Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Manganese Catalysed Enantioselective Hydrogenation of *in-situ*-synthesised imines: efficient asymmetric synthesis of amino-indane derivatives

Conor L. Oates, Alister S. Goodfellow, Michael Bühl and Matthew L. Clarke

Table of Contents:

Section 1.3: A qualitative comparison of the sustainability of the research scale reactions here with other research scale alternatives.

Comparative Methodology:

This research article presents a prototype (research) method to produce a desired target. As discussed in a recent green chemistry editorial [i] a highly appropriate way to compare with the current state-of-the-art research is a qualitative approach that considers as many aspects of the process as is feasible including production of substrates/reagents for each route. In our view, when considering research papers rather than industrial processes, it is more meaningful to exclusively consider core aspects that are fundamental inherent features of the process that was published. Aspects of the processes that might not have been entirely considered as part of a research project are do not then form part of the analysis.

For example, relying on the isolated yields for reactions where conversion to product has been quantitative in each case would seem invalid, as would the solvents used during manipulation of compounds, or the concentration of the reactions unless they have been explicitly found to be required. This approach should then provide a more accurate assessment of the potential each route has after optimisation. In each case where we have omitted a comparison here it was to the advantage of the earlier comparative work, in order that our evaluation should be a worst-case advantage exhibited by the research here.

Finally, it is important to note our comparison is NOT a comparison of the relative merits of the pioneering papers this work is being compared to. Nor is it a comparison of the overall quality of the catalysts discussed in those papers overall, since it does not consider novelty, the degree of mechanistic understanding, molecular beauty, difficulty of other challenges overcome by those catalysts. It is purely a comparison limited to the potential environmental impacts from a synthesis of enantiomerically enriched N-substituted amino-indane. We provide relatively extensive justification, since in our view generalisations can lead to an incorrect conclusion or the reader missing some nuance.

The intrinsic aspects of four reactions used in the synthesis of enantiomerically enriched N-substituted amino-indane were evaluated using a traffic light system on the 'potential environmental impacts matrix' overleaf.

Justification for scoring:

This work: imine formation is quantitative using recyclable drying agent and commodity amine in 1:1 ratio with no purification.

The protocol in reference *ii* was the primary inspiration for this work, and it can be seen that this earlier paper describes a protected imine being formed as a separate step in 60% yield after Kugelrohr distillation and recrystallisation (in diethyl ether). The purification details do not form part of our analysis, since they are unlikely to have been optimised. However, because a separate step is used, with a significant amount of indanone lost, and waste produced, this part of the process is graded red in the potential environmental impact matrix. The protecting group in this case ((*R*)-tert-butyl-sulfinimide), despite its elegant synthesis, is a few steps from a commodity/cheap fine chemical, so is significantly more energetically intensive to prepare, and is used in 1.5 equivalents to generate 0.6 equivalents of product. The difference between 1 equivalent and 2.5 equivalents to convert 1 equivalent of indanone to amine is likely to be a significant one in cost and environmental impact.

In reference iii, the protecting group used is a readily available toluene sulfonyl group. The paper does not, as far as we can perceive, provide the yield for the synthesis of the imine, only reporting

the yield for a group of related imines as being up to 75%. There is therefore another synthetic step required and a waste of at least 25% of the indanone to produce the imine intermediate. We have assumed the best case scenario.
In reference iv, there is no loss of yield associated with making the imine first. However, 1.5 equivalents of ketone are used. Consequently, the yields of 58% for the overall reaction are based on tosyl amine, or ~39% based on indanone; while it may be possible to optimise details, needing an excess of one partner is a disadvantage. The more significant drawback is the noxious fumes and waste associated with the use of 1.2 equivalents of [$Ti(OEt)_4$] as a stoichiometric promoter for imine formation.

Matrix S1: Potential environmental-impacts matrix for catalytic stereoselective imine reduction in the synthesis of amino-indanes.

	This work	Org. Biomol. Chem. 2017, 15, 5685 (ref ii)	Angew. Chem. Int. Ed. 2006, 45, 3842 (ref iii)	Angew. Chem. Int. Ed. 2019, 58, 292 (ref iv)	Comments
Imine synthesis: yield					Yield assumed as 75% for 2006 paper since up to 75% is claimed (best case scenario for 2017 paper).
Imine synthesis, reagents and step-count					
Reduction solvent					2006 paper does not study solvents for this substrate, so its possible this could be less problematic.
Reductant (atom efficiency, toxicity, synthesis impacts)					
Imine reduction: conversion					
Amount of catalyst and promoter used					
Sustainability of metal source (for catalyst production)					
Catalyst removal to API specifications					
Catalyst synthesis: reagents, step count and toxicity					

Key: The colours are approximate scores with green being likely to be favourable in a detailed analysis, orange intermediate and red problematic. Omitted from the chart are any categories where scores may have been arbitrary at research scale such as amounts of work-up solvents or reaction concentrations.

All the reduction reactions work well. The process in reference ii and this work both use non-toxic earth abundant metal catalysts that require multi-step syntheses to make (for our catalyst, it is three steps with good yield and unproblematic reagents from a starting material available in Kg amounts). However, reference ii requires 10 mol% as opposed to just 1 mol% here (both are quite high and likely unoptimised loadings). The activator in our work is a simpler and more benign compound, potassium carbonate and used in smaller amounts (0.1 equivs) than triethylamine N-oxide (0.4

equivs). Reference iii describes the use of a catalyst formed from a precious metal and a diphosphine. Palladium is one of the precious metals that are not considered especially sustainable. There are stricter regulations regarding the removal of all traces of Pd from pharmaceuticals than there are for benign metals such as Mn, Cu and Fe. The catalyst in reference iv is earth abundant, [$NiCl_2$(Dimethylether)$_2$] combined with a diphosphine. The nickel precatalyst is associated with toxicity and carcinogenicity concerns. Further, the process uses 5 mol% of Ni catalyst.
Harmful or toxic waste that is energetic to remove can sometimes be offset by the use of far lower catalyst loadings, but they are either higher (5mol% in reference iv) or the same loadings of 1 mol% (reference iii).
The ligands used in reference iii and iv also require multi-step syntheses, that are arguably somewhat more onerous (requiring the use of primary phosphines) to make than those used in our work, although this was considered an unimportant difference in terms of sustainability.
Reactions in our work and reference ii use similar solvents (EtOH) and reductants, both of which are recommended/desirable. The reaction solvent described in reference iii is dichloromethane, although this might not be an optimised aspect of the protocol. Reference iv describes the use of disadvantageous trifluoroethanol and reports using more common solvents led to almost no product being formed.
The catalytic reduction in reference iv uses triethylamine formic acid azeotrope, which while a readily available reductant is not as atom efficient as hydrogen.

Reactions described in our work and reference ii produce small amounts of undesired stereoisomer. Whilst research scale syntheses and commercial scale syntheses in agrochemical, fragrance, flavours, materials and fine chemical industries frequently and routinely use scalemic chiral starting materials with *er* of ~ 95:5, some upgrade at the expense of yield would be required for pharmaceutical synthesis. The processes in reference iii and iv do give closer to perfect enantiomer ratios, which could be advantageous for some applications.

None of the papers discussed describes conversion to a primary amine product, so was not considered in detail, but we note the literature deprotection conditions for our work and reference ii are the same (DDQ etc) and are not considered disadvantageous. The removal of tosyl groups from ref iii and iv has, at least in our experience and some other colleagues, been one of the more forcing ones. For example, one common process is to heat in concentrated HBr using phenol as solvent!

Other approaches that were considered but not analysed in detail:
As noted in the introduction to the main paper, Morris and co-workers,[v] report some excellent results for other imine reductions using an Fe catalyst, but lower yield and *er* for the synthesis of an amino-indane. There are other reductive amination protocols published that were not applied to this type of substrate to the best of our knowledge.

We felt it reasonable to only consider methods for making an N-substituted amino indane. We did however, check the literature for a method that might not quite fit our criteria but could be competitive, in particular bio-catalysis, as discussed below.

Methods such as enzymatic kinetic resolutions tend to only form the primary amines and are limited with yield below 50% *and* the need to first synthesise a racemate amino-indane: these substrates are likely most efficiently made from indanone using a reductive amination process such as an unselective version of that described here for example (with racemic catalyst). We could point to

other sustainability disadvantages to some of the state of the art methods, even when yields are slightly above 50% due to enantiomer recycling.[vi]

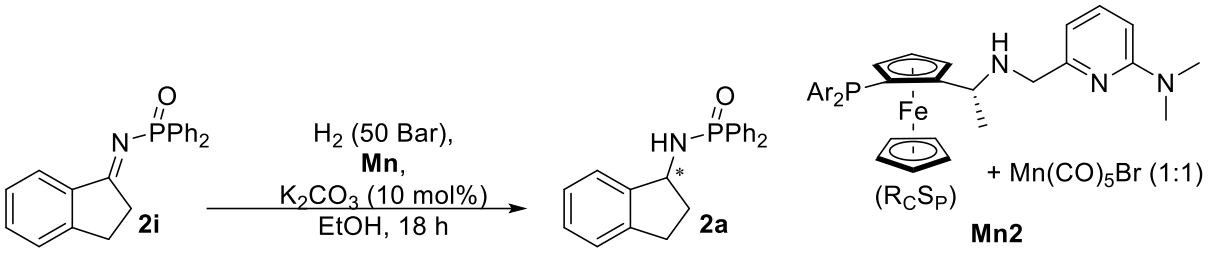
Organocatalytic reductions make use of a heavy dihydropyridine reductant (mwt = 253) as source of H2. 10 mol% of an organocatalyst has been used to directly aminate indanone in benzene as solvent to give a protected amino-indane with an *er* of 93:7. This excellent reaction has drawbacks associated with the need to employ 3 equivalents of indanone so the 75% yield based on anisidine becomes only 25% of indanone converted (albeit with catalysts loading now 3.3%).[vii]
We have not analysed imine hydrosilylations or hydroborations, since we felt it likely that the lower score for a reductant such as SiCl3H would likely make such reactions less competitive by this analysis.
Biocatalytic reductive amination with transaminase enzymes is an emerging and distinct technology with its own advantages and challenges [viii]. However, this was excluded from detailed analysis since it produces primary amine only. In any case, we have not been able to find a preparative process for making the primary amino-indane. If one considers preliminary screening analytic scale reactions for the primary amino-indane with no product isolation, the ammonia surrogates are quite high mass and complex.[viii]

We would stress again that all of the papers discussed here are innovative, well carried out research papers. ***However, from the perspective of the potential for a sustainable and environmentally benign process, a qualitative analysis appears to be sufficient to clearly establish a significant gap in positive attributes between the current work and the previous state of the art methods for producing amino-indanes.***

[i] P. Jessop, *Green Chem.*, 2020, **22**, 13.
[ii] D. Brenna, S. Rossi, F. Cozzi, M. Benagalia, *Org. Biomol. Chem*., 2017, **15**, 5685-5688.
[iii] Q. Yang, G. Shang, W. Gao, J. Deng, X. Zhang, *Angew. Chem. Int. Ed.*, 2006, **45**, 3842.
[iv] X. Zhao, H. Xu, X. Huang, J. S. Zhou, *Angew. Chem. Int. Ed.*, 2019, **58**, 292-296.
[v] C. S. Seo, T. Tannoux, S. A. Smith, A. J. Lough and R. H. Morris, *J. Org. Chem.*, 2019, **84**, 12040–12049.
[vi] G. A. Aleku, J. Mangas-Sanchez, J. Citoler, S. P. France, S. L. Montgomery, R. S. Heath, M. P. Thompson and N. J. Turner, *ChemCatChem*, 2018, **10**, 515.
[vii] R. I. Storer, D. E. Carrera, Y. Ni. and D. W. C. MacMillan, *J. Am. Chem. Soc*., 2006, **128**, 84.
[viii] a) J. H. Schrittwieser, S. Velikogne, W. Kroutil, *Adv. Synth. Catal.*, 2015, **357**, 1655.; b) A. P. Green, N. J. Turner and E. O'Reilly, *Angew. Chem. Int. Ed*., 2014, **53**, 10714.; c) C. A. McKenna, M. Stiblarikova, I. De Silvestro, D. J. Campopiano, A. L. Lawrence, *Green Chem.* 2022, **24**, 2010.

Section 2.1: Comment on selection of catalyst

We recently reported the catalytic system **Mn2** which gave high enantioselectivity in the hydrogenation of cyclic ketones.[1] We therefore investigated the use of **Mn2** in the hydrogenation of **2i** and compared the results to those obtained with **Mn1**:



Entry	Catalyst	Catalyst Loading (mol%)	T (°C)	Yield (%)	e.r (*S*/*R*)
1	**Mn1**	1	50	99	92:8
2	**Mn1**	1	35	99 (96)	94:6
3	**Mn2**	1.5	50	99 (93)	17:83

As the enantioselectivity observed in our benchmarking experiment was lower with **Mn2** than with the simpler **Mn1** we did not use it in further experiments.

Section 2.2: General Information

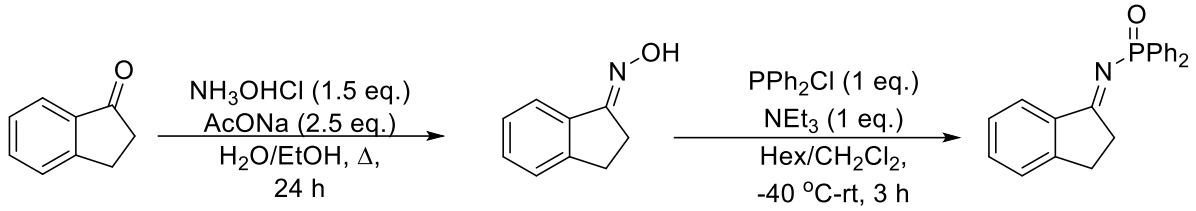
The preparation of solutions for the use in catalytic reactions was carried out under either argon or nitrogen atmosphere. All glassware was flame dried and cooled under vacuum before use. Unless otherwise stated, all chemicals were purchased from SigmaAldrich, Acros, Alfa Aesar, Strem or TCI and used as received. Substrates were not dried before use in catalysis reactions. Unless otherwise stated, solvents used were 'Extra Dry, AcroSeal™, ACROS Organics' purchased from Fisher Scientific. 'Bench-grade' toluene used for imine formation reactions (100 mL at a time) was dried in a Schlenk flask containing activated 3Å molecular sieves (20 g, 20 % w/v) under an argon atmosphere for 72 hours. Room temperature refers to the temperature range 15- 25 °C. Catalyst **Mn1** was prepared in same way as previously reported literature.[2]

Mn1 was stored under dry, inert gas and weighed in air. Heating the reaction mixtures was done with either an oil bath or a Drysyn heating block. Reported temperature is the oil bath or heating block temperature and not internal temperature. In vacuo refers to either the use of a Heidolph Laborota 4001 rotary evaporator or the use of a high-vacuum line. Analytical thin layer chromatography (TLC) was carried out on pre-coated plastic plates (Kieselgel 60 F254 silica). TLC visualization was carried out using a UV lamp (254nm) or using a 1% potassium permanganate aqueous solution. Flash silica chromatography was performed using Kieselgel 60 silica. ^{1}H, ^{13}C, ^{31}P, NMR was carried out using either a Bruker Avance II 400 (400 MHz ^{1}H, 100 MHz ^{13}C, 161 MHz ^{31}P or a Bruker Ultrashield 500 (500 MHz ^{1}H, 125 MHz ^{13}C, 202 MHz ^{31}P). NMR analyses were carried out at room temperature in deuterated solvent. The chemical shifts are quoted as parts per million (ppm). Coupling constants, J, are quoted in Hz. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The abbreviation "b" is used to denote broad peak shape. Mass spectrometric (m/z) data was acquired by electrospray ionisation (ESI) or electron impact (EI) at the University of St Andrews Mass Spectrometry facility (using Micromass LCT spectrometer or Micromass GCT spectrometer). Values are reported as a ratio of mass to charge in Daltons. Optical rotations were measured on a Perkin Elmer 341 polarimeter using a 1 ml cell with a 1 dm path length at room temperature using the sodium D-line, and a suitable solvent that is reported along with the

concentration (c = g/100 mL). HPLC analysis was determined using a Varian Prostar operated by Galaxie workstation PC software. For chromatograms where peak baselines were not fully resolved the lowest point between the two peaks were chosen as the cut-off point. Absolute configuration of amine products was determined by comparison of the sign of [α_D^{20}] values with literature or by analogy of the selectivity of the catalyst with similar substrates.

Section 3.1: Preparation of imine subtrates

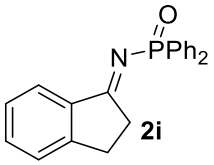
Preparation of (*E*)-*N*-(2,3-dihydro-1H-inden-1-ylidene)-*P*,*P*-diphenylphosphinic amide (**2i**)[3]



(Procedure adapted from ref. S16) To a 50 mL round bottom flask fitted with condenser and charged with a magnetic stirrer was added: indanone (10 mmol, 1 eq.), hydroxylamine HCl (15 mmol, 1.5 eq.) and sodium acetate (25 mmol, 2.5 eq.). The reagents were dissolved in a H_2O (6.25 mL)/ EtOH (3.75 mL) mixture (1 M solution) and stirred at reflux (73 °C) for 24 h. Upon which time the solution was cooled to rt and then to 0 °C resulting in the precipitation of oxime product. This precipitate was collected by filtration, allowed to air dry overnight and used in next step without further purification.

A flame dried, 50 mL 2-neck flask fitted with rubber septa was cycled between vacuum and Ar atmosphere 3 times. A rubber septum was removed and the flask fitted quickly with a thermometer. A rubber septum was briefly removed to allow (E)-2,3-dihydro-1H-inden-1-one oxime (7 mmol, 1 eq.) to be added. NEt_3 (7 mmol, 1 eq.) was then added *via* syringe. The reagents were dissolved in a CH_2Cl_2 (5 mL)/ Hexane (5 mL) mixture (0.7 M solution) and the solution cooled to -40 °C with stirring. Diphenylphosphine chloride (7 mmol, 1 eq. as 1 M solution in CH_2Cl_2) was then added to the flask over 30 minutes whilst maintaining a temperature of -40 °C. The reaction was then warmed to rt and allowed to stir for another 2.5 h. The reaction was then filtered and concentrated *in vacuo*. The crude material was dissolved in Acetone (20 mL) and filtered again to remove insoluble material. The products were then purified by flash column chromatography on silica gel using Hexane/Acetone (1:1) to give:

(*E*)-*N*-(2,3-dihydro-1H-inden-1-ylidene)-*P*,*P*-diphenylphosphinic amide (**2i**)

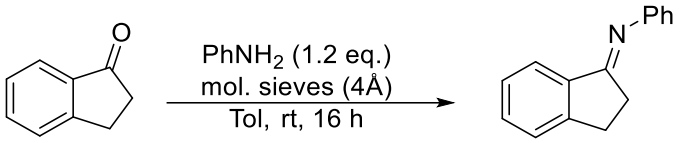


2i

Yield (7 mmol scale): 505.5 mg (22%) of white solid

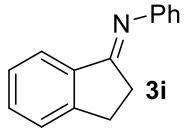
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (5H, m, 5Ar-H), 7.58 – 7.52 (1H, m, Ar-H), 7.49 – 7.36 (8H, m, 8Ar-H), 3.32 – 3.24 (2H, m, C**HH'**-C=N), 3.16 – 3.10 (2H, m, C**HH'**-Ar). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 21.00. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0 (d, J= 7.3 Hz, C=N), 153.5 (Ar-C), 135.0 (d, J= 128.1, Ar-P), 134.2 (Ar-C), 131.8 (d, J= 9.1, Ar-H) 131.4 (d, J= 2.8 Hz, Ar-H), 128.5 (d, J= 12.4, Ar-H), 127.3 (Ar-H), 126.1 (Ar-H), 124.1 (Ar-H), 35.1 (d, J=11.7, CH_2), 28.8 (CH_2). HRMS (ESI+): Calculated for [$C_{21}H_{19}NOP$]: 332.1199 Found: 332.1192.

Preparation of (*E*)-*N*-phenyl-2,3-dihydro-1H-inden-1-imine (**3i**)



A 50 mL Schlenk flask fitted with rubber septum and charged with magnetic stirrer was flame dried under vacuum. The flask was cycled between vacuum and Ar atmosphere 3 times and the rubber septum briefly removed to allow addition of indanone (25 mmol, 1 eq.) and activated 4Å molecular sieves (10 g, 0.5 w/v). Aniline (30 mmol, 1.2 eq.) was then added *via* syringe followed by dried toluene (20 mL) *via* syringe. The reaction was then allowed to stir at rt under Ar atmosphere for 16 h. The reaction was concentrated *in vacuo* and the resulting oil was triturated from hexane at 0 °C. The solid resulting from this was then washed extensively with hexane to give:

(*E*)-*N*-phenyl-2,3-dihydro-1H-inden-1-imine (**3i**)



3i

Yield (25 mmol scale): 1.21 g (23%) of off-white solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (1H, d, *J* = 7.6 Hz, Ar-H), 7.50 – 7.43 (1H, m, Ar-H), 7.42 – 7.31 (4H, m, 4Ar-H), 7.14 – 7.06 (1H, m, Ar-H), 6.97 – 6.88 (2H, m, 2Ar-H), 3.10 – 3.02 (2H, m, C**HH'**-C=N), 2.71 – 2.64 (2H, m, C**HH'**-Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4 (C=N), 152.5 (Ar-C), 150.6 (Ar-C), 139.5 (Ar-C), 132.1 (Ar-H), 129.2 (Ar-H), 127.3 (Ar-H), 125.9 (Ar-H), 123.7 (Ar-H), 123.1 (Ar-H), 119.8 (Ar-H), 29.6 (CH_2), 28.3 (CH_2). HRMS (ESI+): Calculated for [$C_{15}H_{14}N$]: 208.1121 Found: 208.1115.

Section 3.2: General procedures for the asymmetric hydrogenation of (*in situ* formed) imines

Procedure for hydrogenation of *E*-*N*-(2,3-dihydro-1H-inden-1-ylidene)-*P*,*P*-diphenylphosphinic amide (**Method A**):
A microwave vial charged with magnetic stirrer bar and fitted with rubber septum was flame dried under vacuum. The vial was cooled to rt and then cycled between vacuum and Ar atmosphere three times. Working quickly, the rubber septum was removed then: *N*-diphenylphosphinoyl imine (1 eq.), Cat. (0.01 eq.) and K_2CO_3 (0.1 eq.) were added and the vial fitted with a crimp camp and septum. The vial was placed back under vacuum for a further 10 minutes. After cycling vacuum and argon atmosphere three more times, EtOH (0.67 M) was added *via* syringe, the septum pierced by two 21G needles and the vial placed directly into an autoclave which had been cycled between vacuum and Ar atmosphere 3 times. The autoclave was sealed and pressurised to 15 Bar of H_2 which was subsequently vented, this was repeated two more times to degas the solvent. Finally the autoclave was pressurised to 50 Bar H_2 and the autoclave then placed in an oil bath preheated to 35 °C and stirred at 700 rpm for 18 h. Upon which time, the autoclave was cooled to rt, carefully vented in a fume cupboard and 1,4-dimethoxybenzene (0.25 eq. [relative to *N*-diphenylphosphinoyl imine]) was added to the sample as internal standard. The reaction was diluted in $CDCl_3$ (1 mL) and a small aliquot taken for ^{1}H NMR analysis to determine conversion. The NMR sample was retrieved and combined with the reaction mixture and all solvent was removed *in vacuo* prior to chromatographic purification.

Procedure for hydrogenation of (*E*)-*N*-phenyl-2,3-dihydro-1H-inden-1-imine (**Method B**):
A microwave vial charged with magnetic stirrer bar and fitted with rubber septum was flame dried under vacuum. The vial was cooled to rt and then cycled between vacuum and Ar atmosphere three times. Working quickly, the rubber septum was removed then: (*E*)-*N*-phenyl-2,3-dihydro-1H-inden-1-imine (1 eq.), Cat. (0.01 eq.) and K_2CO_3 (0.1 eq.) were added and the vial fitted with a crimp camp and septum. The vial was placed back under vacuum for a further 10 minutes. After cycling vacuum and argon atmosphere three more times, EtOH (0.67 M) was added *via* syringe, the septum pierced by two 21G needles and the vial placed directly into an autoclave which had been cycled between vacuum and Ar atmosphere 3 times. The autoclave was sealed and pressurised to 15 Bar of H_2 which was subsequently vented, this was repeated two more times to degas the solvent. Finally the autoclave was pressurised to 50 Bar H_2 and the autoclave was then placed in an oil bath preheated to 50 °C and stirred at 700 rpm for 18 h. Upon which time, the autoclave was cooled to rt, carefully vented in a fume cupboard and 1,4-dimethoxybenzene (0.25 eq. [relative to (*E*)-*N*-phenyl-2,3-dihydro-1H-inden-1-imine]) was added to the sample as internal standard. The reaction was diluted in $CDCl_3$ (1 mL) and a small aliquot taken for ^{1}H NMR analysis to determine conversion.

General Procedure for hydrogenation of *in situ* generated ketimines (**Method C**):
A microwave vial charged with magnetic stirrer bar and fitted with rubber septum was flame dried under vacuum. The vial was cooled to rt and then cycled between vacuum and Ar atmosphere three times. The septum was briefly removed to allow addition of: activated 4Å molecular sieves (100% w/v with respect to reaction solvent), ketone (1 eq.) (if ketone was solid at rt) and amine (1 eq.) (if amine was solid at rt). If either ketone or amine were liquid at rt, 1 eq. was then added by micro-syringe. Then dried toluene (1M) was added *via* syringe. The reaction was placed in a preheated oil bath at 70 °C and stirred for 4 h under Ar atmosphere.

A separate microwave vial charged with magnetic stirrer bar and fitted with rubber septum was flame dried under vacuum. The vial was cooled to rt and then cycled between vacuum and Ar atmosphere three times. Working quickly, the rubber septum was removed then: Cat. (0.01 eq.) and K_2CO_3 (0.1 eq.) were added and the vial fitted with a crimp camp and septum. The vial was placed back under vacuum for a further 10 minutes. After cycling vacuum and argon atmosphere three more times and allowing the imine formation reaction to cool to rt, the solution was decanted into the vial containing the catalyst and base *via syringe*. EtOH (0.67 M with respect to ketone) was added *via* syringe to the vial in which the imine formation had taken place in two portions and subsequently decanted into the other vial each time. The septum of the vial was then pierced by two 21G needles and the vial placed directly into an autoclave which had been cycled between vacuum and Ar atmosphere 3 times. The autoclave was sealed and pressurised to 15 Bar of H_2 which was subsequently vented, this was repeated two more times to degas the solvent. Finally the autoclave was pressurised to 50 Bar H_2 and the autoclave was then placed in an oil bath preheated to 50 °C and stirred at 700 rpm for 18 h. Upon which time, the autoclave was cooled to rt, carefully vented in a fume cupboard and 1,4-dimethoxybenzene (0.25 eq. [relative to ketone]) was added to the sample as internal standard. The reaction was diluted in $CDCl_3$ (1 mL) and a small aliquot taken for ^{1}H NMR analysis to determine conversion. The NMR sample was retrieved, combined with the reaction mixture and all solvent was removed *in vacuo* prior to chromatographic purification.

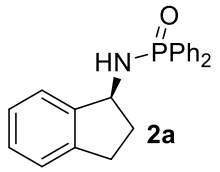
Preparation of racemic samples for HPLC:

A microwave vial charged with magnetic stirrer bar and fitted with rubber septum was flame dried under vacuum. The vial was cooled to rt and then cycled between vacuum and Ar atmosphere three times. The septum was briefly removed to allow addition of: activated 4Å molecular sieves (100% w/v with respect to reaction solvent), ketone (1 eq.) (if ketone was solid at rt) and amine (1 eq.) (if amine was solid at rt). If either ketone or amine were liquid at rt 1 eq. was then added by micro-syringe. Then dried toluene (1M) was added *via* syringe. The reaction was placed in a preheated oil bath at 70 °C and stirred for 4 h under Ar atmosphere.

The reaction was then cooled to rt, decanted into a vial and diluted with MeOH (3 mL). $NaBH_4$ (3 eq.) was then added, the vial loosely capped and stirred at rt for 16 h. The solution was then washed with water (10 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The organic phases were combined, washed with brine and dried over Na_2SO_4. The solution was filtered and solvent removed *in vacuo* and samples were used without further purification.

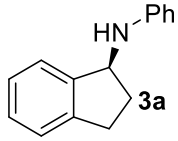
Section 3.3: Characterisation data for amine products:

N-(2,3-dihydro-1H-inden-1-yl)-*P*,*P*-diphenylphosphinic amide (**2a**)



Produced by method A
Purified by flash column chromatography on silica gel using Hexane/EtOAc (9:1 then 4:1)
Yield (0.1 mmol scale): 32.3 mg (96%) of beige solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.95 (4H, m, 4Ar-H), 7.68 (1H, d, *J* = 7.3 Hz, Ar-H), 7.56 – 7.41 (6H, m, 6Ar-H), 7.25 – 7.16 (3H, m, 3Ar-H), 4.71 – 4.57 (1H, m, C**H**-N), 3.27 – 3.12 (1H, m, C**H**H'-Ar), 2.99 – 2.86 (1H, m, CH**H'**-Ar), 2.80 – 2.68 (1H, m, C**H**H'-CH), 2.66 – 2.52 (1H, m, CH**H'**-CH), 2.05 – 1.88 (m, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 22.5. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9 (d, *J* = 6.4 Hz, Ar-C), 142.9 (Ar-C), 132.4 (d, *J* = 9.1 Hz, Ar-P), 132.32 (d, *J* = 9.2 Hz, Ar-H), 132.0 (Ar-H), 128.8 (d, *J* = 3.5 Hz, Ar-H), 128.7 (d, *J* = 3.6 Hz, Ar-H), 127.9 (Ar-H, 126.9 (Ar-H), 124.7 (d, *J* = 6.2 Hz, Ar-H), 57.0 (CH), 37.4 (d, *J* = 3.9 Hz, CH_2), 30.2 (CH_2). [α_D^{20}]: -58.2 (c. 0.28, $CHCl_3$); Lit.[4]: -47.7 (c. 1.0, $CHCl_3$, ee. 93%, *S*). HRMS (ESI+): Calculated for [$C_{21}H_{21}NOP$]: 334.1355 Found: 334.1349. HPLC analysis conducted with Daicel Chiralcel OD-H column, hexane/^{i}PrOH (90:10) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 17.46 min (6%) t_R(*S*)= 21.57 min (94%.) ee= 88%. Compound has been prepared previously by alternative route and data reported here is consistent with previously reported data.[5]

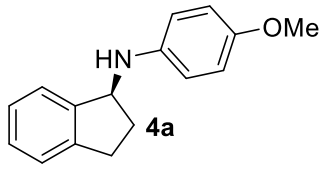
N-phenyl-2,3-dihydro-1H-inden-1-amine (**3a**)



Produced by method B and also by method C
Purified by flash column chromatography on silica gel using Hexane/EtOAc (9:1)

Yield (0.5 mmol scale): 76.3 mg (73%)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (1H, d, *J* = 7.4 Hz, Ar-H), 7.29-7.26 (2H, m, 2Ar-H), 7.25 – 7.19 (3H, m, 3Ar-H), 6.78 – 6.72 (3H, m, 3Ar-H), 5.03 (1H, t, *J* = 6.7 Hz, C**H**-N), 3.10 – 2.98 (1H, m, C**H**H'-Ar), 2.95 – 2.85 (1H, m, CH**H'**-Ar), 2.64 – 2.55 (1H, m, C**H**H'-CHN), 2.00 – 1.88 (1H, m, CH**H'**-CHN). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7 (Ar-C), 144.5 (Ar-C), 143.8 (Ar-H), 129.5 (Ar-H), 128.1 (Ar-H), 126.8 (Ar-H), 125.0 (Ar-H), 124.5 (Ar-H), 117.8 (Ar-C), 113.5 (Ar-H), 58.9 (CH), 33.9 (CH_2), 30.4 (CH_2). [α_D^{20}]: +49.7 (c. 1.0, $CHCl_3$). HRMS (ESI+): Calculated for [$C_{15}H_{16}N$]: 210.1277 Found: 210.1272. Method B: HPLC analysis conducted with Daicel Chiralcel OD-H column, hexane/^{i}PrOH (95:5) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 15.35 min (4%) t_R(*S*)= 16.88 min (96%.) ee= 92%. Method C: HPLC analysis conducted with Daicel Chiralcel OD-H column, hexane/^{i}PrOH (95:5) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 15.35 min (4%) t_R(*S*)= 16.68 min (96%.) ee= 92%. Compound has been prepared previously by alternative route and data reported here is consistent with previously reported data.[6]

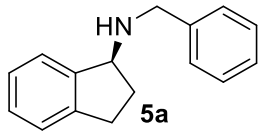
N-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-amine (**4a**)



4a

Produced by method C
Yield: (71%) of yellow oil
Purified by flash column chromatography on silica gel using Hexane/EtOAc (9:1)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (1H, d, *J* = 7.3 Hz, Ar-H), 7.25 – 7.17 (3H, m, 3Ar-H), 6.84 – 6.79 (2H, m, 2Ar-H), 6.73 – 6.66 (2H, m, 2Ar-H), 4.96 (1H, t, *J* = 6.8 Hz, C**H**-N), 3.77 (3H, s, OMe), 3.07 – 2.97 (1H, m, C**H**H'-Ar), 2.94 – 2.85 (1H, m, CH**H'**-Ar), 2.65 – 2.50 (1H, m, C**H**H'-CHN), 1.97 – 1.84 (1H, m, CH**H'**-CHN). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (Ar-C), 145.0 (Ar-C), 143.7 (Ar-O), 142.2 (Ar-N), 128.0 (Ar-H), 126.7 (Ar-H), 125.0 (Ar-H), 124.4 (Ar-H), 115.1 (Ar-H), 114.7 (Ar-H), 59.6 (CH), 56.0 (CH_3), 34.0 (CH_2), 30.4 (CH_2). [α_D^{20}]: +48.1 (c. 0.6, $CHCl_3$). HRMS (ESI+): Calculated for [$C_{16}H_{18}NO$]: 240.1383 Found: 240.1383. HPLC analysis conducted with Daicel Chiralcel OD-H column, hexane/^{i}PrOH (95:5) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 16.06 min (5%) t_R(*S*)= 16.95 min (95%.) ee= 90%. Compound has been prepared previously by alternative route and data reported here is consistent with previously reported data.[7]

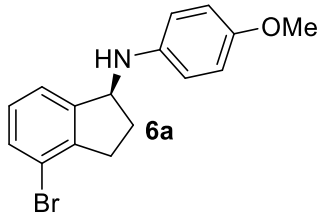
N-benzyl-2,3-dihydro-1H-inden-1-amine (**5a**)



5a

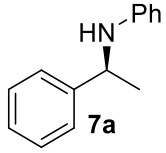
Produced by method C
Yield: n.d
Upon completion, reaction was concentrated to dryness *in vacuo*, dissolved in CH_2Cl_2 (5 mL) and then Boc_2O (43.7 mg, 0.2 mmol, 0.8 eq.) and NEt_3 (0.07 mL, 0.5 mmol, 2 eq.) was added and the reaction stirred at rt for 72 h. The reaction was diluted with water (15 mL) and extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers dried over Na_2SO_4. The solution was filtered and solvent removed before removing remaining imine by flash column chromatography on silica gel using hexane/ EtOAc (14:1) as eluent. The resultant product was not analytically pure but was now amenable to HPLC analysis. (After standard racemate preparation, this procedure was also followed to prepare the racemic HPLC sample).
HPLC analysis conducted with Daicel Chiralcel OD-H column, hexane/^{i}PrOH (99:1) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 9.59 min (2%) t_R(*S*)= 11.63 min (98%.) ee= 96%.

4-bromo-*N*-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-amine (**6a**)



Produced by method C
Purified by flash column chromatography on silica gel using Hexane/EtOAc (9:1 then 4:1)
Yield (0.25 mmol scale): 70.4 mg (88%) of red/ brown oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (1H, d, *J* = 7.7 Hz, Ar-H), 7.29 (1H, d, *J* = 7.7 Hz, Ar-H), 7.07 (1H, t, *J* = 7.7 Hz, Ar-HH), 6.84 – 6.79 (2H, m, 2Ar-H), 6.70 – 6.65 (2H, m, 2Ar-H), 5.03 (1H, t, *J* = 7.0 Hz, C**H**-N), 3.77 (3H, s, OMe), 3.09 – 2.99 (1H, m, C**H**H'-Ar), 2.93 – 2.83 (1H, m, CH**H'**-Ar), 2.64 – 2.54 (1H, m, C**H**H'-CHN), 1.96 – 1.84 (1H, m, CH**H'**-CHN). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5 (Ar-C), 147.0 (Ar-C), 143.9 (Ar-O), 141.7 (Ar-N), 131.0 (Ar-H), 128.6 (Ar-H), 123.3 (Ar-H), 120.4 (Ar-Br), 115.2 (Ar-H), 114.8 (Ar-H), 60.6 (CH), 56.0 (CH_3), 33.1 (CH_2), 31.7 (CH_2). [α_D^{20}]: -6.4 (c. 0.5, $CHCl_3$). HRMS (ESI+): Calculated for [$C_{16}H_{17}NOBr$]: 318.0488 Found: 318.0487. HPLC analysis conducted with Daicel Chiralcel AD-H column, hexane/^{i}PrOH (95:5) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 20.91 min (5%) t_R(*S*)= 22.37 min (95%.) ee= 90%.

N-(1-phenylethyl)aniline (**7a**)



Produced by method C
Purified by flash column chromatography on silica gel using Hexane/Et_2O (2:1)
Yield (0.25 mmol scale): 45.9 mg (93%) pale green oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (2H, m, 2Ar-H), 7.35 – 7.28 (2H, m, 2Ar-H), 7.25 – 7.21 (1H, m, Ar-H), 7.12 – 7.06 (2H, m, 2Ar-H), 6.65 (1H, t, *J* = 7.2 Hz, Ar-H), 6.52 (d, *J* = 8.1 Hz, 2H), 4.49 (1H, q, *J* = 6.7 Hz, CH), 1.52 (3H, d, *J* = 6.7 Hz, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3 (Ar-C), 145.3 (Ar-C), 129.2 (Ar-H), 128.8 (Ar-H), 127.0 (Ar-H), 126.0 (Ar-H), 117.4 (Ar-H), 113.5 (Ar-H), 53.7 (CH), 25.1 (CH_3). [α_D^{20}]: +27.3 (c. 1.1, $CHCl_3$); Lit.[8]: +16.0 (c. 0.001, CH_2Cl_2, ee. 56%, *S*). HRMS (ESI+): Calculated for [$C_{14}H_{16}N$]: 198.1277 Found: 198.1277. HPLC analysis conducted with Daicel Chiralcel OD-H column, hexane/^{i}PrOH (99:1) as mobile phase with a 0.5 mL/min flowrate. t_R(*R*)= 17.97 min (18%) t_R(*S*)= 21.56 min (82%.) ee= 64%. Compound has been prepared previously by alternative route and data reported here is consistent with previously reported data.[9]

Section 3.4: **Experimental References:**

1 C. L. Oates, A. S. Goodfellow, M. Bühl and M. L. Clarke, *Angew. Chem. Int. Ed.*, 2023, **62**, e202212479.
2 M. B. Widegren and M. L. Clarke, *Catal. Sci. Technol.*, 2019, **9**, 6047–6058.
3 J. Huang, X. Liu, Y. Wen, B. Qin and X. Feng, *J. Org. Chem.*, 2007, **72**, 204–208.
4 A. Bezłada, M. Szewczyk and J. Mlynarski, *J. Org. Chem.*, 2016, **81**, 336–342.
5 C. S. G. Seo, T. Tannoux, S. A. M. Smith, A. J. Lough and R. H. Morris, *J. Org. Chem.*, 2019, **84**, 12040–12049.
6 S. Werkmeister, K. Junge and M. Beller, *Green Chem.*, 2012, **14**, 2371–2374.
7 R. Porta, M. Benaglia, R. Annunziata, A. Puglisi and G. Celentano, *Adv. Synth. Catal.*, 2017, **359**, 2375–2382.

