Supporting Information for:

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Transition-Metal-Catalyzed Ring Expansion of Diazocarbonylated Cyclic *N*-Hydroxylamines: A New Approach to Cyclic Ketonitrones

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1- General experimental methods

All the reactions were performed under a positive pressure of dry argon in dried glassware equipped with a magnetic stir bar. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. THF was distilled over sodium in presence of benzophenone. CH_2Cl_2 was distilled over CaH_2.

The reactions were monitored by thin layer chromatography (TLC) using commercial aluminum-backed silica gel plates (Merck, Kieselgel 60 F_{254}). TLC spots were viewed under ultraviolet light and by heating the plate after treatment with 1% triphenyl tetrazolium chloride (TTC) in ethanol (red color) or 3% solution of potassium permanganate in 10% aqueous potassium hydroxide (w/v). Product purification by gravity column chromatography were performed using Macherey-Nagel Silica Gel 60 (70-230 mesh).

Optical rotations were measured on a Perkin Elmer 341 polarimeter. Infrared spectra were obtained from neat compounds, on a Nicolet 'Magna 550' spectrometer using an ATR (Attenuated Total Reflexion) module. The data are reported in reciprocal centimeters (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on either a Brücker Advance 300 (^1H: 300 MHz, ^{13}C: 75 MHz), Advance 400 (^1H: 400 MHz, ^{13}C: 100 MHz) or Varian 500 (^1H: 500 MHz, ^{13}C: 125 MHz) spectrometers. Chemical shifts for ^1H spectra are values from tetramethylsilane in $CDCl_3$ (δ 0.00 ppm), Toluene-d_8 (δ 2.08 ppm) or Acetone-d_6 (δ 2.08 ppm). Chemical shifts for ^{13}C spectra are values from $CDCl_3$ (δ 77.16 ppm), Toluene-d_8 (δ 20.43 ppm) or Acetone-d_6 (δ 29.84 ppm). ^1H NMR spectra are reported as follows: chemical shift (ppm), multiplicity (br: broad; s: singlet; d: doublet; t: triplet; pt: pseudo triplet; q: quadruplet; m: multiplet), coupling constants (Hz) and integration. When ambiguous, proton and carbon assignments were established using COSY, HMQC and ^{13}C mult experiments. High resolution mass spectra (HRMS) were recorded on a MALDI-TOF mass spectrometer. Melting points were measured using a Büchi B-545 apparatus and were not corrected.

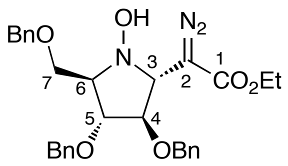
In this Supporting Information the numbering displayed on the structures relates to NMR assignments, not to the IUPAC name of described compounds.

2- Preparation and characterization of new compounds

2a- General method for addition of ethyl diazoacetate to nitrones

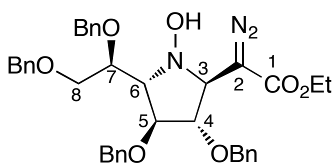
To a solution of nitrone (1.0 equiv) and ethyl diazoacetate (1.5 equiv) in THF at –78 °C, 1.5 equiv of LiHMDS solution (1M in THF) was added dropwise. After 1.5 h a saturated aqueous solution of $NaHCO_3$ was added and the resulting mixture was diluted with dichloromethane. The organic layer was separated, washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography.

Ethyl 2-((2*R*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)-1-hydroxypyrrolidin-2-yl)-2-diazoacetate (3a)



Hydroxylamine **3a** (64 mg, 100%) was obtained following the general method from nitrone **1a** (50 mg, 0.12 mmol). Pale yellow solid; mp 54.2–54.3 °C; $[\alpha]_D^{20}$ +25.5 (*c* 2.05, $CHCl_3$); IR (neat) ν 3456 (OH), 2089 ($C=N_2$), 1664 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 15H, ^{Ar}CH), 6.28 (br s, 1H, OH), 4.55–4.39 (m, 6H, $^{Bn}CH_2$), 4.19–4.11 (m, 4H, ^3CH, ^4CH, $^{OEt}CH_2$) 4.03–3.99 (m, 1H, ^5CH), 3.63–3.54 (m, 2H, $^7CH_2$), 3.50–3.45 (m, 1H, ^6CH), 1.19 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4 ($^1C=O$), 138.0 ($^{Ar}C_q$), 138.0 ($^{Ar}C_q$), 137.8 ($^{Ar}C_q$), 128.4 (^{Ar}CH), 128.4 (^{Ar}CH), 128.0 (^{Ar}CH), 127.8 (^{Ar}CH), 127.8 (^{Ar}CH), 127.7 (^{Ar}CH), 127.7 (^{Ar}CH) , 83.7 (^5CH), 83.4 (^4CH), 73.4 ($^{Bn}CH_2$), 72.1 ($^{Bn}CH_2$), 71.7 ($^{Bn}CH_2$), 71.0 (^6CH), 68.4 (^7CH), 65.1 ($^3CH_2$), 61.0 ($^{OEt}CH_2$), 14.5 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}N_3O_6$ $[M + H]^+$: 532.2442; found 532.2440.
NOESY correlation between ^3H (δ 4.19–4.11 ppm) and ^7H (δ 3.63–3.54 ppm)

Ethyl 2-((2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-5-((*S*)-1,2-bis(benzyloxy)ethyl)-1-hydroxypyrrolidin-2-yl)-2-diazoacetate (3b)

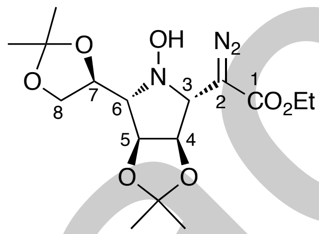


Hydroxylamine **3b** (61 mg, 100%) was obtained following the general method from nitrone **1b** (50 mg, 0.09 mmol). Yellow oil; $[\alpha]^{20}_D$ –58.8 (*c* 1.65, $CHCl_3$); IR (neat) ν 3391 (OH), 2097 ($C=N_2$), 1690 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.20 (m, 20H, ^{Ar}CH), 5.65 (br s, 1H, OH), 4.74

(d, J = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.59 (d, J = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.56 (d, J = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.54–4.45 (m, 3H, $^{Bn}CH_2$), 4.39 (s, 2H, $^{Bn}CH_2$), 4.32 (d, J = 7.5 Hz, 1H, ^{3}CH), 4.26–4.16 (m, 3H, ^{4}CH, $^{OEt}CH_2$), 4.07–4.03 (m, 1H, ^{5}CH), 3.77–3.69 (m, 3H, ^{7}CH, $^{8}CH_2$), 3.55–3.51 (m, 1H, ^{6}CH), 1.32–1.18 (m, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8 (^{1}C=O), 138.3 ($^{Ar}C_q$), 138.3 ($^{Ar}C_q$), 138.0 ($^{Ar}C_q$), 138.0 ($^{Ar}C_q$), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.4 (^{Ar}CH), 128.3 (^{Ar}CH), 128.0 (^{Ar}CH), 127.8 (^{Ar}CH), 127.8 (^{Ar}CH), 127.8 (^{Ar}CH), 127.8 (^{Ar}CH), 84.3 (^{5}CH), 83.9 (^{4}CH), 78.2 (^{7}CH), 73.8 (^{6}CH), 73.5 ($^{Bn}CH_2$), 73.1 ($^{Bn}CH_2$), 72.1 ($^{Bn}CH_2$), 72.0 ($^{Bn}CH_2$), 71.1 ($^{8}CH_2$), 65.0 (^{3}CH), 61.1 ($^{OEt}CH_2$), 14.6 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{38}H_{42}N_3O_7$ $[M + H]^+$: 652.3017; found 652.3013.

NOESY correlation between ^{3}H (δ 4.32 ppm) and ^{5}H (δ 4.07–4.03 ppm) and between ^{3}H (δ 4.32 ppm) and ^{7}H or ^{8}H (δ 3.77–3.69 ppm)

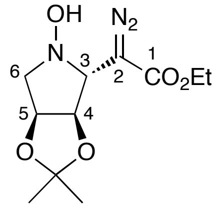
Ethyl 2-diazo-2-((3a*R*,4*R*,6*S*,6a*S*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-5-hydroxy-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyrrol-4-yl)acetate (3c)



Hydroxylamine **3c** (66 mg, 92%) was obtained following the general method from nitrone **1c** (50 mg, 0.19 mmol). Pale yellow solid; mp 104.0–105.0 °C; $[\alpha]^{20}_{D}$ –20.3 (*c* 1.13, $CHCl_3$); IR (neat) ν 3405 (OH), 2100 ($C=N_2$), 1667 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (br s, 1H, OH), 4.58–4.52 (m, 1H, ^{4}CH), 4.35–4.29 (m, 2H, ^{5}CH, ^{7}CH), 4.24 (q, J = 7.0 Hz, 2H, $^{OEt}CH_2$), 4.09 (dd, J = 8.5, 6.5 Hz, 1H, $^{8}CH_2$), 3.97 (dd, J = 8.5, 5.0 Hz, 1H, $^{8}CH_2$), 3.88 (d, J = 6.0 Hz, 1H, ^{3}CH), 3.14 (t, J = 5.5 Hz, 1H, ^{6}CH), 1.55 (s, 3H, $^{iPr}CH_3$), 1.47 (s, 3H, $^{iPr}CH_3$), 1.36 (s, 3H, $^{iPr}CH_3$), 1.31–1.26 (m, 6H, $^{iPr}CH_3$, $^{OEt}CH_3$);^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1 (^{1}C=O), 114.3 ($^{iPr}C_q$), 110.2 ($^{iPr}C_q$), 78.2 (^{4}CH), 77.4 (^{5}CH), 76.4 (^{7}CH), 73.8 (^{6}CH), 68.9 (^{3}CH), 66.3 ($^{8}CH_2$), 61.0 ($^{OEt}CH_2$), 27.3 ($^{iPr}CH_3$), 26.5 ($^{iPr}CH_3$), 25.3 ($^{iPr}CH_3$), 25.3 ($^{iPr}CH_3$), 14.6 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{16}H_{26}N_3O_7$ $[M + H]^+$: 372.1765; found 372.1767.

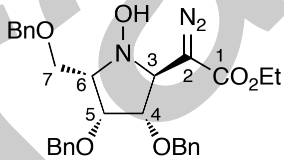
NOESY correlation between ^{3}H (δ 3.88 ppm) and ^{6}H (δ 3.14 ppm)

Ethyl 2-diazo-2-((3a*R*,4*R*,6a*S*)-5-hydroxy-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyrrol-4-yl)acetate (3d)



Hydroxylamine **3d** (80 mg, 93%) was obtained following the general method from nitrone **1d** (50 mg, 0.32 mmol). Yellow oil; $[\alpha]^{20}_{D}$ = +67.1 (*c* 0.75, $CHCl_3$); IR (neat) ν 3420 (OH), 2098 ($C=N_2$), 1686 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (br s, 1H, OH), 4.85–4.74 (m, 2H, ^{5}CH, ^{3}CH), 4.22 (q, *J* = 7.0 Hz, 2H, $^{OEt}CH_2$), 3.95 (d, *J* = 3.0 Hz, 1H, ^{4}CH), 3.47–3.37 (m, 1H, $^6CH_2$), 3.21–3.13 (m, 1H, $^6CH_2$), 1.50 (s, 3H, $^{i\text{-}Pr}CH_3$), 1.31 (s, 3H, $^{i\text{-}Pr}CH_3$), 1.28 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (^{1}C=O), 113.2 ($^{i\text{-}Pr}C_q$), 80.0 (^{5}CH or ^{3}CH), 77.3 (^{5}CH or ^{3}CH), 68.7 (^{4}CH), 61.9 (^{6}CH), 61.1 ($^{OEt}CH_2$), 53.5 (^2C_q), 26.8 ($^{i\text{-}Pr}CH_3$), 24.7 ($^{i\text{-}Pr}CH_3$), 14.6 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{11}H_{18}N_3O_5$ $[M + H]^+$: 272.1241; found 272.1244.

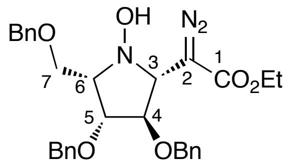
Ethyl 2-((2*S*,3*S*,4*R*,5*S*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)-1-hydroxypyrrolidin-2-yl)-2-diazoacetate (3e)



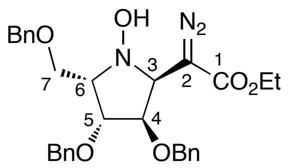
Compound **3e** (92 mg, 78%) was obtained following the general method from nitrone **1e** (90 mg, 0.22 mmol). Yellow oil; $[\alpha]^{20}_{D}$ = −50.4 (*c* 1.15, $CHCl_3$) IR (neat) ν 3368 (OH), 2096 ($C=N_2$), 1689 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.23 (m, 15H, ^{Ar}CH), 6.38 (br s, 1H, OH), 4.75 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.63 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.57 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.52 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.50 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.47 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.24 (d, *J* = 8.5 Hz, 1H, ^{3}CH), 4.22–4.15 (m, 3H, $^{OEt}CH_2$, ^{5}CH), 4.15–4.08 (m, 1H, ^{4}CH), 3.83–3.77 (m, 1H, $^7CH_2$), 3.76–3.70 (m, 1H, $^7CH_2$), 3.65–3.57 (m, 1H, ^{6}CH), 1.24 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6 (^{1}C=O), 138.4 (^{Ar}Cq), 138.2 (^{Ar}Cq), 137.8 (^{Ar}Cq), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 128.4 (^{Ar}CH), 128.0 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 127.8 (^{Ar}CH), 127.7 (^{Ar}CH), 78.9 (^{4}CH), 75.6 (^{5}CH), 73.8 ($^{Bn}CH_2$), 73.5 ($^{Bn}CH_2$), 72.7 ($^{Bn}CH_2$), 70.0 (^{6}CH), 67.5 ($^7CH_2$), 65.4 (^{3}CH), 61.1 ($^{OEt}CH_2$), 14.6 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}N_3O_6$ $[M + H]^+$: 532.2442; found 532.2445.

NOESY correlation between ^{3}H (δ 4.24 ppm) and ^{7}H (δ 3.76–3.70 ppm)

Ethyl 2-((2*R*,3*R*,4*R*,5*S*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)-1-hydroxypyrrolidin-2-yl)-2-diazoacetate (3f) and ethyl 2-((2*S*,3*R*,4*R*,5*S*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)-1-hydroxypyrrolidin-2-yl)-2-diazoacetate (3g)



3f



3g

Compounds **3f** and **3g** (421 mg, 93%) were obtained (60:40) following the general method from nitrone **1f** (357 mg, 0.86 mmol).

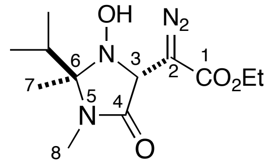
Major diastereomer (3f): Yellow oil; $[\alpha]^{20}_{D}$ = +10.5 (*c* 1.09, $CHCl_3$); IR (neat) ν 3398 (OH), 2093 ($C{=}N_2$), 1683 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.21 (m, 15H, ^{Ar}CH), 5.42 (br s, 1H, OH), 4.59–4.45 (m, 6H, $^{Bn}CH_2$), 4.23 (q, *J* = 7.0 Hz, 2H, $^{OEt}CH_2$), 4.02 (dd, *J* = 6.0, 1.5 Hz, 1H, ^5CH), 3.89 (d, *J* = 5.0 Hz, 1H, ^3CH), 3.88–3.81 (m, 2H, ^4CH, $^7CH_2$), 3.75 (dd, *J* = 9.0, 5.5 Hz, 1H, $^7CH_2$), 3.51 (dd, *J* = 13.0, 6.0 Hz, 1H, ^6CH), 1.27 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3 ($^1C{=}O$), 138.2 (^{Ar}Cq), 137.9 (^{Ar}Cq), 137.7 (^{Ar}Cq), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 127.8 (^{Ar}CH), 127.8 (^{Ar}CH), 83.3 (^4CH), 80.3 (^5CH), 73.5 ($^{Bn}CH_2$), 72.3 ($^{Bn}CH_2$), 71.7 ($^{Bn}CH_2$), 68.8 (^6CH), 68.4 (^3CH), 68.0 ($^7CH_2$), 61.0 ($^{OEt}CH_2$), 14.6 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}N_3O_6$ $[M + H]^+$: 532.2442; found 532.2444.

NOESY correlation between ^3H (δ 3.89 ppm) and ^6H (δ 3.51 ppm)

Minor diastereomer (3g): ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.22 (m, 15H, ^{Ar}CH), 5.24 (br s, 1H, OH), 4.58–4.48 (m, 6H, $^{Bn}CH_2$, ^3CH), 4.47 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.22 (q, *J* = 7.0 Hz, 2H, $^{OEt}CH_2$), 4.22–4.18 (m, 1H, ^4CH), 4.07 (dd, *J* = 6.0, 4.0 Hz, 1H, ^5CH), 3.87 (dd, *J* = 10.0, 5.0 Hz, 1H, $^7CH_2$), 3.74 (dd, *J* = 10.0, 5.0 Hz, 1H, $^7CH_2$), 3.69–3.65 (m, 1H, ^6CH), 1.26 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3 (^{Ar}Cq), 138.0 (^{Ar}Cq), 137.7 (^{Ar}Cq), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 127.8 (^{Ar}CH), 127.7 (^{Ar}CH), 82.7 (^4CH), 81.6 (^5CH), 73.7 ($^{Bn}CH_2$), 72.8 ($^{Bn}CH_2$), 72.7 ($^{Bn}CH_2$), 66.2 ($^7CH_2$), 66.2 (^6CH), 64.3 (^3CH), 61.0 ($^{OEt}CH_2$), 14.7 ($^{OEt}CH_3$).

NOESY correlation between ^3H (δ 4.58–4.48 ppm) and ^7H (δ 3.74 ppm)

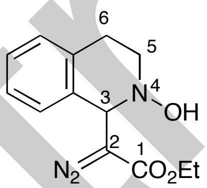
Ethyl 2-diazo-2-((2*S,4*S**)-3-hydroxy-2-isopropyl-1,2-dimethyl-5-oxoimidazolidin-4-yl)acetate (8)**



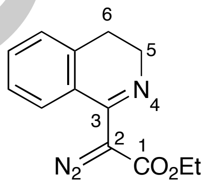
Compound **8** (122 mg, 76%) was obtained following the general method from nitrone **4** (101 mg, 0.59 mmol). Yellow oil; IR (neat) ν 3338 (OH), 2112 (C=N_2), 1689 (C=O); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (br s, 1H, OH), 4.76 (br s, 1H, ^{3}CH), 4.21 (q, *J* = 7.0 Hz, 2H, $^{OEt}CH_2$), 2.85 (s, 3H, $^{8}CH_3$), 2.22–2.13 (m, 1H, $^{i\text{-}Pr}$CH), 1.41 (s, 3H, $^{7}CH_3$), 1.25 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$), 1.05 (d, *J* = 7.0 Hz, 3H, $^{i\text{-}Pr}CH_3$), 1.00 (d, *J* = 7.0 Hz, 3H, $^{i\text{-}Pr}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2 (^{4}C=O), 166.4 (^{1}C=O), 88.0 (^{6}Cq), 64.2 (^{3}CH), 61.3 ($^{OEt}CH_2$), 35.4 ($^{i\text{-}Pr}$CH), 28.0 ($^{8}CH_3$), 18.7 ($^{i\text{-}Pr}CH_3$), 18.0 ($^{i\text{-}Pr}CH_3$), 16.5 ($^{7}CH_3$), 14.6 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{12}H_{21}N_4O_4$ $[M + H]^+$: 285.1557; found 285.1560.

NOESY correlation between ^{3}H (δ 4.76 ppm) and $^{i\text{-}Pr}CH_3$ (δ 1.00 ppm) and between ^{3}H (δ 4.76 ppm) and $^{i\text{-}Pr}$CH (δ 2.22–2.13 ppm)

Ethyl 2-diazo-2-(2-hydroxy-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (9) and ethyl 2-diazo-2-(3,4-dihydroisoquinolin-1-yl)acetate (S-9')



9



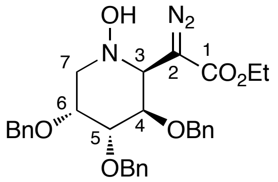
S-9'

Compound **9** (145 mg, 78%) and **S-9'** (26 mg, 15%) were obtained following the general method from nitrone **5** (104 mg, 0.71 mmol).

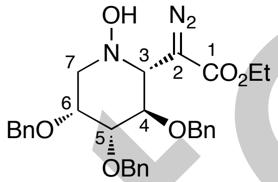
Hydroxylamine **9**: yellow oil; IR (neat) ν 3193 (OH), 2091 (C=N_2), 1694 (C=O); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.87 (br s, 1H, OH), 7.23–7.11 (m, 4H, ^{Ar}CH), 4.84 (br s, 1H, ^{3}CH), 4.25 (q, *J* = 7.0 Hz, 2H, $^{OEt}CH_2$), 3.47–3.40 (m, 1H, $^{5}CH_2$), 3.16–3.04 (m, 2H, $^{5}CH_2$, $^{6}CH_2$), 2.88–2.80 (m, 1H, $^{6}CH_2$), 1.27 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, Acetone-d_6) δ 167.1 (^{1}C=O), 135.7 (^{Ar}Cq), 134.8 (^{Ar}Cq), 129.2 (^{Ar}CH), 128.1 (^{Ar}CH), 128.0 (^{Ar}CH), 127.3 (^{Ar}CH), 65.5 (^{3}CH), 61.3 ($^{OEt}CH_2$), 55.3 ($^{5}CH_2$), 28.7 ($^{6}CH_2$), 14.8 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{13}H_{16}N_3O_3$ $[M + H]^+$: 262.1186; found 262.1185.

Imine **S-9'**: pale yellow solid; mp 123.5–124.2 °C; IR (neat) ν 2090 (C=N_2), 1713 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77–8.69 (m, 1H, ^{Ar}CH), 7.48–7.38 (m, 2H, ^{Ar}CH), 7.38–7.31 (m, 1H, ^{Ar}CH), 4.64–4.58 (m, 2H, $^{6}CH_2$), 4.51 (q, *J* = 7.0 Hz, 2H, $^{OEt}CH_2$), 3.23 (t, *J* = 7.0 Hz, 2H, $^{5}CH_2$), 1.48 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (^{1}C=O), 136.3 (^{Ar}Cq), 133.6 (^{Ar}Cq), 130.8 (^{Ar}CH), 128.9 (^{Ar}CH), 128.2 (^{Ar}CH), 128.1 (^{Ar}CH), 123.6 (^{3}C=N), 61.6 ($^{OEt}CH_2$), 45.1 ($^{6}CH_2$), 29.2 ($^{5}CH_2$), 14.5 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{13}H_{14}N_3O_2$ $[M + H]^+$: 244.1081; found 244.1085.

Ethyl 2-diazo-2-((2*S*,3*R*,4*R*,5*R*)-3,4,5-tris(benzyloxy)-1-hydroxypiperidin-2-yl)acetate (10a) and ethyl 2-diazo-2-((2*R*,3*R*,4*R*,5*R*)-3,4,5-tris(benzyloxy)-1-hydroxypiperidin-2-yl)acetate (10b)



10a



10b

Compounds **10a** and **10b** (137 mg, 97%) were obtained (64:36) following the general method from nitrone **6** (112 mg, 0.27 mmol).

Major diastereomer **10a**: yellow oil; $[\alpha]^{20}_{D}$ = +2.8 (*c* 1.01, acetone); IR (neat) ν 3416 (OH), 2098 ($C=N_2$), 1683 (C=O); ^{1}H NMR (300 MHz, Acetone-d_6) δ 7.62 (br s, 1H, OH), 7.46–7.19 (m, 15H, ^{Ar}CH), 4.81 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.69 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.60 (s, 2H, $^{Bn}CH_2$), 4.55 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.46 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.19–4.08 (m, 2H, $^{OEt}CH_2$), 4.05–4.00 (m, 1H, ^{5}CH), 3.97–3.87 (m, 1H, ^{6}CH), 3.85 (t, *J* = 3.0 Hz, 1H, ^{4}CH), 3.75 (d, *J* = 3.0 Hz, 1H, ^{3}CH), 3.36 (dd, *J* = 9.5, 3.5 Hz, 1H, $^{7}CH_2$), 3.10 (dd, *J* = 11.5, 9.5 Hz, 1H, $^{7}CH_2$), 1.21 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, Acetone-d_6) δ 161.7 (^{1}C=O), 139.9 (^{Ar}Cq), 139.8 (^{Ar}Cq), 138.8 (^{Ar}Cq), 129.2 (^{Ar}CH), 129.1 (^{Ar}CH), 129.0 (^{Ar}CH), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.3 (^{Ar}CH), 128.3 (^{Ar}CH), 79.1 (^{4}CH), 74.2 (^{6}CH), 73.6 ($^{Bn}CH_2$), 73.5 ($^{Bn}CH_2$), 72.8 (^{5}CH), 71.6 ($^{Bn}CH_2$), 61.7 (^{3}CH), 60.9 ($^{OEt}CH_2$), 57.3 ($^{7}CH_2$), 14.8 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}N_3O_6$ $[M + H]^+$: 532.2442; found 532.2441.

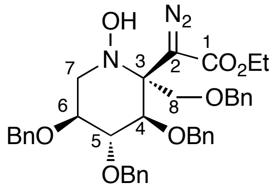
NOESY correlation between ^{3}H (δ 3.75 ppm) and ^{7}H-α (δ 3.10 ppm)

Minor diastereomer **10b**: yellow oil; $[\alpha]^{20}_{D}$ = +8.3 (*c* 1.96, acetone); IR (neat) ν 3397 (OH), 2092 ($C=N_2$), 1694 (C=O); ^{1}H NMR (300 MHz, Acetone-d_6) δ 7.74 (br s, 1H, OH), 7.45-7.23 (m, 15H, ^{Ar}CH), 4.92 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.77–4.60 (m, 5H, $^{Bn}CH_2$), 4.24–4.13 (m, 2H, $^{OEt}CH_2$), 4.13–4.09 (m, 1H, ^{6}CH), 3.92 (t, *J* = 9.5 Hz, 1H, ^{4}CH), 3.72 (dd, *J* = 9.5, 3.5 Hz, 1H, ^{5}CH), 3.65 (dd, *J* = 12.0, 3.5 Hz, 1H, $^{7}CH_2$), 3.42 (d, *J* = 10.0 Hz, 1H, ^{3}CH), 2.70 (dd, *J* = 12.0, 1.5 Hz, 1H, $^{7}CH_2$), 1.22 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (75 MHz, Acetone-d_6) δ 140.12 (^{Ar}Cq), 139.9 (^{Ar}Cq), 139.9 (^{Ar}Cq), 129.1 (^{Ar}CH), 129.0 (^{Ar}CH), 128.9 (^{Ar}CH), 128.5 (^{Ar}CH), 128.4 (^{Ar}CH), 128.4

(^{Ar}CH), 128.2 (^{Ar}CH), 128.1 (^{Ar}CH), 128.1 (^{Ar}CH), 83.8 (^{5}CH), 76.7 (^{4}CH), 75.4 ($^{Bn}CH_2$), 72.9 (^{6}CH), 72.2 ($^{Bn}CH_2$), 72.0 ($^{Bn}CH_2$), 68.2 (^{3}CH), 61.0 ($^{OEt}CH_2$), 58.7 ($^{7}CH_2$), 14.9 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}N_3O_6$ $[M + H]^+$: 532.2442; found 532.2439.

NOESY correlation between ^{3}H (δ 4.42 ppm) and ^{5}H (δ 3.72 ppm)

Ethyl 2-diazo-2-((2*S*,3*R*,4*R*,5*S*)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-1-hydroxy piperidin-2-yl)acetate (11)



Hydroxylamine **11** (135 mg, 79%) was obtained following the general method from nitrone **7** (141 mg, 0.26 mmol). Yellow oil; $[\alpha]^{20}_{D} = -1.4$ (*c* 1.41, $CHCl_3$); IR (neat) ν 3259 (OH), 2105 ($C=N_2$), 1702 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H, OH), 7.37–7.19 (m, 18H, ^{Ar}CH), 7.16–7.09 (m, 2H, ^{Ar}CH), 4.87 (d, *J* = 11.4 Hz, 1H, $^{Bn}CH_2$), 4.86 (d, *J* = 11.0 Hz, 1H, $^{Bn}CH_2$), 4.79–4.62 (m, 5H, $^{Bn}CH_2$), 4.57 (d, *J* = 12.5 Hz, 1H, $^{Bn}CH_2$), 4.22–4.16 (m, 2H, $^{OEt}CH_2$), 4.14 (d, *J* = 10.1 Hz, 1H, ^{4}CH), 3.99 (d, *J* = 10.2 Hz, 1H, $^{8}CH_2$), 3.87–3.79 (m, 1H, ^{6}CH), 3.71 (d, *J* = 10.2 Hz, 1H, $^{8}CH_2$), 3.67 (dd, *J* = 10.6, 6.0 Hz, 1H, $^{7}CH_2$), 3.59 (dd, *J* = 10.0, 8.8 Hz, 1H, ^{5}CH), 2.90 (t, *J* = 10.4 Hz, 1H, $^{7}CH_2$), 1.27 (t, *J* = 7.1 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1 (^{1}C=O), 138.5 (^{Ar}Cq), 138.4 (^{Ar}Cq), 138.2 (^{Ar}Cq), 138.0 (^{Ar}Cq), 128.7 (^{Ar}CH), 128.5 (^{Ar}CH), 128.6 (^{Ar}CH), 128.2 (^{Ar}CH), 128.2 (^{Ar}CH), 128.1 (^{Ar}CH), 128.0 (^{Ar}CH), 128.0 (^{Ar}CH), 127.7 (^{Ar}CH), 127.5 (^{Ar}CH), 127.2 (^{Ar}CH), 83.4 (^{5}CH), 79.7 (^{4}CH), 77.2 (^{6}CH), 76.3 ($^{Bn}CH_2$), 75.8 ($^{Bn}CH_2$), 73.7 ($^{Bn}CH_2$), 73.2 ($^{Bn}CH_2$), 70.3 (^{3}Cq), 68.0 ($^{8}CH_2$),62.1 ($^{OEt}CH_2$), 56.8 (^{2}Cq), 55.9 ($^{7}CH_2$), 14.4 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{38}H_{42}N_3O_7$ $[M + H]^+$: 652.3017; found 652.3007.

