

## Supporting Information

# Iridium-catalyzed Direct Asymmetric Reductive Amination of Aromatic Ketones

Haizhou Huang,<sup>a</sup> Zitong Wu,<sup>a</sup> Guori Gao,<sup>b</sup> Le Zhou<sup>a</sup> and Mingxin Chang<sup>\*a</sup>

<sup>a</sup>Shaanxi Key Laboratory of Natural Products & Chemical Biology, College of Chemistry and Pharmacy, Northwest A&F University, 22 Xinong Road, Yangling, Shaanxi 712100, PR China

<sup>b</sup>College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Shandong Normal University, 88 Wenhudong Road, Jinan 250014, PR China.

Phone/fax: (+86)-29-8709-2662; e-mail: mxchang@nwsuaf.edu.cn

## CONTENTS

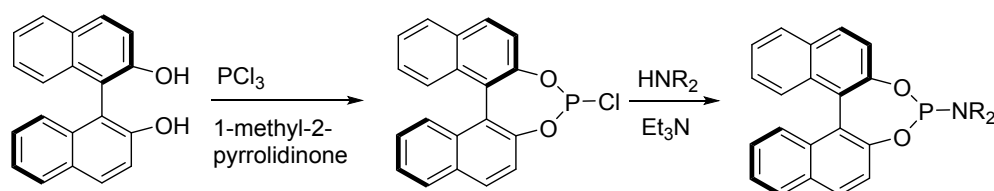
I	General Remarks	S2
II	General Procedure for Preparation of Monophos-type Ligands	S2
III	General Procedure for Asymmetric Reductive Amination	S2
IV	General Procedure for Removal of Diphenylmethyl Group	S23
V	References	S25
VI	NMR & HRMS Spectra	S26

## I. General remarks

All reactions were performed in the nitrogen-filled glovebox or under nitrogen using standard Schlenk techniques unless otherwise noted. Chemicals were purchased from Adamas, Energy Chemicals and other companies. Column chromatography was performed using silica gel 60 (200–300 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data were obtained from Bruker 500 MHz spectrometers. Chemical shifts are reported in ppm. Enantiomeric excess values were determined by chiral HPLC on an Agilent 1220 Series instrument or by  $^1\text{H}$  NMR using (*S*)-2-acetoxy-2-phenylacetic acid as shift reagent. All new products were further characterized by HRMS. A positive ion mass spectrum of sample was acquired on a Thermo Scientific LTQ Orbitrap XL mass spectrometer with an electrospray ionization source.

## II. General Procedure for Preparation of Monophos-type ligands

Ligands **L1a–e** were synthesized according to the reported procedures.<sup>[1]</sup>



A 25 mL Schlenk flask was charged with (*R*)-(+)-1,1'-bi(2-naphthol) (0.57g, 2 mmol), phosphorus trichloride (2.74 g, 20 mmol, 10 equiv), 1-methyl-2-pyrrolidinone (1.6  $\mu\text{L}$ , 0.02 mmol, 0.008 equiv) under nitrogen. The reaction mixture was heated to 90  $^\circ\text{C}$  for 15 min, and all volatiles were removed under reduced pressure.  $\text{CH}_2\text{Cl}_2$  (2 mL  $\times$  2) was used to remove the traces of phosphorus trichloride. The resulting oil was vacuummed for 3 h to give the pale solid which was used directly in next step.

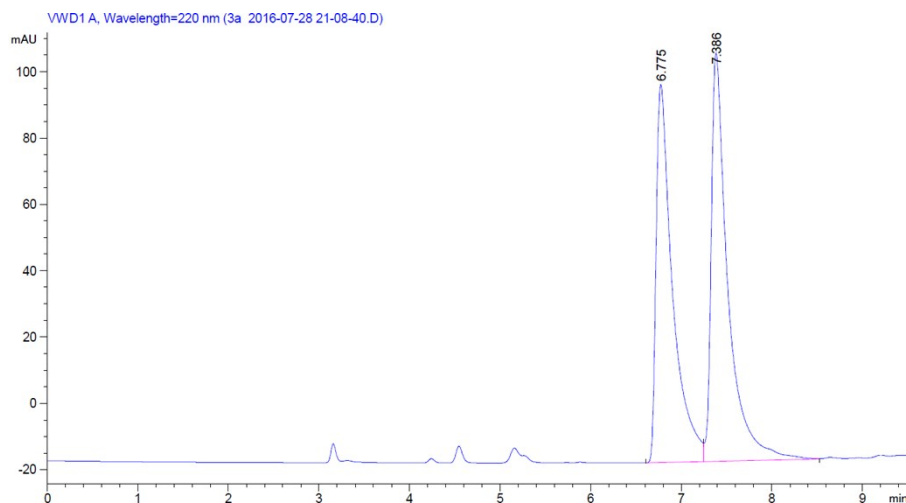
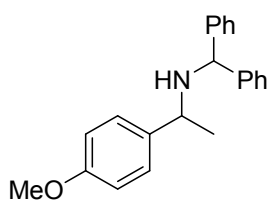
A 25 mL round-bottom flask was charged with 2 mmol of corresponding amine, 3 mmol of  $\text{Et}_3\text{N}$  and 10 ml toluene. The above made chlorophosphite was dissolved in 5 mL toluene and was transferred to the reaction flask. The mixture was stirred for 3 h. The solid was removed by filtration. The filtrate was concentrated and purified by flash column chromatography (EtOAc/Hex) to yield desired ligand (yield: 75–95%).

## III. General Procedure for Asymmetric Reductive amination

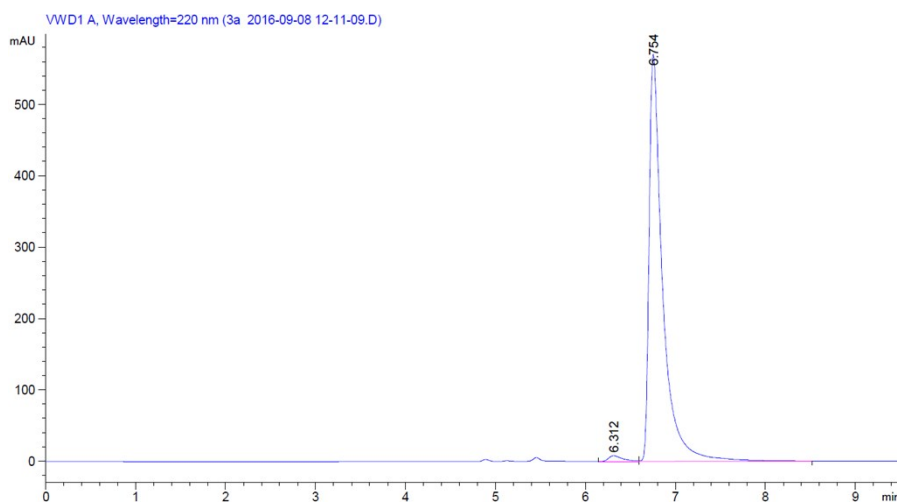
In a nitrogen-filled glovebox, the complex (0.5 mol%) prepared from *in situ* from  $[\text{Ir}(\text{COD})\text{Cl}]_2$  and **L1d** in anhydrous  $\text{CH}_2\text{Cl}_2$  was added to 4-acetoanisole **1a** (0.3 mmol) and diphenylmethylamine **2** (0.39 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  solution (1.0 mL). Then 4 $\text{\AA}$  molecular sieves (0.15 gram),  $\text{Ti}(\text{O}i\text{-Pr})_4$  (0.2 equiv.), and trifluoroacetic acid (0.5 equiv.) were added subsequently and the total solution was made to 3.0 mL. The resulting vial was transferred to an autoclave, which was charged with 60 atm of  $\text{H}_2$ , and stirred at 50  $^\circ\text{C}$  for 24 h. The hydrogen gas was released slowly and the solution was neutralized with aqueous sodium bicarbonate solution. The organic phase was concentrated and passed through a short column of silica gel to remove the metal complex to give the 80mg chiral amine product, which was then analyzed by chiral HPLC to determine the enantiomeric excesses.

$^1\text{H}$  NMR method for determination the ee values: The amine product **3** was mixed with equal amount (mol/mol) of (*S*)-2-acetoxy-2-phenylacetic acid and dissolved in  $\text{CDCl}_3$ . Diastereoisomers are formed and the proton signal of amine  $\beta$ -methyl will be splitted. From integration ratio the ee value could be calculated.

***N*-benzhydryl-1-(4-methoxyphenyl)ethan-1-amine (3a)**: 84% yield, 97% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -49.1^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 4.9$  Hz, 4H), 7.31 (dd,  $J = 14.1, 6.5$  Hz, 5H), 7.23 (d,  $J = 8.6$  Hz, 3H), 6.94 (d,  $J = 8.5$  Hz, 2H), 4.69 (s, 1H), 3.88 (s, 3H), 3.69 (q,  $J = 6.5$  Hz, 1H), 1.41 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 144.7, 143.7, 137.7, 128.5, 128.4, 127.7, 127.7, 127.4, 127.0, 126.8, 113.8, 63.7, 55.3, 54.5, 24.5. IR (KBr)  $\nu$ : 3308.0, 3060.4, 3024.8, 2962.8, 1504.6, 1243.8  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak IB-3 column, Hex/IPA = 99.5:0.5, 1 mL/min, 220 nm, 6.8 min, 7.4 min. HRMS calcd for  $\text{C}_{22}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$ : 318.18504, found: 318.18512.

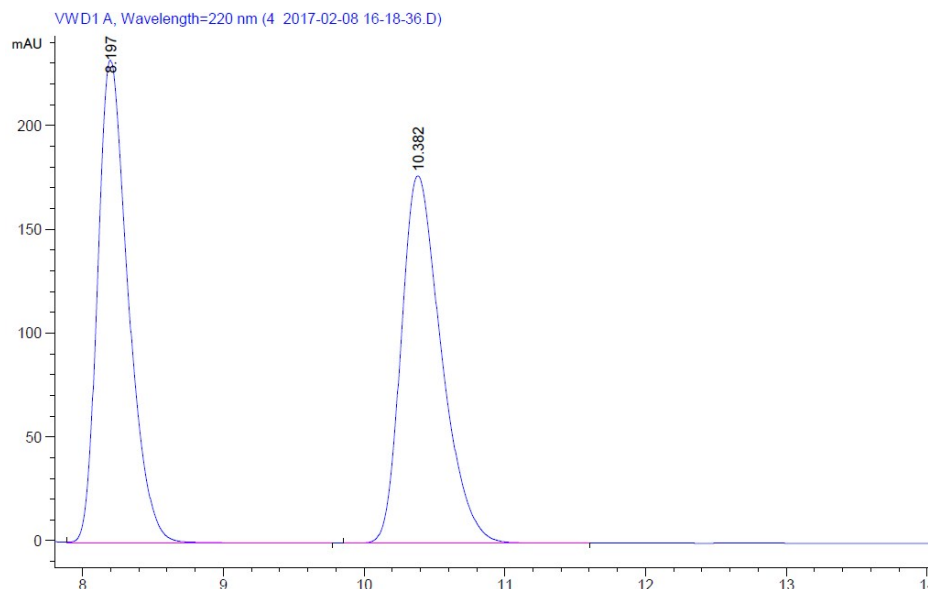
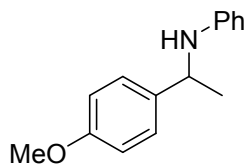


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.775	BV	0.1815	1440.24280	113.94901	47.6601
2	7.386	VV	0.1819	1581.66492	123.11803	52.3399

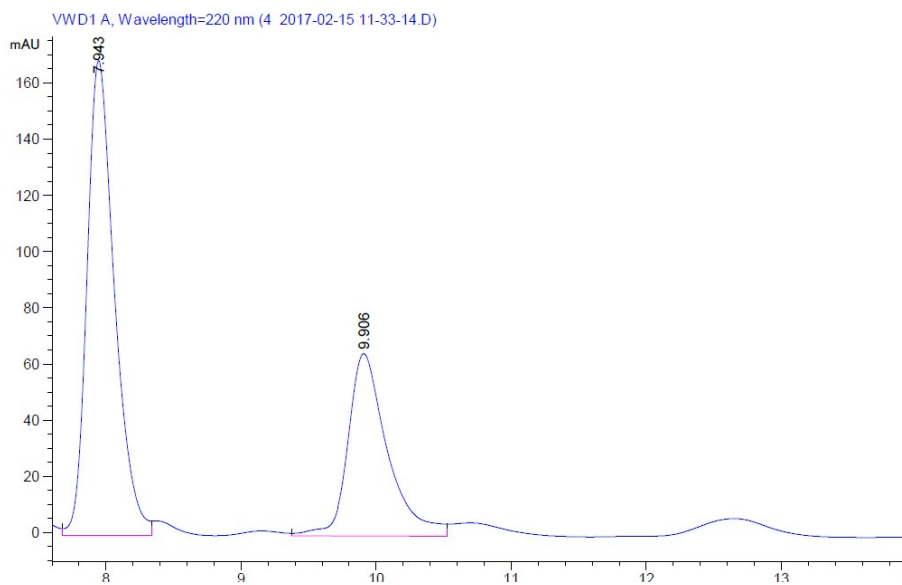


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.312	BV	0.1607	87.42606	8.05050	1.4493
2	6.754	VB	0.1496	5945.05225	570.43250	98.5507

***N*-(1-(4-methoxyphenyl)ethyl)aniline(4):** <sup>[3]</sup> 77% yield, 29% ee, clear oil, known compound. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 8.6 Hz, 2H), 7.20–7.08 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 2H), 4.50 (q, *J* = 6.7 Hz, 1H), 3.84 (s, 3H), 1.55 (d, *J* = 6.7 Hz, 3H). Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 90:10, 1 mL/min, 220 nm, 8.2 min, 10.4 min.

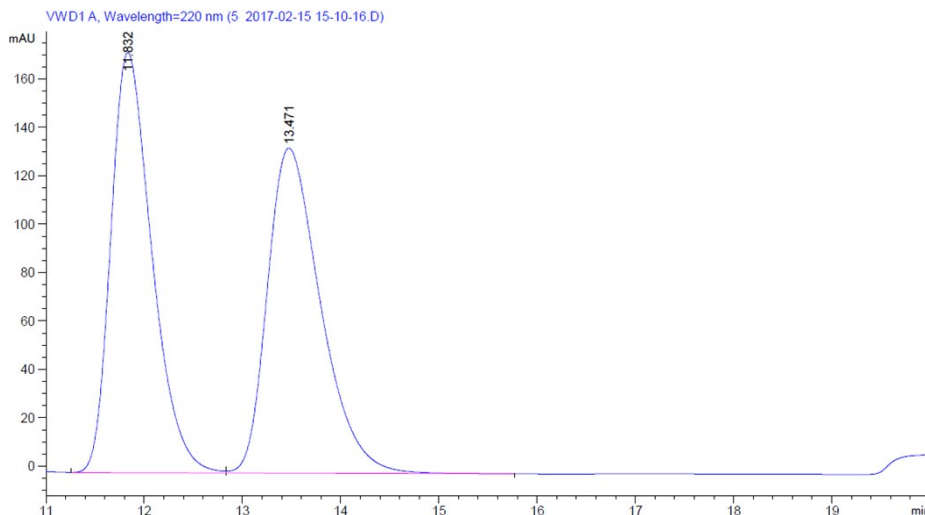
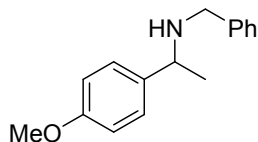


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.197	VB	0.2277	3500.34937	232.46826	50.0163
2	10.382	BB	0.3017	3498.07080	176.92244	49.9837

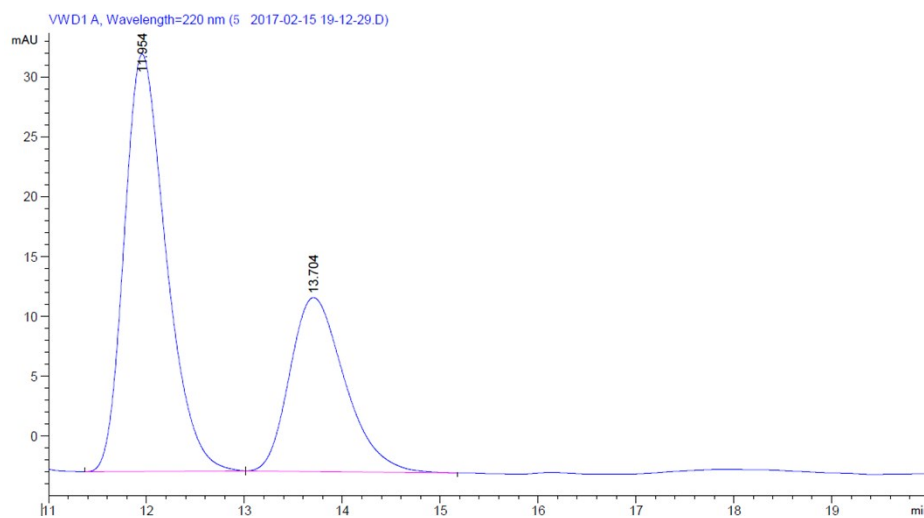


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.943	VV	0.2132	2395.19824	169.14493	64.4247
2	9.906	VV	0.2986	1322.62549	64.93051	35.5753

***N*-benzyl-1-(4-methoxyphenyl)ethan-1-amine(5):**<sup>[4]</sup> 47% yield, 29% ee, clear oil, known compound. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38–7.27 (m, 7H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 3.82 (q, *J* = 6.6 Hz, 1H), 3.74–3.59 (m, 2H), 1.40 (d, *J* = 6.6 Hz, 3H). Enantiomeric excess was determined by chiral HPLC for the corresponding acetamide: Chiralpak OD-H column, Hex/IPA = 90:10, 1 mL/min, 220 nm, 11.8 min, 13.5 min.

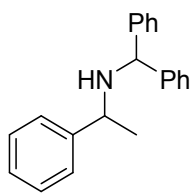


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.832	BV	0.4453	5032.97266	173.56529	49.9189
2	13.471	VB	0.5756	5049.32813	134.31917	50.0811

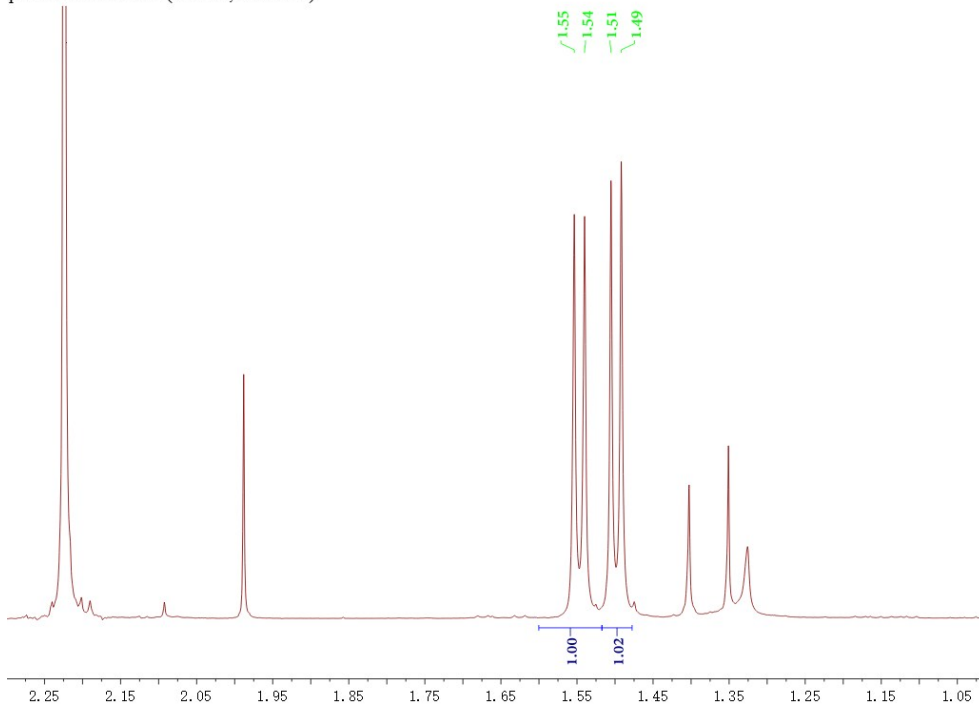


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.954	BB	0.4525	1036.36377	34.89234	64.6333
2	13.704	BB	0.5979	567.08893	14.54519	35.3667

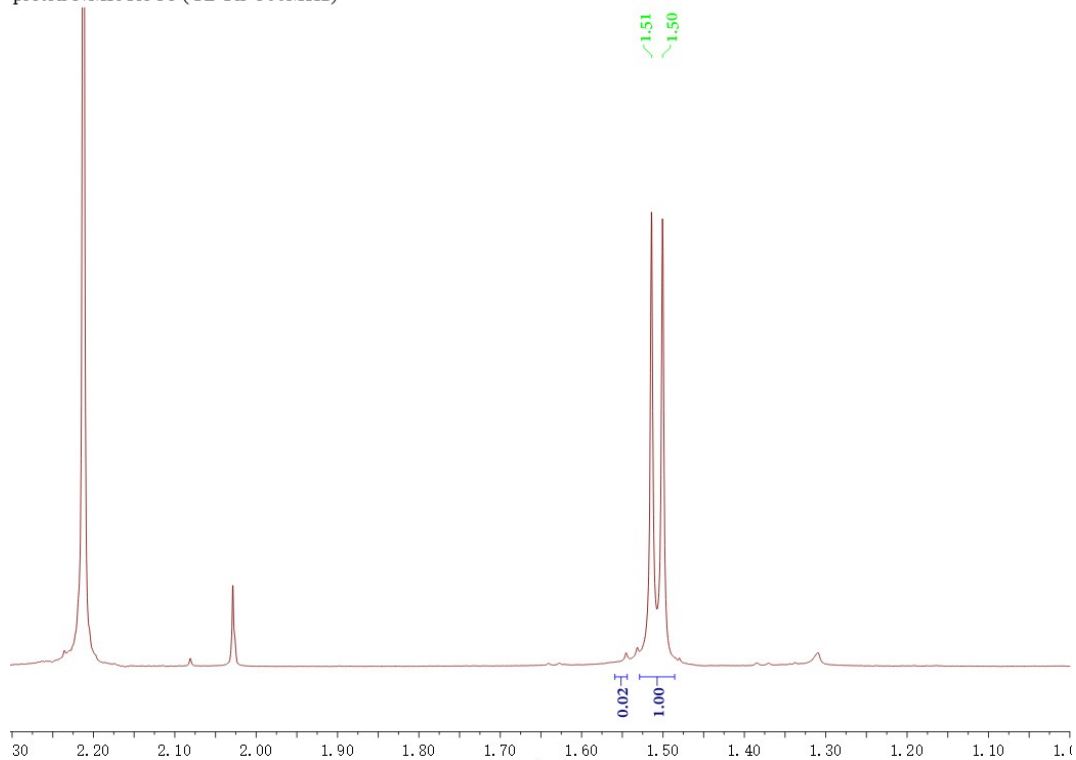
***N*-benzhydryl-1-phenylethan-1-amine (3b):**<sup>[2]</sup> 90% yield, 96% ee, clear oil, known compound.  $[\alpha]_D^{25} = -38.2^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (t,  $J = 7.3$  Hz, 6H), 7.32 (td,  $J = 11.9, 9.9, 7.1$  Hz, 8H), 7.25–7.21 (m, 1H), 4.70 (s, 1H), 3.76 (q,  $J = 6.7$  Hz, 1H), 1.43 (d,  $J = 6.7$  Hz, 3H). IR (KBr)  $\nu$ : 3457.6, 3063.2, 3026.4, 2966.5, 1452.0, 1116.5  $\text{cm}^{-1}$ . Enantiomeric excess was determined by  $^1\text{H NMR}$  using (*S*)-2-acetoxy-2-phenylacetic acid as shift reagent.



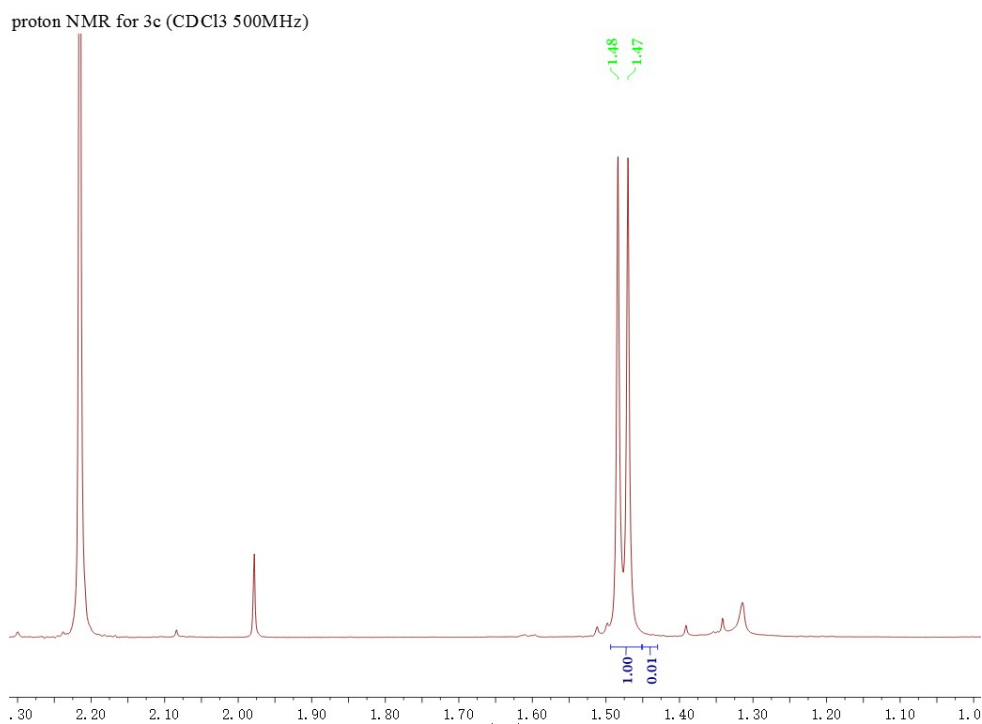
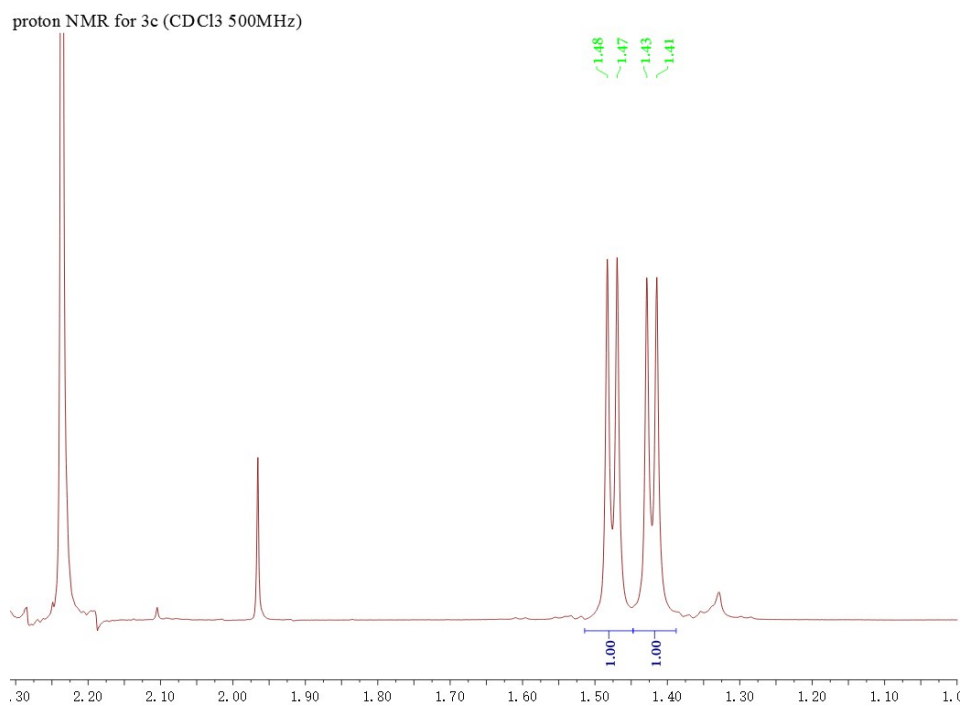
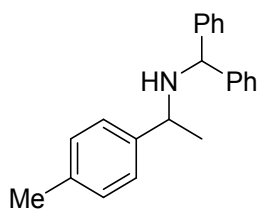
proton NMR for 3b ( $\text{CDCl}_3$ , 500MHz)



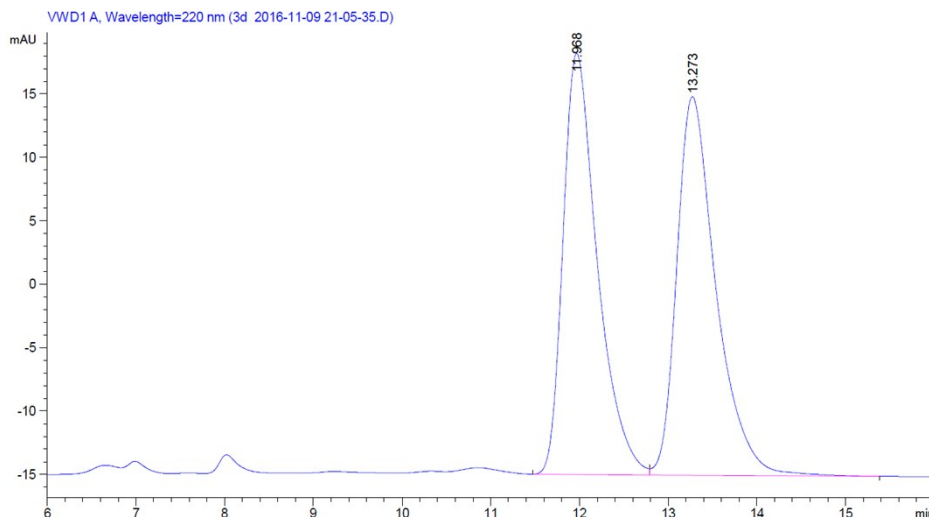
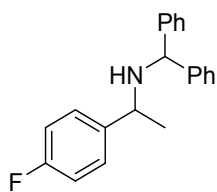
proton NMR for 3b ( $\text{CDCl}_3$  500MHz)



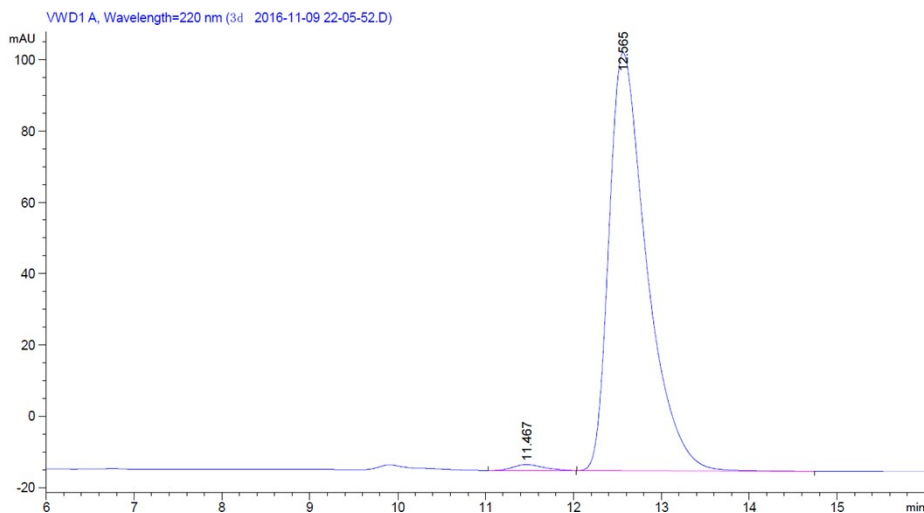
***N*-benzhydryl-1-(*p*-tolyl)ethan-1-amine (3c)**: 83% yield, 99% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -54.0^\circ$  ( $c = 0.4$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (dt,  $J = 15.9, 7.4$  Hz, 6H), 7.31 (t,  $J = 7.6$  Hz, 3H), 7.22 (s, 5H), 4.72 (s, 1H), 3.74 (s, 1H), 2.43 (s, 3H), 1.42 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 143.7, 142.6, 136.4, 129.2, 128.5, 128.4, 127.7, 127.4, 127.0, 126.8, 126.6, 63.7, 54.9, 24.5, 21.2. IR (KBr)  $\nu$ : 3436.1, 3022.6, 3026.4, 2966.5, 1450.8  $\text{cm}^{-1}$ . Enantiomeric excess was determined by  $^1\text{H NMR}$  using (*S*)-2-acetoxy-2-phenylacetic acid as shift reagent. HRMS calcd for  $\text{C}_{22}\text{H}_{22}\text{N}$   $[\text{M}+\text{H}]^+$ : 302.19033, found: 302.1904.



***N*-benzhydryl-1-(4-fluorophenyl)ethan-1-amine (3d)**: 89% yield, 98% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -33.0^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (m, 12H), 7.07 (t,  $J = 8.7$  Hz, 2H), 4.65 (s, 1H), 3.73 (q,  $J = 6.7$  Hz, 1H), 1.40 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  128.6, 128.4, 128.2, 128.2, 127.7, 127.4, 127.1, 127.0, 115.3, 115.2, 63.8, 54.6, 24.5. IR (KBr)  $\nu$ : 3441.4, 2967.2, 1641.6, 1491.4  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 99.6:0.4, 0.9 mL/min, 220 nm, 12.0 min, 13.3 min. HRMS calcd for  $\text{C}_{21}\text{H}_{21}\text{FN}$   $[\text{M}+\text{H}]^+$ : 306.16525, found: 306.16516.



