Supplementary Information for

Secondary Amines as Coupling Partners in Direct Catalytic Asymmetric Reductive Amination

Zitong Wu[1], Shaozhi Du[1], Wenkun Yang[1], Guorui Gao[2], Xiongyu Yang[1], Haizhou Huang[1] and Mingxin Chang[1]*

[1]Shanxi Key Laboratory of Natural Products & Chemical Biology, College of Chemistry & Pharmacy, Northwest A&F University, 22 Xinong Road, Yangling, Shanxi 712100, China. [2]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 Wenhuadong Road, Jinan 250014, China. *e-mail: mxchang@nwsuaf.edu.cn

CONTENTS

I. General remarks

All reactions were performed in the nitrogen-filled glovebox or under nitrogen using standard Schlenk techniques unless otherwise noted. Column chromatography was performed using silica gel 60 (200 – 300 mesh). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectral data were obtaineded 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 using ^{1}H NMR with chemical shift reagent to determine the enantiomeric excesses.. 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 or AB SCIEX LC-30A+SelexION+TripleTOF5600+ with an electrospray ionization source.

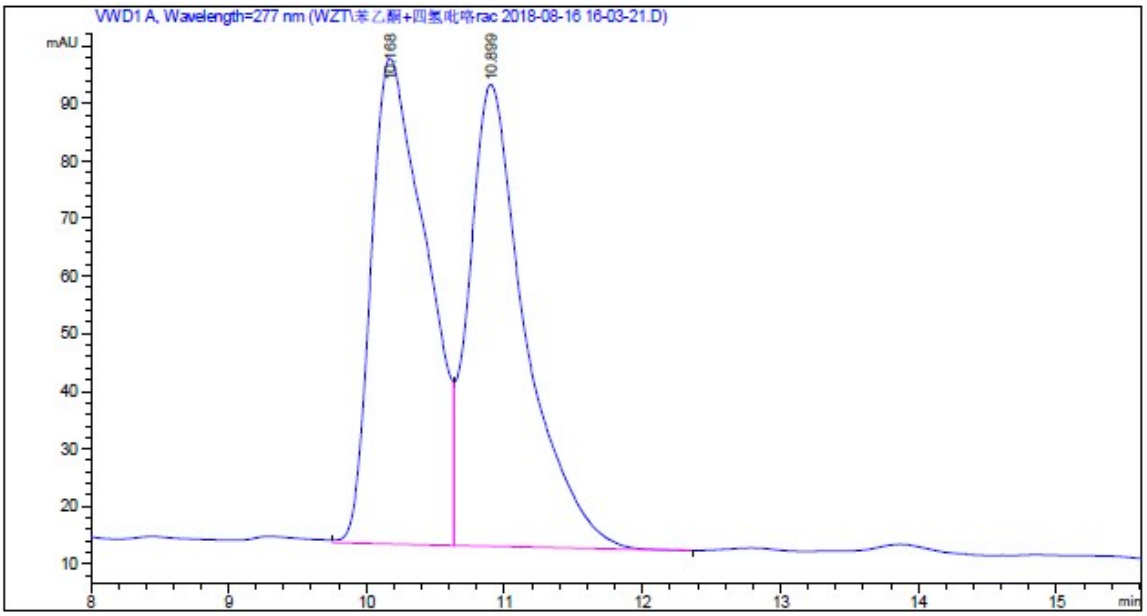
II. General Procedure for Asymmetric Reductive Amination

Chiral ligands **L5**–**L9** were prepared according to literatures.[1]

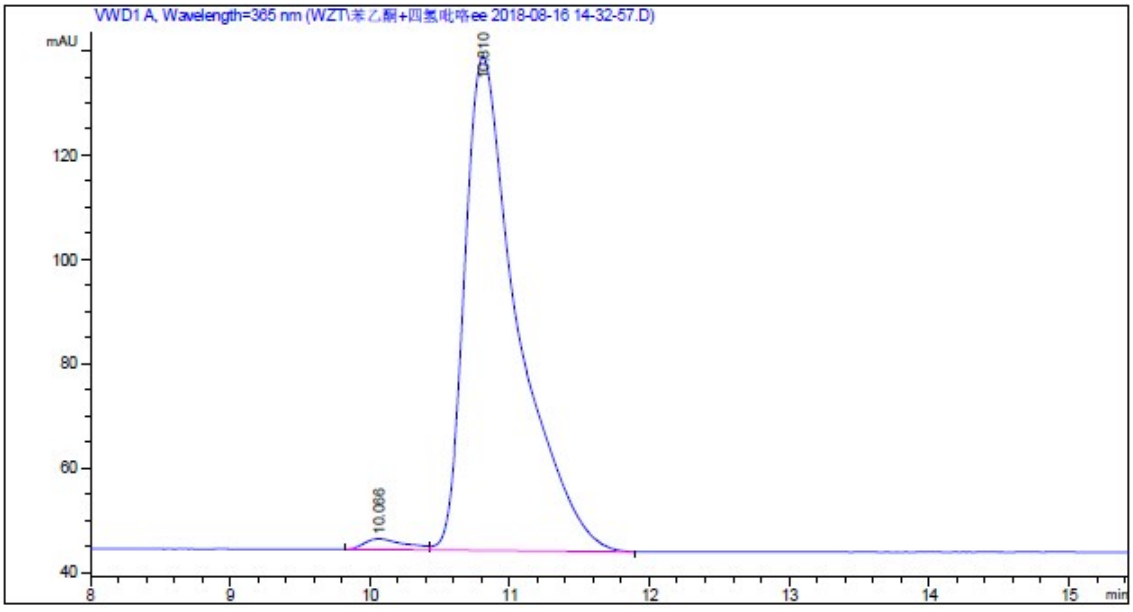
In a nitrogen-filled glovebox, $[Ir(COD)Cl]_2$ (10 μmol) and **L8a** (46 μmol) was dissolved in anhydrous CH_2Cl_2 (1.0 mL), stirred for 20 min, and equally divided into 10 vials charged with ketones (0.2 mmol) and pyrrolidine (0.22 mmol) in anhydrous CH_2Cl_2 solution (0.5 mL). Then $Ti(O\textit{i}\text{-}Pr)_4$ (1.2 equiv.), 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.1 eq), and I_2 (1 mol%) were added and the total solution was made to 2.0 mL (DCM/THF/DCE = 1:1:1.5) for each vial. The resulting vials were transferred to an autoclave, which was charged with 40 atm of H_2, and stirred at 4 ^{o}C for 20 h. The hydrogen gas was released slowly and the solution was quenched 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 crude products, which were purified by column chromotography and then analyzed by chiral HPLC or using ^{1}H NMR with chemical shift reagent to determine the enantiomeric excesses.

^{1}H NMR method for determination the e.e. values: The amine product **3** was mixed with equal amount (mol/mol) of (*S* or *R*)-2-acetoxy-2-phenylacetic acid and dissolved in $CDCl_3$. Diastereoisomers are formed and the proton signal of amine β-methyl will be splitted. From integration ratio the e.e. value could be calculated.

(*S*)-1-(1-phenylethyl)pyrrolidine (3a):[2] 91% yield, 97% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24–7.42 (m, 5H, Ar-H), 3.20 (q, J = 6.3 Hz, 1H, CH), 2.60 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.81 (m, 4H, 2*CH_2), 1.46 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.3 (Ar-CC), 128.3, 127.3, 127.0, 66.1, 53.0, 23.4, 23.1. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-3 column, Hex/IPA=97:3, 0.6 mL/min, 220 nm, 7.08 min, 7.53 min.

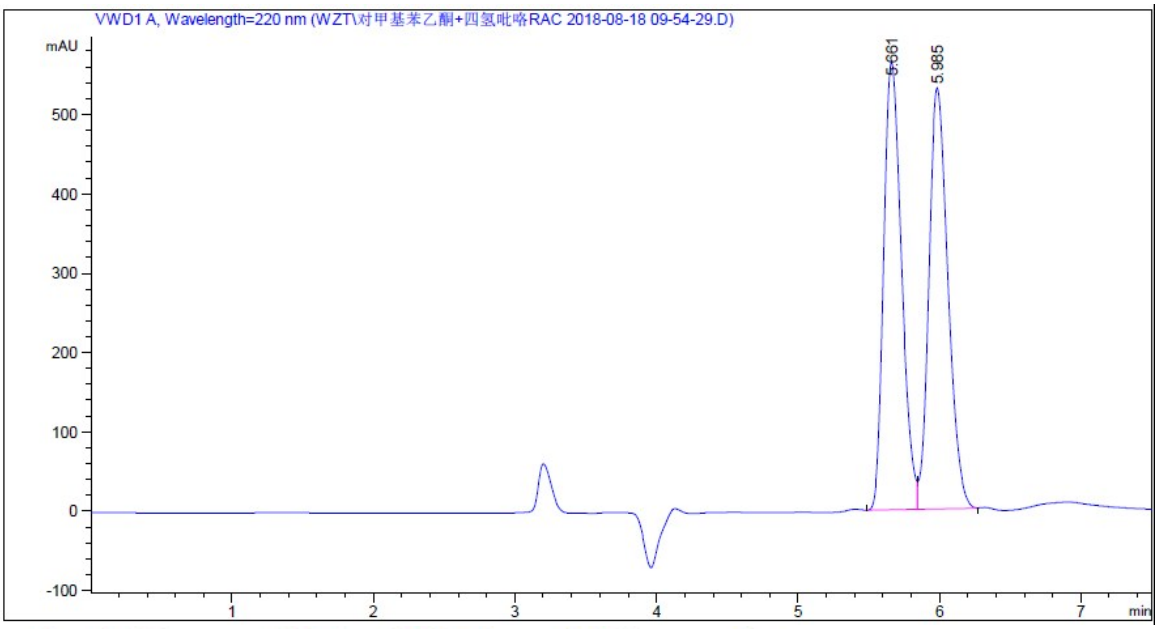


#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.168	VV	0.3954	2350.17651	84.26402	50.7272
2	10.899	VB	0.4122	2282.79297	80.17010	49.2728

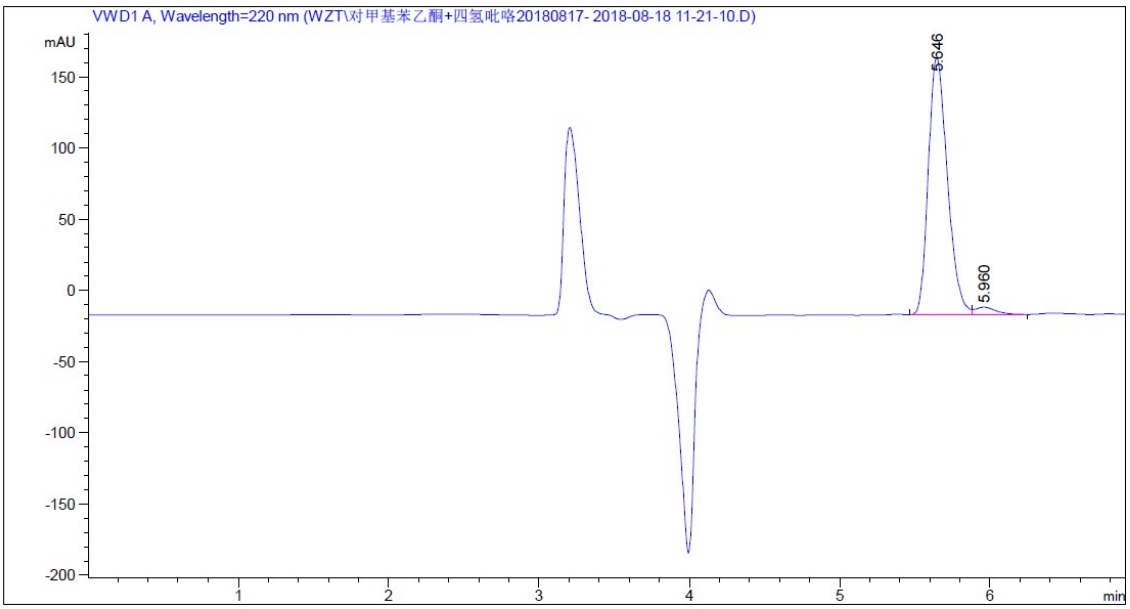


#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.066	VV	0.2948	42.81715	2.10947	1.6913
2	10.810	VB	0.3820	2488.80811	94.57262	98.3087

1-(1-(p-tolyl)ethyl)pyrrolidine (3b):[3] 88% yield, 94% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.0 Hz, 2H, Ar-CH), 7.16 (d, J = 7.9 Hz, 2H, Ar-CH), 3.21 (q, J = 6.6 Hz, 1H, CH), 2.60 (m, 2H, CH_2), 2.42 (m, 2H, N-CH_2), 2.38 (s, 3H, N-CH_3), 1.80 (m, 4H, 2* CH_2), 1.44 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.1, 136.9, 129.1, 127.3, 65.8, 52.9, 23.4, 22.7, 21.1. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-H column, Hex/IPA=99:1, 1 mL/min, 220nm, 4.48 min, 5.67 min.

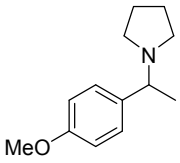


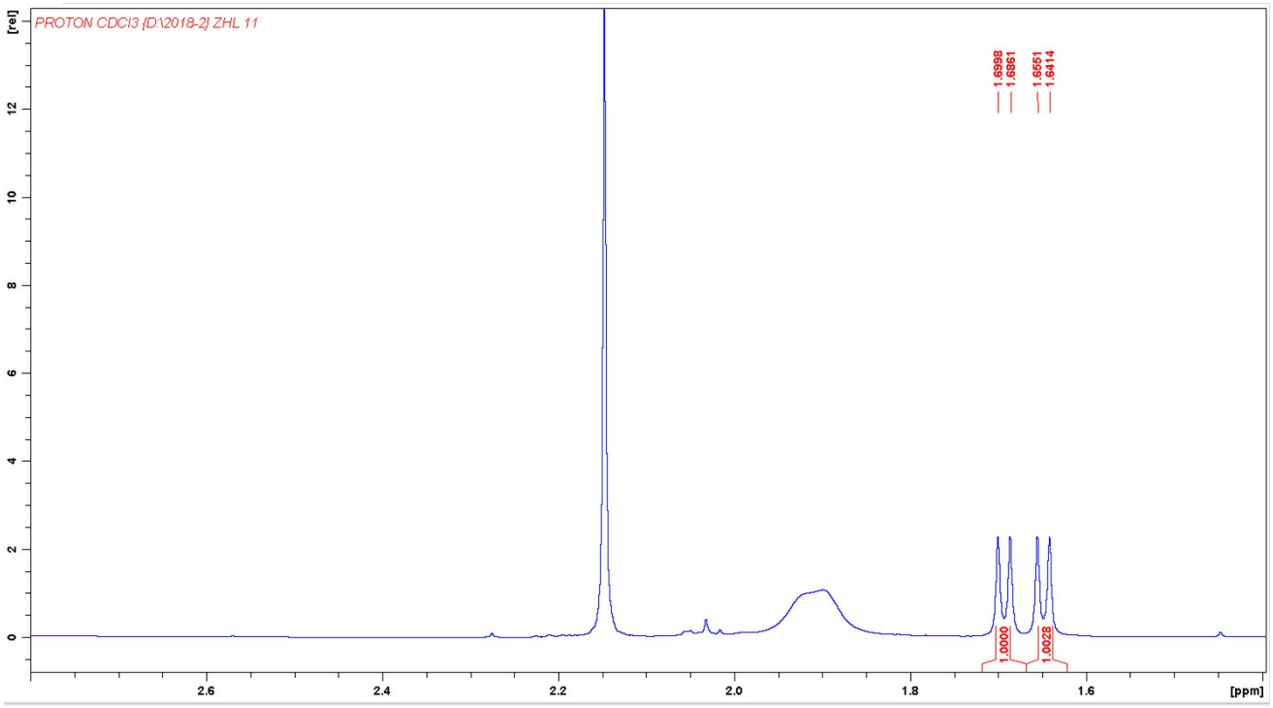
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.661	BV	0.1359	4929.40723	564.19318	49.7128
2	5.985	VB	0.1437	4986.35449	530.23346	50.2872

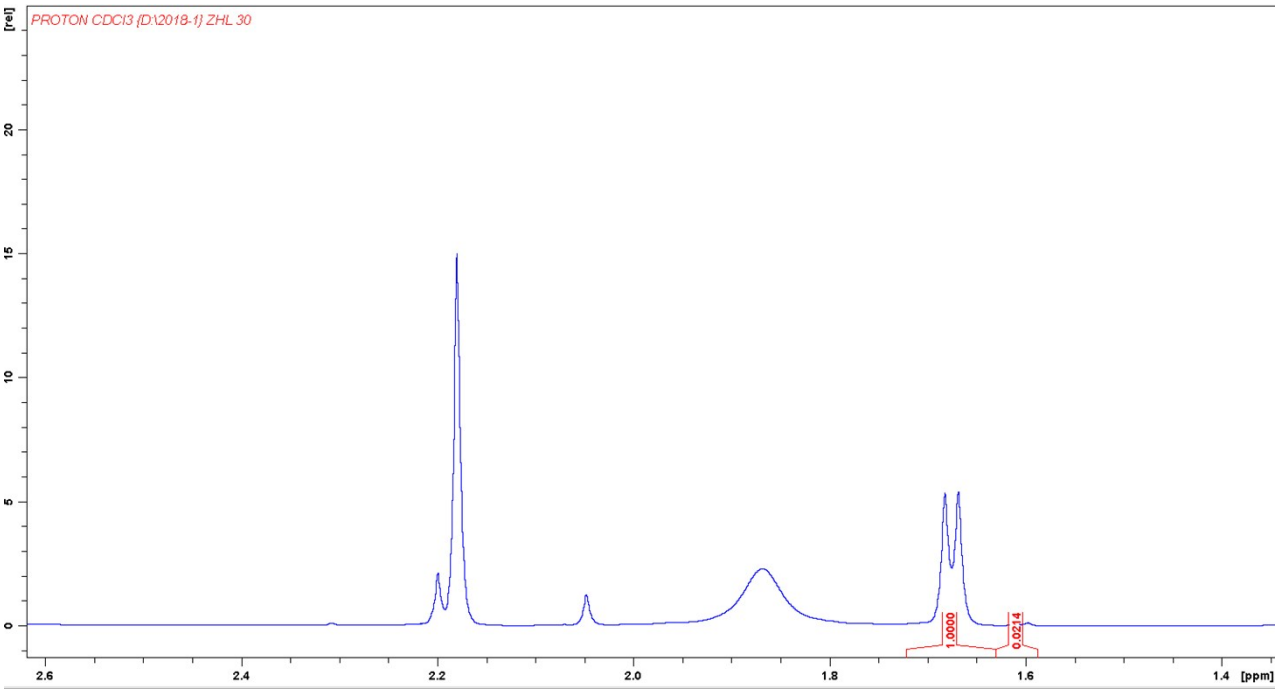


#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.646	BV	0.1372	1593.33813	180.18692	97.0540
2	5.960	VB	0.1387	48.36533	5.19286	2.9460

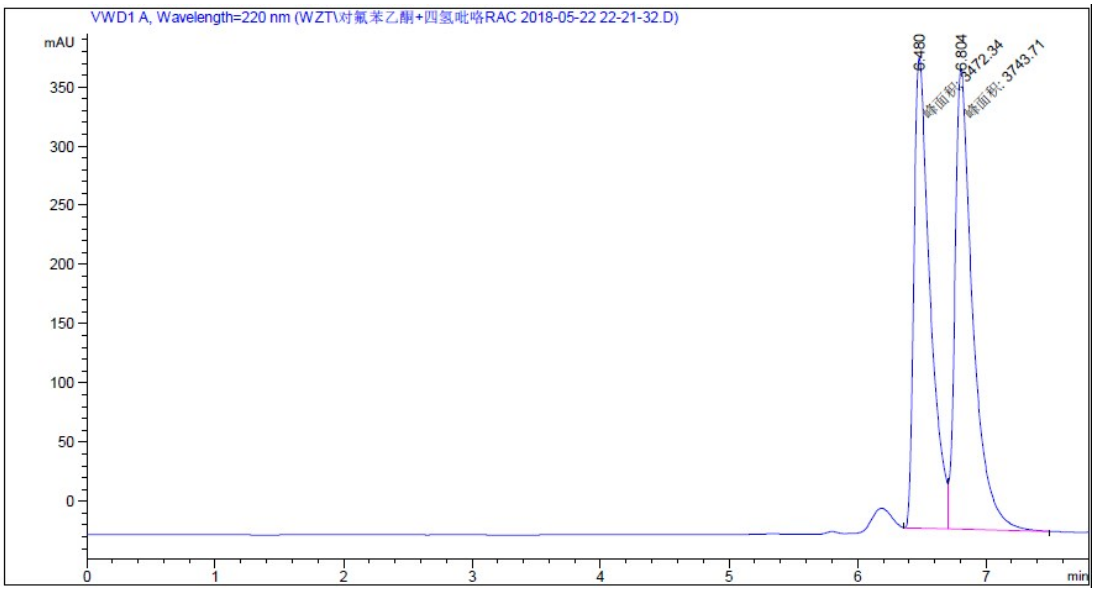
1-(1-(4-methoxyphenyl)ethyl)pyrrolidine (3c):[2] 93% yield, 95% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.7 Hz, 2H, Ar-CH), 6.88 (d, J = 8.7 Hz, 2H, Ar-CH), 3.84 (s, 3H, O-CH_3), 3.18 (q, J = 7.6 Hz, 1H, CH), 2.58 (m, 2H, N-CH_2), 2.39 (m, 2H, N-CH_2), 1.79 (m, 4H, 2*CH_2), 1.42 (d, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2 (Ar-CO), 132.1 (Ar-CC), 128.7, 113.8, 65.2, 55.0, 52.3, 23.0; 20.9. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



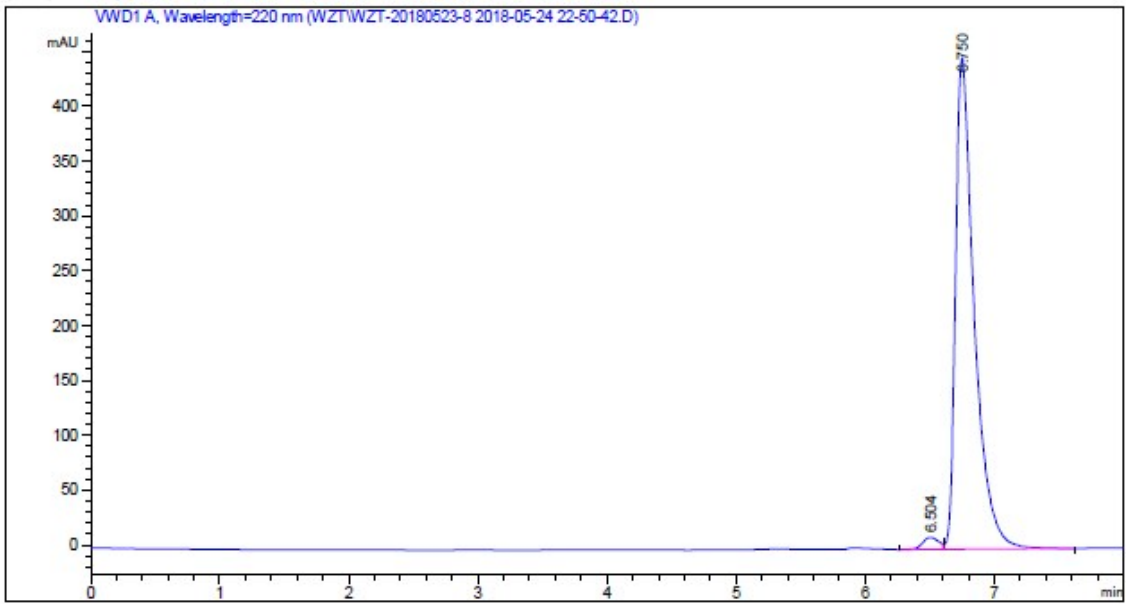




1-(1-(4-fluorophenyl)ethyl)pyrrolidine (3d):[3] 90% yield, 96% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (m, 2H, Ar-CH), 7.02 (m, 2H, Ar-CH), 3.21 (q, J = 6.6 Hz, 1H, CH), 2.57 (m, 2H, N-CH_2), 2.39 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.41 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9 (Ar-CF), 160.9 (Ar-CC), 128.8, 128.7, 115.2, 115.0, 65.3, 52.9, 23.4, 23.0. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-3 column, Hex/IPA=98:2, 0.6 mL/min, 220 nm, 6.48 min, 6.80 min.

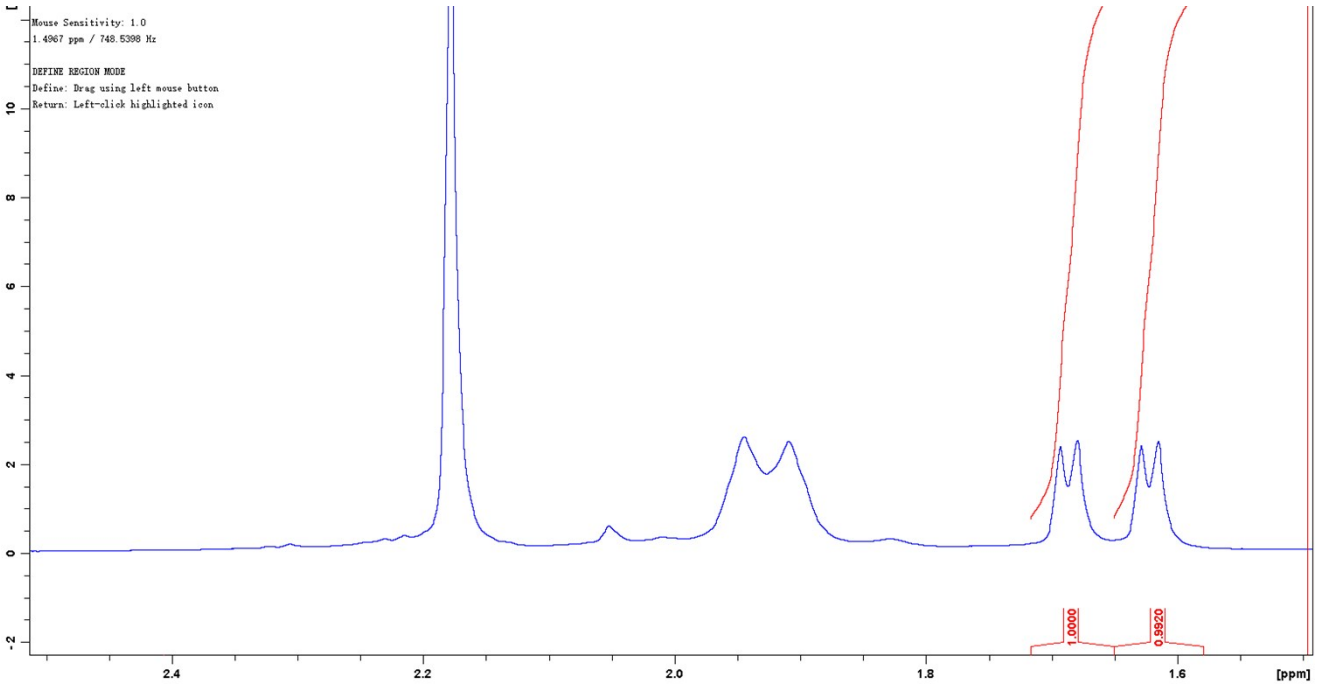


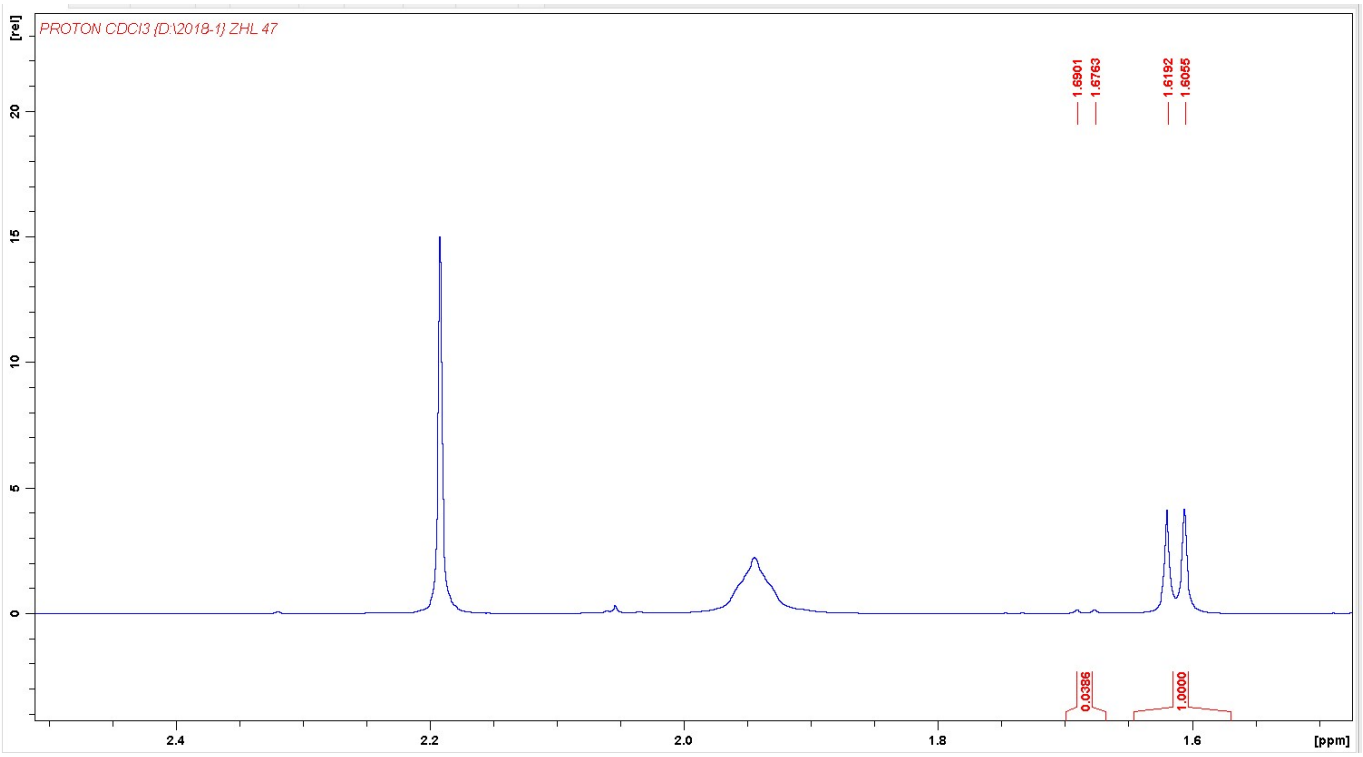
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.480	MF	0.1456	3472.33618	397.57898	48.1196
2	6.804	FM	0.1603	3743.71265	389.23788	51.8804



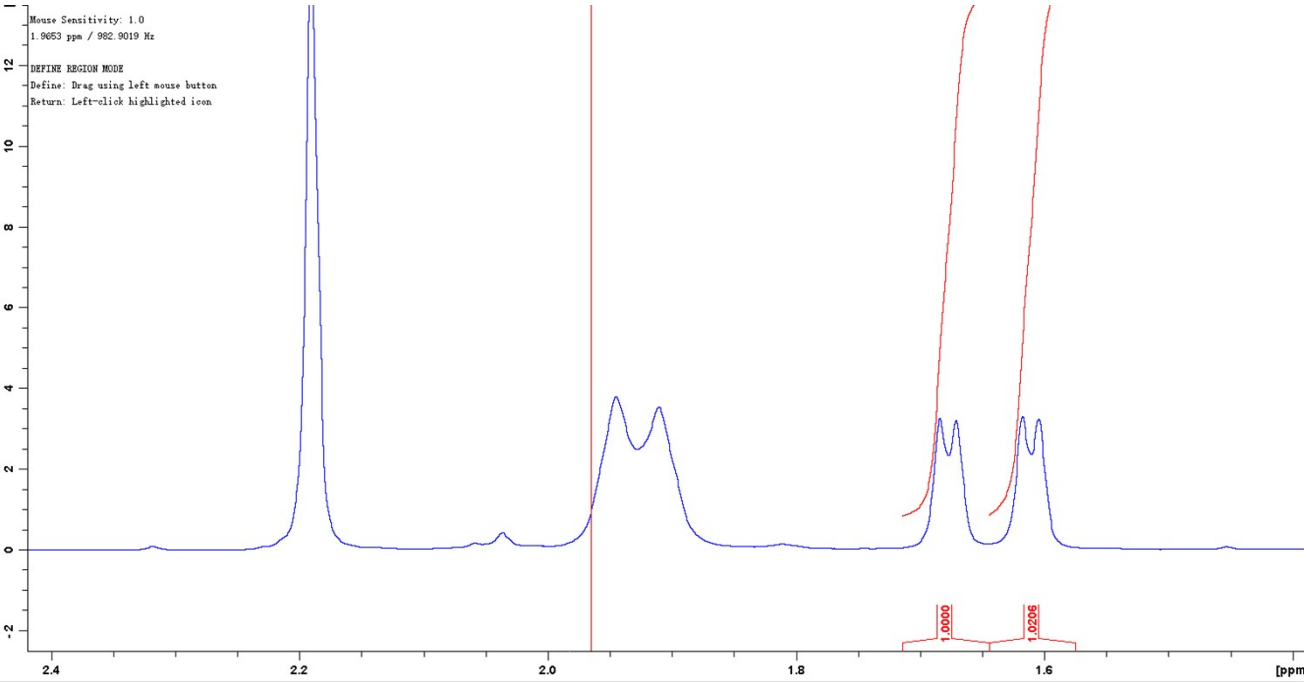
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.504	BV	0.1360	95.05695	10.87021	2.0645
2	6.750	VB	0.1485	4509.29932	447.84070	97.9355

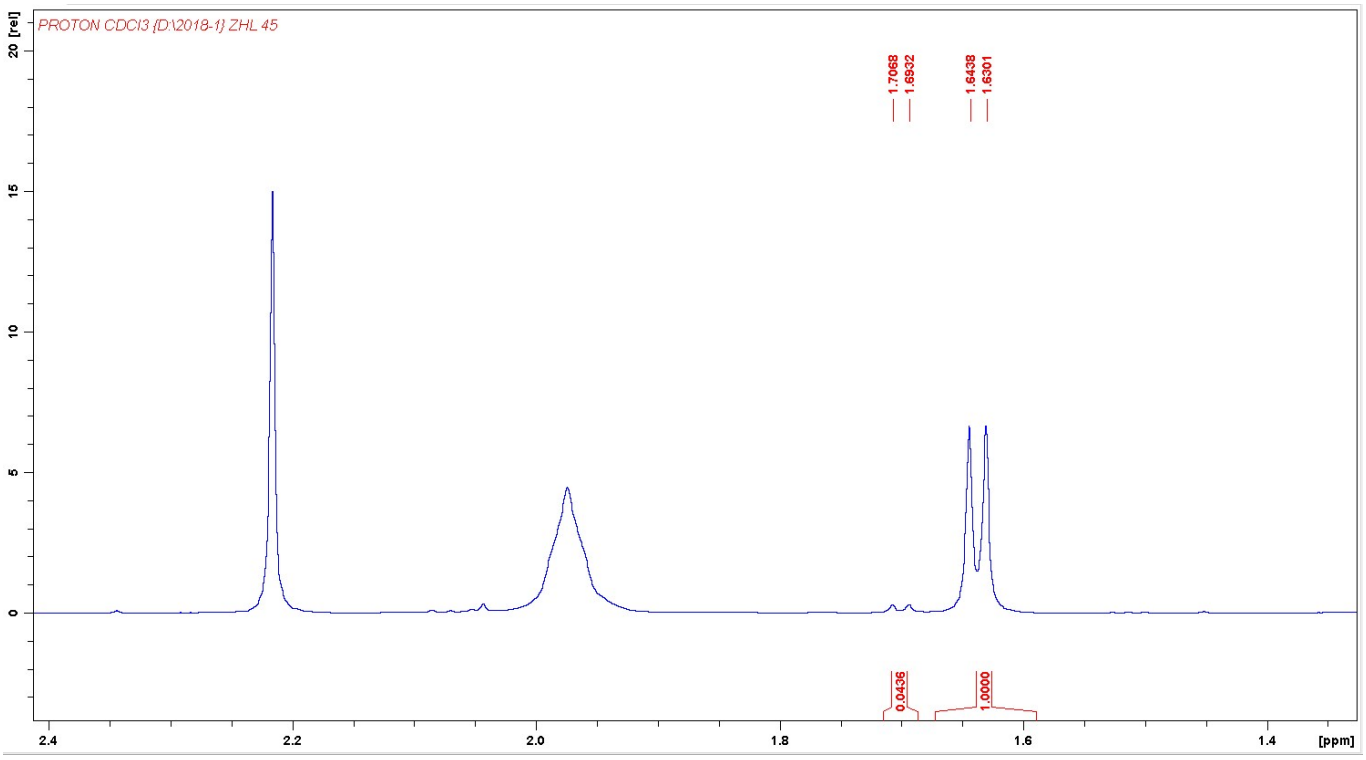
1-(1-(4-chlorophenyl)ethyl)pyrrolidine (3e):[2] 91% yield, 93% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (s, 4H, Ar-CH), 3.21 (q, J = 6.5 Hz, 1H, CH), 2.57 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.42 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3 (Ar-CCl), 132.7 (Ar-C), 128.7, 128.6, 65.4, 52.9, 23.4, 22.9. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



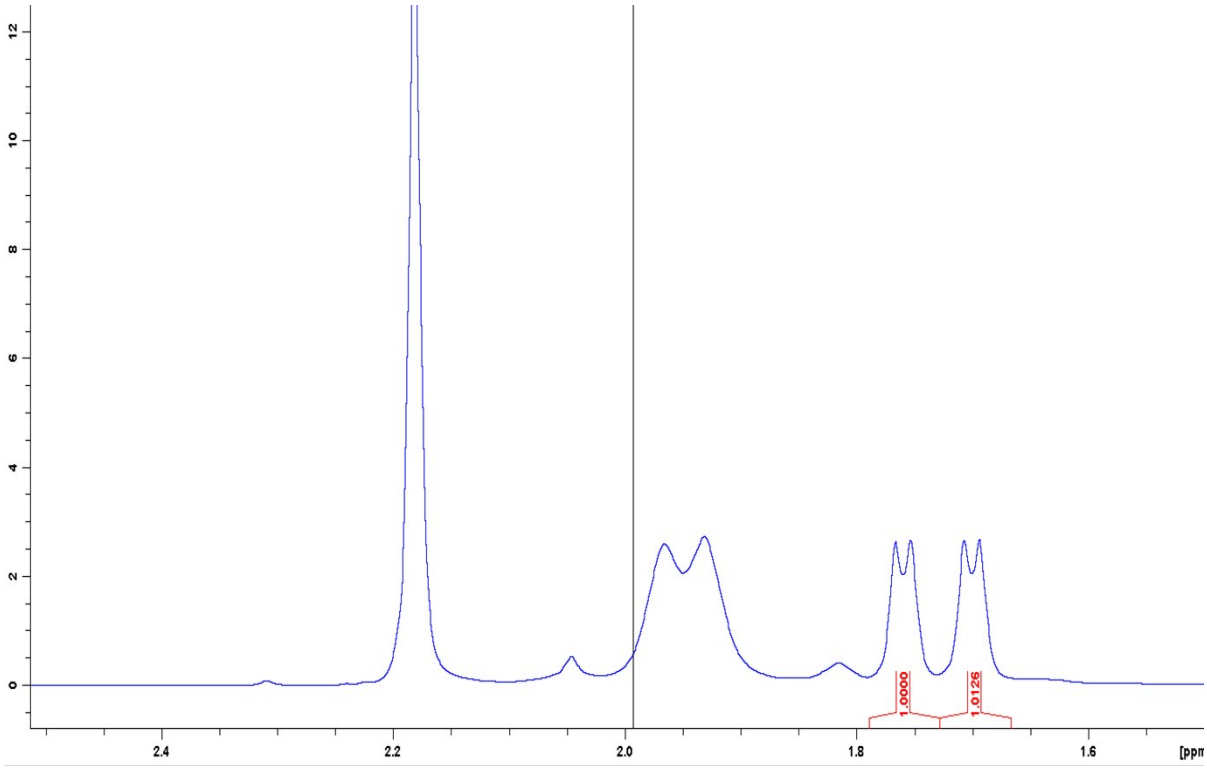


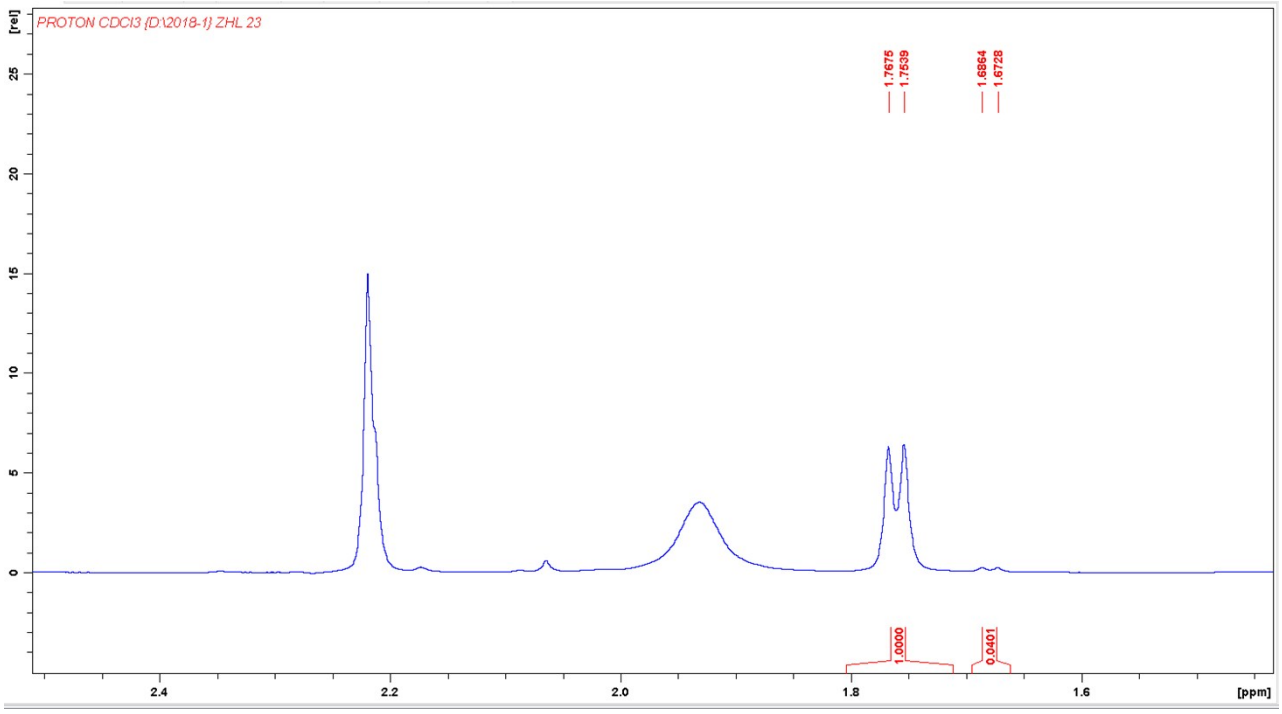
1-(1-(4-bromophenyl)ethyl)pyrrolidine (3f):[4] 84% yield, 92% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 7.9 Hz, 2H, Ar-CH), 7.25 (d, J = 7.8 Hz, 2H, Ar-CH), 3.18 (q, J = 6.2 Hz, 1H, CH), 2.55 (m, 2H, N-CH_2), 2.39 (m, 2H, N-CH_2), 1.79 (m, 4H, 2*CH_2), 1.40 (d, J = 6.3 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 131.4, 129.0, 120.5, 65.4, 52.9, 23.4, 23.1. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



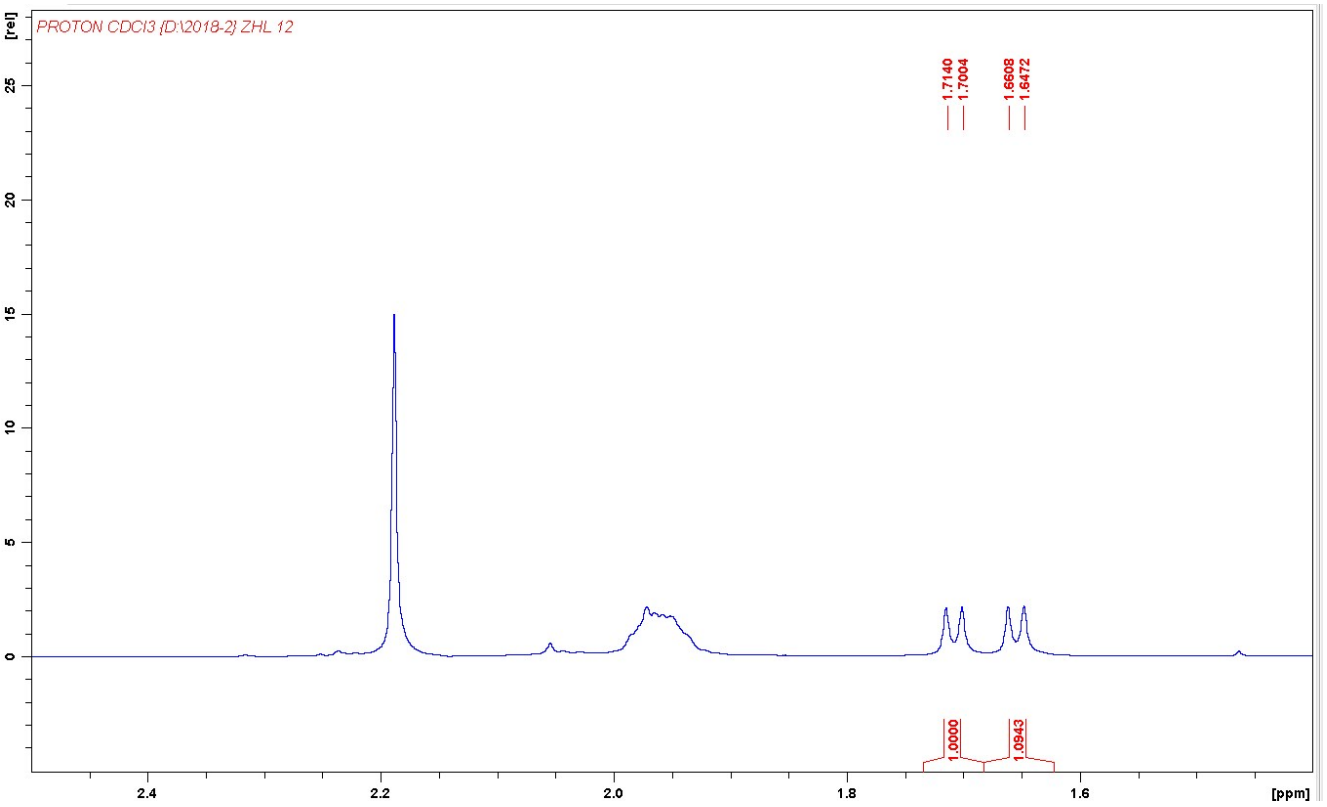


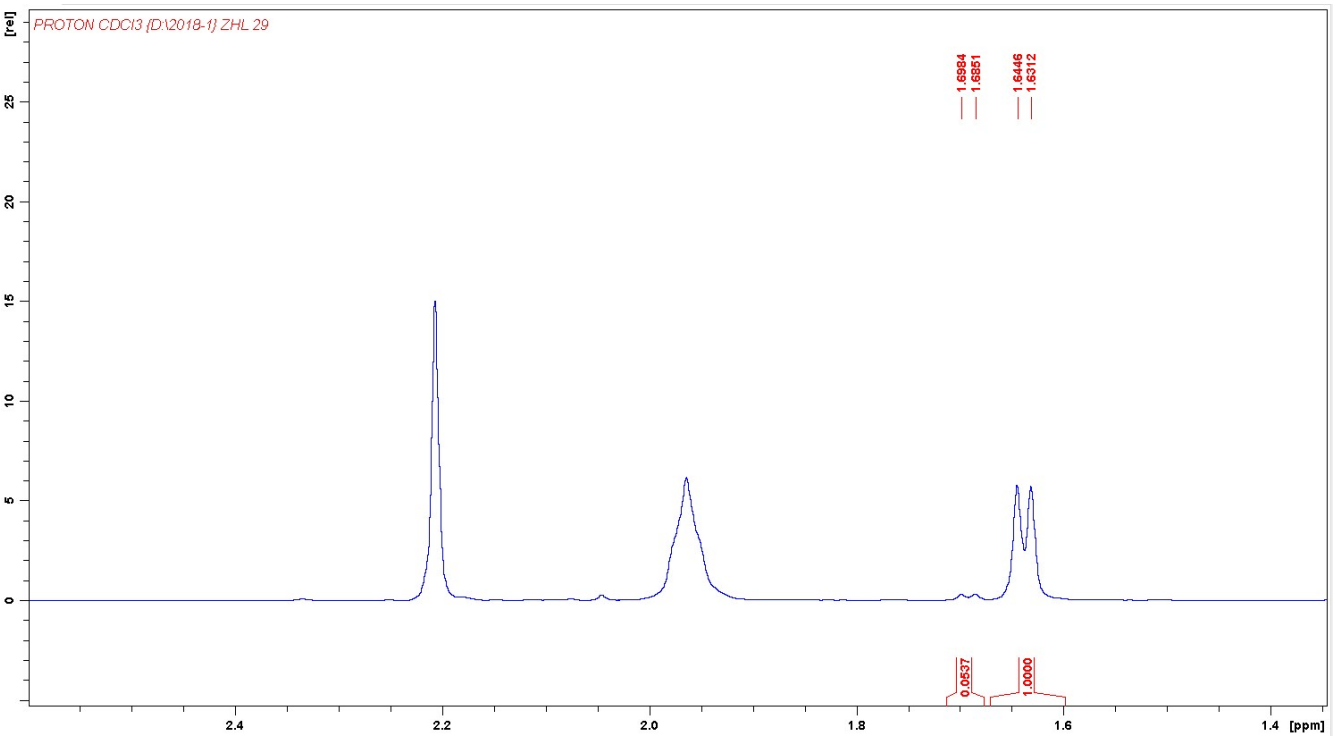
1-(1-([1,1'-biphenyl]-4-yl)ethyl)pyrrolidine (3g): 94% yield, 92% ee, brown oil, unknown compound. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 7.3 Hz, 2H, Ar-CH), 7.59 (d, J = 8.1 Hz, 2H, Ar-CH), 7.47 (m, 4H, Ar-CH), 7.38 (m, 1H, Ar-CH), 3.28 (q, J = 6.5 Hz, 1H, CH), 2.63 (m, 2H, N-CH_2), 2.47 (m, 2H, N-CH_2), 1.83 (m, 4H, 2*CH_2), 1.49 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7, 140.2, 128.8, 128.5, 127.8, 127.7, 127.5, 66.1, 52.9, 23.4, 20.7. HRMS calcd for $C_{18}H_{22}N$ $[M+H]^+$: 252.1674, found: 252.1733. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



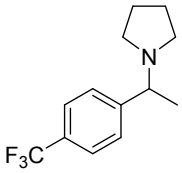


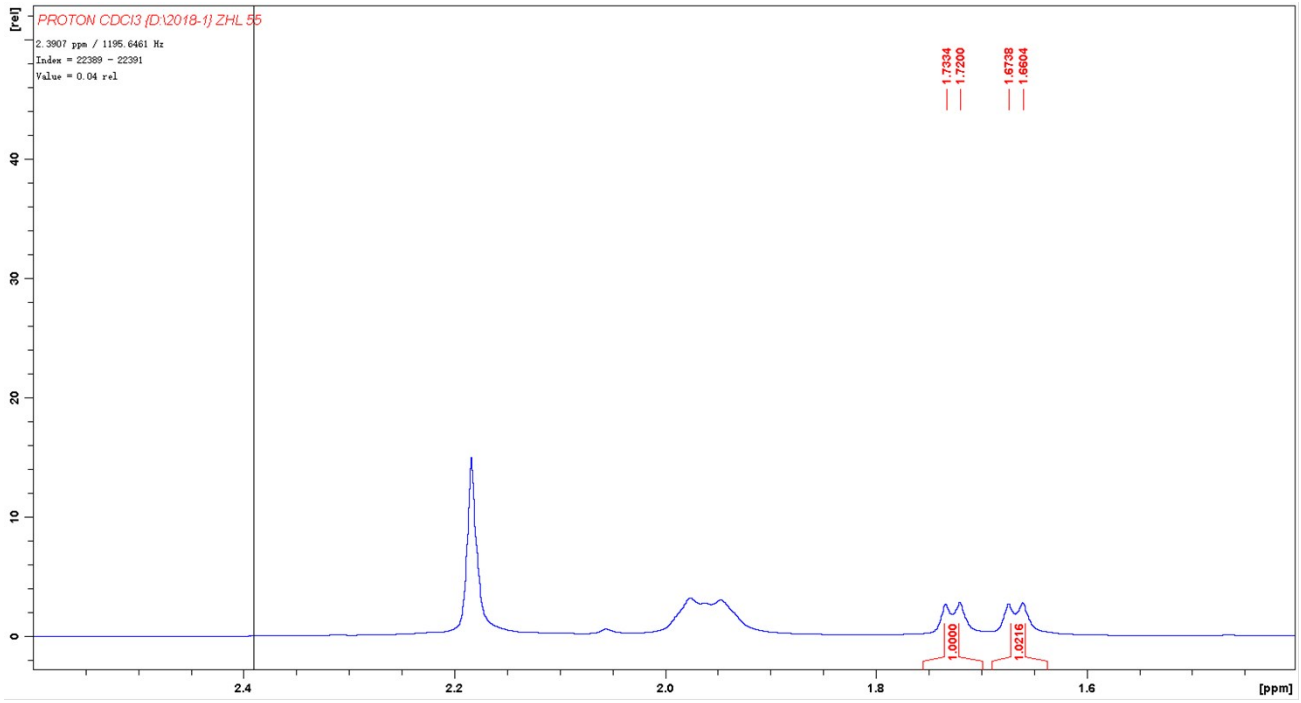
1-(1-(4-nitrophenyl)ethyl)pyrrolidine (3h):[5] 90% yield, 90% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.7 Hz, 2H, Ar-CH), 7.55 (d, J = 8.6 Hz, 2H, Ar-CH), 3.34 (q, J = 6.6 Hz, 1H, CH), 2.57 (m, 2H, N-CH_2), 2.41 (m, 2H, N-CH_2), 1.81 (m, 4H, 2*CH_2), 1.42 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 146.9, 127.9, 123.7, 65.4, 52.9, 23.4, 23.3. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

