Electronic Supplementary Information for

Investigating the Mechanism and Origins of Selectivity in Palladium-Catalysed Carbene Insertion Cross-Coupling Reactions

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Contents

Experimental

General Information

Unless stated otherwise, all chemicals were used as received. Petroleum ether was distilled prior to use. Acetonitrile, hexane, and methanol were HPLC grade. Commercially-sourced $Pd_2(dba)_3{\cdot}CHCl_3$ was recrystallized according to literature procedure prior to use.[1] Benzyl bromide was filtered through a plug of silica and eluted in hexane prior to use. *p*-Acetamidobenzenesulfonyl azide was recrystallized from a binary toluene/dichloromethane solvent system. All reaction solvents were dried over activated 3 Å molecular sieves and stored under an inert N_2 atmosphere 24 h prior to use. *N,N*-Diisopropylethylamine (DIPEA) was dried over activated 3 Å molecular sieves and stored under an inert N_2 atmosphere at least 24 h prior to use if received in Sure-Seal containment. *N,N*-Diisopropylethylamine that was received without Sure-Seal containment was distilled over ninhydrin at atmospheric pressure, redistilled over powdered KOH under inert atmosphere at atmospheric pressure, then dried over 3 Å molecular sieves under an inert N_2 atmosphere at least 24 h prior to use. In the synthesis of $Pd_2(dba)_3{\cdot}CHCl_3$, the chloroform solvent was washed with distilled water, dried over anhydrous magnesium sulfate, filtered, stored over activated 3 Å molecular sieves under an inert N_2 atmosphere, and refrigerated in the absence of light at least 24 h prior to use. All palladium precursors and phosphines were stored under an inert N_2 atmosphere when not in use. All glassware used in air/moisture sensitive reactions was oven-dried at 180 °C for 24 h prior to use. Equipment that was not suited for drying at 180 °C was instead dried at 60 °C for 24 h prior to use. Methyl phenyldiazoacetate (**1**),[2] $Pd_2(dba)_3{\cdot}CHCl_3$,[1] benzyltriphenylphosphonium bromide (**9**),[3] (*E*)-1,2-diphenylmethylacrylate (**5*E***),[2] (*Z*)-1,2-diphenylmethylacrylate (**5*Z***),[4] methyl-2-diazo-4-phenylbutanoate (**3**),[5] bis(triphenylphosphine)palladium(II)benzyl bromide (**6**),[2] carbomethoxybenzylidenephosphorane (**8**),[6] and ethyl 2-diazo-2(4-trifluoromethylphenyl)acetate (**10**)[7] were synthesised and purified according to their respective literature procedures. Unless stated otherwise, the spectral data of all known compounds were in agreement with their literature data.

Flash column chromatography was performed using Fluorochem 40-63 micron silica gel. Thin-layer chromatography was performed using Merck Kieselgel 230-400 mesh silica gel plates and visualized under UV light or by staining with permanganate solution.

^1H, ^{13}C, and ^{31}P NMR analyses were conducted using 400 MHz and 600 MHz Bruker Avance series spectrometers and spectral data was analysed using Bruker TopSpin 4.0 or Mestrenova 11.0 software. Chemical shifts (δ) are quoted in parts per million (ppm), coupling constants (*J*) in Hertz (Hz), and measured against trimethylsilane (TMS), residual chloroform ($CHCl_3$), or 1,3,5-trimethoxybenzene as an internal standard. The ^1H NMR spectra are reported as follows: chemical shift (number of protons, multiplicity, coupling constant). Multiplicity is abbreviated as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet. The ^{13}C spectra are reported as follows: chemical shift. ^{31}P spectra are reported as follows: chemical shift (multiplicity).

GC-FID analysis was conducted using an Agilent 7820A gas chromatography system and an Agilent 19091J-413HP-5 column. The effluent was combusted in a H_2/air flame and detected *via* flame ionization detection. Chromatographic data was analysed using Agilent OpenLabs software.

LC-MS analysis was conducted using an Agilent 1260 HPLC, with an Agilent Infinitylab poroshell 120 column (2.1 x 150 mm, 2.7 μ) and tandem MSD single quadrupole mass spectrometer. Samples were analysed under either an acetonitrile/H_2O gradient with 0.1% formic acid additive.

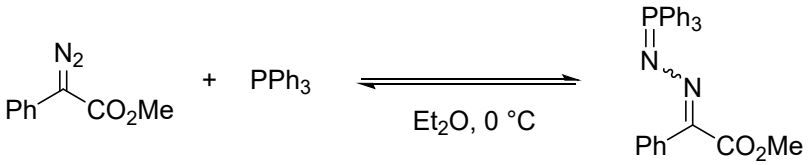
Infra-red (IR) analysis was conducted using an Agilent Cary 630 spectrometer equipped with an attenuated total refractance (ATR) probe. Solid samples were deposited on the ATR directly. Only selected maximum absorbances (ν_{max}) of the most intense peaks are reported and quoted in wavenumber (cm^{-1}).

Melting points were determined using a Stuart SMP10 digital melting point apparatus. Values are given in °C and are uncorrected.

HR-MS analysis was conducted by Analytical Services and Environmental Projects (ASEP) at Queen's University Belfast on a Waters LCT Premier ToF mass spectrometer using the ESI technique in positive-ion mode. Analysis of reaction mixtures was conducted on either a Waters Xevo G2-XS QTOF or Advion Nanomate Injection mass spectrometers in positive-ion and negative-ion mode.

Single X-ray diffraction analysis was conducted using CuKα radiation on an Agilent Supernova diffractometer equipped with an area detector and graphite monochromator. Raw frame data were recorded using CrysAlisPRO and solved using SHELXT. Full-matrix least-squares refinement of the structures were carried out using CRYSTALS.

Synthesis of α-Arylphosphazine Ester (7)

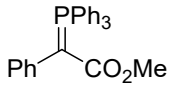


1 **7**

(17% Yield)

The following procedure was adopted from known protocols.[8,9] To an oven-dried 5 mL round-bottomed flask (RBF), PPh_3 (1.0 mmol) was added followed by dry Et_2O and methyl phenyldiazoacetate (**1**) (1.0 mmol). The reaction mixture was submerged in an ice-bath and allowed to stir at 0 – 5 °C for 2 h. The reaction mixture was then sealed with a rubber septum pierced with a syringe and stored in a freezer for 2 – 3 weeks. The yellow precipitate was isolated *via* suction filtration and washed with Et_2O (2 x 5 mL). The crude solid was then redissolved in a warm mixture of Et_2O (anti-solvent) and methanol (solvent) and stored overnight in a fridge. The purified product was isolated *via* suction filtration and washed with cold Et_2O (2 x 5 mL) to yield phosphazine **7** as yellow-green needle-like crystals (0.0741 g, 17% yield). NMR characterization was inconclusive as the desired product immediately reverts to a mixture of phosphazine **7**, liberated methyl phenyldiazoacetate **1**, and liberated PPh_3 in solution phase (see Figure S26 and Figure S27). HRMS (ESI+) found 439.1576; $C_{27}H_{23}N_2O_2P$, $[M+H]^+$ requires 439.1575, ν_{max} (neat): 1681.0, 1433.2, 1291.5, 1205.8, 1056.7, 885.2, 713.8, 687.7 cm^{-1}; m.p: 140 – 144 °C.

Synthesis of Carbomethoxybenzylidenephosphorane (8)



8

(8% Yield)

Compound **8** was synthesised and purified according to literature procedure using benzyltriphenylphosphonium bromide **9** as the starting material (1.3738 g, 8% yield).[6] δ_H (600 MHz, $CDCl_3$): 7.62 – 7.58 (6H, m), 7.50 – 7.47 (3H, m), 7.41 – 7.37 (6H, m), 7.04 – 7.02 (2H, m), 6.97-6.95 (2H, m), 6.91 – 6.88 (1H, m), 3.44 (3H, s); δ_C(151 MHz, $CDCl_3$): 170.14, 170.07, 137.97, 137.89, 134.38, 134.35, 133.90, 133.83, 131.63, 131.61, 128.53, 128.45, 128.01, 127.40, 127.30, 127.29, 124.16, 124.15, 49.95, 48.42, 47.58; δ_P (243 MHz, $CDCl_3$): 19.28 (s). HRMS (ESI+) found 411.1519 ; $C_{27}H_{23}O_2P$, $[M+H]^+$ requires 411.1513; ν_{max} (neat): 1597.2, 1481.6, 1325.1, 1237.5, 1177.8, 1097.7, 1064.2, 971.0, 773.4, 756.6, 693.3 cm^{-1}; m.p: 159 – 161 °C (155 °C lit).[10]

Purity of $Pd_2(dba)_3{\cdot}CHCl_3$

Commercial $Pd_2(dba)_3{\cdot}CHCl_3$

The purity of both commercially sourced and freshly prepared $Pd_2(dba)_3{\cdot}CHCl_3$ was determined by 400 MHz ^1H NMR in $CDCl_3$ according to **Eq. 1** as outlined previously by Zalesskiy and Ananikov.[1] Integrals $\boldsymbol{I_1}$, $\boldsymbol{I_2}$, and $\boldsymbol{I_3}$ correspond to solvated free dibenzylideneacetone, the minor form of $Pd_2(dba)_3$, and the major form of $Pd_2(dba)_3$, respectively.

$$\%\ Purity\ of\ the\ Soluble\ Component\ of\ Pd_2(dba)_2.CHCl_3 = \left(\frac{I_2 + I_3}{I_2 + I_3 + I_1/2}\right) x\ 100 \qquad \textbf{(1)}$$

Commercially-sourced $Pd_2(dba)_3{\cdot}CHCl_3$ is known to possess purities lower than those advertised with a considerable portion of the material's composition being attributed to heterogeneous palladium nanoparticles.[1]

Accordingly, the purity of $Pd_2(dba)_3{\cdot}CHCl_3$ obtained commercially was found to be 43% pure and as such the use of this material was avoided (Figure S1).

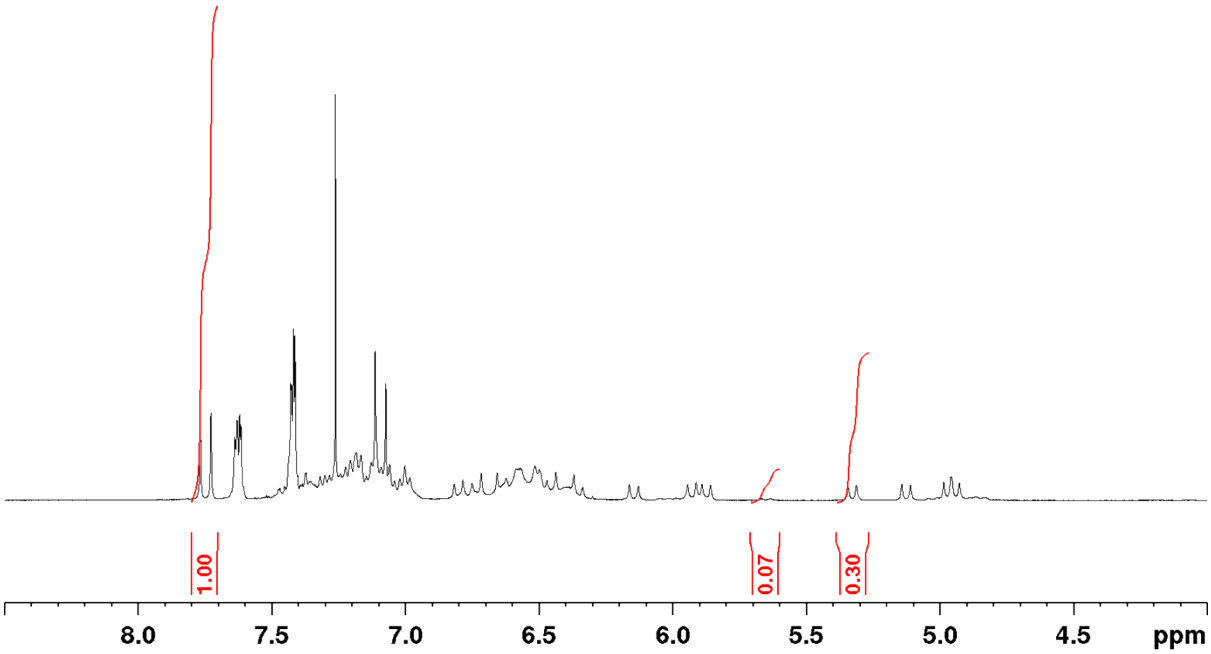


Figure S1: 400 MHz ^{1}H NMR in $CDCl_3$ of commercial $Pd_2(dba)_3{\cdot}CHCl_3$ as received.

Synthesised $Pd_2(dba)_3{\cdot}CHCl_3$

Freshly prepared $Pd_2(dba)_3{\cdot}CHCl_3$ was found to be 97% to 99% pure with high reproducibility (Figure S2). This material was used in the reported studies. Unless stated otherwise, reference to this materials loading in mol% refers to its uncorrected dimeric form whilst absolute concentration values refer to those of monometallic palladium in solution.

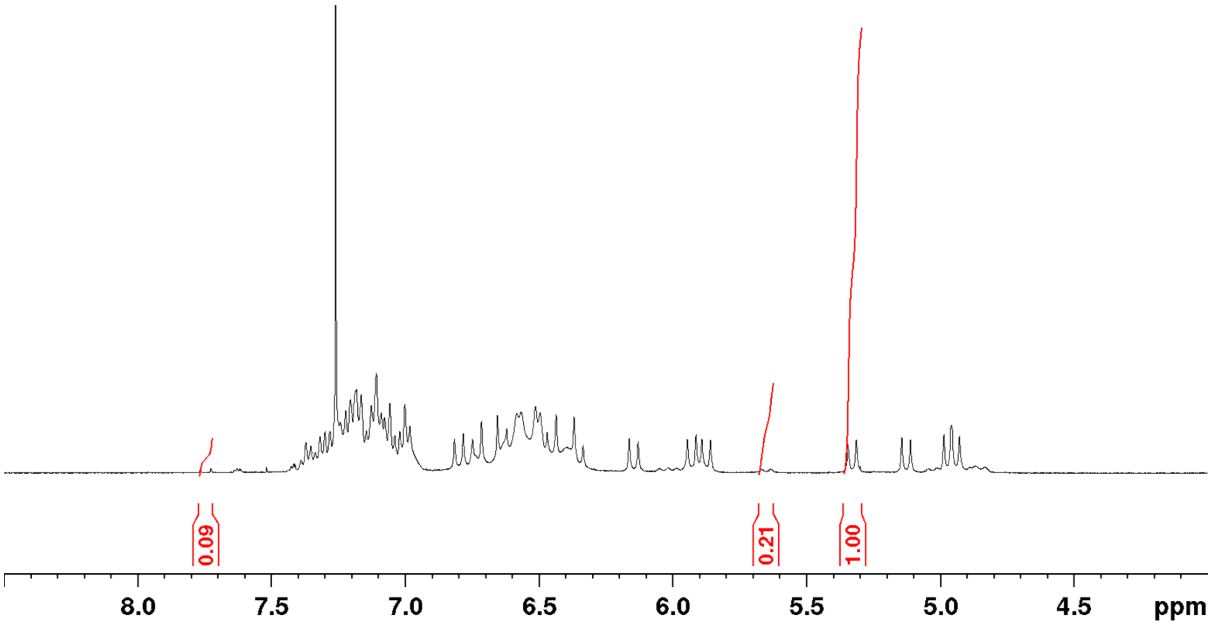


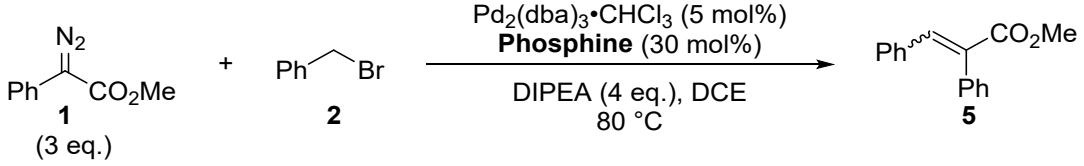
Figure S2: 400 MHz ^{1}H NMR in $CDCl_3$ of $Pd_2(dba)_3{\cdot}CHCl_3$ synthesised in-house.

Model Reaction Optimization

General Procedure

To an oven-dried microwave vial, phosphine (0.04 mmol), palladium precursor (0.005 mmol), and a known amount of internal standard was added. The vial was sealed with a crimped cap then evacuated and flushed with dry N_2 gas three times followed by the addition of solvent (1 mL) and base (0.4 mmol) *via* disposable syringe. The mixture was allowed to stir at 80 °C for 5 min upon which the solution turned clear gold, it was then allowed to cool to room temperature. Benzyl bromide **2** (0.1 mmol) and methyl phenyldiazoacetate **1** (0.3 mmol) were added to the reaction vessel *via* microlitre syringe and the reaction mixture was allowed to stir at 80 °C. After 3 h, an aliquot of the reaction mixture (100 µL) was extracted *via* disposable syringe and eluted through a plug of celite with diethyl ether (1 mL). Product yields were quantified *via* GC-FID analysis of the crude mixture in comparison to benzyl bromide consumption with reference to 1,3,5-trimethoxylbenzene as an internal standard. Where 600 MHz ^{1}H NMR analysis of the crude reaction mixture was used, ^{1}H NMR spectra were analysed using Mestrenova 11 software with the ester methyl resonances of **5(*E*)** (δ 3.793 ppm, s) and **5(*Z*)** (δ 3.787 ppm, s) relative to the aryl proton signal of 1,3,5-trimethoxybenzene (δ 6.09 ppm, s, 3H) being used to monitor product yield and selectivity. All signals integrated were subjected to linear correction with a normalized value of 1.0000 applied to the H_{Aryl} signal of 1,3,5-trimethoxybenzene.

Table S1: Ligand screen.

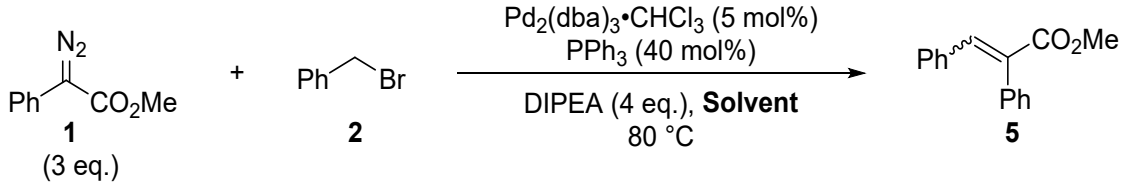


Entry	Phosphine	Conversion 2 (%)	Yield 5 (%)	Selectivity (*E:Z*)
1	PPh_3	100	65	9:1
2	XPhos	96	13	7:1
3	$P(C_6F_5)_3$	43	15	4:1
4	SPhos	91	11	8:1
5	P(*o*-tolyl)$_3$	97	12	7:1
6	JohnPhos	78	13	3:1
7	CataCXium A	99	2	2:1
8[a]	DMPP	100	2	6:1

2 (0.1 mmol), **1** (0.3 mmol), DIPEA (0.4 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mol%), Phosphine (30 mol%), 1,3,5-Trimethoxybenzene (0.06 mmol), Dichloroethane (1 mL), 80 °C, 3 h. Conversion of benzyl bromide is based on the amount of benzyl bromide quantified at t = 0 h with reference to 1,3,5-trimethoxybenzene as an internal standard. [a]DMPP = Tris(2,6-dimethoxyphenyl)phosphine.

As reported in Table S1, more electron-rich phosphines which are known to favour the oxidative addition step in palladium catalysis showed no benefit to the yield of **5** when compared to PPh_3 (Entries 2, 4, 5, 6, 7). Similarly, bulkier phosphines, which are known to promote rapid reductive elimination,[11] showed no positive effect on the desired product yield when compared to PPh_3 (Entries 2, 4, 6, 7). These results are in agreement with the observed reaction kinetics wherein carbene formation is turnover-limiting.

Table S2: Solvent screen.



Entry[a]	Solvent	Yield 5 (%)	Selectivity (E:Z)
1	2-MeTHF	80	21:1
2	Ethyl Acetate	73	17:1
3	Acetonitrile	70	14:1
4	Cyclohexane	89	23:1
5	Toluene	89	20:1[b]
6	Dichloroethane	73	13:1

2 (0.1 mmol), **1** (0.3 mmol), DIPEA (0.4 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mol%), PPh_3 (40 mol%), 1,3,5-Trimethoxybenzene (0.06 mmol), Solvent (3 mL), 80 °C, 3 h. Conversion of benzyl bromide is based on the amount of benzyl bromide quantified at t = 0 h with reference to 1,3,5-trimethoxybenzene as an internal standard.

[a]Yield and selectivity determined *via* ^{1}H NMR analysis of the crude reaction mixture. Benzyl bromide conversions were undetermined due to loss of the substrate *via* rotary evaporation of the reaction sample prior to dissolution in $CDCl_3$.

[b]Selectivity determined *via* GC-FID due to poor **5(*E*)** and **5(*Z*)** signal resolution in the spectra obtained *via* ^{1}H NMR analysis.

All solvents screened, with the exception of dichloroethane, showed an insoluble white solid form over the course of the reaction. Furthermore, analysis of toluene as the reaction solvent showed that toluene was a non-innocent component and partook in a cyclopropanation side-reaction with the diazo compound substrate (*vide infra*).

Side-Reactions, By-Products, and Spectator Species

Cyclopropanation of Toluene

When toluene was employed as the reaction solvent in the model system an impurity that was inseparable from the desired olefin ester product by means of flash column chromatography was observed. Literature data suggested that the impurity was a mixture of the regioisomeric products 2-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**16**) and 3-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**17**) formed from the cyclopropanation of toluene with **1** (Figure S3).[12,13]

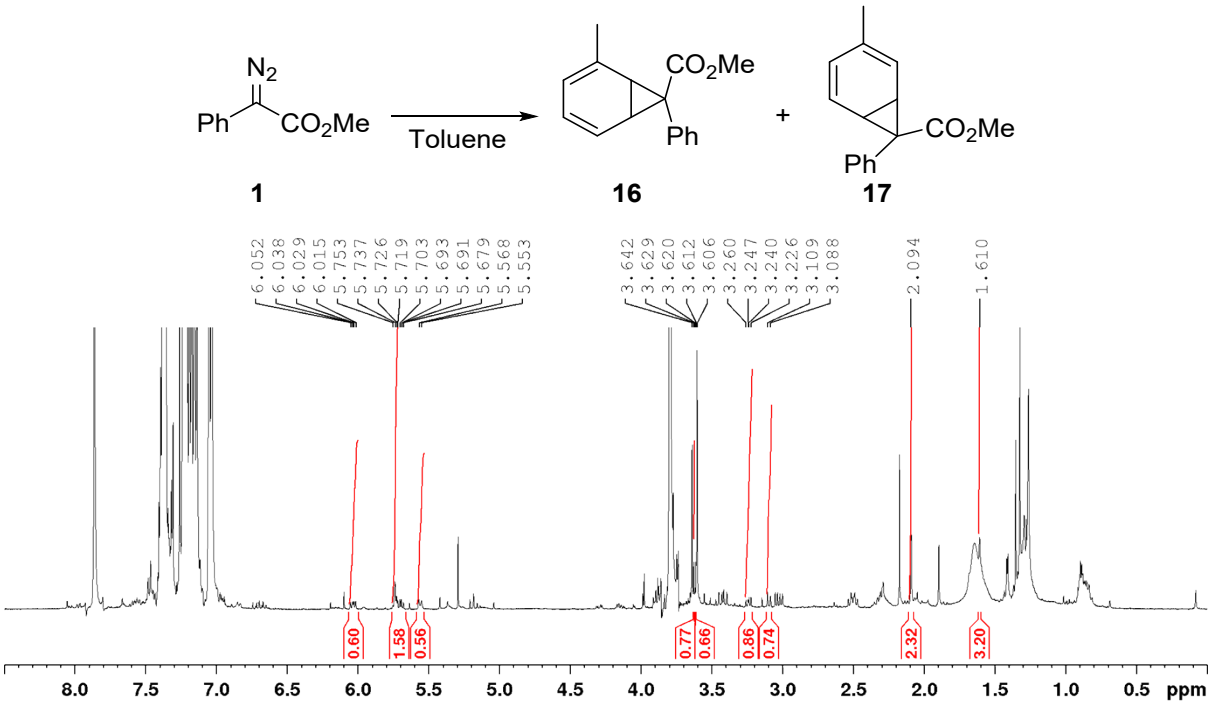


Figure S3: Suspected cyclopropanation side-reaction and 400 MHz ^{1}H NMR spectra in $CDCl_3$ of the **5**/impurity mixture with select characteristic signals of regioisomers **16** and **17** noted.

Identification of an Insoluble Phosphonium Salt (9) By-Product

Benzyl halides are known to react with PPh_3 in the formation of benzyltriphenylphosphonium halide salts.[14,15] ^{1}H NMR analysis in $CDCl_3$ of the crude reaction mixture of the model cross-coupling system showed the presence of a characteristic methylene signal (δ_H 5.40, d, 2H, J = 14.4 Hz) of benzyltriphenylphosphonium bromide (**9**)[16] with a slight downfield shift (δ_H 5.54, d, J = 14.4 Hz) attributed to the chemical environment of the crude sample (Figure S4). The crude mixture was washed with toluene and the insoluble components recovered were analysed *via* LC/MS with the characteristic signal of the cationic moiety of **9** (*i*.e $BnPPh_3^+$) being detected (LC/MS (ESI+): found 353.15, $C_{25}H_{22}P^+$, $[M]^+$ requires 353.20).

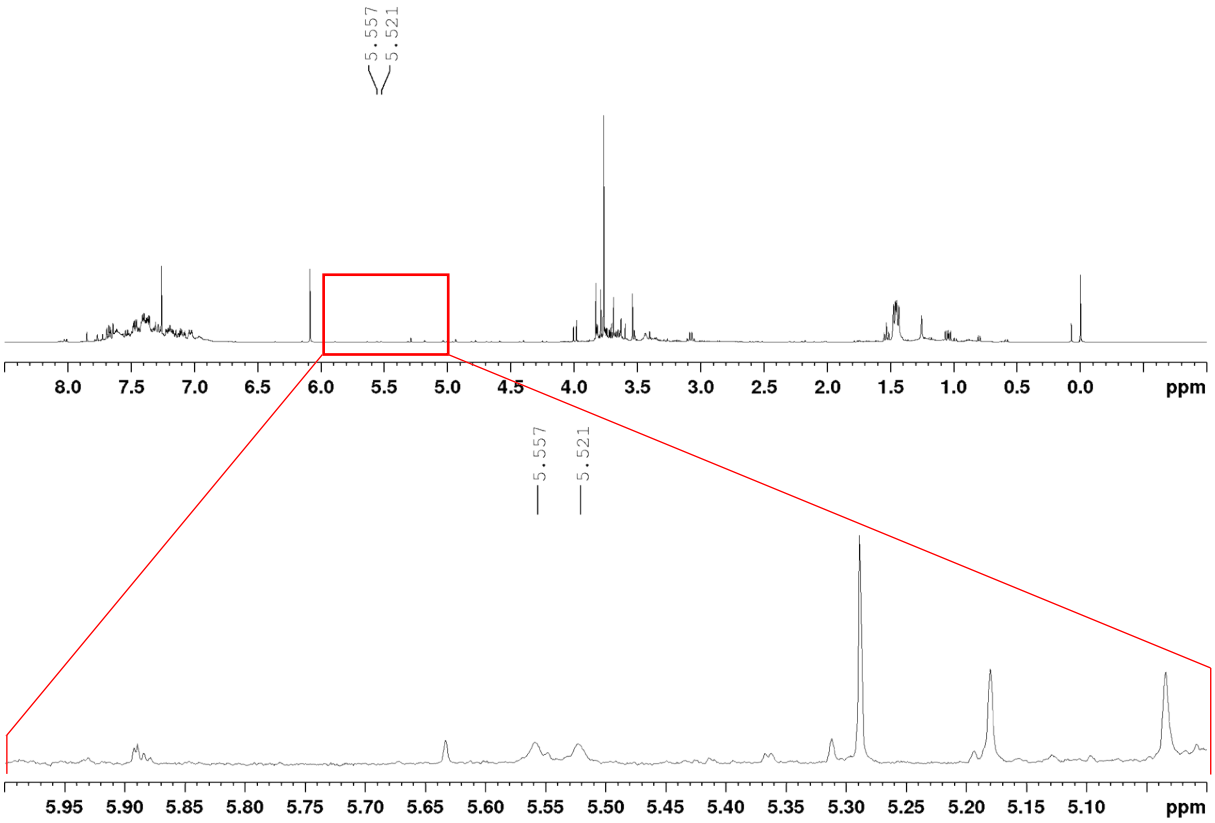
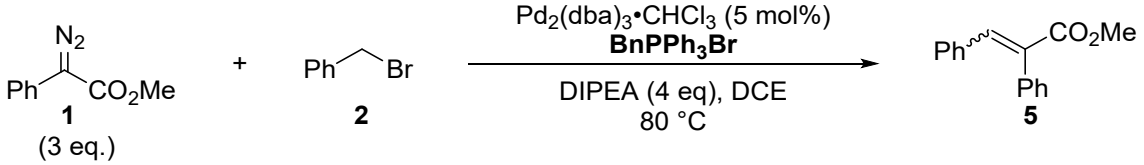


Figure S4: 400 MHz ^{1}H NMR spectra of the crude model reaction mixture in $CDCl_3$ (top). The same spectrum is expanded in the region of δ6.00 – 5.00 ppm to highlight the presence of **9** (bottom).

Phosphonium Salt (9) Decomposition under Standard Conditions

Inclusion of a phosphine source is crucial for the desired catalytic pathway as the absence of PPh_3 resulted in the immediate formation of palladium black with trace amounts of product **5** being detected by ^1H NMR analysis (Table S3) and no detection of product **5** *via* LC/MS analysis.

Table S3: Efficacy of the model reaction in the absence of phosphine and presence of **9** as the phosphine source.



Entry	9 (mmol)	2 (mmol)	Time (h)	Yield 5 (%)[a]
1	0.00	0.10	3	*Trace*
2	0.00	0.10	24	*Trace*
3	0.04	0.10	3	10
4	0.04	0.10	24	10
5	0.30	0.00	3	6
6	0.30	0.00	24	9

2 (0.1 mmol), **1** (0.3 mmol), DIPEA (0.4 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mol%), 1,3,5-Trimethoxybenzene (0.06 mmol), Dichloroethane (1 mL), 80 °C, 3 h.
[a]Yield of **5(*E*)**.

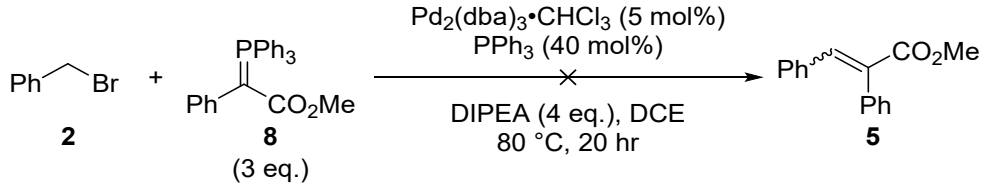
Reversibility of phosphonium salt formation was first investigated by utilizing **9** as the sole phosphine source under standard reaction conditions (Table S3). By ^1H NMR analysis of the reaction mixture, **5(*E*)** was shown to form in 10% yield indicating PPh_3 may be liberated from **9**. Further confidence was gained by detection of the characteristic signal of product **5** *via* LC/MS analysis (LC/MS (ESI+): found 239.10, $C_{16}H_{14}O_2$, $[M+H]^+$ requires 239.10).

To clarify that PPh_3 was liberated from the phosphonium salt by virtue of reversible salt formation, **9** was used in stoichiometric amounts thus acting as the source of both **2** and PPh_3 (Table S3). After 24 h the desired **5(*E*)** product was formed in 9% yield indicating slow reversibility of phosphonium salt formation. Further confidence was gained by detection of the characteristic signal of product **5** *via* LC/MS analysis (LC/MS (ESI+): found 239.50, $C_{16}H_{14}O_2$, $[M+H]^+$ requires 239.10).

Reactivity of Phosphorane (8) under Standard Conditions

As discussed *vide infra*, phosphorane **8** was shown to form irreversibly under standard reaction conditions. Given that similar compounds have been identified as key intermediates in other metal-carbene mediated chemistry[17] the aptitude for olefin formation *via* **8** was investigated. Under standard cross-coupling conditions in which **1** was replaced with **8** no product **5** was detected (Table S4).

Table S4: Model reaction with phosphorane **8** as the carbene precursor.



Time (h)	Yield 5 (%)	Conversion 2 (%)	Yield 9 (%)	Conversion 8 (%)
20	0	46	34	11

2 (0.3 mmol), **8** (0.9 mmol), DIPEA (1.2 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%), PPh_3 (40 mol%), 1,3,5-Trimethoxybenzene (0.06 mmol), Dichloroethane (3 mL), 80 °C, 20 h. Yields and conversions determined *via* 400 MHz ^1H NMR analysis in $CDCl_3$ using 1,3,5-Trimethoxybenzene as an internal standard.

A minor amount of **8** was consumed over a prolonged reaction time whilst moderate consumption of **2** was observed. The majority of **2** depletion can be attributed to the formation of **9** however an amount approximately equal to that of consumed **8** was unaccounted for implying that **8** may sluggishly react with substrate **2**. Given the low conversion of **8** over a relatively long period this possible side-reaction was deemed irrelevant to the model reaction and so no further studies pertaining to this pathway were conducted. At no point was product **5** detected.

Kinetic Analysis

Integral rate data was obtained *via* 400 MHz ^{1}H NMR analysis using an internal standard method of quantification where 1,3,5-trimethoxybenzene was employed as the internal standard. ^{1}H NMR spectra were analysed with the olefinic proton signal for **5(*E*)** (δ 7.87 ppm, s, 1H) relative to the aryl proton signal of 1,3,5-trimethoxybenzene (δ 6.09 ppm, s, 3H) being used to monitor product formation. All signals integrated were subjected to linear correction with a normalized value of 1.0000 applied to the H_{Aryl} signal of 1,3,5-trimethoxybenzene.

General Procedure for Kinetic Profiling Experiments

To an oven-dried microwave vial, 1,3,5-trimethoxybenzene (0.06 mmol) was added. The microwave vial was sealed with a crimped cap then evacuated and flushed with dry N_2 gas three times followed by the addition of an aliquot of catalyst stock solution (0.5 mL, 0.03 M $Pd_2(dba)_3{\cdot}CHCl_3$, 0.24 M PPh_3 in 1,2-dichloroethane, pre-activated at 80 °C), 1,2-dichloroethane (2.5 mL), and DIPEA (1.2 mmol). The mixture was allowed to stir at 80 °C for 5 min after which stirring was ceased and the reaction mixture was allowed to cool to room temperature. **2** (0.3 mmol) and **1** (0.9 mmol) were then added to the reaction vessel and the reaction mixture was allowed to stir at 80 °C.

The reaction was sampled at regular time intervals using disposable 1 mL syringes sparged with dry N_2 gas immediately prior to use. An aliquot of the reaction mixture (100 μL) was withdrawn, dispensed upon a plug of celite, and eluted with diethyl ether (1.2 mL). The sample was then concentrated *in vacuo*, re-dissolved in $CDCl_3$ (0.6 mL) and analysed by 600 MHz or 400 MHz ^{1}H NMR.

^{1}H NMR Repeatability

Following the formation of product **5(*E*)** *via* the olefin proton signal provided time-course data with noticeably less noise than when tracking the combined and independent methyl ester proton signals of the (*E*)/(*Z*)-**5** (Figure S5a). Comparison of time-course data obtained using 400 MHz *versus* 600 MHz NMR spectrometers showed little difference in the resulting kinetic profiles and so 400 MHz ^{1}H NMR spectroscopy was adopted as the preferred analytical method (Figure S5b).

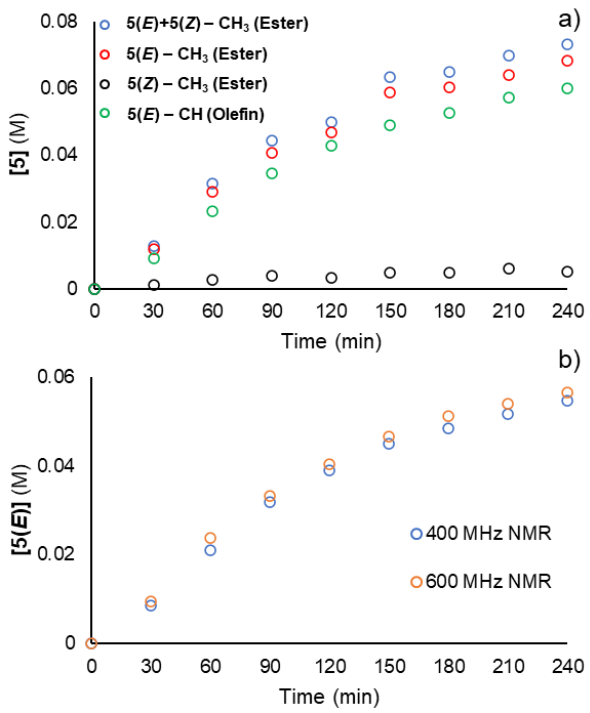


Figure S5: Time-course profiles for the model reaction when observing product formation using various characteristic ^{1}H signals of the resulting (*E*)/(*Z*)-1,2-diarylacrylate **5** (a). Comparison of time-course profiles obtained from 400 MHz versus 600 MHz ^{1}H NMR analysis (b).

The repeatability of standard reaction conditions (Table S5) was monitored across four separate experiments. As well as the standard conditions being highly repeatable (Figure S6), each of the kinetic analysis experiments were conducted with their own reference experiment at standard conditions.

Table S5: Standard reaction conditions for the model palladium-catalysed cross-coupling reaction.

[2] (M)	[1] (M)	[DIPEA] (M)	[$Pd_2(dba)_3$·$CHCl_3$] (M)	[PPh_3] (M)
0.1	0.3	0.4	0.01	0.04

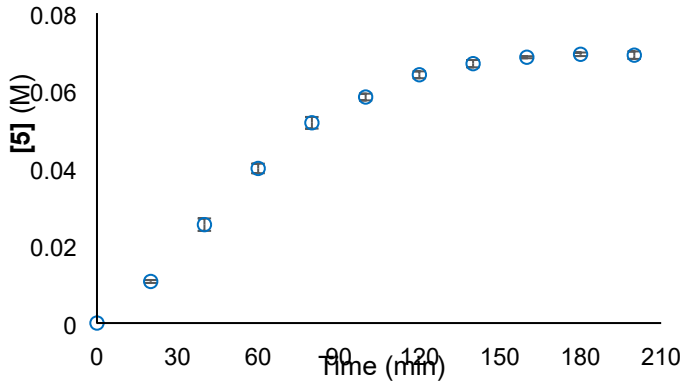


Figure S6: Repeatability of standard reaction conditions averaged over three independent experiments.

Palladium Precursors

Different palladium precursors were investigated, $Pd_2(dba)_3{\cdot}CHCl_3$ and $Pd(PPh_3)_4$, showing identical reaction profiles as well as identical induction periods, suggesting dba is not involved in the induction process (Figure S7).

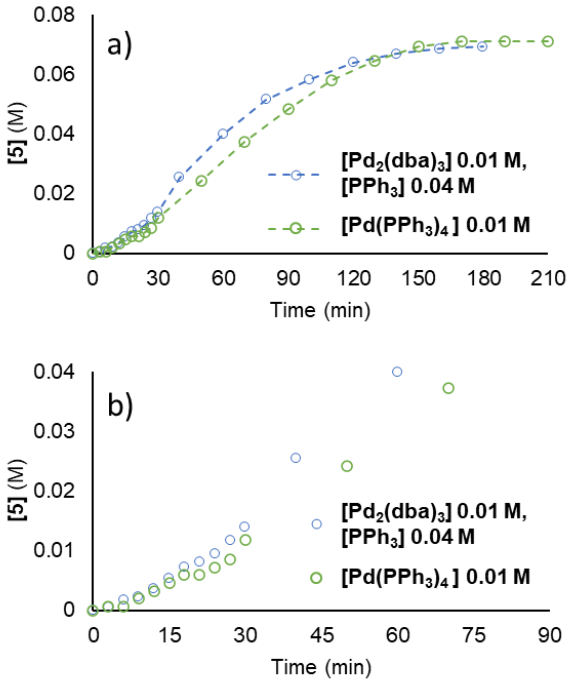


Figure S7: Comparison of palladium precursors $Pd_2(dba)_3$ and $Pd(PPh_3)_4$: a) Full time-course profile, b) induction period only.

