

## Immobilization of (L)-valine and (L)-valinol on SBA-15 nanoporous silica and their application as chiral heterogeneous ligands in Cu-catalyzed asymmetric allylic oxidation of alkenes

Saadi Samadi\*, Akram Ashouri, Hersh I Rashid, Shiva Majidian and Mahsa Mahramasrar

*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*

### Supplementary Information

Page	List of contents	Page	List of contents
S1	Title, author's name, address	S22	Figure 17: <sup>1</sup> HNMR of 9c
S2-S5	Experimental section	S23	Figure 18: <sup>13</sup> CNMR of 9c
S6	Figure 1: <sup>1</sup> HNMR of 2	S24	Figure 19: <sup>1</sup> HNMR of 9d
S7	Figure 2: <sup>13</sup> CNMR of 2	S25	Figure 20: <sup>13</sup> CNMR of 9d
S8	Figure 3: <sup>1</sup> HNMR of 7c	S26	Figure 21: <sup>1</sup> HNMR of 10c
S9	Figure 4: <sup>13</sup> CNMR of 7c	S27	Figure 22: <sup>13</sup> CNMR of 10c
S10	Figure 5: <sup>1</sup> HNMR of 7d	S28	Figure 23: <sup>1</sup> HNMR of 10d
S11	Figure 6: <sup>13</sup> CNMR of 7d	S29	Figure 24: <sup>13</sup> CNMR of 10d
S12	Figure 7: <sup>1</sup> HNMR of 8a	S30	Figure 25: <sup>1</sup> HNMR of 10e
S13	Figure 8: <sup>13</sup> CNMR of 8a	S31	Figure 26: <sup>13</sup> CNMR of 10e
S14	Figure 9: <sup>1</sup> HNMR of 8b	S32	Figure 27: <sup>1</sup> HNMR of 11c
S15	Figure 10: <sup>13</sup> CNMR of 8b	S33	Figure 28: <sup>13</sup> CNMR of 11c
S16	Figure 11: <sup>1</sup> HNMR of 8c	S34	Figure 29: <sup>1</sup> HNMR of 11d
S17	Figure 12: <sup>13</sup> CNMR of 8c	S35	Figure 30: <sup>13</sup> CNMR of 11d
S18	Figure 13: <sup>1</sup> HNMR of 8d	S36	Figure 31: <sup>1</sup> HNMR of 11e
S19	Figure 14: <sup>13</sup> CNMR of 8d	S37	Figure 32: <sup>13</sup> CNMR of 11e
S20	Figure 15: <sup>1</sup> HNMR of 8e	S38	References
S21	Figure 16: <sup>13</sup> CNMR of 8e		

## Experimental

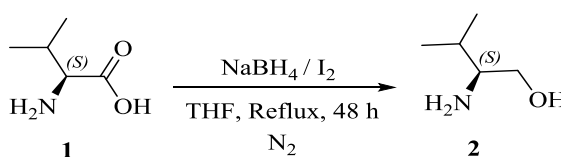
### Materials and characterization methods

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  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The morphology of nanoporous was investigated by a scanning electron microscope (FESEM-TESCAN MIRA3). TGA-DTA analysis was carried out from 0 to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  using a STA PT-1000 LINSEIS. The optical activity of chiral products was measured with Anton Paar Gyromat Digital Automatic 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 dry and oxygen-free nitrogen atmosphere. 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.

### The synthesis of (*S*)-2-amino-3-methylbutane-1-ol (**2**)

To an oven dried 3-neck 250 mL round-bottom flask, 5.5 mmol (1.95 g) of sodium-borohydride and 25 mL of dry tetrahydrofuran were added under nitrogen atmosphere. After 20 minutes, 21.3 mmol (2.5 g) of L-valine amino acid (**1**) was added to the reaction mixture and stirred for 10 minutes. Then the reaction temperature was reduced to  $0^\circ\text{C}$  and a solution of 21.3 mmol (5.4 g) iodine in 6.5 mL of tetrahydrofuran was added slowly. After disappearing of brownish color of solution, the mixture was warmed to room temperature and then refluxed for 48 hours. After completion of the reaction and cooling to room temperature, 10 mL of methanol

was added for completely neutralization of unreacted sodiumborohydride and stirred for one hour. After solvent evaporation the white precipitate was dissolved in 15 mL of KOH (20%) and stirred at room temperature for 4 hours. The aqueous solution was extracted with dichloromethane ( $5 \times 15$  mL) and the organic layer was dried over anhydrous  $\text{MgSO}_4$ . After evaporation of dichloromethane, the *S*-2-amino-3-methylbutane-1-ol (L-valinol) was obtained in 90% yield <sup>1</sup>(Scheme S1). The structure of the product was confirmed by <sup>1</sup>HNMR, <sup>13</sup>CNMR spectra (Figures S6 and S7).



**Scheme S1:** Synthesis of (*S*)-2-amino-3-methylbutane-1-ol

**(*S*)-2-amino-3-methylbutan-1-ol:** <sup>1</sup>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,  $(\text{NH}_2)$ ).; <sup>13</sup>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).

### The synthesis of various peresters from several derivatives of benzoic acid

Under nitrogen atmosphere, to a 50 mL round bottom flask, 5 mmol benzoic acid derivative, and 15 mL dried dichloromethane were added. Then at 0 °C, 20 mmol (1.45 mL) of thionyl chloride was slowly added and stirred for 8 hours. After completion of the reaction, the solvent evaporated and the acyl chloride derivative was obtained in high yields up to 99%. Next, the synthesized acyl chloride derivative was dissolved in 15 mL of dried dichloromethane and cooled to -20 °C, and then 5.75 mmol (0.45 mL) of pyridine and 5.75 mmol (0.55 mL) of *tert*-butylhydroperoxide were added. The reaction progress was monitored by thin-layer chromatography (TLC) and, after completion of the reaction, extracted with dichloromethane ( $4 \times 15$  mL) and washed with 5% sodium bicarbonate (5%) and hydrochloric acid (5%) (Scheme 2). Peresters derivatives were obtained with 85% -95% yields (Scheme 2). The structure of the synthesized peresters was confirmed by FT-IR, <sup>1</sup>HNMR and <sup>13</sup>C NMR spectroscopy techniques<sup>2-4</sup>.

***Tert*-butyl-4-nitrobenzoperoxoate (7c)**<sup>1,5-7</sup>: Mp: 76-78 °C (lit.75-78 °C); <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.

***Tert*-butyl-2-iodobenzoperoxoate (7d)**<sup>1,5-7</sup>: Mp: 47-49 °C.; <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.

## 2.2. Enantioselective allylic C-H bonds oxidation of alkenes

Prior to the reaction, the Schlenk tube was dried for 2 h at 100 °C. Then under nitrogen atmosphere at room temperature, 6 mg of chiral heterogeneous ligand, 0.027 mmol (10 mg) of Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> and 2 mL of acetonitrile were added and stirred for 2 hours. Next, 5 mmol of alkene and 0.85 mmol of perester (Pages S3 and S4 and Figures S8–S11) were added and the reaction temperature was increased to 50 °C (Scheme 2). The reaction progress was monitored by thin layer chromatography (TLC), and after completion of the reaction, the reaction mixture was filtered and the residual catalyst was washed with water and ethyl acetate (3 times) and finally dried. For extraction, 5 mL of ammonia solution (5%) was added to the filtrated solution and then separated organic layers were washed with 5 mL of sodium bicarbonate (5%). The structure of synthesized chiral allylic esters was confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy techniques (Pages S4 and S5 and Figures S12–S37)<sup>3,4</sup>.

***(S)*-Cyclohex-2-en-1-yl benzoate (8a)**<sup>5-7</sup>: [α]<sub>D</sub><sup>20</sup> = –20.3° (c 1.0, CHCl<sub>3</sub>).; The optical purity was determined by HPLC with Chiralcel OD-H column; eluent: *n*-Hexane/Isopropyl alcohol = 99.7/0.3; Flow rate: 0.6 mL/min; t<sub>R</sub> = 16.6 min (*R*), 18.5 min (*S*) (Maximum ee = 25% ).

***(S)*- Cyclohex-2-en-1-yl 4-chlorobenzoate (8b)**<sup>5-7</sup>: [α]<sub>D</sub><sup>20</sup> = –39.4° (c 1.0, CHCl<sub>3</sub>); The optical purity was determined by HPLC with Chiralpak AD column; eluent: *n*-Hexane/Isopropyl alcohol = 99.7/0.3; Flow rate: 0.6 mL/min; t<sub>R</sub> = 22.8 min (*R*), 24.3 min (*S*) (Maximum ee = 30%).

***(S)*-Cyclohex-2-en-1-yl 4-nitrobenzoate (8c)**<sup>5-7</sup>: [α]<sub>D</sub><sup>20</sup> = –50.9° (c 1.0, CHCl<sub>3</sub>); The optical purity was determined by HPLC with Nucleocel Alpha S column; eluent: *n*-Hexane/Isopropyl alcohol = 99.5/0.5; Flow rate: 0.5 mL/min; t<sub>R</sub> = 29.0 min (*R*), 31.5 min (*S*) (Maximum ee = 42% ).

**(S)-Cyclohex-2-en-1-yl 2-iodobenzoate (8d)** <sup>1,5-7</sup>:  $[\alpha]_{\text{D}}^{20} = -37.3^{\circ}$  (c 1.0, CHCl<sub>3</sub>); The optical purity was determined by HPLC with Chiralpak AD column; eluent: *n*-Hexane/Isopropyl alcohol = 99.6/0.4; Flow rate: 0.6 mL/min;  $t_{\text{R}} = 22.3$  min (*R*), 24.9 min (*S*) (Maximum ee = 32%).

**(S) Cyclohex-2-en-1-yl 4-iodobenzoate (8e)** <sup>1,5-7</sup>:  $[\alpha]_{\text{D}}^{20} = -30.0^{\circ}$  (c 1.0, CHCl<sub>3</sub>); The optical purity was determined by HPLC with Chiralpak AD column; eluent: *n*-Hexane/Isopropyl alcohol = 99.7/0.3; Flow rate: 0.5 mL/min;  $t_{\text{R}} = 24.2$  min, 25.8 min (Maximum ee = 34%).

**(S)-Cyclopent-2-en-1-yl 4-nitrobenzoate (9c)** <sup>5-7</sup>:  $[\alpha]_{\text{D}}^{20} = -52.8^{\circ}$  (c 1.0, CHCl<sub>3</sub>); The optical purity was determined by HPLC with Nucleocel Alpha S column; eluent: *n*-Hexane/Isopropyl alcohol = 99.5/0.5; Flow rate: 0.4 mL/min;  $t_{\text{R}} = 35.1$  min (*R*), 36.7 min (*S*) (Maximum ee = 31%).

**(S)-Cyclopent-2-en-1-yl 2-iodobenzoate (9d)** <sup>5-7,8</sup>:  $[\alpha]_{\text{D}}^{20} = -48.0^{\circ}$  (c 1.0, CHCl<sub>3</sub>); The optical purity was determined by HPLC with Chiralpak AD column; eluent: *n*-Hexane/Isopropyl alcohol = 99.6/0.4; Flow rate: 0.6 mL/min;  $t_{\text{R}} = 20.5$  min (*R*), 22.3 min (*S*) (Maximum ee = 23%).

**(S)-Cyclooct-2-en-1-yl 4-nitrobenzoate (10c)** <sup>5-7</sup>:  $[\alpha]_{\text{D}}^{20} = +10.4^{\circ}$  (c 1.0, CHCl<sub>3</sub>); Optical purity was determined by HPLC with Chiralcel OD-H column; eluent: *n*-Hexane/Isopropyl alcohol = 99.5/0.5; Flow rate: 0.4 mL/min;  $t_{\text{R}} = 18.3$  min (*R*), 21.8 min (*S*) (Maximum ee = 26% ).

**(S)-Cyclooct-2-en-1-yl 2-iodobenzoate (10d)** <sup>5-7,9</sup>:  $[\alpha]_{\text{D}}^{20} = +19.5^{\circ}$  (c 1.0, CHCl<sub>3</sub>); Optical purity was determined by HPLC with Chiralpak AD column; eluent: *n*-Hexane/Isopropyl alcohol = 99.6/0.4; Flow rate: 0.6 mL/min;  $t_{\text{R}} = 16.5$  min (*R*), 19.1 min (*S*) (Maximum ee = 20%).

**(S)-Cyclooct-2-en-1-yl 4-iodobenzoate (10 e)** <sup>1,5-7</sup>:  $[\alpha]_{\text{D}}^{20} = +7.6^{\circ}$  (c 1.0, CHCl<sub>3</sub>); Optical purity was determined by HPLC with Chiralcel OD-H column; eluent: *n*-Hexane/Isopropyl alcohol = 99.5/0.5; Flow rate: 0.4 mL/min;  $t_{\text{R}} = 17.0$  min, 20.5 min (Maximum ee = 22% ).

**(S)-Cycloocta-2,6-dien-1-yl 4-nitrobenzoate (11c)** <sup>5-7</sup>:  $[\alpha]_{\text{D}}^{20} = +7.0^{\circ}$  (c 1.0, CHCl<sub>3</sub>); Optical purity was determined by HPLC with Chiralcel OD-H column column; eluent: *n*-Hexane/Isopropyl alcohol = 99.3/0.7; Flow rate: 0.4 mL/min;  $t_{\text{R}} = 31.5$  min (*S*), 33.7 min (*R*) (Maximum ee = 36%).

**(S)-Cycloocta-2,6-dien-1-yl 2-iodobenzoate (11d)**:  $[\alpha]_{\text{D}}^{20} = +8.7^{\circ}$  (c 1.0, CHCl<sub>3</sub>); Optical purity was determined by HPLC with Chiralcel OD-H column; eluent: *n*-Hexane/Isopropyl alcohol = 99.6/0.4; Flow rate: 0.6 mL/min;  $t_{\text{R}} = 28.3$  min (*S*), 30.4 min (*R*) (Maximum ee = 27%).

**(S)-Cycloocta-2,6-dien-1-yl 4-iodobenzoate (11e)** <sup>1,5-7</sup>:  $[\alpha]_{\text{D}}^{20} = +5.8^{\circ}$  (c 1.0, CHCl<sub>3</sub>); Optical purity was determined by HPLC with Chiralcel OD-H column column; eluent: *n*-Hexane/Isopropyl alcohol = 99.3/0.7; Flow rate: 0.4 mL/min;  $t_{\text{R}} = 27.5$  min, 31.2 min (Maximum ee = 32%).

