Electronic Supplementary Material (ESI) for Dalton Transactions.

A Stable Phosphanyl Phosphaketene and Its Reactivity

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Supporting Information

S1: Synthetic Details

S2: Kinetic study for the dimerization of 3

S3: X-Ray Diffraction Studies

S4: Theoretical Details

S5: References

S1: Synthetic Details

General: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk techniques. Dry, oxygen-free solvents were employed unless otherwise mentioned. The sodium phosphaethynolate (**1**)[1] and 2–Chloro–1,3–bis(2,6–diisopropylphenyl)–1,3,2–diazaphospholene (**2**)[2] were prepared following literature procedures while all other starting materials were purchased from commercial sources. 2,3-dimethylbutadiene were distilled from $NaBH_4$ and stored at –20 °C with molecular sieves prior to use. NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers. All spectra were obtained in the solvent indicated at 25 °C. The chemical shifts (δ) were measured according to IUPAC and expressed in ppm relative to $SiMe_4$ (^1H, ^{13}C), and 85% H_3PO_4 (^{31}P). Coupling constants *J* are reported in Hertz [Hz] as absolute values. IR spectra were obtained on a Perkin-Elmer-Spectrum ATR 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500 – 4000 cm^{-1}). The ATR technique was used for the analysis of solid compounds. Melting point (M. P.) were measured on Büchi M-560 apparatus.

Preparation of 2–phosphaketene–1,3–bis(2,6–diisopropylphenyl)–1,3–diazaphospholene 3: 3.02 g (10 mmol) sodium phosphaethynolate [Na(OCP) • $(dioxane)_{2.5}$] was added to a stirred solution of **2** (4.43 g, 10 mmol) in toluene (10 mL). After 1 h stirring, the precipitate of sodium chloride was removed by filtration. The filtrate was dried under reduced pressure and the remaining solid was washed with hexane. Drying the residue *in vacuo* afforded **3** as a yellow powder (3.2 g, 6.8 mmol, 68 % yield). M. P. = 121.6 °C. ^1H NMR (C_6D_6, 500 MHz): δ = 6.86 (m, 2 H, $C_{ar}H$), 6.77 (m, 4 H, $C_{ar}H$), 5.76 (s, 2 H, NC*H*), 3.25 (m, 4 H, C*H*Me_2), 1.06 (d, 12 H, CH_3), 0.83 (d, 12 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz): δ = 198.4 (dd, J_{PC} = 95.6 Hz, *PC*O, J_{PC} = 22.6 Hz, *P*P*C*O), 146.3 (*ipso*-C), 132.7 (d, J_{PC} = 8.8 Hz, *o*-C), 127.8 (*p*-CH), 123.6 (*m*-CH), 121.0 (d, J_{PC} = 8.8 Hz, NCH), 28.0 ($CHMe_2$), 24.0 (CH_3), 23.3 ($CHMe_2$); $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ = 165.1 (d, J_{PP} = 252.5 Hz, *P*PCO), δ = –232.6 (d, J_{PP} = 252.5 Hz, *P*CO). IR (solid): 1881 cm^{-1} (s, PCO).