Following Phosphonium Salt (9) Formation By ^{1}H NMR

The phosphonium salt by-product **9** remains dissolved in dichloroethane at standard operating conditions and shows a distinct signal at 5.45 ppm (d, J = 14.4 Hz) allowing its concentration to be monitored *via* H^1 NMR analysis (Figure S8).

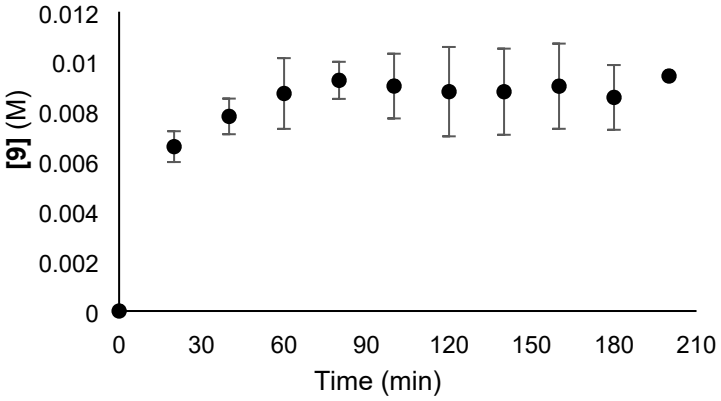


Figure S8: Time-course profile of **9** averaged over three independent experiments under standard reaction conditions.

Analysis of [**9**] under various loadings of $Pd_2(dba)_3$ and PPh_3 showed faster and greater salt formation with increasing [PPh_3]. In contrast, elevated [Pd] slowed the formation of salt **9** and lowered the final concentration (Figure S9).

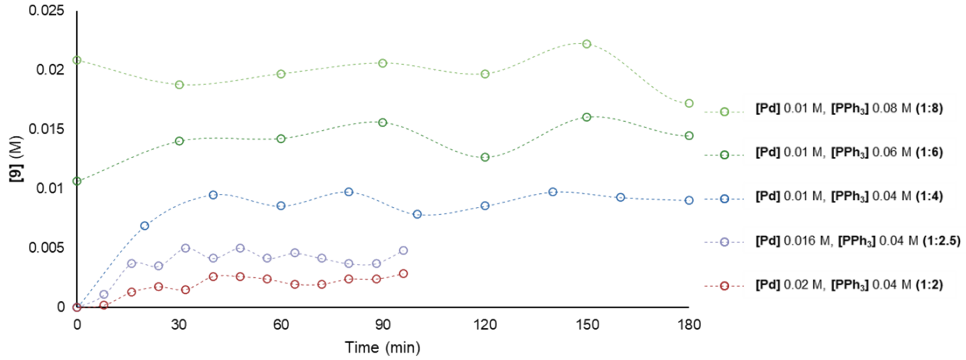


Figure S9: Time-course profiles of **9** formation under various $Pd_2(dba)_3$ and PPh_3 loadings.

Increasing [PPh_3] at a fixed [Pd] leads to elongated induction periods and increased [**9**], however a final maximum [**9**] is achieved rapidly in all cases. This suggests that the origin of the induction period is owed to a different mechanism than **9** formation, as discussed in the main text.

Same Excess Study - Order in $Pd_2(dba)_3{\cdot}CHCl_3$

Pd:PPh_3 1:4 When the t[cat]$^{\alpha}$ parameter, developed by Burés,[18] was employed to determine the order in Pd under same excess conditions at different [Pd] overlay was achieved when the exponent was set equal to 1.30 (Figure S10a). An order in catalyst exceeding 1.0 may imply an on-cycle, catalytically active, Pd dimer,[19,20] marking a mechanistically exceptional reaction.

Auxiliary ligands in Pd pre-catalysts can possess kinetic effects which must be disentangled from that of the Pd.[21]. Dibenzylideneacetone (dba) is known to both stabilize Pd(0) complexes and possess kinetically-relevant effects at the oxidative addition step.[22-24] Due to the use of $Pd_2(dba)_3{\cdot}CHCl_3$, when changing the absolute [Pd] the [dba] also changes However, dba has no effect on the reaction induction period (Figure S7) and was shown to exhibit zero-order kinetics (Figure S14), allowing us to rule out any involvement.

[Pd] and [PPh_3] concentrations were altered simultaneously to hold the ratio of the two constant such that the nature of the active catalyst ([cat]$_{Active}$) was not disturbed,[25] with overlay now describing an order of 0.30 (Figure S10b). As PPh_3 possesses a negative kinetic effect it is likely that the positive kinetic effect of the palladium was counteracted leading to inconclusive results.

Ignoring the induction period[26] to achieve visual overlay resulted in the similar order of 1.15 (Figure S10c).

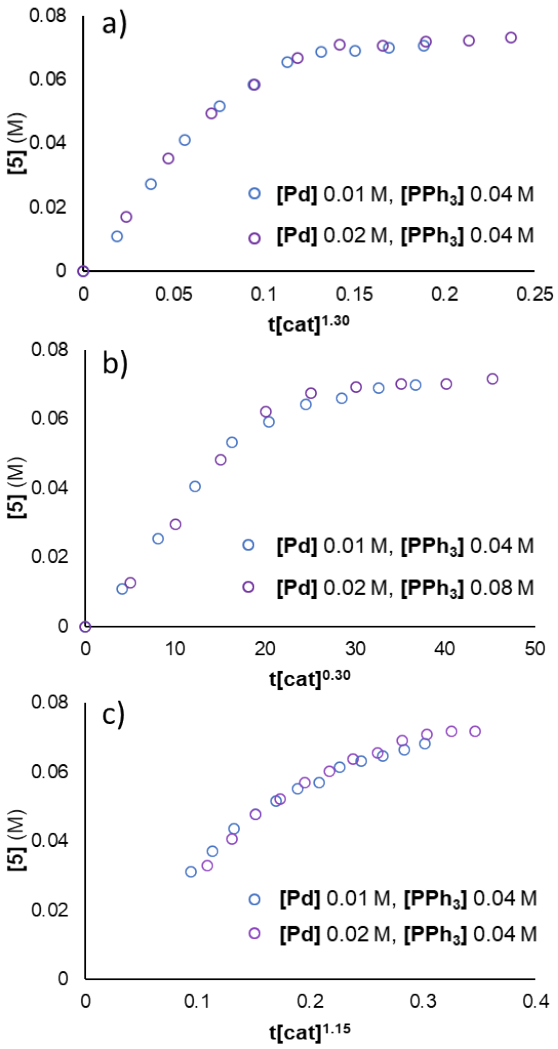


Figure S10: Variable timescale normalization analysis of the model reaction under *same excess* conditions at different [Pd] and: a) Normalized timescale analysis of Pd at fixed [PPh_3], b) Normalized timescale analysis of Pd at [Pd] 0.01 M/0.02 M and [PPh_3] 0.04 M/0.08 M, respectively, c) Post-induction normalized timescale analysis of Pd at fixed [PPh_3].

Influence of PPh_3 Given that each attempt to elucidate the order in Pd resulted in potentially unrealistic orders, the influence of PPh_3 on the system was probed more deeply. The t[cat]$^{\alpha}$ parameter[18] was employed to compare the overlay between different [PPh_3] (Figure S11). The kinetic dependency of PPh_3 remains negative under all loadings studied however the exponent varies according to the initial [PPh_3].

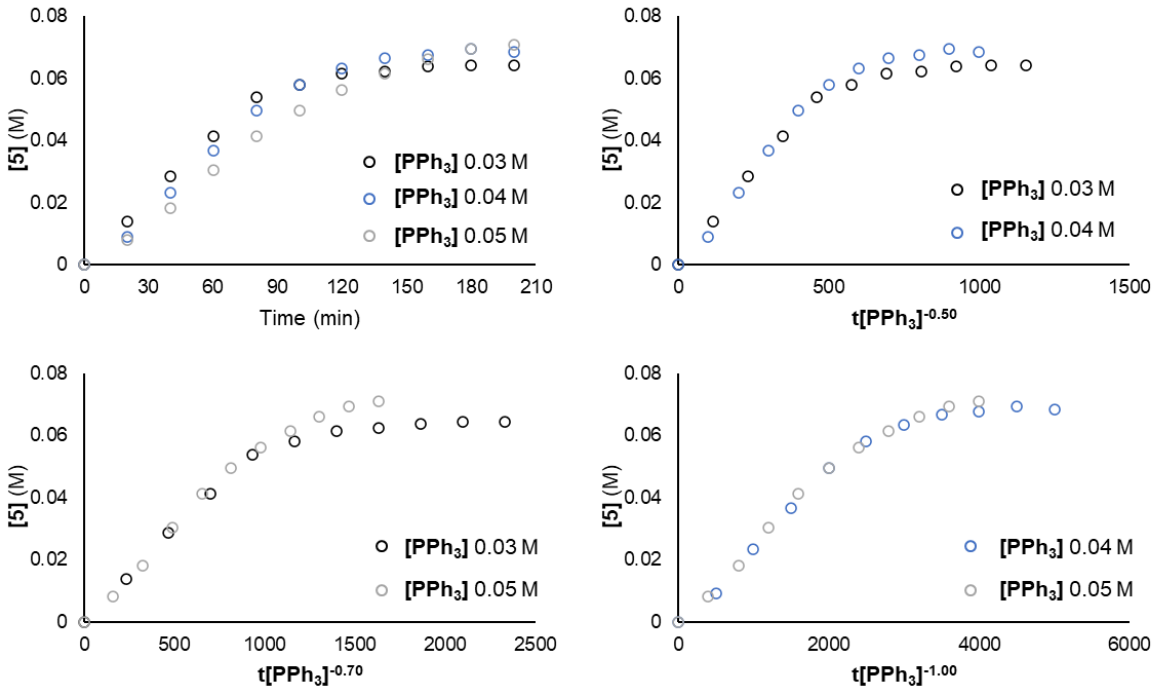


Figure S11: Variable timescale normalization analysis of the model reaction under *same excess* conditions with different [PPh_3] demonstrating the various exponent values lending overlay upon comparison of several [PPh_3].

Flooding conditions are a common approach to determining the order in reaction with respect to a given reagent whilst neglecting the kinetic effects of extraneous reagents. Surprisingly, when attempting to determine the kinetic saturation point of PPh_3 it was found that such a phenomenon wasn't observed even under very high loadings of the phosphine (Figure S12). An increased [PPh_3] at a fixed [Pd] also resulted in reduced reaction rates and product yields for the model reaction (Table S6).

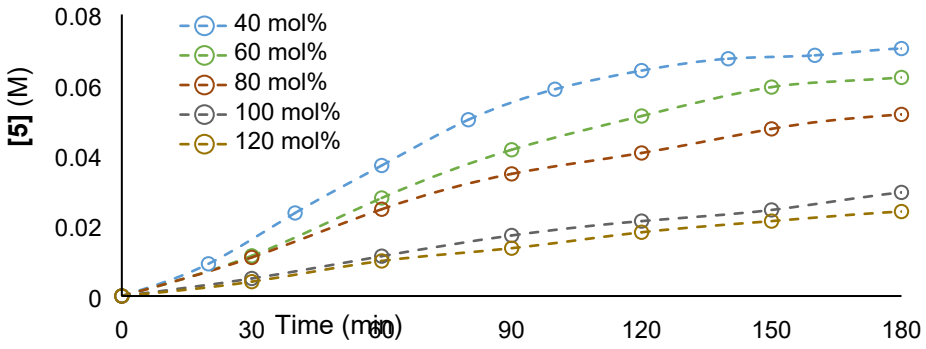


Figure S12: Time-course profiles for the model reaction under different [PPh_3].

Table S6: Yield of **5(*E*)** under various Pd:PPh_3 ratios.

Pd:PPh_3 Ratio	5(*E*) Yield (%)[a]	5(*E*) Yield (%)[b]
1:1	18	-
1:2	56	-
1:3	63	-
1:4	68	-
1:5	71	-
1:6	62	66
1:7	59	64
1:8	52	59
1:10	29	48
1:12	24	40

[**2**] 0.1 M, [**1**] 0.3 M, [DIPEA] 0.4 M, [Pd] 0.01 M, Dichloroethane (3 mL), 80 °C. Yields determined by 400 MHz ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.
[a]Yield after 3 h.
[b]Yield after 24 h.

Judicious Selection of Pd:PPh_3 Evidently, determining the order in Pd under saturation of PPh_3 was not experimentally viable. It was found that the induction period could be removed from the reaction under low a Pd:PPh_3 ratio (see main text). To this extent, the Pd:PPh_3 ratio was selected to minimize the phosphine's intrusive kinetic effects between experiments resulting in an order in Pd of 1.0 as judged by the extent of overlay (Figure S13).

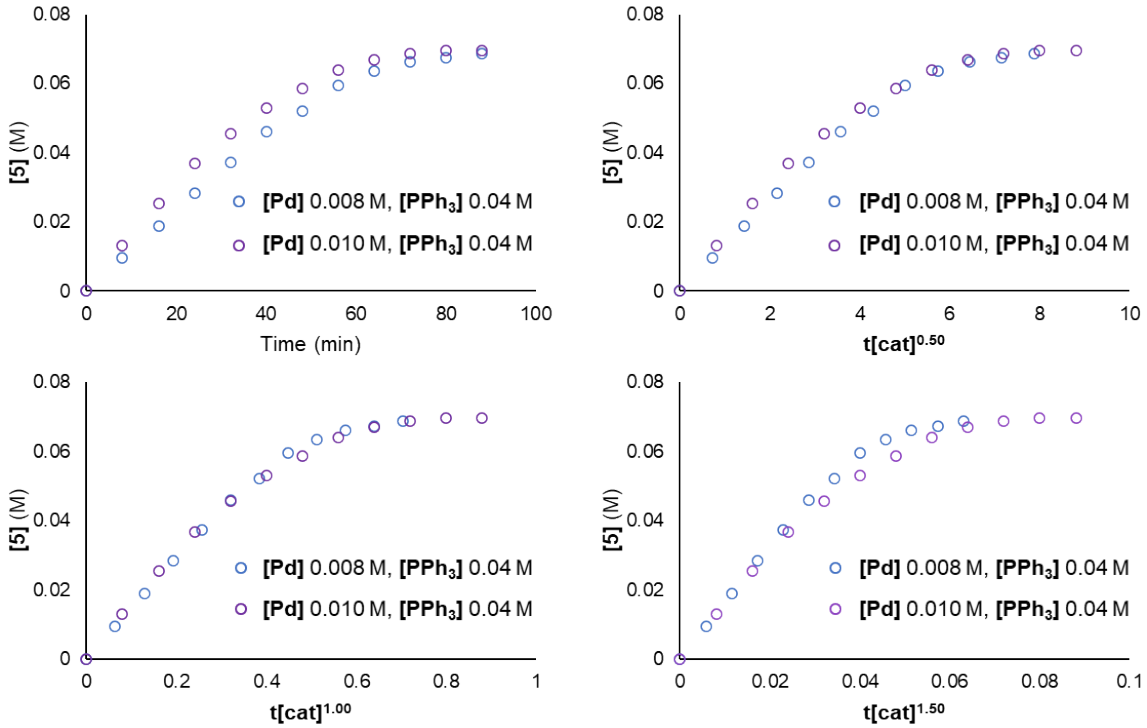


Figure S13: Variable timescale normalization analysis of the model reaction under *same excess* conditions with varying [Pd] demonstrating the overlay, or lack thereof, at different α values.

Different Excess Studies

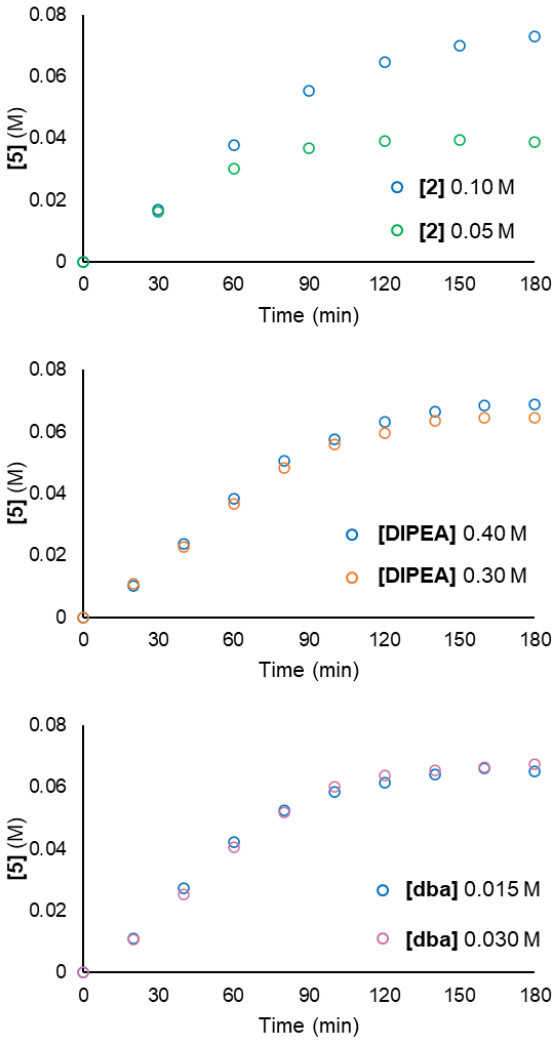


Figure S14: Time-course profiles of the model reaction under different excess conditions with respect to benzyl bromide (**2**), *N,N*-diisopropylethylamine (DIPEA), and dibenzylideneacetone (dba) demonstrating zero order kinetic dependence in each.

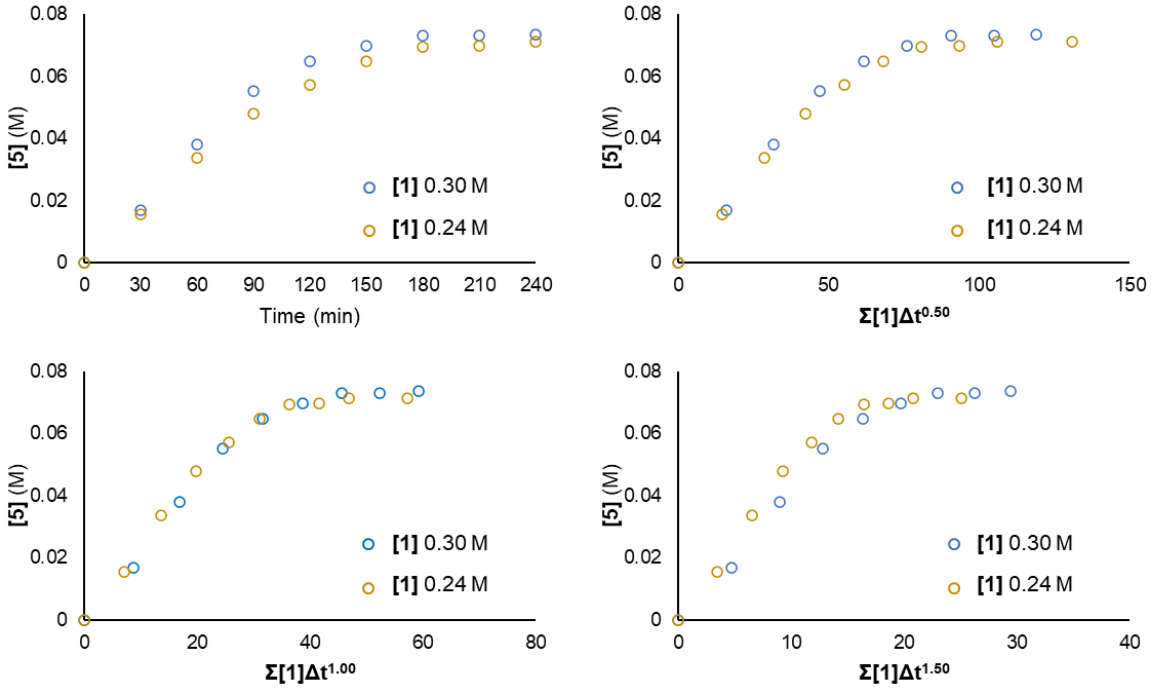


Figure S15: Variable timescale normalization analysis of the model reaction under different excess conditions with respect to methyl phenyldiazoacetate (**1**) demonstrating overlay, or lack thereof, at different exponent values.

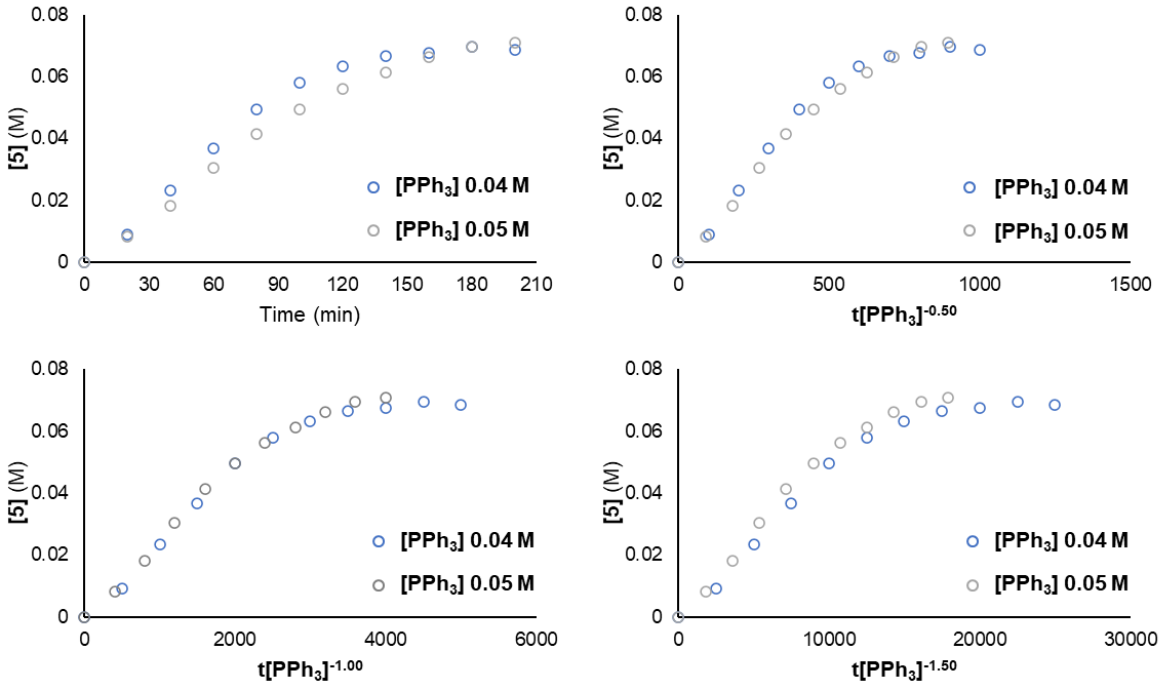


Figure S16: Variable timescale normalization analysis of the model reaction under different excess conditions with respect to PPh_3 demonstrating overlay, or lack thereof, at different exponent values.

Orders During Induction Period

With knowledge that the induction period depended upon the ratio of Pd:PPh_3, further experiments were conducted to ascertain any kinetic differences in the catalytic cycle occurring as a result. During the induction period, **2** was found to possess a partial positive order (Figure S17) implying that the electrophile, which shows global zero order kinetics, is kinetically relevant within this timeframe.

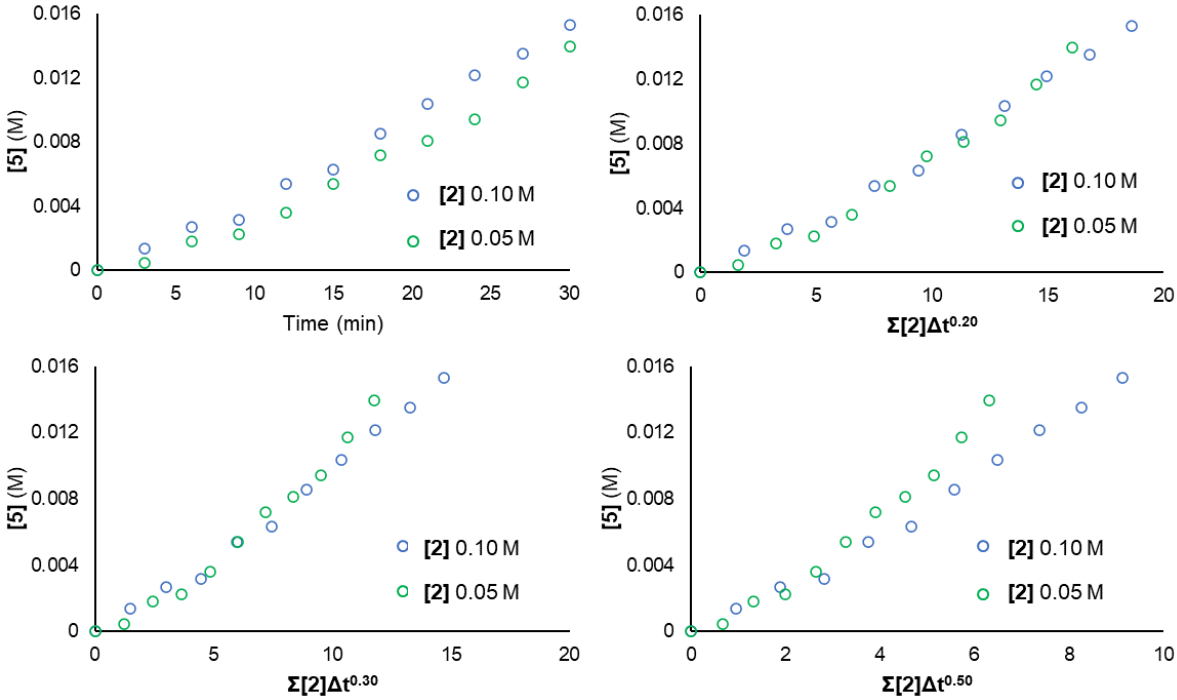


Figure S17: Variable timescale normalization analysis of the model reaction during the induction period under different excess conditions with respect to benzyl bromide (**2**) demonstrating overlay, or lack thereof, at different exponent values.

Different Excess Studies at Lower Pd Loading

A Pd:PPh_3 ratio of 1:8 was adopted, in which the concentration of PPh_3 remained the same but the concentration of Pd was lowered, and further kinetic studies were conducted on this system to understand the irregular nature of the phosphine ligand when attempting to achieve saturation conditions. The catalytic cycle was again shown to be stable under these modified conditions using the same excess protocol (Figure S13a). **2** now demonstrated a half-order dependence whilst **1** maintained global first-order kinetics (Figure S18). This kinetic data is consistent with slower oxidative addition under these conditions.[27]

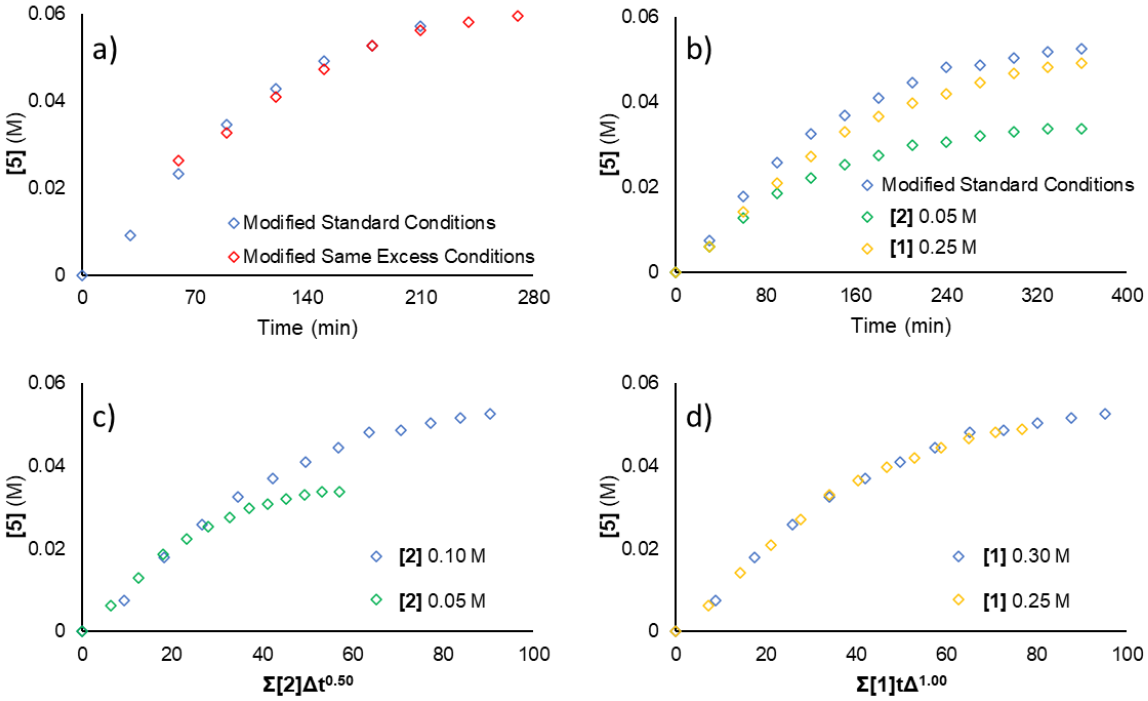


Figure S18: Reaction progress kinetic analysis and variable timescale normalization analysis of the model reaction at a Pd:PPh_3 ratio of 1:8: a) adjusted same excess profile, b) time-course profiles under the modified operating conditions and different [**2**] and [**1**], c) variable timescale normalization analysis under different excess conditions with respect to **2**, d) variable timescale normalization analysis under different excess conditions with respect to **1**. Reaction conditions: [**2**] 0.1 M, [**1**] 0.3 M, [DIPEA] 0.4 M, [Pd] 0.005 M, [PPh_3] 0.04 M, Dichloroethane, 80 °C.

Integral Rate Data

Table S7: Reproducibility of the model reaction time-course under standard conditions averaged over three separate experiments (Figure S6).

Time (min)	[5] (M)	Standard Deviation
0	0	0
20	0.010731415	0.000381891
40	0.025396873	0.001611116
60	0.039901302	0.001233207
80	0.051685594	0.001502026
100	0.058330856	0.000867231
120	0.064075351	0.00088758
140	0.066941653	0.000943761
160	0.068602969	0.000262184
180	0.069360545	0.000458561
200	0.069136096	0.000964867

[2] 0.1 M, [**1**] 0.3 M, [DIPEA**]** 0.4 M, [PPh_3**]** 0.04 M, [Pd**]** 0.01 M, 1,2-dichloroethane (3 mL), 80 °C.

Table S8: Time-course data of the model reaction employing $Pd_2(dba)_3/PPh_3$ versus $Pd(PPh_3)_4$ as the catalyst precursor(s) with emphasis on the induction period (Figure S7).

A[a]		**B**[b]	
Time (min)	**[5] (M)**	**Time (min)**	**[5] (M)**
0	0	0	0
3	0.000450383	3	0.000654022
6	0.001801534	6	0.000654022
9	0.002251917	9	0.001962067
12	0.003603068	12	0.003270111
15	0.005404602	15	0.004578156
18	0.007206136	18	0.0058862
21	0.008106903	21	0.0058862
24	0.009458053	24	0.007194245
27	0.011709971	27	0.008502289
30	0.013961888	30	0.0117724
40	0.025396873	50	0.024198823
60	0.039901302	70	0.037279267
80	0.051685594	90	0.048397646
100	0.058330856	110	0.058207979
120	0.064075351	130	0.064748201
140	0.066941653	150	0.069326357
160	0.068602969	170	0.071288424
180	0.069360545	190	0.071288424

[2] 0.1 M, **[1]** 0.3 M, **[**DIPEA**]** 0.4 M, 1,2-dichloroethane (3 mL), 80 °C.

[a]**[**Pd**]** 0.01 M, **[**PPh_3**]** 0.04 M.

[b]**[**$Pd(PPh_3)_4$**]** 0.01 M.

Table S9: Time-course data and adjusted time-course data under same excess conditions with respect to **2** and **1** (Figure 1).

A[a]		B[b]		Adjusted B	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**	**Adjusted Time (min)[c]**	**Adjusted Concentration (M)[d]**
0	0	0	0	40	0.0335558
20	0.010290445	10	0.003579285	50	0.037135085
40	0.023712765	20	0.007158571	60	0.040714371
60	0.038477317	30	0.011185267	70	0.044741067
80	0.050557405	40	0.015211963	80	0.048767763
100	0.057715976	50	0.020580891	90	0.054136691
120	0.063084904	60	0.025054997	100	0.058610797
140	0.066664189	70	0.029081693	110	0.062637493
160	0.068453832	80	0.032660979	120	0.066216779
180	0.068901243	90	0.034003211	130	0.067559011
200	0.068453832	100	0.034898032	140	0.068453832

[DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C. [Excess] = 0.05 M.
[a]**[2]** 0.10 M, **[1]** 0.30 M.
[b]**[2]** 0.05 M, **[1]** 0.25 M. .
[c]Adjustment Constant = 40
[d]Adjustment Constant = 0.033506748

Table S10: Different excess study in **2** (Figure S14).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
30	0.016884179	30	0.016199685
60	0.03787532	60	0.030117724
90	0.055215827	90	0.036962661
120	0.06479874	120	0.039016142
150	0.06981836	150	0.039472472
180	0.073012664	180	0.038787978
210	0.073012664	210	0.039700636
240	0.073468993	240	0.039700636
300	0.073012664	300	0.039244307

[1] 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C. [Excess] = 0.05 M.
[a]**[2]** 0.10 M.
[b]**[2]** 0.05 M.

Table S11: Different excess study in DIPEA (Figure S14).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
20	0.010290445	20	0.010737856
40	0.023712765	40	0.022817944
60	0.038477317	60	0.036687675
80	0.050557405	80	0.048320352
100	0.057715976	100	0.055926333
120	0.063084904	120	0.059505619
140	0.066664189	140	0.063532315
160	0.068453832	160	0.064427136
180	0.068901243	180	0.064427136
200	0.068453832	200	0.065321957

[2] 0.10 M, **[1]** 0.30 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C. [Excess] = 0.1 M.
[a]**[**DIPEA**]** 0.40 M.
[b]**[**DIPEA**]** 0.30 M.

Table S12: Different excess study in dba (Figure S14).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
20	0.011148106	20	0.010702182
40	0.027201379	40	0.025417682
60	0.042362804	60	0.040579107
80	0.052619062	80	0.051727213
100	0.058416077	100	0.060199774
120	0.061537547	120	0.063767168
140	0.064213092	140	0.065550865
160	0.065996789	160	0.066442714
180	0.065104941	180	0.067334562
200	0.065996789	200	0.069118259

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.4 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C. [Excess] = 0.015 M.
[a]**[**dba**]** 0.015 M.
[b]**[**dba**]** 0.030 M.

Table S13: Different excess study in **1** (Figure S15).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
30	0.016884179	30	0.015515191
60	0.03787532	60	0.033768357
90	0.055215827	90	0.047914561
120	0.06479874	120	0.057041144
150	0.06981836	150	0.06479874
180	0.073012664	180	0.069362031
210	0.073012664	210	0.06981836
240	0.073468993	240	0.071187348
300	0.073012664	300	0.071187348

[2] 0.10 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C. [Excess] = 0.06 M.
[a]**[1]** 0.30 M.
[b]**[1]** 0.24 M.

Table S14: Different excess study in PPh_3 (Figure S11 and S16).

	A[a]	B[b]	C[c]
Time (min)	**[5] (M)**	**[5] (M)**	**[5] (M)**
0	0	0	0
20	0.013793924	0.009037398	0.008086093
40	0.028539152	0.023306974	0.018074796
60	0.041381771	0.036625245	0.030441762
80	0.053748737	0.049467864	0.041381771
100	0.058029609	0.058029609	0.049467864
120	0.061359177	0.063261787	0.056126999
140	0.062310482	0.066591355	0.061359177
160	0.06373744	0.06754266	0.066115702
180	0.064213092	0.06944527	0.06944527
200	0.064213092	0.068493965	0.070872228

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**Pd**]** 0.01 M, 1,2-dichloroethane (3 mL), 80 °C. [Excess] = 0.01 M/0.02 M.
[a]**[**PPh_3**]** 0.03 M.
[b]**[**PPh_3**]** 0.04 M.
[c]**[**PPh_3**]** 0.05 M.

Table S15: Time-course data for the formation of **9** under standard reaction conditions averaged over three independent experiments (Figure S8).

Time (min)	[9] (M)	Standard Deviation (M)
0	0	0
20	0.00659076	0.000618154
40	0.007802436	0.000714354
60	0.00872104	0.001418042
80	0.009248221	0.000743472
100	0.00901857	0.001297626
120	0.008794865	0.001791413
140	0.008792635	0.001727045
160	0.009013368	0.001708124
180	0.008563728	0.001298182
200	0.009420893	0.0000357358

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C.

Table S16: Formation of **9** under various Pd and PPh_3 loadings (Figure S9).

A[a]		B[b]		C[c]	
Time (min)	**[9] (M)**	**Time (min)**	**[9] (M)**	**Time (min)**	**[9] (M)**
0	0	0	0	0	0
8	0.001094992	8	0.000218998	20	0.008213925
16	0.003722972	16	0.00131399	40	0.009582912
24	0.003503974	24	0.001751987	60	0.011180064
32	0.005036962	32	0.001532988	80	0.011180064
40	0.004160969	40	0.00262798	100	0.009354748
48	0.005036962	48	0.00262798	120	0.009354748
56	0.004160969	56	0.002408982	140	0.010723735
64	0.004598965	64	0.001970985	160	0.010039241
72	0.004160969	72	0.001970985	180	0.009354748
80	0.003722972	80	0.002408982	-	-
88	0.003722972	88	0.002408982	-	-

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, 1,2- dichloroethane (3 mL), 80 °C.
[a]**[**Pd**]** 0.016 M, **[**PPh_3**]** 0.04 M.
[b]**[**Pd**]** 0.02 M, **[**PPh_3**]** 0.04 M.
[c]**[**Pd**]** 0.02 M, **[**PPh_3**]** 0.08 M.

Table S17: Formation of **9** under various loadings of PPh_3 at a fixed loading of Pd (Figure S9).

A[a]		B[b]		C[c]	
Time(min)	**[9] (M)**	**Time (min)**	**[9] (M)**	**Time (min)**	**[9] (M)**
0	0	0	0	0	0
20	0.002779595	20	0.006896962	20	0.012842618
40	0.003284975	40	0.009513051	40	0.013080445
60	0.004295737	60	0.008561746	60	0.012604792
80	0.002526904	80	0.009750877	80	0.016172186
100	0.004295737	100	0.007848267	100	0.016172186
120	0.005053808	120	0.008561746	120	0.015696534
140	0.00631726	140	0.009750877	140	0.014983055
160	0.00606457	160	0.009275224	160	0.014269576
180	0.005559189	180	0.009037398	180	0.01593436
200	0.005306499	200	0.008799572	200	0.016647839

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C.
[a]**[**PPh_3**]** 0.03 M.
[b]**[**PPh_3**]** 0.04 M.
[c]**[**PPh_3**]** 0.05 M.

Table S18: Same excess study under different loadings of Pd (Figure S10).

A[a]		**B**[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
20	0.011058921	10	0.017049171
40	0.027186515	20	0.035480706
60	0.041010167	30	0.049304358
80	0.0516083	40	0.058520126
100	0.058520126	50	0.066814317
120	0.065431952	60	0.070961413
140	0.068657471	70	0.070500624
160	0.069118259	80	0.071882989
180	0.070039836	90	0.072343778
200	0.070500624	100	0.073265355

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, 1,2- dichloroethane (3 mL), 80 °C.
[a]**[**Pd**]** 0.01 M.
[b]**[**Pd**]** 0.02 M.

Table S19: Same excess study under different [Pd] and [PPh_3] where Pd:PPh_3 = 1:4 (Figure S10).

A[a]		**B**[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
20	0.0109519	20	0.012777216
40	0.025554432	40	0.029661395
60	0.040613294	60	0.04837089
80	0.053390511	80	0.062060765
100	0.05932279	100	0.067536714
120	0.06434241	120	0.069362031
140	0.066167727	140	0.070274689
160	0.068905702	160	0.070274689
180	0.06981836	180	0.071643677

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, 1,2- dichloroethane (3 mL), 80 °C.
[a]**[**Pd**]** 0.01 M, **[**PPh_3**]** 0.04 M.
[b]**[**Pd**]** 0.02 M, **[**PPh_3**]** 0.08 M.

Table S20: Attempted determination of saturation conditions with respect to PPh_3 (Figure S12).

