SUPPORTING INFORMATION

Broadening the scope of steroidal scaffolds: the umpolung of a bis-primary amine pre-catalyst for the insertion of CO_2 into epoxides

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SYNTHETIC PROCEDURES

General Considerations

All commercially available reagents were used as received unless otherwise stated. THF was distilled from sodium and benzophenone. Acetonitrile was distilled from CaH_2. Epoxides **1a-g** were purchased from commercial suppliers.

Flash chromatography of reaction products was carried out using Silica 60Å, particle size 230-400 micron (Merk). Analytical thin layer chromatography (TLC) was performed on DC-Alufolien Kieselgel $60F_{254}$ 0.2 mm plates (Merk).

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer or Bruker AV-400 spectrometer, using deuterated solvents and were referenced internally to the residual solvent peak (^1H, δ = 7.26 ppm, ^{13}C, δ = 77.2 ppm) signal. [1] Coupling constants (*J*-values) are given in hertzs (Hz). The DEPT 135 technique was used to assign methylene (CH_2) signals. Chemical shifts are reported as follows: value (description of absortion, number of protons, coupling constant(s) where applicable, assignment). NMR spectra assignation was aided by comparison with literature values for similar compounds. Only clear identifiable peaks have been assigned.

FT-IR spectra were measured on a Perkin-Elmer Spectrum 100 spectrophotometer. Samples were prepared as nujol mulls.

Accurate mass of new compounds was measured in a high-resolution mass spectrometer (IMPACT II, BRUKER) with a qudrupole and a TIME-Of-Flight (TOF) tube as analyzers, and a conventional Electrospray Ion Source (ESI). The equipment uses N_2 at the nebulization (2.4 Bar), and as drying gas (250 ºC, 6.0 L/min). Mass spectra were acquired in full scan mode (4 eV) and positive ion polarity.

Calefaction, when necessary, was performed using heating-stirring plates with oil baths.

[1] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.

Standard procedure for the synthesis of cyclic carbonates 2a-g using catalyst 5 + TBAI (SP1)

Inside a 10 mL round bottom flask steroidal catalyst **5** (0.01 eq) and TBAI (0.01 eq) were suspended in 200 µL of the corresponding epoxide **1a-g** (1 eq). A reflux condenser, closed with a septum, was attached and a CO_2 atmosphere was set with a balloon. After flushing the system for 2-3 min through a release needle, the mixture was stirred and heated at 80 ºC (oil bath) for 24 h under 1 atm of CO_2. The conversion of epoxides **1** into the corresponding cyclic carbonates **2** was determined by ^{1}H NMR spectroscopy on crude reaction mixtures. Resonances of cyclic carbonates **2** were quantified against $CHBr_3$, used as an internal standard.

Crude reaction mixtures were filtered through a plug of silica gel (hexane/EtOAc) to afford the tittle products **2a-g** in an analytically pure form.

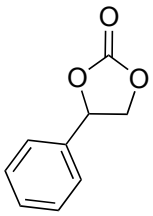
Alternatively, for the experiments of Table 2 (main text), bis-carbamic acid **6** was used instead of **5**.

Standard procedure for the large-scale preparation of carbonate 2a using catalyst 5 + TBAI (SP2)

Inside a 50 mL round bottom flask steroidal catalyst **5** (40.6 mg, 88 µmol) and TBAI (32.4 mg, 88 µmol) were suspended in 1 mL of styrene oxide **1a** (1.05 g, 8.77 mmol). A reflux condenser, closed with a septum, was attached and a CO_2 atmosphere was set with a balloon. After flushing the system for 2-3 min through a release needle, the mixture was stirred and heated at 80 ºC (oil bath) for 24 h under 1 atm of CO_2, before it was allowed to get rt. The crude reaction mixture was filtered through silica gel (Hexane/EtOAc, 3:1) to afford product **2a** (1.07 g, 6.51 mmol, 74% yield) as a white solid.

SPECTROSCOPIC CHARACTERIZATION OF CYCLIC CARBONATES 2a-g

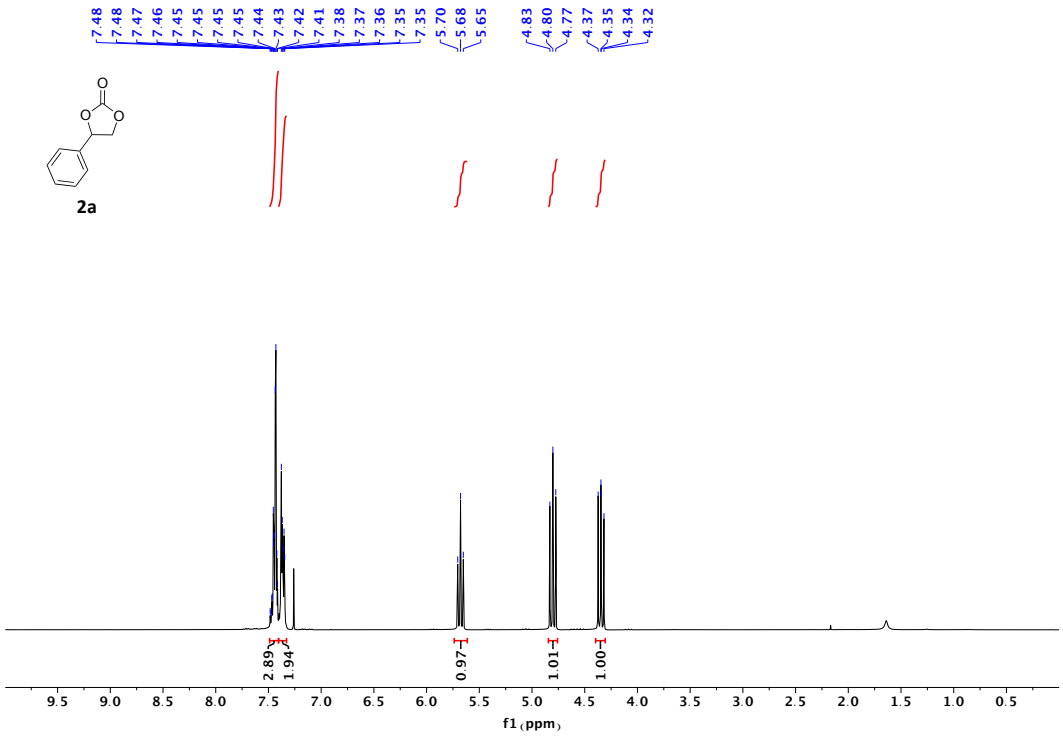
4-Phenyl-1,3-dioxolan-2-one (2a)



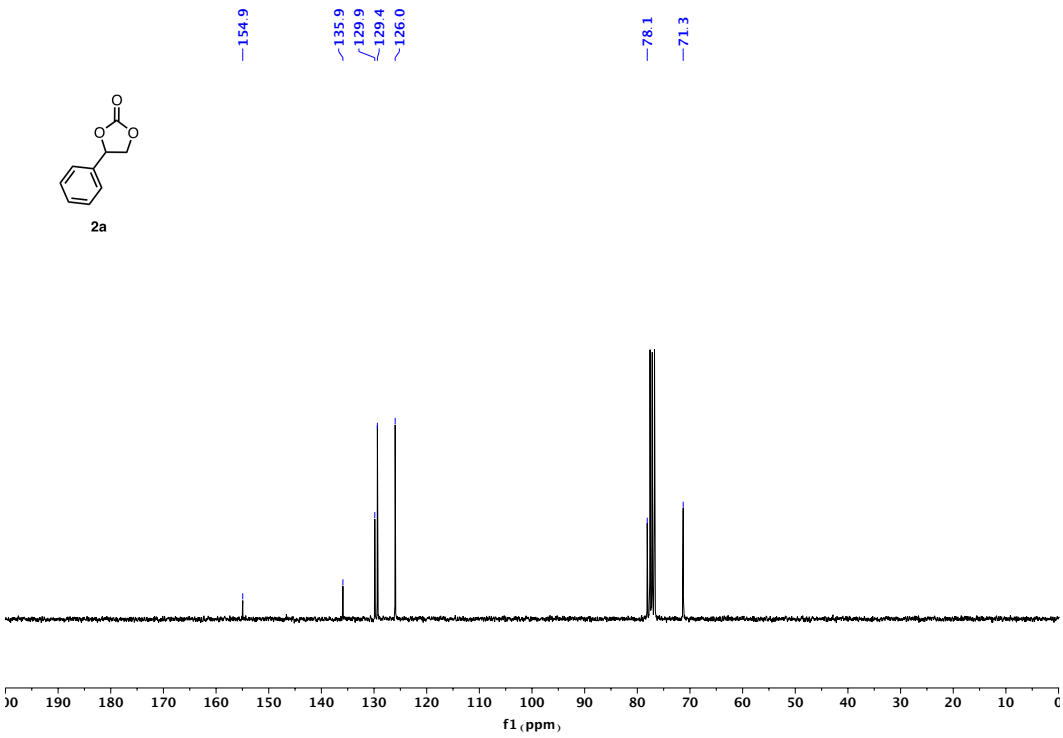
Prepared according to **SP1**, from epoxide styrene oxide **1a** (200 μL, 211 mg, 1.75 mmol). Purified by flash chromatography (Hex/EtOAc, 3:1). Obtained as a white solid (278 mg, 96% isolated yield). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.48–7.41 (m, 3H, H^{Ar}), 7.38–7.35 (m, 2H, H^{Ar}), 5.68 (t, 1H, *J* = 8.0 Hz, C*H*), 4.80 (t, 1H, *J* = 8.4 Hz, C*H*), 4.35 (t, 1H, *J* = 7.9 Hz, C*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 154.9 (*C*O), 135.9 (*C*), 129.9 (Ar*C*H), 129.4 (Ar*C*H), 126.0 (Ar*C*H), 78.1 (*C*H), 71.3 (CH_2).

[2] N. Fanjul-Mosteirín, C. Jehanno, F. Ruipérez, H. Sardon and A. P. Dove, *ACS Sustainable Chem. Eng.*, 2019, **7**, 10633.

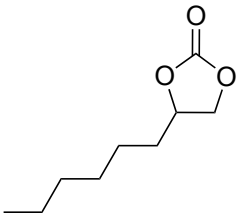
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

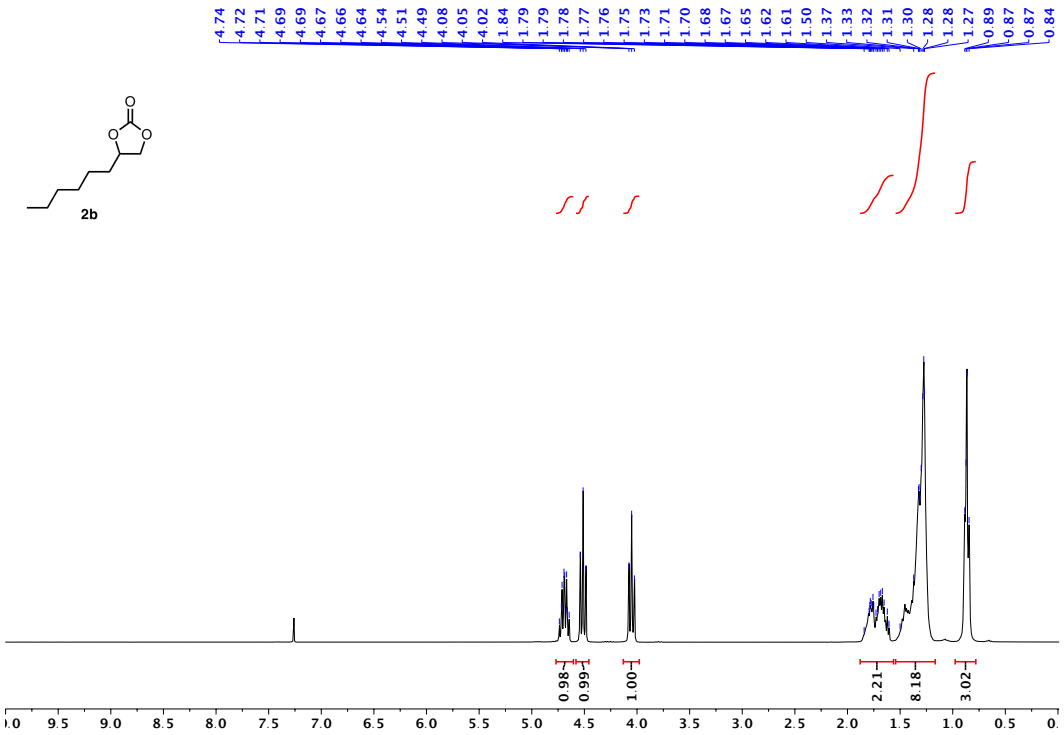


4-Hexyl-1,3-dioxan-2-one (2b)

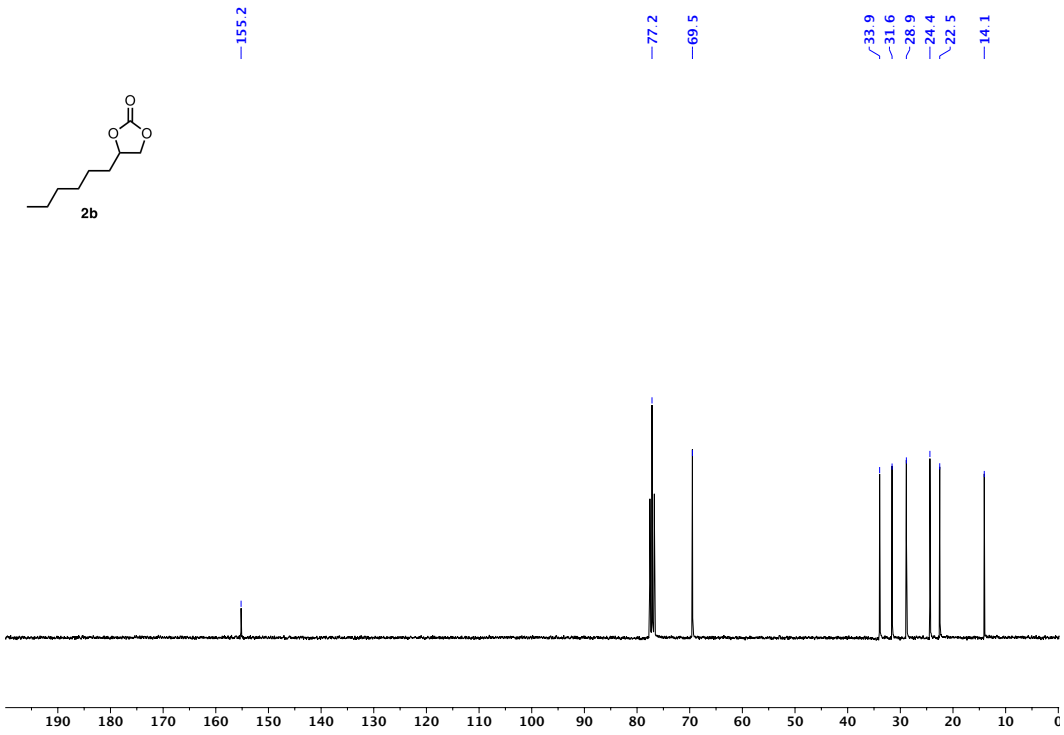


Prepared according to **SP1**, from 1,2-epoxioctane **2a** (200 μL, 168 mg, 1.31 mmol). Purified by flash chromatography (Hex/EtOAc, 5:1). Obtained as a colourless oil (185 mg, 82% isolated yield). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 4.74–4.64 (m, 1H, C*H*), 4.51 (t, 1H, *J* = 8.1 Hz, C*H*), 4.05 (t, 1H, *J* = 8.1 Hz, C*H*), 1.79–1.65 (m, 2H, CH_2), 1.50–1.27 (m, 8H, 4 x CH_2), 0.87 (t, 3H, *J* = 6.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 155.2 (*C*O), 77.2 (*C*H), 69.5 (*C*H_2), 33.9 (*C*H_2), 31.6 (*C*H_2), 28.9 (*C*H_2), 24.4 (*C*H_2), 22.5 (*C*H_2), 14.1 (*C*H_3).

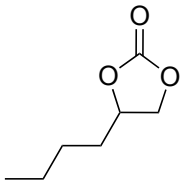
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

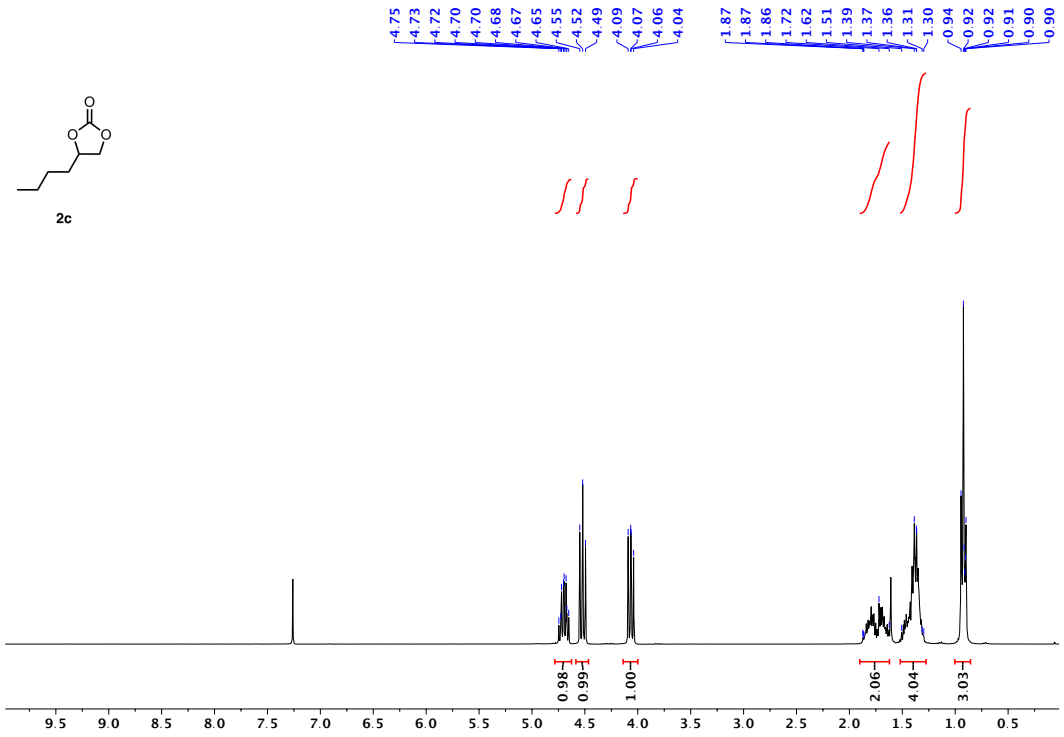


4-Buthyl-1,3-dioxan-2-one (2c)

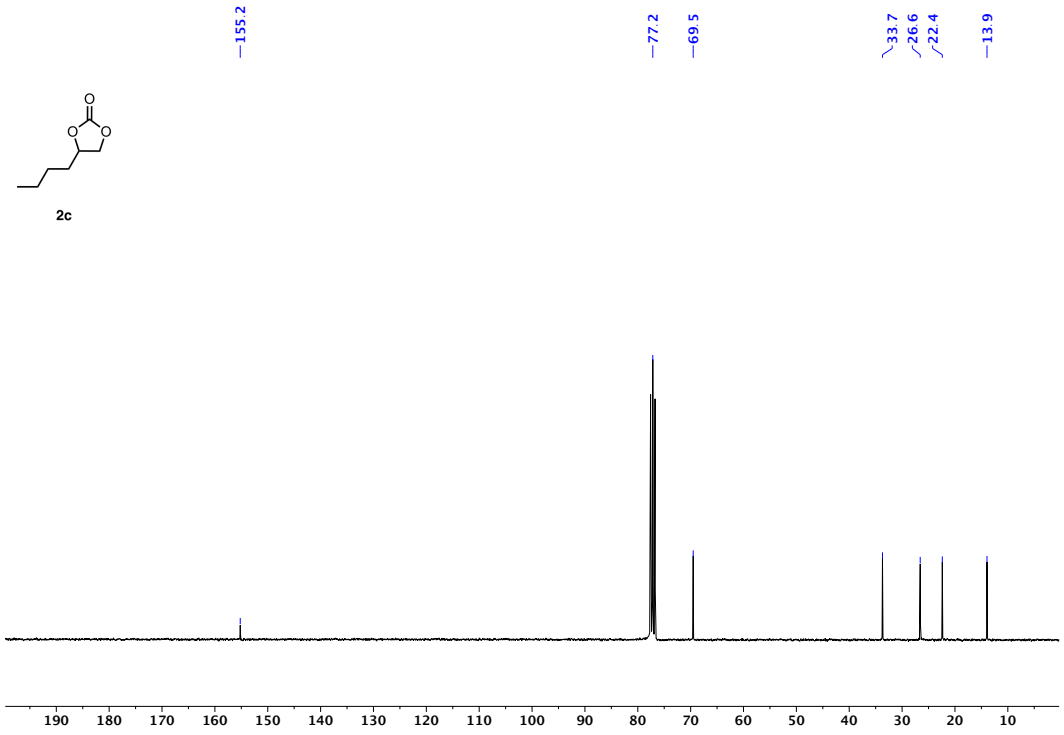


Prepared according to **SP1**, from 1,2-epoxihexane **1c** (200 μL, 166 mg, 1.66 mmol). Isolated as a colourless oil (153 mg, 64% isolated yield). Purified by flash chromatography (Hex/EtOAc, 4:1). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 4.75–4.65 (m, 1H, C*H*), 4.52 (t, 1H, *J* = 8.1 Hz, C*H*), 4.07 (dd, 1H, *J* = 8.4, 7.2 Hz, C*H*), 1.87–1.62 (m, 2H, CH_2), 1.51–1.30 (m, 4H, 2 x CH_2), 0.92 (t, 3H, *J* = 7.0, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 155.2 (*C*O), 77.2 (*C*H), 69.5 (*C*H_2), 33.7 (*C*H_2), 26.6 (*C*H_2), 22.4 (*C*H_2), 13.9 (*C*H_3).