Sample code:Val (Dr.Samadi)



NAME Kurdestan UN  
EXPNO 1  
PROCNO 430  
Date\_ 20180905  
Time 11.01  
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 4.0894956 sec  
RG 62.400 usec  
DE 6.50 usec  
TE 296.3 K  
D1 4.0000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL 0.00 dB  
PL1W 11.86359406 dB  
SFO1 400.2236020 MHz  
SI 32768  
SF 400.2200000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

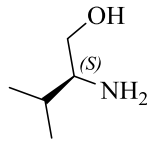
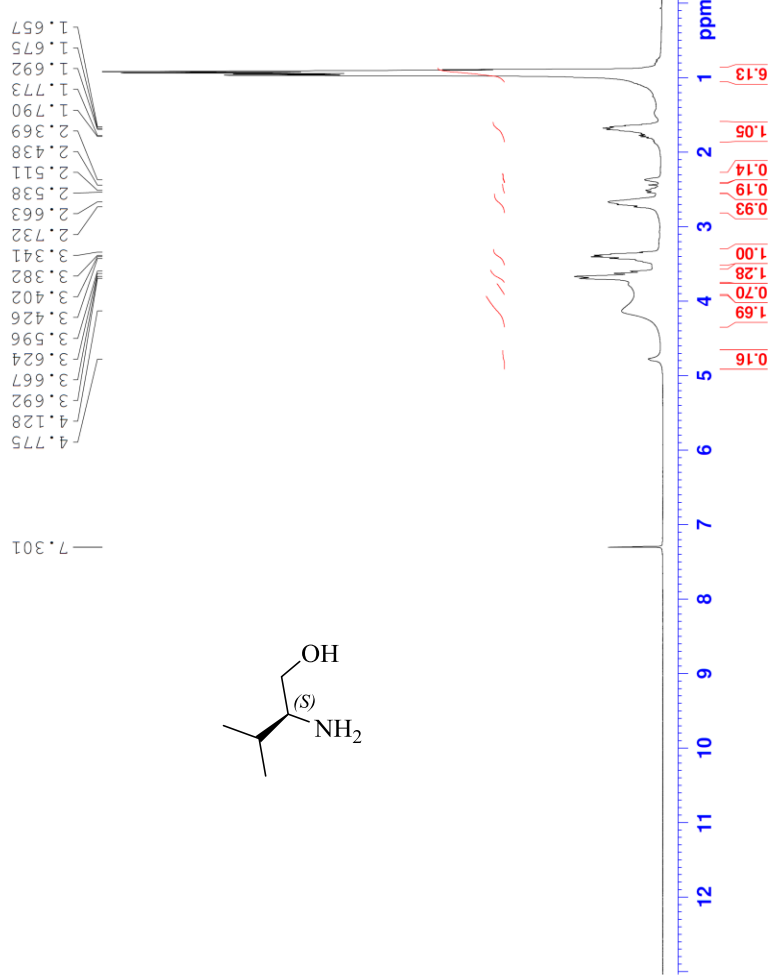


Figure S1: <sup>1</sup>H NMR spectrum of (S)-2-amino-3-methylbutane-1-ol (2)



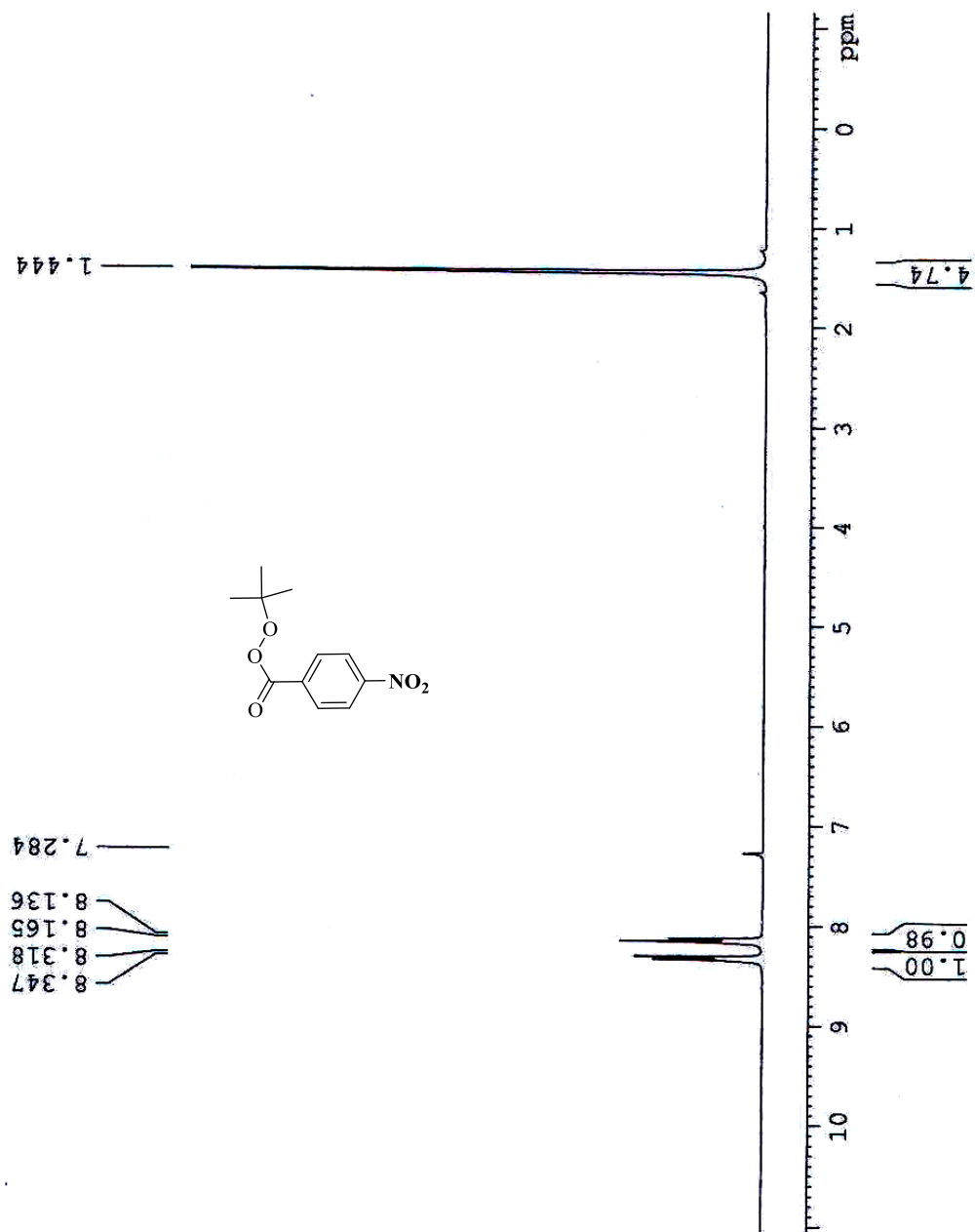


Figure S3: <sup>1</sup>H NMR spectrum of tert-butyl-para-nitrobenzoate (7c)



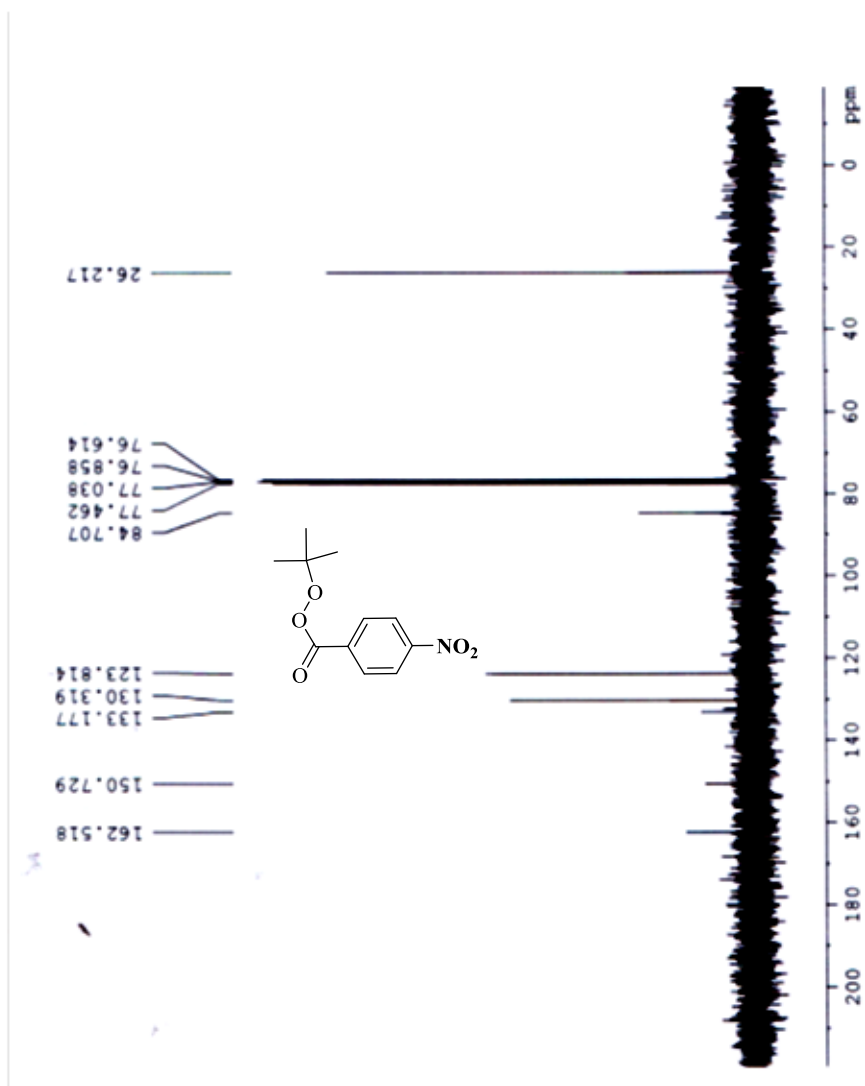


Figure S4:  $^{13}\text{C}$  NMR spectrum of tert-butyl-para-nitroperbenzoate (7c)

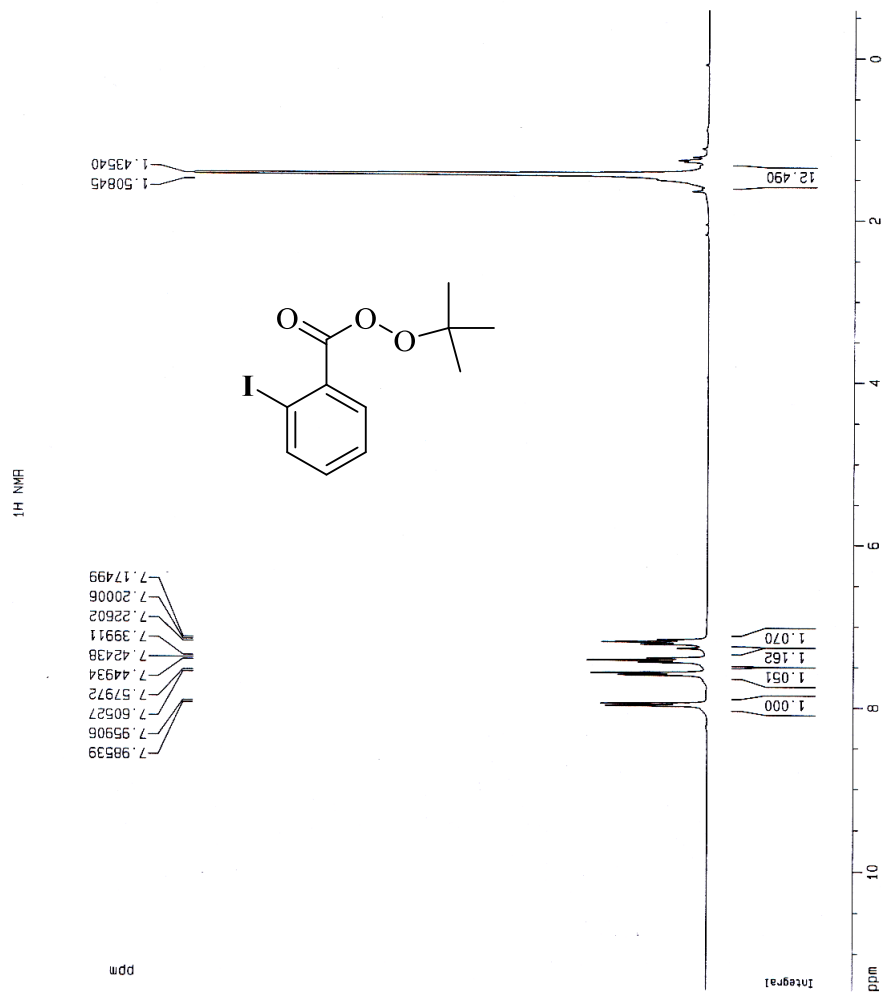


Figure S5: <sup>1</sup>H NMR spectrum of tert-butyl 2-iodobenzoate (7d)



Figure S6: <sup>13</sup>C NMR spectrum of tert-butyl 2-iodobenzoate (7d)

Sample code:E1 (Dr.Samadi)



NAME Kurdestan\_ON  
EXPNO 427  
PROCNO 1  
Time 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 1.00 usec  
TE 293.1 K  
D1 26.01 sec  
D11 4.00000000 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