8 S. Sun, C. Reep, C. Zhang, B. Captain, R. Peverati and N. Takenaka, *Tetrahedron Lett.*, 2021, **81**, 153338.
9 S. Zhou, S. Fleischer, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2011, **50**, 5120–5124.

DFT Computations

Section 4.1: Computational Details

The DFT methodology was chosen following a benchmarking study of the heterolytic metal-hydride bond strengths for a series of 3d transition metal hydride complexes[1] and validated in our previous work on ketone reduction.[2]

Geometry optimisations were performed with the BP86 functional[3,4] using the double-ζ, def2-SVP basis set from the redefinition of the Ahlrichs family of basis sets.[5-8] As a pure functional, density fitting is available and the RI (resolution of identity) approximation has been used to reduce the computational cost whilst using an ultrafine integration grid (99 radial shells with 590 angular points per shell). Implicit solvation was considered through the use of IEF-PCM (Integral Equation Formalism variant of the Polarisable Continuum Model) employing the parameters of ethanol (ε = 24.85).[9-11] All species were formally treated as closed-shell systems and restricted DFT was used throughout. The nature of minima and transition states located were verified by the computation of harmonic frequencies at the same level of theory and transition states were subject to further intrinsic reaction coordinate calculations to formally verify the corresponding minima.[12] Single-point energies were evaluated using the hybrid PBE0 functional[13-15] with a larger, triple-ζ, def2-TZVP basis. Correctional terms to treat dispersion were included with the DFT-D3 empirical correction by Grimme,[16] including Becke-Johnson dampening[17] and implicit solvation corrections were included with this level of theory, using the same ultrafine integration grid (99,590). Thermochemistry was evaluated at 1 atm and 298.15 K using thermodynamic calculations at the level of geometry optimisation in combination with energetics obtained from single-point calculations. Gibbs free energy was calculated at the elevated reaction temperature of 323.15 K using Equation **1**, with additional Martin, Hay, Pratt empirical entropic corrections included (S_{MHP} = 3.929 kcal/mol per particle, evaluated at 454 atm to mimic bulk ethanol following the derivation outlined below).[18] All computations were performed using the Gaussian16, C.01 programme.[19] Visualisation of non-covalent interactions was performed using NCIPlot 4.0.[20]

$$\Delta G_{323.15} = \Delta H_{298.15} - T\,\Delta S_{298.15} \qquad [1]$$

Section 4.2: Derivation of S_{MHP} Entropic Correction

As calculations are performed in the gas phase, with implicit solvation around the cavity, it can be difficult to accurately predict the entropic contribution to Gibbs Free Energy of molecules. In solution, the solvent imposes additional restrictions on translational degrees of freedom that is not accounted for in gas phase calculations.[21] To compensate for this shortcoming, Martin, Hay and Pratt[17] introduced an empirical correction derived by artificially raising the pressure of gaseous water to that of the solvent phase, 1354 atm. In a reaction of mR ⇔ nP, this corresponds to a correctional term of (n - m) x 4.3 kcal/mol, irrespective of the nature of the particles involved in the reaction. This arises due to a change in the number of degrees of translational freedom when there is a change in particle numbers that must be corrected for. The use of this empirical correction has been used by our group in previous studies of catalytic systems and has been shown to be of importance in the prediction of stereochemical outcomes.[1,2,22-28]

The derivation of the correctional term, for the solvent ethanol, is shown below:

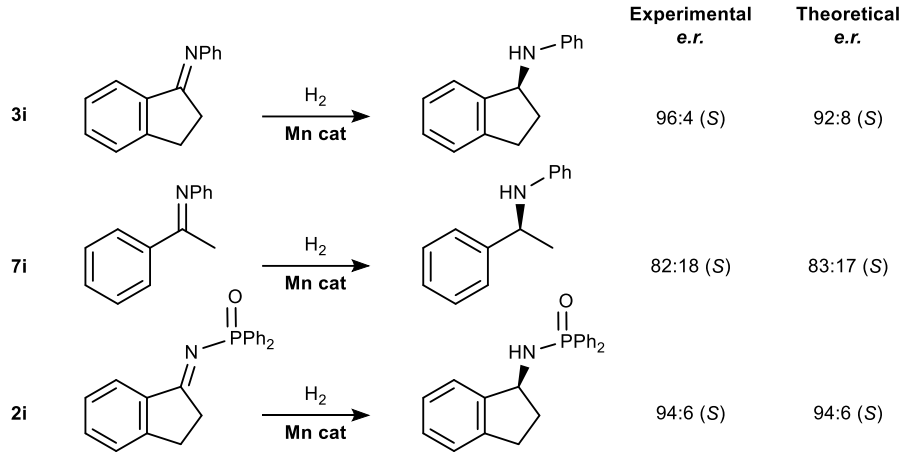
$$p = \frac{\rho RT}{M} = 454.40\ \text{atm}, \qquad [2]$$

$$S_{MHP} = RT\ ln\frac{p}{p^\circ} = 3.929\ \text{kcal/mol per particle}, \qquad [3]$$

where, p = EtOH pressure, ρ = density of EtOH (0.789 g/cm^3), M = molar mass of EtOH (46.07 g/mol), T = 323.15 K, p° = 1 atm, R = ideal gas constant (8.314 J/K.mol) and S_{MHP} = Martin, Hay, Pratt entropic correctional term.

Section 4.3: Computational Discussion

Using **Mn1** as a catalyst, the reduction of indanone-aniline proceeded with enhanced stereocontrol relative to the ketone analogues.



Scheme S1. Experimental and theoretical enantioselectivities obtained for imine hydrogenation.

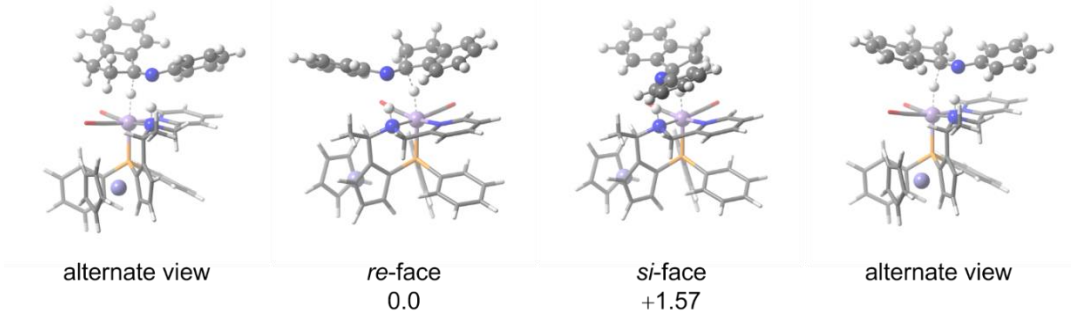


Figure S1. Hydride transfer transition state for diastereomeric transition states with each prochiral face of **3i**. Relative energies given as Gibbs Free Energy at 323.15 K in kcal/mol.

From the *re*-face transition state shown in Figure **S1**, the indan ring system is aligned above the pyridine ring of the ligand backbone and the *N*-phenyl group is orientated away from the rest of the ligand backbone. The *re*-face is favoured, with $\Delta\Delta^{\ddagger}G_{323}$ = −1.57 kcal/mol, corresponding to an *er.* of 92:8 (*S*).

There is a stronger bias for the reduction of **3i** than indanone itself (**3k**), with $\Delta\Delta^{\ddagger}G_{323}$ = −0.70 kcal/mol, and an *er.* of 75:25 (*S*). The imines have a stronger interaction energy than the ketones, due to the additional stabilisation from the *N*-phenyl group. For the *re*-face of **3i** and **3k**, $\Delta\Delta E_{int(imine\text{-}ketone)}$ = −1.69 kcal/mol, with a larger dispersive component $\Delta\Delta D3_{int(imine\text{-}ketone)}$ = −5.39 kcal/mol, indicative of the dispersive interactions from the *N*-phenyl group, which can be visualised from the NCI plots.

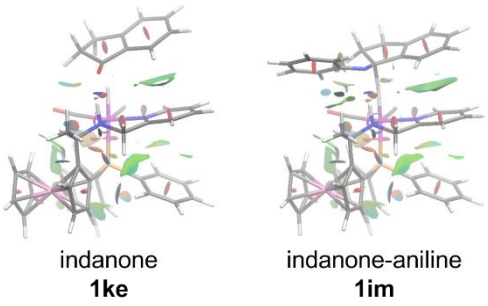


Figure S2. NCI plots of the hydride transfer transition state for the *re*-faces of **3k** and **3i**, with stronger interaction energy driven by dispersive interactions arising from the imine *N*-phenyl substituent.

Compared to the **3k**, there is an additional degree of flexibility associated with the *N*-phenyl substituent of **3i**. The most stable conformation for both prochiral faces have been calculated to be with the *N*-phenyl substituent orientated to the same side as the saturated sp^3 side of the indan ring system (Figure **S3**).

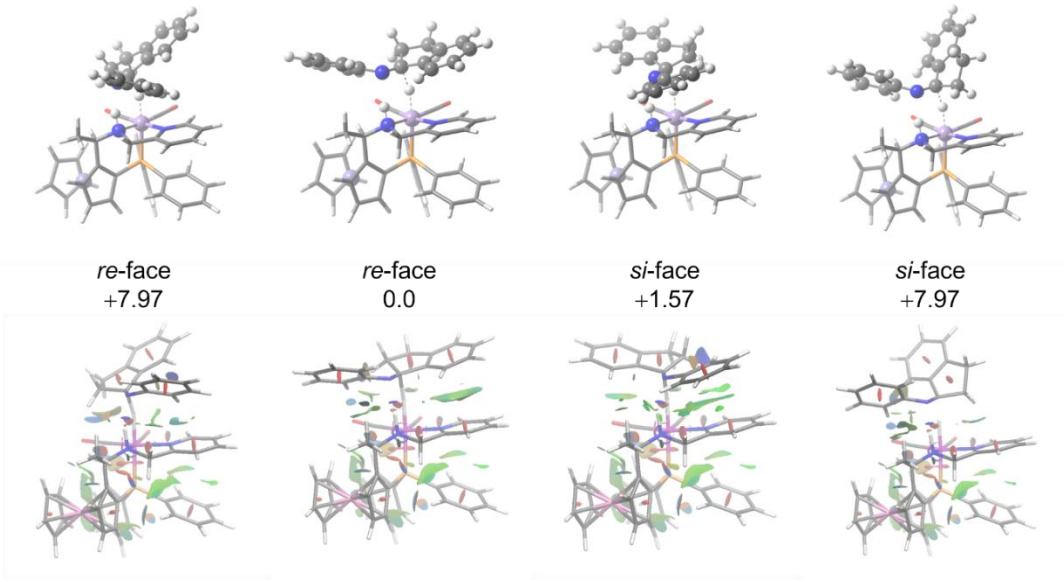


Figure S3. Hydride transfer transition states and visualisation of non-covalent interaction of **3i**, with different orientations of the *N*-phenyl substituent. Relative energies given as Gibbs Free Energy at 323.15 K in kcal/mol.

Between substrates **3i** and **7i**, there was a notable drop in terms of selectivity observed experimentally, from an *er.* of 96:4 to 82:18. Energetically, this variation in *er.* reflects a change in $\Delta\Delta^{\ddagger}G$ of *ca.* 1 kcal/mol. Transition states have been computed for **7i**, with consideration of orientation of the *N*-phenyl group (Figure **S4**). Unlike **3i**, the most stable orientation of *N*-phenyl is different for the approach of each prochiral face without the restriction of a fused ring system. The computed $\Delta\Delta^{\ddagger}G_{323}$ = −1.03 kcal/mol, corresponds to an *er.* of 83:17 (*S*), reduced relative to **3i**,.

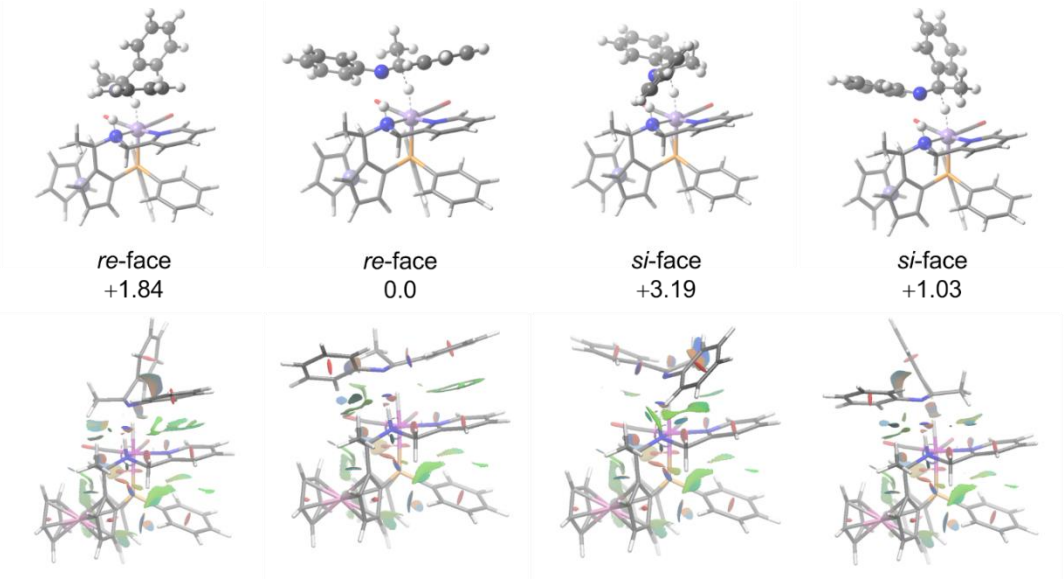


Figure S4. Hydride transfer transition states and visualisation of non-covalent interactions of **7i**. Relative energies given as Gibbs Free Energy at 323.15 K in kcal/mol.

Activated imine **2i**, was reduced with high *er.* using catalyst **Mn1** and has previously been reduced by the Morris group and calculated to proceed through an 8-membered transition state.[29] With **2i**, the reduction may proceed through a 6-membered transition state, similar to those shown in Figure **S3**, with the N-H proton interacting with the imine nitrogen (Figure **S5** [left]), $\Delta\Delta^{\ddagger}G_{323}$ = −1.31 kcal/mol, with an *er.* of 88:12 (*S*). Alternatively, unlike **3i**, the reduction can proceed through an 8-membered transition state, with the phosphinoyl oxygen acting as the hydrogen bond acceptor from the N-H proton donor (Figure **S5** [right]), $\Delta\Delta^{\ddagger}G_{323}$ = −1.75 kcal/mol, with an *er.* of

94:6 (*S*). The formation of this 8-membered transition state is more favourable than the 6-membered analogue by 0.78 kcal/mol. Compared to the imines themselves, the activated phosphinoyl imine has a far lower barrier associated with hydride transfer ($\Delta\Delta^{\ddagger}G_{323}$ = 5.58 kcal/mol, Table **S1**).

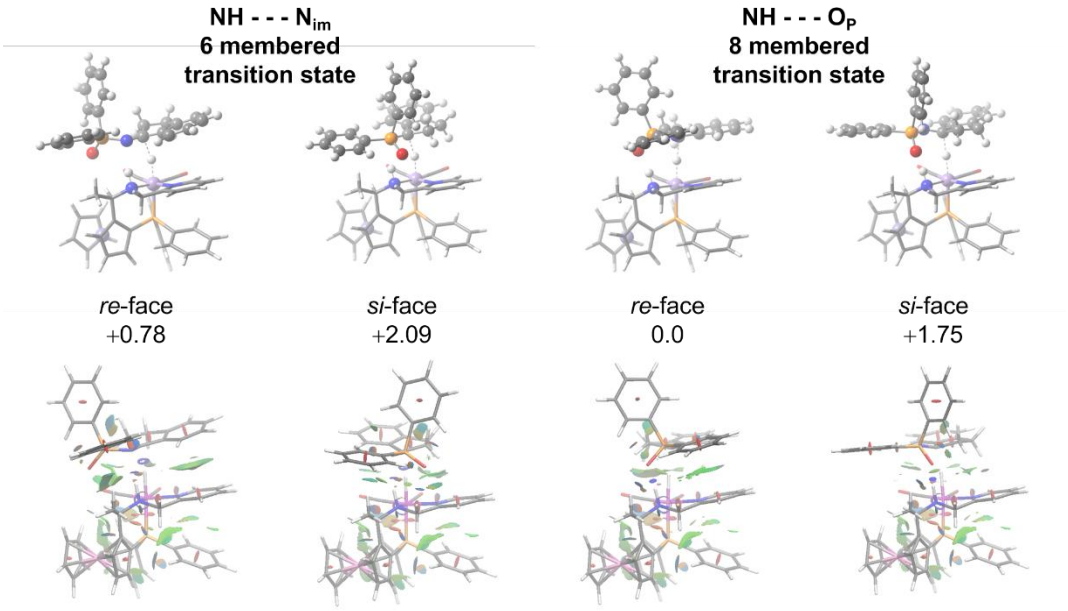


Figure S5. Hydride transfer transition states and visualisation of non-covalent interactions of **3im**, with N-H proton interaction with different hydrogen bond acceptors. Relative energies given as Gibbs Free Energy at 323.15 K in kcal/mol.

Recent work on ketone reduction used catalyst **Mn2**, with an *ortho*-dimethylamino substitution to the pyridine ring of **Mn1**.[2] With **Mn2**, the reaction proceeded with a switch in enantioselectivity, with an *er.* of 17:83 (*R*) observed experimentally. Calculations reveal the reduction to proceed through an 8-membered transition state with $\Delta\Delta^{\ddagger}G_{323}$ = 0.55 kcal/mol, with an *er.* of 30:70 (*R*) (Figure **S6**). In the most favourable orientation, one of the phenyl rings from the *N*-diphenylphosphinoyl group is aligned with the pyridine ring of the catalyst.

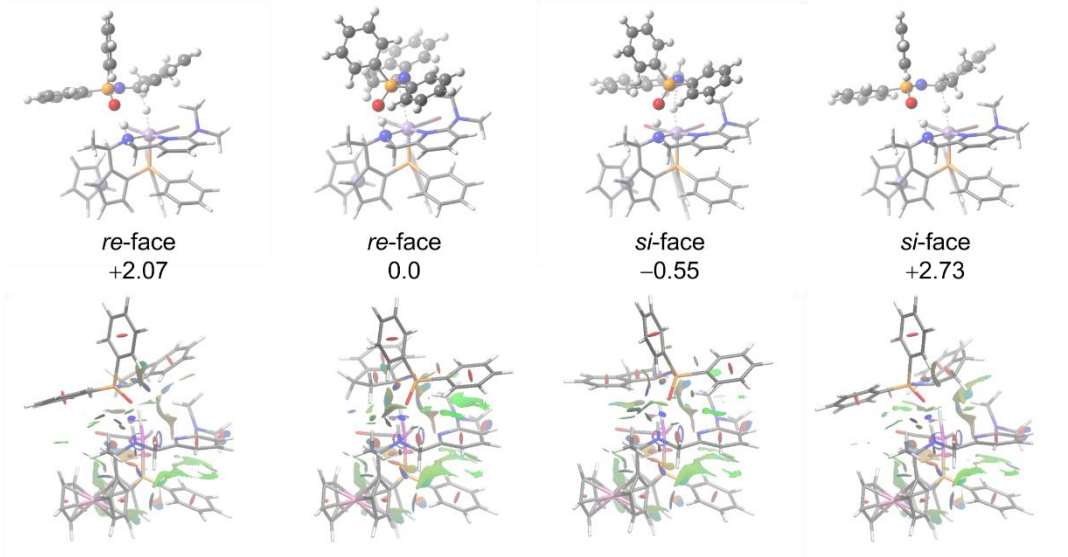
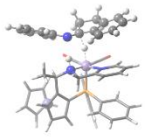
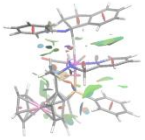
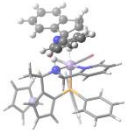
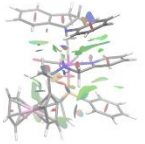
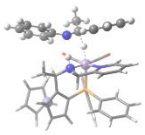
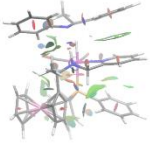
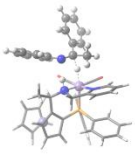
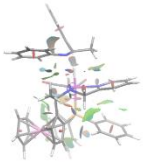
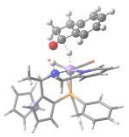
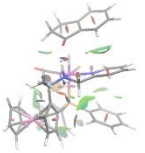
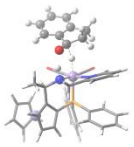
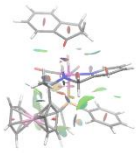
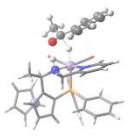
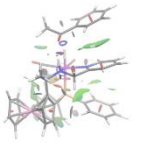
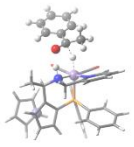
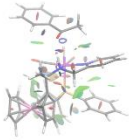
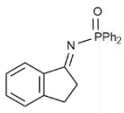
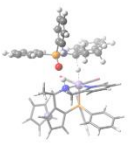
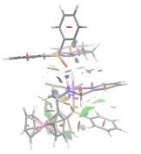
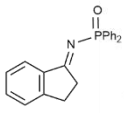
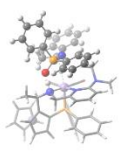
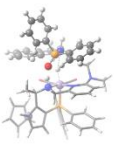
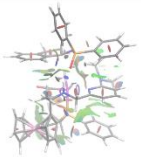


Figure S6. Hydride transfer transition states and visualisation of non-covalent interactions of **2i** with **Mn2**. Relative energies given as Gibbs Free Energy at 323.15 K in kcal/mol.

Table S1. Summary of the diastereomeric transition states for imine and ketone substrates with **Mn1**. Negative energies favour the *re*-face. Energies in kcal/mol and distances in Å.

	***re*-face (*S*)**		$\Delta^{\ddagger}G_{323}$ ***C–H*** ***Mn–H***	$\Delta\Delta^{\ddagger}G_{323}$ *er* $\Delta\Delta^{\ddagger}E$ $\Delta\Delta^{\ddagger}D3$	$\Delta^{\ddagger}G_{323}$ ***C–H*** ***Mn–H***	***si*-face (*R*)**		$\Delta\Delta E_{int}$ $\Delta\Delta D3_{int}$ gas phase
3i			**7.90** *1.607* *1.670*	**−1.57** 92:8 (*S*) −2.28 −0.55	**9.46** *1.618* *1.670*			−2.19 −0.51
7i			**8.80** *1.650* *1.665*	**−1.03** 83:17 (*S*) −0.67 −0.92	**9.83** *1.694* *1.679*			−1.46 −1.80
3k			**4.39** *1.690* *1.655*	**−0.69** 75:25 (*S*) −0.89 −0.64	**5.08** *1.690* *1.653*			−2.04 −0.59
7k			**4.06** *1.776* *1.640*	**−0.74** 76:24 (*S*) −0.97 −0.71	**4.80** *1.756* *1.642*			−2.08 −0.66
2i			**2.32** *1.680* *1.680*	**−1.75** 94:6 (*S*) −2.84 −1.02	**4.07** *1.642* *1.701*			−1.35 −1.14
2i*			**3.10** *1.621* *1.771*	**0.55** 30:70 (*R*) 0.52 0.78	**2.55** *1.678* *1.718*			−1.76 −0.41

* represents the use of **Mn2**

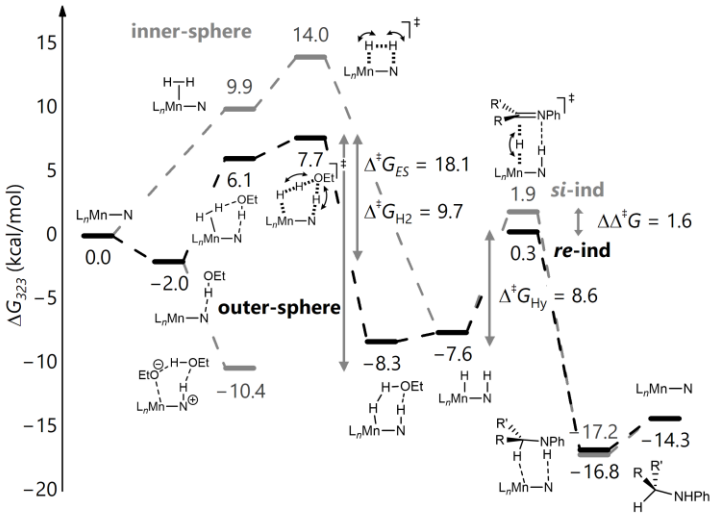


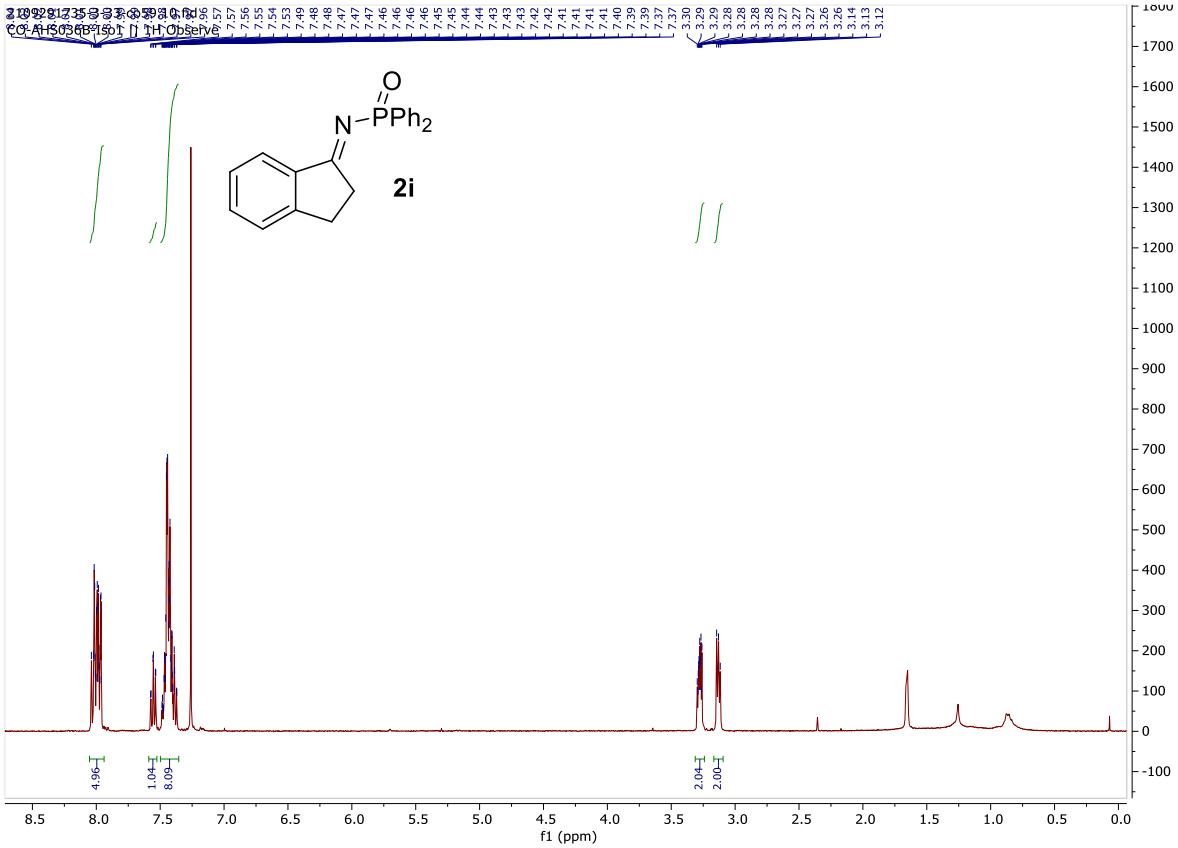
Figure S7. Potential free energy surface for the reduction of **3i** using catalyst **Mn1**, including a relevant ethoxide containing off-cycle species. Note that the barrier for H_2 activation ($\Delta^{\ddagger}G_{H2}$) is computed to be higher than that for subsequent reduction of the substrate ($\Delta^{\ddagger}G_{Hy}$). Also indicated is the overall rate-limiting barrier according to the energy-span model, which involves the low-lying off-cycle intermediate ($\Delta^{\ddagger}G_{ES}$).

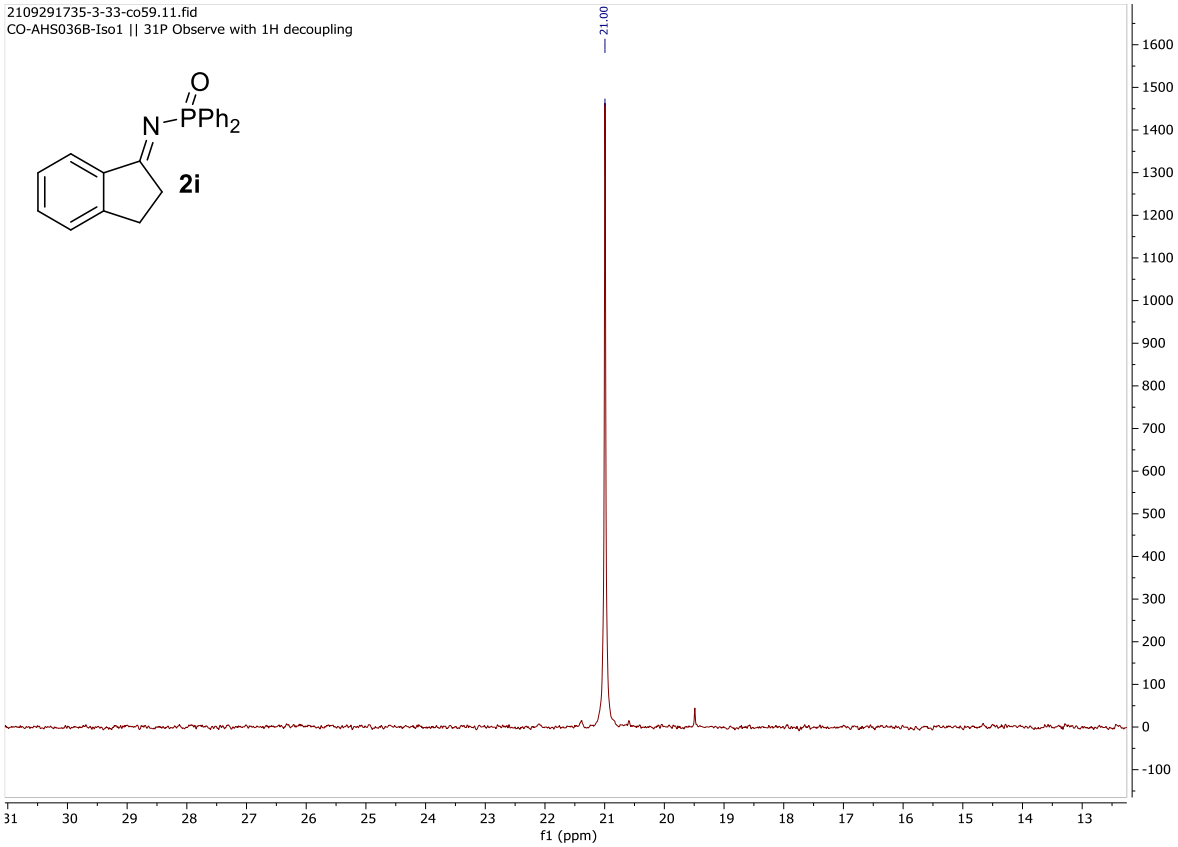
Section 4.4: Computational References

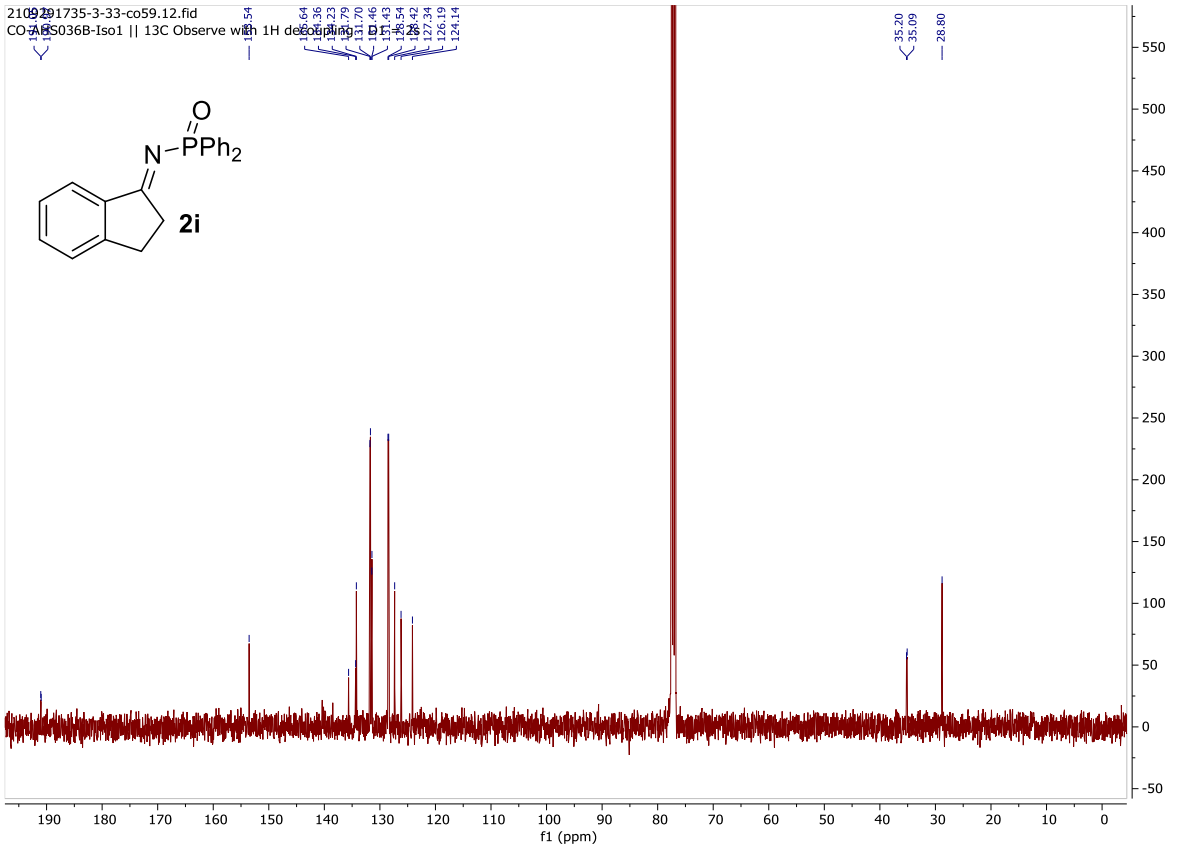
1. A.S. Goodfellow and M. Bühl, *Molecules*, 2021, **26**, 4072.
2. C.L. Oates, A.S. Goodfellow, M. Bühl, M.L. Clarke, *Angew. Chem. Int. Ed.*, 2023, **62**, e202212479.
3. A.D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
4. J.P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.
5. A. Schäfer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
6. A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
7. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
8. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
9. B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151–5158.
10. J. Tomasi, B. Mennucci and E. Cancès, *J. Mol. Struct.*, 1999, **464**, 211–226.
11. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3093.
12. K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368.
13. J.P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B*, 1996, **54**, 16533–16539.
14. J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
15. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
16. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
17. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1457–1465.
18. R.L. Martin, P.J. Hay and L.R. Pratt, *J. Phys. Chem. A*, 1998, **102**, 3565–3573.
19. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman and D.J. Fox, Gaussian 16, Revision C.01, Gaussian Inc., Wallingford CT, 2019.
20. R.A. Boto, F. Peccati, R. Laplaza, C. Quan, A. Carbone, J.-P. Piquemal, Y. Maday and J. Contreras-GarcÍa, *J. Chem. Theory Comput.*, 2020, **16**, 4150–4158.
21. H. Ryu, J. Park, H.K. Kim, J.Y. Park, S.T. Kim and M.H. Baik, *Organometallics*, 2018, **37**, 3228–3239.
22. M. Bühl, N. Sieffert and G. Wipff, *Chem. Phys, Lett.*, 2009, **467**, 287–293.
23. M. Bühl, N. Sieffert, A. Chaumont and G. Wipff, *Inorg. Chem.*, 2012, **51**, 1943–1952.
24. N. Sieffert and M. Bühl, *Inorg. Chem.*, 2009, **48**, 4622–4624.
25. N. Sieffert, and M. Bühl, *J. Am. Chem. Soc.*, 2010, **132**, 8056–8070.

