Effective earth-abundant metal catalysis by exploiting a dynamic coordination sphere

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S2. X-ray data and structures

S0. Author contributions

Mohammed Bahili undertook principal experimental work pertaining to catalyst development and characterization. Assistance with manuscript preparation.

Emily C. Stokes performed experimental work relating to the trimerization catalysis with a focus on substrate scope and product characterization. Assistance in manuscript preparation.

Robert C. Amesbury performed catalytic studies to increase the substrate scope.

Darren M. C. Ould undertook initial experimental work in the trimerization catalysis.

Bashar Christo assisted with catalyst characterization by measuring data for the van't Hoff plot.

Rhian Horne assisted with developing catalyst reactivity and selectivity; grew the crystal of $(TolNCO)_2$.

Benson M. Kariuki measured single-crystal X-ray data for the isocyanurates.

Jack A. Stewart assisted with determining substrate scope and optimizing catalytic reaction conditions.

Rebekah L. Taylor expanded the substrate scope and grew the crystal of $(4\text{-}C_6F_4F\text{-}NCO)_3$.

P. Andrew Williams assisted in the bulk characterization of the $(PhNCO)_3$ trimer by measuring and interpreting powder X-ray diffraction data.

Matthew D. Jones is the co-supervisor of RCA and helped to guide the overall direction of the project.

Kenneth D. M. Harris is PI of the research group that carried out the powder X-ray diffraction study; he assisted in the bulk characterization of the $(PhNCO)_3$ trimer by interpreting the powder X-ray diffraction data, and assisted with manuscript preparation.

Benjamin D. Ward is PI of the research group in which the catalyst was developed; roles included data interpretation, solving and refining crystal structures from single-crystal X-ray diffraction, DFT calculations, and principal role in manuscript preparation.

S1. Experimental Procedures and Characterizing Data

S1.1 General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or of dinitrogen. Solvents were dried by passing through an alumina drying column incorporated into a MBraun SPS800 solvent purification system, except for tetrahydrofuran, which was dried over molten potassium for three days and distilled under argon. Isocyanates were dried over P_2O_5 for three days and distilled under reduced pressure and stored under dinitrogen. Deuterated solvents were dried over molten potassium (C_6D_6) or CaH_2 ($CDCl_3$) for three days, distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Nolan tubes fitted with J. Young Teflon valves. 2-methyl-2-pyridin-2-yl-propane-1,3-diamine {ppda, MeC(2-C_5H_4N)(CH_2NH_2)$_2$} was prepared according to published methods.[1] All other compounds and reagents were purchased from chemical suppliers and used without further purification.

NMR spectra were recorded on Bruker Fourier 300, Avance III HD 400, 500 or 600 spectrometers. ^{1}H and ^{13}C assignments were confirmed with the use of two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR experiments. ^{1}H and ^{13}C spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Infrared spectra of complexes were prepared as KBr pellets and were recorded on a Shimadzu IRAffinity 1 FTIR spectrometer, whilst spectra of the Salpy ligand and isocyanurates were measured by ATR on a Shimadzu IRAffinity 1S FTIR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the EPSRC National Mass spectrometry Service or by the analytical services in the Cardiff School of Chemistry. Elemental analyses were measured by the analytical services at London Metropolitan University.

MALDI mass spectrometry. Spectra were measured on a Bruker AutoFlex speed MALDI Tof mass spectrometer operating in positive mode. Approx. 1 mg of sample was dissolved in DCM and was mixed in a 1:1 (v:v:v) ratio of DCTB (10 mg mL^{-1}) in DCM. 1 μL was spotted on the plate.

Trimerization catalysis. In a nitrogen-filled glove box, [Al(Salpy)(OBn)] (**3**) (3 mg, 7 $\times 10^{-3}$ mmol) was added to a 5 mL screw-cap vial and isocyanate was added *via* a measuring pipette. The vial was sealed and stirred for the appropriate time (see Table 1 for details). For experiments that required heating, the vial was placed in a 20-well thermostat-controlled aluminum heating block with continuous stirring. Temperature was controlled by a thermocouple inserted into a "blank" reaction vial containing 2 mL of paraffin oil. After the required time, a precipitate had formed, or for those experiments with high conversions, the reaction completely solidified. The isolated solids were

washed with hexanes or recrystallized from THF, and characterized by NMR and IR spectroscopies, and by mass spectrometry.

Control experiments were undertaken in which isocyanates were oligomerized using the strong organic nucleophile N,N′-dimethylaminopyridine (DMAP) under otherwise identical conditions to those reported above. In each case, the corresponding trimer was obtained, alongside appreciable quantities of uretidinedione (the isocyanate dimer); the uretidinedione was evident in the mass spectra of the crude product, whereas the corresponding signals were not observed in crude samples prepared using [Al(Salpy)(OBn)] (**3**). The identities of the dimers were confirmed by single-crystal X-ray diffraction of the 4-tolyl and 4-methoxyphenyl derivatives, which were found to preferentially crystallize over the trimer from THF solutions.

Powder X-ray Diffraction. Powder XRD data studies were carried out on a bulk sample of the product obtained from the reaction of **3** with phenyl isocyanate. The powder XRD data were recorded at ambient temperature on a Bruker D8 instrument (Cu Kα_1 radiation, Ge monochromator) operating in transmission mode (data range, $4° \leq 2\theta \leq 70°$; step size, $\Delta 2\theta = 0.017°$; total time, 17 h), with the powder sample held between two pieces of tape in a foil-type sample holder. The powder XRD pattern was indexed using the program LZON [2] within the CRYSFIRE suite,[3] giving the following unit cell with monoclinic metric symmetry: a = 12.68 Å, b = 13.78 Å, c = 9.83 Å, β = 92.1°, V = 1717 Å^3. From systematic absences, the space group was assigned as $I2/a$. Profile fitting and unit cell refinement was carried out using the Le Bail procedure[4] implemented in the GSAS program, leading to an excellent fit (Figure 1) between experimental and calculated powder XRD patterns [R_{wp} = 2.76%, R_p = 2.04%; refined unit cell: a = 12.68201(30) Å, b = 13.77816(30) Å, c = 9.83532(20) Å, β = 92.1448(13)°, V = 1717.37(9) Å^3]. The unit cell obtained matches that (transformed to an alternative setting) of the monoclinic polymorph of N,N′,N″-triphenyl isocyanurate reported previously. Rietveld refinement was carried out using the program GSAS[5] with the known crystal structure of the monoclinic polymorph of N,N′,N″-triphenyl isocyanurate[6] as the initial structural model. Bond distance and bond angle restraints were applied using values taken from the starting structural model. Planar restraints were applied to the phenyl rings and the isocyanurate ring. A common isotropic displacement parameter for all non-hydrogen atoms was refined, with the value for the hydrogen atoms set as 1.2 times the value of the non-hydrogen atoms. The final Rietveld refinement (Figure 2) gave an excellent fit to the experimental powder XRD data [R_{wp} = 2.90%, R_p = 2.13%, with final refined unit cell: $C2/c$, a = 16.3365(4) Å, b = 13.77754(33) Å, c = 9.83486(21) Å, β = 129.1285(9)°, V = 1717.16(7) Å^3; 2θ range, 4°–70°; 3866 profile points; 80 refined variables].

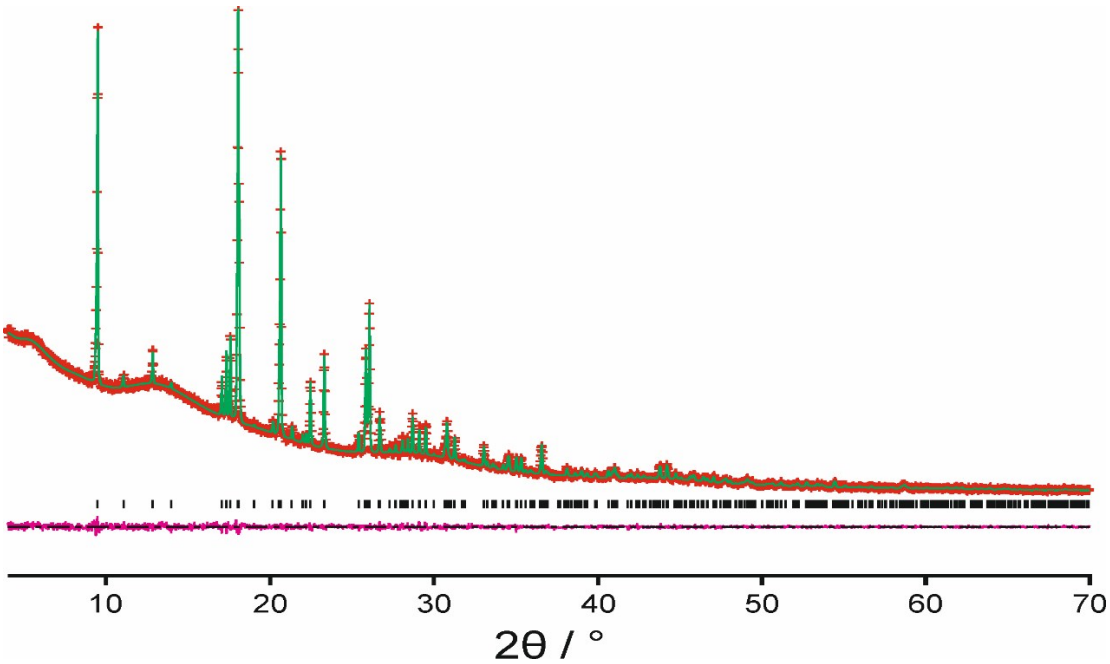


Figure 1 Le Bail fitting of the powder XRD pattern for the product from the reaction of **3** with phenyl isocyanate (PhNCO) discussed in the main text [red + marks, experimental data; green line, calculated data; black tick marks, predicted peak positions; magenta line (at bottom), difference between experimental and calculated powder XRD patterns]. The excellent fit between experimental and calculated powder XRD patterns is indicated by the fact that the difference profile is essentially flat.

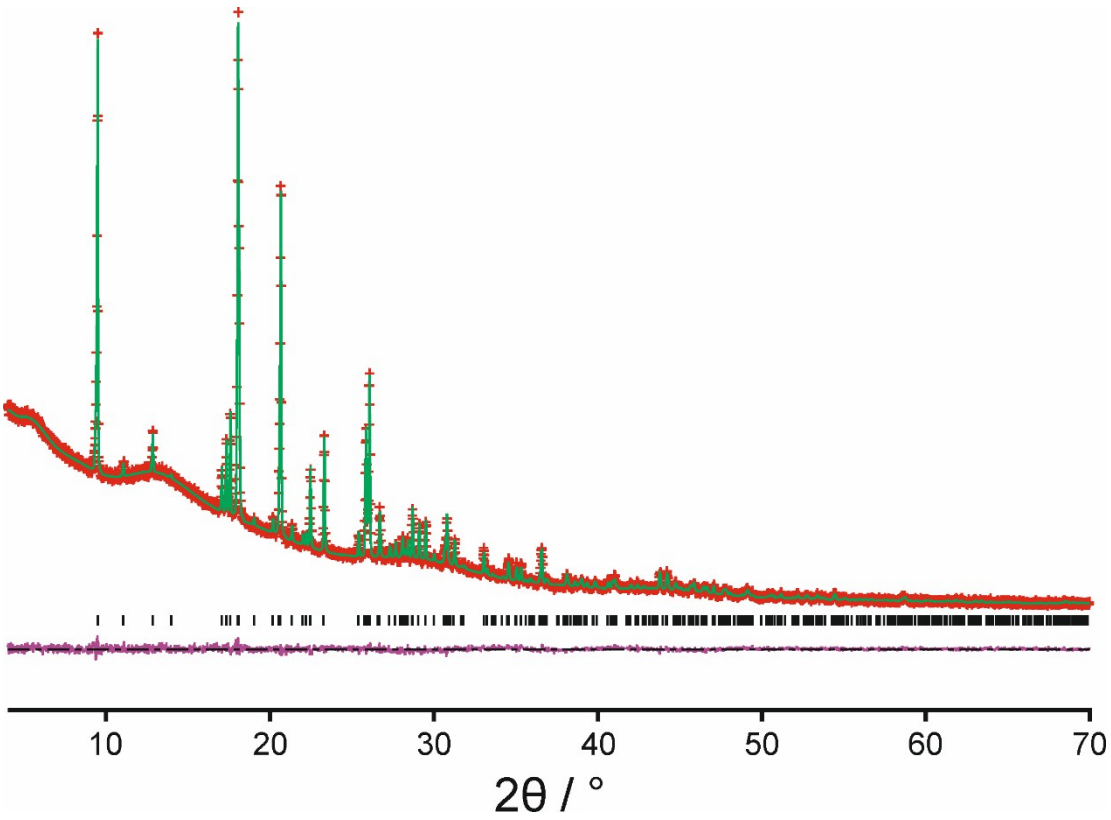


Figure 2 Final Rietveld refinement of the powder XRD pattern for the product from the reaction of **3** with phenyl isocyanate (PhNCO) discussed in the main text [red + marks, experimental data; green line, calculated data; black tick marks, predicted peak positions; magenta line

(at bottom), difference between experimental and calculated powder XRD patterns]. The excellent fit between experimental and calculated powder XRD patterns is indicated by the fact that the difference profile is essentially flat. The molecular structure is given in S2.6 alongside that obtained from single-crystal X-ray analysis.

Single Crystal X-ray Diffraction. Single crystals of the Salpy pro-ligand (**1**), [Al(Salpy)Me] (**2**), and [Al(Salpy)(OTol)] (**4**) were grown from saturated benzene solutions at room temperature, whereas $(PhNCO)_3$,[7] $(4\text{-}C_6H_4F\text{-}NCO)_3$,[8,9] $(4\text{-}C_6H_4Me\text{-}NCO)_3$,[10] $(4\text{-}C_6H_4CF_3\text{-}NCO)_3$, $(4\text{-}C_6H_4OMe\text{-}NCO)_3$,[11] $(4\text{-}C_6H_4OMe\text{-}NCO)_2$ and $(4\text{-}C_6H_4Me\text{-}NCO)_2$ were grown from a saturated THF solutions. Single-crystal X-ray diffraction data (Mo-Kα) for the pro-ligand and complexes were collected on a Rigaku Saturn 724+ CCD diffractometer at low temperature, by the EPSRC National Crystallographic Service;[12] data for the isocyanate oligomers were collected on an Agilent Supernova CCD diffractometer in the Cardiff School of Chemistry. Crystal structures were solved using direct methods with absorption corrections being applied as part of the data reduction scaling procedure. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations and treated with a riding model, with isotropic atomic displacement parameters but not refined. Full least-square refinement was carried out on F^2. A final difference Fourier map revealed no significant maxima or minima of residual electron density other than those discussed below for **4**. The scattering factor coefficients and the anomalous dispersion coefficients were taken from standard sources.[13] Crystal structures were solved using SHELXT[14] and refined using SHELXL-2013.[15] Crystallographic data and experimental details are given in Table S2.1.

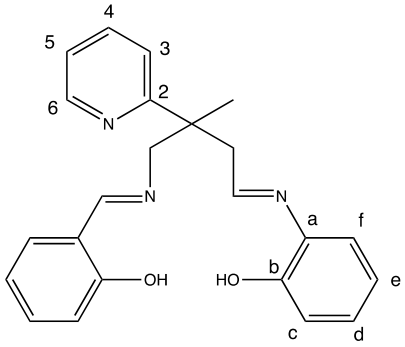
The crystal of **4** was a non-merohedral twin (180° about the direct axis [1 0 0]). The data were processed using CrysalisPro and a hklf5 file produced for the twin refinement. The structure contains residual maxima (1.362 e $Å^{-3}$) which were larger than desired, but these maxima do not correspond to any chemically reasonable atoms and are significantly reduced compared to the hlkf4 refinement. The refinement otherwise proceeded normally.

The structures of $(4\text{-}C_6H_4Me\text{-}NCO)_3$, $(4\text{-}C_6H_4CF_3\text{-}NCO)_3$ and $(4\text{-}C_6H_4OMe\text{-}NCO)_3$ contained a solvent molecule, presumably THF (the recrystallization solvent) with the oxygen atom lying on a special position and the remaining atoms disordered about the C_3 axis. Despite exhaustive attempts to model this disorder, no acceptable (chemically reasonable) model could be obtained. The disorder was therefore modeled using SQUEEZE;[16] the refinement otherwise proceeded as normal. The structures of the cyclotrimers were unaffected by this process.

Two different crystal morphologies of (4-C_6H_4OMe-NCO)$_2$ were formed during the crystallization procedure; data were measured for both morphologies, which correspond to different polymorphs of (4-C_6H_4OMe-NCO)$_2$ (monoclinic and orthorhombic). Both structures are presented for completeness.

Computational details. All calculations were carried out using the Gaussian 09 suite.[17] Molecular geometries were optimized without symmetry restraints and were followed by frequency calculations to ascertain the nature of the stationary point (minimum *vs.* saddle point). Minima on the potential energy surface exhibited no imaginary frequencies, whereas transition state structures were characterized by a single imaginary frequency corresponding to the expected reaction coordinate. Calculations were performed using the restricted M06-2X hybrid functional;[18] employing Dunning's cc-pVTZ triple-ζ basis set for all centers except for the aluminum, for which the cc-pV(T+d)Z functional was used,[19,20] which offers an improved description of the *d*-polarization functions of 3*p* elements. Coordinates of all optimized structures are provided below. NBO analyses were performed using NBO version 6.0,[21] invoked *via* the Gaussian 09 program interface. Solvent was incorporated using the polarizable continuum model,[22] with the molecular cavity defined by a united atom model that incorporates hydrogen into the parent heavy atom. Since the catalytic trimerization reactions were studied in neat isocyanate, it was deemed appropriate to invoke isocyanate as the solvent in calculations (in this case, methylisocyanate). Since methylisocyanate is not pre-defined in Gaussian 09, calculations were performed by reading the pre-defined parameters for methanol, and changing the principal parameters to values that are appropriate for methylisocyanate, as follows: static dielectric constant (EPS) = 29.4 F m^{-1}, solvent radius (RSOLV) = 2.34 Å (estimated using the Stern-Eyring formula),[23] density (DENSITY) = 9.74 × 10^{-3} Å^{-3}, molar volume (VMOL) = 61.8 cm^3. AIM calculations were undertaken with the AIMAll package.[24]

Labelling scheme for Salpy ligand and complexes:



S1.2 H_2Salpy (1)

A solution of salicyldehyde (2.21 g, 18.5 mmol) in methanol (15 mL) was added to a stirred solution of ppda (1.50 g, 9.07 mmol) in methanol (15 mL). The resulting yellow solution was stirred at 50 °C for 2 h. The pale-yellow solution was then allowed to cool to room temperature, whereupon a yellow

precipitate formed, which was filtered and washed with cold methanol (10 mL). The product was dried *in vacuo* for several hours. Yield: 2.97 g, 0.80 mmol (88%). m.p. = 118-120 ˚C.

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 13.21 (s, 2H, OH), 8.63 (ddd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, ^5J = 0.9 Hz, 1 H, H^6), 8.31 (s, 2 H, CH=N), 7.61 (td, ^3J = 7.6 Hz, ^4J = 1.9 Hz, 1 H, H^4), 7.34 (dt, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1 H, H^3), 7.28 (ddd, ^3J = 9.0 Hz, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 2H, H^d), 7.21 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2H, H^c), 7.15 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.0 Hz, 1 H, H^5), 6.91 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 2H, H^f), 6.89 (td, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2H, H^e), 4.13 (dd, ^2J = 12.2 Hz, ^4J = 1.1 Hz, 2H, C<u>H</u>H) 4.00 (dd, ^2J = 12.2 Hz, ^4J = 1.1 Hz, 2 H, CH<u>H</u>), 1.53 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 293 K): δ 166 (CH=N), 163.2 (C^2), 161.1 (C^b), 149.0 (C^6), 136.4 (C^4), 132.3 (C^d), 131.3 (C^c), 121.6 (C^5), 121.16 (C^3), 118.7 (C^a), 118.5 (C^e), 116.9 (C^f), 67.1 (CH_2), 46.1 (Me<u>C</u>), 21.71 (CH_3). IR (cm^{-1}): 3305 (O-H), 3055 (C-H aromatic), 2962 (s, C-H), 2920 (s, C-H), 2864 (s, CH), 1625 (s, C=N_{imine}), 1496 (s, C=N_{py}, C=$C_{aromatic}$), 1452, 1422, 1377, 1334,1273, 1209, 1155, 1038, 1019, 989, 949. HRMS (ES) for $[M+H]^+$: calcd. for $C_{23}H_{24}N_3O_2$: 374.1869; found: 374.1887.