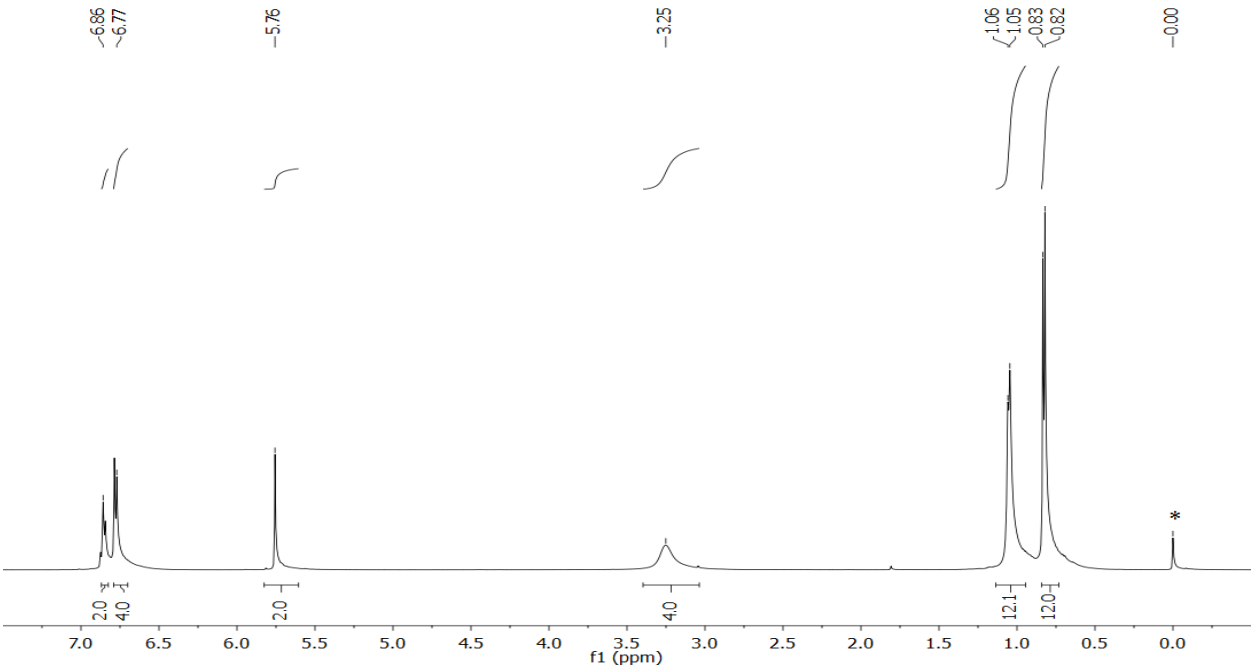

Figure S1. ^{1}H NMR spectrum of **3** in C_6D_6. *$SiMe_4$

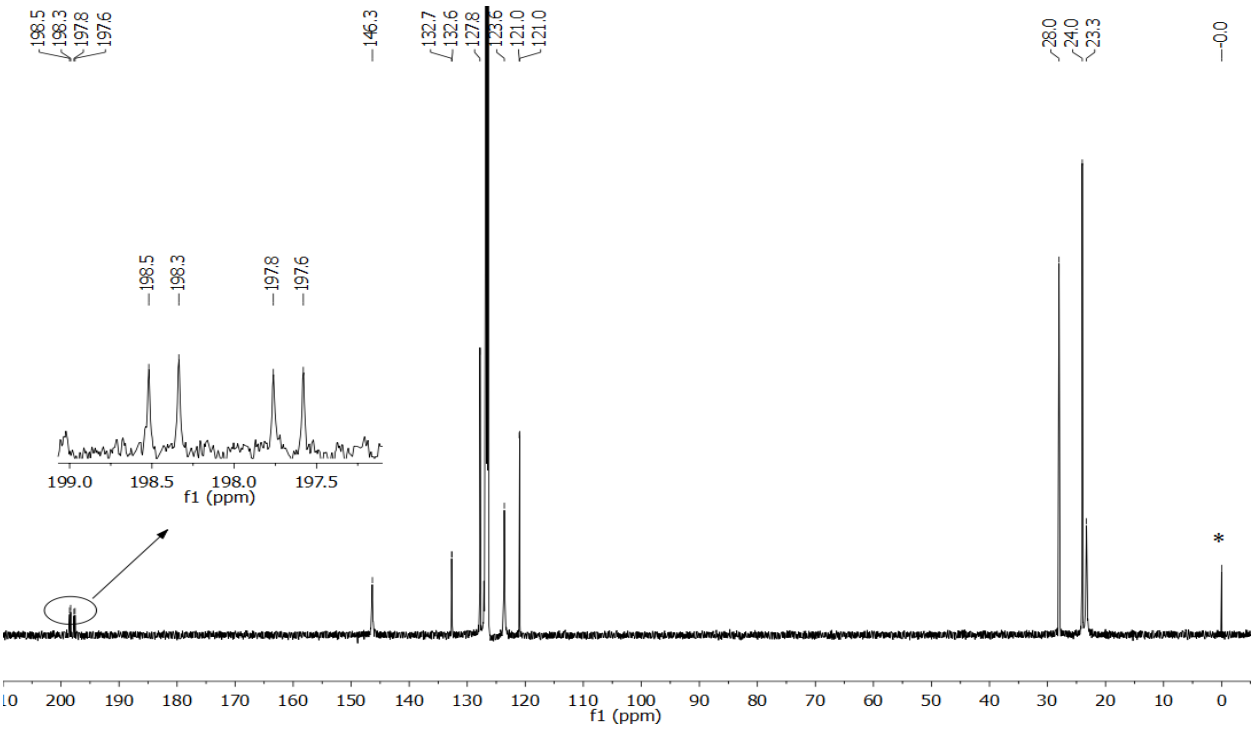

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. *$SiMe_4$

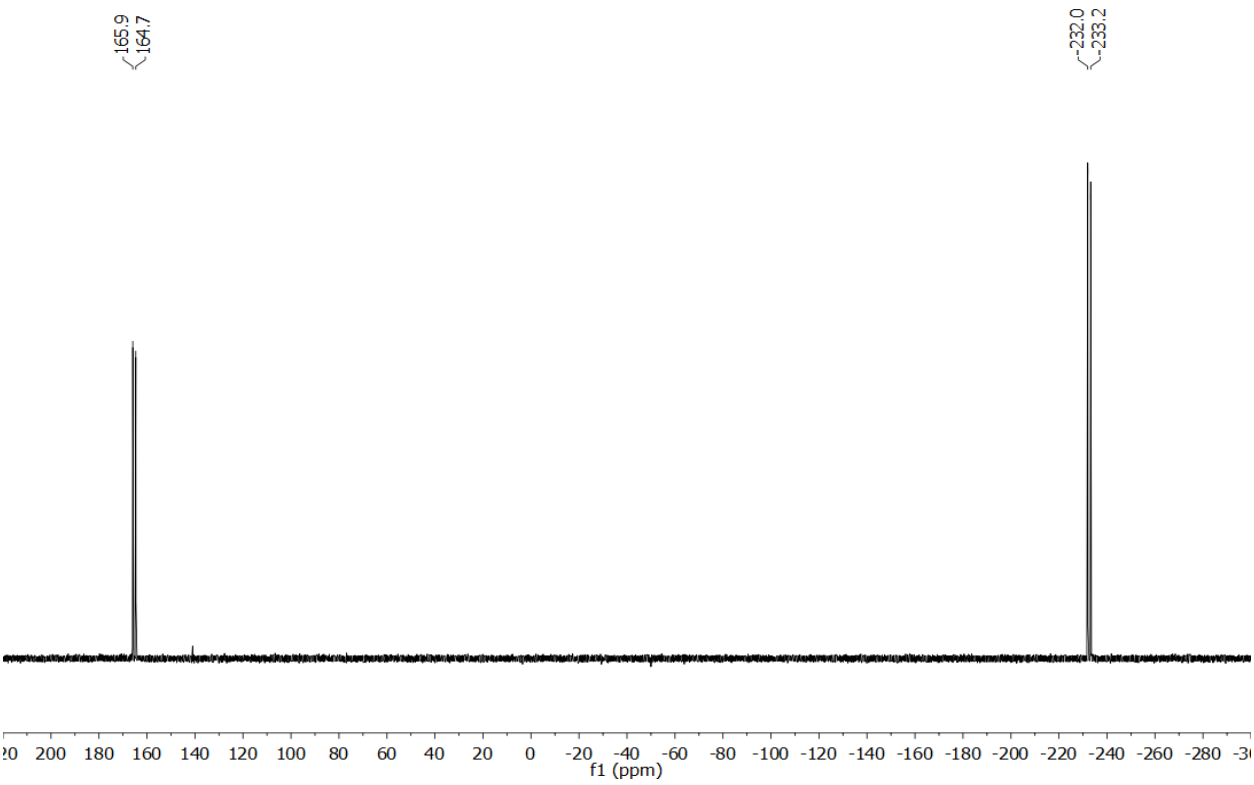

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

Preparation of 5 and 6: 0.5 mL (0.5 mmol) phenylmagnesium bromide (1 M in thf) was added dropwise to a stirred solution of **3** (233 mg, 0.5 mmol) in thf (3 mL) at 0 °C. The mixture was allowed to warm to room temperature under stirring. After 2 hours, the solvent was removed under reduced pressure. The residue was extracted with *n*-hexane (2 × 2 mL) followed by filtration over a glass frit. The filtrate was dried under reduced pressure and washed with acetonitrile (2 × 2 mL) affording **5** as yellow powder (210 mg, 0.43 mmol, 87 % yield). M. P. = 189.2 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.54 (m, 2 H, $C_{ar}H$), 6.88 (m, 4 H, $C_{ar}H$), 6.73 (m, 5 H, $C_{ar}H$), 5.60 (d, J_{PH}= 2.3 Hz, 2 H, NC*H*), 3.59 (m, 2 H, C*H*Me$_2$), 3.22 (m, 2 H, C*H*Me$_2$), 1.23 (d, 6 H, CH_3), 1.07 (M, 12 H, CH_3), 0.91 (d, 6 H, CH_3), 0.20 (d, 6 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 75 MHz): δ = 147.6 (*ipso*-C), 146.9 (d, *ipso*-C′), 143.5, 142.7, 137.1, 136.9, 130.2, 129.8, 129.5, 126.1, 123.4, 123.0, 119.7 (d, J_{PC} = 5.7 Hz, NCH), 27.5 (CHMe$_2$), 27.2 (CH$_3$), 24.5 (CH$_3$), 23.4 (CH$_3$), 23.0 (CHMe$_2$), 22.9 (CH$_3$); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 121 MHz) δ = 102.7. The residue from the filtration above was dried *in vacuo* affording **6** as gray powder (185 mg, 0.487 mmol, 97 % yield).

According to the NMR spectrum and the titration experiment done with ^{1}H NMR spectrum (14 mg product and 6.2 mg benzene were mixed in [D_6]DMSO, see the following spectrum), this solid has the composition [**6**•$(thf)_3$] M. P. = 125.6 °C (decompose, turned black). ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 3.59 (m, 4 H, OC*H*$_2$), 1.75 (m, 4 H, OCH_2CH_2); ^{13}C{^{1}H} NMR ([D_6]DMSO, 75MHz): δ = 169.2 (d, J_{PC} = 60 Hz), 67.0 (OCH_2), 25.1 (OCH_2CH_2); ^{31}P{^{1}H} NMR ([D_6]DMSO, 121 MHz) δ = –381.1. IR (solid): 1736 cm^{-1}(s, OCP).

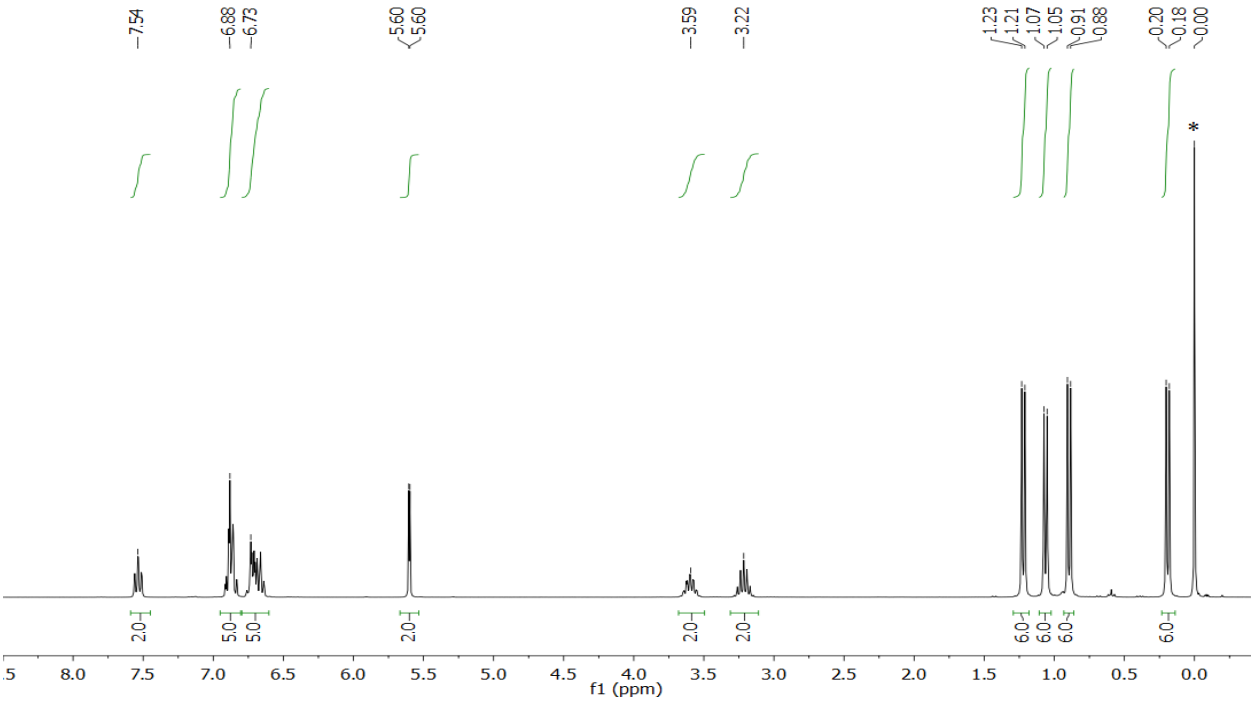

Figure S4. ^{1}H NMR spectrum of **5** in C_6D_6. *$SiMe_4$

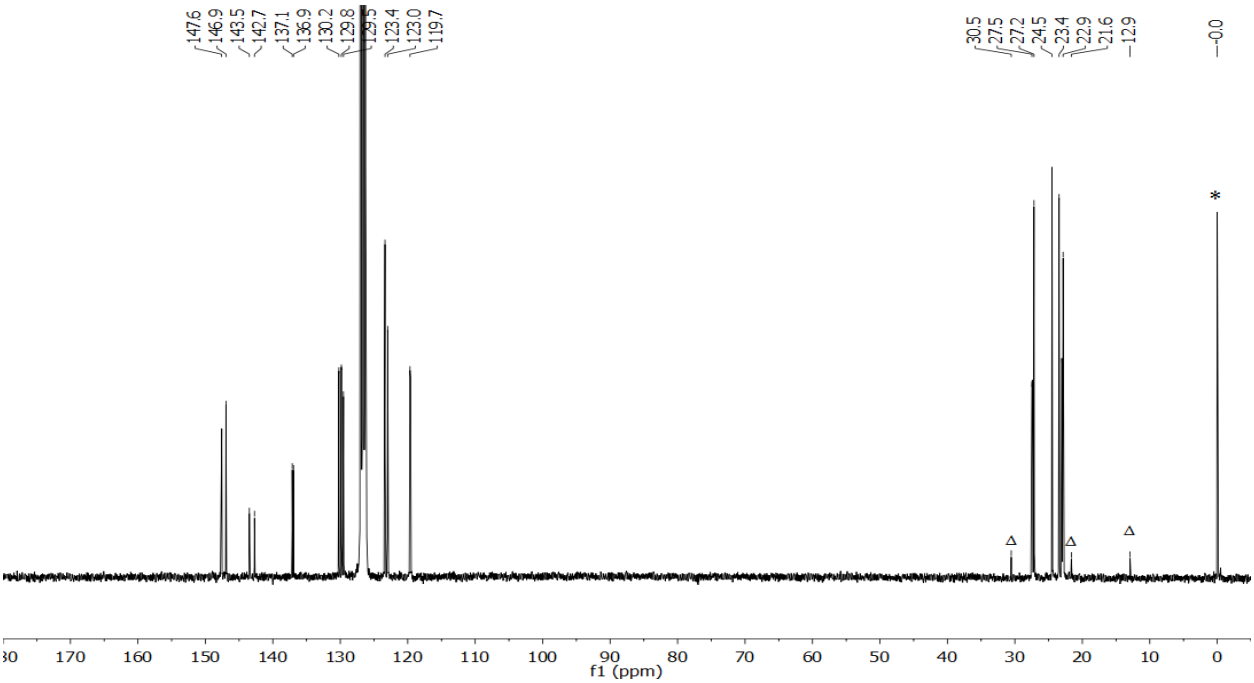

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6. $^{\Delta}$Hexane, *$SiMe_4$