Time (min)	[5] (M)[a]	[5] (M)[b]	[5] (M)[c]	[5] (M)[d]	[5] (M)[e]	[5] (M)[f]
0	0	0	0	0	0	0
13	0.018241275	-	-	-	-	-
20	-	0.009150366	-	-	-	-
28	0.032974612	-	-	-	-	-
30	-	-	0.011415661	0.010959034	0.004981469	0.004075748
40	-	0.023598311	-	-	-	-
42	0.044200012	-	-	-	-	-
56	0.052619062	-	-	-	-	-
60	-	-	0.027854212	0.024657827	0.011321521	0.009962939
70	0.054022237	-	-	-	-	-
60	-	0.037083061	-	-	-	-
80	-	0.050086212	-	-	-	-
84	0.055425412	-	-	-	-	-
90	-	-	0.041553006	0.034703609	0.017208712	0.013585826
98	0.056126999	-	-	-	-	-
100	-	0.058754979	-	-	-	-
112	0.056126999	-	-	-	-	-
120	-	0.06405256	0.051142161	0.040639753	0.02128446	0.018114434
126	0.056828587	-	-	-	-	-
140	0.056126999	0.067423747	-	-	-	-
150	-	-	0.059361436	0.047489149	0.024454486	0.02128446
154	0.055425412	-	-	-	-	-
160	-	0.068386943	-	-	-	-
168	0.056126999	-	-	-	-	-
180	-	0.070313336	0.062101195	0.051598787	0.029435955	0.024001625
200	-	0.06935014	-	-	-	-
210	-	-	-	-	0.03170026	0.025360208
240	-	-	0.068037339	0.056165051	0.033511703	0.027624512

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**Pd**]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C.
[a]**[**PPh_3**]** 0.02 M. [b]**[**PPh_3**]** 0.04 M. [c]**[**PPh_3**]** 0.06 M. [d]**[**PPh_3**]** 0.08 M. [e]**[**PPh_3**]** 0.10 M. [f]**[**PPh_3**]** 0.12 M.

Table S21: Time-course data and adjusted time-course data under same excess conditions with respect to **2** and **1** at a Pd:PPh_3 = 1:8 (Figure S18).

A[a]		B[b]		Adjusted B	
Time (min)	[5] (M)	Time (Min)	[5] (M)	Adjusted Time (min)[c]	Adjusted Concentration (M)[d]
0	0	0	0	60	0.026380879
30	0.009096855	30	0.006367798	90	0.032748677
60	0.02319698	60	0.014554968	120	0.040935846
90	0.034568048	90	0.020922766	150	0.047303645
120	0.042755217	120	0.026380879	180	0.052761758
150	0.049123016	150	0.030019621	210	0.056400499
180	0.052761758	180	0.031838992	240	0.05821987
210	0.057310185	210	0.03320352	270	0.059584399
240	0.060039241	240	0.033658363	300	0.060039241

[DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.005 M, 1,2- dichloroethane (4 mL), 80 °C. [Excess] = 0.05 M.
[a]**[2]** 0.10 M, **[1]** 0.30 M.
[b]**[2]** 0.05 M, **[1]** 0.25 M.
[c]Adjustment Constant = 60
[d]Adjustment Constant = 0.026380879

Table S22: Different excess study in **2** at Pd:PPh_3 = 1:8 (Figure S18).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
30	0.007605981	30	0.006263749
60	0.017896427	60	0.012974909
90	0.025949819	90	0.018791248
120	0.032660979	120	0.022370533
150	0.037135085	150	0.025502408
180	0.041161781	180	0.027739461
210	0.044741067	210	0.029976515
240	0.048320352	240	0.030871336
270	0.048767763	270	0.032213568
300	0.050557405	300	0.033108389
330	0.051899637	330	0.034003211
360	0.052794459	360	0.034003211

[1] 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.005 M, 1,2- dichloroethane (3 mL), 80 °C. [Excess] = 0.05 M. Experimental outcome confirmed over three independent experiments.

[a]**[2]** 0.10 M.

[b]**[2]** 0.05 M.

Table S23: Different excess study in **1** at Pd:PPh_3 = 1:8 (Figure S18).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
30	0.007605981	30	0.006263749
60	0.017896427	60	0.014317141
90	0.025949819	90	0.021028301
120	0.032660979	120	0.027292051
150	0.037135085	150	0.033108389
180	0.041161781	180	0.036687675
210	0.044741067	210	0.039819549
240	0.048320352	240	0.042056603
270	0.048767763	270	0.044741067
300	0.050557405	300	0.04697812
330	0.051899637	330	0.048320352
360	0.052794459	360	0.049215173

[2] 0.10 M, **[**DIPEA] 0.40 M, **[**PPh_3**]** 0.04 M, **[**Pd**]** 0.005 M, 1,2-dichloroethane (3 mL), 80 °C. [Excess] = 0.05 M. Experimental outcome confirmed over three independent experiments.

[a]**[1]** 0.30 M.

[b]**[1]** 0.25 M.

Table S24: Same excess study under different loadings of Pd in the presence of extraneous **9**.

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
20	0.011787264	10	0.015867471
40	0.02584131	20	0.033095012
60	0.038081931	30	0.044882276
80	0.049869196	40	0.053949402
100	0.057122897	50	0.062563173
120	0.062563173	60	0.067550092
140	0.06664338	70	0.069363517
160	0.069816874	80	0.071176943
180	0.071630299	90	0.072990368
200	0.072990368	100	0.073443724

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, **[9]** 0.01 M, 1,2- dichloroethane (3 mL), 80 °C.

[a]**[**Pd**]** 0.01 M.

[b]**[**Pd**]** 0.02 M.

Table S25: Post-induction kinetic analysis under different loadings of Pd.

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
40	0.022742137	20	0.027647304
50	0.031214698	25	0.032998395
60	0.037011713	30	0.040579107
70	0.043700577	35	0.047713895
80	0.047713895	40	0.052173138
90	0.051727213	45	0.057078304
100	0.055294607	50	0.060199774
110	0.057078304	55	0.063767168
120	0.061537547	60	0.065550865
130	0.063321244	65	0.069118259
140	0.064659017	70	0.070901956
150	0.066442714	75	0.071793805
160	0.068226411	80	0.071793805

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, 1,2- dichloroethane (4 mL), 80 °C.
[a]**[**Pd**]** 0.01 M.
[b]**[**Pd**]** 0.02 M.

Table S26: Same excess study under judicious loadings of Pd (Figure 3).

A[a]		B[b]	
Time (min)	**[5] (M)**	**Time (Min)**	**[5] (M)**
0	0	0	0
8	0.009635928	8	0.013139901
16	0.018833859	16	0.025403809
24	0.028469786	24	0.036791724
32	0.03722972	32	0.045551658
40	0.045989655	40	0.052997602
48	0.052121608	48	0.058691559
56	0.059567553	56	0.06394752
64	0.063509523	64	0.067013497
72	0.066137503	72	0.068765483
80	0.067451493	80	0.069641477
88	0.068765483	88	0.069641477

[2] 0.10 M, **[1]** 0.30 M, **[**DIPEA**]** 0.40 M, **[**PPh_3**]** 0.04 M, 1,2- dichloroethane (4 mL), 80 °C.
[a]**[**Pd**]** 0.016 M.
[b]**[**Pd**]** 0.020 M.

Spectroscopic Analysis

General Experimental Procedure for NMR Experiments

To an oven-dried, medium-pressure rated, J-Young NMR tube, $Pd_2(dba)_3 \cdot CHCl_3$ (0.003 mmol), PPh_3 (0.024 mmol), 1,3,5-trimethoxybenzene (0.06 mmol) and/or a sealed capillary containing tributylphosphine oxide (0.049 M in d8-toluene) were added. The vessel was inserted into a sealed Schenk-to-NMR tube adapter then evacuated and flushed with N_2 gas in triplicate. d8-Toluene (0.6 mL) and DIPEA (0.24 mmol) were added and the solution was gently heated until a homogeneous, gold solution was achieved. The mixture was allowed to cool to room temperature before the benzyl bromide (0.06 mmol) and diazo compound (0.18 mmol) derivatives were added. Under a positive pressure of N_2 gas, the reaction vessel was removed from the Schlenk-to-NMR tube adapter and sealed to maintain an inert reaction atmosphere.

The reaction was then immediately loaded onto a Bruker Avance Series 600 MHz NMR spectrometer with the sample probe pre-heated at 80 °C wherein spectroscopic analysis was conducted at the same temperature.

Example Online NMR Analysis

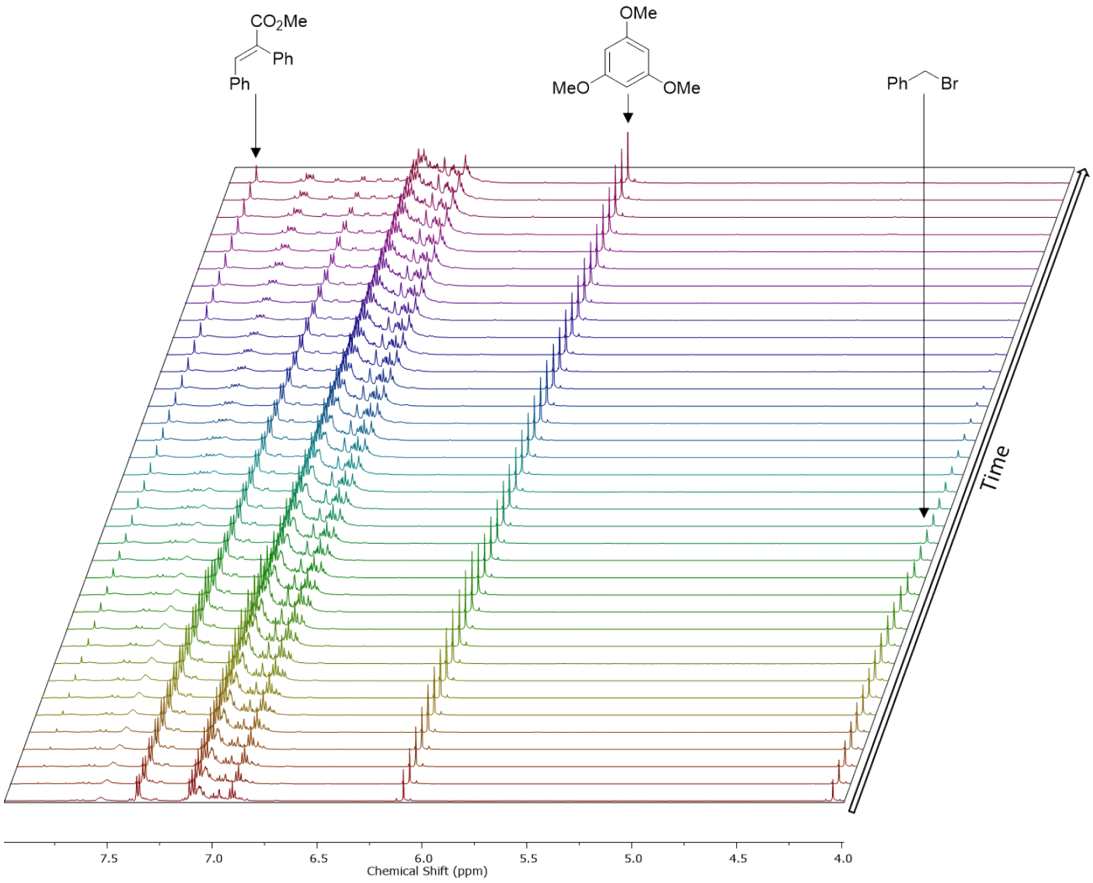


Figure S19: Stacked ^{1}H NMR spectra of the model reaction over the intended reaction time under standard online NMR reaction conditions in d8-toluene.

Figure S20: Time-course profile of the model reaction in d8-toluene monitored *via* online NMR spectroscopy.

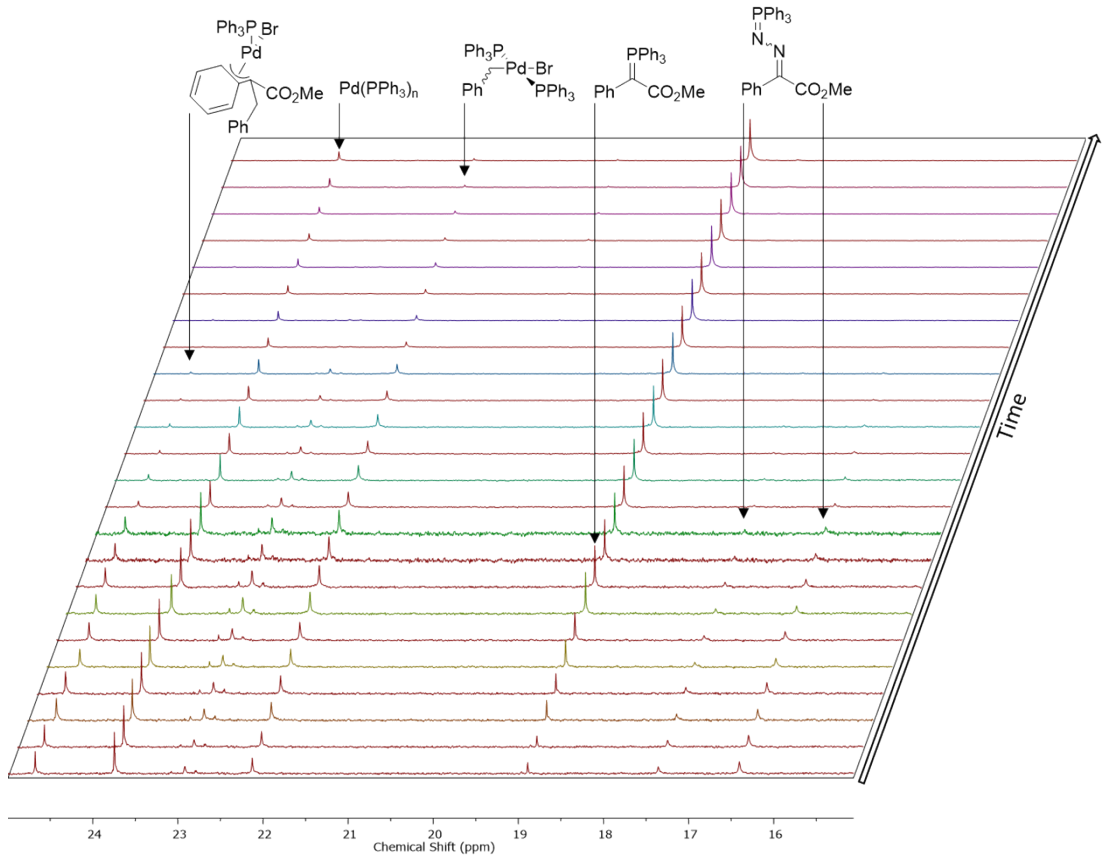


Figure S21: Stacked $^{31}P\{^{1}H\}$ NMR spectra of the model reaction over the intended reaction time under standard online NMR reaction conditions in toluene-d8.

All phosphorous-containing species are observed to decrease over time by $^{31}P\{^{1}H\}$ NMR with the exception of phosphorane **8** due to its formation being irreversible. No free PPh_3 is observed throughout the reaction time-course.

Additional Spectra of the Model Reaction

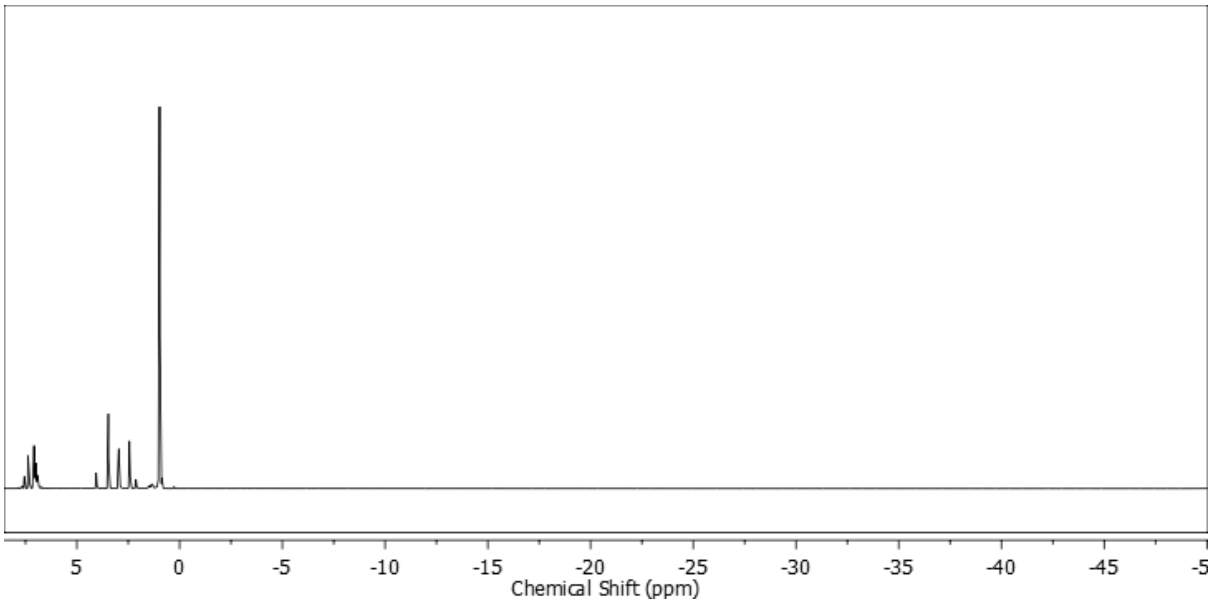


Figure S22: Extended upfield ^{1}H NMR spectrum of the model reaction with the δ8.00 to -50.00 ppm region enhanced to demonstrate the lack of a palladium-hydride signal under standard online NMR reaction conditions.

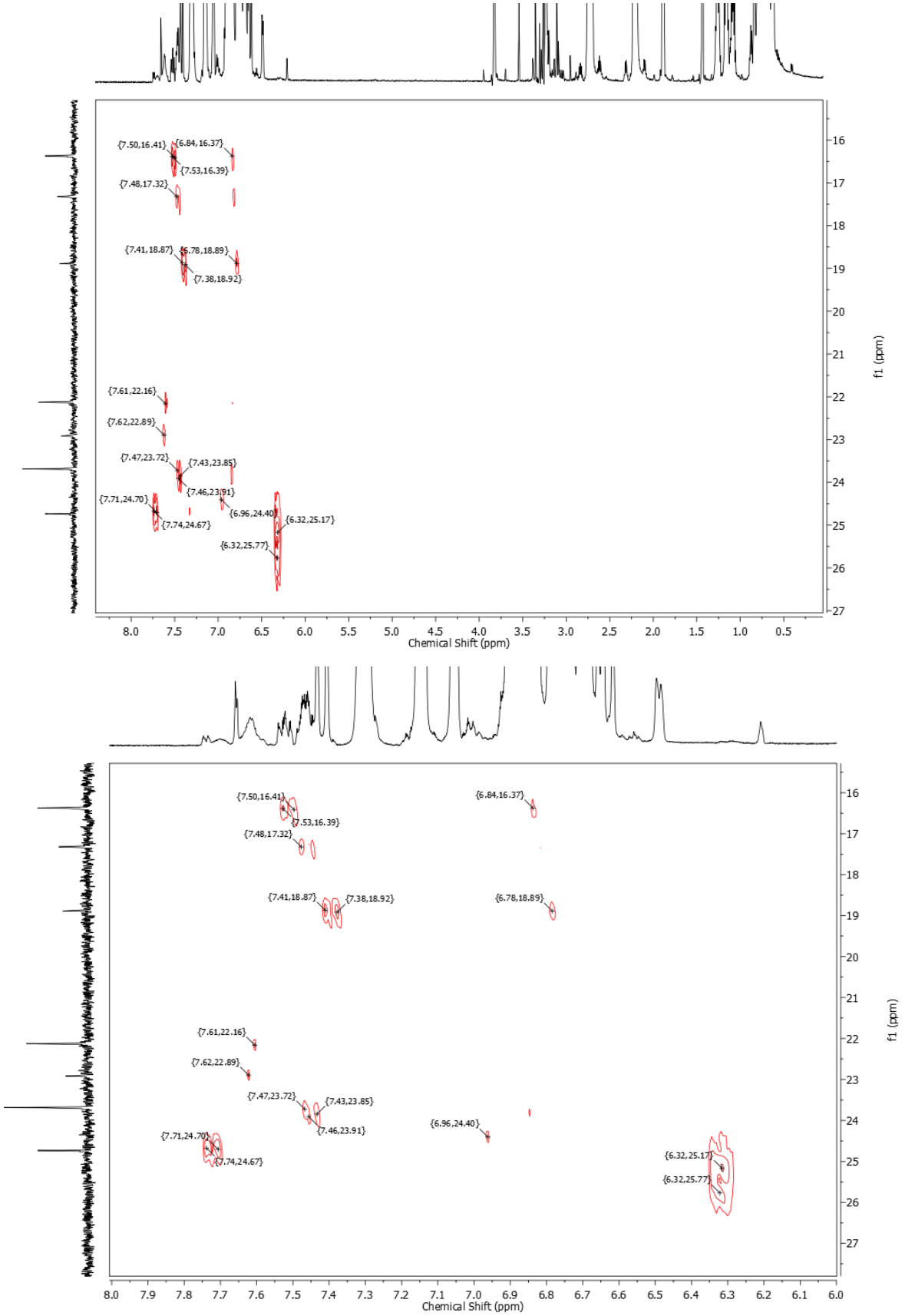


Figure S23: ^{31}P-^{1}H HMBC Spectrum of the model reaction under standard online NMR reaction conditions (top) with the δ8.00 – 6.00 region enhanced (bottom).

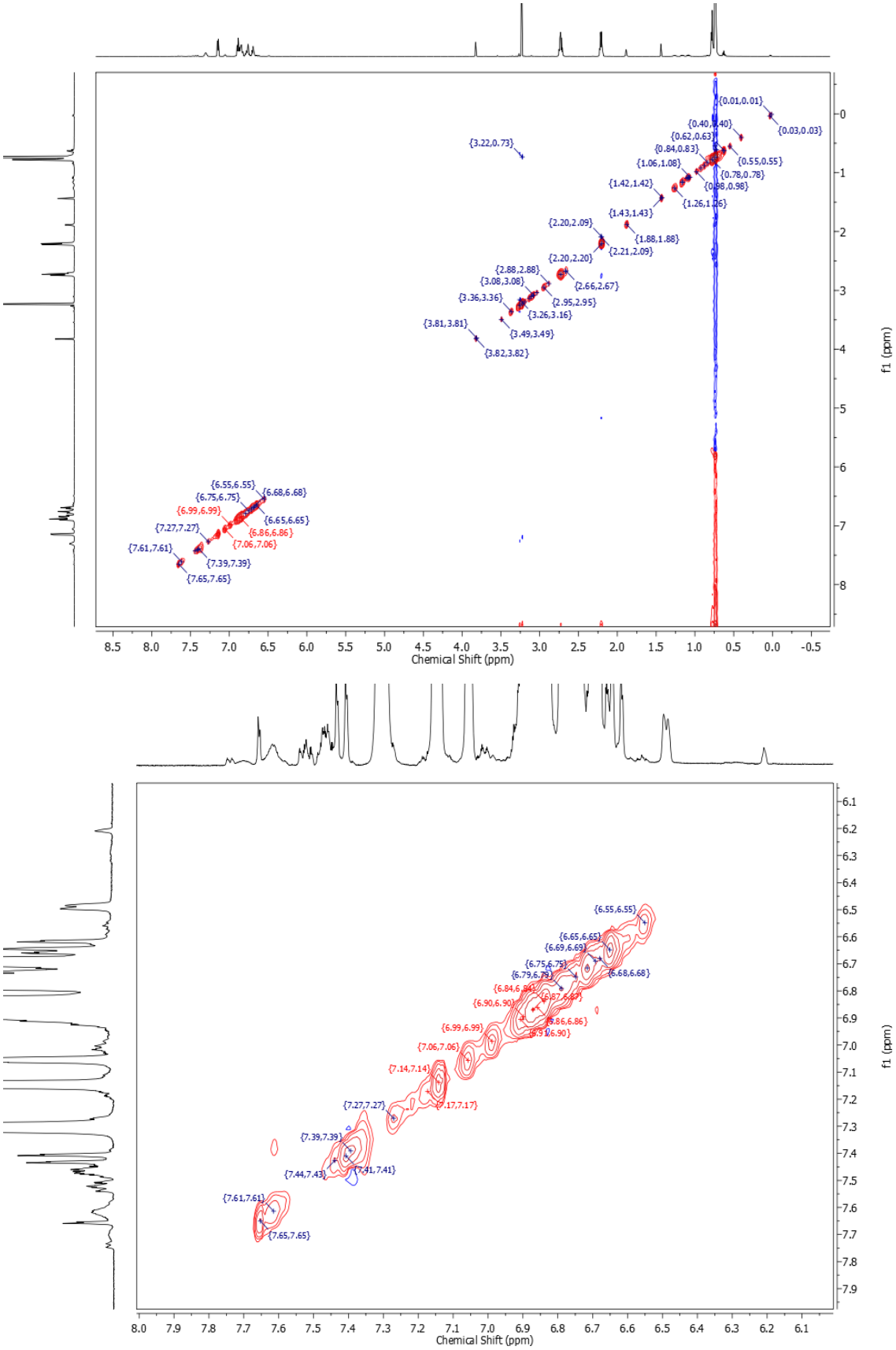
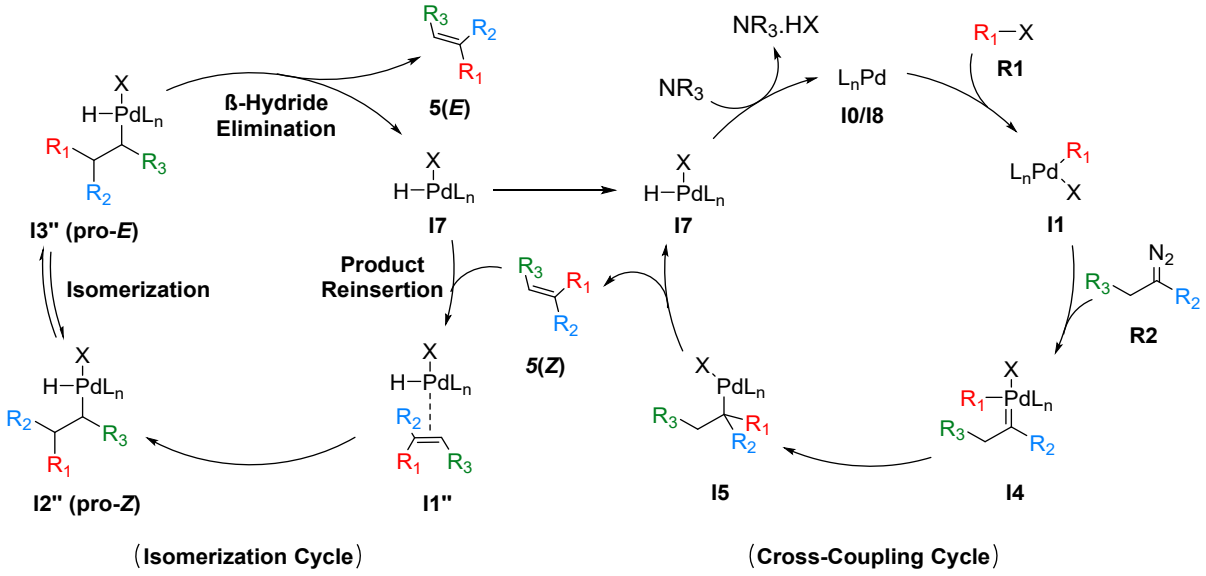


Figure S24: NOESY Spectrum of the model reaction under standard online NMR reaction conditions (top) with the δ8.00 – 6.00 ppm region enhanced (bottom).

Product Re-Insertion Experiments

Product isomerization has previously been observed in palladium-catalysed Heck-type catalytic cycles.[28-30] (*E*)-stereoselectivity in the model cross-coupling reaction could be consequential from the initial formation of **5(*Z*)**, wherein the stereochemistry is set by the preferential sterically unstrained *trans*-geometry of the β-hydride elimination step, followed by re-insertion of the into the catalytic cycle *via* Pd-hydride species **I7**. Subsequent palladium-catalysed isomerization of **5(*Z*)** may then release **5(*E*)** as the apparent product (**Scheme S1**).

This was probed by doping the model reaction with **5(*Z*)**. If product re-insertion and subsequent isomerization were occurring, the presence of **5(*Z*)** dopant would cause an initial spike in the formation of **5(*E*)** in concert with a decline in **5(*Z*)**. Experimentally, both **5(*E*)** and **5(*Z*)** formed steadily throughout the reaction thus eliminating this isomerization mechanism as the origin of (*E*)-stereoselectivity (**Figure S25**).



Scheme S1: Mechanistic proposal for the hypothetical product isomerisation scenario, where R_1 (red) and R_3 (green) are the highest priority groups according to the Cahn-Ingold-Prelog sequence rules.

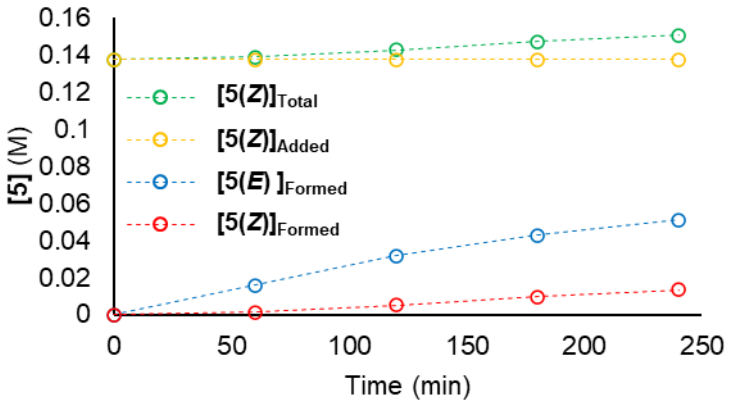


Figure S25: Formation of (*E*)/(*Z*)-**5** in the presence of extraneous **5(*Z*)** dopant in the model cross-coupling system.

NMR Spectra of Novel/Uncharacterised Compounds

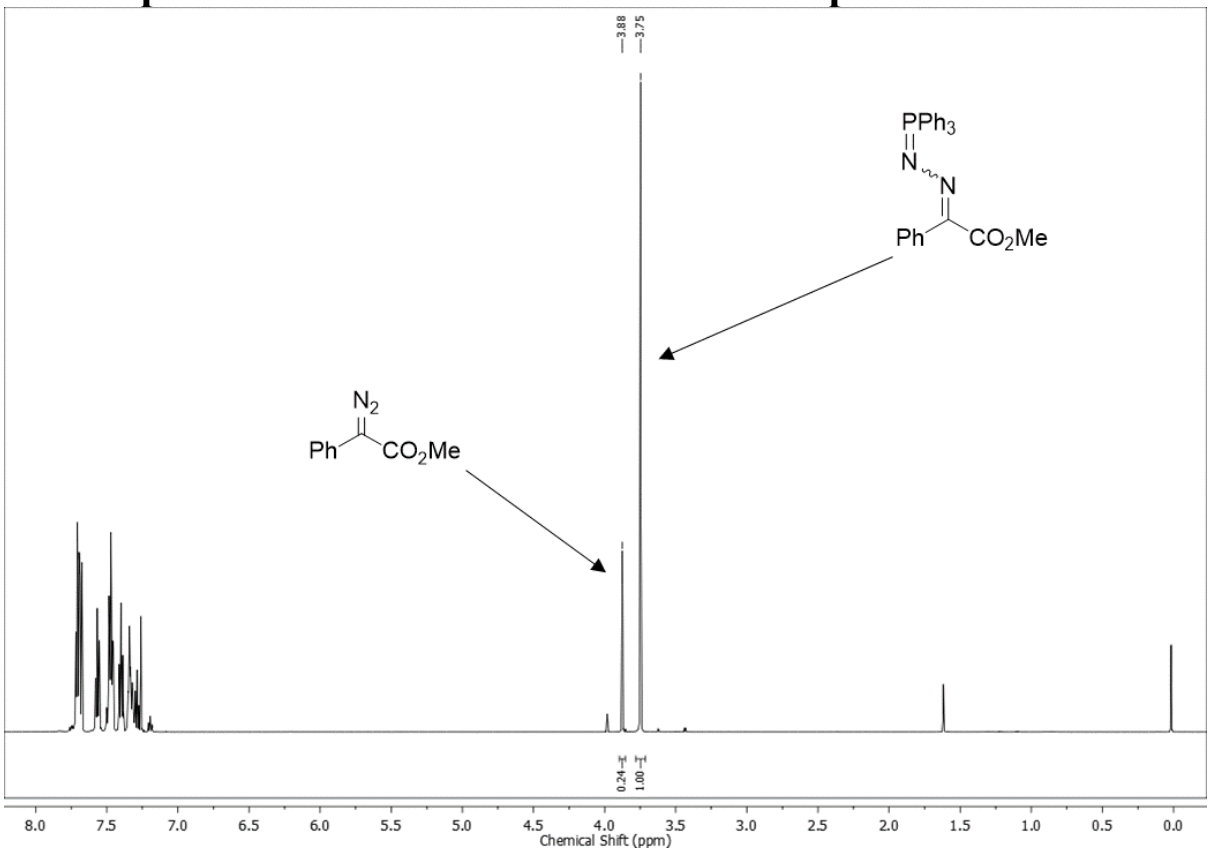


Figure S26: 600 MHz ^{1}H NMR showing decomposition of **7** to liberate **1** upon dissolution in $CDCl_3$.

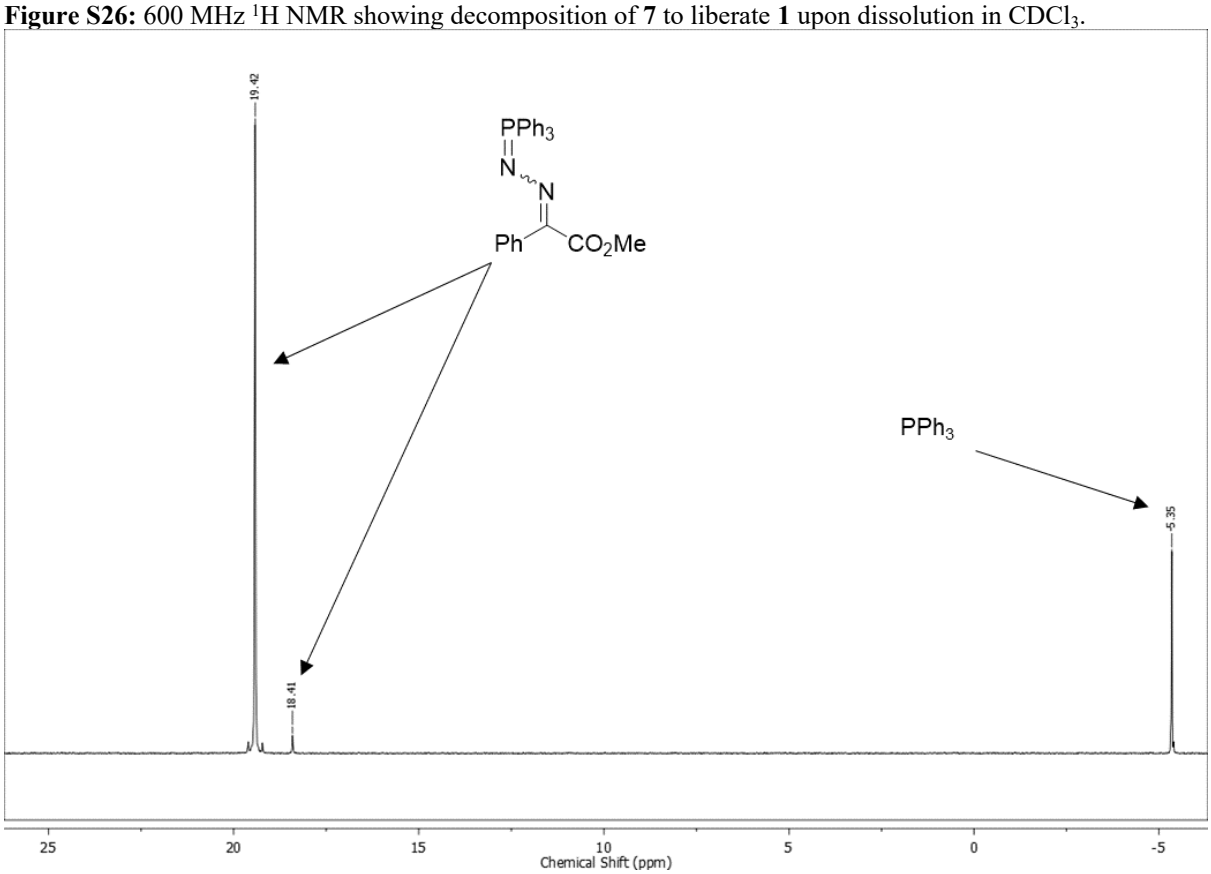


Figure S27: 243 MHz $P^{31}\{^{1}H\}$ NMR showing decomposition of **7** to liberate PPh_3 upon dissolution in $CDCl_3$.

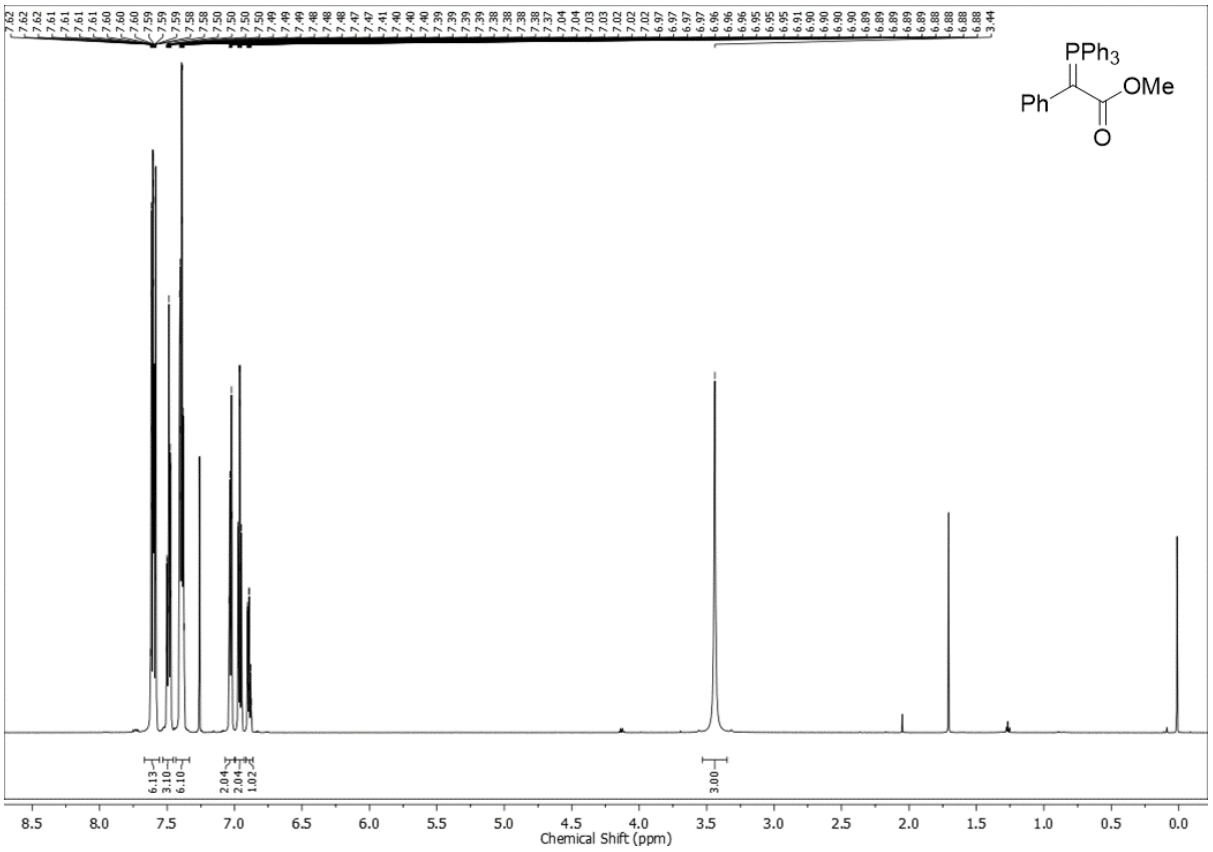


Figure S28: 600 MHz ^{1}H NMR of **8** in $CDCl_3$.

