

# Synthesis of Chiral Allylic Esters by Using the New Recyclable Chiral Heterogeneous Oxazoline-Based Catalysts

Saadi Samadi\*, Akram Ashouri, and Mojgan Samadi

Laboratory of Asymmetric Synthesis, Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj 66177-15175, Iran. Phone: (+9887) 33624133; Email: s.samadi@uok.ac.ir.

## Supporting Information

Page	List of contents	Page	List of contents
S1	Title, author's name, address	S23	Figure S17: <sup>1</sup> HNMR of 7b
S2-S6	Experimental section	S24	Figure S18: <sup>13</sup> CNMR of 7b
S7	Figure S1: <sup>1</sup> HNMR of 2a	S25	Figure S19: <sup>1</sup> HNMR of 8a
S8	Figure S2: <sup>13</sup> CNMR of 2a	S26	Figure S20: <sup>13</sup> CNMR of 8a
S9	Figure S3: <sup>1</sup> HNMR of 2b	S27	Figure S21: <sup>1</sup> HNMR of 8b
S10	Figure S4: <sup>13</sup> CNMR of 2b	S28	Figure S22: <sup>13</sup> CNMR of 8b
S11	Figure S5: <sup>1</sup> HNMR of 2c	S29	Figure S23: <sup>1</sup> HNMR of 8f
S12	Figure S6: <sup>13</sup> CNMR of 2c	S30	Figure S24: <sup>13</sup> CNMR of 8f
S13	Figure S7: <sup>1</sup> HNMR of 2d	S31	Figure S25: <sup>1</sup> HNMR of 9b
S14	Figure S8: <sup>13</sup> CNMR of 2d	S32	Figure S26: <sup>13</sup> CNMR of 9b
S15	Figure S9: <sup>1</sup> HNMR of 3a	S33	Figure S27: <sup>1</sup> H NMR of 10b
S16	Figure S10: <sup>13</sup> CNMR of 3a	S34	Figure S28: <sup>13</sup> C NMR of 10b
S17	Figure S11: <sup>1</sup> HNMR of 3b	S35	Figure S29: <sup>1</sup> HNMR of 11b
S18	Figure S12: <sup>13</sup> CNMR of 3b	S36	Figure S30: <sup>13</sup> C NMR of 11b
S19	Figure S13: <sup>1</sup> HNMR of 3c	S37	Figure S31: Chromatogram of 8a
S20	Figure S14: <sup>13</sup> CNMR of 3c	S38	Figure S32: Chromatogram of 8b
S21	Figure S15: <sup>1</sup> HNMR of 3d	S39	References
S22	Figure S16: <sup>13</sup> CNMR of 3d		

## Experimental

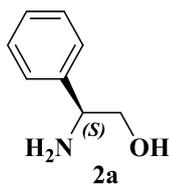
### Materials and characterization methods

Melting points were measured on an Electrothermal 9100 apparatus and were uncorrected. Fourier transform infrared (FT-IR) spectrum of SBA-15 was monitored by Bruker. Vector 22 spectrometer with potassium bromide plate.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13, 400.22 MHz and 75 MHz, 100 MHz in  $\text{CDCl}_3$  using TMS ( $\delta = 0.0$  ppm) an internal standard. X-ray diffraction (XRD) was performed on a Bruker D8 Advance powder diffractometer with Ni filtered CuK $\alpha$  radiation ( $\lambda = 1.54056$  Å). The morphology of nanoporous was investigated by a scanning electron microscope (FESEM-TESCAN MIRA3). TGA–DTA analysis was carried out from 0 to 800°C at a heating rate of 10 °C/min using a STA PT-1000 LINSEIS. Optical rotations were measured with a Perkin–Elmer 341 polarimeter at 589 nm. Enantiomeric excess (ee) of the products were determined by HPLC on chiralpak AD and/or chiralcel OD-H and/or Nucleocel Alpha S columns. All reactions were performed under an atmosphere of dry and oxygen-free nitrogen. All reagents and starting materials were purchased from Aldrich, Merck, Fluka and Sigma. Olefins were distilled from calcium hydride before use. All solvents for the reactions were reagent grade and were dried and distilled immediately before use as follows: acetonitrile and acetone from  $\text{P}_2\text{O}_5$ , methylene chloride from calcium hydride, methanol from Mg and  $\text{I}_2$ , toluene and tetrahydrofuran from sodium and benzophenone. Column chromatography was performed using silica gel 60 (0.063-0.2 mm) eluting with ethyl acetate and *n*-hexane. Thin-layer chromatography (TLC) was performed using silica gel 60 F<sub>256</sub> plates with visualization by UV.

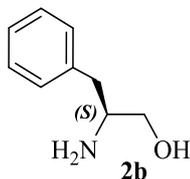
### A typical procedure for the synthesis of chiral amino alcohols 2a–d:

To an oven-dried 3-neck 250 mL round-bottom flask equipped with reflux condenser, sodium borohydride (40.0 mmol, 1.51 g) and 20 mL of dried tetrahydrofuran were added. After 15 minutes, (*S*)-phenylalanine **1b** (16.6 mmol, 2.75 g) was added in one portion to the stirring solution. Then the resulting mixture was cooled to 0 °C, and  $\text{I}_2$  (16.5 mmol, 4.27 g) in 10 mL of tetrahydrofuran was added dropwise by the addition funnel over 30 minutes. After fading

away the brownish color of solution, the mixture was warmed to room temperature and then the white cloudy solution refluxed for 48 hours. After cooling to room temperature, to the cloudy white suspension with fast stirring, 10 mL of CH<sub>3</sub>OH was added dropwise by addition funnel and gas evolution observed. The resulting solution was concentrated, and the obtained residue dissolved in 10 mL of KOH (20%) and then stirred for 4 hours at room temperature. The obtained solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL), the organic layer washed with brine, and then the aqueous layer back extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and concentrated. The white solid **2b** was afforded in 95% yield. Other chiral products **2a**, **2c**, and **2d** were also synthesized from the corresponding amino acids in the similar procedure in a good yields up to 98% <sup>1</sup> (Figures S1-8).



**(S)-2-amino-2-phenylethan-1-ol (2a):** Mp: 75-78°C.; FT-IR (KBr, cm<sup>-1</sup>): 3274, 3062, 2922, 1598, 1489, 1045.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm) = 2.53 (1H, brs, (OH)), 2.75 (2H, brs, (NH<sub>2</sub>)), 3.57 (1H, t, *J* = 9.6 Hz, CH<sub>2</sub>), 3.69 (1H, t, *J* = 8.6 Hz, CH<sub>2</sub>), 4.04-4.05 (1H, m, CH), 7.30-7.37 (5H, m, Ar).; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> (ppm) = 57.4, 67.8, 126.6, 127.4, 127.5, 128.6, 128.8, 142.3.; [α]<sub>D</sub><sup>25</sup> = + 30.5° (*c* = 0.6, HCl (1 M)).

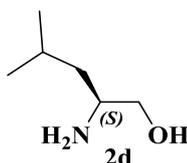


**(S)-2-amino-3-phenylpropan-1-ol (2b):** Mp: 90-92°C.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm) = 2.19 (3H, brs, (NH<sub>2</sub>, OH)), 2.57 (1H, dd, *J* = 12.8, 9.0 Hz, CH<sub>2</sub>), 2.81 (1H, dd, *J* = 12.0, 8.6 Hz, CH<sub>2</sub>), 3.16 (1H, brs, \*CH), 3.44 (1H, d, *J* = 7.6 Hz, H<sub>2</sub>C-OH), 3.67 (1H, d, *J* = 6.8 Hz, H<sub>2</sub>C-

OH), 7.21-7.35 (5H, m, Ar).;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 40.8, 54.2, 66.3, 126.4, 128.6, 129.2, 138.6.;  $[\alpha]_{\text{D}}^{25} = -10.7^\circ$  ( $c = 0.4$ , HCl (1 M)).



**(S)-2-amino-3-methylbutan-1-ol (2c):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 0.92 (6 H, d,  $J = 6.8$  Hz,  $\text{CH}_3$ ), 1.67-1.69 (1 H, m, CH), 2.66-2.73 (1 H, m,  $^*\text{CH}$ ), 3.41-3.42 (1 H, m,  $-\text{CH}_2\text{-OH}$ ), 3.59-3.62 (1 H, m,  $\text{H}_2\text{C-OH}$ ). 4.12 (2 H, brs, ( $\text{NH}_2$ )).;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 19.8, 31.9, 56.6, 64.7.;  $[\alpha]_{\text{D}}^{25} = +3.3^\circ$  ( $c = 0.6$ , EtOH).



**(S)-2-amino-4-methylpentan-1-ol (2d):** Mp: 69-73°C.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 0.94 (6H, d,  $J = 6.8$  Hz,  $\text{CH}_3$ ), 1.24 (2H, brs,  $\text{CH}_2$ ), 1.67-1.75 (1H, m, CH), 2.84 (2H, brs ( $\text{NH}_2$ )), 2.97 (1H, brs,  $^*\text{CH}$ ), 3.29 (1H, t,  $J = 9.0$  Hz,  $\text{H}_2\text{C-OH}$ ), 3.62 (1H, d,  $J = 8.8$  Hz,  $\text{H}_2\text{C-OH}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 22.2, 23.3, 24.7, 43.5, 50.7, 66.9.;  $[\alpha]_{\text{D}}^{25} = +1.3^\circ$  ( $c = 0.5$ , EtOH).

### A typical procedure for the synthesis of Mesoporous silica SBA-15

Mesoporous silica SBA-15 was synthesized according to the described method in the literature <sup>2,3</sup>. In a round bottom flask (250 mL), 6.0 g of Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) as a surfactant was dissolved in deionized water (137 mL) and 30 mL of HCl (37%) at room temperature. After complete copolymer dissolution (0.5-1 hour), 13.7 g of tetraethyl orthosilicate (TEOS) in deionized water (50 mL) was added, and stirred vigorously at 40 °C for 30 minutes. Then the resulting mixture was transferred into a stainless steel jacketed Teflon vessel and heated at 100°C for 48 hours. After cooling to room temperature, the solid product was separated from the mixture of reaction by filtration and then washed by deionized water until pH=7-8 was achieved. Finally the obtained powder was dried at 60 °C, and then calcined

at 550 °C for 5 hours. The mesoporous structure of SBA-15 was characterized by FT-IR, XRD, SEM and BET-BJH techniques.

#### **A typical procedure for the synthesis of functionalized SBA-15 (Cl-SBA-15)**

Functionalization of SBA-15 was carried out as reported in the literature<sup>2, 3 4</sup>. Briefly, 1.0 g of SBA-15 in dried toluene (30 mL) dispersed and, then 3-chloropropyltrimethoxysilane (CPTMS) (4.2 mmol, 0.91 mL) was added. After refluxing the mixture of reaction under nitrogen atmosphere for 24 hours, the modified nonoporous was collected by filtration and washed thoroughly with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH. Then the obtained powder was soxhleted for 24 hours with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1:1) to remove unreacted 3-chloropropyltriethoxysilane. Finally the functionalized SBA-15 was separated as a white solid and dried at room temperature. The synthesis of functionalized SBA-15 (Cl-SBA-15) was proved by FT-IR, TGA, XRD, SEM and BET-BJH techniques.

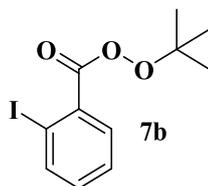
#### **A typical procedure for the Synthesis of benzoyl chloride derivatives 6a-g:**

To a round bottom flask under the nitrogen atmosphere, *o*-iodo-benzoic acids **5b** (1.5 mmol, 0.37 g) and dried methylene chloride (5 mL) were added. After cooling to 0 °C, oxalyl chloride (3 mmol, 0.31 mL) and dimethylformamide (30 µL) were slowly added. The mixture was warmed up to room temperature and stirred for 8 hours (Scheme 1). After completion of the reaction, the solvent was removed on a rotary evaporator to provide the *o*-iodo-benzoyl chloride **6b** (0.4 g, quantitative). Other benzoyl chlorides derivatives **6a** and **6c-g** were also prepared from the corresponding benzoic acids in the similar procedure in good yields up to 99%<sup>4-8</sup>.

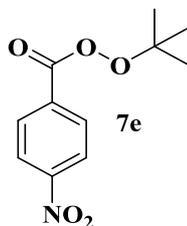
#### **A typical procedure for the Synthesis of *tert*-butyl benzoperoxoate derivatives 7a-g:**

In a 50 mL round bottom flask under the nitrogen atmosphere, *o*-iodo-benzoyl chloride **6b** (1.5 mmol, 0.4 g) was dissolved in dried methylene chloride (3 mL). After cooling to -20 °C, pyridine (1.7 mmol, 0.28 mL) and *tert*-butyl hydroperoxide (1.7 mmol, 0.12 mL) were slowly added and stirred for 4.5 hours at -20 °C (Scheme 1). After consumption of *o*-iodo-benzoyl chloride, the reaction solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> (40 mL) and washed with the saturated NaHCO<sub>3</sub> in the workup. The organic layer was evaporated and the obtained residue was purified by silica gel column chromatography (*n*-hexane: EtOAc; 95:5) to afford the *tert*-butyl-*o*-iodo benzoperoxoates **7b** (98% yield). Other *tert*-butyl benzoperoxoate derivatives **7a**

and **7c-g** were also prepared from the corresponding benzoyl chlorides derivatives in the similar procedure in good yields up to 96%<sup>4-8</sup> (Figures S17-18).



**Tert-butyl-2-iodobenzoperoxoate (7b)**: Mp: 47-49 °C.; FT-IR (KBr, cm<sup>-1</sup>): 2926, 1758, 466.; <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm) = 1.43 (9H, s, CH<sub>3</sub>), 7.20 (1H, t, *J* = 7.6 Hz, Ar), 7.42 (1H, t, *J* = 7.5 Hz, Ar), 7.59 (1H, d, *J* = 7.7 Hz, Ar), 7.97 (1H, d, *J* = 7.9 Hz, Ar).; <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> (ppm) = 26.2, 84.3, 93.3, 127.9, 130.3, 133.0, 134.3, 141.9, 165.2.; m/z (%): 320 (0.2, M), 248 (58), 194 (5), 122 (100), 74 (75).



**Tert-butyl-4-nitrobenzoperoxoate (7e)**: Mp: 76-78 °C (lit. 75-78 °C<sup>2,9</sup>); <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm) = 8.14-8.35 (4H, m, Ar), 1.45 (9H, s, CH<sub>3</sub>); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> (ppm) = 162.5, 150.7, 133.2, 130.3, 123.8, 84.7, 26.2.



