Supplementary Material (ESI) for Chemical Communications

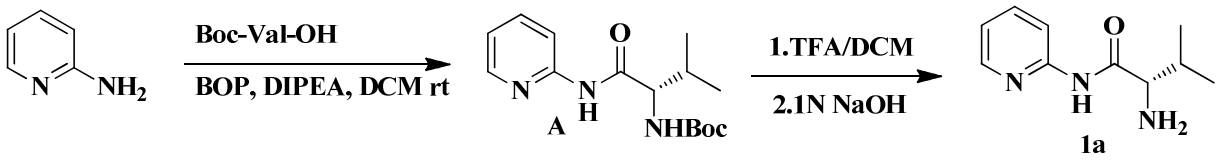
Primary amine-metal Lewis acid bifunctional catalysts based on a simple bidentate ligand: direct asymmetric aldol reaction

Philias Daka, Zhenghu Xu, Alex Alexandru and Hong Wang*

Miami University, Department of Chemistry and Biochemistry, Oxford, Ohio 45056

General: All NMR spectra were recorded on Bruker-500 or 300 MHz spectrometer. *Ee* values were measured by chiral HPLC analysis using Gold Nouveau Chromatography system and the data was recorded on Shimadzu C-R6A Chromatopac integrator. Chiralpak AD-H and As-H columns were purchased from Daicel Chemical Industries. Routine monitoring of the reactions was performed by TLC using precoated silica gel plates. Cyclohexanone was ACS reagent pure and the rest of the solvents were purchased from either Acros or Aldrich and used directly without further purification.

Synthesis of Ligands



To a stirred solution of N-Boc-L-valine (2.17 g, 10 mmol) in CH_2Cl_2 (100 mL), 2-amino-pyridine (10 mmol, 0.94 g), BOP (10 mmol, 4.42 g) and DIPEA (1.25 mL, 10 mmol) at 0 ^oC were added. This reaction mixture was stirred at room temperature for 24 hrs. The solution was washed with aqueous $NaHCO_3$. The organic phase was evaporated under reduced pressure and purified by column chromatography (silica gel, eluent hexane/ethylacetate, 5/1) to give the pure product **A** (2.1 g, 72%). ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 1.47 (s, 9H), 2.22-2.28 (m, 1H), 4.10-4.17 (m, 1H), 4.35 (br, 2H), 5.12 (m, 1H), 6.27 (d, J =7.8 Hz, 1H), 7.28 (t, J =7.8 Hz, 1H), 7.57 (d, J =7.8 Hz, 1H), 8.12 (br, 1H).

The obtained N-Boc compound **A** (2.2 g) was dissolved into DCM (10 mL) and TFA (10 mL) and stirred at rt for 2 hrs. The reaction mixture was evaporated and dissolved in Ethyl Acetate. 1 N NaOH solution was used to tune pH to 8 and the mixture was extracted with Ethyl Acetate. The solvent was evaporated to dryness to get the pure product **1a** (1.20 g, 87%). Similar procedure was followed for other ligands.

General procedure of the enantioselective aldol reaction: A mixture of $CuCl_2$ (5.4 mg, 0.04 mmol, 20 mol%) $AgSbF_6$ (27.5 mg, 0.08 mmol, 40 mol%), and 0.04 mmol, 20 mol% of the appropriate ligand was stirred at room temperature for 4 hrs in 1mL cyclohexanone (*neat*). The appropriate aldehyde (0.2 mmol) was then added. The resulting mixture was stirred for 3-48 hrs. After the reaction was completed (monitored by TLC), the reaction mixture was treated with saturated ammonium chloride solution, and the mixture extracted with ethyl acetate. After removal of the solvent mixture, ^{1}HNMR was taken to determine diastereoselectivity. The residue was purified through column chromatography on silica gel (eluent: mixture of Hexane and ethyl acetate,) to give pure products. All aldol products are known compounds and their spectroscopic data are identical with those reported. The *ee* values were determined by chiral HPLC analysis. HPLC conditions and retention times are incorporated together with NMR data for each respective aldol adduct.

General procedure of the enantioselective aldol reaction in water: A mixture of $CuCl_2$ (5.4 mg, 0.04 mmol, 20 mol%) $AgSbF_6$ (27.5 mg, 0.08 mmol, 40 mol%), and 0.04 mmol, 20 mol% of ligand **1a** in the appropriate cyclohexanone: water ratio (total volume 1mL) was stirred at room temperature for 4 hrs. The aldehyde (0.2mmol) was then added and stirred until reaction was completed. The rest of the procedure is the same as described above under neat conditions.

Table 1 Metal screening using ligand **1a**[a]

Entry	Metal	Yield [%][b]	*Anti/Syn*[c]	*ee* [%][d] (*anti*)
1	$Cu(SbF_6)_2$	80	25/1	98
2	$Cu(OTf)_2$	94	12/1	90
3	$Co(ClO_4)_2$	90	2/1	65
4	$Ni(ClO_4)_2$	80	4/1	61
5	$Yb(OTf)_3$	80	1/1	25
6	$Zn(OAc)_2$	70	1/1	70

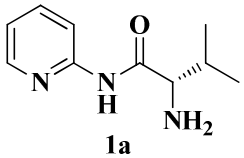
[a]The reactions were carried out with 0.2 mmol of 4-nitrobenzaldehyde and 1 mL cyclohexanone at room temperature between 3-48hrs. [b] Combined yield. [c] Determined by ^{1}H NMR. [d] Determined by chiral HPLC

Table 2. Solvent Screening using ligand **1a**[a]

Entry	Solvent[b]	Yield[%][c]	*Anti/Syn*[d]	*ee*[%][e]
1	DMSO	72	3/1	84
2	CH_3CN	84	4/1	84
3	Toluene	88	8/1	95
4	MeOH	66	9/1	97
5	DCM	90	8/1	96
6	THF	76	6/1	94
7	DMF	64	4/1	86

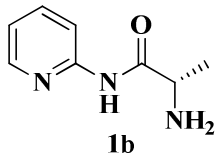
[a]The reactions were performed with 0.2 mmol of 4-nitrobenzaldehyde at room temperature. [b] 0.3 mL cyclohexanone and 0.6 mL solvent. [c] Combined yield. [d] Determined by ^{1}H NMR. [e] Determined by chiral HPLC.

NMR data for ligands and aldol adducts



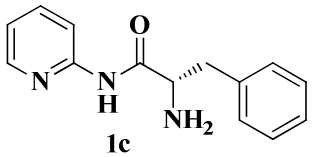
1a

(*S*)-2- amino-3-methyl-*N*- (pyridin-2-yl) butanamide (1a): $[\alpha]_D^{25}$= -21.5(c= 0.20, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H), 1.53 (br, 2H), 2.37-2.42(m, 2H), 3.38 (d, *J* = 2.7Hz, 1H), 6.98-7.03(m, 3H), 7.64-7.71 (m, 1H), 8.24-8.28 (m, 2H), 9.94 (br, 1H). ^{13}C NMR (75Hz, $CDCl_3$) δ 16. 4, 19.6, 31.3, 61.1, 113.8, 119.5, 138.0, 148.0, 151.5, 173.2. MS (ESI) 194.0 $(M+H)^+$; HRMS exact mass calcd for ($C_{10}H_{15}N_3O$+Na) requires m/z 216.1113, found m/z 216.1119.



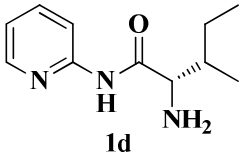
1b

(*S*)-2-amino-*N*- (pyridin-2-yl) propanamide (1b): $[\alpha]_D^{25}$= +5.9 (c= 0.34, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (d, *J* = 6.9 Hz, 3H), 1.65(br, *2*H), 3.63 (dd, *J* = 6.9, 13.8 Hz, 1H), 6.99-7.04 (m, 1H), 7.65-7.71 (m, 1H), 8.20-8.32 (m, 2H), 9.85 (br, 1H). ^{13}C NMR (75Hz, $CDCl_3$) δ 21.5, 51.4, 113.7,119.5, 138, 146.0, 151.5, 174.3. MS (ESI) 188.0 (M+Na); HRMS exact mass calcd for ($C_8H_{11}N_3O$+Na) requires m/z 188.0800, found m/z 188.0805.



1c

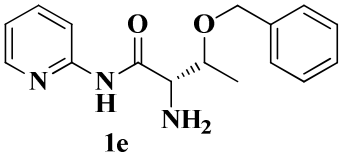
(*S*)-2-amino-3-pheyl-*N*- (pyridin-2-yl) propanamide (1c): $[\alpha]_D^{25}$= -117.1 (c= 0.17, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.62 (br, 2H), 2.78 (dd, *J* = 3.6, 13.8Hz, 2H), 3.38 (dd, *J* = 3.9, 13.8Hz, 2H), 3.42 (d, *J* = 4.8Hz, 1H), 7.02-7.06 (m, 1H), 7.24-7.36 (m, 5H), 7.69-7.75 (m, 1H), 8.28-8.31(m, 1H), 10.00 (br, 1H). ^{13}C NMR (75Hz, $CDCl_3$) δ 40.4, 56.6, 113.2, 119.0, 126.3, 128.2, 128.7, 137.2, 137.4, 147.4, 172.4. MS (ESI) 242.1 $(M+H)^+$; HRMS exact mass calcd for ($C_{14}H_{15}N_3O$+Na) requires m/z 264.1113, found m/z 264.1104.



1d

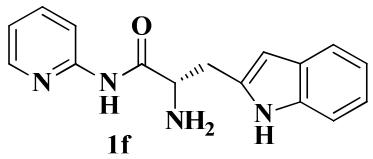
(2*S*,3*S*)-2-amino-3-methyl-*N*- (pyridin-2-yl) pentanamide (1d): $[\alpha]_D^{25}$= -4.07(c= 8.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.90 (m, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 1.39-1.44 (m, 1H), 1.57 (br 1H), 2.11-2.13 (m, 1H), 3.43(d, *J* = 3Hz, 1H), 7.00-7.02 (m, 1H), 7.68-7.70 (m, 1H), 8.25-8.29 (m, 2H), 10.01 (br, 1H). ^{13}C NMR (125Hz, $CDCl_3$) δ 11.9, 16.3, 23.8, 38.0, 60.3, 113.7, 119.6,

138.2, 147.9, 151.2, 173.5. MS (ESI) 208.1 $(M+H)^+$; HRMS exact mass calcd for $(C_{11}H_{17}N_3O+Na)$ requires m/z 230.1269, found m/z 230.1261.



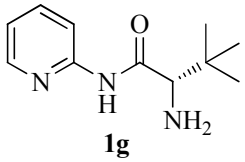
1e

(2*S*,*RS*)-2-amino-3-(benzyloxy)-*N*- (pyridin-2-yl) butanamide (1e): $[\alpha]_D^{25}$= -8.13 (c= 3.42, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, *J* = 6.5 Hz, 3H),1.89 (br, 2H), 3.38 (m, 1H), 4.36 (m, 1H), 4.49 (*d*, *J* = 11.5 Hz, 1H), 4.60 (*d*, *J* = 11.5Hz, 1H), 7.04-7.06 (m, 1H), 7.28 (s, 5H), 7.72 (m, 1H), 8.28-8.34 (m, 2H) 10.22 (br, 1H). ^{13}C NMR (125Hz, $CDCl_3$) δ 17.2, 59.9, 71.5, 74.8, 113.7, 119.7, 127.7, 128.3, 138.2, 138.3, 148.1, 151.3, 172.6. MS (ESI) 286.1 $(M+H)^+$; HRMS exact mass calcd for $(C_{16}H_{19}N_3O_2+Na)$ requires m/z 308.1375, found m/z 308.13.1352.



1f

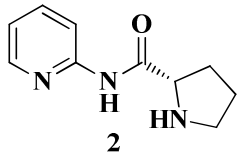
(*S*)-2-amino-3-(1-H-indol-2-yl)-*N*-(pyridin-2-yl) propanamide (1f): $[\alpha]_D^{25}$= -9.40 (c= 3.52, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (br, 2H), 2.92-2.97 (m, 1H), 3.44 (d, *J* = 12 Hz, 1H), 3.79 (d, *J* = 6 Hz, 1H), 6.97-7.16, (m, 4H), 7.31 (*d*, *J* = 8 Hz, 1H), 7.610-7.68 (m, 2H), 8.27 - 8.34 (m, 2H), 9.04 (s, 1H), 10.07 (br, 1H). ^{13}C NMR (125Hz, $CDCl_3$) δ 30.6, 56.1, 111.0, 111.5, 113.9, 118.8, 119.6, 119.9, 122.2, 123.5, 127.4, 136.6, 138.5, 148.0, 151.2, 174.2. MS (ESI) 281.1 $(M+H)^+$



1g

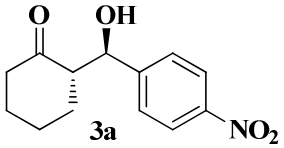
(*S*)-2- amino-3,3-dimethyl-*N*- (pyridin-2-yl) butanamide (1g): $[\alpha]_D^{25}$= -20.0 (c= 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 9H), 1.67 (br, 2H), 3.25 (s, 1H), 6.98-7.00 (m, 1H), 7.64-

7.68 (m, 1H), 8.21-8.26 (m, 2H), 9.45 (br, 1H). ^{13}C NMR (75Hz, $CDCl_3$) δ 26.8, 34.6, 65.0, 113.8, 119.6, 138.2, 147.9, 151.1, 172.6. MS (ESI) 208.1 $(M+H)^+$



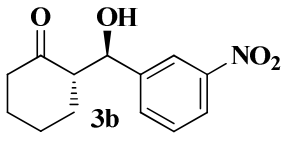
2

(*S*)-*N*-(pyridine-2-yl)pyrrolidine-2-carboxamide (2): $[\alpha]_D^{25}$= -117.1 (c= 0.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, *J* = 6.5 Hz, 3H),1.89 (br, 2H), 3.38 (m, 1H), 4.36 (m, 1H), 4.49 (*d*, 11.5 Hz, 1H), 4.60 (*d*, 11.5Hz, 1H), 7.04-7.06 (m, 1H), 7.28 (s, 5H), 7.72 (m, 1H), 8.28-8.34 (m, 2H) 10.22 (br, 1H). ^{13}C NMR (125Hz, $CDCl_3$) δ 17.2, 59.9, 71.5, 74.8, 113.7, 119.7, 127.7, 128.3, 138.2, 138.3, 148.1, 151.3, 172.6. MS (ESI) 286.1 $(M+H)^+$



3a

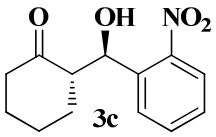
(*S*)-2-((*R*)-hydroxy(4-nitrophenyl)methyl)cyclohexanone(3a)[1]: Using ligand **1a**: yield 80% ; dr 25/1; *ee* 98% ; $[\alpha]_D^{25}$= +11.0 (c= 0.22, $CHCl_3$), Ligand **1g**: yield 90%; dr 9/1; *ee* >99%; HPLC analysis chiralpak AD-H (*i*-PrOH/hexanes = 20:80, 1mL/min, 254nm, t_R = 14.1min and t_R = 18.2min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34-1.82 (m, 5H), 2.07 (m, 1H), 2.33-2.35 (m, 1H), 2.45-2.46 (m, 1H), 2.48-2.56 (m, 1H), 4.04 (s, 1H), 4.87 (dd, *J* = 3 Hz, 8.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.70, 27.63, 30.76, 42.68, 57.20, 74.02, 123.57, 127.87, 147.59, 148.37, 214.70.



3b

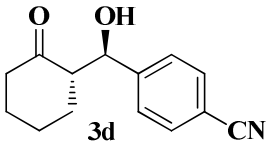
(*S*)-2-((*R*)-hydroxy(3-nitrophenyl)methyl)cyclohexanone (3b)[1]**:** Using ligand **1a:** yield 86% ; dr 17/1; *ee* 96% ; $[\alpha]_D^{25}$= +28.2 (c= 0.14, $CHCl_3$) , Ligand **1g**: yield 90%; dr 3/1; *ee* >99%; HPLC analysis

chiralpak AD-H (*i*-PrOH/hexanes = 20:80, 1mL/min, 254nm) t_R = 11.4 min and t_R = 13.9 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35-1.39 (m, 1H), 1.54-1.67 (m, 4H), 2.08-2.09 (m, 1H), 2.35-2.38 (m, 1H), 2.46-2.49 (m, 1H), 2.61(m, 1H), 4.14 (br, 1H), 4.88 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 2H), 8.12-8.19 (m, 1H), 8.20 (s, 1H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.61, 27.59, 30.69, 42.61, 57.08, 73.96, 121.97, 122.81, 129.26, 133.17, 143.26, 148.25, 214.79.



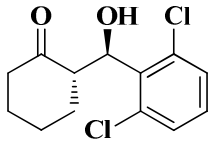
3c

(*S*)-2-((*R*)-hydroxy(2-nitrophenyl)methyl)cyclohexanone (3c)[1]: Using ligand **1a:** yield 84%; dr 30/1; *ee* 95%; $[\alpha]_D^{25}$= +23.9 (c= 0.41, $CHCl_3$), Using ligand **1g**: yield 90%; dr 4/1; *ee* >99%; HPLC analysis chiralpak AD-H (*i*-PrOH/hexanes = 20:80, 1mL/min, 254nm) t_R = 25.4 min and t_R = 27.6 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55-1.84 (m, 5H), 2.05-2.06 (m, 1H), 2.31-2.33 (m, 1H), 2.41-2.44 (m, 1H), 2.72-2.74 (m, 1H), 4.15 (br, 1H), 5.42 (d, *J* = 7.0 Hz, 1H), 7.40-7.42 (m, 1H), 7.61 (m, 1H), 7.81 (m, 1H). 7.83 (m, 1H) ^{13}C NMR (125Hz, $CDCl_3$) δ 24.96, 27.73, 31.09, 42.80, 57.28, 69.76, 124.06, 128.37, 128.98, 133.04, 136.60, 148.72, 214.91



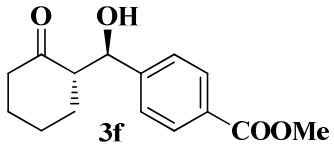
3d

4-((*R*)-hydroxy((*S*)-2-oxocyclohexyl)methyl)benzonitrile (3d)[1]: Using ligand **1a**: yield 83%; dr 16/1 ; *ee* 97% ; $[\alpha]_D^{25}$= +22.2 (c= 0.31, $CHCl_3$), HPLC analysis chiralpak AD-H (*i*-PrOH/hexanes = 20:80, 0.9 mL/min, 254nm) t_R = 16.6 min and t_R = 24.0 min; Using ligand **1g**: yield 85%, dr 3/1, *ee* >99%, HPLC analysis chiralpak AD-H (*i*-PrOH/hexanes = 20:80, 0.9 mL/min, 254nm) t_R = 19.6 min and t_R = 23.9 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34-1.85 (m, 5H), 2.10-2.14 (m, 1H), 2.36-2.39 (m, 1H), 2.49 (m, 1H), 2.51-2.58 (m, 1H), 4.07 (s, 1H), 4.85 (dd, *J* = 3 Hz, 8.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.68, 27.64, 30.73, 42.66, 57.14, 74.20, 111.69, 119.80, 127.78, 132.17, 146.41, 214.76.



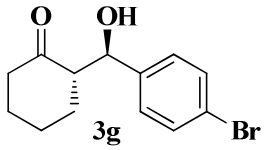
3e

(*S*)-2-((*R*)-(2,6-dichlorophenyl)(hydroxy)methyl)cyclohexanone (3e)[1]: Using ligand **1a**: yield 86% ; dr 14/1 ; *ee* >99% ; $[\alpha]_D^{25}$= -38.5 (c= 0.41, $CHCl_3$); HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 10:90, 1mL/min, 220 nm) t_R = 15.8 min and t_R = 19.6 min. Using ligand **1g**: yield 89%, dr 4/1, *ee* >99%; HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 10:90, 0.7 mL/min, 220 nm) t_R = 17.1 min and t_R = 21.5 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36-1.40 (m, 1H), 1.52-1.85 (m, 4H), 2.08-2.10 (m, 1H), 2.41-2.54 (m, 2H), 3.49-3.52 (m, 1H), 3.70 (br, 1H), 5.85 (d, *J* = 10.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.32-7.33 (m, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.69, 27.63, 29.86, 42.44, 53.65, 70.57, 129.34, 129.75, 134.73, 135.69, 214.39.



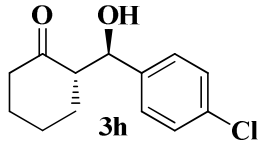
3f

methyl 4-((*R*)-hydroxy((*S*)-2-oxocyclohexyl)methyl)benzoate (3f)[1]: Using ligand **1a**: yield 94% ; dr 12/1 ; *ee* 97% ; $[\alpha]_D^{25}$= +11.6 (c= 0.45, $CHCl_3$); Using ligand **1g**: yield 90%, dr 3/1, *ee* >99%; HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 20:80, 1mL/min, 254 nm), t_R = 16.7 min and t_R = 24.1 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29-1.33 (m, 1H), 1.51-1.79 (m, 4H, 2.06-2.09 (m, 1H), 2.33-2.37 (m, 1H), 2.45-2.46 (m, 1H), 2.48-2.58 (m, 1H), 3.90 (s, 3H), 4.04 (s, 1H), 4.83 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.64, 27.66, 30.71, 42.62, 52.04, 57.24, 74.32, 126.97, 129.62, 129.66, 146.05, 166.81, 215.04.