S1.3 [Al(Salpy)Me] (2)

$AlMe_3$ (1.83 mL, 2.0 M in toluene, 3.6 mmol) was added dropwise to a stirred solution of H_2Salpy (1.37 g, 3.6 mmol) in toluene (20 mL). The reaction mixture was heated at 80 ºC for 18 h, after which the solvent was removed under reduced pressure. The residue was washed with hexanes (2 × 15 mL) to afford an off-white solid. Yield: 1.25 g, 3.0 mmol (82%). Crystals of [Al(Salpy)Me] suitable for structure determination by single-crystal X-ray diffraction were obtained from a concentrated benzene solution. The two phenoxyimine "arms" were observed as equivalent signals due to their rapid interconversion on the NMR timescale.

^{1}H NMR (500 MHz, THF-d_8, 293 K): δ **Isomer 1**: 8.69 (d, ^3J = 4.6 Hz, 1H, H^6), 8.18 (s, 2H, CH=N), 7.79 (t, ^3J = 7.9 Hz, 1H, H^4), 7.52 (d, ^3J = 8.0 Hz, 1H), 7.13 (m, 4H), 6.72 (m, 2H), 6.55 (m, 3H), 4.52 (d, ^2J = 12.5 Hz, 2H, C<u>H</u>H), 3.65 (d, ^2J = 12.5 Hz, 2H, CH<u>H</u>), 1.38 (s, 3H, CH_3), –0.89 (s, 3H, Al-CH_3). **Isomer 2**: 8.53 (d, ^3J = 4.2 Hz, 1H, H^6), 8.34 (s, 2H, CH=N), 7.69 (t, ^3J = 7.6 Hz 1H, H^4), 7.46 (d, ^3J = 8.6 Hz, 1H), 7.26 (m, 4H), 6.77-6.43 (m, 5H), 4.34 (d, ^2J = 12.4 Hz, 2H, C<u>H</u>H), 4.02 (d, ^2J = 12.4 Hz, 2H, CH<u>H</u>), 1.44 (s, 3H, CH_3), –0.89 (s, 3H, Al-CH_3). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8, 293 K): δ, **Isomer 1**: 170.8 (CH=N), 166.8 (C^2), 165.4 (C^b), 149.1 (C^6), 137.0 (C^4), 134.6, 132.8, 132.6, 122.0, 121.1, 120.4, 119.2, 115.5, 68.0 (CH_2), 45.5 (Py-<u>C</u>-CH_3), 21.0 (CH_3), Al-CH_3 (Not observed). **Isomer 2:** 170.8 (CH=N), 166.4 (C^2), 163.4 (C^b), 149.0 (C^6), 136.5 (Py-C), 134.8, 132.8, 122.5, 120.4, 119.3, 114.9, 67.0 (CH_2), 44.2 (Py-<u>C</u>-Me), 21.0 (<u>CH_3</u>), Al-CH_3 (Not observed). Anal. Calcd. for $C_{24}H_{24}AlN_3O_2$ (%): C, 69.72; H, 5.85; N, 10.16. Found (%): C, 69.54; H, 5.92; N, 10.01. HRMS (EI) for $[M-CH_3]^+$: calcd. for $C_{23}H_{21}AlN_3O_2$: 398.1449; found 398.1444.

S1.4 [Al(Salpy)(OBn)] (3)

A solution of dry benzyl alcohol (0.3 mL, 2.9 mmol) in toluene (10 mL) was added to a solution of [Al(Salpy)Me] (**1**) (1.19 g, 2.87 mmol) in toluene (30 mL), and the solution was stirred at room temperature for 24 h. The solvent was concentrated to half the original volume to afford a precipitate, which was filtered, and washed with hexanes (2 × 20 mL) to give an off-white solid. Yield: 1.16 g, 2.29 mmol (80%). The two phenoxyimine "arms" were observed as equivalent signals due to their rapid interconversion on the NMR timescale.

^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ **Isomer 1**: 9.10 (ddd, ^{3}J = 5.3 Hz, ^{4}J = 1.8 Hz, ^{5}J = 0.7 Hz, 1H, H^6), 7.95 (s, 2H, CH=N), 7.74 (td, ^{3}J = 7.7 Hz, ^{4}J = 1.9 Hz 1H, H^4), 7.32 (d, ^{3}J = 8.6 Hz, 1H, H^3), 7.16 (m, 5H), 6.96 (m, 6H), 6.85 (d, ^{3}J = 8.1 Hz, 2H, Ar), 6.58 (td, ^{3}J = 7.1 Hz, ^{4}J = 1.1 Hz, 2H, Ar), 4.76 (br. s, 2H, O$C\underline{H}_2$Ph), 3.91 (d, ^{2}J = 12.9 Hz, 2H, CH_2), 3.81 (d, ^{2}J = 12.9 Hz, 2H, CH_2), 1.52 (s, 3H, CH_3). **Isomer 2**: 8.58 (ddd, ^{3}J = 4.8 Hz, ^{4}J = 1.9 Hz, ^{5}J = 0.9 Hz, 1H, H^6), 8.16 (s, 2 H, CH=N), 7.66 (dt, ^{3}J = 7.8 Hz, ^{4}J = 1.9 Hz, 1H, H^4), 7.40 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 7.1x Hz, ^{4}J = 1.8 Hz, 2H, Ar), 6.74 (ddd, ^{3}J = 7.8 Hz, ^{3}J = 7.1x Hz, ^{4}J = 1.1 Hz, 2H, Ar), 4.69 (br. s, 2H, OCH_2Ph), 4.16 (d, ^{2}J = 12.5 Hz, 2H, C*H*H), *ca.* 3.9 (partially obscured by major isomer 1, 2H, CH*H*), 1.25 (s, 3H, Me), remaining aromatic signals obscured by signals for isomer 1. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 293 K): δ **Isomer 1**: 168.9 (CH=N), 167.4 (C^2), 161.3 (C^b), 151.2 (C^6), 139.0 (C^4), 135.3 (C^d), 133.2, 129.4, 128.6, 127.7, 127.5, 123.3, 122.7, 120.2, 119.8, 115.3, 67.1 (CH_2), 66.8 (O$\underline{C}H_2$Ph), 41.1(Py-$\underline{C}$-Me), 22.9 (CH_3). Signals for isomer 2 are too weak to observe. Anal. Calcd. for $C_{30}H_{28}AlN_3O_3$ (%): C, 71.27; H, 5.58; N, 8.31. Found (%): C, 71.36; H, 5.87; N, 8.03. HRMS (EI) for $[M\text{-}OBn]^+$: calcd. for $C_{23}H_{21}AlN_3O_2$: 398.1449; found: 398.1454.

S1.5 [Al(Salpy)(O-4-C_6H_4Me)] (4)

A solution of *p*-cresol (0.05 g, 0.48 mmol) in toluene (4 mL) was added to a solution of [Al(Salpy)Me] (**1**) (0.2 g, 0.48 mmol) in toluene (10 mL) at room temperature, and the reaction stirred for 20 h. During this time, a precipitate formed which was isolated by cannula filtration and washed with hexanes (3 × 20 mL), affording the title compound as a white solid. Yield: 0.2 g, 0.39 mmol (82%). The two phenoxyimine "arms" were observed as equivalent signals due to their rapid interconversion on the NMR timescale.

^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ 8.79 (d, ^{3}J = 7.9 Hz, 1H, H^6), 7.59 (s, 2H, CH=N), 7.49 (td, ^{3}J = 7.8, ^{4}J =1.7 Hz, 1H, H^4), 7.08 (d, ^{3}J = 8.0 Hz, 1H, H^3), 7.08 (t, ^{3}J = 6.4 Hz, 1H, H^5), 6.91(m, 2H, |Ar), 6.70 (dd, ^{3}J = 7.7, ^{4}J =1.7 Hz, 2H, Ar), 6.48 (s, 2H, Ar), 6.45 (s, 2H, Ar), 6.25 (d, ^{3}J = 8.4 Hz, 2H, Ar), 6.21 (t, ^{3}J = 7.3 Hz, 2H, Ar), 3.53 (Overlapping d, 4H, CH_2), 1.85 (s, 3H, O-4-$C_6H_4\underline{Me}$),

1.25 (s, 3H, MeC$(CH_2)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 293 K): δ 166.9 (C^2), 161.6 (C^b), 160.7, 151.1(C^6), 139.0, 135.0, 132.7 (C^d), 128.7, 123.7, 123.1, 122.4, 120.1, 119.8, 119.3, 114.9, 66.9 (CH_2), 40.1 (Py-C-Me), 22.0 (Ar-CH_3), 20.5 (MeC$(CH_2)_2$). Anal. Calcd. for $C_{30}H_{28}AlN_3O_3$ (%): C, 71.27; H, 5.58; N, 8.31. Found (%): C, 71.13; H, 5.33; N, 8.16. HRMS (EI) for $[M]^+$: calcd. for $C_{30}H_{28}AlN_3O_3$: 505.1946; found: 505.1952.

S1.6 Equilibrium analysis for [Al(Salpy)(OBn)] (3)

^1H NMR spectra (400 MHz) of [Al(Salpy)(OBn)] (**3**) were measured between 25 and 50 °C in $CDCl_3$. The equilibrium coefficients were measured at each temperature from the relative integrations of the pyridyl H^6 resonances, since these resonances were well-separated, unaffected by neighboring signals, and were easily identifiable with no ambiguity as to their assignment (Figure 3). Toluene (*ca.* 0.5 equiv.) was added and used as an internal standard; the sum of H^6 integrations remained constant *vs.* the toluene methyl resonance. The integration values were used to determine the equilibrium coefficient; a van't Hoff plot was constructed from the values of lnK and T^{-1}, a least-squares fit (Microsoft Excel version 16.21) gave a straight line with $R^2 = 0.998$ (Table 1 and Figure 4). The gradient and intercept of the fitted line were used to determine $\Delta H = +13.6 \pm 4.2$ kJ mol^{-1} and $\Delta S = +29.5 \pm 13.5$ J K^{-1} mol^{-1}. Errors were estimated by considering a ±1 K accuracy in the temperature measurement, and by re-placing the start and ends of the integration curves in various positions around the signals and re-calculating the equilibrium coefficients based upon deviations obtained in the integration values. By assuming a constructive addition of errors (to give the greatest possible error in intercept and gradient in one direction, worst-case values were obtained as: $\Delta H = +9.4$ kJ mol^{-1} and $\Delta S = +16.0$ J K^{-1} mol^{-1}.

Diffusion coefficients obtained from DOSY-NMR (Figure 5) were as follows: major isomer: 6.103×10^{-9} m^2 s^{-1}; minor isomer: 6.058×10^{-9} m^2 s^{-1}. Our interpretation that these two components are isomers of the same mass is supported by the two values being almost identical.

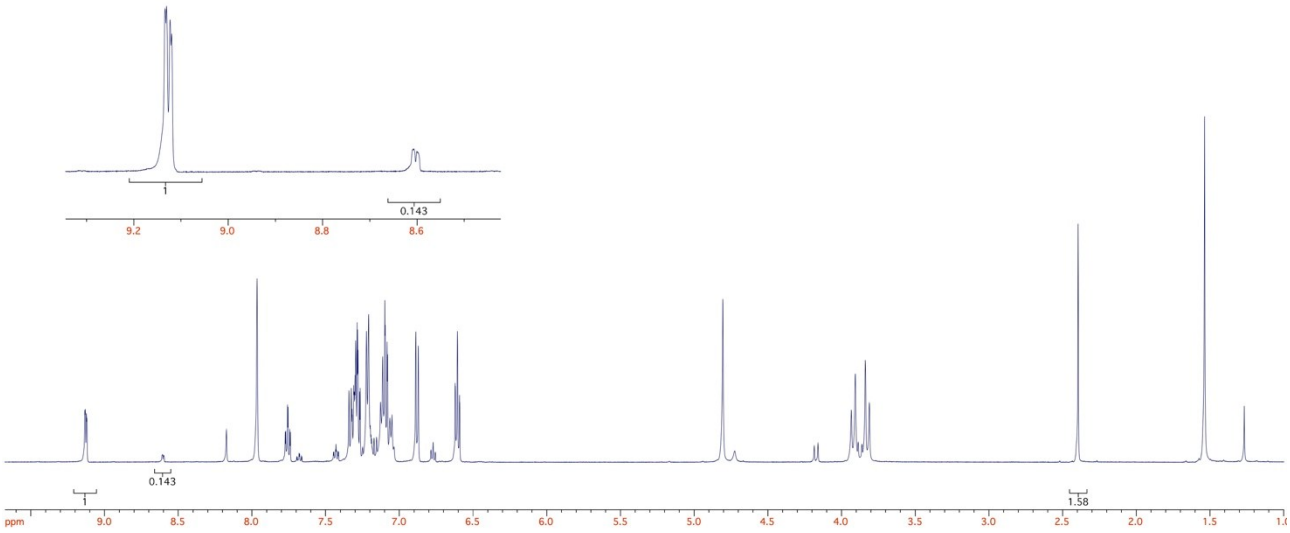


Figure 3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 295 K) of [Al(Salpy)(OBn)] (**3**) used for construction of a van't Hoff plot; toluene was used as an internal standard (methyl signal at 2.36 ppm). Equilibrium coefficients were obtained from the pyridyl H^6 integrations (expansion).

Table 1 Equilibrium coefficients obtained by ^{1}H NMR spectroscopy for [Al(Salpy)(OBn)] (**3**).

Temp (°C)	lnK
25	-1.93
30	-1.86
35	-1.76
40	-1.68
45	-1.59
50	-1.51

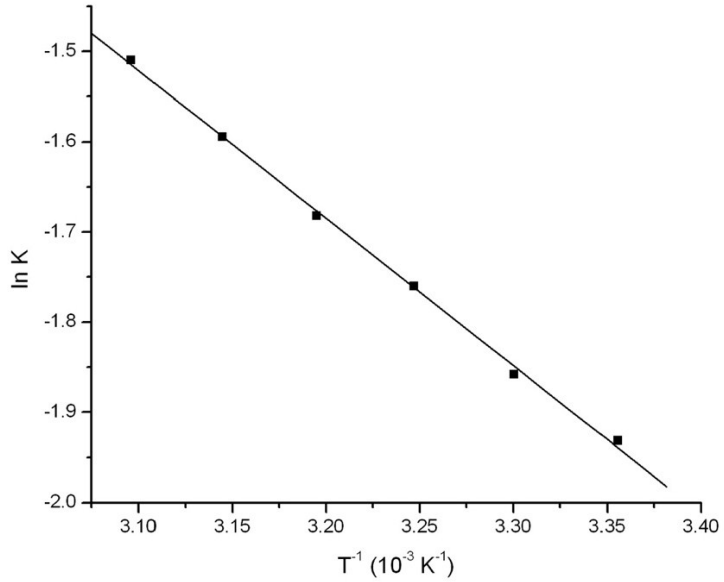


Figure 4 Van't Hoff plot for the equilibrium in [Al(Salpy)(OBn)] (**3**).

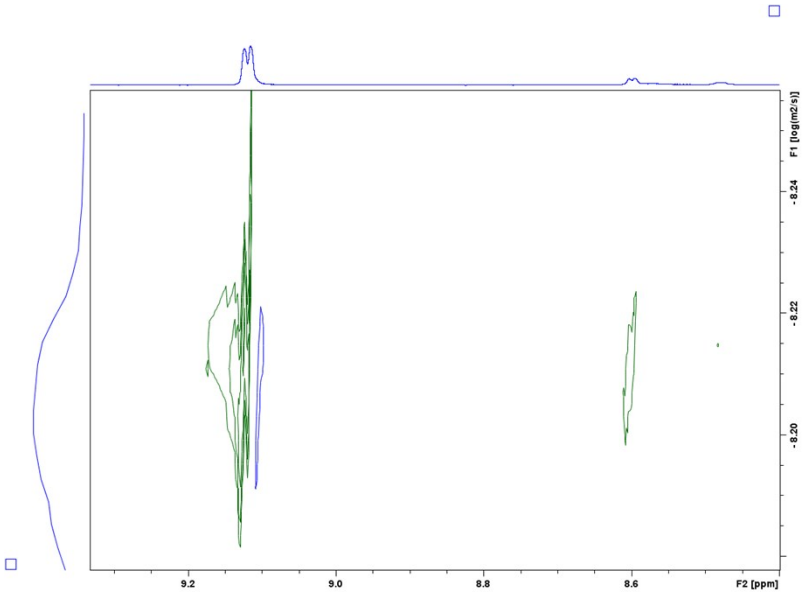


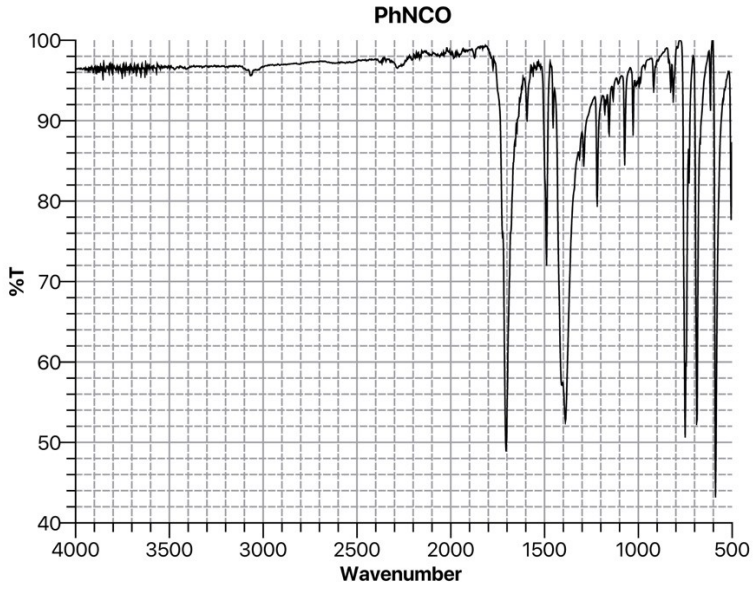
Figure 5 Expansion of the H^6 region of a DOSY NMR spectrum of [Al(Salpy)(OBn)] (**3**) ($CDCl_3$, 600 MHz, 293 K). The two components can be seen to have approximately equal diffusion coefficients.

S1.7 Data for isocyanurates

S1.7.1 N,N′,N″-triphenylisocyanurate

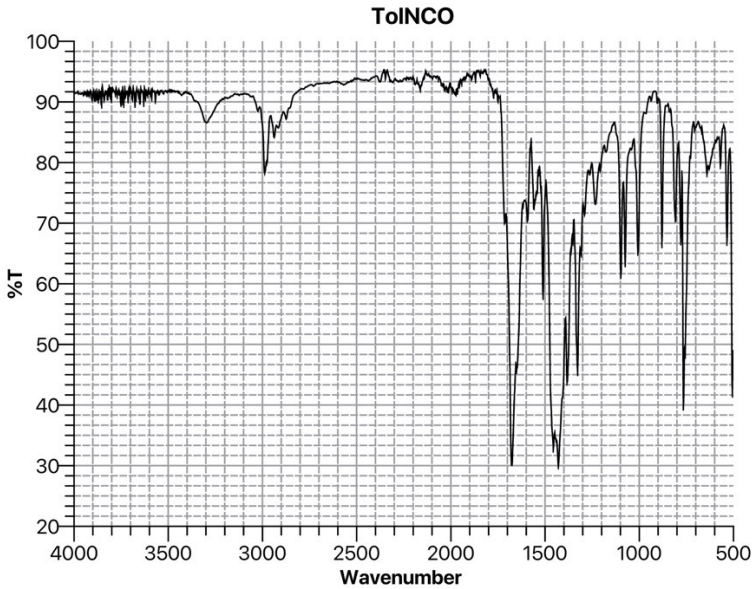
^1H NMR (400 MHz, $CDCl_3$, 293 K): 7.55-7.42 (overlapping m) ppm. HRMS (EI) for $[M]^+$: calcd. for $C_{21}H_{15}N_3O_3$: 357.1113; found: 357.1120. IR (ATR): 1705 (s), 1593 (w), 1489 (m), 1454 (w), 1408

(s), 1388 (s), 1219 (m), 1155 (w), 1072 (w), 1028 (w), 918 (w), 827 (w), 813 (w), 750 (s), 729 (w), 688 (s), 615 (w), 588 (s), 505 (m) cm^{-1}.