Sample code: ph-gly2 (Dr.Samadi)



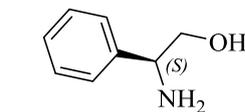
```
NAME Kurdestan_UN
EXPNO 489
PROCNO 1
Date_ 20181019
Time 10.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 2050
DW 14.000 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6478784 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.16 dB
PL13 17.90 dB
PL2W 11.86359406 W
PL12W 0.28722104 W
PL13W 0.12138934 W
SFO2 400.2216009 MHz
SI 32768
SF 100.6355990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
```

77.48  
77.16  
76.84  
70.65  
67.81  
66.65  
63.37  
62.39  
61.62  
57.41  
45.57  
26.51  
24.26  
22.02

142.34  
137.95  
128.83  
128.64  
128.44  
127.55  
127.36  
127.22  
126.62



ppm

Figure S2: <sup>13</sup>CNMR of 2a



NAME Kurdistan UN  
EXPNO 434  
PROCNO 1  
Time 20180901  
Time 11:56  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
DS 20  
SFO1 8012.820 Hz  
SF8H 0.142266 Hz  
FIDRES 4.0894966 sec  
AQ 101  
RG 62.400 usec  
DE 26.50 usec  
TE 300.6 K  
D1 4.00000001 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
PI 14.00 usec  
PL 2.00 dB  
PL1 11.863270 dB  
PL2 22.00 dB  
SFO1 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

Sample code:P-A (Dr.Samadi)

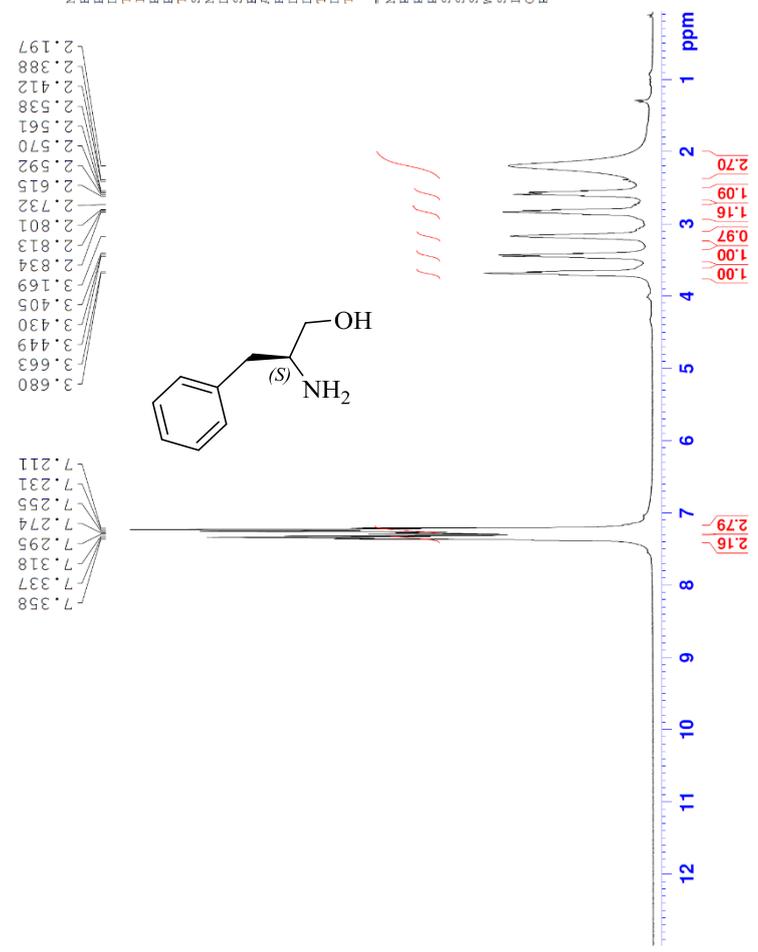


Figure S3: <sup>1</sup>H NMR of 2b



```

NAME Kurdestan_UN
EXPNO 446
PROCNO 1
Date_ 20180910
Time 12.09
INSTRUM spect
PROBHD 5 mm PABBO-BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 804
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 327.5
DM 14.000 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6479784 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 90.00 usec
PCPD2 -2.00 dB
PL2 14.16 dB
PL12 17.90 dB
PL13 11.86359406 W
PL2W 0.13138934 W
PL1W 0.13138934 W
SFO2 400.2216009 MHz
SI 32768
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
  
```

Sample code:P-A (Dr.Samadi)

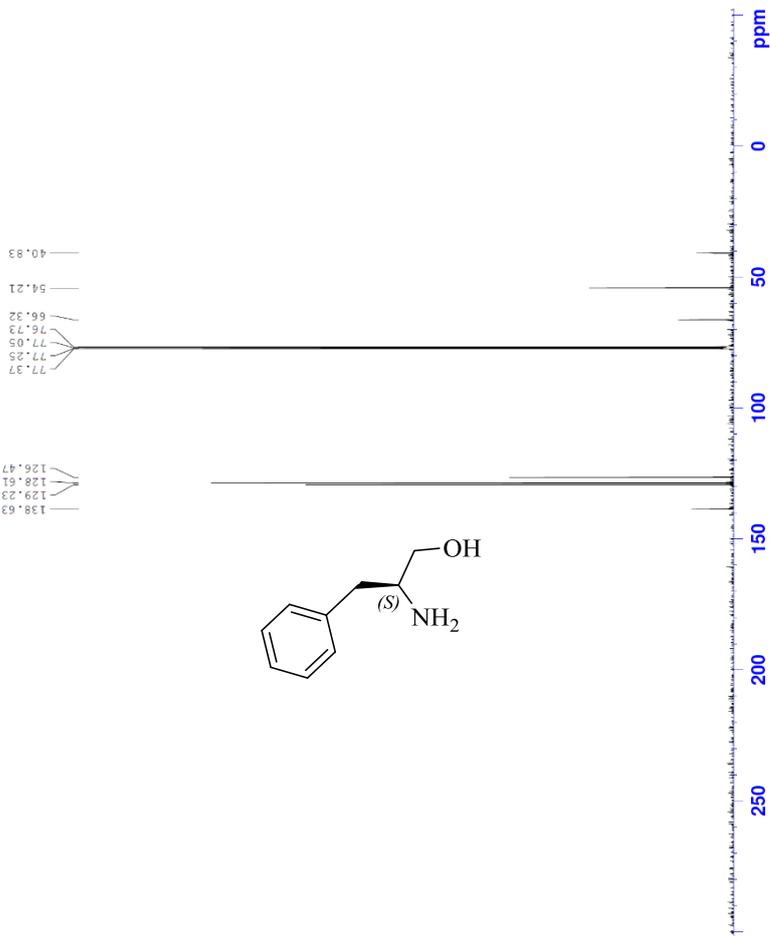


Figure S4:  $^{13}\text{C}$ NMR of **2b**

Sample code :Va1 (Dr. Samadi)

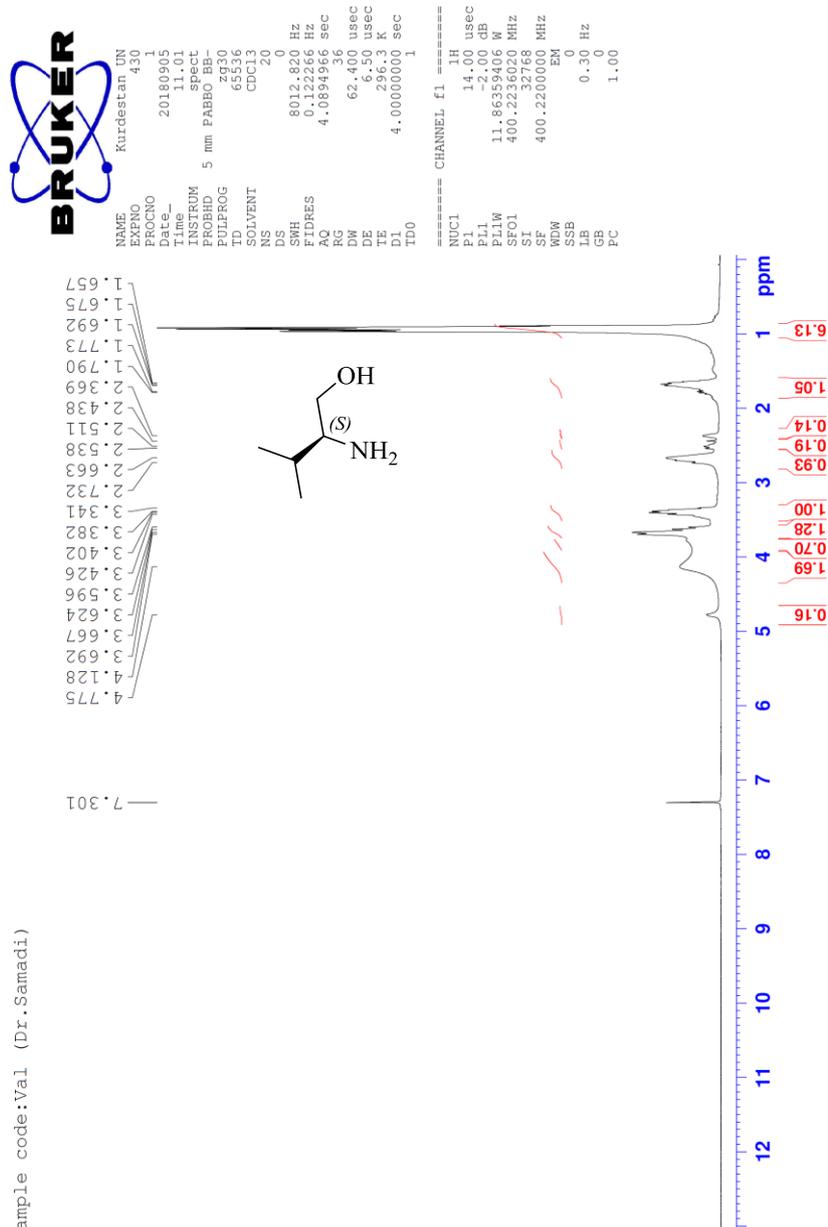


Figure S5:  $^1\text{H}$  NMR of 2c

Sample code: Val (Dr. Samadi)



```

NAME      Kurdistan DX
EXPNO     1
PROCNO    482
Date_     2018-02-1
Time      15:05
INSTRUM   spect
PROBHD    5 mm PABBO 1Hx
PULPROG   zgpg30
TD         65536
SOLVENT   DMS-d6
NS         2386
DS         0
SWH        35714.285 Hz
F2-RES    0.504957 Hz
AQ         0.5175540 sec
RG         2050
CW         14.000 usec
TR         5.00 usec
TE         300.2
D1         1.0000000 sec
D11        0.3300000 sec
TDC        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -0.80 dB
FLLW      42.0280395 K
SFO1      100.6179784 MHz

===== CHANNEL f2 =====
NAME2      val-2-f
NUC2       13C
PCPD2     90.00 usec
PL2       -2.00 dB
FLL2     14.76 dB
PL12     17.80 dB
PL13     11.80 dB
PL14     11.86359406 W
PL15     3.2872104 W
PL16     3.1217334 W
PL17     300.2230000 MHz
PL18     100.6355990 MHz
NUC3       13C
PCPD3     9.00 usec
PL3       -0.80 dB
FLL3     42.0280395 K
SFO3     100.6179784 MHz
  
```

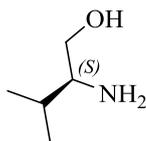
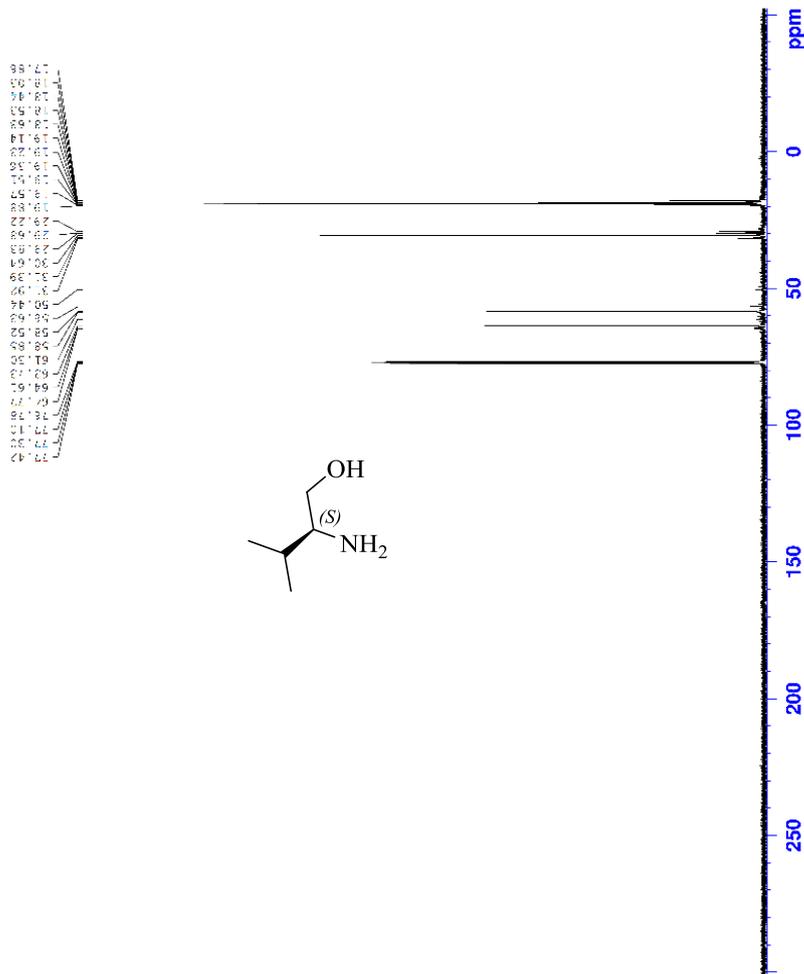


Figure S6: <sup>13</sup>CNMR of 2c

Sample code: Lu (Dr. Samadi)



NAME Kurdestan UN  
EXPNO 433  
PROCNO 1  
Date\_ 20180905  
Time 11.35  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 20  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 101  
DW 62.400 usec  
DE 6.50 usec  
TE 296.2 K  
D1 4.00000000 sec  
ID0 1  
===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -2.00 dB  
PL12 11.8635406 dB  
SFO1 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

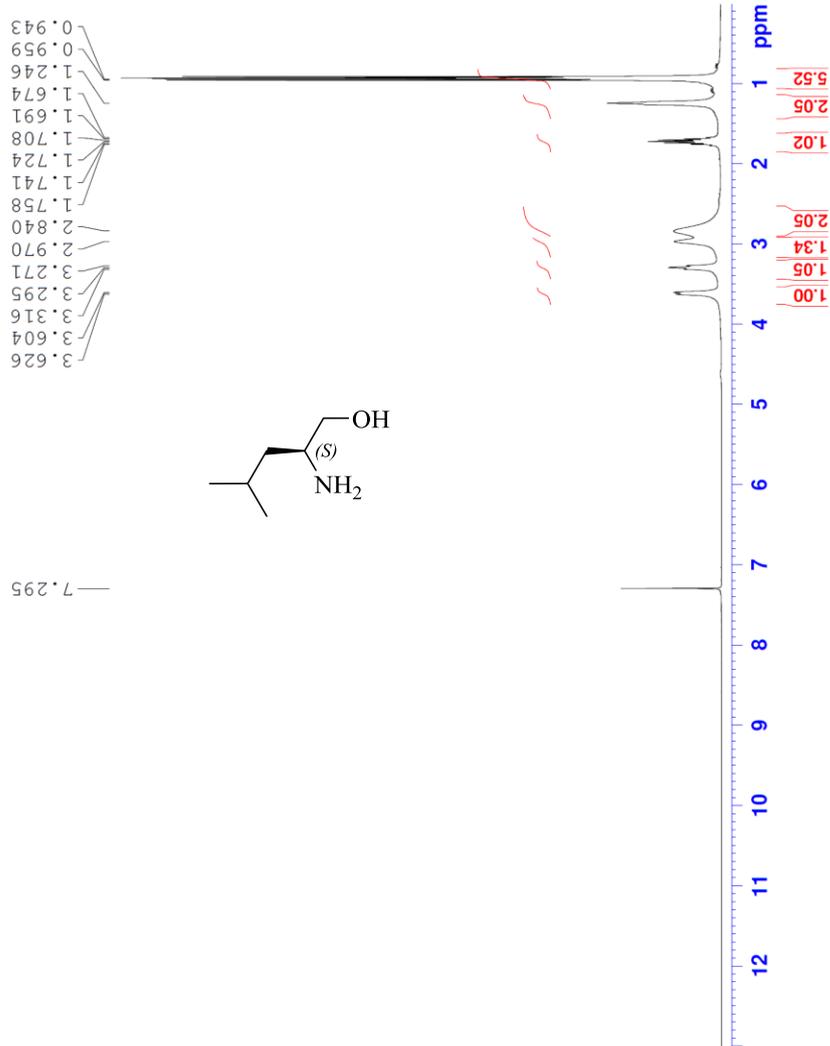


Figure S7:  $^1\text{H}$  NMR of 2d

Sample code: Lu (Dr. Samadi)



