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

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Supporting Information

Experimental

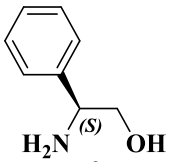
Materials and characterization methods

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. 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 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.

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

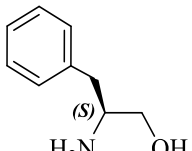
To an oven-dried 3-neck 250 mL round-bottom flask equipped with reflux condenser, sodium borohydride (40.0 mmol, 1.51 g) and 20 mL of dried tetrahydrofuran were added. After 15 minutes, (*S*)-phenylalanine **1b** (16.6 mmol, 2.75 g) was added in one portion to the stirring solution. Then the resulting mixture was cooled to 0 °C, and 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_3OH 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_2Cl_2 (3 x 20 mL), the organic layer washed with brine, and then the aqueous layer back extracted with CH_2Cl_2 (20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ 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% [1] (Figures S1-8).



2a

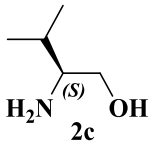
***(S)-2-amino-2-phenylethan-1-ol (2a)*:** Mp: 75-78°C.; FT-IR (KBr, cm^{-1}): 3274, 3062, 2922, 1598, 1489, 1045.; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 2.53 (1H, brs, (OH)), 2.75 (2H, brs, (NH_2)), 3.57 (1H, t, J = 9.6 Hz, CH_2), 3.69 (1H, t, J = 8.6 Hz, CH_2), 4.04-4.05 (1H, m, CH), 7.30-7.37 (5H, m, Ar).; ^{13}C NMR **(**100 MHz, $CDCl_3$): δ_C (ppm) = 57.4, 67.8, 126.6, 127.4, 127.5, 128.6, 128.8, 142.3.; $[\alpha]^{25}_D$ =+ 30.5° (c= 0.6, HCl (1 M)).



2b

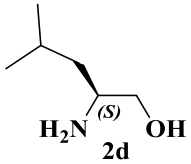
***(S)-2-amino-3-phenylpropan-1-ol (2b)*:** Mp: 90-92°C.; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 2.19 (3H, brs, (NH_2, OH)), 2.57 (1H, dd, J = 12.8, 9.0 Hz, CH_2), 2.81 (1H, dd, J=12.0, 8.6 Hz, CH_2), 3.16 (1H, brs, *CH), 3.44 (1H, d, J =7.6 Hz, H_2C-OH), 3.67 (1H, d, J = 6.8 Hz, H_2C-

OH), 7.21-7.35 (5H, m, Ar).; ^{13}C NMR **(**100 MHz, $CDCl_3$**)**: δ_C (ppm) = 40.8, 54.2, 66.3 , 126.4, 128.6, 129.2, 138.6.; $[\alpha]^{25}_D$ = -10.7° (*c*= 0.4, HCl (1 M)).



2c

(S)-2-amino-3-methylbutan-1-ol (2c)**:** ^{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).



2d

(S)-2-amino-4-methylpentan-1-ol (2d)**:** Mp: 69-73°C.; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) =0.94 (6H, d, *J* = 6.8 Hz, CH_3), 1.24 (2H, brs, CH_2), 1.67-1.75 (1H, m, CH), 2.84 (2H, brs (NH_2)), 2.97 (1H, brs, *CH), 3.29 (1H, t, *J* = 9.0 Hz, H_2C-OH), 3.62 (1H, d, *J* = 8.8 Hz, H_2C-OH).; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) = 22.2, 23.3, 24.7, 43.5, 50.7, 66.9.; $[\alpha]^{25}_D$ = + 1.3° (*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 [2, 3]. In a round bottom flask (250 mL), 6.0 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) 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 ℃ 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 [2, 3 4]. 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_2Cl_2/CH_3OH. Then the obtained powder was soxhleted for 24 hours with CH_2Cl_2/CH_3OH (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.

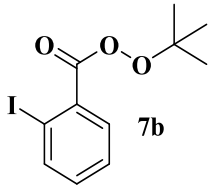
A typical procedure for the Synthesis of benzoyl chloride derivatives 6a-g:

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 ^oC, 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%[4-8].

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

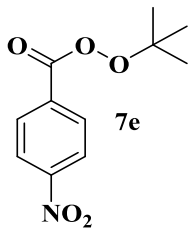
In a 50 mL round bottom flask under the nitrogen atmosphere, *o*-iodo-benzoyl chloride **6b** (1.5 mmol, 0.4 g) was dissolved in dried methylene chloride (3 mL). After cooling to -20 ^oC, pyridine (1.7 mmol, 0.28 mL) and *tert*-butyl hydroperoxide (1.7 mmol, 0.12 mL) were slowly added and stirred for 4.5 hours at -20 ^oC (Scheme 1). After consumption of *o*-iodo-benzoyl chloride, the reaction solution was diluted with CH_2Cl_2 (40 mL) and washed with the saturated $NaHCO_3$ 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% [4-8] (Figures S17-18).



7b

***Tert*-butyl-2-iodobenzoperoxoate (7b**): Mp: 47-49 °C.; FT-IR (KBr, cm^{-1}): 2926, 1758, 466.; ^{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.; m/z (%): 320 (0.2, M), 248 (58), 194 (5), 122 (100), 74 (75).



7e

***Tert*-butyl-4-nitrobenzoperoxoate (7e):** Mp: 76-78 °C (lit.75-78 °C [2, 9]); ^{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.

