Supporting Information

Supporting Information for:

Rhodium complex with Unsymmetrical Vicinal Diamine Ligand: Excellent Catalyst for Asymmetric Transfer Hydrogenation of Ketones

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Contents:

1 Synthesis and characterization of unsymmetrical Vicinal Monotosylated Diamines

1.1 Preparation of ligand 1

In a 3 necked 100 ml round bottom flask 1R, 2S norephedrine compound **9** (3.0g, 20 mmol), triphenyl phosphine (5.2g,20 mmol) and Boc protected *p*- toluene sulfonylamide(5.42 g,20 mmol) were stirred in dichloromethane, (50ml) and the solution was cooled to 0-5^{0}C. To this solution DEAD (3.46 g, 20 mmol) was added slowly over a period of 15 mins. The solution was brought to room temperature and stirred for another 6 h. After 6 h of stirring, reaction mass was washed with 1N HCl (10ml) in water (40 ml). 4N HCl in dioxane (20 ml) was added and the reaction mixture was heated at 50^0 for 2 h. The reaction mass after heating was evaporated to near dryness and dichloromethane (50 ml) and water (50 ml) was added to it. The layers were shaked vigorously and DCM layer was discarded. Aqueous layer was neutralized slowly using dilute NaOH (4N), by drop wise addition to the aqueous layer till the pH was 7. The white solid precipitated was allowed to digest overnight at room temperature and then filtered using sintred glass crucible. The precipitate was washed 2-3 times using water (10 ml) and was dried in oven at 60^{0}C. White solid was crystalized from toluene to get pure sulfonamide Ligand 1, 2 g, (Yield 32.8 %) ligand**1.**

ligand 1

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.52 (d, *J*=8.0 Hz, 2H), 7.14 -7.01 (m, 7H), 4.20 (d, *J*=5.0 Hz, 1H), 3.20 - 3.13 (m, 1H), 2.33 (s, 3H), 0.95 (d, *J*=6.5 Hz, 3H);^{13}C NMR (101MHz, CHLOROFORM-d) δ ppm,142.9, 137.5, 137.2, 129.2,128.1,127.6,127.4,127.0,62.6, 51.0, 21.5, 20.7;FTIR (KBr, cm^{-1})3574,3358, 2878, 1599, 1323, 1162, ;HRMS calculated mass: 304.1245, measured mass: 304.1254;[α] $^{25}_D$= -64.2 (1.0,CHCl3);

1.1.1 Preparation of Ligand 5

The compound **3a** was prepared by using the same procedure presented earlier for compound 3 using 1S, 2R norephedrine as the starting material.

ligand 5

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.51 (d, *J*=7.8 Hz, 2H), 7.17 - 7.01 (m, 7H), 4.18 (d, *J*=5.0 Hz, 1H), 3.15 (dd, *J*=5.3, 6.5 Hz, 1H), 2.33 (s, 3H), 0.94 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (101MHz, CHLOROFORM-d) δ ppm, 142.8, 137.5,137.2,129.2,128.1, 127.6, 127.4, 127.0, 62.6, 51.0, 21.5,20.7;FTIR(KBr,cm^{-1}) 3572,3364, 2878,1599,1323,1160;HRMS calculated mass: 304.1245, measured mass: 304.1249;[α] $^{25}_{D}$= +62.7 (1.0,CHCl3);

1.2 Preparation of compound 11:

Step1:N-[(1S,2R)-2-hydroxy-1-methyl-2-phenyl-ethyl]-4-methyl-benzene sulfonamide

In a 3 necked 250 ml round bottom flask norephedrine compound **9**(15.0 g, 100 mmol) was taken and *tert*-butyl methyl ether (50 ml) and triethyl amine (10 ml) were added to it. *p*-toluene sulfonyl chloride (19 g, 100 mmol) dissolved in *tert*-butyl methyl ether (50 ml) was added drop wise to the solution containing norephedrine at 0^{o}C. The solution was stirred at room temperature for 6 h. After 6 hours the solution was washed with 2 N HCl (50 ml). The tert-butyl methyl ether layer was concentrated to get the crude sulfonamide derivative, which was crystallized from toluene to get the pure product yield (22 g), yield 72%.

Compound **11.**

Yellowish white solid,M.P 79-81,^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 7.69 (d, *J*=7.7 Hz, 2 H),7.13 - 7.24 (m, 7 H),4.72 (d, *J*=3.01 Hz, 1 H),3.47 (dq, *J*=6.7, 3.4 Hz, 1 H),2.33 (s, 3 H), 0.74 (d, *J*=6.8 Hz, 3 H);^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 143.5,140.4, 137.8,129.8, 128.3, 127.6, 127.1, 126.1, 75.8, 55.1, 21.614.5; FT IR (KBr,cm^{-1}): 3500, 3278, 1494, 1326, 1159, 1088 ;HRMS calculated Mass: 305.1086, measured mass: 305.1083;[α] $^{25}_{D}$= -16.8 (1.0, CHCl3);

1.2.1 Preparation of compound 11a

N-[(1R, 2S)-2-hydroxy-1-methyl-2-phenyl-ethyl]-4-methyl-benzene sulfonamide

The enaniomer **11a** was synthesized using the same procedure described in earlier for compound **11** and starting from 1S, 2R norephedrine.

Compound **11a**

Yellowish white solid, M.P 79-81 ,^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm, 7.69 (d, *J*=7.7 Hz, 2 H),7.13 - 7.24 (m, 7 H),4.72 (d, *J*=3.01 Hz, 1 H),3.47 (dq, *J*=6.7, 3.4 Hz, 1 H),2.33

(s, 3 H), 0.74 (d, *J*=6.8 Hz, 3 H); ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm, 143.5,140.4, 137.8,129.8, 128.3, 127.6, 127.1, 126.1, 75.8, 55.1, 21.5 14.6;FTIR (KBr, cm^{-1}); 3480, 3306, 1494,1327, 1200, 1157, 1093;HRMS calculated mass: 305.1086, measured mass: 305.1081 ; [α] $^{25}_{D}$= +16.8 (1.0, CHCl3);

Lit.[1]M.P 79-81 °C; [α]$^{25}_{D}$ +13.40 (*c* 1.0, CHCl3); FTIR (KBr) 3500, 3278, 1494, 1326, 1159, 1088 cm-1; 1H NMR(CDCl3, 400 MHz) δ ppm7.77 (d, *J*) 8.3 Hz, 2H), 7.29 (m, 7H), 5.05(br, 1H, NH), 4.79 (br, 1H), 3.57 (m, 1H), 2.62 (br, 1H, OH), 2.42(s, 3H), 0.83 (d, *J*) 6.8 Hz, 3H); 13C NMR (CDCl3, 100 MHz) δ ppm,143.5, 140.2, 137.7, 129.8, 128.3, 127.6, 126.9, 126.0, 75.7, 54.9,21.5, 14.6

1.3 Preparation of compound 12

Step 2: (2S, 3S)-2-methyl-3-phenyl-1-(p-tolylsulfonyl) aziridine,

In a 100 ml 3 necked flask 6.1 g (20 mmol) of compound **11** was taken and THF (50 ml) was added to it. Triphenyl phosphine (5.26 g, 20 mmol) dissolved in THF (20 ml) was added to the solution. The reaction mixture was cooled to 0^{o}C, DIAD (4.1 g, 20 mmol) was added slowly to the reaction mixture, maintaining the temperature at 0 to 5^{0}C. The reaction mixture was further stirred for 6 h and then concentrated to remove THF. Cyclohexane (50 ml) was added to the solids and contents were heated at 50^{0}C for 1h. The resulting suspension was filtered off, and the cyclohexane layer was concentrated to get the crude tosylated aziridine. Crude product was purified by column chromatography to get pure sample (cyclohexane: ethyl acetate; 9:1), (5g, yield, 86%).

Compound 12

Yellow liquid,[1]H NMR ($CDCl_3$, 400 MHz) *δ*ppm,7.82 (d, *J* = 8.3 Hz, 2H), 7.25 (m,5H), 7.15 (m, 2H), 3.79 (d, *J*= 4.4 Hz, 1H), 2.91 (m, 1H), 2.39 (s,3H), 1.84 (d, *J* = 6.1 Hz, 3H);^{13}C NMR ($CDCl_3$, 101 MHz) *δ*ppm,143.9, 137.9, 135.5, 129.5, 128.5, 128.0, 127.2, 126.3, 49.2, 49.1, 21.5, 14.2,; FT IR (neat,cm^{-1}), 1321, 1159;HRMS,calculated mass: 287.0980, measured mass: 287.0979; [α] $^{25}_{D}$=60.6(1.0, $CHCl_3$);

1.3.1 Preparation of Compound 12a,

Step 2: (2R, 3R)-2-methyl-3-phenyl-1-(p-tolylsulfonyl) aziridine,

The enaniomer **12a** was synthesized using the same procedure used for compound **12** and starting from 1S, 2R norephedrine

Compound 12a

Yellow liquid,^{1}H NMR ($CDCl_3$, 400 MHz) δppm,7.82 (d, *J* = 8.3 Hz, 2H), 7.25 (m,5H), 7.15 (m, 2H), 3.79 (d, *J* =4.4 Hz, 1H), 2.91 (m, 1H), 2.39 (s,3H), 1.84 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz),δppm, 143.9, 137.9, 135.5, 129.5, 128.5, 128.0, 127.2, 126.3, 49.2, 49.1, 21.5, 14.2; FTIR (neat,cm^{-1}) 1321, 1159;HRMS calculated mass: 287.0980, measured mass: 287.0986;[α] $^{25}_{D}$= -62.9(1.0, CHCl3);

Lit[1]. **(2*R*,3*R*)-2-Methyl-3-phenyl-1-(toluene-4-sulfonyl)aziridine:** yellow liquid; $[\alpha]^{25}_{D}$= -64.64 (*c* 1.3, CHCl3); FT IR (neat, cm^{-1}) 1321, 1159;^{1}H NMR (CDCl3, 400 MHz) δ ppm, 7.82 (d, *J*) 8.3 Hz, 2H), 7.25 (m,5H), 7.15 (m, 2H), 3.79 (d, *J*) 4.4 Hz, 1H), 2.91 (m, 1H), 2.39 (s,3H), 1.84 (d, *J*) 6.1 Hz, 3H); ^{13}C NMR (CDCl3, 100 MHz)δ ppm, 143.9, 137.9, 135.5, 129.5, 128.5, 128.0, 127.2, 126.3, 49.2, 49.1,21.5, 14.1.

1.4 Preparation of Compound 13

Step 3: N-[(1S 2R)-2-azido-1-methyl-2-phenyl-ethyl]-4-methyl-benzene sulfonamide,

In a 100 ml, round bottom flask, tosylated aziridine compound **12** (2.87 g, 10 mmol) was dissolved in acetonitrile (40 ml) and sodium azide (1.95 g, 30 mmol) in water (10 ml) was added to it. The contents were stirred at 50 ^{0}C for 8h. After the reaction, acetonitrile was removed under reduced pressure and contents were concentrated to ~10ml. The aqueous layer containing the solid was filtered off and washed with water (10 ml x 2). The product isolated was pure enough to be used for the next step (3.0 g , 90 % yield).

Compound **13**

Off white solid , MP 80-82^{0}C,^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.78 (d, *J*=7.7 Hz, 2H), 7.38 - 7.19 (m, 7H), 4.78 (d, *J*=8.8 Hz, 1H), 4.69 (d, *J*=3.8 Hz, 1H), 3.57 (ddd, *J*=3.9, 6.7, 8.8 Hz, 1H), 2.43 (s, 3H), 0.90 (d, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δppm ,143.6, 137.8,136.3, 129.7, 128.7, 128.3, 126.9, 126.8, 69.6, 54.0, 21.5, 15.2,; FTIR (KBr cm^{-1})3251, 2099, 1378, 1299, 1166; HRMS calculated Mass: 330.1150, measured Mass: 330.1152 difference 0.6 ppm;[α] $^{25}_{D}$= -105.8 (1.0, CHCl3)

1.4.1 Preparation of compound 13a

Step 3 **N-[(1R,2S)-2-azido-1-methyl-2-phenyl-ethyl]-4-methyl-benzenesulfonamide,**

The enaniomer **13a** was synthesized using the procedure described in the synthesis of compound **13** starting from 1S, 2R norephedrine.

Off white solid , M.P 80-82^{0}C,^{1}H NMR (CDCl3, 400 MHz) δppm ,7.78 (d, *J* = 7.9 Hz, 2H), 7.21 (m, 7H), 4.68 (m, 2H), 3.57(m, 1H), 2.43 (s, 3H), 0.89 (d, *J* = 6.7 Hz, 3H); C NMR (CDCl3, 101 MHz) δppm ,143.6, 137.8,136.2, 129.8, 128.8, 128.3, 126.9, 126.8, 69.7, 54.0, 21.5, 15.2; FT IR (KBr, cm $^{-1}$)·3250, 2098, 1370, 1297, 1163;HRMS calculated mass: 330.1150,measured mass: 330.1149;[α] $^{25}_{D}$= +107.8 (1.0, CHCl3);

Lit.[2],(*1R,2S*)-*N*-(2-Azido-1-methyl-2-phenyl-ethyl)-4-methyl-benzenesulfonamideM.P 83-85 °C; [α]$^{25}_{D}$ = +105.8 (1.0, CHCl3); FT IR (KBr, cm^{-1}) 3251, 2099, 1378, 1299, 1166; ^{1}H NMR (CDCl3, 500 MHz) δ ppm, 7.76 (d, *J* = 7.9 Hz, 2H), 7.26 (m, 7H), 4.68 (m, 2H), 3.57(m, 1H), 2.43 (s, 3H), 0.89 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (CDCl3, 125 MHz) δ ppm, 143.6, 137.8,136.2, 129.8, 128.8, 128.3, 126.9, 126.8, 69.7, 54.0, 21.5, 15.2;

1.5 Preparation of ligand 2

Step4:**N-[(1S, 2R)-2-amino-1-methyl-2-phenyl-ethyl]-4-methyl-Benzenesulfonamide**

(1.65 g, 5 mmol) of the compound **13** was dissolved in THF (40 ml) and triphenyl phosphine (1.31 g 5 mmol) was added to it and the resultant mixture was stirred at 50^{0}C for nearly 6 h. After 6 h water (5ml) was added to the reaction mixture and the heating was continued for further 8 h.The reaction mixture was concentrated to (~5ml). The aqueous layer was extracted with DCM (10 ml) and concentrated to get sticky mass. Toluene (10 ml) and the 4 N HCl (1 ml) in dioxane were slowly added to get white precipitate of hydrochloride salt of the resultant amine. The resultant solution was filtered off to get white powder of hydrochloride salt of amine. Traces of toluene were removed by drying under vacuum. Water (5 ml) was added to dissolve the hydrochloride and 1N NaOH was slowly added till the pH reached 7. The solution was extracted with ethyl acetate (10 ml x 2) and concentrated to get sticky mass. (1.0 g, yield = 67%).

Ligand 2

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.73 (d, *J*=8.3 Hz, 2H), 7.33 - 7.13 (m, 7H), 3.95 - 3.87 (m, 1H), 3.50 (dd, *J*=3.8, 6.5 Hz, 1H), 2.39 (s, 3H), 0.79 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (101MHz, CHLOROFORM-d) δ ppm, 143.4, 141.4, 137.8, 129.8, 129.6, 129.1, 128.5, 128.3, 127.5, 127.4, 127.1, 126.8, 59.0, 54.6, 21.6, 16.0;FT IR (KBr, cm $^{-1}$),3288, 3230, 1598,

1328, 1151, ;HRMS calculated mass: 304.1249, measured mass: 304.1245,;[α] $^{25}_{D}$= +13.4 (0.5, CHCl3);

1.5.1 Preparation of ligand 6

N-[(1R, 2S)-2-amino-1-methyl-2-phenyl-ethyl]-4-methyl-benzenesulfonamide

The ligand **6** was synthesized using the procedure described in the synthesis of Ligand 2 and starting from 1S, 2R norephedrine.

ligand 6

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.73 (d, *J*=8.3 Hz, 2H), 7.33 - 7.13 (m, 8H), 3.95 - 3.87 (m, 1H), 3.50 (dd, *J*=3.8, 6.5 Hz, 1H), 2.39 (s, 3H), 0.79 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (101MHz, CHLOROFORM-d) δ ppm, 143.4, 141.4, 137.8, 129.8, 129.6, 129.1, 128.51, 128.3, 127.5, 127.4, 127.1, 126.8, 59.0, 54.6, 21.6, 16.0;FT IR (KBr cm $^{-1}$),3287, 3235, 1595, 1323, 1155, ;HRMS calculated mass: 304.1245, measured mass: 304.1248,;[α] $^{25}_{D}$= -13.4 (0.5, CHCl3);

1.6 Preparation of compound 14

(1S, 2S)-1-chloro-1-phenyl-propan-2-amine.

In a 3 necked round bottom flask 1R, 2S norephedrine hydrochloride (30.0 g, 200 mmol) was taken and thionyl chloride (70.9 g 596 mmol) was added drop wise. After the addition was complete the reaction mixture was stirred for 3h. Vacuum was applied to remove the excess thionyl chloride, and then acetone (50 ml) was slowly added to the slurry. The resultant solution was filtered and washed with acetone and recrystalised from methanol to obtain white solid of compound **14** (22 g, yield 67%).

Compound 14

White solid, MP 206–208°C,^{1}H NMR(400MHz, D_2O)δppm, 7.40-7.44, (5H, m), 4.98-5.01(1H, d 12Hz) 3.86 (1H, m),1.07 (3H d, J= 6.4),; ^{13}C NMR(400MHz, D_2O)δ ppm,137.3, 128.3, 127.5, 126.1, 64.1, 52.4, 16.1, ; FTIR (KBr, cm^{-1}), 3420, 3058, 2996, 2924, 2958, 716, 692;HRMS calculated mass: 169.0658, measured mass: 169.0656, [α] $^{30}_{D}$= 10.4 ,(0.1, water)

1.6.1 Preparation of Compound 14a

(1R, 2R)-1-chloro-1-phenyl-propan-2-amine

The enaniomer **14a** was synthesized using the same procedure used for compound **14** and starting from 1S, 2R norephedrine.

Compound 14a

White solid, MP 206–208°C,[1]H NMR(400MHz D_2O)δppm, 7.40-7.44, (5H, m), 4.98-5.01(1H, d 12Hz) 3.86 (1H, m),1.07 (3H d, J= 6.4) , ; ^{13}C NMR (400MHz D_2O) δ=137.3, 128.3, 127.5, 126.1, 64.1, 52.4, 16.1, ; FTIR (KBr, cm^{-1}) 3425, 3059, 2996, 2924, 2950, 718, 690;HRMS calculated Mass: 169.0659, measured mass: 169.0656,;$[\alpha]^{30}_D$= -10.4,(0.1, water);

Lit.[3]M.P. 205–207°C. IR (KBr, cm^{-1}): 3420, 3058, 2996, 2974, 2958, 716, 692,; $[\alpha]_D^{33}$=−10.4 (H2O, c=0.1). ^{13}C NMR (CDCl3, 137.3 128.3 127.5, 126.1, 64.1, 52.4, 16.1,; 1H NMR (CDCl3), 1.13 (d, *J* 6.20, 3H,), 3.91 (qd, *J* 6.2 and 6.6, 1H,), 5.45 (d, *J* 6.6, 1H,), 7.47 (m, 5H).

1.7 Preparation of compound 15
(2R, 3R)-2-methyl-3-phenyl-aziridin-2-amine

The compound **14** (10.0 g, 50 mmol) was dissolved in methanol (40 ml). NaOH (4 N, 50 ml) was slowly added under stirring to the methanol solution. The mixture was further stirred for 4h, and then was concentrated to 20 ml. The aqueous layer was cooled to 10^0C to get the crystals of aziridine. The solution was filtered and washed 2-3 times with water (10 ml). Light yellow crystals (low melting solid) of aziridine compound **15** (5g, 76 % yield) were obtained after recrystallization from hexane.

Compound 15

[1]H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.32 - 7.16 (m, 5H), 3.19 (d, *J*=6.5 Hz, 1H), 2.39 - 2.32 (m, 1H), 0.87 - 0.84 (m, 3H);[13]C NMR (101MHz, CHLOROFORM-d) δ ppm, 137.7, 127.9, 127.8, 126.7, 37.2, 32.2, 13.7;FTIR (KBr, cm^{-1}):3226, 1612, 1485, 1062, 849HRMS calculated Mass: 133.0891, measured Mass: 133.0895,;$[\alpha]^{25}_D$= -75.2 ,(0.4, $CHCl_3$);

1.7.1 Preparation of compound 15a
(2S, 3S)-2-methyl-3-phenyl-aziridin-2-amine

The enaniomer **15a** was synthesized using the same procedure starting from 1S, 2R norephedrine.

Compound 15a

[1]H NMR (400 MHz, CHLOROFORM-*d*) δ ppm, 7.13 - 7.28 (m, 5 H),3.17 (d, *J*=6.53 Hz, 1 H) 2.33 (quin, *J*=5.90 Hz, 1 H), 0.84 (d, *J*=5.52 Hz, 3 H) ^{13}C NMR (101 MHz, CHLOROFORM-*d*)

δ ppm, 137.6, 128.1, 127.9, 127.8, 127.7, 126.6, 37.2, 32.2, 13.6 ;FTIR ((KBr, cm^{-1})3236, 1602, 1495, 1072, 849;HRMS calculated mass: 133.0891, measured mass: 133.0894,;[α] $^{25}_{D}$= +73.0, (0.4, $CHCl_3$);

1.8 Preparation of compound 16

(2S, 3R)-2-methyl-3-phenyl-aziridine; methylsulfonylbenzene

(5.3g, 40 mmol) of compound **15** was dissolved in TBME (30 ml), and pyridine (5ml) was slowly added to it at 0^0C. *p*-toluene sulfonyl chloride (7.1 g) was dissolved in TBME (*tert* -butyl methyl ether) (30 ml) and the resultant solution was added slowly to the TBME containing compound **15**. The reaction mixture was stirred for 4 h and then of 1 N HCl (20 ml) and 30 ml water was added to the reaction mixture. Contents were shaken vigorously and the layers were separated. Aq. layer was discarded and TBME layer was washed again with 30 ml of water. The TBME layer was concentrated to get the compound **16** which was crystalized from hexane to get off white crystals, (7.5 g, 65 % yield).