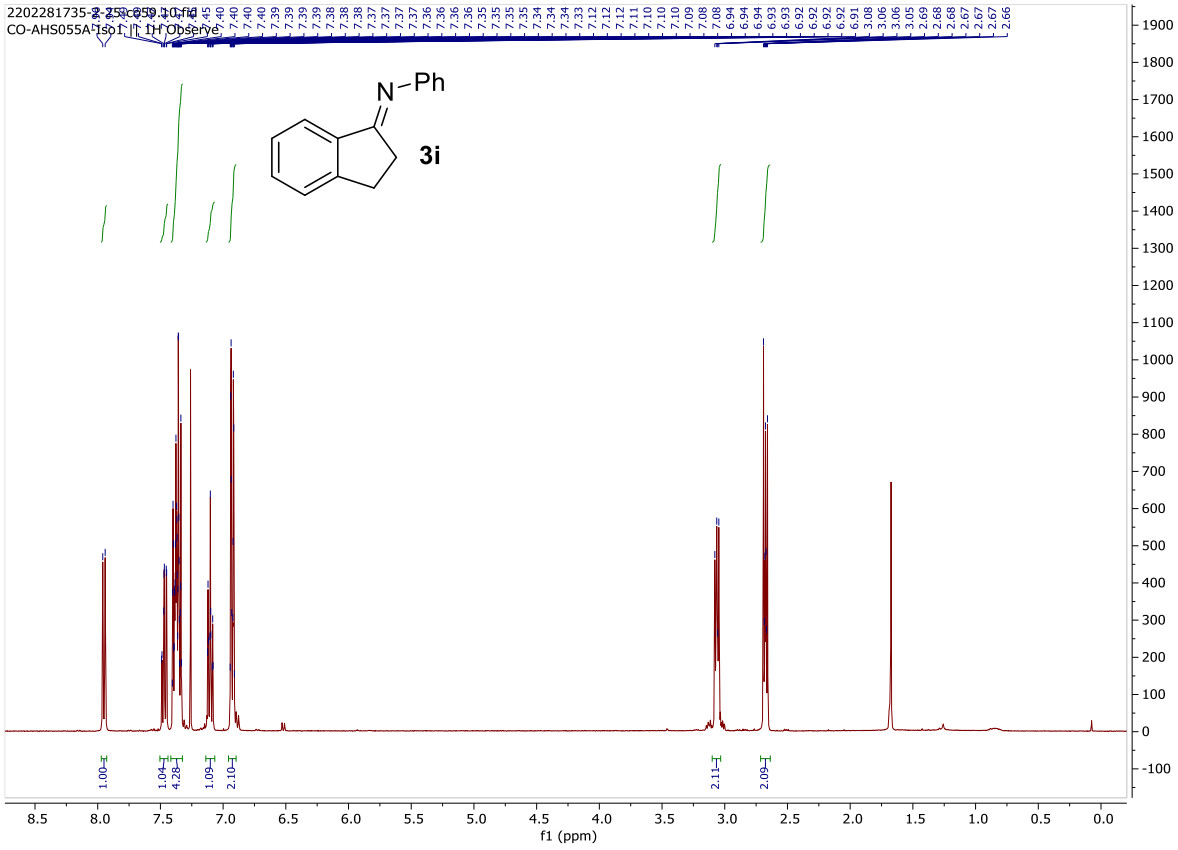
26. N. Sieffert, R. Réocreux, P. Lorusso, D.J. Cole-Hamilton and M. Bühl, *Chem. Eur. J.*, 2014, **20**, 4141–4155.
27. S. Gallarati, P. Dingwall, J.A. Fuentes, M. Bühl and M.L. Clarke, *Organometallics*, 2020, **39**, 4544–4556.
28. A.E. Owen, A. Preiss, A. McLuskie, C. Gao, G. Peters, M. Bühl and A. Kumar, *ACS Catal.*, 2022, **12**, 6923–6933.
29. C. S. Seo, T. Tannoux, S. A. Smith, A. J. Lough and R. H. Morris, *J. Org. Chem.*, 2019, **84**, 12040–12049.

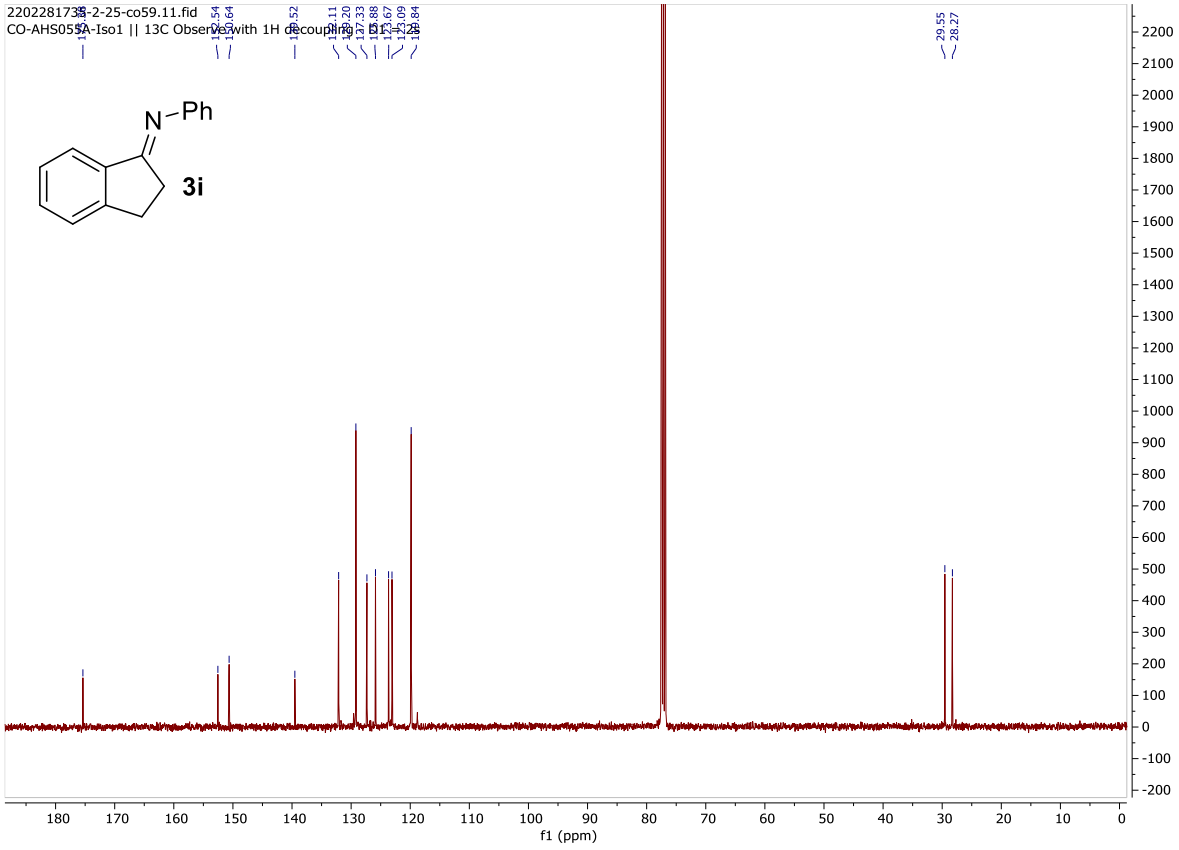
Section 5.1: NMR/ HPLC Data

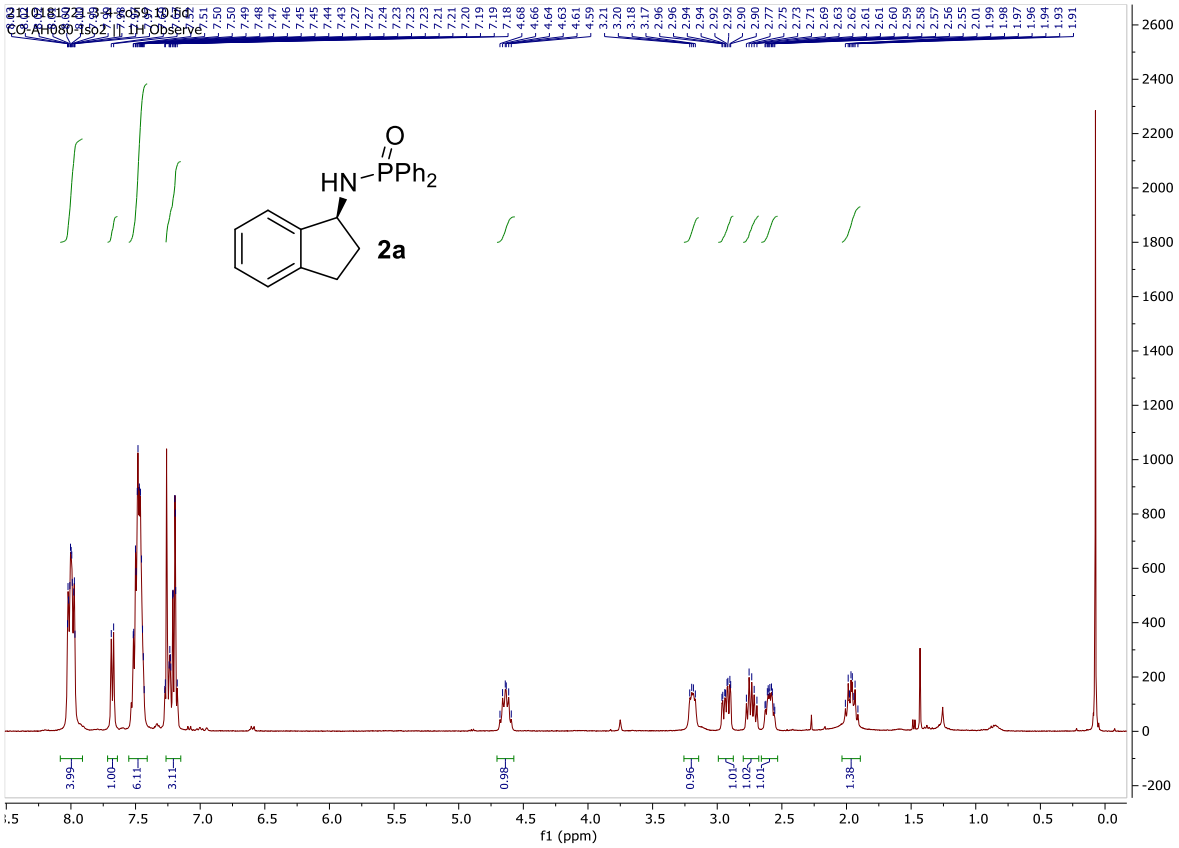


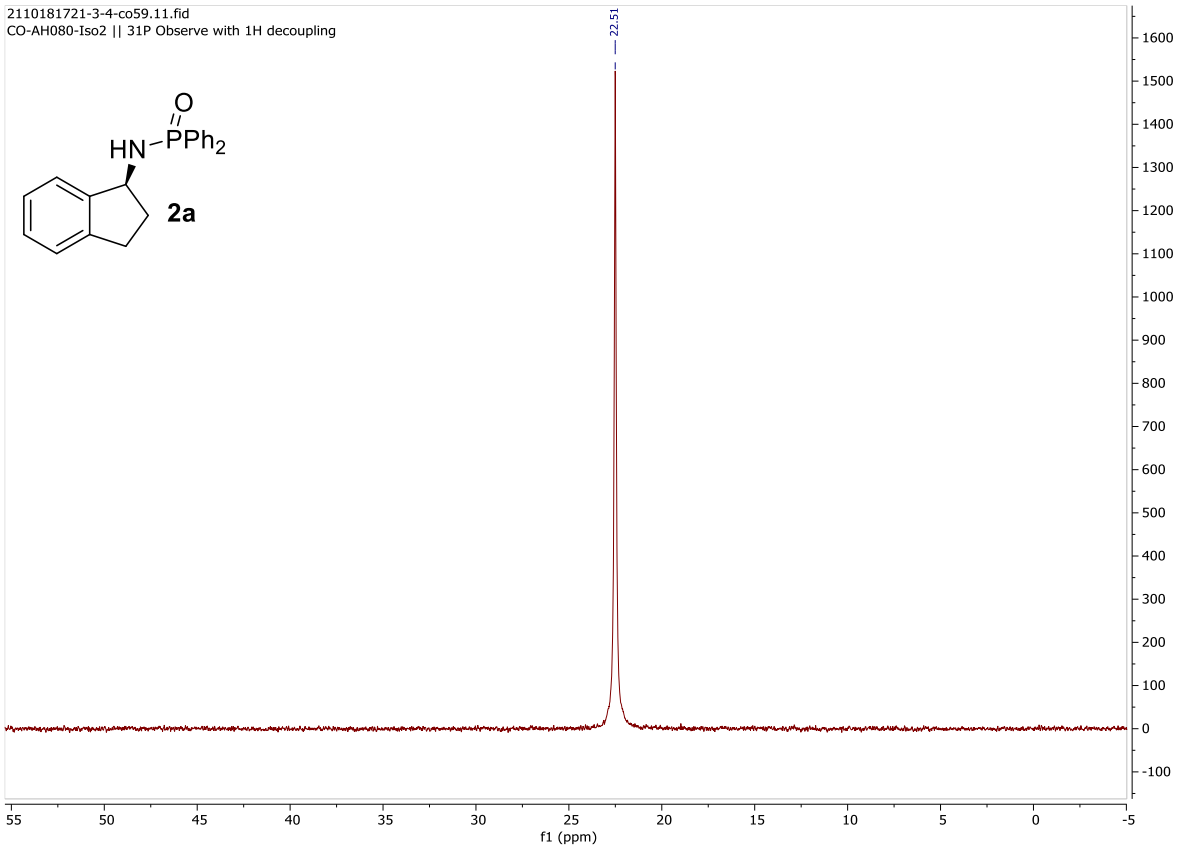


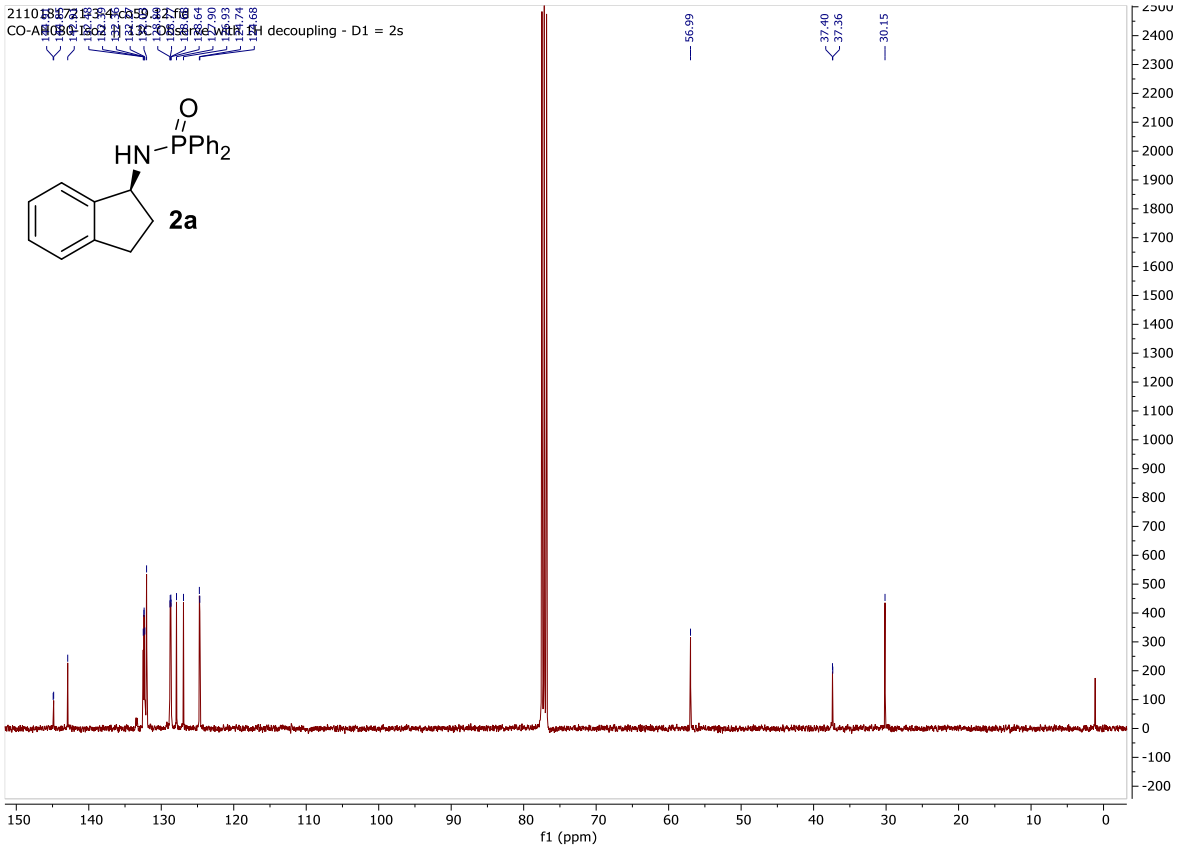

2202281735-3-33-co59.12.fid
CO-AHS036B-Iso1 || 13C Observe with 1H decoupling
O
N–PPh2
2i
f1 (ppm)

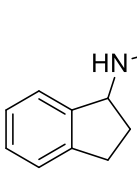

2202281735-2-25-co59.10.fid
CO-AHS055A-Iso1 || 1H Observe
N–Ph
3i
f1 (ppm)


N–Ph
3i
f1 (ppm)

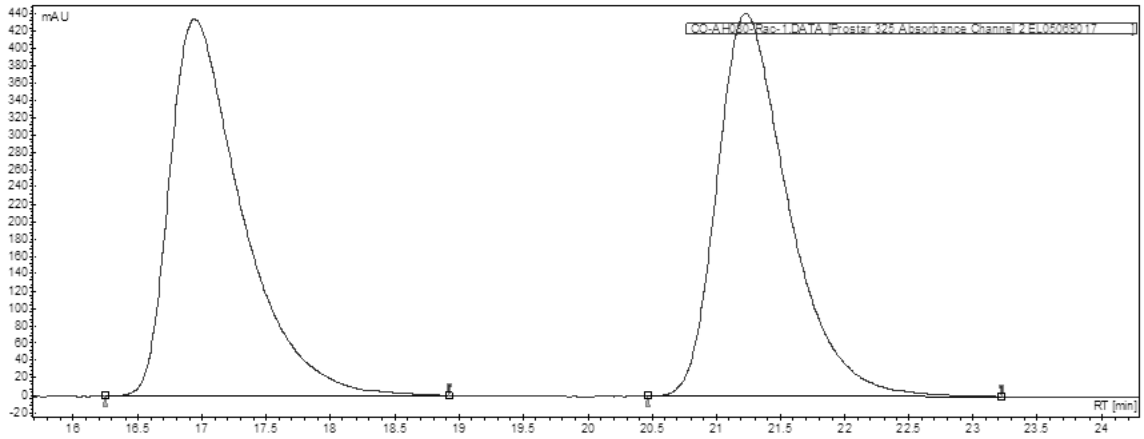

O
HN–PPh2
2a
f1 (ppm)


2110181721-3-4-co59.11.fid
CO-AH080-Iso2 || 31P Observe with 1H decoupling
22.51
HN–PPh2
O
2a
f1 (ppm)

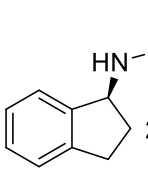

CO-AH080-Iso2 || 13C Observe with 1H decoupling - D1 = 2s
56.99
37.40
37.36
30.15
HN–PPh2
O
2a
f1 (ppm)



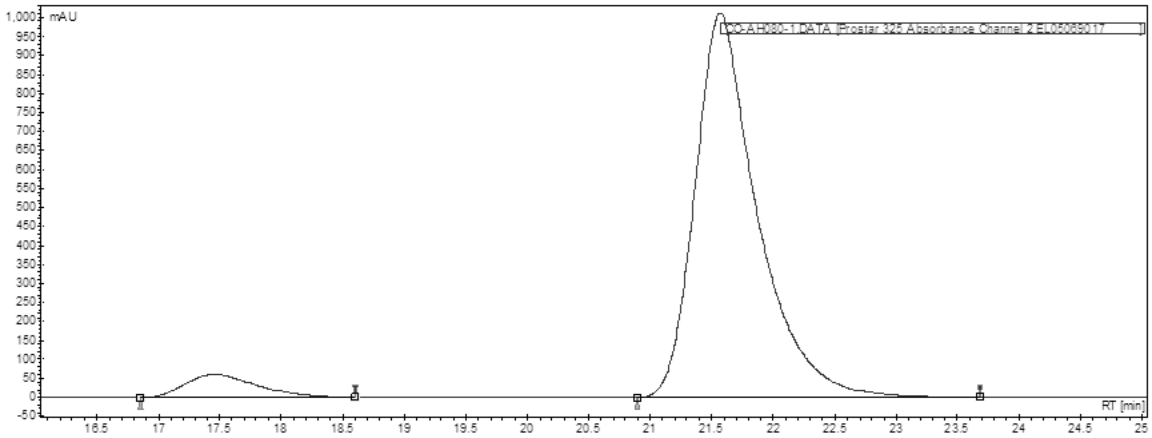
2a (rac)



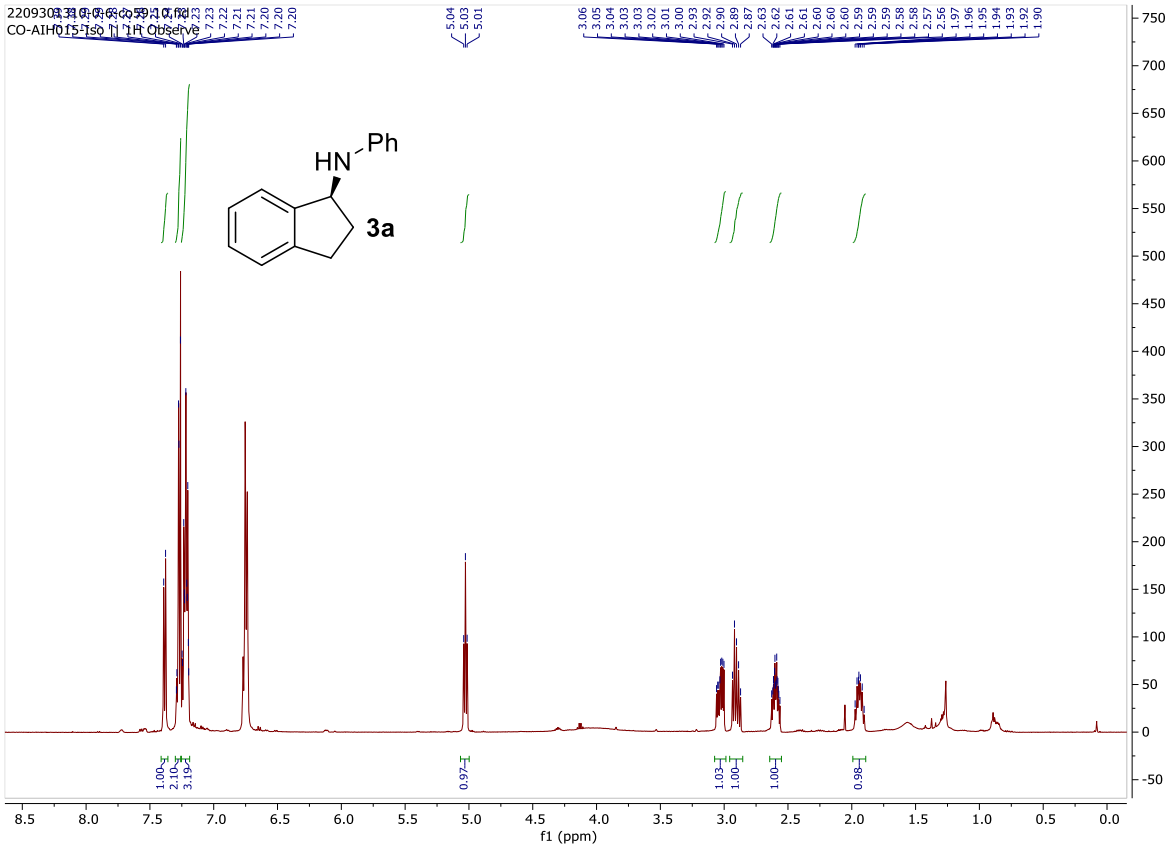
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	16.94	49.91	434.9	282.9	49.909
	2	UNKNOWN	21.23	50.09	441.3	283.9	50.091
	Total			100.00	876.2	566.7	100.000

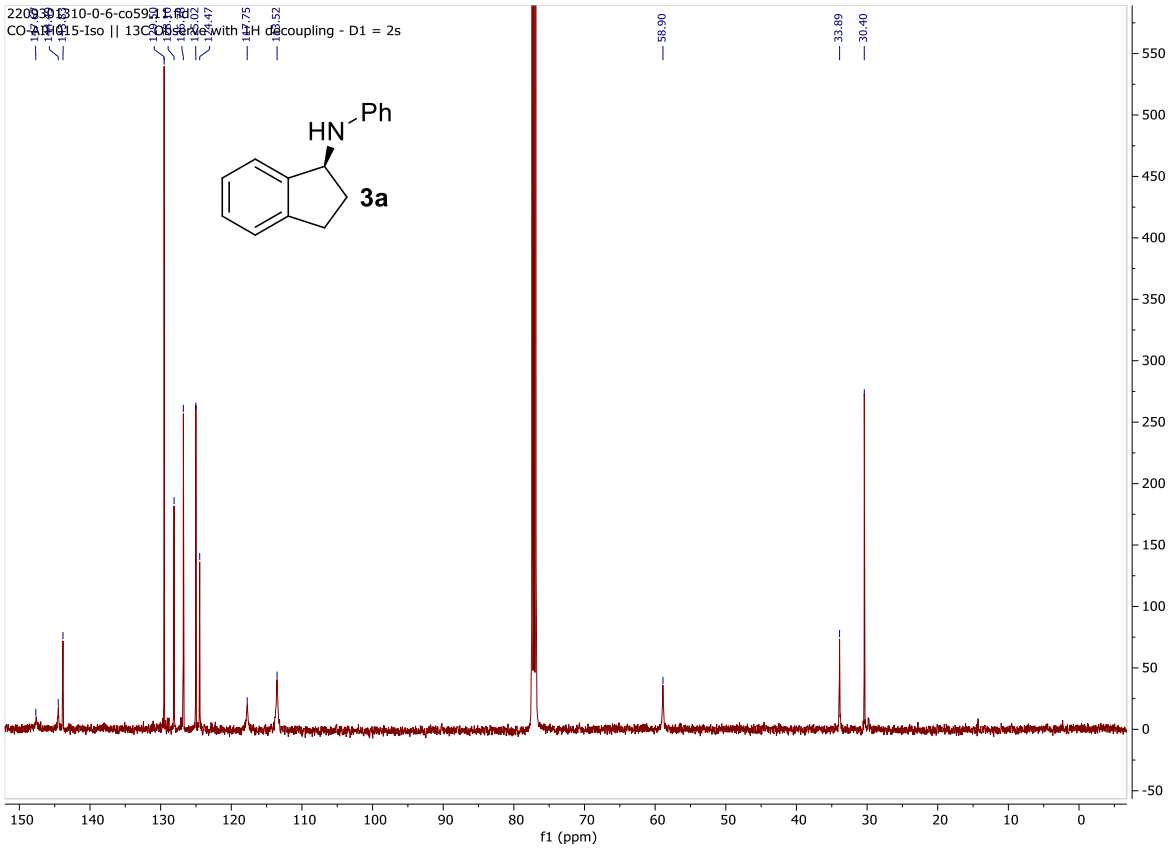


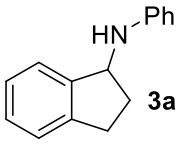
2a



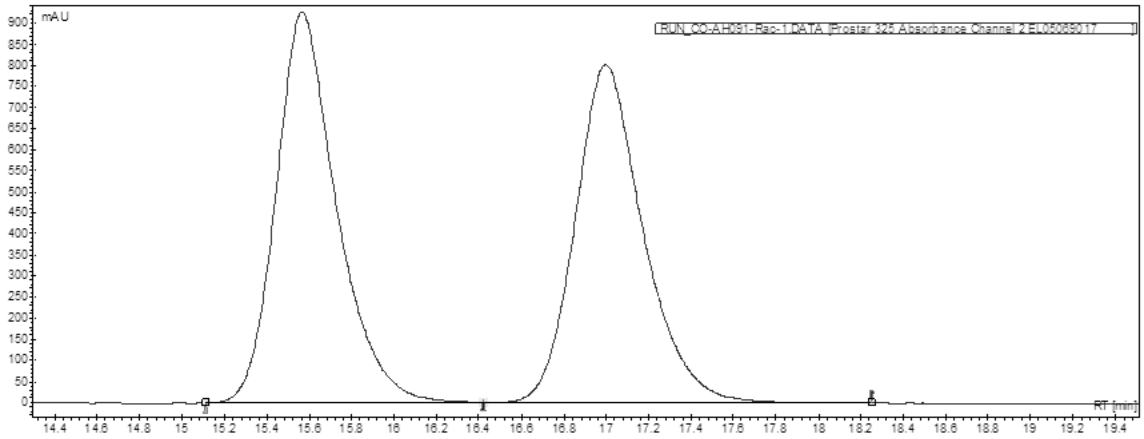
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	17.46	6.40	59.3	40.5	6.396
	2	UNKNOWN	21.57	93.60	1014.3	593.2	93.604
	Total			100.00	1073.6	633.7	100.000


CO-AIH015-Iso || 1H Observe
HN
Ph
3a
f1 (ppm)

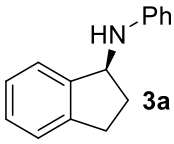

CO-AIH015-Iso || 13C Observe with 1H decoupling - D1 = 2s
58.90
33.89
30.40
HN
Ph
3a
f1 (ppm)



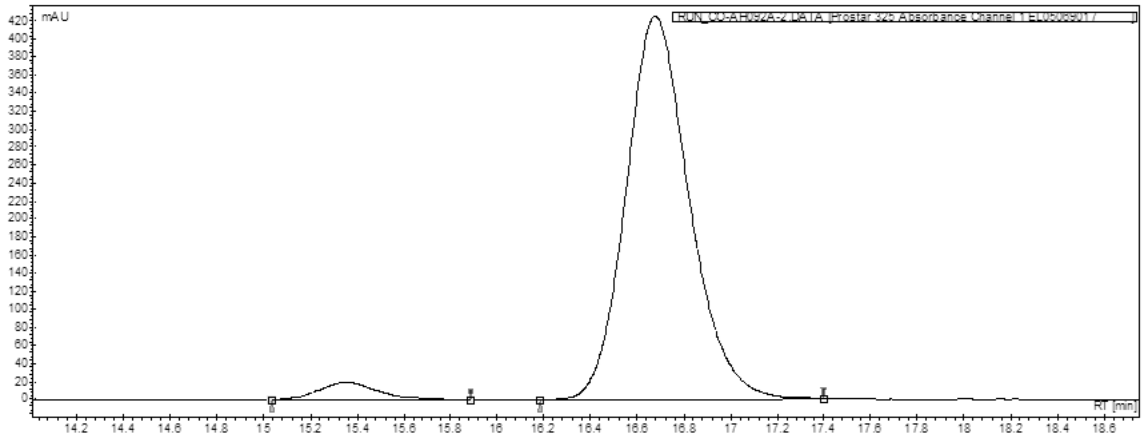
3a (rac)



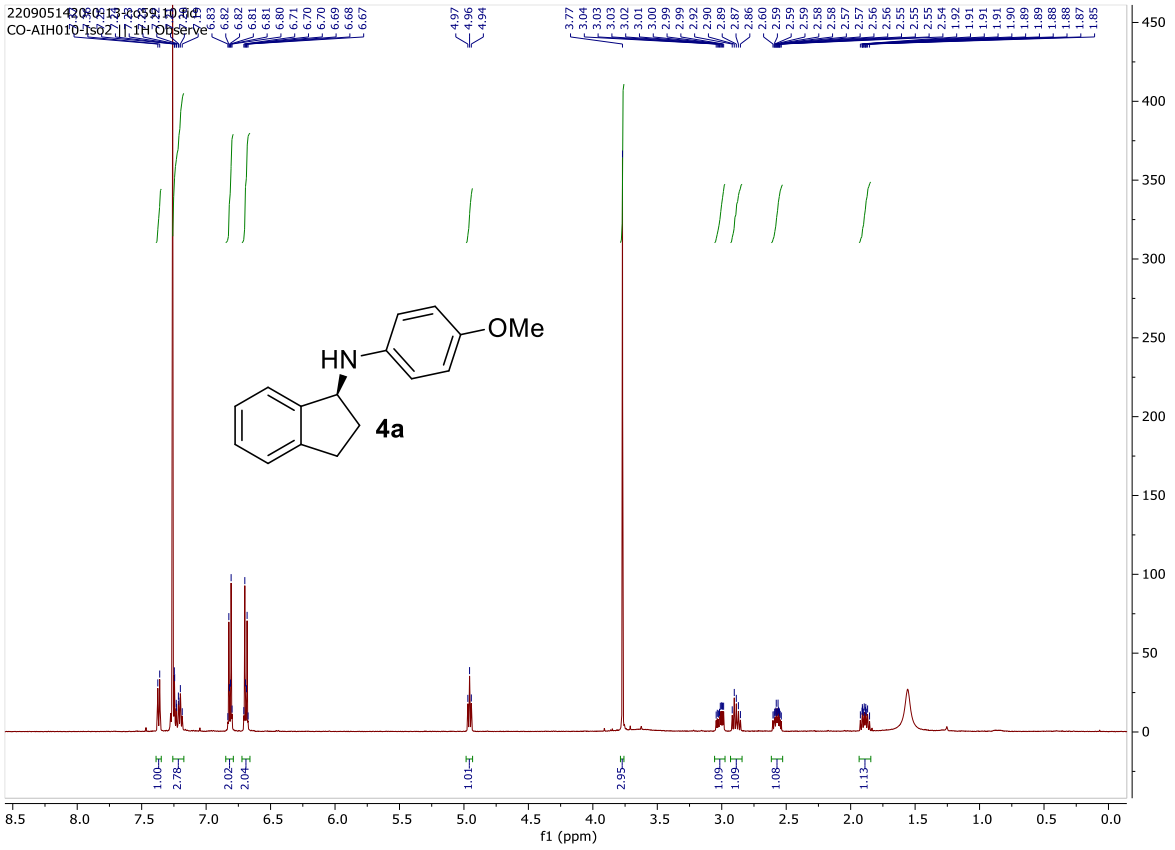
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	15.57	50.73	929.5	307.4	50.732
	2	UNKNOWN	17.00	49.27	803.2	298.6	49.268
	Total			100.00	1732.7	606.0	100.000

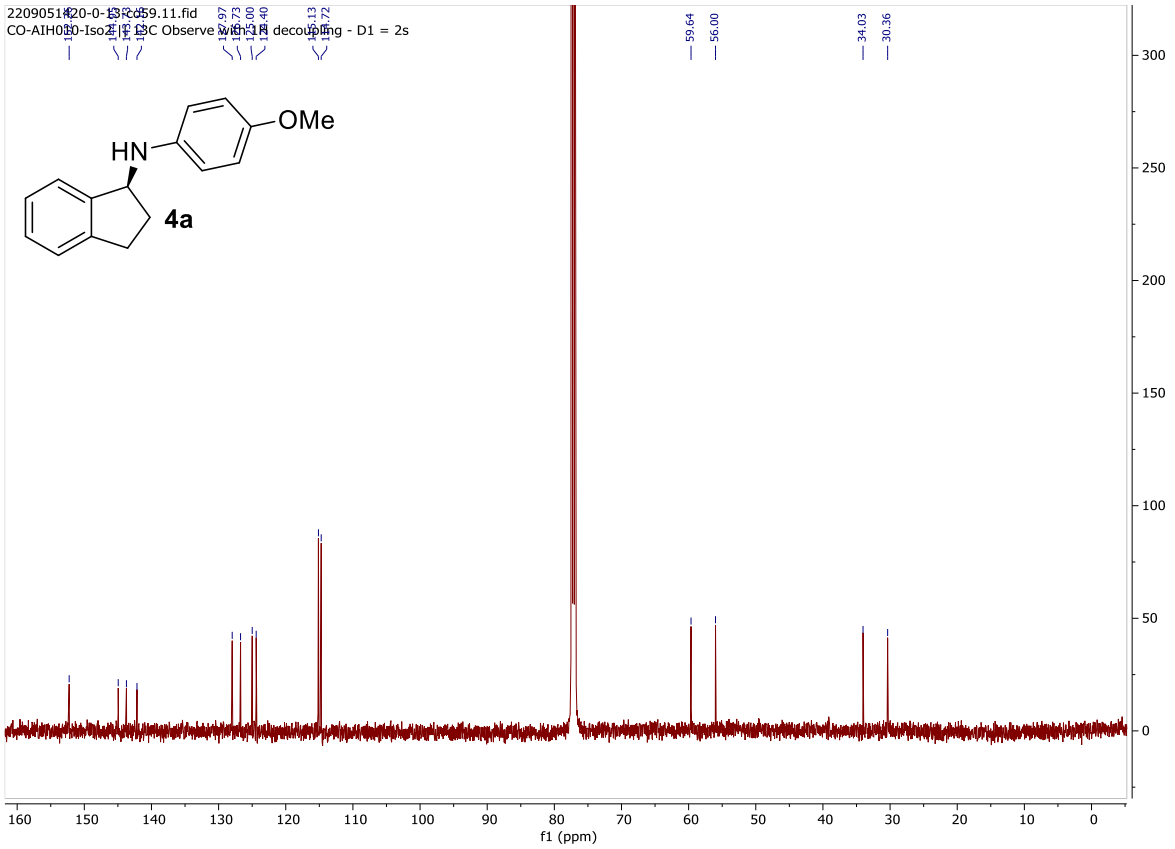


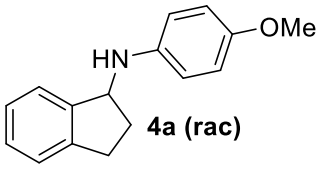
3a



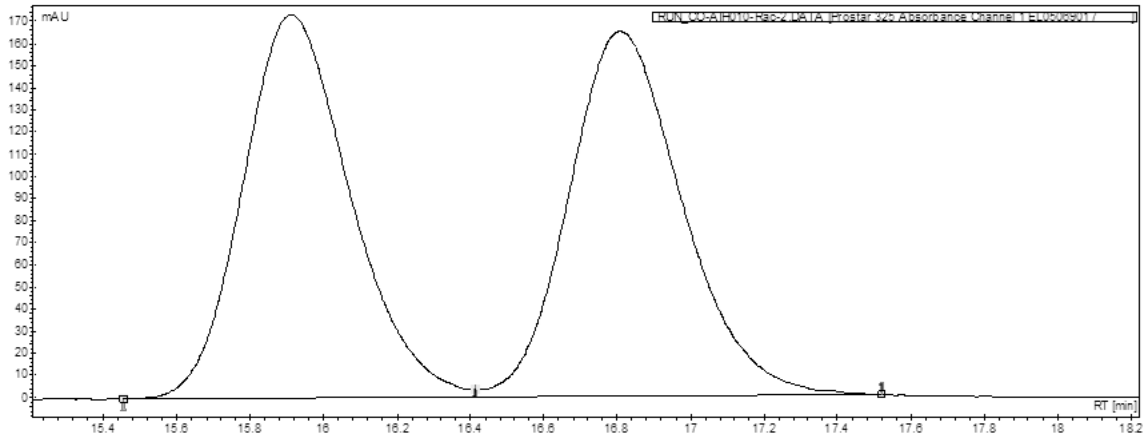
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	15.35	4.02	18.9	5.6	4.016
	2	UNKNOWN	16.68	95.98	425.5	133.6	95.984
	Total			100.00	444.3	139.2	100.000


OMe
HN
4a
f1 (ppm)

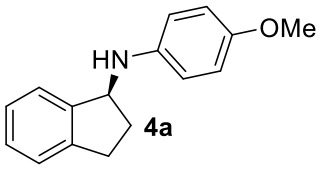

OMe
HN
4a
f1 (ppm)