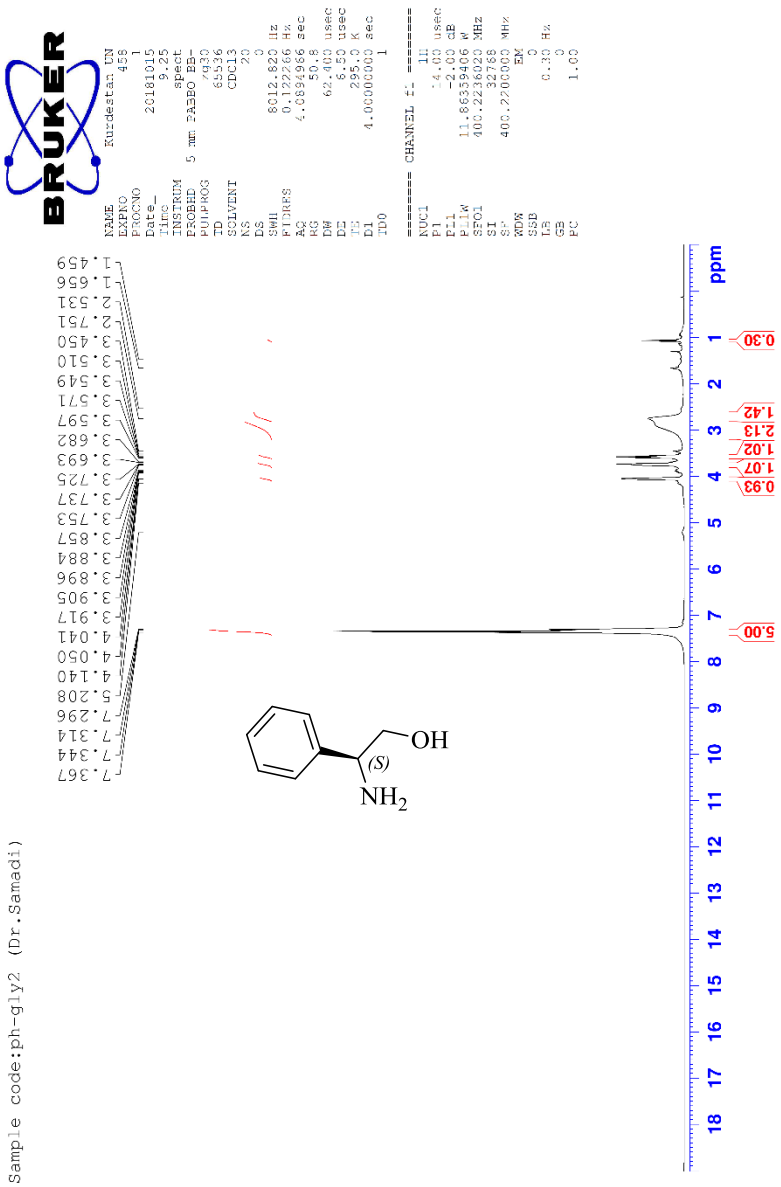


Figure S1: ^{1}H NMR of **2a**

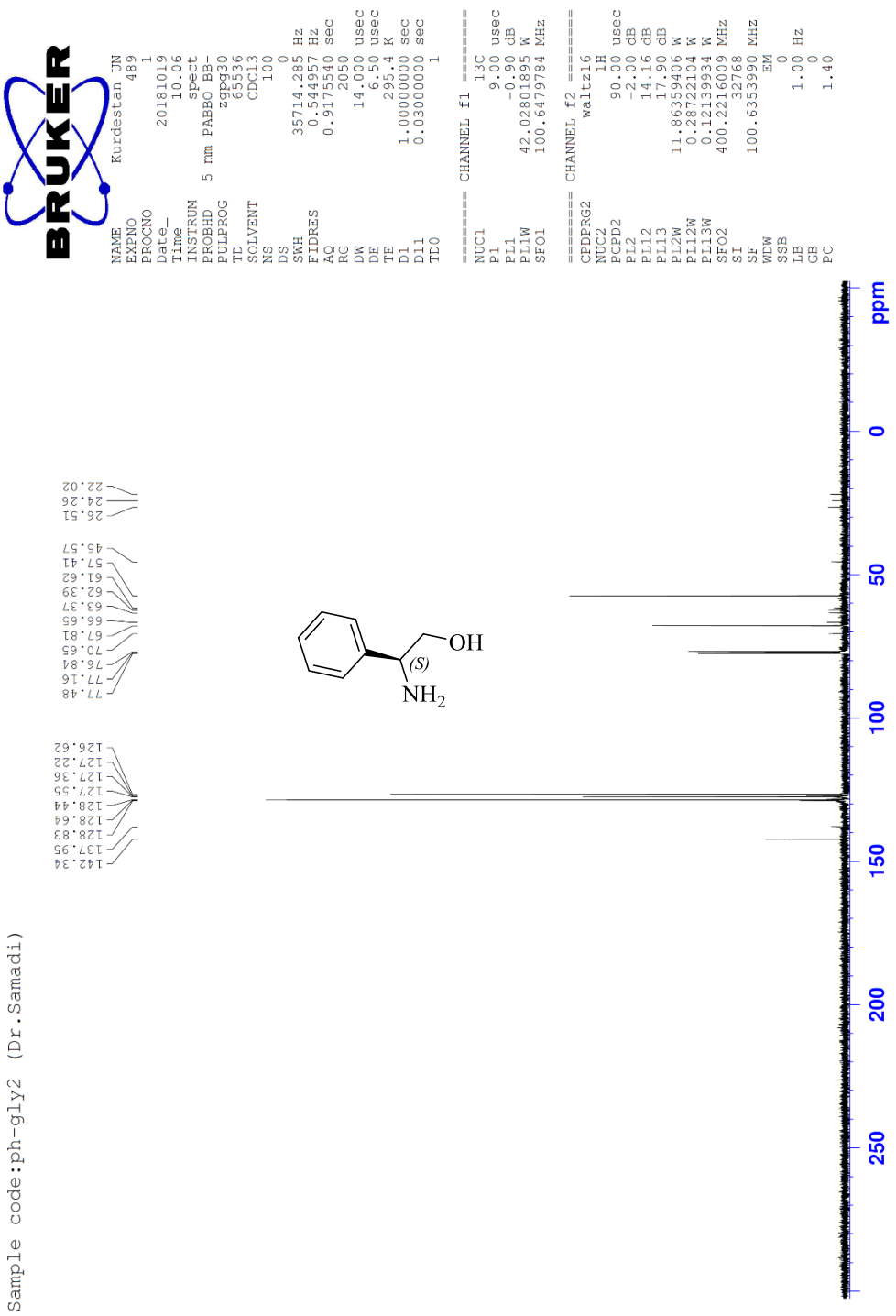


Figure S2: ^{13}CNMR of **2a**

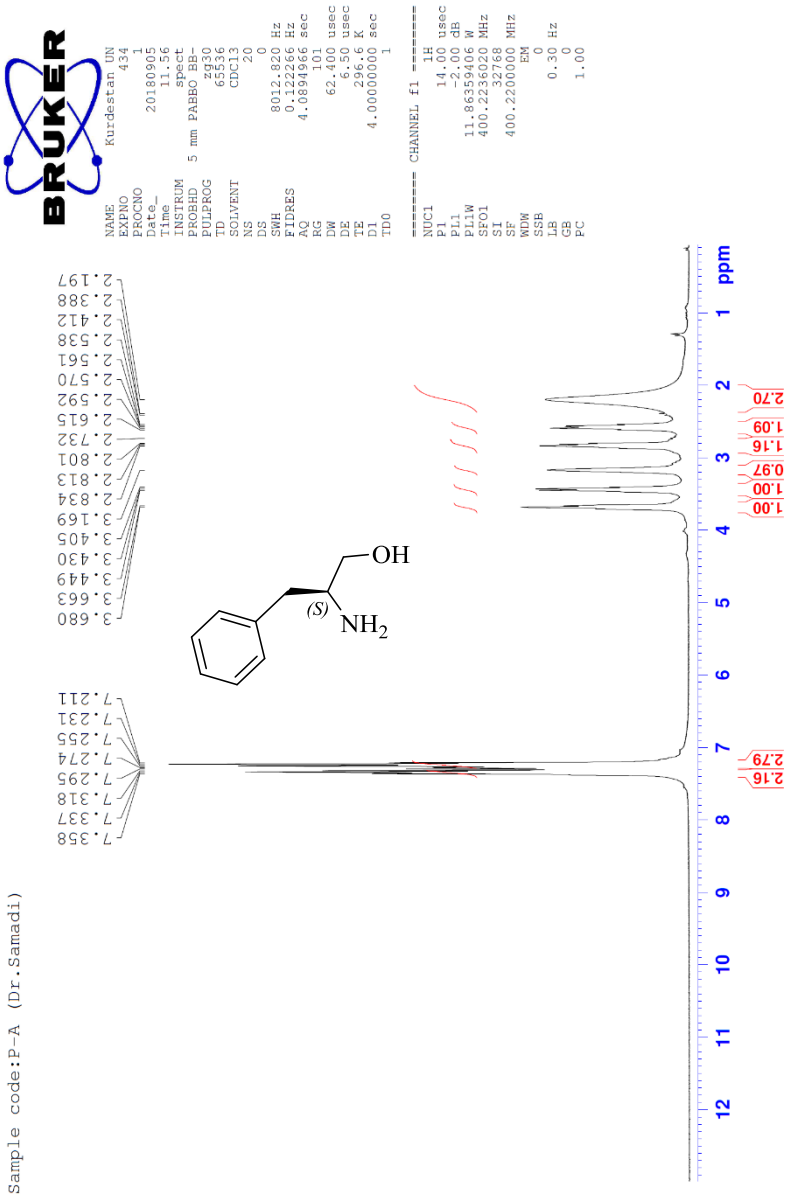


Figure S3: ^{1}H NMR of **2b**

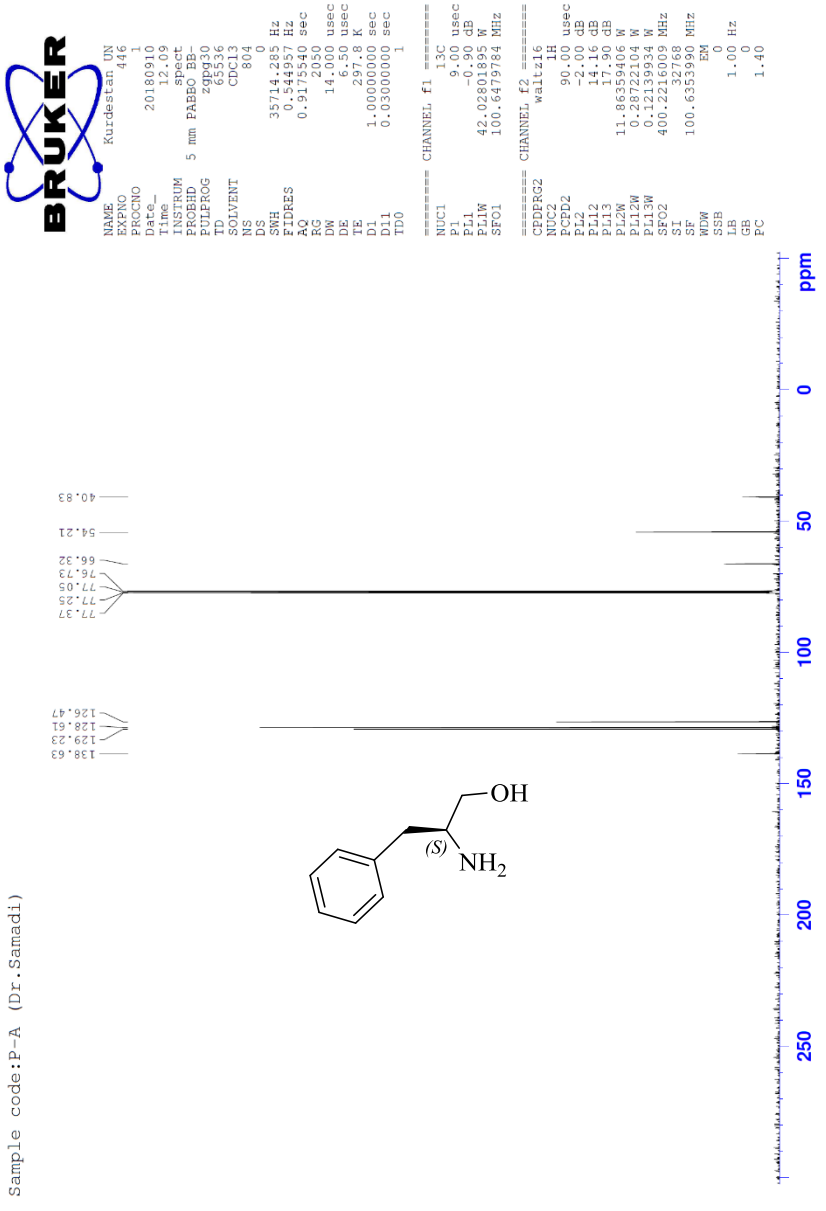


Figure S4: ^{13}CNMR of **2b**

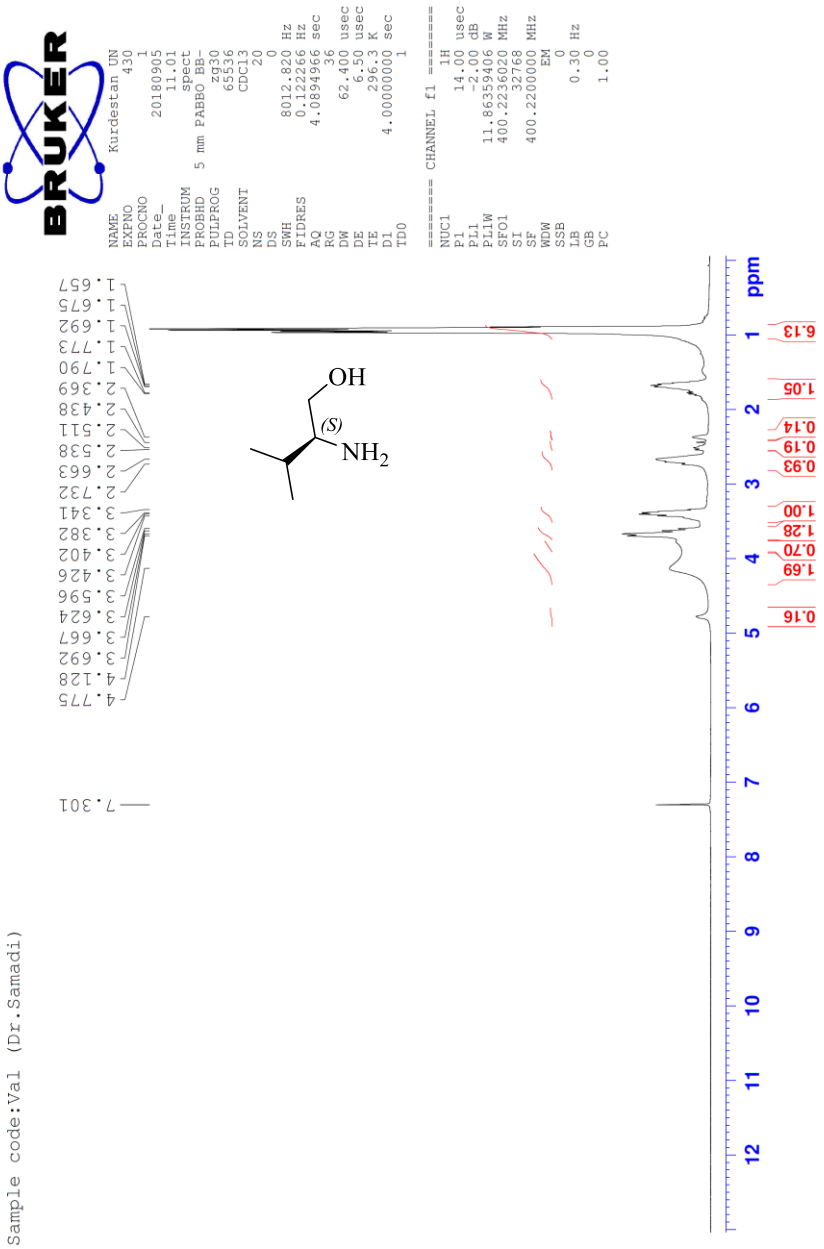