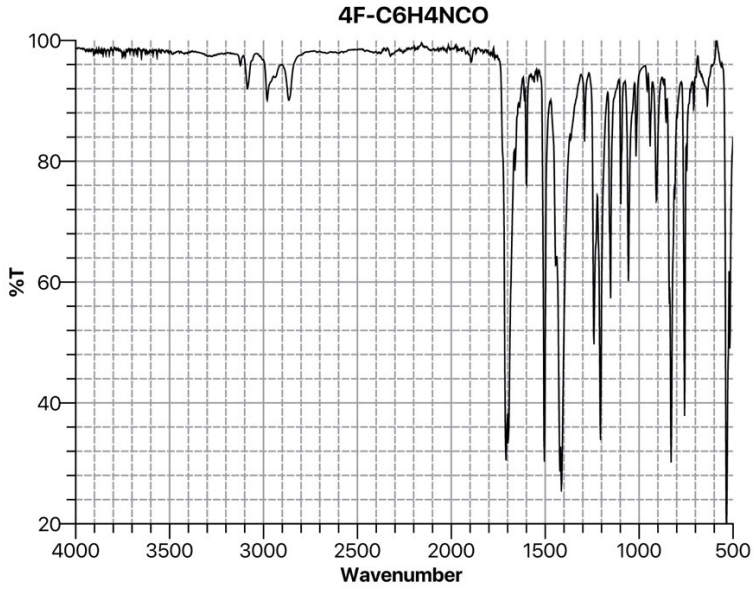
S1.7.2 N,N′,N″-tri(*p*-tolyl)isocyanurate

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 7.13 (2 H, d, ^3J = 8.1 Hz, Ar), 7.00 (2 H, d, ^3J = 8.3 Hz, Ar), 2.35 (3 H, s, Me) ppm. HRMS (EI) for $[M]^+$: calcd. for $C_{24}H_{21}N_3O_3$: 399.1583; found: 399.1587. IR (ATR): 2987 (w), 2976 (w), 1676 (s), 1618 (w), 1510 (m), 1456 (s), 1429 (s), 1382 (m), 1327 (m), 1097 (m), 1074 (m), 1006 (m), 808 (m), 765 (s), 640 (w), 628 (w), 569 (w), 505 (s) cm^{-1}.



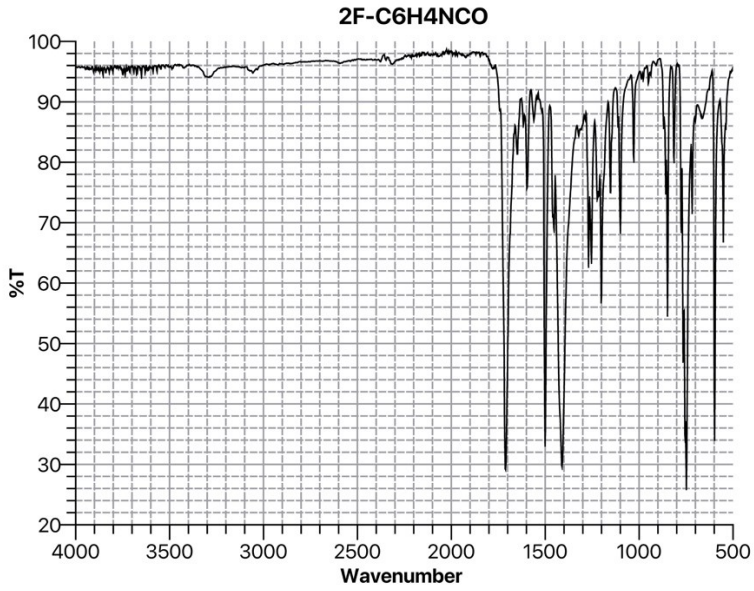
S1.7.3 N,N′,N″-tri(*p*-fluorophenyl)isocyanurate

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 6.88-6.99 (overlapping m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): -115.9 ppm. HRMS (EI) for $[M]^+$: calcd. for $C_{21}H_{12}F_3N_3O_3$: 411.0831; found: 411.0830. IR (ATR):3086 (w), 2980 (w), 2864 (w), 1697 (s), 1600 (m), 1504 (s), 1421 (s), 1408 (s), 1292 (w), 1238 (s), 1207 (s), 1153 (m), 1097 (w), 1056 (w), 1016 (w), 908 (w), 829 (s), 756 (m), 534 (s), 516 (m) cm^{-1}.



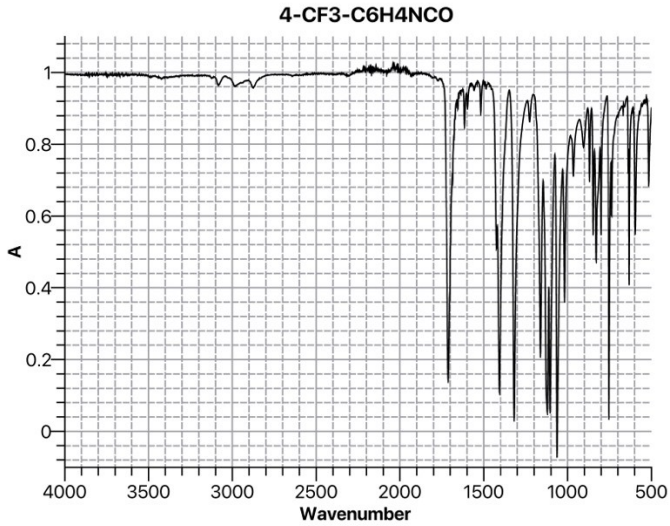
S1.7.4 N,N′,N″-tri(*o*-fluorophenyl)isocyanurate

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 7.23-7.48 (overlapping m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): -122.2 ppm. HRMS (EI) for $[M]^+$: calcd. for $C_{21}H_{12}F_3N_3O_3$: 411.0831; found: 411.0834. IR (ATR): 1710 (s), 1597 (w), 1500 (s), 1452 (w), 1409 (s), 1269 (m), 1253 (m), 1201 (m), 1151 (m), 1099 (m), 1028 (w), 848 (m), 765 (m), 754 (s), 748 (s), 717 (w), 597 (s), 551 (m) cm^{-1}.



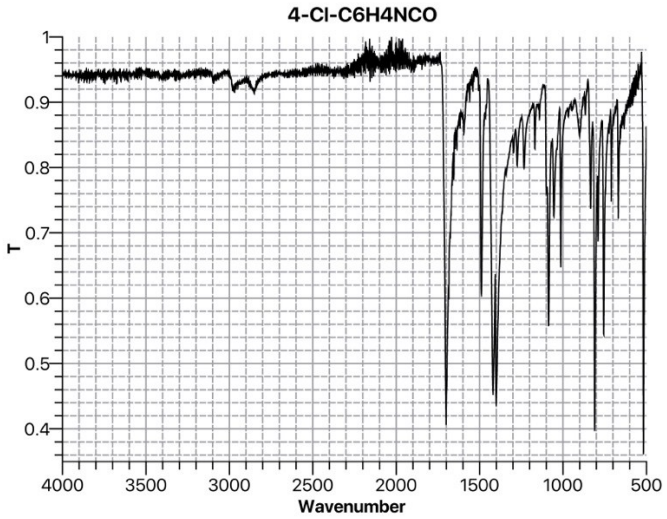
S1.7.5 N,N′,N″-tri{*p*-(trifluoromethyl)phenyl}isocyanurate

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 7.82 (2 H, d, ^{3}J = 8.7 Hz, Ar), 7.58 (2 H, d, ^{3}J = 8.6 Hz, Ar) ppm. ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): –62.8 (3 F, s, CF_3) ppm. HRMS (ASAP) for $[M+H]^+$: calcd. for $C_{24}H_{13}F_9N_3O_3$: 562.0813; found: 562.0814. IR (ATR): 3083 (w), 2980 (w), 2873 (w), 1711 (s), 1406 (s), 1318 (s), 1161 (s), 1120 (s), 1105 (s), 1062 (s), 1017 (m), 965 (w), 903 (w), 869 (w), 847 (m), 829 (m), 800 (m), 752 (s), 736 (m), 632 (m), 596 (m), 516 (m) cm^{-1}.



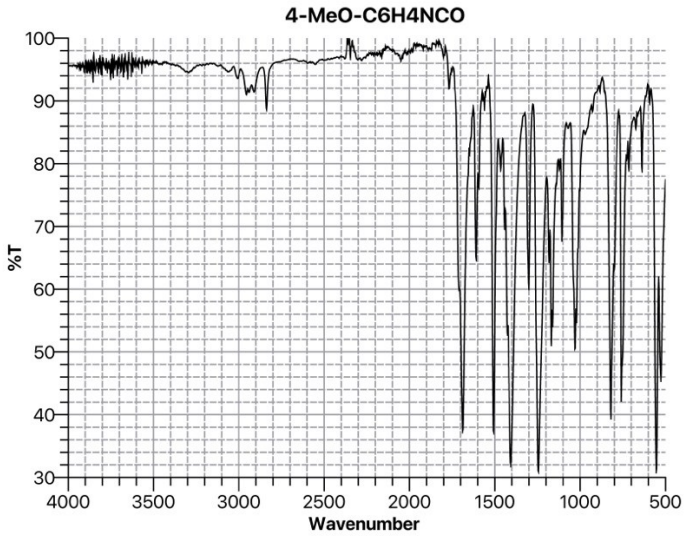
S1.7.6 N,N′,N″-tri(*p*-chlorophenyl)isocyanurate

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 7.49 (2 H, d, ^3J = 9.0 Hz, Ar), 7.33 (2 H, d, ^3J = 8.9 Hz, Ar) ppm. HRMS (ASAP) for $[M+H]^+$: calcd. for $C_{21}H_{13}Cl_3N_3O_3$: 460.0022; found: 460.0030. IR (ATR): 3087 (w), 2964 (w), 2843 (w), 1690 (s), 1478 (m), 1408 (s), 1390 (s), 1265 (w), 1223 (w), 1158 (w), 1076 (s), 1045 (m), 1002 (m), 824 (w), 799 (s), 746 (s), 700 (m), 657 (m), 507 (s) cm^{-1}.



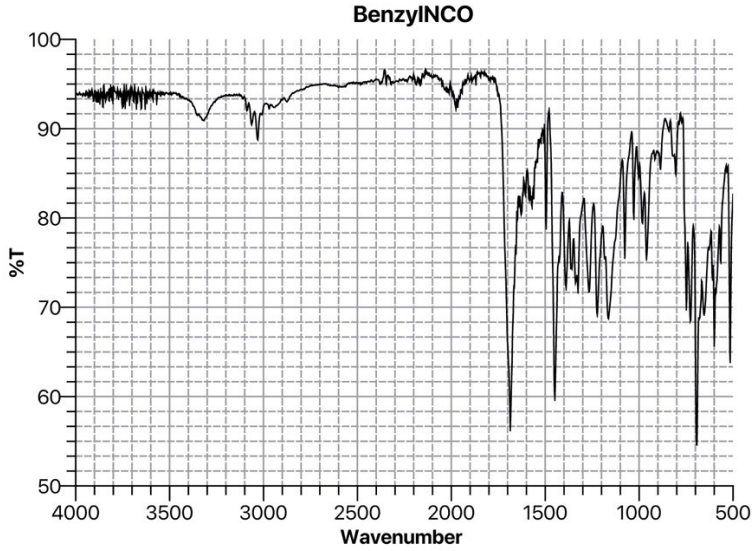
S1.7.7 N,N′,N″-tri(*p*-methoxyphenyl)isocyanurate

^{1}H NMR (500 MHz, $CDCl_3$, 293 K): 7.30 (2 H, d, ^3J = 8.3 Hz, Ar), 7.00 (2 H, d, ^3J = 8.3 Hz, Ar), 3.85 (3 H, s, CH_3) ppm. HRMS (ASAP) for $[M+H]^+$: calcd. for $C_{24}H_{22}N_3O_6$: 448.1509; found: 448.1514. IR (ATR): 3010 (w), 2954 (w), 2951 (w), 2910 (w), 2837 (w), 1687 (s), 1608 (m), 1593 (w), 1506 (s), 1465 (w), 1406 (s), 1300 (m), 1246 (s), 1182 (w), 1168 (m), 1166 (m), 1107 (w), 1029 (s), 1020 (m), 819 (s), 758 (s), 636 (w), 553 (s), 526 (m) cm^{-1}.



S1.7.8 N,N′,N″-tribenzylisocyanurate

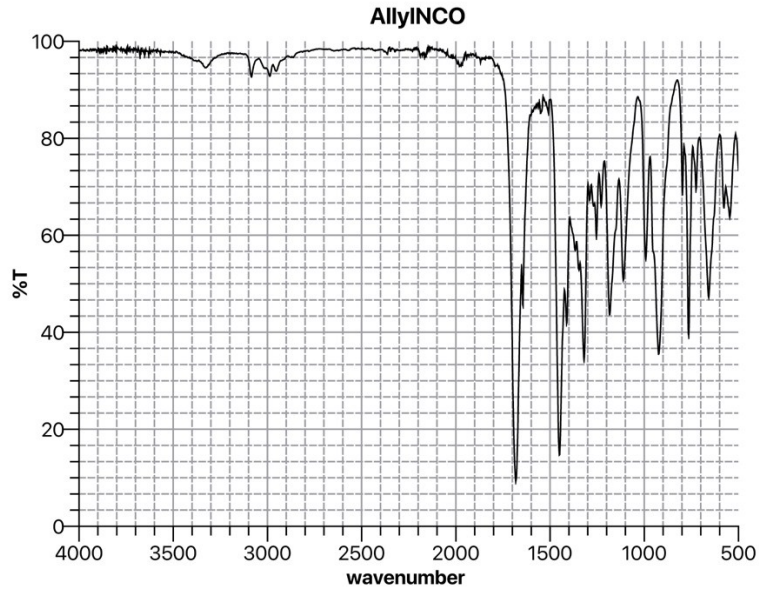
^{1}H NMR (300 MHz, $CDCl_3$, 293 K): 7.52-7.35 (5 H, overlapping, m, C_6H_5), 4.55 (2 H, s, C<u>H</u>$_2$Ph) ppm. HRMS (EI) for $[M]^+$: calcd. for $C_{24}H_{21}N_3O_3$: 399.1583; found: 399.1582. IR (ATR): 1685 (s), 1494 (w), 1448 (s), 1388 (m), 1338 (m), 1325 (m), 1163 (m), 1076 (m), 981 (w), 960 (m), 748 (m), 727 (m), 692 (s), 678 (w), 653 (m), 599 (m), 565 (w), 514 (m) cm^{-1}.



S1.7.9 N,N′,N″-triallylisocyanurate

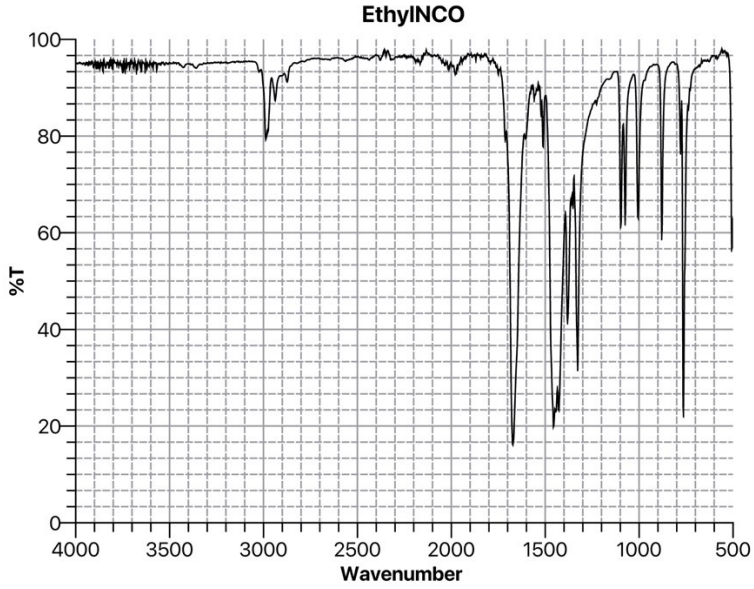
^{1}H NMR (300 MHz, $CDCl_3$, 293 K): 5.89 (1 H, m, C<u>H</u>=CH_2), 5.35 (1 H, d, ^2J = 17.0 Hz, CH=C<u>H</u>$_2$), 5.22 (1 H, d, ^2J = 16.8 Hz, CH=C<u>H</u>$_2$), 3.93 (2 H, m, CH_2) ppm. HRMS (ASAP) for $[M+H]^+$: calcd.

for $C_{12}H_{16}N_3O_3$: 250.1192 found: 250.1203. IR (ATR): 3086 (w), 2981 (w), 2856 (w), 1685 (s), 1602 (w), 1506 (m), 1406 (s), 1319 (m), 1238 (m), 1207 (m), 1186 (w), 1155 (m), 910 (w), 829 (m), 756 (m), 536 (s) cm^{-1}.



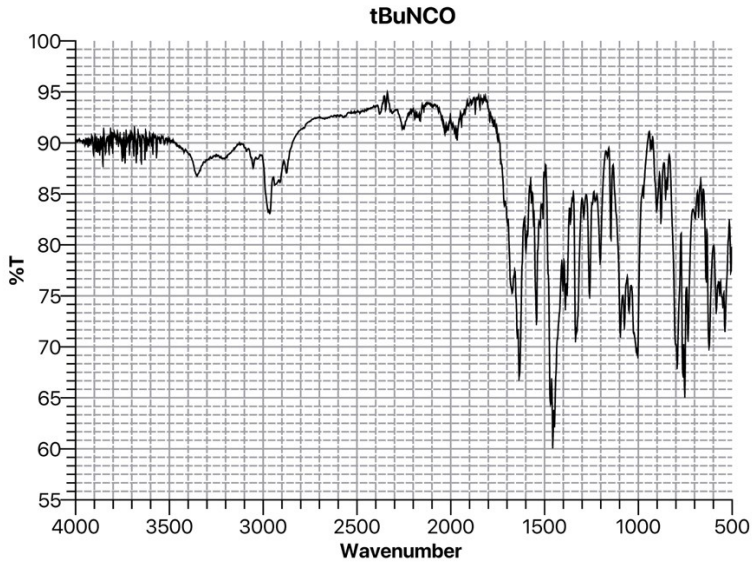
S1.7.10 N,N′,N″-triethylisocyanurate

^{1}H NMR (300 MHz, $CDCl_3$, 293 K): 3.97 (2 H, q, ^3J = 7.1 Hz, CH_2), 1.26 (3 H, t, ^3J = 7.1 Hz, CH_3) ppm. HRMS (EI) for $[M]^+$: calcd. for $C_9H_{15}N_3O_3$: 213.1113; found: 213.1115. IR (ATR): 2987 (w), 1672 (s), 1510 (w), 1456 (s), 1444 (s), 1427 (s), 1381 (m), 1327 (m), 1097 (m), 1074 (m), 1004 (m), 879 (m), 763 (s), 507 (m) cm^{-1}.



S1.7.11 N,N′,N″-tri(*tert*-butyl)isocyanurate

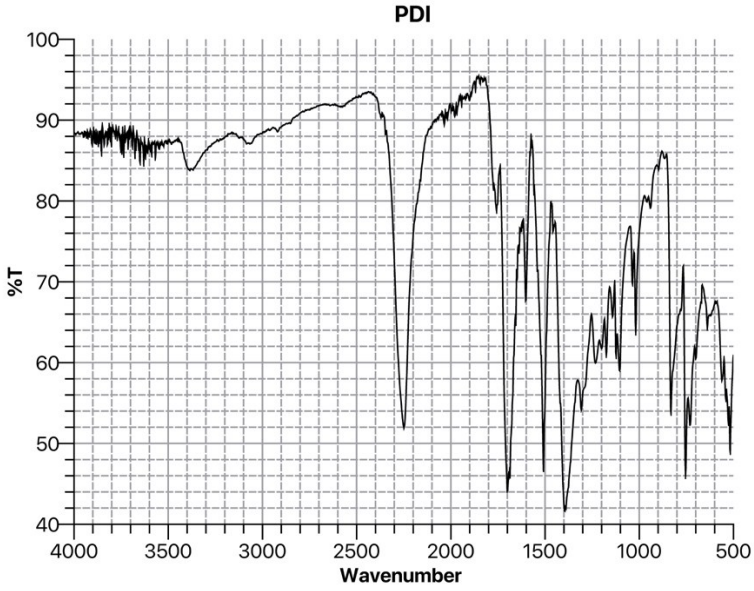
^{1}H NMR (300 MHz, $CDCl_3$, 293 K): 1.38 (9 H, s, CMe_3) ppm. EI-MS (%): $[M]^+$ 297.1 (20). IR (ATR): 3325 (w), 2974 (w), 1674 (m), 1635 (s), 1543 (m), 1456 (s), 1334 (m), 1259 (m), 1203 (m), 1095 (m), 1074 (m), 1008 (s), 792 (s), 752 (s), 734 (m), 507 (w) cm^{-1}.



S1.7.12 N,N′,N″-tri(p-isocyanatophenyl)isocyanurate

^{1}H NMR (300 MHz, $CDCl_3$, 293 K): 7.03 (4 H, overlapping m, 4-C_6H_4NCO) ppm. HRMS (ASAP) for $[M+H]^+$: calcd. for $C_{24}H_{13}N_6O_6$: 481.0897; found: 481.0904. IR (ATR): 2249 (s), 1757 (w), 1697

(s), 1654 (w), 1541 (w), 1508 (s), 1394 (s), 1307 (m), 1232 (w), 1199 (w), 1174 (w), 1103 (w), 1035 (w), 1018 (m), 941 (w), 831 (s), 754 (s), 516 (s) cm^{-1}.