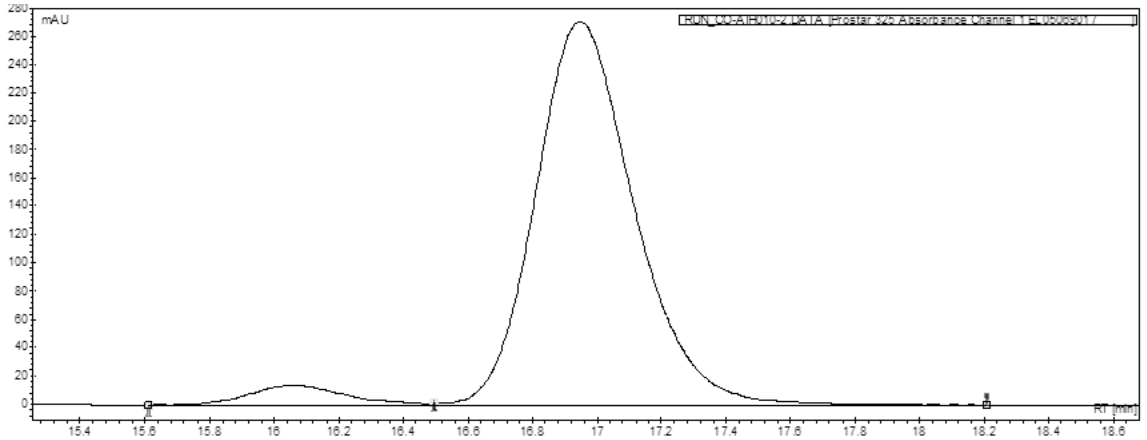
4a (rac)



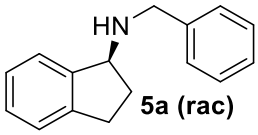
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	15.91	49.87	173.3	58.7	49.869
	2	UNKNOWN	16.81	50.13	164.9	59.0	50.131
	Total			100.00	338.2	117.7	100.000



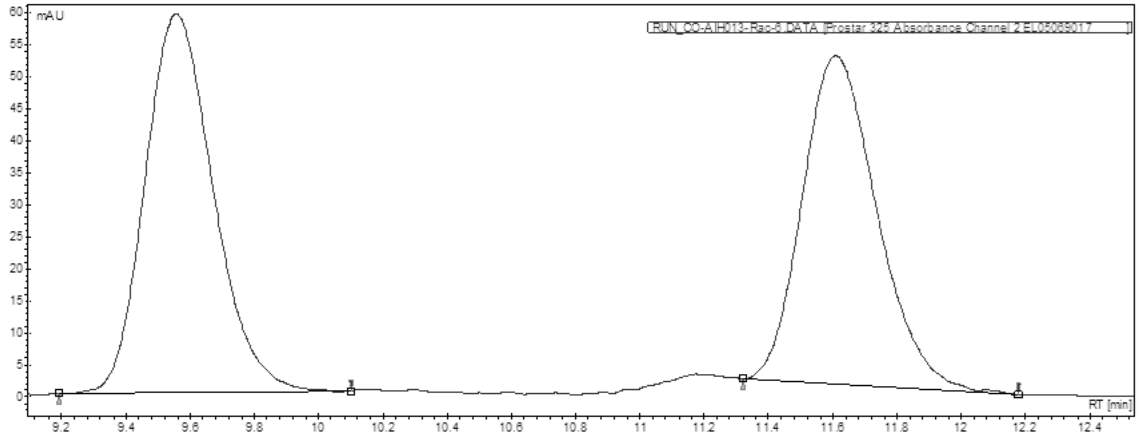
4a



	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	16.06	4.69	13.4	4.7	4.688
	2	UNKNOWN	16.95	95.31	271.3	96.0	95.312
	Total			100.00	284.8	100.7	100.000

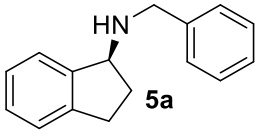


5a (rac)

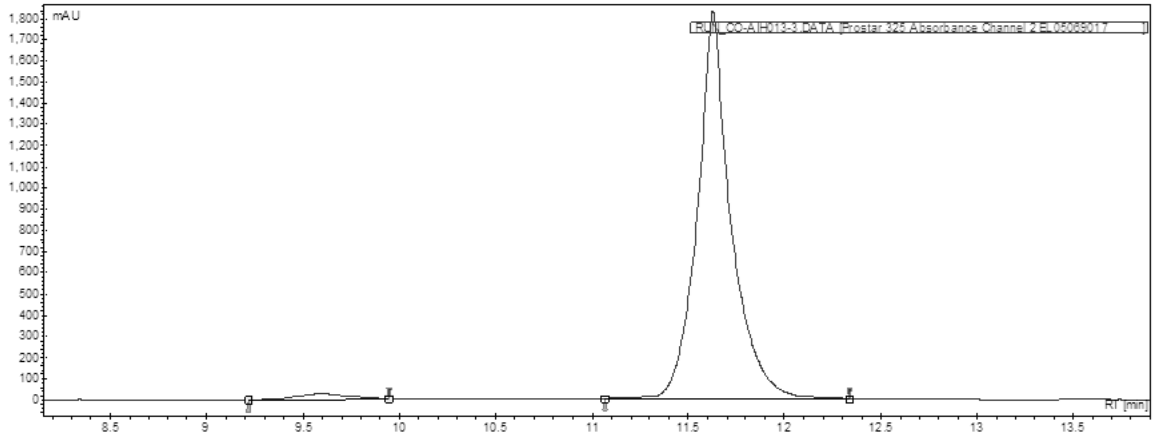


	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	9.56	51.27	59.2	14.5	51.265
	2	UNKNOWN	11.61	48.73	51.4	13.8	48.735
	Total			100.00	110.5	28.3	100.000

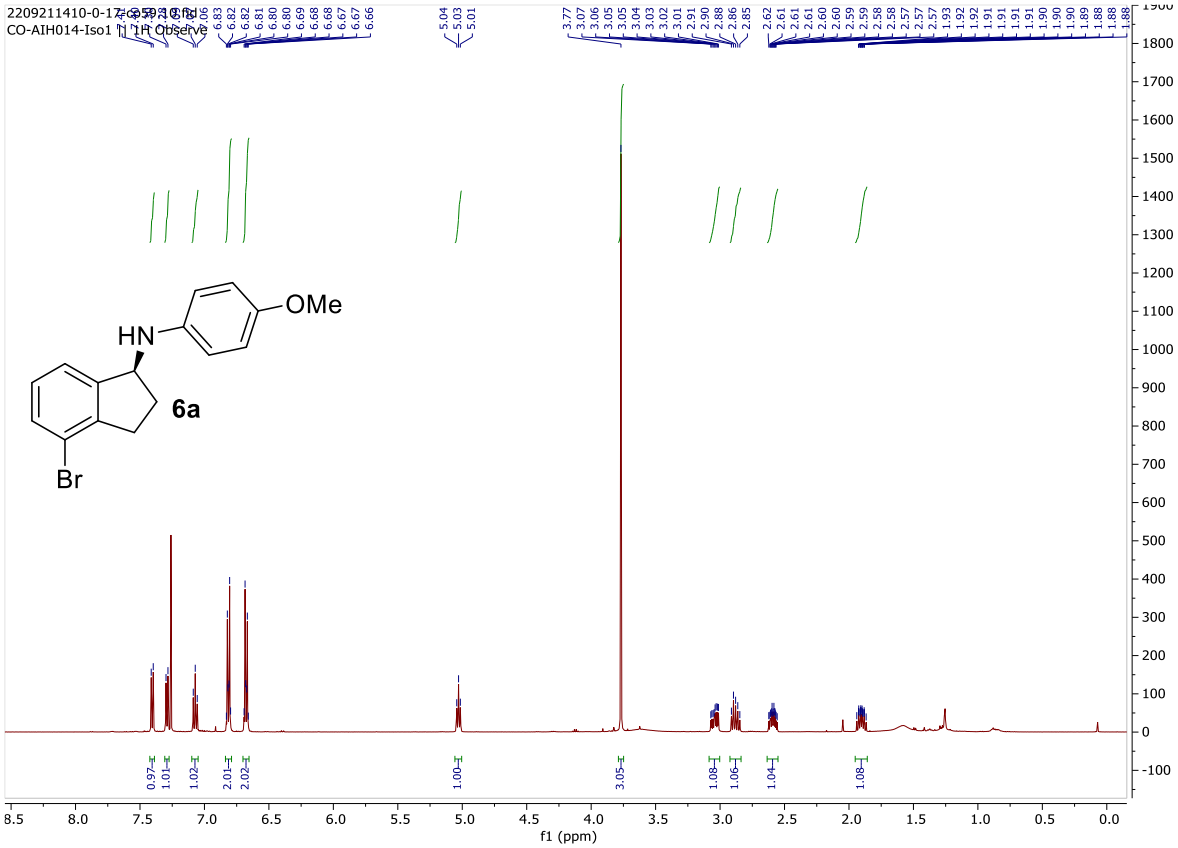
For the racemic sample of **5a** prepared with $NaBH_4$, an impurity eluted at ~11.2 minutes, this impurity was not detected with **5a** produced by asymmetric hydrogenation reaction.

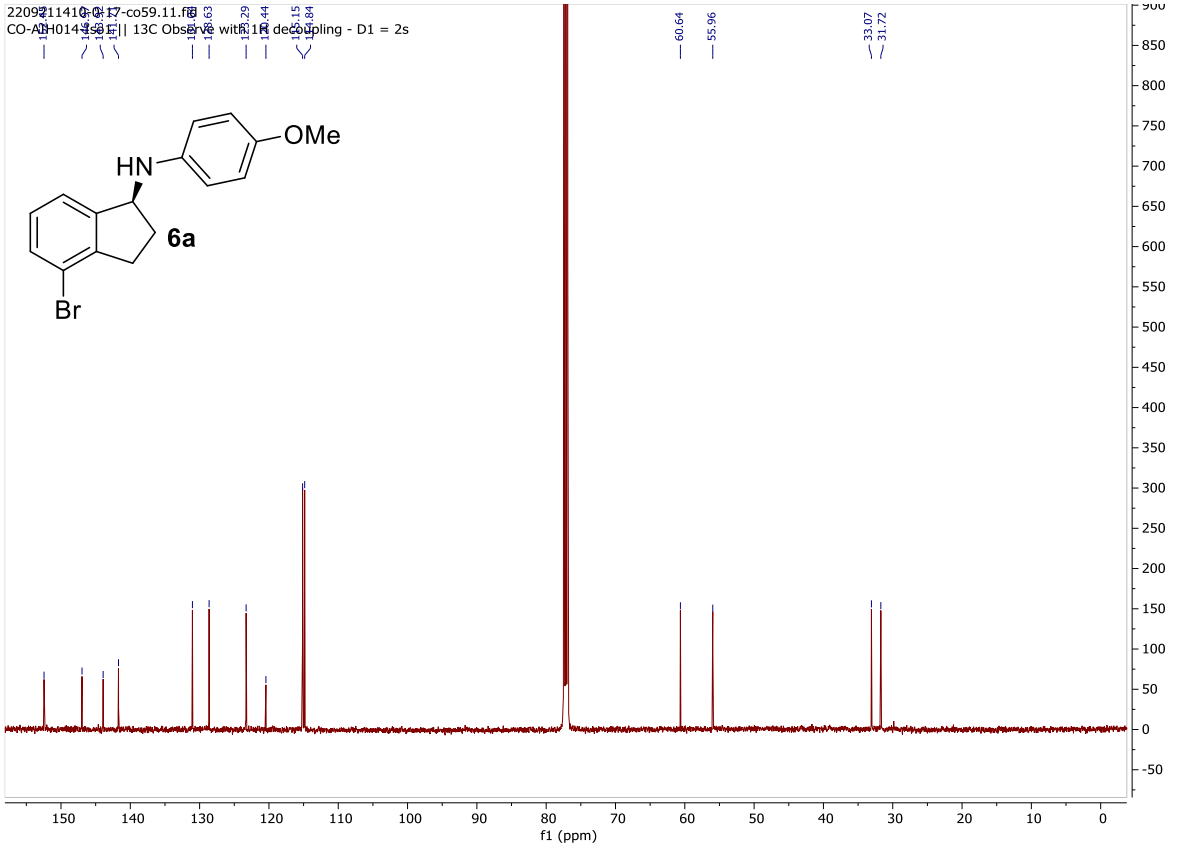


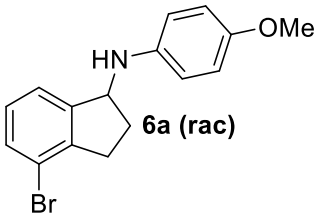
5a

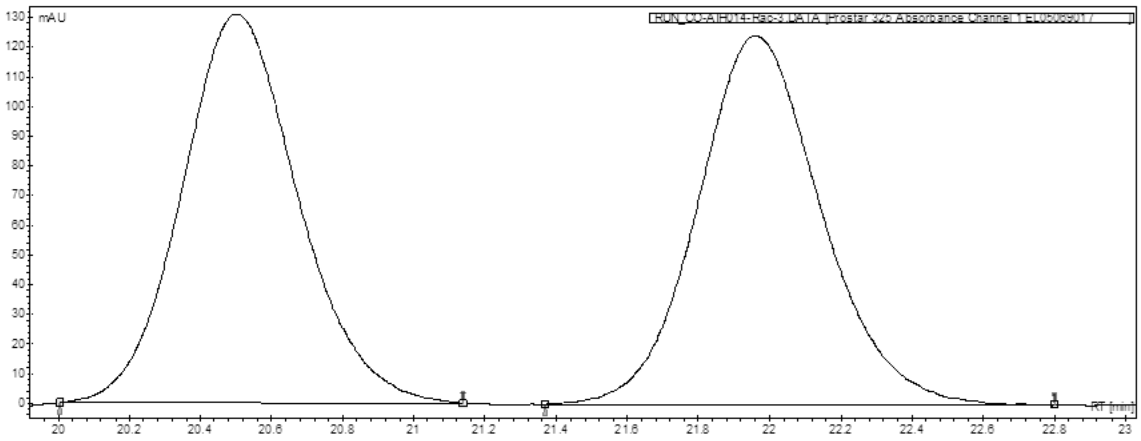


	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	9.59	2.03	26.0	7.7	2.034
	2	UNKNOWN	11.63	97.97	1831.1	370.5	97.966
	Total			100.00	1857.1	378.2	100.000

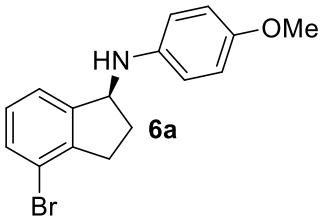

OMe
HN
6a
Br
f1 (ppm)

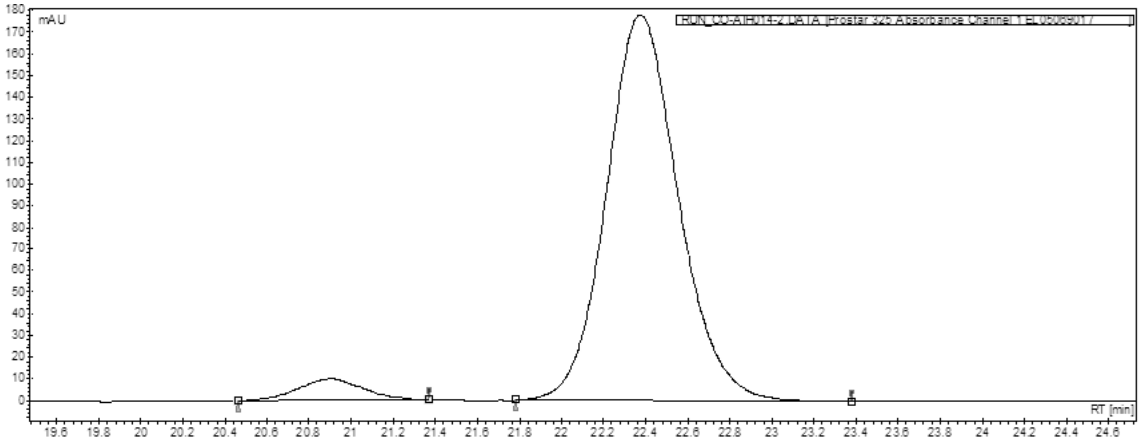

OMe
HN
6a
Br
f1 (ppm)



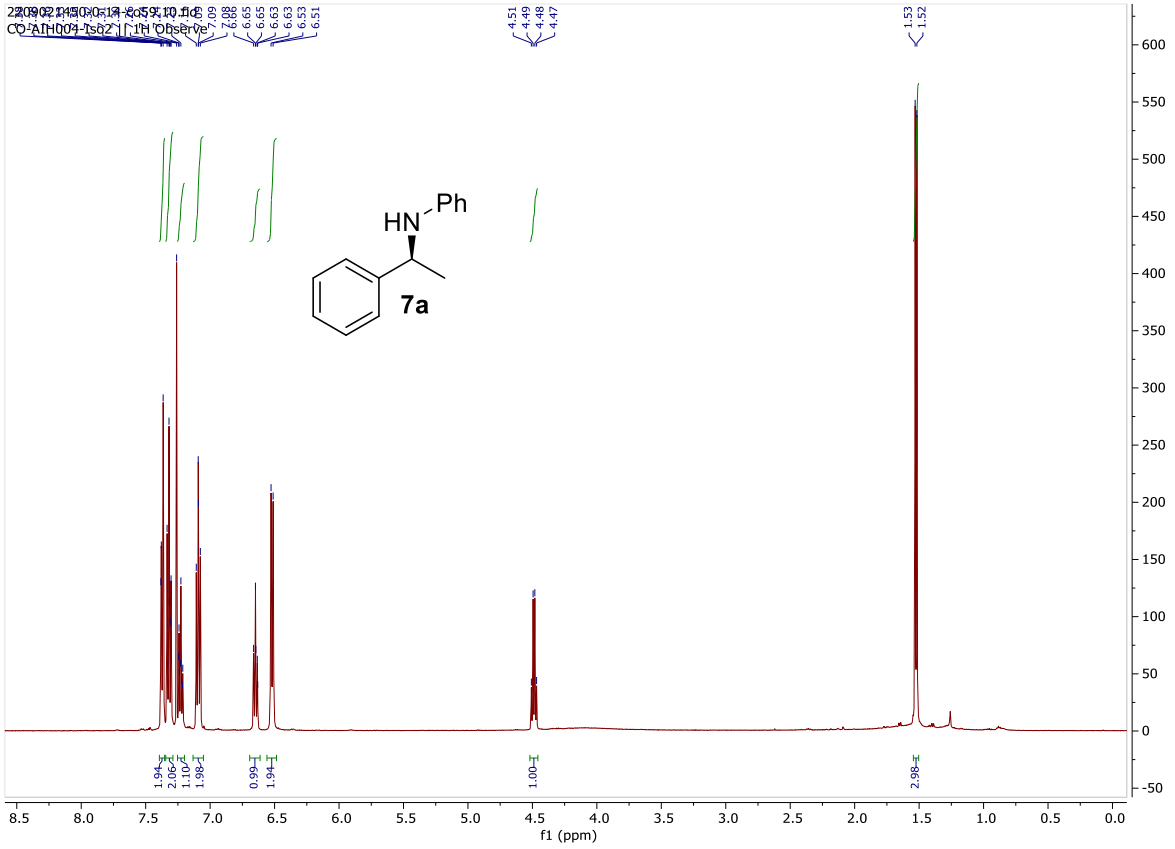


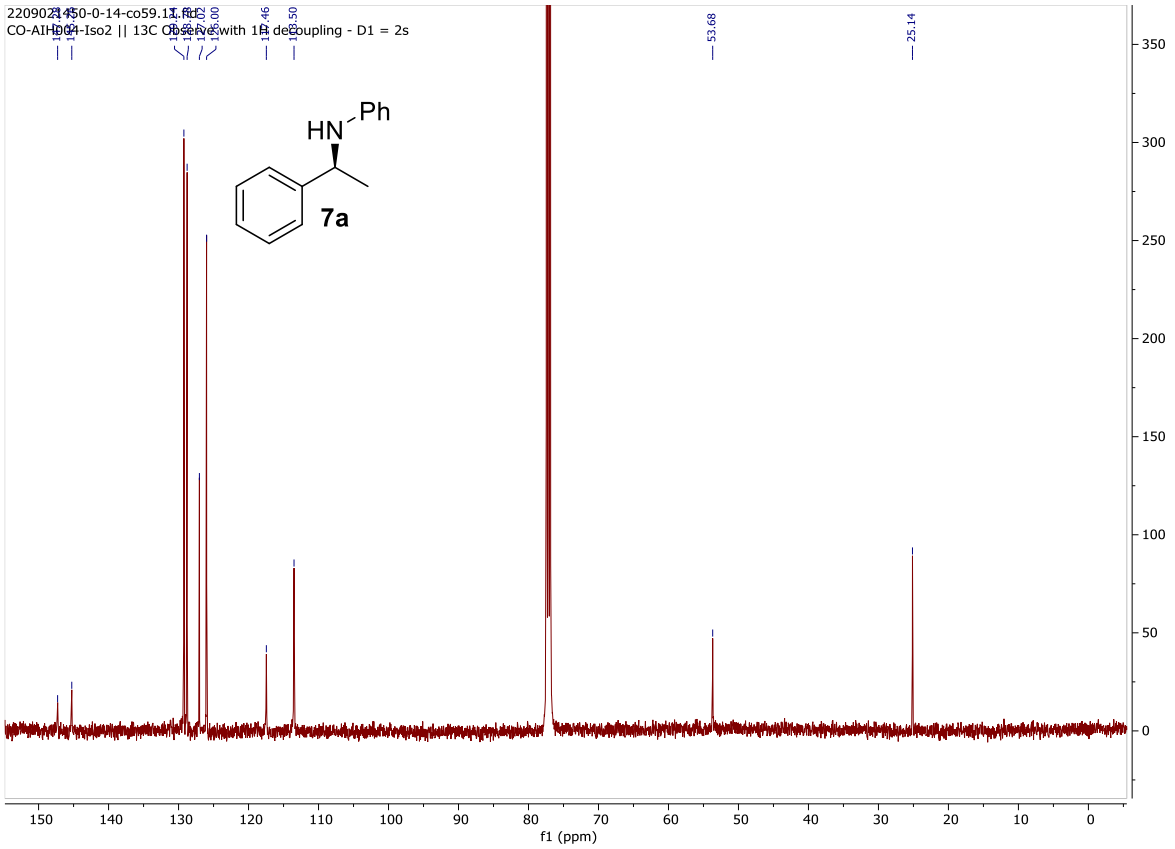
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	20.50	49.80	130.8	49.5	49.800
	2	UNKNOWN	21.96	50.20	124.0	49.9	50.200
	Total			100.00	254.7	99.3	100.000

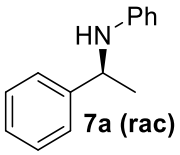




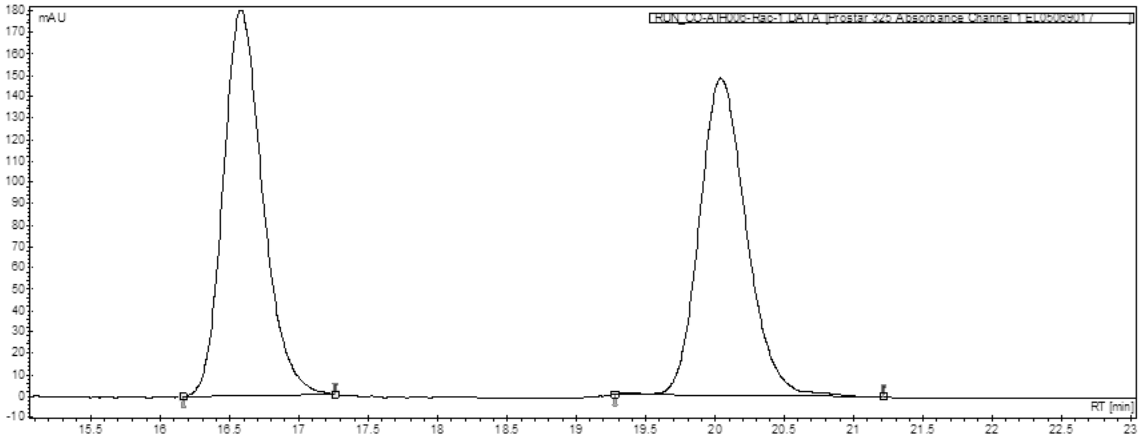
	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	20.91	4.69	9.7	3.5	4.688
	2	UNKNOWN	22.37	95.31	178.3	70.6	95.312
	Total			100.00	188.0	74.1	100.000


HN
Ph
7a
f1 (ppm)

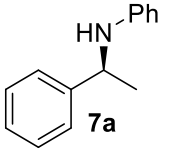

HN
Ph
7a
f1 (ppm)



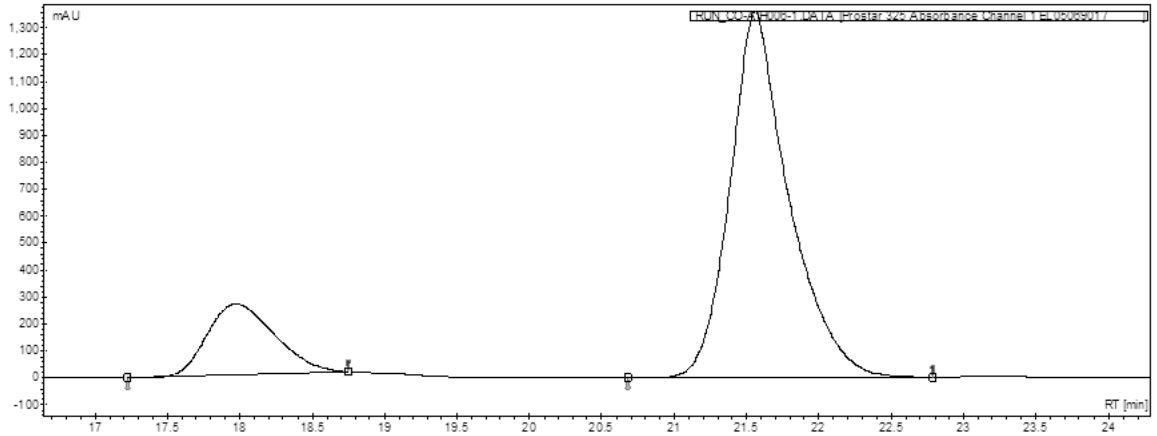
7a (rac)



	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	16.58	50.72	180.2	59.5	50.717
	2	UNKNOWN	20.04	49.28	148.0	57.8	49.283
	Total			100.00	328.3	117.4	100.000



7a



	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
▶	1	UNKNOWN	17.97	17.86	261.8	139.4	17.862
	2	UNKNOWN	21.56	82.14	1361.5	641.3	82.138
	Total			100.00	1623.3	780.7	100.000

Section 5.2: Cartesian Coordinates and Energetics of Optimised Structures

Raw data and cartesian coordinates obtained from geometry optimisation and frequency calculations at the level of RI-BP86(PCM_{EtOH})/def2-SVP and single-point energies at the level of PBE0-D3(PCM_{EtOH})/def2-TZVP.

Gibbs Free Energies for individual species have been evaluated at 323.15 K using the Enthalpy correction (δH) and Entropy (S) obtained from frequency calculations at the level of optimisation:

$$G_{323.15} = E_{sp} + \delta H_{298.15} - T * S_{298.15}.$$

```
Mn1/EtOH
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          245.6449
 E(RB-P86) (a.u.) =                                       -154.922969451
 Thermal correction to Enthalpy (a.u.) =                   0.082426
 Thermal correction to Gibbs Free Energy (a.u.) =          0.051666
 Total Entropy (cal/Kmol) =                                64.739
 E(RPBE1PBE) (a.u.) =                                     -154.927492887
Optimised cartesian coordinates (Angstrom):
 C      1.228762  -0.220241   0.000005
 C     -0.089034   0.542785   0.000003
 H      2.089062   0.479844   0.000002
 H      1.307054  -0.868131   0.898094
 H      1.307052  -0.868130  -0.898087
 H     -0.134881   1.211056   0.896116
 H     -0.134861   1.211081  -0.896093
 O     -1.159836  -0.401017  -0.000021
 H     -1.993111   0.107152   0.000088
---------------------------------------
Mn1/H2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          4268.9553
 E(RB-P86) (a.u.) =                                       -1.17256159454
 Thermal correction to Enthalpy (a.u.) =                   0.013030
 Thermal correction to Gibbs Free Energy (a.u.) =         -0.001825
 Total Entropy (cal/Kmol) =                                31.264
 E(RPBE1PBE) (a.u.) =                                     -1.16813917680
Optimised cartesian coordinates (Angstrom):
 H      0.000000   0.000000   0.383930
 H      0.000000   0.000000  -0.383930
---------------------------------------
Mn1/Mn-H2-EtOH
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          21.7161
 E(RB-P86) (a.u.) =                                       -4407.50616762
 Thermal correction to Enthalpy (a.u.) =                   0.642993
 Thermal correction to Gibbs Free Energy (a.u.) =          0.525677
 Total Entropy (cal/Kmol) =                                246.912
 E(RPBE1PBE) (a.u.) =                                     -4406.83187240
Optimised cartesian coordinates (Angstrom):
 Fe    -2.862066  -1.353924  -0.952208
 Mn     1.299511  -0.156411   1.294935
 P     -0.330133   0.919681   0.130548
 O      1.331545   1.997381   3.325272
 O     -0.519061  -1.737243   2.987459
 N      1.410440  -1.588008  -0.222582
 N      2.842751   0.629656   0.161584
 C     -1.201192  -0.153812  -1.068192
 C     -0.843884  -1.542567  -1.341349
 C     -1.628320  -1.961320  -2.479450
 H     -1.614947  -2.960318  -2.933312
 C     -2.465317  -0.869697  -2.900785
 H     -3.190628  -0.892743  -3.725351
 C     -2.214792   0.245091  -2.029537
 H     -2.697867   1.228694  -2.089770
 C     -3.390420  -1.769932   0.997108
 H     -2.742577  -1.652907   1.874957
 C     -3.496014  -2.952096   0.184318
 H     -2.946762  -3.891012   0.336003
 C     -4.428683  -2.679780  -0.879680
 H     -4.712076  -3.373065  -1.682976
 C     -4.902269  -1.327926  -0.721140
 H     -5.610804  -0.811521  -1.382661
 C     -4.258424  -0.763618   0.436655
 H     -4.390484   0.257148   0.818235
 C      0.330292   2.311246  -0.915335
```

C	0.804631	3.470251	-0.255062
H	0.728684	3.549568	0.841597
C	1.363301	4.531121	-0.986418
H	1.719800	5.429527	-0.457803
C	1.467993	4.446841	-2.388004
H	1.906102	5.279034	-2.961481
C	1.010184	3.295167	-3.050552
H	1.086560	3.220155	-4.147045
C	0.444537	2.232449	-2.319950
H	0.078590	1.342822	-2.855080
C	-1.696802	1.799904	1.044304
C	-2.034193	1.443390	2.367756
H	-1.468552	0.661825	2.893079
C	-3.099346	2.079413	3.031713
H	-3.345854	1.788550	4.065161
C	-3.841554	3.081933	2.383645
H	-4.673953	3.580602	2.905034
C	-3.508237	3.450928	1.067371
H	-4.077341	4.241275	0.552455
C	-2.441637	2.819387	0.404976
H	-2.181587	3.135724	-0.617035
C	0.202093	-2.362560	-0.580188
H	-0.252102	-2.663532	0.386676
C	2.100514	-1.065594	-1.398848
H	2.616205	-1.860112	-1.991535
H	1.398716	-0.577767	-2.130561
C	3.101238	-0.016879	-1.009519
C	3.672340	1.632625	0.549609
C	4.788442	2.024211	-0.196146
C	5.069310	1.351462	-1.398644
C	4.213599	0.319777	-1.804703
C	0.542019	-3.672053	-1.326093
H	-0.353745	-4.320501	-1.414252
H	0.924105	-3.488122	-2.351761
H	1.313715	-4.226556	-0.755355
C	1.334712	1.132945	2.520940
C	0.161794	-1.087860	2.273328
H	2.635925	-0.668567	2.266855
H	2.489391	-1.365099	1.838775
H	2.379748	-2.668078	0.495263
O	2.955656	-3.324140	1.074415
C	4.295208	-3.310321	0.616444
H	4.365955	-3.626687	-0.456820
H	4.737337	-2.280536	0.661549
H	4.395186	-0.235161	-2.737381
H	5.426856	2.841291	0.170255
H	3.427947	2.130181	1.499435
C	5.143454	-4.252201	1.467706
H	4.745551	-5.287879	1.417684
H	6.197778	-4.268164	1.120255
H	5.134012	-3.936718	2.532538
H	5.944126	1.626645	-2.007685

Mn1/Mn-H2

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	23.3751
E(RB-P86) (a.u.) =	-4252.56229993
Thermal correction to Enthalpy (a.u.) =	0.558242
Thermal correction to Gibbs Free Energy (a.u.) =	0.453904
Total Entropy (cal/Kmol) =	219.598
E(RPBE1PBE) (a.u.) =	-4251.88288022

Optimised cartesian coordinates (Angstrom):

Fe	2.939013	-0.831559	0.741325
Mn	-1.230056	-0.409562	-1.752354
P	-0.252497	0.605071	0.013776
O	-2.095658	2.181874	-2.902556
O	1.156377	-0.380474	-3.475237
N	-0.818149	-2.223105	-0.887235
N	-3.021026	-0.755964	-0.769082
C	0.924212	-0.471531	0.916272
C	1.160246	-1.876683	0.601900
C	1.990866	-2.409285	1.655754
H	2.370401	-3.437554	1.713793
C	2.277725	-1.363399	2.602334
H	2.903395	-1.457240	3.500436
C	1.630744	-0.163079	2.147716
H	1.658285	0.811266	2.652085

C	3.685846	-0.197198	-1.073821
H	3.090153	0.022633	-1.968832
C	4.233354	-1.480890	-0.725182
H	4.132984	-2.405618	-1.309278
C	4.915505	-1.347215	0.537279
H	5.422847	-2.152364	1.085605
C	4.791925	0.023076	0.966627
H	5.189694	0.444498	1.899680
C	4.029083	0.733703	-0.026868
H	3.743202	1.792907	0.011510
C	-1.476477	1.109913	1.323369
C	-2.334757	2.201230	1.047385
H	-2.231459	2.756715	0.101022
C	-3.314142	2.592748	1.974837
H	-3.968020	3.450076	1.748481
C	-3.460440	1.892498	3.187655
H	-4.228304	2.199828	3.915266
C	-2.621469	0.799345	3.463920
H	-2.728131	0.245288	4.410269
C	-1.635018	0.408683	2.537868
H	-0.977688	-0.442489	2.772903
C	0.672734	2.208632	-0.217572
C	1.173884	2.579701	-1.483810
H	0.993346	1.940652	-2.358913
C	1.912046	3.767132	-1.643073
H	2.293081	4.040162	-2.639975
C	2.158588	4.602233	-0.539578
H	2.735060	5.532468	-0.665386
C	1.655791	4.246638	0.725698
H	1.835178	4.897819	1.596083
C	0.914636	3.063089	0.884488
H	0.510687	2.811987	1.877505
C	0.562003	-2.615054	-0.605726
H	1.154667	-2.315416	-1.495602
C	-1.737768	-2.583088	0.168436
H	-1.938501	-3.684619	0.227902
H	-1.372124	-2.320371	1.206999
C	-3.051102	-1.874812	0.008029
C	-4.164622	-0.038050	-0.923318
C	-5.374416	-0.401532	-0.325593
C	-5.415389	-1.561967	0.469967
C	-4.238872	-2.302627	0.633530
C	0.738411	-4.144214	-0.465254
H	1.812554	-4.422398	-0.445405
H	0.274333	-4.540894	0.461835
H	0.267947	-4.652014	-1.331837
C	-1.761857	1.136417	-2.461871
C	0.234651	-0.376290	-2.733953
H	-1.795542	-1.726741	-2.785656
H	-2.148453	-1.085000	-3.148820
H	-4.097319	0.857659	-1.557908
H	-6.269076	0.216789	-0.489696
H	-4.223680	-3.218069	1.244338
H	-6.352069	-1.882891	0.951237

Mn1/Mn-R-indNHPh

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	7.7465
E(RB-P86) (a.u.) =	-4886.33598880
Thermal correction to Enthalpy (a.u.) =	0.812019
Thermal correction to Gibbs Free Energy (a.u.) =	0.670964
Total Entropy (cal/Kmol) =	296.875
E(RPBE1PBE) (a.u.) =	-4885.62316586

Optimised cartesian coordinates (Angstrom):

Fe	-3.244637	-2.315077	-1.130866
Mn	0.169975	0.561213	0.528136
P	-2.014012	0.689570	0.369236
O	0.395778	1.763799	3.231166
O	0.247566	-2.077280	1.826070
N	0.422904	-0.080985	-1.267027
N	0.704196	2.334762	-0.379408
C	-2.598885	-0.372444	-1.013552
C	-1.727934	-1.146734	-1.895546
C	-2.554946	-1.670627	-2.956798
H	-2.214136	-2.313972	-3.777887
C	-3.912336	-1.243945	-2.744293
H	-4.775848	-1.502145	-3.372143