Figure S5: ^{1}H NMR of **2c**

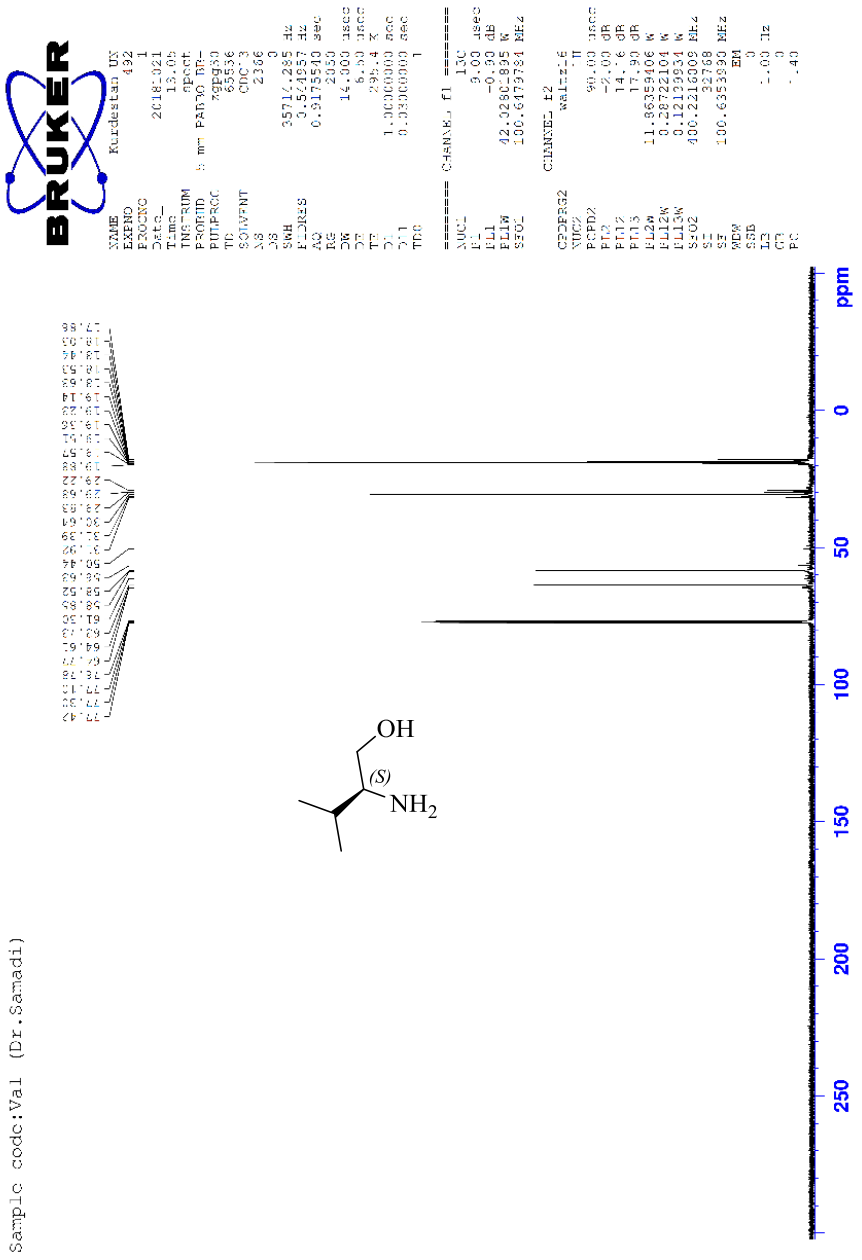


Figure S6: ^{13}CNMR of **2c**

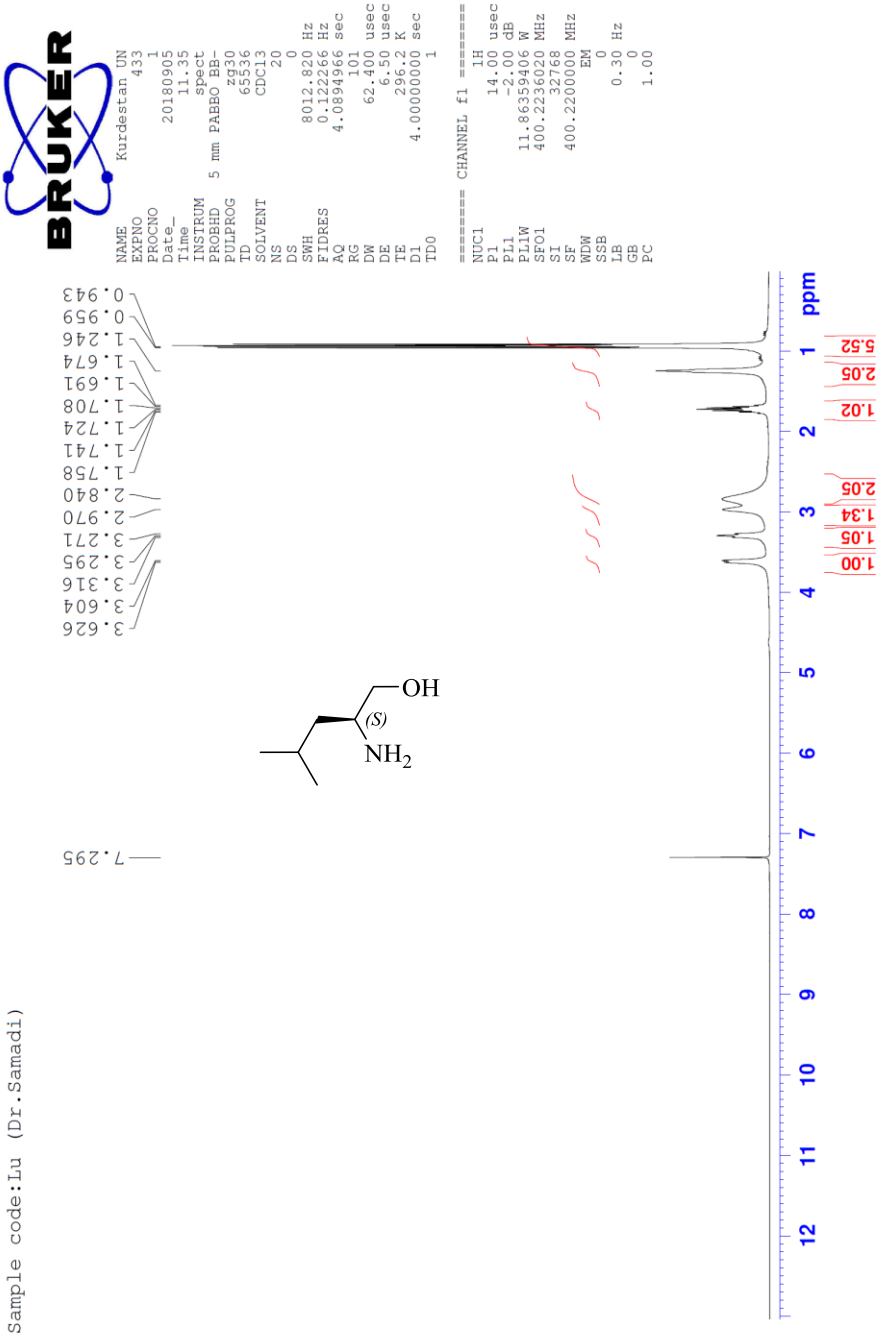


Figure S7: ^{1}H NMR of **2d**

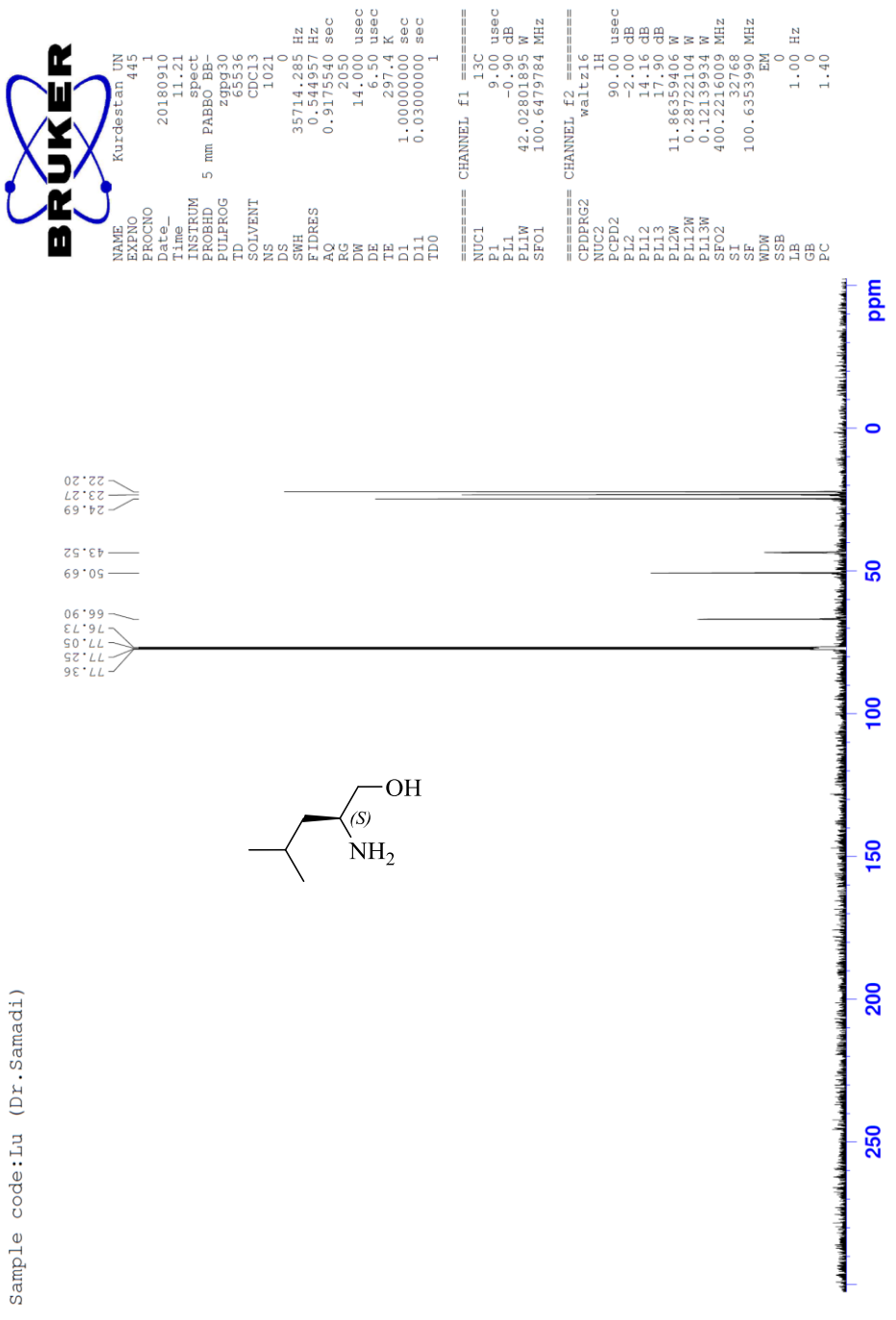


Figure S8: ^{13}CNMR of **2d**

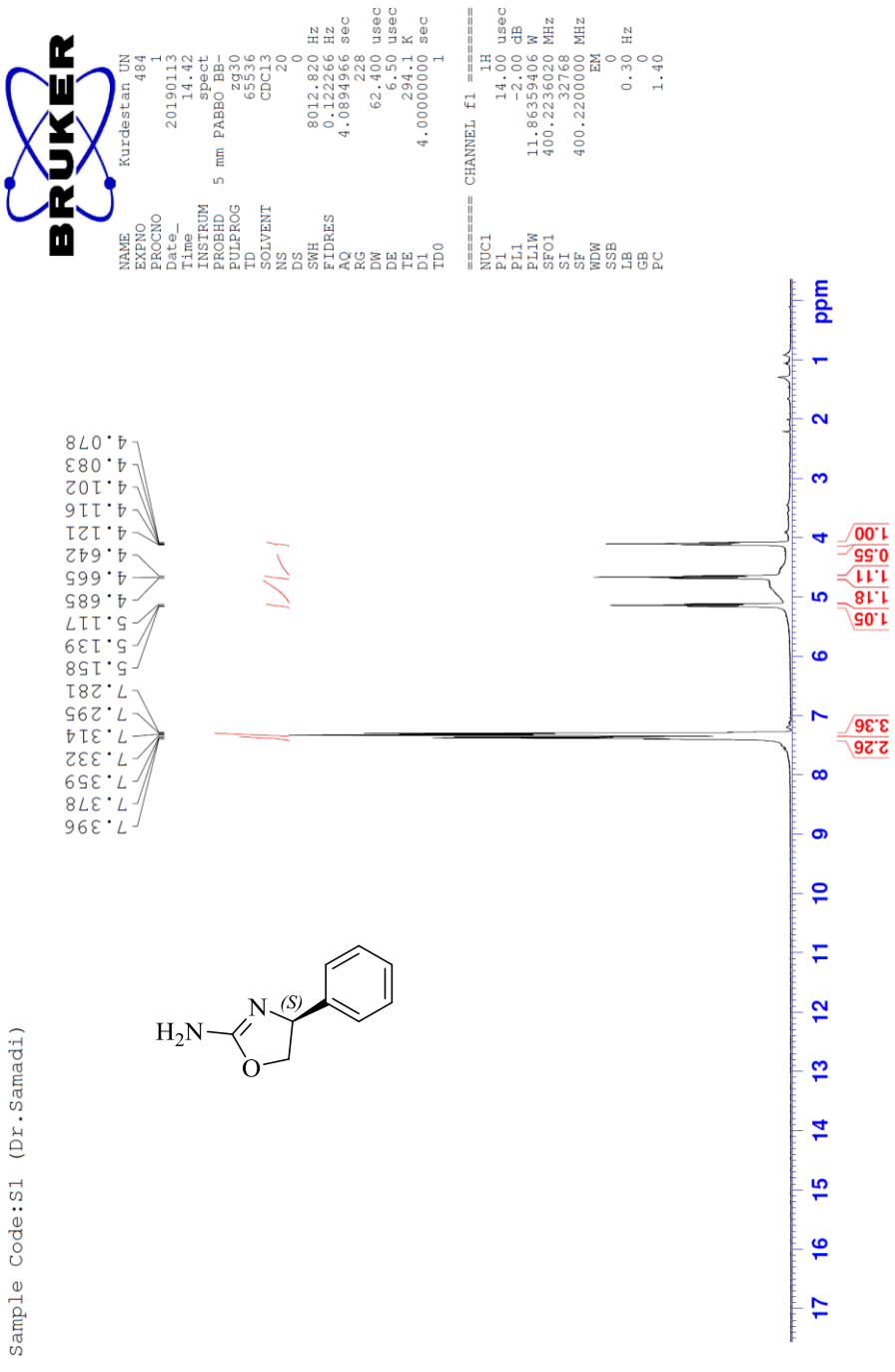


Figure S9: ^{1}H NMR of **3a**

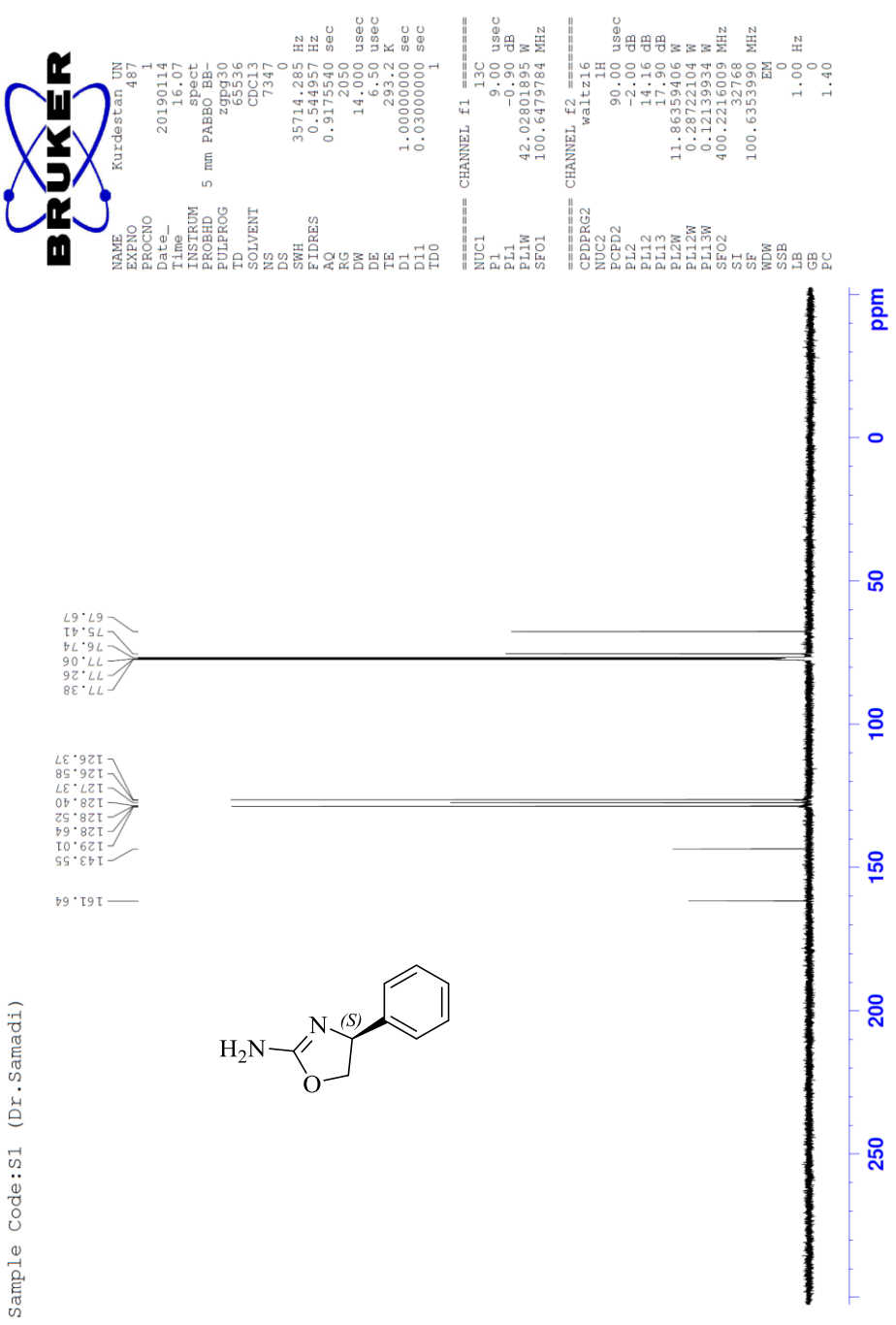