S1.7.13 N,N′,N″-tri(3-isocyanato-4-methyl)phenylisocyanurate / N,N′,N″-tri(3-isocyanato-2-methyl)phenylisocyanurate (75 : 25 mixture of isomers)

^{1}H NMR (300 MHz, $CDCl_3$, 293 K): (major isomer) 7.15 (1 H, d, ^{3}J = 8.1 Hz, Ar), 6.86 (1 H, dd, ^{3}J = 8.2 Hz, ^{4}J = 1.3 Hz, Ar), 6.80 (1 H, s, Ar), 2.32 (3 H, s, Me) ppm; (minor isomer) 7.34 (1 H, d, ^{3}J = 7.9 Hz, Ar), 7.20 (1 H, d, ^{3}J = 8.0 Hz, Ar), 7.18 (1 H, s, Ar) 2.36 (3 H, s, Me) ppm. EI-MS: *m*/*z* (%): 522.12 (10) $[M]^{+}$; Higher order oligomers were detected by MALDI-MS. IR (ATR): 2262 (s), 1685 (s), 1591 (s), 1541 (s), 1406 (s), 1298 (m), 1201 (s), 1076 (w), 873 (m), 810 (m), 752 (s), 590 (m), 553 (s) cm^{-1}.

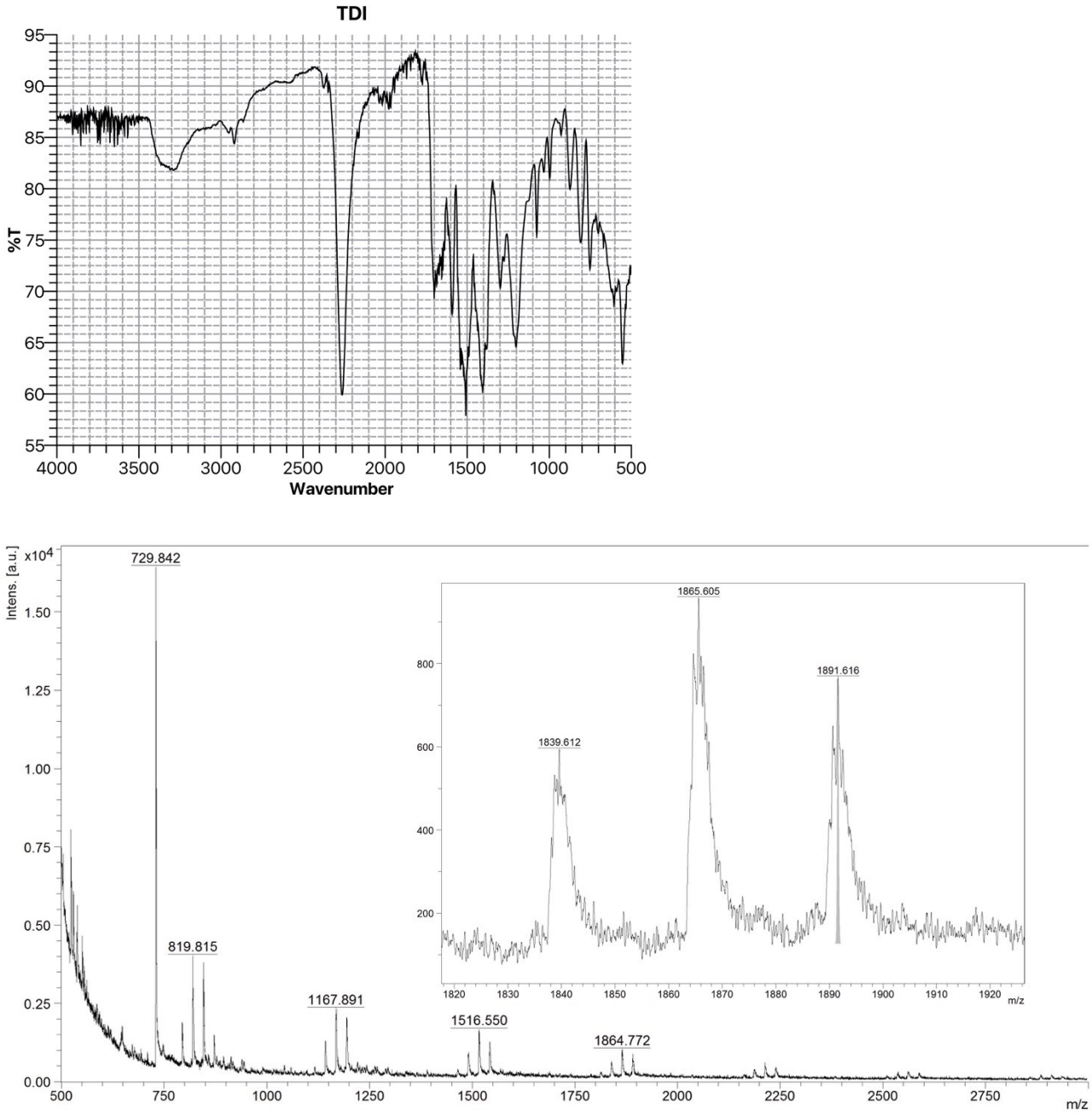


Figure 6 MALDI-mass spectrum of TDI oligomers. The principal separation between ions corresponds to two TDI units (*i.e.* successively linked isocyanurate trimers). The mass distribution of each ion group corresponds to loss of different numbers of NCO termini in favor of NH_2 groups (one of which is protonated to give an ion). The *m/z* of 819 corresponds to 5 TDI units with two NCO groups replaced by NH_2.

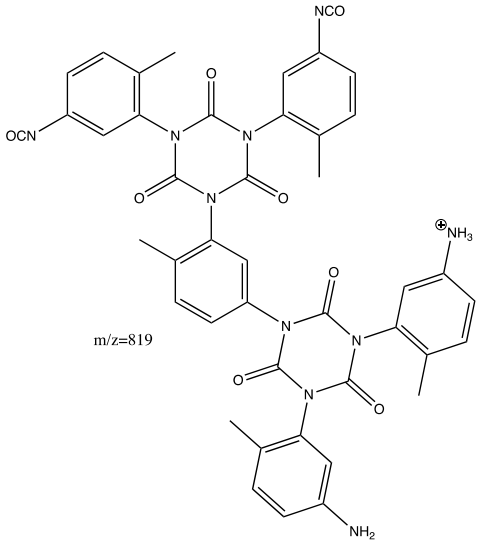
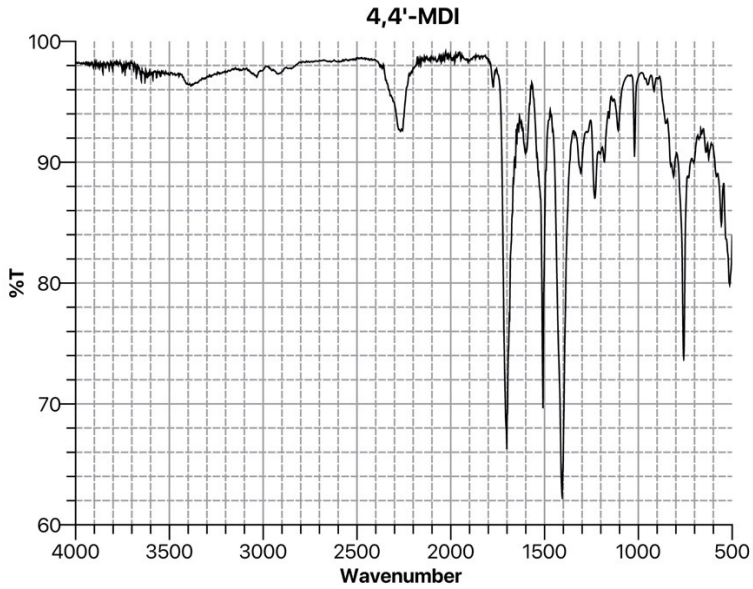


Figure 7 TDI oligomer: ion corresponding to *m/z*=819 in the MALDI mass spectrum

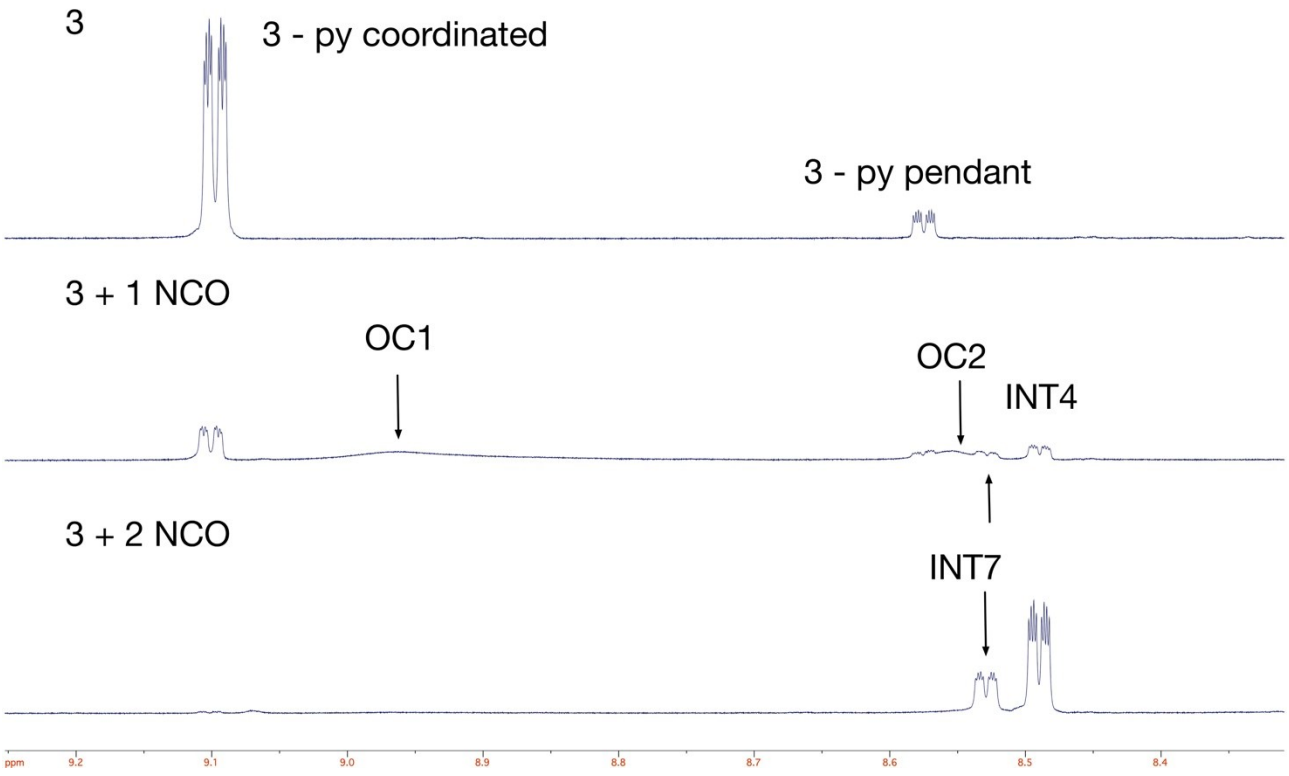
S1.7.14 N,N′,N″-tri(isocyanatephenylmethyl)isocyanurate

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 7.13 (2 H, d, ^3J = 8.7 Hz, Ar), 7.04 (2 H, d, ^3J = 8.6 Hz, Ar), 3.95 (2 H, s, CH_2) ppm. HRMS (ASAP) for $[M+H]^+$: calcd. for $C_{45}H_{30}N_6O_6$: 751.2305; found: 751.2302. IR (ATR): 2268 (w), 1701 (s), 1597 (w), 1508 (s), 1406 (s), 1305 (w), 1232 (w), 1180 (w), 1107 (w), 1020 (w), 812 (w), 758 (m), 513 (m) cm^{-1}. Evidence for an MDI pentamer (presumably two methylene-bridged isocyanurates) seen in MALDI-MS: m/z = 1273.8 $[M+Na]^+$.



S1.8 Stoichiometric NMR tube scale reactions for mechanism verification

The validity of the calculated mechanism was verified by NMR tube experiments of [Al(Salpy)(OBn)] (**3**) (10 mg) in $CDCl_3$ (0.6 mL) with sequential addition of 1 eq. PhNCO (up to 3 eq.). The H^6 resonance was the most useful in identifying key components, as follows.



Before PhNCO added: two isomers, H^6 at 9.10 and 8.58 ppm.

Addition of 1 eq. PhNCO: there was an immediate reduction in relative intensity of signals for **3**, and appearance of several other species: one with a broad H^6 resonance at 8.96 (tentatively assigned to **INT4**, broad due to exchange equilibria), and a second, smaller intensity species with H^6 resonance at 8.49 ppm (presumably **OC1**). Two minor components were also observed with H^6 = 8.53 (see below) and 8.55 (broad) ppm (assigned to **INT7** and **OC2**).

Addition of 2nd eq. PhNCO: almost complete disappearance of signals for **3**, signals for **INT4** still present alongside signals at 8.53 (as seen above) which are increased in intensity (**INT7**).

Addition of 3rd PhNCO: returns to complex **3**.

Summary conclusion: Data are consistent with stepwise addition of isocyanate generating a new species after each equivalent of PhNCO was added, with secondary species often observed consistent with varying states of coordinated/pendant pyridyl donors. None of the species could be isolated in a pure form, presumably because the species are in equilibrium prior to the final cyclization step. These data are consistent with the stepwise coordination-insertion mechanism proposed on the basis of DFT data. Pre-coordination of isocyanate was not observed, nor is it expected since isocyanate coordination is predicted to be synchronous with the corresponding insertion, again consistent with the calculated mechanism.

S2. Crystal Structures Determined from Single-Crystal X-ray Diffraction

Table 2 Crystallographic data and refinement parameters

	1	**2**	**4**	**$(PhNCO)_3$**	**$(TolNCO)_3$**	**$(FC_6H_4NCO)_3\cdot THF$**
Formula	$C_{23}H_{23}N_3O_2$	$C_{24}H_{24}AlN_3O_2\cdot C_6H_6$	$C_{30}H_{28}AlN_3O_3$	$C_{21}H_{15}N_3O_3$	$C_{24}H_{21}N_3O_3$	$C_{25}H_{20}F_3N_3O_4$
Formula weight	373.44	491.55	505.53	357.36	399.44	483.44
Crystal size/mm	0.220 × 0.210 × 0.150	0.175 × 0.106 × 0.098	0.140 × 0.030 × 0.030	0.422 × 0.306 × 0.118	0.263 × 0.210 × 0.112	0.333 × 0.324 × 0.102
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Trigonal	Monoclinic
Space group	*C c*	$P\bar{1}$	$P\bar{1}$	*Fdd*2	*R*3*c*	$P2_1/n$
a/Å	19.1233(13)	8.9816(6)	13.4154(6)	23.3812(16)	12.6283(3)	13.5703(5)
b/Å	11.8499(8)	10.2889(7)	13.5031(6)	37.1191(18)	12.6283(3)	11.6337(5)
c/Å	8.8509(6)	14.1189(10)	14.8493(7)	7.7220(5)	26.6110(10)	14.6589(6)
α/°	90	71.196(3)	79.454(4)	90	90	90
β/°	108.5430(10)	84.480(3)	76.691(4)	90	90	98.895(4)
γ/°	90	88.775(3)	75.227(4)	90	120	90
V/Å^3	1901.6(2)	1229.31(15)	2509.0(2)	6701.8(7)	3675.2(2)	2286.41(16)
Z	4	2	4	16	6	4
D_c/Mg m^{-3}	1.304	1.328	1.338	1.417	1.083	1.404
μ/mm^{-1}	0.085	0.117	0.119	0.097	0.073	0.113
T/K	100(2)	100(2)	100(2)	100(2)	150(2)	150(2)
F(000)	792	520	1064	2976	1260	1000
Refl. collected	10893	26329	17593	12736	6299	12060
Refl. indep. (R_{int})	3659 (0.0227)	5623 (0.0377)	17593 (0)	3863 (0.0361)	2022 (0.0153)	5424 (0.0255)
Data/rest./par.	3659 / 4 / 262	5623 / 72 / 327	17593 / 0 / 672	3863 / 1 / 244	2022 / 1 / 92	5424 / 0 / 316
GooF on F^2	1.068	1.007	1.043	1.100	1.061	0.987
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0309, wR_2 = 0.0784	R_1 = 0.0385, wR_2 = 0.1052	R_1 = 0.0756, wR_2 = 0.1837	R_1 = 0.0419, wR_2 = 0.0972	R_1 = 0.0358, wR_2 = 0.0957	R_1 = 0.0468, wR_2 = 0.1055
R indices (all data)	R_1 = 0.0312, wR_2 = 0.0786	R_1 = 0.0396, wR_2 = 0.1063	R_1 = 0.1095, wR_2 = 0.2050	R_1 = 0.0521, wR_2 = 0.1046	R_1 = 0.0374, wR_2 = 0.0971	R_1 = 0.0703, wR_2 = 0.1233
Largest residual peak and hole/e Å^{-3}	0.175 and –0.220	0.383 and –0.294	1.362 and –0.358	0.209 and –0.238	0.161 and –0.167	0.200 and –0.203

	$(F_3CC_6H_4NCO)_3$	**$(MeOC_6H_4NCO)_3$**	**$(TolNCO)_2$**	**$(MeOC_6H_4NCO)_2$**	**$(MeOC_6H_4NCO)_2$**
Formula	$C_{24}H_{12}F_9N_3O_3$	$C_{24}H_{21}N_3O_6$	$C_{16}H_{14}N_2O_2$	$C_{16}H_{14}N_2O_4$	$C_{16}H_{14}N_2O_4$
Formula weight	561.37	447.44	266.29	298.29	298.29
Crystal size/mm	0.291 × 0.212 × 0.164	0.283 × 0.205 × 0.195	0.360 × 0.220 × 0.040	0.366 × 0.289 × 0.186	0.524 × 0.267 × 0.072
Crystal system	Trigonal	Trigonal	Monoclinic	Monoclinic	Orthorhombic
Space group	$R\bar{3}c$	$R3c$	$C2/m$	$P2_1/c$	$Pbca$
a/Å	16.3987(7)	13.1448(5)	12.3706(9)	15.9239(11)	7.3989(3)
b/Å	16.3987(7)	13.1448(5)	11.2198(7)	5.4001(4)	5.9654(4)
c/Å	18.1743(13)	26.2723(11)	4.8807(3)	8.0430(6)	31.5160(16)
α/°	90	90	90	90	90
β/°	90	90	103.853(6)	99.750(7)	90
γ/°	120	120	90	90	90
V/Å^3	4232.6(5)	3931.3(3)	657.72(8)	681.63(8)	1391.03(13)
Z	6	6	2	2	4
D_c/Mg m^{-3}	1.321	1.134	1.345	1.453	1.424
μ/mm^{-1}	0.128	0.083	0.090	0.106	0.104
T/K	150(2)	150(2)	100(2)	150(2)	150(2)
F(000)	1692	1404	280	312	624
Refl. collected	7152	6859	7323	5462	11260
Refl. indep. (R_{int})	1238 (0.0243)	2162 (0.0185)	798 (0.0619)	1680 (0.0307)	1770 (0.0349)
Data/rest./par.	1238 / 48 / 76	2162 / 1 / 101	798 / 0 / 54	1680 / 0 / 102	1770 / 0 / 101
GooF on F^2	1.119	1.118	1.141	1.037	1.148
Final R indices [I>2σ(I)]	R_1 = 0.0781, wR_2 = 0.2686	R_1 = 0.0428, wR_2 = 0.1304	R_1 = 0.0480, wR_2 = 0.1501	R_1 = 0.0449, wR_2 = 0.1232	R_1 = 0.0519, wR_2 = 0.1226
R indices (all data)	R_1 = 0.0997, wR_2 = 0.2951	R_1 = 0.0472, wR_2 = 0.1346	R_1 = 0.0504, wR_2 = 0.1553	R_1 = 0.0614, wR_2 = 0.1427	R_1 = 0.0707, wR_2 = 0.1347
Largest residual peak and hole/e Å^{-3}	0.305 and –0.343	0.175 and –0.162	0.582 and –0.307	0.243 and –0.187	0.204 and –0.207

S2.2 Structure of H_2Salpy (1)

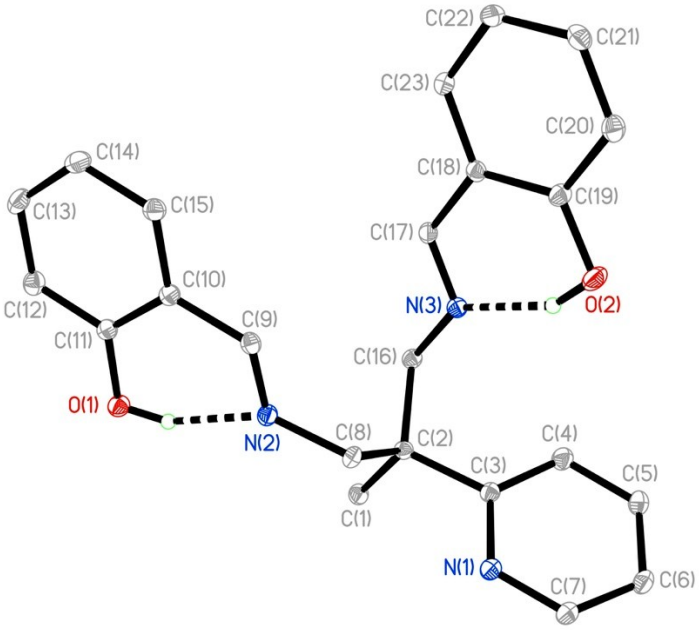


Figure 8 Molecular structure of H_2Salpy. Thermal ellipsoids drawn at 30% probability and H atoms omitted for clarity