Compound 16

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.89 (d, *J*=7.8 Hz, 2H), 7.36 - 7.19 (m, 8H), 3.93 (d, *J*=7.3 Hz, 1H), 3.23 - 3.15 (m, 1H), 2.43 (s, 3H), 1.02 (d, *J*=5.8 Hz, 3H), ;^{13}C(101MHz, CHLOROFORM-d) δppm,18.2, 21.6, 53.7, 69.6, 126.7, 127.7, 127.9, 128.8, 129.4 129.7, 135.6, 137.5, 143.4; FTIR (KBr, cm^{-1}) 2984, 1596, 1320, 1161;HRMS calculated Mass: 287.0980, measured mass: 287.0979,;[α] $^{25}_{D}$= -100.1 ,(1.0, $CHCl_3$);

1.8.1 Preparation of compound 16a

(2S, 3R)-2-methyl-3-phenyl-aziridinemethylsulfonylbenzene

The enaniomer **16a** was synthesized using the same procedure and starting from 1S, 2R norephedrine

Compound 16a

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.85 (d, *J*=7.8 Hz, 2H), 7.30 - 7.19 (m, 7H), 3.92 (d, *J*=7.2 Hz, 1H), 3.21 (qd, *J*=5.8, 7.2 Hz, 1H), 2.42 (s, 3H), 1.02 (d, *J*=5.8 Hz, 3H);^{13}C NMR (101MHz, CHLOROFORM-d) δ = 18.2, 21.6, 53.7, 69.6, 126.7, 127. 7, 127.9, 128.8, 129.4 129.7, 135.6, 137.5, 143.4;FTIR ((KBr, cm^{-1}) 2984, 1596, 1320, 1161; HRMS calculated mass: 287.0980, measured mass: 287.0986,;[α] $^{25}_{D}$= +99.2 ,(1.0, $CHCl_3$);

1.9 Preparation of compound 17 and compound 18 (N-[(1R,2R)-2-azido-1-phenyl-propyl]-4-methyl-benzenesulfonamide)(N-[(1S, 2S)-2-azido-1-methyl-2-phenyl-ethyl]-4-methyl-benzenesulfonamide)

Compound **16** (5.74g, 20 mmol) was dissolved in acetonitrile (40 ml) and DABCO (2.24 g, 20 mmol) was added to it.TMS azide (2.5ml) was slowly added to the reaction mixture. The reaction mixture was heated at 50^0C for 4 h. After 4 h the reaction mixture was cooled to room temperature and concentrated to remove acetonitrile. Distilled water (25 ml) was added to the sticky mass and stirred vigorously. The off white solid precipitated out was filtered through sintred funnel and washed 2-3 times with water. The NMR showed approximately 60:40 ratios of regioisomers, compounds **17** and **18** (combined yield = 6.0g, yield 90%)**.**

Purification of the regioisomers was done by Flash chromatography, to get individually pure azide isomers, compound **11**(2.5g, theoretical yield 69 %), compound **12** (2.0 g, theoretical yield 83%).

Compound 17

^{1}H NMR (CHLOROFORM-d, 400MHz): δ ppm, 7.50 (d, *J*=7.8 Hz, 2H), 7.14-7.21 (m, 3H), 7.02-7.11 (m, 4H), 5.41 (d, *J*=7.3 Hz, 1H), 4.24 (dd, *J*=7.2, 5.4 Hz, 1H), 3.72 (dd, *J*=6.5, 5.5 Hz, 1H), 2.34 (s, 3H), 1.24 ppm (d, *J*=6.5 Hz, 3H) ;^{13}C NMR ^{13}C NMR (101MHz, CHLOROFORM-d) δ = 143.0, 137.6, 137.1, 129.1, 128.3, 127.8, 126. 9, 126.9, , 61.9, 61. 7, 21.30, 16.6;FTIR ((KBr, cm^{-1}) 3255, 2893, 2112, 1445, 1159; HRMS calculated mass: 330.1150, measured mass: 330.1149, ; [α] $^{25}_D$= -66.3 ,(0.5, $CHCl_3$);

Compound 18

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.64 (d, *J*=8.0 Hz, 2H), 7.33 - 7.13 (m, 7H), 4.87 (d, *J*=7.8 Hz, 1H), 4.49 (d, *J*=5.8 Hz, 1H), 3.56 - 3.45 (m, 1H), 2.38 (s, 3H), 2.29 (s, 1H), 0.97 (d, *J*=6.8 Hz, 3H), ;^{13}C NMR (101MHz, CHLOROFORM-d) δ = 142.4, 136.4, 134.4, 128.6, 127.7, 127.6, 126.6, 125.9, 68.5, 52.6, 20.5, 17.2,;FTIR, KBr, cm^{-1}) 3236, 1602, 1495, 1072, 849, ; HRMS calculated mass: 330.1150, measured mass: 330.1152,;[α] $^{25}_D$= +91.3 (1.0, $CHCl_3$);

1.9.1 Preparation of compound 17a and compound 18a (N-[(1S,2S)-2-azido-1-phenyl-propyl]-4-methyl-benzenesulfonamide)and (N-[(1R,2R)-2-azido-1-methyl-2-phenyl-ethyl]-4-methyl-benzenesulfonamide)

The enaniomer **17a** and **18a** was prepared using the procedure starting from 1S, 2R norephedrine

Compound 17a

^{1}H NMR (400MHz, CHLOROFORM-d) δ ppm, 7.49 (d, *J*=7.9 Hz, 2H), 7.22 - 7.15 (m, 3H), 7.11 - 7.03 (m, 4H), 5.25 (d, *J*=7.3 Hz, 1H), 4.76 (br. s., 3H), 4.24 (dd, *J*=5.3, 7.0 Hz, 1H), 3.72 (dd, *J*=5.3, 6.5 Hz, 1H), 2.34 (s, 3H), 1.62 (s, 12H), 1.28 - 1.25 (d, 3H), ;^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 143.2,137.8 , 137.3 , 129.3, 128.5,129.0,127.1, 16.8 , 21.5 , 62.1, 61.8,; FTIR ((KBr, cm^{-1}) 3255, 2893, 2112,1445, 1159;HRMS calculated Mass: 330.1150, measured mass: 330.1143,;[α] $^{25}_{D}$= +64.3 ,(0.5, $CHCl_3$);

Compound 18a

^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.62 (d, *J*=7.7 Hz, 2H), 7.30 - 7.15 (m, 7H), 4.67 (d, *J*=7.8 Hz, 1H), 4.49 (d, *J*=5.8 Hz, 1H), 3.54 - 3.45 (m, 1H), 2.38 (s, 3H), , 0.98 (d, *J*=6.5 Hz, 3H)^{13}C NMR (101MHz, CHLOROFORM-d) δ = 142.4, 136.5, 134.4, 128.6, 127.7, 127.6, 126.6, 126.9, 68.5, 52.6, 20.5, 17.2;FTIR ((KBr, cm^{-1})3269,2987,2119,1599,1328,1161;HRMS calculated Mass: 330.1150, measured Mass: 330.1153,;[α] $^{25}_{D}$= -90.3 ,(1.0, $CHCl_3$);

1.10 Preparation of ligand 3

N-[(1R, 2R)-2-amino-1-phenyl-propyl]-4-methyl benzene sulfonamide

(1.65 g, 5 mmol) of compound **17** was dissolved in THF (40 ml) and triphenyl phosphine (1.31g, 5mmol) was added to the solution and the resultant mixture was stirred at 50^{0}C for nearly 6 h. After 6 h water (5ml) was added to the reaction mixture and the heating was continued for further 8h.The reaction mixture was concentrated to (~5ml) remove THF. The aqueous layer was extracted with DCM (10 ml) and concentrated to get sticky mass. Toluene (10ml) and 4 N HCl (1 ml) in dioxane were slowly added to get white precipitate of hydrochloride. The resultant solution was filtered off to get white powder of hydrochloride. Traces of toluene were removed by drying the precipitate under vacuum. Water 5ml was added to dissolve the hydrochloride and 1N NaOH was slowly added till the pH reached 7.0. The solution was extracted with ethyl acetate (10 ml x 2) and concentrated to get off white solid of ligand **3** (0.8 g, yield=53%).

Ligand 3

^{1}H NMR (CHLOROFORM-d, 400MHz): δ ppm, 7.51 (d, *J*=7.8 Hz, 2H), , 7.10-7.17 (m, 3H), 7.03-7.10 (m, 4H), 4.11 (d, *J*=6.0 Hz, 1H), 3.21-3.28 (m, 2H), 2.33 (s, 3H), 1.01 ppm (d, *J*=6.5 Hz, 3H); ^{13}C NMR (CHLOROFORM-d, 101MHz): δ ppm ,142.7, 139.3, 137.7, 129.1, 128.3, 127.3, 127.1, 127.0, , 63.2, 51.7, 21.4, 20.6 FTIR ((KBr, cm^{-1}) 3288, 3230, 1517, 1328, 1151;HRMS calculated Mass: 304.1245, measured mass: 304.1248 difference 1.0 ppm;[α] $^{25}_{D}$= -90.7 ,(1.0, $CHCl_3$);

Ligand 3 as hydrochloride

^{1}H NMR (400 MHz, METHANOL-d_4) δ ppm 0.97 (d, *J*=6.78 Hz, 3 H) 2.31 (s, 3 H) 3.30 (dt, *J*=3.26, 1.63 Hz, 4 H) 4.13 (d, *J*=10.54 Hz, 1 H) 6.91 (d, *J*=7.48 Hz, 2 H) 7.05 - 7.20 (m, 6 H) 7.43 (d, *J*=7.80 Hz, 2 H) ^{13}C NMR (METHANOL-d_4, 101MHz): δ = 144.8, 138.7, 137.1, 130.4, 129.9, 129.5, 128.5, 128.2, 63.1, 52.6, 21.4, 16.2 ppm

1.10.1 Preparation of ligand 7

N-[(1S, 2S)-2-amino-1-phenyl-propyl]-4-methyl benzene sulfonamide

The ligand 7 was synthesized using the same procedure and starting from 1S, 2R norephedrine.

Ligand 7

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm, 0.92 (3H d, J= 6.4,) 2.41(3H, s) 3.24 (1H,m) 3.77(1H, d, 7.2Hz),7.67, (2H d,8.4),7.17(7H, m); ^{13}C(101MHz, CHLOROFORM-d) δ ppm, 18.8, 21.5, 55.3, 60.4, 127, 127.7, 128.3, 128.5, 128. 7, 129.7, 129.1, 137.8, 141.8, 143.4, (KBr, cm^{-1}) 3385, 3279, 1597, 1328, 1162; HRMS calculated Mass: 304.1245, measured mass: 304.1248 difference 1.0 ppm;[α] $^{25}_{D}$= +92.1 ,(0.5, $CHCl_3$);

1.11 Preparation of ligand 4

N-[(1S2S)-2-amino-1-methyl-2-phenyl-ethyl]-4-methyl-benzenesulfonamide

(1.65 g, 5 mmol) of the compound **18** was dissolved in THF (40 ml) and triphenyl phosphine (1.31 g, 5 mmol) was added to the solution and the resultant mixture was stirred at 50^{0}C for nearly 6 h. After 6 h water (5 ml) was added to the reaction mixture and the heating was continued for further 8 h.The reaction mixture was concentrated to (~5ml) remove the THF. The aqueous layer was extracted with DCM (10 ml) and concentrated to get sticky mass. Toluene (10ml) and the 4 N HCl (1 ml) in dioxane were slowly added to get white precipitate of

hydrochloride. The resultant solution was filtered off to get white powder of hydrochloride. Traces of toluene were removed by drying the powder under vacuum. Water (5 ml) was added to dissolve the hydrochloride and 1N NaOH was slowly added till the pH reached 7.0. The solution was extracted with ethyl acetate (10 ml x 2) and concentrated to get off white sticky mass (0.8 g, yield=53%).

Ligand 4

^{1}H NMR (CHLOROFORM-d, 400MHz): δ = 7.68 (d, *J*=8.3 Hz, 2H), 7.13-7.30 (m, 8H), 3.78 (d, *J*=7.3 Hz, 1H), 3.11-3.40 (m, 2H), 2.41 (s, 1H), 0.92 ppm (d, *J*=6.5 Hz, 3H); ^{13}C NMR (101MHz, CHLOROFORM-d) δ = 143.1, 141.8, 137.9, 137.8, 129.6, 129.1, 128. 7, 128.3, 127.7, 127.0, 127.0, 125.4, , 60.39, 55.33, , 21.57, 18.81 ;FTIR ((KBr, cm^{-1}) 3268, 3240, 1507, 1323, 1152; HRMS calculated Mass: 304.1245, measured mass: 304.1249,

Ligand 4 isolated as hydrochloride,

^{1}H NMR (METHANOL-d_4, 400MHz): δ ppm , 7.83 (d, *J*=7.8 Hz, 2H), 7.40-7.50 (m, 7H),), 3.99 (d, *J*=10.0 Hz, 1H), 3.57-3.65 (m, 1H), 2.43 (s, 3H), 0.55 ppm (d, *J*=6.8 Hz, 3H),;^{13}C NMR (METHANOL-d_4, 101MHz): δ ppm 144.0, 137.7, 134.0, 129.6, 129.6, 129.2, 127.6, 126.8, 60.6, 52.4, 20.1, 15.8 ,; $[\alpha]^{25}_{D}$= -87.7, (0.5, CH_3OH);

1.11.1 Preparation of ligand 8

N-[(1R2R)-2-amino-1-methyl-2-phenyl-ethyl]-4-methyl-benzenesulfonamide

The ligand **8** was synthesized using the same procedure and starting from 1S, 2R norephedrine

ligand 8 as hydrochloride

^{1}H NMR (METHANOL-d_4, 400MHz): δ = 7.84 (d, *J*=8.0 Hz, 2H), 7.40-7.49 (m, 7H), 4.86 (s, 6H), 4.03 (d, *J*=10.3 Hz, 1H), 3.62 (dq, *J*=10.0, 6.8 Hz, 1H), 3.29-3.33 (m, 2H), 2.43 (s, 3H), 0.56 ppm (d, *J*=6.8 Hz, 3H,;^{13}C NMR (METHANOL-d_4, 101MHz): δ = 144.0, 137.8, 134.0, 129.6, 129.5, 129.2, 127.6, 126.8, 60.6, 52.4, , 20.1, 15.8 ppm

;$[\alpha]^{25}_{D}$= +87.0 ,(0.5, CH_3OH);(as **14a** .HCl salt)

2 Mechanism for ATH of ketones

The mechanism proposed by Noyori[4] and Ikaria, and Xiao et al. [5-9 5-9 4-8 3-72-6]for ATH of ketones with Ru-tosylated diamine catalyst with sodium formate as a hydrogen donor in water is as shown in Fig. 1.

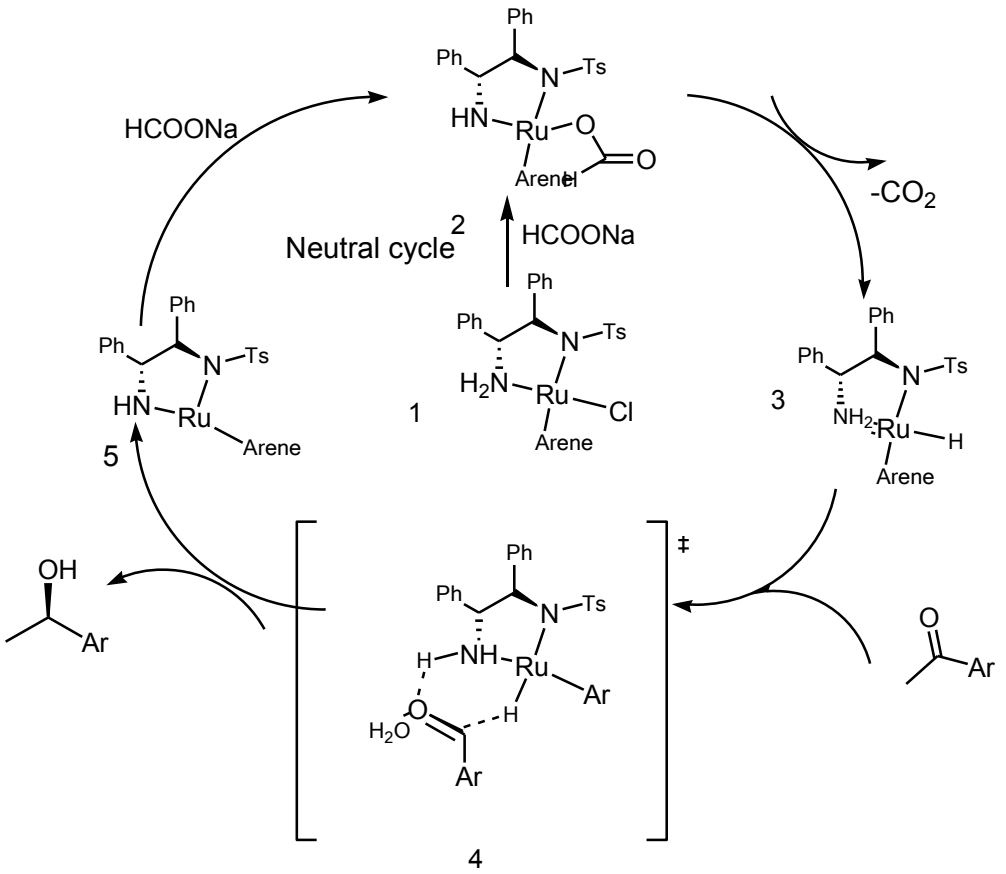


Fig. 1: Mechanism for ATH of ketones with sodium formate as a hydrogen donor in water[9-12]

Precatalyst **1**[5, 13],reacts with sodium formate to generate the active hydride complex (18 electron complex) **3** via carbon dioxide elimination as proposed by Xiao et al.[9, 14] The intermediate **3** interacts with ketone to form a six membered transition state **4.** Simultaneous transfer of hydride and hydrogen of NH to the ketone leads to the formation of enantiopure alcohol as the product and the 16 electron complex**5**is formed. Noyori has isolated species **5**, which is a 16 electron complex and the true active catalytic species.As per the mechanisms reported for ATH of ketones with sodium formate[9, 15]and 2-propanol[5, 6] catalytic intermediate '5' can generate hydride species from either sodium formate or alcohol present in the reaction mixture.

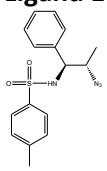
In order to understand the role of methanol (solvent or hydrogen donor) few experiments on ATH of acetophenone were carried out using [Rh (Cp*)Cl_2]$_2$ as a catalyst precursor, with the benchmark ligands like TsDPEN, TsCYDN and ligand 4. In the first experiment ATH of acetophenone was carried out using methanol as a solvent as well as hydrogen donor. The secondexperiment was carried out using methanol *d*-4 as a solvent and sodium formate (five equivalent w.r.t. acetophenone) as a hydrogen donor. Here Threee different experiments were carried out using Rh catalyst and TsDPEN TsCYDN and ligand **9** as the ligands. The results are presented in Table.1With methanol as hydrogen donor trace amount of product was observed after 3h reaction, indicating that methanol was not working as a hydrogen donor efficiently. For other experiments >95 % conversion of acetophenone was observed in 3h reaction time with (96%-97%ee). However, in this experiment deuterium incorporation in the phenethanol formed was not detected, confirming that methanol is not acting as hydrogen donor. Thisclearly showed that sodium formate generates hydride complex faster than methanol and methanol behaves purely as a solvent. Similar experiments by Noyori has reported similar results, for ATH of imine[16]using Ru-TsDPEN and FA:TEA as hydrogen donor and 2-propanol as a solvent. Based on these results, ATH of acetophenone was investigated in detail with methanol as a solvent.

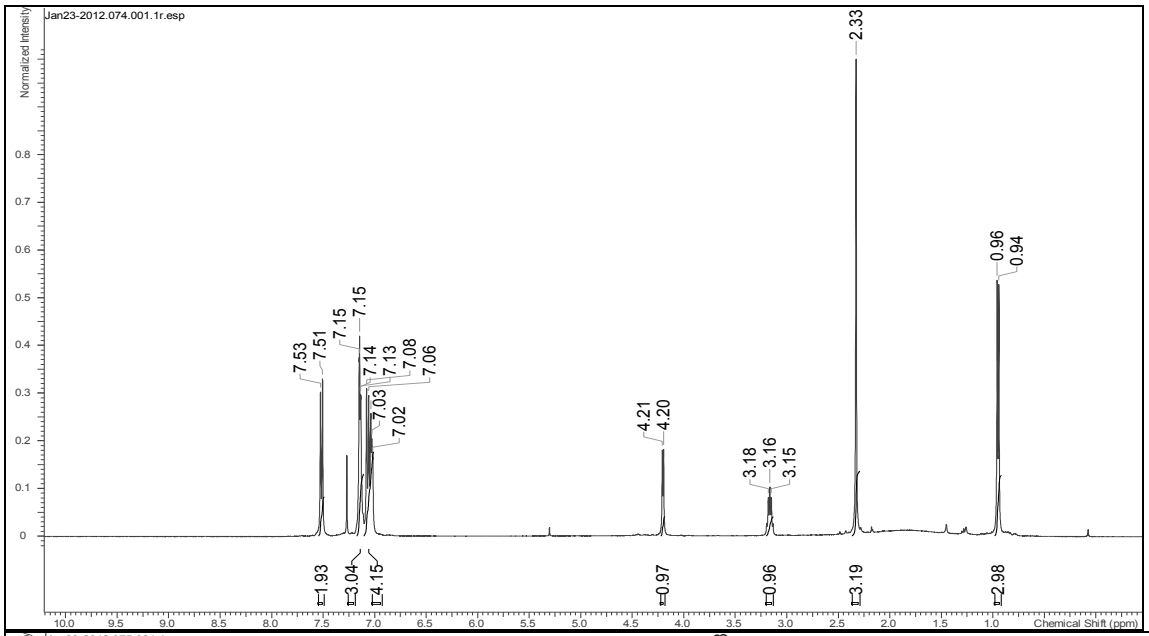
Table 1 ATH of ketone in Deutarated Methanol and sodium formate

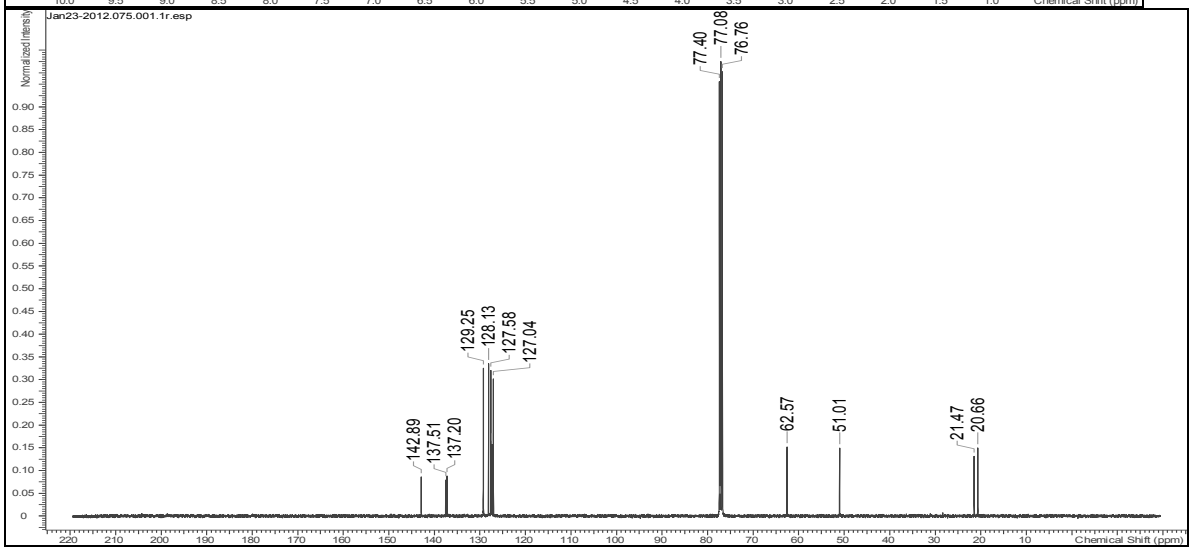
Hydrogen donor	Methanol			Sodium formate in		
				Methanol d-4		
	Time	conv	ee	Time	Conv%.	ee%
Ligand 9	3h	<1		3h	95*	96
TsDPEN	3h	<1		2h	97*	97
TsCYDN	3h	<1		2h	97*	96