Figure S10: ^{13}CNMR of **3a**

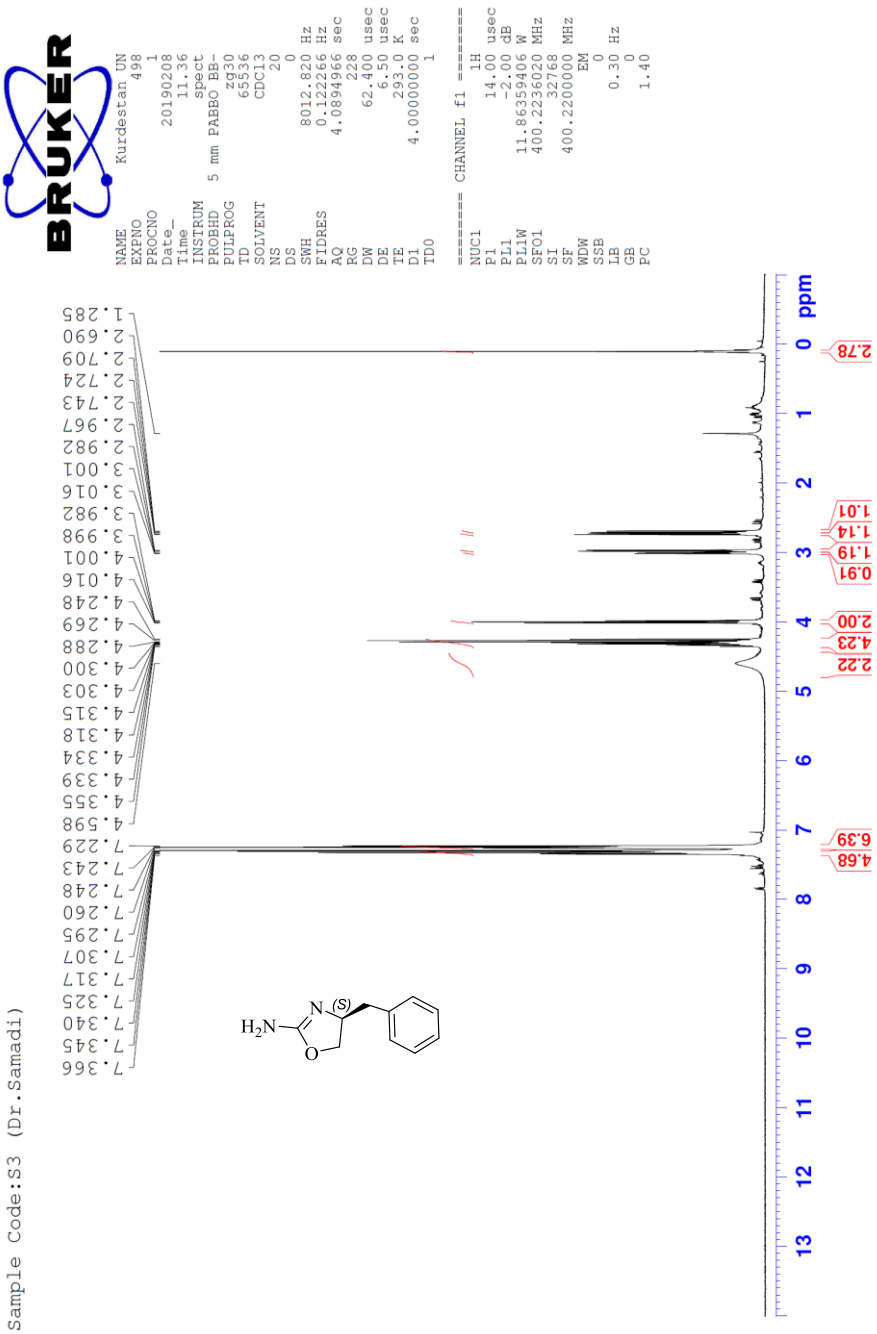


Figure S11: ^{1}H NMR of **3b**

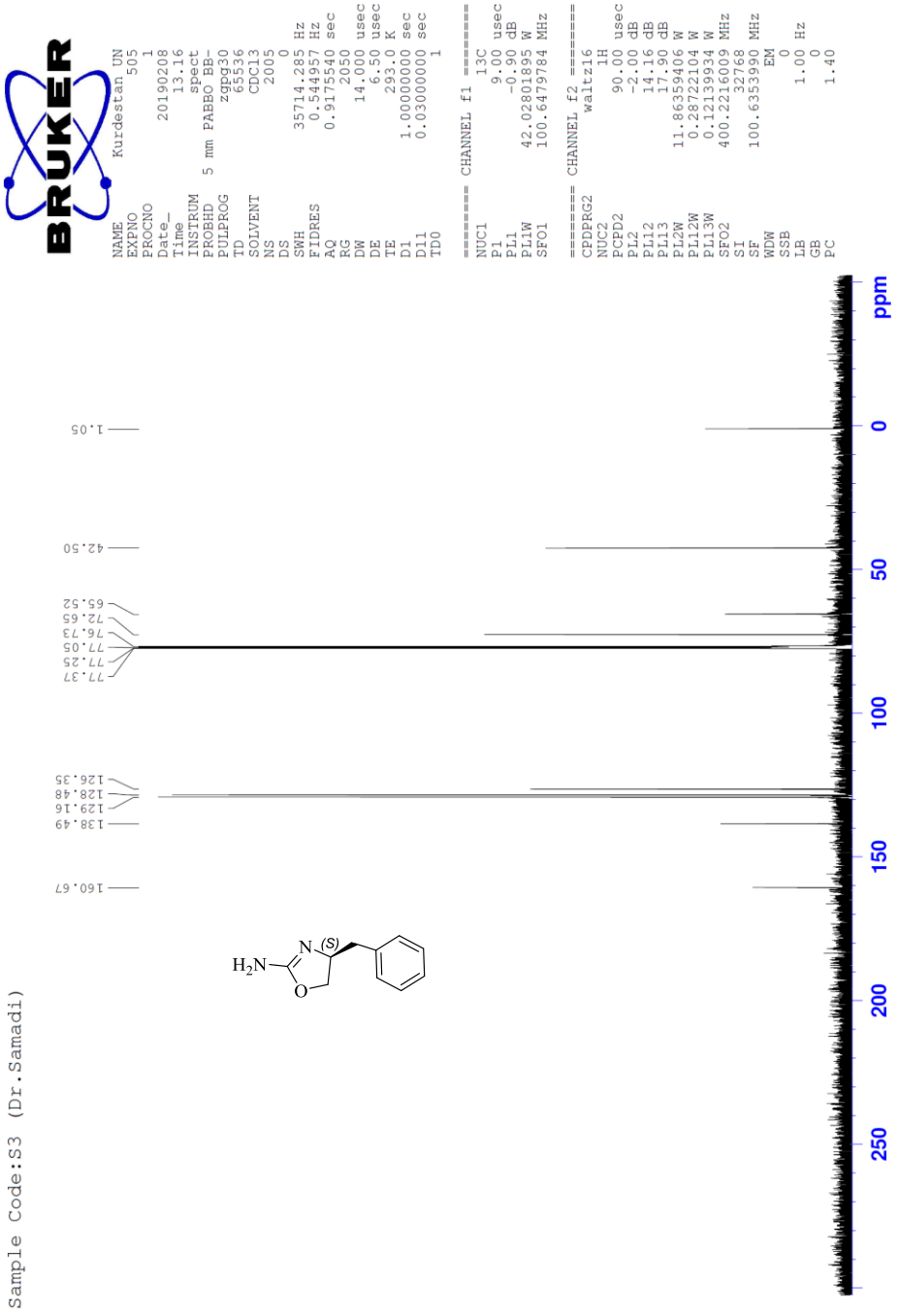


Figure S12: ^{13}CNMR of **3b**

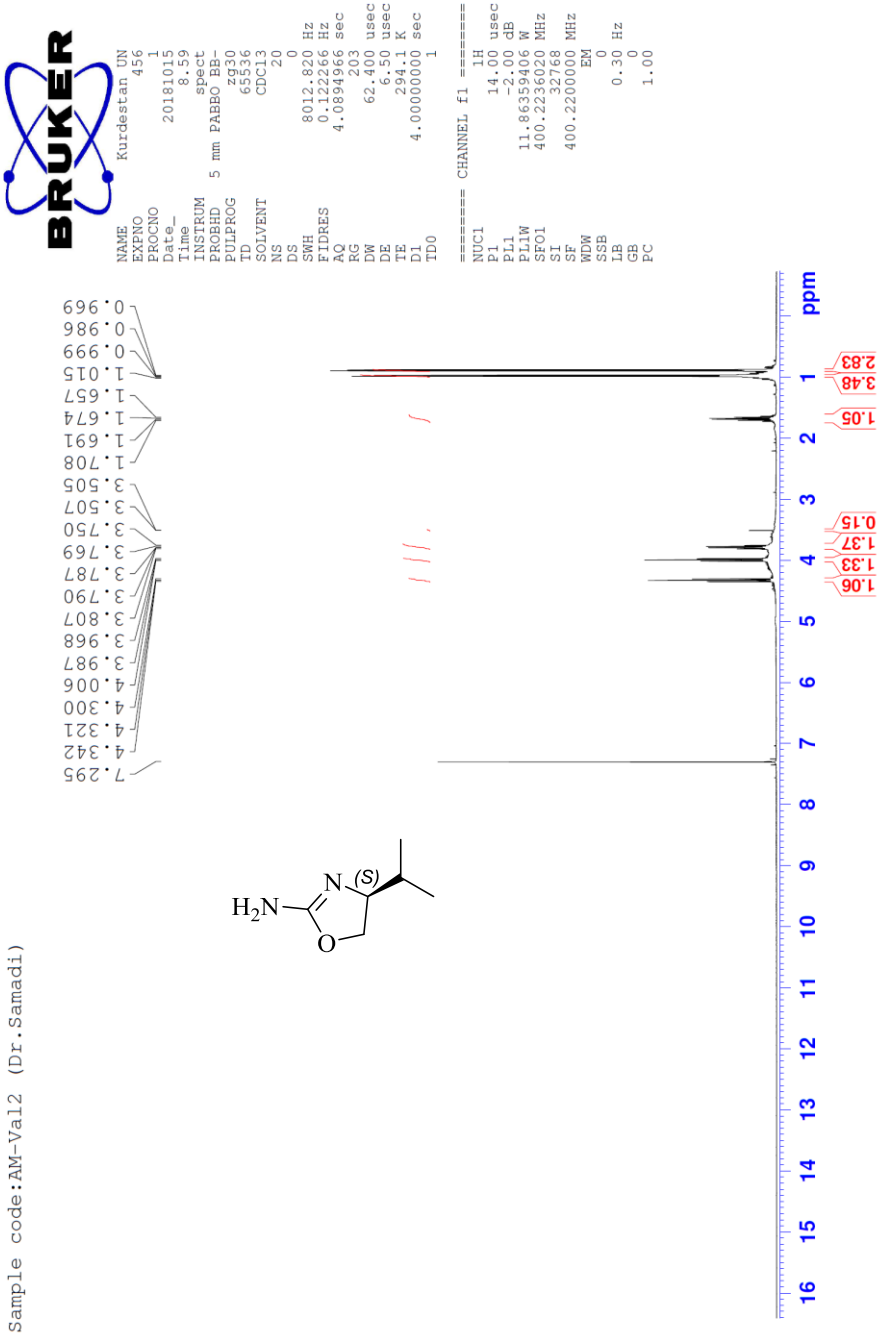


Figure S13: [1]H NMR of **3c**

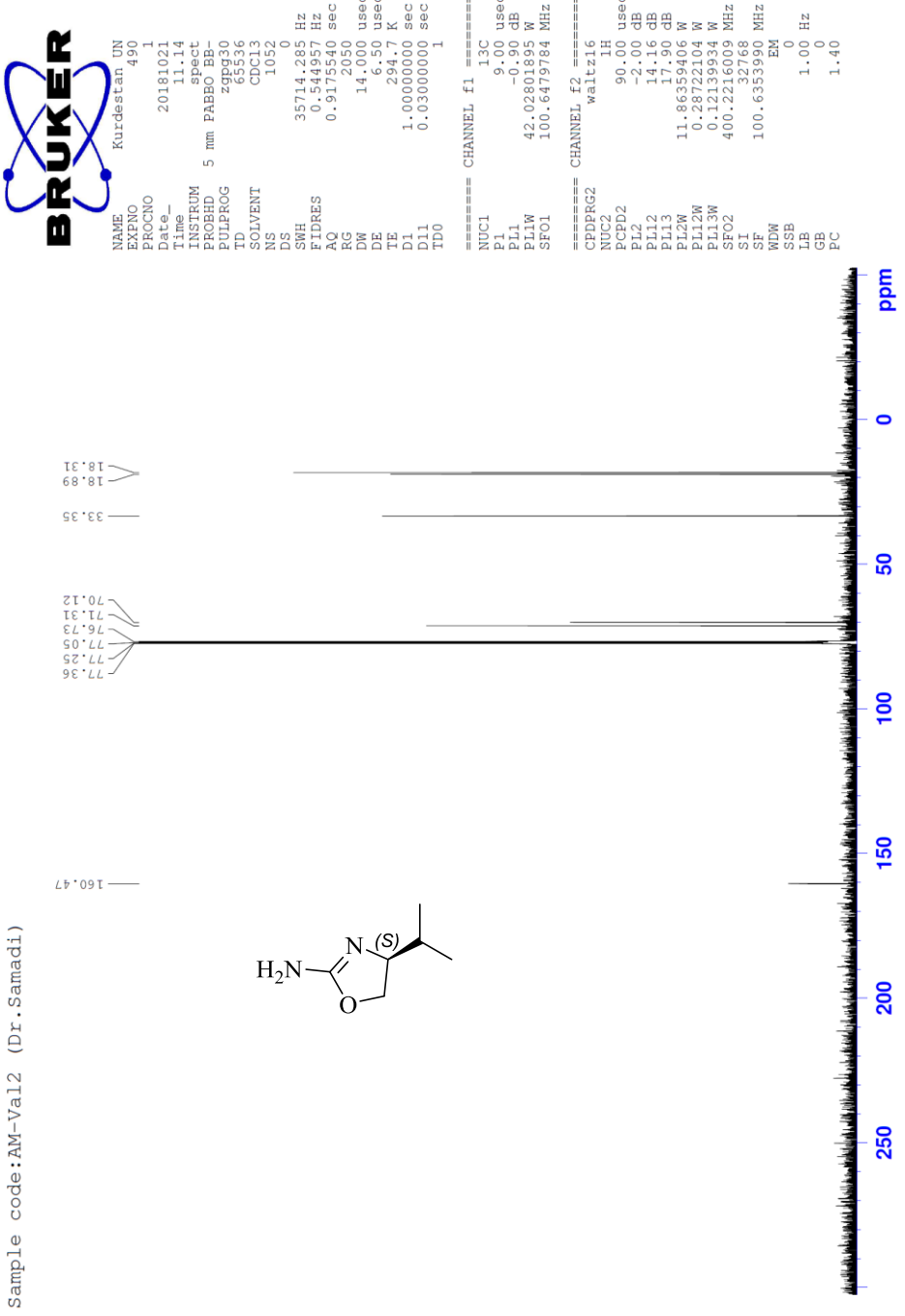


Figure S14: ^{13}CNMR of **3c**