S2.3 Structure of [Al(Salpy)Me] (2)

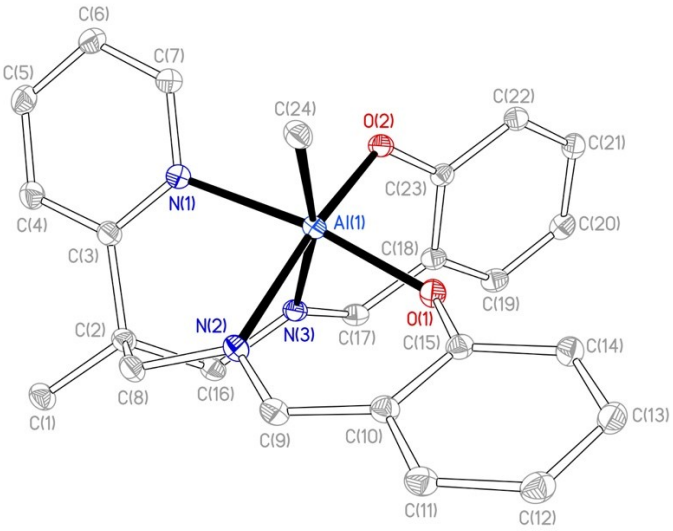


Figure 9 Molecular structure of [Al(Salpy)Me] (**2**). Thermal ellipsoids are drawn at 30% probability. H atoms and solvent molecules included in the crystal structure are omitted for clarity

S2.4 Structure of [Al(Salpy)(OTol)] (4)

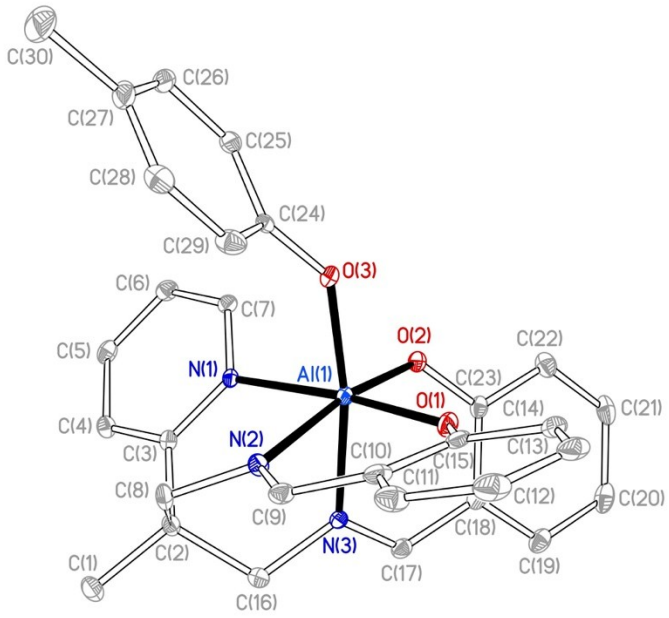


Figure 10 Molecular structure of [Al(Salpy)(OTol)] (**3**). Thermal ellipsoids are drawn at 30% probability. H atoms and the other crystallographically independent molecule are omitted for clarity

S2.5 Principal metric parameters for 2 and 4

Table 3 Selected bond lengths (Å) and angles (°) for [Al(Salpy)Me] (**2**) and [Al(Salpy)(OTol)] (**4**). Numbers in parentheses relate to the equivalent parameters for the crystallographically independent molecule in the asymmetric unit

	2	**4**
Al(1)–N(1)	2.1375(10)	2.128(3) [2.129(3)]
Al(1)–N(2)	2.0829(10)	2.033(3) [2.041(3)]
Al(1)–N(3)	2.0692(10)	2.071(3) [2.066(3)]
Al(1)–O(1)	1.8533(9)	1.837(2) [1.837(2)]
Al(1)–O(2)	1.8550(8)	1.843(2) [1.844(2)]
Al(1)–C(24)	2.0260(12)	–
Al(1)–O(3)	–	1.814(2) [1.811(2)]
N(1)–Al(1)–O(1)	169.76(4)	174.79(12) [175.10(11)]
N(2)–Al(1)–O(2)	167.52(4)	168.09(12) [168.38(12)]
N(3)–Al(1)–C(24)	166.52(5)	–
N(3)–Al(1)–O(3)	–	167.14(11) [166.58(11)]
N(1)–Al(1)–N(2)	87.82(4)	87.36(12) [87.77(11)]
N(1)–Al(1)–N(3)	78.65(4)	79.57(10) [79.28(10)]
N(1)–Al(1)–O(2)	92.44(4)	91.15(11) [90.95(10)]
O(1)–Al(1)–O(2)	90.30(4)	91.34(11) [90.75(11)]
N(2)–Al(1)–O(1)	87.38(4)	89.26(12) [89.65(11)]

N(1)–Al(1)–C(24)	89.64(4)	–
N(1)–Al(1)–O(3)	–	87.69(11) [87.43(10)]
Al(1)–O(3)–C(24)	–	137.9(2) [126.4(2)]

S2.6 Structure of $(PhNCO)_3$

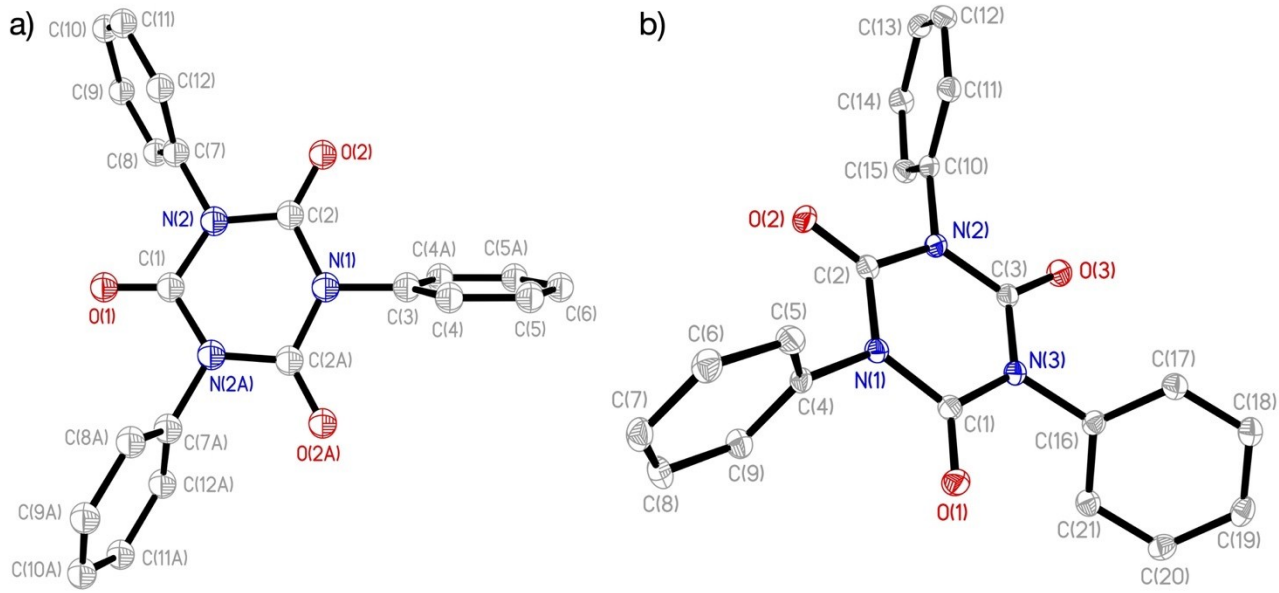


Figure 11 Molecular structure of N,N′,N″-triphenylisocyanurate. a) from Rietveld refinement (powder X-ray refinement); b) from single-crystal refinement with thermal ellipsoids are drawn at 30% probability. H atoms omitted for clarity

S2.7 Structure of $(p\text{-}C_6H_4Me\text{-}NCO)_3$

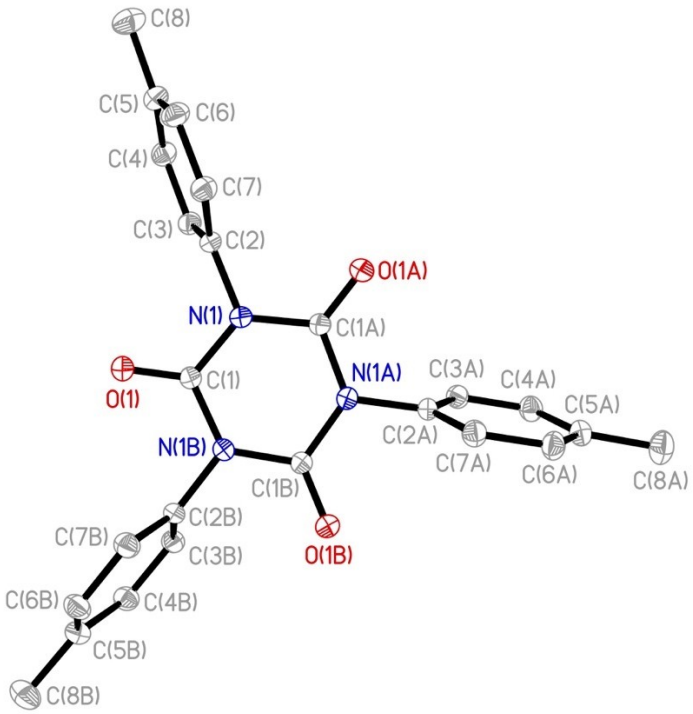


Figure 12 Molecular structure of N,N′,N″-tri(4-tolyl)isocyanurate. Thermal ellipsoids are drawn at 30% probability. H atoms omitted for clarity

S2.8 Structure of (p-C_6H_4F-NCO)$_3$

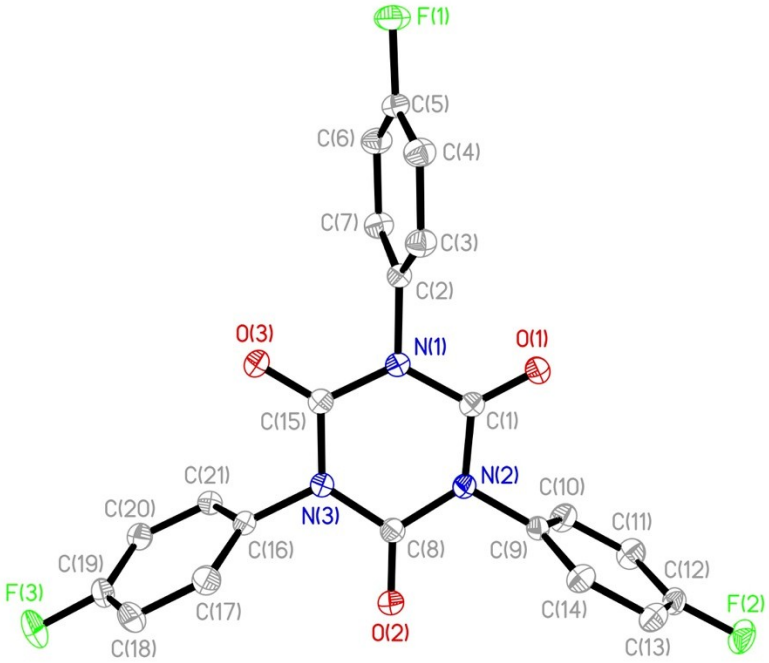


Figure 13 Molecular structure of N,N′,N″-tri(4-fluorophenyl)isocyanurate. Thermal ellipsoids are drawn at 30% probability. H atoms and solvent molecules included in the crystal structure are omitted for clarity

S2.9 Structure of (p-$C_6H_4CF_3$-NCO)$_3$

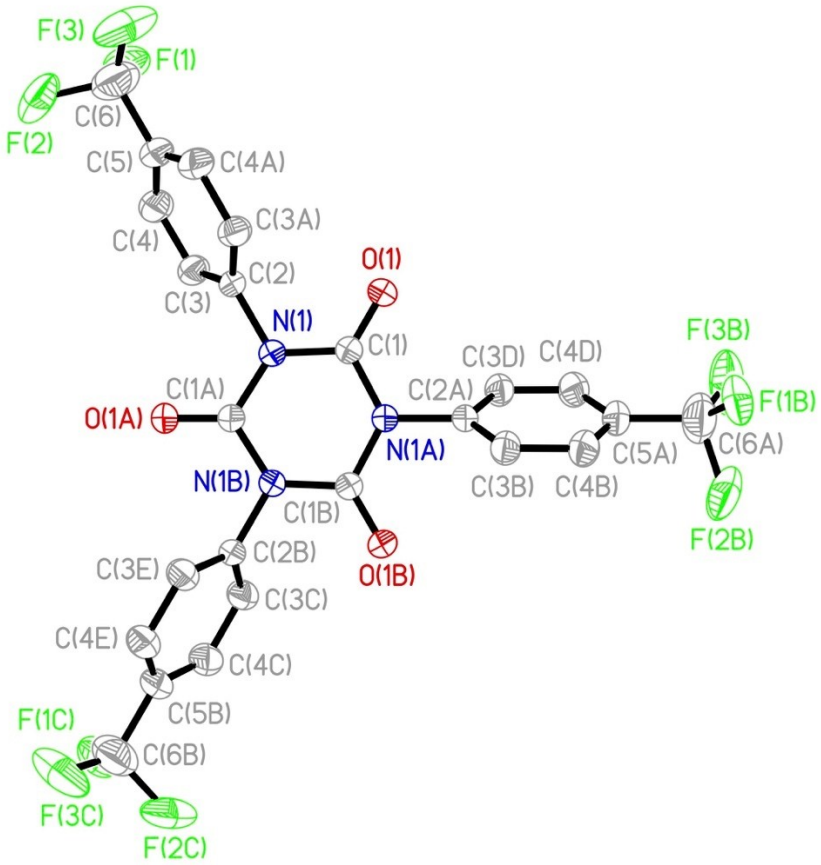


Figure 14 Molecular structure of N,N′,N″-tri{4-(trifluoromethyl)phenyl}isocyanurate. Thermal ellipsoids are drawn at 30% probability. H atoms omitted for clarity

S2.10 Structure of (p-C_6H_4OMe-NCO)$_3$

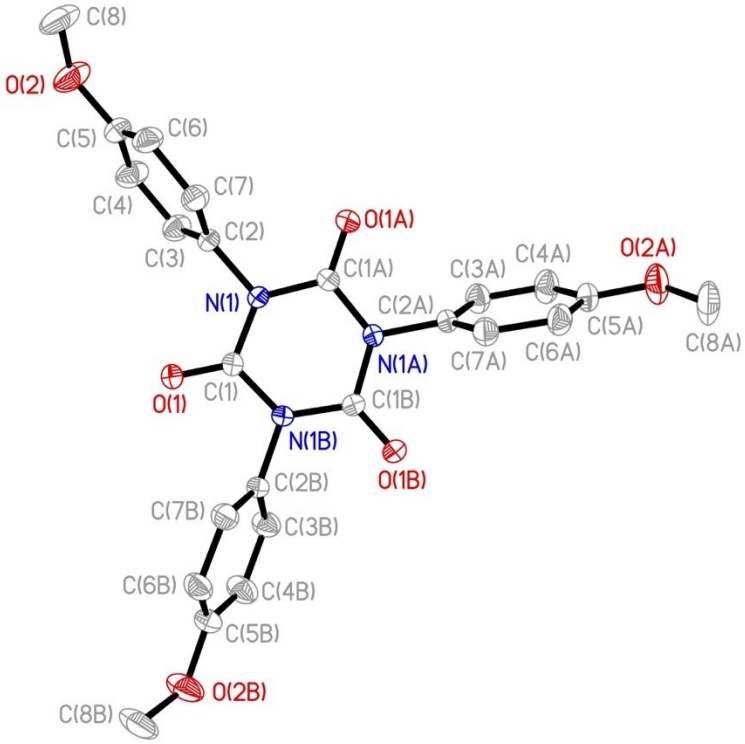


Figure 15 Molecular structure of N,N′,N″-tri(4-methoxyphenyl)isocyanurate. Thermal ellipsoids are drawn at 30% probability. H atoms omitted for clarity

S2.11 Structure of (p-C_6H_4Me-NCO)$_2$

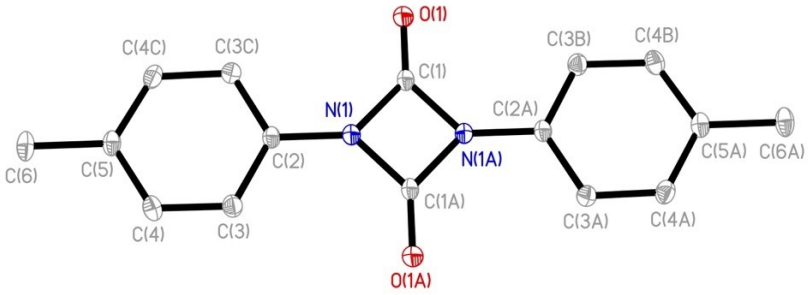


Figure 16 Molecular structure of 1,3-di(4-tolyl)-2,4-uretidinedione. Thermal ellipsoids drawn at 30% probability and H atoms omitted for clarity

S2.12 Structure of (p-C_6H_4OMe-NCO)$_2$

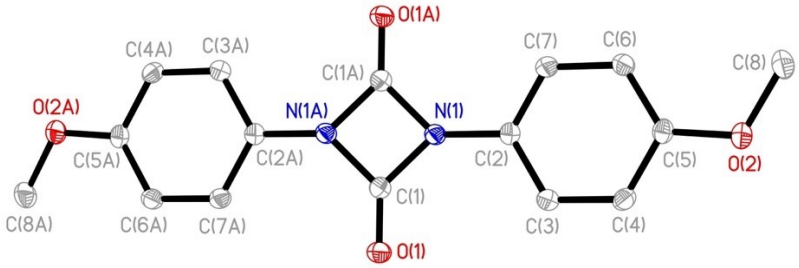


Figure 17 Molecular structure of 1,3-di(4-methoxyphenyl)-2,4-uretidinedione (monoclinic polymorph). Thermal ellipsoids drawn at 30% probability and H atoms omitted for clarity

S3. Calculation data

S3.1 Calculated free energy profile

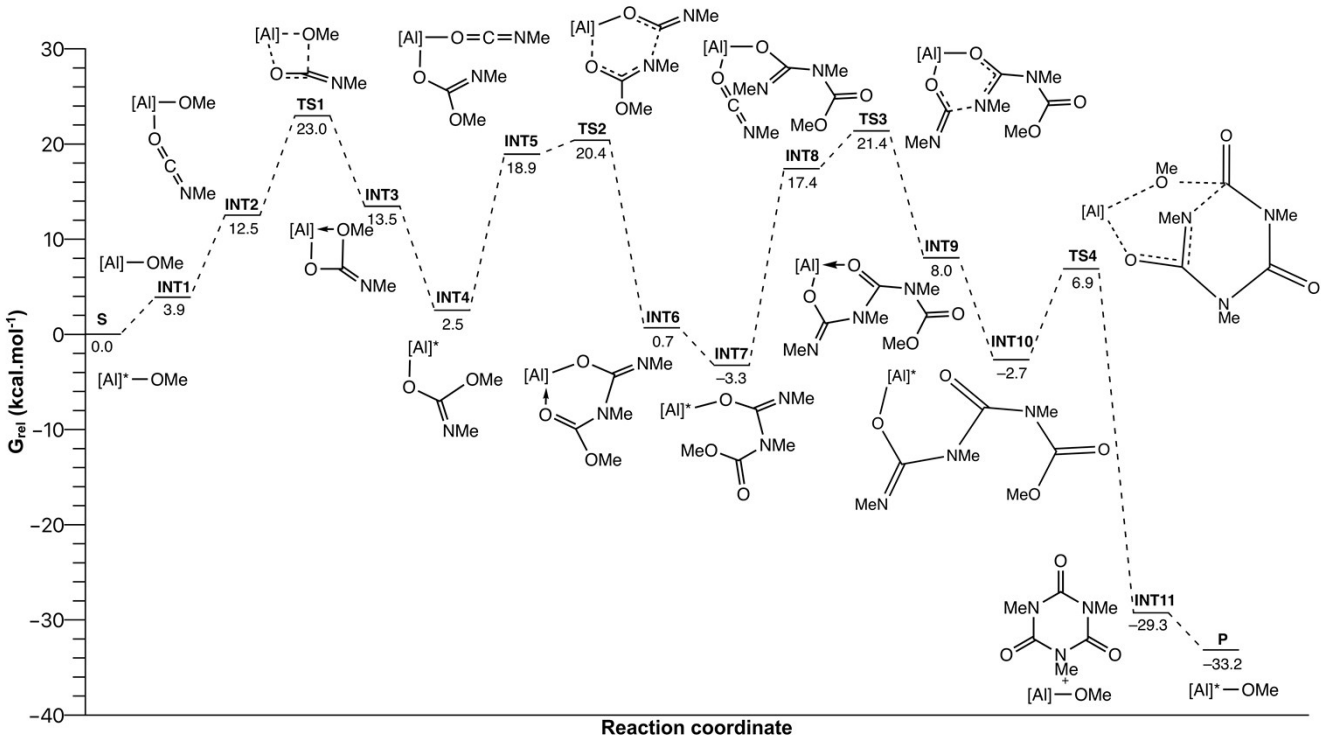


Figure 18 Calculated free energy profile of the trimerization of MeNCO using [Al(Salpy)(OMe)] ($\mathbf{5}_{calc}$). [Al] denotes [Al(κ^4-Salpy)] and [Al]* denotes [Al(κ^5-Salpy)] [M06-2X : cc-pVTZ/cc-pV(T+d)Z]