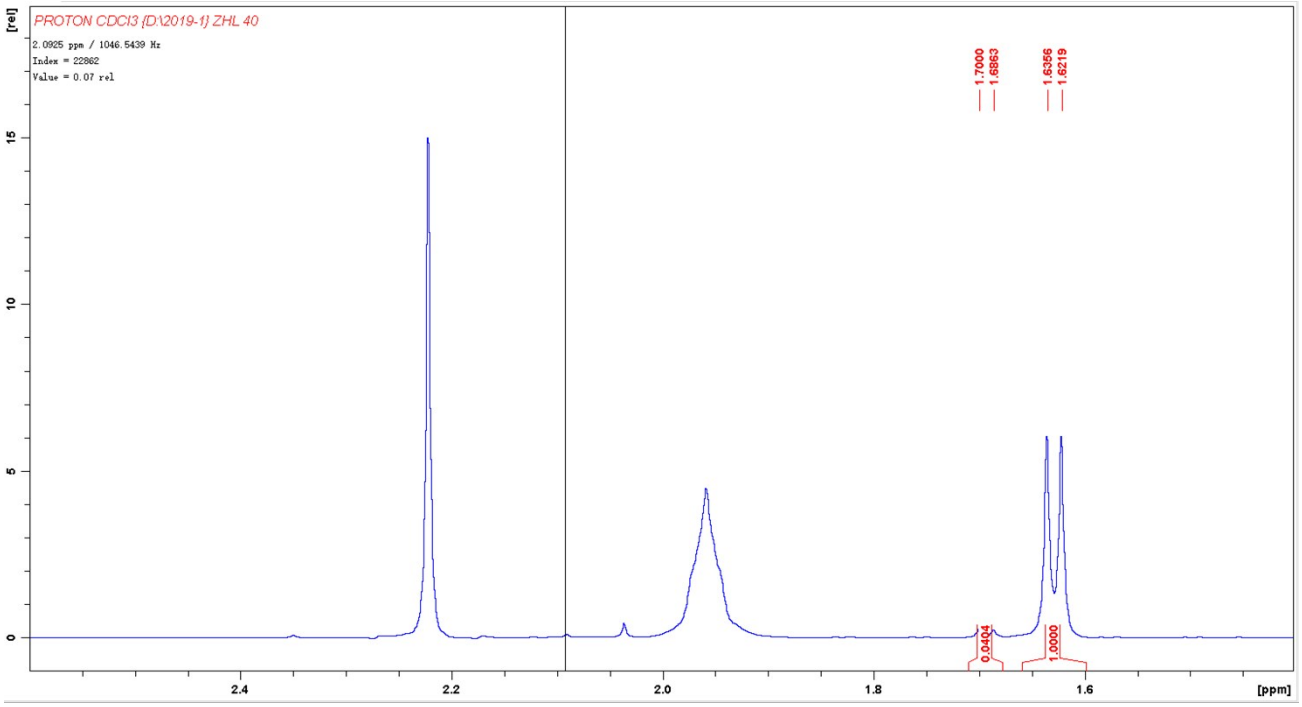




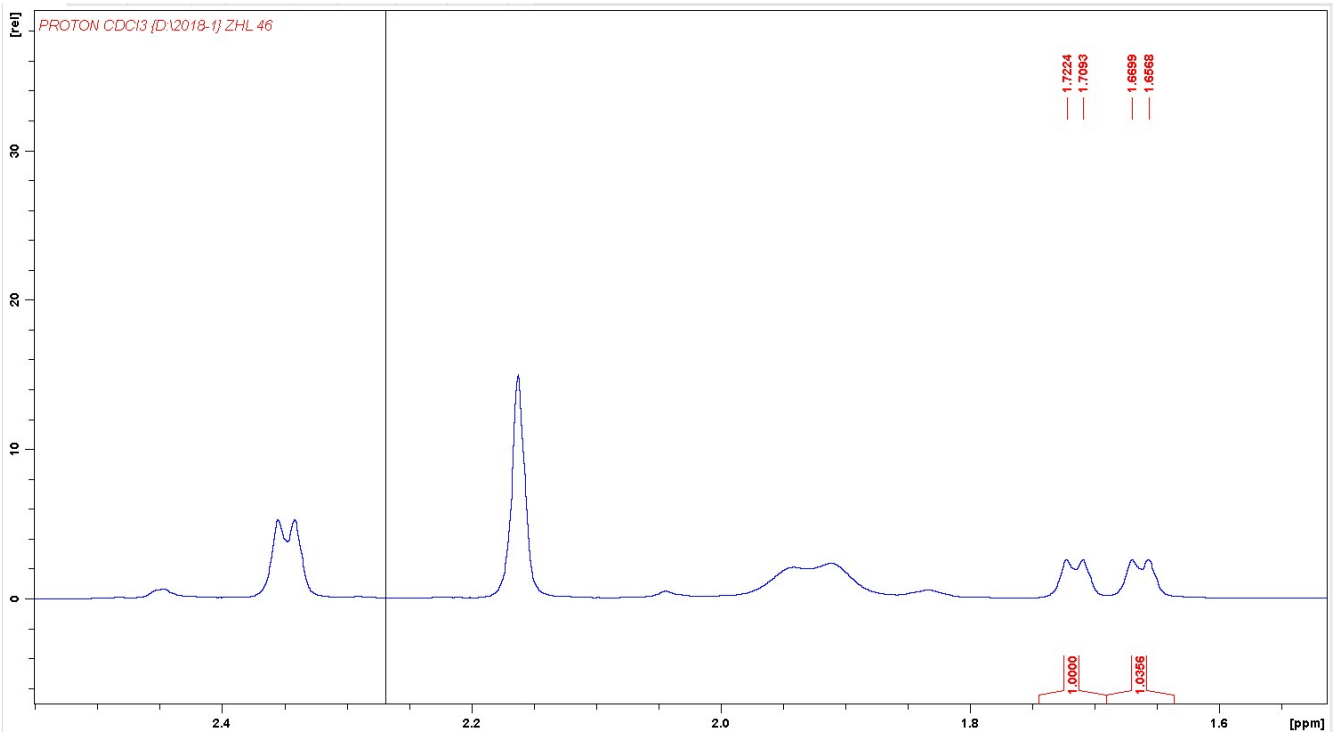
1-(1-(4-trifluoromethylphenyl)ethyl)pyrrolidine (3i):[5] 94% yield, 90% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.1 Hz, 2H, Ar-CH), 7.49 (d, J = 8.1 Hz, 2H, Ar-CH), 3.28 (q, J = 6.6 Hz, 1H, CH), 2.58 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.42 (d, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 129.2, 127.5, 125.3, 125.2, 123.2, 66.3, 53.0, 23.4, 22.3, 21.5. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

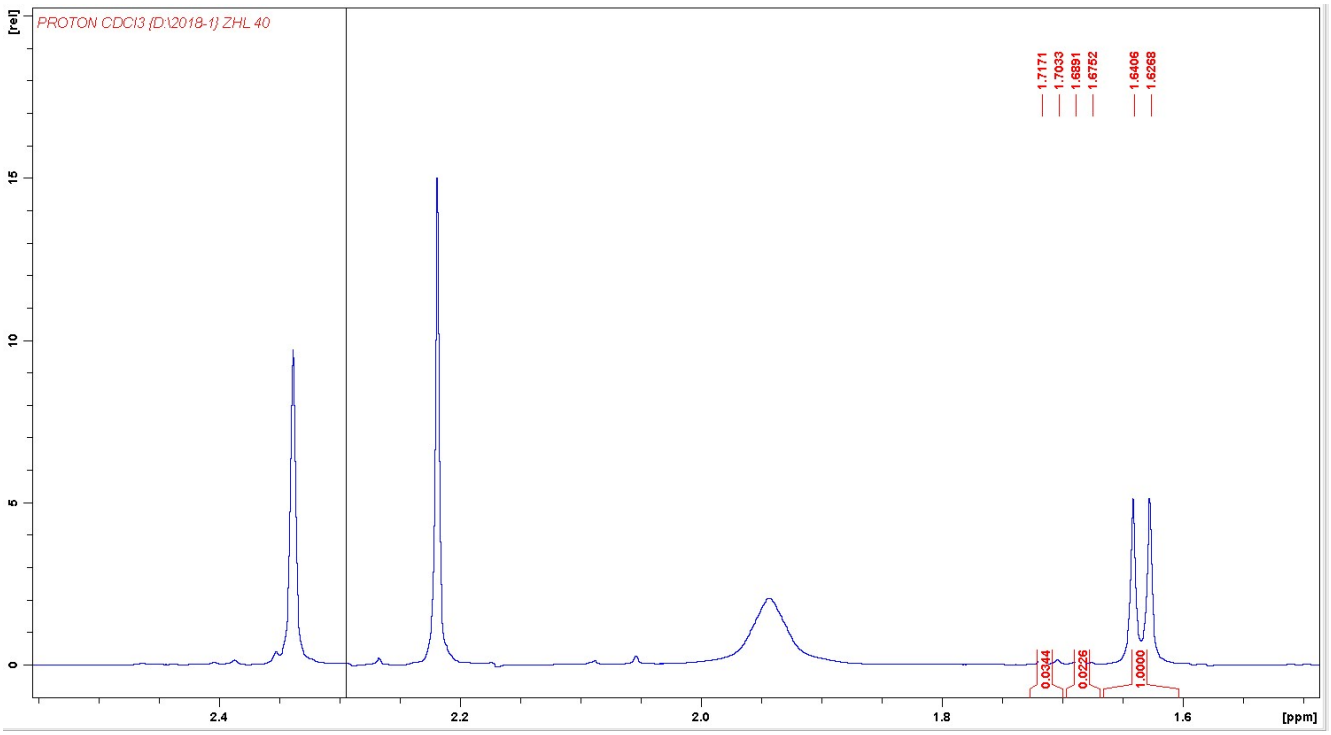




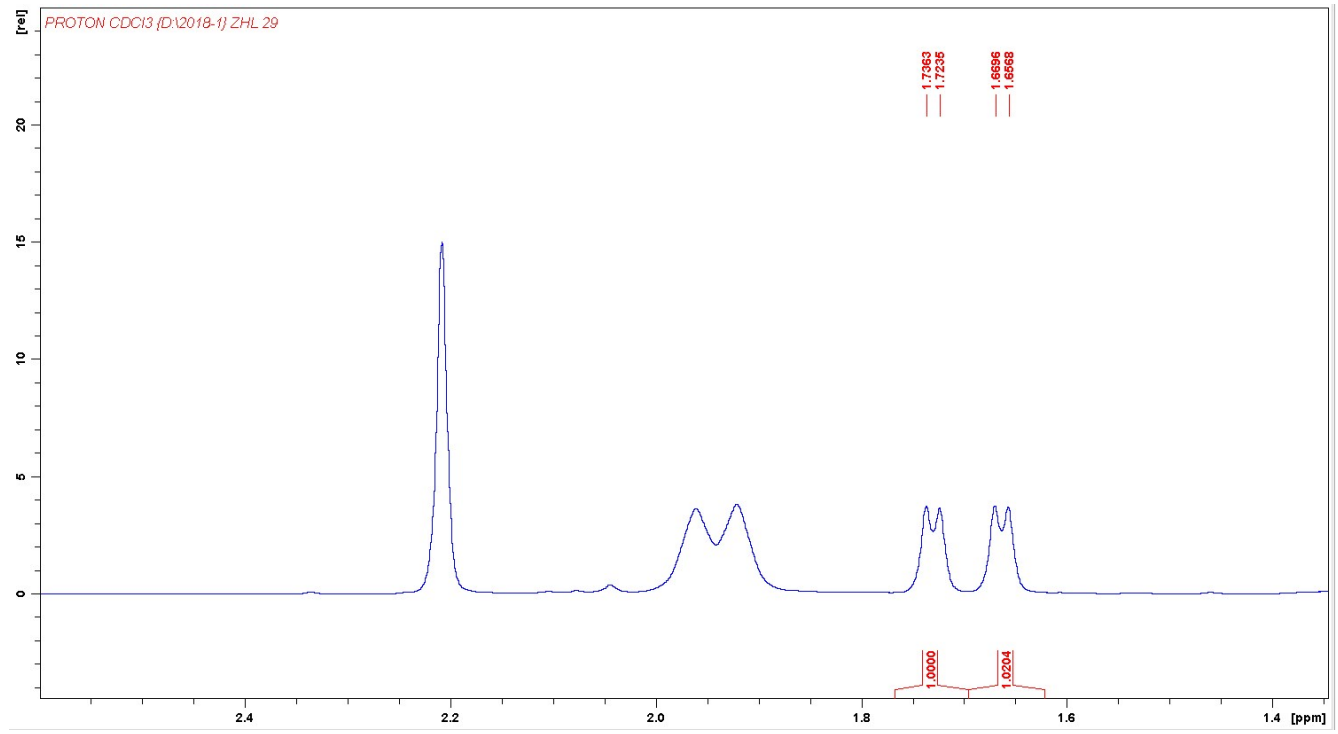


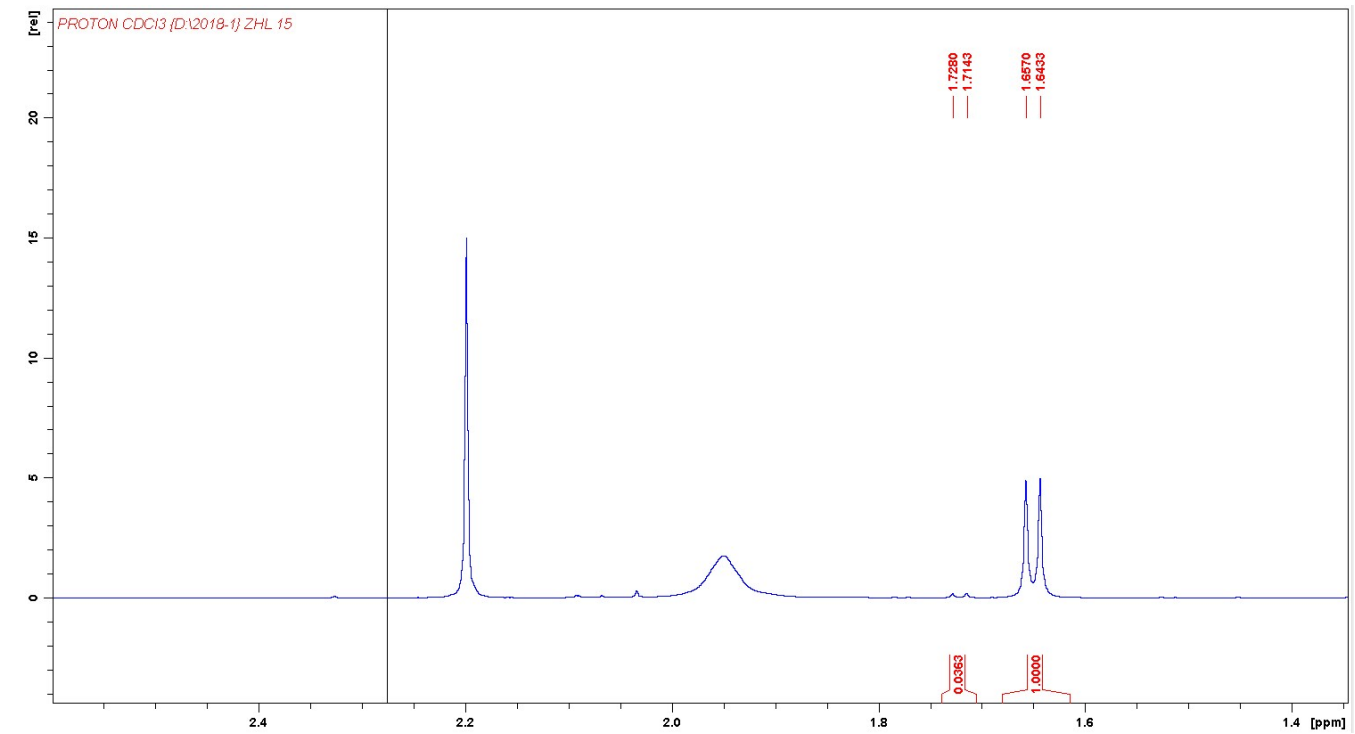
1-(1-(m-tolyl)ethyl)pyrrolidine (3j):[3] 86% yield, 96% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (m, 3H, Ar-CH), 7.11 (m, 1H, Ar-CH), 3.33 (m, 1H, CH), 2.71 (m, 2H, N-CH_2), 2.54 (m, 2H, N-CH_2), 2.38 (s, 3H, Ar-CH_3), 1.86 (m, 4H, 2*CH_2), 1.52 (d, J = 6.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 138.2, 128.4, 128.3, 128.1, 124.6, 65.6, 52.9, 23.4, 23.3. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



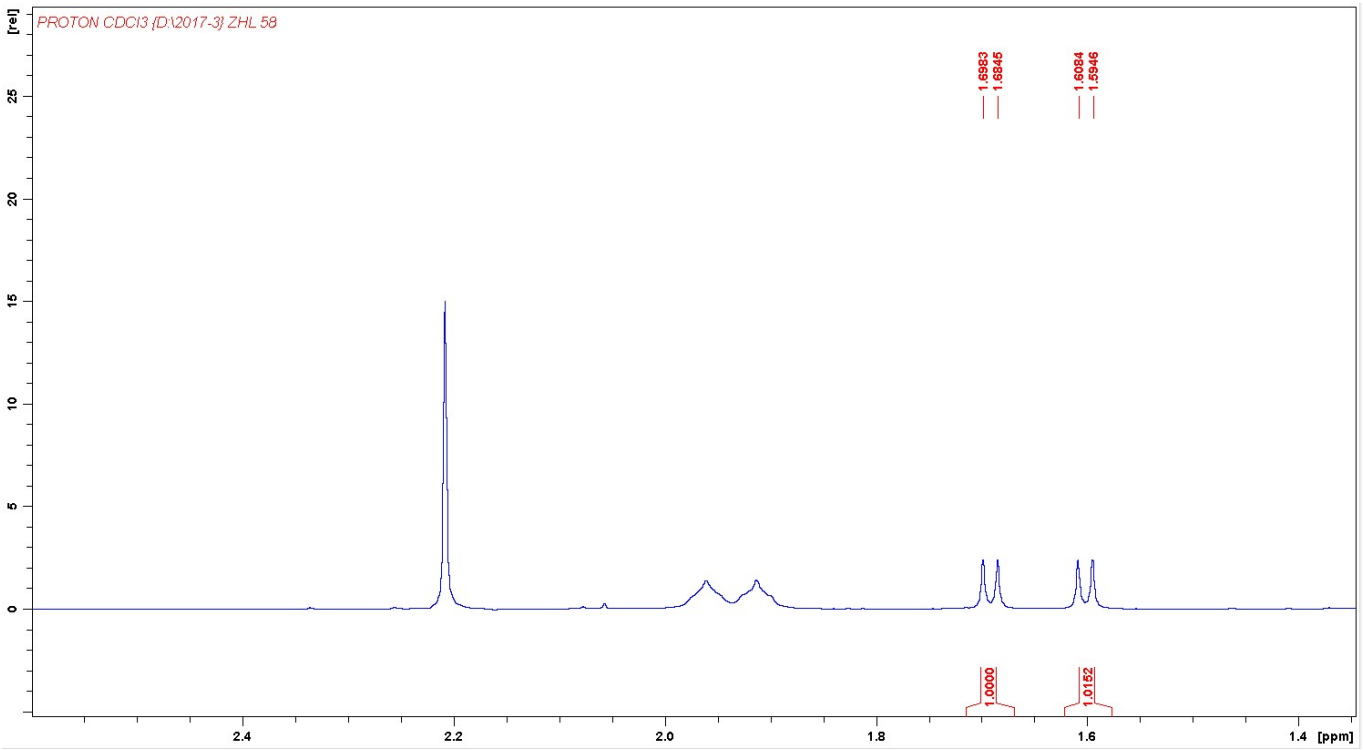


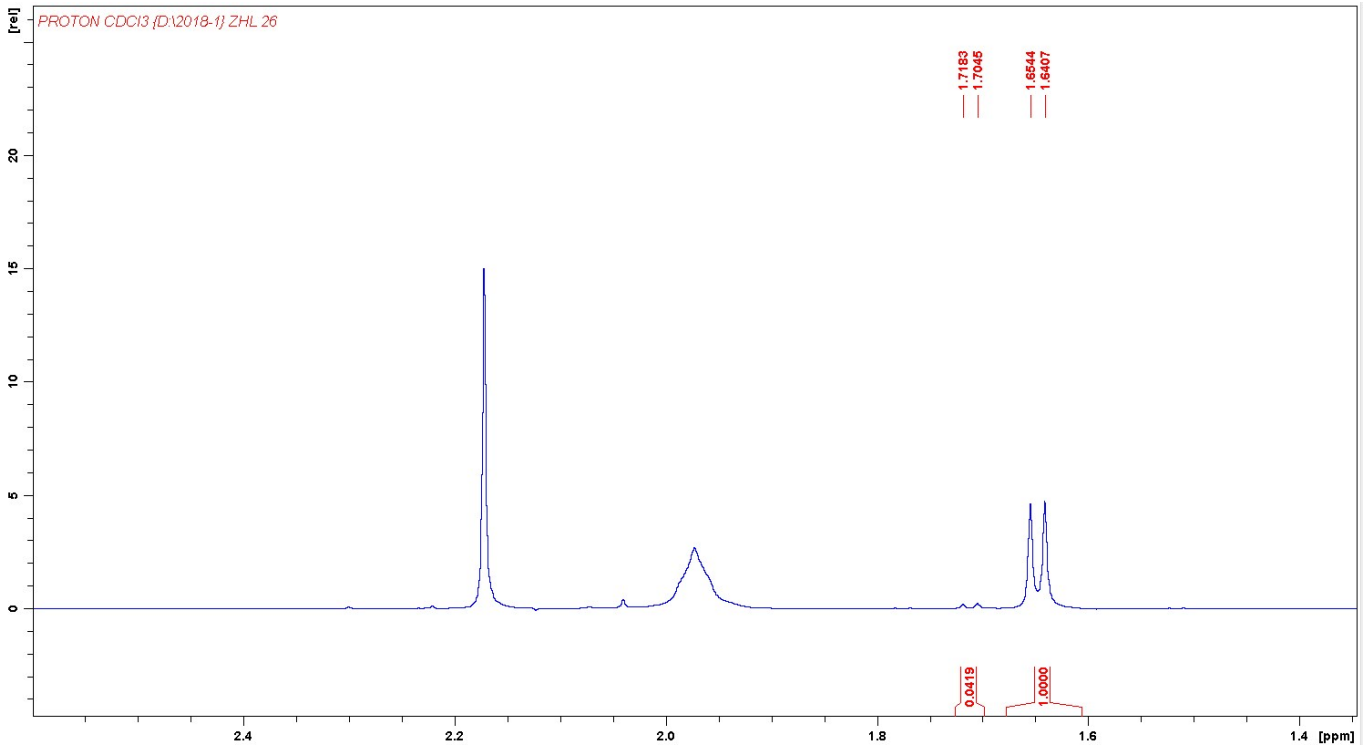
1-(1-(3-methoxyphenyl)ethyl)pyrrolidine (3k):[3] 92% yield, 93% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (m, 1H, Ar-CH), 6.96 (m, 2H, Ar-CH), 6.82 (m, 1H, Ar-CH), 3.84 (s, 3H, O-CH_3), 3.20 (q, J = 6.6 Hz, 1H, CH), 2.60 (m, 2H, N-CH_2), 2.42 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.44 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 147.5, 129.2, 119.7, 112.7, 112.3, 66.1, 55.3, 53.0, 23.5, 23.2. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



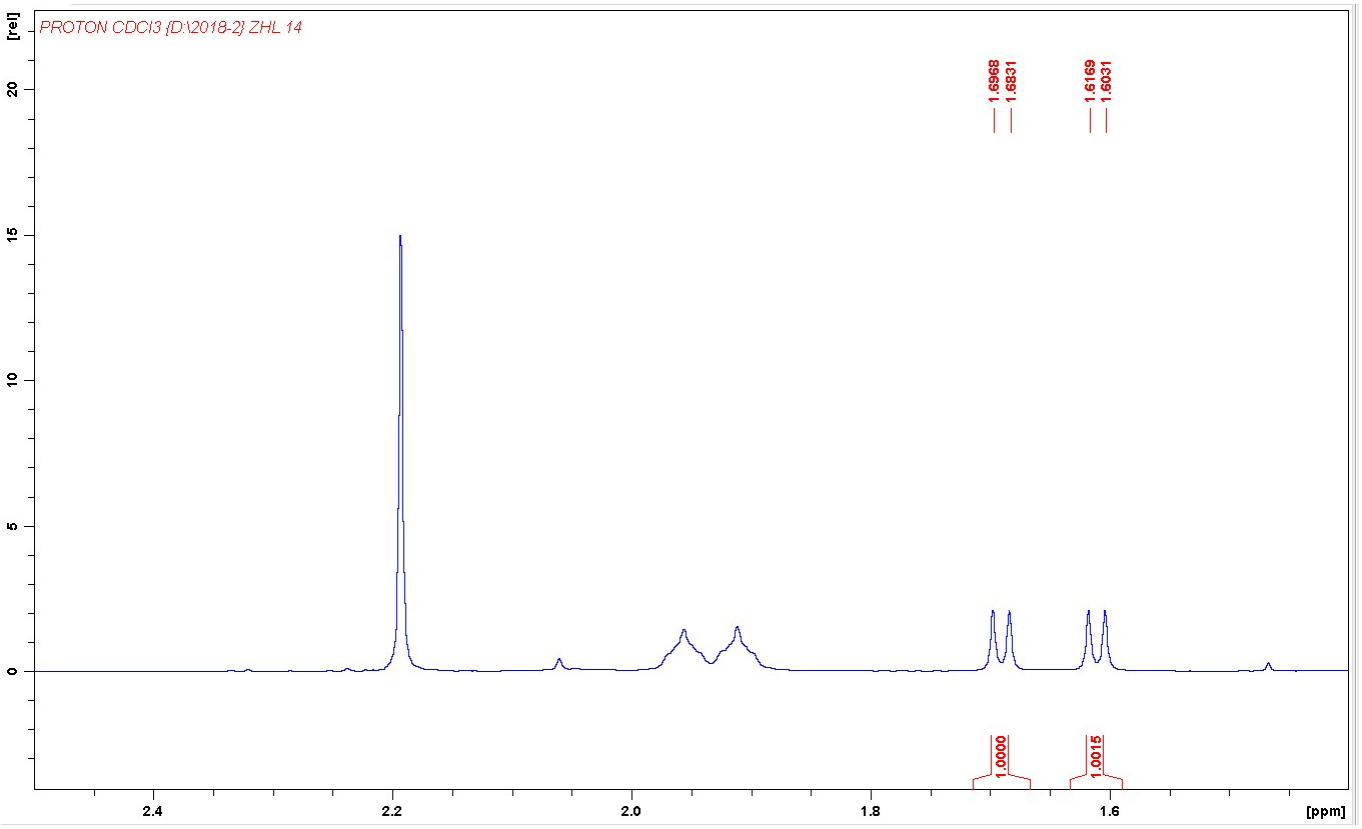


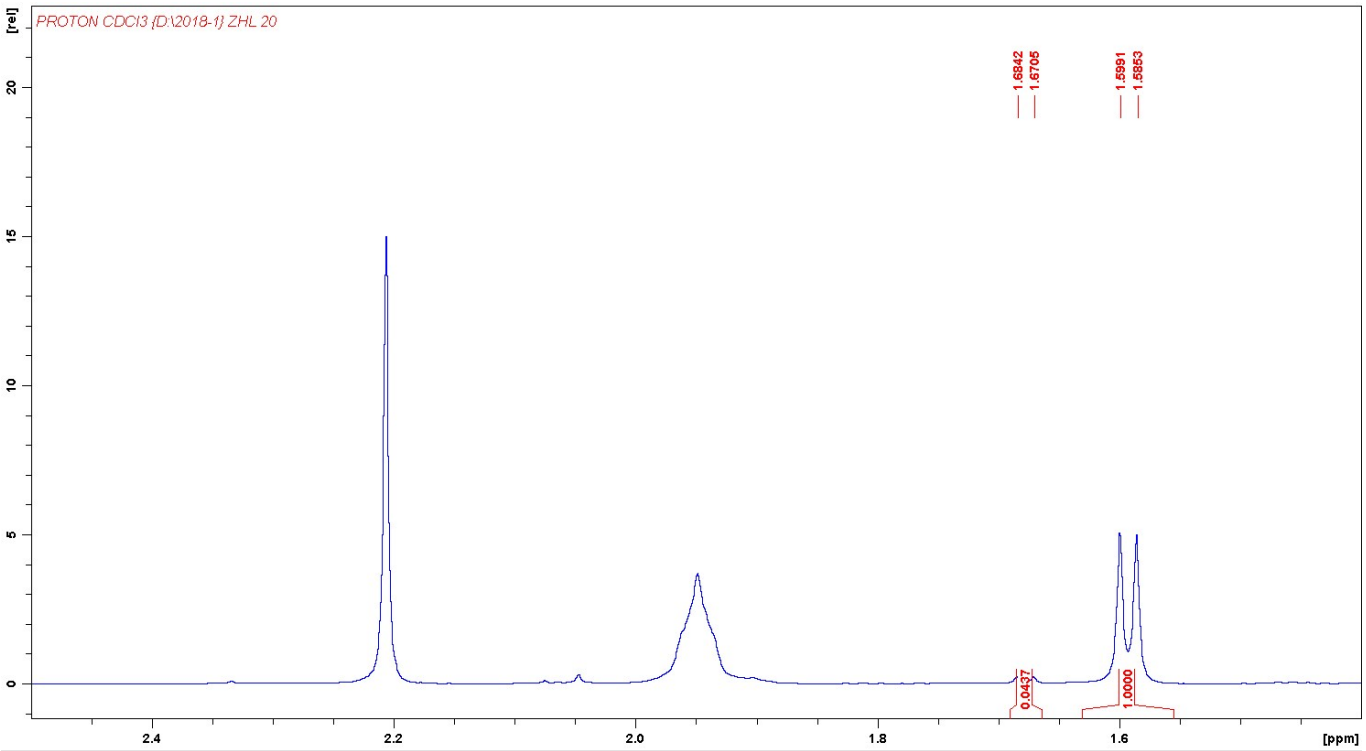
1-(1-(3-chlorophenyl)ethyl)pyrrolidine (3l): 91% yield, 92% ee, brown oil, unkown compound. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 1H, Ar-CH), 7.20–7.30 (m, 3H, Ar-CH), 3.20 (q, J = 6.6 Hz, 1H, CH), 2.58 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.42 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.5 (Ar-CCl), 134.2, 129.7, 127.4, 127.1, 125.4, 65.6, 52.9, 23.4, 23.10. HRMS calcd for $C_{12}H_{17}ClN$ $[M+H]^+$: 210.10440, found 210.10426. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



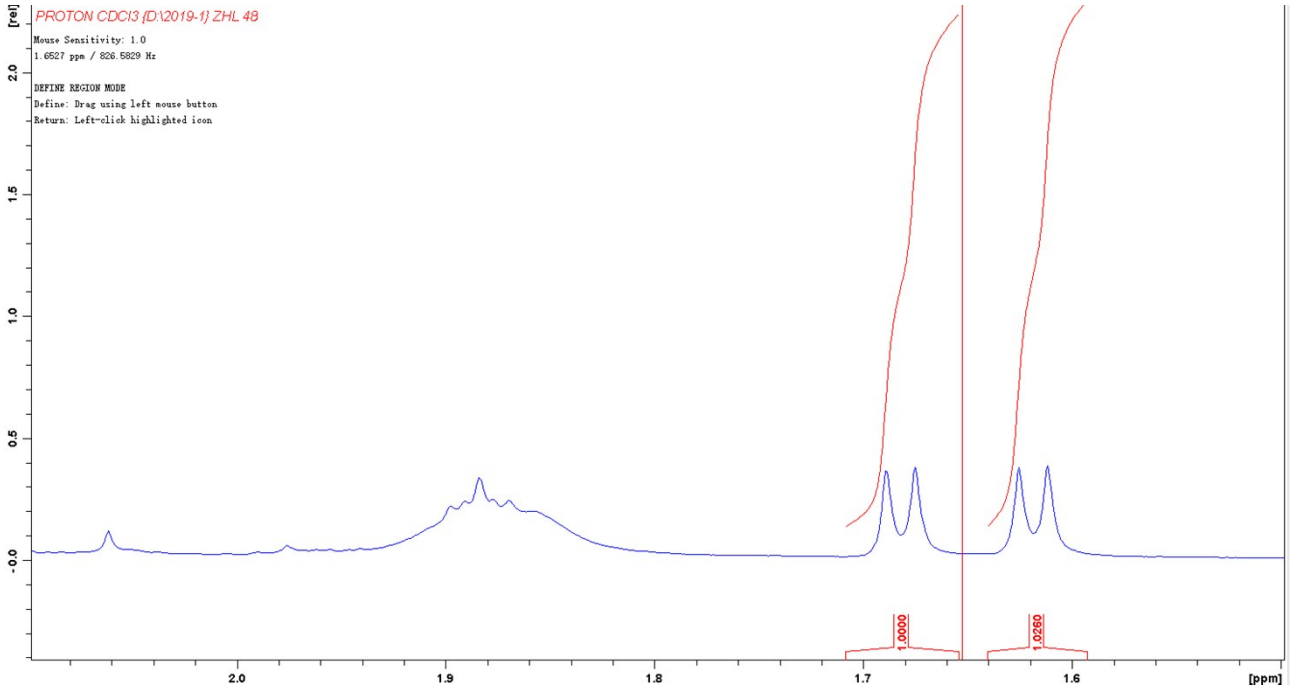


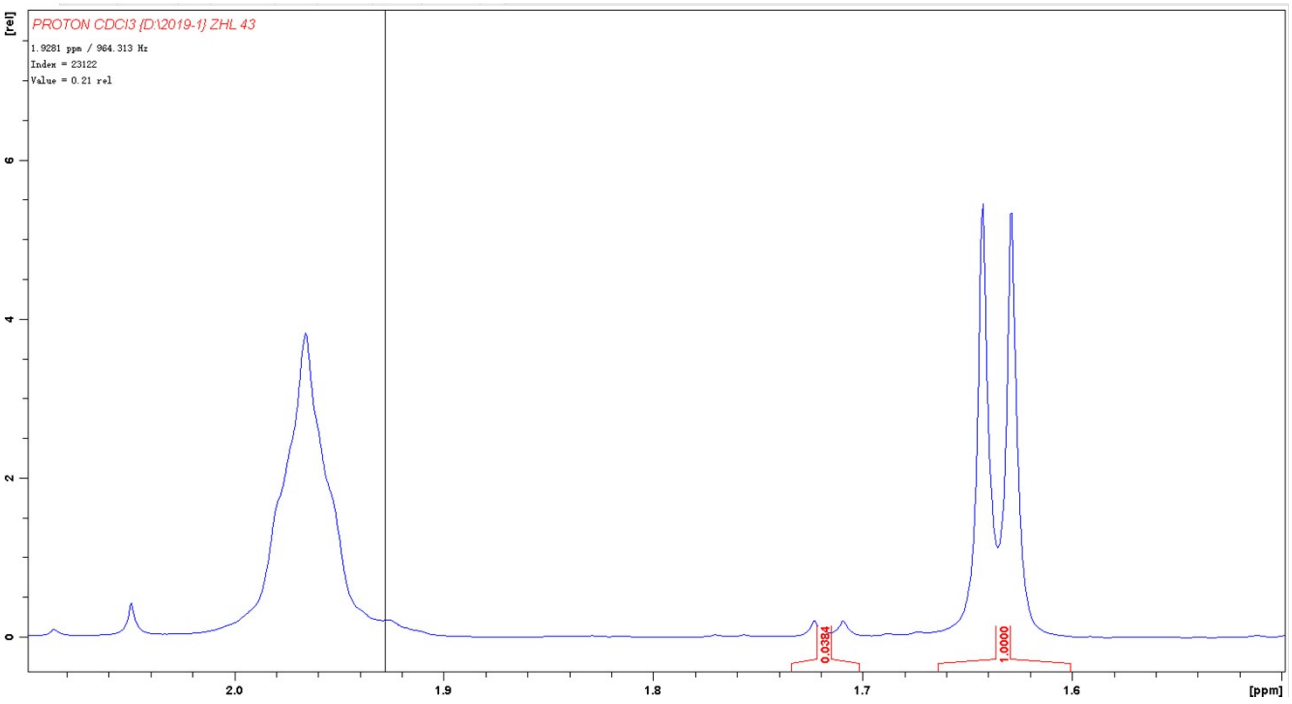
1-(1-(3-bromophenyl)ethyl)pyrrolidine (3m): 89% yield, 92% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (s, 1H, Ar-CH), 7.39 (d, *J* = 7.9 Hz, 1H, Ar-CH), 7.39 (d, *J* = 7.9 Hz, 1H, Ar-CH), 7.20 (t, *J* = 7.8 Hz, 1H, Ar-CH), 3.18 (q, *J* = 6.6 Hz, 1H, CH), 2.57 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.41 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3 (Ar-CBr), 130.2, 129.9, 129.9, 125.9, 122.4, 65.5, 52.9, 23.4, 23.2. HRMS calcd for $C_{12}H_{17}BrN$ $[M+H]^+$: 254.0466, found: 254.0525. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



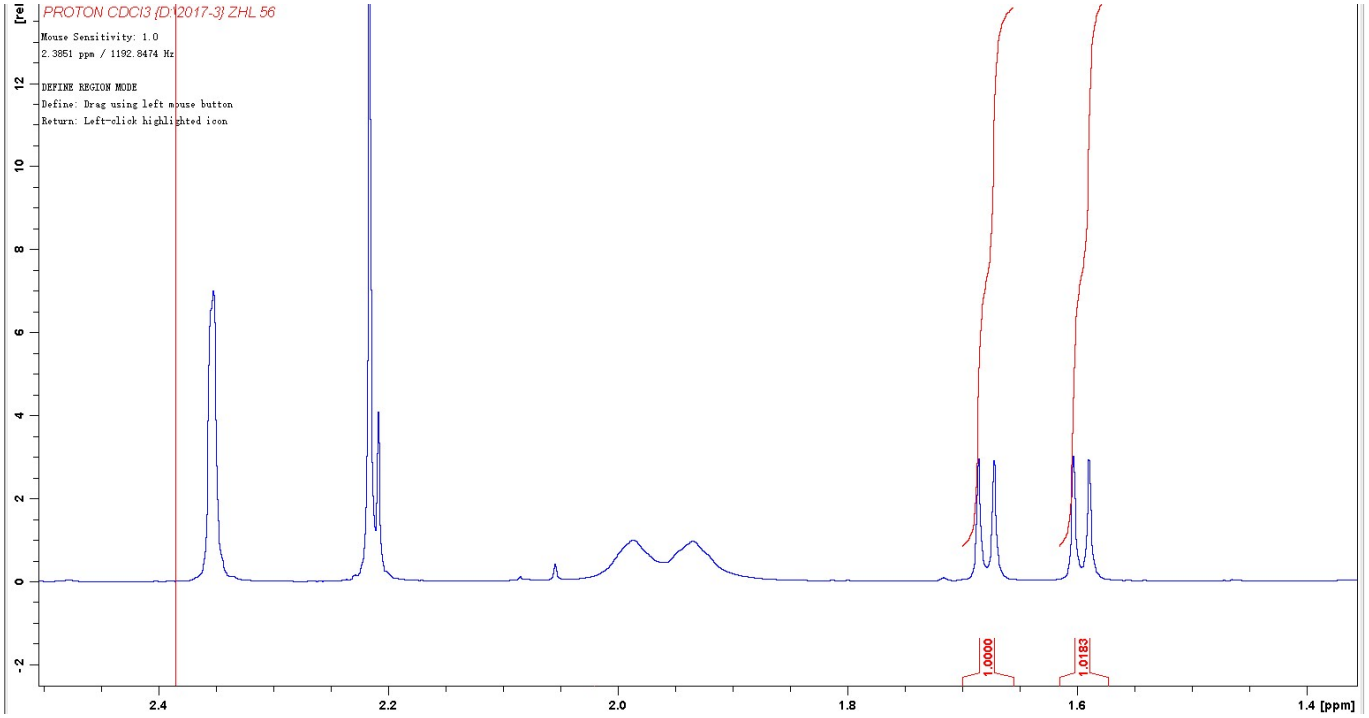


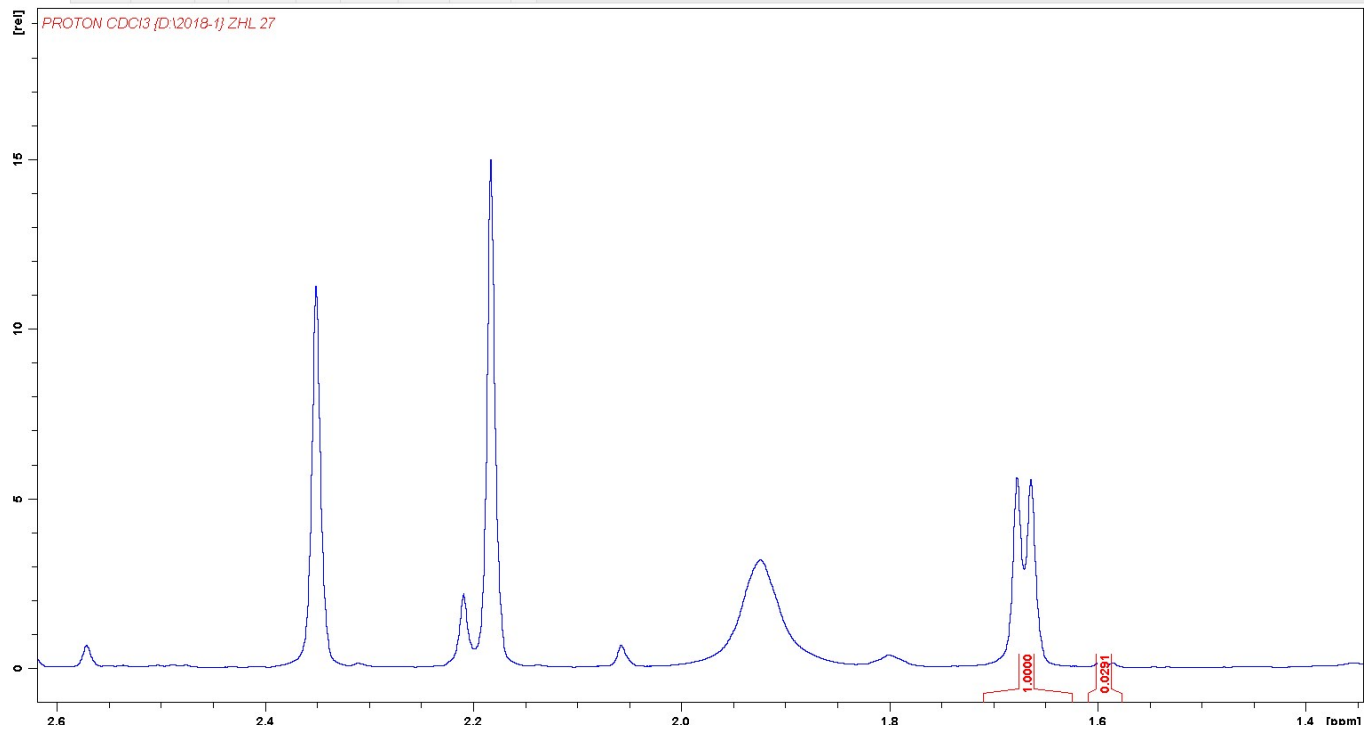
1-(1-(3-trifluoromethylphenyl)ethyl)pyrrolidine (3n): 91% yield, 93% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H, Ar-CH), 7.57 (d, *J* = 7.6 Hz, 1H, Ar-CH), 7.52 (d, *J* = 7.7 Hz, 1H, Ar-CH), 7.45 (t, *J* = 7.7 Hz, 1H, Ar-CH), 3.28 (q, *J* = 6.6 Hz, 1H, CH), 2.58 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.81 (m, 4H, 2*CH_2), 1.43 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.9 (Ar-C-CF_3), 130.6, 128.8, 124.0, 123.7, 65.7, 53.0, 23.4, 23.3. HRMS calcd for $C_{12}H_{17}BrN$ $[M+H]^+$: 254.0466, found: 254.0525. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



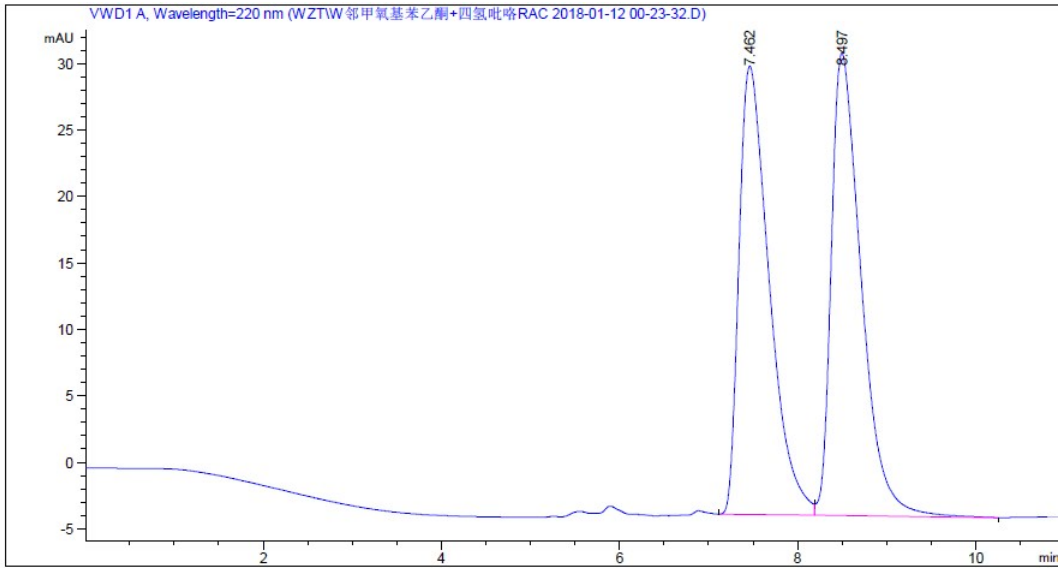


1-(1-(o-tolyl)ethyl)pyrrolidine (3o):[3] 89% yield, 94% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (m, 1H, Ar-CH), 7.24 (m, 1H, Ar-CH), 7.15(m, 1H, Ar-CH), 3.52 (q, J = 6.5 Hz, 1H, CH), 2.58 (m, 2H, N-CH_2), 2.48 (m, 2H, N-CH_2), 2.42 (s, 3H, Ar-CH_3), 1.82 (m, 4H, 2*CH_2), 1.38 (d, J = 6.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 134.5, 130.2, 126.9, 126.2, 126.1, 61.2, 53.0, 23.5, 22.4, 19.6. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

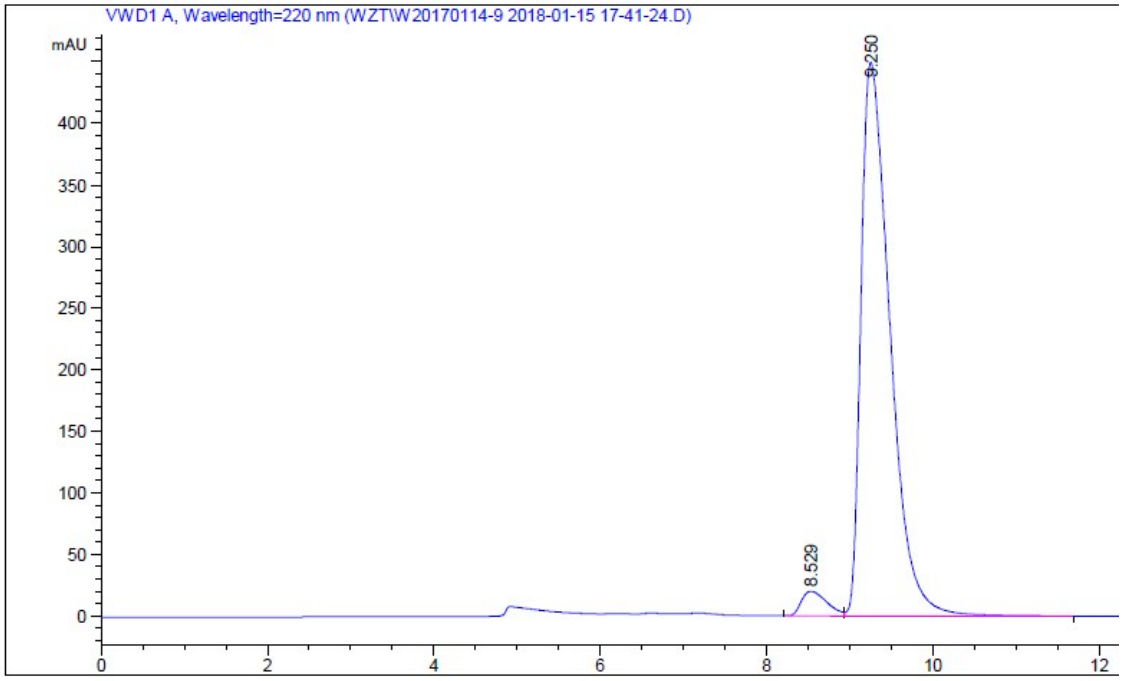




1-(1-(2-methoxyphenyl)ethyl)pyrrolidine (3p):[3] 97% yield, 94% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (m, 1H, Ar-CH), 7.23 (m, 1H, Ar-CH), 7.01 (m, 1H, Ar-CH), 6.90 (m, 1H, Ar-CH), 3.82-3.90 (m, 4H, O-CH_3+CH), 2.60 (m, 2H, N-CH_2), 2.51 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.39 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2 (Ar-COMe), 130.0, 128.9, 121.6, 110.8, 57.8, 55.6, 52.5, 23.4, 19.6. Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA=99.5:0.5, 0.6 mL/min, 220 nm, 7.46 min, 8.50 min.

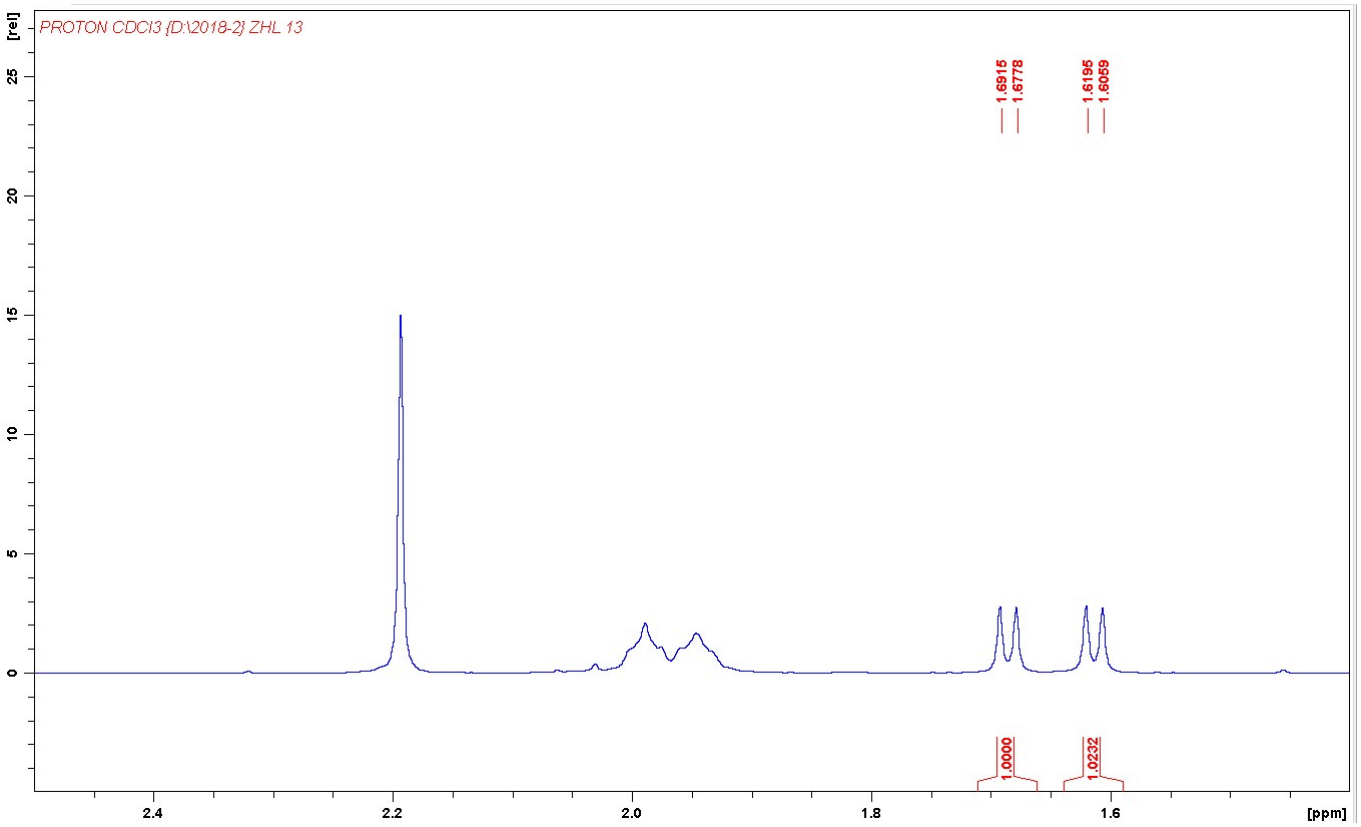


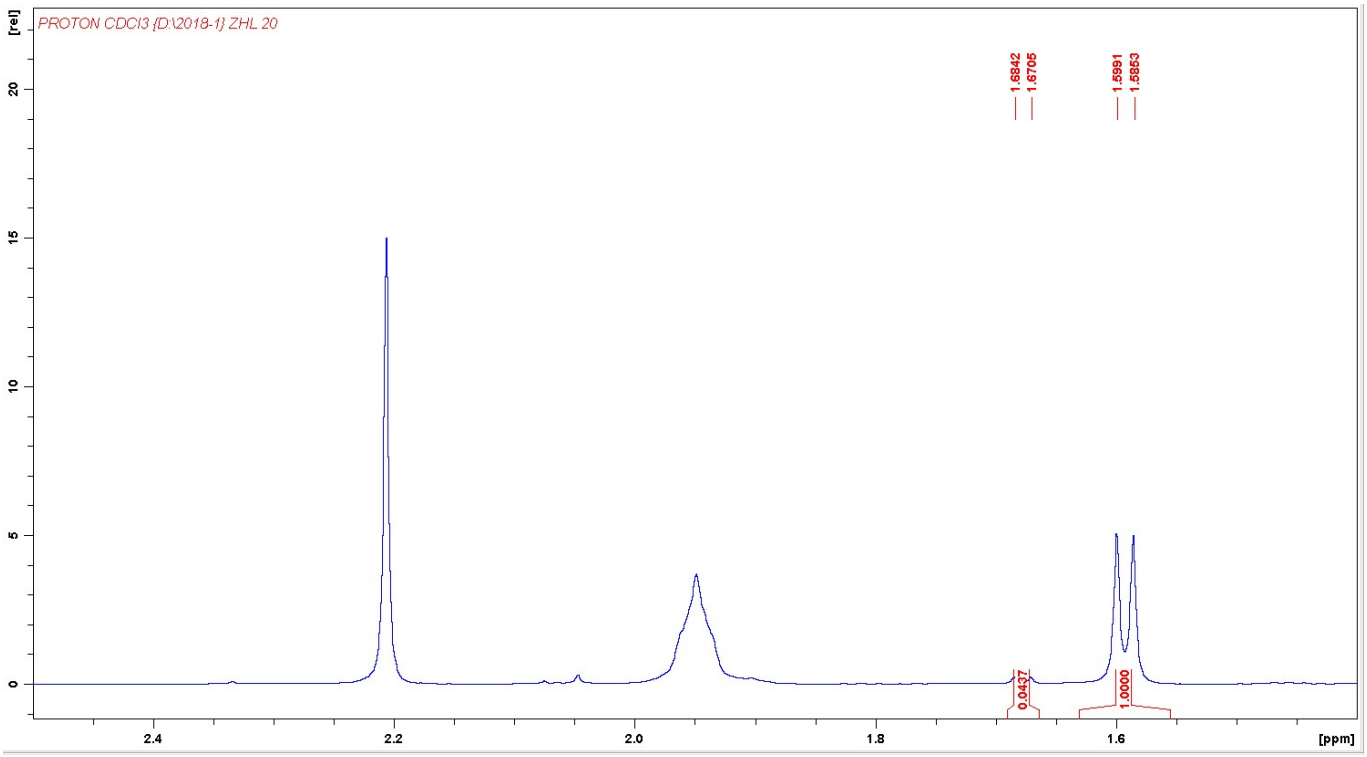
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.462	BV	0.3623	795.36249	33.70512	49.4860
2	8.497	VB	0.3593	811.88580	34.78402	50.5140



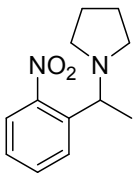
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.529	BV	0.3350	424.18607	20.03264	3.7601
2	9.250	VB	0.3797	1.08571e4	449.61316	96.2399

1-(1-(2-chlorophenyl)ethyl)pyrrolidine (3q): 91% yield, 92% ee, brown oil, unknown compound. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 1H, Ar-CH), 7.20–7.30 (m, 3H, Ar-CH), 3.20 (q, J = 6.6 Hz, 1H, CH), 2.58 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.80 (m, 4H, 2*CH_2), 1.42 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.1, 132.6, 129.3, 128.8, 127.9, 127.2, 61.0, 52.8, 23.5, 21.9. HRMS calcd for $C_{12}H_{17}ClN$ $[M+H]^+$: 210.10440, found 210.10420. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

