Electronic Supplementary Information for

Cycloaddition of CO_2 to epoxides by highly nucleophilic 4-aminopyridines: establishing a relationship between carbon basicity and catalytic performance by experimental and DFT investigations

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Summary

S1. General Information

Experimental details

All chemicals and solvents were obtained commercially and used as received without further purification. All air and water sensitive manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Merrifield resin was purchased from Sigma-Aldrich (Mesh: 100-200, loading: 1.0 to 1.6 mmol/g Cl^-, crosslinked with 1% DVB). NMR spectra were measured on an automated "Bruker" 600 MHz for ^{1}H (150 MHz for ^{13}C). Chemical shifts are reported in ppm (δ, relative to TMS) using $CHCl_3$ residual peak (δ = 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) in $CDCl_3$ as an internal standard or 2.05 ppm for ^{1}H and 29.84 ppm for ^{13}C of acetone-d_6 ($(CD_3)_2CO$) or 4.79 ppm for ^{1}H of D_2O. Mass spectrometry data were collected by using Bruker data analysis Esquire-LC mass spectrometer (APCI mode). FT-IR spectra were recorded on a Frontier FT-IR, Universal-ATR, PerkinElmer (ATR mode). Thermogravimetric analysis was measured on a Rigaku model TG-DTA 8122 with smart loader, 30-800 ℃, 10 ℃/min under N_2 atmosphere. Elemental analysis was measured on CHNS analyzer, Leco model TruSpec Micro. SEM images and compositional analysis mapping were acquired using a JEOL JSM-7610F field emission scanning electron microscope equipped with an Oxford Instruments EDS and *in situ* IR was performed on a METTLER TOLEDO, ReactIR™ 15.

Computational methods

<u>*Epoxide affinity calculations:*</u> Geometry optimizations have been performed using the BP86 hybrid functional[1, 2] complemented by the D3 dispersion correction.[3, 4] The TZVP all electron basis set[5] has been used for all elements. Thermal corrections to enthalpies at 373.15 K have been calculated at the same level using the rigid rotor/harmonic oscillator model. This level of theory will in the following be designated "BP86-D3/TZVP".

Single point energies have subsequently been calculated with the hybrid M06 functional[6] in combination with the TZVP basis set,[5] the ultrafine integration grid, and the PCM continuum solvation model[7] for propylene oxide (PO) as the reaction medium. Estimated values for this latter solvent are eps=13.9 and rsolv=4.26. Enthalpies and free energies at this level of theory are calculated using thermal corrections from the previous gas phase geometry optimizations. This level of theory will in the following be designated "PCM(PO)/M06/TZVP(SP)".

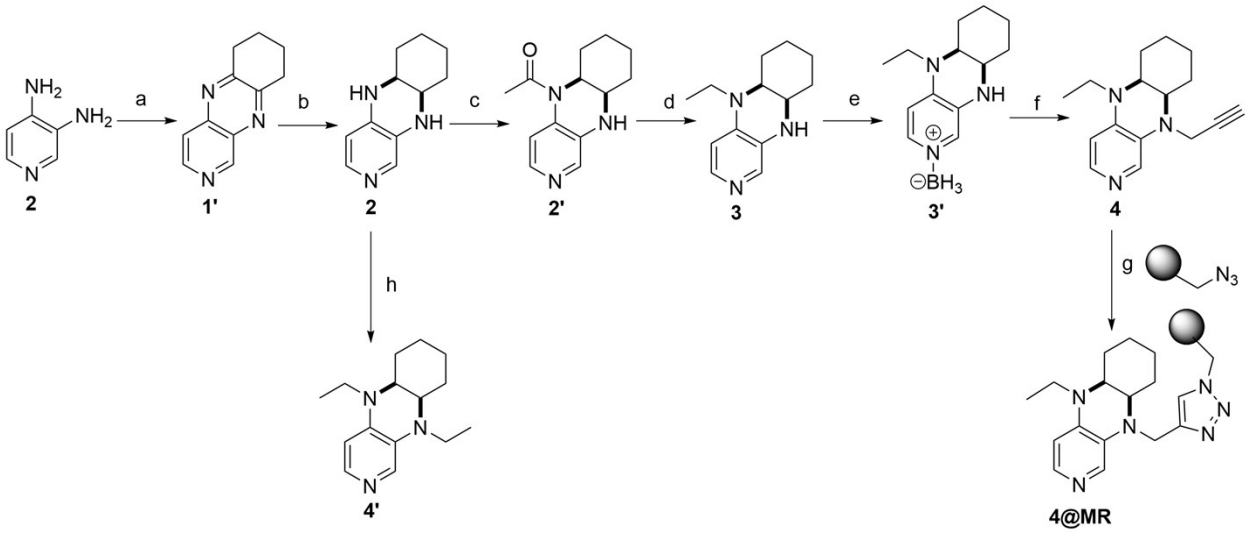
Finally, geometry optimzations have been repeated at the PCM(PO)/M06/TZVP level of theory, again using the ultrafine integration grid. Enthalpies and free energies at 373.15 K are obtained through combination with thermal corrections calculated at this same level. This level of theory will in the following be designated "PCM(PO)/M06/TZVP".

All calculations have been performed with *Gaussian 09, rev. D.01*.[8]

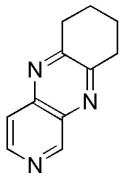
Mechanistic pathways calculations: DFT static calculations were performed with the Gausian09 set of programs,[8] using the BP86 functional of Becke and Perdew,[2, 9, 10] including corrections due to dispersion through the Grimme's method (GD3 keyword in Gaussian).[3, 11] The electronic configuration of the molecular systems was described with the triple-ζ basis set with polarization of Ahlrichs for main-group atoms (TZVP keyword in Gaussian).[12] The geometry optimizations were performed without symmetry constraints, and analytical frequency calculations confirmed the character of the located stationary points. These frequencies were used to calculate unscaled zero-point energies (ZPEs) as well. Energies were obtained by single-point calculations on the optimized geometries with the B3LYP-D3 functional[1, 13, 14] and the triple-ζ basis set TZVP and by estimating solvent effects with the polarizable continuous solvation model (PCM) as implemented in Gaussian09 for the epoxide.[15, 16] The reported free Gibbs free energies in this work include electronic energies obtained at the B3LYP-D3/TZVP//BP86-D3/TZ2P level of theory corrected with zero-point energies, thermal corrections and entropy effects computed with the BP86-D3/TZVP level (see SI for further details).

S2. Experimental section for synthesis catalysts

General procedure for synthesis of aminopyridine-based catalysts

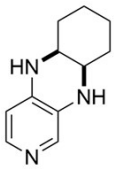


Scheme S1. Synthesis of aminopyridine-based catalysts. Reagents and conditions: a) 1,2-cyclohexadione, EtOH, 70 ˚C, 5 h, b) $LiAlH_4$, THF, -40 ˚C to r.t., 32 h, c) AcCl (1.1 equiv), DMAP (0.2 equiv), Et_3N, CH_2Cl_2, r.t. 3 h, d) $LiAlH_4$ (2.2 equiv), $AlCl_3$ (1.3 equiv), THF, 0 ˚C, then 70 ˚C, overnight, e) BH_3Sme_2, THF, -10 ˚C to r.t., f) 1. n-BuLi, propargyl bromide, THF, -78 ˚C to r.t., 4 days, 2. HCl, MeOH, 0 ˚C to r.t., 5 min, g) Cu(I), DIPEA, THF/DMF, 40 ˚C, 24 h. h) 1. Ac_2O, 25 mol%, pyridine, 100 ℃, 48 h, 2. $LiAlH_4$ (4.2 equiv), $AlCl_3$ (2.6 equiv), THF, 0 ℃, 1 h, then reflux, 8 h.

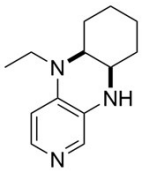


[illegible] of compounds 3. White foam (%yield). ^{1}H-NMR (600 MHz, [illegible]

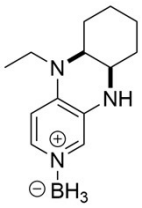
6,7,8,9-Tetrahydropyrido[3,4-*b*]quinoxaline (1'). 3,4-diaminopyridine (4.0 g, 36.65 mmol, 1 equiv.), 1,2-cyclohexadione (4.1096 g, 36.65 mmol, 1 equiv.) and 80 mL of ethanol were added to a 250 mL round bottom flask equipped with a magnetic stirrer. The mixture was placed into oil bath and stirred at 70 ℃ overnight. After cooling the mixture to r.t., the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc:hexane, 1:1) to afford a white solid in 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.66 (d, J = 5.6 Hz, 1H), 7.73 (d, J = 5.6 Hz, 1H), 3.14 (s, 4H), 2.01 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.6, 156.5, 153.6, 143.8, 136.6, 120.8, 33.7, 33.4, 22.6, 22.5. MS (APCI): calcd for [M+H: $C_{11}H_{11}N_3$+H]$^+$: 186.1026; found: 186.1026.



5,5a,6,7,8,9,9a,10-Octahydropyrido[3,4-*b*]quinoxaline (2). Compound **1'** (6.0760 g, 32.84 mmol) was dissolved in 100 mL anhydrous THF. The mixture was cooled to -40 ℃ and $LiAlH_4$ (3.1157 g, 82.10 mmol, 2.5 equiv.) was added in small portions. The solution was allowed to warm to r.t. and stirred for 32 h. After this period, the reaction mixture was poured into ice water. The solution was basified with sat. aq. K_2CO_3 to pH 12 and the precipitate was filtered off and washed with 500 mL CH_2Cl_2. The organic phase was stirred at r.t. for 8 h and subsequently was separated and dried with Na_2SO_4. The crude product was purified by column chromatography (EtOAc:MeOH:Et_3N, 10:1:1) to afford **2** a brown foam in 94% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.63 (d, J = 5.3 Hz, 1H), 6.31 (d, J = 5.3 Hz, 1H), 4.43 (s, 1H), 3.53-3.49 (m, 1H), 3.42-3.39 (m, 1H), 1.72 (dt, J = m, 2H), 1.67-1.55 (m, 4H), 1.34 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.1, 139.7, 134.0, 128.9, 107.6, 50.2, 49.1, 30.8, 30.4, 22.2, 22.0. MS (APCI): calcd for [M+H: $C_{11}H_{15}N_3$+H]$^+$: 190.1339; found: 190.1351.

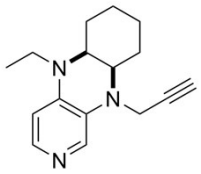


5-Ethyl-5,5a,6,7,8,9,9a,10-octahydropyrido[3,4-b]quinoxaline (3). Compound **2** (7.5033 g, 39.6 mmol, 1equiv.) was dissolved in 160 mL CH_2Cl_2. Et_3N (16.57, 118.8 mmol, 3 equiv.) and DMAP (0.2424 g, 1.98 mmol, 0.05 equiv.) were added to the solution followed by AcCl (3.10 mL, 43.6 mmol, 1.1 equiv.) and the mixture was stirred for 1 h. The reaction was quenched by addition of 15 mL MeOH and stirred for 10 min. The solvent was removed under reduced pressure by rotary evaporator. The crude product was purified by column chromatography (EtOAc:MeOH:Et_3N, 10:1:1) to afford **2'** as a brown liquid in 80% yield. Note: the product still contained traces of DMAP and was used without further purification. 2) $AlCl_3$ (4.5086 g, 33.813 mmol, 1.3 equiv.) was suspended in 220 mL of THF at r.t. and stirred for 45 min. After that, the mixture was cooled to 0 ℃ and $LiAlH_4$ (2.1716 g, 57.222 mmol, 2.2 equiv.) was added in small portions. The mixture was stirred for 15 min. Compound **2'** was added to the mixture and stirred for 1 h at 0 ℃ and then refluxed for 8 h at 70 ℃. After this period, the mixture was cooled to r.t. and poured into ice water. The precipitate was filtered off and washed with 500 mL CH_2Cl_2. The mixture was basified with 30% NaOH to pH 12 and extracted with CH_2Cl_2. The organic layer was combined, dried with Na_2SO_4 and concentrated. The crude product was purified by column chromatography (EtOAc:Et_3N, 10:1) to afford **3** as a brown foam in 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J = 5.5 Hz, 1H), 7.52 (s, 1H), 6.15 (d, J = 5.6 Hz, 1H), 3.74 (s, 2H), 3.25-3.02 (m, 4H), 1.73 (d, J = 13.7 Hz, 1H), 1.61-1.35 (m, 5H), 1.25 (d, J = 12.6 Hz, 1H), 1.14 (d, J = 12.7 Hz, 1H), 1.01 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 140.6, 138.6, 133.1, 129.8, 103.8, 58.2, 47.7, 42.7, 30.8, 26.7, 24.7, 19.1, 12.0. MS (APCI): calcd for [M+H: $C_{13}H_{19}N_3$+H]$^+$: 218.1652; found: 218.1656.

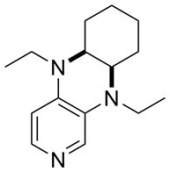


(5-Ethyl-5,5a,6,7,8,9,9a,10-octahydropyrido[3,4-*b*]quinoxalin-2-ium-2-yl) trihydroborate (3'). Compound **3** (1.5245 g, 7.02 mmol, 1.0 equiv.) was dissolved in anhydrous THF (36 mL), and the solution was placed at –10 °C by using an ice/NaCl bath. Then, a solution of BH_3SMe_2 (2 M in THF, 3.51 mL, 7.02 mmol, 1.0 equiv.) was added dropwise through a septum by using a syringe within 10 min. After that, the ice/NaCl bath was removed and the reaction mixture was allowed to warm to r.t. for 10 min. The reaction solvent was removed under reduced pressure, and the residual oil was purified by filtration through silica gel that was previously treated with 1% of Et_3N in hexane (EtOAc:NEt_3:MeOH, 10:1:1) to afford compound **3'** as a white solid in 75 % yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, J = 6.4 Hz, 1H), 7.48 (s, 1H), 6.26 (d, J = 6.5 Hz, 1H), 3.59 (br. s, 1H), 3.44-3.25 (m, 4H), 2.70-2.10 (br. s, 3H), 1.90 (m, 1H),

1.82-1.66 (m, 3H), 1.65-1.40 (m, 3H), 1.33-1.23 (m, 1H), 1.17 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.4, 139.3, 130.4, 129.7, 103.6, 59.2, 47.8, 43.8, 30.9, 27.4, 25.0, 19.2, 12.1.



5-Ethyl-10-(prop-2-ynyl)-5,5a,6,7,8,9,9a,10-octahydropyrido[3,4-*b*]quinoxaline (4). Compound **3'** (2.4000 g, 13.05 mmol, 1.0 equiv.) was dissolved in 70 mL anhydrous THF and placed at –78 °C, then butyllithium (2.0 M in cyclohexane, 10.0 mL, 20.0 mmol, 1.5 equiv.) was added dropwise to this solution through a septum. After 15 min, propargyl bromide (9.2 M in toluene, 2.0 mL, 18.4 mmol, 1.4 equiv.) was added, the reaction mixture was warmed to r.t. and stirred for 4 days. After this period, the reaction was quenched by adding 5 mL EtOH and the solvent was subsequently removed by rotary evaporator. The residual crude was redissolved in 40 mL of MeOH and concentrated HCl (2 mL) was added dropwise to this solution at 0 °C. The reaction mixture was stirred at this temperature for 10 min, then, the solvent was removed, the crude was diluted with 40 mL of CH_2Cl_2 and extracted with saturated K_2CO_3. The aqueous layer was washed with CH_2Cl_2, the combined organic layers were dried with Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (EtOAc: NEt_3:MeOH, 20:2:1) to afford **4** as a pale-yellow solid in 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 5.8 Hz, 1H), 7.79 (s, 1H), 6.39 (d, J = 5.8 Hz, 1H), 4.04 (dd, J = 118.0, 18.8 Hz, 2H), 3.44 (m, 2H), 3.35-3.22 (m, 2H), 2.16 (s, 2H), 1.80-1.56 (m, 4H), 1.53-1.30 (m, 3H), 1.19 (t, J = 7.1 Hz, 3H) ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.2, 139.8, 130.0, 103.9, 78.0, 73.0, 58.2, 52.3, 42.8, 35.2, 28.2, 27.4, 23.7, 20.9, 11.8. MS (APCI): calcd for [M+H: $C_{16}H_{21}N_3$+H]$^+$: 256.1808; found: 256.1811.



5,10-diethyl-5,5a,6,7,8,9,9a,10-octahydropyrido[3,4-*b*]quinoxaline (4'). 1) Compound **2** (4.0000 g, 21.16 mmol) was charged in a 250 mL round bottom flask equipped with magnetic stirrer. Pyridine (130 mL), Ac_2O (50 equiv), and PPY (0.7816 g, 25 mol%) were added under ice cooling. The mixture was refluxed at 100 ℃ for 48 h. After this period, the mixture was cooled to r.t. and solvent was removed to afford brown crude product. Crude product was used without further purification. 2) $AlCl_3$ (6.3000 g, 47.5 mmol) was suspended in 100 mL of THF and stirred at r.t. for 45 min, then, the mixture was cooled to 0 ℃ and $LiAlH_4$ (3.0000 g, 80.49 mmol) was added in small portions. The mixture was stirred for 15 min. After this period, crude product (5.0000 g, ≈ 18.3 mmol) was added to the mixture and stirred at 0 ℃ for 1 h and then refluxed for 8 h. The reaction mixture was cooled to r.t. and poured into ice water. The precipitate was filtered and washed with CH_2Cl_2. The mixture was basified with 30% NaOH to pH 12 and extracted with CH_2Cl_2. The organic layer was combined and dried over Na_2SO_4 and solvent was removed. Crude

product was purified by by column chromatography on silica gel (EtOAc:hexane:NEt_3, 20:5:1) to afford **4'** as a yellow liquid in 42% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 5.5 Hz, 1H), 7.68 (s, 1H), 6.32 (d, *J* = 5.5 Hz, 1H), 3.51-3.36 (m, 2H), 3.32 (dd, *J* = 5.2, 3.1 Hz, 1H), 3.24-3.12 (m, 3H), 1.88 (s, 1H), 1.83-1.75 (m, 1H), 1.61-1.50 (m, 4H), 1.36 (m, 2H), 1.12 (dt, *J* = 11.3, 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.9, 140.1, 131.8, 130.8, 104.5, 56.3, 53.2, 41.7, 40.5, 28.0, 27.4, 23.0, 21.9, 11.8, 10.7. MS (APCI): calcd for [M+H: $C_{15}H_{23}N_3$+H]$^+$: 246.1965; found: 246.1966.

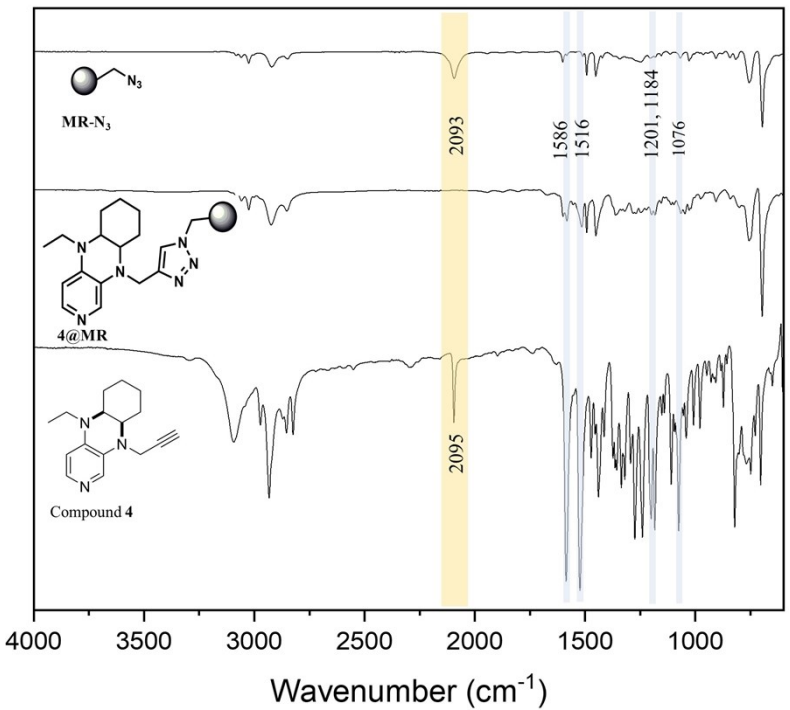
Synthesis of Merrifield resin-Azide (MR-N_3)

Sodium azide (2.25 g, 147 mmol) was added to a mixture of 5 g of Merrifield resin (f = 1.0-1.6 mmol/g) in 50 mL of DMSO. The mixture was heated and stirred at 60 ˚C for 18 h. After this period, the resin was filtered and sequentially washed with water (500 mL), THF (250 mL), 1:1 THF:MeOH (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried under vacuum for 24 h at 40 ˚C. FT-IR (ATR) = 2093 cm^{-1}.

Elemental analysis: N: 5.66%, C: 86.21%, H: 7.38%. (f = 1.35 mmol/g.).

Synthesis of Merrifield resin supported catalyst 4 (4@MR)

Merrifield resin-azide (**MR-N_3**) (1.50 g, 2.1 mmol N_3^-, 1.0 equiv.) was suspended in 20 mL of a 1:1 dry THF/dry DMF mixture in a 100 mL round bottom flask and the suspension was degassed by purging with N_2 for 5 minutes. Compound **4** (0.70 g, 2.7 mmol, 1.3 equiv.) was added, followed by a catalytic amount (10 mol%) of $CuBr(PPh_3)_3$ (0.19 g, 0.2 mmol, 0.1 equiv.) and by DIPEA (0.72 mL, 4.2 mmol, 2.0 equiv.). The mixture was stirred in oil bath at 40 °C for 24 h under nitrogen atmosphere; the color of the reaction mixture turned to brown and later to black. The resin was filtered and washed with: 320 mL of DMF, 320 mL of a 1:1 water/DMF solution, with 320 mL of water, with 320 mL of a 1:1 water/MeOH solution, with 320 mL of MeOH, with 320 mL of a 1:1 THF/MeOH solution, and finally with 600 mL of THF. It was dried with vacuum oven at 60 °C for 24 h, The FT-IR spectrum of the solid shows the disappearance of the azide stretching band at 2093 cm^{-1} (Figure S1). Elemental analysis; C: 81.65%, H: 7.46%, N: 6.47%. Based on the nitrogen content, it is possible to



calculate a loading of 0.77 mmol/g catalyst.

Figure S1. FT-IR Spectra of MR-N_3 (Top), **4@MR** (Middle) and **4** (Bottom).

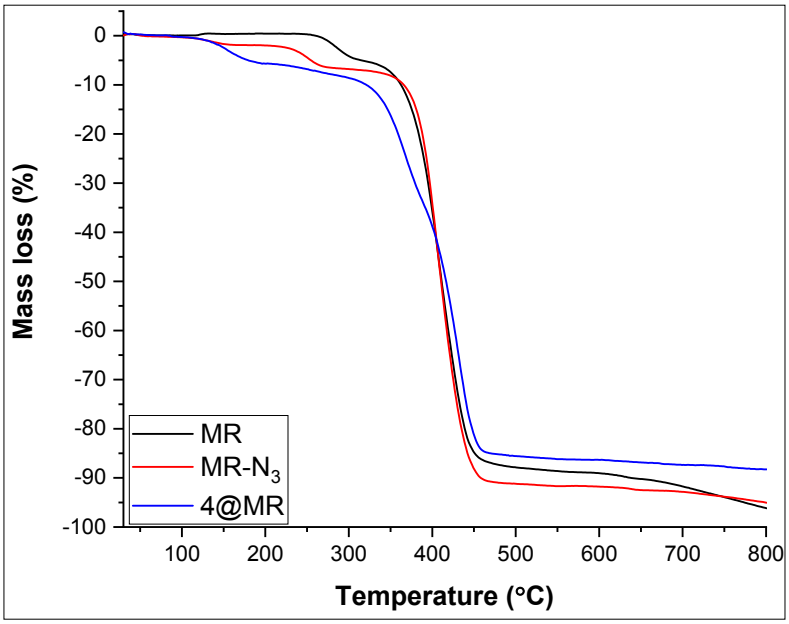


Figure S2. TGA curves of MR (black), **MR-N_3** (red) and **4@MR** (blue).

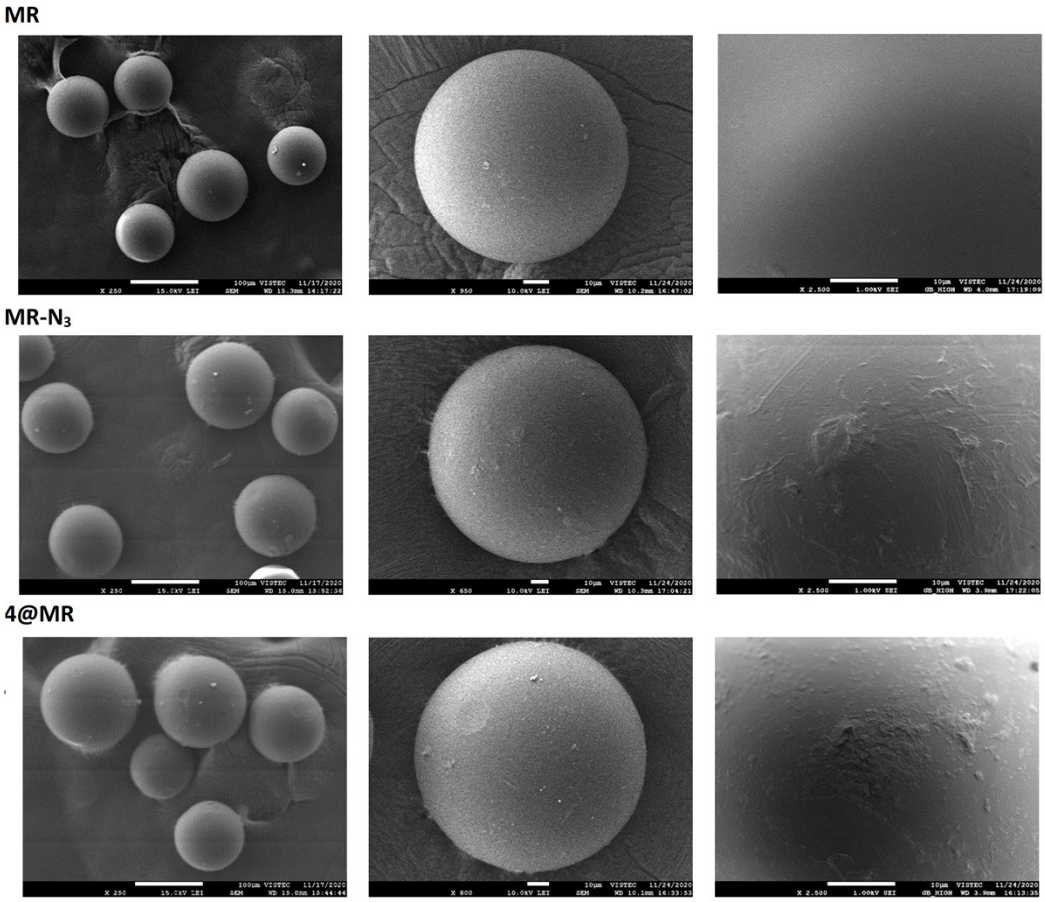


Figure S3. SEM images of polystyrene beads morphology in Merrifield resin (Top), **MR-N_3** (Middle) and **4@MR** (Bottom).

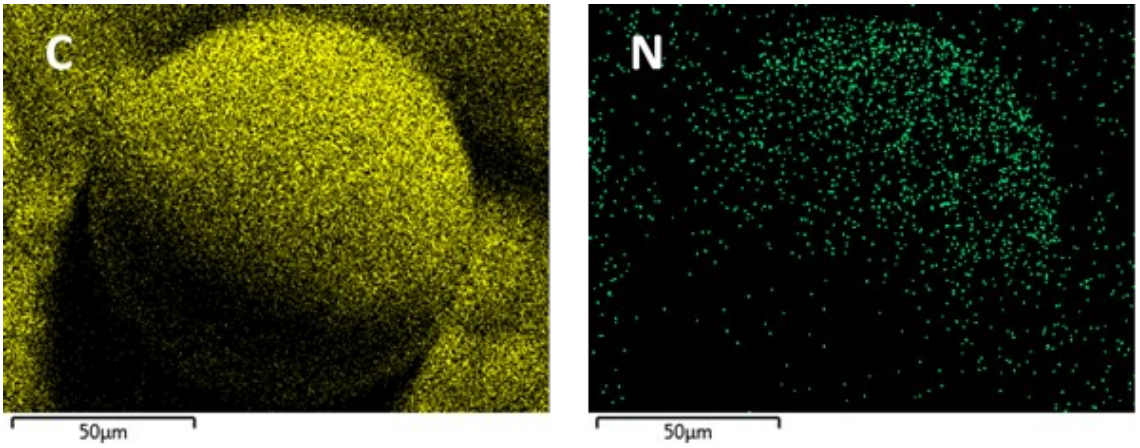


Figure S4. SEM-EDS images of **4@MR** highlighting carbon (Left) and nitrogen (Right) distributions on a polystyrene bead.

S3. Spectral data (^{1}H NMR, ^{13}C NMR) of catalysts

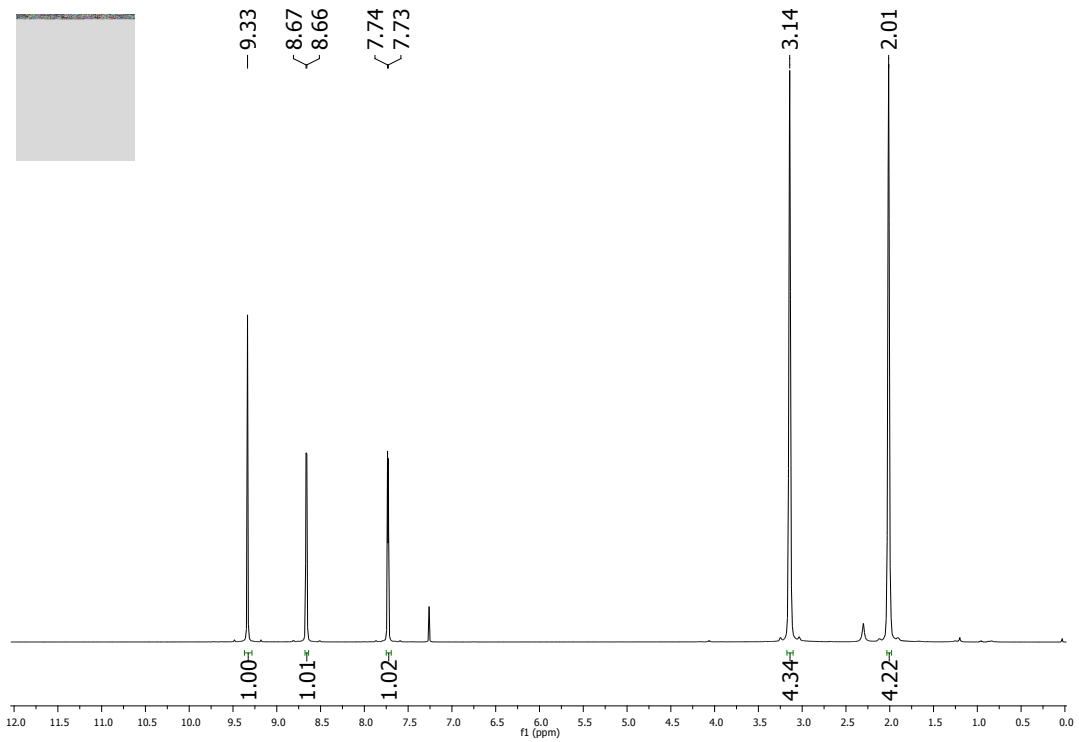


Figure S5. ^{1}H NMR spectrum of **1'**.

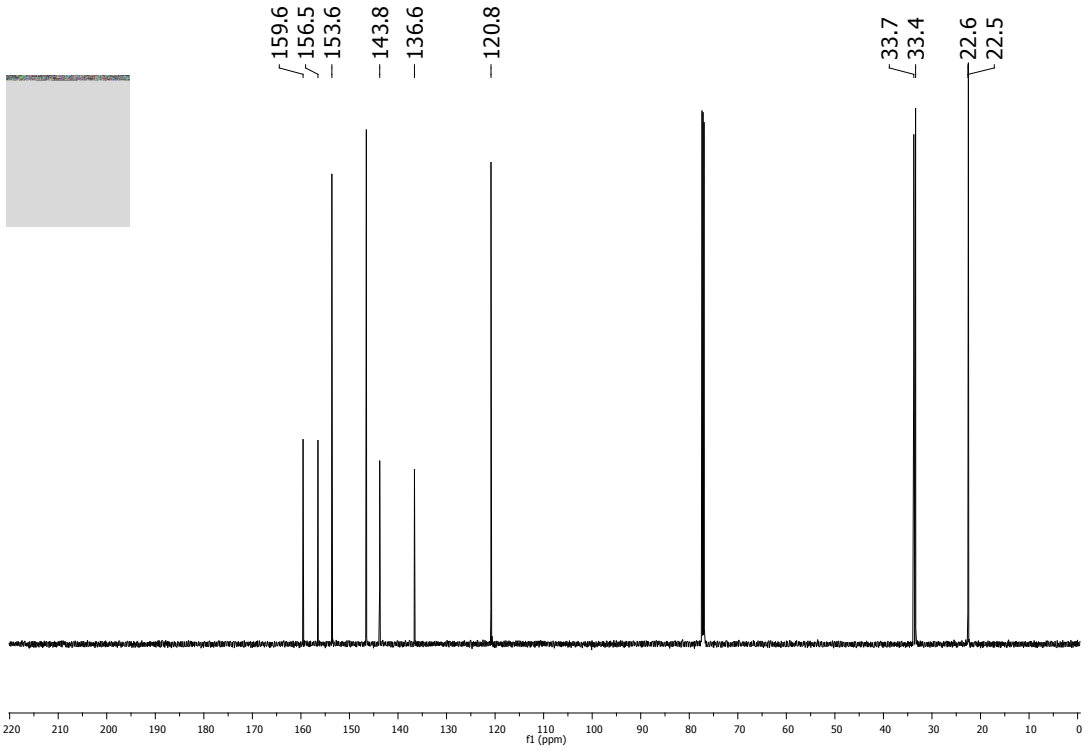


Figure S6. ^{13}C NMR spectrum of **1'**.

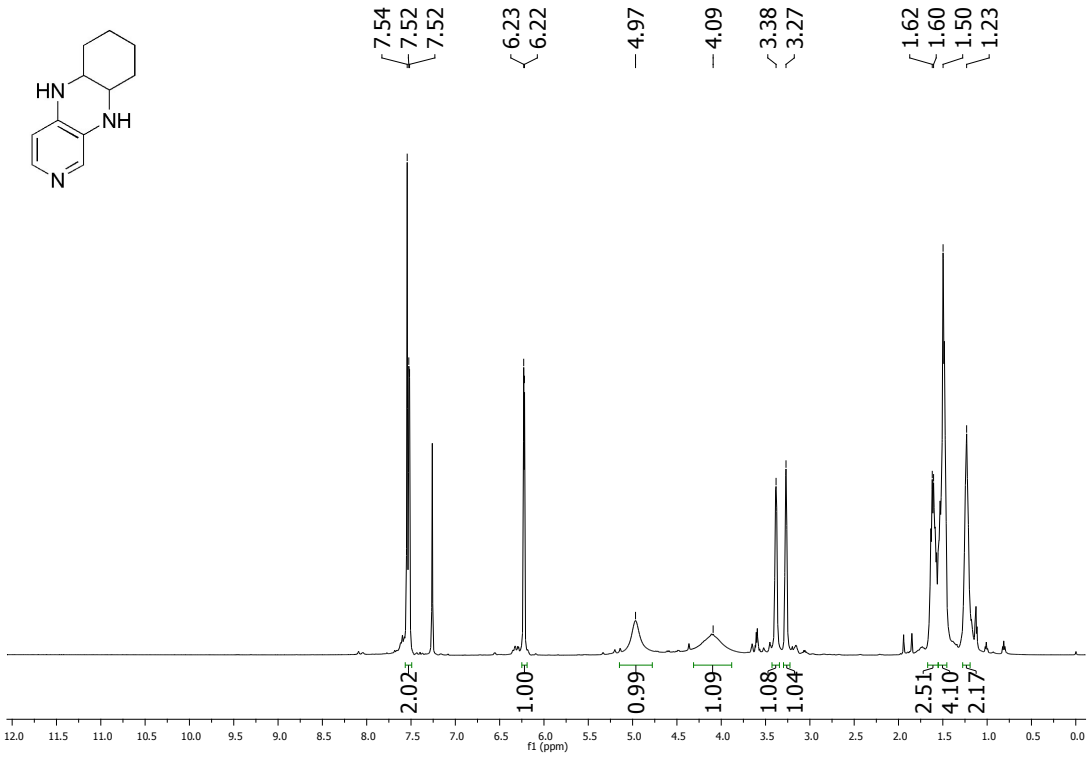


Figure S7. ^{1}H NMR spectrum of **2**.

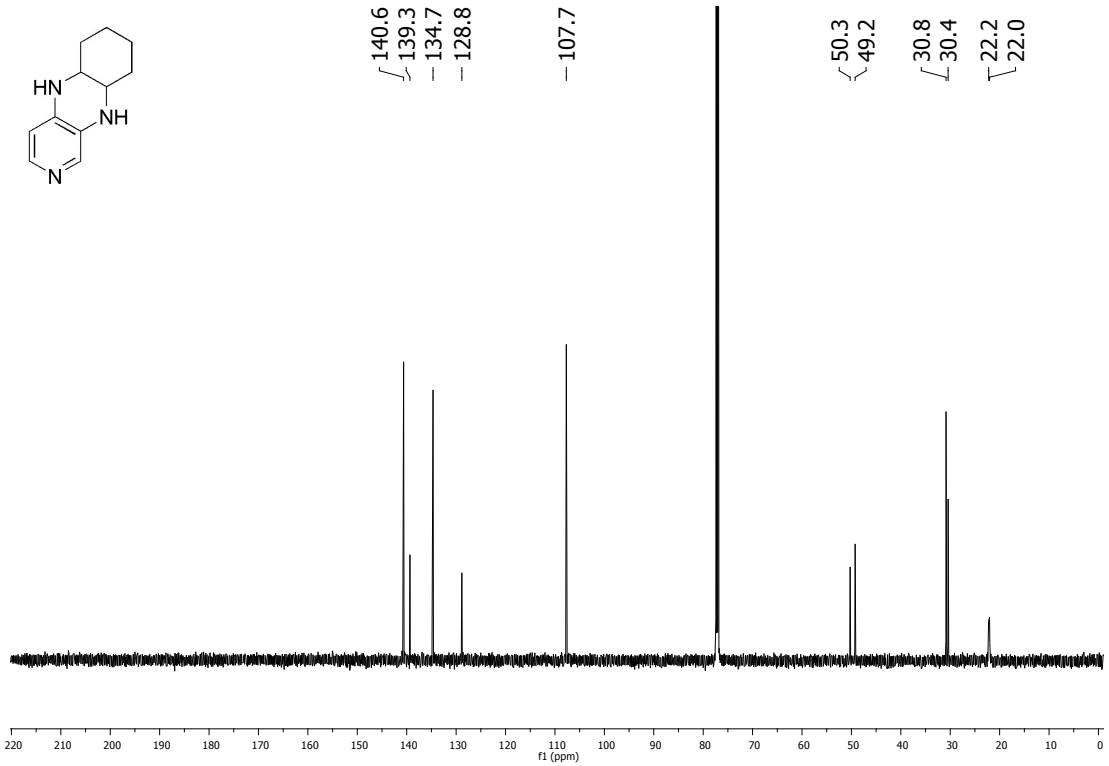


Figure S8. ^{13}C NMR spectrum of **2**.

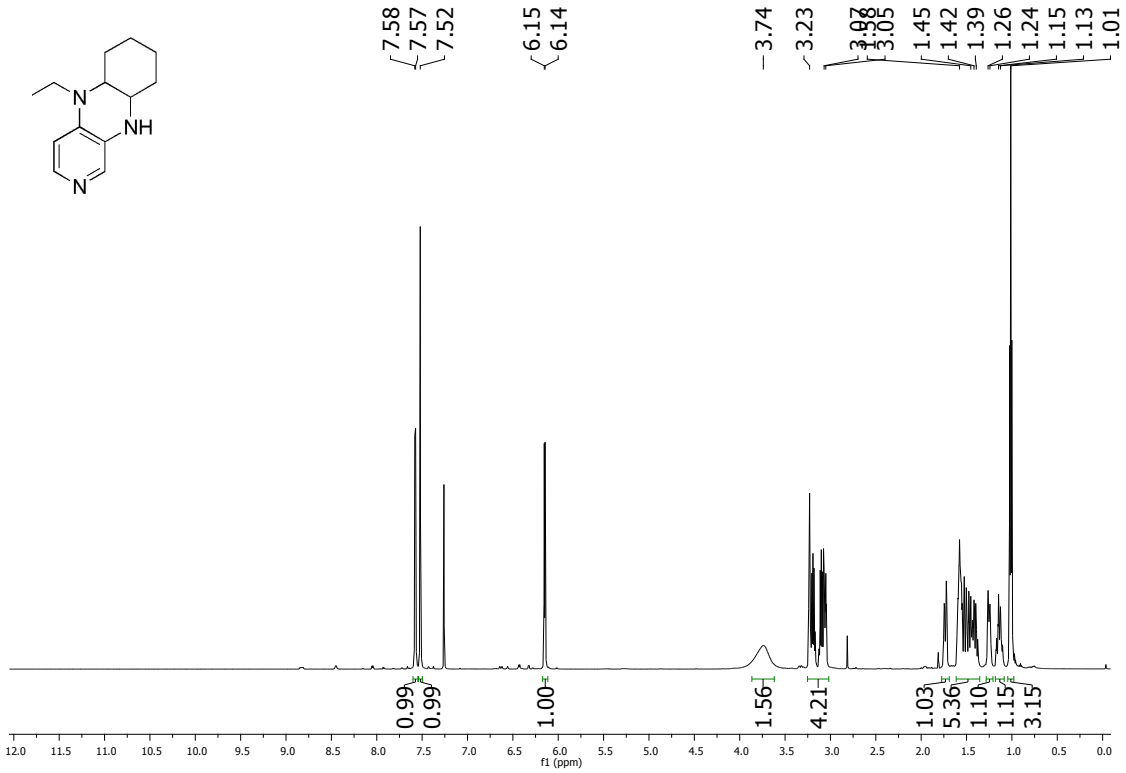


Figure S9. ^{1}H NMR spectrum of **3**.

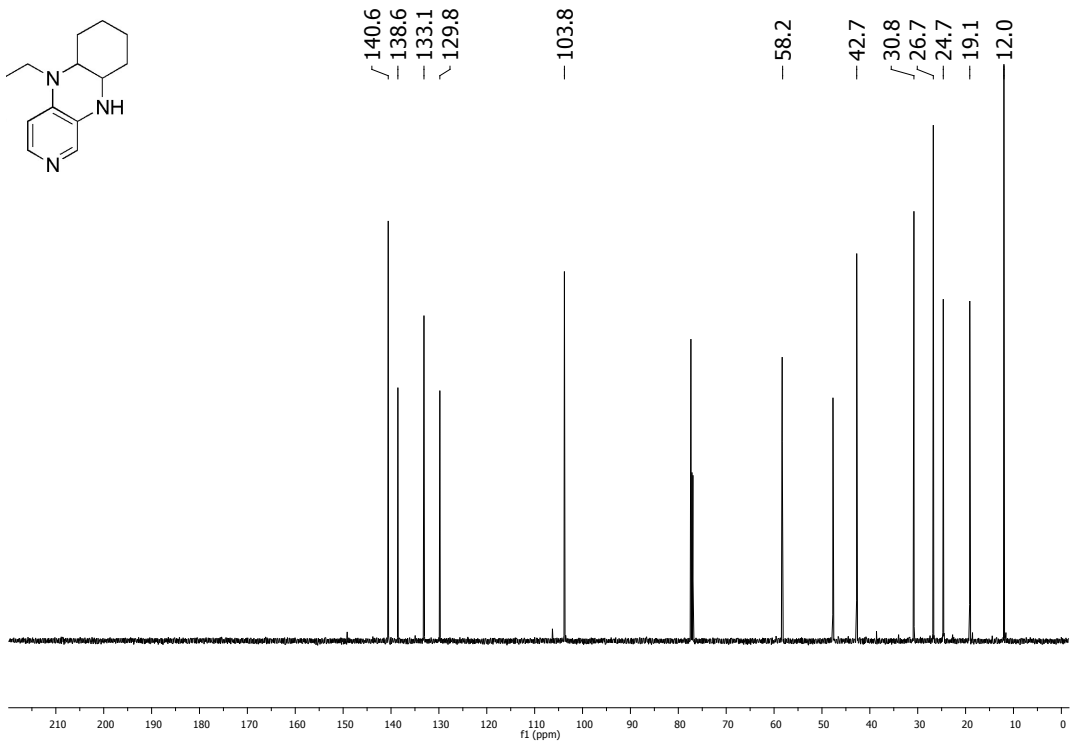


Figure S10. ^{13}C NMR spectrum of **3**.