NOESY correlation between ^{4}H (δ 4.14 ppm) and ^{8}H (δ 3.71 ppm)

2b- Screening of metal complexes as catalysts for transformation of 3a in nitrone 12

entry	catalyst[a]	solvent	temp	time	yield[b] (%)
1	$Rh_2(OAc)_4$	CH_2Cl_2	rt	30 min	53
2[c]	$Cu(acac)_2$[d]	CH_2Cl_2	rt	1.75 h	62
3[e]	$Cu(OTf)_2$	CH_2Cl_2	rt	45 min	77
4	$Cu(CH_3CN)_4PF_6$	CH_2Cl_2	rt	< 5 min	96
5	$Cu(CH_3CN)_4BF_4$	CH_2Cl_2	rt	< 5 min	86
6	$Pd(OAc)_2$	CH_2Cl_2	rt	24 h	56
7[c]	$Pd(OAc)_2$	$PhCH_3$	80 °C	20 min	52

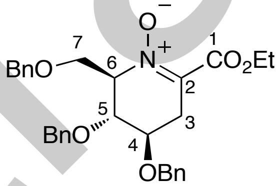
8	$[RuCl_2(p\text{-cymene})]_2$	CH_2Cl_2	rt	1.5 h	58
9	AgOTf	CH_2Cl_2	rt	20 min	97
10	AgOBz	CH_2Cl_2	rt	1.25 h	83
11	$AgBF_4$	CH_2Cl_2	rt	50 min	82
12	AgOAc	CH_2Cl_2	rt	2 h	22[f]
13	no catalyst	CH_2Cl_2	40 °C	120 h	0[g]
14	no catalyst	$PhCF_3$	80 °C	50 min	57

[a] The reactions were performed in the presence of 10 mol % catalyst, unless otherwise stated. [b] Isolated yield after column chromatography. [c] 20 mol % catalyst; [d] acac = acetylacetonate. [e] 15 mol % catalyst. [f] Starting material was recovered in 65% yield. [g] Starting material was totally recovered.

2c- General method for metal-catalyzed ring expansion

To a solution of *β*-diazo-*N*-hydroxylamine (1 equiv) in CH_2Cl_2 (c ~ 0.025 mol/L), the catalyst (0.1 equiv) was added at room temperature. The reaction was followed by TLC. When the starting material was consumed the solution was concentrated and directly purified by column chromatography on silica gel.

(2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-6-(ethoxycarbonyl)-2,3,4,5-tetrahydropyridine 1-oxide (12)

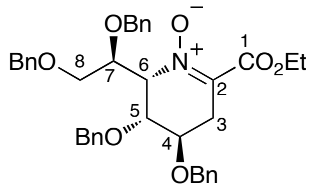


Nitrone **12** (446 mg, 97%) was obtained following the general method from *β*-diazo-hydroxylamine **3a** (486 mg, 0.91 mmol) upon treatment with AgOTf (23 mg, 0.09 mmol).

Nitrone **12** (24 mg, 96%) was obtained following the general method from *β*-diazo-hydroxylamine **3a** (26 mg, 0.49 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (2.0 mg, 0.05 mmol).

Clear oil; $[\alpha]^{20}_{D} = -24.1$ (*c* 0.6, $CHCl_3$); IR (neat) ν 3084, 3057, 3031, 2986, 2930, 2866, 1734 (C=O), 1605, 1457, 1372, 1307, 1269, 1192, 1098, 1068, 1030; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.22 (m, 15H, ^{Ar}CH), 4.87 (br s, 1H, ^4CH), 4.62–4.47 (m, 6H, $^{Bn}CH_2$), 4.31 (dd, *J* = 3.5, 2.5 Hz, 1H, ^5CH), 4.15–4.07 (m, 3H, $^{OEt}CH_2$, $^7CH_2$, ^6CH), 3.80–3.75 (m, 2H, $^7CH_2$, $^3CH_2$), 3.33 (d, *J* = 17.5 Hz, 1H, $^3CH_2$), 1.20 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (^1C=O), 139.5 (^2C=N), 137.7 (^{Ar}Cq), 137.4 (^{Ar}Cq), 137.2 (^{Ar}Cq), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.3 (^{Ar}CH), 128.1 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 127.8 (^{Ar}CH), 127.7 (^{Ar}CH), 127.7 (^{Ar}CH), 84.5 (^4CH), 78.6 (^{5}CH), 77.4 (^{6}CH), 73.4 ($^{Bn}CH_2$), 71.8 ($^{Bn}CH_2$), 71.8 ($^{Bn}CH_2$), 66.5 ($^{7}CH_2$), 61.3 ($^{OEt}CH_2$), 30.6 ($^{3}CH_2$), 14.0 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}NO_6$ $[M + H]^+$: 504.2381; found 504.2382.

(2*S*,3*S*,4*S*)-3,4-bis(benzyloxy)-2-((*S*)-1,2-bis(benzyloxy)ethyl)-6-(ethoxycarbonyl)-2,3,4,5-tetrahydropyridine 1-oxide (13)

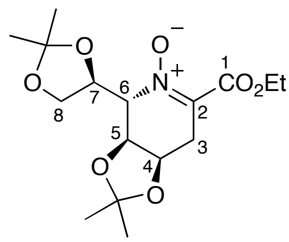


Nitrone **13** (176 mg, 100%) was obtained following the general method from *β*-diazo-hydroxylamine **3b** (184 mg, 0.28 mmol) upon treatment with AgOTf (7.0 mg, 0.027 mmol).

Nitrone **13** (21.7 mg, 100%) was obtained following the general method from *β*-diazo-hydroxylamine **3b** (23 mg, 0.04 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (1.3 mg, 0.004 mmol).

Clear oil; $[\alpha]^{20}_{D}$ = +35.82 (*c* 1.34, $CHCl_3$); IR (neat) ν 3090, 3051, 3031, 2981, 2919, 2869, 1731 (C=O), 1605, 1502, 1451, 1363, 1319; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.15 (m, 20H, ^{Ar}CH), 4.81 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.71 (br s, 1H, ^{4}CH), 4.65 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.51–4.35 (m, 6H, $^{Bn}CH_2$), 4.34–4.30 (m, 1H, ^{7}CH), 4.29–4.25 (m, 1H, ^{6}CH), 4.20 (dd, *J* = 3.0, 1.5 Hz, 1H, ^{5}CH),, 4.12–4.04 (m, 2H, $^{OEt}CH_2$), 3.74 (d, *J* = 5.0 Hz, 2H, $^{8}CH_2$), 3.63 (d, *J* = 17.0 Hz, 1H, $^{3}CH_2$), 3.30 (br d, *J* = 17.0 Hz, 1H, $^{3}CH_2$), 1.18 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (^{1}C=O), 139.9 (^{2}C=N) , 138.3 (^{Ar}Cq), 138.0 (^{Ar}Cq), 137.4 (^{Ar}Cq), 137.4 (^{Ar}Cq), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.4 (^{Ar}CH), 128.1 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 127.7 (^{Ar}CH), 127.6 (^{Ar}CH), 84.9 (^{4}CH), 78.9 (^{6}CH), 77.9 (^{5}CH), 75.2 (^{7}CH), 73.4 ($^{Bn}CH_2$), 73.1 ($^{Bn}CH_2$), 71.8 ($^{Bn}CH_2$), 71.5 ($^{Bn}CH_2$), 70.2 ($^{8}CH_2$), 61.4 ($^{OEt}CH_2$), 30.7 ($^{3}CH_2$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{38}H_{42}NO_7$ $[M + H]^+$: 624.2956; found 624.2956.

(3a*S*,4*S*,7a*R*)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-(ethoxycarbonyl)-2,2-dimethyl-3a,4,7,7a-tetrahydro-[1,3]dioxolo[4,5-c]pyridine 5-oxide (14)

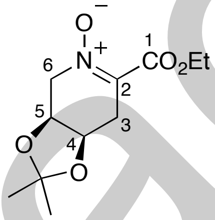


Nitrone **14** (169 mg, 100%) was obtained following the general method from *β*-diazo-hydroxylamine **3c** (183 mg, 0.49 mmol) upon treatment with AgOTf (13 mg, 0.05 mmol).

Nitrone **14** (20 mg, 88%) was obtained following the general method from *β*-diazo-hydroxylamine **3c** (24 mg, 0.065 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (2.4 mg, 0.0065 mmol).

Clear oil; $[\alpha]^{20}_{D} = -6.47$ (*c* 1.22, $CHCl_3$); IR (neat) ν 3054, 2989, 2936, 1740 (C=O), 1596, 1387, 1378, 1269, 1216, 1160, 1089, 1054; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (dd, *J* = 6.0, 0.5 Hz, 1H, ^{4}CH), 4.76 (d, *J* = 6.0 Hz, 1H, ^{5}CH), 4.56 (td, *J* = 6.5, 3.0 Hz, 1H, ^{7}CH), 4.33 (dd, *J* = 9.0, 6.5 Hz, 1H, $^{8}CH_2$), 4.26 (br s, 1H, ^{6}CH), 4.21–4.13 (m, 2H, $^{OEt}CH_2$), 4.05 (dd, *J* = 9.0, 6.5 Hz, 1H, $^{8}CH_2$), 3.84 (d, *J* = 17.5 Hz, 1H, $^{3}CH_2$), 3.30 (d, *J* = 17.5 Hz, 1H, $^{3}CH_2$), 1.36 (s, 6H, $^{i\text{-}Pr}CH_3$), 1.35 (s, 3H, $^{i\text{-}Pr}CH_3$), 1.34 (s, 3H, $^{i\text{-}Pr}CH_3$), 1.26 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (^{1}C=O), 140.6 (^{2}C=N), 111.9 ($^{i\text{-}Pr}C_q$), 110.0 ($^{i\text{-}Pr}C_q$), 80.7 (^{4}CH), 78.4 (^{6}CH), 75.9 (^{5}CH), 74.1 (^{7}CH), 64.9 ($^{8}CH_2$), 61.6 ($^{OEt}CH_2$), 30.4 ($^{3}CH_2$), 27.2 ($^{i\text{-}Pr}CH_3$), 26.1 ($^{i\text{-}Pr}CH_3$), 26.0 ($^{i\text{-}Pr}CH_3$), 25.2 ($^{i\text{-}Pr}CH_3$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{16}H_{26}NO_7$ $[M + H]^+$: 344.1704; found 344.1708.

(3a*S*,7a*R*)-6-(ethoxycarbonyl)-2,2-dimethyl-3a,4,7,7a-tetrahydro-[1,3]dioxolo[4,5-c]pyridine 5-oxide (15)

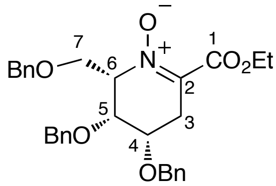


Nitrone **15** (17 mg, 83%) was obtained following the general method from *β*-diazo-hydroxylamine **3d** (23 mg, 0.08 mmol) upon treatment with AgOTf (2.2 mg, 0.009 mmol).

Nitrone **15** (16 mg, 88%) was obtained following the general method from *β*-diazo-hydroxylamine **3d** (20 mg, 0.074 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (2.7 mg, 0.007 mmol).

Clear oil; $[\alpha]^{20}_{D} = +1.0$ (*c* 1.58, $CHCl_3$); IR (neat) ν 2986, 2936, 2850, 1735 (C=O), 1601, 1440, 1374, 1257, 1207, 1154, 1085, 1030; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (br d, *J* = 6.0 Hz, 1H, ^{4}CH), 4.85 (t, *J* = 6.0 Hz, 1H, ^{5}CH), 4.24–4.14 (m, 3H, $^{OEt}CH_2$, $^{6}CH_2$), 4.09 (br d, *J* = 15.0 Hz, 1H, $^{6}CH_2$), 3.86 (d, *J* = 17.5 Hz, 1H, $^{3}CH_2$), 3.30 (br d, *J* = 17.5 Hz, 1H, $^{3}CH_2$), 1.38 (s, 3H, $^{i\text{-}Pr}CH_3$), 1.37 (s, 3H, $^{i\text{-}Pr}CH_3$), 1.27 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8 (^{1}C=O), 139.2 (^{2}C=N), 112.3 ($^{i\text{-}Pr}C_q$), 81.3 (^{4}CH), 71.9 (^{5}CH), 67.6 ($^{6}CH_2$), 61.7 ($^{OEt}CH_2$), 30.3 ($^{3}CH_2$), 27.2 ($^{i\text{-}Pr}CH_3$), 25.9 ($^{i\text{-}Pr}CH_3$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{11}H_{18}NO_5$ $[M + H]^+$: 244.1179; found 244.1182.

(2*S*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-6-(ethoxycarbonyl)-2,3,4,5-tetrahydropyridine 1-oxide (16)

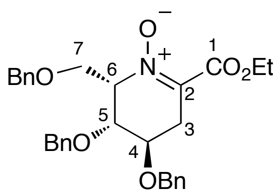


Nitrone **16** (38 mg, 95%) was obtained following the general method from *β*-diazo-hydroxylamine **3e** (42 mg, 0.08 mmol) upon treatment with AgOTf (2.0 mg, 0.008 mmol).

Nitrone **16** (41 mg, 89%) was obtained following the general method from *β*-diazo-hydroxylamine **3e** (49 mg, 0.09 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (3.4 mg, 0.009 mmol).

Clear oil; $[\alpha]^{20}_{D}$ = +21.2 (*c* 1.15, $CHCl_3$); IR (neat) ν 3084, 3065, 3029, 2928, 2889, 1732 (C=O), 1589, 1497, 1454, 1366, 1268, 1248, 1228, 1152, 1098, 1063, 1027; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.10 (m, 15H, ^{Ar}CH), 4.73–4.62 (m, 3H, ^{4}CH, $^{Bn}CH_2$), 4.60–4.41 (m, 4H, $^{Bn}CH_2$), 4.35 (t, *J* = 5.5 Hz, 1H, ^{5}CH), 4.21–4.14 (m, 1H, ^{6}CH), 4.12–3.96 (m, 4H, $^{OEt}CH_2$, $^7CH_2$), 3.76 (d, *J* = 17.5 Hz, 1H, $^3CH_2$), 3.16 (d, *J* = 17.5 Hz, 1H, $^3CH_2$), 1.13 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1 (^{1}C=O), 139.7 (^{2}C=N), 137.9 (^{Ar}Cq), 137.6 (^{Ar}Cq), 137.6 (^{Ar}Cq), 128.7 (^{Ar}CH), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 128.2 (^{Ar}CH), 128.1 (^{Ar}CH), 128.1 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 79.0 (^{4}CH), 74.0 (^{6}CH), 73.8 (^{5}CH), 73.8 ($^{Bn}CH_2$), 73.7 ($^{Bn}CH_2$), 73.4 ($^{Bn}CH_2$), 66.1 ($^7CH_2$), 61.5 ($^{OEt}CH_2$), 30.3 ($^7CH_2$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}NO_6$ $[M + H]^+$: 504.2381; found 504.2381.

(2*S*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-6-(ethoxycarbonyl)-2,3,4,5-tetrahydropyridine 1-oxide (17)



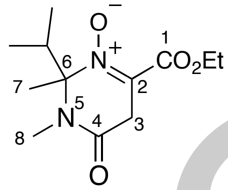
Nitrone **17** (36 mg, 97%) was obtained following the general method from a mixture (60:40) of *β*-diazo-hydroxylamines **3f** and **3g** (39 mg, 0.07 mmol) treated with AgOTf (2.0 mg, 0.008 mmol).

Nitrone **17** (29 mg, 68%) was obtained following the general method from a mixture (60:40) of *β*-diazo-hydroxylamines **3f** and **3g** (45 mg, 0.08 mmol) treated with $Cu(CH_3CN)_4PF_6$ (3.0 mg, 0.008 mmol).

Clear oil; $[\alpha]^{20}_{D}$ = −57.8 (*c* 0.56, $CHCl_3$); IR (neat) ν 3088, 3063, 3031, 2982, 2928, 2870, 1737 (C=O), 1604, 1497, 1455, 1367, 1314, 1249, 1211, 1105, 1028; ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.37–7.23 (m, 15H, ^{Ar}CH), 4.95 (br d, J = 4.0 Hz, 1H, ^{4}CH), 4.65 (d, J = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.61–4.56 (m, 4H, $^{Bn}CH_2$), 4.50 (d, J = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.33 (dd, J = 7.5, 4.5 Hz, 1H, ^{5}CH), 4.25–4.18 (m, 1H, ^{6}CH), 4.05 (q, J = 7.0 Hz, 2H, $^{OEt}CH_2$), 3.99 (dd, J = 10.0, 4.5 Hz, 1H, $^{7}CH_2$), 3.79 (dd, J = 10.0, 2.0 Hz, 1H, $^{7}CH_2$), 3.73 (d, J = 17.0 Hz, 1H, $^{3}CH_2$), 3.37 (br d, J = 17.0 Hz, 1H, $^{3}CH_2$), 1.15 (t, J = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6 (^{1}C=O), 140.8 (^{2}C=N), 138.1 (^{Ar}Cq), 137.6 (^{Ar}Cq), 137.3 (^{Ar}Cq), 128.7 (^{Ar}CH), 128.6 (^{Ar}CH), 128.4 (^{Ar}CH), 128.3 (^{Ar}CH), 128.1 (^{Ar}CH), 127.9 (^{Ar}CH), 127.7 (^{Ar}CH), 127.7 (^{Ar}CH), 84.2 (^{4}CH), 80.2 (^{5}CH), 73.8 (^{6}CH), 73.7 ($^{Bn}CH_2$), 73.5 ($^{Bn}CH_2$), 72.9 ($^{Bn}CH_2$), 64.9 ($^{7}CH_2$), 61.4 ($^{OEt}CH_2$), 30.5 ($^{3}CH_2$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}NO_6$ [M + H]$^+$: 504.2381; found 504.2382.

6-(ethoxycarbonyl)-2-isopropyl-2,3-dimethyl-4-oxo-2,3,4,5-tetrahydropyrimidine 1-oxide (18)

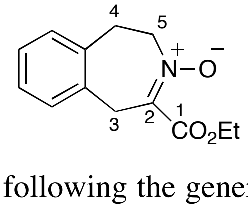


Nitrone **18** (59 mg, 96%) was obtained following the general method from β-diazo-hydroxylamine **8** (69 mg, 0.24 mmol) upon treatment with AgOTf (6.2 mg, 0.024 mmol).

Nitrone **18** (60 mg, 90%) was obtained following the general method from β-diazo-hydroxylamine **8** (74 mg, 0.26 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (9.7 mg, 0.026 mmol).

Clear oil; IR (neat) ν 2975, 1737 (C=O), 1700 (C=O), 1592, 1436, 1388, 1369, 1271, 1238, 1188, 1025; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.15 (q, J = 7.0 Hz, 2H, $^{OEt}CH_2$), 3.60 (d, J = 17.0 Hz, 1H, $^{3}CH_2$), 3.55 (d, J = 17.0 Hz, 1H, $^{3}CH_2$), 3.01 (s, 3H, $^{8}CH_3$), 2.33 (sept, J = 7.0 Hz, 1H, $^{i\text{-}Pr}$CH), 1.64 (s, 3H, $^{7}CH_3$), 1.23 (t, J = 7.2 Hz, 3H, $^{OEt}CH_3$), 1.00 (d, J = 7.0 Hz, 3H, $^{i\text{-}Pr}CH_3$), 0.97 (d, J = 7.0 Hz, 3H, $^{i\text{-}Pr}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7 (^{1}C=O), 162.7 (^{4}C=O), 131.4 (^{2}C=N), 92.8 ($^{6}C_q$), 61.8 ($^{OEt}CH_2$), 34.6 ($^{i\text{-}Pr}$CH), 28.0 ($^{3}CH_2$), 26.5 ($^{8}CH_3$), 21.5 ($^{7}CH_3$), 16.3 ($^{i\text{-}Pr}CH_3$), 15.5 ($^{i\text{-}Pr}CH_3$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{12}H_{21}N_2O_4$ [M + H]$^+$: 257.1496; found 257.1500.

4-(ethoxycarbonyl)-2,5-dihydro-1H-benzo[d]azepine 3-oxide (19)

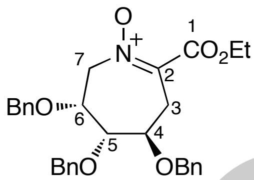


Nitrone **19** (50 mg, 78%) was obtained following the general method from β-diazo-hydroxylamine **9** (72 mg, 0.27 mmol) treated with AgOTf (70 mg, 0.27 mmol).

Nitrone **19** (57 mg, 60%) was obtained following the general method from β-diazo-hydroxylamine **9** (107 mg, 0.41 mmol) treated with $Cu(CH_3CN)_4PF_6$ (15.2 mg, 0.041 mmol).

Clear oil; IR (neat) ν 3501, 2984, 1728 (C=O), 1600, 1446, 1373, 1251, 1160, 1129, 1031; ^{1}H NMR (500 MHz, Toluene-d_8) δ 6.93–6.88 (m, 1H, ^{Ar}CH), 6.86–6.79 (m, 2H, ^{Ar}CH), 6.62 (d, J = 7.5 Hz, 1H, ^{Ar}CH), 3.96 (q, J = 7.0 Hz, 2H, $^{OEt}CH_2$), 3.73 (s, 2H, $^3CH_2$), 3.57 (t, J = 7.5 Hz, 2H, $^4CH_2$), 2.28 (t, J = 7.5 Hz, $^5CH_2$), 0.97 (t, J = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, Toluene-d_8) δ 168.1 (^{1}C=O), 137.0 (^{2}C=N), 131.1 (^{Ar}Cq), 130.6 (^{Ar}Cq), 127.6 (^{Ar}CH), 127.4 (^{Ar}CH), 127.2 (^{Ar}CH), 123.4 (^{Ar}CH), 60.8 ($^{OEt}CH_2$), 58.3 ($^4CH_2$), 32.7 ($^3CH_2$), 27.6 ($^5CH_2$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{13}H_{16}NO_3$ [M + H]$^+$: 234.1125; found 234.1128.

(3*R*,4*S*,5*R*)-3,4,5-tris(benzyloxy)-7-(ethoxycarbonyl)-3,4,5,6-tetrahydro-2H-azepine 1-oxide (20)



Nitrone **20** (37 mg, 96%) was obtained following the general method from *β*-diazo-hydroxylamine **10a** (41 mg, 0.08 mmol) upon treatment with AgOTf (2.0 mg, 0.008 mmol).

Nitrone **20** (26 mg, 64%) was also obtained following the general method from *β*-diazo-hydroxylamine **10b** (42 mg, 0.08 mmol) upon treatment with AgOTf (2.0 mg, 0.008 mmol).

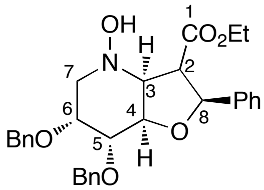
Nitrone **20** (50 mg, 46%) was obtained following the general method from *β*-diazo-hydroxylamine **10a** (115 mg, 0.22 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (2.7 mg, 0.022 mmol).

Nitrone **20** (3.3 mg, 7%) was obtained following the general method from *β*-diazo-hydroxylamine **10b** (47 mg, 0.09 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (3.3 mg, 0.009 mmol).

Clear oil; $[\alpha]^{20}_D$ = −38.8 (c 1.05, $CHCl_3$); IR (neat) ν 3088, 3063, 3031, 2926, 2869, 1732 (C=O), 1600, 1497, 1454, 1368, 1205, 1073, 1026; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.29 (m, 13H, ^{Ar}CH), 7.23–7.19 (m, 2H, ^{Ar}CH), 4.72–4.55 (m, 5H, $^{Bn}CH_2$), 4.48 (d, J = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.42 (br d, J = 5.0 Hz, 1H, ^{4}CH), 4.15 (br dd, J = 15.0, 7.0 Hz, 1H, $^7CH_2$), 4.12–4.05 (m, 3H, $^{OEt}CH_2$, ^{6}CH), 3.96 (br dd, J = 15.0, 4.0 Hz, 1H, $^7CH_2$), 3.89 (dd, J = 5.0, 2.0 Hz, 1H, ^{5}CH), 3.58 (d, J = 16.5 Hz, 1H, $^3CH_2$), 3.33 (br d, J = 16.5 Hz, 1H, $^3CH_2$), 1.18 (t, J = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1 (^{1}C=O), 139.7 (^{2}C=N), 137.7 (^{Ar}Cq), 137.5 (^{Ar}Cq), 137.3 (^{Ar}Cq), 128.7 (^{Ar}CH), 128.7 (^{Ar}CH), 128.6 (^{Ar}CH), 128.3 (^{Ar}CH), 128.2 (^{Ar}CH), 128.1 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 75.5 (^{4}CH), 74.4 (^{5}CH), 73.9 ($^{Bn}CH_2$), 72.4 ($^{Bn}CH_2$), 71.9 ($^{Bn}CH_2$), 70.8 (^{6}CH), 61.1 ($^{OEt}CH_2$), 59.4 ($^7CH_2$), 34.4 ($^3CH_2$), 14.2 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}NO_6$ [M + H]$^+$: 504.2381; found 504.2379.

2d- Characterization of CH-insertion products

Ethyl (2*S*,3a*S*,6*R*,7*R*,7a*R*)-6,7-bis(benzyloxy)-4-hydroxy-2-phenyloctahydrofuro[3,2-b] pyridine-3-carboxylate (S-20'a)

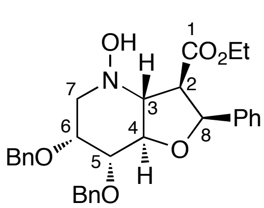


Compound **S-20'a** (59 mg, 54%) was obtained with nitrone **20** (50 mg, 46%) following the general method from *β*-diazo-hydroxylamine **10a** (115 mg, 0.22 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (2.7 mg, 0.022 mmol).

Clear oil; $[\alpha]^{20}_{D}$ = +30.3 (*c* 1.06, $CHCl_3$); IR (neat) ν 3434 (OH), 3088, 3064, 3031, 2868, 1727 (C=O), 1496, 1454, 1177, 1096, 1026; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.23 (m, 15H, ^{Ar}CH), 5.09 (d, *J* = 6.0 Hz, 1H, ^{8}CH), 5.02 (br s, 1H, OH), 4.80 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.74 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.61 (d, *J* = 12.5 Hz, 1H, $^{Bn}CH_2$), 4.59 (d, *J* = 12.5 Hz, 1H, $^{Bn}CH_2$), 4.28 (t, *J* = 4.0 Hz, 1H, ^{4}CH), 4.26–4.13 (m, 2H, $^{OEt}CH_2$), 4.08–4.06 (m, 1H, ^{5}CH), 4.01–3.96 (m, 1H, ^{6}CH), 3.60 (d, *J* = 4.0 Hz, 1H, ^{3}CH), 3.34 (dd, *J* = 10.0, 4.0 Hz, 1H, $^7CH_2$), 3.23–3.16 (m, 2H, $^7CH_2$, ^{2}CH), 1.27 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7 (^{1}C=O), 141.2 (^{Ar}Cq), 138.5 (^{Ar}Cq), 138.4 (^{Ar}Cq), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.0 (^{Ar}CH), 128.0 (^{Ar}CH), 127.8 (^{Ar}CH), 127.8 (^{Ar}CH), 127.7 (^{Ar}CH), 126.4 (^{Ar}CH), 83.2 (^{8}CH), 80.5 (^{4}CH), 74.7 (^{6}CH), 73.1 ($^{Bn}CH_2$), 72.7 (^{5}CH), 71.7 ($^{Bn}CH_2$), 70.3 (^{3}CH), 61.3 ($^{OEt}CH_2$), 57.8 (^{2}CH), 56.4 ($^7CH_2$), 14.4 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}NO_6$ $[M + H]^+$: 504.2381; found 504.2380.

NOESY correlation between ^{8}H (δ 5.09 ppm) and ^{4}H (δ 4.28 ppm)

Ethyl (2*S*,3*R*,3a*R*,6*R*,7*R*,7a*R*)-6,7-bis(benzyloxy)-4-hydroxy-2-phenyloctahydrofuro[3,2-b] pyridine-3-carboxylate (S-20'b)



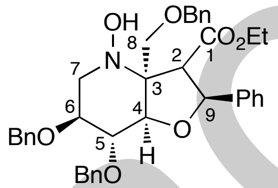
Compound **S-20'b** (30 mg, 66%) was obtained with nitrone **20** (3.3 mg, 7%) following the general method from *β*-diazo-hydroxylamine **10b** (47 mg, 0.09 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (3.3 mg, 0.009 mmol).