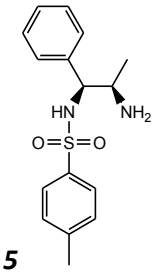
3 1H and 13C spectra of new compounds

Ligand 1

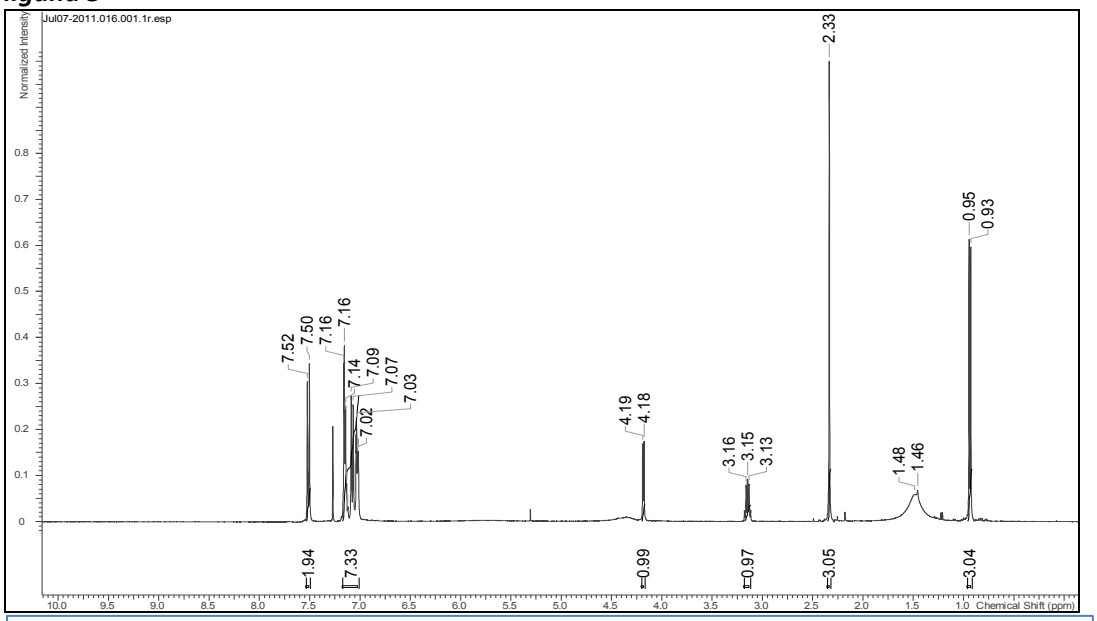







HN
NH2
O=S=O

ligand 5


Jul07-2011.016.001.1r.esp
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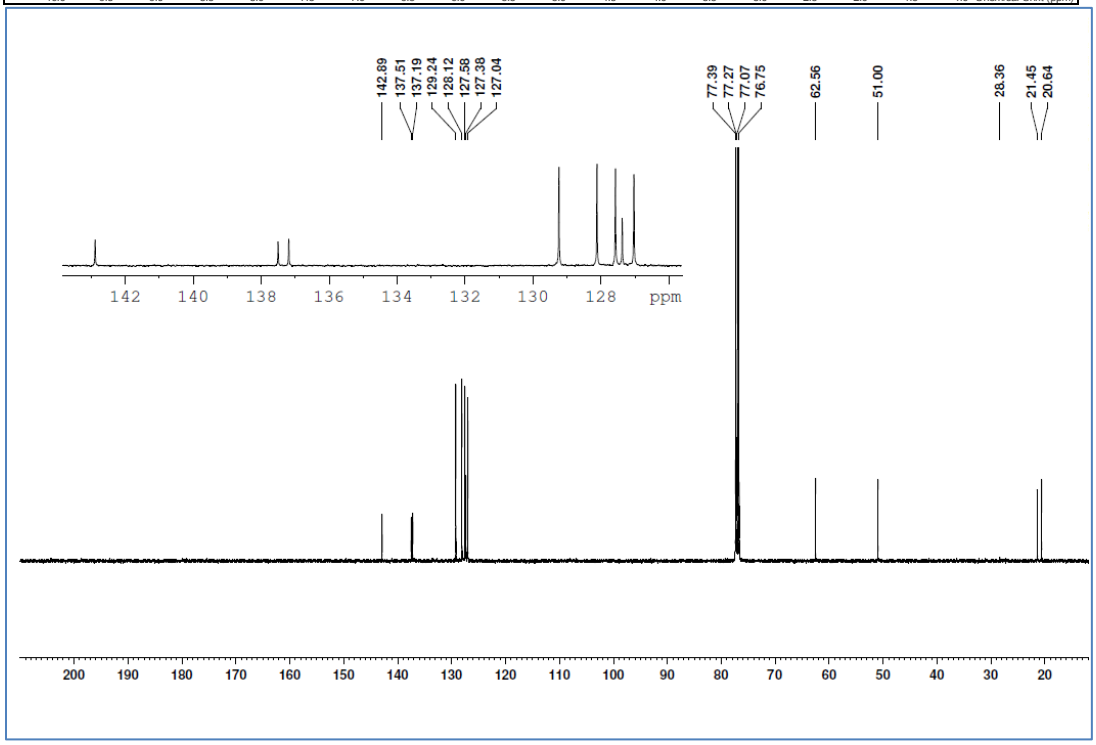
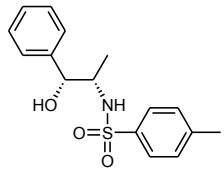
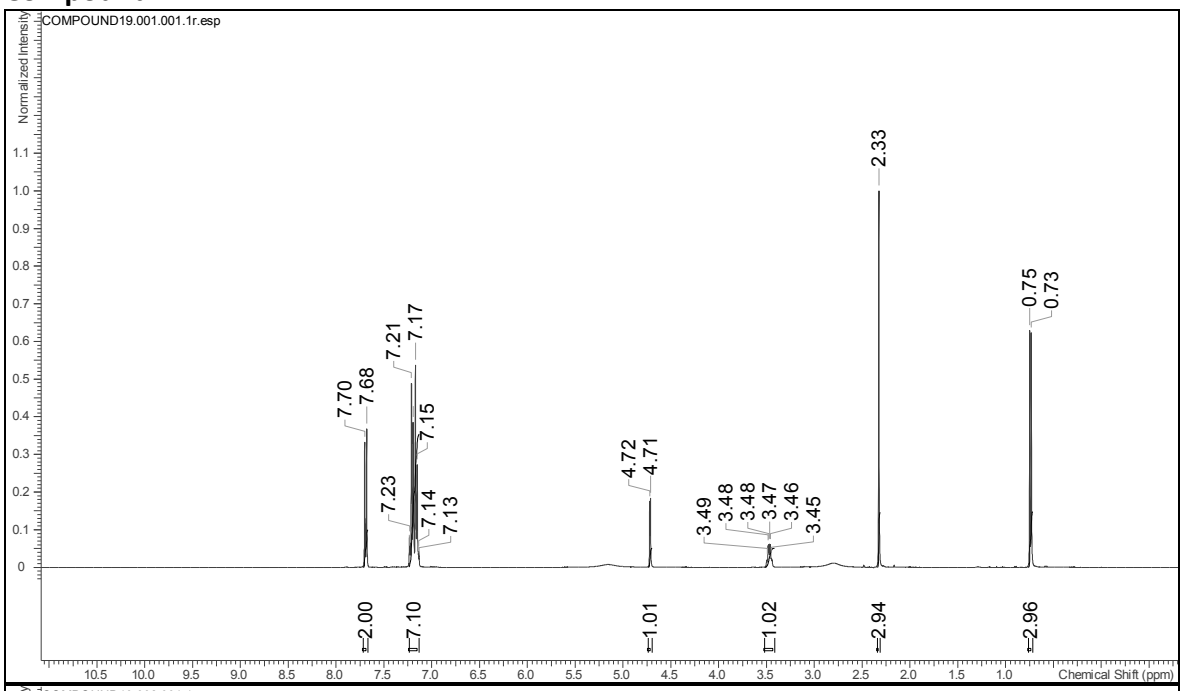
7.50
7.16
7.16
7.14
7.09
7.07
7.03
7.02
4.19
4.18
3.16
3.15
3.13
2.33
1.48
1.46
0.95
0.93
1.94
7.33
0.99
0.97
3.05
3.04
Chemical Shift (ppm)


142.89
137.51
137.19
129.24
128.12
127.58
127.38
127.04
77.39
77.27
77.07
76.75
62.56
51.00
28.36
21.45
20.64
ppm


HO
NH
O
S
O

Compound 11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Normalized Intensity
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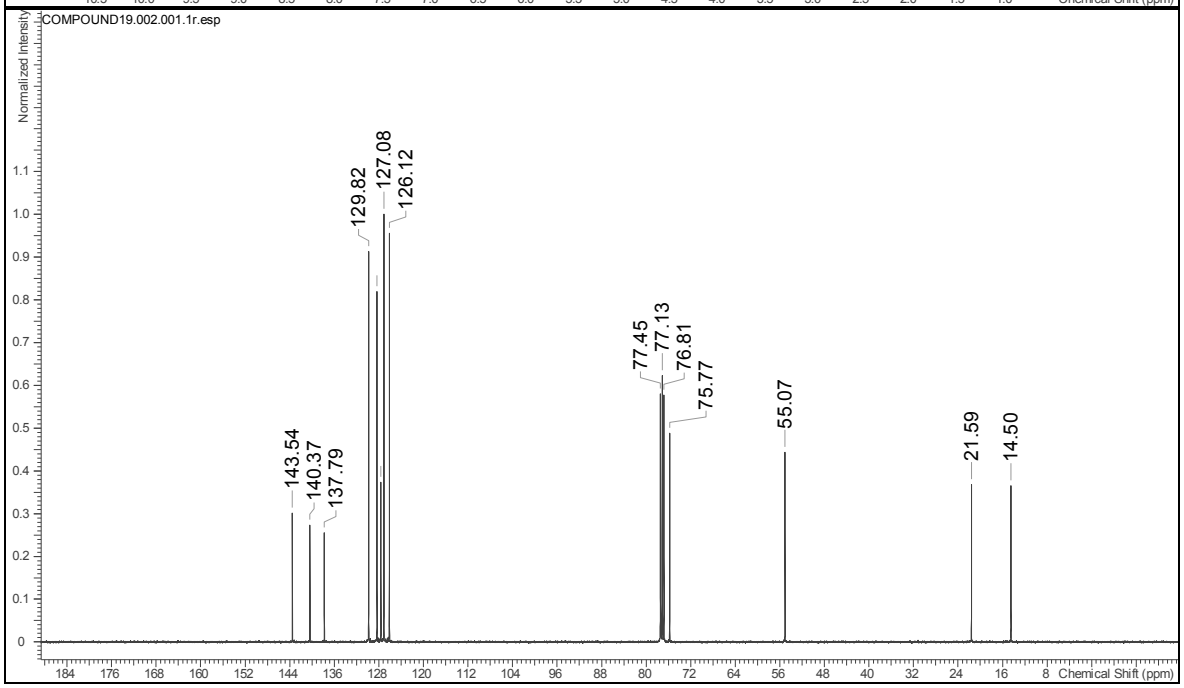
7.68
7.23
7.21
7.17
7.15
7.14
7.13
4.72
4.71
3.49
3.48
3.48
3.47
3.46
3.45
2.33
0.75
0.73
2.00
7.10
1.01
1.02
2.94
2.96
Chemical Shift (ppm)


COMPOUND19.002.001.1r.esp
Normalized Intensity
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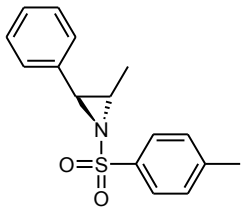
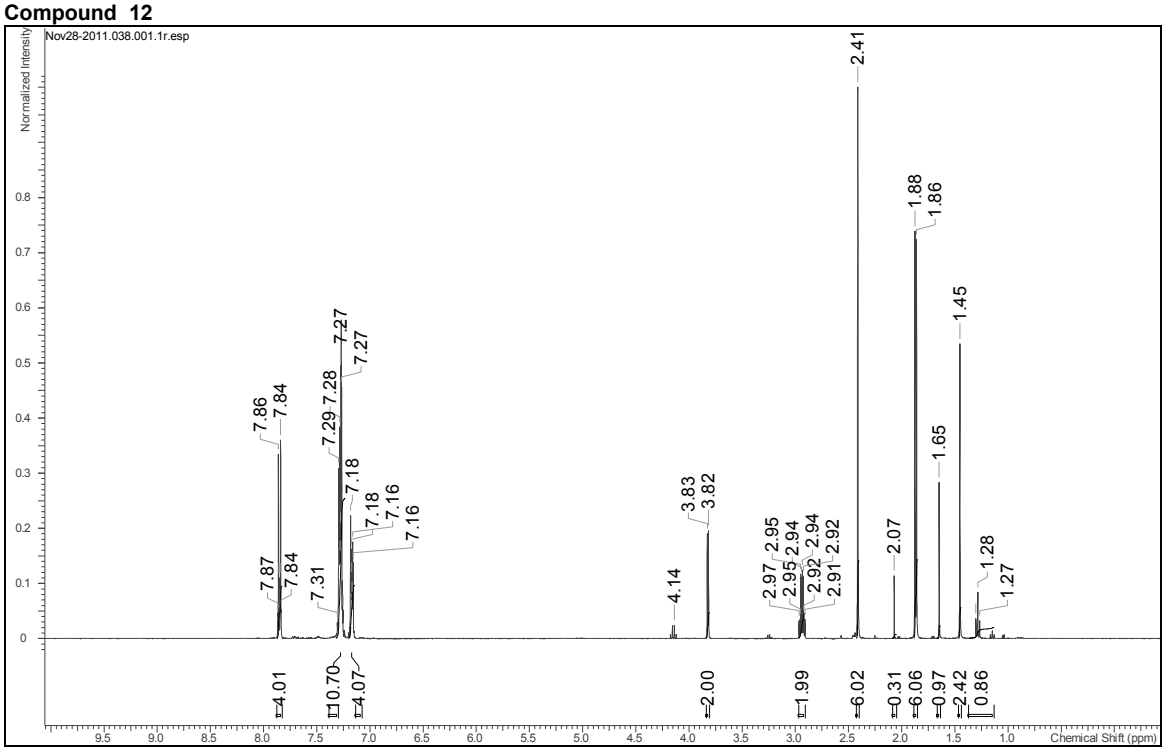
140.37
137.79
129.82
127.08
126.12
77.45
77.13
76.81
75.77
55.07
21.59
14.50
Chemical Shift (ppm)



Compound 12


Nov28-2011.038.001.1r.esp
Normalized Intensity
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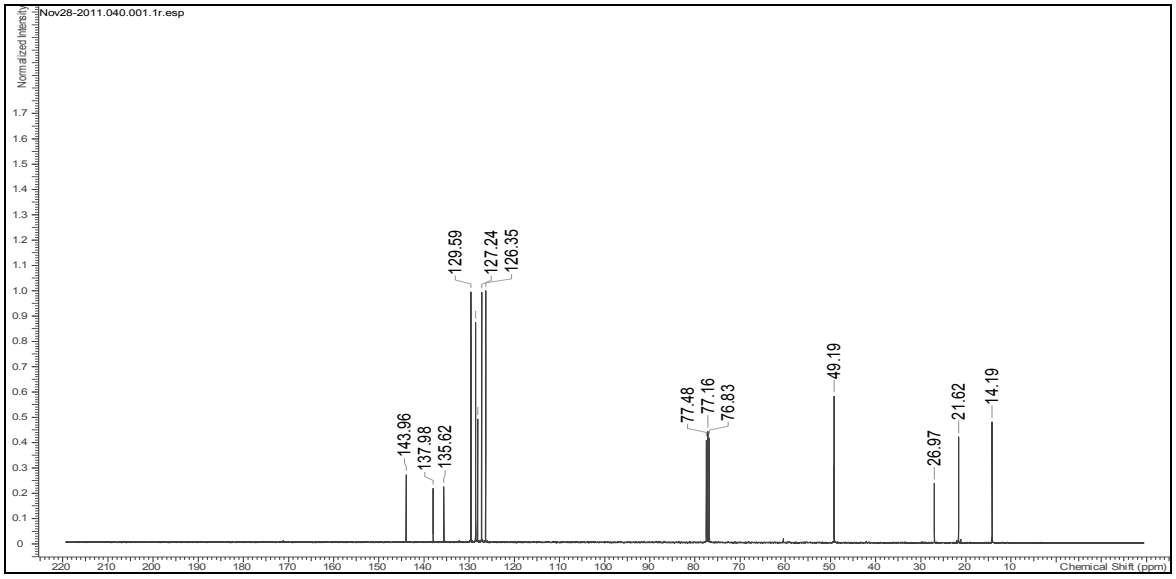
7.84
7.87
7.84
7.31
7.29
7.28
7.27
7.27
7.18
7.18
7.16
7.16
4.14
3.83
3.82
2.97
2.95
2.95
2.94
2.94
2.92
2.92
2.91
2.41
2.07
1.88
1.86
1.65
1.45
1.28
1.27
4.01
0.70
4.07
2.00
1.99
6.02
0.31
6.06
0.97
2.42
0.86
Chemical Shift (ppm)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Normalized Intensity
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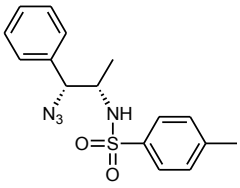
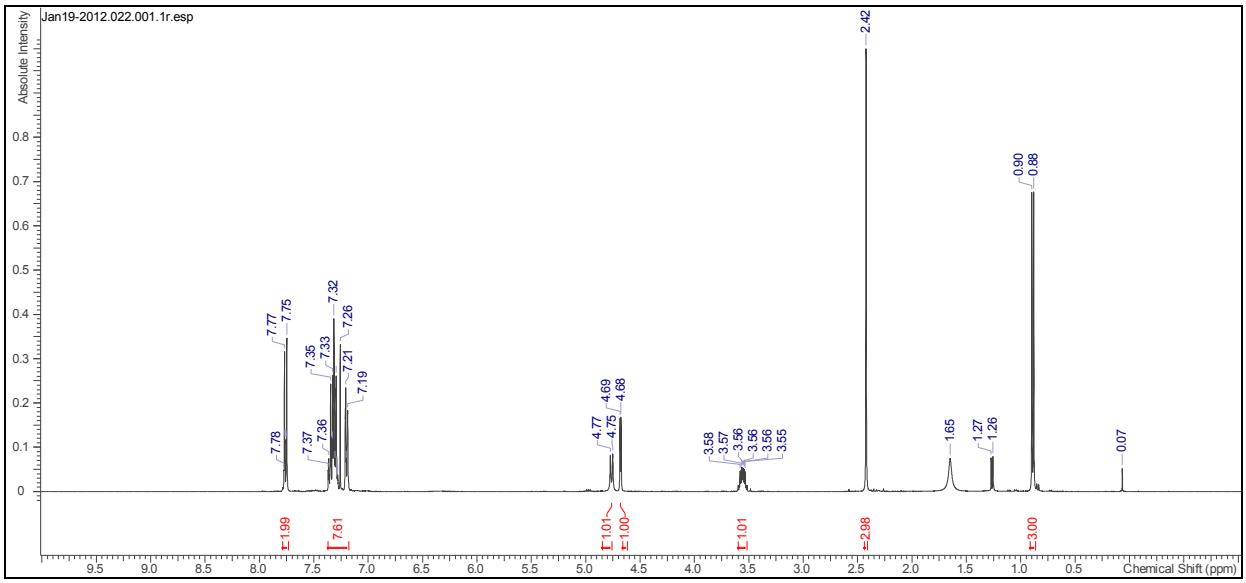
135.62
129.59
127.24
126.35
77.48
77.16
76.83
49.19
26.97
21.62
14.19
Chemical Shift (ppm)


N3
NH
O=S=O

Compound 13


Jan19-2012.022.001.1r.esp
Absolute Intensity
Chemical Shift (ppm)
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7.75
7.37
7.36
7.35
7.33
7.32
7.26
7.21
7.19
4.77
4.75
4.69
4.68
3.58
3.57
3.56
3.56
3.56
3.55
2.42
1.65
1.27
1.26
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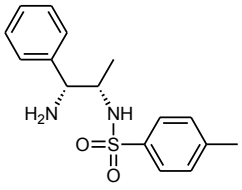
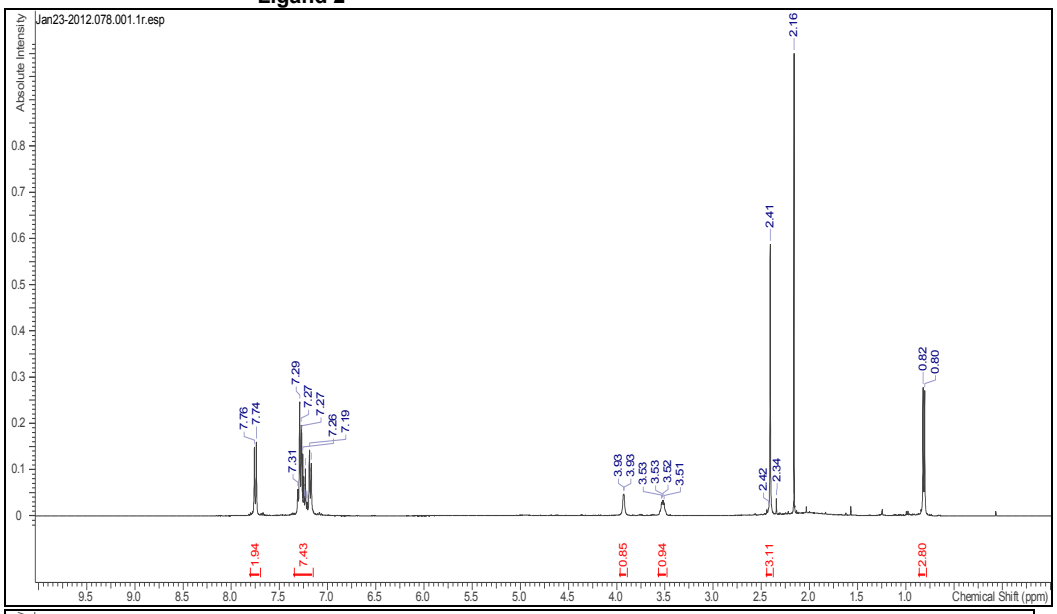
0.88
0.07
1.99
7.61
1.01
1.00
1.01
2.98
3.00