NAME Kurdistan UN  
EXPNO 445  
PROCNO  
Date\_ 20180911  
Time\_ 11.21  
INSTRUM spect  
PROBHD 5 mm PABBOFBB  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 1021  
DS 0  
SWH 35714.285 Hz  
FIDRES 0.544957 Hz  
AQ 0.9175540 sec  
RG 2050  
DM 14.000 usec  
DE 6.50 usec  
TE 297.4 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PL1 -0.90 dB  
PL1W 42.02801895 W  
SF01 100.6479784 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 -2.00 dB  
PL12 14.16 dB  
PL13 17.90 dB  
PL2W 11.86359406 W  
PL12W 0.28722104 W  
PL13W 0.12139934 W  
SFO2 400.2216009 MHz  
SI 32768  
SF 100.6353990 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

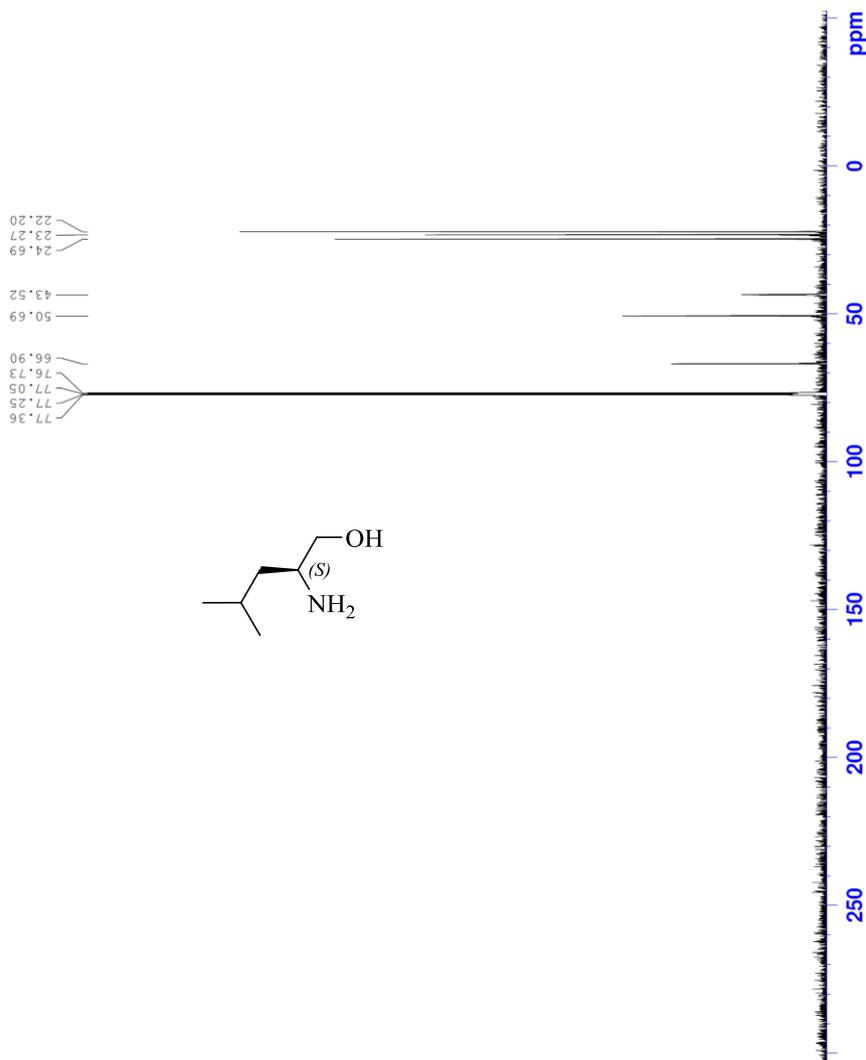


Figure S8: <sup>13</sup>CNMR of 2d

Sample Code:S1 (Dr.Samadi)



NAME Kurdistan\_UN  
EXPNO 484  
PROCNO 1  
Date\_ 20190113  
Time\_ 14.42  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 20  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 228  
DW 62.400 usec  
DE 6.50 usec  
TE 294.1 K  
D1 4.0000000 sec  
TDO 1  
===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -2.00 dB  
PL1W 11.86359406 W  
SFO1 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.40

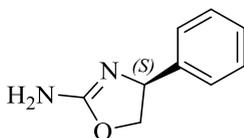
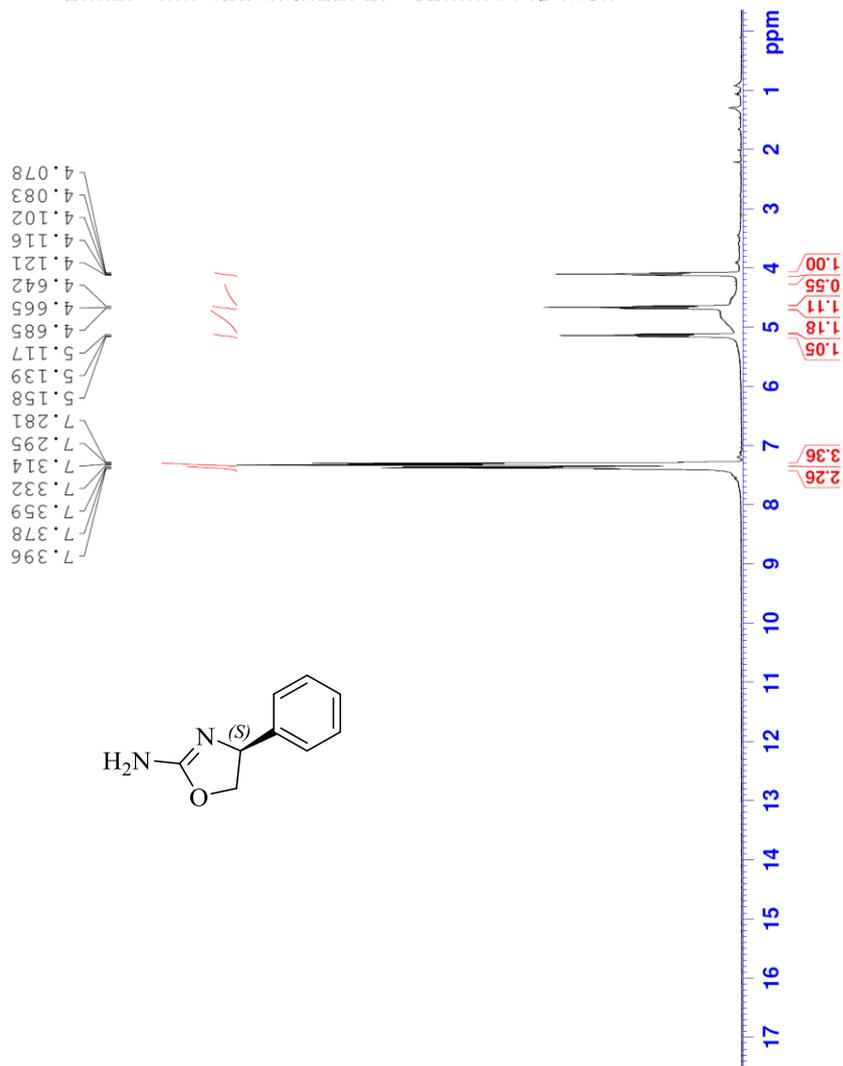


Figure S9:  $^1\text{H}$  NMR of 3a



Sample Code: S1 (Dr. Samadi)

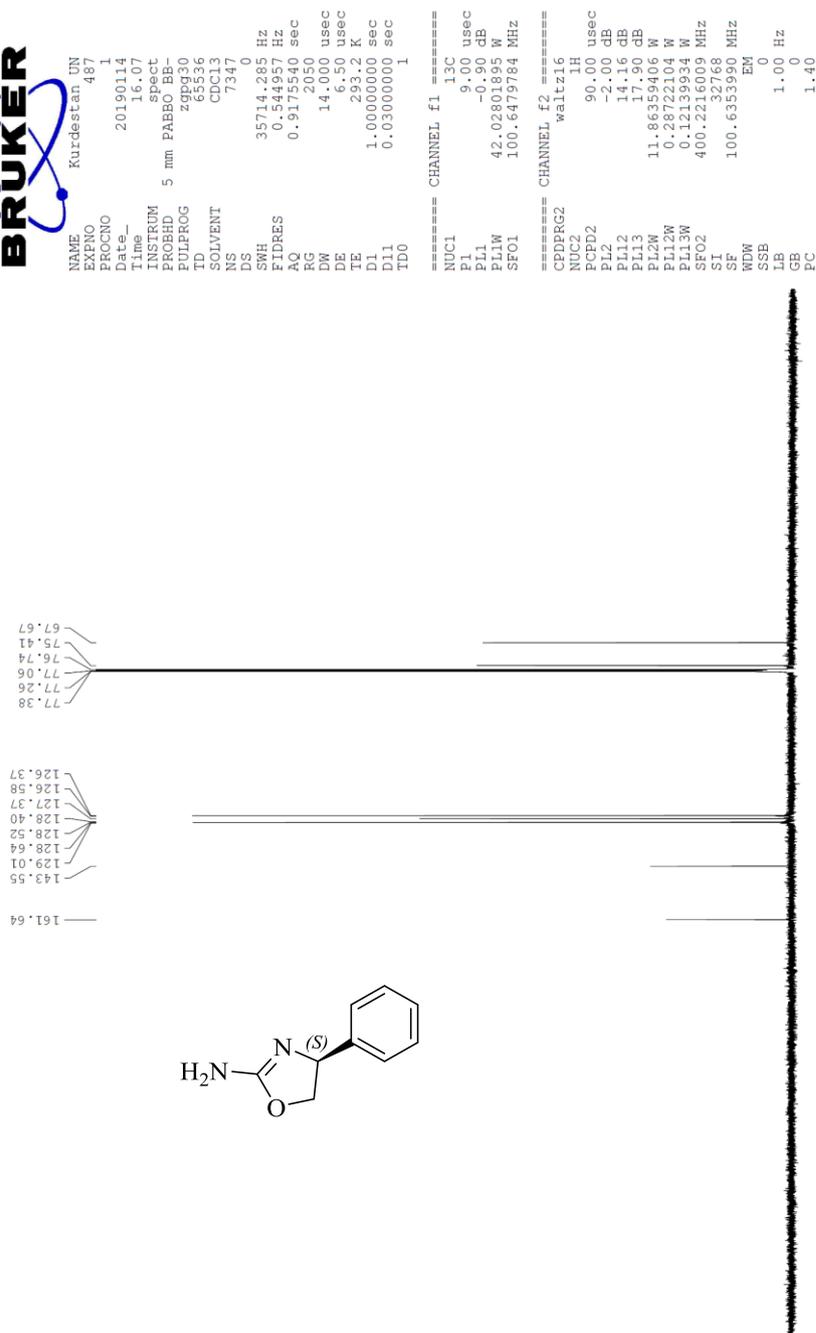


Figure S10:  $^{13}\text{C}$ NMR of 3a



NAME Kurdestan\_UN  
 EXPNO 496  
 PROCNO 1  
 Date\_ 20190208  
 Time 11:36  
 INSTRUM spect  
 PROBHD 5 mm PABBOBB-  
 EUIPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 20  
 DS 0  
 SWH 8012.820 Hz  
 FIDRES 0.122266 Hz  
 AQ 4.0894966 sec  
 RG 228  
 DW 62.400 usec  
 DE 6.50 usec  
 TE 293.0 K  
 D1 4.0000000 sec  
 ID0 1  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -2.00 dB  
 PL1W 11.86359406 W  
 SF01 400.2236020 MHz  
 SI 32768  
 SF 400.2200000 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Sample Code::S3 (Dr.Samadi)

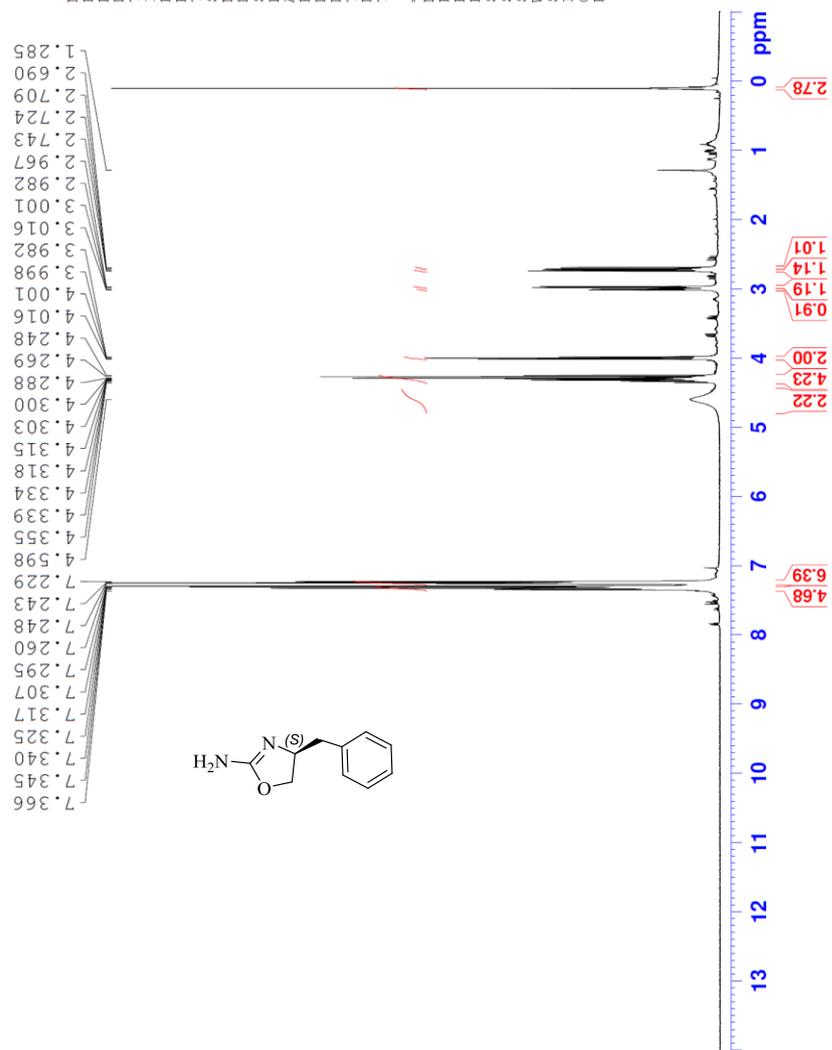


Figure S11: <sup>1</sup>H NMR of 3b



NAME Kurdistan UN  
EXPNO 505  
PROCNO 1  
Date\_ 20190208  
Time\_ 13.16  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 2005  
DS 0  
SWH 35714.285 Hz  
FIDRES 0.544957 Hz  
AQ 0.9175540 sec  
RG 2050  
DW 14.000 usec  
DE 6.50 usec  
TE 293.0 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PL1 -0.90 dB  
PL1W 42.02801895 W  
SFO1 100.6479784 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 1H  
PCPD2 90.00 usec  
PL2 -2.00 dB  
PL12 14.16 dB  
PL13 17.90 dB  
PL2W 11.86359406 W  
PL12W 0.28722104 W  
PL13W 0.12139934 W  
SFO2 400.2216009 MHz  
SI 32768  
SF 100.6353990 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

