Electronic Supplementary Material (ESI) for New Journal of Chemistry.

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

Experimental

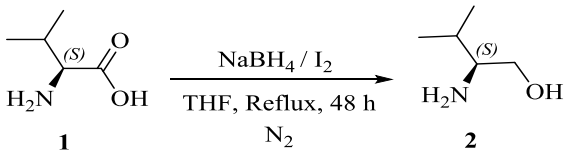
Materials and characterization methods

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}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13, 400.22 MHz and 75 MHz, 100 MHz in $CDCl_3$ using TMS (δ = 0.0 ppm) an internal standard. X-ray diffraction (XRD) was performed *on* a Bruker D8 Advance powder diffractometer with Ni filtered CuKa radiation (λ = 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℃ at a heating rate of 10℃/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 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 P_2O_5, methylene chloride from calcium hydride, methanol from Mg and 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_{256} 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 °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 × 15 mL) and the organic layer was dried over anhydrous $MgSO_4$. After evaporation of dichloromethane, the *S*-2-amino-3-methylbutane-1-ol (L-valinol) was obtained in 90% yield [1](Scheme S1). The structure of the product was confirmed by ^{1}HNMR, ^{13}CNMR spectra (Figures S6 and S7).



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

***(S)-2-amino-3-methylbutan-1-ol*:** ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 0.92 (6 H, d, *J* = 6.8 Hz, CH_3), 1.67-1.69 (1 H, m, CH), 2.66-2.73 (1 H, m, *CH), 3.41-3.42 (1 H, m, -CH_2-OH), 3.59-3.62 (1 H, m, H_2C-OH). 4.12 (2 H, brs, (NH_2)).; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) = 19.8, 31.9, 56.6, 64.7.; $[\alpha]^{25}_D$ = +3.3° (*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 × 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, ^{1}HNMR and ^{13}C NMR spectroscopy techniques[2-4].

***Tert*-butyl-4-nitrobenzoperoxoate (7c)** [1,5-7]: Mp: 76-78 °C (lit.75-78 °C); ^{1}HNMR (300 MHz, $CDCl_3$): δ_H (ppm) = 8.14-8.35 (4H, m, Ar), 1.45 (9H, s, CH_3); ^{13}CNMR (75 MHz, $CDCl_3$): δ_C (ppm)= 162.5, 150.7, 133.2, 130.3, 123.8, 84.7, 26.2.

***Tert*-butyl-2-iodobenzoperoxoate (7d)** [1,5-7]: Mp: 47-49 °C.; ^{1}HNMR (300 MHz, $CDCl_3$): δ_H (ppm) = 1.43 (9H, s, CH_3), 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).; ^{13}CNMR (75 MHz, $CDCl_3$): δ_C (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 $Cu(CH_3CN)_4PF_6$ 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 ^{1}H NMR and ^{13}C NMR spectroscopy techniques (Pages S4 and S5 and Figures S12−S37)[3, 4].

(S)-Cyclohex-2-en-1-yl benzoate (8a) [5-7]: $[\alpha]^{20}_D$ = –20.3° (c 1.0, $CHCl_3$).; 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_R = 16.6 min (*R*), 18.5 min (*S*)) (Maximum ee = 25%).

(S)- Cyclohex-2-en-1-yl 4-chlorobenzoate (8b) [5-7]: $[\alpha]^{20}_D$ = –39.4° (c 1.0, $CHCl_3$); 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_R = 22.8 min (*R*), 24.3 min (*S*)) (Maximum ee = 30%).

(S)-Cyclohex-2-en-1-yl 4-nitrobenzoate (8c) [5-7]: $[\alpha]^{20}_D$ = –50.9° (c 1.0, $CHCl_3$); 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_R = 29.0 min (*R*), 31.5 min (*S*)) (Maximum ee = 42%).

(S)-Cyclohex-2-en-1-yl 2-iodobenzoate (8d) [1,5-7]: $[\alpha]^{20}_{D}$ = –37.3° (c 1.0, $CHCl_3$); 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_R = 22.3 min (R), 24.9 min (*S*)) (Maximum ee = 32%).

(*S*) Cyclohex-2-en-1-yl 4-iodobenzoate (8e) [1,5-7]: $[\alpha]^{20}_{D}$ = –30.0° (c 1.0, $CHCl_3$); 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_R = 24.2 min, 25.8 min (Maximum ee = 34%).

(S)-Cyclopent-2-en-1-yl 4-nitrobenzoate (9c) [5-7]: $[\alpha]^{20}_{D}$ = –52.8° (c 1.0, $CHCl_3$); 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_R = 35.1 min (*R*), 36.7 min (*S*)) (Maximum ee = 31%).

(S)-Cyclopent-2-en-1-yl 2-iodobenzoate (9d) [5-7,8]**:** $[\alpha]^{20}_{D}$ = –48.0° (c 1.0, $CHCl_3$); 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_R = 20.5 min (*R*), 22.3 min (*S*)) (Maximum ee = 23%).

(S)-Cyclooct-2-en-1-yl 4-nitrobenzoate (10c) [5-7]: $[\alpha]^{20}_{D}$ = +10.4° (c 1.0, $CHCl_3$); 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_R = 18.3 min (*R*), 21.8 min (*S*)) (Maximum ee = 26%).

(S)-Cyclooct-2-en-1-yl 2-iodobenzoate (10d) [5-7,9]**:** $[\alpha]^{20}_{D}$ = +19.5° (c 1.0, $CHCl_3$); 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_R = 16.5 min (*R*), 19.1 min (*S*)) (Maximum ee = 20%).

(S)-Cyclooct-2-en-1-yl 4-iodobenzoate (10 e) [1,5-7]: $[\alpha]^{20}_{D}$ = +7.6° (c 1.0, $CHCl_3$); 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_R = 17.0 min, 20.5 min (Maximum ee = 22%).

(S)-Cycloocta-2,6-dien-1-yl 4-nitrobenzoate (11c) [5-7]: $[\alpha]^{20}_{D}$= +7.0° (c 1.0, $CHCl_3$); 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_R = 31.5 min (*S*), 33.7 min (*R*)) (Maximum ee = 36%).

(S)-Cycloocta-2,6-dien-1-yl 2-iodobenzoate (11d): $[\alpha]^{20}_{D}$ = +8.7° (c 1.0, $CHCl_3$); 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_R = 28.3 min (*S*), 30.4 min (*R*)) (Maximum ee = 27%).

(*S*)-Cycloocta-2,6-dien-1-yl 4-iodobenzoate (11e) [1,5-7]: $[\alpha]^{20}_{D}$= +5.8° (c 1.0, $CHCl_3$); 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_R = 27.5 min, 31.2 min (Maximum ee = 32%).

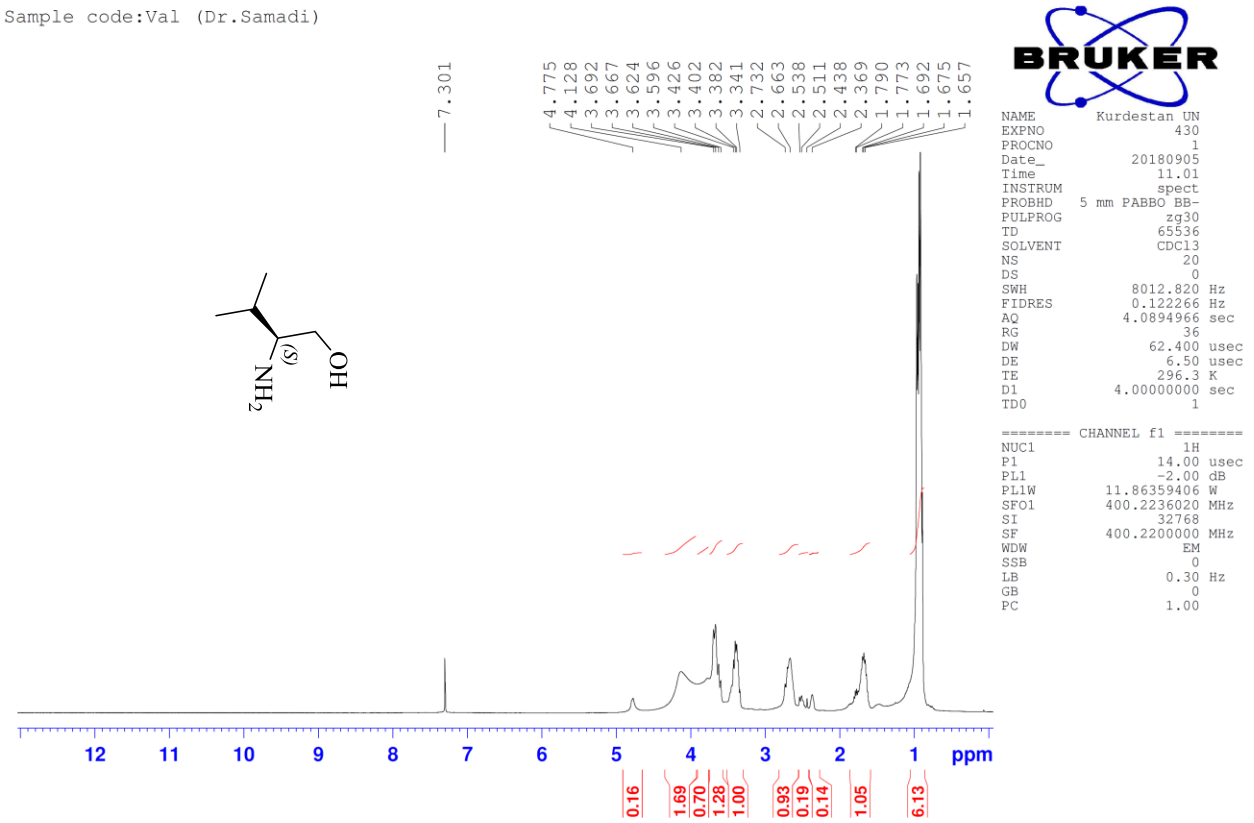


Figure S1: ^{1}H NMR spectrum of (*S*)-2-amino-3-methylbutane-1-ol (2)

