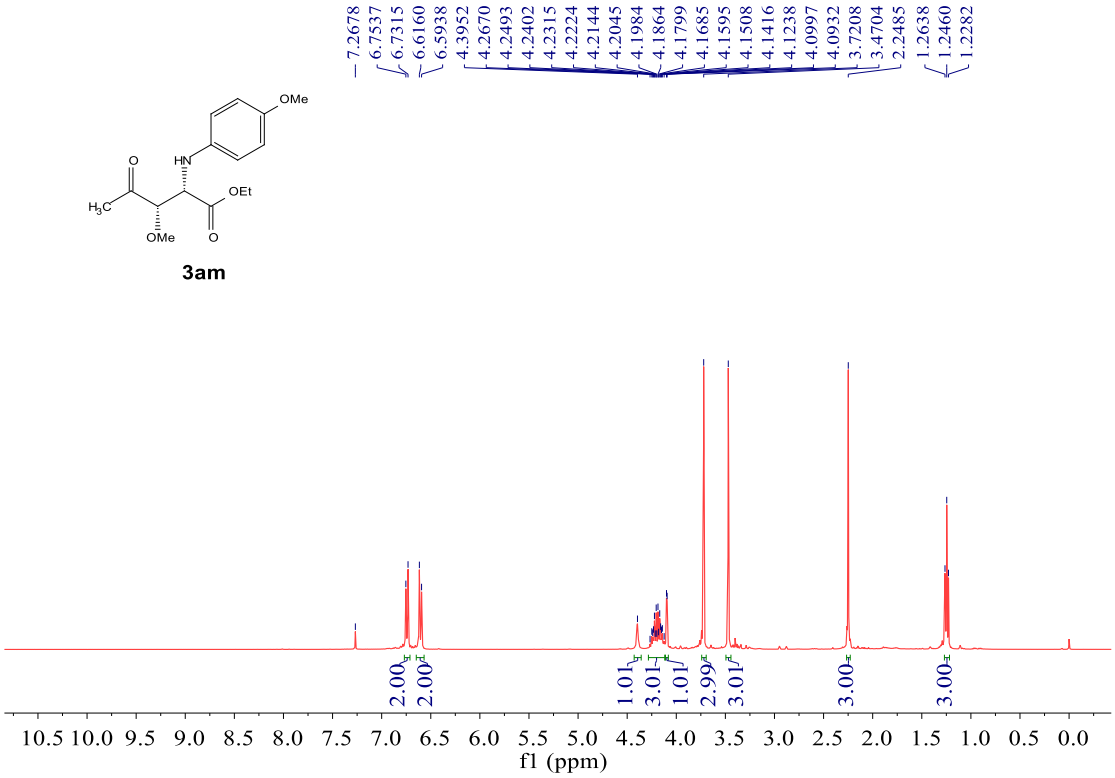
3al

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

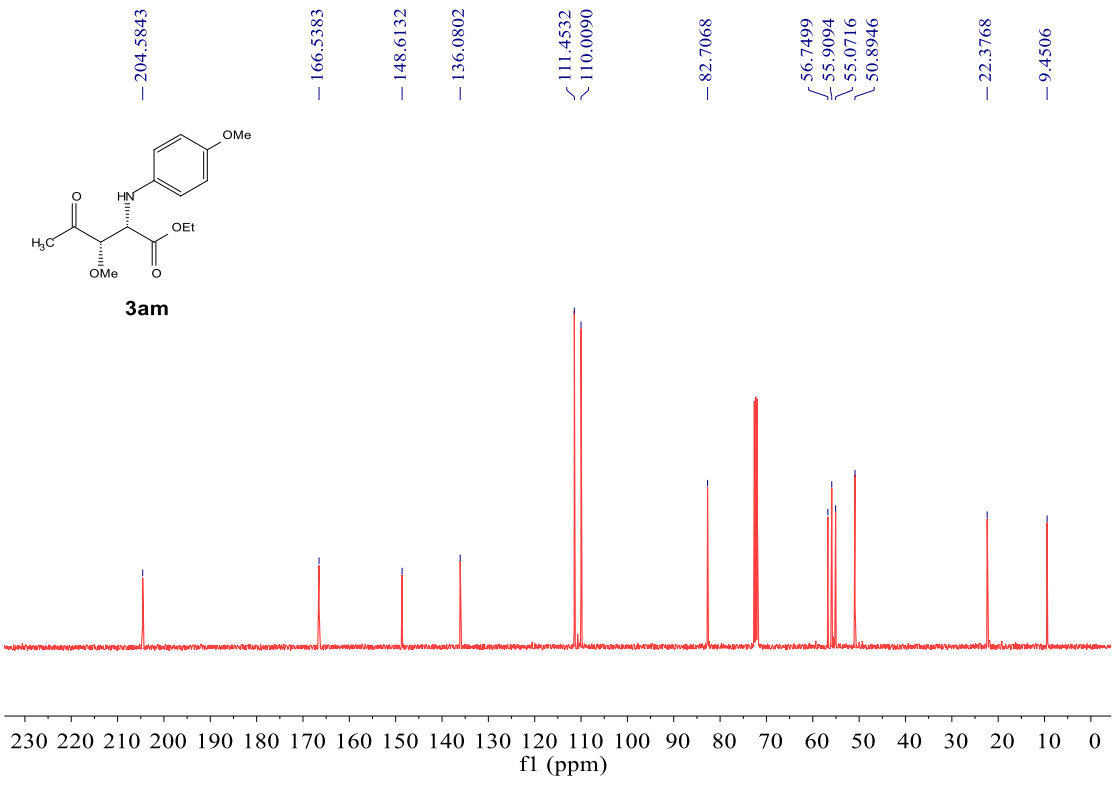


3al

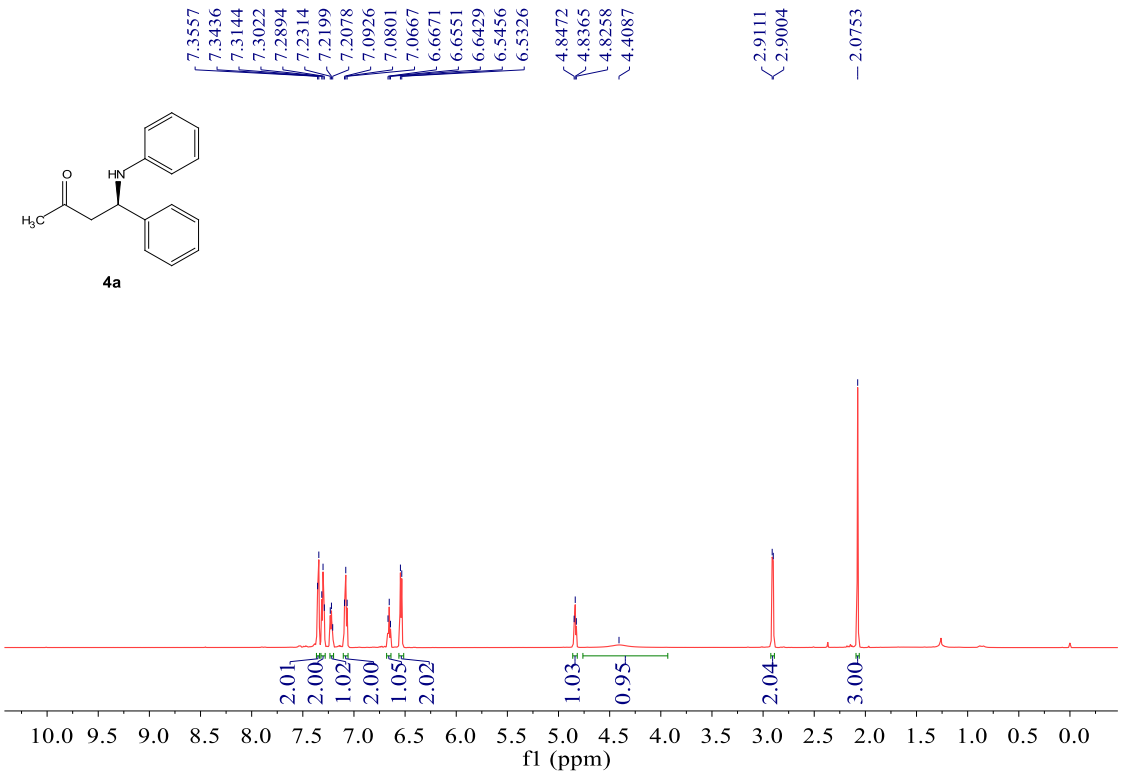
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3am



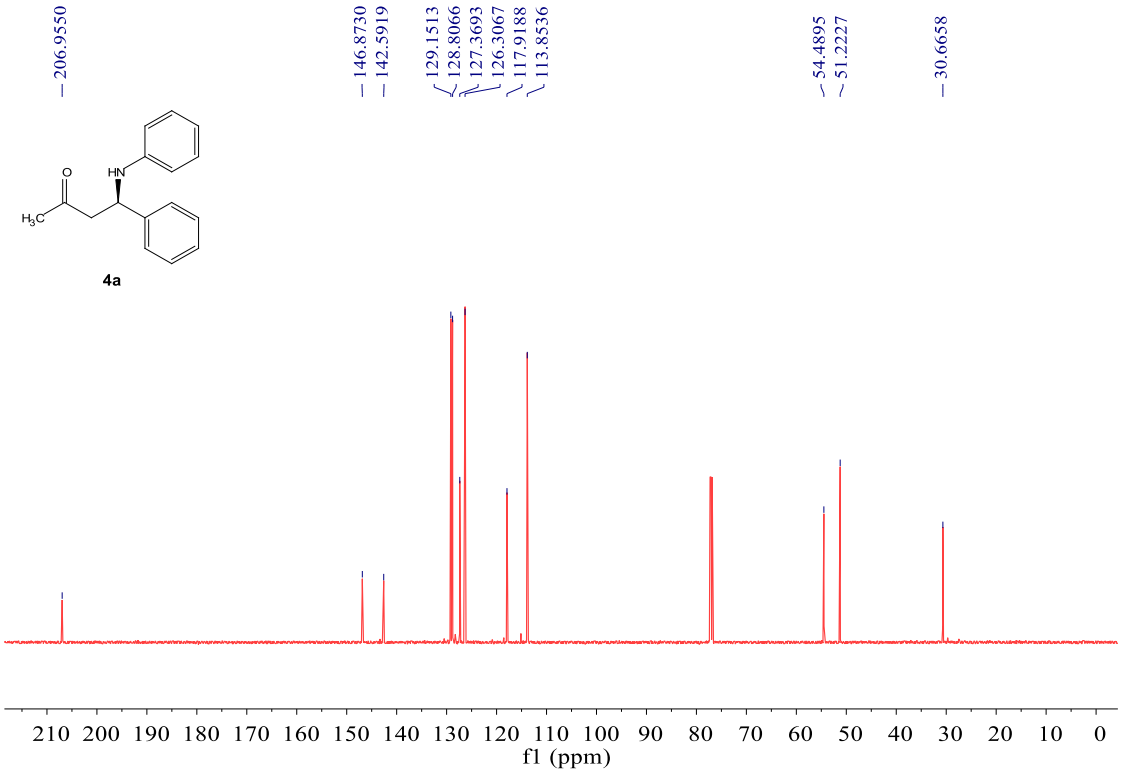
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 3am



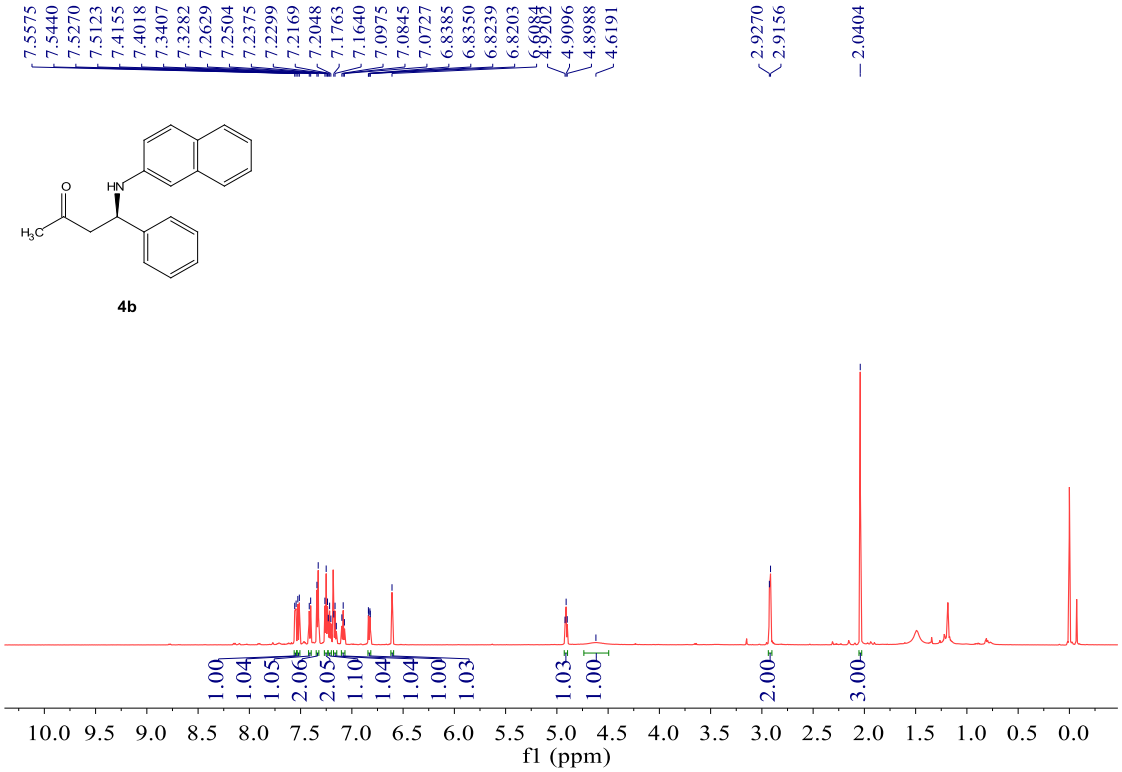
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 4a



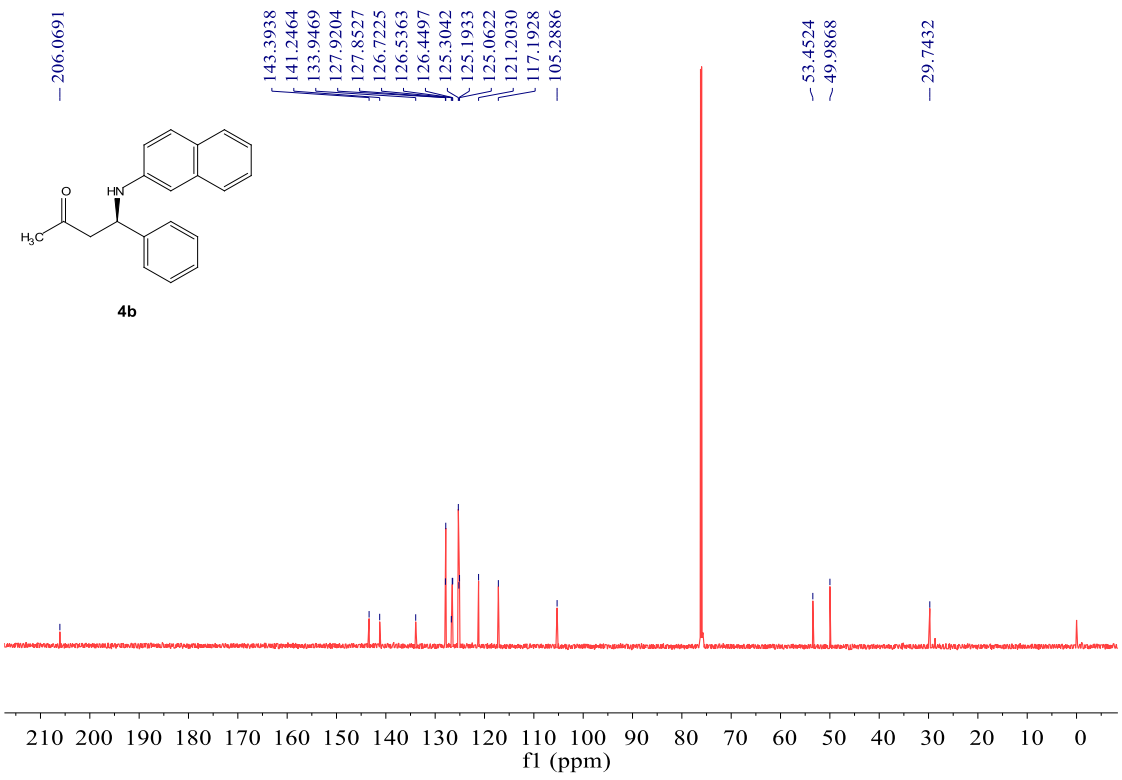
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 4a



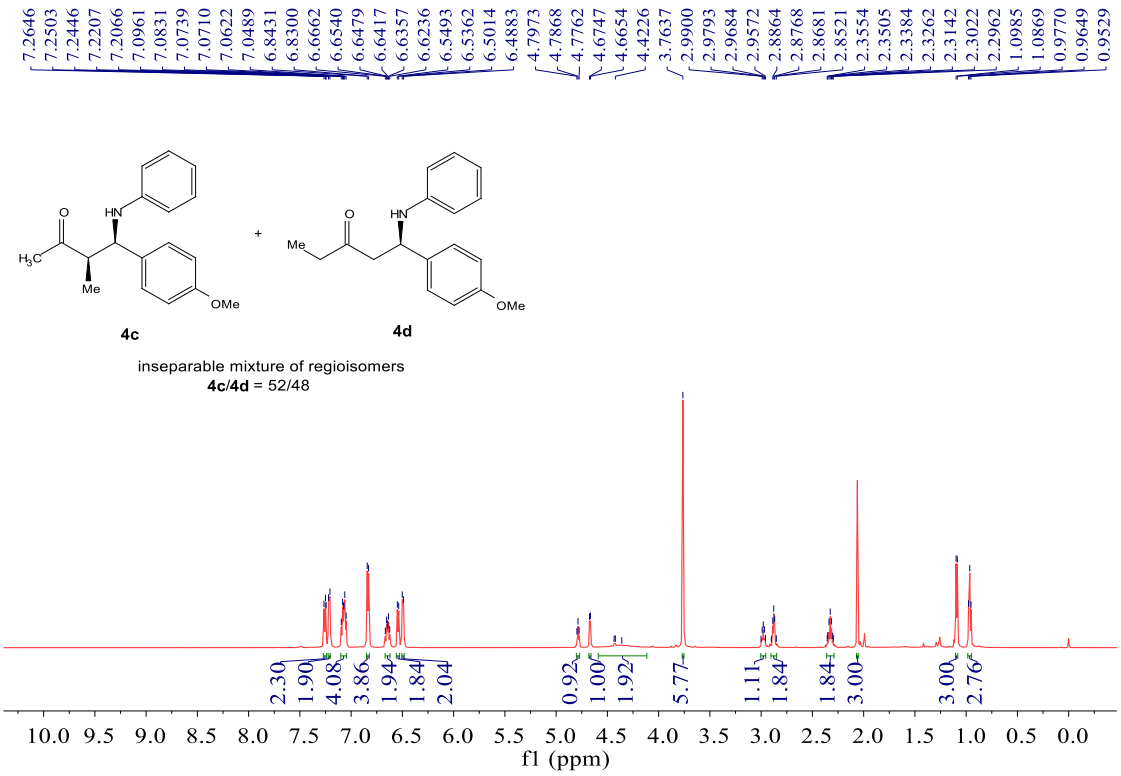
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 4b



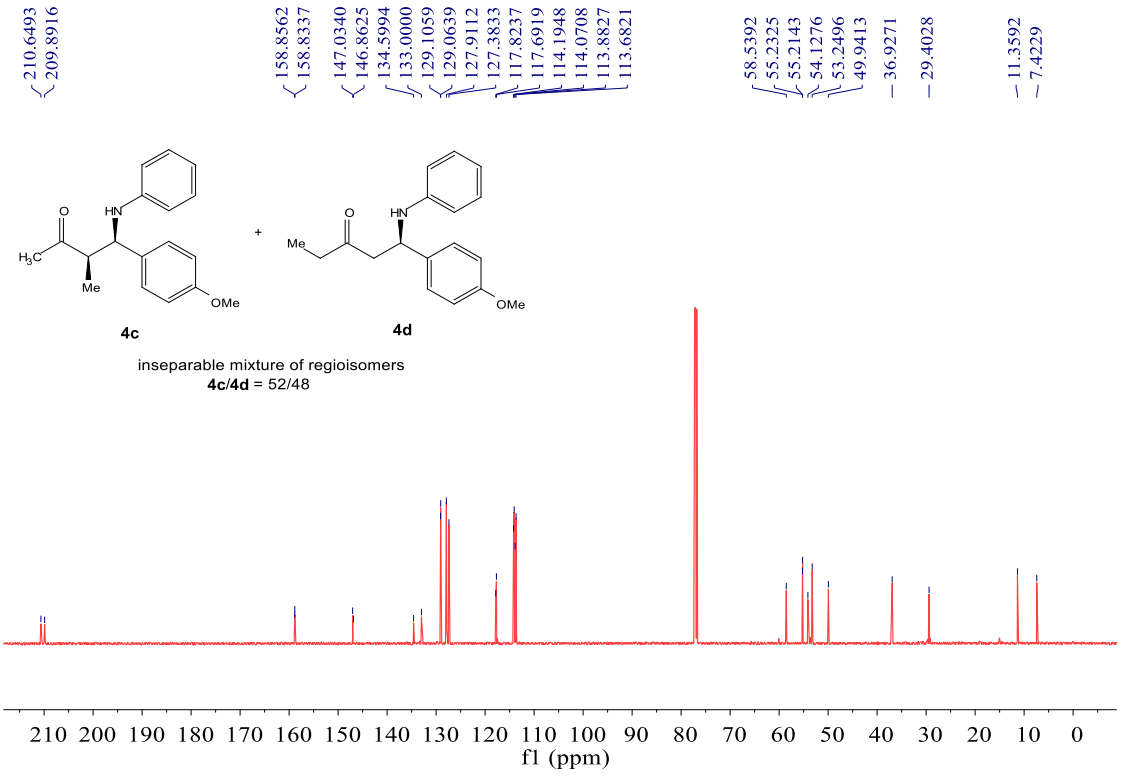
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 4b



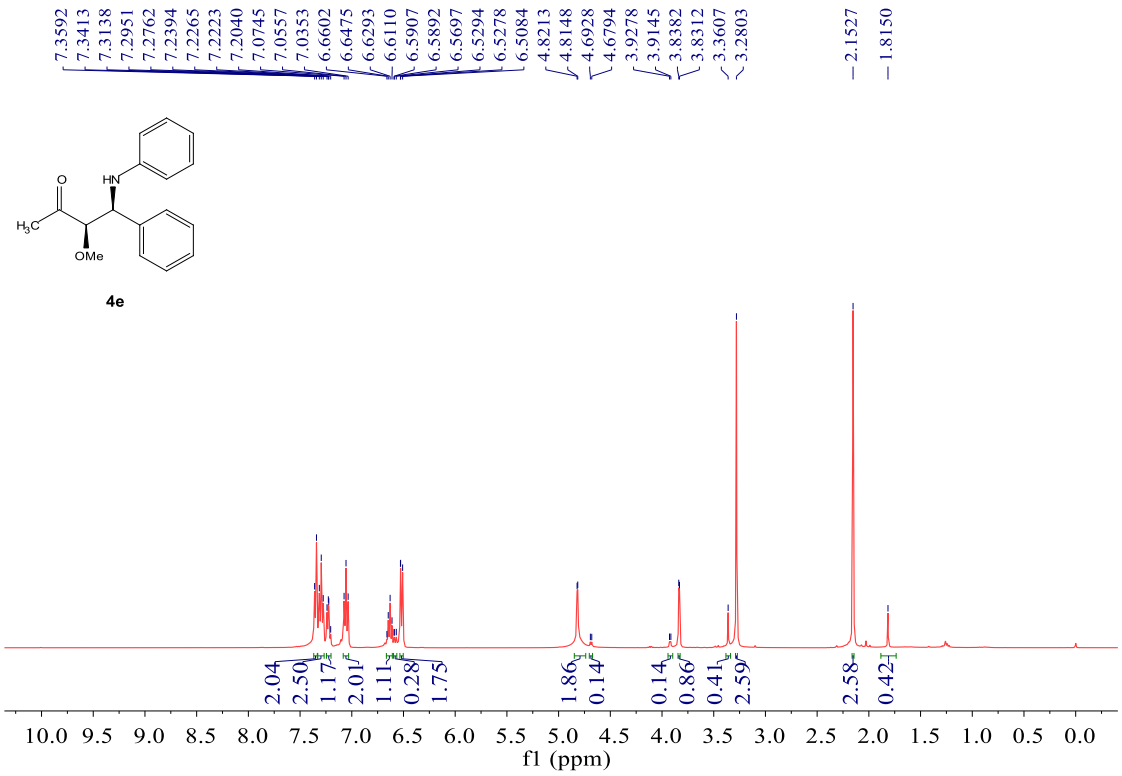
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 4c and 4d



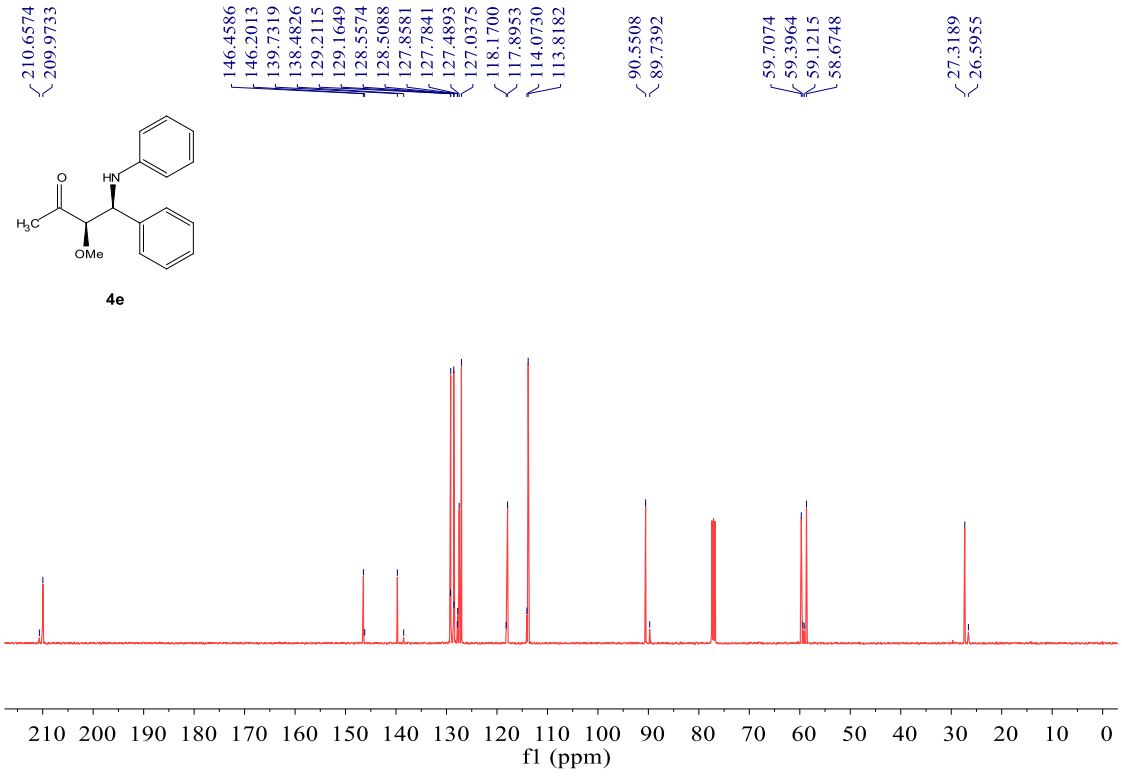
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 4c and 4d



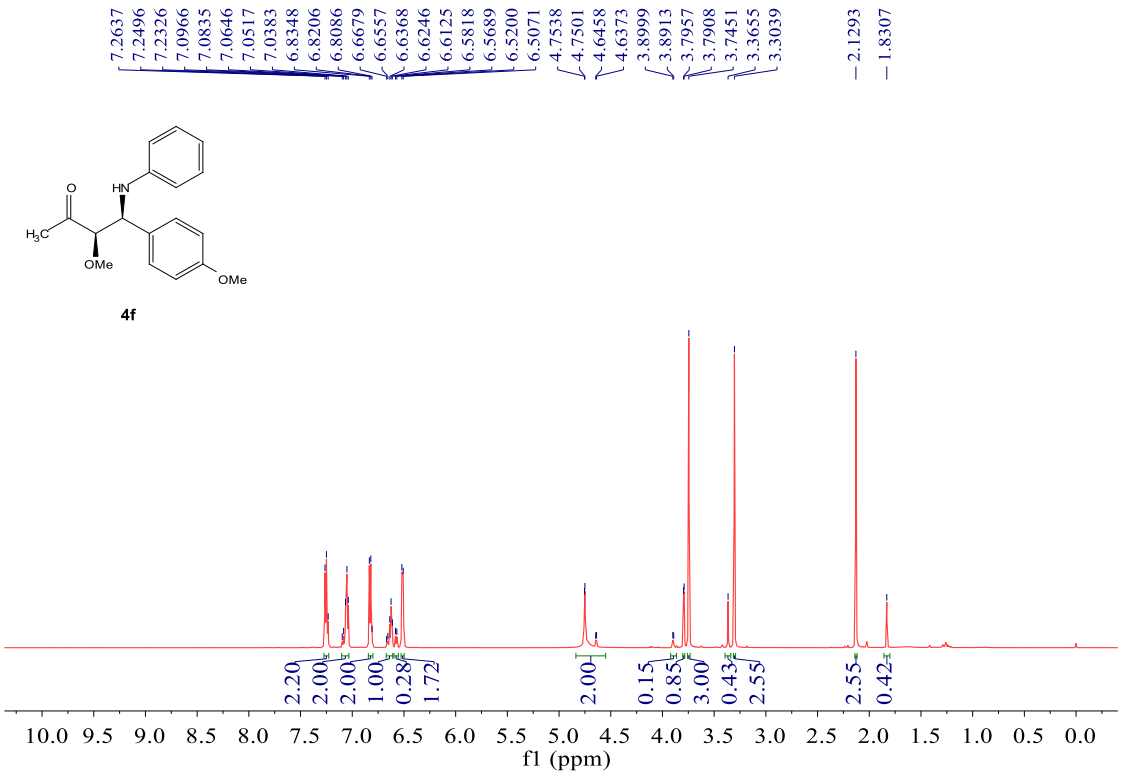
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4e