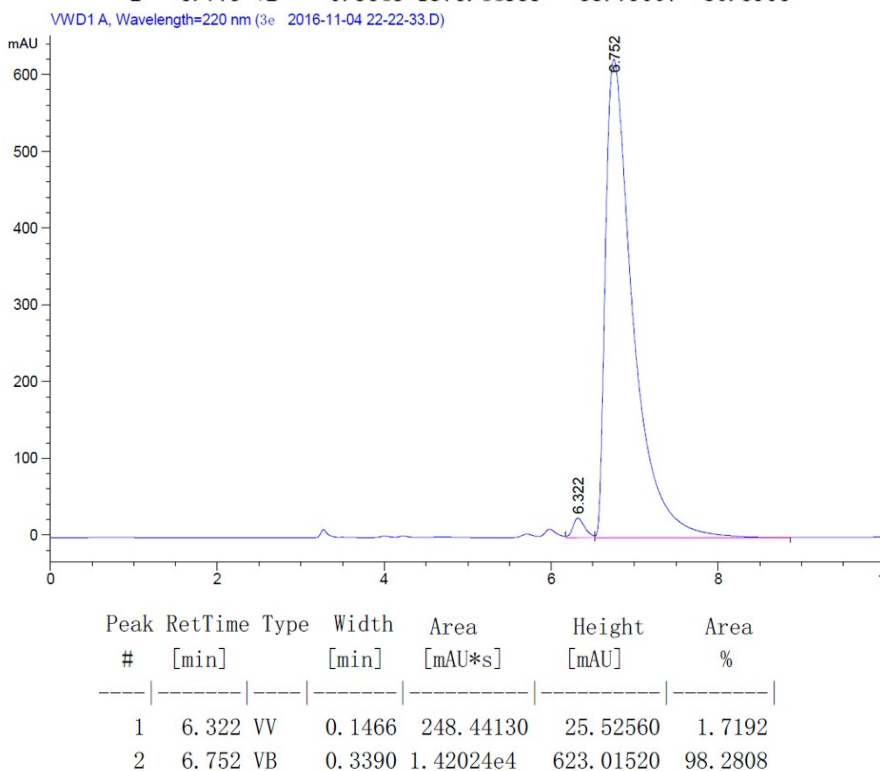
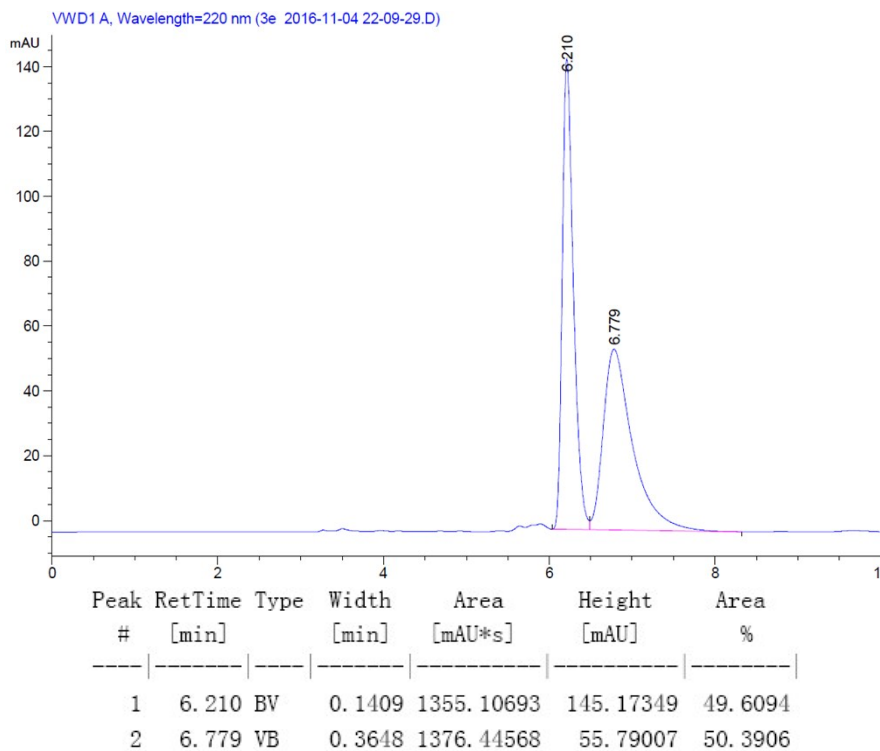
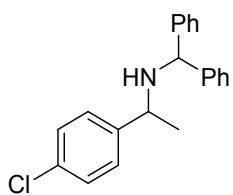
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.968	BV	0.4045	892.36261	33.21243	49.3041
2	13.273	VB	0.4606	917.55286	29.84810	50.6959



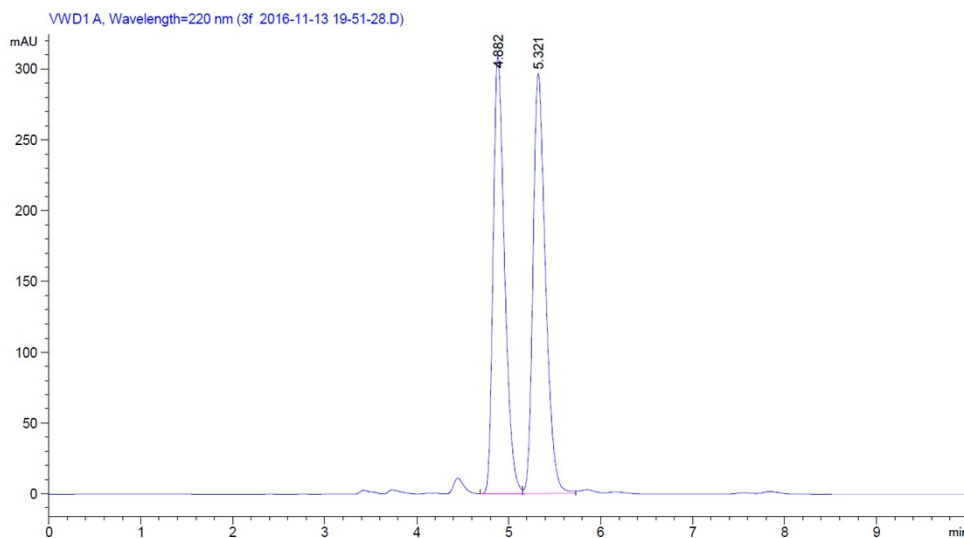
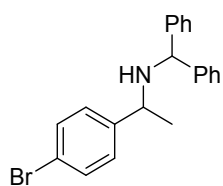
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.467	MM	0.4120	41.96301	1.69744	1.1905
2	12.565	BB	0.4466	3482.93506	117.24285	98.8095



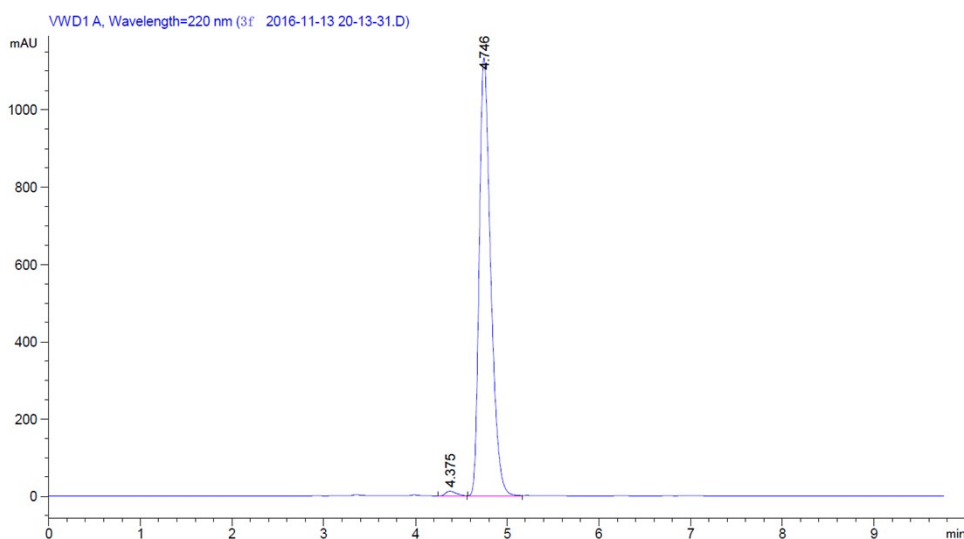
***N*-benzhydryl-1-(4-chlorophenyl)ethan-1-amine (3e)**: 87% yield, 97% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -63.0^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J = 10.7, 7.5$  Hz, 6H), 7.33–7.27 (m, 5H), 7.25 (d,  $J = 8.4$  Hz, 3H), 4.64 (s, 1H), 3.71 (q,  $J = 6.7$  Hz, 1H), 1.39 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 144.1, 143.4, 132.4, 128.6, 128.5, 128.4, 128.1, 127.6, 127.3, 127.1, 127.0, 63.8, 54.6, 24.4. IR (KBr)  $\nu$ : 3463.7, 3061.3, 3026.9, 2969.2, 1488.2, 828.2  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 99.5:0.5, 0.9 mL/min, 220 nm, 6.2min, 6.8 min. HRMS calcd for  $\text{C}_{21}\text{H}_{21}\text{ClN}$   $[\text{M}+\text{H}]^+$ : 322.13570, found: 322.13556.



***N*-benzhydryl-1-(4-bromophenyl)ethan-1-amine (3f)**: 80% yield, 98% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -66.9^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.3$  Hz, 2H), 7.41–7.28 (m, 9H), 7.24 (t,  $J = 6.8$  Hz, 1H), 7.20 (d,  $J = 8.3$  Hz, 2H), 4.65 (s, 1H), 3.71 (q,  $J = 6.6$  Hz, 1H), 1.40 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 144.4, 143.4, 131.6, 128.6, 128.5, 128.4, 127.6, 127.3, 127.1, 127.0, 120.5, 63.8, 54.7, 24.4. IR (KBr)  $\nu$ : 3446.6, 2967.6, 1640.5, 1016.9  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 98:2, 1 mL/min, 220 nm, 4.4 min, 4.8 min. HRMS calcd for  $\text{C}_{21}\text{H}_{21}\text{BrN}$   $[\text{M}+\text{H}]^+$ : 366.08519, found: 366.08524.

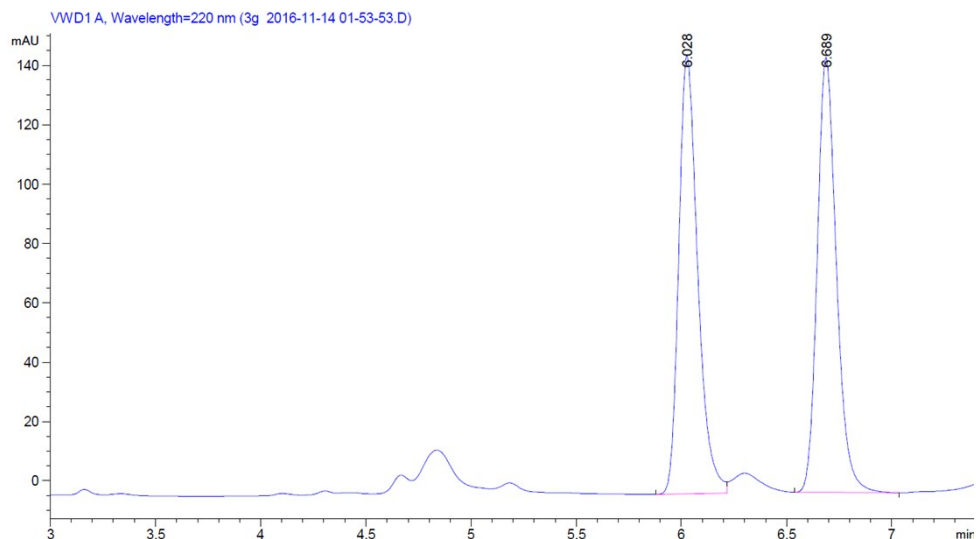
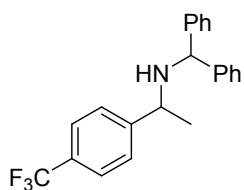


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.415	BV	0.1212	1645.57019	206.03586	48.9521
2	4.808	VV	0.1328	1716.01917	196.65742	51.0479

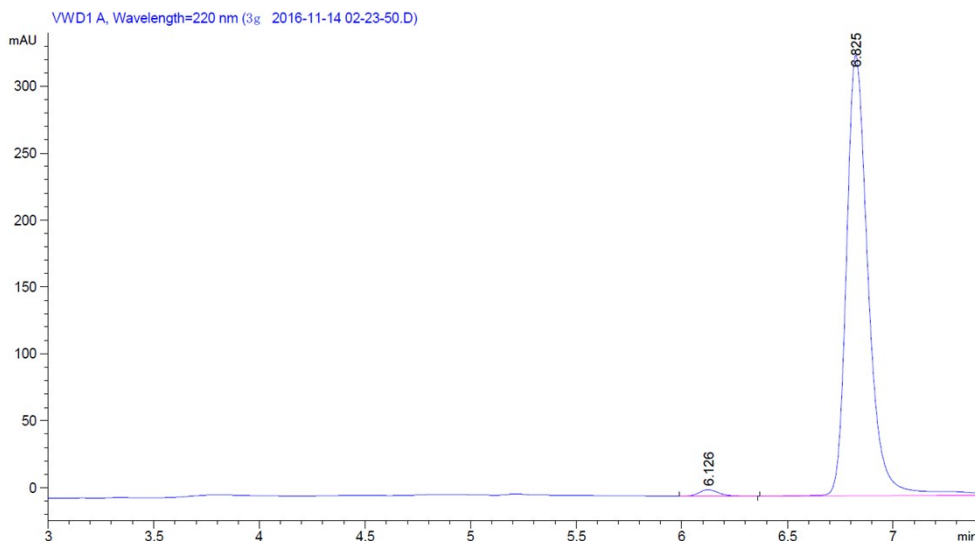


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.375	BV	0.1226	100.61216	12.41213	1.0107
2	4.746	VV	0.1324	9853.84180	1133.45203	98.9893

***N*-benzhydryl-1-(4-(trifluoromethyl)phenyl)ethan-1-amine (3g)**: 93% yield, 97% ee, white solid, unknown compound. Mp: 52–54°C.  $[\alpha]^{25}_D = -46.3^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.1$  Hz, 2H), 7.44 (d,  $J = 8.0$  Hz, 2H), 7.42–7.28 (m, 9H), 7.25 (t,  $J = 7.0$  Hz, 1H), 4.65 (s, 1H), 3.81 (q,  $J = 6.6$  Hz, 1H), 1.43 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 144.2, 143.3, 128.6, 128.4, 127.6, 127.3, 127.1, 127.1, 127.0, 125.5, 125.5, 63.9, 54.9, 24.4. IR (KBr)  $\nu$ : 3349.3, 3061.13028.4, 2973.5, 1323.4, 1123.9  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak IB-3 column, Hex/IPA = 99.5:0.5, 1 mL/min, 220 nm, 6.028 min, 6.689 min. HRMS calcd for  $\text{C}_{22}\text{H}_{21}\text{F}_3\text{N}$   $[\text{M}+\text{H}]^+$ : 356.16206, found: 356.16208.

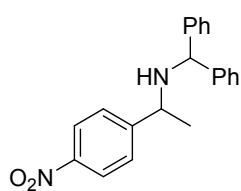


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.028	BV	0.0961	925.52386	147.74202	49.8903
2	6.689	BB	0.0970	929.59540	146.64767	50.1097

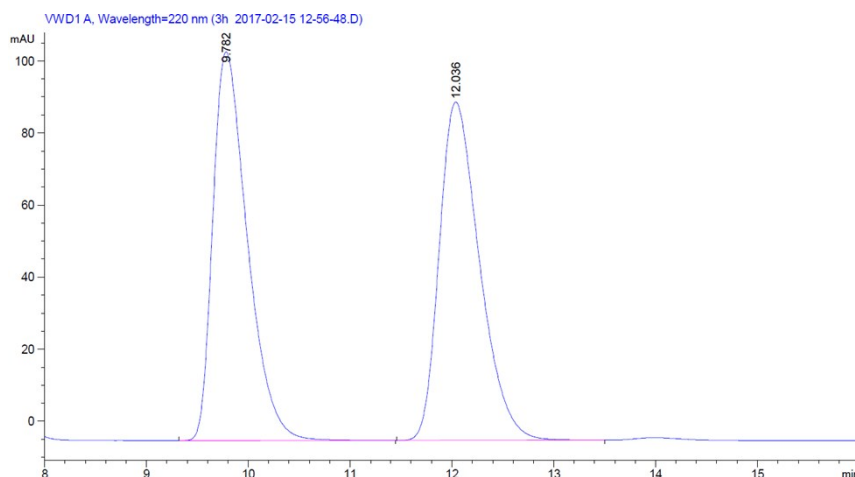


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.126	BB	0.0988	30.86707	4.81507	1.2795
2	6.825	BB	0.1093	2381.49219	329.55951	98.7205

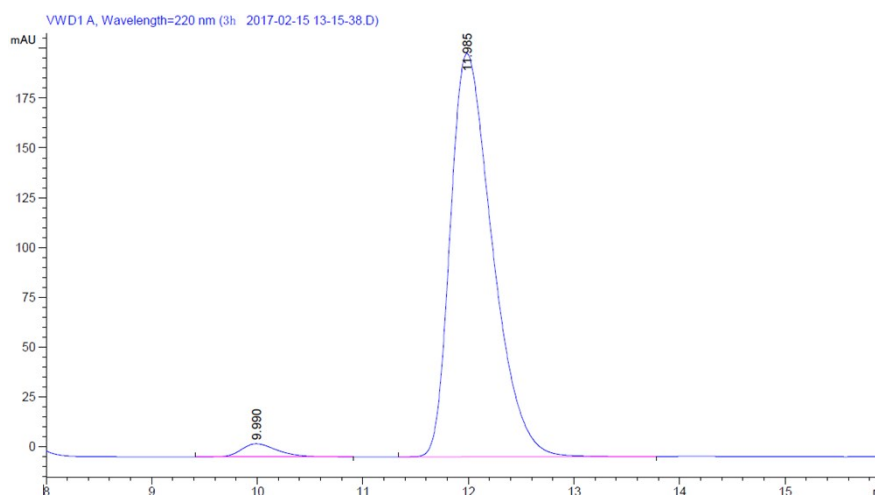
***N*-benzhydryl-1-(4-nitrophenyl)ethan-1-amine (3h)**: 86% yield, 95% ee, white solid, unknown compound. Mp: 107–110°C.



$[\alpha]_D^{25} = -79.4^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J = 8.6$  Hz, 2H), 7.50 (d,  $J = 8.6$  Hz, 2H), 7.39 (t,  $J = 7.5$  Hz, 2H), 7.36–7.28 (m, 7H), 7.24 (t,  $J = 6.8$  Hz, 1H), 4.62 (s, 1H), 3.87 (q,  $J = 6.6$  Hz, 1H), 1.44 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 128.7, 128.4, 127.6, 127.5, 127.3, 127.1, 123.9, 64.1, 55.0, 24.3. IR (KBr)  $\nu$ : 3423.8, 3061.5, 3022.3, 2960.3, 1509.2, 1337.0  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 94:6, 0.9 mL/min, 220 nm, 9.8 min, 12.0 min. HRMS calcd for  $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 333.15975, found: 333.15964.

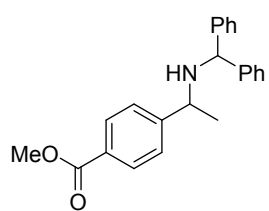


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.782	BB	0.3596	2538.47192	107.86262	49.5975
2	12.036	BB	0.4216	2579.66870	93.88465	50.4025



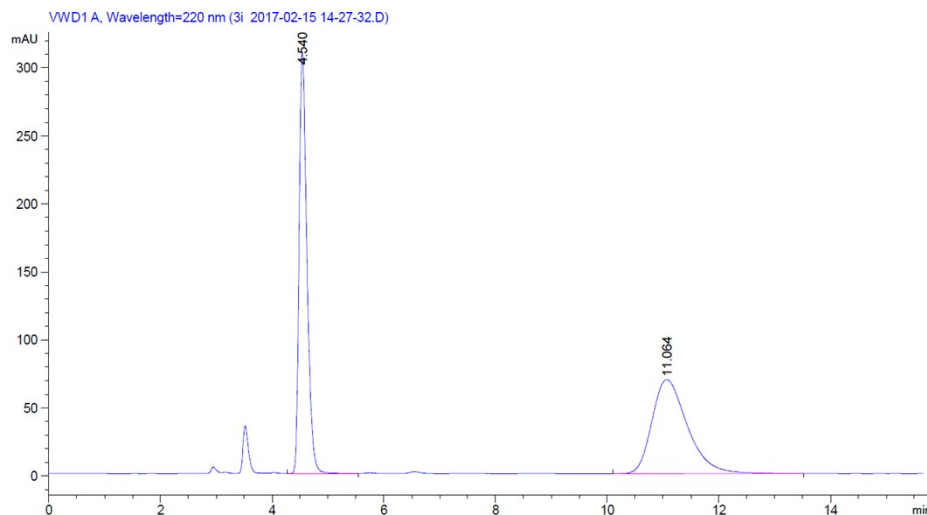
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.990	BB	0.3579	153.80548	6.57567	2.6763
2	11.985	BB	0.4241	5593.15625	202.60150	97.3237

**Methyl 4-(1-(benzhydrylamino)ethyl)benzoate (3i):** 90% yield, 95% ee, white solid, unknown compound. Mp: 58–60°C.

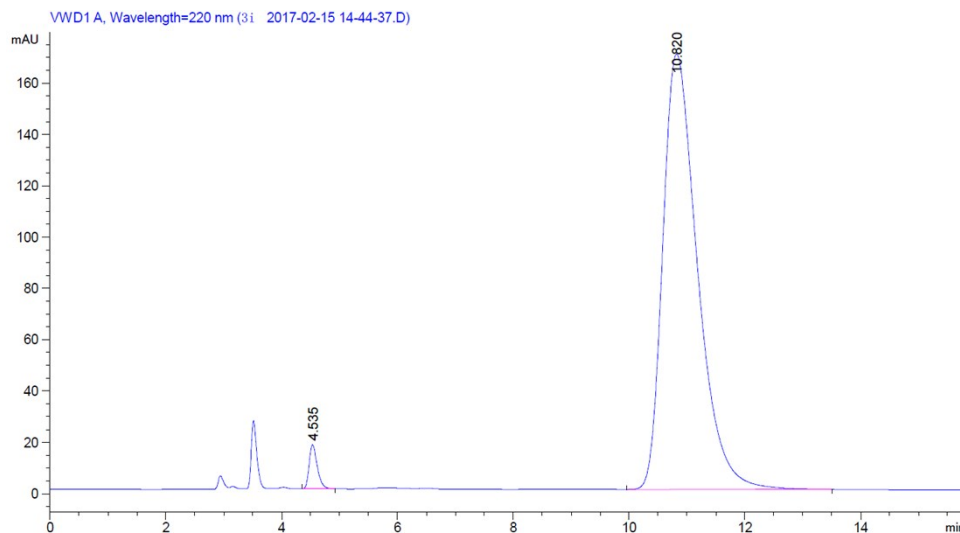


$[\alpha]_D^{25} = -75.1^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.9$  Hz, 2H), 7.37 (q,  $J = 8.4, 7.5$  Hz, 6H), 7.33–7.27 (m, 5H), 7.23 (t,  $J = 6.4$  Hz, 1H), 4.63 (s, 1H), 3.97 (s, 3H), 3.80 (q,  $J = 6.6$  Hz, 1H), 1.43 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.1, 144.3, 143.3, 129.9, 128.9, 128.6, 128.4, 127.6, 127.3, 127.1, 127.0, 126.8, 63.9, 55.1, 52.1, 24.3. IR (KBr)  $\nu$ : 3403.1, 3318.1, 3025.2, 2959.7, 2924.2, 1711.0, 1277.9  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 70:30, 1 mL/min, 220 nm, 4.5 min, 11.1 min.

HRMS calcd for  $\text{C}_{23}\text{H}_{24}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 346.18016, found: 346.18027.

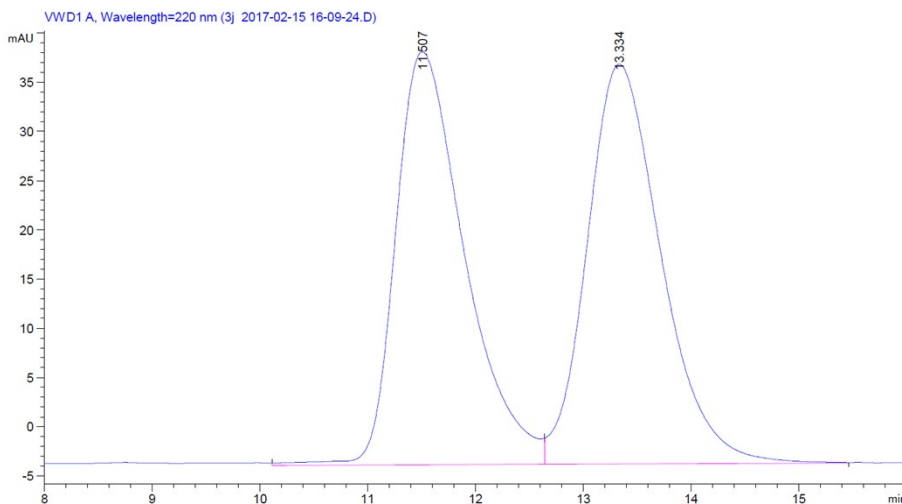
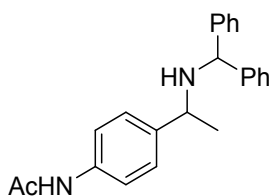


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.540	BB	0.1488	3013.90723	309.05890	49.7491
2	11.064	BB	0.6726	3044.30200	69.15044	50.2509

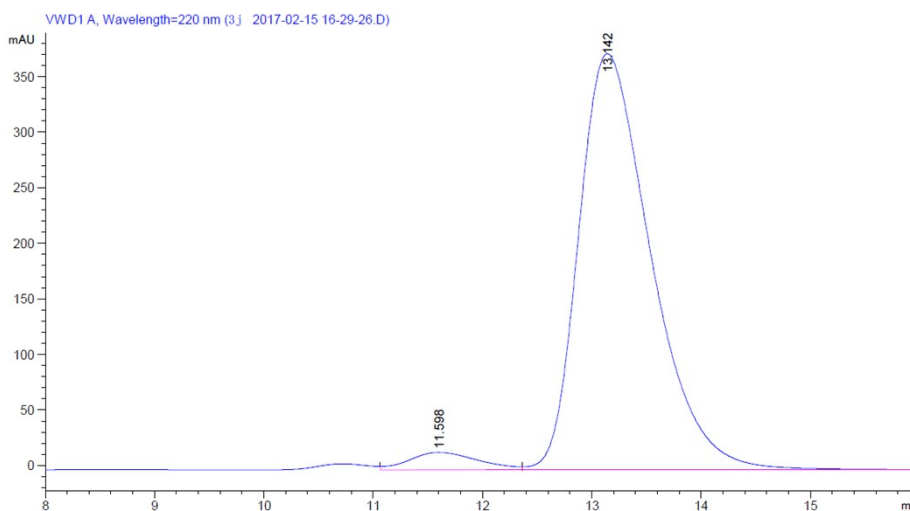


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.535	BB	0.1484	167.06003	17.19346	2.3162
2	10.820	BB	0.6342	7045.52344	169.75066	97.6838

***N*-4-(1-(benzhydrylamino)ethyl)phenylacetamide (3j)**: 91% yield, 92% ee, white solid, unknown compound. Mp: 92–96°C.  $[\alpha]_D^{25} = -68.2^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (s, 2H), 7.37 (d,  $J = 4.1$  Hz, 4H), 7.33–7.21 (m, 8H), 4.66 (s, 1H), 3.70 (q,  $J = 6.6$  Hz, 1H), 2.22 (s, 3H), 1.39 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4, 144.6, 141.6, 136.6, 128.5, 128.4, 127.7, 127.4, 127.3, 127.0, 126.9, 120.1, 63.7, 54.7, 24.6, 24.4. IR (KBr)  $\nu$ : 3294.3, 3190.6, 3061.9, 3029.1, 2963.2, 1662.6, 1542.1  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 90:10, 1 mL/min, 220 nm, 11.5 min, 13.3 min. HRMS calcd for  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 345.19614, found: 345.19614.

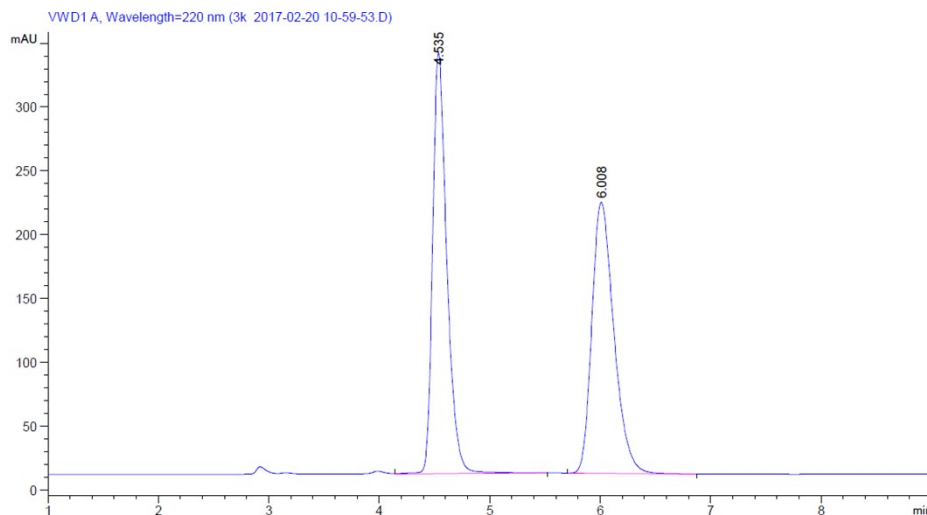
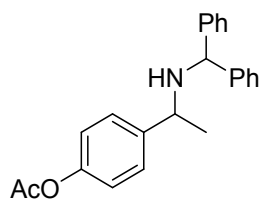


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.507	MF	0.7410	1866.31555	41.97757	49.0664
2	13.334	FM	0.7947	1937.33923	40.63288	50.9336

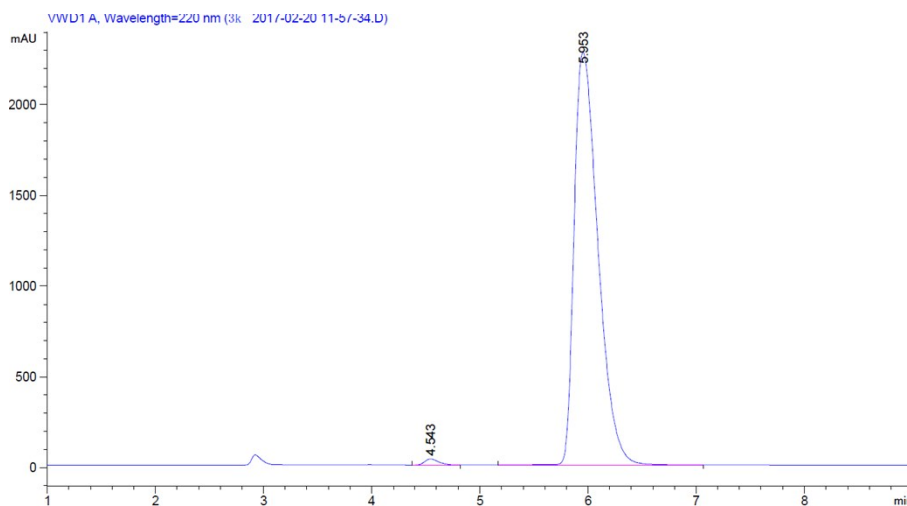


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.598	VV	0.6670	686.02032	15.66234	3.8300
2	13.142	VB	0.7067	1.71253e4	374.37674	95.6099

**4-(1-(benzhydrylamino)ethyl)phenyl acetate (3k)**: 90% yield, 98% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -54.1^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 4.4$  Hz, 4H), 7.32 (dd,  $J = 13.7, 8.1$  Hz, 7H), 7.24 (t,  $J = 6.3$  Hz, 1H), 7.11 (d,  $J = 8.5$  Hz, 2H), 4.70 (s, 1H), 3.75 (q,  $J = 6.6$  Hz, 1H), 2.36 (s, 3H), 1.41 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.5, 144.5, 143.6, 143.1, 128.5, 128.4, 127.7, 127.7, 127.4, 127.0, 126.9, 121.5, 63.7, 54.6, 24.5, 21.2. IR (KBr)  $\nu$ : 3425.6, 1712.0, 1200.2  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA=80:20, 1 mL/min, 220 nm, 4.5 min, 6.0 min. HRMS calcd for  $\text{C}_{23}\text{H}_{24}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 346.18016, found: 346.18015.

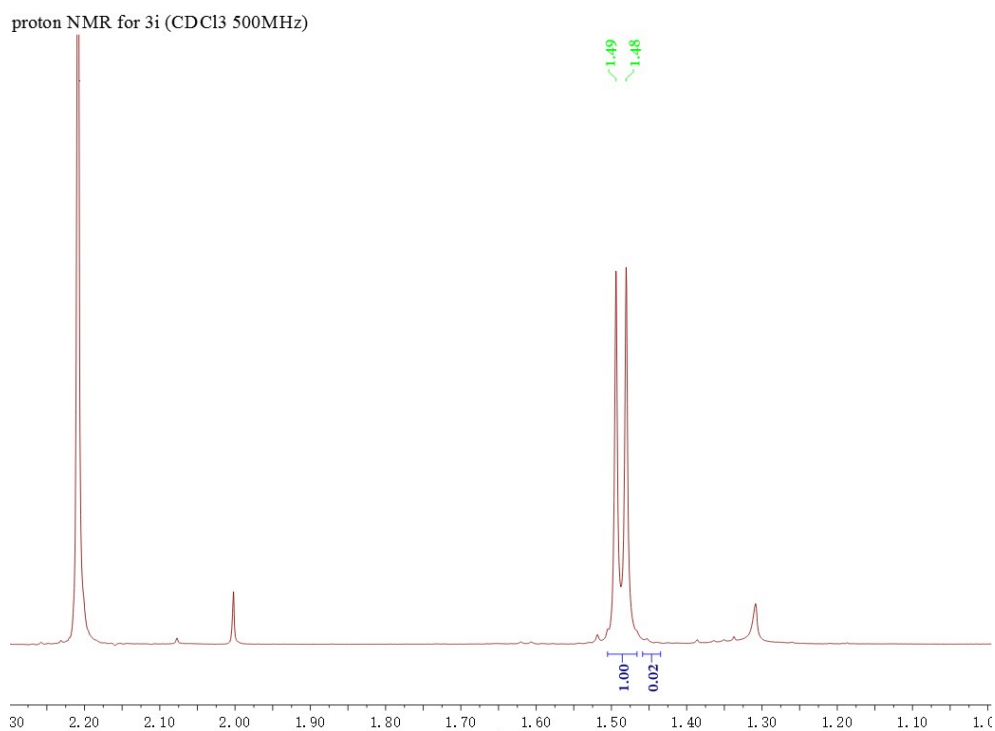
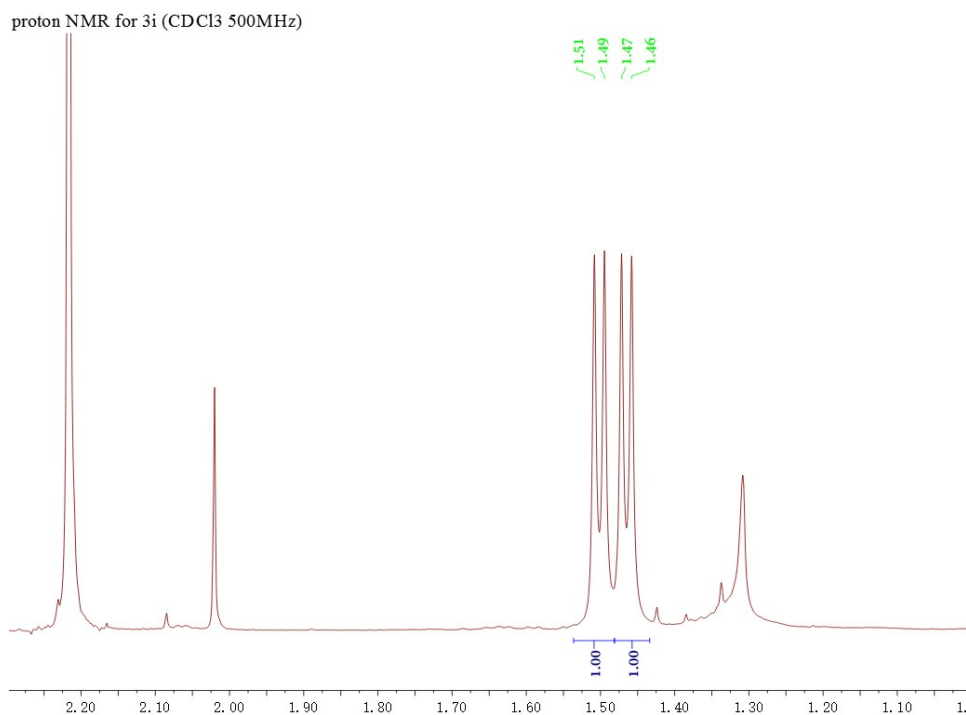
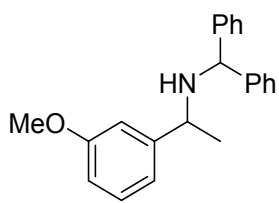


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.535	VB	0.1354	2944.76855	329.13275	50.0836
2	6.008	BB	0.2113	2934.94189	212.30090	49.9164



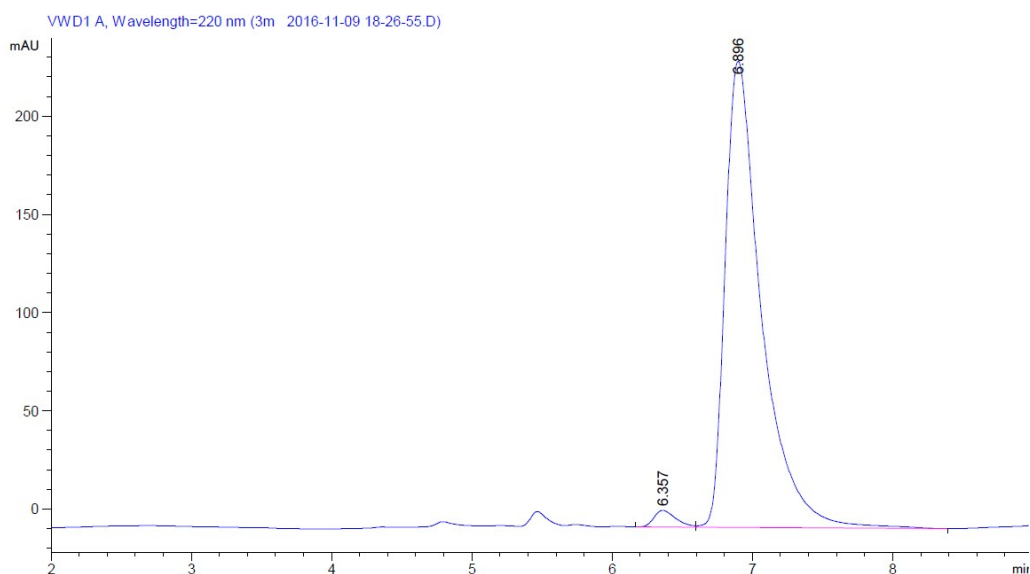
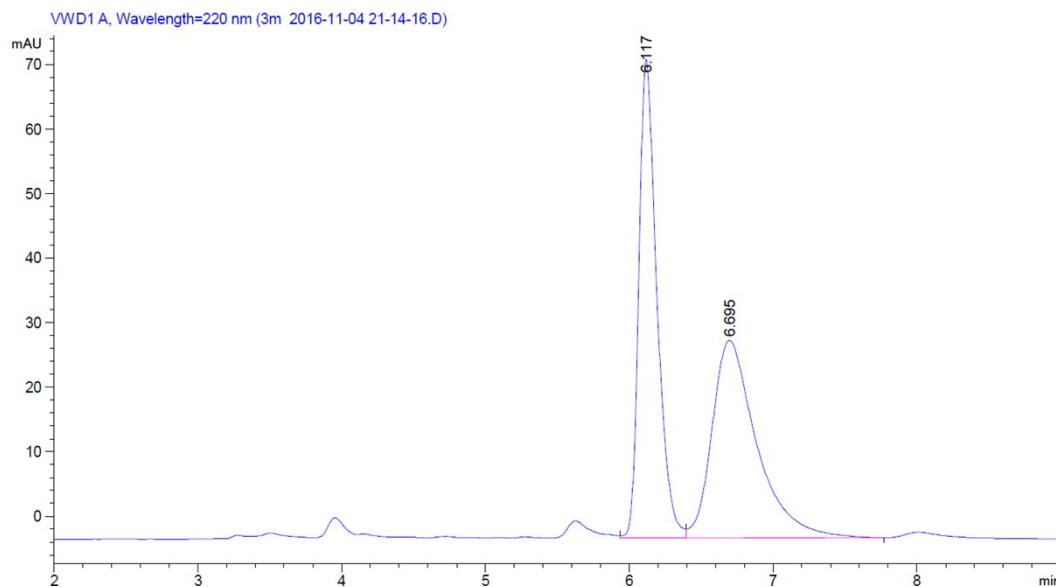
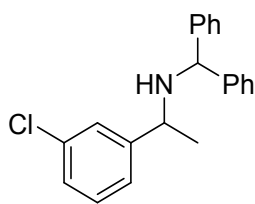
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.543	BV	0.1348	306.52612	34.11092	0.8720
2	5.953	VB	0.2377	3.48470e4	2275.32520	99.1280

***N*-benzhydryl-1-(3-methoxyphenyl)ethan-1-amine (3i)**: 83% yield, 98% ee, clear oil, known compound.  $[\alpha]_D^{25} = -42^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.33 (m, 6H), 7.29 (s, 4H), 7.22 (d,  $J = 7.2$  Hz, 1H), 6.97–6.78 (m, 3H), 4.71 (s, 1H), 3.85 (s, 3H), 3.72 (q,  $J = 6.6$  Hz, 1H), 1.42 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 147.4, 144.7, 143.7, 129.5, 128.5, 128.4, 127.7, 127.4, 127.0, 126.9, 119.1, 112.4, 112.2, 63.8, 55.3, 55.2, 24.4. IR (KBr)  $\nu$ : 3350.4, 3025.5, 2963.0, 2837.4, 1596.0, 1453.0, 1264.4  $\text{cm}^{-1}$ . Enantiomeric excess was determined by  $^1\text{H NMR}$  using (S)-2-acetoxy-2-phenylacetic acid as shift reagent. HRMS calcd for  $\text{C}_{22}\text{H}_{24}\text{NO}$   $[\text{M}+\text{H}]^+$ : 318.18524, found: 318.18502.