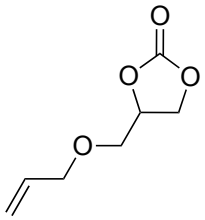
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

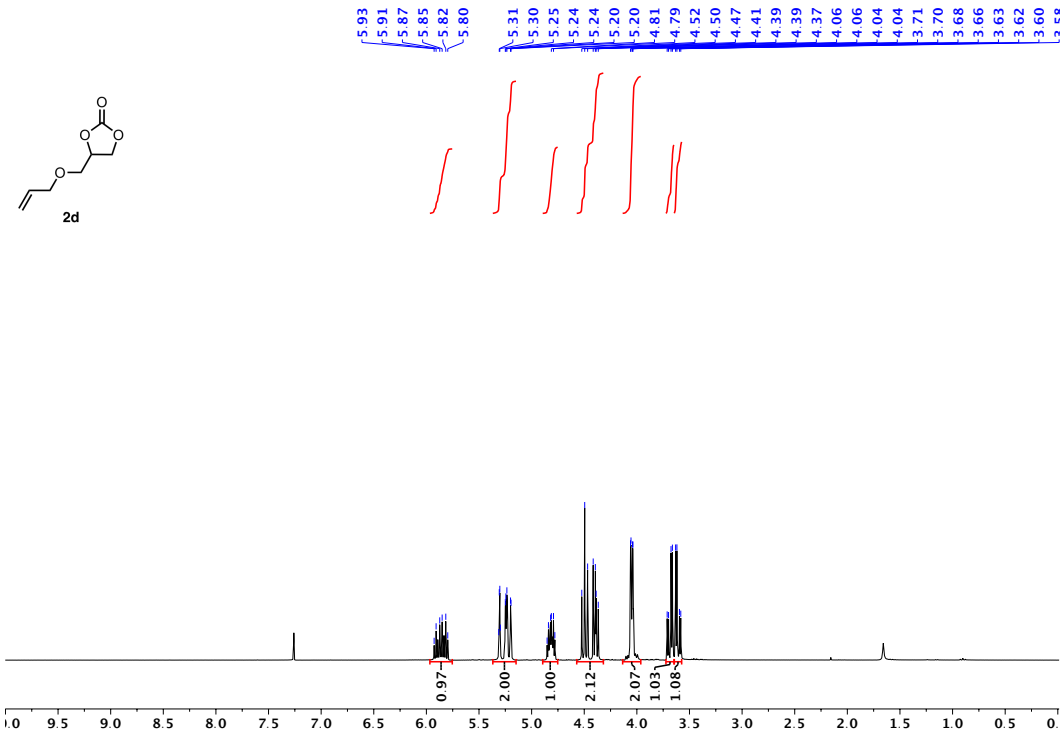


4-Allyloxymethyl-1,3-dioxan-2-one (2d)

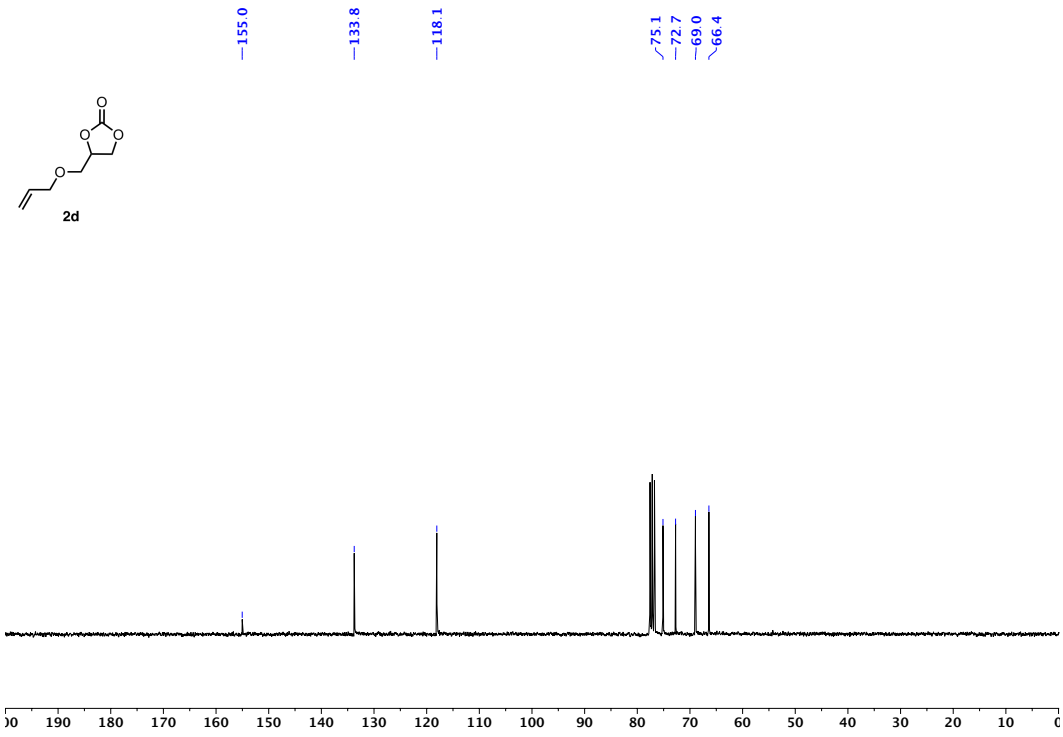


Prepared according to **SP1**, from allyl glycidyl ether **1d** (200 μL, 192 mg, 1.69 mmol). Obtained as a colourless oil (244 mg, 92% isolated yield). Purified by flash chromatography (Hex/EtOAc, 3:1). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 5.93–5.80 (m, 1H, CH_2=C*H*), 5.31–5.20 (m, 2H, CH_2=CH), 4.85–4.78 (m, 1H, C*H*), 4.52–4.37 (m, 2H, CH_2), 4.06–4.04 (m, 2H, CH_2), 3.71–3.66 (dd, 1H, *J* = 11.0, 3.9 Hz, C*H*), 3.63-3.58 (dd, 1H, *J* = 11.1, 3.8 Hz, C*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 155.0 (*C*O), 133.8 (*C*H=CH_2), 118.1 (*C*H_2=CH), 75.1 (*C*H), 72.7 (*C*H_2), 69.0 (*C*H_2), 66.4 (*C*H).

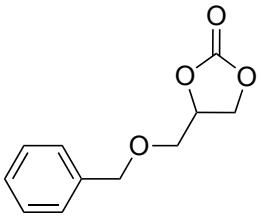
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

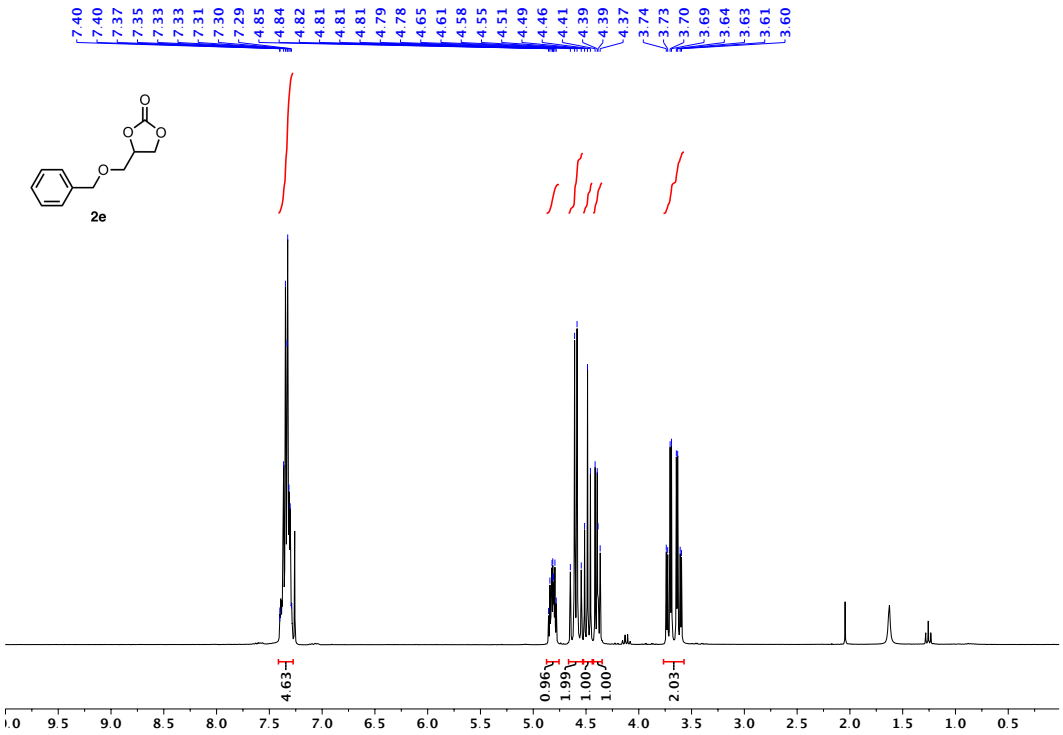


4-((Benzyloxy)methyl)-1,3-dioxan-2-one (2e)

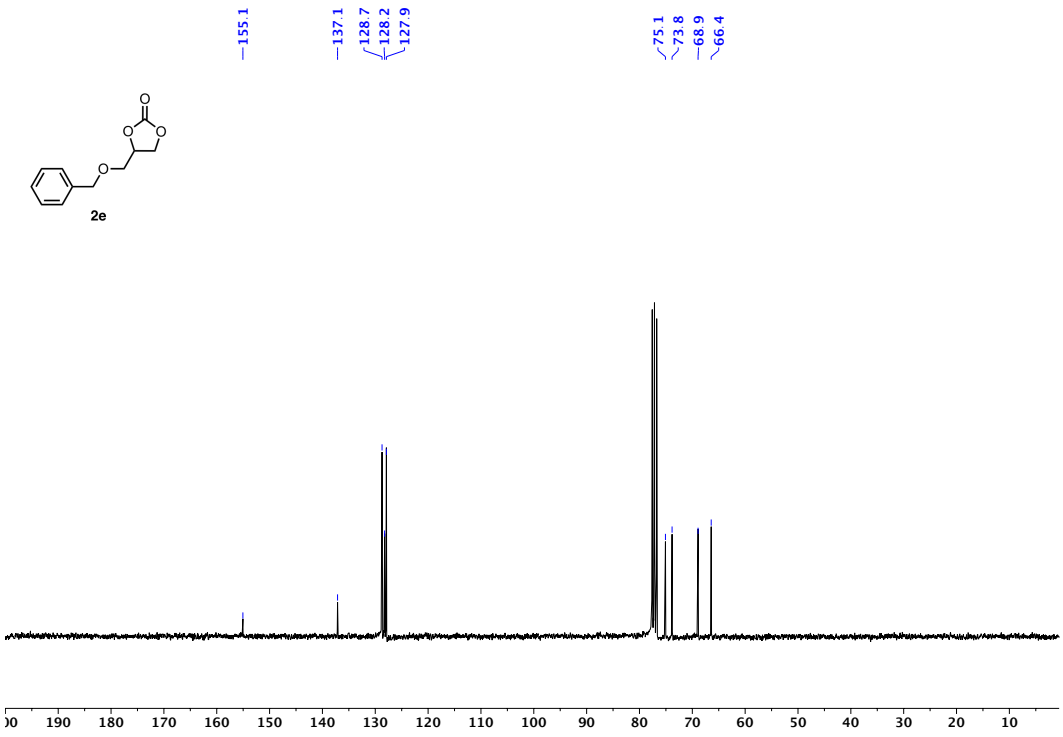


Prepared according to **SP1**, from benzyl glycidyl ether **1e** (200 μL, 215 mg, 1.31 mmol). Obtained a pale-yellow solid (260 mg, 95% isolated yield). Purified by flash chromatography (Hex/EtOAc, 4:1). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.40–7.29 (m, 5H, H^{Ar}), 4.85–4.78 (m, 1H, C*H*), 4.65–4.55 (m, 2H, CH_2), 4.49 (t, 1H, *J* = 8.4 Hz, C*H*), 4.41–4.37 (m, 1H, C*H*), 3.74–3.69 (dd, 1H, *J* = 10.9, 3.8 Hz, C*H*), 3.64–3.60 (dd, 1H, *J* = 10.9, 3.8 Hz, C*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 155.1 (*C*O), 137.1 ($C^{Ar\ ipso}$), 128.7 (C^{Ar}), 128.2 (C^{Ar}), 127.9 (C^{Ar}), 75.1 (*C*H), 73.8 (*C*H_2), 68.9 (*C*H_2), 66.4 (*C*H_2).

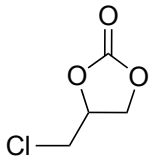
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

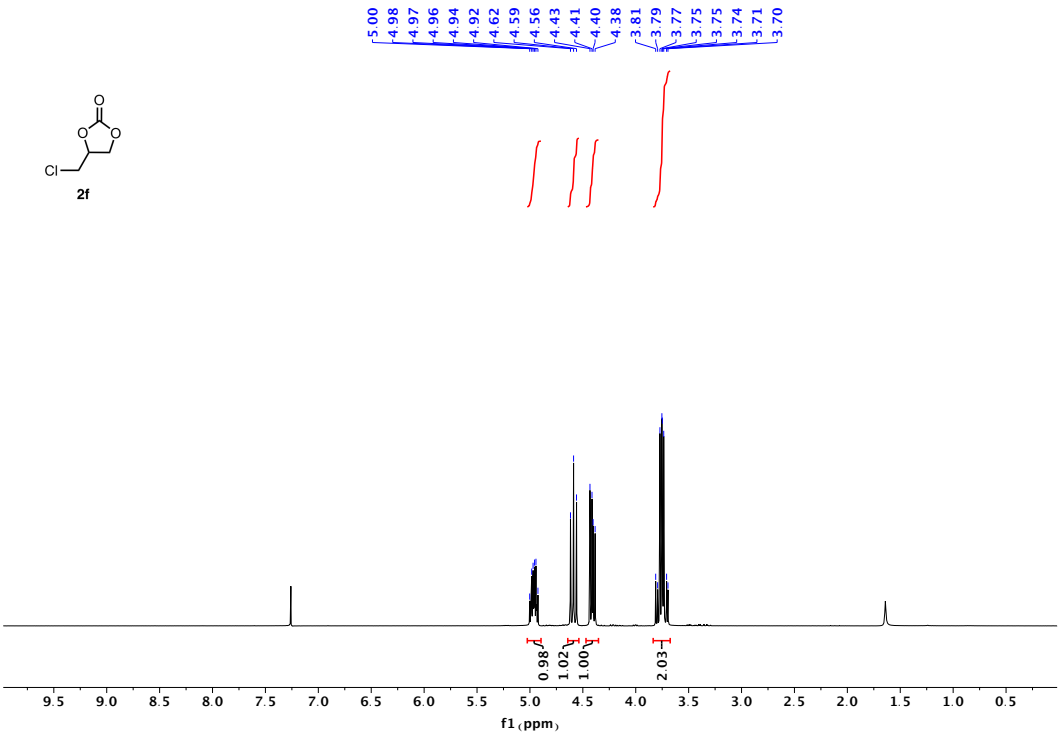


4-(Chloromethyl)-1,3-dioxolan-2-one (2f)

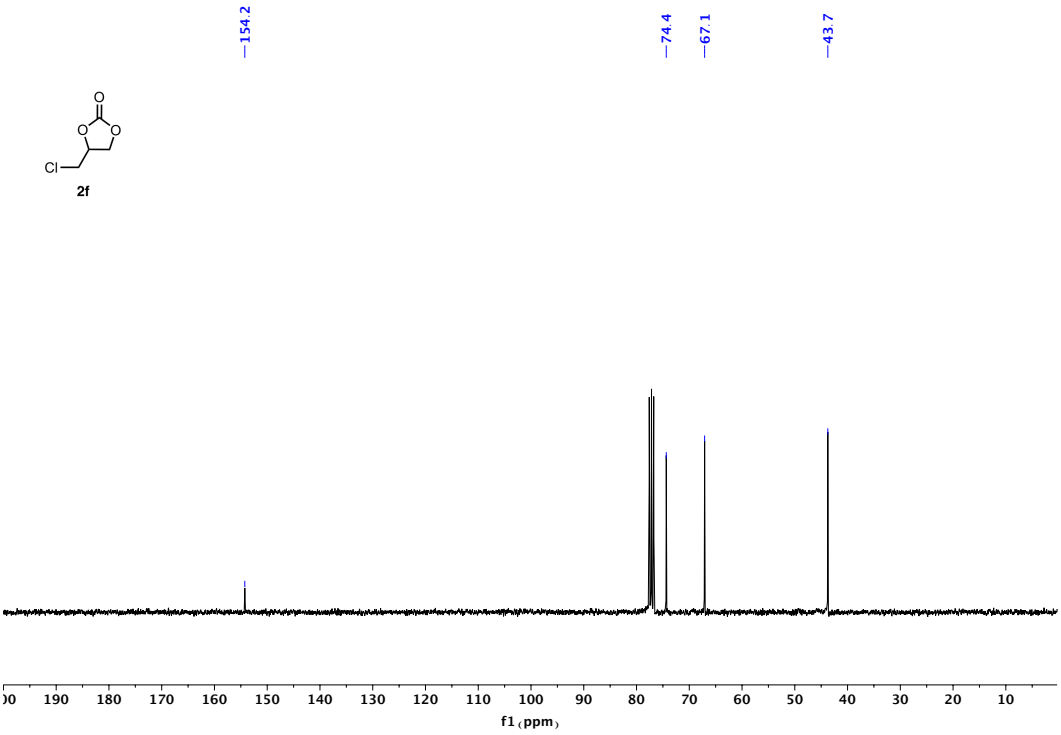


Prepared according to **SP1**, from epichlorohydrine **1f** (200 μL, 234 mg, 2.56 mmol).. Obtained as a colourless oil (248 mg, 71% isolated yield). Purified by flash chromatography (Hex/EtOAc, 3:1). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 5.00–4.92 (m, 1H, C*H*), 4.59 (t, 1H, *J* = 8.7 Hz, C*H*), 4.43–4.38 (m, 1H, C*H*), 3.81–3.70 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 154.3 (*C*O), 74.4 (*C*H), 67.1 (*C*H_2), 43.7 (*C*H_2).