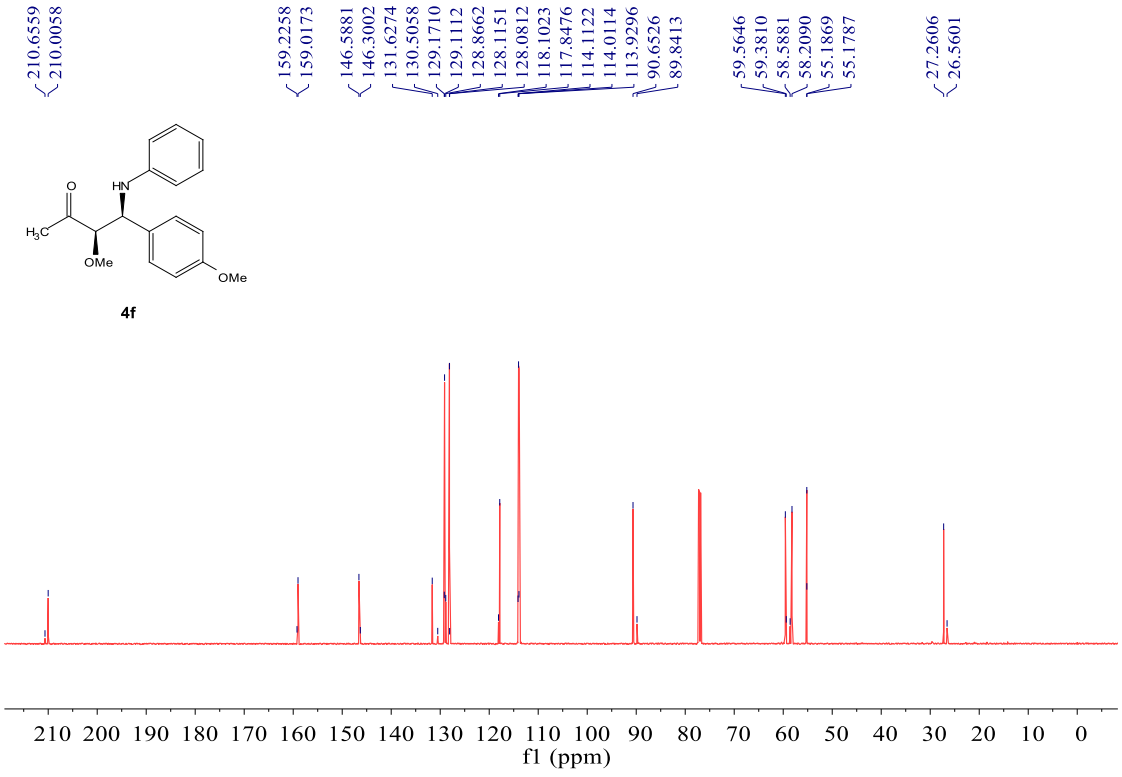
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 4e



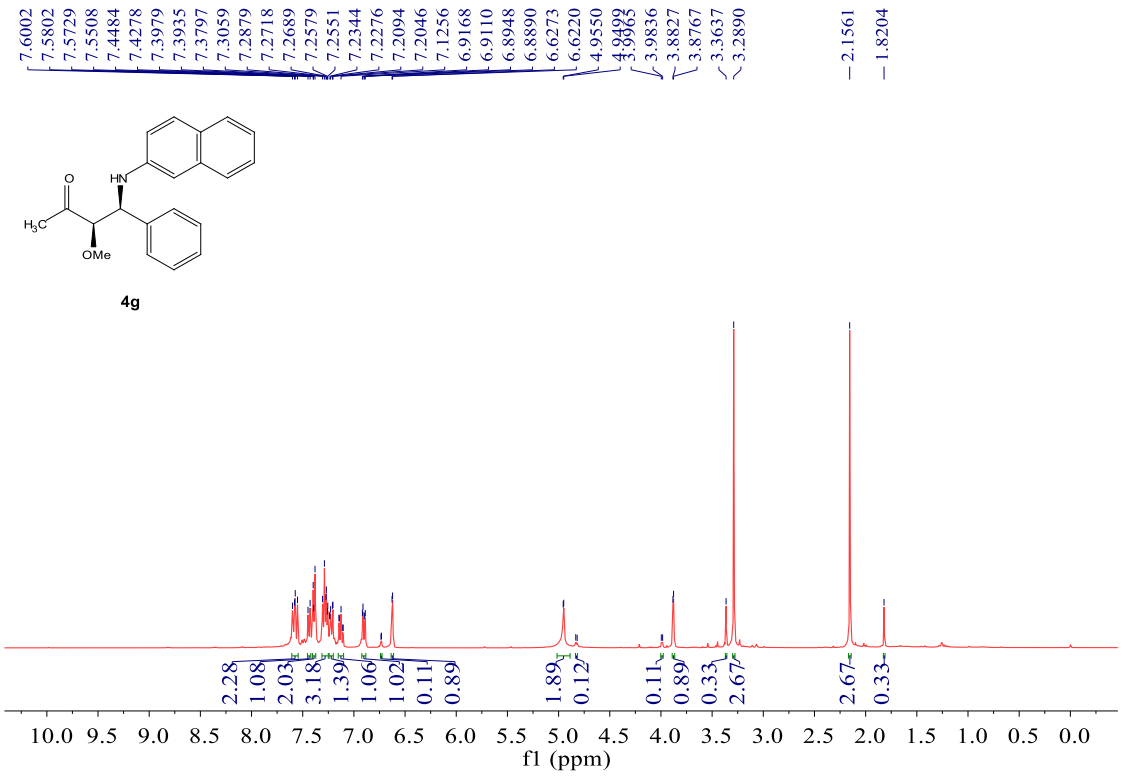
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 4f



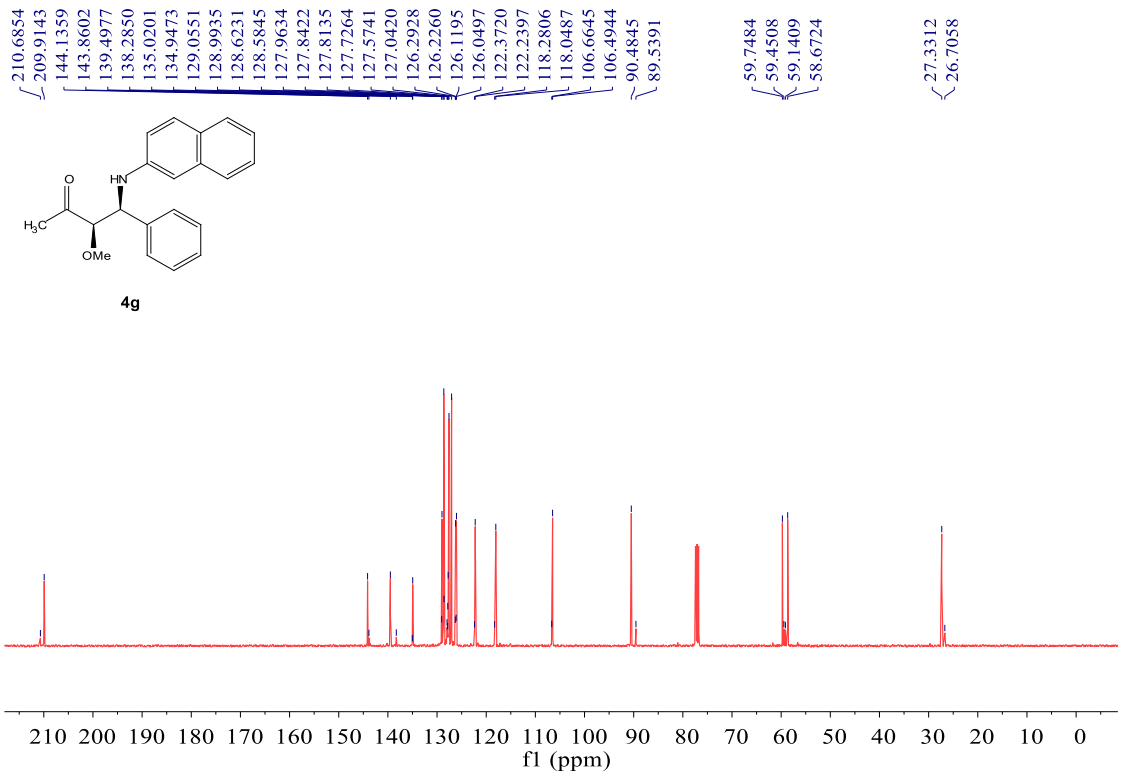
^{13}C NMR Spectrum (151 MHz, $CDCl_3$) of 4f



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4g

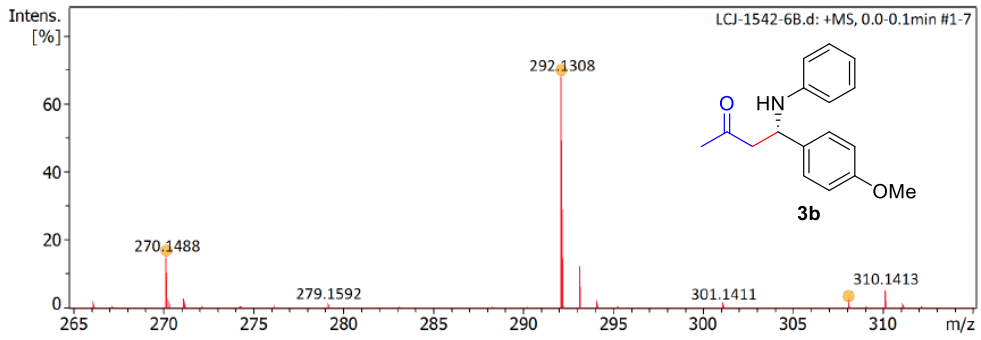


^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 4g



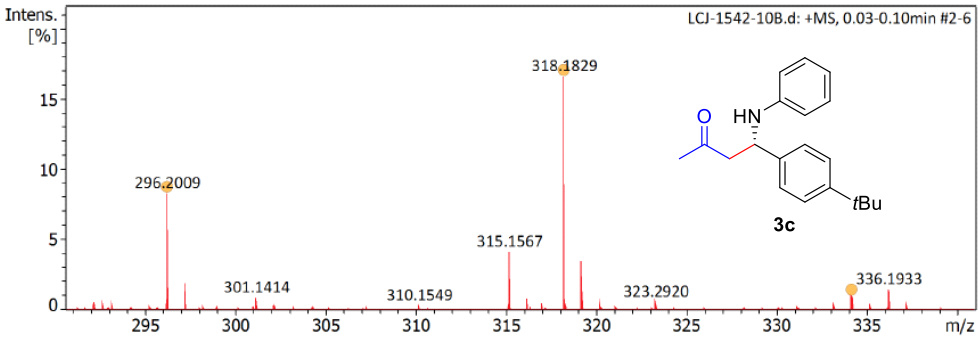
15. HRMS spectra

HRMS spectrum of 3b



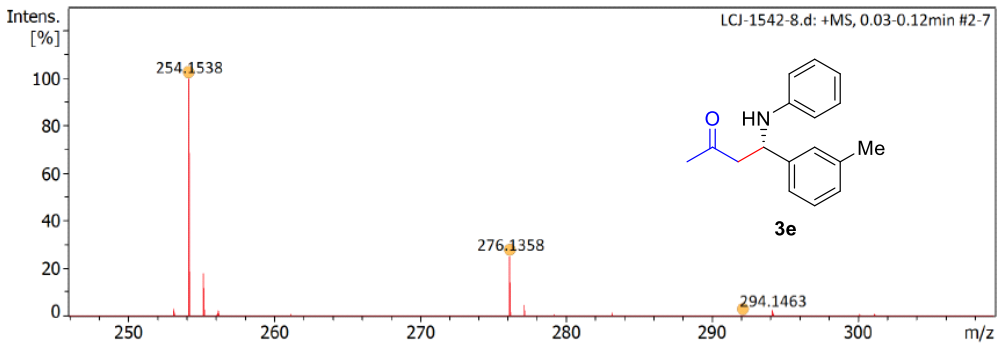
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1488	1	C17H20NO2	270.1489	M+H	0.0	0.5	100.00	9.0	ok
292.1308	1	C17H19NNaO2	292.1308	M+Na	-0.0	4.9	100.00	9.0	ok
308.1046	1	C17H19KNO2	308.1047	M+K	0.3	8.2	100.00	9.0	ok

HRMS spectrum of 3c



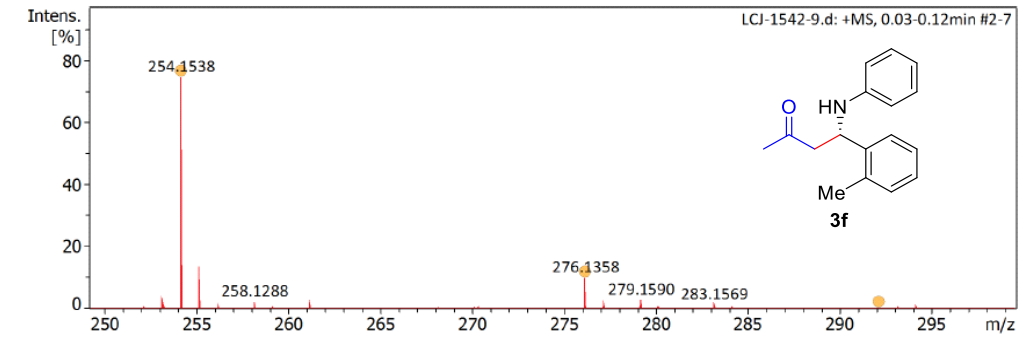
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
296.2009	1	C20H26NO	296.2009	M+H	-0.2	3.6	100.00	9.0	ok
318.1829	1	C20H25NNaO	318.1828	M+Na	-0.1	8.4	100.00	9.0	ok
334.1569	1	C20H25KNO	334.1568	M+K	-0.3	53.8	100.00	9.0	ok

HRMS spectrum of 3e



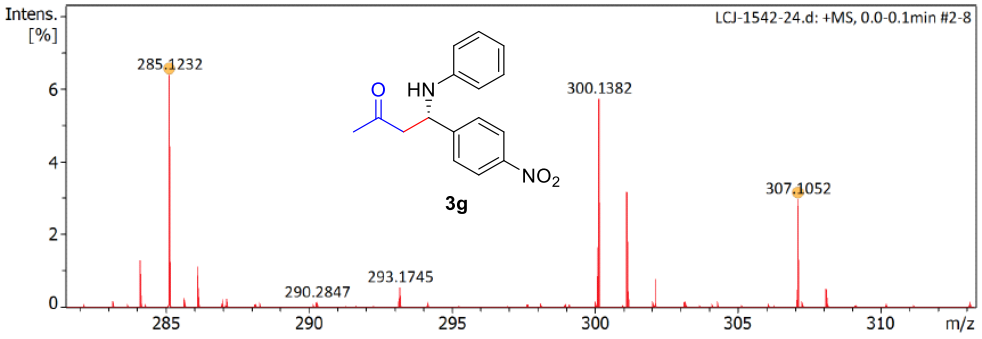
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
254.1538	1	C17H20NO	254.1539	M+H	0.6	5.7	100.00	9.0	ok
276.1358	1	C17H19NNaO	276.1359	M+Na	0.2	7.8	100.00	9.0	ok
292.1097	1	C17H19KNO	292.1098	M+K	0.4	n.a.	100.00	9.0	ok

HRMS spectrum of 3f



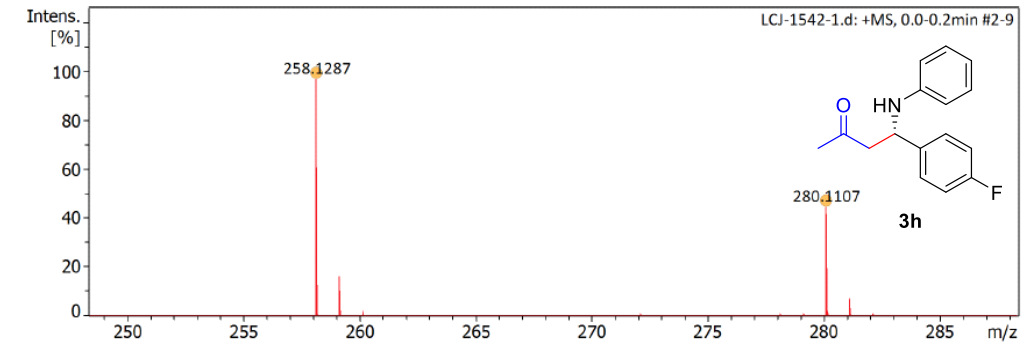
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
254.1538	1	C17H20NO	254.1539	M+H	0.6	5.7	100.00	9.0	ok
276.1358	1	C17H19NNaO	276.1359	M+Na	0.2	7.0	100.00	9.0	ok
292.1100	1	C17H19KNO	292.1098	M+K	-0.8	n.a.	100.00	9.0	ok

HRMS spectrum of 3g



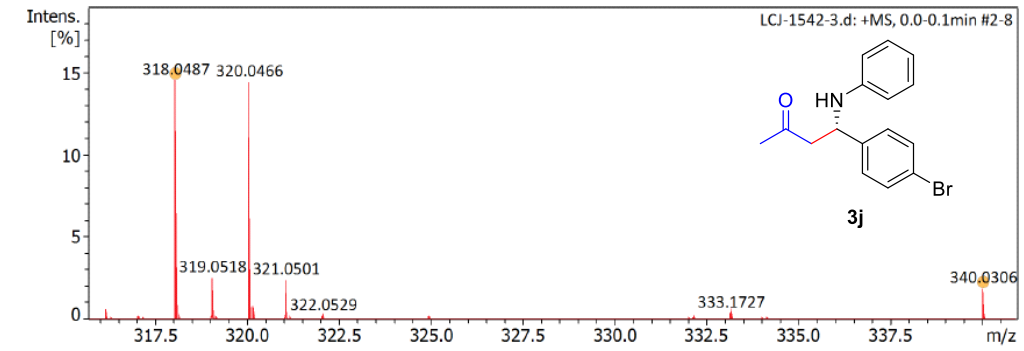
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
285.1232	1	C16H17N2O3	285.1234	M+H	0.7	9.8	100.00	10.0	ok
307.1052	1	C16H16N2NaO3	307.1053	M+Na	0.2	12.9	100.00	10.0	ok

HRMS spectrum of 3h



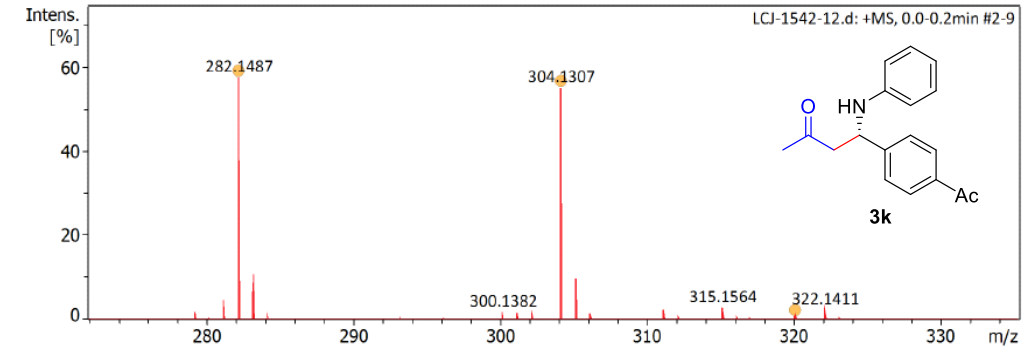
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
258.1287	1	C16H17FNO	258.1289	M+H	0.6	6.6	100.00	9.0	ok
280.1107	1	C16H16FNNaO	280.1108	M+Na	0.4	8.2	100.00	9.0	ok

HRMS spectrum of 3j



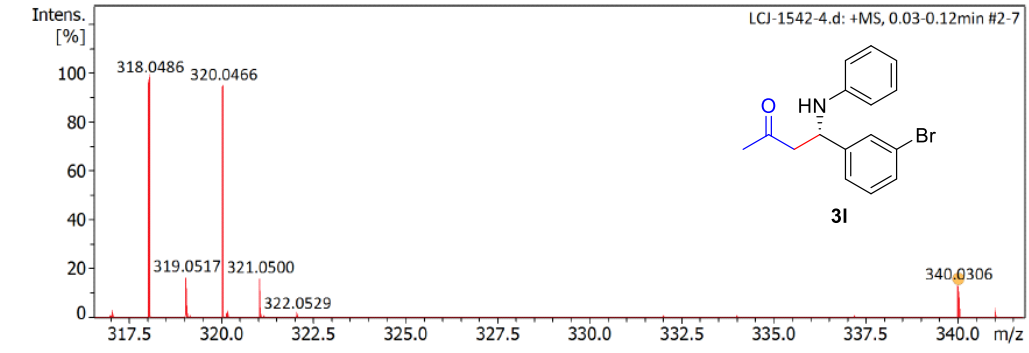
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
318.0487	1	C16H17BrNO	318.0488	M+H	0.5	5.4	100.00	11.0	ok
340.0306	1	C16H16BrNNaO	340.0307	M+Na	0.3	11.7	100.00	11.0	ok

HRMS spectrum of 3k



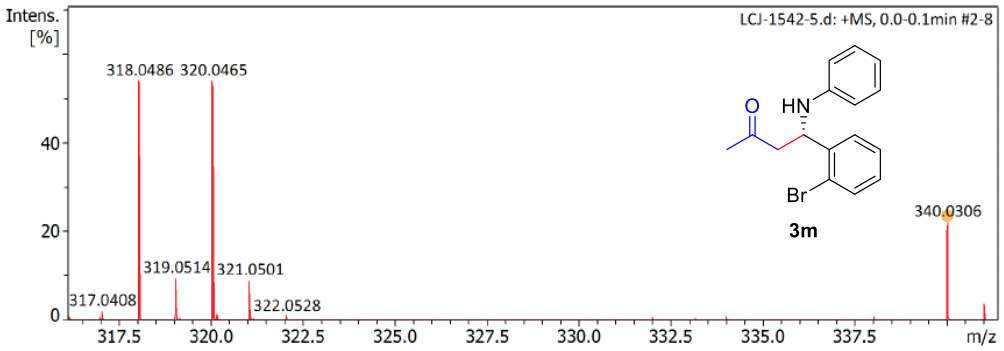
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
282.1487	1	C18H20NO2	282.1489	M+H	0.4	8.7	100.00	10.0	ok
304.1307	1	C18H19NNaO2	304.1308	M+Na	0.3	13.6	100.00	10.0	ok
320.1047	1	C18H19KNO2	320.1047	M+K	0.0	48.5	100.00	10.0	ok

HRMS spectrum of 3l



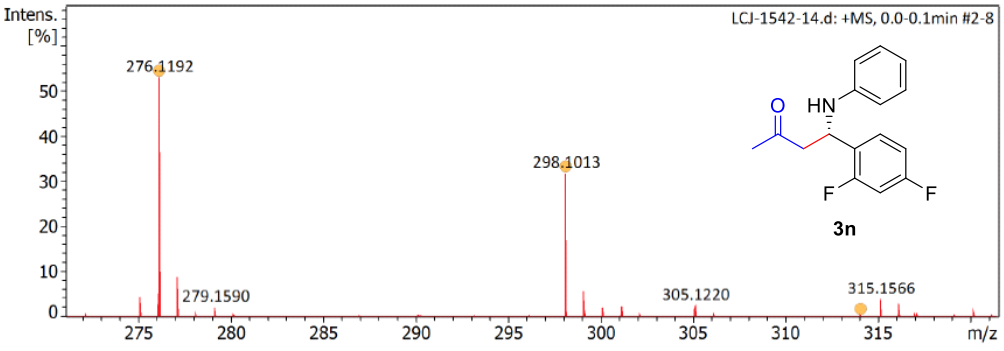
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
318.0486	1	C16H17BrNO	318.0488	M+H	0.6	12.1	100.00	11.0	ok
340.0306	1	C16H16BrNNaO	340.0307	M+Na	0.3	22.7	100.00	11.0	ok

HRMS spectrum of 3m



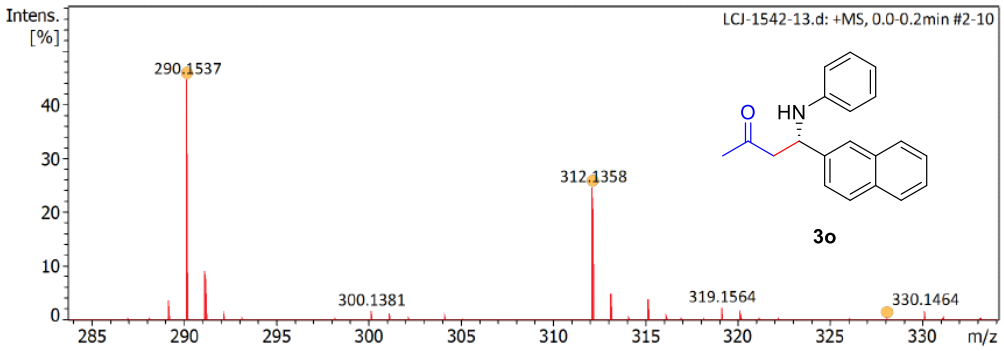
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
318.0486	1	C16H17BrNO	318.0488	M+H	0.6	6.7	100.00	11.0	ok
340.0306	1	C16H16BrNNaO	340.0307	M+Na	0.3	10.9	100.00	11.0	ok

HRMS spectrum of 3n



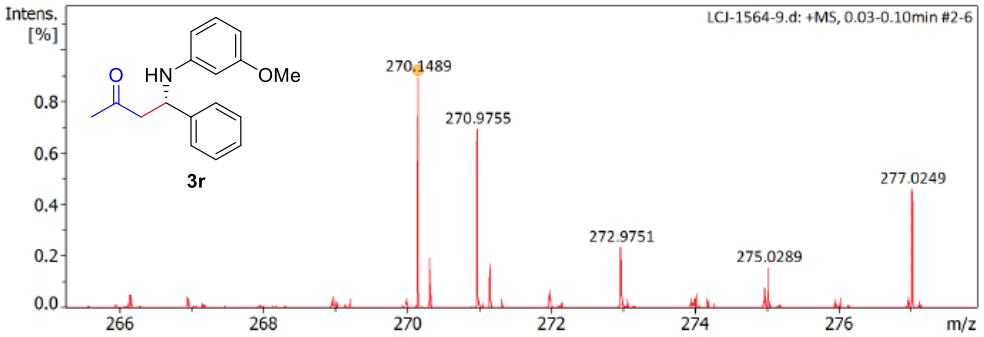
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
276.1192	1	C16H16F2NO	276.1194	M+H	0.9	6.1	100.00	9.0	ok
298.1013	1	C16H15F2NNaO	298.1014	M+Na	0.3	0.8	100.00	9.0	ok
314.0753	1	C16H15F2KNO	314.0753	M+K	0.0	n.a.	100.00	9.0	ok

HRMS spectrum of 3o



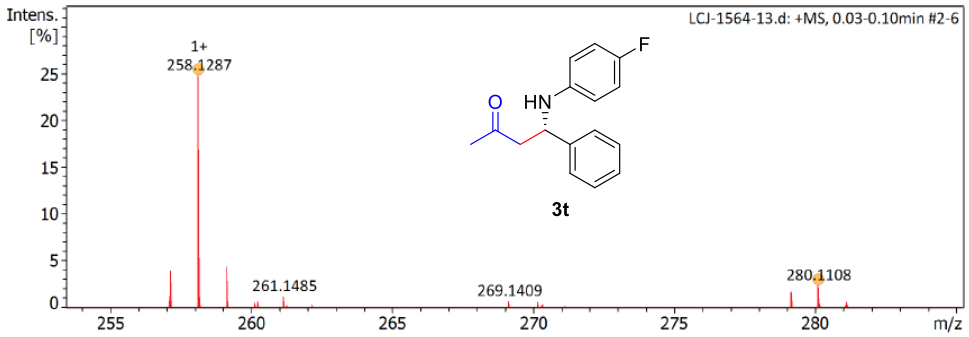
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
290.1537	1	C20H20NO	290.1539	M+H	0.7	11.3	100.00	12.0	ok
312.1358	1	C20H19NNaO	312.1359	M+Na	0.3	15.7	100.00	12.0	ok
328.1099	1	C20H19KNO	328.1098	M+K	-0.1	n.a.	100.00	12.0	ok

HRMS spectrum of 3r



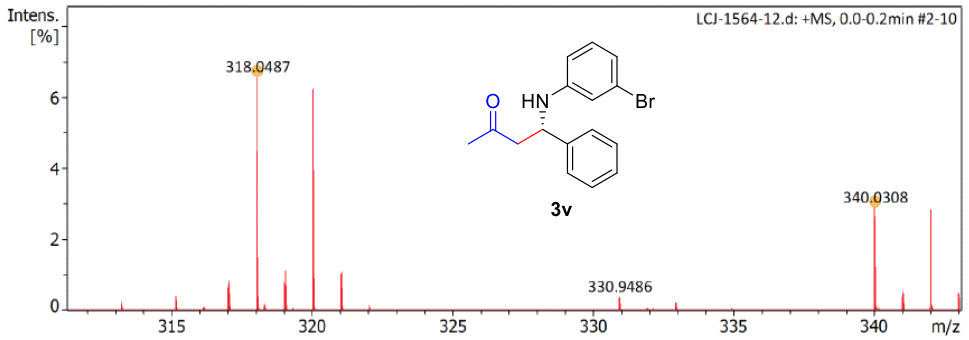
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
270.148871	1	C17H20NO2	100.00	270.148855	-0.0	-0.1	12.3	9.0	M+H

HRMS spectrum of 3t



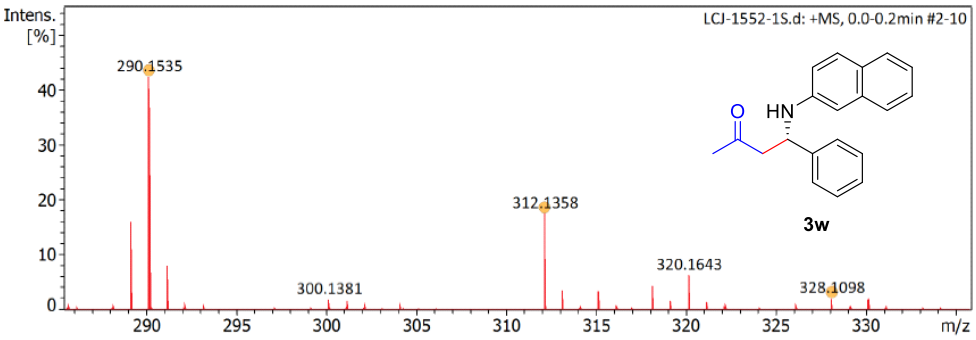
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
258.128734	1	C16H17FNO	100.00	258.128869	0.1	0.5	1.0	9.0	M+H
280.110826	1	C16H16FNNaO	100.00	280.110813	-0.0	-0.0	10.6	9.0	M+Na

HRMS spectrum of 3v



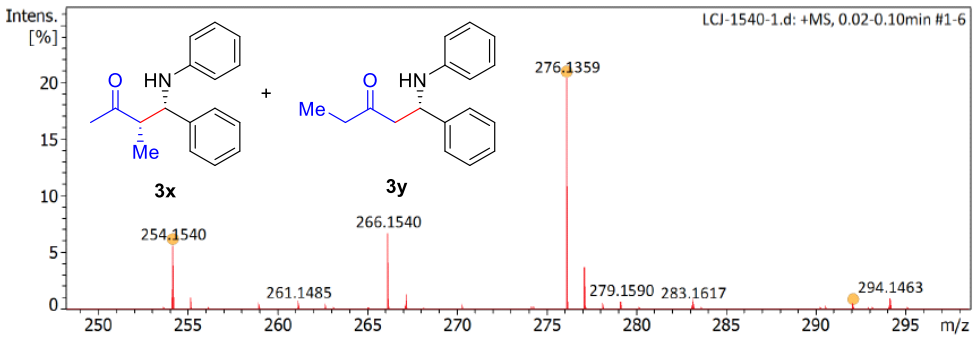
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
318.048660	1	C16H17BrNO	100.00	318.048803	0.1	0.4	17.3	11.0	M+H
340.030778	1	C16H16BrNNaO	100.00	340.030747	-0.0	-0.1	9.2	11.0	M+Na