S3.2 Substrate binding and transition state orbital contribution structures

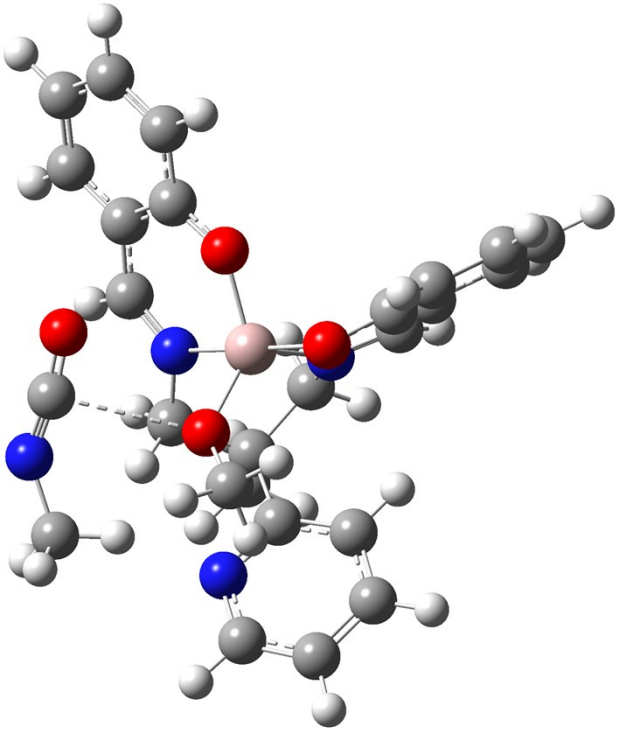


Figure 19 Calculated structure of **INT2** [M06-2X : cc-pVTZ/cc-pV(T+d)Z]

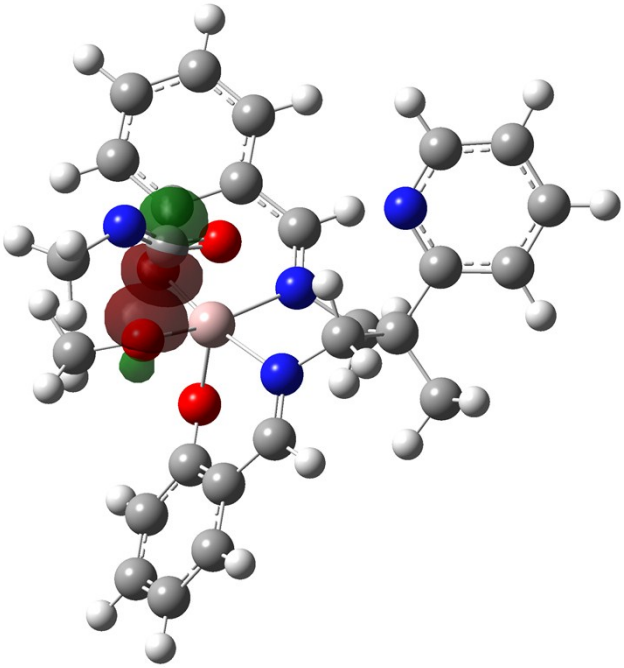


Figure 20 Donor-acceptor NBOs in **TS1** [M06-2X : cc-pVTZ/cc-pV(T+d)Z]

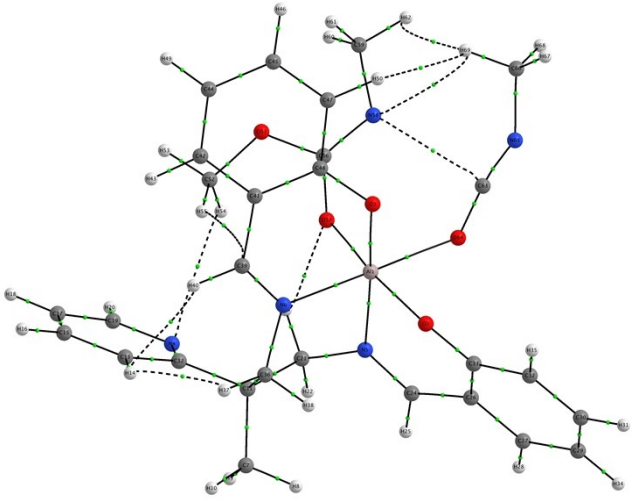


Figure 21 Calculated structure of **INT5**, showing bond critical points [M06-2X : cc-pVTZ/cc-pV(T+d)Z]

S3.3 Cartesian coordinates of calculated species

[Al(κ^5-Salpy)OMe] (S)

Al	-0.085613796451	-0.121390087790	0.455619052451
O	0.536681524816	1.532591133185	0.973449047066
O	-1.682764645098	0.583040439564	-0.145814740674
N	1.796139067566	-0.983406414095	0.816850765353
N	0.837751109270	0.206283275848	-1.363328051060
N	-0.617789756885	-1.908067066076	-0.374097747706
C	2.434667523592	-3.127291068315	-2.186333398051
H	3.365365137820	-2.691603586692	-2.546599047204
H	1.826634660755	-3.381693681473	-3.054269731794
H	2.664423926957	-4.048900765929	-1.651031864472
C	1.666932135502	-2.152748565187	-1.299190226141
C	2.468931087377	-1.713037355050	-0.087470492591
C	3.789778253711	-2.075584988192	0.138358643441
H	4.327644651431	-2.665220240080	-0.586658507686
C	4.411010690442	-1.682746144651	1.313967303543
H	5.439427137047	-1.959517006749	1.500693311305
C	3.700115944080	-0.944536214309	2.244777681532
H	4.144459163497	-0.626974729982	3.175850863504
C	2.389685378947	-0.615271589062	1.953167351766
H	1.774683088788	-0.037472286968	2.629011857556
C	1.255392080888	-0.941499464609	-2.164769031227
H	2.087322431578	-0.659376775822	-2.811941808647
H	0.424414635319	-1.257117063405	-2.801912761319
C	1.070575024958	1.372324657560	-1.833252215117
H	1.516337349282	1.463047412861	-2.826416005171

C	0.820192610737	2.611103584606	-1.135731412096
C	0.913841300762	3.814593627032	-1.848349448972
H	1.117253825468	3.770277886903	-2.911967280421
C	0.749221980639	5.031014042681	-1.223961293136
H	0.811239711598	5.952770813027	-1.783720763392
C	0.513034230203	5.049175188676	0.155484593940
H	0.389144442345	5.997268036939	0.663268944031
C	0.440664690827	3.881348870888	0.883625636640
H	0.266442111225	3.898394949017	1.951408247268
C	0.583705258604	2.623259646153	0.262742150879
C	0.399781026810	-2.868927046124	-0.787917660781
H	0.005693678524	-3.503279093545	-1.584284924854
H	0.663835668629	-3.509816384137	0.056602833987
C	-1.843158467689	-2.257137790765	-0.490750366942
H	-2.069966088808	-3.264032295203	-0.848162004636
C	-2.981729139805	-1.416196668641	-0.213448845635
C	-4.254799204237	-2.004395865278	-0.182472878265
H	-4.330744505103	-3.077420142827	-0.314510205231
C	-5.388376425541	-1.248507046671	0.014306780558
H	-6.363188379901	-1.712550068408	0.048875708310
C	-5.253293425256	0.137948125108	0.155167585091
H	-6.135554153331	0.747874378656	0.302405019906
C	-4.017281744388	0.744152519184	0.103629907601
H	-3.915754133822	1.816633856987	0.204748462014
C	-2.839318430634	-0.011527665072	-0.074456853781
O	-0.617056628911	-0.644943247664	2.075803029457

C	-1.251184909032	0.216182806064	2.966023956834
H	-1.782077067083	-0.350321483896	3.740322482046
H	-0.542894562441	0.883068365977	3.477937498830
H	-1.991487075581	0.862246275753	2.472070852092

INT1

Al	-0.851279560843	0.794830577127	0.343516132255
O	-2.512748931273	1.056038938442	-0.245889773000
O	-0.436054255918	2.540663522842	0.016122001256
N	3.135131401216	-1.899184133473	-0.970048844071
N	-1.250887263615	-1.198564343301	0.463517224157
N	0.610153224932	0.230449995274	-0.870962090781
C	0.257349086453	-3.522574094004	-1.244896778566
H	-0.815151043934	-3.457747591181	-1.439005497440
H	0.445647820832	-4.402476371604	-0.630595528224
H	0.770772264083	-3.650944933005	-2.198450893152
C	0.747696361832	-2.252613584183	-0.536965565145
C	2.216291966865	-2.435796160780	-0.169547635419
C	2.570244608736	-3.190846758124	0.949703777265
H	1.808450825113	-3.625531316550	1.582121366762
C	3.908436651120	-3.384133858105	1.239402580917
H	4.202100445652	-3.966840473154	2.101761664088
C	4.863834918404	-2.818721581133	0.407138842677
H	5.920560079989	-2.939731119610	0.594911068453
C	4.424072036960	-2.087535158261	-0.682070056447
H	5.135238711521	-1.628109706560	-1.358342296257

C	-0.083468184283	-2.017173678841	0.752137490929
H	-0.382412671458	-2.972335185073	1.187870964333
H	0.508094636269	-1.471563057852	1.485832280991
C	-2.404264554291	-1.746171126270	0.404026514155
H	-2.496558114189	-2.814645551093	0.608207871868
C	-3.620604255480	-1.044948495904	0.072921416115
C	-4.824455731210	-1.762962758761	0.050233020798
H	-4.801636336754	-2.816675728986	0.301105894668
C	-6.012695601564	-1.153121894787	-0.284297949845
C	-6.001380673282	0.206619120379	-0.609533949035
H	-6.926438225187	0.700400402337	-0.877258155142
C	-4.829757357651	0.934126714898	-0.595699304379
C	-3.609191703574	0.330962312305	-0.249995336429
H	-6.935770256156	-1.713763753918	-0.298089131350
H	-4.820931280188	1.985970121561	-0.846779295184
C	0.546665611877	-1.085214865215	-1.513247095506
H	1.282949051520	-1.151268182192	-2.310129145849
H	-0.444953804964	-1.178614019082	-1.956175278272
C	1.647806674873	0.957644168707	-1.103699552357
H	2.447466004312	0.528288206152	-1.705789948945
C	1.835474986114	2.308312561755	-0.651977710980
C	3.093097731957	2.909224688542	-0.827508065732
H	3.895596099286	2.315010202054	-1.248182010322
C	3.309607737693	4.218961295575	-0.471184118935
C	2.239488934087	4.961904132258	0.046727235013
H	2.395188301339	5.996778783937	0.323204776942

C	0.990598931248	4.404970651055	0.207109246150
C	0.752587913951	3.056685751771	-0.126629743173
H	4.281578087770	4.672702133698	-0.597074108086
H	0.165073274628	4.982250788079	0.601068983348
O	-0.448088669306	0.746599459756	2.040228040793
C	0.163392478743	1.762586216733	2.783770088857
H	-0.320643488710	2.734513194872	2.639816849843
H	0.120859379030	1.522319962007	3.849839123841
H	1.220415725429	1.886745578885	2.516560401547

INT2

Al	-0.241245234477	0.452114087876	0.256700538516
O	-1.917157198134	1.058166227296	0.131475704214
O	0.364914570441	2.129157428919	0.658632461003
N	2.838304255369	-2.509371773383	0.507352597463
N	-0.857245607423	-1.371208306214	-0.385486815486
N	0.709284459675	0.532232974688	-1.479526486112
C	1.867638230186	-3.010625300267	-2.275593475958
H	1.091188639145	-3.234387629286	-3.008309599666
H	2.070424148580	-3.909148862767	-1.694721997166
H	2.778274147215	-2.727895589481	-2.804095780127
C	1.408589997571	-1.878850300724	-1.339322540435
C	2.595019192208	-1.583475548468	-0.422042461312
C	3.451607670174	-0.500854380328	-0.608204065738
H	3.260532358806	0.240634865408	-1.368179166252
C	4.578919968733	-0.384397604539	0.191593266304

H	5.254526627516	0.449412294297	0.057348111690
C	4.826164680998	-1.346754404730	1.155334680799
H	5.691205448662	-1.296282591076	1.800099349396
C	3.918500065250	-2.388635480525	1.273142221895
H	4.067053440974	-3.164488342414	2.015872227714
C	0.175328184959	-2.392996261654	-0.550444843953
H	-0.254322037116	-3.246708189112	-1.077763061250
H	0.498043782898	-2.719553221763	0.434963336083
C	-2.065876819519	-1.702841791798	-0.643404660225
H	-2.269353618608	-2.722403446508	-0.976523690949
C	-3.212958412050	-0.837461254525	-0.529466991038
C	-4.478915445113	-1.364931957479	-0.816799711683
H	-4.549761491136	-2.403227457438	-1.118219376073
C	-5.613900902676	-0.590652355111	-0.717386165257
C	-5.483092376038	0.744161035823	-0.323137765716
H	-6.364871830439	1.366195024448	-0.239808957792
C	-4.246983638693	1.286455271657	-0.038080503606
C	-3.079963573131	0.510905291555	-0.134015099511
H	-6.586242558405	-1.005464694921	-0.939181274831
H	-4.145589577961	2.319355173226	0.266078465442
C	1.013300075100	-0.697188144397	-2.227972851887
H	1.804787132130	-0.494897708071	-2.951335262565
H	0.124899223588	-0.988443430270	-2.793123988150
C	0.958818510656	1.646194463826	-2.076112402715
H	1.358059131204	1.606441906620	-3.091039803708
C	0.789364471508	2.959439437732	-1.524785193156

C	0.989588090831	4.071876757825	-2.360257989061
H	1.213816168164	3.899708016699	-3.406165603974
C	0.902069018025	5.351831106578	-1.868889809831
C	0.631492643254	5.533338795329	-0.504738004880
H	0.567313084205	6.537195831564	-0.104972659300
C	0.450042592184	4.462154035799	0.340175486249
C	0.514302125290	3.140037638755	-0.145667910582
H	1.047515614067	6.203720969803	-2.516595928935
H	0.248628913932	4.605929029239	1.392974171245
O	0.506658180858	-0.363639614537	1.595521617629
O	-2.322665252142	-0.992346407901	2.594896232620
C	1.438142910612	0.101648954464	2.526282016798
H	1.156192292757	-0.216414593651	3.537098714761
H	2.432626913160	-0.310024594130	2.317464422513
H	1.518724335082	1.191650784329	2.527573059969
C	-1.511621042485	-1.821498446736	2.777474817453
N	-0.823660613767	-2.766754767499	2.997628432189
C	0.562814684227	-3.134800830352	3.140493417614
H	0.857533031501	-3.052126948695	4.185439825493
H	0.689286626570	-4.167647877977	2.825559574988
H	1.185198765642	-2.487742811781	2.526092226625

TS1

Al	-0.817258715227	0.499735704667	-0.103870886325
O	-2.021242554061	0.104983723033	-1.403901134389
O	-0.597659006323	2.257772751635	-0.536802761762

N	3.230395828497	-1.168614101660	0.584389129501
N	-0.754922844273	-1.461316845915	0.396344399179
N	0.877105142035	0.069667293596	-1.090160410473
C	0.990120596464	-3.700217359426	-1.037056337477
H	-0.090036273169	-3.747026369951	-1.181212466636
H	1.280466713352	-4.508320091460	-0.366356079876
H	1.454722206795	-3.868576782205	-2.009157054453
C	1.371360265951	-2.338780946496	-0.459571012173
C	2.850259742164	-2.254005443046	-0.096552500070
C	3.771587177030	-3.219776052050	-0.496937703579
H	3.456344264387	-4.094090516938	-1.044877194320
C	5.110947440384	-3.049348721877	-0.182318364299
H	5.837817138693	-3.791971181228	-0.482066897373
C	5.500712364632	-1.920811681884	0.518434685223
H	6.532829676508	-1.746850244852	0.785289232912
C	4.518215750296	-1.010703918160	0.877263004076
H	4.776178717544	-0.113735135387	1.428326290499
C	0.511736990752	-2.053506849080	0.798432474359
H	0.351184167706	-2.984835977669	1.346155488403
H	1.033607543538	-1.345307510121	1.432441573114
C	-1.798412968813	-2.195480929616	0.308603392086
H	-1.760771962217	-3.218627629340	0.688845580118
C	-3.031750887129	-1.781908679277	-0.322669562860
C	-4.170044029407	-2.583945401750	-0.162466723751
H	-4.106411859771	-3.445038138997	0.492215050587
C	-5.347538659283	-2.295100103939	-0.815928873237

C	-5.383651279358	-1.195367151273	-1.678605646992
H	-6.297985918034	-0.960782963089	-2.208255639935
C	-4.270977074341	-0.403688314395	-1.872299813246
C	-3.066460198576	-0.662426790987	-1.193831615151
H	-6.222215234963	-2.913293071160	-0.676101102491
H	-4.298369348409	0.444046742176	-2.543813382158
C	1.067117834035	-1.294394001629	-1.568664579376
H	1.863380406984	-1.329987292319	-2.314228534361
H	0.137073730113	-1.587372852706	-2.058029807287
C	1.816720263318	0.918237332256	-1.290130187904
H	2.738236756949	0.577733269627	-1.764111611028
C	1.748606756943	2.319592290714	-0.965674102281
C	2.914153794192	3.091910528222	-1.080626787137
H	3.836728613392	2.595206036528	-1.357289990480
C	2.897624574763	4.447988931040	-0.847016135301
C	1.681396644234	5.057222540271	-0.515961503447
H	1.650720566270	6.124505503306	-0.337875916084
C	0.518145442818	4.325366634471	-0.415881494666
C	0.516260708820	2.932429257232	-0.626414079656
H	3.801559700493	5.033781634984	-0.926902614493
H	-0.421423118116	4.799794962875	-0.165940326384
O	-2.036746510183	0.829272437198	1.239427441338
C	-3.053541914792	1.782472206557	1.064239006155
H	-3.313223552947	1.889726879393	0.006797907063
H	-3.954099688221	1.485059397892	1.609093771074
H	-2.742898588581	2.768114216432	1.428751429159

C	-0.455350315093	1.293160377355	2.379246370070
O	0.346511113436	0.853336927382	1.583411861999
N	-0.782247544013	1.831322077576	3.400543920131
C	-2.042390860779	1.979227307827	4.086127994219
H	-1.908395001173	1.712345670938	5.131501576930
H	-2.369839557582	3.015754787020	4.035126300187
H	-2.797143168652	1.335441627677	3.639162954528

INT3

Al	-0.709452170753	0.456347864905	-0.158460931411
O	-2.051223623902	0.104774758041	-1.317640255211
O	-0.702185192936	2.227586905444	-0.577691276091
N	3.326461825606	-0.958442913414	0.566655034319
N	-0.630183131170	-1.513616685974	0.262571465311
N	0.964257143724	0.164241756350	-1.152171547019
C	1.303771699368	-3.590512965532	-1.178111262296
H	0.234130125801	-3.696293838903	-1.363840770485
H	1.615788594084	-4.395392996119	-0.513378280205
H	1.813976659323	-3.709710920238	-2.134525372938
C	1.582367874401	-2.223268575706	-0.557314271732
C	3.039027134063	-2.058374289144	-0.136245751070
C	4.029875864200	-2.965078575502	-0.505696299877
H	3.788436860507	-3.850347273326	-1.073249742144
C	5.343084977694	-2.720117529619	-0.134320705611
H	6.123923632391	-3.416235105013	-0.408866447651
C	5.637112812500	-1.577670119023	0.589954870827