Sample Code:S3 (Dr.Samadi)

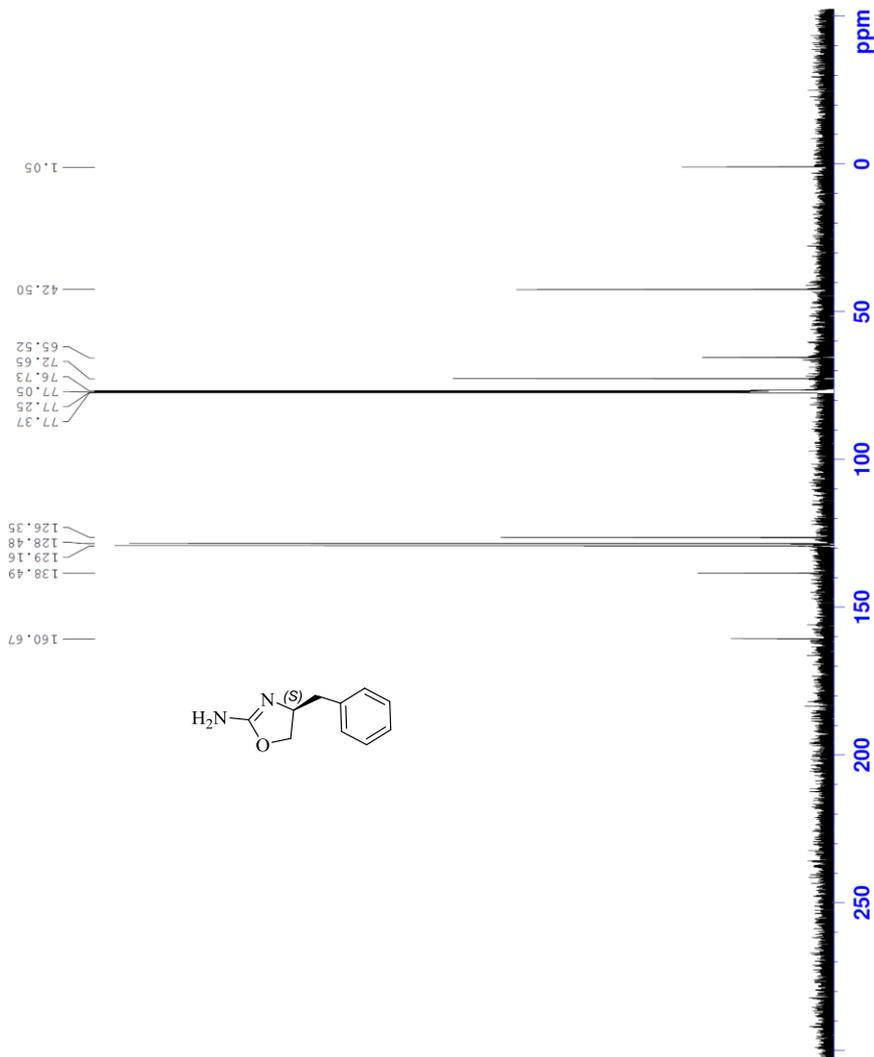


Figure S12: <sup>13</sup>CNMR of 3b

Sample code: AM-Val2 (Dr. Samadi)



NAME Kurdestan UN  
EXPNO 456  
PROCNO 1  
Date\_ 20181015  
Time\_ 8.59  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 20  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 203  
DW 62.400 usec  
DE 6.50 usec  
TE 294.1 K  
D1 4.0000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -2.00 dB  
PL1W 11.86359406 W  
SF01 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

7.295  
4.342  
4.321  
4.300  
4.006  
3.987  
3.968  
3.807  
3.790  
3.787  
3.769  
3.750  
3.507  
3.505  
1.708  
1.691  
1.674  
1.657  
1.015  
0.999  
0.986  
0.969

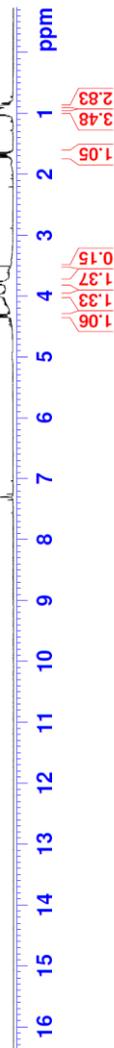
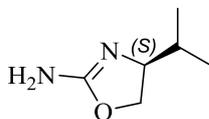


Figure S13: <sup>1</sup>H NMR of 3c



NAME Kurdestan\_UN  
EXPNO 490  
PROCNO 1  
Date\_ 20181021  
Time 11.14  
INSTRUM spect  
PROBHD 5 mm FAPBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 1052  
DS 0  
SWH 35714.285 Hz  
FIDRES 0.544957 Hz  
AQ 0.9175540 sec  
RG 2050  
DW 14.000 usec  
DE 6.50 usec  
TE 294.7 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PL1 -0.90 dB  
PL1W 42.02801895 W  
SFO1 100.6479784 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 -2.00 dB  
PL12 14.16 dB  
PL13 17.90 dB  
PL2W 11.86359406 W  
PL12W 0.2872104 W  
PL13W 0.12139934 W  
SFO2 400.2216009 MHz  
SI 32768  
SF 100.6353990 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

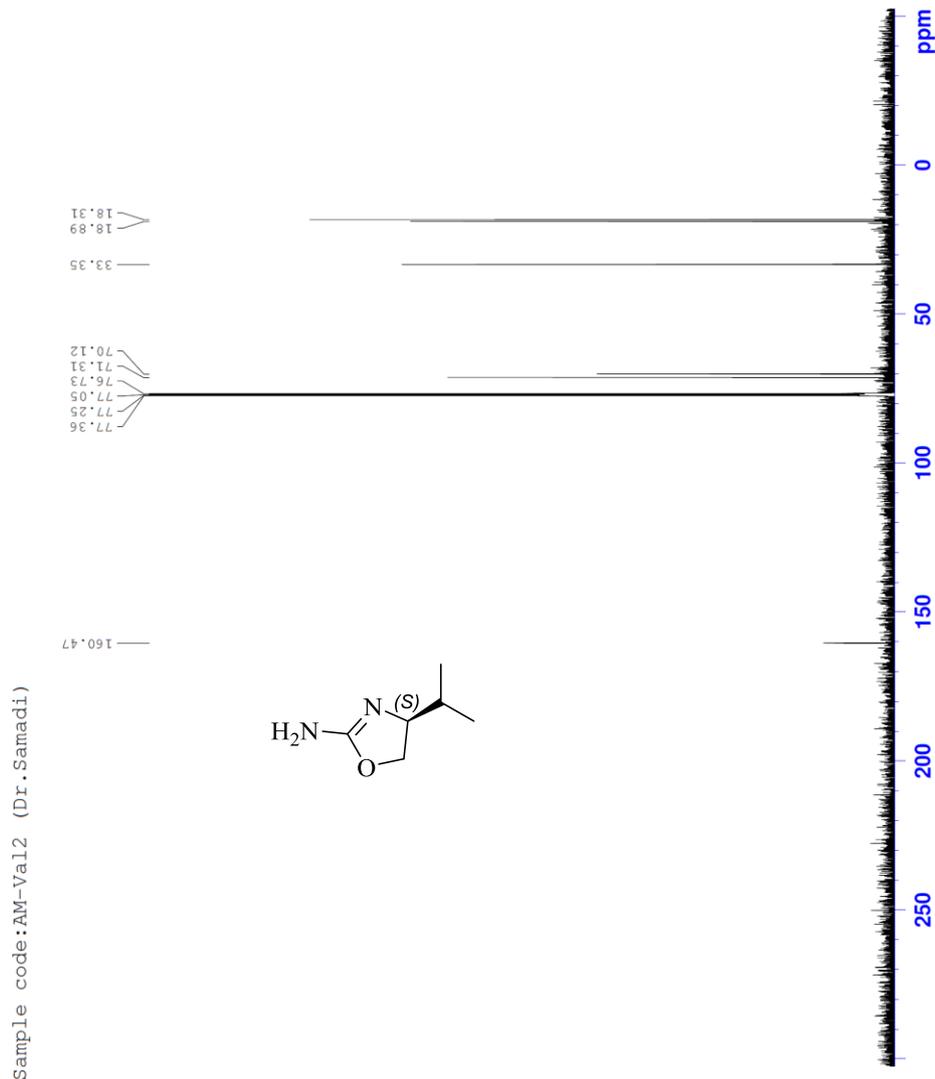


Figure S14:  $^{13}\text{C}$ NMR of **3c**

Sample code: Am-Lu (Dr. Samadi)



NAME Kurdestan UN  
EXPNO 436  
PROCNO 1  
Date\_ 20180905  
Time 12.36  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 20  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 64  
DW 62.400 usec  
DE 6.50 usec  
TE 296.8 K  
D1 4.0000000 sec  
TD0 1

==== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -2.00 dB  
PL1W 11.86359406 W  
SFO1 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

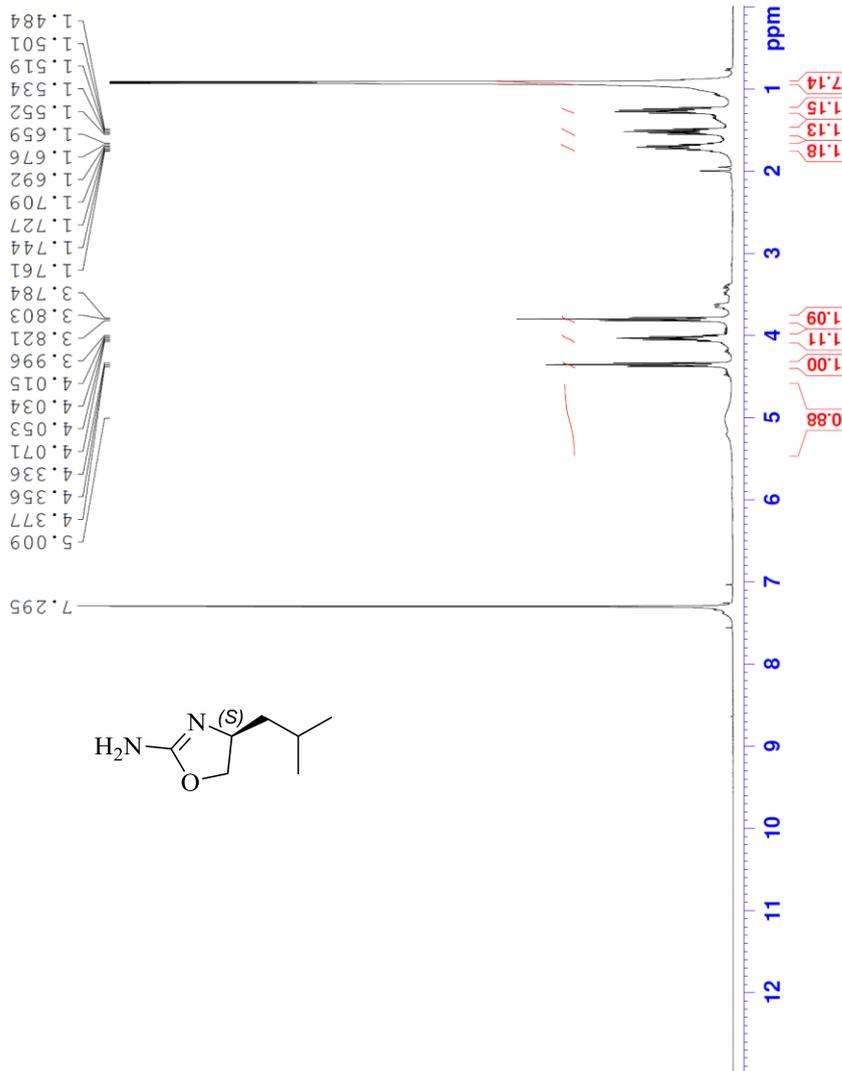


Figure S15: <sup>1</sup>H NMR of 3d

Sample code: Am-Lu (Dr. Samadi)



```
NAME Kurdestan UN
EXPNO 1
PROCNO 447
Date_ 20180910
Time 12.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 355
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 2050
DW 14.000 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.16 dB
PL13 17.90 dB
PL2W 11.86359406 W
PL12W 0.28722104 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
SI 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
```