HRMS spectrum of 3w



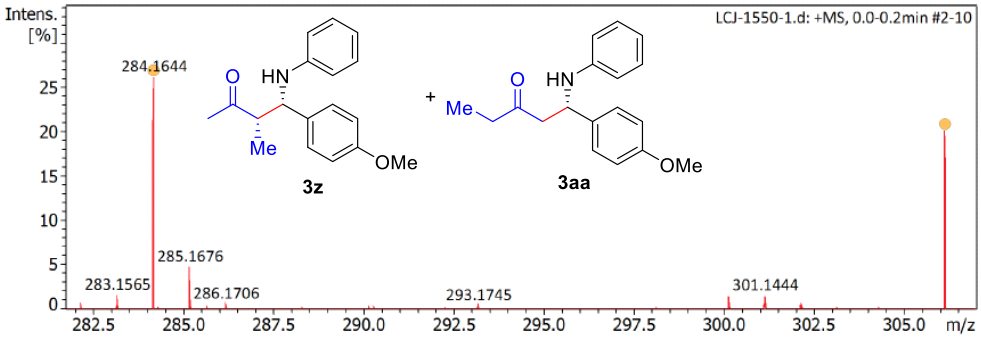
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
290.1535	1	C20H20NO	290.1539	M+H	1.6	18.4	100.00	12.0	ok
312.1358	1	C20H19NNaO	312.1359	M+Na	0.3	9.8	100.00	12.0	ok
328.1098	1	C20H19KNO	328.1098	M+K	0.2	13.8	100.00	12.0	ok

HRMS spectrum of 3x and 3y



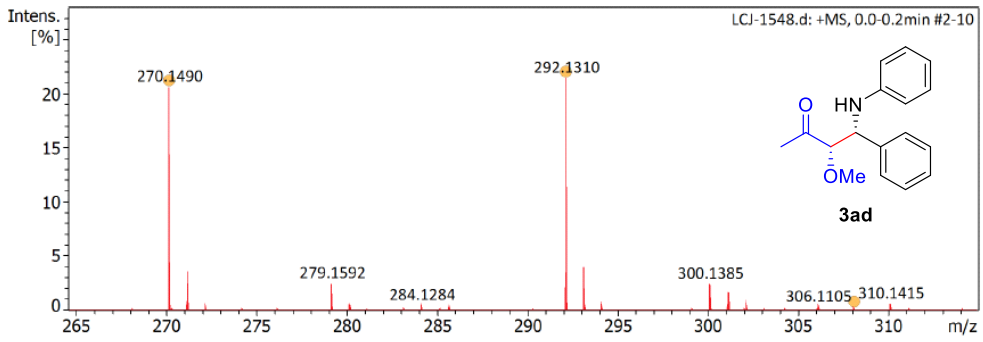
Meas. m/z	#	Ion Formula	Adduct	m/z	err [ppm]	mSigma	Score	rdb	N-Rule
254.1540	1	C17H20NO	M+H	254.1539	-0.1	1.8	100.00	9.0	ok
276.1359	1	C17H19NNaO	M+Na	276.1359	-0.1	6.2	100.00	9.0	ok
292.1098	1	C17H19KNO	M+K	292.1098	0.0	n.a.	100.00	9.0	ok

HRMS spectrum of 3z and 3aa



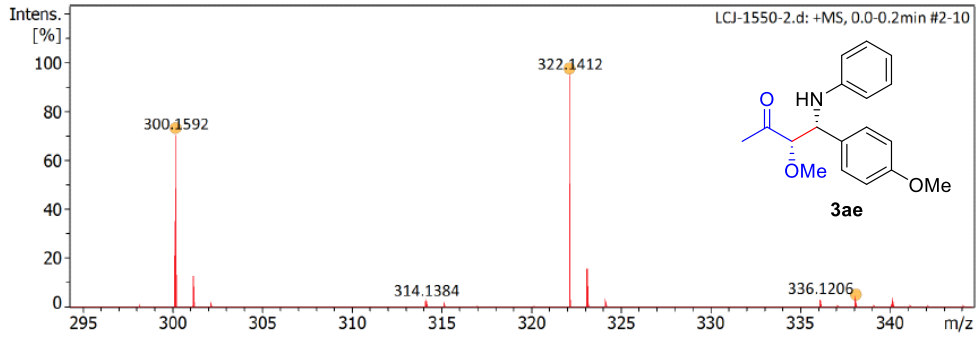
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
284.1644	1	C18H22NO2	284.1645	M+H	0.5	12.3	100.00	9.0	ok
306.1463	1	C18H21NNaO2	306.1464	M+Na	0.3	13.0	100.00	9.0	ok

HRMS spectrum of 3ad



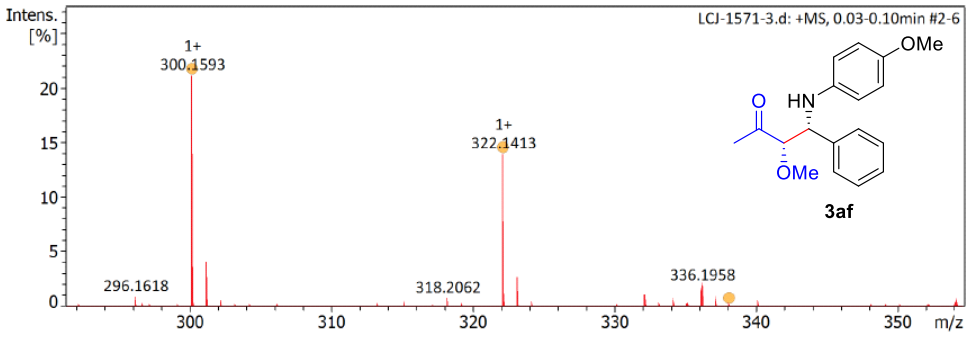
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1490	1	C17H20NO2	270.1489	M+H	-0.6	8.3	100.00	9.0	ok
292.1310	1	C17H19NNaO2	292.1308	M+Na	-0.7	2.8	100.00	9.0	ok
308.1049	1	C17H19KNO2	308.1047	M+K	-0.6	n.a.	100.00	9.0	ok

HRMS spectrum of 3ae



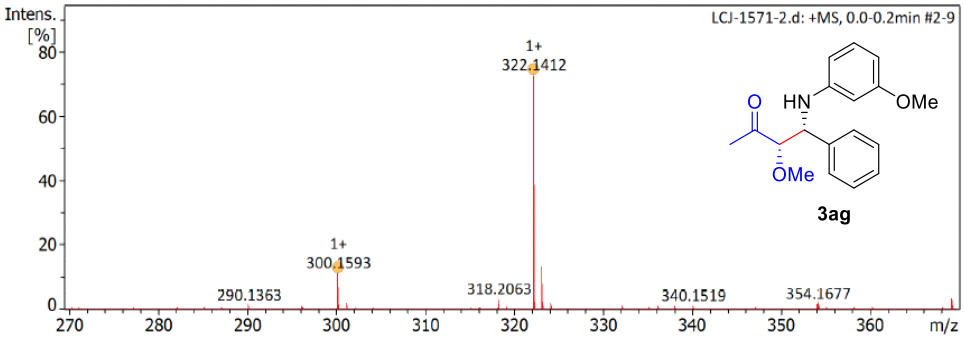
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
300.1592	1	C18H22NO3	300.1594	M+H	0.6	11.1	100.00	9.0	ok
322.1412	1	C18H21NNaO3	322.1414	M+Na	0.5	19.1	100.00	9.0	ok
338.1151	1	C18H21KNO3	338.1153	M+K	0.5	11.2	100.00	9.0	ok

HRMS spectrum of 3af



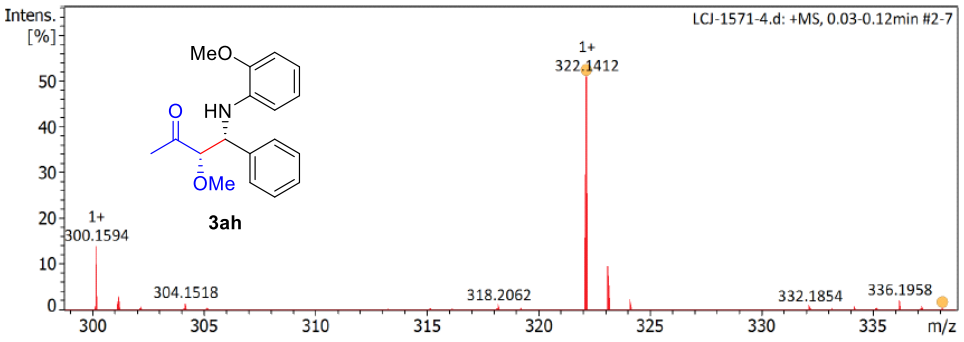
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
300.159336	1	C18H22NO3	100.00	300.159420	0.1	0.3	5.2	9.0	M+H
322.141306	1	C18H21NNaO3	100.00	322.141364	0.1	0.2	5.0	9.0	M+Na
338.115385	1	C18H21KNO3	100.00	338.115301	-0.1	-0.2	n.a.	9.0	M+K

HRMS spectrum of 3ag



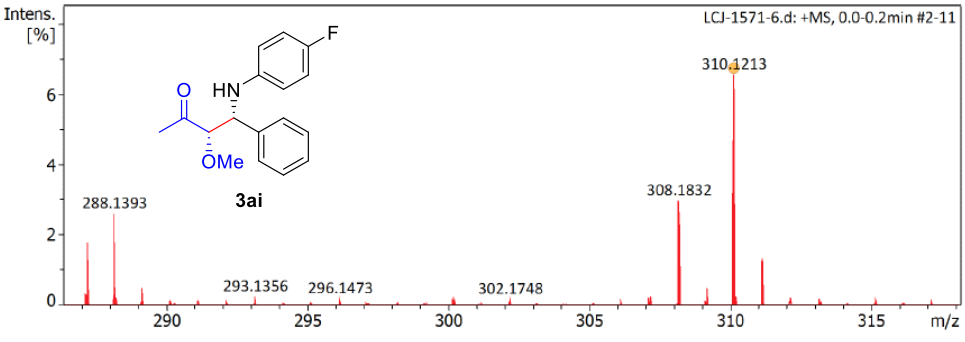
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
300.159350	1	C18H22NO3	100.00	300.159420	0.1	0.2	12.2	9.0	M+H
322.141154	1	C18H21NNaO3	100.00	322.141364	0.2	0.7	8.9	9.0	M+Na

HRMS spectrum of 3ah



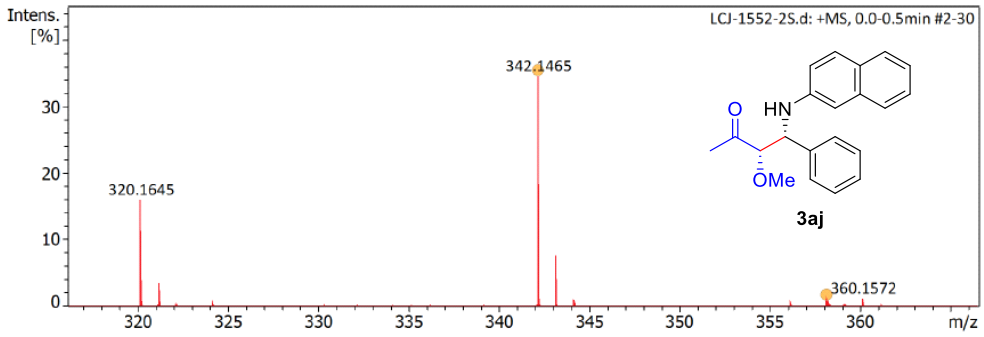
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
300.159375	1	C18H22NO3	100.00	300.159420	0.0	0.1	5.9	9.0	M+H
322.141175	1	C18H21NNaO3	100.00	322.141364	0.2	0.6	7.4	9.0	M+Na
338.115274	1	C18H21KNO3	100.00	338.115301	0.0	0.1	n.a.	9.0	M+K

HRMS spectrum of 3ai



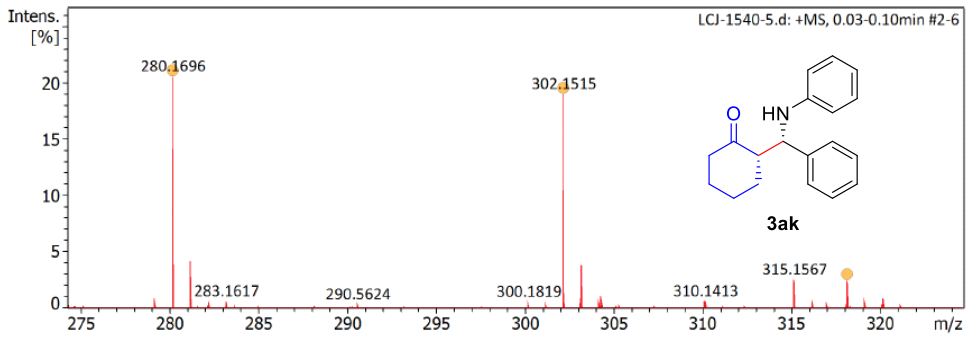
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
288.139349	1	C17H19FNO2	100.00	288.139433	0.1	0.3	13.4	9.0	M+H
310.121252	1	C17H18FNNaO2	100.00	310.121378	0.1	0.4	1.3	9.0	M+Na

HRMS spectrum of 3aj



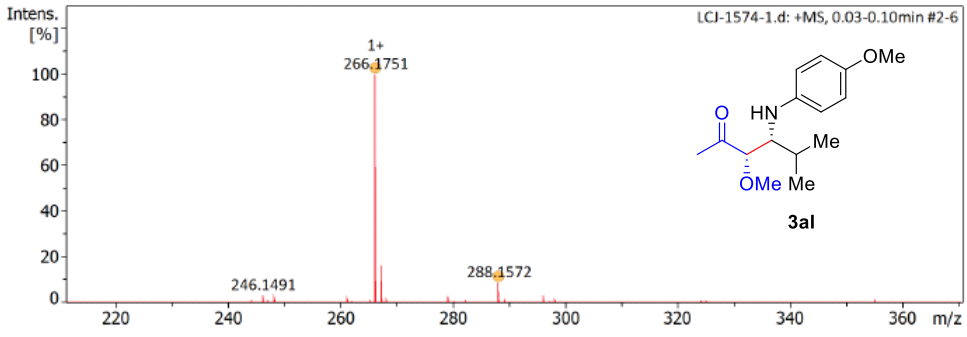
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
320.1645	1	C21H22NO2	320.1645	-0.1	11.6	1	100.00	12.0	even	ok
342.1465	1	C21H21NNaO2	342.1464	-0.2	8.5	1	100.00	12.0	even	ok
358.1207	1	C21H21KNO2	358.1204	-0.9	52.2	1	100.00	12.0	even	ok

HRMS spectrum of 3ak



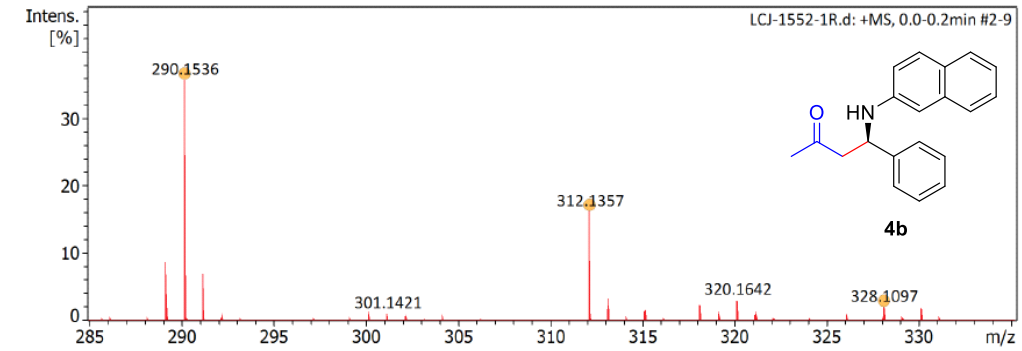
Meas. m/z	#	Ion Formula	Adduct	m/z	err [ppm]	mSigma	Score	rdb	N-Rule
280.1696	1	C19H22NO	M+H	280.1696	0.1	4.9	100.00	10.0	ok
302.1515	1	C19H21NNaO	M+Na	302.1515	-0.0	5.7	100.00	10.0	ok
318.1255	1	C19H21KNO	M+K	318.1255	0.0	12.9	100.00	10.0	ok

HRMS spectrum of 3al



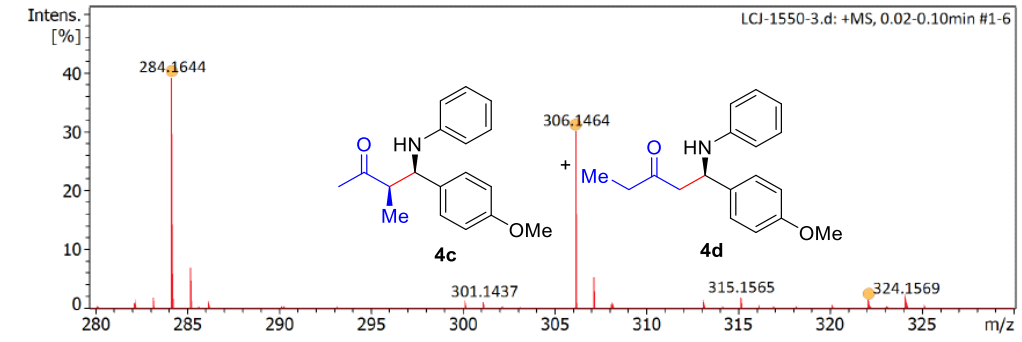
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	Adduct
266.175125	1	C15H24NO3	100.00	266.175070	-0.1	-0.2	4.7	5.0	M+H
288.157164	1	C15H23NNaO3	100.00	288.157014	-0.1	-0.5	6.6	5.0	M+Na

HRMS spectrum of 4b



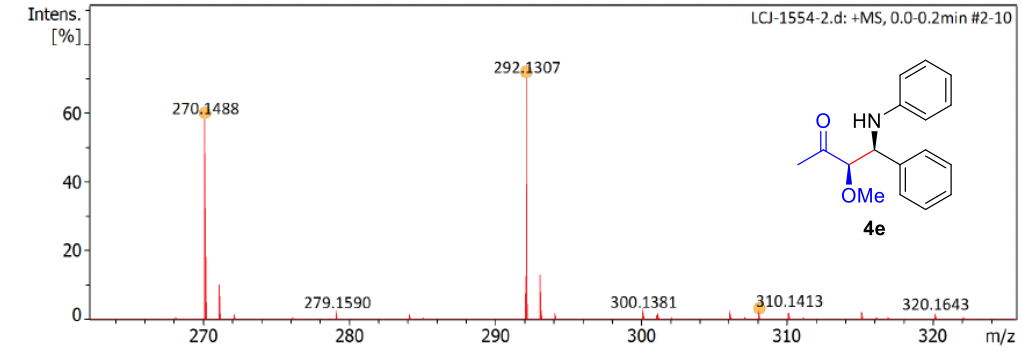
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
290.1536	1	C20H20NO	290.1539	M+H	1.3	17.1	100.00	12.0	ok
312.1357	1	C20H19NNaO	312.1359	M+Na	0.7	10.4	100.00	12.0	ok
328.1097	1	C20H19KNO	328.1098	M+K	0.3	14.1	100.00	12.0	ok

HRMS spectrum of 4c and 4d



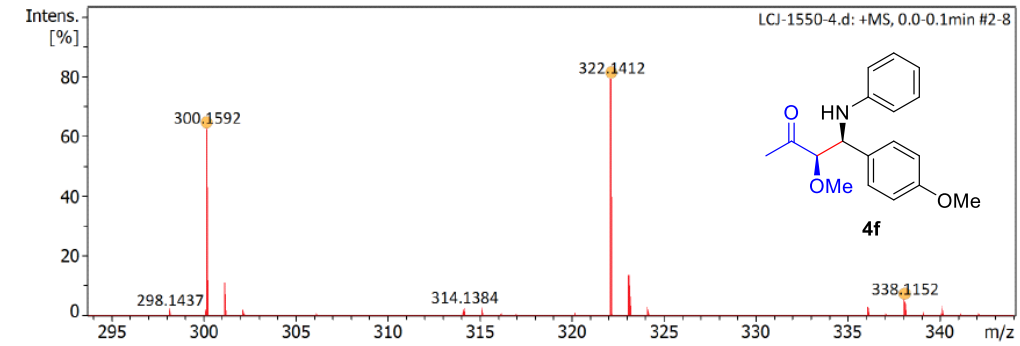
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
284.1644	1	C18H22NO2	284.1645	M+H	0.5	14.8	100.00	9.0	ok
306.1464	1	C18H21NNaO2	306.1464	M+Na	0.2	13.5	100.00	9.0	ok
322.1205	1	C18H21KNO2	322.1204	M+K	-0.2	19.2	100.00	9.0	ok

HRMS spectrum of 4e



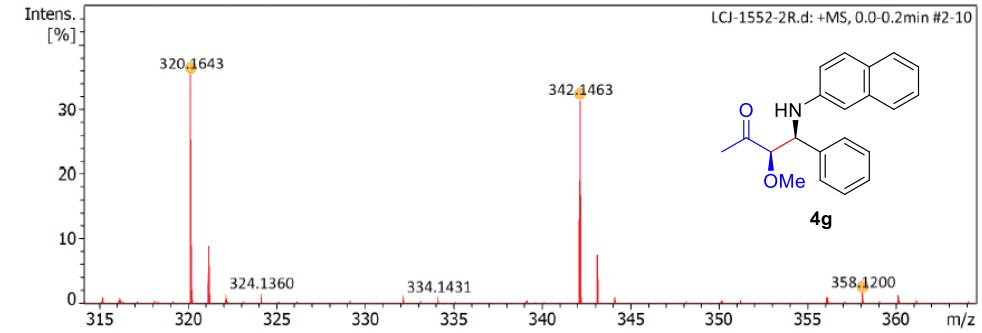
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
270.1488	1	C17H20NO2	270.1489	M+H	0.3	8.6	100.00	9.0	ok
292.1307	1	C17H19NNaO2	292.1308	M+Na	0.4	3.8	100.00	9.0	ok
308.1048	1	C17H19KNO2	308.1047	M+K	-0.3	11.8	100.00	9.0	ok

HRMS spectrum of 4f



Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
300.1592	1	C18H22NO3	300.1594	M+H	0.6	13.9	100.00	9.0	ok
322.1412	1	C18H21NNaO3	322.1414	M+Na	0.4	16.8	100.00	9.0	ok
338.1152	1	C18H21KNO3	338.1153	M+K	0.3	11.5	100.00	9.0	ok

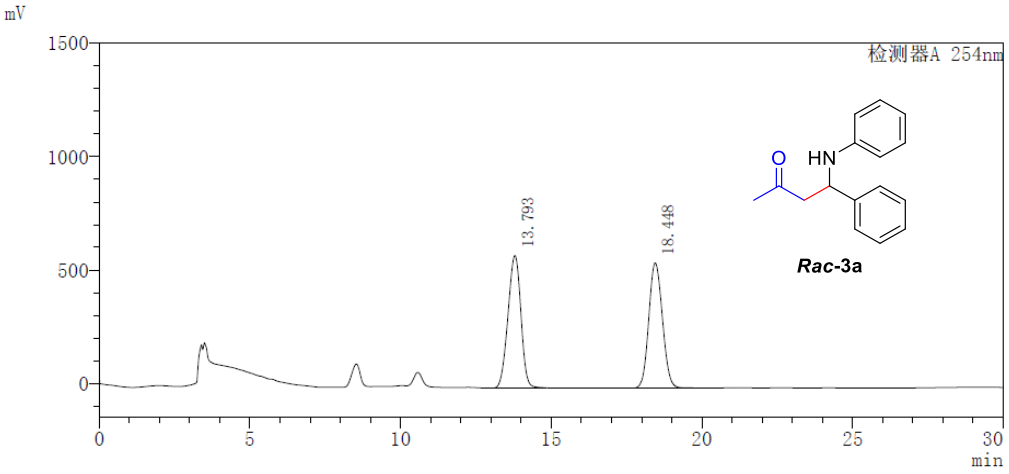
HRMS spectrum of 4g



Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	Score	rdb	N-Rule
320.1643	1	C21H22NO2	320.1645	M+H	0.5	9.4	100.00	12.0	ok
342.1463	1	C21H21NNaO2	342.1464	M+Na	0.6	2.1	100.00	12.0	ok
358.1200	1	C21H21KNO2	358.1204	M+K	1.1	n.a.	100.00	12.0	ok

16. Chiral HPLC spectra

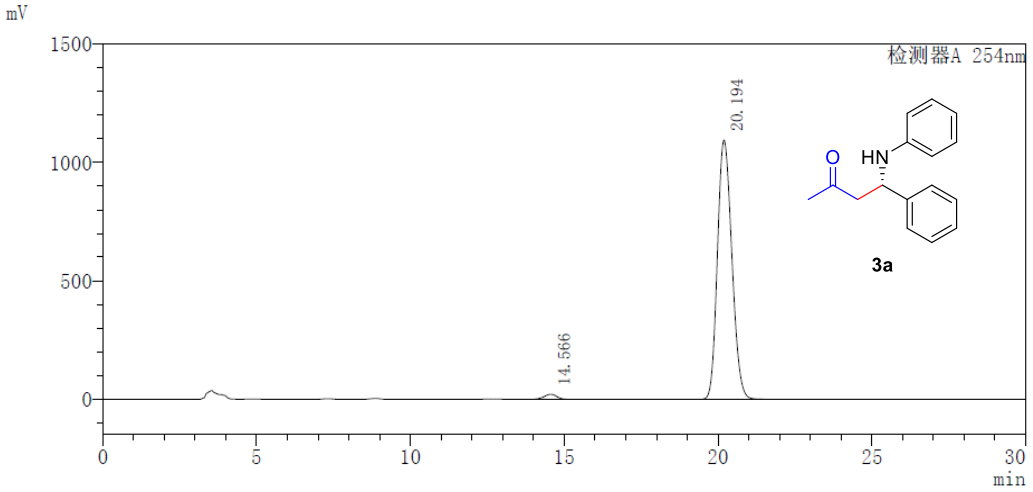
HPLC spectrum of *Rac*-3a



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.793	17298352	582071	49.940
2	18.448	17339828	550914	50.060
总计		34638180	1132986	

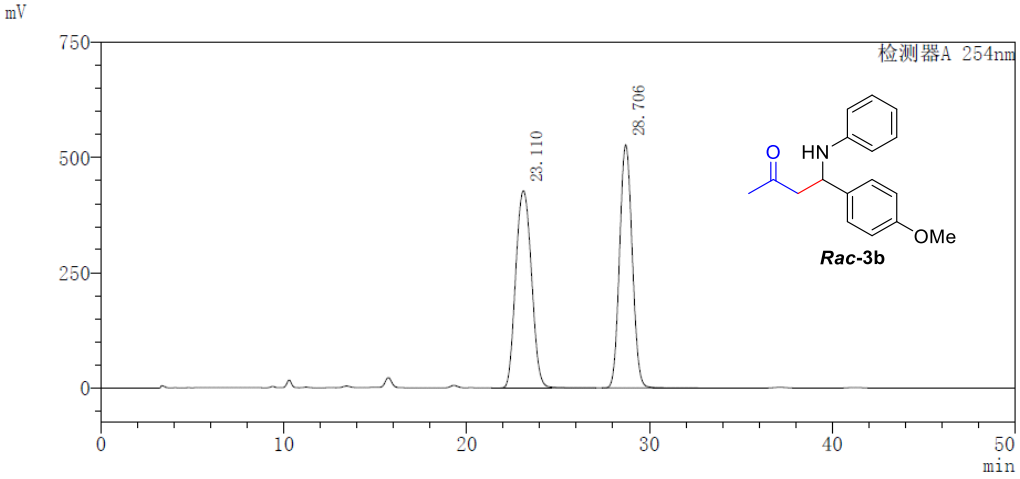
HPLC spectrum of 3a



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.566	580753	21116	1.594
2	20.194	35848146	1094676	98.406
总计		36428899	1115793	

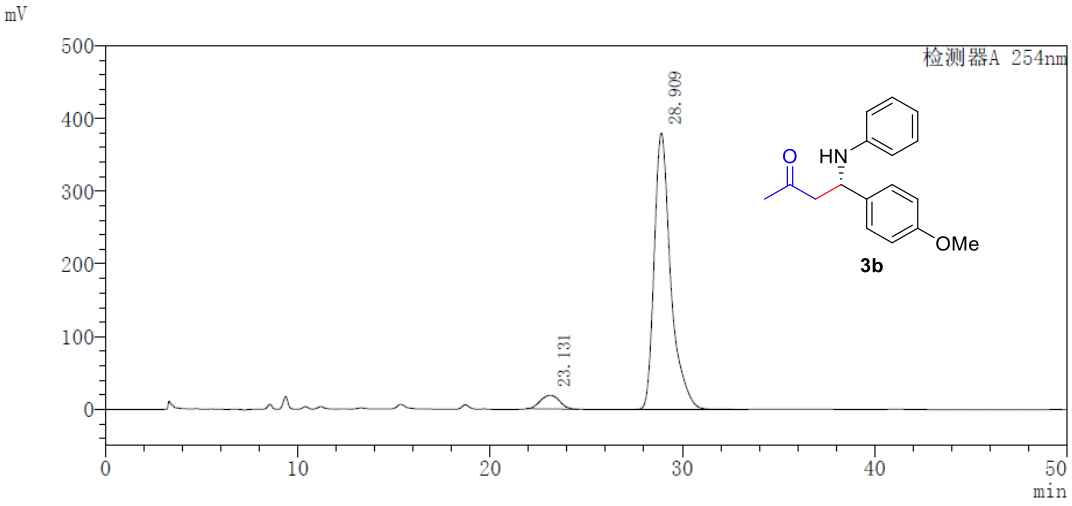
HPLC spectrum of *Rac*-3b



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	23.110	25711822	427918	50.301
2	28.706	25403755	527540	49.699
总计		51115577	955458	