H	6.645510224790	-1.346917198441	0.900763818303
C	4.589642463377	-0.728612468641	0.913642852336
H	4.772268637443	0.177058432129	1.480228575291
C	0.668767011713	-2.023445638598	0.678108907566
H	0.564110315233	-2.973126684336	1.207085318665
H	1.114960115652	-1.287173530810	1.338932418033
C	-1.636212930342	-2.300476720185	0.192847570147
H	-1.537571984648	-3.324704446577	0.557721830708
C	-2.907335946168	-1.929897077984	-0.382602706403
C	-3.989484576912	-2.812206125496	-0.257131731946
H	-3.853064691857	-3.717876657802	0.321670777426
C	-5.201556303252	-2.543924590595	-0.852683307804
C	-5.332910701510	-1.378221524741	-1.613709636469
H	-6.277001880507	-1.157236502182	-2.094509098666
C	-4.277876374311	-0.503220554344	-1.767855931981
C	-3.038483018306	-0.746777567240	-1.150619942609
H	-6.032687369168	-3.225004183322	-0.743180512912
H	-4.378543784094	0.395737875340	-2.361127589663
C	1.260568697556	-1.171661458770	-1.654609710613
H	2.088016672083	-1.136249417433	-2.365144267985
H	0.372918702576	-1.509716992101	-2.191804977940
C	1.836125713148	1.093536858089	-1.302962839409
H	2.791913655604	0.842010713575	-1.763485986012
C	1.647478036787	2.472834324698	-0.933329402972
C	2.755298837194	3.333057963133	-0.990404292805
H	3.718155582208	2.916789391905	-1.262199917552

C	2.633562744669	4.673411190283	-0.705889891457
C	1.369203838392	5.179043776789	-0.380772771321
H	1.256559180263	6.232996843491	-0.161502423545
C	0.260803405926	4.361586362583	-0.338303887873
C	0.365220919449	2.982862075617	-0.602527461563
H	3.493517283046	5.325906847226	-0.741155754987
H	-0.716428145990	4.755956805092	-0.093732437570
O	-2.084892225229	0.775441120110	1.345518121114
C	-3.129211569914	1.753808499314	1.200939702742
H	-3.399877657190	1.758595296877	0.148601030791
H	-3.982962449137	1.475663962734	1.811524655070
H	-2.757174389242	2.735033092535	1.487575118715
C	-0.987510090595	1.051997361860	2.218853733990
O	0.073228663200	0.791391872437	1.533131063717
N	-1.085788540067	1.436343071032	3.412145241880
C	-2.379836920239	1.497125483946	4.068317138066
H	-2.231804629299	1.349384004542	5.136472661613
H	-2.855509160393	2.471902777389	3.939574938217
H	-3.073126446841	0.729393839643	3.716882550950

INT4

Al	0.237386424603	0.042418335220	0.070196565736
O	0.652675955394	1.618540684768	0.893808425396
O	-1.204818675337	0.741675977967	-0.812730261314
N	1.948933229893	-0.846859242464	0.855261308979
N	1.570403615065	0.543902104919	-1.398035910894

N	-0.021120776274	-1.672945067673	-1.007668903379
C	3.442313186458	-2.679793655051	-2.057906602970
H	4.420987928173	-2.204712637501	-2.104581179957
H	3.102562068062	-2.845936032714	-3.079881949787
H	3.546868859197	-3.650725774762	-1.573364596372
C	2.429588798007	-1.804596091300	-1.326074030324
C	2.854922157327	-1.489890185619	0.097796379708
C	4.070386948363	-1.886775405948	0.638078396652
H	4.794568324671	-2.405478541567	0.031019599135
C	4.344376799520	-1.623443972795	1.970987953298
H	5.287886972786	-1.930822342549	2.400223078057
C	3.397342617504	-0.972807176837	2.742585775076
H	3.567046003790	-0.753682801206	3.785678891906
C	2.211505584657	-0.598553537956	2.140823875706
H	1.435433945578	-0.076640272454	2.682045918611
C	2.230104070739	-0.516963567958	-2.155395544287
H	3.197328768553	-0.166000843969	-2.517828662634
H	1.617415815096	-0.775645814188	-3.023633414674
C	1.866974779065	1.754509626666	-1.686895382205
H	2.547843077852	1.947547569205	-2.518404020201
C	1.393464111718	2.912200041157	-0.968428622739
C	1.606711680639	4.183206789115	-1.520311543849
H	2.071496232048	4.251479670842	-2.496933988573
C	1.234580312865	5.325221466827	-0.847299575064
H	1.391638499142	6.300346155565	-1.284573524325
C	0.659189876076	5.198096527770	0.422399337612

H	0.366754198788	6.086891937109	0.966828891635
C	0.462385492903	3.961581878269	0.998355359220
H	0.023705808769	3.865725674221	1.982594458560
C	0.816883628579	2.778226624749	0.320121867203
C	1.098404208418	-2.575991941807	-1.257542245879
H	0.943940031311	-3.100782035234	-2.202149666582
H	1.151901272083	-3.321865364373	-0.460237402718
C	-1.178010005786	-2.044324753606	-1.411026721293
H	-1.278148182582	-3.021140518764	-1.889305083858
C	-2.386773965707	-1.268369373569	-1.292507824580
C	-3.617893630825	-1.896201809821	-1.539638870892
H	-3.621921175461	-2.955352781788	-1.769459213091
C	-4.798447595737	-1.192377976607	-1.485876021237
H	-5.743715197000	-1.684102610302	-1.663201069293
C	-4.750601790871	0.180870123432	-1.210174458388
H	-5.671436374161	0.748763844400	-1.170909507894
C	-3.553993973542	0.824733238305	-0.988417693839
H	-3.518370122448	1.883755507967	-0.771656611860
C	-2.334150314581	0.119609114367	-1.012275507309
O	-0.671829272234	-0.710954402562	1.474310524944
C	-1.832658806122	-0.465713464559	1.997587911929
O	-2.579959120966	-1.575550529782	2.282208496181
C	-1.999046707925	-2.848003247049	2.041094255383
H	-2.741748700702	-3.578417793130	2.350923600336
H	-1.770099109407	-2.983928310884	0.985293284943
H	-1.087044745496	-2.980648789836	2.621470287171

N	-2.301690963121	0.686901159317	2.270608189696
C	-3.644915145278	0.730560044259	2.820365048778
H	-3.908629527227	1.765827649085	3.032321330628
H	-4.386181173508	0.333007750146	2.118743180974
H	-3.742486231393	0.159829172533	3.749083418806

INT5

Al	-0.879389292803	0.021621647582	-0.166727210004
O	-2.268654558119	-0.620909188855	-1.172178440014
O	-0.938141523721	1.623600651703	-1.027815126742
N	3.241927636421	-2.391612518278	1.316917408561
N	-0.773108342015	-1.800317078266	0.681044783428
N	0.609707432651	-0.606208436164	-1.335766646139
C	1.217120256079	-4.218756480255	-0.379921657628
H	0.160525716299	-4.488929878107	-0.437317826402
H	1.666700277614	-4.748715987594	0.458926660929
H	1.704182374909	-4.546247743741	-1.299405289168
C	1.366530707137	-2.702600474623	-0.190633356596
C	2.844360130673	-2.396783943907	0.042551004717
C	3.752267877024	-2.205530364551	-0.998262858257
H	3.442173421330	-2.254433254934	-2.030711746623
C	5.083813799244	-1.961878440577	-0.701560296584
H	5.796654516464	-1.801677864622	-1.498871299551
C	5.484623435362	-1.930301337308	0.623625677772
H	6.510783565268	-1.740222831886	0.901833479809
C	4.523496670249	-2.164968256060	1.593809225042

H	4.793451368181	-2.169249749348	2.643435886528
C	0.555782204796	-2.256366613887	1.065545565229
H	0.489016869307	-3.087691042416	1.768289348379
H	1.061978510216	-1.431927159700	1.551008921959
C	-1.772422414046	-2.587989432647	0.829226342280
H	-1.631696561222	-3.521028450801	1.378736816404
C	-3.075529021336	-2.358574262326	0.256992339678
C	-4.142401414798	-3.187491954084	0.632524464108
H	-3.975639838953	-3.925052921774	1.408588648696
C	-5.376265073478	-3.075181072923	0.033226601619
C	-5.543699616604	-2.133112852899	-0.988450110559
H	-6.505494928622	-2.040741302576	-1.476408790615
C	-4.505167961262	-1.321279494591	-1.390811620573
C	-3.242455530957	-1.398067521205	-0.772575432280
H	-6.196659331073	-3.709822578919	0.334670838533
H	-4.636016927711	-0.598129420843	-2.184444216644
C	0.817141691900	-2.040904535735	-1.472672801461
H	1.463942513227	-2.259048135627	-2.320923659470
H	-0.154428436009	-2.485660474281	-1.690453592068
C	1.421752179329	0.212409418130	-1.891972563257
H	2.263684044944	-0.180078204489	-2.464052791068
C	1.314827980034	1.651798569561	-1.821891247850
C	2.415492620297	2.415409850470	-2.240875174413
H	3.304588835150	1.896375049413	-2.579675712694
C	2.382753876858	3.790744661989	-2.214915847813
C	1.210678353284	4.426660094458	-1.788163615555

H	1.167271493367	5.508082280056	-1.766854842694
C	0.107563122398	3.701101559223	-1.394854797749
C	0.125210433608	2.293638595927	-1.390245078643
H	3.240105285557	4.369557527818	-2.525699697785
H	-0.797935650871	4.192891552257	-1.066076435387
O	1.919376539707	2.074948959597	1.707276789190
C	2.836653611618	1.007249012010	1.507444531424
H	3.826173077267	1.432935994685	1.651366816169
H	2.670910548507	0.208904233873	2.230251357485
H	2.754305949597	0.592673829134	0.502439504357
C	0.591570371918	1.803567333967	1.553236714908
O	0.326407379064	0.622797360137	1.095389546627
N	-0.273244109758	2.689915622163	1.865826778165
C	0.240193591086	3.953433395770	2.367274249668
H	0.990868414046	3.826177505547	3.151412694140
H	0.700870592767	4.546080667026	1.568893573231
H	-0.582546614080	4.535157017030	2.781027906306
C	-2.740170076777	1.749258368696	1.161579149868
O	-2.345332395882	0.622922247237	1.161002726834
N	-3.305348000121	2.775866854154	1.131461014444
C	-3.165008844459	4.197018358533	1.290887083179
H	-3.839768386451	4.701258033882	0.606033275570
H	-3.421286508253	4.471856045398	2.311368507814
H	-2.134847915372	4.475528963374	1.083473549233

TS2

Al	0.072249217113	0.110088864959	0.087749121562
O	0.014166653268	0.141807869414	1.916745448103
O	1.889528095703	0.153849193310	0.083870847783
N	-2.884846870486	2.190378415234	-3.326973910475
N	-1.950458665324	0.124539934798	0.111333496023
N	-0.056149747228	2.096597836264	-0.164682039295
C	-3.747777636438	2.953947524122	-0.455556392813
H	-4.016868355519	2.540730208562	0.518617375894
H	-4.554488708491	2.745849794140	-1.156726216838
H	-3.643085510118	4.035006350839	-0.355741898230
C	-2.441238967552	2.317767619533	-0.956907758809
C	-2.192996304913	2.823018284142	-2.374066179189
C	-1.367240165093	3.901746038492	-2.677728759267
H	-0.842675108223	4.441169304957	-1.905869177798
C	-1.228427353267	4.300693050299	-3.998895435442
H	-0.580724294276	5.129701649999	-4.249673258565
C	-1.930674966361	3.628116275825	-4.983718172846
H	-1.852084696799	3.902607869403	-6.025338888613
C	-2.756862477776	2.586026024609	-4.589677260322
H	-3.340314272507	2.041964040195	-5.323210858913
C	-2.626448517405	0.765396748773	-1.006076597211
H	-3.690590552974	0.526331214493	-0.992217417301
H	-2.198803094479	0.379589640623	-1.922557589560
C	-2.655867421062	-0.371784521166	1.058710759367
H	-3.740914195867	-0.405295355276	0.943168409580
C	-2.124020932341	-0.845482599092	2.311724988614

C	-2.972397668340	-1.527149404513	3.196410064273
H	-3.983399051428	-1.749298247018	2.875786775633
C	-2.540452756004	-1.907859614847	4.446368174994
C	-1.238598518375	-1.573359851812	4.837680092905
H	-0.888473822260	-1.855870036093	5.822230707860
C	-0.392190066624	-0.885717662627	3.995118961607
C	-0.801872523352	-0.512874339813	2.700158655330
H	-3.195863692778	-2.441925907523	5.118618227724
H	0.611283360469	-0.624123952228	4.302630367004
C	-1.348755222379	2.738340112065	0.048699080768
H	-1.242641171211	3.823922633369	0.044875805769
H	-1.691859731790	2.456712473029	1.045134219482
C	0.944192728770	2.820368393804	-0.504286473218
H	0.804438811661	3.897150932954	-0.605591962666
C	2.274972366566	2.341246912910	-0.789844563520
C	3.183255964851	3.241306781015	-1.369220325080
H	2.852132515825	4.255047785960	-1.562348440498
C	4.461135009010	2.854849803051	-1.702019357057
C	4.854155342596	1.537737887295	-1.435706479881
H	5.855953371942	1.217602316151	-1.691844156831
C	3.990961699948	0.639504422608	-0.847651539549
C	2.675026676549	1.010913680057	-0.503936044806
H	5.148652223375	3.552795249286	-2.156685484242
H	4.299004084135	-0.375246010063	-0.633949938419
O	1.157381235156	-0.243371349937	-3.679965185205
C	0.743432595975	1.096773907023	-3.942109863656

H	1.152984364276	1.345893702052	-4.916602933253
H	-0.343095142417	1.171782151659	-3.962045882544
H	1.134818464110	1.777155928194	-3.187465097088
C	0.738171450675	-0.809191162963	-2.525947136413
O	-0.004616916953	-0.081114084937	-1.767474317904
N	1.074727584958	-2.018280641310	-2.261707961326
C	1.940590941193	-2.712632897007	-3.197057399906
H	1.476984835167	-2.833035621164	-4.180850235376
H	2.887538635331	-2.186407367685	-3.341912239103
H	2.160922172473	-3.703679807487	-2.803683268055
C	-0.170860693651	-2.757431508591	-0.528791150653
O	0.080864352318	-1.882375451249	0.257092629438
N	-0.677012787150	-3.763182208642	-0.918859421589
C	-0.661261317787	-4.550730043605	-2.122115126429
H	-1.644599408209	-4.986770253117	-2.272529465039
H	-0.400436991530	-3.921877899735	-2.970786652987
H	0.065839085906	-5.354505800435	-2.024294641487

INT6

Al	0.793237954919	-0.364201795874	-0.483702134130
O	2.183508912373	-0.199102660361	-1.648092149450
O	0.077216803022	-1.819558828123	-1.330490264679
N	-2.177297501809	2.494907981133	1.899472976784
N	1.425191501199	1.327545535061	0.446004066342
N	-0.458030425675	0.877722934072	-1.488305684749
C	-0.314513409467	4.328666149895	0.106380235410

H	0.717752457347	4.545383264705	-0.174756425501
H	-0.498345033936	4.743203239728	1.096891977383
H	-0.980468281115	4.819579557099	-0.603976622783
C	-0.548952164109	2.808016131015	0.121717610428
C	-1.988136089405	2.582677992155	0.581432336207
C	-3.065572249509	2.576087841126	-0.303275663135
H	-2.916619741610	2.692804524734	-1.365130635769
C	-4.352904171511	2.443900769743	0.192058786750
H	-5.196288959915	2.430370270061	-0.484800180963
C	-4.540853531647	2.337340161984	1.560372191976
H	-5.525369924521	2.232955334373	1.992007419074
C	-3.416887594077	2.378226636854	2.370124719369
H	-3.514682834471	2.313764834380	3.447472302858
C	0.452905024841	2.163342420631	1.131715909591
H	0.965293002941	2.947997913087	1.690573806954
H	-0.092779534459	1.549399565012	1.838178907190
C	2.658230948904	1.668694244006	0.473271416229
H	2.951329105410	2.527390690225	1.080509152075
C	3.709955867258	1.032944056527	-0.283686708838
C	5.038351650273	1.397105733630	-0.022675367413
H	5.234120793362	2.090137286197	0.787023003849
C	6.078574041205	0.892134169791	-0.770360174050
C	5.784685437625	0.023245266199	-1.826705815986
H	6.589849533156	-0.374219733618	-2.431285019431
C	4.485470689118	-0.334676475283	-2.117130713314
C	3.408902732349	0.146429751498	-1.347688890981

H	7.099862431024	1.170073227541	-0.554733995365
H	4.260679527731	-1.002327156701	-2.937905334180
C	-0.290071849064	2.317947434291	-1.318980717127
H	-0.934001170322	2.858552132022	-2.013737843977
H	0.738441700305	2.571465459926	-1.577178425441
C	-1.408712979443	0.476831646409	-2.247544480737
H	-2.014459628183	1.222006166524	-2.764505880374
C	-1.790628457447	-0.891716768924	-2.487487843213
C	-2.968551573184	-1.124865962252	-3.215060246368
H	-3.523710024689	-0.270558423699	-3.584330805919
C	-3.424832948144	-2.401537476650	-3.449189009708
C	-2.680464239928	-3.479966694663	-2.955717395175
H	-3.025176875288	-4.490984068763	-3.130913044468
C	-1.513399905872	-3.280416010446	-2.251693948424
C	-1.031010944776	-1.980466389934	-1.993324878917
H	-4.336596068386	-2.569896476023	-4.003087208232
H	-0.937446219727	-4.115265351949	-1.875585774049
O	-2.125945136852	-1.952702305441	1.656930454760
C	-3.189408257525	-1.240200609091	0.999285699502
H	-4.102847515551	-1.711896541715	1.342008920309
H	-3.166052790573	-0.189944648789	1.280596577367
H	-3.085298891848	-1.338159888337	-0.079765086397
C	-0.908960118394	-1.485862625356	1.469594409077
O	-0.706079755140	-0.450925303616	0.807303520272
N	0.057407050704	-2.192486959097	2.055069855603
C	-0.237571366995	-3.484613704332	2.675845932314

H	-0.792454979572	-3.361564674745	3.603448983305
H	-0.817636741967	-4.094079791200	1.987264110888
H	0.705059865848	-3.979304748556	2.882558622790
C	1.440871144274	-1.732577787451	1.909580829675
O	1.762013015113	-1.394792760156	0.704762321373
N	2.239302723006	-1.710606865621	2.892835122244
C	1.791332492380	-1.979525262916	4.243795352726
H	2.353243564885	-1.341557535625	4.924618656268
H	0.727684152557	-1.785395796586	4.403628902319
H	1.997545762978	-3.012602239738	4.534199279982

INT7

Al	-0.746861570791	0.123335465592	-0.075188852045
O	-2.027572380088	0.688840351626	-1.248631075537
O	-0.299273145851	1.852764833636	0.366400460832
N	-1.362668451945	-1.855452591177	-0.322382841934
N	-2.164806107683	-0.002879071669	1.382101114434
N	0.540805624632	-0.525849130486	1.346254423179
C	-1.311287222760	-3.233059453461	3.161734341293
H	-2.346860793872	-3.557181496377	3.253546140110
H	-1.007052318009	-2.807381350221	4.117765268999
H	-0.687598115669	-4.105612532961	2.966012138130
C	-1.148811588567	-2.183547185434	2.067212450751
C	-1.600718303430	-2.683011275074	0.707100113564
C	-2.160323842993	-3.935380563621	0.493983384333
H	-2.346167386157	-4.599796319179	1.322456612229

C	-2.469531164301	-4.330750896125	-0.798138832244
H	-2.906776410990	-5.303500370342	-0.976430072628
C	-2.205060934963	-3.472892616119	-1.851823380319
H	-2.421829655500	-3.745077692556	-2.873575467918
C	-1.646217126967	-2.242136820873	-1.566344278902
H	-1.411739961486	-1.527200319911	-2.341551760911
C	-1.944019781379	-0.927109123703	2.491744187048
H	-2.901675744941	-1.230416697944	2.917547873668
H	-1.371105318196	-0.420037930672	3.272958757860
C	-3.260007434821	0.655469458798	1.352286195331
H	-3.961539412388	0.552016517565	2.182580498861
C	-3.674671770226	1.520936717042	0.273075418339
C	-4.790377465438	2.346346432637	0.473468881951
H	-5.266988945800	2.341554214394	1.446712798975
C	-5.276766819851	3.151237035291	-0.532149758140
H	-6.130073701778	3.791698083249	-0.363664254339
C	-4.650623780801	3.111683453875	-1.782691638773
H	-5.024847468043	3.731415702514	-2.587498960360
C	-3.567106220203	2.291756206610	-2.013300221224
H	-3.090892559395	2.256184617067	-2.983903808221
C	-3.037955297851	1.475441174410	-0.993762435605
C	0.351318125487	-1.836380342756	1.956127230863
H	0.795693411560	-1.846779214483	2.953172716809
H	0.854142886864	-2.588211756884	1.341907442602
C	1.577809525073	0.143040614606	1.686155246322
H	2.287037909397	-0.305261449823	2.382460384894