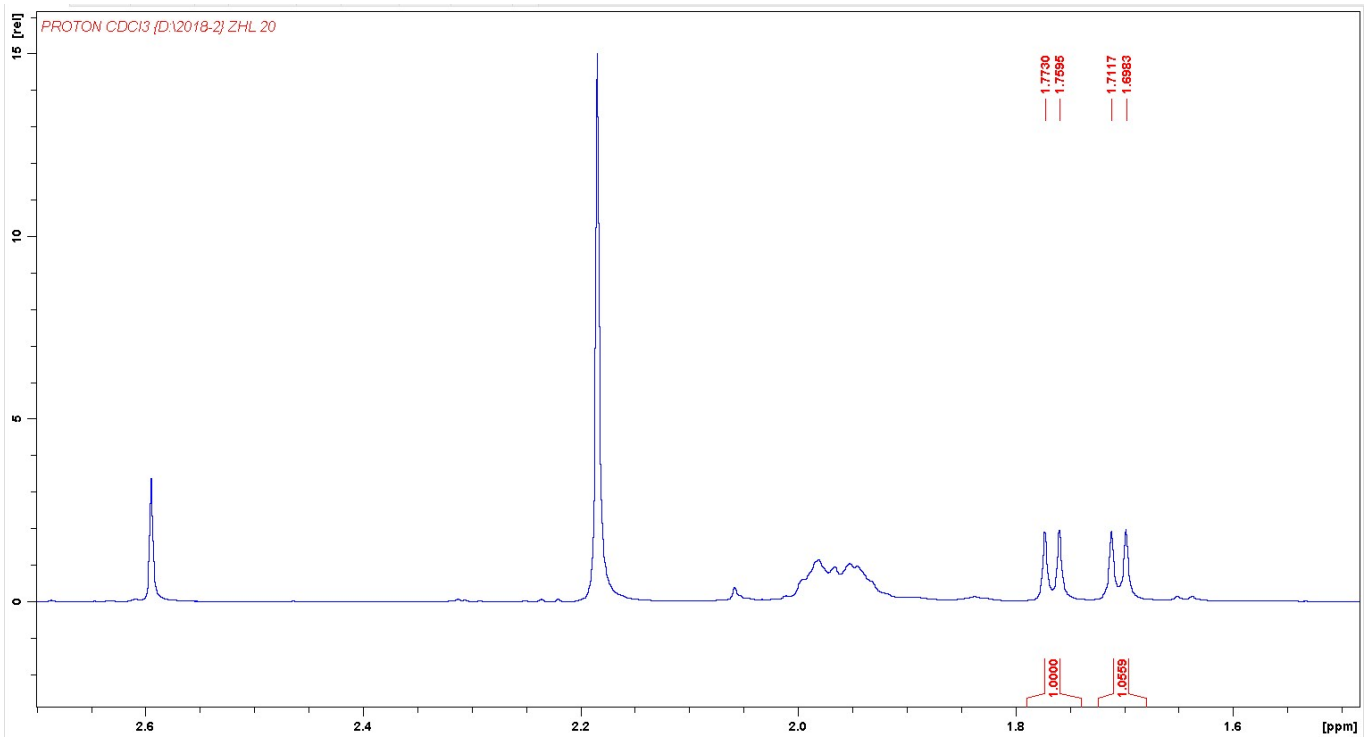


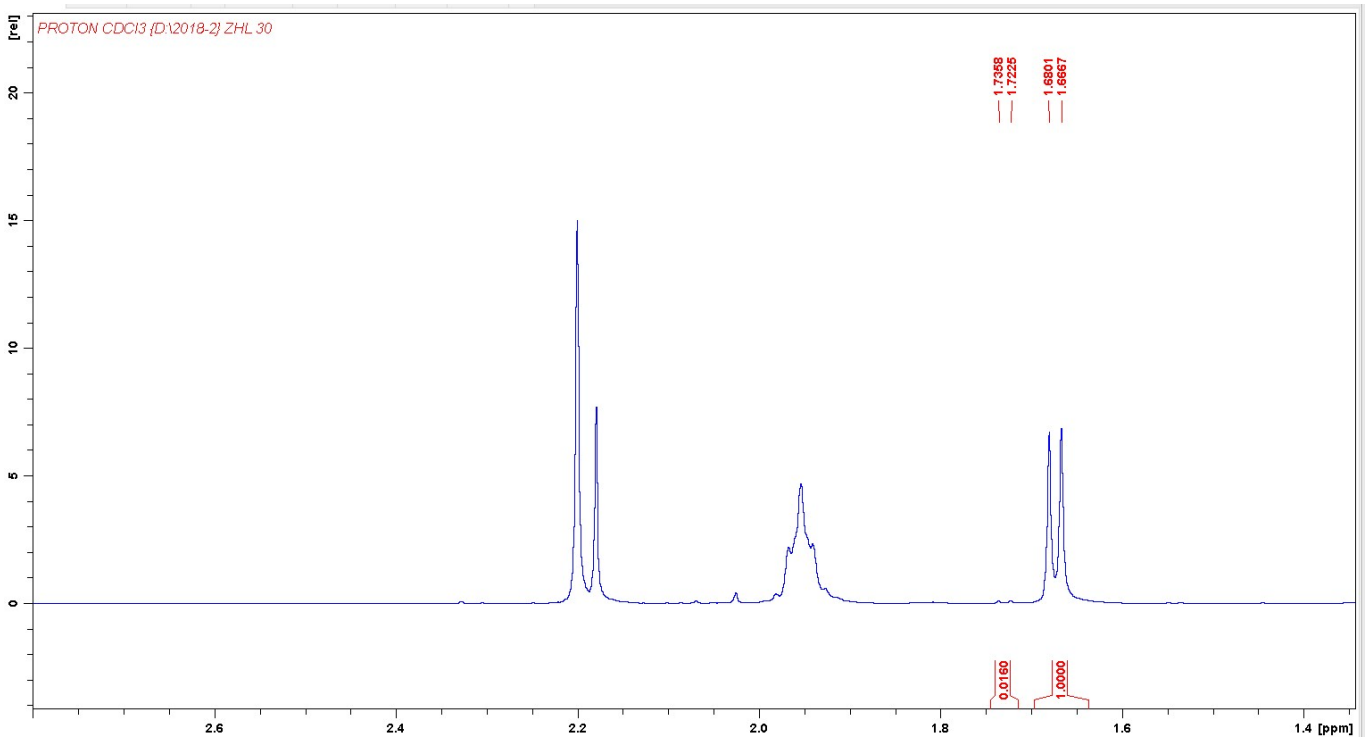


1-(1-(2-nitrophenyl)ethyl)pyrrolidine (3r): 94% yield, 97% ee, brown oil, unknown compound. ^{1}H NMR (500 MHz, $CDCl_3$):

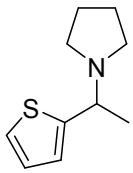


δ 7.90 (d, *J* = 7.7 Hz, 1H, Ar-CH), 7.72 (d, *J* = 8.0 Hz, 1H, Ar-CH), 7.59 (t, *J* = 7.5 Hz, 1H, Ar-CH), 7.37 (q, *J* = 7.5 Hz, 1H, Ar-CH), 3.71 (q, *J* = 6.1 Hz, 1H, CH), 2.54 (m, 2H, N-CH_2), 2.40 (m, 2H, N-CH_2), 1.79 (m, 4H, 2*CH_2), 1.50 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 140.0, 132.6, 129.3, 127.3, 123.3, 59.7, 52.7, 23.5, 22.7. HRMS (ESI) m/z calcd for $C_{12}H_{17}N_2O_2^+$ $[M+H]^+$ 221.12845, found 221.12848. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

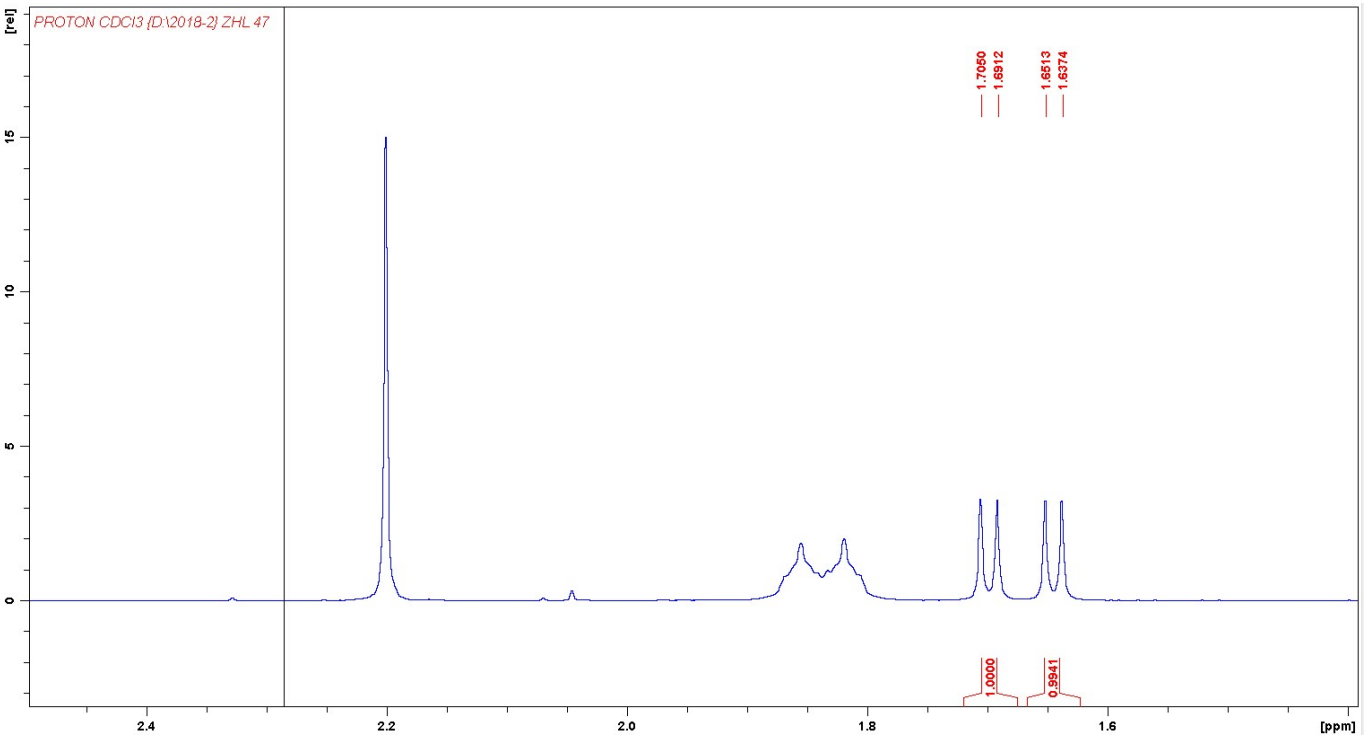


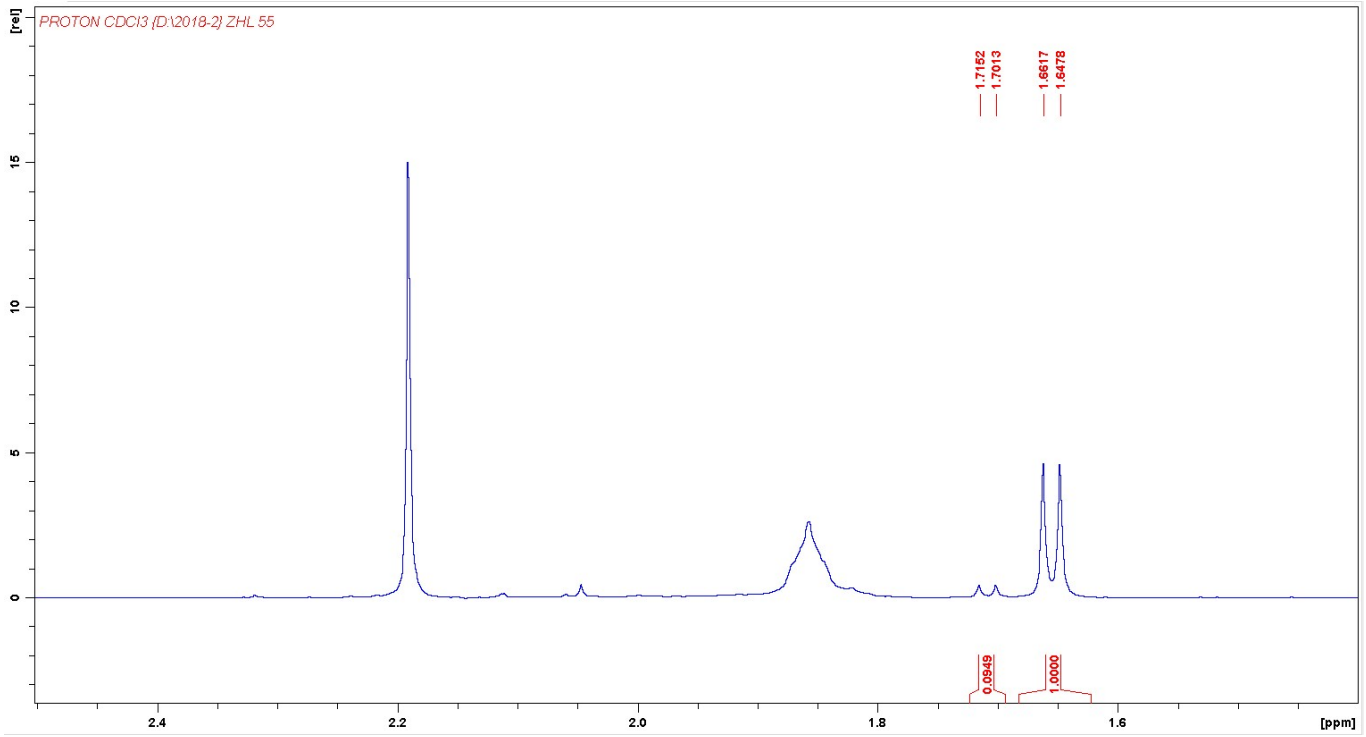


1-(1-(thiophen-2-yl)ethyl)pyrrolidine (3s): 91% yield, 82% ee, brown oil, unknown compound. ^{1}H NMR (500 MHz, $CDCl_3$):

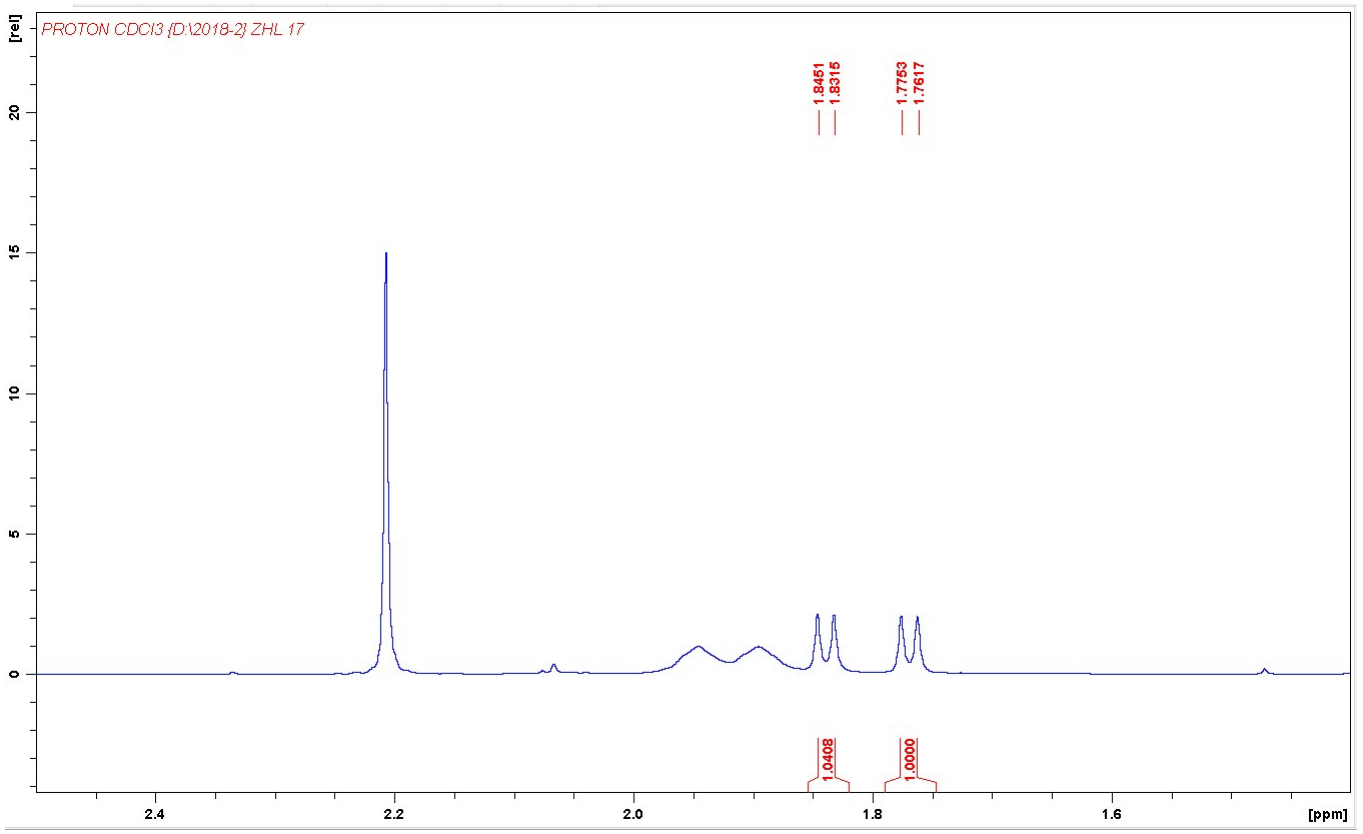


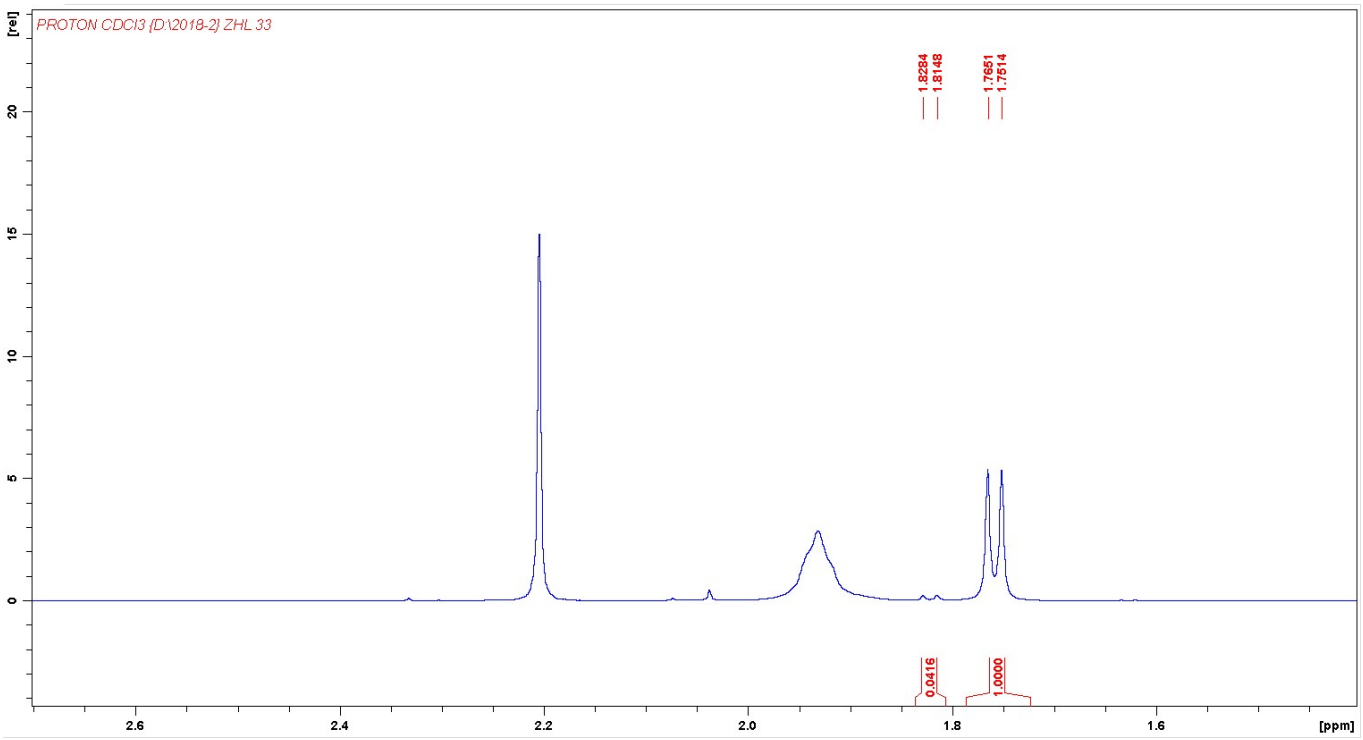
δ 7.22 (m, 1H, Ar-CH), 6.95 (m, 3H, Ar-CH), 3.73 (q, J = 6.6 Hz, 1H, CH), 2.64 (m, 2H, N-CH_2), 2.53 (m, 2H, N-CH_2), 1.81 (m, 4H, 2*CH_2), 1.54 (d, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 126.0, 123.8, 123.7, 59.8, 52.0, 23.5. HRMS (ESI) m/z calcd for $C_{10}H_{16}NS^+$ $[M+H)^+$ 182.09980, found 182.09961. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



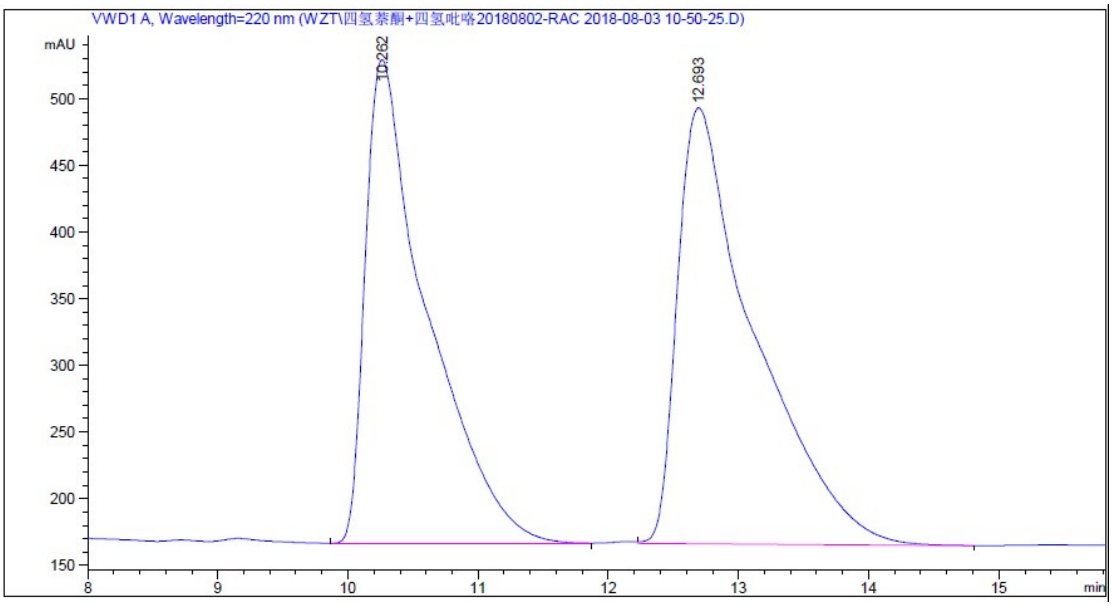


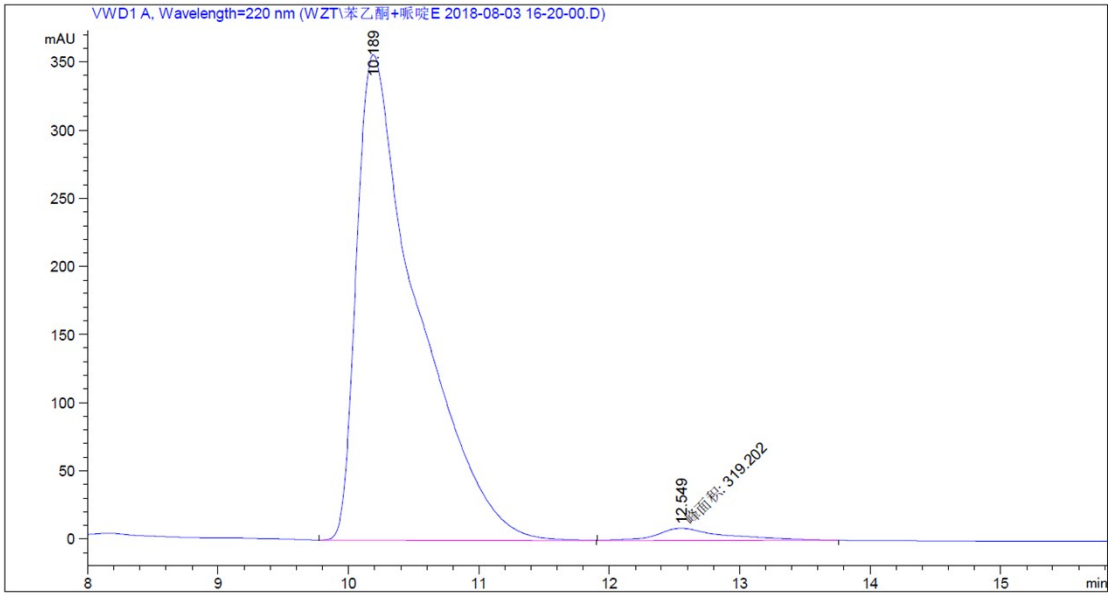
1-(1-(naphthalen-1-yl)ethyl)pyrrolidine (3t):[6] 95% yield, 92% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.51 (d, J = 6.8 Hz, 1H, Ar-CH), 7.93 (d, J = 7.6 Hz, 1H, Ar-CH), 7.80 (m, 2H, Ar-CH), 7.54 (m, 3H), 4.01 (m, 1H, CH), 2.69 (m, 2H, N-CH_2), 2.57 (m, 2H, N-CH_2), 1.86 (m, 4H, 2*CH_2), 1.60 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.8, 134.0, 131.1, 128.9, 127.0, 125.7, 125.5, 125.2, 124.6, 123.7, 62.4, 53.1, 23.6, 22.9. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.





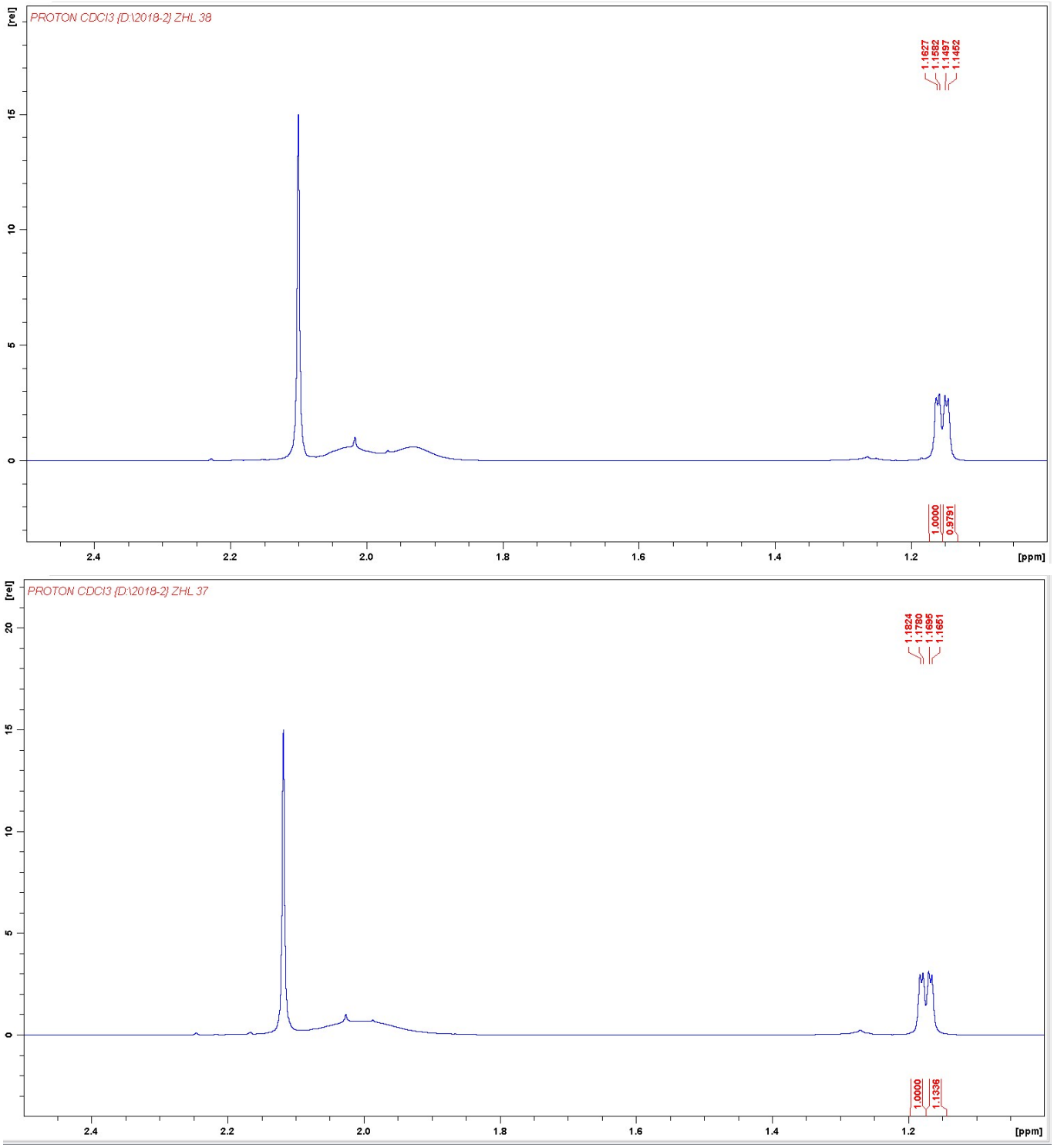
1-(1,2,3,4-tetrahydronaphthalen-1-yl)pyrrolidine (3u):[7] 83% yield, 95% ee, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 7.3 Hz, 1H, Ar-CH), 7.17 (m, 3H, Ar-CH), 3.61 (t, J = 5.0 Hz, 1H, CH), 2.95 (m, 1H, CH_2), 2.80 (m, 1H, CH_2), 2.71 (m, 2H, N-CH_2), 2.54 (m, 2H, N-CH_2), 2.16 (m, 1H, CH_2), 2.00 (m, 1H, CH_2), 1.70–1.90 (m, 6H, 2*CH_2+CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 137.7, 129.4, 129.1, 126.6, 125.0, 60.7, 50.4, 29.1, 24.7, 23.8, 19.4. Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA/TFA/DEA = 92:8:0.2:0.1, 0.5mL/min, 220 nm, 10.19 min, 12.55 min.



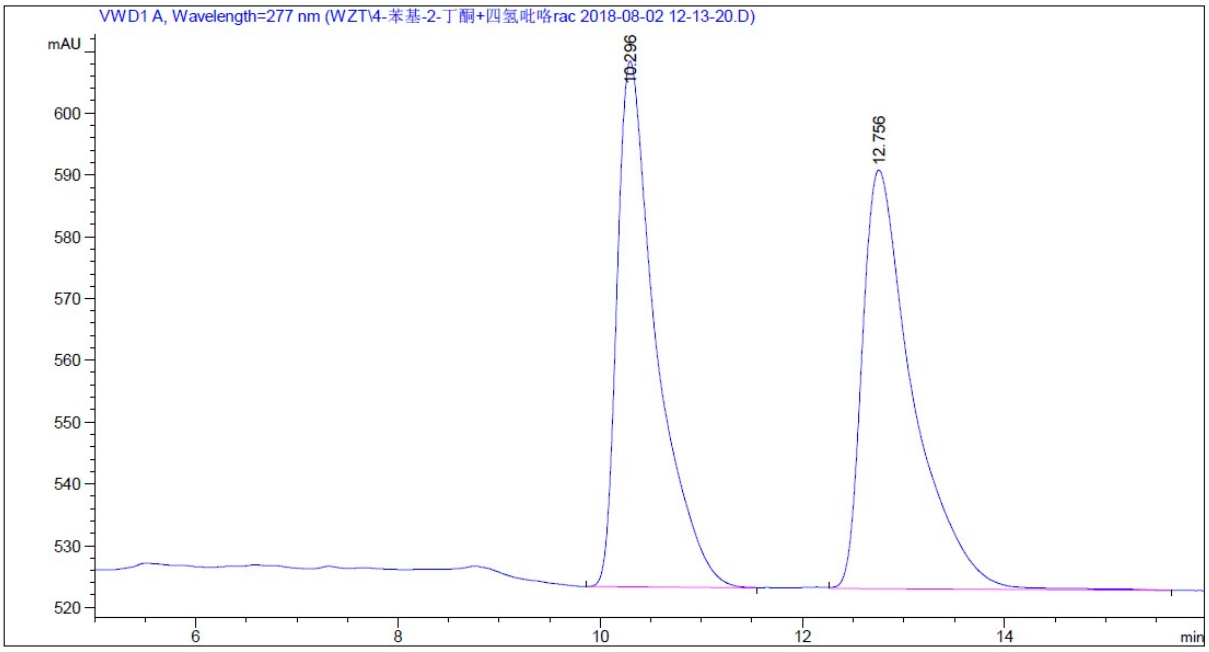


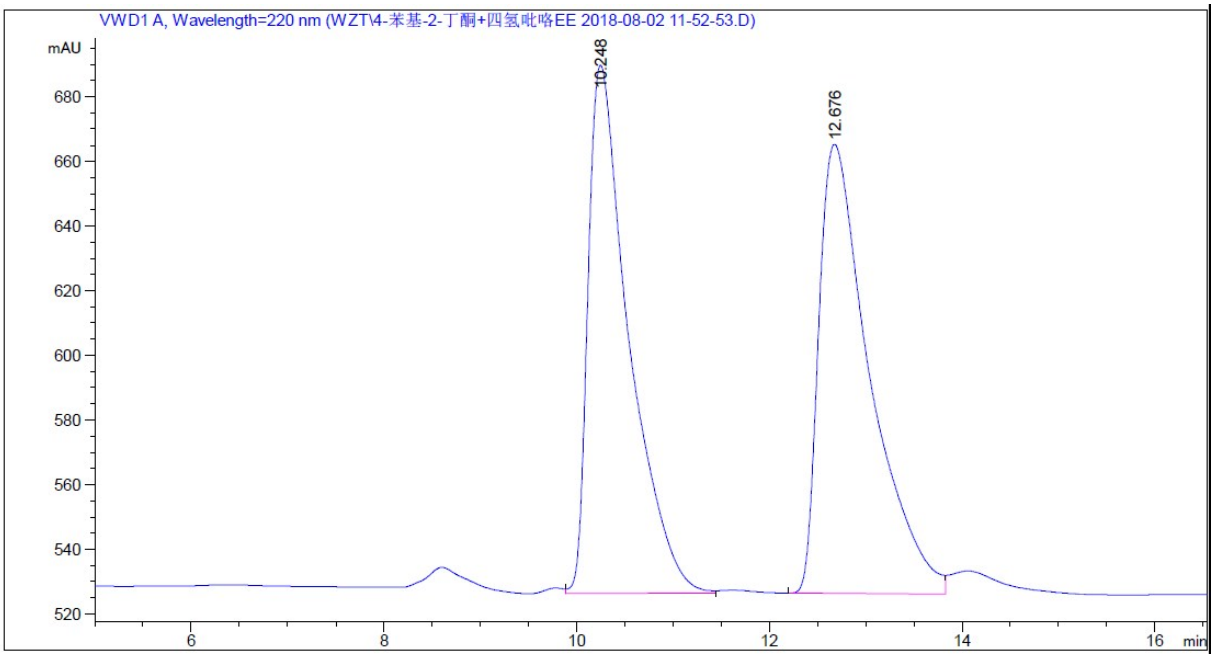
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.189	BV	0.4572	1.15778e4	356.22934	97.3170
2	12.549	MM	0.5936	319.20221	8.96177	2.6830

1-(1-(4-methoxyphenyl)propan-2-yl)pyrrolidine (3v):[8] 97% yield, 6% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (d, J = 8.6 Hz, 2H, Ar-CH), 6.86 (d, J = 8.6 Hz, 2H, Ar-CH), 3.83 (s, 3H, O-CH_3), 3.10 (dd, J = 8.6, 13.5 Hz, 1H, CH), 2.70 (m, 4H, 2*N-CH_2), 2.52 (m, 1H, CH_2), 2.41 (m, 1H, CH_2), 1.85 (m, 4H, 2*CH_2), 1.02 (d, J = 6.3 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 130.7, 130.3, 113.9, 61.6, 55.2, 51.2, 39.9, 23.5, 16.9. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



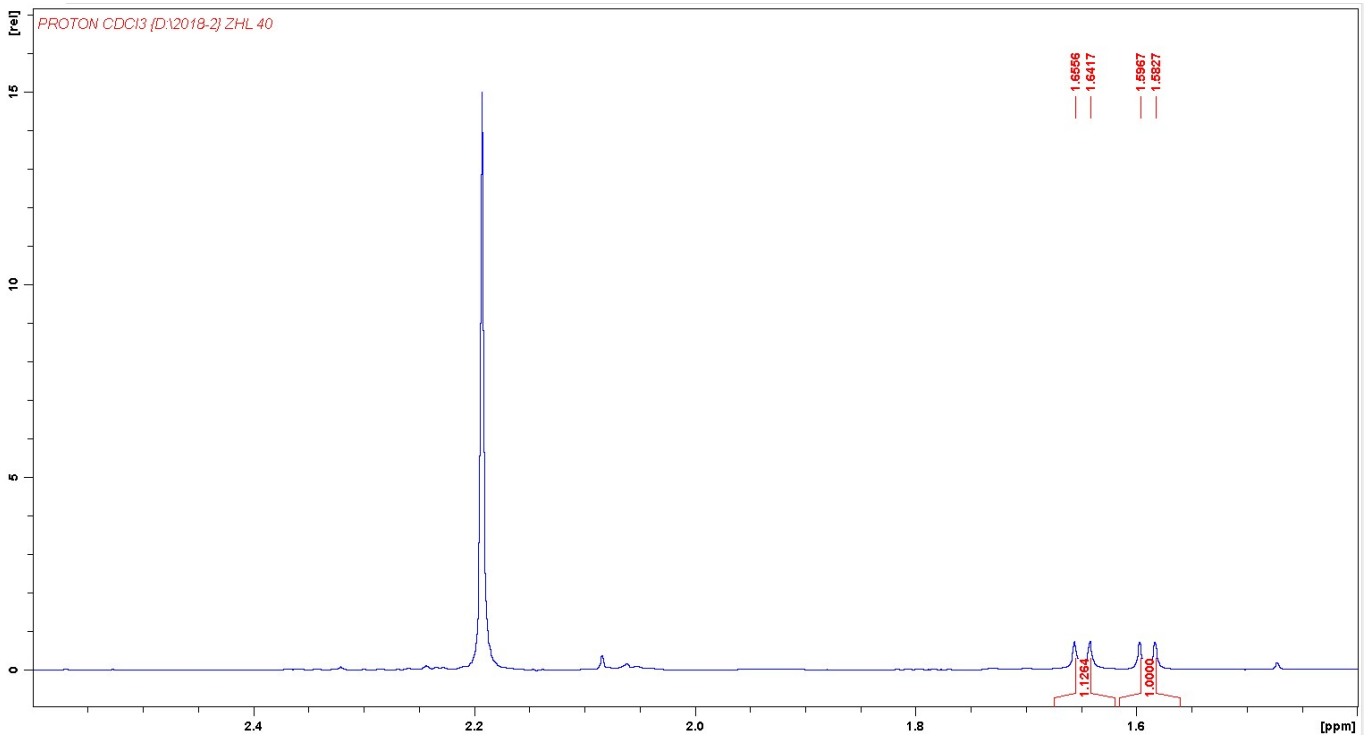
1-(4-phenylbutan-2-yl)pyrrolidine (3w):[9] 95% yield, 3% ee, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (m, 2H, Ar-CH), 7.25 (m, 3H, Ar-CH), 2.78 (m, 1H, CH_2), 2.62 (m, 5H, 2*N-CH_2+CH_2), 2.41 (m, 1H, CH), 1.98 (m, 1H, CH_2), 1.82 (m, 4H, 2*CH_2), 1.74 (m, 1H, CH_2), 1.21 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.1, 128.6, 128.3, 126.2, 59.3, 50.8, 35.2, 32.0, 23.6, 16.4. Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA/TFA/DEA = 92:8:0.2:0.1, 0.5mL/min, 220 nm, 10.26 min, 12.68 min.

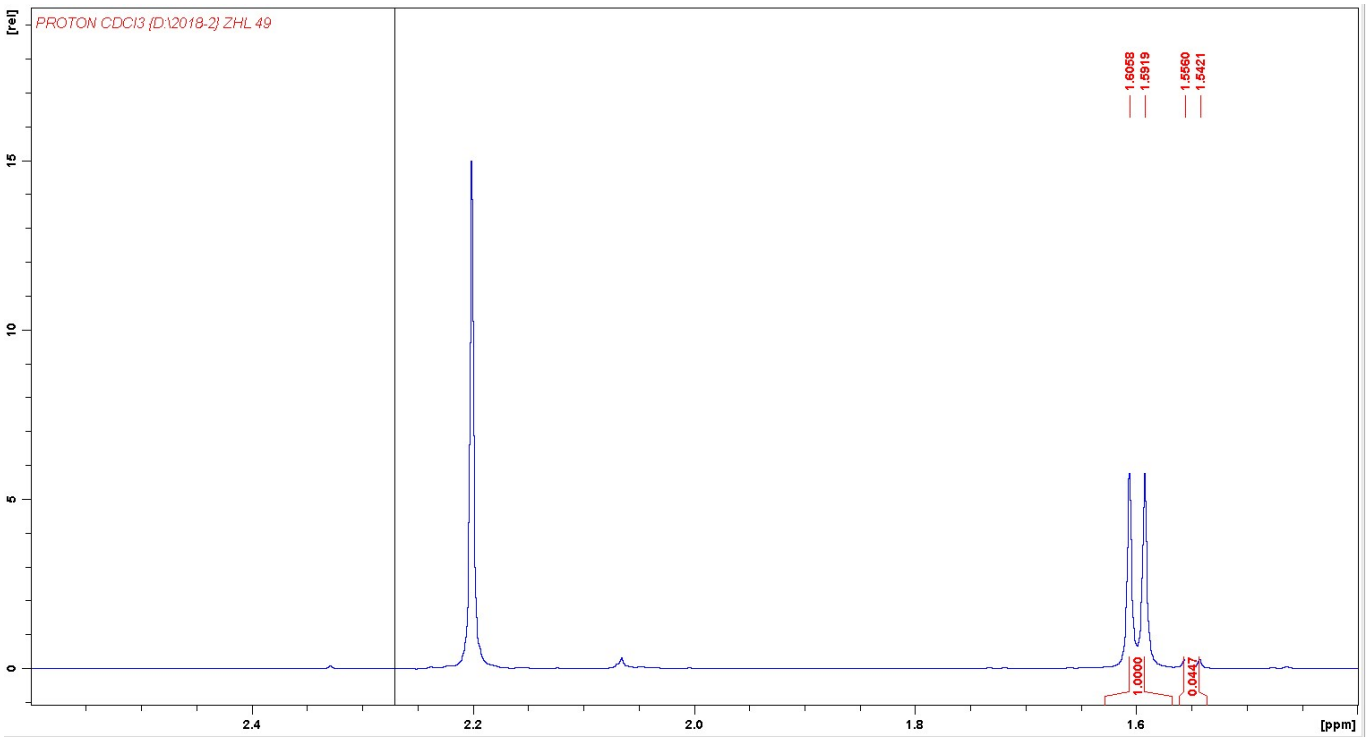




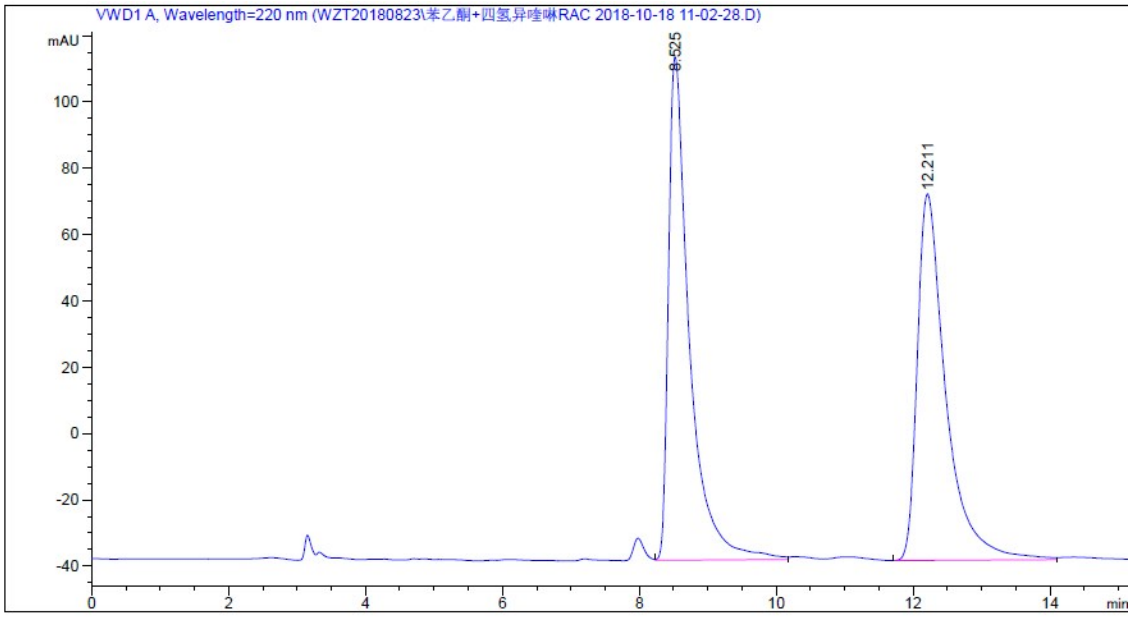
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.248	VV	0.4291	4806.77734	163.45854	48.4685
2	12.676	BV	0.5411	5110.53809	138.94679	51.5315

4-(1-phenylethyl)morpholine (3ab):[2] 89% yield, 92% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34(m, 4H, Ar-CH), 7.28 (m, 1H, Ar-CH), 3.72 (m, 4H, 2*O-CH_2), 3.34 (q, J = 6.7 Hz, 1H, CH), 2.52 (m, 2H, N-CH_2), 2.41 (m, 2H, N-CH_2), 1.40 (d, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 128.3, 127.7, 127.0, 67.3, 65.4, 51.3, 19.9. Enantiomeric excess was determined by ^{1}H NMR using (*R*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

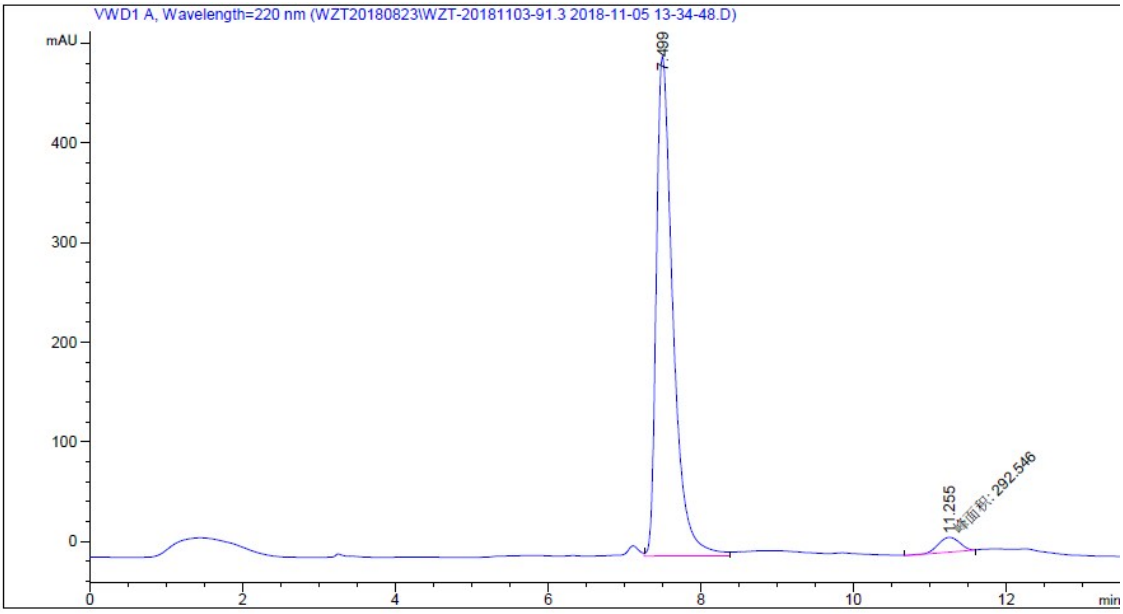




2-(1-phenylethyl)-1,2,3,4-tetrahydroisoquinoline (3ac):[10] 89% yield, 92% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.3 Hz, 2H, Ar-CH), 7.48 (t, *J* = 7.4 Hz, 2H, Ar-CH), 7.40 (m, 1H, Ar-CH), 7.25 (m, 3H, Ar-CH), 7.13 (m, 1H, Ar-CH), 3.98 (d, *J* = 14.8 Hz, 1H, N-CH_2-Ar), 3.72 (m, 2H, CH+N-CH_2-Ar), 2.90-3.10 (m, 3H, CH_2+CH_2), 2.77 (m, 1H, CH_2), 1.62 (d, *J* = 6.7 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 135.4, 134.8, 128.8, 128.5, 127.7, 127.1, 126.9, 126.1, 125.7, 64.6, 53.8, 48.2, 29.5, 20.3. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-H column, Hex/IPA = 95:5, 1 mL/min, 220 nm, 10.52 min, 12.21 min.

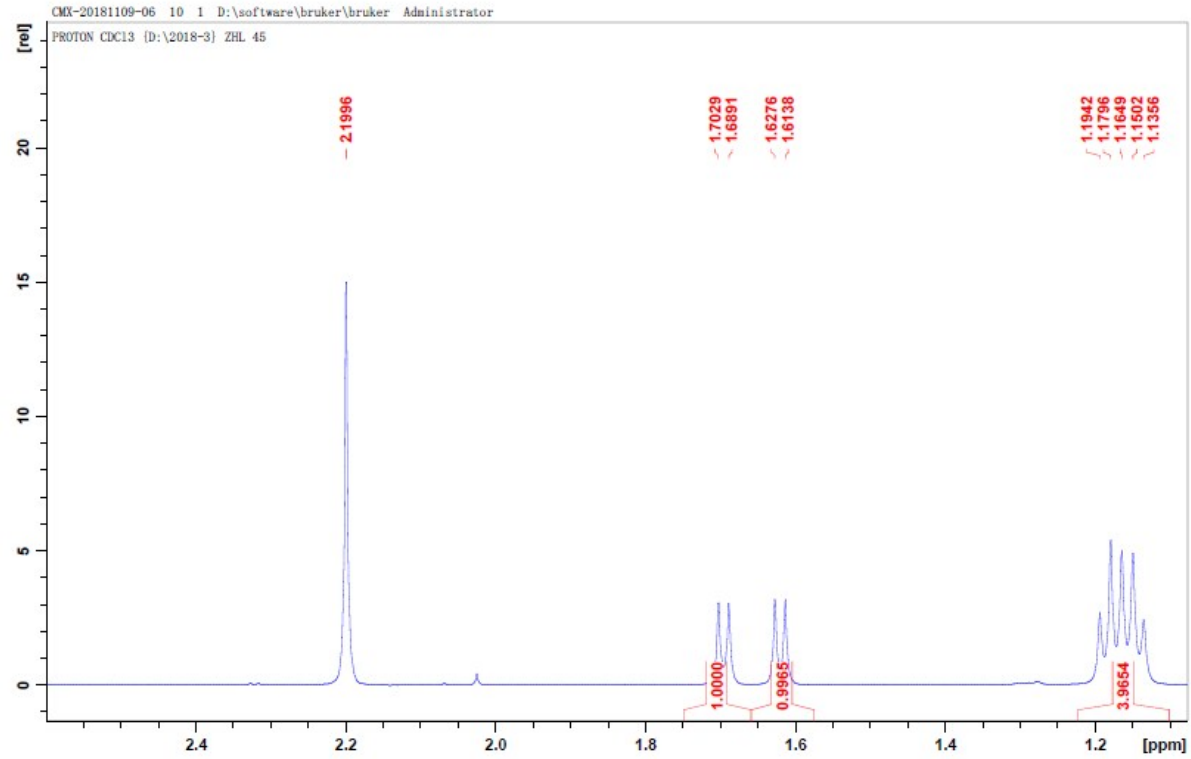


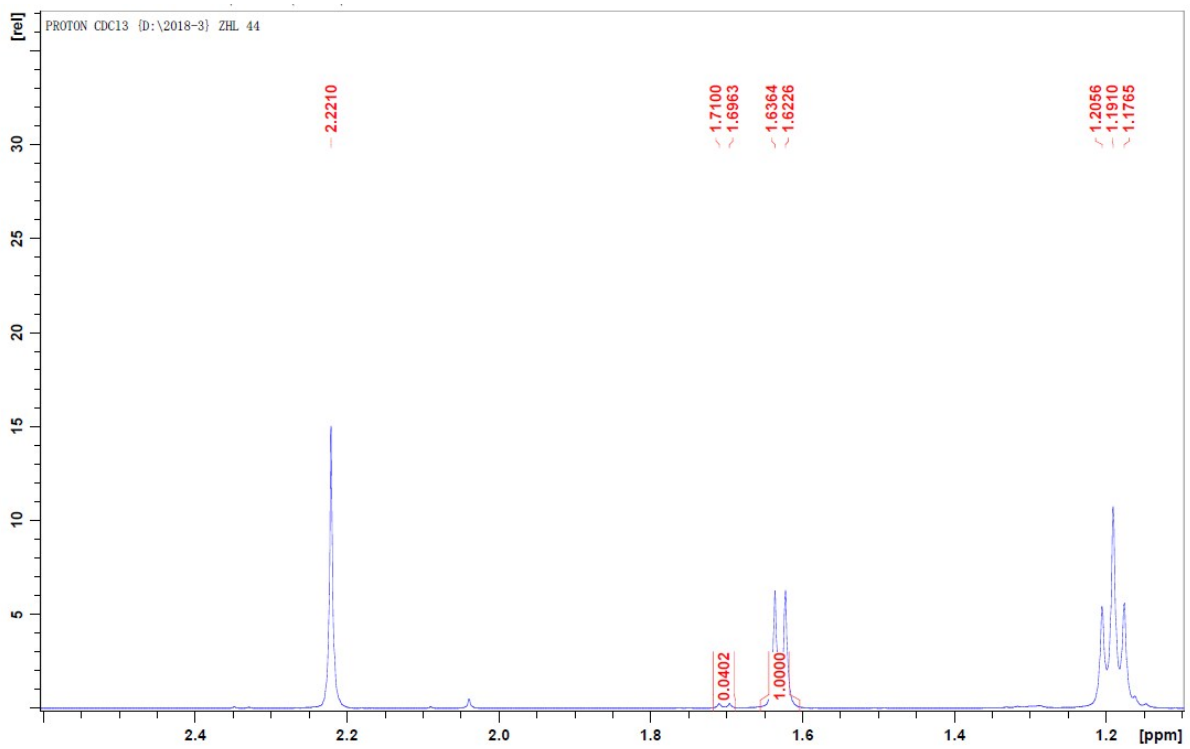
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.525	VV	0.3105	3233.55005	151.79967	50.2380
2	12.211	BV	0.4280	3202.91626	110.54224	49.7620

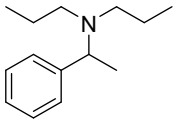


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.499	VV	0.2289	7604.13721	501.39032	96.2953
2	11.255	MM	0.3296	292.54623	14.79080	3.7047

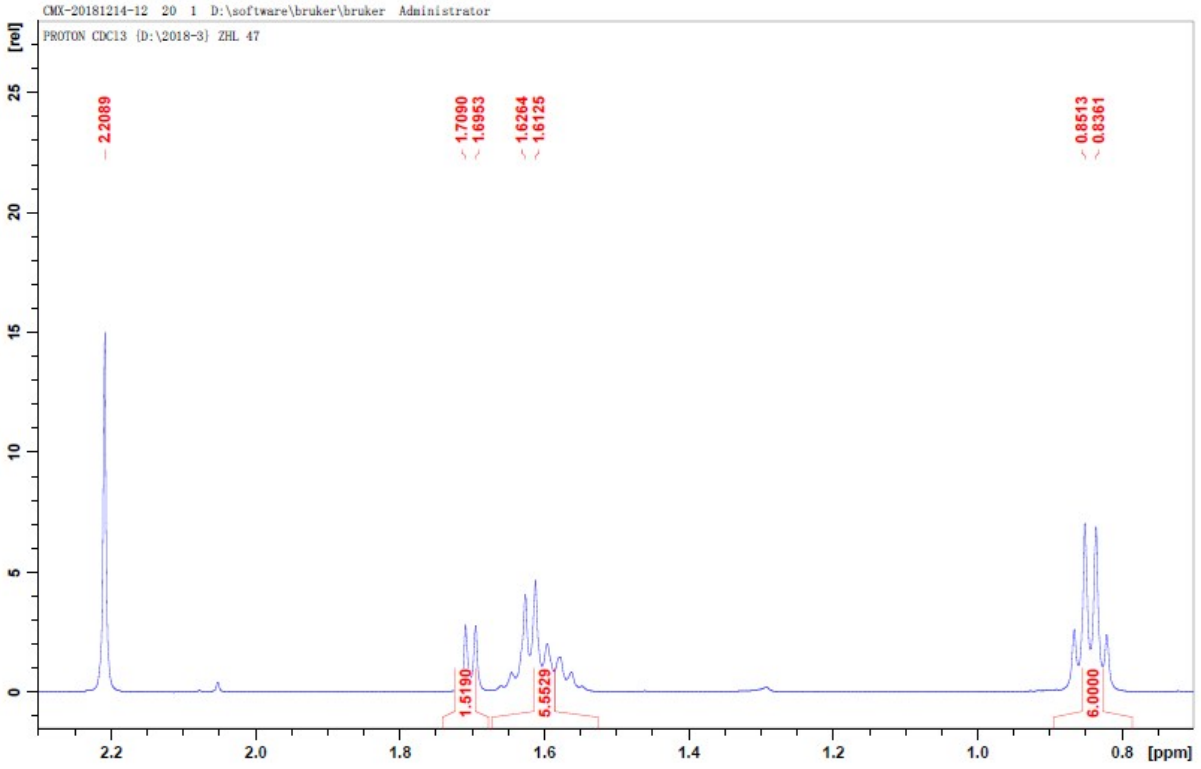
***N,N*-diethyl-1-phenylethan-1-amine (3ad)**:[3] 91% yield, 92% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.4 Hz, 2H, Ar-CH), 7.35 (t, *J* = 7.4 Hz, 2H, Ar-CH), 7.25 (m, 1H, Ar-CH), 3.85 (q, *J* = 6.8 Hz, 1H, CH), 2.50-2.70 (m, 4H, 2*N-CH_2), 1.38 (d, *J* = 6.8 Hz, 3H, CH_3), 1.04 (t, *J* = 7.2 Hz, 6H, 2*CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.3, 128.1, 127.6, 126.5, 59.3, 42.9, 29.7, 18.4, 12.2. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.