Clear oil; $[\alpha]^{20}_{D}$ = −13.2 (*c* 1.22, $CHCl_3$); IR (neat) ν 3227 (OH), 3092, 3062, 3031, 2901, 1732 (C=O), 1496, 1454, 1369, 1320, 1265, 1208, 1149, 1096, 1066, 1025; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.23 (m, 20H, ^{Ar}CH), 5.44 (d, *J* = 10.0 Hz, 1H, ^{8}CH), 5.15 (br s, 1H, OH), 4.86 (d, *J* = 12.5

Hz, 1H, $^{Bn}CH_2$), 4.84–4.76 (m, 2H, $^{Bn}CH_2$), 4.72 (d, *J* = 12.5 Hz, 1H, $^{Bn}CH_2$), 4.22 (t, *J* = 10.0 Hz, 1H, ^{4}CH), 3.99–3.92 (m, 1H, ^{6}CH), 3.80 (dd, *J* = 10.0, 3.5 Hz, 1H, ^{5}CH), 3.67–3.53 (m, 3H, ^{2}CH, $^{OEt}CH_2$), 3.53–3.48 (m, 3H, $^{7}CH_2$), 3.19 (d, *J* = 9.5 Hz, 1H, ^{3}CH), 2.62 (dd, *J* = 12.0, 1.5 Hz, 1H, $^{7}CH_2$), 0.82 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0 (^{1}C=O), 138.5 (^{Ar}Cq), 138.2 (^{Ar}Cq), 138.1 (^{Ar}Cq), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.4 (^{Ar}CH), 128.2 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 127.8 (^{Ar}CH), 127.7 (^{Ar}CH), 127.2 (^{Ar}CH), 82.2 (^{8}CH), 80.3 (^{5}CH), 79.4 (^{4}CH), 74.3 (^{6}CH), 73.5 ($^{Bn}CH_2$), 73.1 (^{3}CH), 72.1 ($^{Bn}CH_2$), 62.5 ($^{7}CH_2$), 60.7 ($^{OEt}CH_2$), 53.8 (^{2}CH), 13.8 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{30}H_{34}NO_6$ $[M + H]^+$: 504.2381; found 504.2380.

NOESY correlations between ^{8}H (δ 5.44 ppm) and ^{4}H (δ 4.22 ppm), ^{4}H (δ 4.22 ppm) and ^{2}H (δ 3.67–3.53ppm) and between ^{5}H (δ 3.80 ppm) and ^{3}H (δ 3.19 ppm)

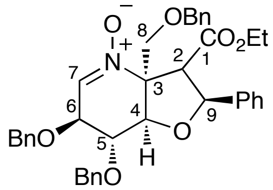
Ethyl (2*S*,3a*R*,6*S*,7*R*,7a*R*)-6,7-bis(benzyloxy)-3a-((benzyloxy)methyl)-4-hydroxy-2-phenyl octahydrofuro[3,2-b]pyridine-3-carboxylate (S-21'a)



Compound **S-21'a** (12 mg, 42%) was obtained following the general method from *β*-diazo-hydroxylamine **11** (30 mg, 0.047 mmol) upon treatment with AgOTf (12 mg, 0.047 mmol). Clear oil; $[\alpha]^{20}_{D}$ = −16.2 (*c* 0.89, $CHCl_3$); IR (neat) ν 3392 (OH), 3088, 3064, 3031, 2926, 2855, 1725 (C=O), 1497, 1454, 1369, 1096, 1028; ^{1}H NMR (500 MHz, Toluene-d_8) δ 7.57 (d, *J* = 7.5 Hz, 2H, ^{Ar}CH), 7.29 – 7.03 (m, 18H, ^{Ar}CH), 5.72 (br s, 1H, OH), 5.41 (d, *J* = 10.0 Hz, 1H, ^{9}CH), 4.67 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.60 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.45 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.39 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.35 (d, *J* = 5.0 Hz, 1H, ^{4}CH), 4.27 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.24 (d, *J* = 12.0 Hz, 1H, $^{Bn}CH_2$), 4.07 – 4.02 (m, 2H, ^{5}CH, $^{8}CH_2$), 3.98 (d, *J* = 9.5 Hz, 1H, $^{8}CH_2$), 3.91 – 3.77 (m, 3H, ^{6}CH, $^{OEt}CH_2$), 3.61 (d, *J* = 10.0 Hz, 1H, ^{2}CH), 3.51 (dd, *J* = 11.0, 6.5 Hz, 1H, $^{7}CH_2$), 3.30 (dd, *J* = 11.0, 7.5 Hz, 1H, $^{7}CH_2$), 0.82 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, Toluene-d_8) δ 171.3 (^{1}C=O), 140.9 (^{Ar}Cq), 139.2 (^{Ar}Cq), 139.2 (^{Ar}Cq), 138.4 (^{Ar}Cq), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 128.5 (^{Ar}CH), 128.3 (^{Ar}CH), 128.0 (^{Ar}CH), 127.9 (^{Ar}CH), 127.7 (^{Ar}CH), 127.6 (^{Ar}CH), 127.6 (^{Ar}CH), 126.6 (^{Ar}CH), 83.0 (^{9}CH), 82.7 (^{4}CH), 80.2 (^{5}CH), 77.0 (^{6}CH), 75.3 (^{3}Cq), 73.8 ($^{Bn}CH_2$), 73.0 ($^{Bn}CH_2$), 72.0 ($^{Bn}CH_2$), 70.5 ($^{8}CH_2$), 60.6 ($^{OEt}CH_2$), 58.0 (^{2}CH), 54.8 ($^{7}CH_2$), 14.0 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{38}H_{42}NO_7$ $[M + H]^+$: 624.2951; found 624.2956.

NOESY correlations between ^{9}H (δ 5.41 ppm) and ^{2}H (δ 3.61 ppm), ^{9}H (δ 5.41 ppm) and ^{8}H (δ 3.98 ppm), and between ^{9}H (δ 5.41 ppm) and ^{4}H (δ 3.35 ppm)

(2*S*,3*R*,3a*R*,6*S*,7*S*,7a*R*)-6,7-bis(benzyloxy)-3a-((benzyloxy)methyl)-3-(ethoxycarbonyl)-2-phenyl-2,3,3a,6,7,7a-hexahydrofuro[3,2-b]pyridine 4-oxide (S-21'b)

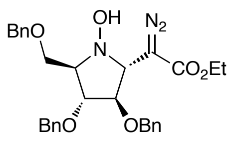


Compound **S-21'b** (7 mg, 23%) was obtained following the general method from from *β*-diazo-hydroxylamine **11** (30 mg, 0.046 mmol) upon treatment with $Cu(CH_3CN)_4PF_6$ (17 mg, 0.046 mmol). Clear oil; $[\alpha]^{20}_D = -20.2$ (*c* 0.55, $CHCl_3$); IR (neat) ν 3088, 3063, 3031, 2924, 2870, 1728 (C=O), 1585, 1497, 1455, 1096, 1027; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.22 (m, 20H, ^{Ar}CH), 7.01 (d, *J* = 2.5 Hz, 1H, ^{7}CH), 5.03 (d, *J* = 10.5 Hz, 1H, ^{9}CH), 4.91 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.80 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.69 (d, *J* = 11.5 Hz, 1H, $^{Bn}CH_2$), 4.67 (d, *J* = 6.5 Hz, 1H, ^{4}CH), 4.60–4.49 (m, 3H, $^{Bn}CH_2$), 4.40 (dd, *J* = 8.5, 2.5 Hz, 1H, ^{6}CH), 4.21 (d, *J* = 10.0 Hz, 1H, $^8CH_2$), 4.13 (d, *J* = 12.0 Hz, 1H, $^8CH_2$), 4.11–4.02 (m, 2H, $^{OEt}CH_2$), 3.88 (dd, *J* = 8.5, 6.5 Hz, 1H, ^{5}CH), 3.37 (d, *J* = 10.5 Hz, 1H, ^{2}CH), 1.07 (t, *J* = 7.0 Hz, 3H, $^{OEt}CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1 (^{1}C=O), 138.0 (^{Ar}Cq), 137.6 (^{Ar}Cq), 137.4 (^{Ar}Cq), 137.4 (^{Ar}Cq), 137.9 (^{7}CH), 128.9 (^{Ar}CH), 128.7 (^{Ar}CH), 128.6 (^{Ar}CH), 128.5 (^{Ar}CH), 128.2 (^{Ar}CH), 128.1 (^{Ar}CH), 128.1 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 127.9 (^{Ar}CH), 126.3 (^{Ar}CH), 83.0 (^{9}CH), 82.7 (^{3}Cq), 81.5 (^{4}CH), 80.0 (^{5}CH), 75.6 (^{6}CH), 73.9 ($^{Bn}CH_2$), 73.8 ($^{Bn}CH_2$), 73.7 ($^{Bn}CH_2$), 71.6 ($^8CH_2$), 61.4 ($^{OEt}CH_2$), 59.7 (^{2}CH), 14.1 ($^{OEt}CH_3$); HRMS (ESI): calcd for $C_{38}H_{40}NO_7$ $[M + H]^+$: 622.2799; found 622.2793.

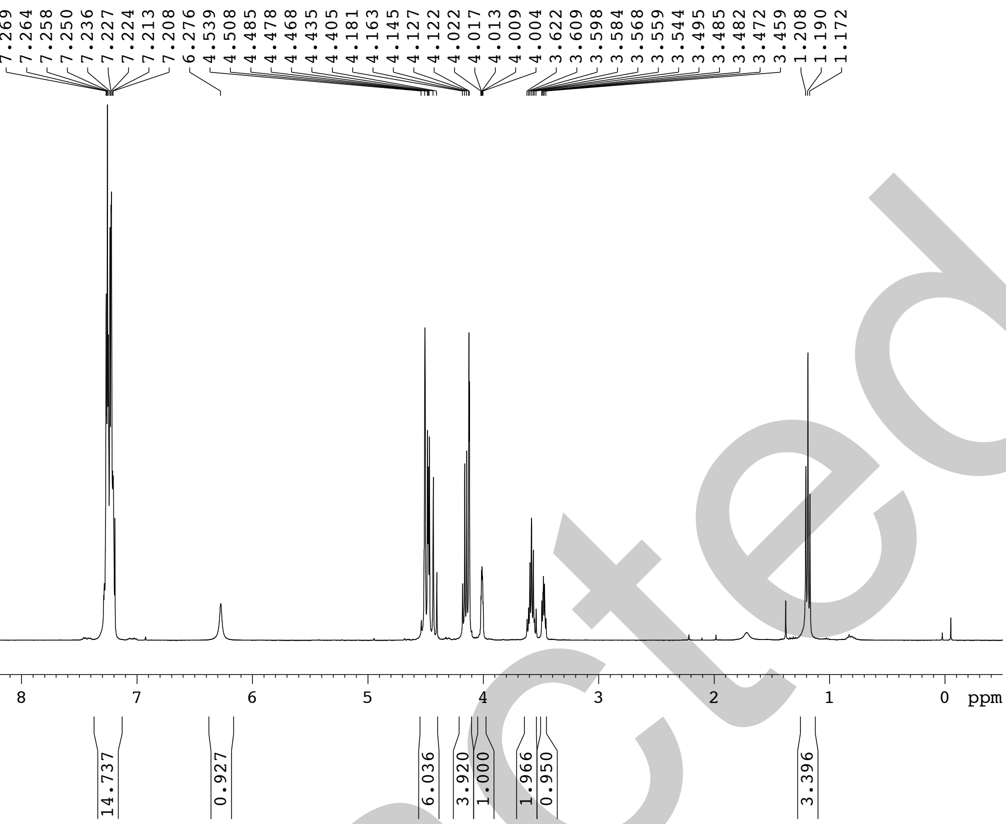
NOESY correlation between ^{9}H (δ 5.03 ppm) and ^{2}H (δ 3.37 ppm), ^{9}H (δ 5.03 ppm) and ^{8}H (δ 4.13 ppm), and between ^{9}H (δ 5.03 ppm) and ^{4}H (δ 4.67 ppm)

3- Copies of ^{1}H and ^{13}C NMR spectra

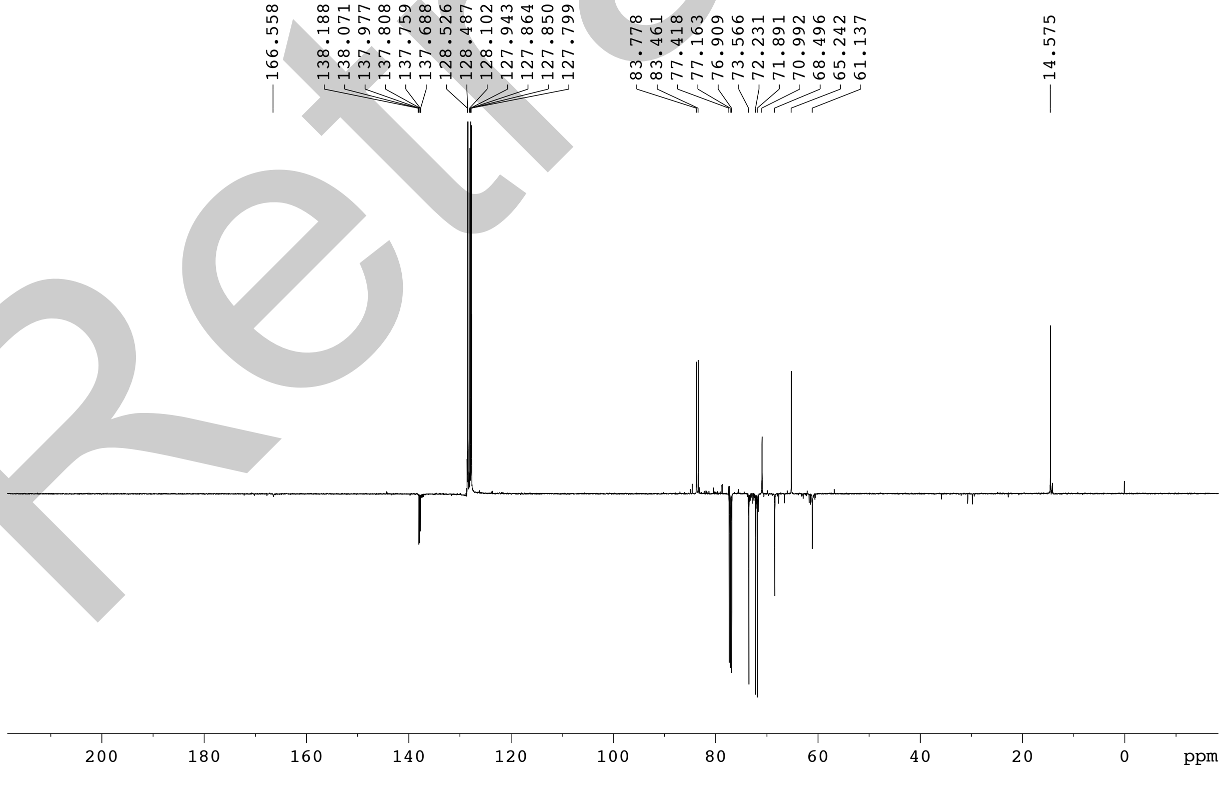
^{1}H NMR (400 MHz, $CDCl_3$)



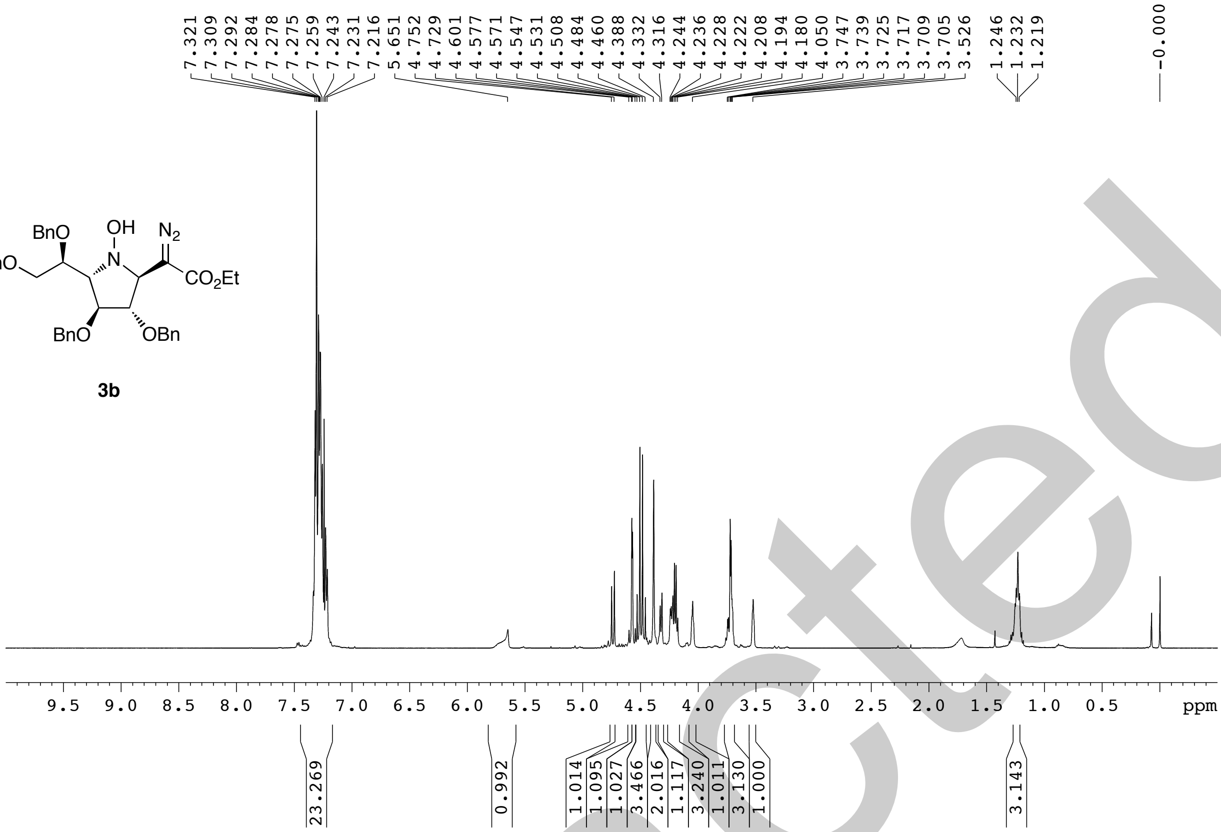
3a



^{13}C NMR (125 MHz, $CDCl_3$)

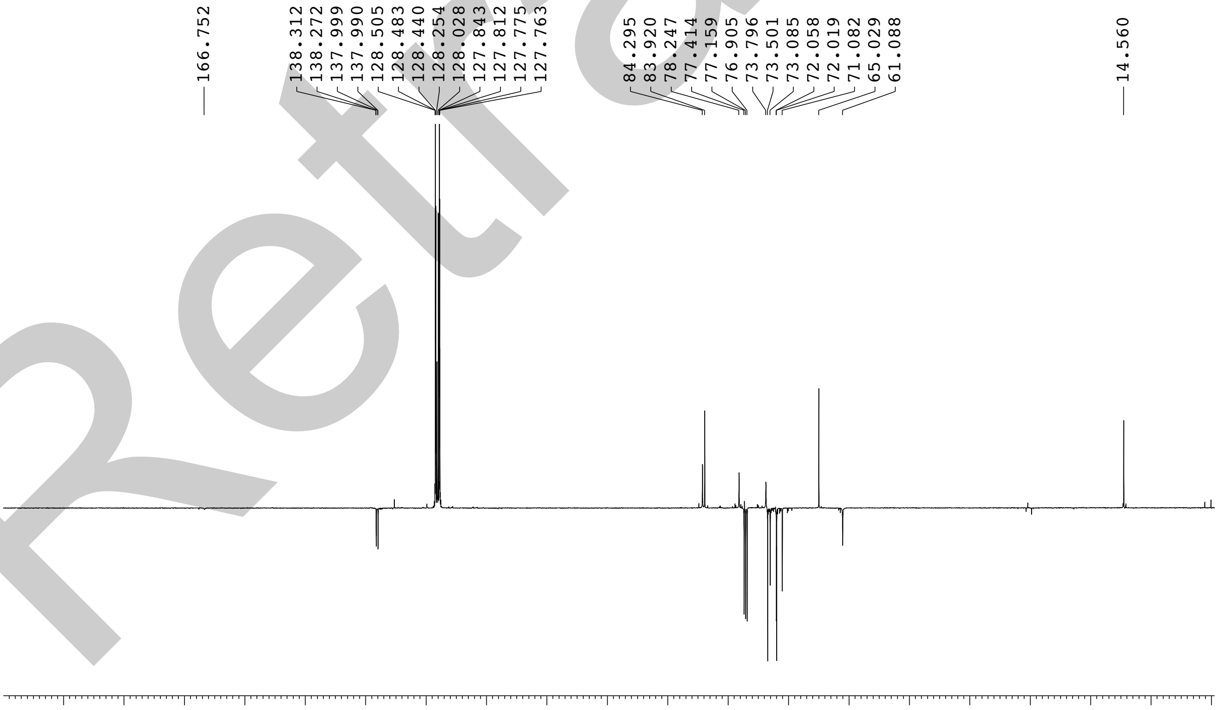


^{1}H NMR (500 MHz, $CDCl_3$)

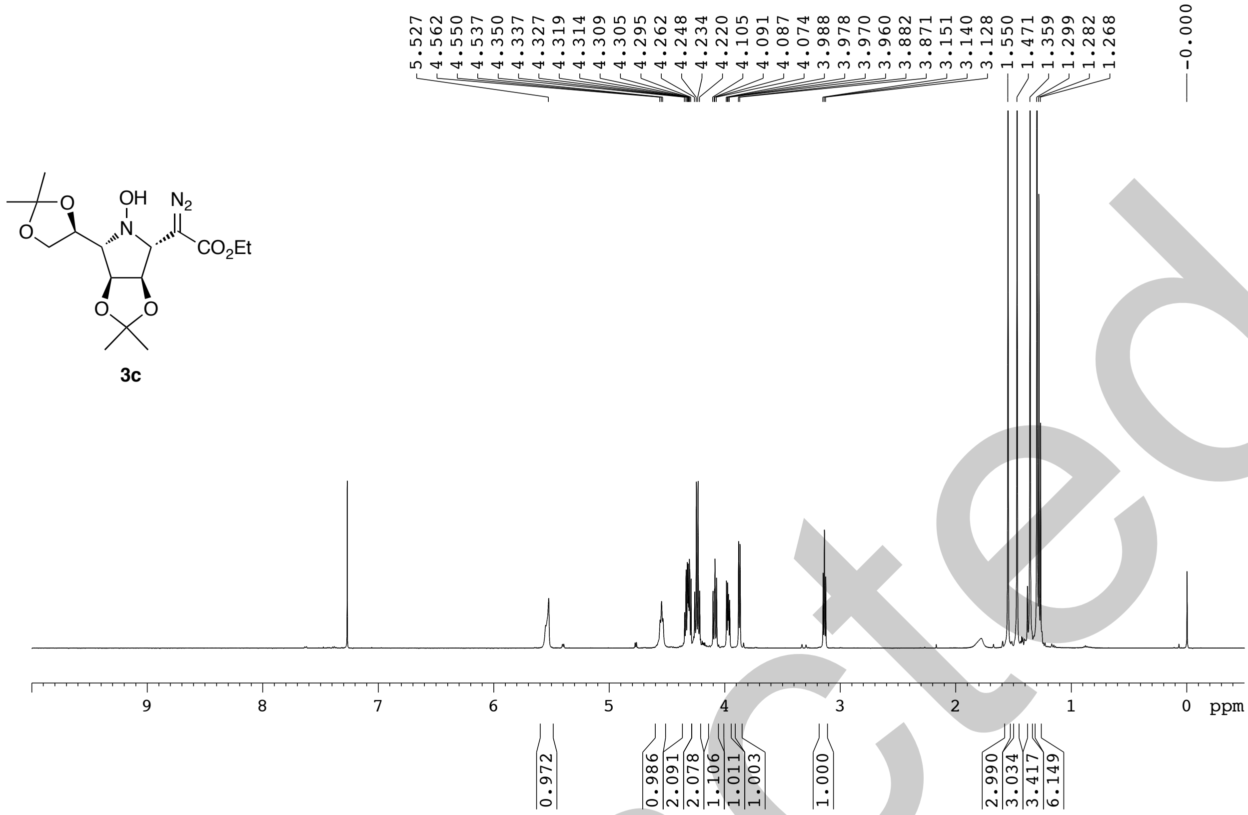


3b

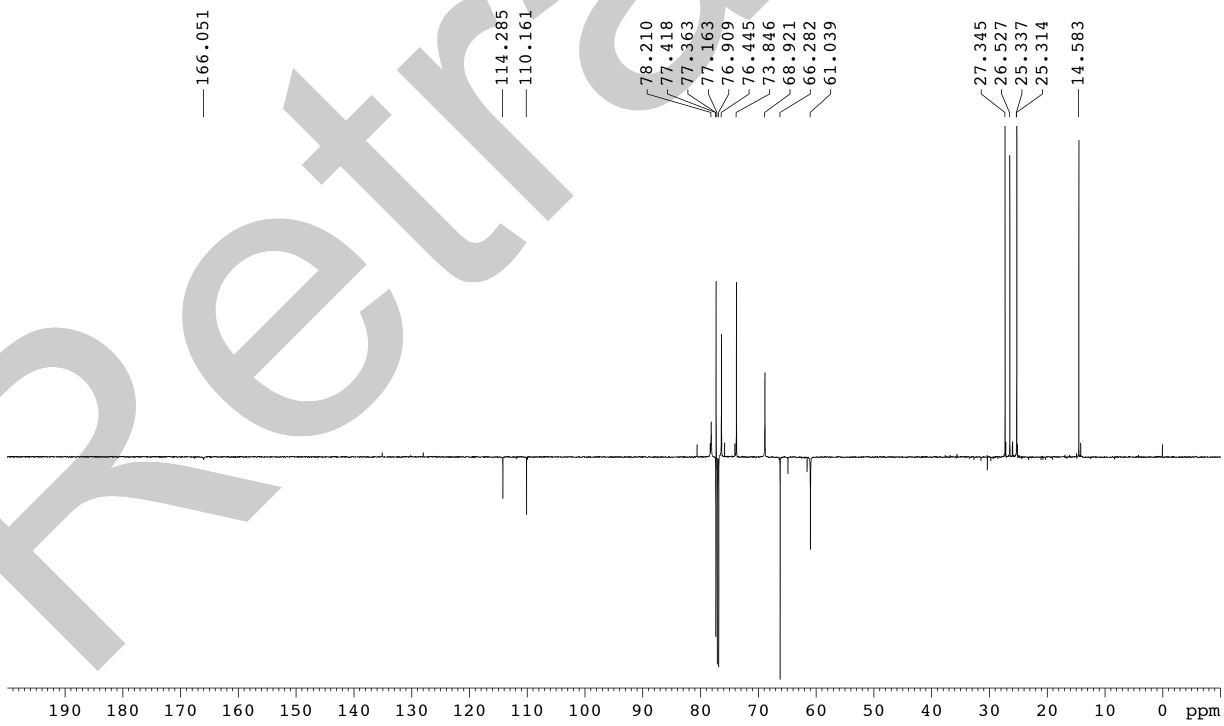
^{13}C NMR (125 MHz, $CDCl_3$)



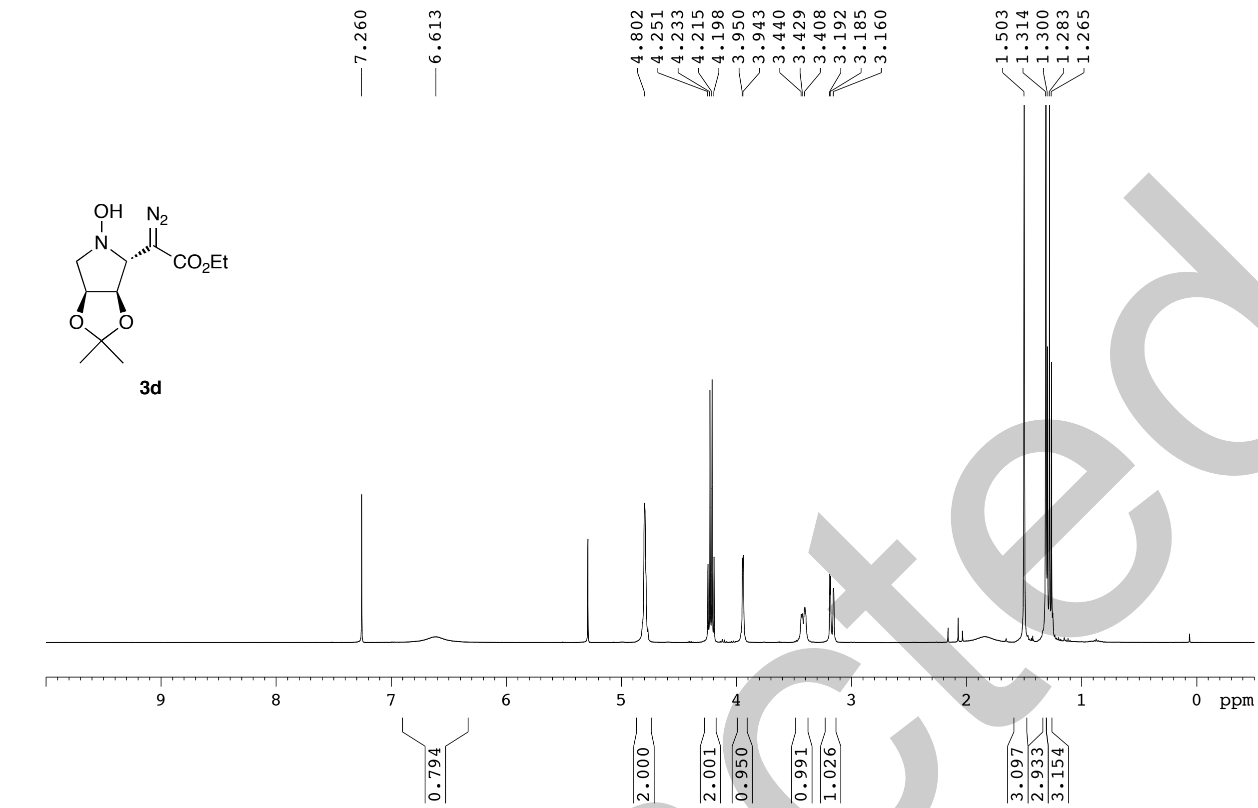
^{1}H NMR (500 MHz, $CDCl_3$)