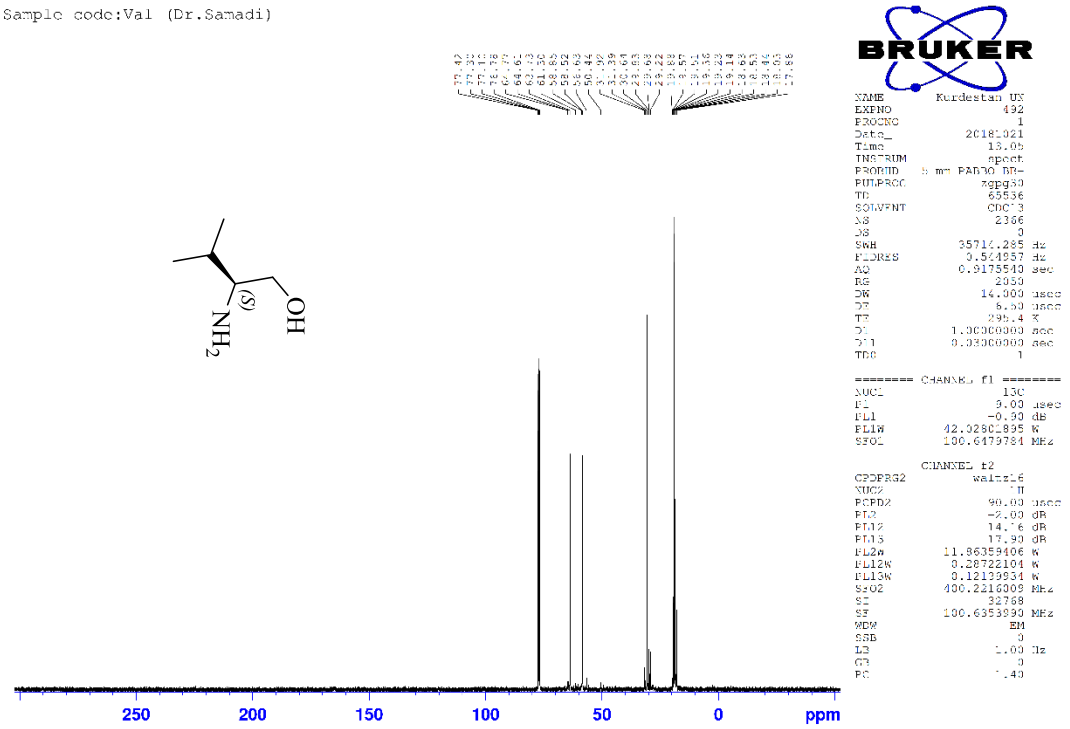


Figure S2: ^{13}C NMR spectrum of (*S*)-2-amino-3-methylbutane-1-ol

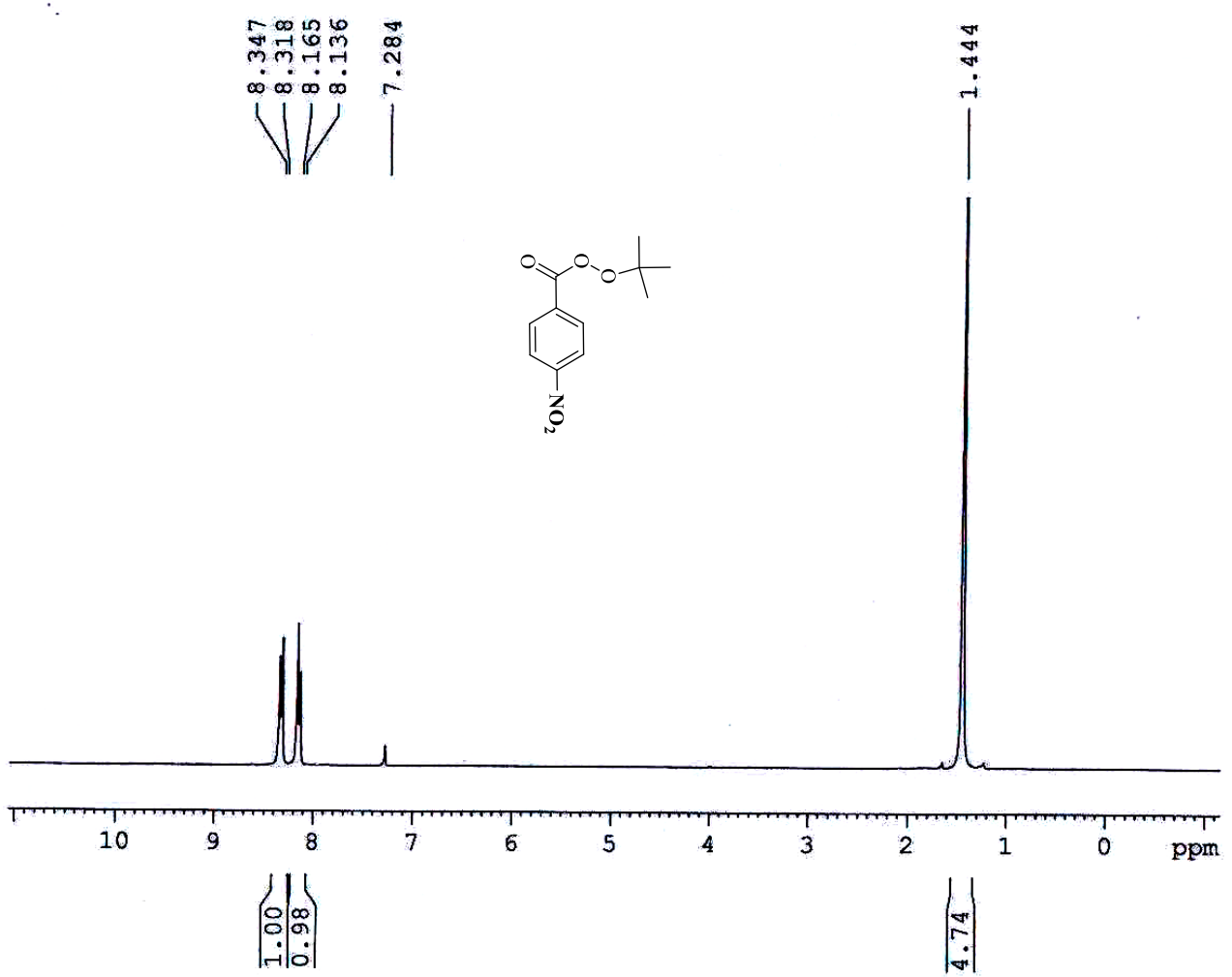


Figure S3: ^{1}H NMR spectrum of tert-butyl-para-nitroperbenzoate (7c)

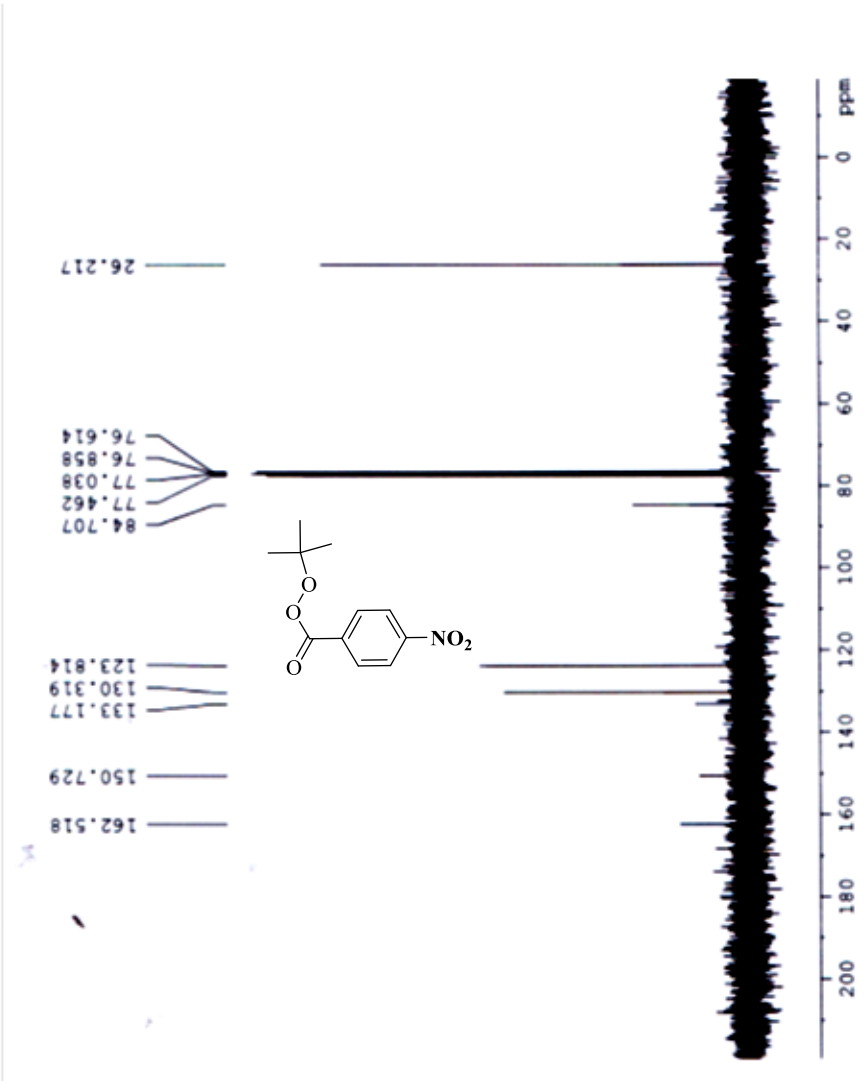


Figure S4: ^{13}C NMR spectrum of tert-butyl-para-nitroperbenzoate (7c)

Figure S5: ^{1}H NMR spectrum of tert-butyl 2-iodoperbenzoate (7d)

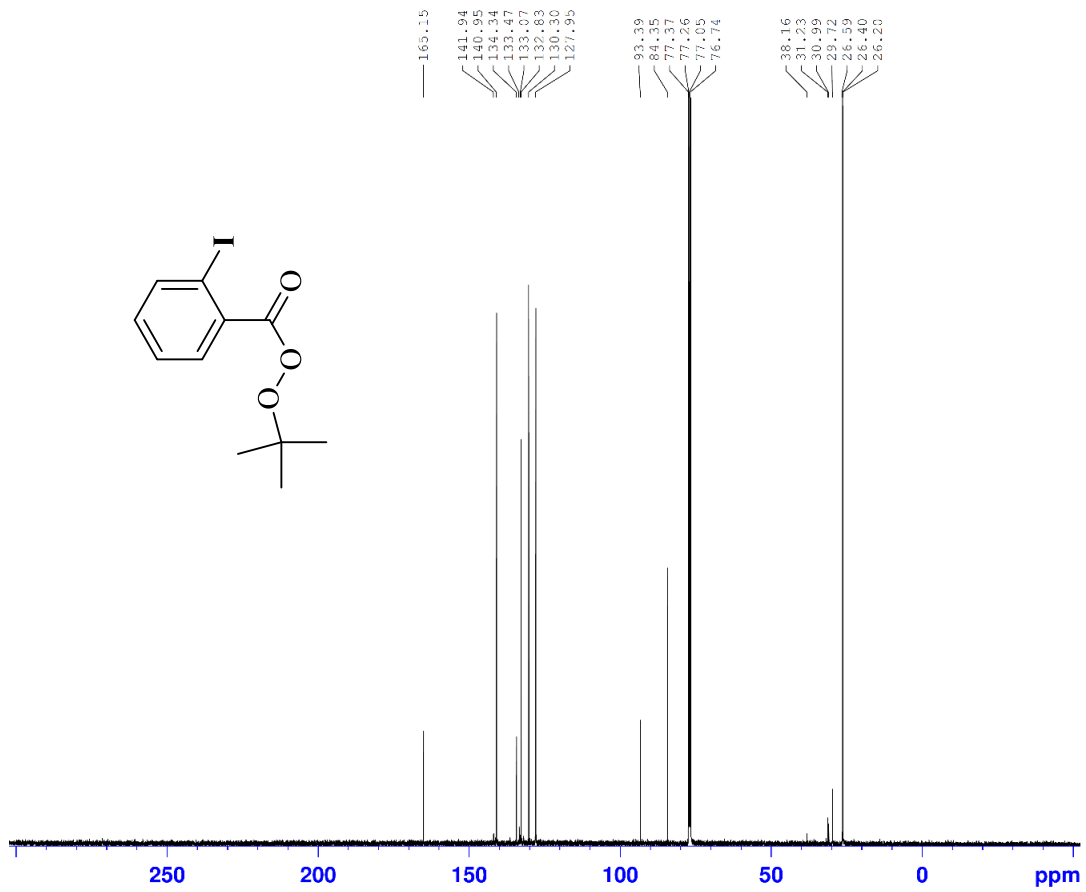


Figure S6: ^{13}C NMR spectrum of tert-butyl -2-iodoperbenzoate (7d)