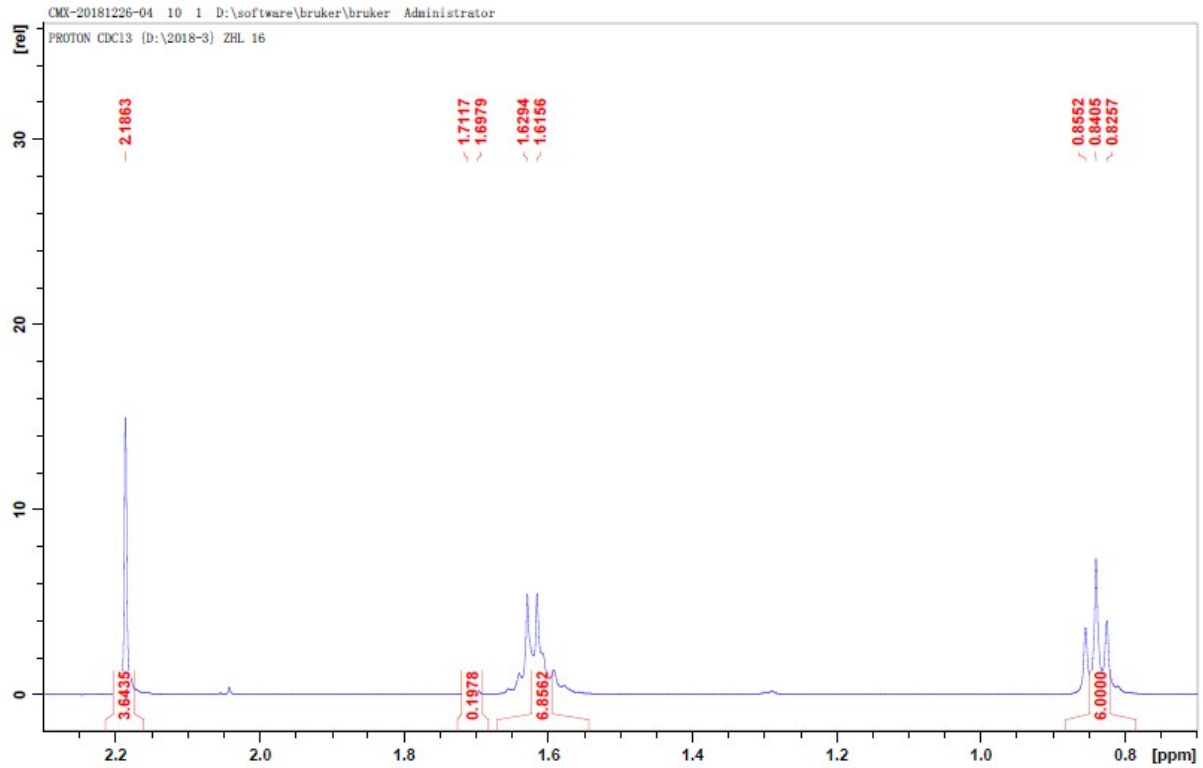




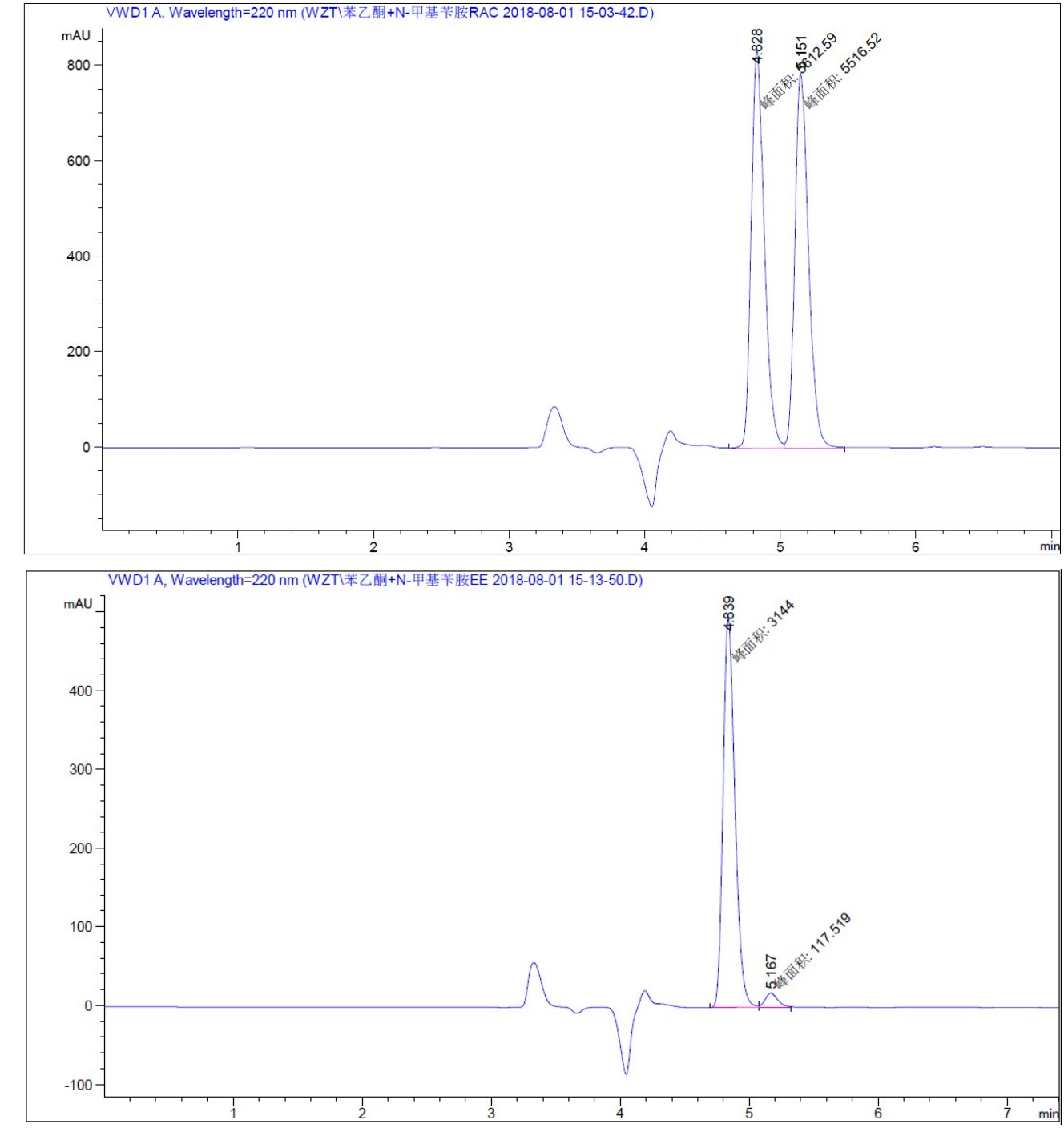


***N,N*-dipropyl-1-phenylethan-1-amine (3ae)**:[11] 89% yield, 87% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.5 Hz, 2H, Ar-CH), 7.34 (t, *J* = 7.4 Hz, 2H, Ar-CH), 7.25 (m, 1H, Ar-CH), 3.87 (q, *J* = 6.7 Hz, 1H, CH), 2.30-2.52 (m, 4H, 2*N-CH_2), 1.48 (m, *J* = 7.4 Hz, 4H, 2*CH_2), 1.36 (d, *J* = 6.8 Hz, 3H, CH_3), 0.86 (t, *J* = 7.2 Hz, 6H, 2*CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.3, 128.2, 127.9, 127.0, 59.9, 51.9, 20.2, 16.8, 11.8. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.



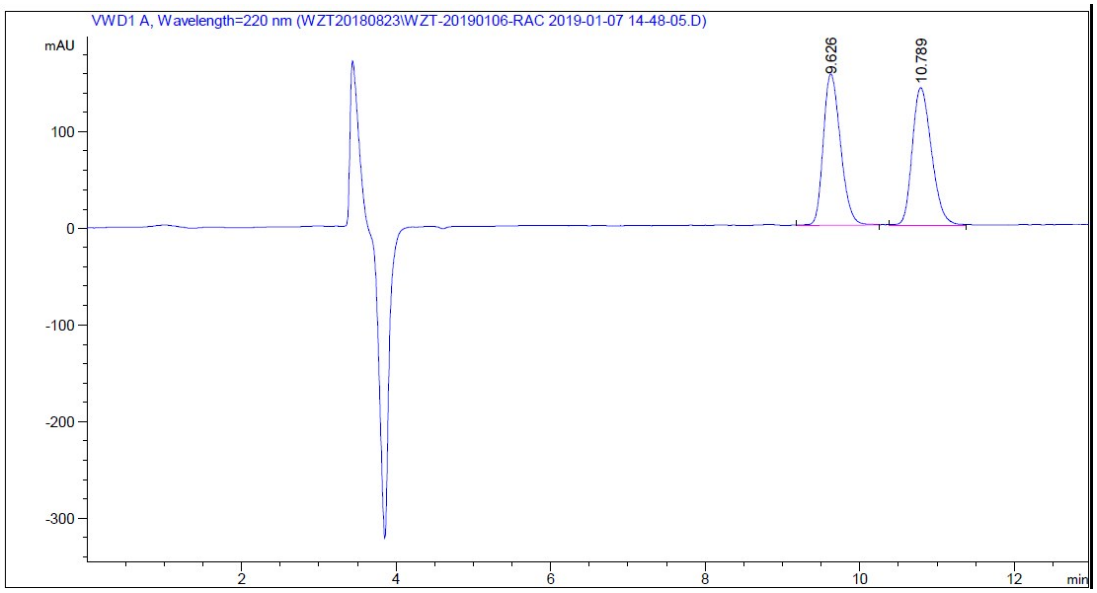


***N*-benzyl-*N*-methyl-1-phenylethan-1-amine (3af)**:[2] 92% yield, 93% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.48 (m, 10H, Ar-CH), 3.68 (m, 1H, CH), 3.63 (m, 1H, CH_2), 3.37 (m, 1H, CH_2), 2.19 (m, 3H, N-CH_3), 1.48 (m, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 140.2, 128.9, 128.3, 128.2, 127.8, 126.9, 126.8, 63.4, 59.0, 38.5, 18.5. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-H column, Hex/IPA/TFA/DEA=90:10:0.2:0.1, 1 mL/min, 220 nm, 4.83 min, 5.15 min.

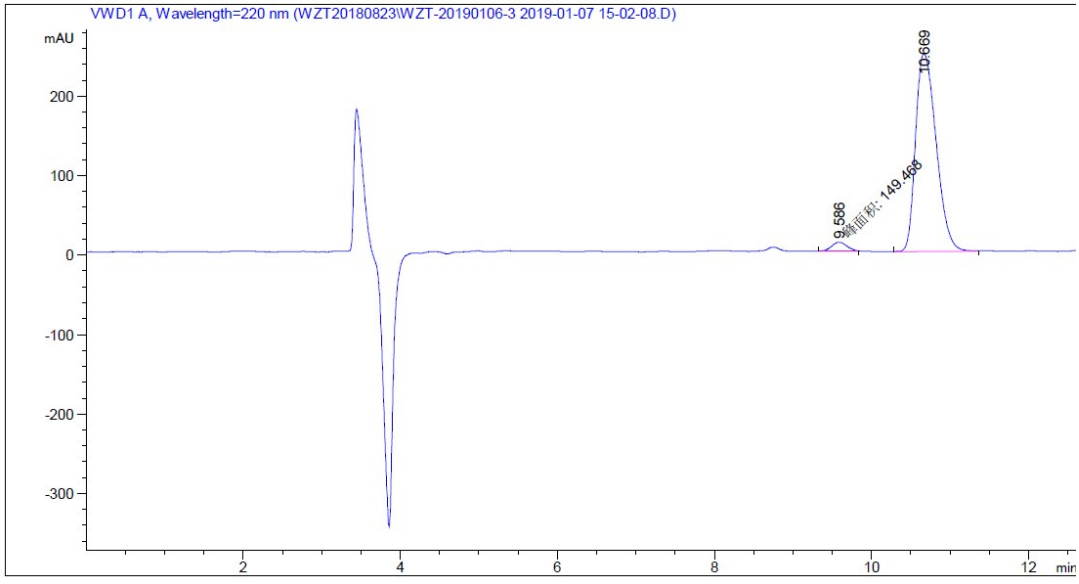


#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.839	MF	0.1060	3143.99683	494.14529	96.3968
2	5.167	FM	0.1092	117.51907	17.94036	3.6032

***N*-(4-methoxybenzyl)-*N*-methyl-1-phenylethan-1-amine (3ag)**:[12] 90% yield, 94% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.46 (d, *J* = 7.3 Hz, 2H, Ar-CH), 7.38 (t, *J* = 7.0 Hz, 2H, Ar-CH), 7.28 (m, 3H, Ar-CH), 6.90 (d, *J* = 7.7 Hz, 2H, Ar-CH), 3.84 (s, 3H, O-CH_3), 3.68 (q, *J* = 6.1 Hz, 1H, CH), 3.56 (d, *J* = 13 Hz, 1H, CH_2), 3.30 (d, *J* = 13 Hz, 1H, CH_2), 2.17 (s, 3H, N-CH_3), 1.46 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 144.3, 132.1, 129.9, 128.2, 127.7, 126.8, 113.6, 63.1, 58.2, 55.3, 38.2, 18.4. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-H column, Hex/IPA/DEA=97:3:0.1, 1 mL/min, 220 nm, 9.63 min, 10.78 min.

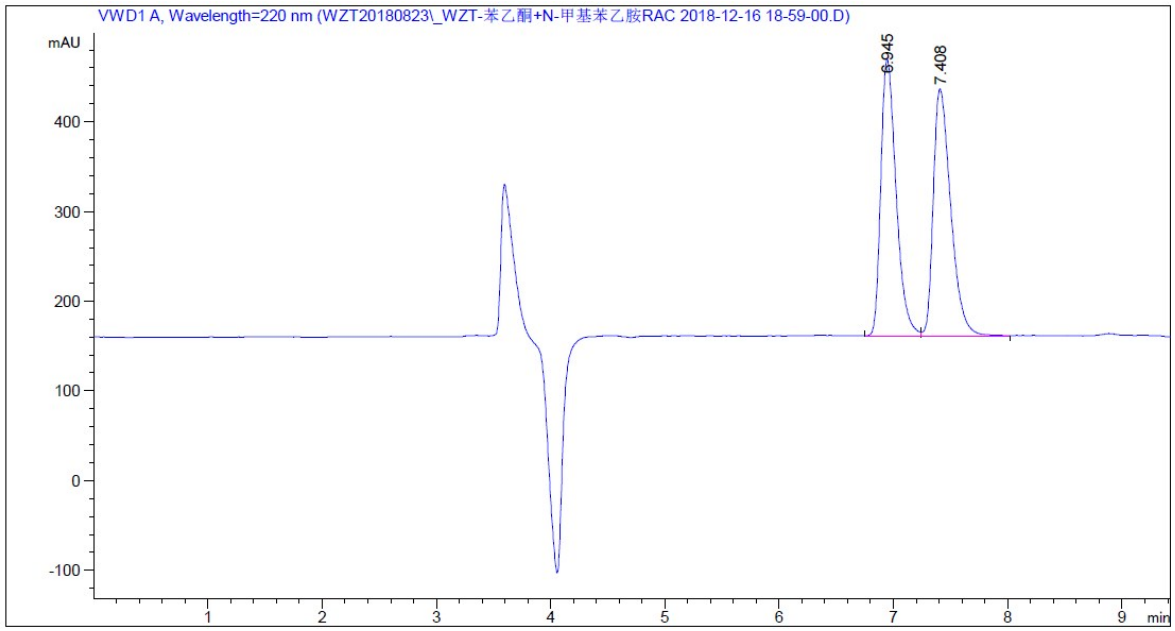


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.626	VV	0.2412	2416.86694	156.50574	49.6375
2	10.789	VV	0.2684	2452.16968	142.04248	50.3625

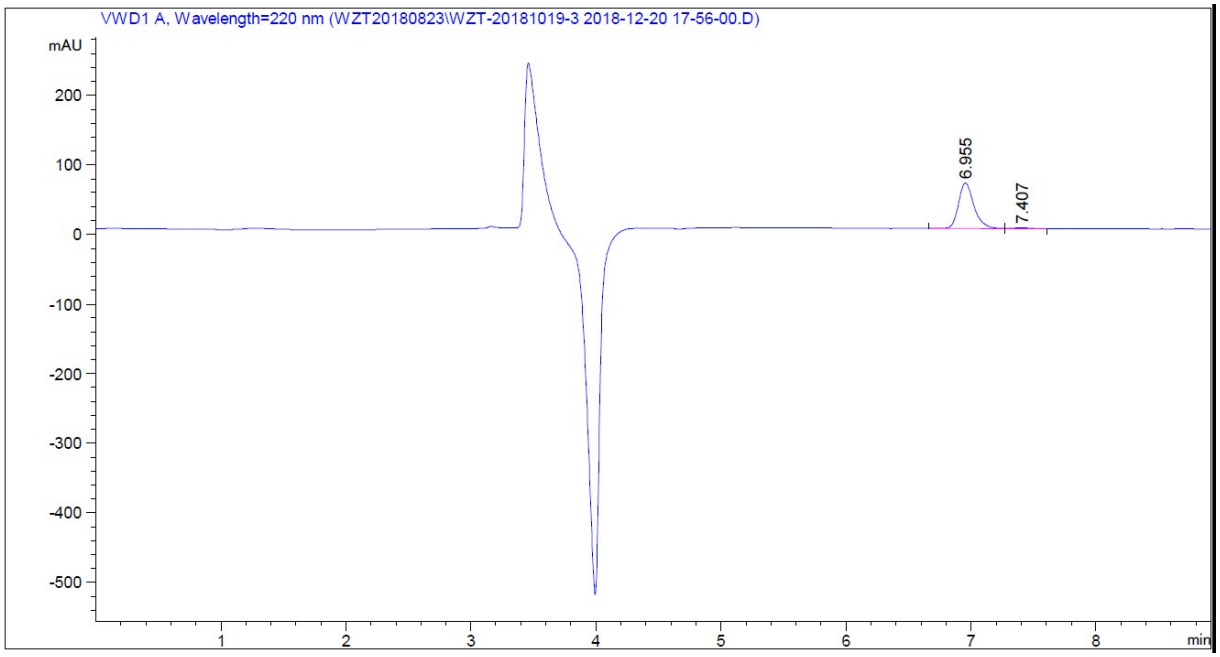


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.586	MM	0.2221	149.46837	11.21587	3.1838
2	10.669	VV	0.2890	4545.12305	249.00073	96.8162

***N*-methyl-*N*-phenethyl-1-phenylethan-1-amine (3ah)**:[13] 96% yield, 96% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-7.40 (m, 10H, Ar-CH), 3.70 (q, J = 6.7 Hz, 1H, CH), 2.60-2.90 (m, 4H, 2*CH_2), 2.37 (s, 3H, N-CH_3), 1.44 (d, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 140.1, 128.8, 128.4, 128.3, 127.9, 127.3, 126.1, 63.6, 56.2, 38.5, 33.3, 18.7. Enantiomeric excess was determined by chiral HPLC: Chiralpak OJ-3 column, Hex/IPA/DEA=97:3:0.1, 1 mL/min, 220 nm, 6.94 min, 7.41 min.

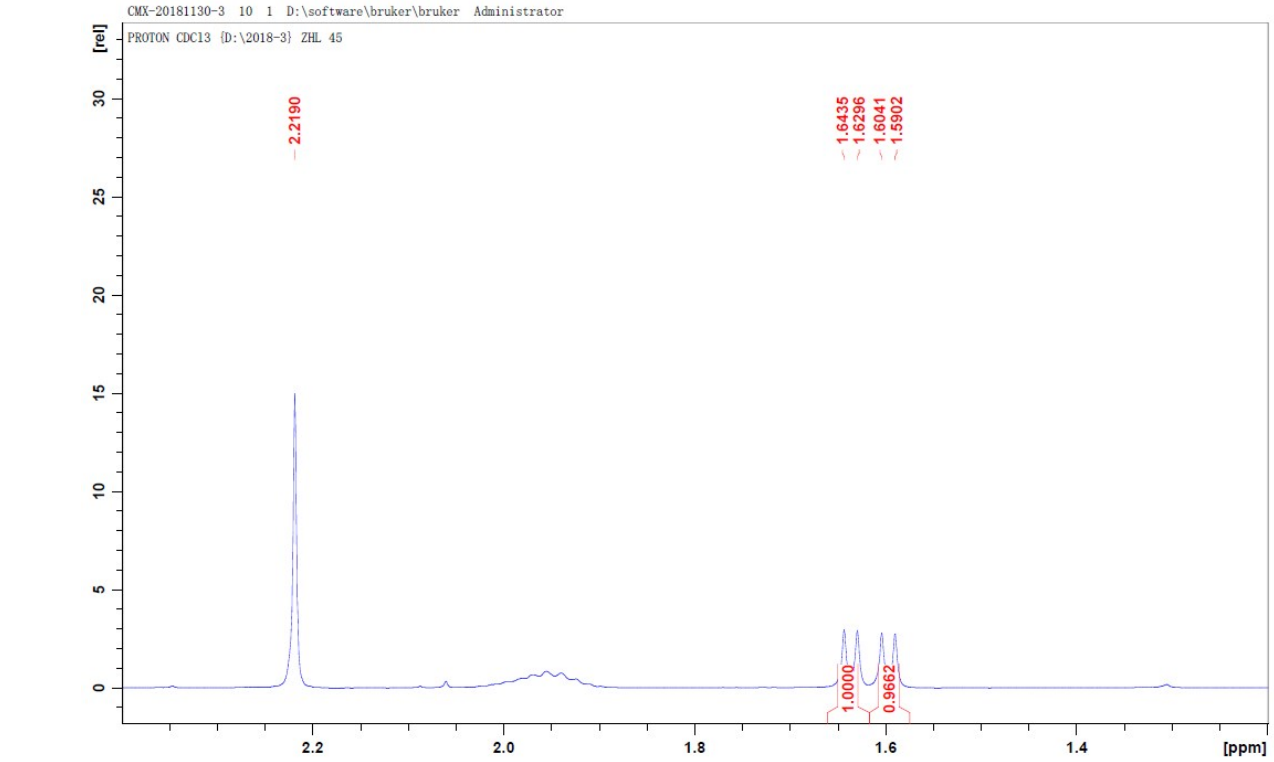


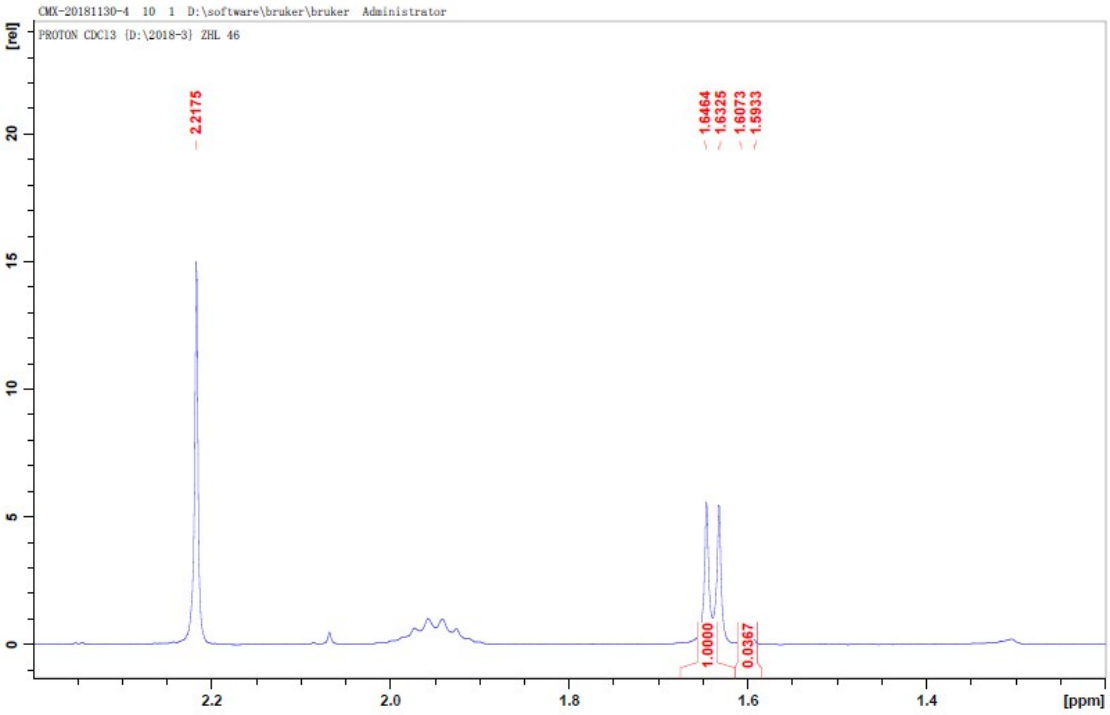
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.945	BV	0.1435	2868.82544	308.38168	49.5930
2	7.408	VB	0.1637	2915.91235	275.07419	50.4070



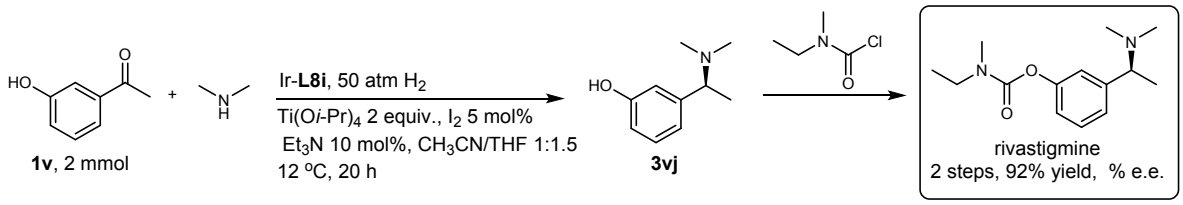
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.955	BV	0.1307	564.60931	65.42831	97.9282
2	7.407	VB	0.1385	11.94481	1.33325	2.0718

***N*-methyl-*N*-phenpropyl-1-phenylethan-1-amine (3ai)**: 96% yield, 93% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-7.40 (m, 10H), 3.62 (q, J = 6.8 Hz, 1H), 2.35-2.73 (m, 4H), 2.24 (s, 3H), 1.84 (m, J = 7.6 Hz, 2H), 1.40 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.12, 142.6, 128.4, 128.3, 128.1, 127.4, 126.7, 125.7, 63.3, 53.9, 38.4, 33.6, 29.0, 18.4. Enantiomeric excess was determined by ^{1}H NMR using (*S*)-2-acetoxy-2-phenylacetic acid as chemical shift reagent.





III Procedure for the Synthesis of rivastigmine



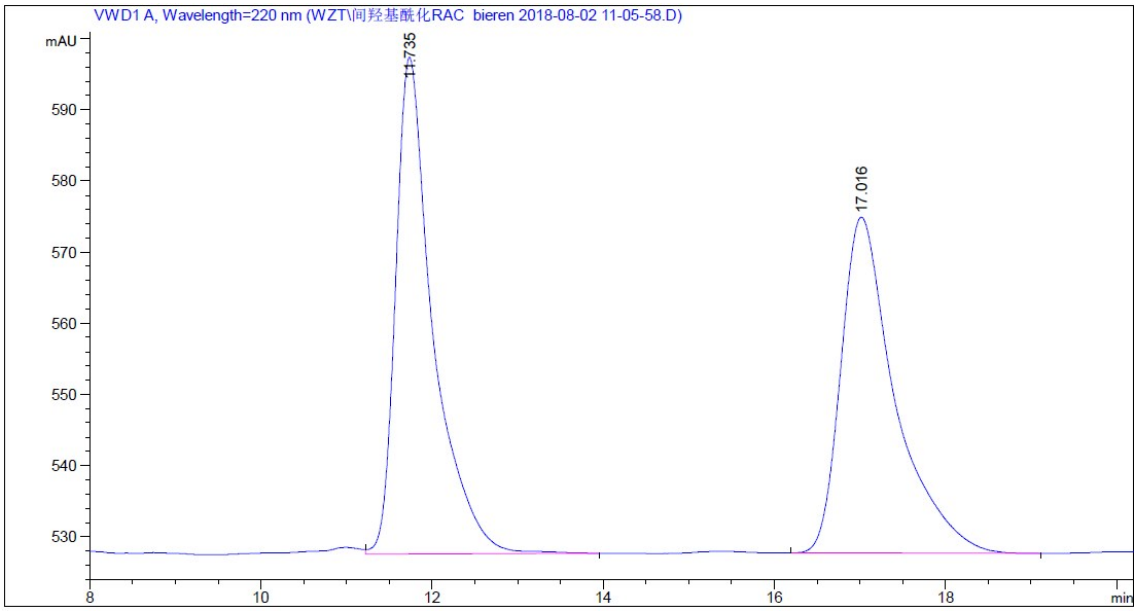
Step 1：

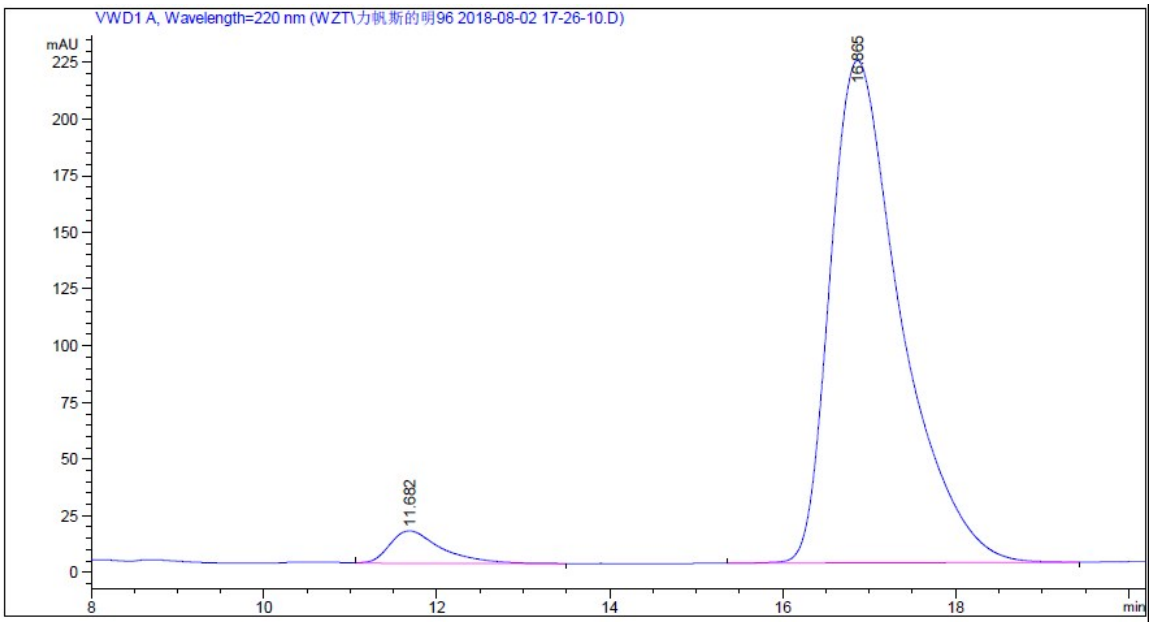
In a nitrogen-filled glovebox, the *in situ* generated complex Ir-**L8i** (20 μmol) was added to the vial charged with ketones (2 mmol) and dimethylamine in THF (2 mol/L, 2 mL, 4 mmol) in anhydrous acetonitrile solution (5.0 mL). $Ti(O^iPr)_4$ (2 equiv.), Et_3N (0.1 eq), and I_2 (5 mol%) were added and the total solution was made to 15 mL at a ratio CH_3CN/THF 1:1.5. The resulting vials were transferred to an autoclave, which was charged with 50 atm of H_2, and stirred at 12 °C for 20 h. The hydrogen gas was released slowly and the solution was quenched 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 crude products **3vj**, which were used in next step without purification.

Step 2:

NaOH (2.5 mmol) was added to the solution of **3vj** in CH_3CN (15 mL). The the above solution was stirred for 1 h at room temperature, then ethyl(methyl)carbamic chloride (2.2 mmol) was added. The reaction mixture was stirred for 12 h, quenched by aq. NH_4Cl solution. CH_3CN was removed under vaccumn and the solution was extracted by EtOAc (15 mL*3). The organic phase was dried over anhydrous Na_2SO_4, concentrated and purified with column chromatograpgy (EtOAc/PE) to give rivastigmine (461 mg, 92% yield for 2 steps).

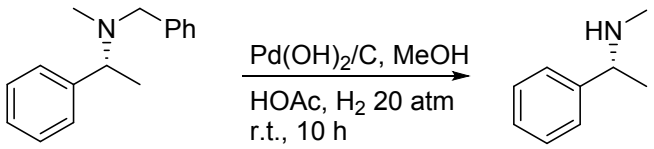
(*S*)-3-[1-(Dimethylamino)ethyl]phenyl Ethyl-(methyl)carbamate (Rivastigmine):[10] 93% yield for 2 steps, 91% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.10 (m, 1H), 7.05 (m, 1H), 3.50 (dq, *J* = 6.7 Hz, 31.2 Hz, 2H), 3.28 (t, *J* = 6.7 Hz, 1H), 3.05 (d, *J* = 37.2 Hz, 1H), 2.24 (s, 6H), 1.39 (d, *J* = 6.7 Hz, 3H), 1.27 (dt, *J* = 7.7 Hz, 26.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6, 151.6, 145.8, 128.9, 124.2, 120.7, 120.3, 65.6, 44.0, 43.2, 34.2, 33.8, 20.1, 13.2, 12.5. HRMS (ESI) m/z calcd for $C_{14}H_{23}N_2O_2^+$ $[M+H]^+$ 251.17540, found 251.17538. Enantiomeric excess was determined by chiral HPLC: Chiralpak OD-H column, Hex/IPA/TFA/DEA = 92:8:0.2:0.1, 1 mL/min, 220 nm, 11.74 min, 17.02 min.





#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.682	VB	0.6138	598.98987	14.35594	4.5502
2	16.865	VB	0.8506	1.25651e4	221.56683	95.4498

IV Debenzylation of 3ae

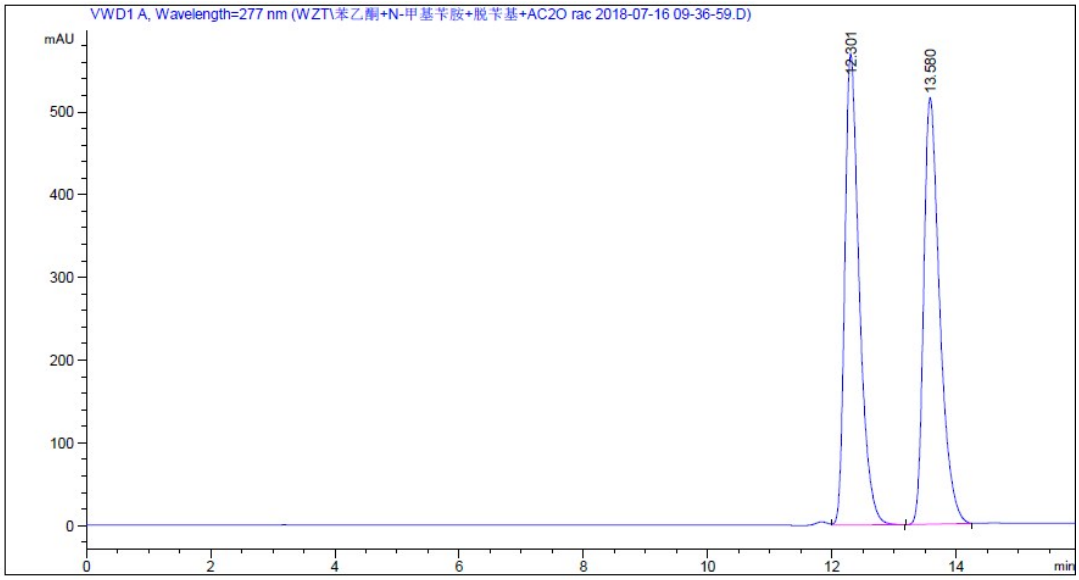


3af **4**

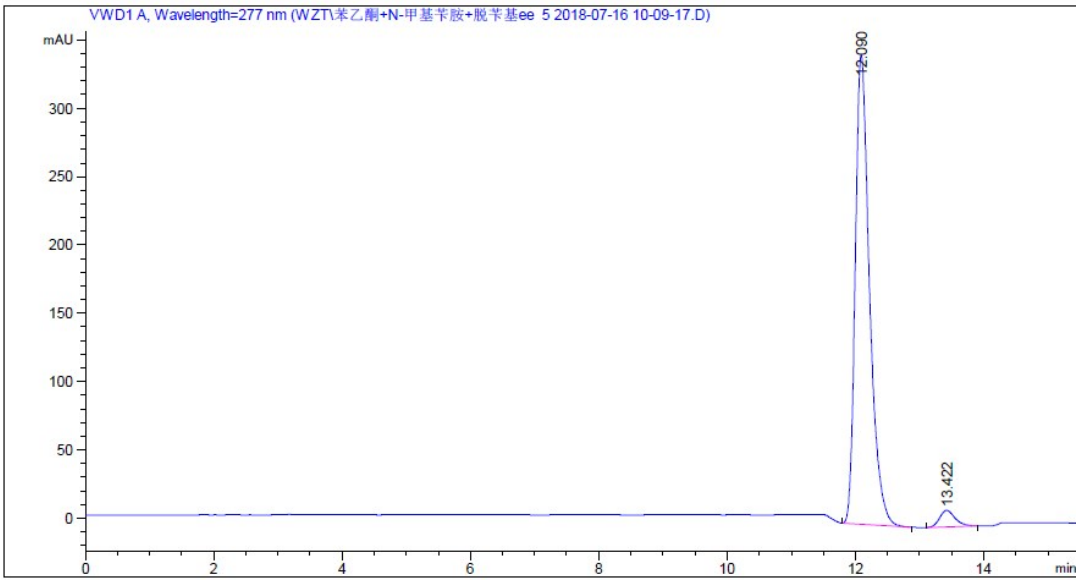
$Pd(OH)_2$ on carbon (10%, 4.5 mg) was added to the solution of (*R*)-**3af** (45 mg, 0.2 mmol) and acetic acid (1 drop) in MeOH (2 mL). The resulting mixture was transferred to an autoclave, which was charged with 20 atm of H_2, and stirred at r.t. for 10 h. The hydrogen gas was released slowly and the solution was filter and quenched 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 crude product, which was purified with column chromotography to afford **4** (26 mg, 95% yield).

***(R)-N*-methyl-1-phenylethan-1-amine (4)**:[11] 26 mg, 95% yield, 93% *ee*, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.36 (m, 4H, Ar-CH), 7.23 (m, 1H, Ar-CH), 3.67 (q, J = 6.6 Hz, 1H, CH), 2.34 (s, 3H, N-CH_3), 1.86 (bs, 1H, NH), 1.39 (d, J =

6.7 Hz, 3H, CH_3). Enantiomeric excess was determined for the corresponding acetamide by chiral HPLC: Chiralpak AD-H column, Hex/IPA=97:3, 1 mL/min, 220 nm, 12.3 min (major), 13.6 min (minor).



#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.301	VB	0.2451	9230.26953	569.60980	49.9640
2	13.580	BB	0.2712	9243.55957	515.57379	50.0360



#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.090	BB	0.2338	5299.50635	343.80060	96.3059
2	13.422	BB	0.2532	203.27594	12.14922	3.6941

V Mechanistic study

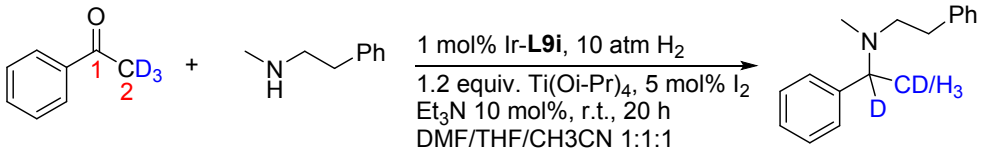
1. ^{31}P spectra.

^{31}P NMR for **L9i** (202 MHz, $CDCl_3$): δ 147.5;

^{31}P NMR for Ir:**L9i** 1:1 (202 MHz, $CDCl_3$): δ 113.2;

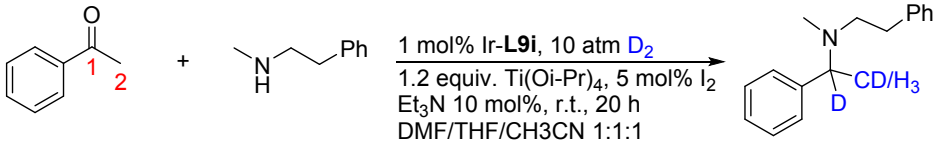
^{31}P NMR for Ir:**L9i** 1:2 (202 MHz, $CDCl_3$): δ 147.5, 113.2;

2. Deuterium incorporation study for the DARA of 1a with 2h.



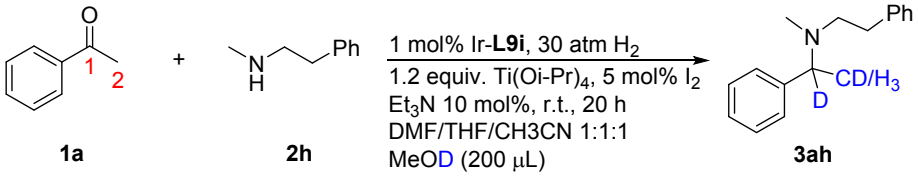
d_3-**1a** **2h** **3ah**

***N*-methyl-*N*-phenethyl-1-phenylethan-1-amine-*d* (3ah)**:[13] 82% yield, 94% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-7.40 (m, 10H), 3.70 (q, J = 6.7 Hz, 0.93H), 2.60-2.90 (m, 4H), 2.37 (s, 3H), 1.44 (m, J = 6.8 Hz, 1.76H).



1a **2h** **3ah**

***N*-methyl-*N*-phenethyl-1-phenylethan-1-amine-*d* (3ah)**:[13] 82% yield, 94% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-7.40 (m, 10H), 3.70 (q, J = 6.7 Hz, 0.28H), 2.60-2.90 (m, 4H), 2.37 (s, 3H), 1.44 (m, J = 6.8 Hz, 1.16H).



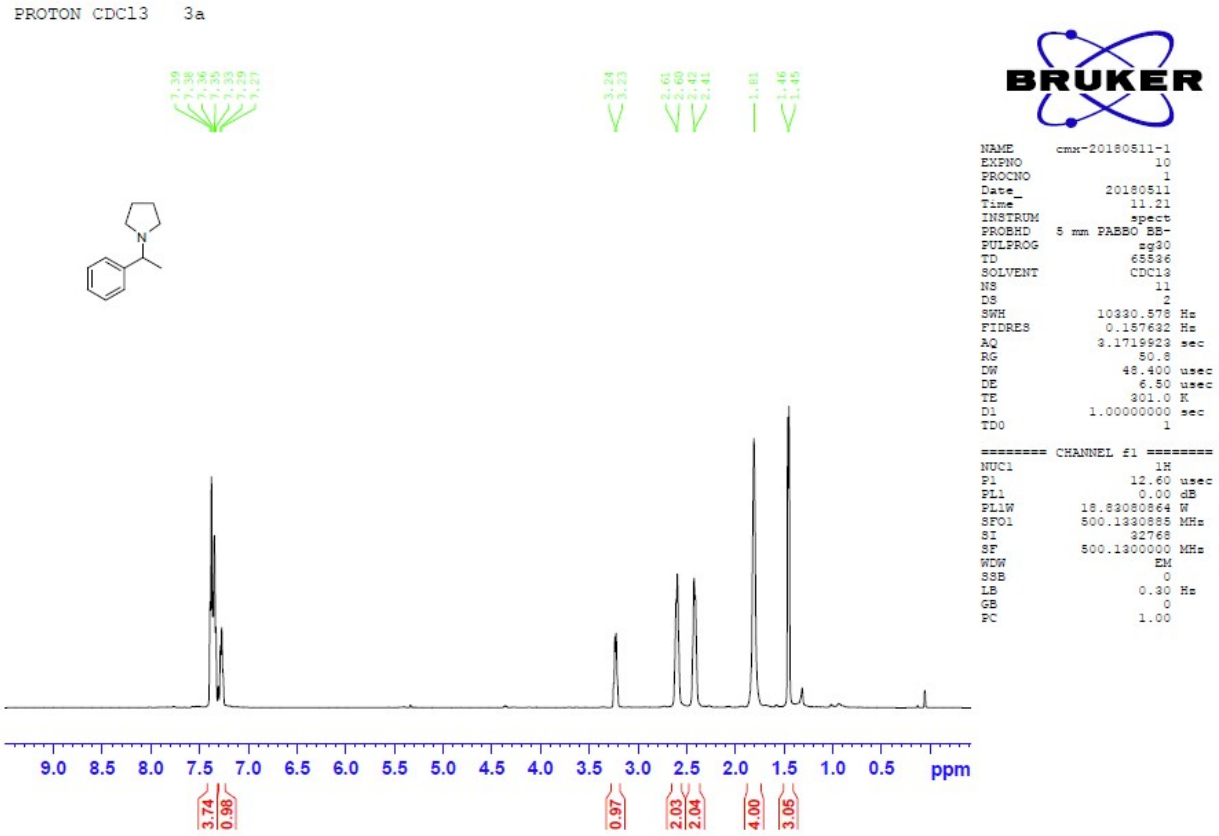
1a **2h** **3ah**

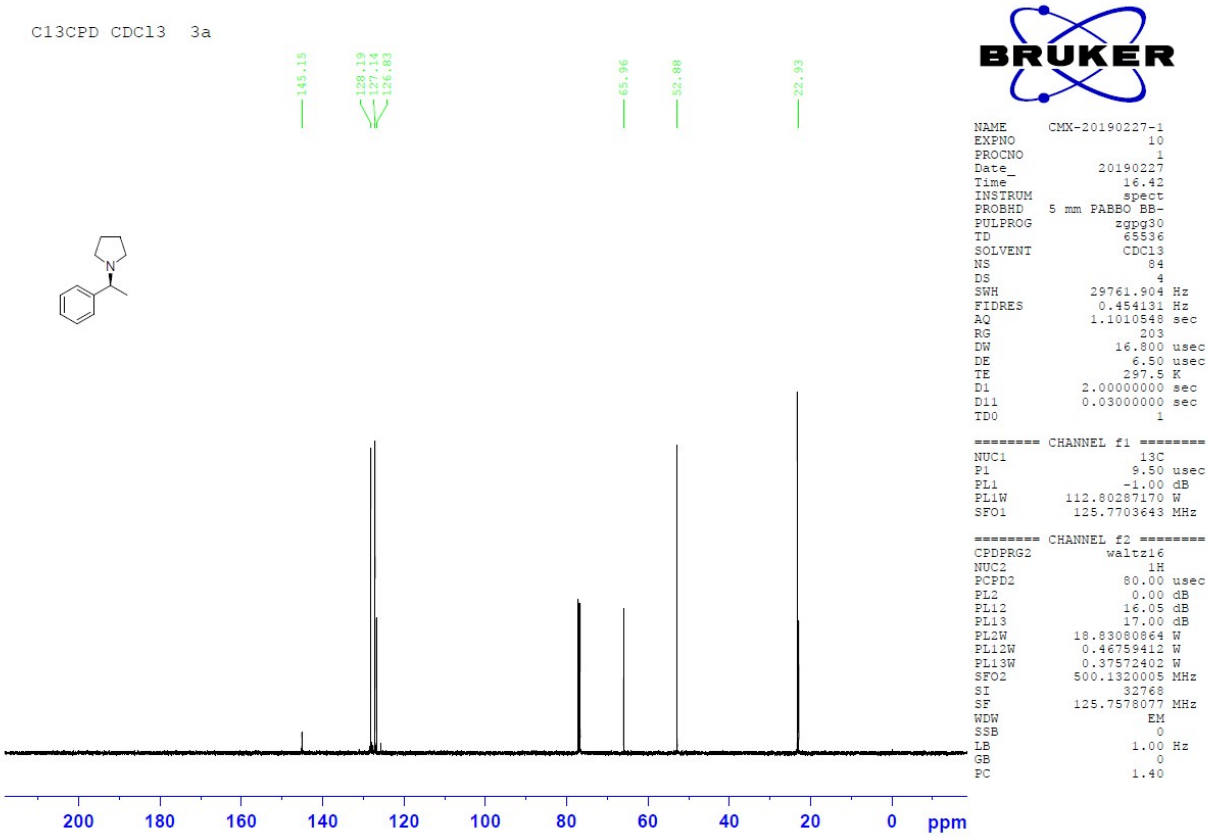
***N*-methyl-*N*-phenethyl-1-phenylethan-1-amine-*d* (3ah)**:[13] 67% yield, 93% *ee*, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-7.40 (m, 10H), 3.70 (q, J = 6.7 Hz, 0.81H), 2.60-2.90 (m, 4H), 2.37 (s, 3H), 1.44 (m, J = 6.8 Hz, 0.66 H).

VI References:

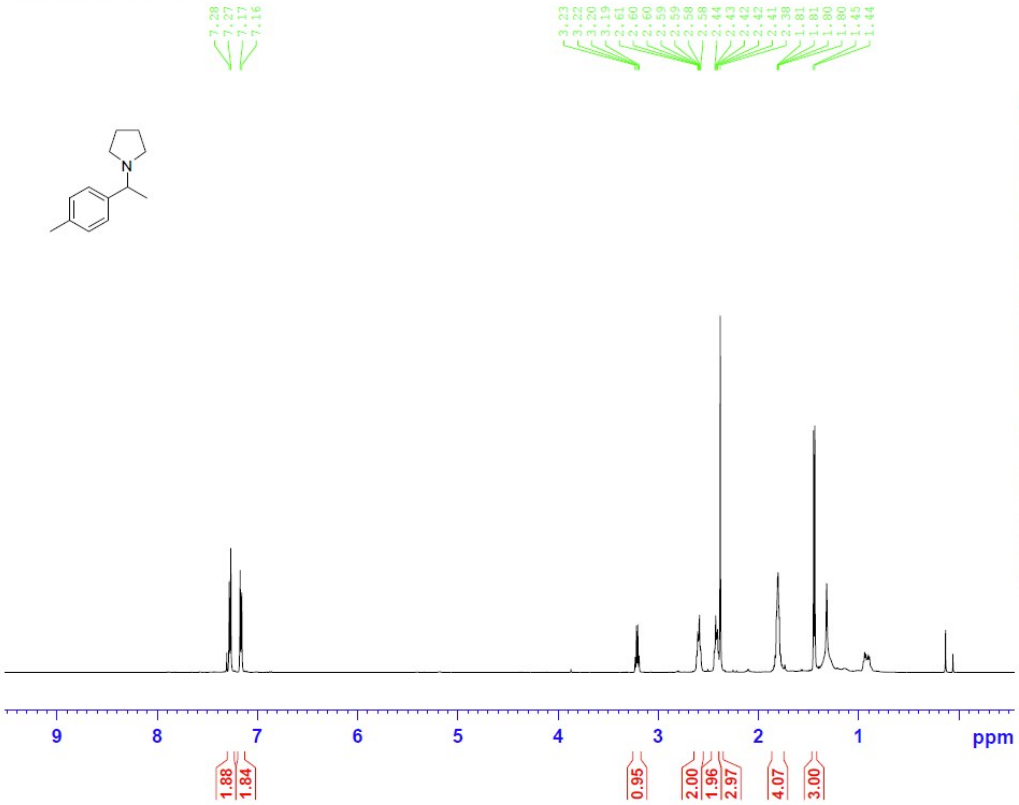
1. a) L. Lefort, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, *Org. Lett.* **2004**, *6*, 1733. b) C. R. Smith, D. J. Mans and T. V. RajanBabu, *Org. Synth.* **2008**, *85*, 238-247. c) B. Wang, X. Feng, Y. Huang, H. Liu, X. Cui, Y. Jiang, *J. Org. Chem*. **2002**, 67, 2175. d) C. R. Graves, H. Zhou, C. L. Stern, S. T. Nguyen, *J. Org. Chem*. **2007**, *72*, 9121. e) W. Zhao, T. Wang, R. Zhao, H. Xie, L. Liu, *Tetrahedron: Asymmetry*, **2016**, *27*, 157.
2. N. E. Lee, S. L. Buchwald, *J. Am. Chem. Soc*. **1994**, *116*, 5985.
3. P. Yan, J. Xie, Q. Zhou, *Chin. J. Chem.* **2010**, *28*, 1736.
4. H. Kleijn, E. Rijnberg, J. T. B. H. Jastrzebski, G. van Koten*, Org. Lett*. **1999**, *1*, 853.
5. S. E. Varjosaari, V. Skrypai, P. Suating, J. J. M. Hurley, A. M. De Lio, T. M. Gilbert, M. J. Adler, *Adv. Synth. Catal*. **2017**, *359*, 1872.
6. A. Tarasewicz, D. Ensan, R. A. Batey, *Chem. Eur. J.* **2018**, 24, 6071.
7. M. Lindqvist, K. Borre, K. Axenov, B. Kótai, M. Nieger, M. Leskelä, I. Pápai, T. Repo, *J. Am. Chem. Soc*. **2015**, *137*, 4038−4041.
8. R. V. Heinzelman, B. D. Aspergeen, *J. Am. Chem. Soc*. **1953**, *75*, 3409.
9. H. Guan, M. Iimura, M. P. Magee, J. R. Norton, G. Zhu, *J. Am. Chem. Soc*. **2005**, *127*, 7805−7814.
10. L. Benmekhbi, F. Louafi, T. Roisnel, J.-P. Hurvois, *J. Org. Chem*. **201**6, *81*, 6721−6739.
11. R. J. W. Schuurman, A. d. Linden, R. P. F. Grimbergen, R. J. M. Nolte, H. W. Scheeren, *Tetrahedron*, **1996**, *52*, 8307−8314.
12. R. Baltzly, P. B. Russell, *J. Am. Chem. Soc*. **1953,** *75*, 5598.
13. P. Blaney, R. Grigg, Z. Rankovic, M. Thoroughgood, *Tetrahedron Lett*, **2000**, *41*, 6639−6642.
14. P.-C. Yan, G.-L. Zhu, J.-H. Xie, X.-D. Zhang, Q.-L. Zhou, Y.-Q. Li, W.-H. Shen, D.-Q. Che, *Org. Process Res. Dev*. **2013**, *17*, 307.
15. V. N. Wakchaure, P. S. J. Kaib, M. Leutzsch, B. List, *Angew. Chem. Int. Ed*. **2015**, *54*, 11852.