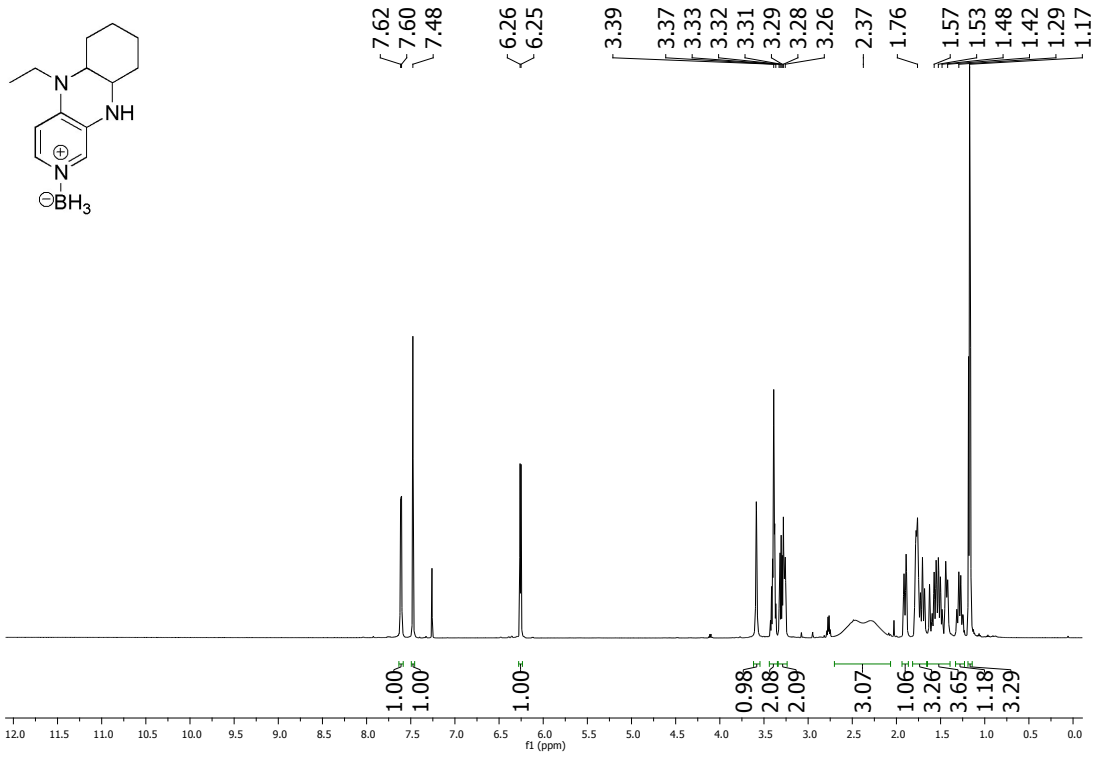


Figure S11. ^{1}H NMR spectrum of **3'**.

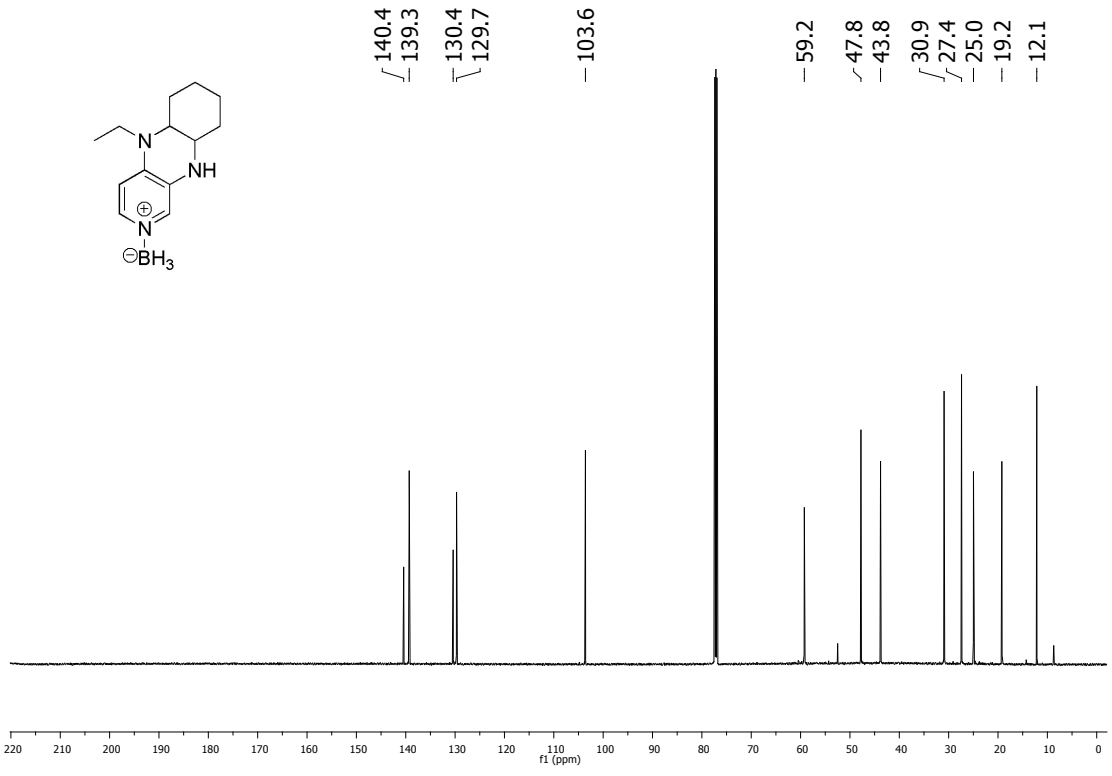


Figure S12. ^{13}C NMR spectrum of **3'**.

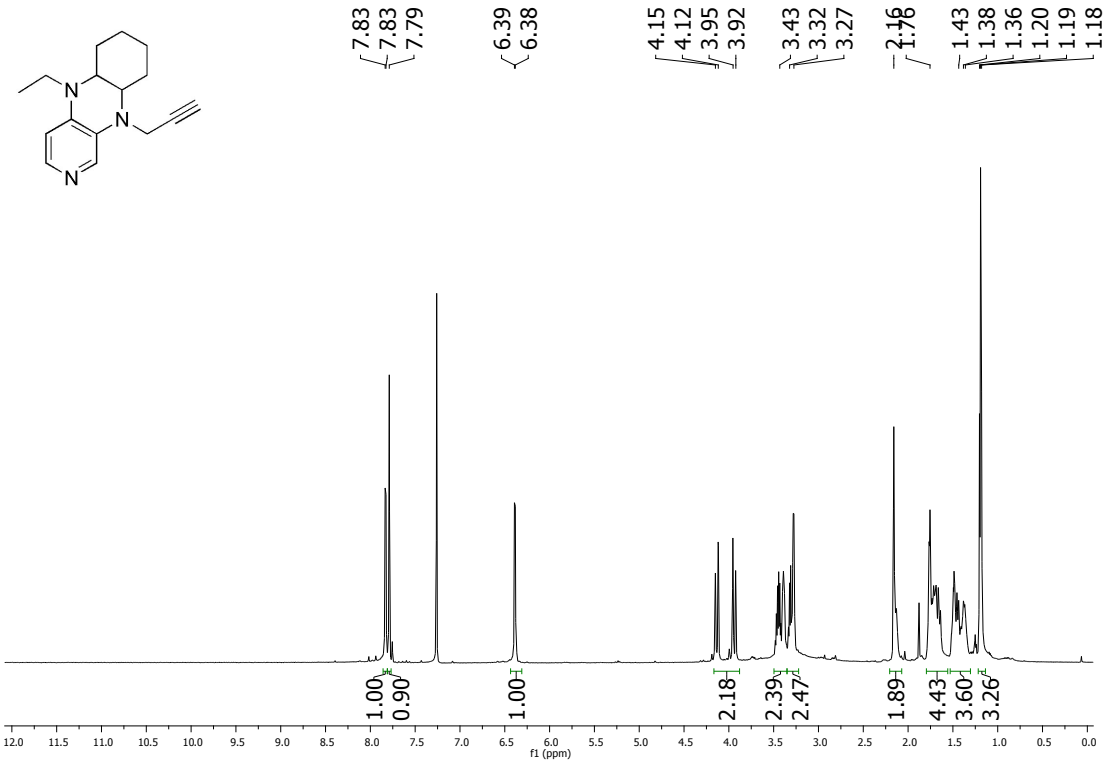


Figure S13. ^{1}H NMR spectrum of **4**.

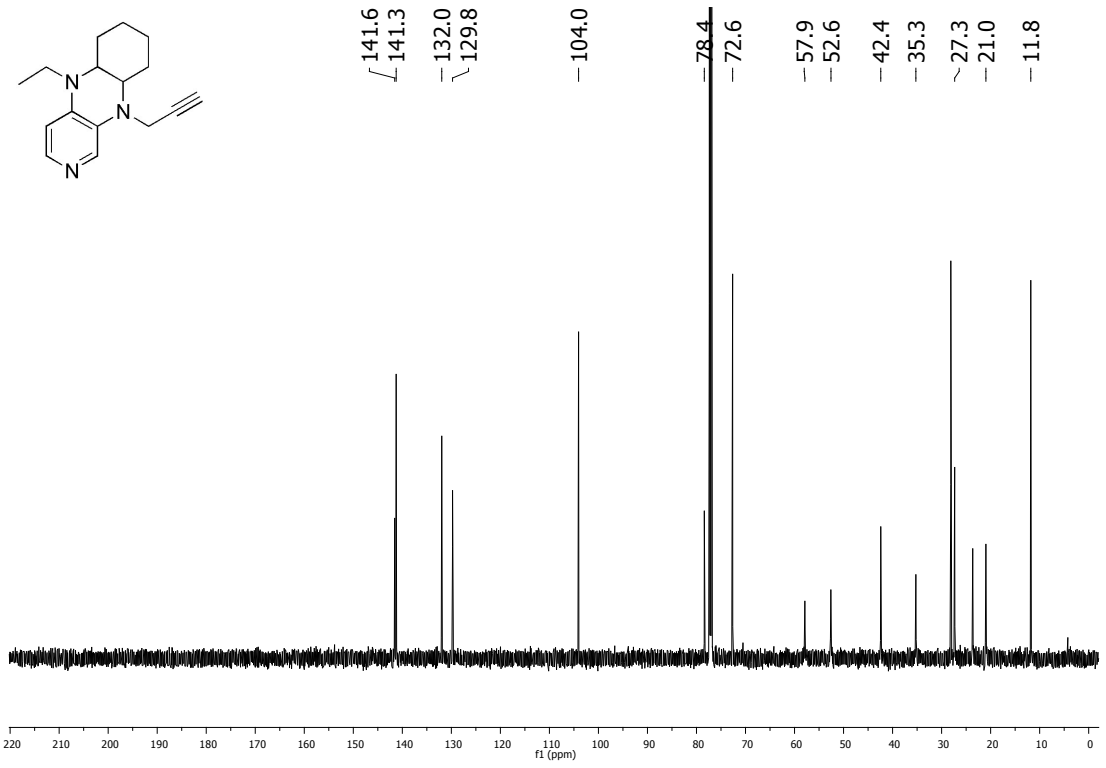


Figure S14. ^{13}C NMR spectrum of **4**.

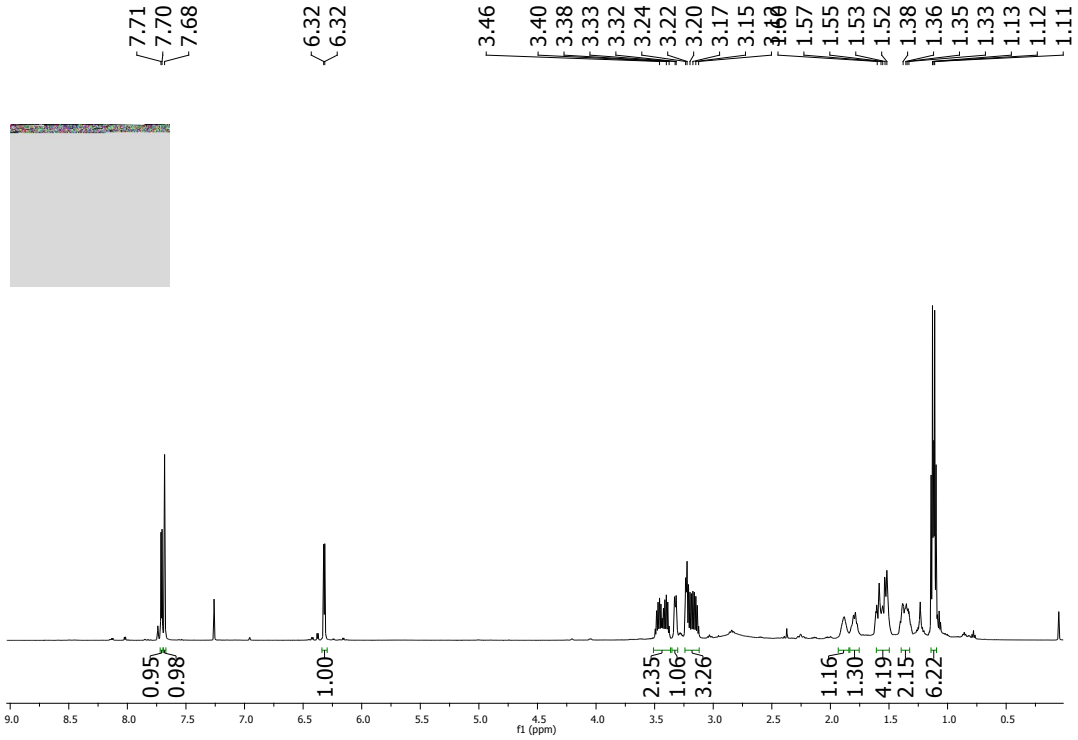


Figure S15. ^{1}H NMR spectrum of **4'**.

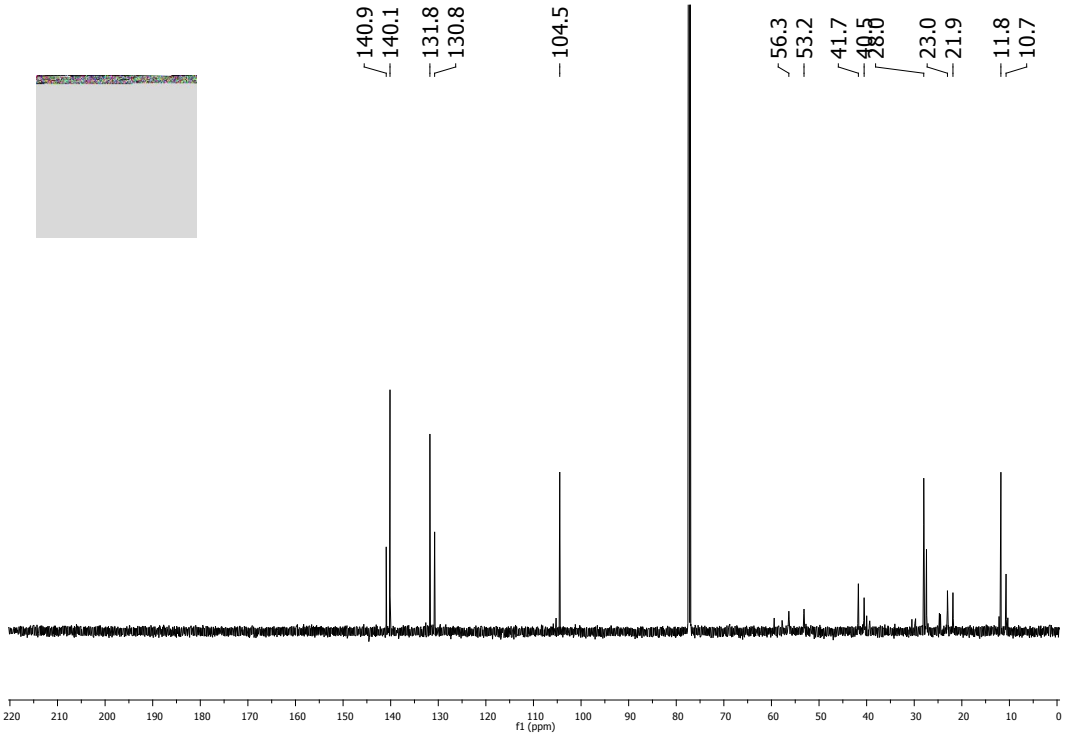
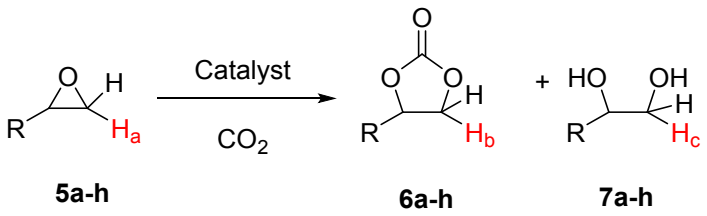


Figure S16. ^{13}C NMR spectrum of **4'**.

S4. ^{1}H NMR methods for determination of conversion and selectivity

The conversion of epoxide **5a-5h** was determined *via* ^{1}H NMR by comparison of the integrals of one of the two diastereotopic OCH_2CHR protons in the starting material (H_a) and in the carbonated product (H_b) and diol by-product (H_c) shown in **Scheme S1.** according to **equation S1.**



Scheme S2. CO_2 conversion with epoxides into cyclic carbonates

Equation S1. Conversion (%) calculated from the integral values (I) of the OCH_2CHR protons in the starting material (H_a), cyclic carbonate product (H_b) and diol by-product (H_c)

$$\text{Conversion (\%)} = \frac{I_{Hb} + I_{Hc}}{I_{Ha} + I_{Hb} + I_{Hc}} \text{x100} \qquad \textbf{(eq. S1)}$$

Table S1 Chemical Shifts (δ, ppm, $CDCl_3$) for the corresponding OCH_2CHR protons in the epoxides, carbonate products and the diol by-product (See also the ^{1}H NMR spectra in the following section).

Compound	**δ (H_a) (ppm)**	**δ (H_b) (ppm)**	**δ (H_c) (ppm)**
5a/6a/7a	3.14	4.79	3.77
5b/6b/7b	2.74	4.51	3.63
5c/6c/7c	2.89	4.59	3.70
5d/6d/7d	3.35	5.02	3.84
5e/6e/7e	2.80	4.48	3.78
5f/6f/7f	2.79	4.78	3.75
5g/6g/7g	2.75	4.51	3.83
5h/6h/7h	2.90	4.96	3.74

The selectivity for the carbonate product was determined *via* ^{1}H NMR from the integrals of protons of carbonated product (H_b) and diol by-product (H_c) shown in **Scheme S1.** according to **equation S2.**

Equation S2. Selectivity (%) calculated from the integral values (I) of the $RHCOCOOCH_2$ protons in cyclic carbonate product (H_b) and $RHCOHCOHH_2$ protons in diol by-product (H_c).

$$\text{Selectivity of cyclic carbonate (\%)} = \frac{I_{Hb}}{I_{Hb} + I_{Hc}} x100 \qquad \textbf{(eq. S2)}$$

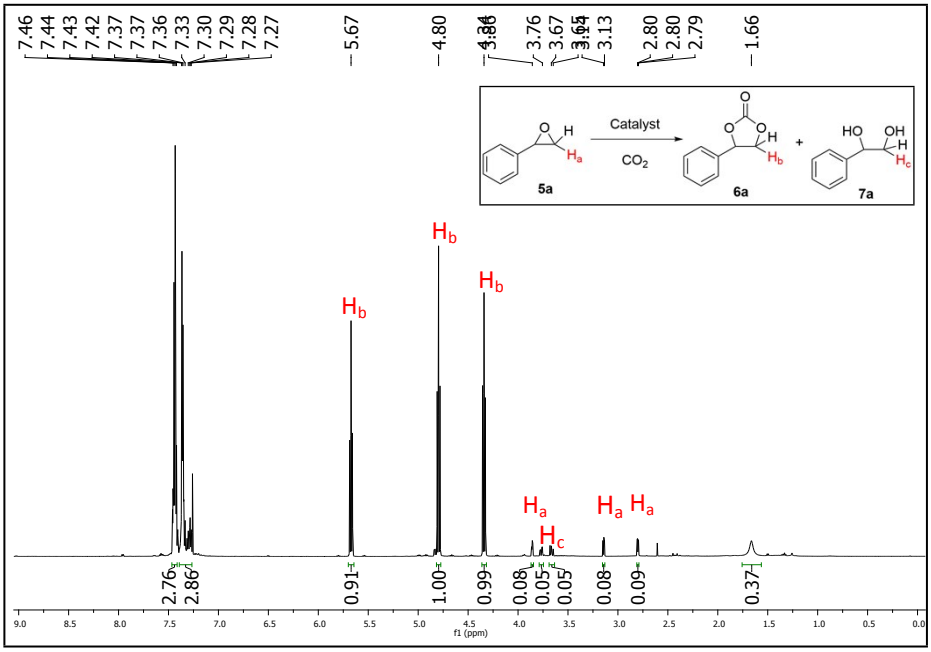


Figure S17. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 6.

$$\text{Conversion (\%)} = \frac{I_{Hb} + I_{Hc}}{I_{Ha} + I_{Hb} + I_{Hc}} x100$$
$$= \frac{1.00 + 0.05}{1.00 + 0.05 + 0.08} x100$$
$$= \frac{1.05}{1.13} x100$$
$$= 93\%$$

$$\text{Selectivity of cyclic carbonate (\%)} = \frac{I_{Hb}}{I_{Hb} + I_{Hc}} x100$$
$$= \frac{1.00}{1.00 + 0.08} x100$$
$$= \frac{1.00}{1.08} x100$$
$$= 93\%$$

S5. Copies of ^{1}H NMR crude reaction

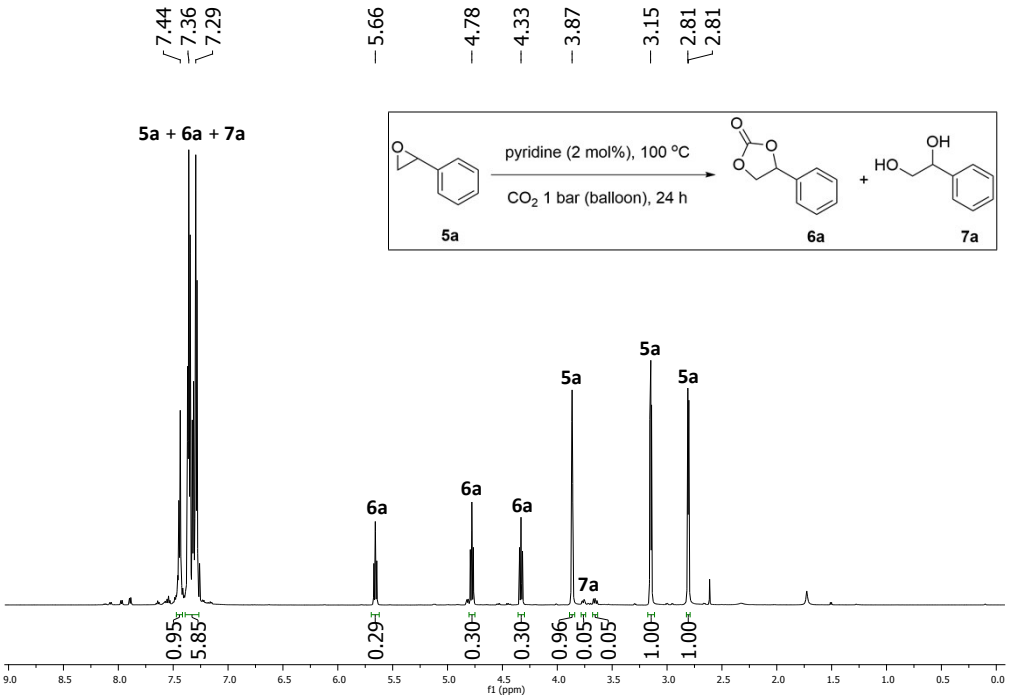


Figure S18. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% pyridine, 100 °C, 1 bar CO_2, 24 h; Table 1, Entry 1.

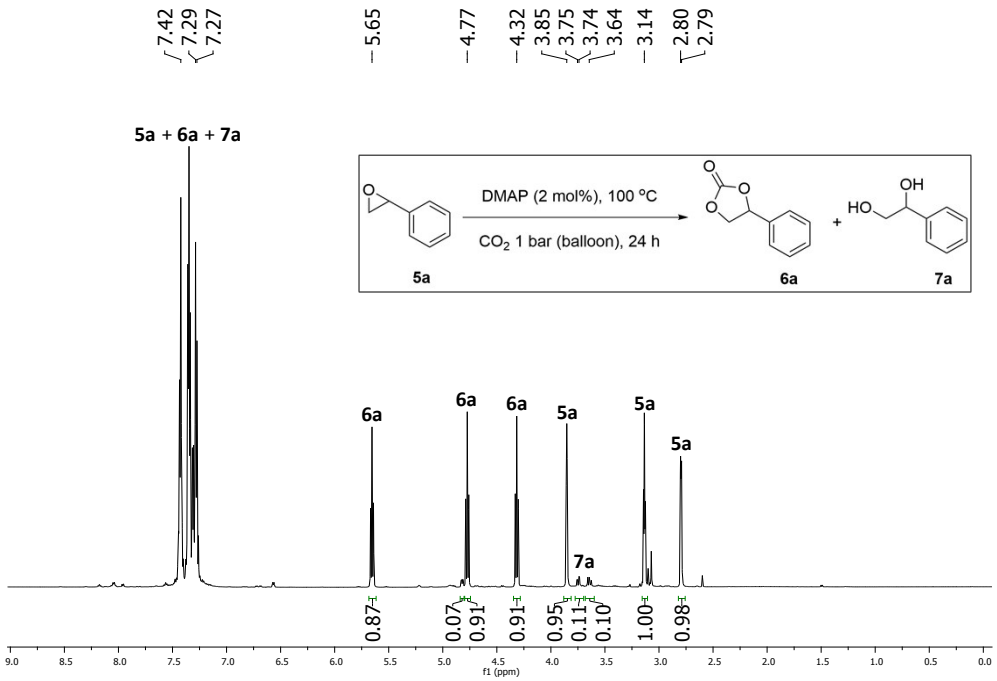


Figure S19. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% DMAP, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 2.

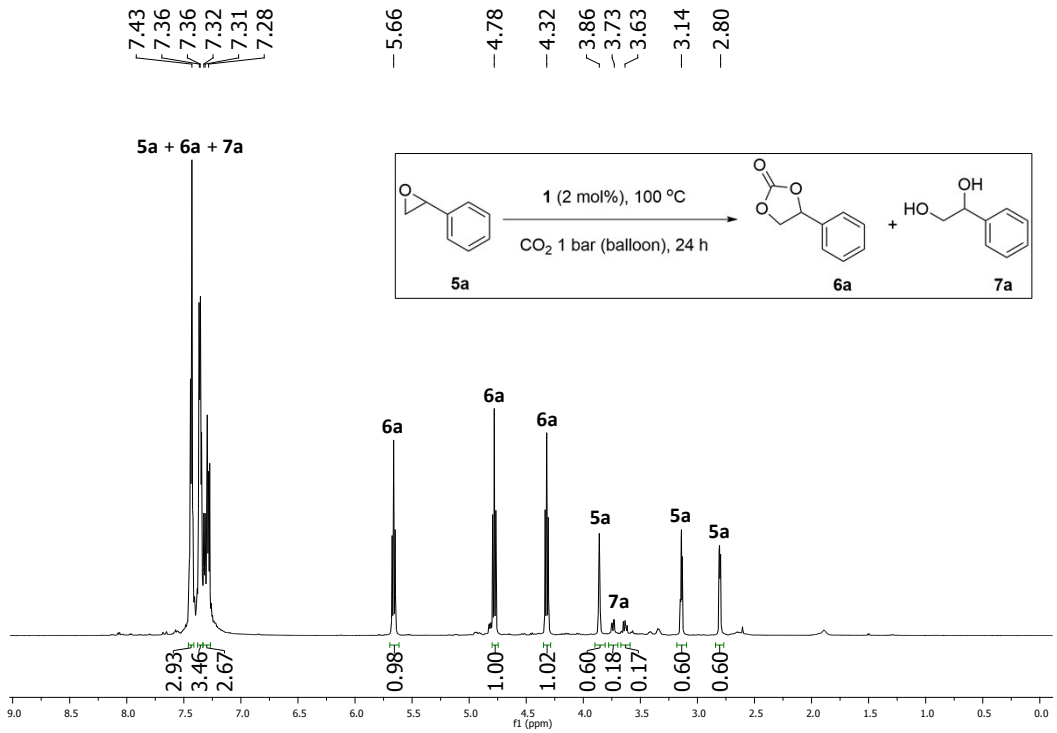


Figure S20. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% 9-Azajulolidine (**1**), 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 3.

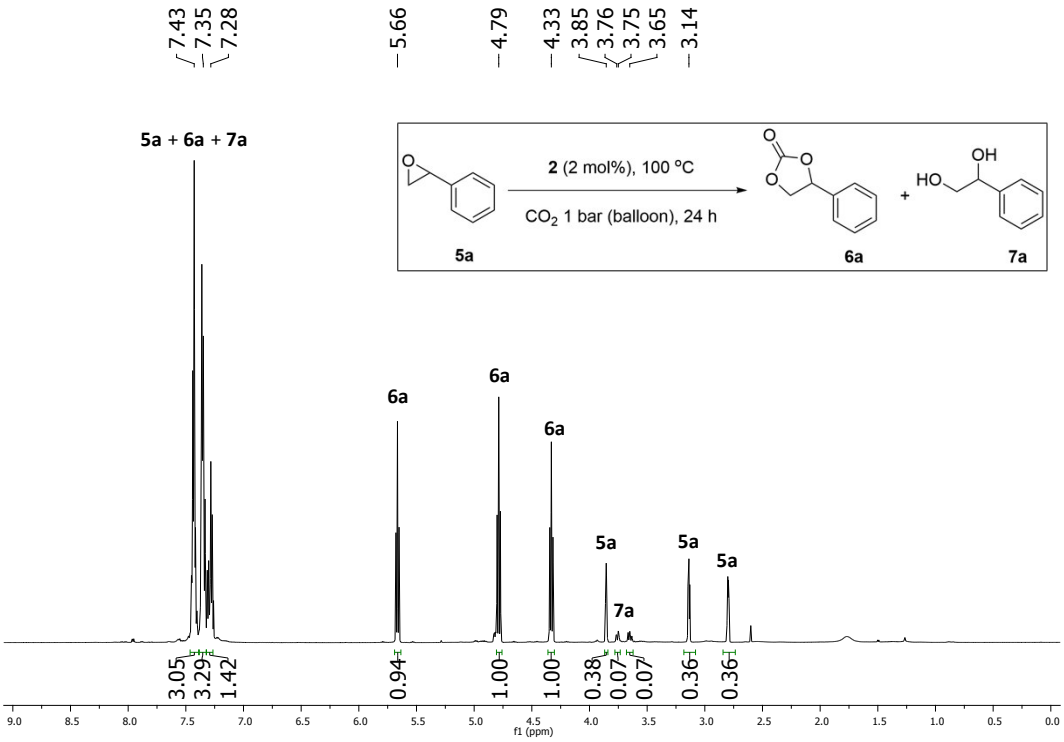


Figure S21. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% **2**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 4.

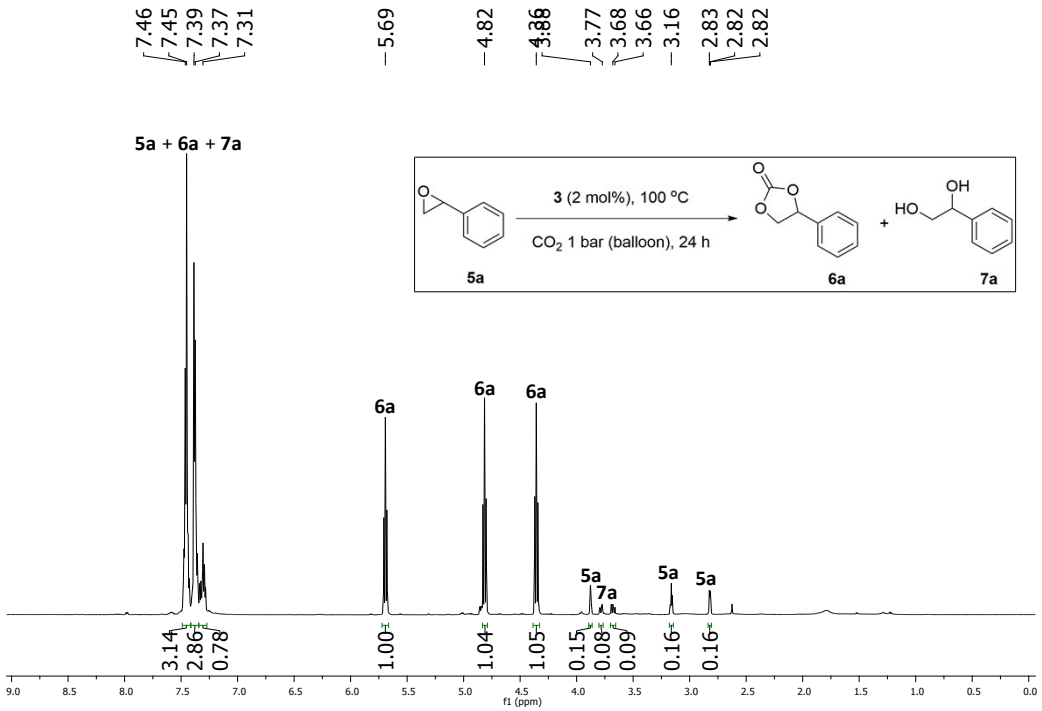


Figure S22. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% **3**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 5.

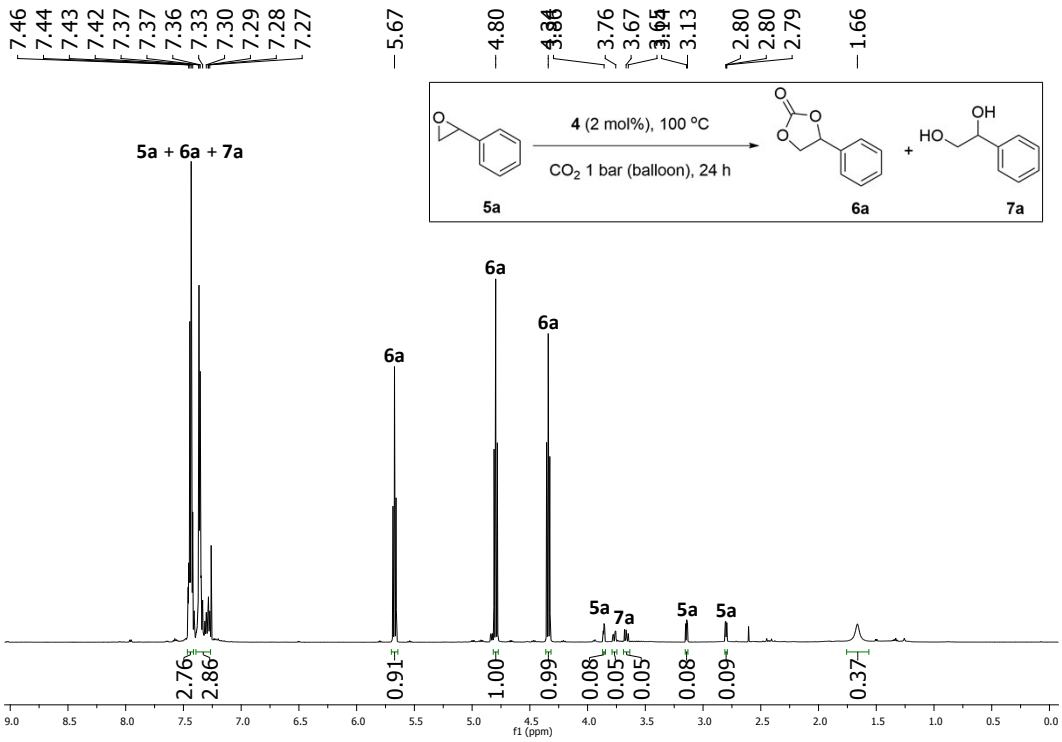


Figure S23. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 6.

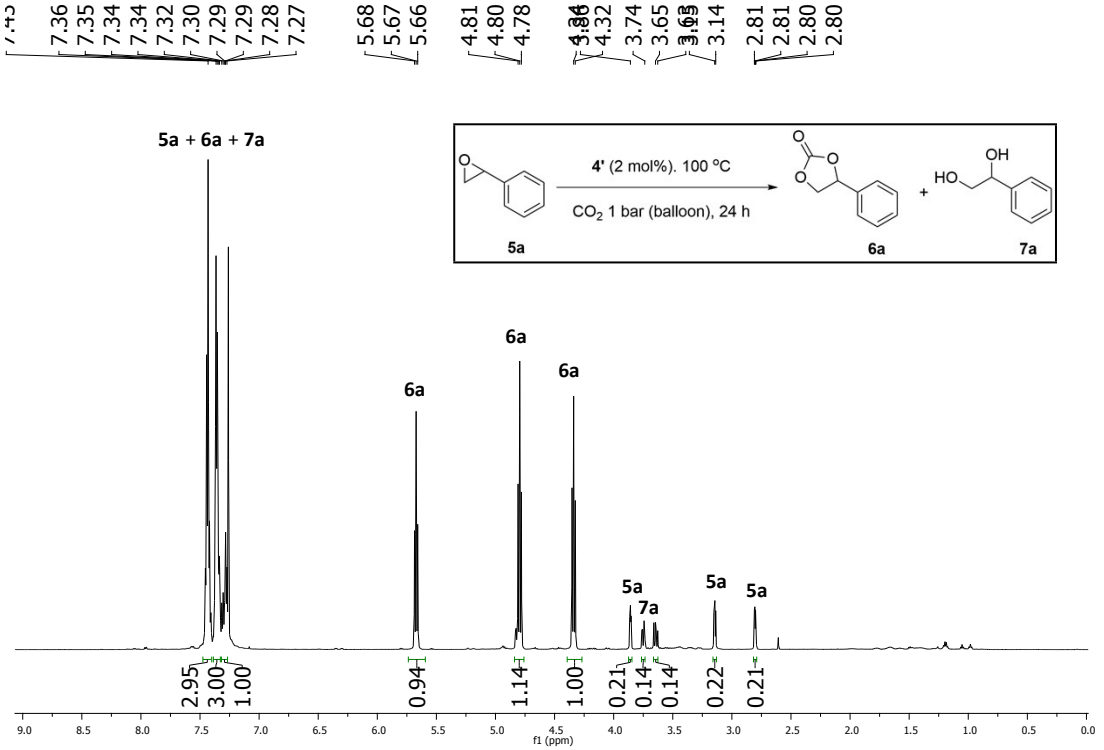


Figure S24. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% **4'**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 7.

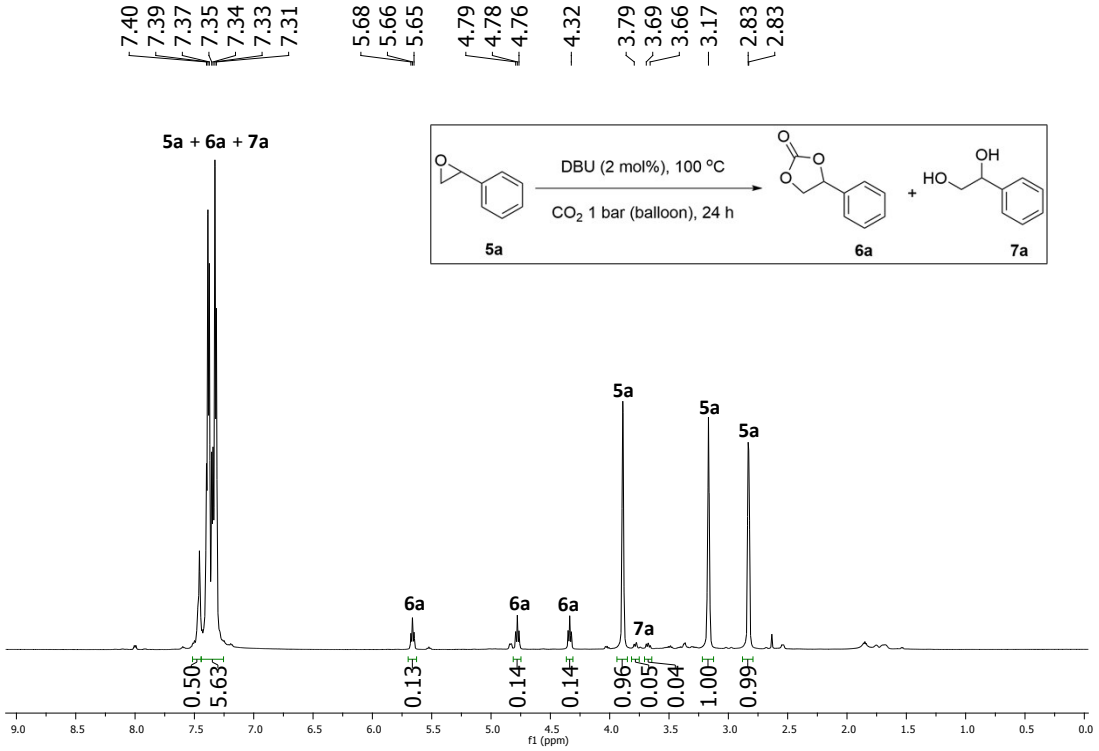


Figure S25. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% DBU, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 8.

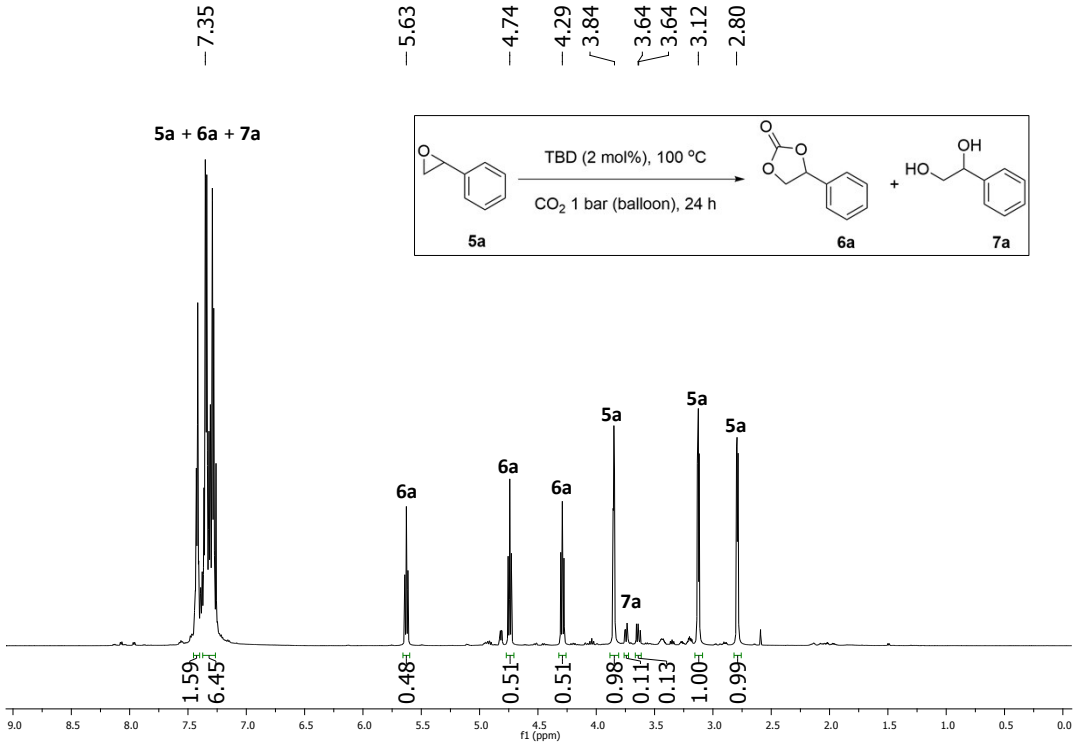


Figure S26. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5a**; **5a** (16.6 mmol), 2 mol% TBD, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 9.

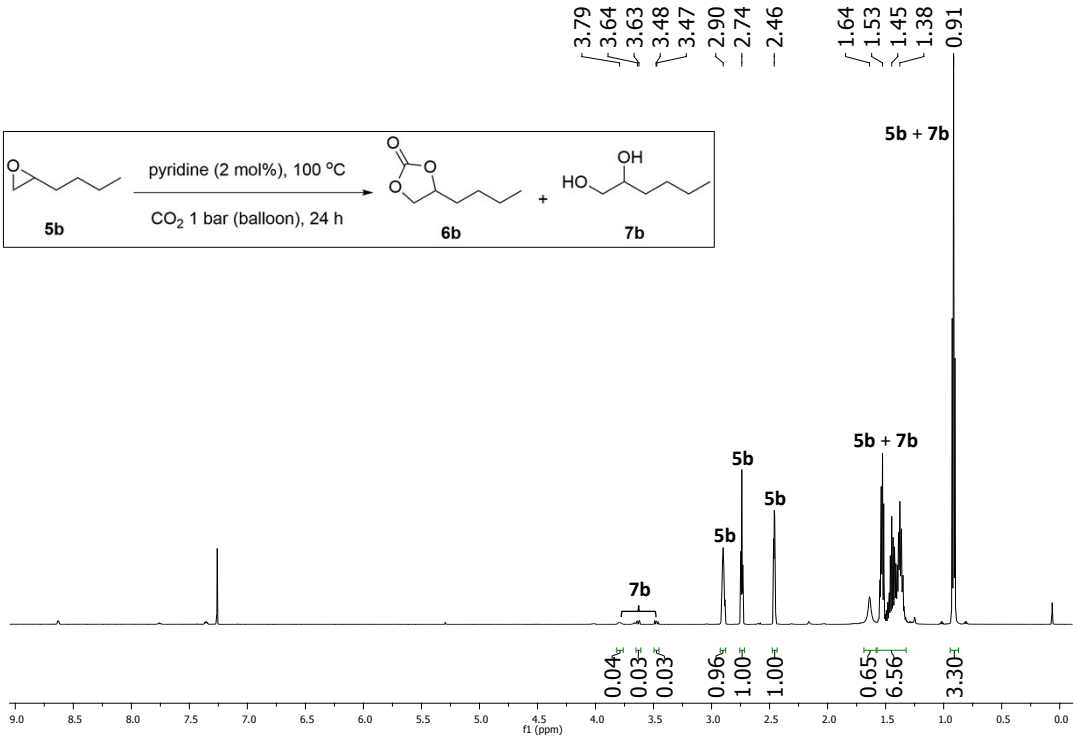


Figure S27. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% pyridine, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 1.