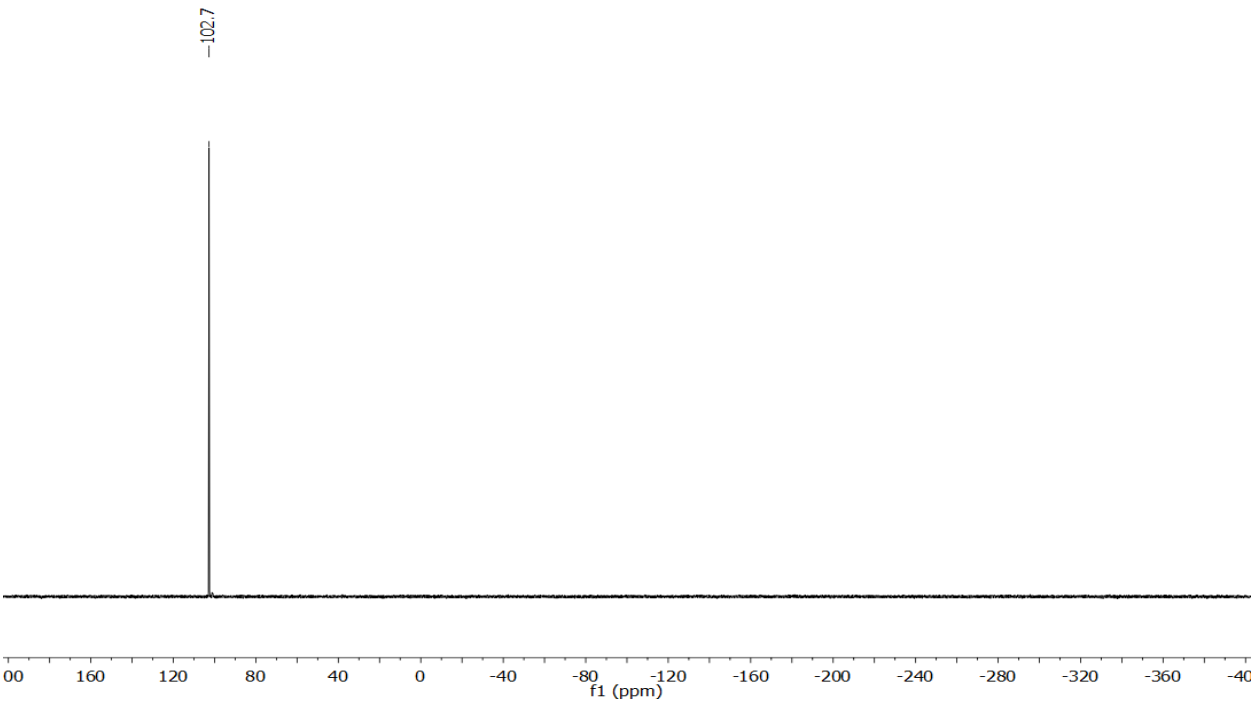

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

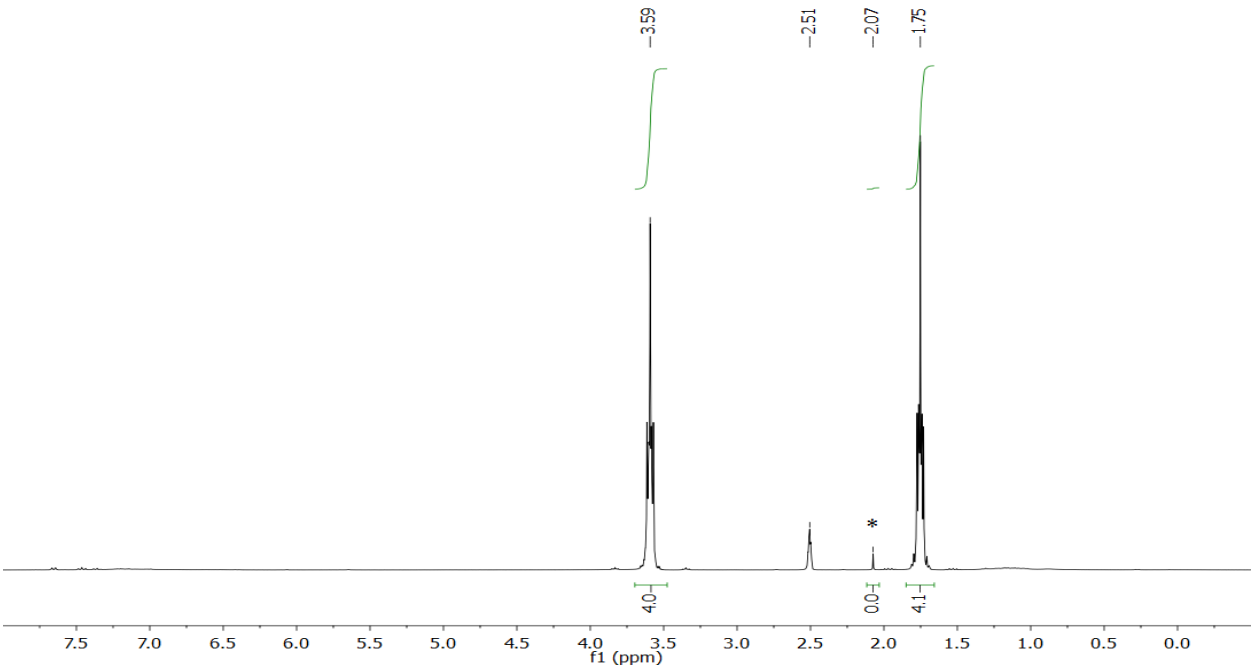

Figure S7. ^{1}H NMR spectrum of **6**•$(thf)_3$ in $[D_6]$DMSO. *Impurity

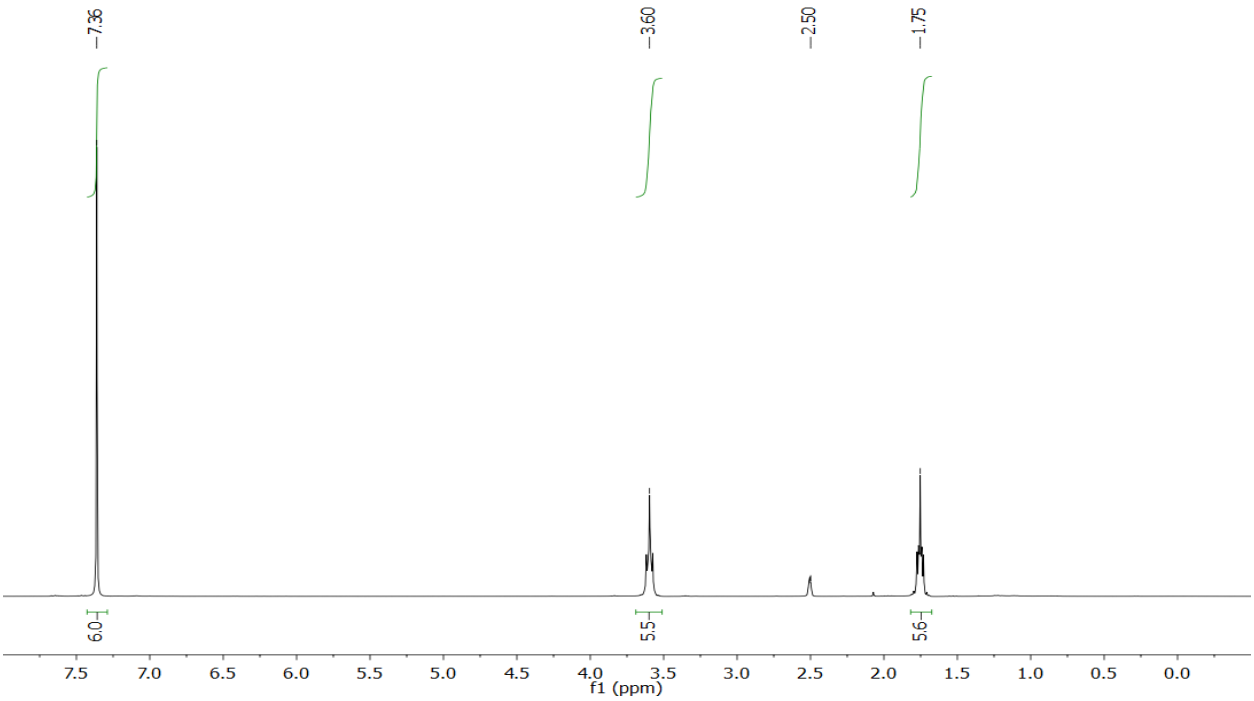

Figure S8. ^{1}H NMR spectrum of **6**•$(thf)_3$ (14 mg) and benzene (6.2 mg) in $[D_6]$DMSO.

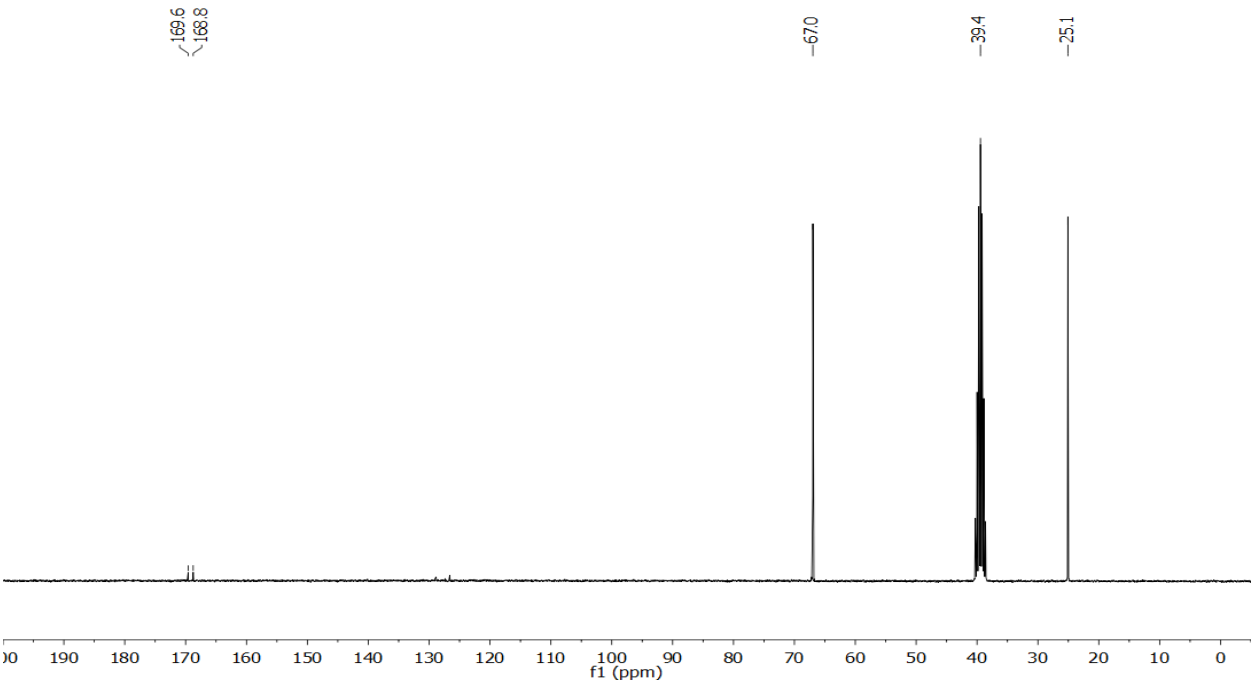

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **6**•$(thf)_3$ in $[D_6]$DMSO.