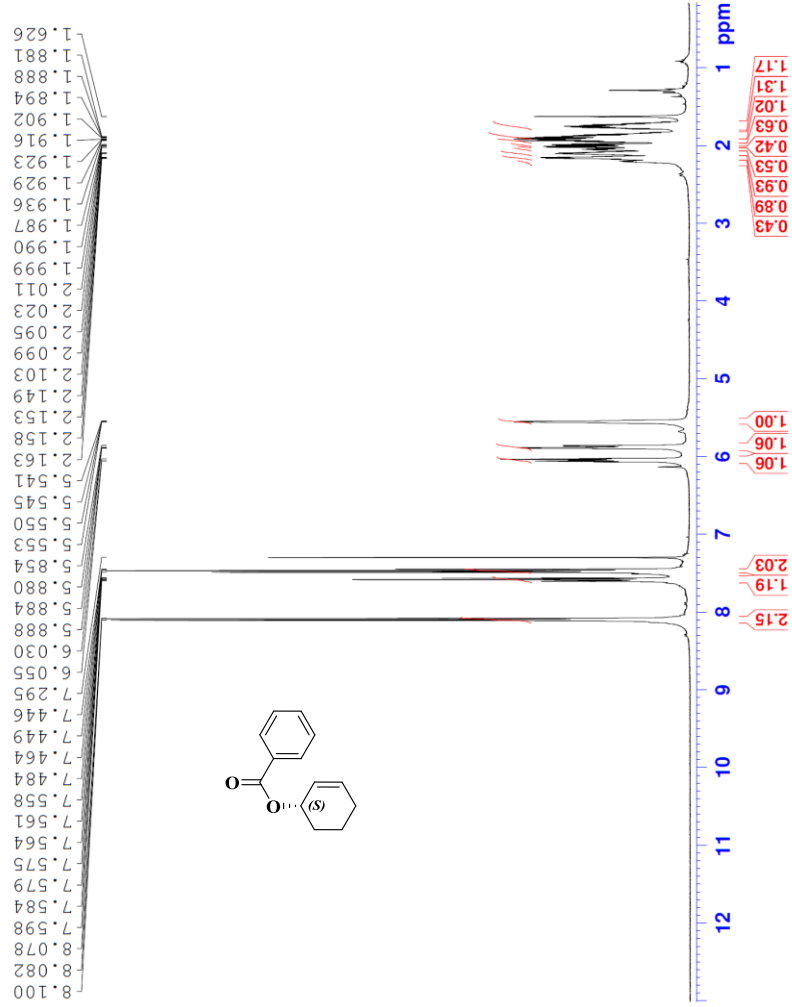


Figure S7: <sup>1</sup>H NMR spectrum of (S)-cyclohex-2-en-1-yl-benzoate (8a)

Sample code: E1 (Dr. Samadi)



NAME Kurdistan UN  
EXPNO 440  
PROCNO 1  
Date\_ 20180910  
Time 8.10  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
ID 65536  
SOLVENT CDCl3  
NS 320  
DS 3  
SRH 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 <sup>13</sup>C  
PI 9.00 usec  
PL1 -0.30 dB  
PL1W 42.02801895 W  
SFO1 100.6479784 MHz

===== CHANNEL f2 =====  
CFDPRG2 waltz16  
NUC2 <sup>1</sup>H  
PCPD2 90.00 usec  
PL2 -2.00 dB  
PL12 14.16 dB  
PL13 11.86350406 dB  
PL12W 0.28722104 W  
PL13W 0.12139934 W  
SFO2 400.2216009 MHz  
SI 32768  
SF 100.6353990 MHz  
WDW EM  
SBB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

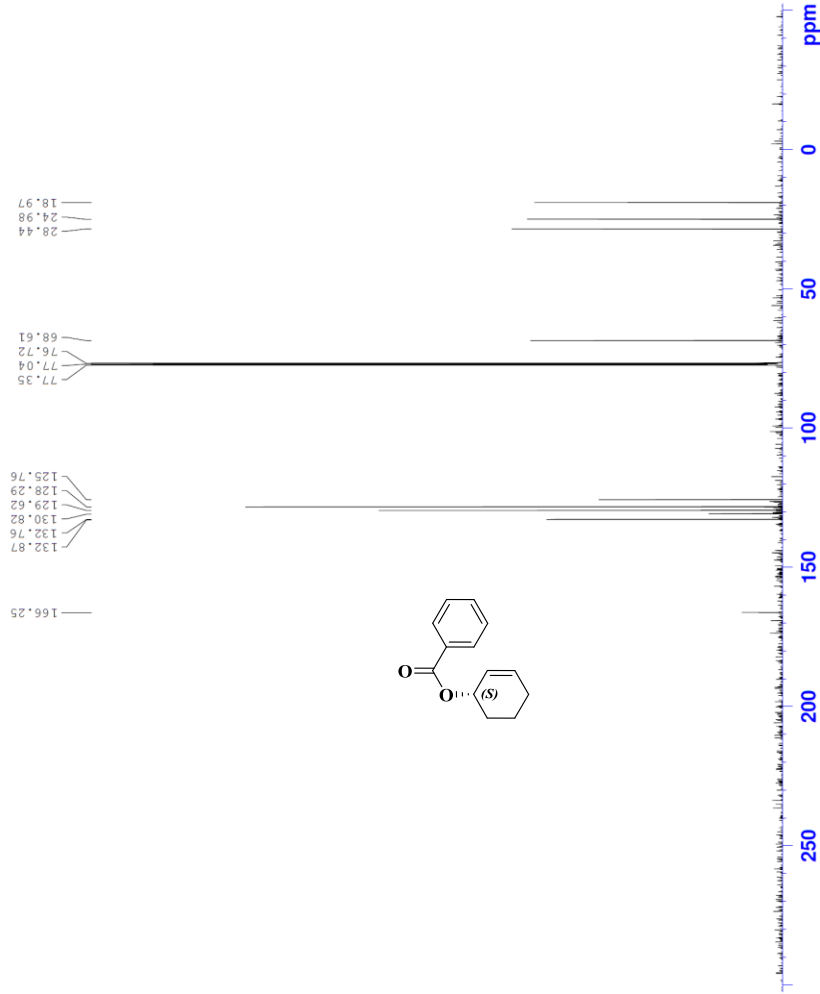


Figure S8: <sup>13</sup>C NMR spectrum of (S)-cyclohex-2-en-1-yl-benzoate (8a)



Sample code: E2 (Dr. Samadi)

1.730  
1.736  
1.744  
1.750  
1.756  
1.764  
1.842  
1.849  
1.856  
1.867  
1.874  
1.882  
1.888  
1.901  
1.908  
1.915  
1.921  
1.934  
1.966  
1.976  
1.987  
2.000  
2.011  
2.084  
2.090  
2.094  
2.097  
2.147  
2.152  
2.156  
2.524  
5.529  
5.835  
5.839  
5.843  
5.860  
5.864  
6.022  
6.031  
6.040  
6.056  
7.295  
7.419  
7.440  
8.004  
8.025

NAME Kurdestan\_UN  
EXPNO 426  
PROCNO 1  
Date\_ 20180905  
Time 9:52  
INSTRUM spect  
PROBHD 5 mm PABBO  
PULPROG zgpg30  
TD 65536  
FIDRES 0.2370  
SOLVENT CDCl3  
NS 20  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 327.680  
WDW 62.400 usec  
DE 6.50 usec  
TE 295.7 K  
D1 4.00000000 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

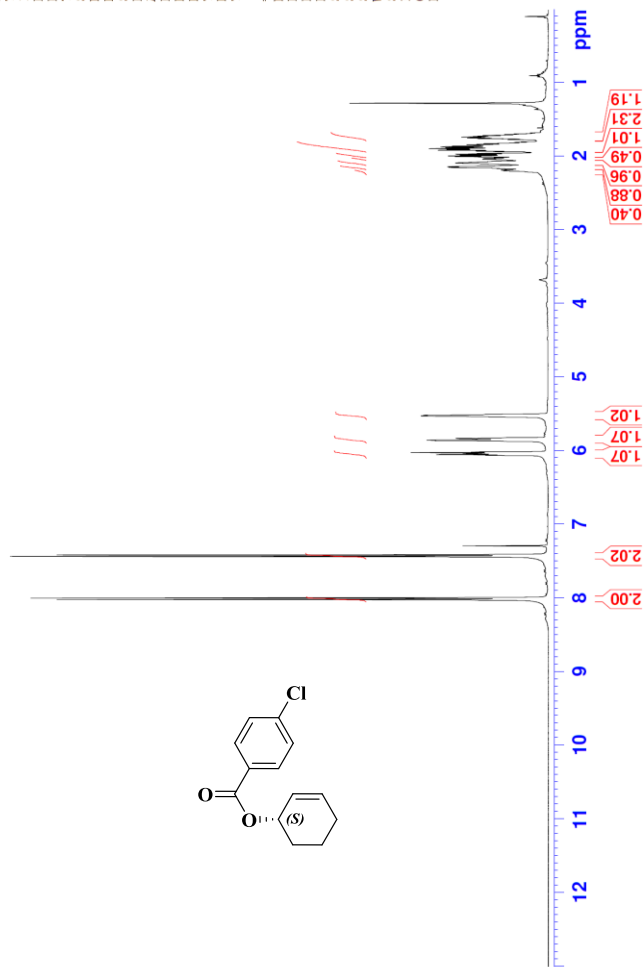


Figure S9: <sup>1</sup>H NMR spectrum of (S)-cyclohex-2-en-1-yl-4-chlorobenzoate (8b)



N2  
1H NMR

```

Current Data Parameters
NAME      8c-1
EXPNO     47
PROCNO    1

F2 - Acquisition Parameters
Date_     20110902
Time      15:51
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         10
DS         1
SWH        7912.500 Hz
FIDRES     0.211500 Hz
AQ         2.6972021 sec
RG         50.8
DW         64.000 usec
DE         16.00 usec
TE         300.2 K
D1         2.00000000 sec

***** CHANNEL f1 *****
NUC1       13C
P1         14.00 usec
PL1        3.00 dB
SFO1       300.13223986 MHz

F2 - Processing parameters
SI         32768
SF         300.1300000 MHz
EQ         EM
SSB        0
GB         0
CB         0
PC         1.00
  
```

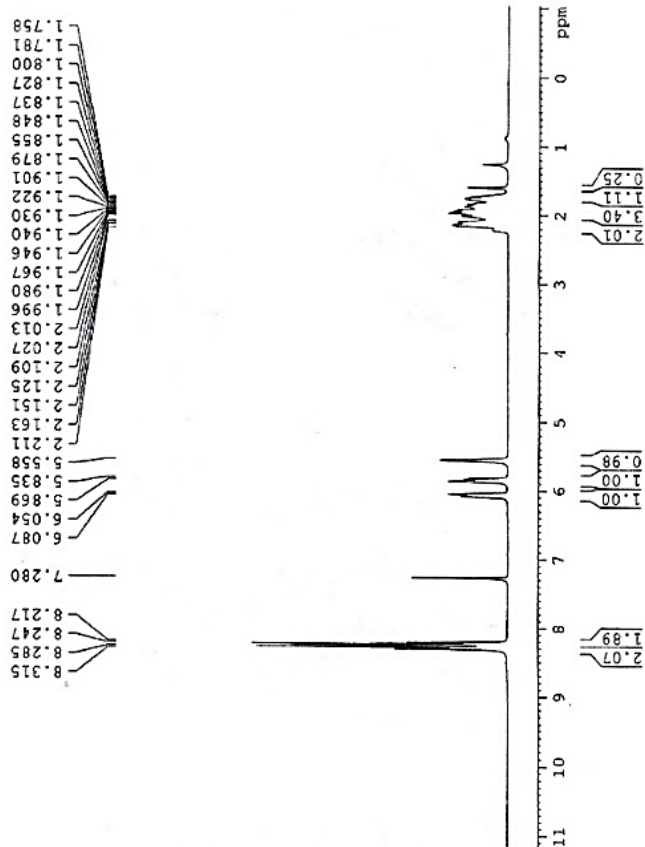


Figure S11: <sup>1</sup>H NMR spectrum of (S)-cyclohex-2-en-1-yl-4-nitrobenzoate (8c)



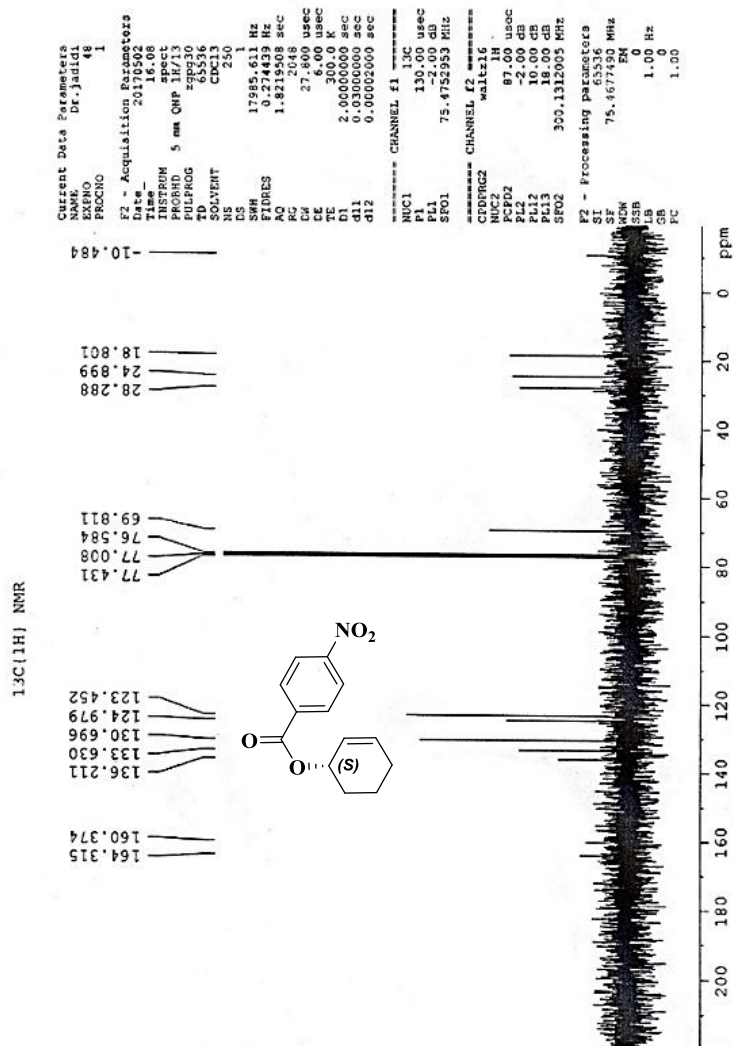


Figure S12: <sup>13</sup>C NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-nitrobenzoate (8c)