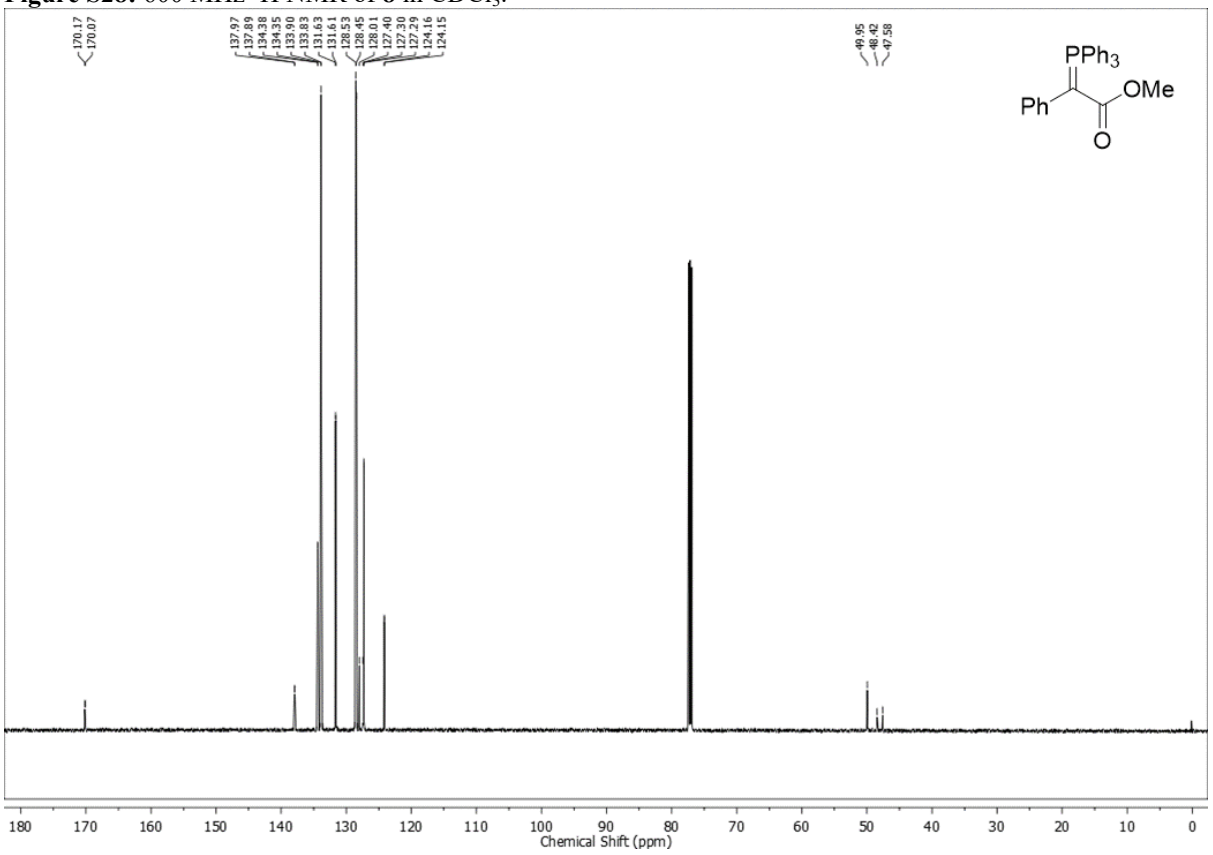


Figure S29: 151 MHz ^{13}C NMR of **8** in $CDCl_3$.

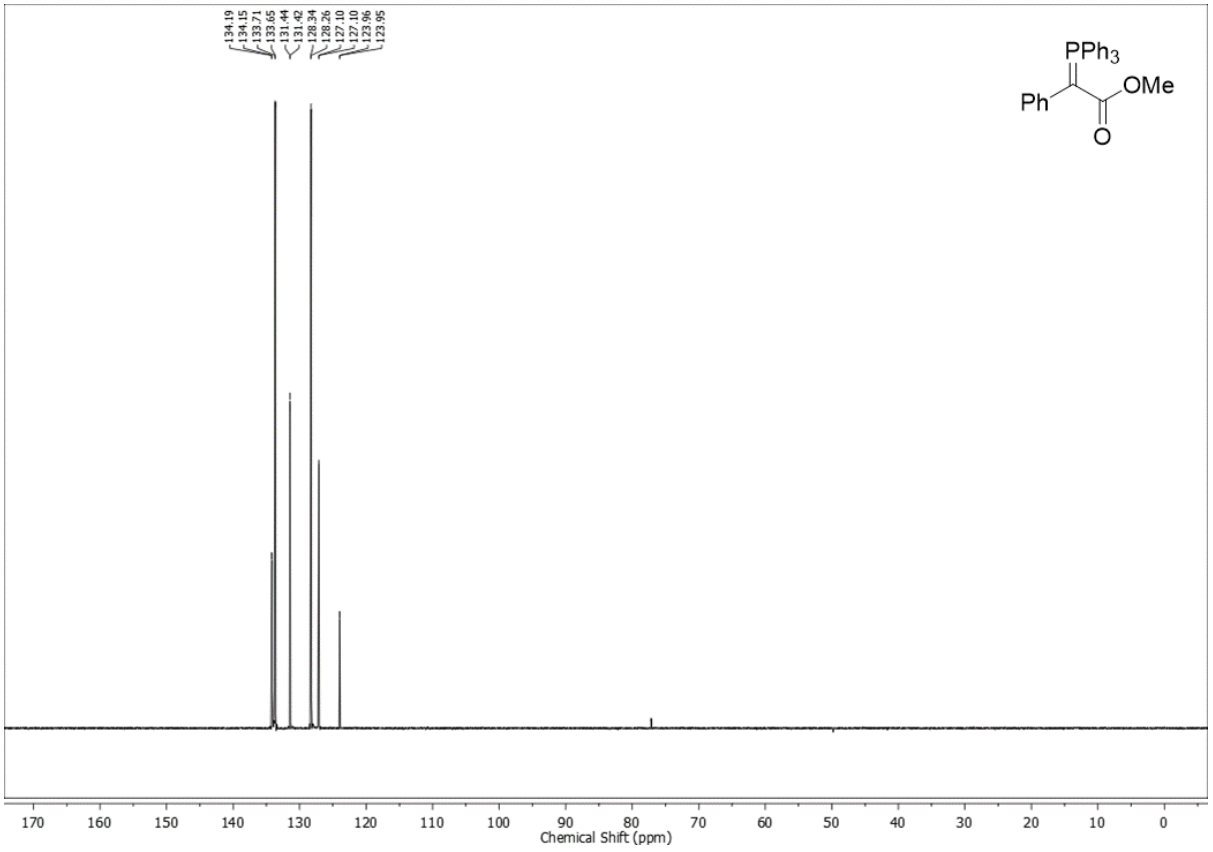


Figure S30: 151 MHz DEPT-90 NMR of **8** in $CDCl_3$.

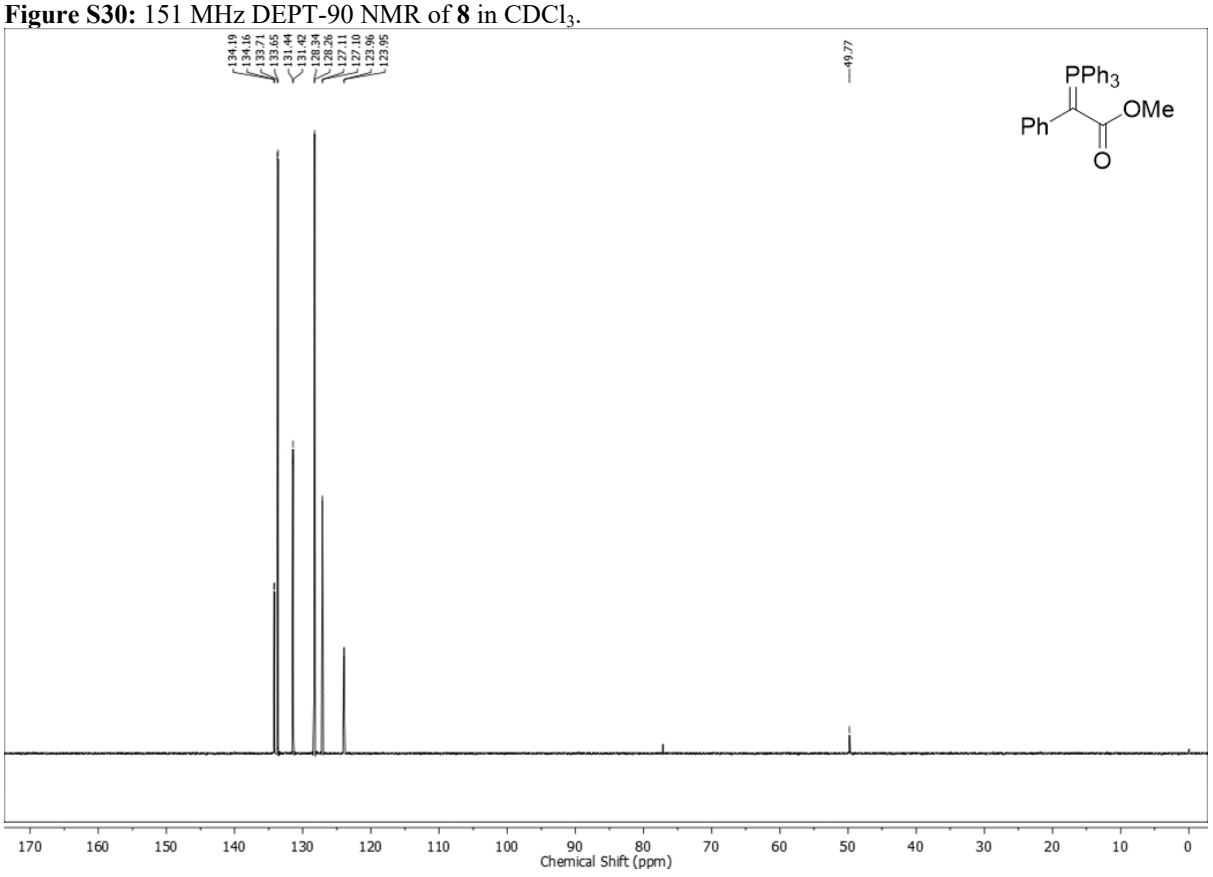


Figure S31: 151 MHz DEPT-135 NMR of **8** in $CDCl_3$.

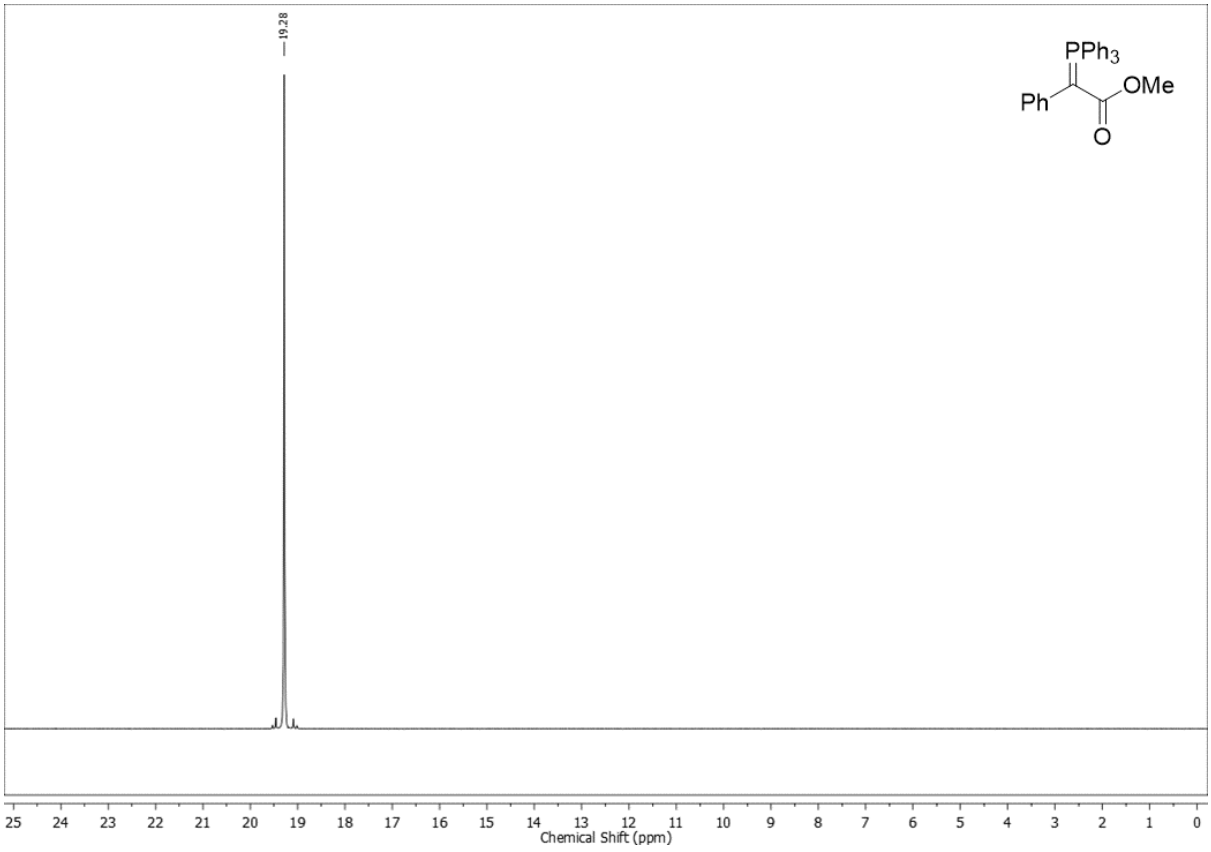


Figure S32: 243 MHz $^{31}P\{^{1}H\}$ NMR of **8** in $CDCl_3$.

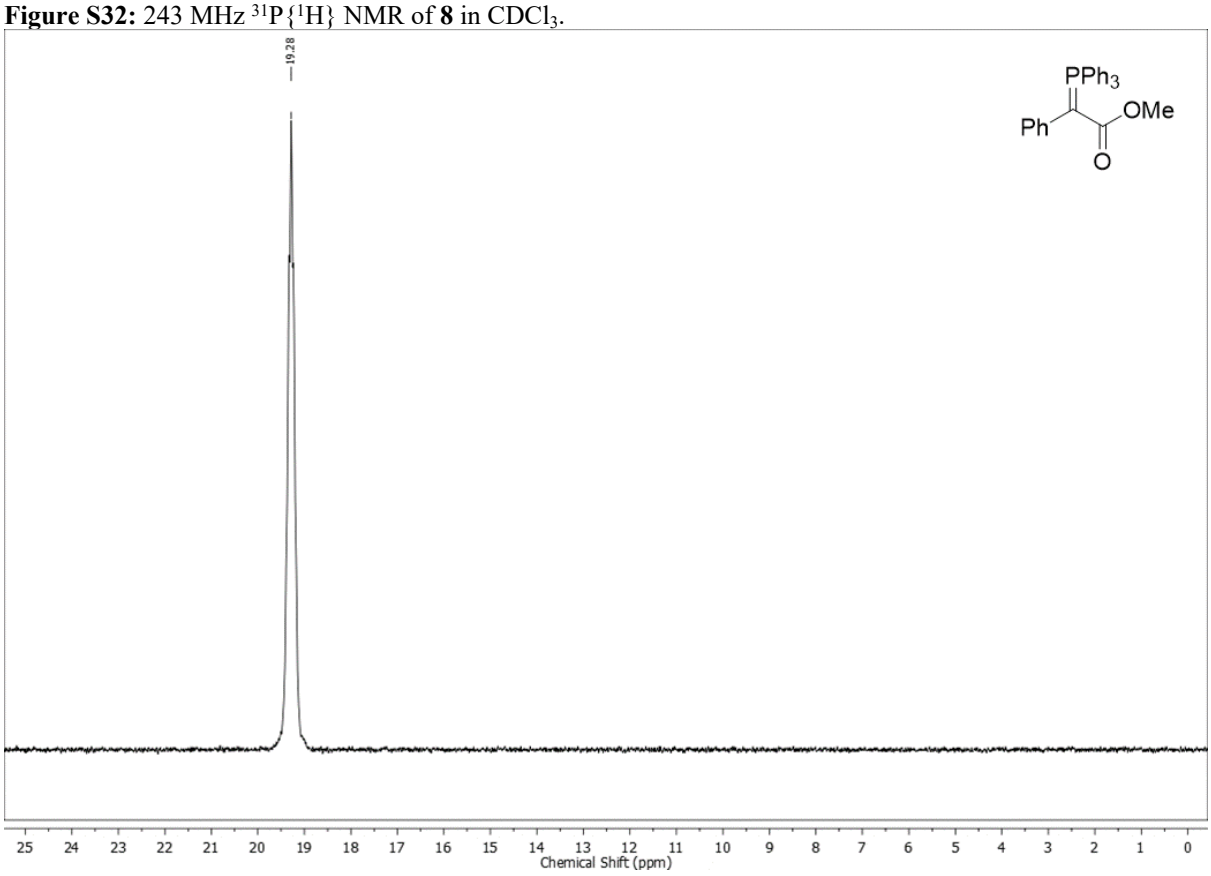


Figure S33: 243 MHz ^{31}P NMR of **8** in $CDCl_3$.

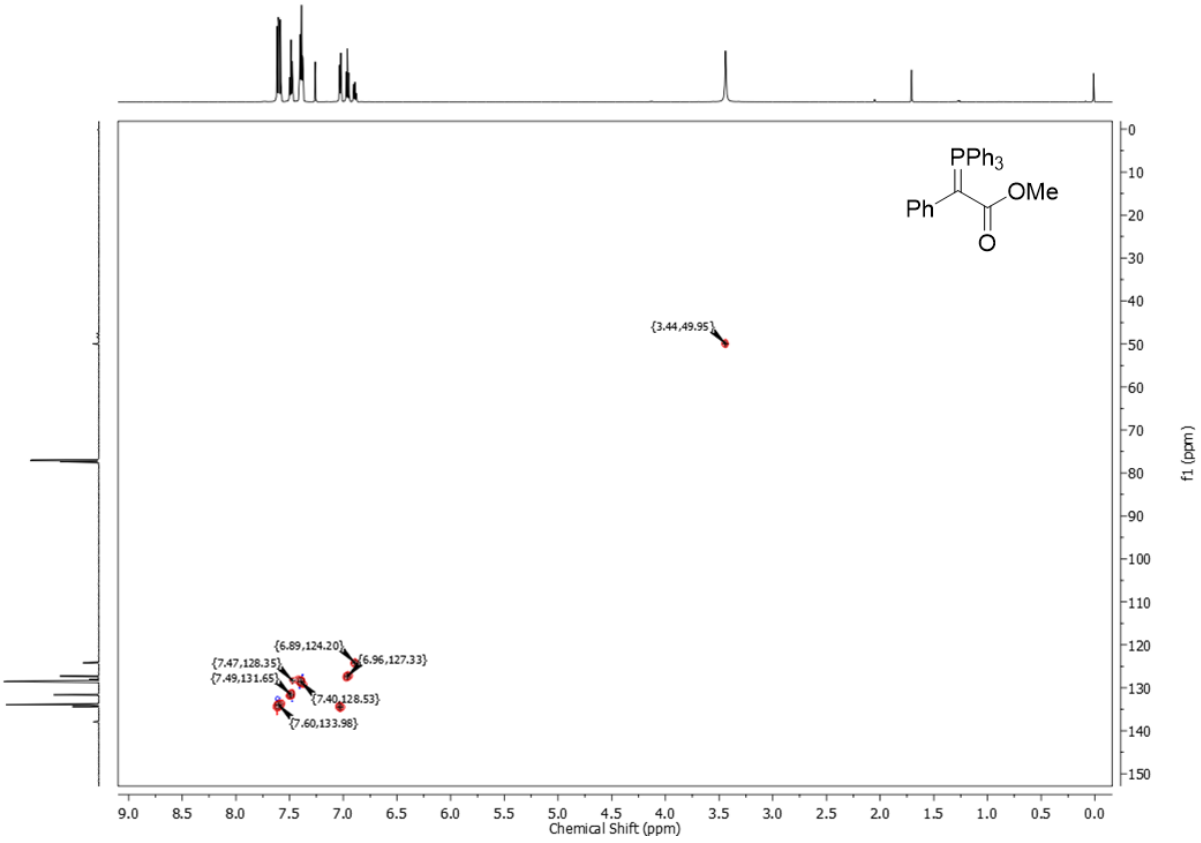


Figure S34: HSQC of **8** in $CDCl_3$.

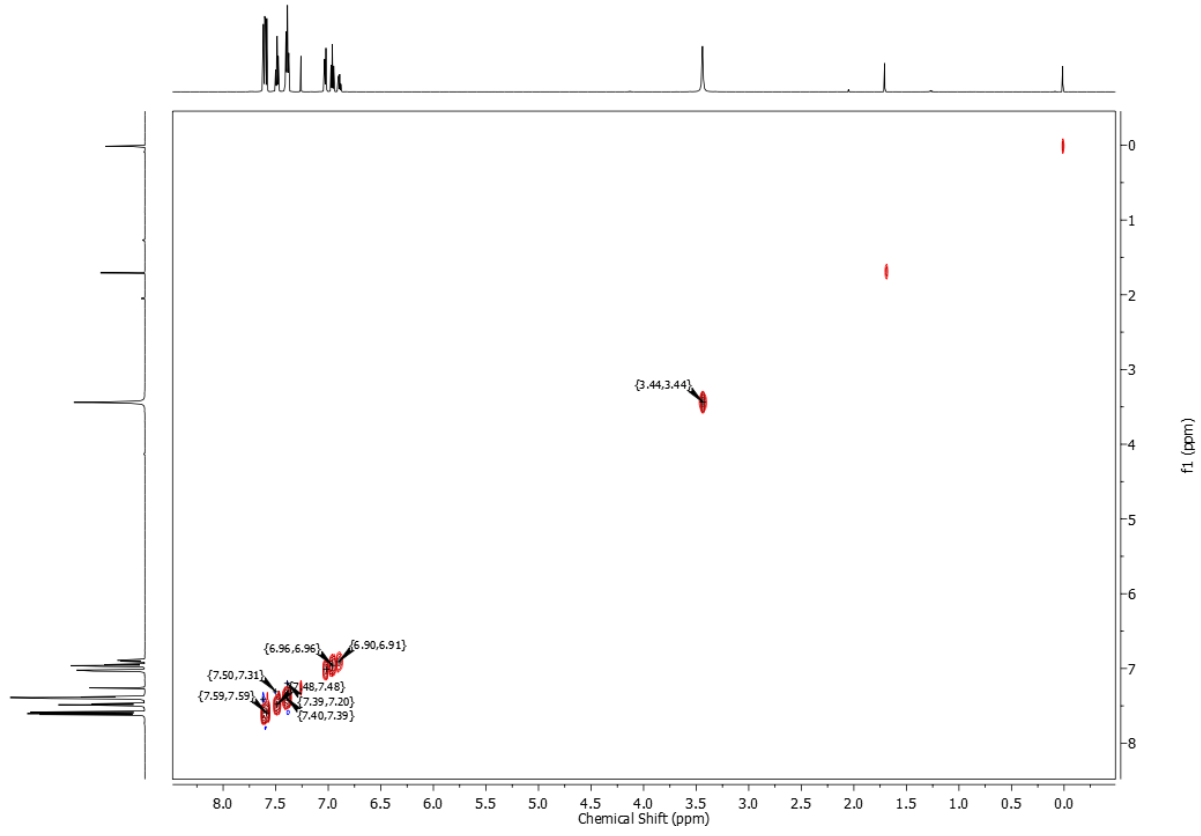


Figure S35: NOESY of **8** in $CDCl_3$.

Mass Spectrometry Analysis of Reaction Mixture

General Procedure for Mass Spectrometry Analysis of Reaction Mixture

To an oven-dried microwave vial, 4-(trifluoromethyl)benzyl bromide **11** (0.1 mmol), PPh_3 (0.04 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (0.005 mmol) was added. The microwave vial was sealed with a crimped cap then evacuated and flushed with dry N_2 gas three times followed by the addition of toluene (1 mL), and DIPEA (0.4 mmol). The mixture was allowed to stir at 80 °C for 5 min after which stirring was ceased and the reaction mixture was allowed to cool to room temperature. Methyl phenyldiazoacetate **1** (0.9 mmol) was then added to the reaction vessel and the reaction mixture was allowed to stir at 80 °C.

After *c.a* 15 min, an aliquot (1-3 droplets of undefined volume) was withdrawn from the reaction mixture using a disposable 1 mL syringe sparged with dry N_2 gas immediately prior to use and transferred to an oven-dried 1.8 mL glass screw-cap sample vial under inert atmosphere. The reaction sample was diluted in dry acetonitrile (1.0 – 1.2 mL) and the sample vial was capped under positive pressure of dry N_2 gas. The sample vial was wrapped in parafilm and immediately analysed *via* high resolution mass spectrometry using the ESI technique in positive-ion and negative-ion modes. Theoretical *m/z* values and isotopic distributions were calculated using MassLynx 4.1 software and signals were assigned in accordance with literature protocols out.[31]

For LC/HRMS, the sample was analysed using a Waters Xevo G2-XS QTOF mass spectrometer. Here, the sample was placed onto the autosampler of the instrument and autonomously injected with the analytes being ionized according to the conditions in Table S28.

Table S28: Waters Xevo G2-XS QTOF instrument settings used here in positive-ion and negative-ion modes.

Source	Positive Ion Mode Setting	Negative Ion Mode Setting
Capillary (kV)	3.0000	3.0000
Sampling Cone	50.0000	50.0000
Source Temperature (°C)	150	150
Source Offset	80	80
Desolvation Temp. (°C)	350	450

For direct sample infusion analysis, the sample was analysed using an Advion Nanomate mass spectrometer with the sample being manually dispensed directly into the ionization segment of the instrument. Here, an aliquot of the original sample (100 μL) was diluted in acetonitrile (1 mL) then an aliquot of this solution (10 μL) was further diluted in acetonitrile (1 mL) with the twice-diluted solution being used for analysis. Analytes were ionized according to the conditions in Table S29.

Table S29: Advion Nanomate instrument settings used here in positive-ion and negative-ion modes.

Source	Positive Ion Mode Setting	Negative Ion Mode Setting
Capillary (V)	3400.0	3500.0
Sample Cone (V)	120.0	120.0
Source Temperature (°C)	130.0	130.0
Desolvation Temp. (°C)	20.0	400.0
MCP Detector (V)	2050.0	2000.0

High Resolution Mass Spectra

Due to the operational nature of the HRMS equipment, an absolute inert atmosphere of the sample was not guaranteed during this analysis. Organometallic decomposition is evident from the small signals scattered throughout the spectra making total spectral assignment difficult.[32] HRMS results were duplicated over two independent experiments using separate reaction samples under identical operating conditions.

The de-brominated, bis-phosphine ligated oxidative addition complex **14** was observed in positive-ion mode using both LC/HRMS and direct sample infusion HRMS methods (Figure S36 and Figure S38, respectively) with good agreement between the theoretical and experimental isotopic distribution pattern for the same complex (Figure S37 and Figure S39).

The de-brominated, bis-phosphine ligated β-hydride elimination precursor complex **15** was only detected *via* LC/HRMS in positive-ion mode (Figure S40), again with good agreement between the theoretical and experimental isotopic distribution pattern (Figure S41). Due to the more dilute nature of the direct infusion MS sample and the low relative abundance of complex **15** (see Figure S36and Figure S40) it is expected that this complex may not be detected *via* direct infusion HRMS analysis, however decomposition of the complex may have also contributed to this species' absence.

In both cases, free bromide was observed in negative-ion mode analysis of the samples validating the de-brominated nature of the observed structures for **14** and **15**.

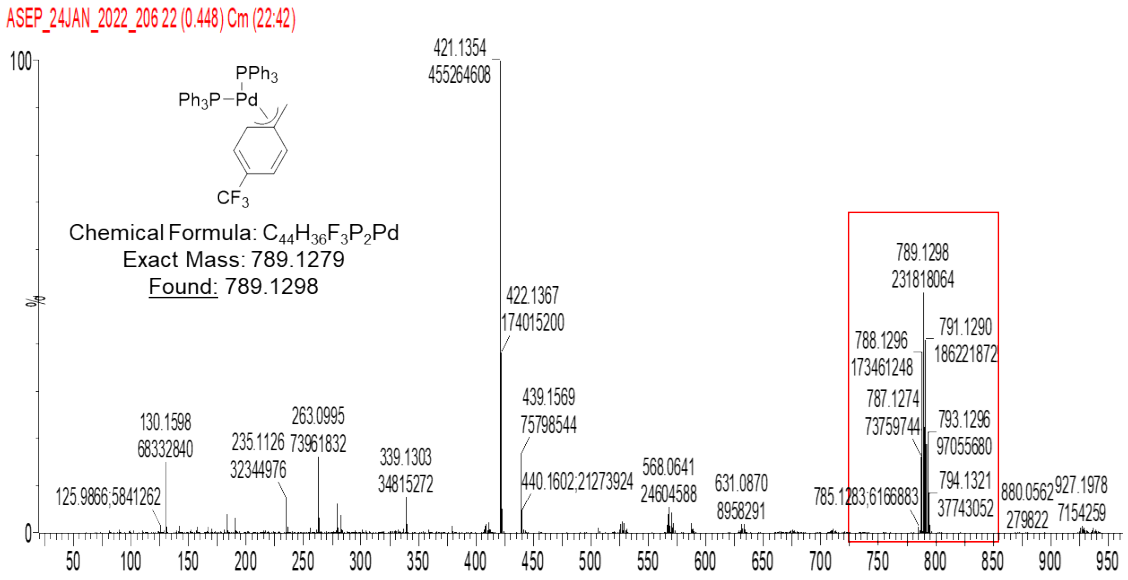


Figure S36: High resolution mass spectrum of crude reaction mixture obtained *via* LC/HRMS in positive-ion mode with the characteristic signal of the oxidative addition complex **14** highlighted in red.

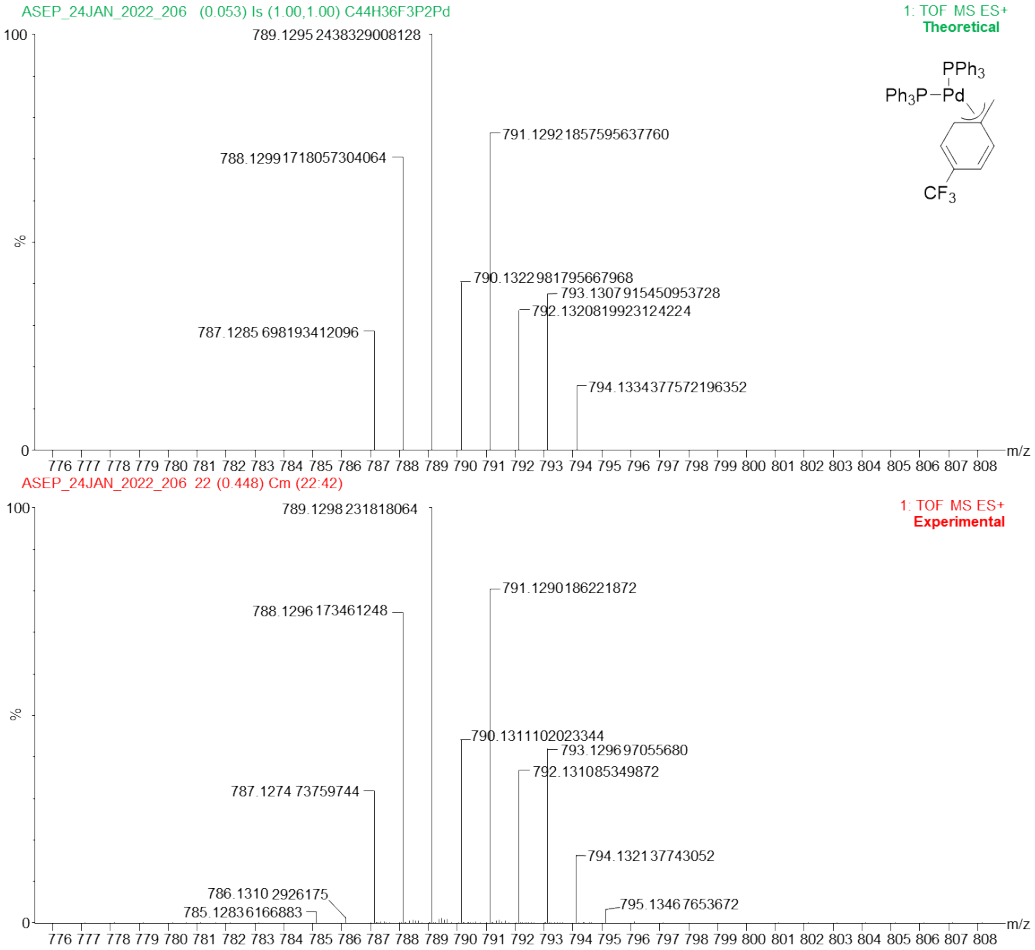


Figure S37: Enhanced LC/HRMS spectrum of the crude reaction mixture with the theoretical isotopic distribution of the oxidative addition complex **14** (top) and experimentally observed signal (bottom).

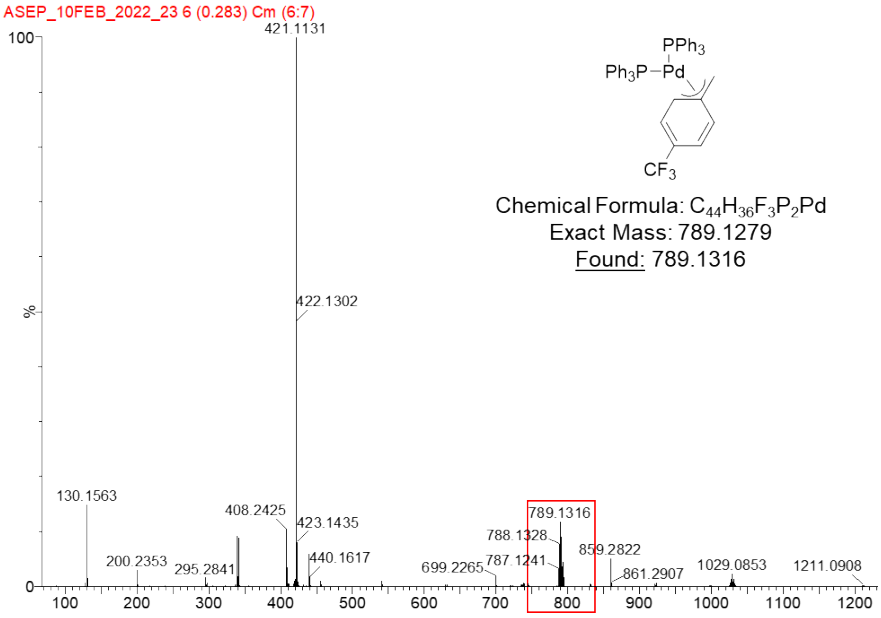


Figure S38: High resolution mass spectrum of crude reaction mixture obtained *via* direct infusion HRMS in positive-ion mode with the characteristic signal of the oxidative addition complex **14** highlighted in red.

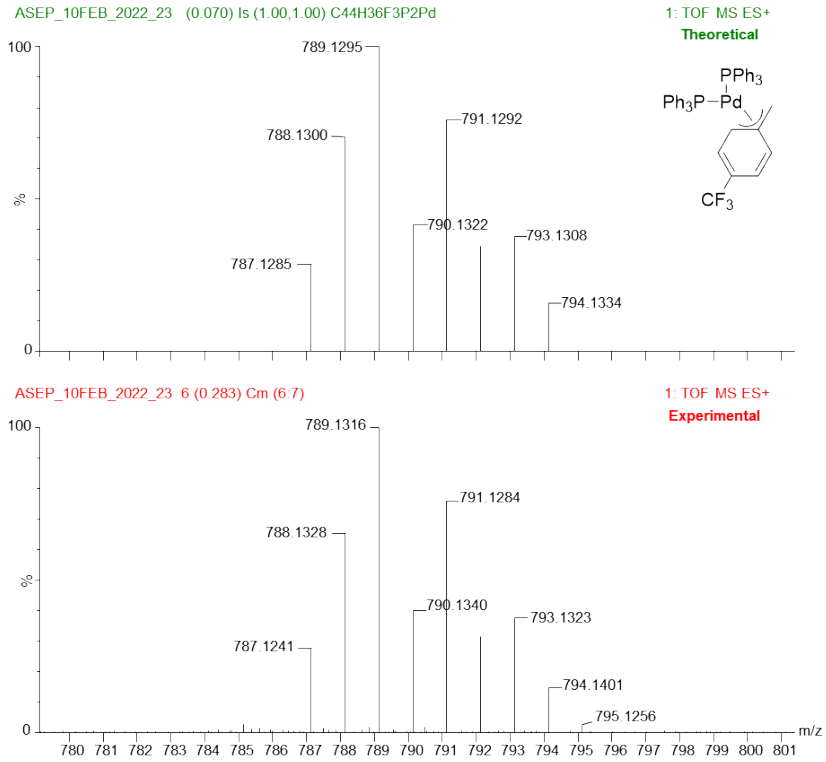


Figure S39: Enhanced HRMS spectrum obtained *via* direct infusion HRMS of the crude reaction mixture with the theoretical isotopic distribution of the oxidative addition complex **14** (top) and experimentally observed signal (bottom).

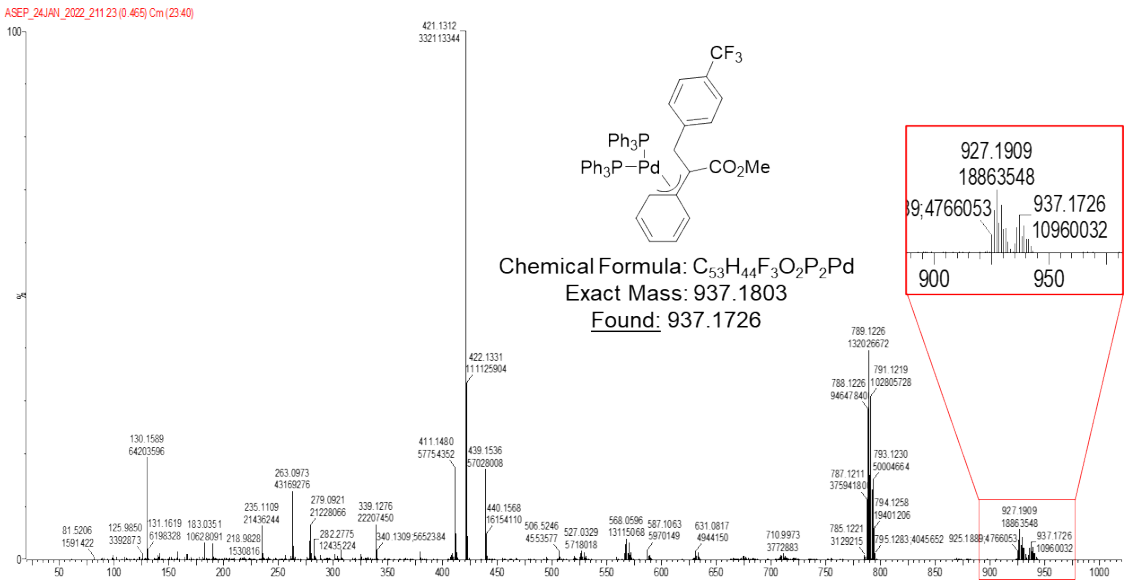


Figure S40: High resolution mass spectrum of crude reaction mixture obtained *via* LC/HRMS in positive-ion mode with the characteristic signal of the β-hydride elimination precursor complex **15** highlighted in red.