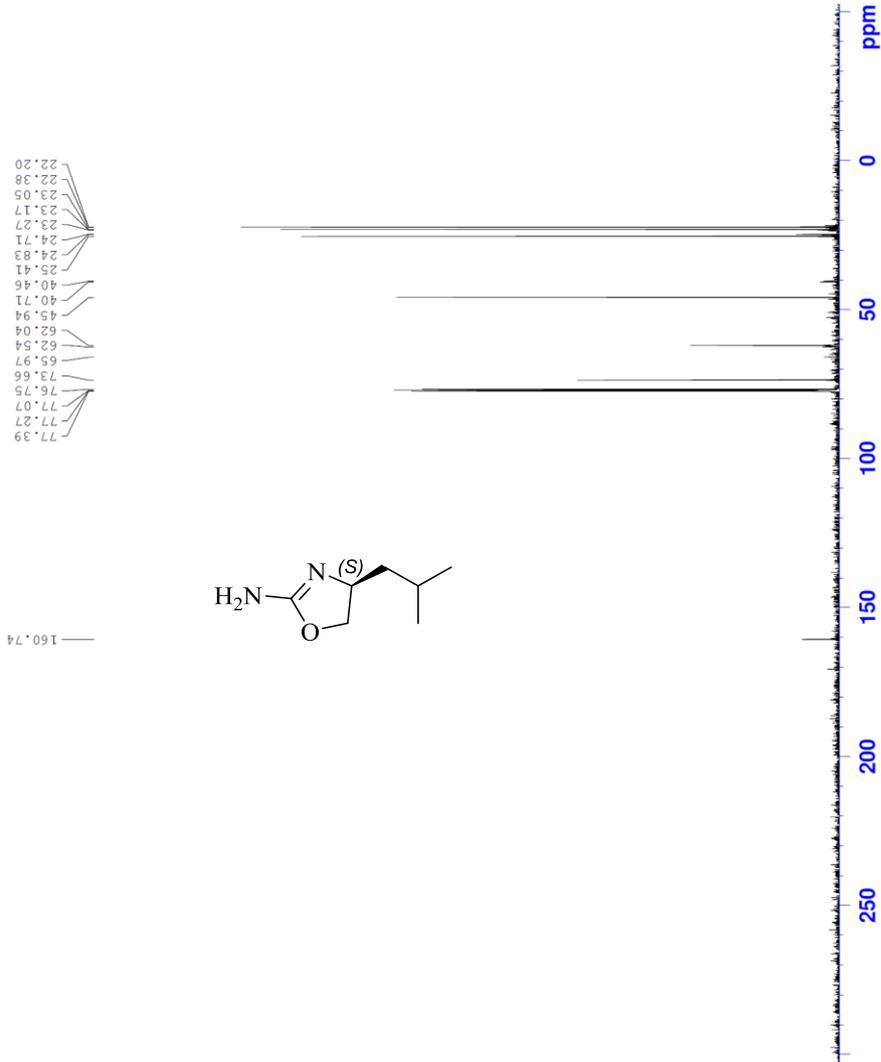


Figure S16:  $^{13}\text{C}$ NMR of 3d

Current Data Parameters

NAME: Semad1  
 EXPNO: 888  
 PROCNO: 1

F2 - Acquisition Parameters

File: 20111226  
 Time: 14:05  
 INSTRUM: spect  
 PROBHD: 5 mm BB0 BB-FH  
 PULPROG: zg30  
 TD: 32768  
 SOLVENT: CDCl3  
 NS: 10  
 DS: 1  
 SWH: 7812.500 Hz  
 FIDRES: 0.226449 Hz  
 AQ: 2.0975021 sec  
 RG: 655.36  
 DW: 64.000 usec  
 DE: 6.00 usec  
 TE: 380.0 K  
 D1: 2.00000000 sec

===== CHANNEL f1 =====

NUC1: 1H  
 P1: 19.00 usec  
 PL1: 0.00 dB  
 SF01: 300.1300000 MHz

F2 - Processing parameters

SI: 65536  
 SF: 300.1300000 MHz  
 WDW: EM  
 SSB: 0  
 LB: 0.30 Hz  
 GB: 0  
 PC: 1.00

1D NMR plot parameters

CX: 20.00 cm  
 CY: 50.85 cm  
 F1P: 11.452 ppm  
 F1: 3437.22 Hz  
 F2P: -0.592 ppm  
 F2: -177.71 Hz  
 PPMCM: 0.60253 ppm/cm  
 HZCM: 180.74646 Hz/cm

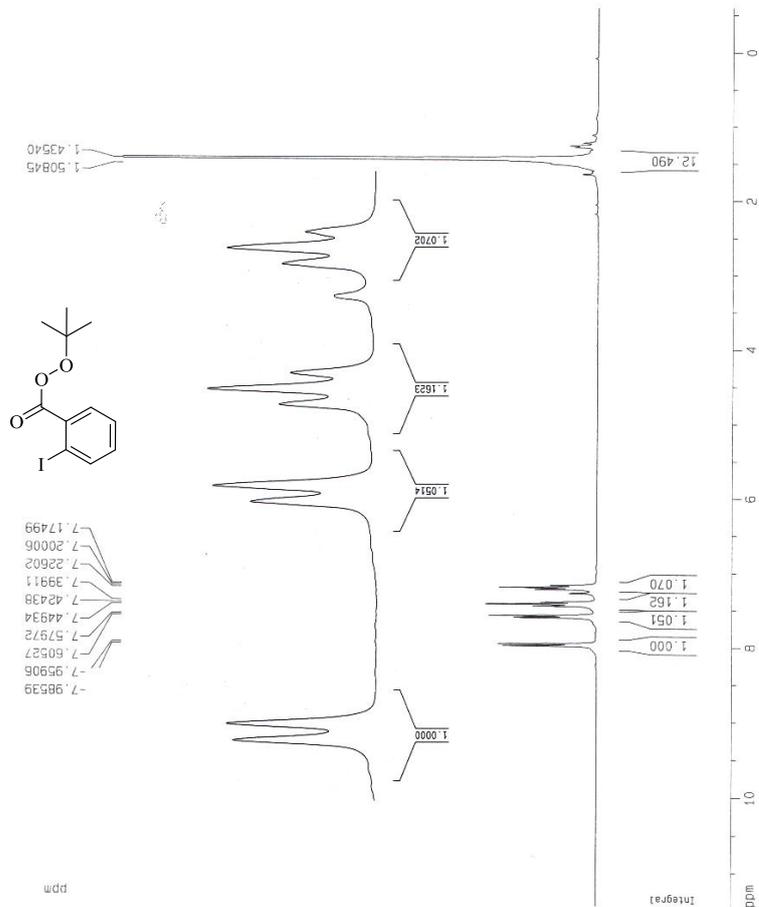


Figure S17: <sup>1</sup>H NMR of 7b

Sample code: 5 (samadi)

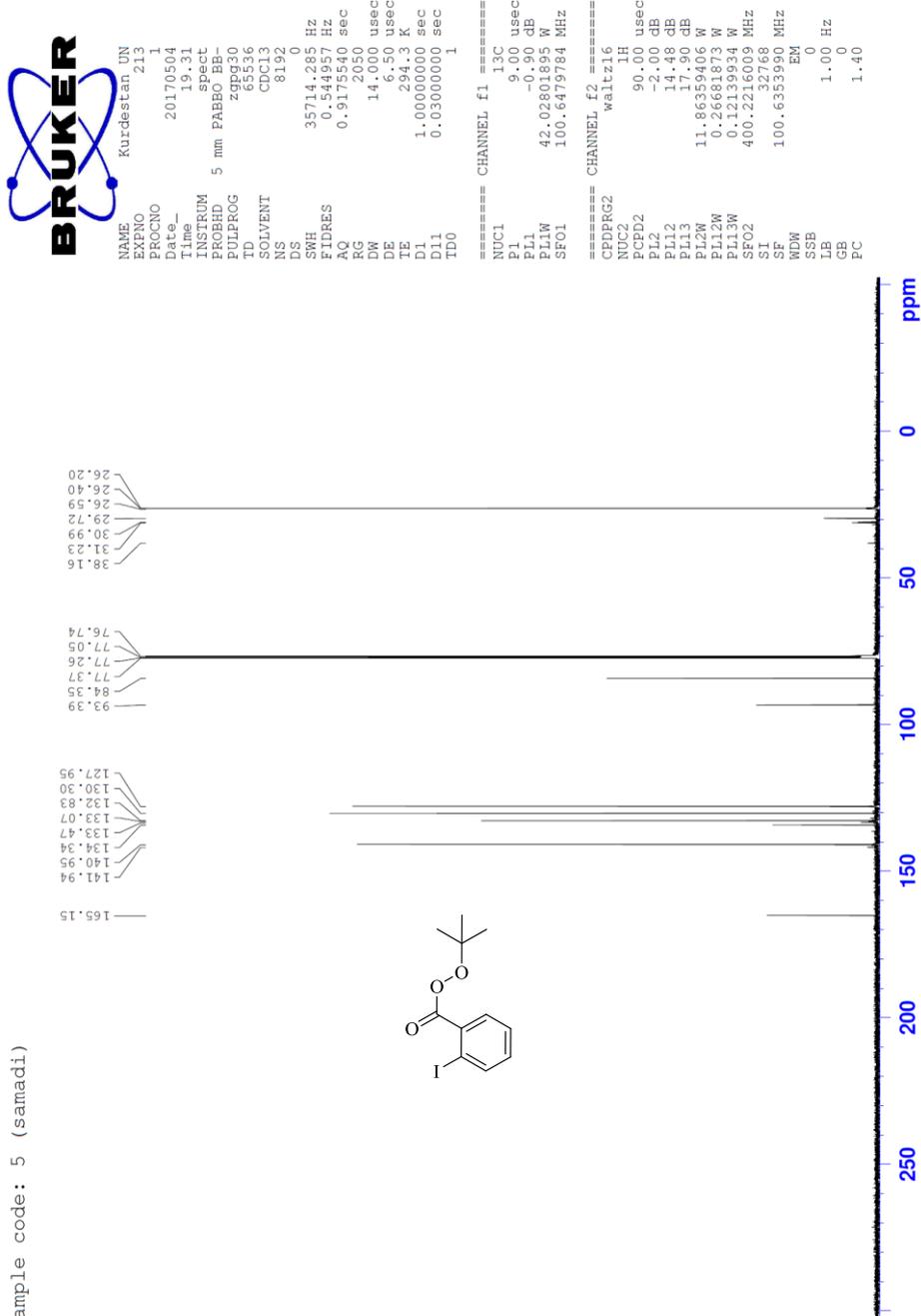


Figure S18:  $^{13}\text{C}$ NMR of 7b



NAME Kurdestan UN  
EXPNO 427  
PROCNO 1  
Date\_ 20180905  
Time\_ 10.15  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 20  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 181  
DW 62.400 usec  
DE 6.50 usec  
TE 296.1 K  
D1 4.0000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -2.00 dB  
PL1W 11.86359406 W  
SF01 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

Sample code: E1 (Dr..Samadi)

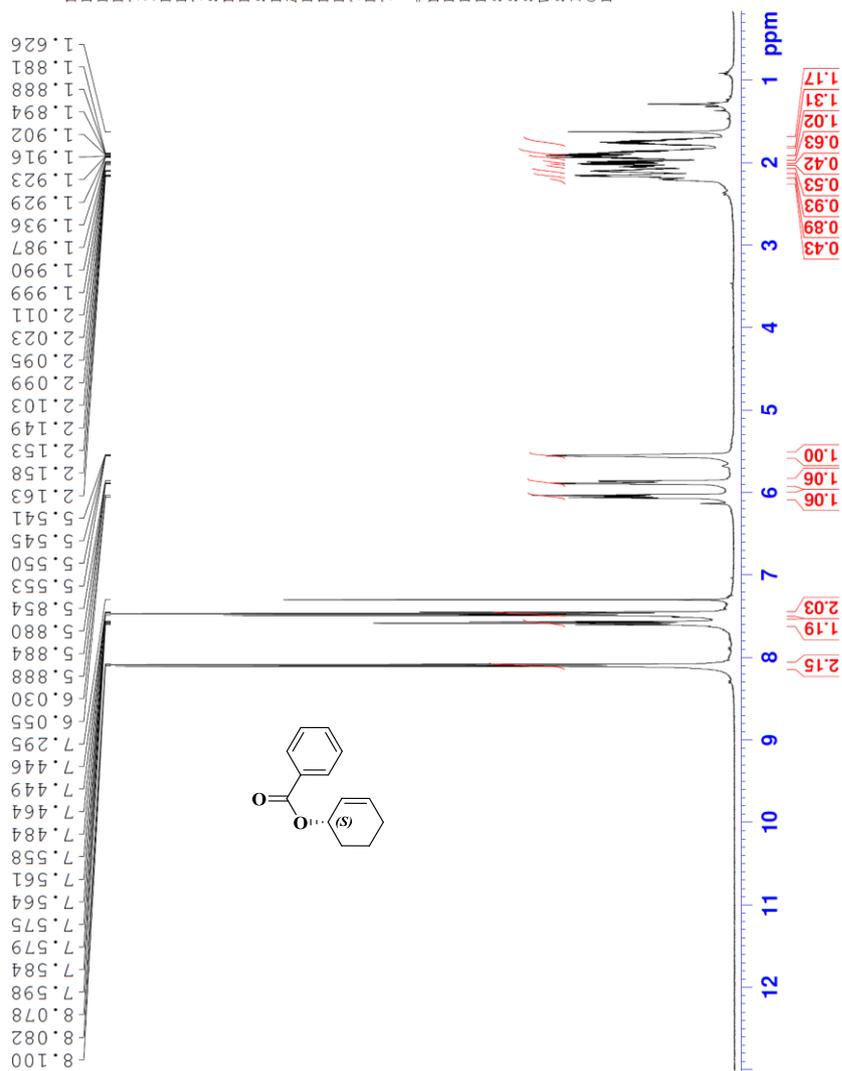


Figure S19:  $^1\text{H}$  NMR of 8a

Sample code:E1 (Dr.Samadi)



NAME Kurdestan\_UN  
EXPNO 440  
PROCNO 1  
Date\_ 20180910  
Time 8.10  
INSTRUM spect  
PROBHD 5 mm FAPBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 351  
DS 0  
SWH 35714.285 Hz  
FIDRES 0.544957 Hz  
AQ 0.9175540 sec  
RG 2050  
DW 14.000 usec  
DE 6.50 usec  
TE 297.2 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PL1 -0.90 dB  
PL1W 42.02801895 W  
SFO1 100.6479784 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 -2.00 dB  
PL2 14.16 dB  
PL2W 11.86350490 dB  
PL3 0.28726094 W  
PL3W 0.12139934 W  
SFO2 400.2216709 MHz  
SI 100.6353990 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