VII NMR & HRMS Spectra



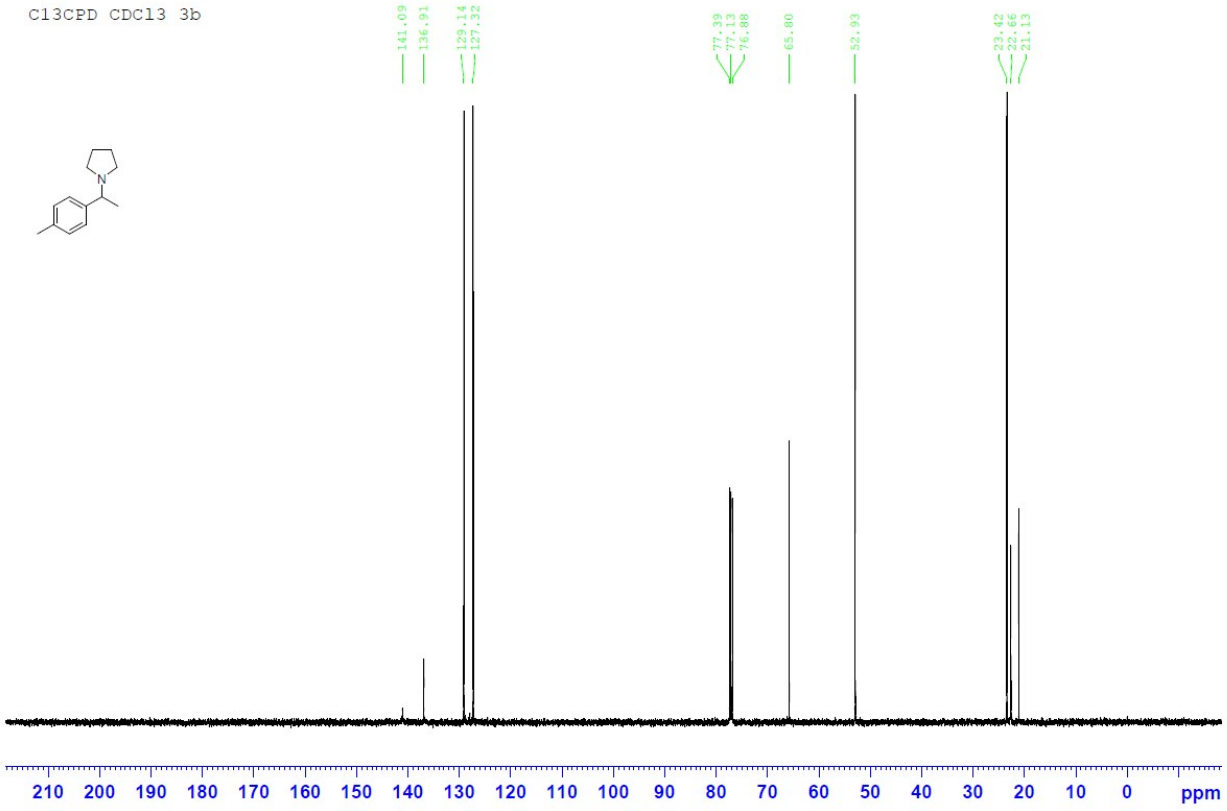


PROTON CDCl3 3b

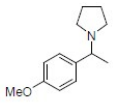


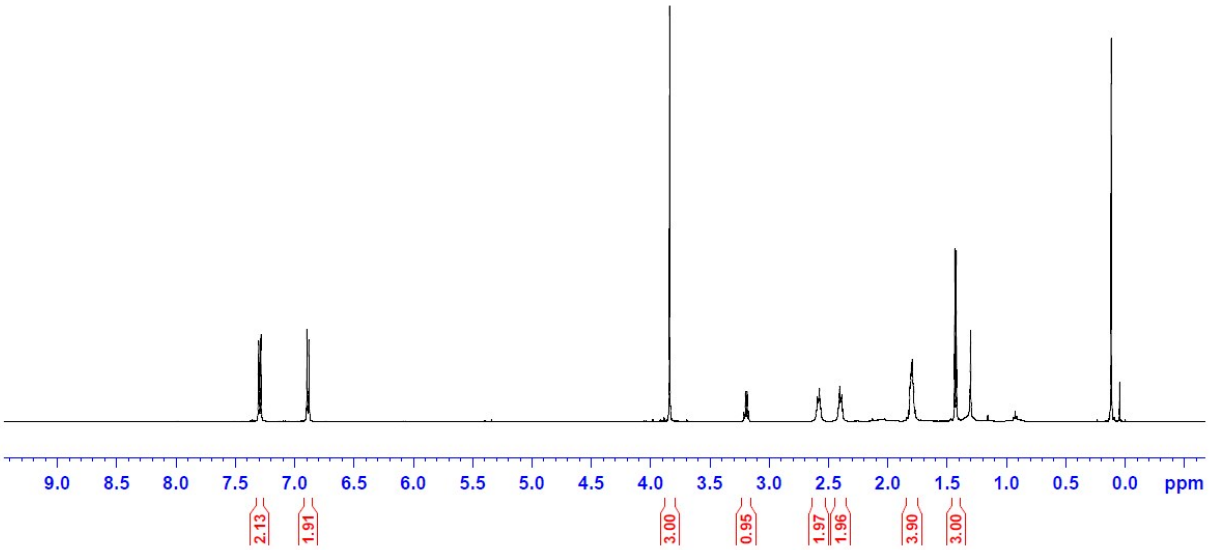

```
NAME        CMX-20170919-8
EXPNO               10
PROCNO               1
Date_         20170919
Time_            11.41
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                40.3
DW              48.400 usec
DE               6.50 usec
TE              303.4 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1              12.60 usec
PL1              0.00 dB
PL1W       18.83080864 W
SFO1       500.1330885 MHz
SI               32768
SF         500.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

C13CPD CDCl3 3b

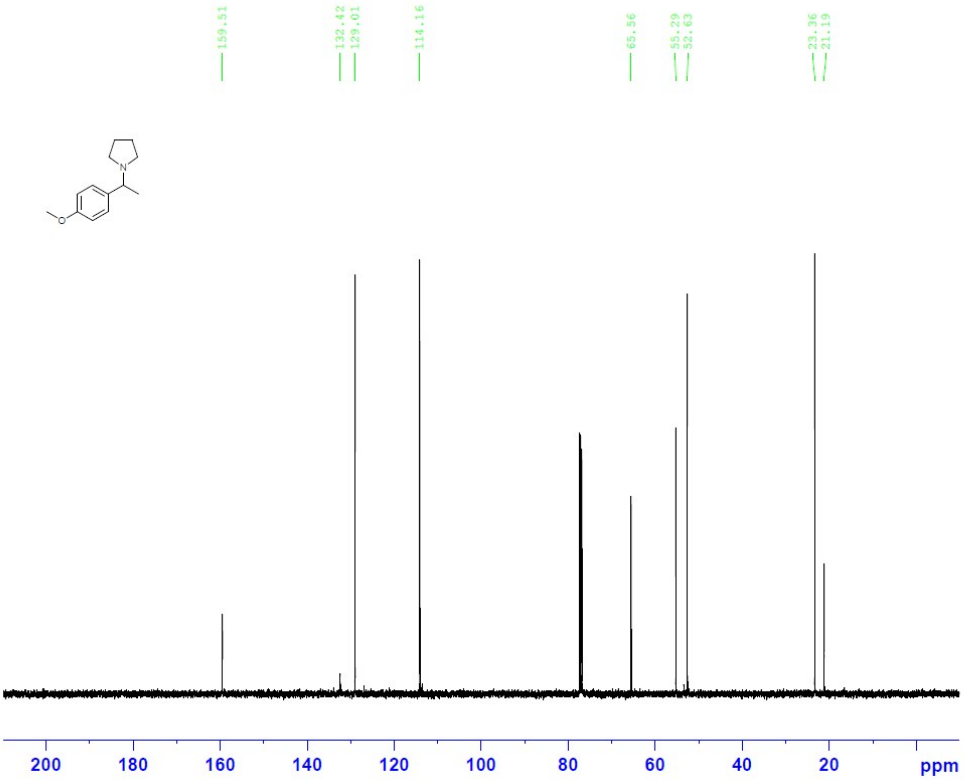


PROTON CDCl3 3c





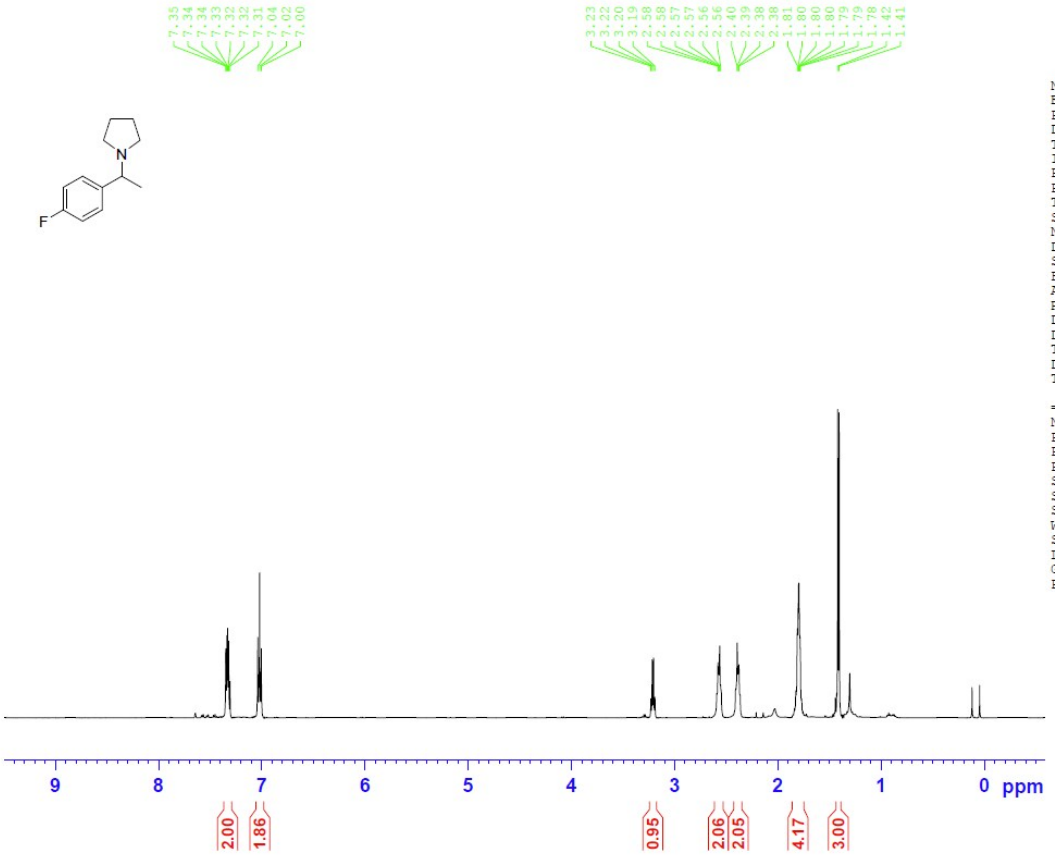
C13CPD CDCl3 3c



BRUKER

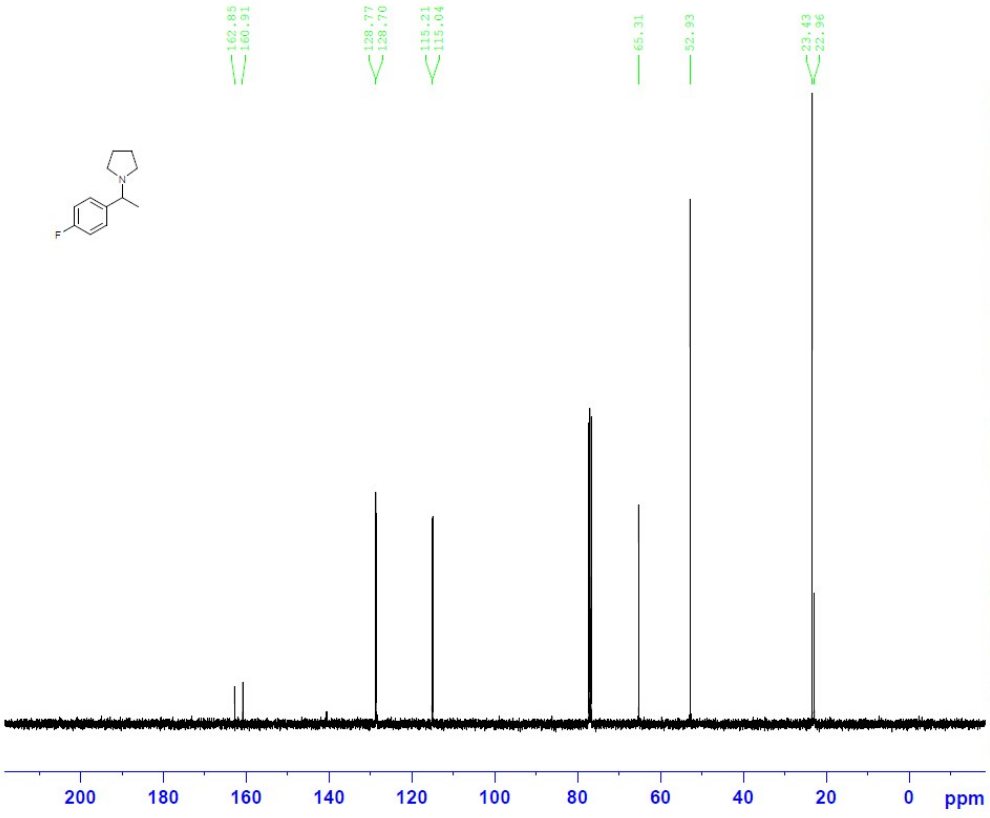
```
NAME          CMX-20190225-3
EXPNO                     11
PROCNO                     1
Date_               20190225
Time                   11.49
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                CDCl3
NS                         64
DS                          4
SWH                29761.904 Hz
FIDRES                 0.454131 Hz
AQ                     1.1010548 sec
RG                        203
DW                      16.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -1.00 dB
PL1W             112.80287170 W
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W              18.83080864 W
PL12W              0.46759412 W
PL13W              0.37572402 W
SFO2              500.1320005 MHz
SI                      32768
SF                125.7577890 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

PROTON CDCl3 3d



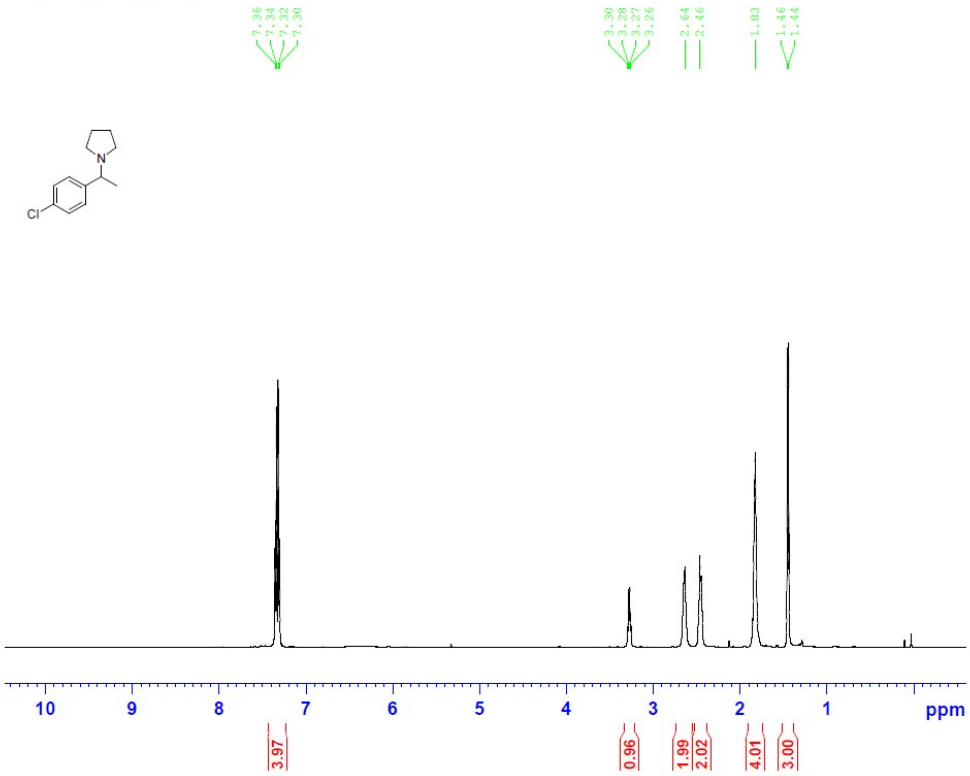

```
NAME      CMX-20170919-9
EXPNO                 10
PROCNO                 1
Date_           20170919
Time               11.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                  71.8
DW                48.400 usec
DE                 6.50 usec
TE                303.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.60 usec
PL1                0.00 dB
PL1W         18.83080864 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

C13CPD CDCl3 3d



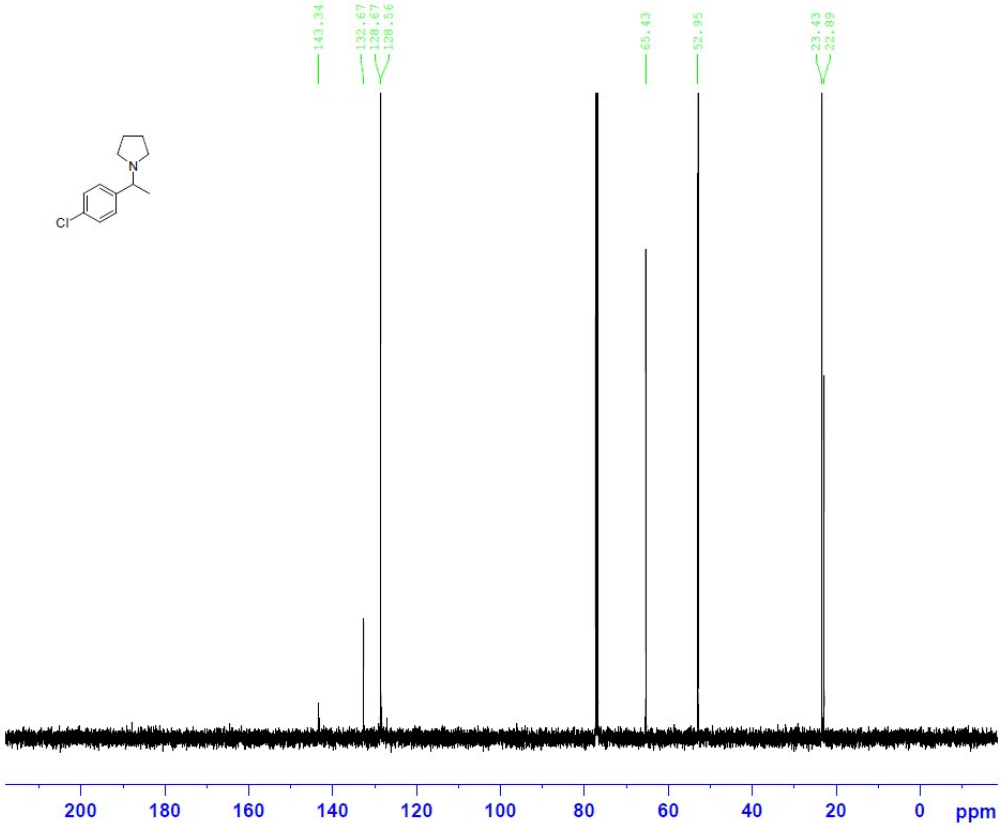

```
NAME      CMX-20190225-4
EXPNO                 11
PROCNO                 1
Date_           20190225
Time               16.38
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   203
DW                16.800 usec
DE                 6.50 usec
TE                300.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -1.00 dB
PL1W        112.80287170 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                0.00 dB
PL12              16.05 dB
PL13              17.00 dB
PL2W         18.83080864 W
PL12W         0.46759412 W
PL13W         0.37572402 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

PROTON CDCl3 3e



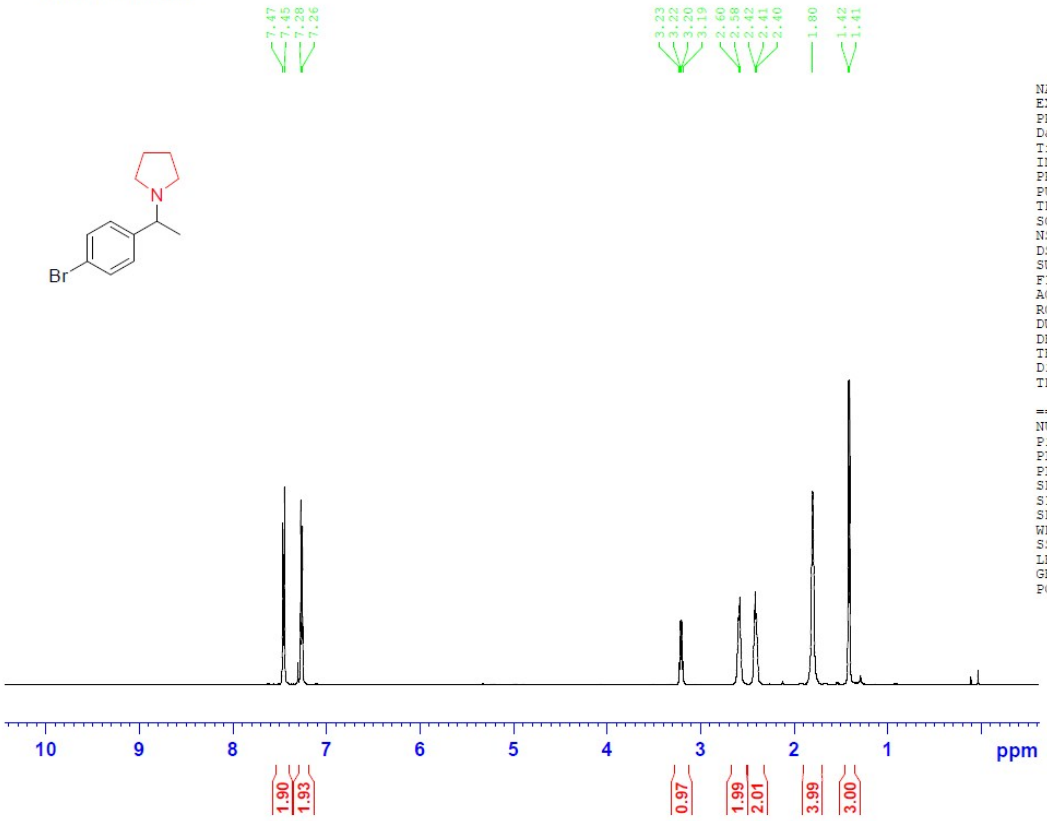

```
NAME      CMX-20190227-14
EXPNO                 10
PROCNO                 1
Date_           20190228
Time_               9.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                  45.2
DW                48.400 usec
DE                 6.50 usec
TE                296.9 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.60 usec
PL1                 0.00 dB
PL1W         18.83080864 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

C13CPD CDCl3 3e



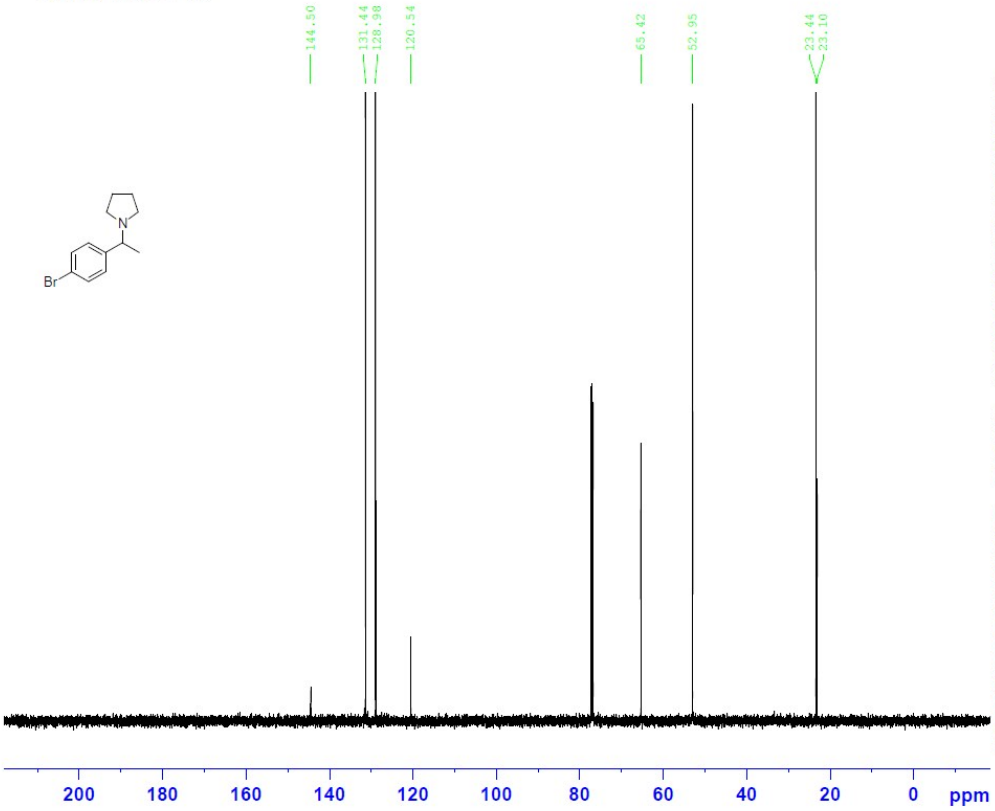

```
NAME      CMX-20190227-14
EXPNO                 11
PROCNO                 1
Date_           20190228
Time_               9.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                   203
DW                16.800 usec
DE                 6.50 usec
TE                297.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -1.00 dB
PL1W        112.80287170 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.05 dB
PL13               17.00 dB
PL2W         18.83080864 W
PL12W         0.46759412 W
PL13W         0.37572402 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

PROTON CDCl3 3f



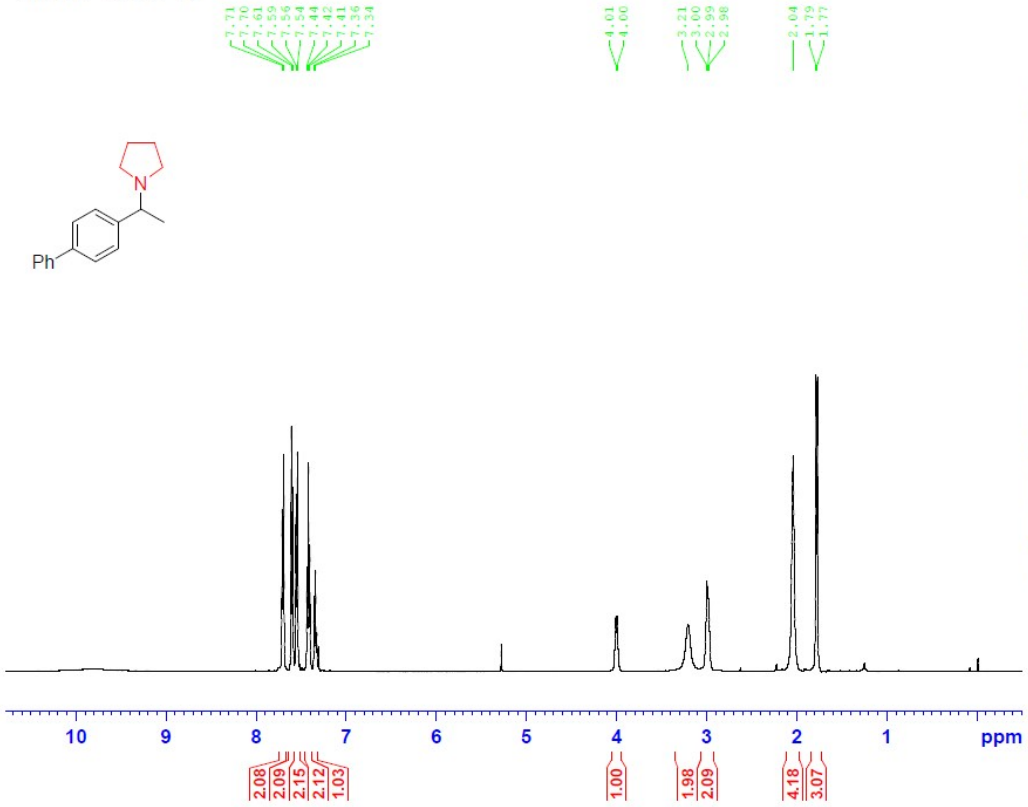

```
NAME          CMX-20190227-4
EXPNO                     10
PROCNO                     1
Date_               20190227
Time                   17.09
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                      40.3
DW                    48.400 usec
DE                     6.50 usec
TE                    297.5 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.60 usec
PL1                     0.00 dB
PL1W           18.83080864 W
SFO1           500.1330885 MHz
SI                     32768
SF             500.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

C13CPD CDCl3 3f




```
NAME          CMX-20190227-4
EXPNO                     11
PROCNO                     1
Date_               20190227
Time                   17.11
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       64
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      203
DW                    16.800 usec
DE                     6.50 usec
TE                    298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.50 usec
PL1                    -1.00 dB
PL1W          112.80287170 W
SFO1           125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  16.05 dB
PL13                  17.00 dB
PL2W           18.83080864 W
PL12W           0.46759412 W
PL13W           0.37572402 W
SFO2           500.1320005 MHz
SI                     32768
SF             125.7577890 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

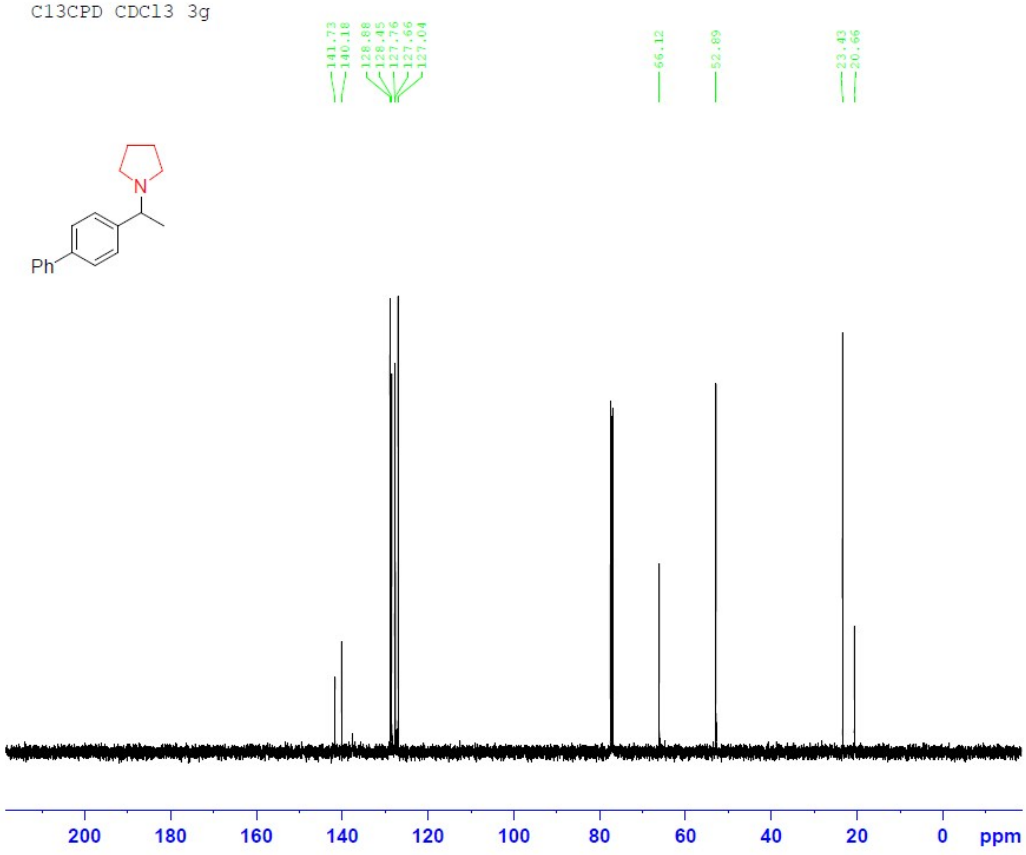
PROTON CDCl3 3g



BRUKER

```
NAME          CMX-20190227-5
EXPNO                     10
PROCNO                     1
Date_               20190227
Time                   17.26
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                         8
DS                         2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                        32
DW                   48.400 usec
DE                    6.50 usec
TE                   297.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.60 usec
PL1                     0.00 dB
PL1W              18.83080864 W
SFO1              500.1330885 MHz
SI                       32768
SF                500.1300000 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```

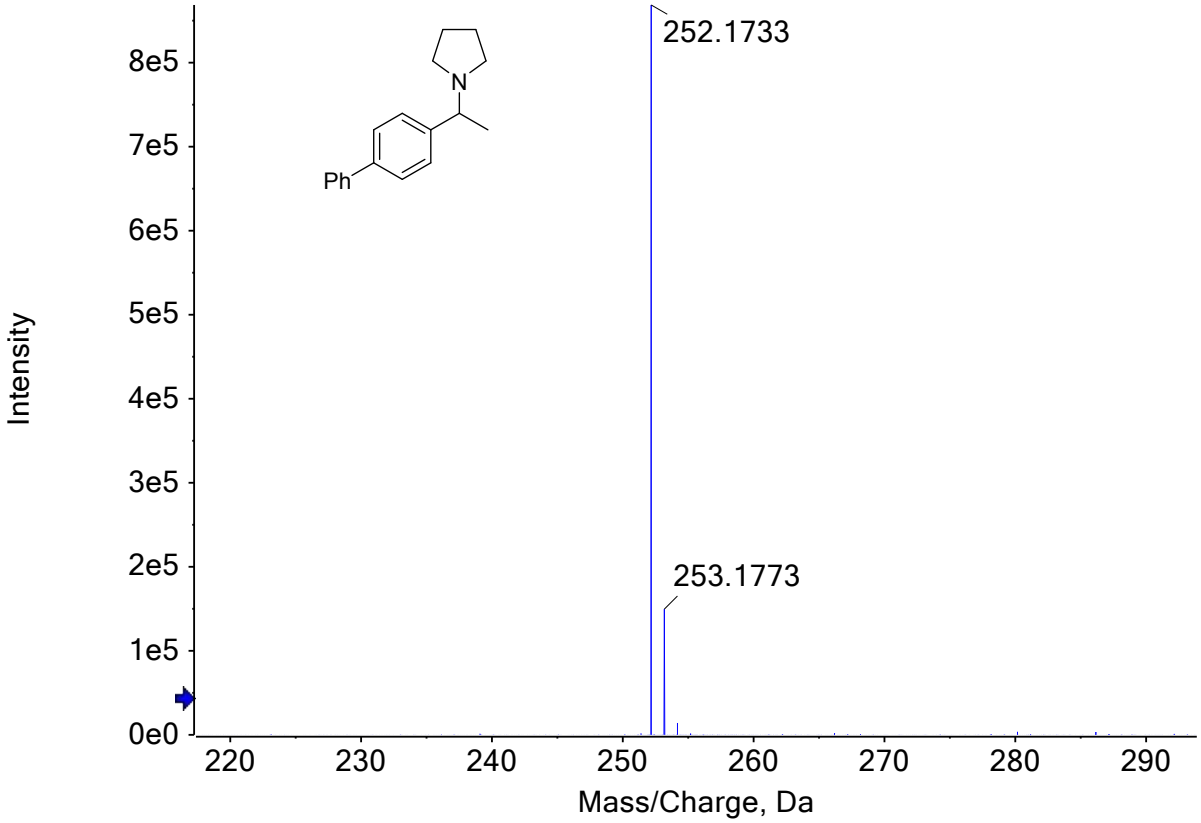
C13CPD CDCl3 3g

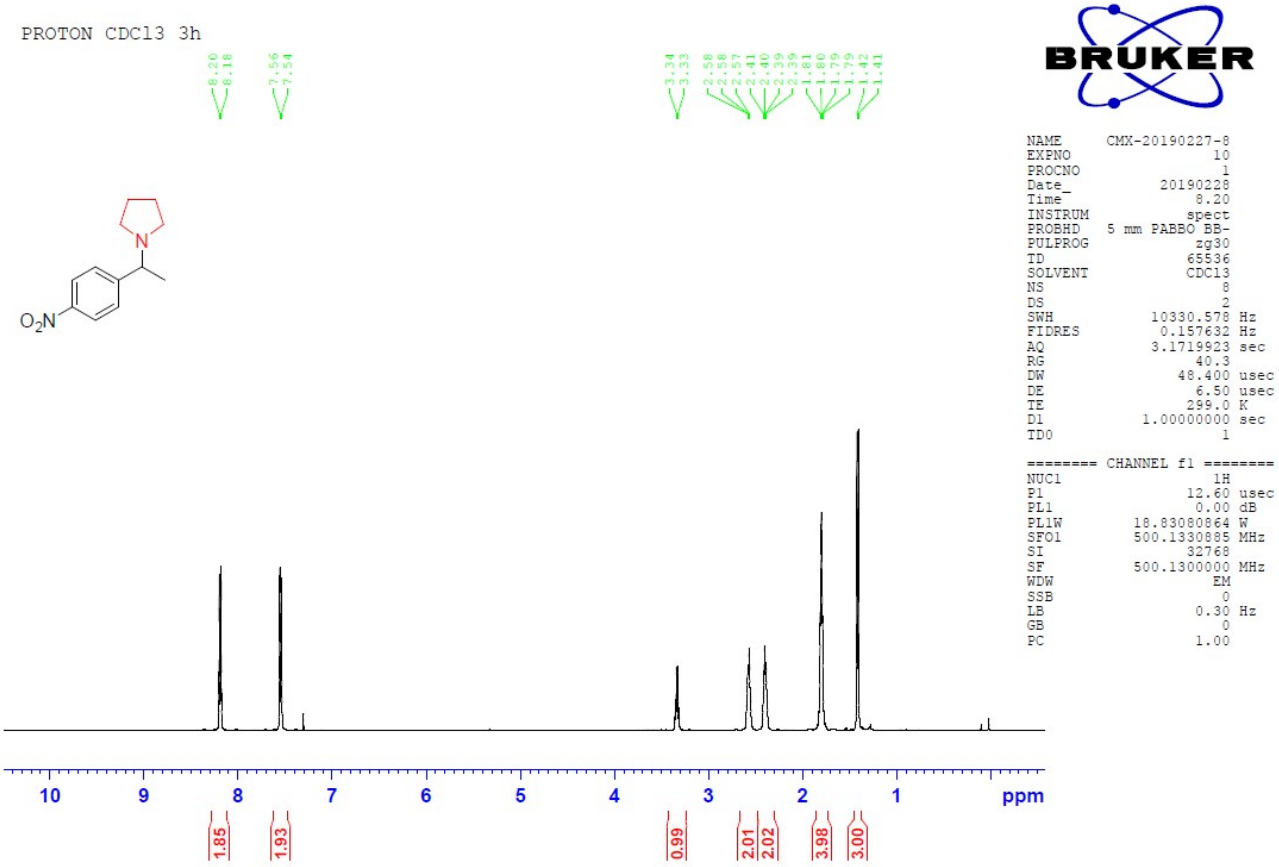


BRUKER

```
NAME          CMX-20190227-5
EXPNO                     11
PROCNO                     1
Date_               20190227
Time                   17.28
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                        17
DS                         4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                       203
DW                   16.800 usec
DE                    6.50 usec
TE                   297.3 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.50 usec
PL1                    -1.00 dB
PL1W             112.80287170 W
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  16.05 dB
PL13                  17.00 dB
PL2W              18.83080864 W
PL12W              0.46759412 W
PL13W              0.37572402 W
SFO2              500.1320005 MHz
SI                       32768
SF                125.7577890 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

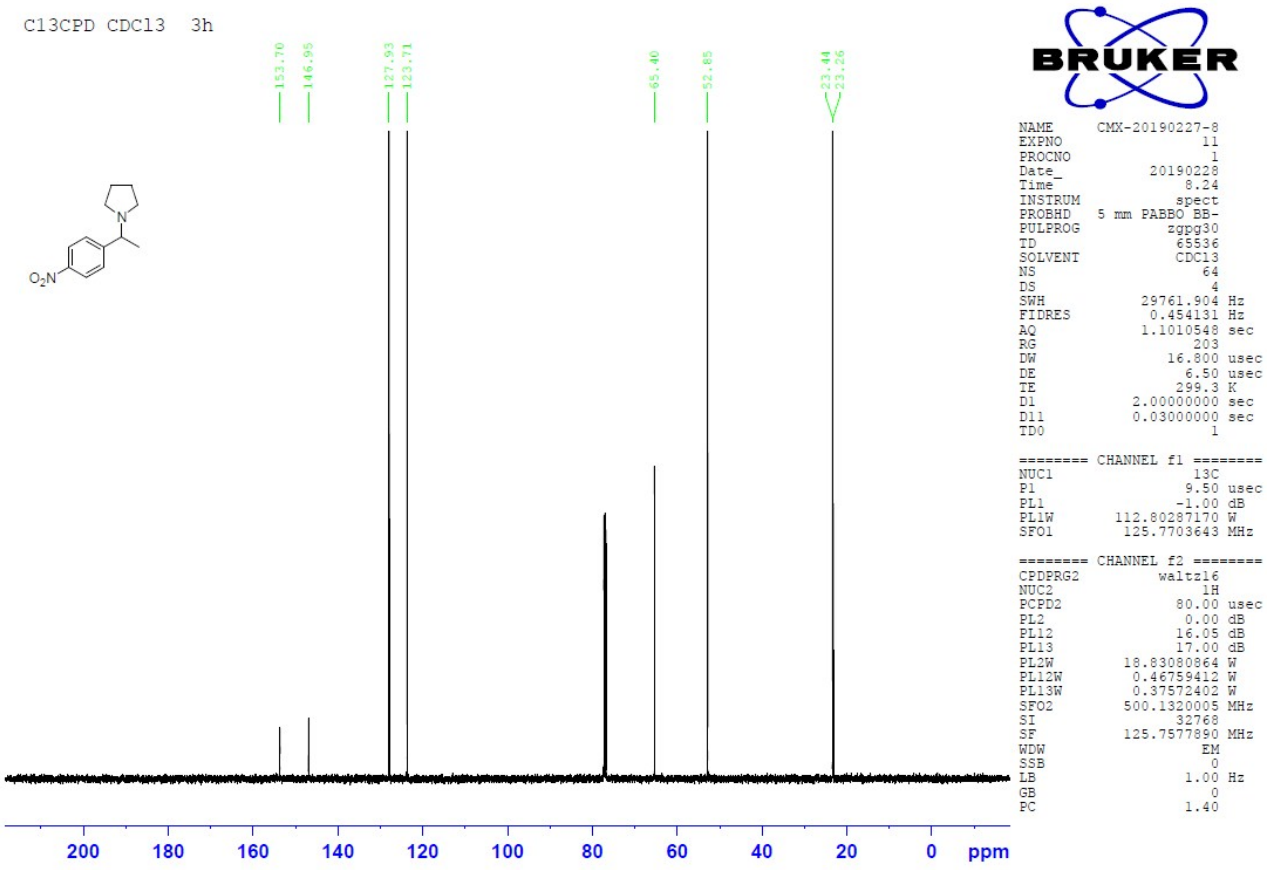
Spectrum from CMXWZT2018717-1.wiff (sam...MS (100 - 3000) from 0.054 to 0.101 min



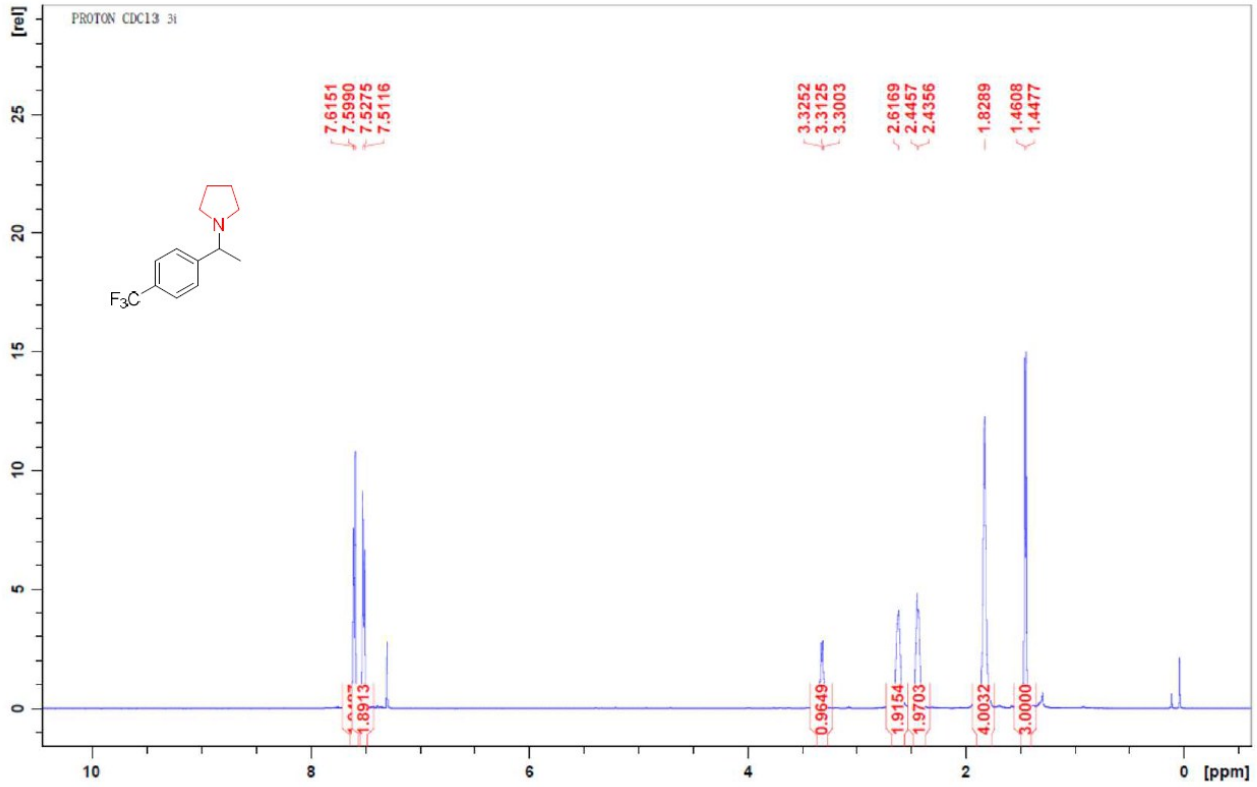


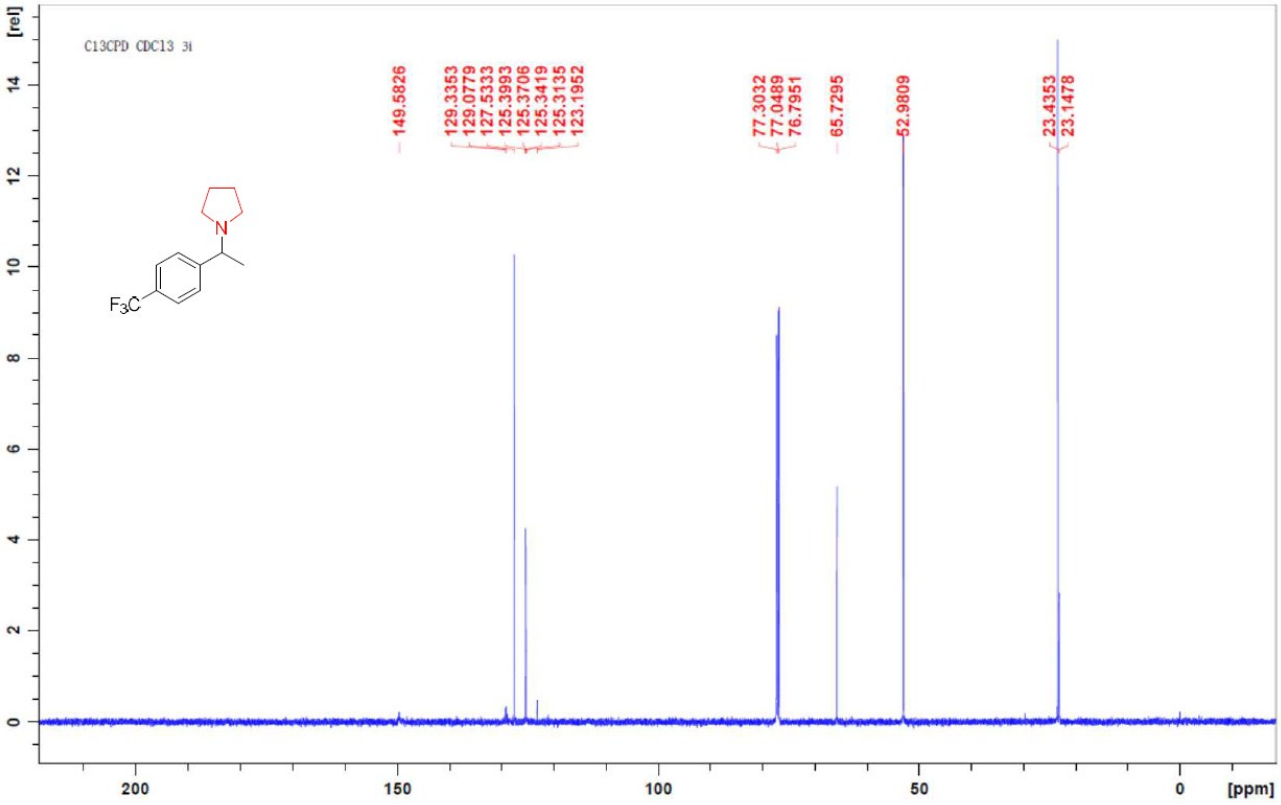
BRUKER

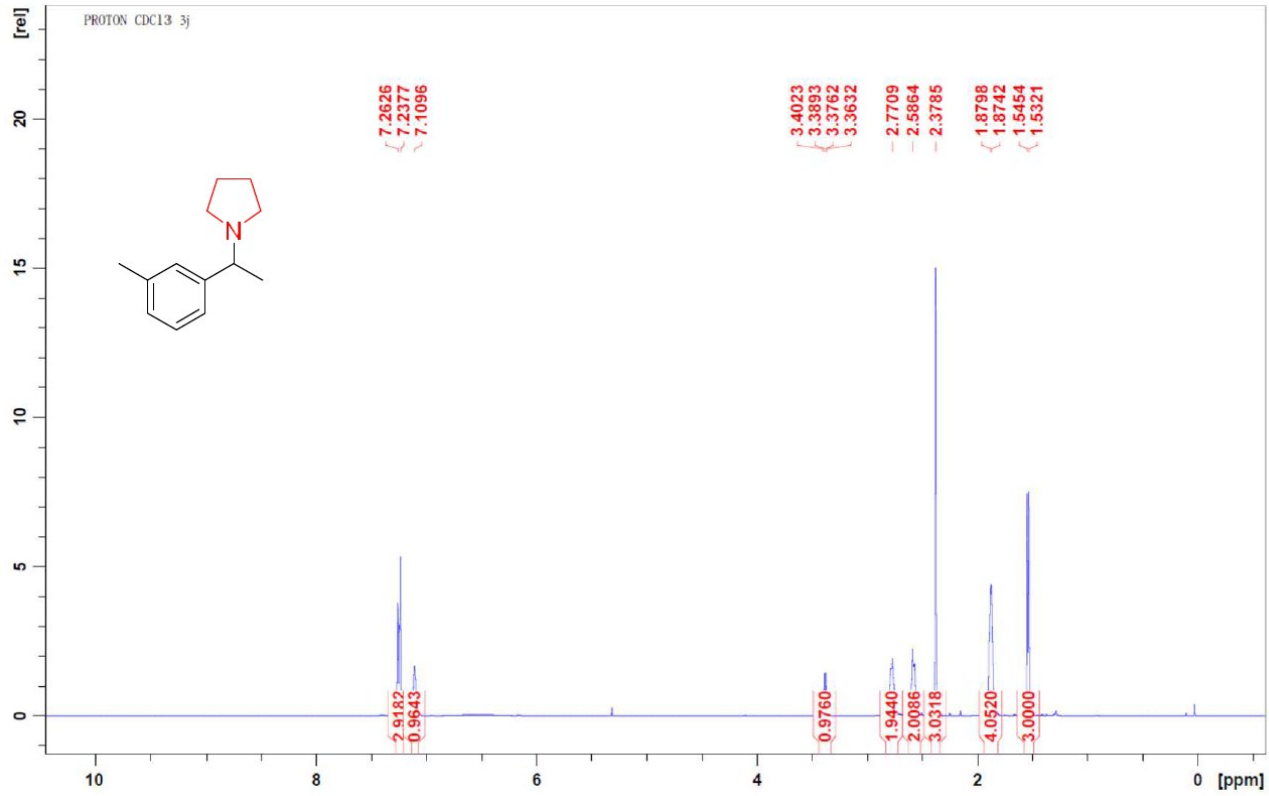
```
NAME        CMX-20190227-8
EXPNO                   10
PROCNO                   1
Date_             20190228
Time                 8.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                    40.3
DW                  48.400 usec
DE                    6.50 usec
TE                   299.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.60 usec
PL1                  0.00 dB
PL1W         18.83080864 W
SFO1         500.1330885 MHz
SI                   32768
SF           500.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



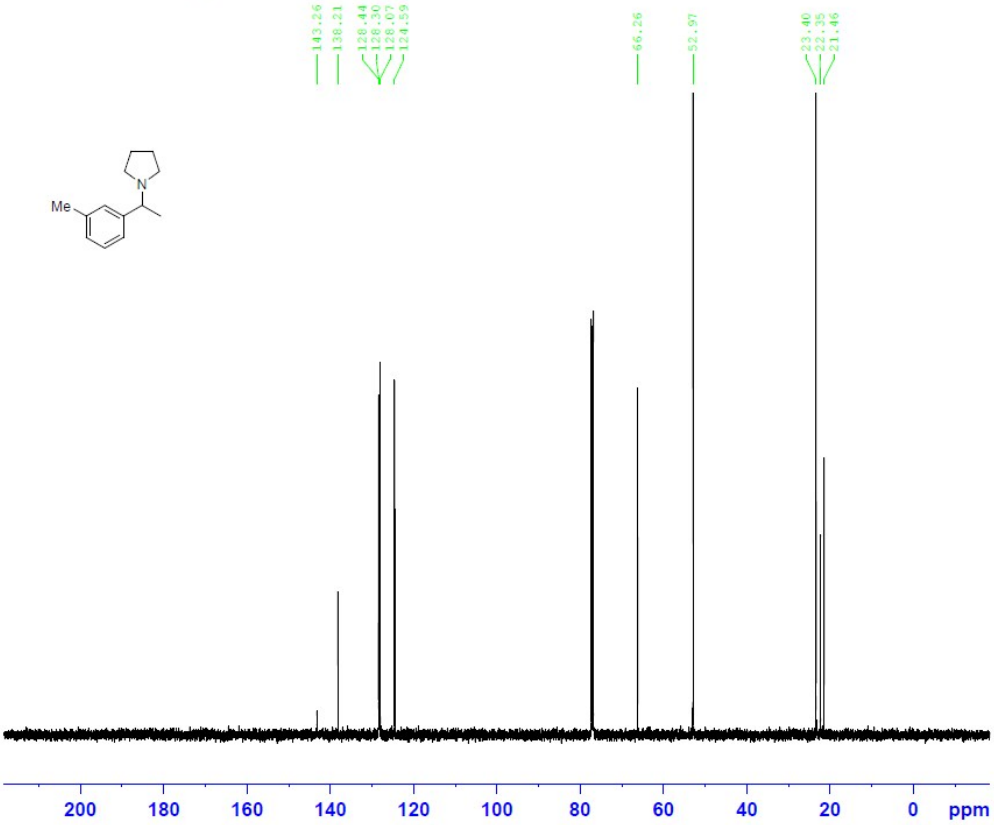

```
NAME      CMX-20190227-8
EXPNO                 11
PROCNO                 1
Date_           20190228
Time_               8.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                  203
DW               16.800 usec
DE                6.50 usec
TE                299.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -1.00 dB
PL1W       112.80287170 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.05 dB
PL13               17.00 dB
PL2W        18.83080864 W
PL12W        0.46759412 W
PL13W        0.37572402 W
SFO2        500.1320005 MHz
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




C13CPD CDCl3 3i
[rel]
149.5826
129.3353
129.0779
127.5333
125.3993
125.3706
125.3419
125.3135
123.1952
77.3032
77.0489
76.7951
65.7295
52.9809
23.4353
23.1478
F3C
N
200
150
100
50
0
[ppm]

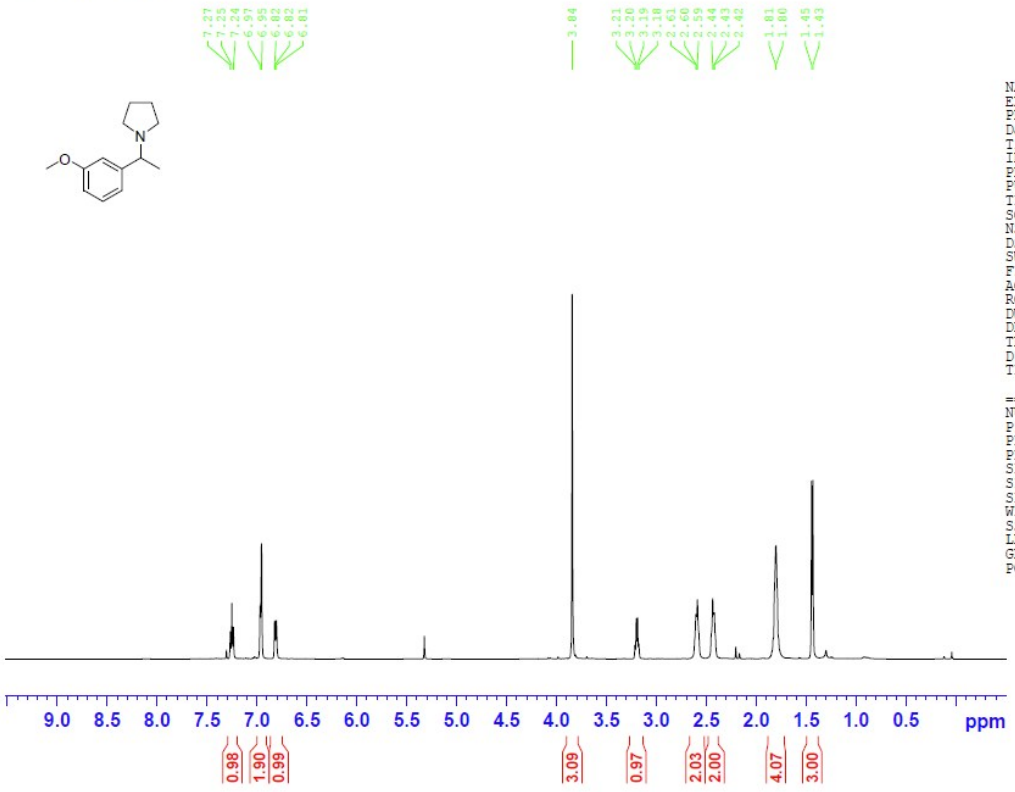

PROTON CDCl3 3j
[rel]
7.2626
7.2377
7.1096
3.4023
3.3893
3.3762
3.3632
2.7709
2.5864
2.3785
1.8798
1.8742
1.5454
1.5321
2.9182
0.9643
0.9760
1.9440
2.0086
3.0318
4.0520
3.0000
N
10
8
6
4
2
0
[ppm]