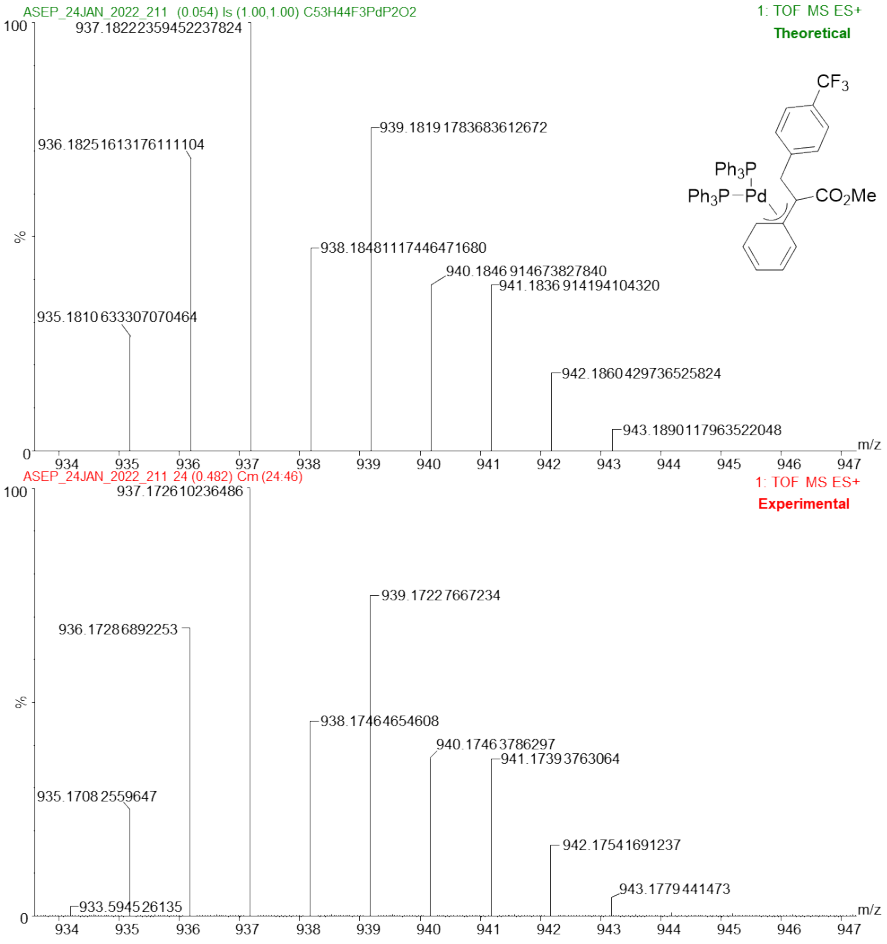


Figure S41: Enhanced LC/HRMS spectrum of the crude reaction mixture with the theoretical isotopic distribution of the β-hydride elimination precursor **15** complex (top) and experimentally observed signal (bottom).

Computational Details

Computational Methods

All optimisation, frequency, and single point calculations were performed with *Gaussian 16*, rev C.01. The hybrid B3PW91[33-35] functional was used for all geometry optimisation with the 6-31G(d,p) basis set on all non-metal atoms and the SDD[36] valence basis set and pseudopotential to describe Pd. Grimme's DFT-D3[37] correction was included in the optimisation procedure. Transition states on the potential energy surface were located using scans and a coordinate driving methodology. All optimised structures were confirmed as either minima or saddle points by the presence of zero or one imaginary harmonic frequency respectively. All transition states were further analysed via intrinsic reaction coordinate (IRC) calculations to ensure intermediates connected to their corresponding transition state structures. On the basis of the optimised structures, single point refinements with the 6-311+G(d,p) basis set for non-metal atoms and the SDD[36] valence basis set and effective core potential pairing for Pd. Grimme's DFT-D3[37] correction was again included as were further corrections for bulk solvation through a polarisable continuum model (PCM)[38] approach (toluene). Free energies were determined from thermochemical corrections of the geometries applied to electronic energies. Considerable care was taken to identify low energy conformers of intermediates and transition states through extensive conformational sampling. All structures reported are the most energetically stable of those sampled. Non-covalent interaction (NCI) surfaces were calculated using promolecular densities in nciplot.[39] Structures are displayed with PyMOL, shamelessly rendered with the excellent Paton group display settings.[40]

Carbene Trans to Br

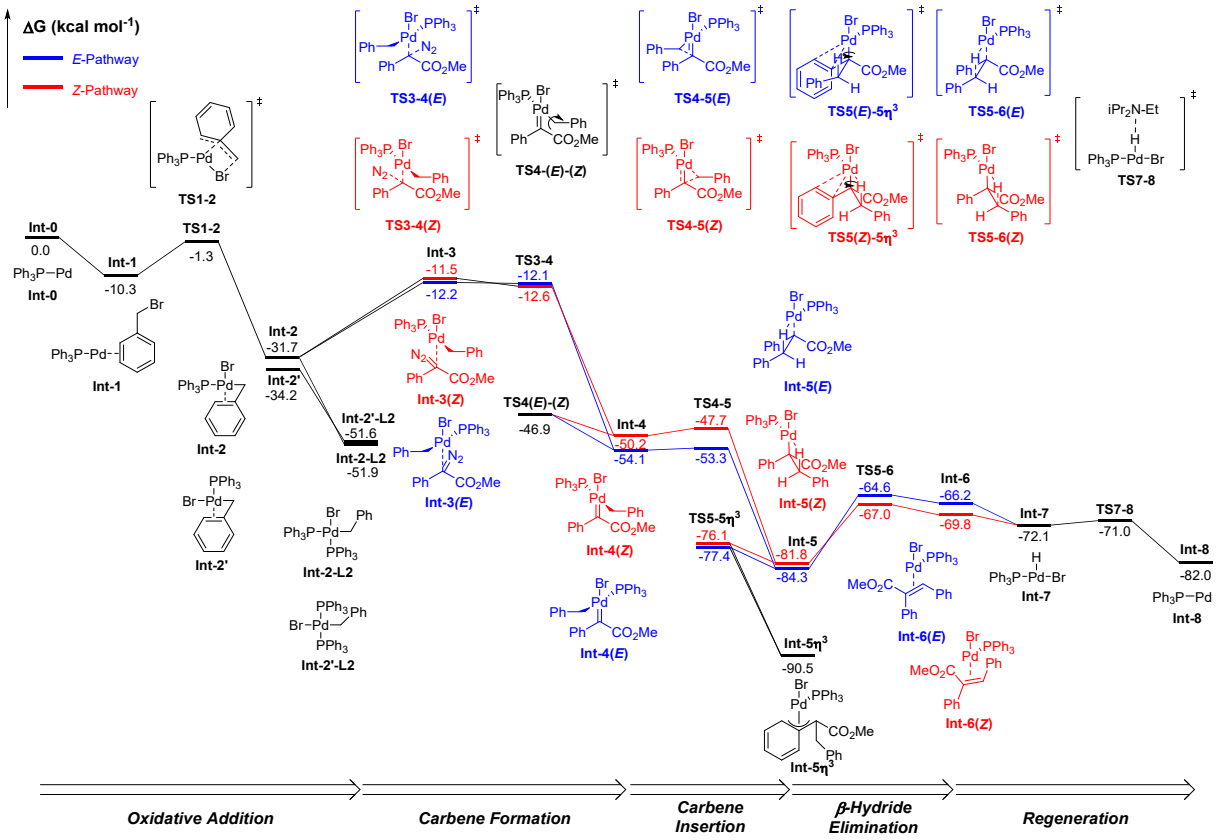
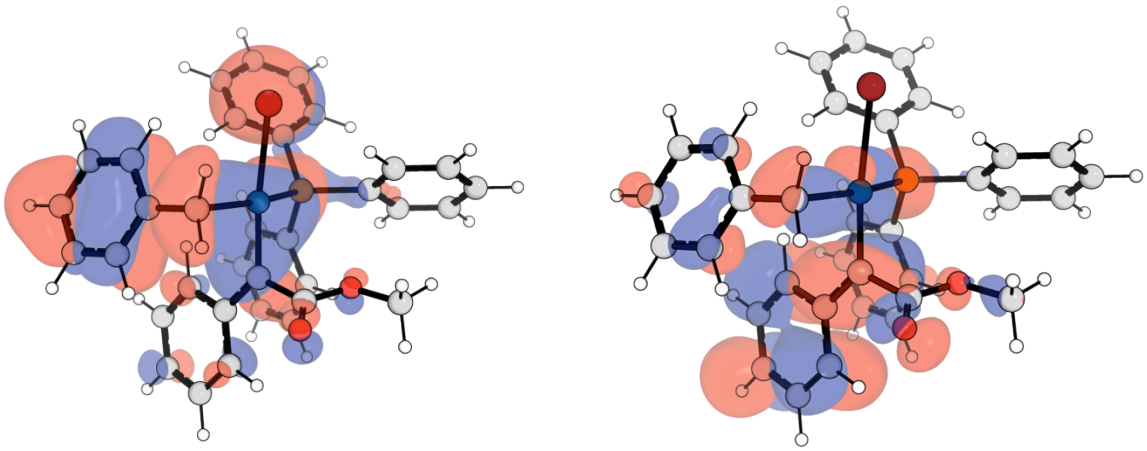


Figure S42:Free energy profiles for the alternative, higher energy, catalytic cycle in which the carbene forms trans to bromine, showing the major (E)-selective (blue) and minor (Z)-selective (red) reaction pathways. Theoretical reaction analysis performed at B3PW91-D3-PCM$_{Toluene}$/6-311+G(d,p)/SDD//B3PW91-D3/6-31G(d,p)/SDD energies are Gibbs free energies in kcal mol^{-1}.

Two isomers of the oxidative addition product exist, **Int-2** and **Int-2'**, meaning there are two potential vacant sites on palladium at which to form the carbene during **TS3-4**. The pathway in which the carbene forms trans to the bromine ligand of **Int-2** was found to be unproductive, Figure S42. Here, **TS3-4** 1.4 kcal mol^{-1} higher than productive pathway details in main body of paper in which the carbene forms trans to the PPh_3 ligand of **Int-2'**. Nevertheless, we fully investigated this pathway as well to contrast and compare the behaviour of the two possible mechanisms. Carbene insertion **TS4-5** is highly E-selective, favoured by 5.6 kcal mol^{-1}, much like the productive pathway. The same favourable HOMO-LUMO overlap is observed in the pro-(*E*) transition state, Figure S43.



HOMO **LUMO**

Figure S43: Molecular orbitals of Pd-carbene **TS4-5(*E*)** in the trans Br pathway where the HOMO resides predominantly on the migrating benzyl group and the LUMO predominantly on the carbene phenyl ring.

However, the barrier for rotation between **Int-4(*E*)** and **Int-4(*Z*)** is higher than the barrier to carbene insertion **TS4-5** making equilibration at this step much less likely than in the productive pathway. It is unlikely that carbene insertion could set selectivity in this pathway. β-hydride elimination, **TS5-6**, is much higher in energy than in the productive pathway, by 4.5-8.8 kcal mol^{-1}, which has significant consequences. Firstly, the barrier to rotation via **TS5-5η³**, of a similar magnitude to the productive pathway, is 9.1 kcal mol^{-1} lower than β-hydride insertion **TS5-6**. This equilibration can now be thought of as rapid, meaning a Curtin-Hammett like situation is operating. Any selectivity set earlier in the catalytic cycle will be nullified by the rapid equilibration, meaning it is likely β-hydride elimination is the selectivity determining step. However, **TS5-6(*Z*)** is 2.4 kcal mol^{-1} lower in energy than **TS5-6(*E*)**, resulting in 58:1 Z-product selectivity. The prediction of high (*Z*)-selectivity for this catalytic cycle goes against the high (*E*)-selectivity overwhelmingly observed in experiment. Neither can this possibly pathway account for the differences in experimentally observed selectivity for changes in starting material (Scheme 2). Together, the evidence suggest that this pathway is not operating and that carbene formation must occur trans to PPh_3 from intermediate **Int-2'**.

Carbene Intermediate Int-4 Dispersion Effects

The thermodynamic preference for carbene intermediate **Int-4(*E*)** over **Int-4(*Z*)** is not due to similar HOMO-LUMO overlap, as is suggested for the proceeding migratory insertion transition state but is more likely the result of favourable non-covalent interactions (Figure S44). **Int-4(*E*)** is favoured due to what appears to be two strong CH-π interactions between the benzyl ring and the triphenylphosphine ligand as well as the benzyl and carbene phenyl rings. Removal of dispersion corrections at SP level in fact results in the pro-(*Z*) carbene **Int-4(*Z*)** being favoured by 0.8 kcal mol^{-1}.

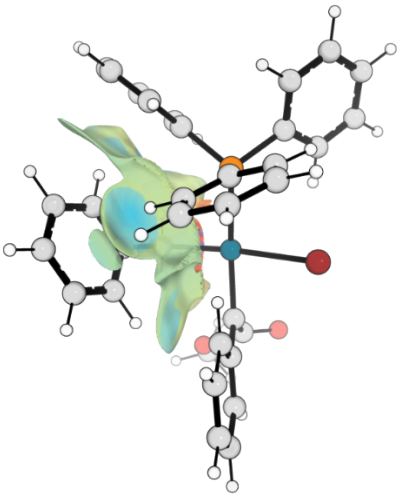


Figure S44: Noncovalent interactions favouring **Int-4(*E*)**. NCI cutoffs 0.01 and 1. The colour spectrum ranges from blue (strongly attractive) to green (weekly attractive) to yellow (mildly repulsive) to red (strongly repulsive).

Computational vs Experimental Selectivities

Both carbene insertion (TS4-5) and β-hydride elimination (TS5-6) are (*E*)-selective. However, the degrees of selectivity are different. Carbene insertion, with 3.5 kcal mol^{-1} favouring pro-(*E*) selectivity at TS4-5(*E*) over TS4-5(*Z*) would result in near perfect selectivity of 372:1 in favour of Int-5(*E*). From Int-5(*E*), β-hydride elimination at TS5-6(*E*) favours the (*E*)-product over the (*Z*)-product forming TS5-6(*Z*) by 1.9 kcal mol^{-1}, leading to a predicted (*E*)-selectivity of 25:1. The absolute values of these predicted selectivities suffer from inaccuracies related both to DFT and the application of simple transition state theory. These values do allow boundaries for each scenario to be set, depending on the degree of interconversion prior to β-hydride elimination, selectivity with a pendant migrating group will be in the range 372-25:1, whereas if selectivity is set solely during β-hydride insertion it can be no higher than 25:1. Although these are not quantitative, the calculated selectivities for each of these steps qualitatively match experimental results (Scheme 2) where a reaction at which selectivity can be determined during migratory insertion has much higher (*E*)-selectivity (>20:1) than a reaction at which selectivity can only occur during β-hydride elimination (5:1).

cβ-H Elimination TS5-6(*E*) Dispersion Effects

(*E*)-selectivity during β-hydride elimination is not immediately expected, at first glance it would seem that the steric clash between phenyl groups would disfavour this transition state. Stabilising non-covalent interactions, particularly between the triphenylphosphine ligand and phenyl ring of the product coming from the benzyl group appear to be the cause of the added stability of the pro-(*E*) pathway in comparison to the pro-(*Z*) (Figure S45). Removal of dispersion corrections during SP results in a drop from 1.9 to 0.2 kcal mol^{-1} preference for pro-(*E*).

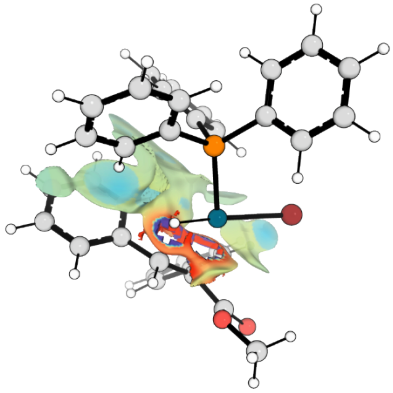


Figure S45: Strong non-covalent interaction between tripheylphosphine ligand and phenyl group of product during β-hydride elimination appears to preferentially stabilize the pro-(*E*) pathway **TS5-6(E)**. NCI cutoffs 0.01 and 1. The colour spectrum ranges from blue (strongly attractive) to green (weekly attractive) to yellow (mildly repulsive) to red (strongly repulsive).

Cartesian Coordinates

Starting Materials and Products

2 (benzyl bromide)

Energy: -1783742.0168202

C	3.21567	-0.19994	-0.44471
C	2.45092	-1.29833	-0.04873
C	1.16141	-1.11055	0.43618
C	0.62139	0.17681	0.53553
C	1.39010	1.27099	0.12995
C	2.68267	1.08433	-0.35552
H	4.22334	-0.34637	-0.82291
H	2.86152	-2.30148	-0.11940
H	0.55719	-1.96473	0.73113
H	0.97262	2.27274	0.19396
H	3.27265	1.94232	-0.66477
C	-0.75855	0.37250	1.06624
H	-0.98530	-0.28826	1.90320
H	-0.95988	1.40644	1.34566
Br	-2.12925	-0.07130	-0.29944

1 (diazo)

Energy: -381197.4901761

C	-3.69184	-0.51217	-0.00002
C	-2.74728	-1.53556	0.00035
C	-1.38399	-1.25434	0.00036
C	-0.93971	0.07769	0.00000
C	-1.89807	1.10595	-0.00040
C	-3.25622	0.81177	-0.00039
H	-4.75328	-0.74133	-0.00002
H	-3.06947	-2.57316	0.00064
H	-0.65946	-2.05797	0.00062
H	-1.58946	2.14777	-0.00072
H	-3.97631	1.62512	-0.00071
C	0.49891	0.39847	0.00005
C	1.61900	-0.54964	-0.00008
O	1.51822	-1.75975	-0.00026
O	2.80650	0.09814	0.00005
C	3.95559	-0.75415	-0.00019
H	3.96438	-1.39164	-0.88840
H	4.81555	-0.08474	-0.00147
H	3.96587	-1.39006	0.88914
N	1.12029	2.76766	0.00040
N	0.84631	1.66531	0.00024

DIPEA

Energy: -232781.4037305

N	0.01171	-0.01763	-0.48071
C	-0.51865	1.19313	-1.07248
H	-0.04176	1.33953	-2.05390
H	-1.57998	1.02569	-1.28842
C	-0.37261	2.49664	-0.27305
H	0.68097	2.74535	-0.10940

H	-0.82346	3.33128	-0.82231
H	-0.85742	2.43097	0.70444
C	1.43742	-0.03608	-0.17870
H	1.87866	0.75260	-0.80334
C	-0.87748	-0.86459	0.30525
H	-0.23398	-1.60620	0.79378
C	-1.83442	-1.64539	-0.60357
H	-1.26956	-2.19810	-1.35896
H	-2.43983	-2.35226	-0.02534
H	-2.52599	-0.97332	-1.12405
C	1.79733	0.28164	1.28232
H	2.88398	0.32662	1.41507
H	1.37362	1.23853	1.59800
H	1.41834	-0.49379	1.95741
C	-1.65441	-0.14333	1.41794
H	-2.23424	-0.85925	2.01099
H	-0.9789	0.39067	2.09161
H	-2.36158	0.58095	0.99883
C	2.07600	-1.35929	-0.61734
H	1.69536	-2.20049	-0.02708
H	1.85136	-1.55728	-1.66891
H	3.16329	-1.33455	-0.48562

HBr

Energy: -1614136.8656230

Br	0.00000	0.00000	0.03927
H	0.00000	0.00000	-1.37459

N_2

Energy: -68697.9195631

N	0.00000	0.00000	0.55225
N	0.00000	0.00000	-0.55225

Int-0 (PdPPh3)

Energy: -730438.0818779

Pd	0.00067	0.00408	2.59536
P	0.00052	0.00105	0.40415
C	-1.27208	1.05970	-0.40338
C	-1.94702	0.68257	-1.57072
C	-1.53970	2.31182	0.16642
C	-2.87100	1.54689	-2.15767
H	-1.75107	-0.28574	-2.02175
C	-2.45379	3.17710	-0.42792
H	-1.02908	2.59608	1.08385
C	-3.12375	2.79486	-1.59089
H	-3.39333	1.24249	-3.06070
H	-2.65146	4.14610	0.02220
H	-3.84489	3.46567	-2.04979
C	-0.28210	-1.63190	-0.39921
C	0.38440	-2.03403	-1.56297
C	-1.2376	-2.48451	0.17036
C	0.09542	-3.26737	-2.14672
H	1.12862	-1.38426	-2.01393
C	-1.53237	-3.70962	-0.42092
H	-1.74119	-2.17964	1.0851
C	-0.86393	-4.1049	-1.58044
H	0.62215	-3.57236	-3.04699
H	-2.27661	-4.36114	0.02883
H	-1.08619	-5.06554	-2.03694
C	1.55471	0.57106	-0.40301
C	1.5677	1.34116	-1.57233
C	2.77187	0.17687	0.16914
C	2.77929	1.70656	-2.15866
H	0.63205	1.65526	-2.02547
C	3.97932	0.53325	-0.42456
H	2.7611	-0.40552	1.0878
C	3.98538	1.30176	-1.58938
H	2.77851	2.30884	-3.06321
H	4.91649	0.21996	0.02734
H	4.92771	1.5888	-2.04793

PPh_3

Energy: -650126.6936949

P	-0.00047	-0.00060	-1.27816
C	0.22158	1.63165	-0.45007
C	1.17108	2.50357	-1.00200
C	-0.48782	2.03795	0.68712
C	1.41847	3.74479	-0.42196
H	1.72018	2.20505	-1.89208
C	-0.24855	3.28649	1.25936
H	-1.22739	1.37500	1.12622
C	0.70613	4.14046	0.70989
H	2.16101	4.40706	-0.85845
H	-0.80792	3.59032	2.14010
H	0.89160	5.11234	1.15862
C	-1.52527	-0.62518	-0.45052
C	-1.52225	-1.43874	0.68964
C	-2.75527	-0.24248	-1.00461

C	-2.72288	-1.85555	1.26244
H	-0.57817	-1.74499	1.13017
C	-3.95379	-0.64838	-0.42381
H	-2.7715	0.37948	-1.89664
C	-3.93996	-1.4591	0.71086
H	-2.70609	-2.48872	2.14547
H	-4.89879	-0.33917	-0.86185
H	-4.87423	-1.784	1.1602
C	1.30311	-1.00813	-0.45019
C	1.59073	-2.26315	-1.00556
C	2.00312	-0.59878	0.6919
C	2.5425	-3.09665	-0.42413
H	1.06284	-2.58823	-1.89913
C	2.96523	-1.42867	1.26548
H	1.79332	0.37084	1.13354
C	3.23467	-2.67931	0.71241
H	2.75054	-4.06843	-0.86329
H	3.50276	-1.09752	2.14997
H	3.98393	-3.32481	1.16214

(*E*)-5 (Prod-(*E*))

Energy: -482137.1846484

C	0.47347	3.79456	0.27443
C	-0.11900	2.96295	1.22427
C	0.03732	1.58354	1.13684
C	0.78433	1.01372	0.09728
C	1.39183	1.85719	-0.84089
C	1.23035	3.23764	-0.75536
H	0.35159	4.87209	0.34062
H	-0.70196	3.38910	2.03589
H	-0.42924	0.93156	1.86930
H	1.99309	1.42478	-1.63299
H	1.70165	3.88038	-1.49360
C	0.91224	-0.46165	0.01087
C	2.30780	-0.98883	-0.02295
O	3.29873	-0.29544	-0.13168
O	2.37283	-2.33587	0.07090
C	3.69526	-2.8748	0.02638
H	4.30078	-2.48611	0.84997
H	3.57714	-3.95496	0.11542
H	4.18716	-2.61958	-0.91654
C	-0.12998	-1.32554	-0.0115
H	0.12133	-2.38249	0.03574
C	-1.56575	-1.04625	-0.098
C	-2.4572	-1.99987	0.42224
C	-2.10095	0.09436	-0.72274
C	-3.83327	-1.80495	0.36218
H	-2.05919	-2.89831	0.8879
C	-3.47596	0.27957	-0.79622
H	-1.4339	0.82868	-1.15947
C	-4.34792	-0.66163	-0.24641
H	-4.50348	-2.5492	0.78276
H	-3.8708	1.16356	-1.28884
H	-5.42197	-0.5089	-0.30231

(*Z*)-5 (Prod-(*Z*))

Energy: -482134.4469470

C	-4.80480	-0.81458	0.06663
C	-4.29599	0.41075	0.49484
C	-2.92797	0.65583	0.44816
C	-2.03722	-0.32202	-0.02155
C	-2.56534	-1.54290	-0.46941
C	-3.93327	-1.78875	-0.41889
H	-5.87381	-1.00420	0.09859
H	-4.96709	1.17957	0.86699
H	-2.54434	1.61442	0.78530
H	-1.89975	-2.29177	-0.88857
H	-4.32187	-2.73823	-0.77628
C	-0.58453	-0.06771	-0.02404
C	-0.16694	1.35862	-0.22076
O	-0.49803	2.05204	-1.15816
O	0.61288	1.78604	0.78827
C	1.1653	3.09326	0.61313
H	0.37938	3.82919	0.42458
H	1.69345	3.31788	1.53942
H	1.86279	3.09642	-0.2303
C	0.3353	-1.04666	0.12635
H	-0.03558	-2.04492	0.35517
C	1.79167	-0.93289	0.01939
C	2.60207	-1.778	0.79387
C	2.41698	-0.03354	-0.86117
C	3.98912	-1.69558	0.72859
H	2.13329	-2.49315	1.46538
C	3.80321	0.04541	-0.92896
H	1.81089	0.58414	-1.51763
C	4.59557	-0.77923	-0.12974
H	4.59819	-2.35014	1.34563
H	4.26796	0.74256	-1.62059
H	5.67857	-0.71845	-0.18715

Shared Pathway

Int-1

Energy: -2514015.9480380

P	1.34726	-0.09580	0.04067
C	1.79607	0.82128	1.57052
C	2.04223	2.19902	1.59727
C	1.91229	0.08279	2.75596
C	2.40502	2.82406	2.79011
H	1.94637	2.78359	0.68685
C	2.28493	0.70698	3.94320
H	1.70046	-0.98430	2.74010
C	2.53055	2.08048	3.96249
H	2.58855	3.89510	2.80198
H	2.37304	0.12402	4.85594
H	2.81176	2.57047	4.89066
C	0.84828	1.24628	-1.11258
C	1.75272	1.93284	-1.93185
C	-0.50717	1.59985	-1.13917
C	1.30407	2.96082	-2.76102
H	2.80491	1.66247	-1.92537
C	-0.95008	2.63366	-1.9591
H	-1.21788	1.05886	-0.51941
C	-0.04492	3.31463	-2.77394
H	2.01131	3.48532	-3.39814
H	-2.00498	2.89352	-1.95973
H	-0.39031	4.11594	-3.42179
C	2.98929	-0.60614	-0.6128
C	4.19275	-0.01394	-0.21095
C	3.01611	-1.61851	-1.58152
C	5.40043	-0.42495	-0.77439
H	4.18603	0.76682	0.54428
C	4.22203	-2.02049	-2.14959
H	2.08209	-2.09085	-1.8781
C	5.41745	-1.42498	-1.74552
H	6.32952	0.03789	-0.45258
H	4.23051	-2.8057	-2.90071
H	6.35995	-1.74419	-2.18199
Pd	-0.21638	-1.7127	0.2566
C	-3.65518	-1.17451	-0.19592
C	-2.83579	-1.68141	-1.20131
C	-3.51064	-1.65489	1.12119
C	-1.90918	-2.71069	-0.93163
H	-2.91783	-1.29526	-2.21373
C	-2.59356	-2.65267	1.41245
H	-4.11943	-1.22743	1.91327
C	-1.79998	-3.22723	0.38561
H	-1.40684	-3.20459	-1.75864
H	-2.50596	-3.03281	2.42576
H	-1.24699	-4.14506	0.57573
C	-4.65775	-0.11934	-0.5005
H	-5.59423	-0.25622	0.04072
H	-4.85662	-0.01985	-1.56726
Br	-4.03768	1.69131	0.07277

TS1-2

Energy: -2514008.0634443

P	0.98627	0.14024	-0.00693
C	1.53364	-0.59118	1.58704
C	2.66101	-0.15652	2.29228
C	0.77397	-1.65709	2.09251
C	3.02576	-0.78279	3.48458
H	3.25178	0.67268	1.91412
C	1.14802	-2.28529	3.27643
H	-0.11340	-1.98417	1.55419
C	2.27410	-1.84833	3.97627
H	3.89908	-0.43455	4.02951
H	0.55333	-3.11023	3.65937
H	2.56024	-2.33319	4.90565
C	1.96288	1.68696	-0.14627
C	3.29257	1.71862	-0.58621
C	1.33042	2.88088	0.22380
C	3.9827	2.92807	-0.64102
H	3.7837	0.79797	-0.88995
C	2.02589	4.08716	0.17435
H	0.28798	2.85699	0.5353
C	3.35189	4.11195	-0.25743
H	5.01297	2.94667	-0.98621
H	1.52801	5.00899	0.46194
H	3.89138	5.05407	-0.30372
C	1.77865	-0.96536	-1.24499
C	2.80093	-1.86585	-0.92505
C	1.31184	-0.90352	-2.56541
C	3.34628	-2.68915	-1.91072
H	3.16581	-1.92878	0.09621
C	1.86329	-1.71893	-3.54926
H	0.50531	-0.2159	-2.81025
C	2.88083	-2.61725	-3.22233
H	4.13613	-3.3888	-1.65065
H	1.49451	-1.66057	-4.56982
H	3.3053	-3.26148	-3.98741
Pd	-1.24853	0.23001	-0.17966
C	-3.18298	-0.90215	-0.4192

C	-2.17797	-1.48948	-1.26689
C	-3.52689	-1.58684	0.78469
C	-1.6633	-2.77249	-0.9521
H	-2.03126	-1.10134	-2.27389
C	-2.98561	-2.82051	1.07534
H	-4.24022	-1.12211	1.4601
C	-2.05778	-3.42538	0.19753
H	-0.93698	-3.21822	-1.62478
H	-3.28189	-3.33637	1.98421
H	-1.64912	-4.40328	0.43516
C	-3.83557	0.34228	-0.78327
H	-4.80943	0.51878	-0.33948
H	-3.76593	0.64293	-1.82465
Br	-3.01133	2.29283	0.12644

Int-2'

Energy: -2514041.9836632

P	0.97196	0.10438	0.01823
C	1.89399	-1.19601	-0.88092
C	3.22928	-1.47490	-0.56038
C	1.27482	-1.88440	-1.92907
C	3.93716	-2.42725	-1.28731
H	3.71243	-0.95452	0.26145
C	1.98926	-2.83533	-2.65625
H	0.22919	-1.69447	-2.15148
C	3.31812	-3.10681	-2.33778
H	4.97054	-2.64318	-1.03079
H	1.49921	-3.37296	-3.46277
H	3.87099	-3.85351	-2.90116
C	1.45282	-0.10746	1.77478
C	2.61538	0.47553	2.30000
C	0.65608	-0.91906	2.59364
C	2.97401	0.24951	3.62702
H	3.23662	1.11331	1.6779
C	1.02403	-1.14222	3.91877
H	-0.23844	-1.38398	2.18645
C	2.17868	-0.55879	4.43855
H	3.87506	0.7073	4.02595
H	0.40105	-1.77395	4.54552
H	2.45858	-0.73198	5.4741
C	1.8126	1.65325	-0.48812
C	2.55358	1.72815	-1.67211
C	1.63123	2.81351	0.27997
C	3.10611	2.94285	-2.07871
H	2.70492	0.83699	-2.27385
C	2.19175	4.02103	-0.12397
H	1.05972	2.76342	1.2035
C	2.9293	4.08923	-1.30737
H	3.68104	2.98852	-2.99944
H	2.05205	4.91029	0.48441
H	3.3641	5.03288	-1.62446
Pd	-1.25406	0.08298	-0.34968
C	-2.83134	1.6891	-0.57502
C	-3.42079	0.62741	-1.32305
C	-3.47946	2.09556	0.62627
C	-4.61188	0.01883	-0.88504
H	-3.01282	0.3644	-2.29702
C	-4.65301	1.49537	1.02814
H	-3.02831	2.88687	1.21834
C	-5.22185	0.44698	0.27731
H	-5.03505	-0.79433	-1.46529
H	-5.13893	1.82387	1.94278
H	-6.13758	-0.02553	0.61951
C	-1.47586	2.07545	-0.90653
H	-1.00464	2.83794	-0.28995
H	-1.19655	2.14184	-1.95888
Br	-1.70456	-2.31941	0.10029

Int-2

Energy: -2514040.4888290

P	-0.73879	0.27028	-0.00966
C	-1.21295	0.14075	1.75628
C	-2.31416	0.84205	2.26702
C	-0.44905	-0.66047	2.61170
C	-2.64032	0.74830	3.61602
H	-2.91685	1.46165	1.60974
C	-0.78060	-0.75293	3.96356
H	0.38674	-1.22725	2.21219
C	-1.87217	-0.04946	4.46672
H	-3.49552	1.29451	4.00429
H	-0.18676	-1.38350	4.61908
H	-2.13031	-0.12461	5.51956
C	-2.28544	-0.09044	-0.93055
C	-3.29211	0.87176	-1.10316
C	-2.47627	-1.38191	-1.43783
C	-4.47007	0.54481	-1.76936
H	-3.14984	1.88391	-0.73534
C	-3.6596	-1.70342	-2.10114
H	-1.70598	-2.13533	-1.29708
C	-4.65638	-0.74433	-2.26911
H	-5.24163	1.29867	-1.90023
H	-3.79744	-2.70899	-2.4884

H	-5.5757	-0.9977	-2.79009
C	-0.51005	2.07094	-0.26269
C	-0.07737	2.89776	0.77961
C	-0.61637	2.60456	-1.5562
C	0.23278	4.23557	0.53532
H	0.01842	2.49569	1.78359
C	-0.31332	3.94168	-1.79565
H	-0.94422	1.97094	-2.37605
C	0.11606	4.76166	-0.74948
H	0.56586	4.86688	1.35454
H	-0.41052	4.34459	-2.80003
H	0.35501	5.80468	-0.93693
Pd	1.17796	-0.9606	-0.55058
C	3.31721	-0.39323	-0.67579
C	2.63768	0.64681	-1.3962
C	3.94393	-0.0506	0.56378
C	2.67147	1.97852	-0.91395
H	2.31334	0.46381	-2.41948
C	3.94605	1.24876	1.00945
H	4.42307	-0.83974	1.13571
C	3.30614	2.27216	0.27068
H	2.17923	2.76213	-1.47957
H	4.4412	1.49484	1.94495
H	3.31477	3.29247	0.64106
C	3.06737	-1.74282	-1.08071
H	3.43573	-2.55835	-0.46504
H	2.95916	-1.97671	-2.1388
Br	0.35381	-3.22194	-0.00903

Int-2'-L2

Energy: -3164199.0934825

P	-2.22902	-0.43250	-0.13931
C	-2.75115	0.04584	1.54229
C	-3.22663	-0.88415	2.47087
C	-2.54168	1.37629	1.93464
C	-3.51395	-0.47975	3.77332
H	-3.35058	-1.92325	2.18507
C	-2.83607	1.77367	3.23526
H	-2.14466	2.09945	1.22942
C	-3.32359	0.84673	4.15717
H	-3.87746	-1.20858	4.49232
H	-2.67294	2.80801	3.52447
H	-3.54643	1.15570	5.17489
C	-2.86531	-2.12254	-0.44245
C	-4.24444	-2.36481	-0.36642
C	-2.00231	-3.15859	-0.81129
C	-4.74924	-3.63326	-0.63562
H	-4.92053	-1.55666	-0.09959
C	-2.5135	-4.42482	-1.09199
H	-0.93397	-2.97541	-0.85275
C	-3.88286	-4.66519	-1.00015
H	-5.81818	-3.81516	-0.56719
H	-1.83631	-5.2261	-1.37393
H	-4.27738	-5.65487	-1.21393
C	-3.3189	0.5162	-1.26862
C	-4.30241	1.41021	-0.83618
C	-3.12884	0.32049	-2.64412
C	-5.06792	2.11378	-1.76578
H	-4.46286	1.57062	0.22461
C	-3.89122	1.02577	-3.56971
H	-2.37809	-0.38809	-2.98657
C	-4.85897	1.9318	-3.13107
H	-5.82518	2.81107	-1.41818
H	-3.72877	0.87174	-4.63274
H	-5.4499	2.48882	-3.85276
C	-0.49334	2.61698	-0.81073
C	-1.66514	3.30362	-1.17115
C	0.21193	3.0892	0.3134
C	-2.12776	4.38833	-0.42758
H	-2.22654	2.97185	-2.03943
C	-0.24192	4.17708	1.05174
H	1.10339	2.56532	0.64322
C	-1.42311	4.82975	0.69161
H	-3.04839	4.88394	-0.7246
H	0.32083	4.50403	1.92232
H	-1.78696	5.67097	1.27514
C	-0.04285	1.41711	-1.57176
H	0.94326	1.56387	-2.01465
H	-0.73984	1.18177	-2.37916
Br	0.18705	-1.9626	1.59356
Pd	0.07905	-0.18774	-0.2426
P	2.41341	-0.10293	-0.19745
C	3.15659	-1.77435	-0.21354
C	3.07576	0.7468	1.28661
C	3.29422	0.74289	-1.57088
C	4.34815	-2.07387	0.4513
C	2.51702	-2.76638	-0.96788
C	4.37209	1.28343	1.30195
C	2.26637	0.87345	2.42402
C	3.90655	0.02046	-2.60169
C	3.28416	2.1454	-1.63725
C	4.89618	-3.35226	0.35793
H	4.84115	-1.31777	1.05443
C	3.0748	-4.03679	-1.07128

H	1.5725	-2.53927	-1.45534
C	4.85123	1.93156	2.43777
H	5.00229	1.2051	0.42069
C	2.75064	1.52669	3.55549
H	1.26633	0.45023	2.42391
C	4.50077	0.68693	-3.67271
H	3.92954	-1.06422	-2.56503
C	3.88123	2.80681	-2.70638
H	2.81241	2.7244	-0.8486
C	4.26485	-4.33231	-0.40578
H	5.8168	-3.58228	0.88702
H	2.57104	-4.80144	-1.65581
C	4.04007	2.05613	3.56566
H	5.85657	2.34358	2.43874
H	2.1132	1.62047	4.43004
C	4.49076	2.07906	-3.72844
H	4.97759	0.11272	-4.46232
H	3.86564	3.89246	-2.74105
H	4.69393	-5.3281	-0.47507
H	4.41275	2.56738	4.44914
H	4.95545	2.59567	-4.56358

Int-2-L2

Energy: -3164200.1133611

P	1.56118	0.83943	-0.22347
C	1.63698	0.51072	1.57957
C	1.89849	1.49156	2.54362
C	1.39552	-0.80821	1.99043
C	1.90256	1.16024	3.89651
H	2.05172	2.52316	2.24800
C	1.38616	-1.13296	3.34463
H	1.19792	-1.58117	1.25433
C	1.63588	-0.14893	4.30021
H	2.09316	1.93165	4.63758
H	1.16863	-2.15394	3.64201
H	1.61949	-0.39889	5.35748
C	1.14078	2.60999	-0.47620
C	2.01325	3.63063	-0.06640
C	-0.01657	2.95223	-1.18002
C	1.69919	4.96434	-0.30675
H	2.9571	3.3792	0.4095
C	-0.32361	4.28765	-1.4332
H	-0.67354	2.16572	-1.53763
C	0.52584	5.29574	-0.98655
H	2.37935	5.7455	0.02105
H	-1.23081	4.5349	-1.97675
H	0.28547	6.33744	-1.18015
C	3.32743	0.90028	-0.71094
C	4.37097	0.68096	0.19315
C	3.62536	1.19114	-2.04941
C	5.69586	0.74444	-0.23941
H	4.15011	0.44425	1.22899
C	4.94729	1.25026	-2.47806
H	2.81586	1.3675	-2.75405
C	5.9861	1.02385	-1.57305
H	6.50075	0.56814	0.46874
H	5.16767	1.46909	-3.51895
H	7.01839	1.06512	-1.90887
C	2.11302	-2.62832	-1.07498
C	3.34462	-2.4664	-0.41495
C	1.29483	-3.70172	-0.66629
C	3.70625	-3.28064	0.6553
H	4.02278	-1.68945	-0.74956
C	1.6589	-4.51775	0.39973
H	0.35675	-3.86588	-1.18943
C	2.85723	-4.30017	1.08434
H	4.65883	-3.11843	1.15359
H	1.0041	-5.33393	0.69569
H	3.13466	-4.93192	1.92376
C	1.67201	-1.67531	-2.12279
H	1.19386	-2.15346	-2.97668
H	2.47592	-1.01725	-2.45261
Br	-1.46267	-2.13323	-2.44139
Pd	0.09252	-0.61745	-1.19325
P	-1.84707	0.0168	0.14769
C	-1.91681	1.55502	1.16083
C	-2.12611	-1.28807	1.41004
C	-3.4008	0.17508	-0.81156
C	-2.56365	2.70181	0.68044
C	-1.25255	1.62416	2.3929
C	-2.90208	-1.06069	2.55683
C	-1.50684	-2.5327	1.24688
C	-3.31878	0.68977	-2.11139
C	-4.65435	-0.11004	-0.26374
C	-2.52693	3.89166	1.40231
H	-3.09891	2.6671	-0.26331
C	-1.21966	2.81505	3.11346
H	-0.76886	0.74319	2.80096
C	-3.04866	-2.05741	3.51849
H	-3.37261	-0.0943	2.71245
C	-1.6469	-3.5242	2.21457
H	-0.90976	-2.72355	0.36249
C	-4.477	0.94182	-2.84157
H	-2.34443	0.85392	-2.56257