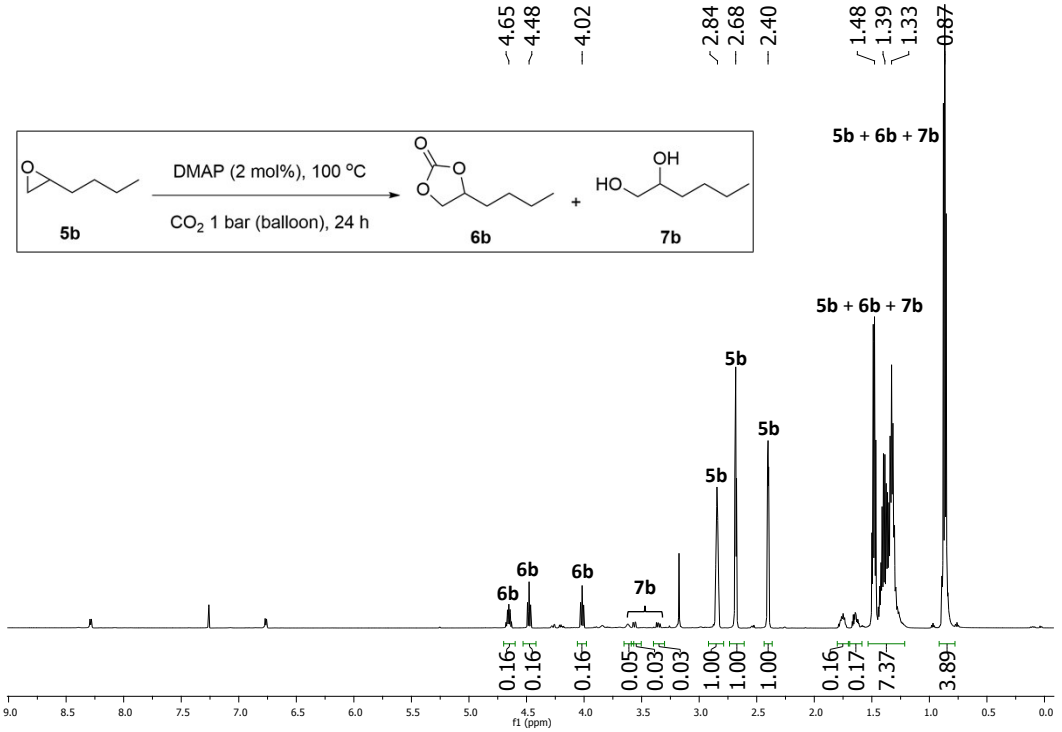


Figure S28. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% DMAP, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 2.

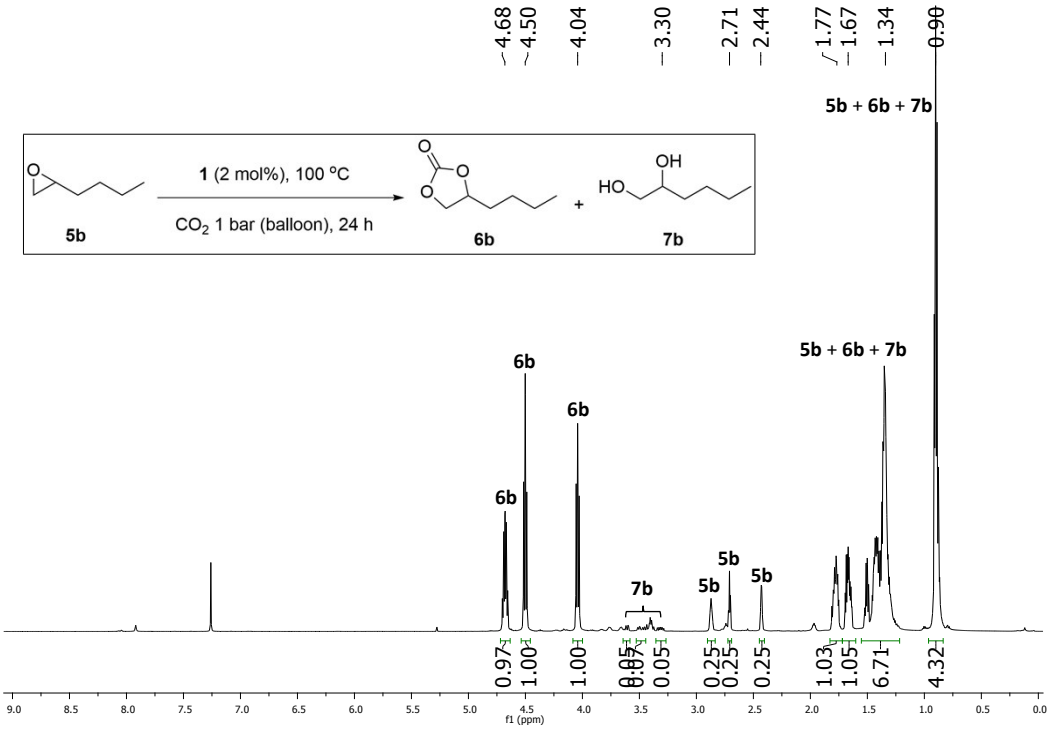


Figure S29. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% **1**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 3.

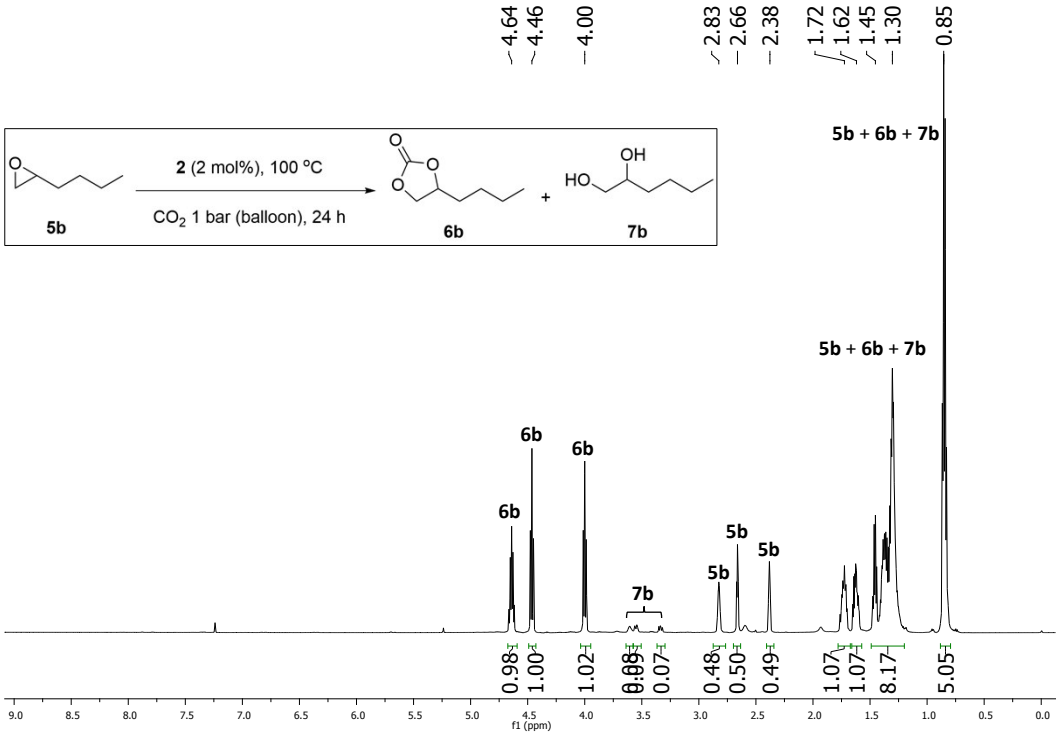


Figure S30. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% **2**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 4.

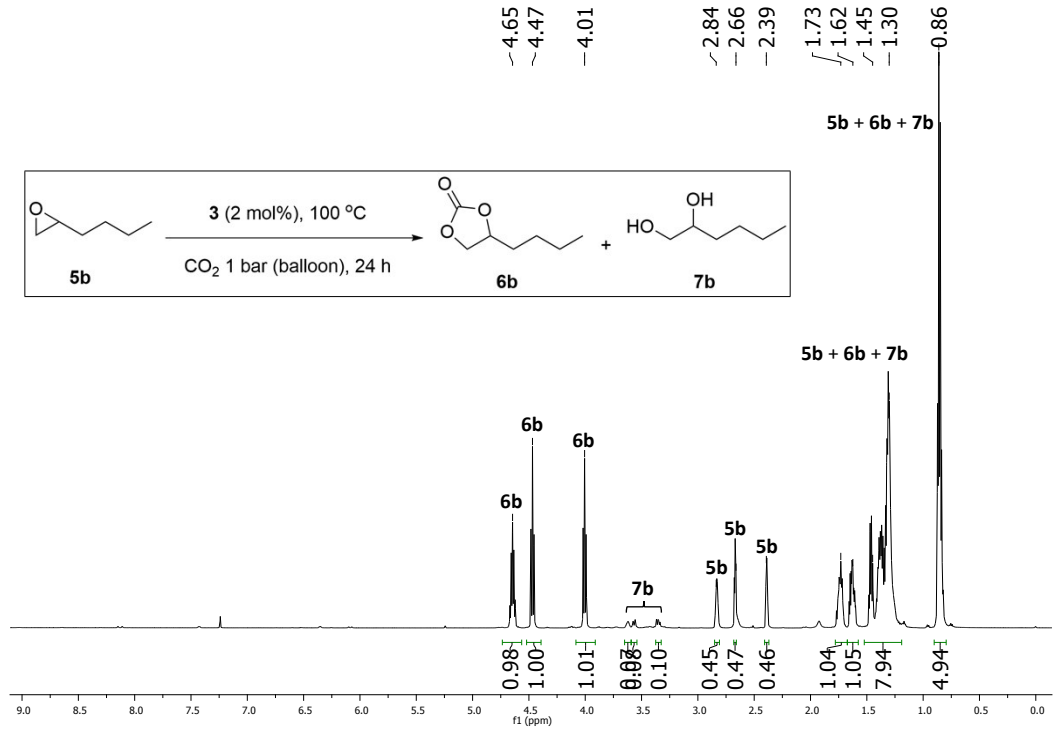


Figure S31. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% **3**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 5.

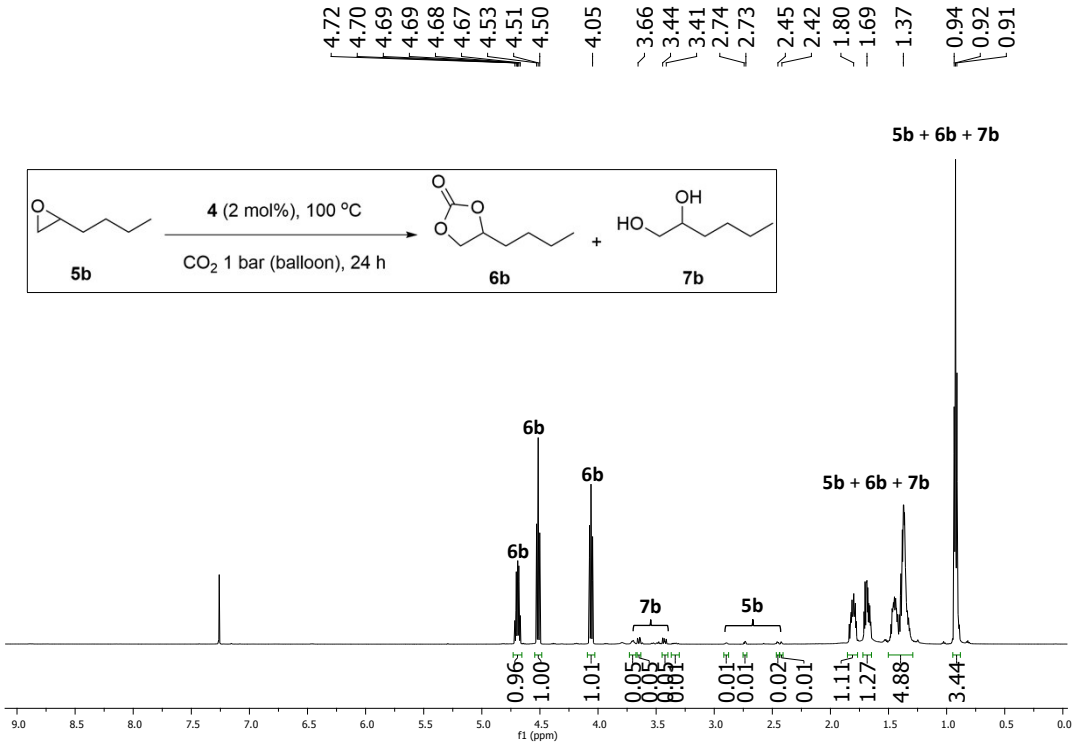


Figure S32. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 6.

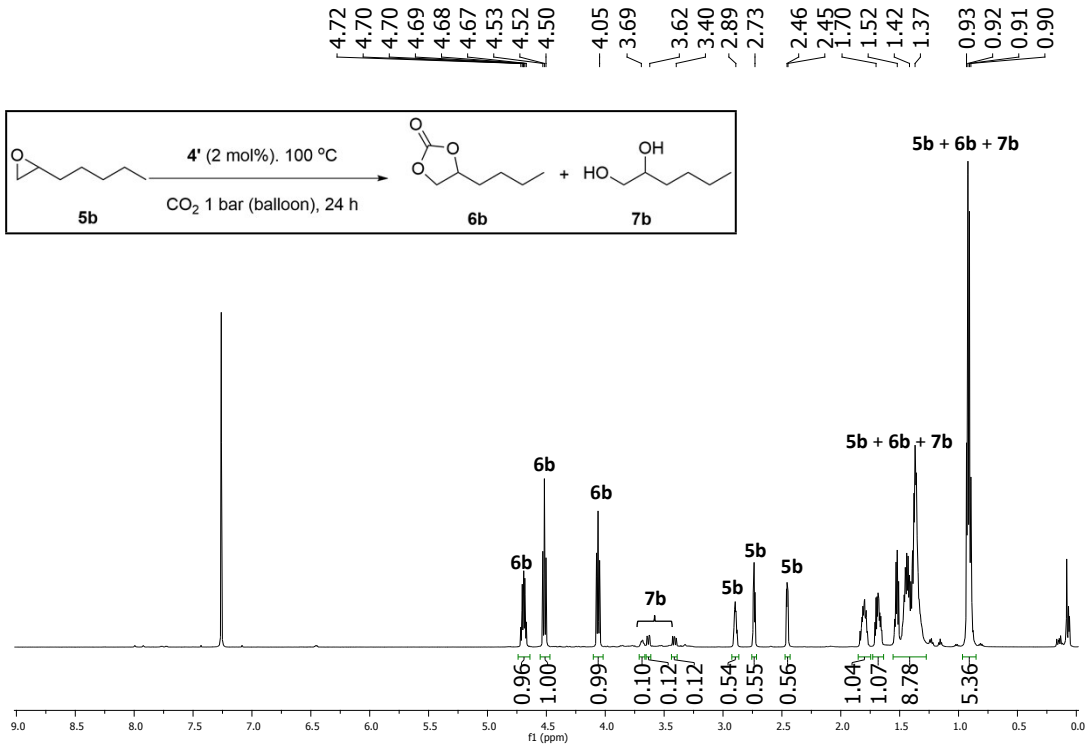


Figure S33. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% **4'**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 7.

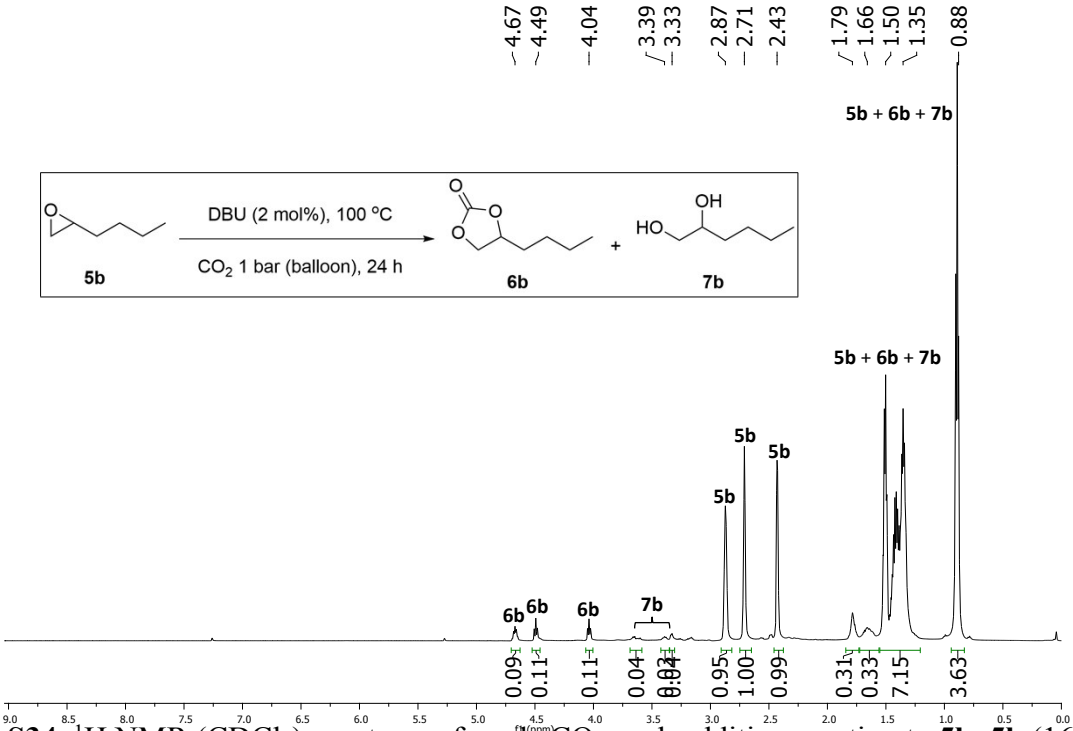


Figure S34. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% DBU, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 8.

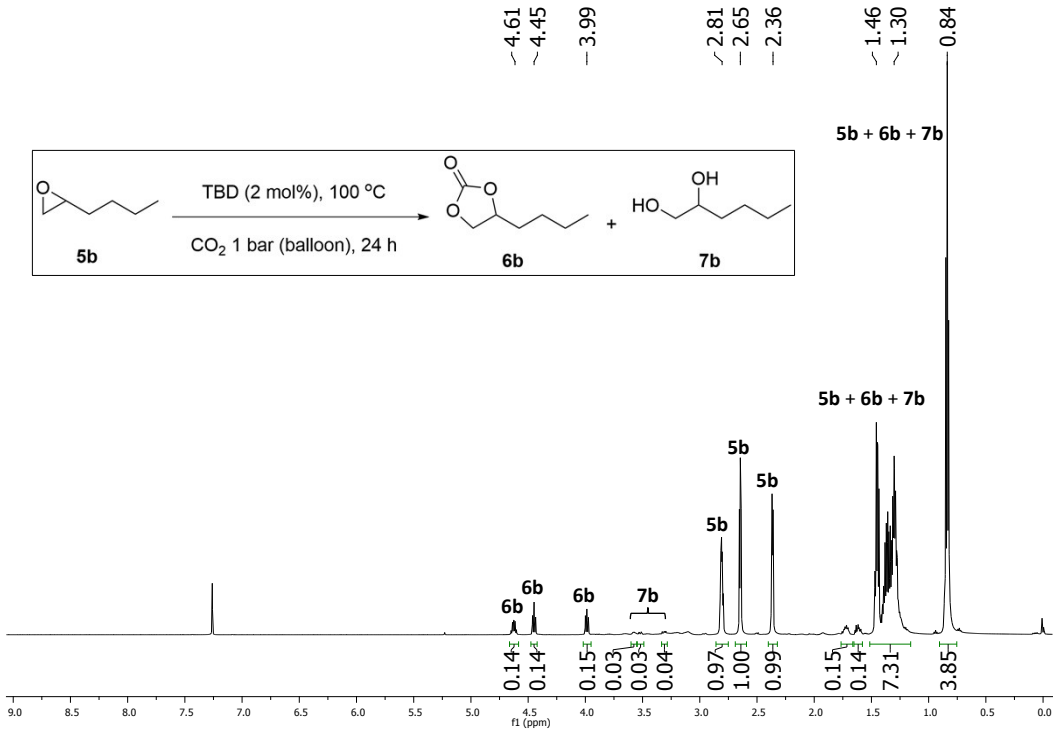


Figure S35. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5b**; **5b** (16.6 mmol), 2 mol% TBD, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 1, Entry 9.

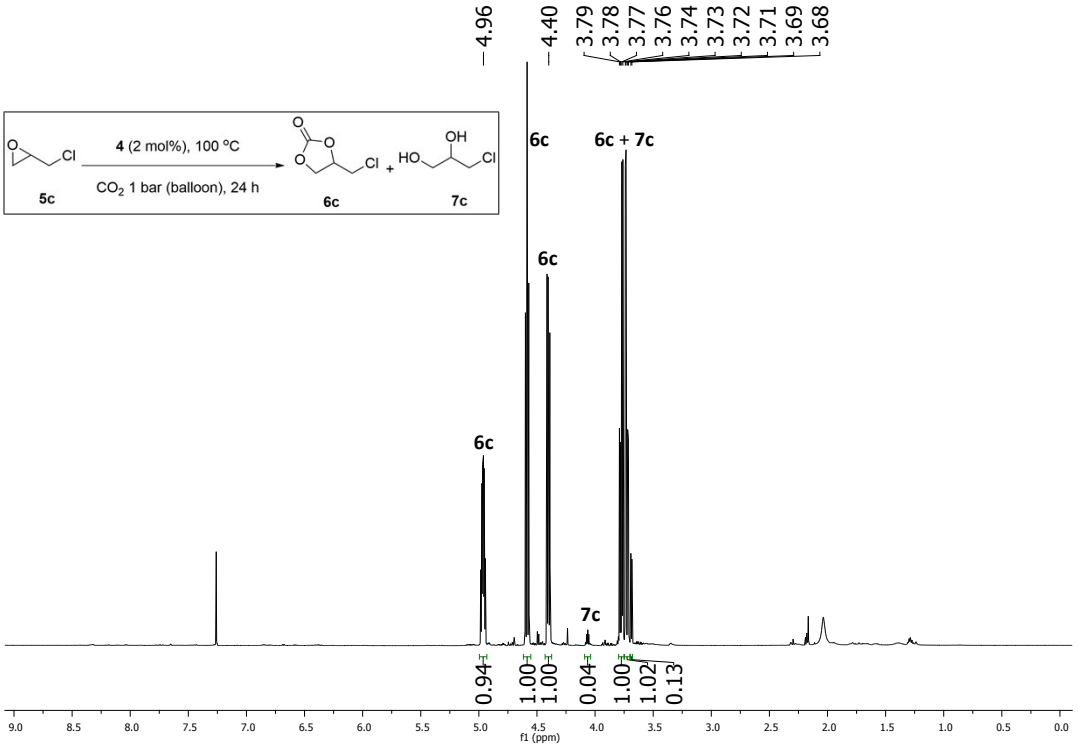


Figure S36. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5c**; **5c** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 2, Entry 3.

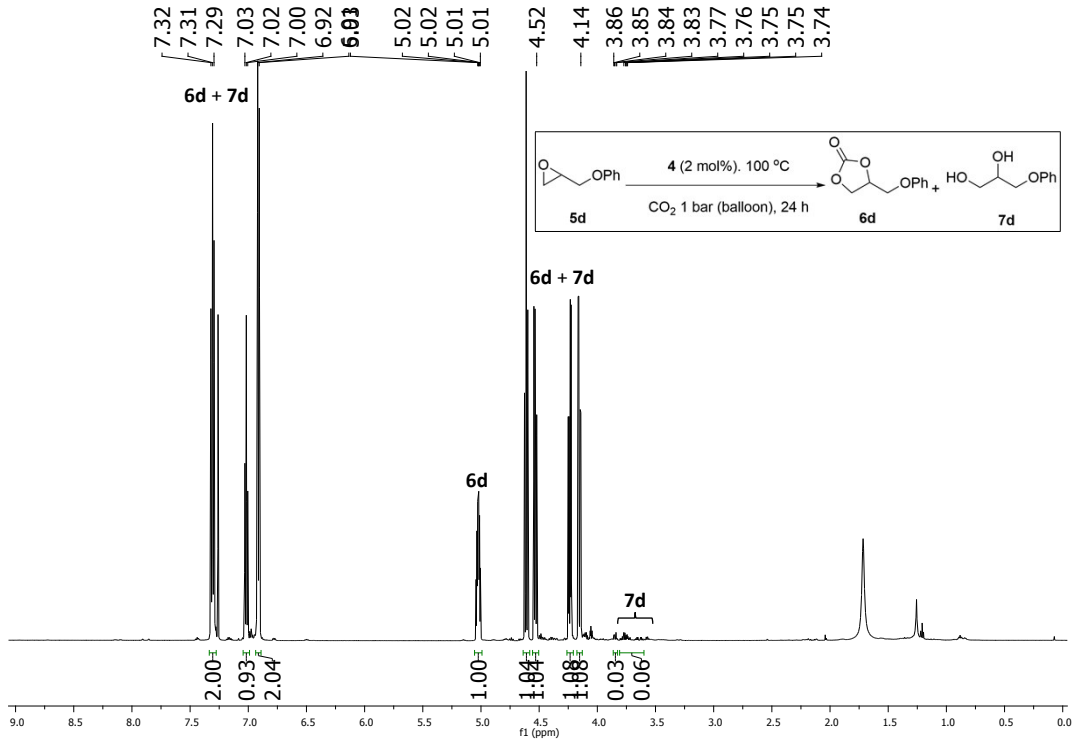


Figure S37. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5d**; **5d** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 2, Entry 4.

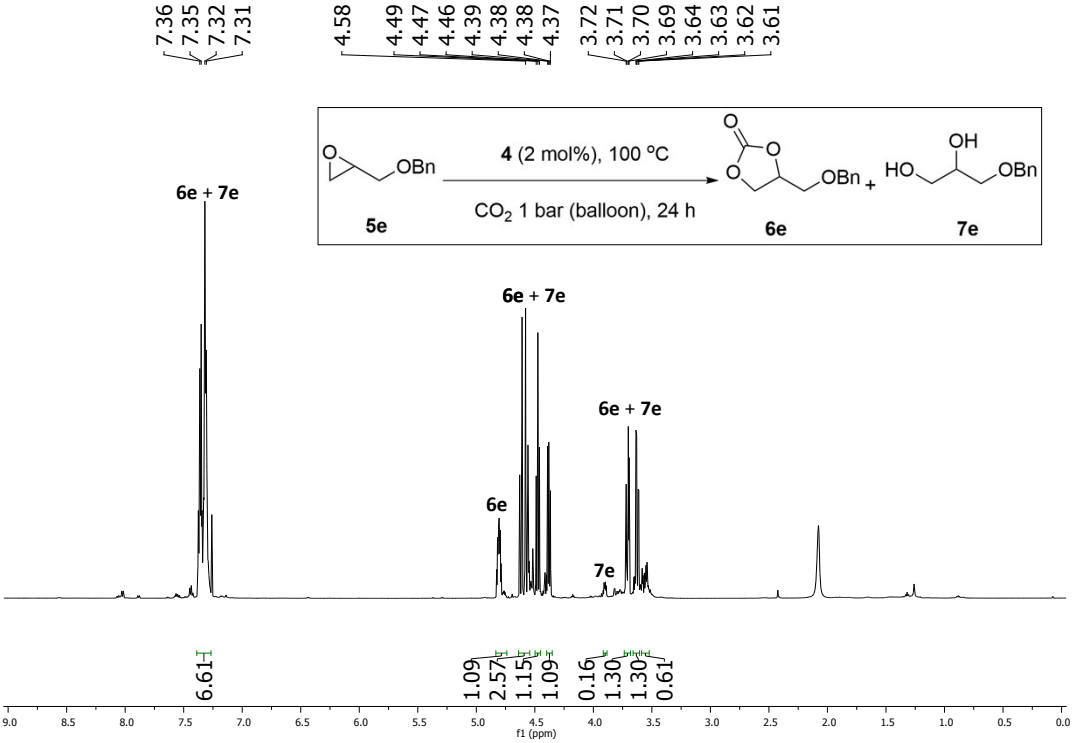


Figure S38. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5e**; **5e** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 2, Entry 5.

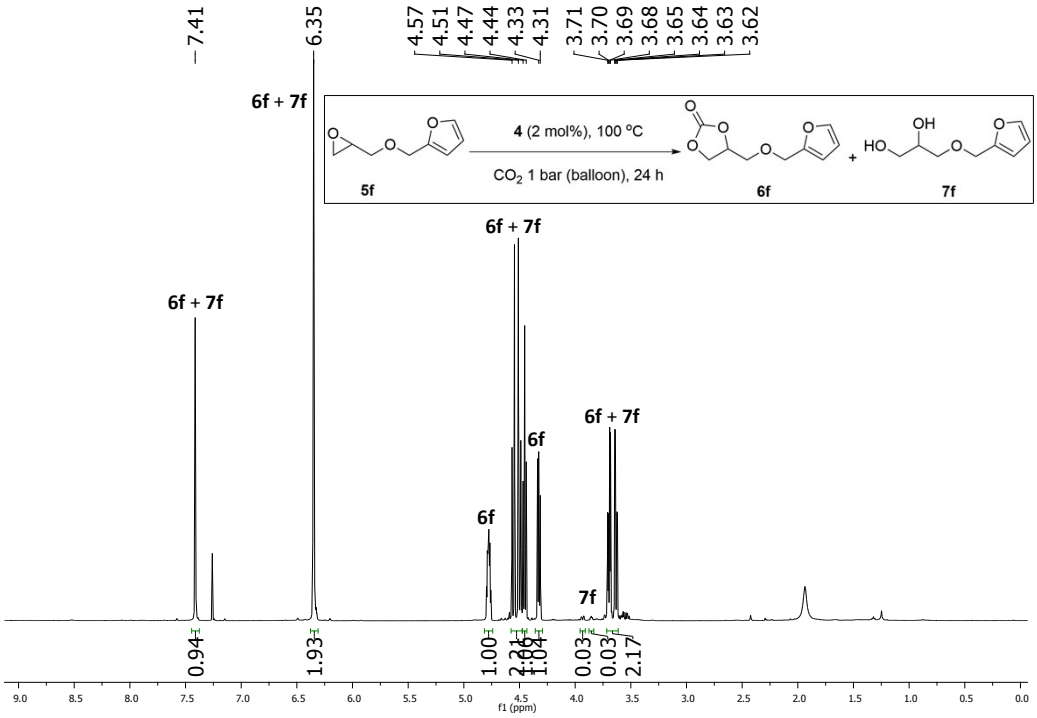


Figure S39. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5f**; **5f** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 2, Entry 6.

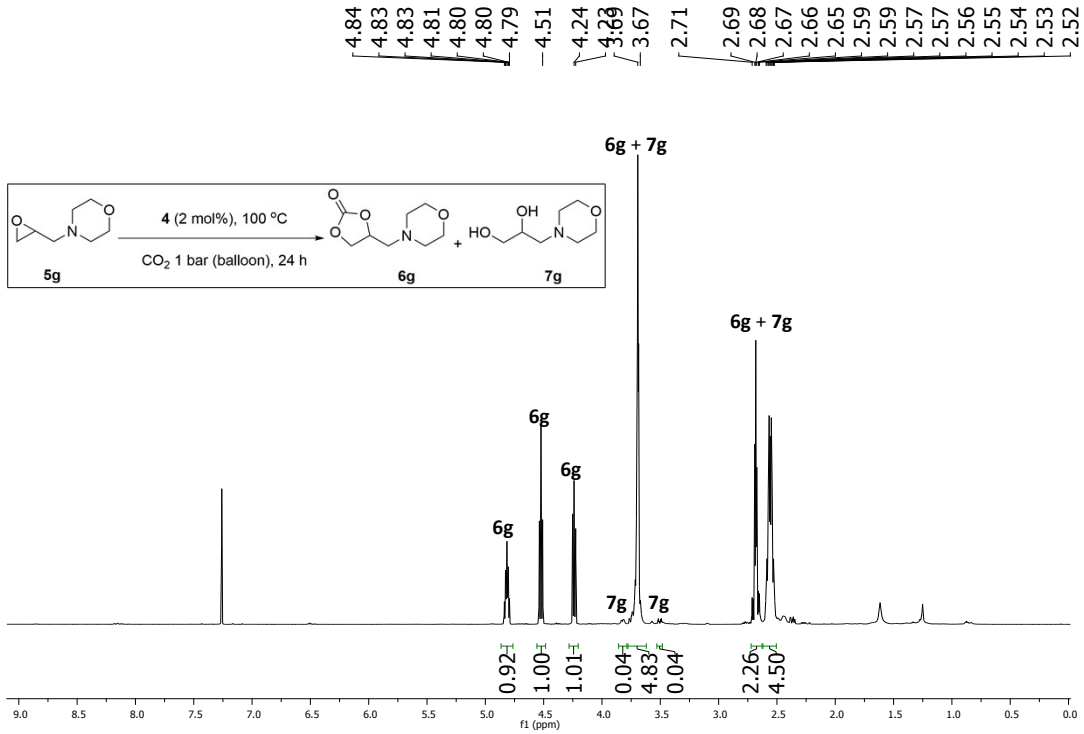


Figure S40. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5g**; **5g** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 2, Entry 7.

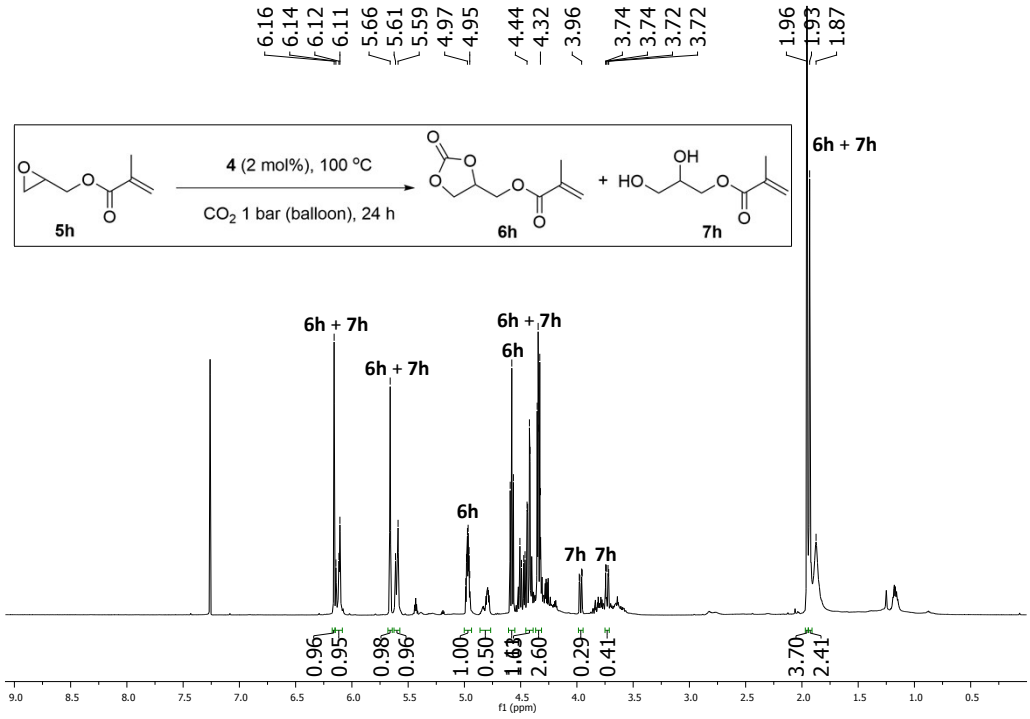


Figure S41. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5h**; **5h** (16.6 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h; Table 2, Entry 8.

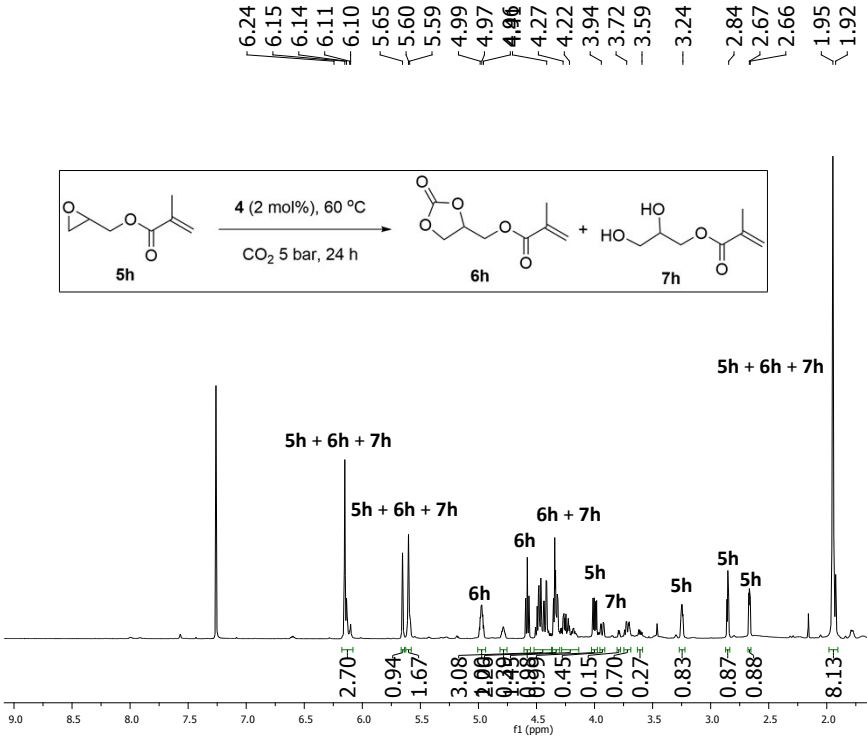


Figure S42. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5h**; **5h** (16.6 mmol), 2 mol% **4**, 60 °C, 5 bar CO_2, 24 h.

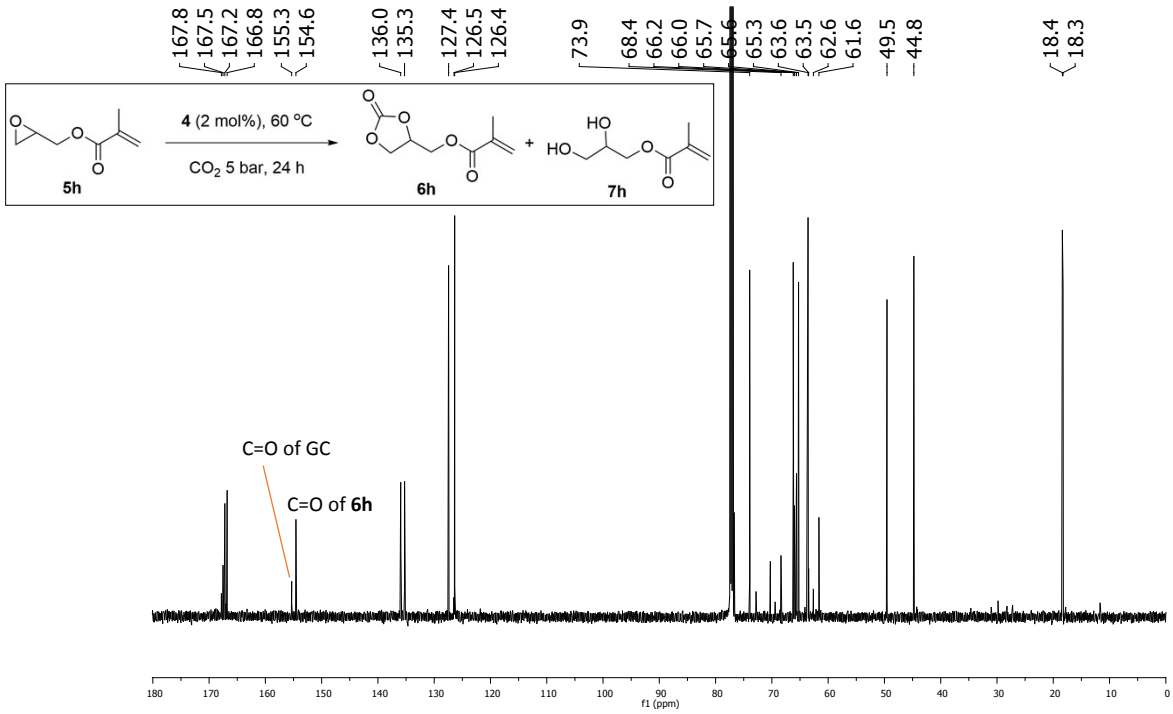
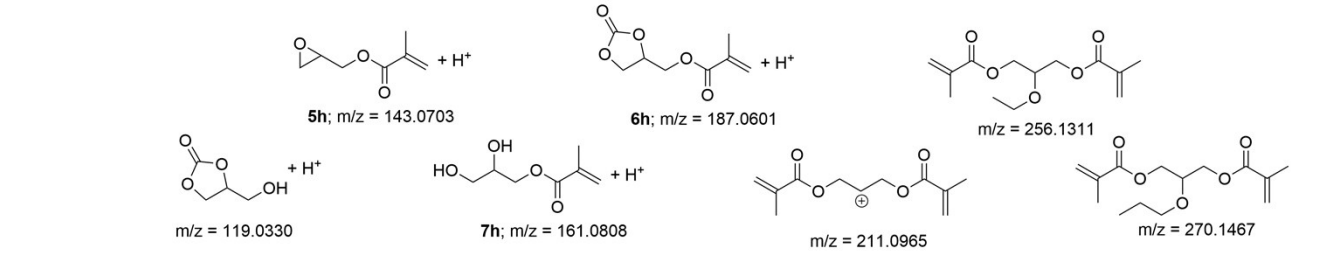


Figure S43. ^{13}C NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5h**; **5h** (16.6 mmol), 2 mol% **4**, 60 °C, 5 bar CO_2, 24 h. (GC: glycerol carbonate).



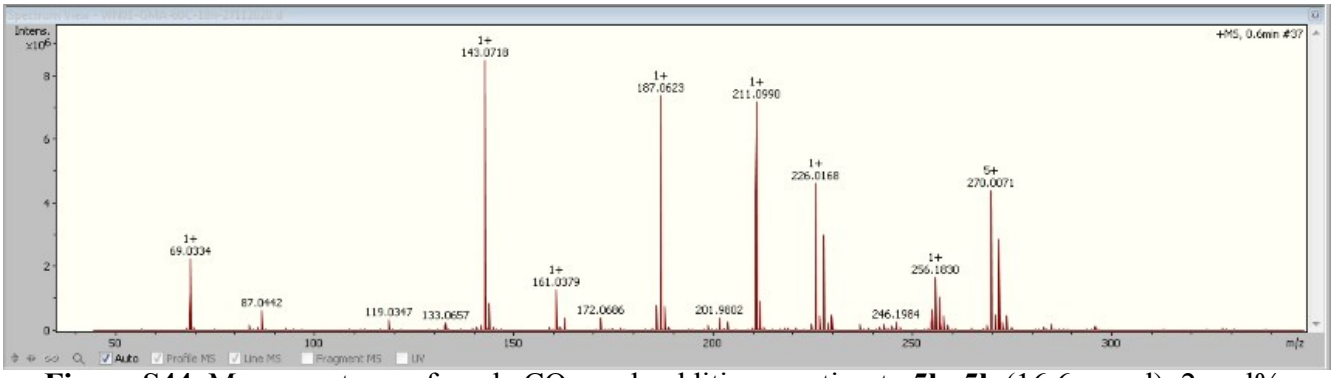
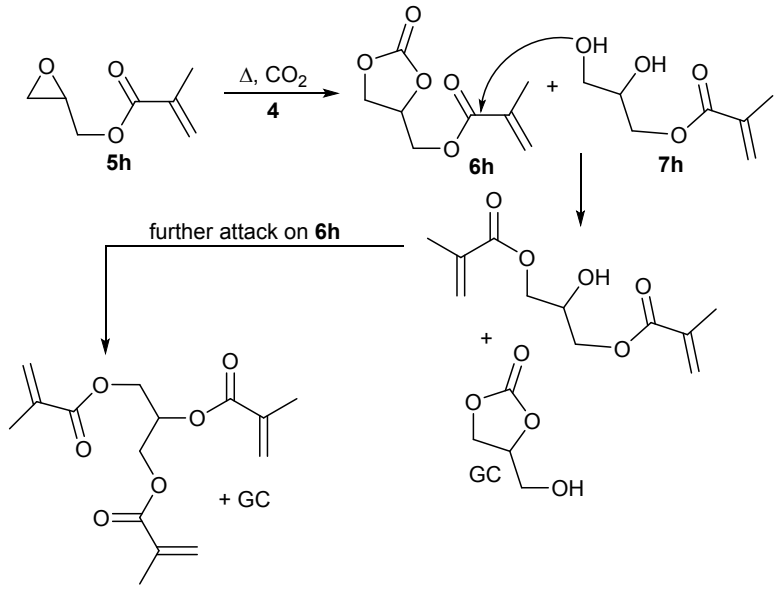


Figure S44. Mass spectrum of crude CO_2 cycloaddition reaction to **5h**; **5h** (16.6 mmol), 2 mol% **4**, 60 °C, 5 bar CO_2, 24 h.