C13CPD CDCl3 3j



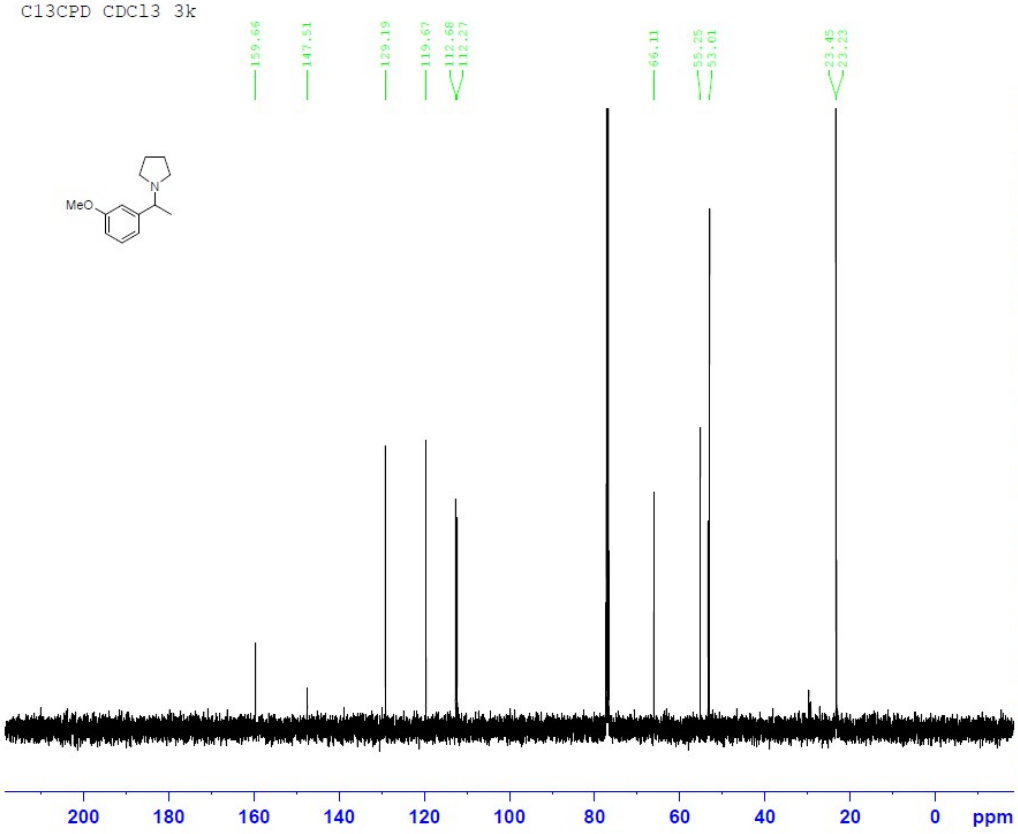

```
NAME          CMX-20190227-6
EXPNO                     11
PROCNO                     1
Date_               20190227
Time                   17.36
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         64
DS                          4
SWH                 29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                        203
DW                     16.800 usec
DE                      6.50 usec
TE                     297.9 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -1.00 dB
PL1W             112.80287170 W
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   16.05 dB
PL13                   17.00 dB
PL2W             18.83080864 W
PL12W             0.46759412 W
PL13W             0.37572402 W
SFO2              500.1320005 MHz
SI                       32768
SF                125.7577890 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

PROTON CDCl3 3k



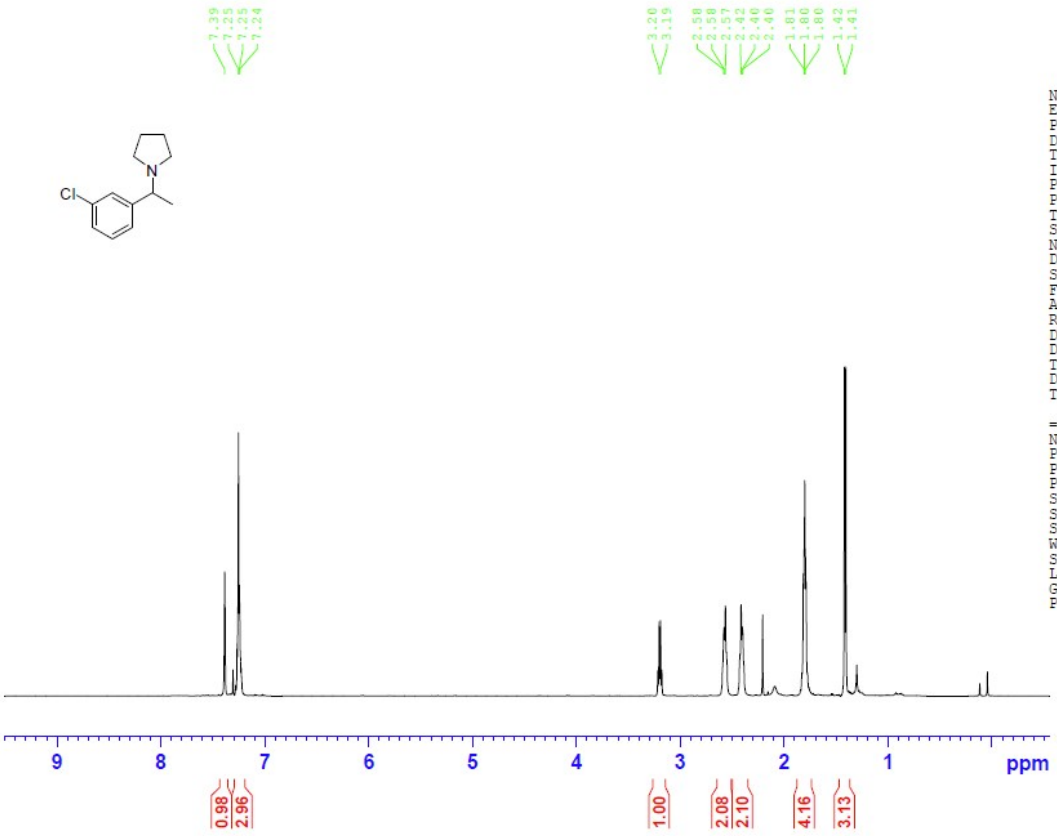

```
NAME          CMX-20180109-16
EXPNO                     10
PROCNO                     1
Date_               20180109
Time                   11.36
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                         32
DW                     48.400 usec
DE                      6.50 usec
TE                     295.8 K
D1                  1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.60 usec
PL1                     0.00 dB
PL1W             18.83080864 W
SFO1              500.1330885 MHz
SI                       32768
SF                500.1300000 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```

C13CPD CDCl3 3k

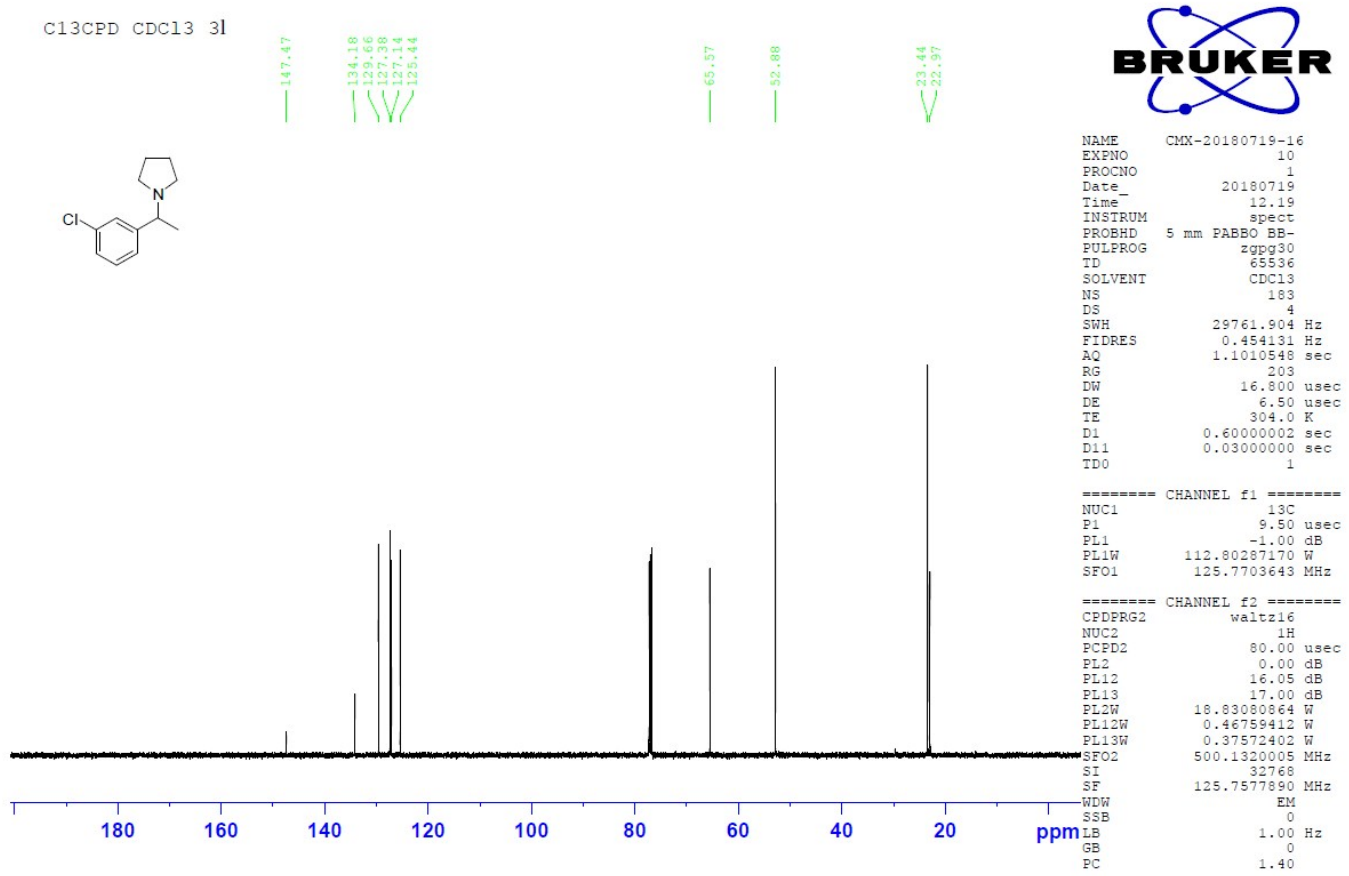



```
NAME        CMX-20190225-6
EXPNO               11
PROCNO              1
Date_           20190225
Time              12.10
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  64
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 203
DW              16.800 usec
DE               6.50 usec
TE              300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -1.00 dB
PL1W       112.80287170 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             16.05 dB
PL13             17.00 dB
PL2W       18.83080864 W
PL12W       0.46759412 W
PL13W       0.37572402 W
SFO2       500.1320005 MHz
SI              32768
SF         125.7577890 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

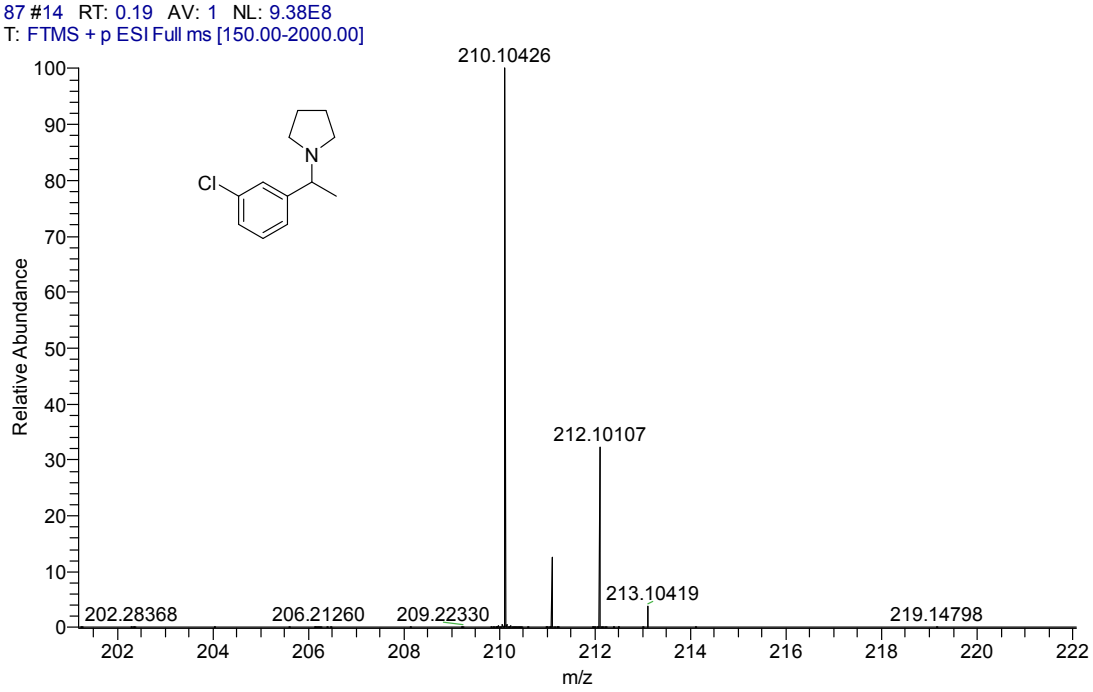
PROTON CDCl3 31



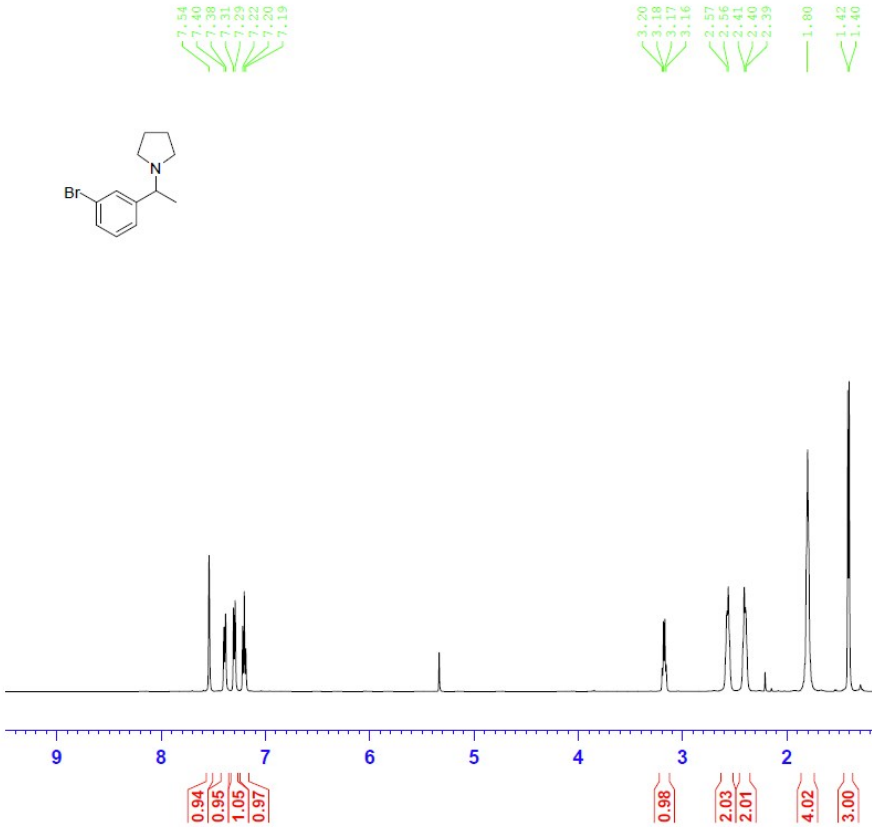

```
NAME        CMX-20170925-5
EXPNO               10
PROCNO              1
Date_           20170926
Time               9.11
INSTRUM           spect
PROBHD   5 mm PASEI 1H/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                  64
DW              48.400 usec
DE               6.50 usec
TE              302.0 K
D1           1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1                6.80 usec
PL1               0.00 dB
PL1W       18.83080864 W
SFO1       500.1330885 MHz
SI              32768
SF         500.1300000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```




```
NAME        CMX-20180719-16
EXPNO                    10
PROCNO                    1
Date_              20180719
Time                  12.19
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     183
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                     203
DW                  16.800 usec
DE                   6.50 usec
TE                  304.0 K
D1              0.60000002 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -1.00 dB
PL1W         112.80287170 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 16.05 dB
PL13                 17.00 dB
PL2W          18.83080864 W
PL12W          0.46759412 W
PL13W          0.37572402 W
SFO2          500.1320005 MHz
SI                   32768
SF            125.7577890 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

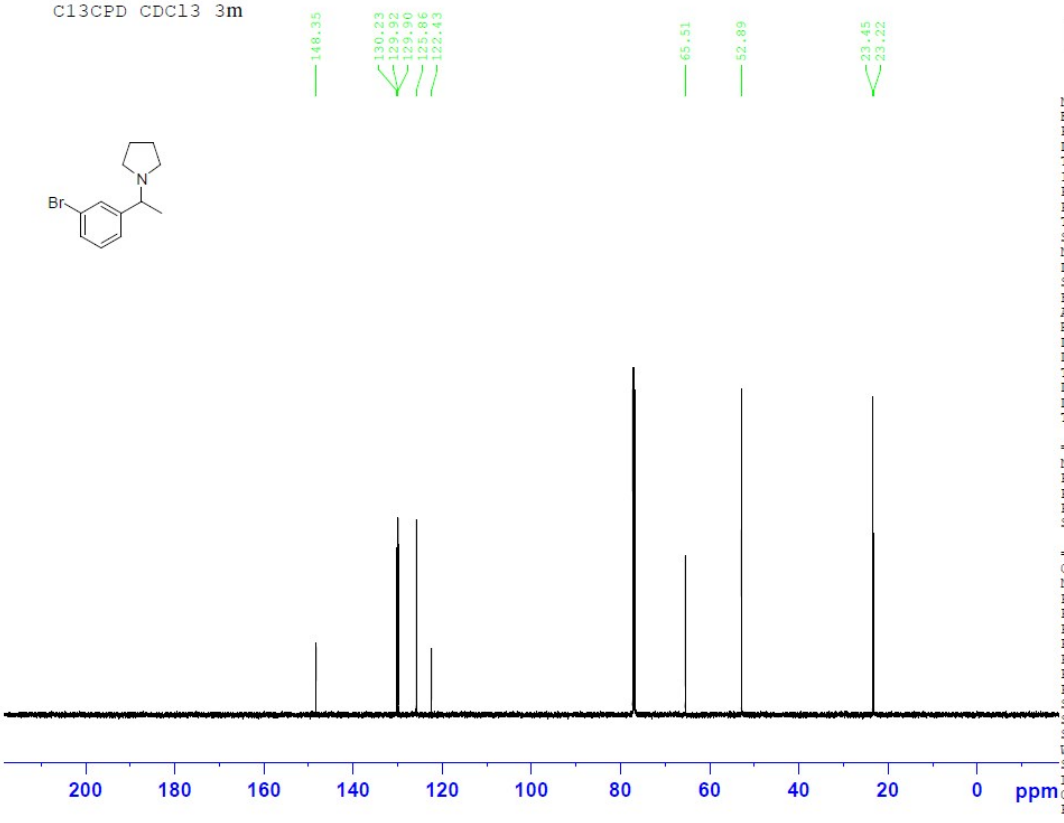


PROTON CDCl3 3m

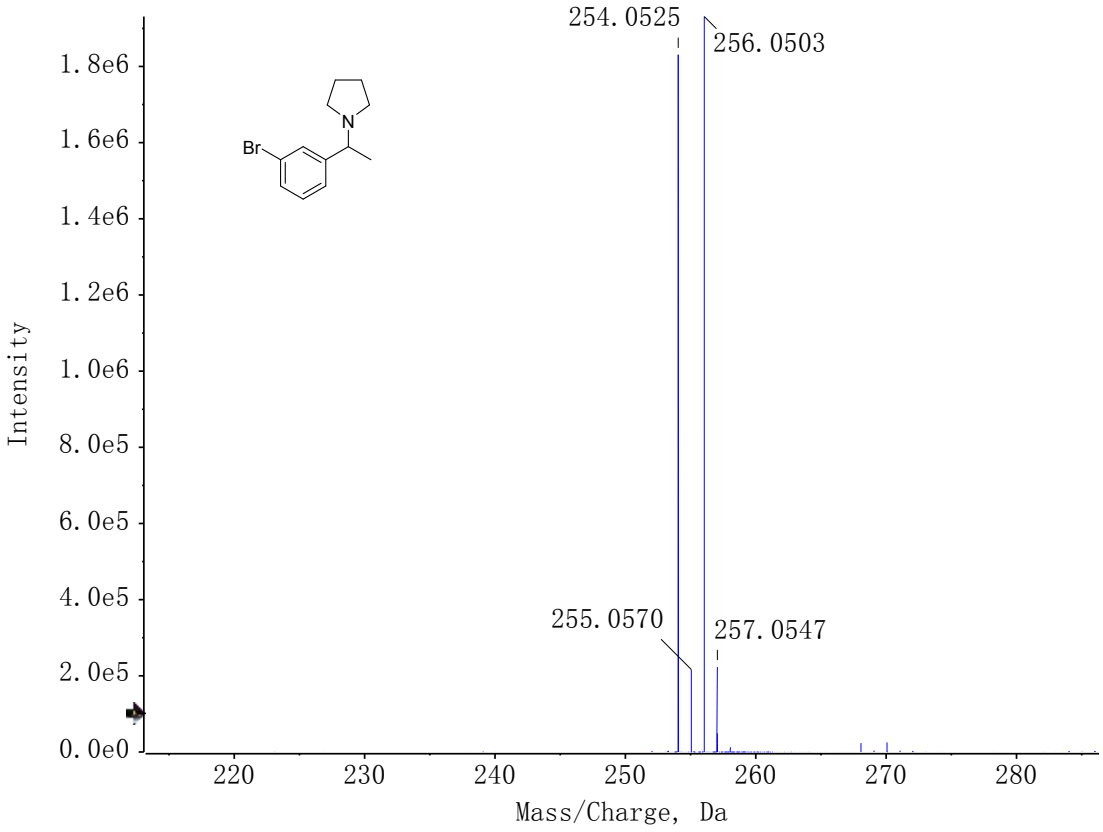


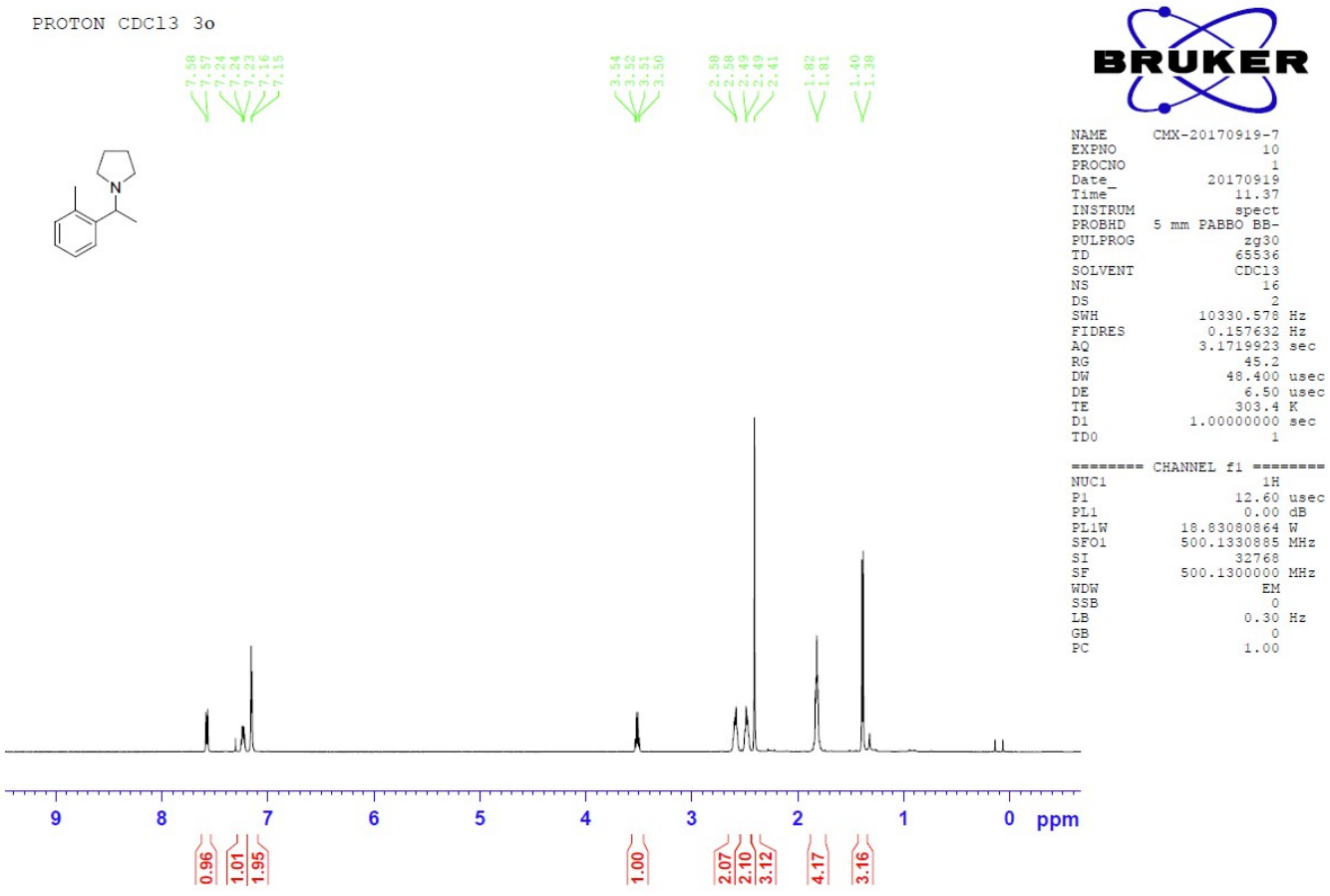

```
NAME          CMX-20180109-15
EXPNO                      10
PROCNO                      1
Date_                20180109
Time                    11.13
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         16
DS                          2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719923 sec
RG                       45.2
DW                     48.400 usec
DE                      6.50 usec
TE                     295.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.60 usec
PL1                      0.00 dB
PL1W               18.83080864 W
SFO1               500.1330885 MHz
SI                       32768
SF                 500.1300000 MHz
WDW                         EM
SSB                          0
LB                       0.30 Hz
GB                           0
PC                       1.00
```

C13CPD CDCl3 3m

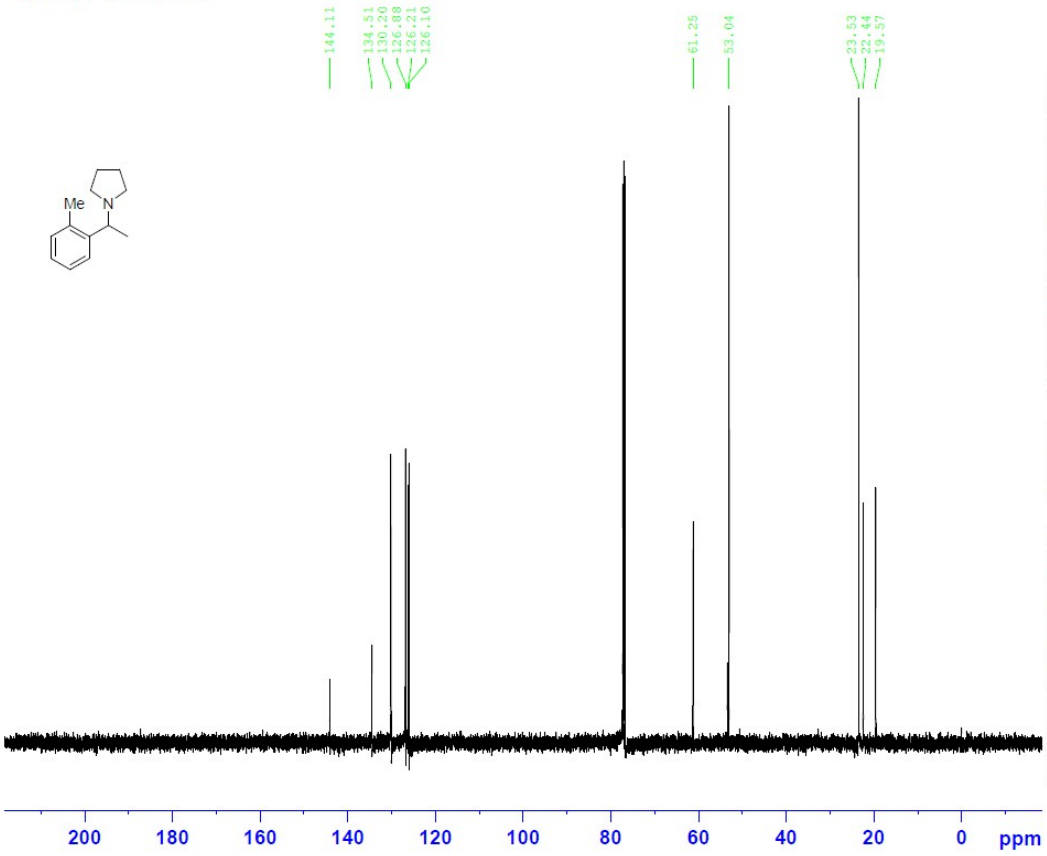



```
NAME          CMX-20180719-14
EXPNO                      10
PROCNO                      1
Date_                20180719
Time                    12.04
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        256
DS                          4
SWH                29761.904 Hz
FIDRES              0.454131 Hz
AQ                  1.1010548 sec
RG                        203
DW                     16.800 usec
DE                      6.50 usec
TE                     304.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       9.50 usec
PL1                     -1.00 dB
PL1W              112.80287170 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W               18.83080864 W
PL12W               0.46759412 W
PL13W               0.37572402 W
SFO2               500.1320005 MHz
SI                       32768
SF                 125.7577890 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```


Spectrum from CMXWZT2018717-2.wiff (s...(100 - 3000) from 0.054 to 0.116 min
254.0525
256.0503
255.0570
257.0547
Br
N
Intensity
1.8e6
1.6e6
1.4e6
1.2e6
1.0e6
8.0e5
6.0e5
4.0e5
2.0e5
0.0e0
220
230
240
250
260
270
280
Mass/Charge, Da

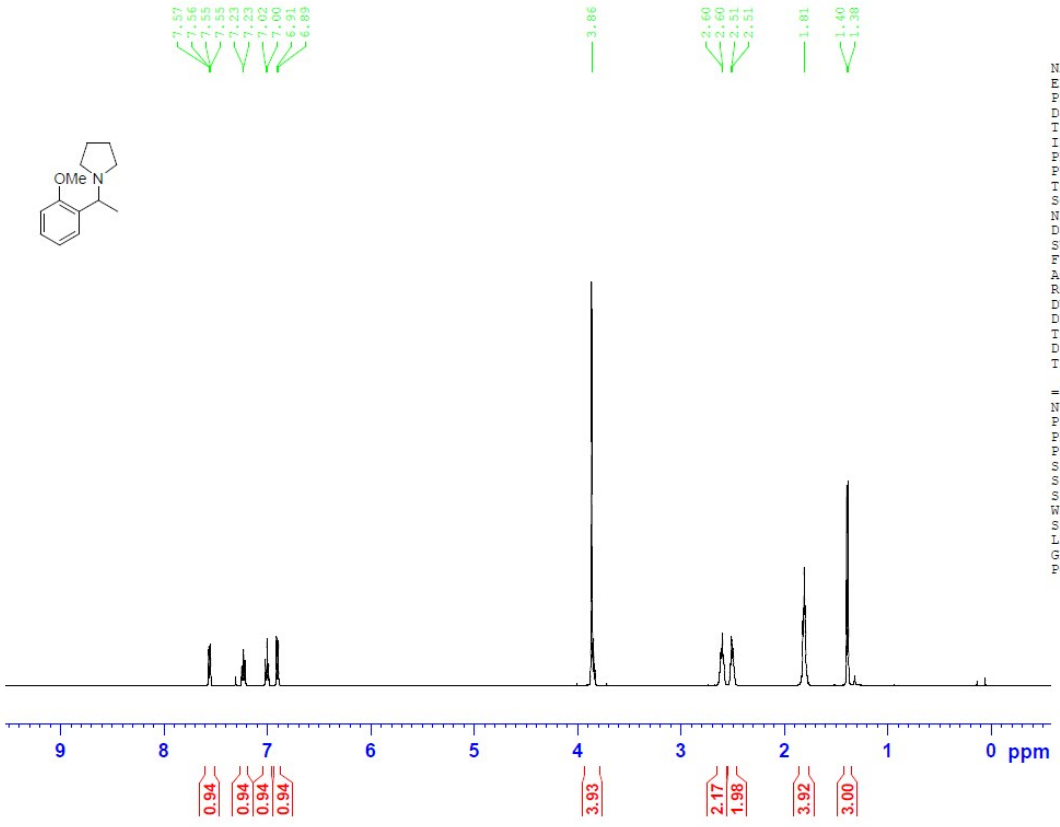

PROTON CDCl3 3o
BRUKER
NAME CMX-20170919-7
EXPNO 10
PROCNO 1
Date_ 20170919
Time 11.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 45.2
DW 48.400 usec
DE 6.50 usec
TE 303.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.60 usec
PL1 0.00 dB
PL1W 18.83080864 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.96
1.01
1.95
1.00
2.07
2.10
3.12
4.17
3.16

C13CPD CDCl3 3o

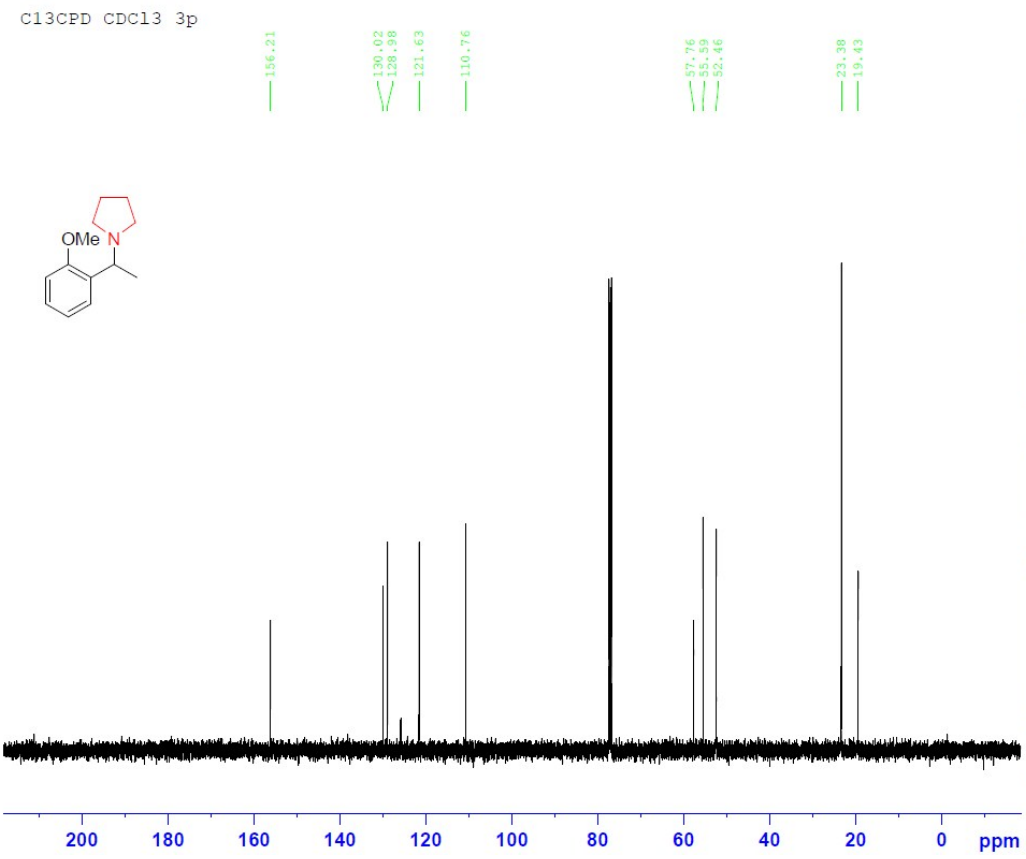



```
NAME      CMX-20190225-9
EXPNO                 11
PROCNO                 1
Date_           20190225
Time_              12.35
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                  203
DW               16.800 usec
DE                6.50 usec
TE               300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -1.00 dB
PL1W       112.80287170 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.05 dB
PL13               17.00 dB
PL2W       18.83080864 W
PL12W       0.46759412 W
PL13W       0.37572402 W
SFO2        500.1320005 MHz
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

PROTON CDCl3 3p

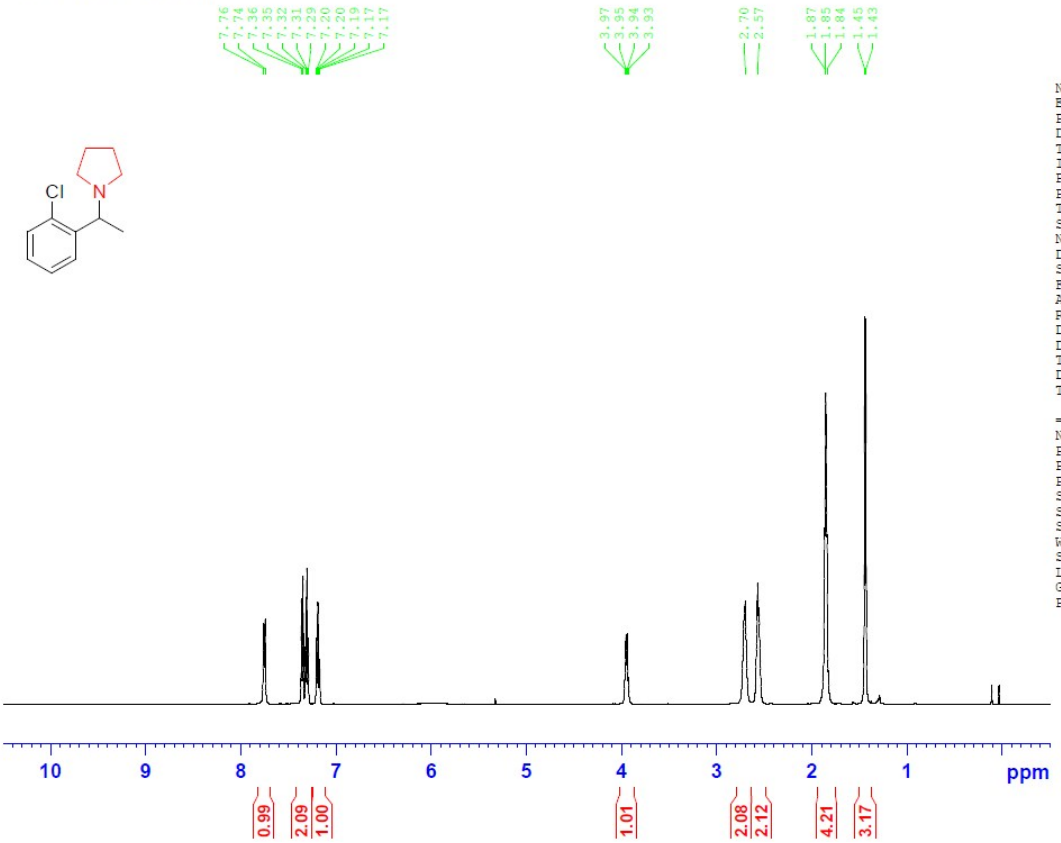



```
NAME      CMX-20170919-5
EXPNO                 10
PROCNO                 1
Date_           20170919
Time_              11.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                   32
DW               48.400 usec
DE                6.50 usec
TE               303.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                12.60 usec
PL1                0.00 dB
PL1W       18.83080864 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



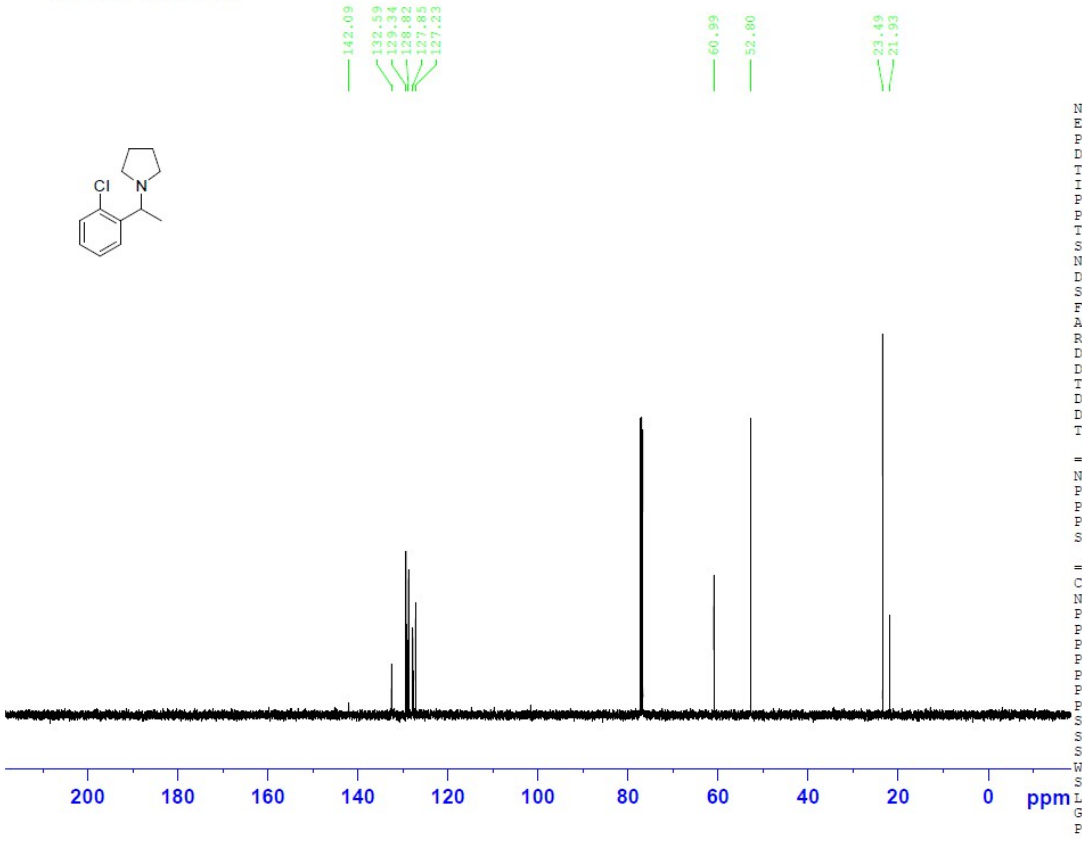

```
NAME          CMX-20190225-10
EXPNO                      11
PROCNO                      1
Date_                20190225
Time                    12.40
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          21
DS                           4
SWH                  29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                          203
DW                     16.800 usec
DE                      6.50 usec
TE                      300.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                        9.50 usec
PL1                      -1.00 dB
PL1W              112.80287170 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                   80.00 usec
PL2                       0.00 dB
PL12                     16.05 dB
PL13                     17.00 dB
PL2W               18.83080864 W
PL12W               0.46759412 W
PL13W               0.37572402 W
SFO2               500.1320005 MHz
SI                       32768
SF                 125.7577890 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

PROTON CDCl3 3q

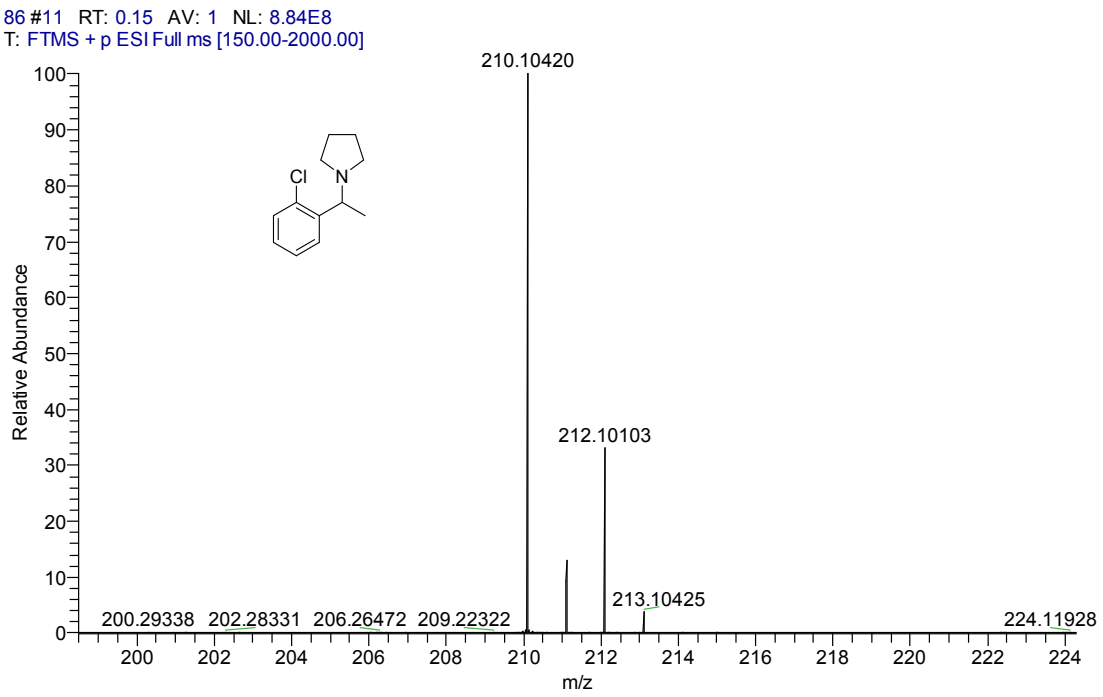


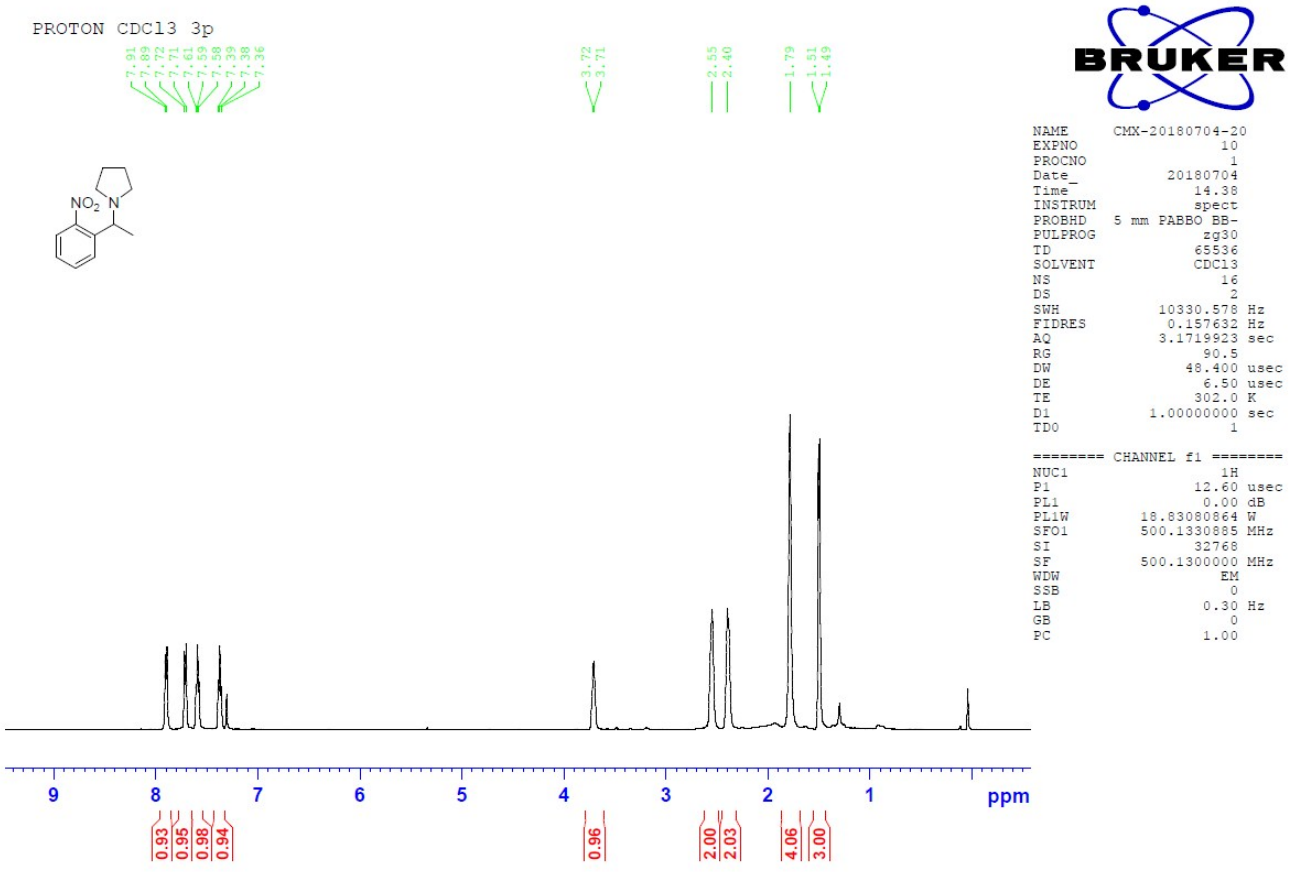

```
NAME          CMX-20190227-7
EXPNO                     10
PROCNO                     1
Date_               20190227
Time                   17.41
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                     40.3
DW                   48.400 usec
DE                    6.50 usec
TE                   297.1 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.60 usec
PL1                     0.00 dB
PL1W             18.83080864 W
SFO1            500.1330885 MHz
SI                        32768
SF              500.1300000 MHz
WDW                       EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

C13CPD CDCl3 3q

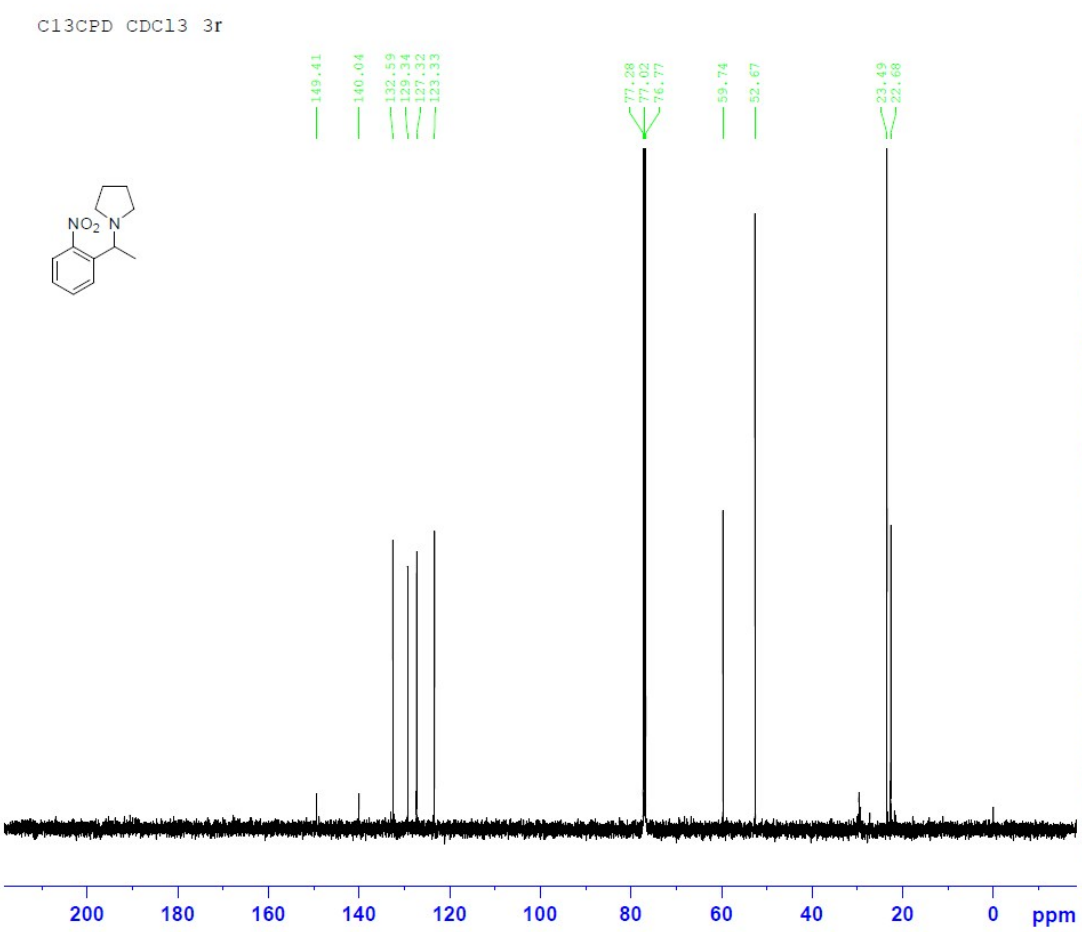



```
NAME          CMX-20180719-15
EXPNO                     10
PROCNO                     1
Date_               20180719
Time                   12.09
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       48
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      203
DW                   16.800 usec
DE                    6.50 usec
TE                   303.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                     9.50 usec
PL1                   -1.00 dB
PL1W            112.80287170 W
SFO1             125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  16.05 dB
PL13                  17.00 dB
PL2W             18.83080864 W
PL12W             0.46759412 W
PL13W             0.37572402 W
SFO2            500.1320005 MHz
SI                        32768
SF              125.7577890 MHz
WDW                       EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



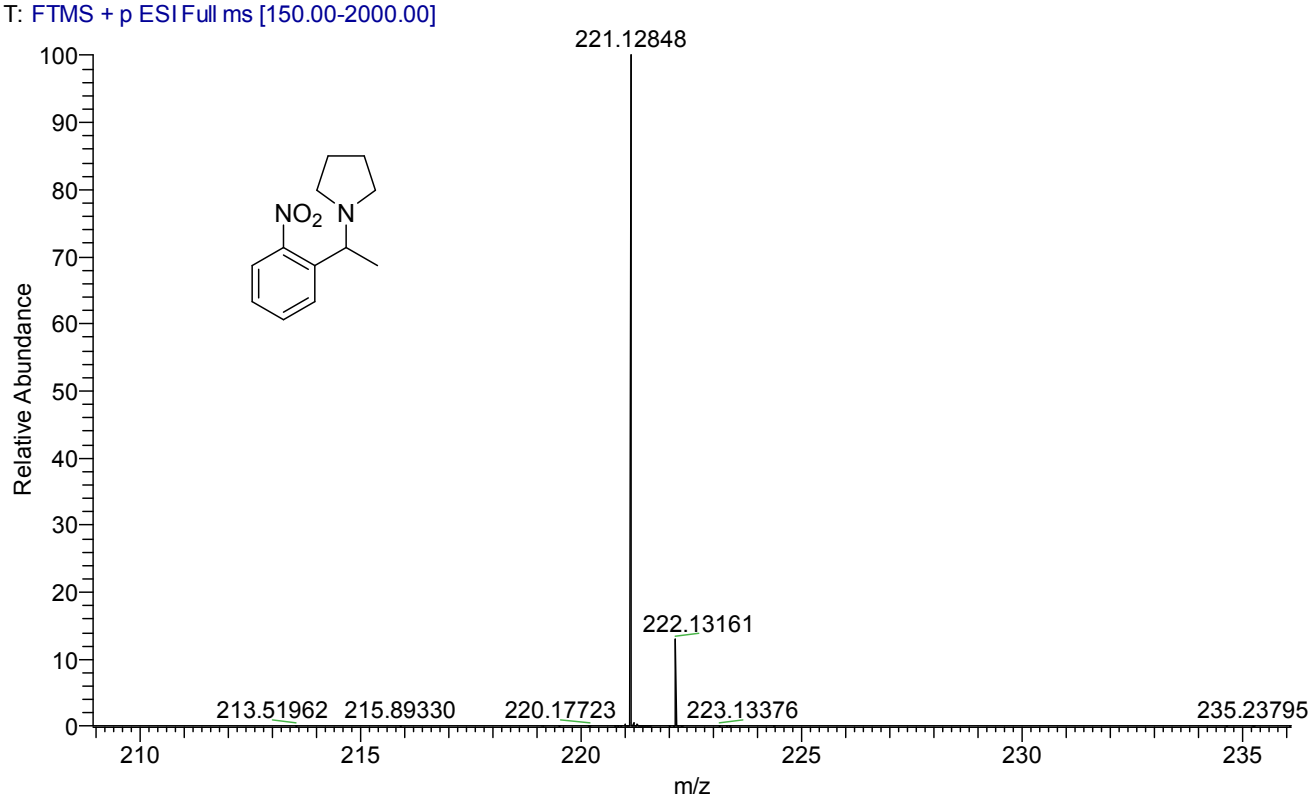



```
NAME        CMX-20180704-20
EXPNO                    10
PROCNO                    1
Date_              20180704
Time                  14.38
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1719923 sec
RG                     90.5
DW                   48.400 usec
DE                    6.50 usec
TE                   302.0 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.60 usec
PL1                   0.00 dB
PL1W         18.83080864 W
SFO1         500.1330885 MHz
SI                    32768
SF           500.1300000 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