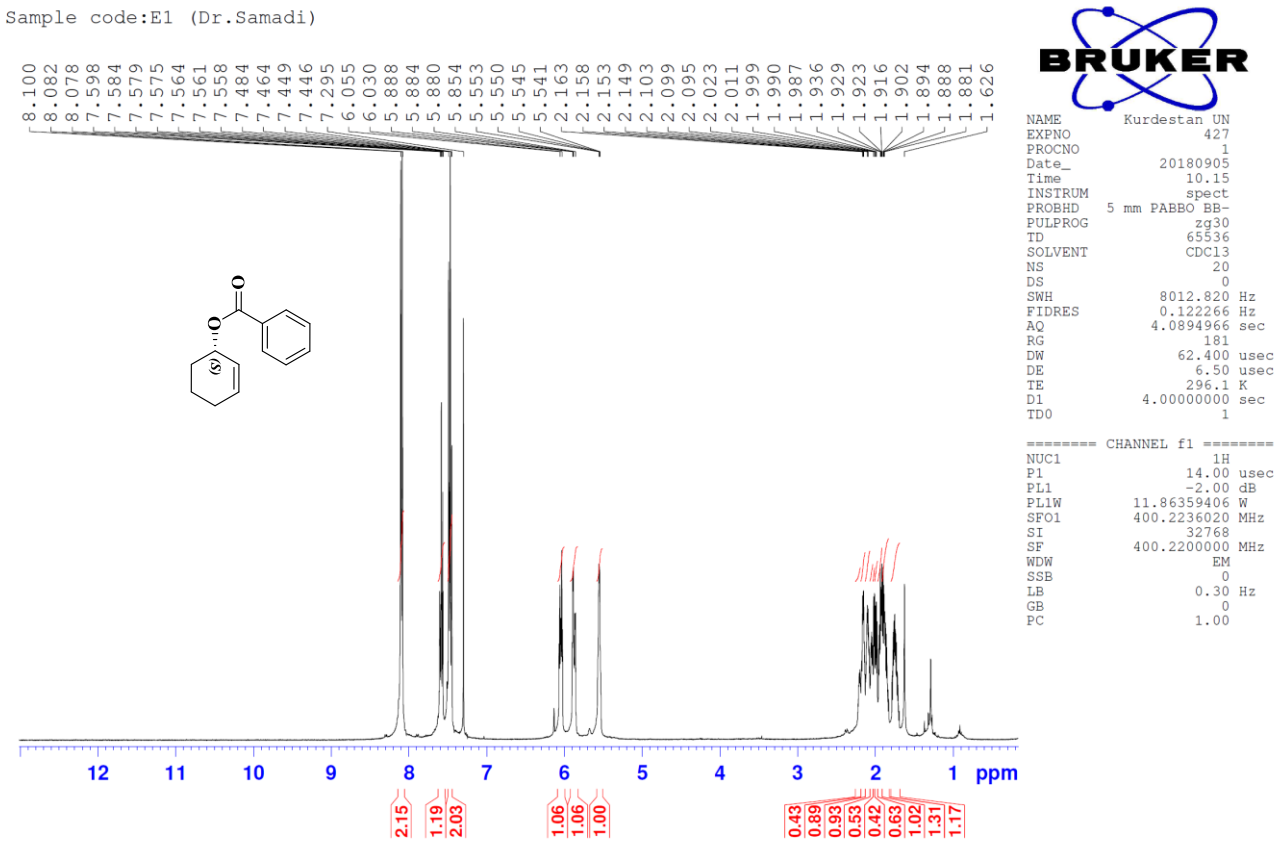


Figure S7: ^{1}H NMR spectrum of (*S*)-cyclohex-2-en-1-yl-benzoate (8a)

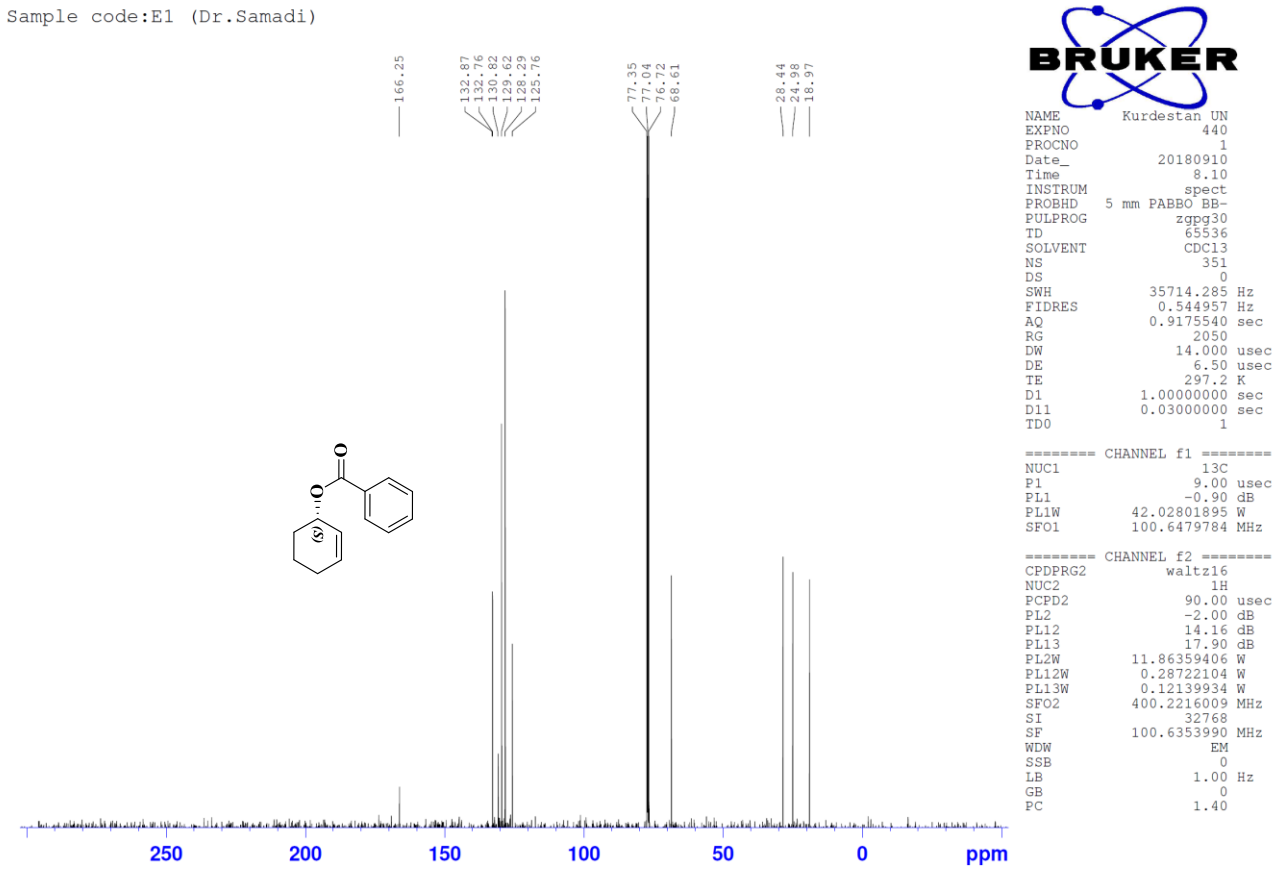


Figure S8: ^{13}C NMR spectrum of (*S*)-cyclohex-2-en-1-yl-benzoate (8a)

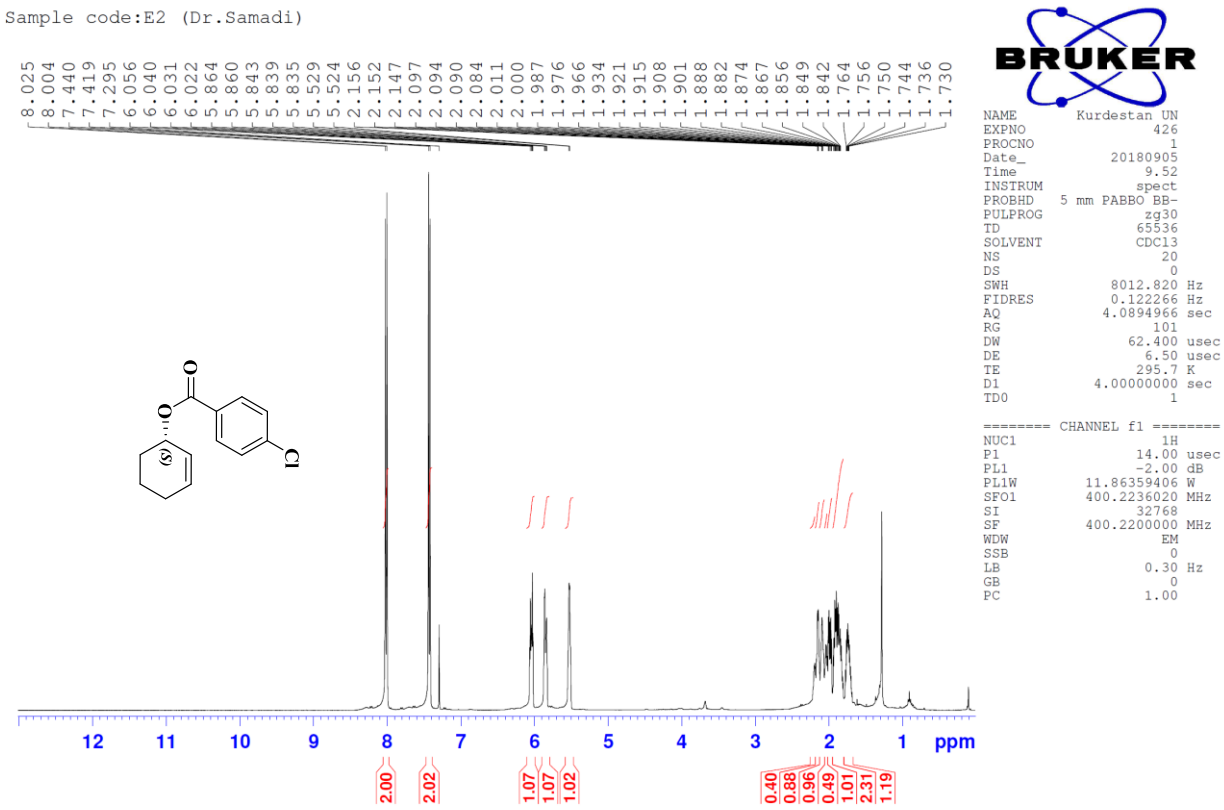


Figure S9: ^{1}H NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-chlorobenzoate (8b)

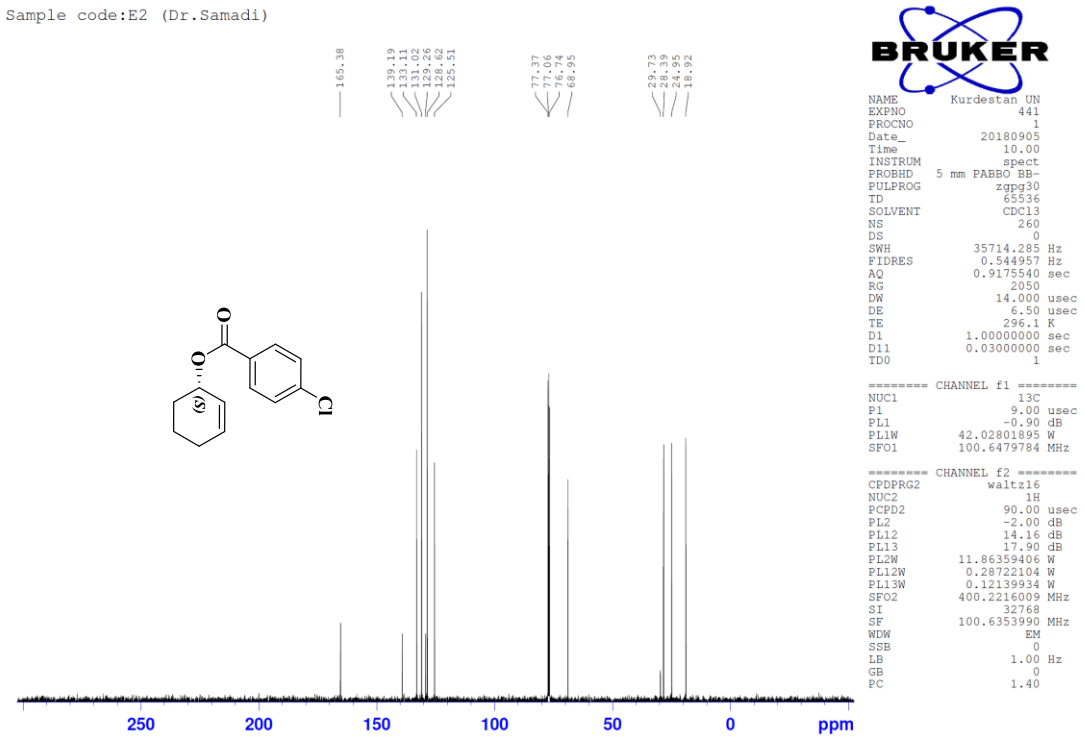


Figure S10: ^{13}C NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-chlorobenzoate (8b)