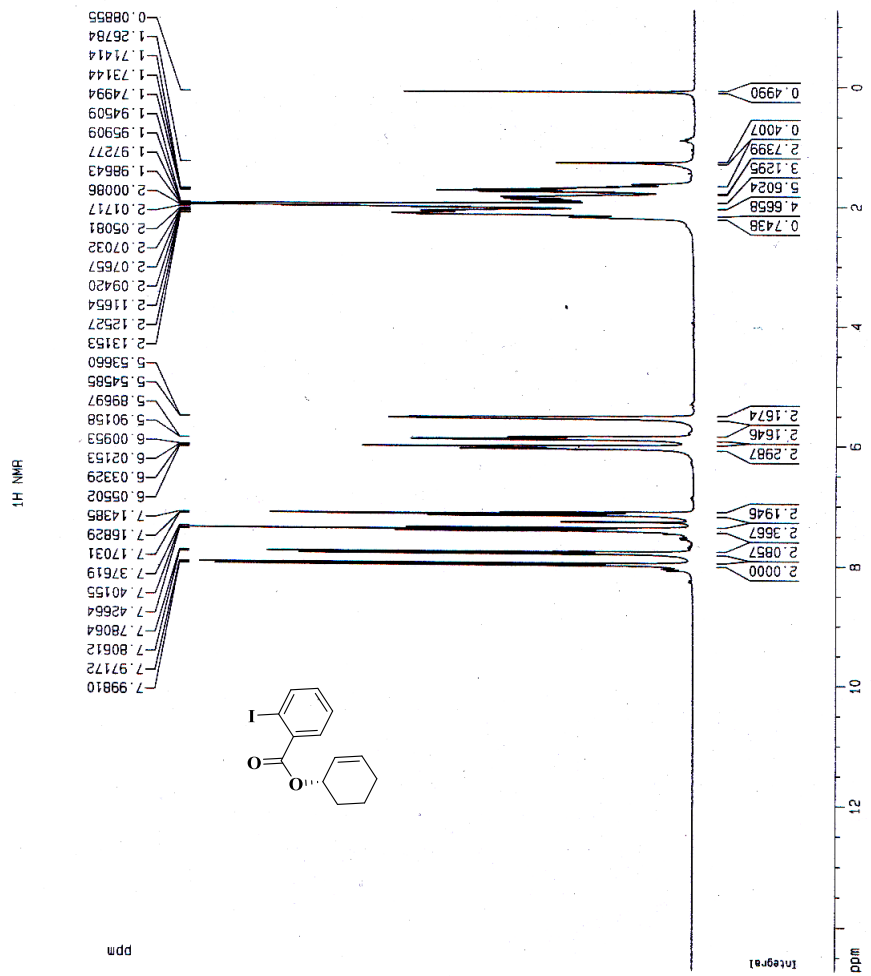


Figure S13: <sup>1</sup>H NMR spectrum of (*S*)-cyclohex-2-en-1-yl-2-iodobenzoate (8d)

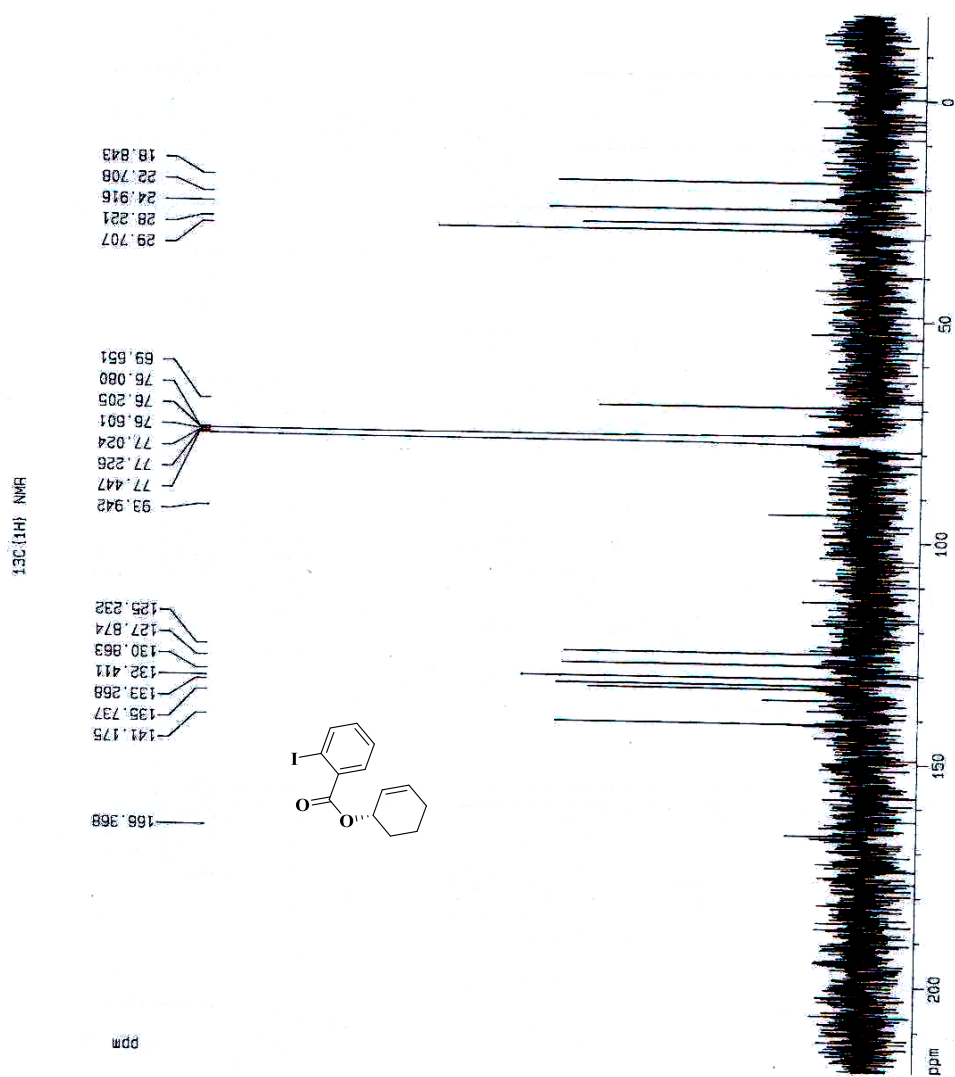


Figure S14: <sup>13</sup>C NMR spectrum of (S)-cyclohex-2-en-1-yl-2-iodobenzoate (8d)

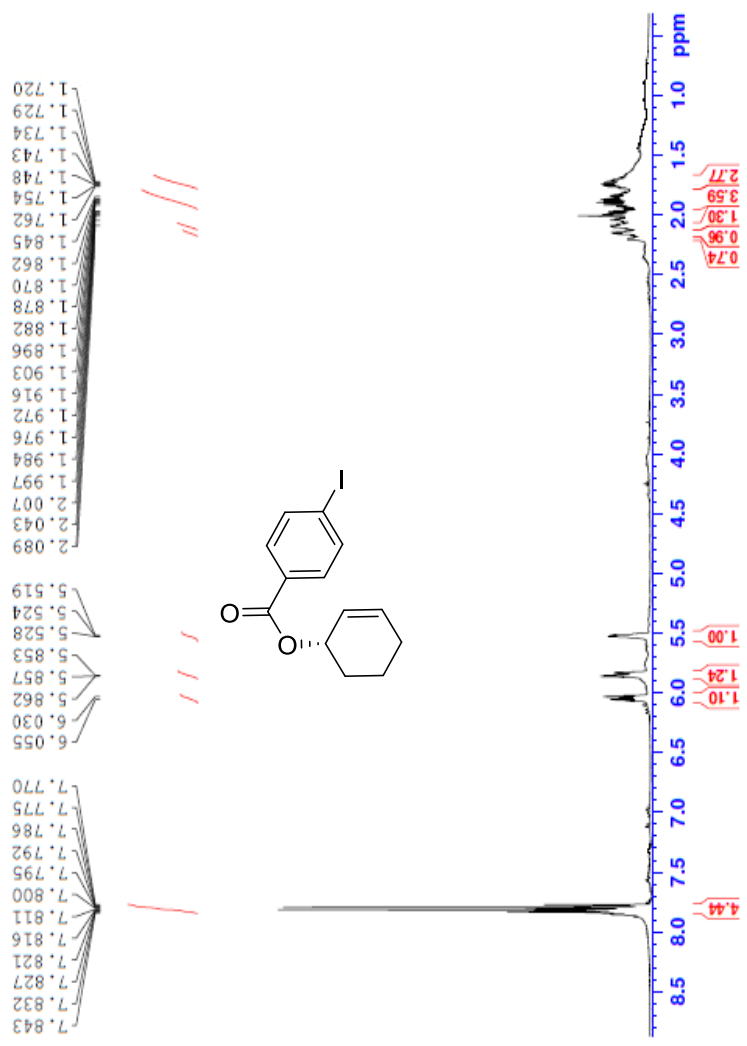


Figure S15:  $^1\text{H}$  NMR spectrum of (S)-cyclohex-2-en-1-yl-4-iodobenzoate (8c)

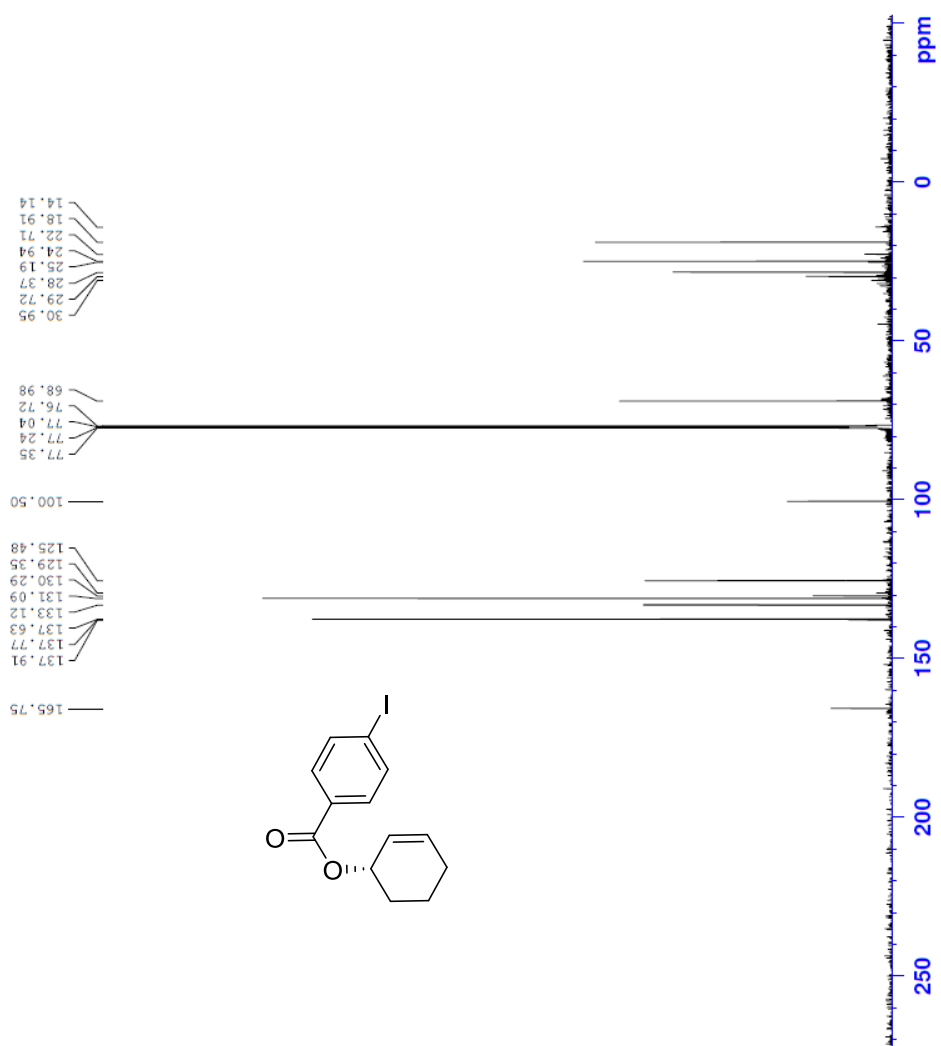


Figure S16: <sup>13</sup>C NMR spectrum of (S)-cyclohex-2-en-1-yl-4-iodobenzoate (8e)

<sup>1</sup>H NMR

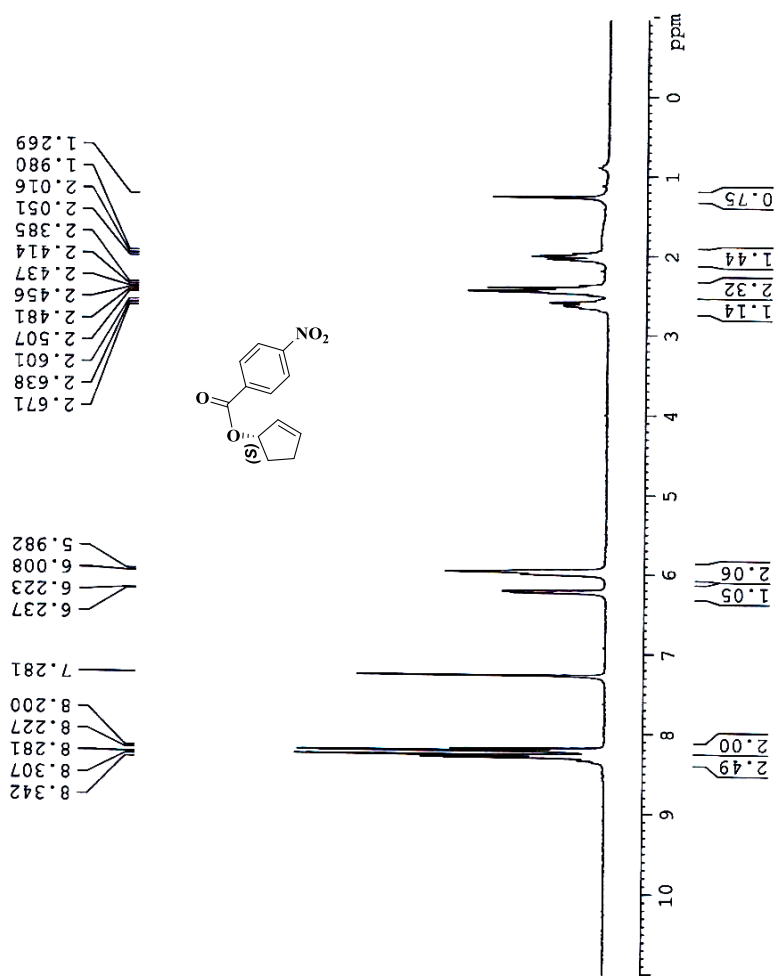


Figure S17: <sup>1</sup>H NMR spectrum of (S)-cyclopenta-2-en-1-yl-4-nitrobenzoate (9c)