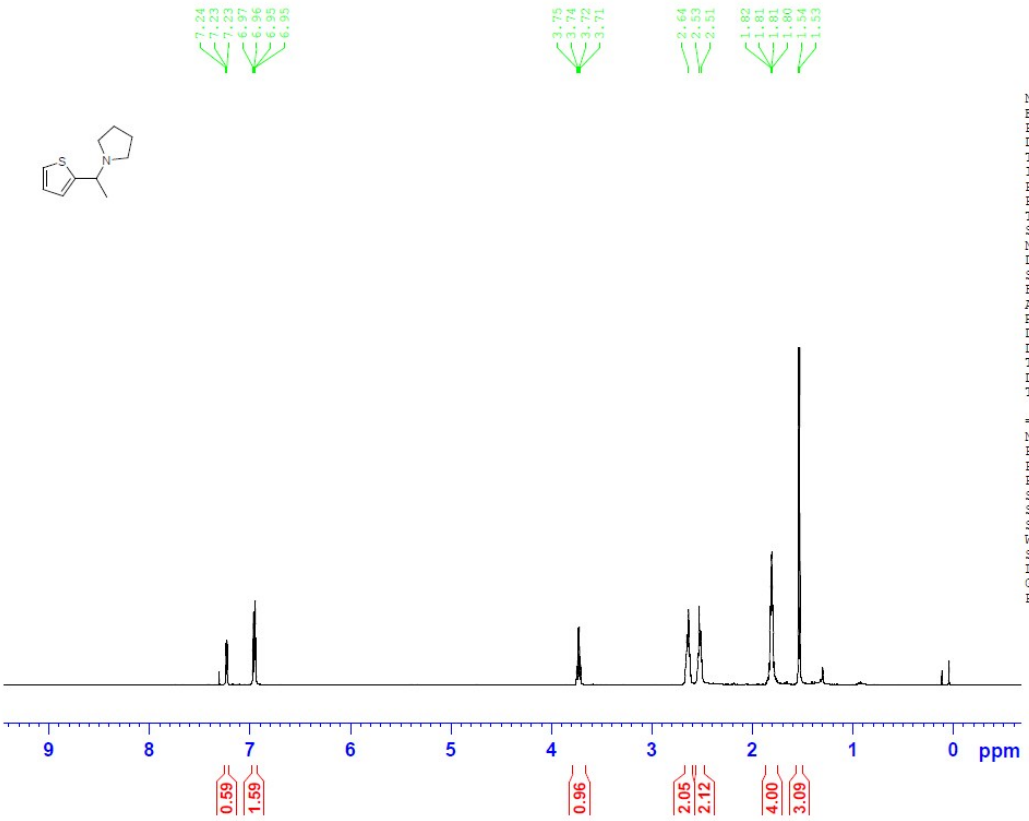



```
NAME        CMX-20180801-2
EXPNO                   12
PROCNO                   1
Date_             20180801
Time                 10.59
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDC13
NS                   1024
DS                      4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                    203
DW                16.800 usec
DE                 6.50 usec
TE                304.7 K
D1             0.60000002 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -1.00 dB
PL1W        112.80287170 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.05 dB
PL13               17.00 dB
PL2W         18.83080864 W
PL12W         0.46759412 W
PL13W         0.37572402 W
SFO2        500.1320005 MHz
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

33 #10 RT: 0.12 AV: 1 NL: 6.16E8
T: FTMS + p ESI Full ms [150.00-2000.00]

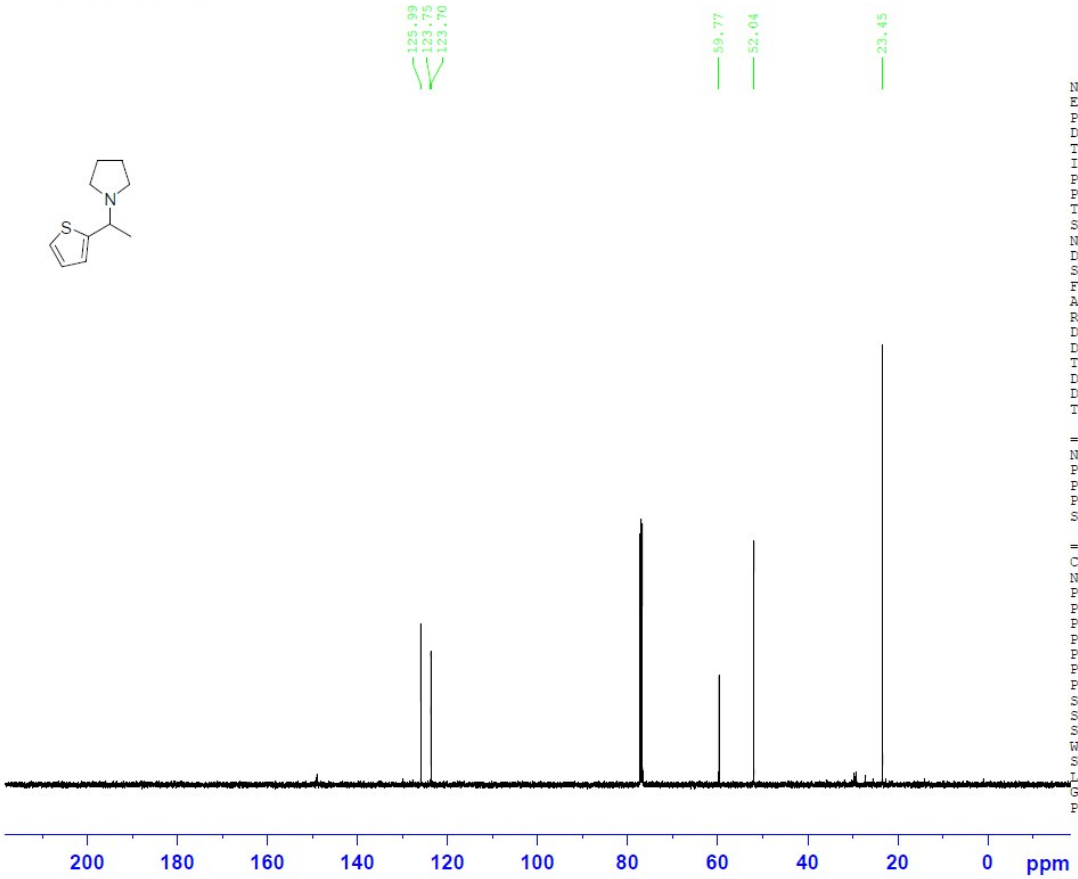


PROTON CDCl3 3s



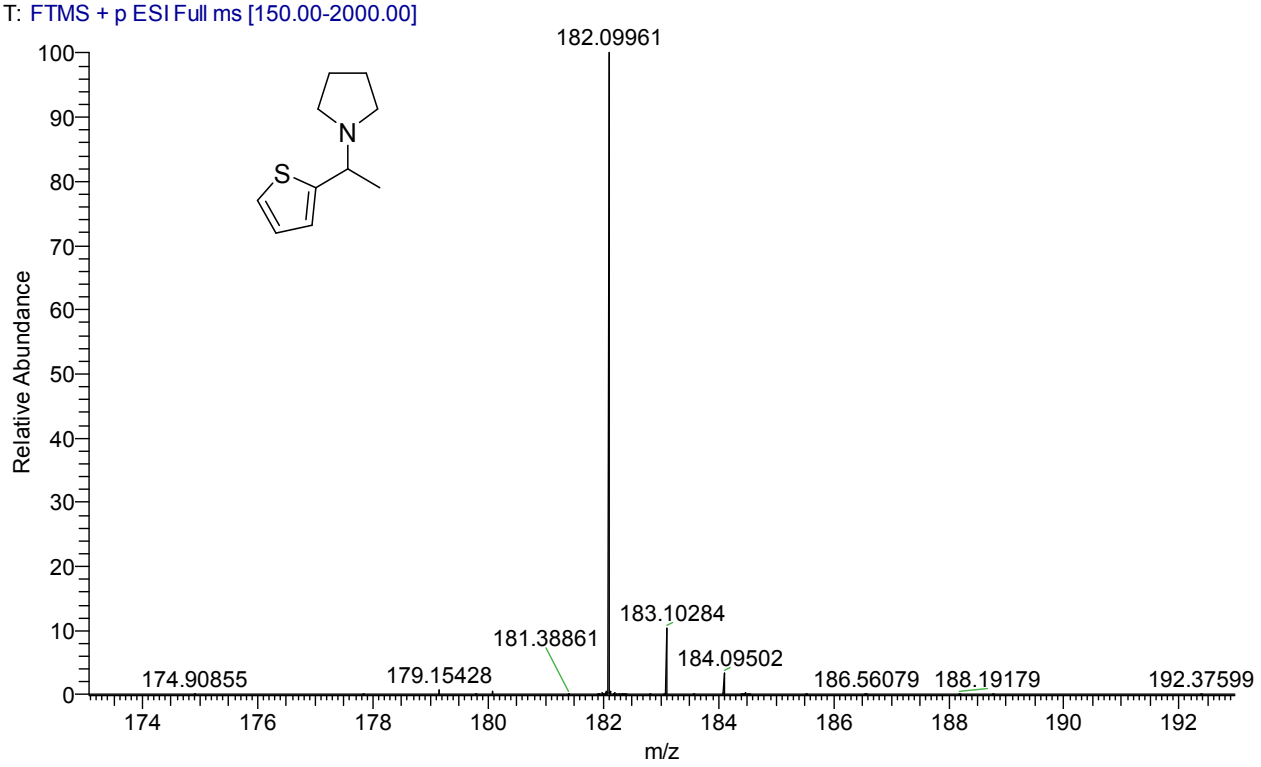

```
NAME      CMX-20180725-9
EXPNO                 10
PROCNO                 1
Date_           20180725
Time                14.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                  71.8
DW                48.400 usec
DE                 6.50 usec
TE                303.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.60 usec
PL1                0.00 dB
PL1W        18.83080864 W
SFO1        500.1330885 MHz
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

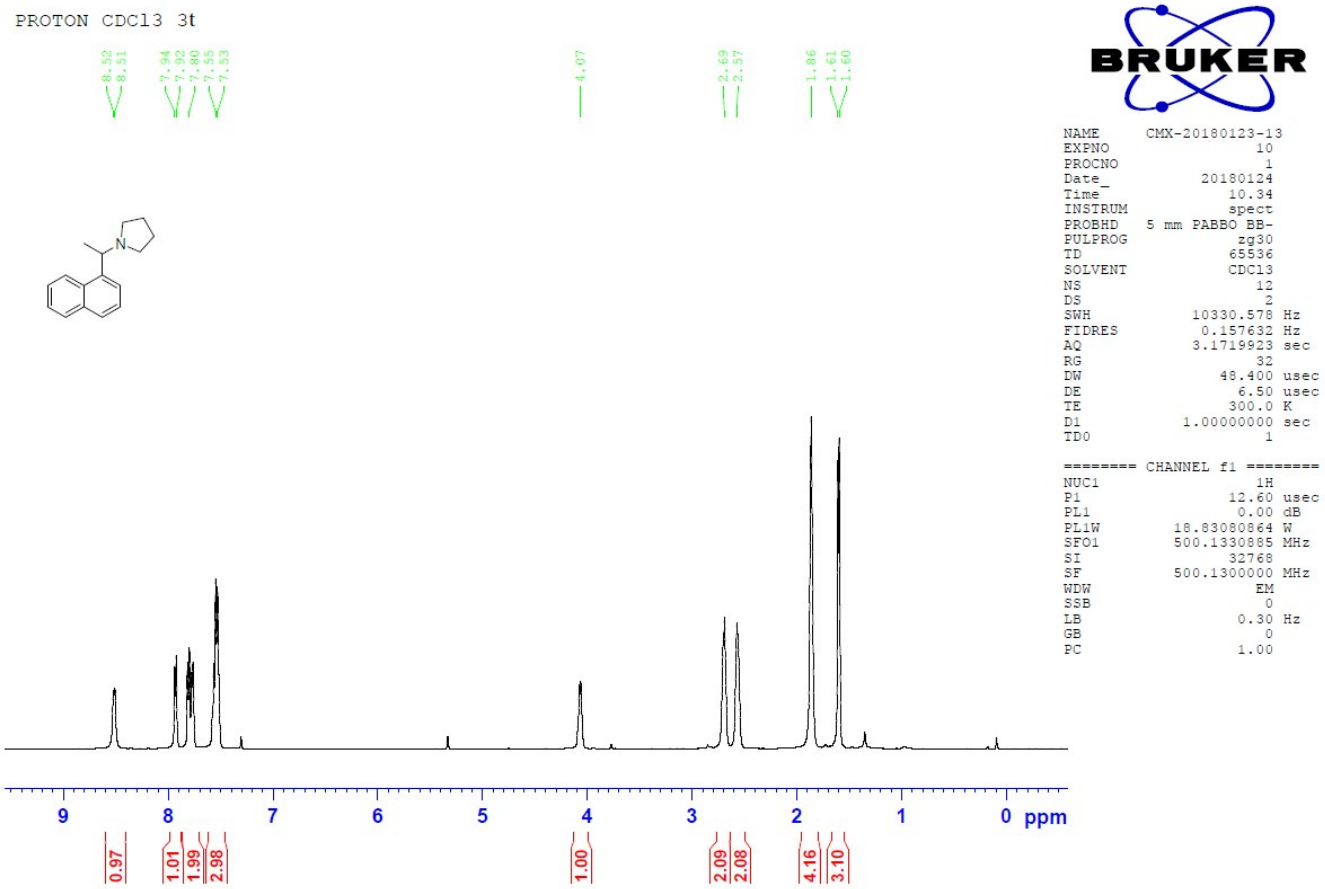
C13CPD CDCl3 3s



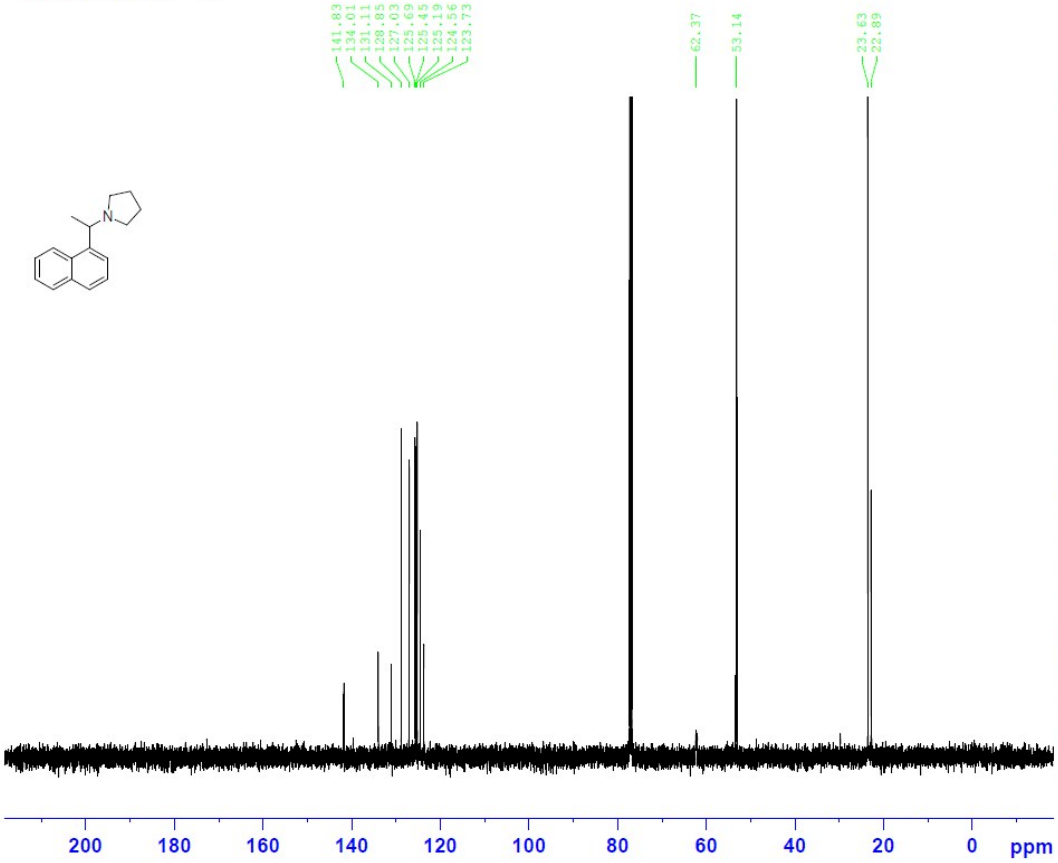

```
NAME      CMX-20180731-4
EXPNO                 11
PROCNO                 1
Date_           20180731
Time                11.26
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   203
DW                16.800 usec
DE                 6.50 usec
TE                304.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.50 usec
PL1                -1.00 dB
PL1W       112.80287170 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.05 dB
PL13               17.00 dB
PL2W        18.83080864 W
PL12W        0.46759412 W
PL13W        0.37572402 W
SFO2        500.1320005 MHz
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

34 #12 RT: 0.16 AV: 1 NL: 2.04E8
T: FTMS + p ESI Full ms [150.00-2000.00]



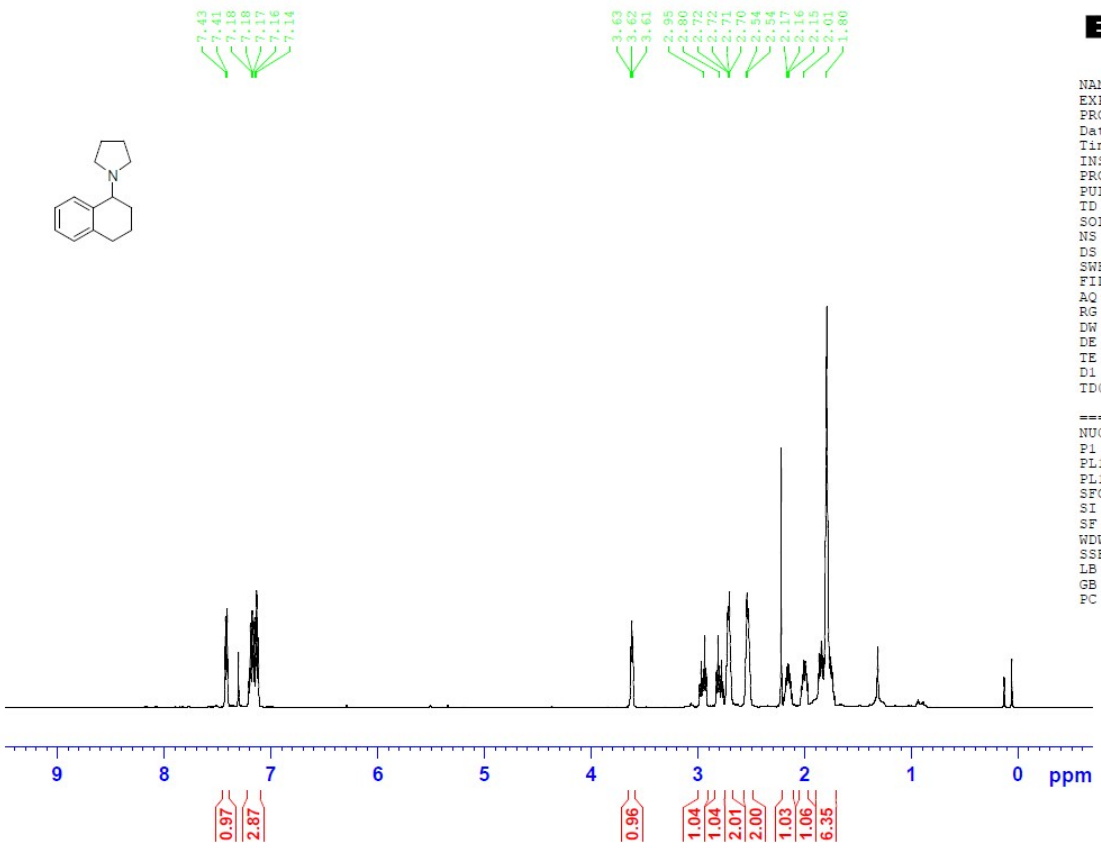


C13CPD CDCl3 3t



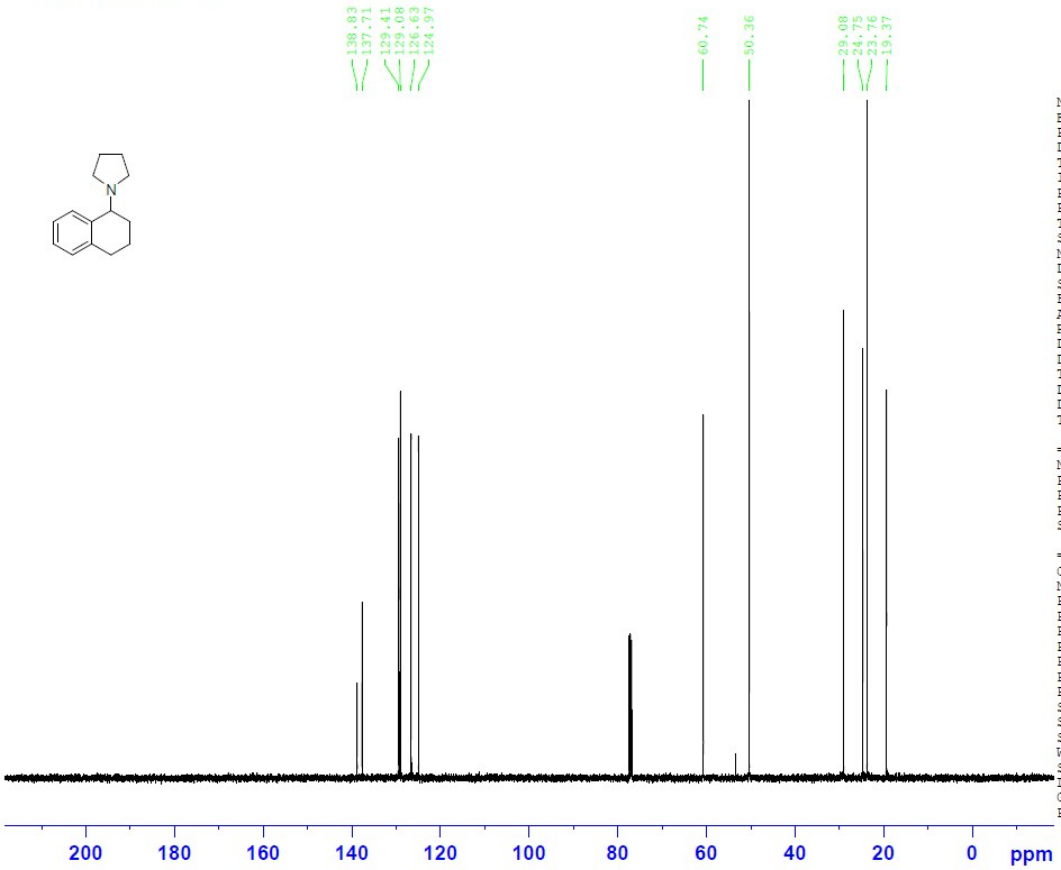

```
NAME          CMX-20190225-11
EXPNO                      11
PROCNO                      1
Date_                20190225
Time                    12.46
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          64
DS                           4
SWH                  29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                         203
DW                      16.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                        9.50 usec
PL1                      -1.00 dB
PL1W              112.80287170 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                       0.00 dB
PL12                     16.05 dB
PL13                     17.00 dB
PL2W               18.83080864 W
PL12W               0.46759412 W
PL13W               0.37572402 W
SFO2               500.1320005 MHz
SI                       32768
SF                 125.7577890 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

PROTON CDCl3 3u



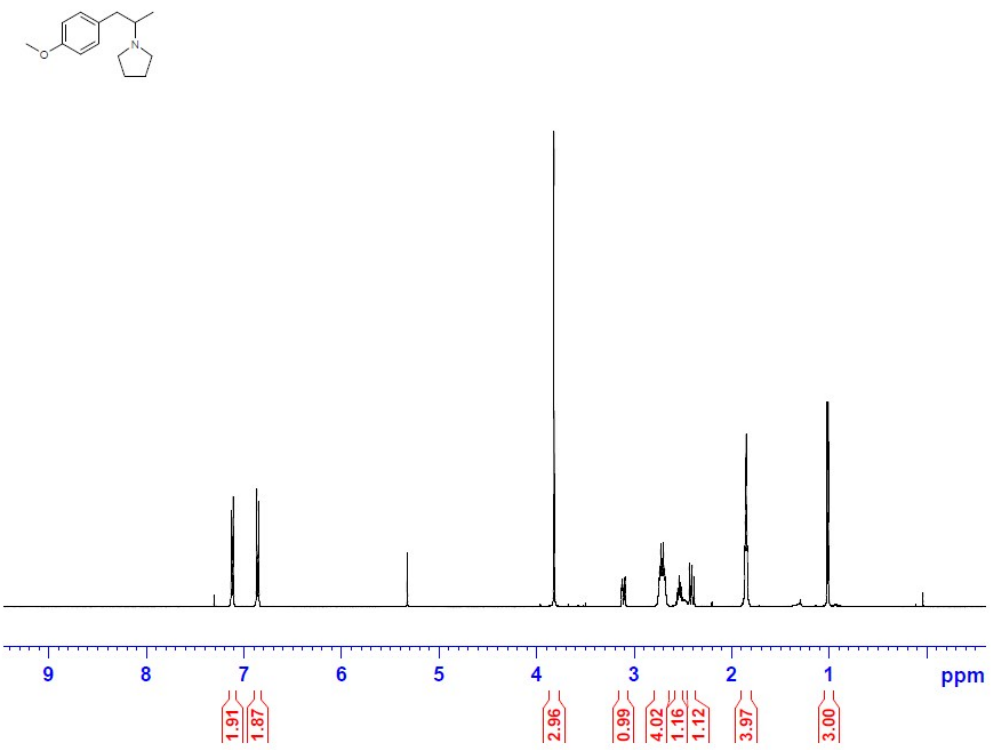

```
NAME          CMX-20170925-6
EXPNO                      10
PROCNO                      1
Date_                20170926
Time                     9.15
INSTRUM                 spect
PROBHD   5 mm PASEI 1H/
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                          71.8
DW                      48.400 usec
DE                       6.50 usec
TE                      301.9 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                        6.80 usec
PL1                       0.00 dB
PL1W               18.83080864 W
SFO1               500.1330885 MHz
SI                       32768
SF                 500.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

C13CPD CDCl3 3u



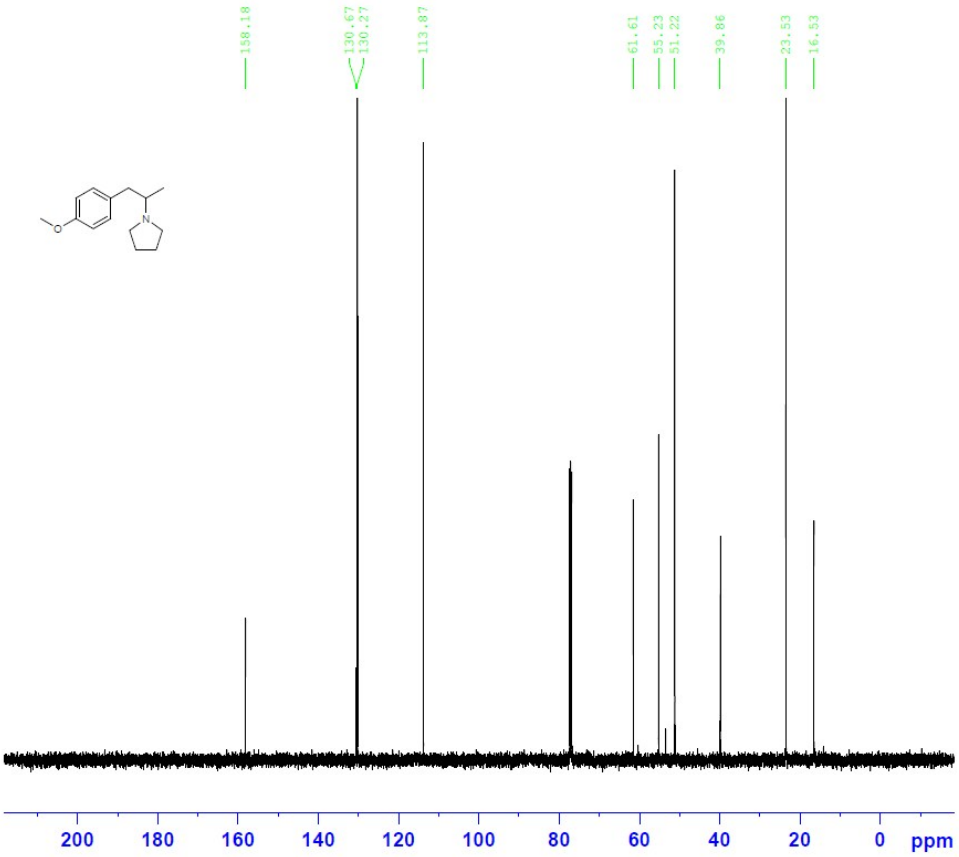

```
NAME        CMX-20190225-12
EXPNO                    11
PROCNO                    1
Date_              20190225
Time                  14.11
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       51
DS                        4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010548 sec
RG                      203
DW                  16.800 usec
DE                   6.50 usec
TE                  301.5 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.50 usec
PL1                  -1.00 dB
PL1W           112.80287170 W
SFO1            125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 16.05 dB
PL13                 17.00 dB
PL2W           18.83080864 W
PL12W           0.46759412 W
PL13W           0.37572402 W
SFO2           500.1320005 MHz
SI                    32768
SF             125.7577890 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

PROTON CDCl3 3t



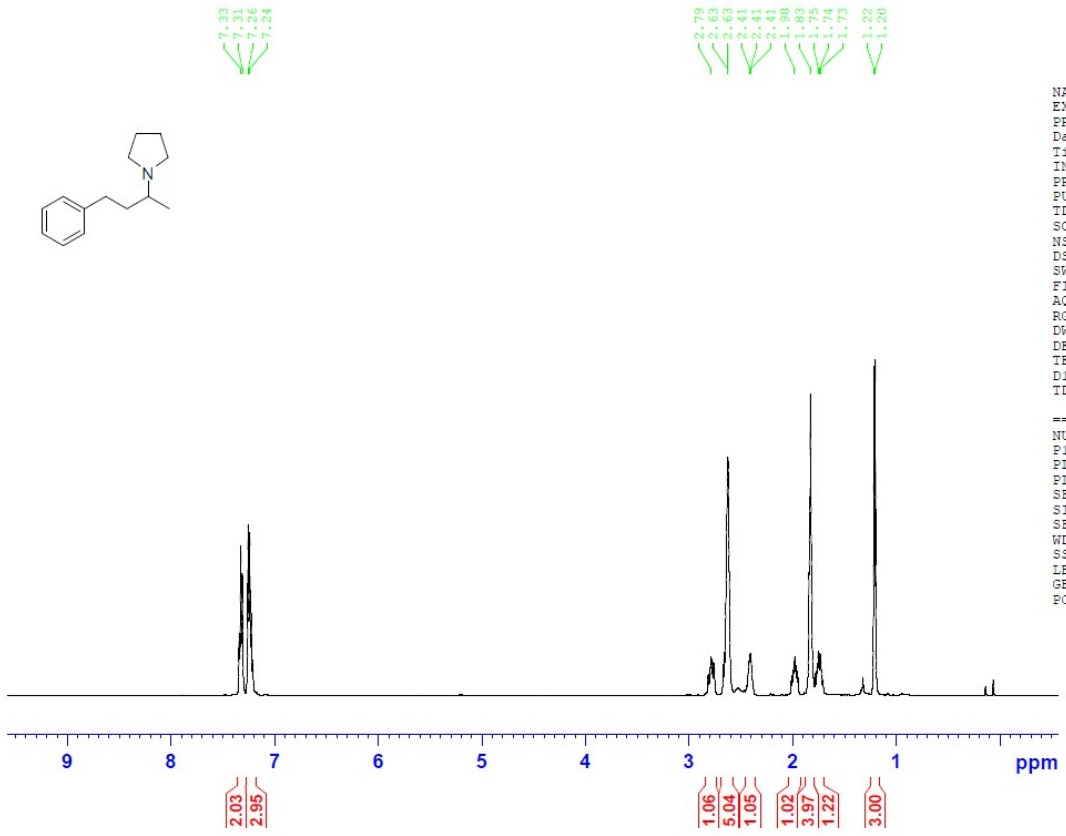

```
NAME        CMX-20180730-7
EXPNO                    10
PROCNO                    1
Date_              20180730
Time                  11.06
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719923 sec
RG                     50.8
DW                  48.400 usec
DE                   6.50 usec
TE                  302.6 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.60 usec
PL1                   0.00 dB
PL1W           18.83080864 W
SFO1           500.1330885 MHz
SI                    32768
SF             500.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

C13CPD CDCl3 3v

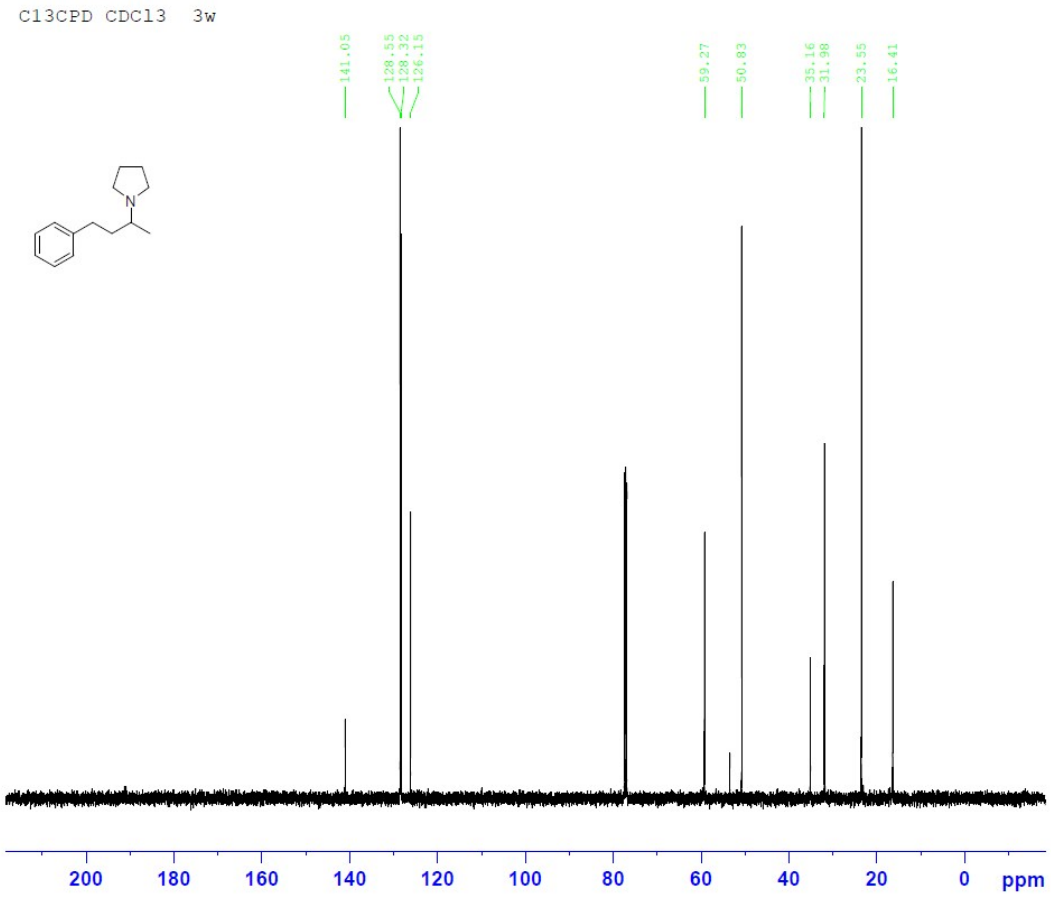



```
NAME          CMX-20190225-13
EXPNO                      11
PROCNO                      1
Date_                20190225
Time                    14.18
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         40
DS                          4
SWH                 29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                        203
DW                     16.800 usec
DE                      6.50 usec
TE                     300.8 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       9.50 usec
PL1                     -1.00 dB
PL1W              112.80287170 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W              18.83080864 W
PL12W              0.46759412 W
PL13W              0.37572402 W
SFO2               500.1320005 MHz
SI                        32768
SF                 125.7577890 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

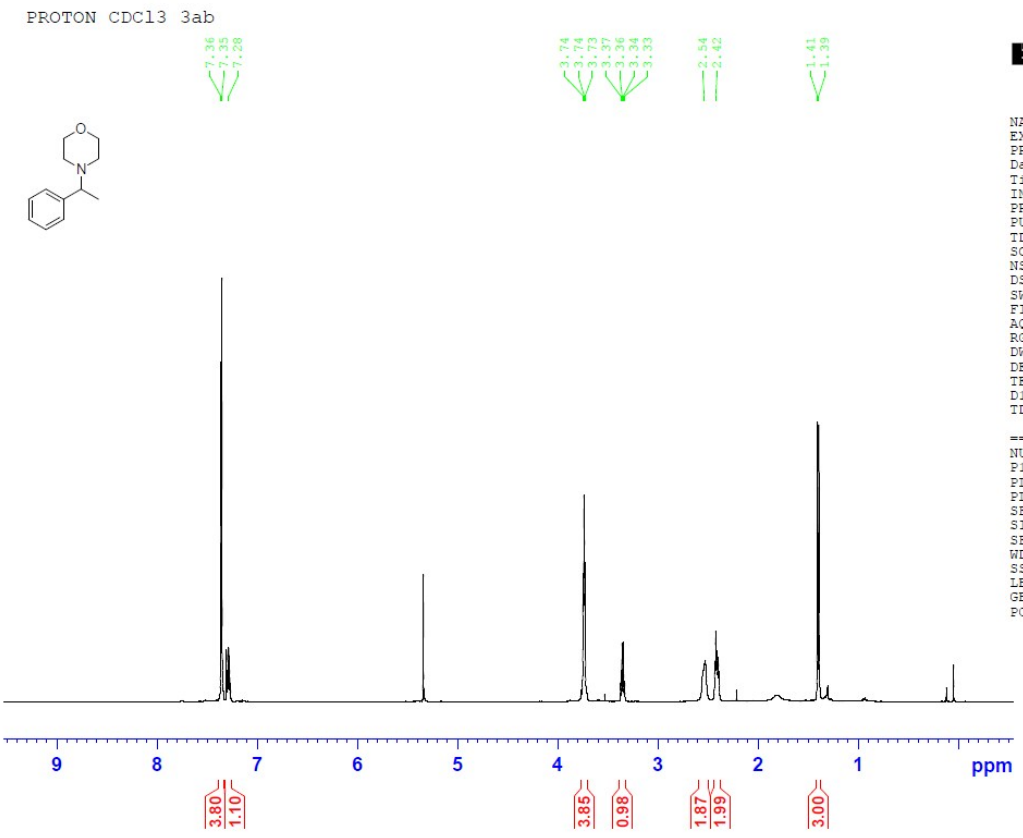
PROTON CDCl3 3u




```
NAME          CMX-20170919-6
EXPNO                      10
PROCNO                      1
Date_                20170919
Time                    11.32
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                         36
DW                     48.400 usec
DE                      6.50 usec
TE                     303.4 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.60 usec
PL1                      0.00 dB
PL1W              18.83080864 W
SFO1               500.1330885 MHz
SI                        32768
SF                 500.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

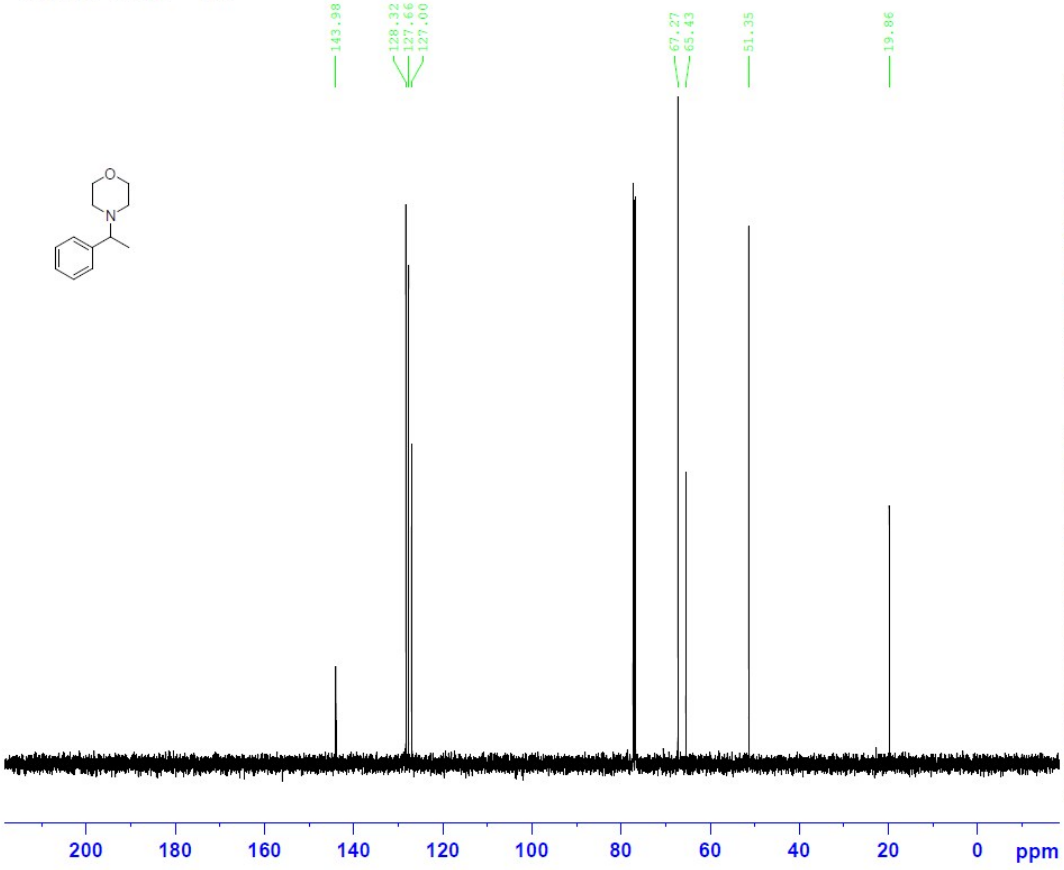



```
NAME          CMX-20190225-14
EXPNO                      11
PROCNO                      1
Date_                20190225
Time                    14.27
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          47
DS                           4
SWH                  29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                          203
DW                       16.800 usec
DE                        6.50 usec
TE                       301.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.50 usec
PL1                       -1.00 dB
PL1W               112.80287170 W
SFO1                125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PL2                        0.00 dB
PL12                      16.05 dB
PL13                      17.00 dB
PL2W                18.83080864 W
PL12W                0.46759412 W
PL13W                0.37572402 W
SFO2                500.1320005 MHz
SI                         32768
SF                  125.7577890 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```



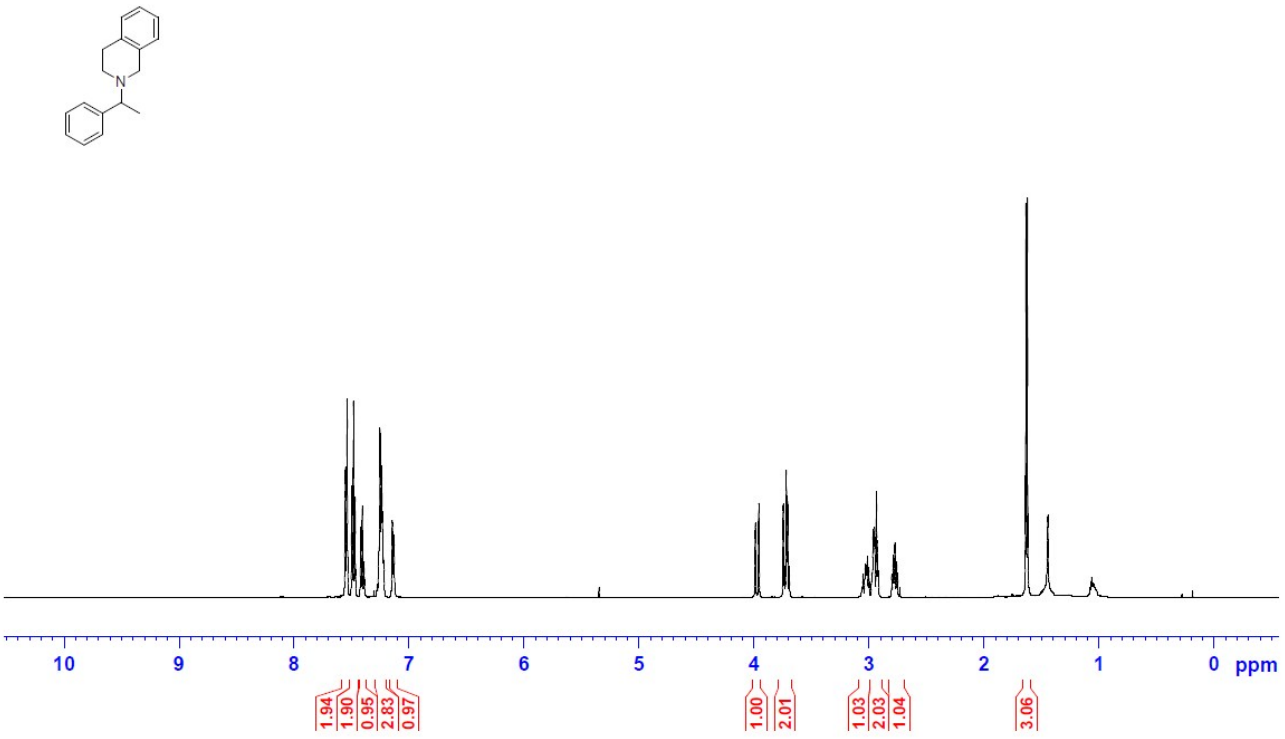

```
NAME          CMX-20180730-5
EXPNO                      10
PROCNO                      1
Date_                20180730
Time                    10.56
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                          80.6
DW                       48.400 usec
DE                        6.50 usec
TE                       302.8 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                        12.60 usec
PL1                        0.00 dB
PL1W               18.83080864 W
SFO1               500.1330885 MHz
SI                         32768
SF                 500.1300000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

C13CPD CDCl3 3ab

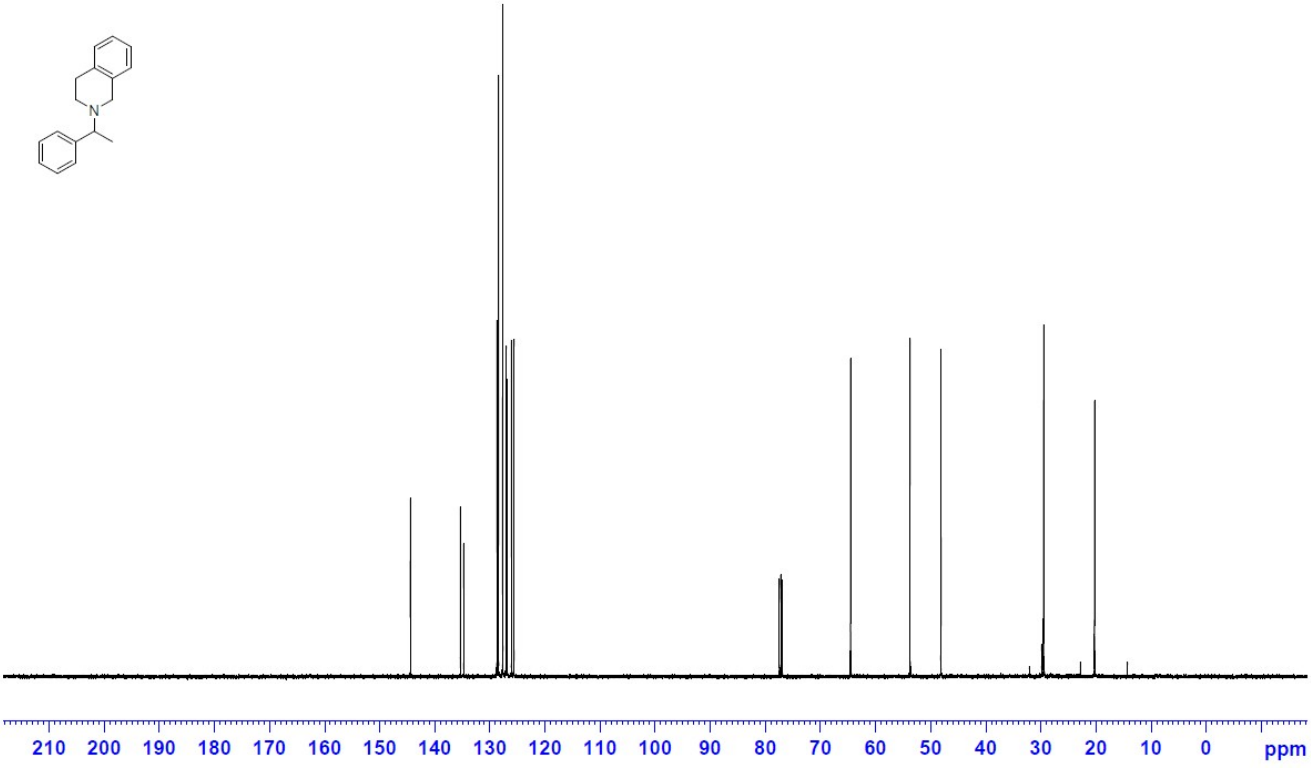



```
NAME        CMX-20190225-21
EXPNO                    11
PROCNO                    1
Date_              20190225
Time                  15.41
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       64
DS                        4
SWH               29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010548 sec
RG                      203
DW                   16.800 usec
DE                    6.50 usec
TE                   300.4 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.50 usec
PL1                  -1.00 dB
PL1W          112.80287170 W
SFO1           125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 16.05 dB
PL13                 17.00 dB
PL2W           18.83080864 W
PL12W           0.46759412 W
PL13W           0.37572402 W
SFO2          500.1320005 MHz
SI                    32768
SF             125.7577890 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

