Reversible Insertion of CO into an Aluminium–Carbon Bond

Electronic Supporting Information

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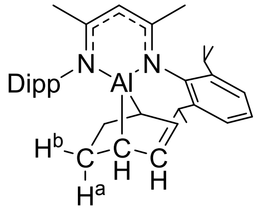
General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. A MBraun Labmaster glovebox was employed, operating at <0.1 ppm O_2 and <0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120°C prior to use. Benzene-d_6 was dried over 3 Å molecular sieves and subjected to the freeze-pump-thaw degassed thrice before use. 1,3-cyclohexadiene was dried over molecular sieves and freeze-pump-thaw degassed thrice before use.

NMR Spectra were recorded on Bruker 400 MHz or 500 MHz at 298 K unless otherwise stated and values recorded in ppm. Data were processed in MestReNova software. Where needed, chemical shifts were assigned with the assistance of 2D NMR (HSQC, HMBC, COSY) spectra. **1** and **4** were prepared according to literature procedure.[1]

*Synthesis of **2**:*



In a glovebox, **1** (18 mg, 0.040 mmol) was dissolved in toluene (~ 3 mL). To this solution, 1,3-cyclohexadiene (5 µL, 0.052 mmol) was added *via* micropipette. An instantaneous colour change from the characteristic orange-red of **1** to yellow was observed. The reaction was stirred for approximately 20 minutes before volatiles were removed *in vacuo*, to afford **2** as a pale yellow powder. The product thus obtained is sufficiently pure for use and characterisation, however **2** can be recrystallised from mixtures of toluene:hexane (1:3) as pale yellow blocks (Yield: 16 mg, 0.030 mmol, 75%).

^{1}H NMR (400 MHz, C_6D_6, 298 K)

δ 7.21-706 (m, 6H, Ar**H**),6.02 (m, 2H, **H**C=C**H**), 4.84 (s, 1H, $(CH_3)C(C\mathbf{H})C(CH_3)$), 3.41 (hept, $^3J_{HH}$ = 6.8 Hz, 2H, $(CH_3)_2C\mathbf{H}$), 3.21 (hept, $^3J_{HH}$ = 6.8 Hz, 2H, $(CH_3)_2C\mathbf{H}$), 2.09 – 2.00 (m, 2H, AlC**H**), 1.56 (s, 3H, $(C\mathbf{H_3})C(CH)C(CH_3)$), 1.52 (s, 3H, $(CH_3)C(CH)C(C\mathbf{H_3})$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $(C\mathbf{H_3})_2CH$)), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $(C\mathbf{H_3})_2CH$)), 1,40 (m, 2H, $(CH)(C\mathbf{H_aH_b})(C\mathbf{H_aH_b})(CH)$, 1.29 (dd, $^3J_{HH}$ = 10.0, 3.8 Hz, 2H, $(CH)(C\mathbf{H_aH_b})(C\mathbf{H_aH_b})(CH)$), 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 8H, $(C\mathbf{H_3})_2CH$)), 1.02 (d, ^3J = 6.8 Hz, 6H, $(C\mathbf{H_3})_2CH$)).*

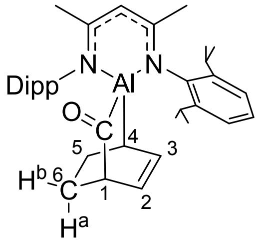
$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298K)

δ 171.6 (**C**N), 169.5 (**C**N), 144.1 (Ar**C**), 143.5 (Ar**C**), 142.3 (Ar**C**), 140.5 (Ar**C**), 131.3 (H**C**=**C**H), 127.6 (Ar**C**), 126.7 (Ar**C**), 124.3 (Ar**C**), 124.0 (Ar**C**), 96.0 ($(CH_3)C(\mathbf{C}H)C(CH_3)$), 29.9 (br, Al**C**H), 28.5 ($(CH)(\mathbf{C}H_aH_b)(\mathbf{C}H_aH_b)(CH)$), 28.4 $(CH_3)_2\mathbf{C}H$), 28.1 $(CH_3)_2\mathbf{C}H$), 24.9 ($(\mathbf{C}H_3)_2CH$), 24.8 ($(\mathbf{C}H_3)_2CH$), 24.4 ($(\mathbf{C}H_3)C(CH)C(CH_3)$), 23.4 ($(\mathbf{C}H_3)_2CH$), 23.2 ($(\mathbf{C}H_3)_2CH$), 23.1 ($(CH_3)C(CH)C(\mathbf{C}H_3)$).

Elemental analysis for $C_{35}H_{49}AlN_2$ calculated: C 80.11, H 9.41, N 5.34. Found: C 80.04, H 9.50, N 5.39.

* Unequivocal assignment of the diastereotopic methylene protons is not possible due to the overlap between the multiplet at 1.40 ppm with the di-isopropyl methyl groups.

<u>*Synthesis of **3**:*</u>



In a glovebox, **1** (40.5 mg, 0.091 mmol) was dissolved in ~0.5 mL of C_6D_6 and transferred to a J-Young NMR tube. 1,3-cyclohexadiene (12.5 µL, 0.137 mmol) was added to the NMR tube *via* micropipette and the tube was shaken to allow the reagents to mix. An immediate colour change was observed from the characteristic orange-red colour of **1** to the light yellow colour of **2**. The reaction was checked by ^{1}H NMR spectroscopy to ensure the complete conversion to **2**. The NMR tube was returned to the glovebox and all volatiles were removed *in vacuo*. The resultant yellow powder was redissolved in 0.600 mL of C_6D_6 and freeze-pump thaw degassed thrice before an atmosphere of CO (~1.1 bar) was introduced. The reaction was heated at 100°C for 1 h and then at 40°C for 7 days.† ^{1}H NMR spectroscopy was used to monitor the reaction progress. Upon completion, the NMR tube was returned to the glovebox, the solution decanted into a 20 mL scintillation vial and all volatiles were removed *in vacuo*. The resultant powder was washed once with toluene (1 x 3 mL) and thrice with pentane (3 x 3 mL) affording **3** as a bright yellow powder (19 mg, 0.035 mmol, 38% yield).

^{1}H NMR (400 MHz, C_6D_6, 298 K)

δ 7.03-7.16 (m, 6H, Ar**H**), 5.63 – 5.56 (m, 1H, C^{3}**H**), 5.54 (m, 1H, C^{2}-**H**), 4.78 (s, 1H, (CH$_3$)C(C**H**)C(CH$_3$)), 3.42 (hept, $^{2}J_{HH}$ = 6.6 Hz, 1H), (CH$_3$)$_2$C**H**), 3.38 – 3.30 (hept, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 1H, (CH$_3$)$_2$C**H**), 3.28 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, (CH$_3$)$_2$C**H**), 3.27 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, (CH$_3$)$_2$C**H**), 2.80-2.75 (m, C^{1}**H**, 1H), 1.73 – 1.62 (m, 1H, C^{6}-**H^{a}**H^{b}), 1.62 – 1.55 (m, 1H, C^{4}-**H**), 1.52 (s, 3H, (C**H$_3$**)C(CH)C(CH$_3$)), 1.51 (s, 3H, (C**H$_3$**)C(CH)C(CH$_3$)), 1.48 (m, 1H, C^{6}-H^{a}**H^{b}**), 1.41 (m, 1H, C^{5}-**H^{a}**H^{b}), 1.36 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, (C**H$_3$**)CH(CH$_3$)), 1.33 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, (C**H$_3$**)CH(CH$_3$)), 1.26 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, (C**H$_3$**)CH(CH$_3$)), 1.04 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, (C**H$_3$**)CH(CH$_3$)), 1.04 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, (C**H$_3$**)CH(CH$_3$)), 1.03 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, (C**H$_3$**)CH(CH$_3$)), 1.02 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, (C**H$_3$**)CH(CH$_3$)), 0.93 (s, 1H, C^{5}-H^{a}**H^{b}**).

† The reaction rate is concentration dependent and repeating this procedure with 9 mg of **1** results in the reaction completion after approximately 48 h. We treat the reaction as complete upon >95% consumption of starting materials.

^{13}C NMR (101 MHz, C_6D_6)

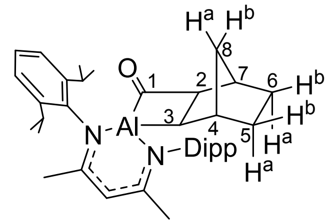
δ 254.1 (**C**O), 171.4 (**C**N), 171.1 (**C**N), 145.9 (Ar**C**), 145.7 (Ar**C**), 143.7 (Ar**C**), 143.1 (Ar**C**), 140.3 (Ar**C**), 139.6 (Ar**C**), 139.4 (**C**^{3}-H), 125.4 (Ar**C**), 125.2 (Ar**C**), 123.9 (Ar**C**), 123.7 (Ar**C**), 121.8 (**C**^{2}-H), 97.1 ((CH_3)C(**C**H)C(CH_3)), 61.5 (**C**^{1}-H), 29.1 (CH_3)$_2$**C**H), 28.9 (CH_3)$_2$**C**H), 28.1 (br, **C**^{4}-H), 27.7 (CH_3)$_2$**C**H), 25.9 (**C**^{6}-H_aH_b), 25.7 (**C**H_3)$_2$CH), 25.6 (**C**H_3)$_2$CH), 25.5 (**C**H_3)$_2$CH), 25.1 (overlapping, **C**H_3)$_2$CH), 25.1 (overlapping, **C**H_3)$_2$CH), 24.9 (**C**H_3)$_2$CH), 23.8 (**C**H_3)$_2$CH), 23.6 (**C**H_3)$_2$CH), 23.3 (overlapping, (**C**H_3)C(CH)C(CH_3)), 23.3 (overlapping, (**C**H_3)C(CH)C(CH_3), 22.5 (**C**^{5}-H_aH_b).

IR (ATR), cm^{-1}: 1620 (CO).

Elemental analysis for $C_{36}H_{49}AlN_2O$ calculated: C 78.22, H 8.94, N 5.07. Found: C 72.57, H 9.32, N, 4.83.‡

‡ Thermal sensitivity of **3** prevented attainment of accurate elemental analysis.

<u>*Synthesis of **5**:*</u>



In a glovebox, **1** (9 mg, 0.020 mmol) and norbornene (5 mg, 0.050 mmol) were dissolved in C_6D_6 (0.600 mL) and transferred to a J-young NMR tube. The formation of **4** was monitored by NMR spectroscopy, and upon reaction completion, all volatiles were removed *in vacuo*. The residue was redissolved in C_6D_6 (0.600 mL) and freeze-pump-thaw degassed thrice before an atmosphere of CO was introduced to the sample. An instantaneous colour change from the characteristic dark-red of **4** to yellow was observed. An NMR taken after reaction completion shows the formation of **5** (95% yield, vs. internal ferrocene standard). Allowing **5** to stand under these conditions results in decomposition over the course of 12 h. X-ray quality were grown by rapidly transferring a solution of **5** in C_6D_6 to a vial, diluting with toluene and concentrating *in vacuo* and setting vapour diffusion of pentane into a concentrated toluene solution of **5** at -35°C. While **5** is amenable to X-ray diffraction analysis as single crystals, it decomposes as a solid under inert atmosphere, and vacuum, at ambient temperature thus precluding attainment of elemental analysis and meaningful isolated yields.

^{1}H NMR (400 MHz, C_6D_6, 298 K)

δ 7.08-7.28 (m, Ar**H**), 5.00 (s, 1H, $(CH_3)C(C\mathbf{H})C(CH_3)$), 3.46 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, $(CH_3)_2C\mathbf{H}$), 3.46 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, $(CH_3)_2C\mathbf{H}$), 3.33 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, 3.46 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, $(CH_3)_2C\mathbf{H}$), 3.09 (hept, $^3J_{HH}$ = 6.6 Hz, 1H, 2.85 – 2.83 (m, 1H, C^7-**H**), 2.47 (m, 1H, C^6-**H**), 1.63 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $(C\mathbf{H_3})_2CH$), 1.61 (s, H, $(C\mathbf{H_3})C(CH)C(CH_3)$), 1.60 (m, overlapping, 1H, C^2-**H**), 1.59 (s, 3H, $(C\mathbf{H_3})C(CH)C(CH_3)$), 1.55 (m, 1H, C^6-**H^a**) 1.47 (d, $^3J_{HH}$ = 6.7 Hz, 3H, $(C\mathbf{H_3})_2CH$)), 1.33 (d, $^3J_{HH}$ = 6.7 Hz, 3H, $(C\mathbf{H_3})_2CH$), 1.25 (m, overlapping, 1H, C^5-**H^b**), 1.22 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $(C\mathbf{H_3})_2CH$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $(C\mathbf{H_3})_2CH$), 1.15 (m, overlapping, 1H, C^3-**H**), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $(C\mathbf{H_3})_2CH$), 1.02 (d, $^3J_{HH}$ = 6.7 Hz, 3H, $(C\mathbf{H_3})_2CH$), 0.97 (m, 1H, C^5-**H^a**), 0.92 (m, 1H, C6-**H^b**), 0.66 (m, 1H, C^8-**H^a**), 0.30 (m, 1H, C^8-**H^b**).