Scheme S3. Possible pathway of formation of the by-products of Figure S44 in the cycloaddition of CO_2 to **5h** catalyzed by **4**.

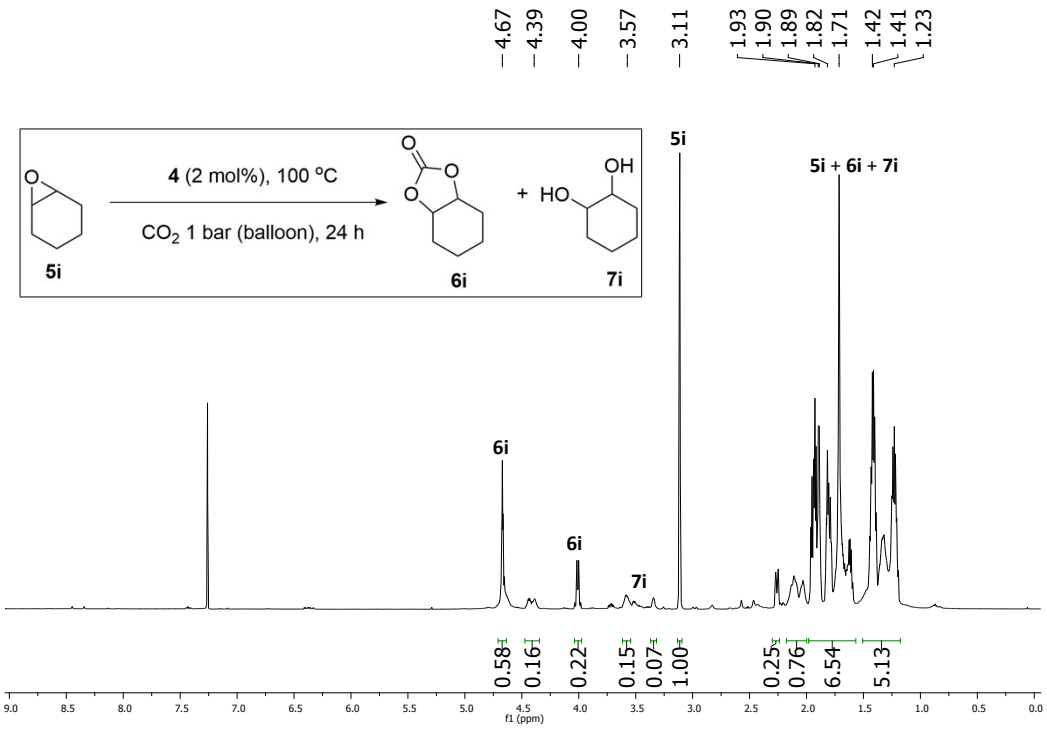

4.67
4.39
4.00
3.57
3.11
1.93
1.90
1.89
1.82
1.71
1.42
1.41
1.23
4 (2 mol%), 100 °C
CO2 1 bar (balloon), 24 h
5i
6i
7i
OH
HO
5i
5i + 6i + 7i
6i
6i
7i
0.58
0.16
0.22
0.15
0.07
1.00
0.25
0.76
6.54
5.13
f1 (ppm)

Figure S45. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5i**; **5i** (16.6 mmol), 2 mol% **4**, 100 °C, 20 bar CO_2, 24 h; Table S2, Entry 2.

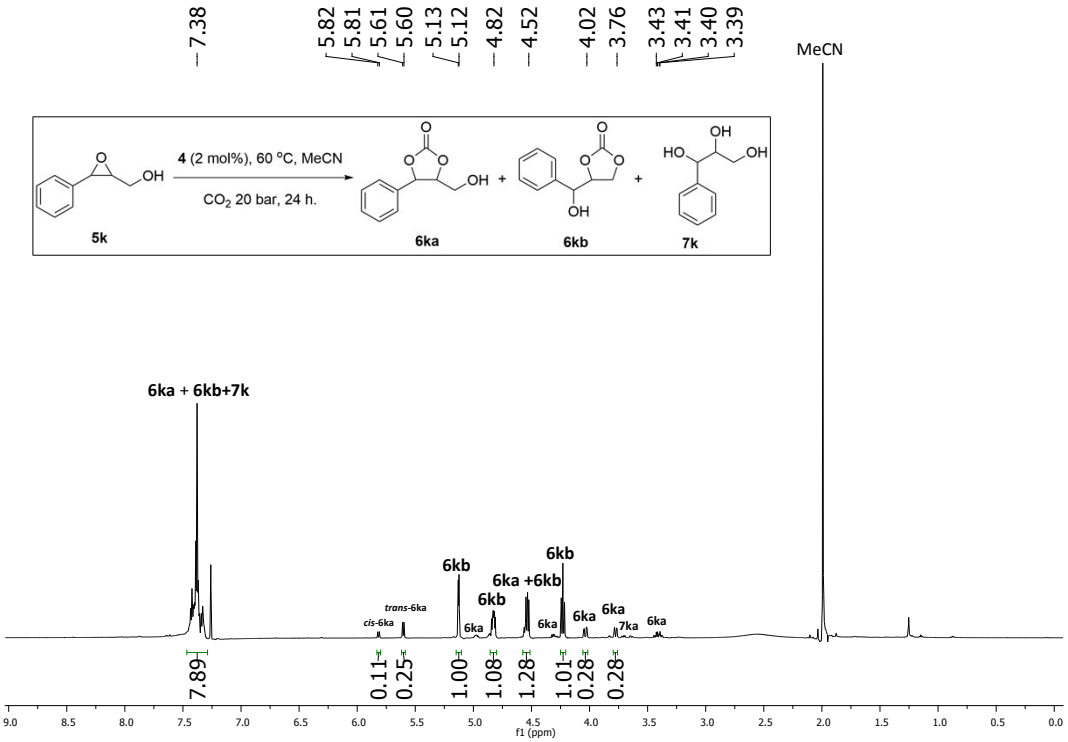


Figure S46. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5k**; **5k** (2 mmol), 2 mol% **4**, 60 °C, 20 bar CO_2, 24 h, acetonitrile 4 mL.

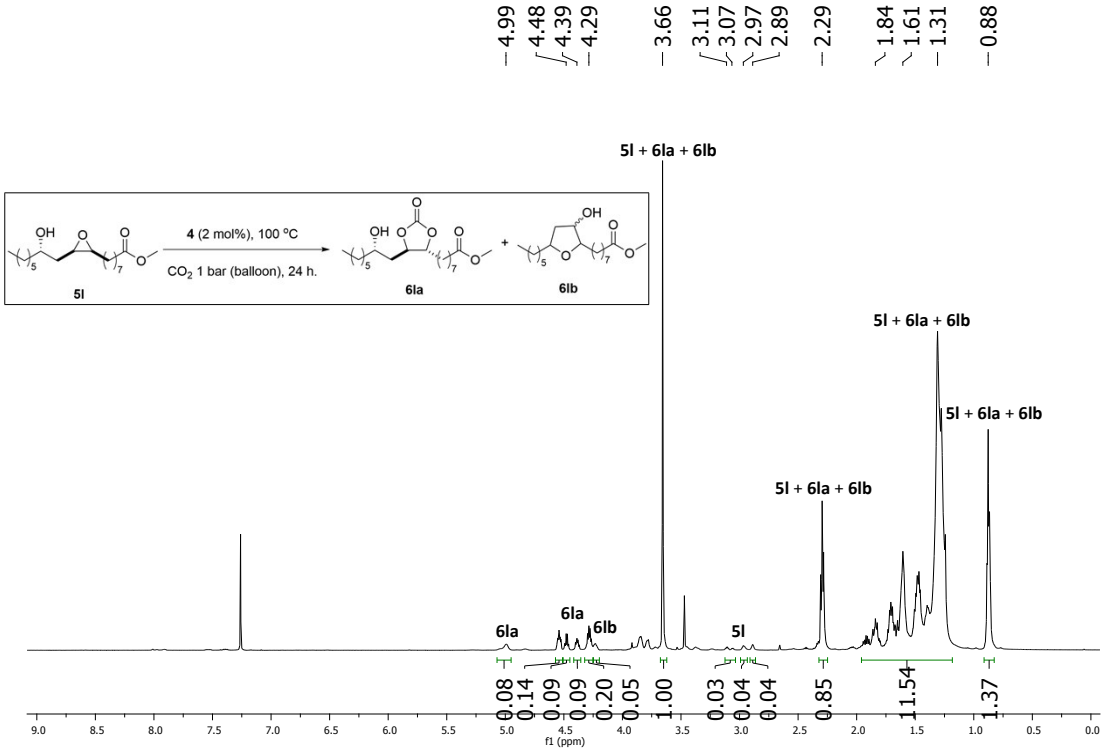


Figure S47. ^{1}H NMR ($CDCl_3$) spectrum of crude CO_2 cycloaddition reaction to **5l**; **5l** (4.2 mmol), 2 mol% **4**, 100 °C, 1 bar CO_2 (balloon), 24 h.

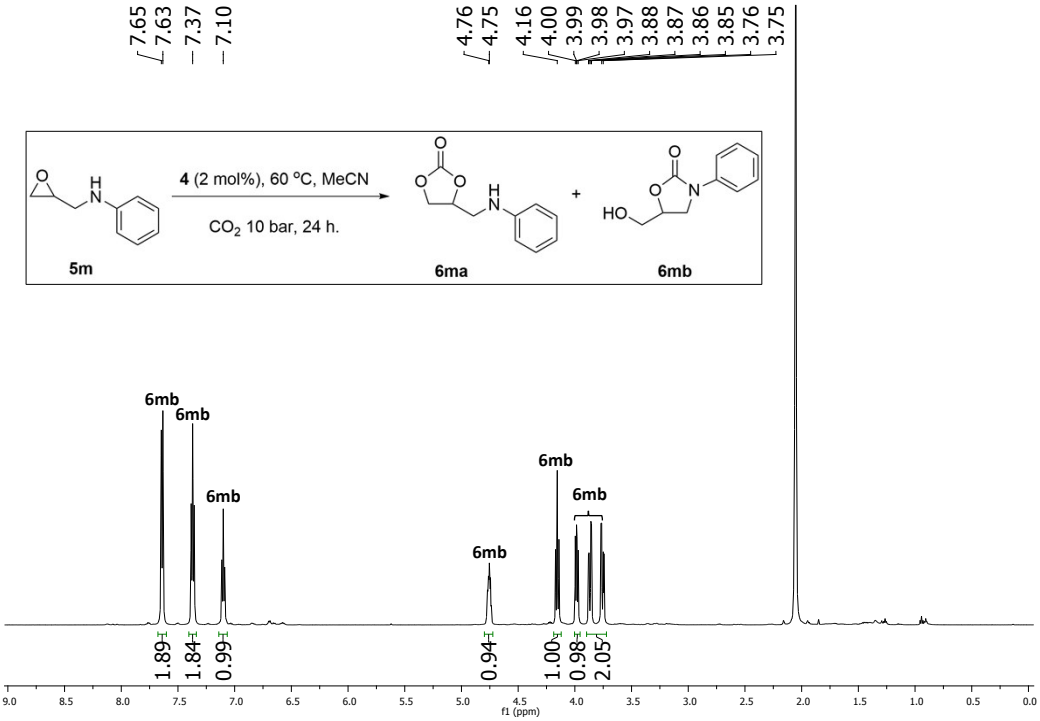


Figure S48. ^{1}H NMR (Acetone-d_6) spectrum of crude CO_2 cycloaddition reaction to **5m**; **5m** (1 mmol), 2 mol% **4**, 60 °C, 10 bar CO_2, 24 h, acetonitrile 2 mL.

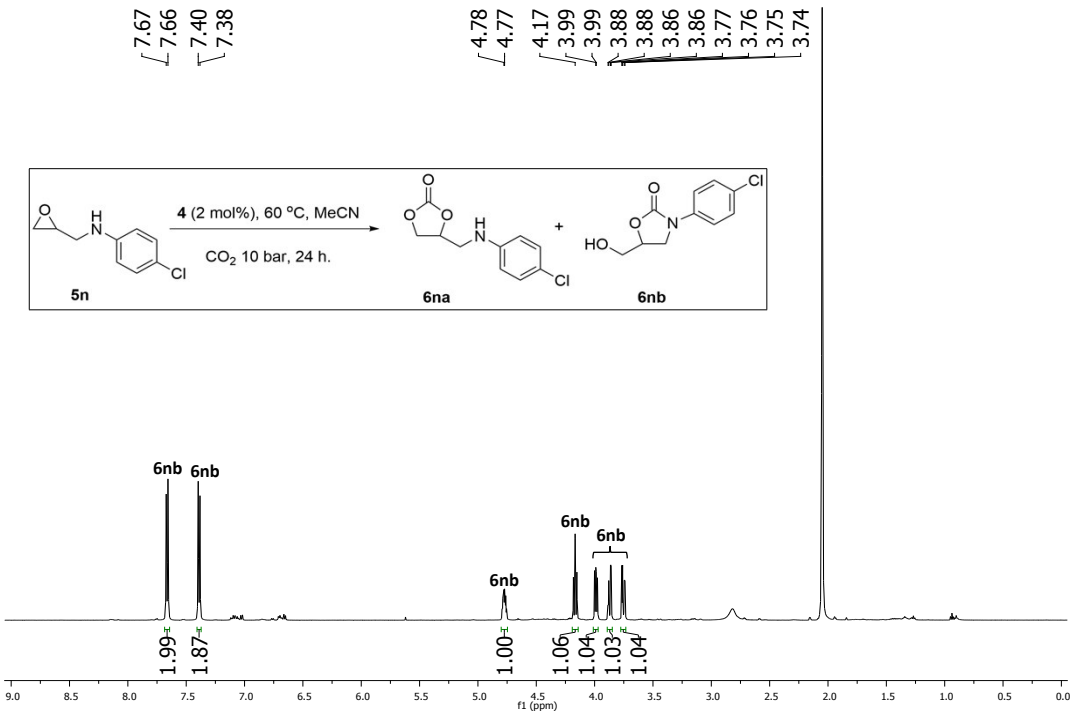
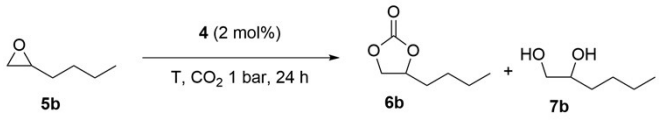


Figure S49. ^{1}H NMR (Acetone-d_6) spectrum of crude CO_2 cycloaddition reaction to **5n**; **5n** (1 mmol), 2 mol% **4**, 60 °C, 10 bar CO_2, 24 h, acetonitrile 2 mL.

S6. Supplementary catalytic results



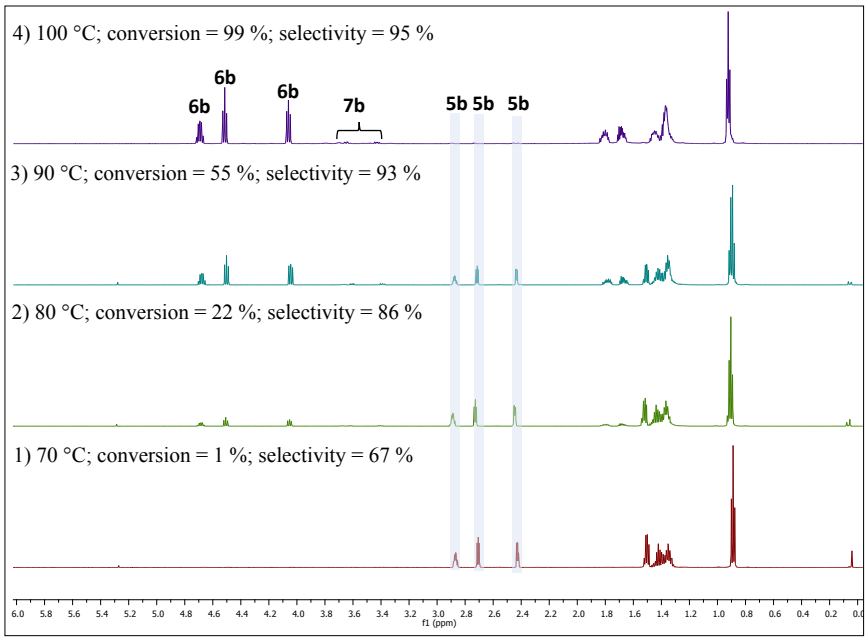


Figure S50. ^{1}H NMR of the cycloaddition of CO_2 to epoxyhexane; **5b** for different reaction temperatures. (catalyst: **4** (2 mol%); P_{CO2} = 1 bar (balloon); 24 h).

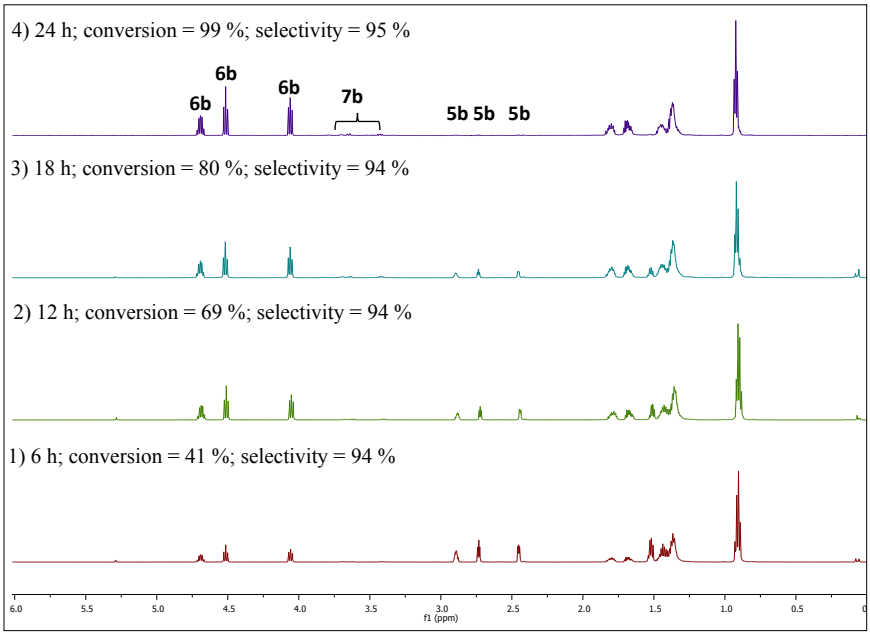
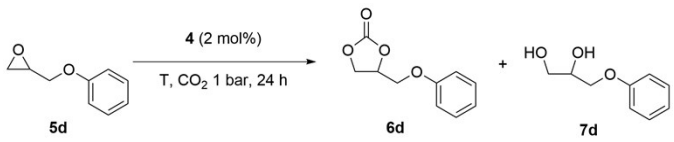


Figure S51. ^{1}H NMR of the cycloaddition of CO_2 to epoxyhexane; **5b** for different reaction times. (catalyst: **4** (2 mol%); P_{CO2} = 1 bar (balloon); 100 °C).



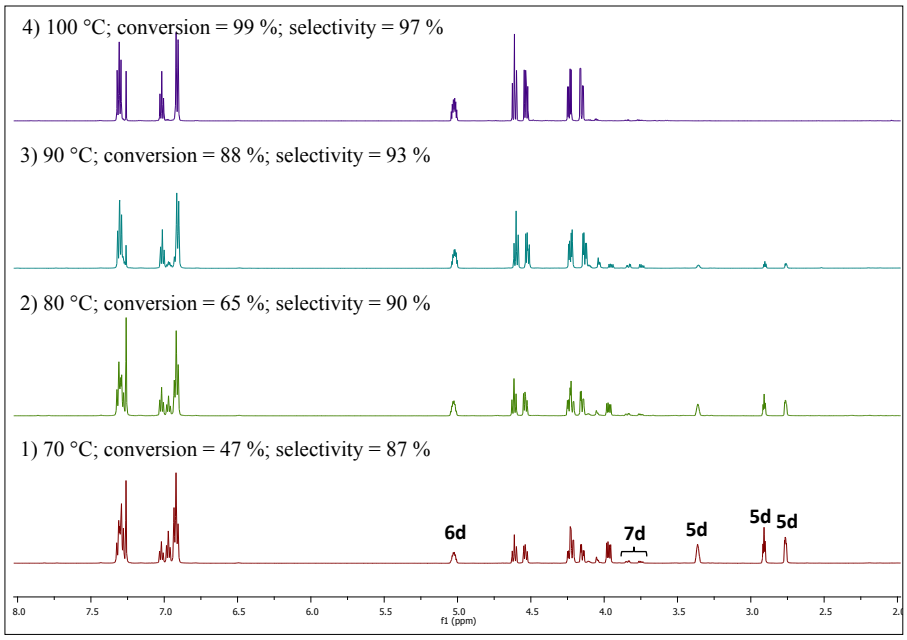


Figure S52. ^{1}H NMR of the cycloaddition of CO_2 to phenyl glycidyl ether; **5d** for different reaction temperatures. (catalyst: **4** (2 mol%); P_{CO2} = 1 bar (balloon); 24 h).

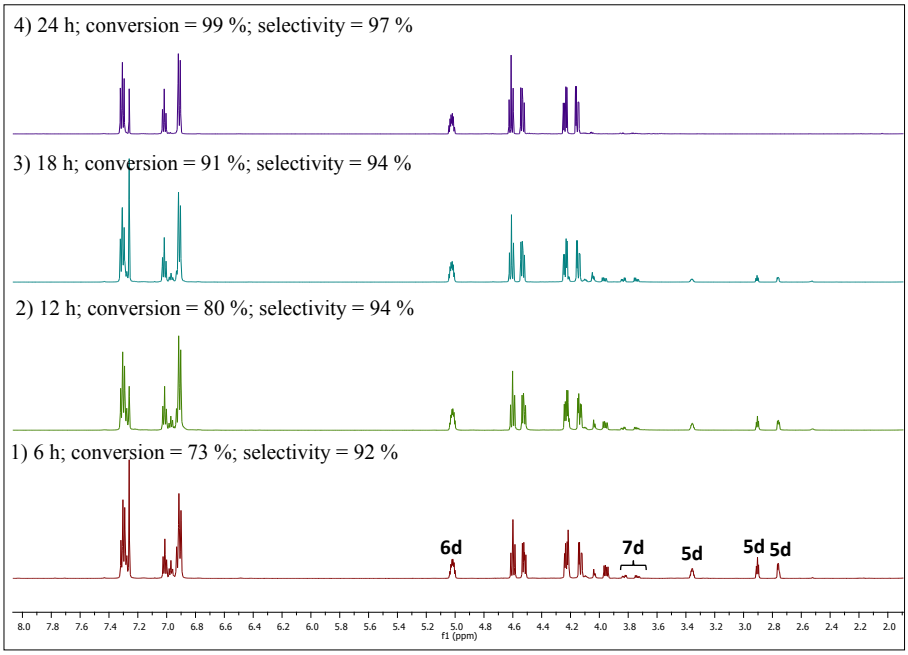
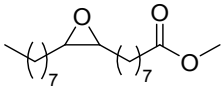
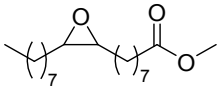


Figure S53. ^{1}H NMR of the cycloaddition of CO_2 to phenyl glycidyl ether; **5d** for different reaction times. (catalyst: **4** (2 mol%); P_{CO2} = 1 bar (balloon); 100 °C).

Table S2. The cycloaddition of CO_2 to internal epoxides. [a]

Entry	Substrate	Pressure of CO_2 (bar)	Conversion of 5[b](%)	Yield (%)[c]
1	 **5i**	1	17	-
2	 **5i**	20	47	18
3	 **5j**	1	0	-
4	 **5j**	20	0	-

[a] Condition: epoxide 16.6 mmol; catalyst **4** (2 mol%, 0.332 mmol, 84.6 mg); 100 °C; 24h; solvent free.

S7. Study of CO_2 interaction with different catalysts by ^{13}C NMR

DMAP, compound **4**, DBU and TBD were dissolved in 5 mL of anhydrous acetonitrile. A CO_2 balloon was connected to the solutions thorough a long needle and CO_2 was bubbled through the solutions for 3 h. In the cases of DBU and TBD, white precipitates formed whereas no precipitate was observed for DMAP and **4**. In the former cases, acetonitrile was dried under vacuum and the solid products were redissolved in D_2O and analyzed by ^{13}C NMR.

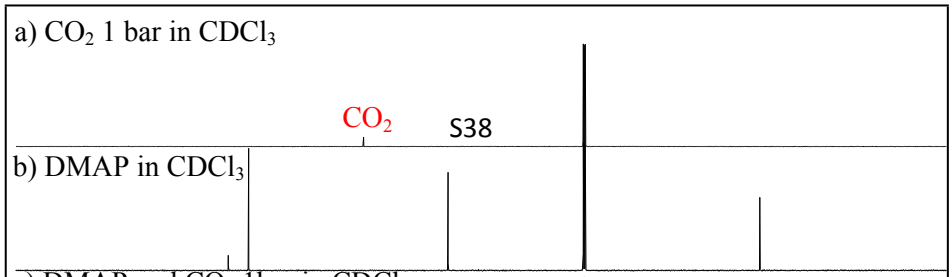


Figure S54. ^{13}C NMR spectra ($CDCl_3$) of a) CO_2, b) DMAP, c) DMAP under 1 bar of CO_2, d) compound **4**, and e) compound **4** under 1 bar of CO_2.

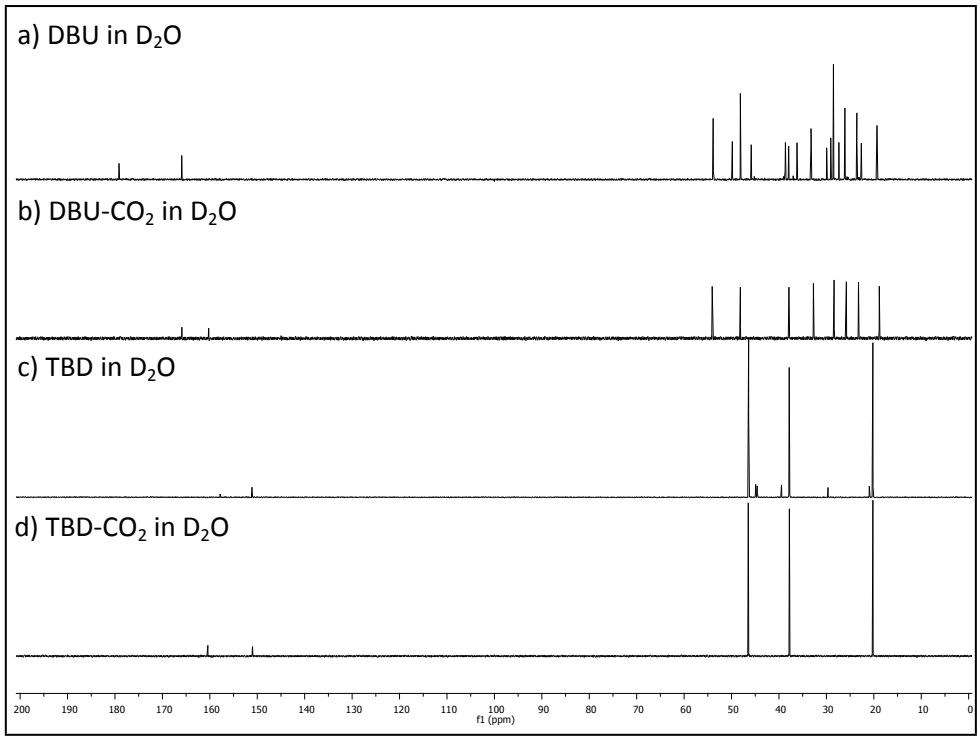


Figure S55. ^{13}C NMR spectra (D_2O) of a) DBU, b) DBU-CO_2, c) TBD and d) TBD-CO_2.

S8. In situ IR spectroscopy: IR signal assignment and kinetic studies in the pyridine asymmetric ring stretching (ARS) region

The measurement of the reaction profiles of: a) interaction between epoxide and catalyst b) the cycloaddition reactions of CO_2 to **5b** was performed by *in-situ IR* spectroscopy (METTLER TOLEDO, ReactIR™ 15): **5b** (16.6 mmol) and compound **4**, 84.6 mg (0.332 mmol) were charged into a 50 mL of Schenck flask equipped with a magnetic stirrer and a fitting for the *in situ* IR probe. The mixture was placed into an oil bath at 100 °C and stirred at 530 rpm. IR spectra were recorded every 30 second for 45 min. After this period, CO_2 was added *via* a rubber balloon and IR spectra still recorded for 2h. (monitored frequency: $\nu_{c=c}$ = 1585 and 1645 cm^{-1}; $\nu_{c=o}$ = 1680, 1814 cm^{-1}).

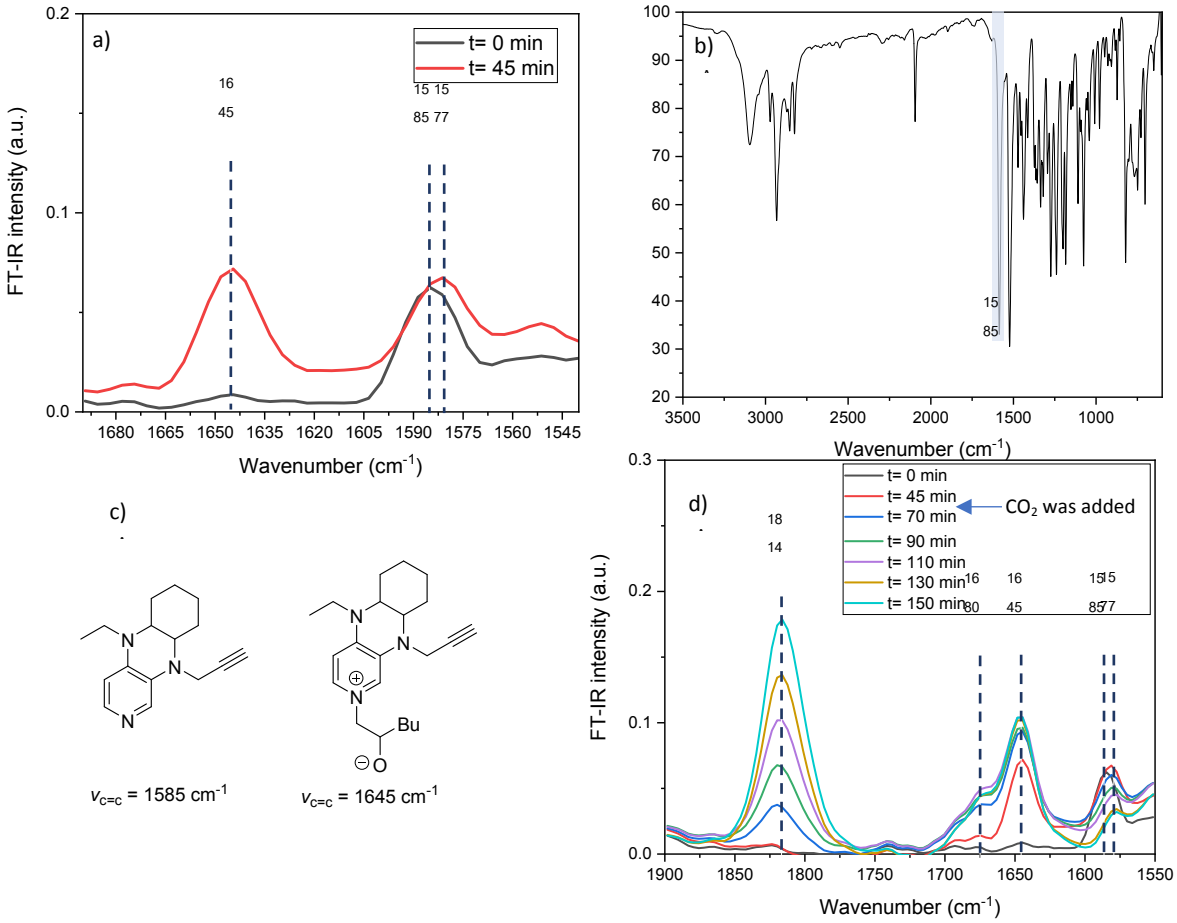
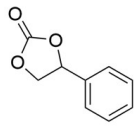
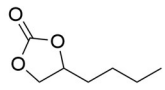


Figure S56. a) IR spectra of the ARS region at t = 0 min (black) and at t = 45 min (red), b) IR spectrum of compound **4**, c) The two different compound **4** species and their corresponding vibrational shifts of the ARS, and d) IR spectra of the ARS region ($\nu_{C=C}$ = 1585 and 1645 cm^{-1}), hemi-carbonate ($\nu_{C=O}$ = 1680 cm^{-1}) and cyclic carbonate ($\nu_{C=O}$ = 1814 cm^{-1}).

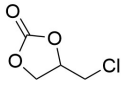
S9. ^{1}H NMR, ^{13}C NMR and mass data of products



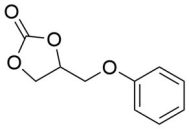
4-Phenyl-1,3-dioxolan-2-one (**6a**). Yellow liquid, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.40 (m, 3H), 7.39-7.33 (m, 2H), 5.67 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 4.34 (t, J = 8.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 135.9, 129.8, 129.4, 126.0, 78.11, 71.3. MS (APCI): calcd for [M+H: $C_9H_8O_3$+H]$^{+}$: 165.0546; found: 165.0548.



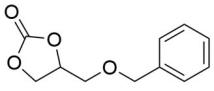
4-Butyl-1,3-dioxolan-2-one (**6b**). Yellow liquid, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.73-4.65 (m, 1H), 4.51 (t, J = 8.1 Hz, 1H), 4.06 (dd, J = 8.2, 7.4 Hz, 1H), 1.85-1.75 (m, 1H), 1.72-1.64 (m, 1H), 1.55-1.30 (m, 4H), 0.92 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 69.5, 33.7, 26.6, 22.4, 13.9. MS (APCI): calcd for [M+H: $C_7H_{12}O_3$+H]$^{+}$: 145.0859; found: 145.0857.



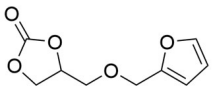
4-(Chloromethyl)-1,3-dioxolan-2-one (**6c**). Yellow liquid, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.00-4.92 (m, 1H), 4.58 (t, J = 8.6 Hz, 1H), 4.40 (dd, J = 8.9, 5.7 Hz, 1H), 3.75 (ddd, J = 15.8, 12.1, 4.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 74.4, 67.1, 43.7. MS (APCI): calcd for [M+H: $C_4H_5ClO_3$+H]$^{+}$: 137.0000; found: 137.0004.



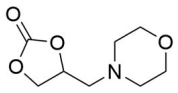
4-(Phenoxymethyl)-1,3-dioxolan-2-one (**6d**). White solid, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, J = 8.0 Hz, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 5.02 (m, 1H), 4.60 (t, J = 8.5 Hz, 1H), 4.52 (dd, J = 8.5, 5.9 Hz, 1H), 4.19 (ddd, J = 53.9, 10.6, 3.9 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9, 154.8, 129.8, 122.1, 114.8, 74.3, 67.1, 66.4. MS (APCI): calcd for [M+H: $C_{10}H_{10}O_4$+H]$^{+}$: 195.0652; found: 195.0649.



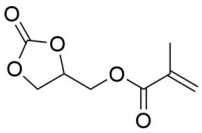
4-((Benzyloxy)methyl)-1,3-dioxolan-2-one (**6e**). Yellow liquid, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.33-7.29 (m, 3H), 4.84-4.77 (m, 1H), 4.59 (dd, J = 30.0, 12.0 Hz, 2H), 4.47 (t, J = 8.4 Hz, 1H), 4.38 (dd, J = 8.2, 6.2 Hz, 1H), 3.67 (ddd, J = 50.4, 10.9, 3.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 137.2, 128.7, 128.2, 127.9, 75.1, 73.9, 69.0, 66.4. MS (APCI): calcd for [M+H: $C_{11}H_{12}O_4$+H]$^{+}$: 209.0808; found: 209.0811.



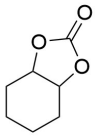
4-((Furan-2-ylmethoxy)methyl)-1,3-dioxolan-2-one (**6f**). Yellow liquid, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 1H), 6.35 (s, 2H), 4.78 (m, 1H), 4.53 (dd, J = 33.9, 13.1 Hz, 2H), 4.45 (t, J = 8.4 Hz, 1H), 4.32 (dd, J = 8.3, 6.2 Hz, 1H), 3.66 (ddd, J = 38.9, 11.0, 4.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 150.8, 143.3, 110.5, 110.2, 75.0, 68.6, 66.4, 65.4. MS (APCI): calcd for [M+H: $C_9H_{10}O_5$+H]$^{+}$: 199.0601; found: 199.0598.



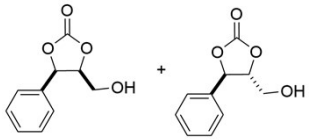
4-(Morpholinomethyl)-1,3-dioxolan-2-one (**6g**). Yellow liquid, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.84-4.77 (m, 1H), 4.51 (t, *J* = 8.3 Hz, 1H), 4.22 (dd, *J* = 8.2, 7.3 Hz, 1H), 3.77-3.60 (m, 4H), 2.71-2.61 (m, 2H), 2.60-2.47 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 75.1, 67.9, 66.9, 60.4, 54.5. MS (APCI): calcd for [M+H: $C_8H_{13}NO_4$+H]$^+$: 188.0917; found: 188.0919.



(2-Oxo-1,3-dioxolan-4-yl)methyl methacrylate (**6h**). Yellow liquid, 39% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.13 (s, 1H), 5.63 (s, 1H), 4.96 (m, 1H), 4.57 (t, *J* = 8.6 Hz, 1H), 4.41 (dd, *J* = 12.6, 3.1 Hz, 1H), 4.36-4.27 (m, 2H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 154.6, 135.3, 127.3, 74.0, 66.2, 63.5, 18.2. MS (APCI): calcd for [M+H: $C_8H_{10}O_5$+H]$^+$: 187.0601; found: 187.0601.

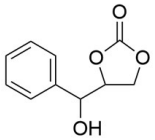


Hexahydrobenzo[*d*][1,3]dioxol-2-one (**6i**). Yellow liquid, 18% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.71-4.60 (m, 1H, *cis* isomer), 4.04-3.93 (m, 1H, *trans* isomer), 2.29-1.00 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 155.1, 83.6, 28.2, 26.7, 23.2, 19.1. MS (APCI): calcd for [M+H: $C_7H_{10}O_3$+H]$^+$: 143.0703; found: 143.0705.

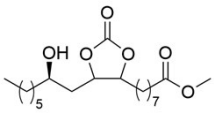


cis:*trans* = 26:74

4-(Hydroxymethyl)-5-phenyl-1,3-dioxolan-2-one (**6ka**). Colorless liquid, 20% yield. ^{1}H NMR (600 MHz, $CDCl_3$) *cis* isomer: δ 7.46-7.40 (m, 3H), 7.35-7.31 (m, 2H), 5.83 (d, *J* = 8.2 Hz, 1H), 4.98 (ddd, *J* = 8.1, 6.2, 4.2 Hz, 1H), 3.47-3.35 (m, 2H). *trans* isomer: δ 7.46-7.40 (m, 3H), 7.38-7.36 (m, 2H), 5.61 (d, *J* = 7.1 Hz, 1H), 4.59-4.56 (m, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 3.79 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 136.0, 132.6, 129.9, 129.7, 129.4, 129.2, 129.1, 127.0, 126.1, 125.9, 83.9, 80.2, 79.5, 79.2, 61.2, 60.9. calcd for [M+H: $C_{10}H_{10}O_4$+H]$^+$: 195.0652; found: 195.0659.

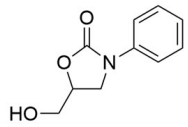


4-(Hydroxy(phenyl)methyl)-1,3-dioxolan-2-one (**6kb**). Colorless liquid, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.34 (m, 5H), 7.34-7.30 (m, 1H), 5.11 (t, *J* = 3.6 Hz, 1H), 4.82 (ddd, *J* = 8.5, 6.4, 3.5 Hz, 1H), 4.52 (dd, *J* = 8.5, 6.4 Hz, 1H), 4.20 (t, *J* = 8.5 Hz, 1H), 3.70 (d, *J* = 4.2 Hz, 1H), 2.13 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 137.3, 129.0, 128.6, 126.0, 79.4, 71.7, 64.7. MS (APCI): calcd for [M+H: $C_{10}H_{10}O_4$+H]$^+$: 195.0652; found: 195.0655.

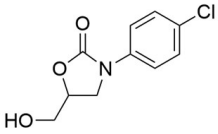


Methyl 8-(5-(2-hydroxyoctyl)-2-oxo-1,3-dioxolan-4-yl)octanoate (**6la**). Yellow oil, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.57-4.25 (m, 2H), 3.87-3.75 (m, 1H), 3.65 (s, 3H), 2.29 (t, *J* = 7.4 Hz, 2H), 2.00-1.20 (m, 44H), 0.86 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 154.8, 154.8, 82.6, 82.2, 80.0, 79.6, 51.6, 41.4, 40.4, 38.3, 37.7, 34.1, 33.7, 33.5, 31.8, 29.3, 29.3, 29.0, 29.0, 28.9, 25.5, 25.4, 24.9, 24.6, 24.6, 22.7,

14.2. MS (APCI): calcd for [M+H: $C_{20}H_{36}O_6$+H]$^+$: 373.2585; found: 373.2584.



5-**(Hydroxymethyl)-3-phenyloxazolidin-2-one** (**6mb**). Yellow solid, 95% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.75 (td, *J* = 9.9, 3.9 Hz, 1H), 4.15 (t, *J* = 8.9 Hz, 1H), 3.98 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.81 (ddd, *J* = 66.3, 12.3, 3.8 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 155.42, 140.13, 129.63, 124.01, 118.62, 74.04, 63.15, 47.04. MS (APCI): calcd for [M+H: $C_{10}H_{11}NO_3$+H]$^+$: 194.0812; found: 194.0814.



3-(4-Chlorophenyl)-5-(hydroxymethyl)oxazolidin-2-one (**6nb**). Pale yellow solid, 91% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.66 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 4.78 (qd, *J* = 7.5, 3.8 Hz, 1H), 4.28 (d, *J* = 112.6 Hz, 1H), 4.16 (d, *J* = 8.9 Hz, 1H), 3.98 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.82 (ddd, *J* = 72.1, 12.3, 3.7 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 155.3, 139.0, 129.5, 128.6, 120.1, 74.2, 63.2, 47.0. MS (APCI): calcd for [M+H: $C_{10}H_{10}ClNO_3$+H]$^+$: 228.0422; found: 228.0425.

S10. Copies of ^{1}H NMR, ^{13}C NMR spectra of products

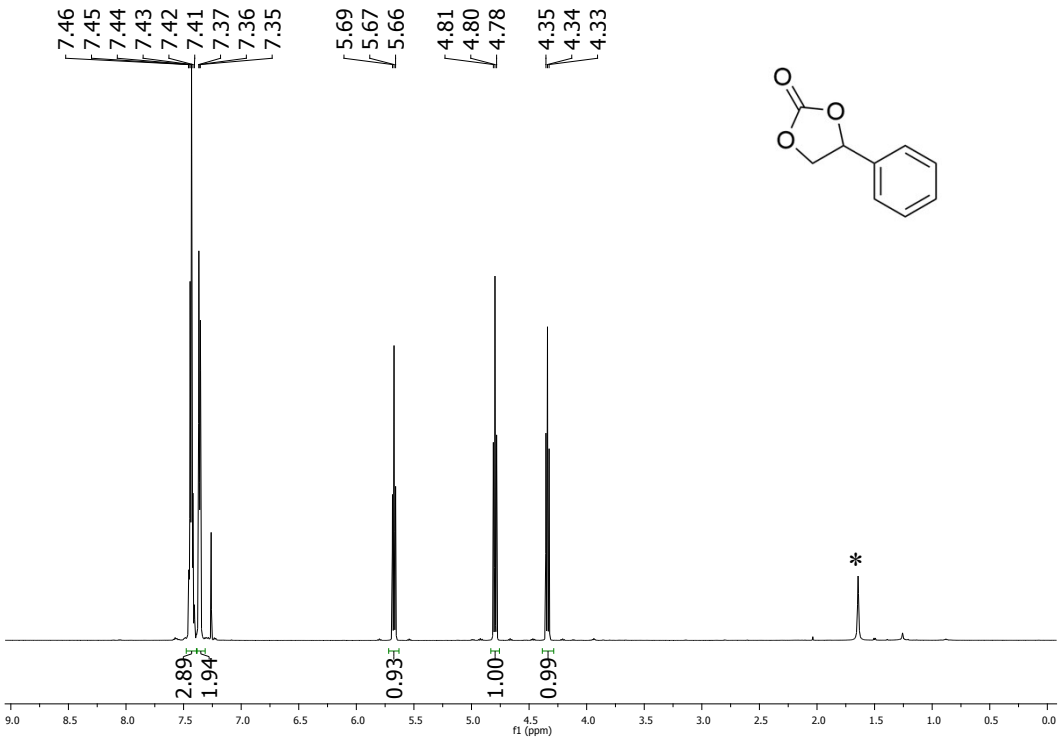


Figure S57. ^{1}H NMR ($CDCl_3$) spectrum of **6a**. (*) signal for residual water in $CDCl_3$.