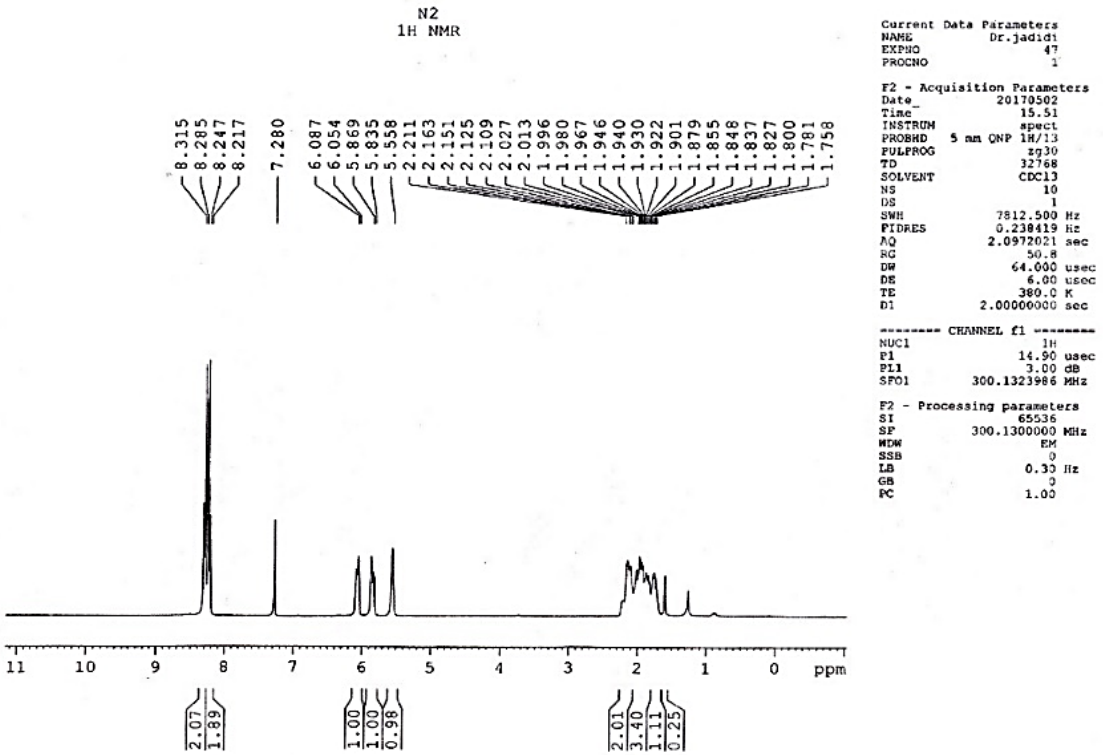


Figure S11: ^{1}H NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-nitrobenzoate (8c)

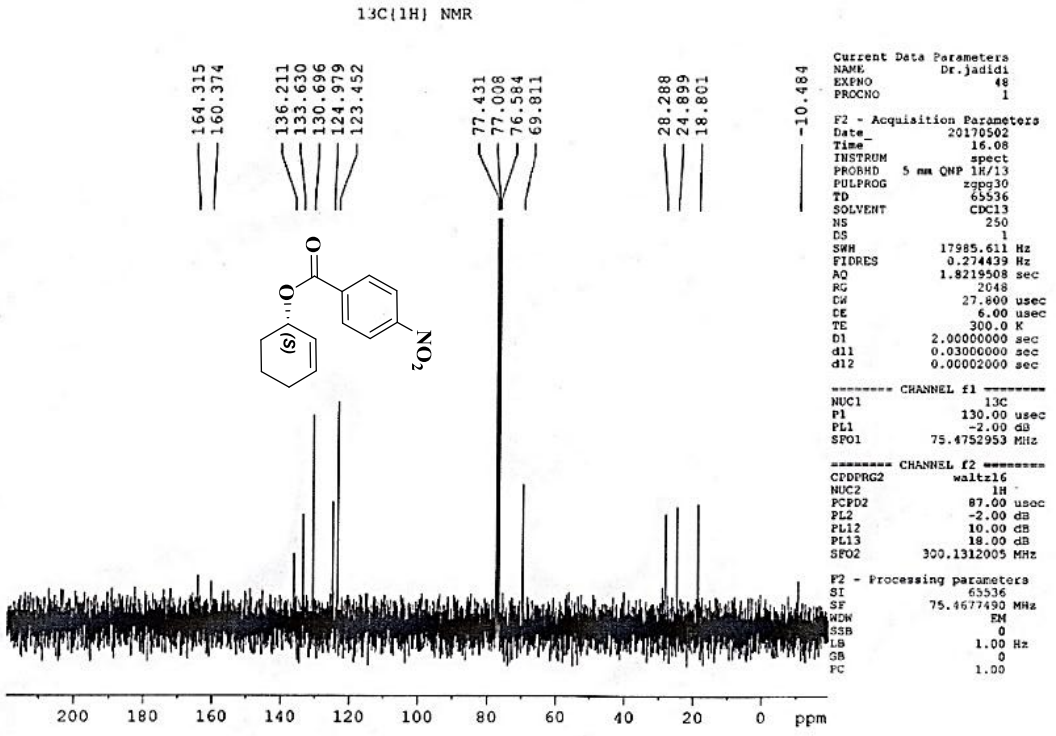


Figure S12: ^{13}C NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-nitrobenzoate (8c)

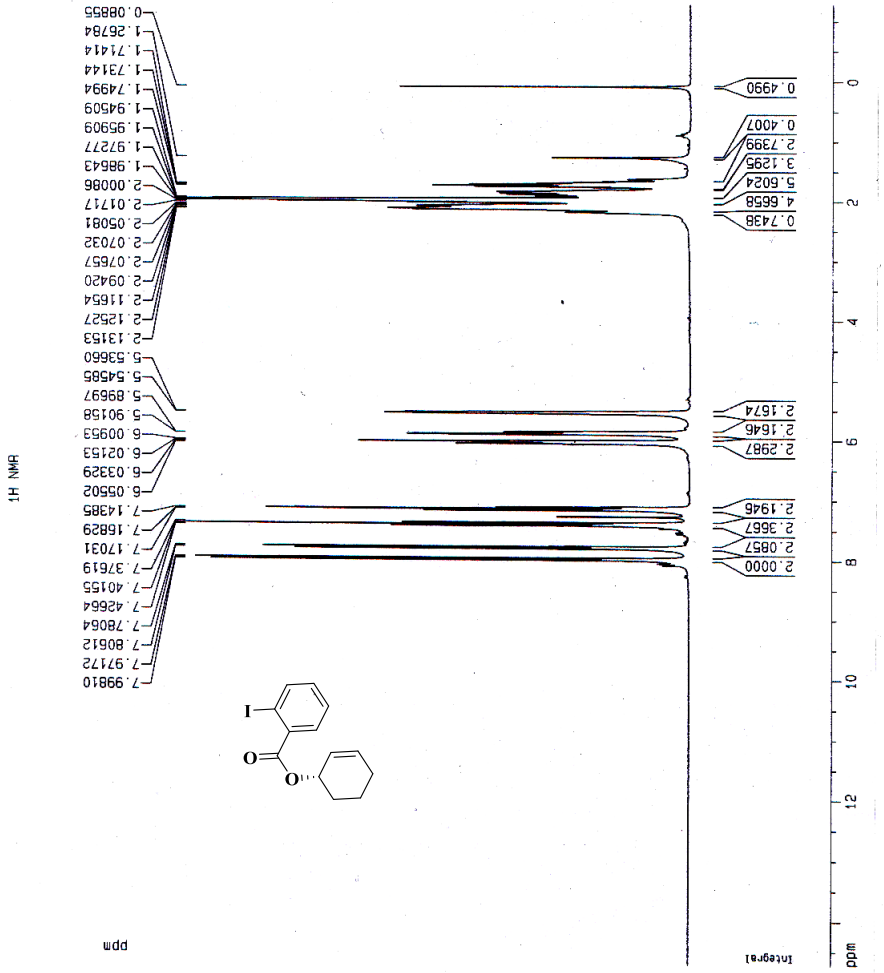


Figure S13: ^{1}H NMR spectrum of (*S*)-cyclohex-2-en-1-yl-2-iodobenzoate (8d)

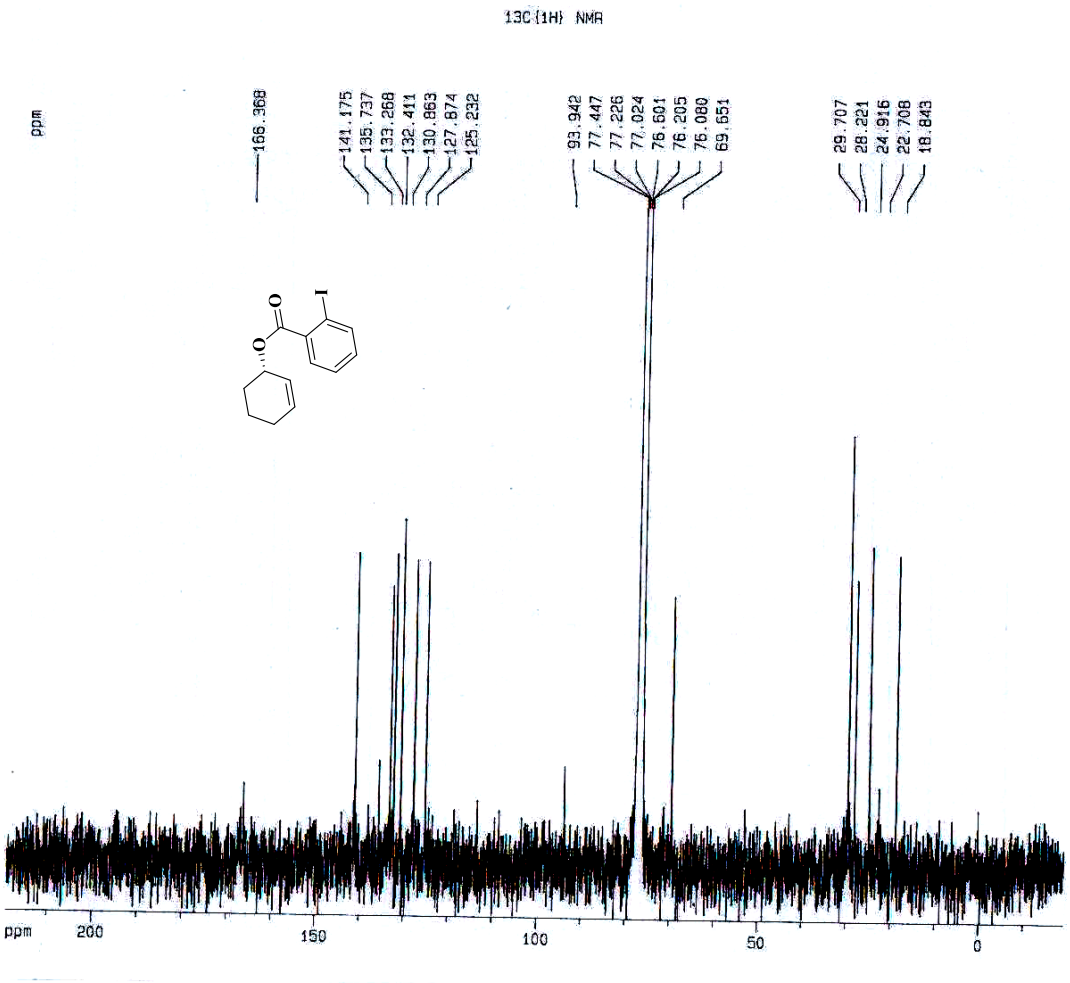


Figure S14: ^{13}C NMR spectrum of (*S*)-cyclohex-2-en-1-yl-2-iodobenzoate (8d)