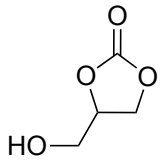
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

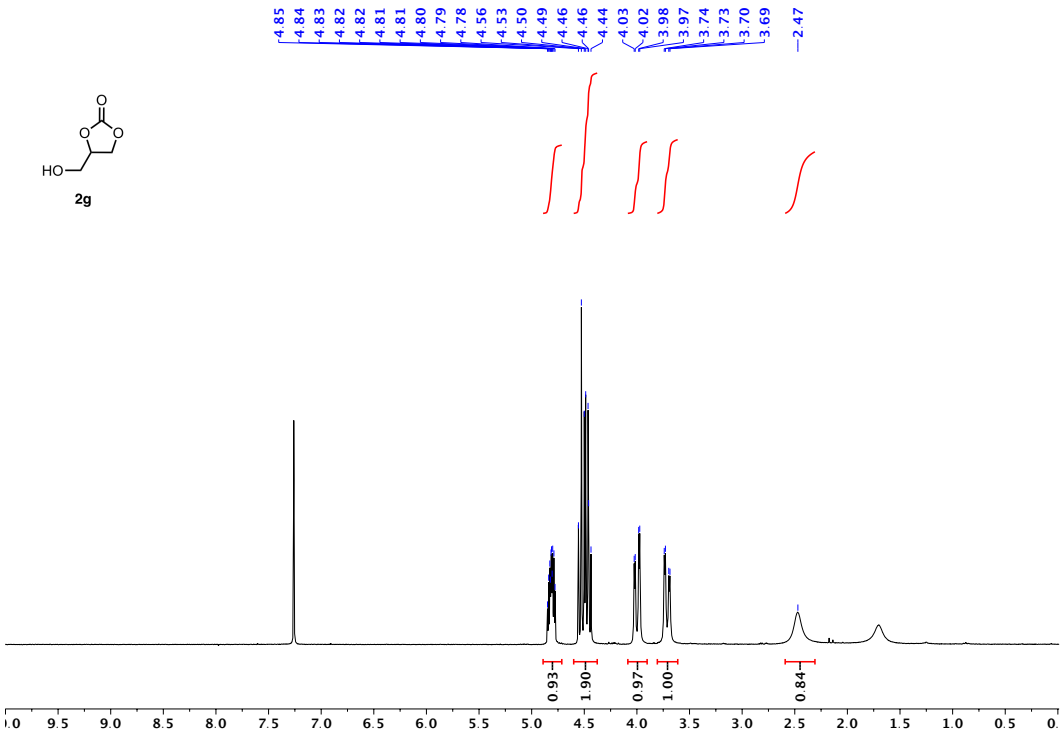


4-(Hydroxymethyl)-1,3-dioxolan-2-one (2g)

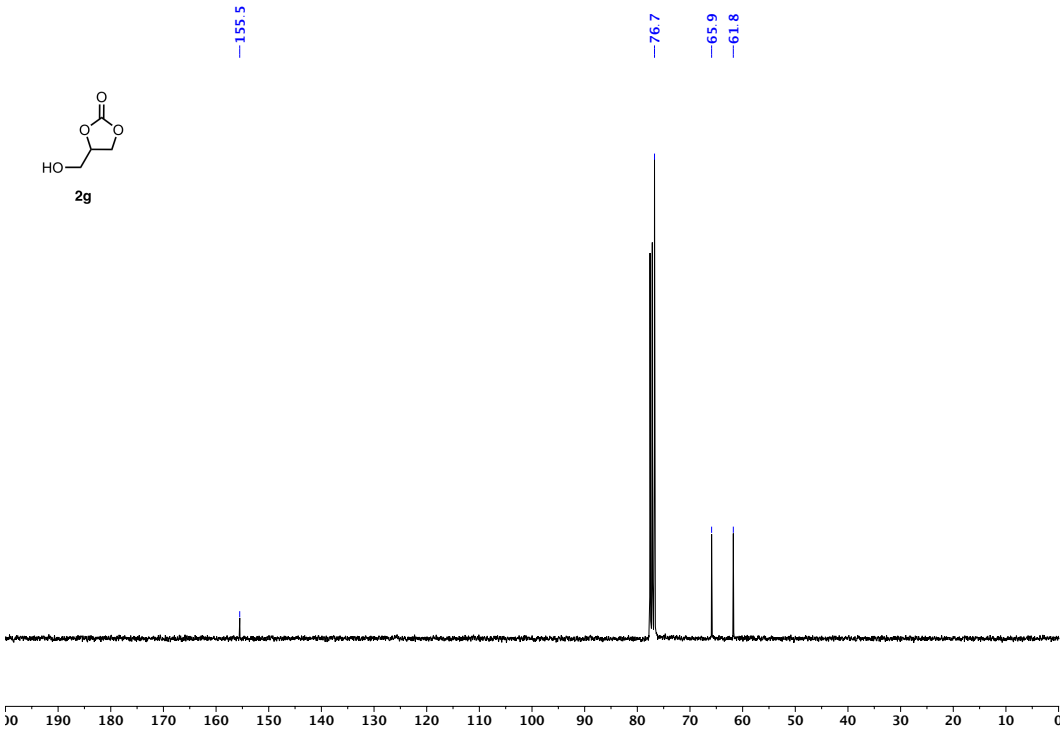


Prepared according to **SP1**, from glycidol **1g** (200 μL, 223 mg, 3.02 mmol). Obtained as a colourless oil (251 mg, 70% isolated yield). Purified by flash chromatography (Hex/EtOAc, 1:1). Characterization data agrees with those reported previously.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 4.85–4.78 (m, 1H, C*H*), 4.56–4.44 (m, 2H, CH_2), 4.02–3.97 (m, 1H, C*H*), 3.74-3.69 (m, 1H, C*H*), 2.47 (broad s, 1H, O*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 155.5 (*C*O), 76.7 (*C*H), 65.9 (*C*H_2), 61.8 (*C*H_2).

^{1}H NMR (300 MHz, $CDCl_3$):

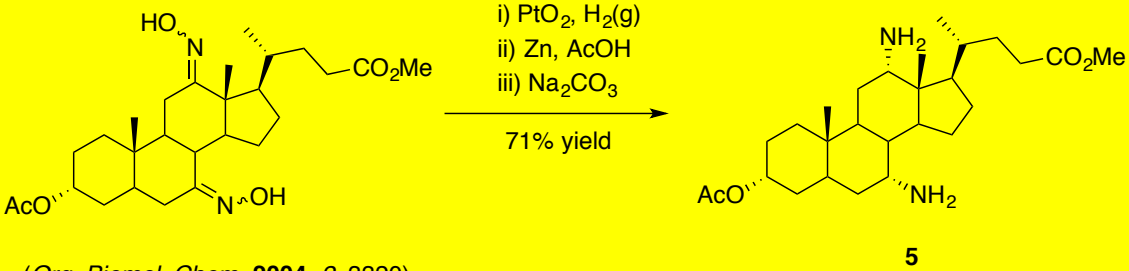


^{13}C NMR (75 MHz, $CDCl_3$):



SYNTHETIC PROCEDURES AND SPECTROSCOPIC CHARACTERIZATION OF STEROIDAL DERIVATIVES 4–6

Steroid 5:[3]

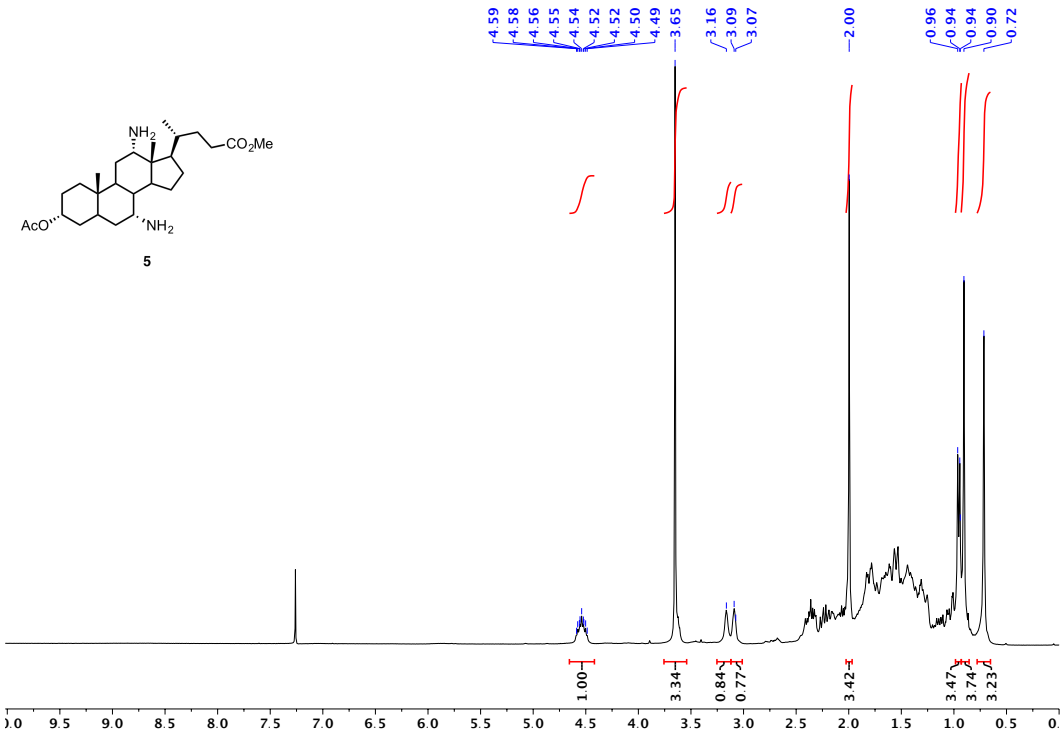


(*Org. Biomol. Chem.* **2004**, *2*, 3320)

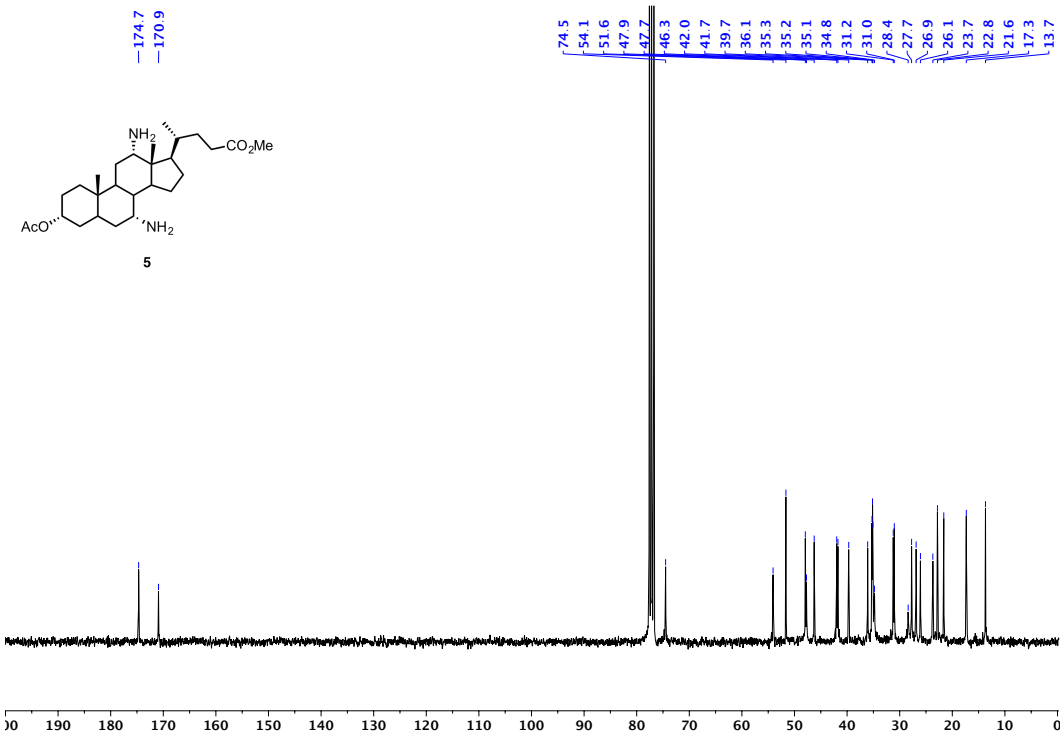
Bis-amine **5** was prepared following a procedure previously described in the literature,[3] which was slightly modified. A mixture of the bis-oxime indicated above (1.50 g, 3.06 mmol) and platinum (IV) oxide hydrate (Adams' catalyst) (150 mg) in glacial acetic acid (6.5 mL) was stirred under 1 atm of H_2 for 3 d at R.T. The catalyst was filtered off, and washed with acetic acid. Zinc powder (3.00 g, 45.89 mmol) was added to the combined filtrates. The mixture was stirred for 4 d at R.T before removing the zinc by filtration. The solvent and volatiles were evacuated under reduced pressure to afford a dense colourless oil. A solution of Na_2CO_3 (aq. sat.) was then added until a basic pH was observed. The resulting white foam was filtered off, washed thoroughly with distilled water and dried, to render bis-amine **5** (1.00 g, 71%) as a white solid. Spectroscopic data agreed with those reported previously. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 4.59–4.49 (m, 1H, 3β-*H*), 3.65 (s, 3H, CO_2CH_3), 3.16 (broad s, 1H, 7β-*H*), 3.09 (broad s, 1H, 12β-*H*), 2.00 (s, 3H, CH_3CO_2), 0.95 (d, 3H, J = 5.9 Hz, CH_3), 0.90 (s, 3H, CH_3), 0.72 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 174.7 (CO_2CH_3) , 170.9 (CH_3CO_2), 74.5 (*C*H), 54.1 (*C*H), 51.6 (*C*H), 47.9 (*C*H), 47.7 (*C*H), 46.3 (*C*), 42.0 (*C*H), 41.7 (*C*H), 39.7 (*C*H), 36.1 (CH_2), 35.3 (*C*H), 35.2 (CH_2), 35.1 (*C*), 34.8 (*C*), 31.2 (CH_2), 31.0 (CH_2), 28.4 (*C*), 27.7 (CH_2), 26.9 (CH_2), 26.1 (*C*H), 23.7 (CH_2), 22.8 (CH_3), 21.6 (CH_3CO_2), 17.3 (CH_3), 13.7 (CH_3).

[3] V. del Amo, L. Siracusa, T. Markidis, B. Baragaña, K. M. Bhattarai, M. Galobardes, G. Naredo, M. N. Pérez-Payán and A. P. Davis, *Org. Biomol. Chem.*, 2004, **2**, 3320.

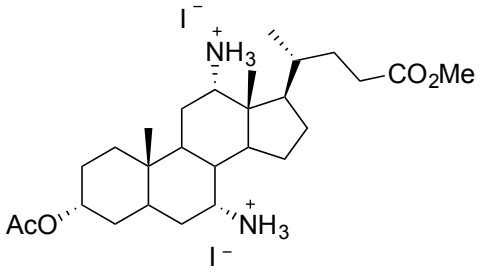
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):

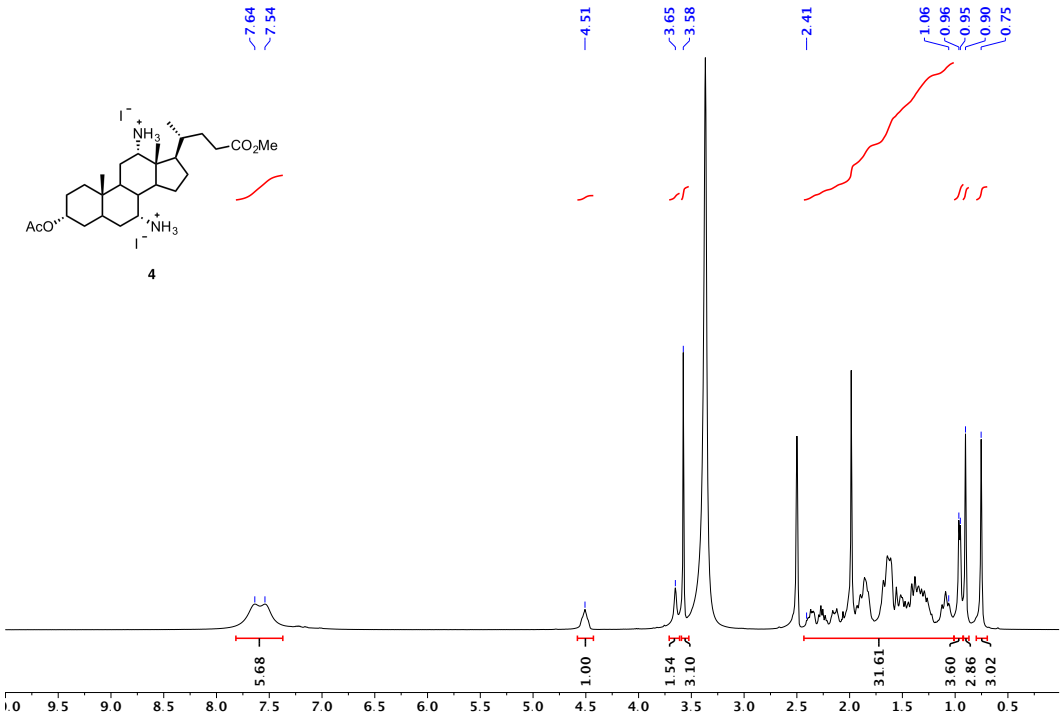


Steroid 4:

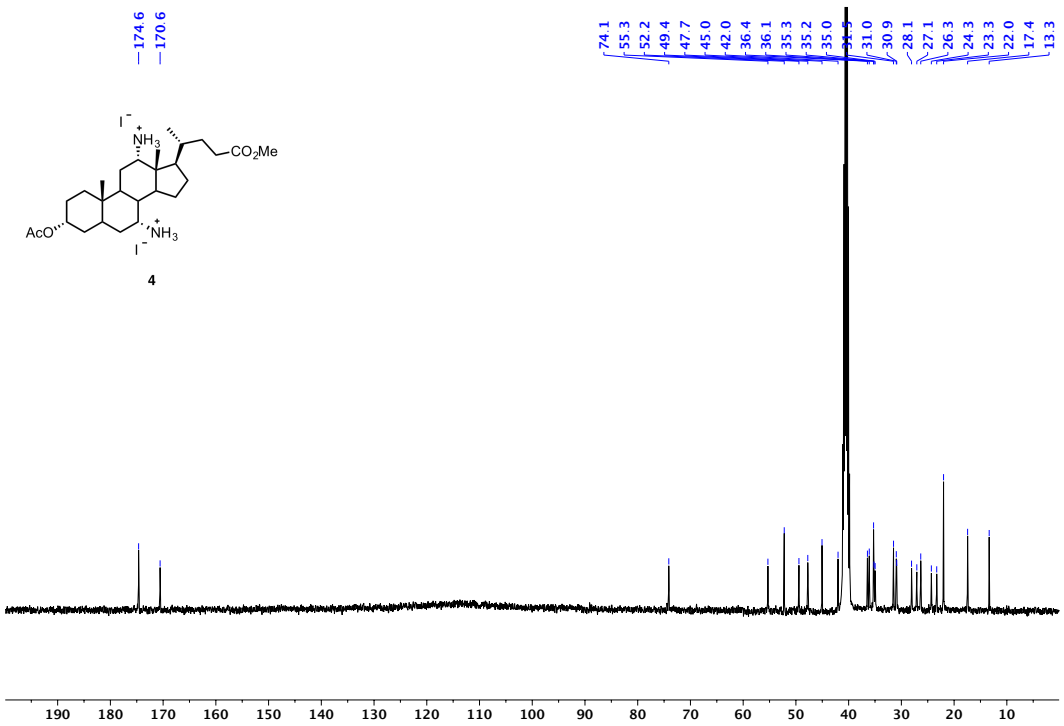


Inside a 10 mL round bottomed flask steroid **5** (200 mg, 0.43 mmol) and NH_4I (127.8 mg, 0.88 mmol) were dissolved in 4.3 mL of dry MeCN. The mixture was refluxed for 8 h before the solvent and volatiles were evacuated under high vacuum to render catalyst **4** (304 mg, 98%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.59 (m, 6H, 2 x N*H*$_3$), 4.51 (m, 1H, 3β-*H*), 3.65 (s, 1*H*), 3.58 (s, 3H, CO_2CH_3), 2.41–1.06 (m, 31H), 0.96 (d, 3H, *J* = 5.7 Hz, C*H*$_3$), 0.90 (s, 3H, C*H*$_3$), 0.75 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 174.7 (CO_2CH_3), 170.6 (CH_3CO_2), 74.1 (*C*H), 55.3 (*C*H), 52.2 (*C*H), 49.4 (*C*H), 47.8 (*C*H), 45.1 (*C*), 42.0 (*C*H), 40.3 (*C*H), 36.4 (*C*H), 36.1 (*C*H), 35.3 (*C*), 35.2 (CH_2), 35.0 (CH_2), 31.5 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 28.1 (CH_2), 27.1 (CH_2), 26.3 (CH_3), 24.3 (CH_2), 23.3 (CH_2), 22.0 (CH_3), 17.4 (CH_3), 13.4 (CH_3); MS (ESI-): *m/z* (%) = 127 (100) $[I]^-$, 381 (21) $[I_3]^-$, 717 (4) [**4** – H]$^-$; HRMS (ESI-) m/z: [**4** – H]$^-$ Calcd for $C_{27}H_{47}N_2O_4I_2$ 717.1631; Found 717.1631; MS (ESI+): *m/z* (%) = 463 (100) [**5** + H]$^+$, 232 (20) [**5** + 2H]$^{2+}$; HRMS (ESI+) m/z: [**5** + H]$^+$ Calcd for $C_{27}H_{47}N_2O_4$ 463.3536; Found 463.3530.