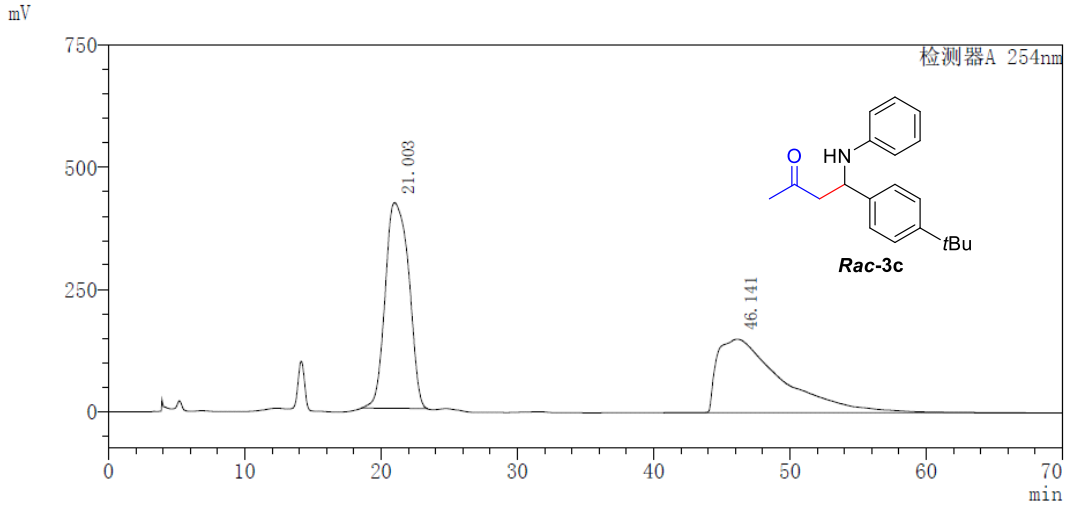
HPLC spectrum of 3b



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	23.131	1298524	18706	5.399
2	28.909	22750813	380107	94.601
总计		24049337	398812	

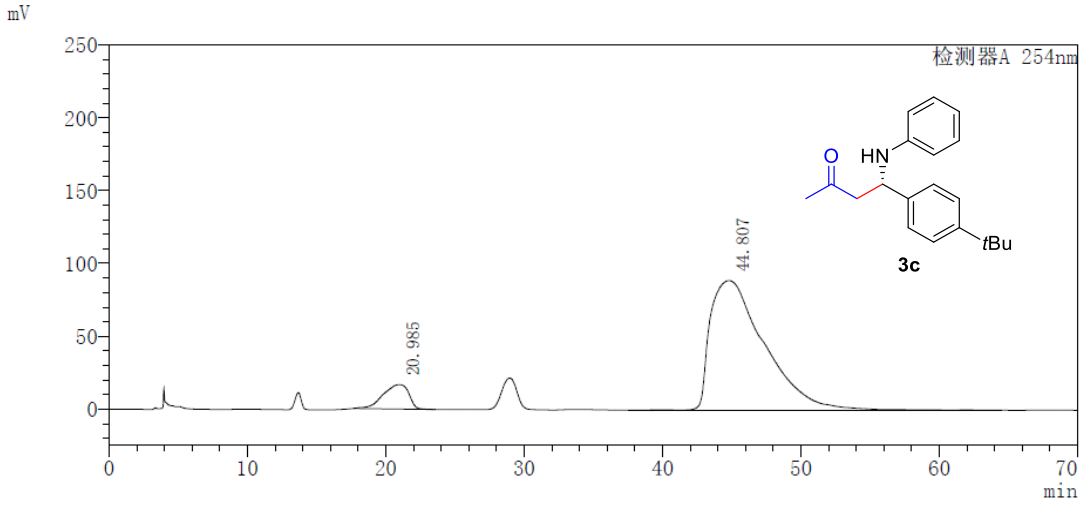
HPLC spectrum of *Rac*-3c



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	21.003	50756399	420770	50.506
2	46.141	49738554	150384	49.494
总计		100494952	571154	

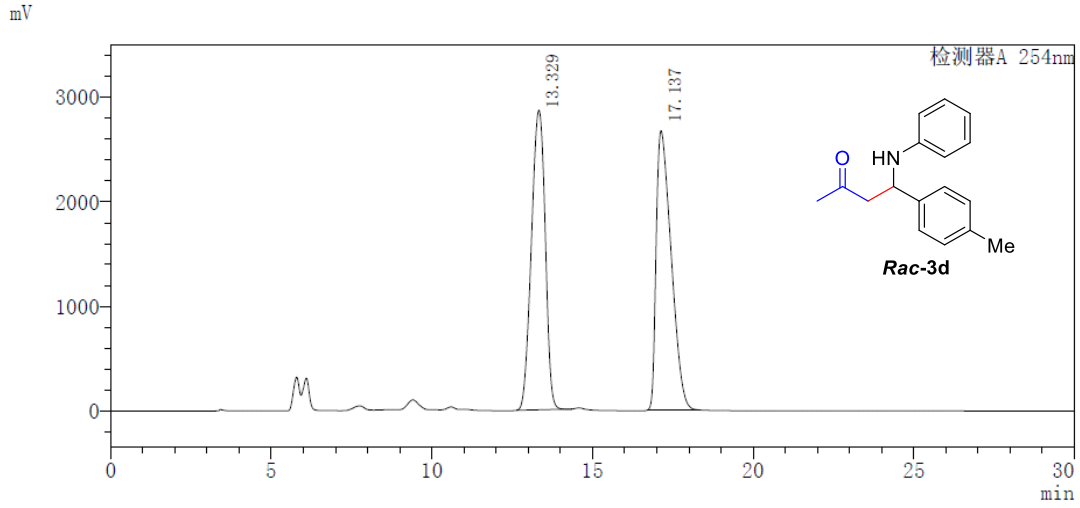
HPLC spectrum of 3c



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.985	2162867	16784	8.223
2	44.807	24140643	88744	91.777
总计		26303509	105528	

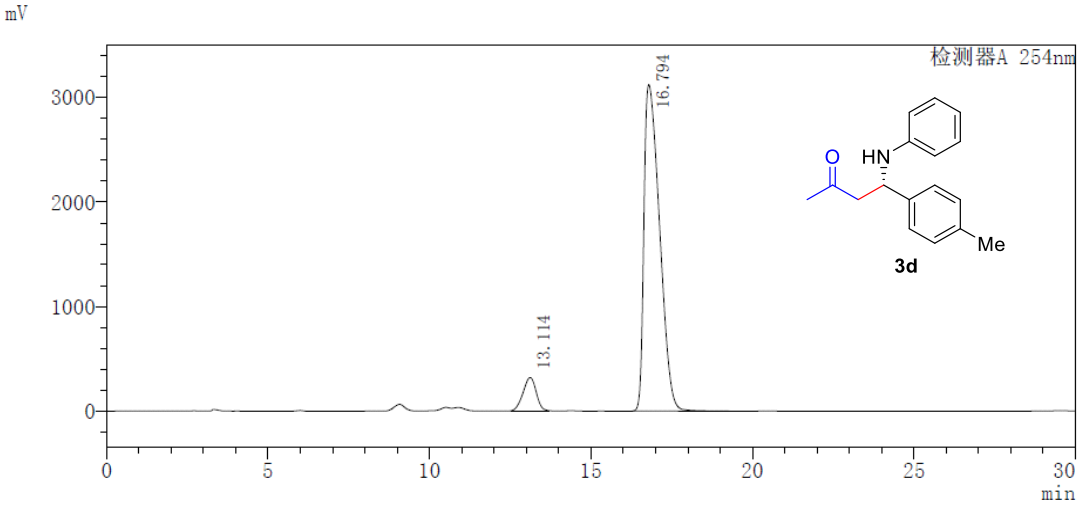
HPLC spectrum of *Rac*-3d



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.329	85705965	2863611	49.690
2	17.137	86776305	2672221	50.310
总计		172482270	5535832	

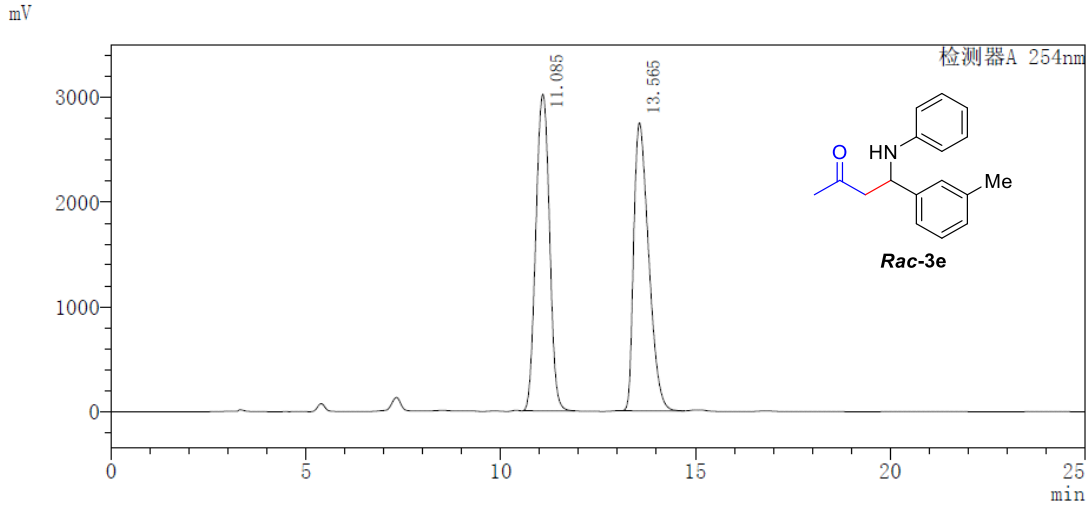
HPLC spectrum of 3d



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.114	8868157	317493	7.768
2	16.794	105293975	3122794	92.232
总计		114162132	3440287	

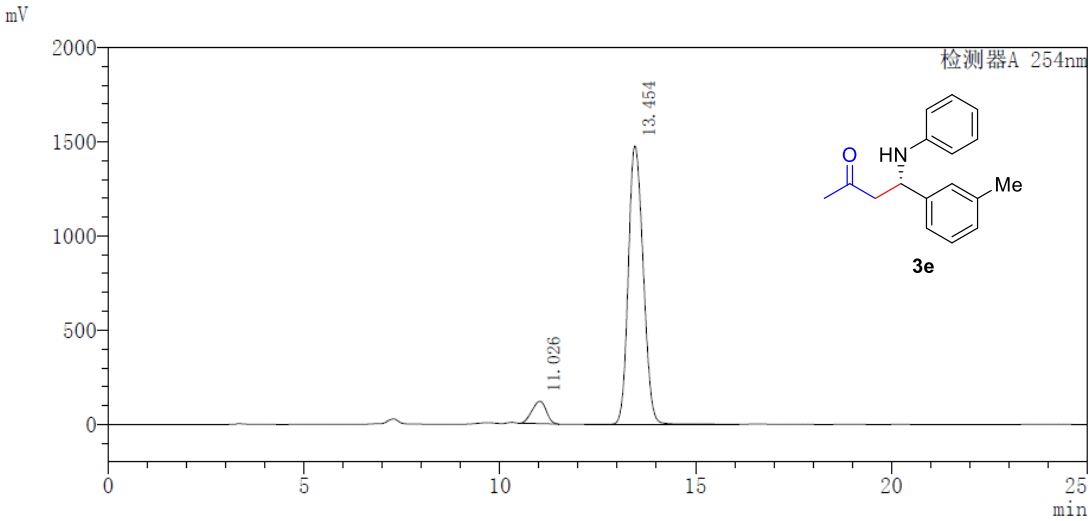
HPLC spectrum of *Rac*-3e



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.085	73545034	3022307	50.033
2	13.565	73446743	2751768	49.967
总计		146991777	5774076	

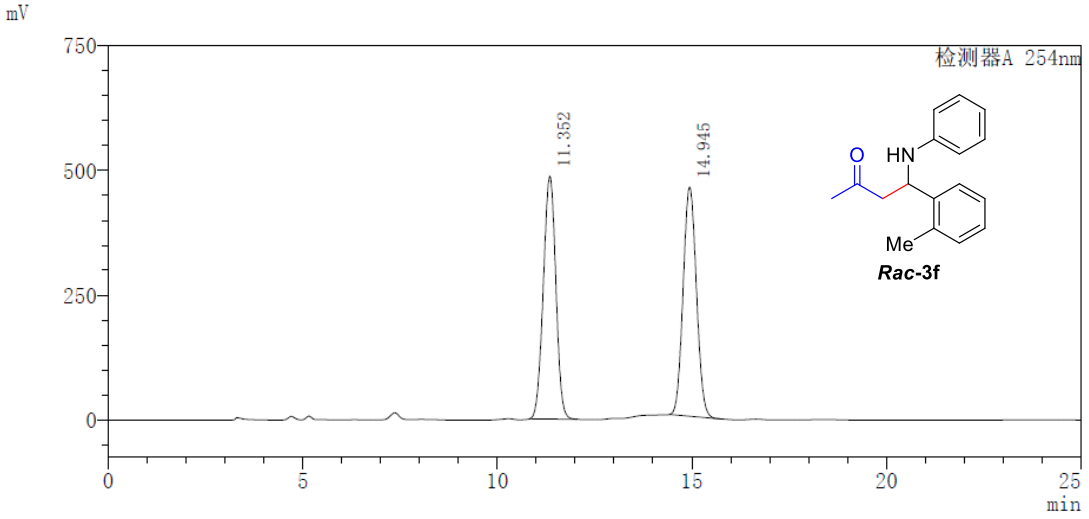
HPLC spectrum of 3e



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.026	2992771	118599	7.089
2	13.454	39226898	1477467	92.911
总计		42219668	1596066	

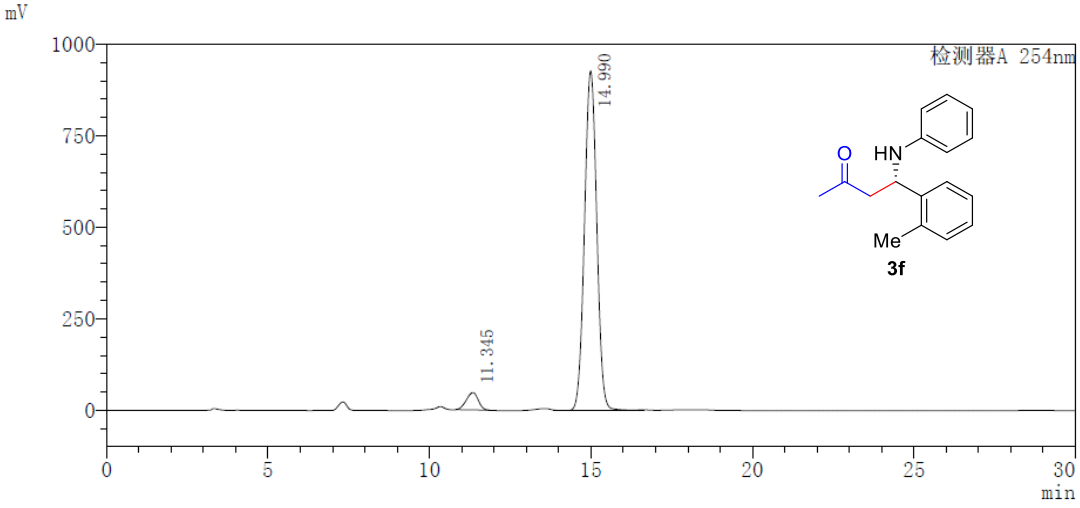
HPLC spectrum of *Rac*-3f



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.352	10904811	486349	50.070
2	14.945	10874229	458775	49.930
总计		21779040	945124	

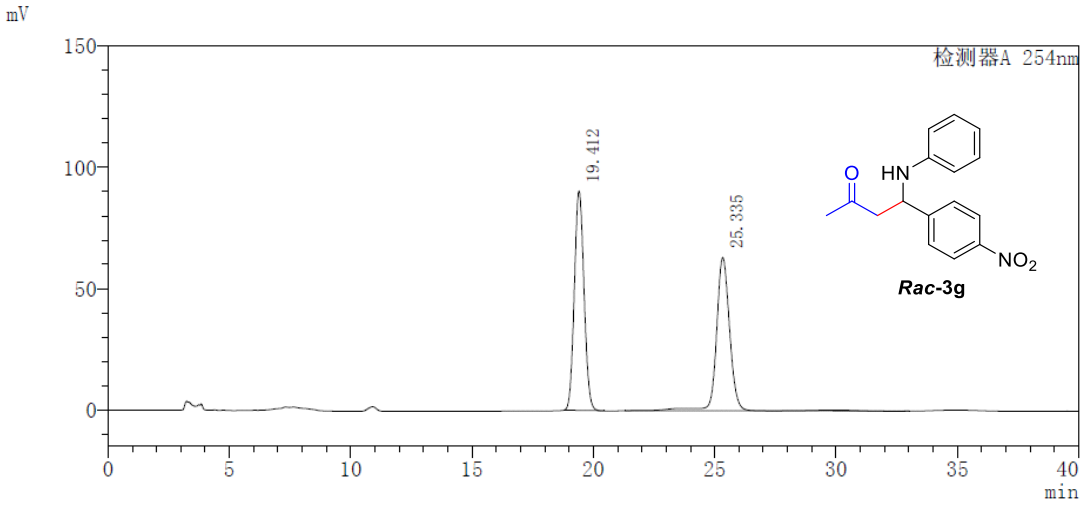
HPLC spectrum of 3f



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.345	1222300	47497	4.794
2	14.990	24274435	925955	95.206
总计		25496735	973452	

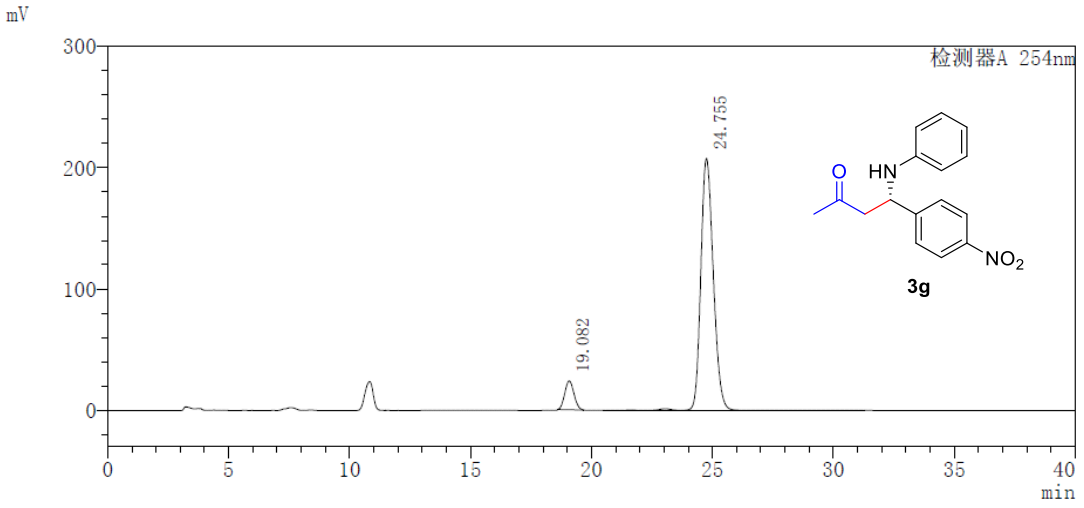
HPLC spectrum of *Rac*-3g



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.412	2510402	90361	50.702
2	25.335	2440849	63192	49.298
总计		4951251	153553	

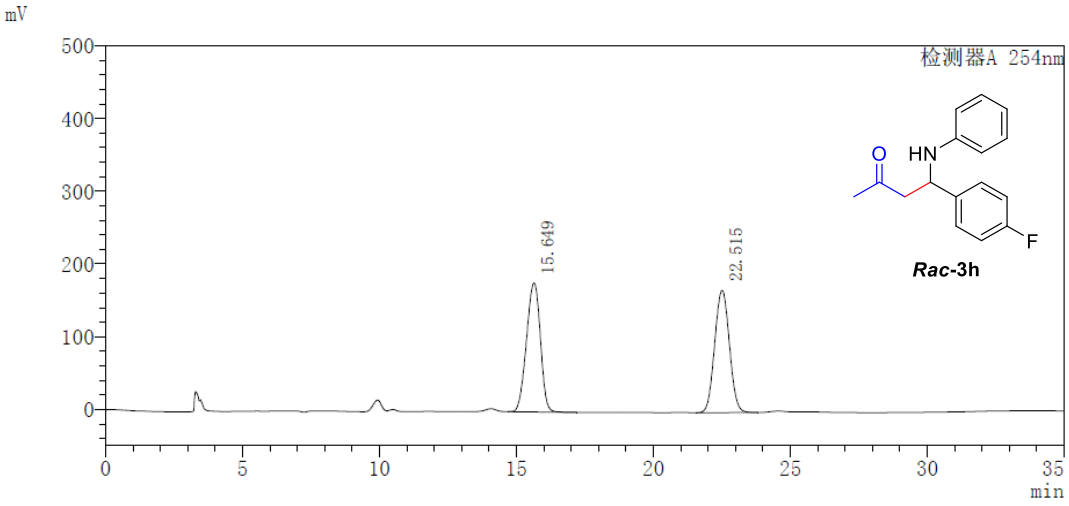
HPLC spectrum of 3g



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.082	630027	23749	7.771
2	24.755	7477222	207572	92.229
总计		8107249	231322	

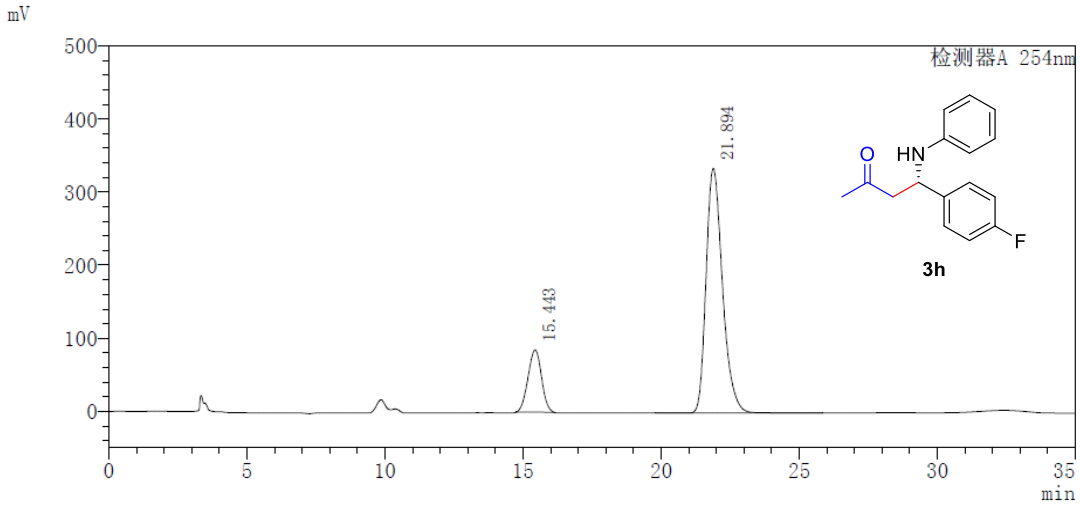
HPLC spectrum of *Rac*-3h



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	15.649	6264032	177462	49.893
2	22.515	6290845	168328	50.107
总计		12554876	345790	

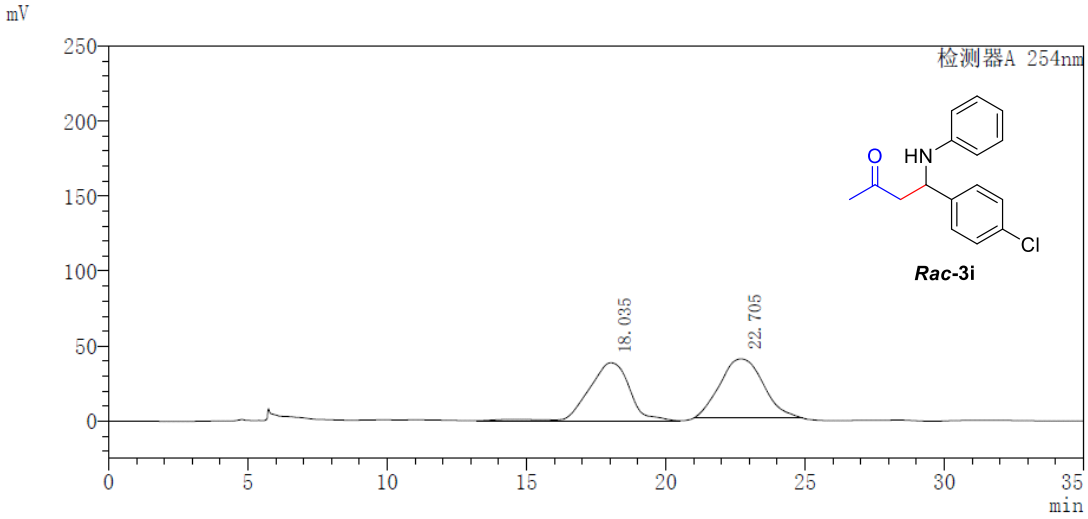
HPLC spectrum of 3h



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	15.443	2897809	85142	17.317
2	21.894	13836054	334836	82.683
总计		16733862	419977	

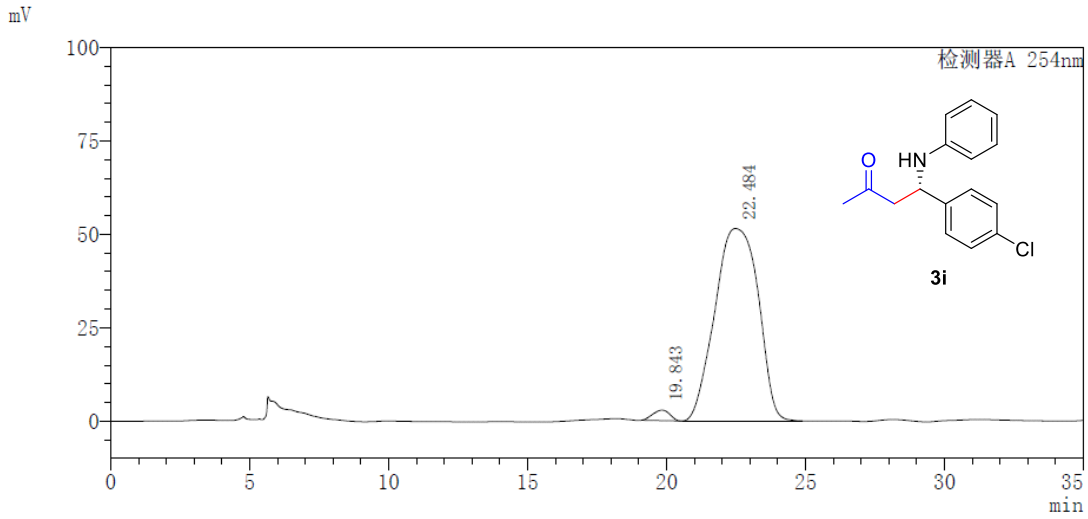
HPLC spectrum of *Rac*-3i



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	18.035	3904688	38643	47.598
2	22.705	4298796	39427	52.402
总计		8203484	78070	

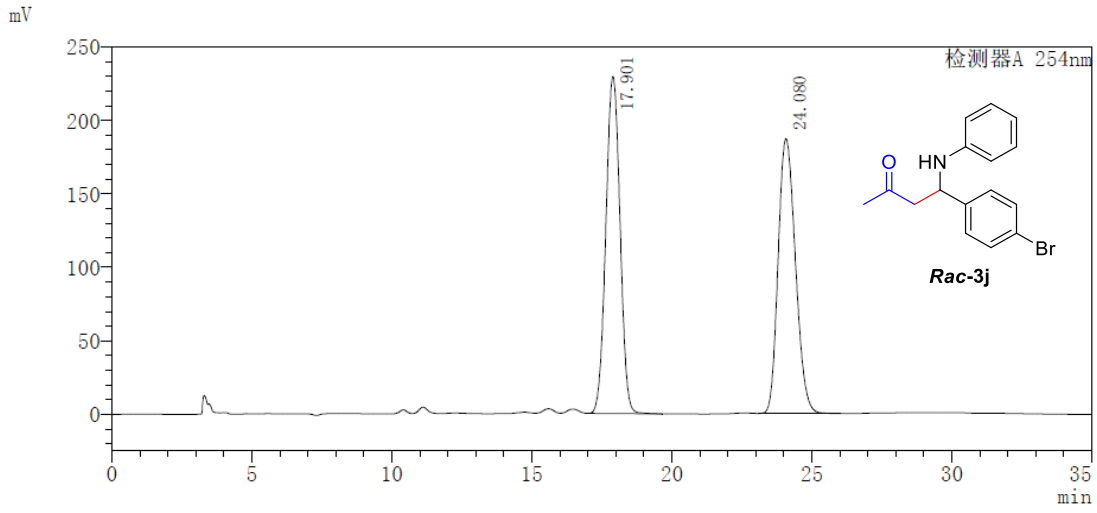
HPLC spectrum of 3i



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	19.843	120277	2795	2.102
2	22.484	5601409	51474	97.898
总计		5721687	54269	

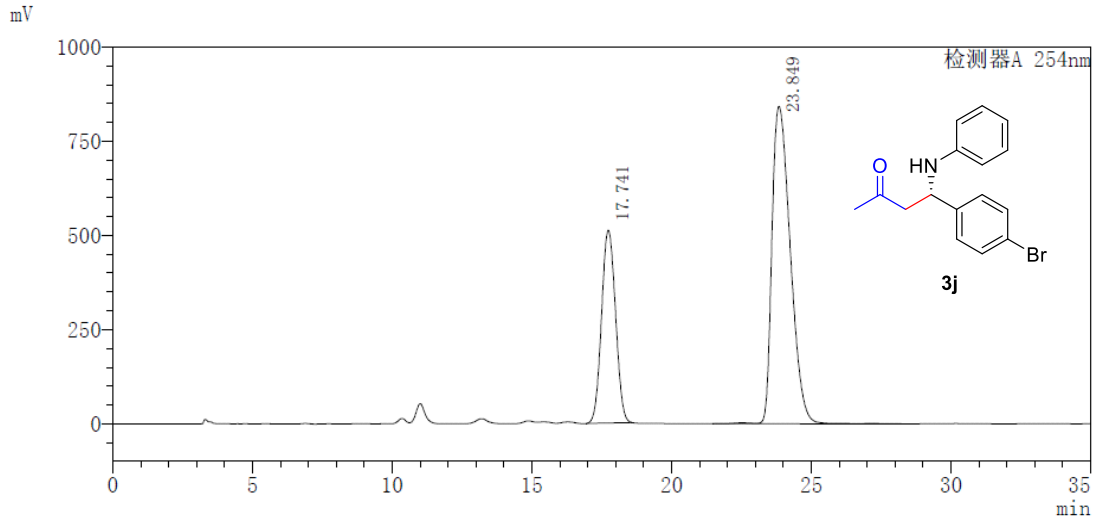
HPLC spectrum of *Rac*-3j



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	17.901	8081210	229506	50.124
2	24.080	8041180	187141	49.876
总计		16122390	416647	