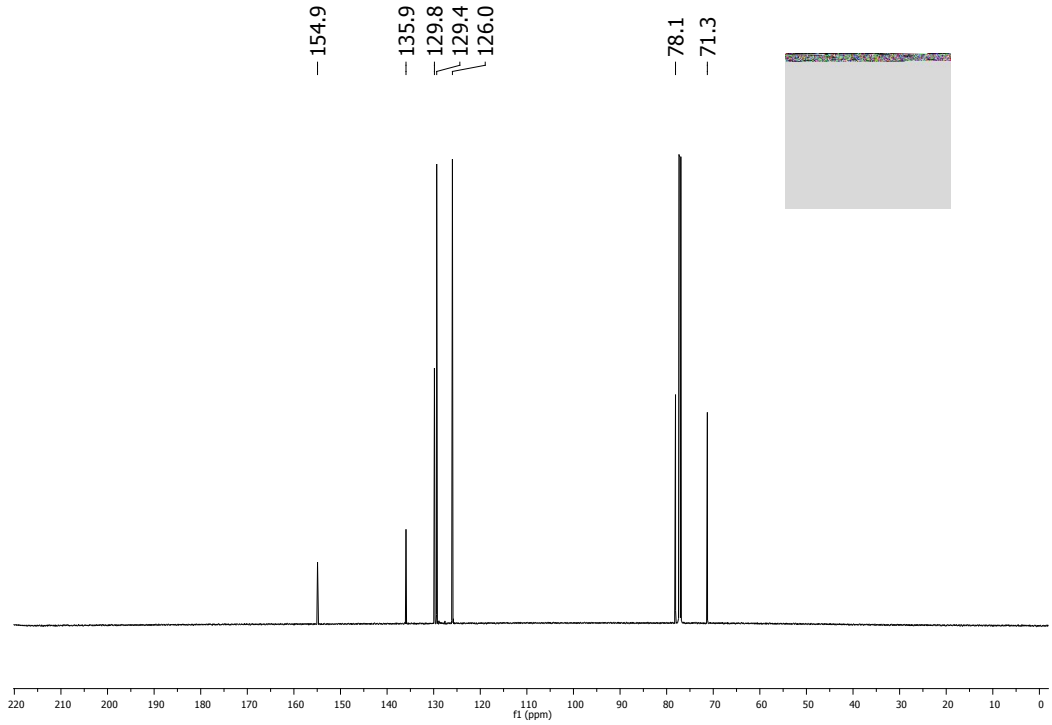


Figure S58. ^{13}C NMR ($CDCl_3$) spectrum of **6a**.

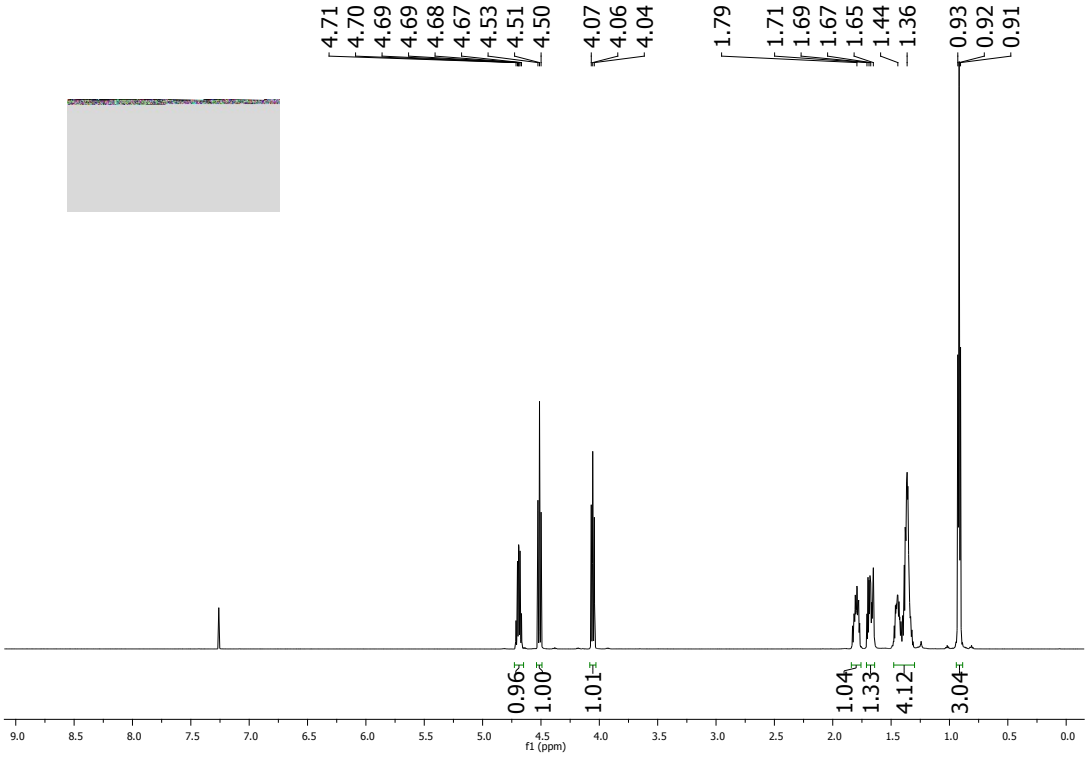


Figure S59. ^{1}H NMR ($CDCl_3$) spectrum of **6b**.

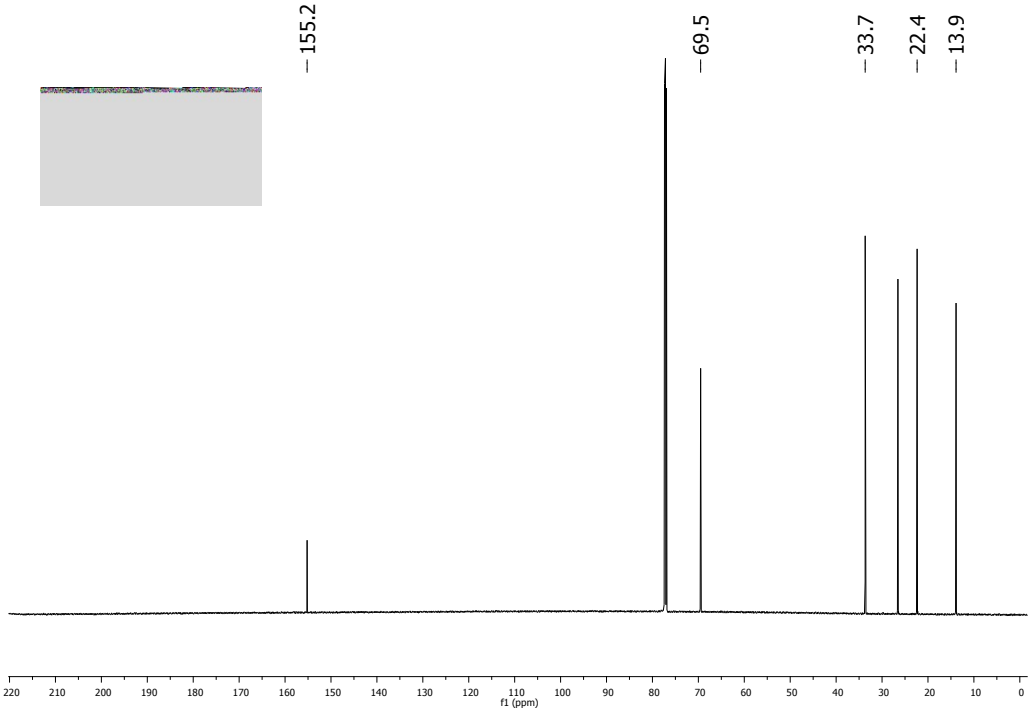


Figure S60. ^{13}C NMR ($CDCl_3$) spectrum of **6b**.

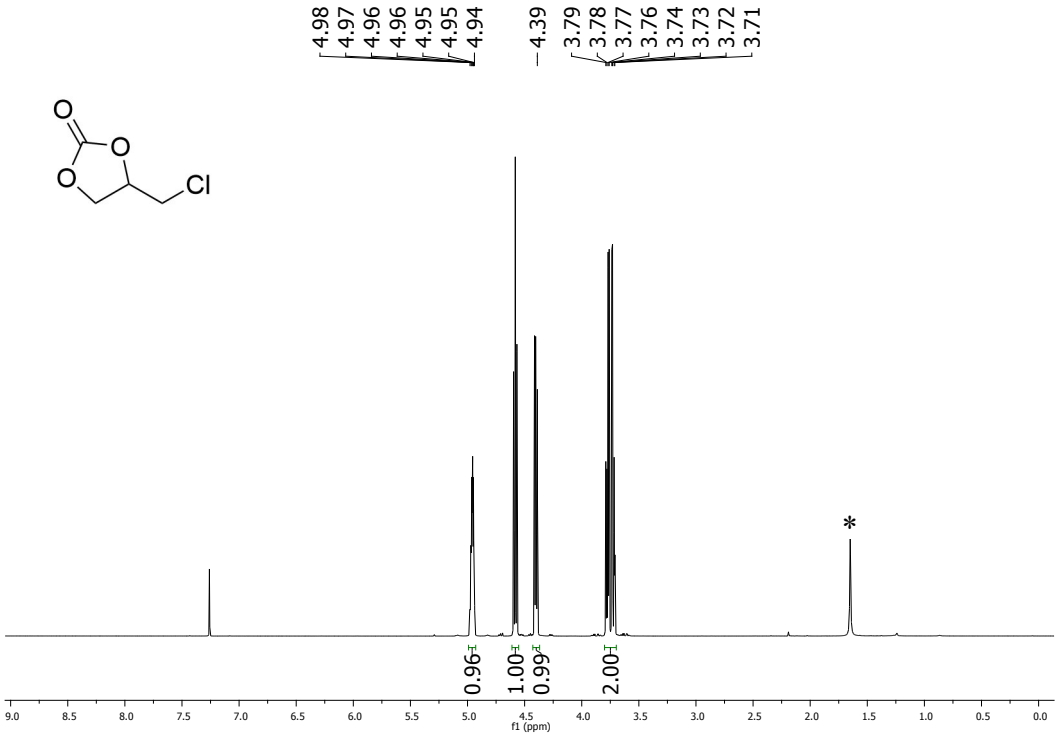


Figure S61. ^{1}H NMR ($CDCl_3$) spectrum of **6c**. (*) signal for residual water in $CDCl_3$.

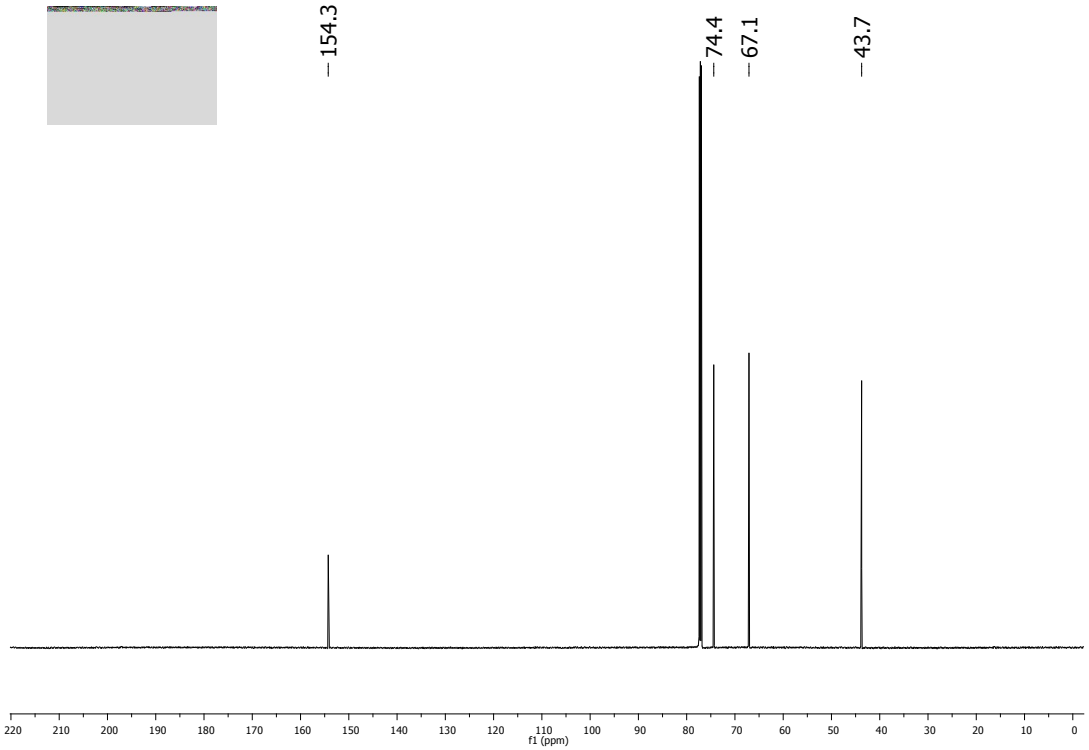


Figure S62. ^{13}C NMR ($CDCl_3$) spectrum of **6c**.

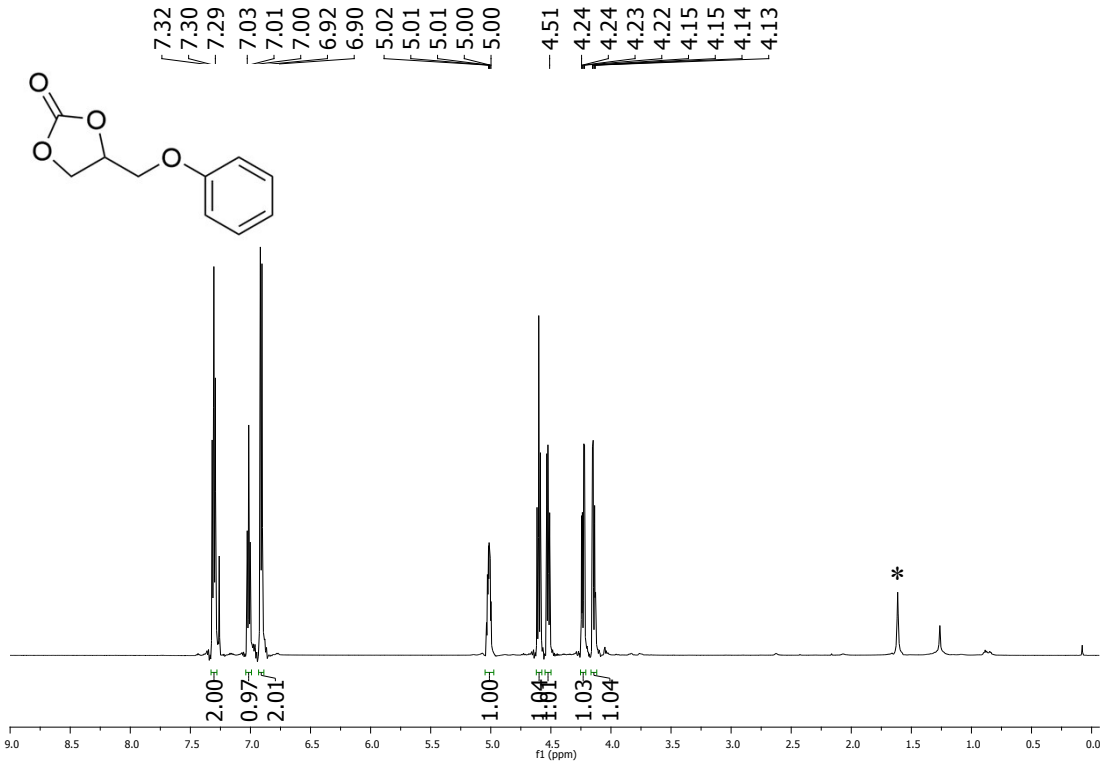


Figure S63. ^{1}H NMR ($CDCl_3$) spectrum of **6d**. (*) signal for residual water in $CDCl_3$.

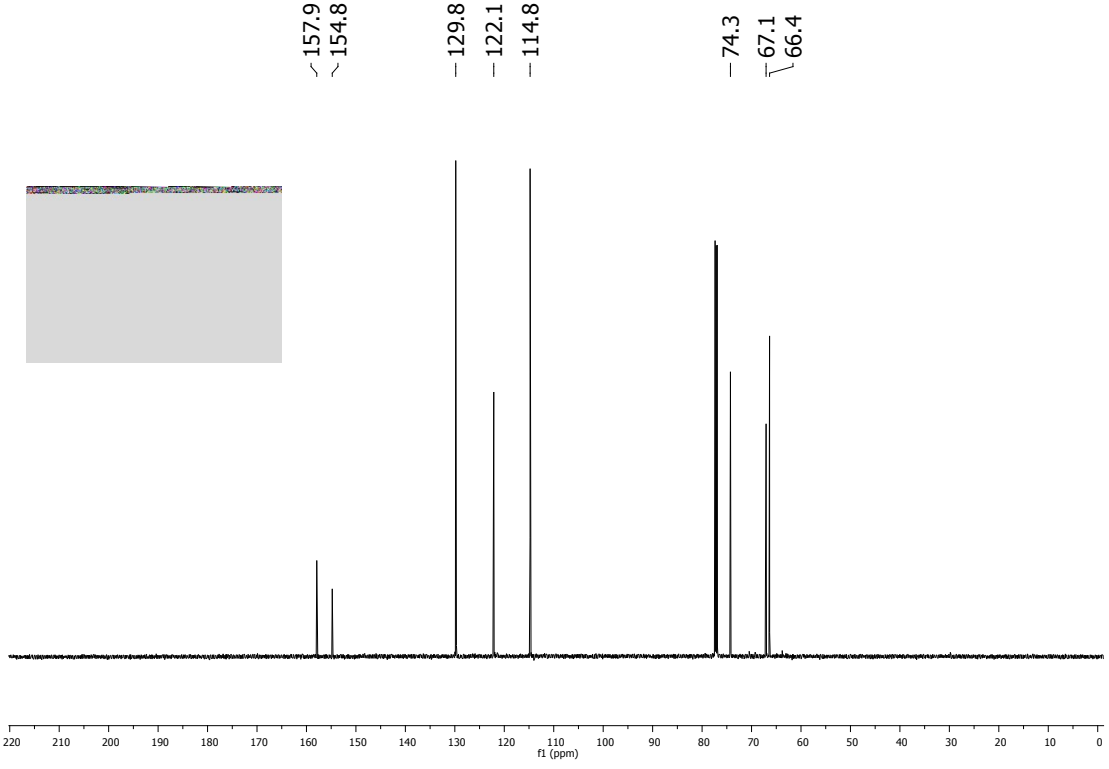


Figure S64. ^{13}C NMR ($CDCl_3$) spectrum of **6d**.

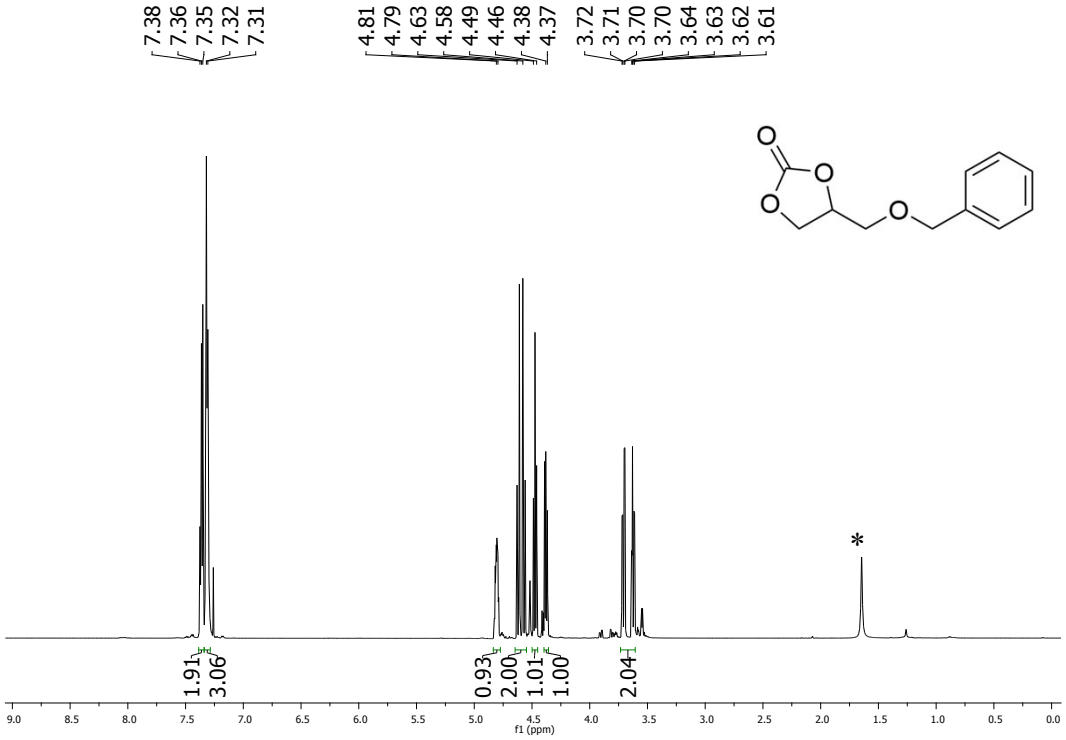


Figure S65. ^{1}H NMR ($CDCl_3$) spectrum of **6e**. (*) signal for residual water in $CDCl_3$.

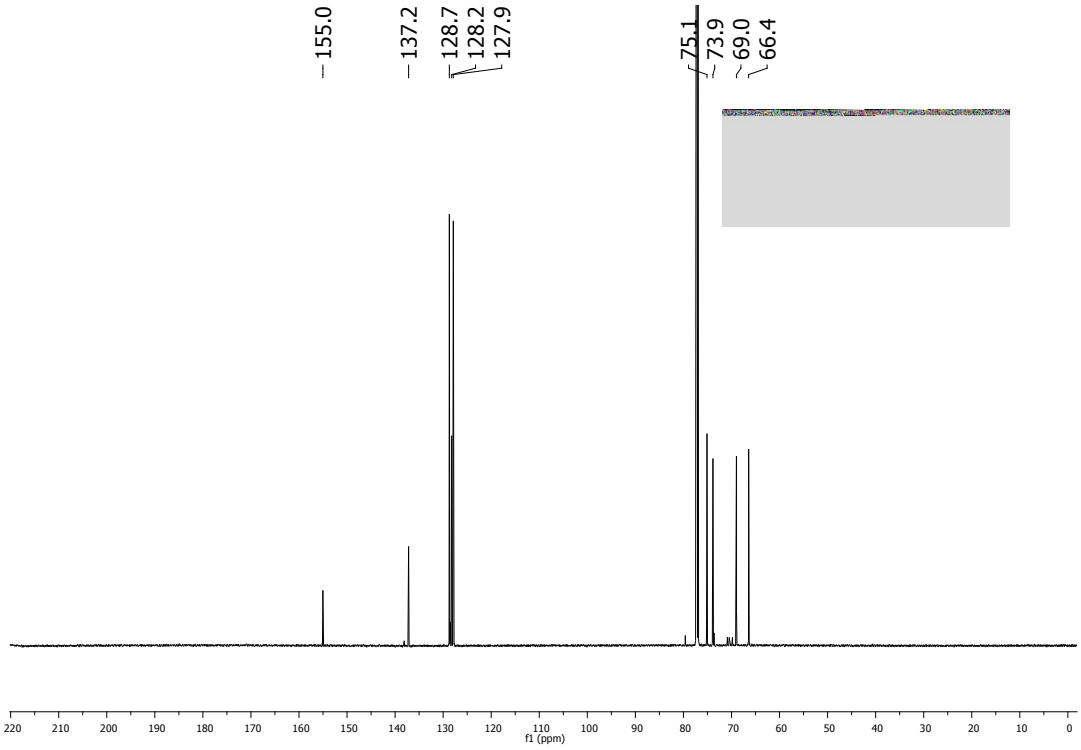


Figure S66. ^{13}C NMR ($CDCl_3$) spectrum of **6e**.

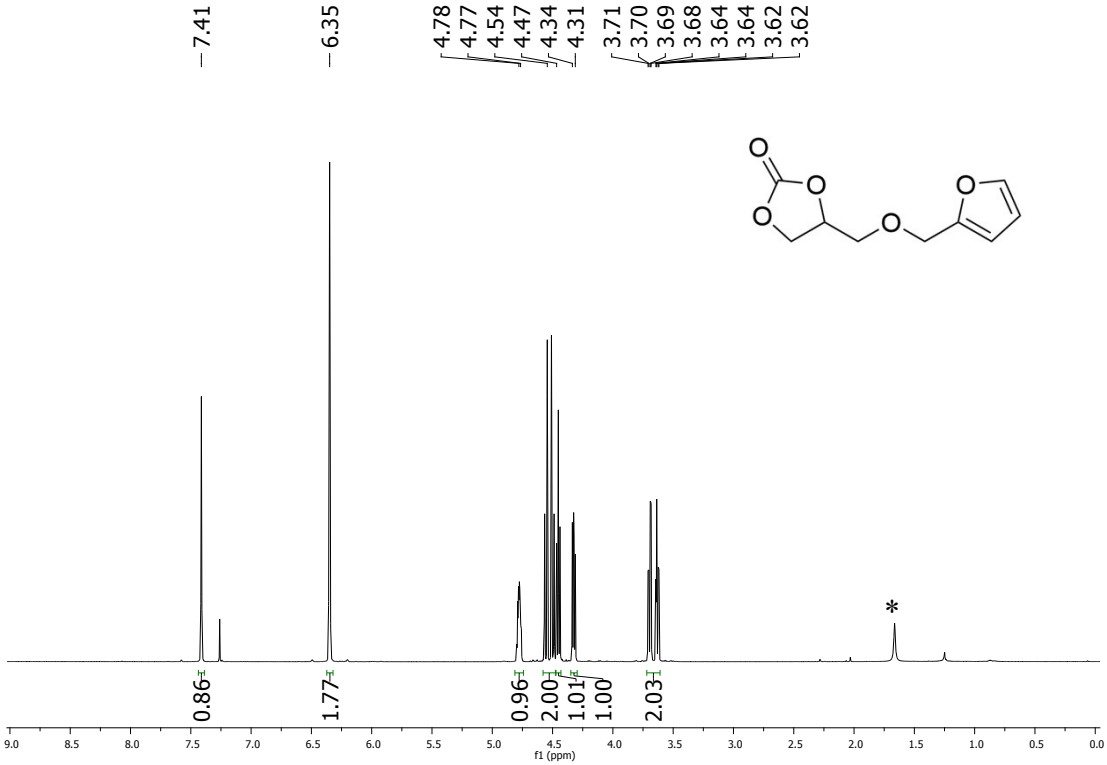


Figure S67. ^{1}H NMR ($CDCl_3$) spectrum of **6f**. (*) signal for residual water in $CDCl_3$.

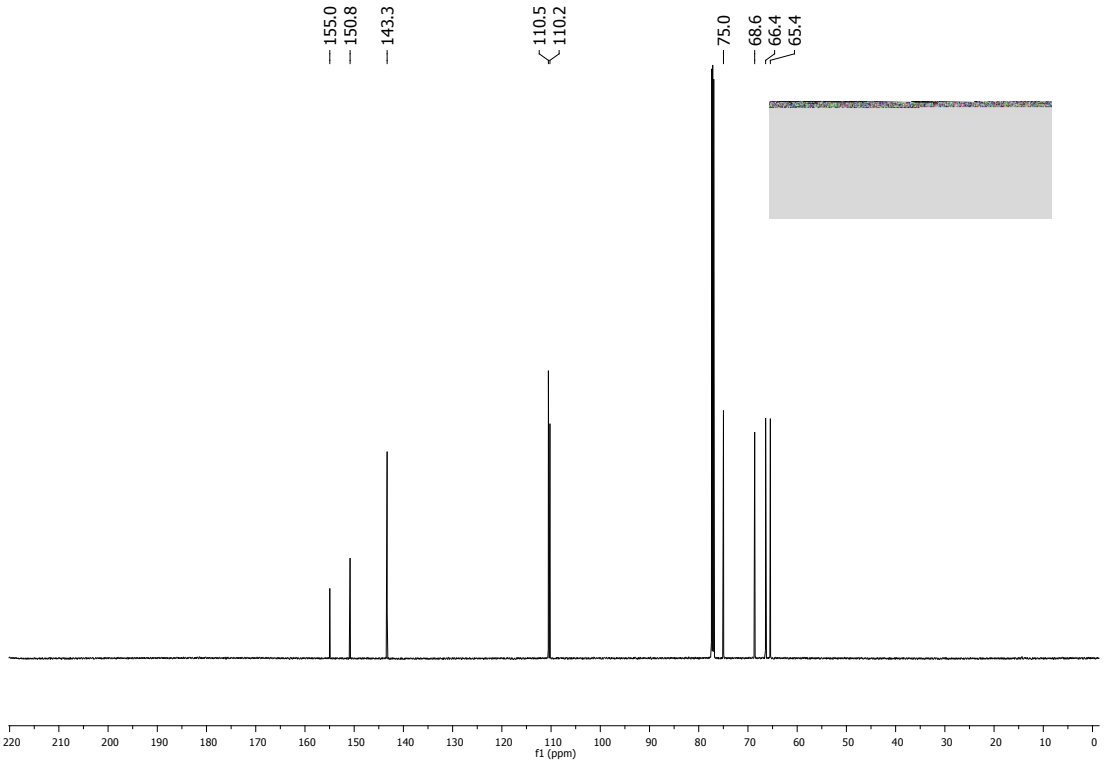


Figure S68. ^{13}C NMR ($CDCl_3$) spectrum of **6f**.

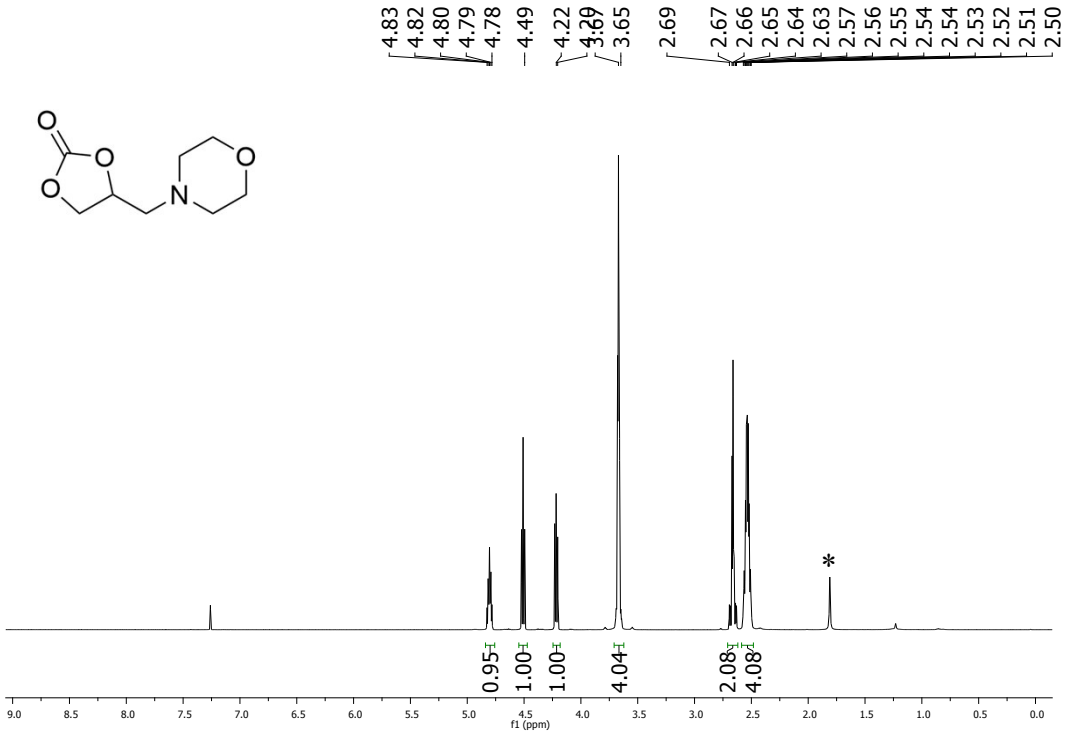


Figure S69. ^{1}H NMR ($CDCl_3$) spectrum of **6g**. (*) signal for residual water in $CDCl_3$.

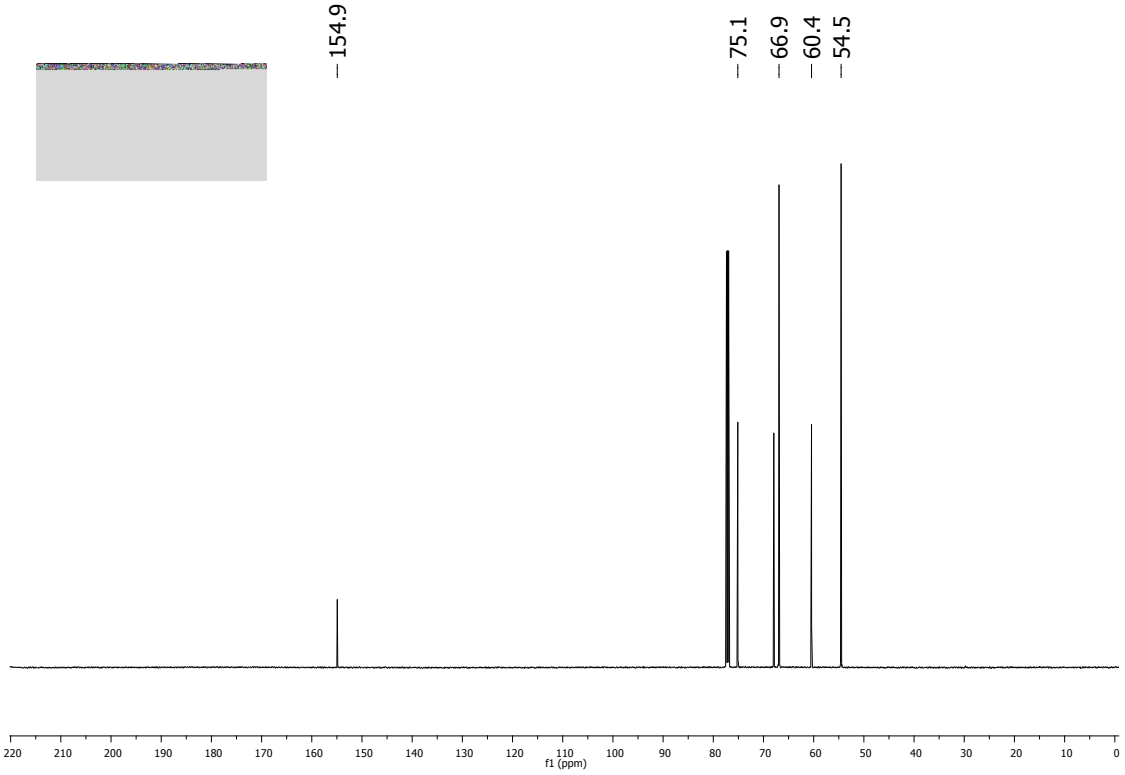


Figure S70. ^{13}C NMR ($CDCl_3$) spectrum of **6g**.

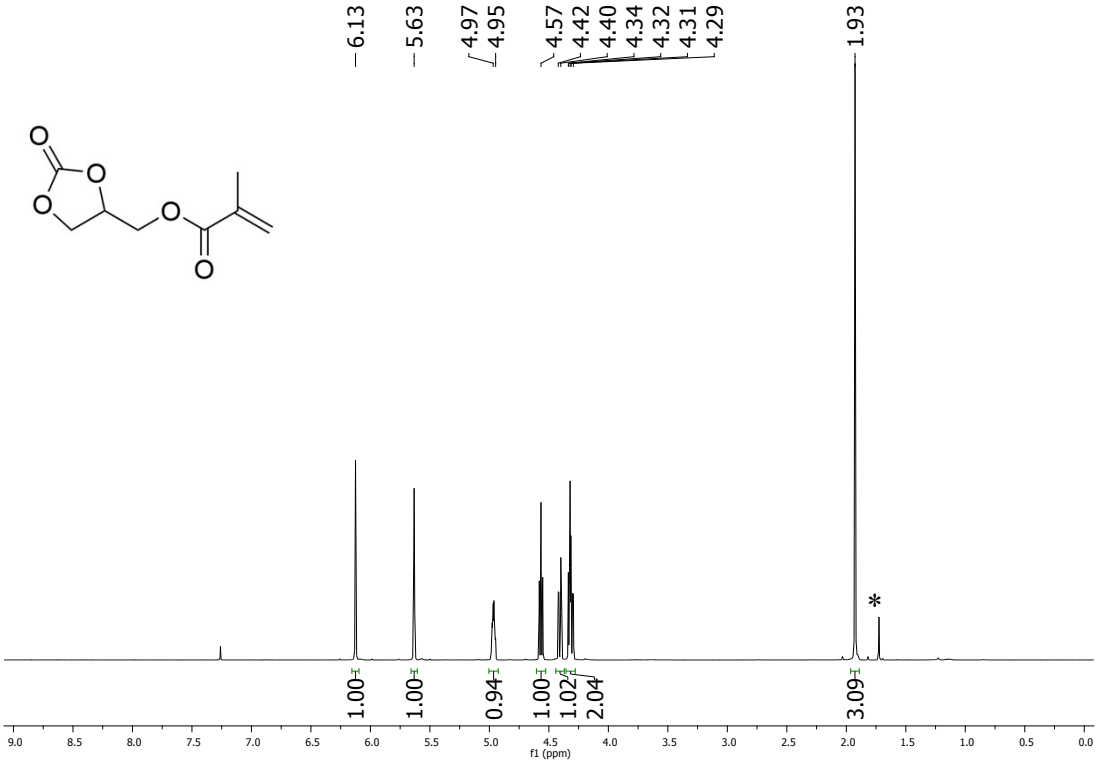


Figure S71. ^{1}H NMR ($CDCl_3$) spectrum of **6h**. (*) signal for residual water in $CDCl_3$.

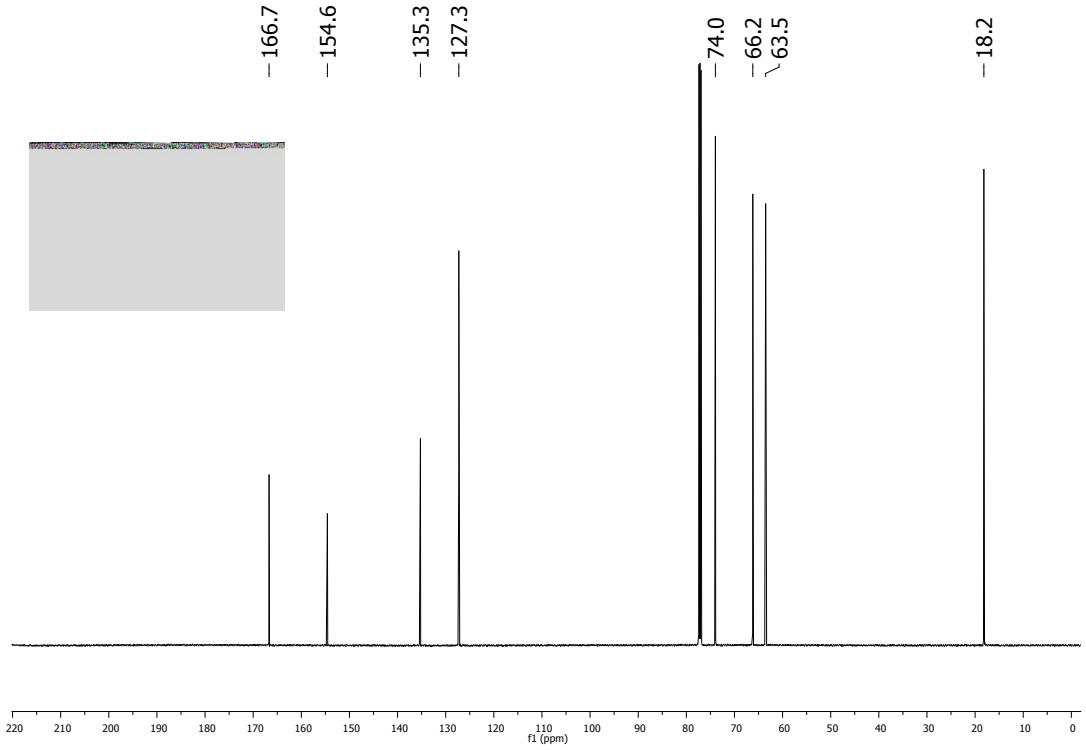


Figure S72. ^{13}C NMR ($CDCl_3$) spectrum of **6h**.

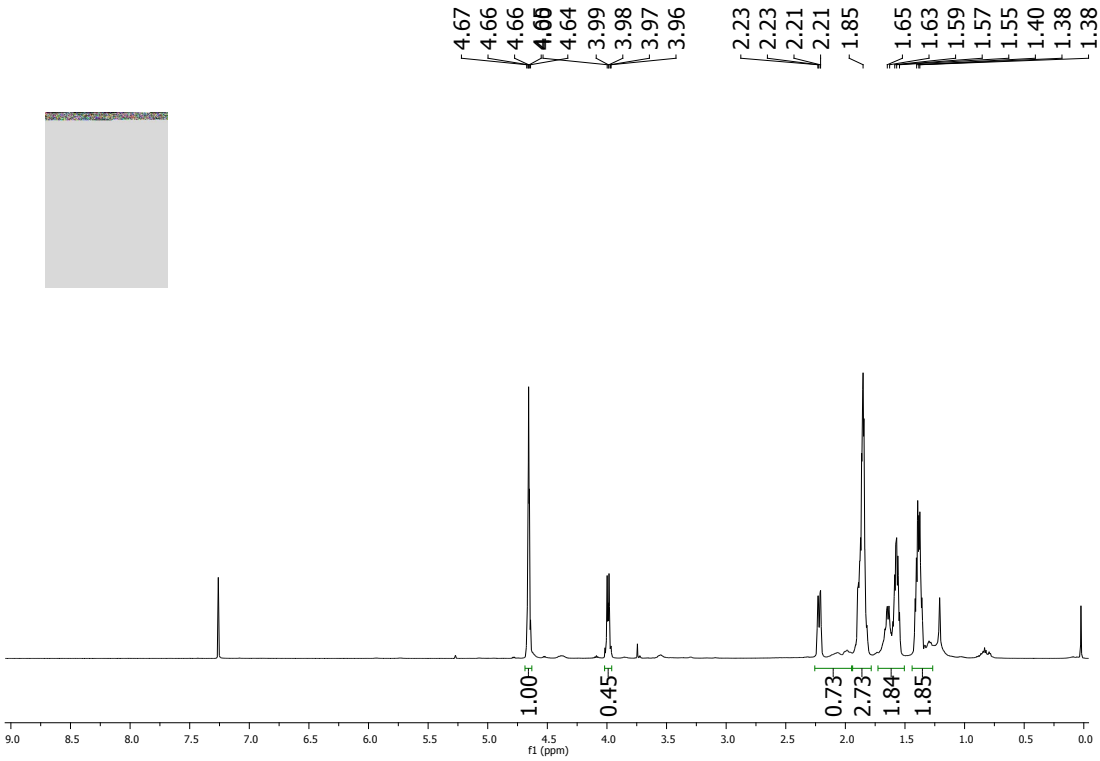


Figure S73. ^{1}H NMR ($CDCl_3$) spectrum of **6i**.

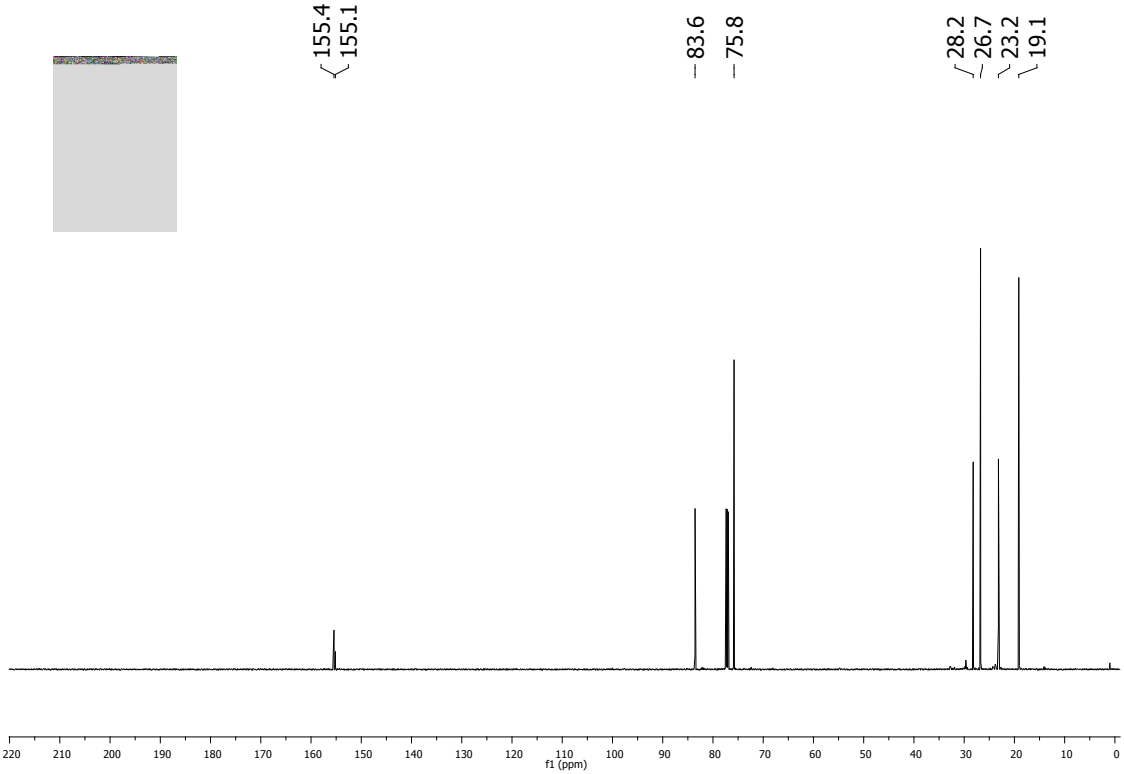


Figure S74. ^{13}C NMR ($CDCl_3$) spectrum of **6i**.