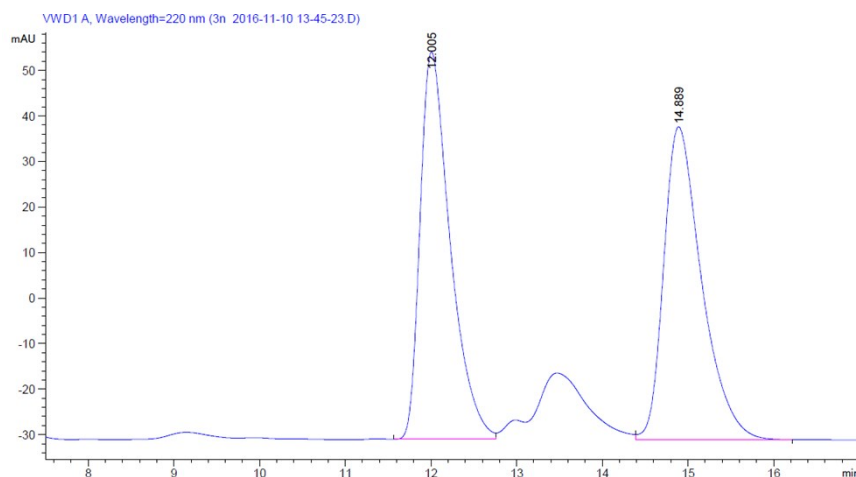
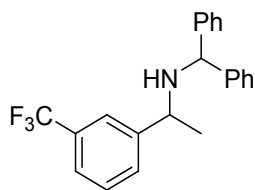




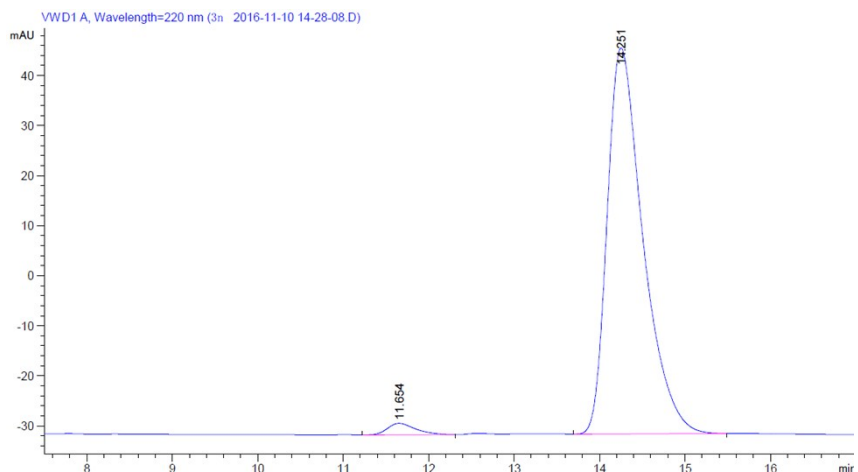
***N*-benzhydryl-1-(3-chlorophenyl)ethan-1-amine (3m)**: 88% yield, 97% ee, clear oil, unknown compound.  $[\alpha]_{D}^{25} = -48.7^{\circ}$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 6.1$  Hz, 4H), 7.37–7.27 (m, 8H), 7.25 (t,  $J = 7.0$  Hz, 1H), 7.19 (d,  $J = 6.9$  Hz, 1H), 4.69 (s, 1H), 3.72 (q,  $J = 6.5$  Hz, 1H), 1.41 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 144.3, 143.5, 134.4, 129.8, 128.6, 128.4, 127.6, 127.4, 127.1, 127.0, 126.9, 124.9, 63.9, 54.9, 24.4. IR (KBr)  $\nu$ : 3450.5, 3046.3, 3027.5, 2969.0, 1636.8, 1455.8  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 99.5:0.5, 0.9 mL/min, 220 nm, 6.1 min, 7.0 min. HRMS calcd for  $\text{C}_{21}\text{H}_{21}\text{ClN}$   $[\text{M}+\text{H}]^+$ : 322.13570, found: 322.13580.



***N*-benzhydryl-1-(3-(trifluoromethyl)phenyl)ethan-1-amine (3n)**: 87% yield, 96% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -34.7^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (s, 2H), 7.51 (q,  $J = 8.7, 7.5$  Hz, 2H), 7.43–7.29 (m, 9H), 7.24 (t,  $J = 6.9$  Hz, 1H), 4.65 (s, 1H), 3.83 (q,  $J = 6.5$  Hz, 1H), 1.44 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  130.2, 128.9, 128.6, 128.4, 127.6, 127.4, 127.2, 127.0, 123.8, 123.7, 64.0, 55.1, 24.3. IR (KBr)  $\nu$ : 3457.2, 3027.1, 2968.7, 1450.7, 1327.5, 1166.9  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 99.4:0.6, 0.9 mL/min, 220 nm, 12.0 min, 14.9 min. HRMS calcd for  $\text{C}_{22}\text{H}_{21}\text{F}_3\text{N}$   $[\text{M}+\text{H}]^+$ : 356.16206, found: 356.16193.

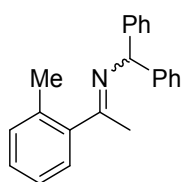


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.005	BV	0.3682	2079.99146	85.08228	49.6038
2	14.889	VB	0.4629	2113.21484	68.69870	50.3962

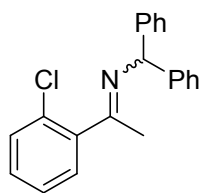


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.654	BB	0.3397	51.96469	2.29058	2.2627
2	14.251	BB	0.4376	2244.57690	77.11256	97.7373

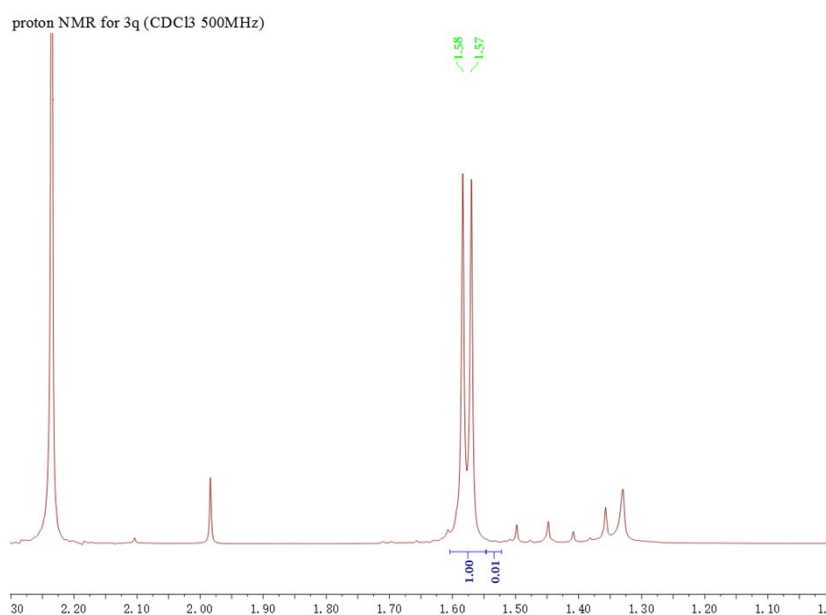
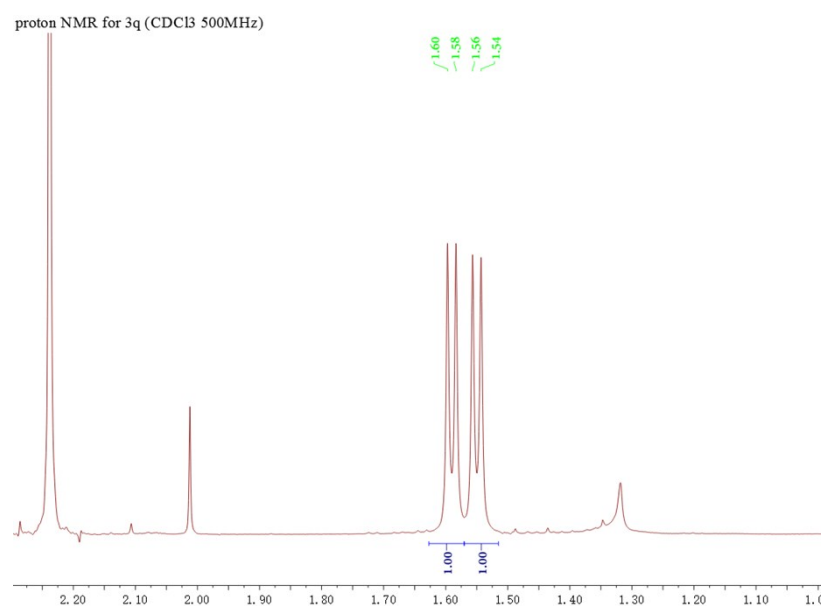
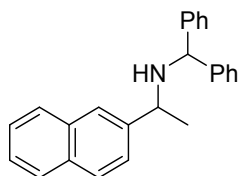
***N*-benzhydryl-1-(*o*-tolyl)ethan-1-imine (3o')**: white solid, unknown compound. (Major):  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54–7.18 (m, 13H), 6.90 (dd,  $J = 7.5, 1.4$  Hz, 1H), 5.30 (s, 1H), 2.40 (s, 3H), 2.31 (s, 1H), 2.02 (s, 3H). HRMS calcd for  $\text{C}_{22}\text{H}_{22}\text{N}$   $[\text{M}+\text{H}]^+$ : 300.17577, found: 300.17526.



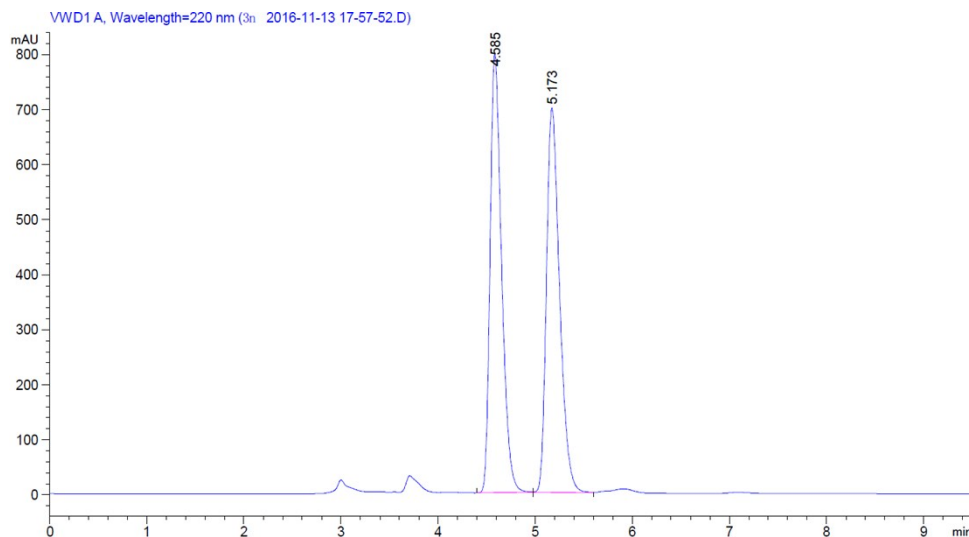
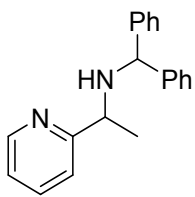
***N*-benzhydryl-1-(2-chlorophenyl)ethan-1-imine (3p')**: white solid, unknown compound. (Major): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50–7.19 (m, 13H), 6.89 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.28 (s, 1H), 2.45 (s, 3H). HRMS calcd for C<sub>21</sub>H<sub>19</sub>ClN [M+H]<sup>+</sup>: 320.12005, found: 320.12003.



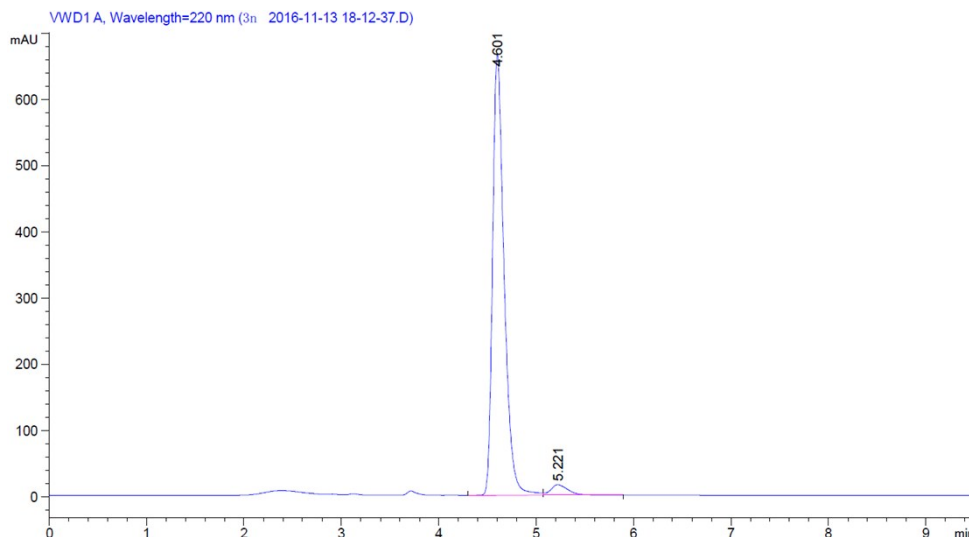
***N*-benzhydryl-1-(naphthalen-2-yl)ethan-1-amine (3q)**: 94% yield, 99% ee, white solid, unknown compound. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -53.3° (c = 0.3, MeOH). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.69 (s, 1H), 7.58–7.48 (m, 3H), 7.40 (dd, *J* = 4.1, 1.6 Hz, 4H), 7.33 (dd, *J* = 16.7, 8.3 Hz, 5H), 7.24 (t, *J* = 7.1 Hz, 1H), 4.72 (s, 1H), 3.92 (q, *J* = 6.4 Hz, 1H), 1.52 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.6, 143.6, 143.0, 133.5, 132.9, 128.5, 128.4, 127.8, 127.7, 127.4, 127.0, 126.9, 126.0, 125.5, 124.8, 63.8, 55.4, 24.4. IR (KBr)  $\nu$ : 3447.9, 3054.3, 2966.5, 1637.8, 1449.9 cm<sup>-1</sup>. Enantiomeric excess was determined <sup>1</sup>H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as shift reagent. HRMS calcd for C<sub>25</sub>H<sub>24</sub>N [M+H]<sup>+</sup>: 338.19033, found: 338.19043.



***N*-benzhydryl-1-(pyridin-2-yl)ethan-1-amine (3r)**: 76% yield, 93% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -50.4^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 4.6$  Hz, 1H), 7.66 (td,  $J = 7.6, 1.8$  Hz, 1H), 7.45 (d,  $J = 7.5$  Hz, 2H), 7.37 (dd,  $J = 12.8, 7.3$  Hz, 4H), 7.33–7.26 (m, 3H), 7.22 (dd,  $J = 10.9, 7.3$  Hz, 3H), 4.67 (s, 1H), 3.85 (q,  $J = 6.7$  Hz, 1H), 1.47 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 149.6, 144.6, 143.6, 136.28, 128.5, 128.4, 127.7, 127.4, 127.0, 126.9, 121.9, 64.5, 56.5, 23.1. IR (KBr)  $\nu$ : 3314.8, 3060.6, 3022.0, 2969.1, 1586.1, 1442.5  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 90:10, 1 mL/min, 220 nm, 4.6 min, 5.2 min. HRMS calcd for  $\text{C}_{20}\text{H}_{21}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 289.16993, found: 289.17007.

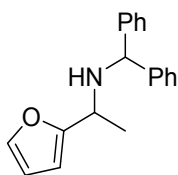


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.585	BB	0.1246	6526.83105	796.68225	49.9490
2	5.173	BV	0.1432	6540.14844	698.47717	50.0510

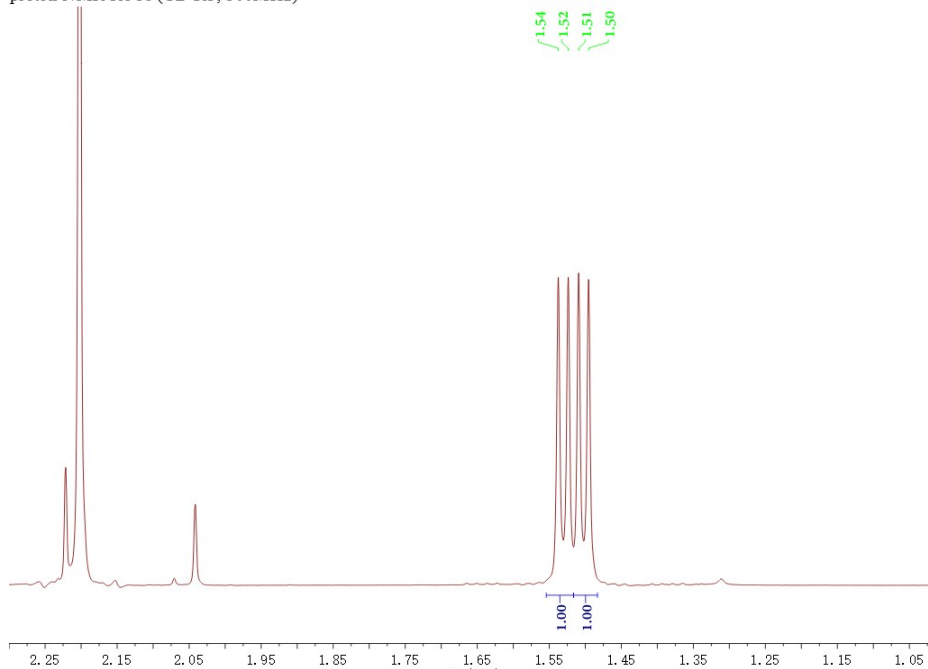


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.601	BV	0.1228	5465.53906	665.49359	96.5024
2	5.221	VB	0.1930	198.09058	15.83363	3.4976

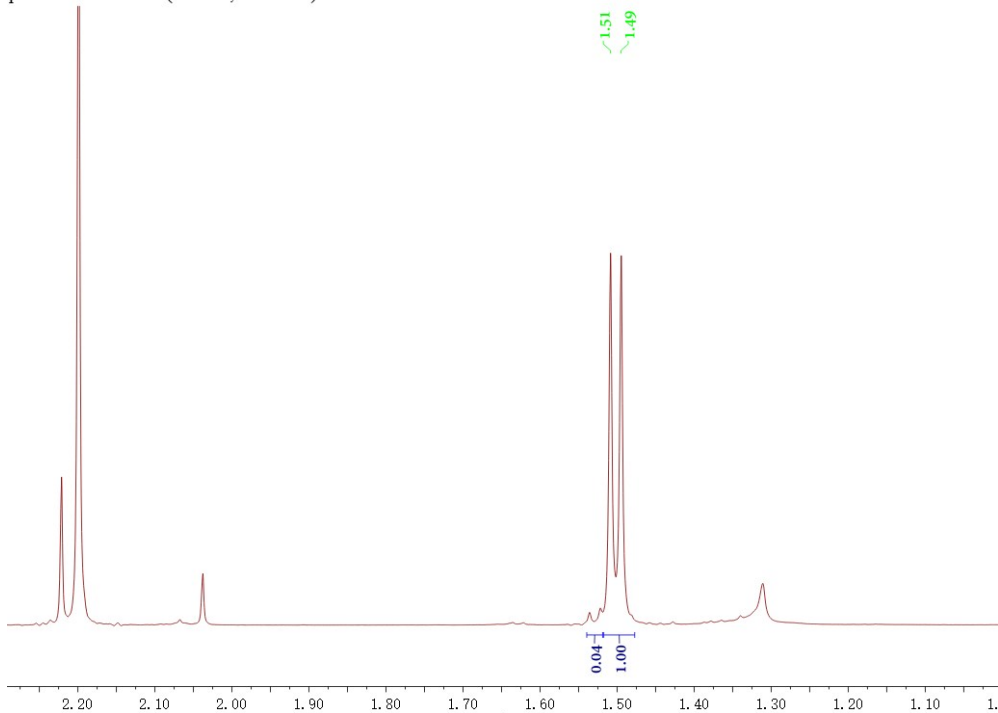
***N*-benzhydryl-1-(furan-2-yl)ethan-1-amine (3s)**: 94% yield, 92% ee, clear oil, unknown compound.  $[\alpha]^{25}_D = -59.4^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.0$  Hz, 2H), 7.43 (s, 1H), 7.37 (d,  $J = 3.9$  Hz, 4H), 7.31 (q,  $J = 7.7$  Hz, 3H), 7.24 (t,  $J = 7.8$  Hz, 1H), 6.38 (s, 1H), 6.13 (s, 1H), 4.82 (s, 1H), 3.80 (q,  $J = 6.8$  Hz, 1H), 1.49 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9, 144.5, 143.6, 141.4, 128.5, 128.5, 127.6, 127.4, 127.0, 127.0, 109.8, 105.6, 64.3, 48.9, 21.0. IR (KBr)  $\nu$ : 3461.7, 3062.1, 3027.9, 2974.2, 1453.6  $\text{cm}^{-1}$ . Enantiomeric excess was determined by  $^1\text{H NMR}$  using (*S*)-2-acetoxy-2-phenylacetic acid as shift reagent. HRMS calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}$   $[\text{M}+\text{H}]^+$ : 278.15394, found: 278.15436.



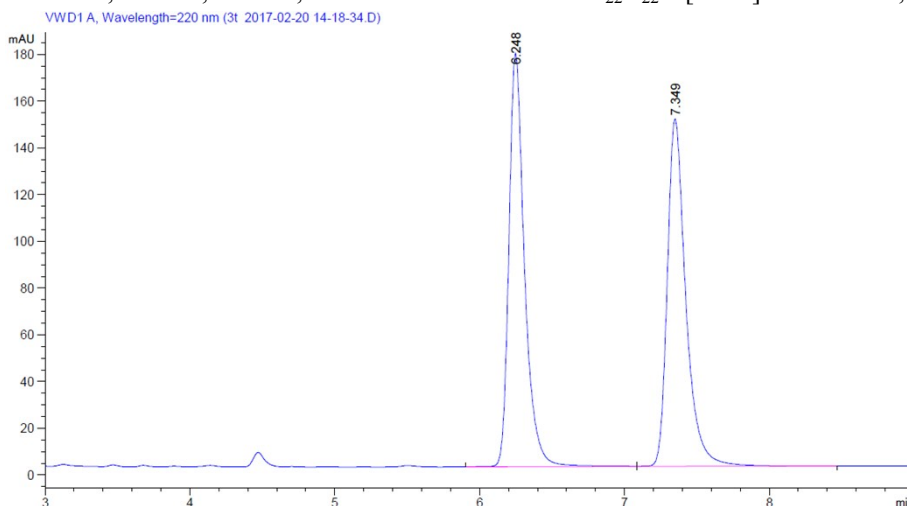
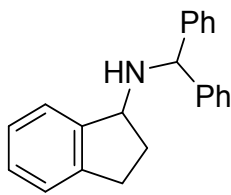
proton NMR for 3s ( $\text{CDCl}_3$ , 500MHz)



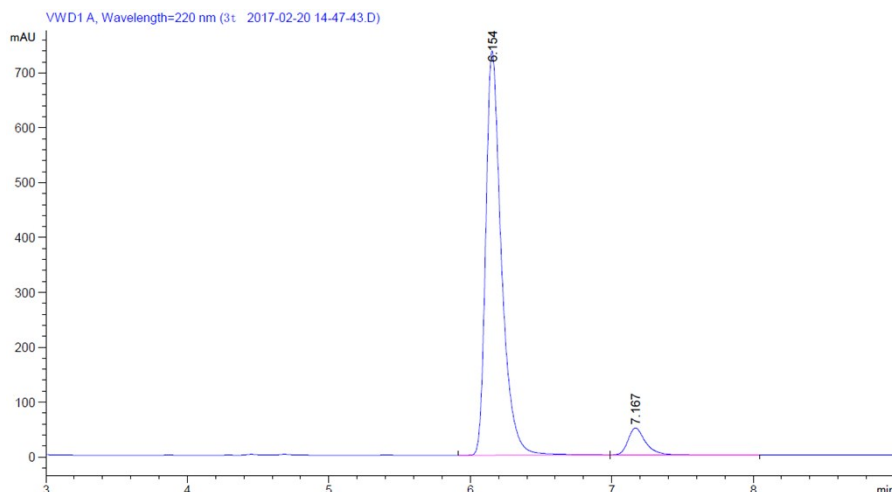
proton NMR for 3s ( $\text{CDCl}_3$ , 500MHz)



***N*-benzhydryl-1-(pyridin-2-yl)ethan-1-amine (3t)**: 90% yield, 86% ee, clear oil, unknown compound.  $[\alpha]^{25}_D = -9.4^\circ$  ( $c = 0.3$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 7.7$  Hz, 2H), 7.57 (d,  $J = 6.7$  Hz, 1H), 7.54 (d,  $J = 7.2$  Hz, 2H), 7.38 (dt,  $J = 13.0, 7.6$  Hz, 4H), 7.28 (q,  $J = 8.2, 7.4$  Hz, 5H), 5.20 (s, 1H), 4.23 (t,  $J = 6.9$  Hz, 1H), 3.03 (ddd,  $J = 15.8, 8.5, 3.9$  Hz, 1H), 2.81 (dt,  $J = 15.9, 8.0$  Hz, 1H), 2.59–2.46 (m, 1H), 1.88 (ddd,  $J = 15.3, 12.4, 8.3$  Hz, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 143.3, 128.5, 127.5, 127.4, 127.1, 127.1, 126.3, 124.7, 124.3, 65.2, 61.0, 34.6, 30.3. IR (KBr)  $\nu$ : 3427.1, 3026.6, 2944.1, 1451.1, 1026.6  $\text{cm}^{-1}$ . Enantiomeric excess was determined by chiral HPLC: Chiralpak IA-3 column, Hex/IPA = 99.5:0.5, 1 mL/min, 220 nm, 6.2 min, 7.3 min. HRMS calcd for  $\text{C}_{22}\text{H}_{22}\text{N}$   $[\text{M}+\text{H}]^+$ : 300.17468, found: 300.17490.

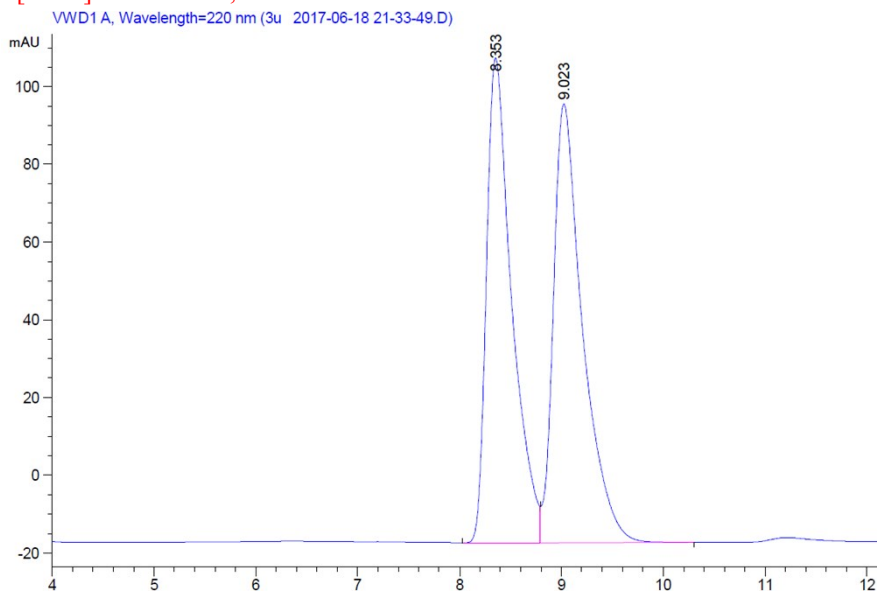
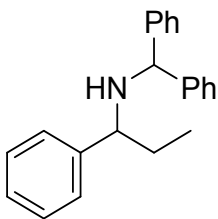


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.248	BB	0.1121	1321.68103	177.01202	50.0853
2	7.349	BB	0.1334	1317.17871	148.67311	49.9147

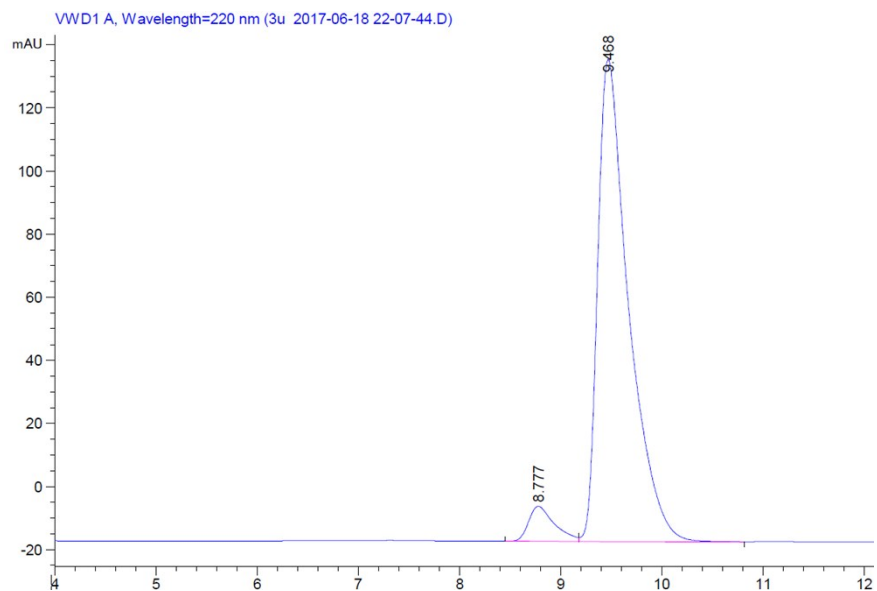


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.154	BV	0.1158	5673.66553	736.93341	92.8364
2	7.167	VB	0.1312	437.80048	49.49916	7.1636

***N*-benzhydryl-1-phenylpropan-1-amine (3u)**: 51% yield, 90% ee, clear oil, unknown compound.  $[\alpha]_D^{25} = -35.0^\circ$  ( $c = 0.4$ , MeOH).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.29 (m, 6H), 7.23 (dq,  $J = 17.9, 9.9, 8.4$  Hz, 8H), 7.15 (t,  $J = 7.1$  Hz, 1H), 4.59 (s, 1H), 3.40 (t,  $J = 7.0$  Hz, 1H), 1.70 (dtt,  $J = 64.3, 14.7, 7.3$  Hz, 3H), 0.81 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ -*d*)  $\delta$  128.46, 128.38, 128.33, 127.83, 127.38, 126.94, 126.85, 63.63, 61.80, 31.16, 11.01. Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 99.6:0.4, 0.8 mL/min, 220 nm, 8.4 min, 9.0 min. HRMS calcd for  $\text{C}_{22}\text{H}_{22}\text{N}$   $[\text{M}+\text{H}]^+$ : 300.17468, found: 300.17490.