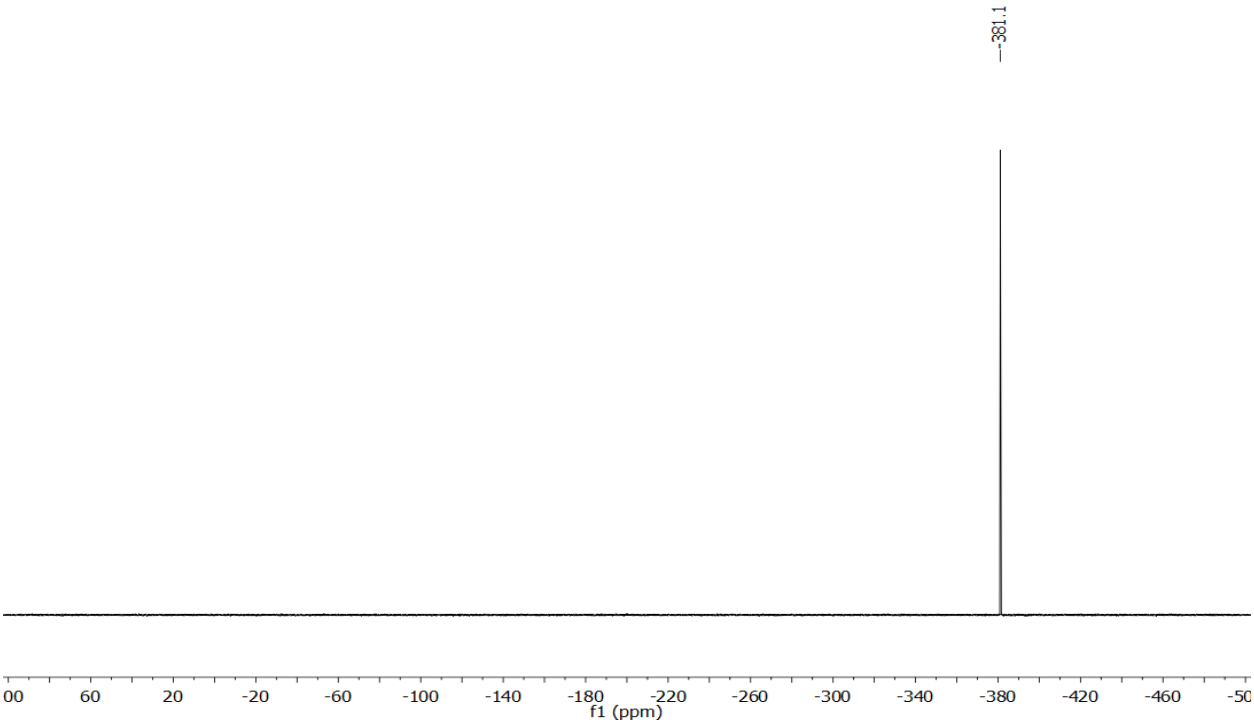

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **6**•$(thf)_3$ in $[D_6]$DMSO.

Preparation of 7: Water (5.4 mg, 0.3 mmol) was added dropwise to a stirred solution of **3** (117 mg, 0.25 mmol) in toluene (2 mL). After stirring for 3 minutes, the reaction mixture was dried under reduced pressure to yield an orange-red solid **7** (97.7 mg, 0.23 mmol, 92 % yield). M. P. = 69.3 °C (decompose). ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.48 (d, J_{PH}= 642 Hz, 1 H, P*H*), 6.91 (m, 4 H, C_{ar}*H*), 6.75 (m, 2 H, C_{ar}*H*), 5.44 (d, J_{PH}= 15 Hz, 2 H, NC*H*), 5.39 (S, 1 H, NC*H*), 3.77 (m, 2 H, C*H*Me$_2$), 2.91 (m, 2 H, C*H*Me$_2$), 1.20 (d, 6 H, C*H*$_3$), 0.86 (m, 12 H, C*H*$_3$), 0.77 (d, 6 H, C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 149.1 (d, J_{PC} = 1.6 Hz, *ipso*-C), 146.9 (d, J_{PC} = 3.2 Hz, *ipso*-C′), 131.6 (d, J_{PC} = 3.7 Hz, *o*-C), 128.0 (*p*-CH), 123.6 (*m*-CH), 122.8 (*m*-C′H), 115.8 (d, J_{PC} = 11.6 Hz, NCH), 27.4 (CH$_3$), 23.9 (CHMe$_2$), 23.6 (C′HMe$_2$), 23.1 (C″HMe$_2$), 22.7 (C‴HMe$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ = 2.9 (td, J_{HP} = 15 Hz, *H*CNP, J_{HP} = 639 Hz, *H*P).