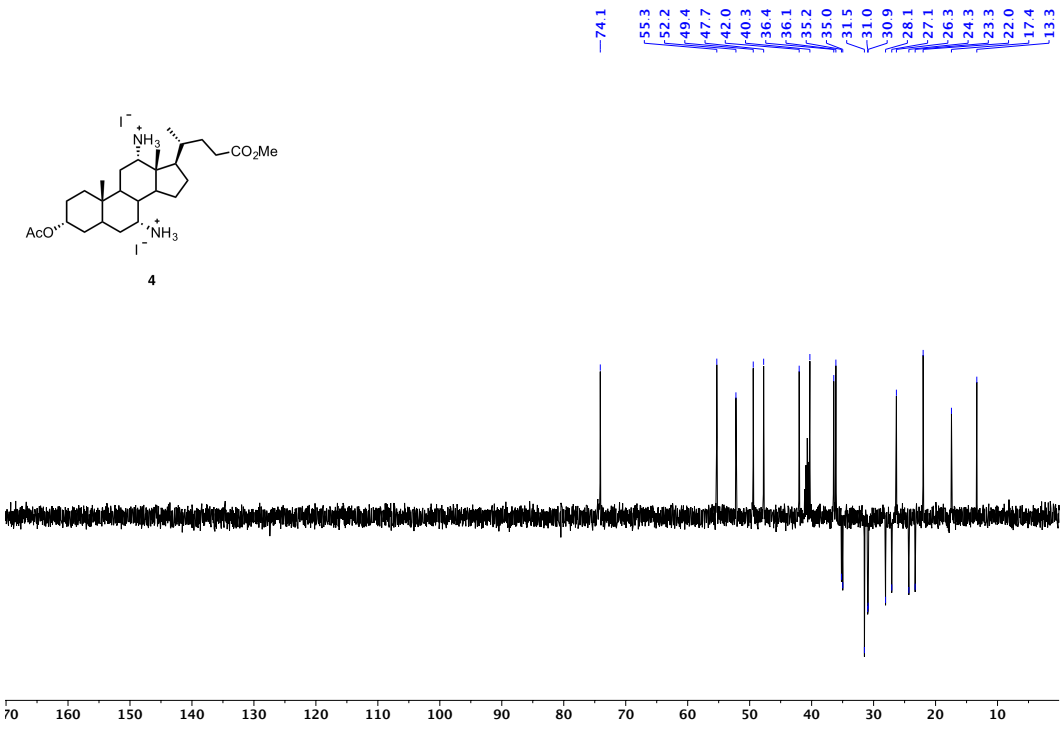
^{1}H NMR (400 MHz, DMSO-d_6):



^{13}C NMR (100 MHz, DMSO-d_6):



DEPT-135 NMR (100 MHz, DMSO-d_6):



Mass Spectrum SmartFormula Report

Analysis Info

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Method	FantasmaMASAEXACTA_POS_Tun_Mix_neg.m	Operator	Demo User
Sample Name	MNF_411_NEG	Instrument	impact II 1825265.10101
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	2.4 Bar
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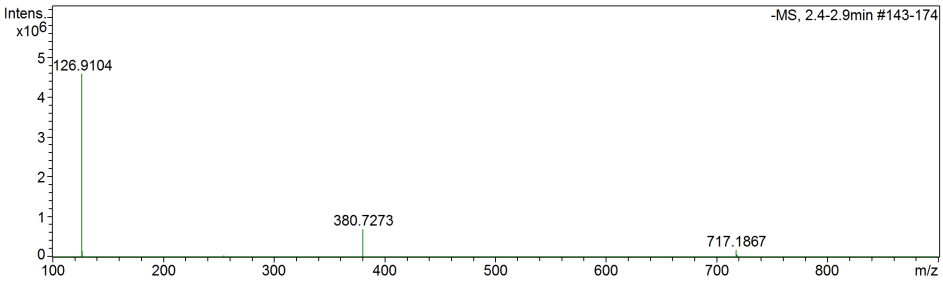
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	mnf_411_neg	Instrument	impact II 1825265.10101
Comment			

Acquisition Parameter

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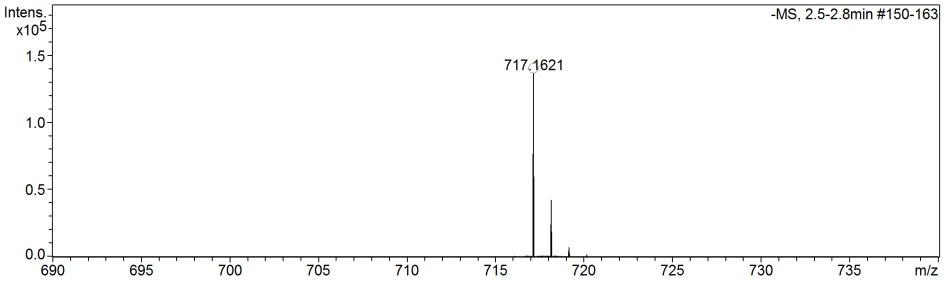
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
717.1621	1	C27H47I2N2O4	717.1631	1.3	2.8	1	100.00	4.0	even	ok	M-H

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MNF_411_POS_BA1_01_5038.d	Acquisition Date	6/18/2020 11:15:35 AM
Method	FantasmaMASAEXACTA_POS_Tun_Mix.m	Operator	Demo User
Sample Name	MNF_411_POS	Instrument	impact II 1825265.10101
Comment			

Acquisition Parameter

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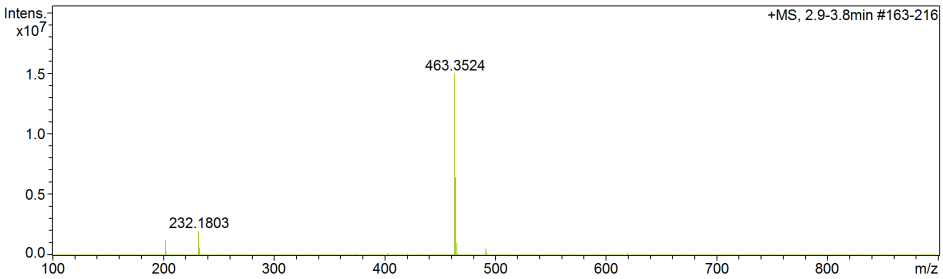
Focus	Active	Set Capillary	3000 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



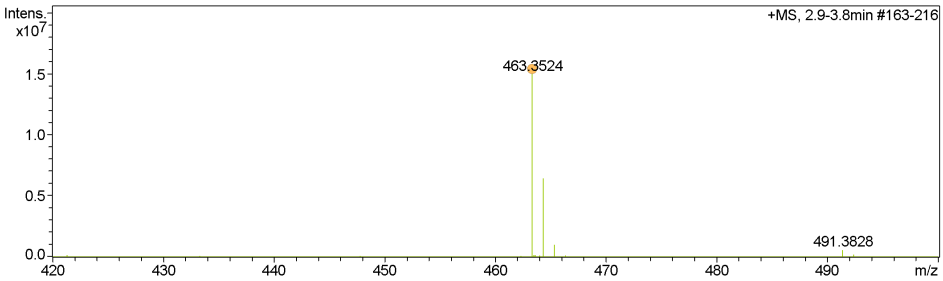
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MNF_411_POS_BA1_01_5038.d	Acquisition Date	6/18/2020 11:15:35 AM
Method	FantasmaMASAEXACTA_POS_Tun_Mix.m	Operator	Demo User
Sample Name	MNF_411_POS	Instrument	impact II 1825265.10101
Comment			

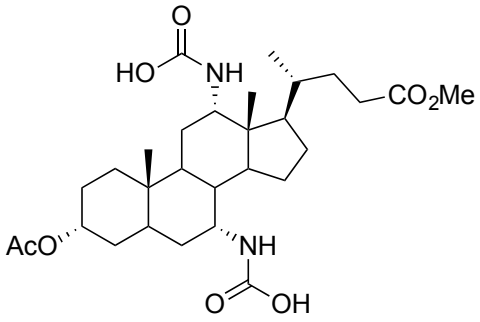
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.4 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



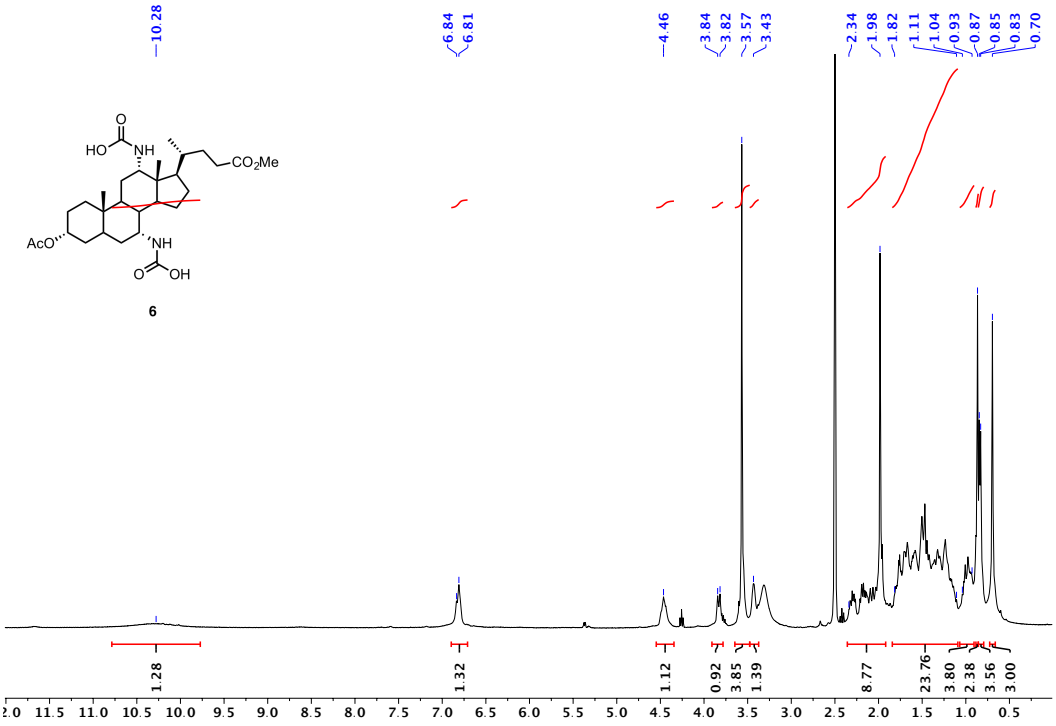
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule	Adduct
463.3524	1	C27H47N2O4	463.3530	1.4	62.4	1	100.00	6.0	even	ok	M

Catalyst 6:

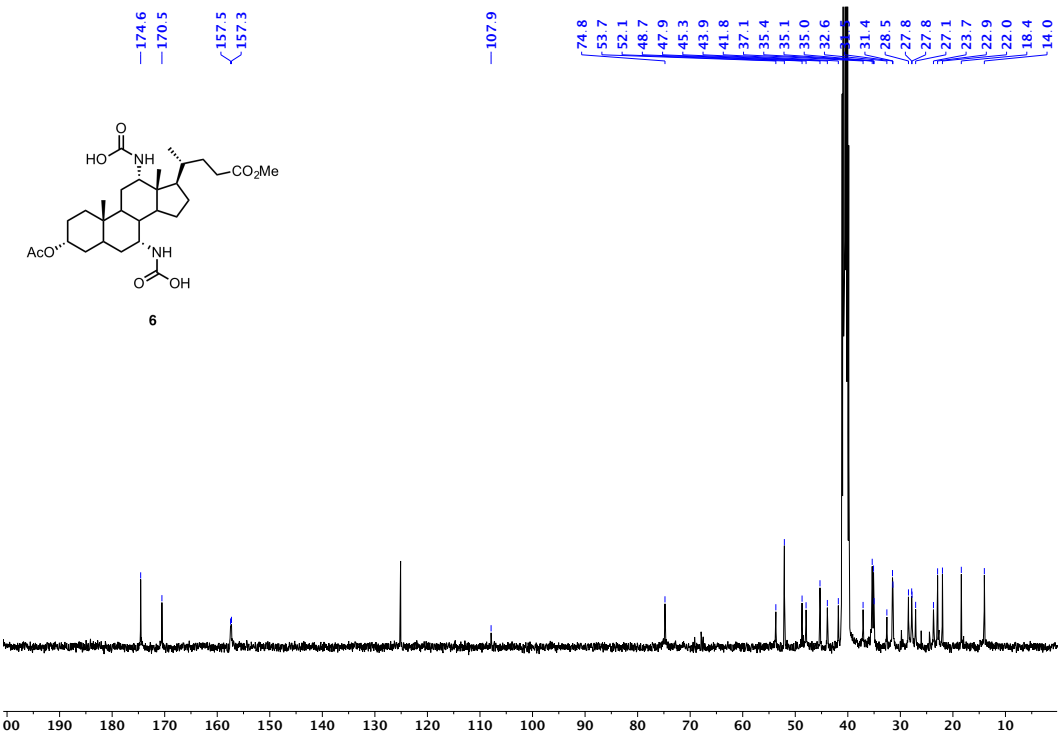


A suspension of steroid **5** (100 mg, 0.22 mmol) in 10.8 mL of freshly dried and degassed THF was passed through 13 mm syringe filters (0.2 µm PTFE) until a clear solution was obtained. It was transferred to a 25 mL round bottomed flash, closed with a septum, degassed, by means of 3 freeze-thaw cycles, cooled to 0 ºC and saturated with CO_2. The formation of a white precipitate was observed. The mixture was allowed to get to rt and it was stirred overnight under CO_2 atmosphere. The precipitate was allowed to settle and the supernatant liquid was syringed out. The solid was dried with a continuous CO_2 flush until all the THF was evaporated to afford bis-carbamic acid **6** (55 mg, 47% isolated yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 10.28 (s, 2H, NHCO$_2$*H*), 6.84 (s, 1H, N*H*CO$_2$H), 6.81 (s, 1H, N*H*CO$_2$H), 4.46 (m, 1H, 3β-*H*), 3.83 (d, 1H, *J* = 11.0 Hz, 12β-*H*), 3.57 (s, 3H, CO$_2$C*H*$_3$), 3.43 (bs, 1H, 7β-*H*), 2.34–1.98 (m, 9H), 1.82–1.11 (m, 24H), 1.04–0.93 (m, 4H), 0.86 (s, 3H, CH$_3$), 0.84 (d, 3H, *J* = 6.4 Hz, CH$_3$), 0.70 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 174.6 (*C*(O)O), 170.5 (*C*(O)O), 157.5 (*C*(O)NH), 157.3 (*C*(O)NH), 107.9 (*C*), 74.8 (*C*H), 53.7 (*C*H), 52.1 (*C*H), 48.7 (*C*H), 47.9 (*C*H), 45.3 (*C*), 43.9 (*C*H), 41.8 (*C*H), 37.1 (*C*H), 35.4 (*C*H$_2$), 35.1 (*C*H), 35.0 (*C*H$_2$), 32.6 (*C*H$_2$), 31.5 (*C*H$_2$), 31.4 (*C*H$_2$), 28.5 (*C*H$_3$), 27.8 (*C*H$_2$), 27.8 (*C*H$_2$), 27.1 (*C*H$_2$), 23.7 (*C*H$_2$), 22.9 (*C*H$_3$), 22.0 (*C*H$_3$), 18.4 (*C*H$_3$), 14.0 (*C*H$_3$).

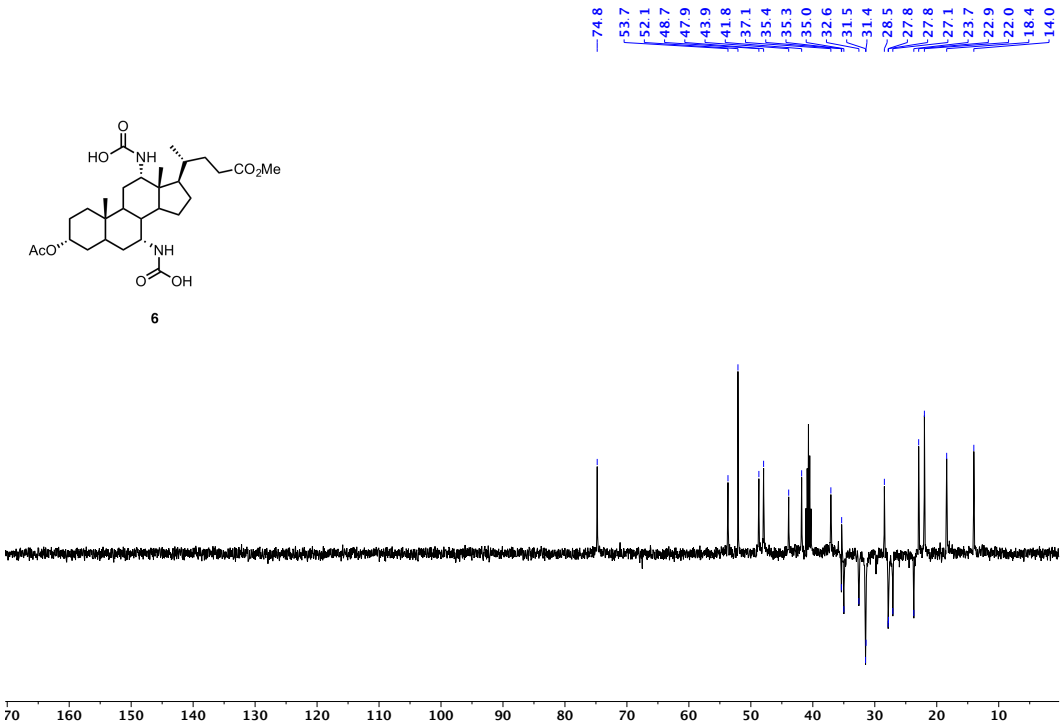
^{1}H NMR (400 MHz, DMSO-d_6):



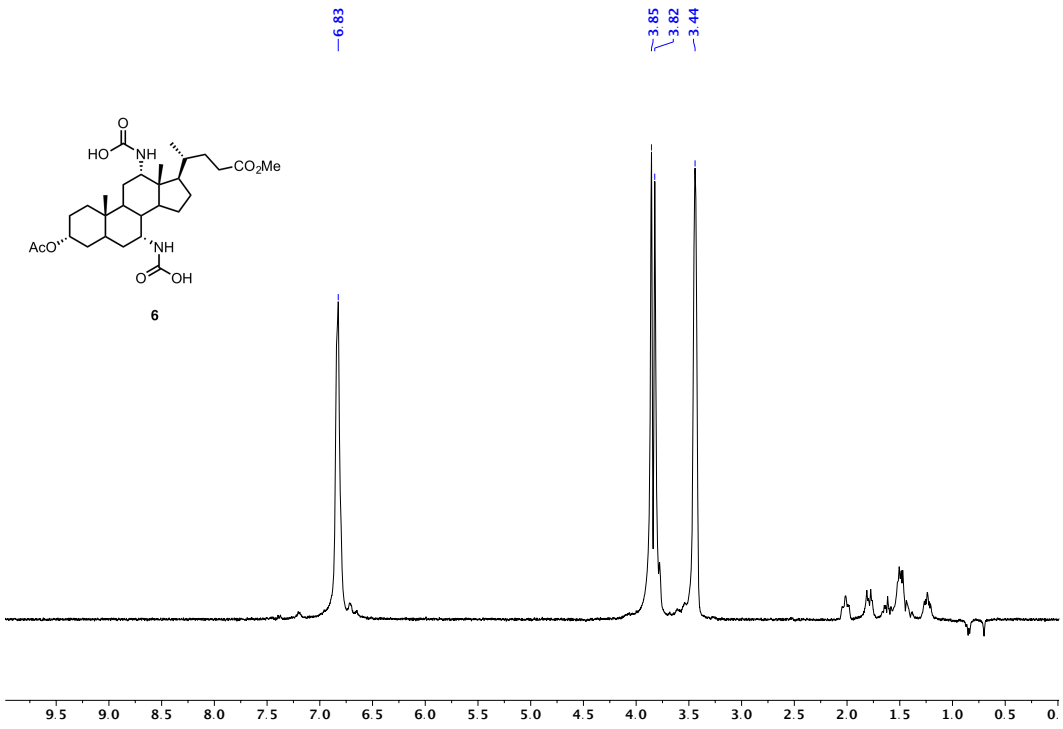
^{13}C NMR (100 MHz, DMSO-d_6):