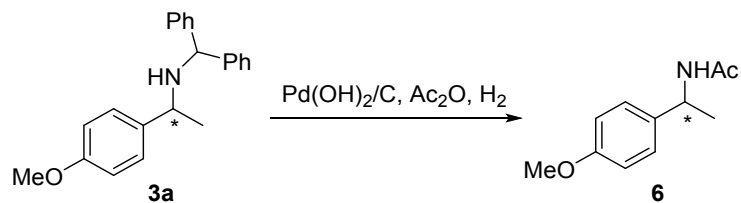


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.353	BV	0.2546	2155.42358	124.73232	48.9154
2	9.023	VB	0.2927	2251.00977	112.87238	51.0846



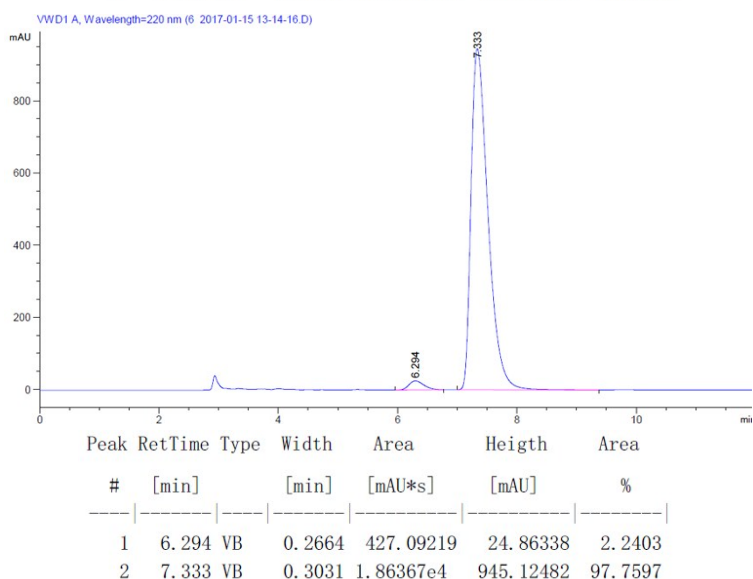
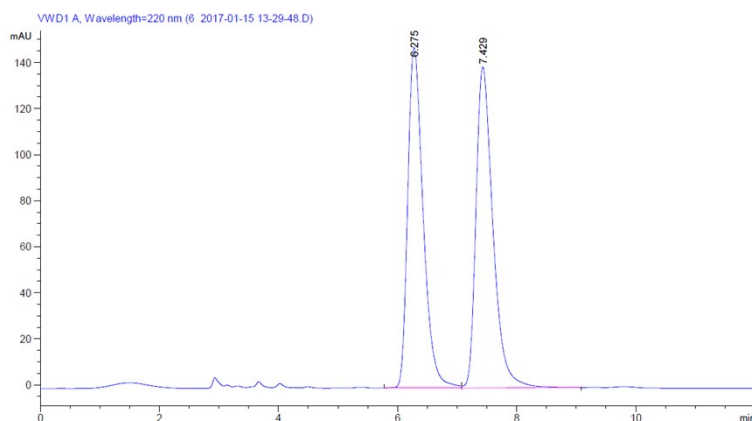
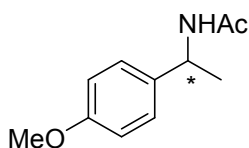
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.777	BV	0.2606	195.82176	11.05770	5.7006
2	9.468	VB	0.3125	3239.27124	152.69235	94.2994

## VI General Procedure for Removal of Diphenylmethyl Group



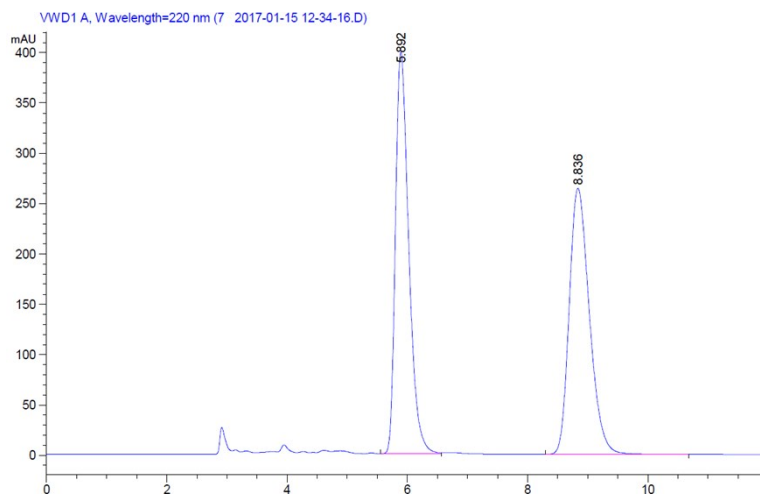
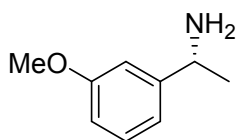
**3a** (0.2 mmol), acetic anhydride (2 drops), 6 mg of Pd(OH)<sub>2</sub>/C (20%, 50% wetted with water) and CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) were added to a vial. The resulting vial was transferred to an autoclave, which was charged with 25 atm of H<sub>2</sub>, and stirred at 40 °C for 20 h. The hydrogen gas was released slowly and the solution was filtered to remove Pd(OH)<sub>2</sub>/C. The filtrate was concentrated and then purified by flash column chromatography (EtOAc/Hex) to yield the desired product **6** (95% yield).

**N-(1-(4-methoxyphenyl)ethyl)acetamide (6)**:<sup>[5]</sup> 95% yield, 96% ee, white solid, known compound.  $[\alpha]_D^{25} = -138.0^\circ$  (c = 0.4, MeOH). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.72 (s, 1H), 5.13 (p, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 2.01 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H). IR (KBr) ν: 3255.3, 3076.2, 3011.2, 2958.7, 1639.1, 1245.6 cm<sup>-1</sup>. Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA = 85:15, 1 mL/min, 220nm, 6.3 min, 7.4 min.

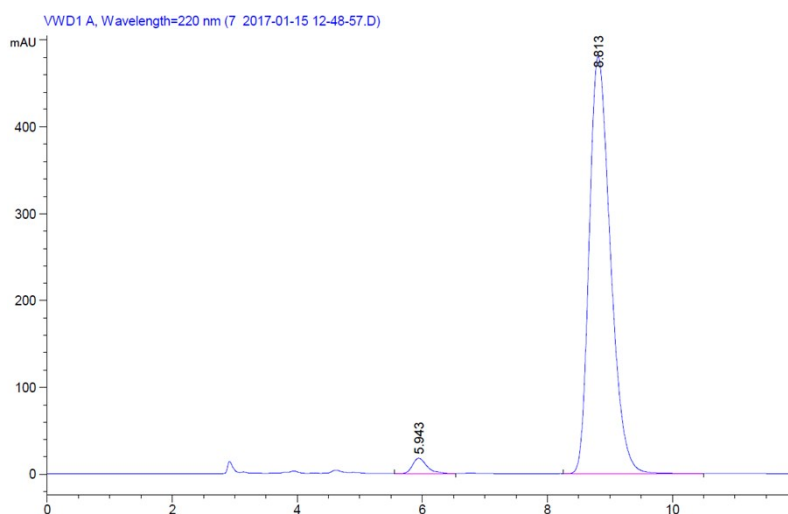




***N*-**(1-(3-methoxyphenyl)ethyl)acetamide (**7**):<sup>[5]</sup> 93% yield, 95% ee, white solid, known compound.  $[\alpha]_D^{25} = -108.3^\circ$  ( $c = 0.4$ , MeOH). Enantiomeric excess was determined by chiral HPLC after it was transformed to the corresponding acetamide: Chiralpak OD-H column, Hex/IPA=75:25, 1 mL/min, 220nm, 5.9 min, 8.8 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.892	BV	0.2354	6134.65283	398.95340	50.0188
2	8.836	BB	0.3587	6130.04688	264.15176	49.9812



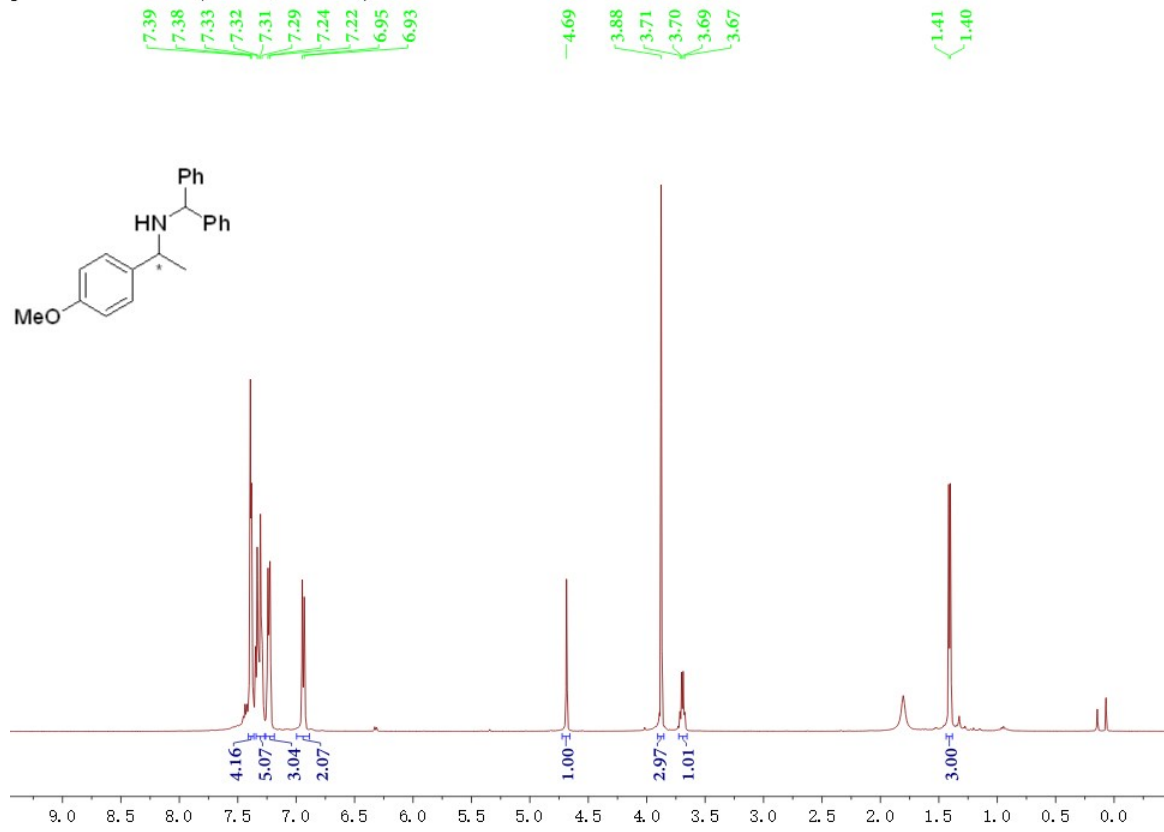
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.943	BB	0.2429	282.61298	17.73931	2.4443
2	8.813	BB	0.3640	1.12795e4	480.32599	97.5557

## V References:

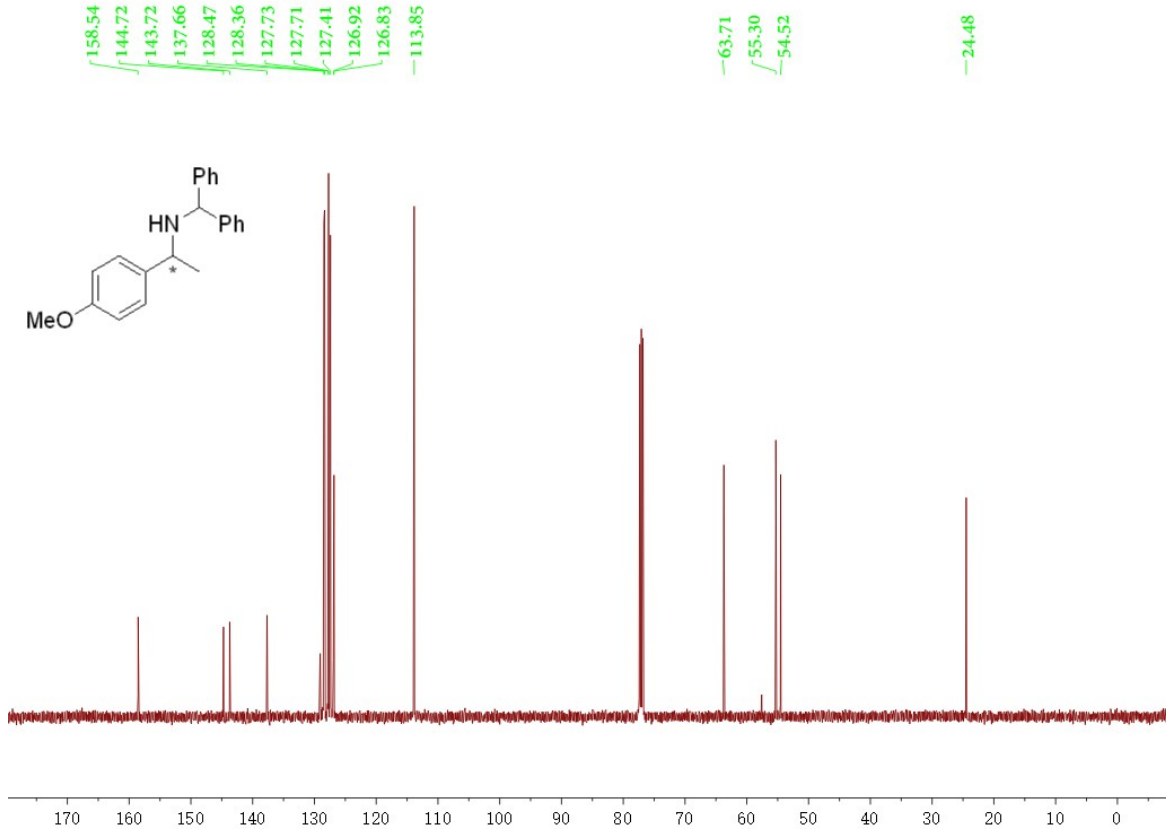
- [1] H. Huang, X. Liu, L. Zhou, M. Chang, X. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 5309–5312.
- [2] A. Nodzevska, K. Sidorowicz, M. Sienkiewicz, *Synthesis*, **2014**, *46*, 1475–1480.
- [3] W. J. Lu, Y. W. Chen, X. L. Hou, *Adv. Synth. Catal.*, **2010**, *352*, 103–107.
- [4] C. Wang, X. J. Wu, L. Zhou, J. Sun, *Chem. Eur. J.*, **2008**, *14*, 8789–8792.
- [5] G. Li, J.C. Antilla, *Org. Lett.*, **2009**, *11*(5):1075–1078.

## VI NMR & HRMS Spectra

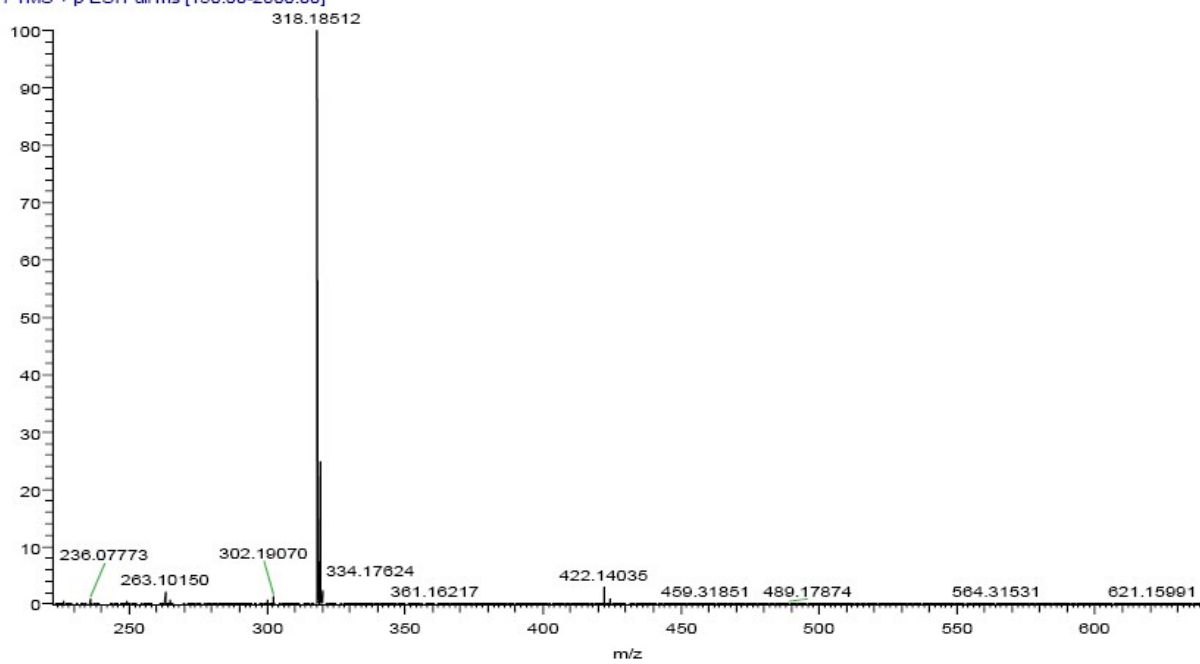
proton NMR for 3a (CDCl<sub>3</sub>, 500MHz)



C13 for 3a (CDCl<sub>3</sub>, 125MHz)

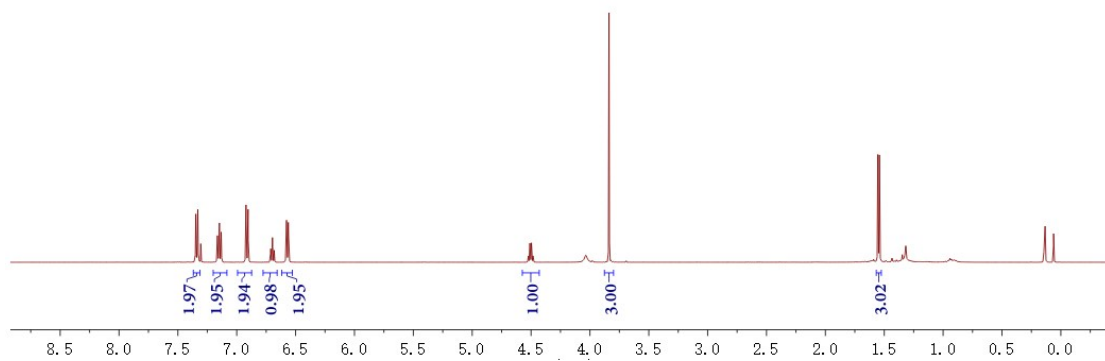
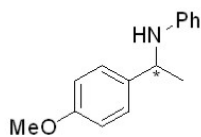


00088 #14 RT: 0.39 AV: 1 NL: 1.58E7  
T: FTMS + p ESI Full ms [150.00-2000.00]

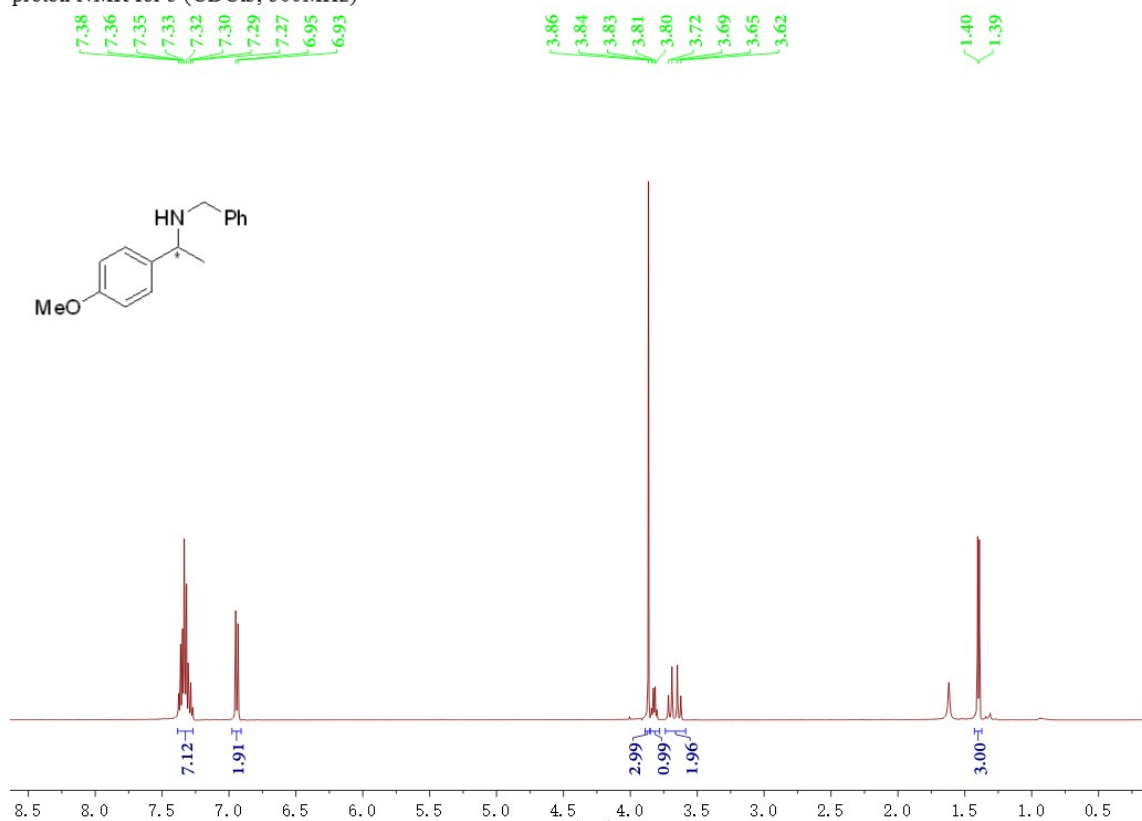


proton NMR for 4 (CDCl<sub>3</sub>, 500MHz)

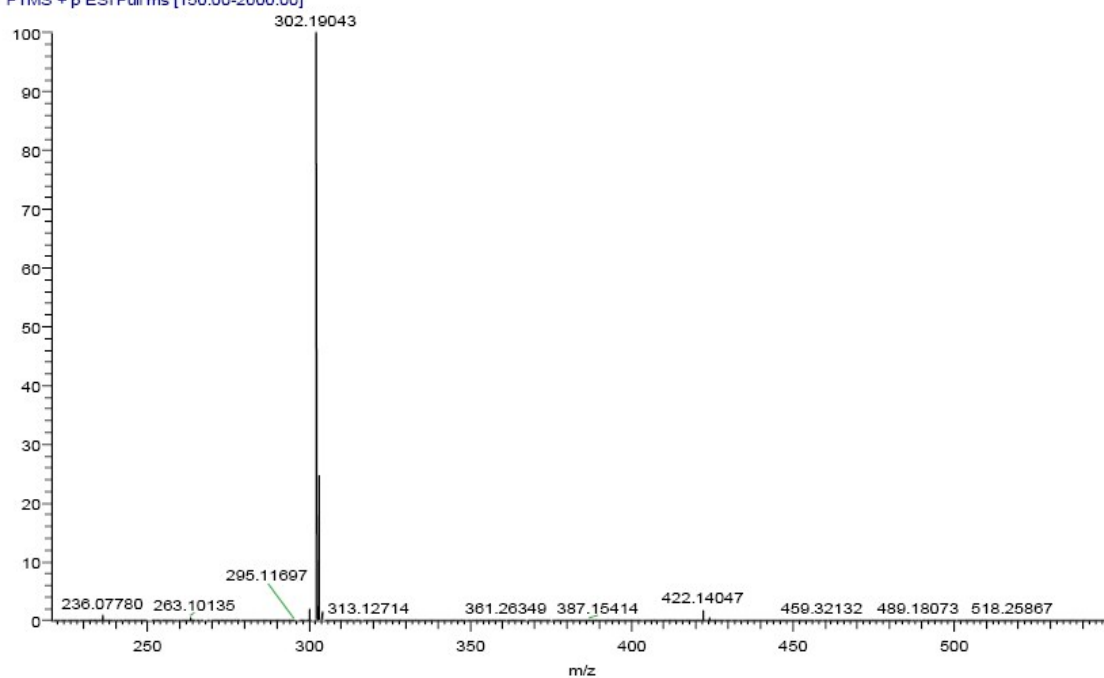
7.35, 7.33, 7.16, 7.15, 7.13, 6.92, 6.90, 6.71, 6.70, 6.68, 6.58, 6.56, 4.52, 4.51, 4.50, 4.48, 3.84, 1.55, 1.54



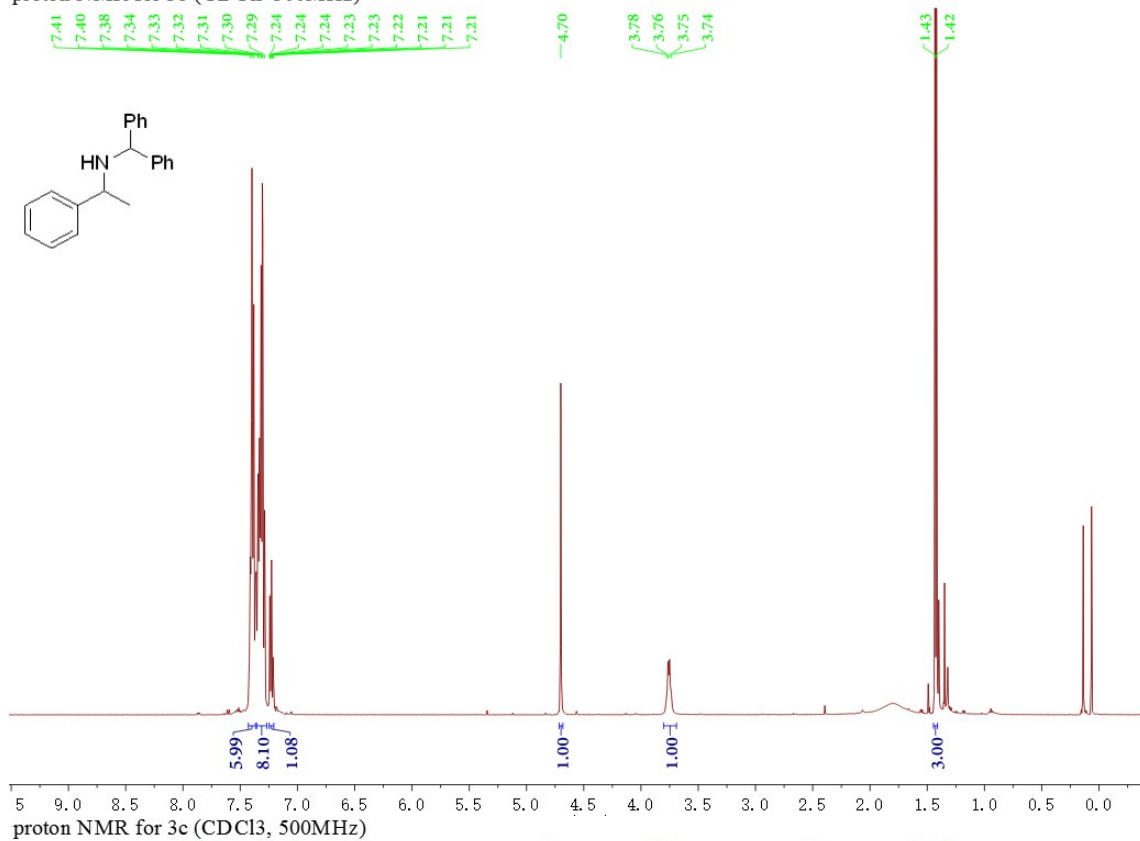
proton NMR for 5 (CDCl<sub>3</sub>, 500MHz)



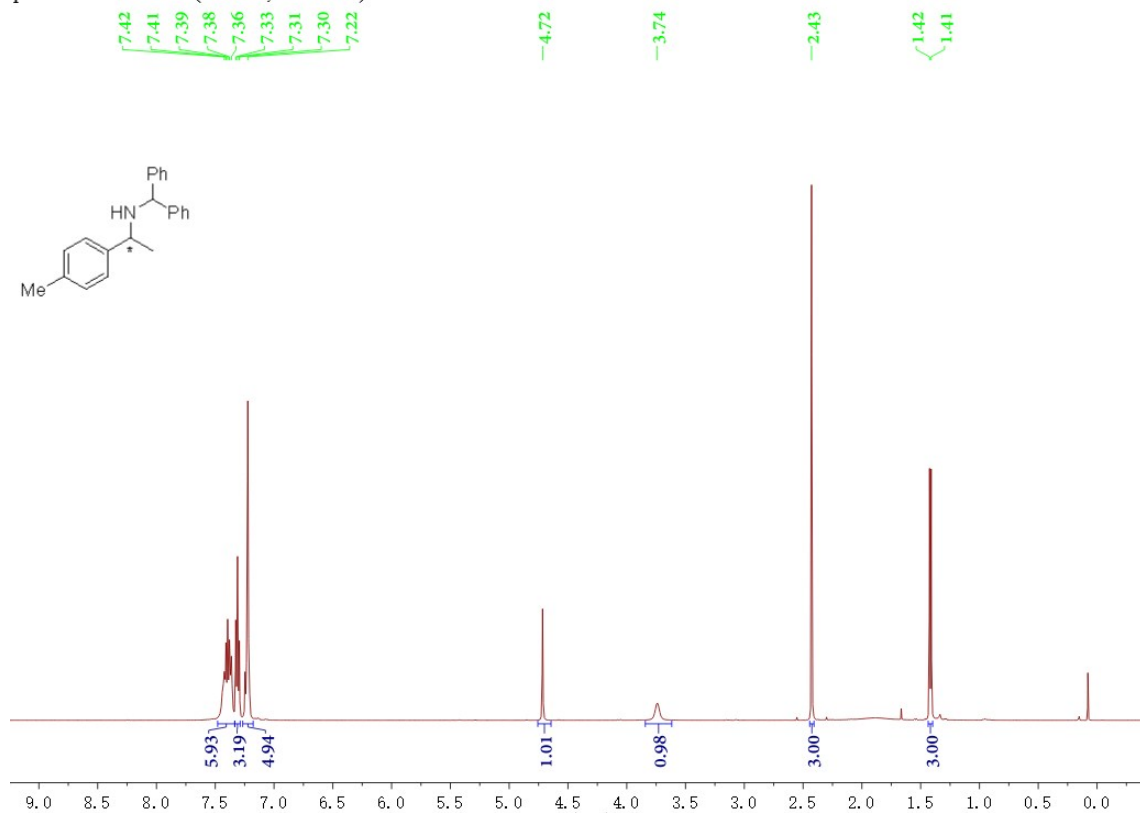
00083 #13 RT: 0.38 AV: 1 NL: 3.84E7  
T: FTMS + p ESI Full ms [150.00-2000.00]



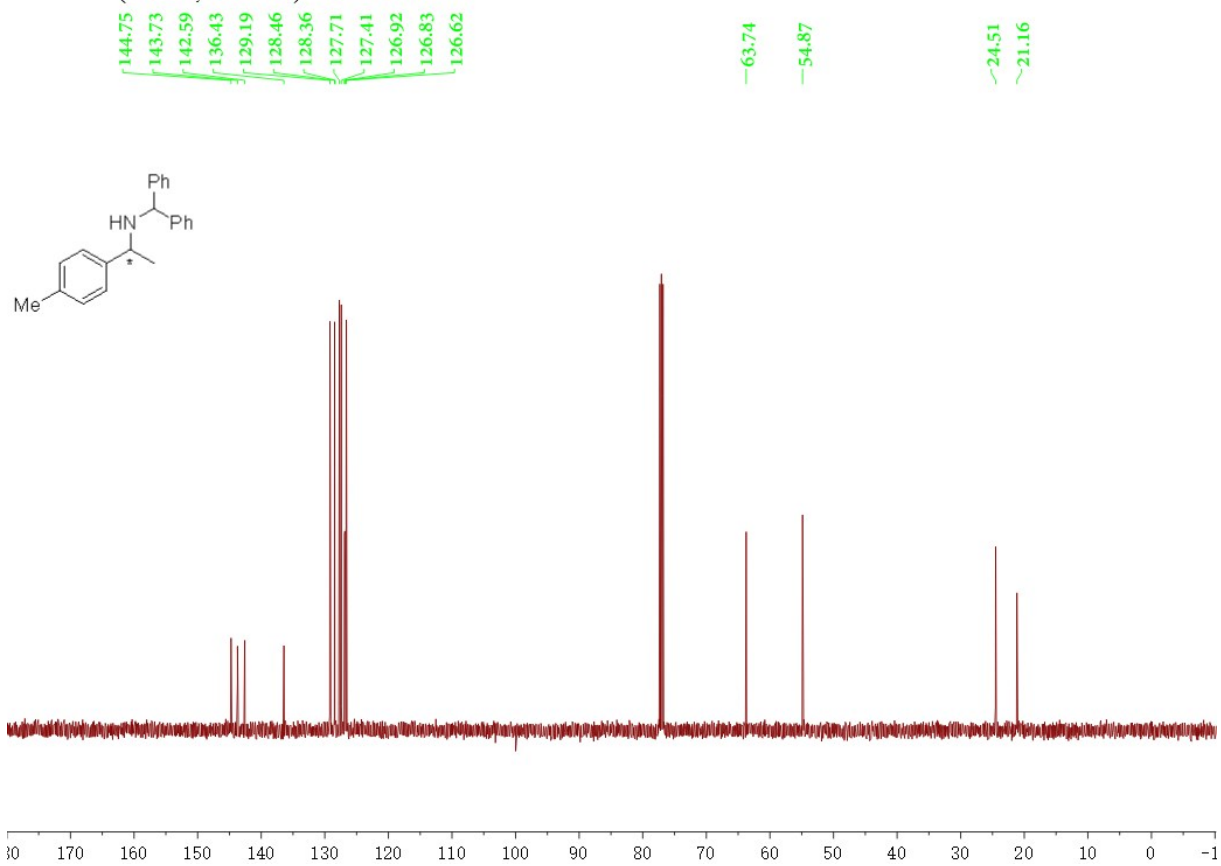
proton NMR for 3b (CDCl<sub>3</sub> 500MHz)



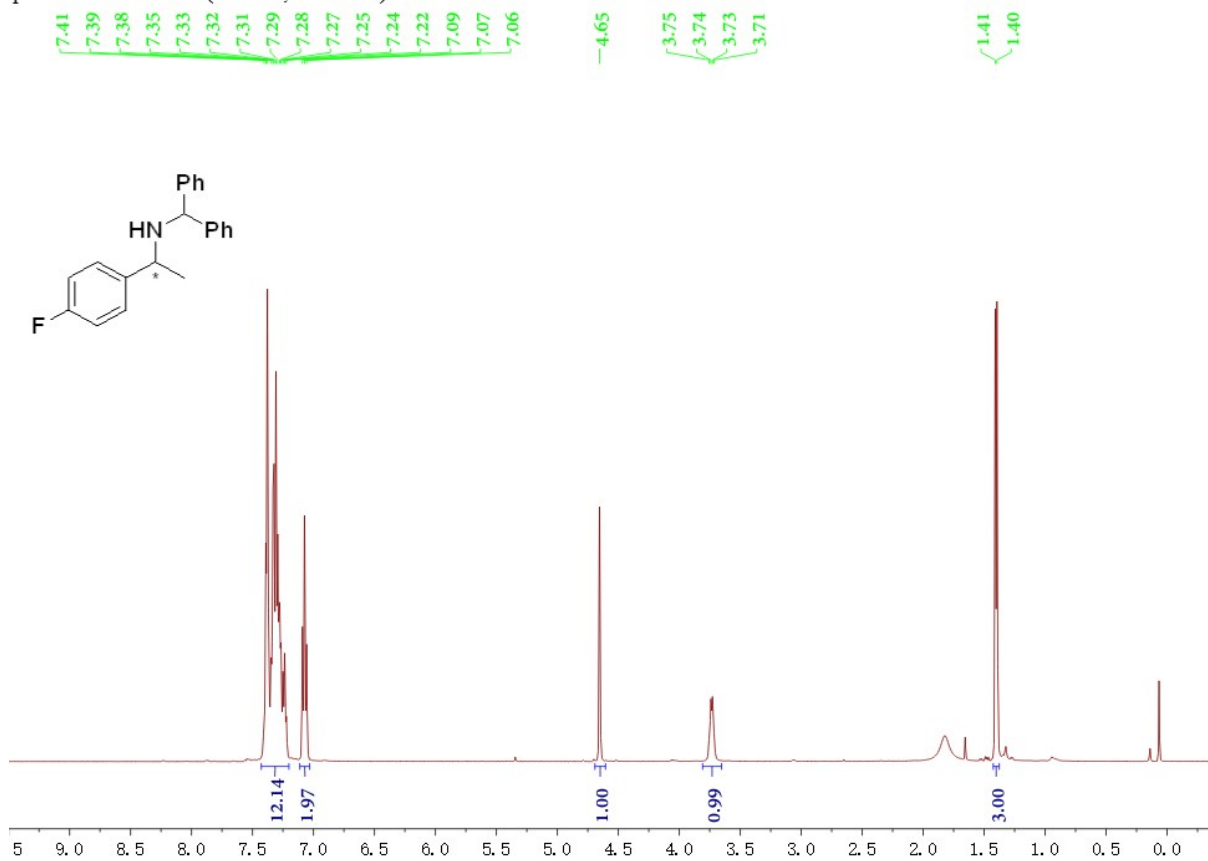
proton NMR for 3c (CDCl<sub>3</sub>, 500MHz)