H2N
NH
O=S
O

Ligand 2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Absolute Intensity
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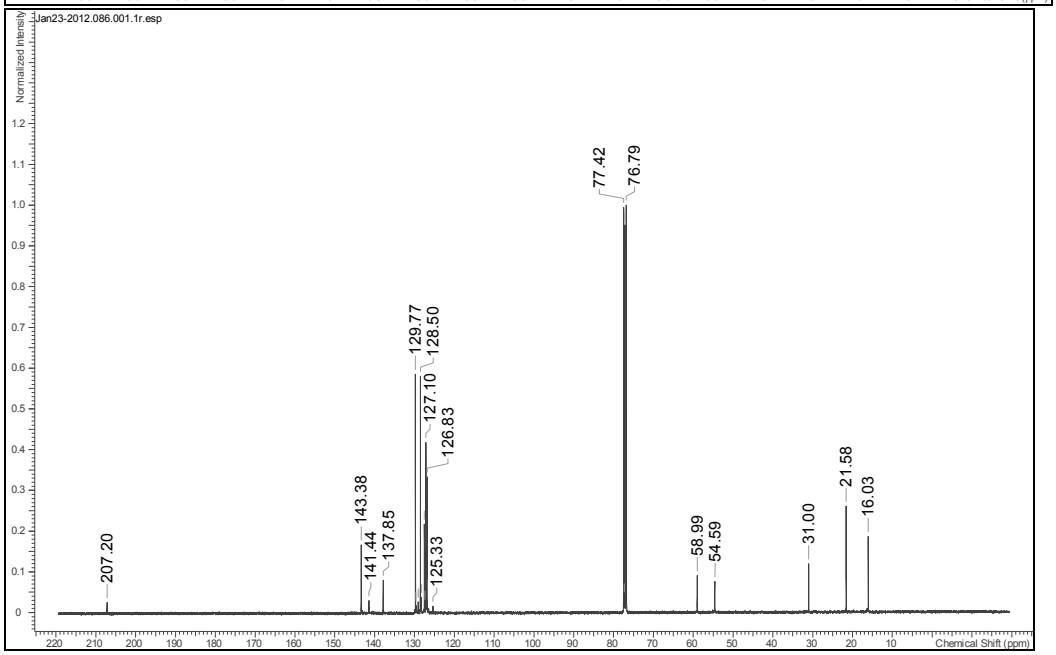
7.74
7.31
7.29
7.27
7.27
7.26
7.19
3.93
3.93
3.53
3.53
3.52
3.51
2.42
2.34
2.41
2.16
0.82
0.80
1.94
7.43
0.85
0.94
3.11
2.80
Chemical Shift (ppm)


Jan23-2012.086.001.1r.esp
Normalized Intensity
207.20
143.38
141.44
137.85
129.77
128.50
127.10
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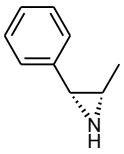
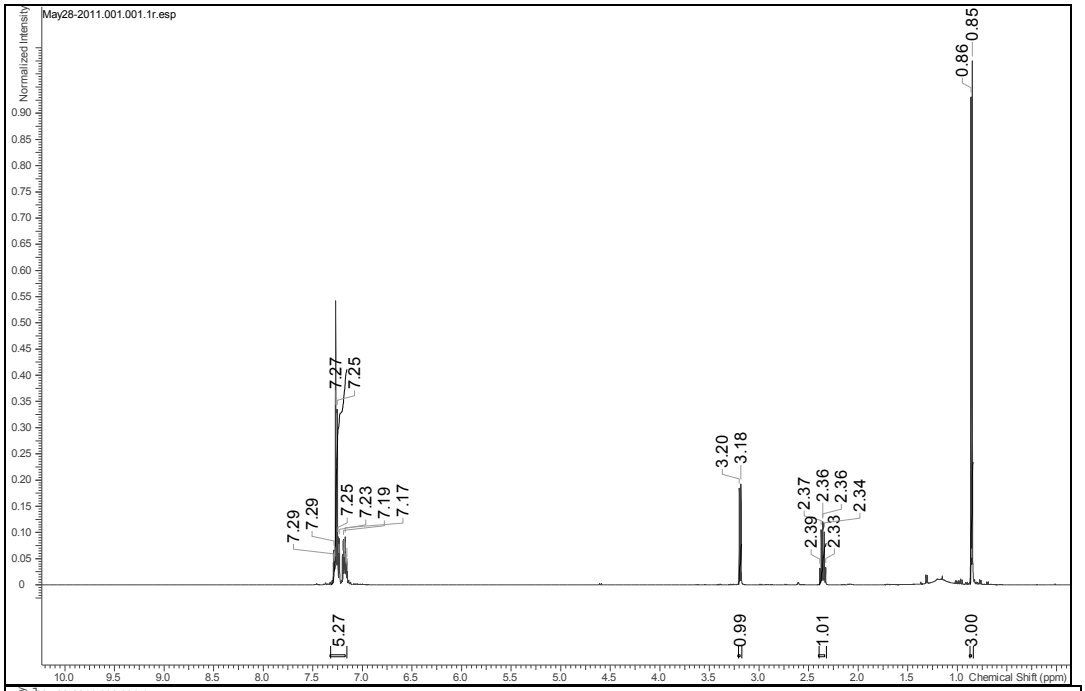
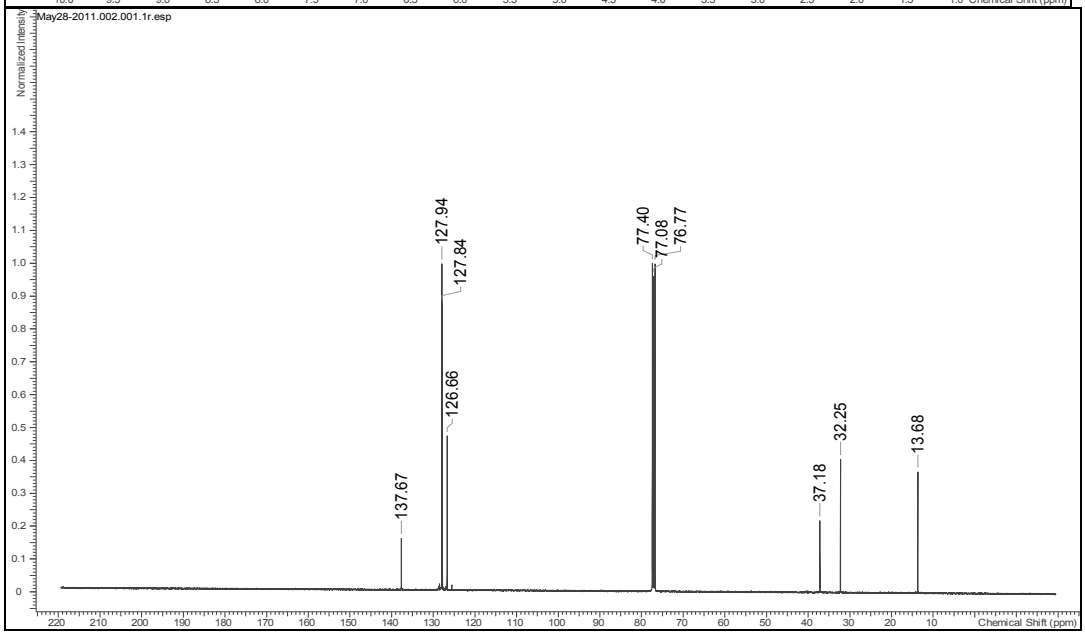
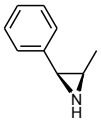
76.79
58.99
54.59
31.00
21.58
16.03
Chemical Shift (ppm)



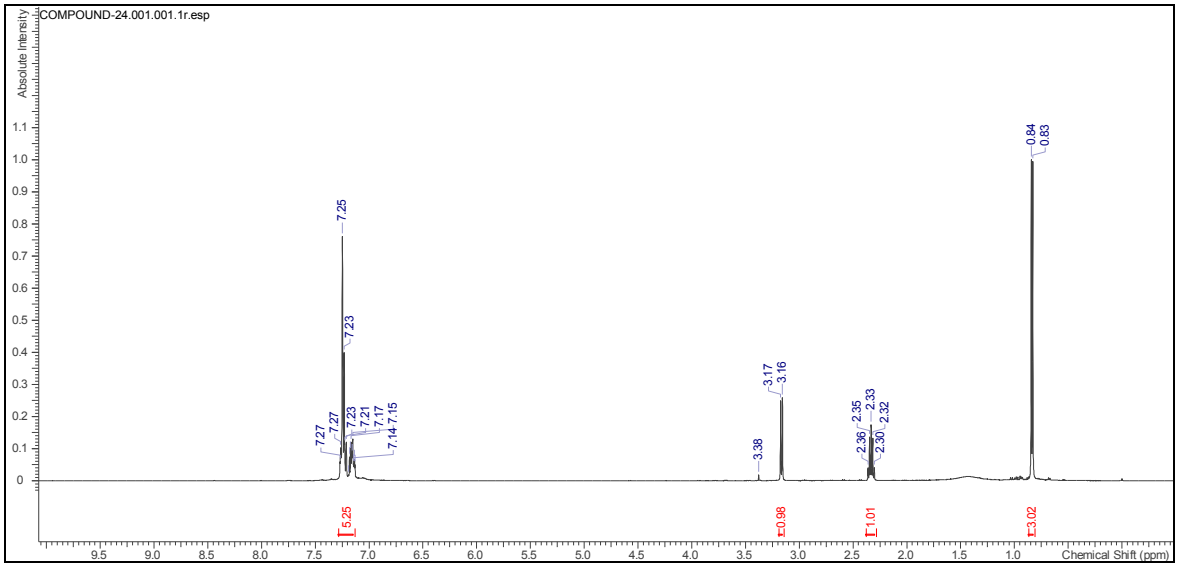
Compound 14

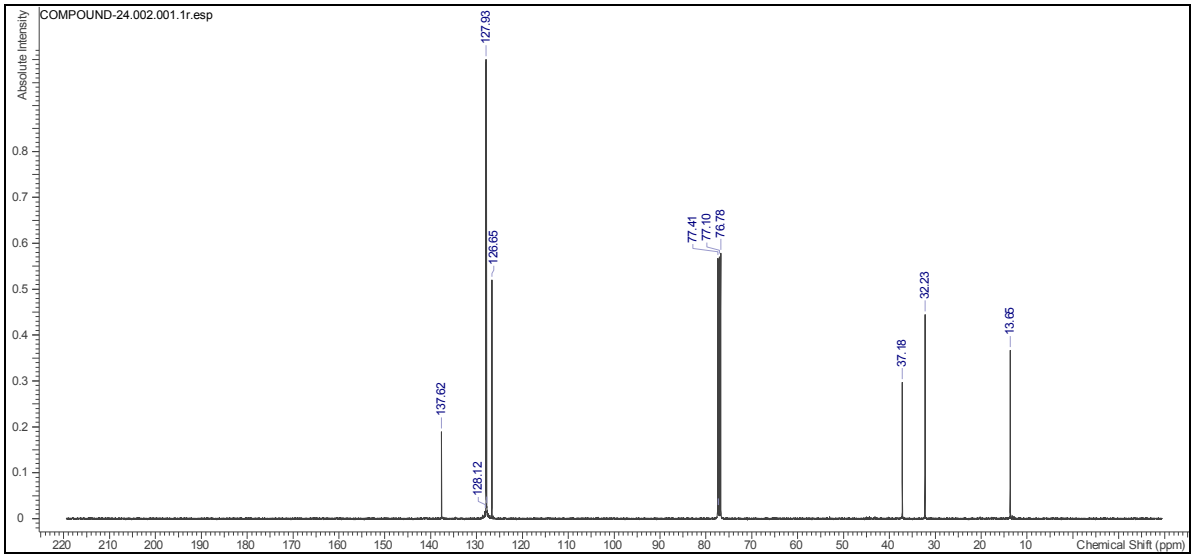

May28-2011.001.001.1r.esp
Normalized Intensity
0.86
0.85
7.27
7.25
3.20
3.18
2.37
2.36
2.34
7.29
7.29
7.25
7.23
7.19
7.17
2.39
2.33
5.27
0.99
1.01
3.00
Chemical Shift (ppm)

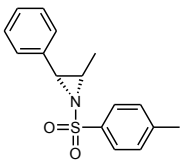

May28-2011.002.001.1r.esp
Normalized Intensity
127.94
127.84
77.40
77.08
76.77
126.66
32.25
13.68
137.67
37.18
Chemical Shift (ppm)



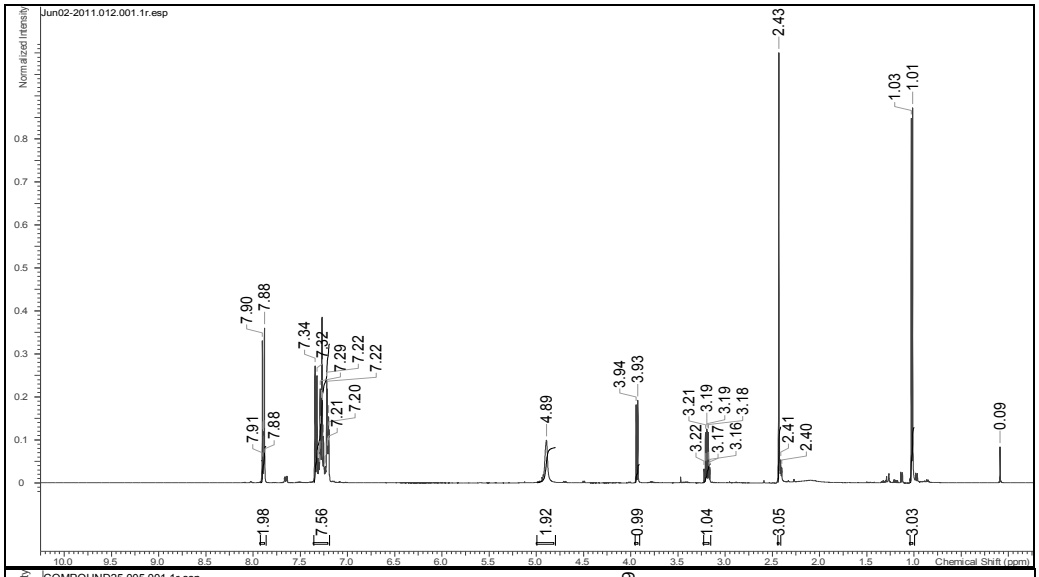
compound 14a

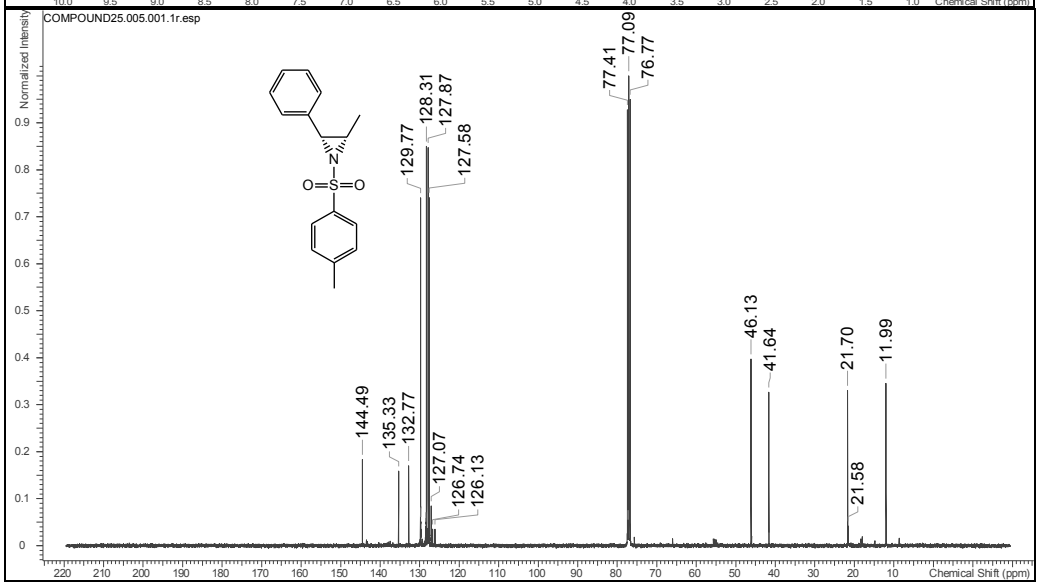


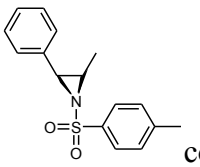




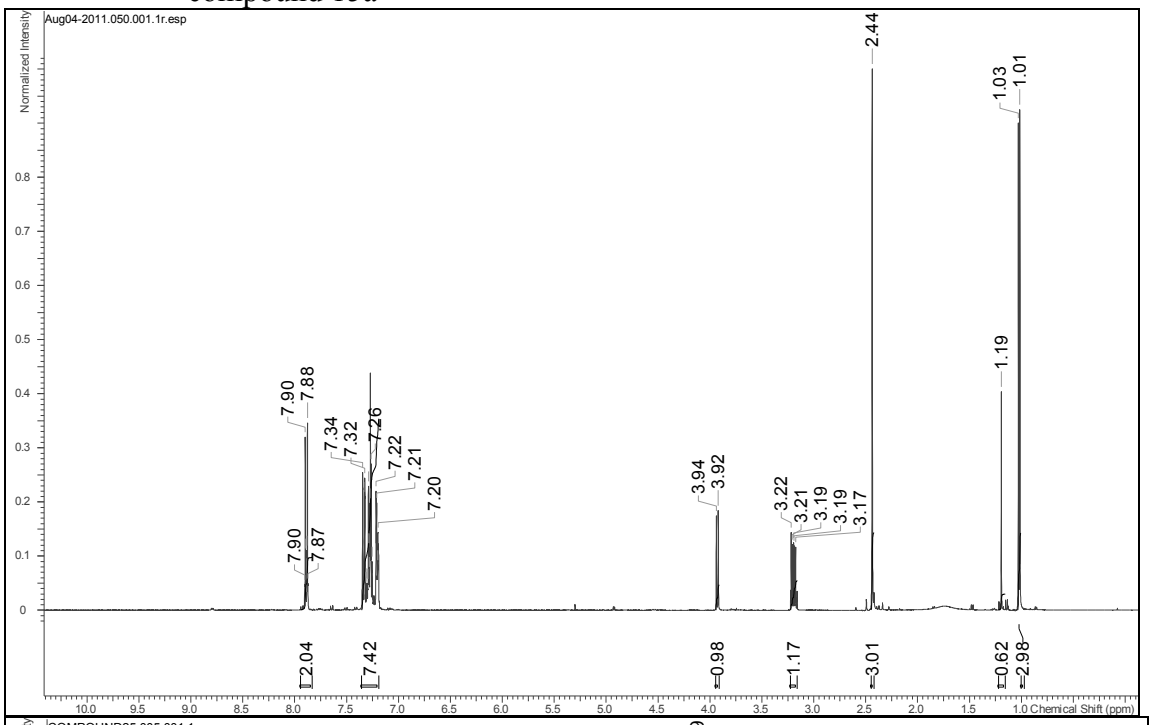
Compound 15

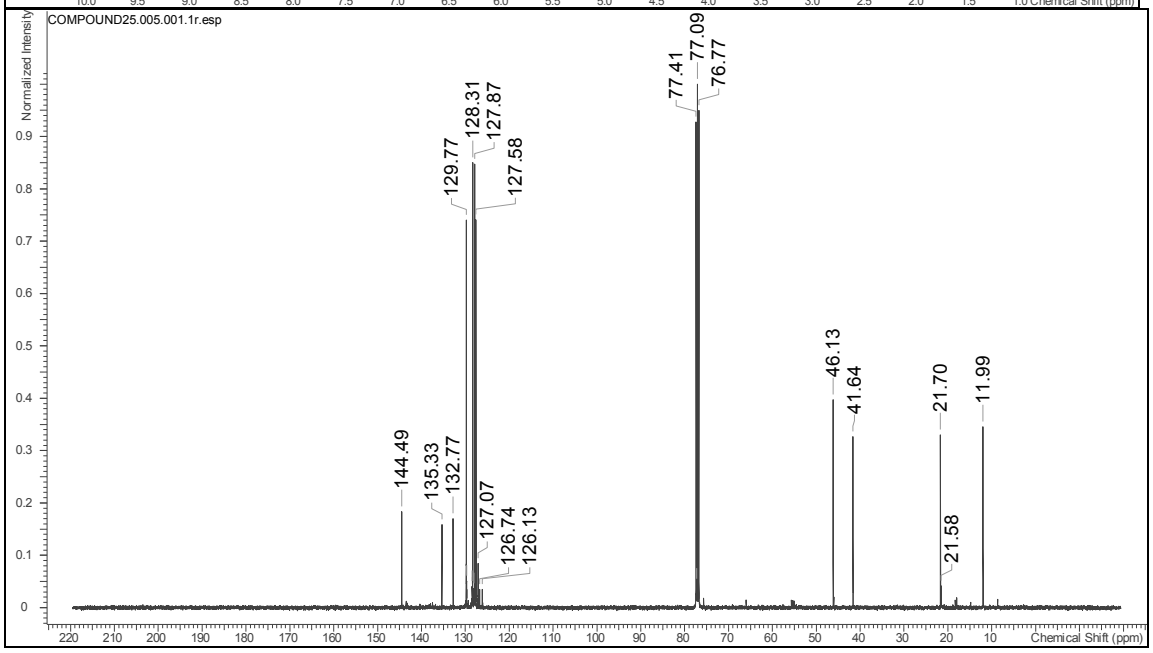

Jun02-2011.012.001.1r.esp
Normalized Intensity
2.43
1.03
1.01
7.90
7.88
7.34
7.32
7.29
7.22
7.22
7.91
7.88
7.21
7.20
4.89
3.94
3.93
3.21
3.19
3.19
3.18
3.22
3.17
3.16
2.41
2.40
0.09
1.98
7.56
1.92
0.99
1.04
3.05
3.03
Chemical Shift (ppm)

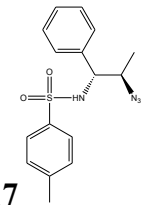

COMPOUND25.005.001.1r.esp
Normalized Intensity
77.41
77.09
76.77
128.31
127.87
129.77
127.58
46.13
41.64
21.70
11.99
144.49
135.33
132.77
127.07
126.74
126.13
21.58
Chemical Shift (ppm)