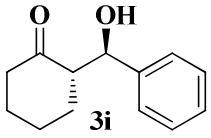
3g

(*S*)-2-((*R*)-(4-bromophenyl)(hydroxy)methyl)cyclohexanone (3g)[1]: Using ligand **1a:** yield 70% ; dr 12/1; *ee* 94%; $[\alpha]_D^{25}$= +20.2 (c= 0.30, $CHCl_3$); HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 2.5:97.5, 0.5mL/min, 220 nm) t_R = 41.3 min and t_R = 45.8min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27-1.30 (m, 1H), 1.52-1.78 (m, 4H), 2.33-2.35 (m, 1H), 2.07-2.08 (m, 1H), 2.33-2.35 (m, 1H), 2.45-2.54 (m, 2H), 3.98 (s, 1H), 4.74 (d, *J* = 9 Hz, 1H), 7.18 (dd, *J* = 1.5, 6.5 Hz, 2H), 7.46 (dd, *J* = 2.0, 6.5 Hz, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.68, 27.69, 30.72, 42.63, 57.33, 74.17, 121.68, 128.71, 131.45, 140.00, 215.21.



3h

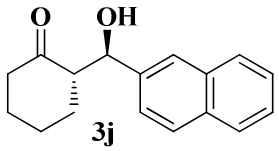
(*S*)-2-((*R*)-(4-chlorophenyl)(hydroxy)methyl)cyclohexanone (3h)[1]: Using ligand **1a**: yield 84% ; dr 7/1 ; *ee* 97%; $[\alpha]_D^{25}$= +19.2 (c= 0.25, $CHCl_3$); HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 2.5:97.5, 0.5mL/min, 220 nm) t_R = 39.7 min and t_R = 43.5min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29-1.33 (m, 1H), 1.55-1.81 (m, 4H), 2.09-2.58 (m, 3H), 4.04 (s, 1H), 4.78 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.72, 27.72, 30.76, 42.68, 57.38, 74.14, 128.39, 128.54, 138.59, 139.50, 215.29.



3i

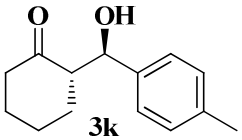
(*S*)-2-((*R*)-hydroxy(phenyl)methyl)cyclohexanone (3i)[1]: Using ligand **1a**: yield 75% ; dr 10/1 ; *ee* 83% ; $[\alpha]_D^{25}$= +18.9 (c= 0.56, $CHCl_3$); Using ligand **1g**: yield 83%, dr 4/1, *ee* 89%; HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 5:95, 0.6 mL/min, 220 nm) t_R = 35.6 min and t_R = 40.5 min. ^{1}H NMR (500

MHz, $CDCl_3$) δ 1.28-1.31 (m, 1H), 1.52-1.77 (m, 4H), 2.35-2.36 (m, 1H), 2.06 (m, 1H), 2.35-2.36 (m, 1H), 2.46-2.47 (m, 1H), 2.49-2.62 (m, 1H), 3.94 (s, 1H), 4.78 (d, J = 8.5 Hz, 1H), 7.2-7.34 (m, 5H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.68, 27.77, 30.81, 42.63, 57.40, 74.71, 126.99, 127.85, 128.33, 140.92, 215.48.



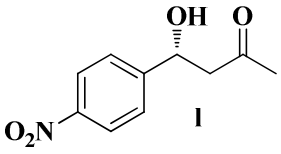
3j

(*S*)-2-((*R*)-hydroxy(naphthalen-2-yl)methyl)cyclohexanone (3j)[2]: Using ligand **1a**: yield 70% ; dr 8/1 ; *ee* 92% ; $[\alpha]_D^{25}$= +5.3 (c= 0.50, $CHCl_3$); HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 10:90, 0.7mL/min, 220 nm) t_R = 20.3 min and t_R = 23.2 min. ^1H NMR (500 MHz, $CDCl_3$) δ 1.32-1.35 (m, 1H), 1.50-1.76 (m, 4H), 2.06 (m, 1H), 2.36-2.38 (m, 1H), 2.48 (m, 1H), 2.72 (m, 1H), 2.49-2.62 (m, 1H), 4.08 (br, 1H), 4.96 (d, J = 9.0 Hz, 1H), 7.46-7.49 (m, 3H), 7.76 (s, 1H), 7.82-7.85 (m, 3H). ^{13}C NMR (125Hz, $CDCl_3$) δ 24.71, 27.80, 30.92, 42.71, 57.41, 74.92, 124.68, 125.95, 126.15, 126.26, 127.70, 127.99, 128.28, 133.17, 133.21, 138.38, 215.49.



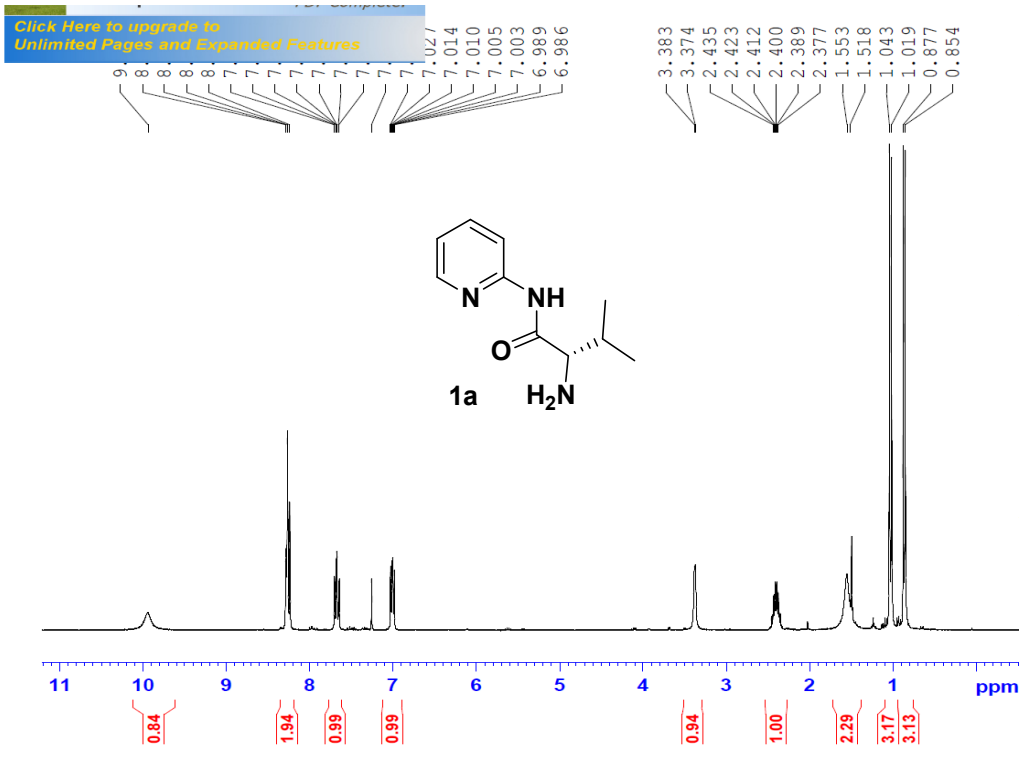
3k

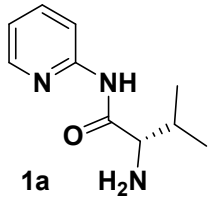
(*S*)-2-(*R*)- hydroxy (*p*-tolyl) methy) cyclohexanone (3k)[3]: Using ligand **1a**:yield 70%, dr 5/1; *ee* 82% ; $[\alpha]_D^{25}$= +5.3 (c = 0.50, $CHCl_3$); HPLC analysis chiralpak AS-H (*i*-PrOH/hexanes = 10:90, 0.7mL/min, 220 nm) t_R = 12.9 min and t_R = 15.4 min. ^1H NMR (500 MHz, $CDCl_3$) δ 1.23-1.28 (m, 1H), 1.51-2.04 (m, 4H), 2.04-2.07 (m, 1H), 2.32-2.58 (m 4H), 3.81-3.95 (br, 1H), 4.74 (d, J = 8.5 Hz, 1H), 2.48 (m, 1H), 7.12-7.14 (m, 2H), 7.16-7.24 (m, 1H),. ^{13}C NMR (75Hz, $CDCl_3$) δ 21.04, 24.88, 26.11, 27.81, 40.66, 67.45, 70.54.68, 125.70, 126.90, 128.83, 129.04, 215.52.

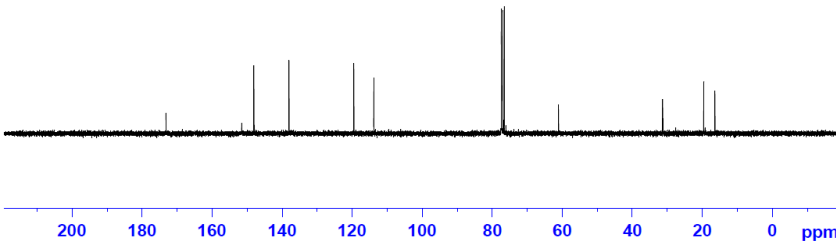


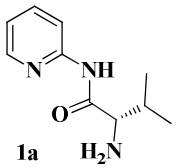
(*R*)-4-hydroxy-4-(4-nitrophenyl)butan-2-one (l)[4] Using ligand **1g:** yield 65%; *ee* 81 %; $[\alpha]_D^{25}$= 35.2 (c= 0.2, $CHCl_3$). HPLC analysis chiralpak AD-H (*i*-PrOH/hexanes = 30:70, 0.9mL/min, 220 nm) t_R = 20.0 min and t_R = 26.5 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.82 (m, 2H), 3.65 (s, 1H), 5.23 (t, *J* = 6 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125Hz, $CDCl_3$) δ 30.70, 51.52, 68.91, 123.75, 126.43, 147.10, 150.06, 208.44

NMR SPECTRA FOR LIGANDS





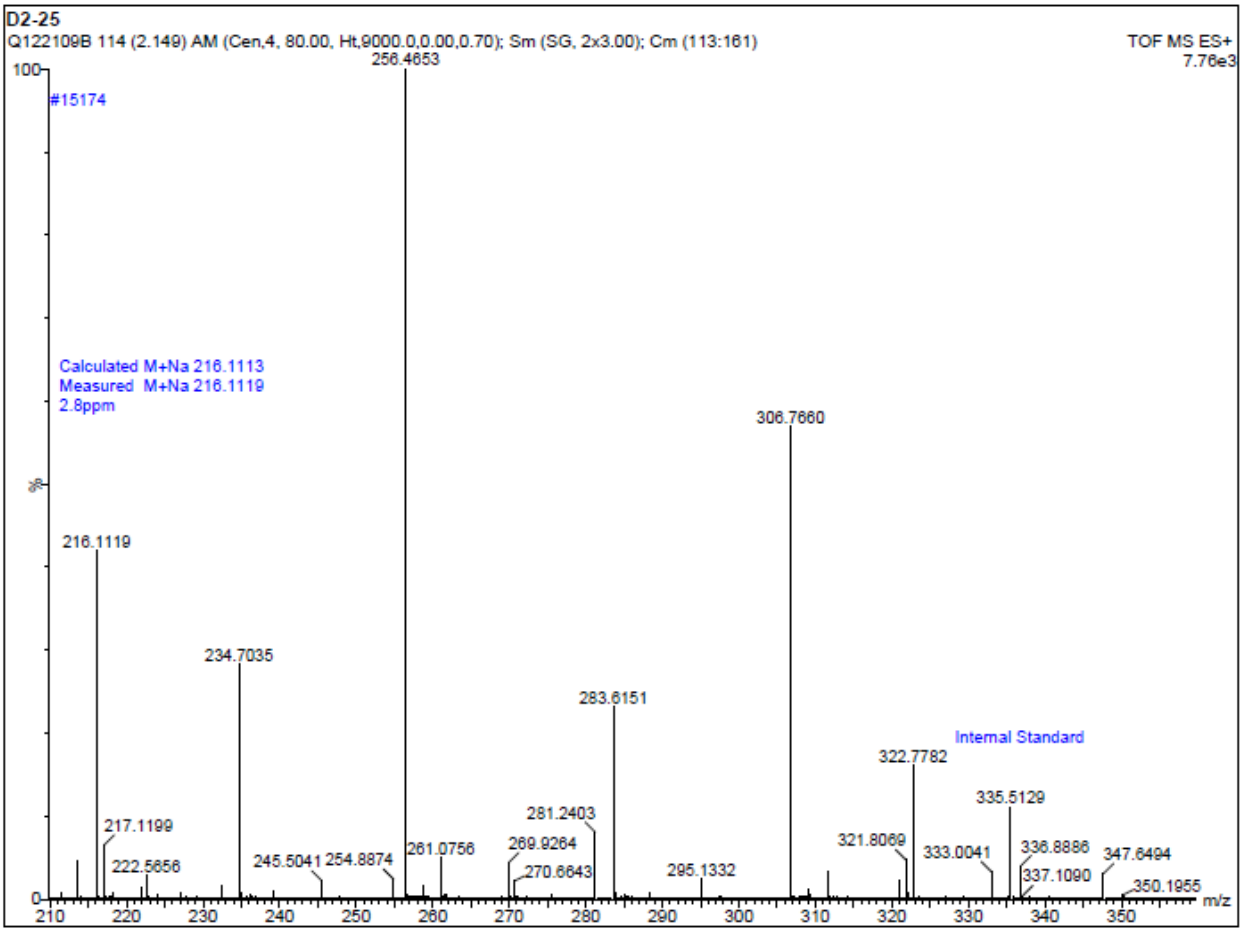


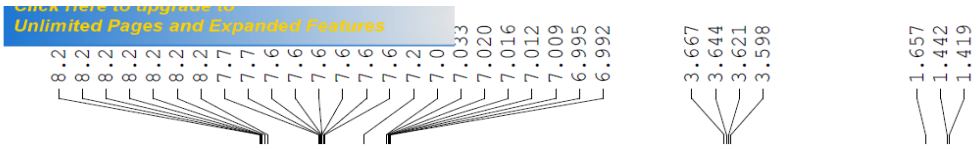


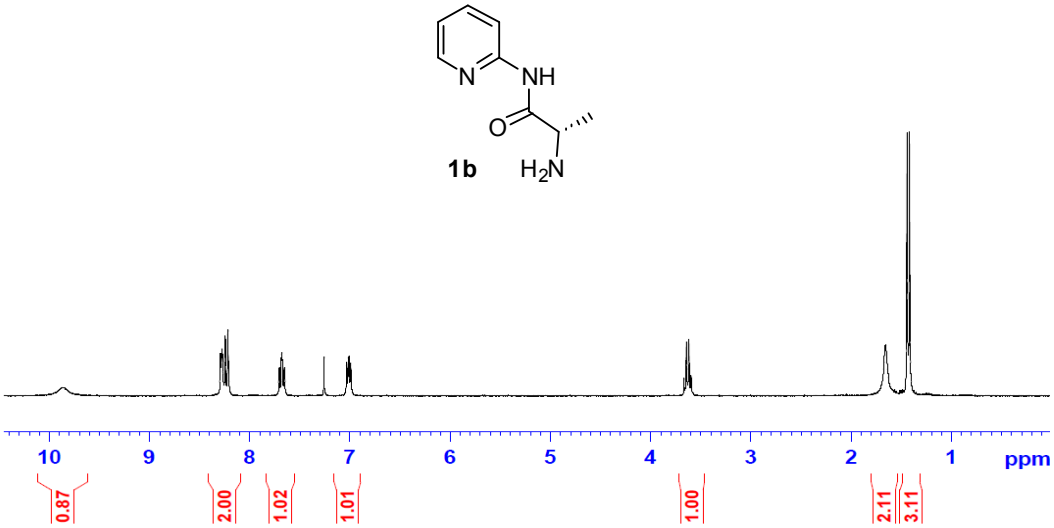
1a

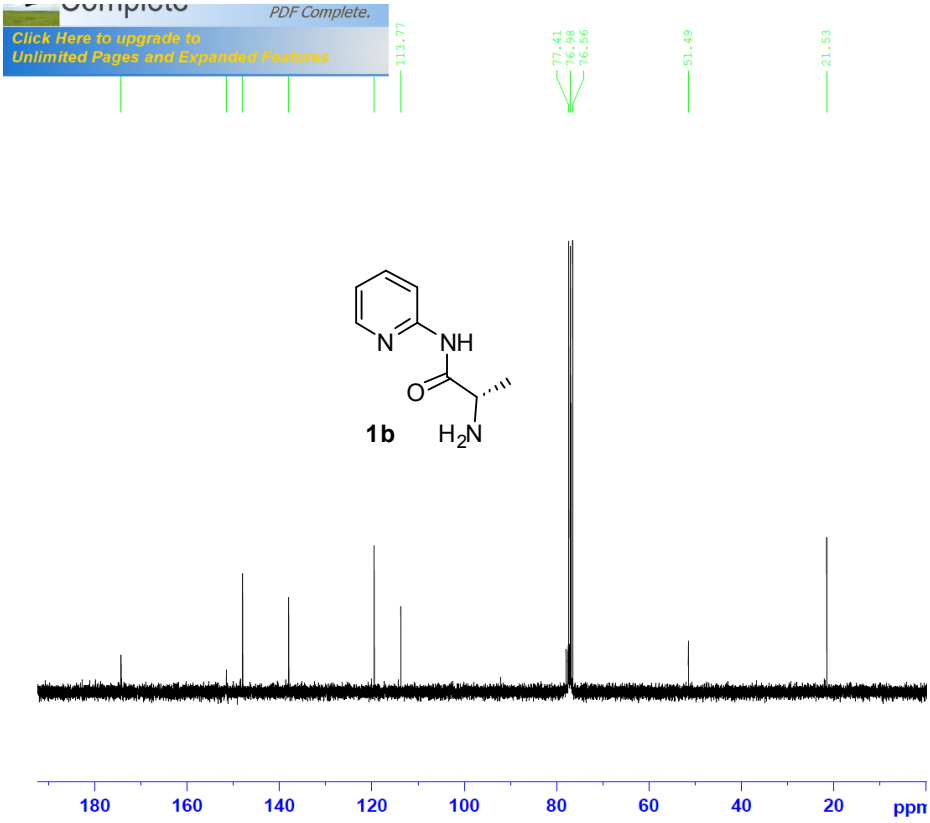
Chemical Formula: $C_{10}H_{15}N_3O$
Exact Mass: 193.12
Molecular Weight: 193.25
m/z: 193.12 (100.0%), 194.12 (11.9%)
Elemental Analysis: C, 62.15; H, 7.82; N, 21.74; O, 8.28