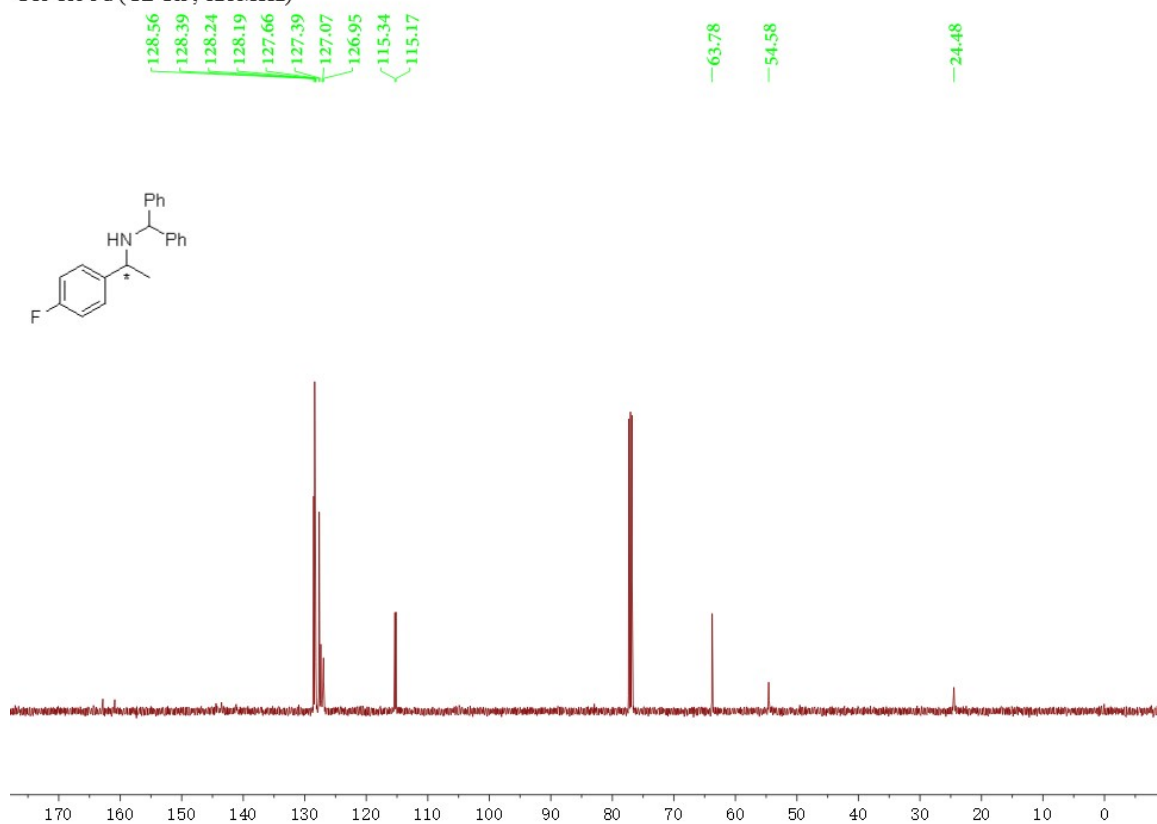
C13 for 3c (CDCl<sub>3</sub>, 125MHz)



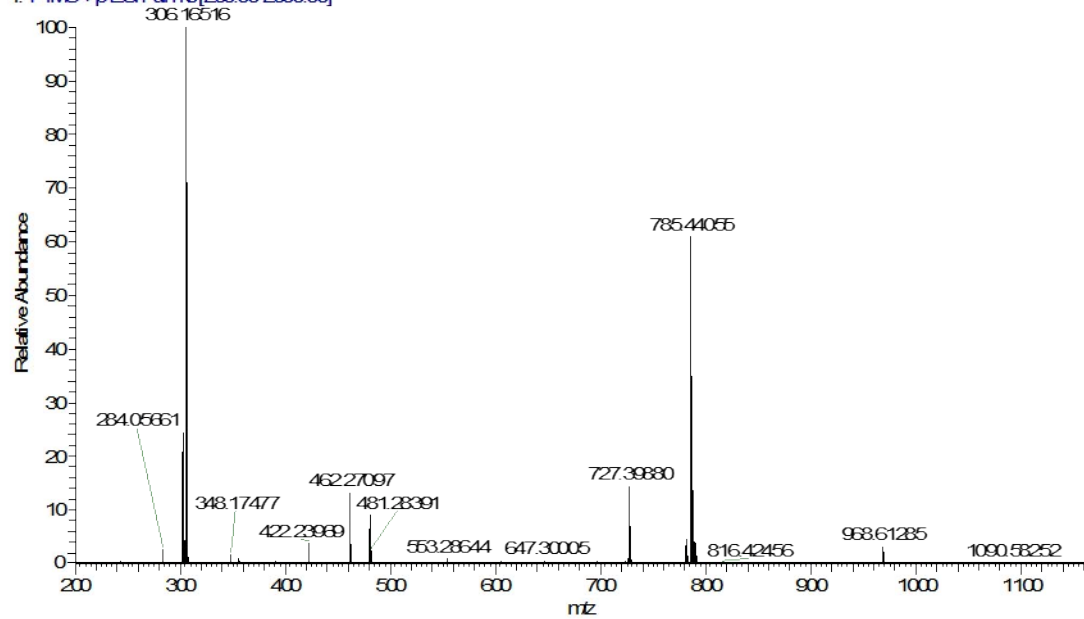
proton NMR for 3d (CDCl<sub>3</sub>, 500MHz)



C13 for 3d (CDCl<sub>3</sub>, 125MHz)

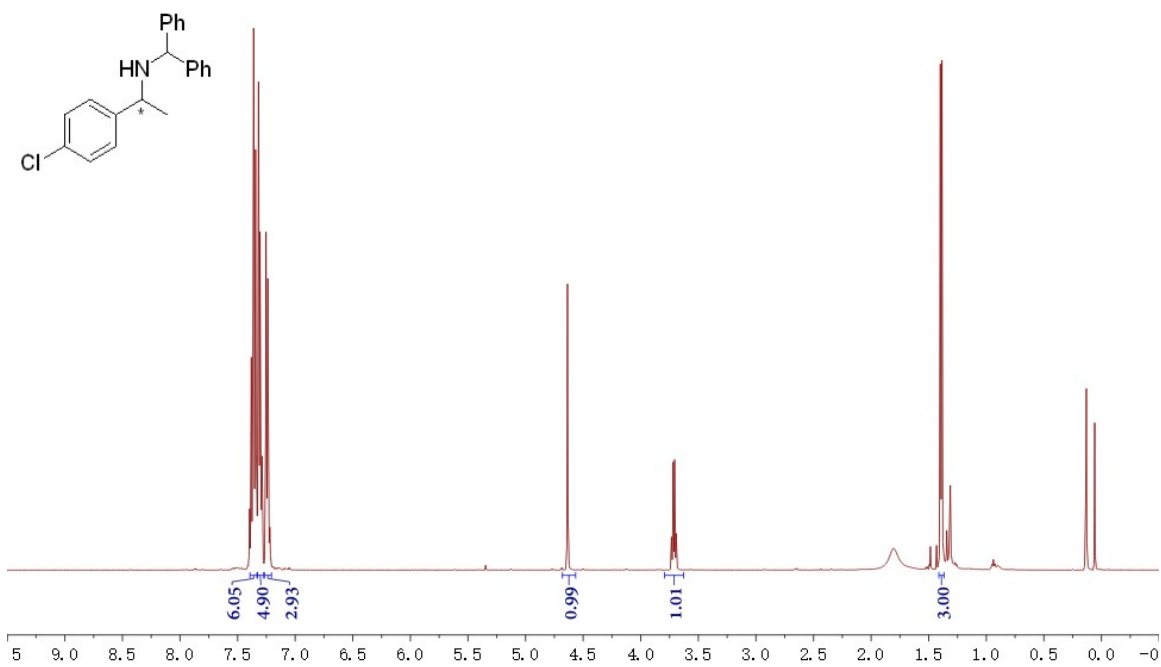


0031#23 RT: 0.35 AV: 1 NL: 1.38EB  
T: FIMS+pESI Full ms [200.00-2000.00]



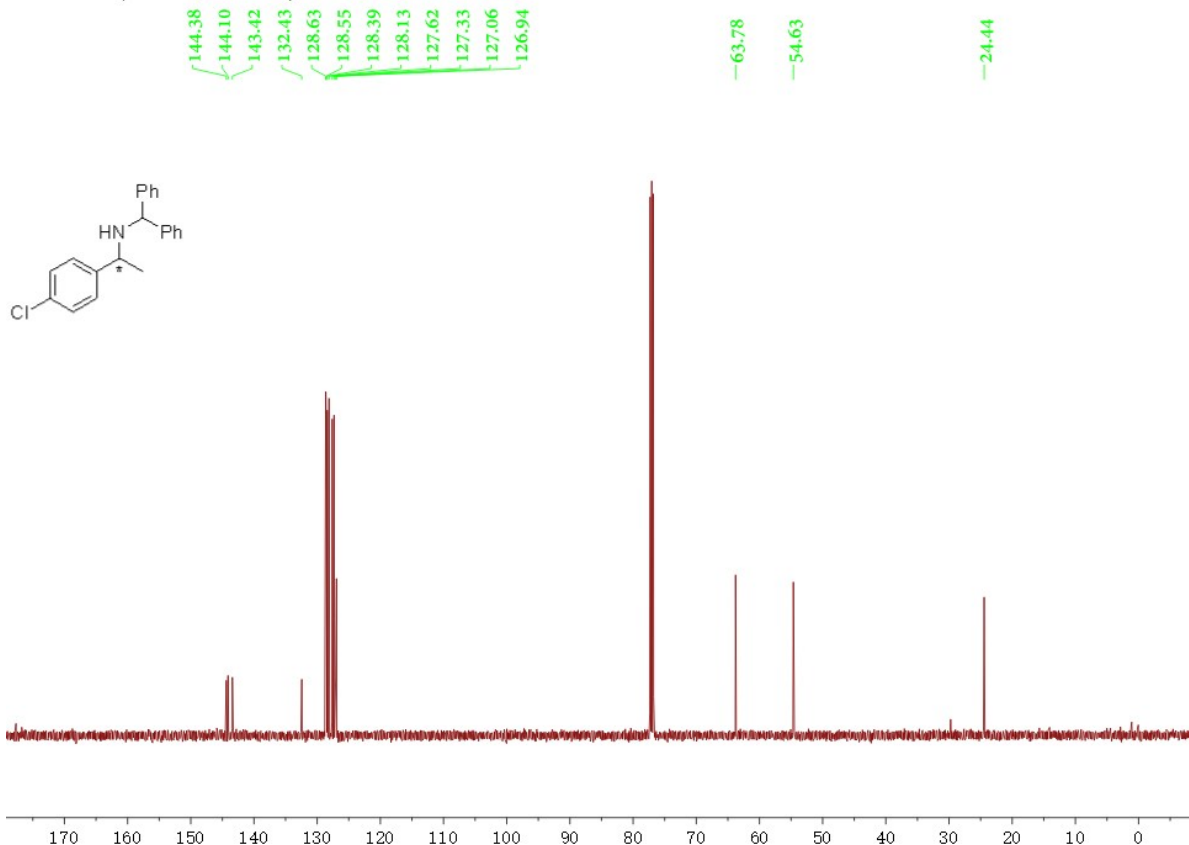
proton NMR for 3e (CDCl<sub>3</sub>, 500MHz)

7.38, 7.38, 7.37, 7.36, 7.34, 7.32, 7.32, 7.31, 7.30, 7.29, 7.25, 7.24, -4.64, 3.73, 3.72, 3.71, 3.69, 1.40, 1.39

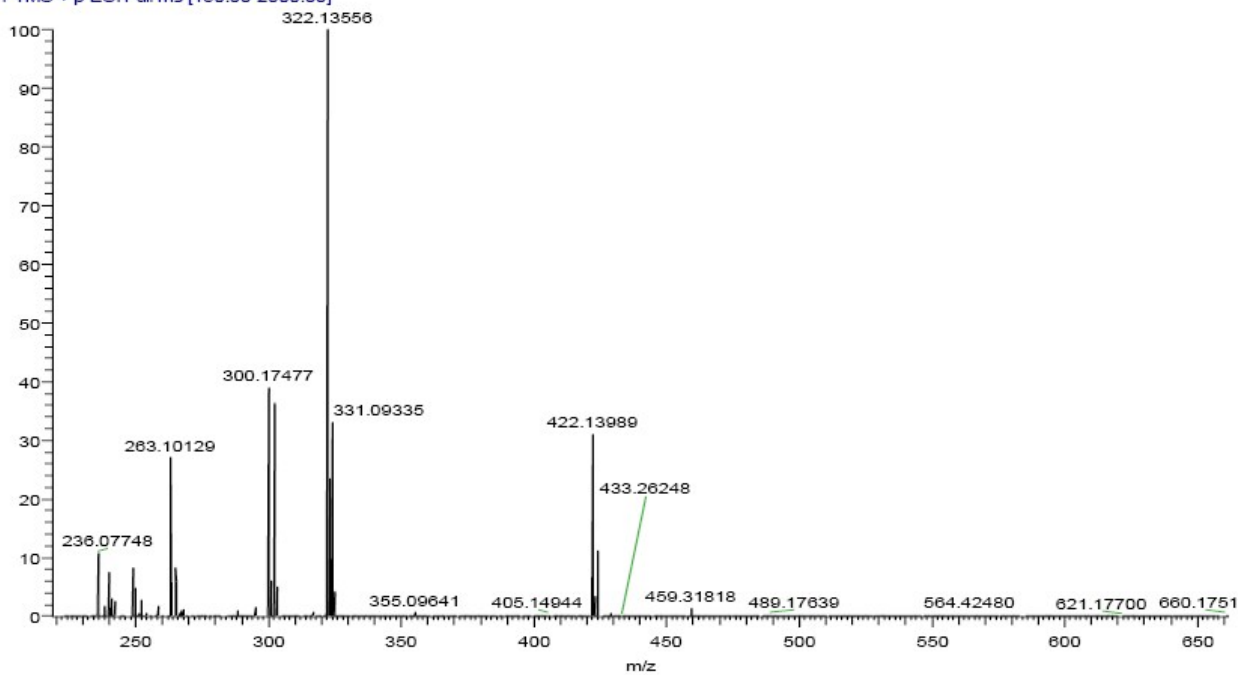




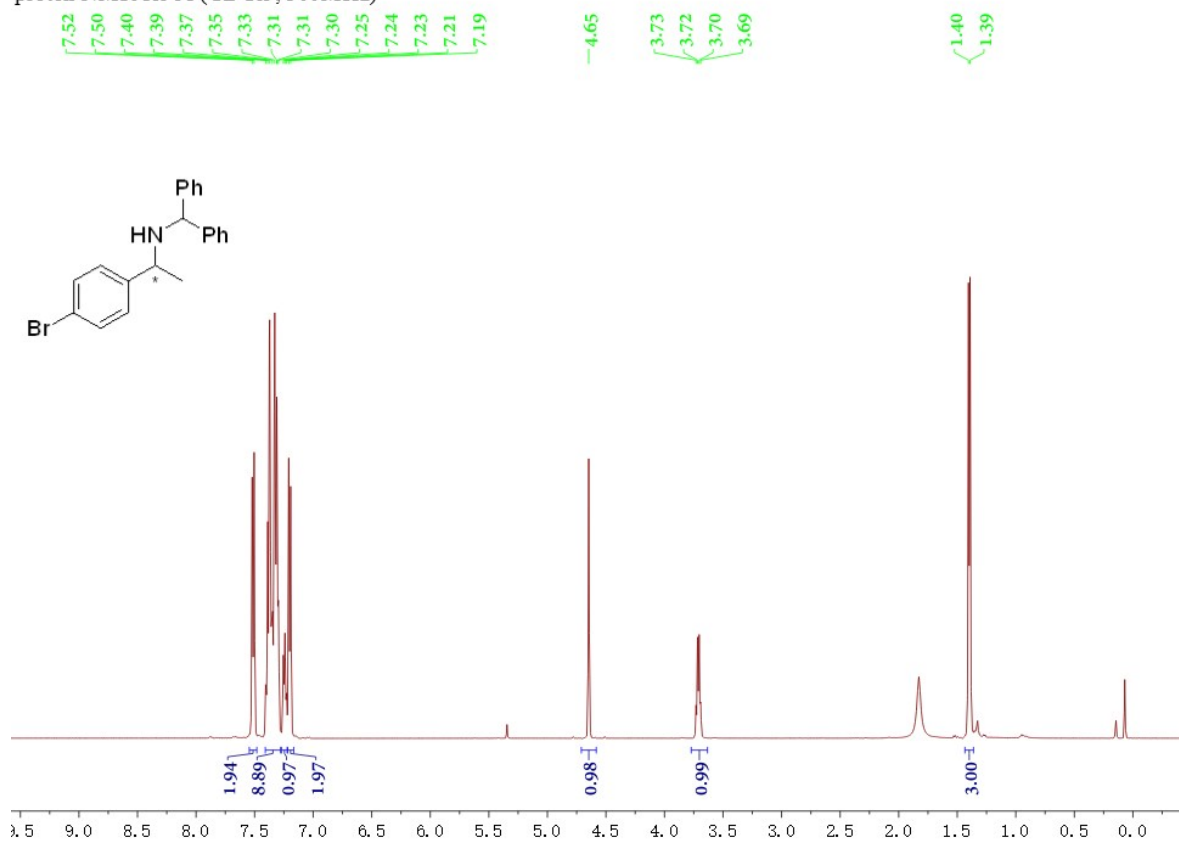
C13 for 3e (CDCl3, 125MHz)



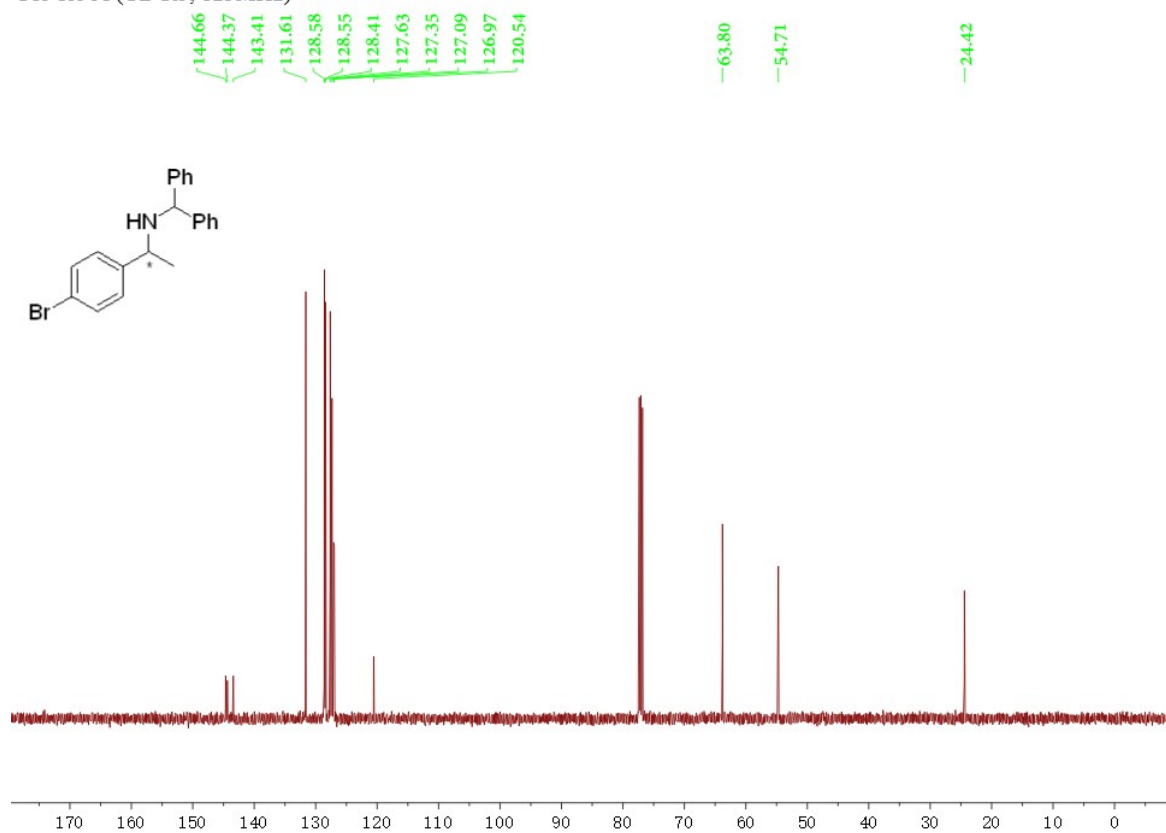
00085 #21 RT: 0.64 AV: 1 NL: 9.26E5  
T: FTMS + p ESI Full ms [150.00-2000.00]



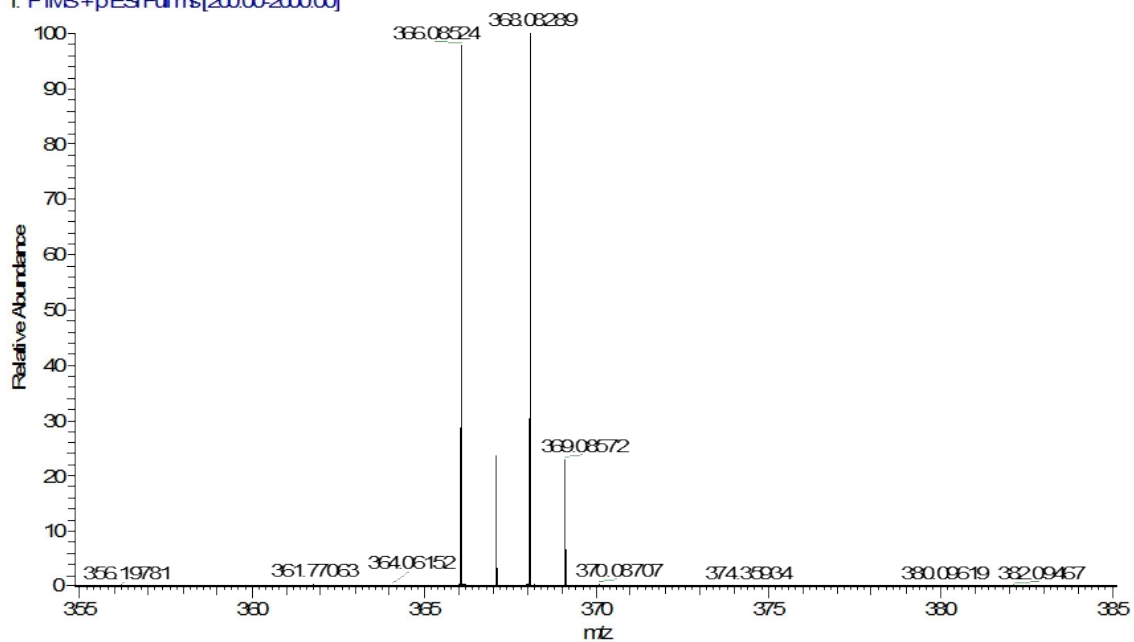
proton NMR for 3f (CDCl<sub>3</sub>, 500MHz)



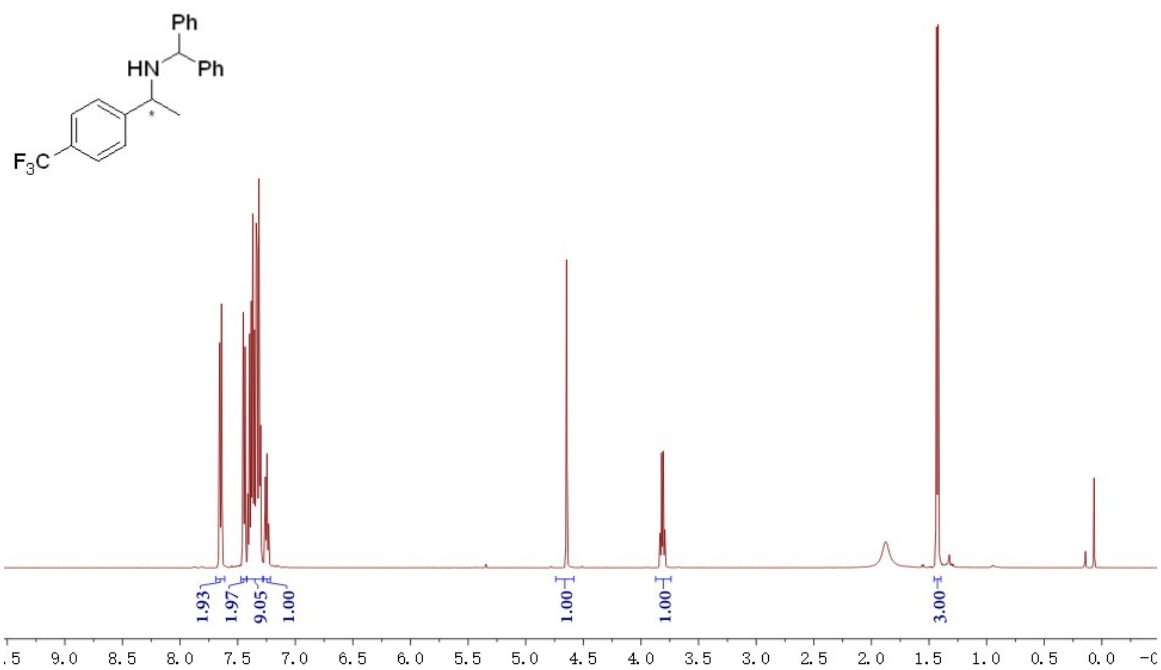
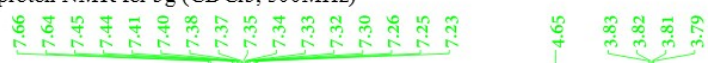
C13 for 3f (CDCl<sub>3</sub>, 125MHz)



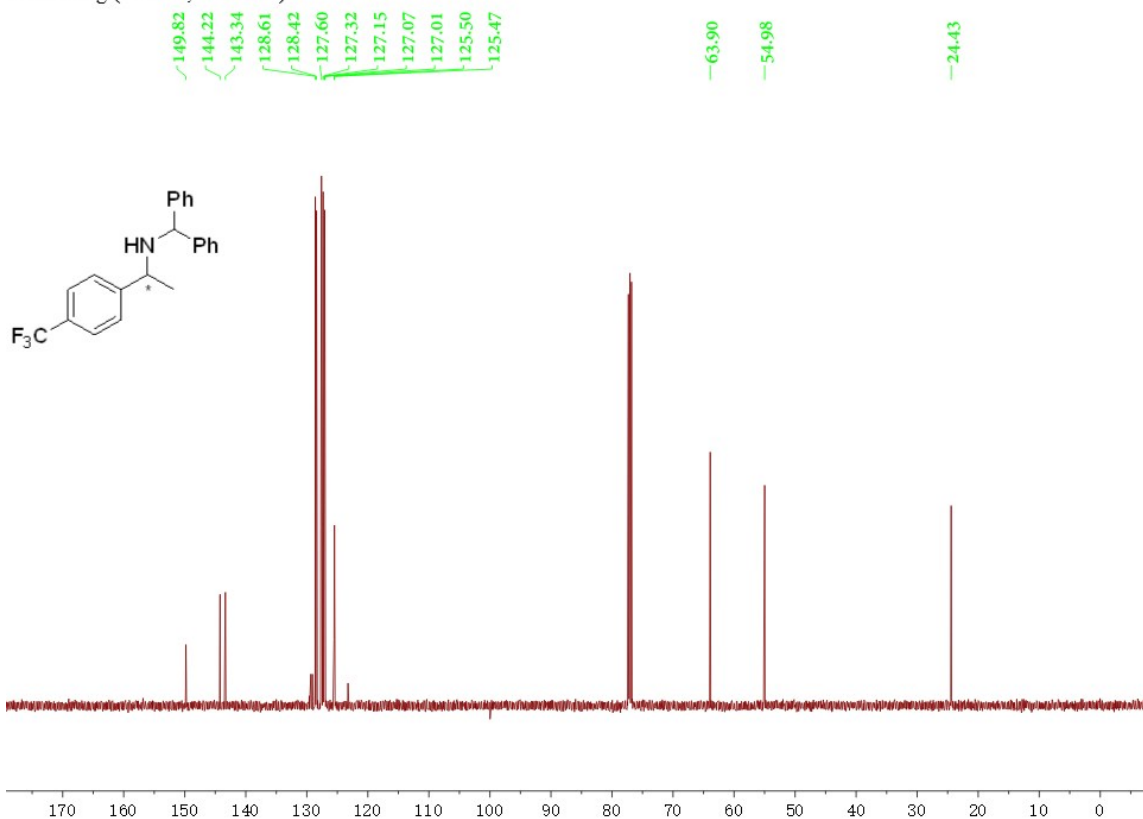
0003 #9 RT: 0.13 AV: 1 NL: 1.61EB  
T: FIMS+pESI Full ms[200.00-2000.00]



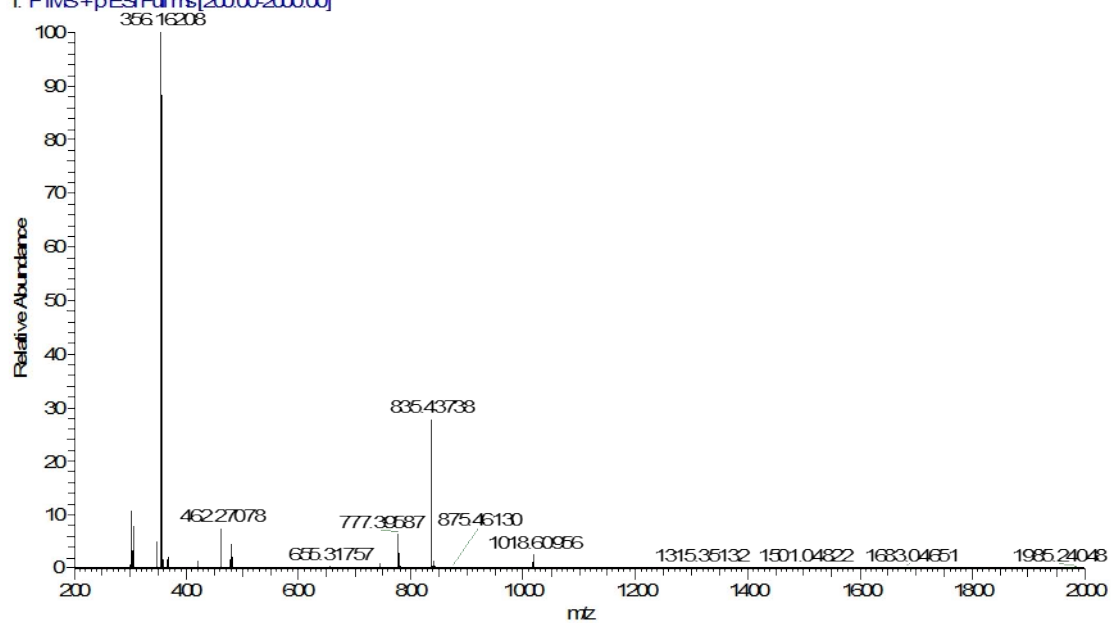
proton NMR for 3g (CDCl<sub>3</sub>, 500MHz)



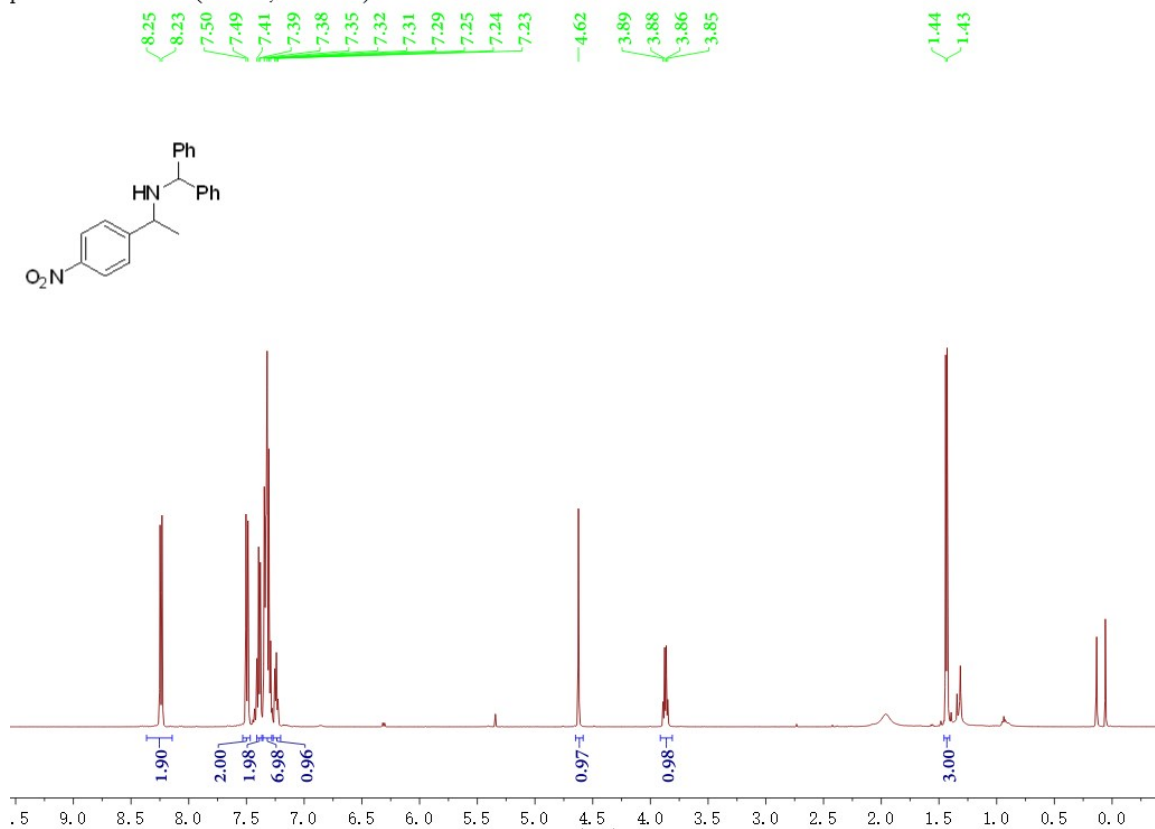
C13 for 3g (CDCl3, 125MHz)



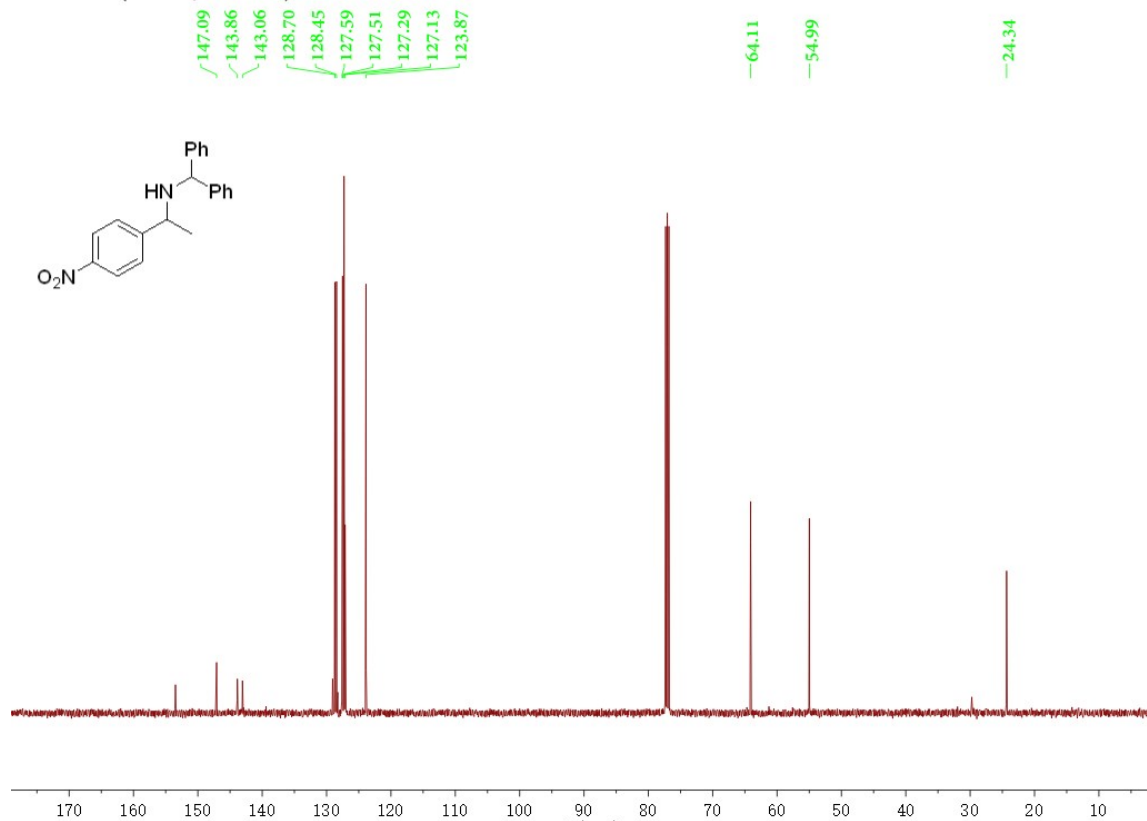
0003 #19 RT: 0.28 AV: 1 NL: 246EB  
T: FTMS+pESI Full ms [200.00-2000.00]