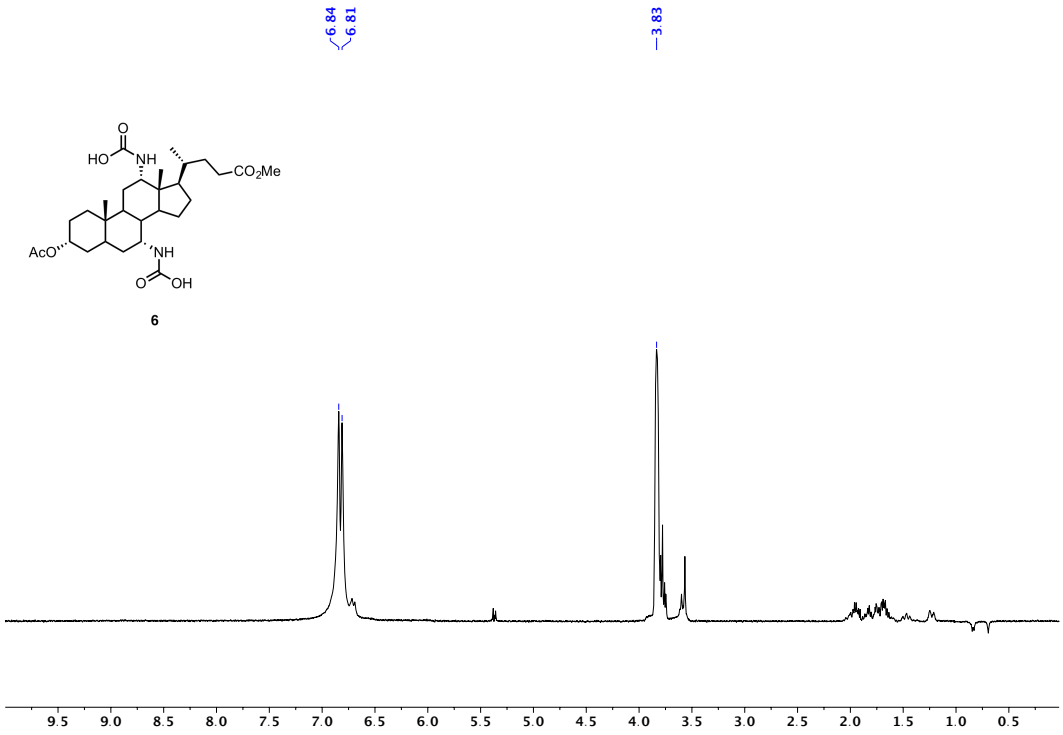
DEPT-135 NMR (100 MHz, DMSO-d_6):



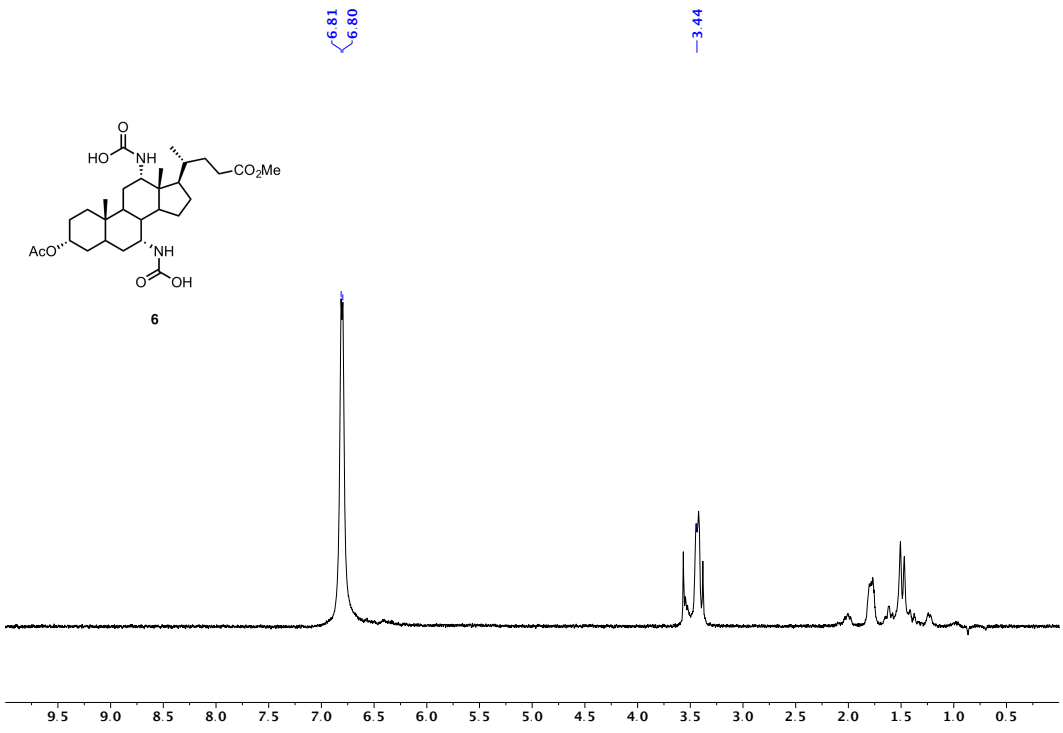
^{1}H–^{1}H selective TOCSY NMR (400 MHz, DMSO-d_6), irradiation at 6.83 ppm:



^{1}H–^{1}H selective TOCSY NMR (400 MHz, DMSO-d_6), irradiation at 3.83 ppm:



^{1}H–^{1}H selective TOCSY NMR (400 MHz, DMSO-d_6), irradiation at 3.44 ppm:



FT–IR SPECTRA OF STEROIDAL CATALYSTS 5 & 6

Figure SI-1. Full FT-IR spectra of steroidal bis-amine **5** (nujol mull).

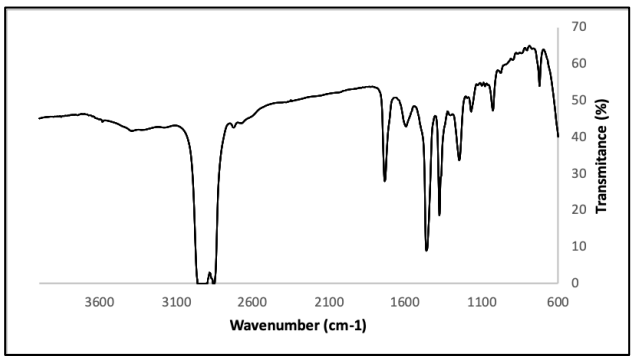


Figure SI-2. Full FT-IR spectra of steroidal bis-carbamic acid **6** (nujol mull).

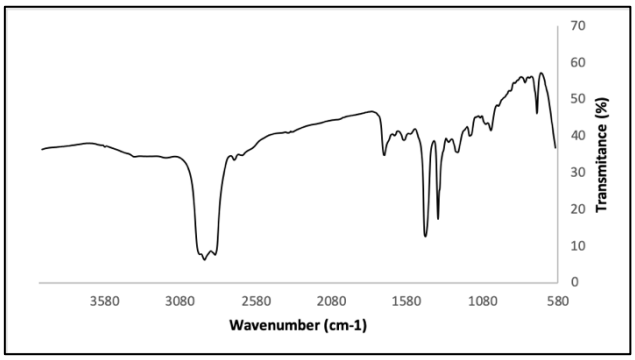
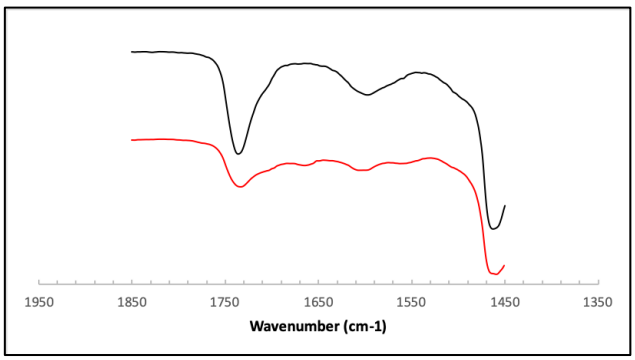
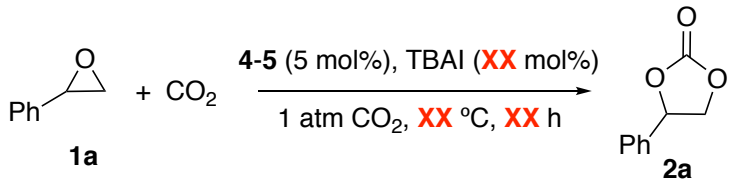


Figure SI-3. Comparison of FT-IR spectra of bis-carbamic acid **6** (red trace), and bis-amine **5** (black trace), zoomed from Figures SI-1 and SI-2 respectively.



OPTIMIZATION OF THE REACTION CONDITIONS

Table SI-1. Initial screening of reaction parameters for the potential steroid-based catalysts **4** and **5** on the insertion reaction of CO_2 into styrene oxide **1a**.[a]



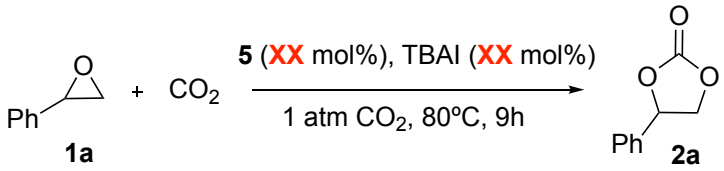
1a **2a**

entry	Catalyst	TBAI (mol%)	Temp. (ºC)	time (h)	Conv. (%)[b]
1	**4**	-	70	3	4
2	**5**	5	70	3	67
3	**5**	5	70	9	88
4	**5**	5	80	6	86
5	**5**	5	80	9	99

[a] General conditions: steroidal catalyst **4** or **5** (87.5 µmol) and TBAI (stated amount) were suspended in styrene oxide **1a** (200 µL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at the indicated temperature, the stated time, under 1 atm of CO_2 (standard balloon).

[b] Conversion of styrene oxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixtures.

Table SI-2. Screening of the amount of steroid **5** and TBAI employed on the insertion reaction of CO_2 into styrene oxide **1a**.[a]

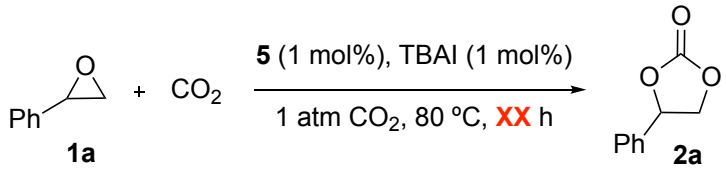


entry	**5** (mol%)	TBAI (mol%)	Conv. (%)[b]
1	5	5	99
2	2.5	2.5	93
3	1	1	78
4	0.5	0.5	44
5	1	0.5	55
6	0.5	1	63

[a] General conditions: steroidal bis-amine **5** (stated amount, respect to epoxide **1a**) and TBAI (stated amount, respect to epoxide **1a**) were suspended in styrene oxide **1a** (200 µL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at 80 ºC for 9 h under 1 atm of CO_2 (standard balloon).

[b] Conversion of epoxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixtures.

Table SI-3. Screening of the reaction time for the CO_2 insertion reaction into expoxide **1a**.[a]

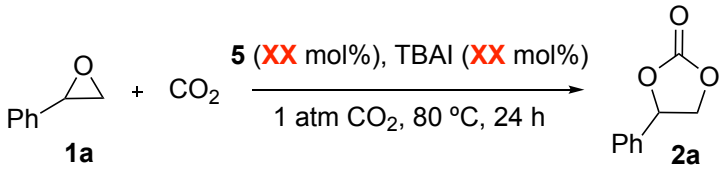


entry	time (h)	Conv. (%)[b]
1	12	81
2	18	86
3	24	99

[a] General conditions: steroidal bis-amine **5** (8.1 mg, 17.5 μmol) and TBAI (6.5 mg, 17.5 μmol) were suspended in styrene oxide **1a** (200 μL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at 80 ºC for the stated time, under 1 atm of CO_2 (standard balloon).

[b] Conversion of epoxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixtures.

Table SI-4. Further screening of the amount of steroid **5** and TBAI employed on the insertion reaction of CO_2 into styrene oxide **1a**.[a]



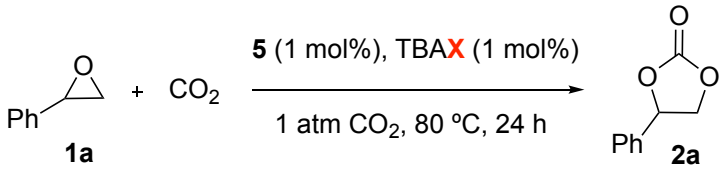
entry	**5** (mol%)	TBAI (mol%)	Conv. (%)[b]
1	1	1	99
2	1	0.5	78
3	0.5	0.5	77
4	0.5	1	67

[a] General conditions: steroidal bis-amine **5** (stated amount, respect to epoxide **1a**) and TBAI (stated amount, respect to epoxide **1a**) were suspended in styrene oxide **1a** (200 µL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at 80 ºC for 24 h under 1 atm of CO_2 (standard balloon).

[b] Conversion of epoxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixtures.

CONTROL EXPERIMENTS

Table SI-5. Screening of different TBA salts, with varying anions, on the insertion of CO_2 into expoxide **1a.**[a]

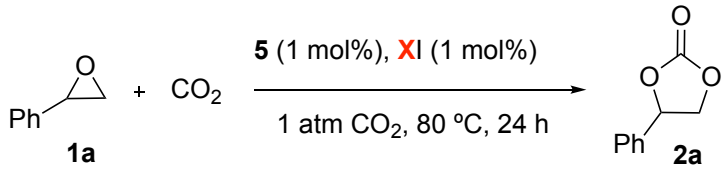


entry	X	Conv. (%)[b]
1	Cl	76
2	Br	89
3	I	99

[a] General conditions: steroidal bis-amine **5** (8.1 mg, 17.5 μmol) and TBAX (17.5 μmol) were suspended in styrene oxide **1a** (200 μL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at 80 ºC for 24 h, under 1 atm of CO_2 (standard balloon).

[b] Conversion of epoxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixtures.

Table SI-6. Screening of different iodide salts, with varying cations, on the insertion of CO_2 into expoxide **1a.**[a]

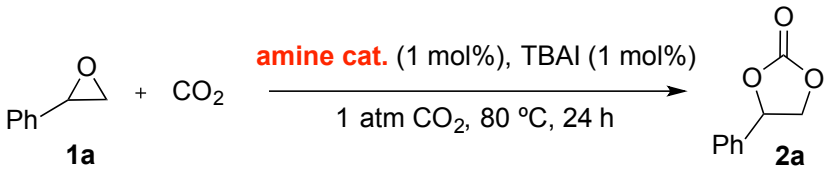


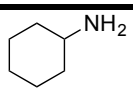
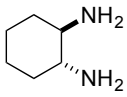
entry	XI	Conv. (%)[b]
1	NaI	5
2	KI	4
3	Me_4NI	0
4	Et_4NI	81

[a] General conditions: steroidal bis-amine **5** (8.1 mg, 17.5 μmol) and salt XI (17.5 μmol) were suspended in styrene oxide **1a** (200 μL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at 80 ºC for 24 h, under 1 atm of CO_2 (standard balloon).

[b] Conversion of epoxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixture.

Table SI-7. Screening of different primary amines as catalysts for the insertion of CO_2 into expoxide **1a.**[a]



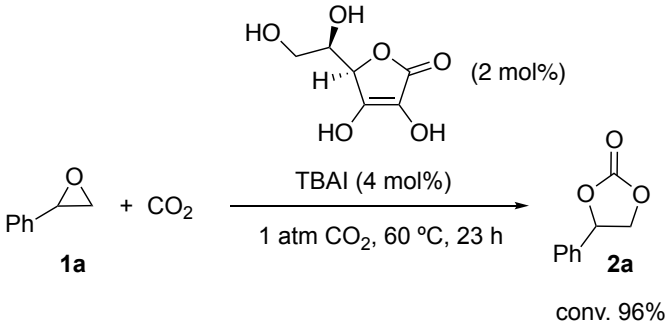
entry	catalyst	Conv. (%)[b]
1		34
2		40

[a] General conditions: primary amine catalyst (17.5 µmol) and TBAI (6.5 mg, 17.5 µmol) were suspended in styrene oxide **1a** (200 µL, 211 mg, 1.75 mmol). The reactions were vigorously stirred at 80 ºC for 24 h, under 1 atm of CO_2 (standard balloon).

[b] Conversion of epoxide **1a** into the corresponding cyclic carbonate **2a**, as determined by ^{1}H NMR spectroscopy on crude reaction mixture.

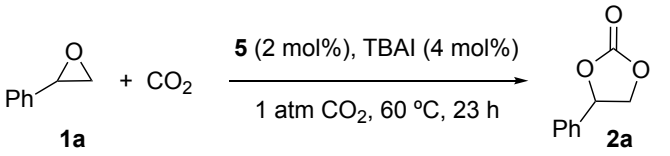
COMPARISON OF CATALYTIC SYSTEM 5/TBAI *versus* OTHER KNOWN ORGANOCATALYSTS OPERATING UNDER RELATED MILD CONDITIONS

A) Work published in *ACS Sus. Chem. Eng.* **2017**, *5*, 6392–6397, due to V. D'Elia and co-workers.



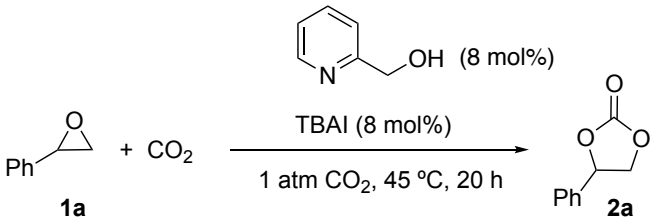
conv. 96%

Our system:



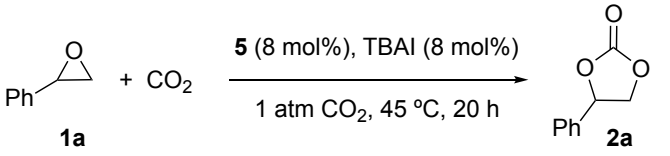
conv. 95%

B) Work published in *Green Chem.* **2016**, *18*, 1229–1233, due to T. Hirose and co-workers.



conv. 85%

Our system:

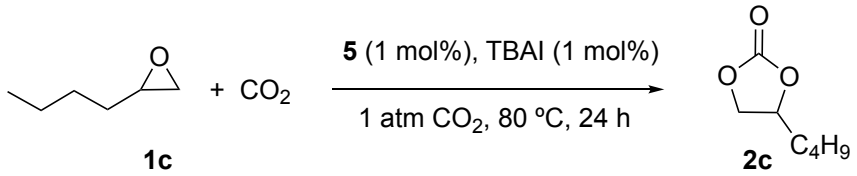


conv. 91%

RECICLABILITY OF THE CATALYTIC SYSTEM 5 + TBAI

A reaction with 1,2-epoxyhexane, **1c**, was set up as in Table 1, entry 7 (main text), according to the conditions of **SP1**. With the completion of the reaction (full conversion) cyclic carbonate **2c** was distilled off under reduced pressure. The residue left over inside the distillation flask was reused as the catalyst in subsequent **1c→2c** transformations.