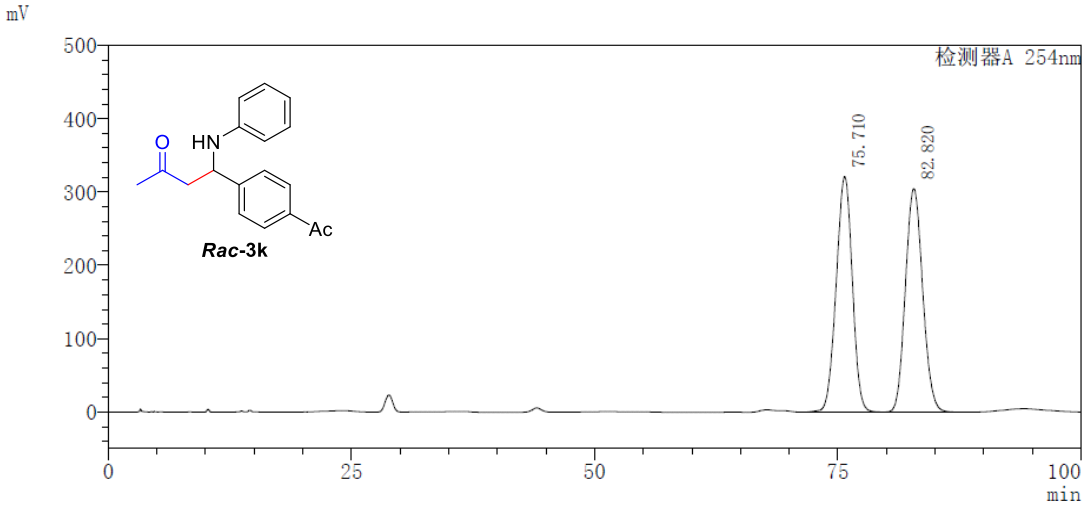
HPLC spectrum of 3j



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	17.741	17785103	511741	31.614
2	23.849	38472636	842736	68.386
总计		56257739	1354477	

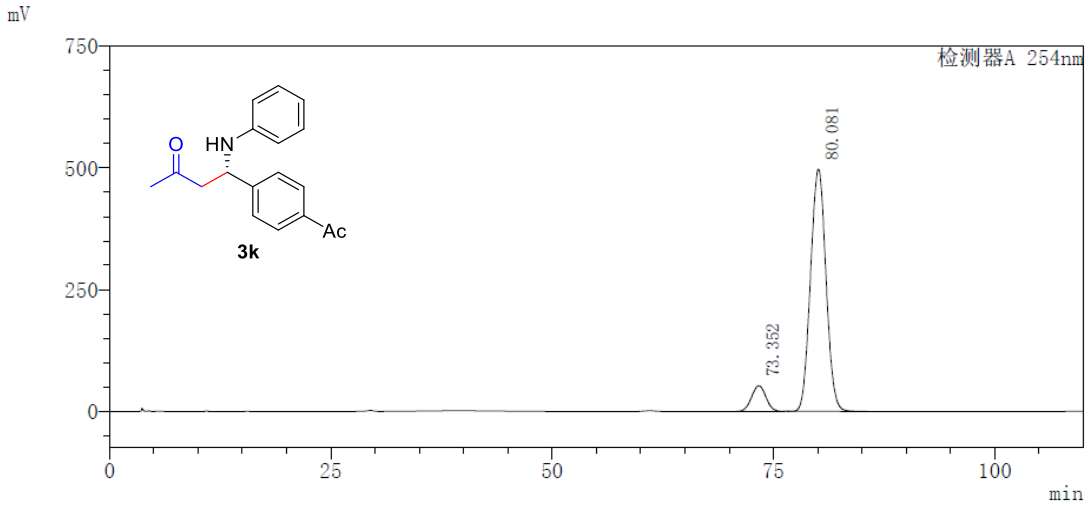
HPLC spectrum of *Rac*-3k



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	75.710	37138987	321319	49.593
2	82.820	37749177	304821	50.407
总计		74888165	626141	

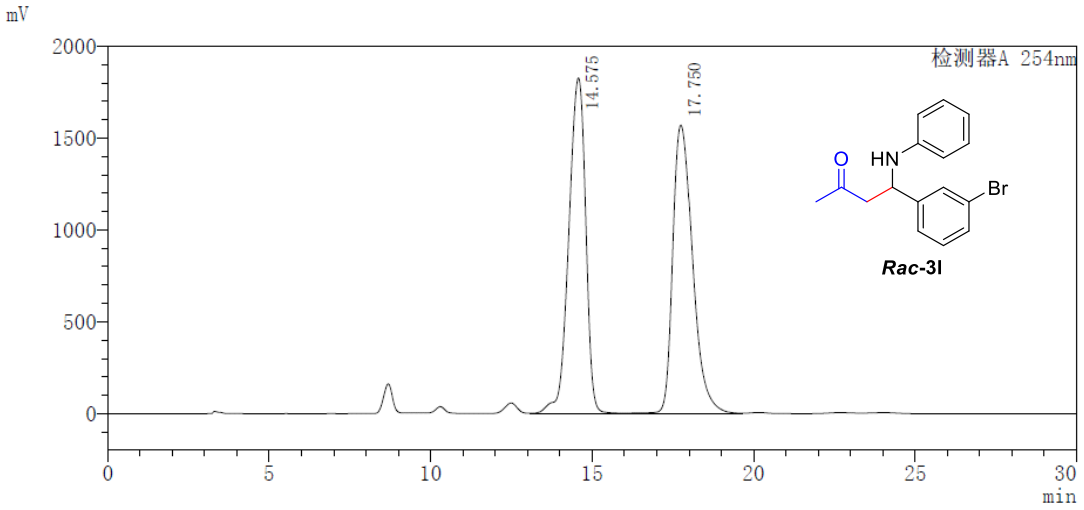
HPLC spectrum of 3k



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	73.352	5925311	52571	8.893
2	80.081	60700886	497214	91.107
总计		66626197	549786	

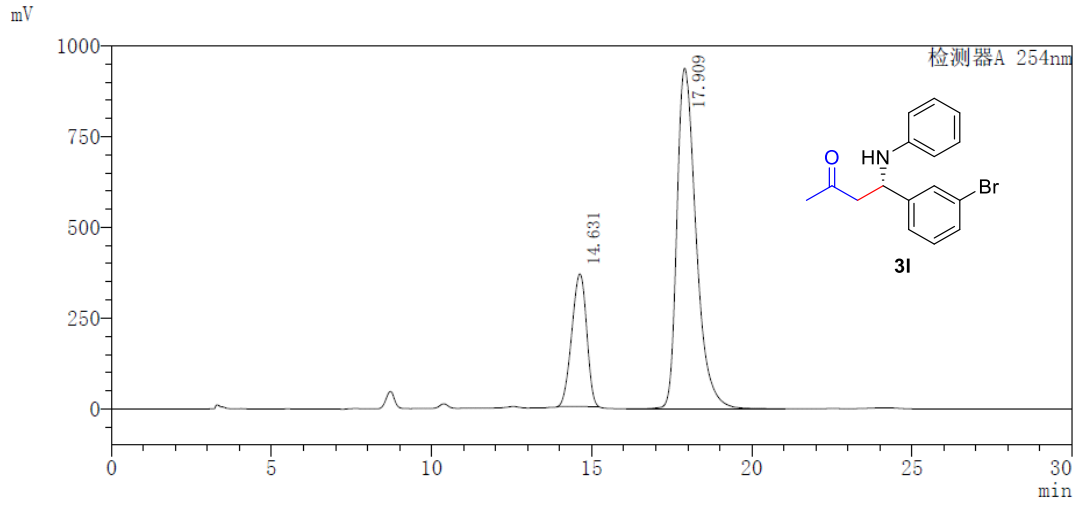
HPLC spectrum of *Rac*-3l



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.575	66716361	1826711	50.072
2	17.750	66525308	1569246	49.928
总计		133241668	3395957	

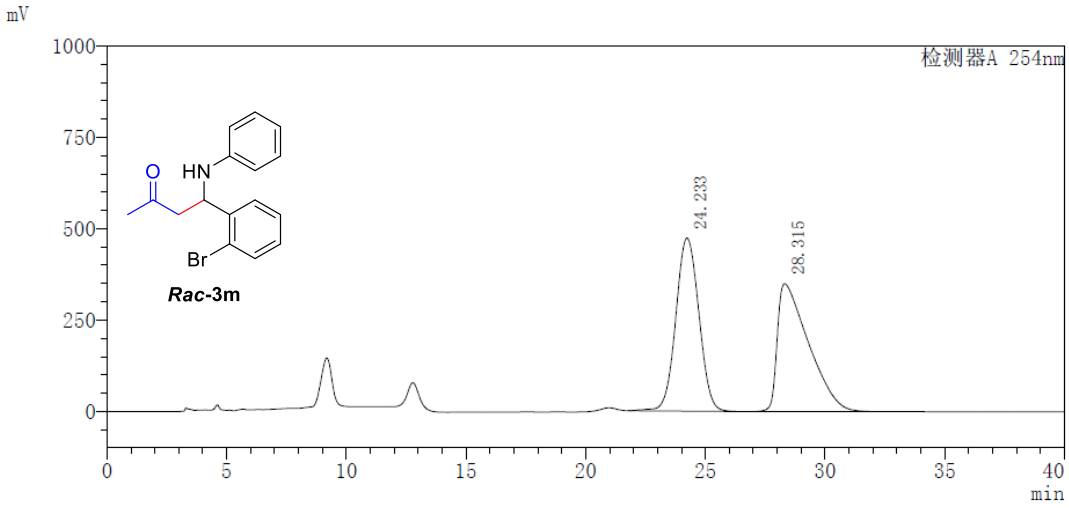
HPLC spectrum of 3l



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.631	11773871	365332	23.320
2	17.909	38714202	938699	76.680
总计		50488072	1304030	

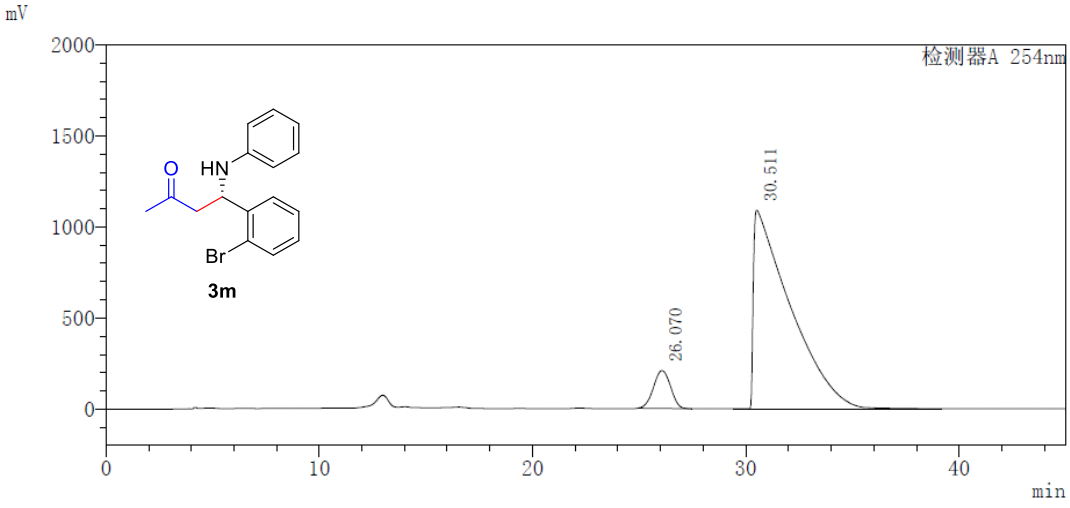
HPLC spectrum of *Rac*-3m



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	24.233	31818690	474067	50.093
2	28.315	31700421	350041	49.907
总计		63519110	824108	

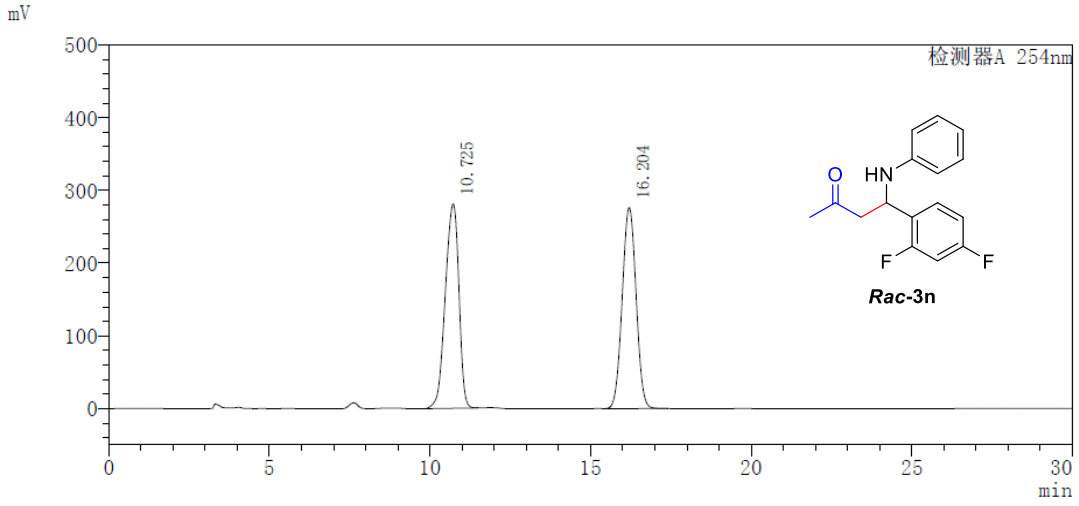
HPLC spectrum of 3m



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	26.070	11629549	207997	8.127
2	30.511	131475123	1090508	91.873
总计		143104672	1298505	

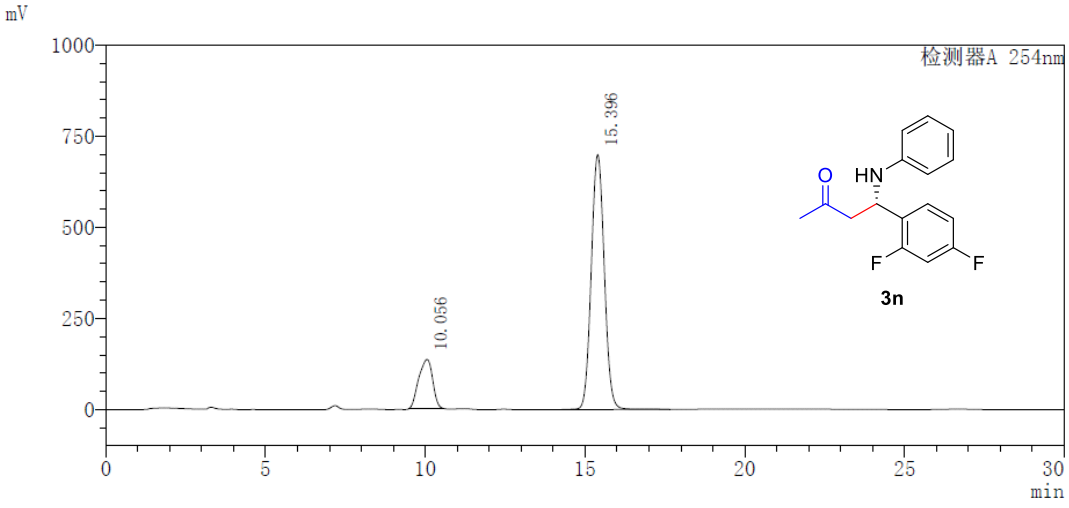
HPLC spectrum of *Rac*-3n



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.725	8288294	281055	49.884
2	16.204	8326980	276668	50.116
总计		16615275	557723	

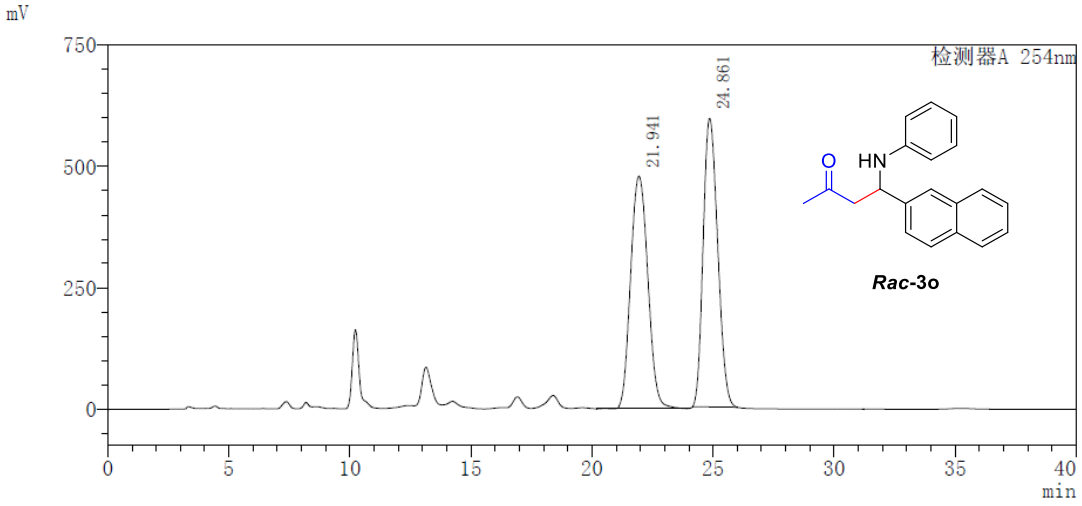
HPLC spectrum of 3n



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.056	4097811	135221	17.087
2	15.396	19884798	699505	82.913
总计		23982609	834726	

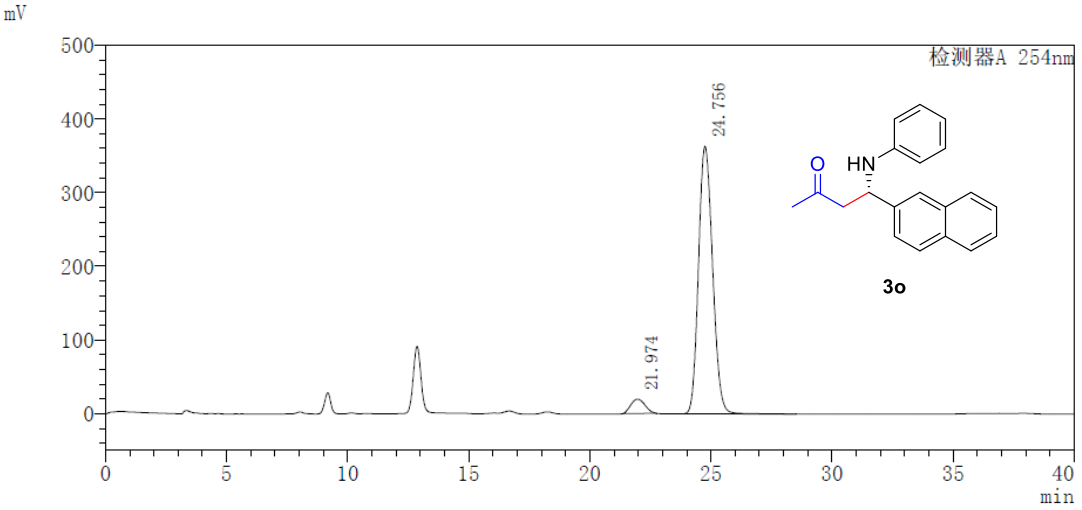
HPLC spectrum of *Rac*-3o



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	21.941	23712287	478713	48.866
2	24.861	24812747	594243	51.134
总计		48525035	1072956	

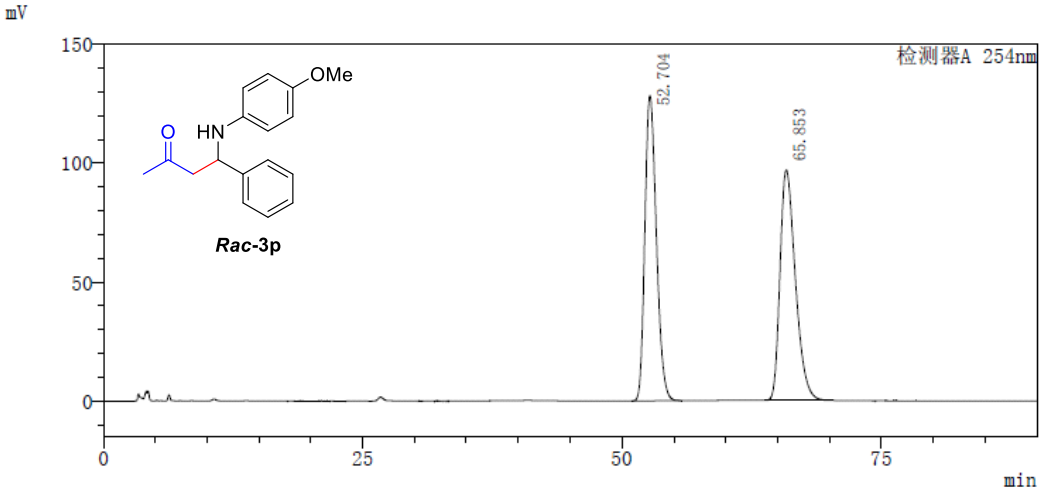
HPLC spectrum of 3o



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	21.974	783990	19251	5.053
2	24.756	14730790	363209	94.947
总计		15514780	382460	

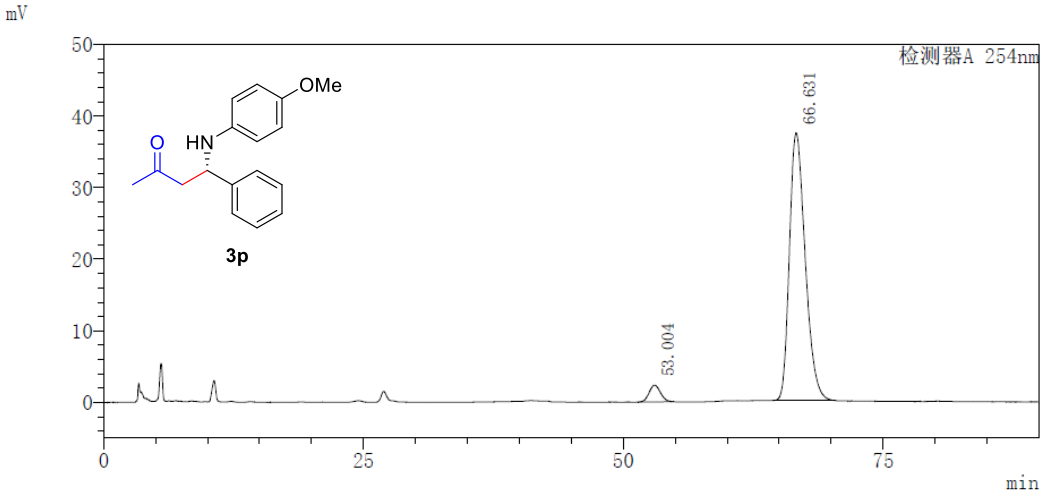
HPLC spectrum of *Rac*-3p



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	52.704	9909718	128286	49.844
2	65.853	9971752	96931	50.156
总计		19881470	225217	

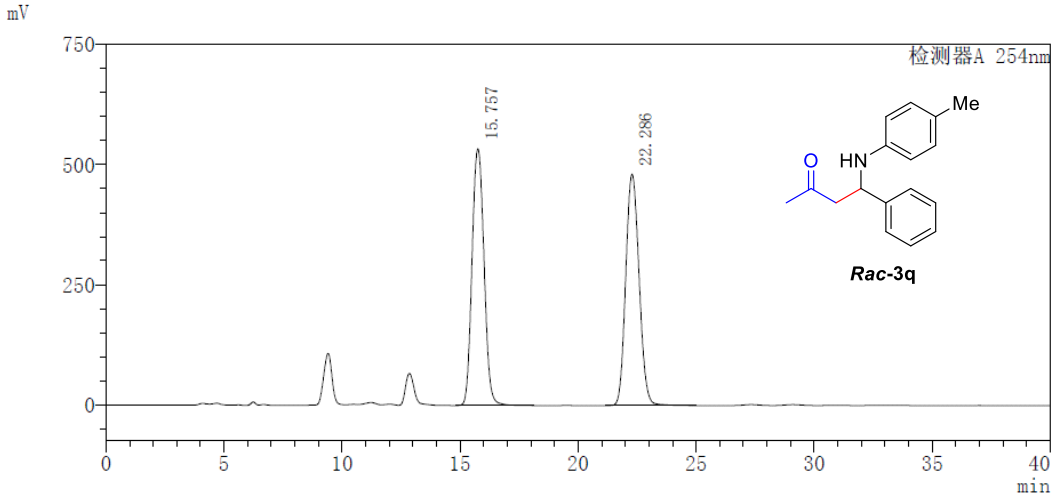
HPLC spectrum of 3p



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	53.004	178446	2348	4.329
2	66.631	3943312	37355	95.671
总计		4121757	39704	

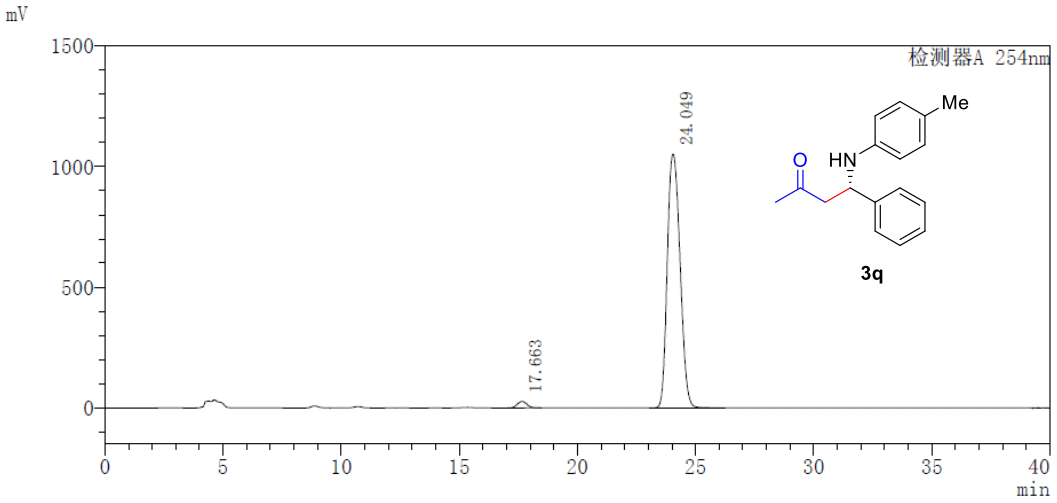
HPLC spectrum of *Rac*-3q



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	15.757	18849285	534289	49.918
2	22.286	18911229	481089	50.082
总计		37760515	1015378	

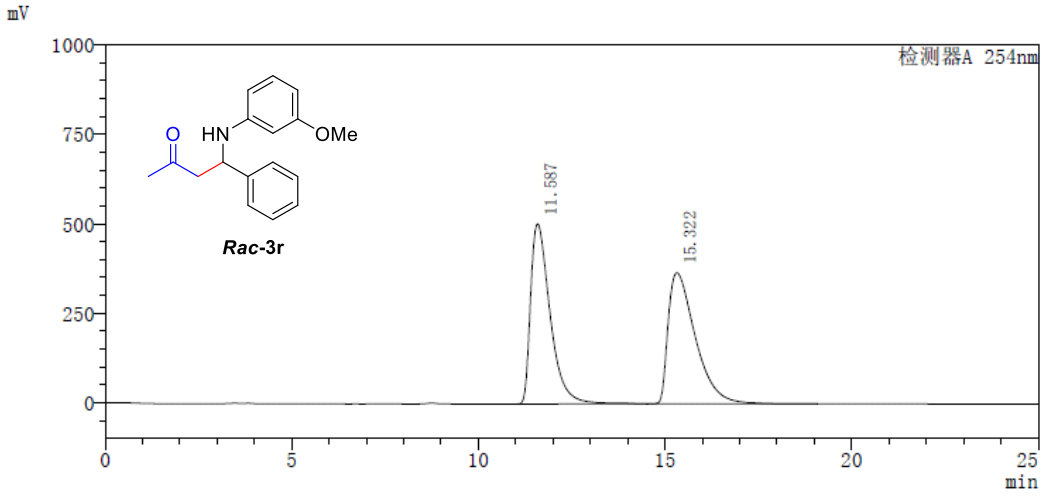
HPLC spectrum of 3q



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	17.663	761540	26694	1.895
2	24.049	39419943	1051871	98.105
总计		40181483	1078564	

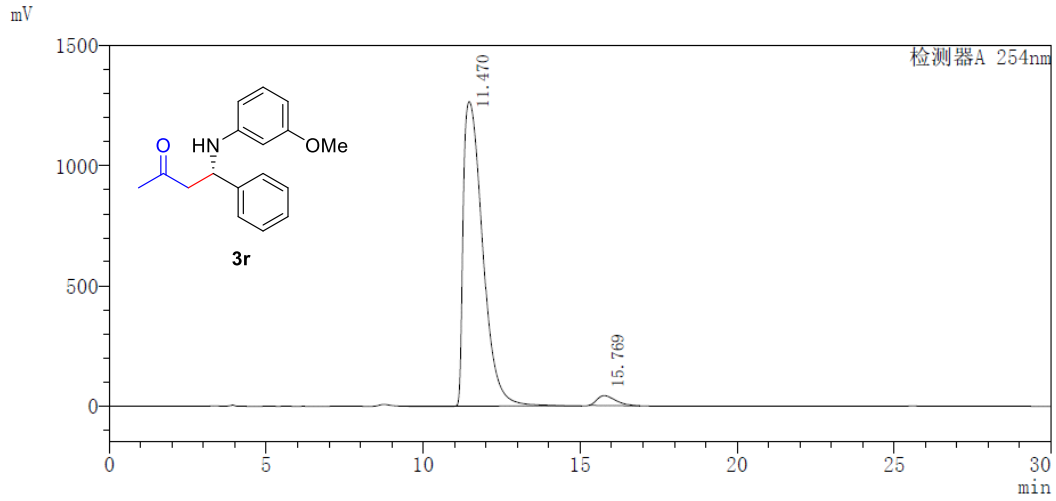
HPLC spectrum of *Rac*-3r



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.587	18391791	504034	49.760
2	15.322	18569474	366301	50.240
总计		36961265	870335	

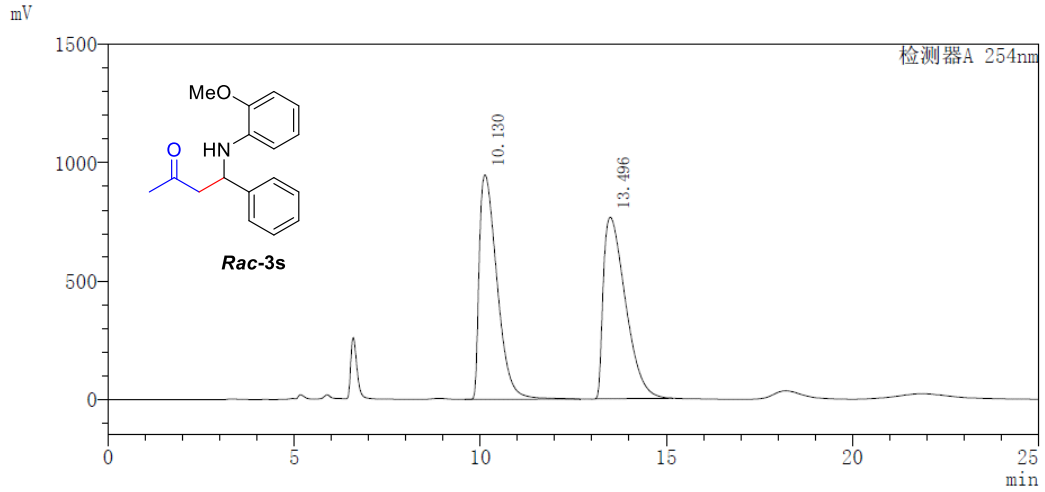
HPLC spectrum of 3r



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.470	54330255	1267118	96.982
2	15.769	1690497	40842	3.018
总计		56020752	1307960	