C	-5.81169	0.12725	-1.00303
H	-4.73061	-0.52969	0.73429
C	-1.84976	3.95518	2.61862
H	-3.02897	4.77149	1.00976
H	-0.6928	2.84452	4.06286
C	-2.41663	-3.28988	3.35243
H	-3.65078	-1.86668	4.40262
H	-1.14432	-4.47685	2.07534
C	-5.72584	0.66091	-2.28805
H	-4.40196	1.33485	-3.8515
H	-6.78178	-0.10727	-0.57352
H	-1.81941	4.88496	3.17994
H	-2.52329	-4.06245	4.10919
H	-6.62972	0.84555	-2.86208

Int-5η3

Energy: -2826595.2712710

Pd	-0.22811	-0.34007	-0.00081
C	-2.34091	-0.14809	0.20760
C	-2.75793	-1.09868	1.28176
O	-2.44081	-1.03259	2.45680
O	-3.49903	-2.10403	0.78906
C	-1.77686	1.13910	0.60982
C	-1.80217	1.68608	1.92872
C	-0.96698	1.81370	-0.36622
C	-1.10444	2.83554	2.22364
H	-2.38784	1.18188	2.68507
C	-0.24709	2.98433	-0.02549
H	-1.06166	1.57758	-1.42256
C	-0.30850	3.48477	1.25425
H	-1.16459	3.24804	3.22718
H	0.34239	3.47644	-0.79237
H	0.24218	4.38249	1.51921
H	-2.5201	0.27065	-1.90532
H	-3.03508	-1.33387	-1.42919
C	-4.47875	0.23325	-1.04673
C	-3.05697	-0.2846	-1.13084
C	-4.72128	1.61063	-0.98669
C	-5.56717	-0.64222	-1.00191
C	-6.02018	2.10285	-0.88688
H	-3.88125	2.30124	-1.01687
C	-6.869	-0.15301	-0.90397
H	-5.38392	-1.71189	-1.03216
C	-7.10001	1.22043	-0.84527
H	-6.19045	3.17542	-0.84391
H	-7.70469	-0.84721	-0.87215
H	-8.11454	1.60174	-0.76776
P	2.06577	0.02388	-0.15441
C	2.8049	0.55168	1.43216
C	3.19292	-1.29127	-0.72656
C	2.36454	1.41936	-1.30248
C	4.19221	0.54048	1.63281
C	1.96082	0.99915	2.45446
C	4.09724	-1.10763	-1.77842
C	3.1524	-2.51883	-0.05049
C	1.73442	1.36297	-2.55514
C	3.09515	2.55818	-0.95239
C	4.72539	0.98823	2.83883
H	4.84856	0.17501	0.8475
C	2.49908	1.44718	3.65903
H	0.88409	0.98727	2.30955
C	4.95367	-2.14337	-2.15027
H	4.13652	-0.15858	-2.30467
C	4.01451	-3.54527	-0.4226
H	2.43714	-2.67081	0.75144
C	1.83255	2.4319	-3.44033
H	1.15521	0.48214	-2.82444
C	3.18486	3.63181	-1.83932
H	3.57789	2.61613	0.01813
C	3.8797	1.44417	3.85156
H	5.801	0.97503	2.99135
H	1.83613	1.78804	4.44916
C	4.91397	-3.36083	-1.47331
H	5.6531	-1.9954	-2.96844
H	3.97407	-4.4957	0.1015
C	2.55283	3.57334	-3.08
H	1.34024	2.37955	-4.40737
H	3.74716	4.51725	-1.55588
H	4.29832	1.78753	4.79362
H	5.58081	-4.16725	-1.76589
H	2.61941	4.41327	-3.76574
Br	-0.29614	-2.76434	-0.34363
C	-3.73892	-3.17786	1.69994
H	-4.26615	-2.82403	2.58998
H	-4.3486	-3.89646	1.15198
H	-2.78921	-3.63065	1.99668

Int-7

Energy: -2344423.6743579

Pd	-1.75359	0.00784	-0.11296
Br	-4.14431	0.01197	-0.11743
P	0.49613	0.00477	-0.05989

C	1.31767	1.48371	-0.74848
C	0.59986	2.68575	-0.79027
C	2.64948	1.45541	-1.18141
C	1.21278	3.84926	-1.25040
H	-0.43921	2.70260	-0.47023
C	3.25552	2.62045	-1.64537
H	3.20824	0.52422	-1.16407
C	2.53958	3.81747	-1.67786
H	0.64972	4.77743	-1.28295
H	4.28676	2.59240	-1.98568
H	3.01434	4.72372	-2.04328
C	1.06455	-0.08486	1.67622
C	1.88766	0.8863	2.25571
C	0.61006	-1.16308	2.45181
C	2.25682	0.77446	3.59584
H	2.24032	1.72466	1.66266
C	0.98503	-1.27069	3.78715
H	-0.03054	-1.92042	2.00497
C	1.80836	-0.30052	4.36113
H	2.89671	1.53092	4.04122
H	0.63092	-2.10829	4.38097
H	2.09665	-0.38206	5.40523
C	1.30998	-1.41841	-0.86685
C	2.49928	-1.96378	-0.36429
C	0.74054	-1.95323	-2.02932
C	3.11545	-3.02331	-1.02657
H	2.93622	-1.56562	0.54734
C	1.36303	-3.00988	-2.68941
H	-0.19574	-1.55022	-2.40566
C	2.55005	-3.5451	-2.18982
H	4.03553	-3.44393	-0.63077
H	0.91359	-3.42219	-3.58807
H	3.0297	-4.37453	-2.70177
H	-1.59313	0.30035	-1.57232

TS7-8

Energy: -2577151.0017734

Pd	0.0893	1.56	-0.028
Br	-1.13497	3.62839	-0.07699
H	-1.09115	0.61762	0.09162
N	-3.19024	-0.64168	0.05026
C	-2.54109	-1.81834	0.61837
H	-1.52669	-1.8755	0.20043
H	-2.41046	-1.63268	1.6902
C	-3.18618	-3.20083	0.43362
H	-3.22878	-3.4882	-0.62134
H	-2.57556	-3.95273	0.9473
H	-4.19787	-3.25518	0.84315
C	-3.45995	-0.69921	-1.39502
H	-2.67994	-1.35893	-1.79928
C	-4.17471	0.05895	0.89101
H	-4.67201	0.77207	0.22377
C	-3.48665	0.88629	1.981
H	-2.77528	1.59119	1.54497
H	-4.22882	1.45203	2.55504
H	-2.95253	0.24516	2.693
C	-4.82342	-1.2891	-1.80178
H	-4.87921	-1.38012	-2.89241
H	-4.9982	-2.27892	-1.37369
H	-5.64471	-0.63349	-1.4921
C	-5.27007	-0.82126	1.51914
H	-6.00314	-0.18935	2.03271
H	-5.80486	-1.41708	0.77548
H	-4.85208	-1.50261	2.26871
C	-3.28016	0.6687	-2.05981
H	-4.03764	1.38654	-1.72751
H	-2.30272	1.09758	-1.8282
H	-3.37992	0.57533	-3.14716
P	1.45302	-0.23429	0.01681
C	3.14015	0.34568	-0.4214
C	3.9108	-0.23384	-1.43564
C	3.6471	1.451	0.28068
C	5.17152	0.28112	-1.73738
H	3.5276	-1.08442	-1.99109
C	4.90654	1.95944	-0.02298
H	3.05458	1.91336	1.06747
C	5.67053	1.37552	-1.03399
H	5.76277	-0.17534	-2.52639
H	5.2876	2.81624	0.52522
H	6.65095	1.77648	-1.27513
C	1.10011	-1.57933	-1.17756
C	1.38569	-2.92613	-0.92273
C	0.53385	-1.21813	-2.40878
C	1.11514	-3.89454	-1.88887
H	1.80865	-3.22213	0.03245
C	0.27568	-2.18742	-3.37516
H	0.28652	-0.17632	-2.5987
C	0.56487	-3.52725	-3.11571
H	1.33333	-4.93808	-1.67955
H	-0.16144	-1.89645	-4.32611
H	0.35447	-4.28439	-3.86595
C	1.68219	-1.0384	1.64701

C	2.85785	-1.73209	1.96965
C	0.66219	-0.93473	2.60101
C	2.99689	-2.33181	3.21916
H	3.66977	-1.7898	1.24958
C	0.80554	-1.53666	3.84996
H	-0.23248	-0.36572	2.36391
C	1.96988	-2.23773	4.1587
H	3.91147	-2.86556	3.46223
H	0.01126	-1.44642	4.5855
H	2.08346	-2.70054	5.1351

Int-8

Energy: -2577234.6449202

Pd	0.20926	-1.39583	-0.01371
Br	2.35740	-2.66333	0.04663
H	3.07122	-0.61281	-0.06098
N	3.25769	0.42961	0.00927
C	2.52515	0.75004	1.29045
H	1.63783	0.09417	1.24879
H	3.15993	0.38550	2.10155
C	2.07420	2.17896	1.51804
H	1.35196	2.50026	0.76598
H	1.54807	2.20049	2.47686
H	2.88969	2.90325	1.57005
C	2.58755	0.96987	-1.24700
H	1.52020	0.89584	-1.00600
C	4.76750	0.56222	0.05343
H	5.07441	0.58170	-0.99646
C	5.37053	-0.68074	0.70252
H	5.05411	-1.59415	0.19396
H	6.46124	-0.61078	0.66326
H	5.07783	-0.76805	1.75338
C	2.95906	2.40498	-1.59249
H	2.35751	2.70277	-2.4553
H	2.74973	3.11571	-0.79381
H	4.01004	2.49227	-1.88647
C	5.25342	1.83664	0.73302
H	6.34155	1.88467	0.63255
H	4.83725	2.74228	0.29057
H	5.02481	1.83139	1.80245
C	2.86439	0.03572	-2.42135
H	3.91014	0.07655	-2.74584
H	2.60068	-0.99636	-2.17859
H	2.24644	0.35352	-3.26585
P	-1.58313	-0.14578	0.0092
C	-2.79004	-0.34128	-1.37323
C	-3.59673	0.69765	-1.85721
C	-2.90695	-1.61465	-1.94575
C	-4.50734	0.46387	-2.88653
H	-3.50641	1.69517	-1.4354
C	-3.82381	-1.8491	-2.9681
H	-2.26096	-2.41353	-1.58815
C	-4.62524	-0.81013	-3.44123
H	-5.12502	1.27856	-3.25557
H	-3.90423	-2.84165	-3.40305
H	-5.33434	-0.99066	-4.24468
C	-1.26864	1.67561	-0.04611
C	-1.47717	2.51953	1.05087
C	-0.71523	2.22023	-1.21688
C	-1.13052	3.87011	0.98392
H	-1.91244	2.12	1.96196
C	-0.38042	3.56927	-1.2868
H	-0.55943	1.57564	-2.07954
C	-0.57977	4.40006	-0.18105
H	-1.29594	4.50952	1.84709
H	0.0348	3.97597	-2.20517
H	-0.31346	5.45209	-0.23246
C	-2.66447	-0.27788	1.50137
C	-3.98854	0.17899	1.53333
C	-2.10638	-0.82674	2.66277
C	-4.73526	0.09434	2.70618
H	-4.44054	0.59507	0.63779
C	-2.85229	-0.90469	3.83833
H	-1.08529	-1.2017	2.62491
C	-4.16773	-0.4442	3.86182
H	-5.76328	0.44691	2.71774
H	-2.40838	-1.33598	4.7316
H	-4.75321	-0.51146	4.77494

Productive (Trans PPh_3) (*E*)-Pathway

Int-3(*E*)

Energy: -2895258.4650738

Pd	0.61387	0.73564	0.15924
C	0.91880	-2.86654	0.70220
O	0.91886	-2.60962	1.89578
O	-0.00746	-3.64216	0.10816
C	-1.00949	-4.18415	0.97159
H	-1.60367	-3.38868	1.42501
H	-0.55038	-4.79027	1.75767
C	3.19586	-1.74065	0.07633

C	3.89742	-1.02461	-0.90786
C	3.74066	-1.83510	1.36734
C	5.11904	-0.43124	-0.60904
H	3.45710	-0.87926	-1.88907
C	4.95816	-1.22319	1.65780
H	3.20090	-2.36933	2.13903
C	5.65745	-0.52375	0.67478
H	5.64101	0.12391	-1.38338
H	5.36131	-1.29819	2.66387
H	6.60561	-0.04861	0.90854
C	0.76096	0.93634	2.22818
H	-0.13138	1.19431	2.79389
H	1.23904	0.00639	2.54095
C	1.58642	2.01887	1.74795
C	1.17268	3.38312	1.77697
C	2.70883	1.67241	0.94139
C	1.84972	4.33069	1.04276
H	0.3093	3.65362	2.37876
C	3.37329	2.65938	0.1864
H	3.13593	0.67824	1.01768
C	2.94828	3.9707	0.23117
H	1.52823	5.36838	1.07705
H	4.21671	2.36435	-0.42811
H	3.45663	4.73169	-0.35337
P	-1.59085	0.22542	0.0688
C	-2.47659	1.57715	-0.79474
C	-2.14913	-1.28277	-0.81203
C	-2.4432	0.06907	1.68505
C	-3.73526	1.37018	-1.37373
C	-1.88866	2.84669	-0.8547
C	-3.25083	-2.02895	-0.37159
C	-1.48611	-1.65617	-1.98716
C	-1.90929	-0.83697	2.6147
C	-3.59714	0.78831	2.01157
C	-4.4032	2.42582	-1.99009
H	-4.18855	0.38321	-1.34947
C	-2.56139	3.89895	-1.47113
H	-0.89447	2.99982	-0.44243
C	-3.6748	-3.14246	-1.09544
H	-3.77447	-1.74496	0.53648
C	-1.91108	-2.77284	-2.70116
H	-0.64129	-1.06743	-2.33687
C	-2.5369	-1.03362	3.84085
H	-0.99184	-1.37388	2.38559
C	-4.21482	0.59641	3.24865
H	-4.01648	1.49521	1.30229
C	-3.81833	3.69129	-2.03732
H	-5.37723	2.2572	-2.44094
H	-2.09365	4.87798	-1.52267
C	-3.00187	-3.52012	-2.25687
H	-4.52924	-3.71648	-0.74688
H	-1.3811	-3.05968	-3.60469
C	-3.69172	-0.31691	4.16122
H	-2.11487	-1.73873	4.55159
H	-5.10882	1.16264	3.49515
H	-4.3376	4.5115	-2.5254
H	-3.32952	-4.39243	-2.81601
H	-4.17627	-0.46516	5.12231
Br	1.1099	0.8629	-2.28591
H	-1.6437	-4.79041	0.32694
C	1.92097	-2.39732	-0.25077
N	1.66898	-2.65344	-1.51589
N	1.4635	-2.86099	-2.61047

TS3-4(*E*)

Energy: -2895233.8820766

Pd	0.59013	-0.12421	-0.22656
C	1.62946	-2.33223	1.06087
O	1.74114	-2.20715	2.26859
O	0.87870	-3.28116	0.47413
C	0.02207	-4.01935	1.35064
H	-0.78647	-3.37217	1.70454
H	0.57984	-4.41743	2.20141
C	3.57466	-0.82449	0.23367
C	4.05774	-0.00819	-0.80644
C	4.37037	-1.03001	1.37163
C	5.31971	0.56382	-0.72478
H	3.41615	0.17820	-1.66432
C	5.61474	-0.41116	1.46766
H	3.99104	-1.63721	2.18523
C	6.09732	0.37368	0.42001
H	5.68345	1.18555	-1.53732
H	6.21438	-0.5511	2.36259
H	7.07386	0.84335	0.49861
C	1.09062	0.79985	1.59753
H	0.22739	0.80907	2.25849
H	1.91434	0.2746	2.07931
C	1.45073	2.13129	1.07505
C	0.45576	3.0813	0.76458
C	2.79197	2.48693	0.84229
C	0.78398	4.30778	0.20101
H	-0.58278	2.84428	0.97801
C	3.12032	3.71555	0.27738
H	3.57716	1.79146	1.11905

C	2.11936	4.62719	-0.05795
H	-0.00297	5.01955	-0.03477
H	4.16422	3.96239	0.10228
H	2.37646	5.58467	-0.50252
P	-1.70428	0.1247	0.11147
C	-2.64892	1.16198	-1.05805
C	-2.46335	-1.55059	-0.0141
C	-2.27947	0.69278	1.7546
C	-4.01983	0.96869	-1.26818
C	-1.98343	2.20327	-1.71432
C	-3.50895	-1.95145	0.83086
C	-1.98897	-2.44721	-0.98249
C	-1.87819	-0.0375	2.8855
C	-3.03516	1.85689	1.92719
C	-4.7196	1.81711	-2.12226
H	-4.53509	0.15241	-0.76921
C	-2.69002	3.0538	-2.56207
H	-0.91487	2.33323	-1.57156
C	-4.05622	-3.22892	0.71961
H	-3.89446	-1.27031	1.5828
C	-2.54687	-3.71813	-1.09479
H	-1.18386	-2.14838	-1.64588
C	-2.24166	0.38242	4.16052
H	-1.27354	-0.93336	2.76129
C	-3.38834	2.2806	3.20888
H	-3.35144	2.43088	1.06137
C	-4.05562	2.86197	-2.76673
H	-5.78182	1.66046	-2.28839
H	-2.16764	3.85699	-3.07377
C	-3.57509	-4.11665	-0.24126
H	-4.86205	-3.52662	1.38495
H	-2.16677	-4.40053	-1.84997
C	-2.9963	1.54561	4.32512
H	-1.926	-0.19227	5.02656
H	-3.97441	3.18716	3.33119
H	-4.60277	3.52091	-3.43544
H	-4.00158	-5.11252	-0.32579
H	-3.27274	1.8783	5.3216
Br	0.34106	-0.28749	-2.71501
H	-0.39686	-4.82078	0.74431
C	2.2125	-1.36221	0.08975
N	2.39962	-2.42512	-1.38739
N	2.19614	-2.51278	-2.48075

Int-4(*E*)

Energy: -2826551.9492598

Pd	-0.53451	-0.48262	-0.66774
C	-2.47247	-0.65575	-0.72838
C	-3.01913	-1.26552	-1.96035
O	-2.98071	-2.44104	-2.24489
O	-3.51583	-0.29915	-2.76474
C	-3.92810	-0.74880	-4.06335
H	-4.72878	-1.48853	-3.98000
H	-3.08637	-1.19832	-4.59692
C	-3.35785	-0.31053	0.34132
C	-2.83701	0.27468	1.52395
C	-4.75609	-0.50429	0.23680
C	-3.68386	0.65216	2.55129
H	-1.76325	0.41291	1.60688
C	-5.59918	-0.11596	1.26649
H	-5.16699	-0.95848	-0.65968
C	-5.06339	0.46018	2.42248
H	-3.27305	1.09433	3.45352
H	-6.67108	-0.26497	1.17923
H	-5.72684	0.75915	3.22975
C	-0.53518	1.19804	-1.95082
H	0.35668	1.12509	-2.57715
H	-1.42682	1.08179	-2.57023
C	-0.55915	2.4559	-1.16296
C	0.54574	3.32443	-1.13494
C	-1.68241	2.81194	-0.39228
C	0.55219	4.45976	-0.32652
H	1.41269	3.10105	-1.74774
C	-1.67883	3.94462	0.4137
H	-2.55788	2.1719	-0.41672
C	-0.55237	4.76964	0.46615
H	1.4311	5.09899	-0.31485
H	-2.55715	4.18144	1.009
H	-0.54312	5.64866	1.10469
P	1.70694	-0.24435	-0.00315
C	1.48109	0.25012	1.74281
C	2.80731	-1.70228	-0.01103
C	2.80439	1.01832	-0.74231
C	1.74822	-0.62575	2.79908
C	0.84367	1.47465	2.0021
C	4.08092	-1.6253	0.57022
C	2.40619	-2.87863	-0.65123
C	3.0288	0.92763	-2.12322
C	3.4007	2.0539	-0.0172
C	1.40047	-0.2719	4.10186
H	2.20208	-1.59131	2.60214
C	0.50196	1.82212	3.30585
H	0.60387	2.15139	1.18773
C	4.93611	-2.72184	0.52654

H	4.40034	-0.70471	1.05211
C	3.27098	-3.97135	-0.70131
H	1.41404	-2.94241	-1.08636
C	3.82092	1.87037	-2.77131
H	2.57329	0.11847	-2.68954
C	4.19243	2.99847	-0.66932
H	3.23164	2.136	1.05161
C	0.7792	0.94913	4.35896
H	1.60586	-0.96093	4.91624
H	0.01204	2.7743	3.48923
C	4.53066	-3.89626	-0.11066
H	5.91988	-2.65943	0.98342
H	2.95274	-4.8844	-1.19614
C	4.39758	2.91437	-2.04519
H	3.98233	1.79622	-3.84298
H	4.6446	3.80544	-0.09939
H	0.50668	1.21728	5.37619
H	5.19991	-4.7516	-0.147
H	5.00682	3.65752	-2.55187
Br	-0.72991	-2.52282	0.83585
H	-4.28018	0.14175	-4.58322

TS4-5(*E*)

Energy: -2826549.3872390

Pd	-0.33454	-0.75580	-0.09332
C	-2.14722	-1.38772	0.16563
C	-2.25890	-2.69834	0.85954
O	-2.81078	-3.65341	0.34994
O	-1.62699	-2.74633	2.04650
C	-3.34083	-0.80146	-0.37449
C	-3.22618	0.23373	-1.33086
C	-4.62702	-1.14822	0.09891
C	-4.35069	0.90447	-1.78508
H	-2.23663	0.48088	-1.70114
C	-5.74697	-0.46418	-0.34824
H	-4.73178	-1.95499	0.81694
C	-5.60892	0.56454	-1.28533
H	-4.24791	1.70347	-2.51199
H	-6.73088	-0.72786	0.02833
H	-6.48949	1.10049	-1.62927
H	-1.94897	-0.32654	2.26608
H	-0.38191	0.43763	2.10924
C	-2.02646	1.51459	1.17396
C	-1.33361	0.27792	1.59779
C	-3.34674	1.75708	1.58926
C	-1.43787	2.45126	0.3051
C	-4.04568	2.88251	1.16325
H	-3.83393	1.03645	2.24103
C	-2.128	3.58509	-0.1109
H	-0.44362	2.2652	-0.08796
C	-3.4392	3.80581	0.31208
H	-5.07076	3.03392	1.49058
H	-1.64337	4.286	-0.7855
H	-3.98487	4.68276	-0.02503
P	1.80616	0.24033	0.06196
C	3.21545	-0.82832	-0.39782
C	1.9768	1.73365	-0.98794
C	2.26436	0.8191	1.74394
C	4.43449	-0.29089	-0.826
C	3.08139	-2.21386	-0.25046
C	2.73735	2.84715	-0.60692
C	1.30356	1.74692	-2.21882
C	1.60372	1.92378	2.30576
C	3.19137	0.11617	2.5235
C	5.50988	-1.13248	-1.09987
H	4.5406	0.78268	-0.95297
C	4.16264	-3.05095	-0.51643
H	2.12446	-2.6315	0.04758
C	2.81499	3.96158	-1.44032
H	3.2602	2.84872	0.34487
C	1.3886	2.86259	-3.04799
H	0.72483	0.87807	-2.52266
C	1.87295	2.31798	3.61362
H	0.88222	2.48576	1.71983
C	3.45343	0.51122	3.83462
H	3.71431	-0.73783	2.10407
C	5.37599	-2.51206	-0.9421
H	6.45184	-0.71081	-1.4395
H	4.05002	-4.12579	-0.40761
C	2.1385	3.97274	-2.65941
H	3.40373	4.82203	-1.13439
H	0.86387	2.86331	-3.99928
C	2.79721	1.61137	4.38306
H	1.35585	3.17751	4.03077
H	4.17791	-0.04218	4.42574
H	6.21523	-3.16715	-1.15936
H	2.1967	4.84447	-3.30546
H	3.00457	1.91792	5.40445
Br	0.21515	-1.85177	-2.23673
C	-1.61496	-4.03798	2.66449
H	-1.07484	-4.75358	2.03871
H	-1.10639	-3.90107	3.61845
H	-2.6334	-4.4054	2.81964

TS4-5-(E)-(Z)

Energy: -2826548.7694810

Pd	-0.34773	-0.23709	-0.13408
C	-2.20359	-0.64046	-0.58158
C	-2.38410	-1.01044	-2.01253
O	-2.78906	-2.10938	-2.33682
O	-1.96673	-0.07849	-2.88295
C	-2.02148	-0.47586	-4.25775
H	-3.03566	-0.77392	-4.53833
H	-1.34405	-1.31491	-4.43719
C	-3.31564	-0.79202	0.30105
C	-3.08875	-0.76756	1.69785
C	-4.64202	-0.95074	-0.16950
C	-4.14009	-0.92071	2.58660
H	-2.06576	-0.65877	2.04305
C	-5.69198	-1.08100	0.72327
H	-4.82857	-0.97385	-1.23717
C	-5.44007	-1.07285	2.09906
H	-3.95428	-0.92025	3.65605
H	-6.7074	-1.19649	0.35704
H	-6.26623	-1.18736	2.79603
C	-0.74085	1.8055	-0.49504
H	-0.03467	2.35208	0.13327
H	-0.49629	1.97006	-1.5478
C	-2.13953	2.17967	-0.1715
C	-2.53558	2.37094	1.16241
C	-3.12708	2.28505	-1.16632
C	-3.86603	2.60013	1.49421
H	-1.78489	2.2947	1.94609
C	-4.45993	2.52063	-0.83591
H	-2.83977	2.15198	-2.20438
C	-4.84198	2.66561	0.49648
H	-4.14821	2.71851	2.53722
H	-5.20504	2.58859	-1.62494
H	-5.88289	2.83451	0.75662
P	1.97503	0.17983	0.09362
C	2.70397	-0.38913	1.67037
C	2.97498	-0.60281	-1.23139
C	2.495	1.93551	0.00375
C	4.06498	-0.68558	1.79975
C	1.86999	-0.46648	2.7919
C	4.20597	-0.06211	-1.63301
C	2.50773	-1.77369	-1.84306
C	2.36795	2.61133	-1.21947
C	2.91533	2.64454	1.13383
C	4.58572	-1.04781	3.03993
H	4.71557	-0.64438	0.93126
C	2.3957	-0.81907	4.03232
H	0.8071	-0.27307	2.67977
C	4.95743	-0.68532	-2.6265
H	4.57246	0.85279	-1.1765
C	3.26474	-2.39175	-2.83664
H	1.56533	-2.20923	-1.52436
C	2.6696	3.96597	-1.31114
H	2.03711	2.06873	-2.10114
C	3.21016	4.00485	1.03964
H	3.01892	2.13344	2.08632
C	3.75339	-1.11079	4.1574
H	5.64198	-1.28478	3.13249
H	1.74122	-0.88323	4.89693
C	4.48738	-1.85092	-3.23106
H	5.90925	-0.2575	-2.9293
H	2.89358	-3.30075	-3.30167
C	3.09008	4.66723	-0.17993
H	2.57131	4.47674	-2.26494
H	3.5391	4.54471	1.9233
H	4.16148	-1.39636	5.12309
H	5.0731	-2.33495	-4.00791
H	3.32151	5.72631	-0.25058
Br	-0.004	-2.62141	0.65517
H	-1.70716	0.39872	-4.82671

Int-5(*E*)

Energy: -2826584.1822375

Pd	0.27252	-0.56755	-0.31160
C	2.32564	-0.59303	-0.83044
C	2.30960	-1.74100	-1.78276
O	1.77942	-1.71505	-2.88357
O	2.90594	-2.82405	-1.26948
C	3.37827	-0.56636	0.23232
C	3.25167	-1.26580	1.43692
C	4.55405	0.16095	-0.00445
C	4.26879	-1.22169	2.38755
H	2.35105	-1.84264	1.61681
C	5.56959	0.20370	0.94624
H	4.66965	0.70256	-0.93893
C	5.42830	-0.48505	2.15016
H	4.15113	-1.76825	3.31947
H	6.47089	0.77635	0.74493
H	6.21789	-0.45001	2.89595
H	1.87778	0.63843	-2.52624
H	0.62201	0.73932	-1.37442

C	2.25065	2.01167	-0.86783
C	1.83833	0.68117	-1.4324
C	2.80606	2.97833	-1.7078
C	2.04151	2.31989	0.48207
C	3.16208	4.23049	-1.20603
H	2.96285	2.74978	-2.75922
C	2.39331	3.56854	0.98272
H	1.60448	1.56892	1.13692
C	2.95586	4.5285	0.13906
H	3.59623	4.97307	-1.86968
H	2.22667	3.79332	2.03224
H	3.22865	5.50477	0.52965
P	-1.89674	0.18071	0.0414
C	-3.25124	-0.9912	-0.28646
C	-2.16249	0.76917	1.75362
C	-2.27383	1.65027	-0.98743
C	-4.51379	-0.83662	0.29942
C	-3.01848	-2.04688	-1.17568
C	-2.89711	1.92836	2.03472
C	-1.61778	0.01857	2.80541
C	-1.37221	2.72531	-0.93905
C	-3.38545	1.72413	-1.83183
C	-5.53868	-1.72592	-0.01374
H	-4.69008	-0.02721	1.0027
C	-4.04894	-2.93063	-1.4882
H	-2.02786	-2.18457	-1.59977
C	-3.08689	2.33068	3.35561
H	-3.31396	2.51823	1.22342
C	-1.81483	0.42626	4.12235
H	-1.04794	-0.88109	2.58637
C	-1.58127	3.85437	-1.72324
H	-0.50402	2.68223	-0.28533
C	-3.58784	2.85698	-2.62183
H	-4.08967	0.89882	-1.87604
C	-5.3072	-2.77094	-0.90912
H	-6.51626	-1.60653	0.44494
H	-3.86307	-3.7523	-2.17368
C	-2.54615	1.58144	4.39985
H	-3.65625	3.23154	3.56738
H	-1.39017	-0.15923	4.93291
C	-2.68982	3.92069	-2.57017
H	-0.87285	4.67653	-1.67722
H	-4.451	2.90405	-3.27994
H	-6.10693	-3.46655	-1.14818
H	-2.6924	1.89901	5.42863
H	-2.85005	4.79893	-3.18926
Br	-0.02081	-2.73605	0.79493
C	2.7059	-4.03285	-2.00456
H	3.05073	-3.92558	-3.03659
H	3.285	-4.7933	-1.48106
H	1.64439	-4.29624	-2.00209

TS5-6(*E*)

Energy: -2826577.4393031

Pd	0.30274	-0.70508	-0.58989
C	2.49543	-0.49358	-0.92520
C	2.78685	-1.71945	-1.72789
O	3.52958	-2.60696	-1.37558
O	2.10325	-1.74643	-2.90127
C	3.35515	-0.31000	0.28430
C	3.27755	-1.15740	1.39424
C	4.31308	0.71386	0.28016
C	4.11413	-0.95848	2.48941
H	2.54846	-1.95970	1.39294
C	5.15083	0.90907	1.37437
H	4.39935	1.36337	-0.58606
C	5.04833	0.07670	2.48805
H	4.03621	-1.62208	3.34639
H	5.88499	1.70983	1.35390
H	5.6992	0.22844	3.34501
H	1.77591	0.55437	-2.63843
H	0.16649	0.45612	-1.60312
C	1.79826	2.00905	-1.02026
C	1.8474	0.61534	-1.55285
C	1.88742	3.07387	-1.92265
C	1.54001	2.28745	0.33166
C	1.72734	4.39014	-1.48802
H	2.06799	2.87037	-2.97548
C	1.36919	3.59687	0.7618
H	1.43943	1.47107	1.03918
C	1.46138	4.65467	-0.14649
H	1.79931	5.20527	-2.20268
H	1.14167	3.7853	1.80648
H	1.31902	5.67765	0.19022
P	-1.77585	0.01315	0.05257
C	-3.09064	-1.20124	0.37001
C	-1.4803	0.86772	1.64908
C	-2.55703	1.28934	-1.00614
C	-4.09119	-0.95201	1.31728
C	-3.11548	-2.37977	-0.38327
C	-1.97553	2.14855	1.91746
C	-0.67167	0.22328	2.59939
C	-1.79314	2.40952	-1.3702
C	-3.87087	1.17419	-1.46911

C	-5.11723	-1.87552	1.50056
H	-4.06237	-0.0415	1.90981
C	-4.14742	-3.29681	-0.1989
H	-2.31297	-2.58427	-1.08547
C	-1.65151	2.78625	3.11472
H	-2.60065	2.65678	1.19022
C	-0.35217	0.86732	3.79078
H	-0.28517	-0.77259	2.39494
C	-2.33997	3.39814	-2.1802
H	-0.77532	2.52005	-1.00568
C	-4.41014	2.16314	-2.29386
H	-4.47274	0.31468	-1.19043
C	-5.14644	-3.0458	0.74101
H	-5.89085	-1.68412	2.23882
H	-4.16044	-4.21568	-0.77765
C	-0.83404	2.15201	4.04828
H	-2.03598	3.78302	3.31266
H	0.28432	0.36618	4.51424
C	-3.64977	3.27443	-2.64923
H	-1.7372	4.2617	-2.44632
H	-5.42927	2.06098	-2.65611
H	-5.94485	-3.76762	0.88959
H	-0.57377	2.65551	4.97529
H	-4.07397	4.0424	-3.29001
Br	0.2329	-2.8784	0.61652
C	2.21857	-2.97473	-3.62363
H	1.82406	-3.80025	-3.02473
H	1.62625	-2.84091	-4.52921
H	3.26229	-3.18392	-3.87338

TS5(*E*)-5η^3

Energy: -2826581.6967540

Pd	-0.20967	-0.71183	-0.45643
C	-2.30392	-0.97497	-0.36211
C	-2.75828	-2.28545	-0.91395
O	-3.32648	-3.16846	-0.30585
O	-2.44679	-2.39719	-2.22518
C	-2.30843	-0.71592	1.09615
C	-2.48623	-1.74213	2.05169
C	-1.91270	0.55863	1.57750
C	-2.27137	-1.50115	3.40131
H	-2.76726	-2.72943	1.71396
C	-1.69476	0.78482	2.93406
H	-1.78981	1.39353	0.89889
C	-1.87131	-0.24143	3.85568
H	-2.40926	-2.31382	4.10921
H	-1.38542	1.77283	3.26293
H	-1.70221	-0.06586	4.91437
H	-2.45481	-0.19154	-2.33925
H	-1.16832	0.57704	-1.40715
C	-3.08287	1.41744	-1.05621
C	-2.26392	0.17721	-1.32966
C	-2.52287	2.68702	-1.21879
C	-4.41804	1.30325	-0.66016
C	-3.28512	3.8293	-0.98611
H	-1.47647	2.78323	-1.49942
C	-5.18134	2.44559	-0.43224
H	-4.84953	0.31654	-0.51335
C	-4.61744	3.7119	-0.59306
H	-2.82956	4.80873	-1.10317
H	-6.21722	2.34672	-0.1198
H	-5.21307	4.60109	-0.40657
P	1.77805	0.38328	-0.15005
C	2.32933	0.30689	1.59207
C	3.25126	0.02623	-1.16175
C	1.39701	2.15835	-0.41813
C	3.48871	0.97071	2.01608
C	1.54163	-0.37961	2.52341
C	4.22446	0.99059	-1.45867
C	3.4119	-1.28981	-1.61588
C	1.43243	2.70569	-1.70896
C	0.88335	2.92551	0.63626
C	3.85027	0.95336	3.35923
H	4.10981	1.49633	1.29638
C	1.90647	-0.38872	3.86913
H	0.65144	-0.91034	2.19887
C	5.34952	0.63921	-2.20051
H	4.09565	2.01689	-1.1254
C	4.54404	-1.63415	-2.3518
H	2.65463	-2.03514	-1.38166
C	0.98515	4.00619	-1.93331
H	1.81418	2.1147	-2.53726
C	0.42565	4.22081	0.4045
H	0.8354	2.50186	1.63554
C	3.0567	0.27558	4.28783
H	4.75132	1.46683	3.683
H	1.28497	-0.92053	4.58326
C	5.51086	-0.6733	-2.64561
H	6.09954	1.39048	-2.432
H	4.66611	-2.65593	-2.69958
C	0.4806	4.76705	-0.87758
H	1.02601	4.42335	-2.93557
H	0.02454	4.8041	1.22837
H	3.341	0.26412	5.33659

H	6.38925	-0.94484	-3.22465
H	0.12726	5.77871	-1.05529
Br	0.43113	-3.0447	0.02304
C	-2.661	-3.69604	-2.78149
H	-3.71139	-3.98874	-2.69904
H	-2.3642	-3.61934	-3.82761
H	-2.0402	-4.42907	-2.25962

Int-6(*E*)

Energy: -2826579.1378332

Pd	0.24815	-0.63973	-0.86847
C	2.63136	-0.27134	-0.89205
C	3.03670	-1.55078	-1.55908
O	3.84004	-2.32746	-1.09765
O	2.39183	-1.75211	-2.73244
C	3.26134	-0.02096	0.43591
C	3.08509	-0.89298	1.51580
C	4.09180	1.09704	0.59542
C	3.68632	-0.62220	2.74187
H	2.46514	-1.77286	1.38355
C	4.69658	1.36287	1.82033
H	4.25586	1.76458	-0.24526
C	4.48640	0.50862	2.90241
H	3.53442	-1.30631	3.57260
H	5.33425	2.23597	1.92743
H	4.95535	0.7163	3.86055
H	1.89128	0.53788	-2.69469
H	-0.25577	0.47264	-1.78631
C	1.66753	2.1071	-1.21058
C	1.97864	0.7161	-1.62438
C	1.58453	3.08579	-2.21013
C	1.3465	2.47052	0.10943
C	1.20297	4.39218	-1.90574
H	1.80729	2.81577	-3.23965
C	0.96039	3.77045	0.41026
H	1.36302	1.72423	0.89531
C	0.88731	4.73917	-0.59383
H	1.14558	5.13401	-2.69748
H	0.69326	4.01633	1.43326
H	0.57826	5.75289	-0.35501
P	-1.73415	-0.078	0.03205
C	-2.89993	-1.4136	0.43216
C	-1.26012	0.68881	1.63052
C	-2.74291	1.21037	-0.79354
C	-3.72429	-1.33514	1.56087
C	-2.98934	-2.51281	-0.42837
C	-1.7527	1.93675	2.02803
C	-0.30327	0.03535	2.42404
C	-2.09445	2.35346	-1.28487
C	-4.13305	1.10701	-0.90202
C	-4.64442	-2.34906	1.81742
H	-3.64186	-0.48741	2.23569
C	-3.91516	-3.51961	-0.16923
H	-2.31358	-2.58711	-1.27504
C	-1.27975	2.53299	3.19684
H	-2.4885	2.45367	1.42059
C	0.1728	0.64333	3.58092
H	0.08332	-0.93341	2.11849
C	-2.82971	3.37948	-1.86717
H	-1.01563	2.45034	-1.19962
C	-4.86402	2.13251	-1.50402
H	-4.64603	0.22898	-0.52211
C	-4.74157	-3.43842	0.95142
H	-5.28092	-2.29081	2.6958
H	-3.97743	-4.37721	-0.83254
C	-0.30855	1.8955	3.96667
H	-1.66447	3.50396	3.49662
H	0.93901	0.14473	4.1664
C	-4.21697	3.26889	-1.98333
H	-2.31256	4.2613	-2.23403
H	-5.94248	2.03891	-1.5955
H	-5.45563	-4.23112	1.1569
H	0.07446	2.37296	4.86432
H	-4.78999	4.06585	-2.44907
Br	0.45061	-2.91493	0.19604
C	2.56528	-3.06002	-3.28659
H	2.16161	-3.80435	-2.59448
H	2.00374	-3.05968	-4.22094
H	3.6224	-3.26854	-3.47036

Productive (Trans PPh_3) (*Z*)-Pathway

Int-3(*Z*)

Energy: -2895250.6696178

Pd	0.05100	-0.73640	-1.03075
C	-2.38984	-2.67235	1.04594
O	-2.17521	-2.42541	2.22021
O	-2.11544	-3.87169	0.48121
C	-1.52806	-4.83212	1.36419
H	-2.18498	-5.02798	2.21565
H	-0.56356	-4.47325	1.73455