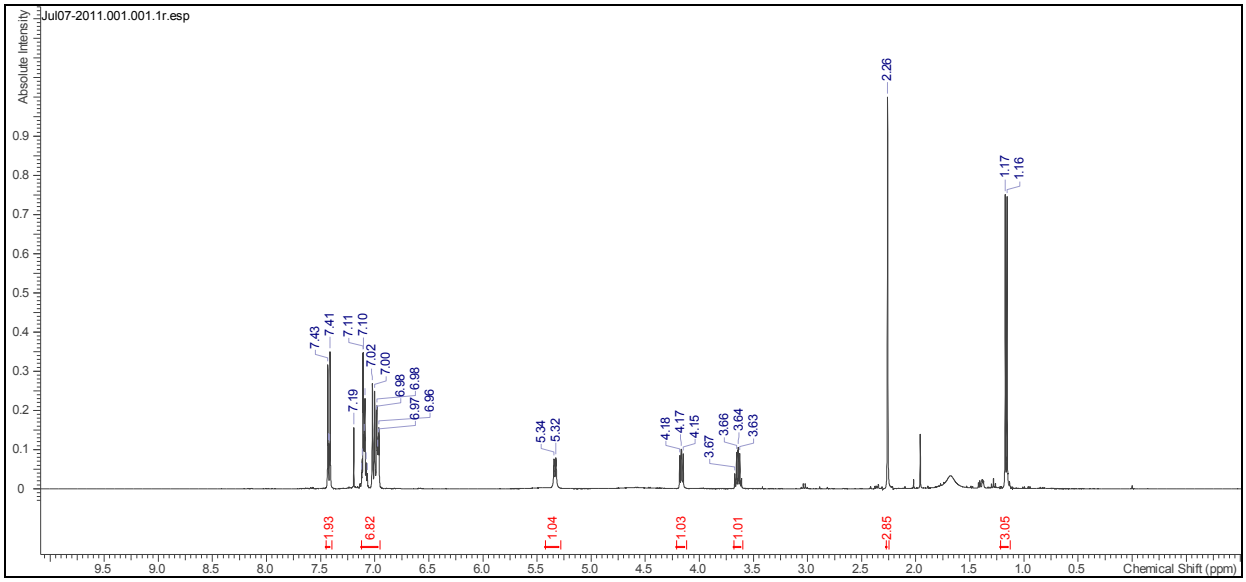
compound 15a

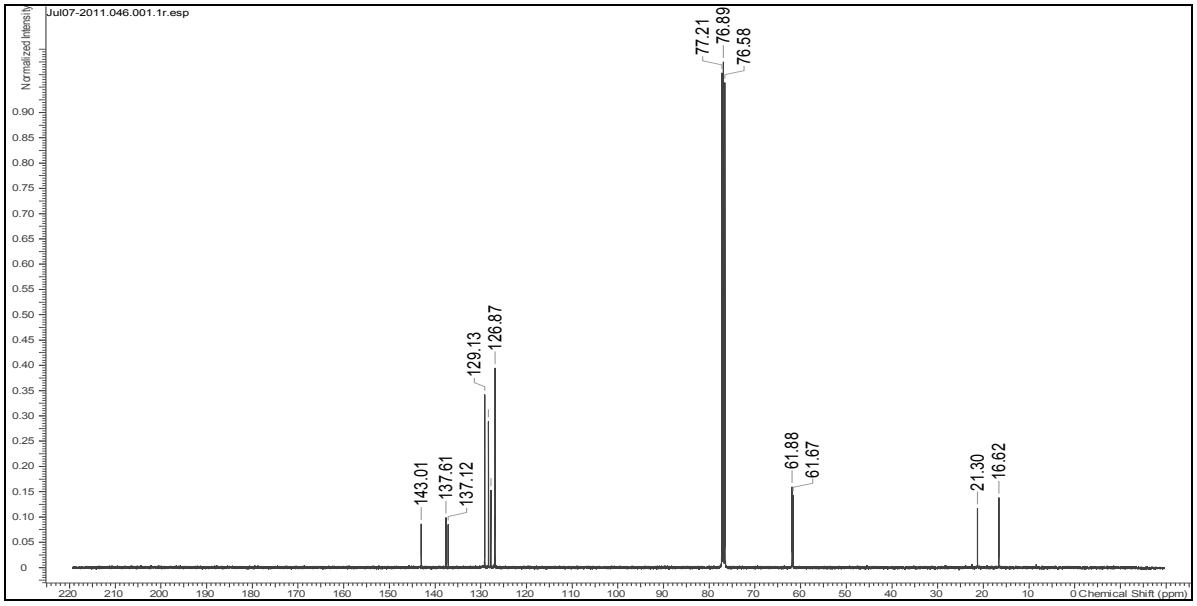


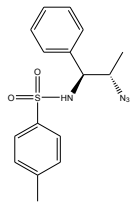




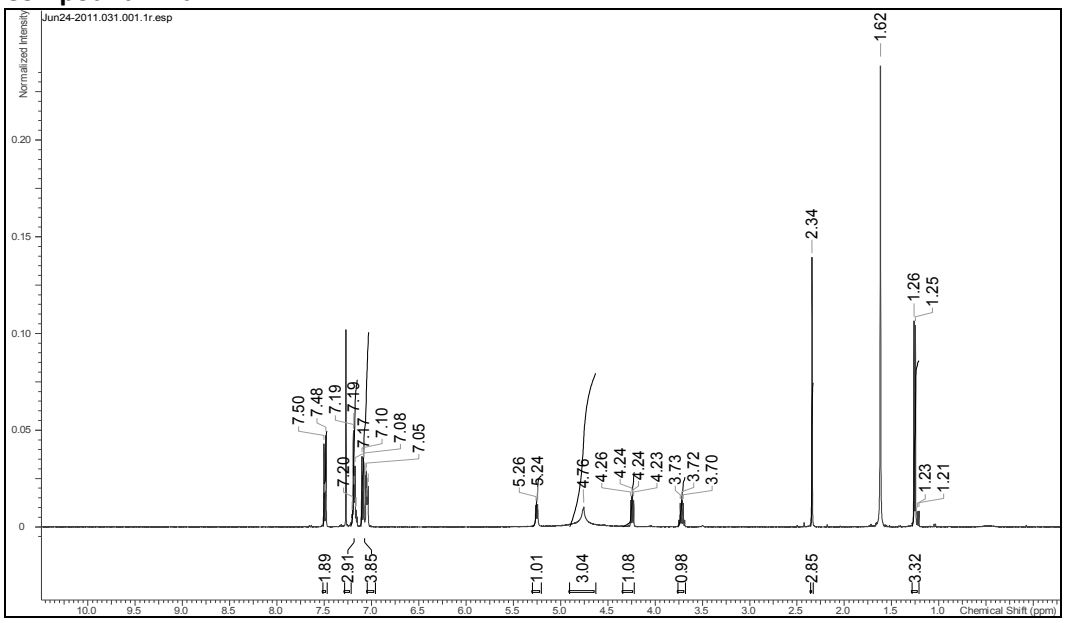
Compound 17

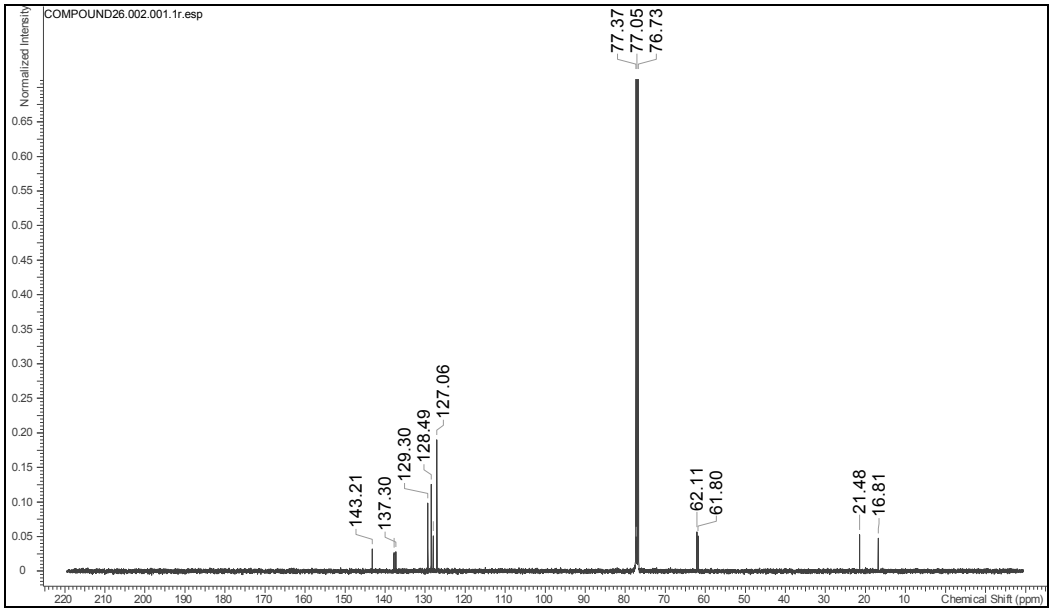

Jul07-2011.001.001.1r.esp
Absolute Intensity
7.43
7.41
7.11
7.10
7.02
7.00
6.98
6.98
6.97
6.96
7.19
5.34
5.32
4.18
4.17
4.15
3.67
3.66
3.64
3.63
2.26
1.17
1.16
1.93
6.82
1.04
1.03
1.01
2.85
3.05
Chemical Shift (ppm)

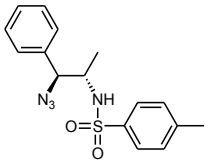

Jul07-2011.046.001.1r.esp
Normalized Intensity
77.21
76.89
76.58
129.13
126.87
143.01
137.61
137.12
61.88
61.67
21.30
16.62
Chemical Shift (ppm)



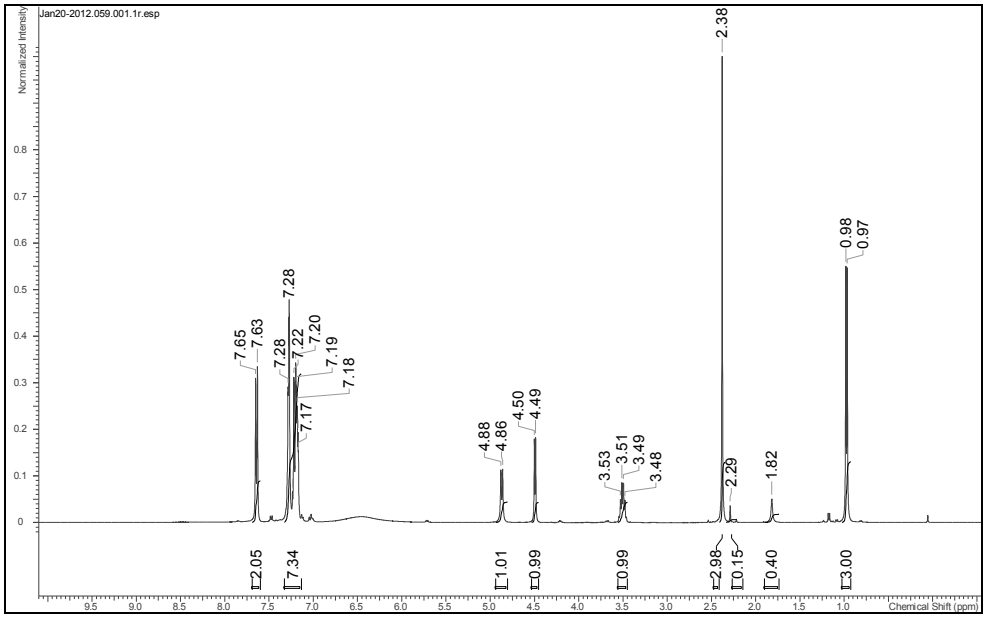
Compound 17a

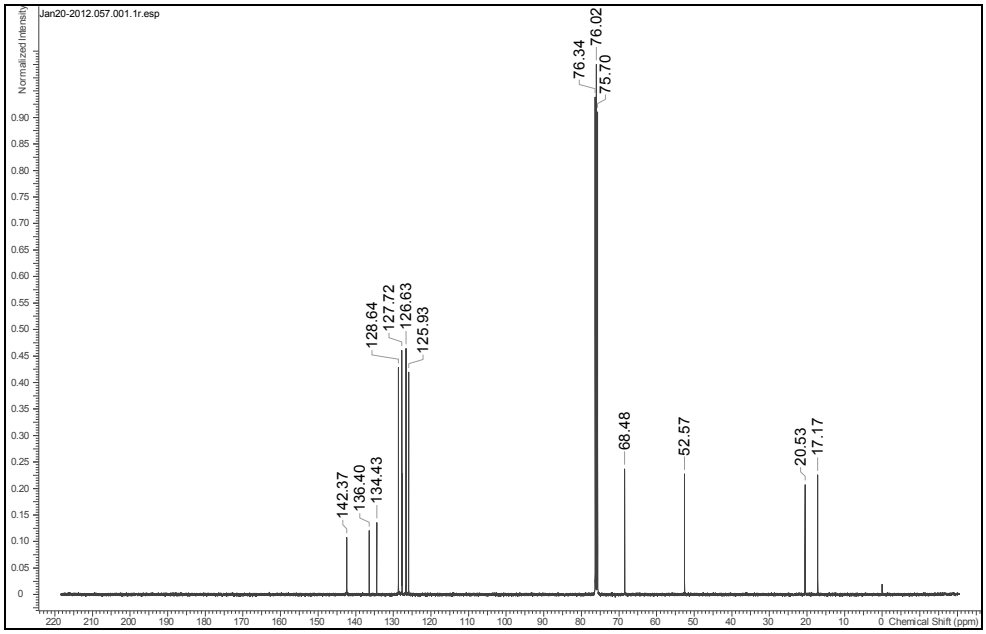


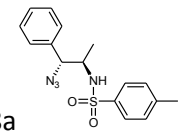




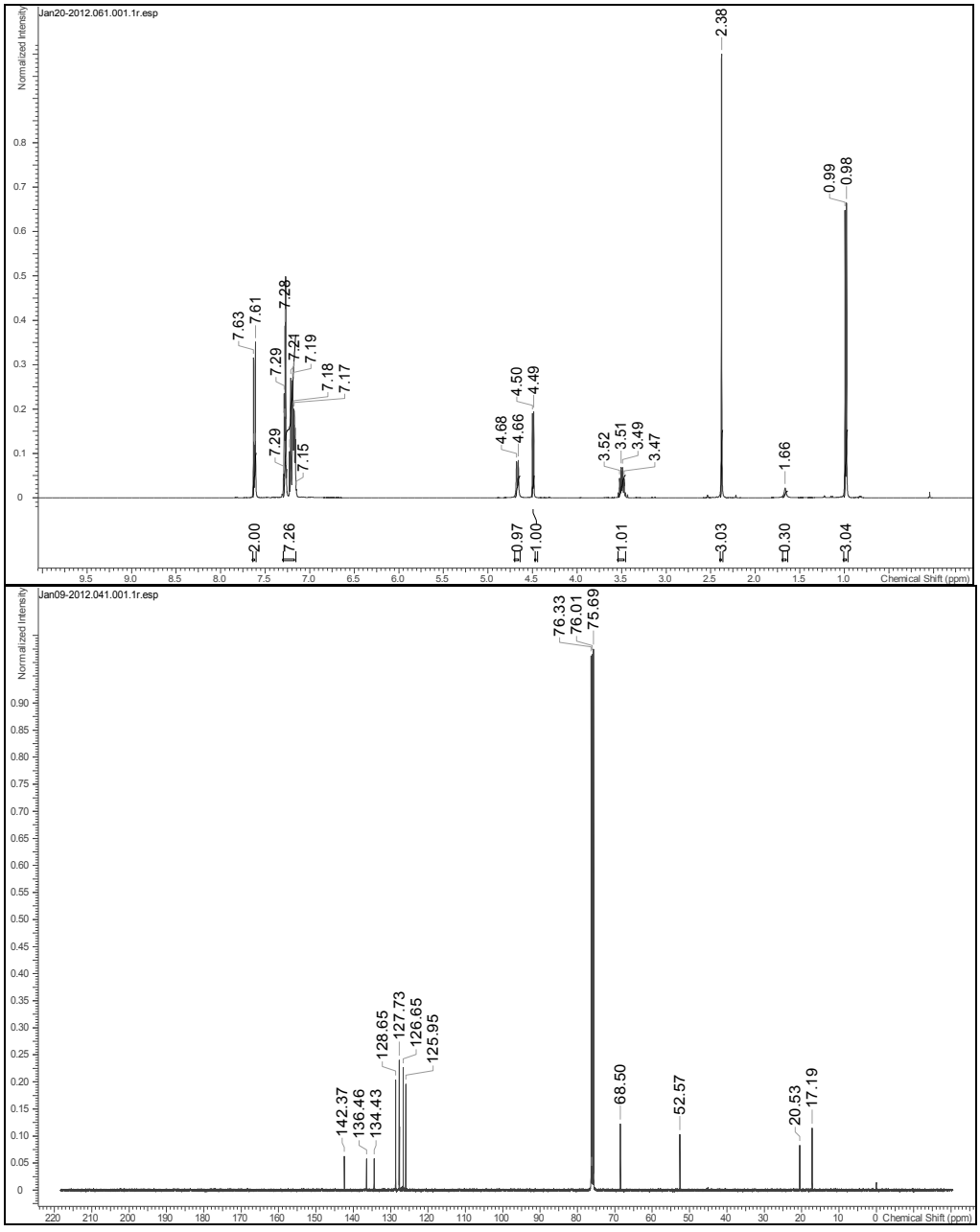
Compound 18

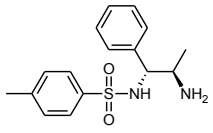

Jan20-2012.059.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.65
7.63
7.28
7.28
7.22
7.20
7.19
7.18
7.17
4.88
4.86
4.50
4.49
3.53
3.51
3.49
3.48
2.38
2.29
1.82
0.98
0.97
2.05
7.34
1.01
0.99
0.99
2.98
0.15
0.40
3.00


Jan20-2012.057.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
76.34
76.02
75.70
128.64
127.72
126.63
125.93
142.37
136.40
134.43
68.48
52.57
20.53
17.17