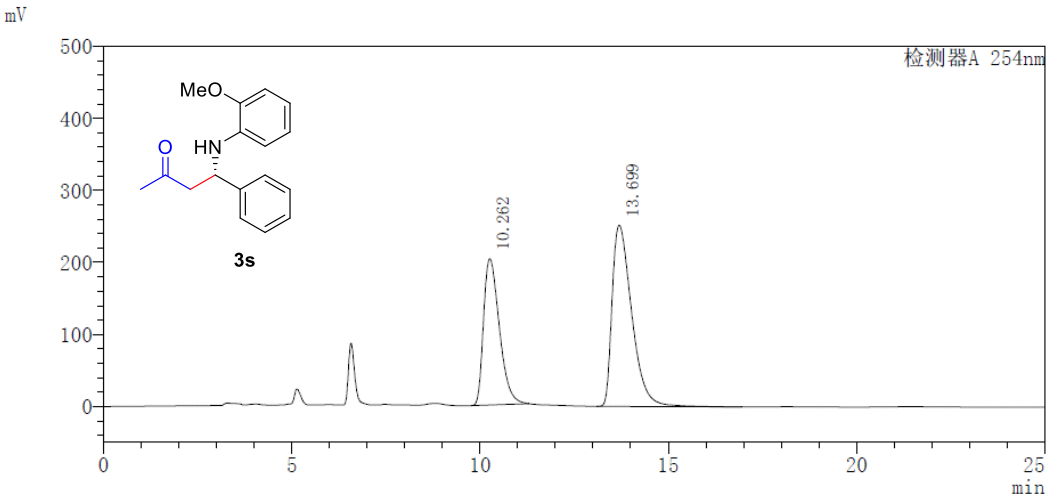
HPLC spectrum of *Rac*-3s



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.130	31522366	948476	49.833
2	13.496	31733087	765658	50.167
总计		63255453	1714135	

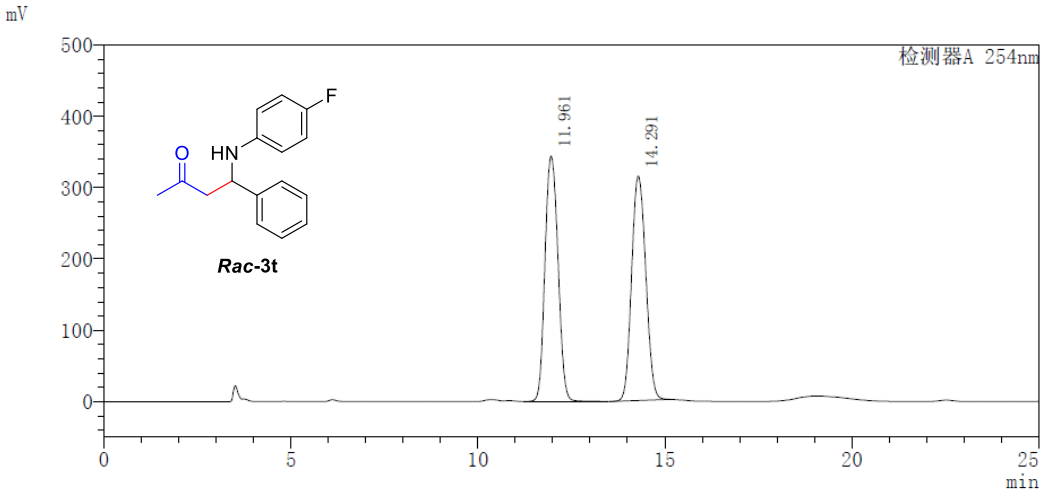
HPLC spectrum of 3s



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.262	5940262	203277	39.461
2	13.699	9113256	251682	60.539
总计		15053519	454959	

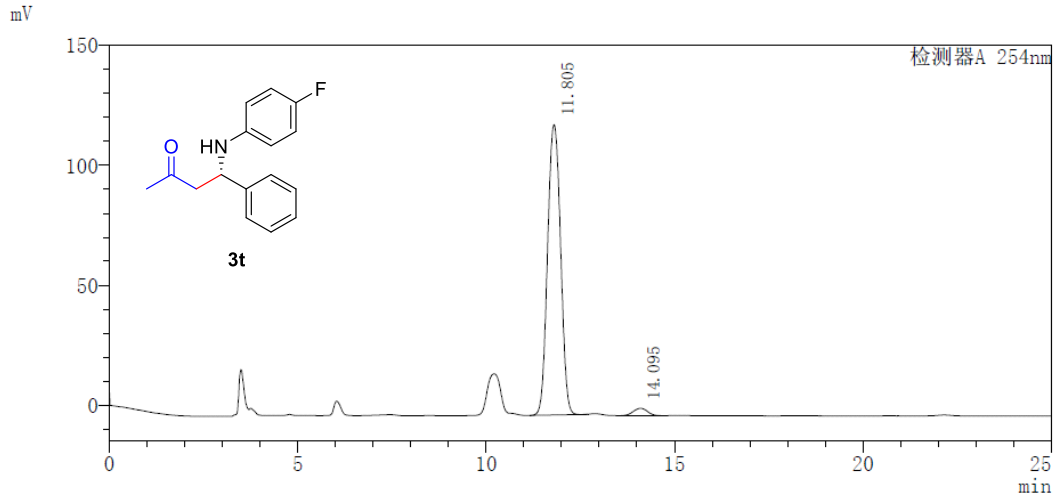
HPLC spectrum of *Rac*-3t



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.961	8317069	343751	50.079
2	14.291	8290663	314652	49.921
总计		16607731	658403	

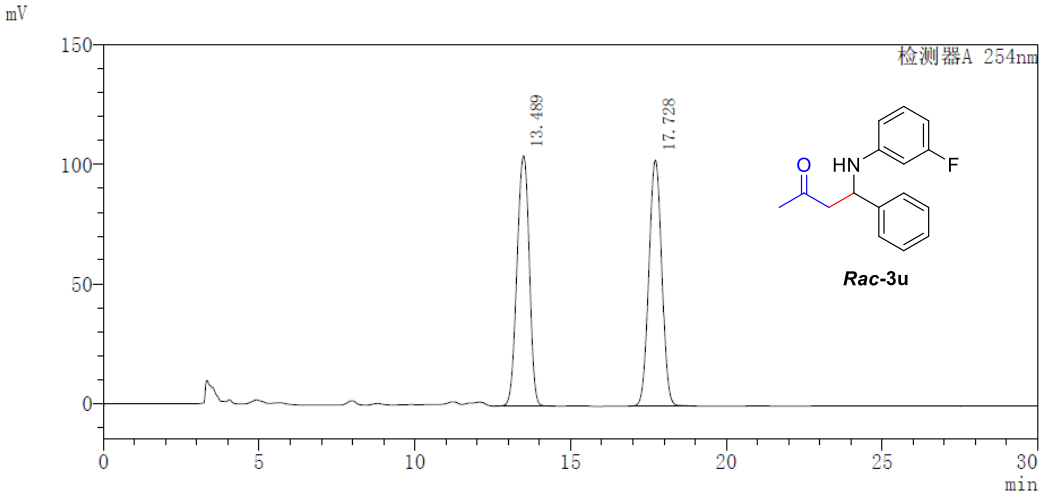
HPLC spectrum of 3t



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.805	2898902	120950	97.377
2	14.095	78096	3023	2.623
总计		2976998	123973	

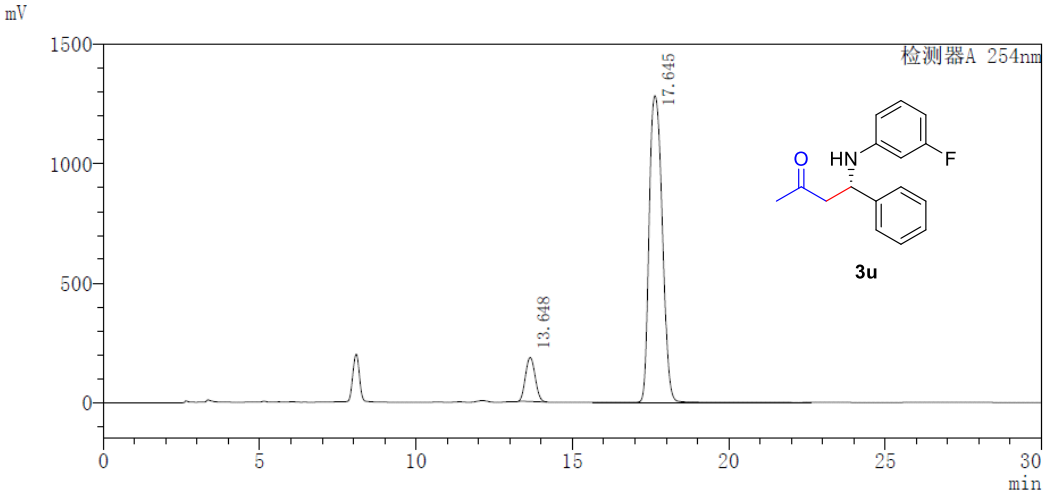
HPLC spectrum of *Rac*-3u



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.489	2874563	104710	49.369
2	17.728	2948080	102912	50.631
总计		5822643	207622	

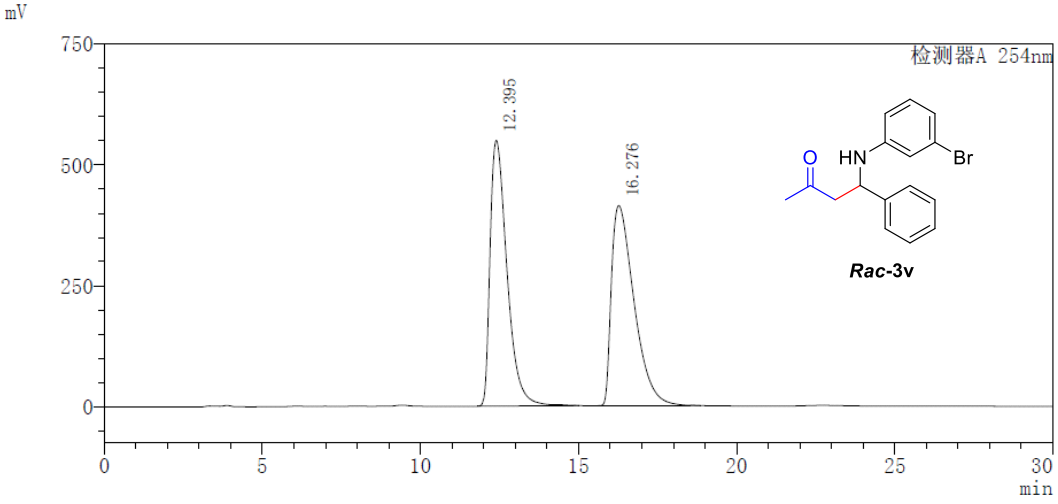
HPLC spectrum of 3u



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.648	3978314	184008	9.646
2	17.645	37265672	1283095	90.354
总计		41243986	1467103	

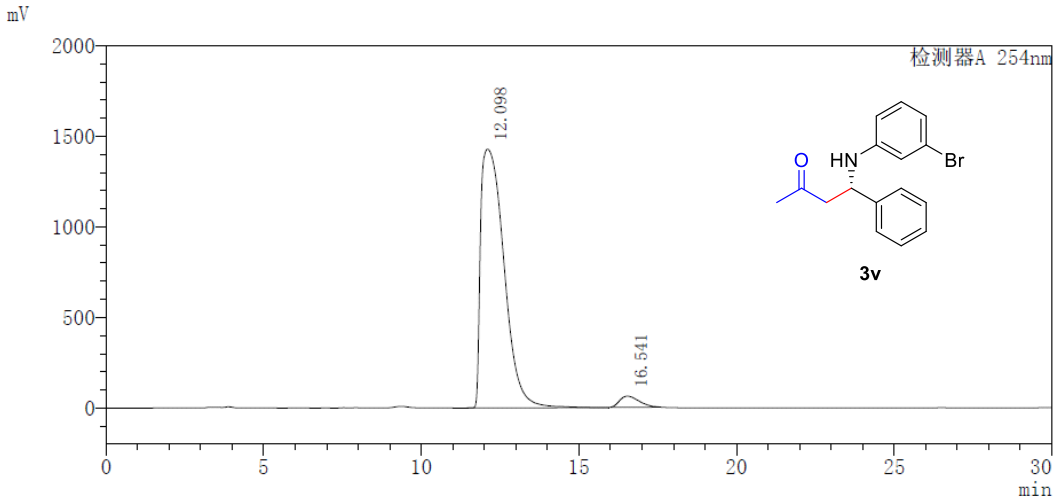
HPLC spectrum of *Rac*-3v



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.395	20479247	549359	49.788
2	16.276	20653310	413818	50.212
总计		41132557	963177	

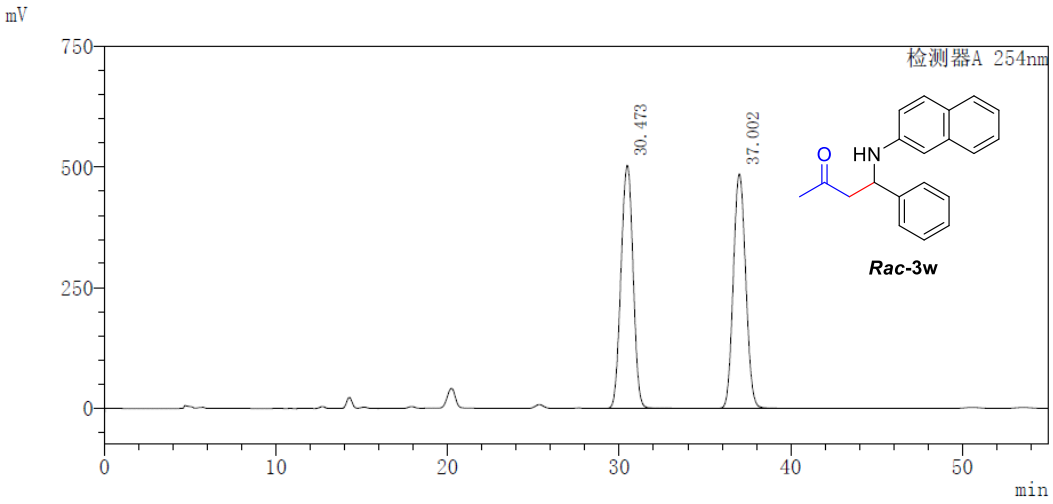
HPLC spectrum of 3v



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.098	73181778	1428731	96.525
2	16.541	2634573	61600	3.475
总计		75816351	1490331	

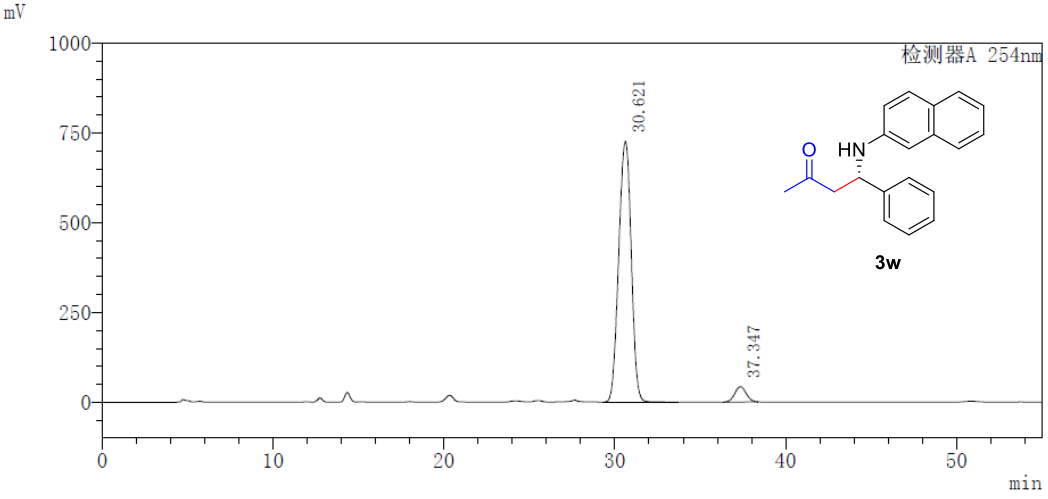
HPLC spectrum of *Rac*-3w



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	30.473	24759110	503934	50.302
2	37.002	24461397	486009	49.698
总计		49220506	989943	

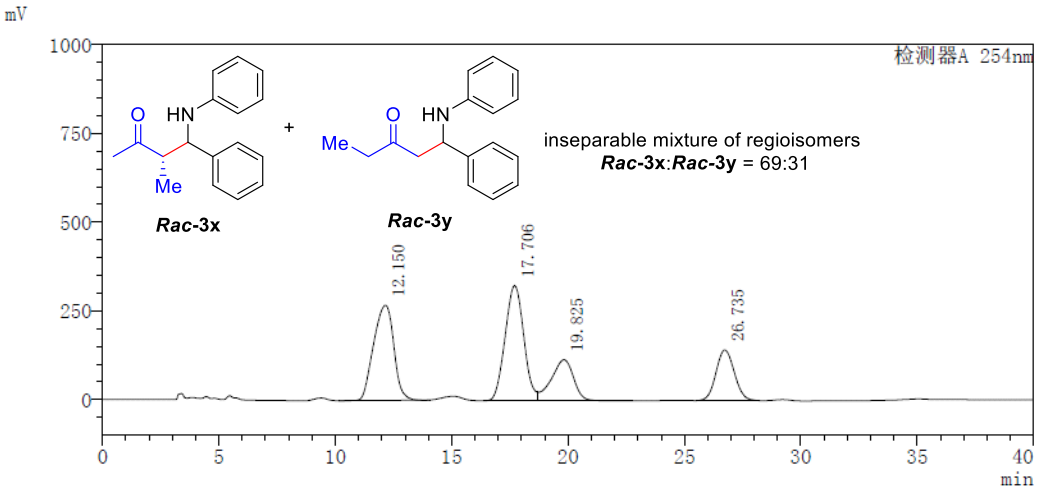
HPLC spectrum of 3w



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	30.621	37008118	726484	94.911
2	37.347	1984491	42386	5.089
总计		38992609	768870	

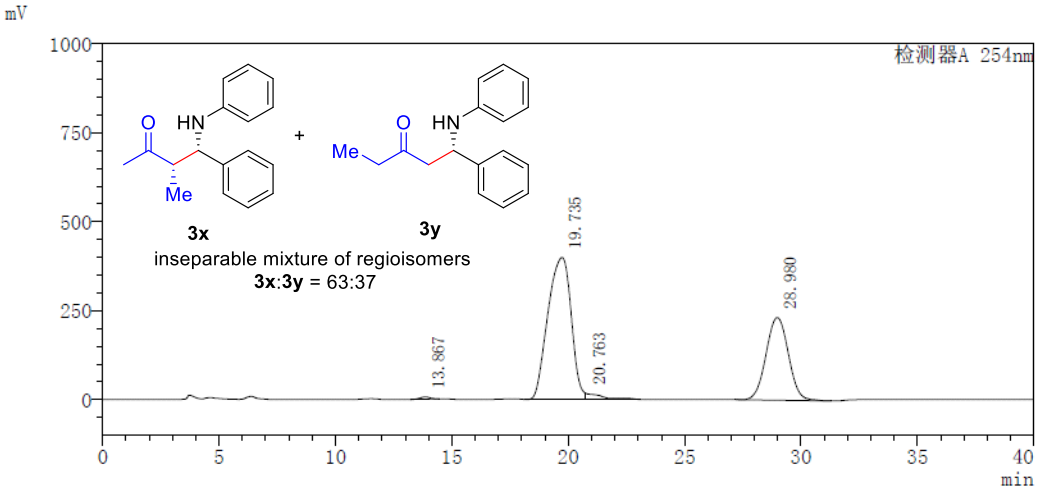
HPLC spectrum of *Rac*-3x and *Rac*-3y



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.150	16133583	267776	32.547
2	17.706	18050218	324084	36.414
3	19.825	7675784	115335	15.485
4	26.735	7709782	141732	15.554
总计		49569366	848927	

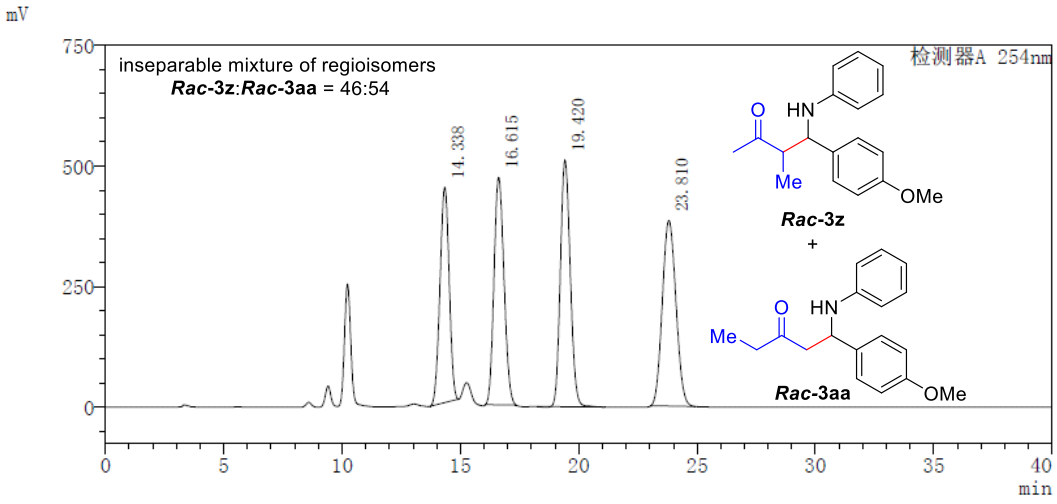
HPLC spectrum of 3x and 3y



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.867	189225	6276	0.426
2	19.735	27790910	399155	62.555
3	20.763	833813	16851	1.877
4	28.980	15612331	232514	35.142
总计		44426279	654796	

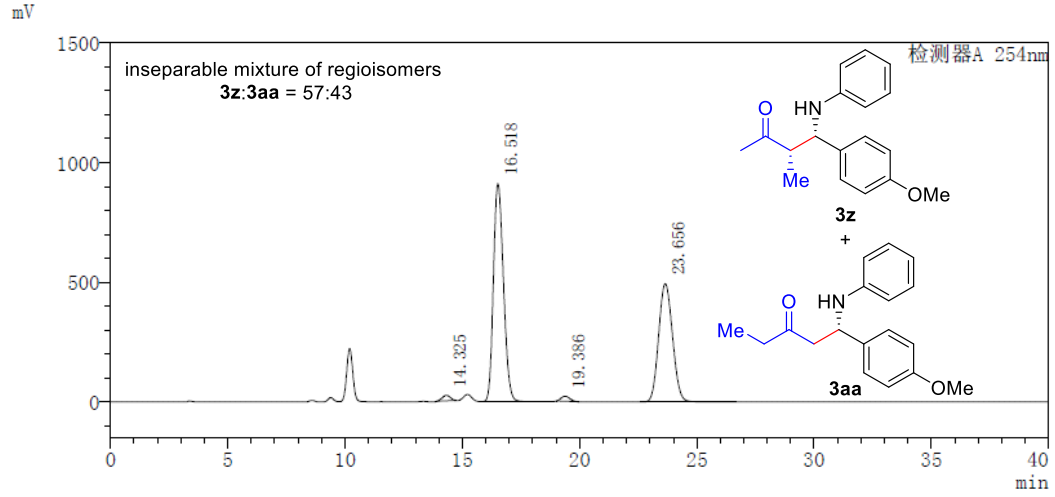
HPLC spectrum of *Rac*-3z and *Rac*-3aa



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.338	12092532	446138	21.493
2	16.615	13893959	471479	24.695
3	19.420	14902202	510749	26.487
4	23.810	15373957	384940	27.325
总计		56262650	1813306	

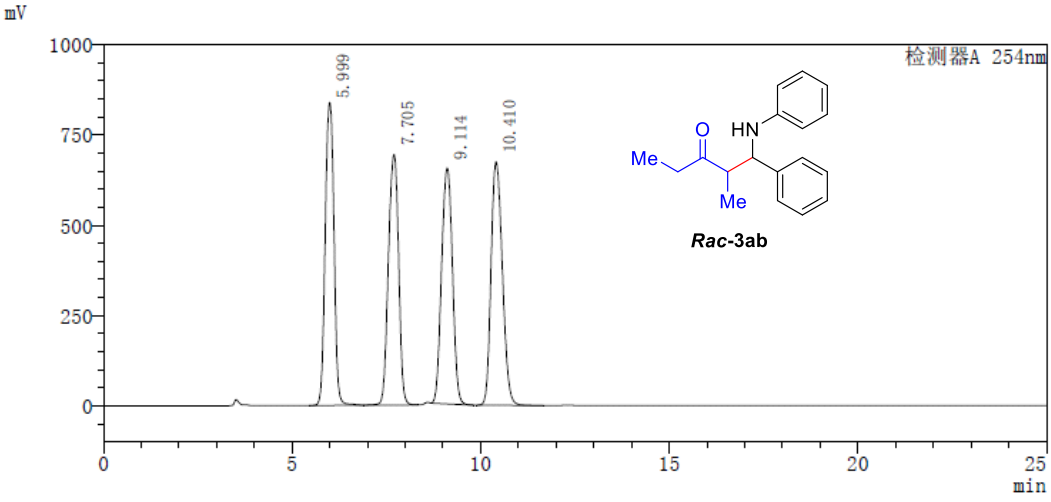
HPLC spectrum of 3z and 3aa



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.325	554383	22864	1.143
2	16.518	27125390	909735	55.917
3	19.386	528571	20959	1.090
4	23.656	20302109	493780	41.851
总计		48510453	1447338	

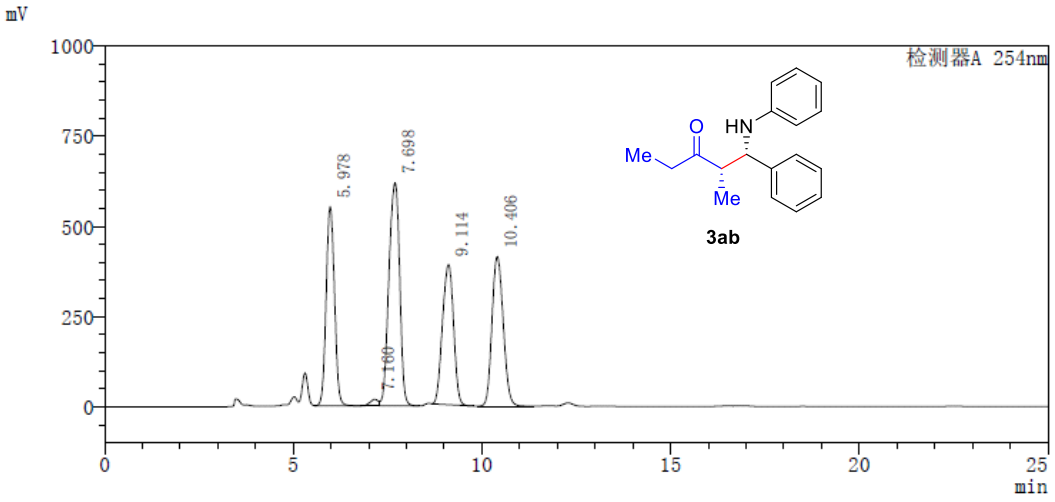
HPLC spectrum of *Rac*-3ab



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	5.999	13478591	839109	25.073
2	7.705	13106221	694261	24.381
3	9.114	13071344	653628	24.316
4	10.410	14100731	674327	26.231
总计		53756887	2861324	

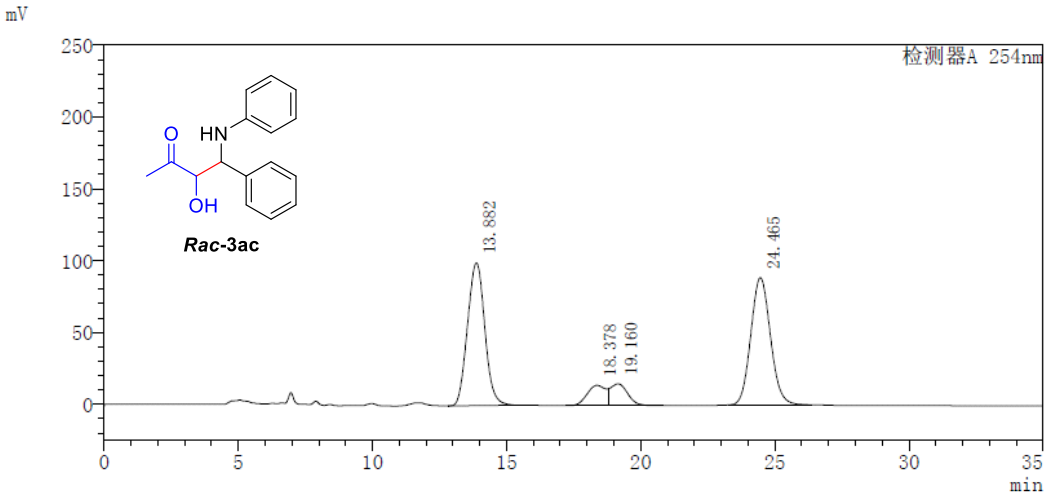
HPLC spectrum of 3ab



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	5.978	8474214	552525	22.509
2	7.160	278525	18536	0.740
3	7.698	12291072	619090	32.647
4	9.114	7953531	388165	21.126
5	10.406	8651098	414941	22.979
总计		37648439	1993256	

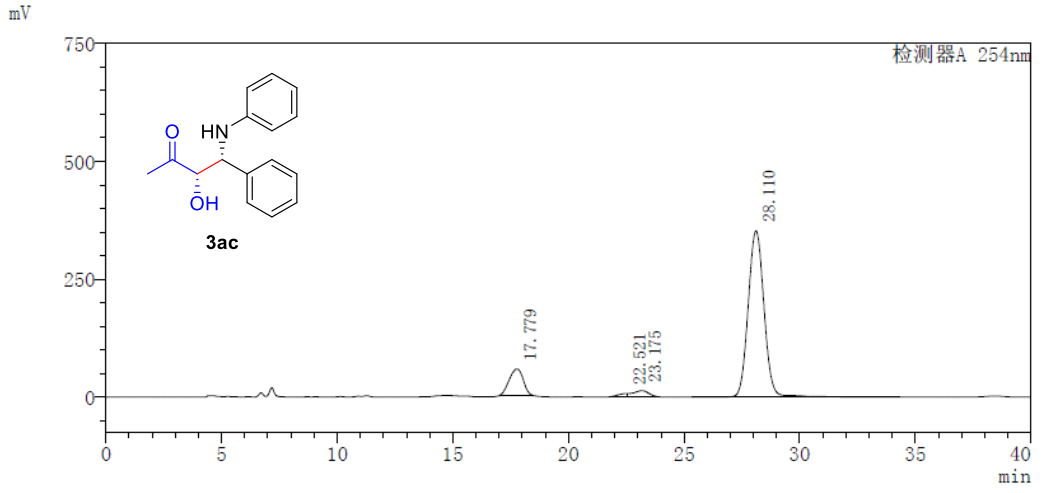
HPLC spectrum of *Rac*-3ac



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.882	4464762	99388	43.170
2	18.378	683405	14137	6.608
3	19.160	688807	15161	6.660
4	24.465	4505327	88517	43.562
总计		10342301	217202	