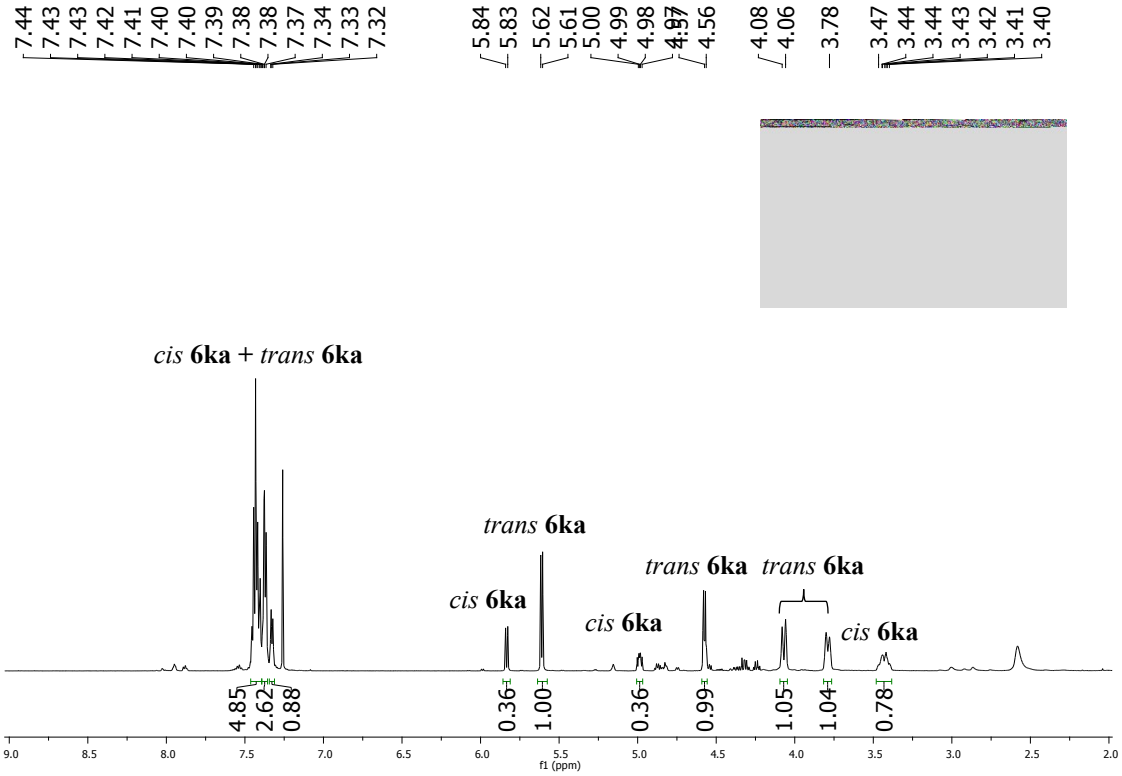


Figure S75. ^{1}H NMR ($CDCl_3$) spectrum of **6ka**.

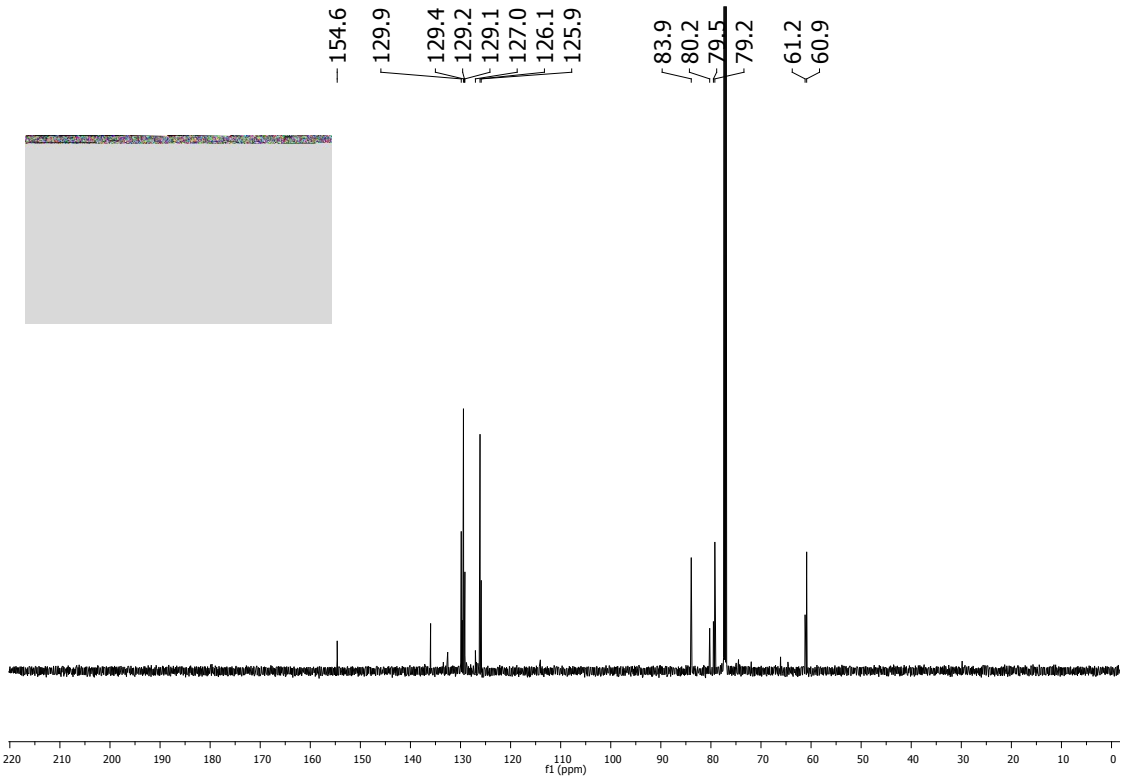


Figure S76. ^{13}C NMR ($CDCl_3$) spectrum of **6ka**.

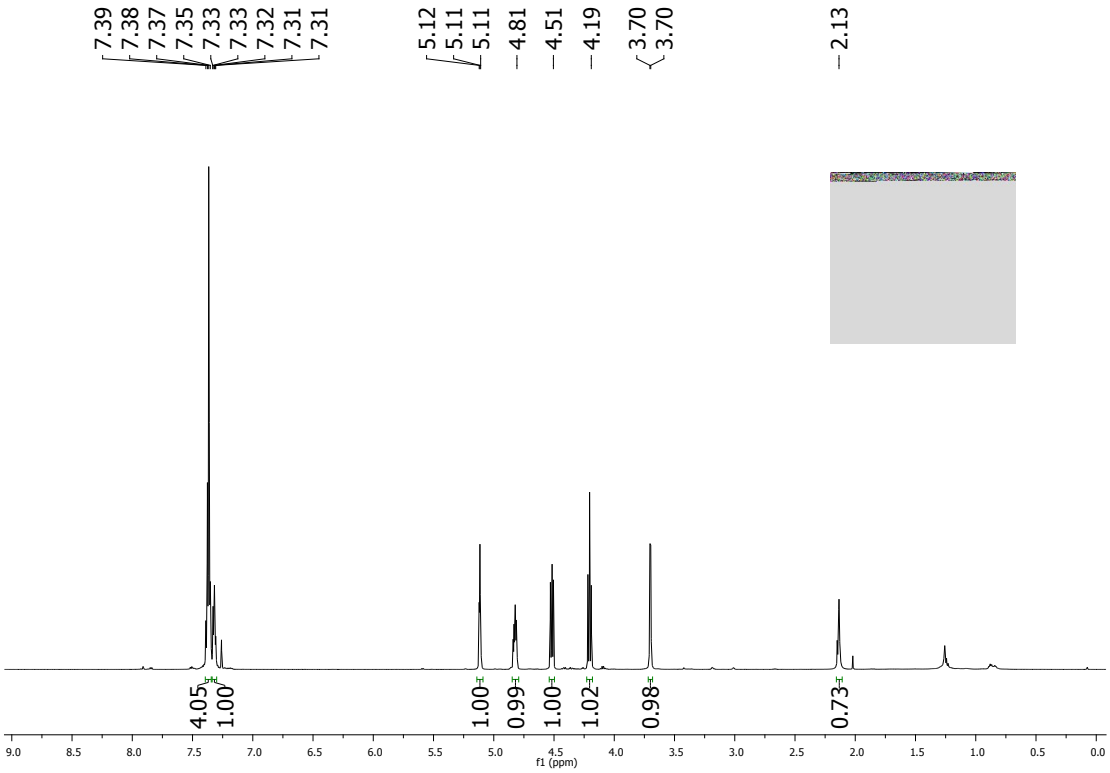


Figure S77. ^{1}H NMR ($CDCl_3$) spectrum of **6kb**.

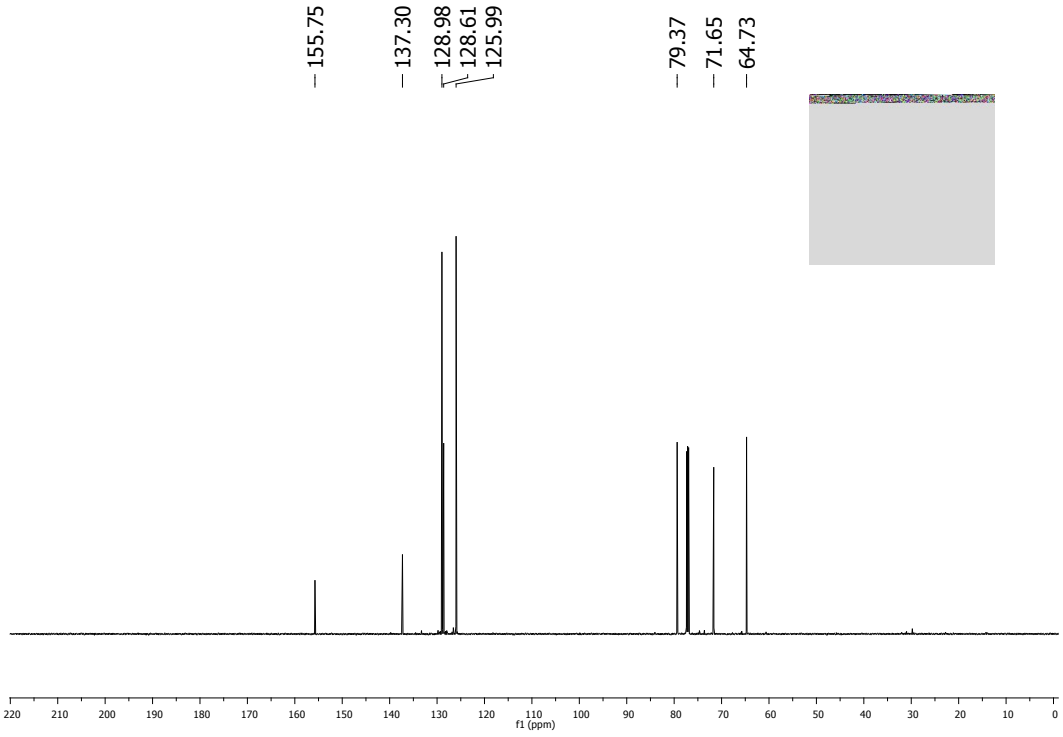


Figure S78. ^{13}C NMR ($CDCl_3$) spectrum of **6kb**.

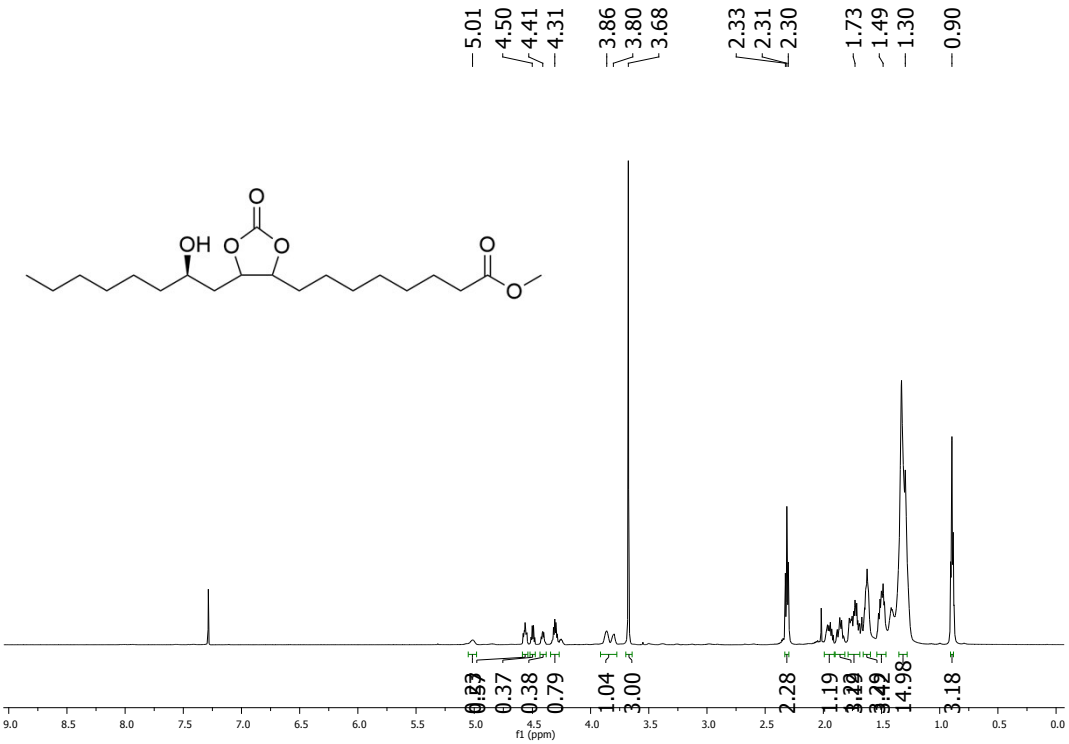


Figure S79. ^{1}H NMR ($CDCl_3$) spectrum of **6la**.

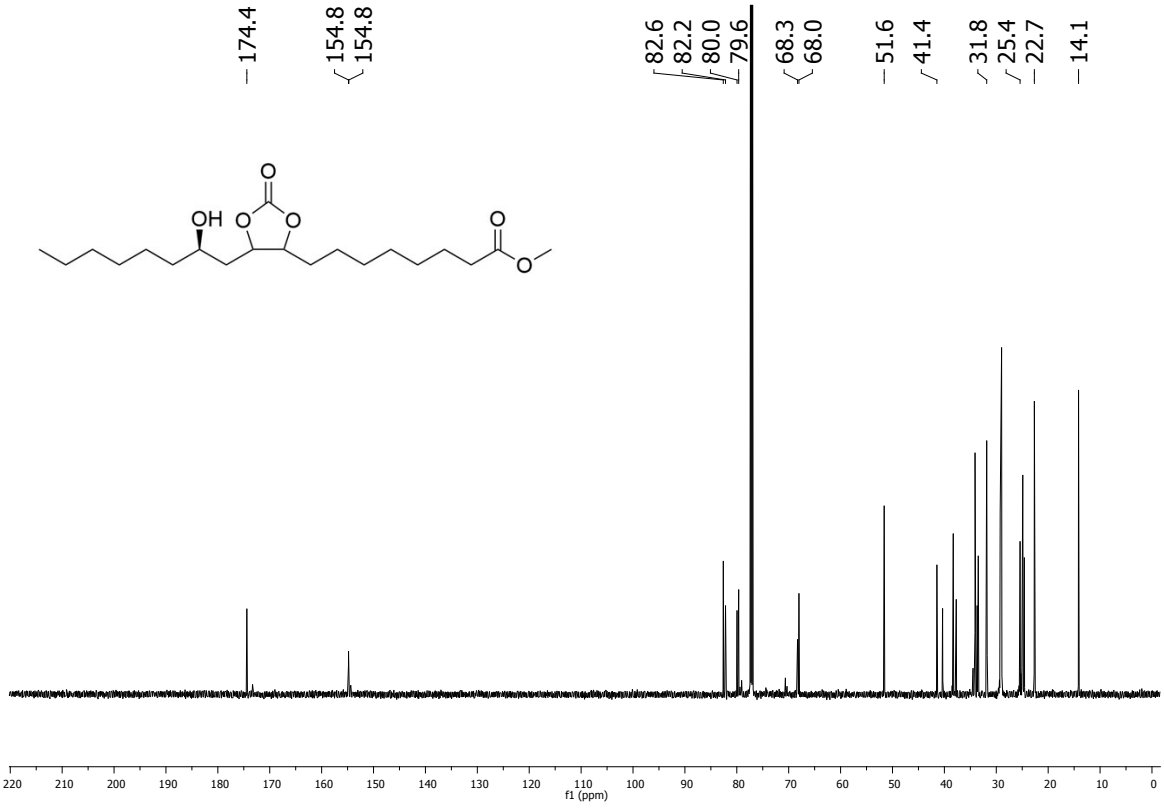


Figure S80. ^{13}C NMR ($CDCl_3$) spectrum of **6la**.

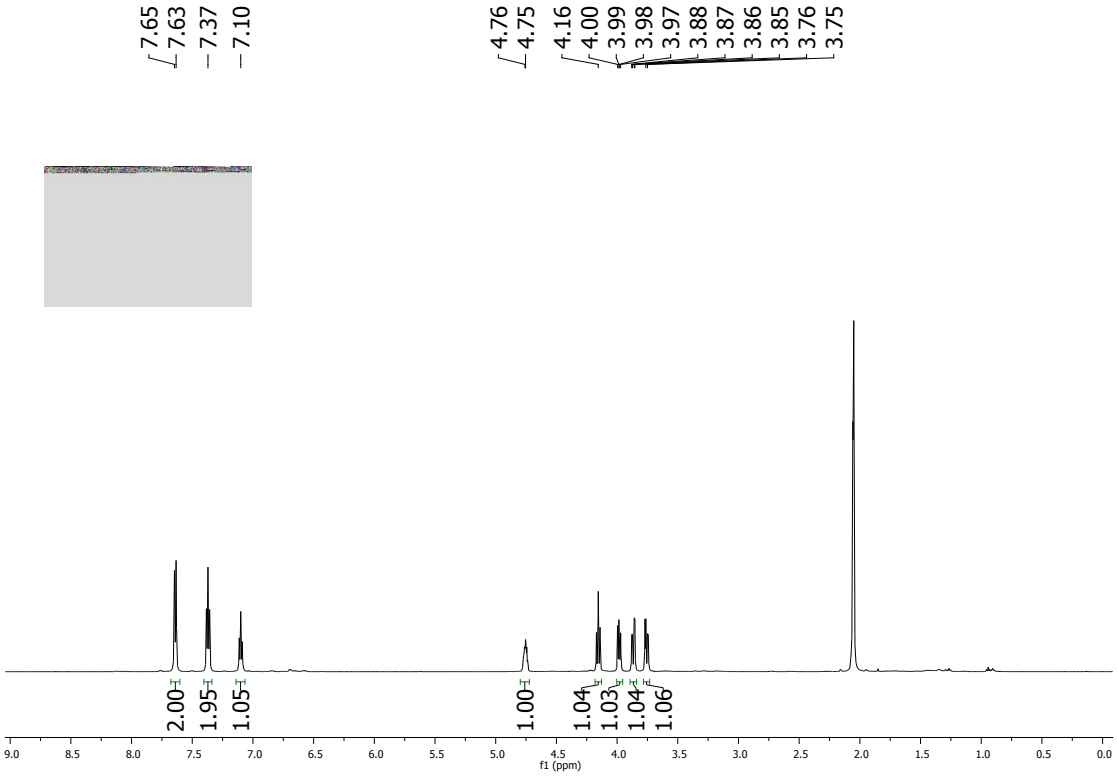


Figure S81. ^{1}H NMR (Acetone-d_6) spectrum of **6mb**.

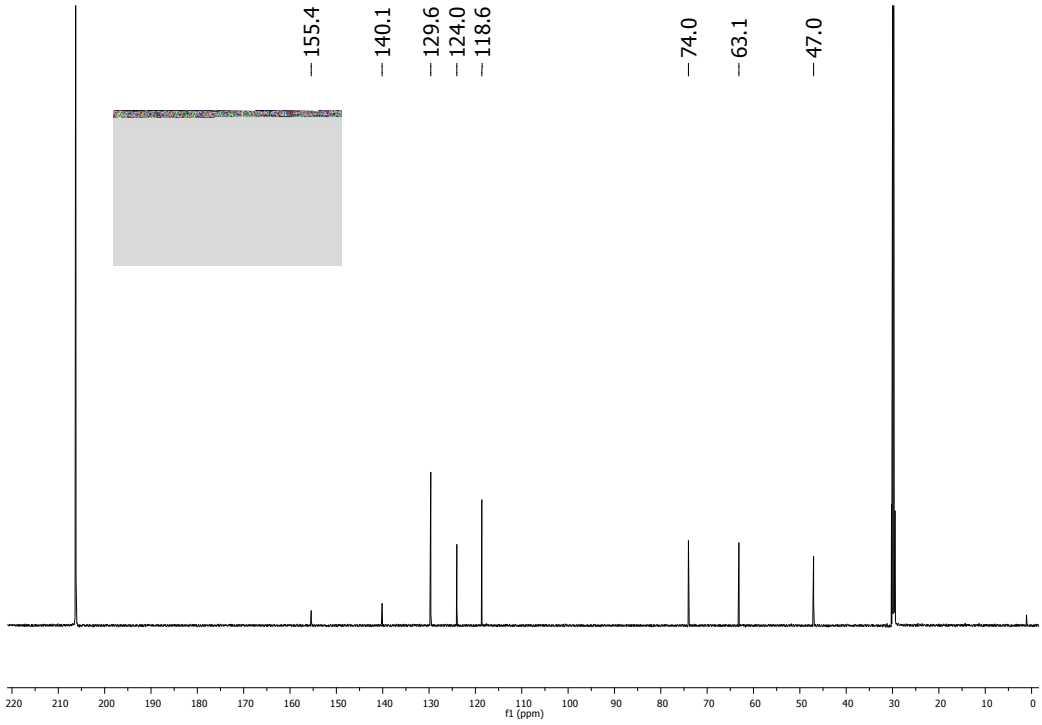


Figure S82. ^{13}C NMR (Acetone-d_6) spectrum of **6mb**.

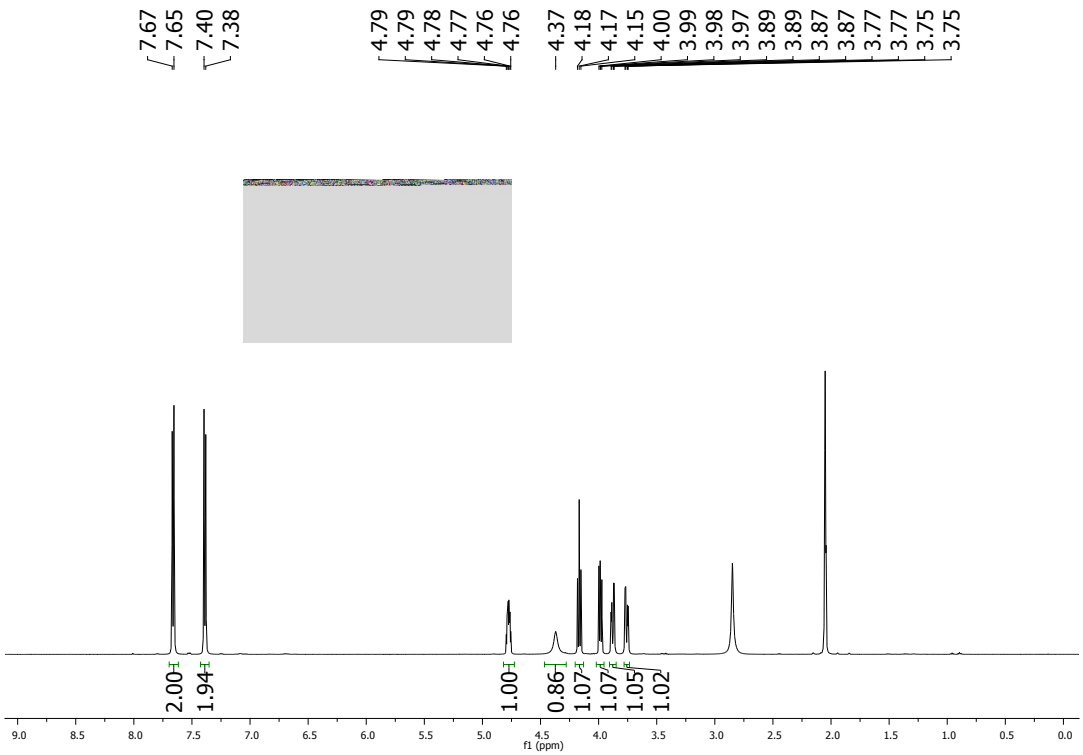


Figure S83. ^{1}H NMR (Acetone-d_6) spectrum of **6nb**.

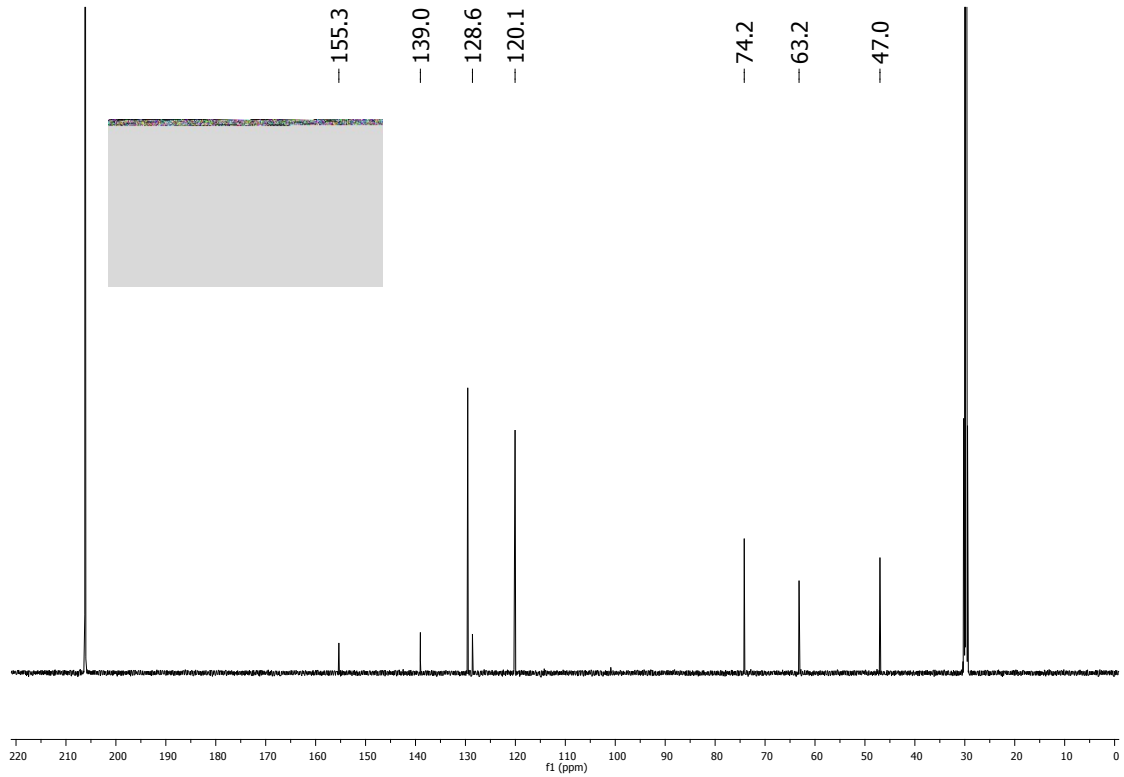


Figure S84. ^{13}C NMR (Acetone-d_6) spectrum of **6nb**.

S11. Computational data

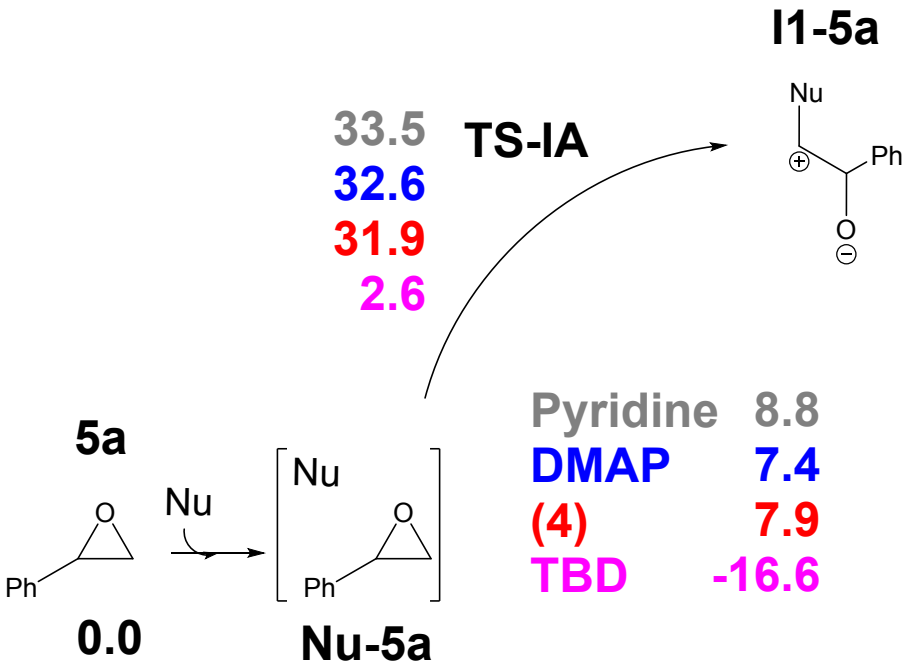


Figure S85. Reaction barriers (kcal/mol) for the ring-opening of epoxide **5a** by several nucleophiles.

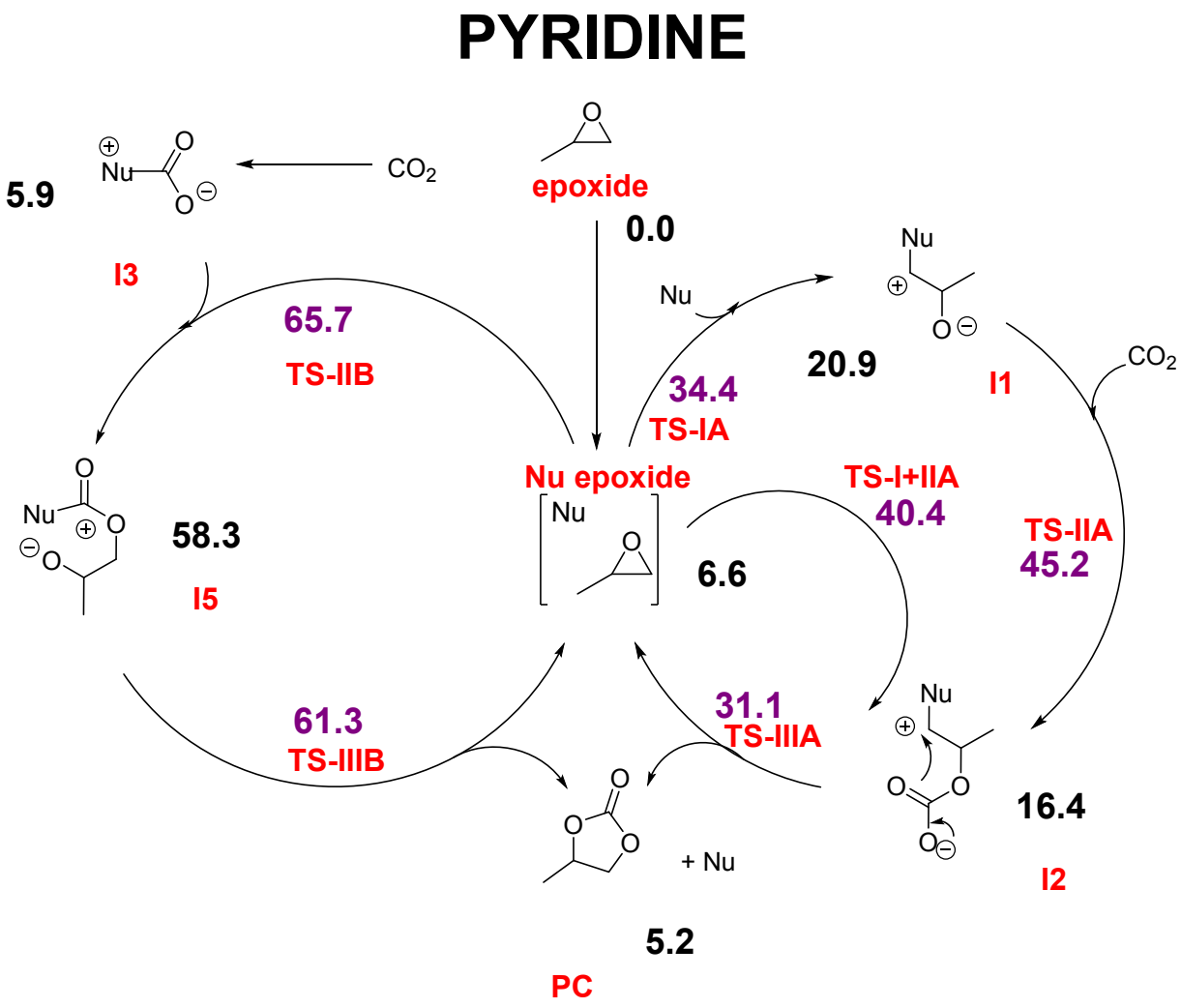


Figure S86. Reaction barriers (kcal/mol) for the cycloaddition of CO_2 to propylene oxide catalyzed by pyridine according to two different pathways.

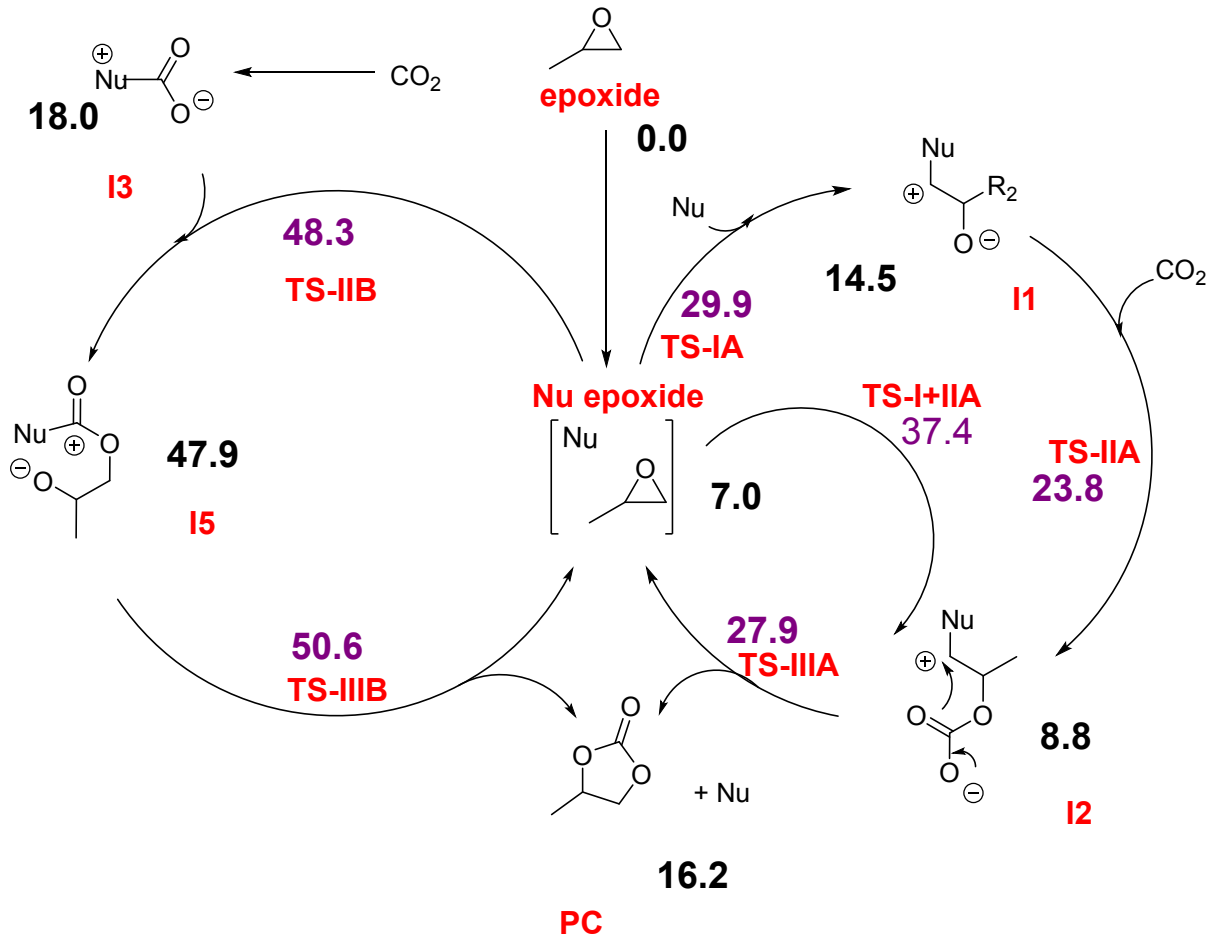


Figure S87. Reaction barriers (kcal/mol) for the cycloaddition of CO_2 to propylene oxide catalyzed by DMAP according to two different pathways.

(4)

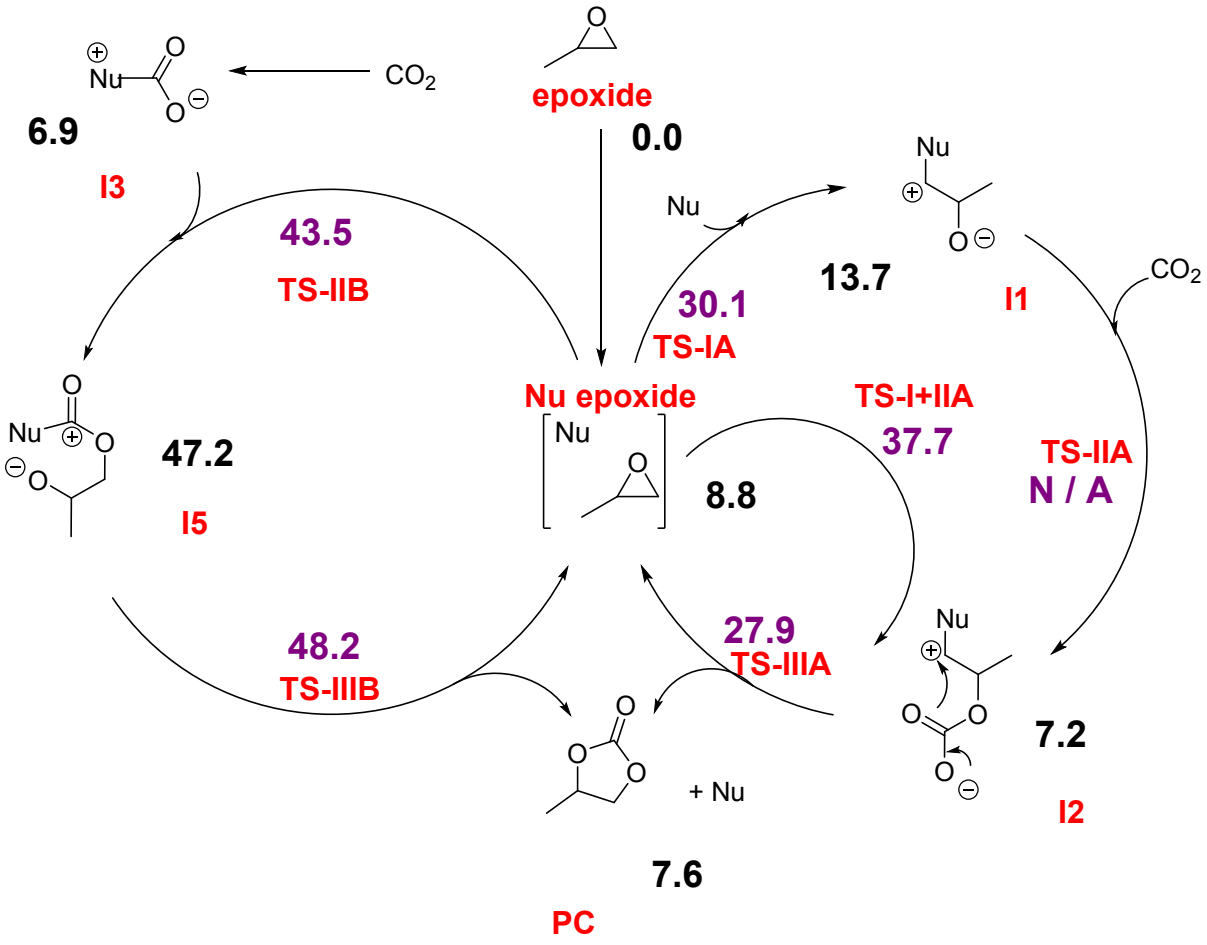


Figure S88. Reaction barriers (kcal/mol) for the cycloaddition of CO_2 to propylene oxide catalyzed by nucleophile **4** according to two different pathways.

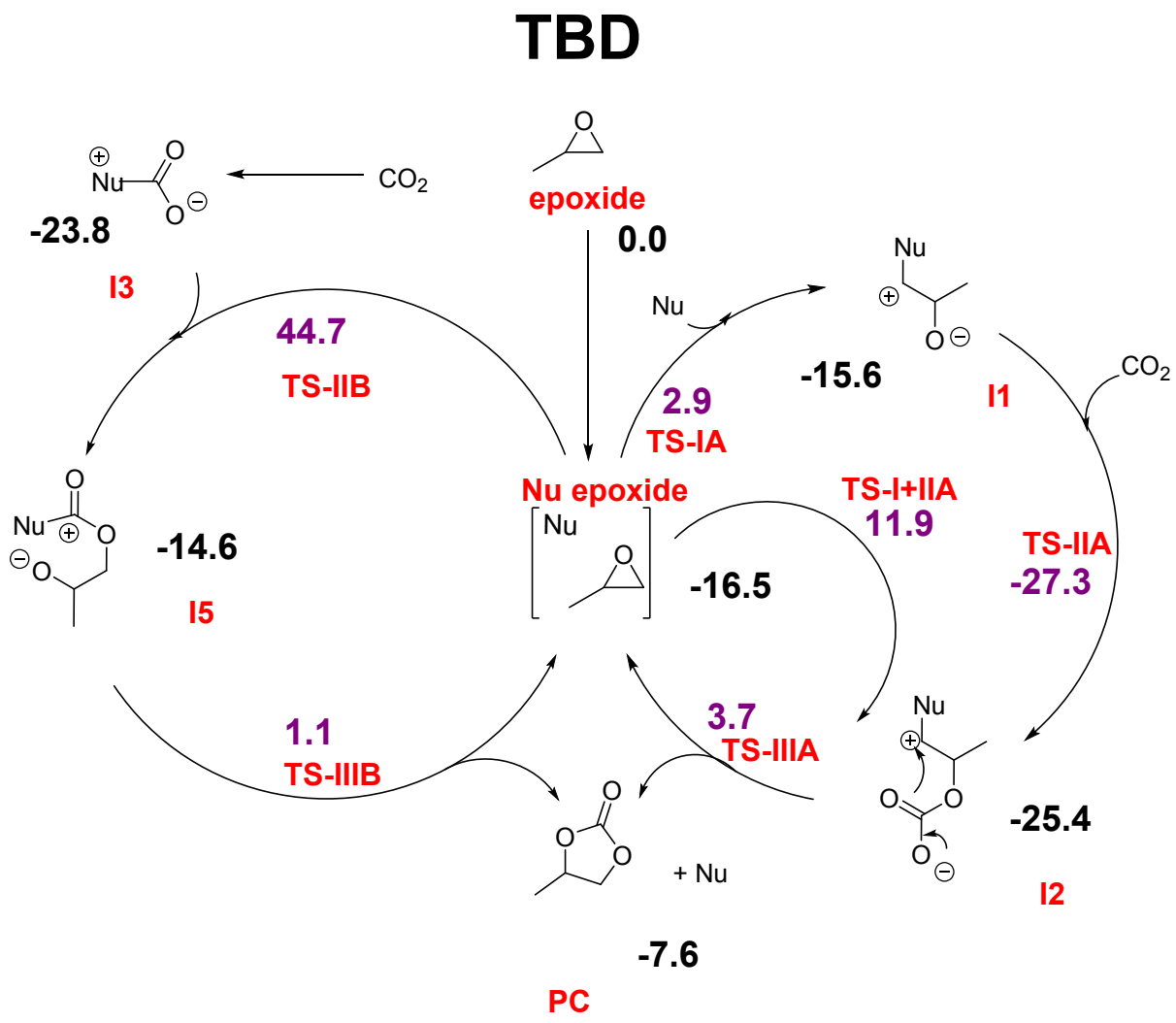


Figure S89. Reaction barriers (kcal/mol) for the cycloaddition of CO_2 to propylene oxide catalyzed by TBD according to two different pathways.