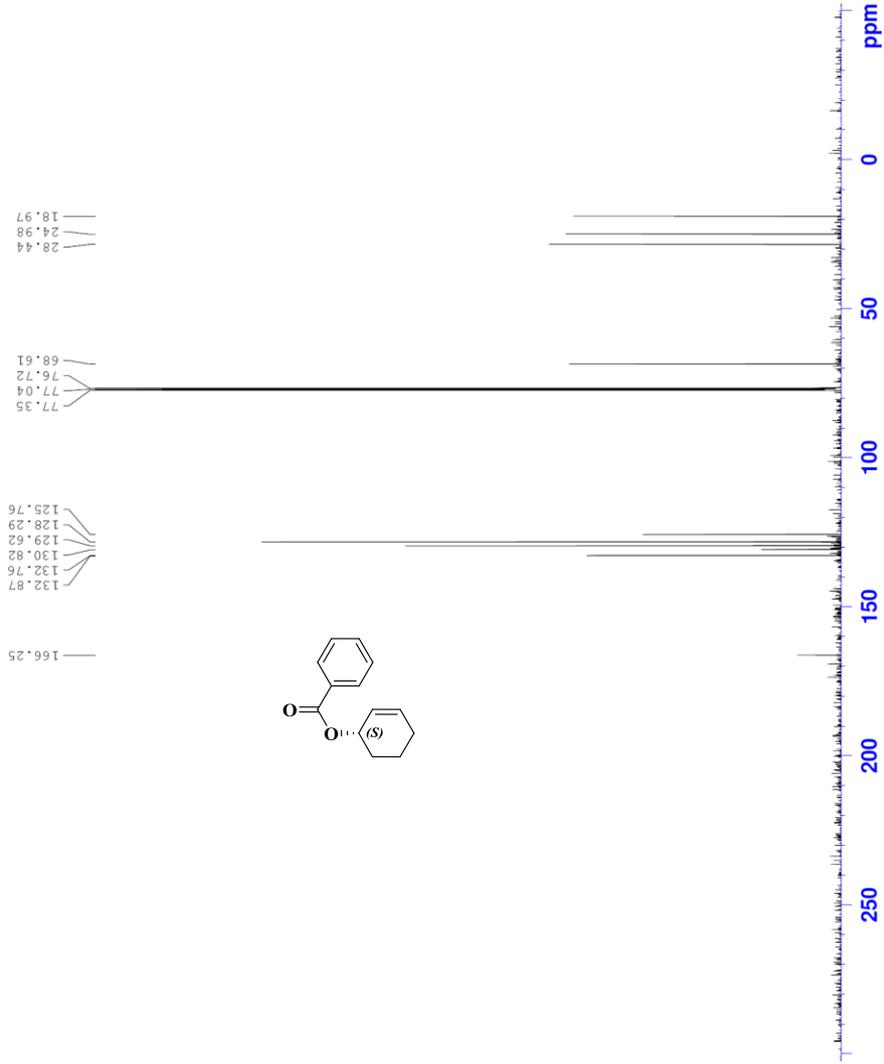


Figure S20:  $^{13}\text{C}$ NMR of 8a

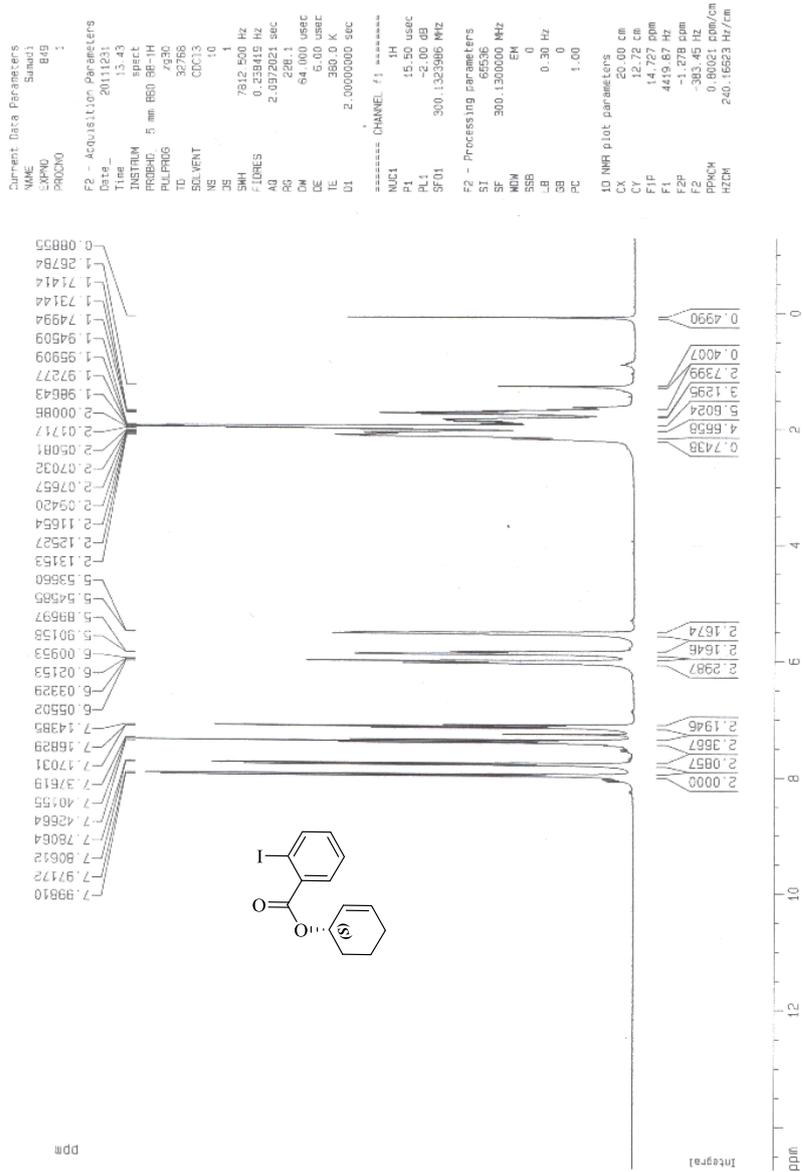


Figure S21: <sup>1</sup>H NMR of 8b

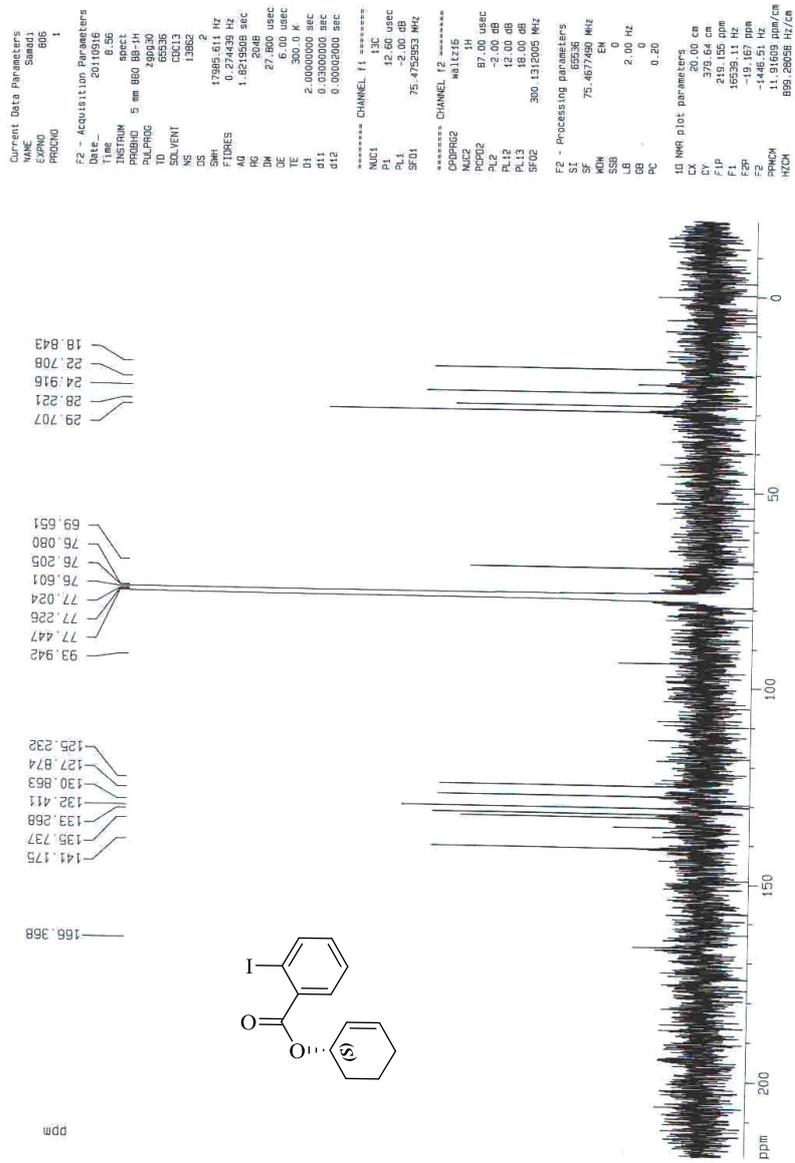


Figure S22: <sup>13</sup>CNMR of 8b



NAME Kurdestan UN  
 EXPNO 426  
 PROCNO 1  
 Date\_ 20180905  
 Time\_ 9.52  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg30  
 ID 65536  
 SOLVENT CDCl3  
 NS 20  
 DS 0  
 SWH 8012.820 Hz  
 FIDRES 0.122266 Hz  
 AQ 4.0894966 sec  
 RG 101  
 DW 62.400 usec  
 DE 6.50 usec  
 TE 295.7 K  
 D1 4.0000000 sec  
 TD0 1  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -2.00 dB  
 PL1W 11.86359406 W  
 SFO1 400.2236020 MHz  
 SI 32768  
 SF 400.2200000 MHz  
 EM  
 WDW 0  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

Sample code: E2 (Dr. Samadi)

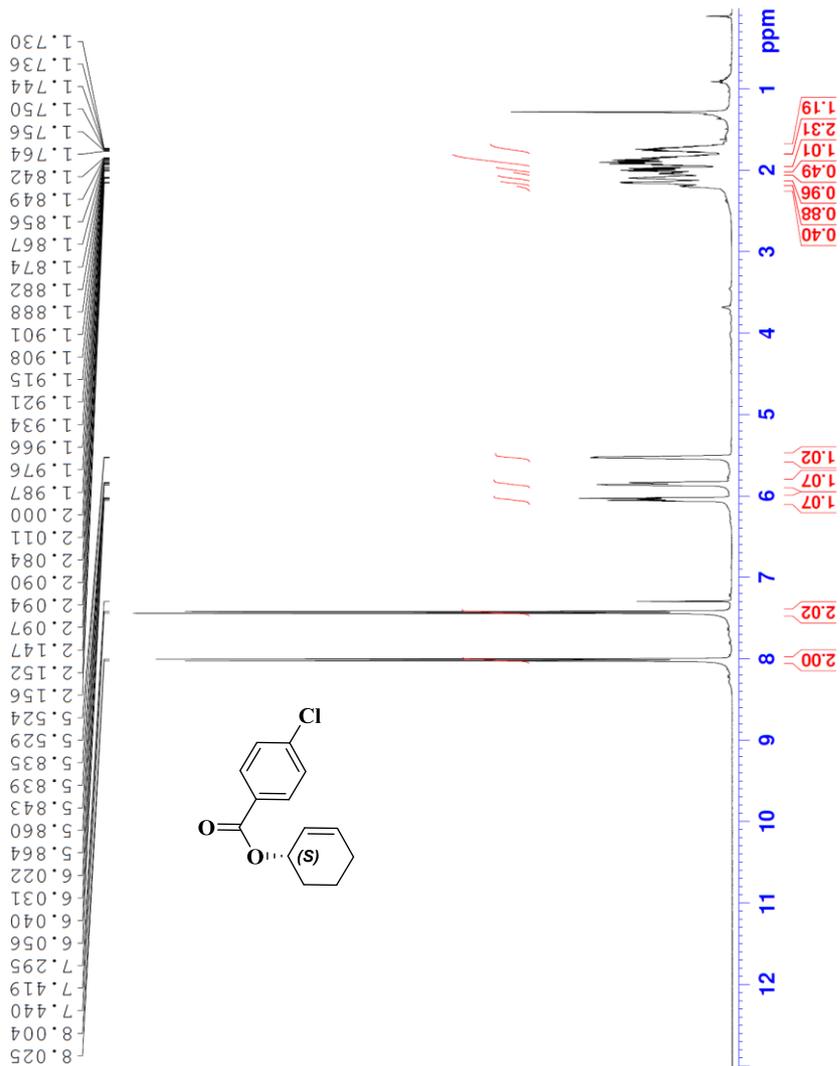


Figure S23: <sup>1</sup>H NMR of 8f



NAME Kurdistan UN  
 EXPNO 441  
 PROCNO 1  
 Date\_ 20180905  
 Time 10.00  
 INSTRUM spect  
 PROBHD 5 mm FABEO BB-  
 PULPROG zgpg30  
 ID 65335  
 SOLVENT CDCl3  
 NS 260  
 DS 0  
 SWH 35714.285 Hz  
 FIDRES 0.544587 Hz  
 AQ 0.9175540 sec  
 RG 2050  
 DW 14.000 usec  
 DE 6.50 usec  
 TE 296.1 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 9.00 usec  
 PL1 -0.90 dB  
 PL1W 42.02801895 W  
 SF01 100.6479784 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 90.00 usec  
 PL2 -2.00 dB  
 PL12 14.16 dB  
 PL13 17.90 dB  
 PL2W 11.86359406 W  
 PL12W 0.28722104 W  
 PL13W 0.12139934 W  
 SF02 400.2216009 MHz  
 SI 32768  
 SF 100.6353990 MHz  
 EM 0  
 SSB 1.00 Hz  
 LB 0  
 GB 0  
 PC 1.40

Sample code:E2 (Dr.Samadi)