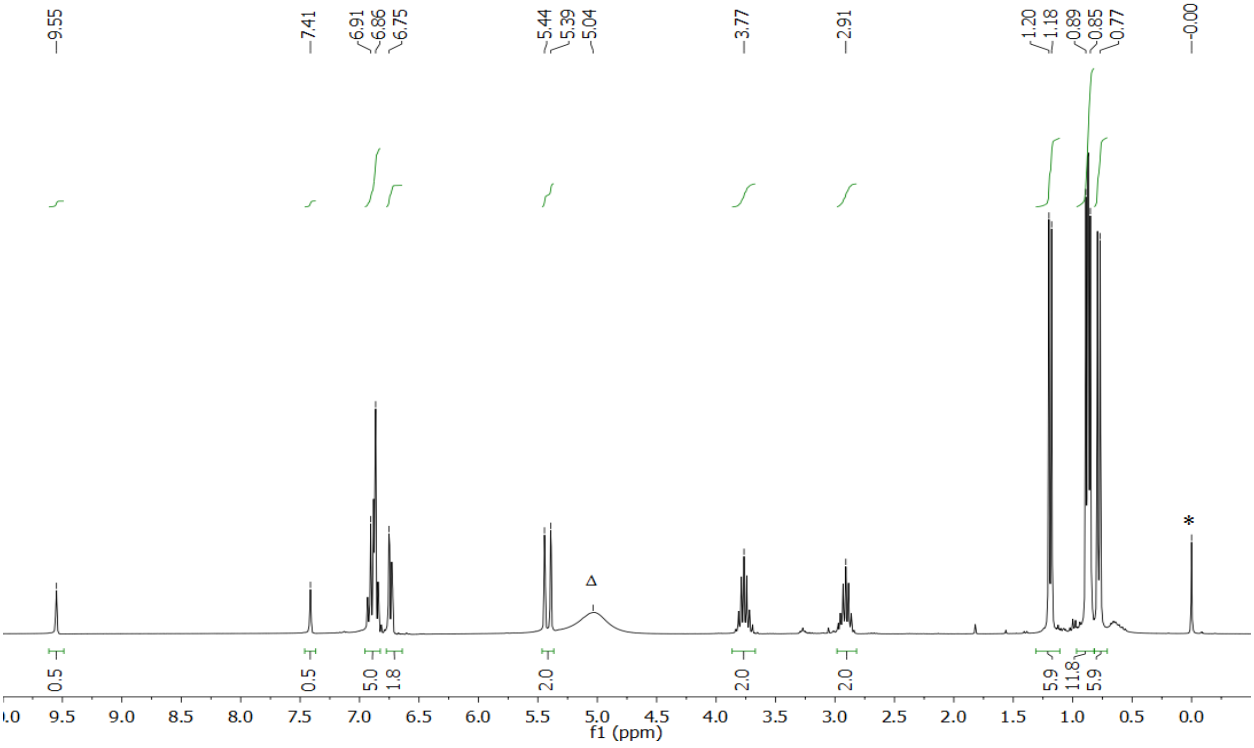

Figure S11. ^{1}H NMR spectrum of **7** in C_6D_6. $^{\Delta}H_2O$, *SiMe$_4$

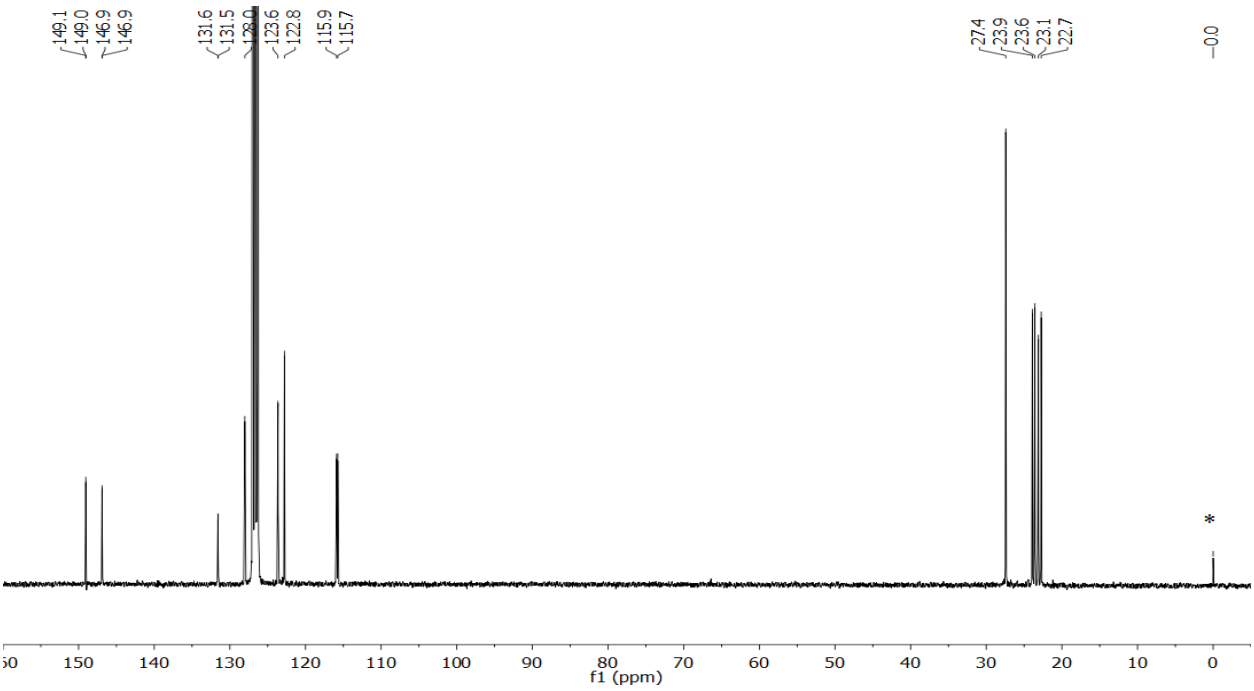

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6. *$SiMe_4$

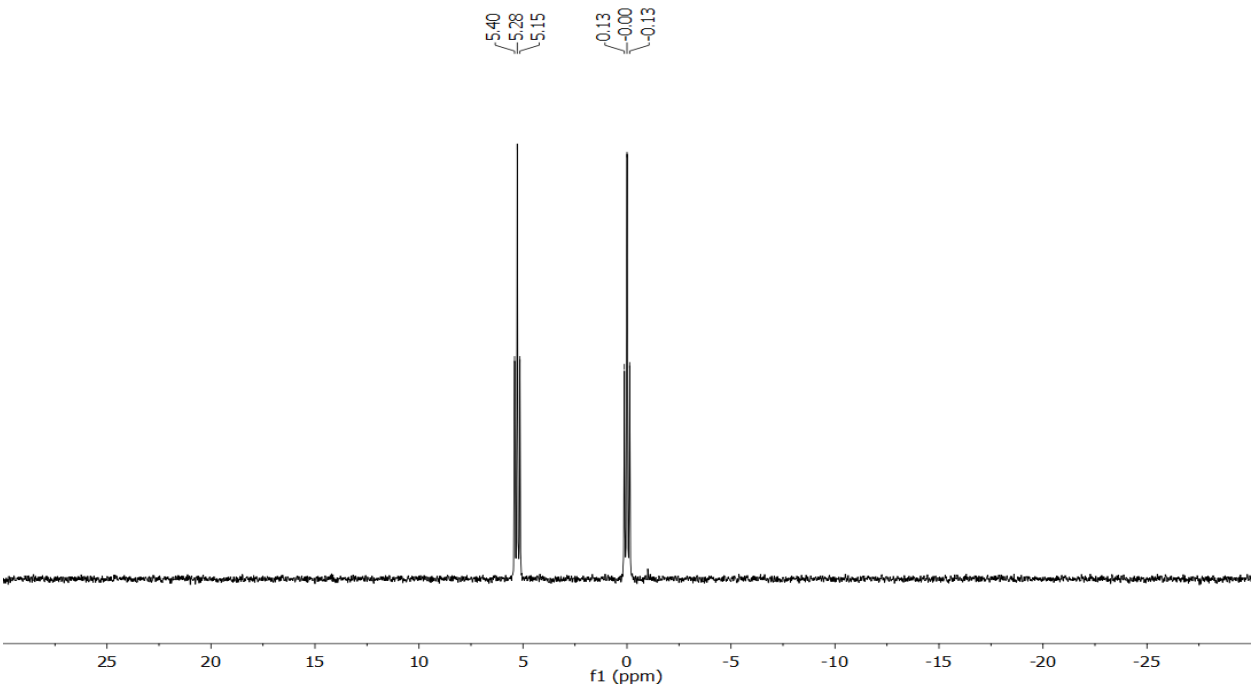

Figure S13. ^{31}P NMR spectrum of **7** in C_6D_6.

Preparation of 8: A solution of **3** (117 mg, 0.25 mmol) in THF (2 mL) was stirred for 60 hours at room temperature or in toluene (3 mL) at 60 °C for 2 hours. The solvent was removed under reduced pressure, and the remaining solid was dissolved in acetonitrile (2 mL) and diethyl ether (0.5 mL). After 24 hours yellow crystals of **8** precipitated from the solution which were filtered off, washed with acetonitrile, and dried *in vacuo*. (81 mg, 0.09 mmol, 71 % yield). M. P. = 189.2 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.14 (d, 1 H, $C_{ar}H$), 6.79 (br, 9 H, $C_{ar}H$), 6.61 (m, 2 H, $C_{ar}H$), 5.63 (d, 2 H, J_{PH} = 51 Hz, NC*H*), 4.45 (s, 1 H, NC*H*), 3.72 (m, 1 H, C*H*Me$_2$), 3.14 (m, 3 H, C*H*Me$_2$), 2.76 (m, 2 H, C*H*Me$_2$), 1.30 (d, 3 H, CH_3), 0.92 (br, 42 H, CH_3) , 0.64 (d, 3 H, CH_3); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 162.6, 148.1, 147.6, 146.4, 145.6, 135.8, 135.6, 134.5, 135.2, 135.1, 134.9, 127.3, 123.5, 123.3, 123.2, 123.1, 121.2, 117.6, 117.1, 69.1, 28.0, 27.8, 27.5, 26.8, 26.4, 25.7, 24.9, 24.2, 24.1, 23.5, 23.3, 22.6, 22.3, 21.6; ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ = 118.0 (dt, J_{PP} = 145.4 Hz, J_{PP} = 34.3 Hz), 0.1 (td, J_{PP} = 207.4 Hz, J_{PP} = 32.4 Hz), –263.4, – (ddd, J_{PP} = 33.9 Hz, J_{PP} = 145.2 Hz, J_{PP} = 208.8 Hz), –272.1 (dt, J_{PP} = 206.1 Hz, J_{PP} = 36.4 Hz).

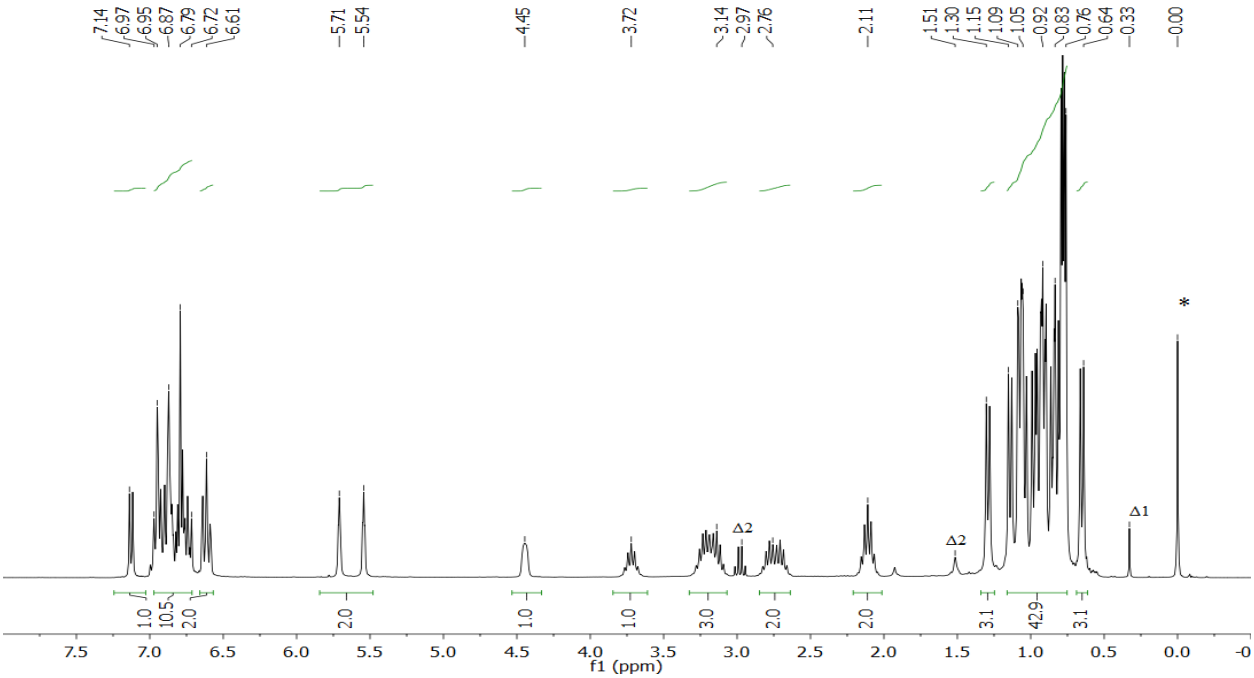

Figure S14. ^{1}H NMR spectrum of **8** in C_6D_6. *$SiMe_4$, $^{\Delta 1}$Water, $^{\Delta 2}$Diethyl ether