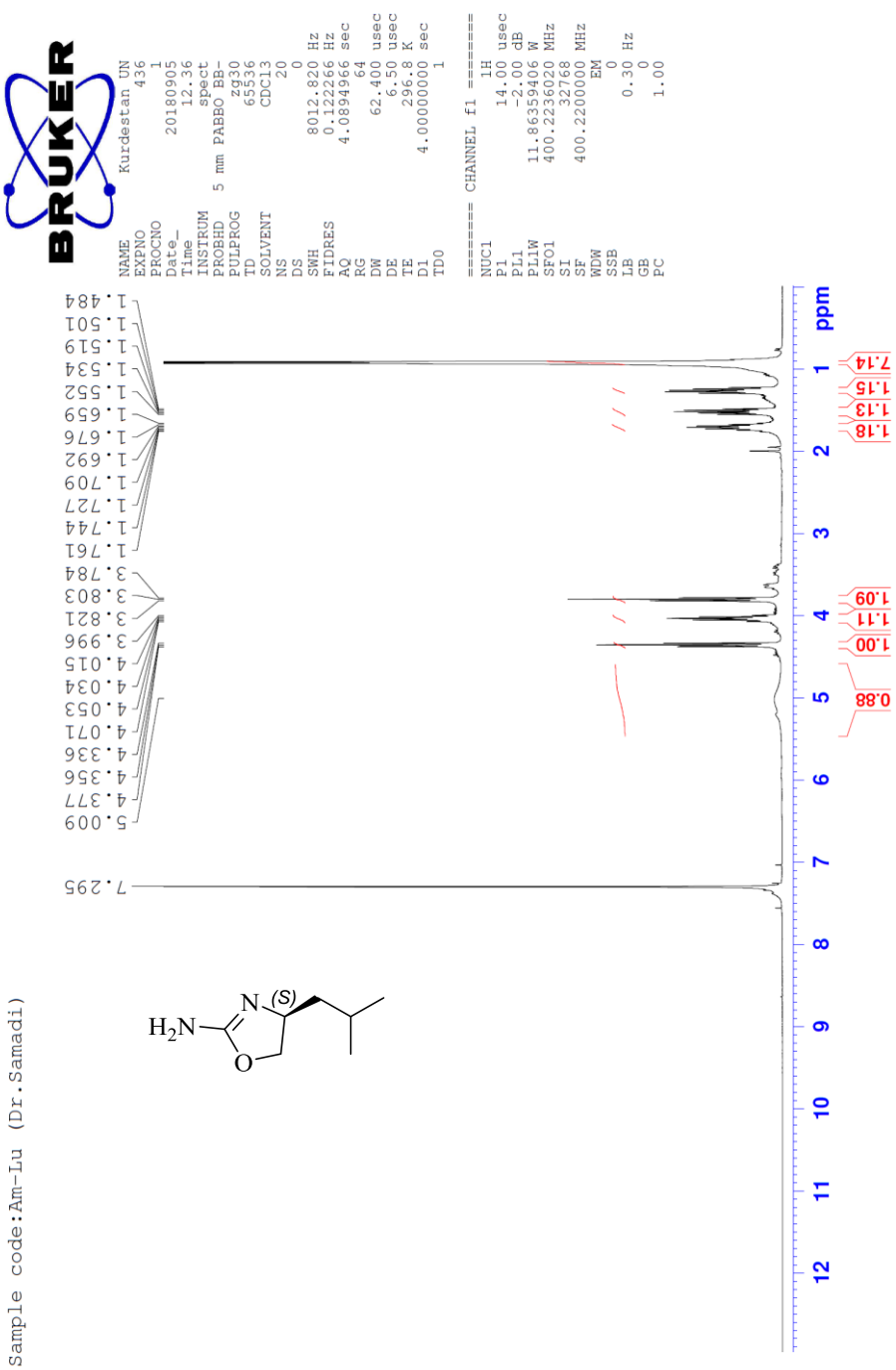


Figure S15: ^{1}H NMR of **3d**

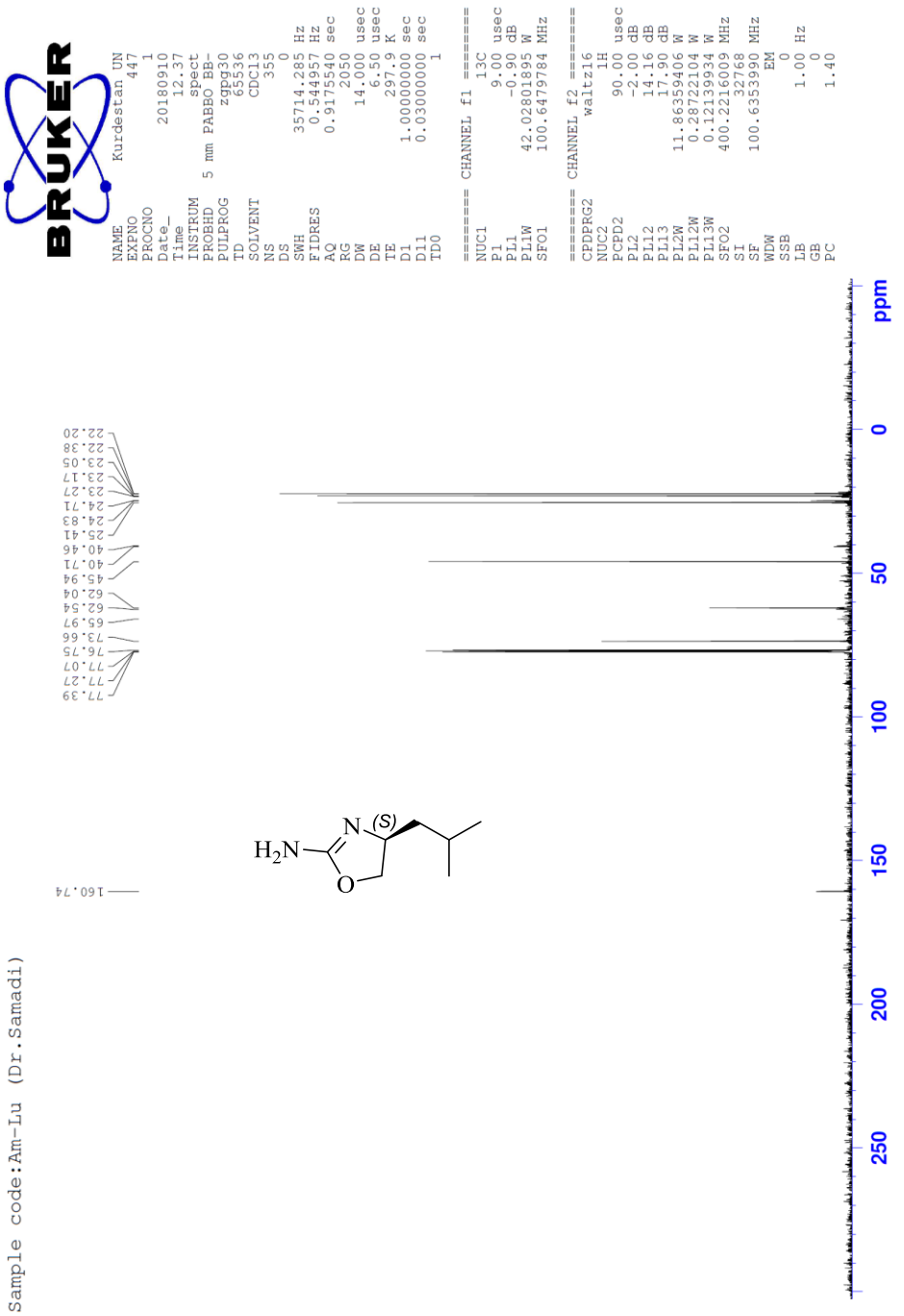


Figure S16: ^{13}CNMR of **3d**

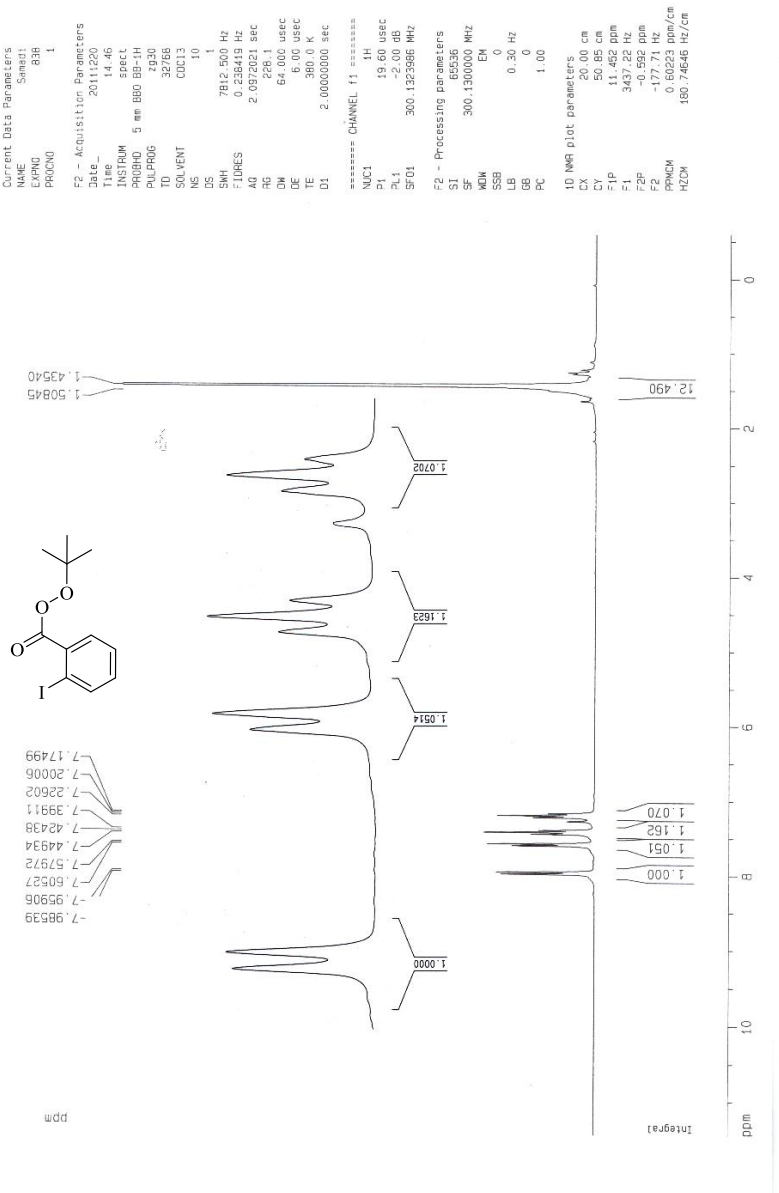


Figure S17: ^{1}H NMR of **7b**

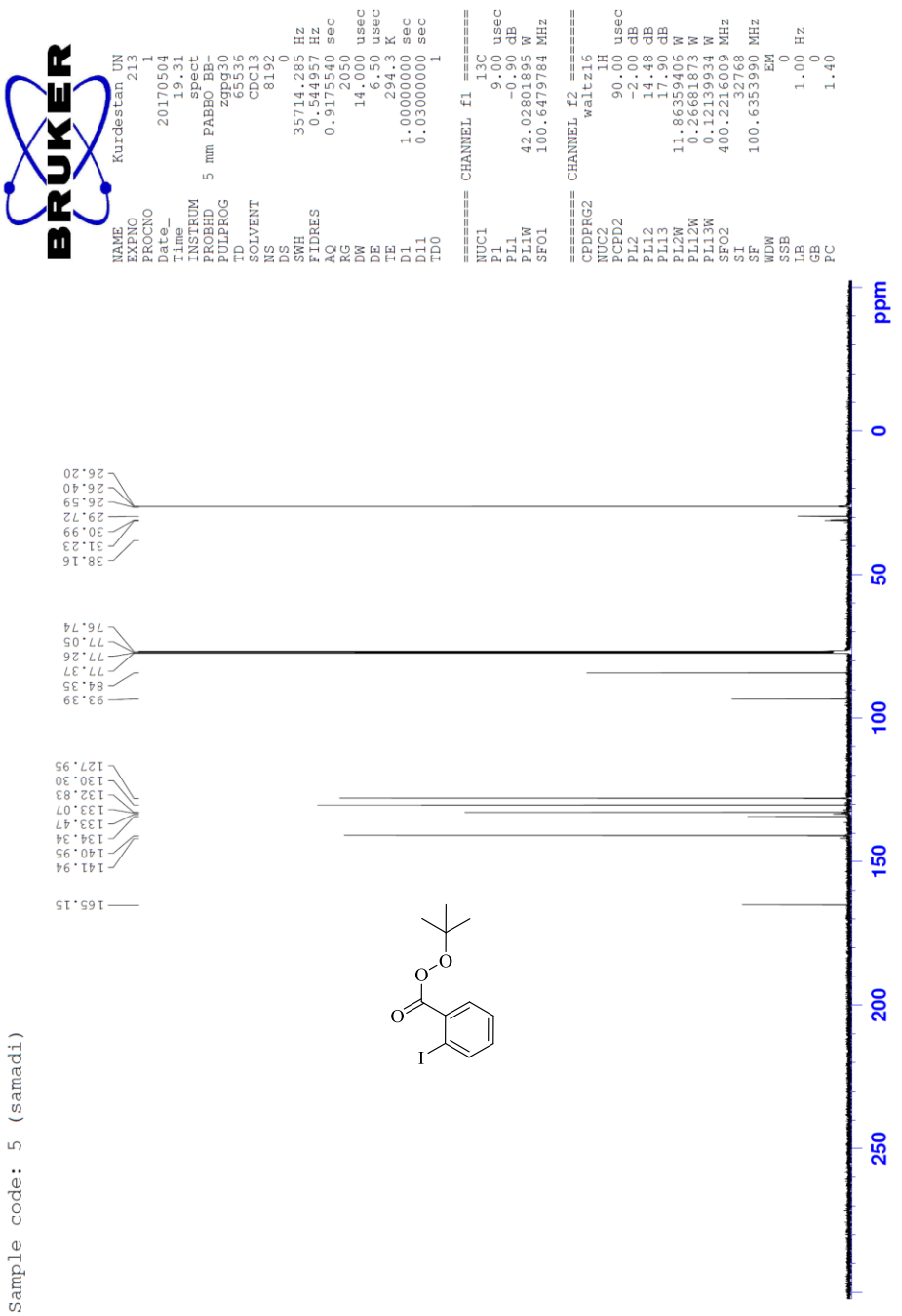


Figure S18: ^{13}CNMR of **7b**

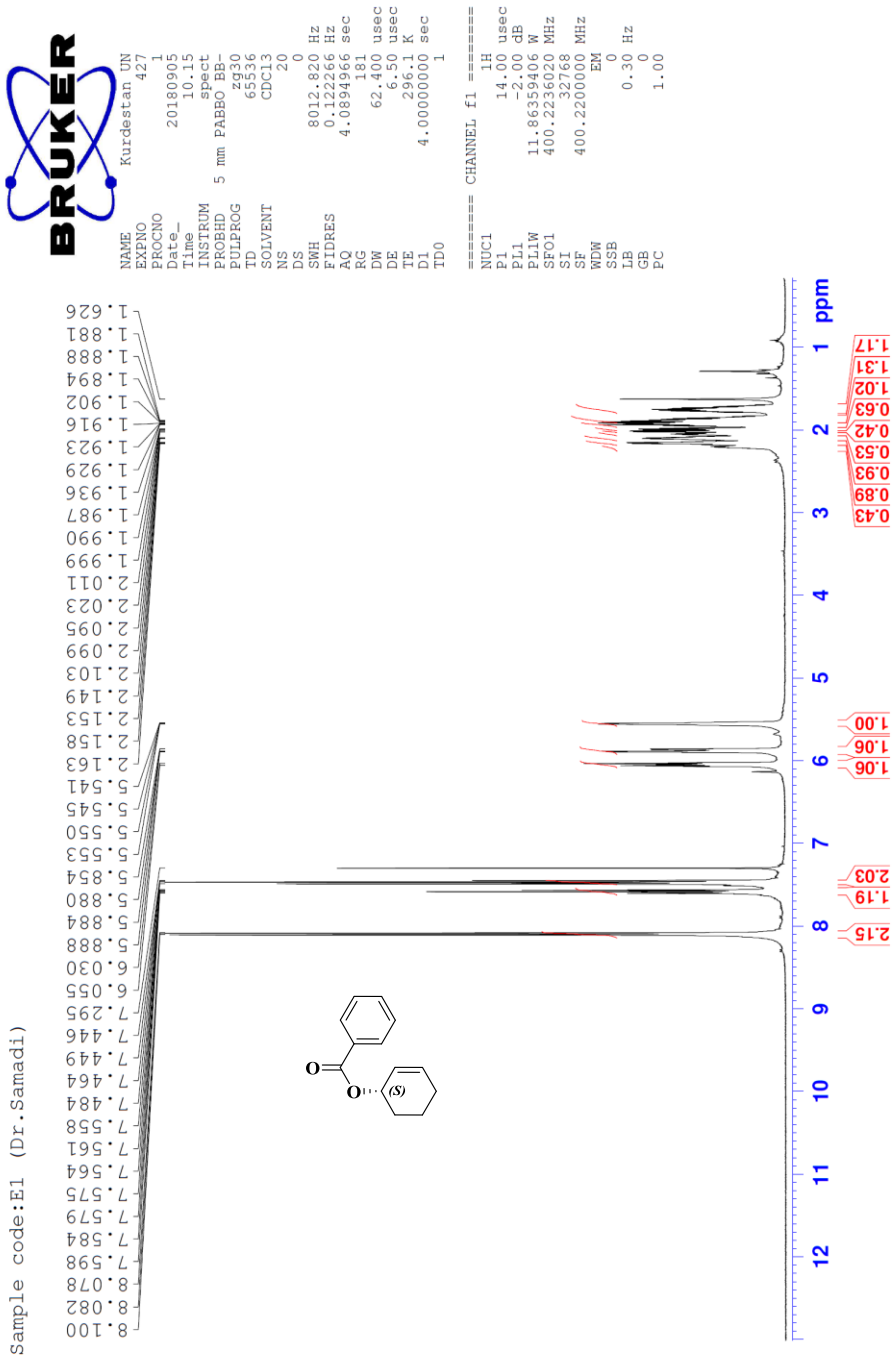


Figure S19: ^{1}H NMR of **8a**