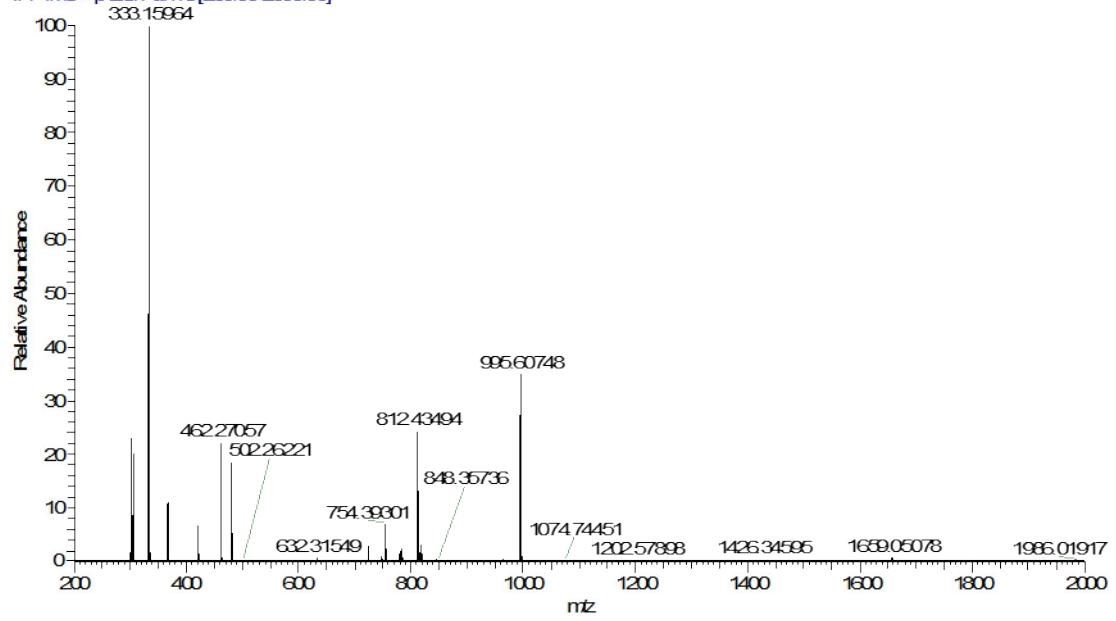
proton NMR for 3h (CDCl<sub>3</sub>, 500MHz)



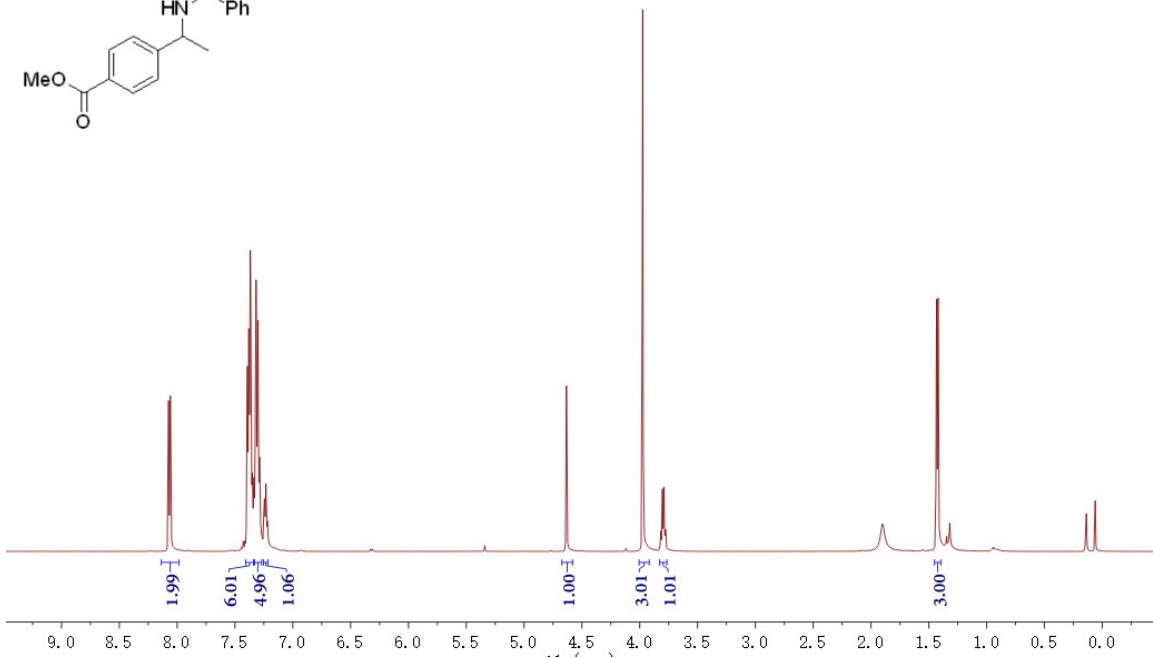
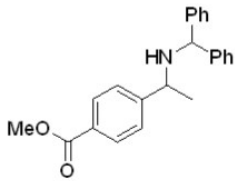
C13 for 3h (CDCl<sub>3</sub>, 125MHz)



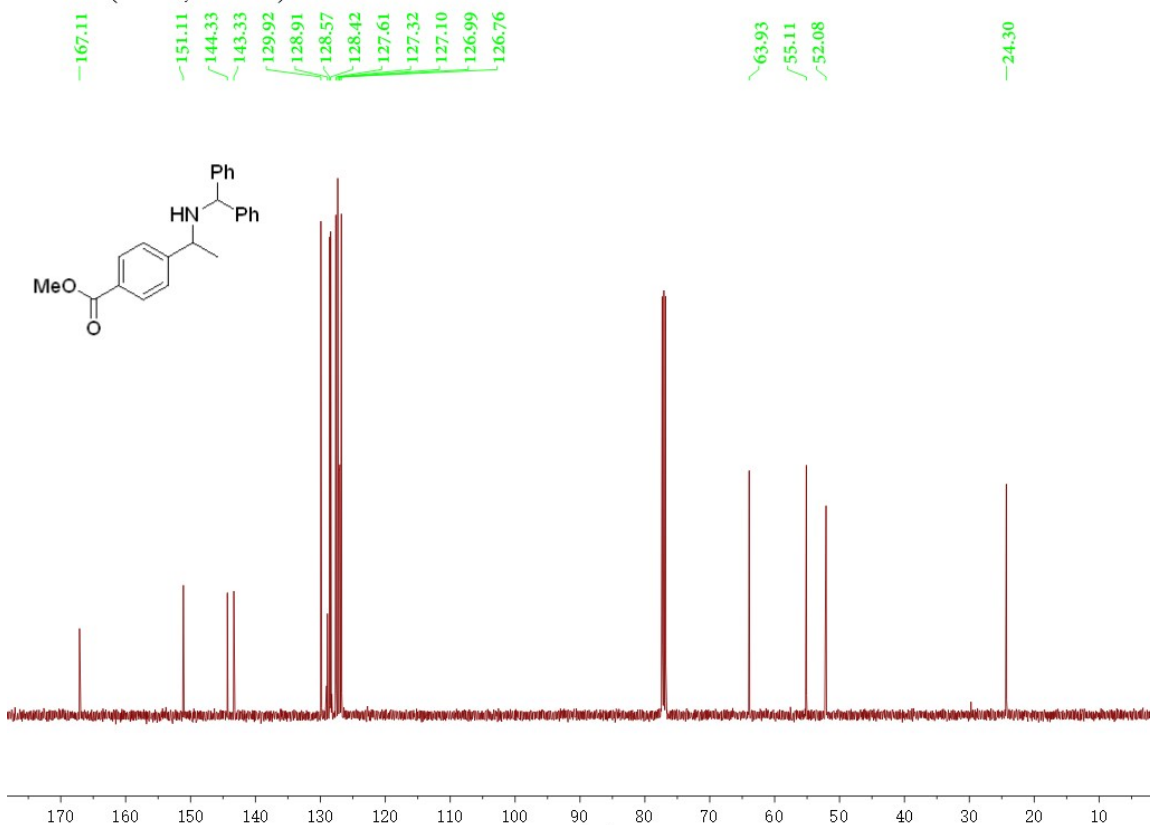
003: #19 RT: 0.28 AV: 1 NL: 1.32EB  
T: FIMS+pESI Full ms [200.00-2000.00]



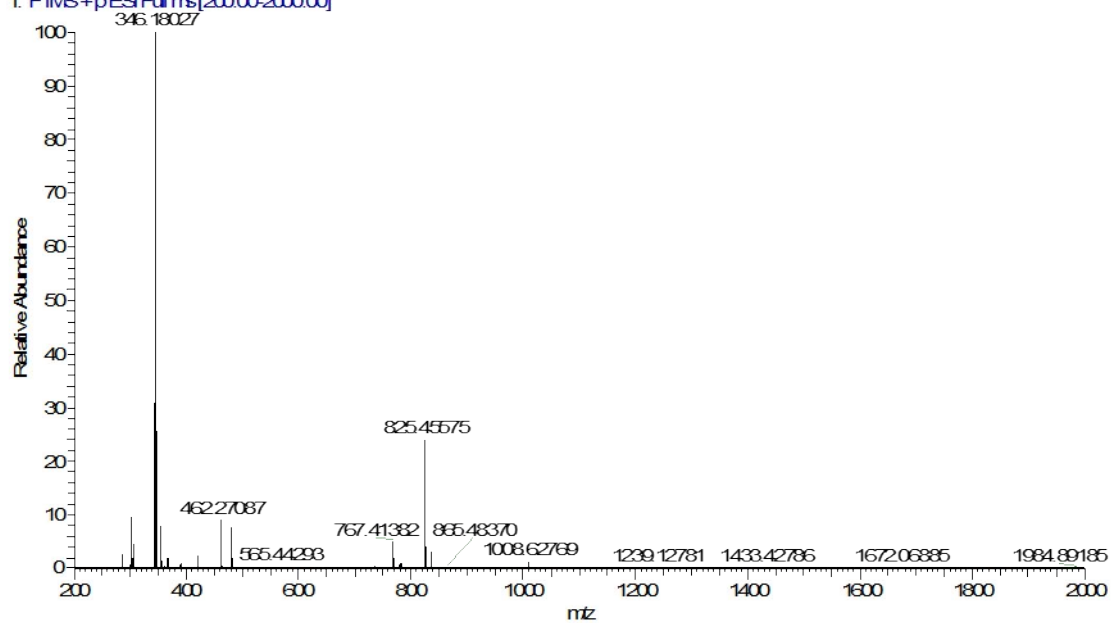
proton NMR for 3i (CDCl<sub>3</sub>, 500MHz)



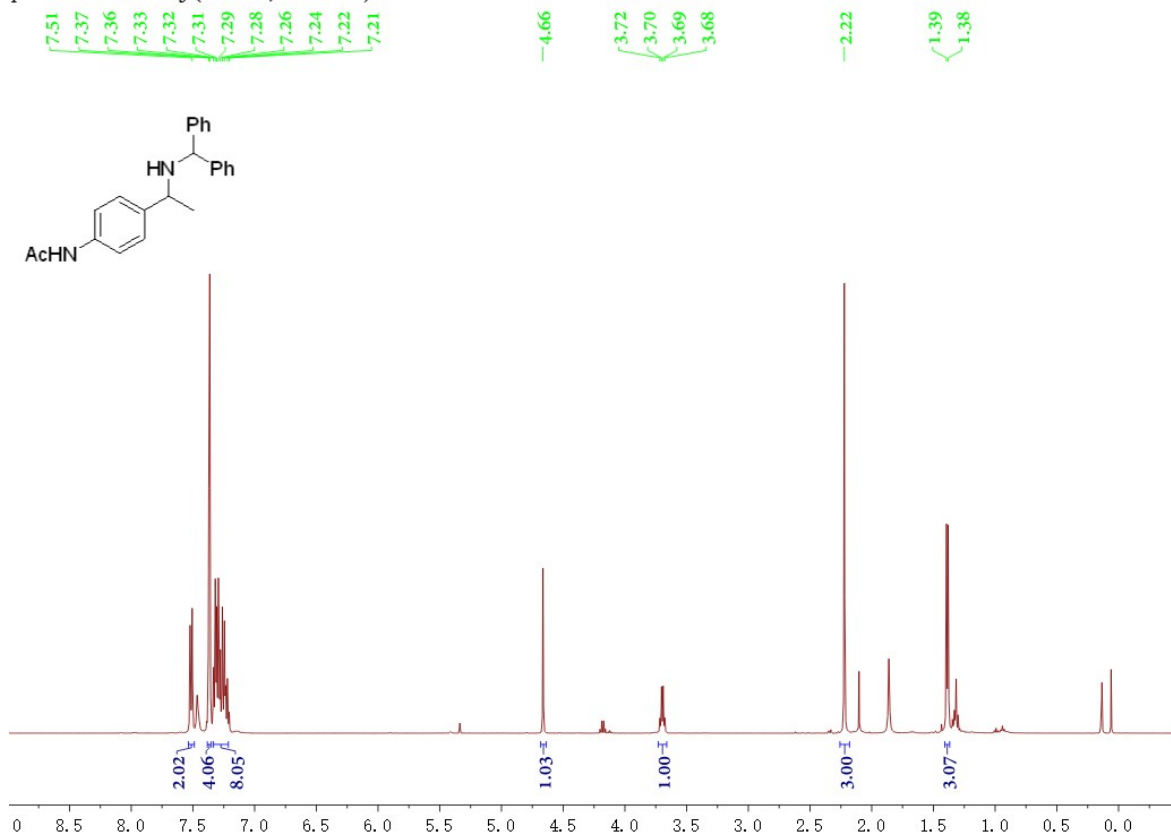
C13 for 3i (CDCl3, 125MHz)



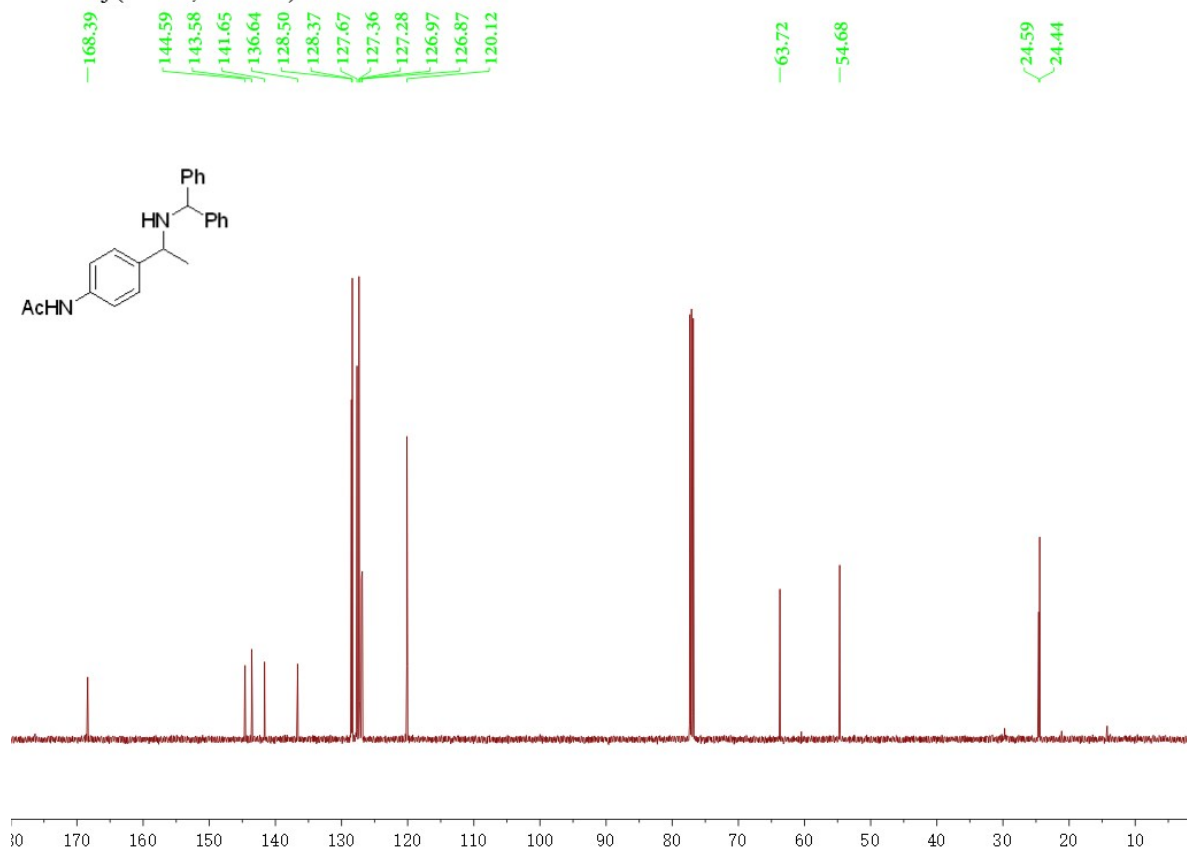
0003E #10 RT: 0.13 AV: 1 NL: 271EB  
T: FTMS+pESI Full ms [200.00-2000.00]



proton NMR for 3j (CDCl<sub>3</sub>, 500MHz)

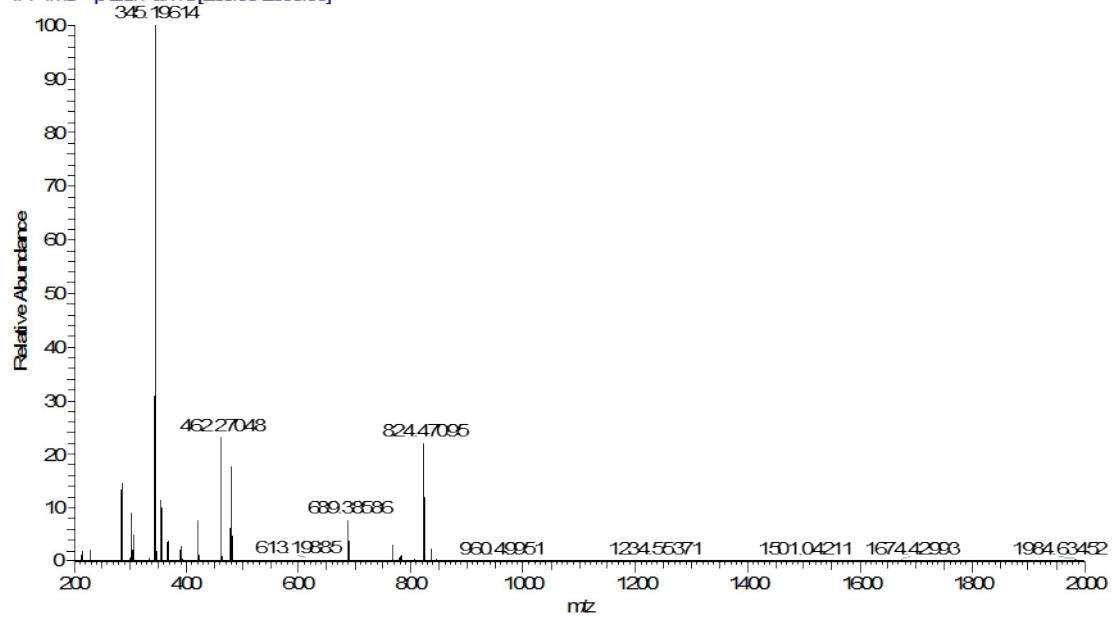


C13 for 3j (CDCl<sub>3</sub>, 125MHz)



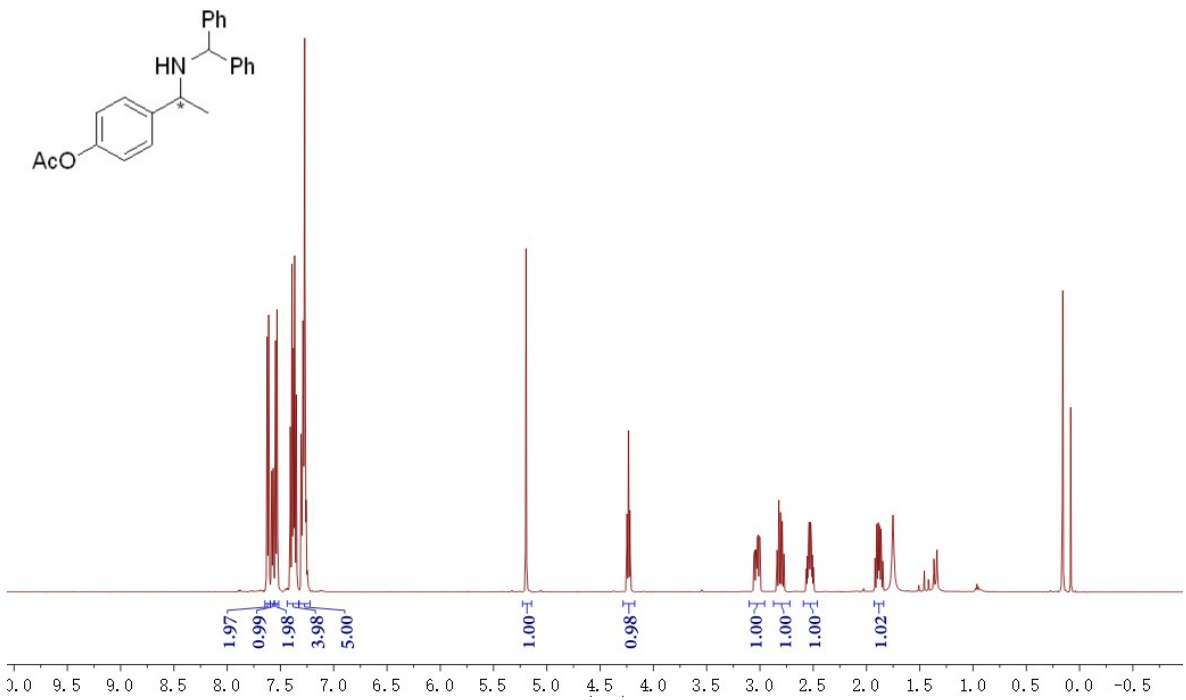


003E #26 RT: 0.40 AV: 1 NL: 1.50EB  
T: FTMS+pESI Full ms [200.00-2000.00]

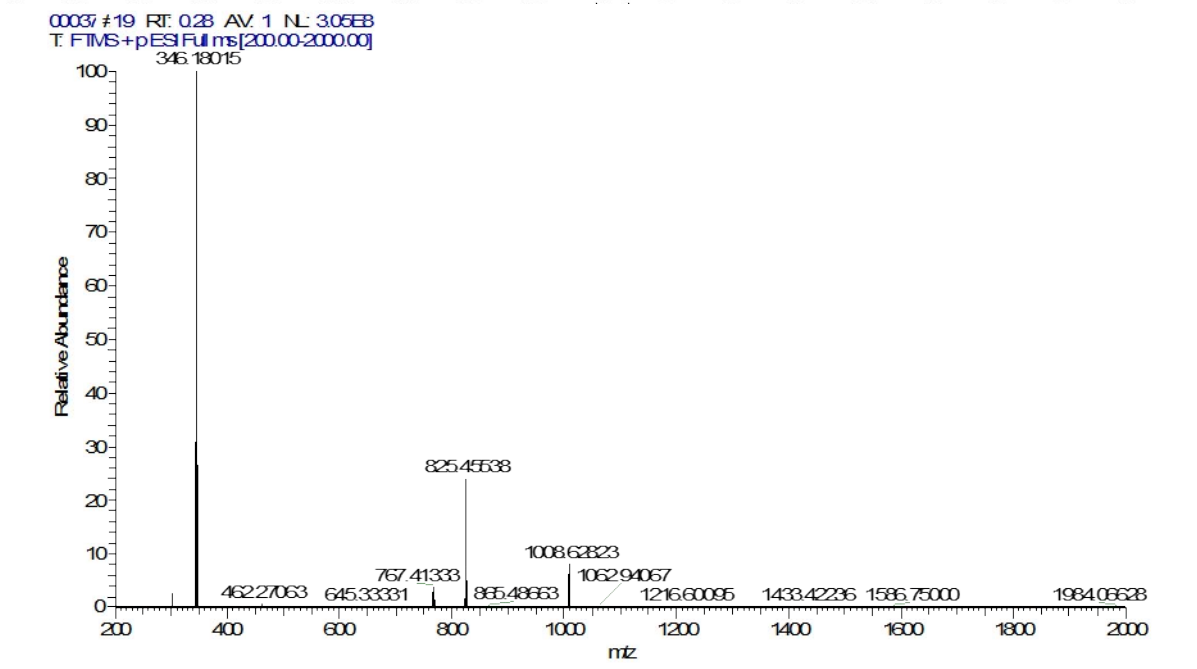
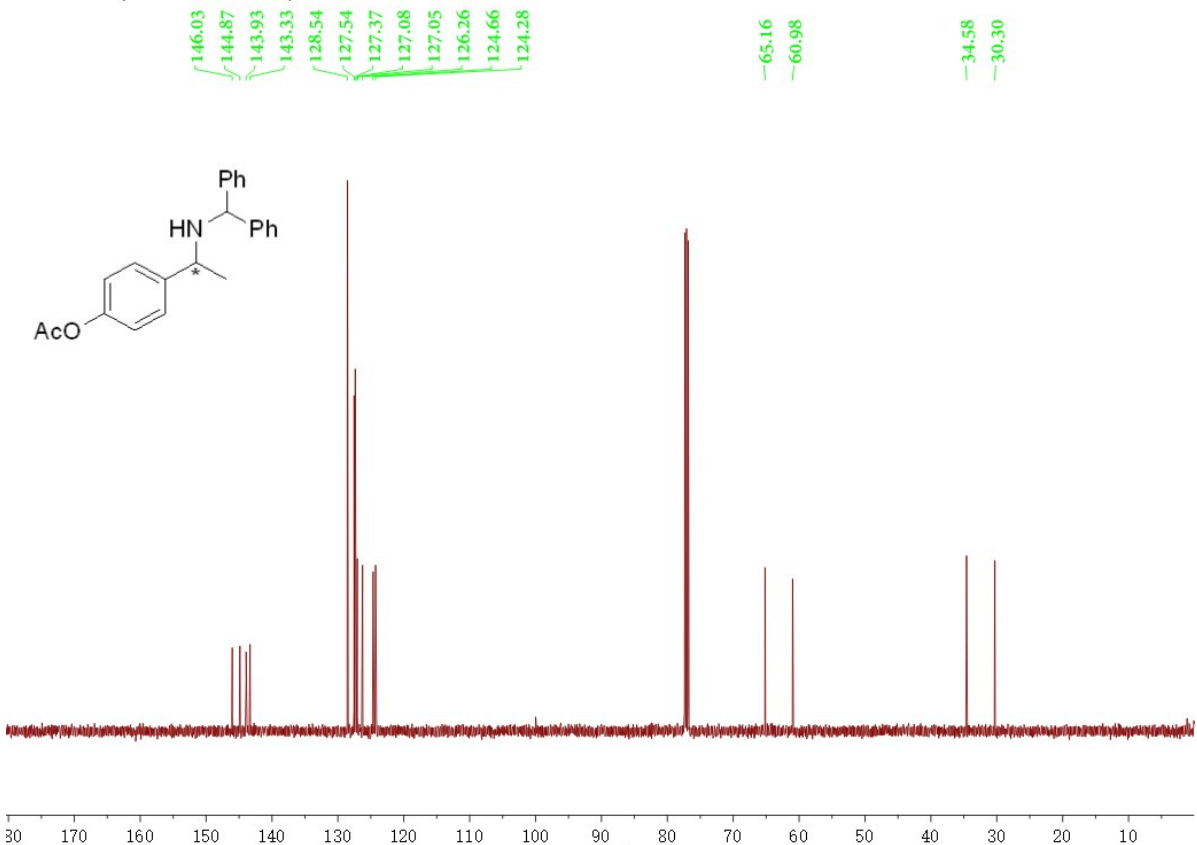


Proton NMR for 3k (CDCl<sub>3</sub>, 500MHz)

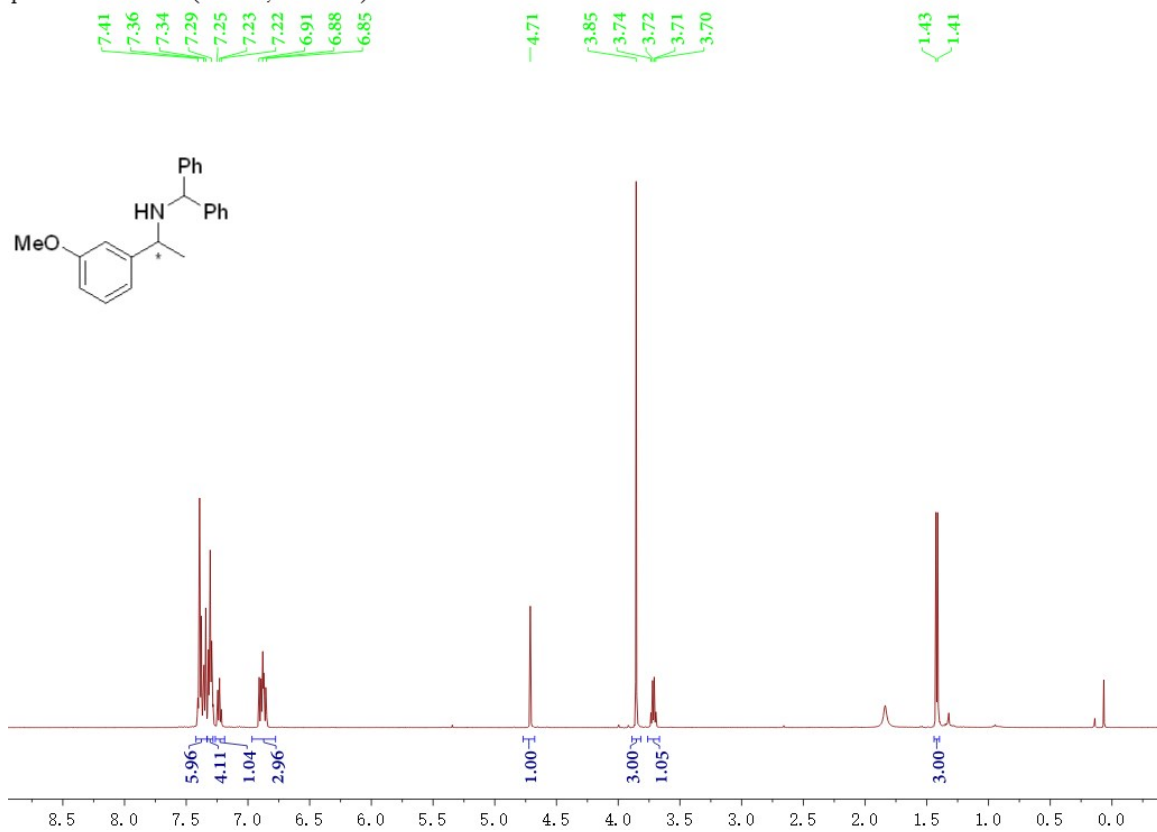
7.63 7.61 7.58 7.57 7.55 7.53 7.41 7.39 7.38 7.38 7.37 7.35 7.31 7.29 7.27 7.26 5.20 4.25 4.23 4.22 3.04 3.03 3.02 3.02 3.01 3.00 2.84 2.82 2.81 2.79 2.55 2.54 2.53 2.52 2.52 2.52 1.90 1.89 1.88 1.86



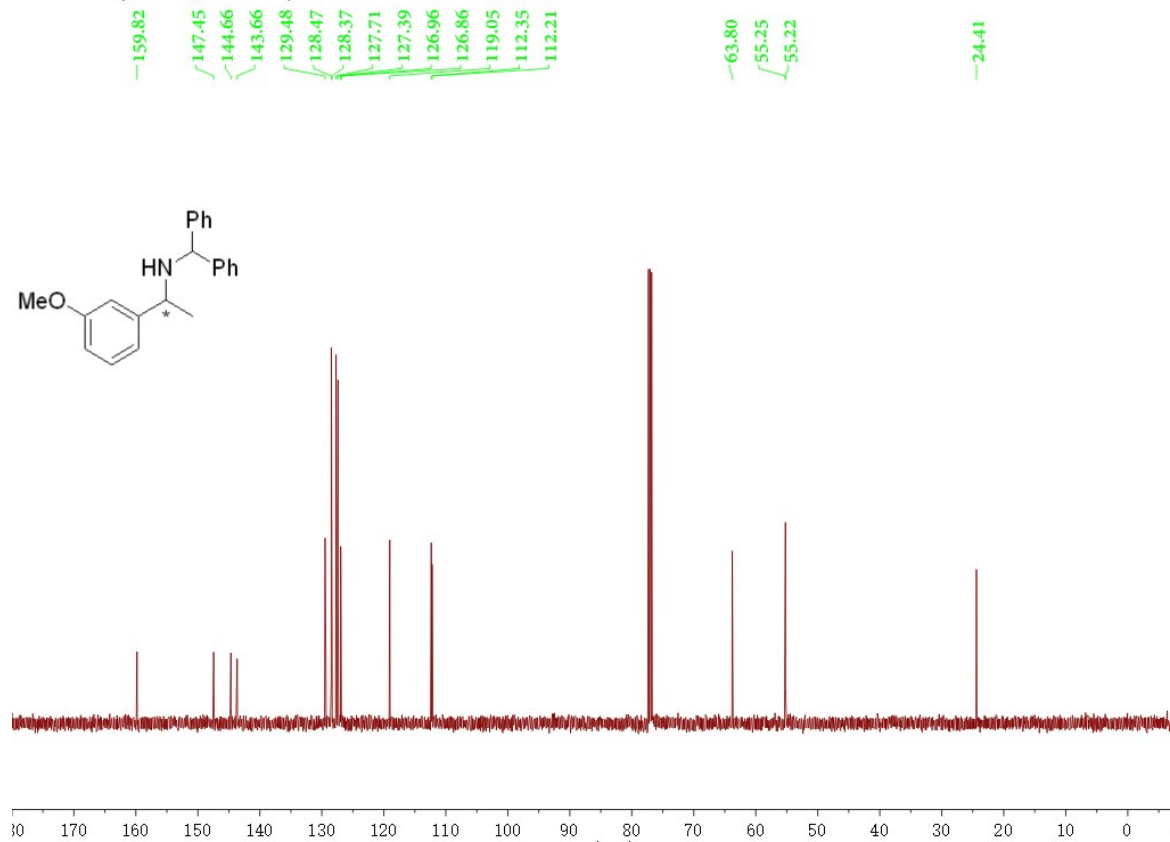
C13 for 3k (CDCl3, 125MHz)



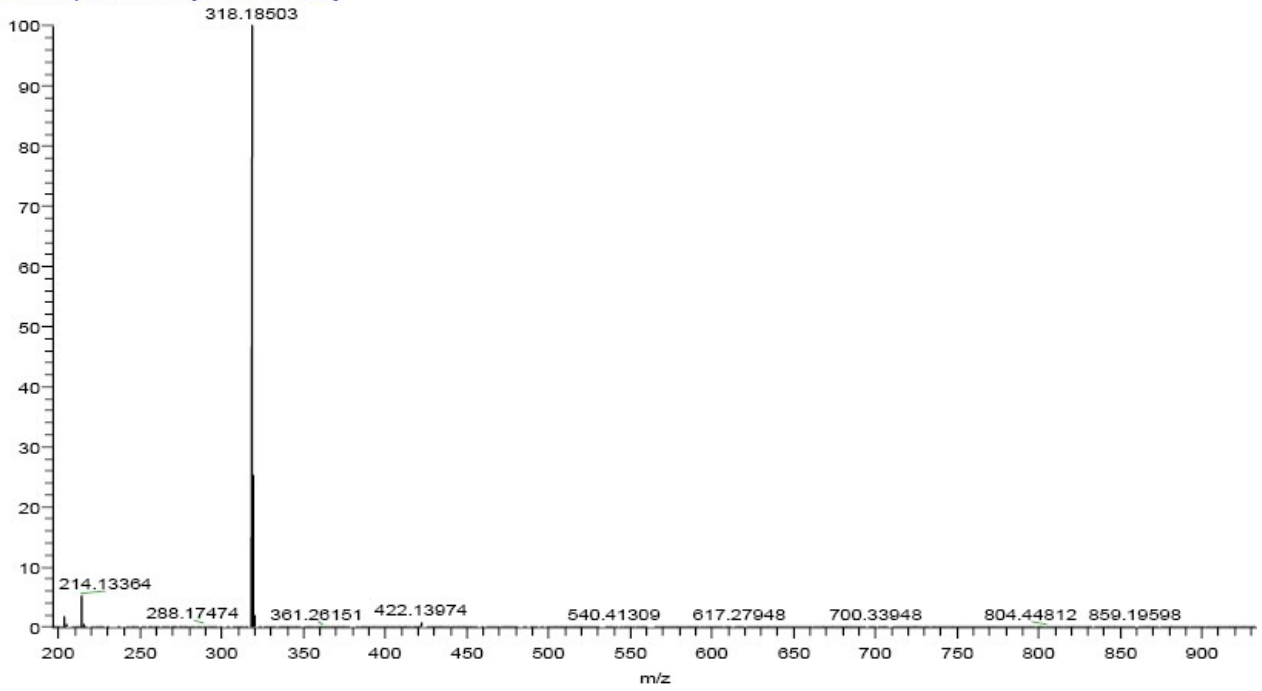
proton NMR for 31 (CDCl<sub>3</sub>, 500MHz)