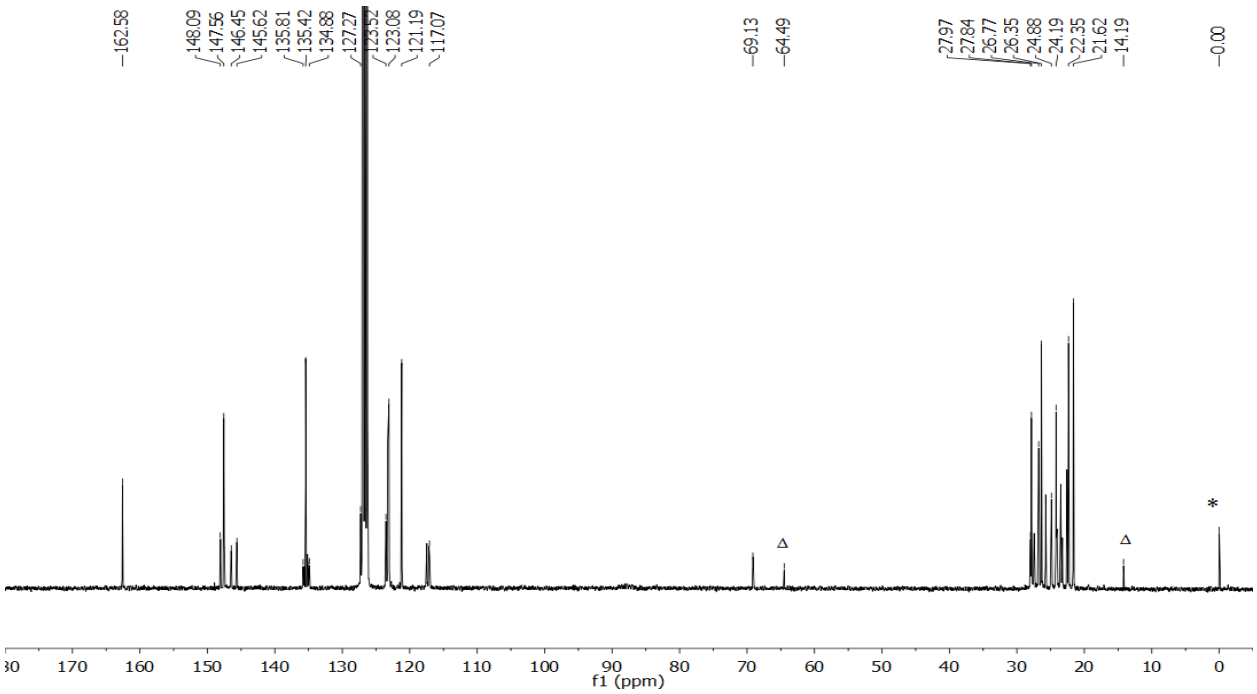

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6. *$SiMe_4$, $^{\Delta}$Diethyl ether

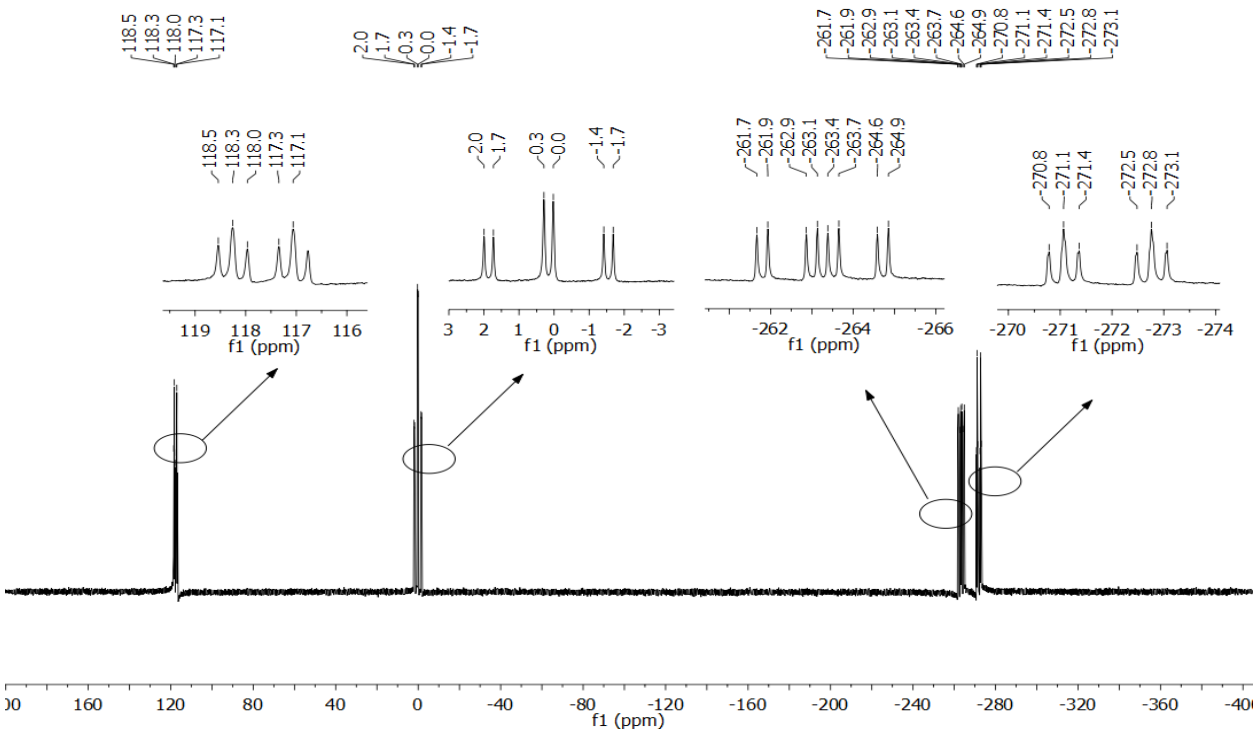

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **8** in C_6D_6.

Preparation of 9: A solution of **3** (233 mg, 0.5 mmol) in 2,3–dimethylbutadiene (3 mL) was stirred for 72 hours at room temperature. The solvent was removed under reduced pressure, and the remaining solid was dissolved in acetonitrile (1 mL) and diethyl ether (1 mL). After 48 hours, the precipitate was removed by filtration from the solution. The filtrate was dried under reduced pressure to give a yellow-red residue. This residue was dissolved in 1 mL *n*-hexane and filtered over a 6 × 1c m column of alumina which was washed with 3 mL hexane. The solvent was removed under reduced pressure to give product **9** as a yellow solid (31 mg, 0.056 mmol, 11 % yield). According to NMR-data, this solid contains both the *trans* and *cis* isomer in a ratio of about 2:1. M. P. = 163.7 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 10.29 (d, *J* = 12 Hz, 1 H, N*H*), 6.95 (s, 2 H, C_{ar}*H*), 6.87 (m, 1 H, C_{ar}*H*), 6.77 (m, 3 H, C_{ar}*H*), 6.72 (m, 3 H, C_{ar}*H*), 6.49 (d, *J* = 12 Hz, 0.5 H, N*H′*), 5.62 (d, *J* = 12 Hz, 1 H, NC*H*), 4.97 (d, *J* = 12 Hz, 0.5 H, NC*H′*), 3.80 (m, 0.5 H, C*H′*Me_2), 3.27 (m, 2.5 H, C*H*Me_2), 2.80 (m, 5 H, C*H′*Me_2 and PCH_2), 2.40 (m, 1 H, C*H*Me_2), 1.76 (m, 1 H, PCH_2), 1.59 (m, 9 H, CH_2CH_3), 1.48 (m, 2 H, PCH'_2), 1.24 (d, *J* = 6 Hz, 3 H, CH_3), 1.25 (d, *J* = 6 Hz, 1.5 H, CH'_3), 1.11 (d, *J* = 6 Hz, 1.5 H, CH'_3), 1.07 (d, *J* = 6 Hz, 3 H, CH_3), 0.96 (d, *J* = 6 Hz, 3 H, CH_3), 0.78 (m, 24 H, CH_3 and CH'_3); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 215.2 (dd, J_{PC} = 37.5 Hz, *PC*O, J_{PC} = 7.5 Hz, *P*P*C*O), 148.8, 148.8, 148.2, 147.4, 143.9, 143.5, 142.6, 142.1, 136.9, 136.3, 135.0, 128.7, 126.8, 126.7, 125.7, 125.4, 124.4, 124.3, 123.9, 123.7, 123.0, 123.1, 122.4, 38.1, 37.7, 37.4, 37.1, 31.8, 29.1, 29.0, 28.4, 28.3, 28.1, 27.6, 27.5, 27.1, 26.1, 25.9, 25.3, 25.1, 24.0, 23.6, 23.5, 23.4, 22.9, 22.8, 22.2, 21.8, 21.7, 21.0, 20.6; ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ = 39.4 (d, J_{PP} = 290.4 Hz, trans), 36.2 (d, $J_{P'P'}$ = 290.4 Hz, cis), –45.8 (d, J_{PP} = 290.4 Hz, trans), –51.2 (d, J_{PP} = 290.4 Hz, cis).