Computational data* (*Epoxide-basicity calculations)

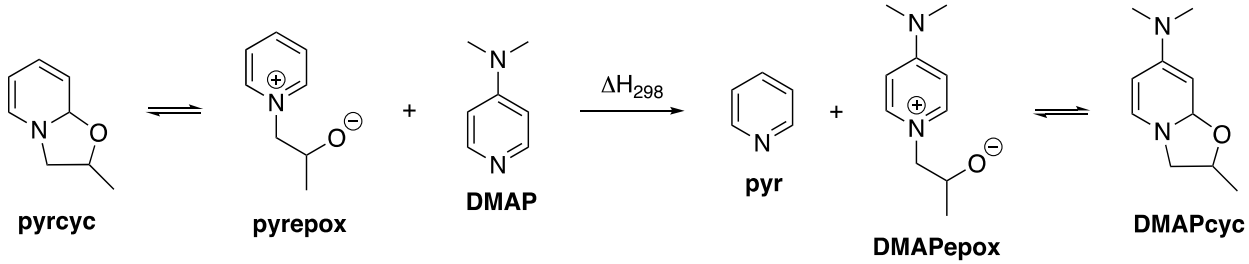


Figure S90. Formal propylene oxide (PO) transfer from pyridine to DMAP.

Table S3a. Total energies and enthalpies for the systems shown in Figure S1 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/T ZVP (SP)	E_{tot} PCM/M06/T ZVP (opt)	H_{373} PCM/M06/T ZVP (opt)	G_{373} PCM/M06/T ZVP (opt)
pyr							
v2020_004	-248.3666737	-248.272946; 0.093728	-248.316938; 0.049735	-248.1733623	-248.1747374	-248.078837	-248.122506
pyrepox							
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**
v2020_001	-441.5358646	-441.349816; 0.186049	-441.412343; 0.123522	-441.2096693	-441.2154689	-441.024248	-441.085326
pyrcyc							
v2020_003c	**-441.5679829**	**-441.379827**	**-441.439467**	**-441.2369168**	**-441.2398363**	**-441.047047**	**-441.105622**
v2020_002c	-441.5671169	-441.379020	-441.439447	-441.2361960	-441.2391496	-441.046352	-441.105318
DMAP							
v2020_006	-382.3905399	-382.219628; 0.170912	-382.279343; 0.111197	-382.0942390	-382.0962779	-381.921453	-381.981098
DMAPepox							
v2020_008b	(collapse)	-	-	-	**-575.1505343**	**-574.880006**	-574.956436

v2020_007	(collapse)	-	-	-	- 575.1503472	- 574.879908	**- 574.956646**
v2020_005	- 575.5606500	- 575.297470	- 575.376546	- 575.1400157	- 575.1462886	- 574.875781	- 574.952465
DMAPcyc							
v2020_008c	**- 575.5876952**	**- 575.322391**	**- 575.397437**	**- 575.1529598**	**- 575.1566920**	**- 574.885215**	**- 574.960066**
v2020_007c	- 575.5868439	- 575.321645	- 575.397719	- 575.1523775	- 575.1560744	- 574.884547	- 574.958972
propylene oxide (PO) transfer							
ΔE (kcal/mol)	-0.58	-0.61	-1.13	-5.94	-4.51	**-4.34**	-4.02
zwitterion collapse energy (pyrepox)							
ΔE (kcal/mol)	-20.16	-18.83	-17.02	-17.10	-11.32	**-10.40**	-8.91
zwitterion collapse energy (DMAPepox)							
ΔE (kcal/mol)	-16.97	-15.64	-13.11	-8.12	-3.86	**-3.27**	-2.15

Table S3b. Enthalpies and free energies for the systems shown in Figure S1 (in Hartree).

system	H_{373} BP86-D3/ TZVP (gas)	G_{373} BP86-D3/ TZVP (gas)	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)
pyr						
v2020_004	- 248.272946	- 248.316938	- 248.0796346	- 248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	**-**		**-441.030468**	-441.091186
v2020_002	-	-	-		-441.030317	**-441.091431**
v2020_001	- 441.34981	- 441.41234	- 441.0236207	- 441.0861477	-441.024248	-441.085326

	6	3				
DMAP						
v2020_006	-382.219628	-382.279343	-381.9233271	-381.9830421	-381.921453	-381.981098
DMAPepox						
v2020_008b	-	-			**-574.880006**	-574.956436
v2020_007	-	-			-574.879908	**-574.956646**
v2020_005	-575.297470	-575.376546	-574.8768357	-574.9559117	-574.875781	-574.952465
propylene oxide (PO) transfer						
ΔE (kcal/mol)	-0.61	-1.13	-5.98	-6.50	**-4.34**	-4.02

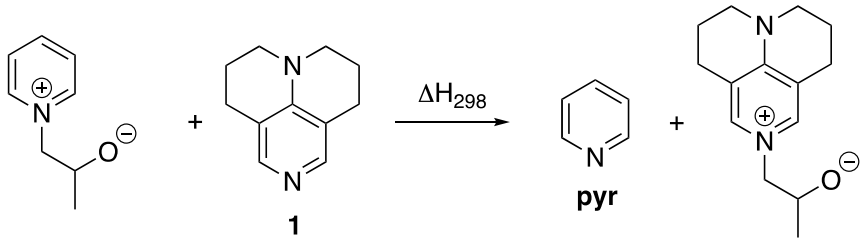


Figure S91. Formal propylene oxide (PO) transfer from pyridine to TCAP (**1**).

Table S4a. Total energies and enthalpies for the systems shown in Figure S2 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/TZ VP (SP)	E_{tot} PCM/M06/TZ VP (opt)	H_{373} PCM/M06/TZ VP (opt)	G_{373} PCM/M06/TZ VP (opt)
pyr							
v2020_004	-248.366737	-248.272946	-248.316938	-248.1733623	-248.1747374	-248.078837	-248.122506
pyrepox							
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**
v2020_001	-441.535864	-441.349816	-441.412343	-441.2096693	-441.2154689	-441.024248	-441.085326
1							
v2020_009	**-537.3069539**	**-537.061515**	**-537.127081**	**-536.8835532**	**-536.8863919**	**-536.635428**	**-536.700254**
v2020_010	-537.306630	-537.061236	-537.127053	-536.8835057	-536.8863336	-536.635335	-536.700131
1epox							
v2020_016	-	-	-	-	**-729.9430173**	-729.596072	**-729.677459**
v2020_018	-	-	-	-	-729.9430055	**-729.596151**	-729.677421
v2020_015	-	-	-	-	-729.9428554	-729.595991	-729.677187
v2020_019	-	-	-	-	-729.9428181	-729.595927	-729.677421
v2020_017	-	-	-	-	-729.9424321	-729.595626	-729.677205
v2020_014	(collapse)	-	-	-	-729.9423493	-729.595468	-729.677281
v2020_012	-730.479321	-730.141461	**-730.225893**	**-729.9328153**	-729.9397373	-729.592765	-729.674315
v2020_013	-730.479300	-730.141322	-730.225227	-729.9327568	-729.9396990	-729.592804	-729.674399
v2020_020	-	-	-	-	-729.9390833	-729.592248	-729.674352

v2020_011	**-730.4794871**	**-730.141614**	-730.225832	-729.9317013	-729.9389824	-729.592183	-729.675228
1cyc							
v2020_017c	**-730.5038870**	**-730.164252**	-730.244986	**-729.9413574**	**-729.9457360**	**-729.598111**	**-729.677422**
v2020_014c	-730.5030107	-730.163385	-730.245058	-729.9408050	-729.9451987	-729.597586	-729.677336
v2020_018c	-730.5021443	-730.162580	-730.244573	-729.9392726	-729.9438538	-729.596302	-729.676482
v2020_016c	-730.5024031	-730.162880	-730.244688	-729.9393418	-729.9437952	-729.596347	-729.676932
v2020_019c	-730.5013040	-730.161718	-730.244541	-729.9388187	-729.9433514	-729.595766	-729.676264
v2020_015c	-730.5013856	-730.161921	**-730.245070**	-729.9386968	-729.9431864	-729.595704	-729.676515
propylene oxide (PO) transfer							
ΔE (kcal/mol)	-2.10	-2.03	-2.14	-8.13	-6.00	**-5.71**	-5.20
zwitterion collapse energy (3epox)							
ΔE (kcal/mol)	-15.32	-14.20	-12.03	-5.35	-1.70	**-1.22**	+0.02

Table S4b. Enthalpies and free energies for the systems shown in Figure S2 (in Hartree).

system	H_{373} BP86-D3/TZVP	G_{373} BP86-D3/TZVP	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)
pyr						
v2020_004	-248.272946	-248.316938	-248.0796346	-248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	-	**-**	**-441.030468**	-441.091186
v2020_002	-	-	-	-	-441.030317	**-441.091431**
v2020_001	-441.349816	-441.412343	-441.0236207	-441.0861477	-441.024248	-441.085326
1						
v2020_009	**-537.061515**	**-537.127081**	**-536.6381143**	-536.7036803	**-536.635428**	**-536.700254**
v2020_010	-	-	-536.6381112	**-536.7039282**	-536.635335	-536.700131

	537.061236	537.127053				
1epox						
v2020_016	-	-	-	**-**	-729.596072	**-729.677459**
v2020_018	-	-	-	-	**-729.596151**	-729.677421
v2020_015	-	-	-	-	-729.595991	-729.677187
v2020_019	-	-	-	-	-729.595927	-729.677421
v2020_017	-	-	-	-	-729.595626	-729.677205
v2020_014	-	-	-	-	-729.595468	-729.677281
v2020_012	- 730.141461	**- 730.225893**	**-729.5949550**	**-729.6793870**	-729.592765	-729.674315
v2020_013	- 730.141322	- 730.225227	-729.5947781	-729.6786831	-729.592804	-729.674399
v2020_020	-	-	-	-	-729.592248	-729.674352
v2020_011	**- 730.141614**	- 730.225832	-729.5938282	-729.6780462	-729.592183	-729.675228
propylene oxide (PO) transfer						
ΔE (kcal/mol	-2.03	-2.14	-8.07	-8.12	**-5.71**	-5.20

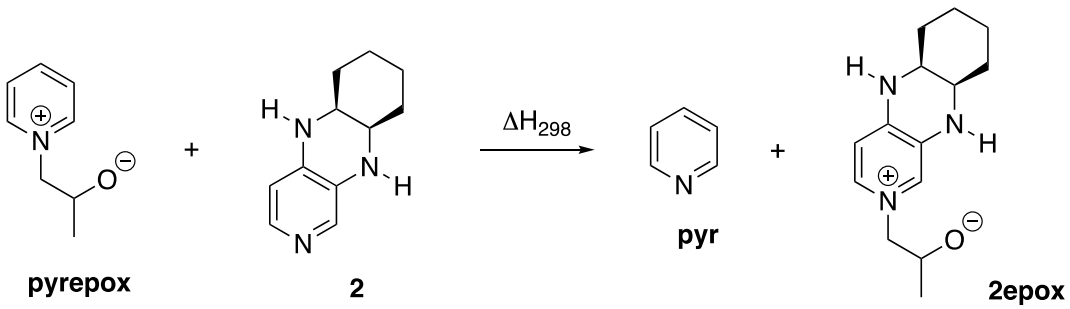


Figure S92. Formal propylene oxide (PO) transfer from pyridine to catalyst **2**.

Conformational space selection for catalyst **2** and adduct **2epox**: the attached cyclohexane ring is assumed to occupy a chair conformation, which puts the two amino substituents either in an axial/equatorial (ae) or in an equatorial/axial (ea) orientation.

Table S5a. Total energies and enthalpies for the systems shown in Figure S3 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/TZVP (SP)	E_{tot} PCM/M06/TZVP (opt)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)	conf
pyr								
v2020_004	-248.3666737	-248.272946	-248.316938	-248.1733623	-248.1747374	-248.078837	-248.122506	
pyrepox								
v2020_001	-441.5358646	-441.349816	-441.412343	-441.2096693	-441.2154689	-441.024248	-441.085326	
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**	
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186	
2								
v2020_068	**-592.6873395**	**-592.423408**	-592.491790	**-592.2276932**	**-592.2309309**	**-591.961258**	**-592.029207**	ae
v2020_069	-592.6871398	-592.423281	**-592.491961**	-592.2276376	-592.2308737	-591.961113	-592.028822	ea
v2020_070	-592.6760170	-592.412037	-592.482032	-592.2161398	-592.2194858	-591.949547	-592.019452	bb
v2020_071	-592.6763741	-592.412284	-592.482538	-592.2160801	-592.2192087	-591.949006	-592.017527	bb
2epox								
v2020_241	-	-	-	-	**-785.2862458**	**-784.920710**	-785.004738	ae.d+g-g
v2020_240	-	-	-	-	-785.2860202	-784.920547	-785.005832	ea.u+g-g
v2020_247	-	-	-	-	-785.2859394	-784.920406	-785.005021	ae.u+g-g
v2020_235	-	-	-	-	-785.2857965	-784.920235	-785.004609	ea.d+g-g
v2020_242	-	-	-	-	-785.2857952	-784.920305	**-785.006140**	ae.d+ga
v2020_2	-	-	-	-	-	-	-	ae.d-

43					785.2857161	784.920047	785.004219	g+g
v2020_238	-	-	-	-	-785.2855456	-784.919964	-785.005011	ea.u-g+g
v2020_248	-	-	-	-	-785.2855422	-784.920160	-785.005665	ae.u+ga
v2020_245	-	-	-	-	-785.2855325	-784.919998	-785.004527	ae.u-g+g
v2020_244	-	-	-	-	-785.2855118	-784.920106	-785.005623	ae.d-ga
v2020_239	-	-	-	-	-785.2854669	-784.919818	-785.004545	ea.u-ga
v2020_234	-	-	-	-	-785.2854375	-784.919842	-785.003795	ea.d-g+g
v2020_246	-	-	-	-	-785.2854029	-784.919918	-785.004670	ae.u-ga
v2020_233	-	-	-	-	-785.2853797	-784.919774	-785.005239	ea.d+ga
v2020_236	-	-	-	-	-785.2852612	-784.919793	-785.005484	ea.d-ga
v2020_254	-785.8589508	-785.502619	-785.589912	-785.2749269	-785.2829231	-784.917279	-785.002162	ae.da-g
v2020_251	-785.8589695	-785.502743	**-785.590756**	-785.2744257	-785.2828989	-784.917288	-785.002455	ae.ua-g
v2020_226	**-785.8593832**	**-785.503035**	-785.590206	**-785.2751923**	-785.2827674	-784.917239	-785.002181	ea.ua-g
v2020_237	-785.8587558	-785.502353	-785.589219	-785.2747801	-785.2826839	-784.917168	-785.002214	ea.da-g
v2020_249	-785.8580595	-785.501676	-785.589150	-785.2745065	-785.2826383	-784.917047	-785.001903	ae.da+g
v2020_252	-785.8581522	-785.501730	-785.588799	-785.2746795	-785.2826172	-784.917003	-785.002125	ae.ua+g
v2020_250	-785.8584737	-785.501979	-785.589041	-785.2750534	-785.2825340	-784.916983	-785.002129	ea.ua+g
v2020_228	-785.8579767	-785.501480	-785.588104	-785.2747742	-785.2824808	-784.916729	-785.001229	ea.da+g
2cyc								
v2020_240c	-785.8846470	-785.526300	**-785.610372**	-785.2839966	**-785.2892831**	**-784.922584**	**-785.004868**	
v2020_241c	-785.8845125	-785.526188	-785.609815	-785.2838197	-785.2890253	-784.922313	-785.004296	
v2020_2	**-**	**-**	-	**-**	-	-	-	

47c	**785.8848264**	**785.526499**	785.610364	**785.2840564**	785.2889876	784.922305	785.004743	
v2020_242c	-785.8834120	-785.525166	-785.609747	-785.2828663	-785.2882965	-784.921672	-785.004368	
v2020_235c	-785.8817770	-785.523625	-785.607648	-785.2830217	-785.2882543	-784.921702	-785.004011	
v2020_243c	-785.8774843	-785.519403	-785.603214	-785.2793595	-785.2844230	-784.918061	-785.000728	
propylene oxide (PO) transfer								
ΔE (kcal/mol)	-1.79	-1.73	-2.13	-7.02	-5.18	**-4.91**	-5.02	
zwitterion collapse energy (6epox)								
ΔE (kcal/mol)	-15.97	-14.72	-12.31	-5.56	-1.90	**-1.18**	+0.79	

Table S5b. Enthalpies and free energies for the systems shown in Figure S3 (in Hartree).

system	H_{373} BP86-D3/TZVP (gas)	G_{373} BP86-D3/TZVP (gas)	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)
pyr						
v2020_004	-248.272946	-248.316938	-248.0796346	-248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	**-**		**-441.030468**	-441.091186
v2020_002	-	-	-		-441.030317	**-441.091431**
v2020_001	-441.349816	-441.412343	-441.0236207	-441.0861477	-441.024248	-441.085326
2						
v2020_068	**-592.423408**	-592.491790	**-591.9637617**	**-592.0321437**	**-591.961258**	**-592.029207**
v2020_069	-592.423281	**-592.491961**	**-591.9637788**	**-592.0324588**	-591.961113	-592.028822
v2020_070	-	-	-	-	-591.949547	-592.019452

	592.412037	592.482032	591.9521598	592.0221548		
v2020_071	-592.412284	-592.482538	-591.9519900	-592.0222440	-591.949006	-592.017527
2epox						
v2020_241	-	-	-	-	**-784.920710**	-785.004738
v2020_240	-	-	-	-	-784.920547	-785.005832
v2020_247	-	-	-	-	-784.920406	-785.005021
v2020_235	-	-	-	-	-784.920235	-785.004609
v2020_242	-	-	-	-	-784.920305	**-785.006140**
v2020_243	-	-	-	-	-784.920047	-785.004219
v2020_238	-	-	-	-	-784.919964	-785.005011
v2020_248	-	-	-	-	-784.920160	-785.005665
v2020_245	-	-	-	-	-784.919998	-785.004527
v2020_244	-	-	-	-	-784.920106	-785.005623
v2020_239	-	-	-	-	-784.919818	-785.004545
v2020_234	-	-	-	-	-784.919842	-785.003795
v2020_246	-	-	-	-	-784.919918	-785.004670
v2020_233	-	-	-	-	-784.919774	-785.005239
v2020_236	-	-	-	-	-784.919793	-785.005484
v2020_254	-785.502619	-785.589912	-784.9185951	-785.0058881	-784.917279	-785.002162
v2020_251	-785.502743	**-785.590756**	-784.9181992	**-785.0062122**	-784.917288	-785.002455
v2020_226	**-785.503035**	-785.590206	**-784.9188441**	-785.0060151	-784.917239	-785.002181
v2020_237	-785.502353	-785.589219	-784.9183773	-785.0052433	-784.917168	-785.002214
v2020_249	-785.501676	-785.589150	-784.9181230	-785.0055970	-784.917047	-785.001903
v2020_252	-785.501730	-785.588799	-784.9182573	-785.0053263	-784.917003	-785.002125
v2020_250	-785.501979	-785.589041	-784.9185587	-785.0056207	-784.916983	-785.002129
v2020_228	-785.501480	-785.588104	-784.9182775	-785.0049015	-784.916729	-785.001229
propylene oxide (PO) transfer						
ΔE (kcal/mol)	-1.73	-2.13	-6.95	-7.05	**-4.91**	-5.02

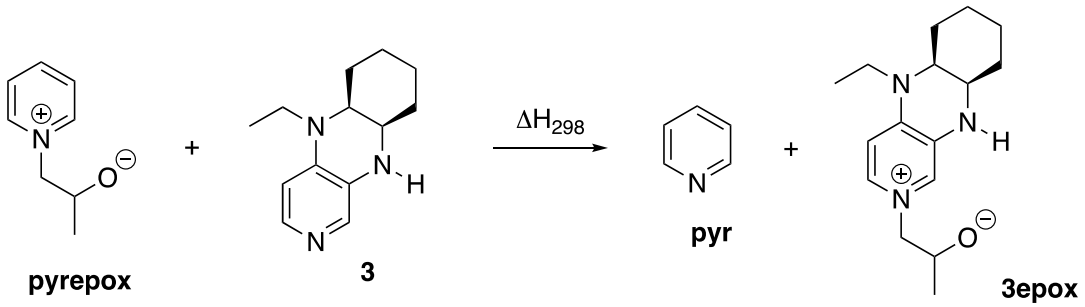


Figure S93. Formal propylene oxide (PO) transfer from pyridine to catalyst **3**.

Conformational space selection for catalyst **3** and adduct **3epox**: the attached cyclohexane ring is assumed to occupy a chair conformation, which puts the two amino substituents either in an axial/equatorial (ae) or in an equatorial/axial (ea) orientation.

Table S6a. Total energies and enthalpies for the systems shown in Figure S4 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/TZVP (SP)	E_{tot} PCM/M06/TZVP (opt)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)	conf
pyr								
v2020_004	-248.3666737	-248.272946	-248.316938	-248.1733623	-248.1747374	-248.078837	-248.122506	
pyrepox								
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186	
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**	
v2020_001	-441.5358646	-441.349816	-441.412343	-441.2096693	-441.2154689	-441.024248	-441.085326	
3								
v2020_072	**-671.3360865**	**-671.013242**	**-671.092003**	**-670.8085993**	**-670.8121904**	**-670.482294**	**-670.559482**	ae-d
v2020_073	-671.3357660	-671.012815	-671.091797	-670.8075308	-670.8113558	-670.481350	-670.558145	ae-u
v2020_074	-671.3340343	-671.010822	-671.087938	-670.8057035	-670.8093099	-670.479055	-670.555178	ea-d
v2020_075	-671.3335027	-671.010412	-671.087028	-670.8049959	-670.8085148	-670.478503	-670.554594	ea-u
v2020_076	-671.3226624	-670.999539	-671.078426	-670.7942894	-670.7979242	-670.467489	-670.545944	bb-d
3epox								
v2020_341	-	-	-	-	**-863.86785**	**-863.44216**	**-863.53675**	ae-d.d+

					75	**2**	**7**	g-g
v2020_347	-	-	-	-	-863.8674987	-863.441920	-863.536128	ae-d.u+g-g
v2020_361	-	-	-	-	-863.8674987	-863.441920	-863.536128	ae-d.u+g-g
v2020_342	-	-	-	-	-863.8674771	-863.441844	-863.536445	ae-d.d+ga
v2020_343	-	-	-	-	-863.8674272	-863.441684	-863.535402	ae-d.d-g+g
v2020_362	-	-	-	-	-863.8674272	-863.441684	-863.535402	ae-d.d-g+g
v2020_344	-	-	-	-	-863.8673287	-863.441660	-863.536371	ae-d.d-ga
v2020_345	-	-	-	-	-863.8672505	-863.441449	-863.535207	ae-d.u-g+g
v2020_348	-	-	-	-	-863.8671147	-863.441384	-863.535555	ae-d.u+ga
v2020_346	-	-	-	-	-863.8670785	-863.441338	-863.535614	ae-d.u-ga
v2020_353	-	-	-	-	-863.8668412	-863.441032	-863.534513	ae-u.d+g-g
v2020_358	-	-	-	-	-863.8664849	-863.440711	-863.534137	ae-u.u+g-g
v2020_354	-	-	-	-	-863.8664130	-863.440719	-863.535831	ae-u.d+ga
v2020_356	-	-	-	-	-863.8663167	-863.440522	-863.534823	ae-u.d-ga
v2020_355	-	-	-	-	-863.8663147	-863.440502	-863.533604	ae-u.d-g+g
v2020_359	-	-	-	-	-863.8662268	-863.440353	-863.534520	ae-u.u-g+g
v2020_357	-	-	-	-	-863.8660926	-863.440314	-863.534262	ae-u.u+ga
v2020_360	-	-	-	-	-863.8660824	-863.440227	-863.535313	ae-u.u-ga
v2020_350	**-864.5088121**	**-864.093388**	-864.190135	**-863.8568400**	-863.8647108	-863.438872	-863.532886	ae-d.da-g
v2020_351	-864.5085193	-864.093144	**-864.190448**	-863.8564414	-863.8646240	-863.438988	-863.533827	ae-d.ua-g
v2020_349	-864.5080219	-864.092585	-864.189840	-863.8565976	-863.8644108	-863.438675	-863.532456	ae-d.da+g
v2020_3	-	-	-	-	-	-	-	ae-

52	864.5076671	864.092322	864.189909	863.8559040	863.8643734	863.438601	863.533391	d.ua+g
v2020_340	-	-	-	-	-863.8640749	-863.438217	-863.531720	ea-d.u+g-g
v2020_335	-	-	-	-	-863.8638773	-863.437977	-863.531016	ea-d.d+g-g
v2020_338	-	-	-	-	-863.8636398	-863.437492	-863.530292	ea-d.u-g+g
v2020_339	-	-	-	-	-863.8635305	-863.437527	-863.531012	ea-d.u-ga
v2020_334	-	-	-	-	-863.8635090	-863.437526	-863.531571	ea-d.d-g+g
v2020_333	-	-	-	-	-863.8634679	-863.437568	-863.532409	ea-d.d+ga
v2020_336	-	-	-	-	-863.8633722	-863.437394	-863.531735	ea-d.d-ga
v2020_328	-864.5055457	-864.089735	-864.185334	-863.8526579	-863.8606290	-863.434579	-863.527845	ea-d.da+g
3cyc								
v2020_347c	-864.5313941	-864.114167	-864.208251	-863.8609066	**-863.8697290**	**-863.443089**	**-863.534402**	
v2020_341c	**-864.5325517**	**-864.115618**	**-864.209790**	**-863.8634218**	-863.8688882	-863.442435	-863.535424	
v2020_342c	-864.5314820	-864.114459	-864.209325	-863.8622786	-863.8680778	-863.441665	-863.534823	
v2020_344c	-864.5265382	-864.109417	-864.203419	-863.8607391	-863.8661152	-863.439632	-863.531766	
v2020_354c	-864.5291420	-864.112106	-864.207393	-863.8596791	-863.8658232	-863.439184	-863.531461	
propylene oxide (PO) transfer								
ΔE (kcal/mol)	-2.22	-2.06	-1.91	-7.49	-5.40	-5.17	-5.24	
zwitterion collapse energy (7epox)								
ΔE (kcal/m	-14.89	-13.96	-12.14	-4.14	-1.17	**-0.58**	+1.48	

ol)								

Table S6b. Enthalpies and free energies for the systems shown in Figure S4 (in Hartree).

system	H_{373} BP86-D3/ TZVP (gas)	G_{373} BP86-D3/ TZVP (gas)	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)
pyr						
v2020_004	-248.272946	-248.316938	-248.0796346	-248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	**-**		**-441.030468**	-441.091186
v2020_002	-	-	-		-441.030317	**-441.091431**
v2020_001	-441.349816	-441.412343	-441.0236207	-441.0861477	-441.024248	-441.085326
3						
v2020_072	**-671.013242**	**-671.092003**	**-670.4857548**	**-670.5645158**	**-670.482294**	**-670.559482**
v2020_073	-671.012815	-671.091797	-670.4845798	-670.5635618	-670.481350	-670.558145
v2020_074	-671.010822	-671.087938	-670.4824912	-670.5596072	-670.479055	-670.555178
v2020_075	-671.010412	-671.087028	-670.4819052	-670.5585212	-670.478503	-670.554594
v2020_076	-670.999539	-671.078426	-670.4711660	-670.5500530	-670.467489	-670.545944
3epox						
v2020_341	-	-	-	-	**-863.442162**	**-863.536757**
v2020_347	-	-	-	-	-863.441920	-863.536128
v2020_361	-	-	-	-	-863.441920	-863.536128
v2020_342	-	-	-	-	-863.441844	-863.536445
v2020_343	-	-	-	-	-863.441684	-863.535402
v2020_362	-	-	-	-	-863.441684	-863.535402
v2020_344	-	-	-	-	-863.441660	-863.536371
v2020_345	-	-	-	-	-863.441449	-863.535207
v2020_348	-	-	-	-	-863.441384	-863.535555
v2020_346	-	-	-	-	-863.441338	-863.535614
v2020_353	-	-	-	-	-863.441032	-863.534513
v2020_358	-	-	-	-	-863.440711	-863.534137
v2020_354	-	-	-	-	-863.440719	-863.535831
v2020_356	-	-	-	-	-863.440522	-863.534823
v2020_355	-	-	-	-	-863.440502	-863.533604
v2020_359	-	-	-	-	-863.440353	-863.534520
v2020_357	-	-	-	-	-863.440314	-863.534262
v2020_360	-	-	-	-	-863.440227	-863.535313
v2020_350	**-**	-	**-**	-	-863.438872	-863.532886

	864.093388	864.190135	**863.4414159**	863.5381629		
v2020_351	-864.093144	**-864.190448**	-863.4410661	-863.5383701	-863.438988	-863.533827
v2020_349	-864.092585	-864.189840	-863.4411607	**-863.5384157**	-863.438675	-863.532456
v2020_352	-864.092322	-864.189909	-863.4405589	-863.5381459	-863.438601	-863.533391
v2020_340	-	-	-	-	-863.438217	-863.531720
v2020_335	-	-	-	-	-863.437977	-863.531016
v2020_338	-	-	-	-	-863.437492	-863.530292
v2020_339	-	-	-	-	-863.437527	-863.531012
v2020_334	-	-	-	-	-863.437526	-863.531571
v2020_333	-	-	-	-	-863.437568	-863.532409
v2020_336	-	-	-	-	-863.437394	-863.531735
v2020_328	-864.089735	-864.185334	-863.1166355	-862.4637477	-863.434579	-863.527845
propylene oxide (PO) transfer						
ΔE (kcal/mol)	-2.06	-1.91	-7.33	-7.14	-5.17	-5.24

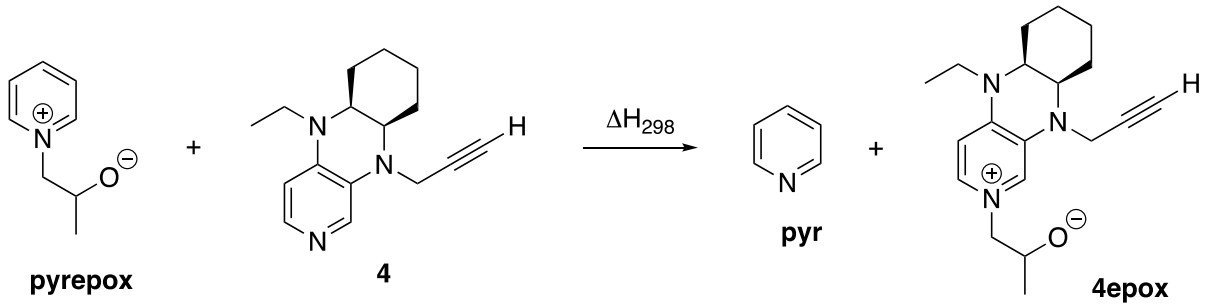


Figure S94. Formal propylene oxide (PO) transfer from pyridine to catalyst **4**.

Conformational space selection for catalyst **4** and adduct **4epox**: the attached cyclohexane ring is assumed to occupy a chair conformation, which puts the two amino substituents either in an axial/equatorial (ae) or in an equatorial/axial (ea) orientation.

Table S7a. Total energies and enthalpies for the systems shown in Figure S5 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/TZVP (SP)	E_{tot} PCM/M06/TZVP (opt)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)	conf
pyr								
v2020_004	-248.3666737	-248.272946	-248.316938	-248.1733623	-248.1747374	-248.078837	-248.122506	
pyrepox								
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186	
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**	
v2020_001	-441.5358646	-441.349816	-441.412343	-441.2096693	-441.2154689	-441.024248	-441.085326	
4								
v2020_061	**-786.8170817**	**-786.452818**	**-786.542697**	**-786.2011883**	**-786.2053505**	**-785.832862**	**-785.920535**	aedd
v2020_062	-786.8162911	-786.452114	-786.542560	-786.2002813	-786.2044790	-785.831941	-785.919349	aedu
v2020_063	-786.8137273	-786.449689	-786.540167	-786.1975237	-786.2016744	-785.829367	-785.918623	eadd
v2020_065	-786.8147425	-786.450894	-786.540785	-786.1974126	-786.2016431	-785.829467	-785.917942	aeud
v2020_064	-786.8132170	-786.449161	-786.537901	-786.1975250	-786.2016303	-785.829313	-785.916637	eadu
v2020_066	-786.8144454	-786.450682	-786.540743	-786.1970883	-786.2012634	-785.829101	-785.917286	aeuu
v2020_067	-786.8025367	-786.438528	-786.530255	-786.1866180	-786.1909051	-785.818309	-785.907553	bbdd
4epox								
v2020_147	-	-	-	-	**-979.2612766**	**-978.793103**	**-978.898027**	aedd.u+g-g
v2020_143	-	-	-	-	-979.2611610	-978.792889	-978.896815	aedd.d-g+g
v2020_148	-	-	-	-	-979.2607338	-978.792579	-978.897398	aedd.u+ga
v2020_144	-	-	-	-	-979.2603968	-978.792132	-978.897145	aedd.d-ga
v2020_158	-	-	-	-	-979.2602546	-978.792064	-978.896038	aedu.u+g-g
v2020_145	-	-	-	-	-979.2601919	-978.792003	-978.896536	aedd.u-g+g

v2020_155	-	-	-	-	-979.2601360	-978.7919066	-978.8956066	aedu.d-g+g
v2020_141	-	-	-	-	-979.2601005	-978.7919666	-978.8954444	aedd.d+g-g
v2020_146	-	-	-	-	-979.2600464	-978.7919044	-978.8966344	aedd.u-ga
v2020_157	-	-	-	-	-979.2597217	-978.7914442	-978.8958088	aedu.u+ga
v2020_142	-	-	-	-	-979.2596188	-978.7913779	-978.8949550	aedd.d+ga
v2020_156	-	-	-	-	-979.2593132	-978.7912115	-978.8961855	aedu.d-ga
v2020_159	-	-	-	-	-979.2592277	-978.7910669	-978.8955773	aedu.u-g+g
v2020_160	-	-	-	-	-979.2591010	-978.7909499	-978.8950700	aedu.u-ga
v2020_153	-	-	-	-	-979.2590860	-978.7908466	-978.8932477	aedu.d+g-g
v2020_154	-	-	-	-	-979.2584986	-978.7902220	-978.8936671	aedu.d+ga
v2020_149	-979.9902360	-979.533490	-979.642070	**-979.2495485**	-979.2579248	-978.7895771	-978.8929779	aedd.da+g
v2020_150	-979.9897867	-979.533010	-979.641303	-979.2493864	-979.2577790	-978.7894772	-978.8939774	aedd.da-g
v2020_134	-	-	-	-	-979.2575626	-978.7893332	-978.8934009	eadd.d-g+g
v2020_140	-	-	-	-	-979.2574149	-978.7892441	-978.8939440	eadd.u+g-g
v2020_151	**-979.9905853**	**-979.533874**	**-979.642319**	-979.2491612	-979.2572839	-978.7890118	-978.8941045	aedd.ua-g
v2020_162	-	-	-	-	-979.2572553	-978.7891840	-978.8942343	aeud.d-g+g
v2020_152	-979.9898829	-979.533003	-979.640702	-979.2490205	-979.2570361	-978.7888355	-978.8940801	aedd.ua+g
v2020_138	-	-	-	-	-979.2568888	-978.7885610	-978.8935055	eadd.u-g+g
v2020_136	-	-	-	-	-979.2568034	-978.7886833	-978.8941336	eadd.d-ga
v2020_139	-	-	-	-	-979.2566317	-978.7883773	-978.8932004	eadd.u-ga
v2020_161	-	-	-	-	-979.25625	-978.78808	-978.89174	aeud.u+g-g

					60	7	5	
v2020_135	-	-	-	-	-979.2557445	-978.787571	-978.891775	eadd.d+g-g
v2020_133	-	-	-	-	-979.2557073	-978.787454	-978.891504	eadd.d+ga
v2020_128	-979.9876669	-979.530948	-979.639030	-979.2461491	-979.2544012	-978.786171	-978.890165	eadd.da+g
v2020_137	-979.9875007	-979.531005	-979.640249	-979.2458324	-979.2543820	-978.786098	-978.891621	eadd.da-g
v2020_129	-979.9880249	-979.531287	-979.639458	-979.2455073	-979.2538310	-978.785671	-978.891192	eadd.ua-g
v2020_127	-979.9867620	-979.530107	-979.637189	-979.2453468	-979.2537288	-978.785546	-978.889077	eadu.da+g
v2020_126	-979.9871424	-979.530695	-979.638163	-979.2450269	-979.2531480	-978.785072	-978.889200	eadu.ua-g
4cyc								
v2020_147c	-980.0151148	-979.556768	-979.661553	**-979.2572827**	**-979.2636880**	-978.794490	-978.897043	
v2020_158c	**-980.0151204**	**-979.556824**	**-979.661684**	-979.2569740	-979.2635160	**-978.794628**	**-978.897054**	
v2020_148c	-980.0142743	-979.555887	-979.661420	-979.2565644	-979.2632283	-978.794057	-978.897239	
v2020_143c	-980.0112061	-979.553018	-979.658818	-979.2561608	-979.2621589	-978.793252	-978.895591	
v2020_155c	-980.0105131	-979.551924	-979.655726	-979.2554379	-979.2613907	-978.792275	-978.894703	
v2020_145c	-980.0102675	-979.551929	-979.656630	-979.2555734	-979.2613778	-978.792245	-978.893994	
v2020_144c	-980.0096782	-979.551230	-979.657021	-979.2549966	-979.2611301	-978.792110	-978.895011	
propylene oxide (PO) transfer								
ΔE (kcal/mol)	-2.71	-2.63	-2.65	-7.56	-5.56	**-5.40**	-5.28	
zwitterion collapse energy (6epox)								

ΔE (kcal/mol)	-15.39	-14.41	-12.14	-4.85	-1.51	**-0.96**	+0.62	

Table S7b. Enthalpies and free energies for the systems shown in Figure S5 (in Hartree).

system	H_{373} BP86-D3/ TZVP (gas)	G_{373} BP86-D3/ TZVP (gas)	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)
pyr						
v2020_004	-248.272946	-248.316938	-248.0796346	-248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	-		**-441.030468**	-441.091186
v2020_002	-	-	-		-441.030317	**-441.091431**
v2020_001	-441.349816	-441.412343	-441.0236207	-441.0861477	-441.024248	-441.085326
4						
v2020_061	**-786.452818**	**-786.542697**	**-785.8369246**	**-785.9268036**	**-785.832862**	**-785.920535**
v2020_062	-786.452114	-786.542560	-785.8361042	-785.9265502	-785.831941	-785.919349
v2020_065	-786.450894	-786.540785	-785.8335641	-785.9234551	-785.829467	-785.917942
v2020_063	-786.449689	-786.540167	-785.8334854	-785.9239634	-785.829367	-785.918623
v2020_064	-786.449161	-786.537901	-785.8334690	-785.9222090	-785.829313	-785.916637
v2020_066	-786.450682	-786.540743	-785.8333249	-785.9233859	-785.829101	-785.917286
v2020_067	-786.438528	-786.530255	-785.8226093	-785.9143363	-785.818309	-785.907553
4epox						
v2020_147	-	-	-	-	**-978.793103**	**-978.898027**
v2020_143	-	-	-	-	-978.792889	-978.896815
v2020_148	-	-	-	-	-978.792579	-978.897398
v2020_144	-	-	-	-	-978.792132	-978.897145
v2020_158	-	-	-	-	-978.792064	-978.896038
v2020_145	-	-	-	-	-978.792003	-978.896536
v2020_155	-	-	-	-	-978.791906	-978.895606
v2020_141	-	-	-	-	-978.791966	-978.895444
v2020_146	-	-	-	-	-978.791904	-978.896634
v2020_157	-	-	-	-	-978.791442	-978.895808
v2020_142	-	-	-	-	-978.791379	-978.894950
v2020_156	-	-	-	-	-978.791215	-978.896185

v2020_159	-	-	-	-	-978.791069	-978.895573
v2020_160	-	-	-	-	-978.790949	-978.895070
v2020_153	-	-	-	-	-978.790846	-978.893247
v2020_154	-	-	-	-	-978.790220	-978.893671
v2020_149	-979.533490	-979.642070	**-978.7928025**	**-978.9013825**	-978.789571	-978.892979
v2020_150	-979.533010	-979.641303	-978.7926097	-978.9009027	-978.789472	-978.893974
v2020_134	-	-	-	-	-978.789332	-978.893409
v2020_140	-	-	-	-	-978.789241	-978.893940
v2020_151	**-979.533874**	**-979.642319**	-978.7924499	-978.9008949	-978.789018	-978.894105
v2020_162	-	-	-	-	-978.789180	-978.894233
v2020_152	-979.533003	-978.790846	-978.7921406	-978.8998396	-978.788835	-978.894081
v2020_138	-	-	-	-	-978.788560	-978.893505
v2020_136	-	-	-	-	-978.788683	-978.894136
v2020_139	-	-	-	-	-978.788373	-978.893204
v2020_161	-	-	-	-	-978.788087	-978.891745
v2020_135	-	-	-	-	-978.787571	-978.891775
v2020_133	-	-	-	-	-978.787454	-978.891504
v2020_128	-979.530948	-979.639030	-978.7894302	-978.8975122	-978.786171	-978.890165
v2020_137	-979.531005	-979.640249	-978.7893367	-978.8985807	-978.786098	-978.891621
v2020_129	-979.531287	-979.639458	-978.7887694	-978.8969404	-978.785671	-978.891192
v2020_127	-979.530107	-979.637189	-978.7886918	-978.8957738	-978.785546	-978.889077
v2020_126	-979.530695	-979.638163	-978.7885795	-978.8960475	-978.785072	-978.889200
propylene oxide (PO) transfer						
ΔE (kcal/mol)	-2.63	-2.65	-7.46	-7.57	**-7.57**	-5.38

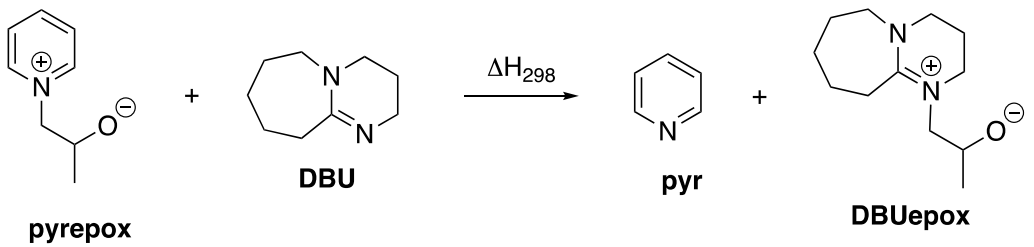


Figure S95. Formal propylene oxide (PO) transfer from pyridine to DBU.