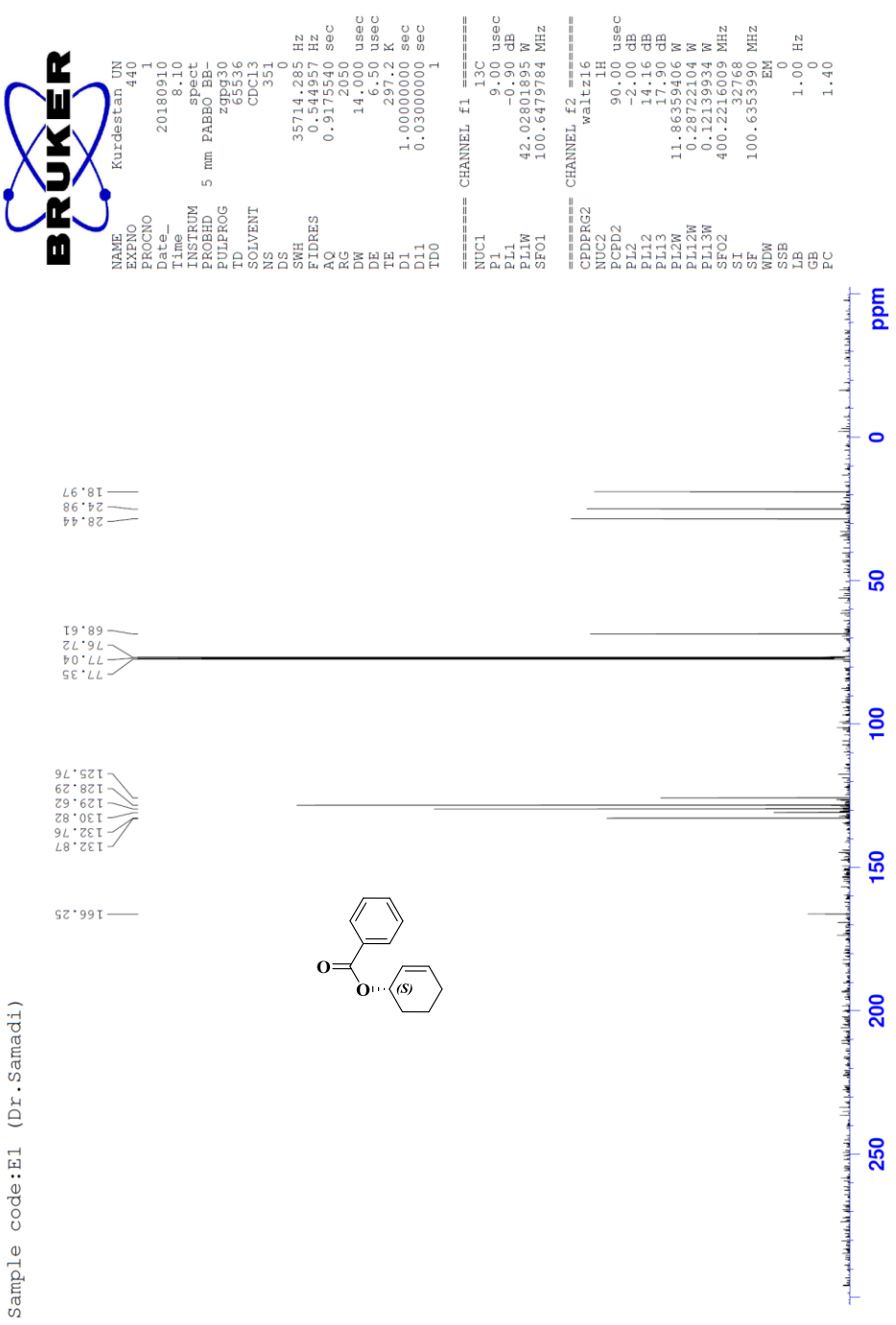


Figure S20: ^{13}CNMR of **8a**

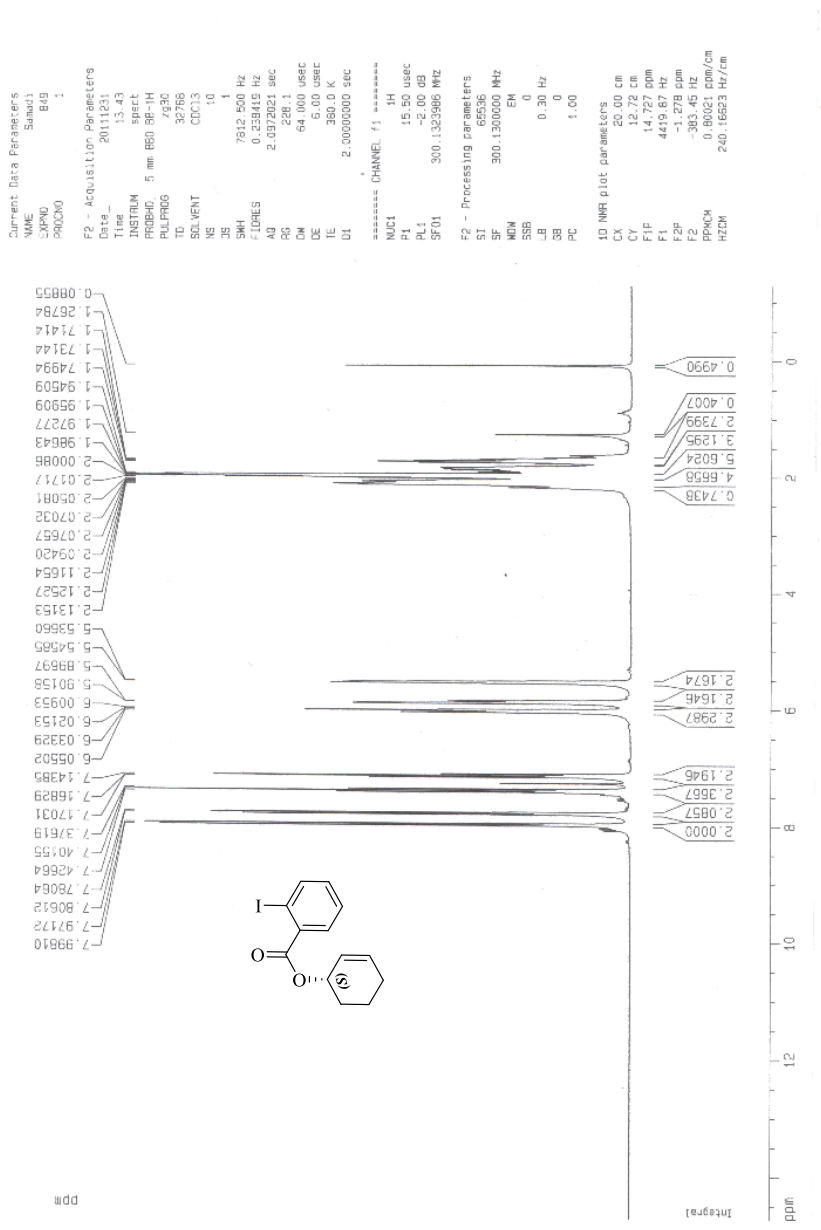


Figure S21: ^{1}H NMR of **8b**

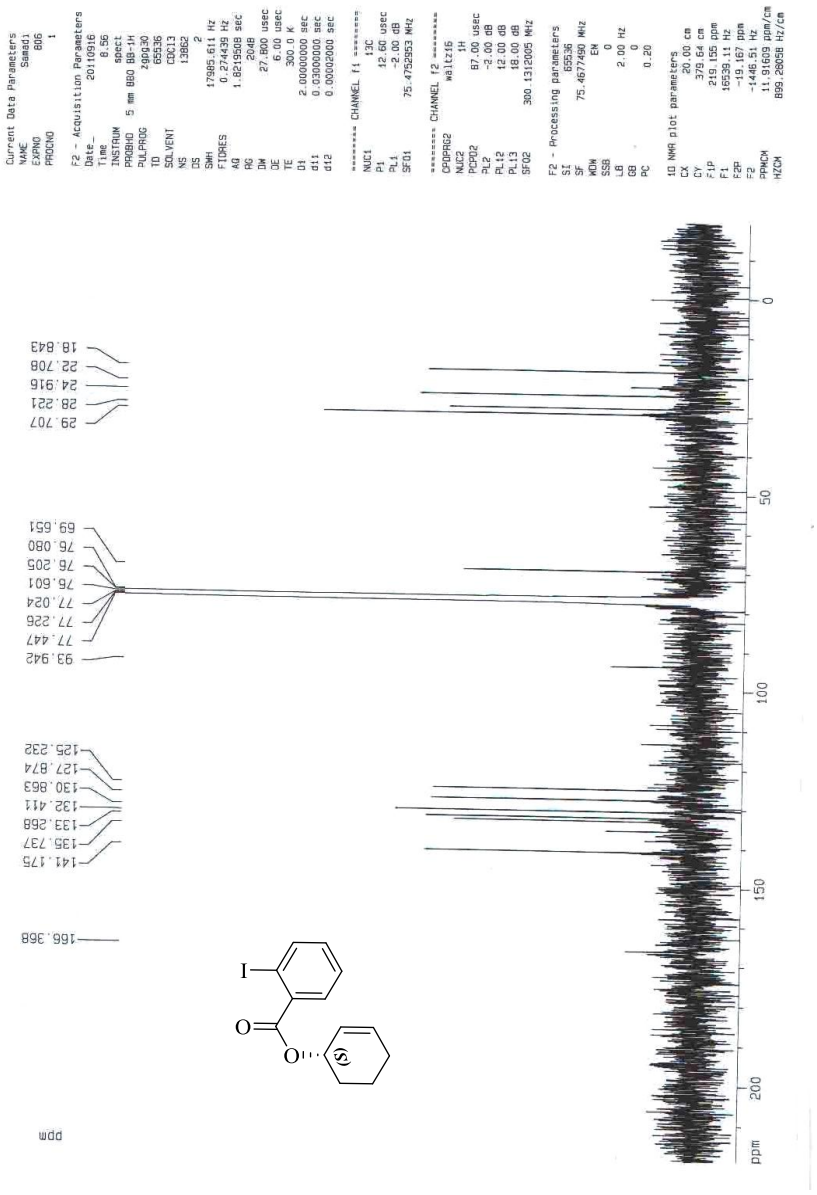


Figure S22: ^{13}CNMR of **8b**

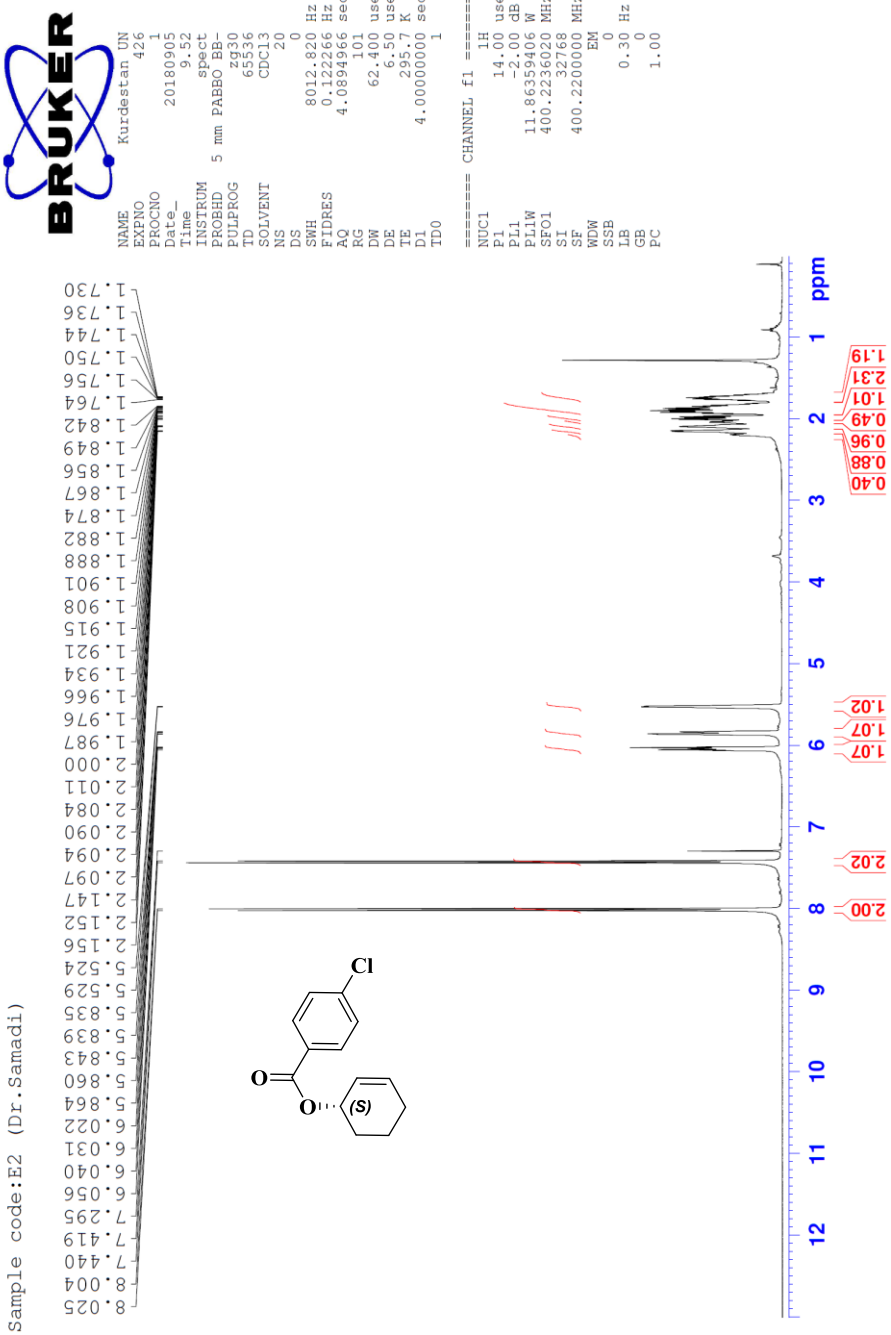


Figure S23: ^{1}H NMR of **8f**

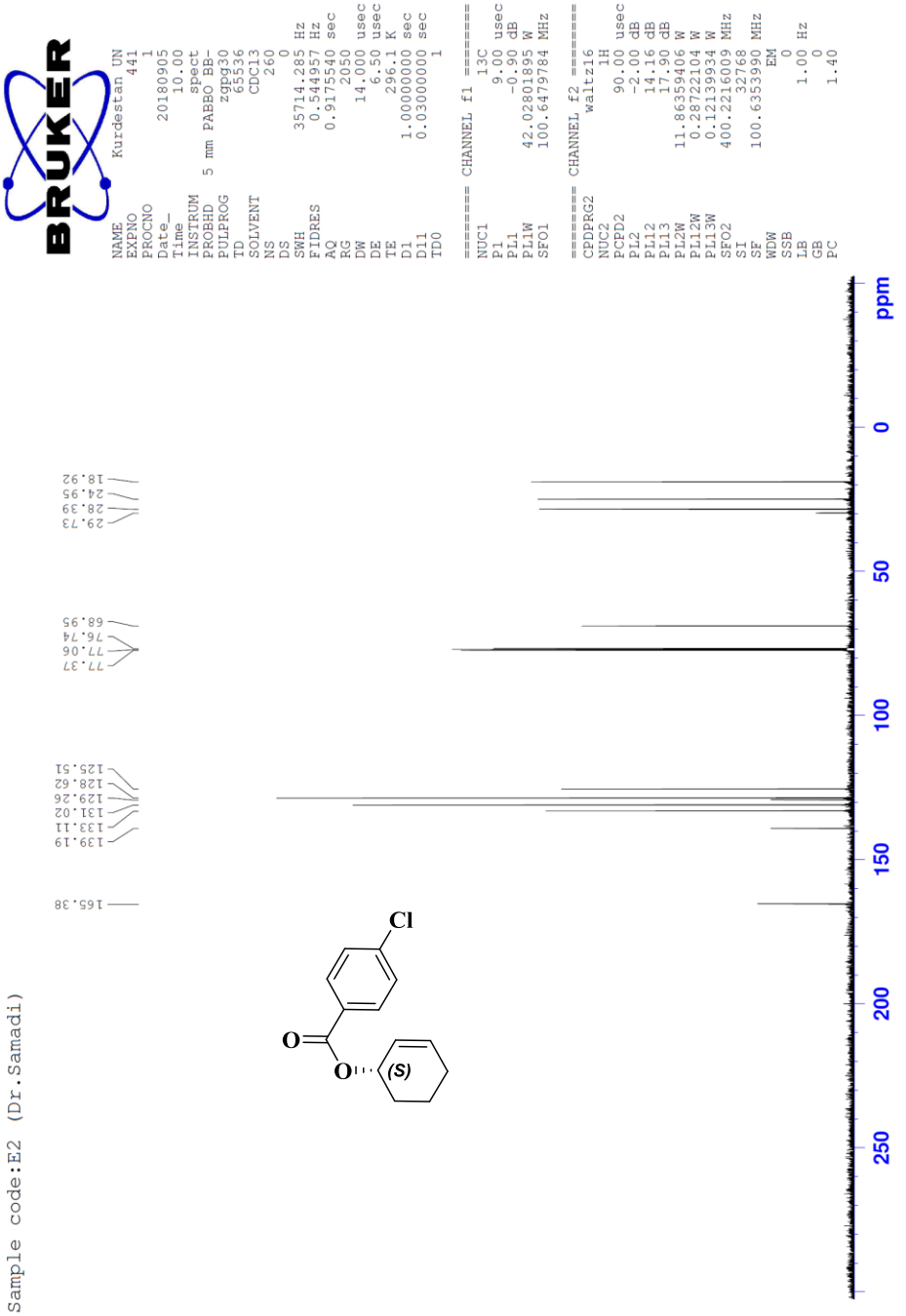