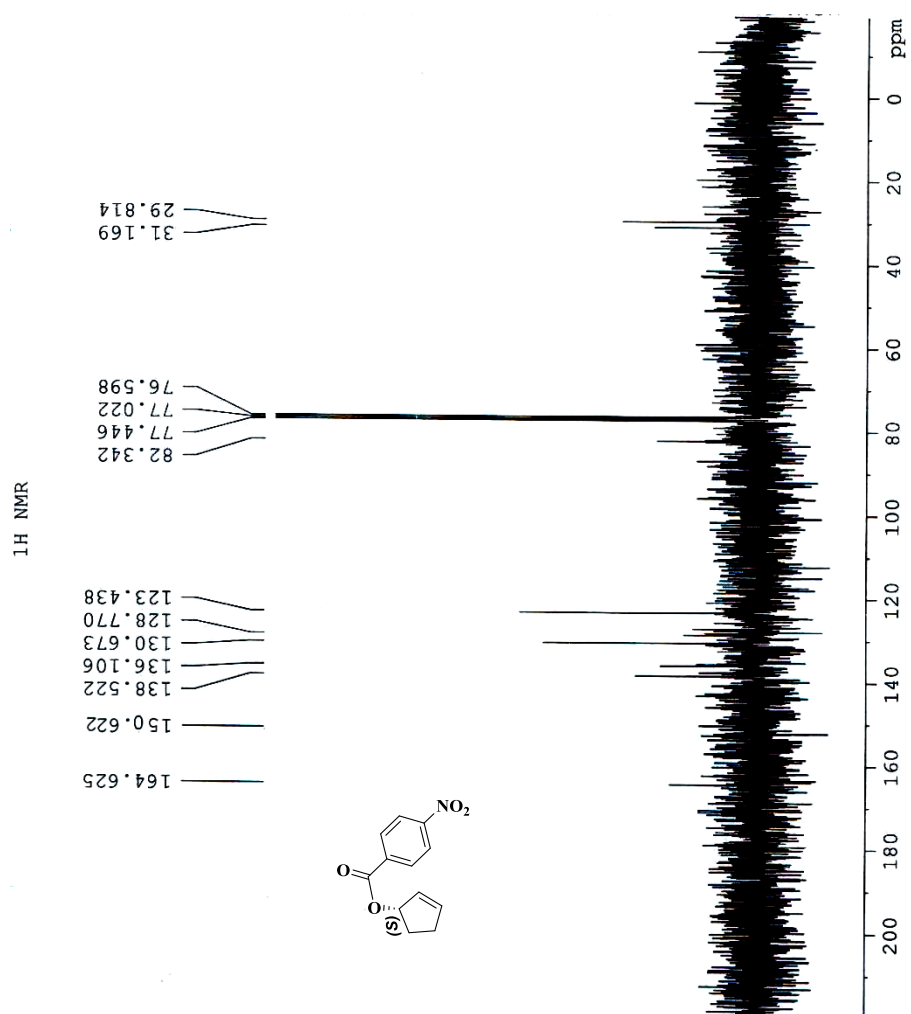


Figure S18: <sup>13</sup>C NMR spectrum of (S)-cyclopenta-2-en-1-yl-4-nitrobenzoate (9c)

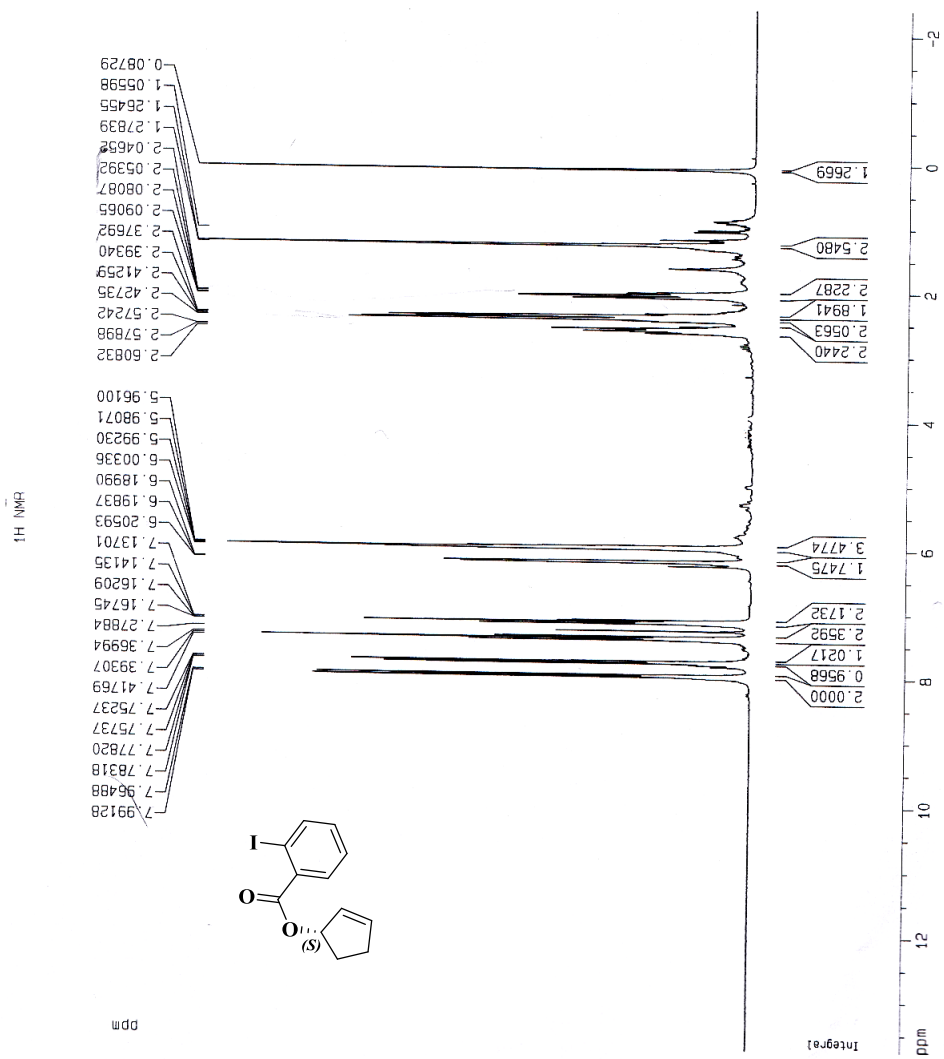


Figure S19: <sup>1</sup>H NMR spectrum of (*S*)-cyclopenta-2-en-1-yl-2-iodobenzoate (9d)



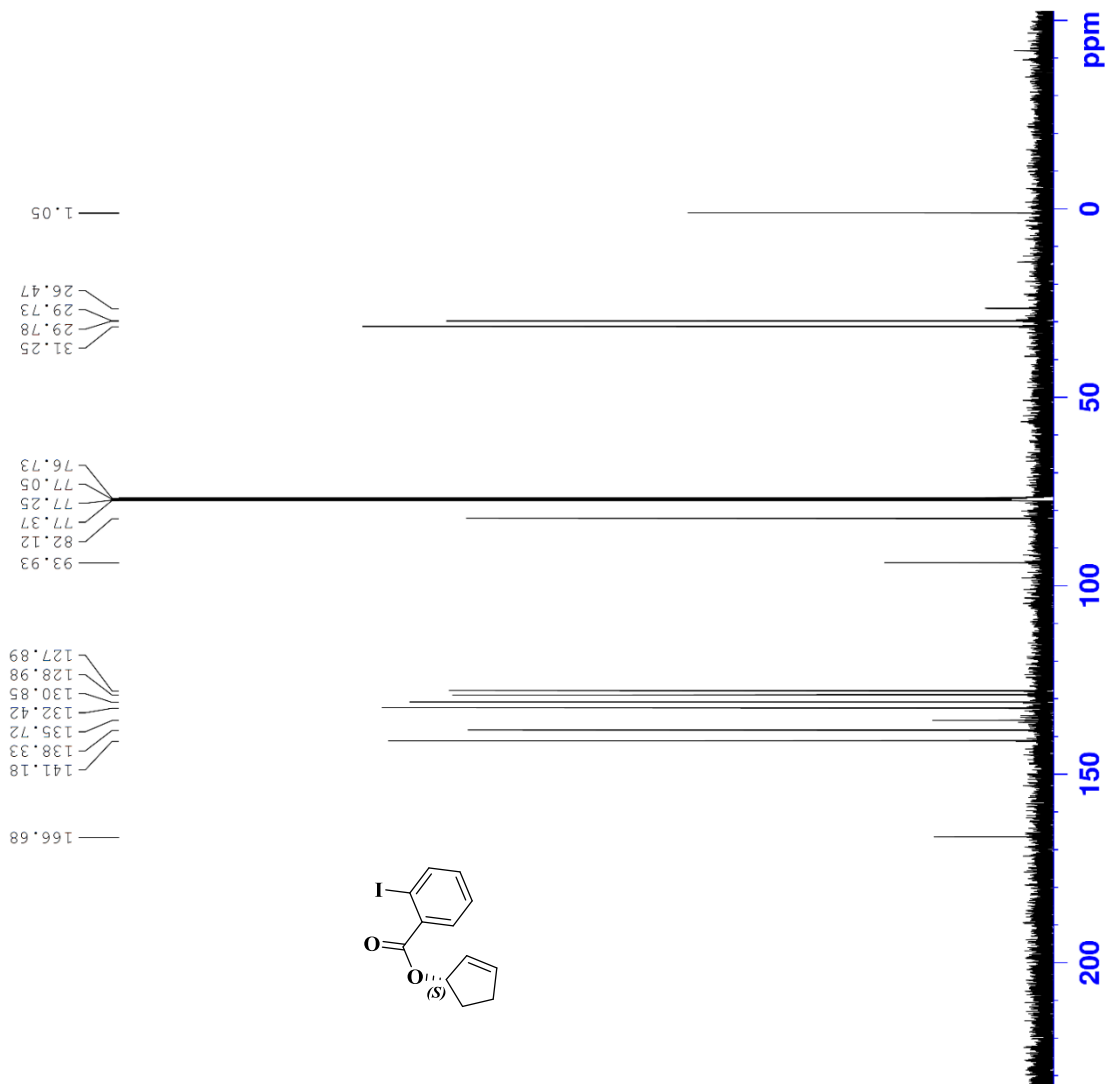


Figure S20: <sup>13</sup>C NMR spectrum of (S)-cyclopenta-2-en-1-yl-2-iodobenzoate (9d)

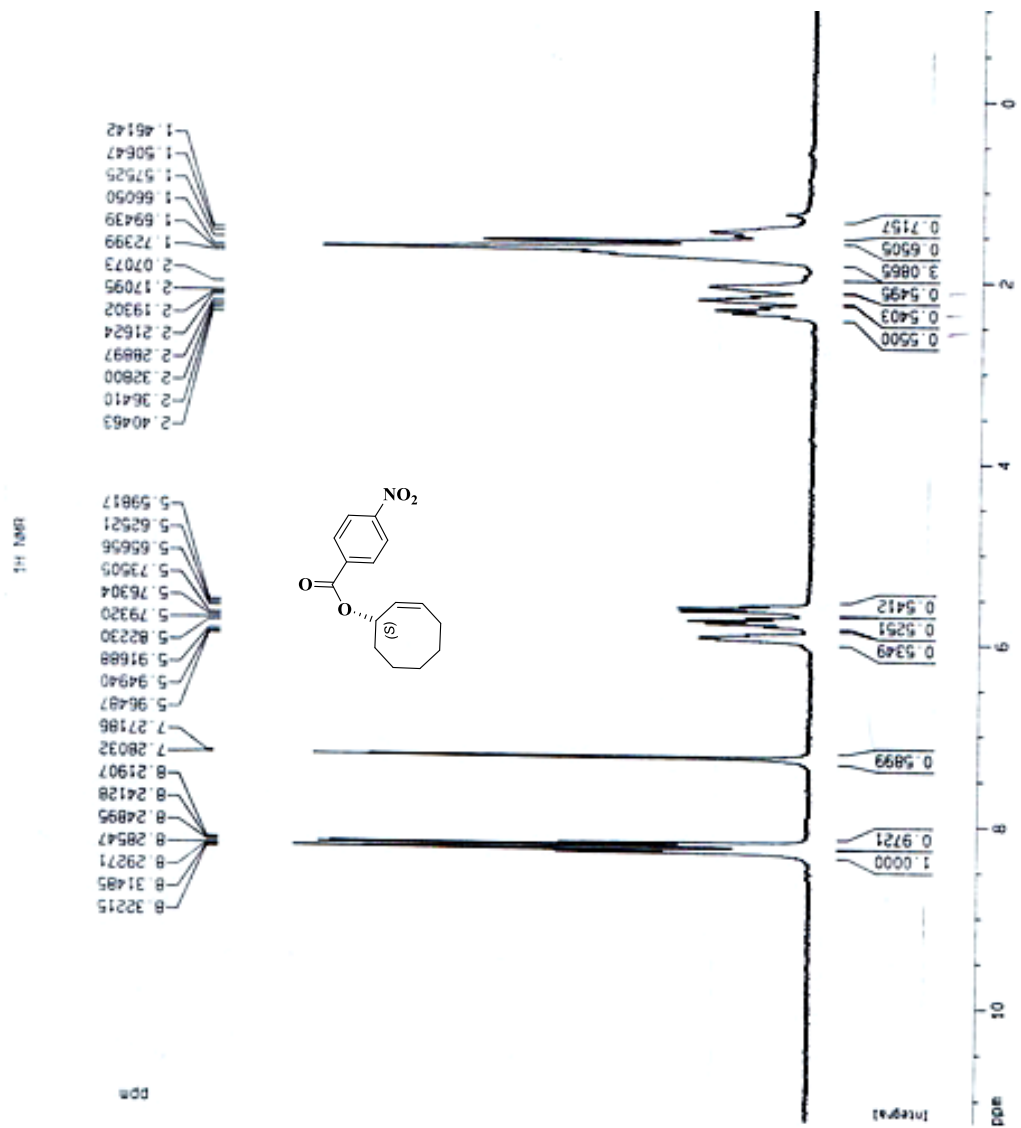


Figure S21: <sup>1</sup>H NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-4-nitrobenzoate (**10c**)