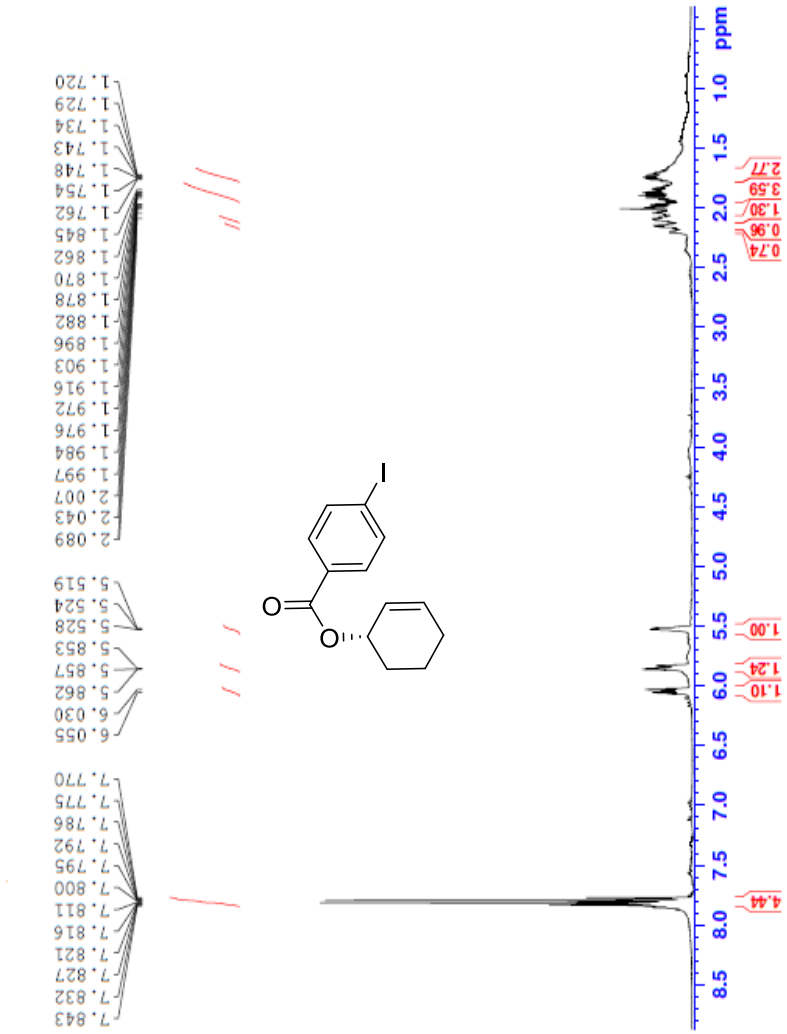


Figure S15: ^{1}H NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-iodobenzoate (8e)

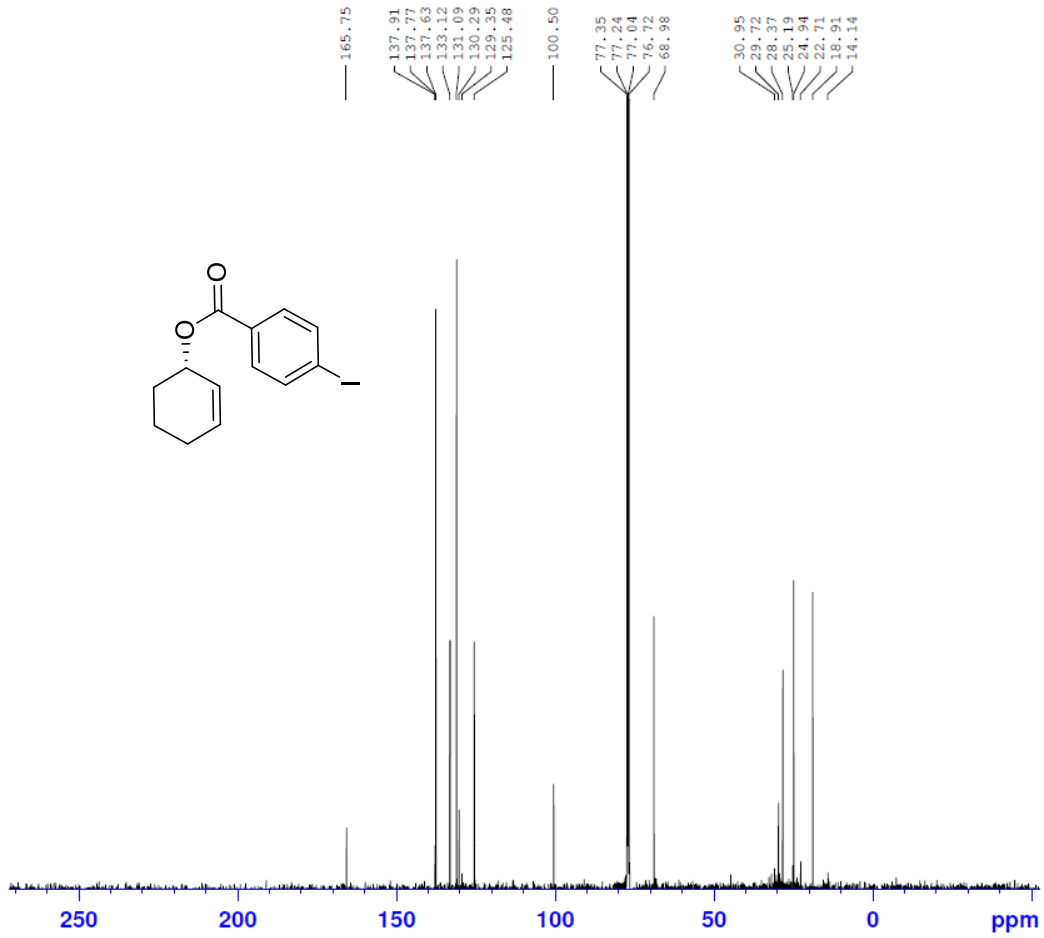


Figure S16: ^{13}C NMR spectrum of (*S*)-cyclohex-2-en-1-yl-4-iodobenzoate (8e)

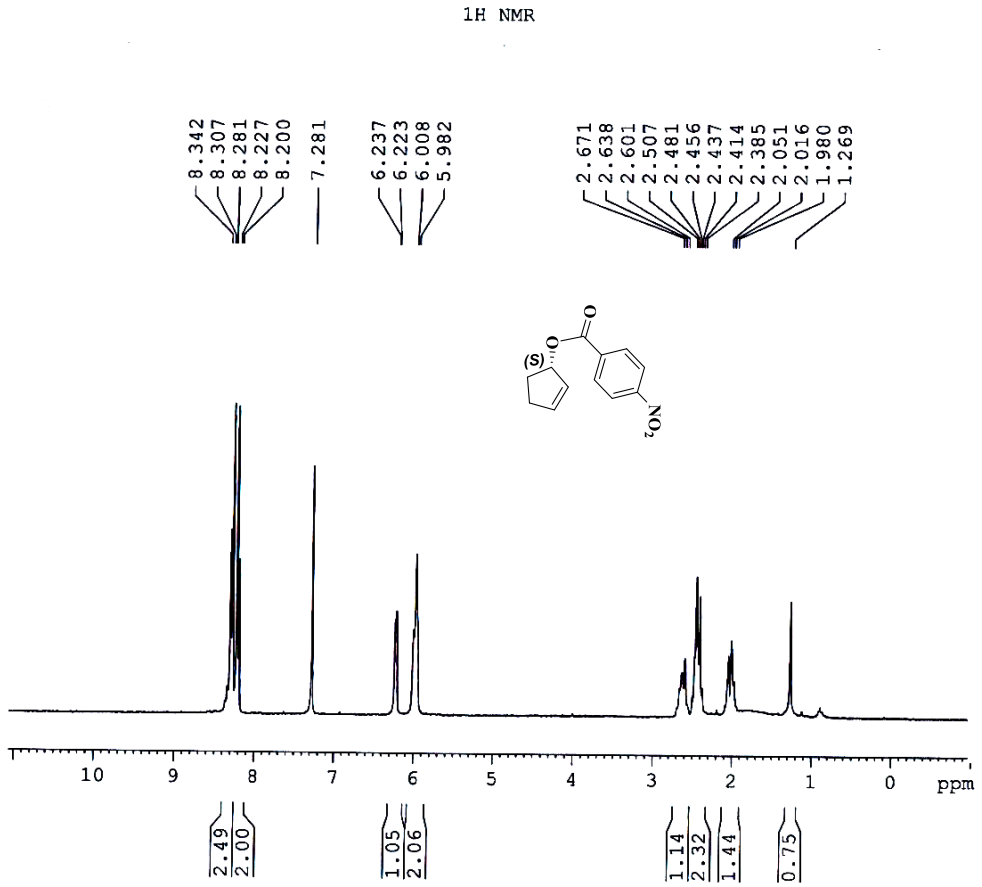


Figure S17: ^{1}H NMR spectrum of (*S*)-cyclopenta-2-en-1-yl-4-nitrobenzoate (9c)

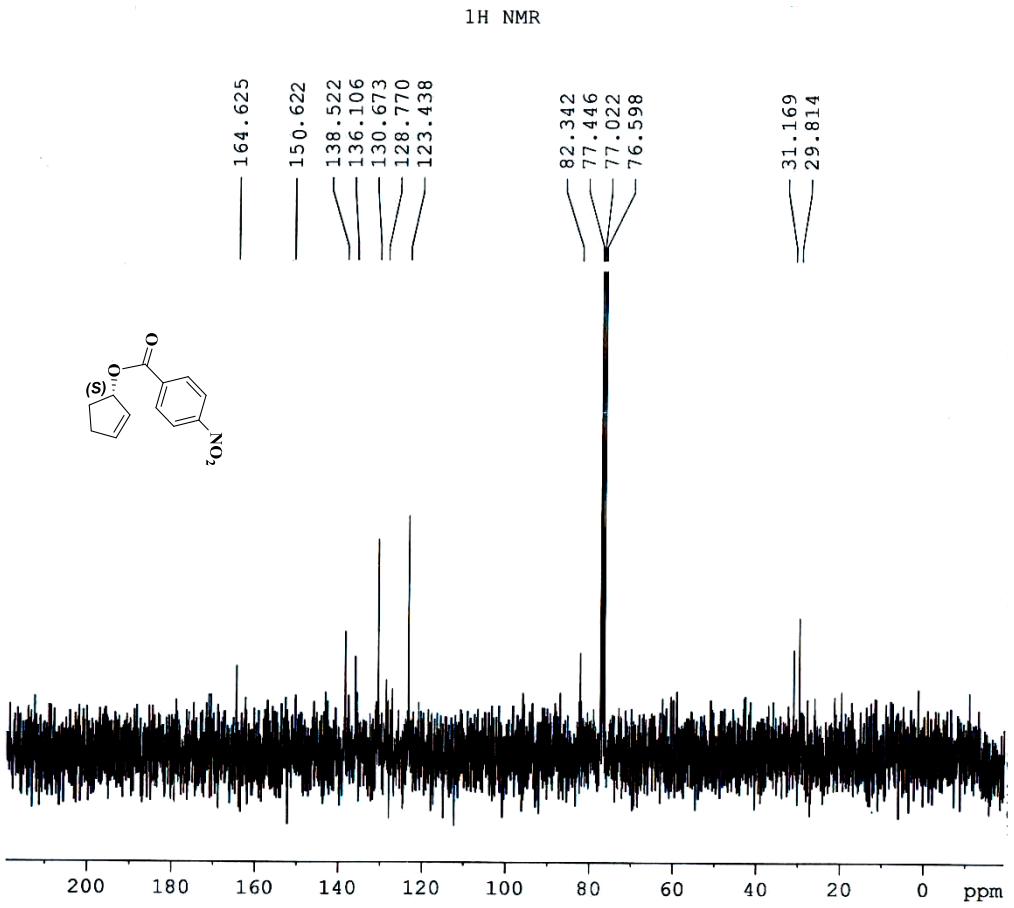


Figure S18: ^{13}C NMR spectrum of (*S*)-cyclopenta-2-en-1-yl-4-nitrobenzoate (9c)