^{13}C NMR (101 MHz, C_6D_6, 298 K)

δ 292.3 (**C**O), 170.6 (**C**N), 170.0 (**C**N), 145.1 (Ar**C**), 144.6 (Ar**C**), 143.1 (Ar**C**), 142.7 (Ar**C**), 139.9 (Ar**C**), 139.3 (Ar**C**), 125.1 (Ar**C**), 124.8 (Ar**C**), 124.0 (Ar**C**), 123.9(Ar**C**), 97.8 ($(CH_3)C(\mathbf{C}H)C(CH_3)$), 69.1 (**C**2-H), 43.9 (**C**3-H), 40.1 (**C**6-H), 38.7 (**C**7-H_2), 34.5 (br, **C**8-

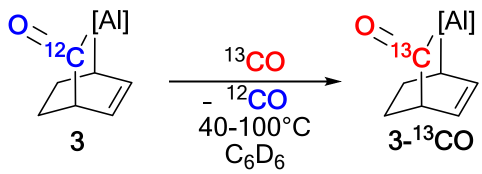
H), 34.4 (**C**4-H_2), 29.4 $(CH_3)_2$**C**H), 29.4 $(CH_3)_2$**C**H), 29.0 (**C**5-H), 27.7 $(CH_3)_2$**C**H), 27.4 $(CH_3)_2$**C**H), 25.0 (**C**$H_3)_2$CH), 24.8 (**C**$H_3)_2$CH), 24.8 (**C**$H_3)_2$CH), 24.7 (**C**$H_3)_2$CH), 24.6 (**C**$H_3)_2$CH), 24.1 (**C**$H_3)_2$CH), 23.9 (**C**$H_3)_2$CH), 23.9 (**C**$H_3)_2$CH), 23.1 (**C**H_3)C(CH)C(CH_3), 22.9 (CH_3)C(CH)C(**C**H_3).

Elemental analysis for $C_{37}H_{51}AlN_2O$ calculated: C 78.40, H 9.07, N 4.94. Found: C 76.11, H 9.59, N 4.79.§

IR (ATR), cm^{-1}: 1652 (CO).

<u>*^{13}CO Exchange Experiments*</u>

*Exchange of ^{13}CO into **3***



In a glovebox, **3** (5 mg, 0.009 mmol) was dissolved in 0.600 mL C_6D_6 and transferred to a J-Young NMR tube. An initial time point (t1) ^{1}H (16 scans) and ^{13}C NMR spectrum was taken (Figure S1,S2). The tube was degassed *via* the freeze-pump-thaw procedure thrice before the introduction of ^{13}CO gas (~1 bar). The solution was heated at 100 °C for 3 hours before a second timepoint ^{1}H NMR spectrum was taken (t2) (Figure S3). The $^{2}J_{CH}$ coupling of the α-carbonyl methine resonance to ^{13}CO was observed, signalling the completion of the degenerate isotope exchange. The sample was heated at 40°C until **3-^{13}CO** was the predominant species at which point a third point taken (Figure S4, S5).

§ Thermal sensitivity of **5** prevented attainment of accurate elemental analysis.

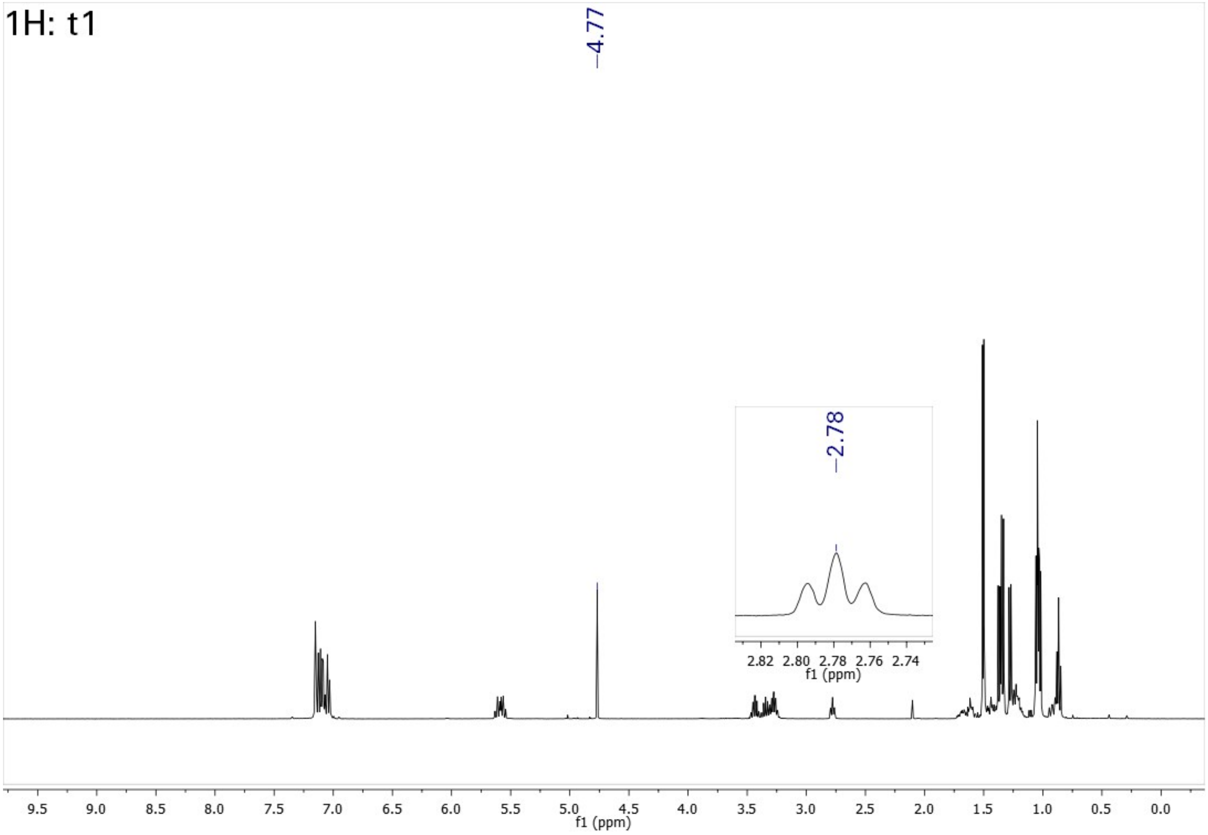


Figure S1: ^{1}H spectrum at initial timepoint of exchange experiment.

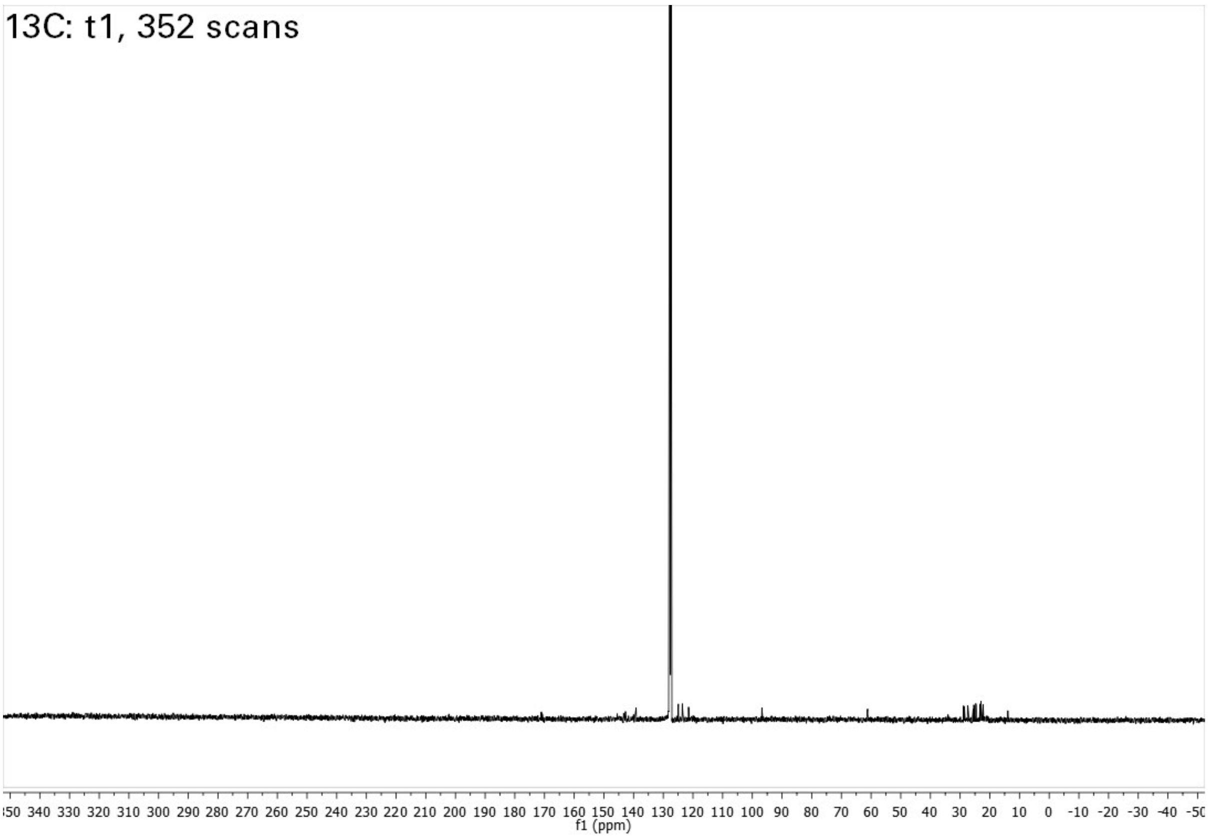


Figure S2: ^{13}C spectrum at initial timepoint of exchange experiment.

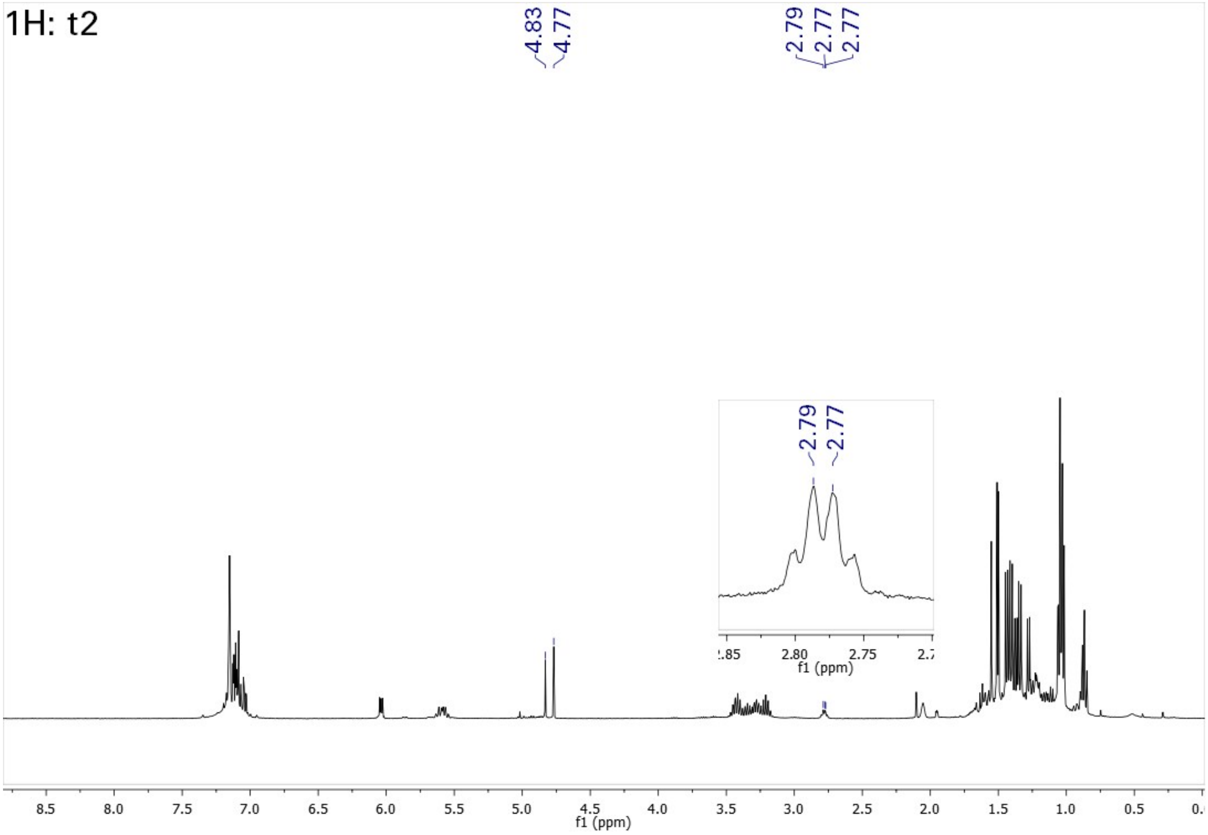


Figure S3: ^{1}H spectrum at 2nd timepoint in exchange experiment showing completion of exchange.