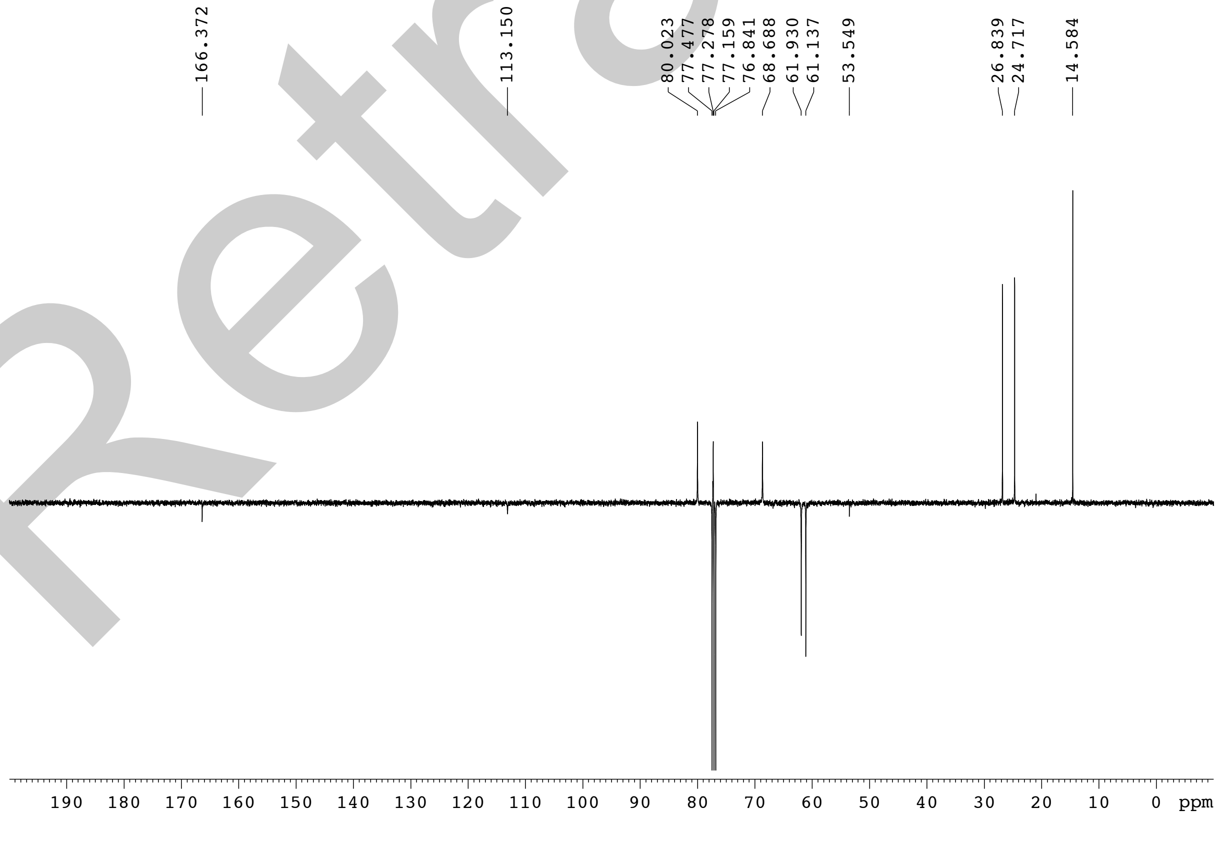
^{13}C NMR (125 MHz, $CDCl_3$)



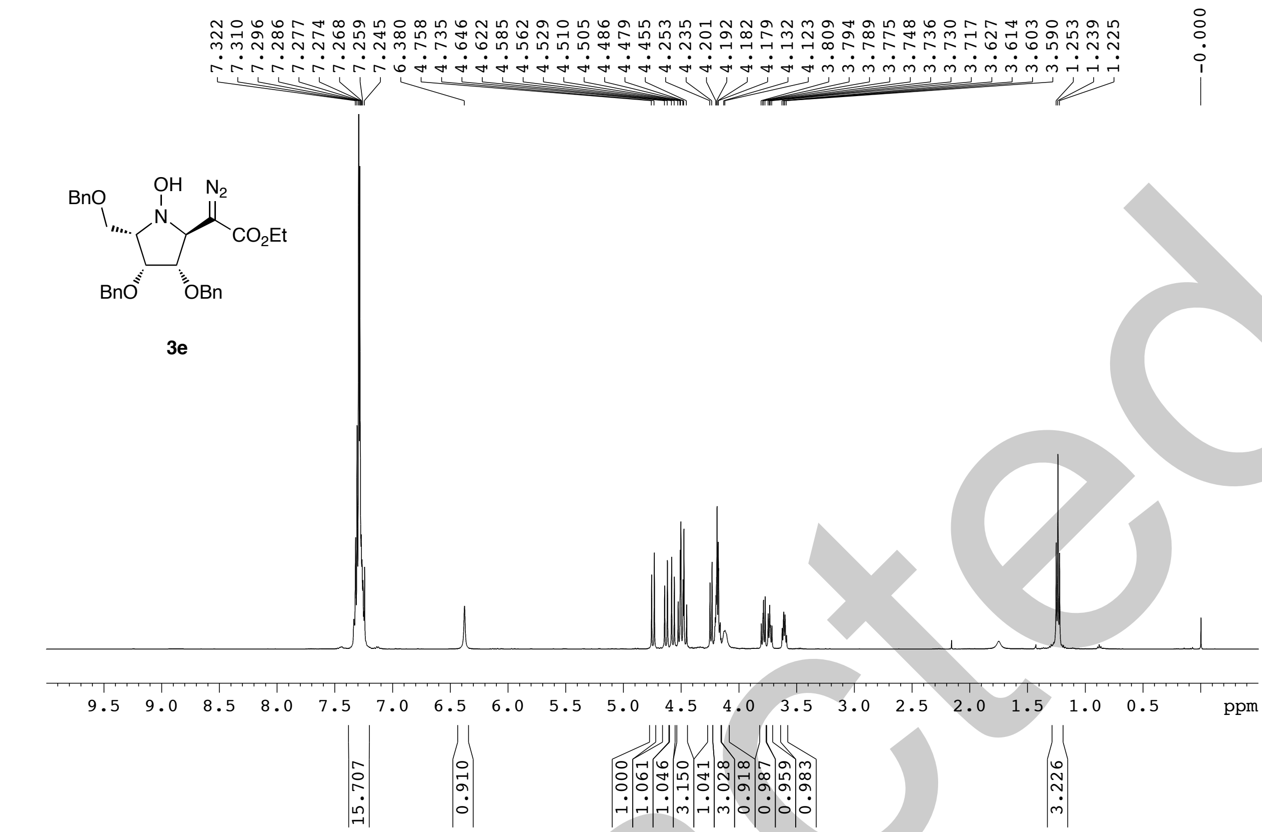
^{1}H NMR (400 MHz, $CDCl_3$)



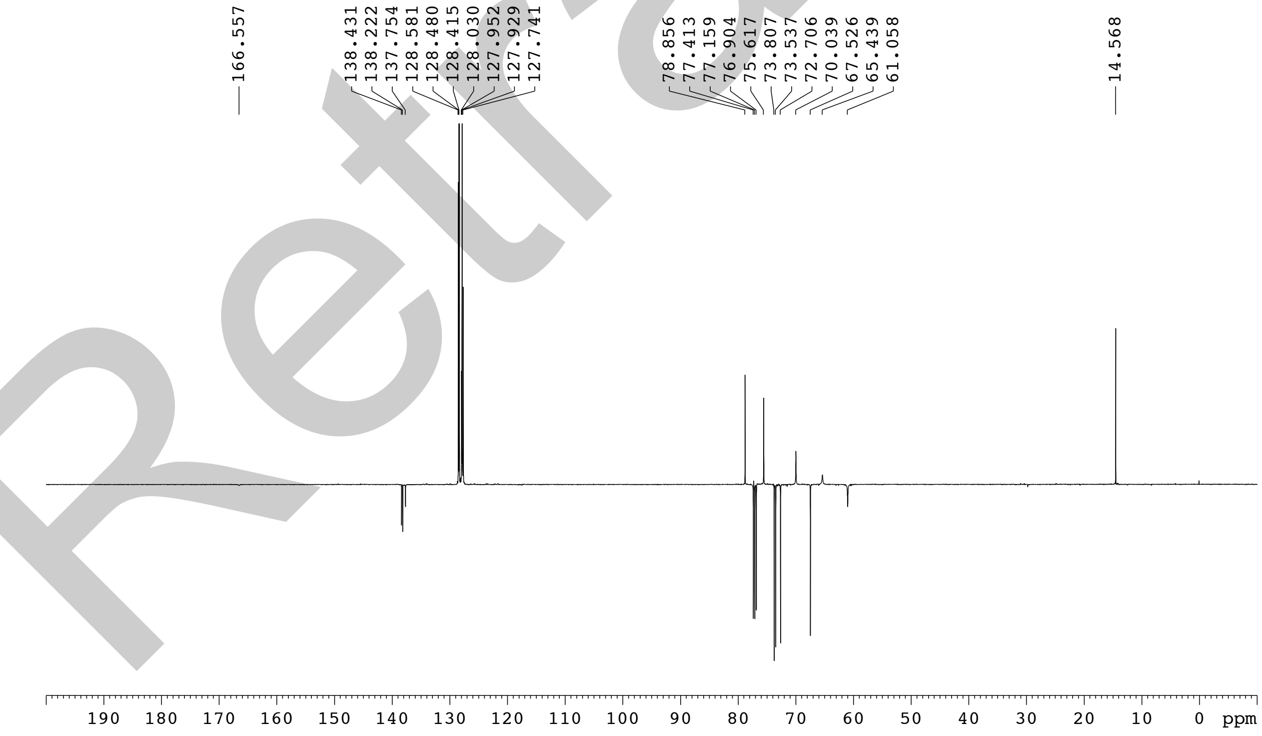
^{13}C NMR (100 MHz, $CDCl_3$)

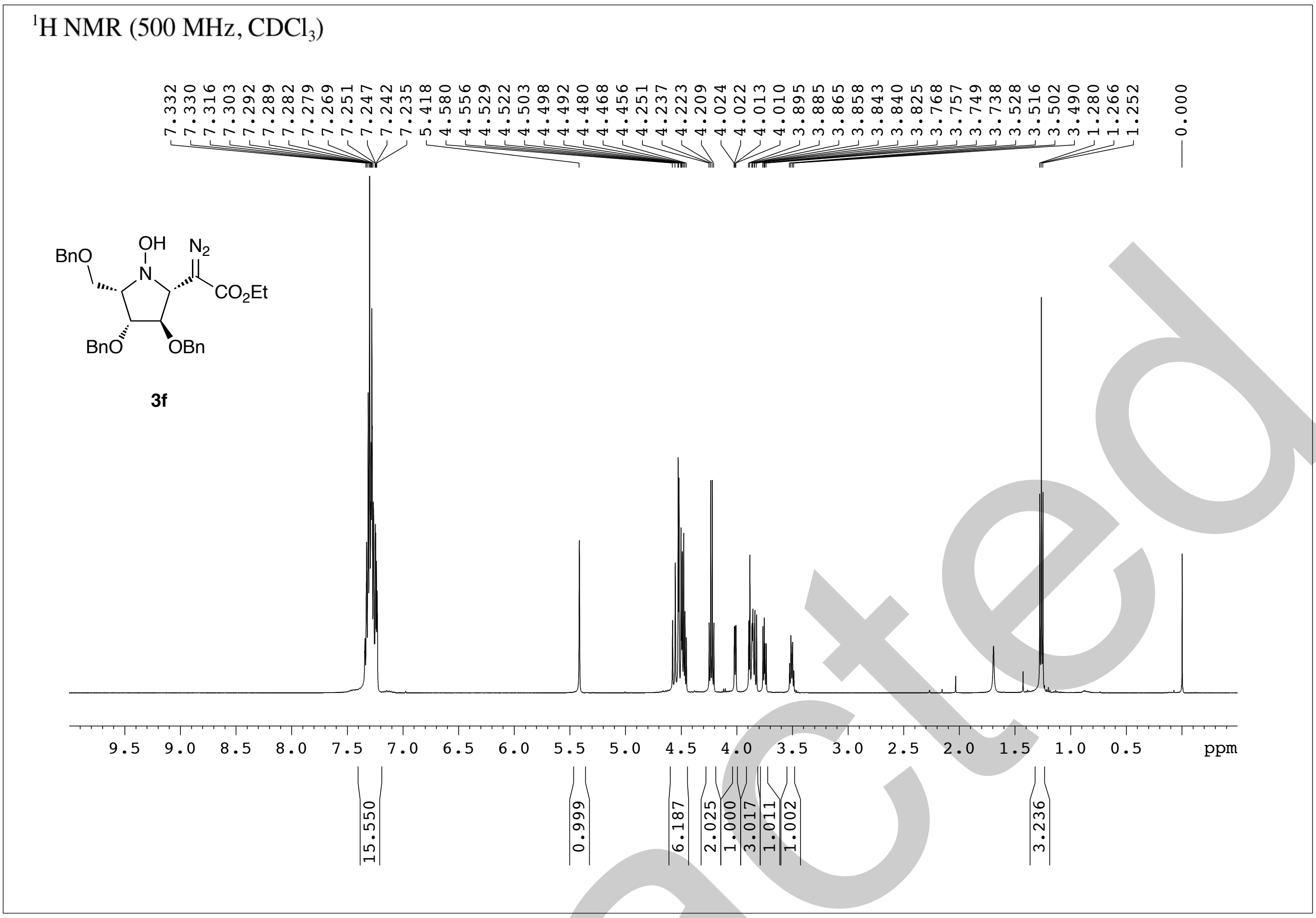


^{1}H NMR (500 MHz, $CDCl_3$)

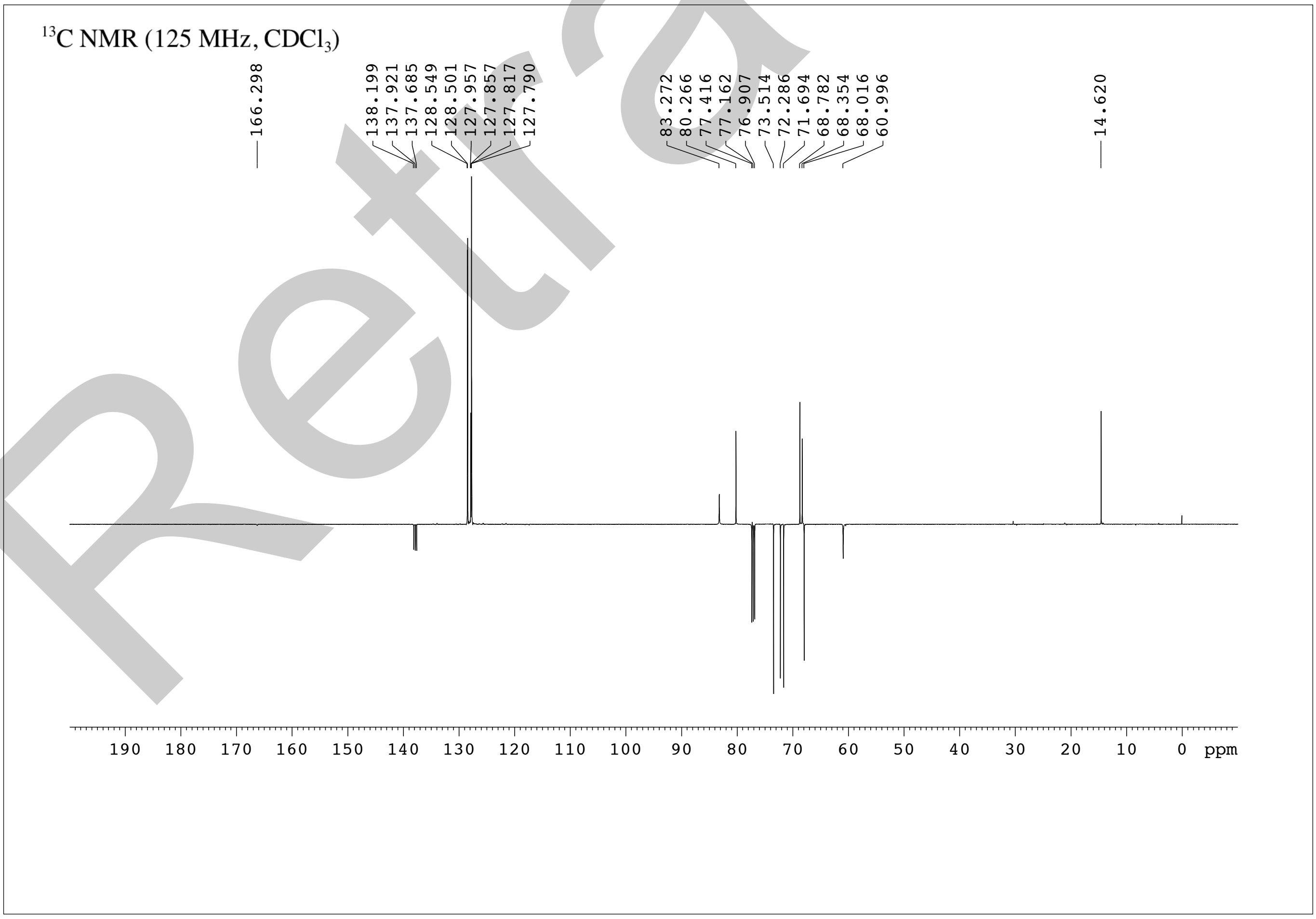


^{13}C NMR (125 MHz, $CDCl_3$)



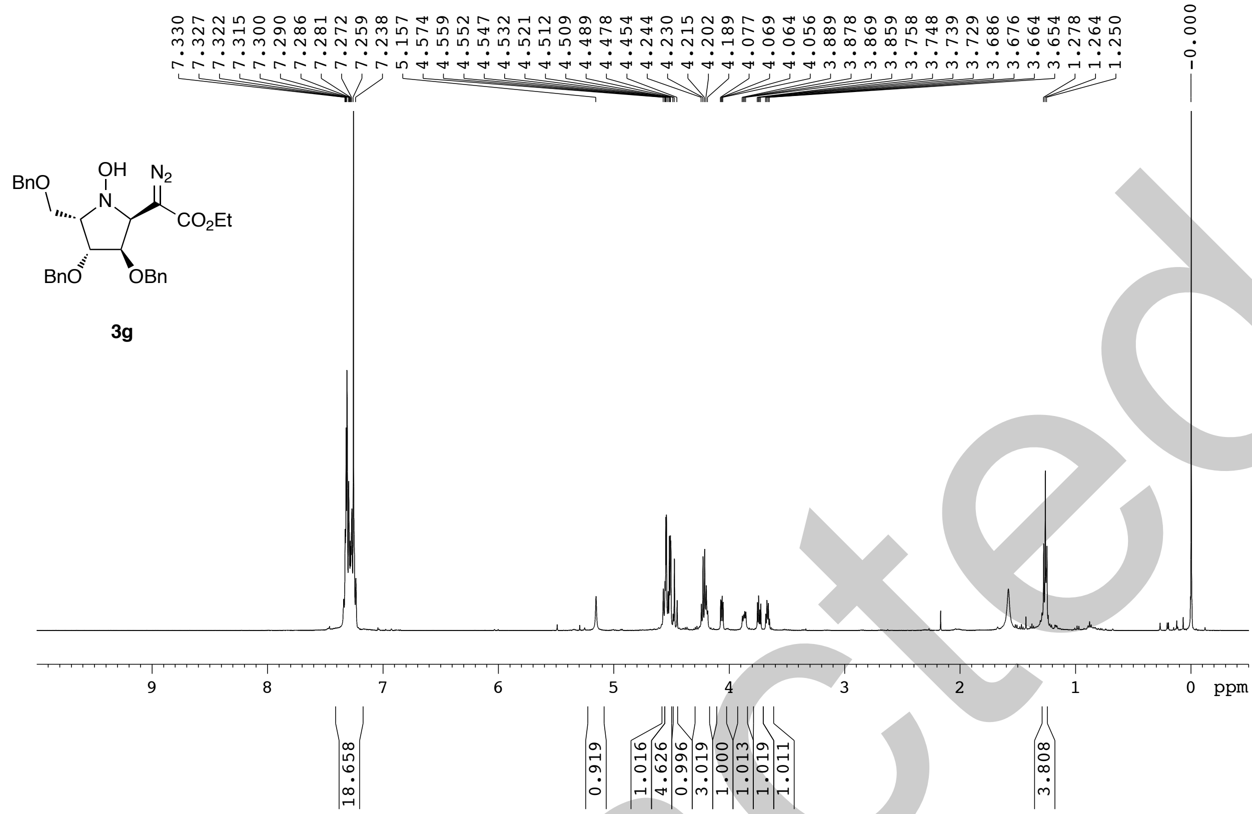


1H NMR (500 MHz, CDCl3)
BnO
OH
N
N2
CO2Et
BnO
OBn
3f
ppm
15.550
0.999
6.187
2.025
1.000
3.017
1.011
1.002
3.236

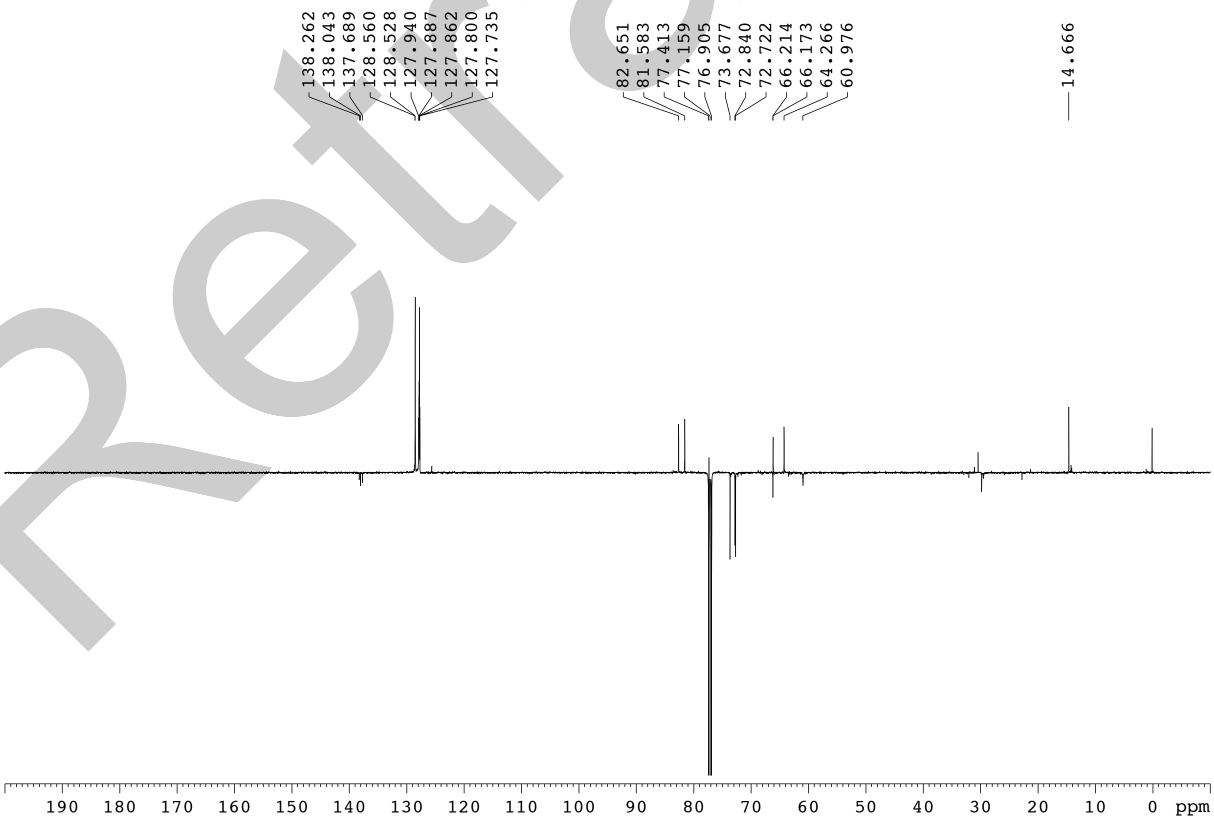


13C NMR (125 MHz, CDCl3)
166.298
138.199
137.921
137.685
128.549
128.501
127.957
127.857
127.817
127.790
83.272
80.266
77.416
77.162
76.907
73.514
72.286
71.694
68.782
68.354
68.016
60.996
14.620
ppm

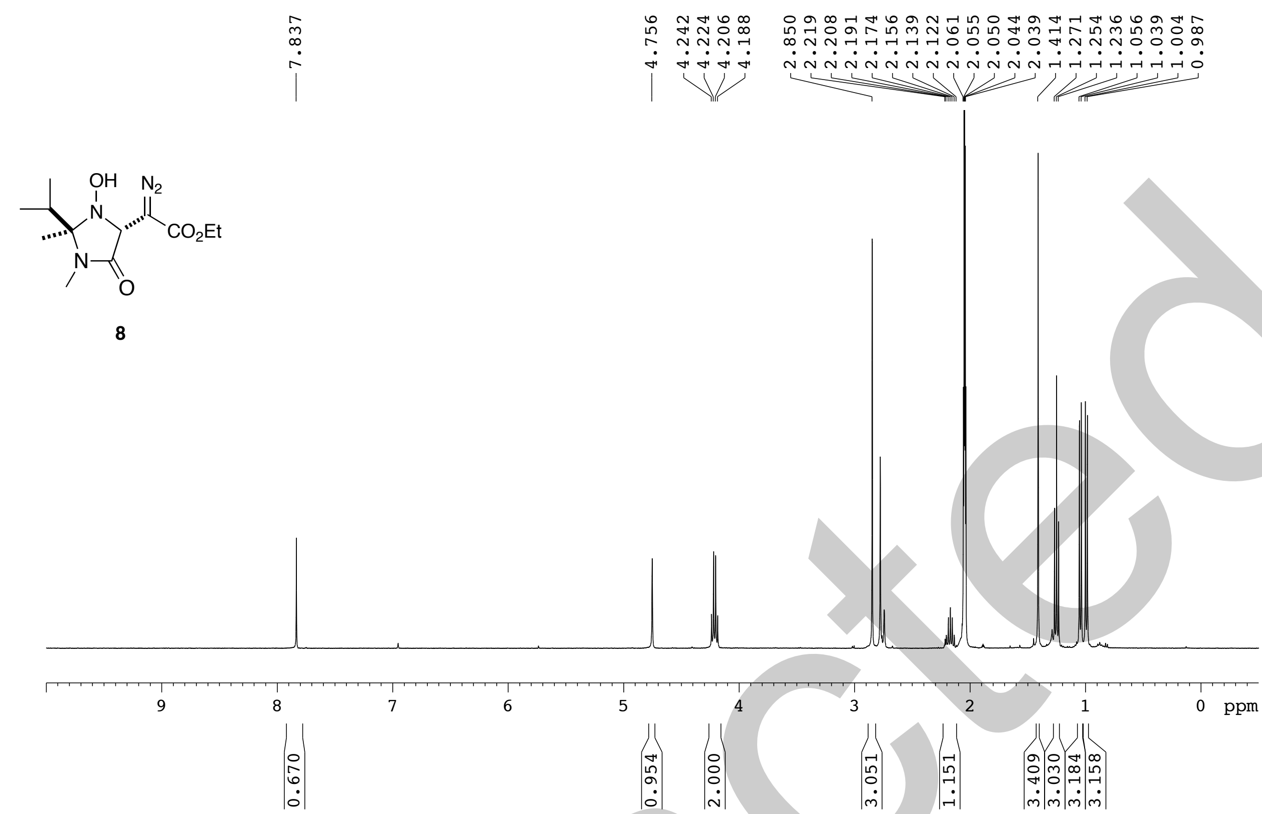
^1H NMR (500 MHz, $CDCl_3$)