Figure S19: ^{1}H NMR spectrum of (*S*)-cyclopenta-2-en-1-yl-2-iodobenzoate (9d)

Figure S20: ^{13}C NMR spectrum of (*S*)-cyclopenta-2-en-1-yl-2-iodobenzoate (9d)

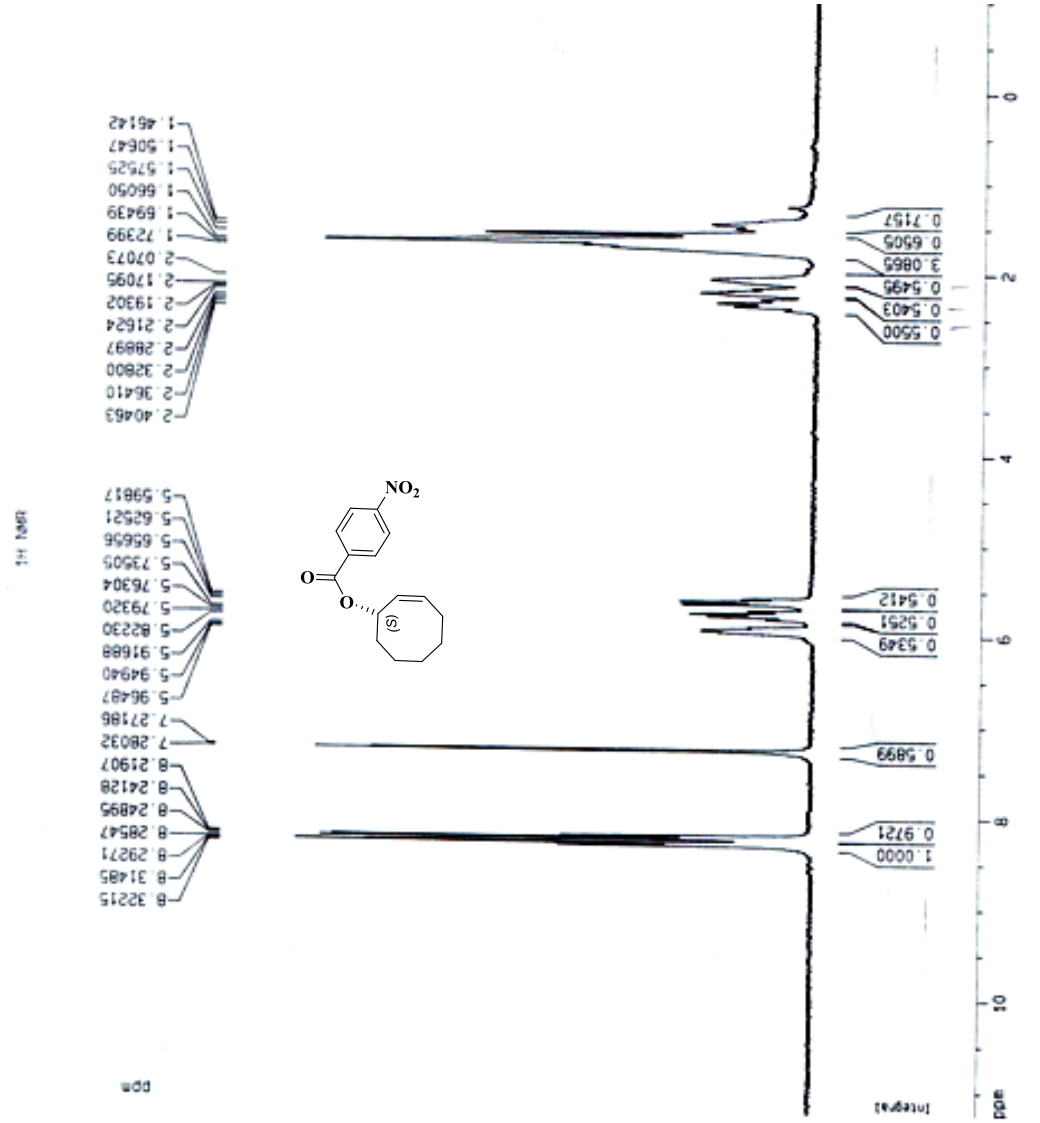


Figure S21: ^{1}H NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-4-nitrobenzoate (10c)

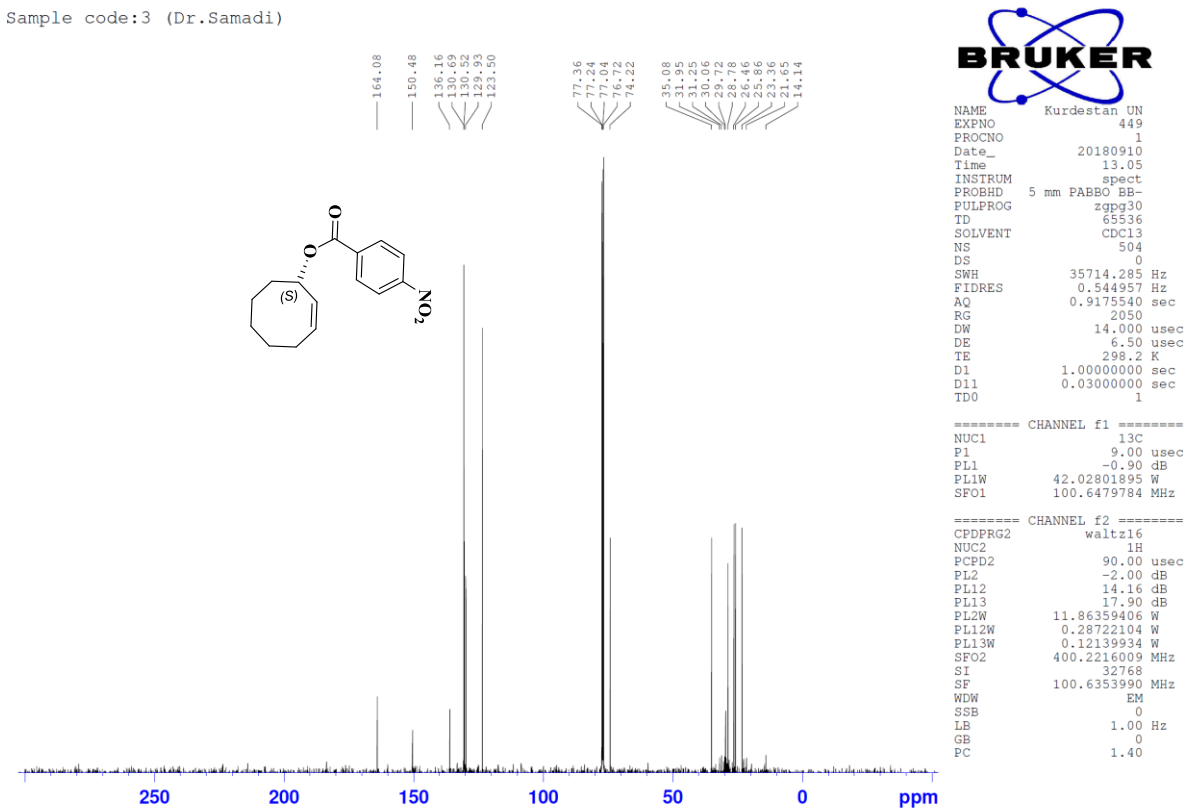


Figure S22: ^{13}C NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-4-nitrobenzoate (10c)

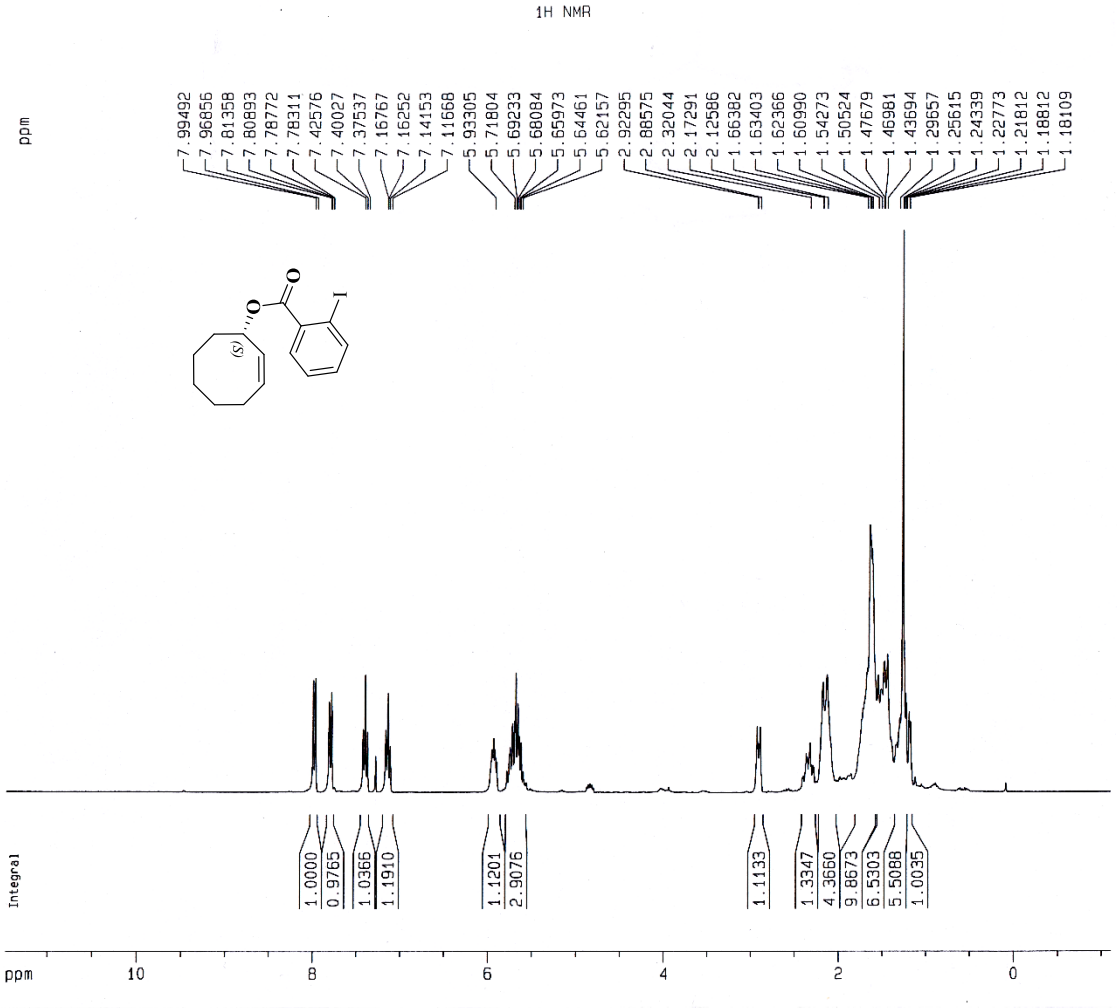


Figure S23: ^{1}H NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-2-iodobenzoate (10d)