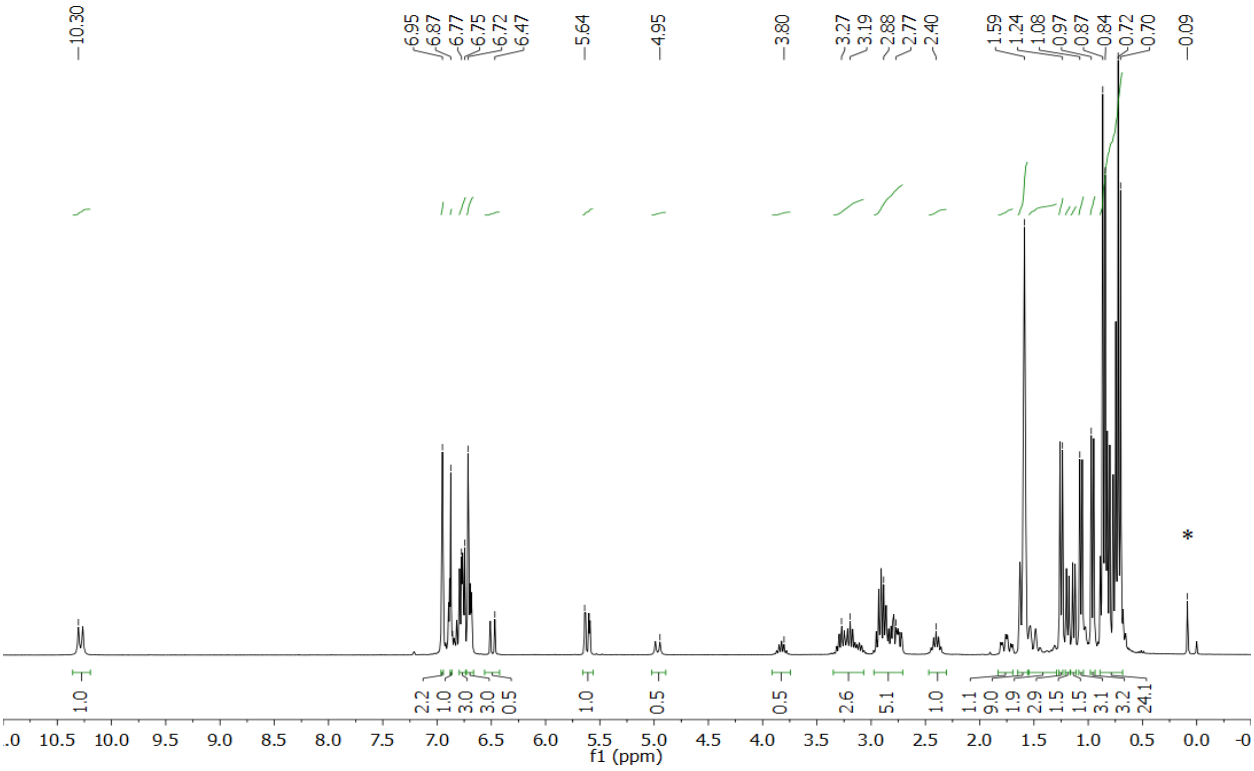

Figure S17. ^{1}H NMR spectrum of **9** in C_6D_6. *$SiMe_4$

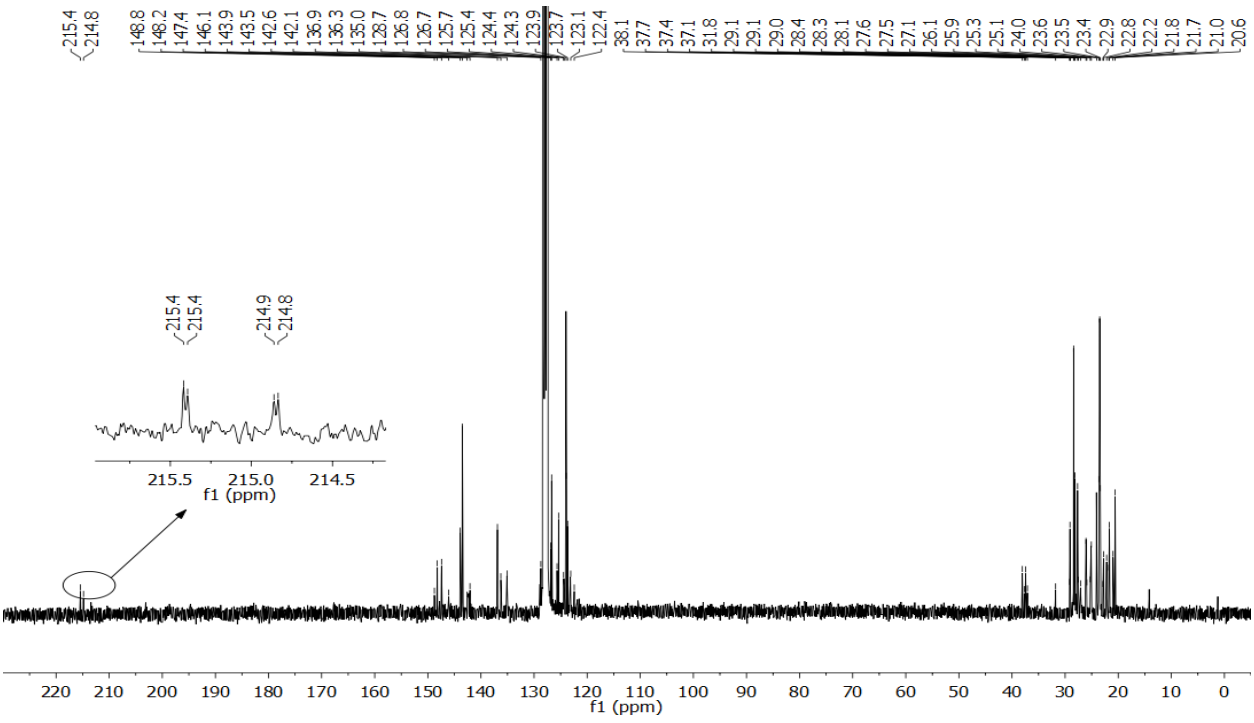

Figure S18. ^{13}C{^{1}H} NMR spectrum of **9** in C_6D_6.

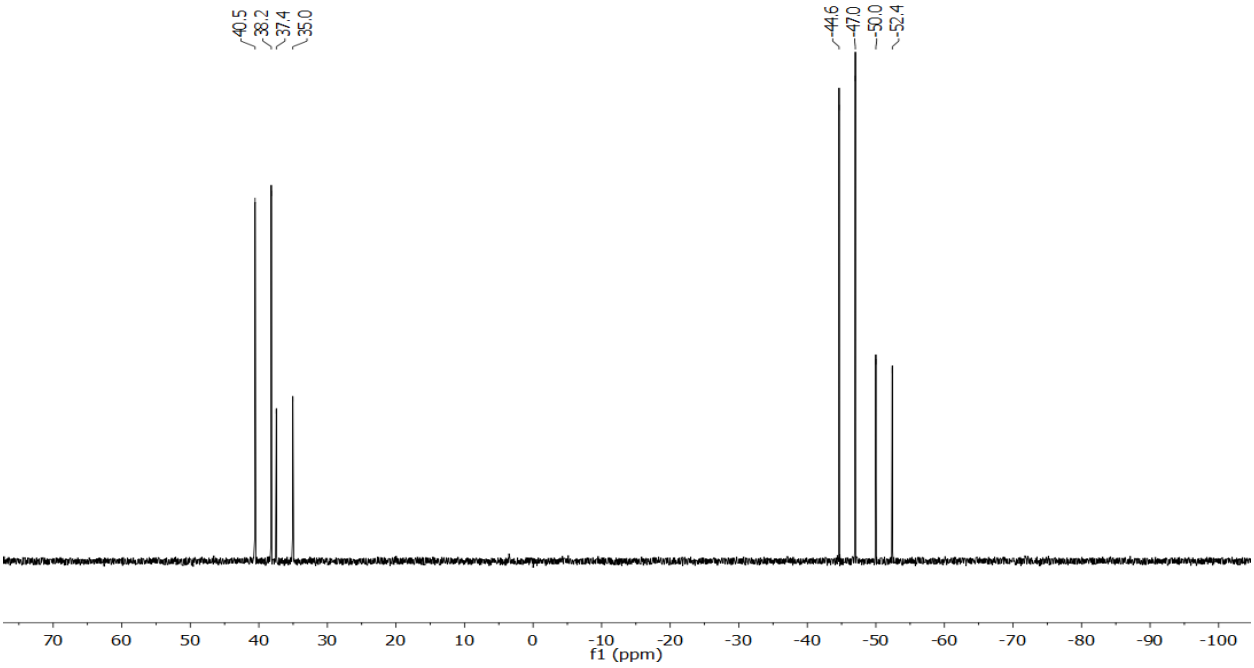

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **9** in C_6D_6.

Preparation of 11: Tetraphenylcyclopentadienone (288 mg, 0.75 mmol) was added to a stirred solution of **3** (117 mg, 0.25 mmol) in THF (3 mL). After stirring for 48 hours, the solvent was removed under reduced pressure, followed by extraction with *n*-hexane (2 × 5 mL) and filtration. The filtrate was dried under reduced pressure and washed with acetonitrile to yield **11** as yellow powder. (57 mg, 0.07 mmol, 28 % yield). M. P. = 157.5 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.31 (m, 2 H, $C_{ar}H$), 7.15 (m, 2 H, $C_{ar}H$), 6.92 (m, 2 H, $C_{ar}H$), 6.76 (m, 5 H, $C_{ar}H$), 6.67 (m, 5 H, $C_{ar}H$), 6.60 (m, 3 H, $C_{ar}H$), 6.48 (m, 1 H, $C_{ar}H$), 6.33 (m, 6 H, $C_{ar}H$), 5.61 (m, 1 H, NC*H*), 5.44 (m, 1 H, NC*H*), 3.66 (m, 1 H, C*H*Me_2), 3.37 (m, 1 H, C*H*Me_2), 3.03 (m, 1 H, C*H*Me_2), 2.67 (m, 1 H, C*H*Me_2), 1.36 (m, 6 H, CH_3), 1.04 (d, 3 H, CH_3), 0.89 (m, 6 H, CH_3), 0.78 (d, 3 H, CH_3), 0.70 (d, 3 H, CH_3), 0.37 (d, 3 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 75 MHz): δ = 158.5 (d, J_{PC} = 1.6 Hz), 148.6, 147.9, 147.1, 146.1, 145.9, 145.8, 145.7, 141.4, 139.4, 136.8, 136.2, 135.0, 133.5, 133.4, 130.3, 129.6, 129.1, 126.9, 126.7, 126.5, 125.3, 125.6, 124.3, 124.8, 121.4, 121.0, 117.2, 66.6 (dd, J_{PC} = 52.2 Hz, *P*C, J_{PC} = 7.5 Hz, *P*PC), 65.7, 31.8, 29.6, 29.0, 28.2, 26.6, 26.2, 26.0, 25.0, 24.2, 23.7,

22.6, 22.2, 15.4, 14.2; $^{31}P\{^{1}H\}$ NMR (C_6D_6, 121 MHz) δ = 118.2, 112.8 (d, J_{PP} = 651 Hz), δ = –140.5, –145.9 (d, J_{PP} = 651 Hz).