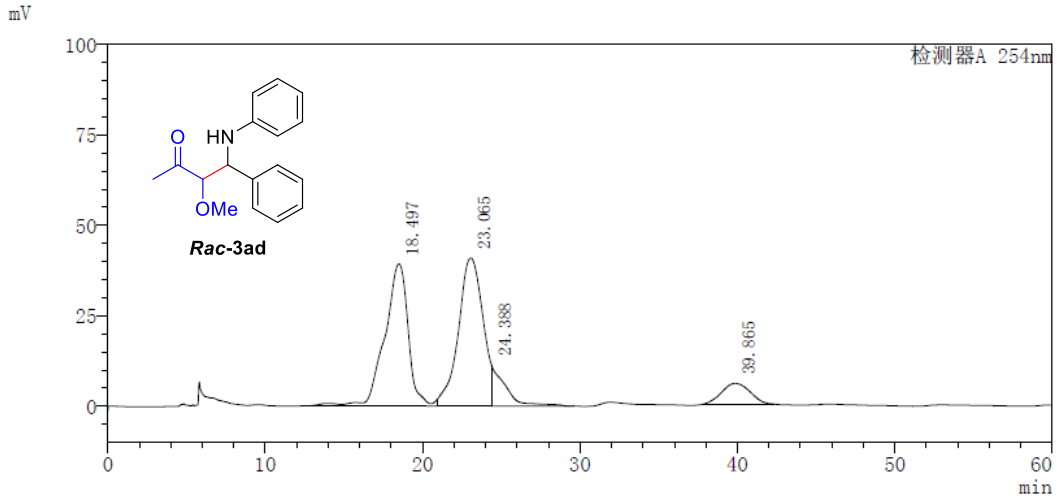
HPLC spectrum of 3ac



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	17.779	2344638	55775	11.826
2	22.521	165981	6746	0.837
3	23.175	619605	12750	3.125
4	28.110	16695519	352442	84.211
总计		19825742	427712	

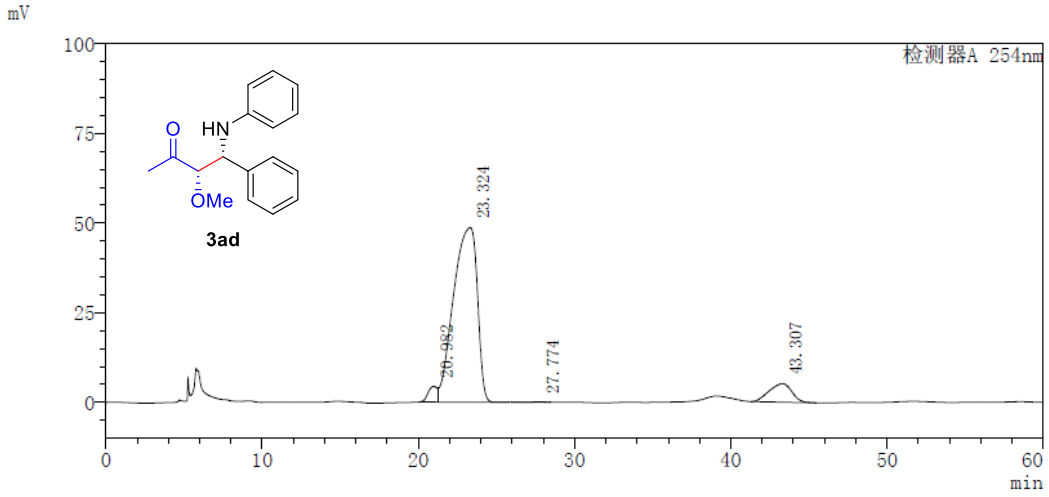
HPLC spectrum of *Rac*-3ad



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	18.497	4055546	39268	41.100
2	23.065	4393606	40964	44.526
3	24.388	697707	11271	7.071
4	39.865	720581	5721	7.303
总计		9867439	97224	

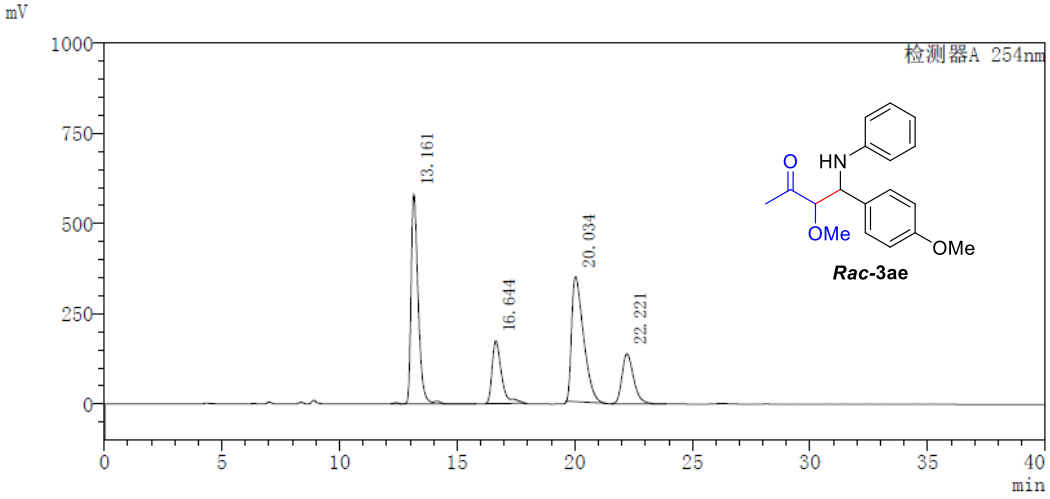
HPLC spectrum of 3ad



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.982	172306	4333	2.926
2	23.324	5187235	48710	88.101
3	27.774	8161	126	0.139
4	43.307	520155	5153	8.834
总计		5887858	58323	

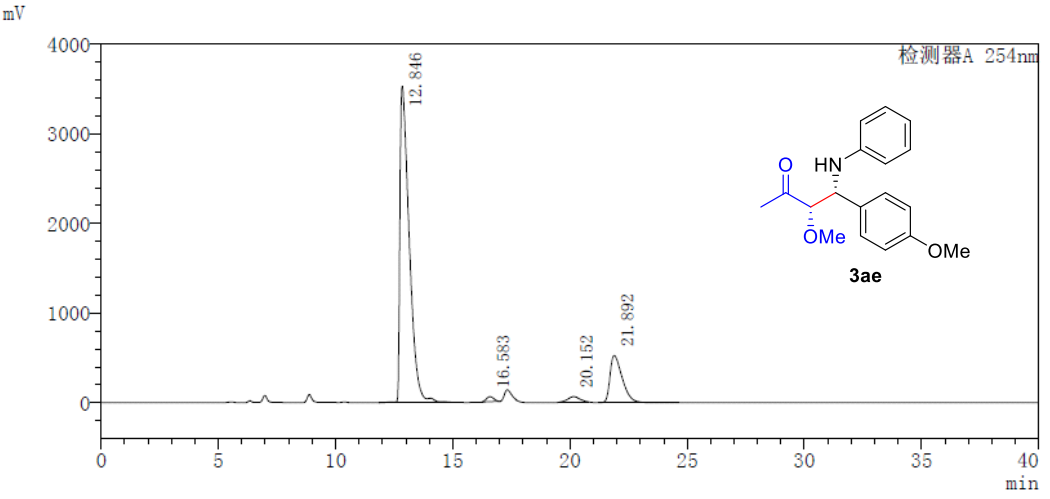
HPLC spectrum of *Rac*-3ae



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.161	12207029	580706	35.883
2	16.644	4867054	173552	14.307
3	20.034	12166936	346606	35.765
4	22.221	4777768	138889	14.044
总计		34018787	1239754	

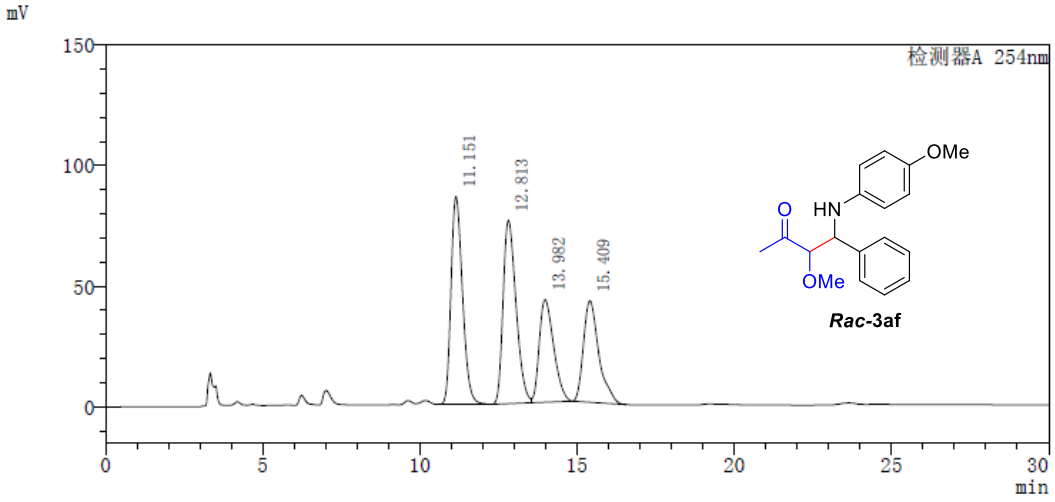
HPLC spectrum of 3ae



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.846	96950854	3527224	81.377
2	16.583	1225897	56447	1.029
3	20.152	2048794	59828	1.720
4	21.892	18912538	526788	15.874
总计		119138083	4170287	

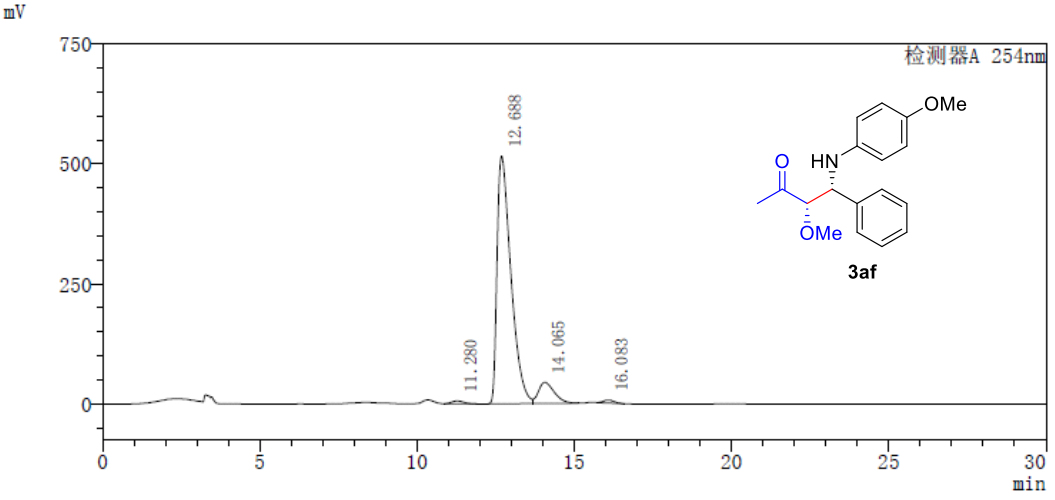
HPLC spectrum of *Rac*-3af



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.151	2189728	86109	30.576
2	12.813	2179205	75999	30.429
3	13.982	1362001	42518	19.018
4	15.409	1430734	42007	19.978
总计		7161668	246633	

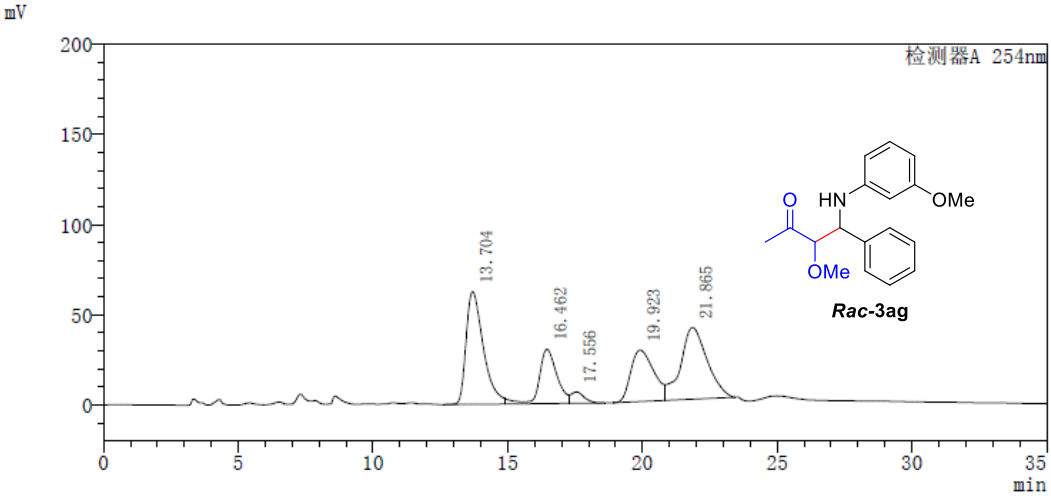
HPLC spectrum of 3af



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	11.280	153595	6114	0.868
2	12.688	15842790	515810	89.536
3	14.065	1554711	44235	8.786
4	16.083	143306	6410	0.810
总计		17694402	572569	

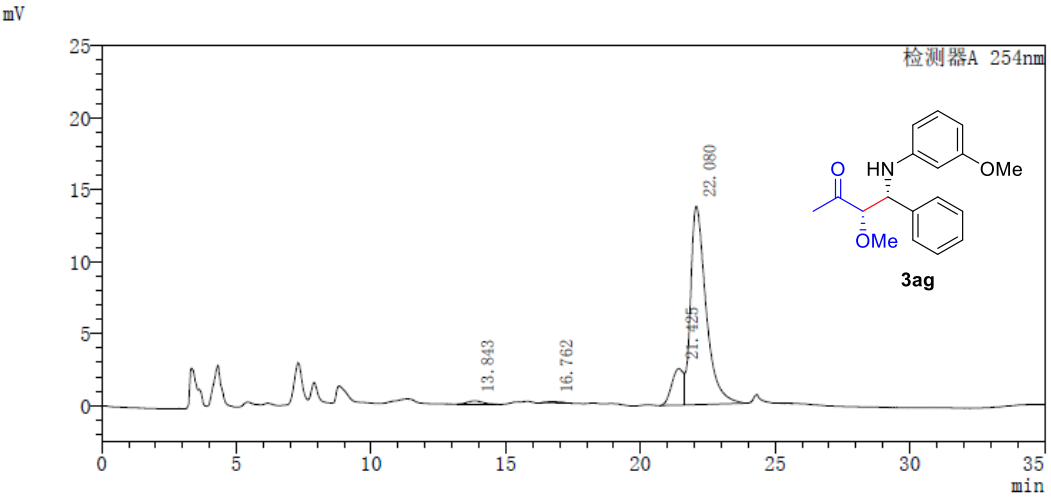
HPLC spectrum of *Rac*-3ag



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.704	2774164	62493	31.446
2	16.462	1376328	30133	15.601
3	17.556	223293	6345	2.531
4	19.923	1706228	28550	19.340
5	21.865	2742033	39826	31.082
总计		8822046	167348	

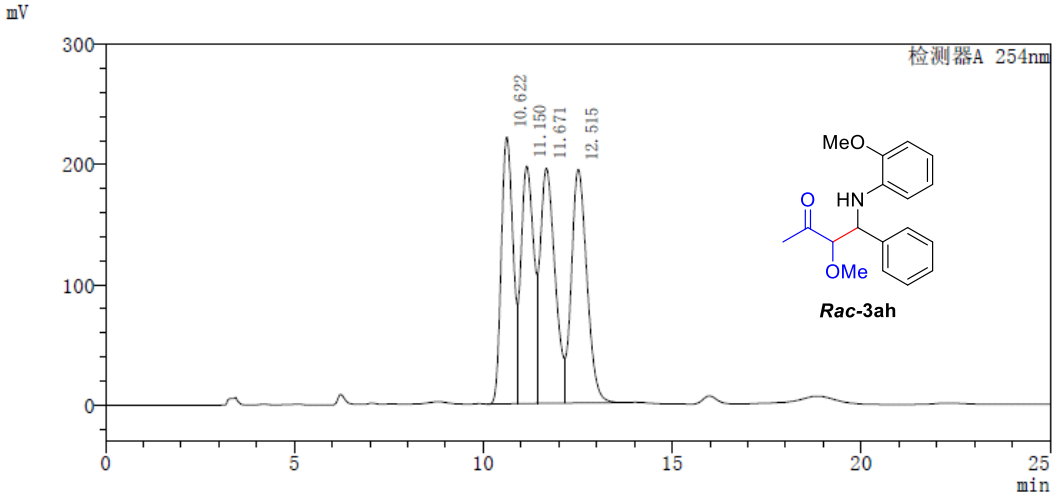
HPLC spectrum of 3ag



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.843	8895	224	1.390
2	16.762	3800	95	0.594
3	21.425	76569	2528	11.965
4	22.080	550672	13772	86.051
总计		639936	16618	

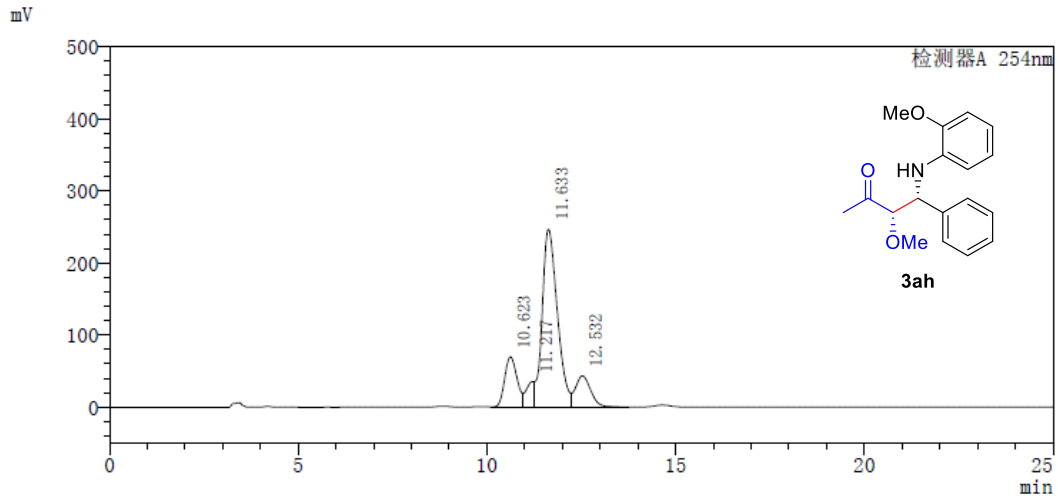
HPLC spectrum of *Rac*-3ah



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.622	4819800	221719	23.666
2	11.150	4606410	197412	22.618
3	11.671	5385490	195486	26.444
4	12.515	5554295	194359	27.272
总计		20365995	808976	

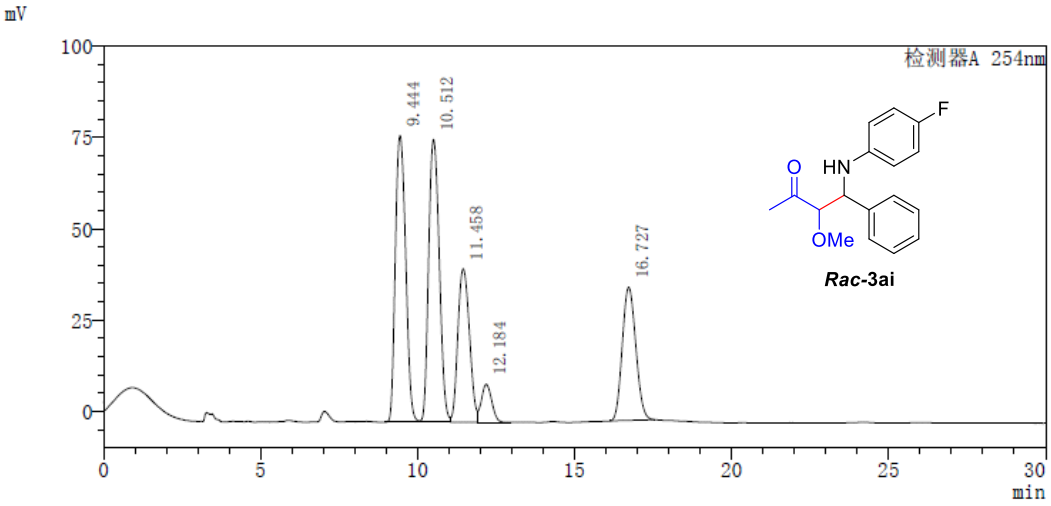
HPLC spectrum of 3ah



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.623	1592634	69449	15.612
2	11.217	520801	35238	5.105
3	11.633	6872395	246428	67.366
4	12.532	1215742	43084	11.917
总计		10201572	394199	

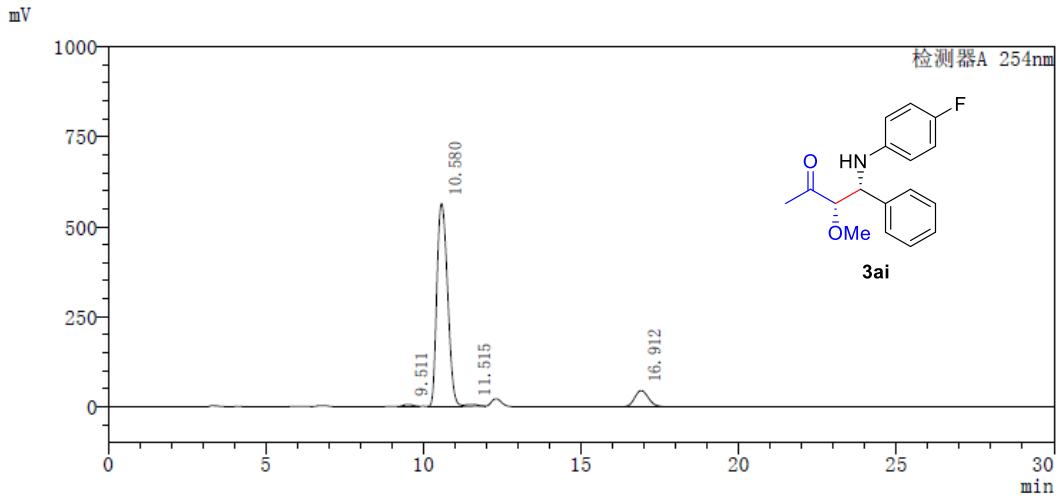
HPLC spectrum of *Rac*-3ai



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	9.444	1795703	78487	29.711
2	10.512	1832244	77469	30.316
3	11.458	1084629	42043	17.946
4	12.184	237274	10406	3.926
5	16.727	1094050	36452	18.102
总计		6043901	244857	

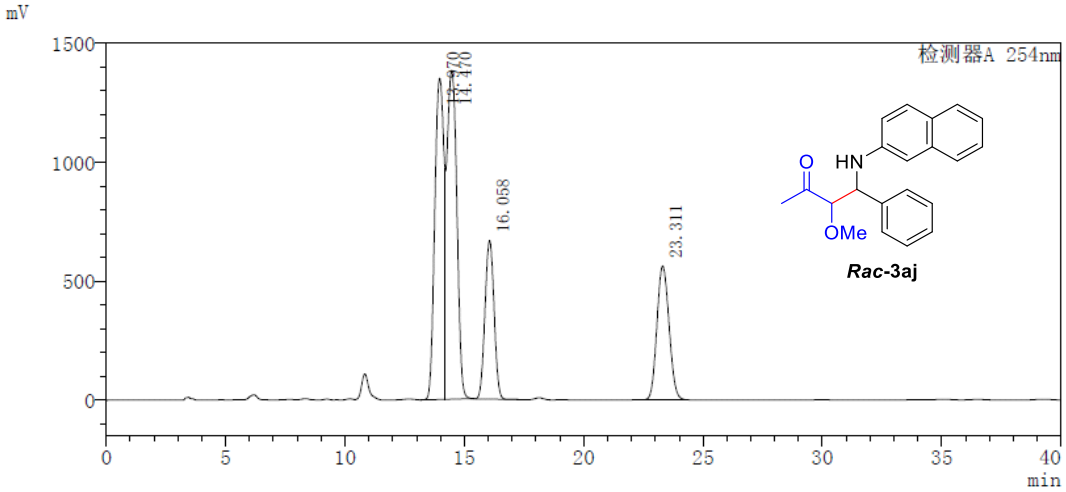
HPLC spectrum of 3ai



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	9.511	98415	4881	0.661
2	10.580	13317156	563811	89.488
3	11.515	128064	5038	0.861
4	16.912	1337870	44678	8.990
总计		14881506	618408	

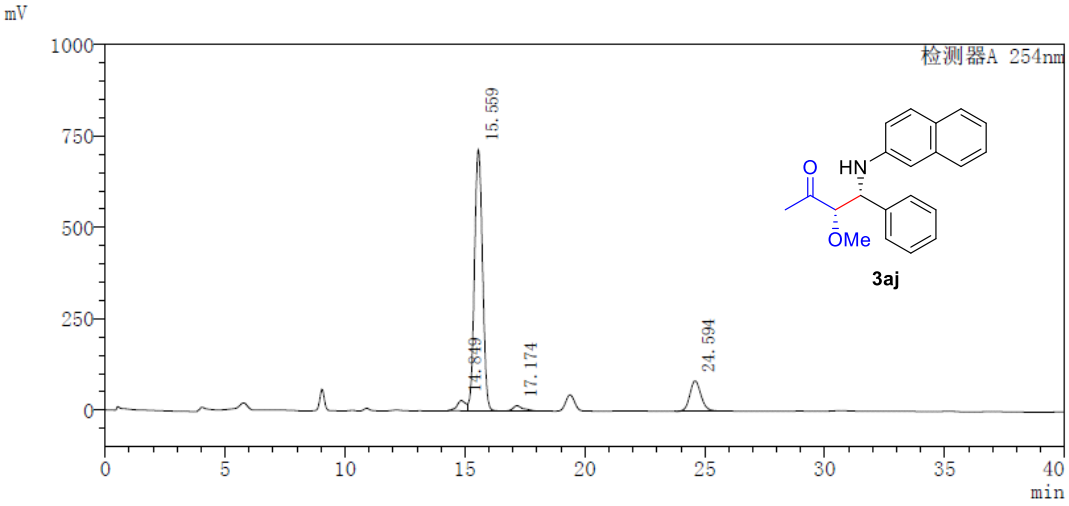
HPLC spectrum of *Rac*-3aj



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.970	35213422	1349077	31.127
2	14.470	40594571	1378470	35.884
3	16.058	17579209	666429	15.539
4	23.311	19739584	560217	17.449
总计		113126786	3954193	

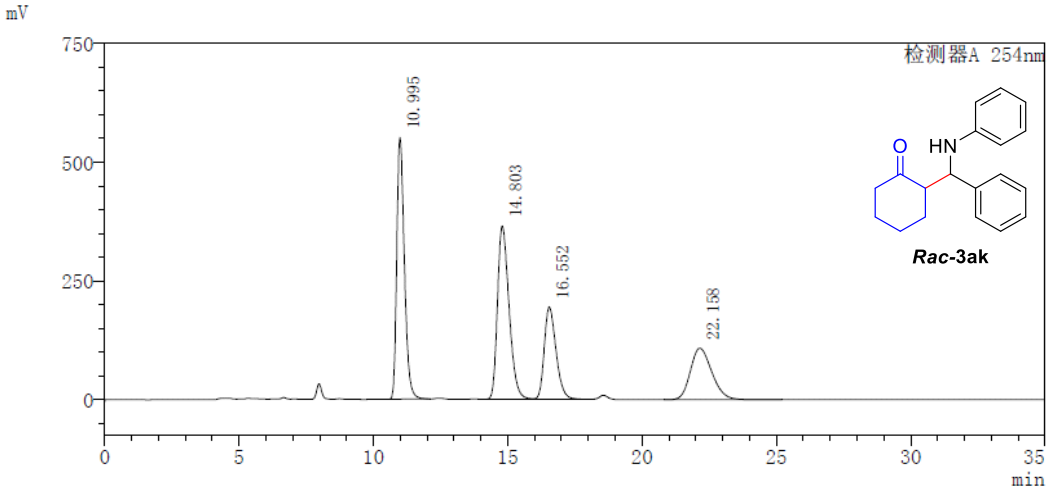
HPLC spectrum of 3aj



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.849	697129	28110	3.396
2	15.559	16794462	714230	81.813
3	17.174	401246	13801	1.955
4	24.594	2634962	82447	12.836
总计		20527799	838587	

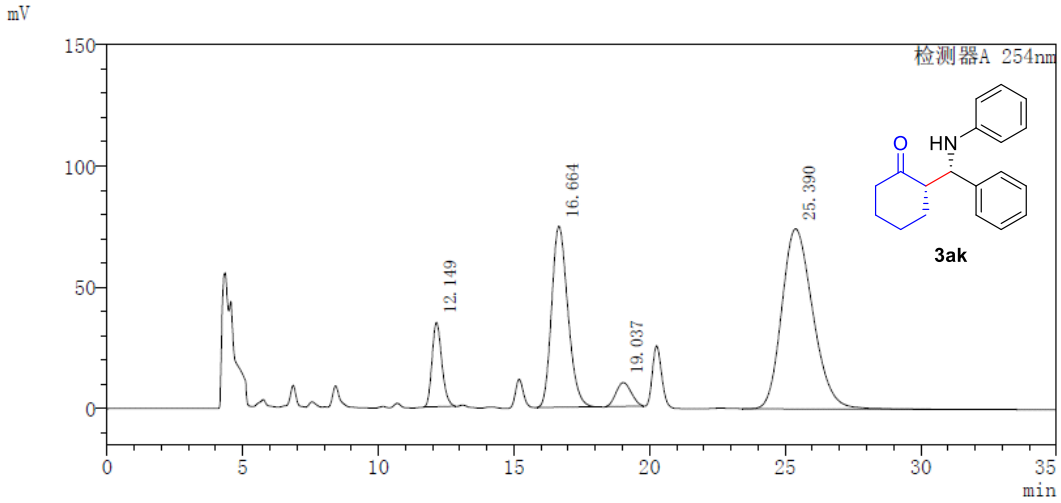
HPLC spectrum of *Rac*-3ak



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	10.995	10845118	550533	32.201
2	14.803	10933003	364964	32.462
3	16.552	5908103	193950	17.542
4	22.158	5993649	108212	17.796
总计		33679873	1217658	