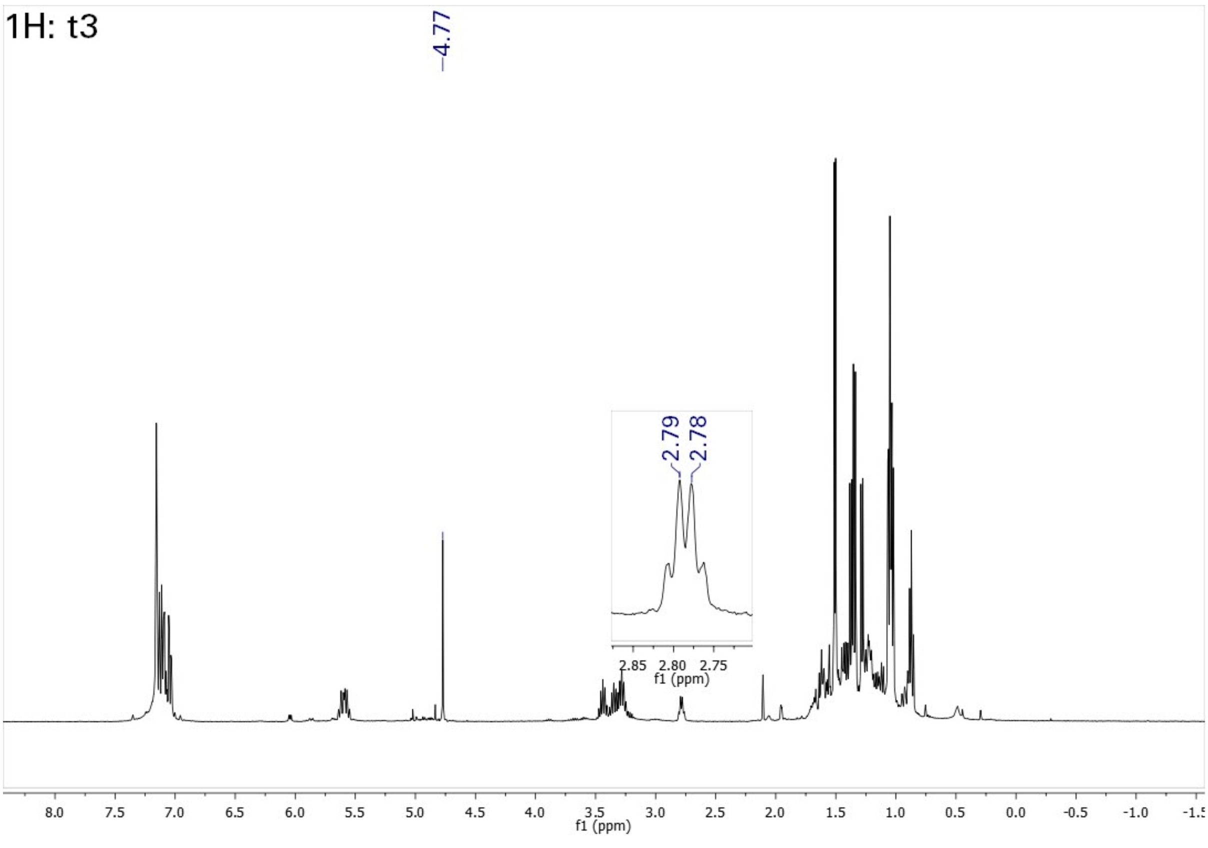


Figure S4: ^{1}H spectrum of ^{13}CO enriched **3**.

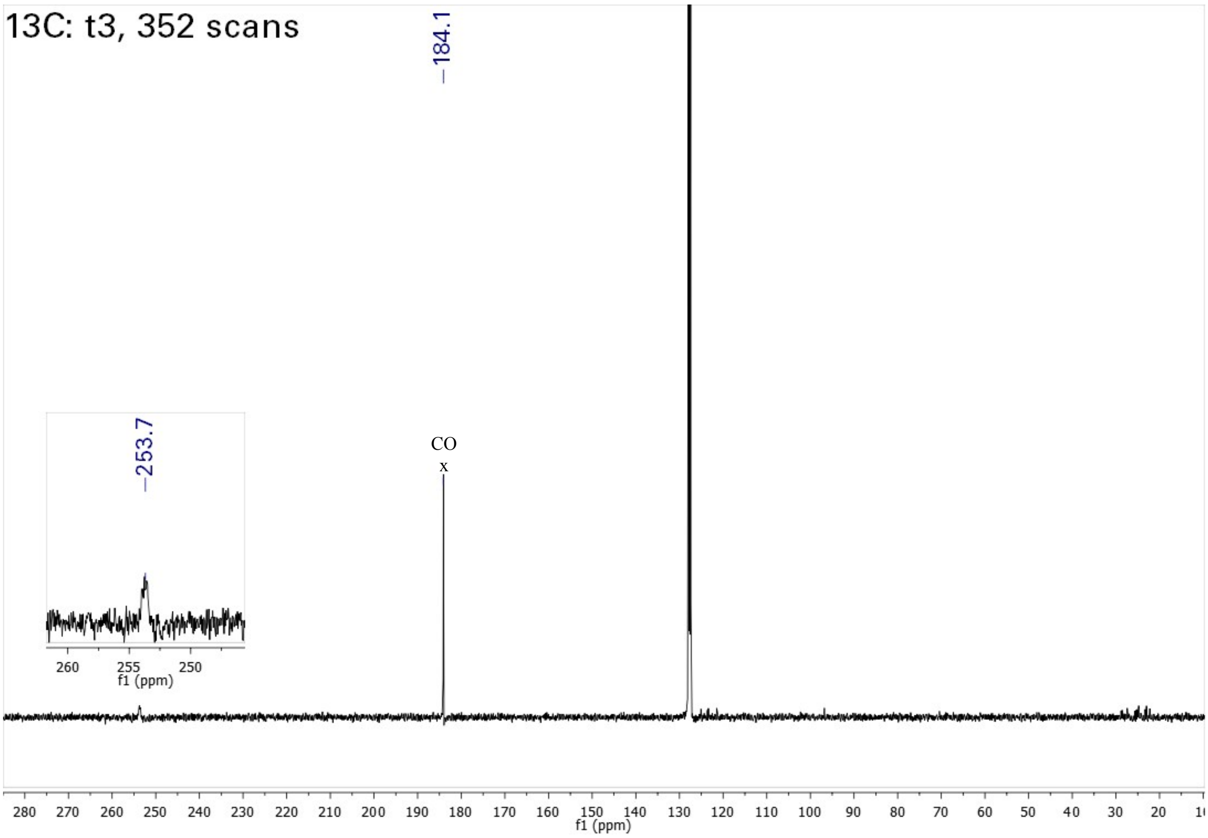


Figure S5: ^{13}C spectrum of ^{13}CO enriched **3**.

*Kinetic experiments on the elimination of CO from **3** to form **2***

In a glovebox, complex **3** (3 mg, 0.005 mmol) in d8-toluene (2.5 mL) and a small amount of ferrocene (1 mg) was added to be used as an internal standard. The solution of **3** (2 mM, 2.5 mL) was portioned into 4x0.550 mL aliquots and transferred into four separate J-Young NMR tubes and kept at –35°C in the glovebox.** The NMR tubes were removed from the glovebox and inserted into a pre-heated NMR spectrometer probe. ^1H NMR spectra were recorded at 2 minute intervals.

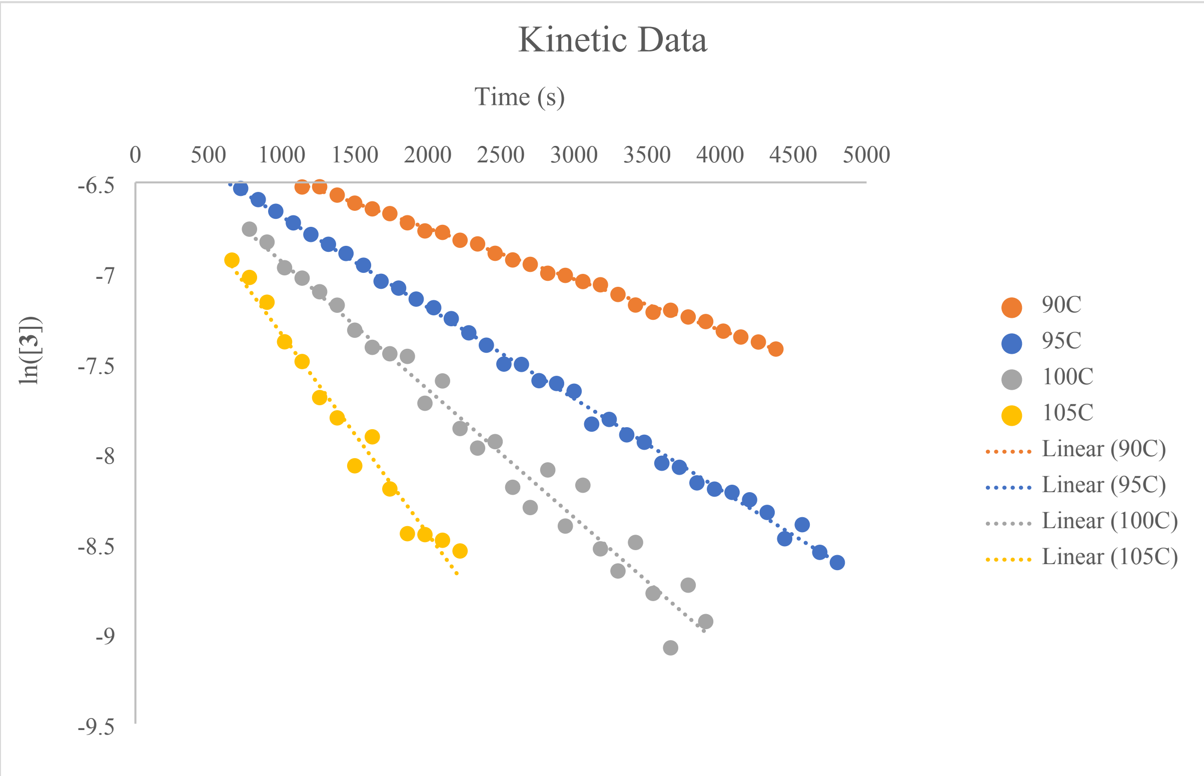


Figure S6: Kinetic data for the transformation from **3** to **2** at varying temperatures.