C13 for 31 (CDCl<sub>3</sub>, 125MHz)

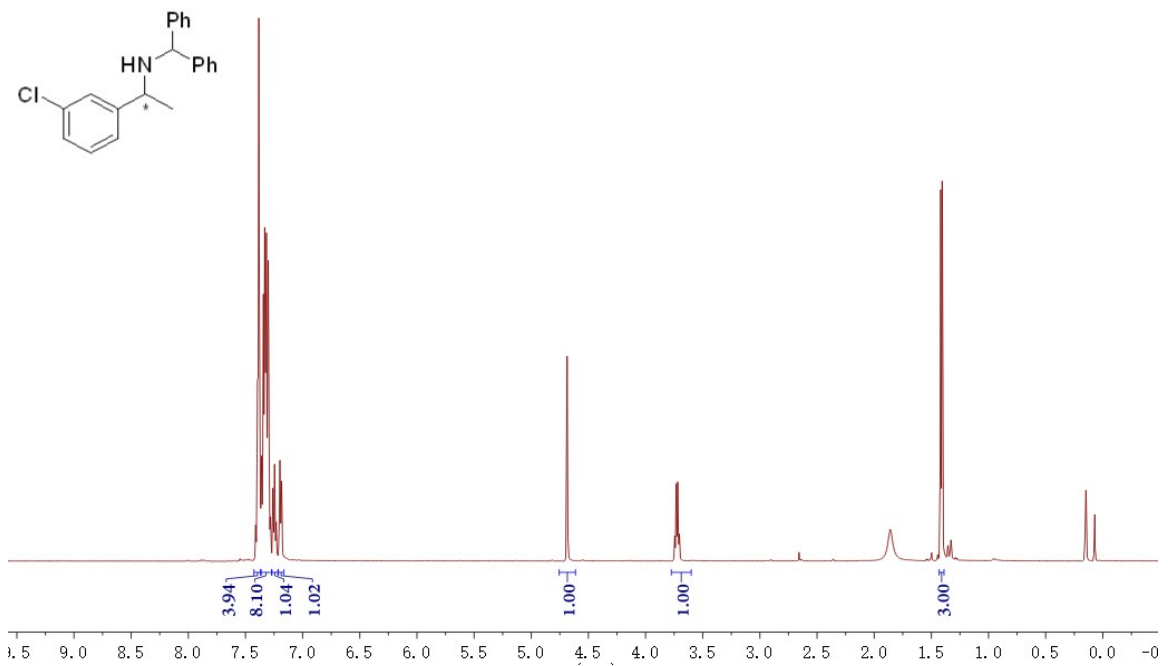


00087 #5 RT: 0.12 AV: 1 NL: 8.95E7  
T: FTMS + p ESI Full ms [150.00-2000.00]

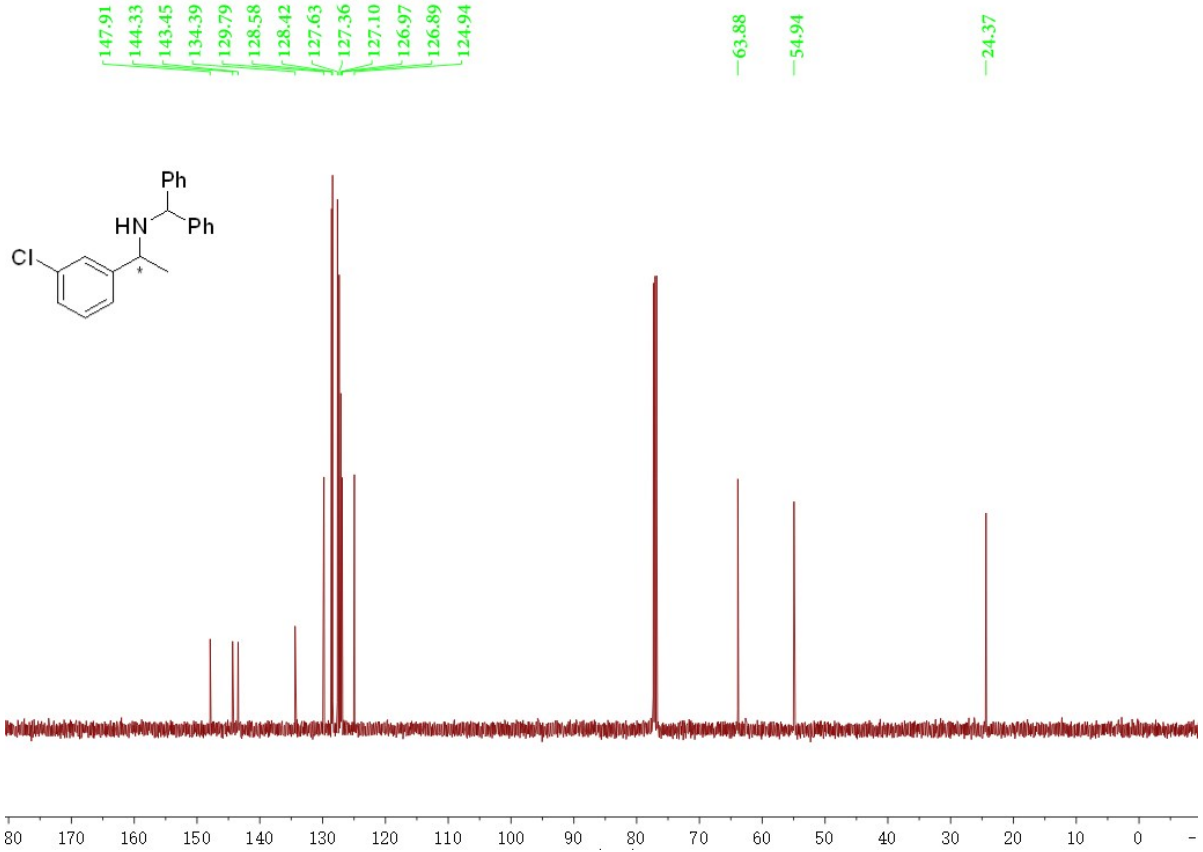


proton NMR for 3m (CDCl<sub>3</sub>, 500MHz)

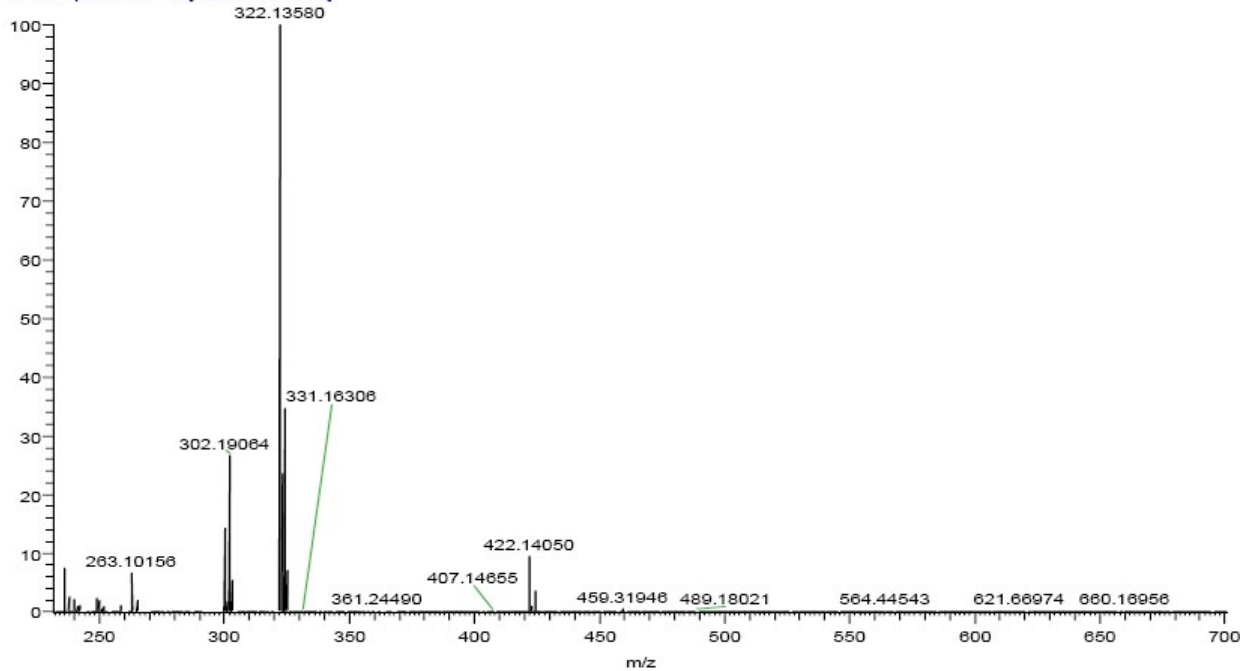
7.41 7.40 7.38 7.36 7.34 7.33 7.32 7.31 7.30 7.26 7.25 7.23 7.20 7.19 -4.69 3.74 3.73 3.72 3.71 1.42 1.41



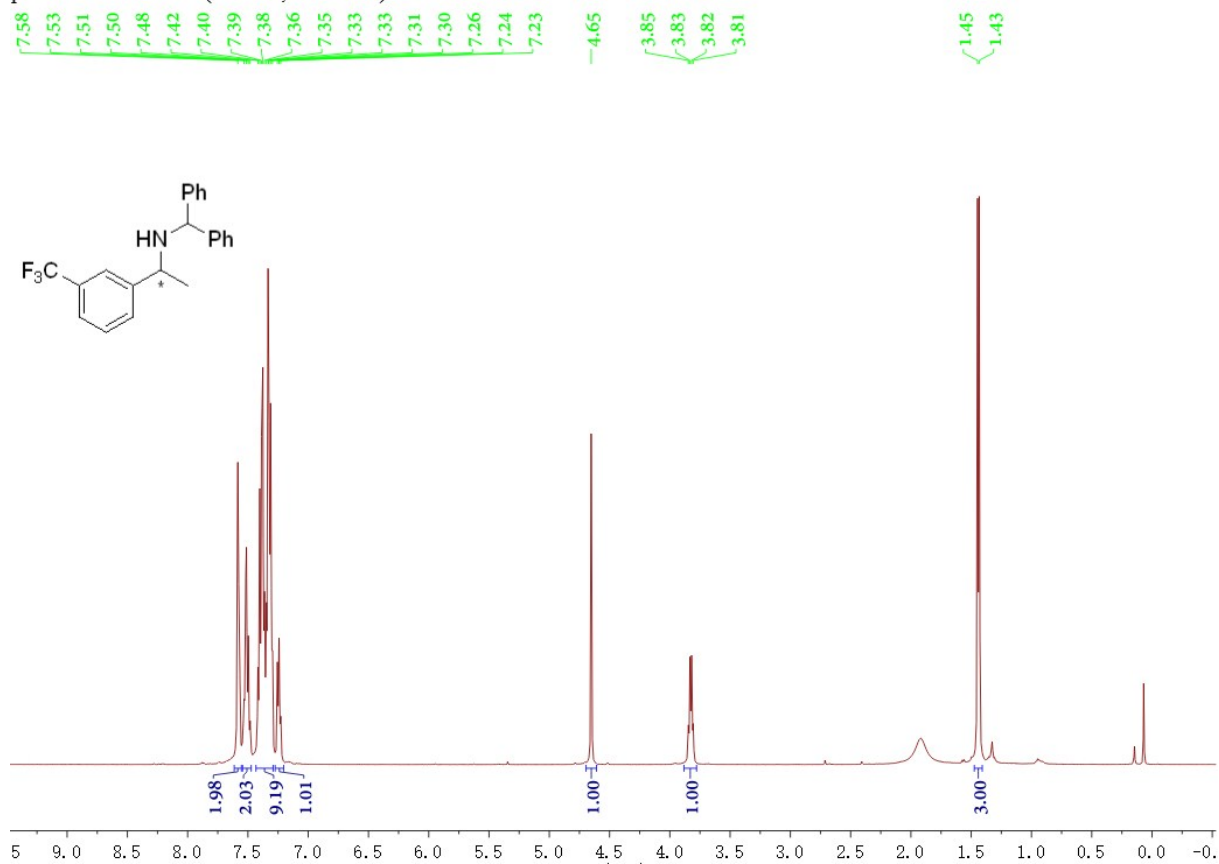
C13 for 3m (CDCl3, 125MHz)



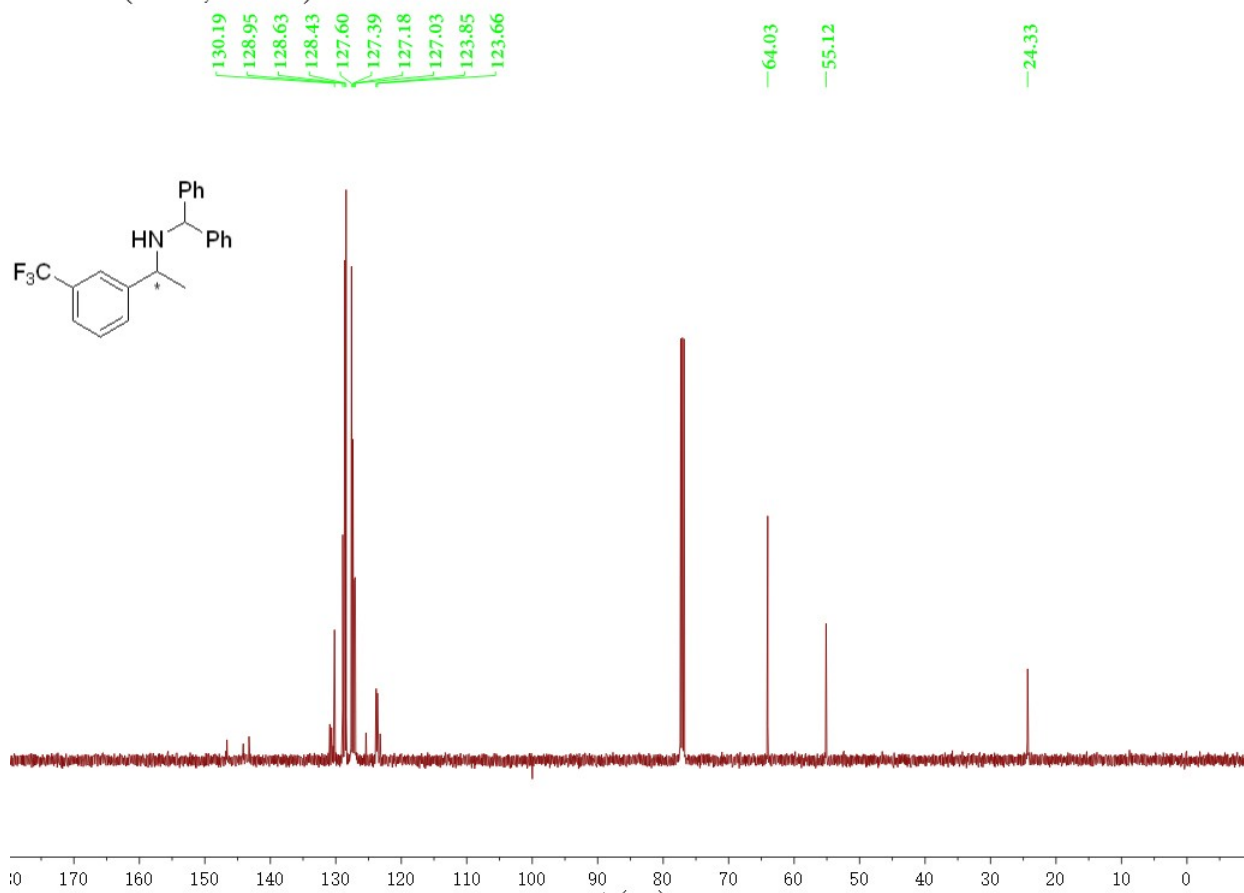
00084 #26 RT: 0.77 AV: 1 NL: 6.47E6  
T: FTMS + p ESI Full ms [150.00-2000.00]



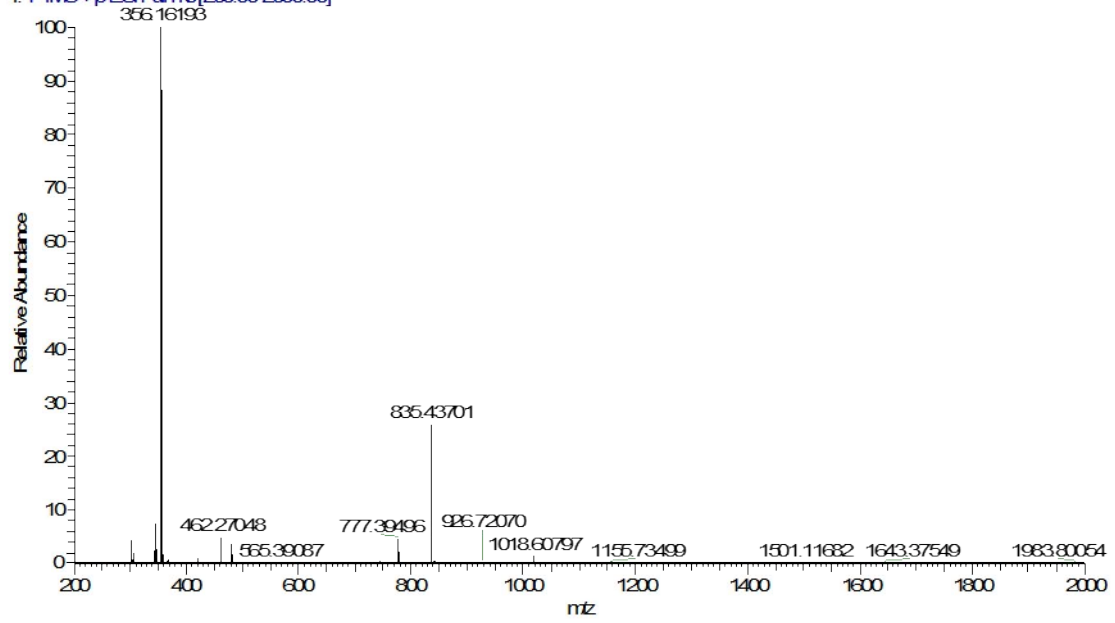
proton NMR for 3n (CDCl<sub>3</sub>, 500MHz)



C13 for 3n (CDCl<sub>3</sub>, 125MHz)

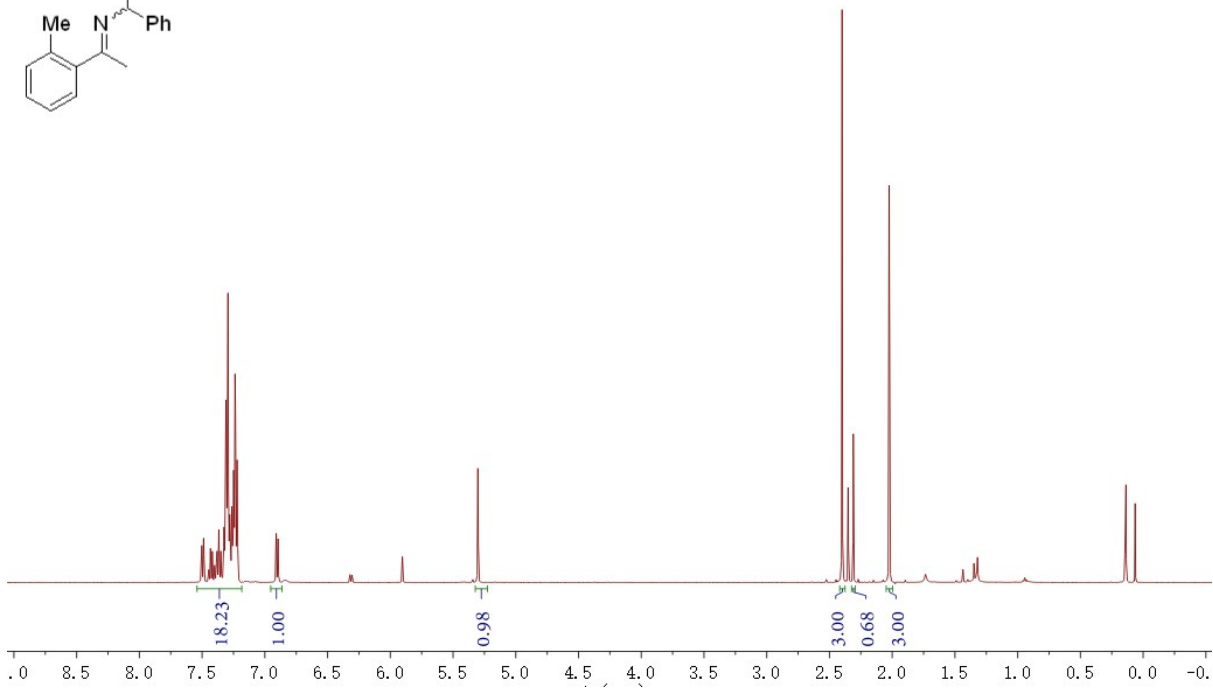
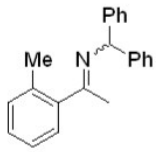


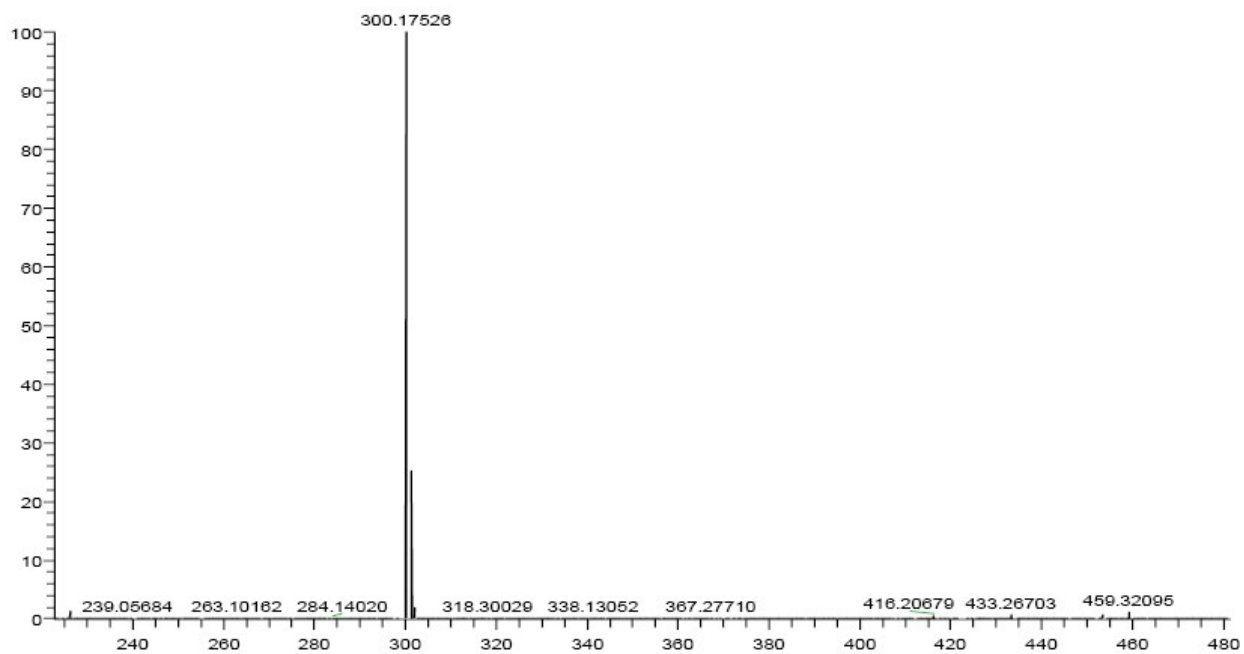
003E #18 RT: 0.26 AV: 1 NL: 261EB  
T: FIMS+pESI Full ms [200.00-2000.00]



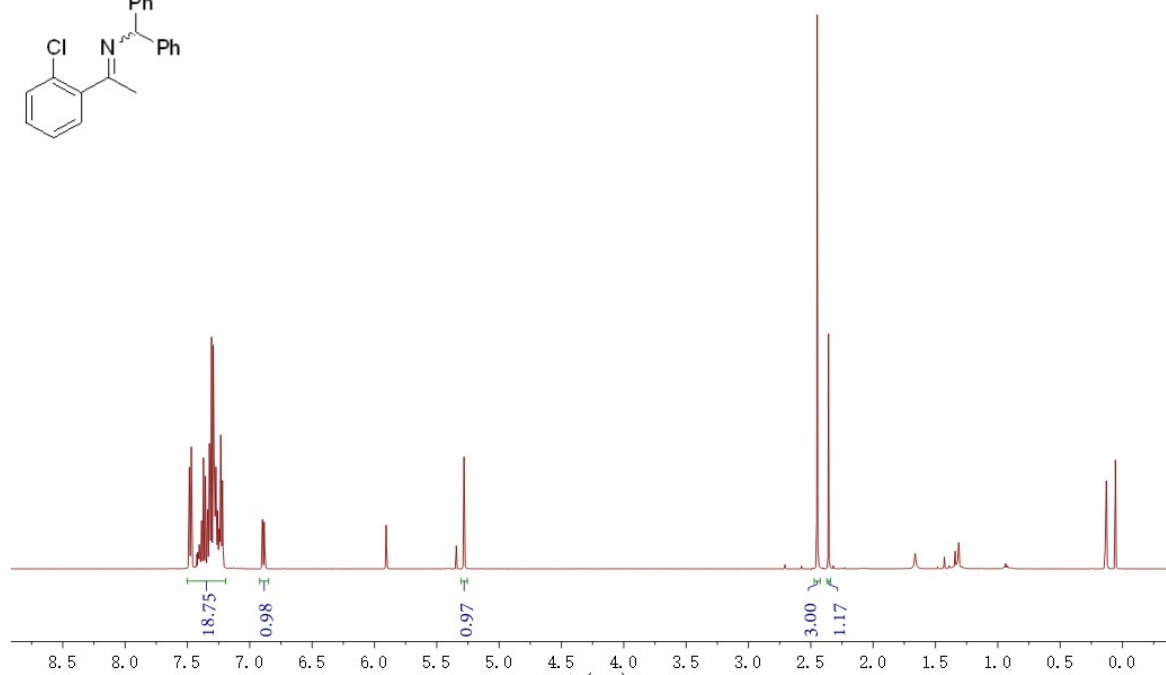
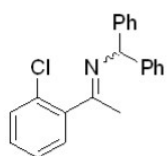
proton NMR for 3o' (CDCl<sub>3</sub>, 500MHz)

7.50  
7.49  
7.37  
7.31  
7.30  
7.29  
7.26  
7.24  
7.22  
6.91  
6.91  
6.90  
6.89  
-5.30  
-2.40  
-2.02



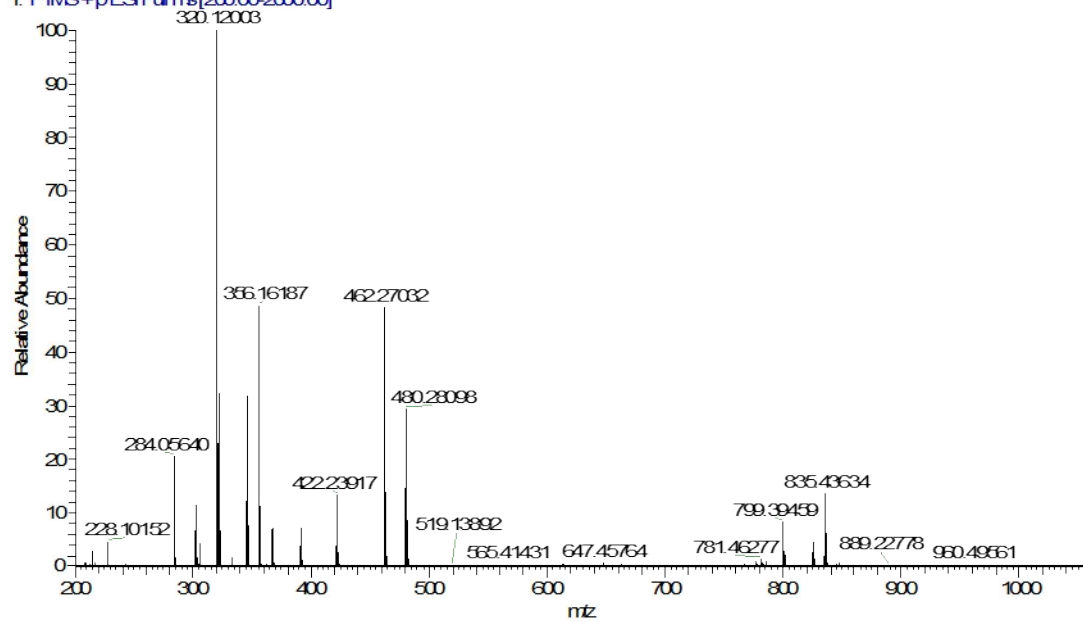


proton NMR for 3p' (CDCl<sub>3</sub>, 500MHz)

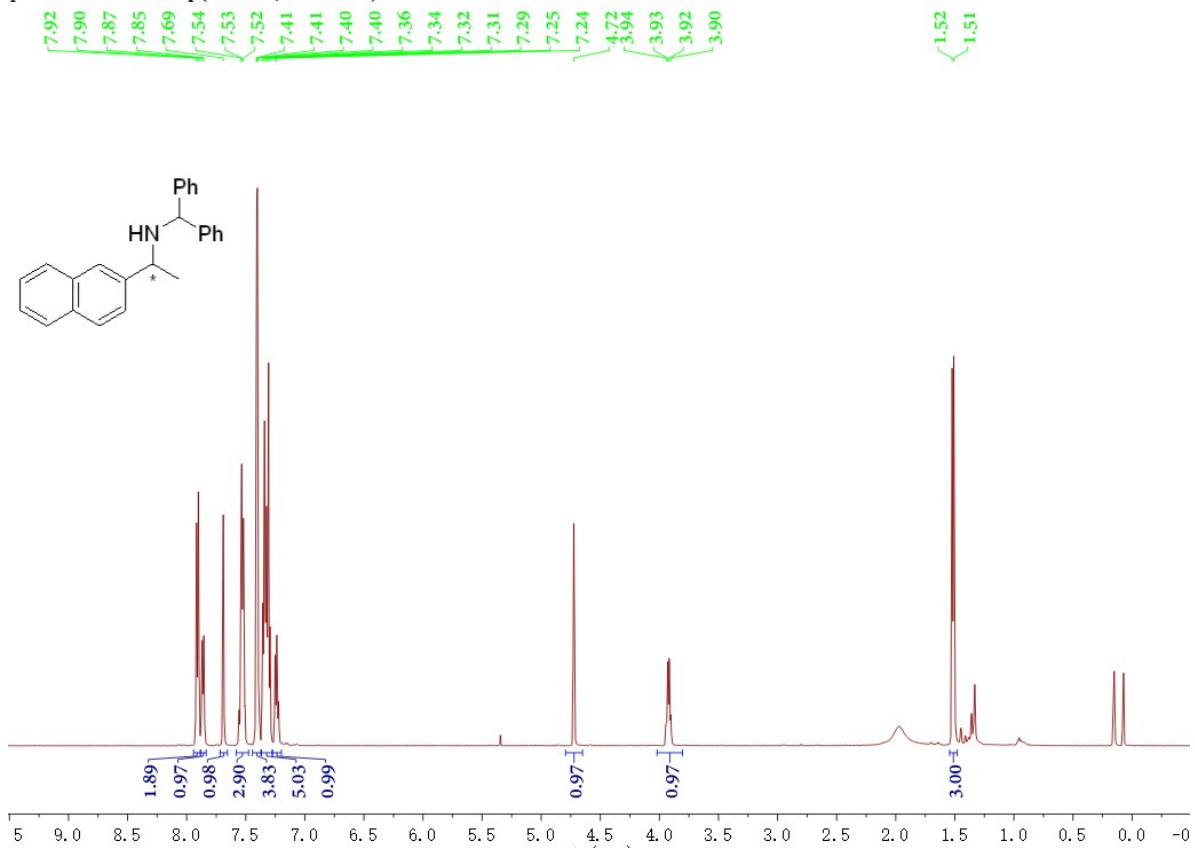




003 #31 RT: 0.48 AV: 1 NL: 6.56E7  
T: FIMS+pESI Full ms [200.00-2000.00]

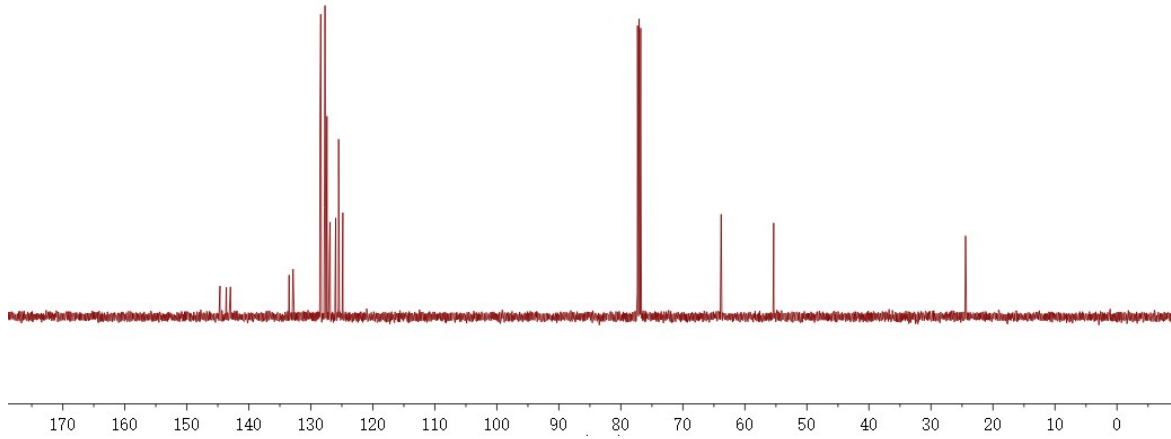
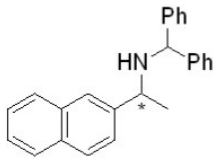


proton NMR for 3q (CDCl<sub>3</sub>, 500MHz)

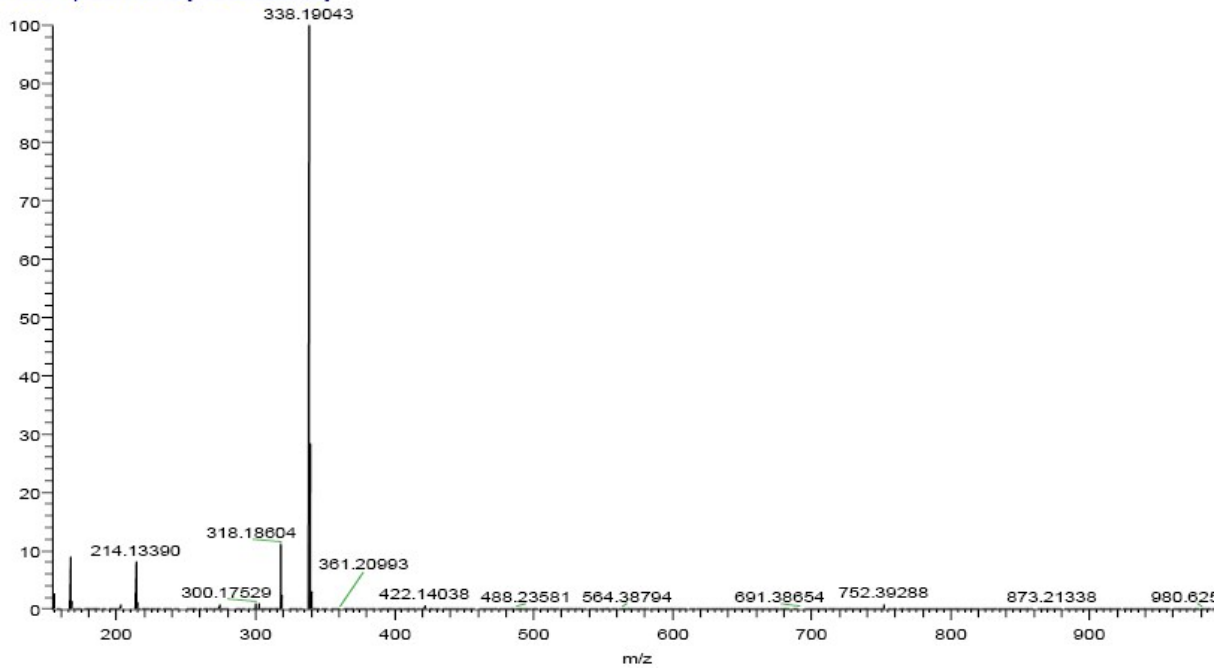


C13 for 3q (CDCl3, 125MHz)