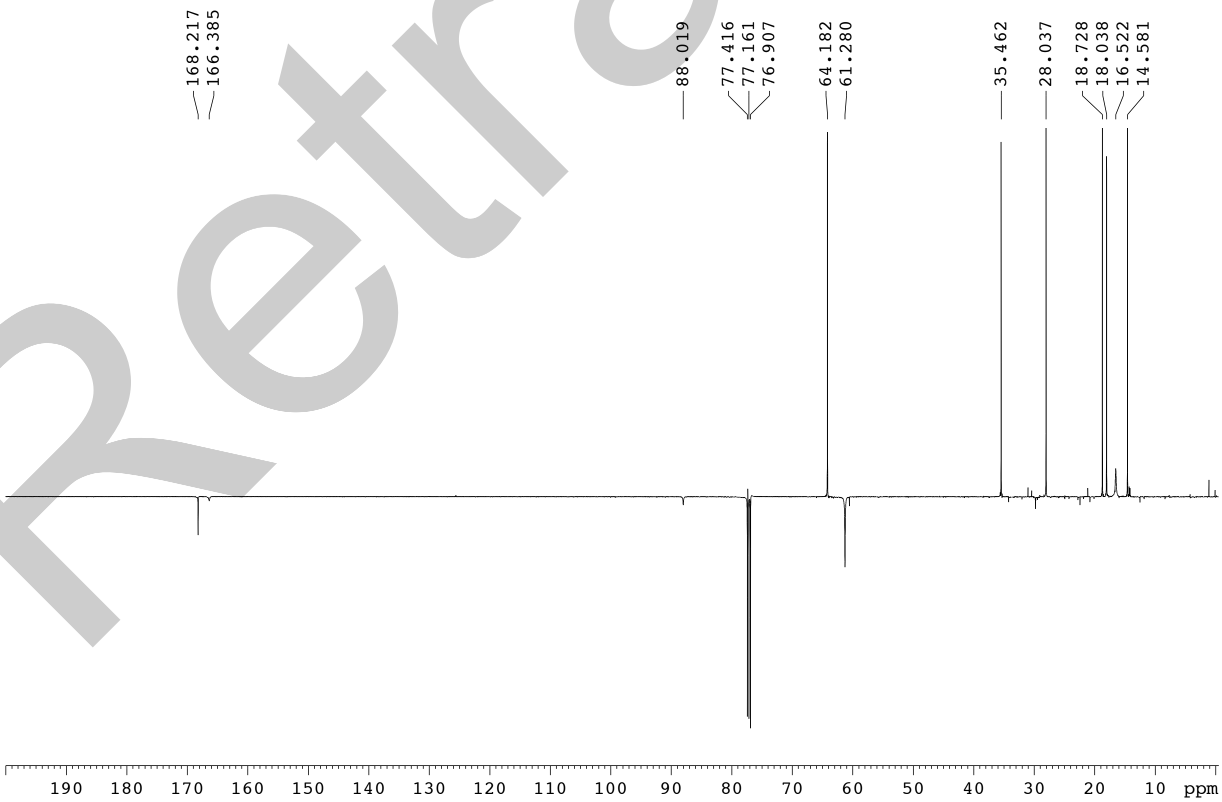
^{13}C NMR (125 MHz, $CDCl_3$)



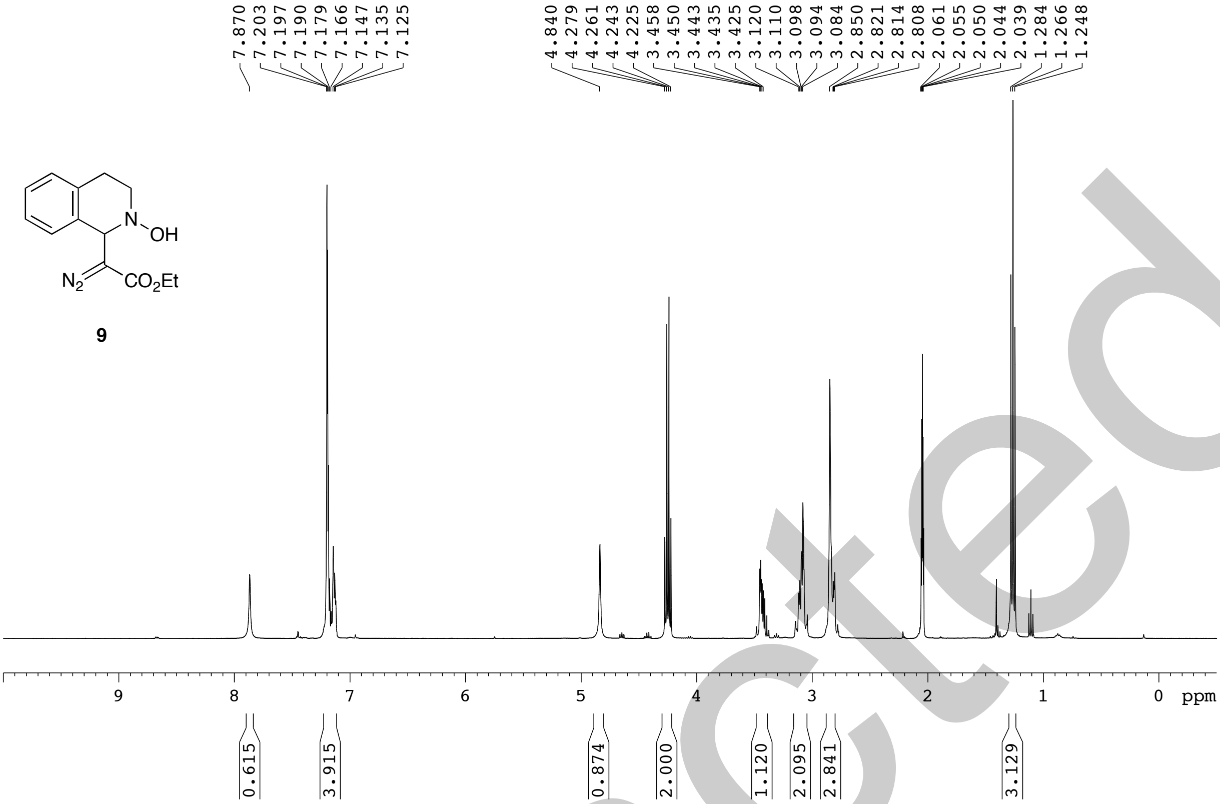
[1]H NMR (400 MHz, Acetone-d_6)



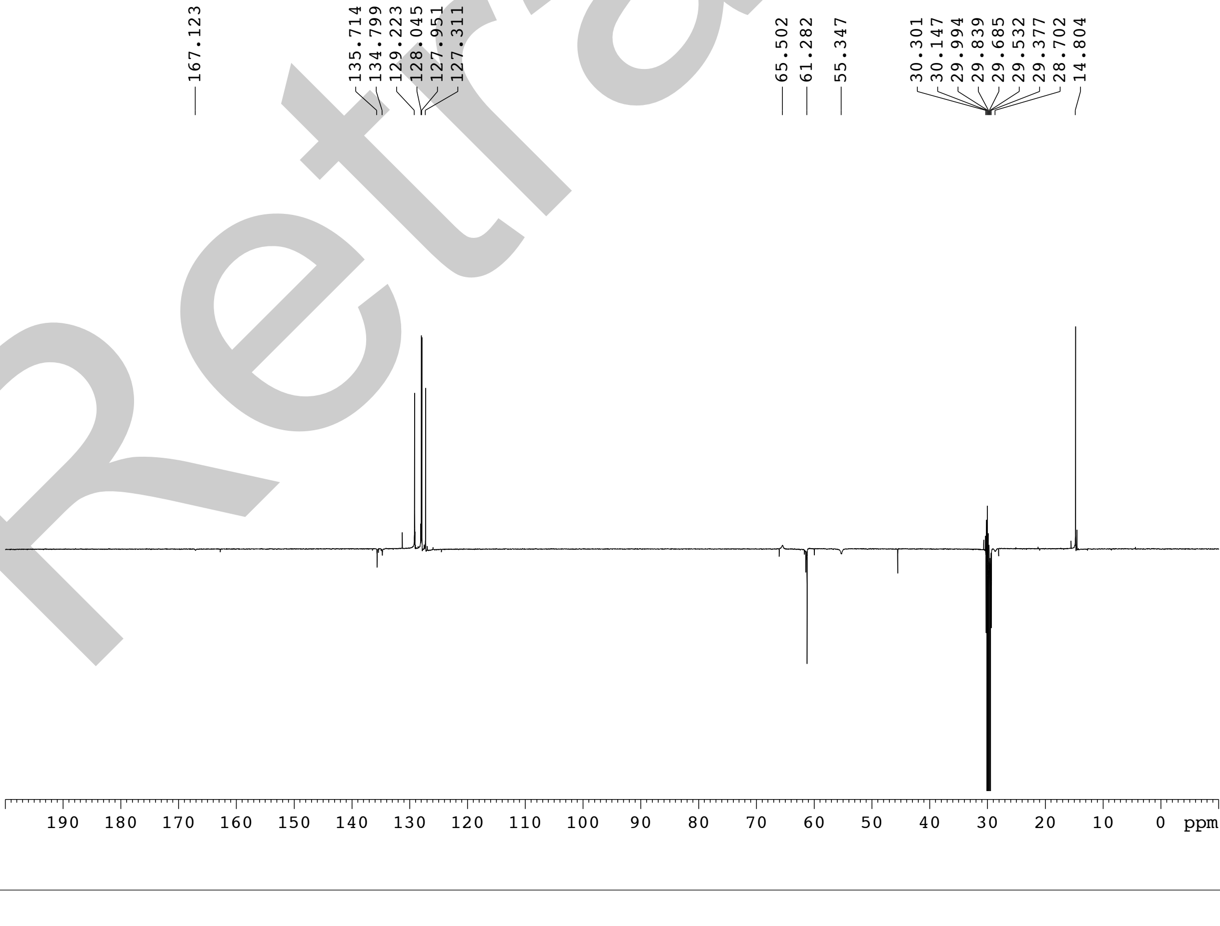
[13]C NMR (125 MHz, $CDCl_3$)



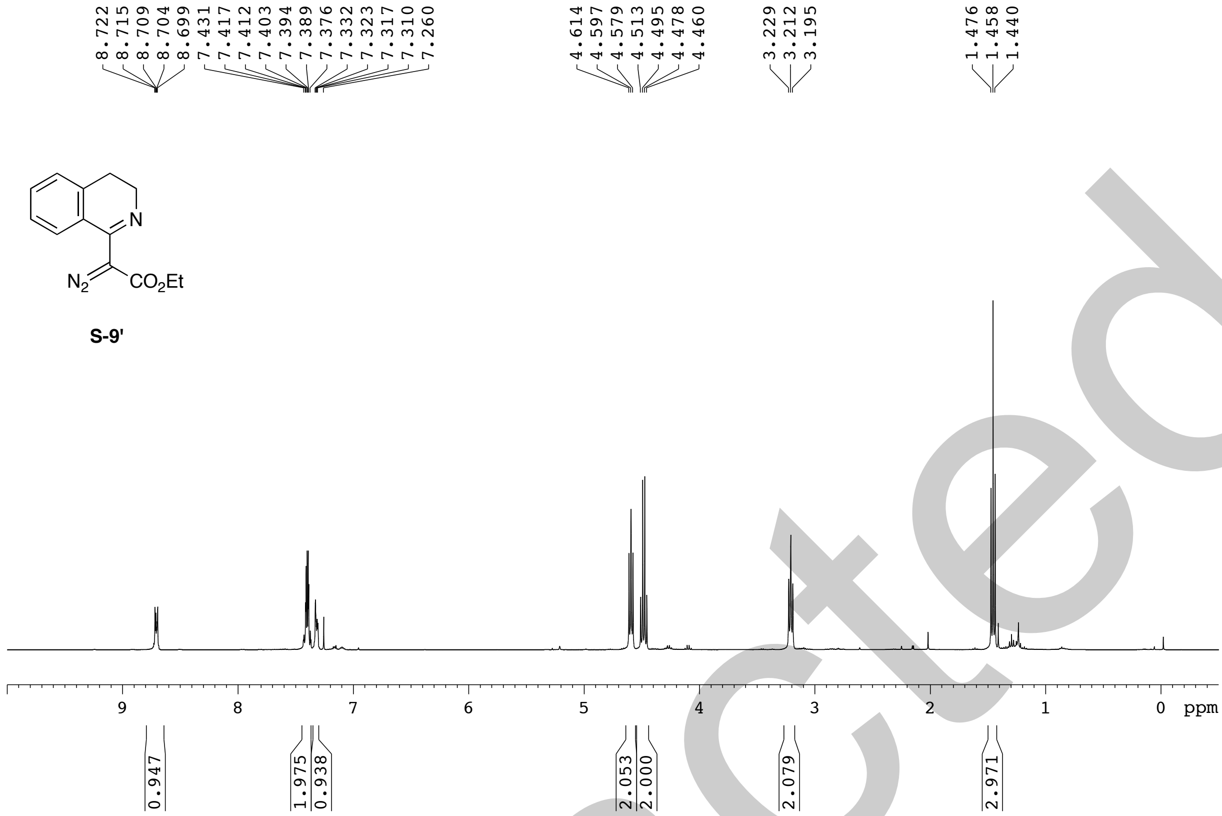
[1]H NMR (400 MHz, Acetone-d_6)



[13]C NMR (125 MHz, Acetone-d_6)

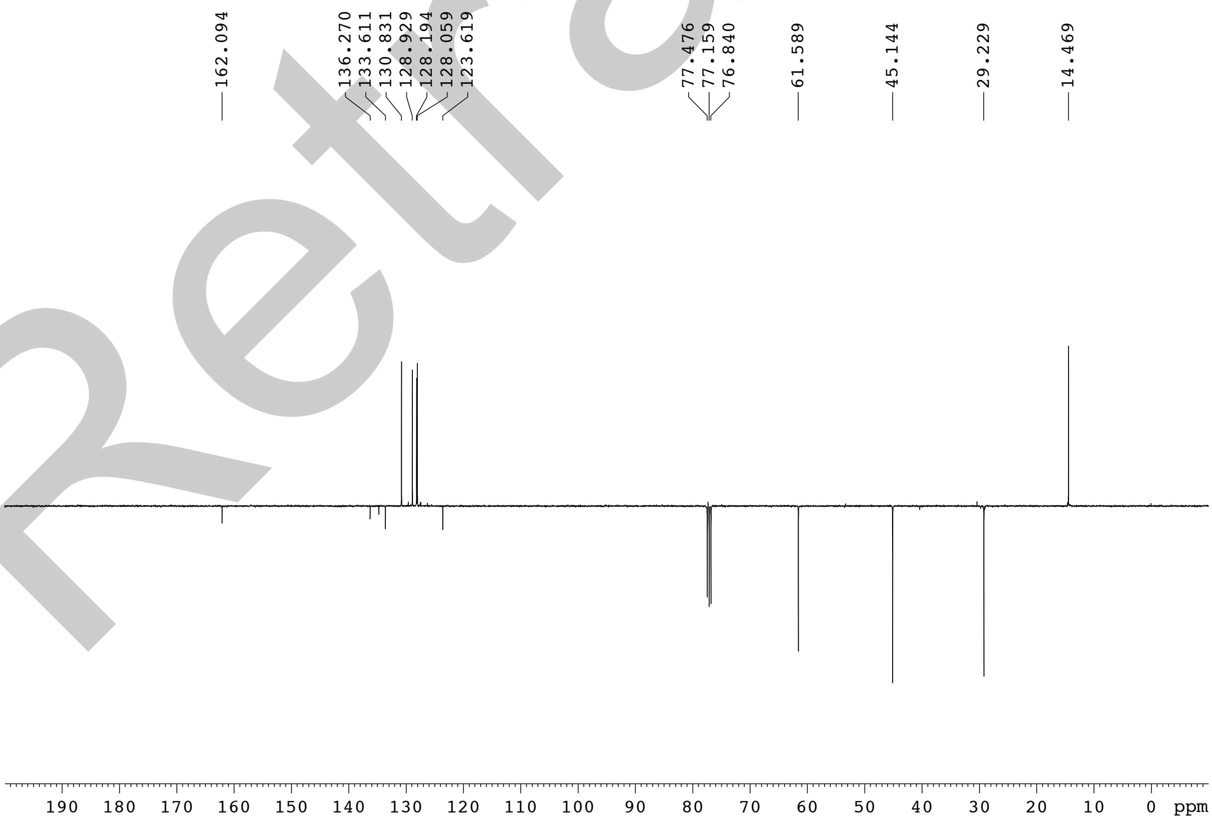


^{1}H NMR (400 MHz, $CDCl_3$)

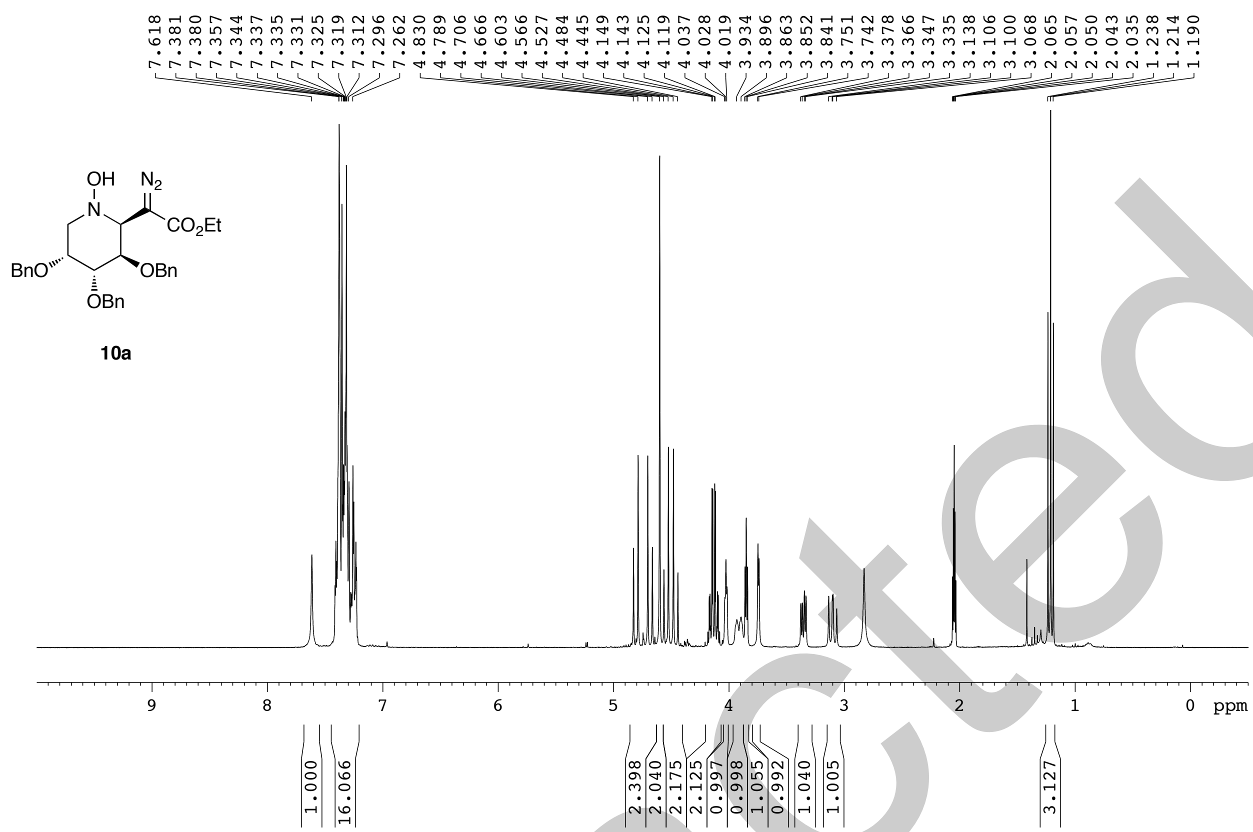


S-9'

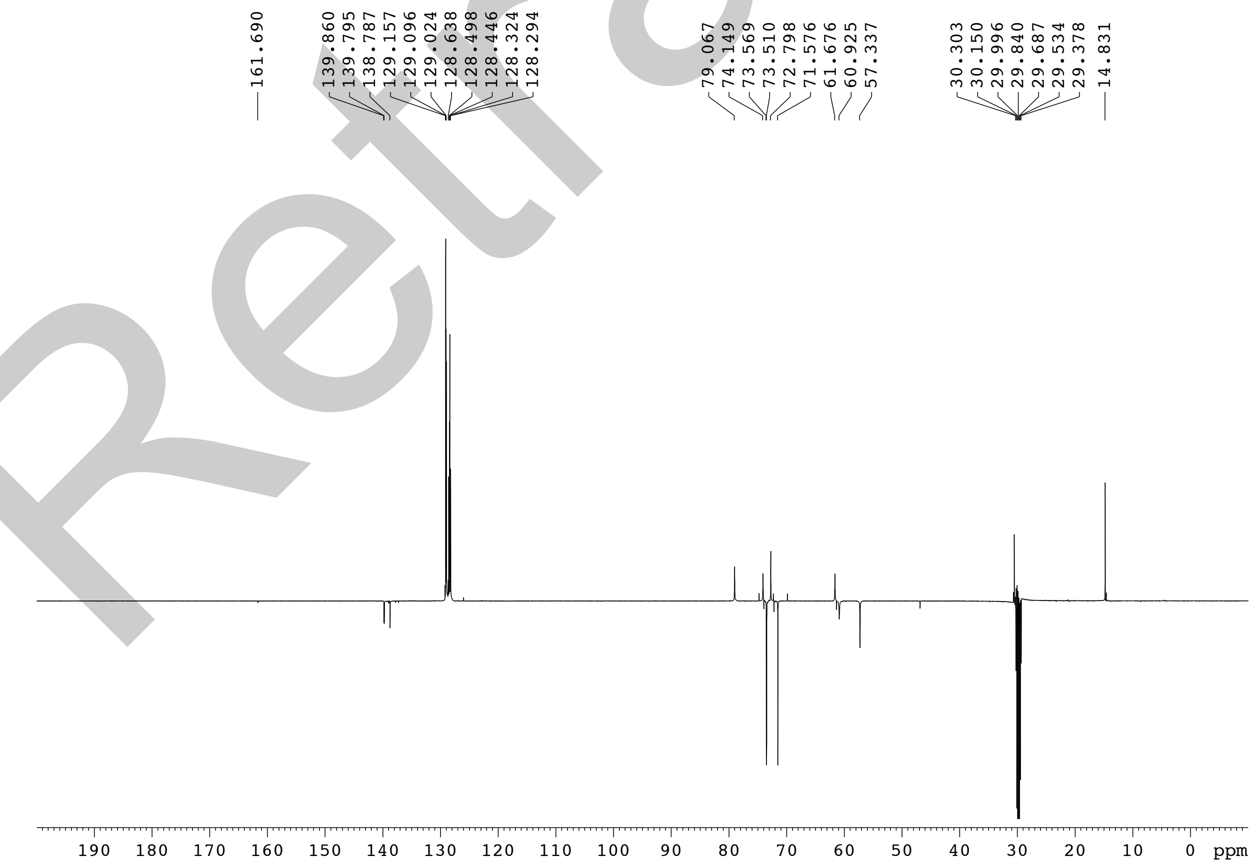
^{13}C NMR (100 MHz, $CDCl_3$)



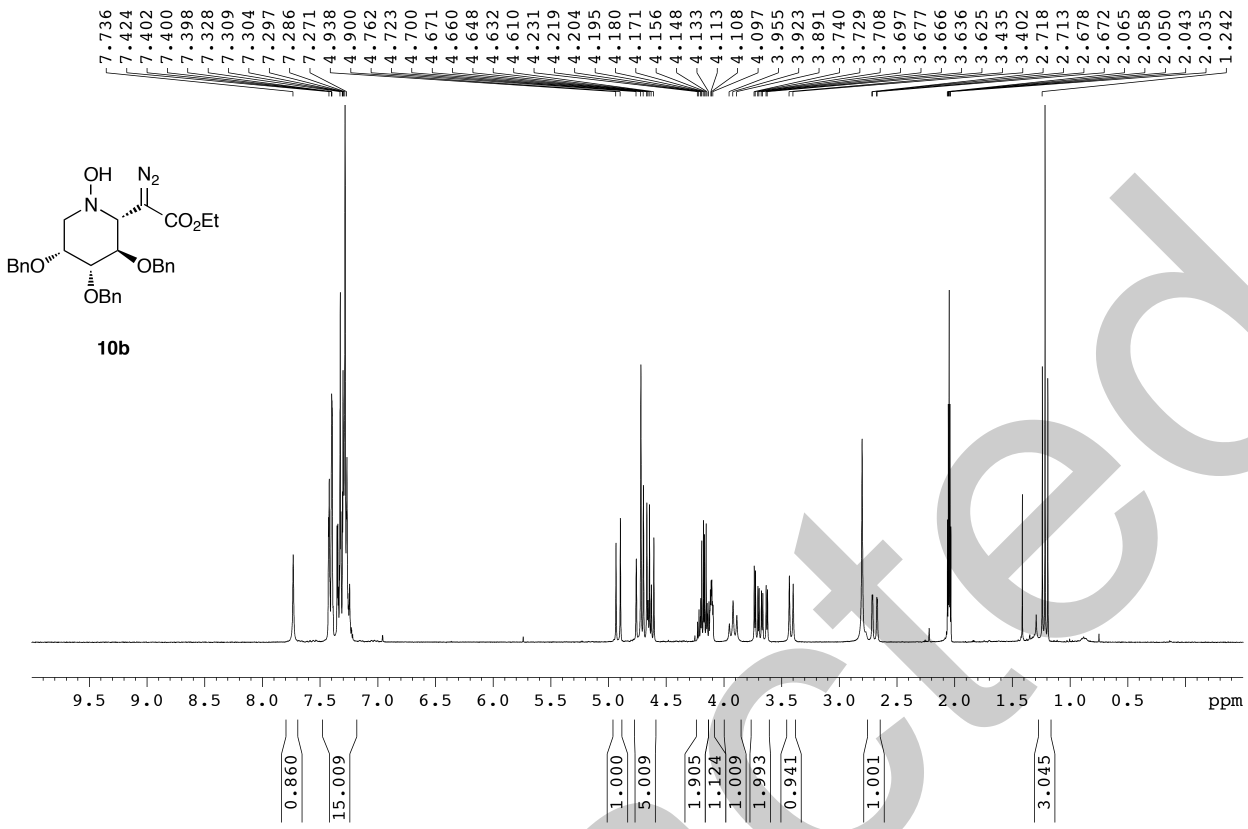
[1]H NMR (300 MHz, Acetone-d_6)



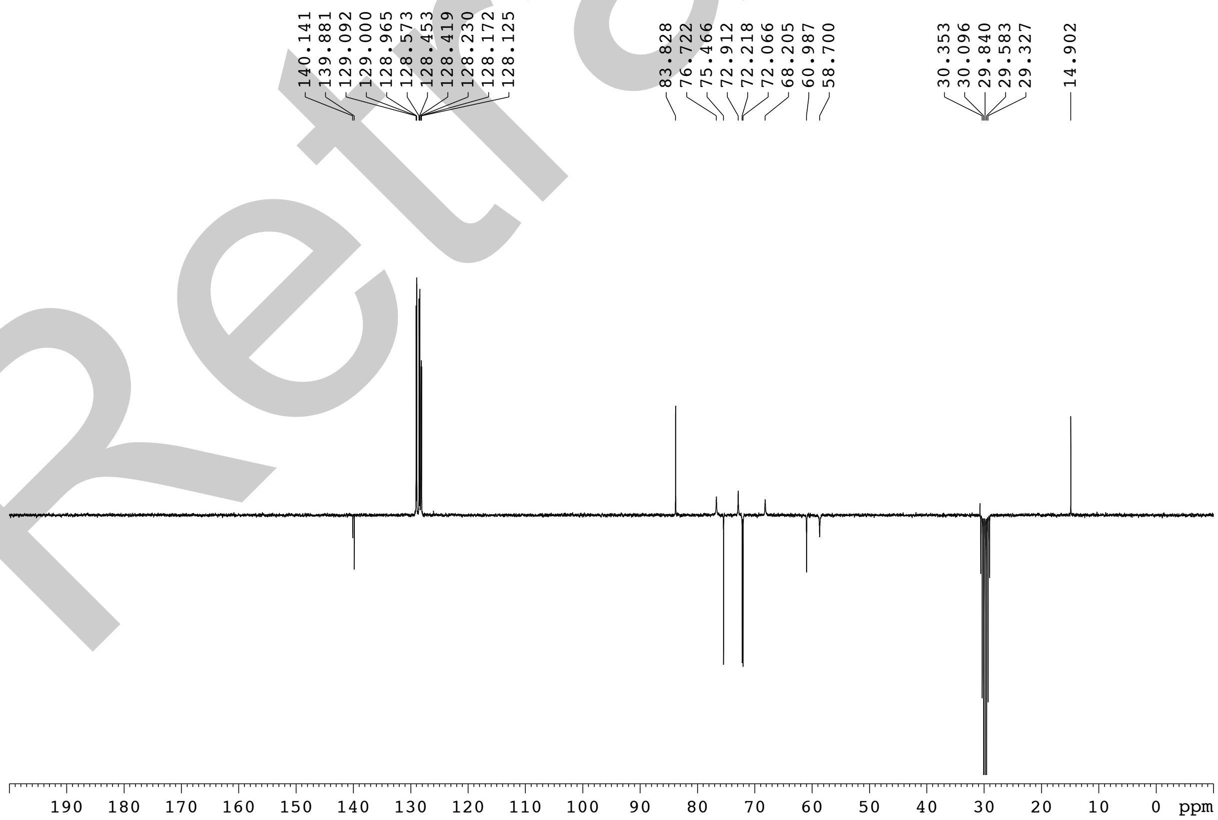
[13]C NMR (125 MHz, Acetone-d_6)