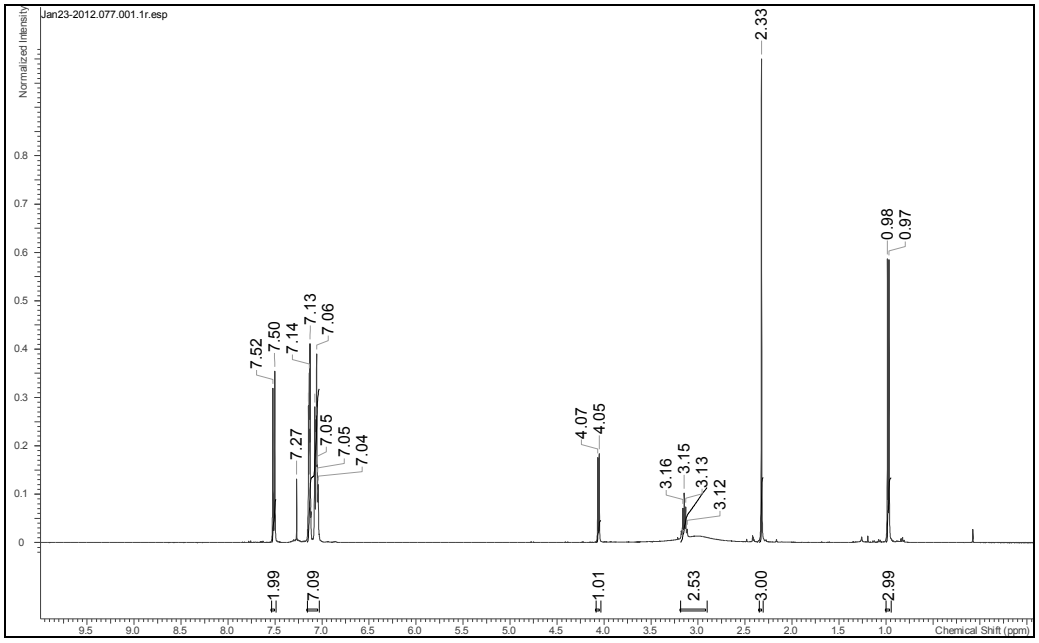


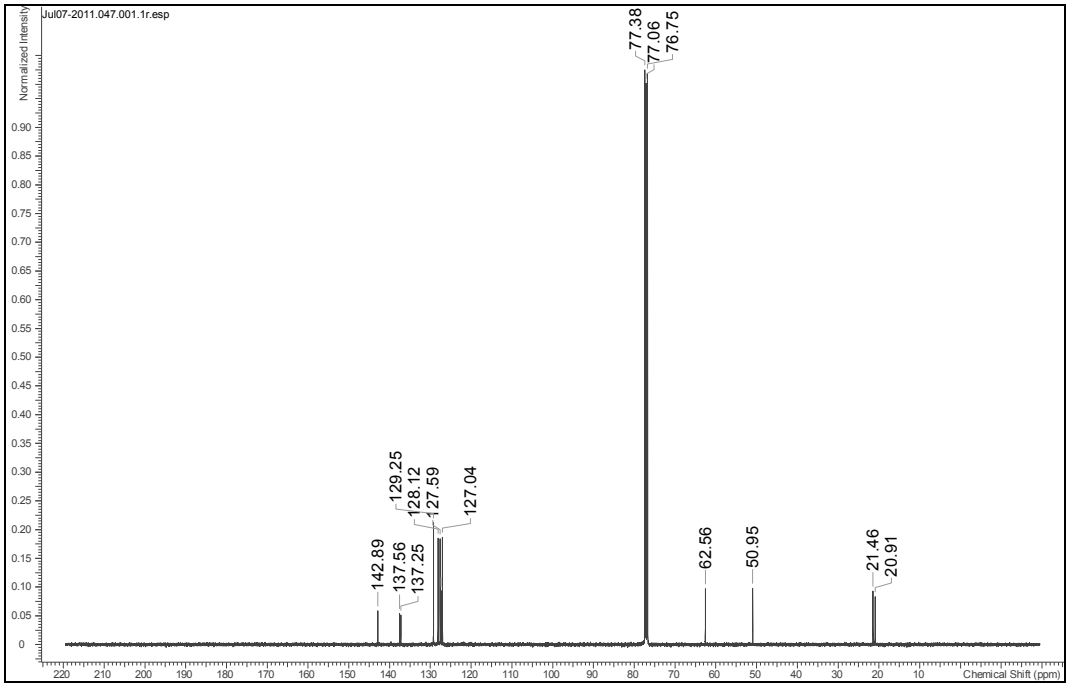
Compound 18a



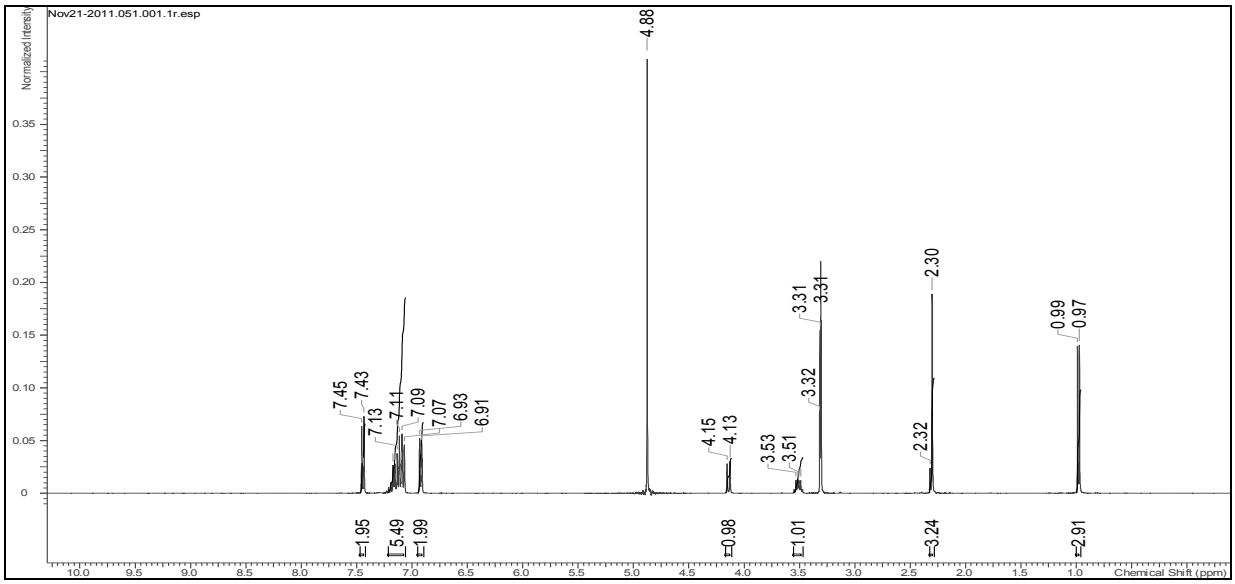


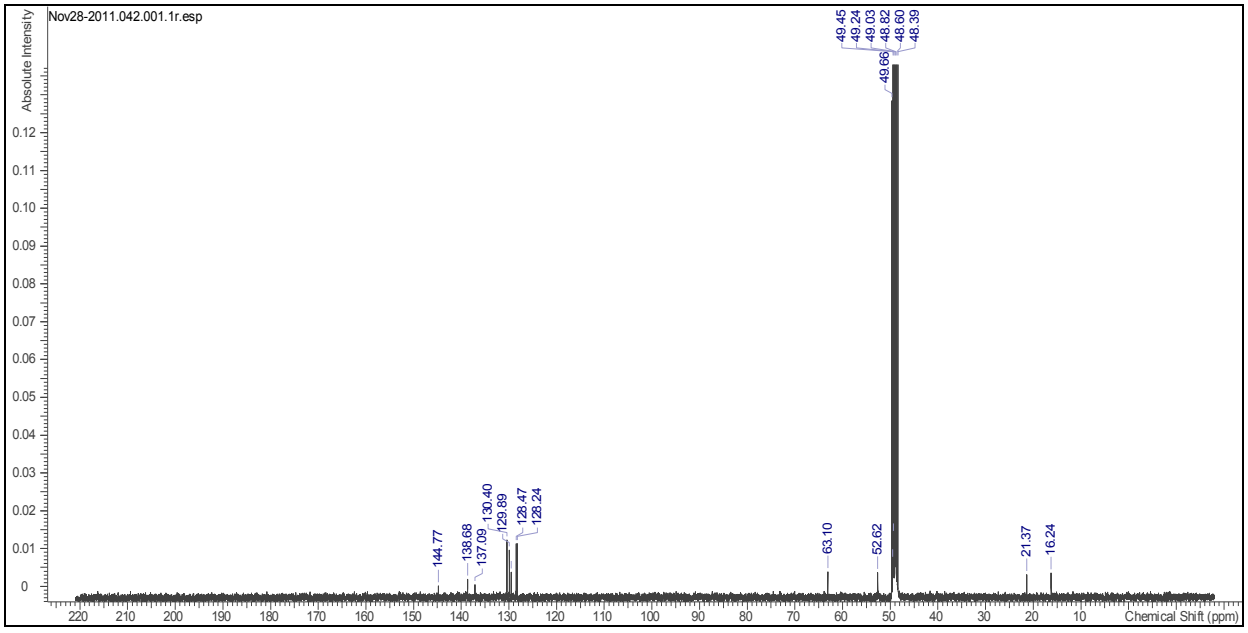
Ligand 3

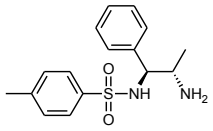

Jan23-2012.077.001.1r.esp
Normalized Intensity
2.33
0.98
0.97
7.52
7.50
7.14
7.13
7.06
7.27
7.05
7.05
7.04
4.07
4.05
3.16
3.15
3.13
3.12
1.99
7.09
1.01
2.53
3.00
2.99
Chemical Shift (ppm)


Jul07-2011.047.001.1r.esp
Normalized Intensity
77.38
77.06
76.75
129.25
128.12
127.59
127.04
142.89
137.56
137.25
62.56
50.95
21.46
20.91
Chemical Shift (ppm)

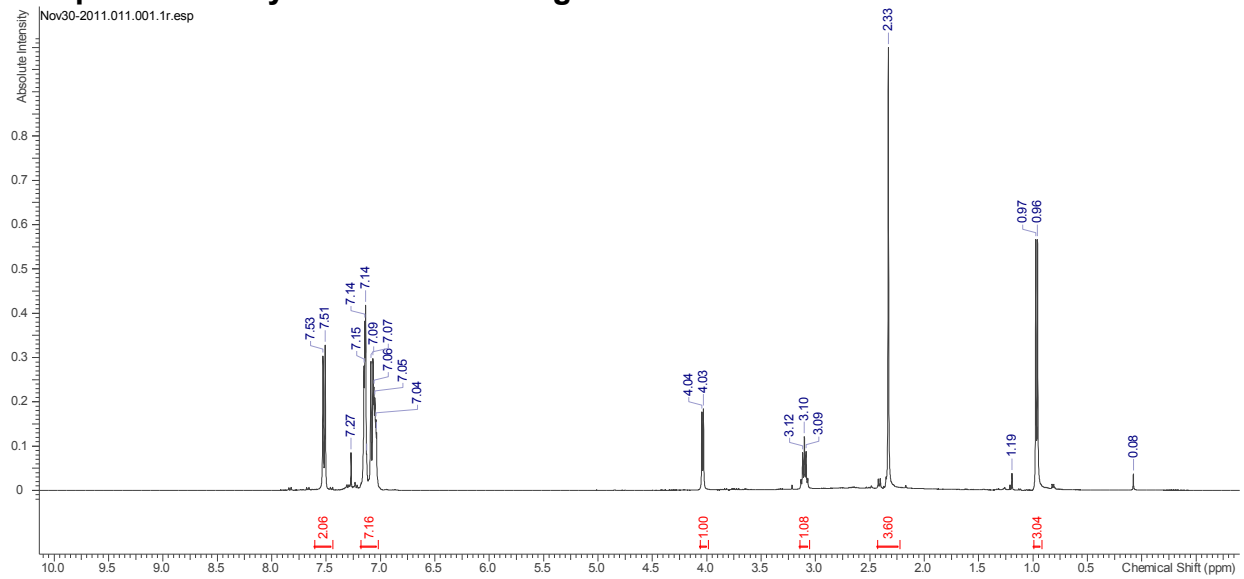
ligand 3 in hydrochloride form

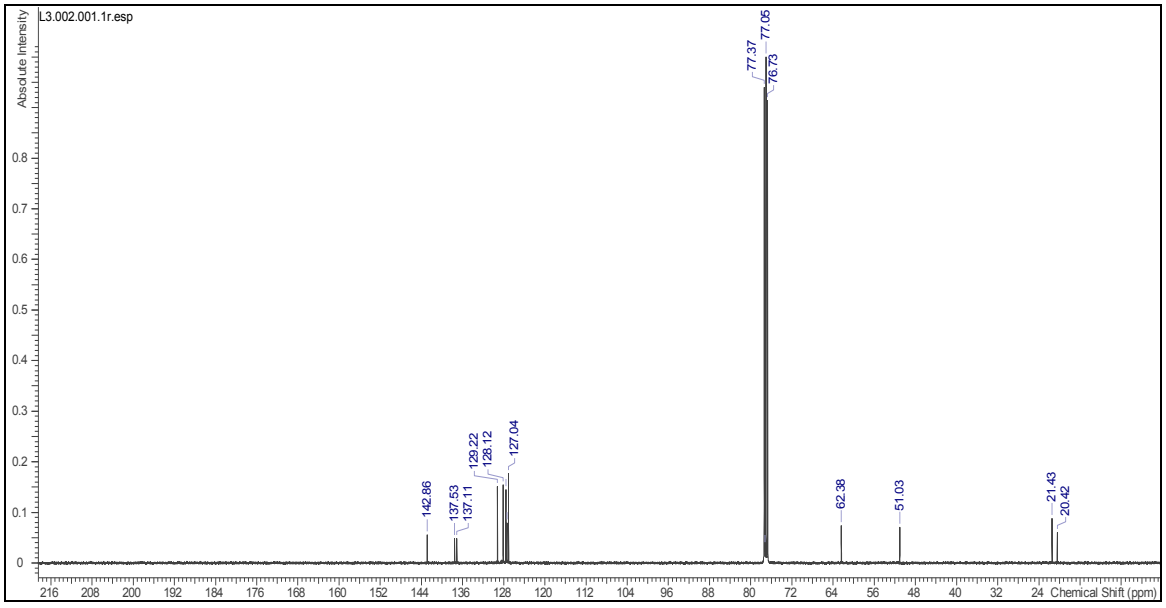


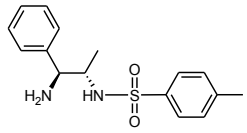




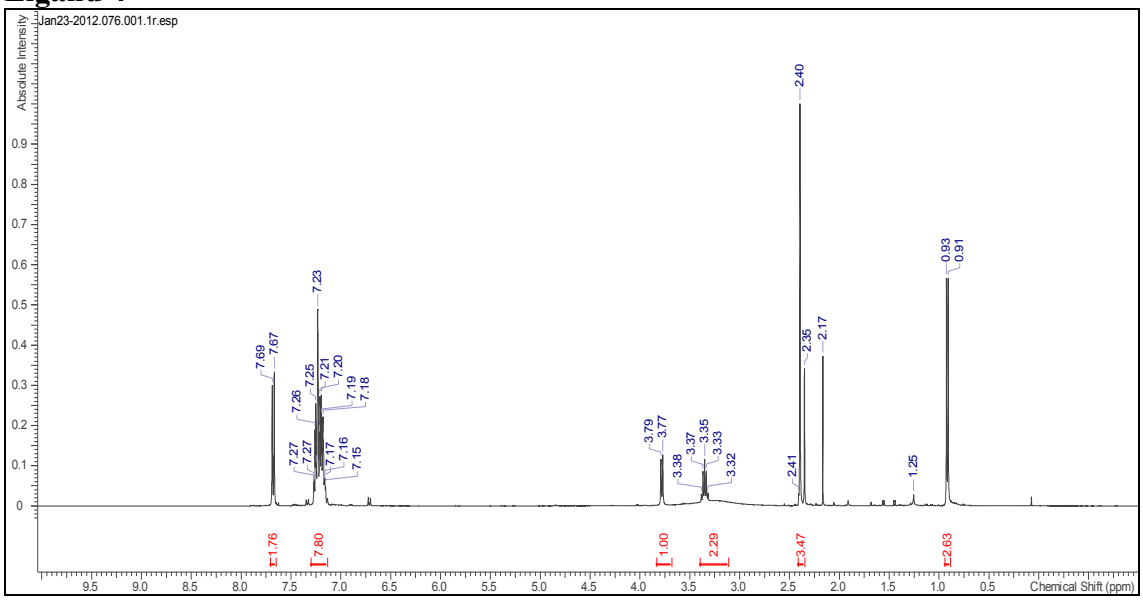
Compound 13a Hydrochloride salt ligand 7

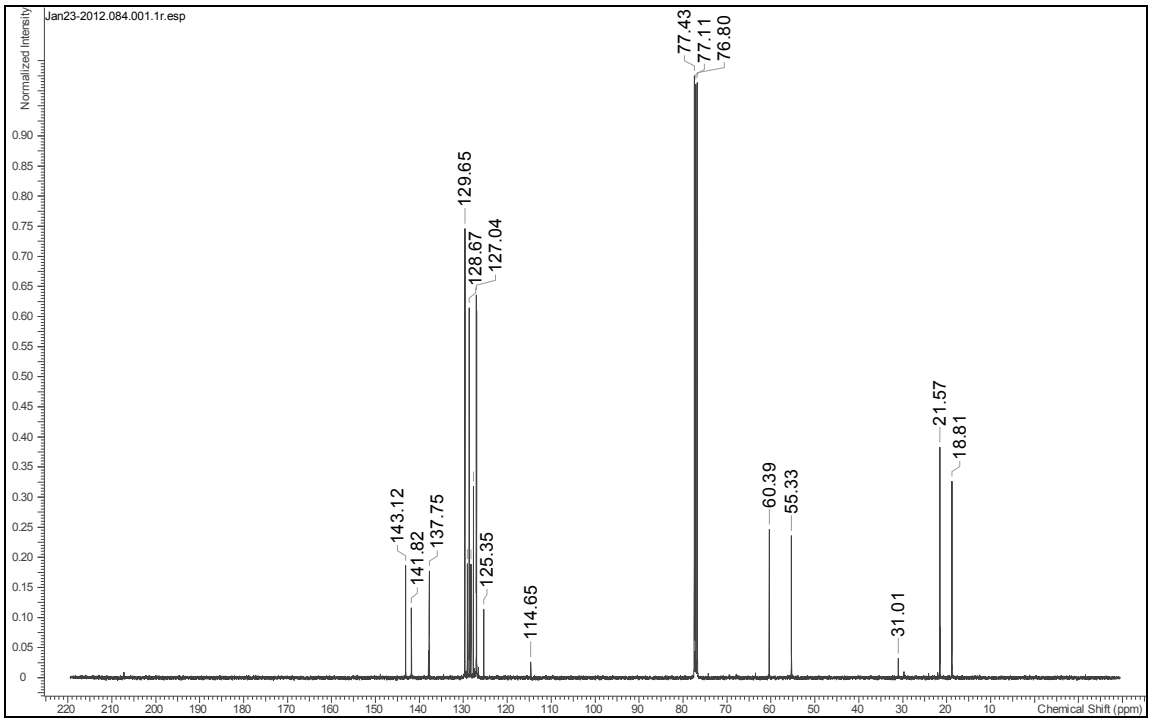




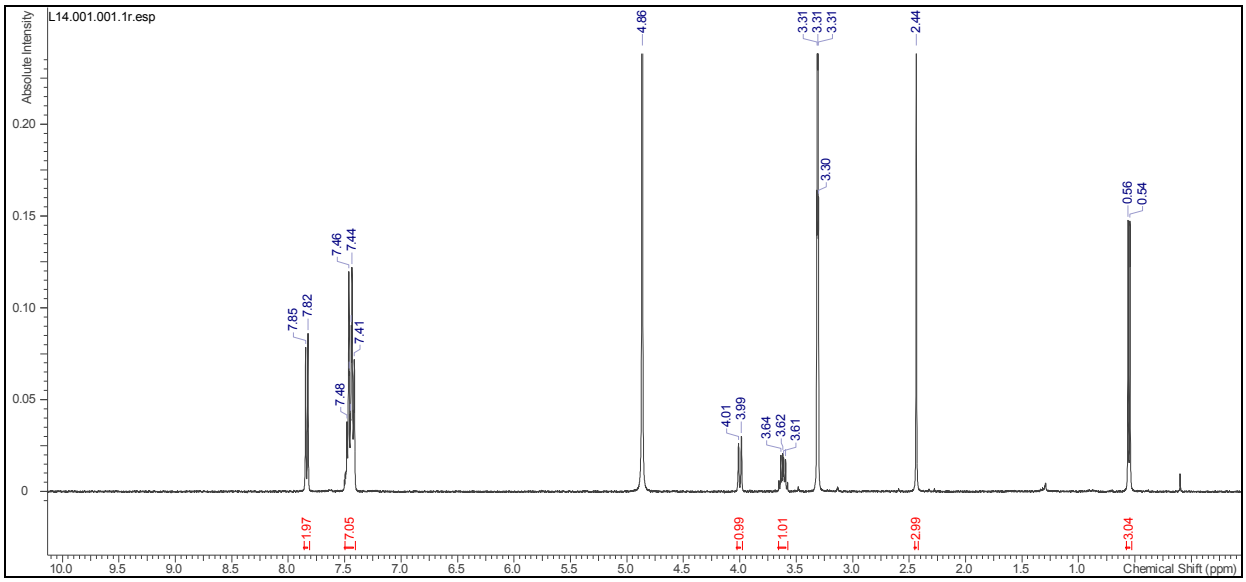


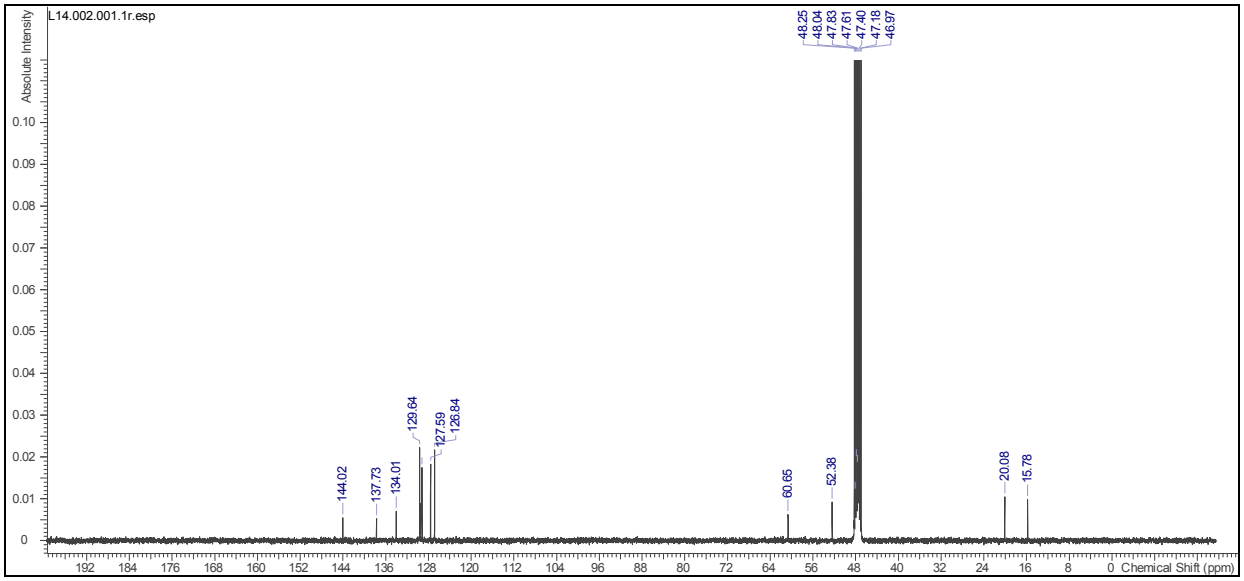
Ligand 4


Jan23-2012.076.001.1r.esp
Absolute Intensity
Chemical Shift (ppm)
7.69
7.67
7.25
7.23
7.21
7.20
7.19
7.18
7.26
7.27
7.27
7.17
7.16
7.15
3.79
3.77
3.38
3.37
3.35
3.33
3.32
2.41
2.40
2.35
2.17
1.25
0.93
0.91
1.76
7.80
1.00
2.29
3.47
2.63

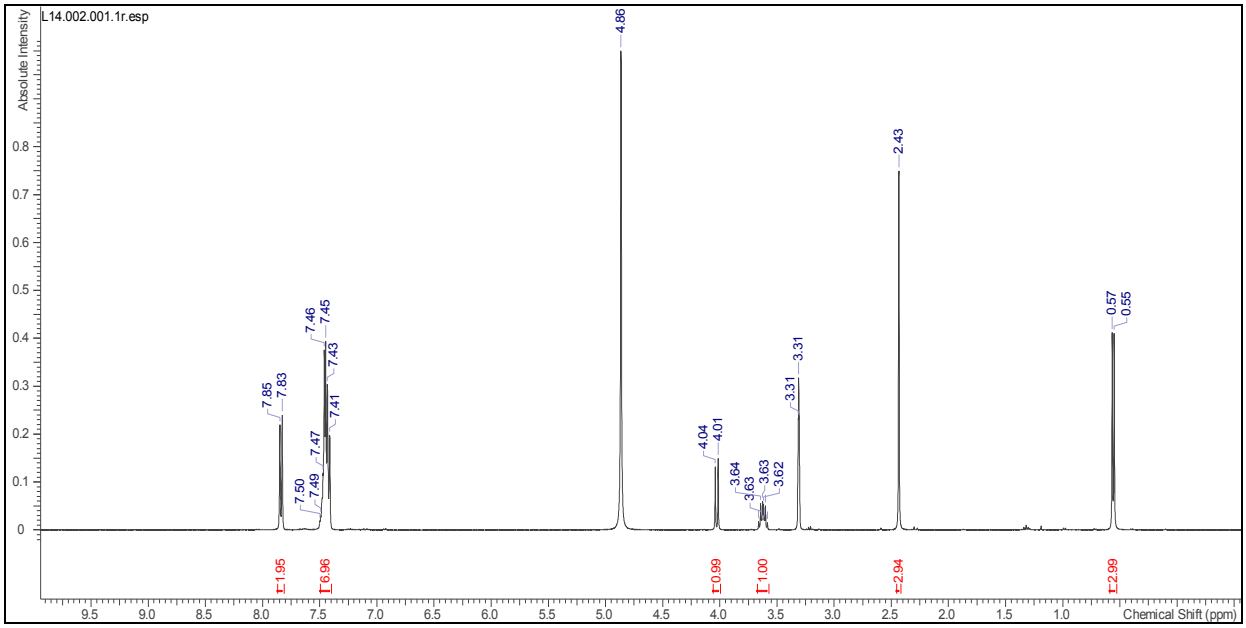

Jan23-2012.084.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.43
77.11
76.80
129.65
128.67
127.04
143.12
141.82
137.75
125.35
114.65
60.39
55.33
31.01
21.57
18.81