C	-3.36335	-0.34708	0.37740
C	-3.36359	0.62385	-0.63608
C	-3.77977	0.01163	1.66909
C	-3.78503	1.91959	-0.36261
H	-2.99462	0.37657	-1.62794
C	-4.17418	1.32008	1.93563
H	-3.77717	-0.73011	2.45840
C	-4.18625	2.27729	0.92309
H	-3.75912	2.66255	-1.15249
H	-4.48354	1.58611	2.94284
H	-4.49009	3.29795	1.1348
C	0.69498	-2.12817	0.33022
H	0.33677	-1.9675	1.34744
H	0.12592	-2.9335	-0.16002
C	2.1517	-2.30889	0.22895
C	3.00838	-1.8814	1.25841
C	2.72808	-2.84217	-0.94076
C	4.38924	-1.9374	1.10335
H	2.57759	-1.48636	2.17324
C	4.10956	-2.89682	-1.09398
H	2.07707	-3.1877	-1.74077
C	4.94663	-2.43447	-0.07595
H	5.03517	-1.58864	1.9045
H	4.53524	-3.29998	-2.00875
H	6.02556	-2.47355	-0.19636
P	0.71595	0.97064	0.22099
C	2.36686	1.59144	-0.26994
C	-0.34069	2.44985	0.00958
C	0.8059	0.72475	2.026
C	2.7412	2.90672	0.04349
C	3.27018	0.75427	-0.93248
C	-0.80724	3.18688	1.10255
C	-0.5927	2.9005	-1.29373
C	-0.30179	0.13074	2.64518
C	1.93102	1.05794	2.78816
C	4.01204	3.36771	-0.2886
H	2.03652	3.56776	0.5405
C	4.5405	1.22162	-1.26216
H	2.9841	-0.25817	-1.1939
C	-1.50755	4.37442	0.89187
H	-0.62546	2.83991	2.11436
C	-1.28566	4.08919	-1.49469
H	-0.26263	2.31096	-2.14457
C	-0.28441	-0.1309	4.01085
H	-1.17043	-0.15029	2.05898
C	1.94276	0.79471	4.15783
H	2.79949	1.50373	2.31392
C	4.91403	2.5246	-0.93972
H	4.29543	4.38786	-0.04515
H	5.23351	0.55971	-1.77258
C	-1.74173	4.83075	-0.40282
H	-1.87046	4.94013	1.74528
H	-1.47662	4.43211	-2.50756
C	0.83959	0.19959	4.76945
H	-1.14312	-0.61316	4.46721
H	2.82071	1.04871	4.74532
H	5.90412	2.888	-1.20104
H	-2.28526	5.75783	-0.56323
H	0.8594	-0.01363	5.83468
Br	-0.7847	-0.22644	-3.28369
H	-1.39462	-5.73366	0.76673
C	-2.9428	-1.72897	0.08264
N	-3.10922	-2.18606	-1.14348
N	-3.25773	-2.5725	-2.19778

TS3-4(*Z*)

Energy: -2895232.9555150

Pd	-0.51756	-0.78174	-0.40019
C	-2.91214	-2.08016	0.93363
O	-2.84717	-1.95365	2.14211
O	-3.19372	-3.25251	0.33803
C	-3.42806	-4.34447	1.23562
H	-4.28056	-4.13272	1.88641
H	-2.54647	-4.52809	1.85551
C	-3.04969	0.37465	0.18995
C	-2.91547	1.33614	-0.83128
C	-3.60113	0.77594	1.42069
C	-3.31630	2.64848	-0.62572
H	-2.47308	1.05130	-1.78075
C	-3.96896	2.10301	1.62645
H	-3.70563	0.05564	2.22177
C	-3.83211	3.04359	0.60801
H	-3.18593	3.37307	-1.42232
H	-4.373	2.39776	2.59121
H	-4.1182	4.07821	0.7742
C	-0.01105	-2.13523	1.10795
H	-0.07421	-1.71134	2.10915
H	-0.7471	-2.93071	0.98383
C	1.33481	-2.59404	0.71372
C	2.47883	-2.25903	1.45928
C	1.50423	-3.37249	-0.44921
C	3.74411	-2.66013	1.0431
H	2.3643	-1.68007	2.37002
C	2.77043	-3.77324	-0.86328

H	0.62947	-3.63713	-1.03852
C	3.89759	-3.41288	-0.12186
H	4.61571	-2.38321	1.62991
H	2.87895	-4.36397	-1.7687
H	4.88729	-3.72088	-0.447
P	1.03549	0.81966	0.21954
C	2.66823	0.90364	-0.58607
C	0.31964	2.47131	-0.15208
C	1.34276	0.87315	2.02074
C	3.45601	2.06262	-0.52114
C	3.12704	-0.21136	-1.2916
C	-0.10154	3.35944	0.84272
C	0.20363	2.84234	-1.50019
C	0.23272	0.7211	2.86701
C	2.61836	1.00679	2.5783
C	4.70227	2.0914	-1.13955
H	3.08657	2.93929	0.00464
C	4.37602	-0.17711	-1.90882
H	2.50438	-1.09651	-1.36484
C	-0.62568	4.6038	0.494
H	-0.0183	3.09087	1.89027
C	-0.31134	4.08836	-1.84059
H	0.50241	2.14639	-2.27834
C	0.39954	0.71538	4.2487
H	-0.75901	0.59167	2.43769
C	2.78156	0.98744	3.96327
H	3.48519	1.10425	1.93246
C	5.16389	0.9692	-1.83152
H	5.31057	2.99025	-1.08889
H	4.72594	-1.04977	-2.45204
C	-0.72739	4.97381	-0.8446
H	-0.95137	5.28443	1.27562
H	-0.393	4.3648	-2.8881
C	1.67574	0.84344	4.79953
H	-0.46626	0.59499	4.89351
H	3.77728	1.08115	4.38785
H	6.13558	0.99533	-2.31739
H	-1.13254	5.94579	-1.11282
H	1.80736	0.82457	5.87778
Br	-0.44458	-0.40671	-2.88989
H	-3.63531	-5.20401	0.59904
C	-2.52231	-1.00461	-0.02383
N	-3.35614	-1.5264	-1.51893
N	-3.29158	-1.55126	-2.63375

Int-4(*Z*)

Energy: -2826549.6160917

Pd	0.66076	-0.32689	-0.12360
C	2.59360	-0.23445	0.03127
C	3.04234	0.95973	0.78816
O	2.85316	1.11593	1.97497
O	3.63088	1.85053	-0.02441
C	3.88240	3.13773	0.56595
H	4.61504	3.04887	1.37250
H	2.95290	3.55868	0.95456
C	3.57167	-1.19165	-0.38540
C	3.16566	-2.33622	-1.11381
C	4.94672	-1.02572	-0.08927
C	4.09778	-3.26979	-1.53447
H	2.10705	-2.46231	-1.31584
C	5.87502	-1.96482	-0.50977
H	5.27168	-0.15338	0.46865
C	5.45037	-3.08462	-1.23143
H	3.77922	-4.14658	-2.08956
H	6.92755	-1.83376	-0.2781
H	6.18029	-3.82057	-1.55818
C	0.73067	1.26399	-1.49162
H	1.59265	1.12885	-2.15273
H	-0.16665	1.1585	-2.10933
C	0.77417	2.63238	-0.87472
C	1.31881	3.70337	-1.60288
C	0.25919	2.91477	0.39957
C	1.32168	5.0004	-1.09609
H	1.74128	3.50913	-2.58604
C	0.2577	4.21251	0.91222
H	-0.12974	2.10344	1.00691
C	0.78573	5.26439	0.16574
H	1.7465	5.8084	-1.68671
H	-0.14941	4.39276	1.90356
H	0.78959	6.27517	0.56428
P	-1.72238	-0.34282	-0.10129
C	-2.4686	-2.00964	-0.1861
C	-2.38387	0.42222	1.42792
C	-2.59496	0.55725	-1.44258
C	-3.7149	-2.29638	0.37938
C	-1.78868	-3.00277	-0.90105
C	-3.64199	1.04039	1.46124
C	-1.60345	0.38681	2.59224
C	-2.5583	1.96004	-1.46557
C	-3.22109	-0.12462	-2.49275
C	-4.27655	-3.56215	0.22551

H	-4.24185	-1.53621	0.9483
C	-2.35846	-4.26264	-1.06385
H	-0.80469	-2.78792	-1.30737
C	-4.11055	1.61558	2.64035
H	-4.25005	1.08364	0.56239
C	-2.07757	0.96599	3.76736
H	-0.63239	-0.10038	2.57922
C	-3.14221	2.66291	-2.51499
H	-2.06807	2.50407	-0.66392
C	-3.80233	0.58421	-3.54367
H	-3.26262	-1.20953	-2.48754
C	-3.60217	-4.54418	-0.49928
H	-5.24102	-3.78165	0.67497
H	-1.82274	-5.02974	-1.61575
C	-3.32804	1.58186	3.79424
H	-5.08595	2.09411	2.65489
H	-1.46212	0.93604	4.6619
C	-3.76536	1.97702	-3.5579
H	-3.10312	3.7485	-2.51828
H	-4.28906	0.04286	-4.3503
H	-4.0416	-5.531	-0.61635
H	-3.69222	2.03657	4.71151
H	-4.21937	2.52657	-4.37786
Br	0.6987	-2.29933	1.462
H	4.26619	3.75715	-0.24279

TS4-5(*Z*)

Energy: -2826545.2132343

Pd	-0.53157	-0.54683	-0.19498
C	-2.46536	-0.54356	-0.18911
C	-3.10975	0.49591	-1.05095
O	-2.86497	0.63270	-2.22805
O	-3.94645	1.28961	-0.35542
C	-4.37689	2.46977	-1.05130
H	-4.93417	2.20393	-1.95290
H	-3.50823	3.07639	-1.32037
C	-3.29778	-1.56275	0.41838
C	-2.68155	-2.62356	1.12028
C	-4.70484	-1.56685	0.29356
C	-3.43919	-3.64049	1.67871
H	-1.59730	-2.62984	1.18861
C	-5.45956	-2.59168	0.84918
H	-5.19956	-0.75878	-0.23341
C	-4.83048	-3.62634	1.5437
H	-2.95101	-4.45191	2.21002
H	-6.54029	-2.58629	0.74256
H	-5.42464	-4.4262	1.97726
C	-1.42958	0.87082	1.24571
H	-2.3428	0.62025	1.79142
H	-0.59686	0.66009	1.9266
C	-1.46375	2.28617	0.77235
C	-2.2062	3.23764	1.49055
C	-0.77719	2.71918	-0.37128
C	-2.23287	4.57358	1.10105
H	-2.7655	2.91941	2.36691
C	-0.7999	4.05694	-0.76424
H	-0.23512	1.99262	-0.9694
C	-1.5255	4.99175	-0.02808
H	-2.81028	5.29135	1.67806
H	-0.25354	4.35919	-1.65327
H	-1.54881	6.03389	-0.33429
P	1.77093	-0.13299	0.14766
C	2.89482	-1.57269	0.12347
C	2.4314	1.01323	-1.11929
C	2.1676	0.67073	1.74971
C	4.25031	-1.44233	-0.199
C	2.38968	-2.82149	0.50309
C	3.40231	1.98247	-0.83701
C	1.92063	0.90381	-2.42148
C	1.73388	1.98503	1.98354
C	2.79784	-0.03153	2.78459
C	5.09204	-2.55019	-0.13643
H	4.64486	-0.47779	-0.50571
C	3.23689	-3.92505	0.57387
H	1.33042	-2.9267	0.71624
C	3.85068	2.83735	-1.84233
H	3.79923	2.07747	0.16946
C	2.37512	1.76038	-3.42135
H	1.17165	0.14754	-2.6456
C	1.93139	2.58282	3.22499
H	1.24262	2.54351	1.19262
C	2.98967	0.57024	4.02776
H	3.14431	-1.04704	2.61805
C	4.58709	-3.79093	0.25331
H	6.14215	-2.44516	-0.39463
H	2.83728	-4.89311	0.86217
C	3.33599	2.72991	-3.13383
H	4.60108	3.5894	-1.61423
H	1.97118	1.67078	-4.42574
C	2.55796	1.87631	4.2519
H	1.58961	3.60108	3.38792
H	3.48288	0.0152	4.82107

H	5.24488	-4.65462	0.29868
H	3.68304	3.40116	-3.91469
H	2.70942	2.3423	5.22162
Br	-0.1248	-2.29812	-1.88518
H	-5.00812	3.00894	-0.34618

TS4(*E*)-(*Z*)

Energy: -2826545.4748367

Pd	-0.35844	-0.44660	0.30047
C	-2.20050	-0.89042	-0.10766
C	-2.37690	-1.31870	-1.53305
O	-3.02456	-2.29856	-1.84162
O	-1.66805	-0.58306	-2.39936
C	-1.65201	-1.07568	-3.74257
H	-2.66197	-1.10040	-4.16141
H	-1.23100	-2.08458	-3.76547
C	-3.35616	-0.91240	0.73410
C	-3.17715	-0.92275	2.13748
C	-4.67024	-0.84249	0.21412
C	-4.26860	-0.87529	2.98780
H	-2.16326	-0.98311	2.52100
C	-5.75711	-0.75985	1.07076
H	-4.81911	-0.82901	-0.85888
C	-5.55821	-0.78143	2.45309
H	-4.12509	-0.90032	4.06368
H	-6.76158	-0.67971	0.66695
H	-6.41414	-0.72444	3.1204
C	-1.04075	1.44586	0.93344
H	-1.20845	1.29565	2.00679
H	-0.20972	2.14185	0.81777
C	-2.26001	1.98679	0.26625
C	-3.43107	2.25799	0.9881
C	-2.28017	2.2133	-1.12028
C	-4.58628	2.7056	0.34962
H	-3.44295	2.08198	2.06067
C	-3.42874	2.6694	-1.75995
H	-1.39116	1.97653	-1.69818
C	-4.59338	2.91258	-1.0292
H	-5.4864	2.88388	0.93239
H	-3.41916	2.82575	-2.83588
H	-5.4943	3.25729	-1.52927
P	1.9099	0.26224	0.18236
C	3.11555	-0.77737	1.07997
C	2.45871	0.28344	-1.57078
C	2.32502	1.95641	0.74981
C	4.4535	-0.88333	0.68639
C	2.67982	-1.43532	2.23627
C	3.50375	1.11525	-2.00039
C	1.82512	-0.5532	-2.49962
C	1.85926	3.0554	0.01044
C	3.01149	2.18418	1.94732
C	5.34724	-1.63313	1.44764
H	4.79562	-0.39147	-0.21912
C	3.57863	-2.17498	3.00068
H	1.63174	-1.38621	2.51717
C	3.9093	1.10691	-3.3331
H	3.99333	1.78072	-1.29515
C	2.23568	-0.55696	-3.83114
H	1.02473	-1.20936	-2.17348
C	2.08626	4.3539	0.45632
H	1.32487	2.89075	-0.92198
C	3.23359	3.487	2.393
H	3.38139	1.34425	2.52774
C	4.91245	-2.2751	2.60699
H	6.38348	-1.71877	1.13254
H	3.23187	-2.68839	3.89286
C	3.27497	0.27133	-4.25183
H	4.71971	1.75611	-3.65294
H	1.74077	-1.21485	-4.54031
C	2.77365	4.57274	1.65078
H	1.72196	5.19452	-0.12737
H	3.77269	3.65094	3.32198
H	5.61102	-2.86154	3.19751
H	3.59045	0.26689	-5.29164
H	2.94912	5.58625	2.00033
Br	0.39075	-2.84497	-0.05046
H	-1.02012	-0.38214	-4.29655

Int-5(*Z*)

Energy: -2826580.9773395

Pd	-0.44438	-0.45055	0.11030
C	-2.51647	0.01153	0.14408
C	-2.77102	0.18006	-1.31808
O	-2.24782	1.01507	-2.03298
O	-3.62368	-0.75035	-1.77598
C	-3.39724	-0.91407	0.92290
C	-3.36749	-2.30216	0.72044
C	-4.29716	-0.39767	1.86700
C	-4.19614	-3.14175	1.45624
H	-2.67871	-2.70814	-0.01259

C	-5.12909	-1.24011	2.60213
H	-4.37437	0.67782	2.00734
C	-5.07744	-2.61755	2.40327
H	-4.14926	-4.21481	1.29134
H	-5.82226	-0.81624	3.32373
H	-5.7218	-3.27776	2.9773
H	-2.24674	1.10072	1.94432
H	-0.73237	0.8658	1.17526
C	-1.82106	2.55456	0.41255
C	-1.89641	1.13102	0.9082
C	-2.75643	3.47695	0.88626
C	-0.81802	2.98823	-0.45863
C	-2.69774	4.8117	0.48689
H	-3.53693	3.1512	1.57034
C	-0.75067	4.32166	-0.84861
H	-0.10623	2.27014	-0.85511
C	-1.69138	5.2381	-0.37769
H	-3.43476	5.51802	0.85883
H	0.03461	4.63927	-1.52857
H	-1.64053	6.27937	-0.68351
P	1.85823	-0.20189	0.22392
C	2.91437	-1.6809	0.12864
C	2.38987	0.89397	-1.14325
C	2.42007	0.67425	1.73277
C	4.22457	-1.61638	-0.36044
C	2.4046	-2.89498	0.60305
C	3.38342	1.86725	-0.97667
C	1.74387	0.7647	-2.38214
C	1.85176	1.92496	2.02247
C	3.35677	0.1259	2.61409
C	5.0214	-2.75853	-0.36437
H	4.61582	-0.67746	-0.74233
C	3.20841	-4.03255	0.6024
H	1.37526	-2.94813	0.94516
C	3.72545	2.70416	-2.0373
H	3.87832	1.98037	-0.01637
C	2.09136	1.60531	-3.43643
H	0.9663	0.01595	-2.51227
C	2.22078	2.61421	3.17243
H	1.13047	2.36975	1.33989
C	3.71577	0.81697	3.77235
H	3.80598	-0.83852	2.39711
C	4.5148	-3.96525	0.11958
H	6.03616	-2.70755	-0.74896
H	2.80738	-4.97476	0.96431
C	3.07812	2.5766	-3.26589
H	4.4941	3.45981	-1.90059
H	1.57901	1.50675	-4.38893
C	3.15144	2.05878	4.05341
H	1.77904	3.58432	3.38217
H	4.44116	0.3808	4.45346
H	5.1369	-4.85604	0.11148
H	3.33959	3.23657	-4.0885
H	3.43391	2.59436	4.95537
Br	-0.42408	-2.31503	-1.49433
C	-3.70559	-0.83554	-3.20049
H	-2.7267	-1.10105	-3.60959
H	-4.43091	-1.62305	-3.40521
H	-4.03476	0.11403	-3.63108

TS5-6(*Z*)

Energy: -2826576.9386572

Pd	0.59267	-0.33394	-0.16773
C	2.60666	0.52702	-0.07154
C	2.88406	0.53617	1.39846
O	2.31433	1.22172	2.22434
O	3.85790	-0.33157	1.70775
C	3.57681	-0.17342	-0.97500
C	3.74199	-1.56566	-0.94133
C	4.34835	0.57379	-1.87499
C	4.63924	-2.18830	-1.80230
H	3.15355	-2.14616	-0.23798
C	5.24815	-0.05204	-2.73632
H	4.26323	1.65804	-1.88329
C	5.39273	-1.43698	-2.70584
H	4.74770	-3.26901	-1.76942
H	5.84066	0.54563	-3.42373
H	6.09178	-1.9283	-3.37708
H	1.98954	1.62692	-1.74494
H	0.42767	0.71485	-1.30465
C	1.09684	2.73479	-0.14472
C	1.75757	1.50869	-0.68514
C	1.21775	3.90653	-0.90343
C	0.253	2.745	0.97515
C	0.53213	5.06571	-0.5438
H	1.84778	3.90929	-1.79032
C	-0.44783	3.89415	1.32156
H	0.13281	1.84383	1.56106
C	-0.30981	5.06011	0.56657
H	0.64485	5.96563	-1.14193
H	-1.11527	3.86585	2.17773
H	-0.86172	5.95597	0.83735

P	-1.69901	-0.4674	-0.27117
C	-2.46719	-2.11595	-0.31049
C	-2.39594	0.37162	1.20332
C	-2.43705	0.445	-1.67957
C	-3.78872	-2.30737	0.11244
C	-1.72701	-3.19539	-0.80444
C	-3.45518	1.28194	1.10843
C	-1.81267	0.11349	2.45291
C	-2.06805	1.78848	-1.85677
C	-3.3264	-0.14877	-2.57867
C	-4.36808	-3.57056	0.0279
H	-4.3568	-1.47101	0.51103
C	-2.31347	-4.45619	-0.88958
H	-0.69005	-3.04899	-1.09193
C	-3.91765	1.93721	2.24889
H	-3.9112	1.49189	0.14599
C	-2.27954	0.77302	3.58618
H	-0.98623	-0.58902	2.53007
C	-2.58775	2.52265	-2.91663
H	-1.38669	2.26526	-1.15538
C	-3.83473	0.59008	-3.64897
H	-3.62098	-1.1856	-2.44815
C	-3.63136	-4.64388	-0.47529
H	-5.39186	-3.71877	0.3597
H	-1.73418	-5.29448	-1.26532
C	-3.3276	1.68939	3.48701
H	-4.7366	2.64634	2.16558
H	-1.81357	0.57642	4.54739
C	-3.46932	1.92279	-3.81931
H	-2.29946	3.5629	-3.03823
H	-4.519	0.11824	-4.34857
H	-4.08355	-5.63004	-0.53505
H	-3.6827	2.20877	4.3729
H	-3.86806	2.49471	-4.6525
Br	0.92465	-2.21303	1.4453
C	4.03056	-0.56148	3.10851
H	3.11062	-0.98077	3.52488
H	4.84765	-1.27842	3.18759
H	4.27906	0.36719	3.62922

TS5(*Z*)-5η^3

Energy: -2826578.5052911

Pd	-0.42417	-0.19859	-0.09343
C	-2.20927	-1.13697	0.47082
C	-3.29973	-1.35927	-0.53059
O	-3.85274	-2.42365	-0.72629
O	-3.61573	-0.23358	-1.17539
C	-1.36859	-2.27663	0.89139
C	-1.22906	-3.44098	0.09471
C	-0.48997	-2.13497	1.99747
C	-0.26805	-4.39161	0.39189
H	-1.86768	-3.56491	-0.76907
C	0.48461	-3.09607	2.27633
H	-0.56866	-1.28785	2.67044
C	0.60105	-4.22600	1.47878
H	-0.18155	-5.27071	-0.24058
H	1.14946	-2.94454	3.12147
H	1.35922	-4.97377	1.6928
H	-2.45552	-0.40081	2.47559
H	-1.32634	0.52441	1.53635
C	-3.37292	1.07772	1.21512
C	-2.34718	0.00543	1.46135
C	-4.66677	0.93576	1.72108
C	-3.05095	2.21839	0.47557
C	-5.63079	1.91223	1.47688
H	-4.92386	0.04925	2.29634
C	-4.01071	3.19675	0.2339
H	-2.04998	2.3161	0.05937
C	-5.3049	3.04515	0.73255
H	-6.63611	1.78817	1.86995
H	-3.74987	4.07565	-0.34919
H	-6.05531	3.80774	0.54356
P	1.72808	0.59496	-0.00665
C	2.94937	-0.62951	-0.58445
C	2.14804	2.15817	-0.84736
C	2.15684	0.8816	1.75263
C	4.26636	-0.27155	-0.89722
C	2.55425	-1.97091	-0.65683
C	3.05881	3.07841	-0.31259
C	1.53547	2.41646	-2.08167
C	1.40649	1.83319	2.46126
C	3.11666	0.12351	2.43004
C	5.18288	-1.25182	-1.26993
H	4.57007	0.77103	-0.85666
C	3.4776	-2.94723	-1.02253
H	1.52598	-2.24651	-0.4403
C	3.35865	4.24649	-1.01097
H	3.52476	2.8852	0.64992
C	1.84513	3.58418	-2.77499
H	0.82601	1.6994	-2.48981
C	1.6209	2.02834	3.82153
H	0.65271	2.42092	1.94111

C	3.32169	0.31511	3.7972
H	3.69886	-0.61795	1.89138
C	4.7899	-2.58985	-1.32926
H	6.20261	-0.9712	-1.51853
H	3.16268	-3.98515	-1.07858
C	2.7535	4.49923	-2.24196
H	4.06366	4.95953	-0.59245
H	1.37005	3.78098	-3.73192
C	2.57801	1.2648	4.49418
H	1.03861	2.77165	4.35895
H	4.06814	-0.27996	4.3162
H	5.50648	-3.352	-1.6233
H	2.98741	5.41158	-2.78383
H	2.74054	1.41105	5.55828
Br	-0.52817	-0.76276	-2.49816
C	-4.64442	-0.35024	-2.15682
H	-5.56244	-0.74442	-1.71198
H	-4.80204	0.66093	-2.53057
H	-4.32039	-1.01268	-2.96366

Int-6(*Z*)

Energy: -2826578.7963990

Pd	-0.63179	-0.23958	0.25437
C	-2.66909	0.75150	0.07398
C	-3.00923	0.73175	-1.38533
O	-2.48331	1.41104	-2.24319
O	-4.01130	-0.12098	-1.63625
C	-3.61418	0.07969	1.02585
C	-3.82002	-1.30759	0.99322
C	-4.30508	0.84162	1.97606
C	-4.67813	-1.91202	1.90553
H	-3.29435	-1.89804	0.24916
C	-5.16600	0.23364	2.88870
H	-4.18319	1.92207	1.98707
C	-5.35154	-1.14646	2.85911
H	-4.81947	-2.98895	1.87318
H	-5.69673	0.84191	3.61612
H	-6.02108	-1.62308	3.56985
H	-1.88037	1.7808	1.70123
H	-0.27048	0.35082	1.61561
C	-0.87043	2.72946	0.0833
C	-1.75554	1.6707	0.62492
C	-0.60116	3.80973	0.94092
C	-0.15225	2.64402	-1.12178
C	0.34562	4.77574	0.60893
H	-1.12693	3.87975	1.89052
C	0.81486	3.59071	-1.43688
H	-0.33707	1.81957	-1.79602
C	1.06849	4.66082	-0.57757
H	0.53148	5.60404	1.28705
H	1.38758	3.47195	-2.35172
H	1.82905	5.39527	-0.8276
P	1.62797	-0.55197	0.28619
C	2.22145	-2.27097	0.25544
C	2.38953	0.26315	-1.17269
C	2.4825	0.24723	1.69504
C	3.51337	-2.577	-0.19122
C	1.37775	-3.29005	0.70958
C	3.53434	1.06007	-1.04575
C	1.8016	0.09356	-2.43399
C	2.20233	1.60252	1.93085
C	3.38919	-0.42574	2.51644
C	3.96105	-3.89516	-0.1672
H	4.1606	-1.78657	-0.56183
C	1.83252	-4.60643	0.73324
H	0.3631	-3.05122	1.01471
C	4.07723	1.68803	-2.1655
H	3.9984	1.20277	-0.0753
C	2.34846	0.7264	-3.54663
H	0.91106	-0.5211	-2.53734
C	2.82959	2.27239	2.97435
H	1.50297	2.13454	1.29031
C	4.00474	0.24965	3.57267
H	3.61373	-1.47294	2.33803
C	3.12174	-4.90888	0.29706
H	4.96181	-4.13209	-0.51713
H	1.17281	-5.39719	1.07807
C	3.48332	1.52791	-3.41601
H	4.96282	2.30772	-2.05565
H	1.87816	0.59695	-4.51715
C	3.72934	1.59525	3.80163
H	2.61059	3.32303	3.14236
H	4.7015	-0.28161	4.21497
H	3.47087	-5.9377	0.30867
H	3.90254	2.02595	-4.28603
H	4.21222	2.11725	4.62303
Br	-1.09771	-1.90085	-1.59564
C	-4.2805	-0.33468	-3.02419
H	-3.39289	-0.75184	-3.50717
H	-5.10462	-1.04725	-3.05472
H	-4.55983	0.60117	-3.51571

Unproductive (Trans Br) (E)-Pathway

Int-3(*E*)

Energy: -2895239.3153925

Pd	-0.69393	-0.69774	-0.99708
C	0.05079	1.44383	-2.62101
O	-0.14218	1.24331	-3.80185
O	1.24400	1.74165	-2.09203
C	2.32635	1.73448	-3.03644
H	2.20209	2.54390	-3.76014
H	2.36713	0.77847	-3.56013
C	-1.16971	2.29442	-0.37516
C	-2.06227	1.93754	0.64413
C	-0.47880	3.50657	-0.29957
C	-2.27041	2.79529	1.71943
H	-2.59521	0.99316	0.59146
C	-0.67828	4.34987	0.78992
H	0.23071	3.77581	-1.07334
C	-1.57998	4.00361	1.79446
H	-2.96945	2.50869	2.49948
H	-0.11631	5.27588	0.85679
H	-1.73066	4.66745	2.64081
C	-2.49302	-1.45774	-1.77406
H	-2.78109	-0.94778	-2.6978
H	-2.30359	-2.51141	-1.97157
C	-3.41016	-1.21633	-0.63693
C	-4.51239	-0.34465	-0.733
C	-3.16931	-1.81764	0.62007
C	-5.28419	-0.02184	0.38188
H	-4.7794	0.0665	-1.70129
C	-3.94224	-1.49623	1.72949
H	-2.34375	-2.51724	0.71542
C	-4.99218	-0.57955	1.6254
H	-6.12277	0.66119	0.27408
H	-3.72292	-1.96714	2.68429
H	-5.58971	-0.32516	2.49641
P	1.21725	-0.19492	0.43057
C	0.99264	-1.27426	1.89921
C	2.8387	-0.63701	-0.30241
C	1.6072	1.42613	1.23797
C	1.99661	-2.08811	2.42716
C	-0.27796	-1.28136	2.49195
C	4.04655	-0.38655	0.36708
C	2.87439	-1.21831	-1.57519
C	2.4893	2.33474	0.63448
C	1.03439	1.77658	2.46666
C	1.73643	-2.8872	3.53984
H	2.97443	-2.12325	1.95862
C	-0.52991	-2.06815	3.61102
H	-1.08094	-0.68925	2.05995
C	5.26345	-0.71434	-0.22548
H	4.03408	0.07952	1.34834
C	4.09386	-1.54109	-2.16792
H	1.94406	-1.43081	-2.09244
C	2.80402	3.5436	1.24725
H	2.95616	2.08254	-0.30852
C	1.34853	2.98805	3.07877
H	0.35051	1.09844	2.96409
C	0.47812	-2.87555	4.13789
H	2.52064	-3.52733	3.93455
H	-1.51896	-2.06226	4.06075
C	5.28886	-1.29108	-1.49578
H	6.19135	-0.5172	0.30428
H	4.10589	-1.99366	-3.15547
C	2.23711	3.87499	2.47674
H	3.5013	4.22343	0.7648
H	0.89347	3.2348	4.03382
H	0.27949	-3.50199	5.00303
H	6.23854	-1.5449	-1.95885
H	2.4864	4.81528	2.96066
Br	0.00483	-3.07976	-0.78279
H	3.23163	1.87349	-2.44725
C	-1.04703	1.39645	-1.58384
N	-2.21694	1.4662	-2.29368
N	-3.18755	1.48485	-2.8539

TS3-4(*E*)

Energy: -2895231.2398664

Pd	-0.62436	0.59790	1.08189
C	0.16466	-1.78599	2.38611
O	-0.03105	-1.93250	3.57474
O	1.37498	-1.88924	1.81753
C	2.46322	-2.06645	2.73608
H	2.40197	-3.04836	3.21216
H	2.44359	-1.28867	3.50151
C	-1.19616	-2.25311	0.20278
C	-2.12576	-1.79360	-0.74465
C	-0.61765	-3.51935	0.03887
C	-2.48786	-2.59753	-1.81848
H	-2.56948	-0.81082	-0.62292
C	-0.96146	-4.30808	-1.05355

H	0.12304	-3.87120	0.74905
C	-1.90620	-3.85572	-1.97454
H	-3.21801	-2.23441	-2.53547
H	-0.48657	-5.27451	-1.18976
H	-2.17698	-4.47933	-2.82195
C	-2.41588	1.30282	1.93807
H	-2.71494	0.68287	2.78645
H	-2.18589	2.31325	2.27272
C	-3.35855	1.25486	0.79615
C	-4.46463	0.38418	0.77307
C	-3.14354	2.05581	-0.34793
C	-5.2669	0.25574	-0.36003
H	-4.71057	-0.18587	1.66285
C	-3.94675	1.92961	-1.4747
H	-2.31074	2.75345	-0.34605
C	-5.00302	1.01398	-1.49878
H	-6.1075	-0.43329	-0.34609
H	-3.74762	2.55373	-2.34227
H	-5.62572	0.91414	-2.38354
P	1.23691	0.23721	-0.43955
C	1.01954	1.45761	-1.7931
C	2.88783	0.53634	0.29348
C	1.49754	-1.3193	-1.40599
C	2.06446	2.21748	-2.32223
C	-0.27502	1.61942	-2.30571
C	4.07113	0.27967	-0.41591
C	2.97046	1.01023	1.60825
C	2.38714	-2.31364	-0.97398
C	0.77999	-1.54037	-2.58871
C	1.81875	3.1173	-3.35874
H	3.06558	2.13212	-1.91315
C	-0.51379	2.50705	-3.34926
H	-1.10536	1.07218	-1.86674
C	5.31175	0.49288	0.18061
H	4.02182	-0.10354	-1.4312
C	4.21306	1.21995	2.20275
H	2.05963	1.22647	2.15742
C	2.57106	-3.47935	-1.7122
H	2.95784	-2.16841	-0.06619
C	0.95939	-2.71015	-3.32243
H	0.08379	-0.79317	-2.95234
C	0.53411	3.26011	-3.87879
H	2.63583	3.71409	-3.75464
H	-1.52286	2.62242	-3.73493
C	5.38439	0.96193	1.49244
H	6.22061	0.29077	-0.37936
H	4.26239	1.58949	3.22307
C	1.85912	-3.68249	-2.89252
H	3.27759	-4.22777	-1.36329
H	0.3899	-2.85786	-4.2355
H	0.34726	3.96469	-4.68439
H	6.35219	1.12634	1.95831
H	2.00332	-4.59062	-3.47122
Br	0.11164	3.00527	1.06002
H	3.3694	-1.97446	2.13842
C	-0.88446	-1.389	1.37157
N	-2.23566	-1.7598	2.40291
N	-3.2451	-1.64911	2.85408

Int-4(*E*)

Energy: -2826560.7271195

Pd	0.22466	0.43962	-1.16010
C	1.12136	-1.24457	-1.04617
C	0.56270	-2.20173	-2.02918
O	1.16828	-2.59024	-3.00950
O	-0.70435	-2.54255	-1.73190
C	2.15622	-1.66887	-0.16405
C	2.55531	-0.80991	0.88941
C	2.75164	-2.95375	-0.25741
C	3.46591	-1.24134	1.84343
H	2.10371	0.17378	0.95445
C	3.68137	-3.36290	0.68019
H	2.47805	-3.60472	-1.08171
C	4.02738	-2.51241	1.74037
H	3.74217	-0.58301	2.66017
H	4.13684	-4.34572	0.60262
H	4.74453	-2.84777	2.48494
H	2.2894	0.28309	-2.98695
H	1.34604	1.82577	-3.02471
C	2.78212	1.66566	-1.40219
C	1.86837	1.10089	-2.40253
C	3.96677	0.99585	-1.03655
C	2.48316	2.87986	-0.74259
C	4.81868	1.51517	-0.06258
H	4.21479	0.05981	-1.52982
C	3.32664	3.38451	0.2372
H	1.56629	3.40028	-1.00726
C	4.5002	2.70496	0.58644
H	5.72656	0.97693	0.19667
H	3.07492	4.31986	0.73097
H	5.1589	3.10675	1.35153
P	-1.29517	0.01461	0.57273
C	-1.79157	1.50446	1.4999
C	-2.8299	-0.80722	0.02363

C	-0.60572	-1.07332	1.879
C	-3.03177	1.5895	2.13929
C	-0.86794	2.55035	1.62579
C	-3.51648	-1.72822	0.82437
C	-3.30975	-0.50635	-1.25846
C	-0.39007	-2.43098	1.5977
C	-0.15538	-0.55078	3.09667
C	-3.34468	2.71266	2.90286
H	-3.75479	0.78577	2.03389
C	-1.18023	3.66239	2.40224
H	0.08182	2.49934	1.10006
C	-4.669	-2.34821	0.3439
H	-3.14533	-1.96967	1.81616
C	-4.46486	-1.12535	-1.72942
H	-2.77737	0.21436	-1.87432
C	0.26465	-3.24491	2.51552
H	-0.71928	-2.8398	0.6468
C	0.50506	-1.37027	4.01193
H	-0.31574	0.49683	3.33128
C	-2.419	3.74628	3.03849
H	-4.31355	2.78013	3.38968
H	-0.46297	4.47298	2.49286
C	-5.14295	-2.04959	-0.93315
H	-5.19551	-3.06465	0.96843
H	-4.8326	-0.88694	-2.72347
C	0.72051	-2.71542	3.72373
H	0.43443	-4.29145	2.27954
H	0.85238	-0.95085	4.95211
H	-2.66623	4.62179	3.63253
H	-6.04038	-2.53526	-1.30671
H	1.24196	-3.34998	4.43466
Br	-1.06958	2.50796	-1.82416
C	-1.40387	-3.30639	-2.72142
H	-0.95258	-4.29562	-2.83858
H	-2.42568	-3.38336	-2.35108
H	-1.38322	-2.78666	-3.6825

TS4-5(*E*)

Energy: -2826560.2390615

Pd	0.21113	0.48978	-1.02308
C	1.21429	-1.13430	-0.95210
C	0.76741	-2.09855	-1.99154
O	1.42472	-2.42261	-2.96111
O	-0.48151	-2.53381	-1.74203
C	2.22101	-1.53560	-0.02253
C	2.51506	-0.69426	1.07709
C	2.89087	-2.78036	-0.12344
C	3.39413	-1.10781	2.06760
H	2.01015	0.26346	1.14250
C	3.78381	-3.17549	0.85710
H	2.70225	-3.41575	-0.98316
C	4.02514	-2.34586	1.96076
H	3.59092	-0.46278	2.91745
H	4.29300	-4.13136	0.77555
H	4.71551	-2.66948	2.73518
H	2.48466	0.01948	-2.75451
H	1.50416	1.52918	-2.88488
C	2.97892	1.52494	-1.28176
C	2.06585	0.87087	-2.22043
C	4.16628	0.88797	-0.87031
C	2.68509	2.79311	-0.73256
C	5.02967	1.49225	0.04183
H	4.40939	-0.0884	-1.2808
C	3.54431	3.38701	0.18079
H	1.76479	3.28834	-1.03123
C	4.72108	2.73988	0.57682
H	5.93993	0.97885	0.33977
H	3.30078	4.36535	0.58728
H	5.39012	3.21072	1.29201
P	-1.40872	0.00451	0.53293
C	-2.13682	1.41741	1.42603
C	-2.8066	-0.91113	-0.2023
C	-0.75291	-1.05725	1.87616
C	-3.42718	1.35186	1.96245
C	-1.352	2.55857	1.63273
C	-3.46248	-1.9569	0.45672
C	-3.20869	-0.5395	-1.49319
C	-0.40375	-2.38702	1.59608
C	-0.44609	-0.52221	3.13241
C	-3.9267	2.42007	2.70414
H	-4.04227	0.47237	1.79428
C	-1.8522	3.61781	2.38559
H	-0.36504	2.62098	1.18384
C	-4.50559	-2.63363	-0.17496
H	-3.1529	-2.25028	1.45554
C	-4.25629	-1.21413	-2.11405
H	-2.69648	0.27521	-2.0007
C	0.2364	-3.16363	2.55567
H	-0.61527	-2.80119	0.61476
C	0.20423	-1.30269	4.08812
H	-0.7103	0.50479	3.36517
C	-3.139	3.55074	2.9192
H	-4.9324	2.36968	3.11194
H	-1.24276	4.50385	2.5378

C	-4.90211	-2.2649	-1.45997
H	-5.00842	-3.44814	0.33916
H	-4.56387	-0.92187	-3.11409
C	0.54889	-2.62163	3.80302
H	0.51068	-4.18802	2.32106
H	0.44064	-0.87409	5.05813
H	-3.53189	4.38386	3.4955
H	-5.71423	-2.79444	-1.95071
H	1.06117	-3.22529	4.54676
Br	-0.90927	2.60291	-1.80859
C	-1.0935	-3.33139	-2.76167
H	-0.56998	-4.28491	-2.87543
H	-2.11864	-3.48459	-2.4255
H	-1.07936	-2.79893	-3.71582

Int-5(*E*)