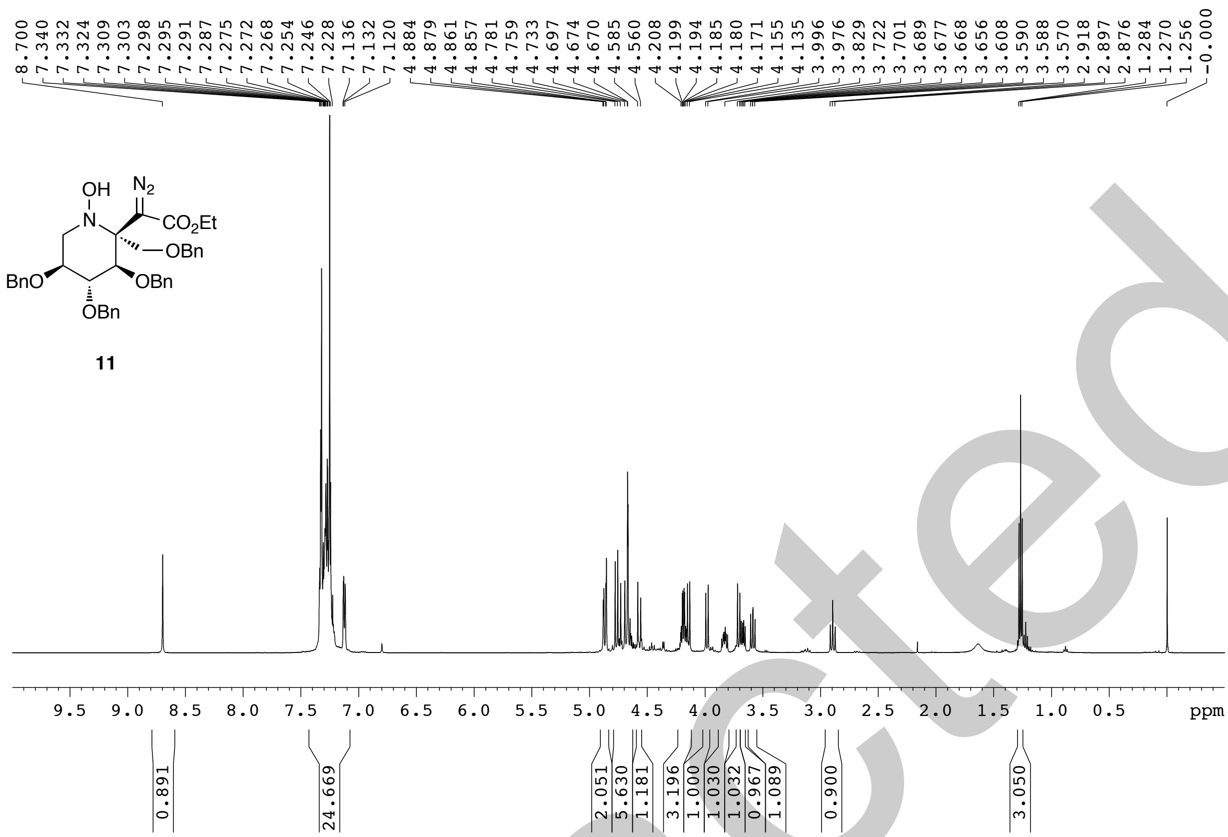
[1]H NMR (300 MHz, Acetone-d_6)



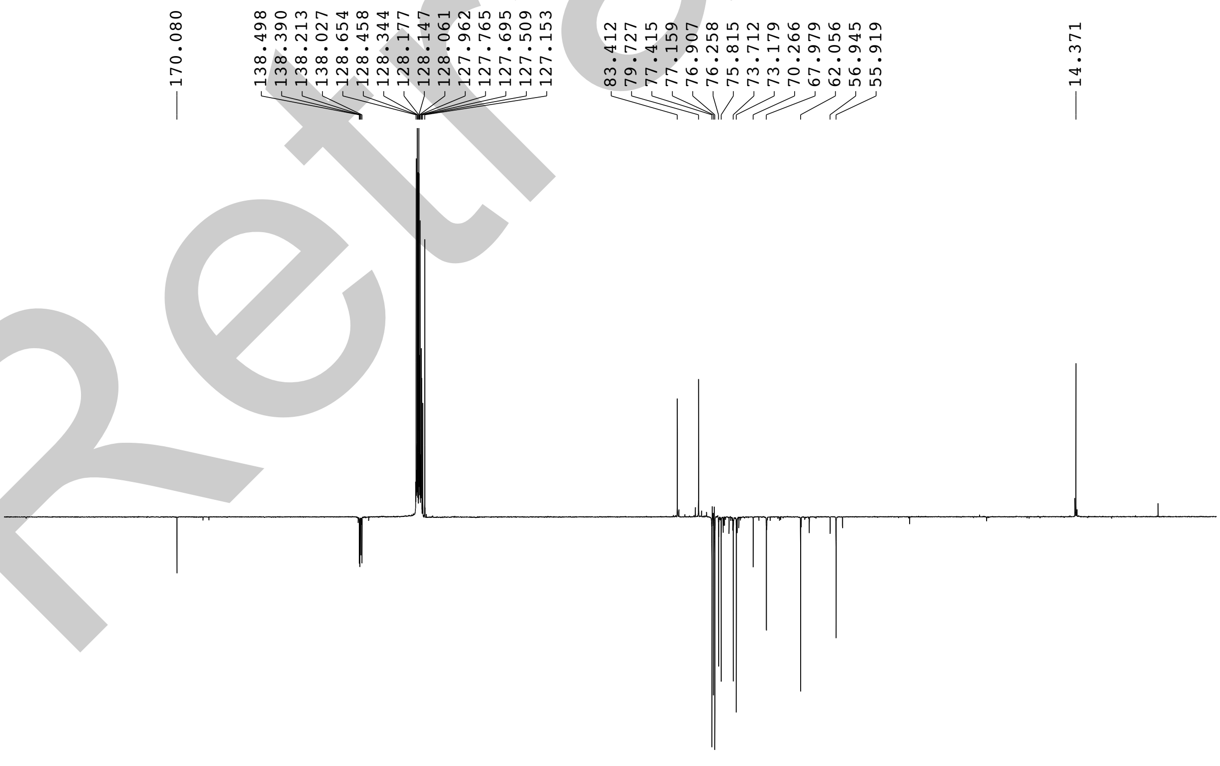
[13]C NMR (75 MHz, Acetone-d_6)



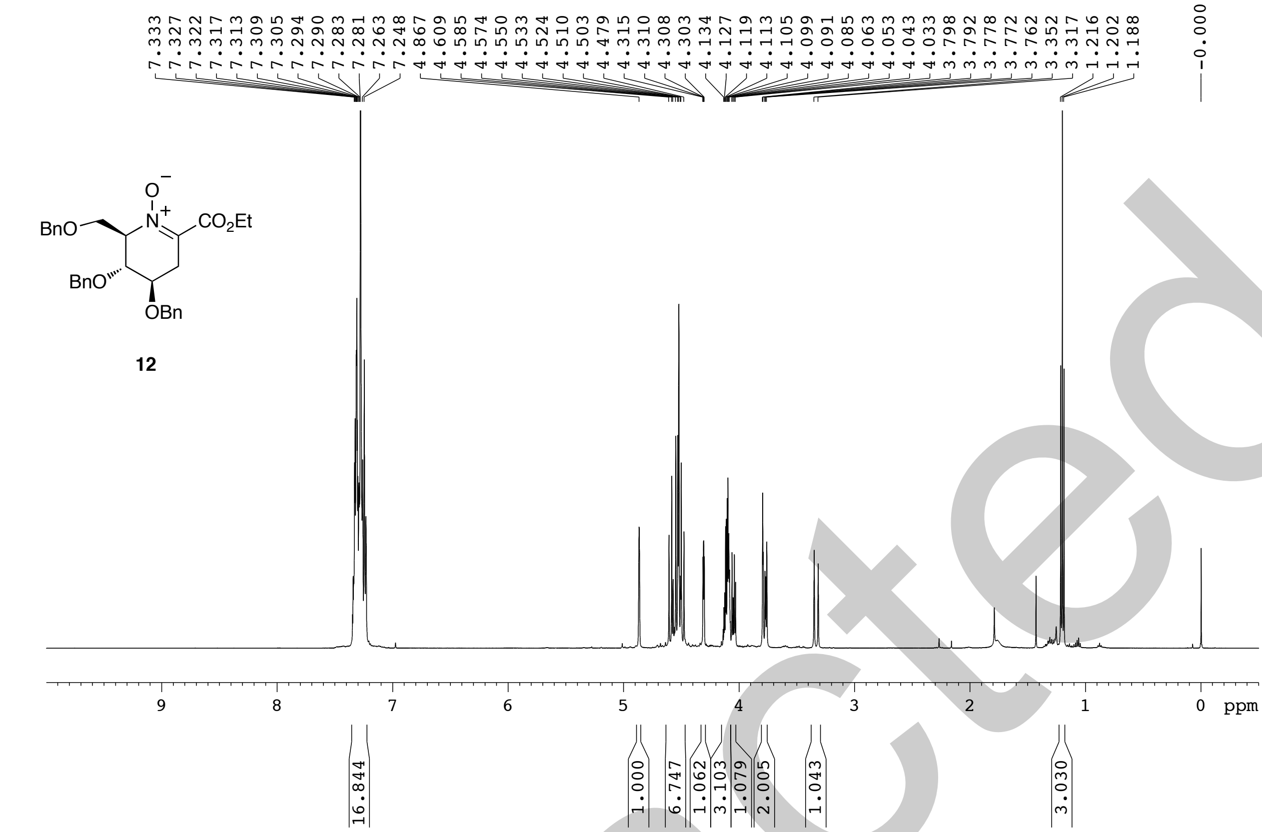
^{1}H NMR (500 MHz, $CDCl_3$)



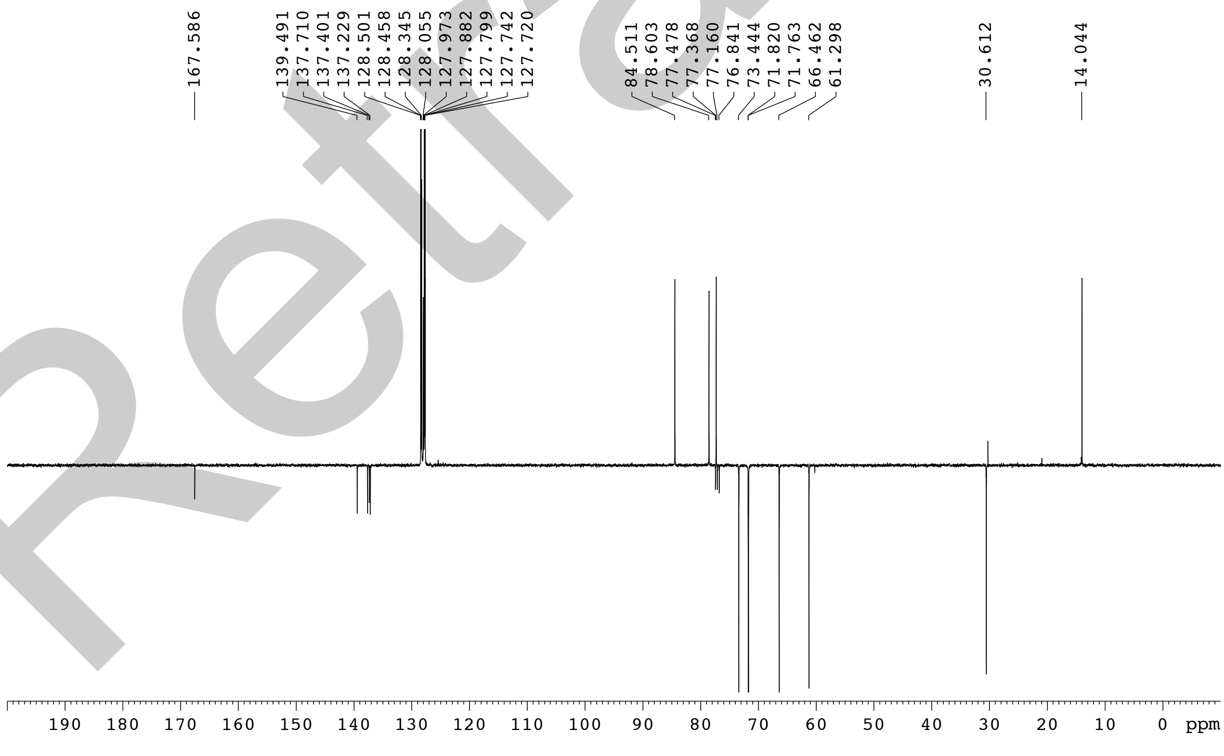
^{13}C NMR (125 MHz, $CDCl_3$)



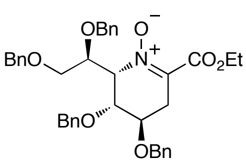
^{1}H NMR (500 MHz, $CDCl_3$)



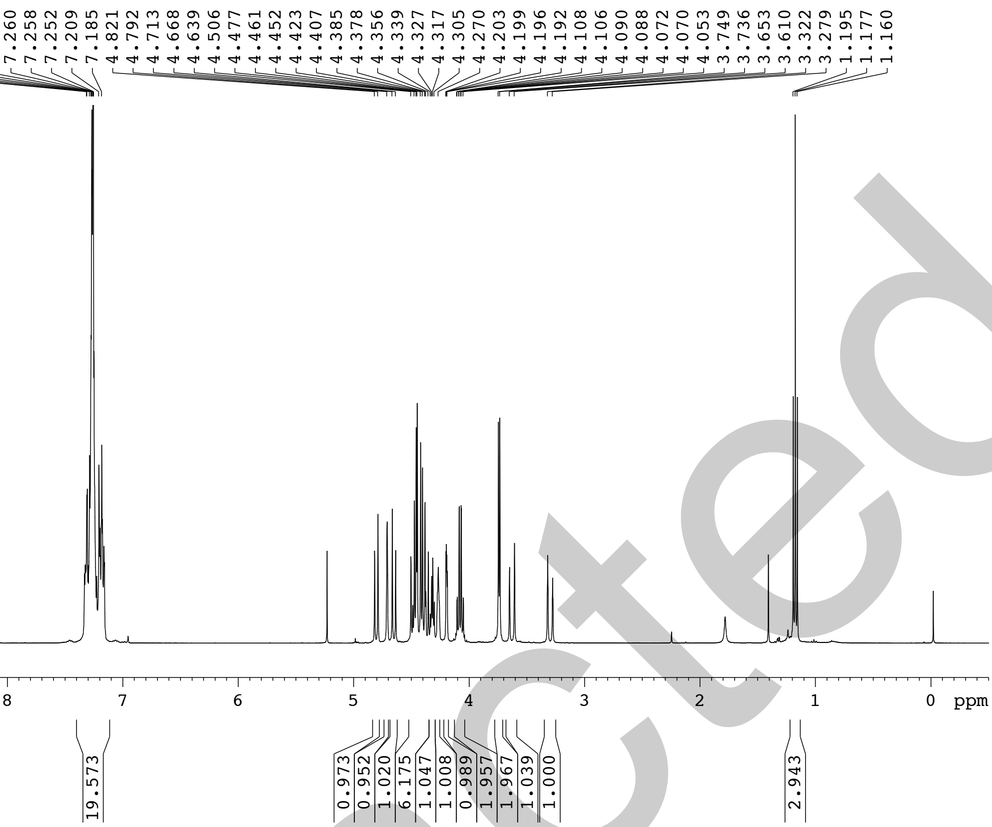
^{13}C NMR (100 MHz, $CDCl_3$)



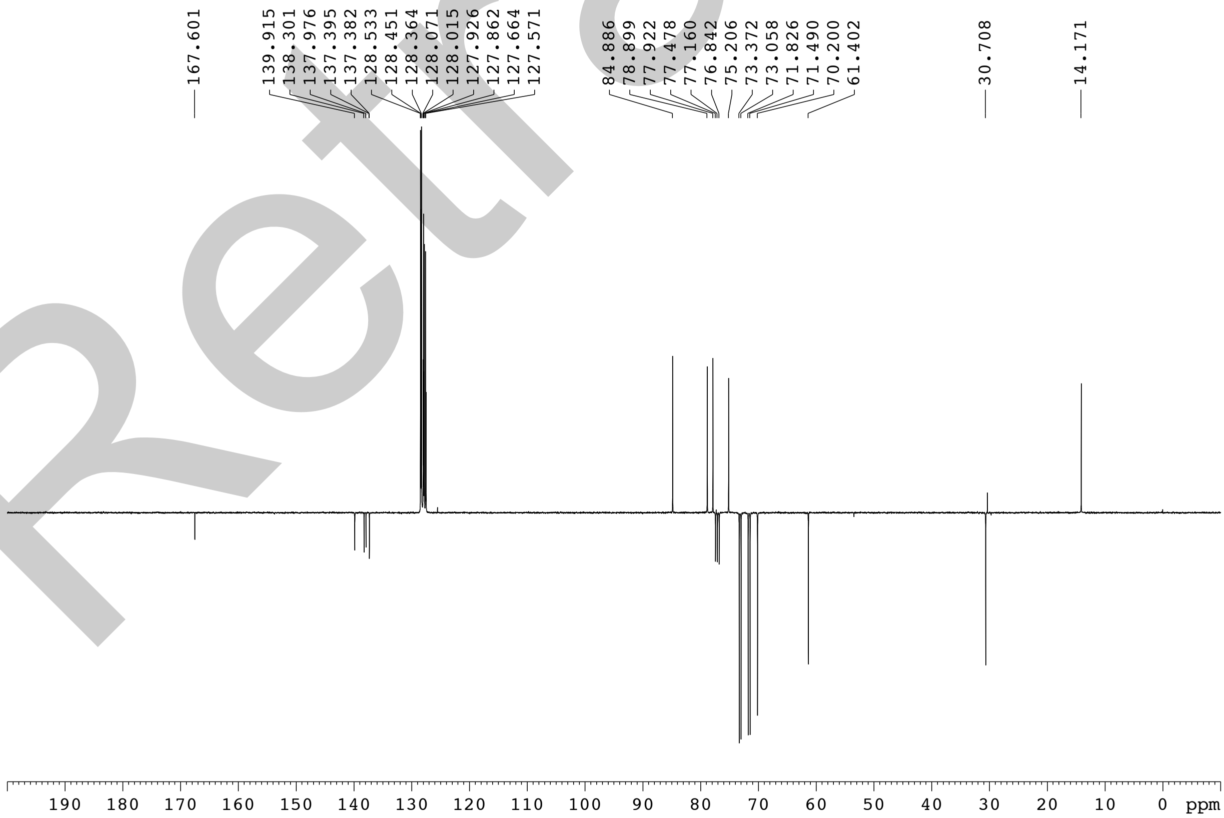
[1]H NMR (400 MHz, $CDCl_3$)



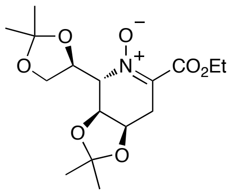
13



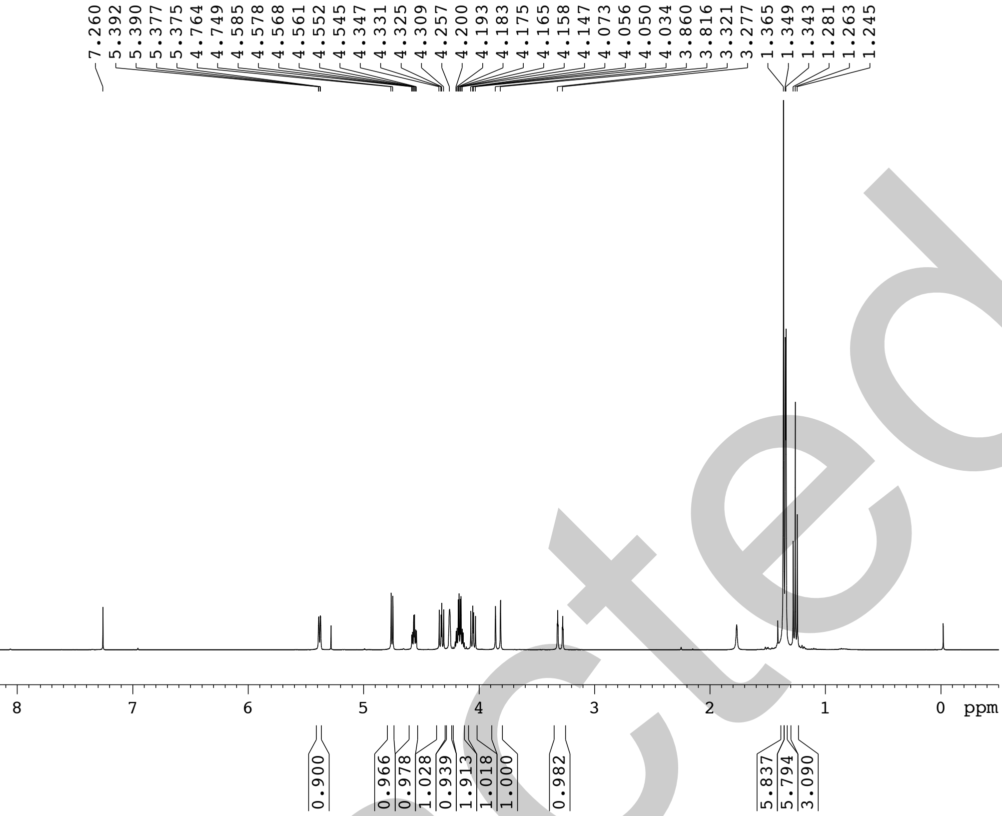
[13]C NMR (100 MHz, $CDCl_3$)



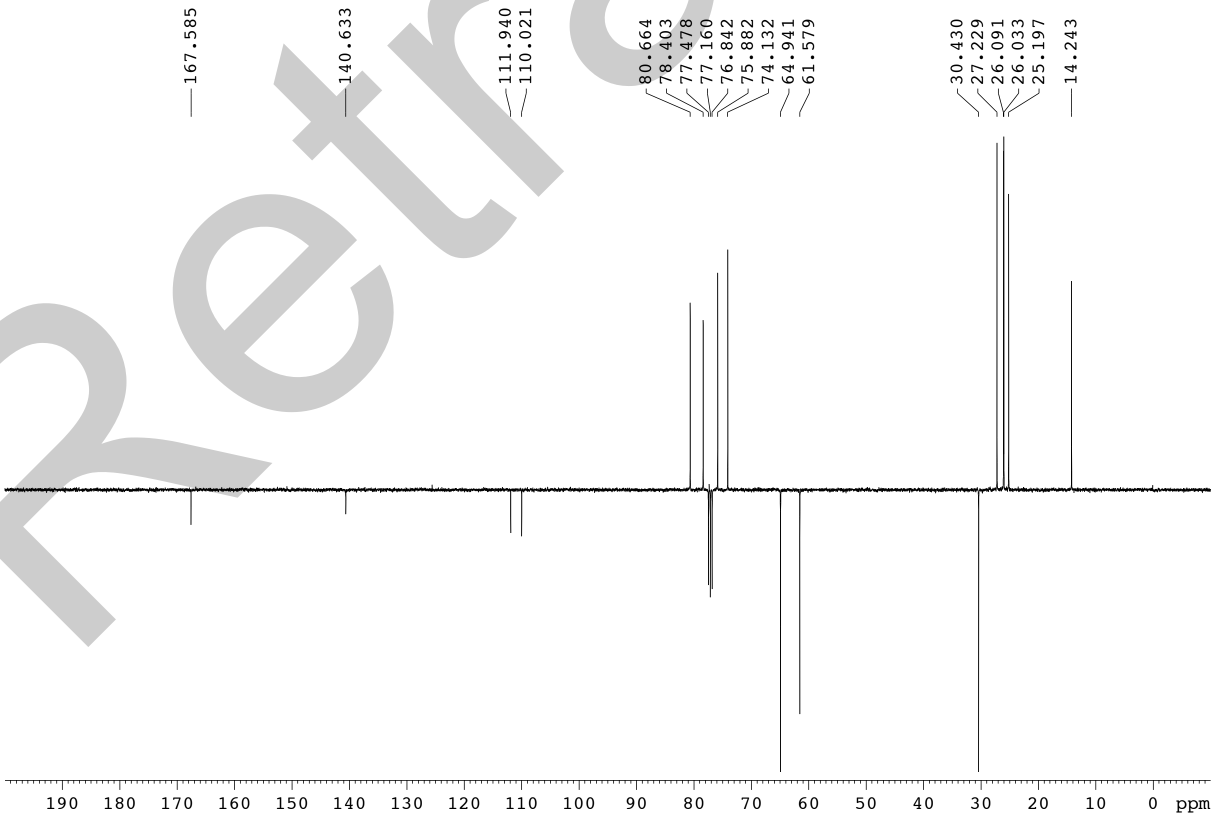
[1]H NMR (400 MHz, $CDCl_3$)



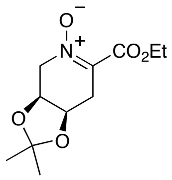
14



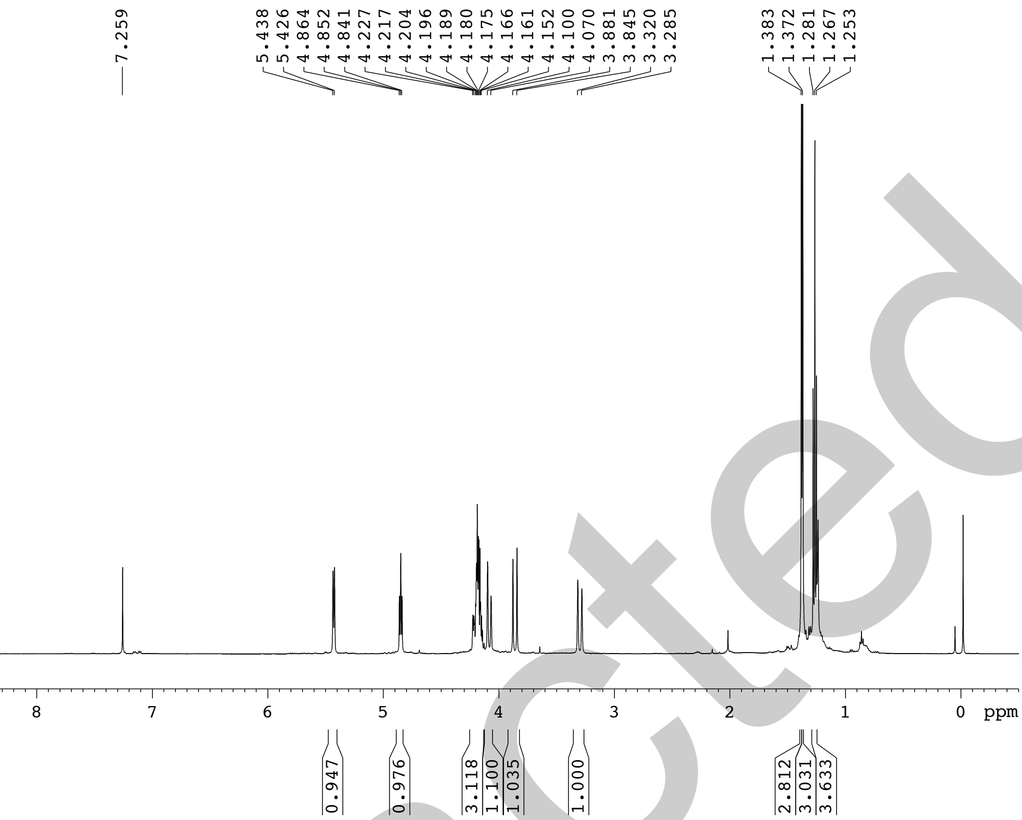
[13]C NMR (100 MHz, $CDCl_3$)



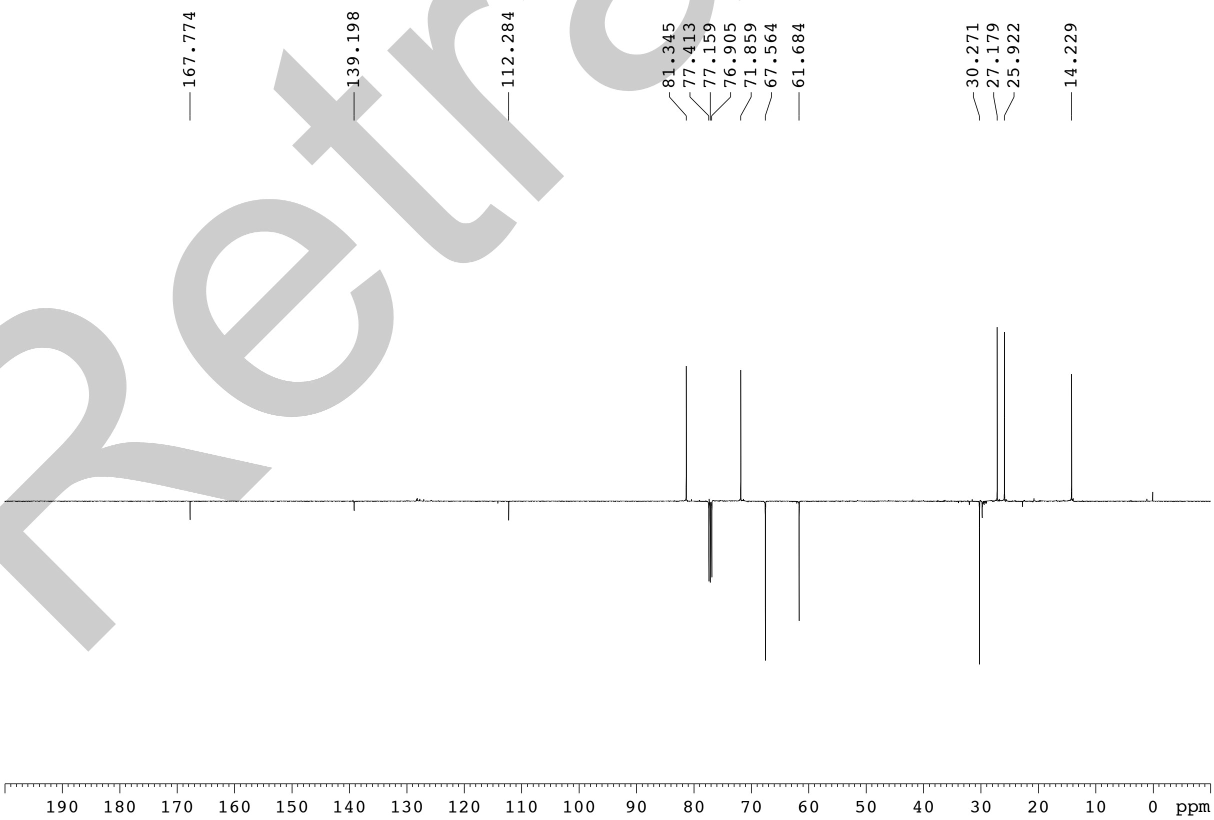
[1]H NMR (500 MHz, $CDCl_3$)