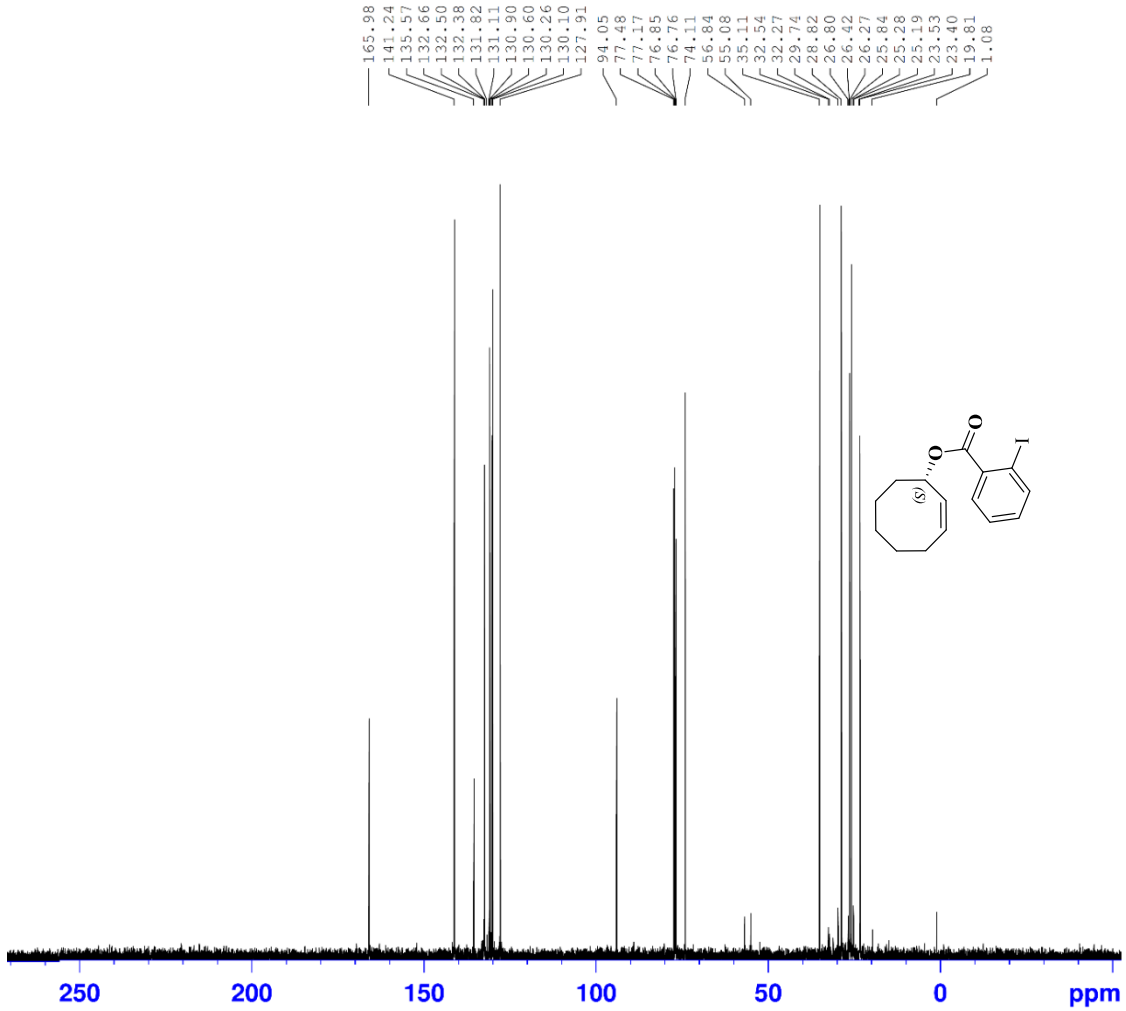


Figure S24: ^{13}C NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-2-iodobenzoate (10d)

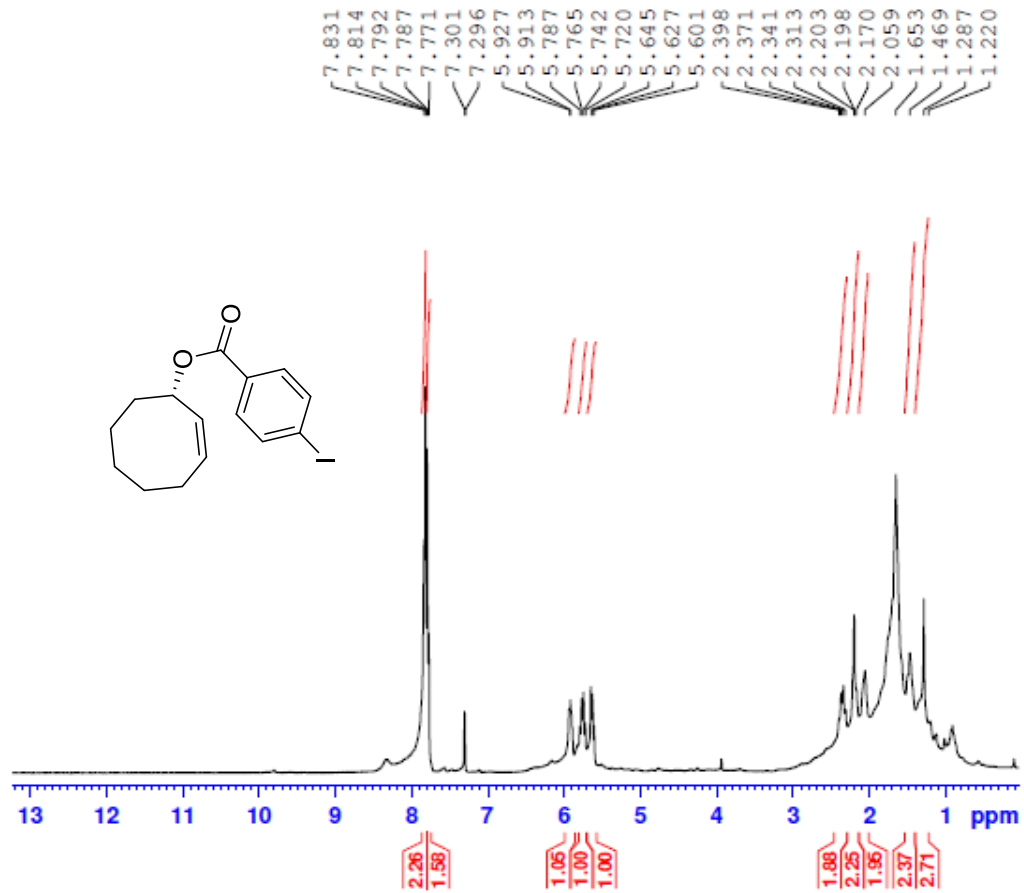


Figure S25: ^{1}H NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-4-iodobenzoate (10e)

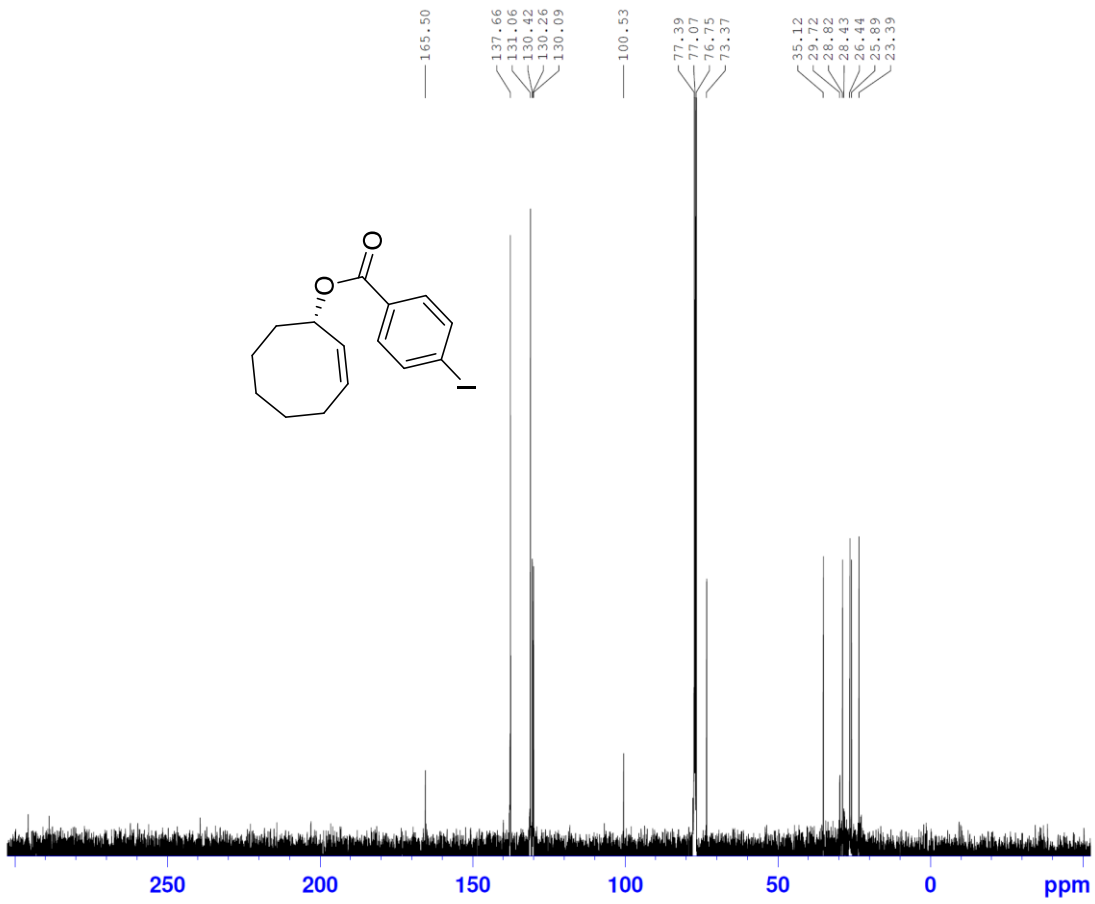


Figure S26: ^{13}C NMR spectrum of the (*S*)-cyclooct-2-en-1-yl-4-iodorobenzoate (10e)

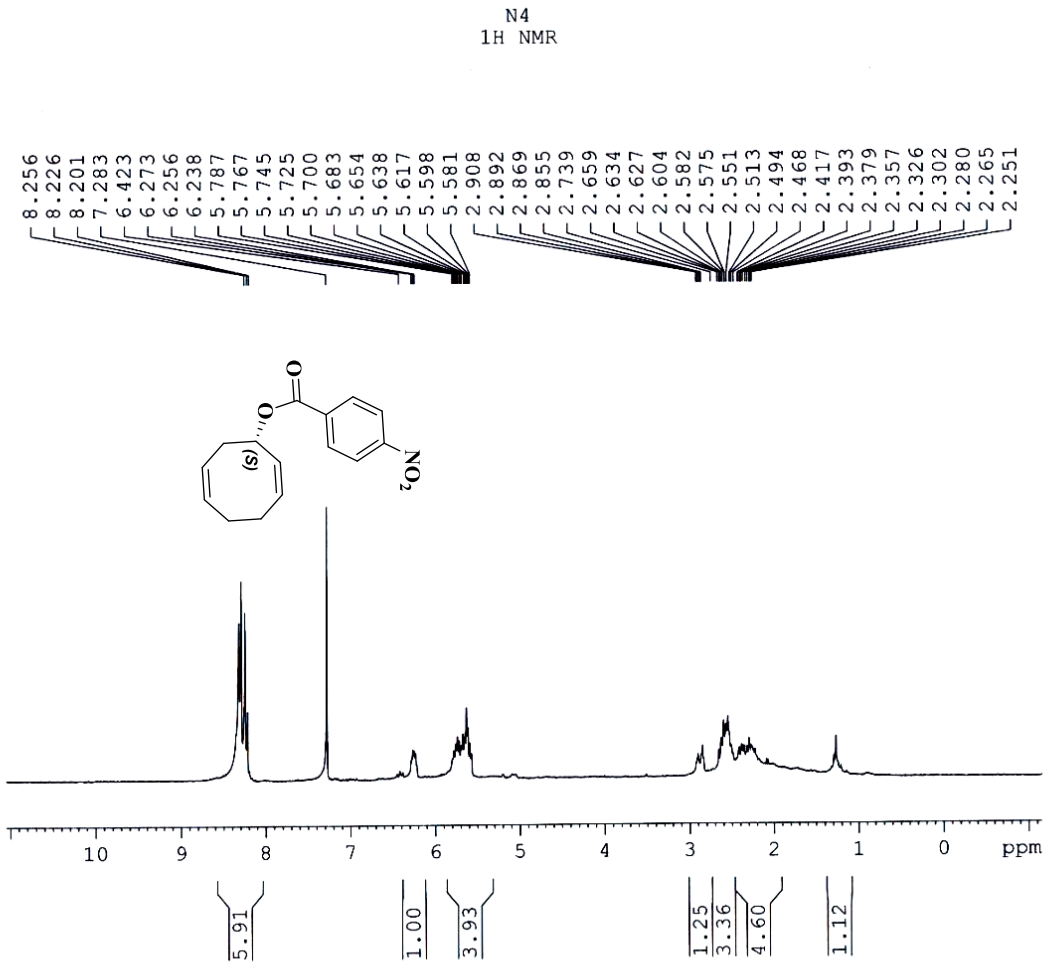


Figure S27: ^{1}H NMR spectrum of (*S*)-cycloocta-2,6-dien-1-yl-4-nitrobenzoate (11c)