Table SI-8. Recyclability of catalysts **5** + TBAI on the insertion reaction of CO_2 into 1,2-epoxyhexane **1c.**[a]



1c **2c**

cycle	Conv. (%)[b]	TON[c]	TOF (h^{-1})[d]
1	99	99	4,1
2	99	198	8,3
3	92	290	12,1
4	93	383	16,0
5	93	476	19,8
6	89	565	23,5

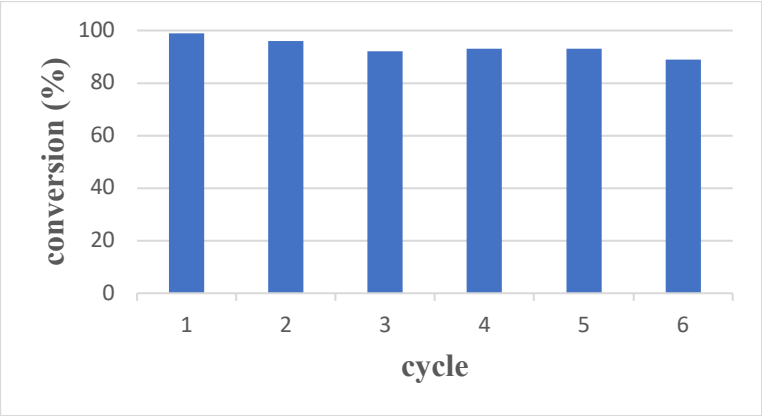
[a] Inside a 10 mL round bottomed flask catalyst **5** (7.7 mg, 16.6 μmol) and TBAI (6.1 mg, 16.6 μmol) were dissolved in 1,2-epoxyhexane **1c** (200 μL, 166 mg, 1.66 mmol). A reflux condenser, closed with a septum, was attached and a standard balloon filled with CO_2 was inserted using a needle. After flushing the system for 2-3 min through a release needle, the mixture was stirred and heated at 80 ºC for 24 h under 1 atm of CO_2. The catalytic system (**5** + TBAI) was recovered by distilling the product **2c** under reduced pressure. Then, another fresh batch of 1,2-epoxyhexane **1c** was added and the subsequent reaction was carried out under the same experimental conditions.

[b] Conversion of epoxide **1c** to cyclic carbonate **2c**, as determined by ^{1}H NMR spectroscopy on crude reaction mixtures.

[c] Accumulative turn over number. TON is defined by the expression = (mol of product)/(mol of catalyst).

[d] Accumulative turn over frequency. TOF is defined by the expression = (mol of product/reaction time)/(mol of catalyst).

Figure SI-4. Bars-chart representation of the recyclability of catalysts **5** + TBAI on the insertion reaction of CO_2 into 1,2-epoxyhexane **1c.** Reaction conditions as indicated in Table SI-8.



KINETIC STUDY

A kinetic study was carried out for the transformation **1a→2a** employing either TBAI, TBAI + **5**, or TBAI + **6**. Each plotted point on Figures SI-5, and SI-6 corresponds to a different experiment. They were set up according to the conditions specified in Table 1 (main text): styrene oxide **1a** (200 µL, 211 mg, 1.75 mmol), 1 mol% of the catalysts (respect to epoxide **1a**). The reaction mixtures were heated at 80 ºC for the stated times under 1 atm of CO_2 (standard balloon). The reaction mixtures were quickly cooled to rt and the conversion of epoxide **1a** to cyclic carbonate **2a** was determined by ^{1}H NMR spectroscopy ($CDCl_3$) on crude reaction mixtures.

Figure SI-5: Kinetic course of the transformation **1a→2a** catalyzed by TBAI.

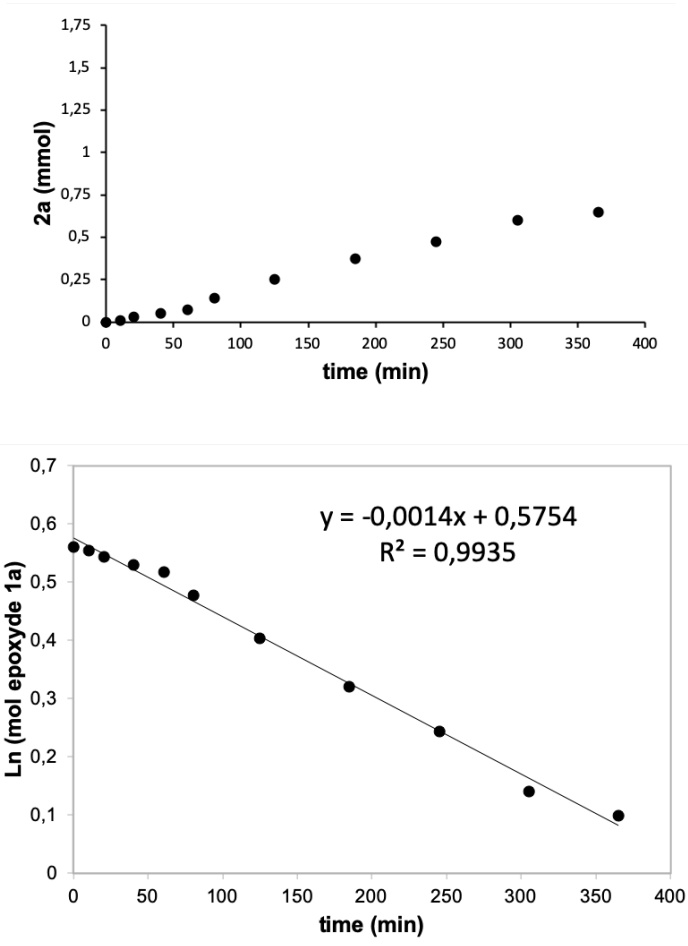
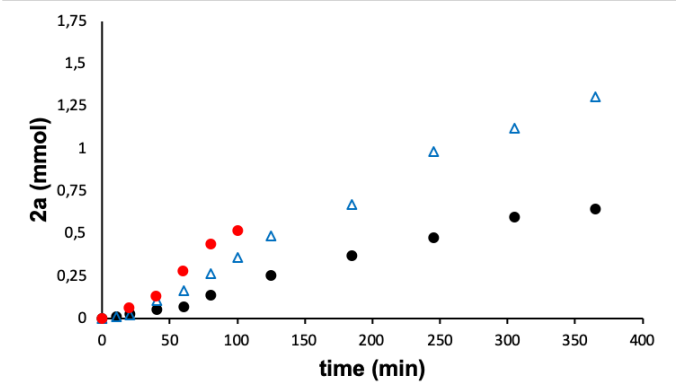


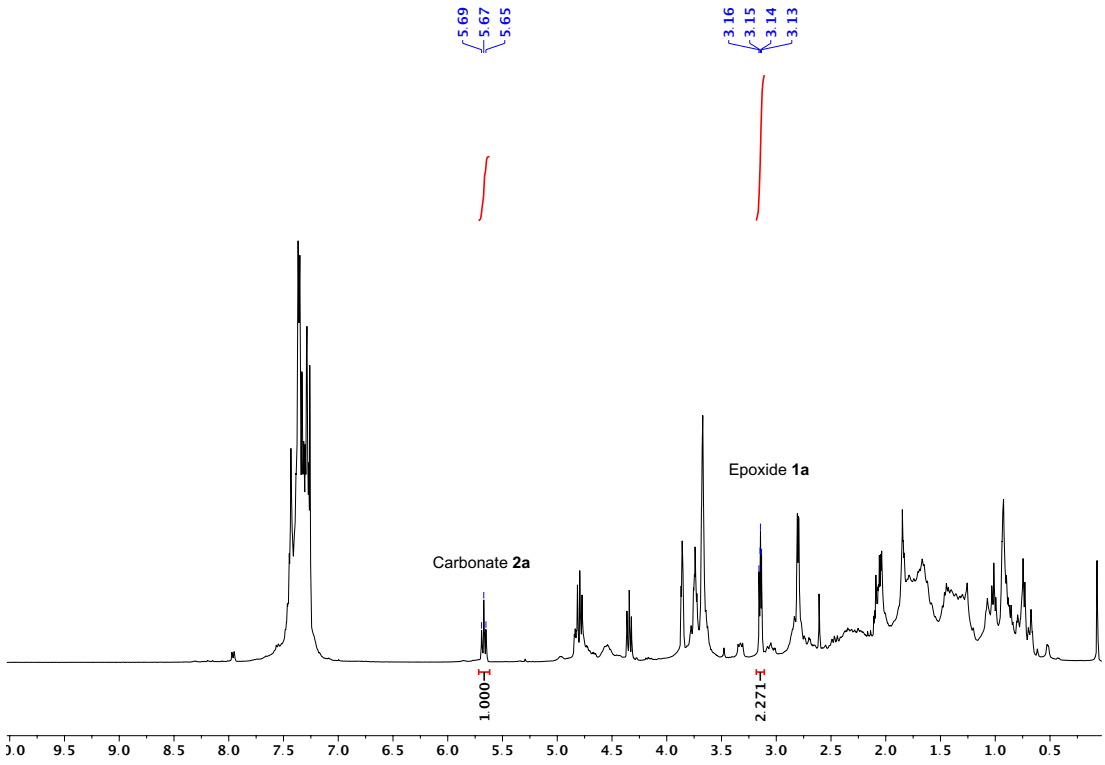
Figure SI-6: Comparative plot for the kinetic courses of the transformation **1a→2a** catalyzed by TBAI (black dots), TBAI + **5** (empty blue triangles), TBAI + **6** (red dots).



MECHANISTIC PROOF

An experiment was set up to determine the concurrence of Cycle B (main text, Scheme 2) in the transformation **1→2**. The reaction conditions were as followed: inside a 10 mL round bottom flask steroidal catalyst **6** (121 mg) and TBAI (3.3 mg) were suspended in styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol). A reflux condenser, closed with a septum, was attached. The mixture was stirred and heated at 80 ºC for 24 h under air. The resulting reaction mixture was analyzed by ^{1}H NMR spectroscopy. The resonances of cyclic carbonate **2a** were integrated against epoxide **1a**, resulting in a 30% conversion.

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

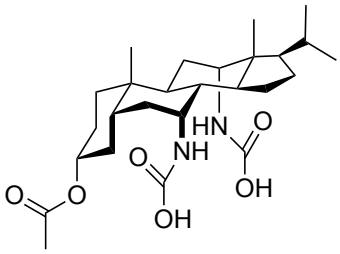


MOLECULAR MODELLING STUDY

Methods: All calculations were performed with the Gaussian09 package of programs.[4] Full geometry optimizations were carried out employing the b3lyp hybrid functional with the 6-31+G** basis set for C, H, O, and N and the effective core potential lanl2dz for Iodine. Harmonic force constants were computed at the optimized geometries employing the same level of theory to characterize the stationary points as minima or saddle points. Zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies E_{el} to Gibbs free energies G. Computational data, three-dimensional models and cartesian coordinates for all the stationary points found are included below. The three-dimensional models have been rendered with CYLview.[5]

As a consequence of the complexity of steroid **6**, in the molecular modelling study it was replaced by the surrogate **6***, missing the alkyl chain at C_{22}, which is not likely to participate in the catalytic process. It was used as a simplified model.

Figure SI-7: Chemical structure of **6*** used in the molecular modelling study.

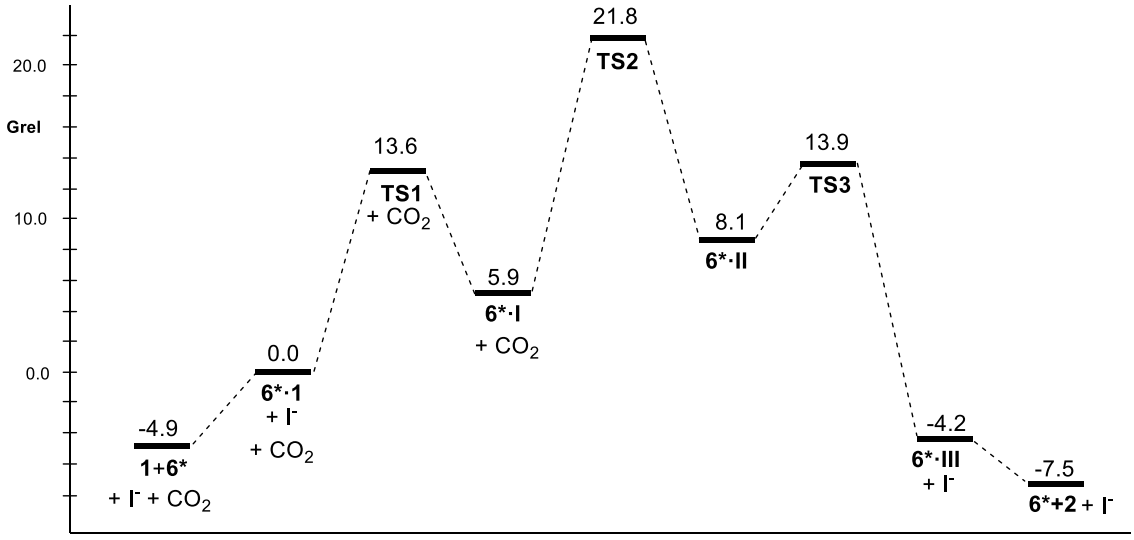


6*

[4] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V.Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

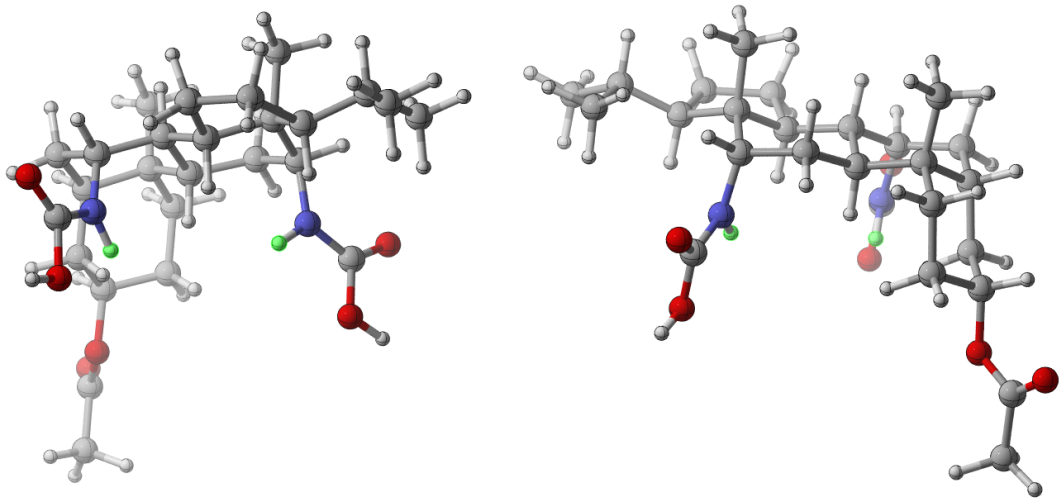
[5] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

Figure SI-8: Energy profile calculated for the carboxylation reaction of propylene oxide co-catalyzed by **6*** and iodide at the b3lyp/6-31+G**+lanl2dz.



Energies, 3D models and Cartesian coordinates for the stationary points

Ligand 6*



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Thermal correction to Gibbs Free Energy=         0.600789
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Sum of electronic and thermal Energies=             -1576.416132
Sum of electronic and thermal Enthalpies=           -1576.415188
Sum of electronic and thermal Free Energies=        -1576.518564

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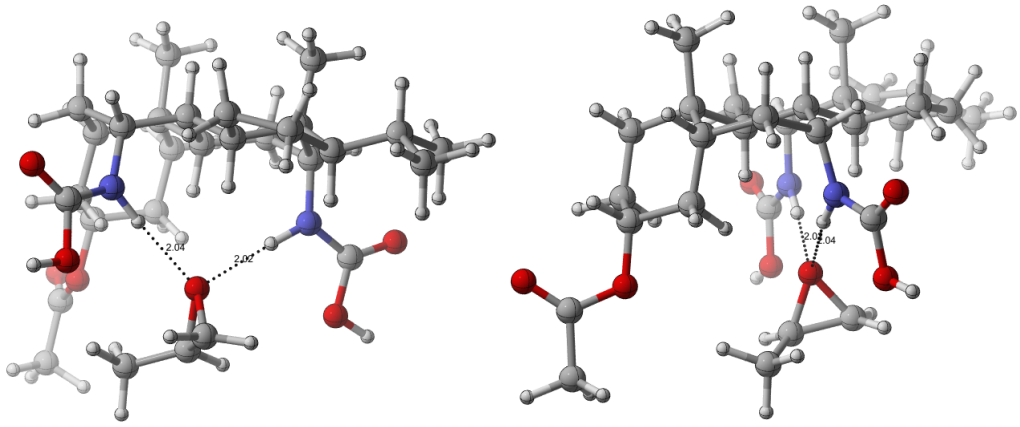
Initial complex [6*·1]



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TS1

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Sum of electronic and thermal Free Energies=        -1781.045368

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  C    -1.454616   -2.542183    2.334761
  C    -2.851302   -2.832836    1.721312
  C    -2.670738   -2.930063    0.166826
  C    -3.662738   -3.937941   -0.466404
  C    -3.498118   -4.126992   -1.983615
  C    -5.114913   -3.510652   -0.170483
  C     5.127935    2.877251   -1.485091
  C     0.611165    0.760075    3.492161
  C    -1.328513   -1.177278   -3.074220
  O    -1.446551   -2.020112   -3.963487
  O     6.173674    2.364651   -1.843425
  O     0.941165    0.433396    4.632311
  H     4.984567   -1.750261   -1.163945
  H     3.566756   -2.149834   -2.106920
  H     4.347136    0.160123   -2.578816
  H     2.740362    0.234492   -1.843471
  H     5.404635    0.637011   -0.402180
  H     2.543641    0.853909    0.652547
  H     4.000843    1.141360    1.586928
  H     4.739708   -1.170282    1.341323
  H     3.242717   -0.499989    3.261736
  H     3.283493   -2.213042    2.896034
  H     1.058561   -1.719179    3.374169
  H     1.242237   -3.210259    1.580565
  H     1.381478   -0.821819   -0.308090
  H     3.227037   -3.799914    1.246718
  H     4.777420   -3.362307    0.528551
  H     3.501437   -4.046692   -0.478857
  H     1.390578   -3.756733   -1.137581
  H     1.459327   -2.359203   -2.191475
  H    -0.758841   -3.383753   -2.148701
  H    -1.288955   -5.011650    1.140786
  H     0.293772   -4.793870    0.406931
  H    -1.082135   -5.252905   -0.592700
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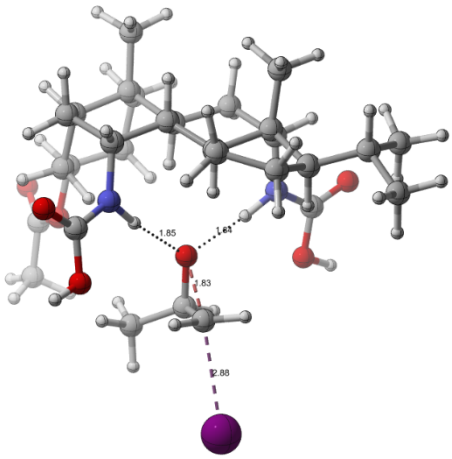

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H	-3.264710	-3.769303	2.117069
H	-2.894655	-1.946163	-0.265860
H	-3.505979	-4.915234	0.015880
H	-4.287786	-4.783530	-2.370034
H	-2.540167	-4.578616	-2.252764
H	-3.565484	-3.174452	-2.519497
H	-5.316853	-3.433990	0.902231
H	-5.328969	-2.532920	-0.620673
H	-5.824238	-4.232651	-0.592888
C	4.745742	4.317682	-1.739220
H	4.368351	4.783272	-0.824821
H	5.610553	4.862671	-2.118855
H	3.938339	4.353917	-2.478371
O	-1.609241	0.144696	-3.305977
H	-1.907870	0.189873	-4.225975
N	-0.944161	-1.378088	-1.797439
H	-0.782866	-0.535704	-1.216973
O	-0.021142	1.950868	3.242208
H	-0.131208	2.377206	4.104849
N	0.802005	0.051983	2.362833
H	0.417833	0.432332	1.482892
O	-0.372664	0.888074	-0.128608
C	-1.845829	1.932959	0.187430
H	-1.800693	2.100902	1.253008
H	-2.659834	1.361295	-0.229063
C	-0.659104	2.194595	-0.623727
I	-3.647395	4.175887	0.033605
H	-0.845393	2.197381	-1.703381
C	0.300695	3.289604	-0.203089
H	1.268946	3.155955	-0.698973
H	-0.114370	4.265056	-0.477302
H	0.455732	3.269583	0.880093