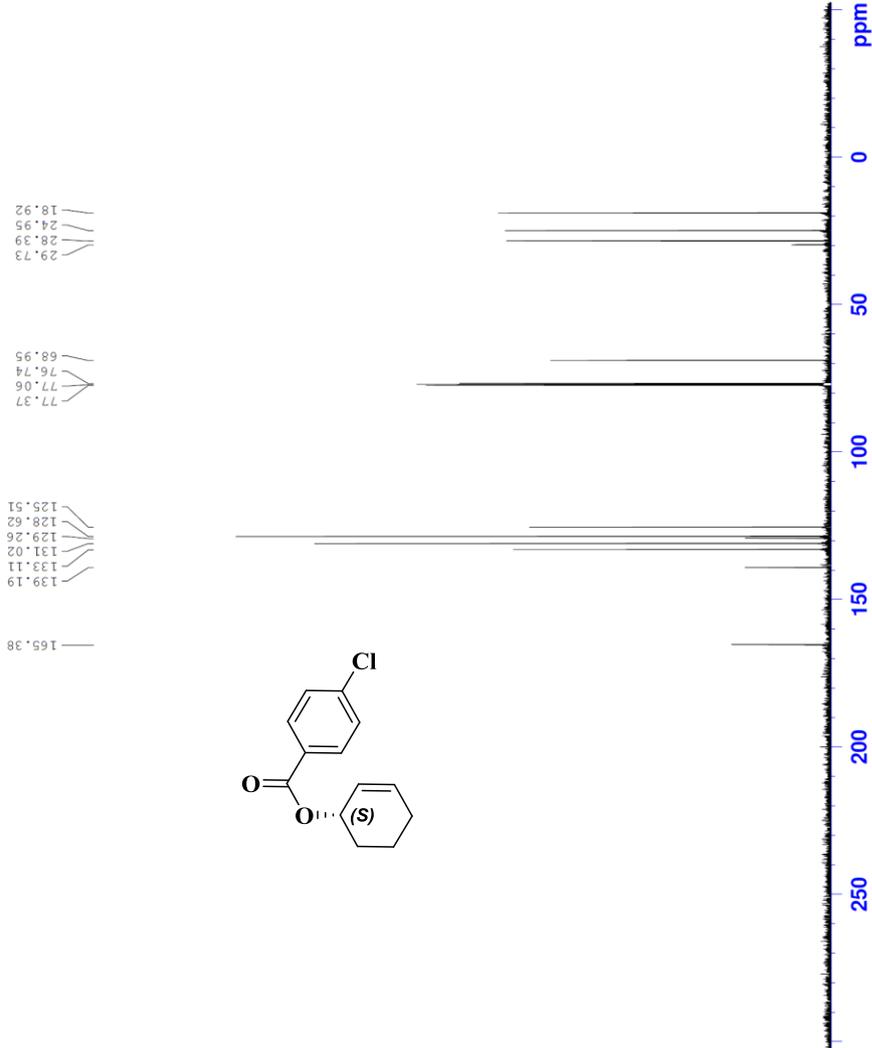
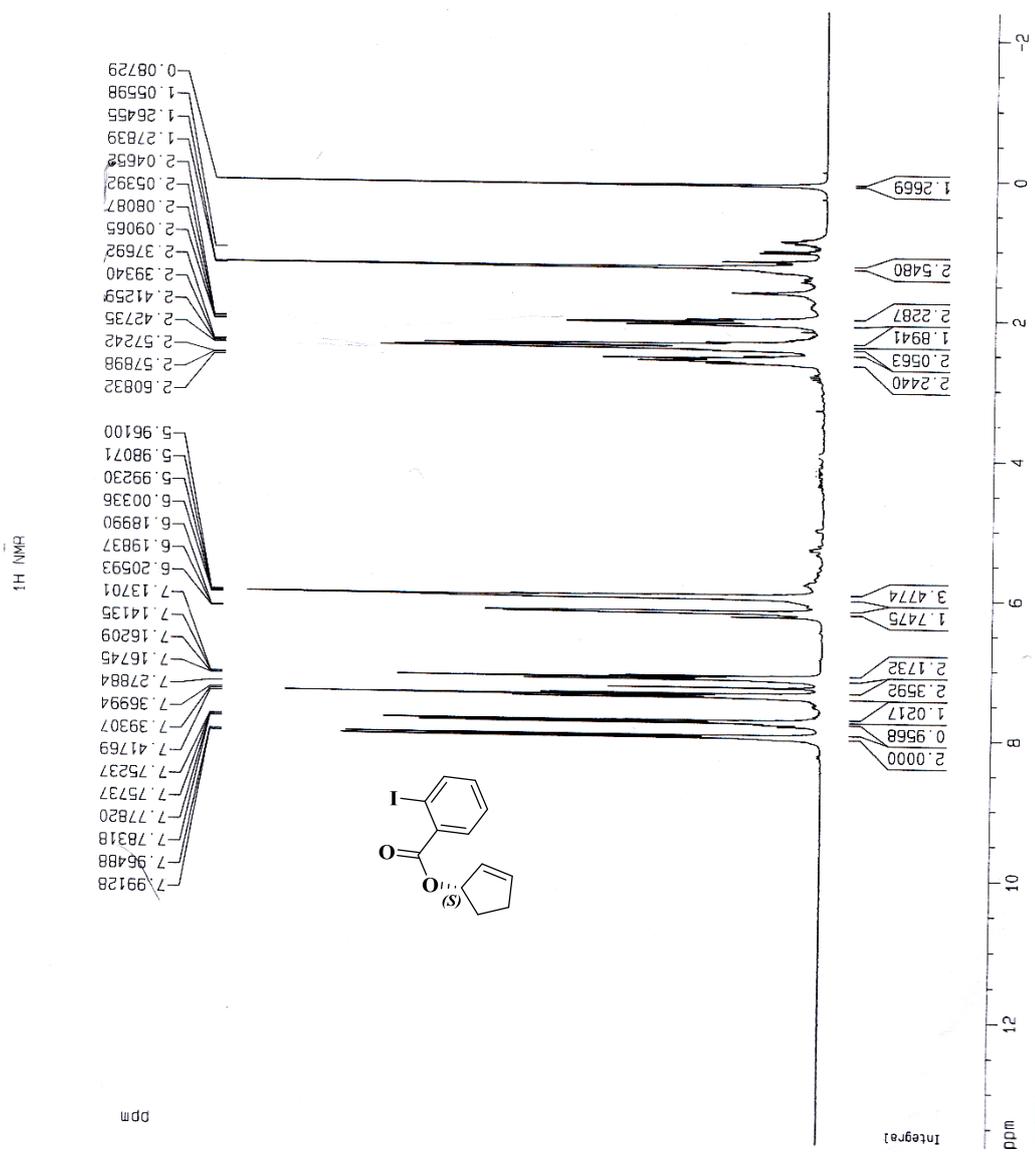