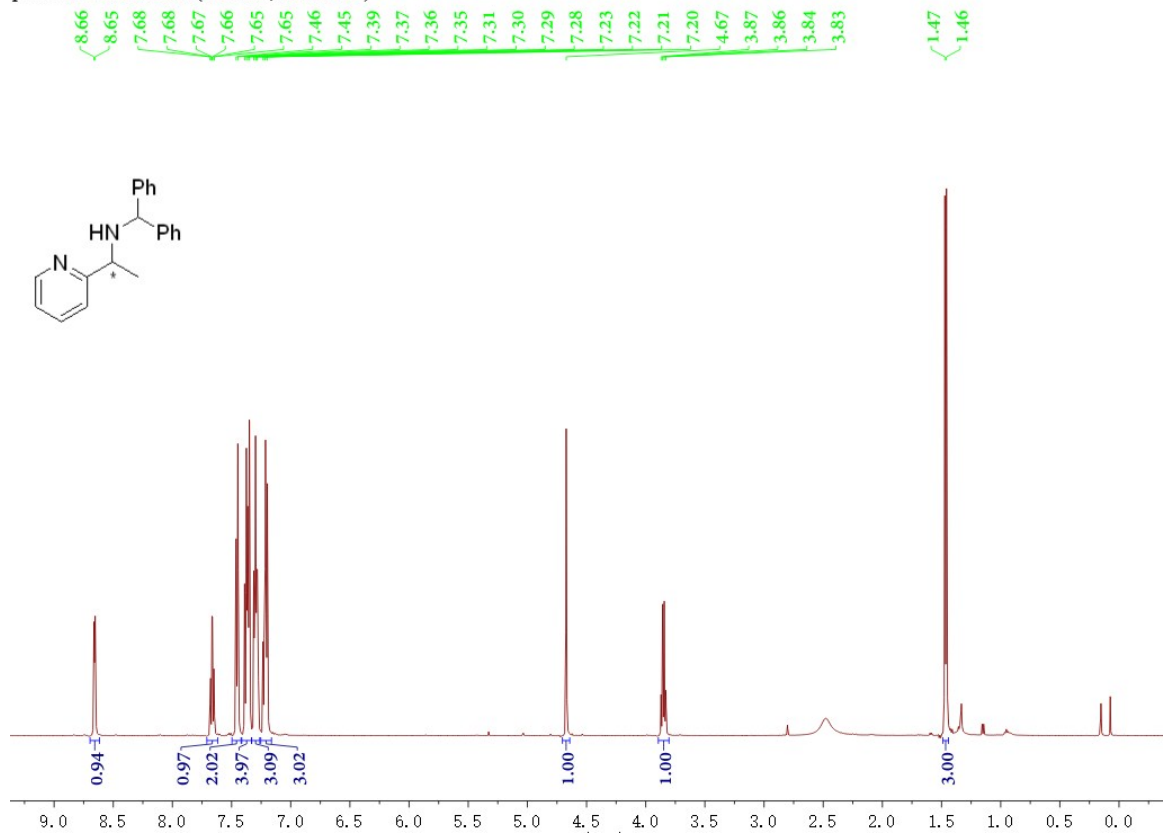
144.65  
143.62  
142.96  
133.51  
132.87  
128.52  
128.40  
127.81  
127.71  
127.40  
127.00  
126.89  
126.00  
125.51  
124.84  
63.83  
55.37  
24.42



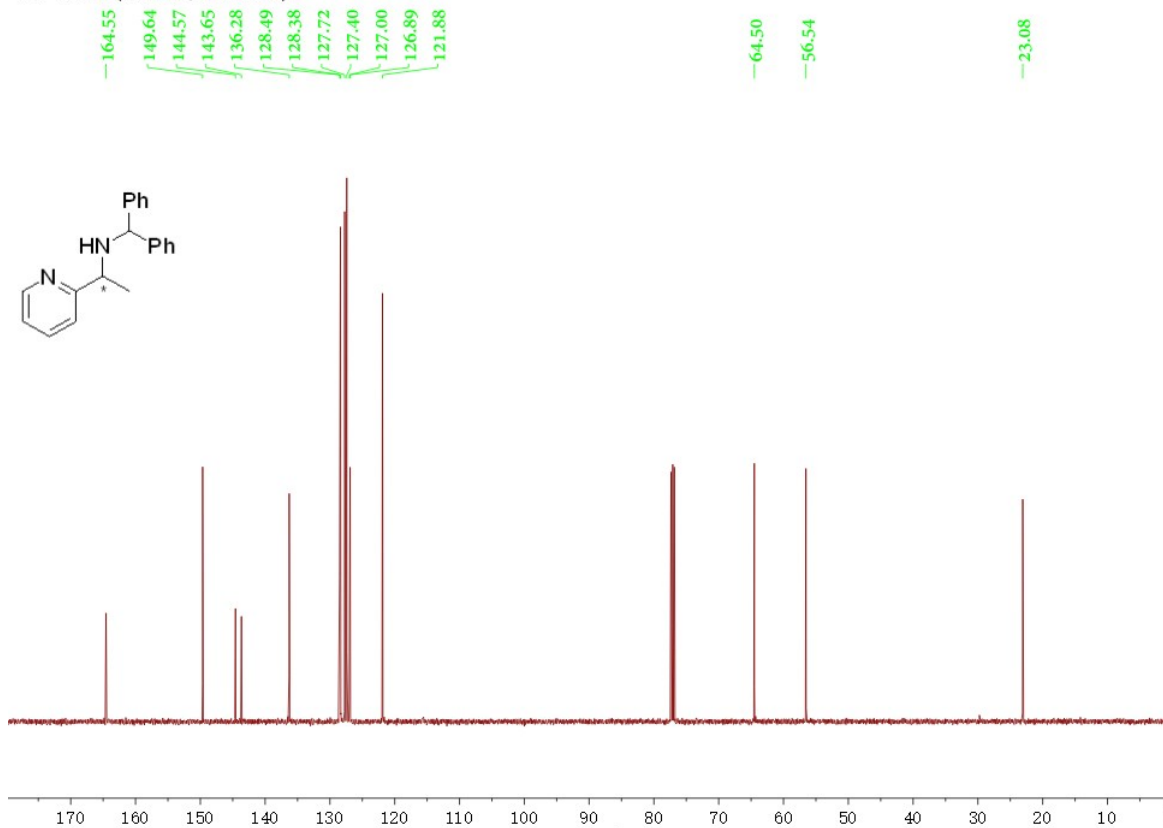
00089 #3 RT: 0.07 AV: 1 NL: 3.90E7  
T: FTMS + p ESI Full ms [150.00-2000.00]



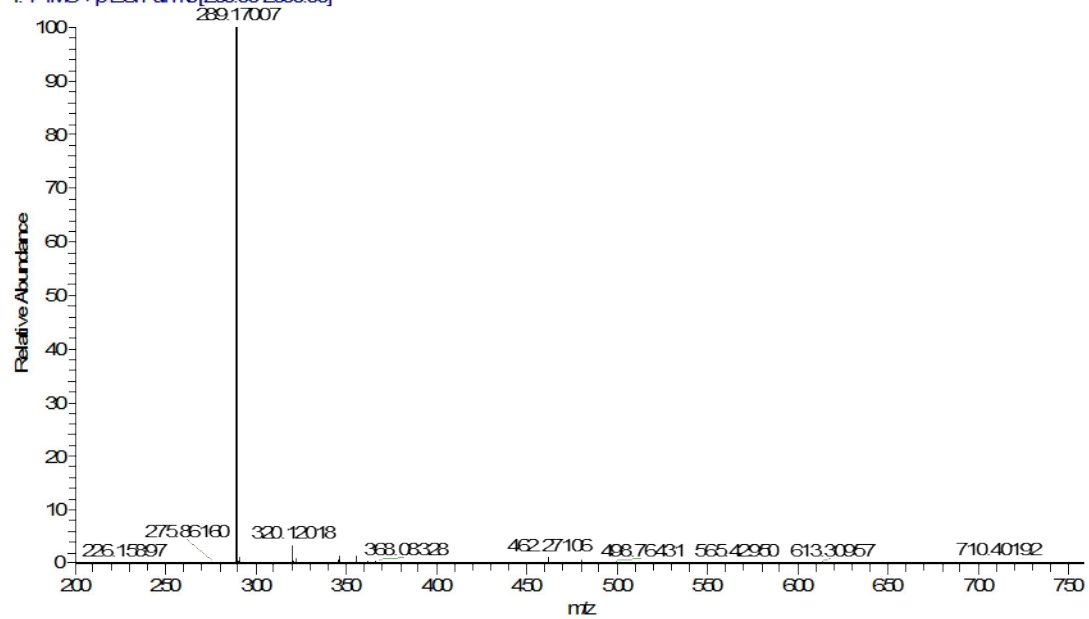
proton NMR for 3r (CDCl<sub>3</sub>, 500MHz)



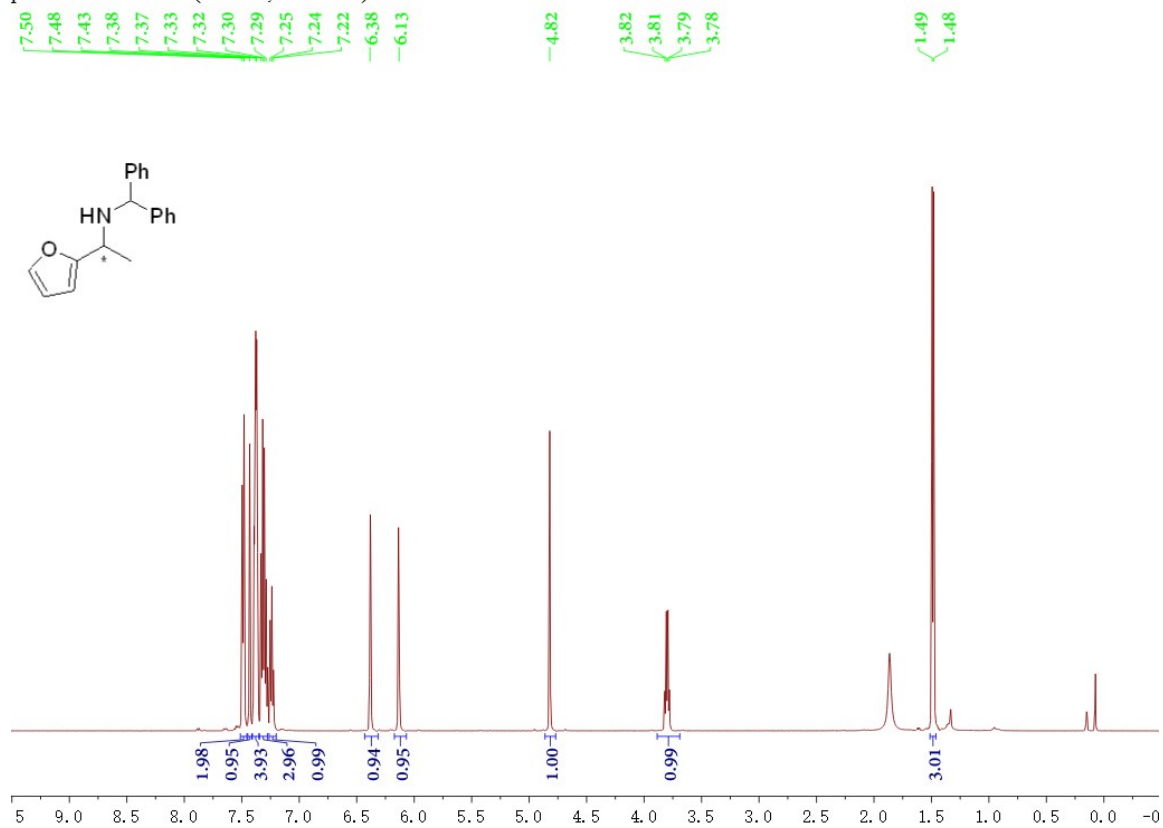
C13 for 3r (CDCl<sub>3</sub>, 125MHz)



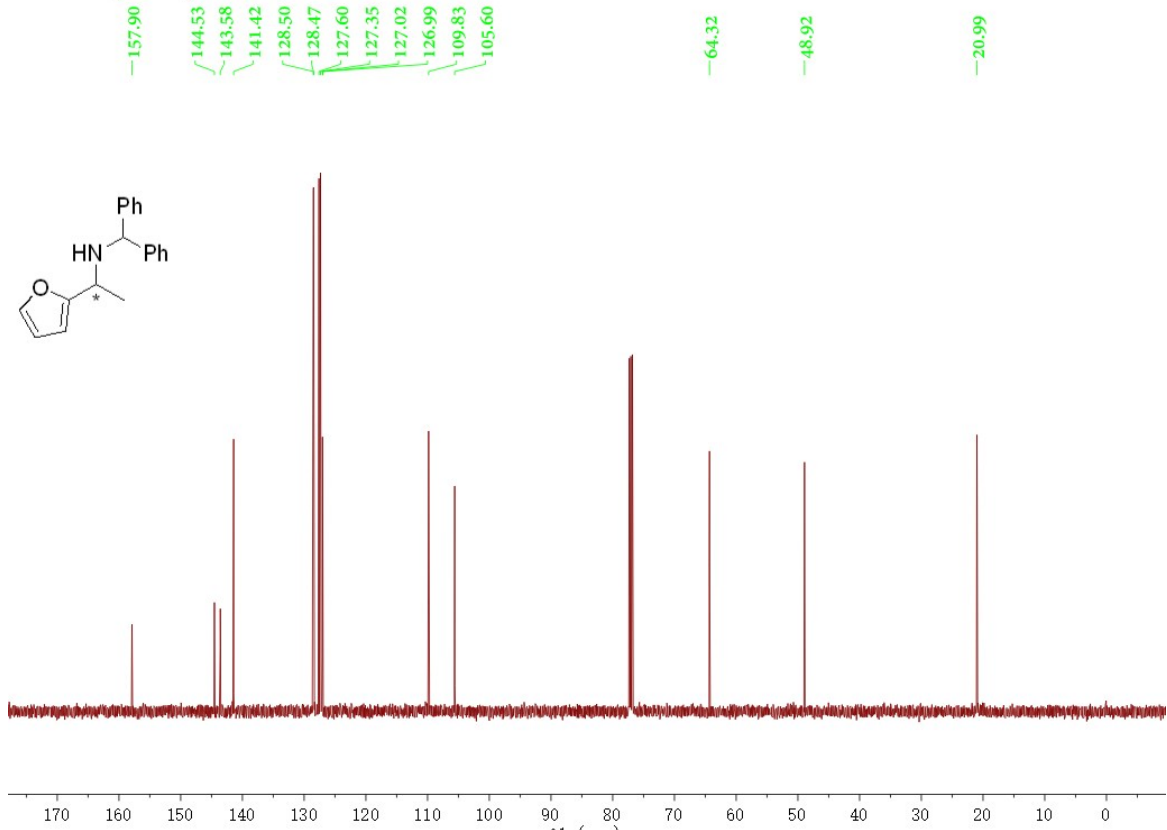
004C #25 RT: 0.38 AV: 1 NL: 280EB  
T: FTMS+pESI Full ms[200.00-2000.00]



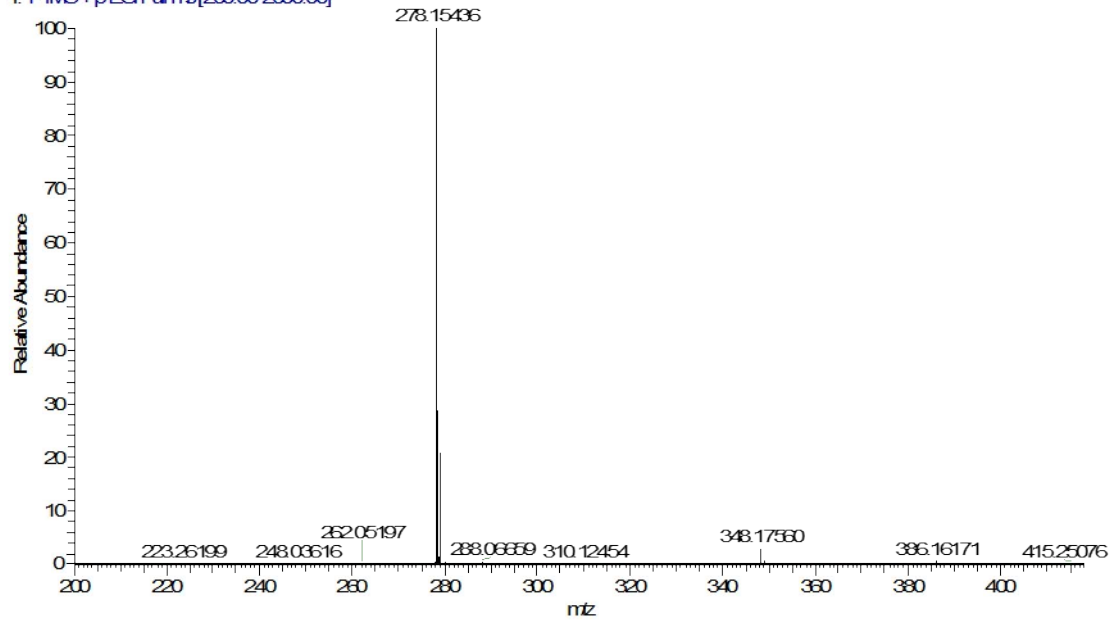
proton NMR for 3s (CDCl<sub>3</sub>, 500MHz)



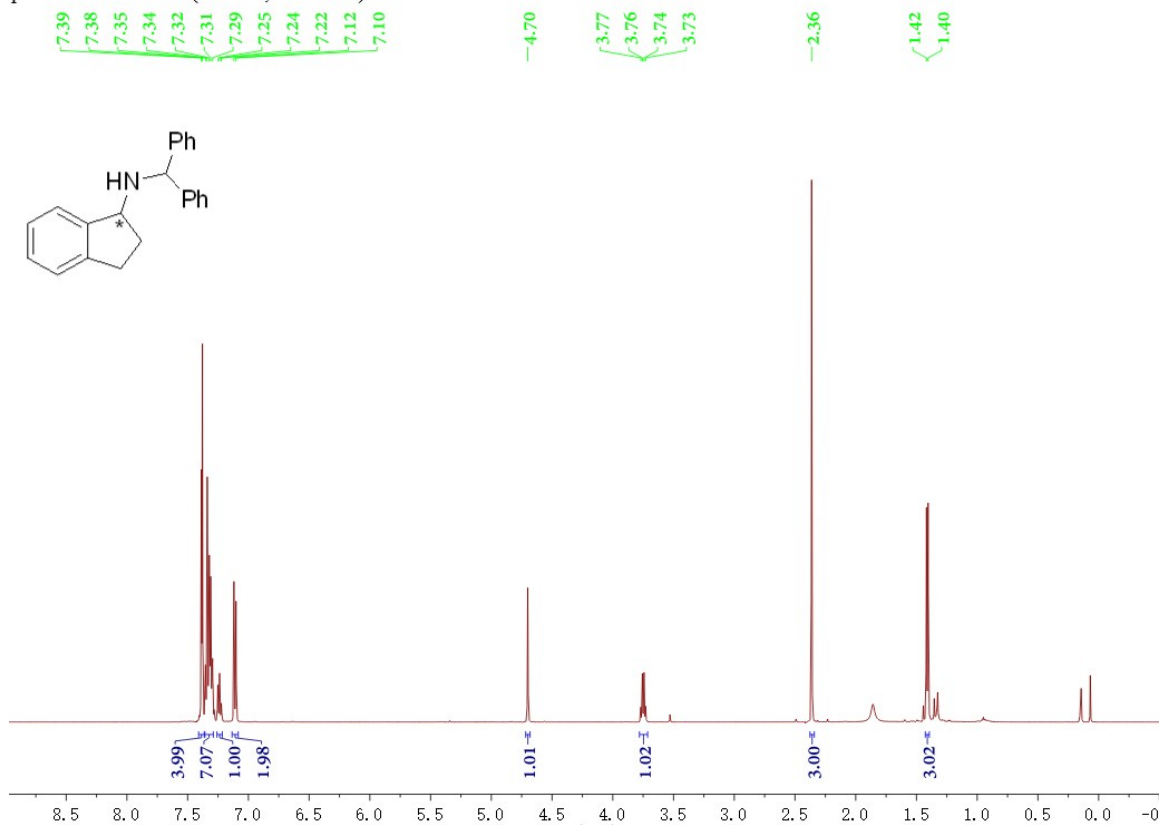
C13 for 3s (CDCl3, 125MHz)



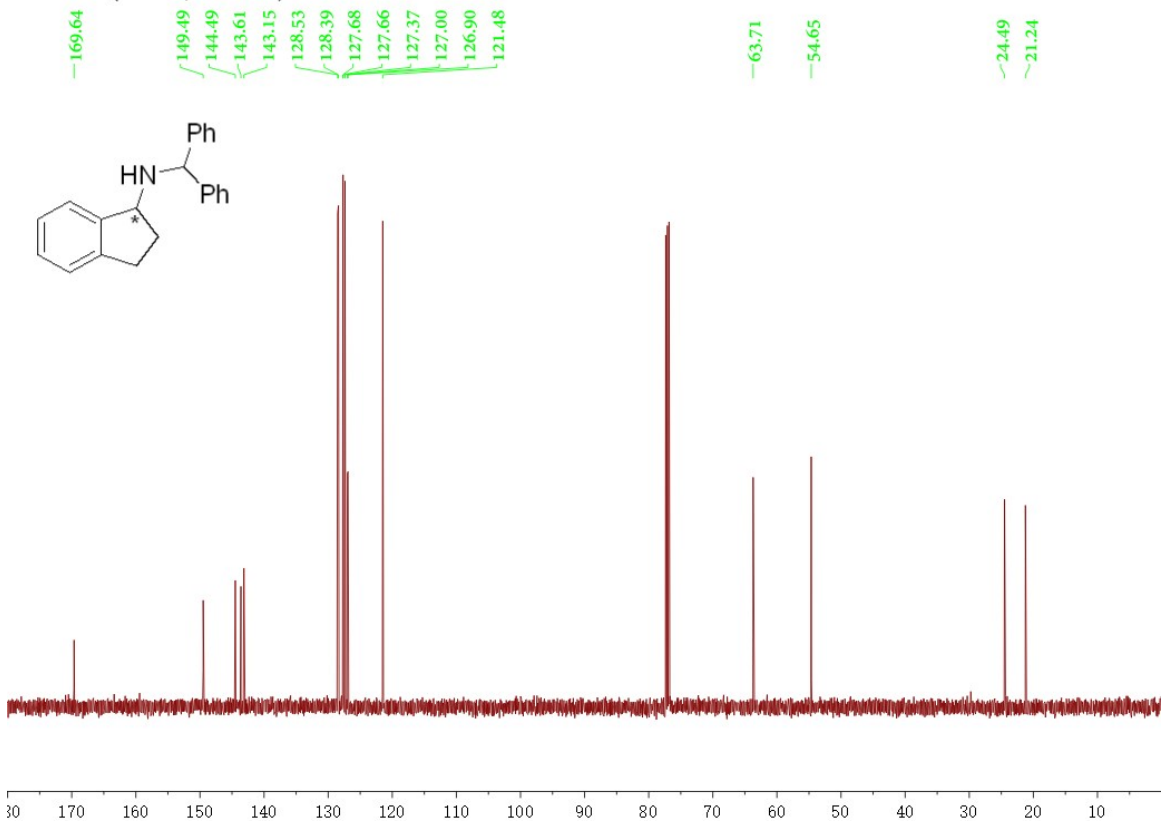
0010E #74 RT: 1.20 AV: 1 NL: 1.39EB  
T: FTMS+pESI Full ms [200.00-2000.00]



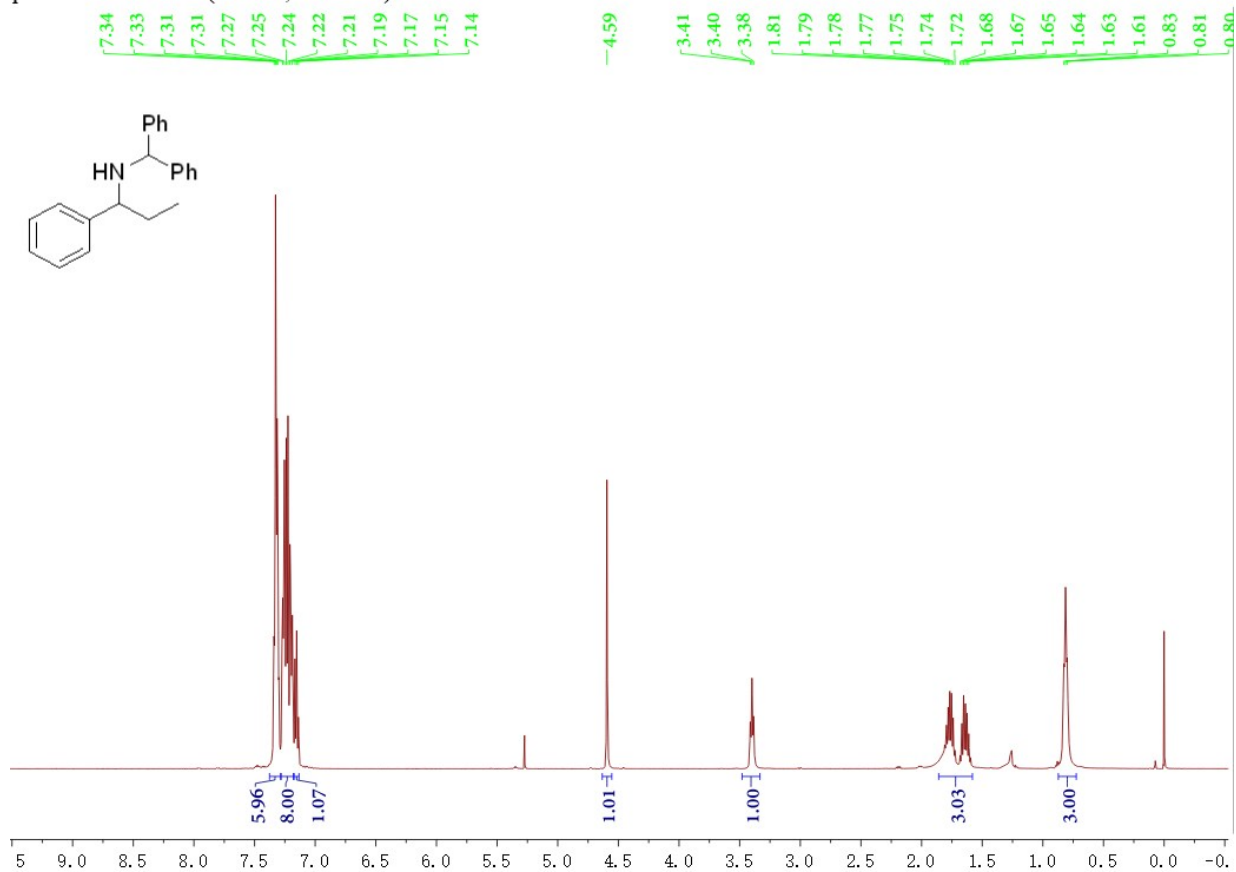
proton NMR for 3t (CDCl<sub>3</sub>, 500MHz)



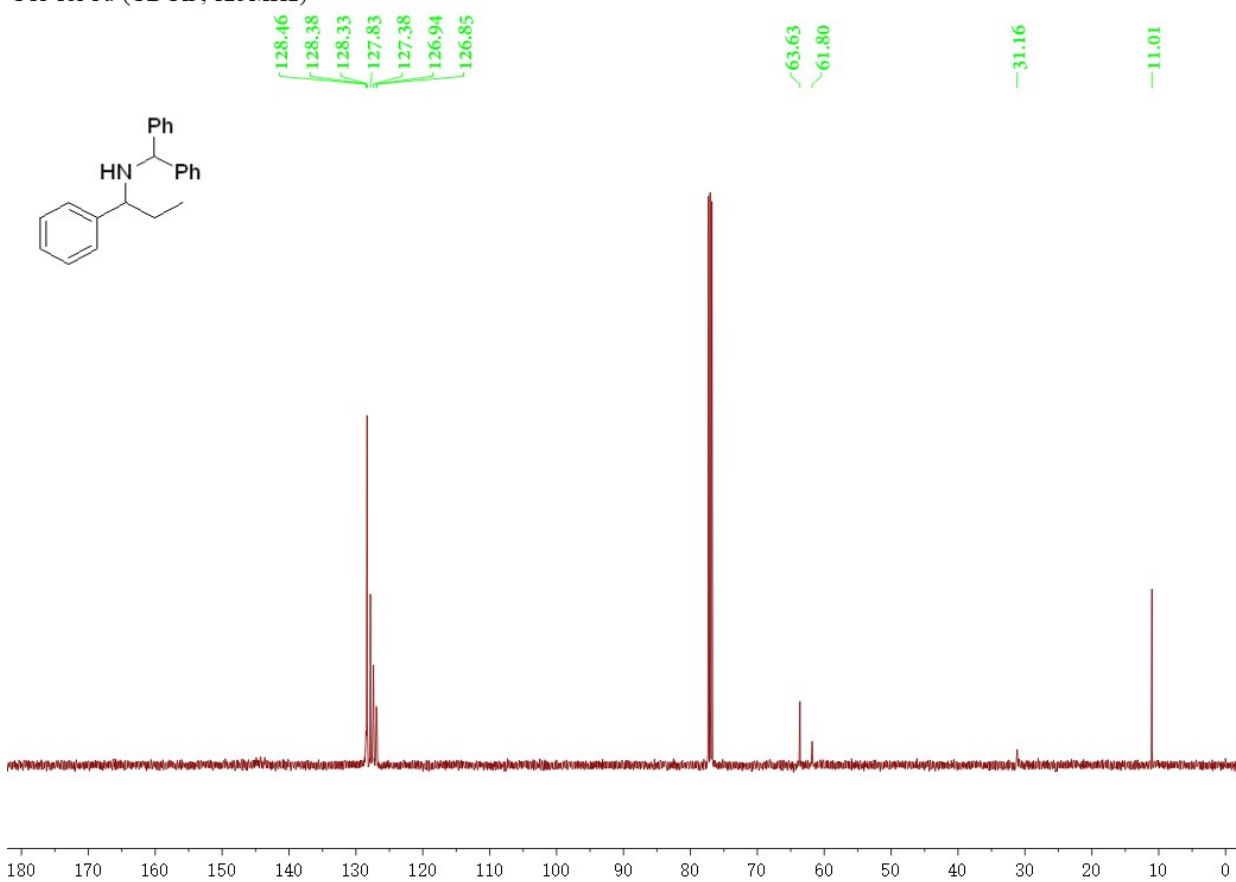
C13 for 3t (CDCl<sub>3</sub>, 125MHz)

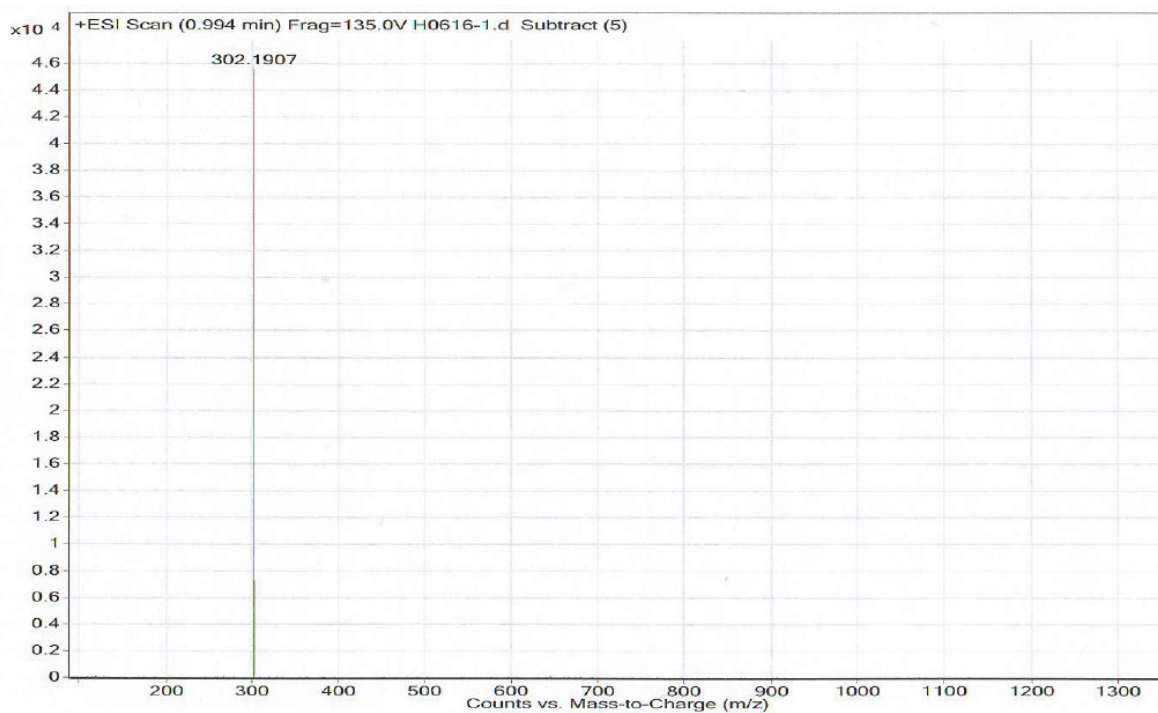


proton NMR for 3u (CDCl<sub>3</sub>, 500MHz)

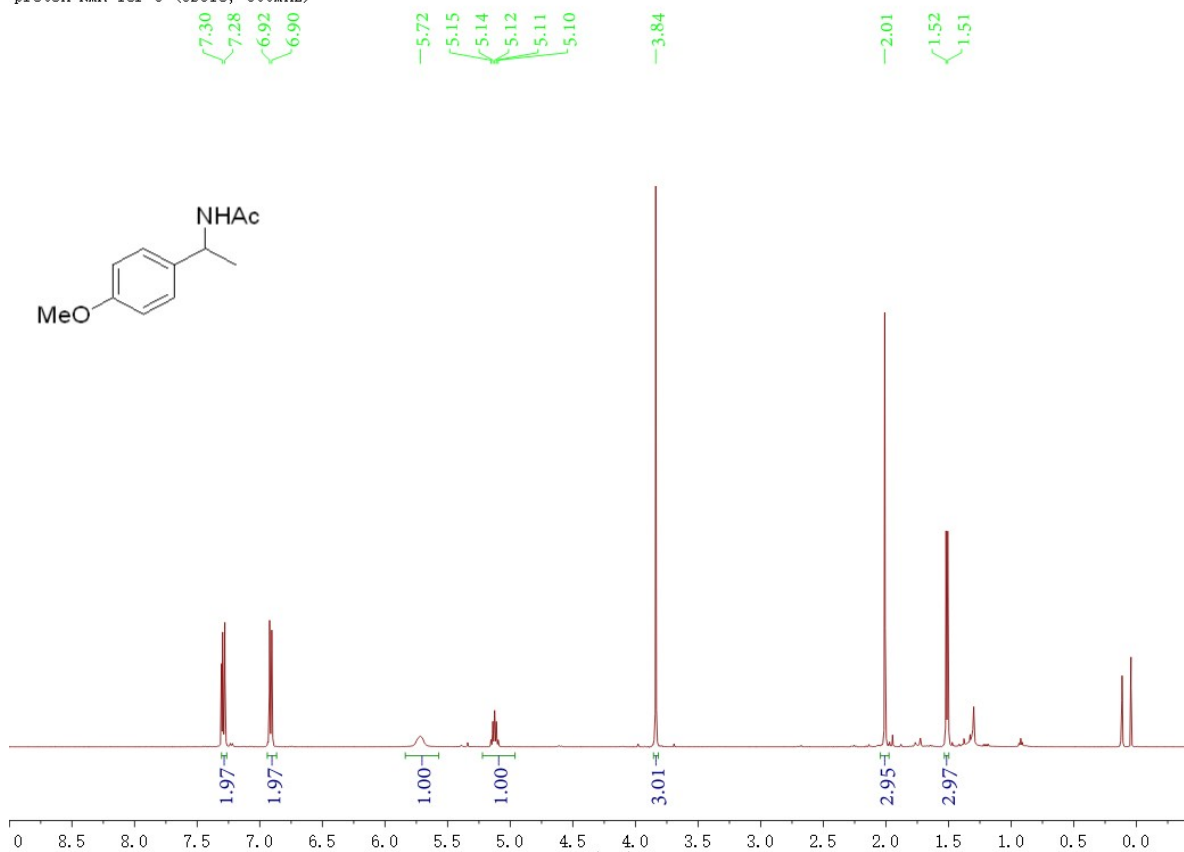


C13 for 3u (CDCl<sub>3</sub>, 125MHz)





proton NMR for 6 (CDC13, 500MHz)





proton NMR for 7 (CDCl<sub>3</sub>, 500MHz)