6*·I

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E(RB3LYP) =  -1781.73464484
Zero-point correction=                           0.754955 (Hartree/Particle)
Thermal correction to Energy=                    0.796826
Thermal correction to Enthalpy=                  0.797770
Thermal correction to Gibbs Free Energy=         0.677055
Sum of electronic and zero-point Energies=          -1780.979690
Sum of electronic and thermal Energies=             -1780.937819
Sum of electronic and thermal Enthalpies=           -1780.936874
Sum of electronic and thermal Free Energies=        -1781.057590
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  C    0.758940   -1.778771    2.375285
  C   -0.030066   -2.409799    1.202526
  C    0.740928   -2.299299   -0.149729
  C    2.156938   -2.972890   -0.067315
  C    2.060782   -4.495780    0.197527
  C   -0.115057   -2.796407   -1.336737
  C   -1.534965   -2.175198   -1.405587
  C   -2.296954   -2.440751   -0.072437
  C   -2.518241   -3.963772    0.098293
  C   -1.446209   -1.829956    1.076522
  C   -2.368563   -1.889150    2.301703
  C   -3.775299   -1.604627    1.709210
  C   -3.652330   -1.684130    0.147245
  C    0.798604    0.353774    3.516868
  C   -1.803000   -0.325787   -2.967487
  O   -2.293509   -0.985889   -3.888979
  O    1.001693   -0.123877    4.637695
  H    3.868192   -3.441010   -1.297085
  H    2.398272   -3.245307   -2.226423
  H    3.880748   -2.899142    1.224286
  H    2.761302   -1.764594    3.188873
  H    2.153931   -3.356997    2.782387
  H    0.281255   -2.088844    3.311536
  H   -0.123679   -3.472219    1.466629
  H    0.901147   -1.228961   -0.320752
  H    1.486414   -4.745247    1.093073
  H    3.064880   -4.919164    0.324947
  H    1.595246   -5.015140   -0.647443
  H   -0.212948   -3.888287   -1.315709
  H    0.381286   -2.551550   -2.281350
  H   -2.060255   -2.645218   -2.239526
  H   -3.144647   -4.179328    0.969631
  H   -1.584821   -4.515476    0.230387
  H   -3.024285   -4.385249   -0.777260
  H   -1.334853   -0.768917    0.828615
  H   -2.084414   -1.161398    3.067501
  H   -2.334024   -2.879934    2.774832
  H   -4.142400   -0.620549    2.017912
  H   -4.508465   -2.336352    2.073160
  H   -3.499207   -0.667164   -0.237272
  O   -1.570343    1.019614   -3.125924
  H   -1.864972    1.218146   -4.026482
  N   -1.450635   -0.750576   -1.742518
  H   -0.916644   -0.081643   -1.118861
  O    0.651342    1.713247    3.356379
  H    0.750159    2.078218    4.247892
  N    0.693738   -0.311085    2.357166
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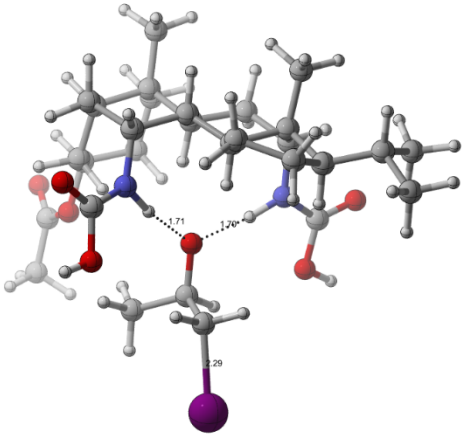

C	-1.043799	2.825560	0.404246
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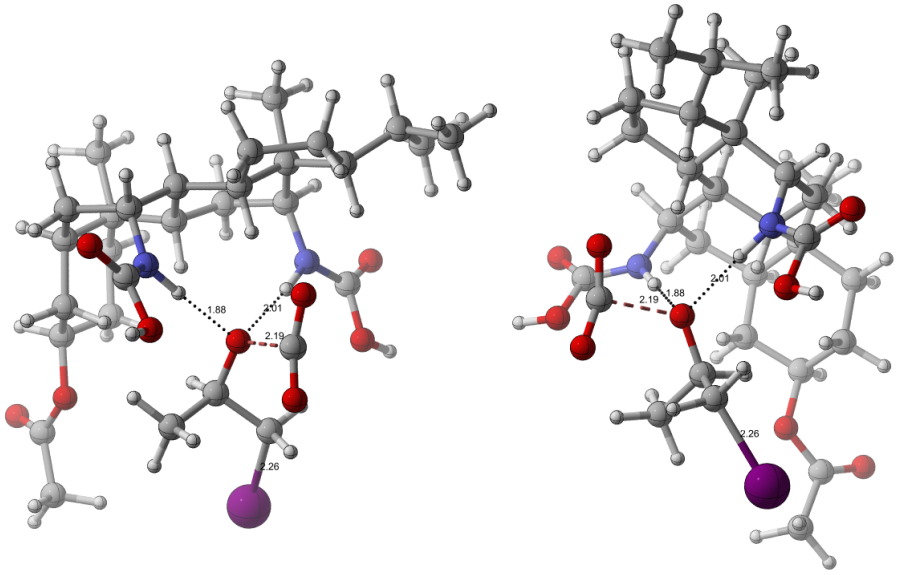
H	-1.995038	2.397291	0.097117
C	0.124144	2.203074	-0.368852
H	-0.048172	2.374264	-1.446908
I	-1.400475	5.054486	0.047346
C	-4.950803	-2.227272	-0.501898
H	-5.159514	-3.214908	-0.062103
C	-4.881508	-2.395129	-2.028885
H	-4.159655	-3.155144	-2.337284
H	-5.861381	-2.697513	-2.420529
H	-4.593426	-1.464010	-2.527519
C	-6.143284	-1.312855	-0.153556
H	-7.072251	-1.705654	-0.585039
H	-6.292944	-1.215565	0.926286
H	-5.988619	-0.305534	-0.561416
C	3.447580	-0.863326	0.728445
H	2.604605	-0.174718	0.629793
H	4.073279	-0.484290	1.546186
C	3.400961	-1.389027	-1.725508
H	3.987619	-1.385254	-2.651334
H	2.534685	-0.734375	-1.875347
C	4.239145	-0.844947	-0.572807
H	5.166723	-1.421128	-0.483882
O	4.614117	0.544416	-0.827719
C	5.750195	0.796004	-1.498324
O	6.519983	-0.057242	-1.905932
C	5.951019	2.285366	-1.672686
H	5.089886	2.721224	-2.188165
H	6.018596	2.769488	-0.693324
H	6.862838	2.466470	-2.242592
C	1.487311	2.806154	0.003009
H	1.554882	3.864957	-0.273949
H	1.662582	2.714189	1.080953
H	2.277779	2.257353	-0.519473

TS2



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Zero-point correction=	0.768841 (Hartree/Particle)
Thermal correction to Energy=	0.813719
Thermal correction to Enthalpy=	0.814663
Thermal correction to Gibbs Free Energy=	0.688648
Sum of electronic and zero-point Energies=	-1969.551702
Sum of electronic and thermal Energies=	-1969.506823
Sum of electronic and thermal Enthalpies=	-1969.505879
Sum of electronic and thermal Free Energies=	-1969.631894

90

C	-0.911801	2.753073	-2.609698
C	-0.525495	3.703604	-0.294779
C	0.459684	3.944381	0.868471
C	1.324838	2.730614	1.279616
C	1.976052	2.075360	0.041846
C	0.931581	1.753547	-1.069604
C	0.171924	3.050651	-1.534901
C	1.131371	4.080273	-2.182630
C	1.560577	0.958276	-2.237332
C	2.424168	-0.259667	-1.819553
C	3.524559	0.175407	-0.808113
C	4.507148	1.140518	-1.516999
C	2.806548	0.836628	0.400179
C	3.906263	0.987717	1.460434
C	4.793792	-0.267580	1.250745
C	4.331169	-0.954387	-0.078862
C	0.538333	1.985590	3.445022
C	1.384811	-2.443491	-2.101117
O	1.852452	-2.658189	-3.219971
O	0.922690	2.996499	4.038095
H	-1.272211	3.720591	-2.990614
H	-0.460266	2.247056	-3.469836
H	-0.877597	4.694940	-0.624751
H	-0.078453	4.307218	1.751308
H	1.152245	4.747928	0.584815
H	2.126765	3.127964	1.911073
H	2.666381	2.838622	-0.340915
H	0.190200	1.087299	-0.611597
H	1.967872	4.365096	-1.539852
H	0.581012	4.997255	-2.426073
H	1.551106	3.697796	-3.119510

H	2.181839	1.616452	-2.854607
H	0.772701	0.578704	-2.895547
H	2.886474	-0.650930	-2.727088
H	5.343444	1.407201	-0.863255
H	4.035216	2.074785	-1.830035
H	4.931774	0.675553	-2.413499
H	2.120854	0.078873	0.790115
H	3.493892	1.035056	2.471852
H	4.480883	1.910514	1.301173
H	4.695493	-0.959073	2.091602
H	5.854350	0.010419	1.188457
H	3.605427	-1.734645	0.181404
O	0.572900	-3.369855	-1.497277
H	0.470403	-4.077848	-2.150420
N	1.583087	-1.358610	-1.325601
H	1.014565	-1.258553	-0.465871
O	-0.034672	0.944136	4.124473
H	-0.030223	1.217286	5.053435
N	0.609307	1.757442	2.119320
H	0.322227	0.821852	1.765549
O	-0.154305	-0.883298	1.128158
C	-1.776462	-2.518913	0.655202
H	-1.686054	-3.146065	1.539102
H	-1.143611	-2.873497	-0.151402
C	-1.538304	-1.031699	0.951044
H	-1.867859	-0.466612	0.057971
I	-3.850102	-3.004480	-0.115805
O	1.935687	-1.606545	2.529706
C	0.834381	-1.984224	2.743943
O	-0.042072	-2.584304	3.268232
C	5.511679	-1.646487	-0.806335
H	6.286820	-0.886923	-0.992343
C	5.149094	-2.289048	-2.155568
H	4.833469	-1.557363	-2.903415
H	6.017241	-2.820851	-2.565907
H	4.333520	-3.012466	-2.053509
C	6.139065	-2.721753	0.104657
H	6.996660	-3.196128	-0.388561
H	6.486921	-2.308680	1.056338
H	5.407916	-3.508544	0.330748
C	-1.779480	2.931301	0.177024
H	-1.507622	1.961880	0.600109
H	-2.261602	3.496473	0.984291
C	-2.127551	1.958263	-2.115179
H	-2.849572	1.834541	-2.929501
H	-1.838765	0.955693	-1.778996
C	-2.776687	2.702529	-0.952104
H	-3.198475	3.649752	-1.307434
O	-3.868520	1.915933	-0.392705
C	-5.081023	1.985568	-0.972320
O	-5.354332	2.716604	-1.909095
C	-6.046742	1.035877	-0.303804
H	-5.667289	0.011471	-0.379515
H	-6.126225	1.270629	0.762283
H	-7.024840	1.114314	-0.779480
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H	-3.440560	-0.639241	1.955971
H	-2.109822	-1.103749	3.047778
H	-2.155975	0.517047	2.345691

6*II

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E(RB3LYP) =  -1970.34189578
Zero-point correction=                           0.771158 (Hartree/Particle)
Thermal correction to Energy=                    0.816060
Thermal correction to Enthalpy=                  0.817004
Thermal correction to Gibbs Free Energy=         0.688203
Sum of electronic and zero-point Energies=          -1969.570738
Sum of electronic and thermal Energies=             -1969.525835
Sum of electronic and thermal Enthalpies=           -1969.524891
Sum of electronic and thermal Free Energies=        -1969.653692

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  C    1.431943    3.595983    1.302087
  C    2.049863    2.236095    1.692493
  C    2.794569    1.606380    0.491928
  C    1.911425    1.548560   -0.792862
  C    1.368050    2.968409   -1.197916
  C    2.517154    3.924740   -1.606153
  C    2.658795    0.831232   -1.941140
  C    3.259801   -0.552620   -1.575901
  C    4.191677   -0.430475   -0.335005
  C    5.434477    0.405593   -0.725729
  C    3.371155    0.219455    0.816947
  C    4.276426    0.076545    2.048730
  C    4.974283   -1.293559    1.828787
  C    4.648077   -1.756052    0.367170
  C    0.738092    1.431123    3.577248
  C    1.884172   -2.374066   -2.436721
  O    2.471580   -2.482047   -3.515253
  O    1.140266    2.289132    4.366907
  H    0.251217    3.942778   -2.766479
  H    0.900359    2.396039   -3.258789
  H    0.414365    4.648181   -0.252144
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  H    2.261435    4.305879    1.183852
  H    2.782791    2.439782    2.481341
  H    3.637432    2.285751    0.303153
  H    1.043014    0.925932   -0.547772
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  H    2.123456    4.935984   -1.765065
  H    2.981103    3.607825   -2.546339
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  H    3.834936   -0.886925   -2.441139
  H    6.156235    0.456023    0.095203
  H    5.184898    1.433644   -0.998441
  H    5.948482   -0.042446   -1.583332
  H    2.523173   -0.451012    0.986993
  H    3.708282    0.108248    2.982963
  H    5.011923    0.891046    2.094566
  H    4.626418   -2.035157    2.554506
  H    6.059764   -1.206061    1.968714
  H    3.762566   -2.403547    0.404663
  O    0.785426   -3.136548   -2.149959
  H    0.648740   -3.689822   -2.932547
  N    2.203391   -1.555429   -1.413340
  H    1.532970   -1.491559   -0.632075
  O   -0.144056    0.460255    3.975412
  H   -0.299686    0.634501    4.915068
  N    1.072805    1.312264    2.280846
  H    0.715523    0.501657    1.750095
  O   -1.797400   -0.592440    0.801444
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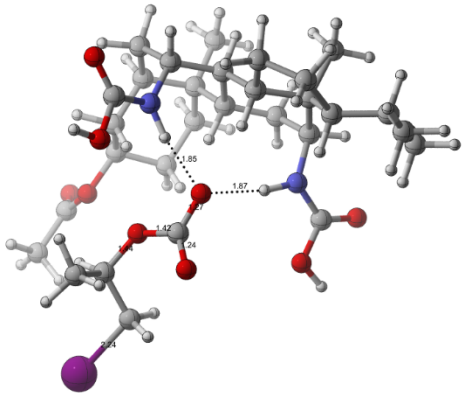

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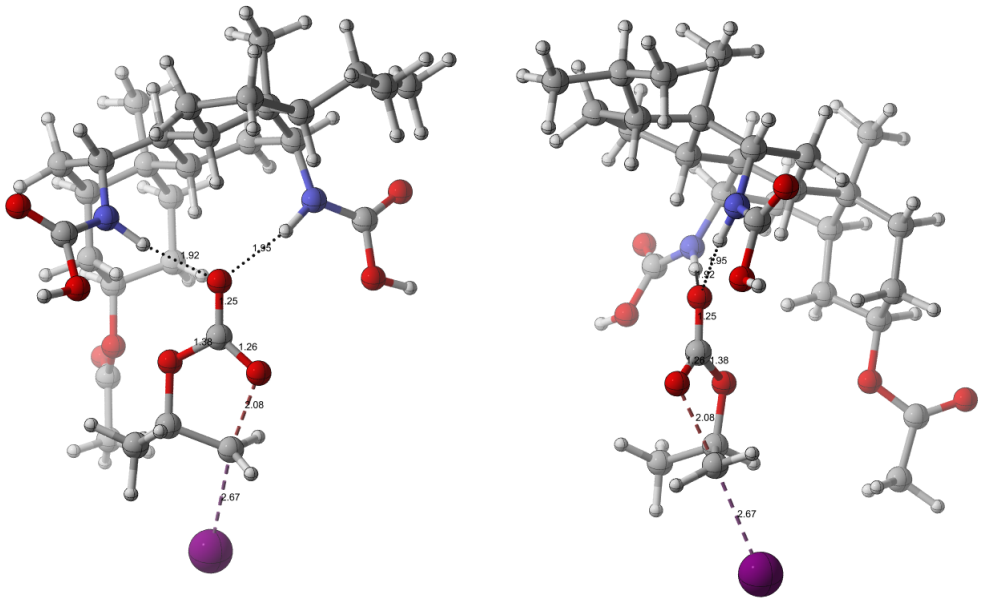
C	-3.150884	-0.967762	1.097939
H	-3.702455	-0.049935	0.869681
I	-5.826267	-2.137257	-0.079251
O	0.371618	-1.007219	0.745169
C	-0.759197	-1.553162	0.920941
O	-1.054921	-2.729795	1.152493
C	5.797772	-2.595939	-0.244170
H	6.712261	-1.982572	-0.230429
C	5.551394	-3.046793	-1.693639
H	5.486730	-2.210053	-2.392825
H	6.369166	-3.695060	-2.033381
H	4.618246	-3.613272	-1.783408
C	6.070819	-3.840290	0.625262
H	6.893075	-4.432675	0.205377
H	6.339249	-3.580159	1.653810
H	5.183238	-4.484983	0.664568
C	-0.814567	2.976023	0.233863
H	-0.765857	1.930615	0.549140
H	-1.314165	3.526760	1.040930
C	-0.969924	2.286540	-2.163782
H	-1.575450	2.337063	-3.075831
H	-0.889439	1.232533	-1.872840
C	-1.646924	3.061306	-1.038202
H	-1.792307	4.103086	-1.344587
O	-2.968322	2.513418	-0.746016
C	-4.025828	3.012616	-1.411022
O	-3.960423	3.893965	-2.251453
C	-5.308041	2.343250	-0.972001
H	-5.261743	1.266502	-1.161557
H	-5.448238	2.472492	0.105724
H	-6.148689	2.779246	-1.512590
C	-3.355880	-1.320157	2.572437
H	-4.422325	-1.447262	2.788560
H	-2.823464	-2.240054	2.823907
H	-2.966503	-0.508509	3.194330

TS3



1 imaginary frequency: -339.68

E(RB3LYP) = -1970.33286241
Zero-point correction= 0.770987 (Hartree/Particle)
Thermal correction to Energy= 0.815375
Thermal correction to Enthalpy= 0.816319
Thermal correction to Gibbs Free Energy= 0.688487
Sum of electronic and zero-point Energies= -1969.561875
Sum of electronic and thermal Energies= -1969.517488
Sum of electronic and thermal Enthalpies= -1969.516543
Sum of electronic and thermal Free Energies= -1969.644376

90

C	0.632970	3.052529	-2.348561
C	0.730405	3.601998	0.119910
C	1.529435	3.532038	1.437078
C	2.107114	2.143634	1.789941
C	2.861041	1.530807	0.584607
C	2.025406	1.566088	-0.732299
C	1.541926	3.019702	-1.087122
C	2.735584	3.957828	-1.397218
C	2.793028	0.878725	-1.885080
C	3.323473	-0.545439	-1.570031
C	4.199232	-0.529886	-0.284226
C	5.495768	0.263547	-0.578552
C	3.359069	0.103399	0.863338
C	4.199987	-0.145015	2.123598
C	4.841613	-1.535357	1.865611
C	4.564243	-1.908798	0.368867
C	0.791027	1.275920	3.648390
C	1.931327	-2.268283	-2.600451
O	2.566830	-2.331409	-3.653016
O	1.234131	2.070657	4.478885
H	0.498776	4.108299	-2.627819
H	1.147239	2.587829	-3.196335
H	0.582076	4.671807	-0.100833
H	0.912211	3.877736	2.273968
H	2.376209	4.228318	1.377076
H	2.829953	2.301350	2.597687
H	3.740739	2.175668	0.452829
H	1.128512	0.962855	-0.549114