NAME Kurdestan UN  
 EXPNO 449  
 PROCNO 1  
 Date\_ 20180910  
 Time 13.05  
 INSTRUM spect  
 PULPROG zgpg30  
 TD 65536  
 F2 55536  
 SOLVENT CDCl3  
 NS 504  
 DS 0  
 SWH 35714.285 Hz  
 FIDRES 0.141857 Hz  
 A 0.917540 sec  
 RG 2050  
 DW 14.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.0000000 sec  
 D11 0.0300000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUCL 13C  
 P1 9.00 usec  
 PL1 -0.90 dB  
 PLW 42.02801395 W  
 SFO1 100.6419784 MHz  
 ===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 NUC2 90.00 usec  
 FCPD2 -2.00 dB  
 PL2 17.00 dB  
 PL12 17.00 dB  
 PL13 17.00 dB  
 PL14 17.00 dB  
 PL15 17.00 dB  
 PL16 17.00 dB  
 PL17 17.00 dB  
 PL18 17.00 dB  
 PL19 17.00 dB  
 PL20 17.00 dB  
 PL21 17.00 dB  
 PL22 17.00 dB  
 PL23 17.00 dB  
 PL24 17.00 dB  
 PL25 17.00 dB  
 PL26 17.00 dB  
 PL27 17.00 dB  
 PL28 17.00 dB  
 PL29 17.00 dB  
 PL30 17.00 dB  
 PL31 17.00 dB  
 PL32 17.00 dB  
 PL33 17.00 dB  
 PL34 17.00 dB  
 PL35 17.00 dB  
 PL36 17.00 dB  
 PL37 17.00 dB  
 PL38 17.00 dB  
 PL39 17.00 dB  
 PL40 17.00 dB  
 PL41 17.00 dB  
 PL42 17.00 dB  
 PL43 17.00 dB  
 PL44 17.00 dB  
 PL45 17.00 dB  
 PL46 17.00 dB  
 PL47 17.00 dB  
 PL48 17.00 dB  
 PL49 17.00 dB  
 PL50 17.00 dB  
 PL51 17.00 dB  
 PL52 17.00 dB  
 PL53 17.00 dB  
 PL54 17.00 dB  
 PL55 17.00 dB  
 PL56 17.00 dB  
 PL57 17.00 dB  
 PL58 17.00 dB  
 PL59 17.00 dB  
 PL60 17.00 dB  
 PL61 17.00 dB  
 PL62 17.00 dB  
 PL63 17.00 dB  
 PL64 17.00 dB  
 PL65 17.00 dB  
 PL66 17.00 dB  
 PL67 17.00 dB  
 PL68 17.00 dB  
 PL69 17.00 dB  
 PL70 17.00 dB  
 PL71 17.00 dB  
 PL72 17.00 dB  
 PL73 17.00 dB  
 PL74 17.00 dB  
 PL75 17.00 dB  
 PL76 17.00 dB  
 PL77 17.00 dB  
 PL78 17.00 dB  
 PL79 17.00 dB  
 PL80 17.00 dB  
 PL81 17.00 dB  
 PL82 17.00 dB  
 PL83 17.00 dB  
 PL84 17.00 dB  
 PL85 17.00 dB  
 PL86 17.00 dB  
 PL87 17.00 dB  
 PL88 17.00 dB  
 PL89 17.00 dB  
 PL90 17.00 dB  
 PL91 17.00 dB  
 PL92 17.00 dB  
 PL93 17.00 dB  
 PL94 17.00 dB  
 PL95 17.00 dB  
 PL96 17.00 dB  
 PL97 17.00 dB  
 PL98 17.00 dB  
 PL99 17.00 dB  
 PL100 17.00 dB  
 SFO2 400.2216009 MHz  
 SI 32768  
 SF 32768  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 FC 1.40

Sample code:3 (Dr.Samadi)

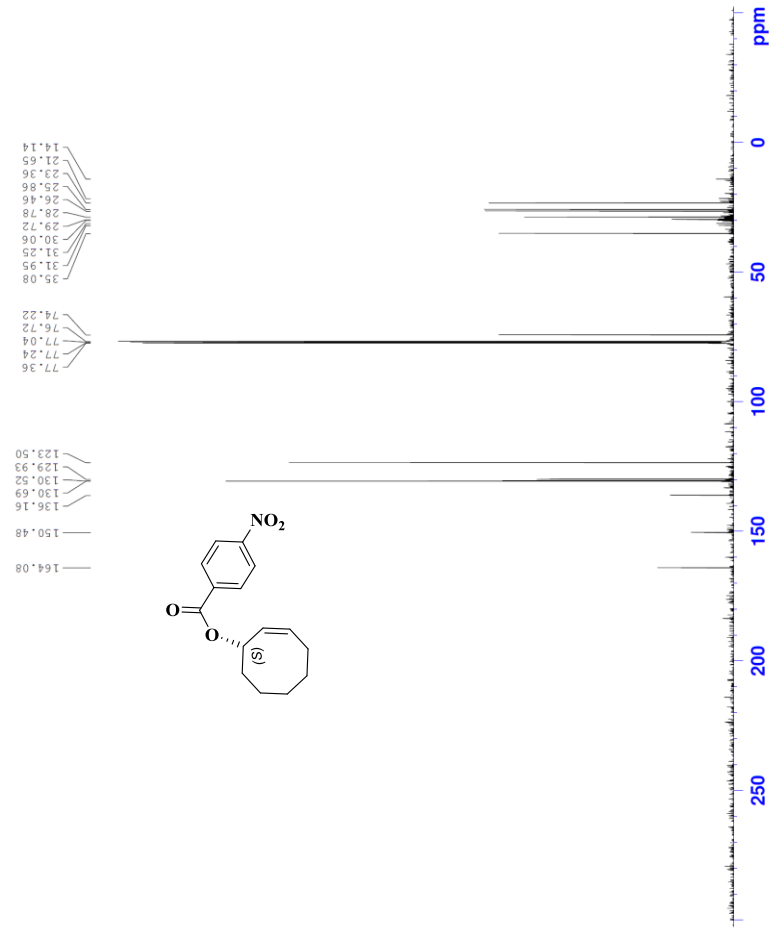


Figure S22: <sup>13</sup>C NMR spectrum of the (S)-cyclooct-2-en-1-yl-4-nitrobenzoate (10c)

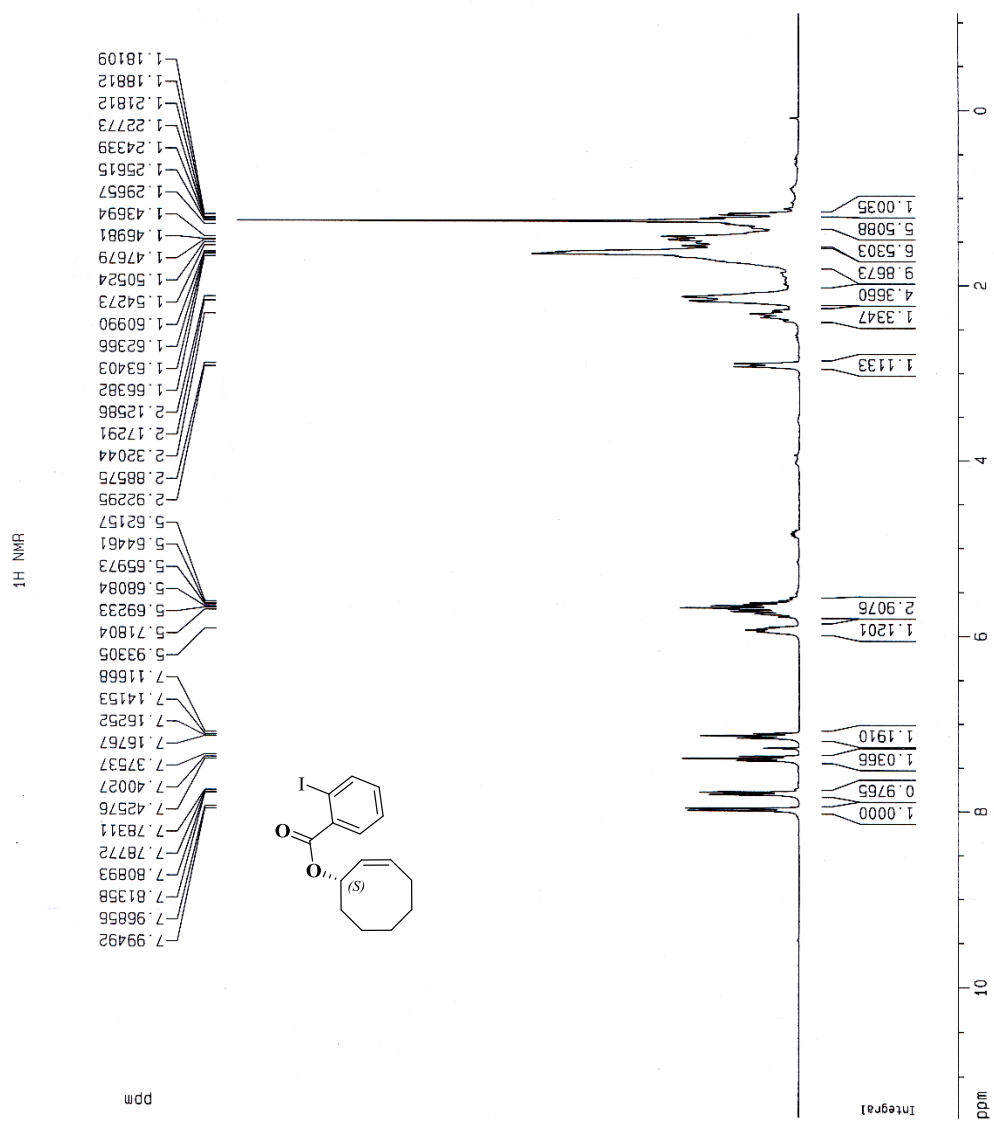


Figure S23: <sup>1</sup>H NMR spectrum of the (S)-cyclooct-2-en-1-yl-2-iodobenzoate (10d)

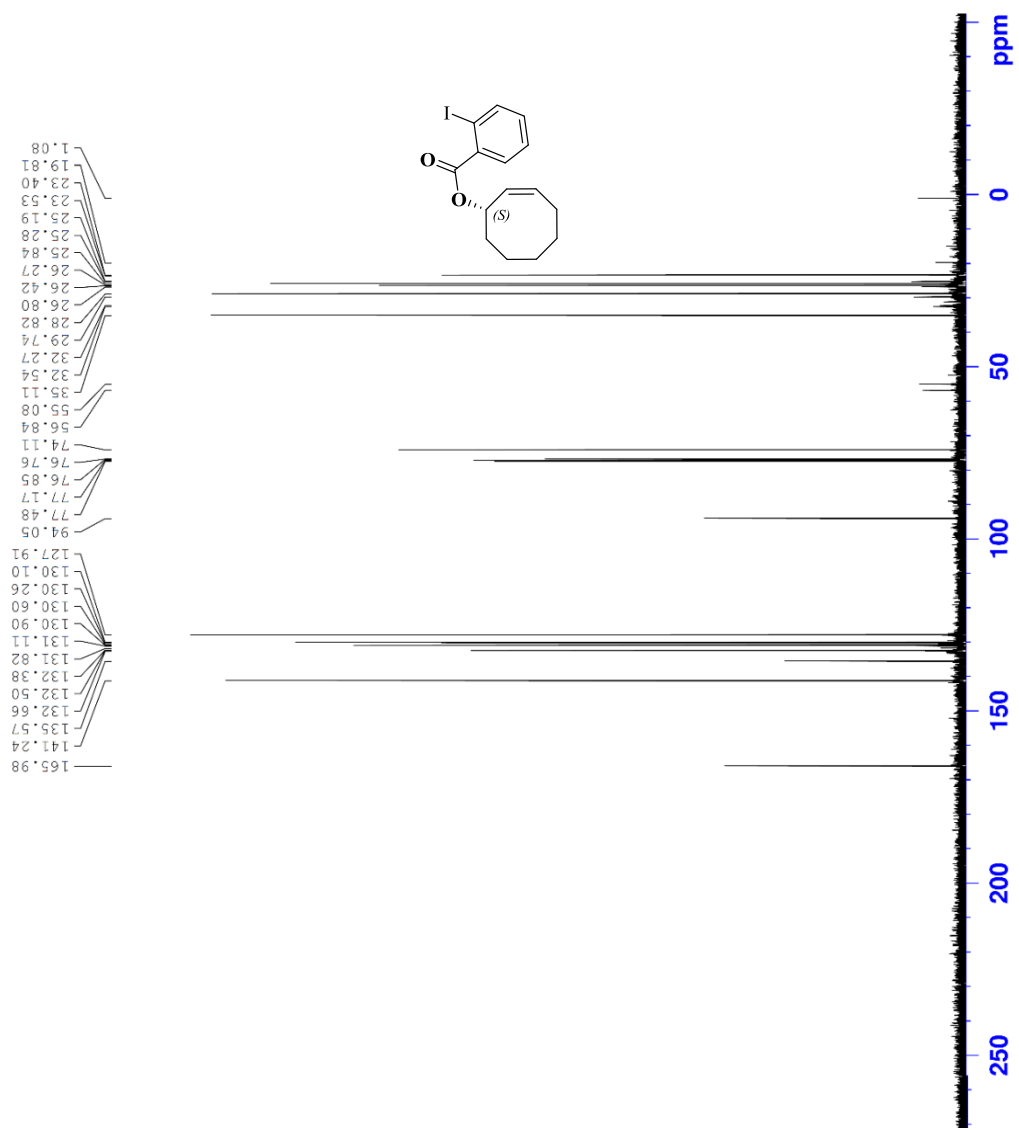


Figure S24:  $^{13}\text{C}$  NMR spectrum of the (S)-cyclooct-2-en-1-yl-2-iodobenzoate (10d)