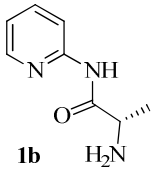
HRMS = 216.1119 $(M+Na)^+$







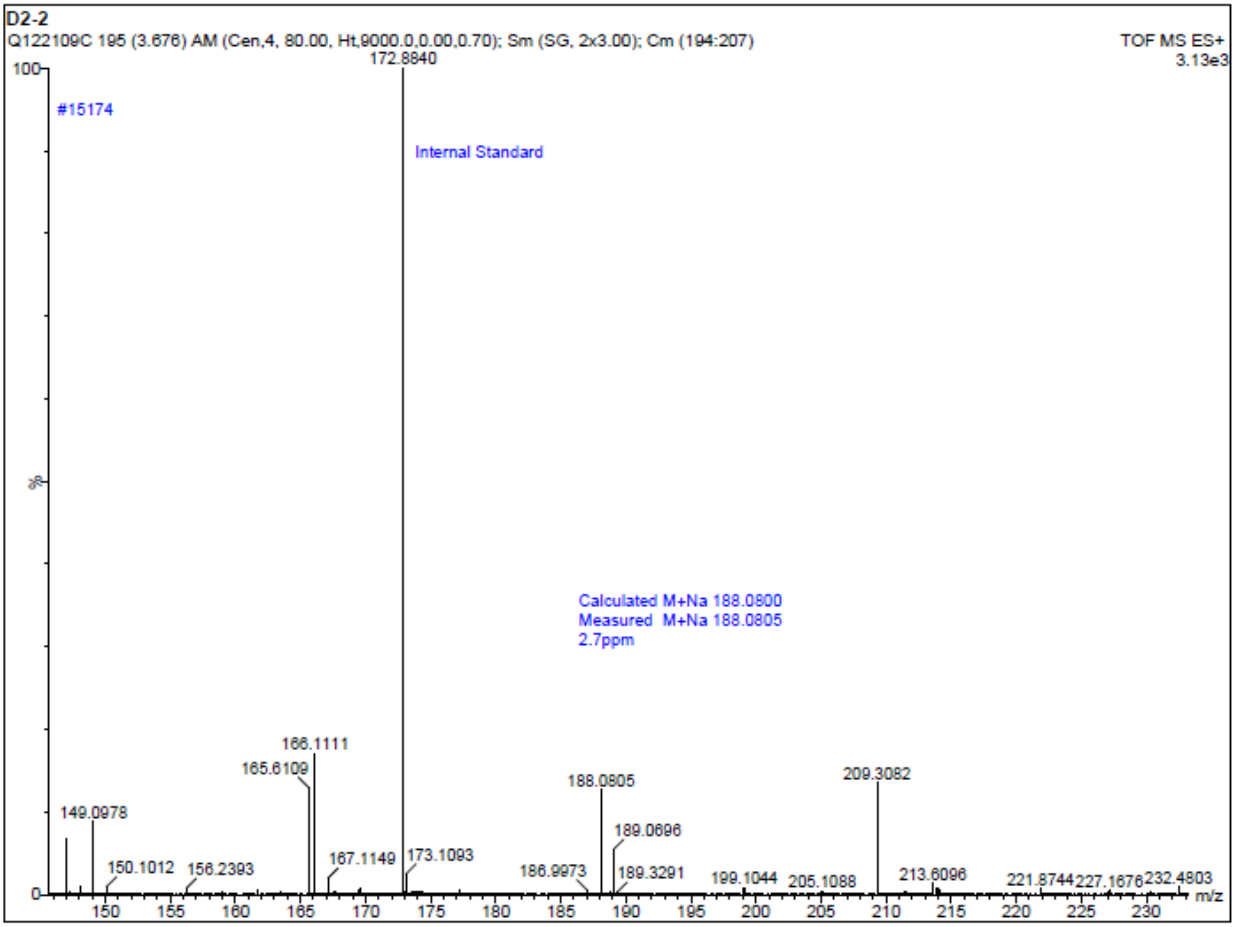


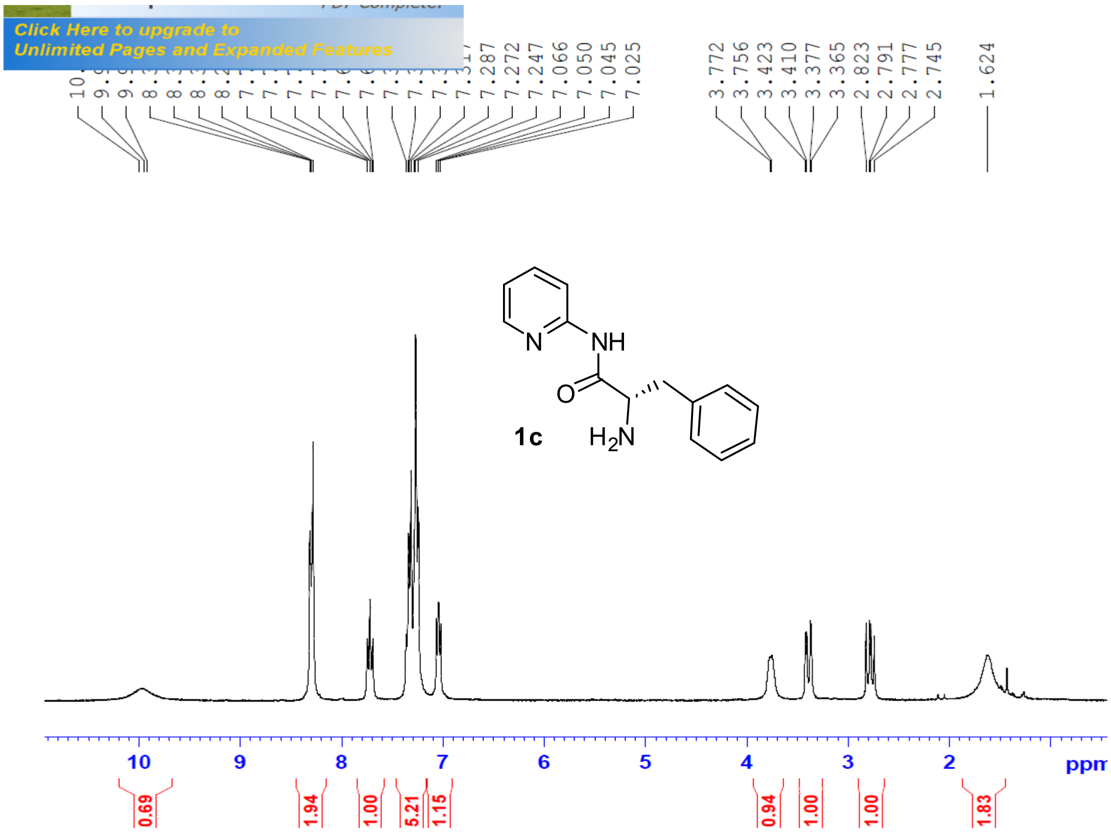


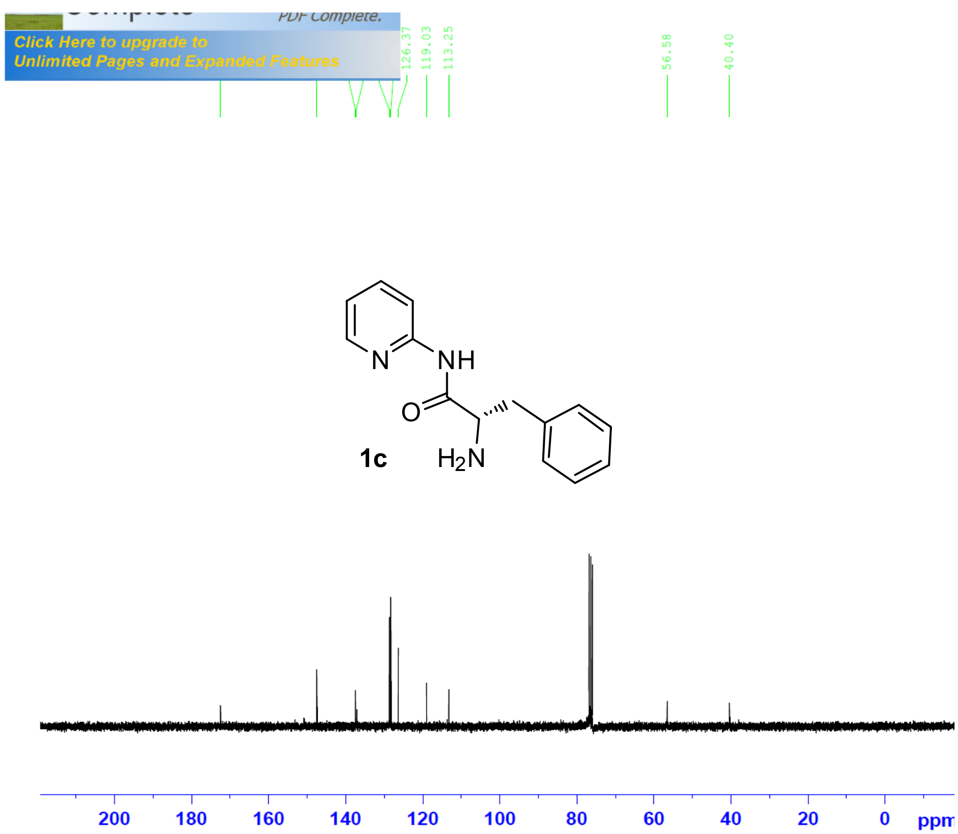
1b

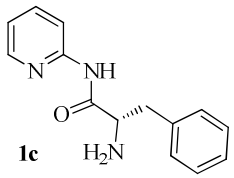
Chemical Formula: $C_8H_{11}N_3O$
Exact Mass: 165.09
Molecular Weight: 165.19
m/z: 165.09 (100.0%), 166.09 (9.8%)
Elemental Analysis: C, 58.17; H, 6.71; N, 25.44; O, 9.69

HRMS = 188.0805 $(M+Na)^+$




Click Here to upgrade to
Unlimited Pages and Expanded Features
7.287
7.272
7.247
7.066
7.050
7.045
7.025
3.772
3.756
3.423
3.410
3.377
3.365
2.823
2.791
2.777
2.745
1.624
NH
N
O
1c
H2N
10
9
8
7
6
5
4
3
2
ppm
0.69
1.94
1.00
5.21
1.15
0.94
1.00
1.00
1.83

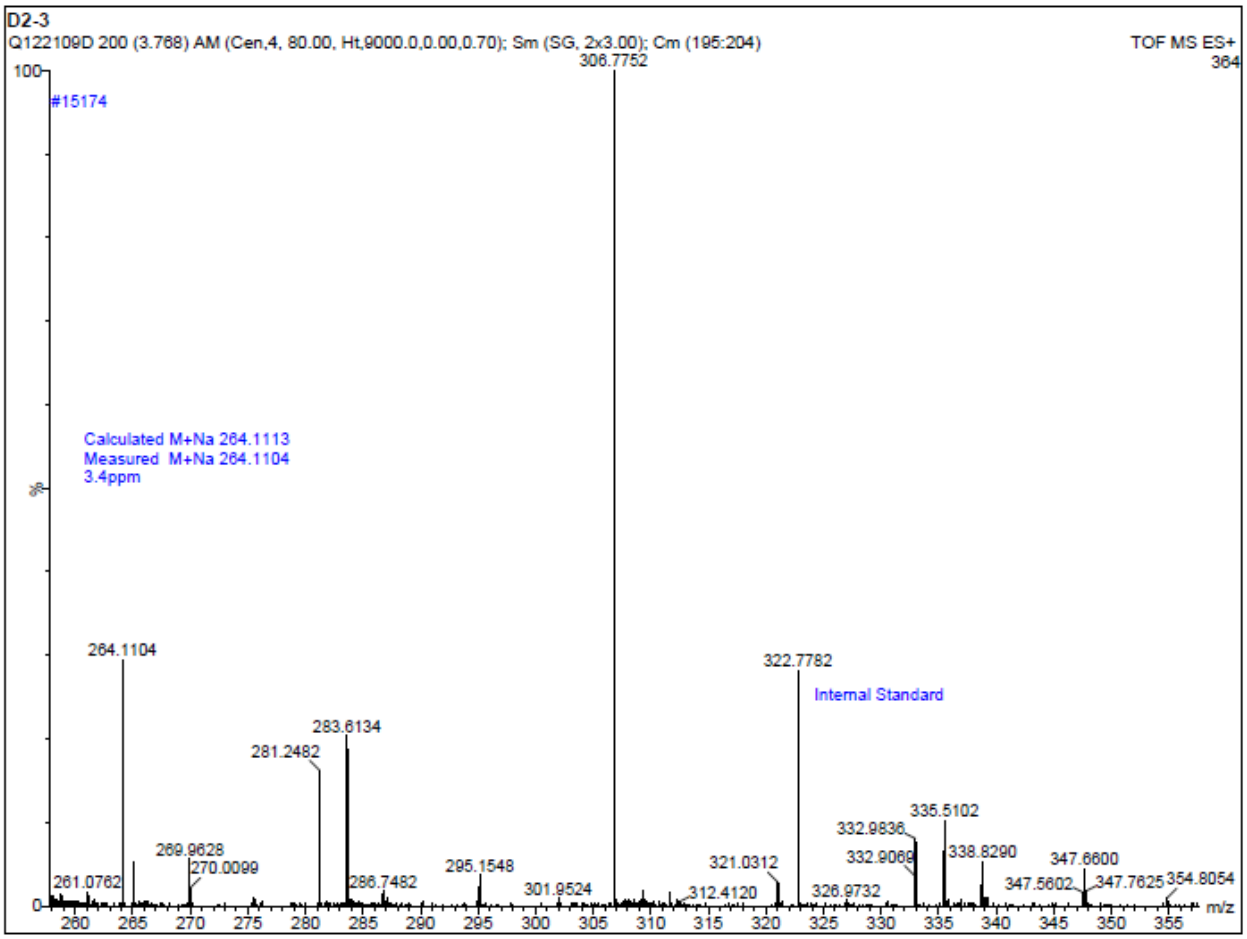

Click Here to upgrade to
Unlimited Pages and Expanded Features
126.37
119.03
113.25
56.58
40.40
NH
N
O
1c
H2N
200
180
160
140
120
100
80
60
40
20
0
ppm



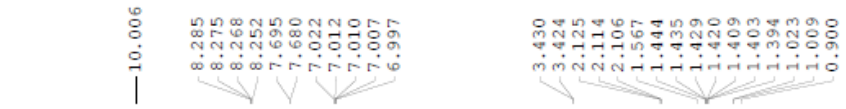
1c

Chemical Formula: $C_{14}H_{15}N_3O$
Exact Mass: 241.12
Molecular Weight: 241.29
m/z: 241.12 (100.0%), 242.12 (16.3%), 243.13 (1.3%)
Elemental Analysis: C, 69.69; H, 6.27; N, 17.41; O, 6.63

HRMS = 264.1104 $(M+Na)^+$

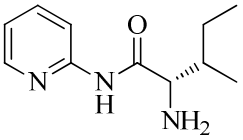


isol8-H

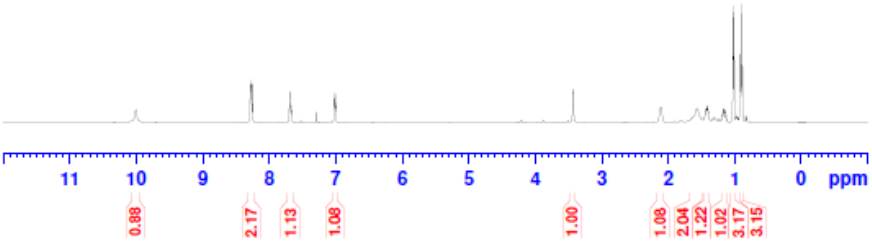


BRUKER

NAME	isol8-H
EXPNO	7
PROCNO	1
Date_	20100118
Time	12.34
INSTRUM	spect
PROBHD	5 mm TXI 1H-13
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1720407 sec
RG	32
DW	48.400 usec
DE	7.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	6.70 usec
PL1	0.00 dB
PL1W	15.07131863 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



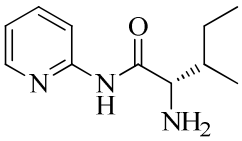
1d



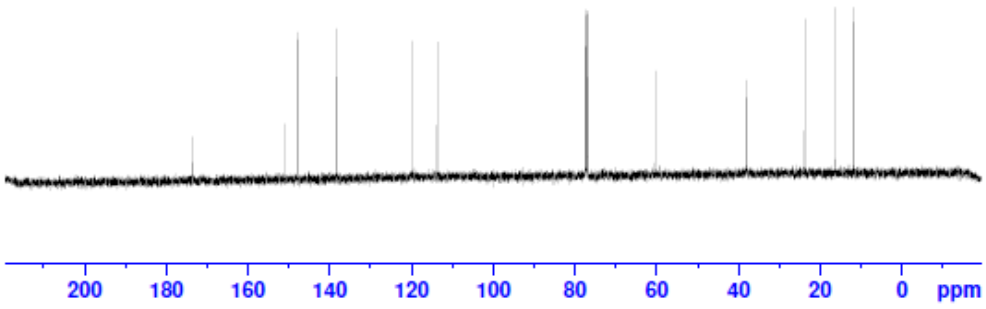
isol8-C

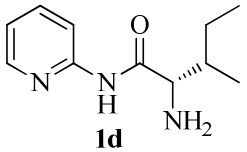
BRUKER

NAME	isol8-C
EXPNO	7
PROCNO	1
Date_	20100118
Time	12.51
INSTRUM	spect
PROBHD	5 mm TXI 1H-13
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	87
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912410 sec
RG	1149.4
DW	16.650 usec
DE	7.50 usec
TE	297.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	12.20 usec
PL1	-3.00 dB
PL1W	190.45114136 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	23.48 dB
PL13	25.00 dB
PL2W	15.07131863 W
PL12W	0.06763186 W
PL13W	0.04765970 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