Plotting ln[**3**] (concentration determined by the integration of the internal ferrocene standard) against time showed a linear relationship indicating that the reaction is first order in [**3**]. Four rate constants were determined in the temperature range of 90 °C to 105°C at 5°C intervals and a plot of $\ln(k_{obs})$ against 1/T allowed calculation of the thermodynamic parameters using the Eyring equation. Standard errors were calculated using regression analysis in the Microsoft Excel program. The activation parameters for the reverse reaction were found to be: $\Delta H^{\ddagger} = 23.5 \pm 1.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -10.3 \pm 4.5$ cal K^{-1} mol^{-1} and an associated $\Delta G^{\ddagger}_{298K} = 26.5 \pm 3.0$ kcal mol^{-1}.

** Assuming a standard 7-inch J-Young NMR tube with usable volume of approx. 2.4 mL, the maximum concentration of CO in the headspace (1.85 mL) should not exceed 15 ppm.

T (K)	K_{obs} (s^{-1})	1/T (K^{-1})	ln(k/T)
363	0.000282	0.002755	-14.0679
368	0.000505	0.002717	-13.4993
373	0.000709	0.002681	-13.1732
378	0.001107	0.002646	-12.7406

Table S1: Rate constants extracted from kinetic experiments.

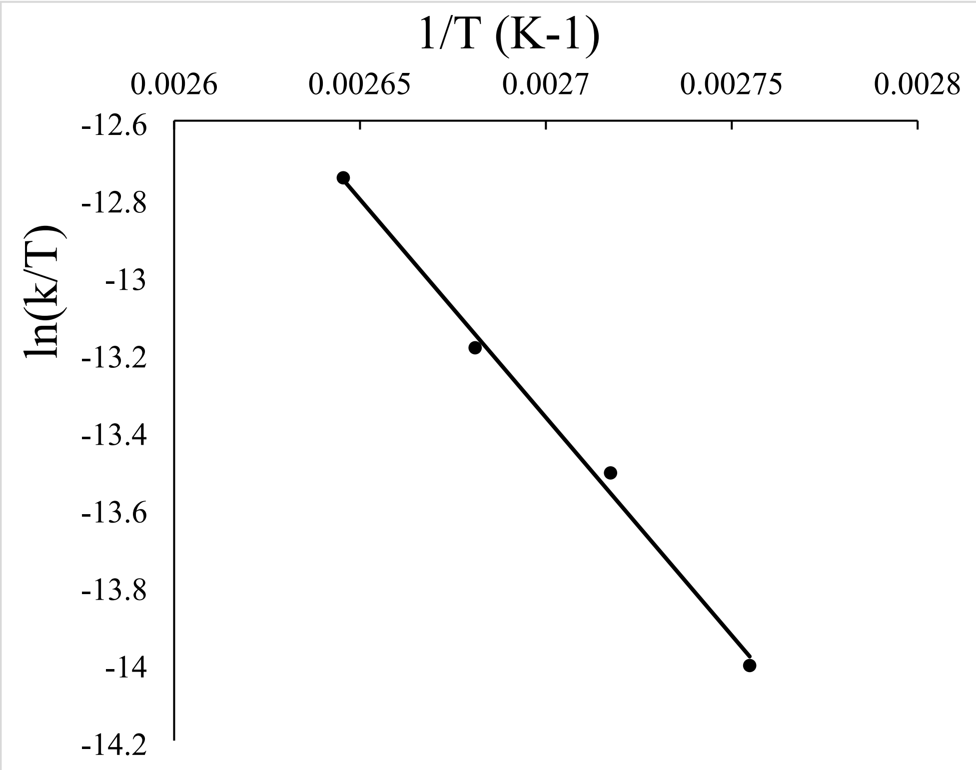


Figure S7: Eyring plot of data from Table S1.

X-ray Structures

The X-ray crystal structure of **2**

Crystal Data for $C_{35}H_{51}AlN_2$, M =526.75, monoclinic, space group P2/n (no. 13), a = 12.7484(13) Å, b = 9.4906(9) Å, c = 13.5651(15) Å, β = 105.015(11)°, V = 1585.2(3) Å^3, Z = 2, ρ_{calc}g/cm^3 = 1.104, μ(MoKα) = 0.089 mm^{-1}, T = 173.00(10), yellow plates, F^2 refinement, R_1(obs) = 0.0567, wR_2(all) = 0.1604, 3191 independent observed reflections (R_{int} = 0.0259), 2414 independent measured reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 56.576], 189 parameters.

The structure of **2** was found to have C_{2v} symmetry which passes through the Al1-C6 axis. The entirety of the cyclohexene fragment was found to be disordered over C_{2v} symmetry and was modelled using one complete 50% occupancy orientation (with the mirror symmetry generating a second 50% orientation). Distance restraints between the C2–C3 and C5–C6 bonds were used to model the double and single bonds respectively. The geometries of both orientations were optimised and the thermal parameters of the entirety of the disordered fragment were restrained to be similar.

The carbon atoms (C14, C15) in the C13 isopropyl group were found to be disordered and two orientations were identified to *ca.* 75% and 25% occupancy. The geometries of both orientations were optimised and the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The X-ray crystal structure of ***5.toluene***

Crystal Data for $C_{44}H_{59}AlN_2O$, M =658.91, orthorhombic, space group Pnma (no. 62), a = 24.3410(10) Å, b = 14.7167(6) Å, c = 10.9529(5) Å, V = 3923.5(3) Å^3, Z = 4, ρ_{calc}g/cm^3 = 1.115, μ(MoKα) = 0.086 mm^{-1}, T = 173.00(10), yellow plates, F^2 refinement, R_1(obs) = 0.0644, wR_2(all) = 0.1703, 4102 independent observed reflections (R_{int} = 0.0393), 2954 independent measured reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 56.402], 274 parameters.

The structure of **5** was found to have C_s symmetry which passes through the Al1, C6 axis. The whole of the acyl-norbornane fragment was found to be disordered over the mirror plane and was modelled using one complete 50% occupancy orientation (with the mirror symmetry generating a second 50% occupancy orientation).

NMR Data (C_6D_6, 298 K)

Compound 2

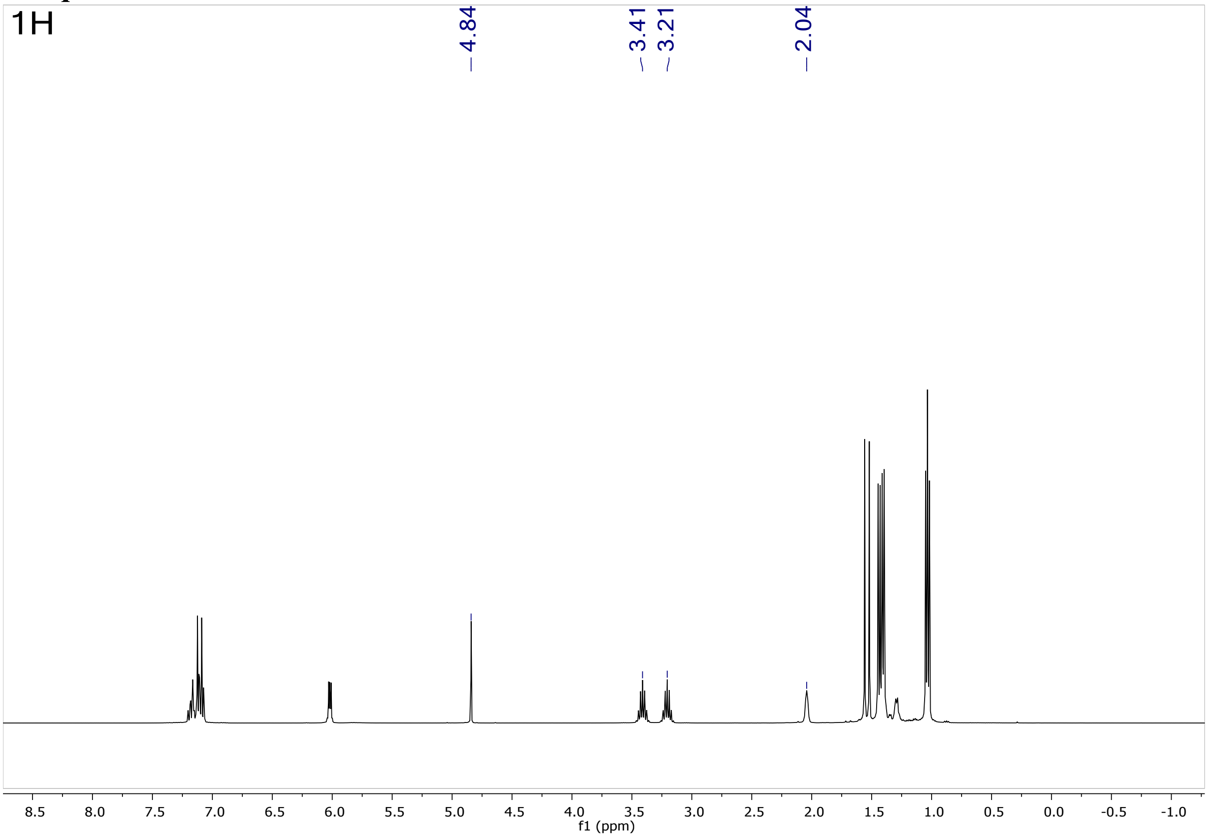


Figure S8: ^{1}H spectrum of **2**.

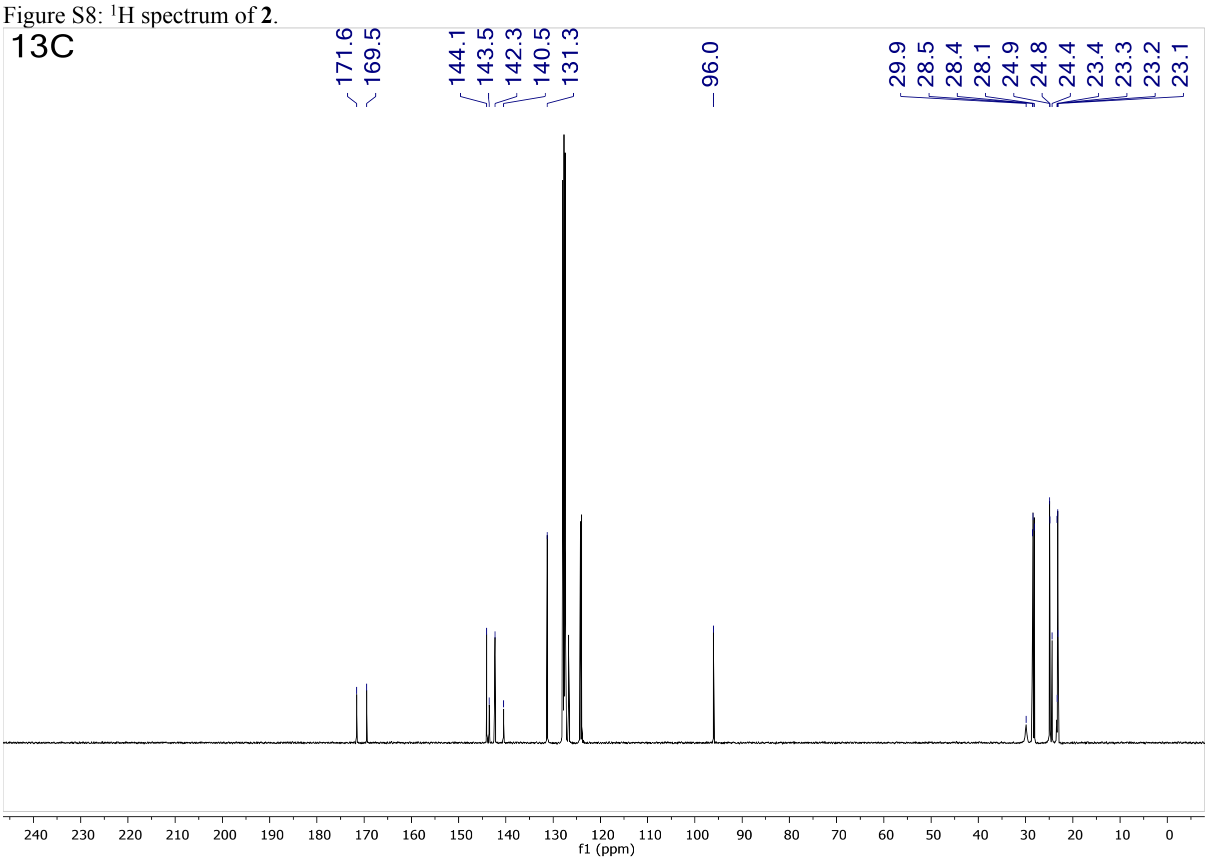


Figure 9: ^{13}C spectrum of **2**.