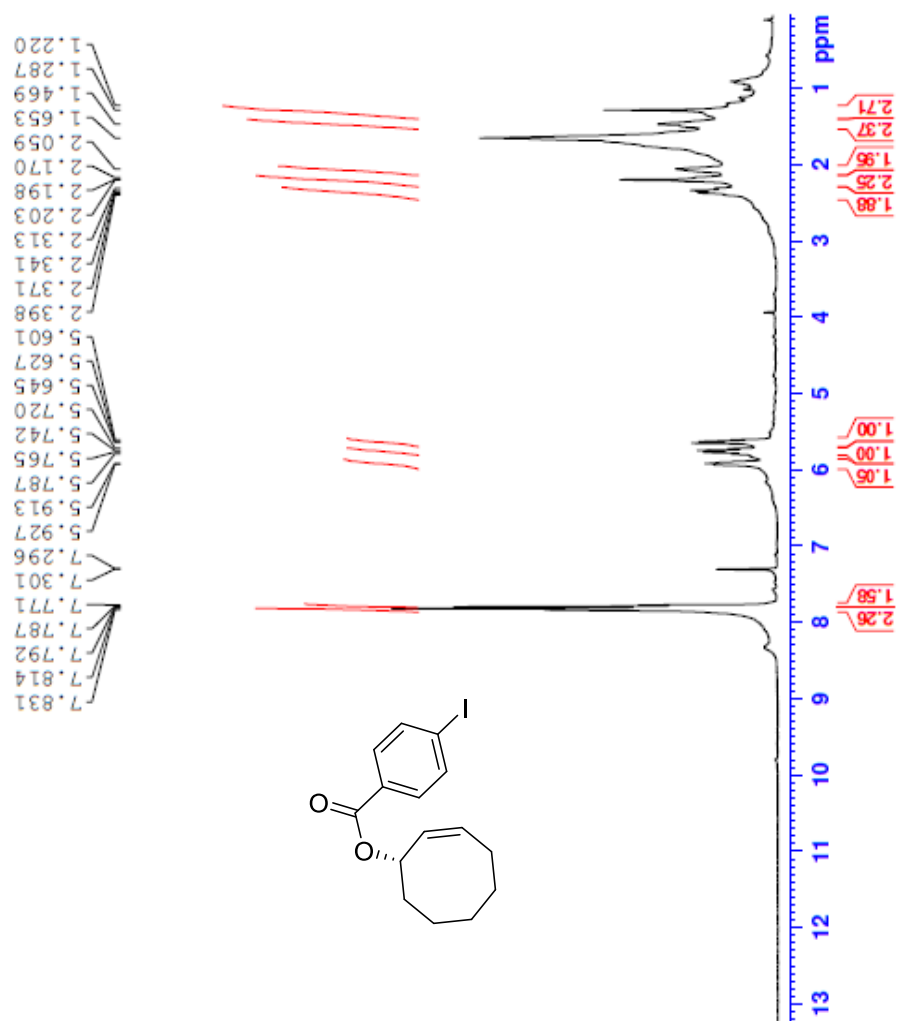


Figure S25:  $^1\text{H}$  NMR spectrum of the (S)-cyclooct-2-en-1-yl-4-iodobenzoate (10e)

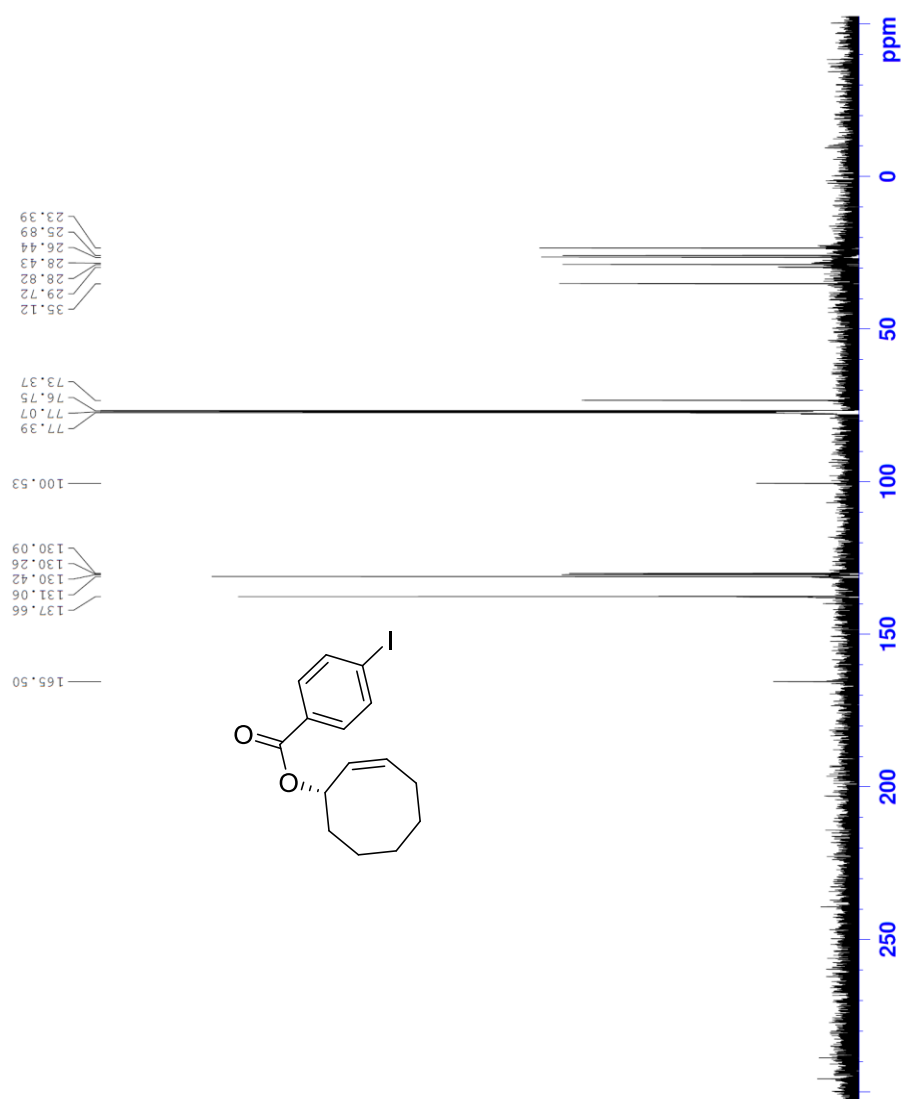


Figure S26:  $^{13}\text{C}$  NMR spectrum of the (S)-cyclooct-2-en-1-yl-4-iodobenzoate (10e)

<sup>14</sup>N  
<sup>1</sup>H NMR

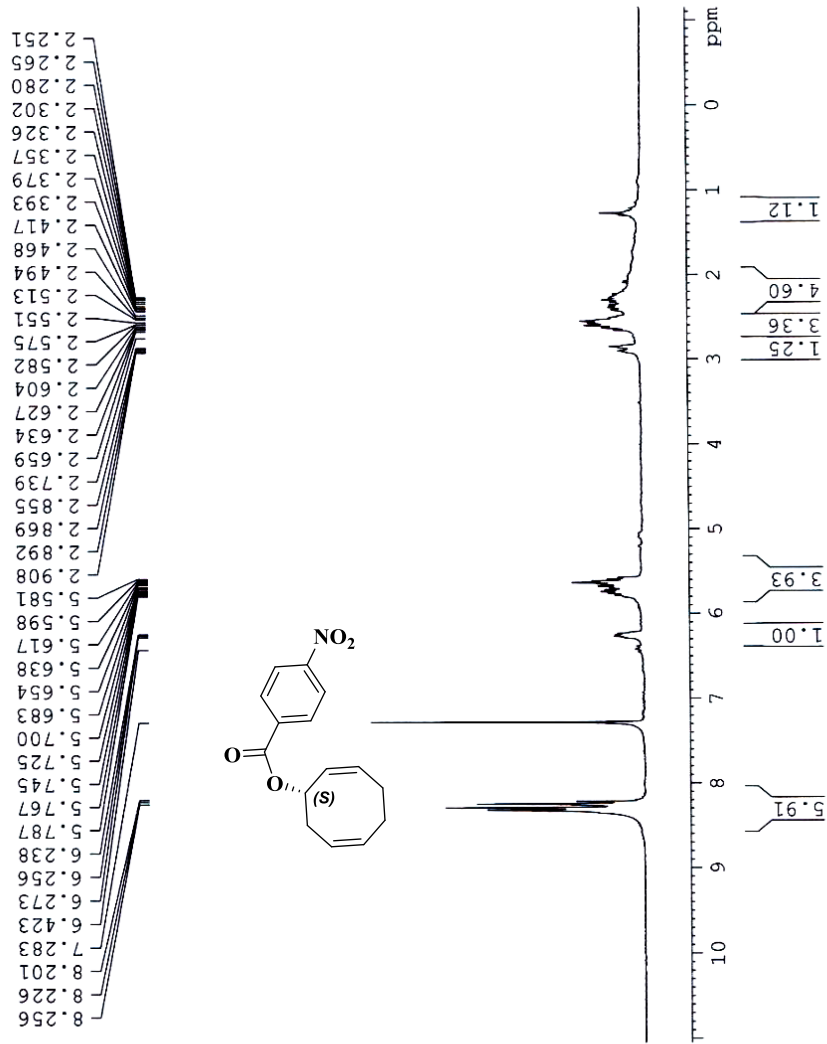


Figure S27: <sup>1</sup>H NMR spectrum of (S)-cycloocta-2,6-dien-1-yl-4-nitrobenzoate (11c)



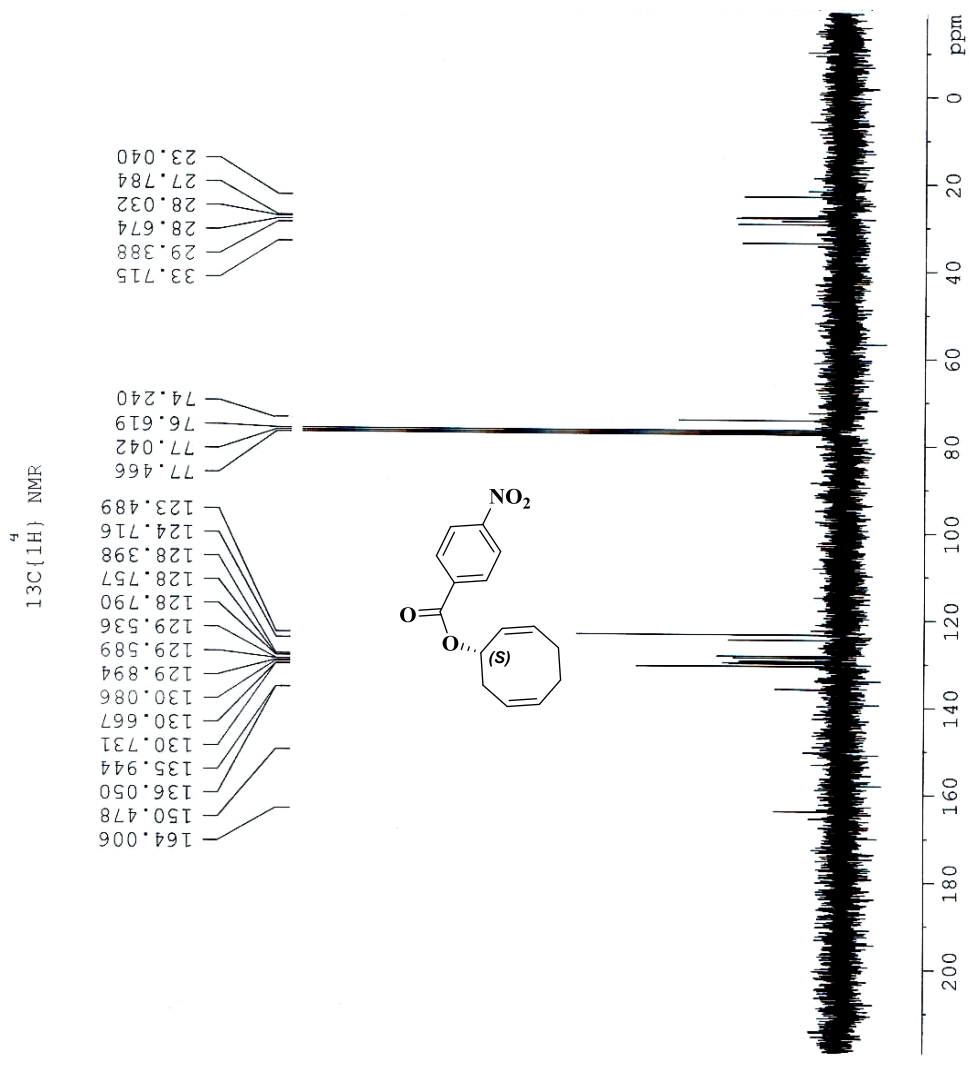


Figure S28: <sup>13</sup>C NMR spectrum of (*S*)-cycloocta-2,6-dien-1-yl-4-nitrobenzoate (**11c**)