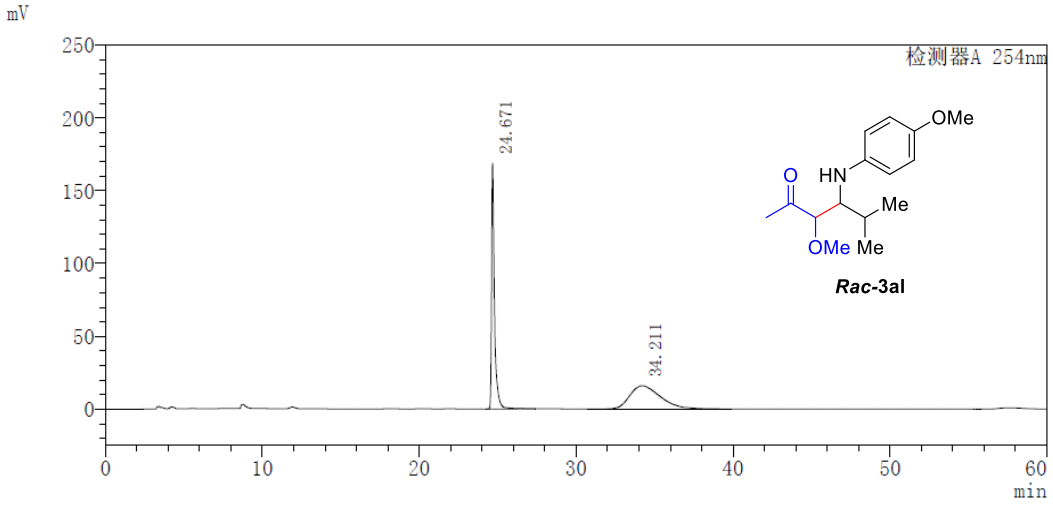
HPLC spectrum of 3ak



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.149	871622	34754	8.463
2	16.664	3109569	74608	30.192
3	19.037	383158	9766	3.720
4	25.390	5934820	74283	57.624
总计		10299169	193411	

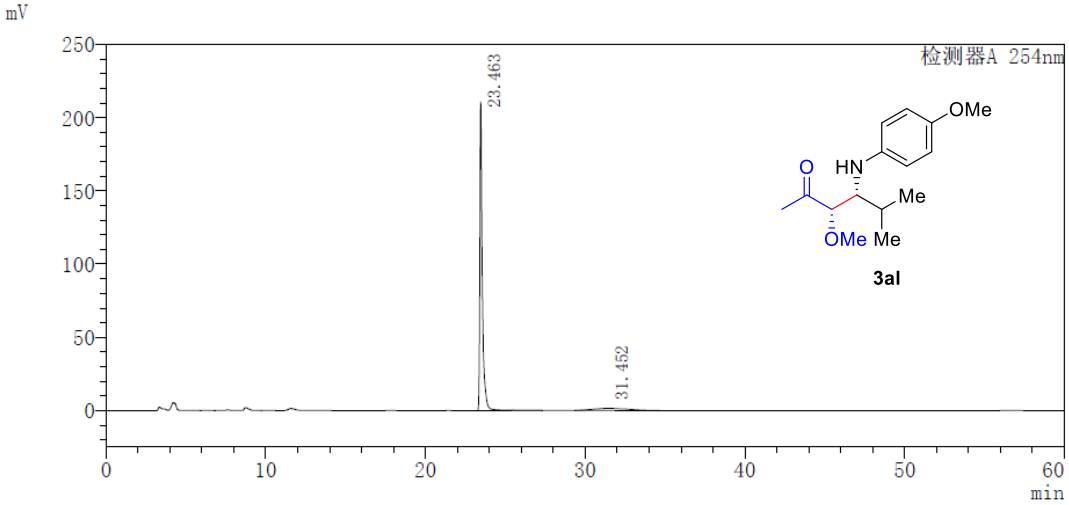
HPLC spectrum of *Rac*-3al



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	24.671	2166855	168975	50.051
2	34.211	2162402	15862	49.949
总计		4329257	184837	

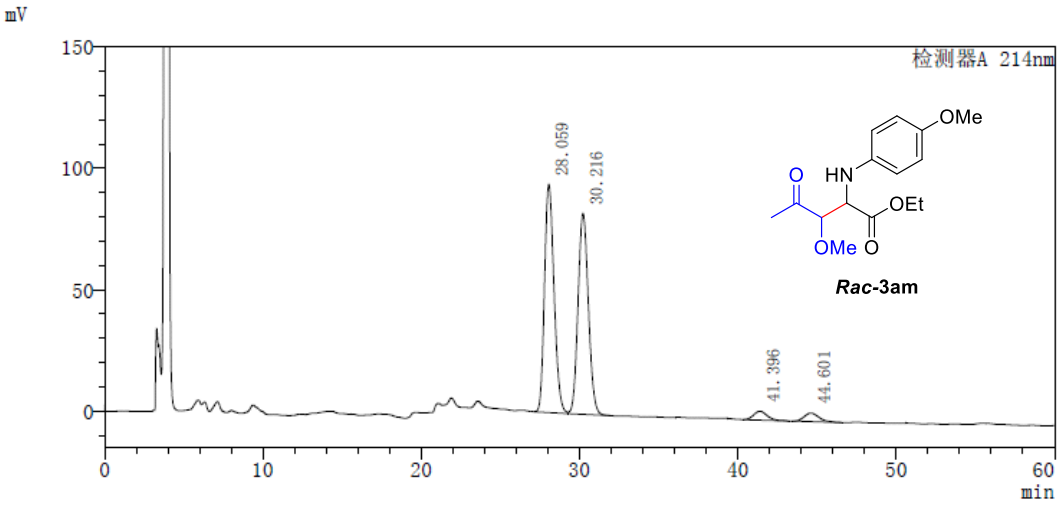
HPLC spectrum of 3al



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	23.463	2276615	210864	91.315
2	31.452	216519	1495	8.685
总计		2493134	212360	

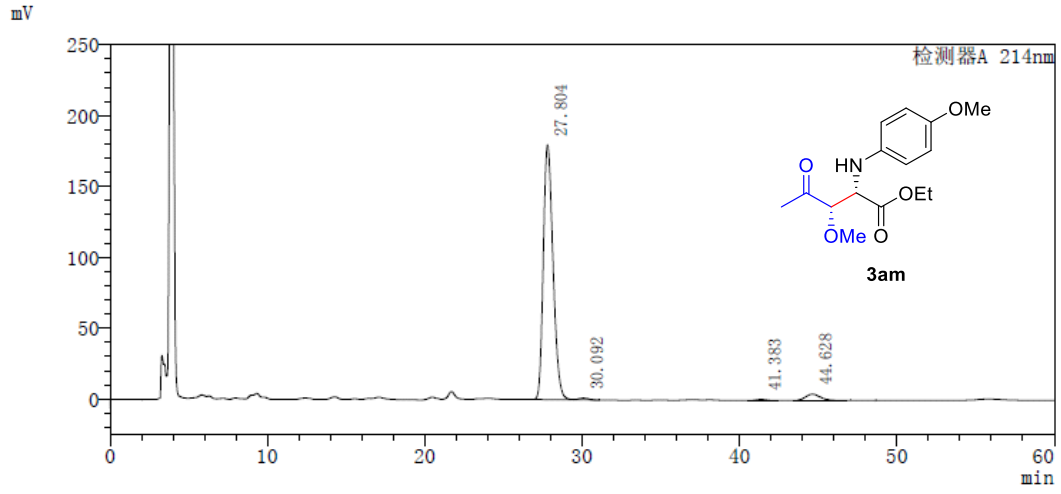
HPLC spectrum of *Rac*-3am



检测器A 214nm

No.	Retention Time	Area	Height	Concentration
1	28.059	3924433	93884	48.382
2	30.216	3733797	82751	46.032
3	41.396	221407	3691	2.730
4	44.601	231652	3536	2.856
总计		8111288	183862	

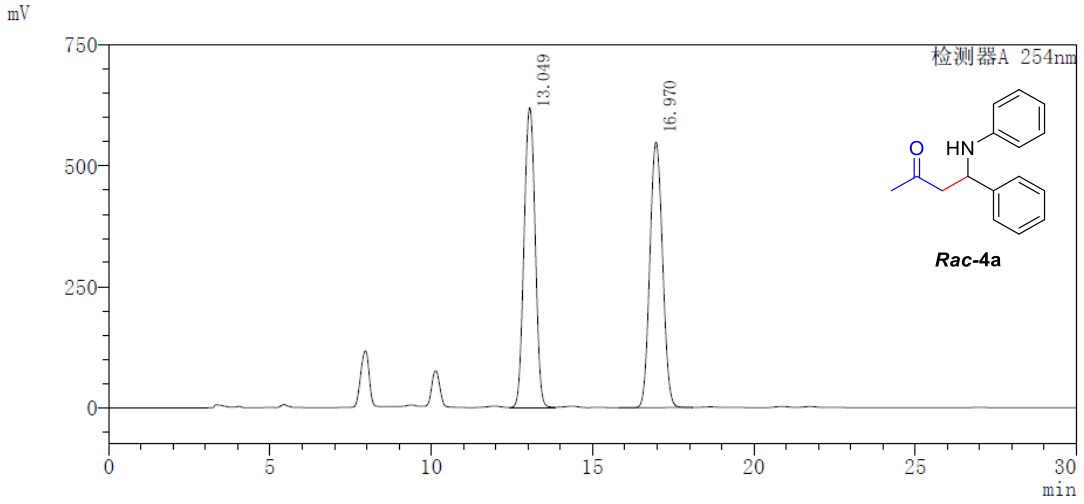
HPLC spectrum of 3am



检测器A 214nm

No.	Retention Time	Area	Height	Concentration
1	27.804	7688640	179610	95.365
2	30.092	59761	1332	0.741
3	41.383	31667	615	0.393
4	44.628	282260	4370	3.501
总计		8062328	185927	

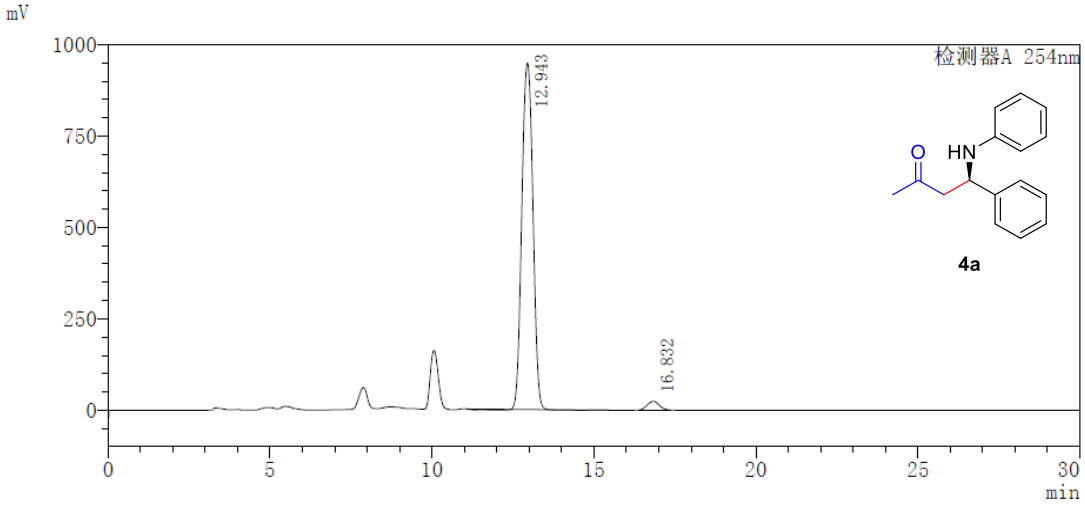
HPLC spectrum of *Rac*-4a



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.049	14853059	619249	49.676
2	16.970	15047056	548490	50.324
总计		29900115	1167739	

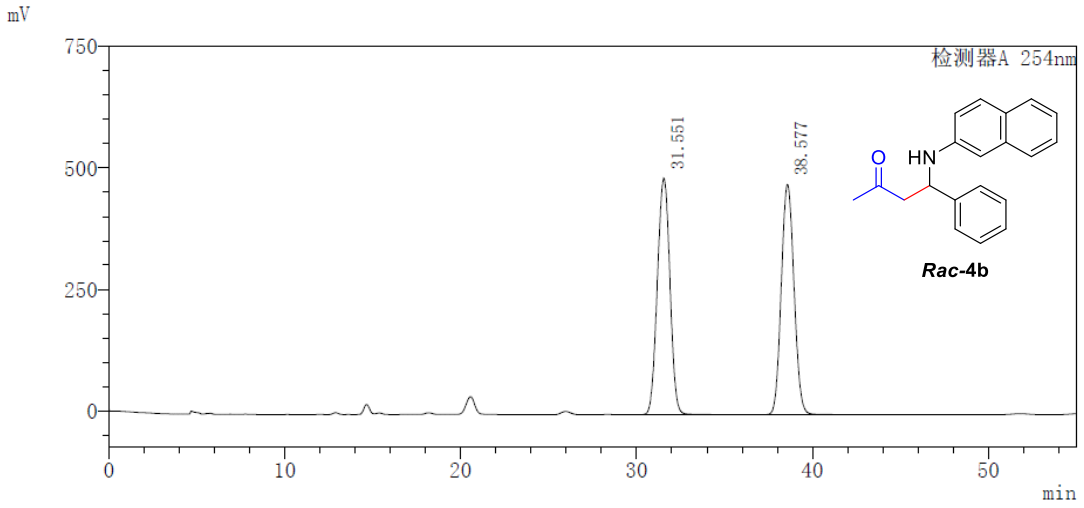
HPLC spectrum of 4a



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	12.943	22417274	948331	97.372
2	16.832	604957	24023	2.628
总计		23022230	972354	

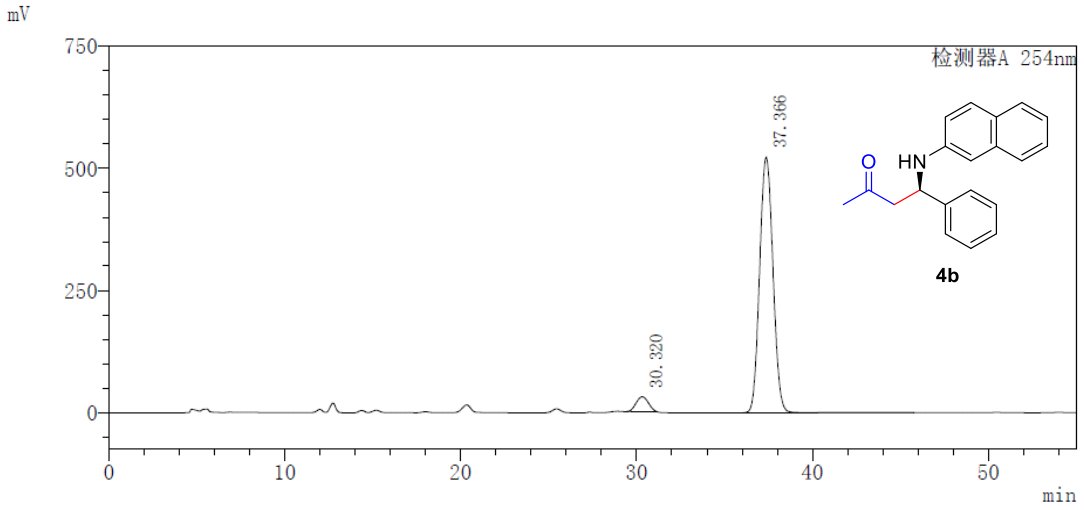
HPLC spectrum of *Rac*-4b



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	31.551	24173100	485771	50.312
2	38.577	23872976	473308	49.688
总计		48046076	959080	

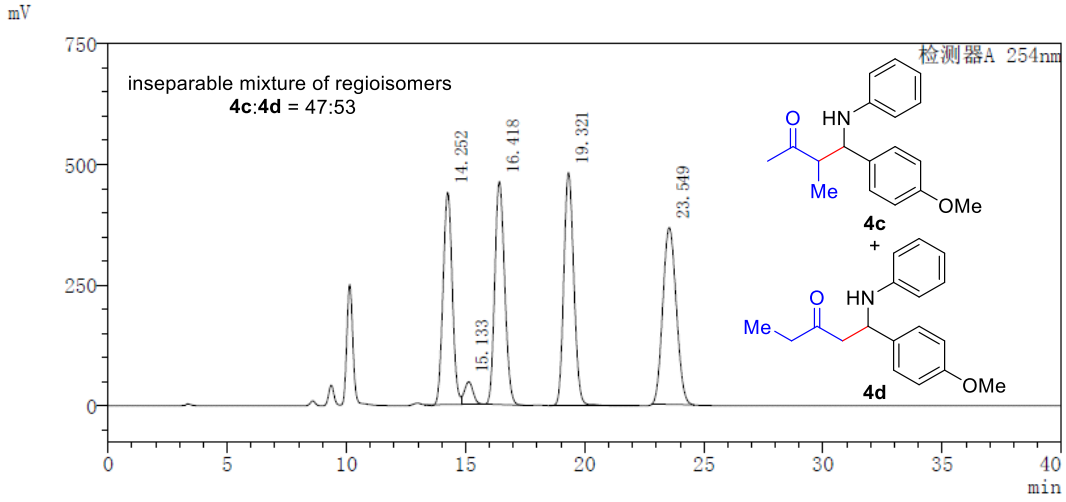
HPLC spectrum of 4b



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	30.320	1480819	30535	5.096
2	37.366	27576134	522405	94.904
总计		29056953	552940	

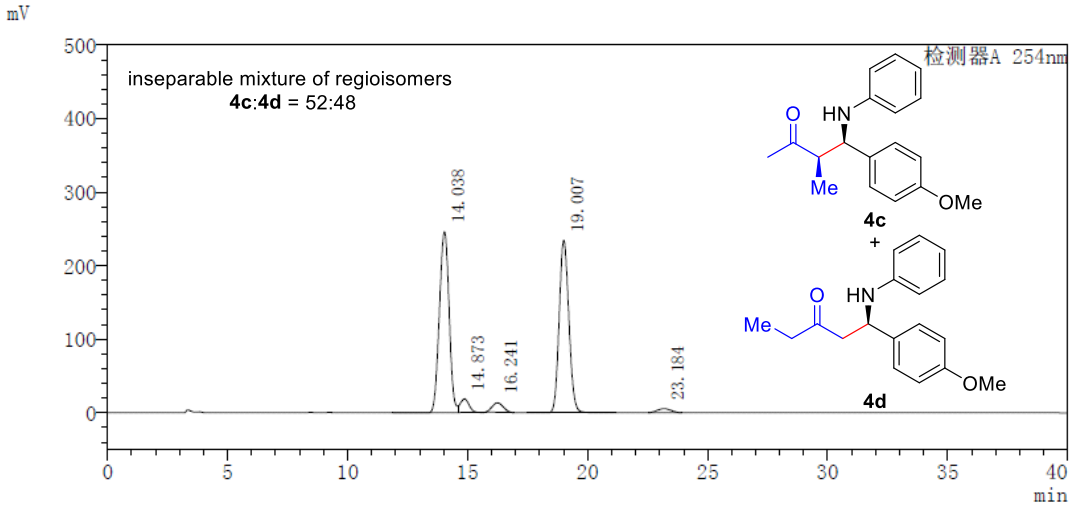
HPLC spectrum of *Rac*-4c and *Rac*-4d



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.252	11854063	439571	21.584
2	15.133	1181434	46745	2.151
3	16.418	13325754	461627	24.264
4	19.321	14130994	482755	25.730
5	23.549	14427114	366662	26.270
总计		54919359	1797360	

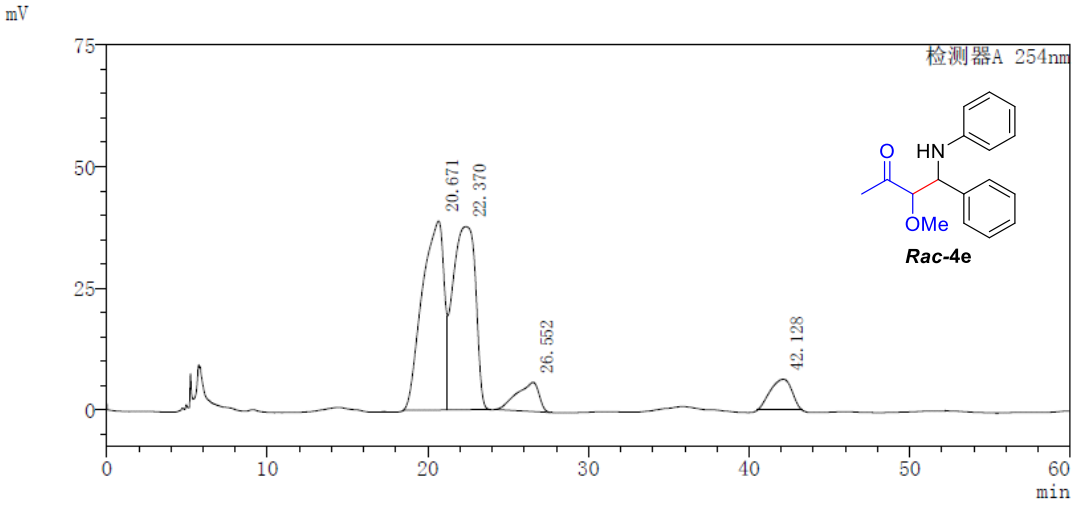
HPLC spectrum of 4c and 4d



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.038	6902397	245828	47.270
2	14.873	463776	18338	3.176
3	16.241	412298	12907	2.824
4	19.007	6604605	234504	45.230
5	23.184	219066	5428	1.500
总计		14602142	517005	

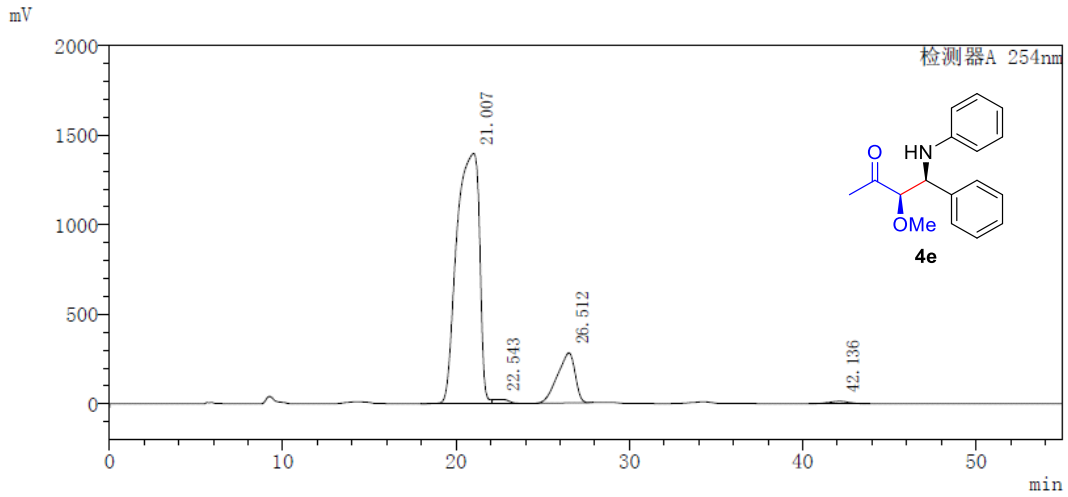
HPLC spectrum of *Rac*-4e



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	20.671	3712079	38835	43.246
2	22.370	3710810	37636	43.231
3	26.552	574835	5995	6.697
4	42.128	585966	6304	6.827
总计		8583690	88770	

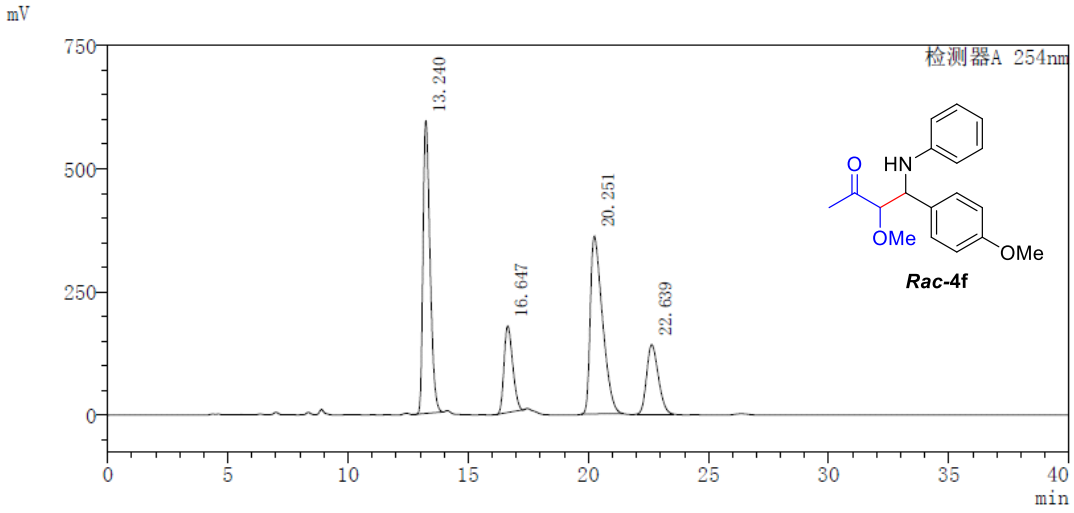
HPLC spectrum of 4e



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	21.007	126808201	1396919	85.162
2	22.543	1383489	21959	0.929
3	26.512	19762638	279239	13.272
4	42.136	948666	12365	0.637
总计		148902994	1710481	

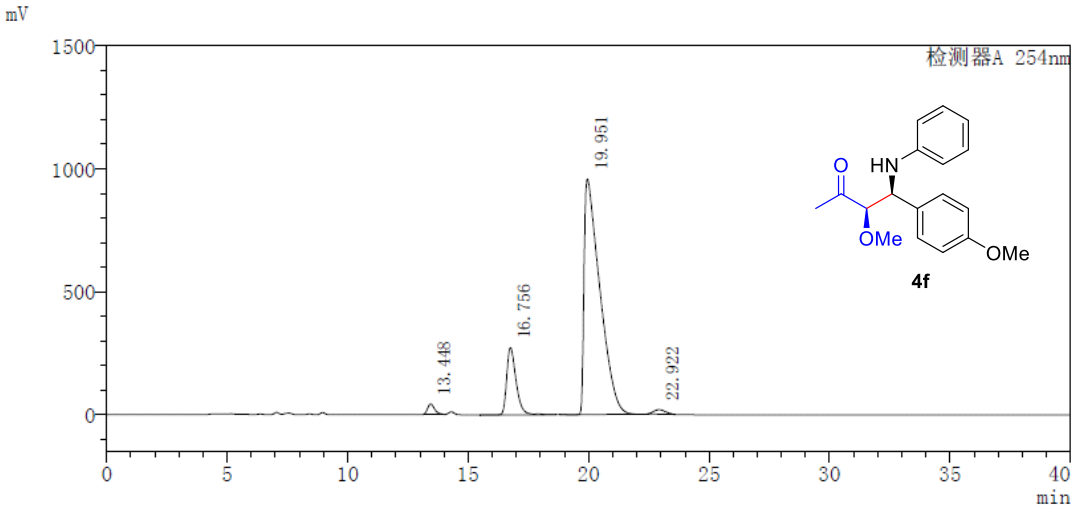
HPLC spectrum of *Rac*-4f



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.240	11985141	594082	35.323
2	16.647	4419346	176029	13.025
3	20.251	12750932	360545	37.580
4	22.639	4774588	140941	14.072
总计		33930008	1271598	

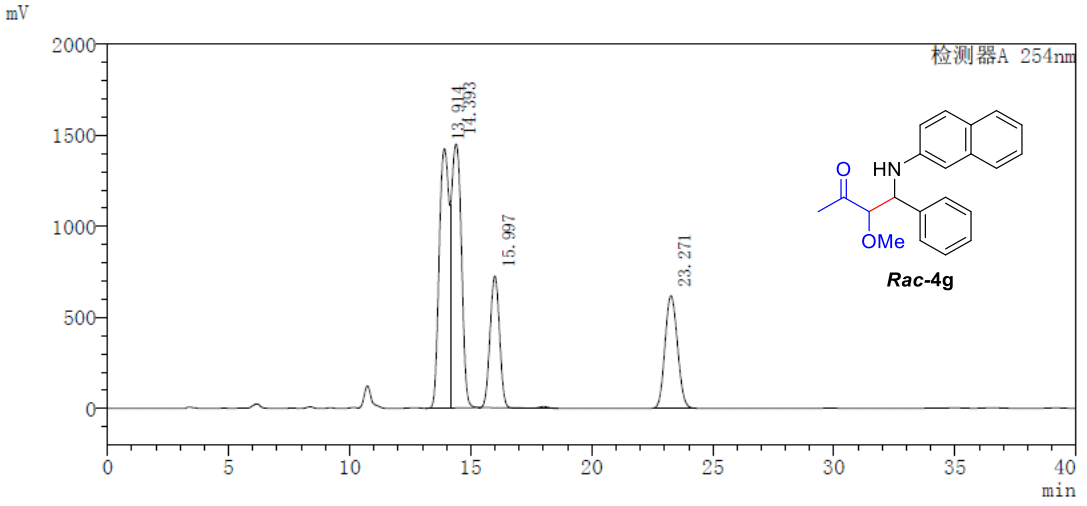
HPLC spectrum of 4f



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.448	807153	41426	1.547
2	16.756	7400046	273727	14.181
3	19.951	43376115	958641	83.123
4	22.922	599813	17808	1.149
总计		52183127	1291602	

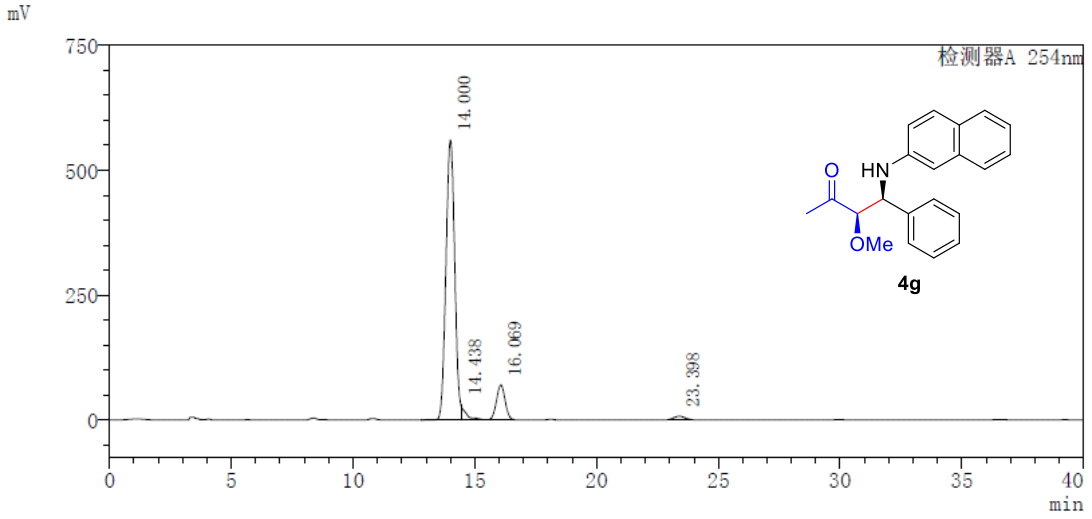
HPLC spectrum of *Rac*-4g



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	13.914	40017783	1423786	32.564
2	14.393	41121893	1449377	33.463
3	15.997	19833856	721905	16.140
4	23.271	21915001	615831	17.833
总计		122888533	4210899	

HPLC spectrum of 4g



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	14.000	13820479	559848	86.116
2	14.438	395704	28802	2.466
3	16.069	1638031	68564	10.207
4	23.398	194504	6742	1.212
总计		16048719	663955	