Compound 3

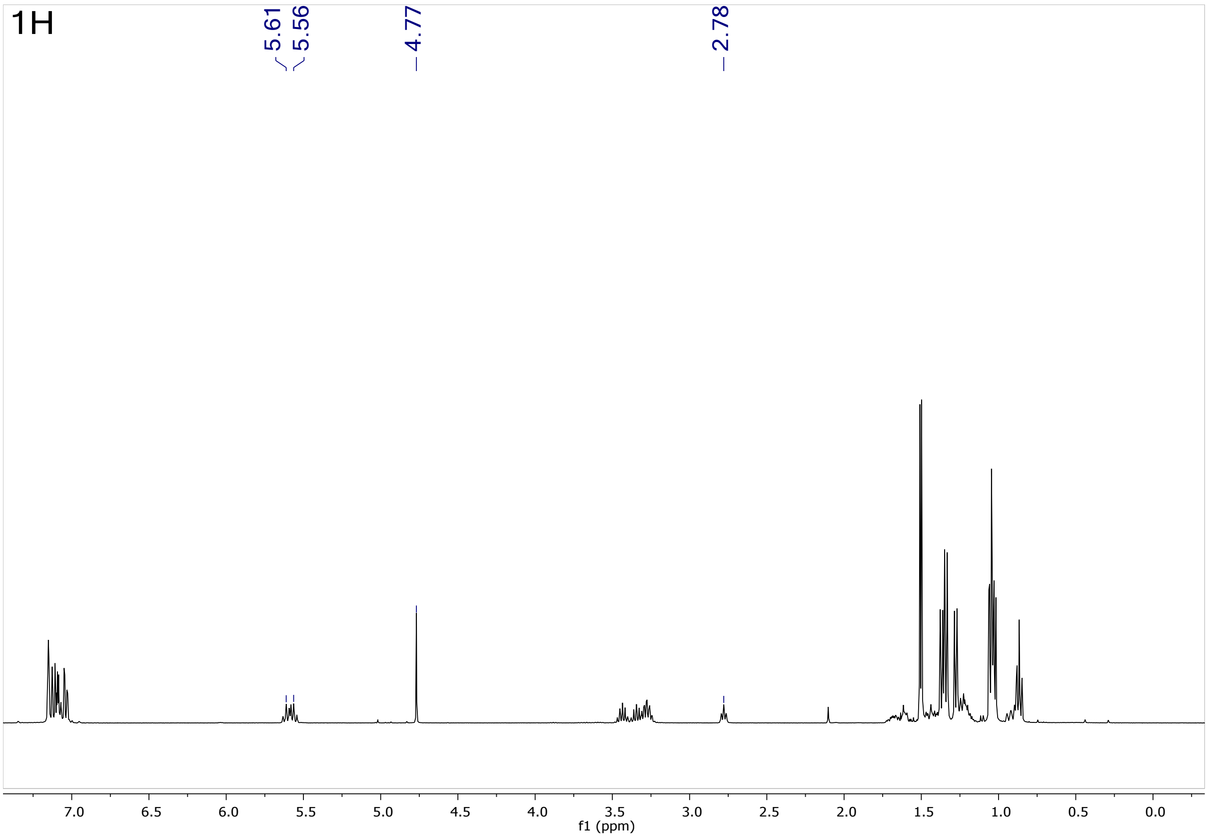


Figure S10: [1]H spectrum of **3**.

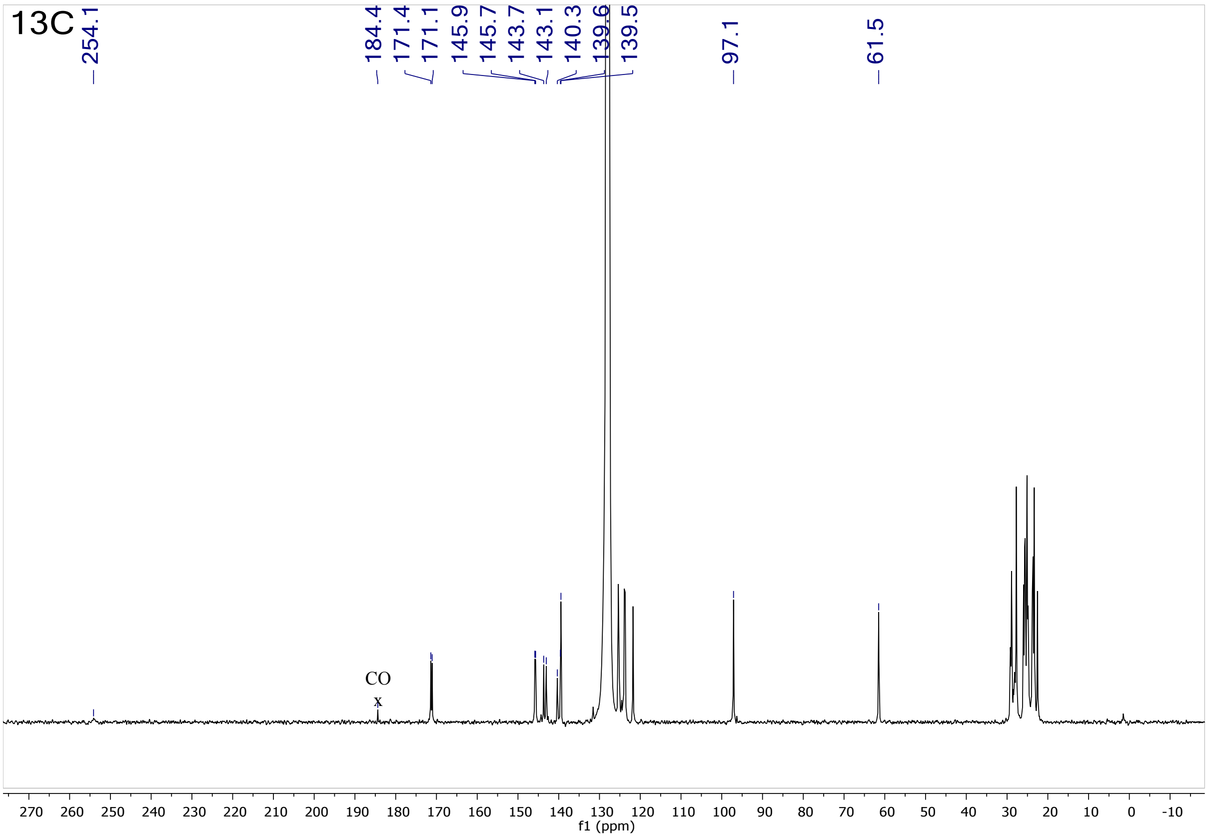


Figure S11: [13]C spectrum of **3**.

Compound 5

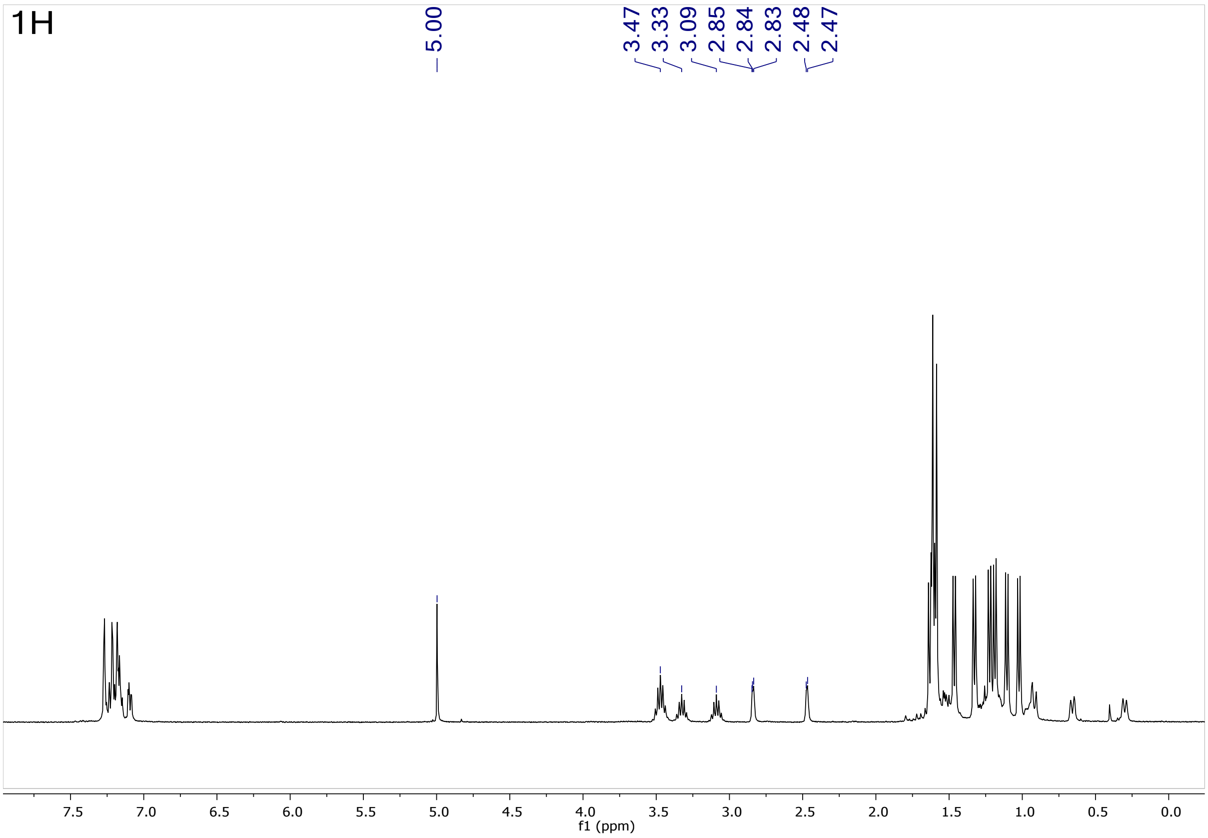


Figure S12: [1]H spectrum of **5**.