C	1.887660106410	1.478392984723	1.234373155112
C	3.162004050829	1.995399258991	1.504074556384
H	3.879741776124	1.354435676248	2.002938754235
C	3.502877561281	3.281754613450	1.149801255011
H	4.492861258349	3.665762012776	1.348667453360
C	2.532787412174	4.088177543646	0.542675984503
H	2.779907139101	5.105931789846	0.268881553469
C	1.264506090356	3.612206949489	0.288978317274
H	0.515413677516	4.238744513728	-0.176407774430
C	0.905159391229	2.286941150459	0.610099083588
O	3.810402696732	-1.173134762276	0.228078641151
C	3.817006898254	-0.351145024412	-0.666391838776
O	4.867110112102	0.452415632100	-0.907726874530
C	5.995729457888	0.255912148887	-0.058364228535
H	6.732738104751	0.986395831742	-0.374489818528
H	5.725807035439	0.418659509368	0.982442903074
H	6.387115725466	-0.752461761227	-0.174531450775
N	2.800490725897	-0.103344279384	-1.537310762784
C	2.795143293630	1.142563241531	-2.305003915734
H	1.917809782071	1.140111250611	-2.941286330182
H	2.751034060855	2.008869188979	-1.642879792855
H	3.689930872762	1.201891552423	-2.918141296648
O	0.522012676118	-0.070708032271	-1.380409295883
C	1.569352742300	-0.848097855327	-1.442448062659
N	1.509229229074	-2.114839300260	-1.481543465948
C	2.679891153460	-2.924455298180	-1.729882872355

H	2.385668877851	-3.778377201080	-2.340895767510
H	3.481893602677	-2.390832121172	-2.249325710233
H	3.092015209425	-3.308593890468	-0.795788841075

INT8

Al	-0.021232872491	0.365849569190	-0.749137267914
O	-0.984441001349	-0.206402668652	-2.170621150601
O	0.655832332207	1.876959748290	-1.494044358175
N	3.165635341768	-1.955757182272	1.948400349317
N	-0.442534279403	-1.358378255836	0.226072275277
N	1.684766617193	-0.608876657823	-1.225885010481
C	1.225446397565	-4.164186345225	-0.002298930584
H	0.196687662052	-4.229930716021	-0.362131085781
H	1.294594151919	-4.694222155278	0.946983247677
H	1.863041575881	-4.669090372997	-0.727650859287
C	1.623154890849	-2.692894802377	0.173562622433
C	3.017472927786	-2.606557944503	0.797517863599
C	4.102373423452	-3.218424763407	0.163134021484
H	3.968067946370	-3.754303101382	-0.765918843316
C	5.358029777057	-3.135931398606	0.734553536717
H	6.207764600368	-3.601296278842	0.254037023621
C	5.507734190087	-2.449922156746	1.931719818997
H	6.468930800406	-2.358733368699	2.415859678579
C	4.380113562311	-1.883014823356	2.496679897533
H	4.447556979004	-1.343296557244	3.433742201467
C	0.568870340307	-1.984426026703	1.066382435987

H	0.112020988439	-2.713214426415	1.739423250311
H	1.048805743666	-1.221185453661	1.663440920361
C	-1.552323636833	-1.966783462182	0.028289819832
H	-1.776460603170	-2.855097736695	0.623369309810
C	-2.519154990926	-1.609591640526	-0.982650852387
C	-3.779650125127	-2.223896846867	-0.948864129859
H	-4.017050589978	-2.871512587841	-0.112760158572
C	-4.701781299039	-2.018490395987	-1.950015430142
C	-4.348690110026	-1.203526863252	-3.031326335235
H	-5.058166215782	-1.042582893644	-3.832786524535
C	-3.108546205930	-0.606102533984	-3.100342498106
C	-2.161816361310	-0.775334462160	-2.073331178150
H	-5.673875712367	-2.488138041798	-1.909975297874
H	-2.835118871041	0.017720509030	-3.940377383332
C	1.645192804657	-2.066848900649	-1.240221784911
H	2.491662068194	-2.462663467514	-1.801153154754
H	0.736106992980	-2.360569969762	-1.765642333927
C	2.796954058596	-0.033782075417	-1.502188654427
H	3.672532901013	-0.654316366186	-1.701538279654
C	2.990908479817	1.389173144036	-1.610507092811
C	4.297035215255	1.876352423215	-1.779926920625
H	5.117428553363	1.168527183260	-1.768217113052
C	4.540474854914	3.218201910663	-1.956597484662
C	3.452573720473	4.099767056583	-1.992862724713
H	3.627764184114	5.157689167994	-2.140038746661
C	2.160411228903	3.646379815636	-1.847841641992

C	1.890131039704	2.279503446490	-1.639735816998
H	5.549066174629	3.585601117416	-2.076285082375
H	1.320774451129	4.327791825888	-1.876034814391
O	-5.093362654384	-0.226241181851	1.215460802446
C	-6.353344628416	-0.090551356583	0.558561710284
H	-6.977418764791	-0.886760339813	0.950856245208
H	-6.792601223874	0.879680955717	0.781286500738
H	-6.232073522669	-0.198767980089	-0.516685446380
C	-4.154713736252	0.657323669588	0.834009074611
O	-4.339793691510	1.506319544393	-0.012223212197
N	-3.011155237631	0.495633304578	1.548124645523
C	-2.902287841993	-0.497797027844	2.609856284607
H	-3.528768081172	-0.248241597880	3.465848002084
H	-3.194454814422	-1.478221372409	2.237190336963
H	-1.863748993066	-0.538602319841	2.929856870619
C	-1.874647549181	1.339277568835	1.254831803263
O	-1.411791935524	1.228360442736	0.050366637698
N	-1.373243717468	2.107997532765	2.135253123263
C	-2.013511634290	2.265043757077	3.425861786632
H	-1.825321626054	3.274488483014	3.790081665048
H	-3.094861408799	2.108553824328	3.395067338059
H	-1.592720257350	1.574987110038	4.161948895094
O	1.114768085179	0.909899311782	1.006290441532
C	1.217025725742	2.052667288010	1.333963551276
N	1.494264902130	3.157081755511	1.611773385454
C	1.002852341237	4.413261731172	2.105380472666

H	1.205373218915	5.185664739953	1.368156267975
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H	1.518783396787	4.661784243385	3.028790684151

TS3

Al	0.037412567027	0.025132491558	0.056548560975
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O	1.839576290175	0.089589572462	-0.165468598339
N	-2.398395430527	2.678439897739	-3.058981877028
N	-1.990181086047	0.157761739769	0.075522916290
N	-0.068456286444	2.016187015586	-0.218880672997
C	-3.719395922946	2.918117030024	0.222099393671
H	-3.848146879428	2.257818753135	1.082027657303
H	-4.627657975228	2.884863690018	-0.378599187065
H	-3.591802273868	3.931976973943	0.600550495965
C	-2.510236564665	2.463954637834	-0.605633226404
C	-2.410933226918	3.300412324960	-1.882993191699
C	-2.341540159979	4.693916839843	-1.796645932610
H	-2.360709675526	5.188609950734	-0.835828724549
C	-2.247431411791	5.442295530574	-2.954543768185
H	-2.190083397416	6.521026109610	-2.903856649359
C	-2.229427850700	4.787572694146	-4.178265166719
H	-2.157028413195	5.329711211097	-5.109629963327
C	-2.310483313595	3.407261459788	-4.173493724069
H	-2.304674348960	2.853599194953	-5.104801479050
C	-2.661905393444	0.956048431531	-0.939481201443

H	-3.722427379004	0.700133998753	-0.993452879714
H	-2.207564433905	0.747288407835	-1.898616632169
C	-2.676874759473	-0.376030031646	1.015292647742
H	-3.767295618178	-0.354824955208	0.949828919018
C	-2.108977936629	-0.964000768172	2.206170448976
C	-2.935478781498	-1.736398511872	3.034217796211
H	-3.952162297563	-1.932284660676	2.713303682396
C	-2.477102377896	-2.240145212563	4.230951132906
C	-1.170890771199	-1.936731557027	4.630088127715
H	-0.799583307292	-2.315231321769	5.573767507049
C	-0.346336969587	-1.157671936720	3.846422533205
C	-0.779947896552	-0.661480420002	2.603497439601
H	-3.116996238961	-2.845127413825	4.856788868766
H	0.661402512049	-0.921604011074	4.160113431976
C	-1.257117483895	2.705274095405	0.268987915252
H	-1.069593130069	3.776243767515	0.347186510473
H	-1.456729878391	2.330194052651	1.273117899770
C	0.833456790420	2.703982254319	-0.816510036004
H	0.663257962008	3.771252422333	-0.971097693493
C	2.095882012504	2.188208252793	-1.280845182947
C	2.916224137445	3.027925283355	-2.051191581945
H	2.545013702454	4.011420119118	-2.313963229406
C	4.162490867599	2.622805232549	-2.468229986406
C	4.619279210496	1.355171095942	-2.085947974160
H	5.601715119584	1.025298316761	-2.398411655953
C	3.843249230639	0.518916894903	-1.314887844004

C	2.553136623324	0.902494884699	-0.898149285974
H	4.782316471968	3.272137244096	-3.068869812805
H	4.197607584270	-0.459253781126	-1.018813130986
O	-2.602588362647	-4.625587011887	1.482358327604
C	-2.416633768721	-5.460161188853	2.626470348916
H	-3.410997565090	-5.772593115113	2.927106710103
H	-1.808256293990	-6.324235548910	2.368383773806
H	-1.936966760100	-4.899347936737	3.425411855483
C	-1.476070609690	-4.116080853877	0.962749794771
O	-0.372221866358	-4.334377677356	1.408757616191
N	-1.745349953362	-3.374893536695	-0.152053979021
C	-3.113596599626	-3.200885405813	-0.635756209561
H	-3.505070122964	-4.118672885638	-1.072074329056
H	-3.761043477877	-2.896548790204	0.184524679173
H	-3.112953566270	-2.418686882207	-1.390320385669
C	-0.695052874623	-2.605502941524	-0.753732554628
O	-0.049569741310	-1.821188775944	0.033394293768
N	-0.461909999518	-2.673349645910	-2.010123126557
C	-1.151830715551	-3.606563423514	-2.877063510897
H	-0.485579657924	-3.896316317146	-3.687372143855
H	-1.465036159006	-4.509111925799	-2.348707490426
H	-2.033708660877	-3.148258060647	-3.329919429896
O	-0.115991562189	-0.071751114549	-1.997374735181
C	0.537711661116	-0.861922336507	-2.636137375532
N	1.399794974069	-1.165597725255	-3.411739179820
C	1.932694594949	-2.421354138827	-3.869633555270

H	3.016988255177	-2.350876533199	-3.902173601416
H	1.637908677299	-3.221868446094	-3.193290214006
H	1.570702259201	-2.631245364205	-4.874500354000

INT9

Al	0.079820418047	0.440738651554	-0.749865163585
O	-0.887946132834	-0.088001209611	-2.217145184464
O	0.516495940260	2.052279053229	-1.477536397330
N	3.355044991180	-1.843948376415	1.737884948124
N	-0.274871558286	-1.433216209517	0.003460614797
N	1.827340117075	-0.334651097976	-1.316842068304
C	1.648055374885	-4.023036087263	-0.479399819971
H	0.633152456784	-4.132515144141	-0.866746573418
H	1.748613649824	-4.646997845723	0.408028914469
H	2.334385822811	-4.392057073618	-1.241206039993
C	1.916994078619	-2.552202864013	-0.135644144977
C	3.283267556138	-2.418180105658	0.539904935544
C	4.425835668207	-2.902018536003	-0.104082737609
H	4.353552431248	-3.374630264977	-1.073488210615
C	5.657464792470	-2.772769304244	0.509067704045
H	6.550691184912	-3.139583281515	0.022125365695
C	5.726853558122	-2.167558931345	1.756231068989
H	6.666548905301	-2.043774134759	2.274197906649
C	4.547227885965	-1.724872190610	2.325715414642
H	4.551990668022	-1.250661940949	3.299902623486
C	0.787932727005	-2.034734481094	0.794324669996

H	0.405392029112	-2.863417527716	1.395085440037
H	1.181912478306	-1.273246246172	1.454657455950
C	-1.349884640434	-2.088041154200	-0.228009252783
H	-1.516707739315	-3.039021599661	0.284592051536
C	-2.355468632336	-1.665505410691	-1.174539742362
C	-3.604100913508	-2.302717857345	-1.171081471662
H	-3.802341543795	-3.050809045229	-0.411864509932
C	-4.564220682471	-1.994626314662	-2.109108606292
C	-4.257566430178	-1.053019586114	-3.098164255348
H	-4.997446315600	-0.808999750619	-3.849669075263
C	-3.027929789459	-0.431075146327	-3.138458801535
C	-2.043465437506	-0.699846675955	-2.168387640160
H	-5.528541540193	-2.481476810939	-2.093255650176
H	-2.794864764758	0.294583300769	-3.905827862827
C	1.926986475539	-1.778751404046	-1.475931800292
H	2.824561962939	-2.038644108528	-2.037771970301
H	1.064296665608	-2.095984495906	-2.063004194914
C	2.872100407661	0.386058691547	-1.496080641648
H	3.819024940316	-0.108620582924	-1.722027486580
C	2.898149740053	1.826980674765	-1.463494639661
C	4.147073711689	2.466395485177	-1.513017336296
H	5.039875762914	1.852191461002	-1.513135554185
C	4.249737737646	3.837225850801	-1.558506628313
C	3.073259627076	4.596619077774	-1.585012209025
H	3.135861792202	5.676355980253	-1.631058831653
C	1.834742029807	3.995781207553	-1.557784771930

C	1.703252147518	2.594051933068	-1.482206878354
H	5.216135790148	4.318945013128	-1.585206394922
H	0.927396298405	4.584287032221	-1.581785664374
O	-5.120265433203	-0.459438568956	1.174374242064
C	-6.383097243577	-0.281414739559	0.522342161185
H	-7.002728379410	-1.105249177545	0.857983767087
H	-6.820907877305	0.670972354115	0.811126607376
H	-6.249622699491	-0.316782643155	-0.556278160729
C	-4.204112989995	0.461815278437	0.887403548652
O	-4.378619305922	1.398433179824	0.151942906788
N	-3.038749117942	0.227311745697	1.605654272223
C	-2.924910637943	-0.949643693651	2.479397275134
H	-3.446362296150	-0.797089364904	3.421296228168
H	-3.347543820197	-1.810006581438	1.967781852785
H	-1.873895736567	-1.144884734820	2.668442225124
C	-1.878601554372	0.907956739876	1.218159235443
O	-1.615071806357	1.068412244318	0.008984057544
N	-1.047653718414	1.338091684439	2.159706942720
C	-1.296580058397	1.254935155950	3.596205918604
H	-0.761619684400	2.057598783672	4.088453068743
H	-2.359967998676	1.366205018667	3.790350944743
H	-0.942238011251	0.308408709805	4.000296718731
O	0.842228873748	0.908355498753	0.910464857478
C	0.278985514923	1.787594630400	1.672641988043
N	0.769836727866	2.903264760411	1.997154063322
C	0.018161832937	3.906348309507	2.721313057305

H	0.236167222153	4.877386916125	2.278102014579
H	-1.064774105551	3.761013722065	2.693489898601
H	0.338720600354	3.956564155594	3.764609405380

INT10

Al	0.469154533051	0.514465112176	-0.123241550794
O	0.604102567791	-0.423379333179	1.446636468960
O	-0.836017948148	1.585362224667	0.596326352270
N	2.052355956380	-0.570620341582	-0.948009434390
N	2.047432296697	1.668122250922	0.475067387365
N	0.506525935393	1.718298331001	-1.766782829554
C	4.120560203683	2.024367577821	-2.677413939771
H	5.075830285724	1.898709705524	-2.169957011771
H	3.969674931977	3.089994261588	-2.848226392303
H	4.171868553337	1.528750617337	-3.647123047207
C	2.967508460076	1.478054633076	-1.842578546969
C	3.120569067338	0.004002675818	-1.527438813794
C	4.237546800862	-0.748121203810	-1.857601501281
H	5.090830900990	-0.282859065907	-2.324525760295
C	4.242304217790	-2.111034477911	-1.598102773954
H	5.106205467051	-2.707658233099	-1.856441821196
C	3.129797890873	-2.694051727072	-1.018055214919
H	3.081633341727	-3.752458252246	-0.810444746811
C	2.057474233694	-1.881332077884	-0.702265411596
H	1.165408882284	-2.267068843570	-0.236511989546
C	2.877810152306	2.310536710047	-0.543253120332

H	3.881970451935	2.477091120147	-0.151302011516
H	2.448771231081	3.283281255284	-0.798094198223
C	2.370395058500	1.830645234870	1.702081826223
H	3.209215110174	2.486066515223	1.944972984986
C	1.723639834625	1.184583598341	2.818397007423
C	2.028431934702	1.630627633748	4.112691737869
H	2.702198407110	2.472217373194	4.222778869815
C	1.486623828721	1.025419078645	5.223965677503
H	1.718917766804	1.383018961373	6.216450425319
C	0.634879887417	-0.069650487187	5.041081019568
H	0.201522082472	-0.557904773405	5.904763134980
C	0.337255029318	-0.544600600320	3.781293567542
H	-0.327106267358	-1.386472741028	3.638060717444
C	0.870101601841	0.067604055103	2.629375054973
C	1.660944956521	1.638938073187	-2.655560145404
H	1.725590138986	2.546180852310	-3.258529410059
H	1.547854376349	0.787925384825	-3.330210159276
C	-0.382712892503	2.596941291131	-2.048155514046
H	-0.265483097087	3.175275059059	-2.966319452899
C	-1.518501024690	2.948464198812	-1.237782913730
C	-2.435823882959	3.878676526558	-1.748552889568
H	-2.290785248751	4.245610380190	-2.757803963921
C	-3.496624124736	4.324741257575	-0.993704075731
H	-4.203080704020	5.035079197558	-1.397326300193
C	-3.629401544819	3.853708121278	0.317760003339
H	-4.447269353518	4.207971803434	0.932089139129

C	-2.733948643745	2.950066668200	0.847402679847
H	-2.836104974463	2.593280847945	1.863382773737
C	-1.661905759931	2.451493227790	0.079148176697
O	-0.110898249826	-4.191820983491	-1.305992304820
C	-1.009225479082	-3.596761062598	-0.755114591239
O	-2.179017845713	-3.328426763799	-1.329569543920
C	-2.223873129884	-3.498863561290	-2.748121578541
H	-3.216852079285	-3.181680583321	-3.047633594930
H	-1.469500384977	-2.871240237186	-3.218403051123
H	-2.057590981150	-4.540978769333	-3.008979584250
N	-0.954695576549	-3.167748882586	0.551991021033
C	0.020037880237	-3.793363043651	1.447137341892
H	0.541841439161	-3.015367628576	2.000377959140
H	-0.479171771263	-4.461684163587	2.144677094779
H	0.723934473954	-4.351460609218	0.840216161927
O	-2.078776106400	-2.422099978984	2.366554932741
C	-1.841380007753	-2.267599074462	1.179428424867
N	-2.395904773351	-1.250668372932	0.467619972488
C	-3.314371715685	-0.405137659665	1.227858925852
H	-2.806633023095	-0.002735934151	2.103072931313
H	-3.628803731693	0.416925198136	0.596351715046
C	-1.928233572705	-0.757936876183	-0.809117299814
O	-0.631078677838	-0.711727691072	-0.939530562440
H	-4.184305780101	-0.975131704224	1.551037223070
N	-2.723519831300	-0.395690077415	-1.728824199911
C	-4.140834916561	-0.669964400769	-1.631752070575

H	-4.697818819710	0.221333987345	-1.328852003537
H	-4.509187807504	-0.948228188423	-2.619871795802
H	-4.383350440783	-1.478332596122	-0.935651587186

TS4

Al	0.640321734980	0.959072476170	0.724121130057
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O	-0.506071981132	0.495406895831	2.046709107498
N	2.454513872593	-2.587014725661	-0.768597557578
N	2.001640719950	1.364857596835	-0.707304094511
N	1.919426625290	-0.394057590158	1.333329924262
C	4.985571150544	0.179143289635	-0.789923614394
H	4.890299326823	1.261184705825	-0.689433540461
H	5.328659567385	-0.041021448880	-1.800240987825
H	5.747769130475	-0.149254474304	-0.082726056488
C	3.636400733070	-0.480246725740	-0.512872867133
C	3.645605012326	-1.980860650001	-0.787041093005
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H	1.408306002846	-4.346733746041	-0.917938426033
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H	-3.279587803218	2.836425451166	-0.353211060015

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