1d

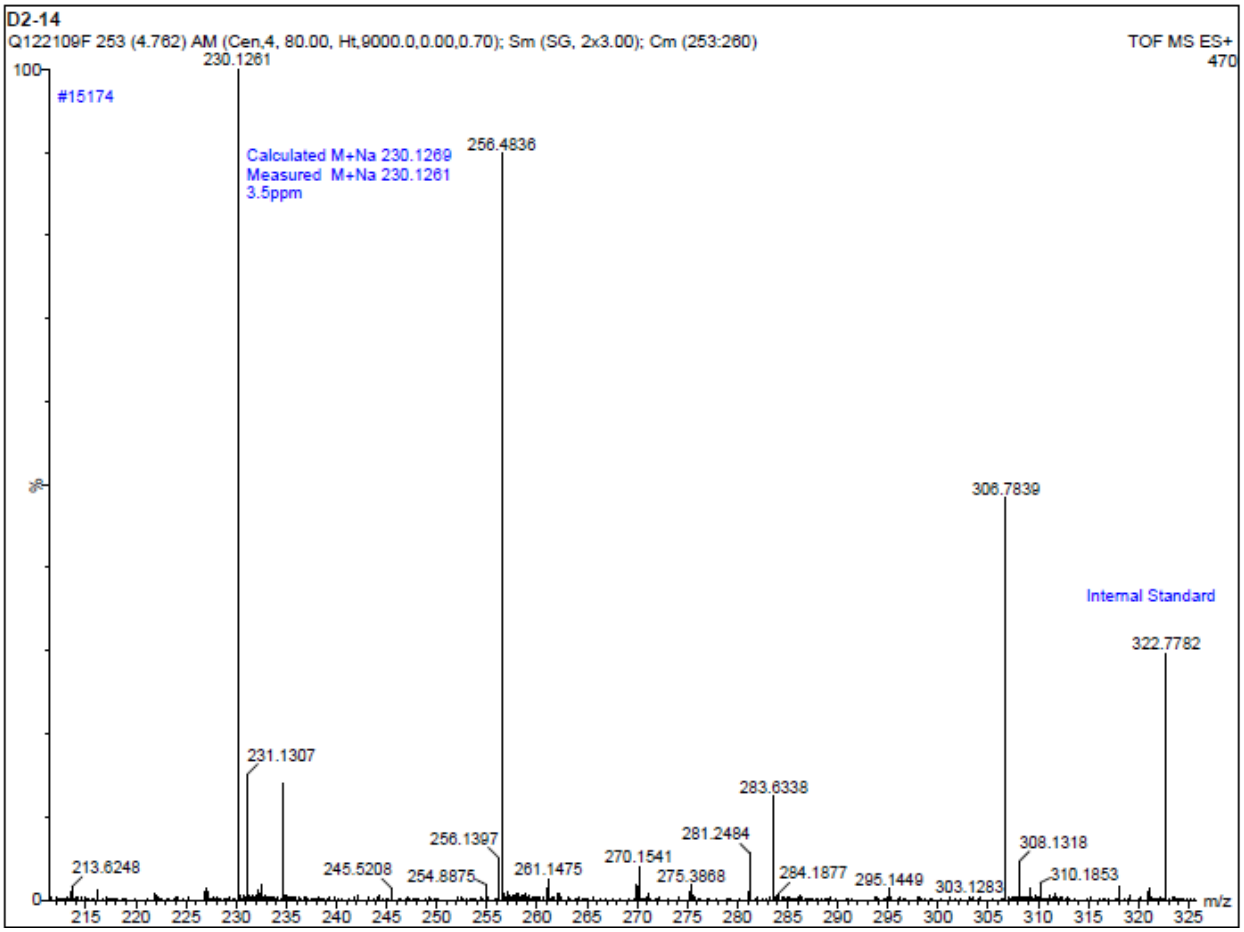


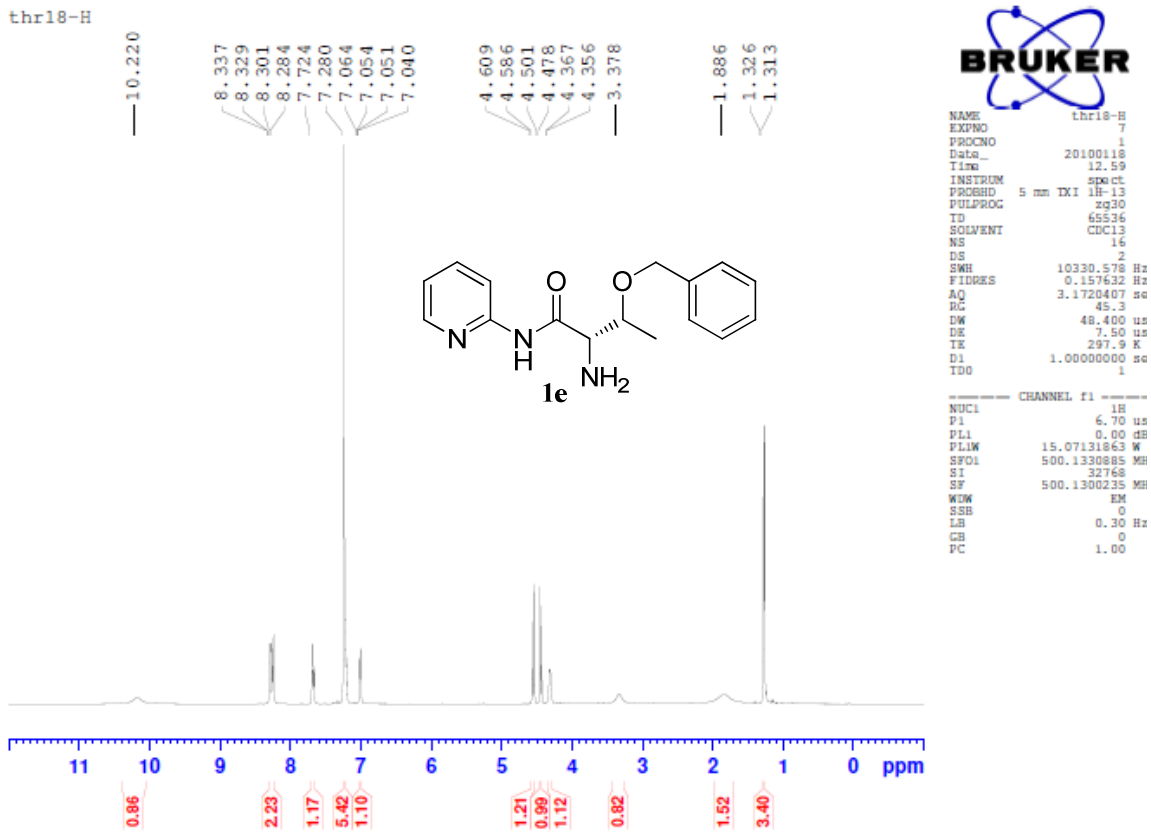


1d

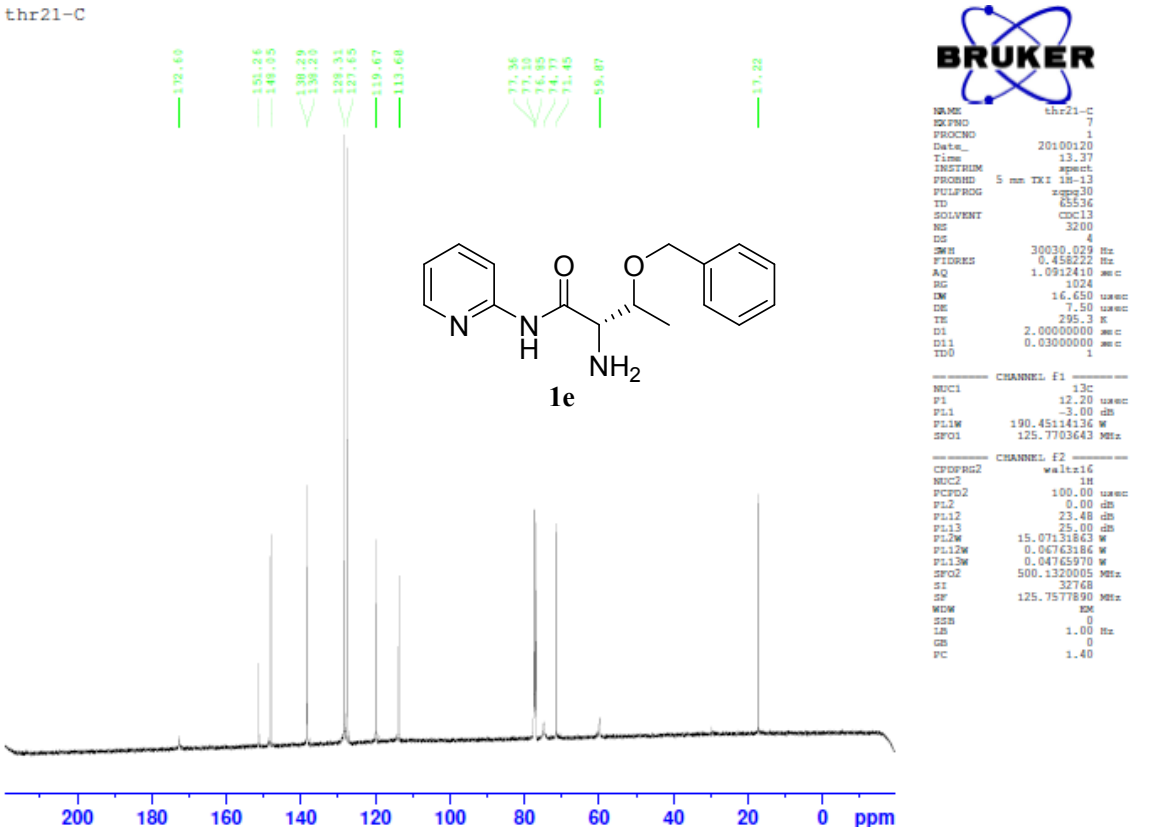
Chemical Formula: $C_{11}H_{17}N_3O$
Exact Mass: 207.14
Molecular Weight: 207.27
m/z: 207.14 (100.0%), 208.14 (12.1%), 208.13 (1.1%)
Elemental Analysis: C, 63.74; H, 8.27; N, 20.27; O, 7.72

HRMS = 230.1261 $(M+Na)^+$

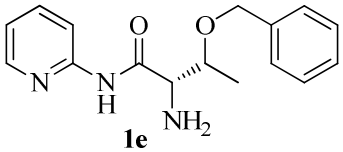



thr18-H
10.220
8.337
8.329
8.301
8.284
7.724
7.280
7.064
7.054
7.051
7.040
4.609
4.586
4.501
4.478
4.367
4.356
3.378
1.886
1.326
1.313
1e
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.86 2.23 1.17 5.42 1.10 1.21 0.99 1.12 0.82 1.52 3.40

BRUKER
NAME thr18-H
EXPNO 7
PROCNO 1
Date_ 20100118
Time 12.59
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 45.3
DW 48.400 usec
DE 7.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 6.70 usec
PL1 0.00 dB
PL1W 15.07131863 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300235 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


thr21-C
172.60
151.26
148.05
138.29
138.20
129.31
127.65
119.67
113.68
77.36
77.10
76.85
74.77
71.45
59.87
17.22
1e
200 180 160 140 120 100 80 60 40 20 0 ppm

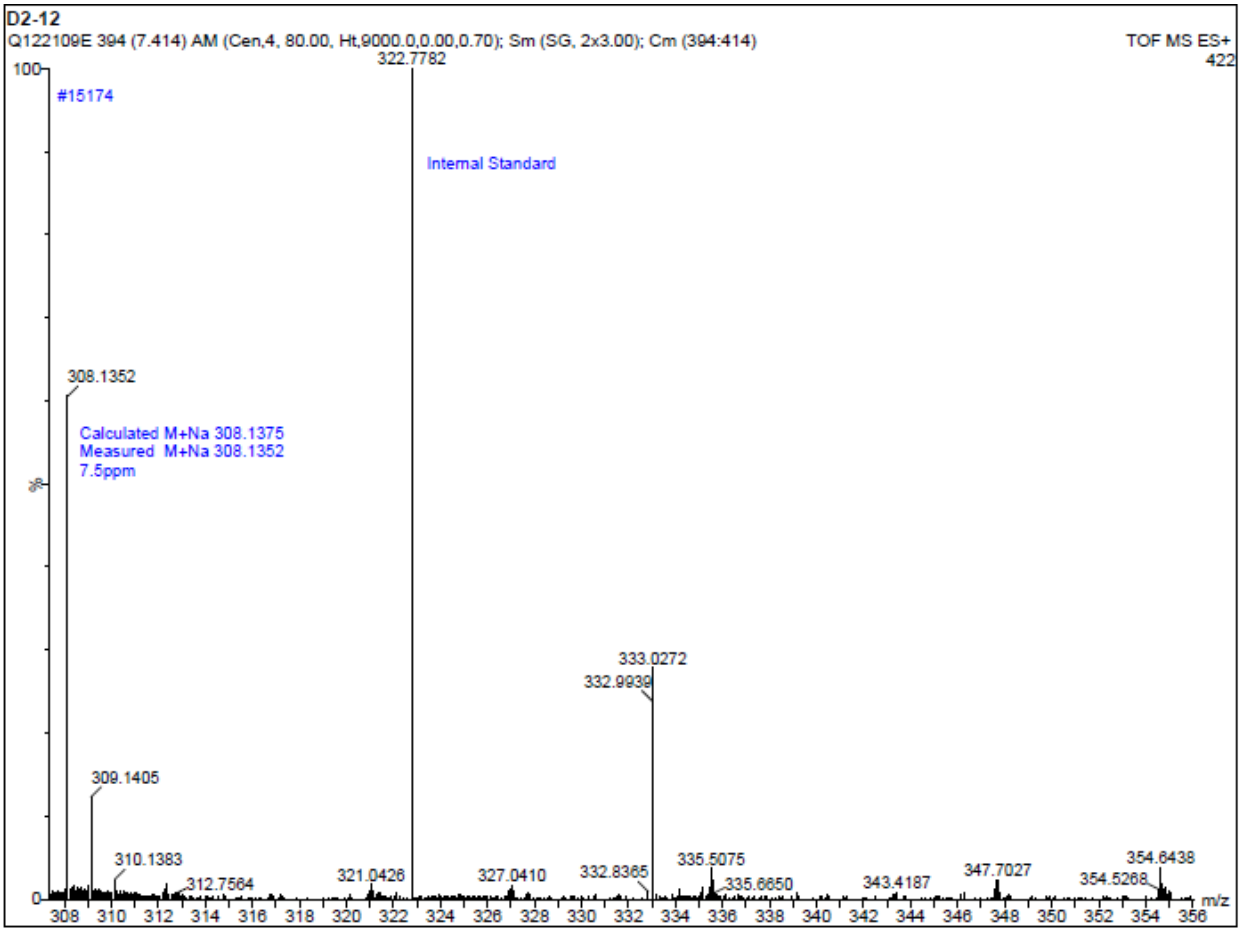
BRUKER
NAME thr21-C
EXPNO 7
PROCNO 1
Date_ 20100120
Time 13.37
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3200
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 1024
DW 16.650 usec
DE 7.50 usec
TE 295.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 12.20 usec
PL1 -3.00 dB
PL1W 190.45114136 W
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 23.48 dB
PL13 25.00 dB
PL2W 15.07131863 W
PL12W 0.06763186 W
PL13W 0.04765970 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



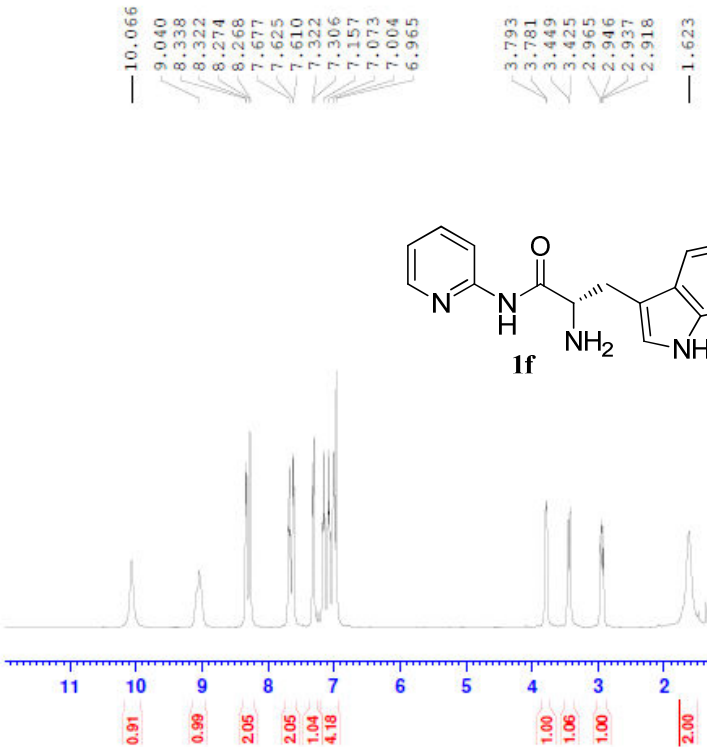
1e

Chemical Formula: $C_{16}H_{19}N_3O_2$
Exact Mass: 285.15
Molecular Weight: 285.34
m/z: 285.15 (100.0%), 286.15 (17.6%), 287.15 (2.0%), 286.14 (1.1%)
Elemental Analysis: C, 67.35; H, 6.71; N, 14.73; O, 11.21

HRMS = 308.1352 $(M+Na)^+$



dthr-H

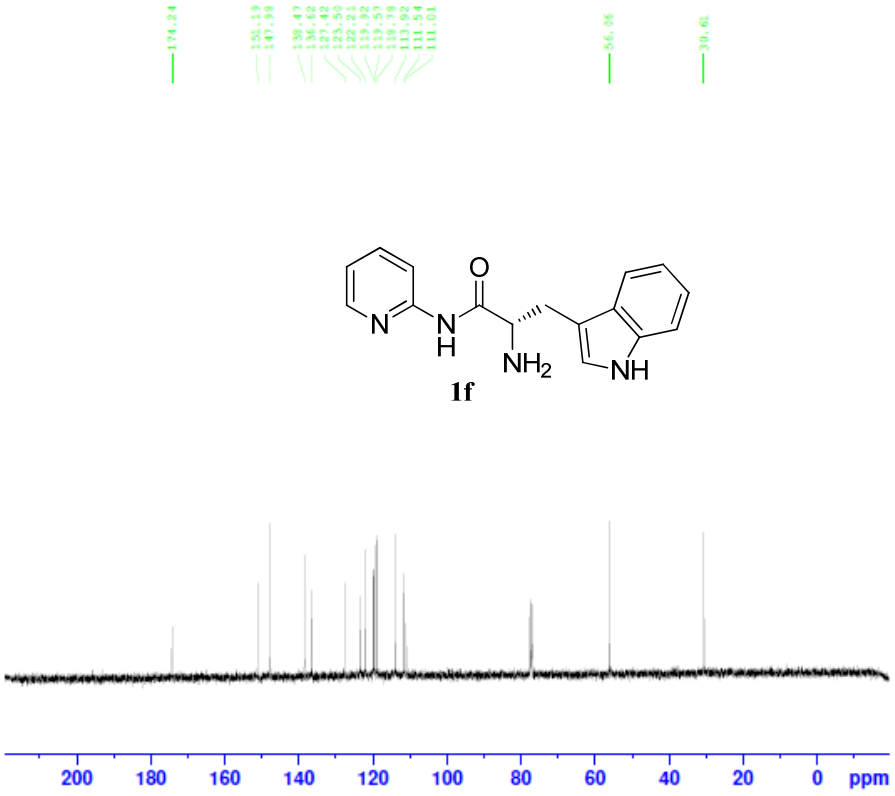


BRUKER

```
NAME                 dthr-H
EXPNO                     7
PROCNO                    1
Date_              20100122
Time                   9.17
INSTRUM                spect
PROBHD   5 mm TXI 1H-13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1720407 sec
RG                      25.4
DW                    48.400 usec
DE                     7.50 usec
TE                   295.2 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                     6.70 usec
PL1                    0.00 dB
PL1W              15.07131863 W
SFO1             500.1330885 MHz
SI                       32768
SF               500.1300227 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

dtrp-C

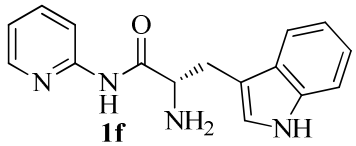


BRUKER

```
NAME                 dtrp-C
EXPNO                     7
PROCNO                    1
Date_              20100122
Time                   9.38
INSTRUM                spect
PROBHD   5 mm TXI 1H-13
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       84
DS                        4
SWH               30030.029 Hz
FIDRES             0.458222 Hz
AQ                 1.0912410 sec
RG                     1024
DW                    16.650 usec
DE                     7.50 usec
TE                   295.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                    12.20 usec
PL1                   -3.00 dB
PL1W             190.45114136 W
SFO1             125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  23.48 dB
PL13                  25.00 dB
PL2W              15.07131863 W
PL12W              0.06763186 W
PL13W              0.04765970 W
SFO2             500.1320005 MHz
SI                       32768
SF               125.7577890 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



1f

Chemical Formula: $C_{16}H_{16}N_4O$
Exact Mass: 280.13
Molecular Weight: 280.32
m/z: 280.13 (100.0%), 281.14 (17.5%), 282.14 (1.7%), 281.13 (1.5%)
Elemental Analysis: C, 68.55; H, 5.75; N, 19.99; O, 5.71