Energy: -2826594.6553266

Pd	-0.08113	-1.02195	-0.76761
C	-1.56356	0.36368	-1.25174
C	-0.85713	1.01459	-2.40298
O	-0.80135	0.55225	-3.52872
O	-0.20867	2.15116	-2.05980
C	-2.21901	1.23124	-0.23214
C	-2.39267	0.78655	1.08725
C	-2.76012	2.47417	-0.58822
C	-3.07806	1.55565	2.01833
H	-1.97383	-0.17180	1.37668
C	-3.44937	3.24672	0.34389
H	-2.63887	2.84146	-1.60261
C	-3.61019	2.79135	1.65097
H	-3.18584	1.19408	3.03635
H	-3.86236	4.20662	0.04527
H	-4.1423	3.39655	2.37962
H	-2.75566	-0.63393	-2.7376
H	-1.6473	-1.70106	-1.99718
C	-3.41239	-1.3928	-0.80735
C	-2.36033	-0.861	-1.74
C	-4.66338	-0.7722	-0.73479
C	-3.14386	-2.47902	0.03099
C	-5.62185	-1.2165	0.17123
H	-4.87182	0.08264	-1.3728
C	-4.10356	-2.92629	0.938
H	-2.17498	-2.97358	-0.02443
C	-5.34317	-2.29369	1.01304
H	-6.58609	-0.71862	0.22379
H	-3.88133	-3.77188	1.58316
H	-6.09113	-2.64035	1.72079
P	1.36576	0.18778	0.4354
C	2.40242	-0.83378	1.54099
C	2.54838	0.98983	-0.70583
C	0.73691	1.48913	1.55242
C	3.72343	-0.4644	1.81655
C	1.84185	-1.94495	2.18149
C	3.05597	2.27698	-0.49524
C	2.98081	0.24438	-1.81341
C	0.20725	2.67864	1.02957
C	0.70614	1.27575	2.9371
C	4.47695	-1.20389	2.72545
H	4.16519	0.39367	1.31846
C	2.59589	-2.67284	3.09787
H	0.82764	-2.24956	1.94281
C	3.97086	2.82129	-1.39602
H	2.73665	2.85517	0.36596
C	3.90111	0.79199	-2.70311
H	2.59524	-0.76033	-1.9733
C	-0.32108	3.64267	1.88089
H	0.18338	2.83158	-0.04222
C	0.16296	2.24081	3.78213
H	1.10976	0.36123	3.35896
C	3.91371	-2.3054	3.36846
H	5.50558	-0.91971	2.92857
H	2.15831	-3.53896	3.58547
C	4.39142	2.08306	-2.50109
H	4.35617	3.82348	-1.22998
H	4.2281	0.20984	-3.55965
C	-0.34833	3.42592	3.25765
H	-0.74147	4.55098	1.46117
H	0.14484	2.06434	4.85392
H	4.50442	-2.88245	4.07448
H	5.10198	2.51125	-3.20259
H	-0.77462	4.17527	3.91867
Br	1.10158	-3.17568	-0.93788
C	0.62591	2.71034	-3.07929
H	0.03497	2.98245	-3.95768
H	1.08237	3.59174	-2.62973
H	1.40009	1.9968	-3.36987

TS5-6(*E*)

Energy: -2826571.5131099

Pd	-0.02569	-0.68063	-1.36309
C	-1.88207	0.48242	-1.42292
C	-1.61293	1.17730	-2.73577

O	-1.94465	0.76104	-3.82589
O	-0.90807	2.31642	-2.57539
C	-2.32410	1.28997	-0.25117
C	-2.23443	0.80760	1.06136
C	-2.91276	2.54753	-0.45273
C	-2.68674	1.56593	2.13443
H	-1.79541	-0.16450	1.24622
C	-3.36014	3.30893	0.62368
H	-3.00988	2.94716	-1.45626
C	-3.24264	2.82644	1.92500
H	-2.59634	1.16720	3.14094
H	-3.80185	4.28451	0.44041
H	-3.58288	3.42429	2.76548
H	-2.47166	-1.16709	-2.61513
H	-0.61415	-1.60789	-2.44167
C	-2.80579	-1.73774	-0.52473
C	-2.2047	-0.89215	-1.59502
C	-4.18009	-1.61429	-0.28593
C	-2.04915	-2.60588	0.26893
C	-4.78005	-2.32992	0.74678
H	-4.77054	-0.93434	-0.89421
C	-2.65137	-3.31639	1.30492
H	-0.98236	-2.70358	0.08677
C	-4.01622	-3.17783	1.54919
H	-5.84492	-2.2171	0.93043
H	-2.04162	-3.96482	1.92658
H	-4.48473	-3.72728	2.36097
P	1.23266	0.28179	0.47685
C	0.89548	-0.87966	1.85958
C	3.04757	0.21686	0.25874
C	1.00683	1.95653	1.181
C	1.32318	-2.20951	1.71713
C	0.12454	-0.52766	2.97422
C	3.91725	-0.12098	1.30045
C	3.56916	0.58488	-0.98638
C	0.33809	2.92369	0.4274
C	1.54465	2.30464	2.42871
C	0.97946	-3.16267	2.67135
H	1.90538	-2.49631	0.84576
C	-0.224	-1.48905	3.92185
H	-0.2127	0.49562	3.09957
C	5.29549	-0.08162	1.09916
H	3.51975	-0.43049	2.26293
C	4.94634	0.63194	-1.18143
H	2.89259	0.80367	-1.80778
C	0.17013	4.21233	0.9319
H	-0.06251	2.66737	-0.54589
C	1.37634	3.59191	2.92865
H	2.09176	1.56755	3.0095
C	0.20005	-2.80771	3.77334
H	1.31691	-4.18781	2.54688
H	-0.82848	-1.20265	4.77805
C	5.81108	0.29861	-0.13919
H	5.96641	-0.35164	1.91003
H	5.3438	0.90979	-2.15335
C	0.6808	4.54621	2.18352
H	-0.37204	4.94869	0.34611
H	1.79036	3.85235	3.89886
H	-0.07344	-3.55541	4.51271
H	6.886	0.32497	-0.29514
H	0.544	5.54898	2.57907
Br	1.79759	-2.25618	-1.91175
C	-0.52989	2.97388	-3.78944
H	-1.41353	3.25782	-4.3672
H	0.02899	3.85706	-3.48061
H	0.09489	2.31567	-4.39878

TS5(*E*)-5η^3

Energy: -2826587.3671555

Pd	-0.25361	-0.94978	-0.32357
C	-1.69254	0.56031	-0.30000
C	-1.27928	1.93199	-0.72142
O	-1.56684	2.44673	-1.78608
O	-0.51196	2.55285	0.19539
C	-2.24469	0.36428	1.07492
C	-2.57226	-0.94599	1.48716
C	-2.43417	1.40296	2.00371
C	-2.98800	-1.21067	2.78778
H	-2.50442	-1.77881	0.79241
C	-2.87699	1.13731	3.29563
H	-2.21509	2.42451	1.72073
C	-3.14029	-0.17072	3.70198
H	-3.20715	-2.23400	3.07741
H	-3.01889	1.96191	3.98912
H	-3.47778	-0.37423	4.71412
H	-2.12049	0.24155	-2.37082
H	-2.0622	-1.26331	-1.45195
C	-3.92225	-0.23397	-1.29587
C	-2.41565	-0.20003	-1.41585
C	-4.63566	0.96968	-1.30235
C	-4.6176	-1.43757	-1.17124
C	-6.02204	0.96493	-1.17871
H	-4.09328	1.90466	-1.41349
C	-6.00661	-1.44296	-1.04783

H	-4.06809	-2.37662	-1.16748
C	-6.71186	-0.24136	-1.04787
H	-6.56691	1.90522	-1.18551
H	-6.53559	-2.38692	-0.94908
H	-7.79379	-0.24345	-0.94866
P	1.70584	0.09926	-0.04706
C	3.12697	-0.99686	-0.40261
C	2.00569	1.52844	-1.15016
C	2.06011	0.6838	1.65014
C	4.00413	-0.75878	-1.46512
C	3.328	-2.10771	0.42894
C	2.89605	2.55418	-0.80858
C	1.38481	1.54288	-2.40422
C	0.99882	1.02409	2.49427
C	3.37872	0.79917	2.1148
C	5.07644	-1.62241	-1.68965
H	3.85795	0.09766	-2.11538
C	4.40357	-2.95853	0.20552
H	2.63199	-2.31105	1.23673
C	3.16218	3.5773	-1.71499
H	3.37504	2.55685	0.16553
C	1.65016	2.5707	-3.30712
H	0.68248	0.75527	-2.66394
C	1.25063	1.49187	3.78139
H	-0.02123	0.92197	2.14809
C	3.62521	1.27293	3.4013
H	4.20755	0.50551	1.47687
C	5.27894	-2.7189	-0.85543
H	5.75298	-1.43311	-2.5183
H	4.54953	-3.81939	0.85121
C	2.54063	3.58728	-2.96483
H	3.85231	4.37108	-1.44304
H	1.15031	2.58076	-4.27076
C	2.56231	1.621	4.23569
H	0.41488	1.74394	4.42792
H	4.64861	1.35977	3.75544
H	6.11417	-3.39066	-1.03303
H	2.74478	4.39048	-3.66717
H	2.75816	1.98159	5.24181
Br	0.26556	-3.3449	-0.43306
C	-0.1109	3.88538	-0.1372
H	-0.97937	4.55093	-0.14788
H	0.58998	4.17902	0.64338
H	0.37268	3.91037	-1.11495

Int-6(*E*)

Energy: -2826574.6720679

Pd	0.53238	0.22871	-0.79877
C	2.07458	0.50659	0.73326
C	1.26543	1.41784	1.62534
O	0.52810	1.03142	2.51211
O	1.45777	2.70308	1.31546
C	3.43930	0.98748	0.34677
C	4.53788	0.40061	0.98547
C	3.65584	2.03223	-0.55832
C	5.83267	0.83381	0.70710
H	4.37384	-0.40816	1.69178
C	4.94934	2.46360	-0.83507
H	2.80392	2.49224	-1.04835
C	6.04217	1.86446	-0.20656
H	6.67595	0.36172	1.20339
H	5.10429	3.26818	-1.54842
H	7.0512	2.20017	-0.42918
H	0.94948	-1.06873	1.55046
H	1.77119	0.52514	-1.64138
C	2.42958	-2.00999	0.27766
C	1.69483	-0.84283	0.79067
C	2.29219	-3.224	0.97073
C	3.25194	-1.97824	-0.86213
C	2.96028	-4.36967	0.54702
H	1.65986	-3.26035	1.85411
C	3.91271	-3.12431	-1.28627
H	3.36303	-1.05239	-1.41592
C	3.77141	-4.32414	-0.58532
H	2.84552	-5.29731	1.1009
H	4.54054	-3.08229	-2.17169
H	4.28897	-5.21749	-0.92327
P	-1.68072	-0.17845	0.18569
C	-2.31755	1.35142	0.95762
C	-2.9606	-0.61624	-1.05271
C	-1.92623	-1.55851	1.36735
C	-2.68501	2.39522	0.09308
C	-2.34603	1.56473	2.34089
C	-4.31023	-0.298	-0.8642
C	-2.57969	-1.37717	-2.16313
C	-1.11599	-2.68623	1.187
C	-2.95496	-1.60554	2.31679
C	-3.11476	3.61446	0.61068
H	-2.61982	2.2509	-0.98215
C	-2.79086	2.78287	2.85233
H	-1.99516	0.79594	3.0186
C	-5.26517	-0.73003	-1.78139
H	-4.6143	0.29509	-0.00636
C	-3.53837	-1.81581	-3.07302
H	-1.53068	-1.60484	-2.32781

C	-1.30176	-3.8257	1.96693
H	-0.34577	-2.67948	0.42061
C	-3.13201	-2.74116	3.10354
H	-3.62645	-0.76101	2.43567
C	-3.18204	3.80719	1.99166
H	-3.39708	4.41413	-0.06815
H	-2.816	2.93318	3.92794
C	-4.88086	-1.49042	-2.88569
H	-6.31033	-0.47286	-1.63262
H	-3.23219	-2.39823	-3.93723
C	-2.3023	-3.85032	2.93661
H	-0.66335	-4.69116	1.81209
H	-3.92776	-2.76332	3.84299
H	-3.52577	4.75629	2.3937
H	-5.62678	-1.82462	-3.60158
H	-2.44512	-4.73425	3.55183
Br	-0.438	1.27057	-2.78638
C	0.62012	3.64344	1.9987
H	0.61745	3.45149	3.0741
H	1.04176	4.62402	1.77926
H	-0.4011	3.57255	1.61741

Unproductive (Trans Br) (*Z*)-Pathway

Int-3(*Z*)

Energy: -2895237.3110457

Pd	0.81217	0.16318	-1.14051
C	1.05029	2.52230	0.64355
O	1.92825	3.34673	0.78004
O	0.62443	1.70279	1.60341
C	1.41792	1.70269	2.80250
H	1.33753	2.66445	3.31521
H	2.46076	1.50052	2.54830
C	-1.16267	2.49899	-0.79503
C	-1.82937	2.05702	-1.94388
C	-1.85771	3.22542	0.17387
C	-3.17700	2.35113	-2.12454
H	-1.28535	1.47436	-2.68334
C	-3.21034	3.50286	-0.00478
H	-1.35208	3.55629	1.07506
C	-3.86912	3.07704	-1.15589
H	-3.68743	2.00355	-3.01794
H	-3.75088	4.04204	0.76614
H	-4.92457	3.29495	-1.28918
C	2.67447	0.54693	-2.02276
H	2.79469	-0.16614	-2.83662
H	2.6949	1.56671	-2.41722
C	3.61806	0.33777	-0.90313
C	4.06581	-0.95323	-0.55171
C	4.07524	1.41855	-0.12732
C	4.89518	-1.14979	0.54613
H	3.71874	-1.80017	-1.13531
C	4.89763	1.22	0.97899
H	3.7755	2.42672	-0.39174
C	5.30572	-0.06697	1.32909
H	5.22232	-2.15627	0.79487
H	5.22612	2.07686	1.56156
H	5.94936	-0.22438	2.19041
P	-0.93945	-0.75554	0.34383
C	-1.85054	-2.15083	-0.42291
C	-0.03418	-1.4539	1.78257
C	-2.35059	0.12539	1.16313
C	-2.1474	-3.34132	0.24327
C	-2.30533	-1.96596	-1.73542
C	-0.68333	-1.87297	2.95422
C	1.36324	-1.53023	1.72062
C	-2.18304	0.81946	2.37131
C	-3.62335	0.11709	0.57765
C	-2.90195	-4.32801	-0.39041
H	-1.77747	-3.51175	1.24907
C	-3.07393	-2.94351	-2.35899
H	-2.0304	-1.06176	-2.2715
C	0.05204	-2.34853	4.03817
H	-1.76506	-1.80845	3.02816
C	2.0972	-2.00102	2.80662
H	1.88514	-1.20808	0.82449
C	-3.2534	1.46854	2.97986
H	-1.21536	0.83303	2.85421
C	-4.69338	0.76943	1.18613
H	-3.79056	-0.41314	-0.35337
C	-3.37321	-4.12855	-1.68644
H	-3.11873	-5.25615	0.13134
H	-3.41809	-2.79113	-3.3781
C	1.44454	-2.4094	3.96845
H	-0.46441	-2.66782	4.93935
H	3.18031	-2.03241	2.73499
C	-4.51644	1.44533	2.39071
H	-3.09882	1.98696	3.92253
H	-5.67083	0.74394	0.71252
H	-3.96092	-4.89958	-2.17699
H	2.01622	-2.77249	4.81835

H	-5.35438	1.94595	2.86798
Br	1.07102	-2.12417	-2.05876
H	1.0173	0.89234	3.41087
C	0.32576	2.26486	-0.66097
N	0.95515	3.04049	-1.60764
N	1.48632	3.61354	-2.41167

TS3-4(*Z*)

Energy: -2895230.9564330

Pd	-0.75184	-0.06385	-1.16255
C	-1.20993	-2.29191	0.73916
O	-1.92924	-3.24956	0.93298
O	-0.99921	-1.31960	1.62605
C	-1.77309	-1.38609	2.83225
H	-1.55341	-2.30555	3.38112
H	-2.83589	-1.34428	2.58359
C	0.91787	-2.54216	-0.67930
C	1.67152	-2.23177	-1.82164
C	1.46405	-3.38768	0.29349
C	2.94598	-2.75858	-1.98733
H	1.23765	-1.57252	-2.56964
C	2.74940	-3.89748	0.13520
H	0.88931	-3.63832	1.17935
C	3.48700	-3.59209	-1.00673
H	3.52076	-2.5141	-2.87574
H	3.17601	-4.5284	0.90819
H	4.48843	-3.99478	-1.12859
C	-2.59626	-0.35859	-2.1219
H	-2.68171	0.43372	-2.86351
H	-2.61286	-1.3338	-2.61363
C	-3.55802	-0.23161	-1.0057
C	-3.96574	1.03772	-0.54319
C	-4.06462	-1.35994	-0.33493
C	-4.80438	1.16571	0.55773
H	-3.57929	1.91981	-1.0458
C	-4.90309	-1.23108	0.76958
H	-3.79482	-2.35352	-0.67791
C	-5.2711	0.03308	1.2306
H	-5.1	2.15736	0.89163
H	-5.2707	-2.12443	1.26768
H	-5.92595	0.13513	2.09169
P	0.99343	0.77546	0.32683
C	2.09731	1.98102	-0.50188
C	0.1634	1.64994	1.70944
C	2.23195	-0.26682	1.22131
C	2.55475	3.15402	0.10185
C	2.52327	1.66378	-1.79841
C	0.86542	2.0833	2.84445
C	-1.223	1.83713	1.65621
C	1.92103	-0.87086	2.44925
C	3.49897	-0.49431	0.66922
C	3.44017	3.98996	-0.57716
H	2.20621	3.43229	1.09074
C	3.42041	2.49041	-2.46706
H	2.12442	0.78046	-2.28908
C	0.19283	2.69985	3.89748
H	1.93635	1.9161	2.91748
C	-1.89455	2.44483	2.71412
H	-1.78323	1.49135	0.79395
C	2.85406	-1.6649	3.11022
H	0.95215	-0.70062	2.90104
C	4.42976	-1.29171	1.33107
H	3.76945	-0.03854	-0.2772
C	3.88128	3.65678	-1.85621
H	3.78146	4.907	-0.1048
H	3.7405	2.23705	-3.47382
C	-1.18937	2.88033	3.83513
H	0.74873	3.03179	4.77005
H	-2.97254	2.56409	2.65615
C	4.1146	-1.87785	2.5547
H	2.5954	-2.1116	4.06665
H	5.40695	-1.45217	0.88433
H	4.57076	4.31121	-2.38229
H	-1.71362	3.35356	4.66105
H	4.84527	-2.49321	3.07233
Br	-0.89369	2.29557	-1.9871
H	-1.4831	-0.50322	3.40149
C	-0.46514	-1.98666	-0.54904
N	-1.29627	-3.10813	-1.53562
N	-1.75132	-3.52371	-2.46114

Int-4(*Z*)

Energy: -2826557.9935816

Pd	0.59391	0.03898	-1.13218
C	0.29780	1.79946	-0.44110
C	1.19179	2.20854	0.66862
O	1.74476	3.29271	0.71133
O	1.39734	1.22017	1.54872
C	-0.79585	2.66000	-0.80254
C	-1.53288	2.37957	-1.97837

C	-1.21503	3.73544	0.01446
C	-2.65239	3.12497	-2.30999
H	-1.19134	1.56476	-2.61170
C	-2.33362	4.48150	-0.32486
H	-0.66207	3.96376	0.91767
C	-3.05398	4.17786	-1.48210
H	-3.20922	2.89878	-3.21437
H	-2.65548	5.29515	0.31783
H	-3.92985	4.766	-1.74263
H	2.27305	-0.17027	-3.10578
H	2.07951	1.59413	-2.76437
C	3.39104	0.56381	-1.3958
C	2.26189	0.60512	-2.34196
C	3.94291	-0.6631	-0.96869
C	3.93879	1.74875	-0.86918
C	4.98345	-0.69645	-0.0485
H	3.51989	-1.5848	-1.35863
C	4.98923	1.7127	0.04311
H	3.52343	2.7049	-1.17339
C	5.51377	0.49006	0.46619
H	5.39025	-1.65459	0.2655
H	5.39509	2.6443	0.42891
H	6.33134	0.46178	1.18153
P	-0.96445	-0.82749	0.43195
C	-2.15435	-2.02376	-0.26796
C	-0.08629	-1.63733	1.81385
C	-2.05663	0.40752	1.2463
C	-2.68312	-3.08488	0.47178
C	-2.57528	-1.82276	-1.58878
C	-0.72456	-1.91047	3.03247
C	1.27081	-1.94934	1.66222
C	-1.63613	1.10092	2.39029
C	-3.2651	0.77239	0.63889
C	-3.63695	-3.92502	-0.0999
H	-2.3409	-3.27125	1.48447
C	-3.53915	-2.65458	-2.15042
H	-2.11981	-1.03371	-2.18032
C	-0.0173	-2.49715	4.07958
H	-1.7683	-1.64234	3.17189
C	1.97449	-2.53036	2.7145
H	1.77465	-1.73191	0.72557
C	-2.42118	2.11957	2.92572
H	-0.69332	0.84344	2.8595
C	-4.04038	1.79963	1.17141
H	-3.60491	0.25135	-0.25075
C	-4.07169	-3.70703	-1.40612
H	-4.03673	-4.75444	0.47674
H	-3.85568	-2.49561	-3.17724
C	1.3337	-2.80663	3.92201
H	-0.52026	-2.70522	5.01983
H	3.02811	-2.76116	2.58668
C	-3.62553	2.4724	2.31907
H	-2.08704	2.63939	3.81962
H	-4.97122	2.07439	0.6838
H	-4.81401	-4.36525	-1.84894
H	1.88625	-3.25839	4.74138
H	-4.2341	3.27044	2.73484
Br	0.84571	-2.31367	-2.02733
C	2.37351	1.45782	2.56843
H	2.13932	2.36942	3.12555
H	2.32541	0.58036	3.21318
H	3.36361	1.54571	2.11515

TS4-5(*Z*)

Energy: -2826556.0880863

Pd	0.57871	-0.22676	-0.84980
C	0.95785	1.52394	-0.18983
C	1.98194	1.63588	0.88569
O	2.81257	2.52467	0.94573
O	1.94560	0.59186	1.72535
C	0.26453	2.71940	-0.60428
C	-0.53511	2.68214	-1.77140
C	0.27478	3.90758	0.16123
C	-1.29482	3.77584	-2.15194
H	-0.53351	1.77014	-2.36266
C	-0.49677	4.99708	-0.21881
H	0.87771	3.95807	1.05919
C	-1.27941	4.93664	-1.37260
H	-1.89921	3.73029	-3.05295
H	-0.49277	5.89720	0.38859
H	-1.87769	5.79473	-1.66695
H	2.19719	-0.27587	-2.70034
H	2.593	1.39789	-2.15576
C	3.6426	-0.14824	-1.07997
C	2.50642	0.35247	-1.86286
C	3.76916	-1.51636	-0.75723
C	4.63821	0.73459	-0.61943
C	4.84186	-1.97169	-0.00238
H	3.00358	-2.20635	-1.10139
C	5.71674	0.27241	0.13018
H	4.55495	1.79181	-0.85026
C	5.82113	-1.08161	0.44961

H	4.91825	-3.02949	0.23539
H	6.47485	0.97376	0.46851
H	6.66035	-1.44269	1.03802
P	-1.3506	-0.59392	0.3461
C	-2.82662	-1.02782	-0.63958
C	-1.21618	-1.86344	1.65563
C	-1.86526	0.92682	1.23277
C	-3.99468	-1.49326	-0.02298
C	-2.80674	-0.82461	-2.02359
C	-1.96314	-1.78786	2.8402
C	-0.35355	-2.94807	1.44936
C	-1.16405	1.32304	2.38138
C	-2.82866	1.78239	0.68999
C	-5.13239	-1.74528	-0.78434
H	-4.01257	-1.66758	1.04881
C	-3.95023	-1.07268	-2.78083
H	-1.88741	-0.50456	-2.50397
C	-1.85018	-2.78745	3.80372
H	-2.62107	-0.94179	3.01746
C	-0.2479	-3.94461	2.41722
H	0.2164	-3.014	0.52636
C	-1.44391	2.54361	2.98791
H	-0.39123	0.67827	2.78803
C	-3.09354	3.01198	1.29287
H	-3.36713	1.49308	-0.20724
C	-5.11228	-1.53145	-2.16333
H	-6.03393	-2.11238	-0.30189
H	-3.92524	-0.92253	-3.85633
C	-0.99194	-3.8666	3.5938
H	-2.43099	-2.72062	4.71957
H	0.42169	-4.78328	2.24886
C	-2.40968	3.39222	2.44458
H	-0.90116	2.83617	3.88268
H	-3.83374	3.67459	0.85385
H	-6.00045	-1.73194	-2.75626
H	-0.90269	-4.64408	4.34765
H	-2.61958	4.34983	2.91256
Br	0.40553	-2.40115	-2.13098
C	3.00893	0.52725	2.6848
H	3.07455	1.45811	3.255
H	2.75885	-0.30987	3.33561
H	3.95625	0.34521	2.17162

TS4(E)-(Z)

Energy: -2826552.1429218

Pd	0.37345	-0.83193	-0.65743
C	1.50076	0.43672	0.20911
C	1.90211	-0.04597	1.55611
O	3.03563	-0.36344	1.84871
O	0.84478	-0.14023	2.38294
C	1.97629	1.71052	-0.24017
C	1.40690	2.28160	-1.40180
C	2.95258	2.44565	0.47306
C	1.75544	3.56062	-1.80196
H	0.66592	1.70379	-1.94547
C	3.32451	3.71023	0.04502
H	3.42635	1.99430	1.33807
C	2.71577	4.27505	-1.08003
H	1.28612	4.00429	-2.67424
H	4.08424	4.26519	0.58736
H	2.99767	5.27447	-1.40034
H	1.73983	-2.57391	-1.99327
H	2.01846	-0.91098	-2.61582
C	3.40649	-1.55144	-1.09578
C	2.08186	-1.57061	-1.74454
C	3.8037	-2.60075	-0.25153
C	4.3066	-0.49021	-1.2948
C	5.04857	-2.59069	0.36915
H	3.11356	-3.42413	-0.08209
C	5.54924	-0.47735	-0.6713
H	4.0179	0.331	-1.94698
C	5.92777	-1.52774	0.16581
H	5.33305	-3.41459	1.01873
H	6.22952	0.35324	-0.84372
H	6.89923	-1.51832	0.65238
P	-1.64291	0.16086	0.13071
C	-3.10435	-0.0274	-0.94576
C	-2.15389	-0.47291	1.76596
C	-1.50295	1.98405	0.30634
C	-4.39977	0.00772	-0.41883
C	-2.91915	-0.13024	-2.32981
C	-2.69992	0.34177	2.76416
C	-1.96679	-1.84114	2.00929
C	-0.71636	2.53044	1.33202
C	-2.0346	2.83841	-0.66729
C	-5.50011	-0.05529	-1.27107
H	-4.54873	0.07657	0.6549
C	-4.0223	-0.18013	-3.17794
H	-1.91381	-0.19918	-2.73369

C	-3.04537	-0.20487	4.00007
H	-2.84899	1.40186	2.58183
C	-2.32253	-2.38112	3.24219
H	-1.54731	-2.47213	1.2289
C	-0.46642	3.89809	1.37802
H	-0.28486	1.87596	2.08272
C	-1.77479	4.20796	-0.62121
H	-2.65036	2.43603	-1.46565
C	-5.31266	-0.14499	-2.64993
H	-6.50416	-0.03645	-0.85657
H	-3.87237	-0.268	-4.25006
C	-2.85608	-1.56511	4.24138
H	-3.46544	0.43371	4.77234
H	-2.17602	-3.44209	3.42389
C	-0.98872	4.74158	0.39703
H	0.15117	4.30357	2.17435
H	-2.19178	4.85719	-1.38621
H	-6.17226	-0.19695	-3.31244
H	-3.12556	-1.98894	5.20495
H	-0.78321	5.80778	0.42795
Br	-0.93009	-2.80292	-1.52943
C	1.08167	-0.76614	3.64915
H	1.80231	-0.19111	4.23735
H	0.1079	-0.79431	4.13712
H	1.46544	-1.77845	3.50116

Int-5(*Z*)

Energy: -2826591.9841443

Pd	0.24412	-0.03257	-1.21795
C	1.28001	1.52192	-0.33674
C	1.78214	1.32618	1.07092
O	2.17674	2.20658	1.80546
O	1.81375	0.02167	1.39784
C	0.49163	2.75319	-0.61299
C	0.29446	3.18346	-1.94198
C	-0.15620	3.46942	0.40741
C	-0.51977	4.27210	-2.23428
H	0.76667	2.65594	-2.76571
C	-0.96476	4.56152	0.11047
H	-0.02235	3.17578	1.44005
C	-1.15593	4.97001	-1.20789
H	-0.65516	4.57553	-3.26874
H	-1.45266	5.09082	0.92400
H	-1.78914	5.8232	-1.43441
H	1.93608	0.67855	-2.25421
H	2.76643	2.13179	-1.78751
C	3.53373	0.33604	-0.86808
C	2.39374	1.19406	-1.35809
C	3.53719	-1.04622	-1.07947
C	4.58326	0.91896	-0.15106
C	4.56453	-1.83451	-0.56669
H	2.72351	-1.50562	-1.63874
C	5.61299	0.13007	0.36018
H	4.57961	1.99115	0.02659
C	5.60392	-1.24982	0.15684
H	4.55386	-2.90759	-0.73676
H	6.42174	0.59507	0.91718
H	6.40612	-1.86504	0.55491
P	-1.19863	-0.56641	0.41116
C	-2.81994	-1.08552	-0.26115
C	-0.5764	-1.96198	1.41615
C	-1.65185	0.7367	1.61418
C	-3.65819	-1.95706	0.44311
C	-3.24792	-0.546	-1.48019
C	-1.05111	-2.21926	2.70984
C	0.41076	-2.79084	0.86769
C	-0.89938	0.95782	2.77672
C	-2.71623	1.59888	1.31951
C	-4.91403	-2.27878	-0.06554
H	-3.3291	-2.39752	1.37893
C	-4.50964	-0.86171	-1.97822
H	-2.58239	0.09853	-2.04712
C	-0.5377	-3.28521	3.4464
H	-1.8093	-1.57867	3.15093
C	0.91918	-3.85516	1.60752
H	0.77862	-2.59318	-0.135
C	-1.21501	2.01034	3.63178
H	-0.07217	0.30186	3.01723
C	-3.02925	2.64934	2.17819
H	-3.30308	1.44945	0.41865
C	-5.34309	-1.72822	-1.27297
H	-5.55596	-2.96422	0.48066
H	-4.83137	-0.44391	-2.92764
C	0.4504	-4.1021	2.89806
H	-0.90863	-3.47365	4.44995
H	1.68785	-4.48855	1.1744
C	-2.28131	2.85906	3.33538
H	-0.62049	2.16945	4.52653
H	-3.85632	3.3098	1.93494
H	-6.32228	-1.98337	-1.66856
H	0.85408	-4.92911	3.47563
H	-2.52534	3.68116	4.00213

Br	-0.2168	-1.8008	-2.87618
C	2.53202	-0.33137	2.5815
H	2.26036	0.32269	3.41439
H	2.25588	-1.36592	2.78683
H	3.60556	-0.24995	2.38985

TS5-6(*Z*)

Energy: -2826574.9929574

Pd	-0.55981	-0.54864	-1.18168
C	-1.45002	1.26246	-0.38173
C	-1.83590	1.09783	1.06812
O	-2.13628	2.00418	1.81407
O	-1.90304	-0.19597	1.42815
C	-0.69096	2.49021	-0.79306
C	0.23228	2.41907	-1.84762
C	-0.87157	3.72407	-0.15168
C	0.98514	3.52742	-2.22308
H	0.39117	1.46687	-2.34929
C	-0.12075	4.83409	-0.53363
H	-1.57296	3.79859	0.66862
C	0.81793	4.74223	-1.55970
H	1.71408	3.43109	-3.02246
H	-0.26828	5.77723	-0.01422
H	1.41153	5.60752	-1.84116
H	-2.40163	1.15659	-2.28375
H	-1.59049	-0.81736	-2.31394
C	-3.63413	0.01486	-0.87826
C	-2.34982	0.65737	-1.31587
C	-4.58003	0.84038	-0.25394
C	-3.9381	-1.33537	-1.07311
C	-5.80205	0.3231	0.17068
H	-4.3474	1.8887	-0.08769
C	-5.16284	-1.84964	-0.65189
H	-3.19923	-1.988	-1.52908
C	-6.09752	-1.02492	-0.0278
H	-6.52156	0.97578	0.65729
H	-5.38105	-2.9028	-0.80558
H	-7.04896	-1.43049	0.30471
P	1.29751	-0.35467	0.3404
C	1.59439	-1.94815	1.1847
C	2.86216	0.12401	-0.48119
C	1.19167	0.83467	1.7347
C	2.86796	-2.37624	1.5679
C	0.47532	-2.73237	1.49549
C	3.93853	0.63976	0.25677
C	2.98711	-0.01161	-1.86937
C	1.42805	2.19797	1.50759
C	0.79179	0.41565	3.01039
C	3.01962	-3.57382	2.26471
H	3.74238	-1.7861	1.31168
C	0.63076	-3.92063	2.20343
H	-0.50904	-2.41219	1.16596
C	5.11851	1.00869	-0.3838
H	3.84686	0.76919	1.33131
C	4.16862	0.36291	-2.50596
H	2.16816	-0.42973	-2.44611
C	1.25637	3.1211	2.53538
H	1.74498	2.5423	0.52811
C	0.62038	1.34438	4.03383
H	0.61428	-0.6376	3.20343
C	1.90325	-4.34339	2.58821
H	4.01316	-3.90716	2.55124
H	-0.24008	-4.5267	2.43706
C	5.23445	0.87344	-1.76714
H	5.94487	1.40732	0.19807
H	4.25367	0.25203	-3.58326
C	0.84824	2.6994	3.79854
H	1.43062	4.17422	2.3362
H	0.31092	1.00581	5.01893
H	2.02545	-5.2772	3.13001
H	6.15353	1.16682	-2.267
H	0.708	3.42258	4.59686
Br	0.44869	-2.60069	-2.08782
C	-2.51967	-0.44661	2.69443
H	-3.57773	-0.17333	2.64969
H	-2.40853	-1.51724	2.86404
H	-2.02268	0.12539	3.48085

TS5(*Z*)-5η^3

Energy: -2826588.8459255

Pd	0.27134	-0.81548	-0.87034
C	-0.60244	-1.98775	0.61690
C	-1.14869	-1.48869	1.92779
O	-1.01751	-2.03787	3.00142
O	-1.91358	-0.40079	1.74215
C	0.69394	-2.69750	0.65225
C	1.13109	-3.41652	-0.49197
C	1.62915	-2.49853	1.70034
C	2.44658	-3.87737	-0.59100
H	0.45257	-3.64192	-1.30740

C	2.91964	-2.98287	1.59540
H	1.32979	-1.95196	2.58550
C	3.34242	-3.66656	0.44720
H	2.75517	-4.40558	-1.48779
H	3.61377	-2.81278	2.41343
H	4.36192	-4.03442	0.37468
H	-1.35347	-3.26627	-0.97768
H	-2.17585	-3.43984	0.54836
C	-2.87405	-1.8189	-0.6804
C	-1.76288	-2.69145	-0.14385
C	-2.77315	-1.25493	-1.95856
C	-4.02681	-1.57227	0.06984
C	-3.78543	-0.43507	-2.45646
H	-1.89145	-1.44124	-2.56912
C	-5.04098	-0.75489	-0.42324
H	-4.12837	-2.02645	1.05259
C	-4.92105	-0.17898	-1.68845
H	-3.68129	0.00066	-3.44591
H	-5.92805	-0.5725	0.17736
H	-5.71378	0.45386	-2.07845
P	0.48058	1.16427	0.19442
C	1.56447	2.32064	-0.73838
C	-1.01212	2.13647	0.58892
C	1.37438	0.92195	1.78162
C	1.3218	3.69962	-0.76461
C	2.6784	1.81076	-1.42042
C	-1.0129	3.15146	1.55638
C	-2.18428	1.85905	-0.12202
C	0.70512	0.85644	3.01039
C	2.74778	0.63928	1.74801
C	2.19019	4.55251	-1.44336
H	0.45103	4.11474	-0.26909
C	3.5493	2.66851	-2.08548
H	2.84345	0.73906	-1.46879
C	-2.17713	3.87511	1.80985
H	-0.1067	3.37398	2.11282
C	-3.34451	2.5853	0.13287
H	-2.19535	1.05462	-0.85003
C	1.3886	0.51178	4.17438
H	-0.35179	1.08041	3.06156
C	3.43048	0.30671	2.91372
H	3.28857	0.67205	0.8088
C	3.30866	4.0414	-2.09828
H	1.98549	5.61936	-1.46239
H	4.40342	2.25632	-2.61467
C	-3.34404	3.59175	1.09894
H	-2.17132	4.65865	2.56241
H	-4.24904	2.34486	-0.41655
C	2.75314	0.23343	4.1306
H	0.84805	0.45666	5.11471
H	4.4944	0.09294	2.86653
H	3.98194	4.70853	-2.62935
H	-4.25204	4.15323	1.30135
H	3.28513	-0.03808	5.03784
Br	0.96361	-0.57298	-3.22243
C	-2.69413	0.05196	2.84816
H	-3.61464	-0.53521	2.91506
H	-2.1417	-0.04699	3.7854
H	-2.93133	1.09415	2.63254

Int-6(*Z*)

Energy: -2826575.8658043

Pd	-0.55318	0.07458	1.09030
C	-2.09846	0.98588	-0.11741
C	-3.42818	1.32018	0.53037
O	-3.63053	1.68430	1.66572
O	-4.38722	1.21302	-0.40211
C	-1.37718	2.19202	-0.62078
C	-0.78313	2.22151	-1.88987
C	-1.26686	3.32260	0.20803
C	-0.06359	3.33860	-2.30475
H	-0.87588	1.37144	-2.55722
C	-0.55333	4.43881	-0.21606
H	-1.71077	3.29529	1.19832
C	0.05760	4.44935	-1.47142
H	0.40248	3.33458	-3.28571
H	-0.46327	5.29774	0.44263
H	0.62212	5.31804	-1.79768
H	-1.18885	-0.36886	-1.48184
H	-1.66772	0.34752	2.10549
C	-2.75025	-1.46962	-0.48865
C	-1.87264	-0.29675	-0.6417
C	-2.81804	-2.38196	-1.55255
C	-3.51651	-1.72308	0.66166
C	-3.63944	-3.50362	-1.48138
H	-2.23033	-2.19466	-2.44763
C	-4.33751	-2.84276	0.72971
H	-3.44414	-1.05684	1.51594
C	-4.40417	-3.73766	-0.3398
H	-3.68172	-4.19533	-2.31823
H	-4.9182	-3.02559	1.62952
H	-5.04154	-4.61519	-0.27881

P	1.47791	-0.45754	-0.17497
C	2.76168	0.80764	0.11501
C	2.23669	-2.0792	0.21007
C	1.35412	-0.52618	-2.00514
C	4.1277	0.5148	0.17137
C	2.33052	2.13474	0.23931
C	3.13956	-2.68605	-0.67689
C	1.90911	-2.72731	1.40742
C	0.6365	-1.58684	-2.58108
C	1.8521	0.48559	-2.83279
C	5.05291	1.54333	0.34006
H	4.46872	-0.51332	0.09657
C	3.25948	3.1598	0.39061
H	1.27002	2.36526	0.22415
C	3.71106	-3.91671	-0.36522
H	3.38677	-2.19868	-1.61597
C	2.4833	-3.96036	1.7128
H	1.2223	-2.25832	2.10521
C	0.4094	-1.62416	-3.95412
H	0.2575	-2.38596	-1.94804
C	1.62436	0.44416	-4.20837
H	2.40687	1.31214	-2.4004
C	4.62173	2.86563	0.44358
H	6.1127	1.30995	0.39363
H	2.91218	4.18485	0.4815
C	3.38282	-4.556	0.83076
H	4.40957	-4.37784	-1.05805
H	2.22276	-4.45461	2.64433
C	0.89825	-0.60356	-4.77179
H	-0.14654	-2.45183	-4.38624
H	2.01788	1.23542	-4.84071
H	5.34667	3.66431	0.57504
H	3.82629	-5.51826	1.07182
H	0.71925	-0.63026	-5.84289
Br	0.74173	0.27944	3.15646
C	-5.7136	1.49686	0.05831
H	-5.77318	2.50937	0.46591
H	-6.3564	1.39245	-0.81524
H	-6.00225	0.78258	0.83454

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