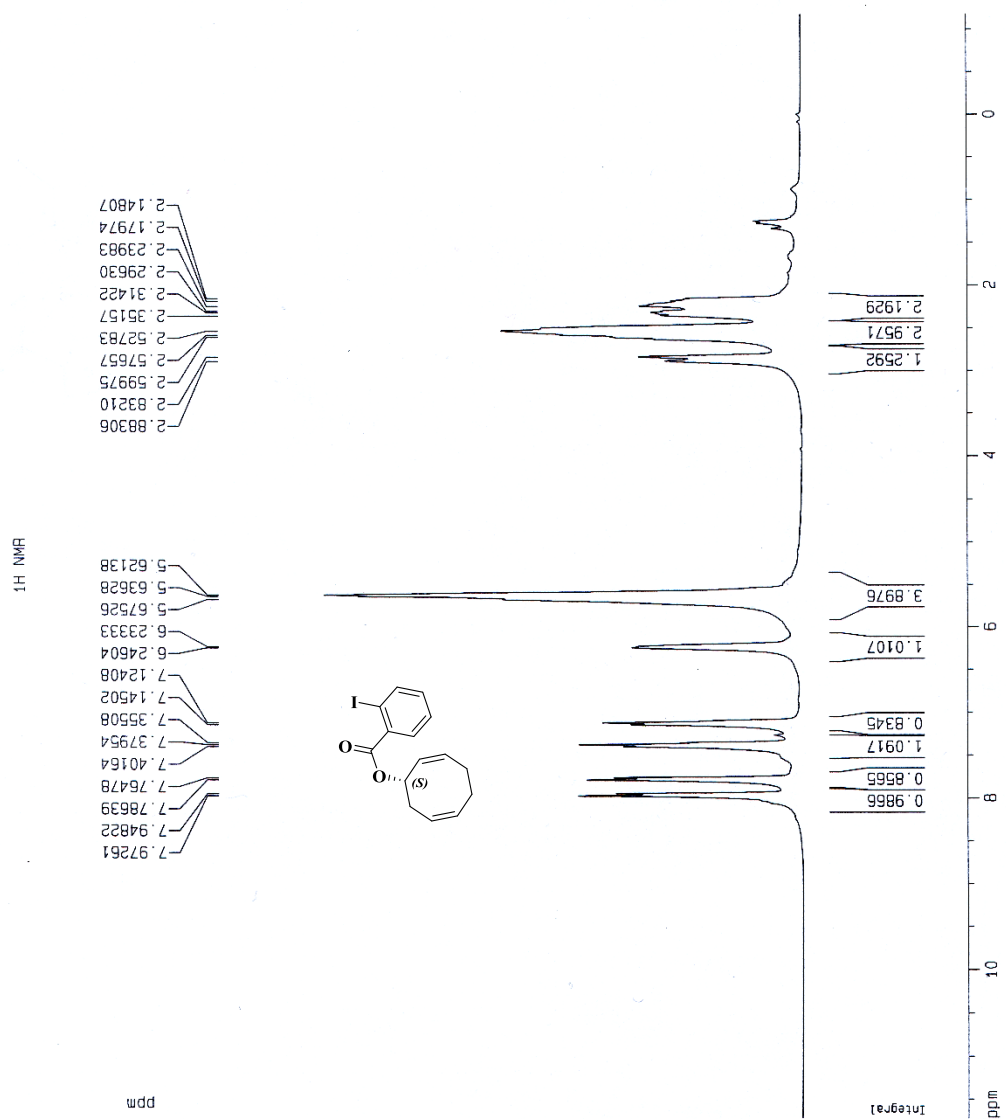
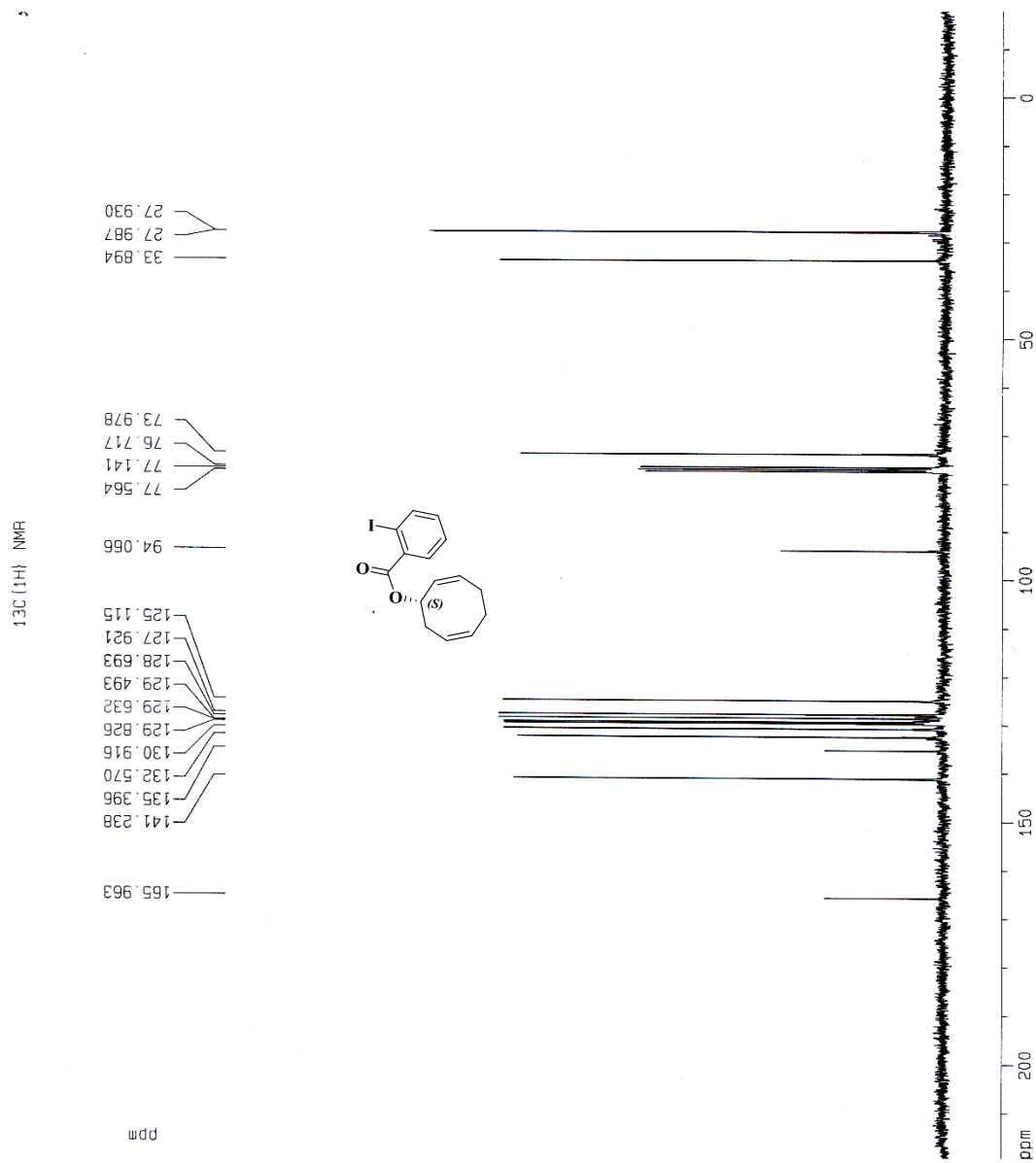


Figure S29: <sup>1</sup>H NMR spectrum of (S)-cycloocta-2,6-dien-1-yl-2-iodobenzoate (11d)



**Figure S30: <sup>13</sup>C NMR spectrum of (S)-cycloocta-2,6-dien-1-yl-2-iodobenzoate (11d)**

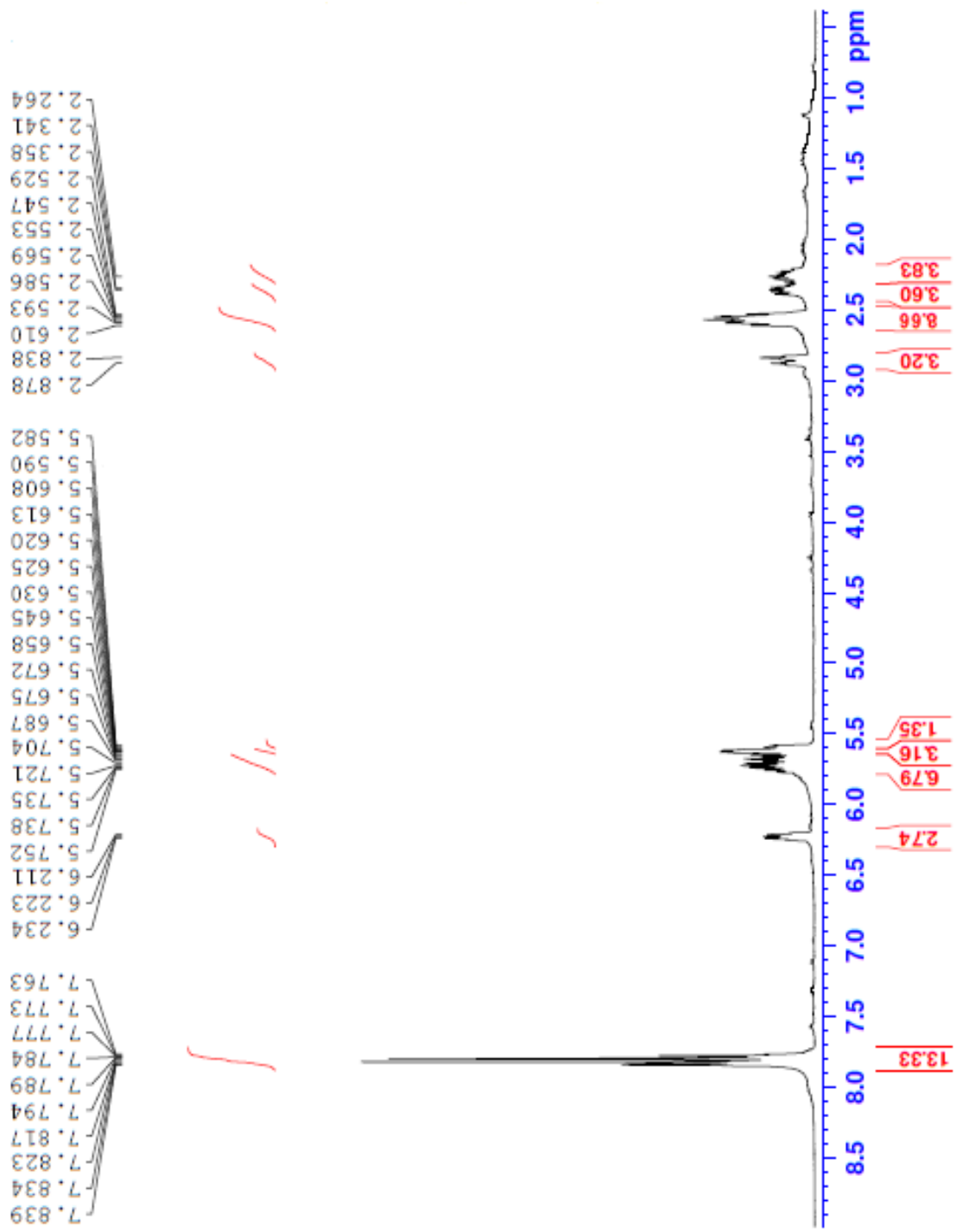


Figure S31: <sup>1</sup>H NMR spectrum of (S)-cycloocta-2,6-dien-1-yl-4-iodobenzoate (11e)

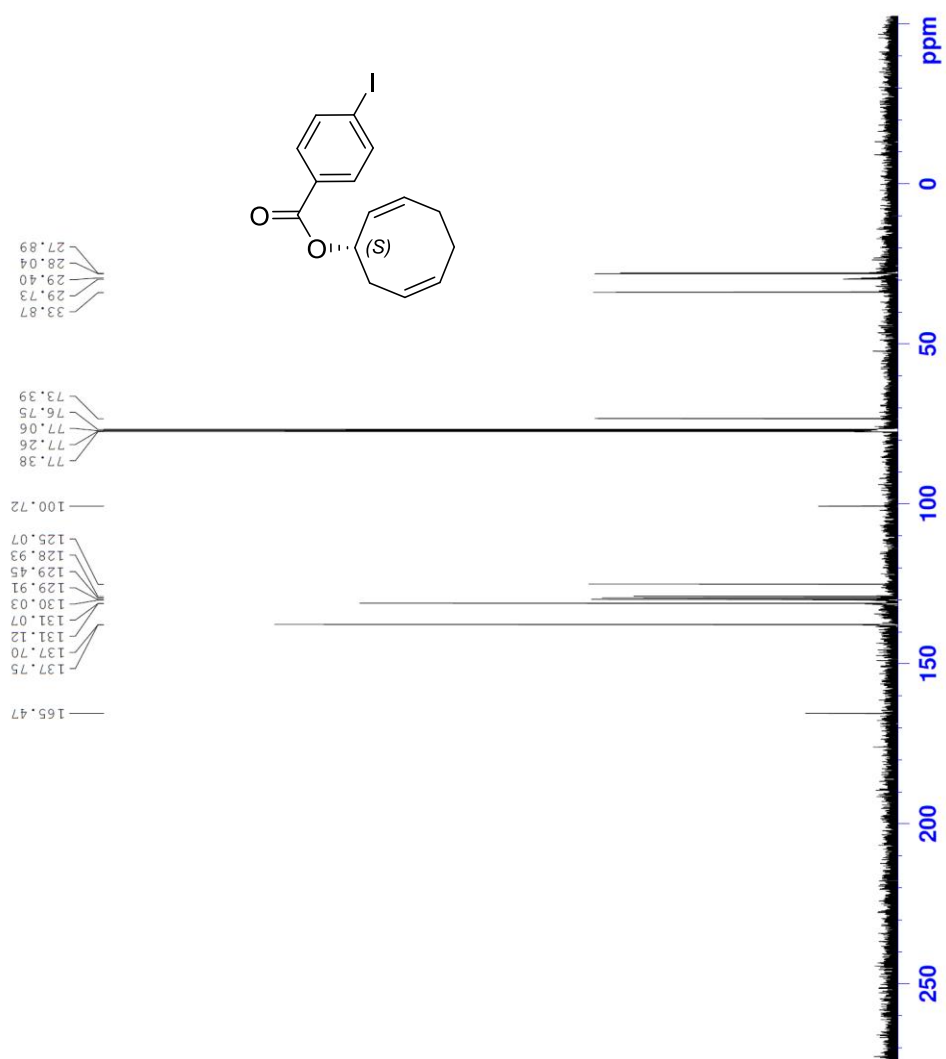


Figure S32: <sup>13</sup>C NMR spectrum of (S)-cycloocta-2,6-dien-1-yl-4-iodobenzoate (11e)

## References

1. M. J. McKennon, A. Meyers, K. Drauz and M. Schwarm, A convenient reduction of amino acids and their derivatives, *J.Org.Chem*, 1993, **58**, 3568-3571.
2. S. Samadi, A. Ashouri, S. Majidian and H. I. Rashid, Synthesis of new alkenyl iodobenzoate derivatives via Kharasch-Sosnovsky reaction using tert-butyl iodo benzoperoxoate and copper (I) iodide, *J. Chem. Sci.*, 2020, **132**, 1-9.
3. S. Sadjadi, S. Samadi and M. Samadi, 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.
4. S. Samadi, A. Ashouri, S. Kamangar and F. Pourakbari, 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.
5. S. Samadi, K. Jadidi, B. Khanmohammadi and N. Tavakoli, 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.
6. S. Samadi, K. Jadidi, M. Samadi, A. Ashouri and B. Notash, Designing chiral amido-oxazolines as new chelating ligands devoted to direct Cu-catalyzed oxidation of allylic CH bonds in cyclic olefins, *Tetrahedron*, 2019, **75**, 862-867.
7. S. Samadi, A. Ashouri and M. Samadi, Synthesis of chiral allylic esters by using the new recyclable chiral heterogeneous oxazoline-based catalysts, *ACS Omega*, 2020, **5**, 22367-22378.
8. M. B. Andrus and D. Asgari, Asymmetric allylic oxidation with biarylbisoxazoline-copper (I) catalysis, *Tetrahedron*, 2000, **56**, 5775-5780.
9. K.-i. Kawasaki and T. Katsuki, Enantioselective allylic oxidation of cycloalkenes by using Cu (II)-tris (oxazoline) complex as a catalyst, *Tetrahedron*, 1997, **53**, 6337-6350.