MS (ESI) = 281.1 $(M+H)^+$

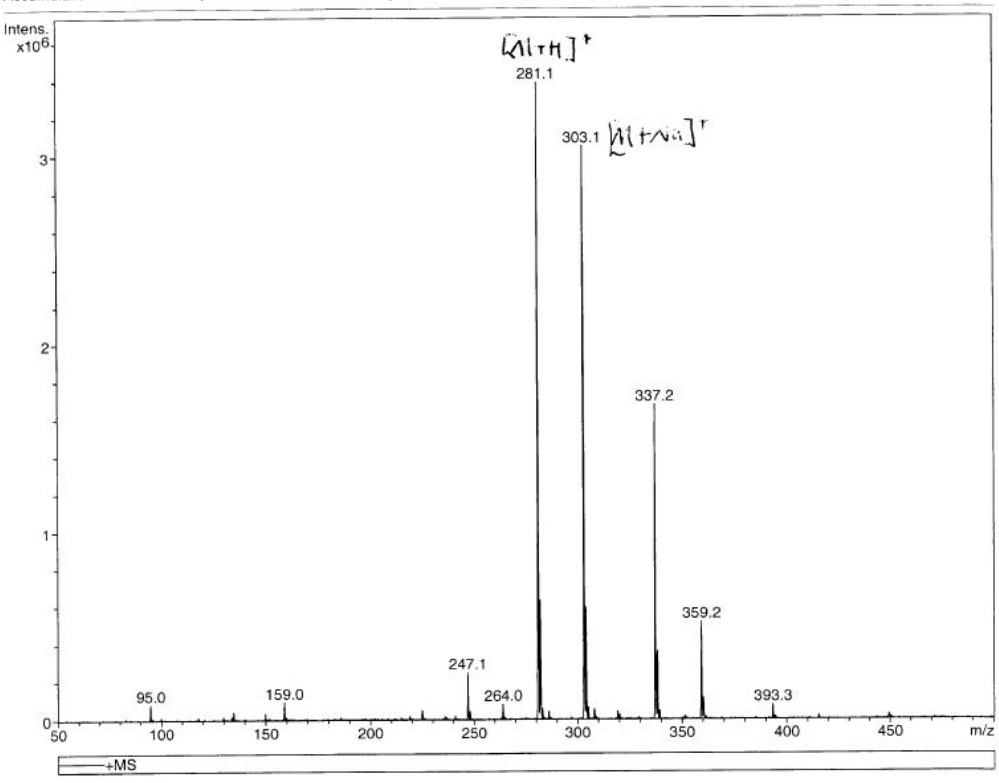
Display Report

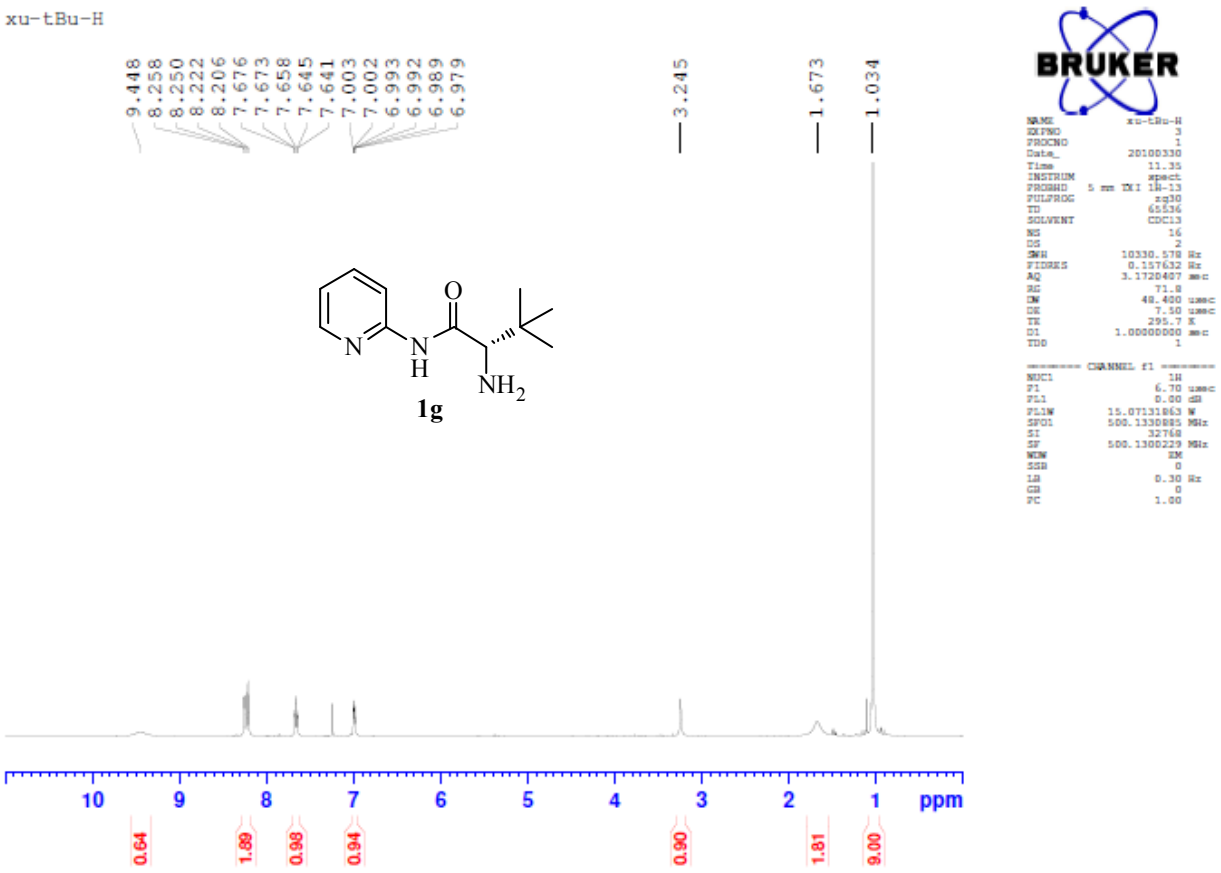
Analysis Info

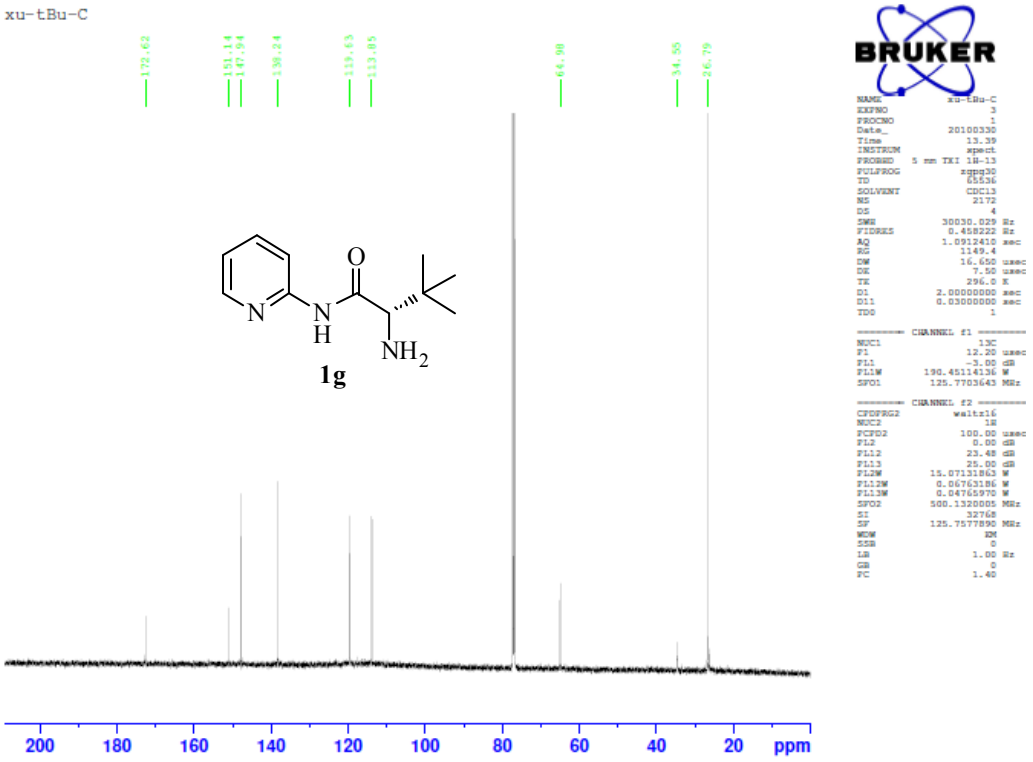
Analysis Name	d2-13000.d	Acquisition Date	09/23/09 11:29:30
Method	PTSHMSMS.M	Operator	Administrator
Sample Name	d2-13	Instrument	Esquire-LC_00137
Comment	Diluted 1/40 in MEOH		

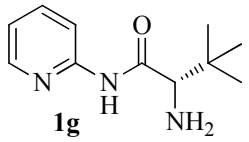
Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	50.00 m/z	Scan End	500.00 m/z
Capillary Exit	79.2 Volt	Skim 1	12.7 Volt	Trap Drive	30.7
Accumulation Time	647 µs	Averages	20 Spectra	Auto MS/MS	Off




xu-tBu-H
9.448
8.258
8.250
8.222
8.206
7.676
7.673
7.658
7.645
7.641
7.003
7.002
6.993
6.992
6.989
6.979
3.245
1.673
1.034
BRUKER
NAME xu-tBu-H
EXPNO 3
PROCNO 1
Date_ 20100330
Time 11.35
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 71.8
DW 48.400 usec
DE 7.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 6.70 usec
PL1 0.00 dB
PL1W 15.07131863 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300229 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
N
H
O
NH2
1g
10
9
8
7
6
5
4
3
2
1
ppm
0.64
1.89
0.98
0.94
0.90
1.81
9.00


xu-tBu-C
172.62
151.14
147.94
138.24
119.63
113.85
64.98
34.55
26.79
O
N
H
N
NH2
1g
200
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME xu-tBu-C
EXPNO 3
PROCNO 1
Date_ 20100330
Time 13.39
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2172
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 1149.4
DW 16.650 usec
DE 7.50 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 12.20 usec
PL1 -3.00 dB
PL1W 190.45114136 W
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 23.48 dB
PL13 25.00 dB
PL2W 15.07131863 W
PL12W 0.06763186 W
PL13W 0.04765970 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



1g

Chemical Formula: $C_{11}H_{17}N_3O$
Exact Mass: 207.14
Molecular Weight: 207.27
m/z: 207.14 (100.0%), 208.14 (12.1%), 208.13 (1.1%)
Elemental Analysis: C, 63.74; H, 8.27; N, 20.27; O, 7.72

MS (ESI) = 230.1 $(M+Na)^+$

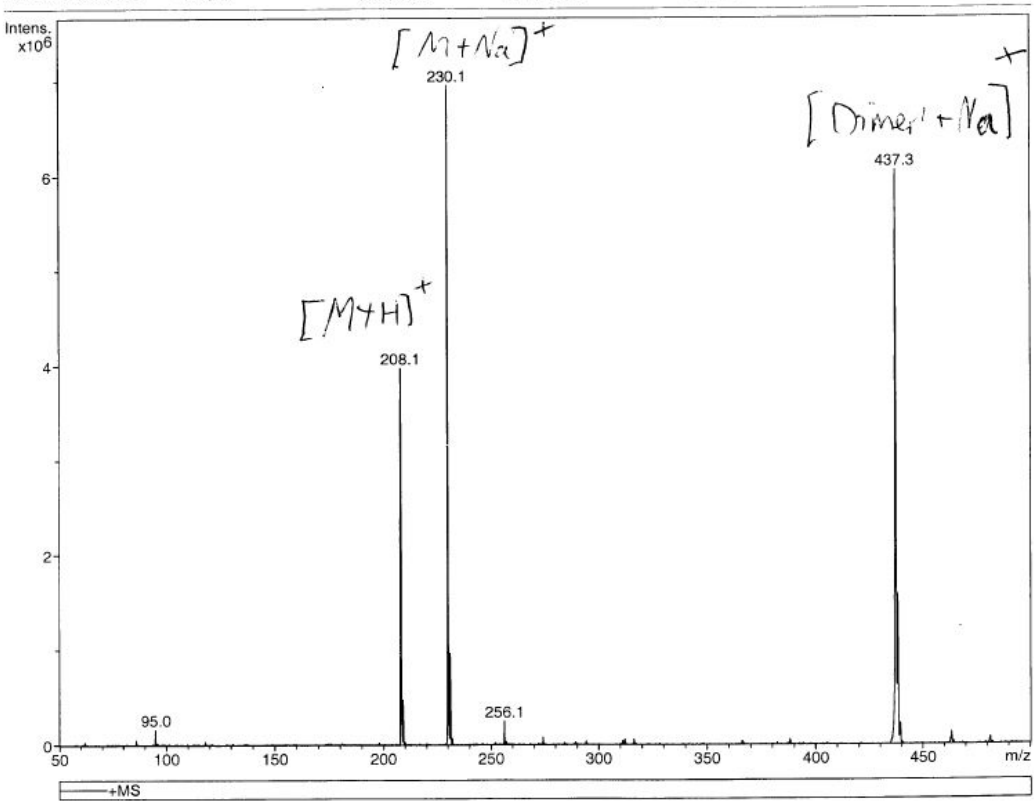
Display Report

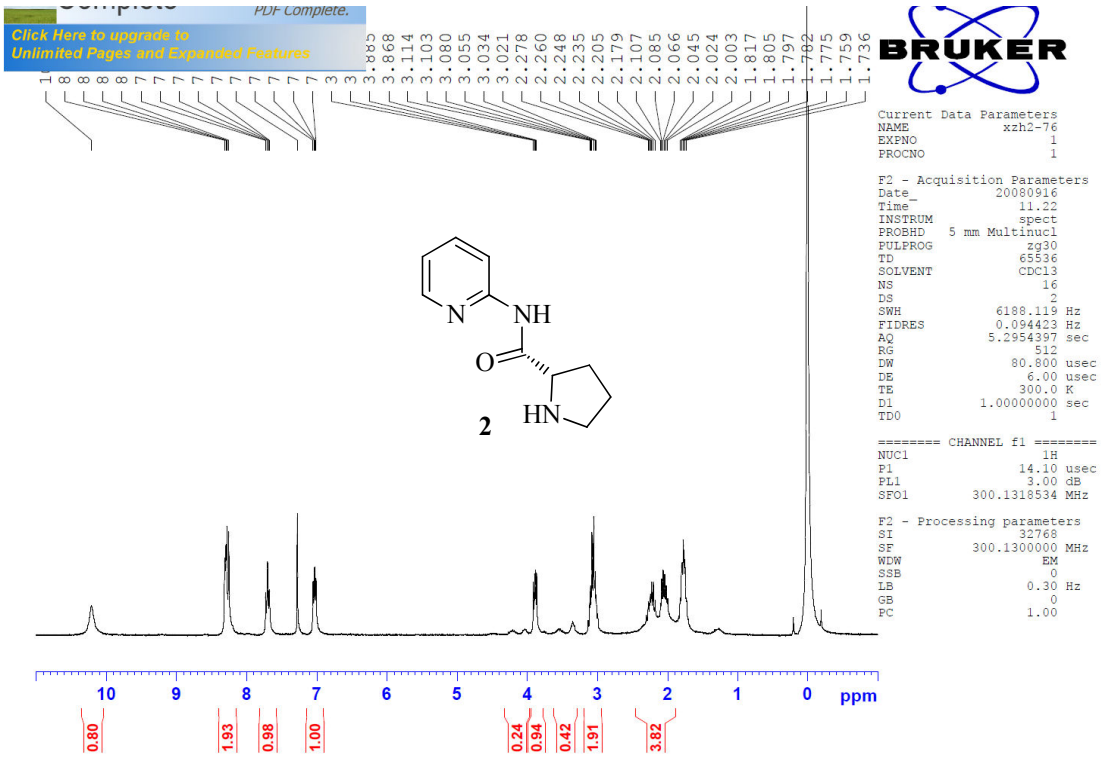
Analysis Info

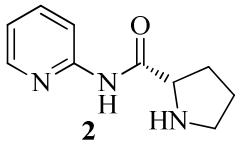
Analysis Name	d2-79000.d	Acquisition Date	03/30/10 13:59:19
Method	NOVAKS.M	Operator	Administrator
Sample Name	d2-79	Instrument	Esquire-LC_00137
Comment	Diluted 1/50 in MEOH		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	50.00 m/z	Scan End	500.00 m/z
Capillary Exit	76.7 Volt	Skim 1	10.5 Volt	Trap Drive	29.6
Accumulation Time	300 μs	Averages	20 Spectra	Auto MS/MS	Off



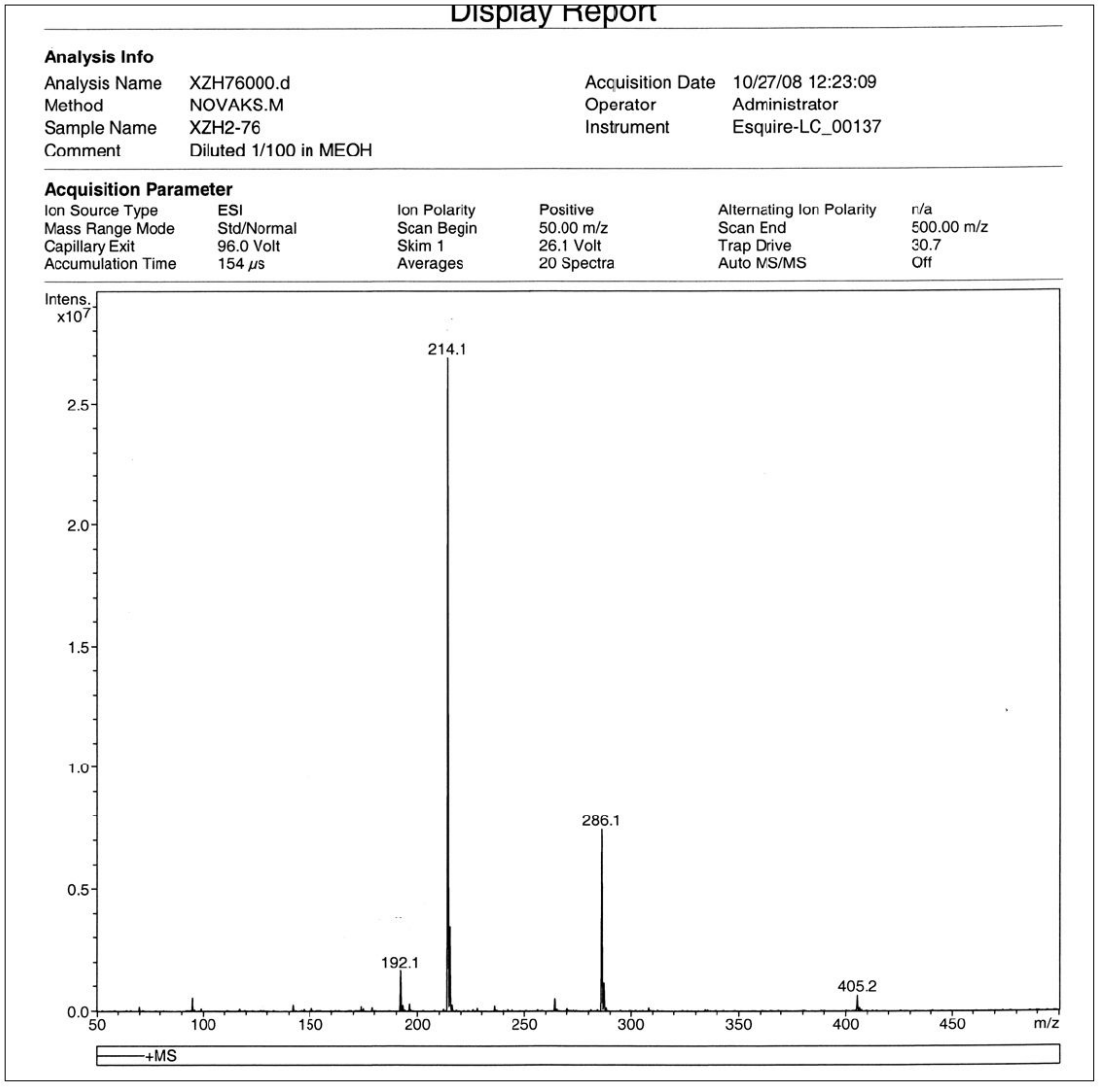




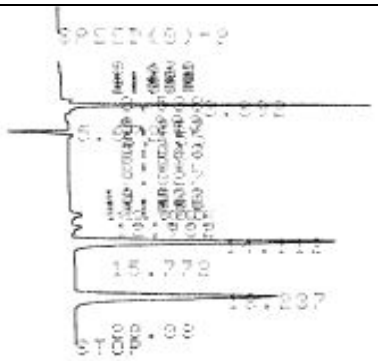
2

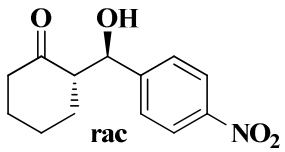
Chemical Formula: $C_{10}H_{13}N_3O$
Exact Mass: 191.11
Molecular Weight: 191.23
m/z: 191.11 (100.0%), 192.11 (11.0%), 192.10 (1.1%)
Elemental Analysis: C, 62.81; H, 6.85; N, 21.97; O, 8.37

MS (ESI) = 214.1 $(M+Na)^+$



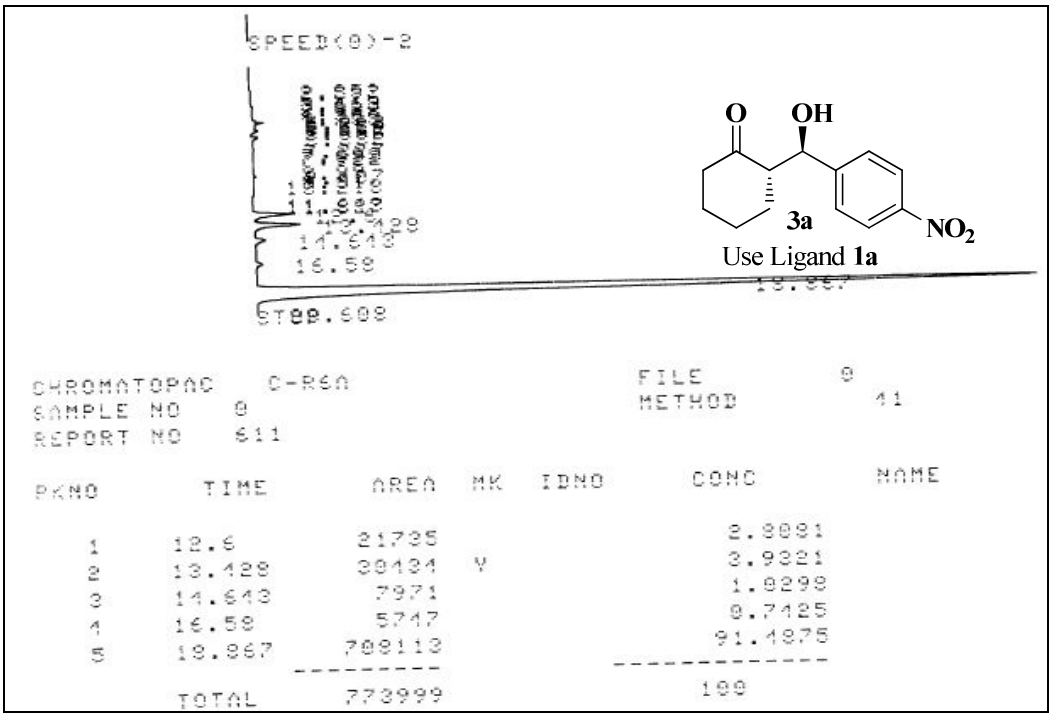
HPLC DATA FOR ALDOL ADDUCTS





CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 750

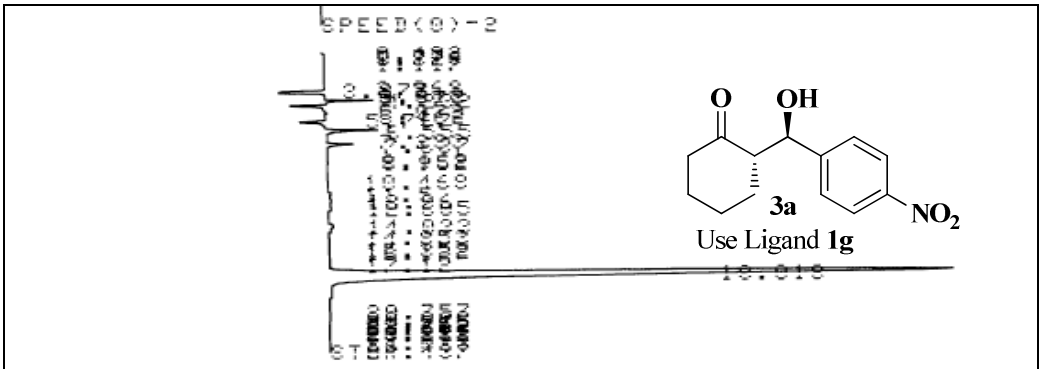
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.539	11612			1.647	
2	3.892	119552	V		16.9576	
3	4.892	27323	V		3.8755	
4	5.217	26199	V		3.7149	
5	5.357	26407	V		3.7456	
6	5.672	32605	V		4.6249	
7	6.155	51079			7.245	
8	6.71	27608	V		3.916	
9	7.943	25019	V		3.5489	
10	7.557	18326	V		2.5994	
11	14.112	170635	V		24.2033	
12	19.237	168652			23.9221	
	TOTAL	705006			100	



CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 611

FILE 0
METHOD 41

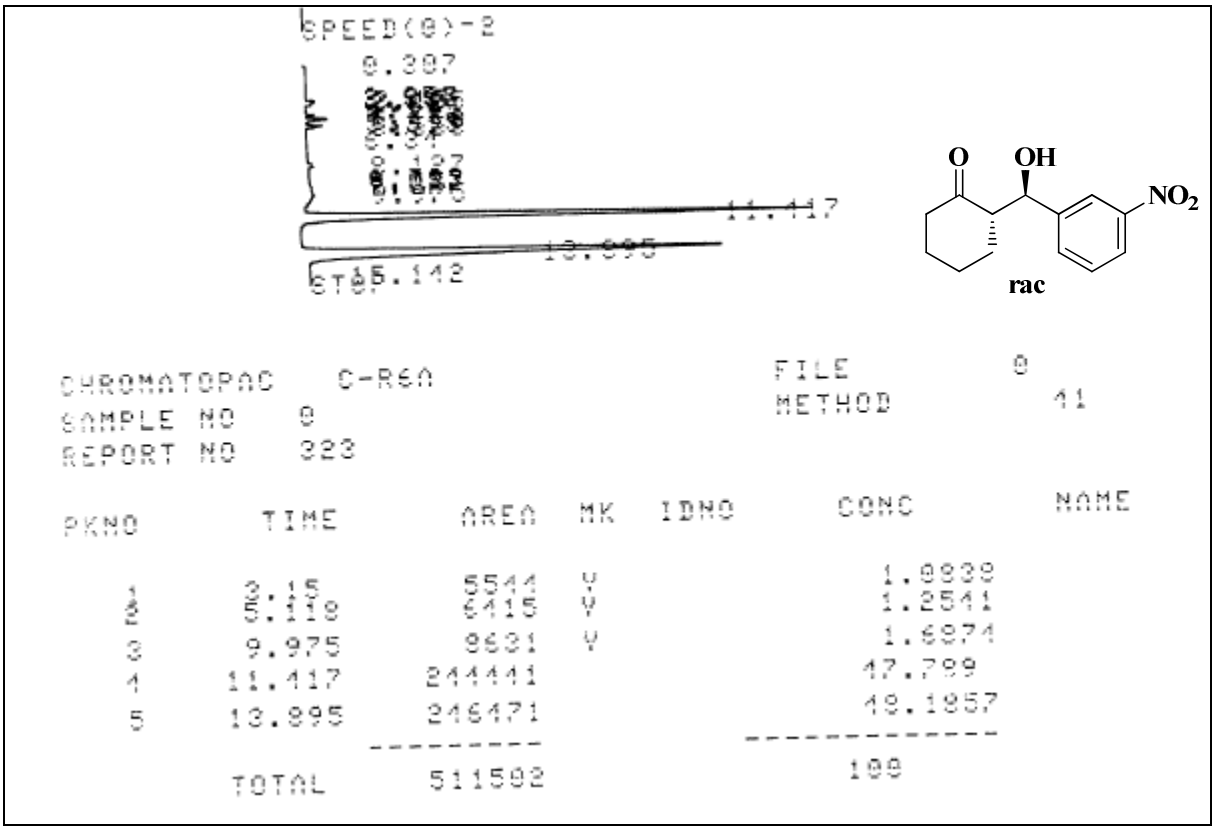
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.6	21735			2.8081	
2	13.428	30134	V		3.9021	
3	14.643	7971			1.0299	
4	16.59	5747			0.7425	
5	19.867	709113			91.4975	
	TOTAL	773999			100	



CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 945

FILE 0
METHOD 41

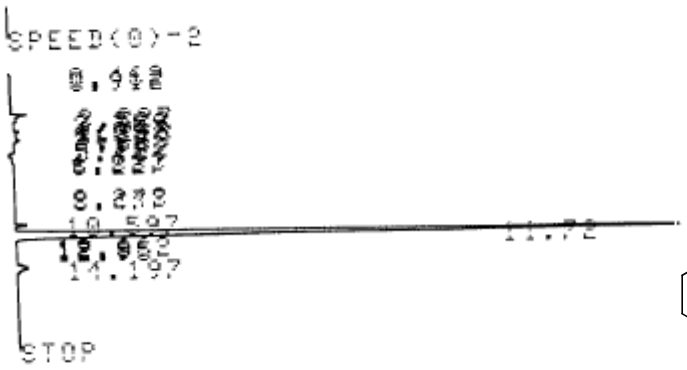
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.277	13097	V		1.6773	
2	3.912	19906			2.4984	
3	3.973	11192	V		1.4333	
4	4.232	52142	V		6.6772	
5	5.072	42351	V		5.4218	
6	5.462	21465	V		2.7488	
7	5.767	10325	V		1.3222	
8	6.555	59605	V		7.633	
9	7.283	17591	V		2.2527	
10	7.637	24318	V		3.118	
11	9.162	12541	V		1.606	
12	19.919	497411	V		63.6993	
	TOTAL	780985			100	

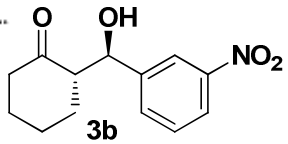


CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 323

FILE 0
METHOD 41

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.15	5541	V		1.0939	
2	5.119	6415	V		1.2541	
3	9.975	9631	V		1.6974	
4	11.417	244441			47.799	
5	13.895	246471			48.1957	
	TOTAL	511502			100	



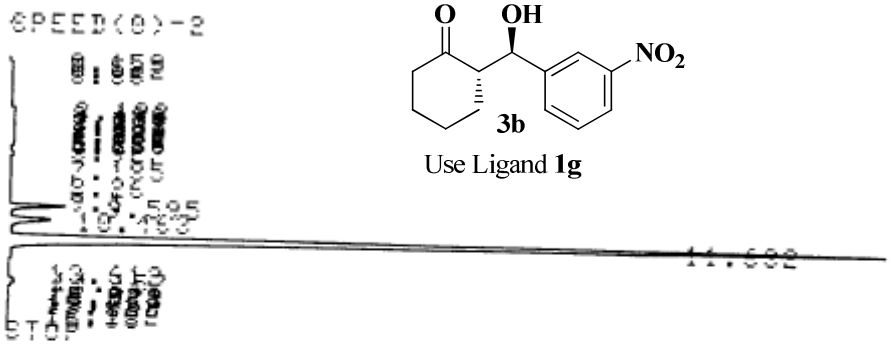


3b

Use Ligand **1a**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 324

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.597	6219			1.9319	
2	11.72	310427	SV		95.9927	
3	14.197	6745			2.0956	
	TOTAL	323420			100	

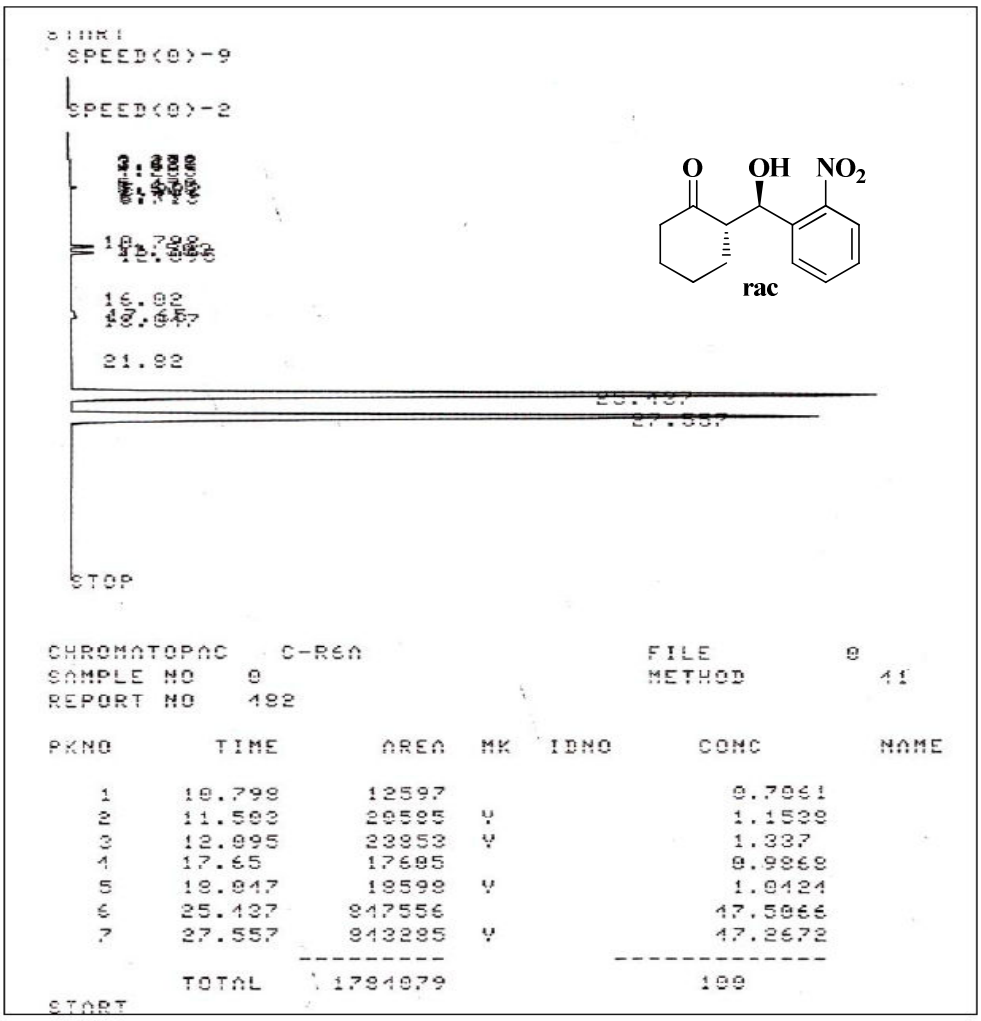


3b

Use Ligand **1g**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 939

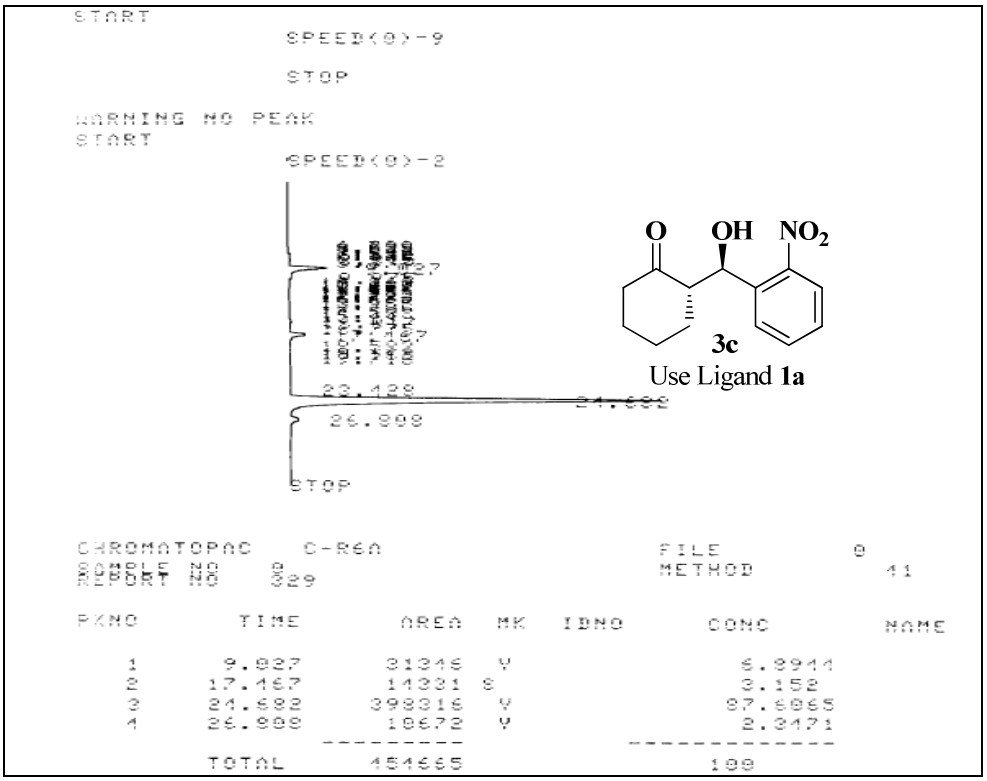
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	9.595	22029			1.9767	
2	10.463	20254	V		1.8265	
3	11.632	425047	V		90.7969	
	TOTAL	469130			100	



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 482

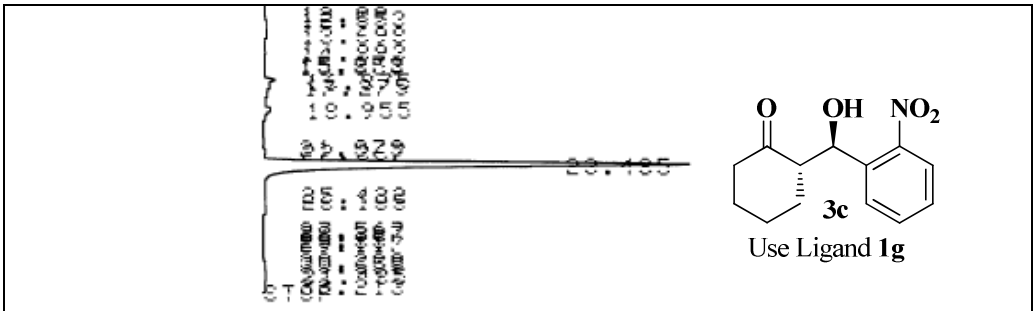
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.798	12597			0.7061	
2	11.503	20585	V		1.1538	
3	12.095	23853	V		1.337	
4	17.65	17685			0.9868	
5	18.947	18598	V		1.0424	
6	25.437	847556			47.5066	
7	27.557	843285	V		47.2672	
	TOTAL	1784079			100	

START



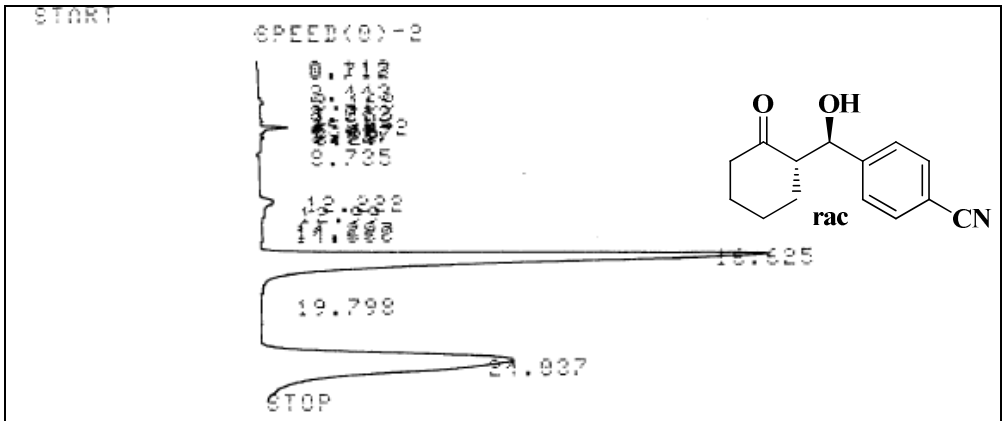
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 329

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	9.927	31346	V		6.9911	
2	17.467	14331	B		3.152	
3	21.692	398316	V		87.6065	
4	26.999	10672	V		2.3471	
	TOTAL	454665			100	



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 926

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	2.728	12992			2.9413	
2	8.925	27711			6.3224	
3	10.89	10304	V		2.3509	
4	22.185	387286	V		88.3853	
	TOTAL	438292			100	



CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 343

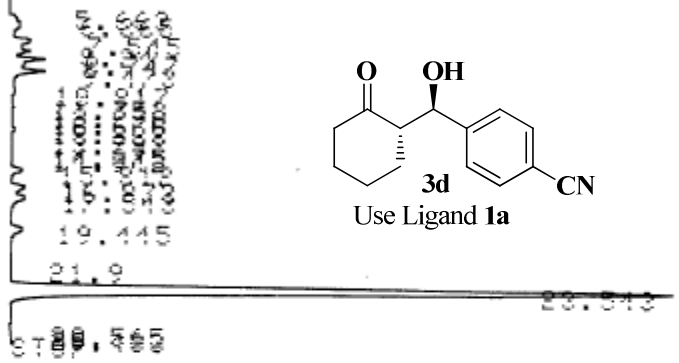
FILE 0
METHOD 41

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	5.172	12737	V		0.738	
2	12.222	16976			0.9837	
3	12.99	6539	V		0.3789	
4	16.625	956919	BV		49.651	
5	21.037	932613			48.2491	

START

SPEED(0)-9

SPEED(0)-2

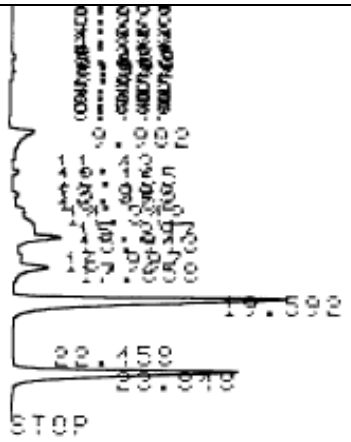


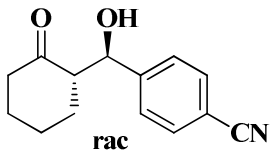
3d

Use Ligand **1a**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 342

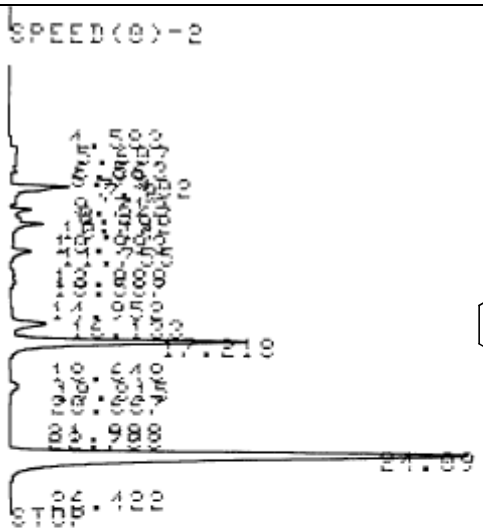
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	6.365	20221	V		2.5097	
2	7.545	17761	V		2.2041	
3	9.24	14143	V		1.7551	
4	9.747	22391	V		2.7779	
5	9.473	24943	V		3.0953	
6	10.917	8557	V		1.0619	
7	15.912	11092	V		1.3763	
8	16.979	12734	V		1.5802	
9	17.543	15119	V		1.8762	
10	19.445	12991	V		1.6122	
11	23.543	645995			80.1524	
	TOTAL	805934			100	

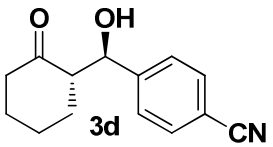




CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 974

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	9.902	36391			6.1135	
2	14.342	16399	V		2.7549	
3	15.297	39174	V		6.5811	
4	15.943	49690	V		8.3441	
5	16.997	12662	V		2.0263	
6	17.659	35890	V		6.0295	
7	19.592	206452	V		34.6835	
8	23.918	208199	V		34.977	
	TOTAL	595216			100	