H	3.495318	3.966791	-0.611597
H	2.379650	4.987830	-1.520381
H	3.230969	3.673830	-2.331904
H	3.644451	1.496553	-2.192806
H	2.150116	0.785428	-2.765660
H	3.925946	-0.854680	-2.425660
H	6.177697	0.249776	0.276966
H	5.305269	1.311543	-0.821278
H	6.031400	-0.174583	-1.427822
H	2.472470	-0.531803	0.962887
H	3.593220	-0.128930	3.033462
H	4.969637	0.629131	2.241336
H	4.425126	-2.293737	2.535748
H	5.921573	-1.509134	2.059676
H	3.652180	-2.518650	0.333209
O	0.801200	-3.010363	-2.403655
H	0.673254	-3.508932	-3.223782
N	2.226253	-1.516395	-1.516936
H	1.521290	-1.475617	-0.772605
O	-0.111027	0.306544	4.002441
H	-0.259787	0.436988	4.950428
N	1.101279	1.226322	2.339826
H	0.690228	0.479407	1.767685
O	-1.887506	-0.428403	0.974549
C	-3.426470	-2.176083	0.320017
H	-3.585837	-3.158209	0.730716
H	-3.268582	-2.093443	-0.743539
C	-3.209069	-0.965439	1.213656
H	-3.875959	-0.159404	0.909786
I	-6.058256	-2.012083	-0.088680
O	0.236865	-0.985877	0.611959
C	-0.945032	-1.391333	0.686570
O	-1.395243	-2.560881	0.514900
C	5.704121	-2.768141	-0.233711
H	6.640774	-2.195183	-0.153059
C	5.501817	-3.141224	-1.711742
H	5.490011	-2.271586	-2.372499
H	6.311684	-3.799307	-2.050871
H	4.556278	-3.673064	-1.863322
C	5.889959	-4.061829	0.585524
H	6.703400	-4.668927	0.169880
H	6.127561	-3.861291	1.634817
H	4.976314	-4.669862	0.559973
C	-0.687431	2.997611	0.264806
H	-0.660748	1.941739	0.543858
H	-1.211169	3.519971	1.075172
C	-0.760513	2.430436	-2.175567
H	-1.332823	2.539467	-3.103133
H	-0.694195	1.359638	-1.949929
C	-1.479568	3.137185	-1.029879
H	-1.627076	4.192104	-1.287656
O	-2.796935	2.557570	-0.806391
C	-3.834479	3.040362	-1.519843
O	-3.741192	3.939682	-2.338246
C	-5.117730	2.330318	-1.162089
H	-5.027731	1.252529	-1.329061
H	-5.337153	2.467551	-0.098523
H	-5.934510	2.731375	-1.762657
C	-3.397732	-1.278630	2.695493
H	-4.429512	-1.595039	2.877272
H	-2.716866	-2.076515	3.008364
H	-3.184879	-0.386857	3.291241

6*·2

```
E(RB3LYP) =  -1958.87647454
Zero-point correction=                           0.773192 (Hartree/Particle)
Thermal correction to Energy=                    0.816002
Thermal correction to Enthalpy=                  0.816946
Thermal correction to Gibbs Free Energy=         0.691999
Sum of electronic and zero-point Energies=          -1958.103283
Sum of electronic and thermal Energies=             -1958.060472
Sum of electronic and thermal Enthalpies=           -1958.059528
Sum of electronic and thermal Free Energies=        -1958.184475

89
  C    2.096598   -2.909149   -1.524587
  C    2.226873   -2.594833    0.983275
  C    1.473664   -2.507878    2.326788
  C    0.239010   -1.583180    2.332214
  C   -0.690927   -1.887319    1.132666
  C    0.078695   -1.911286   -0.225034
  C    1.269245   -2.938660   -0.207995
  C    0.764573   -4.393987   -0.052969
  C   -0.888870   -2.113678   -1.416705
  C   -2.114442   -1.165732   -1.434998
  C   -2.896577   -1.258661   -0.092308
  C   -3.507179   -2.675249    0.035691
  C   -1.897879   -0.940013    1.059171
  C   -2.790988   -0.793354    2.299580
  C   -4.087467   -0.142784    1.745299
  C   -4.003445   -0.182553    0.180912
  C    0.824272    0.458116    3.573915
  C   -1.845385    0.724543   -2.995633
  O   -2.406725    0.212225   -3.954881
  O    0.824871   -0.057348    4.684638
  H    2.786932   -3.764352   -1.496733
  H    1.445044   -3.088132   -2.385854
  H    2.925620   -3.441421    1.068480
  H    2.155358   -2.191385    3.124163
  H    1.125769   -3.509872    2.607050
  H   -0.311159   -1.786514    3.256068
  H   -1.073526   -2.896395    1.328996
  H    0.526501   -0.917642   -0.355193
  H    0.114098   -4.541172    0.812630
  H    1.617133   -5.072555    0.063163
  H    0.212874   -4.720820   -0.940168
  H   -1.256279   -3.144537   -1.432287
  H   -0.356684   -1.965412   -2.360843
  H   -2.752811   -1.466661   -2.266908
  H   -4.128640   -2.761285    0.931371
  H   -2.752529   -3.462358    0.092572
  H   -4.145950   -2.900580   -0.824146
  H   -1.512607    0.066947    0.850126
  H   -2.321429   -0.187363    3.079694
  H   -3.000800   -1.773911    2.744434
  H   -4.197880    0.886264    2.100580
  H   -4.973952   -0.685532    2.094341
  H   -3.595803    0.777698   -0.163621
  O   -1.278036    1.975931   -3.077019
  H   -1.422657    2.257438   -3.993135
  N   -1.701885    0.205867   -1.756281
  H   -1.091747    0.713096   -1.124370
  O    1.077327    1.800569    3.399123
  H    1.249999    2.139563    4.290631
  N    0.588500   -0.156291    2.397508
  H    0.599762    0.418113    1.562760
  O    1.332516    3.770971   -0.300961
  C   -0.477782    4.970326    0.524762
  H   -0.347086    5.203066    1.586897
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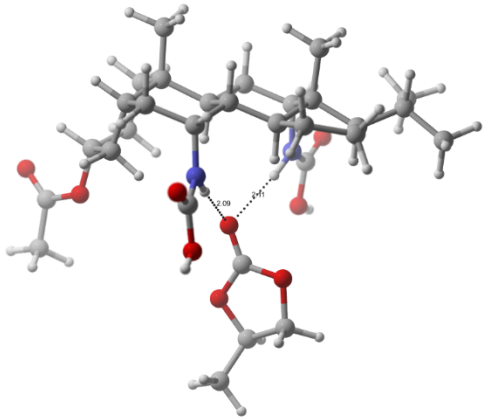

H	-1.319136	5.533196	0.118656
C	0.822635	5.134241	-0.277742
H	0.608696	5.402901	-1.318464
O	0.432602	1.709697	-0.066294
C	0.343921	2.912771	0.005296
O	-0.769618	3.563660	0.401426
C	-5.399735	-0.337526	-0.471935
H	-5.855661	-1.258346	-0.079153
C	-5.376125	-0.438524	-2.006087
H	-4.877241	-1.342281	-2.364252
H	-6.399165	-0.457553	-2.399325
H	-4.862802	0.416392	-2.459281
C	-6.313223	0.834552	-0.061106
H	-7.309215	0.720823	-0.503664
H	-6.439246	0.906747	1.023297
H	-5.901063	1.788515	-0.415328
C	3.102683	-1.343059	0.732389
H	2.504735	-0.428727	0.699352
H	3.801620	-1.226484	1.569323
C	2.929674	-1.639462	-1.752885
H	3.501081	-1.733636	-2.682308
H	2.290745	-0.752668	-1.847251
C	3.877959	-1.444505	-0.574226
H	4.600726	-2.266397	-0.542137
O	4.631104	-0.204061	-0.718489
C	5.794681	-0.244581	-1.403036
O	6.260880	-1.251254	-1.900529
C	6.431458	1.124028	-1.465564
H	5.779856	1.809235	-2.017139
H	6.554793	1.530640	-0.457506
H	7.398289	1.052608	-1.963633
C	1.852833	6.068305	0.322686
H	1.455710	7.088926	0.349600
H	2.106472	5.762608	1.342073
H	2.765083	6.073602	-0.279258

1 (PO)

```
E(RB3LYP) =  -193.126404591
Zero-point correction=                           0.085390 (Hartree/Particle)
Thermal correction to Energy=                    0.089809
Thermal correction to Enthalpy=                  0.090753
Thermal correction to Gibbs Free Energy=         0.059006
Sum of electronic and zero-point Energies=           -193.041015
Sum of electronic and thermal Energies=              -193.036595
Sum of electronic and thermal Enthalpies=            -193.035651
Sum of electronic and thermal Free Energies=         -193.067398
```

CO_2

```
E(RB3LYP) =  -188.590392621
Zero-point correction=                           0.011565 (Hartree/Particle)
Thermal correction to Energy=                    0.014202
Thermal correction to Enthalpy=                  0.015146
Thermal correction to Gibbs Free Energy=        -0.009149
Sum of electronic and zero-point Energies=           -188.578828
Sum of electronic and thermal Energies=              -188.576191
Sum of electronic and thermal Enthalpies=            -188.575246
Sum of electronic and thermal Free Energies=         -188.599542
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2

```
E(RB3LYP) =  -381.743438049
Zero-point correction=                           0.102677 (Hartree/Particle)
Thermal correction to Energy=                    0.108931
Thermal correction to Enthalpy=                  0.109875
Thermal correction to Gibbs Free Energy=         0.072335
Sum of electronic and zero-point Energies=           -381.640761
Sum of electronic and thermal Energies=              -381.634507
Sum of electronic and thermal Enthalpies=            -381.633563
Sum of electronic and thermal Free Energies=         -381.671103
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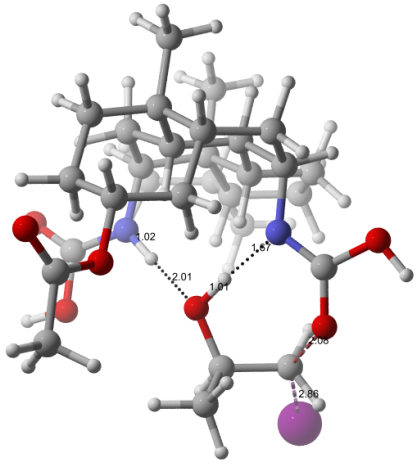
TS4



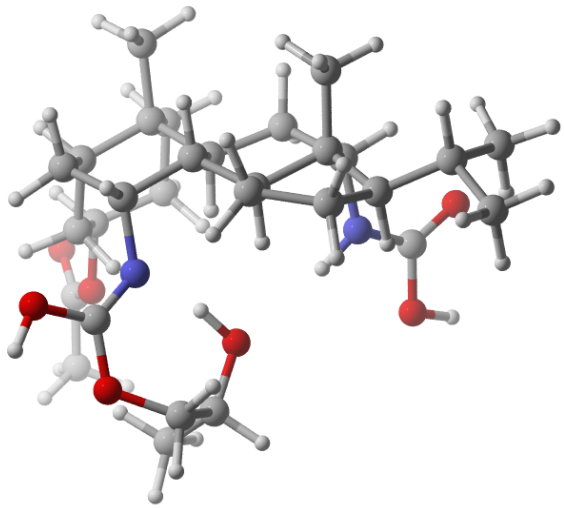
1 imaginary frequency: -340.7259

E(RB3LYP) = -1781.70163442
Zero-point correction= 0.755171 (Hartree/Particle)
Thermal correction to Energy= 0.796407
Thermal correction to Enthalpy= 0.797351
Thermal correction to Gibbs Free Energy= 0.678532
Sum of electronic and zero-point Energies= -1780.946463
Sum of electronic and thermal Energies= -1780.905228
Sum of electronic and thermal Enthalpies= -1780.904284
Sum of electronic and thermal Free Energies= -1781.023103

C	4.04460500	1.99476600	0.45009900
C	3.56791300	0.72741600	-1.68777100
C	2.62868600	0.51511900	-2.89504800
C	1.12185000	0.42449300	-2.54942400
C	0.69854900	1.63916300	-1.67830100
C	1.60502100	1.75612400	-0.41443700
C	3.11925300	1.93554700	-0.79777100
C	3.36033700	3.25618900	-1.57020100
C	1.08599100	2.81903900	0.57877300
C	-0.41465900	2.67829100	0.94526400
C	-1.28762700	2.69307800	-0.34148100
C	-1.17858500	4.08950500	-1.00180000
C	-0.78124200	1.55603100	-1.27318000
C	-1.84152300	1.48044100	-2.38106300
C	-3.17069300	1.79400400	-1.64056800
C	-2.79748100	2.29159600	-0.20247200
C	0.50238100	-1.90128800	-2.50875700
C	-0.70806000	1.60648600	3.12799000
O	-0.68769900	2.64398800	3.78999700
O	0.71767300	-1.95144000	-3.87889000
H	5.05117900	2.27280100	0.10253600
H	3.72900600	2.80426500	1.11663100
H	4.55799300	0.99585100	-2.09290000
H	2.92140600	-0.39094600	-3.43839000
H	2.75807700	1.34864600	-3.59908200
H	0.57908200	0.48952000	-3.50383500
H	0.83399300	2.53417900	-2.30142800
H	1.52461700	0.79232000	0.10091000
H	2.74750600	3.34678600	-2.47009300
H	4.41050400	3.32157300	-1.88062200
H	3.15380700	4.12825800	-0.93995200
H	1.24917800	3.82828700	0.18348500
H	1.64630100	2.76471100	1.51768300
H	-0.67115700	3.52501300	1.58392800

H	-1.85597000	4.17744800	-1.85643700
H	-0.17208900	4.30795200	-1.36672800
H	-1.44762400	4.87934000	-0.29140100
H	-0.89289100	0.63209700	-0.69766200
H	-1.86001500	0.50007800	-2.86658500
H	-1.64076100	2.22036200	-3.16779000
H	-3.81156200	0.90963500	-1.58403200
H	-3.74305100	2.56317500	-2.17551800
H	-2.83224500	1.42582800	0.47116900
O	-0.82190300	0.38149800	3.73114700
H	-0.88920600	0.57169300	4.67812500
N	-0.63898400	1.49431500	1.78542600
H	-0.56193500	0.54530500	1.40697600
O	0.05559000	-2.99020300	-1.99239700
N	0.75112900	-0.80834500	-1.85803000
H	0.30831800	-1.08830900	-0.27252600
O	-0.09243000	-1.24731800	0.64138200
C	-1.47334500	-2.82351900	-0.59275100
H	-1.69916800	-3.83238700	-0.89031300
H	-1.87124500	-2.01248900	-1.17891800
C	-0.69758900	-2.53342700	0.67629800
I	-4.18905800	-2.95114600	0.28878100
C	-3.81835600	3.32280400	0.33959900
H	-3.84419000	4.17513700	-0.35709800
C	-3.48439400	3.86602900	1.73945700
H	-2.55814000	4.44560200	1.76094500
H	-4.28892300	4.52331600	2.09289900
H	-3.37596000	3.05376100	2.46652200
C	-5.23307000	2.70929700	0.36670800
H	-5.96309100	3.43948200	0.73771000
H	-5.56364200	2.38072400	-0.62306400
H	-5.26473500	1.83669000	1.03071100
C	3.76166300	-0.58732200	-0.89346000
H	2.79912200	-0.97585600	-0.55309200
H	4.18111500	-1.34535800	-1.56704700
C	4.16172400	0.68214000	1.23753200
H	4.84715600	0.81258200	2.08279100
H	3.19071200	0.37397300	1.64268300
C	4.68227100	-0.40672300	0.30567700
H	5.70399800	-0.16650900	-0.00773000
O	4.73288100	-1.69064500	1.00314800
C	5.85854400	-2.03024000	1.65279300
O	6.86985800	-1.35074500	1.69306400
C	5.70154700	-3.37312400	2.33185400
H	4.93411800	-3.30360900	3.10964300
H	5.36536200	-4.12523800	1.61212700
H	6.65172300	-3.67097100	2.77621400
C	0.32286100	-3.63622500	0.99656000
H	1.06174400	-3.72192100	0.19633200
H	0.83050500	-3.38738600	1.93330800
H	-0.18220200	-4.60233100	1.11757300
H	-1.42681500	-2.50116200	1.48988600
H	0.40395900	-2.82820000	-4.14603200

IV



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E(RB3LYP) =  -1770.25612522
Zero-point correction=                           0.758873 (Hartree/Particle)
Thermal correction to Energy=                    0.797788
Thermal correction to Enthalpy=                  0.798732
Thermal correction to Gibbs Free Energy=         0.687520
Sum of electronic and zero-point Energies=          -1769.497252
Sum of electronic and thermal Energies=             -1769.458337
Sum of electronic and thermal Enthalpies=           -1769.457393
Sum of electronic and thermal Free Energies=        -1769.568605
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C	-2.04491000	-2.14506200	-1.97619400
C	-2.23564600	0.36368100	-2.23755000
C	-1.51342300	1.70775300	-2.46386700
C	-0.25481000	1.93449000	-1.59558600
C	0.70825300	0.71984900	-1.69333600
C	-0.04773800	-0.60440500	-1.36030400
C	-1.25665100	-0.85359900	-2.33129800
C	-0.79033700	-1.02655500	-3.79821400
C	0.91297400	-1.80914400	-1.23659600
C	2.12237400	-1.57665900	-0.29496200
C	2.91942000	-0.32517700	-0.76695400
C	3.51725300	-0.59461000	-2.16873700
C	1.93475900	0.87806300	-0.77696800
C	2.84022300	2.10153500	-0.97311800
C	4.11949000	1.74062300	-0.16998900
C	4.03226800	0.21762600	0.19438600
C	-0.96144600	3.32375200	0.23793800
C	1.93294200	-2.51255700	1.97111900
O	2.57211800	-3.53478600	1.75194500
O	-1.12880200	4.39626600	-0.57766600
H	-2.77173000	-2.31927400	-2.78287900
H	-1.37791800	-3.01315000	-1.99114200
H	-2.95161500	0.24621300	-3.06610800
H	-2.21132200	2.53833800	-2.30605400
H	-1.19811700	1.77216300	-3.51249000
H	0.26484800	2.81439500	-1.99644000
H	1.05995100	0.69571200	-2.73202800
H	-0.47915200	-0.45581500	-0.36180800
H	-0.20276600	-0.18422900	-4.17127800
H	-1.65958000	-1.13409500	-4.45743000
H	-0.18272800	-1.92964500	-3.91731100
H	1.29962900	-2.09148800	-2.22129700
H	0.37244800	-2.68166500	-0.85721200
H	2.75171600	-2.46708200	-0.33728300
H	4.17847000	0.21954500	-2.47983600

H	2.75508100	-0.70094100	-2.94417500
H	4.11278700	-1.51286200	-2.17102000
H	1.55527400	0.95522500	0.24575200
H	2.37349900	3.02580900	-0.61651900
H	3.06897700	2.25324000	-2.03573200
H	4.19889600	2.34744900	0.73738700
H	5.02164000	1.94475400	-0.75896300
H	3.63130600	0.13451800	1.21345100
O	1.35518600	-2.26643900	3.18906000
H	1.60517300	-3.02269100	3.74152200
N	1.70204400	-1.49631600	1.10910600
H	1.08531700	-0.75844500	1.44184500
O	-1.19420200	3.60581600	1.51366600
N	-0.60461600	2.17096700	-0.18429700
H	-0.85410600	1.01389400	0.77422900
O	-0.70077800	0.53602800	1.67656300
C	-0.36081200	2.83407700	2.54903200
H	-0.50963500	3.51543000	3.38092400
H	0.61874200	2.88280900	2.08099800
C	-0.93447500	1.43043000	2.75003100
C	5.42947100	-0.45305600	0.20730200
H	5.88988900	-0.29232300	-0.77927100
C	5.41018200	-1.96633900	0.48030100
H	4.93265400	-2.53421400	-0.32245800
H	6.43481900	-2.34464800	0.57794600
H	4.87578200	-2.20721500	1.40513800
C	6.33348900	0.23368300	1.25024600
H	7.33360300	-0.21471600	1.25046000
H	6.45016100	1.30524400	1.06026700
H	5.91721400	0.11810600	2.25927800
C	-3.06982600	0.38691900	-0.93426900
H	-2.43673700	0.60160700	-0.06802100
H	-3.80029400	1.20340800	-0.99847000
C	-2.81407400	-2.09528200	-0.64920700
H	-3.35509000	-3.03495400	-0.49605500
H	-2.13515400	-1.96192500	0.20205100
C	-3.79664500	-0.92893900	-0.68940500
H	-4.55525700	-1.11486500	-1.45714000
O	-4.49042700	-0.79549400	0.58665900
C	-5.60738600	-1.52952500	0.77719000
O	-6.08591000	-2.27957300	-0.05149100
C	-6.17648700	-1.29289400	2.15686400
H	-5.45982200	-1.62555000	2.91476900
H	-6.34848000	-0.22449500	2.31839000
H	-7.11011800	-1.84513700	2.26404200
C	-2.42011500	1.43768500	3.12675800
H	-3.02946500	1.85676200	2.32209200
H	-2.74460800	0.40980100	3.31053700
H	-2.58720100	2.02516300	4.03761500
H	-0.37616400	1.04038300	3.61483900
H	-1.32017200	5.15617700	-0.00632800