Figure S24: <sup>13</sup>C NMR of 8f



**Figure S25:  $^1\text{H}$  NMR of 9b**

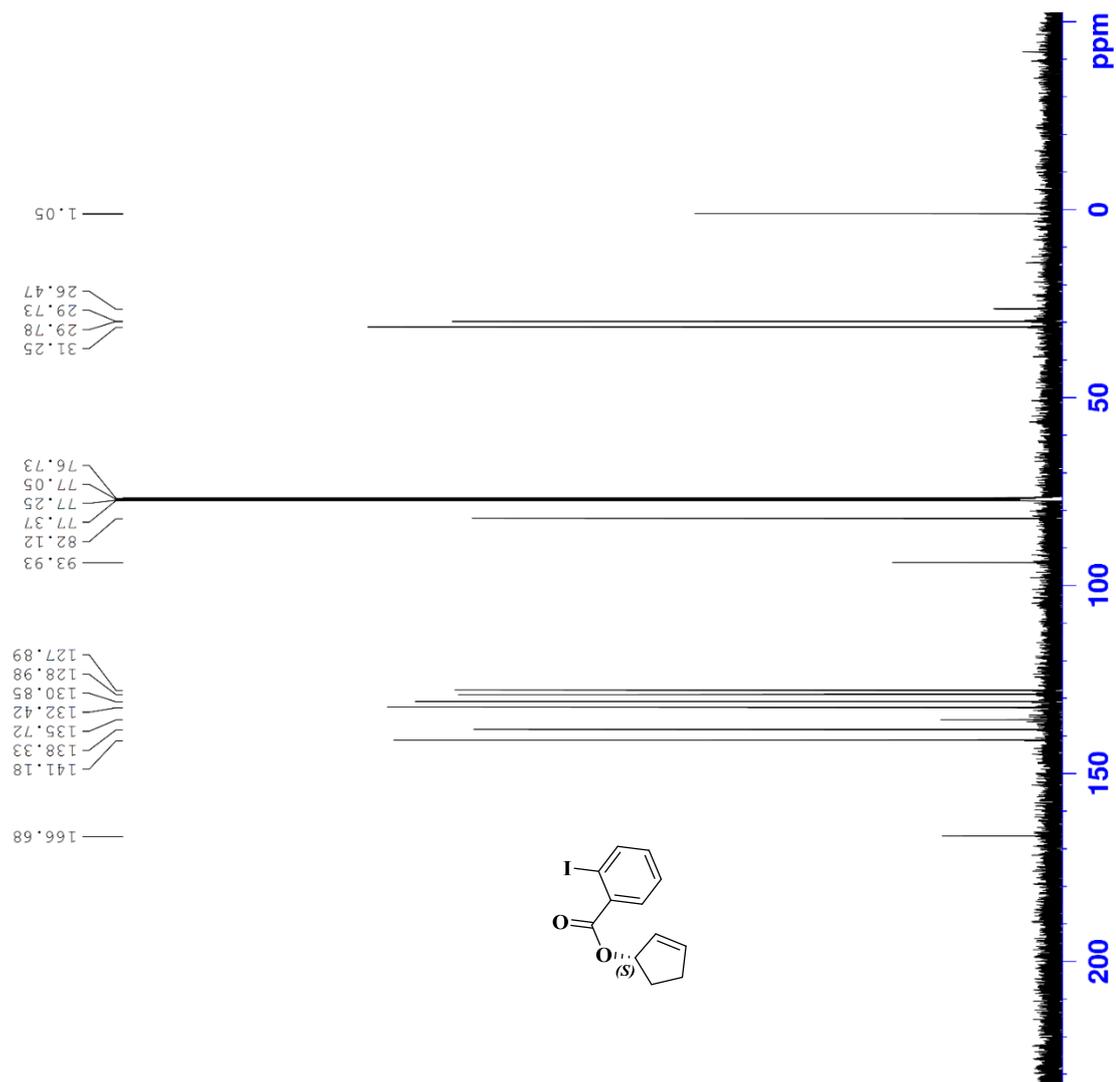


Figure S26:  $^{13}\text{C}$ NMR of 9b

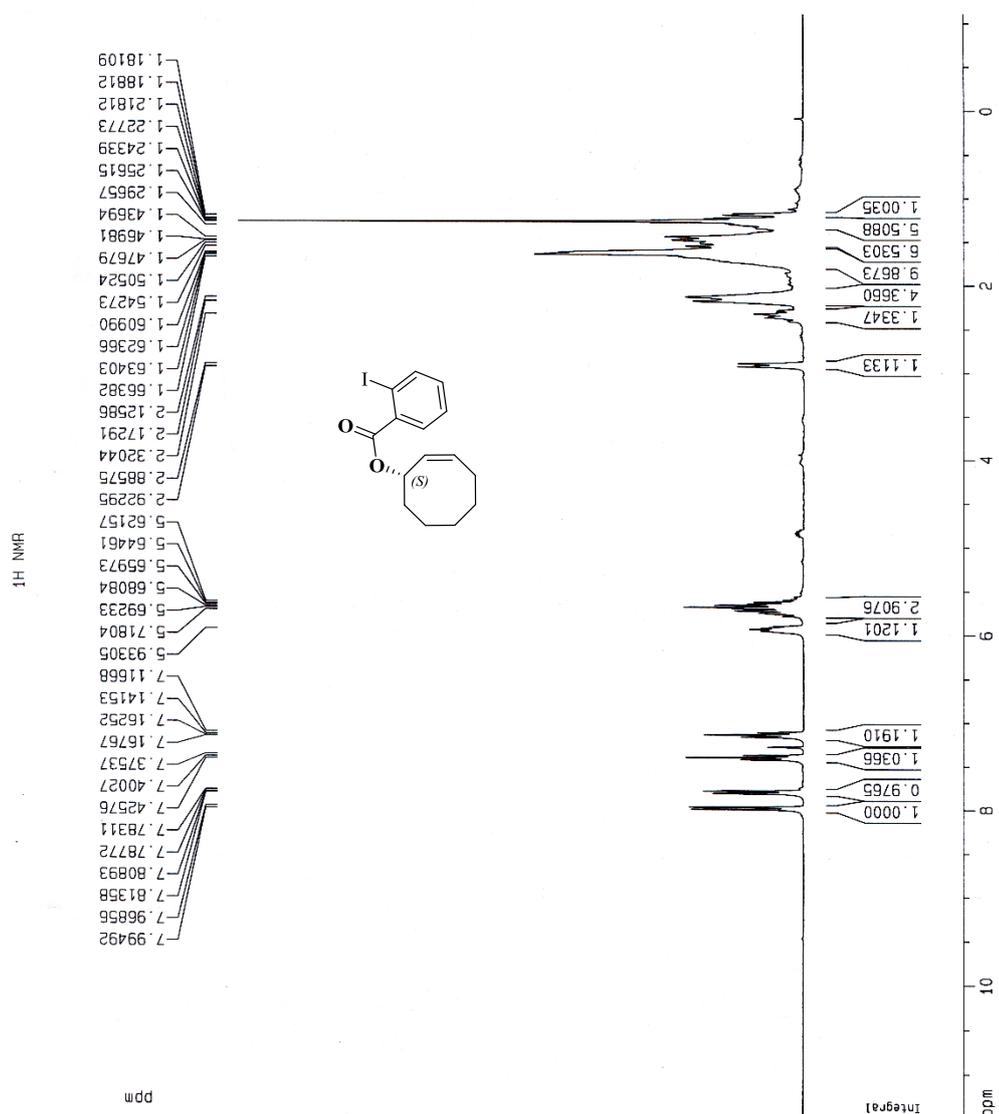


Figure S27: <sup>1</sup>H NMR of 10b

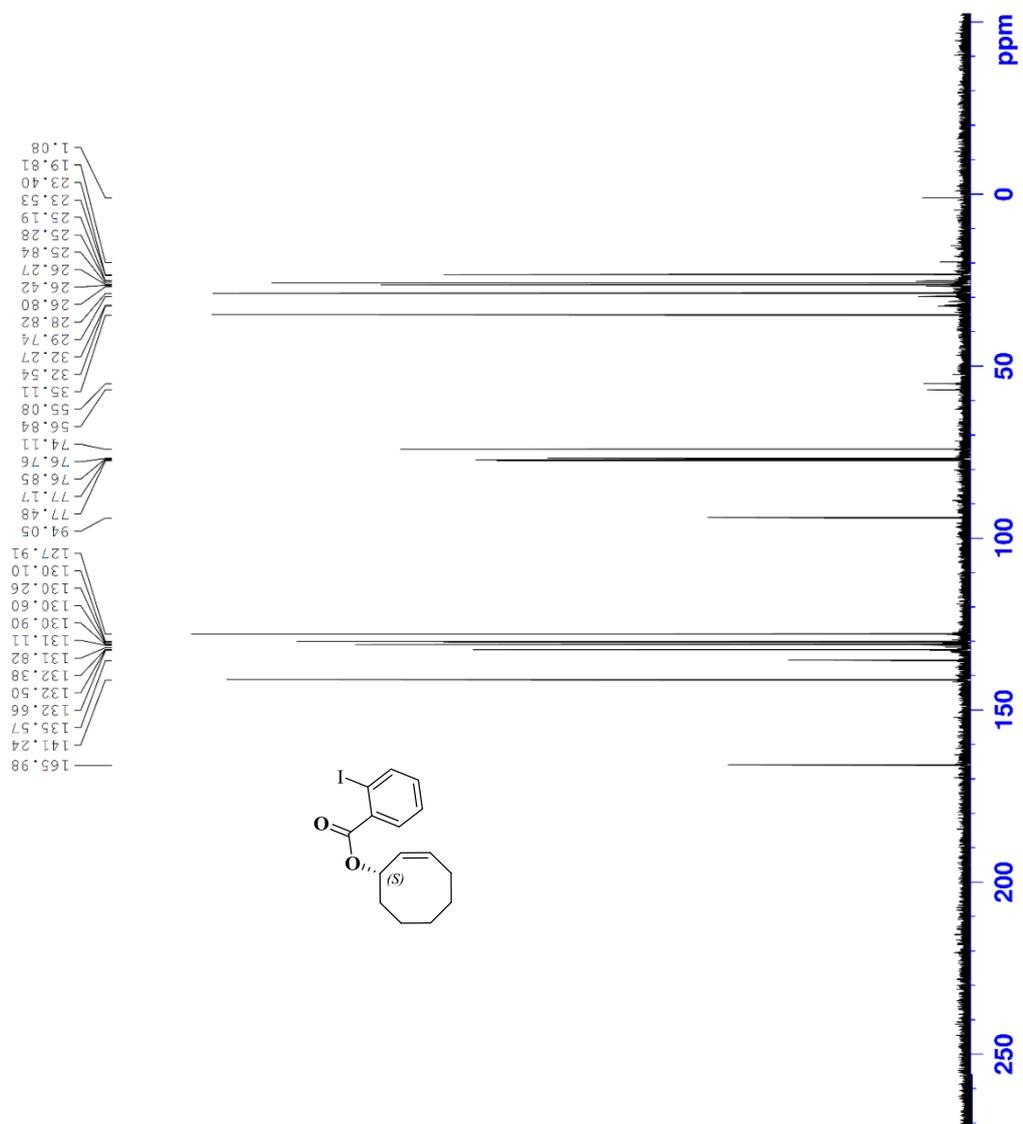


Figure S28: <sup>13</sup>CNMR of 10b

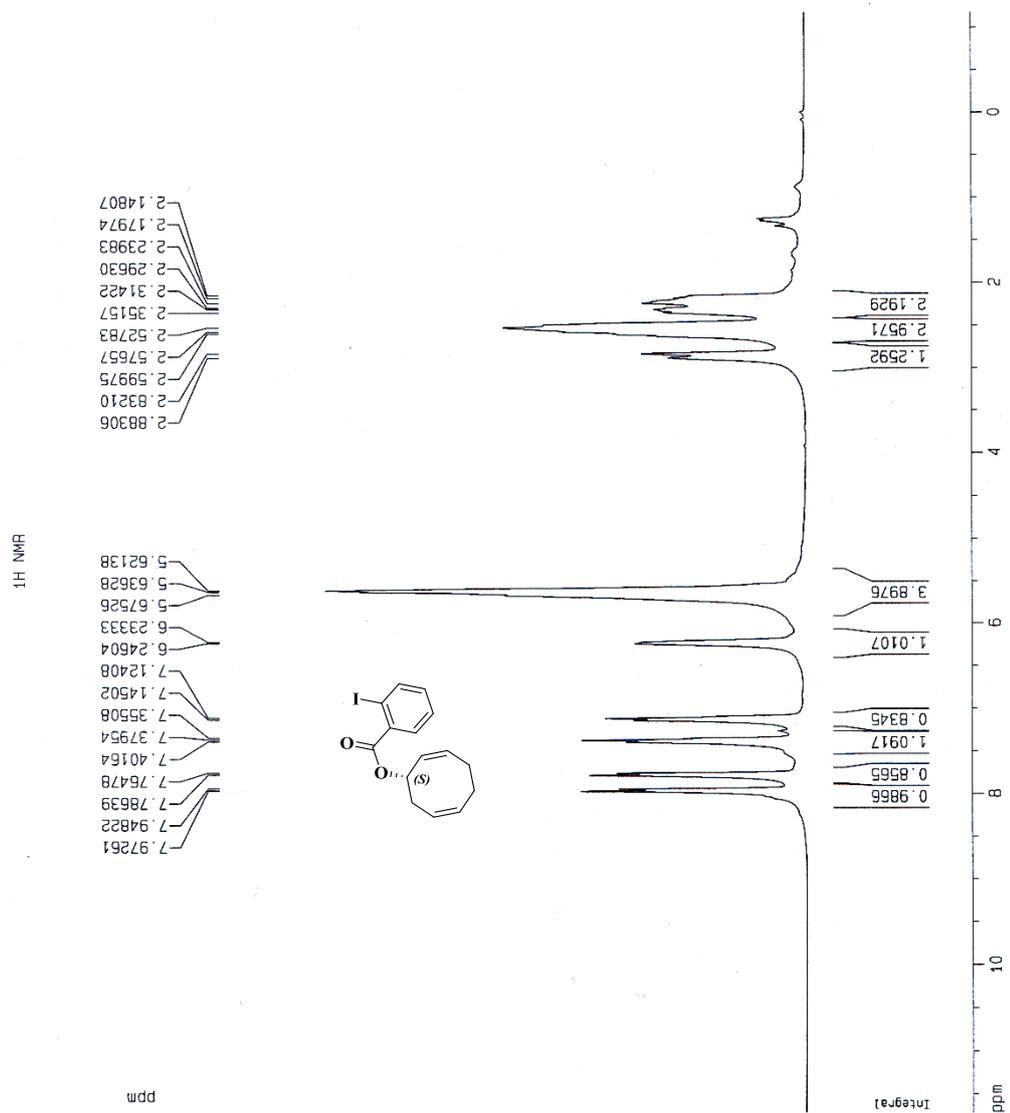


Figure S29: <sup>1</sup>H NMR of 11b

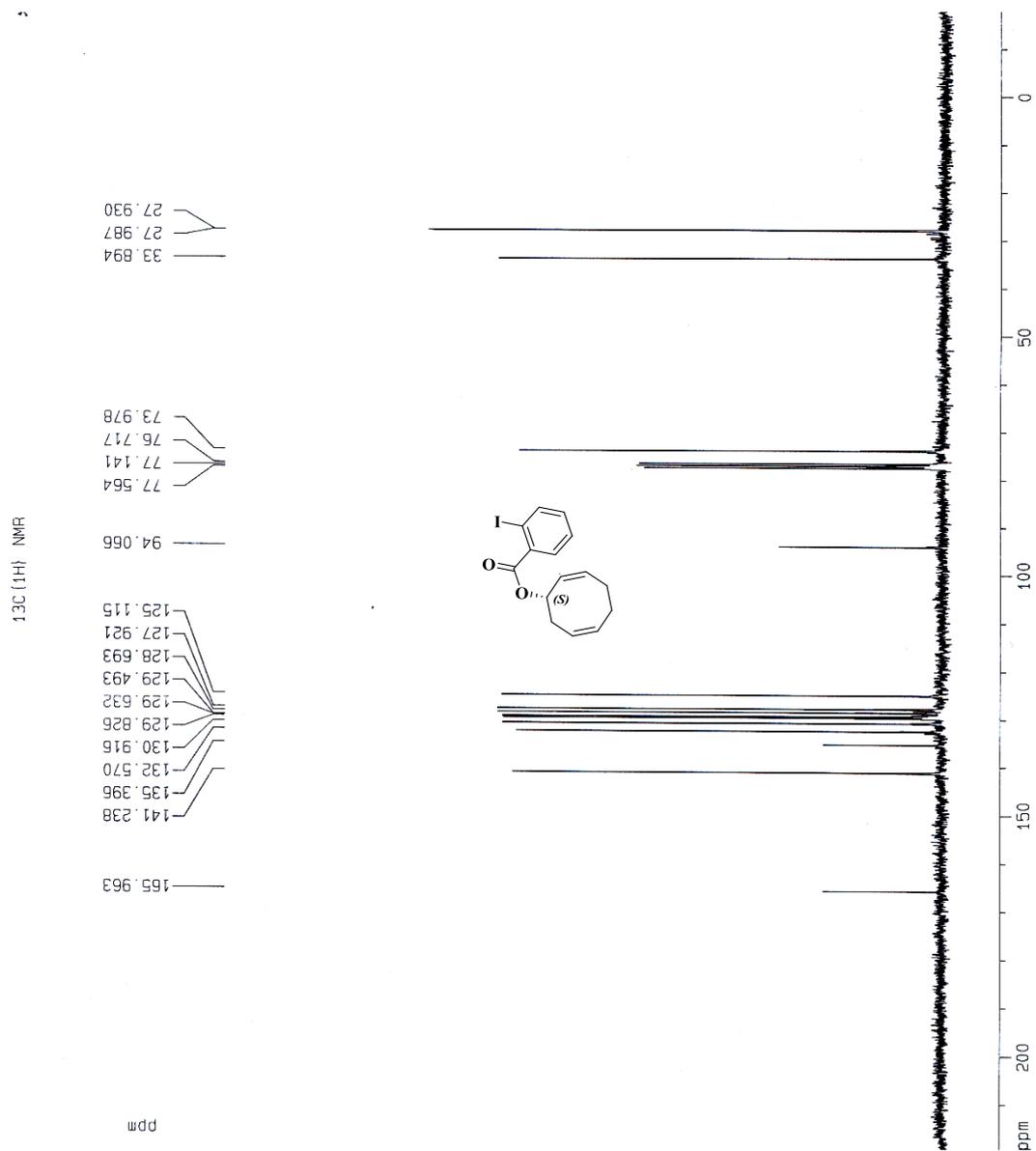
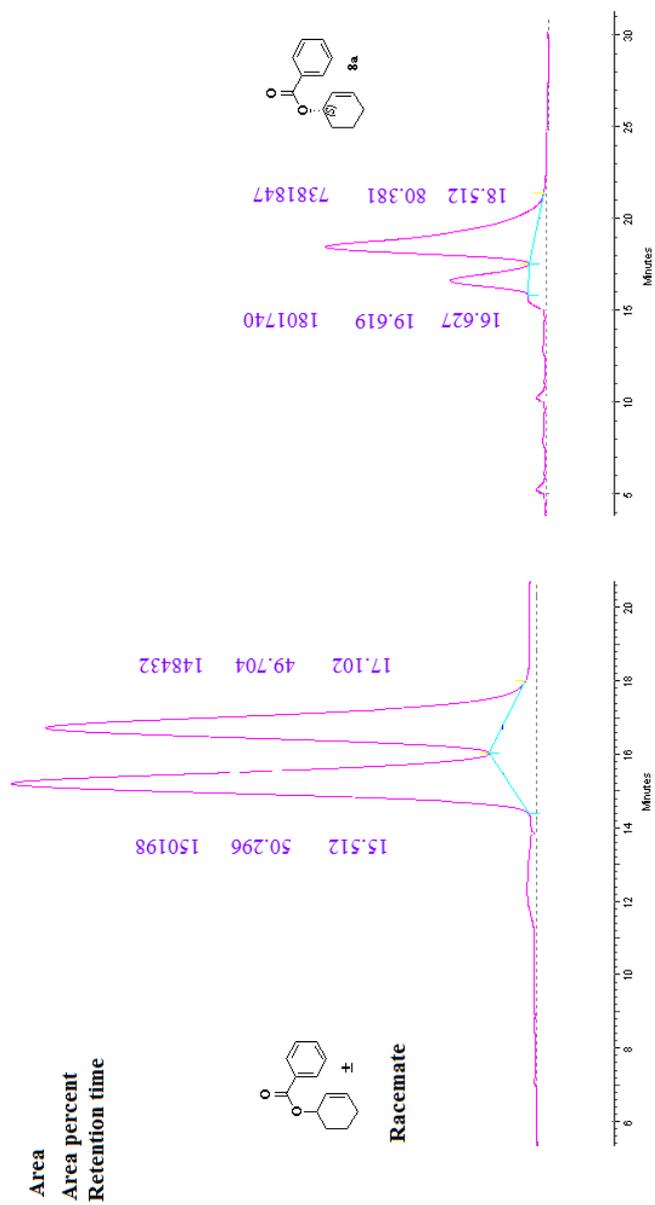
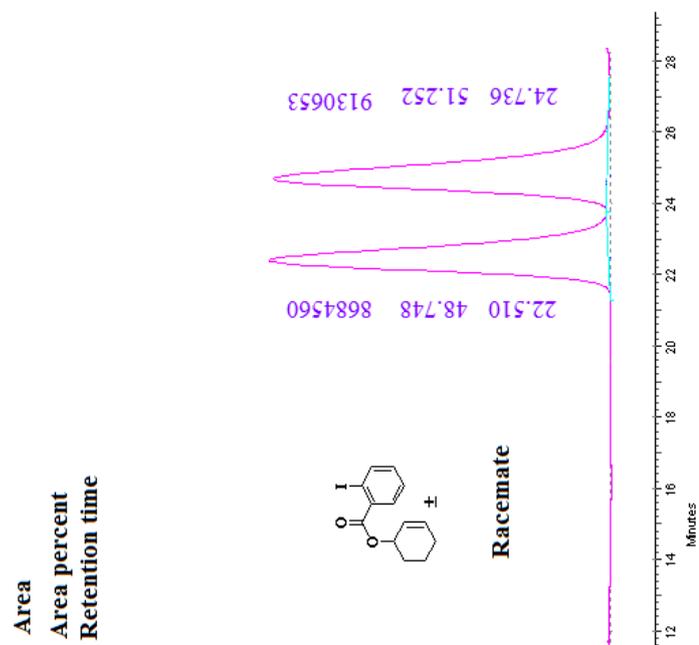
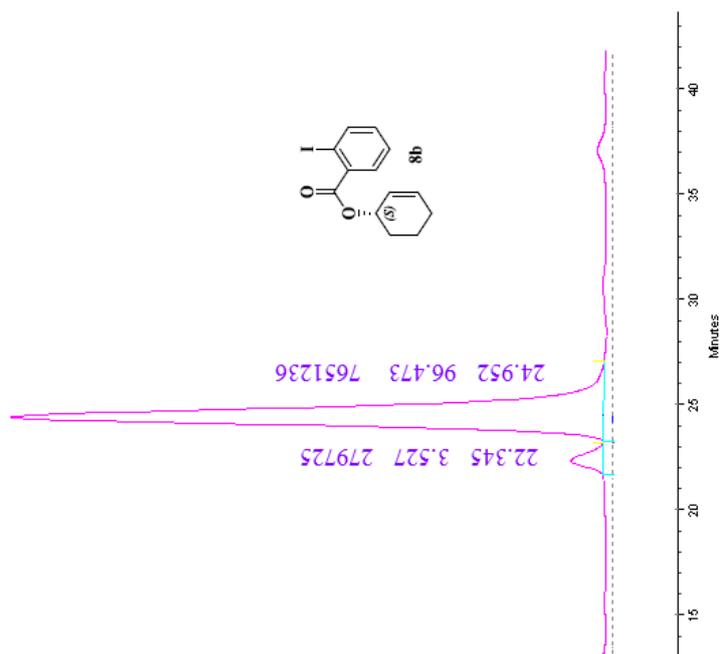


Figure S30: <sup>13</sup>CNMR of 11b



**Figure S31: Chromatogram of 8a**



**Figure S32: Chromatogram of 8b**

## REFERENCES:

- (1) McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. A convenient reduction of amino acids and their derivatives. *J. Org. Chem.* **1993**, *58*, 3568–3571.
- (2) Samadi, S.; Ashouri, A.; Ghambarian, M. Use of CuO encapsulated in mesoporous silica SBA-15 as a recycled catalyst for allylic C–H bond oxidation of cyclic olefins at room temperature. *RSC Adv.* **2017**, *7*, 19330–19337.
- (3) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* **1998**, *279*, 548–552.
- (4) Samadi, S.; Jadidi, K.; Khanmohammadi, B.; Tavakoli, N. Heterogenization of chiral mono oxazoline ligands by grafting onto mesoporous silica MCM-41 and their application in copper-catalyzed asymmetric allylic oxidation of cyclic olefins. *J. Catal.* **2016**, *340*, 344–353.
- (5) Andrus, M. B.; Asgari, D. Asymmetric allylic oxidation with biarylbisoxazoline-copper (I) catalysis. *Tetrahedron* **2000**, *56*, 5775–5780.
- (6) Sadjadi, S.; Samadi, S.; Samadi, M. Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> immobilized on halloysite as efficient heterogeneous catalyst for oxidation of allylic C–H bonds in olefins under mild reaction condition. *Res. Chem. Intermed.* **2019**, *45*, 2441–2455.
- (7) Samadi, S.; Ashouri, A.; Kamangar, S.; Pourakbari, F. 2-Aminopyrazine-functionalized MCM-41 nanoporous silica as a new efficient heterogeneous ligand for Cu-catalyzed allylic C–H bonds oxidation of olefins. *Res. Chem. Intermed.* **2020**, *46*, 557–569.
- (8) Samadi, S.; Jadidi, K.; Samadi, M.; Ashouri, A.; Notash, B. Designing chiral amido-oxazolines as new chelating ligands devoted to direct Cu-catalyzed oxidation of allylic C–H bonds in cyclic olefins. *Tetrahedron* **2019**, *75*, 862–867.
- (9) Samadi, S.; Jadidi, K.; Notash, B. Chiral bisoxazoline ligands with a biphenyl backbone: development and application in catalytic asymmetric allylic oxidation of cycloolefins. *Tetrahedron: Asymmetry* **2013**, *24*, 269–277.