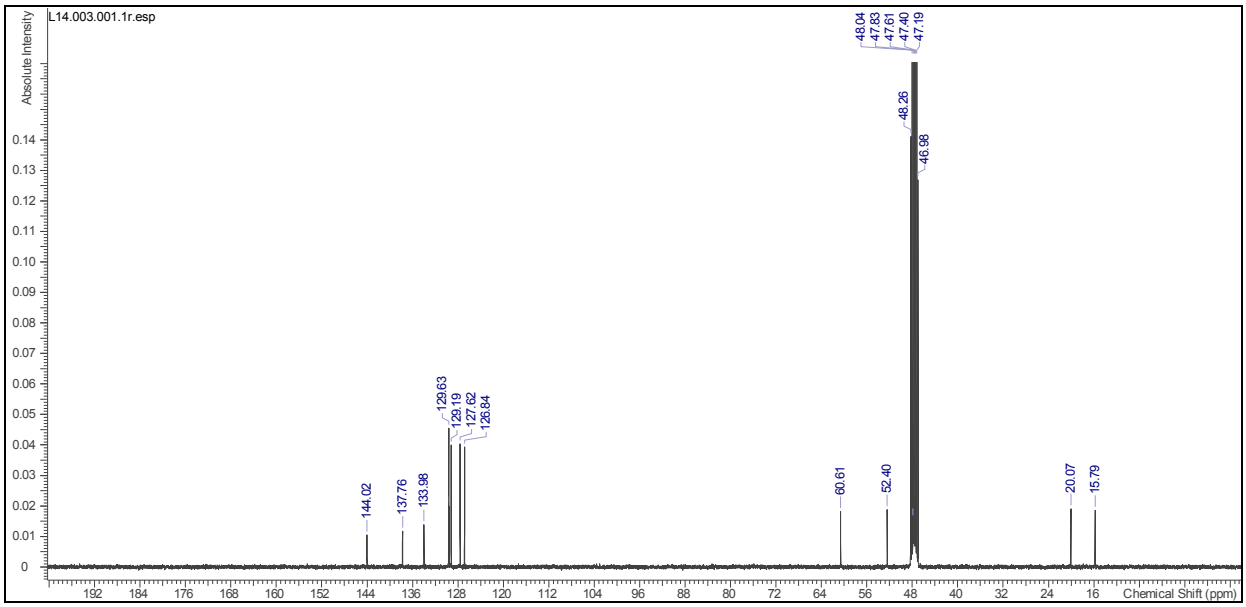
(Ligand 4)as hydrochloride



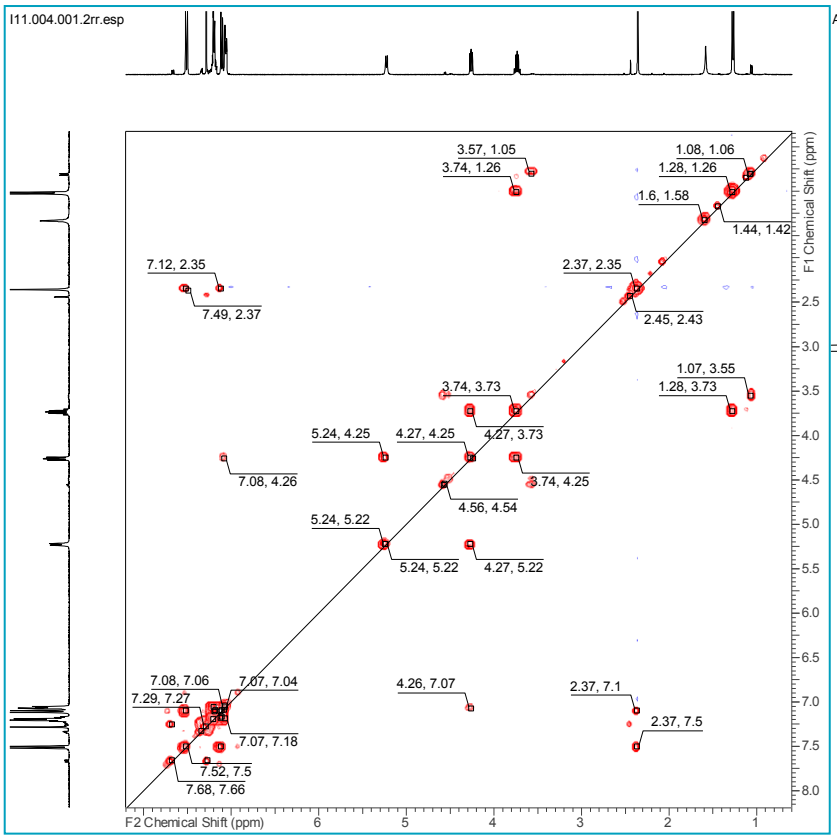


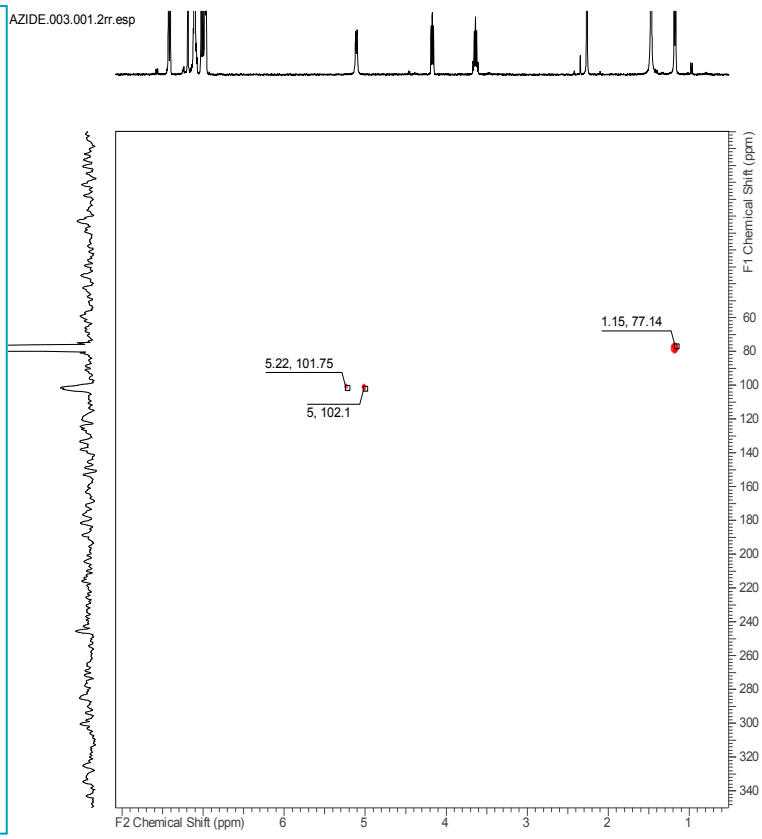
Compound 14a as hydrochloride (Ligand 8)

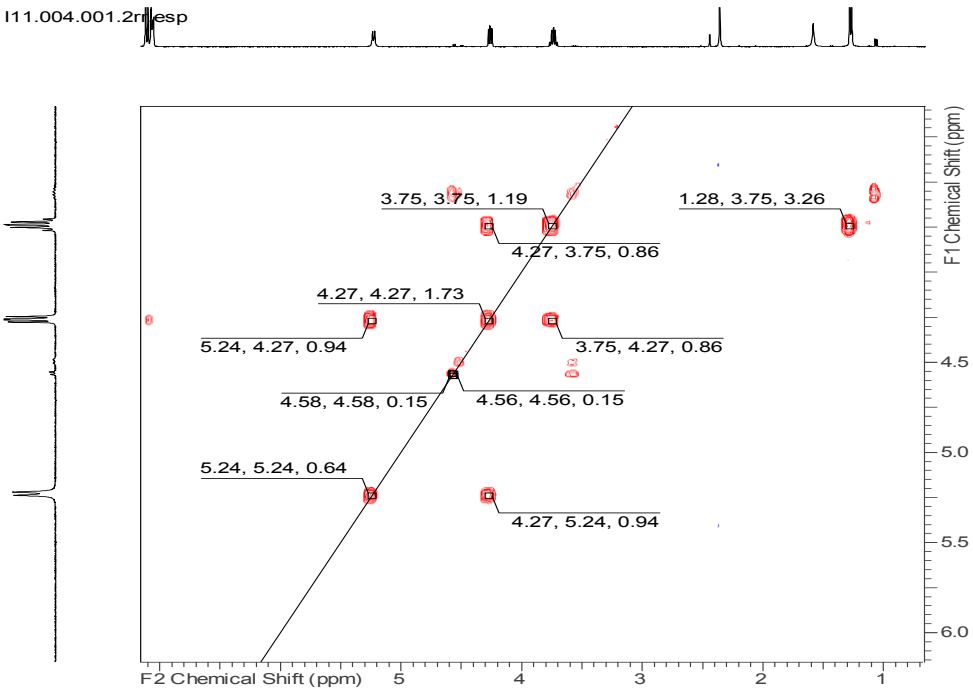




4 ^{1}H-^{1}H COSY and ^{1}H-^{15}N HMBC of compound 17a^{1}H-^{15}N HMBC

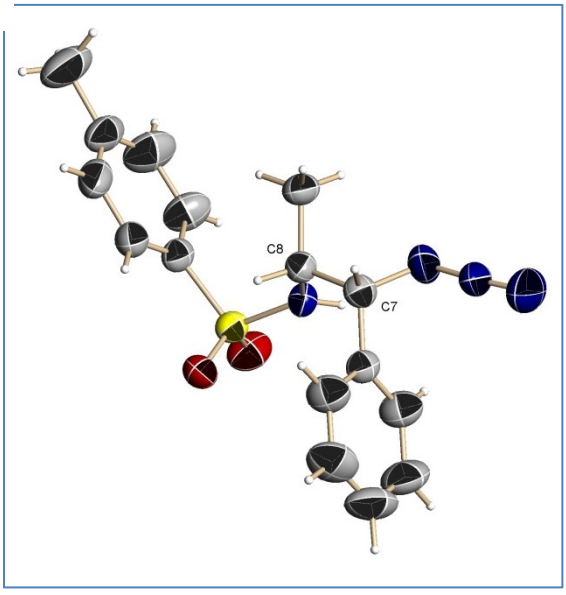






5 X-ray Crystal Structure Analysis of compound 18a (CCDC Depositary number CCDC 1018428)

Crystal Data: Single crystals of the compound 12a were grown by slow evaporation from Acetonitrile**.** Pale yellow plate like crystal of approximate size 0.34 x 0.32 x 0.16 mm^3 was used for data collection. Data were collected at T = 296K on SMART APEX-II CCD single crystal X-ray diffractometer using Mo-K_α radiation (λ = 0.7107 Å). Crystal to detector distance 5.00 cm, 512 x 512 pixels / frame, Oscillation / frame -0.5º, maximum detector swing angle = –30.0º, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration. Multirun data acquisition. Total scans = 3, total frames = 1439, exposure / frame = 8.0 sec / frame,θ range = 2.84 to 24.99º, completeness to θ of 24.99º is 99.40 %, SADABS correction applied. All the structures were solved by direct methods using SHELXTL. All the data were corrected for Lorentzian, polarization and absorption effects. C_{16} H_{18} N_4 O_2 S, M = 330.40. Crystals belong to Monoclinic , space group $P2_1$, a = 8.2251(1) Å , b = 10.3695(1) Å , c = 9.9358(1) Å , V = 845.09(2) $Å^3$, Z = 2 , D_c = 1.298 g/cc,μ (Mo–Kα) = 0.206 mm^{-1}, 6855 reflections measured, 2791unique , R1 = 0.0291, wR2 = 0.0791. SHELX-97 (ShelxTL) was used for structure solution and full matrix least squares refinement on F2. Hydrogen atoms were included in the refinement as per the riding model. The refinements were carried out using SHELXL-97. Largest diff. peak and hole 0.210 and -0.265 e.Å-3 .The conformation of the molecule was established by single crystal X-ray analysis shows C7 and C8 both to have R configuration.



Analysis of Potential Hydrogen Bonds

Donor --- H....Acceptor	D-H	H...A	D...A	D-H...A
N(1) --H(1N) ..O(1)^{i}	0.86	2.42	3.047(2)	130
C(3) --H(3) ..N(4)^{ii}	0.93	2.53	3.451(4)	173
C(7) --H(7) ..O(2)^{iii}	0.98	2.57	3.426(2)	146
C(8) --H(8) ..O(1)^{Intra}	0.98	2.58	3.025(2)	108
C(8) --H(8) ..N(4)^{iv}	0.98	2.61	3.341(4)	131'
C(11) --H(11) ..O(1)^{Intra}	0.93	2.57	2.921(2)	103

Equivalent Position Code

^{i} = 2-x,-1/2+y,-z
^{ii} = 1-x,1/2+y,-1-z
^{iii} = -1+x,y,z
^{iv} = 1-x,1/2+y,-z

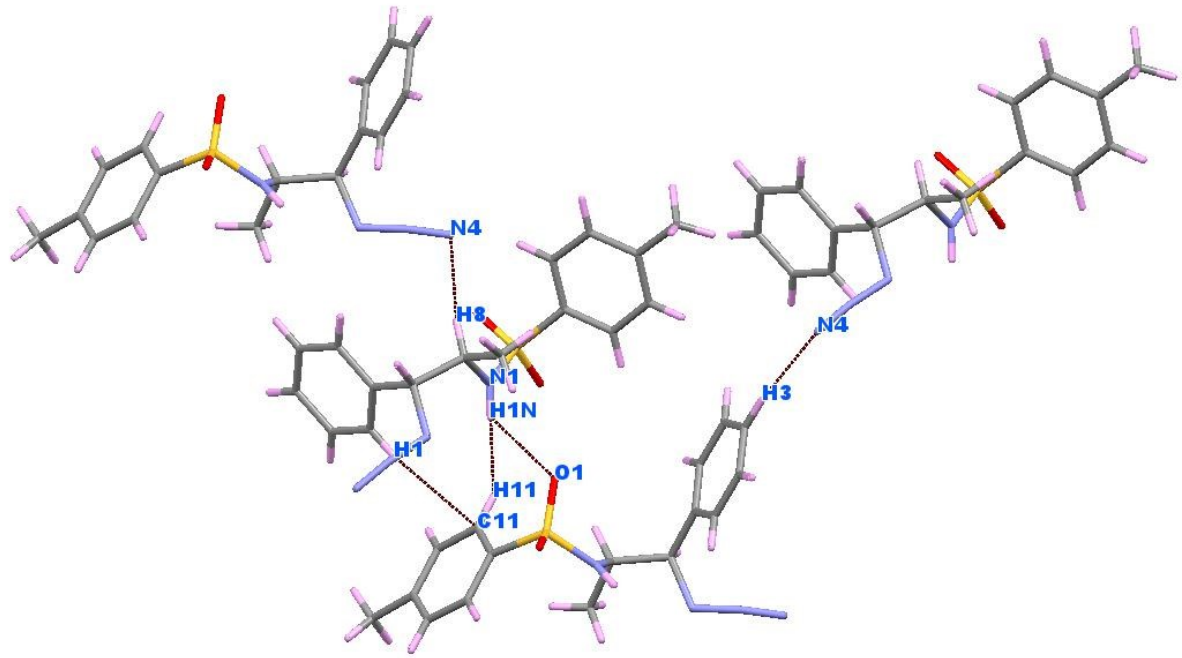


Table 1. Crystal data and structure refinement for compound 18a

Empirical formula	C16 H18 N4 O2 S
Formula weight	330.4
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 8.2251 (1) Å α= 90°. b = 10.3695 (1) Å β= 94.2510(7)°. c = 9.9358 (1) Å γ = 90°.
Volume	845.095(16) $Å^3$
Z	2
Density (calculated)	1.298 g/cc
Absorption coefficient	0.206 mm^{-1}
F(000)	348
Crystal size	0.34 x 0.32 x 0.16 mm^3
Theta range for data collection	2.84 to 24.99°.
Index ranges	-9<=h<=9, -11<=k<=12, -11<=l<=11
Reflections collected	6855
Independent reflections	2791 [R(int) = 0.0197]
Completeness to theta = 24.99°	99.40%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9682 and 0.9323
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2791 / 1 / 210
Goodness-of-fit on F2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0791
R indices (all data)	R1 = 0.0297, wR2 = 0.0800
Absolute structure parameter	0.04(6)
Largest diff. peak and hole	0.210 and -0.265 e.$Å^{-3}$

Table 2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters ($Å^2$x 103) for 0m. (compound 18 a)U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	10635(1)	2529(1)	131(1)	44(1)
O(1)	10194(2)	3747(1)	-450(1)	58(1)
O(2)	11974(2)	1832(2)	-340(2)	67(1)
N(1)	9067(2)	1588(1)	-91(1)	43(1)
N(2)	5966(3)	262(2)	-689(2)	69(1)
N(3)	4845(3)	-98(2)	-1471(2)	78(1)
N(4)	3858(4)	-547(4)	-2171(3)	121(1)
C(1)	6935(3)	1634(3)	-3031(2)	66(1)
C(2)	6967(3)	2174(3)	-4287(3)	83(1)
C(3)	6273(4)	3373(4)	-4537(3)	92(1)
C(4)	5599(4)	4028(3)	-3527(3)	85(1)
C(5)	5573(3)	3486(2)	-2269(2)	66(1)
C(6)	6224(2)	2278(2)	-2011(2)	45(1)
C(7)	6092(2)	1694(2)	-641(2)	47(1)
C(8)	7506(2)	1998(2)	390(2)	43(1)
C(9)	7214(3)	1401(2)	1762(2)	61(1)
C(10)	10963(2)	2760(2)	1890(2)	48(1)
C(11)	10278(3)	3802(2)	2494(2)	58(1)
C(12)	10400(3)	3884(3)	3896(2)	73(1)
C(13)	11181(3)	2958(3)	4690(2)	75(1)
C(14)	11882(4)	1949(4)	4055(3)	90(1)
C(15)	11775(3)	1827(3)	2659(2)	72(1)
C(16)	11252(4)	3038(5)	6212(3)	117(1)

Table 3. Bond lengths [Å] and angles [°] for compound 18a.

S(1)-O(1)	1.4245(15)
S(1)-O(2)	1.4250(15)
S(1)-N(1)	1.6195(15)
S(1)-C(10)	1.7644(18)
N(1)-C(8)	1.466(2)
N(1)-H(1N)	0.86
N(2)-N(3)	1.219(3)
N(2)-C(7)	1.489(3)
N(3)-N(4)	1.129(3)
C(1)-C(2)	1.370(3)
C(1)-C(6)	1.380(3)
C(1)-H(1)	0.93
C(2)-C(3)	1.383(5)
C(2)-H(2)	0.93
C(3)-C(4)	1.363(5)
C(3)-H(3)	0.93
C(4)-C(5)	1.373(4)
C(4)-H(4)	0.93
C(5)-C(6)	1.378(3)
C(5)-H(5)	0.93
C(6)-C(7)	1.501(3)
C(7)-C(8)	1.525(2)
C(7)-H(7)	0.98
C(8)-C(9)	1.532(3)
C(8)-H(8)	0.98
C(9)-H(9A)	0.96
C(9)-H(9B)	0.96
C(9)-H(9C)	0.96
C(10)-C(15)	1.375(3)
C(10)-C(11)	1.377(3)
C(11)-C(12)	1.392(3)
C(11)-H(11)	0.93
C(12)-C(13)	1.372(4)
C(12)-H(12)	0.93
C(13)-C(14)	1.370(4)
C(13)-C(16)	1.512(3)
C(14)-C(15)	1.389(4)
C(14)-H(14)	0.93
C(15)-H(15)	0.93

C(16)-H(16A)	0.96
C(16)-H(16B)	0.96
C(16)-H(16C)	0.96
O(1)-S(1)-O(2)	119.77(10)
O(1)-S(1)-N(1)	107.64(8)
O(2)-S(1)-N(1)	106.03(9)
O(1)-S(1)-C(10)	107.26(9)
O(2)-S(1)-C(10)	109.20(9)
N(1)-S(1)-C(10)	106.19(8)
C(8)-N(1)-S(1)	119.22(12)
C(8)-N(1)-H(1N)	120.4
S(1)-N(1)-H(1N)	120.4
N(3)-N(2)-C(7)	112.0(2)
N(4)-N(3)-N(2)	173.5(3)
C(2)-C(1)-C(6)	120.6(2)
C(2)-C(1)-H(1)	119.7
C(6)-C(1)-H(1)	119.7
C(1)-C(2)-C(3)	119.7(3)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	120.0(2)
C(4)-C(3)-H(3)	120
C(2)-C(3)-H(3)	120
C(3)-C(4)-C(5)	120.1(3)
C(3)-C(4)-H(4)	120
C(5)-C(4)-H(4)	120
C(4)-C(5)-C(6)	120.6(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	118.9(2)
C(5)-C(6)-C(7)	118.80(17)
C(1)-C(6)-C(7)	122.24(19)
N(2)-C(7)-C(6)	112.52(16)
N(2)-C(7)-C(8)	106.00(16)
C(6)-C(7)-C(8)	115.04(14)
N(2)-C(7)-H(7)	107.7
C(6)-C(7)-H(7)	107.7
C(8)-C(7)-H(7)	107.7

N(1)-C(8)-C(7)	111.30(14)
N(1)-C(8)-C(9)	111.83(16)
C(7)-C(8)-C(9)	110.62(15)
N(1)-C(8)-H(8)	107.6
C(7)-C(8)-H(8)	107.6
C(9)-C(8)-H(8)	107.6
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(15)-C(10)-C(11)	120.51(19)
C(15)-C(10)-S(1)	119.15(17)
C(11)-C(10)-S(1)	120.05(16)
C(10)-C(11)-C(12)	118.9(2)
C(10)-C(11)-H(11)	120.6
C(12)-C(11)-H(11)	120.6

C(13)-C(12)-C(11)	121.9(2)
C(13)-C(12)-H(12)	119
C(11)-C(12)-H(12)	119
C(14)-C(13)-C(12)	117.7(2)
C(14)-C(13)-C(16)	121.1(3)
C(12)-C(13)-C(16)	121.2(3)
C(13)-C(14)-C(15)	122.1(3)
C(13)-C(14)-H(14)	118.9
C(15)-C(14)-H(14)	118.9
C(10)-C(15)-C(14)	118.9(3)
C(10)-C(15)-H(15)	120.6
C(14)-C(15)-H(15)	120.6
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for aakd2(compound 18a) .The anisotropic displacement factor exponent takes the form: $-2\alpha^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
S(1)	38(1)	54(1)	41(1)	-2(1)	4(1)	-5(1)
O(1)	66(1)	54(1)	52(1)	6(1)	1(1)	-16(1)
O(2)	44(1)	99(1)	59(1)	-8(1)	12(1)	5(1)
N(1)	42(1)	41(1)	44(1)	-8(1)	2(1)	-2(1)
N(2)	87(1)	56(1)	60(1)	5(1)	-13(1)	-25(1)
N(3)	104(2)	82(2)	48(1)	-3(1)	3(1)	-51(1)
N(4)	138(2)	152(3)	72(1)	-16(2)	1(2)	-88(2)
C(1)	67(1)	74(1)	56(1)	0(1)	13(1)	8(1)
C(2)	85(2)	118(3)	49(1)	-1(1)	20(1)	-8(2)
C(3)	88(2)	135(3)	53(1)	34(2)	-5(1)	-22(2)
C(4)	86(2)	84(2)	82(2)	34(1)	-7(1)	11(1)
C(5)	69(1)	66(1)	61(1)	9(1)	2(1)	13(1)
C(6)	36(1)	55(1)	43(1)	-1(1)	1(1)	-2(1)
C(7)	40(1)	52(1)	49(1)	0(1)	4(1)	-6(1)
C(8)	42(1)	45(1)	42(1)	-2(1)	5(1)	-5(1)
C(9)	63(1)	78(1)	41(1)	2(1)	6(1)	-19(1)
C(10)	38(1)	63(1)	44(1)	-4(1)	0(1)	-12(1)
C(11)	63(1)	58(1)	53(1)	-6(1)	8(1)	-14(1)
C(12)	81(2)	79(2)	62(1)	-23(1)	20(1)	-27(1)
C(13)	63(1)	115(2)	46(1)	-8(1)	0(1)	-34(1)
C(14)	75(2)	134(3)	57(1)	10(2)	-15(1)	6(2)
C(15)	66(1)	95(2)	52(1)	4(1)	-6(1)	17(1)
C(16)	107(2)	193(4)	49(1)	-13(2)	-1(1)	-46(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for aakd2(compound 18a).

	x	y	z	U(eq)
H(1N)	9149	855	-487	51
H(1)	7397	825	-2864	79
H(2)	7454	1737	-4969	100
H(3)	6265	3733	-5395	111
H(4)	5156	4843	-3691	101
H(5)	5113	3938	-1583	79
H(7)	5093	2026	-286	56
H(8)	7548	2936	507	52
H(9A)	7281	478	1702	91
H(9B)	6151	1641	2015	91
H(9C)	8026	1708	2430	91
H(11)	9742	4440	1974	70
H(12)	9940	4587	4307	88
H(14)	12447	1326	4575	108
H(15)	12245	1126	2251	86
H(16A)	11253	3927	6484	175
H(16B)	12229	2628	6588	175
H(16C)	10319	2612	6532	175

Table 6.Torsion angles [°] for compound 18a.