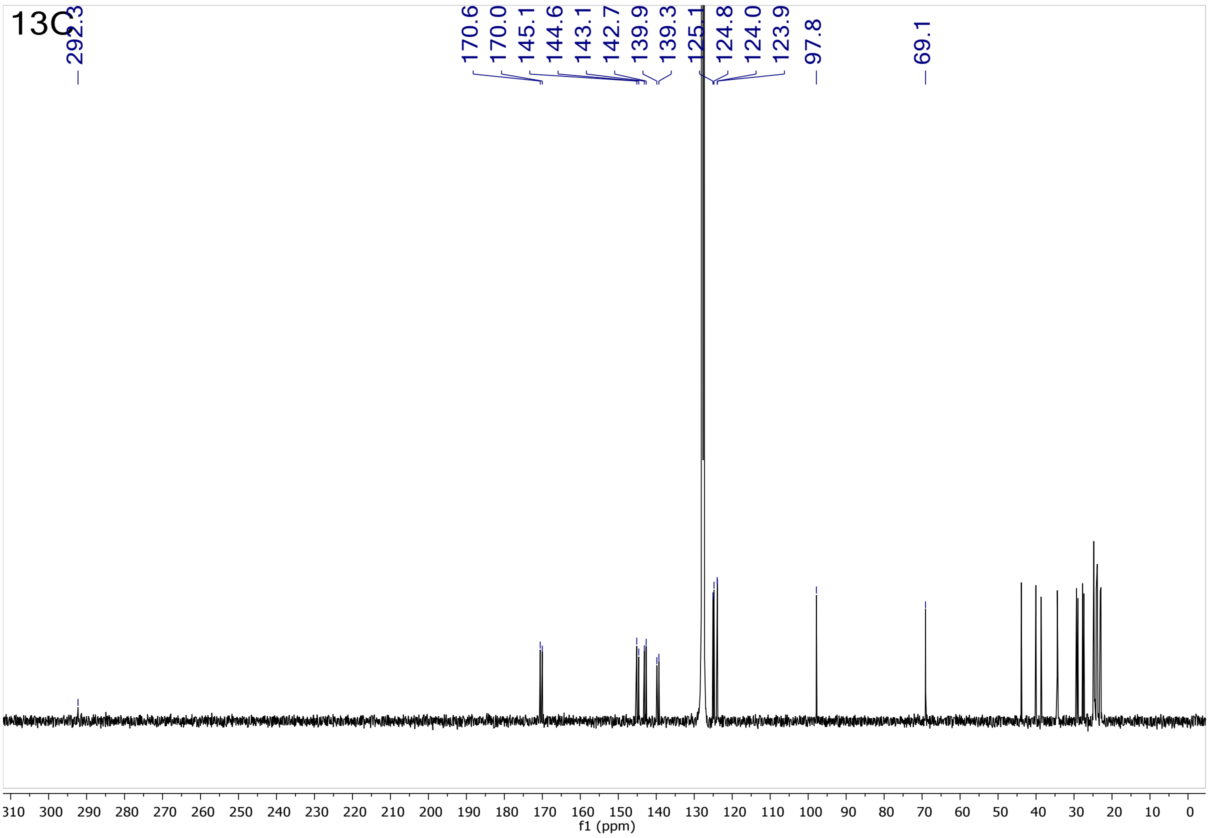


Figure S13: [13]C spectrum of **5.**

IR Data

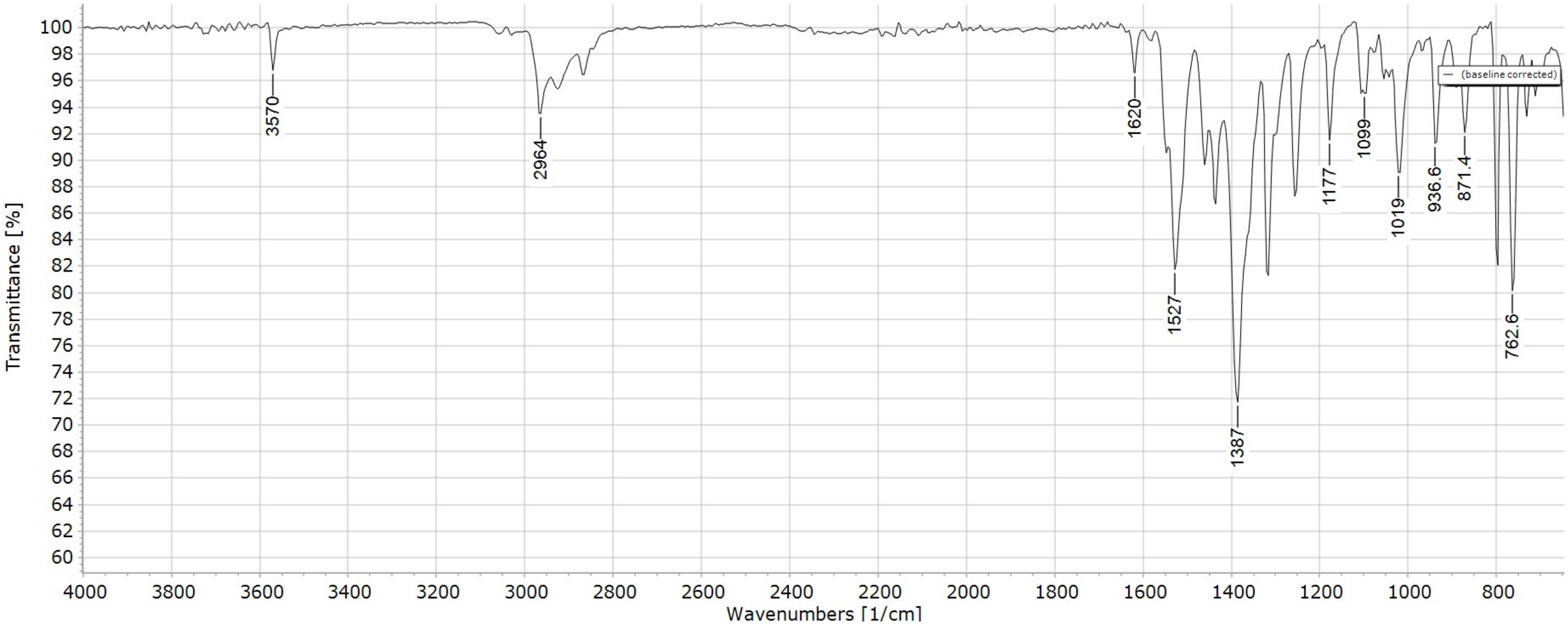


Figure S14: Solid state IR (ATR) of Compound **3**.

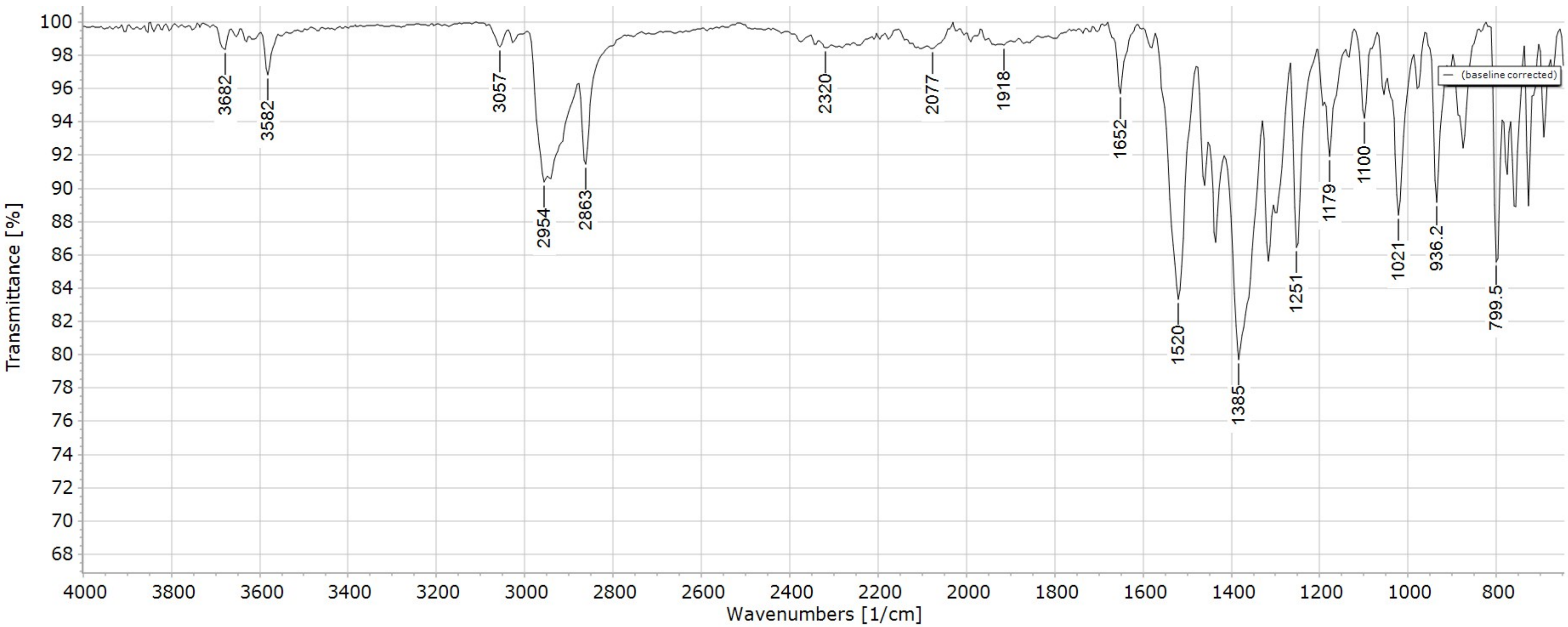


Figure S15: Solid state IR (ATR) of Compound **5**

Computational details

DFT calculations were run using Gaussian 09 (Revision D.01)[3] using the M06l Minnesota functional.[4] Other functionals investigated were Al centres were described with Stuttgart SDDAll RECPs and associated basis sets and the 6-31G** basis sets were used for all other atoms.[5] Other functionals investigated were the m062x, B3PW91, and the ωB97X functional.

Geometry optimisation calculations were performed without symmetry constraints. Frequency analyses for all stationary points were performed using the enhanced criteria to confirm the nature of the structures as either minima (no imaginary frequency) or transition states (only one imaginary frequency). Single point solvent corrections (benzene, $\varepsilon = 2.2706$) were applied using the polarizable continuum model (PCM) to free energies reported in the main text. Single point dispersion corrections were applied to the free energies; to the ωB97X energies using the ωB97X-D functional, to the B3PW91 energies using Grimme's D3 correction with Becke-Johnson damping, and to the Minnesota functional (m06l, m062x) energies, using Grimme's D3 correction.[6]

Intrinsic reaction coordinate (IRC) calculations were used to connect transition states and minima located on the potential energy surface allowing a full energy profile (calculated at 298.15 K, 1 atm) of the reaction to be constructed.[7] Natural Bond Orbital analysis was carried out using NBO 6.0.[8]

NBO Data

Structures have been abbreviated for clarity; charges are bolded and Wiberg bond indices are italicised.

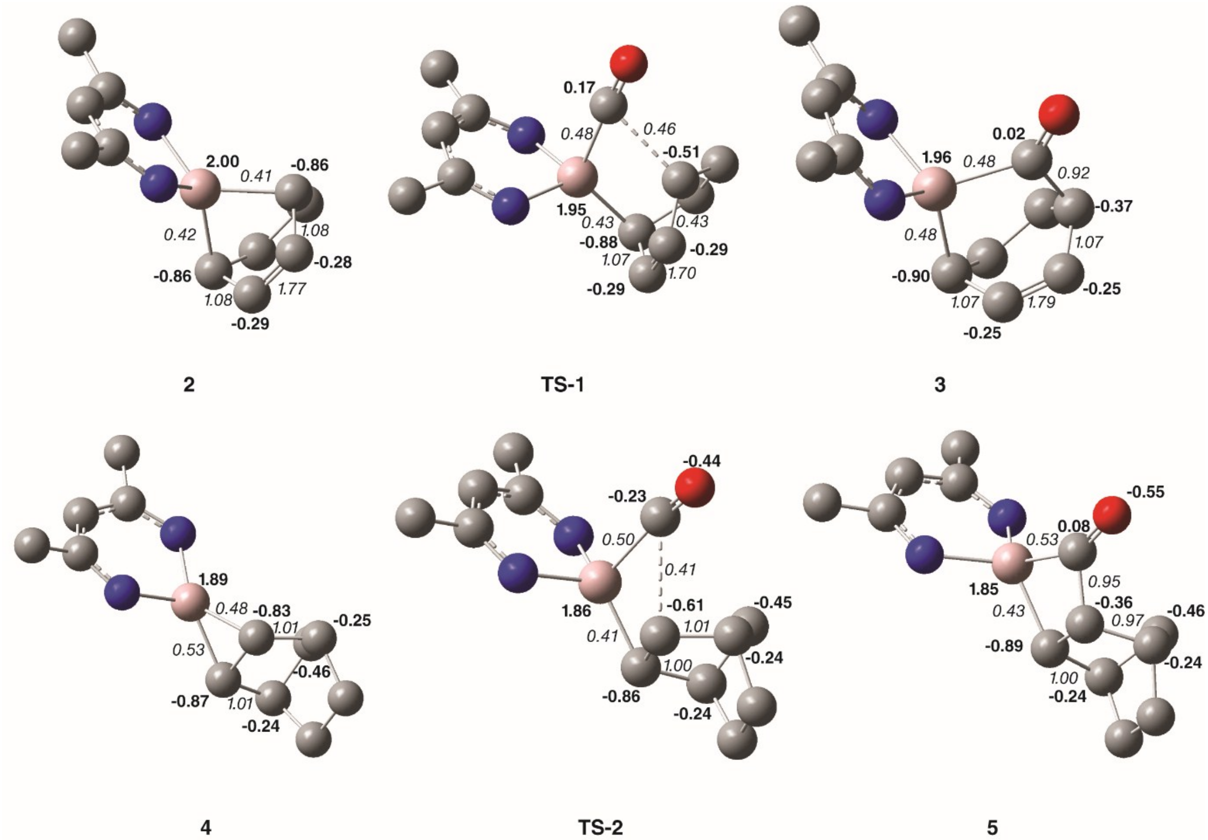
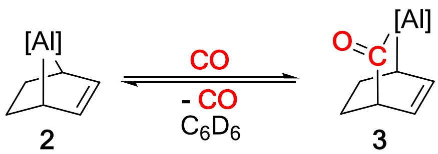


Figure S16: NBO data on compounds **2-5, TS-1** and **TS-2**. Wiberg bond indices are provided in *italics* and NPA charges provided in **bold**.