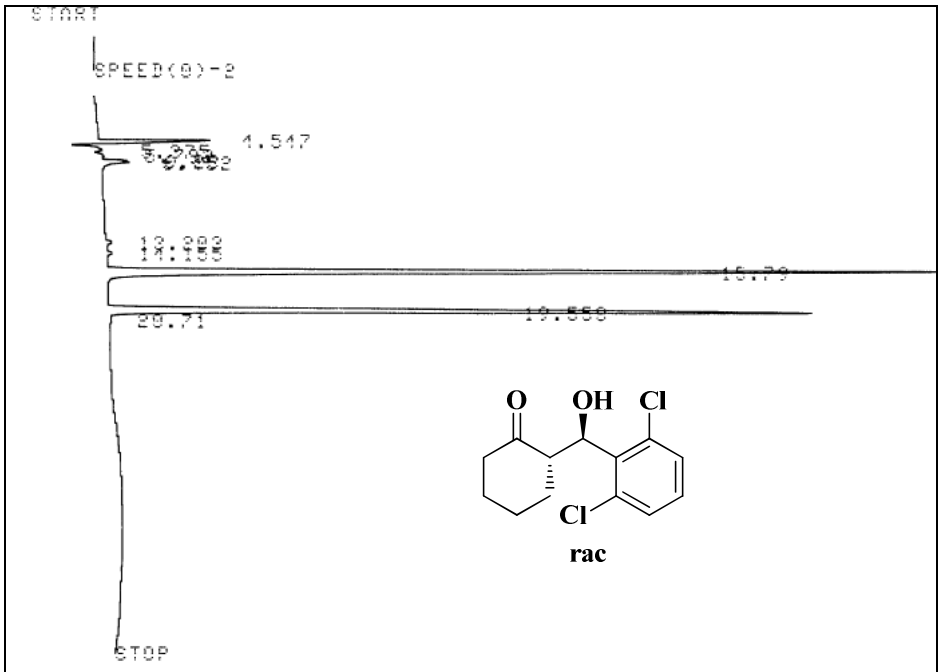




Use Ligand **1g**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 972

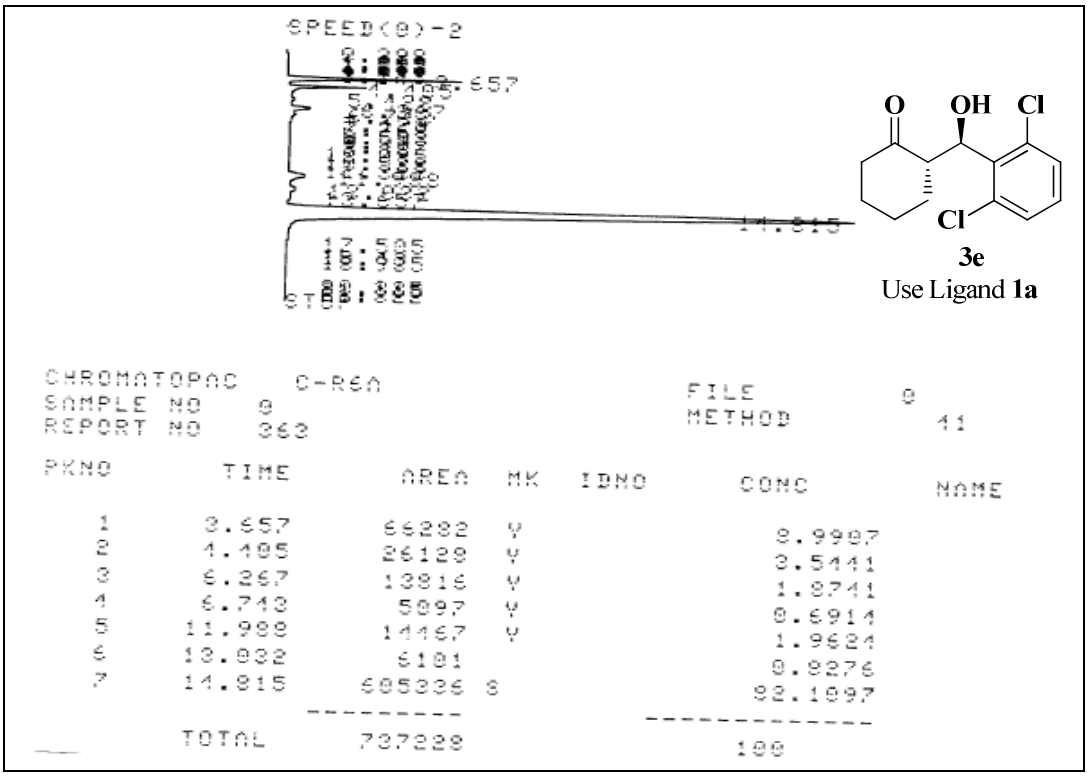
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	5.687	10203	V		1.4347	
2	7.9	38851	SV		5.4631	
3	9.267	10339			1.4537	
4	10.14	18523	V		2.6047	
5	11.755	13925	V		1.9581	
6	16.133	29162	V		4.1007	
7	17.219	154059	V		21.6632	
8	24.09	436888	SV		61.3217	
	TOTAL	711149			100	



rac

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 710

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.547	70568			4.5366	
2	5.375	29717			1.9178	
3	5.792	17500	V		1.1284	
4	6.29	20679	V		1.3275	
5	6.452	23024	V		1.5294	
6	15.79	698905			44.8673	
7	19.558	696422			44.7079	
	TOTAL	1557714			100	



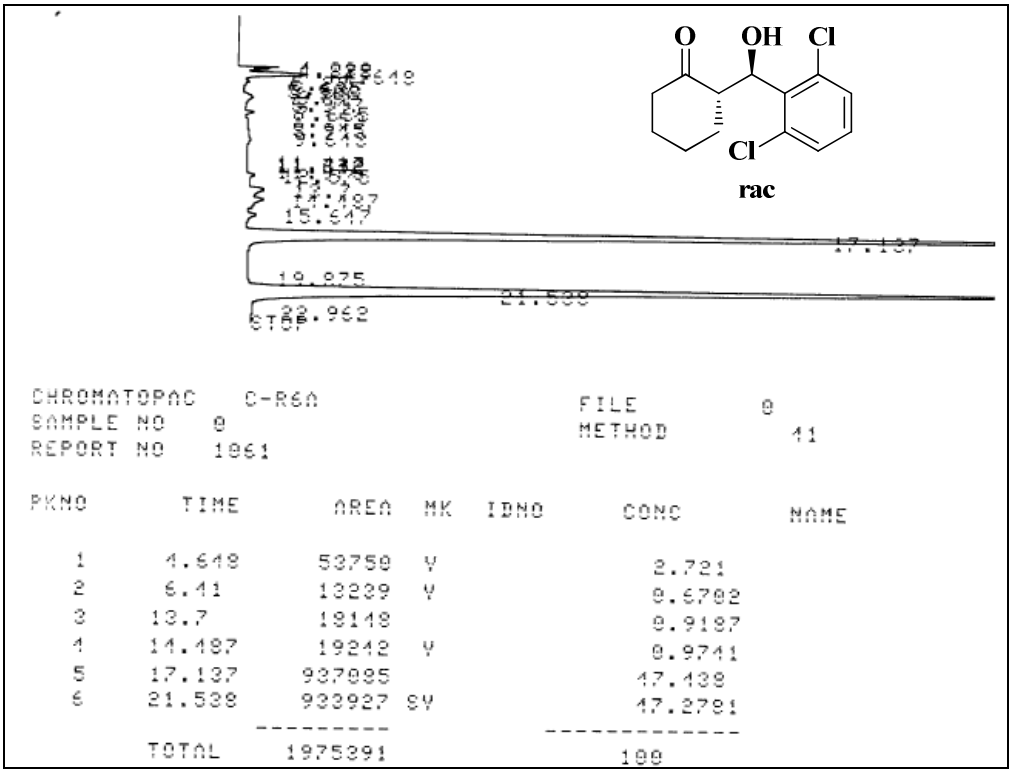
3e

Use Ligand **1a**

CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 363

FILE 0
METHOD 41

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.657	66282	V		0.9907	
2	4.105	26129	V		3.5141	
3	6.267	13816	V		1.8741	
4	6.743	5097	V		0.6914	
5	11.988	14467	V		1.9624	
6	13.032	6101			0.8276	
7	14.815	605336	S		82.1097	
	TOTAL	737228			100	

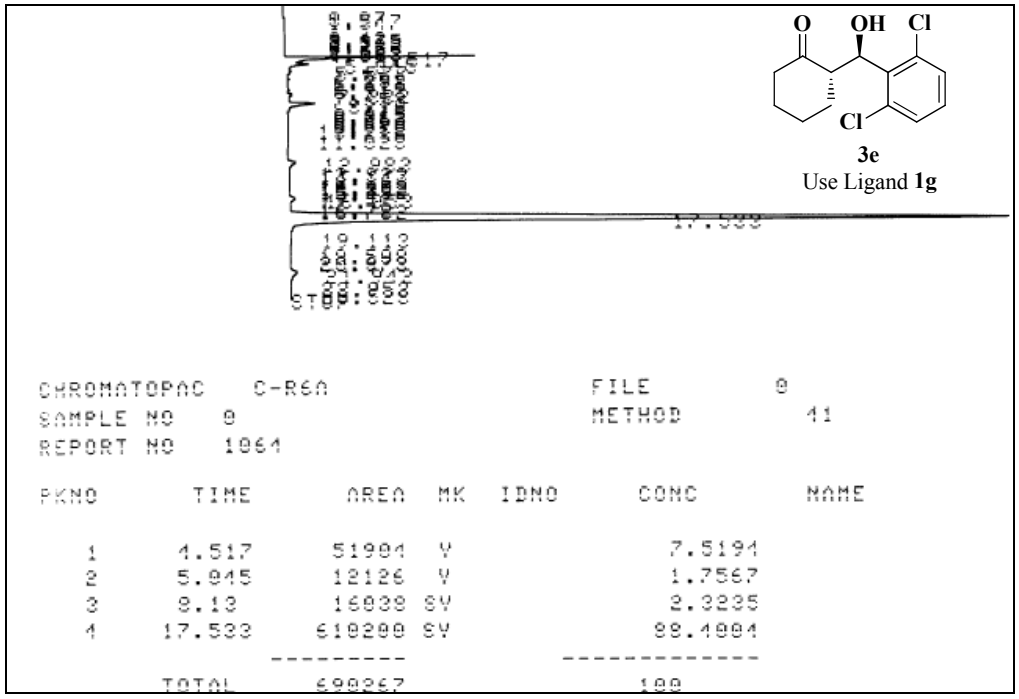


rac

CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 1061

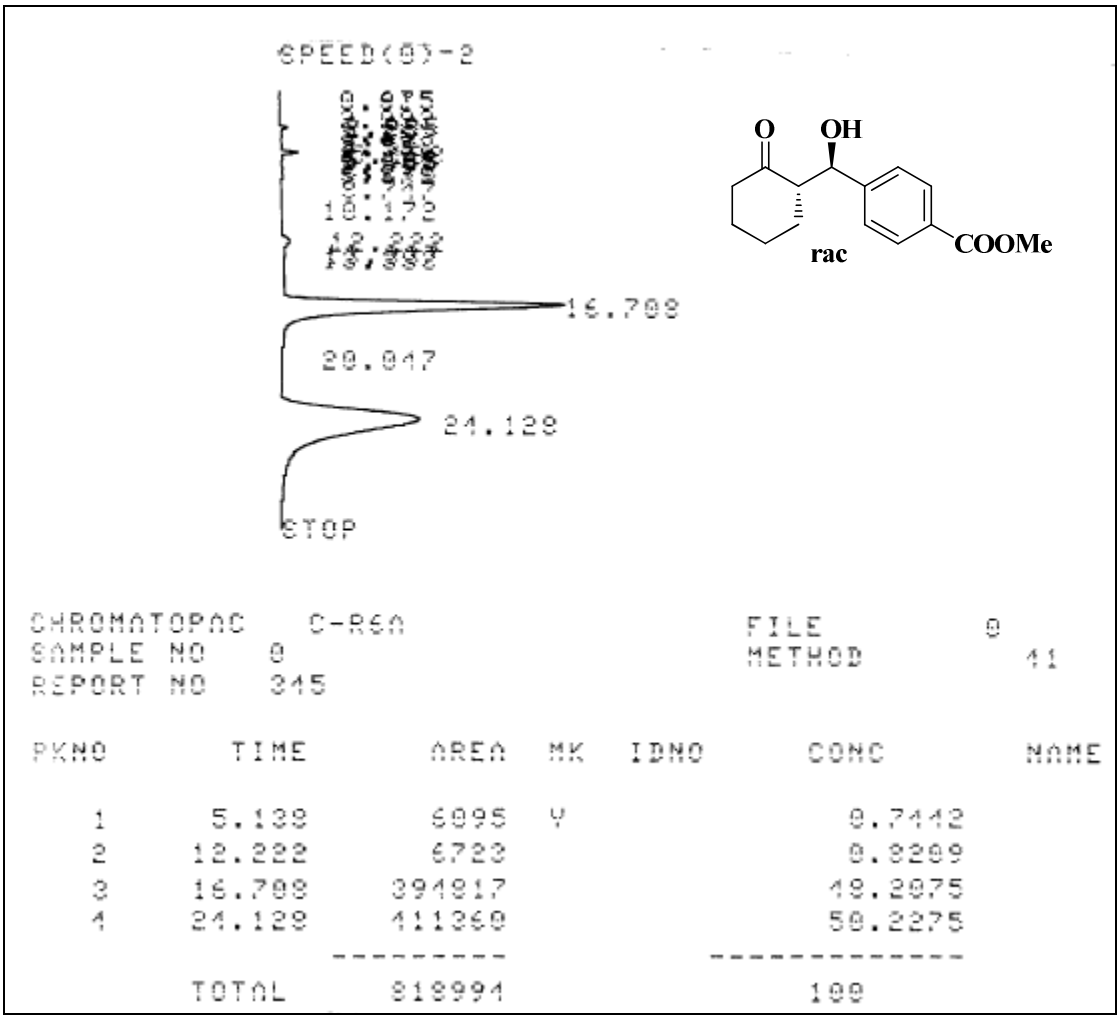
FILE 0
METHOD 41

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.648	53750	V		2.721	
2	6.41	13229	V		0.6702	
3	13.7	18148			0.9187	
4	14.487	19242	V		0.9741	
5	17.137	937095			47.439	
6	21.538	933927	SV		47.2791	
	TOTAL	1975391			100	



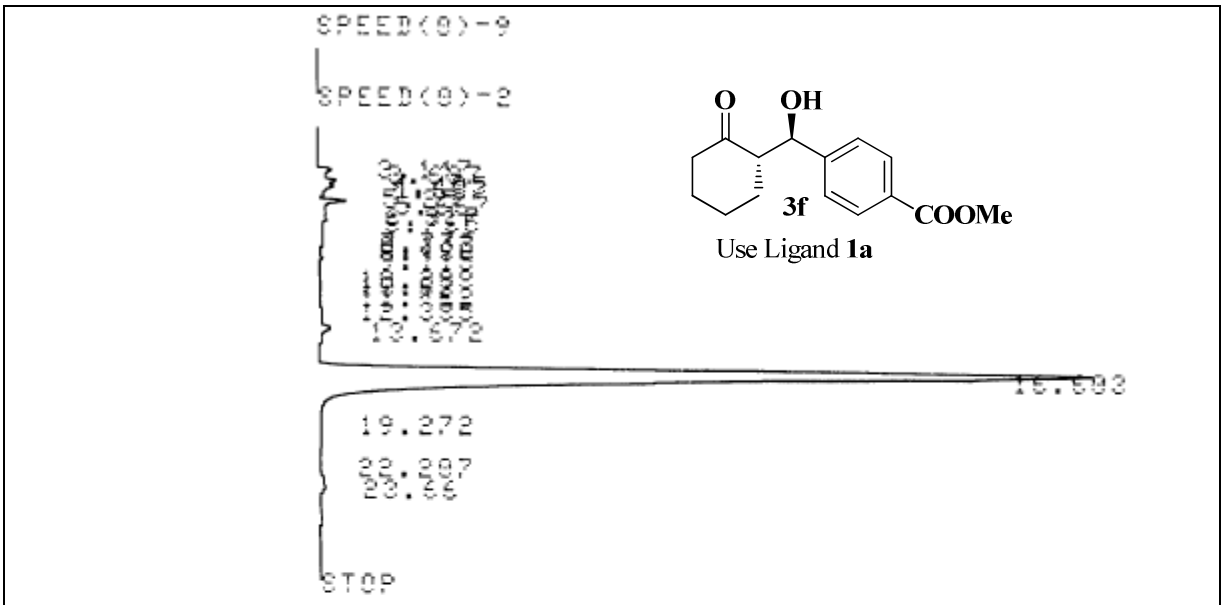
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 1061

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.517	51904	V		7.5191	
2	5.045	12126	V		1.7567	
3	8.13	16038	SV		2.3235	
4	17.533	610200	SV		88.4004	
TOTAL		690267			100	



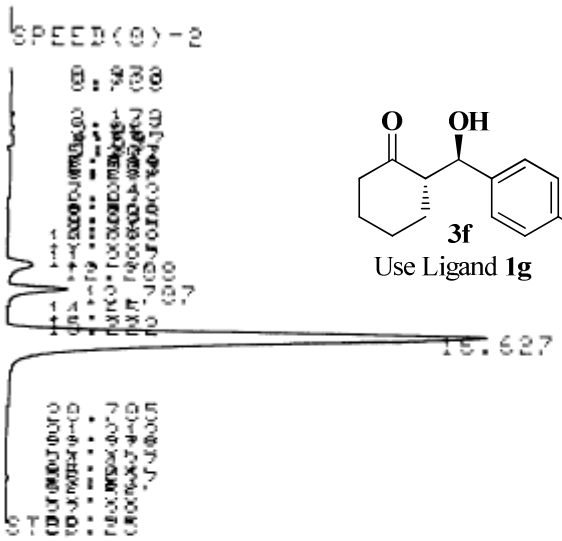
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 345

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	5.139	6095	V		0.7412	
2	12.222	6723			0.8209	
3	16.708	391917			19.2075	
4	24.129	411360			50.2275	
	TOTAL	816991			100	



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 11
REPORT NO 352

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.697	11519	V		1.0236	
2	4.105	10944	V		0.9819	
3	4.687	8101	V		0.7102	
4	5.667	13167	V		1.16	
5	6.317	5616	V		0.4918	
6	6.765	6031	V		0.5311	
7	13.672	7509			0.6616	
8	16.603	1055093	B		92.9567	
9	23.66	17559	V		1.5469	
	TOTAL	1135039			100	



3f

Use Ligand **1g**

CHROMATOPAC C-R6A

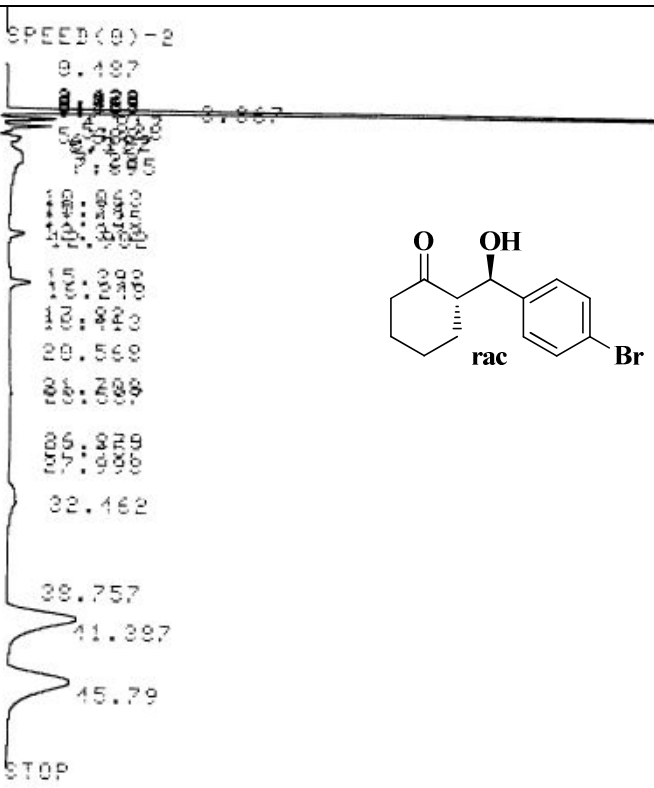
SAMPLE NO 9

REPORT NO 990

FILE 9

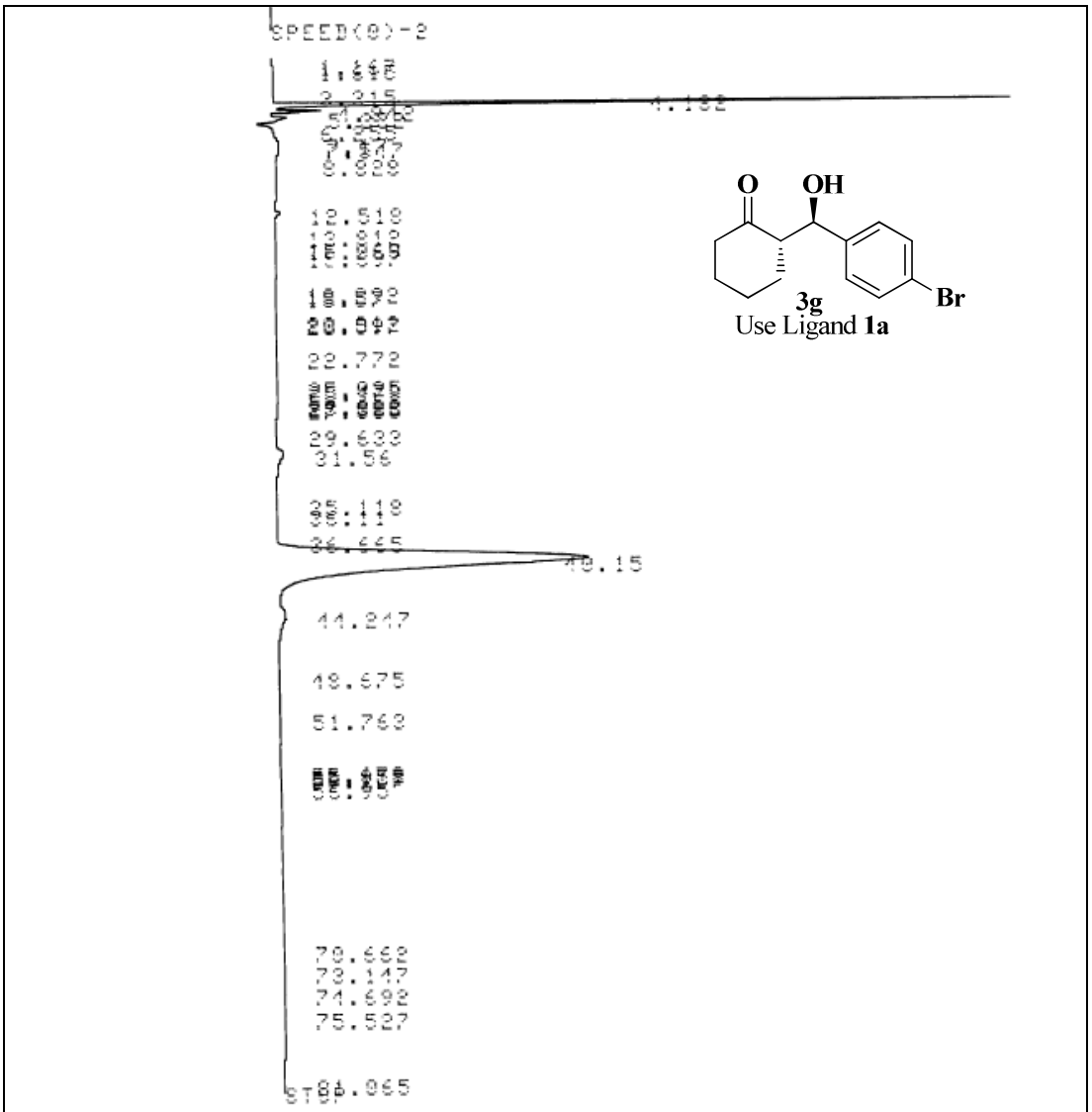
METHOD 11

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.209	29563	V		3.7147	
2	13.707	46599	SV		5.854	
3	16.627	719790	V		90.4313	
	TOTAL	795952			100	