Table S8a. Total energies and enthalpies for the systems shown in Figure S6 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/T ZVP (SP)	E_{tot} PCM/M06/T ZVP (opt)	H_{373} PCM/M06/T ZVP (opt)	G_{373} PCM/M06/T ZVP (opt)	conf
pyr								
v2020_004	-248.3666737	-248.272946	-248.316938	-248.1733623	-248.1747374	-248.078837	-248.122506	
pyrepox								
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186	
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**	
v2020_001	-441.5358646	-441.349816	-441.412343	-441.2096693	-441.2154689	-441.024248	-441.085326	
DBU								
v2020_077	**-462.2608538**	**-462.005712**	**-462.069913**	**-461.8948908**	**-461.8974988**	**-461.636672**	**-461.699770**	
v2020_078	-462.2604346	-462.005343	-462.069546	-461.8940753	-461.8966632	-461.635746	-461.699173	
v2020_083	-462.2569382	-462.001649	-462.066555	-461.8906027	-461.8932830	-461.632168	-461.695710	
v2020_084	-462.2572745	-462.001861	-462.065801	-461.8905449	-461.8931776	-461.632113	-461.695203	
v2020_095	-462.2532332	-461.998140	-462.062481	-461.8874952	-461.8900293	-461.629183	-461.692686	
v2020_094	-462.2534111	-461.998250	-462.062481	-461.8868615	-461.8894267	-461.628433	-461.692006	
DBUepox								
v2020_089	-	-	-	-	**-654.9607549**	**-654.603508**	**-654.680962**	
v2020_081	**-655.4433168**	**-655.095004**	**-655.176928**	**-654.9500740**	-654.9576032	-654.600047	-654.678638	
v2020_090	-	-	-	-	-654.9562642	-654.599097	-654.677596	
v2020_079	-655.4331412	-655.085253	-655.167288	-654.9424883	-654.9556454	-654.598096	-654.677265	
v2020_082	-655.4410928	-655.092925	-655.175079	-654.9446106	-654.9543134	-654.597063	-654.677801	

v2020_080	-655.4320791	-655.083862	-655.165836	-654.9452968	-654.9537424	-654.596333	-654.676872	
v2020_088	-655.4395416	-655.091387	-655.171556	-654.9438519	-654.9523566	-654.594747	-654.673461	
v2020_086	-655.4293157	-655.080993	-655.163717	-654.9432151	-654.9511107	-654.593463	-654.673058	
v2020_085	(collapse)	-	-	-	-654.9499864	-654.592235	-654.672684	
v2020_087	-655.4375106	-655.089465	-655.170827	-654.9406602	-654.9492955	-654.591746	-654.672045	
v2020_097	-655.4378167	-655.090204	-655.169996	-654.9368085	-654.9463777	-654.589362	-654.668544	
v2020_096	(H-transfer)	-	-	-	-654.9452592	-654.587613	-654.667595	
DBUcyc								
v2020_092	-	-	-	-	**-654.9844972**	**-654.627059**	**-654.702385**	
v2020_091	-	-	-	-	-654.9835643	-654.626033	-654.701238	
v2020_089c	**-655.4813058**	**-655.131720**	**-655.208141**	**-654.976253**	-654.9803547	-654.622912	-654.697846	
v2020_085c	-655.4784395	-655.128717	-655.205912	-654.9749952	-654.9788906	-654.621128	-654.697178	
v2020_093	-	-	-	-	-654.9783710	-654.620754	-654.697322	
propylene oxide (PO) transfer								
ΔE (kcal/mol)	-8.33	-7.79	-7.28	-11.85	-10.16	**-9.54**	-7.70	
zwitterion collapse energy (8epox)								
ΔE (kcal/mol)	-23.83	-23.04	-19.59	-16.43	-14.90	**-14.78**	-13.44	

Table S6b. Enthalpies and free energies for the systems shown in Figure S6 (in Hartree).

system	H_{373} BP86-D3/TZVP (gas)	G_{373} BP86-D3/TZVP (gas)	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)

pyr						
v2020_004	-248.272946	-248.316938	-248.0796346	-248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	**-**		**-441.030468**	-441.091186
v2020_002	-	-	-		-441.030317	**-441.091431**
v2020_001	-441.349816	-441.412343	-441.0236207	-441.0861477	-441.024248	-441.085326
DBU						
v2020_077	**-462.005712**	**-462.069913**	**-461.6397490**	**-461.7039500**	**-461.636672**	**-461.699770**
v2020_078	-462.005343	-462.069546	-461.6389837	-461.7031867	-461.635746	-461.699173
v2020_083	-462.001649	-462.066555	-461.6353135	-461.7002195	-461.632168	-461.695710
v2020_084	-462.001861	-462.065801	-461.6351314	-461.6990714	-461.632113	-461.695203
v2020_095	-461.998140	-462.062481	-461.6324020	-461.6967430	-461.629183	-461.692686
v2020_094	-461.998250	-462.062481	-461.6317004	-461.6959314	-461.628433	-461.692006
DBUepox						
v2020_089	-	-	-	-	**-654.603508**	**-654.680962**
v2020_081	**-655.095004**	**-655.176928**	**-654.6017612**	**-654.6836852**	-654.600047	-654.678638
v2020_090	-	-	-	-	-654.599097	-654.677596
v2020_079	-655.085253	-655.167288	-654.5946001	-654.6766351	-654.598096	-654.677265
v2020_082	-655.092925	-655.175079	-654.5964428	-654.6785968	-654.597063	-654.677801
v2020_080	-655.083862	-655.165836	-654.5970797	-654.6790537	-654.596333	-654.676872
v2020_088	-655.091387	-655.171556	-654.5956973	-654.6758663	-654.594747	-654.673461
v2020_086	-655.080993	-655.163717	-654.5948924	-654.6776164	-654.593463	-654.673058
v2020_085	-	-	-	-	-654.592235	-654.672684
v2020_087	-655.089465	-655.170827	-654.5926146	-654.6739766	-654.591746	-654.672045
v2020_097	-655.090204	-655.169996	-654.5891958	-654.6689878	-654.589362	-654.668544

v2020_096	-	-	-	-	-654.587613	-654.667595
propylene oxide (PO) transfer						
ΔE (kcal/mol)	-7.79	-7.28	-11.31	-10.80	**-9.54**	-7.70

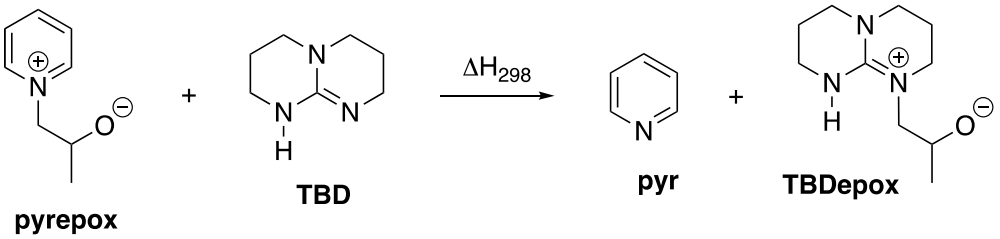


Figure S96. Formal propylene oxide (PO) transfer from pyridine to TBD.

Table S9a. Total energies and enthalpies for the systems shown in Figure S7 (in Hartree).

system	E_{tot} BP86-D3/ TZVP	H_{373} BP86-D3/ TZVP	G_{373} BP86-D3/ TZVP	E_{tot} PCM/M06/TZVP (SP)	E_{tot} PCM/M06/TZVP (opt)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)	conf
pyr								
v2020_004	-248.3666737	-248.272946	-248.316938	-248.1733623	-248.1747374	-248.078837	-248.122506	
pyrepox								
v2020_003	(collapse)	-	-	-	**-441.2217974**	**-441.030468**	-441.091186	
v2020_002	(collapse)	-	-	-	-441.2215652	-441.030317	**-441.091431**	
v2020_001	-441.5358646	-441.349816	-441.412343	-441.2096693	-441.2154689	-441.024248	-441.085326	

pyrcyc								**1cyc**
v2020_003c	**-441.5679829**	**-441.379827**	**-441.439467**	-441.2369168	**-441.2398363**	**-441.047047**	**-441.105622**	v2020_003c
v2020_002c	-441.5671169	-441.379020	-441.439447	-441.2361960	-441.2391496	-441.046352	-441.105318	v2020_002c
TBD								
v2020_401	**-438.9861877**	**-438.772107**	**-438.831930**	**-438.6522323**	**-438.6547290**	**-438.435721**	**-438.495268**	
v2020_402	-438.9850665	-438.770955	-438.831389	-438.6517495	-438.6543298	-438.435329	-438.495110	
v2020_403	-438.9861877	-	-	-	-	-	-	
TBDepox								
v2020_406	(collapse)	-	-	-	**-631.7187100**	**-631.403592**	**-631.480873**	
v2020_411	**-632.1693472**	**-631.862409**	**-631.940037**	**-631.7103361**	-631.7177313	-631.402425	-631.479338	
v2020_408	(collapse)	-	-	-	-631.7169950	-631.401597	-631.478372	
v2020_405	-632.1566752	-631.849613	-631.928718	-631.7100899	-631.7164114	-631.401124	-631.478340	
v2020_404	-632.1569398	-631.849880	-631.928616	-631.7077091	-631.7152094	-631.399761	-631.477268	
v2020_410	-632.1684253	-631.860899	-631.936898	-631.7067397	-631.7150627	-631.399954	-631.476644	
v2020_409	(H-transf.)	-	-	-	(H-transf.)	-	-	
v2020_407	(H-transf.)	-	-	-	(H-transf.)	-	-	
TBDcyc								
v2020_406c	**-632.2079074**	**-631.899438**	**-631.970989**	**-631.7363074**	**-631.7402084**	**-631.424625**	**-631.495378**	
v2020_413c	-632.2035357	-631.895375	-631.967161	-631.7342217	-631.7384474	-631.422707	-631.492764	
v2020_412c	-632.2058980	-631.897631	-631.969438	-631.7340067	-631.7378774	-631.422345	-631.493161	
v2020_408c	-632.2024768	-631.894032	-631.965444	-631.7333034	-631.7374504	-631.421739	-631.491746	
propylene oxide (PO)								

transfer								
ΔE (kcal/mol)	-0.98	-0.57	-0.87	-13.52	-10.62	**-10.19**	-10.47	
zwitterion collapse energy (9epox)								
ΔE (kcal/mol)	-24.20	-23.24	-19.42	-16.30	-13.49	**-13.20**	-9.10	

Table S9b. Enthalpies and free energies for the systems shown in Figure S7 (in Hartree).

system	H_{373} BP86-D3/ TZVP (gas)	G_{373} BP86-D3/ TZVP (gas)	H_{373} PCM/M06/TZVP (SP)	G_{373} PCM/M06/TZVP (SP)	H_{373} PCM/M06/TZVP (opt)	G_{373} PCM/M06/TZVP (opt)
pyr						
v2020_004	-248.272946	-248.316938	-248.0796346	-248.1236266	-248.078837	-248.122506
pyrepox						
v2020_003	-	-	**-**		**-441.030468**	-441.091186
v2020_002	-	-	-		-441.030317	**-441.091431**
v2020_001	-441.349816	-441.412343	-441.0236207	-441.0861477	-441.024248	-441.085326
TBD						
v2020_401	**-438.772107**	**-438.831930**	**-438.4381516**	-438.4979746	**-438.435721**	**-438.495268**
v2020_402	-438.770955	-438.831389	-438.4376380	**-438.4980720**	-438.435329	-438.495110
TBDepox						
v2020_406	-	-	-	-	**-631.403592**	**-631.480873**
v2020_411	**-631.862409**	**-631.940037**	**-631.4033979**	-631.4810259	-631.402425	-631.479338
v2020_408	-	-	-	-	-631.401597	-631.478372
v2020_405	-631.849613	-631.928718	-631.4030277	**-631.4821327**	-631.401124	-631.478340
v2020_404	-631.849880	-631.928616	-631.4006493	-631.4793853	-631.399761	-631.477268
v2020_410	-631.860899	-631.936898	-631.3992134	-631.4752124	-631.399954	-631.476644
propylene oxide						

(PO) transfer						
ΔE (kcal/mol)	-0.57	-0.87	-13.34	-13.52	-10.19	-10.47

Structures of Important Stationary Points
(optimized at PCM/M06/TZVP level, best conformer only)

pyr

C	-0.00000	1.37383	0.00000
C	1.19061	0.66754	0.00000
C	1.13635	-0.71697	0.00000
N	0.00000	-1.40918	0.00000
C	-1.13634	-0.71697	0.00000
C	-1.19061	0.66754	0.00000
H	-0.00001	2.45762	0.00000
H	2.14681	1.17593	0.00000
H	2.05540	-1.29751	0.00000
H	-2.05539	-1.29752	0.00000
H	-2.14681	1.17592	0.00000

pyrepox

C	-2.12303	-0.13643	0.02874
O	-1.83770	-1.32889	0.54146
C	-1.18568	0.20883	-1.19113
H	-1.34165	-0.53780	-1.96982
H	-1.35559	1.20785	-1.59381
C	2.59712	-0.12948	0.55294
C	2.10863	1.12778	0.20699
C	0.89956	1.22086	-0.42504
N	0.19506	0.11283	-0.73962
C	0.64515	-1.11294	-0.40287
C	1.85987	-1.25138	0.24090
H	3.55360	-0.22319	1.05141
H	2.66011	2.02996	0.43135
H	0.45160	2.16340	-0.71068
H	0.01416	-1.93939	-0.68735

H	2.21082	-2.24335	0.48957
H	-3.12829	-0.07176	-0.46516
C	-2.06446	1.00705	1.04548
H	-2.28094	1.98773	0.60550
H	-2.79332	0.81709	1.83663
H	-1.07731	1.04496	1.52183

pyrcyc

C	1.63557	-1.23698	0.00571
C	2.37202	-0.25142	0.53611
C	1.93730	1.11722	0.47564
C	0.82120	1.40465	-0.21906
N	0.13000	0.45018	-0.92544
C	0.31174	-0.94414	-0.59118
O	-0.76272	-1.22981	0.33571
C	-1.85330	-0.36114	0.01591
C	-1.30917	0.56505	-1.09173
C	-2.26845	0.38730	1.25691
H	-1.59086	0.20158	-2.08336
H	-1.63901	1.59878	-0.98675
H	3.32063	-0.48146	1.00981
H	2.50710	1.90785	0.94293
H	0.43747	2.41447	-0.31882
H	0.12184	-1.54082	-1.49629
H	1.94898	-2.27261	0.04430
H	-2.68655	-0.96025	-0.37024
H	-3.14182	1.01326	1.05924
H	-2.51681	-0.30624	2.06224
H	-1.45056	1.02945	1.59941

DMAP

C	0.18234	0.00000	-0.00001
C	-0.56593	1.19189	-0.00000
C	-1.94231	1.12689	0.00000
N	-2.65579	-0.00000	0.00000
C	-1.94231	-1.12689	0.00000
C	-0.56592	-1.19188	-0.00000
H	-0.08387	2.16013	-0.00000
H	-2.51018	2.05484	0.00000
H	-2.51017	-2.05484	-0.00000
H	-0.08386	-2.16013	-0.00001
N	1.54046	0.00000	0.00000
C	2.26522	-1.25134	0.00000
H	2.03780	-1.85302	0.88667
H	2.03781	-1.85302	-0.88667
H	3.33307	-1.04611	0.00001
C	2.26523	1.25134	-0.00000
H	2.03782	1.85301	-0.88667
H	2.03782	1.85301	0.88667
H	3.33308	1.04611	-0.00000

DMAPepox

C	-3.23787	-0.19281	0.31866
O	-2.90002	-1.44144	0.64587
C	-2.54664	0.27538	-0.99832
H	-2.82907	-0.40373	-1.80494

H	-2.81213	1.29684	-1.27899
C	1.59951	0.01524	-0.13561
C	0.95448	1.26865	-0.28457
C	-0.36109	1.32397	-0.61979
N	-1.09305	0.21232	-0.84588
C	-0.51150	-1.00028	-0.70766
C	0.80695	-1.12654	-0.37487
H	1.48182	2.19794	-0.12911
H	-0.88485	2.26525	-0.72665
H	-1.16572	-1.84363	-0.87032
H	1.21689	-2.12230	-0.29484
N	2.89673	-0.07425	0.20241
C	3.52022	-1.37503	0.36329
H	3.02984	-1.95865	1.14755
H	3.49281	-1.94923	-0.56722
H	4.56052	-1.23746	0.64449
C	3.68142	1.12525	0.43213
H	3.71661	1.75692	-0.45986
H	3.28097	1.71423	1.26231
H	4.69959	0.83976	0.68170
C	-2.95007	0.82866	1.42587
H	-1.88894	0.79655	1.70239
H	-3.21064	1.85722	1.14655
H	-3.52256	0.56025	2.31696
H	-4.32326	-0.05986	0.05246

DMAPcyc

C	0.65384	-1.03384	-0.49371
C	1.41664	0.05073	-0.17790
C	0.77815	1.35413	-0.15216
C	-0.49299	1.47788	-0.56843
N	-1.22279	0.43085	-1.06966
C	-0.79545	-0.90189	-0.70988
O	-1.57134	-1.18830	0.49241
C	-2.81906	-0.50944	0.37194
C	-2.66157	0.39729	-0.87026
C	-3.08244	0.26758	1.63685
N	2.76569	-0.03302	0.07108
C	3.49179	1.08772	0.62883
C	3.36235	-1.34230	0.16717
H	-3.13963	-0.04701	-1.74686
H	-3.06390	1.39991	-0.72091
H	1.31021	2.23892	0.16229
H	-0.99595	2.43924	-0.58137
H	-1.15899	-1.59566	-1.48309
H	1.05903	-2.03477	-0.52726
H	2.93833	-1.93715	0.98838
H	3.21736	-1.90608	-0.75967
H	4.43356	-1.24232	0.33179
H	3.41138	1.97367	-0.00469
H	3.15698	1.35623	1.63925
H	4.54773	0.82851	0.68388
H	-2.31511	1.03712	1.76947
H	-4.05954	0.75513	1.59812
H	-3.05982	-0.38995	2.50789
H	-3.61882	-1.24144	0.19895

compound 1

C	0.00000	0.08879	-0.05165
C	-1.20465	0.81790	-0.04612
C	-1.12777	2.19587	0.00324
N	0.00000	2.90454	0.03094
C	1.12777	2.19587	0.00324
C	1.20465	0.81790	-0.04612
H	-2.05798	2.76409	0.02254
H	2.05798	2.76409	0.02254
N	0.00000	-1.28004	-0.03890
C	1.23808	-2.00646	-0.24810
H	1.44606	-2.11683	-1.32486
H	1.10415	-3.01391	0.15534
C	-1.23808	-2.00646	-0.24810
H	-1.44606	-2.11683	-1.32486
H	-1.10415	-3.01391	0.15534
C	2.52437	0.10654	-0.10228
H	2.87658	0.06431	-1.14101
H	3.27802	0.67180	0.45310
C	-2.52437	0.10654	-0.10228
H	-2.87658	0.06431	-1.14101
H	-3.27802	0.67180	0.45310
C	2.39484	-1.30748	0.43275
H	3.31363	-1.87398	0.26822
H	2.21258	-1.28587	1.51255
C	-2.39484	-1.30748	0.43275
H	-2.21258	-1.28587	1.51255
H	-3.31363	-1.87398	0.26822

1epox

C	-3.76906	-0.10456	0.32390
O	-3.48762	-1.30967	0.82290
C	-3.03895	0.16022	-1.02473
H	-3.31849	-0.62368	-1.73158
H	-3.28577	1.13369	-1.45464
C	1.09330	-0.00545	-0.14316
C	0.47569	1.23002	-0.47331
C	-0.84823	1.23548	-0.78826
N	-1.58680	0.10602	-0.84535
C	-1.01335	-1.07869	-0.54006
C	0.30345	-1.17695	-0.18592
H	-1.36969	2.15574	-1.02437
H	-1.67629	-1.93251	-0.57068
N	2.39609	-0.05588	0.18921
C	3.09369	-1.31869	0.40734
H	3.19030	-1.49352	1.48737
H	4.10662	-1.20379	0.00966
C	3.20456	1.14515	0.37007
H	3.87574	0.96189	1.21468
H	3.83655	1.28982	-0.51670
C	0.92785	-2.49356	0.15307
H	0.85742	-2.66968	1.23355
H	0.38267	-3.30516	-0.33324
C	2.38905	-2.47761	-0.25807
H	2.88828	-3.40696	0.02012
H	2.46586	-2.37850	-1.34590
C	1.29187	2.48342	-0.45423

H	0.64914	3.35175	-0.29460
H	1.77863	2.62342	-1.42739
C	2.35580	2.36911	0.62233
H	2.99683	3.25172	0.63913
H	1.87984	2.29147	1.60525
C	-3.46748	1.04556	1.29341
H	-2.41139	1.02250	1.58948
H	-3.69407	2.03528	0.87703
H	-4.06067	0.91146	2.20129
H	-4.84481	0.03073	0.01713

1cyc

C	3.30897	0.34242	0.42352
O	2.09443	1.05274	0.65148
C	3.10462	-0.36614	-0.93500
H	3.59226	0.18668	-1.74226
H	3.47440	-1.39221	-0.94053
C	-0.93163	0.00438	-0.13777
C	-0.35005	-1.32496	-0.28773
C	0.90752	-1.41603	-0.74733
N	1.66376	-0.32310	-1.12216
C	1.29039	0.94928	-0.56141
C	-0.15140	1.10552	-0.29404
H	1.38335	-2.38033	-0.90122
H	1.65272	1.74274	-1.23745
N	-2.29531	0.10641	0.10239
C	-2.78163	1.38906	0.57033
H	-2.53217	1.52946	1.63701
H	-3.87274	1.38413	0.49360
C	-3.04013	-1.04441	0.57569
H	-2.90388	-1.18352	1.66389
H	-4.10246	-0.83687	0.41528
C	-0.67731	2.49876	-0.14606
H	-0.36248	2.92950	0.81589
H	-0.23596	3.14638	-0.91443
C	-2.19196	2.51704	-0.24880
H	-2.59943	3.47275	0.08872
H	-2.49500	2.38393	-1.29294
C	-1.14570	-2.54055	0.08533
H	-1.00461	-2.76683	1.15188
H	-0.78544	-3.41254	-0.46709
C	-2.62472	-2.30314	-0.14919
H	-2.82780	-2.18861	-1.21987
H	-3.21818	-3.14670	0.21143
H	4.13995	1.05615	0.34948
C	3.54381	-0.61766	1.56239
H	2.74387	-1.36423	1.59415
H	4.49807	-1.13646	1.44329
H	3.55622	-0.09007	2.51804

compound 2

C	-1.08816	0.98965	0.55878
C	-1.11201	-0.48619	0.95407
N	-0.15967	-1.19971	0.11696
C	1.12240	-0.67734	0.02269
C	1.32449	0.69703	0.26368
N	0.27523	1.47438	0.67650

C	2.61571	1.18998	0.10300
C	3.63302	0.33252	-0.27610
N	3.45704	-0.96635	-0.50076
C	2.21969	-1.43931	-0.34470
H	-1.69571	1.52651	1.29886
H	2.81752	2.24178	0.27652
H	2.07263	-2.50344	-0.52876
H	4.64144	0.71852	-0.40272
H	-0.81756	-0.54544	2.01446
C	-2.50425	-1.07485	0.79607
H	-2.46872	-2.14569	1.02391
H	-3.14897	-0.61848	1.55674
C	-1.68669	1.22196	-0.82306
H	-1.68337	2.29601	-1.03471
H	-1.04204	0.74833	-1.57311
C	-3.09855	-0.83077	-0.58206
H	-4.11627	-1.22892	-0.61904
H	-2.51954	-1.37550	-1.33633
C	-3.09297	0.65248	-0.91476
H	-3.74539	1.18346	-0.20790
H	-3.50751	0.82667	-1.91131
H	-0.20049	-2.20631	0.20157
H	0.40971	2.47342	0.64725

2epox

C	-2.52704	0.78722	0.67972
C	-2.06952	-0.65559	0.88045
N	-1.03382	-0.94578	-0.10290
C	0.03157	-0.06994	-0.16797
C	-0.16167	1.27125	0.24593
N	-1.36061	1.65434	0.72892
C	0.92253	2.15068	0.13874
C	2.11812	1.71736	-0.35800
N	2.27915	0.44495	-0.76332
C	1.26227	-0.44115	-0.65259
H	-3.16526	1.04562	1.53312
H	0.81507	3.18335	0.44488
H	1.50327	-1.45585	-0.93933
H	2.97826	2.36578	-0.45413
H	-1.66068	-0.73451	1.89957
C	-3.22912	-1.62659	0.73701
H	-2.84926	-2.65054	0.81508
H	-3.89390	-1.47816	1.59601
C	-3.31989	0.97056	-0.60770
H	-3.65682	2.00951	-0.67251
H	-2.65086	0.79882	-1.45939
C	-4.01547	-1.43029	-0.54916
H	-4.86292	-2.12047	-0.56861
H	-3.38689	-1.67959	-1.41166
C	-4.49341	0.00730	-0.67029
H	-5.18983	0.22836	0.14996
H	-5.04999	0.15368	-1.59946
C	3.59754	-0.06954	-1.14308
H	3.47722	-0.66036	-2.05334
H	4.23901	0.78858	-1.35498
C	4.17891	-0.98498	-0.02456
H	5.19675	-1.21599	-0.44897

C	4.43568	-0.13634	1.22739
H	5.05520	0.74776	1.03090
H	3.48434	0.19297	1.66354
H	4.94125	-0.74903	1.97762
O	3.42347	-2.06123	0.20412
H	-1.49844	2.62901	0.94676
H	-0.78947	-1.92343	-0.18217

2cyc

C	-1.69685	-0.09595	-0.98730
C	-0.26808	0.20791	-0.79309
C	0.12318	1.15683	0.08358
C	-0.86591	1.93163	0.79062
C	-2.16546	1.76461	0.50693
N	-2.58937	0.92091	-0.50606
N	1.47799	1.35823	0.35733
C	2.41813	0.81741	-0.61465
C	1.99574	-0.60461	-0.98705
N	0.64240	-0.57213	-1.52880
C	2.15829	-1.56473	0.18532
C	3.58421	-1.54617	0.71303
C	4.00106	-0.14003	1.11419
C	3.82844	0.82902	-0.04545
C	-3.85908	0.22471	-0.38370
C	-3.44483	-1.16754	0.13008
O	-2.08061	-1.30745	-0.26723
C	-3.54611	-1.29639	1.62970
H	2.39921	1.41313	-1.54174
H	2.67007	-0.92906	-1.79166
H	1.88051	-2.57267	-0.14198
H	1.45660	-1.28551	0.98045
H	3.68632	-2.23387	1.55716
H	4.26187	-1.91221	-0.07083
H	5.04178	-0.13087	1.45061
H	3.39171	0.19165	1.96216
H	4.08523	1.84963	0.25892
H	4.52204	0.56217	-0.85233
H	-0.55426	2.65409	1.53480
H	-1.91603	-0.29404	-2.05082
H	-2.95300	2.32345	0.99858
H	-4.33117	0.15295	-1.36766
H	-4.53386	0.74851	0.29379
H	-4.04181	-1.94467	-0.36213
H	-2.99237	-0.48536	2.11317
H	-4.58817	-1.24932	1.95518
H	-3.12324	-2.24502	1.96559
H	0.28909	-1.50554	-1.70640
H	1.70090	2.30289	0.64260

compound 3

C	-1.09461	0.74740	0.06374
C	-1.18223	-0.48808	0.95195
N	-0.39086	-1.53771	0.33092
C	0.93781	-1.20643	0.08930
C	1.27523	0.14663	-0.15763
N	0.29931	1.10284	-0.17006
C	2.62859	0.41134	-0.38755

C	3.54332	-0.62708	-0.40190
N	3.22963	-1.90010	-0.18949
C	1.94344	-2.15483	0.06075
C	0.61213	2.51578	-0.27303
C	1.01065	3.11924	1.05979
H	-1.55041	1.57268	0.63082
H	-0.27548	3.01883	-0.66686
H	1.39401	2.66788	-1.02226
H	1.91104	2.64116	1.45237
H	1.20677	4.18906	0.96485
H	0.21189	2.98393	1.79436
H	2.97621	1.42127	-0.56242
H	1.67599	-3.19369	0.25394
H	4.59110	-0.40725	-0.59279
H	-0.75736	-0.21460	1.93372
C	-2.62229	-0.93246	1.14446
H	-2.63603	-1.86057	1.72601
H	-3.12595	-0.17649	1.75872
C	-1.85828	0.57222	-1.24278
H	-1.79936	1.50073	-1.81958
H	-1.35794	-0.20271	-1.83505
C	-3.37534	-1.09809	-0.16596
H	-4.41526	-1.36625	0.03960
H	-2.94408	-1.92595	-0.74017
C	-3.30369	0.17780	-0.98887
H	-3.81216	0.98721	-0.44697
H	-3.83445	0.05700	-1.93699
H	-0.51336	-2.44806	0.75553

3epox

C	-2.41124	0.34693	0.21590
C	-1.80943	-0.87530	0.89602
N	-0.74504	-1.37691	0.04049
C	0.23808	-0.46238	-0.28475
C	-0.09526	0.92032	-0.33179
N	-1.36205	1.31951	-0.08730
C	0.94547	1.80958	-0.65273
C	2.19782	1.34705	-0.94111
N	2.47735	0.03362	-0.92626
C	1.51868	-0.85690	-0.57946
C	-1.73171	2.72654	-0.01799
C	-1.42890	3.32911	1.33865
H	-3.08149	0.81954	0.94740
H	-2.80091	2.78834	-0.23373
H	-1.23490	3.27794	-0.81985
H	-0.35930	3.29321	1.55698
H	-1.75027	4.37109	1.38038
H	-1.95073	2.78023	2.12688
H	0.77743	2.87606	-0.68502
H	1.85441	-1.88299	-0.50199
H	3.01429	2.01009	-1.19355
H	-1.39848	-0.54603	1.86455
C	-2.85899	-1.94543	1.14144
H	-2.37367	-2.83181	1.56271
H	-3.54051	-1.57084	1.91411
C	-3.21132	-0.01474	-1.02831
H	-3.65622	0.89279	-1.44780

H	-2.52241	-0.41017	-1.78359
C	-3.65447	-2.29605	-0.10569
H	-4.42546	-3.02888	0.14601
H	-2.99855	-2.77057	-0.84442
C	-4.27838	-1.04898	-0.71008
H	-4.99883	-0.62236	0.00098
H	-4.84146	-1.29631	-1.61354
C	3.85132	-0.45472	-1.07027
H	3.83911	-1.29304	-1.76985
H	4.44670	0.35751	-1.49292
C	4.40894	-0.95457	0.29484
H	5.47383	-1.19358	0.01483
C	4.49158	0.23181	1.26393
H	5.05126	1.08431	0.85871
H	3.48312	0.57043	1.53271
H	4.98071	-0.09240	2.18566
O	3.72337	-1.99206	0.78014
H	-0.39954	-2.29319	0.29311

3cyc

C	2.20326	0.26788	0.44788
C	2.05508	-0.30141	-0.97711
N	0.69737	-0.75301	-1.21782
C	-0.30606	0.03557	-0.64096
C	-0.05968	1.06099	0.21372
N	1.22434	1.31299	0.70841
C	-1.17137	1.86605	0.67276
C	-2.40864	1.62888	0.21468
N	-2.66842	0.67337	-0.75202
C	-1.69249	-0.35815	-0.96326
C	1.71226	2.68619	0.69393
C	2.01935	3.23334	-0.68756
H	3.19881	0.72708	0.51392
H	2.60452	2.72296	1.32652
H	0.97225	3.32387	1.18427
H	1.13705	3.16962	-1.33116
H	2.32380	4.28080	-0.63113
H	2.82842	2.67737	-1.16896
H	-1.01348	2.65490	1.39537
H	-1.75941	-0.70655	-2.00679
H	-3.26879	2.20850	0.53016
H	2.25303	0.52240	-1.67609
C	3.05527	-1.41695	-1.23222
H	2.88534	-1.83347	-2.23041
H	4.05839	-0.97459	-1.24185
C	2.12462	-0.84237	1.48691
H	2.25834	-0.40441	2.48025
H	1.11794	-1.28038	1.47230
C	3.00884	-2.50799	-0.17111
H	3.79382	-3.24343	-0.36813
H	2.06180	-3.06044	-0.22648
C	3.16521	-1.91874	1.22149
H	4.16758	-1.47787	1.31207
H	3.10168	-2.70417	1.97970
C	-3.92478	-0.05680	-0.71755
H	-4.70174	0.51578	-0.21017
H	-4.25174	-0.26660	-1.73961

C	-3.55248	-1.35894	0.02118
O	-2.13612	-1.46631	-0.12747
C	-3.89992	-1.32546	1.48846
H	-4.98310	-1.30301	1.63047
H	-3.50398	-2.20477	1.99993
H	-3.46871	-0.43451	1.95580
H	-4.03039	-2.21783	-0.46582
H	0.56372	-1.74676	-1.06191

compound 4

C	0.82824	-1.35290	0.16942
C	1.14916	0.07722	0.58482
N	0.51496	0.98174	-0.38198
C	-0.87653	0.80901	-0.46210
C	-1.42097	-0.48450	-0.23690
N	-0.60656	-1.53964	0.04552
C	-2.80982	-0.60720	-0.33891
C	-3.57940	0.48979	-0.67308
N	-3.08559	1.70113	-0.88848
C	-1.76179	1.83465	-0.76152
C	-1.12954	-2.84782	0.39631
C	-1.54739	-2.93615	1.85119
C	1.00938	2.34528	-0.41298
H	1.17054	-1.99708	0.99326
H	0.58198	2.85976	-1.27706
H	2.08487	2.32688	-0.59931
H	-0.34386	-3.57794	0.18358
H	-1.95843	-3.10513	-0.26839
H	-2.34843	-2.22798	2.07435
H	-1.90132	-3.93924	2.09677
H	-0.70331	-2.70430	2.50643
H	-3.29521	-1.55854	-0.16690
H	-1.38452	2.84086	-0.91269
H	-4.65735	0.37667	-0.76237
H	0.70889	0.24854	1.58372
C	2.65922	0.24152	0.69353
H	2.91662	1.25501	1.01154
H	2.97972	-0.41070	1.51463
C	1.56059	-1.75838	-1.10397
H	1.30631	-2.79444	-1.34840
H	1.18969	-1.13647	-1.92700
C	3.40607	-0.15993	-0.56910
H	4.48193	-0.05311	-0.40677
H	3.14725	0.51172	-1.39671
C	3.06285	-1.58841	-0.95778
H	3.43203	-2.27154	-0.18093
H	3.56795	-1.86915	-1.88564
C	0.74361	3.10171	0.81045
C	0.52808	3.67442	1.84237
H	0.33439	4.19369	2.75181

4epox

C	-2.38048	0.65708	-0.17386
C	-1.99490	-0.65604	0.49480
N	-0.67022	-1.04240	-0.00675
C	0.30794	-0.07475	0.21476
C	-0.06246	1.30255	0.21456

N	-1.34765	1.66364	0.03757
C	0.96826	2.24298	0.39947
C	2.26481	1.84514	0.54251
N	2.58927	0.54384	0.56481
C	1.62720	-0.39829	0.42484
C	-1.79252	3.04840	0.12896
C	-2.01871	3.48172	1.56265
C	-0.27052	-2.43016	0.15242
H	-3.28371	1.01596	0.33932
H	0.65119	-2.59722	-0.41281
H	-1.01670	-3.06901	-0.32315
H	-2.72012	3.12362	-0.44305
H	-1.07800	3.69975	-0.37927
H	-1.09425	3.43267	2.14208
H	-2.39107	4.50660	1.60197
H	-2.75383	2.83406	2.04709
H	0.75615	3.30167	0.41430
H	2.00951	-1.40725	0.42744
H	3.07851	2.54934	0.65323
H	-1.93281	-0.48328	1.58316
C	-3.07954	-1.69165	0.23395
H	-2.82845	-2.63954	0.71627
H	-3.97737	-1.33128	0.74970
C	-2.68608	0.48204	-1.65587
H	-2.96824	1.44919	-2.08236
H	-1.76697	0.16568	-2.16247
C	-3.40126	-1.87600	-1.24096
H	-4.21307	-2.59981	-1.34873
H	-2.53807	-2.29429	-1.77262
C	-3.78149	-0.54745	-1.87262
H	-4.71517	-0.18590	-1.42152
H	-3.97703	-0.66869	-2.94086
C	3.98266	0.09212	0.54515
H	4.61298	0.94965	0.78980
H	4.10059	-0.67264	1.31589
C	4.33358	-0.53256	-0.83848
O	3.59638	-1.61224	-1.11972
C	4.25091	0.56137	-1.91024
H	4.85738	1.44460	-1.67350
H	4.59367	0.15520	-2.86484
H	3.20961	0.87834	-2.04696
H	5.43017	-0.74788	-0.70399
C	-0.09806	-2.83229	1.54704
C	0.00906	-3.12078	2.70630
H	0.11380	-3.38797	3.73197

4cyc

C	-2.11088	0.80532	-0.61578
C	-2.01277	-0.39410	0.33348
N	-0.68028	-0.97974	0.19595
C	0.36169	-0.02868	0.26110
C	0.16561	1.29059	-0.00732
N	-1.09093	1.80416	-0.34422
C	1.29891	2.18851	-0.04465
C	2.52126	1.75005	0.27930
N	2.73033	0.46111	0.72679
C	1.74643	-0.54165	0.41959

C	-1.53661	3.01790	0.33162
C	-1.85939	2.83699	1.80298
C	-0.48163	-2.22625	0.91641
H	-3.08578	1.27354	-0.42766
H	0.47068	-2.67146	0.61677
H	-1.23952	-2.94305	0.59459
H	-2.41205	3.38907	-0.20998
H	-0.76712	3.78500	0.21640
H	-0.99565	2.43339	2.33996
H	-2.12925	3.79140	2.26029
H	-2.69651	2.14900	1.94953
H	1.16139	3.21732	-0.34637
H	1.81101	-1.30097	1.21287
H	3.39885	2.38598	0.26535
H	-2.14344	-0.02153	1.36480
C	-3.13729	-1.37260	0.01865
H	-3.13752	-2.21503	0.71588
H	-4.07726	-0.83924	0.20707
C	-2.07208	0.35717	-2.07121
H	-2.16860	1.24119	-2.70866
H	-1.08847	-0.08040	-2.27932
C	-3.11212	-1.84101	-1.42730
H	-3.95159	-2.51695	-1.61332
H	-2.19757	-2.41495	-1.61756
C	-3.16926	-0.65159	-2.37348
H	-4.14607	-0.15983	-2.26662
H	-3.10181	-0.98353	-3.41331
C	3.98520	-0.20859	0.42584
H	4.78521	0.51204	0.25459
H	4.26403	-0.85281	1.26422
C	3.64672	-1.04513	-0.82469
O	2.22355	-1.17486	-0.79897
C	4.06144	-0.37847	-2.11212
H	5.14995	-0.31787	-2.18461
H	3.68937	-0.93593	-2.97363
H	3.65202	0.63563	-2.15792
H	4.09837	-2.04130	-0.74542
C	-0.53568	-2.07638	2.37051
C	-0.59344	-1.88119	3.55348
H	-0.64161	-1.72391	4.60567

DBU

C	0.90656	1.28799	-0.80744
C	1.95908	1.29779	0.29074
C	-0.39986	-0.77725	-0.36868
C	2.73680	-0.00363	0.38765
C	0.88465	-1.54518	-0.50230
C	1.88492	-1.24244	0.61518
H	1.32528	0.86729	-1.72843
H	1.46421	1.51892	1.24559
H	3.30774	-0.13920	-0.54109
H	1.35059	-1.36236	-1.47810
H	0.61294	2.31127	-1.05494
H	2.65807	2.11924	0.10365
H	3.47648	0.07618	1.19030
H	0.60276	-2.59827	-0.48058
H	2.54919	-2.10395	0.72809

H	1.33891	-1.15115	1.56366
C	-1.41100	1.43217	0.01661
H	-0.99086	2.21974	0.65368
H	-1.88098	1.93105	-0.84202
C	-2.68957	-0.66290	0.01366
H	-3.44045	-1.27594	0.51958
H	-3.10760	-0.41439	-0.97429
C	-2.42797	0.61861	0.77921
H	-2.03421	0.36539	1.77004
H	-3.33998	1.20117	0.92517
N	-0.31656	0.58652	-0.44816
N	-1.47684	-1.44308	-0.14442

DBUepox

C	2.53958	0.77611	-0.08952
C	2.88588	-0.36949	0.84779
C	0.23825	0.23036	-0.72753
C	2.73568	-1.73351	0.19817
C	0.75585	-1.06108	-1.28431
C	1.32642	-2.04982	-0.26917
H	2.92894	0.58470	-1.09447
H	2.25362	-0.29667	1.74183
H	3.42367	-1.78622	-0.65716
H	1.52225	-0.79802	-2.02646
H	3.01116	1.70017	0.24777
H	3.91932	-0.23834	1.18124
H	3.06129	-2.50762	0.89916
H	-0.04239	-1.53500	-1.84952
H	1.32668	-3.03895	-0.73634
H	0.62587	-2.08074	0.57187
C	0.69406	2.21949	0.64749
H	1.12032	2.08194	1.64704
H	1.15152	3.11525	0.21278
C	-1.33948	2.02634	-0.66826
H	-2.42127	2.13356	-0.72635
H	-0.89499	2.69159	-1.41707
C	-0.80427	2.35210	0.70752
H	-1.21586	1.64203	1.42765
H	-1.07651	3.36432	1.00911
N	1.10637	1.06869	-0.16588
N	-1.00339	0.64395	-1.01606
C	-2.10094	-0.30926	-0.90799
H	-1.85669	-1.22474	-1.44991
H	-2.98453	0.13133	-1.37773
C	-2.31369	-0.66358	0.59466
H	-2.87466	0.21378	1.02474
C	-3.28802	-1.84125	0.64000
H	-2.82127	-2.71859	0.17678
H	-3.52066	-2.09436	1.67725
H	-4.22903	-1.62962	0.11735
O	-1.13796	-0.89458	1.19262

DBUcyc

C	-1.90216	0.04551	1.29451
C	-3.13711	-0.26797	0.46701
C	0.18452	-0.12422	0.00800
C	-2.92360	-1.39954	-0.52572

C	-0.37138	-1.43447	-0.56776
C	-1.65929	-1.29682	-1.37241
H	-1.51849	-0.85900	1.78153
H	-3.41890	0.65055	-0.06391
H	-2.88320	-2.34881	0.02610
H	-0.52146	-2.13361	0.26143
H	-2.16291	0.72667	2.11004
H	-3.97324	-0.51961	1.12914
H	-3.79668	-1.47054	-1.18258
H	0.40618	-1.88322	-1.18789
H	-1.68900	-2.09470	-2.12110
H	-1.64313	-0.35250	-1.92954
C	-0.62356	2.07767	0.76602
H	-1.58675	2.55114	0.97712
H	0.01182	2.21723	1.66002
C	1.29155	1.95961	-0.73864
H	1.79343	2.35839	-1.62461
H	1.98730	2.08838	0.10939
C	0.02839	2.71726	-0.43377
H	-0.65628	2.67367	-1.28804
H	0.26232	3.76621	-0.23683
N	-0.87390	0.68258	0.48365
N	1.01981	0.54070	-0.99472
C	2.27204	-0.20490	-0.92855
H	3.09559	0.40488	-1.30196
H	2.22945	-1.10665	-1.54713
C	2.43039	-0.57672	0.55552
O	1.11889	-0.46504	1.08820
C	3.00492	-1.95448	0.77086
H	2.37886	-2.70926	0.28621
H	4.01051	-2.01891	0.34588
H	3.06983	-2.19260	1.83405
H	3.06406	0.16404	1.06412

TBD

C	-1.19582	-1.38817	-0.22211
C	-2.41295	-0.67045	0.30903
C	0.06367	0.72630	0.03369
C	-2.39763	0.75193	-0.19545
H	-1.29517	-1.54062	-1.30988
H	-2.39873	-0.67232	1.40336
H	-2.52456	0.75470	-1.28970
H	-1.10067	-2.38063	0.22887
H	-3.31853	-1.18485	-0.01793
H	-3.22099	1.32977	0.22867
C	1.25602	-1.36748	-0.19744
H	1.16860	-2.36266	0.24916
H	1.39136	-1.51087	-1.28199
C	2.40649	0.80295	-0.17862
H	3.15680	1.42021	0.32714
H	2.71211	0.77423	-1.23570
C	2.42336	-0.60502	0.38099
H	2.32576	-0.57447	1.47162
H	3.36236	-1.11173	0.14641
N	0.02257	-0.65172	0.07150
N	1.11777	1.45376	-0.06575

N	-1.14882	1.36961	0.20572
H	-1.05782	2.35728	0.01913

TBDepox

C	2.99627	-0.07759	-0.31646
C	3.04350	-1.50694	0.16048
C	0.59519	-0.16431	0.21240
C	1.81610	-2.22583	-0.33911
H	3.17498	-0.02095	-1.39749
H	3.06979	-1.53914	1.25354
H	1.82802	-2.28519	-1.43438
H	3.76804	0.52034	0.17458
H	3.94743	-1.98979	-0.21114
H	1.76060	-3.24239	0.05014
C	1.69728	2.00601	-0.01183
H	2.01762	2.37797	0.96927
H	2.43751	2.33291	-0.74607
C	-0.68827	1.88685	0.55863
H	-0.58065	2.26414	1.58361
H	-1.70428	2.06445	0.19953
C	0.32273	2.51186	-0.36273
H	0.28876	3.59850	-0.27977
H	0.08105	2.24455	-1.39660
N	1.71060	0.54702	-0.01099
N	-0.54026	0.42959	0.56802
N	0.64088	-1.50635	0.12078
H	-0.24620	-1.98214	0.07190
C	-1.76412	-0.31797	0.85800
H	-2.33593	0.29768	1.56159
H	-1.51312	-1.24526	1.38561
C	-2.62662	-0.55036	-0.40453
H	-2.02822	-1.28801	-1.02393
C	-3.86978	-1.32370	0.05249
H	-3.62985	-2.27195	0.55047
H	-4.45149	-0.70381	0.74551
H	-4.50320	-1.53933	-0.81165
O	-2.89914	0.58596	-1.05418

TBDcyc

C	-2.04297	0.21238	1.15196
C	-2.99051	-0.46224	0.18085
C	-0.21025	-0.14319	-0.37980
C	-2.23192	-1.43701	-0.69580
H	-1.68728	-0.51170	1.90619
H	-3.46005	0.30123	-0.44814
H	-1.88719	-2.28637	-0.08533
H	-2.55390	1.01354	1.69370
H	-3.78230	-0.98156	0.72642
H	-2.87919	-1.83824	-1.47894
C	-0.05429	1.65041	1.20408
H	-0.67686	2.24675	1.87485
H	0.60938	1.04723	1.84748
C	0.82007	1.92718	-1.12651
H	-0.07601	2.18868	-1.69498
H	1.67589	2.30615	-1.69082
C	0.75582	2.55268	0.26884
H	0.29652	3.54167	0.19208

H	1.75867	2.70582	0.67697
N	-0.93480	0.80352	0.42119
N	0.90707	0.47796	-1.08107
N	-1.11846	-0.73570	-1.32801
H	-0.58374	-1.35043	-1.93235
C	2.14477	-0.06130	-0.54737
H	2.55023	0.53671	0.28587
H	2.91356	-0.13215	-1.32170
C	1.70132	-1.41210	-0.03334
H	1.63240	-2.11982	-0.87630
C	2.55248	-1.98744	1.06183
H	3.57183	-2.15263	0.70614
H	2.58723	-1.29543	1.90802
H	2.15342	-2.94149	1.40959
O	0.39921	-1.14184	0.46351

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