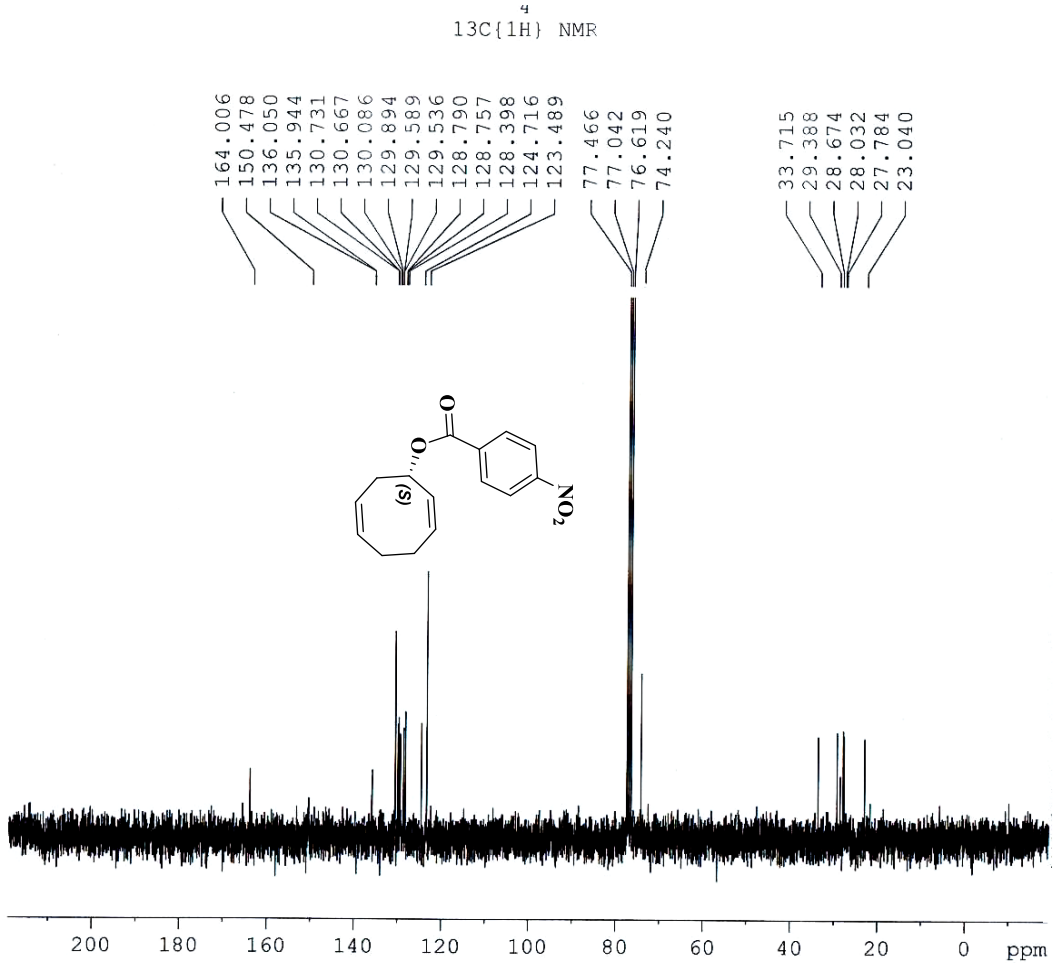


Figure S28: ^{13}C NMR spectrum of (*S*)-cycloocta-2,6-dien-1-yl-4-nitrobenzoate (11c)

Figure S29: ^{1}H NMR spectrum of (*S*)-cycloocta-2,6-dien-1-yl-2-iodobenzoate (11d)

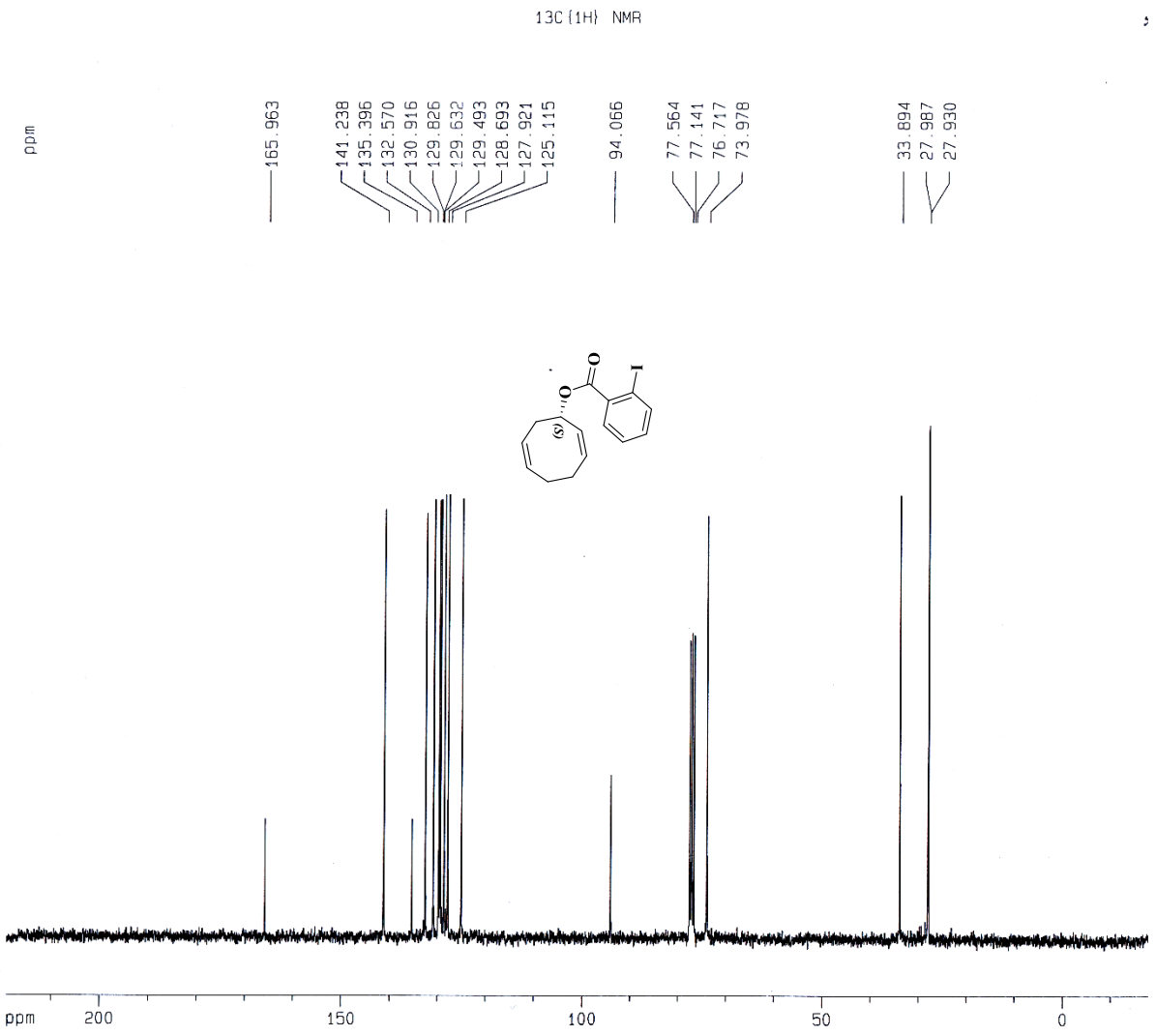


Figure S30: ^{13}C NMR spectrum of (*S*)-cycloocta-2,6-dien-1-yl-2-iodobenzoate (11d)

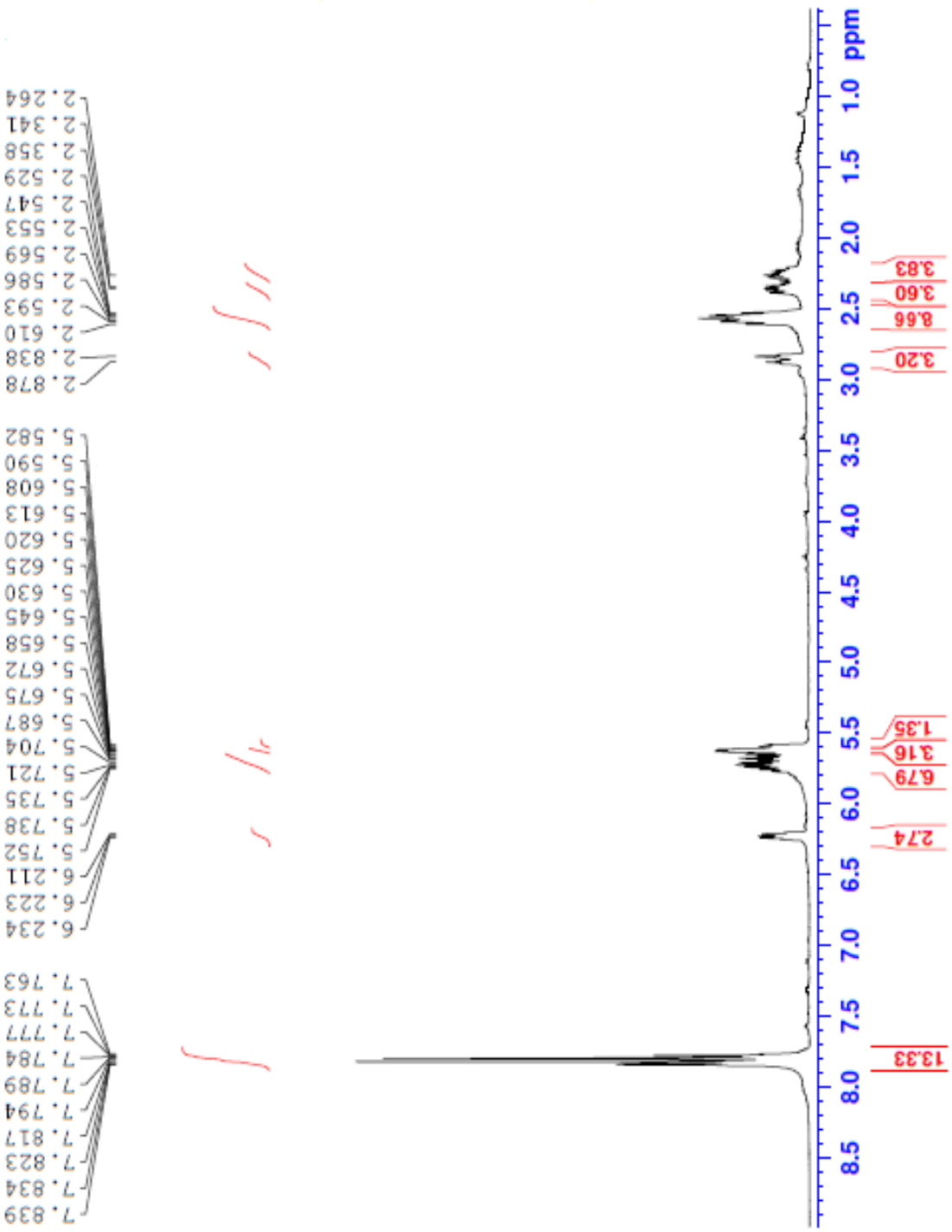


Figure S31: ^{1}H NMR spectrum of (*S*)-cycloocta-2,6-dien-1-yl-4-iodobenzoate (11e)

Figure S32: ^{13}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 $(CH_3CN)_4PF_6$ 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.