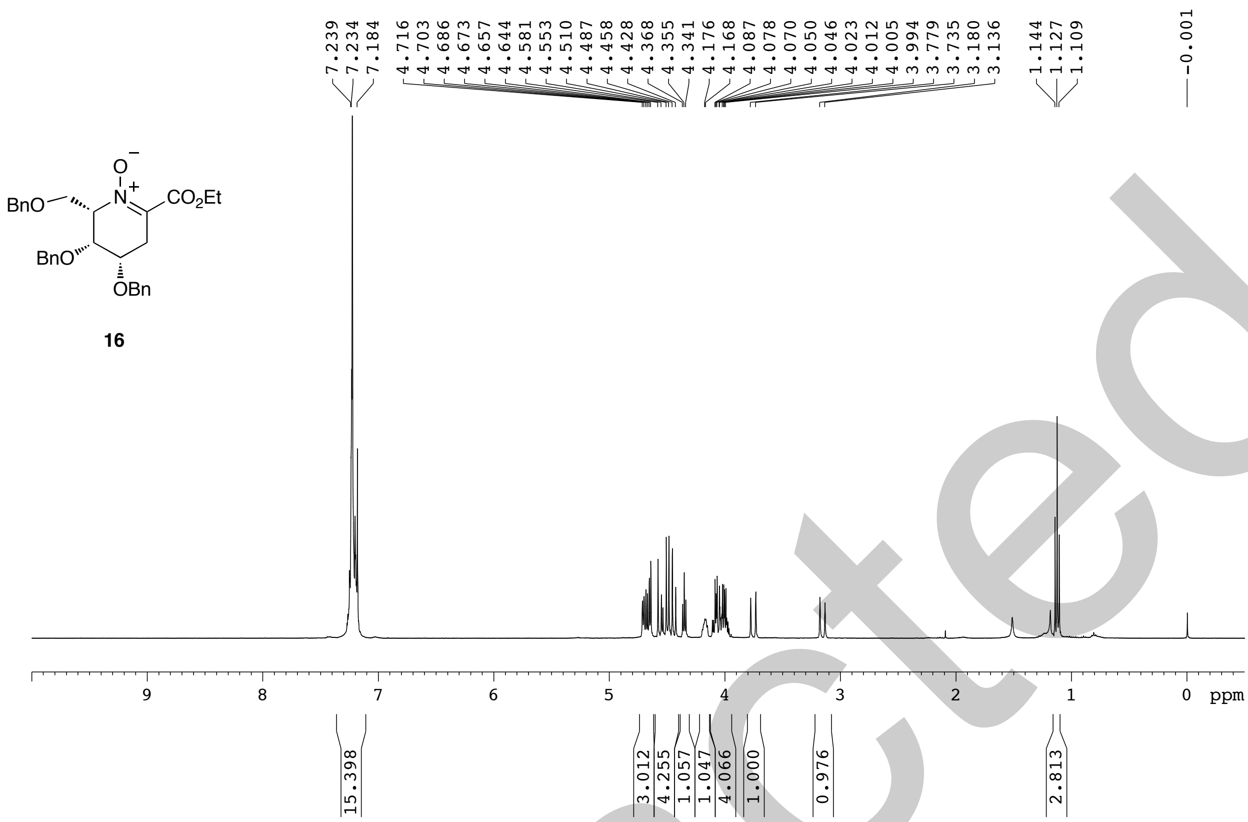
15



[13]C NMR (125 MHz, $CDCl_3$)

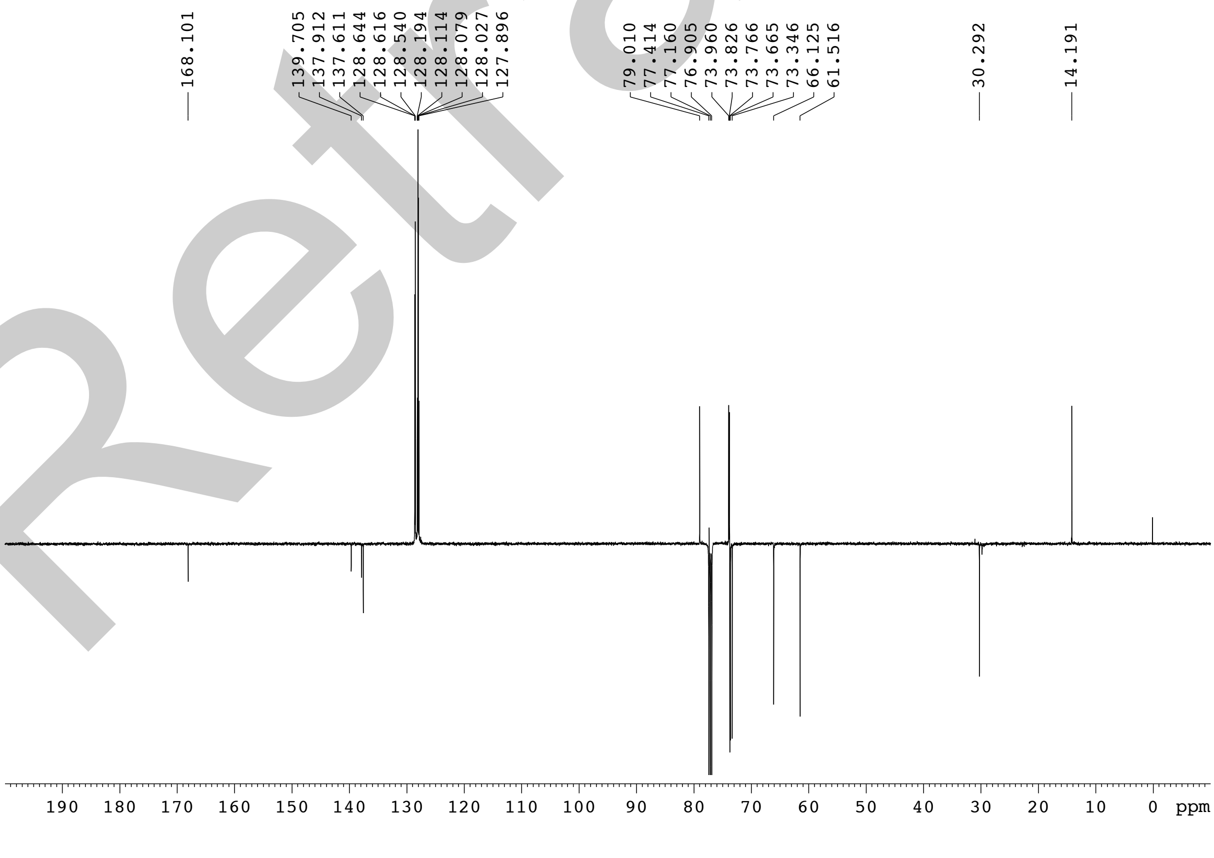


^{1}H NMR (400 MHz, $CDCl_3$)

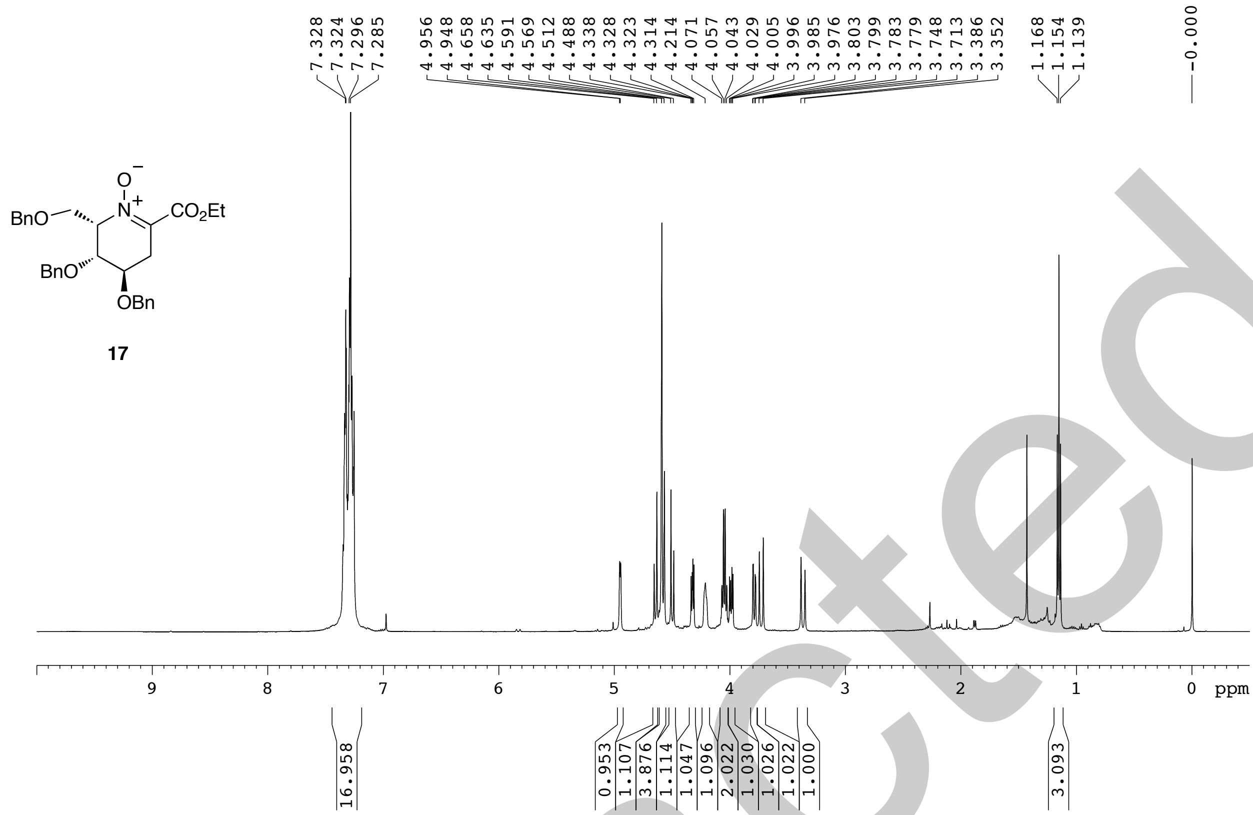


16

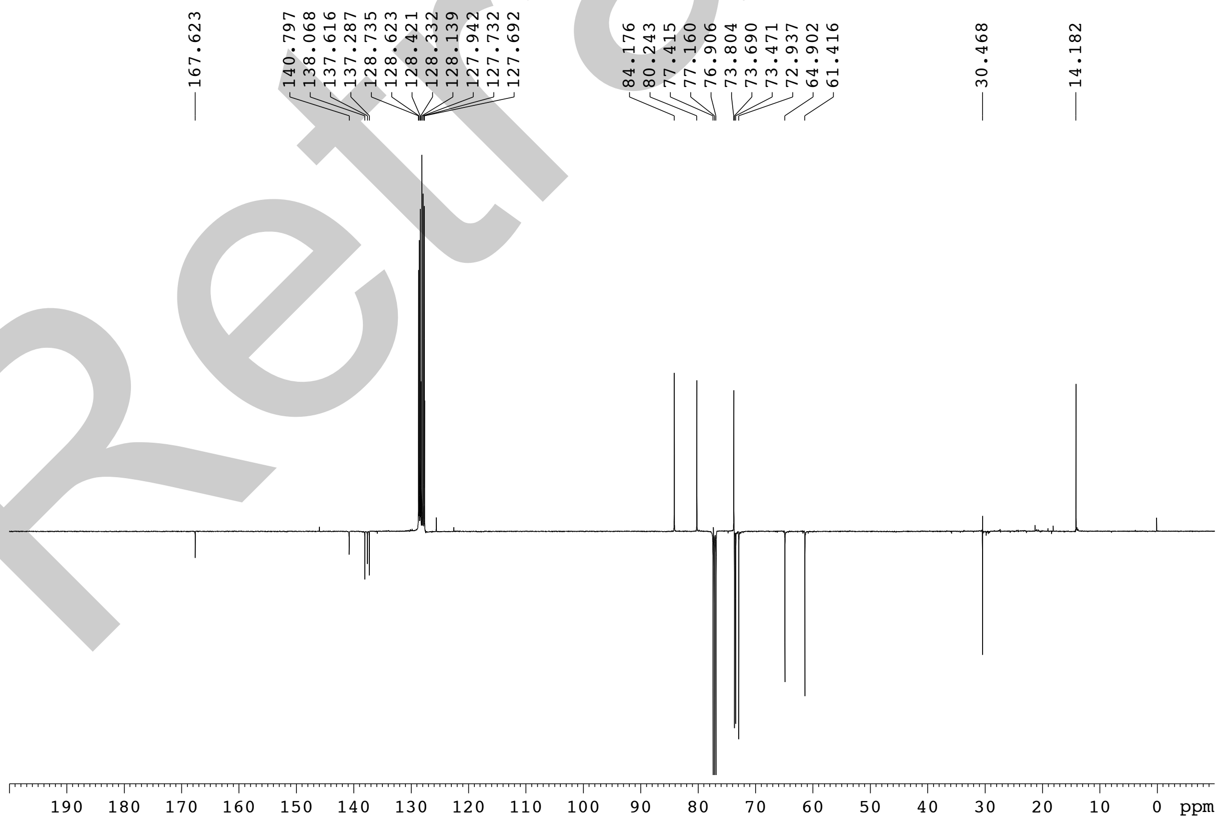
^{13}C NMR (125 MHz, $CDCl_3$)



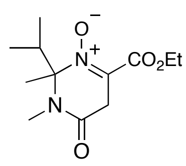
^{1}H NMR (500 MHz, $CDCl_3$)



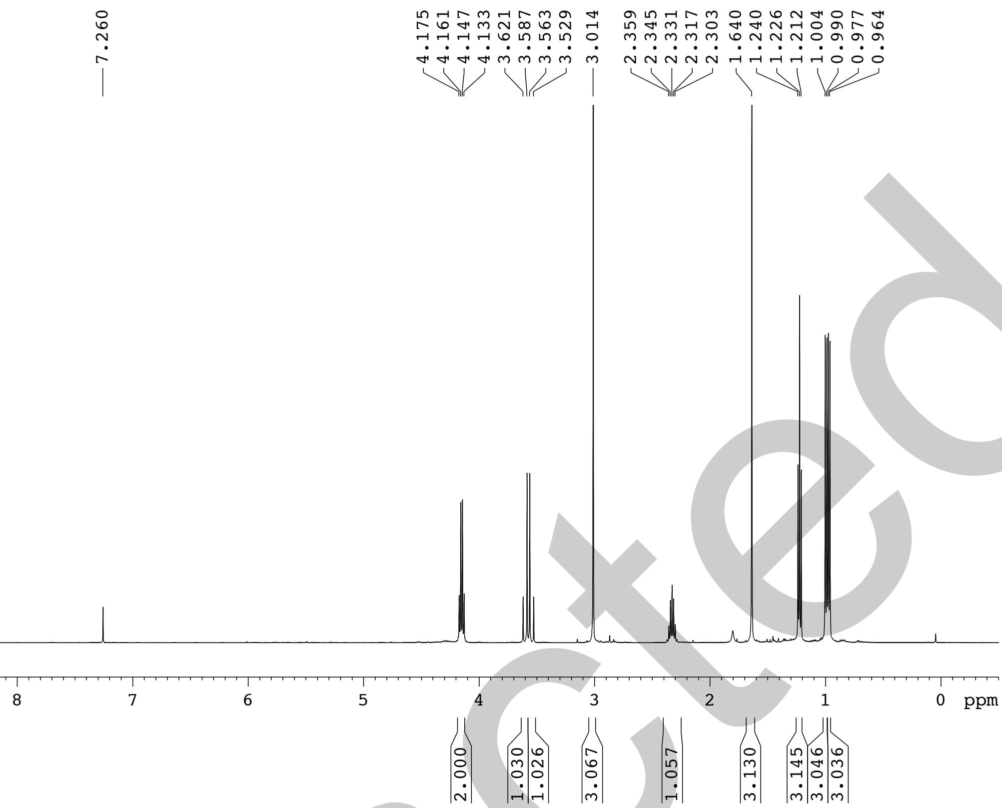
^{13}C NMR (125 MHz, $CDCl_3$)



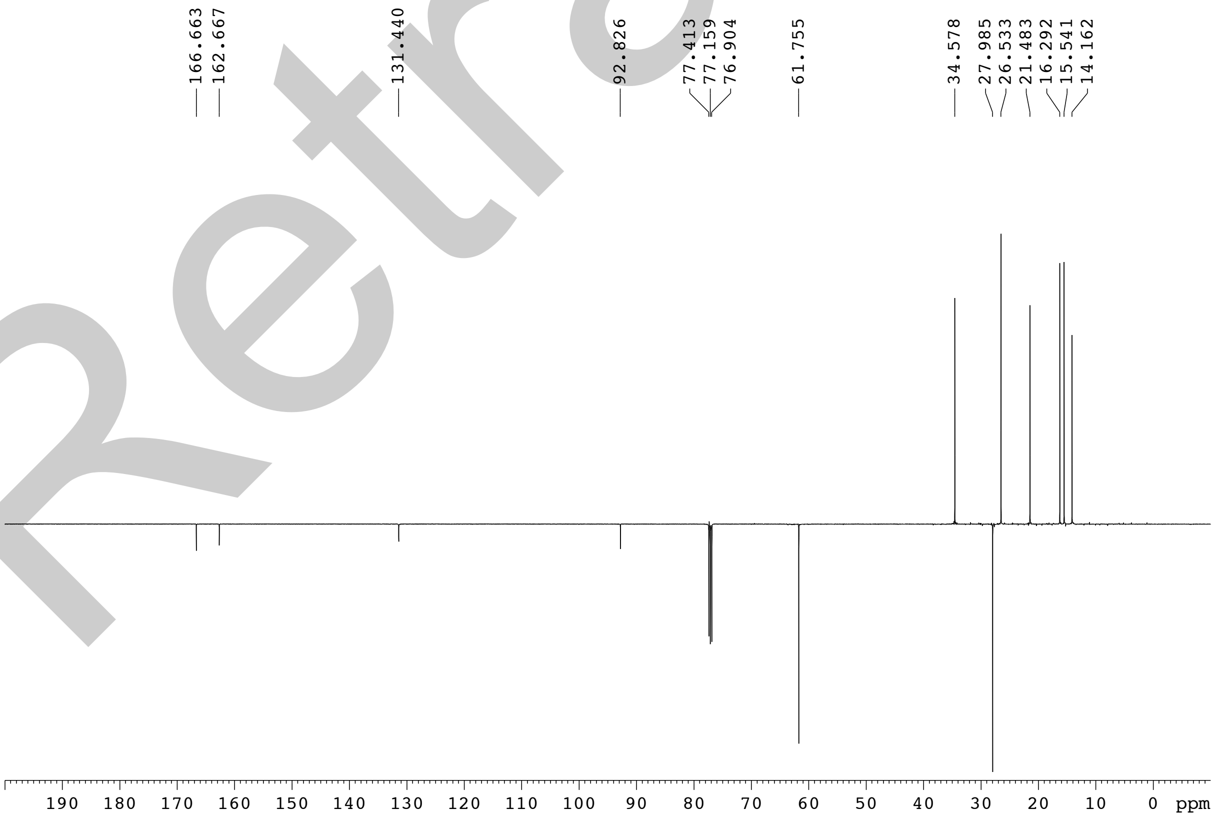
^{1}H NMR (500 MHz, $CDCl_3$)



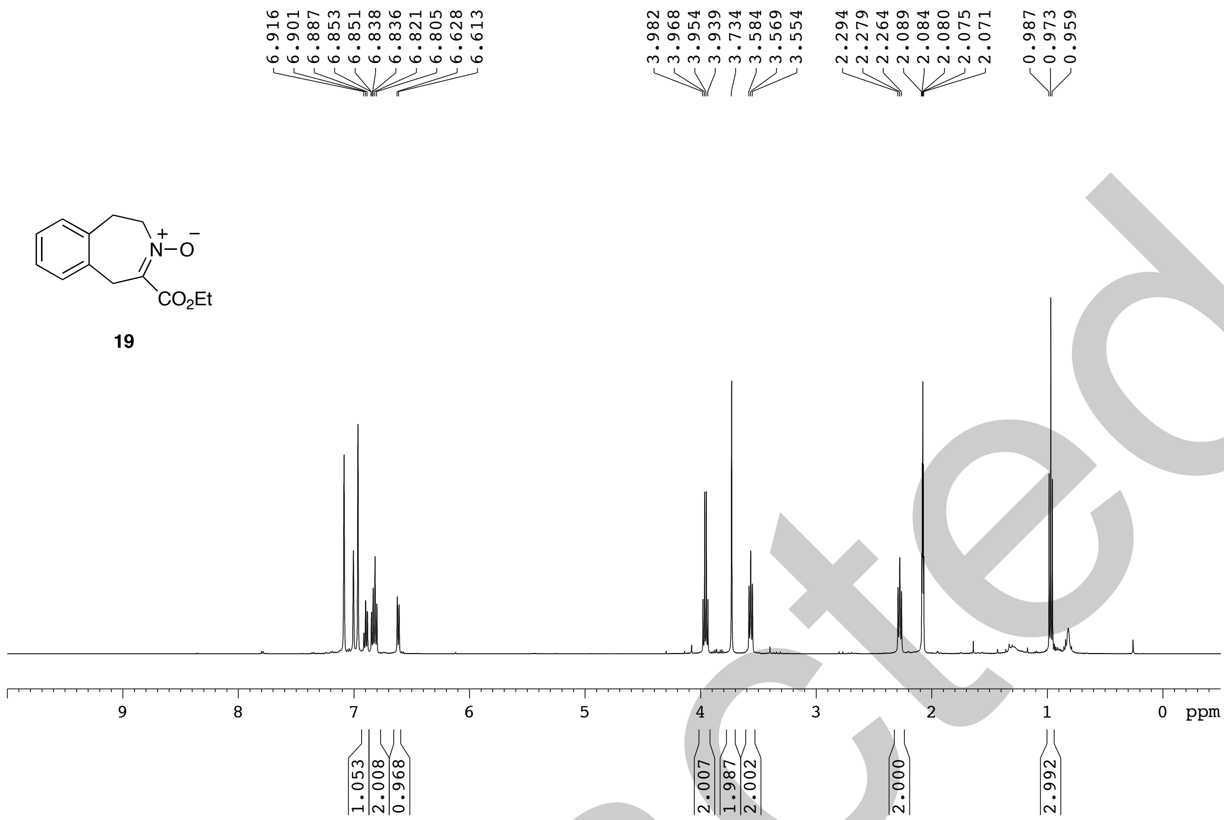
18



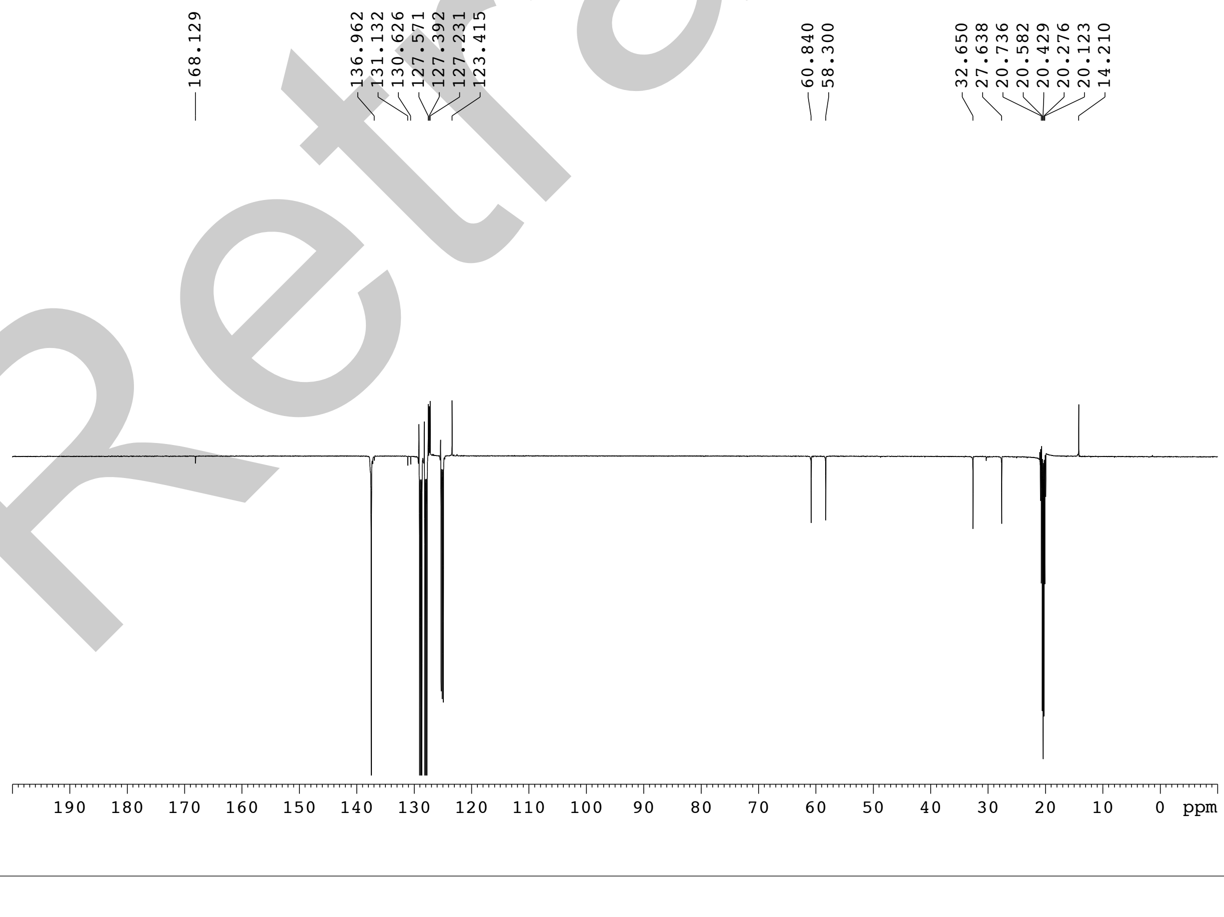
^{13}C NMR (125 MHz, $CDCl_3$)

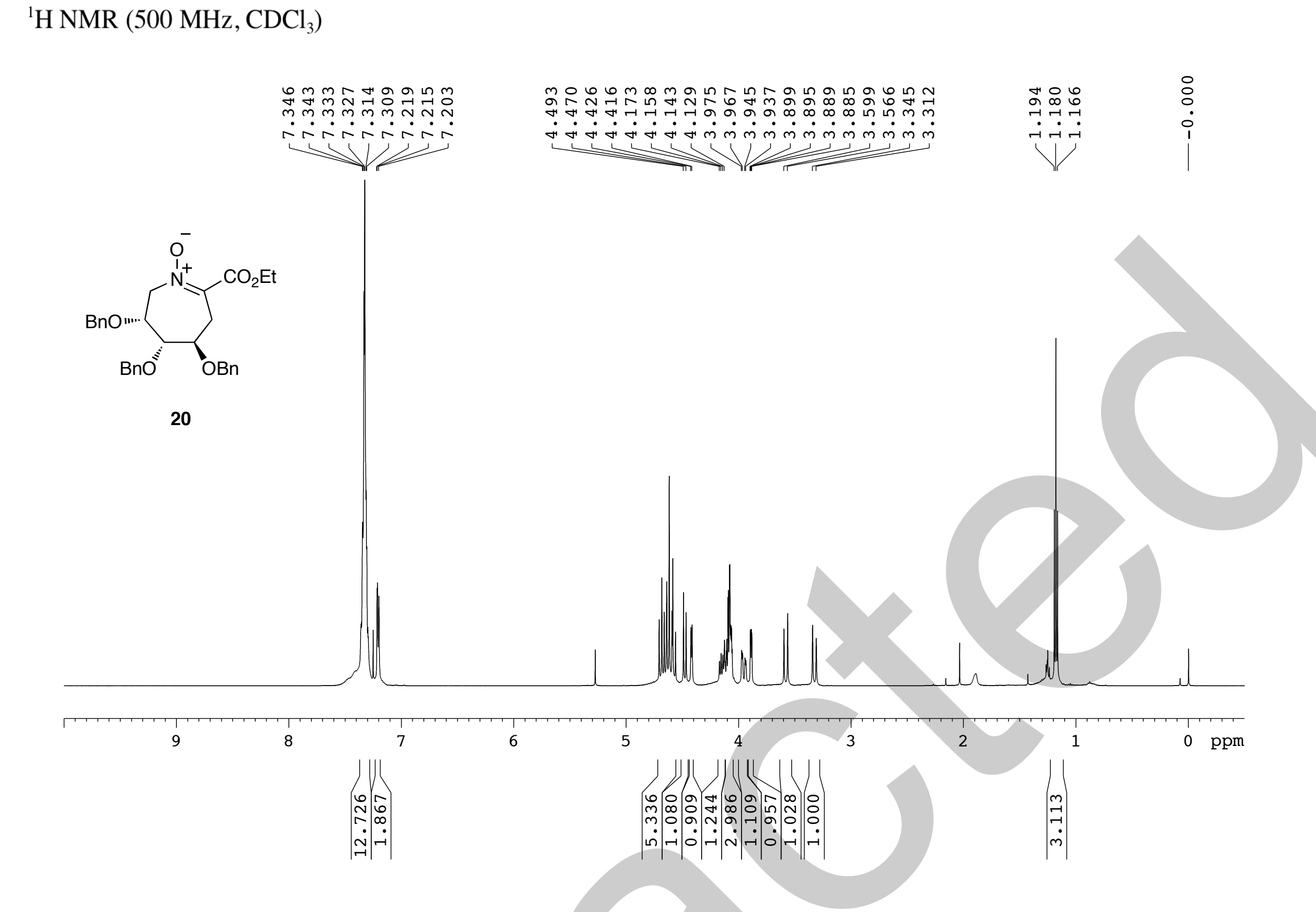


^{1}H NMR (500 MHz, Toluene-d_8)