C	-3.947719	-0.451299	-1.546178
H	-4.840591	0.019825	-1.115592
C	-2.709925	-3.403105	0.535907
H	-1.929060	-3.125764	1.255497
C	-2.513793	-4.182746	-0.657361
H	-1.561283	-4.607979	-1.001254
C	-3.780659	-4.287724	-1.335595
H	-3.962081	-4.802261	-2.288769
C	-4.761850	-3.574505	-0.557839
H	-5.822371	-3.450620	-0.815127
C	-4.100364	-3.024991	0.597306
H	-4.566212	-2.410314	1.378531
C	-2.564767	2.394452	-0.126730
C	-2.561109	3.411075	0.858406
H	-2.305083	3.164029	1.901716
C	-2.885729	4.734474	0.519379
H	-2.888736	5.512591	1.299310
C	-3.203586	5.066441	-0.812002
H	-3.457433	6.104877	-1.077736
C	-3.193907	4.066340	-1.799281
H	-3.440896	4.317288	-2.843247
C	-2.876346	2.736786	-1.460862
H	-2.887267	1.960863	-2.241659
C	-3.163526	0.330635	1.785723
C	-2.718188	-0.409724	2.901692
H	-1.676365	-0.755353	2.954791
C	-3.600327	-0.715260	3.954490
H	-3.235994	-1.293134	4.818615
C	-4.936958	-0.282045	3.907057
H	-5.626310	-0.520151	4.732609
C	-5.387235	0.466487	2.803640
H	-6.430095	0.819120	2.762087
C	-4.506535	0.775437	1.752832
H	-4.868823	1.380371	0.907003
C	-0.213560	-1.338328	-1.716135
H	-0.068480	-2.054968	-0.883709
C	0.506836	0.922937	-2.318599
H	1.247013	0.665849	-3.114825
H	-0.467954	1.030987	-2.865536
C	0.853566	2.256447	-1.732633
C	0.964036	3.525663	0.229020
C	1.387004	4.656550	-0.472213
H	1.585163	5.589951	0.074781
C	1.553598	4.573082	-1.868159
C	1.283287	3.354202	-2.501135
H	1.397633	3.239125	-3.589625
C	0.433749	-1.972072	-2.961065
H	0.010298	-2.980774	-3.141106
H	0.275617	-1.374108	-3.881896
H	1.524028	-2.095856	-2.803383
C	0.300498	1.281640	2.153506
C	0.158214	-1.028612	1.280397
H	2.605539	-0.354043	-1.021008
H	2.560601	0.195175	1.057012
C	3.637462	0.070246	0.750377
C	4.356357	1.428378	1.028689
C	4.773177	1.361173	2.519409
H	1.889399	5.445504	-2.449260
N	3.560429	-0.377594	-0.624412
C	4.277064	-0.871739	1.767139
C	4.249976	-2.274314	1.807717
C	4.921300	-0.128309	2.780774
C	4.889215	-2.937412	2.874091
H	3.743726	-2.843467	1.011042
C	5.554190	-0.790659	3.846348
C	5.537932	-2.200066	3.885510
H	4.886484	-4.038633	2.916315
H	6.063391	-0.219203	4.640087
H	6.039653	-2.729796	4.711420
H	5.257568	1.503142	0.384230
H	3.706381	2.293851	0.791464
H	5.693125	1.938834	2.748496
H	3.968785	1.776385	3.169341
C	4.615911	-0.613859	-1.485864
C	4.361118	-0.787913	-2.879117
C	5.970898	-0.711347	-1.052652
C	5.399636	-1.049495	-3.782370

```
 H      3.325216  -0.708803  -3.246031
 C      7.001953  -0.966611  -1.972388
 H      6.214578  -0.603747   0.013374
 C      6.735959  -1.140068  -3.343097
 H      5.159035  -1.178101  -4.850690
 H      8.037793  -1.035848  -1.600465
 H      7.551155  -1.341345  -4.055263
 H      0.828189   3.556370   1.319441
---------------------------------------
Mn1/Mn-S-indNHPh
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          9.4585
 E(RB-P86) (a.u.) =                                    -4886.33617026
 Thermal correction to Enthalpy (a.u.) =                   0.812190
 Thermal correction to Gibbs Free Energy (a.u.) =          0.671663
 Total Entropy (cal/Kmol) =                              295.764
 E(RPBE1PBE) (a.u.) =                                  -4885.62333227
Optimised cartesian coordinates (Angstrom):
 Fe     3.673923   2.237485  -0.156270
 Mn    -0.165498  -0.527461   0.411652
 P      1.957350  -0.901562   0.010519
 O     -0.513203  -2.750218   2.346439
 O      0.228439   1.257099   2.714872
 N     -0.326969   0.864462  -0.906577
 N     -1.046893  -1.613819  -1.104861
 C      2.704051   0.557283  -0.822268
 C      1.969020   1.758653  -1.211282
 C      2.860413   2.560098  -2.016184
 H      2.626122   3.539271  -2.452762
 C      4.126341   1.884888  -2.123219
 H      5.013475   2.257310  -2.653170
 C      4.039548   0.655687  -1.383965
 H      4.842836  -0.083801  -1.272251
 C      3.338597   2.585209   1.847596
 H      2.517719   2.162529   2.441111
 C      3.292188   3.818763   1.108416
 H      2.433916   4.501094   1.044247
 C      4.560081   3.990471   0.445913
 H      4.835896   4.823299  -0.214772
 C      5.392475   2.862650   0.779533
 H      6.414196   2.686081   0.417363
 C      4.637419   1.992296   1.643180
 H      4.980968   1.036271   2.059225
 C      2.181979  -2.270328  -1.227419
 C      1.995212  -3.604063  -0.790821
 H      1.792650  -3.810822   0.272816
 C      2.069974  -4.670101  -1.701649
 H      1.932732  -5.703363  -1.344873
 C      2.316580  -4.419933  -3.065706
 H      2.374051  -5.256478  -3.780047
 C      2.487367  -3.097798  -3.510281
 H      2.680126  -2.892880  -4.575503
 C      2.420780  -2.027138  -2.597911
 H      2.571798  -0.997812  -2.957676
 C      3.173310  -1.390530   1.328687
 C      2.892503  -1.143776   2.689673
 H      1.936879  -0.686232   2.981567
 C      3.830322  -1.477149   3.684139
 H      3.594798  -1.279399   4.741880
 C      5.058589  -2.063539   3.331523
 H      5.791275  -2.326161   4.111030
 C      5.343233  -2.322445   1.977912
 H      6.298865  -2.790431   1.692600
 C      4.406159  -1.993181   0.983499
 H      4.634639  -2.222009  -0.069161
 C      0.514245   2.078688  -0.832970
 H      0.509352   2.374421   0.234863
 C     -0.606654   0.444092  -2.272340
 H     -1.290339   1.140105  -2.816297
 H      0.326304   0.420416  -2.896997
 C     -1.196528  -0.932047  -2.276415
 C     -1.528282  -2.885865  -1.033720
 C     -2.172318  -3.511053  -2.103200
 H     -2.543329  -4.539668  -1.985323
 C     -2.335897  -2.804698  -3.310507
 C     -1.841409  -1.497537  -3.391951
 H     -1.945859  -0.904680  -4.313180
```

```
 C     -0.029741   3.280992  -1.625940
 H      0.562611   4.189766  -1.397231
 H      0.006727   3.126334  -2.723780
 H     -1.078502   3.489102  -1.333237
 C     -0.376772  -1.861668   1.575748
 C      0.133995   0.549524   1.767262
 H     -2.456474   1.284766  -0.418086
 H     -2.508846  -0.119348   1.224145
 C     -3.487683   0.435851   1.188288
 C     -4.589502  -0.612634   1.307404
 C     -3.620310   1.244277   2.519502
 C     -5.022052  -0.715709   2.648137
 C     -5.129612  -1.439952   0.310196
 C     -4.261029   0.259566   3.530160
 C     -6.010906  -1.650613   2.999588
 C     -6.124713  -2.372969   0.663260
 H     -4.786328  -1.349696  -0.733181
 C     -6.562826  -2.476533   1.999180
 H     -6.357466  -1.735553   4.042904
 H     -6.566752  -3.022698  -0.109335
 H     -2.842643  -3.267978  -4.170854
 H     -7.345675  -3.206017   2.262732
 H     -4.295316   2.109692   2.349997
 H     -4.906231   0.758479   4.283536
 H     -3.475880  -0.285985   4.102441
 H     -2.643189   1.644708   2.854073
 N     -3.417172   1.190234  -0.046781
 C     -4.392210   2.016826  -0.576266
 C     -4.091150   2.805585  -1.726922
 C     -5.713486   2.110578  -0.048900
 C     -5.052347   3.641736  -2.309457
 H     -3.081672   2.747499  -2.164495
 C     -6.666375   2.953863  -0.645180
 H     -5.999582   1.510805   0.825792
 C     -6.354289   3.729916  -1.776310
 H     -4.777068   4.234720  -3.197320
 H     -7.678164   2.999996  -0.209013
 H     -7.108146   4.388434  -2.234864
 H     -1.389682  -3.407307  -0.076013
---------------------------------------
Mn1/Mn-actcat-EtOH
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          15.2660
 E(RB-P86) (a.u.) =                                     -4407.53470683
 Thermal correction to Enthalpy (a.u.) =                   0.647685
 Thermal correction to Gibbs Free Energy (a.u.) =          0.529622
 Total Entropy (cal/Kmol) =                                248.485
 E(RPBE1PBE) (a.u.) =                                   -4406.85863799
Optimised cartesian coordinates (Angstrom):
 Fe    -2.946279  -1.235552  -0.957429
 Mn     1.366866  -0.282407   1.100895
 P     -0.333967   0.927399   0.183527
 O      1.734598   1.519841   3.394307
 O     -0.214203  -2.092446   2.798750
 N      1.349918  -1.586238  -0.611211
 N      2.854413   0.562477  -0.039897
 C     -1.304956  -0.009695  -1.069337
 C     -0.977829  -1.361391  -1.524833
 C     -1.848826  -1.659856  -2.639450
 H     -1.875325  -2.601764  -3.201395
 C     -2.711287  -0.533256  -2.869332
 H     -3.499840  -0.471556  -3.631274
 C     -2.386279   0.480051  -1.904849
 H     -2.870644   1.460931  -1.816808
 C     -3.286228  -1.882899   0.967683
 H     -2.549180  -1.874013   1.781339
 C     -3.492084  -2.957142   0.032189
 H     -2.947119  -3.910628   0.013798
 C     -4.522179  -2.554328  -0.890954
 H     -4.895255  -3.143610  -1.739344
 C     -4.956021  -1.230777  -0.523060
 H     -5.718255  -0.634645  -1.042528
 C     -4.191105  -0.813976   0.623358
 H     -4.266757   0.154273   1.134702
 C      0.230770   2.430350  -0.764260
 C      0.787498   3.498982  -0.019509
 H      0.803411   3.448330   1.081740
```

C	1.313451	4.628440	-0.667726
H	1.732297	5.454414	-0.070685
C	1.308883	4.704436	-2.074045
H	1.722621	5.589542	-2.582864
C	0.774940	3.641998	-2.823105
H	0.766959	3.690480	-3.923929
C	0.239179	2.512471	-2.173991
H	-0.189204	1.697294	-2.777775
C	-1.639562	1.690924	1.276247
C	-1.855739	1.186222	2.576470
H	-1.235723	0.359749	2.951974
C	-2.862830	1.726995	3.397190
H	-3.017104	1.320237	4.409382
C	-3.665240	2.783383	2.930997
H	-4.452157	3.208104	3.574458
C	-3.450680	3.301317	1.640079
H	-4.068078	4.134909	1.268627
C	-2.442797	2.762876	0.821131
H	-2.274194	3.192802	-0.178690
C	0.071895	-2.302005	-0.946431
H	-0.293314	-2.669778	0.033194
C	1.982466	-0.910161	-1.763939
H	2.405535	-1.623937	-2.503755
H	1.198260	-0.327809	-2.298291
C	3.042726	0.048300	-1.290113
C	3.737147	1.497111	0.401903
C	4.829189	1.934748	-0.356104
C	5.038155	1.386621	-1.632511
C	4.126113	0.427886	-2.099757
C	0.323284	-3.531611	-1.835766
H	-0.596883	-4.143464	-1.919027
H	0.640232	-3.256444	-2.862448
H	1.107876	-4.170546	-1.381933
C	1.576608	0.799075	2.465495
C	0.372843	-1.344298	2.088928
H	2.587292	-1.151762	1.667652
H	2.875976	-2.554327	1.365309
H	2.006593	-2.322943	-0.274526
O	3.069937	-3.414317	0.876101
C	4.487067	-3.501105	0.697132
H	4.660811	-4.286577	-0.070325
H	4.896250	-2.549717	0.279390
H	4.242754	-0.029937	-3.093703
H	5.507985	2.692472	0.062496
H	3.557649	1.895181	1.410940
C	5.218895	-3.861919	1.989541
H	4.832418	-4.815229	2.406520
H	6.308401	-3.978224	1.807686
H	5.085812	-3.071295	2.758319
H	5.893222	1.698126	-2.251491

Mn1/Mn-actcat

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	22.8984
E(RB-P86) (a.u.) =	-4252.59625634
Thermal correction to Enthalpy (a.u.) =	0.563059
Thermal correction to Gibbs Free Energy (a.u.) =	0.459114
Total Entropy (cal/Kmol) =	218.770
E(RPBE1PBE) (a.u.) =	-4251.91602182

Optimised cartesian coordinates (Angstrom):

Fe	2.929780	-0.835431	0.735619
Mn	-1.259583	-0.397702	-1.708544
P	-0.249528	0.662580	0.033109
O	-2.200394	2.042618	-3.048429
O	0.985879	-0.554665	-3.601720
N	-0.831721	-2.300219	-0.800680
N	-3.033888	-0.770169	-0.750561
C	0.932578	-0.414412	0.949965
C	1.140486	-1.837558	0.675462
C	1.981102	-2.359052	1.730262
H	2.342747	-3.391331	1.815027
C	2.306289	-1.290883	2.635117
H	2.952234	-1.371596	3.519659
C	1.670495	-0.094932	2.158021
H	1.729195	0.894732	2.628739
C	3.634866	-0.315107	-1.128848
H	3.017684	-0.151088	-2.022155

```
 C      4.193522  -1.574637  -0.712249
 H      4.083199  -2.534655  -1.234400
 C      4.905286  -1.361270   0.522043
 H      5.425375  -2.130390   1.108654
 C      4.789485   0.032633   0.866618
 H      5.206195   0.512036   1.762579
 C      4.002720   0.679126  -0.151080
 H      3.714543   1.738015  -0.171196
 C     -1.421347   1.220902   1.372471
 C     -2.314719   2.274376   1.057372
 H     -2.239286   2.781171   0.081087
 C     -3.292844   2.686568   1.977111
 H     -3.971089   3.515310   1.717463
 C     -3.409759   2.041992   3.223939
 H     -4.178268   2.363555   3.944723
 C     -2.540595   0.983784   3.539888
 H     -2.623525   0.471467   4.512011
 C     -1.553281   0.575553   2.621791
 H     -0.871504  -0.245286   2.893974
 C      0.714660   2.234486  -0.250642
 C      1.198531   2.534818  -1.542104
 H      0.984231   1.850811  -2.376021
 C      1.956852   3.697841  -1.771029
 H      2.326595   3.916374  -2.785644
 C      2.237571   4.579934  -0.712361
 H      2.828905   5.491946  -0.892060
 C      1.750305   4.295394   0.576995
 H      1.957348   4.984725   1.411315
 C      0.990911   3.134306   0.805215
 H      0.599846   2.935780   1.815526
 C      0.600004  -2.645227  -0.498601
 H      1.145158  -2.340148  -1.413943
 C     -1.767415  -2.547101   0.318269
 H     -1.914128  -3.628267   0.529026
 H     -1.321150  -2.100071   1.234697
 C     -3.088201  -1.873376   0.052978
 C     -4.187959  -0.078627  -0.950877
 H     -4.115619   0.806885  -1.598476
 C     -5.413964  -0.457874  -0.392431
 H     -6.310022   0.146057  -0.599203
 C     -5.473467  -1.607702   0.412337
 C     -4.285333  -2.322029   0.633140
 H     -4.275256  -3.228139   1.257832
 C      0.802256  -4.158995  -0.319487
 H      1.882884  -4.401258  -0.283354
 H      0.338170  -4.543240   0.611558
 H      0.371092  -4.710081  -1.180640
 C     -1.810415   1.066637  -2.495556
 C      0.119100  -0.468315  -2.794717
 H     -1.114473  -2.891829  -1.593884
 H     -1.921183  -1.272907  -2.854240
 H     -6.422646  -1.941937   0.858045
----------------------------------------
Mn1/Mn-alkox-EtOH
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          15.2679
 E(RB-P86) (a.u.) =                                    -4561.29174882
 Thermal correction to Enthalpy (a.u.) =                   0.711699
 Thermal correction to Gibbs Free Energy (a.u.) =          0.585348
 Total Entropy (cal/Kmol) =                                265.928
 E(RPBE1PBE) (a.u.) =                                  -4560.62416478
Optimised cartesian coordinates (Angstrom):
 Fe    -3.107117  -1.523989  -0.789165
 Mn     1.226354  -0.010541   0.908054
 P     -0.659890   0.936847   0.085223
 O      1.347180   2.056443   2.997000
 O     -0.128228  -1.858097   2.752196
 N      1.217384  -1.397843  -0.742167
 N      2.472916   0.970527  -0.434083
 C     -1.606429  -0.151205  -1.056854
 C     -1.174114  -1.480617  -1.484197
 C     -2.079494  -1.911884  -2.524467
 H     -2.044826  -2.875497  -3.047861
 C     -3.064143  -0.886307  -2.736483
 H     -3.901966  -0.934735  -3.444889
 C     -2.783792   0.194638  -1.833081
 H     -3.358050   1.125997  -1.749405
```

C	-3.278579	-2.102438	1.180778
H	-2.509625	-1.974082	1.953360
C	-3.413280	-3.239839	0.309568
H	-2.770422	-4.130365	0.305912
C	-4.525161	-2.996368	-0.573464
H	-4.873950	-3.664984	-1.371873
C	-5.080119	-1.708039	-0.245117
H	-5.926405	-1.223221	-0.750014
C	-4.308634	-1.153583	0.836760
H	-4.462204	-0.172991	1.305421
C	-0.329145	2.448506	-0.956297
C	0.119485	3.618506	-0.296704
H	0.196064	3.634030	0.802695
C	0.461250	4.767308	-1.028654
H	0.799081	5.671615	-0.497616
C	0.374649	4.763628	-2.434228
H	0.643716	5.664345	-3.008432
C	-0.057480	3.603408	-3.098872
H	-0.130483	3.590006	-4.198172
C	-0.408164	2.452965	-2.365822
H	-0.761693	1.559579	-2.903361
C	-1.961244	1.607199	1.243008
C	-2.048948	1.146801	2.574511
H	-1.328856	0.408394	2.952728
C	-3.058577	1.620982	3.432375
H	-3.109328	1.250139	4.468433
C	-3.994177	2.564357	2.973077
H	-4.783258	2.936278	3.645764
C	-3.910208	3.037480	1.650528
H	-4.632480	3.783389	1.282097
C	-2.899249	2.567231	0.794634
H	-2.835858	2.964515	-0.230289
C	0.011512	-2.269800	-0.948657
H	-0.239588	-2.628517	0.069402
C	1.689862	-0.736034	-1.977068
H	2.160279	-1.447603	-2.689733
H	0.812478	-0.298094	-2.504596
C	2.646158	0.379309	-1.646336
C	3.260465	2.024894	-0.111731
C	4.244722	2.528953	-0.970156
C	4.437156	1.911885	-2.217292
C	3.625308	0.819740	-2.555096
C	0.339534	-3.508135	-1.800664
H	-0.504944	-4.225644	-1.779993
H	0.540390	-3.252691	-2.861257
H	1.230300	-4.017504	-1.381432
C	1.311634	1.217257	2.161930
C	0.367281	-1.096042	1.994341
H	3.215622	-2.244830	0.800103
H	1.980238	-2.056686	-0.439939
O	3.270685	-3.128817	0.220068
C	4.515570	-3.147413	-0.463752
H	4.386170	-3.724520	-1.409543
H	4.825912	-2.115934	-0.765681
H	3.740186	0.303228	-3.519932
H	4.852586	3.389414	-0.654130
H	3.090589	2.477443	0.875619
C	5.630557	-3.790764	0.365991
H	5.348987	-4.823260	0.662557
H	6.580587	-3.842490	-0.208289
H	5.823501	-3.211025	1.293745
H	5.208889	2.273286	-2.914118
O	3.000577	-0.947824	1.407386
C	3.489449	-0.996412	2.728001
C	4.477522	0.130504	3.058185
H	4.014771	-1.976015	2.881323
H	2.662835	-0.983162	3.483713
H	4.895417	0.002451	4.081011
H	5.323476	0.133843	2.338201
H	3.985530	1.123976	3.015453

Mn1/Mn-precat-EtOH
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) = 20.8357
 E(RB-P86) (a.u.) = -4406.33359366
 Thermal correction to Enthalpy (a.u.) = 0.626987
 Thermal correction to Gibbs Free Energy (a.u.) = 0.508376

Total Entropy (cal/Kmol) = 249.638
E(RPBE1PBE) (a.u.) = -4405.66239607
Optimised cartesian coordinates (Angstrom):

Fe	-2.856548	-1.323029	-0.988718
Mn	1.268364	-0.169377	1.099869
P	-0.363611	0.964167	0.178129
O	1.713232	1.641078	3.405533
O	-0.412574	-1.792409	2.881842
N	1.380856	-1.460424	-0.324588
N	2.899562	0.597989	0.092882
C	-1.228601	-0.078561	-1.066898
C	-0.844559	-1.443057	-1.422700
C	-1.637539	-1.824615	-2.566736
H	-1.608003	-2.799271	-3.070388
C	-2.504274	-0.731366	-2.918474
H	-3.241385	-0.728192	-3.732851
C	-2.263111	0.343173	-1.995063
H	-2.768653	1.317299	-1.999302
C	-3.325071	-1.849239	0.948249
H	-2.653915	-1.766231	1.812757
C	-3.435489	-2.988667	0.076626
H	-2.868523	-3.925299	0.163737
C	-4.401429	-2.676884	-0.946015
H	-4.696667	-3.331978	-1.776611
C	-4.890515	-1.343296	-0.704010
H	-5.624504	-0.804541	-1.318235
C	-4.223748	-0.830047	0.464690
H	-4.359845	0.167686	0.901789
C	0.283816	2.389993	-0.824507
C	0.729591	3.543825	-0.135903
H	0.619376	3.607039	0.959058
C	1.308000	4.614352	-0.836738
H	1.640559	5.509887	-0.287897
C	1.464667	4.543161	-2.234721
H	1.919369	5.382782	-2.783978
C	1.038839	3.395092	-2.924372
H	1.157672	3.330735	-4.017811
C	0.451385	2.323112	-2.225160
H	0.109137	1.436331	-2.780267
C	-1.715026	1.785800	1.155899
C	-1.978764	1.392462	2.485513
H	-1.366657	0.614295	2.962653
C	-3.026486	1.987879	3.211922
H	-3.217977	1.670271	4.249170
C	-3.821326	2.985419	2.620489
H	-4.639913	3.452439	3.190795
C	-3.559165	3.391609	1.298842
H	-4.170089	4.179425	0.830024
C	-2.510955	2.800288	0.573002
H	-2.305039	3.144393	-0.452571
C	0.214243	-2.289066	-0.703422
H	-0.229154	-2.623550	0.255851
C	2.232386	-1.121701	-1.456870
H	2.798230	-1.999584	-1.851706
H	1.630834	-0.753743	-2.329941
C	3.197447	-0.042419	-1.073884
C	3.715470	1.610135	0.499225
C	4.842437	2.008276	-0.222259
C	5.156663	1.341602	-1.422429
C	4.321195	0.302237	-1.847894
C	0.584647	-3.563367	-1.485365
H	-0.291391	-4.238823	-1.560411
H	0.933577	-3.349982	-2.516515
H	1.386634	-4.098902	-0.938117
C	1.531357	0.919250	2.484683
C	0.211132	-1.127736	2.123793
H	2.372711	-2.677641	0.706195
O	2.827874	-3.442541	1.164827
C	4.225198	-3.346016	0.922724
H	4.625698	-2.347096	1.229922
H	4.461691	-3.456026	-0.166839
H	4.526267	-0.249506	-2.777841
H	5.466729	2.830220	0.157748
H	3.445586	2.105266	1.442930
C	4.947352	-4.438578	1.703490
H	6.042643	-4.392849	1.531476
H	4.761109	-4.330045	2.792708

```
 H      4.589144  -5.443434   1.395083
 H      6.040286   1.629018  -2.012644
---------------------------------------
Mn1/Mn-precat
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          23.9444
 E(RB-P86) (a.u.) =                                     -4251.39884820
 Thermal correction to Enthalpy (a.u.) =                   0.542229
 Thermal correction to Gibbs Free Energy (a.u.) =          0.438928
 Total Entropy (cal/Kmol) =                                217.415
 E(RPBE1PBE) (a.u.) =                                   -4250.71884842
Optimised cartesian coordinates (Angstrom):
 Fe     2.917887  -0.911218   0.714619
 Mn    -1.205675  -0.381228  -1.607893
 P     -0.214139   0.693098   0.019465
 O     -2.232962   1.969720  -3.101141
 O      1.069091  -0.405194  -3.468128
 N     -0.881739  -2.095930  -0.861035
 N     -3.069846  -0.733089  -0.795709
 C      0.928851  -0.443878   0.912034
 C      1.090828  -1.864165   0.610934
 C      1.906876  -2.432854   1.656813
 H      2.234781  -3.478475   1.718254
 C      2.255113  -1.395064   2.591133
 H      2.886086  -1.514044   3.482459
 C      1.662672  -0.167814   2.134191
 H      1.745363   0.807274   2.631163
 C      3.666455  -0.382513  -1.132297
 H      3.068647  -0.193348  -2.033553
 C      4.189991  -1.658820  -0.723089
 H      4.067147  -2.609149  -1.259911
 C      4.883590  -1.477719   0.526943
 H      5.377100  -2.265577   1.111718
 C      4.791084  -0.086132   0.888999
 H      5.202412   0.372177   1.798444
 C      4.036737   0.590584  -0.134082
 H      3.772150   1.655895  -0.145372
 C     -1.419603   1.202395   1.341268
 C     -2.235375   2.335982   1.109901
 H     -2.090116   2.940690   0.199769
 C     -3.227395   2.702884   2.033765
 H     -3.846495   3.594425   1.844439
 C     -3.432185   1.933917   3.195988
 H     -4.211185   2.221420   3.919848
 C     -2.638174   0.797148   3.425484
 H     -2.791785   0.189051   4.331394
 C     -1.637368   0.431734   2.504749
 H     -1.013545  -0.453140   2.704021
 C      0.754204   2.261805  -0.225313
 C      1.216808   2.618052  -1.510380
 H      0.981430   1.981835  -2.375464
 C      1.983535   3.783192  -1.696094
 H      2.335996   4.047520  -2.705780
 C      2.294422   4.608630  -0.601062
 H      2.892870   5.521815  -0.747619
 C      1.828605   4.267228   0.682332
 H      2.059058   4.912824   1.544818
 C      1.060446   3.105005   0.868922
 H      0.685831   2.862555   1.875736
 C      0.482495  -2.589755  -0.600257
 H      1.078973  -2.298271  -1.487596
 C     -1.881235  -2.655604   0.028862
 H     -2.076299  -3.737820  -0.169409
 H     -1.557142  -2.619540   1.103903
 C     -3.166642  -1.897764  -0.092111
 C     -4.190626   0.030918  -0.928338
 H     -4.078568   0.964875  -1.497373
 C     -5.425286  -0.336513  -0.390672
 H     -6.295721   0.320279  -0.535591
 C     -5.528703  -1.546097   0.324417
 C     -4.380416  -2.333313   0.471111
 H     -4.408547  -3.286121   1.021488
 C      0.592559  -4.120965  -0.476446
 H      1.657393  -4.429947  -0.475866
 H      0.130631  -4.512357   0.452963
 H      0.101909  -4.607731  -1.344028
 C     -1.814880   1.034858  -2.504092
```

```
 C      0.192848  -0.383443  -2.667582
 H     -6.488796  -1.865812   0.757583
---------------------------------------
Mn1/TSH2-EtOH
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -748.4830
 E(RB-P86) (a.u.) =                                       -4407.50399496
 Thermal correction to Enthalpy (a.u.) =                   0.639186
 Thermal correction to Gibbs Free Energy (a.u.) =          0.523276
 Total Entropy (cal/Kmol) =                                243.952
 E(RPBE1PBE) (a.u.) =                                     -4406.82702017
Optimised cartesian coordinates (Angstrom):
 Fe    -2.902525  -1.261186  -0.959042
 Mn     1.315847  -0.227590   1.257345
 P     -0.295405   0.921578   0.138927
 O      1.473818   1.859894   3.342092
 O     -0.522519  -1.777306   2.957743
 N      1.362388  -1.644520  -0.297274
 N      2.869177   0.522864   0.115577
 C     -1.210944  -0.105627  -1.071908
 C     -0.899287  -1.499522  -1.378380
 C     -1.708042  -1.873051  -2.515160
 H     -1.728945  -2.862498  -2.989118
 C     -2.516772  -0.748957  -2.903789
 H     -3.252248  -0.734518  -3.719392
 C     -2.222783   0.340127  -2.014046
 H     -2.677675   1.338234  -2.048597
 C     -3.415367  -1.701376   0.988486
 H     -2.751470  -1.622150   1.858637
 C     -3.569260  -2.862630   0.153305
 H     -3.047280  -3.820979   0.277374
 C     -4.508534  -2.539953  -0.890468
 H     -4.824584  -3.207210  -1.703535
 C     -4.937985  -1.178088  -0.697178
 H     -5.639444  -0.626480  -1.337439
 C     -4.260336  -0.657898   0.461881
 H     -4.355385   0.358330   0.865899
 C      0.391322   2.311457  -0.892202
 C      0.913378   3.440588  -0.216155
 H      0.853455   3.500540   0.882754
 C      1.499783   4.495697  -0.933913
 H      1.893060   5.370968  -0.392707
 C      1.585912   4.434866  -2.338030
 H      2.046163   5.262336  -2.900884
 C      1.081228   3.312513  -3.016550
 H      1.142678   3.255952  -4.115089
 C      0.487137   2.256070  -2.299405
 H      0.083513   1.391040  -2.847679
 C     -1.626524   1.822938   1.083127
 C     -1.952920   1.455425   2.406334
 H     -1.400473   0.650750   2.910469
 C     -2.990110   2.109791   3.096307
 H     -3.228774   1.809976   4.129042
 C     -3.714397   3.141869   2.474882
 H     -4.524835   3.654836   3.016607
 C     -3.391182   3.522093   1.159232
 H     -3.946219   4.335538   0.665363
 C     -2.352579   2.872047   0.470771
 H     -2.099224   3.197040  -0.550260
 C      0.117659  -2.375283  -0.648965
 H     -0.326819  -2.668092   0.324194
 C      2.063757  -1.120427  -1.474368
 H      2.541867  -1.921549  -2.085096
 H      1.356582  -0.602080  -2.171386
 C      3.101202  -0.112870  -1.067066
 C      3.734651   1.491234   0.512916
 C      4.859477   1.856053  -0.233718
 C      5.112689   1.192127  -1.446584
 C      4.220202   0.195773  -1.862942
 C      0.408973  -3.684272  -1.410900
 H     -0.507314  -4.303599  -1.492421
 H      0.784985  -3.503029  -2.438991
 H      1.168009  -4.268688  -0.852988
 C      1.421132   1.022510   2.511070
 C      0.168695  -1.139182   2.242693
 H      2.632630  -0.858350   2.145486
 H      2.507429  -1.616642   1.760723
```

```
 H      2.143302  -2.502094   0.331444
 O      2.783120  -3.171048   1.099649
 C      4.144129  -3.265306   0.752665
 H      4.276991  -3.477606  -0.341694
 H      4.688899  -2.297518   0.935107
 H      4.378483  -0.351356  -2.804408
 H      5.526631   2.645896   0.141194
 H      3.513458   1.981283   1.472073
 C      4.839370  -4.369880   1.553656
 H      4.353505  -5.351175   1.366058
 H      5.913411  -4.455578   1.281567
 H      4.774324  -4.164613   2.643601
 H      5.993476   1.446170  -2.055944
---------------------------------------
Mn1/TSH2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -635.0178
 E(RB-P86) (a.u.) =                                        -4252.55916938
 Thermal correction to Enthalpy (a.u.) =                    0.557285
 Thermal correction to Gibbs Free Energy (a.u.) =           0.454058
 Total Entropy (cal/Kmol) =                                 217.259
 E(RPBE1PBE) (a.u.) =                                      -4251.87662437
Optimised cartesian coordinates (Angstrom):
 Fe     2.925876  -0.824346   0.742419
 Mn    -1.213095  -0.449467  -1.735452
 P     -0.257116   0.639994   0.015126
 O     -2.167456   1.975664  -3.131911
 O      1.173626  -0.416996  -3.455349
 N     -0.835999  -2.294650  -0.829359
 N     -3.015332  -0.767010  -0.755152
 C      0.913227  -0.451154   0.916556
 C      1.146541  -1.865866   0.621734
 C      1.976297  -2.382932   1.685228
 H      2.353104  -3.410937   1.759730
 C      2.268258  -1.324551   2.614426
 H      2.896773  -1.406880   3.511520
 C      1.623597  -0.130717   2.142759
 H      1.656232   0.851506   2.631290
 C      3.678592  -0.210795  -1.077818
 H      3.085396   0.003595  -1.975630
 C      4.218856  -1.494181  -0.716203
 H      4.114979  -2.423745  -1.291941
 C      4.900293  -1.352076   0.545480
 H      5.402396  -2.154641   1.102327
 C      4.783207   0.022753   0.961719
 H      5.181334   0.450676   1.891635
 C      4.025463   0.727926  -0.039427
 H      3.744486   1.788758  -0.010940
 C     -1.466043   1.170238   1.328934
 C     -2.333388   2.248087   1.028297
 H     -2.238636   2.777604   0.065994
 C     -3.310725   2.658924   1.949514
 H     -3.971375   3.505467   1.702978
 C     -3.446982   1.991006   3.181643
 H     -4.213613   2.312800   3.904274
 C     -2.599996   0.910574   3.482682
 H     -2.698998   0.381163   4.443898
 C     -1.615828   0.500889   2.562401
 H     -0.953453  -0.340872   2.816991
 C      0.682834   2.230186  -0.237465
 C      1.162055   2.583582  -1.517238
 H      0.960776   1.933901  -2.380208
 C      1.903811   3.764822  -1.704031
 H      2.268299   4.024271  -2.710720
 C      2.174199   4.611482  -0.614929
 H      2.753229   5.537012  -0.762018
 C      1.691549   4.274286   0.663345
 H      1.889385   4.935514   1.522107
 C      0.947468   3.096613   0.849770
 H      0.558815   2.859610   1.852397
 C      0.556377  -2.656339  -0.556811
 H      1.126950  -2.375728  -1.466696
 C     -1.754848  -2.579004   0.254499
 H     -1.957985  -3.671519   0.386851
 H     -1.364170  -2.240261   1.256665
 C     -3.063270  -1.865780   0.049572
 C     -4.153403  -0.049629  -0.942395
```

C	-5.372646	-0.390878	-0.348686
C	-5.430724	-1.529710	0.474032
C	-4.260087	-2.273596	0.668859
C	0.750352	-4.177218	-0.369589
H	1.827238	-4.442279	-0.338864
H	0.287190	-4.549889	0.567704
H	0.289471	-4.716603	-1.221865
C	-1.785554	1.006456	-2.573872
C	0.254007	-0.418251	-2.710589
H	-1.498201	-2.021978	-2.253729
H	-1.888947	-1.492427	-2.903250
H	-4.076194	0.826877	-1.601758
H	-6.261137	0.228848	-0.538995
H	-4.258153	-3.174929	1.300323
H	-6.374840	-1.833776	0.951735

Mn1/TSHy-re-AcPh

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-184.5546
E(RB-P86) (a.u.) =	-4637.21573152
Thermal correction to Enthalpy (a.u.) =	0.705418
Thermal correction to Gibbs Free Energy (a.u.) =	0.581370
Total Entropy (cal/Kmol) =	261.080
E(RPBE1PBE) (a.u.) =	-4636.52516560

Optimised cartesian coordinates (Angstrom):

Fe	-3.566530	-1.255761	-0.827929
Mn	0.922326	-0.253006	0.720679
P	-0.940534	0.938627	0.230103
O	1.585491	1.214427	3.183974
O	-0.344273	-2.333762	2.367298
N	0.749414	-1.324881	-1.086470
N	2.191999	0.831383	-0.470909
C	-2.021562	0.084706	-0.991824
C	-1.687305	-1.175917	-1.655368
C	-2.685169	-1.399103	-2.676836
H	-2.736923	-2.266679	-3.346433
C	-3.629591	-0.315760	-2.648288
H	-4.516452	-0.217963	-3.288692
C	-3.231254	0.594685	-1.611300
H	-3.750076	1.522080	-1.337136
C	-3.616993	-2.153888	1.025466
H	-2.781696	-2.195920	1.736580
C	-3.889798	-3.117375	-0.008320
H	-3.304988	-4.023253	-0.217720
C	-5.051046	-2.674187	-0.736756
H	-5.502393	-3.178969	-1.601435
C	-5.498424	-1.436877	-0.149905
H	-6.350890	-0.833448	-0.489585
C	-4.611322	-1.113074	0.936967
H	-4.668241	-0.221740	1.575082
C	-0.597379	2.578220	-0.586531
C	-0.009757	3.593201	0.207639
H	0.159612	3.417708	1.282856
C	0.353329	4.826375	-0.357711
H	0.799268	5.607921	0.278184
C	0.151783	5.062543	-1.731426
H	0.437760	6.029260	-2.175441
C	-0.414773	4.055844	-2.531736
H	-0.576352	4.229940	-3.607713
C	-0.787290	2.821544	-1.964515
H	-1.244640	2.050747	-2.604044
C	-2.114726	1.471006	1.577693
C	-2.113886	0.805792	2.822534
H	-1.402314	-0.011547	3.006290
C	-3.020913	1.175119	3.833035
H	-3.005236	0.644987	4.798665
C	-3.938858	2.217543	3.614621
H	-4.647092	2.508127	4.406822
C	-3.941239	2.893942	2.380475
H	-4.650619	3.717953	2.202276
C	-3.033425	2.527042	1.371780
H	-3.034589	3.080041	0.419396
C	-0.512692	-2.096601	-1.345657
H	-0.716486	-2.608887	-0.384500
C	1.186815	-0.500597	-2.233509
H	1.573685	-1.113336	-3.076314
H	0.305470	0.056103	-2.625316

```
 C      2.221593   0.498680  -1.793517
 C      3.054746   1.788743  -0.036700
 H      3.010633   2.032495   1.034249
 C      3.958972   2.440693  -0.881792
 H      4.627236   3.209659  -0.467171
 C      3.996449   2.090732  -2.242095
 C      3.115852   1.098591  -2.696502
 H      3.106188   0.786673  -3.751854
 C     -0.312256  -3.186548  -2.412400
 H     -1.192629  -3.858796  -2.446384
 H     -0.168348  -2.766562  -3.428827
 H      0.572148  -3.804046  -2.155751
 C      1.308330   0.634918   2.187450
 C      0.113730  -1.476288   1.686115
 H      1.509138  -2.042402  -0.927345
 H      2.240129  -1.191597   0.986093
 C      3.293668  -2.552688   0.547984
 C      4.558610  -1.720439   0.650903
 C      2.897373  -3.388480   1.763205
 C      5.081259  -1.250203   1.878827
 C      5.278330  -1.455986  -0.536458
 C      6.289388  -0.534055   1.914672
 C      6.488079  -0.744290  -0.501786
 H      4.866085  -1.836994  -1.483058
 C      6.998670  -0.280025   0.725083
 H      6.681223  -0.171713   2.878638
 H      7.039924  -0.553220  -1.436362
 H      7.948289   0.277860   0.755627
 O      2.901662  -2.920648  -0.597038
 H      1.873067  -3.780880   1.627164
 H      3.597619  -4.252197   1.819917
 H      4.700065   2.577853  -2.934230
 H      4.536073  -1.431213   2.817760
 H      2.949130  -2.843381   2.724013
---------------------------------------
Mn1/TSHy-re-AcPhNPh
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -386.8602
 E(RB-P86) (a.u.) =                                        -4848.21569378
 Thermal correction to Enthalpy (a.u.) =                    0.800145
 Thermal correction to Gibbs Free Energy (a.u.) =           0.665452
 Total Entropy (cal/Kmol) =                                 283.487
 E(RPBE1PBE) (a.u.) =                                      -4847.50324800
Optimised cartesian coordinates (Angstrom):
 Fe    -3.673968  -1.768895  -0.958970
 Mn     0.421022   0.084547   0.837748
 P     -1.623180   0.903294   0.274336
 O      0.692533   1.530428   3.383447
 O     -0.633105  -2.161842   2.416165
 N      0.569460  -0.901492  -1.030262
 N      1.446466   1.494136  -0.253565
 C     -2.443678  -0.127504  -1.013969
 C     -1.821172  -1.265552  -1.693441
 C     -2.706802  -1.658326  -2.766466
 H     -2.545740  -2.492789  -3.460239
 C     -3.860513  -0.801410  -2.755135
 H     -4.721450  -0.871922  -3.433327
 C     -3.707831   0.135702  -1.677781
 H     -4.423974   0.921069  -1.404810
 C     -3.646153  -2.685293   0.886879
 H     -2.875961  -2.543032   1.655558
 C     -3.612519  -3.668374  -0.163553
 H     -2.819161  -4.409801  -0.328886
 C     -4.789547  -3.494670  -0.975768
 H     -5.047909  -4.075775  -1.871183
 C     -5.553046  -2.404124  -0.424489
 H     -6.495459  -2.009029  -0.826970
 C     -4.845649  -1.901791   0.724817
 H     -5.152670  -1.057648   1.355845
 C     -1.599441   2.599631  -0.500084
 C     -1.269466   3.692763   0.338106
 H     -1.099617   3.525783   1.414665
 C     -1.167512   4.992325  -0.184195
 H     -0.921091   5.831749   0.485579
 C     -1.375992   5.221662  -1.557967
 H     -1.294989   6.240745  -1.968289
 C     -1.687113   4.141638  -2.401412
```