Functional Testing



A series of functionals (Table S2) were tested. The M06l functional gave the activation parameter for the deinsertion of CO from **3** to form 2 closest to the measured value ($\Delta G^{\ddagger}_{298K}$ = 26.5 ±3.0 kcal mol^{-1}).

M06l	**M062x**	**ωB97X**	**B3PW91**
28.7	36.5	39.7	30.8

Table S2: Calculated free-energy barriers using the respective functional. All energies provided in kCal mol^{-1}.

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Comptuational Coordinates

*Optimised Structure of **2***

H_{298K} = -1473.879286

G_{298K} = -1473.988554

Lowest frequency: 27.75 cm^{-1}

Al	7.111567	2.141978	9.978898
N	7.871209	3.463051	8.770135
C	8.222175	0.632464	10.757134
H	9.102559	0.736023	11.397614
C	8.522497	2.958451	7.591140
C	7.079862	5.406096	9.972213
H	7.093687	6.489867	9.981834
C	7.709803	2.544636	6.514727
C	7.793557	4.791771	8.936369
C	9.921480	2.829650	7.550143
C	10.825754	3.296513	8.676242
H	10.217276	3.862905	9.392070
C	10.492969	2.240948	6.418272
H	11.573310	2.116288	6.377237
C	6.201241	2.713988	6.559239
H	5.888642	2.620756	7.606939
C	11.443656	2.123499	9.435767
H	10.680475	1.511589	9.921087
H	12.133362	2.482859	10.206712
H	12.011439	1.475295	8.758165
C	8.512067	0.088333	9.395455
H	9.511136	-0.190602	9.064583
C	9.711818	1.817579	5.352826
H	10.176569	1.362871	4.482394
C	8.331869	1.982677	5.399715
H	7.724355	1.653939	4.560625
C	7.127516	-0.251115	11.411261
H	7.515708	-1.267416	11.566308
H	6.863133	0.131549	12.405044
C	8.504260	5.701345	7.975518
H	9.579064	5.711308	8.188065
H	8.137449	6.724876	8.062230
H	8.398358	5.368385	6.940091
C	11.929536	4.220511	8.159271
H	12.639615	3.675661	7.527769
H	12.499129	4.646391	8.991248
H	11.534233	5.046570	7.559093
C	5.452457	1.639113	5.780219
H	5.576222	1.752266	4.697248
H	4.379576	1.702722	5.988505
H	5.788632	0.634318	6.054439
C	5.777203	4.106650	6.089651
H	6.179361	4.897064	6.730631
H	4.685829	4.201319	6.100046
H	6.119113	4.298136	5.065750
N	6.206892	3.465406	11.095562
C	5.286623	2.925265	12.057333
C	5.793933	2.427546	13.277748
C	6.284536	4.792159	10.948126
C	3.915434	2.846994	11.744352
C	3.336926	3.361553	10.438539
H	4.118457	3.917911	9.904695
C	3.061348	2.241750	12.670441
H	2.001725	2.160344	12.436538
C	7.268133	2.555450	13.620969

H	7.832700	2.348132	12.701452
C	2.906086	2.204192	9.538278
H	3.739984	1.530123	9.329202
H	2.517832	2.576685	8.583638
H	2.112380	1.616151	10.013285
C	3.541880	1.738667	13.870447
H	2.862681	1.267687	14.575573
C	4.895911	1.838094	14.169641
H	5.264239	1.442670	15.111792
C	5.457345	5.696364	11.815514
H	4.450884	5.797818	11.393481
H	5.893956	6.695530	11.862898
H	5.335991	5.306284	12.828349
C	2.160496	4.309330	10.672413
H	1.305883	3.780777	11.108505
H	1.821992	4.745715	9.727556
H	2.413405	5.128576	11.353186
C	7.737245	1.562471	14.678032
H	7.334143	1.802024	15.668914
H	8.827538	1.593488	14.760967
H	7.449908	0.534471	14.438137
C	7.624279	3.976812	14.063136
H	7.480379	4.709454	13.265357
H	8.674247	4.030344	14.368700
H	7.013507	4.284100	14.920289
C	6.162843	0.518891	9.211629
H	5.314837	0.521125	8.523639
C	5.878709	-0.294950	10.498247
H	4.999036	0.113264	11.018712
H	5.632152	-1.335987	10.246809
C	7.424949	0.026841	8.584847
H	7.481560	-0.292706	7.544914

*Optimised Structure of **TS-1***

H_{298K} = -1587.152791

G_{298K} = -1587.266906

Lowest frequency: -285.98 cm^{-1}

Al	7.431639	2.487525	10.069943
N	9.115019	3.024143	9.294691
C	6.845257	0.588220	10.226288
H	7.333882	-0.000408	11.010916
C	9.650069	2.392984	8.113866
C	9.470452	4.713869	11.011259
H	10.083664	5.571921	11.261181
C	9.481150	2.988753	6.849825
C	9.796012	4.065962	9.811909
C	10.315077	1.156175	8.257196
C	10.483141	0.513591	9.622330
H	9.534367	0.655247	10.158174
C	10.808899	0.533820	7.110221
H	11.317778	-0.421476	7.198489
C	8.734873	4.292800	6.632649
H	8.514976	4.736365	7.612813
C	10.734538	-0.988132	9.561256
H	10.000386	-1.504067	8.934911
H	10.679795	-1.419127	10.565520
H	11.730612	-1.219319	9.167039
C	7.241104	0.179988	8.845207
H	8.003250	-0.572036	8.656269
C	10.649701	1.107224	5.853776
H	11.036275	0.603512	4.972191

C	9.990311	2.320106	5.732016	C	8.992181	1.002748	13.122794
H	9.855154	2.764002	4.747796	H	9.132780	1.262477	12.065066
C	5.309676	0.564031	10.387796	C	3.921826	4.067371	12.007371
H	4.955027	-0.475307	10.375390	H	4.081134	3.279568	11.265551
H	5.027304	0.968924	11.371538	H	3.516515	4.940296	11.486302
C	11.028156	4.556508	9.108714	H	3.159894	3.706918	12.707840
H	11.569143	5.274867	9.724885	C	5.668529	1.365967	14.965811
H	10.778195	5.038212	8.159681	H	5.117353	0.857131	15.751635
H	11.695849	3.725434	8.862778	C	6.898046	0.870928	14.544160
C	11.577548	1.187110	10.452850	H	7.303624	-0.023001	15.010622
H	12.538732	1.163883	9.926313	C	8.581322	5.035632	13.308398
H	11.710534	0.660971	11.405597	H	8.404831	4.378038	14.163140
H	11.343101	2.229553	10.688919	H	7.768713	5.771750	13.302569
C	7.402663	4.040483	5.927285	H	9.516735	5.576979	13.458246
H	7.570942	3.636102	4.922433	C	4.946061	5.499067	13.788001
H	6.832464	4.969386	5.824600	H	4.183664	5.173406	14.504307
H	6.788459	3.324801	6.475171	H	4.576529	6.413748	13.314115
C	9.549536	5.301874	5.821104	H	5.842057	5.751819	14.363514
H	10.546067	5.482652	6.236137	C	9.160413	-0.505836	13.250585
H	9.027397	6.262025	5.768567	H	9.152391	-0.833970	14.295833
H	9.690469	4.955332	4.791589	H	10.125126	-0.811817	12.831542
N	7.776746	3.238732	11.832951	H	8.373507	-1.053059	12.721496
C	7.070469	2.659758	12.938776	C	10.086186	1.725926	13.911882
C	7.620500	1.502454	13.532052	H	10.084682	2.803378	13.721403
C	8.583585	4.284340	12.010667	H	11.077612	1.346594	13.642059
C	5.835053	3.180997	13.361390	H	9.951796	1.575925	14.989278
C	5.214530	4.416998	12.742033	C	5.683506	1.905556	8.265939
H	5.917990	4.820267	12.001448	H	5.231015	2.486535	7.460675
C	5.150829	2.512493	14.381846	C	4.647108	1.356532	9.241056
H	4.189913	2.901301	14.713465	H	4.025571	2.180306	9.621049

H	3.947952	0.701342	8.700739
C	6.675210	0.921029	7.853871
H	6.984756	0.826139	6.812287
C	6.169606	3.863801	9.305809
O	5.395263	4.631346	8.872493

*Optimised Structure of **3***

H_{298K} = -1587.19922

G_{298K} = -1587.311848

Lowest frequency: 36.46 cm^{-1}

Al	7.620386	2.440642	10.043556
N	9.273371	3.144384	9.350237
C	7.351215	0.464982	9.778243
H	8.182753	-0.206502	10.017986
C	9.788525	2.502445	8.174152
C	9.613788	4.689157	11.164979
H	10.214689	5.526734	11.500148
C	9.471302	2.982664	6.891188
C	9.930543	4.170971	9.902608
C	10.549056	1.326499	8.355624
C	10.909058	0.835676	9.746099
H	10.093523	1.131451	10.420016
C	10.992719	0.646475	7.220440
H	11.581701	-0.259398	7.337362
C	8.648401	4.234879	6.662835
H	8.410545	4.673506	7.640118
C	11.045509	-0.679759	9.834092
H	10.176437	-1.193457	9.410391
H	11.146142	-0.989254	10.879456
H	11.936326	-1.042777	9.309541
C	7.089773	0.502467	8.305793
H	7.824087	0.098102	7.608283
C	10.687490	1.105632	5.943559
H	11.036678	0.559542	5.071555
C	9.935281	2.260696	5.787219
H	9.693529	2.616722	4.787606
C	6.050370	-0.013552	10.457995
H	5.809824	-1.016622	10.077516
H	6.183553	-0.112804	11.542138
C	11.059590	4.815489	9.155008
H	11.696143	5.398788	9.821687
H	10.654198	5.495806	8.397265
H	11.671532	4.083453	8.622126
C	12.179754	1.513534	10.263167
H	13.020525	1.337660	9.582242
H	12.458060	1.118684	11.245997
H	12.054317	2.595024	10.369303
C	7.325893	3.907950	5.971958
H	7.501453	3.510965	4.964984
H	6.704785	4.803697	5.879122
H	6.757132	3.164778	6.534835
C	9.421330	5.269008	5.842870
H	10.398583	5.504361	6.276468
H	8.852639	6.200361	5.760518
H	9.600849	4.906907	4.824240
N	7.837363	3.192419	11.814915
C	6.970984	2.675199	12.838888
C	7.326529	1.449004	13.447127
C	8.682415	4.192533	12.089731
C	5.769182	3.333073	13.170663
C	5.316313	4.631251	12.528357

H	6.076396	4.946082	11.802231
C	4.944504	2.747673	14.137493
H	4.012276	3.243716	14.400121
C	8.610267	0.733727	13.065825
H	8.725119	0.845434	11.979617
C	3.997694	4.453493	11.773981
H	4.059461	3.682715	11.004347
H	3.715272	5.384332	11.273404
H	3.189630	4.184455	12.464096
C	5.285614	1.555212	14.755768
H	4.628749	1.119479	15.503451
C	6.468752	0.913003	14.408594
H	6.725138	-0.028070	14.886388
C	8.669643	4.831793	13.446178
H	7.883843	5.592758	13.493770
H	9.620021	5.325143	13.654826
H	8.458885	4.107768	14.237106
C	5.140500	5.738557	13.571194
H	4.301298	5.512159	14.238615
H	4.919605	6.694214	13.086025
H	6.022182	5.874135	14.204388
C	8.579853	-0.762091	13.355843
H	8.604958	-0.972536	14.431042
H	9.456239	-1.247722	12.916301
H	7.688303	-1.241721	12.939802
C	9.841481	1.370795	13.713432
H	10.008797	2.395558	13.368628
H	10.741592	0.795236	13.470116
H	9.745777	1.390141	14.805214
C	5.047227	1.728296	8.851581
H	4.079353	2.020379	8.428959
C	4.878034	0.930500	10.167688
H	4.775494	1.648145	10.997929
H	3.937126	0.370677	10.143073
C	5.928550	1.031898	7.860153
H	5.695795	1.086026	6.800043
C	5.871193	3.024075	9.158314
O	5.437760	4.126367	8.847224