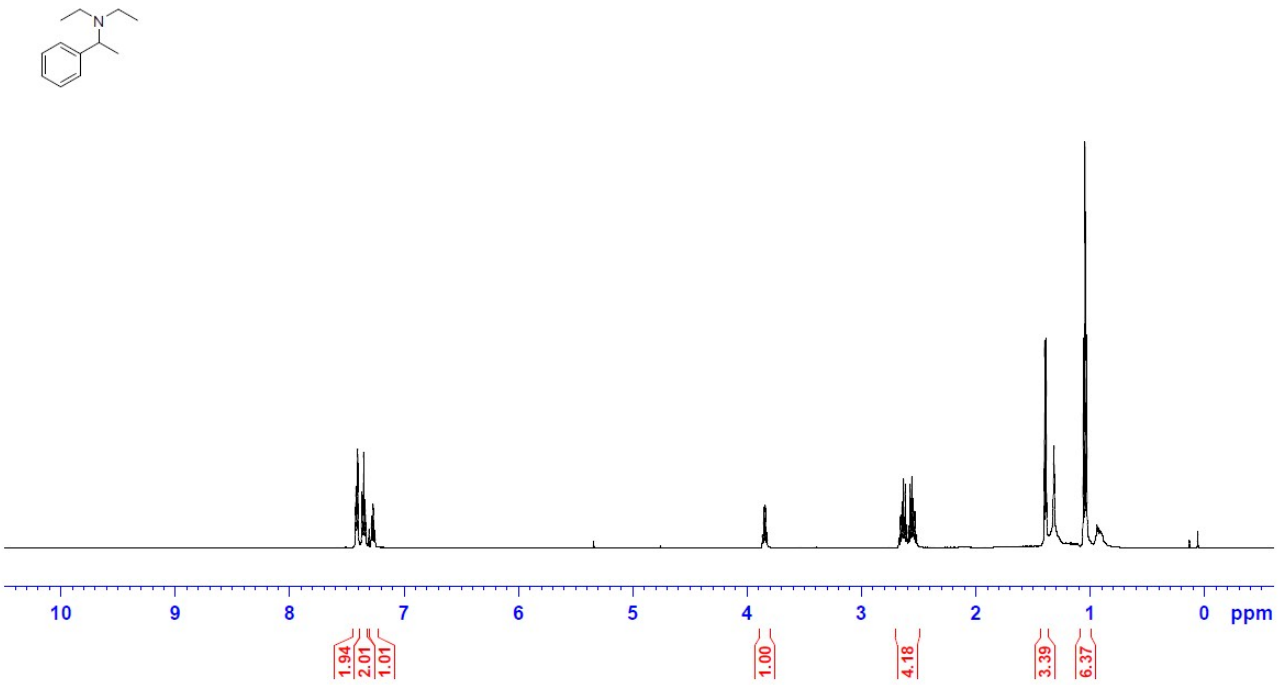
PROTON CDCl3 for 3ac



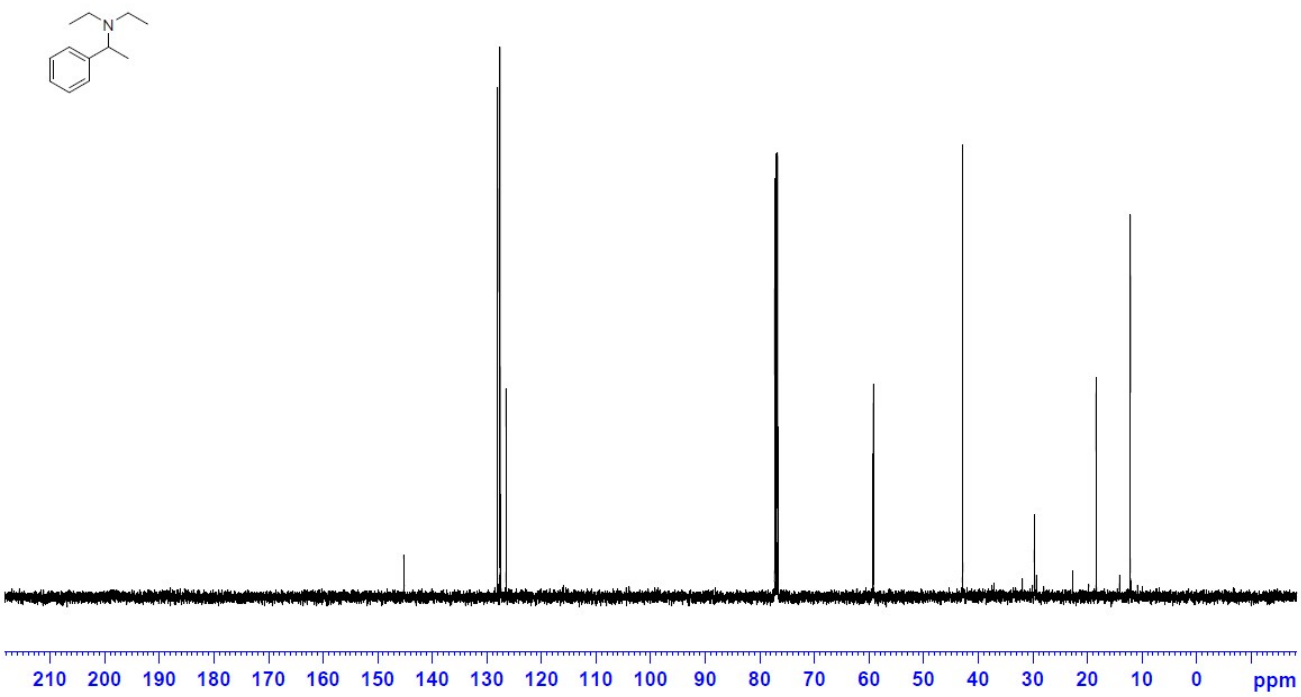
C13CPD CDCl3 3ac



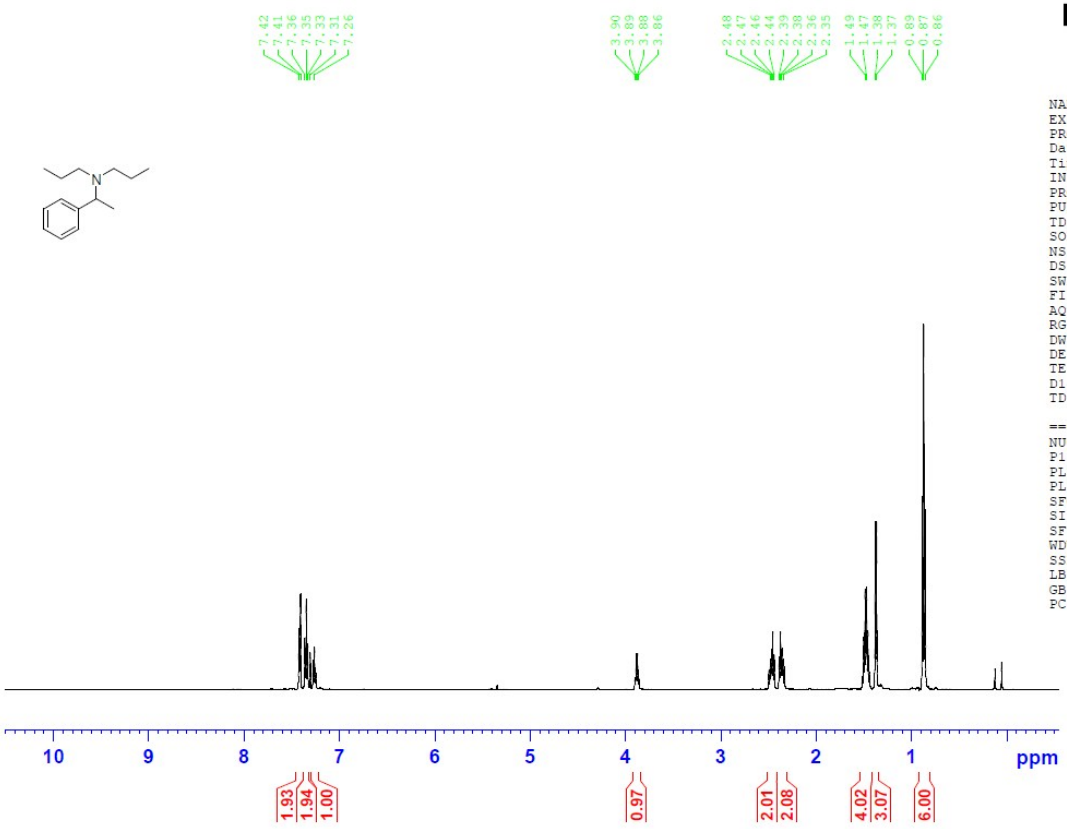
PROTON CDCl3 for 3ad



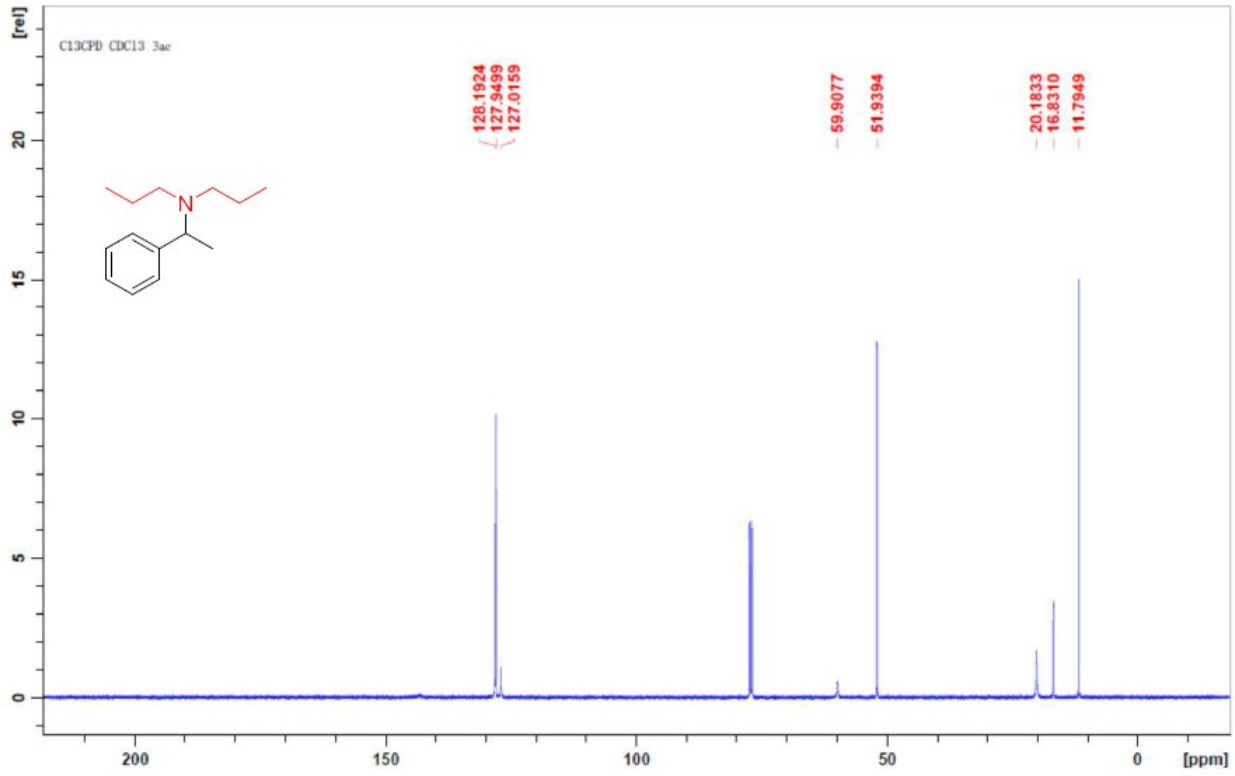
C13CPD CDCl3 3ad

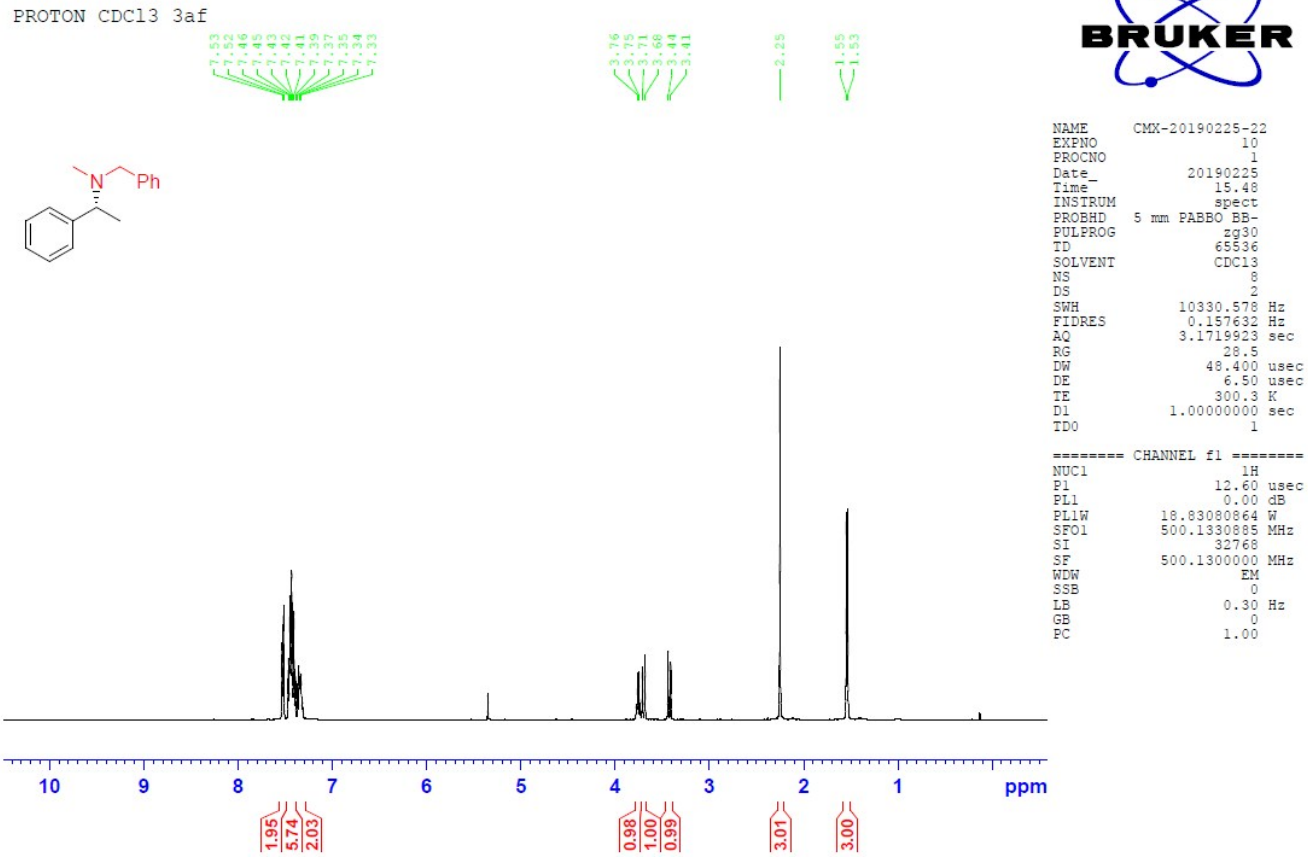


PROTON CDCl3 for 3ae



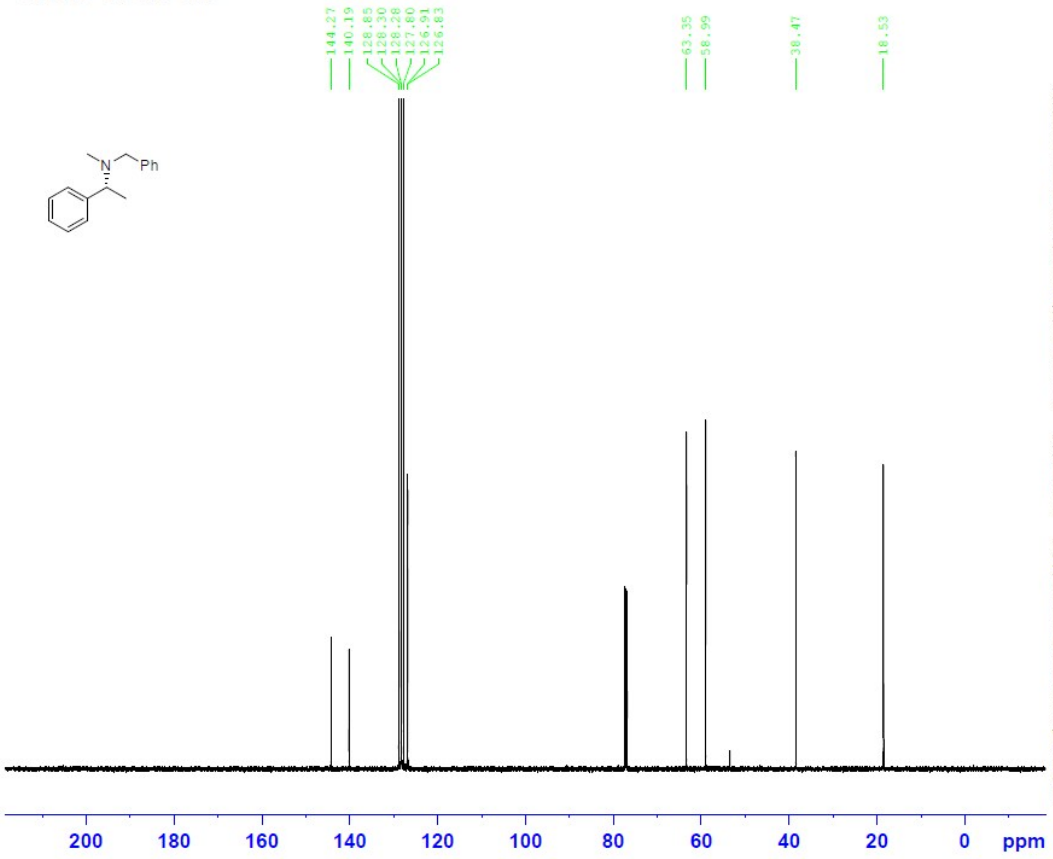

```
NAME        CMX-20181214-10
EXPNO                   20
PROCNO                   1
Date_             20181214
Time                 10.14
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                     64
DW               48.400 usec
DE                6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.60 usec
PL1                 0.00 dB
PL1W         18.83080864 W
SFO1         500.1330885 MHz
SI                  32768
SF           500.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```





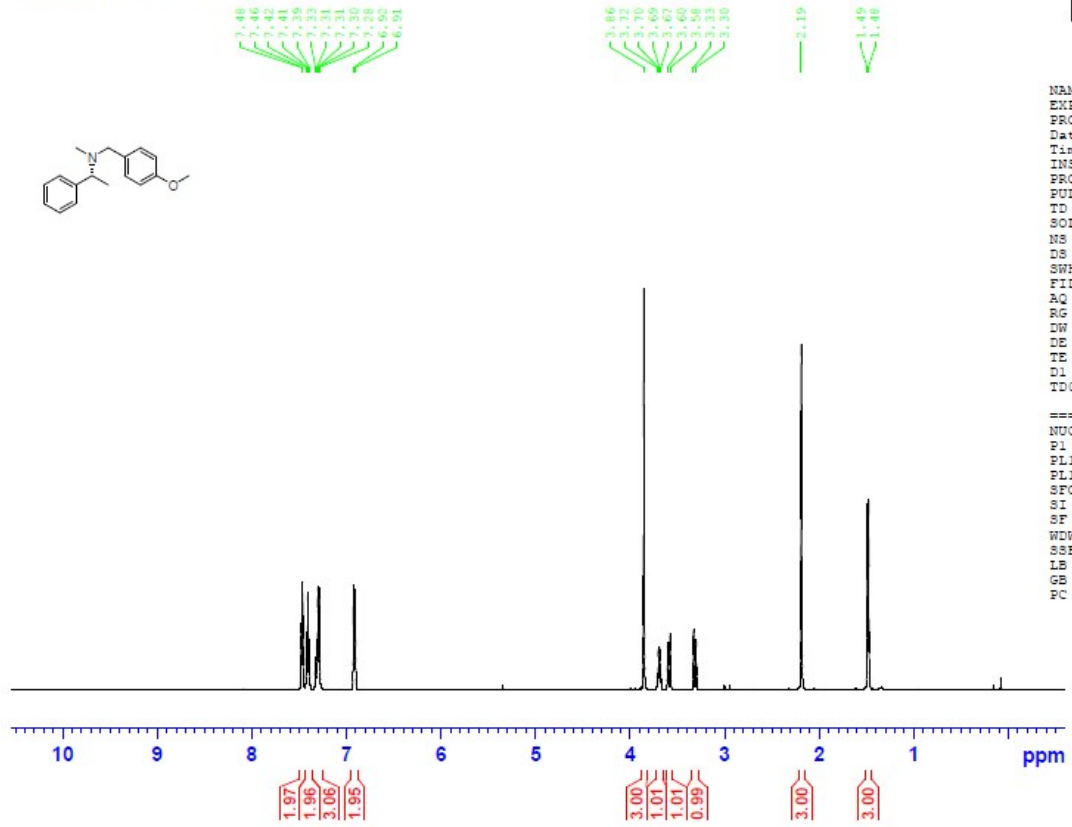

```
NAME          CMX-20190225-22
EXPNO                      10
PROCNO                      1
Date_                20190225
Time_                   15.48
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                 3.1719923 sec
RG                      28.5
DW                    48.400 usec
DE                     6.50 usec
TE                    300.3 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.60 usec
PL1                     0.00 dB
PL1W              18.83080864 W
SFO1              500.1330885 MHz
SI                     32768
SF                500.1300000 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
```

C13CPD CDCl3 3af



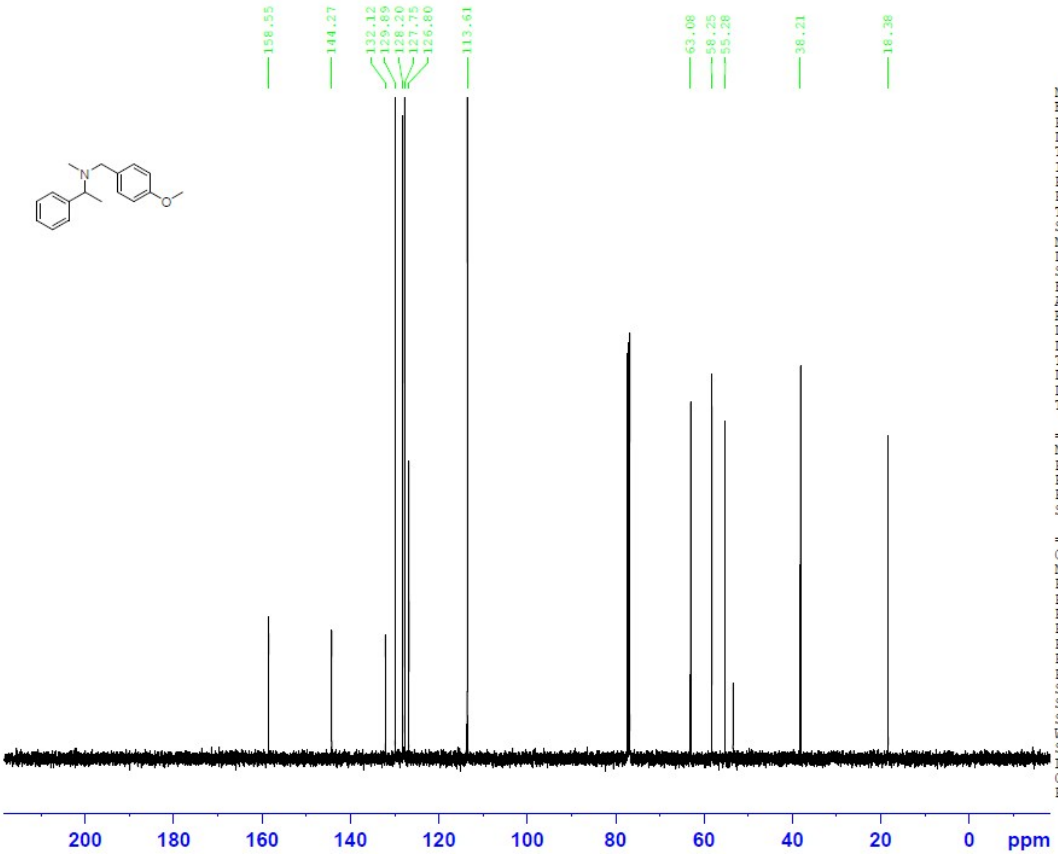

```
NAME          CMX-20190302-22
EXPNO                      10
PROCNO                      1
Date_                20190302
Time                    11.17
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        116
DS                          4
SWH                 29761.904 Hz
FIDRES              0.454131 Hz
AQ                  1.1010548 sec
RG                        203
DW                    16.800 usec
DE                     6.50 usec
TE                     298.5 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -1.00 dB
PL1W             112.80287170 W
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   16.05 dB
PL13                   17.00 dB
PL2W              18.83080864 W
PL12W              0.46759412 W
PL13W              0.37572402 W
SFO2             500.1320005 MHz
SI                      32768
SF               125.7577890 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

PROTON CDCl3 for 3ag



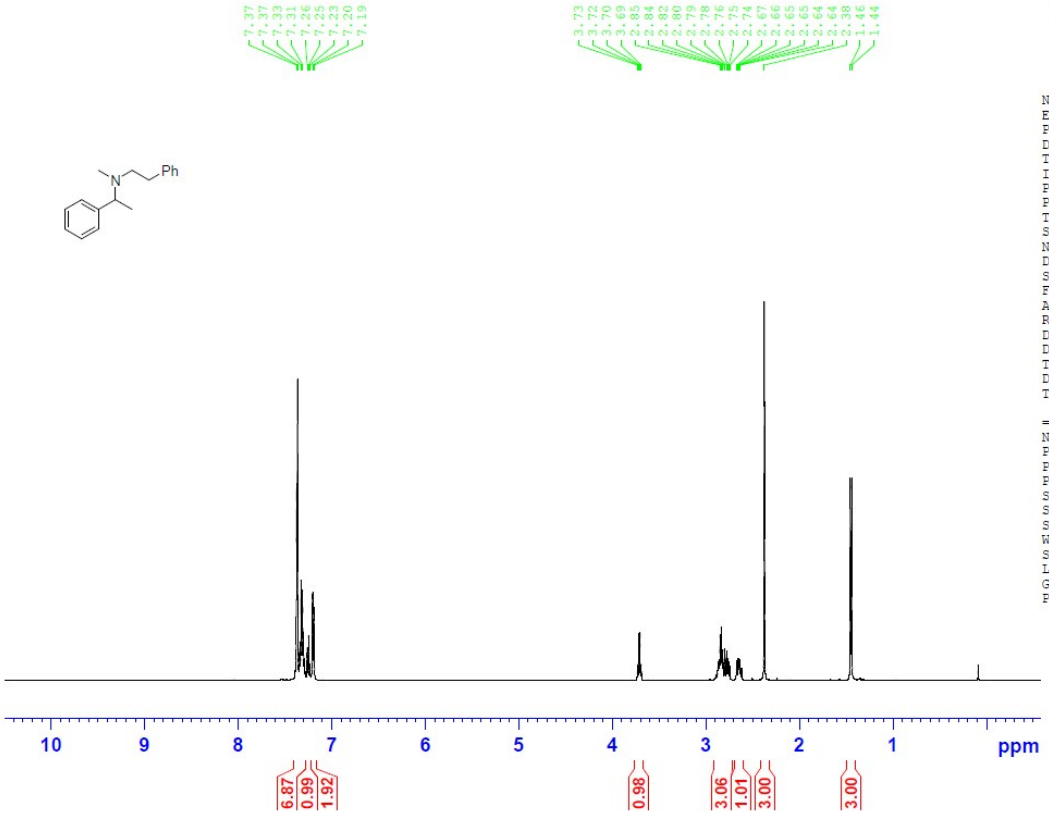

```
NAME          CMX-20190108-1
EXPNO                      10
PROCNO                      1
Date_                20190108
Time                    10.18
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719923 sec
RG                         40.3
DW                    48.400 usec
DE                     6.50 usec
TE                     299.1 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     12.60 usec
PL1                     0.00 dB
PL1W              18.83080864 W
SFO1             500.1330885 MHz
SI                      32768
SF               500.1300000 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```

C13CPD CDCl3 3ag

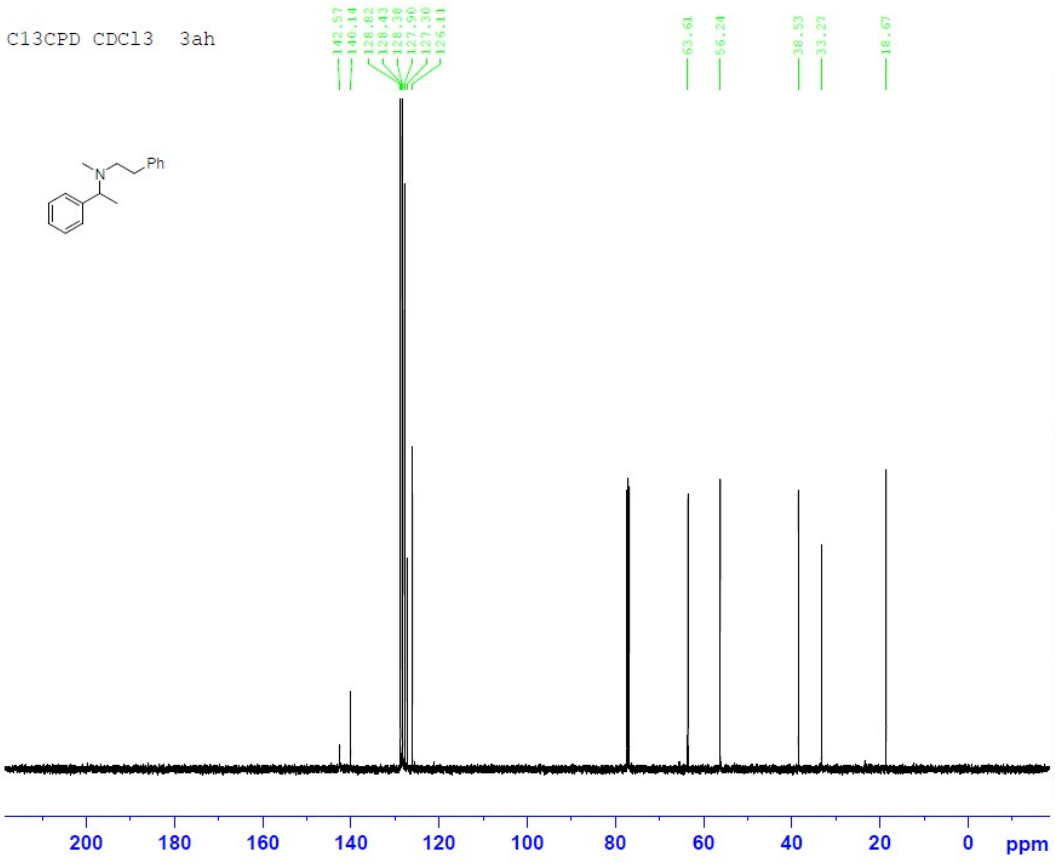



```
NAME      CMX-20190225-15
EXPNO                  11
PROCNO                  1
Date_            20190225
Time                14.34
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     54
DS                      4
SWH             29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                    203
DW                16.800 usec
DE                 6.50 usec
TE                301.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -1.00 dB
PL1W        112.80287170 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.05 dB
PL13               17.00 dB
PL2W         18.83080864 W
PL12W         0.46759412 W
PL13W         0.37572402 W
SFO2         500.1320005 MHz
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

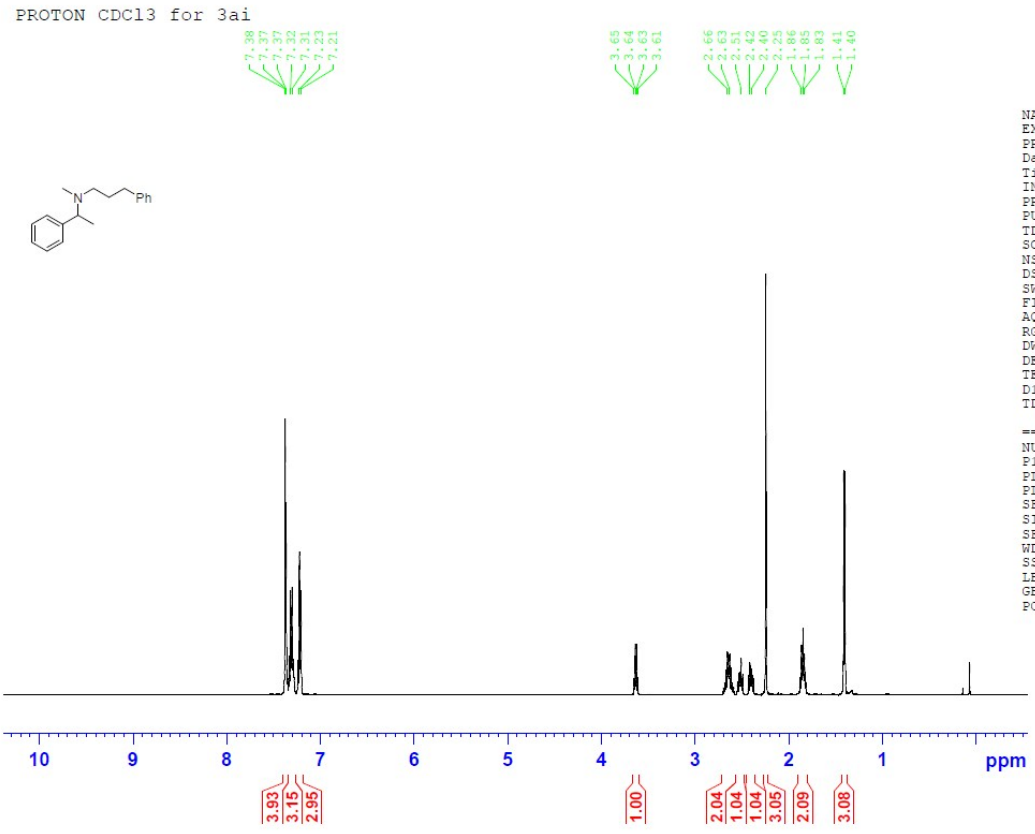
PROTON CDCl3 for 3ah




```
NAME      CMX-20181130-1
EXPNO                  10
PROCNO                  1
Date_            20181130
Time                22.34
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                   45.2
DW                48.400 usec
DE                 6.50 usec
TE                301.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.60 usec
PL1                0.00 dB
PL1W        18.83080864 W
SFO1         500.1330885 MHz
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```

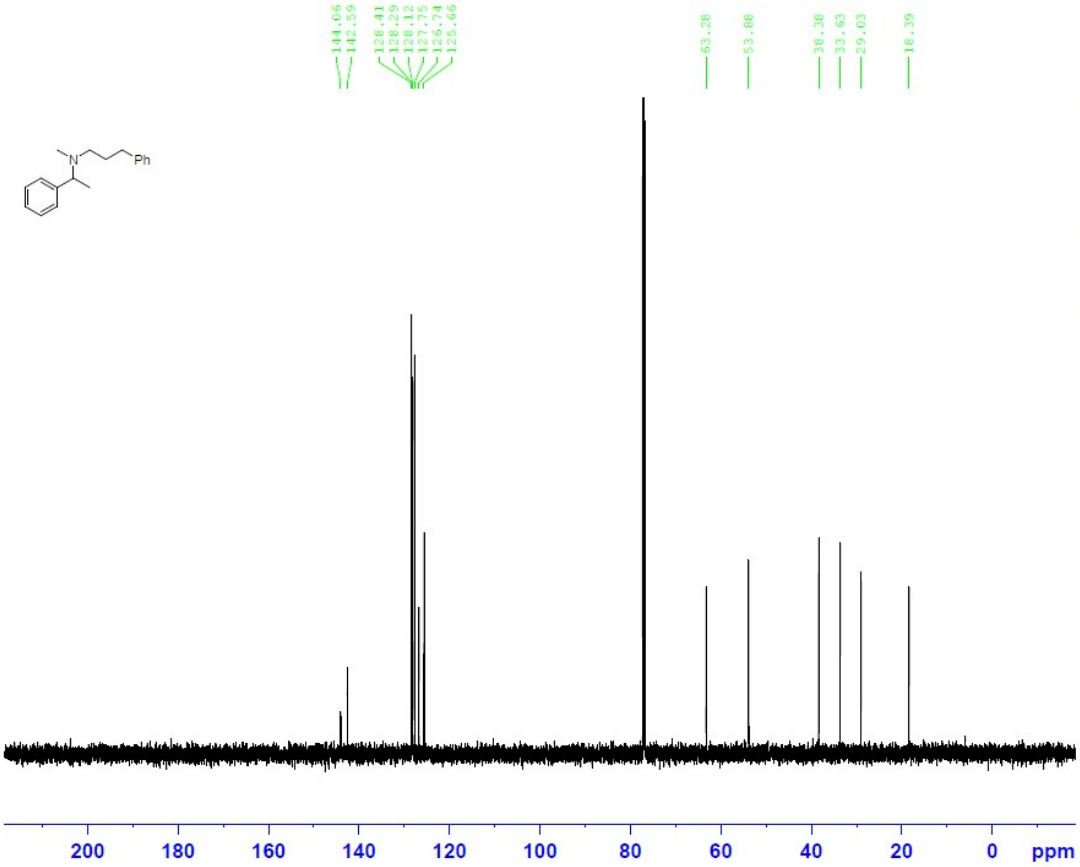



```
NAME        CMX-20190227-15
EXPNO                    11
PROCNO                    1
Date_              20190228
Time                   9.11
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      64
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                     203
DW                  16.800 usec
DE                   6.50 usec
TE                  296.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -1.00 dB
PL1W         112.80287170 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 16.05 dB
PL13                 17.00 dB
PL2W          18.83080864 W
PL12W          0.46759412 W
PL13W          0.37572402 W
SFO2          500.1320005 MHz
SI                   32768
SF            125.7577890 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



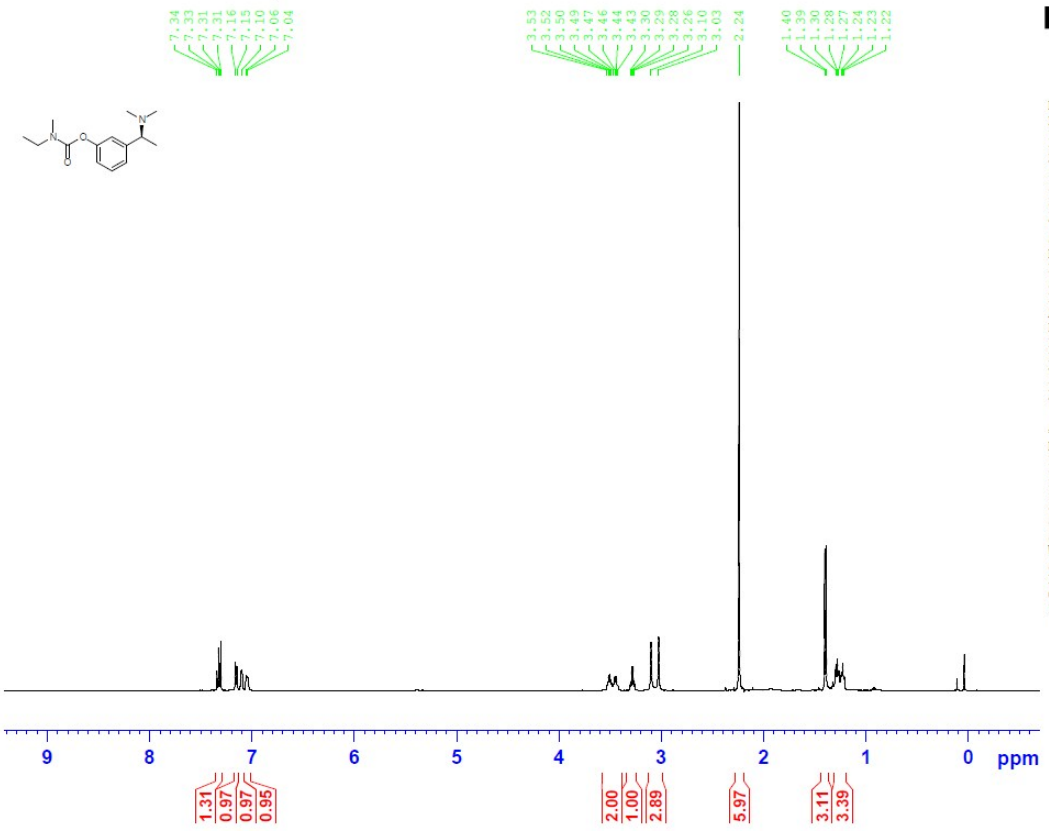

```
NAME        CMX-20181130-2
EXPNO                    10
PROCNO                    1
Date_              20181130
Time                  22.38
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                      64
DW                  48.400 usec
DE                   6.50 usec
TE                  301.3 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.60 usec
PL1                   0.00 dB
PL1W          18.83080864 W
SFO1          500.1330885 MHz
SI                   32768
SF            500.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

C13CPD CDCl3 3ai



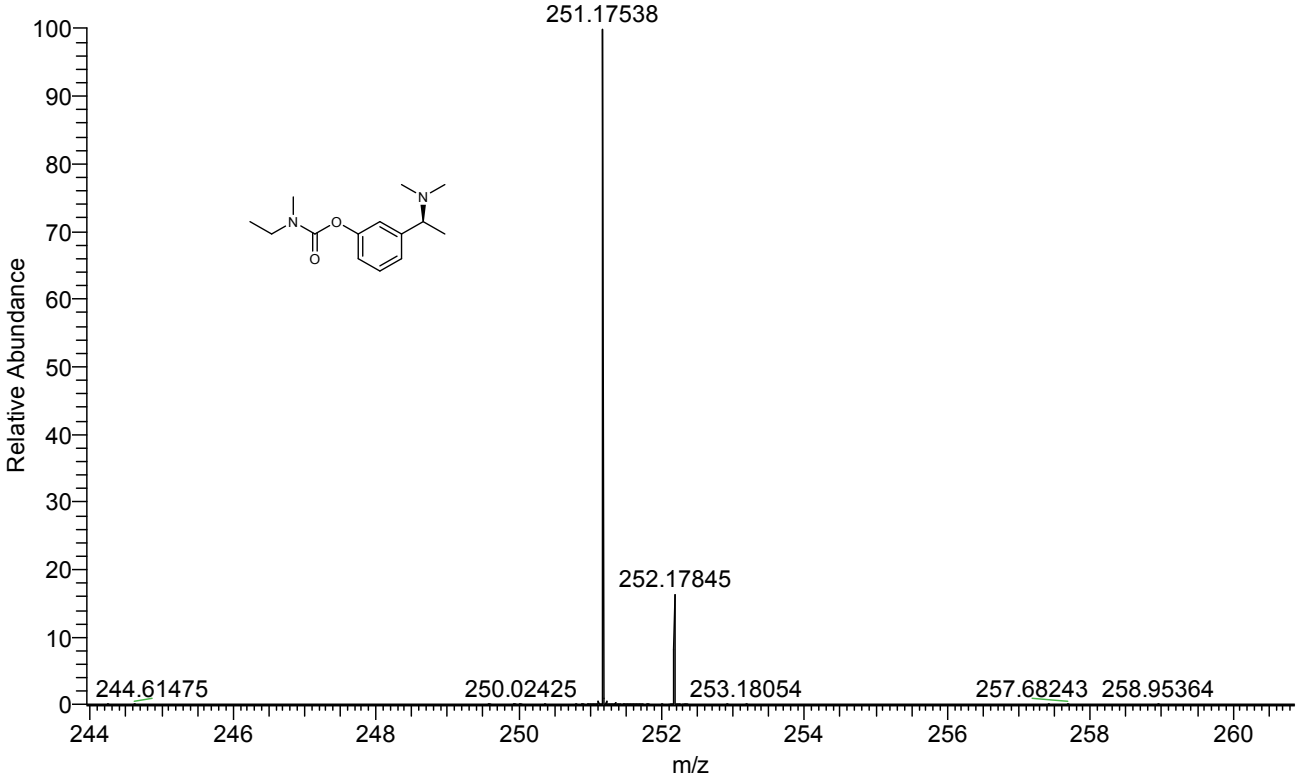

```
NAME          CMX-20181207-02
EXPNO                      11
PROCNO                      1
Date_                20181207
Time                    14.53
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          46
DS                           4
SWH                  29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                         203
DW                      16.800 usec
DE                       6.50 usec
TE                      297.7 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       9.50 usec
PL1                     -1.00 dB
PL1W              112.80287170 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W              18.83080864 W
PL12W              0.46759412 W
PL13W              0.37572402 W
SFO2               500.1320005 MHz
SI                       32768
SF                 125.7577890 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

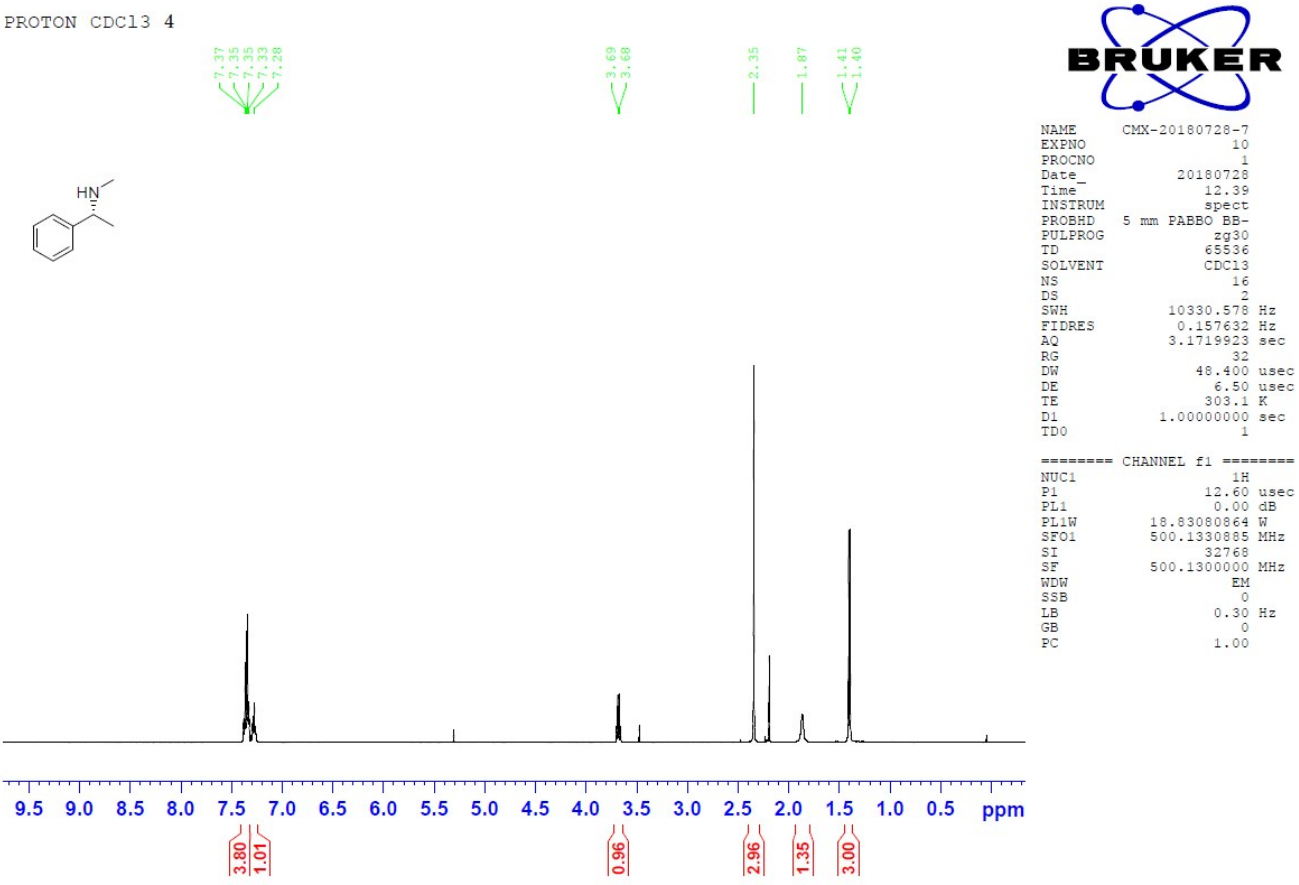
PROTON CDCl3 rivastigmine




```
NAME          CMX-20180116-05
EXPNO                      10
PROCNO                      1
Date_                20180116
Time                    11.34
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                          90.5
DW                      48.400 usec
DE                       6.50 usec
TE                      299.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                        1H
P1                       12.60 usec
PL1                       0.00 dB
PL1W              18.83080864 W
SFO1               500.1330885 MHz
SI                       32768
SF                 500.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

35 #15 RT: 0.21 AV: 1 NL: 9.48E8
T: FTMS + p ESI Full ms [150.00-2000.00]

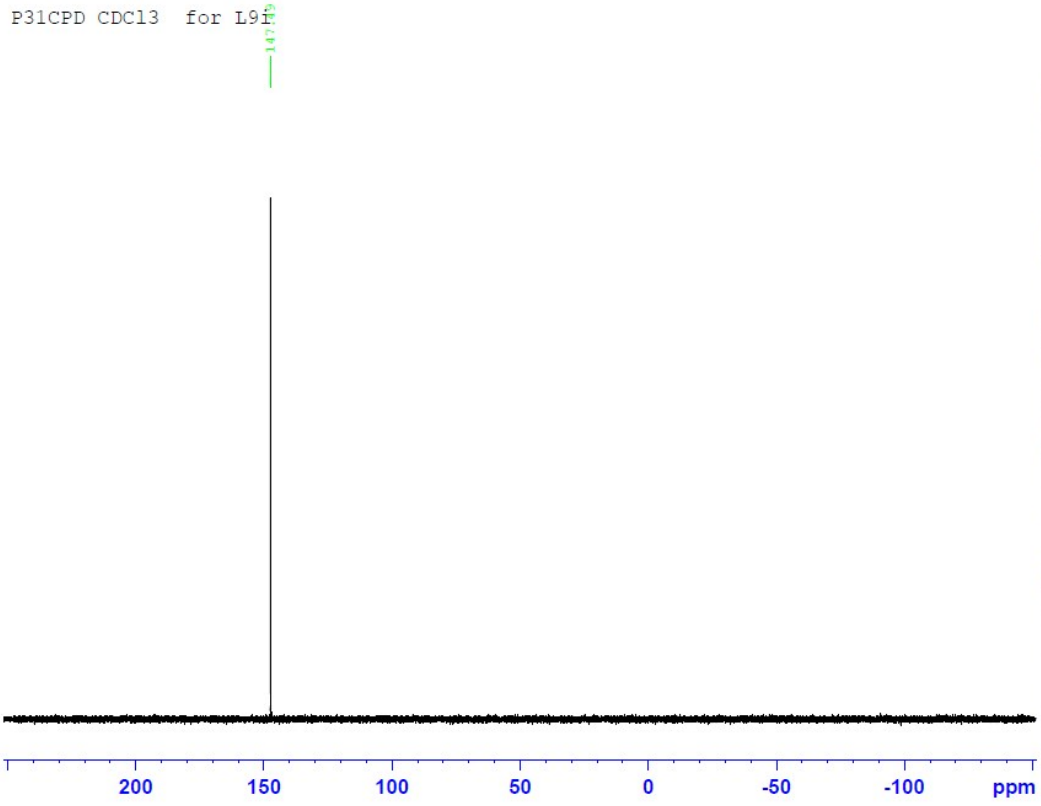




BRUKER

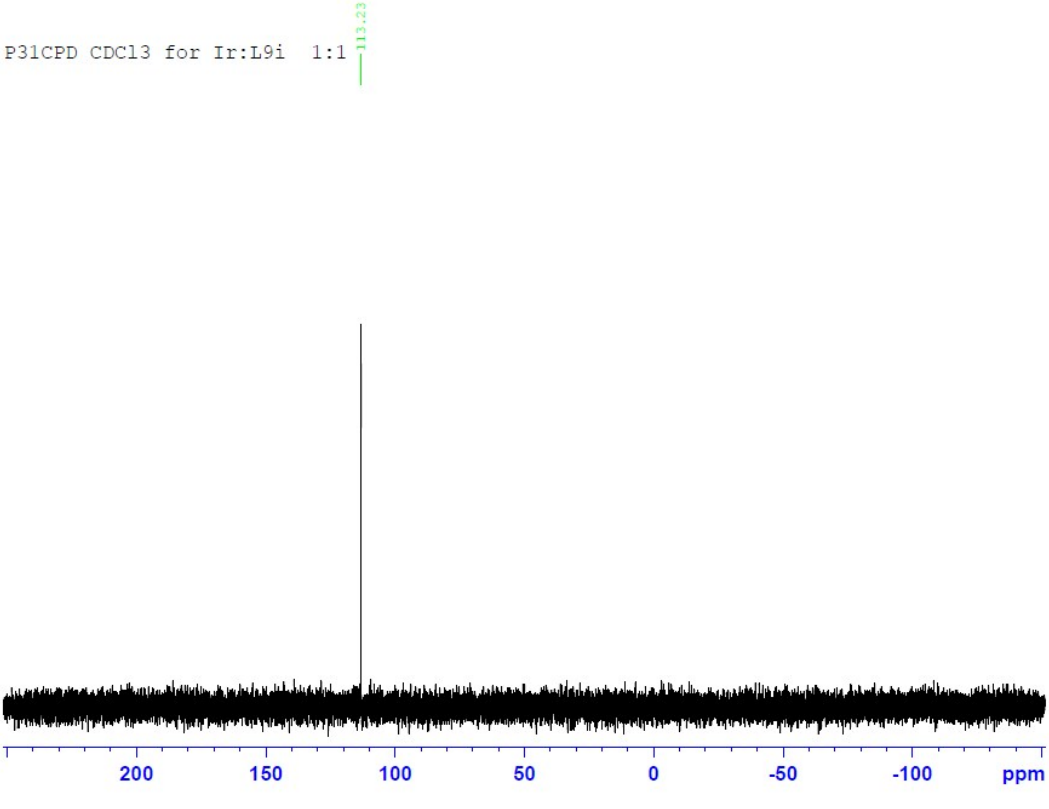
NAME	CMX-20180728-7
EXPNO	10
PROCNO	1
Date_	20180728
Time	12.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	32
DW	48.400 usec
DE	6.50 usec
TE	303.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.60 usec
PL1	0.00 dB
PL1W	18.83080864 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

P31CPD CDCl3 for L9i



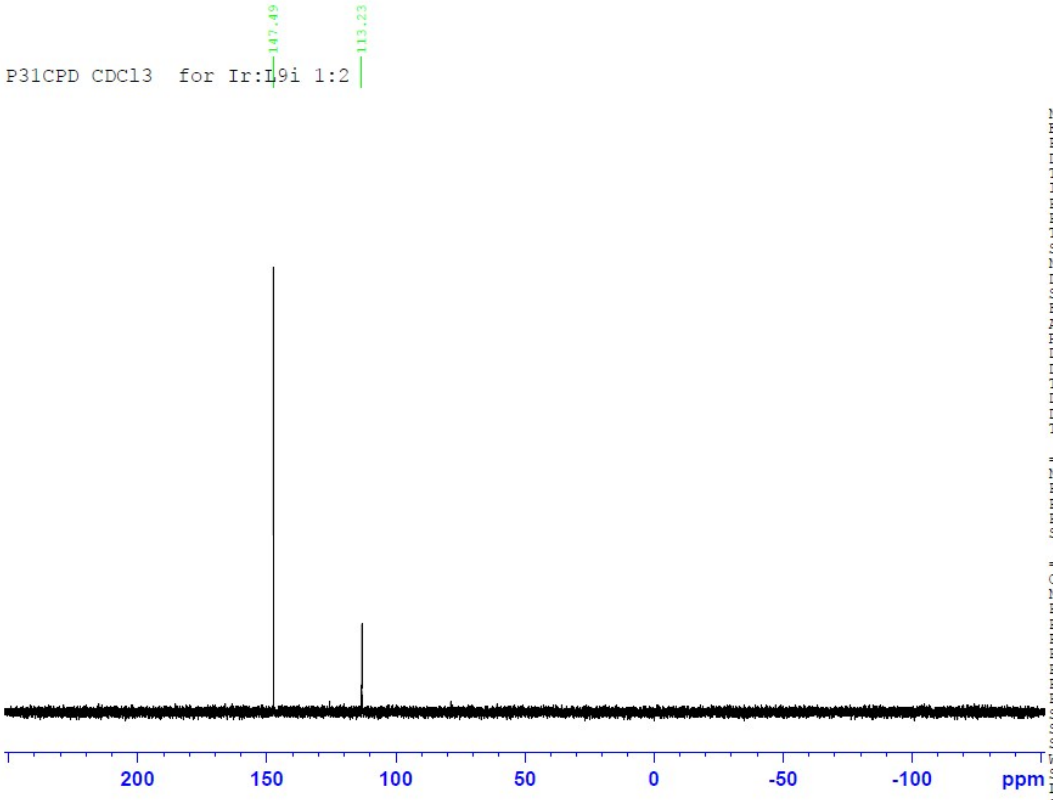

```
NAME          CMX-20190103-09
EXPNO                      10
PROCNO                      1
Date_                20190103
Time                     9.30
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                81521.742 Hz
FIDRES              1.243923 Hz
AQ                  0.4020041 sec
RG                        203
DW                      6.133 usec
DE                      6.50 usec
TE                      298.4 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       31P
P1                      11.30 usec
PL1                      0.00 dB
PL1W               82.64508057 W
SFO1              202.4664578 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W               18.83080864 W
PL12W               0.46759412 W
PL13W               0.37572402 W
SFO2              500.1320005 MHz
SI                        32768
SF                202.4563350 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

P31CPD CDCl3 for Ir:L9i 1:1



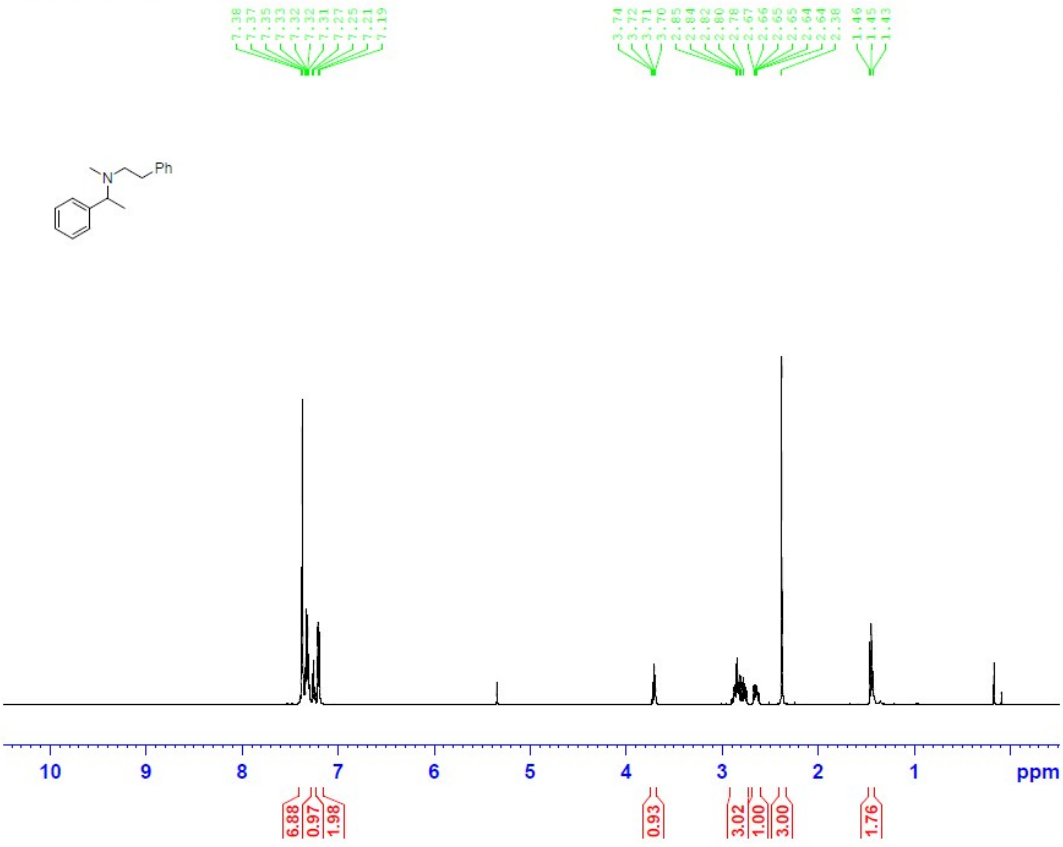

```
NAME          CMX-20190103-04
EXPNO                      10
PROCNO                      1
Date_                20190103
Time                     9.03
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                81521.742 Hz
FIDRES              1.243923 Hz
AQ                  0.4020041 sec
RG                        203
DW                      6.133 usec
DE                      6.50 usec
TE                      298.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       31P
P1                      11.30 usec
PL1                      0.00 dB
PL1W               82.64508057 W
SFO1              202.4664578 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W               18.83080864 W
PL12W               0.46759412 W
PL13W               0.37572402 W
SFO2              500.1320005 MHz
SI                        32768
SF                202.4563350 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

P31CPD CDCl3 for Ir:19i 1:2



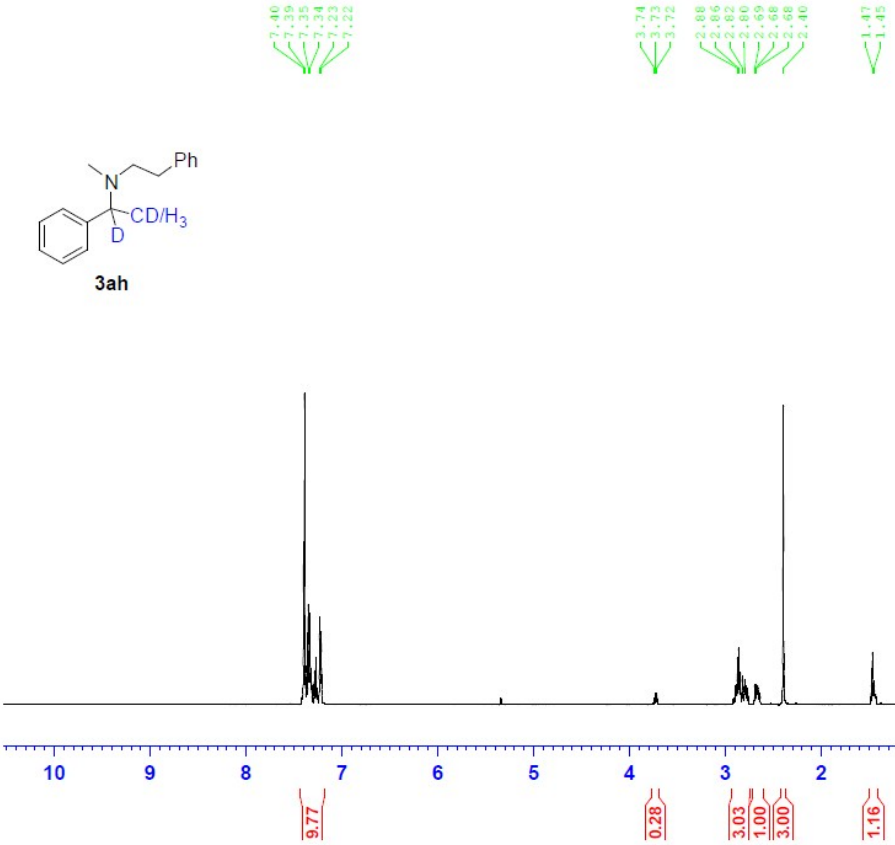

```
NAME          CMX-20190103-05
EXPNO                      10
PROCNO                      1
Date_                20190103
Time                     9.07
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                81521.742 Hz
FIDRES              1.243923 Hz
AQ                  0.4020041 sec
RG                        203
DW                      6.133 usec
DE                      6.50 usec
TE                      298.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       31P
P1                      11.30 usec
PL1                      0.00 dB
PL1W               82.64508057 W
SFO1              202.4664578 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    16.05 dB
PL13                    17.00 dB
PL2W               18.83080864 W
PL12W               0.46759412 W
PL13W               0.37572402 W
SFO2              500.1320005 MHz
SI                        32768
SF                202.4563350 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

PROTON CDCl3 for 3ah from 1a-d3




```
NAME          CMX-20190103-01
EXPNO                      10
PROCNO                      1
Date_                20190103
Time                     8.48
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719923 sec
RG                       40.3
DW                     48.400 usec
DE                      6.50 usec
TE                      298.7 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.60 usec
PL1                      0.00 dB
PL1W               18.83080864 W
SFO1              500.1330885 MHz
SI                        32768
SF                500.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

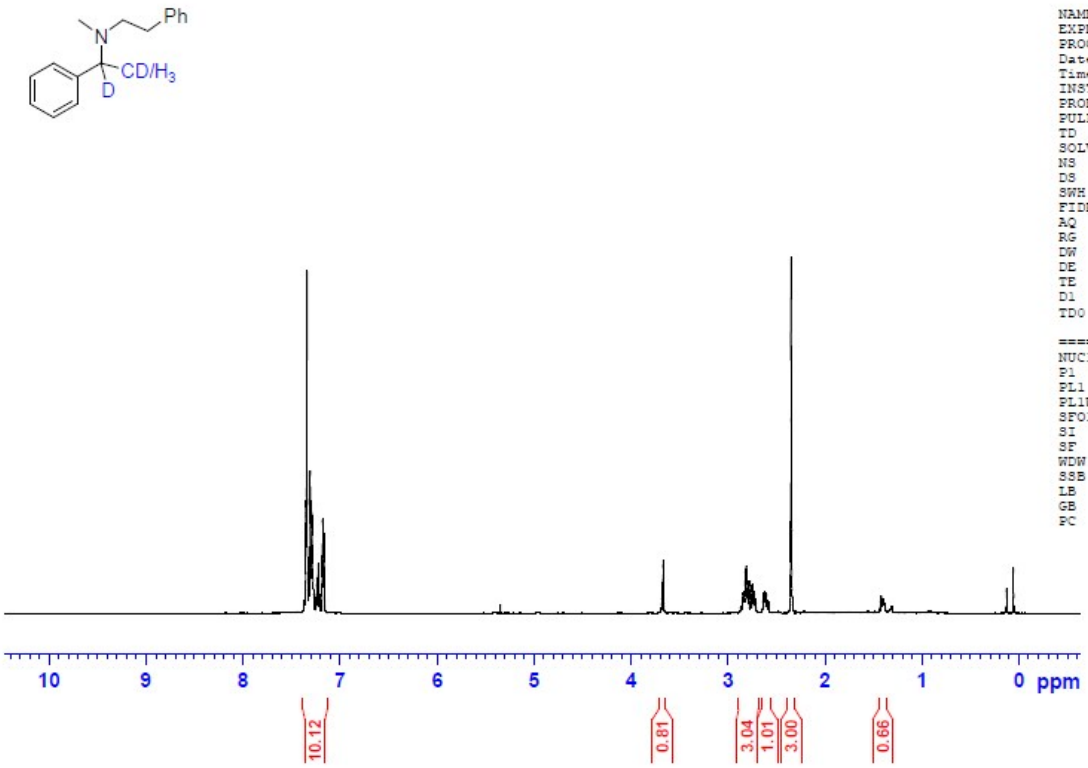
PROTON CDCl3 for 3ah with D2



3ah

```
NAME        CMX-20181226-01
EXPNO                   10
PROCNO                   1
Date_             20181226
Time                  8.42
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                      32
DW                 48.400 usec
DE                  6.50 usec
TE                 299.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  12.60 usec
PL1                  0.00 dB
PL1W          18.83080864 W
SFO1          500.1330885 MHz
SI                   32768
SF            500.1300000 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

PROTON CDCl3 for 3ah with MeOD




```
NAME        CMX-20181214-11
EXPNO                   20
PROCNO                   1
Date_             20181214
Time                 10.19
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                    90.5
DW                 48.400 usec
DE                  6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  12.60 usec
PL1                  0.00 dB
PL1W          18.83080864 W
SFO1          500.1330885 MHz
SI                   32768
SF            500.1300000 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```