H	-1.852281	4.309919	-3.477735
C	-1.798273	2.838895	-1.877403
H	-2.060394	2.008486	-2.551117
C	-2.950922	1.155855	1.561936
C	-2.882062	0.488864	2.803962
H	-2.031617	-0.168837	3.028805
C	-3.899532	0.651278	3.762643
H	-3.827108	0.122835	4.726598
C	-4.999030	1.485538	3.495507
H	-5.793873	1.614163	4.247360
C	-5.072797	2.163122	2.264328
H	-5.925195	2.826744	2.047648
C	-4.055259	2.003723	1.307797
H	-4.118396	2.559102	0.359076
C	-0.482748	-1.921641	-1.369764
H	-0.599924	-2.512230	-0.438983
C	0.810325	0.072244	-2.120386
H	1.376716	-0.372053	-2.967446
H	-0.173232	0.391057	-2.532004
C	1.526768	1.288525	-1.598550
C	2.047500	2.601389	0.258910
C	2.727409	3.533637	-0.531154
H	3.191110	4.409877	-0.054636
C	2.800073	3.327117	-1.919386
C	2.193035	2.182500	-2.453213
H	2.232555	1.968782	-3.531820
C	-0.012006	-2.884618	-2.472950
H	-0.716822	-3.734088	-2.571610
H	0.064173	-2.390628	-3.463089
H	0.981523	-3.300706	-2.209357
C	0.564505	0.959494	2.350937
C	-0.240964	-1.266036	1.742902
H	1.473588	-1.434442	-0.898574
H	1.924025	-0.642435	1.099363
C	3.121644	-1.825405	0.832667
C	4.225582	-1.288196	1.736015
C	2.362184	-2.971958	1.495117
C	3.988571	-0.399070	2.806080
C	5.531213	-1.810757	1.570349
C	5.031027	-0.023729	3.673032
C	6.571146	-1.439792	2.439099
H	5.729492	-2.520902	0.752086
C	6.326964	-0.539146	3.492356
H	4.826067	0.678154	4.497531
H	7.579533	-1.859309	2.292142
H	7.142671	-0.244468	4.171773
N	3.246411	-1.938343	-0.492381
C	4.148563	-1.190479	-1.263589
C	4.555632	-1.769457	-2.499732
C	4.665153	0.096115	-0.940097
C	5.458468	-1.116714	-3.351578
H	4.150882	-2.760002	-2.762243
C	5.562310	0.748071	-1.801588
H	4.346152	0.592569	-0.013058
C	5.974107	0.148336	-3.006730
H	5.762431	-1.599231	-4.294999
H	5.941922	1.746041	-1.527357
H	6.681946	0.664789	-3.674282
H	1.973220	2.734859	1.347570
H	3.325704	4.040832	-2.571774
H	2.977532	0.008875	2.952116
H	3.064812	-3.829855	1.590231
H	2.004010	-2.713005	2.508188
H	1.507404	-3.301103	0.874324

Mn1/TSHy-re-AcPhNPh_2
Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-307.9091
E(RB-P86) (a.u.) =	-4848.21912743
Thermal correction to Enthalpy (a.u.) =	0.800276
Thermal correction to Gibbs Free Energy (a.u.) =	0.665534
Total Entropy (cal/Kmol) =	283.587
E(RPBE1PBE) (a.u.) =	-4847.50626610

Optimised cartesian coordinates (Angstrom):

Fe	3.352674	1.667837	-0.876579
Mn	-0.652655	-0.453056	0.794946
P	1.412745	-1.150277	0.184103

O	-0.881507	-2.094367	3.224770
O	0.187182	1.748662	2.549473
N	-0.859926	0.684416	-0.982742
N	-1.646843	-1.800798	-0.395898
C	2.189041	-0.013317	-1.036613
C	1.522725	1.138174	-1.648042
C	2.395622	1.627964	-2.692178
H	2.205344	2.496093	-3.335081
C	3.581304	0.817168	-2.728158
H	4.439700	0.961786	-3.397764
C	3.462945	-0.188220	-1.710369
H	4.207397	-0.961654	-1.482562
C	3.248155	2.509642	1.001254
H	2.457034	2.325285	1.739578
C	3.232345	3.532830	-0.010800
H	2.431839	4.266767	-0.174619
C	4.438746	3.410348	-0.788551
H	4.716274	4.030091	-1.651710
C	5.202656	2.311904	-0.254274
H	6.164815	1.948360	-0.639344
C	4.466493	1.753089	0.849639
H	4.767408	0.890202	1.457655
C	1.444648	-2.792312	-0.696350
C	1.178229	-3.952999	0.070356
H	1.031861	-3.868011	1.159793
C	1.107842	-5.215585	-0.540604
H	0.910867	-6.108736	0.073775
C	1.284653	-5.339788	-1.932195
H	1.228244	-6.329829	-2.411866
C	1.532139	-4.192044	-2.704543
H	1.671858	-4.277954	-3.794134
C	1.611785	-2.926228	-2.092175
H	1.823613	-2.040636	-2.711129
C	2.744384	-1.429543	1.460058
C	2.643149	-0.837202	2.737068
H	1.765405	-0.226732	2.990417
C	3.661302	-1.014373	3.692237
H	3.564230	-0.544753	4.684057
C	4.793484	-1.789532	3.385612
H	5.589120	-1.930070	4.134482
C	4.899640	-2.392922	2.118658
H	5.778335	-3.009769	1.871061
C	3.881446	-2.218542	1.165349
H	3.970008	-2.715211	0.186531
C	0.168219	1.742501	-1.284851
H	0.274168	2.295662	-0.330808
C	-1.131077	-0.194508	-2.143235
H	-1.726844	0.314540	-2.931205
H	-0.155897	-0.462624	-2.608469
C	-1.811542	-1.461780	-1.706854
C	-2.178075	-2.980166	0.023880
C	-2.868853	-3.851426	-0.824565
H	-3.268456	-4.793131	-0.420836
C	-3.044740	-3.497171	-2.172249
C	-2.510684	-2.277454	-2.611879
H	-2.622148	-1.950795	-3.656855
C	-0.321972	2.737979	-2.350073
H	0.365246	3.605199	-2.407423
H	-0.376602	2.283361	-3.360105
H	-1.323662	3.128705	-2.080479
C	-0.769883	-1.445912	2.238642
C	-0.098363	0.865433	1.806002
H	-1.760730	1.183609	-0.763496
H	-2.137183	0.211032	1.154043
C	-3.530028	1.086275	1.020794
C	-4.399381	-0.133799	0.759629
C	-3.568646	1.577880	2.470426
C	-4.534344	-1.176088	1.707914
C	-5.189368	-0.193960	-0.411076
C	-5.447054	-2.224203	1.505255
C	-6.095640	-1.247491	-0.621312
H	-5.088778	0.624965	-1.138820
C	-6.236725	-2.263831	0.340962
H	-5.538356	-3.020151	2.261839
H	-6.707664	-1.266114	-1.537873
H	-3.589245	-4.155647	-2.866022
H	-6.956627	-3.083234	0.184945

N	-3.406225	1.924516	-0.012607
C	-3.057714	3.279386	0.076082
C	-3.800719	4.177829	-0.744753
C	-1.982866	3.829239	0.832853
C	-3.514704	5.550211	-0.779287
H	-4.620856	3.761869	-1.351378
C	-1.691947	5.204434	0.780452
H	-1.352577	3.178345	1.453542
C	-2.455199	6.077803	-0.014975
H	-4.121862	6.214952	-1.415593
H	-0.850025	5.596081	1.375047
H	-2.223367	7.154109	-0.046087
H	-2.037361	-3.226503	1.085265
H	-3.909067	-1.179415	2.613820
H	-2.788564	2.327544	2.684062
H	-4.559870	2.049459	2.651605
H	-3.454381	0.750308	3.193822

Mn1/TSHy-re-ind

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-246.9177
E(RB-P86) (a.u.) =	-4675.30396284
Thermal correction to Enthalpy (a.u.) =	0.712461
Thermal correction to Gibbs Free Energy (a.u.) =	0.589480
Total Entropy (cal/Kmol) =	258.836
E(RPBE1PBE) (a.u.) =	-4674.61436103

Optimised cartesian coordinates (Angstrom):

Fe	-3.642701	-1.202629	-0.855907
Mn	0.923649	-0.272107	0.489268
P	-1.005852	0.902787	0.354360
O	1.742051	0.772806	3.116173
O	-0.145069	-2.652645	1.842700
N	0.636066	-1.031042	-1.453503
N	2.055107	1.055236	-0.593148
C	-2.159464	0.214858	-0.904808
C	-1.842578	-0.899049	-1.799413
C	-2.914803	-0.990632	-2.764157
H	-2.995155	-1.733634	-3.567442
C	-3.887211	0.028152	-2.476213
H	-4.827430	0.192483	-3.019512
C	-3.432375	0.766966	-1.331579
H	-3.955535	1.610005	-0.862453
C	-3.513929	-2.407541	0.811458
H	-2.623192	-2.535971	1.440140
C	-3.842000	-3.189705	-0.351166
H	-3.250037	-4.020024	-0.759257
C	-5.071688	-2.678583	-0.900845
H	-5.577131	-3.046022	-1.803989
C	-5.505812	-1.581159	-0.074575
H	-6.400598	-0.965698	-0.238165
C	-4.542489	-1.411158	0.981838
H	-4.572702	-0.646289	1.768566
C	-0.778427	2.665910	-0.204111
C	-0.154503	3.563052	0.696914
H	0.109208	3.224603	1.712494
C	0.126029	4.884759	0.313849
H	0.602118	5.571503	1.031984
C	-0.196234	5.329943	-0.982804
H	0.025199	6.366141	-1.283995
C	-0.800680	4.442933	-1.889825
H	-1.056879	4.780969	-2.906786
C	-1.090588	3.119564	-1.504456
H	-1.579224	2.443677	-2.223241
C	-2.074701	1.155909	1.860864
C	-1.954407	0.290429	2.969316
H	-1.211266	-0.519270	2.954066
C	-2.781768	0.450365	4.096232
H	-2.673161	-0.234147	4.952588
C	-3.738141	1.480448	4.132382
H	-4.383826	1.607117	5.015925
C	-3.859397	2.354866	3.036381
H	-4.599760	3.170537	3.058328
C	-3.031272	2.197115	1.911419
H	-3.125107	2.902043	1.070550
C	-0.617385	-1.804283	-1.744330
H	-0.723778	-2.480803	-0.873328
C	0.954171	-0.011208	-2.475531

H	1.295481	-0.460456	-3.433242
H	0.027710	0.562073	-2.706540
C	1.986596	0.948940	-1.951400
C	2.917074	1.966735	-0.068753
H	2.954278	2.024690	1.028320
C	3.724725	2.793935	-0.856541
H	4.397543	3.514447	-0.368814
C	3.663227	2.676238	-2.255153
C	2.783743	1.731701	-2.803999
H	2.698741	1.599293	-3.893197
C	-0.472293	-2.688359	-2.994862
H	-1.329522	-3.386142	-3.074850
H	-0.429053	-2.097222	-3.932366
H	0.450574	-3.298172	-2.917951
C	1.403272	0.365893	2.055586
C	0.229261	-1.671363	1.288222
H	1.433365	-1.729939	-1.475670
H	2.298291	-1.193689	0.472013
C	3.325365	-2.332998	-0.236769
C	4.564131	-1.535947	0.072122
C	3.194915	-3.338696	0.933916
C	4.978893	-1.788252	1.399556
C	5.309139	-0.710314	-0.785840
C	3.998885	-2.716241	2.096123
C	6.157017	-1.198617	1.886231
C	6.490150	-0.123879	-0.296079
H	4.971137	-0.544354	-1.821418
C	6.907965	-0.365964	1.030781
H	6.499261	-1.388510	2.916972
H	7.098483	0.521528	-0.949962
H	7.838347	0.095377	1.399775
O	2.879298	-2.534239	-1.402008
H	4.501863	-3.464844	2.742535
H	3.328447	-2.120238	2.756585
H	2.146264	-3.590247	1.177167
H	3.690359	-4.271528	0.578024
H	4.290530	3.304637	-2.905597

Mn1/TSHy-re-indNPh

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-475.3349
E(RB-P86) (a.u.) =	-4886.29877445
Thermal correction to Enthalpy (a.u.) =	0.807091
Thermal correction to Gibbs Free Energy (a.u.) =	0.673201
Total Entropy (cal/Kmol) =	281.795
E(RPBE1PBE) (a.u.) =	-4885.58546240

Optimised cartesian coordinates (Angstrom):

Fe	-3.656312	-1.753915	-0.986328
Mn	0.455721	0.124022	0.763410
P	-1.603952	0.921942	0.247973
O	0.782642	1.533576	3.326251
O	-0.643785	-2.138719	2.287755
N	0.592193	-0.872832	-1.088857
N	1.423939	1.550491	-0.352419
C	-2.425043	-0.113564	-1.037507
C	-1.802720	-1.250511	-1.720780
C	-2.689043	-1.640593	-2.794107
H	-2.528020	-2.473440	-3.489806
C	-3.842346	-0.783595	-2.780676
H	-4.703601	-0.852328	-3.458603
C	-3.689378	0.150928	-1.701259
H	-4.406035	0.935537	-1.428011
C	-3.645127	-2.662130	0.864378
H	-2.883335	-2.513480	1.639909
C	-3.596774	-3.649952	-0.180917
H	-2.799383	-4.389668	-0.333934
C	-4.765389	-3.483858	-1.006594
H	-5.012283	-4.069927	-1.902000
C	-5.538177	-2.392941	-0.468934
H	-6.477158	-2.002601	-0.883872
C	-4.844808	-1.882958	0.685654
H	-5.160773	-1.035954	1.308516
C	-1.619355	2.624492	-0.511163
C	-1.318118	3.718011	0.337160
H	-1.141774	3.545379	1.411755
C	-1.254040	5.024818	-0.172773
H	-1.029829	5.864385	0.504535

C	-1.473032	5.261222	-1.543682
H	-1.423002	6.286205	-1.944113
C	-1.754865	4.181038	-2.397112
H	-1.927209	4.354973	-3.471374
C	-1.826723	2.870518	-1.885928
H	-2.065691	2.039522	-2.567252
C	-2.910383	1.147852	1.562123
C	-2.789395	0.515872	2.818232
H	-1.907533	-0.098551	3.043674
C	-3.792725	0.662776	3.794404
H	-3.679150	0.162482	4.769318
C	-4.929512	1.446247	3.530954
H	-5.713360	1.562155	4.296268
C	-5.054292	2.091391	2.286376
H	-5.935391	2.717397	2.072766
C	-4.051139	1.947907	1.312715
H	-4.154171	2.479994	0.354250
C	-0.460250	-1.902653	-1.406117
H	-0.564139	-2.486078	-0.470061
C	0.807173	0.088755	-2.197513
H	1.409355	-0.347943	-3.023564
H	-0.183093	0.346858	-2.634262
C	1.456831	1.351950	-1.700070
C	2.008523	2.675056	0.142617
C	2.617627	3.636436	-0.670096
H	3.073907	4.524180	-0.208213
C	2.624560	3.446154	-2.062975
C	2.039316	2.281775	-2.577981
H	2.037232	2.077255	-3.658989
C	0.004401	-2.872735	-2.504725
H	-0.701278	-3.722526	-2.593903
H	0.076903	-2.385911	-3.498667
H	0.998435	-3.287812	-2.241133
C	0.635950	0.981739	2.288079
C	-0.221554	-1.230766	1.648687
H	1.496754	-1.407023	-0.949658
H	2.023516	-0.580349	0.984135
C	3.166900	-1.608202	0.810276
C	4.185422	-0.933291	1.727407
C	2.556931	-2.707115	1.716130
C	3.890141	-1.283231	3.073967
C	5.316798	-0.132914	1.461068
C	2.678127	-2.184264	3.154826
C	4.690703	-0.826818	4.132937
C	6.124218	0.312972	2.525012
H	5.592428	0.135455	0.433475
C	5.811279	-0.021311	3.856207
H	4.450187	-1.109665	5.171064
H	7.012018	0.928473	2.307938
H	6.449713	0.337477	4.679585
H	3.217548	-3.593159	1.584248
H	2.790755	-2.988320	3.911219
H	1.780848	-1.593798	3.443588
H	1.538804	-3.008234	1.414139
N	3.266776	-1.946293	-0.488151
C	4.095328	-1.376835	-1.454476
C	4.611640	-2.260848	-2.449843
C	4.415410	0.004448	-1.594322
C	5.426268	-1.800847	-3.493679
H	4.357798	-3.329624	-2.363957
C	5.223099	0.462498	-2.649347
H	4.007762	0.726857	-0.873628
C	5.743632	-0.431938	-3.602900
H	5.816691	-2.518815	-4.233786
H	5.443953	1.539868	-2.727011
H	6.379957	-0.066839	-4.424389
H	1.977994	2.798484	1.234440
H	3.086252	4.186884	-2.733393

Mn1/TSHy-re-indNPh_2
Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-347.0476
E(RB-P86) (a.u.) =	-4886.31099273
Thermal correction to Enthalpy (a.u.) =	0.807280
Thermal correction to Gibbs Free Energy (a.u.) =	0.673808
Total Entropy (cal/Kmol) =	280.915
E(RPBE1PBE) (a.u.) =	-4885.59881135

Optimised cartesian coordinates (Angstrom):

Fe	3.491001	1.602641	-0.767322
Mn	-0.652000	-0.429749	0.660437
P	1.438387	-1.166867	0.201161
O	-1.030216	-2.025656	3.101741
O	0.100272	1.785113	2.439318
N	-0.723946	0.681823	-1.142694
N	-1.596085	-1.778011	-0.564760
C	2.311078	-0.060594	-0.980600
C	1.705305	1.092822	-1.648159
C	2.651922	1.553754	-2.639987
H	2.518179	2.415824	-3.304903
C	3.823134	0.722883	-2.589328
H	4.725093	0.843904	-3.204119
C	3.622347	-0.266154	-1.568423
H	4.336890	-1.048658	-1.283129
C	3.285593	2.467859	1.091849
H	2.448585	2.305417	1.783294
C	3.347760	3.479530	0.070107
H	2.570778	4.224231	-0.149080
C	4.597110	3.329673	-0.631200
H	4.936663	3.935345	-1.482087
C	5.309358	2.225797	-0.039833
H	6.287292	1.843222	-0.361500
C	4.498546	1.691001	1.022930
H	4.747758	0.830493	1.657207
C	1.496133	-2.821237	-0.654190
C	1.157825	-3.966522	0.107358
H	0.943974	-3.865360	1.184196
C	1.101477	-5.235330	-0.492040
H	0.847453	-6.116356	0.118882
C	1.365005	-5.381241	-1.867683
H	1.319455	-6.376175	-2.338274
C	1.685684	-4.248843	-2.635735
H	1.894207	-4.351731	-3.712781
C	1.751347	-2.976951	-2.034438
H	2.021514	-2.104085	-2.648810
C	2.679652	-1.447378	1.564369
C	2.511343	-0.824961	2.819890
H	1.633524	-0.190419	3.004387
C	3.463043	-1.002408	3.841220
H	3.314219	-0.509093	4.814949
C	4.594761	-1.807618	3.623058
H	5.338321	-1.948269	4.423626
C	4.767243	-2.440528	2.378033
H	5.646101	-3.080502	2.199308
C	3.815286	-2.266047	1.358500
H	3.954923	-2.785683	0.397677
C	0.338930	1.720989	-1.383983
H	0.384994	2.282371	-0.429446
C	-0.928328	-0.216559	-2.302235
H	-1.457522	0.285167	-3.140976
H	0.072034	-0.511490	-2.691393
C	-1.661996	-1.463349	-1.889858
C	-2.185051	-2.934102	-0.156683
C	-2.836682	-3.808169	-1.032164
H	-3.287552	-4.730369	-0.637478
C	-2.904749	-3.483129	-2.397271
C	-2.313600	-2.286206	-2.824427
H	-2.342729	-1.982492	-3.881814
C	-0.061275	2.712005	-2.489889
H	0.644284	3.566127	-2.510920
H	-0.057636	2.246299	-3.496420
H	-1.070883	3.124434	-2.291376
C	-0.863408	-1.395631	2.110673
C	-0.147298	0.899641	1.685505
H	-1.628273	1.201311	-0.994808
H	-2.159597	0.253308	0.884822
C	-3.488713	1.131546	0.672574
C	-4.389907	-0.045113	0.427044
C	-3.666492	1.459543	2.178015
C	-4.845105	-0.579665	1.653775
C	-4.865500	-0.541397	-0.798483
C	-4.220454	0.162219	2.816803
C	-5.772449	-1.635165	1.661160
C	-5.791963	-1.599513	-0.788264
H	-4.530472	-0.081989	-1.741046

```
 C     -6.241075  -2.144755   0.433503
 H     -6.142527  -2.050592   2.613028
 H     -6.181713  -1.997081  -1.739101
 H     -3.412918  -4.146273  -3.113770
 H     -6.975003  -2.966872   0.427623
 H     -4.415229   2.281470   2.247631
 H     -4.938775   0.354559   3.640761
 H     -3.391939  -0.442019   3.249941
 H     -2.743792   1.812754   2.670625
 N     -3.294257   1.987961  -0.336261
 C     -2.915841   3.324460  -0.184105
 C     -3.365066   4.217951  -1.203512
 C     -2.104005   3.876499   0.849810
 C     -3.056148   5.584249  -1.174756
 H     -3.981933   3.796030  -2.013111
 C     -1.785871   5.246411   0.863355
 H     -1.685686   3.227555   1.629362
 C     -2.262375   6.113329  -0.136794
 H     -3.435174   6.244542  -1.972112
 H     -1.149544   5.640173   1.673337
 H     -2.012578   7.185845  -0.113617
 H     -2.126199  -3.156440   0.918048
---------------------------------------
Mn1/TSHy-si-AcPh
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -195.0199
 E(RB-P86) (a.u.) =                                        -4637.21506298
 Thermal correction to Enthalpy (a.u.) =                    0.705308
 Thermal correction to Gibbs Free Energy (a.u.) =           0.581015
 Total Entropy (cal/Kmol) =                                 261.597
 E(RPBE1PBE) (a.u.) =                                      -4636.52361268
Optimised cartesian coordinates (Angstrom):
 Fe    -2.883132  -1.844489  -1.145271
 Mn     1.158303   0.345235   0.404070
 P     -1.064863   0.753994   0.517189
 O      1.735039   1.067188   3.198148
 O      1.109672  -2.485437   1.201007
 N      1.018700  -0.055006  -1.660798
 N      1.673327   2.177437  -0.353395
 C     -1.994097  -0.015359  -0.873533
 C     -1.373996  -0.733819  -1.987328
 C     -2.413716  -0.998865  -2.956020
 H     -2.288313  -1.539233  -3.902525
 C     -3.656472  -0.474359  -2.459534
 H     -4.631187  -0.545946  -2.960514
 C     -3.406405   0.124854  -1.178559
 H     -4.155245   0.611327  -0.540545
 C     -2.215492  -3.238734   0.216349
 H     -1.289661  -3.165191   0.801654
 C     -2.338969  -3.830112  -1.089937
 H     -1.527806  -4.291477  -1.669254
 C     -3.708042  -3.690218  -1.515955
 H     -4.121764  -4.020132  -2.478334
 C     -4.432358  -3.014783  -0.469701
 H     -5.495398  -2.740051  -0.495432
 C     -3.510584  -2.733265   0.599857
 H     -3.744983  -2.208752   1.535116
 C     -1.505508   2.558498   0.370758
 C     -1.170666   3.403174   1.457307
 H     -0.736728   2.970140   2.373655
 C     -1.392264   4.787998   1.384041
 H     -1.135471   5.427836   2.243525
 C     -1.937112   5.357311   0.216741
 H     -2.109675   6.443720   0.158473
 C     -2.257196   4.530108  -0.873336
 H     -2.683649   4.965273  -1.791441
 C     -2.043506   3.139871  -0.798278
 H     -2.315582   2.505643  -1.656242
 C     -2.044856   0.285628   2.032823
 C     -1.548745  -0.689984   2.924060
 H     -0.571450  -1.156900   2.736928
 C     -2.296862  -1.077311   4.051225
 H     -1.893469  -1.840076   4.736179
 C     -3.549618  -0.491656   4.305483
 H     -4.133921  -0.793279   5.189356
 C     -4.048745   0.489462   3.428622
 H     -5.025268   0.960996   3.623606
```

C	-3.300418	0.878631	2.304004
H	-3.695638	1.662551	1.639140
C	0.089288	-1.139717	-2.124899
H	0.286028	-1.977911	-1.427241
C	0.895725	1.199558	-2.434083
H	1.300285	1.105981	-3.464966
H	-0.185489	1.445745	-2.537967
C	1.571960	2.328885	-1.706428
C	2.206899	3.203871	0.362303
H	2.275012	3.054191	1.449214
C	2.662654	4.388533	-0.225877
H	3.085087	5.179618	0.411072
C	2.578313	4.535449	-1.620824
C	2.025533	3.483587	-2.366393
H	1.935763	3.548845	-3.461275
C	0.436007	-1.628756	-3.541794
H	-0.132031	-2.549727	-3.780896
H	0.200764	-0.875427	-4.321105
H	1.515124	-1.875395	-3.603638
C	1.489561	0.782613	2.073621
C	1.072765	-1.346982	0.872649
H	2.000521	-0.412031	-1.826079
H	2.748288	-0.021415	0.224524
C	4.126964	-0.467603	-0.767978
C	4.525325	-1.605832	0.155244
C	4.838701	0.872029	-0.584579
C	5.153169	-1.403121	1.406471
C	4.304687	-2.930505	-0.284149
H	5.888910	0.753222	-0.934572
C	5.544680	-2.497612	2.196062
C	4.698006	-4.025067	0.501516
H	3.824073	-3.075058	-1.263699
C	5.319803	-3.812586	1.746588
H	6.030313	-2.322806	3.169559
H	4.521362	-5.051626	0.141517
H	5.629740	-4.669639	2.365730
O	3.643925	-0.744318	-1.904801
H	4.352636	1.634640	-1.221473
H	2.937253	5.449314	-2.118131
H	4.866549	1.232255	0.460792
H	5.332084	-0.382679	1.778055

Mn1/TSHy-si-AcPhNPh
Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-336.8116
E(RB-P86) (a.u.) =	-4848.21828597
Thermal correction to Enthalpy (a.u.) =	0.800325
Thermal correction to Gibbs Free Energy (a.u.) =	0.666066
Total Entropy (cal/Kmol) =	282.571
E(RPBE1PBE) (a.u.) =	-4847.50519907

Optimised cartesian coordinates (Angstrom):

Fe	-2.476037	-2.762780	-0.583425
Mn	0.446138	0.952101	0.428466
P	-1.795220	0.632562	0.331904
O	0.410932	2.512140	2.920518
O	1.076299	-1.390300	2.089645
N	0.707888	0.033733	-1.466926
N	0.435930	2.606282	-0.786296
C	-2.250656	-0.736546	-0.807298
C	-1.306057	-1.460275	-1.659474
C	-2.088065	-2.295926	-2.544082
H	-1.688637	-2.983920	-3.299224
C	-3.482180	-2.113620	-2.247473
H	-4.317188	-2.634561	-2.734821
C	-3.588139	-1.162136	-1.177705
H	-4.521876	-0.811946	-0.719639
C	-1.592402	-3.453736	1.145441
H	-0.831101	-2.921779	1.730576
C	-1.335005	-4.355047	0.053320
H	-0.345889	-4.633064	-0.334891
C	-2.602431	-4.810108	-0.458319
H	-2.749167	-5.490476	-1.307868
C	-3.644463	-4.191269	0.320698
H	-4.724705	-4.318305	0.168572
C	-3.021311	-3.351151	1.310149
H	-3.540378	-2.725985	2.048099
C	-2.744805	2.081871	-0.354409

C	-2.833629	3.245660	0.447951
H	-2.411294	3.242499	1.466339
C	-3.463423	4.403938	-0.035692
H	-3.532665	5.296085	0.607147
C	-4.001155	4.426887	-1.337087
H	-4.493832	5.335846	-1.717221
C	-3.903792	3.282829	-2.147351
H	-4.321355	3.289824	-3.166990
C	-3.280438	2.117373	-1.660516
H	-3.229717	1.225117	-2.303641
C	-2.782217	0.285438	1.875879
C	-2.144794	-0.207666	3.034645
H	-1.057844	-0.367769	3.037428
C	-2.889764	-0.505274	4.190811
H	-2.374472	-0.888551	5.085927
C	-4.282098	-0.310552	4.206442
H	-4.864463	-0.541097	5.112686
C	-4.926229	0.189466	3.059547
H	-6.015674	0.353778	3.063639
C	-4.182162	0.489560	1.905259
H	-4.699104	0.899695	1.023658
C	0.218534	-1.378353	-1.651282
H	0.597505	-1.910769	-0.756113
C	0.271809	0.944412	-2.550043
H	0.807188	0.756171	-3.505445
H	-0.807216	0.756293	-2.748719
C	0.434064	2.379908	-2.132234
C	0.508090	3.896379	-0.360855
C	0.589300	4.985433	-1.234694
H	0.646843	6.003941	-0.823456
C	0.605382	4.750480	-2.620034
C	0.528260	3.423809	-3.068355
H	0.537073	3.185296	-4.142650
C	0.835710	-2.049565	-2.889784
H	0.607479	-3.133838	-2.888968
H	0.449258	-1.624424	-3.838434
H	1.939157	-1.945863	-2.875270
C	0.407455	1.885359	1.913105
C	0.778908	-0.478037	1.390046
H	1.759236	0.003140	-1.507149
H	2.123108	1.026664	0.389926
C	3.693059	1.006176	-0.244726
C	3.670785	2.475705	-0.658236
H	0.678292	5.582877	-3.336314
N	3.692257	0.136385	-1.257347
C	4.484092	0.784525	1.039495
C	4.010056	1.175134	2.310848
C	5.807481	0.291288	0.938616
C	4.824074	1.054323	3.451299
H	2.988625	1.571546	2.405715
C	6.622929	0.174826	2.077044
C	6.132445	0.550143	3.341107
H	4.430420	1.357686	4.434889
H	7.650301	-0.210226	1.973847
H	6.769135	0.454828	4.235198
C	3.996237	-1.226181	-1.126585
C	3.682573	-2.043671	-0.004753
C	4.606477	-1.853908	-2.250284
C	3.977823	-3.417861	-0.013747
H	3.190241	-1.602444	0.871896
C	4.917645	-3.221441	-2.242986
H	4.837644	-1.227027	-3.126441
C	4.603070	-4.017185	-1.123350
H	3.715225	-4.029452	0.865384
H	5.403737	-3.673421	-3.123153
H	4.836911	-5.093570	-1.119037
H	0.510470	4.049513	0.727645
H	6.204303	0.003856	-0.047352
H	4.714664	2.779545	-0.896300
H	3.060836	2.620810	-1.569920
H	3.304112	3.136789	0.149882

Mn1/TSHy-si-AcPhNPh_2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) = -305.9456
 E(RB-P86) (a.u.) = -4848.21709086
 Thermal correction to Enthalpy (a.u.) = 0.800221

Thermal correction to Gibbs Free Energy (a.u.) = 0.665781
Total Entropy (cal/Kmol) = 282.952
E(RPBE1PBE) (a.u.) = -4847.50145954
Optimised cartesian coordinates (Angstrom):

Fe	3.163978	-1.204190	1.979213
Mn	-0.461985	0.040868	-0.980732
P	1.591940	0.857672	-0.496758
O	-0.303500	0.338774	-3.902948
O	0.352359	-2.767451	-1.309547
N	-0.938724	-0.145155	1.070899
N	-1.464778	1.798745	-0.686460
C	2.136751	0.390369	1.199034
C	1.311485	-0.336659	2.165770
C	2.014816	-0.313718	3.429041
H	1.679634	-0.784839	4.361316
C	3.253749	0.394428	3.259141
H	4.015787	0.552567	4.033998
C	3.336932	0.823554	1.891338
H	4.166131	1.387142	1.444946
C	3.215119	-2.795947	0.672493
H	2.540494	-2.939235	-0.181329
C	2.978641	-3.255266	2.015807
H	2.099701	-3.816123	2.361167
C	4.085407	-2.830705	2.834389
H	4.194964	-3.005108	3.913153
C	5.008565	-2.110496	1.994971
H	5.945253	-1.639946	2.322658
C	4.470313	-2.086256	0.659700
H	4.923596	-1.596684	-0.211951
C	1.678884	2.719195	-0.468408
C	1.566542	3.395337	-1.708032
H	1.506414	2.815694	-2.644033
C	1.538415	4.798375	-1.760049
H	1.461575	5.306765	-2.734556
C	1.604682	5.552799	-0.572543
H	1.580927	6.653363	-0.612944
C	1.699047	4.891592	0.663810
H	1.751035	5.471928	1.599029
C	1.736337	3.484482	0.717037
H	1.828029	2.985019	1.693997
C	3.063938	0.466405	-1.572322
C	3.035733	-0.650819	-2.434487
H	2.134987	-1.278310	-2.489256
C	4.154528	-0.974459	-3.224365
H	4.114312	-1.849915	-3.891948
C	5.315386	-0.183229	-3.166749
H	6.189986	-0.435394	-3.787304
C	5.349988	0.938942	-2.318126
H	6.251475	1.570747	-2.272313
C	4.231724	1.264126	-1.530814
H	4.267581	2.157386	-0.887643
C	-0.038452	-1.003698	1.919492
H	0.127231	-1.909324	1.303600
C	-1.202772	1.193240	1.646595
H	-1.856628	1.157599	2.543660
H	-0.231043	1.623675	1.976535
C	-1.795442	2.099553	0.603365
C	-1.906160	2.632307	-1.667010
C	-2.686767	3.764351	-1.410539
H	-3.012127	4.397006	-2.249486
C	-3.044159	4.061958	-0.084320
C	-2.589024	3.210640	0.933221
H	-2.841752	3.399174	1.987219
C	-0.717623	-1.454196	3.222957
H	-0.089072	-2.203594	3.743589
H	-0.893003	-0.614370	3.925974
H	-1.688363	-1.940855	2.998997
C	-0.346426	0.232476	-2.722150
C	0.060323	-1.629100	-1.153575
H	-1.862859	-0.646228	0.989826
H	-1.973822	-0.597987	-1.161198
C	-3.504763	-1.165707	-0.900698
C	-4.123216	-0.211622	-1.922576
H	-3.665943	4.938637	0.152510
N	-3.733229	-1.099801	0.416826
C	-3.161717	-2.549417	-1.423531
C	-3.228090	-3.661701	-0.552968

C	-2.849066	-2.785567	-2.783094
C	-2.988723	-4.964397	-1.020895
H	-3.486797	-3.476818	0.500340
C	-2.618581	-4.088071	-3.255402
C	-2.686775	-5.185670	-2.377067
H	-3.049154	-5.815134	-0.322690
H	-2.378968	-4.246377	-4.319285
H	-2.506710	-6.207147	-2.748796
C	-4.632717	-0.275330	1.081771
C	-4.383605	0.008046	2.461022
C	-5.879765	0.190644	0.556454
C	-5.276757	0.753882	3.241113
H	-3.469914	-0.401519	2.917491
C	-6.775881	0.926723	1.348510
H	-6.172142	-0.061607	-0.470660
C	-6.482027	1.232802	2.690160
H	-5.035478	0.950718	4.298664
H	-7.728923	1.260072	0.905101
H	-7.189223	1.813932	3.302430
H	-1.621140	2.366550	-2.694942
H	-2.767518	-1.943023	-3.485939
H	-5.121464	-0.580332	-2.244307
H	-4.242793	0.803883	-1.501099
H	-3.493687	-0.132098	-2.828121

Mn1/TSHy-si-ind

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-245.8578
E(RB-P86) (a.u.) =	-4675.30344377
Thermal correction to Enthalpy (a.u.) =	0.712351
Thermal correction to Gibbs Free Energy (a.u.) =	0.589178
Total Entropy (cal/Kmol) =	259.239
E(RPBE1PBE) (a.u.) =	-4674.61294299

Optimised cartesian coordinates (Angstrom):