*Optimised Structure of **4***

H_{298K} = -1513.13341

G_{298K} = -1513.24496

Lowest frequency: 25.01 cm^{-1}

Al	16.299946	11.196159	8.145650
C	18.053315	11.552905	7.407943
H	18.234786	12.479836	6.848974
C	19.061592	10.856586	9.523367
H	18.989221	10.588324	10.584245
C	19.027021	9.678731	8.542353
H	19.854160	8.972766	8.685804
H	18.086703	9.112916	8.569925
C	20.413613	11.498488	9.151768
H	21.241187	11.009255	9.681001
H	20.441871	12.559363	9.423889
C	19.192609	10.549261	7.289133
H	19.219327	10.003302	6.337106
C	17.944994	11.758208	9.015871
H	18.054384	12.795725	9.352308
C	20.513898	11.267076	7.620580

H	20.619658	12.198987	7.054956	C	14.244050	13.310717	3.817941
H	21.379656	10.639221	7.372711	H	13.368668	13.780791	4.277525
C	13.090458	11.063590	8.069086	H	13.893641	12.492531	3.180055
H	12.007452	11.023773	8.093383	H	14.705604	14.058353	3.163263
N	14.967688	12.532306	7.762031	C	16.882996	15.310544	10.412512
C	15.501140	13.753300	7.227273	H	17.888158	15.078334	10.047388
C	13.654690	12.314451	7.755714	H	16.833935	15.024048	11.466980
C	15.648928	13.883720	5.833456	H	16.753267	16.398062	10.370733
C	15.958509	14.744435	8.118229	C	14.418495	15.004689	10.093656
C	15.808161	14.576683	9.619086	H	14.216557	16.048251	9.824632
H	15.915477	13.506087	9.838105	H	14.339042	14.920327	11.182382
C	15.239901	12.796138	4.857086	H	13.627365	14.387343	9.659083
H	14.752361	11.987625	5.418161	N	15.092517	9.708434	8.139505
C	12.709821	13.392376	7.313555	C	15.658041	8.388763	8.068429
H	13.106004	14.395126	7.482914	C	13.753626	9.836483	8.167874
H	11.745611	13.291383	7.816212	C	15.786206	7.619889	9.240924
H	12.523759	13.296875	6.237316	C	16.140566	7.930532	6.823609
C	16.534488	15.894918	7.575399	C	16.044308	8.794248	5.577893
H	16.891455	16.675705	8.241238	H	16.301964	9.821740	5.881496
C	16.236548	15.052596	5.343365	C	15.375731	8.161190	10.597427
H	16.364403	15.168604	4.268745	H	14.606042	8.927355	10.444015
C	16.670704	16.053430	6.201104	C	12.904833	8.599827	8.240124
H	17.127193	16.954403	5.800697	H	13.161432	7.906079	7.432973
C	16.463339	12.196026	4.162269	H	11.845640	8.847623	8.166254
H	16.996673	12.958145	3.582496	H	13.068560	8.052247	9.173591
H	16.160440	11.405541	3.465539	C	16.729957	6.665071	6.778737
H	17.163022	11.769696	4.888339	H	17.112549	6.288607	5.834808

C	16.386804	6.362788	9.139826
H	16.503134	5.755689	10.033934
C	16.849263	5.884258	7.921790
H	17.314824	4.904283	7.863591
C	16.564141	8.856616	11.262908
H	17.407269	8.164901	11.375966
H	16.293680	9.226650	12.257552
H	16.910333	9.710168	10.669642
C	14.784102	7.094467	11.513330
H	13.973566	6.539143	11.029380
H	14.384170	7.553417	12.422288
H	15.537339	6.366049	11.831514
C	17.037957	8.397040	4.493213
H	18.056753	8.316083	4.883472
H	17.042988	9.148051	3.697595
H	16.777163	7.438816	4.028787
C	14.628601	8.829160	4.998348
H	14.285922	7.820724	4.737438
H	14.606528	9.432205	4.082977
H	13.902401	9.265930	5.689936

Optimised Structure of ***TS-2***

H_{298K} = -1626.429519

G_{298K} = -1626.546098

Lowest frequency: -105.95 cm^{-1}

Al	-0.003792	-0.189126	0.096530
O	0.065207	-3.351494	-0.191204
C	0.929385	-1.087960	1.804498
H	2.013128	-0.992736	1.931047
C	-0.972619	-0.235130	3.030794
H	-1.865084	0.400277	3.081362
C	-1.227929	-1.690031	2.635419
H	-1.857935	-2.234872	3.347977
H	-1.687969	-1.777672	1.640770
C	-0.254010	-0.425437	4.381220
H	-0.974962	-0.546363	5.198863
H	0.370851	0.439566	4.629258
C	0.254133	-2.103849	2.705818
H	0.469462	-3.152275	2.463817
C	0.066239	0.195286	1.998353
H	0.642356	1.079778	2.295220
C	0.572355	-1.721937	4.165729
H	1.646215	-1.573056	4.318958
H	0.253236	-2.513568	4.856135
C	-0.096497	-2.196154	-0.177460
C	0.056318	0.781627	-2.958686
H	0.092300	0.990567	-4.022040
N	1.433456	0.428347	-0.996171
C	2.742706	0.522399	-0.405652
C	1.293043	0.708297	-2.305375
C	3.651500	-0.547895	-0.504660
C	3.062498	1.690596	0.320183
C	2.059197	2.821113	0.473972
H	1.071510	2.356392	0.590276
C	3.316896	-1.860824	-1.186686
H	2.324883	-1.766165	-1.648854
C	2.518440	0.983786	-3.125145
H	3.151701	1.740558	-2.652371
H	2.254361	1.319719	-4.128318

H	3.135406	0.083998	-3.213058
C	4.328100	1.778296	0.903902
H	4.595184	2.668439	1.465962
C	4.903586	-0.409297	0.100827
H	5.612909	-1.232089	0.035222
C	5.248320	0.743151	0.790560
H	6.227083	0.831377	1.253909
C	3.257717	-2.998444	-0.165215
H	4.244583	-3.160456	0.283551
H	2.950684	-3.933841	-0.643388
H	2.551029	-2.780257	0.638346
C	4.322841	-2.217510	-2.282367
H	4.437106	-1.427894	-3.031622
H	4.018231	-3.131396	-2.801576
H	5.315482	-2.402600	-1.857151
C	2.300211	3.667867	1.718333
H	2.395687	3.052046	2.618089
H	1.466400	4.359685	1.870813
H	3.206394	4.277845	1.631095
C	1.984563	3.715456	-0.764754
H	2.968865	4.129639	-1.012901
H	1.306893	4.557637	-0.585008
H	1.608642	3.179574	-1.641490
N	-1.400286	0.443286	-1.092839
C	-2.674546	0.547800	-0.446642
C	-1.223962	0.716936	-2.384663
C	-2.885698	1.683172	0.367099
C	-3.618786	-0.494891	-0.504422
C	-3.440170	-1.724783	-1.373252
H	-2.464910	-1.651154	-1.872618

C	-1.887449	2.823487	0.372124
H	-0.910656	2.406695	0.096492
C	-2.399563	0.966321	-3.281378
H	-2.711680	0.029771	-3.757763
H	-2.142789	1.665266	-4.079933
H	-3.260698	1.351755	-2.730155
C	-4.779229	-0.374487	0.267446
H	-5.518408	-1.172645	0.232925
C	-4.061293	1.756578	1.113446
H	-4.240556	2.626732	1.740143
C	-5.001890	0.733053	1.072181
H	-5.908678	0.801945	1.666619
C	-1.720087	3.484931	1.733261
H	-2.629376	4.000261	2.061691
H	-0.927278	4.239468	1.688247
H	-1.446411	2.753463	2.500538
C	-2.253171	3.849623	-0.701775
H	-2.272531	3.398556	-1.699661
H	-1.531028	4.672692	-0.722263
H	-3.244379	4.277750	-0.512759
C	-3.443866	-3.012542	-0.550291
H	-2.680886	-3.004868	0.231769
H	-3.254790	-3.880403	-1.190044
H	-4.414124	-3.165291	-0.064452
C	-4.532443	-1.800996	-2.442333
H	-5.514527	-1.955753	-1.981342
H	-4.355698	-2.640468	-3.122465
H	-4.597398	-0.886341	-3.038698

*Optimised Structure of **5***

H_{298K} = -1626.469816

G_{298K} = -1626.586578

Lowest frequency: 19.29 cm^{-1}

Al	16.209853	10.995071	7.085888
O	17.704688	10.479711	4.356906
C	18.623297	11.530394	6.376110
H	18.842472	12.557696	6.047098
C	18.982085	10.415498	8.490299
H	18.576708	9.899695	9.367821
C	19.358946	9.499576	7.321422
H	20.133459	8.767052	7.578508
H	18.499812	8.965496	6.896648
C	20.329184	11.109544	8.757088
H	20.983656	10.479269	9.372040
H	20.199431	12.056645	9.292951
C	19.866647	10.638817	6.426283
H	20.220407	10.353984	5.430616
C	18.030429	11.430349	7.828263
H	18.066704	12.392198	8.357516
C	20.917097	11.295960	7.332722
H	21.077907	12.347757	7.072506
H	21.885920	10.791984	7.236646
C	17.501304	10.933002	5.469033
C	13.000304	10.930329	7.412929
H	11.917027	10.889507	7.429262
N	14.888523	12.406073	7.176658
C	15.429376	13.736784	7.177232
C	13.567974	12.199274	7.219363
C	15.569121	14.462893	5.980034
C	15.905815	14.246965	8.406750
C	15.749324	13.457247	9.693669
H	15.850002	12.393256	9.438122
C	15.094321	13.944674	4.636775
H	14.624740	12.965037	4.793141
C	12.628553	13.357275	7.058718
H	13.006643	14.261119	7.543173
H	11.639498	13.123935	7.455522
H	12.513900	13.594330	5.994958
C	16.503197	15.507548	8.410426
H	16.875017	15.917936	9.344990
C	16.179649	15.720067	6.040012
H	16.295947	16.291490	5.121235
C	16.640536	16.242870	7.238156
H	17.113524	17.220648	7.261559
C	16.261523	13.754230	3.668337
H	16.753672	14.711244	3.460709
H	15.909799	13.350211	2.714107
H	17.014135	13.066301	4.058411
C	14.059842	14.883490	4.012298
H	13.226083	15.100186	4.687279
H	13.650915	14.453452	3.092687
H	14.515003	15.844067	3.746343
C	16.822163	13.773056	10.728758
H	17.830063	13.680230	10.311070
H	16.745645	13.083043	11.574240
H	16.716969	14.785667	11.133553
C	14.356484	13.640590	10.299167
H	14.165805	14.695018	10.530073
H	14.262600	13.072791	11.231704
H	13.566007	13.296646	9.625685
N	14.999593	9.616194	7.676925

C	15.645447	8.443968	8.194177
C	13.668047	9.738588	7.727856
C	15.786466	8.289428	9.587185
C	16.223038	7.530469	7.286176
C	16.050105	7.701442	5.787670
H	16.056946	8.776461	5.567979
C	15.221538	9.286406	10.583241
H	14.556851	9.978709	10.050622
C	12.832787	8.586521	8.203359
H	13.268162	7.621302	7.934845
H	11.818983	8.651242	7.803961
H	12.754511	8.605935	9.296800
C	16.937581	6.450758	7.809194
H	17.394293	5.737835	7.128595
C	16.517604	7.195149	10.056662
H	16.647833	7.067120	11.129387
C	17.089077	6.282859	9.180482
H	17.657804	5.441084	9.565589
C	16.336742	10.126672	11.205151
H	17.060209	9.491811	11.729646
H	15.927989	10.836726	11.933044
H	16.885142	10.694384	10.445815
C	14.401194	8.601165	11.674995
H	13.620691	7.954984	11.260254
H	13.920249	9.343292	12.319979
H	15.031383	7.975655	12.316311
C	17.174087	7.084574	4.965295
H	18.159348	7.421985	5.301788
H	17.069720	7.380550	3.918433
H	17.157628	5.989138	5.001213
C	14.694746	7.160618	5.328746
H	14.593353	6.097529	5.577077
H	14.586754	7.263289	4.244528
H	13.861584	7.695310	5.794264