O(1)-S(1)-N(1)-C(8)	-55.10(15)
O(2)-S(1)-N(1)-C(8)	175.60(13)
C(10)-S(1)-N(1)-C(8)	59.52(15)
C(7)-N(2)-N(3)-N(4)	174(2)
C(6)-C(1)-C(2)-C(3)	-0.3(4)
C(1)-C(2)-C(3)-C(4)	1.8(4)
C(2)-C(3)-C(4)-C(5)	-1.6(5)
C(3)-C(4)-C(5)-C(6)	-0.1(4)
C(4)-C(5)-C(6)-C(1)	1.5(3)
C(4)-C(5)-C(6)-C(7)	-176.9(2)
C(2)-C(1)-C(6)-C(5)	-1.3(3)
C(2)-C(1)-C(6)-C(7)	177.0(2)
N(3)-N(2)-C(7)-C(6)	-54.7(2)
N(3)-N(2)-C(7)-C(8)	178.74(18)
C(5)-C(6)-C(7)-N(2)	148.54(19)
C(1)-C(6)-C(7)-N(2)	-29.7(3)
C(5)-C(6)-C(7)-C(8)	-89.9(2)
C(1)-C(6)-C(7)-C(8)	91.8(2)
S(1)-N(1)-C(8)-C(7)	137.43(13)
S(1)-N(1)-C(8)-C(9)	-98.28(17)
N(2)-C(7)-C(8)-N(1)	67.74(18)
C(6)-C(7)-C(8)-N(1)	-57.3(2)
N(2)-C(7)-C(8)-C(9)	-57.2(2)
C(6)-C(7)-C(8)-C(9)	177.75(17)
O(1)-S(1)-C(10)-C(15)	-164.41(17)
O(2)-S(1)-C(10)-C(15)	-33.2(2)
N(1)-S(1)-C(10)-C(15)	80.72(18)
O(1)-S(1)-C(10)-C(11)	21.75(17)
O(2)-S(1)-C(10)-C(11)	152.95(16)
N(1)-S(1)-C(10)-C(11)	-93.13(16)
C(15)-C(10)-C(11)-C(12)	-0.9(3)
S(1)-C(10)-C(11)-C(12)	172.82(16)
C(10)-C(11)-C(12)-C(13)	-0.1(3)
C(11)-C(12)-C(13)-C(14)	1.6(4)
C(11)-C(12)-C(13)-C(16)	-177.8(2)
C(12)-C(13)-C(14)-C(15)	-2.1(4)
C(16)-C(13)-C(14)-C(15)	177.3(3)
C(11)-C(10)-C(15)-C(14)	0.5(3)
S(1)-C(10)-C(15)-C(14)	-173.4(2)
C(13)-C(14)-C(15)-C(10)	1.1(4)

6 Analytical methods for alcohols using Chiral HPLC.

The enantiomeric excess of all the chiral alcohols were determined on HPLC or GC using chiral columns. For this, racemic alcohols were obtained by reductions of all the ketone with $NaBH_4$ using standard procedure. Using GC/HPLC and chiral columns from Daicel, these alcohols were separated such that two distinct peaks of both the isomers are obtained with 50% (equal) areas .The analytical methods used were based on literature reports for all the alcohols which were obtained as products. The conditions for GC/HPLC to get chiral separation along with retention times of isomers of particular alcohol are given below.

Column : Chiralpak IB, 250X 4.6, 5u

Conditions for Acetophenone, R and S phenethanol: HPLC, λ-216 nm, solvent Hexane: IPA 92:8, Flow-0.8ml, Injection volume- 2µl., acetophenone 5.7 min6.4 min (R), 7.0 min (S) alcohol,

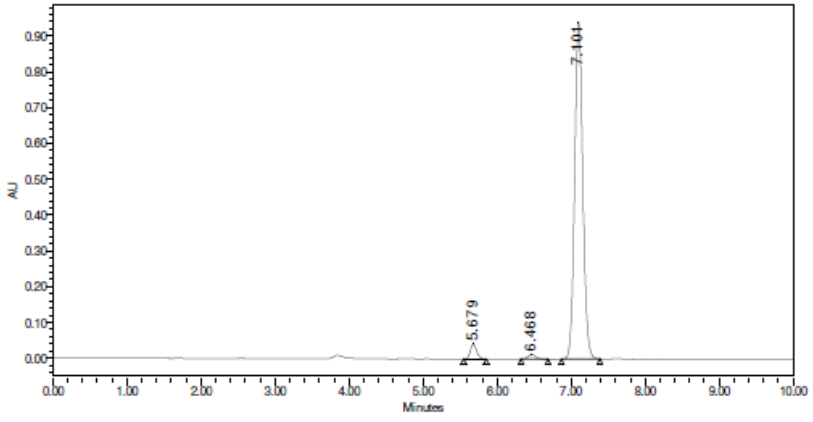
1. Acetophenone, R and S phenethanol HPLC, λ-216 nm, solvent Hexane: IPA 92:8, Flow-0.8ml, Injection volume- 2µl., acetophenone 5.7 min 6.5 min (R), 7.10 min (S) alcohol**,**

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	RHSL1460MINS	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	10042013
Vial:	1:F,7	Acq. Method Set:	ACPR
Injection #:	1	Processing Method	chiral
Injection Volume:	2.00 ul	Channel Name:	216.0nm
Run Time:	10.0 Minutes	Proc. Chnl. Descr.:	PDA 216.0 nm
Date Acquired:	4/13/2013 4:27:12 PM IST	Column Name:	
Date Processed:	4/15/2013 11:15:28 AM IST		



	RT	Area	% Area	Height
1	5.679	245993	3.28	41291
2	6.468	87552	1.17	12791
3	7.101	7160396	95.55	941181

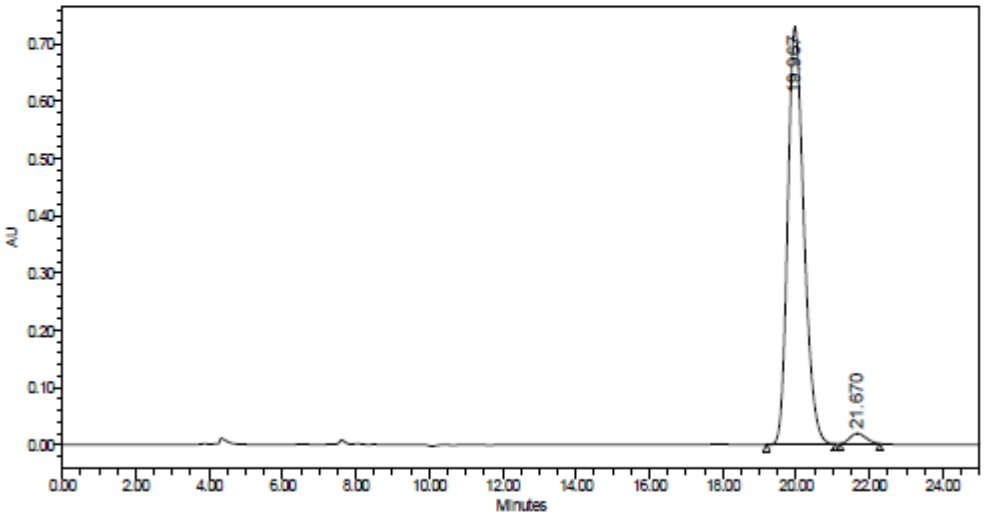
2. 1-p-Bromophenylethanol-HPLC, λ-220 nm, solvent Hexane: IPA 98:2, Flow-0.8ml, Injection volume- 1µl. 19.97 min (isomer 1), 21.7 min (isomer 2)

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	pbap	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	170712
Vial:	2:E,4	Acq. Method Set:	ACP
Injection #:	1	Processing Method	chiral
Injection Volume:	1.00 ul	Channel Name:	220.0nm
Run Time:	25.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	7/17/2012 6:26:47 PM IST		
Date Processed:	7/17/2012 7:14:59 PM IST		



	RT	Area	% Area	Height
1	19.967	22332660	97.65	728154
2	21.670	536828	2.35	17895

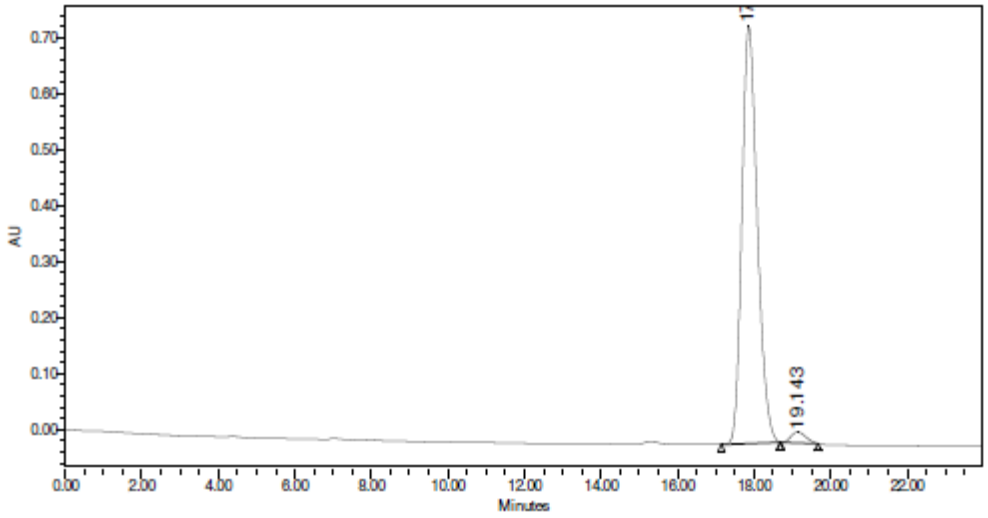
3. 1-p-Chlorophenylethanol-HPLC, λ-220 nm, solvent Hexane: IPA 98:2, Flow-0.8 ml, Injection volume- 2µl. 17.9 min(isomer 1), 19.2 min (isomer 2).

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	pcalcohol	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	230712s
Vial:	2:f,4	Acq. Method Set:	ACP
Injection #:	1	Processing Method	chiral2
Injection Volume:	2.00 ul	Channel Name:	220.0nm
Run Time:	25.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	7/23/2012 5:07:43 PM IST		
Date Processed:	7/25/2012 2:40:14 PM IST		



	RT	Area	% Area	Height
1	17.860	20914538	97.52	745090
2	19.143	532812	2.48	19821

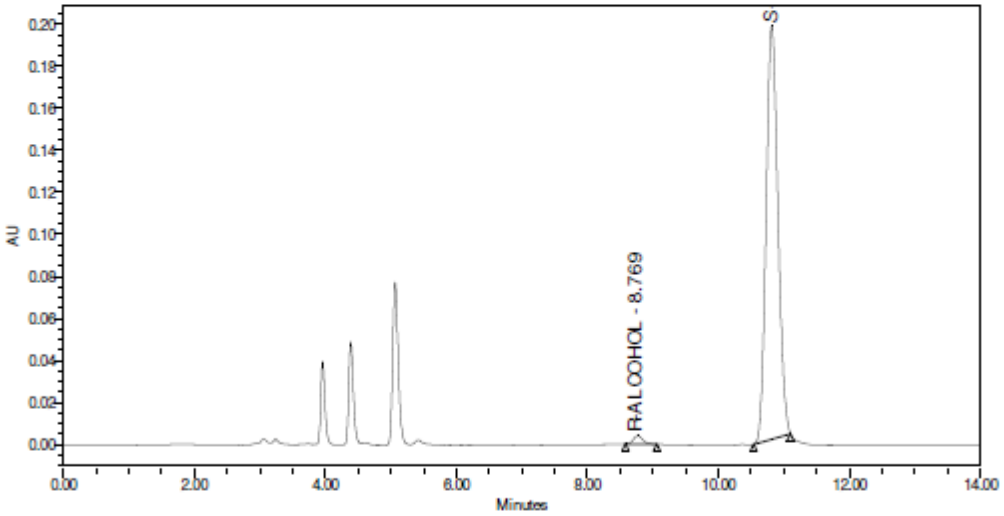
4. 1-p-methylphenylethanol- - HPLC, λ-220 nm, solvent Hexane: IPA 95:5, Flow-0.8 ml, Injection volume- 2µl. 8.8 min (isomer 1), 10.8 min (isomer2).

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	MEAP 120MINS	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	210712S
Vial:	2:E,4	Acq. Method Set:	ACP
Injection #:	1	Processing Method	METHLPHENETHANOL
Injection Volume:	2.00 ul	Channel Name:	220.0nm
Run Time:	14.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	7/21/2012 2:54:54 PM IST		
Date Processed:	7/21/2012 3:42:25 PM IST		



	Peak Name	RT	Area	% Area	Height
1	R-ALCOHOL	8.769	39501	1.58	3986
2	S-ALCOHOL	10.814	2462631	98.42	196458

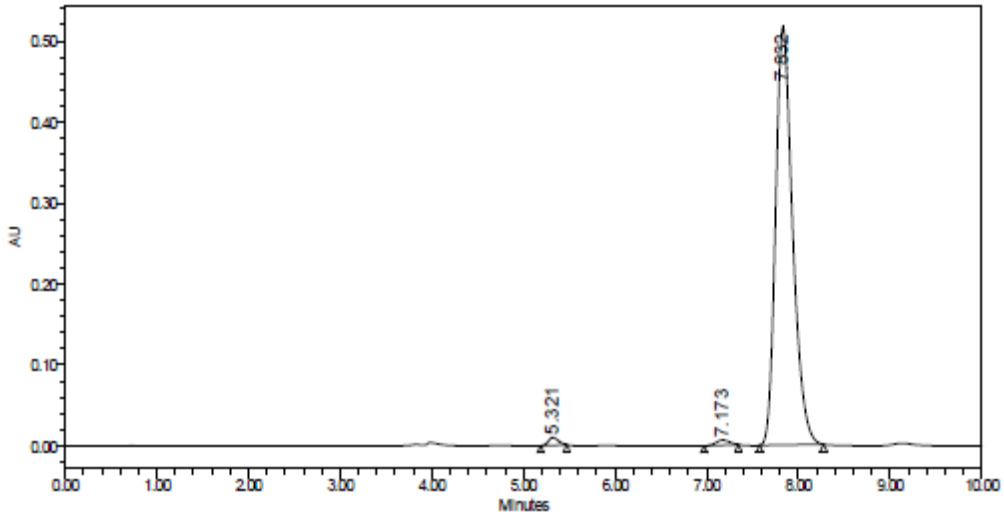
5. 1-p-Isobutylphenylethanol-HPLC λ-220 nm, solvent Hexane: IPA 98:2, Flow-0.8 ml, Injection volume- 2µl. 7.2 min (isomer 1), 7.8 min (isomer 2)

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	ibap210mins	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	140712
Vial:	2:E,6	Acq. Method Set:	ibap
Injection #:	1	Processing Method	ACP
Injection Volume:	2.00 ul	Channel Name:	220.0nm
Run Time:	10.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	7/14/2012 3:50:09 PM IST		
Date Processed:	7/14/2012 4:07:24 PM IST		



	RT	Area	% Area	Height
1	5.321	72069	1.06	9716
2	7.173	64413	0.95	6368
3	7.832	6669913	97.99	516593

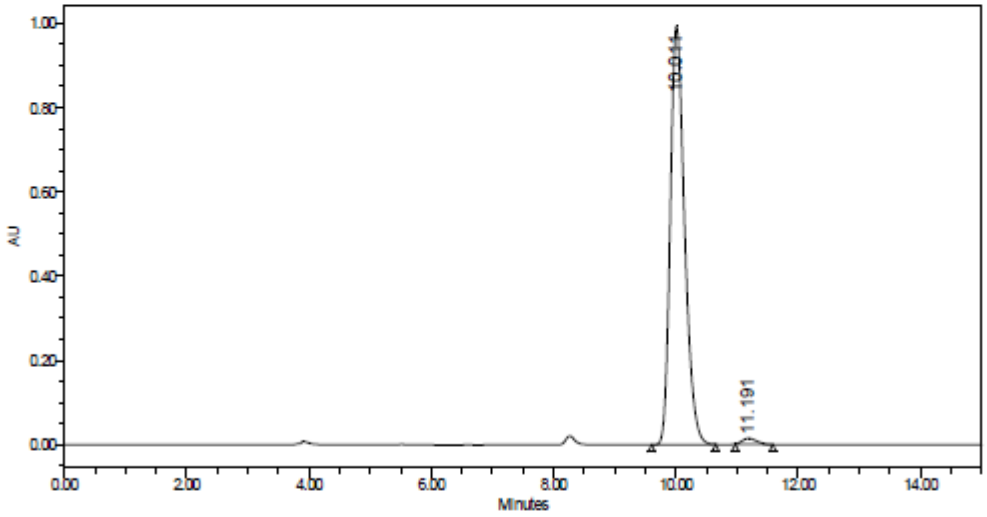
6. Indanone - HPLC, λ-215nm, solvent Hexane: IPA 95:5, Flow-1ml, Injection volume- 2µl. 10.0 min (isomer1), 11.2 min (isomer 2)

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	indanone120mins	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	120712s
Vial:	2:F,8	Acq. Method Set:	indanol
Injection #:	1	Processing Method	chiral
Injection Volume:	2.00 ul	Channel Name:	215.0nm
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	PDA 215.0 nm
Date Acquired:	7/12/2012 6:55:52 PM IST		
Date Processed:	7/12/2012 7:18:37 PM IST		



	RT	Area	% Area	Height
1	10.011	16109524	98.62	992232
2	11.191	225056	1.38	13842

7. 1-p-Methoxyphenylethanol-HPLC, λ-220 nm, solvent Hexane: IPA 98:2, Flow-0.8ml, Injection volume- 2µl. 34.9 min (R), 37.0 min (S) alcohol.

8 Tetralone - HPLC, λ-215nm, solvent Hexane: IPA 95:5, Flow-1ml, Injection volume- 2µl. 10.8 min (isomer1), 11.4 min (isomer 2)

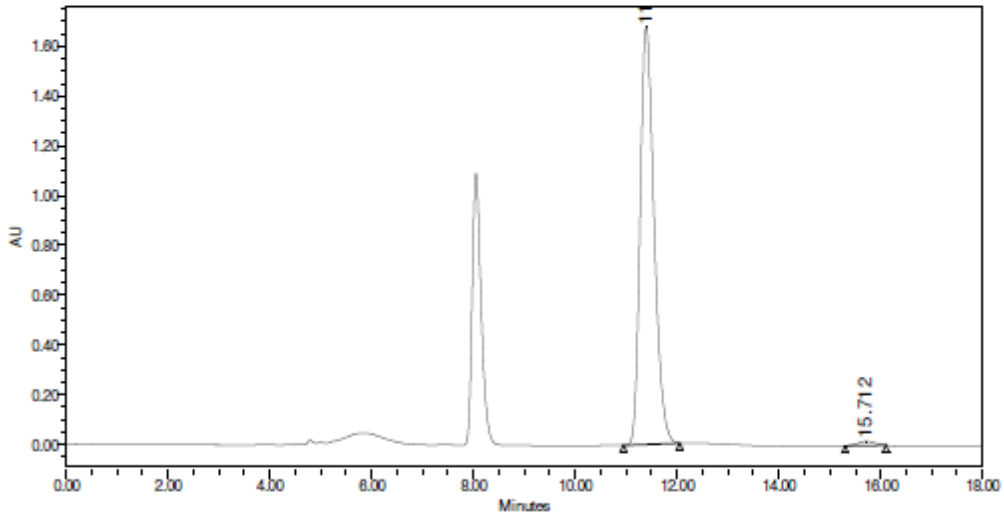
8. 1-(6-Methoxynaphthalen-2-yl) ethanol- HPLC, λ-235 nm, solvent Hexane: IPA 90:10, Flow-0.5ml, Injection volume- 1µl. 11.4 min (isomer 1), 15.7 min (isomer 2).

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	mnafinal	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	240712
Vial:	1:F,7	Acq. Method Set:	ACP
Injection #:	1	Processing Method	ACP
Injection Volume:	1.00 ul	Channel Name:	235.0nm
Run Time:	18.0 Minutes	Proc. Chnl. Descr.:	PDA 235.0 nm
Date Acquired:	7/24/2012 9:43:40 AM IST		
Date Processed:	7/24/2012 2:00:17 PM IST		



	RT	Area	% Area	Height
1	11.391	31782504	98.80	1675966
2	15.712	386820	1.20	16830

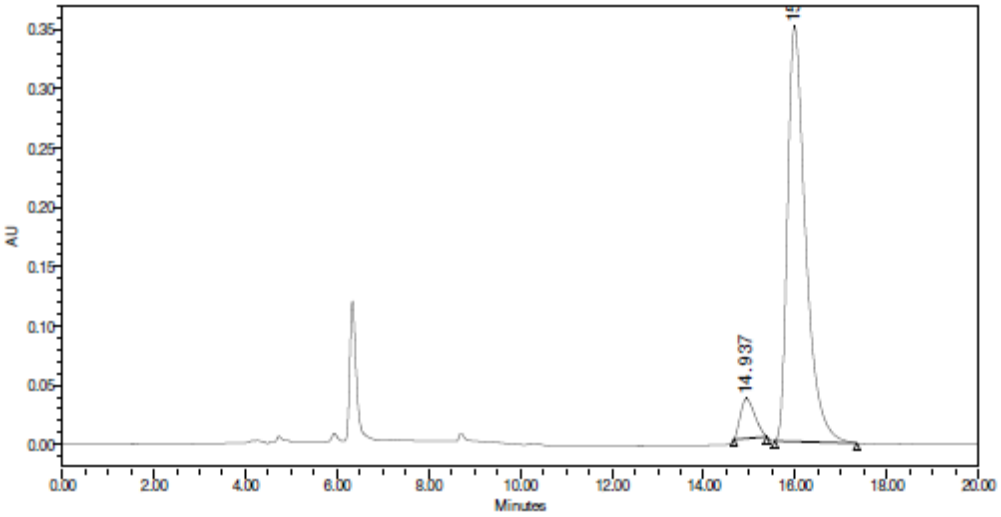
9.1-(pyridin-3-yl) ethanol- - HPLC, λ-260 nm, solvent Hexane: IPA 90:100.1 DEA, Flow-1ml, Injection volume- 2µl. 15.0 min (isomer1), 16.0 min (isomer 2).

Empower 3

LC Default Individual Report

SAMPLE INFORMATION

Sample Name:	acetylpyridine	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	240712s
Vial:	1:E,5	Acq. Method Set:	ACETYLPYRIDINE
Injection #:	1	Processing Method	chiral2
Injection Volume:	2.00 ul	Channel Name:	260.0nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	7/24/2012 4:49:51 PM IST		
Date Processed:	7/25/2012 2:28:00 PM IST		



	RT	Area	% Area	Height
1	14.937	733407	7.10	33556
2	15.986	9590829	92.90	349913

7 References

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