Fe	-3.109463	-1.736164	-1.058360
Mn	1.087275	0.255866	0.320028
P	-1.105335	0.773625	0.523708
O	1.855422	0.939248	3.076933
O	0.911214	-2.566229	1.128373
N	0.842909	-0.124664	-1.737341
N	1.659039	2.066156	-0.455748
C	-2.124173	0.048810	-0.827744
C	-1.585677	-0.698124	-1.965306
C	-2.676196	-0.914114	-2.889094
H	-2.615700	-1.459809	-3.838969
C	-3.871114	-0.331677	-2.342264
H	-4.868270	-0.357400	-2.801811
C	-3.539923	0.255064	-1.073901
H	-4.237846	0.776036	-0.406176
C	-2.463089	-3.151651	0.291745
H	-1.518831	-3.115623	0.850281
C	-2.648599	-3.743142	-1.007083
H	-1.874661	-4.241616	-1.606229
C	-4.021987	-3.546705	-1.395232
H	-4.476539	-3.862984	-2.343667
C	-4.686894	-2.836007	-0.332942
H	-5.737494	-2.515967	-0.330516
C	-3.723891	-2.589270	0.708615
H	-3.908925	-2.050374	1.646854
C	-1.464373	2.597366	0.391259
C	-1.045320	3.425362	1.461246
H	-0.593914	2.972913	2.359616
C	-1.205928	4.818940	1.395141
H	-0.883827	5.446012	2.241928
C	-1.773150	5.413045	0.251108
H	-1.897992	6.506241	0.198444
C	-2.177118	4.601786	-0.822922
H	-2.621940	5.056288	-1.722740
C	-2.024489	3.203172	-0.754714
H	-2.362220	2.582515	-1.599154
C	-2.046710	0.353693	2.077380
C	-1.562900	-0.642201	2.952682
H	-0.615778	-1.153742	2.730661
C	-2.285033	-0.992895	4.108416
H	-1.891621	-1.772364	4.780222
C	-3.498974	-0.349612	4.407545
H	-4.062902	-0.622561	5.313684

```
 C     -3.984836   0.652374   3.546960
 H     -4.930361   1.169063   3.777092
 C     -3.262395   1.004786   2.393690
 H     -3.645906   1.805429   1.742013
 C     -0.148520  -1.167267  -2.165100
 H      0.040330  -2.016708  -1.478781
 C      0.741734   1.137641  -2.500456
 H      1.090854   1.029688  -3.549960
 H     -0.329402   1.438547  -2.550539
 C      1.508690   2.226583  -1.802965
 C      2.268094   3.065563   0.238809
 H      2.370617   2.911561   1.322444
 C      2.755084   4.228966  -0.366731
 H      3.238892   4.998103   0.253165
 C      2.621302   4.382602  -1.757188
 C      1.988750   3.360593  -2.479874
 H      1.856164   3.433238  -3.569910
 C      0.119243  -1.665831  -3.595751
 H     -0.496798  -2.560888  -3.813423
 H     -0.113863  -0.900682  -4.364109
 H      1.183579  -1.958494  -3.700487
 C      1.525897   0.669695   1.970021
 C      0.925945  -1.428343   0.796127
 H      1.806877  -0.510369  -1.948081
 H      2.654951  -0.198344   0.056717
 C      3.933481  -0.654008  -0.950660
 C      4.317420  -1.829752  -0.091097
 C      4.848092   0.502272  -0.476976
 C      5.134665  -1.397354   0.977066
 C      4.021627  -3.188619  -0.285944
 C      5.292249   0.113121   0.950036
 H      5.721042   0.498298  -1.169913
 C      5.663008  -2.337872   1.876660
 C      4.554742  -4.128373   0.614231
 H      3.392437  -3.500420  -1.135037
 H      6.321683   0.442140   1.201770
 C      5.367604  -3.703692   1.687974
 H      6.306511  -2.019438   2.713398
 H      4.344728  -5.201891   0.481064
 H      5.782727  -4.451185   2.383325
 O      3.448360  -0.745655  -2.113663
 H      4.368617   1.495791  -0.559372
 H      4.614802   0.569610   1.707264
 H      3.002552   5.279740  -2.268172
---------------------------------------
Mn1/TSHy-si-indNPh
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -311.0848
 E(RB-P86) (a.u.) =                                        -4886.30095071
 Thermal correction to Enthalpy (a.u.) =                    0.807397
 Thermal correction to Gibbs Free Energy (a.u.) =           0.672922
 Total Entropy (cal/Kmol) =                                 283.028
 E(RPBE1PBE) (a.u.) =                                      -4885.58513249
Optimised cartesian coordinates (Angstrom):
 Fe    -2.936358  -2.482927  -0.597634
 Mn     0.445728   0.816322   0.450436
 P     -1.817039   0.787472   0.324698
 O      0.626244   2.390755   2.929052
 O      0.755255  -1.574373   2.129899
 N      0.619012  -0.158927  -1.426313
 N      0.658337   2.441508  -0.787537
 C     -2.431115  -0.509512  -0.827104
 C     -1.576680  -1.362846  -1.654732
 C     -2.445761  -2.091532  -2.552213
 H     -2.127501  -2.833687  -3.294613
 C     -3.807808  -1.717360  -2.288526
 H     -4.695611  -2.122756  -2.792079
 C     -3.805615  -0.750815  -1.227043
 H     -4.692825  -0.270922  -0.794908
 C     -2.188368  -3.265001   1.155224
 H     -1.374045  -2.831437   1.750102
 C     -2.033806  -4.206380   0.077455
 H     -1.083975  -4.620274  -0.287108
 C     -3.340918  -4.493088  -0.455927
 H     -3.561562  -5.158318  -1.301469
 C     -4.304790  -3.730064   0.295332
 H     -5.389177  -3.712426   0.122153
```

C	-3.593368	-2.969129	1.289318
H	-4.037854	-2.271101	2.010586
C	-2.567591	2.347213	-0.364854
C	-2.545226	3.503628	0.452583
H	-2.161682	3.437908	1.484154
C	-3.016326	4.734394	-0.032871
H	-3.001461	5.620707	0.621525
C	-3.503004	4.836569	-1.350435
H	-3.871673	5.802009	-1.731834
C	-3.514072	3.698741	-2.175272
H	-3.893130	3.767534	-3.207596
C	-3.049721	2.461827	-1.687167
H	-3.082801	1.577428	-2.342270
C	-2.857485	0.567013	1.857054
C	-2.291598	0.030333	3.033271
H	-1.226449	-0.238208	3.057417
C	-3.080482	-0.170951	4.181248
H	-2.620649	-0.590393	5.090261
C	-4.445481	0.165233	4.171030
H	-5.062102	0.009549	5.070547
C	-5.017396	0.711403	3.006796
H	-6.083962	0.987261	2.990851
C	-4.229041	0.915313	1.861133
H	-4.687504	1.363769	0.966002
C	-0.056702	-1.491588	-1.608091
H	0.219179	-2.058898	-0.697093
C	0.345803	0.783602	-2.535200
H	0.887873	0.511561	-3.466447
H	-0.740285	0.733083	-2.775024
C	0.674042	2.194237	-2.129111
C	0.859043	3.723671	-0.377107
C	1.092332	4.781698	-1.261814
H	1.247572	5.794769	-0.862565
C	1.133617	4.521091	-2.641952
C	0.921843	3.203974	-3.074620
H	0.940396	2.947889	-4.144703
C	0.497100	-2.259948	-2.820248
H	0.126076	-3.304014	-2.813640
H	0.197837	-1.801591	-3.784765
H	1.603978	-2.302640	-2.775643
C	0.535321	1.763454	1.927627
C	0.580490	-0.629626	1.428252
H	1.658060	-0.342264	-1.441409
H	2.105455	0.689295	0.440319
C	3.636691	0.436109	-0.203886
C	3.909158	1.881825	-0.669968
C	5.366976	2.132832	-0.206476
H	1.326638	5.326830	-3.366392
N	3.536323	-0.486892	-1.161960
C	4.443328	0.301953	1.073833
C	4.338583	-0.576736	2.168709
C	5.475155	1.275670	1.040656
C	5.285264	-0.494136	3.208594
H	3.511439	-1.295359	2.240029
C	6.422761	1.347505	2.074192
C	6.325797	0.453993	3.158901
H	5.201723	-1.170554	4.074269
H	7.225386	2.102706	2.044332
H	7.056679	0.508956	3.981755
H	3.756979	1.982148	-1.761254
H	3.240633	2.592545	-0.146302
H	6.092333	1.781988	-0.975409
H	5.588119	3.203246	-0.015691
C	3.773411	-1.860957	-1.009775
C	3.174352	-2.709745	-0.039491
C	4.614999	-2.469802	-1.985239
C	3.426990	-4.094100	-0.038425
H	2.480502	-2.291265	0.700724
C	4.878167	-3.846723	-1.965723
H	5.064221	-1.821689	-2.754547
C	4.284591	-4.672908	-0.990213
H	2.942504	-4.726934	0.723354
H	5.548555	-4.282032	-2.724907
H	4.482511	-5.756355	-0.979427
H	0.838840	3.895041	0.708537

Mn1/TSHy-si-indNPh_2

Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-371.0482
E(RB-P86) (a.u.) =	-4886.30856450
Thermal correction to Enthalpy (a.u.) =	0.807124
Thermal correction to Gibbs Free Energy (a.u.) =	0.672751
Total Entropy (cal/Kmol) =	282.812
E(RPBE1PBE) (a.u.) =	-4885.59518065

Optimised cartesian coordinates (Angstrom):

Fe	-3.305428	-0.993147	-1.952638
Mn	0.494096	-0.056264	0.904783
P	-1.553135	0.851070	0.574444
O	0.450621	0.066473	3.843329
O	-0.421180	-2.845409	1.106356
N	0.864251	-0.103324	-1.177719
N	1.523134	1.699338	0.676653
C	-2.192641	0.515626	-1.119534
C	-1.437901	-0.164263	-2.173685
C	-2.201434	-0.035661	-3.394764
H	-1.926103	-0.450164	-4.372462
C	-3.408771	0.691932	-3.114611
H	-4.202810	0.923566	-3.837108
C	-3.411948	1.027404	-1.718358
H	-4.200411	1.581411	-1.193249
C	-3.338872	-2.677264	-0.765373
H	-2.625319	-2.905503	0.036843
C	-3.191189	-3.040419	-2.150151
H	-2.351641	-3.599158	-2.585287
C	-4.325826	-2.522786	-2.871199
H	-4.499587	-2.611754	-3.951967
C	-5.177419	-1.841322	-1.929905
H	-6.114177	-1.319949	-2.168411
C	-4.566905	-1.933905	-0.629211
H	-4.955144	-1.498661	0.300718
C	-1.586813	2.712078	0.673898
C	-1.410600	3.301158	1.949988
H	-1.332718	2.659858	2.843430
C	-1.343500	4.696554	2.093125
H	-1.217380	5.136735	3.095297
C	-1.433996	5.529877	0.961361
H	-1.380048	6.624424	1.073174
C	-1.592130	4.955135	-0.311202
H	-1.663961	5.597686	-1.203435
C	-1.668154	3.556033	-0.455434
H	-1.809555	3.125236	-1.458773
C	-2.986166	0.429801	1.691498
C	-2.955275	-0.742258	2.477301
H	-2.074016	-1.398023	2.449291
C	-4.047923	-1.085748	3.294979
H	-4.005571	-2.004161	3.901958
C	-5.185287	-0.260478	3.341435
H	-6.039416	-0.528497	3.983490
C	-5.222229	0.915532	2.569282
H	-6.105071	1.573749	2.605024
C	-4.129812	1.260562	1.754691
H	-4.166282	2.194849	1.172892
C	-0.094290	-0.875434	-2.043092
H	-0.251961	-1.823405	-1.491731
C	1.146681	1.260006	-1.682611
H	1.794048	1.253256	-2.586218
H	0.182489	1.728795	-1.982049
C	1.772190	2.100575	-0.603304
C	2.020807	2.458637	1.690574
C	2.770048	3.619638	1.475766
H	3.144262	4.188631	2.339580
C	3.029537	4.030226	0.156774
C	2.521636	3.252765	-0.893113
H	2.703145	3.527274	-1.942901
C	0.515201	-1.233383	-3.408662
H	-0.143760	-1.940609	-3.950382
H	0.662866	-0.344621	-4.055435
H	1.494142	-1.734486	-3.268001
C	0.451404	0.028851	2.656877
C	-0.086349	-1.713191	0.999107
H	1.782257	-0.628530	-1.185823
H	2.009173	-0.755992	0.972641
C	3.422426	-1.392806	0.508321
C	4.183811	-0.886490	1.757652

```
 C      3.699894  -1.784600   2.920781
 H      3.618880   4.936642  -0.049092
 N      3.594932  -1.088320  -0.783446
 C      3.045158  -2.807569   0.848057
 C      2.633909  -3.836313  -0.015396
 C      3.237926  -3.048707   2.227192
 C      2.405032  -5.117685   0.517182
 H      2.514076  -3.633120  -1.090985
 C      3.005963  -4.328391   2.757577
 C      2.587354  -5.361711   1.895060
 H      2.089536  -5.939874  -0.145337
 H      3.160019  -4.528424   3.830785
 H      2.411141  -6.372047   2.298458
 H      5.269881  -1.055801   1.577507
 H      4.040367   0.193449   1.951889
 H      4.484953  -1.968781   3.683137
 H      2.844680  -1.306148   3.448952
 C      4.411425  -0.095261  -1.318528
 C      4.416932  -0.006687  -2.747068
 C      5.287748   0.797795  -0.624867
 C      5.231085   0.900698  -3.435815
 H      3.764506  -0.699780  -3.301329
 C      6.109772   1.697564  -1.324029
 H      5.331519   0.799188   0.469671
 C      6.092405   1.764368  -2.729143
 H      5.201473   0.928641  -4.537544
 H      6.774532   2.365985  -0.751926
 H      6.739920   2.475697  -3.265568
 H      1.803582   2.109481   2.710189
---------------------------------------
Mn1/TSHy_6-re-indNPOPh2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -220.8149
 E(RB-P86) (a.u.) =                                        -5534.28929411
 Thermal correction to Enthalpy (a.u.) =                    0.909702
 Thermal correction to Gibbs Free Energy (a.u.) =           0.755631
 Total Entropy (cal/Kmol) =                                 324.270
 E(RPBE1PBE) (a.u.) =                                      -5533.56181283
Optimised cartesian coordinates (Angstrom):
 Fe    -2.899725  -3.106971  -0.499346
 Mn    -0.565873   0.956570   0.619549
 P     -2.710356   0.396733   0.174152
 O     -1.211927   2.665900   2.920965
 O      0.030435  -1.148028   2.583389
 N      0.125968  -0.075726  -1.104326
 N     -0.470037   2.508841  -0.713004
 C     -2.832944  -1.095191  -0.889380
 C     -1.693465  -1.777096  -1.503880
 C     -2.235356  -2.766743  -2.410275
 H     -1.652331  -3.467981  -3.019580
 C     -3.670379  -2.716184  -2.357519
 H     -4.358266  -3.365543  -2.915492
 C     -4.043578  -1.695078  -1.420388
 H     -5.069487  -1.411140  -1.153396
 C     -2.273357  -3.534554   1.416497
 H     -1.692551  -2.863307   2.061869
 C     -1.724721  -4.483390   0.483952
 H     -0.656851  -4.664150   0.301431
 C     -2.820801  -5.136012  -0.185455
 H     -2.735593  -5.898100  -0.971715
 C     -4.048532  -4.591134   0.336266
 H     -5.062777  -4.866378   0.017144
 C     -3.710963  -3.599423   1.324350
 H     -4.420188  -2.985962   1.894866
 C     -3.645417   1.680719  -0.800047
 C     -3.989630   2.886589  -0.141676
 H     -3.769627   3.006907   0.931904
 C     -4.619536   3.930192  -0.839311
 H     -4.889953   4.856578  -0.307591
 C     -4.901854   3.795240  -2.212377
 H     -5.394651   4.614227  -2.759996
 C     -4.549748   2.609044  -2.878924
 H     -4.766594   2.492812  -3.952994
 C     -3.926113   1.558114  -2.178747
 H     -3.673613   0.629144  -2.713249
 C     -3.919479   0.068340   1.555896
 C     -3.452205  -0.271944   2.843713
```

H	-2.372159	-0.320086	3.040621
C	-4.357609	-0.558400	3.882122
H	-3.974150	-0.821603	4.880826
C	-5.743237	-0.505275	3.649270
H	-6.451610	-0.727397	4.463200
C	-6.219744	-0.157650	2.371659
H	-7.303532	-0.104800	2.180408
C	-5.315563	0.131607	1.334781
H	-5.705197	0.421985	0.346580
C	-0.203102	-1.535988	-1.274901
H	0.115267	-1.986948	-0.314560
C	-0.138231	0.720950	-2.323476
H	0.597894	0.521162	-3.131338
H	-1.133305	0.416356	-2.720077
C	-0.187182	2.190861	-2.008837
C	-0.606433	3.825064	-0.398419
C	-0.476498	4.851912	-1.339057
H	-0.604508	5.896146	-1.018482
C	-0.178699	4.524187	-2.672102
C	-0.025306	3.170449	-3.003378
H	0.209009	2.859538	-4.032792
C	0.644522	-2.188904	-2.379702
H	0.544390	-3.291310	-2.332748
H	0.342822	-1.865411	-3.396764
H	1.716402	-1.957812	-2.230206
C	-0.966941	1.977807	1.985154
C	-0.250886	-0.351493	1.751525
H	1.152803	-0.030317	-0.909719
H	1.027805	1.247335	0.881570
C	2.790029	1.206699	0.758172
C	2.852223	2.669315	0.475915
C	2.937977	1.070647	2.283035
C	2.782137	3.396262	1.689090
C	3.058563	3.320306	-0.753398
C	2.566073	2.457131	2.857387
C	2.919151	4.793755	1.676469
C	3.194568	4.719243	-0.760203
H	3.127952	2.734132	-1.682798
C	3.126647	5.449627	0.446160
H	2.877744	5.371414	2.614318
H	3.366781	5.250249	-1.709856
H	-0.064156	5.306940	-3.437308
H	3.244899	6.545049	0.426183
H	4.012834	0.858379	2.479895
H	3.163837	2.734821	3.749850
H	1.496755	2.482571	3.163949
H	2.356781	0.225565	2.697360
N	3.101365	0.317510	-0.183011
H	-0.826423	4.052458	0.654141
P	3.569877	-1.284413	0.074227
O	2.508336	-2.314461	0.471146
C	4.344523	-1.714930	-1.538498
C	4.796975	-0.745022	-2.459173
C	4.501482	-3.087025	-1.839939
C	5.405482	-1.144266	-3.663362
H	4.654739	0.321597	-2.227019
C	5.111081	-3.482707	-3.042452
H	4.129399	-3.841603	-1.128493
C	5.565352	-2.511416	-3.955151
H	5.754025	-0.382932	-4.379638
H	5.228428	-4.553902	-3.272102
H	6.042053	-2.821995	-4.898669
C	4.975616	-1.323117	1.273452
C	4.868271	-2.179040	2.390009
C	6.141593	-0.543625	1.100577
C	5.913809	-2.252135	3.327962
H	3.954570	-2.782978	2.508848
C	7.184275	-0.617692	2.040269
H	6.238838	0.124279	0.229175
C	7.071422	-1.471583	3.154783
H	5.824700	-2.922523	4.197911
H	8.091370	-0.007830	1.901958
H	7.890862	-1.529337	3.888944

Mn1/TSHy_6-si-indNPOPh2
Frequencies, energies and thermodynamic properties:
Lowest Vibrational Mode (1/cm) = -233.7156

```
 E(RB-P86) (a.u.) =                                      -5534.28941800
 Thermal correction to Enthalpy (a.u.) =                  0.909579
 Thermal correction to Gibbs Free Energy (a.u.) =         0.755912
 Total Entropy (cal/Kmol) =                               323.420
 E(RPBE1PBE) (a.u.) =                                    -5533.56004615
Optimised cartesian coordinates (Angstrom):
 Fe    -3.574151  -2.713998   0.038302
 Mn    -0.522801   1.046586   0.419427
 P     -2.656557   0.728217  -0.265141
 O     -1.037108   3.551207   1.872118
 O     -0.707344  -0.426194   2.959509
 N      0.163819  -0.636548  -0.661365
 N      0.067930   1.960603  -1.316732
 C     -2.944756  -0.986439  -0.866763
 C     -1.912838  -2.021286  -0.948508
 C     -2.491733  -3.144571  -1.652036
 H     -1.991062  -4.096484  -1.867377
 C     -3.852400  -2.830706  -1.990728
 H     -4.557610  -3.497345  -2.504895
 C     -4.137778  -1.509510  -1.506812
 H     -5.094428  -0.981726  -1.609171
 C     -3.410209  -2.605857   2.087921
 H     -2.783546  -1.892829   2.639496
 C     -2.996133  -3.901924   1.618192
 H     -2.003695  -4.351979   1.755447
 C     -4.103707  -4.497039   0.915133
 H     -4.101526  -5.476193   0.417731
 C     -5.204955  -3.569146   0.953716
 H     -6.189612  -3.717769   0.490526
 C     -4.776884  -2.399641   1.676161
 H     -5.376042  -1.499107   1.862771
 C     -3.138123   1.769765  -1.732150
 C     -3.371020   3.150259  -1.519154
 H     -3.345338   3.558987  -0.495681
 C     -3.644808   4.006469  -2.598498
 H     -3.834880   5.075635  -2.411901
 C     -3.673571   3.502294  -3.912927
 H     -3.887553   4.173619  -4.759688
 C     -3.425599   2.137026  -4.136839
 H     -3.444656   1.732208  -5.161473
 C     -3.159220   1.275842  -3.054997
 H     -2.982234   0.206397  -3.248133
 C     -4.092579   1.062215   0.876975
 C     -3.891092   1.120686   2.272567
 H     -2.880654   0.994306   2.685868
 C     -4.974571   1.333600   3.145153
 H     -4.797777   1.376422   4.231701
 C     -6.274302   1.495390   2.634238
 H     -7.121987   1.664218   3.317269
 C     -6.484661   1.449646   1.243311
 H     -7.497879   1.584259   0.831967
 C     -5.402253   1.239650   0.371499
 H     -5.581381   1.227413  -0.714924
 C     -0.491543  -1.967471  -0.397857
 H     -0.541428  -2.027982   0.707219
 C      0.308861  -0.331139  -2.105869
 H      1.169918  -0.866245  -2.556063
 H     -0.618709  -0.664310  -2.622814
 C      0.479765   1.145890  -2.328731
 C      0.143603   3.306287  -1.509322
 C      0.629357   3.881166  -2.687505
 H      0.663813   4.976678  -2.780231
 C      1.068221   3.040526  -3.725562
 C      0.992471   1.654852  -3.534605
 H      1.331602   0.953393  -4.310625
 C      0.367604  -3.142229  -0.890155
 H     -0.048294  -4.101697  -0.523626
 H      0.417799  -3.194419  -1.996707
 H      1.400039  -3.056252  -0.496448
 C     -0.849637   2.541392   1.278496
 C     -0.675278   0.152616   1.924819
 H      1.121291  -0.697277  -0.248861
 H      1.056295   1.176586   0.860483
 C      2.783124   0.887409   1.107510
 C      3.182081   2.243286   0.504633
 C      2.761292   3.301316   1.549473
 H      1.464922   3.458382  -4.663456
```

N	3.062413	-0.324905	0.628212
C	2.616127	1.123745	2.570388
C	2.514400	0.182377	3.609532
C	2.659808	2.512874	2.838796
C	2.452454	0.646896	4.934410
H	2.489007	-0.893627	3.378706
C	2.597757	2.971766	4.164325
C	2.493219	2.031420	5.208975
H	2.377472	-0.071690	5.766199
H	2.636901	4.050173	4.388844
H	2.449416	2.380115	6.253407
H	4.291214	2.229304	0.399490
H	2.766460	2.396607	-0.508975
H	3.467750	4.154008	1.618620
H	1.764433	3.728090	1.299706
H	-0.203232	3.936277	-0.678058
P	3.950715	-0.615068	-0.776314
O	3.435624	-0.143074	-2.141496
C	5.650579	0.050364	-0.479167
C	6.348841	-0.161140	0.731097
C	6.262372	0.784853	-1.517533
C	7.644925	0.357029	0.896224
H	5.878894	-0.728848	1.549996
C	7.559840	1.301381	-1.349384
H	5.703231	0.946252	-2.452917
C	8.252124	1.087697	-0.143478
H	8.185025	0.190554	1.841986
H	8.032001	1.874562	-2.163456
H	9.268488	1.491937	-0.011561
C	4.152281	-2.441825	-0.748078
C	4.112984	-3.203309	0.440993
C	4.385545	-3.089459	-1.981829
C	4.311133	-4.594974	0.394036
H	3.909533	-2.699712	1.398266
C	4.583432	-4.480400	-2.025255
H	4.398545	-2.492179	-2.907400
C	4.548261	-5.234427	-0.837208
H	4.275510	-5.184753	1.324018
H	4.761604	-4.979594	-2.991187
H	4.702565	-6.324791	-0.871393

Mn1/TSHy_8-re-indNPOPh2
Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-352.8927
E(RB-P86) (a.u.) =	-5534.29443392
Thermal correction to Enthalpy (a.u.) =	0.909405
Thermal correction to Gibbs Free Energy (a.u.) =	0.755780
Total Entropy (cal/Kmol) =	323.332
E(RPBE1PBE) (a.u.) =	-5533.56324461

Optimised cartesian coordinates (Angstrom):

Fe	3.930323	-2.652895	-0.032019
Mn	0.412534	0.708217	-0.462899
P	2.562577	0.637071	0.237547
O	0.832693	3.239170	-1.898833
O	0.746885	-0.794937	-2.970135
N	-0.056447	-1.071349	0.636370
N	-0.343660	1.533479	1.243851
C	3.082706	-1.011583	0.857014
C	2.194806	-2.168685	0.956626
C	2.918621	-3.198522	1.669036
H	2.546861	-4.204882	1.897509
C	4.228712	-2.706297	1.996062
H	5.016976	-3.269105	2.513829
C	4.337869	-1.365230	1.494595
H	5.217730	-0.715403	1.583995
C	3.750334	-2.591516	-2.082651
H	3.038824	-1.970054	-2.642011
C	3.501988	-3.922972	-1.595726
H	2.573339	-4.495118	-1.724803
C	4.676292	-4.365947	-0.888409
H	4.797273	-5.331348	-0.378958
C	5.652979	-3.308171	-0.941913
H	6.649276	-3.326783	-0.480114
C	5.080981	-2.210540	-1.677505
H	5.562753	-1.244884	-1.878093
C	2.889523	1.751489	1.694043
C	2.909200	3.149770	1.470398

H	2.814979	3.542588	0.444864
C	3.056398	4.045432	2.542475
H	3.080144	5.129658	2.347681
C	3.170793	3.561327	3.859744
H	3.285555	4.263669	4.700586
C	3.136273	2.175809	4.094025
H	3.224840	1.786033	5.120856
C	2.996236	1.276247	3.019739
H	2.986150	0.193762	3.220778
C	3.944236	1.148102	-0.906636
C	3.749029	1.143245	-2.304454
H	2.770263	0.865211	-2.719992
C	4.798841	1.487605	-3.175985
H	4.627715	1.478626	-4.264252
C	6.057728	1.845474	-2.662219
H	6.878666	2.117256	-3.344714
C	6.260141	1.863120	-1.269579
H	7.240275	2.150198	-0.856210
C	5.210718	1.521940	-0.398727
H	5.379971	1.559899	0.688774
C	0.778129	-2.305386	0.409515
H	0.836677	-2.385706	-0.694264
C	-0.242341	-0.752630	2.067789
H	-0.956679	-1.445177	2.563242
H	0.735209	-0.875840	2.587980
C	-0.687229	0.673989	2.247249
C	-0.625054	2.853262	1.411182
H	-0.333465	3.519360	0.587467
C	-1.252072	3.360147	2.555171
H	-1.447517	4.440013	2.629675
C	-1.625248	2.473411	3.578350
C	-1.337636	1.110392	3.413573
H	-1.604526	0.375740	4.187934
C	0.080675	-3.575952	0.928094
H	0.605832	-4.478836	0.557523
H	0.068839	-3.625045	2.036475
H	-0.963920	-3.601324	0.562443
C	0.662418	2.223928	-1.311669
C	0.659832	-0.192808	-1.950339
H	-1.008641	-1.325853	0.267481
H	-1.194109	0.778548	-0.948280
H	-2.129123	2.835574	4.487417
C	-2.829198	0.939916	-1.300893
C	-2.788674	2.397581	-1.628598
C	-2.695470	0.214836	-2.659303
N	-3.509815	0.520734	-0.231110
C	-2.398775	2.582525	-2.975129
C	-3.148009	3.488696	-0.817630
P	-3.814875	-1.095318	0.053314
C	-2.358776	3.875577	-3.521437
C	-3.104670	4.781856	-1.367934
H	-3.471001	3.318688	0.220900
O	-2.625547	-2.077920	-0.026863
C	-4.569983	-1.101815	1.724792
C	-5.154548	-1.668483	-1.079600
C	-2.711110	4.972515	-2.710423
H	-2.064163	4.033420	-4.571828
H	-3.388895	5.651578	-0.754019
C	-5.131203	0.057892	2.302583
C	-4.593215	-2.319626	2.441698
C	-6.330550	-0.909683	-1.277206
C	-4.989370	-2.890519	-1.765738
H	-2.688216	5.990899	-3.131010
C	-5.719353	-0.004789	3.578818
H	-5.089316	1.007243	1.747324
C	-5.180672	-2.377886	3.717138
H	-4.141535	-3.221216	1.997828
C	-7.329052	-1.372751	-2.151086
H	-6.466133	0.048499	-0.749944
C	-5.991322	-3.351427	-2.638874
H	-4.065461	-3.469423	-1.609267
C	-5.746749	-1.221121	4.285981
H	-6.155207	0.903096	4.025771
H	-5.194453	-3.329679	4.271884
C	-7.161141	-2.594230	-2.831912
H	-8.243484	-0.777322	-2.303174
H	-5.857199	-4.306284	-3.172168

```
 H     -6.207567  -1.267701   5.285649
 H     -7.945596  -2.955468  -3.515960
 C     -2.079693   1.252555  -3.625094
 H     -0.978106   1.120364  -3.698385
 H     -2.478443   1.173481  -4.657836
 H     -2.138263  -0.737328  -2.589454
 H     -3.733239  -0.031028  -2.980323
---------------------------------------
Mn1/TSHy_8-si-indNPOPh2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -427.9492
 E(RB-P86) (a.u.) =                                        -5534.29118691
 Thermal correction to Enthalpy (a.u.) =                    0.909063
 Thermal correction to Gibbs Free Energy (a.u.) =           0.754152
 Total Entropy (cal/Kmol) =                                 326.037
 E(RPBE1PBE) (a.u.) =                                      -5533.55872103
Optimised cartesian coordinates (Angstrom):
 Fe     3.283085   2.886192  -0.341291
 Mn     0.390004  -0.966313   0.266534
 P      2.595607  -0.611704  -0.093163
 O      0.893254  -3.041177   2.288056
 O      0.004867   1.041712   2.380696
 N     -0.120380   0.380799  -1.315951
 N      0.158863  -2.287741  -1.286425
 C      2.940187   0.964736  -0.970981
 C      1.910115   1.867046  -1.484422
 C      2.584656   2.875789  -2.271261
 H      2.104421   3.718930  -2.782876
 C      3.998871   2.621477  -2.243399
 H      4.772500   3.232509  -2.727457
 C      4.224371   1.452284  -1.440964
 H      5.200685   1.000300  -1.224310
 C      2.698623   3.168516   1.613597
 H      2.013952   2.518278   2.173102
 C      2.313851   4.295830   0.805881
 H      1.288899   4.658331   0.649558
 C      3.505958   4.851402   0.218115
 H      3.548626   5.707186  -0.468924
 C      4.629212   4.068075   0.666044
 H      5.678194   4.223309   0.380086
 C      4.131005   3.026594   1.526497
 H      4.731227   2.248268   2.015136
 C      3.393776  -1.887002  -1.191696
 C      3.583364  -3.187703  -0.664221
 H      3.331180  -3.393928   0.388926
 C      4.100083  -4.218486  -1.466311
 H      4.250958  -5.221280  -1.035432
 C      4.421697  -3.973052  -2.815092
 H      4.826247  -4.781537  -3.444487
 C      4.221917  -2.689811  -3.352689
 H      4.470592  -2.486750  -4.406754
 C      3.711439  -1.653144  -2.547744
 H      3.577700  -0.649936  -2.981456
 C      3.790959  -0.600666   1.339328
 C      3.330524  -0.367345   2.652981
 H      2.257874  -0.219607   2.840946
 C      4.233801  -0.316939   3.730856
 H      3.855409  -0.134602   4.749306
 C      5.610110  -0.502480   3.511576
 H      6.316553  -0.465210   4.356056
 C      6.078783  -0.745292   2.207029
 H      7.154286  -0.900513   2.024984
 C      5.176344  -0.798740   1.130595
 H      5.557465  -1.009415   0.119162
 C      0.403268   1.791880  -1.259634
 H      0.186174   2.115141  -0.221888
 C      0.097845  -0.263671  -2.628599
 H     -0.571576   0.148157  -3.413671
 H      1.142679  -0.060305  -2.957181
 C     -0.072576  -1.753575  -2.522144
 C      0.154734  -3.643836  -1.172687
 H      0.380212  -4.046921  -0.175137
 C     -0.114686  -4.501362  -2.244867
 H     -0.104885  -5.589097  -2.081815
 C     -0.399264  -3.949142  -3.504951
 C     -0.371597  -2.553002  -3.638406
 H     -0.570625  -2.070501  -4.607179
```

```
 C     -0.367432   2.728114  -2.208297
 H     -0.138988   3.786727  -1.973251
 H     -0.105054   2.554425  -3.272209
 H     -1.456127   2.565489  -2.085067
 C      0.692935  -2.202256   1.475356
 C      0.208739   0.251058   1.521962
 H     -1.166078   0.470315  -1.232911
 H     -1.267978  -1.112165   0.617132
 H     -0.630387  -4.592326  -4.367637
 C     -2.849344  -1.119829   1.058681
 N     -3.285170   0.144092   1.001163
 C     -2.649677  -1.761580   2.397866
 C     -3.264481  -2.270460   0.110854
 P     -3.799603   0.857378  -0.412129
 C     -2.695485  -3.168363   2.276533
 C     -2.506252  -1.144468   3.652718
 O     -2.910395   0.686299  -1.666558
 C     -2.599178  -3.975942   3.422149
 C     -2.403261  -1.955473   4.796585
 H     -2.482624  -0.046758   3.727401
 C     -2.451215  -3.361975   4.681324
 H     -2.643368  -5.074460   3.341209
 H     -2.293666  -1.493140   5.790775
 H     -2.377541  -3.985407   5.587098
 C     -2.848033  -3.576134   0.825513
 H     -3.580870  -4.398096   0.685739
 H     -1.877143  -3.952412   0.437374
 H     -2.858707  -2.152822  -0.911272
 H     -4.373640  -2.220432   0.028610
 C     -3.987937   2.626732   0.041746
 C     -3.619862   3.114148   1.314119
 C     -4.471222   3.528220  -0.935175
 C     -3.738612   4.485295   1.606817
 H     -3.236876   2.403195   2.061567
 C     -4.591831   4.895934  -0.638535
 H     -4.755945   3.158958  -1.934174
 C     -4.226023   5.376514   0.633858
 H     -3.449310   4.859140   2.602159
 H     -4.972346   5.591644  -1.403381
 H     -4.321715   6.449313   0.865861
 C     -5.506825   0.281140  -0.804487
 C     -6.515933   0.242623   0.184507
 C     -5.799401  -0.144682  -2.117627
 C     -7.803852  -0.215193  -0.141534
 H     -6.292272   0.567455   1.213651
 C     -7.090282  -0.600992  -2.440938
 H     -5.001024  -0.116210  -2.876134
 C     -8.092482  -0.636625  -1.454356
 H     -8.587509  -0.245111   0.632346
 H     -7.314293  -0.931505  -3.467961
 H     -9.103177  -0.994745  -1.707509
---------------------------------------
Mn1/indNHPh
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          32.5272
 E(RB-P86) (a.u.) =                                      -634.934670927
 Thermal correction to Enthalpy (a.u.) =                   0.268181
 Thermal correction to Gibbs Free Energy (a.u.) =          0.213422
 Total Entropy (cal/Kmol) =                                115.251
 E(RPBE1PBE) (a.u.) =                                    -634.886020135
Optimised cartesian coordinates (Angstrom):
 H     -0.408205   0.988170  -1.152331
 H      0.081937  -0.684004   1.243128
 C      0.347504  -0.442491   0.186847
 C      1.734223   0.191467   0.187493
 C      0.587015  -1.772887  -0.598490
 C      2.718030  -0.778922  -0.105274
 C      2.088121   1.523803   0.451136
 C      2.070476  -2.132344  -0.336553
 C      4.075410  -0.417450  -0.133807
 C      3.449895   1.885492   0.415553
 H      1.311592   2.273557   0.674103
 C      4.435445   0.920717   0.126023
 H      4.851032  -1.165897  -0.365379
 H      3.745605   2.928617   0.611915
 H      5.496627   1.216309   0.096187
 H      0.437931  -1.558308  -1.679100
```

```
 H      2.537449  -2.705764  -1.164207
 H      2.169752  -2.761412   0.577973
 H     -0.121107  -2.576571  -0.314498
 N     -0.678227   0.445174  -0.327892
 C     -2.042774   0.282358  -0.138809
 C     -2.952476   1.096143  -0.874479
 C     -2.587940  -0.647575   0.789925
 C     -4.335489   0.991814  -0.677652
 H     -2.552659   1.819824  -1.604454
 C     -3.977627  -0.735577   0.979804
 H     -1.924954  -1.309848   1.366056
 C     -4.867251   0.077098   0.254204
 H     -5.009717   1.637477  -1.264185
 H     -4.368340  -1.465030   1.708423
 H     -5.954722  -0.003218   0.406073
---------------------------------------
Mn1/indNPh
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          26.2219
 E(RB-P86) (a.u.) =                                     -633.725638982
 Thermal correction to Enthalpy (a.u.) =                   0.244580
 Thermal correction to Gibbs Free Energy (a.u.) =          0.189713
 Total Entropy (cal/Kmol) =                                115.479
 E(RPBE1PBE) (a.u.) =                                   -633.674525286
Optimised cartesian coordinates (Angstrom):
 C      0.320330   0.055398  -0.019371
 C      1.754214  -0.292522   0.044825
 C      0.214093   1.565987  -0.257200
 C      2.541009   0.864554  -0.160356
 C      2.345287  -1.552681   0.268058
 C      1.671111   2.086014  -0.386130
 C      3.943649   0.767293  -0.141366
 C      3.744965  -1.643120   0.287005
 H      1.707971  -2.437501   0.423182
 C      4.536828  -0.489112   0.083839
 H      4.572573   1.658184  -0.299790
 H      4.233056  -2.615174   0.460938
 H      5.635156  -0.575962   0.102134
 H     -0.327951   2.048154   0.582278
 H      1.899196   2.883259   0.353034
 H      1.866496   2.530112  -1.385997
 H     -0.396551   1.760447  -1.164331
 N     -0.625797  -0.818140   0.081570
 C     -1.985176  -0.466082   0.056213
 C     -2.796524  -0.876829  -1.032909
 C     -2.599623   0.206390   1.144656
 C     -4.172400  -0.596699  -1.042047
 H     -2.326699  -1.415531  -1.870818
 C     -3.979968   0.468137   1.132282
 H     -1.984541   0.503516   2.008889
 C     -4.774619   0.075013   0.039189
 H     -4.782773  -0.914184  -1.903137
 H     -4.438586   0.987077   1.989793
 H     -5.855831   0.284133   0.032709
---------------------------------------
Mn2/Mn-actcat
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          19.6732
 E(RB-P86) (a.u.) =                                    -4386.45866100
 Thermal correction to Enthalpy (a.u.) =                   0.637322
 Thermal correction to Gibbs Free Energy (a.u.) =          0.525625
 Total Entropy (cal/Kmol) =                                235.085
 E(RPBE1PBE) (a.u.) =                                  -4385.77799462
Optimised cartesian coordinates (Angstrom):
 Fe     3.406489  -0.682557   0.369539
 Mn    -1.057548  -0.393765  -1.510524
 P      0.026007   0.551591   0.256095
 O     -2.017305   2.214967  -2.477957
 O      1.014455  -0.113726  -3.561606
 N     -0.403773  -2.315405  -0.825931
 N     -2.776853  -1.068136  -0.440365
 C      1.422131  -0.485954   0.875882
 C      1.714801  -1.844213   0.416200
 C      2.730702  -2.384942   1.291909
 H      3.186488  -3.379866   1.212781
 C      3.082346  -1.387218   2.265124
 H      3.846293  -1.492442   3.047185
```

```
 C      2.288125  -0.217942   2.009281
 H      2.325473   0.720543   2.577412
 C      3.815817   0.124540  -1.481129
 H      3.070527   0.345289  -2.256237
 C      4.504999  -1.127869  -1.313269
 H      4.385090  -2.020402  -1.942158
 C      5.363221  -1.014874  -0.161572
 H      6.006441  -1.806943   0.244813
 C      5.206365   0.310518   0.381091
 H      5.709786   0.705185   1.273885
 C      4.248596   1.013936  -0.431882
 H      3.893030   2.039946  -0.272218
 C     -0.995009   0.824542   1.797523
 C     -2.051642   1.764199   1.707190
 H     -2.192374   2.338007   0.776209
 C     -2.918833   1.978573   2.790683
 H     -3.725872   2.723955   2.704720
 C     -2.761095   1.241912   3.981122
 H     -3.443182   1.407096   4.830275
 C     -1.728427   0.293702   4.075672
 H     -1.596106  -0.289370   5.001410
 C     -0.850831   0.086735   2.993160
 H     -0.038123  -0.649350   3.093558
 C      0.808943   2.239317   0.079100
 C      1.163184   2.720577  -1.200228
 H      0.951496   2.111672  -2.090442
 C      1.789404   3.971747  -1.347985
 H      2.057211   4.330748  -2.354687
 C      2.068483   4.763215  -0.219389
 H      2.556460   5.744064  -0.336040
 C      1.712648   4.296923   1.059533
 H      1.920256   4.911447   1.950324
 C      1.084308   3.047442   1.206920
 H      0.796430   2.704503   2.213102
 C      1.074053  -2.583061  -0.752685
 H      1.472056  -2.161701  -1.697133
 C     -1.137425  -2.687173   0.397680
 H     -1.189577  -3.787867   0.550436
 H     -0.575466  -2.278955   1.265961
 C     -2.528140  -2.103963   0.411829
 C     -4.047337  -0.531492  -0.433324
 C     -5.006897  -0.939041   0.529161
 H     -6.005473  -0.482402   0.521966
 C     -4.712523  -1.966168   1.427904
 C     -3.458790  -2.587991   1.343461
 H     -3.183737  -3.424363   2.002919
 C      1.386009  -4.088874  -0.743165
 H      2.473409  -4.257522  -0.873952
 H      1.078642  -4.581090   0.201986
 H      0.871444  -4.594692  -1.586252
 C     -1.687036   1.152683  -2.063738
 C      0.225627  -0.210212  -2.674892
 H     -0.767472  -2.874899  -1.609339
 H     -1.658082  -1.221278  -2.727724
 H     -5.464682  -2.302887   2.158124
 N     -4.378686   0.425152  -1.396448
 C     -4.366440  -0.004499  -2.797267
 H     -5.311346  -0.540001  -3.062127
 H     -3.493832  -0.663382  -2.974018
 H     -4.263066   0.881219  -3.456142
 C     -5.451646   1.362211  -1.094824
 H     -5.366992   2.226278  -1.785897
 H     -5.357879   1.741240  -0.058448
 H     -6.475568   0.930055  -1.225343
---------------------------------------
Mn2/TSHy_6-re-indNPOPh2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                        -383.1383
 E(RB-P86) (a.u.) =                                      -5668.14427169
 Thermal correction to Enthalpy (a.u.) =                  0.983688
 Thermal correction to Gibbs Free Energy (a.u.) =         0.822759
 Total Entropy (cal/Kmol) =                               338.703
 E(RPBE1PBE) (a.u.) =                                    -5667.41921109
Optimised cartesian coordinates (Angstrom):
 Fe     2.353099  -3.561329   0.278767
 Mn     0.635814   0.867803  -0.529736
 P      2.686674  -0.011905  -0.143395
```