Figure S24: ^{13}C NMR of **8f**

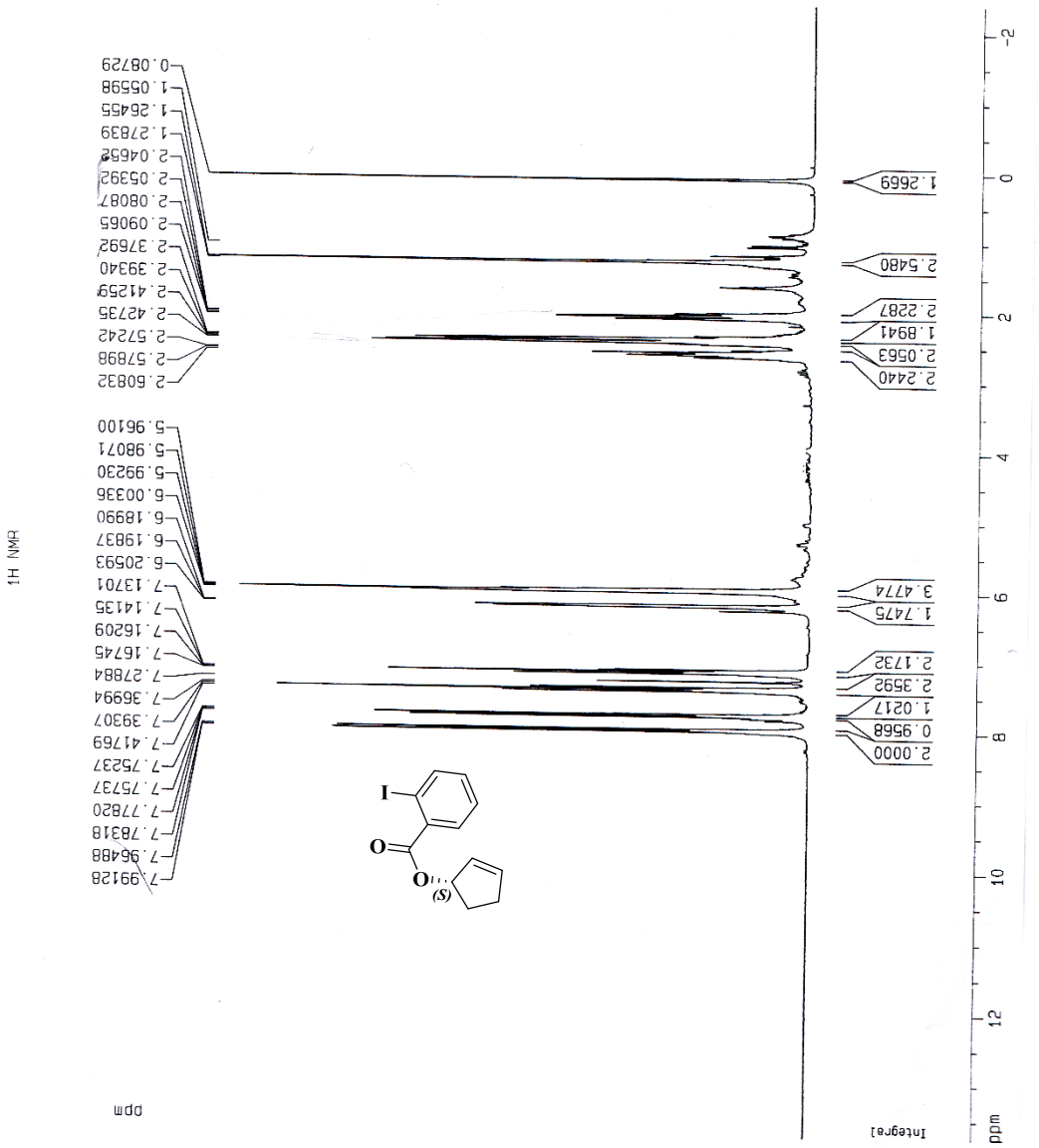


Figure S25: ^{1}H NMR of **9b**

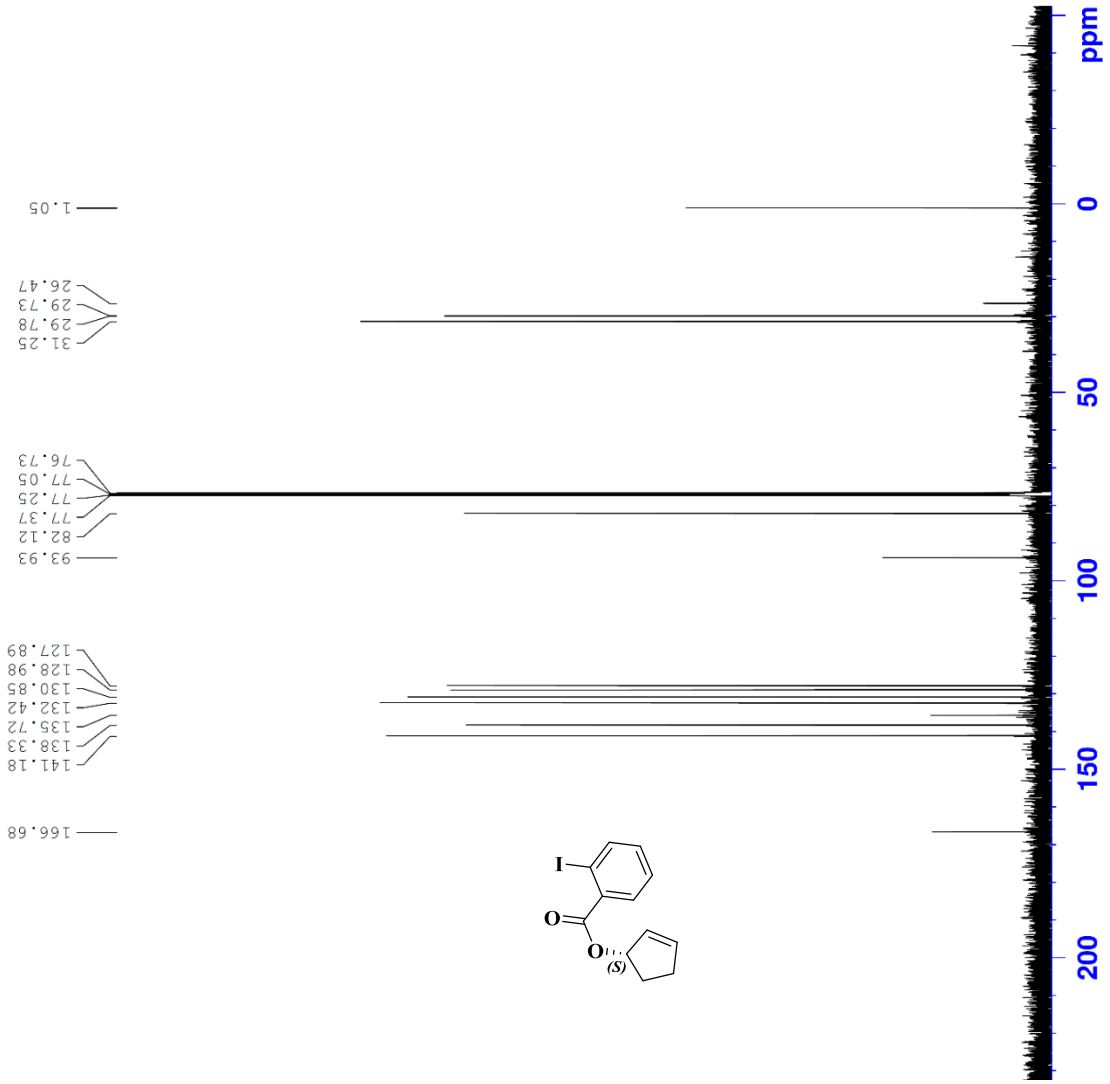


Figure S26: ^{13}CNMR of **9b**

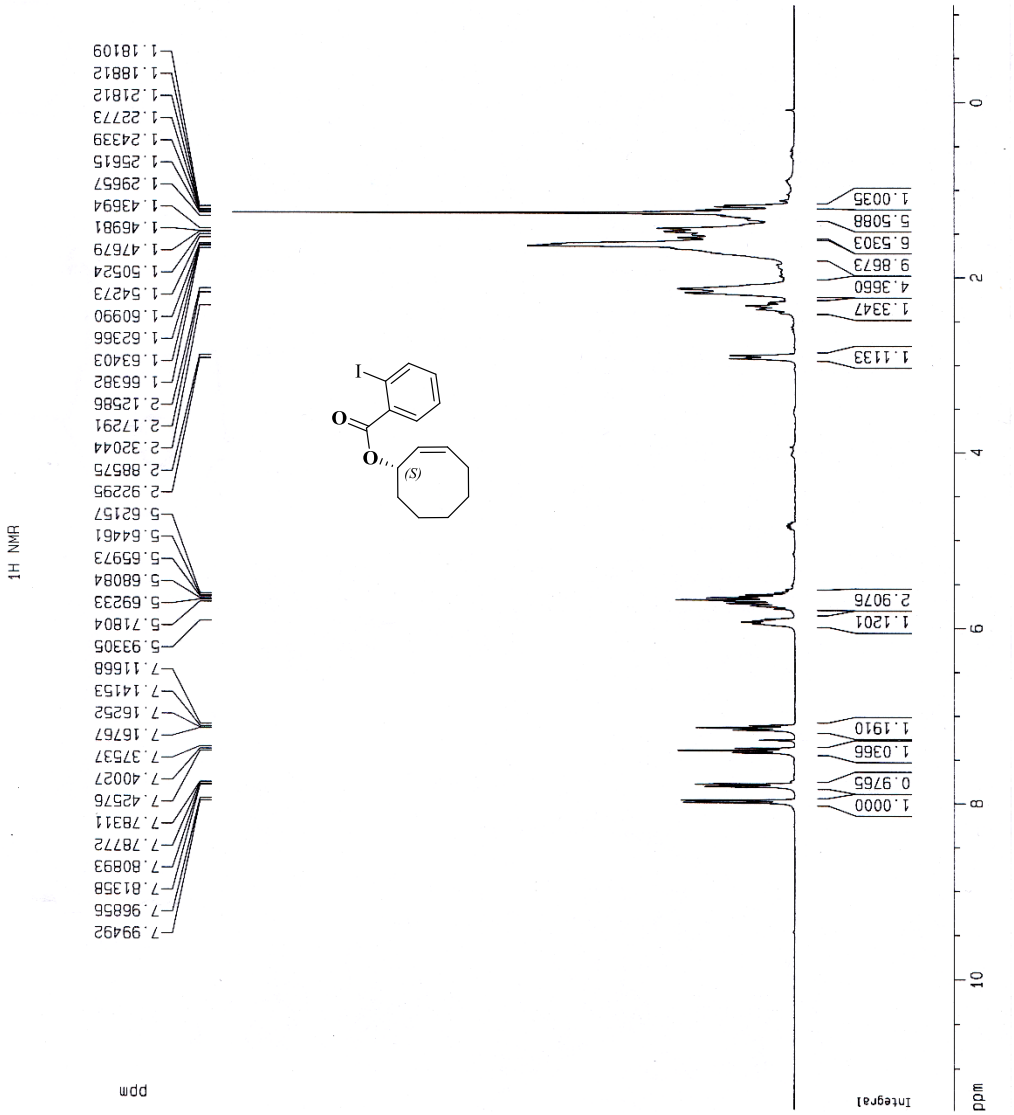


Figure S27: ^{1}H NMR of **10b**

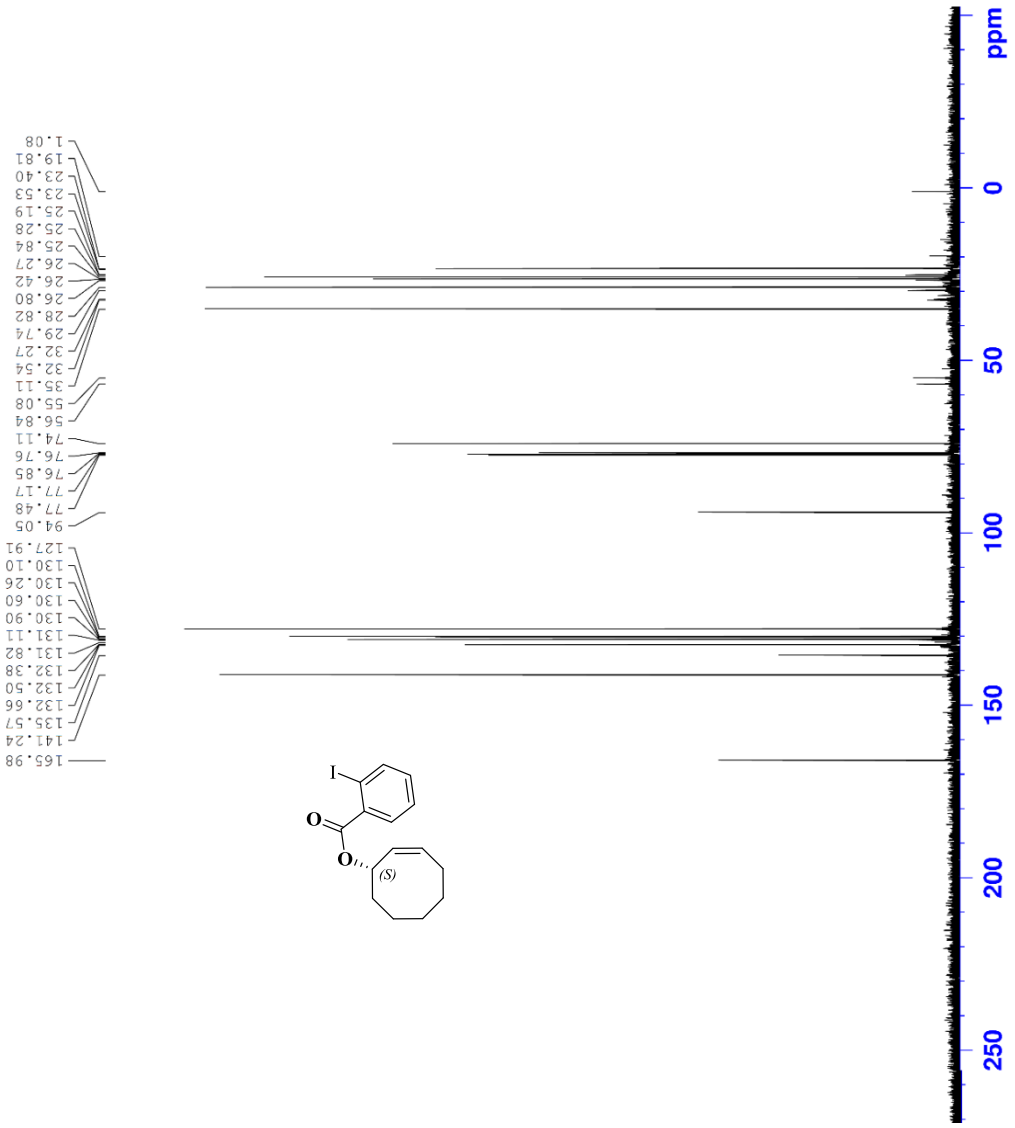


Figure S28: ^{13}CNMR of **10b**