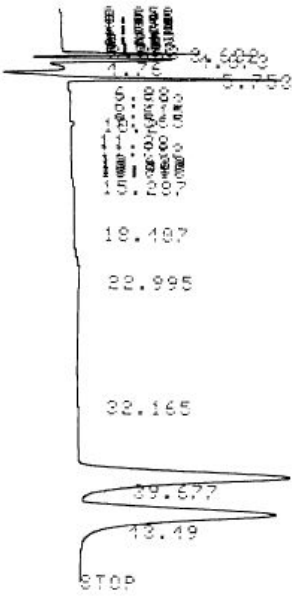
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 11
REPORT NO 153

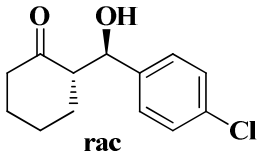
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.169	683913	V		51.927	
2	1.917	20827			1.5804	
3	5.328	23196	V		1.7601	
4	6.132	11634			0.8828	
5	6.317	9720	V		0.7375	
6	7.32	37902	V		2.8761	
7	7.695	56040	V		4.2523	
8	10.74	9707	V		0.7366	
9	12.372	5524	V		0.4192	
10	12.902	12504	V		0.9488	
11	15.292	5023			0.3811	
12	16.249	17717	V		1.3446	
13	32.462	31553			2.3942	
14	41.387	197363	V		14.9759	
15	45.79	196219	V		14.8891	
	TOTAL	1317879			100	



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 455

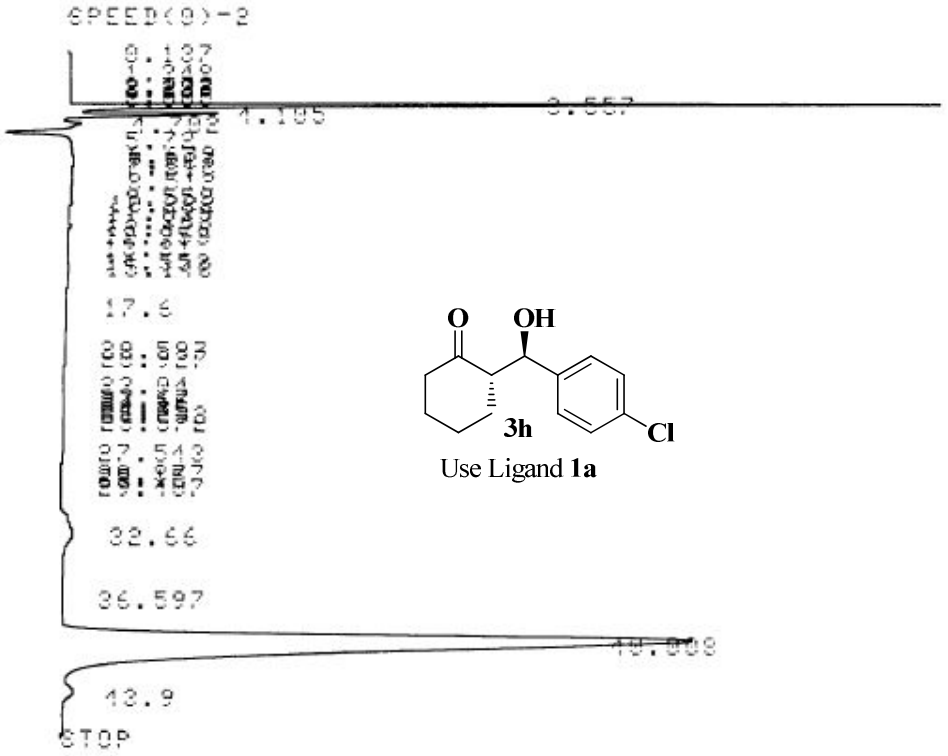
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.182	233947	BV		18.0118	
2	4.942	14169	T		1.0909	
3	5.332	18356			1.4139	
4	6.255	16960			1.3062	
5	7.17	31918	V		2.3925	
6	7.547	28746	V		2.2173	
7	8.929	7927	V		0.6115	
8	31.56	25511			1.9677	
9	40.15	892148	V		68.8131	
10	44.247	27697	V		2.1363	
	TOTAL	1296480			100	





CHROMATOPAC C-R6A FILE 9
SAMPLE NO 0 METHOD 41
REPORT NO 152

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.342	5944	V		0.1175	
2	1.997	14381	V		0.2892	
3	2.21	10739	V		0.2159	
4	2.357	5323	V		0.1071	
5	2.48	7899	V		0.1586	
6	2.697	13383	V		0.2691	
7	3.003	16715	V		0.3367	
8	3.363	14543	V		0.2925	
9	3.602	83442	V		1.679	
10	4.072	99047			1.9717	
11	4.76	72433	V		1.4566	
12	5.753	202940			4.081	
13	6.99	167030	V		3.3591	
14	7.593	109939	V		2.1907	
15	8.615	119502	V		2.4031	
16	9.565	99019	V		1.9912	
17	10.2	153612	V		3.0891	
18	11.29	99119	V		1.9932	
19	11.792	84659	V		1.7025	
20	12.633	128990	V		2.5939	
21	13.413	36707	V		0.7382	
22	13.707	24214	V		0.4869	
23	13.915	29188	V		0.5869	
24	15.287	233169	V		4.6889	
25	19.407	386587	V		8.7686	
26	22.995	613917	V		12.3456	
27	32.165	577975	V		11.6229	
28	39.677	929466	V		18.6911	
29	43.49	685957	V		13.7943	
	TOTAL	4972764			100	

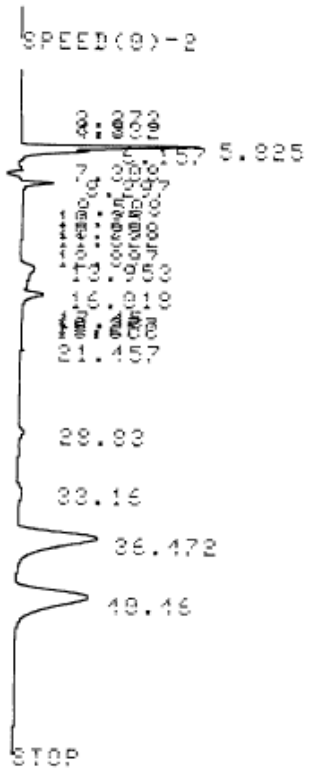


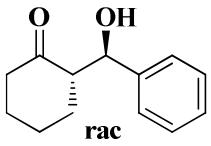
3h

Use Ligand **1a**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 450

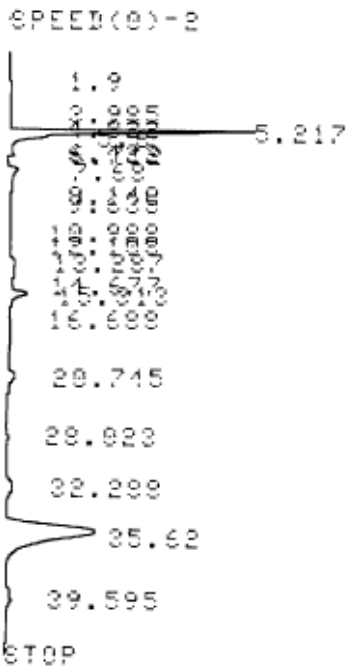
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.557	254097			10.0529	
2	4.105	56596	V		2.2391	
3	4.702	39593			1.566	
4	5.72	64821			2.5645	
5	6.673	97042	V		3.8393	
6	7.007	49750	V		1.9683	
7	7.513	51799	V		2.0295	
8	8.512	110425	V		4.3689	
9	9.559	28102	V		1.1119	
10	10.292	49886	V		1.9736	
11	11.099	29331	V		1.1604	
12	11.917	10972	V		0.4341	
13	12.422	21490	V		0.8502	
14	32.66	47313			1.8719	
15	40.009	1592410	B		63.001	
16	43.9	24192	T		0.9596	
	TOTAL	2527697			100	

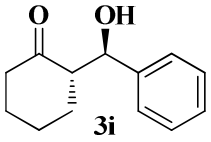




CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 424

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	5.925	89671			12.0031	
2	6.157	30273	V		4.0522	
3	7.300	9492			1.2705	
4	9.297	63443			8.4922	
5	9.500	9170	V		1.2295	
6	10.25	20608	V		2.7595	
7	10.999	12806	V		1.7142	
8	11.692	15096	V		2.0207	
9	12.887	18723	V		2.5057	
10	13.953	68849	V		9.039	
11	16.019	32939	V		4.3959	
12	21.457	6125			0.9199	
13	28.93	11709			1.5673	
14	33.16	12881			1.7242	
15	36.472	179851	V		23.9101	
16	40.16	177283			23.7305	
	TOTAL	747968			100	



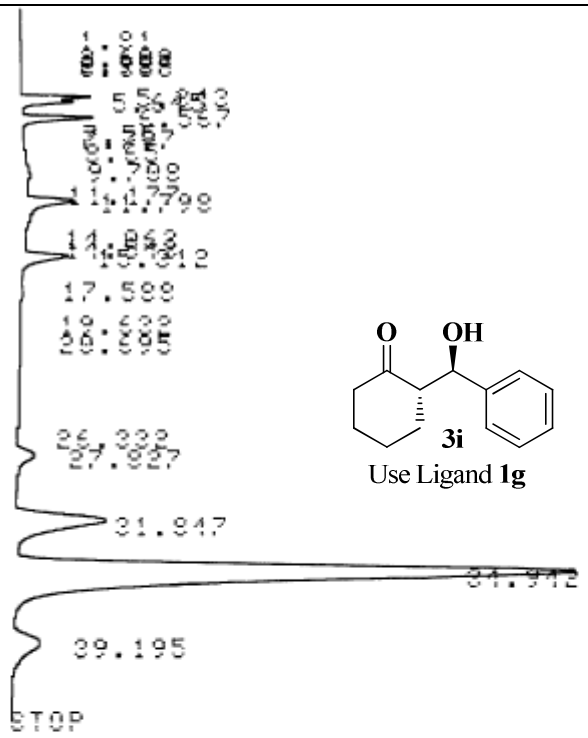


3i

Use Ligand **1a**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 11
REPORT NO 125

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	5.217	103316	V		26.2992	
2	5.6	21092	V		5.3672	
3	7.69	17971			4.5731	
4	10.297	10954	V		2.7875	
5	15.313	14922	V		3.7716	
6	20.745	9065			2.3069	
7	28.023	5910			1.4795	
8	32.299	13013			3.3113	
9	35.62	100499			15.9296	
10	39.595	16416			4.1773	
	TOTAL	392977			100	

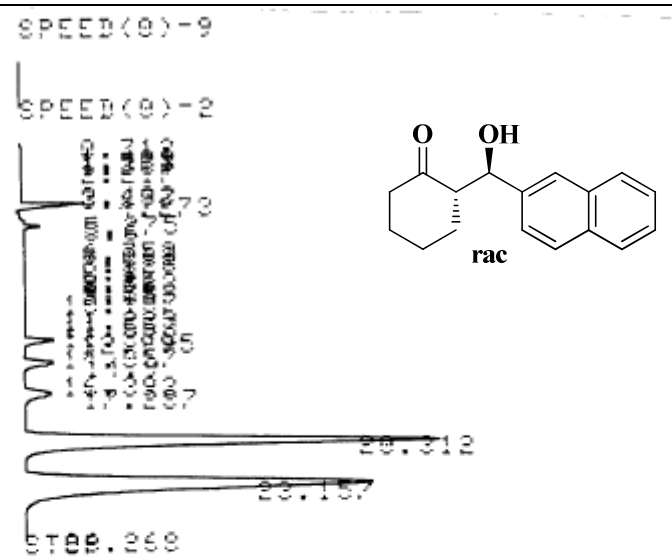


3i

Use Ligand **1g**

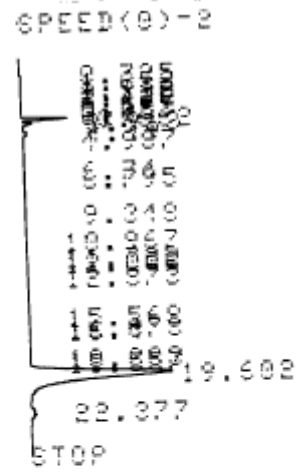
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 1005

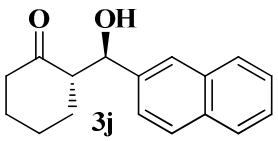
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	5.343	29621			1.7966	
2	5.645	20310	V		1.2749	
3	6.567	49194	BV		3.0246	
4	9.799	21670	V		1.3602	
5	11.799	73645	BV		4.6227	
6	15.312	52038	V		3.3167	
7	27.827	30216	V		1.8967	
8	31.847	169946			10.6019	
9	34.942	1094320	V		68.0637	
10	39.195	64346			4.0391	
	TOTAL	1592096			100	



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 164

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.273	25059	V		2.3429	
2	5.275	5391			0.504	
3	5.6	6610	V		0.618	
4	12.995	20638	V		1.9296	
5	14.9	28480	SV		2.6628	
6	17.287	27970			2.615	
7	20.312	479177			44.8005	
8	23.157	476252	V		44.5271	
	TOTAL	1069579			100	





3j

Use Ligand **1a**

CHROMATOPAC C-R6A

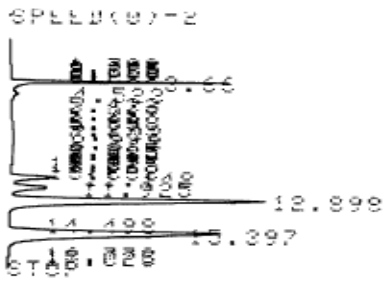
SAMPLE NO 0

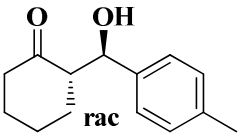
REPORT NO 167

FILE 0

METHOD 41

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.662	11311	V		6.3941	
2	19.602	159335	V		89.6699	
3	22.377	7014	V		3.9471	
	TOTAL	177693			100	

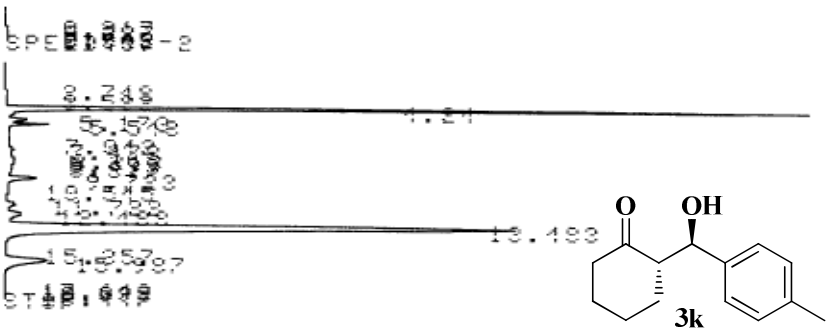




CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 475

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.66	66324			12.6932	
2	4.523	7010	SV		1.3379	
3	7.602	6564	V		1.2474	
4	11.149	27926			5.2977	
5	11.925	29039	V		5.328	
6	12.898	195479	V		37.146	
7	15.397	194974	V		37.0499	
	TOTAL	526245			100	

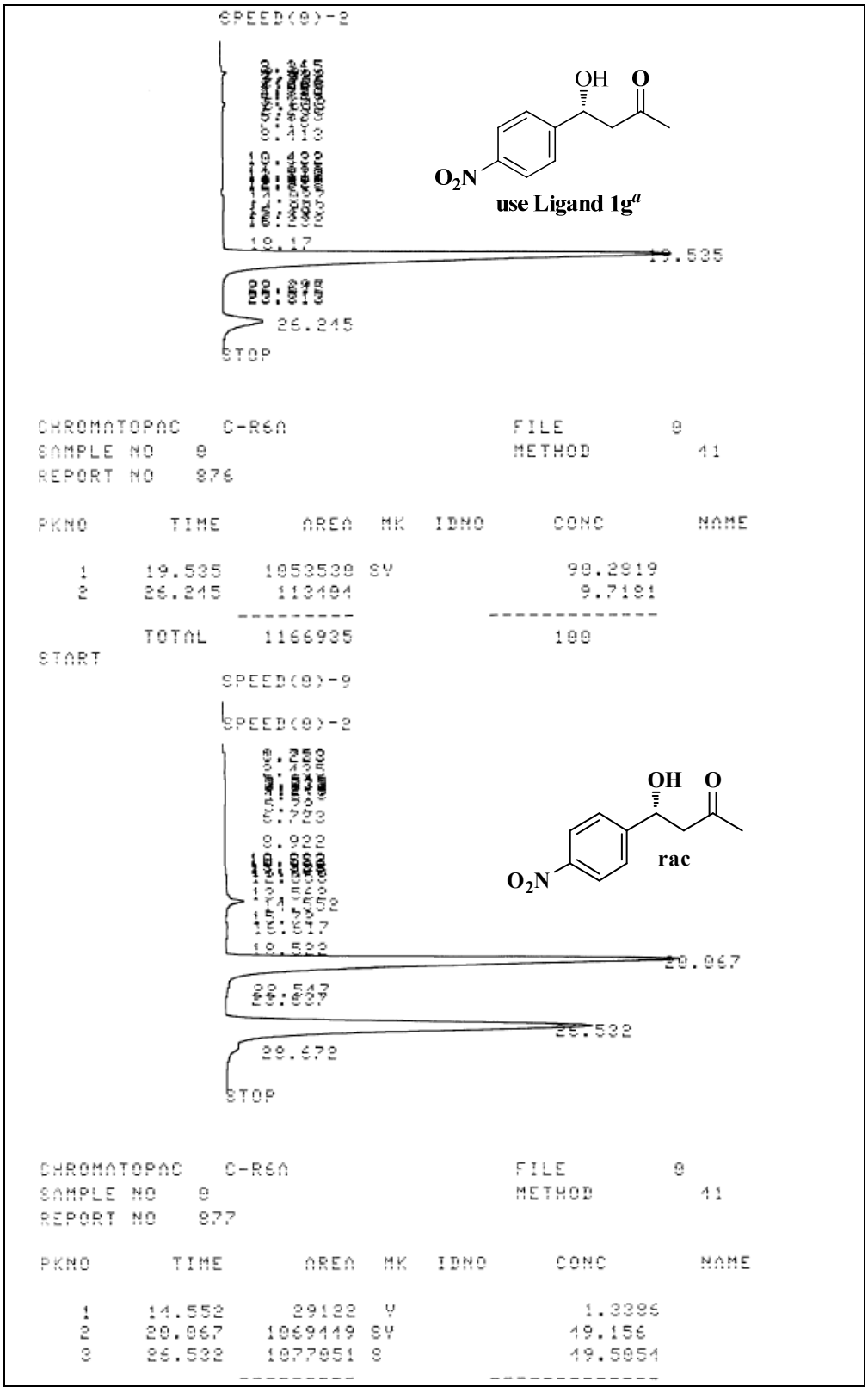
START



Use Ligand **1a**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 476

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.21	219291	SV		39.5729	
2	5.173	6682	T		1.202	
3	5.549	12624	TV		1.7691	
4	8.213	6134	V		0.8591	
5	9.723	14403	V		2.0172	
6	11.722	6394			0.8955	
7	12.498	13669	V		1.9144	
8	13.493	394575	V		55.2625	
9	15.987	39331	V		5.5095	
	TOTAL	714092			100	



[a] The reaction was performed with 0.2mmol aldehyde at rt for 45hrs in 1mL acetone (*neat*), with ligand **1g**

1 N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc*., **2006**, *128*, 734

2 H. Yang, R. G. Carter, *Org. Lett*., **2008**, *10*, 4649

3 Y. Wu, Y. Zhang, M. Yu, G. Zhao, S. Wang, *Org. Lett*., **2006**, *8*, 4417

4 Z. Tang, Z. Yang, X. Chen, L. Cun, A. Mi and L. Gong, *J. Am. Chem. Soc*., **2005**, *127*, 9285.