O	1.568111	2.250358	-2.951919
O	-0.191425	-1.087866	-2.543986
N	-0.164565	-0.151158	1.148964
N	0.821478	2.408224	0.952762
C	2.598547	-1.588205	0.794301
C	1.388035	-2.131880	1.404985
C	1.798011	-3.250897	2.227147
H	1.132312	-3.897179	2.812046
C	3.222644	-3.410772	2.125445
H	3.819713	-4.191130	2.616157
C	3.719422	-2.396587	1.239331
H	4.768426	-2.249159	0.952474
C	1.690145	-3.766746	-1.663446
H	1.259590	-2.966440	-2.277684
C	0.951020	-4.633065	-0.784171
H	-0.134970	-4.607947	-0.621841
C	1.887957	-5.516401	-0.137963
H	1.643045	-6.283755	0.608657
C	3.207738	-5.195655	-0.620957
H	4.143478	-5.677199	-0.306523
C	3.086094	-4.111611	-1.561559
H	3.910324	-3.621207	-2.095768
C	3.824196	1.015986	0.920550
C	4.404473	2.176100	0.353391
H	4.216407	2.420290	-0.704640
C	5.231367	3.012737	1.121191
H	5.692809	3.899397	0.657321
C	5.473885	2.719749	2.477150
H	6.121319	3.376906	3.079138
C	4.885434	1.582266	3.055434
H	5.068458	1.342704	4.115241
C	4.068825	0.734086	2.282763
H	3.637099	-0.166263	2.746577
C	3.831846	-0.426815	-1.560047
C	3.313680	-0.673167	-2.850321
H	2.235190	-0.585948	-3.037731
C	4.166457	-1.035311	-3.909181
H	3.741914	-1.220948	-4.908710
C	5.551076	-1.155662	-3.696697
H	6.218131	-1.436382	-4.527280
C	6.079210	-0.907872	-2.416590
H	7.163095	-0.993769	-2.238206
C	5.227839	-0.543494	-1.358649
H	5.661504	-0.338010	-0.367838
C	-0.052410	-1.651944	1.254101
H	-0.485819	-2.016525	0.301524
C	0.228499	0.515294	2.402804
H	-0.542641	0.411741	3.196938
H	1.137497	0.001593	2.789339
C	0.577350	1.967470	2.220271
C	1.257607	3.709697	0.811646
C	1.507100	4.527849	1.940280
H	1.853299	5.558812	1.789611
C	1.250415	4.055078	3.229095
C	0.753366	2.754741	3.370548
H	0.530958	2.326079	4.358887
C	-0.932489	-2.208074	2.387379
H	-1.049953	-3.303527	2.273441
H	-0.504538	-2.015633	3.392253
H	-1.947684	-1.769986	2.345759
C	1.204661	1.769024	-1.931733
C	0.174058	-0.355308	-1.683032
H	-1.183828	0.033853	0.979803
H	-0.985006	1.298888	-0.779253
C	-2.723184	1.213640	-0.701678
C	-2.878077	2.673094	-0.419387
C	-2.904753	1.066629	-2.223022
C	-2.938577	3.393574	-1.637117
C	-3.066461	3.317761	0.816674
C	-2.660584	2.474381	-2.808145
C	-3.219734	4.769603	-1.624453
C	-3.331297	4.698554	0.824255
H	-3.024420	2.739809	1.753118
C	-3.416726	5.416914	-0.388457
H	-3.288226	5.337306	-2.566703
H	-3.490015	5.222186	1.780545
H	1.414787	4.699989	4.106221

H	-3.642874	6.495135	-0.367295
H	-3.966512	0.778346	-2.386161
H	-3.287028	2.696747	-3.696219
H	-1.598860	2.585798	-3.126486
H	-2.279378	0.264434	-2.656314
N	-3.040780	0.313126	0.237524
P	-3.645701	-1.237418	-0.035912
O	-2.710392	-2.354837	-0.509987
C	-4.405444	-1.649004	1.591284
C	-4.772424	-0.670236	2.540108
C	-4.656797	-3.012462	1.865965
C	-5.386601	-1.051796	3.747204
H	-4.558740	0.388560	2.327668
C	-5.272063	-3.390453	3.071310
H	-4.352569	-3.775204	1.131324
C	-5.638946	-2.410224	4.013274
H	-5.667343	-0.283671	4.485699
H	-5.462474	-4.455444	3.280146
H	-6.120109	-2.707144	4.958933
C	-5.109884	-1.126394	-1.162797
C	-5.153083	-1.994564	-2.274061
C	-6.180649	-0.233168	-0.933000
C	-6.252214	-1.966970	-3.151337
H	-4.311863	-2.687172	-2.436107
C	-7.276925	-0.206386	-1.812160
H	-6.159749	0.446371	-0.065565
C	-7.313755	-1.072588	-2.922385
H	-6.280195	-2.647193	-4.017785
H	-8.108771	0.492762	-1.630061
H	-8.174979	-1.050687	-3.609152
N	1.450559	4.223098	-0.478877
C	2.415911	5.304443	-0.638286
C	0.228789	4.451906	-1.254473
H	3.342832	5.083724	-0.075037
H	2.674554	5.385879	-1.714242
H	2.027845	6.302752	-0.314097
H	0.474061	4.520464	-2.332495
H	-0.464469	3.605736	-1.109555
H	-0.278810	5.395140	-0.937202

Mn2/TSHy_6-si-indNPOPh2
Frequencies, energies and thermodynamic properties:

Lowest Vibrational Mode (1/cm) =	-461.5285
E(RB-P86) (a.u.) =	-5668.14624258
Thermal correction to Enthalpy (a.u.) =	0.983638
Thermal correction to Gibbs Free Energy (a.u.) =	0.823065
Total Entropy (cal/Kmol) =	337.956
E(RPBE1PBE) (a.u.) =	-5667.42359945

Optimised cartesian coordinates (Angstrom):

Fe	3.550928	2.134000	-1.802795
Mn	0.446563	-0.289998	1.024175
P	2.520291	-0.674343	0.191343
O	1.267883	-0.969398	3.768388
O	1.091733	2.411923	1.951321
N	-0.254550	0.258915	-0.888034
N	-0.331828	-2.171708	0.341159
C	2.814959	0.264839	-1.366715
C	1.808874	1.071392	-2.057037
C	2.369064	1.450788	-3.335049
H	1.878393	2.073728	-4.093086
C	3.697055	0.911408	-3.439196
H	4.385405	1.053184	-4.283133
C	3.979484	0.189543	-2.230230
H	4.914895	-0.336470	-2.001140
C	3.568158	3.370092	-0.153058
H	2.988702	3.209593	0.764964
C	3.115640	4.087715	-1.315469
H	2.139783	4.578065	-1.431995
C	4.157098	4.030677	-2.309112
H	4.112527	4.463694	-3.317443
C	5.256170	3.279219	-1.758225
H	6.195534	3.039412	-2.274304
C	4.891906	2.868673	-0.427106
H	5.503904	2.262895	0.253761
C	2.888485	-2.434809	-0.307288
C	3.067460	-3.382040	0.730106
H	3.021718	-3.055937	1.782029

C	3.316834	-4.731797	0.433269
H	3.472501	-5.451446	1.253035
C	3.369510	-5.164501	-0.906055
H	3.565124	-6.223223	-1.139115
C	3.171032	-4.236501	-1.942182
H	3.208549	-4.564400	-2.993431
C	2.932504	-2.880240	-1.646147
H	2.800189	-2.164741	-2.472236
C	4.048442	-0.310950	1.205257
C	3.997353	0.573453	2.304416
H	3.046513	1.037059	2.597292
C	5.160828	0.878153	3.035327
H	5.098192	1.569224	3.891043
C	6.393780	0.304048	2.680289
H	7.303443	0.542320	3.254168
C	6.455576	-0.584241	1.590789
H	7.414351	-1.046725	1.306480
C	5.292907	-0.892819	0.863656
H	5.357947	-1.605724	0.027240
C	0.411329	1.429743	-1.563249
H	0.503072	2.190989	-0.763471
C	-0.368472	-0.916652	-1.770820
H	-1.183966	-0.801437	-2.518996
H	0.574802	-1.011595	-2.352469
C	-0.569243	-2.195365	-1.000873
C	-0.454598	-3.362610	1.026879
C	-0.713336	-4.577546	0.345514
H	-0.802506	-5.509157	0.919047
C	-0.923081	-4.582003	-1.035046
C	-0.875962	-3.362505	-1.719258
H	-1.047918	-3.301645	-2.803689
C	-0.462244	2.027657	-2.677899
H	-0.036479	2.989560	-3.026612
H	-0.547636	1.355880	-3.556008
H	-1.482437	2.227945	-2.294835
C	0.911664	-0.770647	2.655984
C	0.852554	1.329209	1.527949
H	-1.241484	0.560792	-0.660247
H	-1.121641	0.230396	1.489275
C	-2.629357	0.997607	1.285994
C	-3.262870	0.366735	2.539016
C	-2.564265	1.059141	3.728641
H	-1.148557	-5.521577	-1.563009
N	-2.995996	0.793319	0.009295
C	-2.174792	2.350008	1.737586
C	-1.883262	3.488217	0.967063
C	-2.171426	2.404223	3.151928
C	-1.572224	4.690020	1.627357
H	-1.921792	3.438130	-0.132281
C	-1.856852	3.604702	3.807381
C	-1.555583	4.745990	3.036989
H	-1.351141	5.597206	1.042486
H	-1.859673	3.662091	4.908200
H	-1.317570	5.696564	3.541187
H	-4.338285	0.659604	2.519370
H	-3.235449	-0.736738	2.529611
H	-3.203124	1.140421	4.631574
H	-1.651126	0.492736	4.023486
P	-4.116476	-0.410506	-0.386680
O	-3.981883	-1.828157	0.177314
C	-5.768791	0.293912	0.060461
C	-6.054905	1.676365	0.001128
C	-6.776020	-0.607612	0.468656
C	-7.337073	2.146642	0.336197
H	-5.266870	2.387445	-0.292852
C	-8.057664	-0.134585	0.801844
H	-6.535612	-1.680903	0.530760
C	-8.340329	1.242285	0.733390
H	-7.553608	3.226063	0.291367
H	-8.838600	-0.843588	1.120784
H	-9.344147	1.613211	0.995444
C	-4.096298	-0.434469	-2.226360
C	-4.056400	0.737059	-3.014686
C	-4.174151	-1.694805	-2.857450
C	-4.089826	0.644909	-4.417238
H	-3.999125	1.724501	-2.531165
C	-4.205456	-1.784611	-4.260795

```
 H     -4.204294  -2.598510  -2.228634
 C     -4.163280  -0.615127  -5.041785
 H     -4.057506   1.561712  -5.027350
 H     -4.263839  -2.771799  -4.746675
 H     -4.189808  -0.684103  -6.141059
 N     -0.315262  -3.358808   2.419046
 C      0.076800  -4.601737   3.071589
 C     -1.324620  -2.617270   3.175730
 H      0.904505  -5.086097   2.518549
 H      0.437653  -4.361585   4.092830
 H     -0.761143  -5.335276   3.177715
 H     -0.938047  -2.380229   4.186431
 H     -1.538460  -1.666388   2.658148
 H     -2.268226  -3.207323   3.278548
---------------------------------------
Mn2/TSHy_8-re-indNPOPh2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -578.5019
 E(RB-P86) (a.u.) =                                        -5668.14639679
 Thermal correction to Enthalpy (a.u.) =                    0.983616
 Thermal correction to Gibbs Free Energy (a.u.) =           0.821510
 Total Entropy (cal/Kmol) =                                 341.180
 E(RPBE1PBE) (a.u.) =                                      -5667.42311227
Optimised cartesian coordinates (Angstrom):
 Fe     4.037732  -2.013149   1.708539
 Mn     0.422752   0.110098  -0.751074
 P      2.539538   0.688281  -0.150489
 O      0.919422   0.857877  -3.554504
 O      1.260160  -2.535605  -1.680121
 N      0.016243  -0.430111   1.267115
 N     -0.458494   1.928233   0.006239
 C      3.104442  -0.214621   1.352345
 C      2.260081  -1.083872   2.171817
 C      3.005831  -1.395001   3.370720
 H      2.665013  -2.039778   4.190233
 C      4.289807  -0.752947   3.300752
 H      5.088356  -0.826272   4.051187
 C      4.360033  -0.034567   2.059133
 H      5.215315   0.555858   1.706668
 C      3.974295  -3.272509   0.076305
 H      3.290078  -3.170314  -0.775143
 C      3.702386  -4.001799   1.286588
 H      2.784018  -4.560866   1.511189
 C      4.835444  -3.850200   2.163175
 H      4.930543  -4.267749   3.174532
 C      5.809841  -3.027661   1.491889
 H      6.777233  -2.709478   1.903219
 C      5.276747  -2.667966   0.203554
 H      5.765240  -2.029787  -0.544307
 C      2.794237   2.479251   0.310081
 C      2.702722   3.434106  -0.731908
 H      2.522366   3.099150  -1.766542
 C      2.853833   4.804154  -0.463577
 H      2.796758   5.531654  -1.289116
 C      3.077557   5.247577   0.854363
 H      3.194877   6.322428   1.065027
 C      3.150583   4.309664   1.897911
 H      3.325099   4.645422   2.932729
 C      3.011202   2.934122   1.628784
 H      3.093105   2.213567   2.456964
 C      3.965315   0.468000  -1.339919
 C      3.884066  -0.443220  -2.415249
 H      2.963270  -1.014586  -2.588872
 C      4.979993  -0.636379  -3.276587
 H      4.893985  -1.350187  -4.111336
 C      6.174720   0.077220  -3.078057
 H      7.031061  -0.073736  -3.754428
 C      6.265328   0.992207  -2.013221
 H      7.193453   1.563208  -1.850443
 C      5.169434   1.189086  -1.155221
 H      5.253135   1.923891  -0.339712
 C      0.835122  -1.539885   1.874716
 H      0.870424  -2.321862   1.089722
 C     -0.030312   0.769377   2.125196
 H     -0.684279   0.610086   3.008560
 H      0.991527   0.977118   2.510712
 C     -0.497681   1.981495   1.368406
```

```
 C     -0.800216   3.073006  -0.683119
 C     -1.090334   4.282106  -0.002412
 H     -1.356387   5.176172  -0.581089
 C     -1.110951   4.315865   1.392859
 C     -0.835448   3.135531   2.093581
 H     -0.846426   3.100548   3.192682
 C      0.149704  -2.149882   3.109861
 H      0.656473  -3.090065   3.405643
 H      0.169001  -1.464893   3.981929
 H     -0.908664  -2.382846   2.879795
 C      0.684384   0.621794  -2.418696
 C      0.941147  -1.466968  -1.264118
 H     -0.981314  -0.756887   1.263324
 H     -1.154362  -0.586806  -1.153386
 H     -1.366739   5.245098   1.925292
 C     -2.630234  -1.251367  -1.242126
 C     -2.698054  -1.478646  -2.727980
 C     -2.273938  -2.643456  -0.644924
 N     -3.492046  -0.376517  -0.690244
 C     -2.214935  -2.765768  -3.056787
 C     -3.260334  -0.649846  -3.716617
 P     -3.839810  -0.406739   0.937421
 C     -2.235056  -3.206928  -4.391624
 C     -3.279262  -1.093073  -5.050556
 H     -3.705204   0.316764  -3.437847
 O     -2.716874  -0.729261   1.948693
 C     -4.583236   1.238658   1.270674
 C     -5.227451  -1.604793   1.181472
 C     -2.756773  -2.360068  -5.388163
 H     -1.864851  -4.211528  -4.654447
 H     -3.716108  -0.454865  -5.835345
 C     -5.078002   2.064882   0.238322
 C     -4.671429   1.671849   2.612843
 C     -6.307316  -1.681762   0.272924
 C     -5.197074  -2.464386   2.300560
 H     -2.779155  -2.698323  -6.436749
 C     -5.663062   3.306015   0.547950
 H     -4.989336   1.726798  -0.805293
 C     -5.258002   2.911900   2.918645
 H     -4.270525   1.034335   3.417108
 C     -7.345586  -2.604347   0.487648
 H     -6.330142  -1.023467  -0.610189
 C     -6.237761  -3.386971   2.512734
 H     -4.345749  -2.402985   2.996718
 C     -5.756946   3.729326   1.886705
 H     -6.046336   3.947769  -0.261602
 H     -5.323554   3.244321   3.967058
 C     -7.313038  -3.456947   1.608238
 H     -8.184175  -2.661442  -0.224801
 H     -6.207880  -4.056016   3.387843
 H     -6.217109   4.701139   2.127062
 H     -8.127828  -4.179714   1.774376
 C     -1.779373  -3.521358  -1.819626
 H     -0.677795  -3.647076  -1.804475
 H     -2.216994  -4.542066  -1.792265
 H     -1.563796  -2.587875   0.199352
 H     -3.221298  -3.055188  -0.232372
 N     -0.851894   3.024132  -2.076174
 C     -0.680723   4.264080  -2.820628
 C     -1.849177   2.133012  -2.668581
 H      0.154429   4.858079  -2.401946
 H     -0.429841   4.008828  -3.870847
 H     -1.599395   4.902077  -2.842620
 H     -1.516750   1.802014  -3.671858
 H     -1.983426   1.244715  -2.027330
 H     -2.832723   2.655144  -2.771118
---------------------------------------
Mn2/TSHy_8-re-indNPOPh2_2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -545.8603
 E(RB-P86) (a.u.) =                                        -5668.14271360
 Thermal correction to Enthalpy (a.u.) =                    0.983766
 Thermal correction to Gibbs Free Energy (a.u.) =           0.822554
 Total Entropy (cal/Kmol) =                                 339.300
 E(RPBE1PBE) (a.u.) =                                      -5667.42092994
Optimised cartesian coordinates (Angstrom):
 Fe     3.233867   3.054850  -0.444011
```

Mn	0.452591	-0.825083	0.511412
P	2.644186	-0.449775	0.061607
O	1.136635	-2.453465	2.863789
O	0.190425	1.350364	2.453762
N	-0.142662	0.404805	-1.134599
N	0.251787	-2.316240	-1.041220
C	2.911340	1.082923	-0.917999
C	1.845138	1.924962	-1.456407
C	2.469897	2.886199	-2.339488
H	1.954487	3.680535	-2.892956
C	3.889164	2.662099	-2.344702
H	4.632050	3.251020	-2.899213
C	4.167377	1.560499	-1.467264
H	5.160072	1.143832	-1.254882
C	2.712538	3.487023	1.502988
H	2.059787	2.873077	2.136732
C	2.277904	4.537199	0.620140
H	1.241181	4.868349	0.472374
C	3.437620	5.061892	-0.054312
H	3.439723	5.858355	-0.810527
C	4.590901	4.336864	0.415216
H	5.626005	4.485218	0.079343
C	4.143358	3.362417	1.375961
H	4.775290	2.637462	1.905146
C	3.494914	-1.743741	-0.977593
C	3.854281	-2.968222	-0.364560
H	3.676245	-3.114452	0.712950
C	4.454869	-3.994928	-1.112070
H	4.749075	-4.932469	-0.613443
C	4.684980	-3.826717	-2.491143
H	5.156105	-4.631908	-3.076916
C	4.311107	-2.623502	-3.113591
H	4.485927	-2.480658	-4.192023
C	3.721487	-1.588415	-2.362941
H	3.456961	-0.644492	-2.863940
C	3.876151	-0.283740	1.457665
C	3.449891	0.049791	2.761532
H	2.381019	0.177748	2.977212
C	4.383650	0.226395	3.799450
H	4.029171	0.484464	4.810118
C	5.758673	0.071885	3.551572
H	6.488706	0.208615	4.365167
C	6.195072	-0.266268	2.257379
H	7.269535	-0.396445	2.051176
C	5.262227	-0.446713	1.221483
H	5.622238	-0.729520	0.220375
C	0.346990	1.834081	-1.183534
H	0.144879	2.225372	-0.166958
C	0.066361	-0.284852	-2.420781
H	-0.705712	0.003196	-3.166690
H	1.044338	0.040530	-2.840324
C	0.108121	-1.783557	-2.289070
C	0.411516	-3.684783	-0.956359
C	0.493699	-4.490640	-2.118925
H	0.621834	-5.575658	-2.013612
C	0.338573	-3.922833	-3.384696
C	0.117830	-2.543978	-3.470362
H	-0.011308	-2.039112	-4.439033
C	-0.458083	2.682840	-2.184015
H	-0.254632	3.759923	-2.021965
H	-0.197771	2.444872	-3.235797
H	-1.541063	2.501708	-2.045349
C	0.859928	-1.861904	1.875544
C	0.338194	0.491887	1.645999
H	-1.182177	0.477871	-1.032358
H	-1.228956	-0.885720	0.960401
H	0.367934	-4.551594	-4.288114
C	-2.755807	-0.570570	1.526436
C	-3.386968	-1.852042	1.049289
C	-2.503261	-0.761562	3.043594
N	-3.069963	0.673527	1.139202
C	-3.500575	-2.762685	2.127838
C	-3.864239	-2.195057	-0.231986
P	-3.720911	1.181228	-0.294849
C	-4.156918	-3.992612	1.946841
C	-4.503837	-3.433896	-0.410363
H	-3.722793	-1.500221	-1.074755

```
 O     -3.036770   0.727843  -1.608419
 C     -4.664805  -4.320834   0.675755
 H     -4.264468  -4.696980   2.787992
 H     -4.885698  -3.713615  -1.405284
 H     -5.180157  -5.282929   0.523851
 C     -2.808057  -2.240232   3.369368
 H     -1.874827  -2.817940   3.549239
 H     -3.428188  -2.360248   4.282775
 H     -1.491021  -0.436657   3.345345
 H     -3.221167  -0.087548   3.556411
 C     -3.685577   3.015156  -0.133942
 C     -3.121459   3.653493   0.991267
 C     -4.211269   3.800632  -1.186005
 C     -3.083929   5.058440   1.063036
 H     -2.711635   3.028676   1.799327
 C     -4.176010   5.203017  -1.109959
 H     -4.651929   3.313955  -2.071597
 C     -3.611882   5.834633   0.015423
 H     -2.641413   5.549414   1.944757
 H     -4.590062   5.807400  -1.932868
 H     -3.585549   6.934501   0.074733
 C     -5.521986   0.780840  -0.361644
 C     -6.335681   0.873283   0.789592
 C     -6.097439   0.400530  -1.593057
 C     -7.709298   0.587419   0.707028
 H     -5.890589   1.166069   1.754217
 C     -7.473247   0.118965  -1.673475
 H     -5.452901   0.321814  -2.483114
 C     -8.279912   0.211838  -0.524496
 H     -8.339045   0.657030   1.608459
 H     -7.917250  -0.177258  -2.637498
 H     -9.357158  -0.010501  -0.587342
 N      0.483960  -4.278908   0.309210
 C      1.158937  -5.566619   0.418194
 C     -0.744829  -4.224960   1.102884
 H      2.113791  -5.553060  -0.141358
 H      1.386863  -5.751324   1.488104
 H      0.541396  -6.426838   0.056679
 H     -0.510016  -4.400519   2.170912
 H     -1.203256  -3.226089   1.006387
 H     -1.478206  -4.996325   0.763734
---------------------------------------
Mn2/TSHy_8-si-indNPOPh2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -458.4039
 E(RB-P86) (a.u.) =                                        -5668.14561579
 Thermal correction to Enthalpy (a.u.) =                    0.983369
 Thermal correction to Gibbs Free Energy (a.u.) =           0.821442
 Total Entropy (cal/Kmol) =                                 340.804
 E(RPBE1PBE) (a.u.) =                                      -5667.42393828
Optimised cartesian coordinates (Angstrom):
 Fe    -3.874707  -2.098704  -1.565455
 Mn    -0.420946   0.314286   0.834858
 P     -2.521172   0.788921   0.116526
 O     -0.929483   1.231774   3.584455
 O     -1.178593  -2.302552   1.903028
 N      0.088335  -0.377213  -1.114816
 N      0.447672   2.089455  -0.037674
 C     -3.000966  -0.251966  -1.328001
 C     -2.103233  -1.162263  -2.040697
 C     -2.795754  -1.593413  -3.234896
 H     -2.408552  -2.294816  -3.984268
 C     -4.097041  -0.984288  -3.266331
 H     -4.864096  -1.142793  -4.036236
 C     -4.232084  -0.166803  -2.093364
 H     -5.114544   0.427261  -1.823758
 C     -3.860952  -3.198344   0.179882
 H     -3.227467  -2.994296   1.051824
 C     -3.499914  -4.025931  -0.940495
 H     -2.553256  -4.569282  -1.062561
 C     -4.587393  -3.997749  -1.884951
 H     -4.613869  -4.510884  -2.855654
 C     -5.622519  -3.152234  -1.345693
 H     -6.575531  -2.909216  -1.834582
 C     -5.172403  -2.655612  -0.070997
 H     -5.720540  -1.968357   0.586647
 C     -2.823141   2.525528  -0.500323
```

C	-2.804471	3.564992	0.461454
H	-2.657907	3.320456	1.526285
C	-2.984600	4.903263	0.076136
H	-2.984591	5.696549	0.840898
C	-3.164258	5.231180	-1.281802
H	-3.304287	6.280965	-1.584839
C	-3.163618	4.209636	-2.246572
H	-3.302406	4.454594	-3.311888
C	-2.995201	2.865682	-1.859813
H	-3.017329	2.078252	-2.628826
C	-3.979267	0.612037	1.274290
C	-3.893610	-0.193197	2.430879
H	-2.953368	-0.701705	2.681136
C	-5.006986	-0.357295	3.275760
H	-4.917665	-0.988363	4.174435
C	-6.223803	0.281542	2.980034
H	-7.093943	0.153997	3.643531
C	-6.319017	1.092389	1.834188
H	-7.264614	1.604897	1.594973
C	-5.205971	1.259370	0.992005
H	-5.294372	1.913642	0.110924
C	-0.676257	-1.552533	-1.663285
H	-0.711274	-2.276751	-0.825371
C	0.147475	0.746559	-2.068060
H	0.849429	0.538296	-2.903346
H	-0.859238	0.884894	-2.519507
C	0.536276	2.034570	-1.397300
C	0.727748	3.297181	0.564871
C	0.991540	4.459282	-0.200499
H	1.202614	5.406341	0.313294
C	1.056583	4.384195	-1.593453
C	0.854089	3.140306	-2.202746
H	0.904497	3.017298	-3.294535
C	0.064887	-2.225449	-2.831853
H	-0.407525	-3.197005	-3.079043
H	0.058237	-1.602322	-3.749273
H	1.119164	-2.420483	-2.553710
C	-0.708106	0.932305	2.459522
C	-0.904824	-1.245750	1.434036
H	1.086639	-0.673729	-1.013440
H	1.095098	-0.311541	1.346852
H	1.291006	5.278343	-2.191736
C	2.585082	-0.964632	1.758603
N	3.498664	-0.190163	1.161044
C	2.238313	-2.403315	1.456494
C	2.454895	-0.834987	3.293628
P	3.972996	-0.240404	-0.429717
C	1.766658	-3.035866	2.633843
C	2.381180	-3.144488	0.265141
O	2.930402	-0.529393	-1.533928
C	4.749555	1.403103	-0.703775
C	5.379936	-1.431855	-0.571772
C	1.468430	-4.408372	2.635076
C	2.073130	-4.516509	0.269722
H	2.725212	-2.652286	-0.656827
C	5.331104	2.142820	0.349225
C	4.792177	1.913707	-2.019773
C	6.252801	-1.682255	0.510226
C	5.590443	-2.091233	-1.802672
C	1.625580	-5.148215	1.448871
H	1.113016	-4.899922	3.555474
H	2.189846	-5.103634	-0.655258
C	5.955416	3.374740	0.085117
H	5.277383	1.749956	1.376182
C	5.417012	3.146097	-2.280578
H	4.323904	1.341342	-2.835964
C	7.324634	-2.579672	0.359414
H	6.084897	-1.179168	1.475731
C	6.664525	-2.986724	-1.950933
H	4.898185	-1.903528	-2.638906
H	1.397556	-6.226327	1.439848
C	6.001778	3.876450	-1.229349
H	6.405473	3.948841	0.910939
H	5.444800	3.540189	-3.309131
C	7.533256	-3.230986	-0.871104
H	7.999653	-2.774451	1.208219
H	6.822218	-3.499619	-2.913379

```
 H      6.491771   4.841791  -1.434219
 H      8.373822  -3.933679  -0.987343
 C      1.641424  -2.051387   3.773827
 H      2.000294  -2.463808   4.739809
 H      0.569992  -1.788825   3.917237
 H      2.032215   0.136504   3.603317
 H      3.493868  -0.880559   3.688029
 N      0.750778   3.355557   1.961608
 C      0.477439   4.635544   2.600834
 C      1.824958   2.610523   2.619924
 H     -0.389054   5.131622   2.122557
 H      0.224224   4.449025   3.665037
 H      1.347690   5.338807   2.584494
 H      1.517939   2.336898   3.649789
 H      2.053521   1.690532   2.052498
 H      2.755593   3.227316   2.680806
---------------------------------------
Mn2/TSHy_8-si-indNPOPh2_2
Frequencies, energies and thermodynamic properties:
 Lowest Vibrational Mode (1/cm) =                          -500.0568
 E(RB-P86) (a.u.) =                                        -5668.14298754
 Thermal correction to Enthalpy (a.u.) =                    0.983751
 Thermal correction to Gibbs Free Energy (a.u.) =           0.822141
 Total Entropy (cal/Kmol) =                                 340.135
 E(RPBE1PBE) (a.u.) =                                      -5667.41943127
Optimised cartesian coordinates (Angstrom):
 Fe     2.994071   3.225004  -0.271879
 Mn     0.401228  -0.877833   0.246863
 P      2.591210  -0.328732   0.016261
 O      1.099226  -2.554755   2.559369
 O     -0.258342   1.128278   2.276520
 N     -0.123759   0.409486  -1.386412
 N      0.406635  -2.297319  -1.362412
 C      2.852803   1.262932  -0.862862
 C      1.786846   2.061548  -1.461837
 C      2.423899   3.103547  -2.238032
 H      1.909544   3.890304  -2.803146
 C      3.849625   2.970624  -2.116220
 H      4.599026   3.632677  -2.570433
 C      4.119445   1.845817  -1.265726
 H      5.113517   1.481507  -0.976827
 C      2.252583   3.526101   1.627037
 H      1.580446   2.844316   2.164081
 C      1.841888   4.591427   0.750839
 H      0.806003   4.866320   0.510928
 C      3.027243   5.218116   0.223959
 H      3.053689   6.050005  -0.492619
 C      4.171930   4.541362   0.778737
 H      5.223817   4.768309   0.559005
 C      3.694215   3.494364   1.643839
 H      4.315413   2.783296   2.203582
 C      3.599563  -1.522022  -1.002174
 C      3.953861  -2.764809  -0.423685
 H      3.683074  -2.979457   0.622542
 C      4.662258  -3.724564  -1.165765
 H      4.950032  -4.676923  -0.692050
 C      5.007583  -3.471347  -2.507398
 H      5.561792  -4.224965  -3.089068
 C      4.641749  -2.249435  -3.097296
 H      4.906895  -2.039710  -4.145987
 C      3.945453  -1.280086  -2.350053
 H      3.689267  -0.319069  -2.822262
 C      3.684571  -0.161467   1.522553
 C      3.124678   0.111125   2.789556
 H      2.035314   0.186802   2.905890
 C      3.949485   0.293443   3.914848
 H      3.492171   0.503468   4.894885
 C      5.347284   0.205469   3.792280
 H      5.992159   0.346427   4.674251
 C      5.916277  -0.071076   2.535544
 H      7.010070  -0.147978   2.427456
 C      5.092172  -0.257073   1.411823
 H      5.554963  -0.489332   0.440241
 C      0.280940   1.864843  -1.325645
 H     -0.028940   2.186547  -0.311421
 C      0.250913  -0.213716  -2.667226
 H     -0.428748   0.090344  -3.493098
```

H	1.264230	0.150406	-2.950673
C	0.320655	-1.716686	-2.596207
C	0.604294	-3.663866	-1.320232
C	0.769248	-4.419156	-2.508406
H	0.920356	-5.504130	-2.438650
C	0.670947	-3.804709	-3.757780
C	0.420906	-2.428341	-3.802788
H	0.334718	-1.888919	-4.757466
C	-0.490649	2.722482	-2.345411
H	-0.350830	3.798572	-2.120288
H	-0.142515	2.547929	-3.384397
H	-1.570235	2.483566	-2.289122
C	0.808254	-1.944945	1.586543
C	0.053622	0.346312	1.437775
H	-1.173299	0.431418	-1.369671
H	-1.290644	-1.104484	0.485882
H	0.766603	-4.395927	-4.681701
C	-2.910354	-1.122943	0.764172
N	-3.295603	0.159958	0.835139
C	-2.892805	-1.907706	2.047682
C	-3.351573	-2.132759	-0.338880
P	-3.770372	1.007819	-0.519666
C	-3.514190	-3.161187	1.857195
C	-2.445181	-1.507027	3.319485
O	-2.964948	0.785527	-1.821721
C	-3.682608	-4.036442	2.945821
C	-2.606590	-2.387801	4.402706
H	-1.965742	-0.525460	3.452081
C	-3.220711	-3.646063	4.216678
H	-4.172777	-5.014239	2.808048
H	-2.250439	-2.097535	5.404249
H	-3.340760	-4.326845	5.074905
C	-3.974097	-3.334659	0.422589
H	-5.085733	-3.304044	0.375794
H	-3.672452	-4.314590	-0.002840
H	-2.479323	-2.455612	-0.939300
H	-4.060818	-1.661886	-1.045531
C	-3.734317	2.761561	0.027377
C	-3.109467	3.145637	1.233683
C	-4.295416	3.751850	-0.811992
C	-3.051733	4.504340	1.595709
H	-2.667436	2.367743	1.874510
C	-4.238106	5.106854	-0.445601
H	-4.785960	3.463126	-1.756270
C	-3.616650	5.485127	0.760233
H	-2.564196	4.798038	2.539229
H	-4.681975	5.871932	-1.102438
H	-3.574672	6.547630	1.048767
C	-5.552139	0.654943	-0.841360
C	-6.492436	0.606835	0.212670
C	-5.975750	0.420190	-2.167054
C	-7.842842	0.331182	-0.061399
H	-6.163776	0.779662	1.250181
C	-7.328956	0.146194	-2.437793
H	-5.230213	0.449909	-2.977638
C	-8.262596	0.102307	-1.386480
H	-8.572890	0.292536	0.762902
H	-7.655339	-0.035500	-3.474418
H	-9.322056	-0.113091	-1.598548
N	0.646543	-4.308931	-0.077609
C	1.378408	-5.567209	0.008905
C	-0.603189	-4.339392	0.683753
H	2.350208	-5.487539	-0.514773
H	1.577898	-5.781002	1.079143
H	0.816285	-6.441364	-0.405494
H	-0.390781	-4.551589	1.749242
H	-1.091172	-3.352038	0.629214
H	-1.294528	-5.125190	0.291050