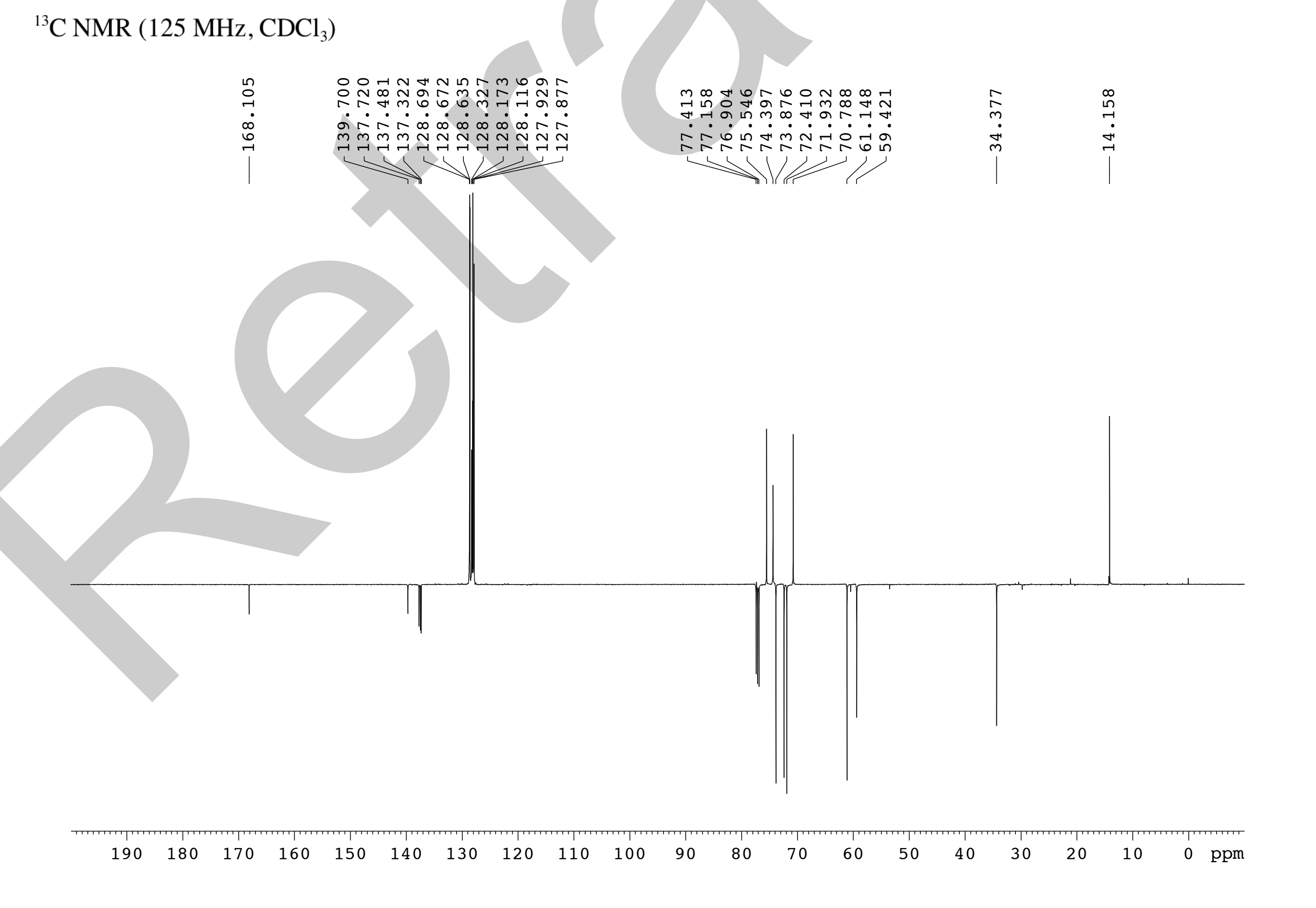


^{13}C NMR (125 MHz, Toluene-d_8)



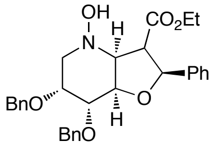


^{1}H NMR (500 MHz, CDCl$_3$)
7.346
7.343
7.333
7.327
7.314
7.309
7.219
7.215
7.203
4.493
4.470
4.426
4.416
4.173
4.158
4.143
4.129
3.975
3.967
3.945
3.937
3.899
3.895
3.889
3.885
3.599
3.566
3.345
3.312
1.194
1.180
1.166
-0.000
CO2Et
BnO
BnO
OBn
20
9
8
7
6
5
4
3
2
1
0 ppm
12.726
1.867
5.336
1.080
0.909
1.244
2.986
1.109
0.957
1.028
1.000
3.113

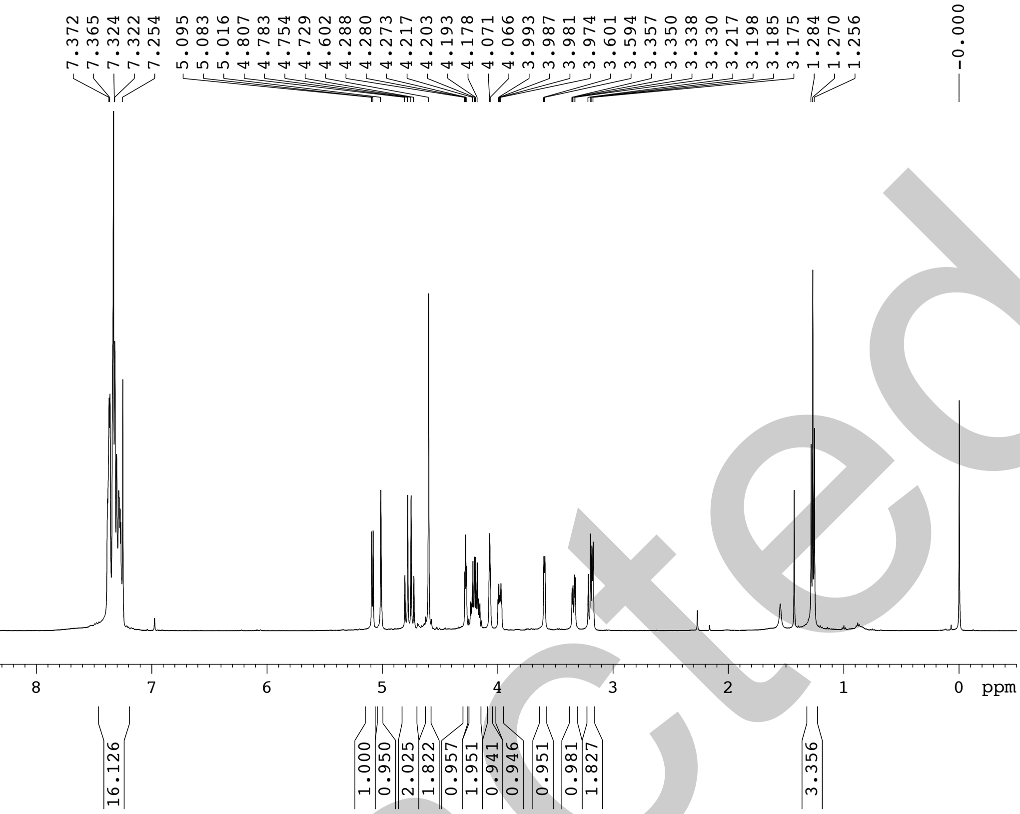


^{13}C NMR (125 MHz, CDCl$_3$)
168.105
139.700
137.720
137.481
137.322
128.694
128.672
128.635
128.327
128.173
128.116
127.929
127.877
77.413
77.158
76.904
75.546
74.397
73.876
72.410
71.932
70.788
61.148
59.421
34.377
14.158
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

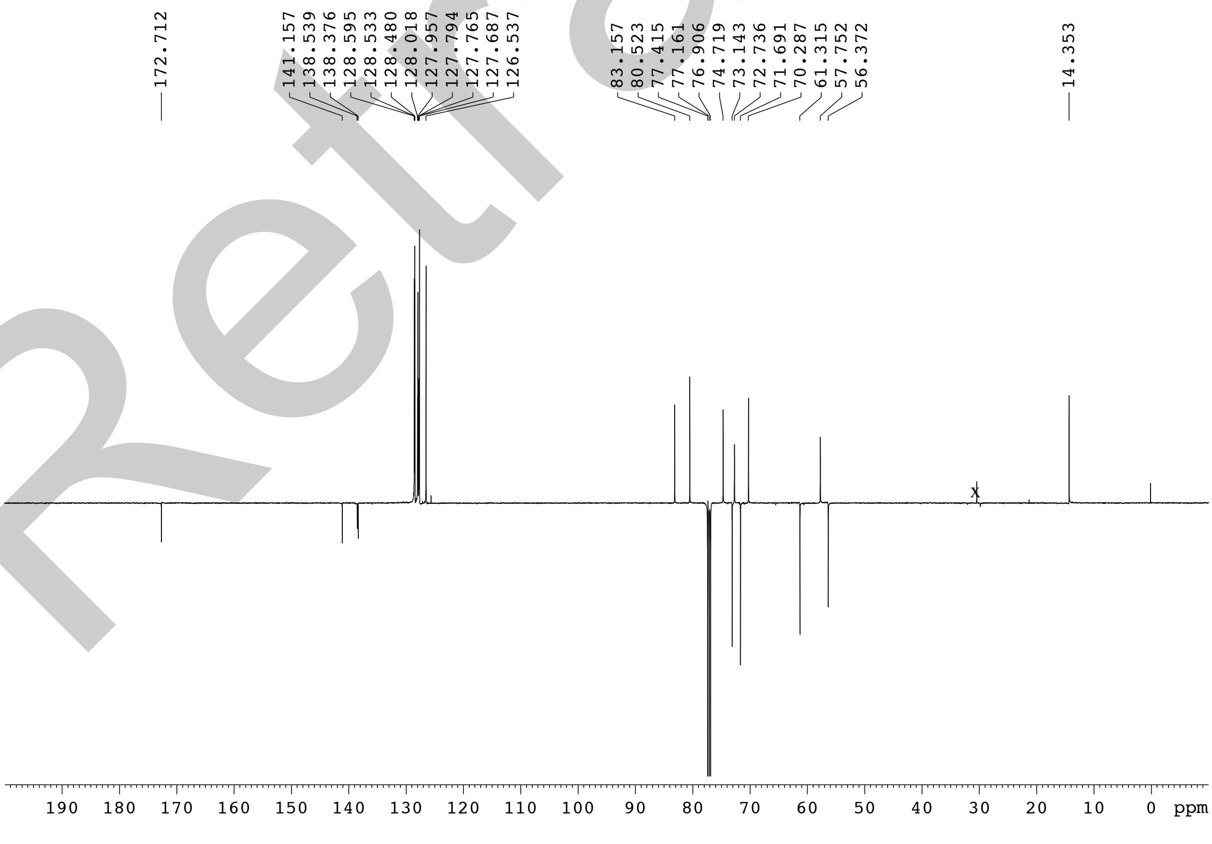
^{1}H NMR (500 MHz, $CDCl_3$)



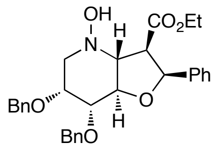
S-20'a



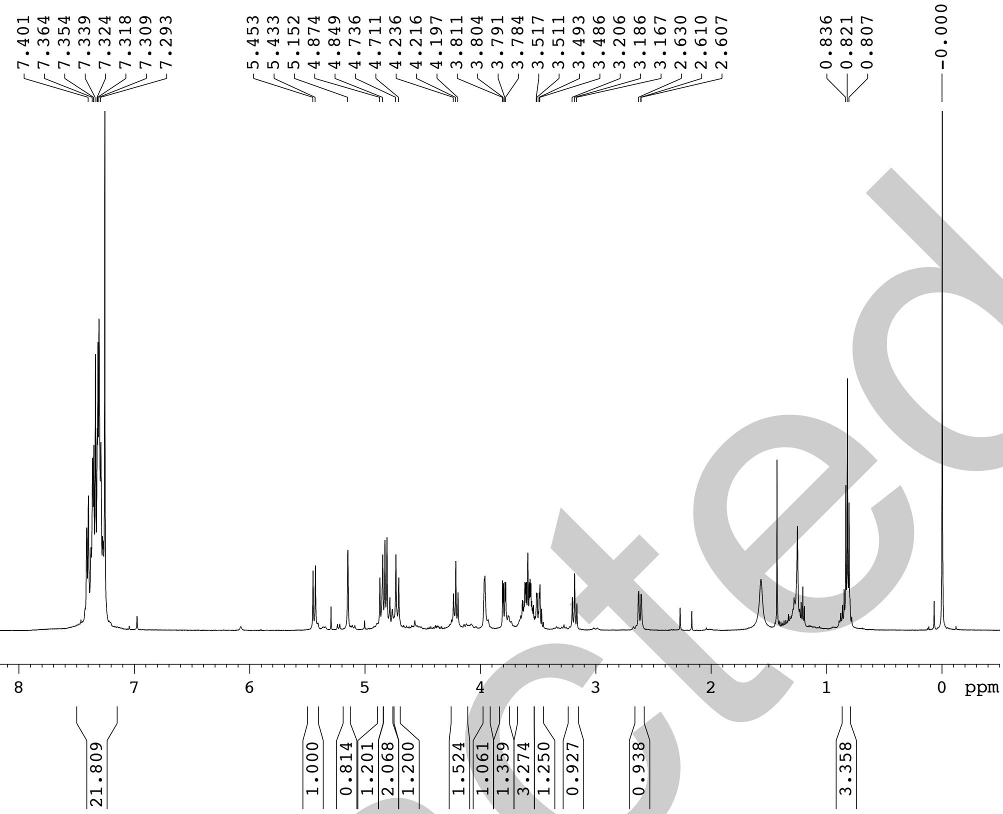
^{13}C NMR (125 MHz, $CDCl_3$)



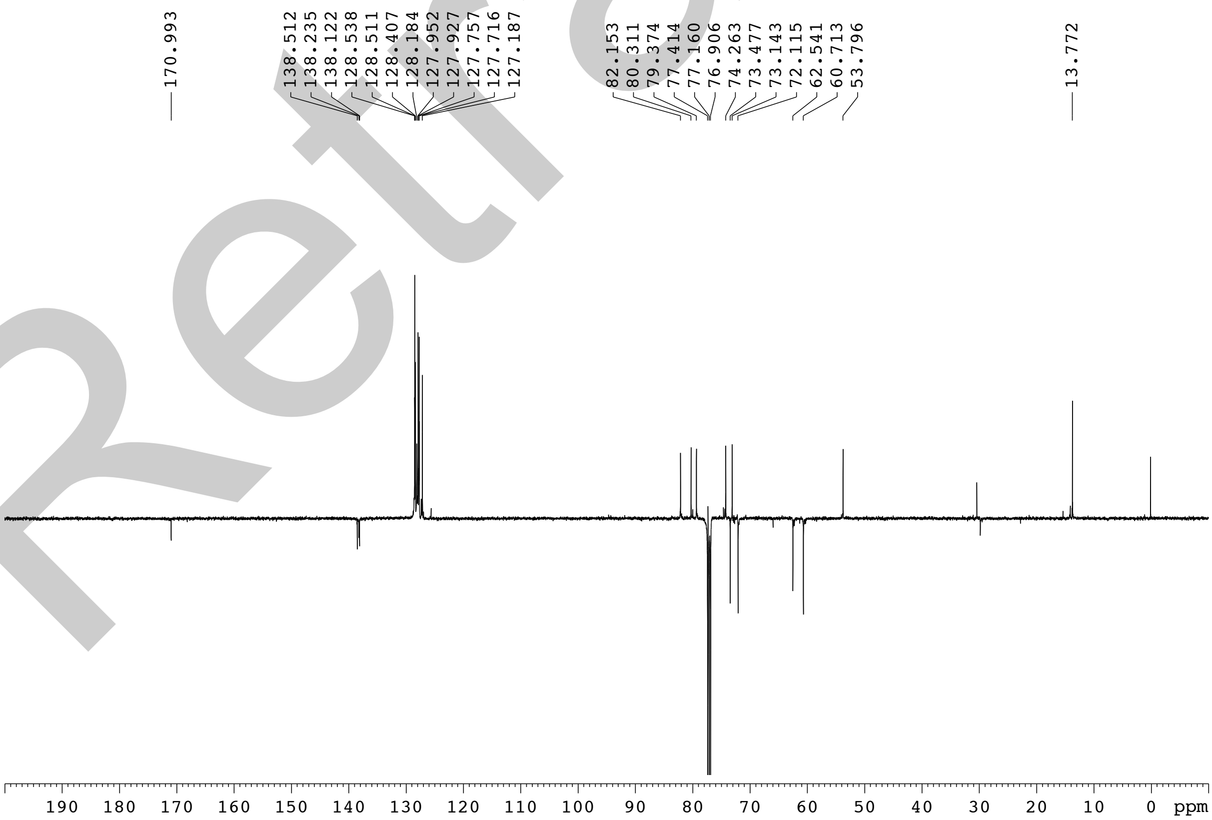
^1H NMR (500 MHz, $CDCl_3$)



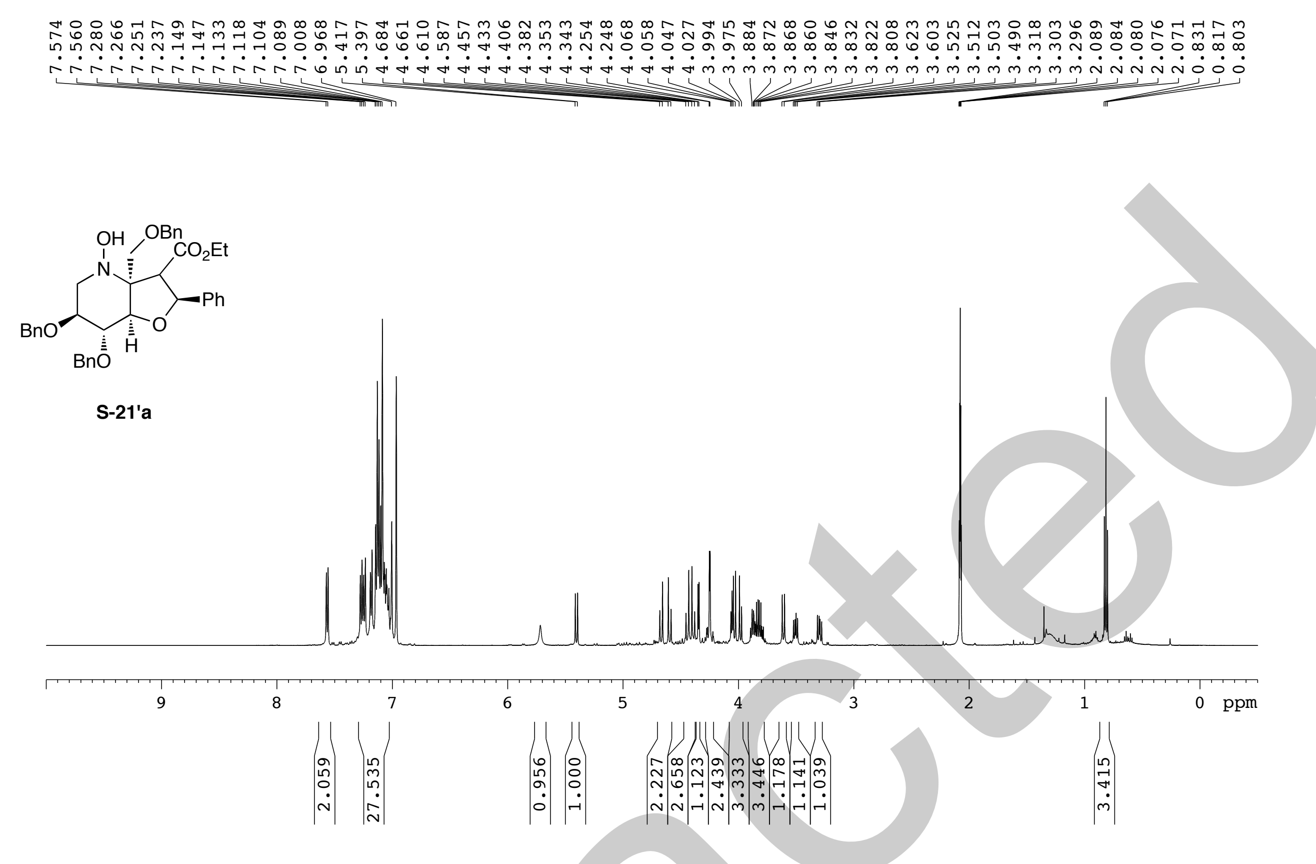
S-20'b



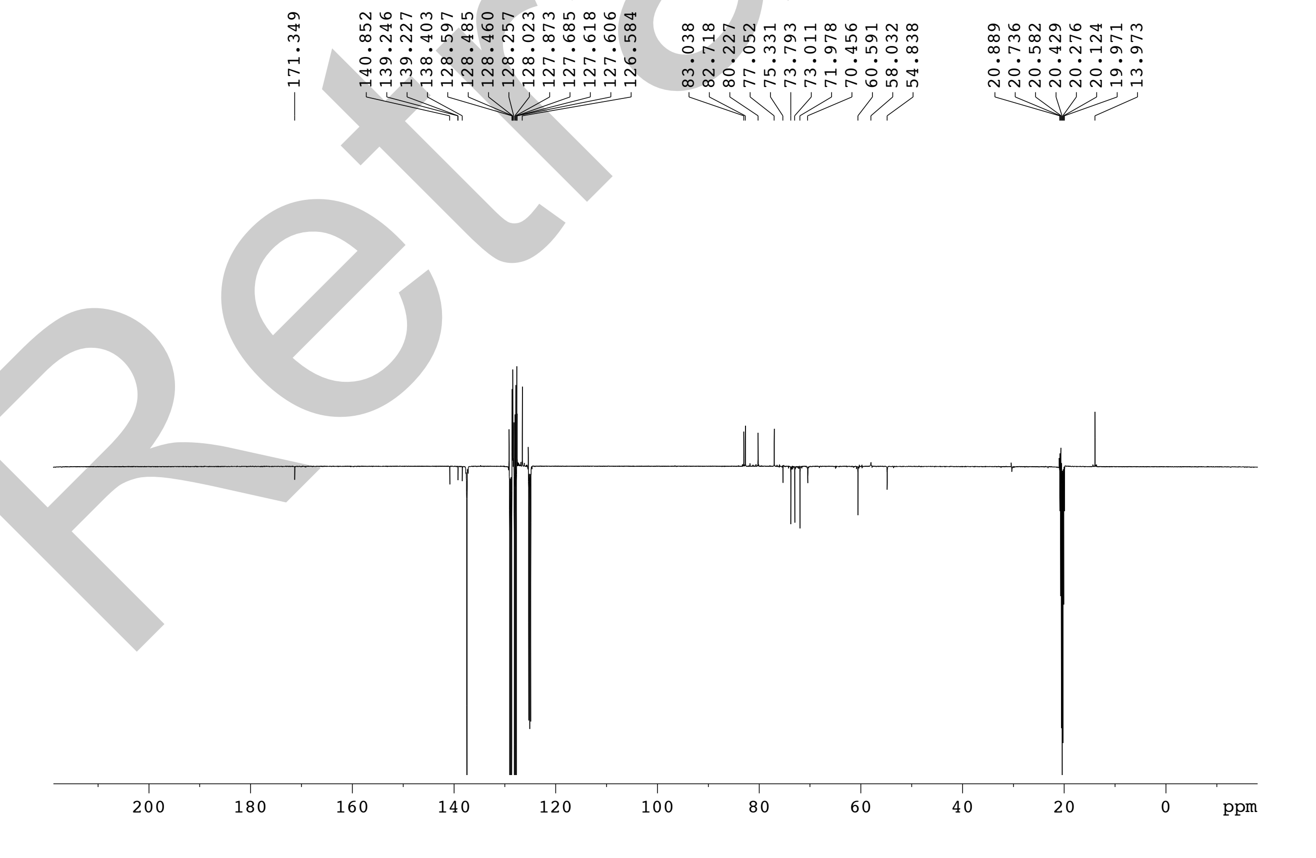
^{13}C NMR (125 MHz, $CDCl_3$)



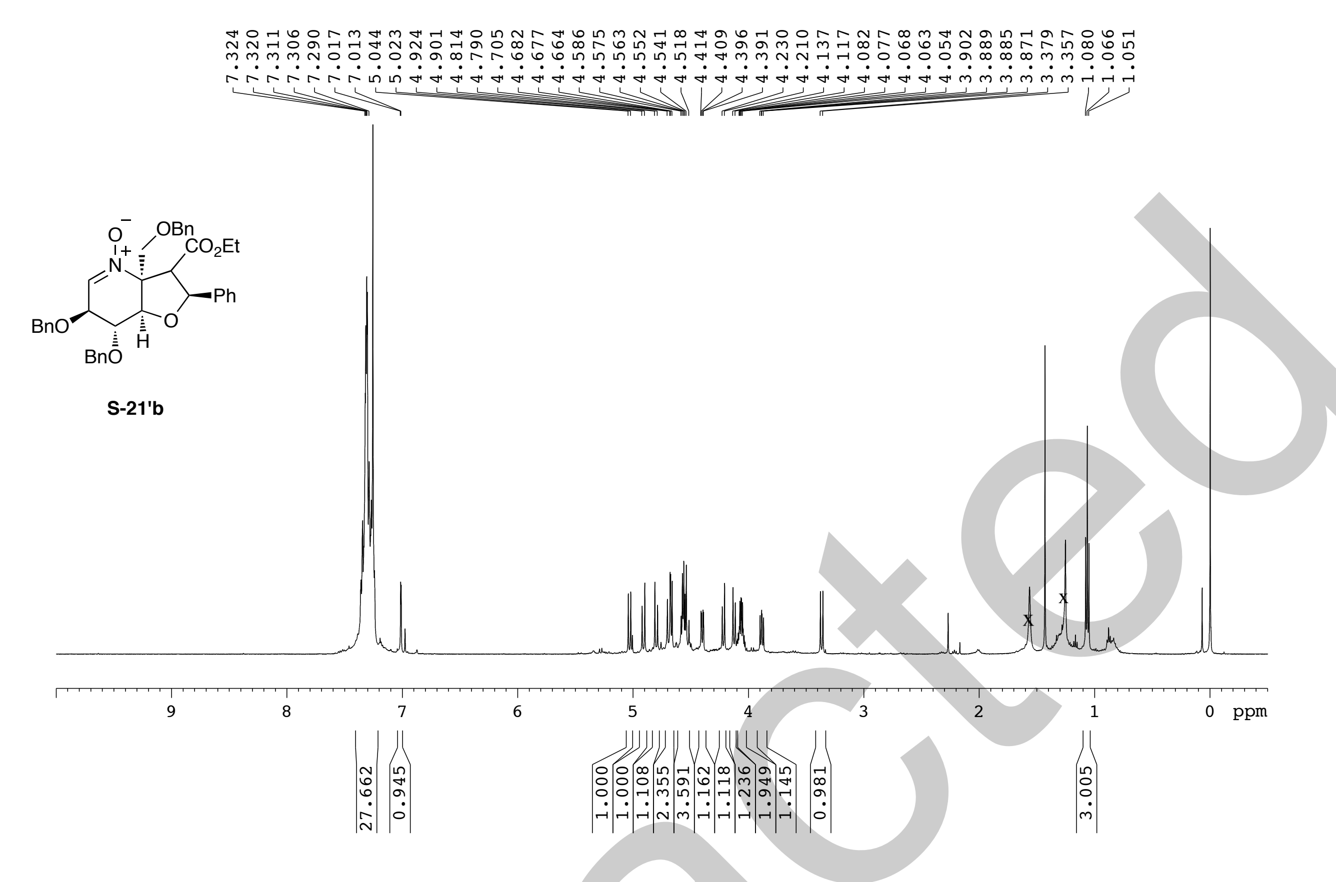
^{1}H NMR (500 MHz, Toluene-d_8)



^{13}C NMR (125 MHz, Toluene-d_8)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)