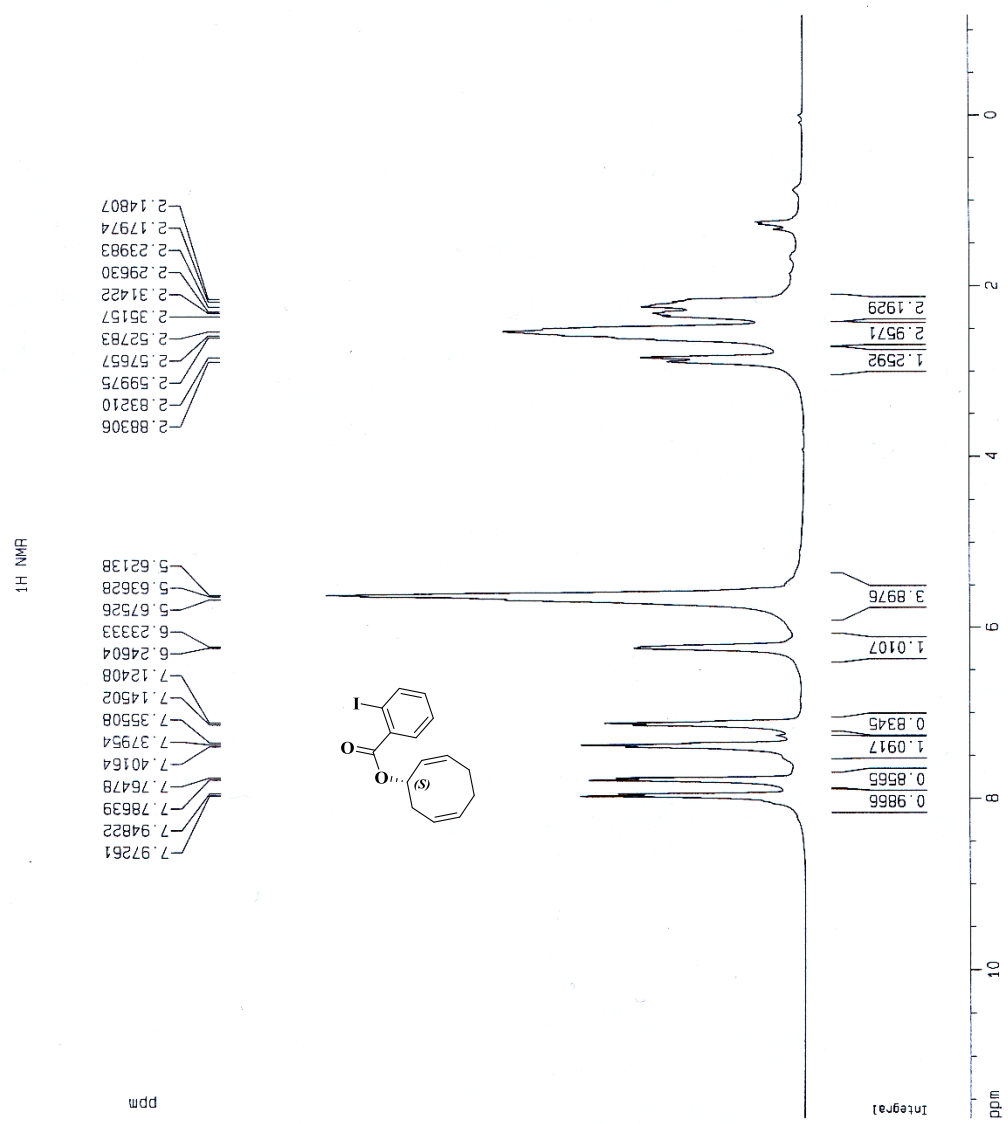


Figure S29: ^{1}H NMR of **11b**

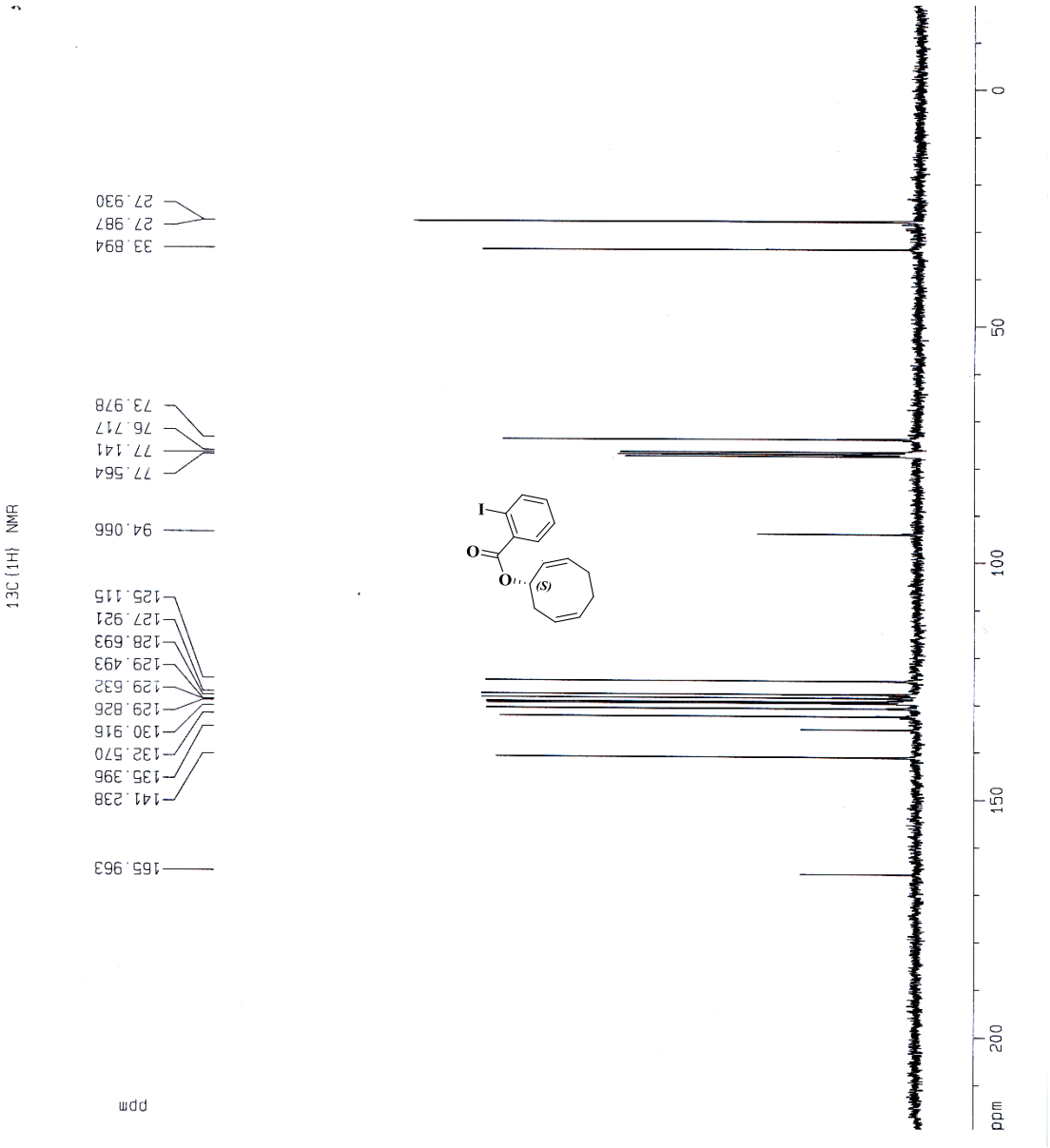


Figure S30: ^{13}CNMR of **11b**

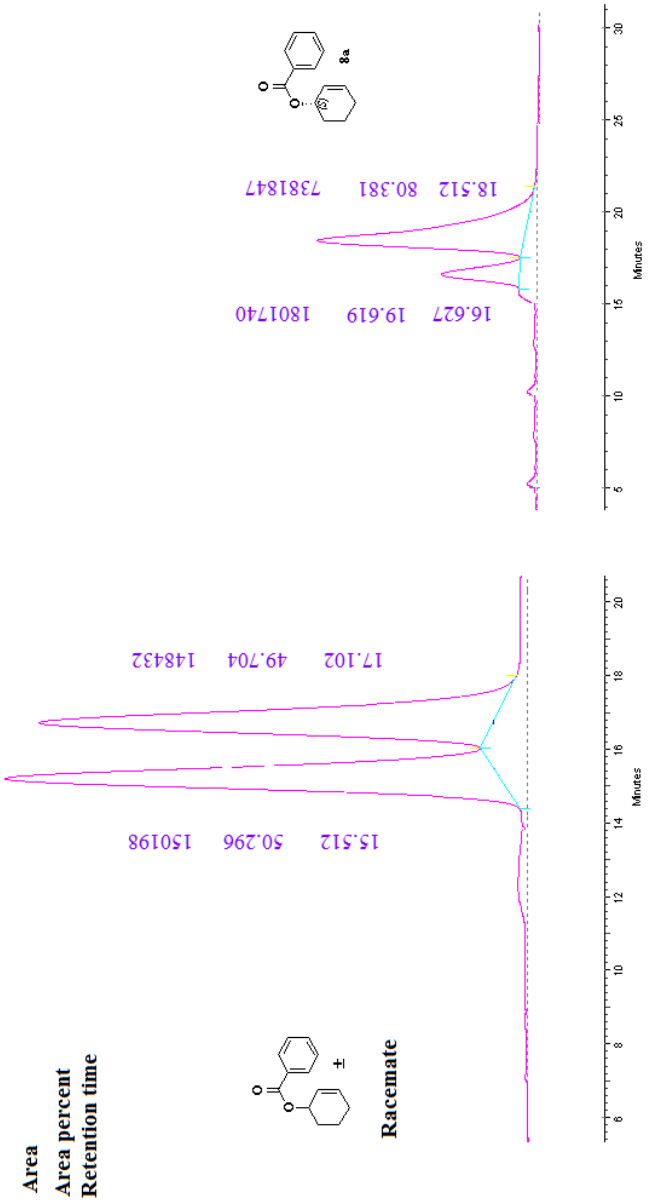


Figure S31: Chromatogram of **8a**

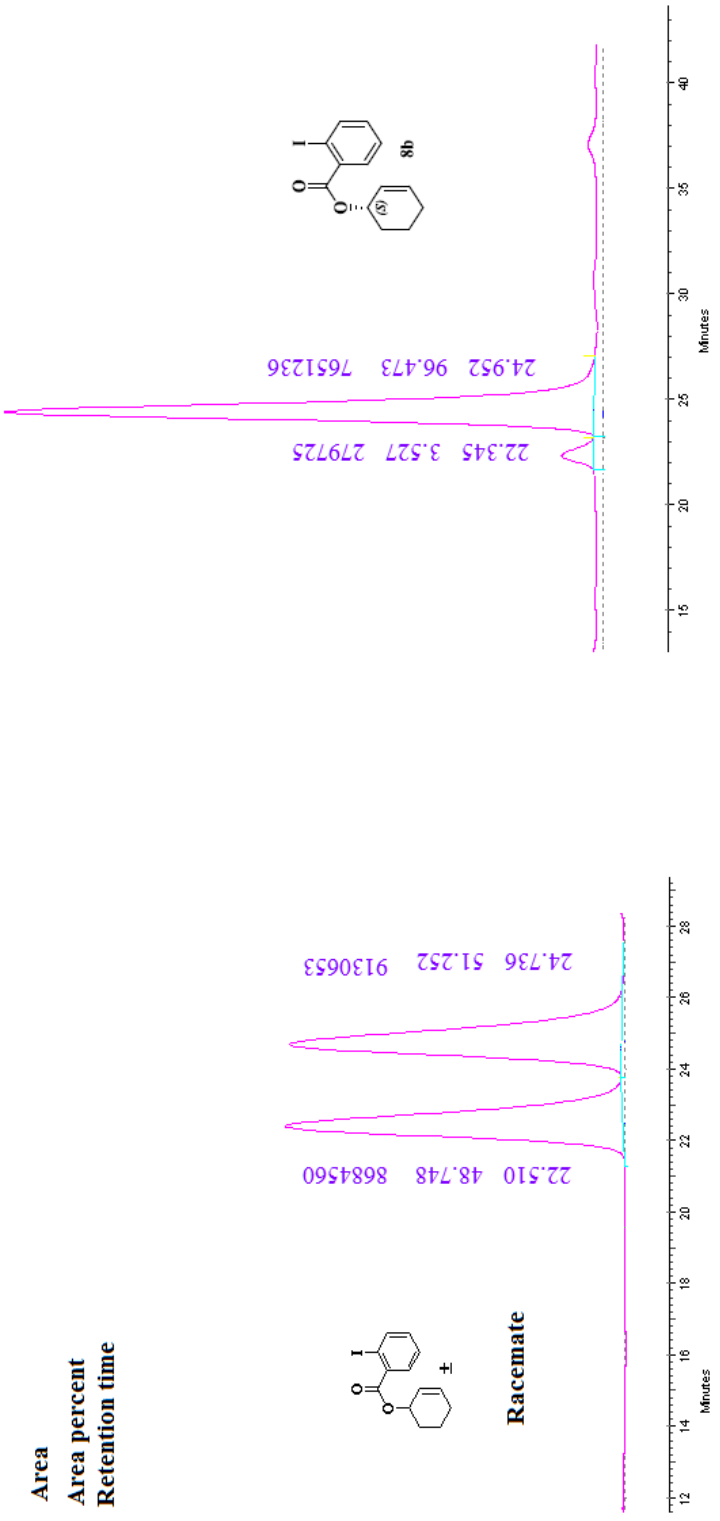


Figure S32: Chromatogram of **8b**

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