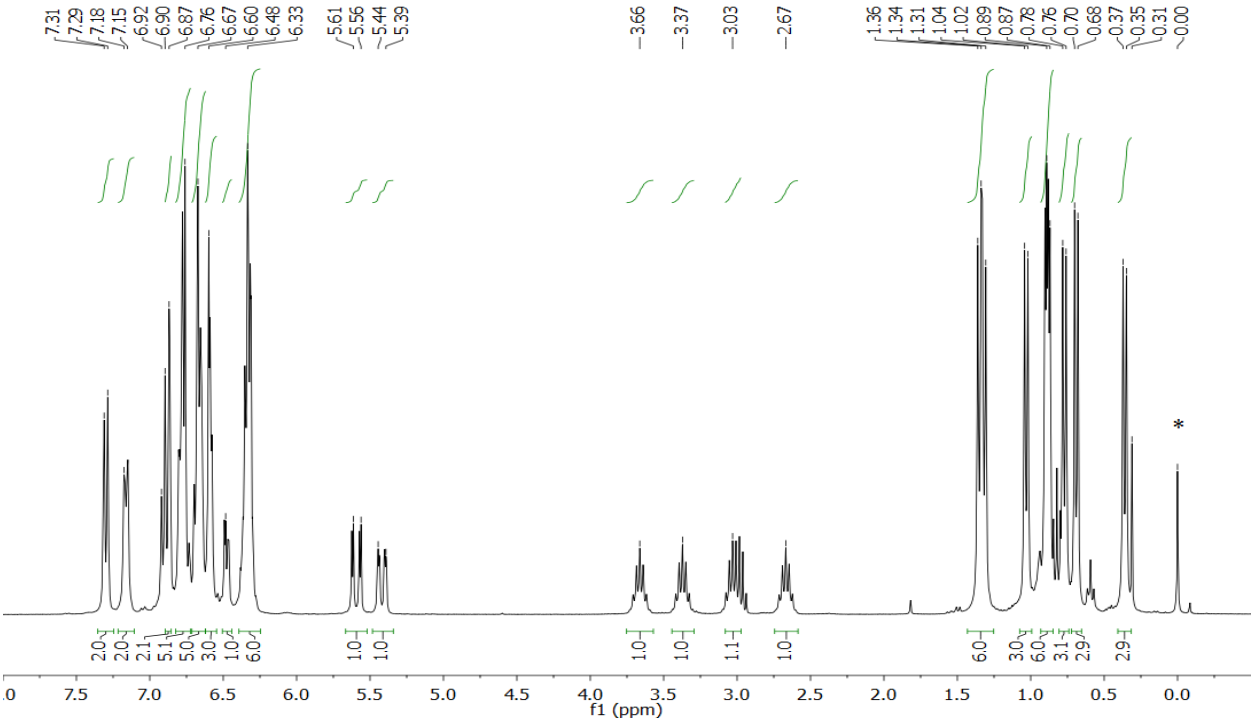

Figure S20. ^{1}H NMR spectrum of **11** in C_6D_6. *$SiMe_4$

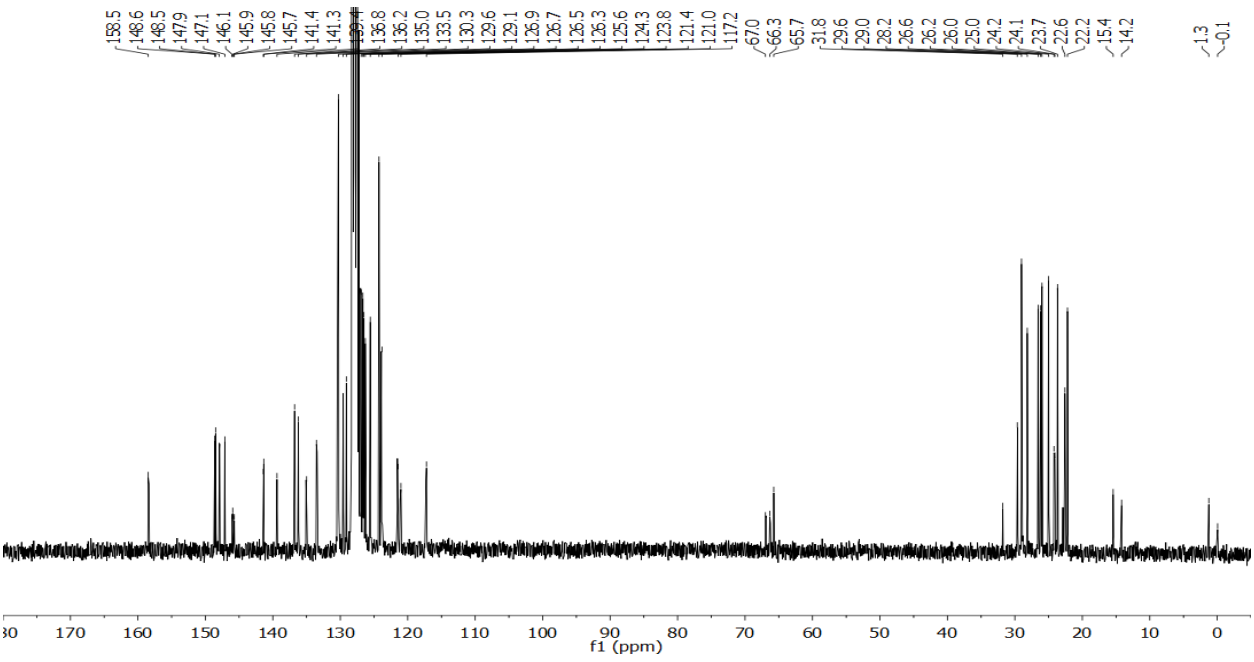

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **11** in C_6D_6.

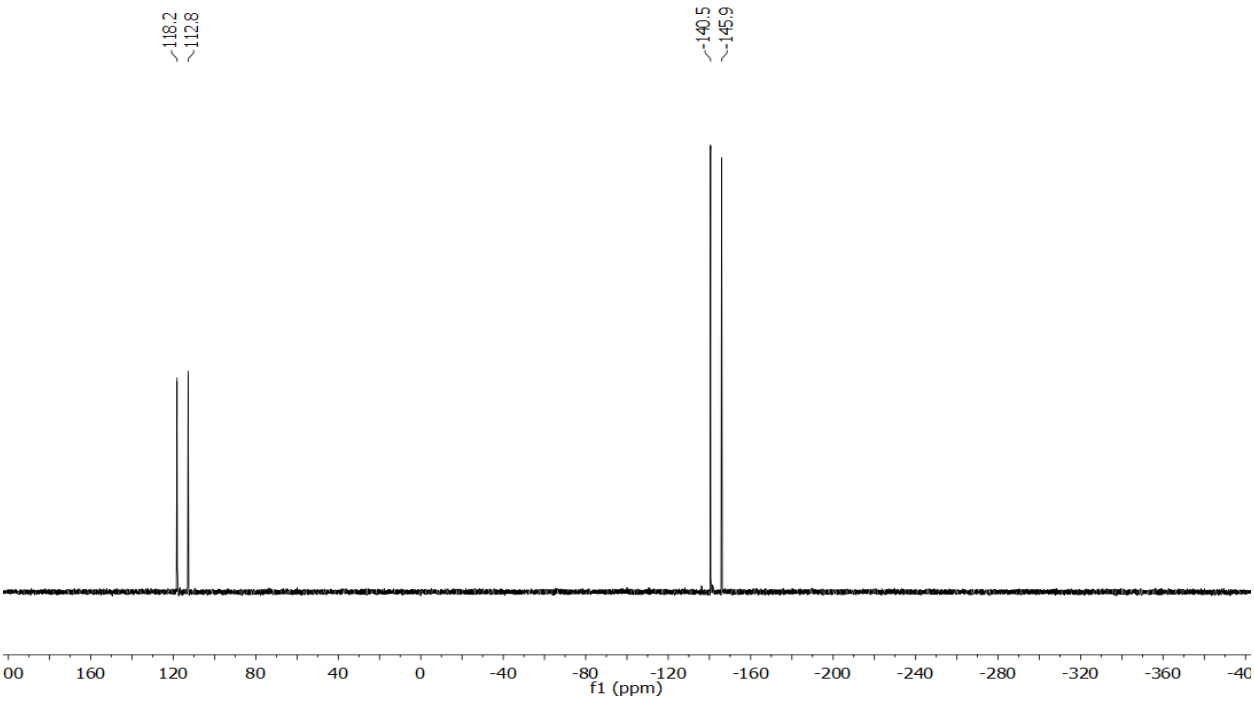

Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **11** in C_6D_6.

S2: Kinetic measurement and analysis for the dimerization of 3

The ^{31}P NMR data for kinetic analysis were acquired on Bruker-200 spectrometers. All integrals were normalized versus the started concentration of **3** and plotted versus the time. The values of the integrals were fit by a non-linear least squares method to the first order equations $[\mathbf{3}] = Ae^{-kt}$ and $[\mathbf{8}] = B - Ce^{-kt}$(where A, B, C and k were allowed to vary freely) using the automated routine of Gnuplot.

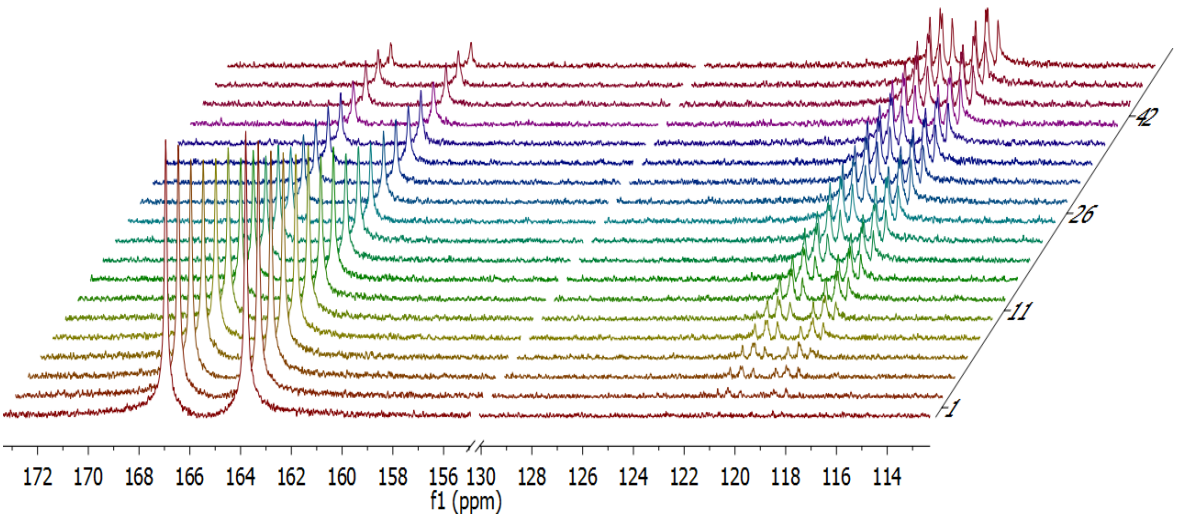

Figure S23. Dimerization of **3** to **8** in toluene followed by ^{31}P NMR form t = 0 h to 75 h (front to back). The signals on the left show the doublet of **3** the right side shows the multiplet for **8**.

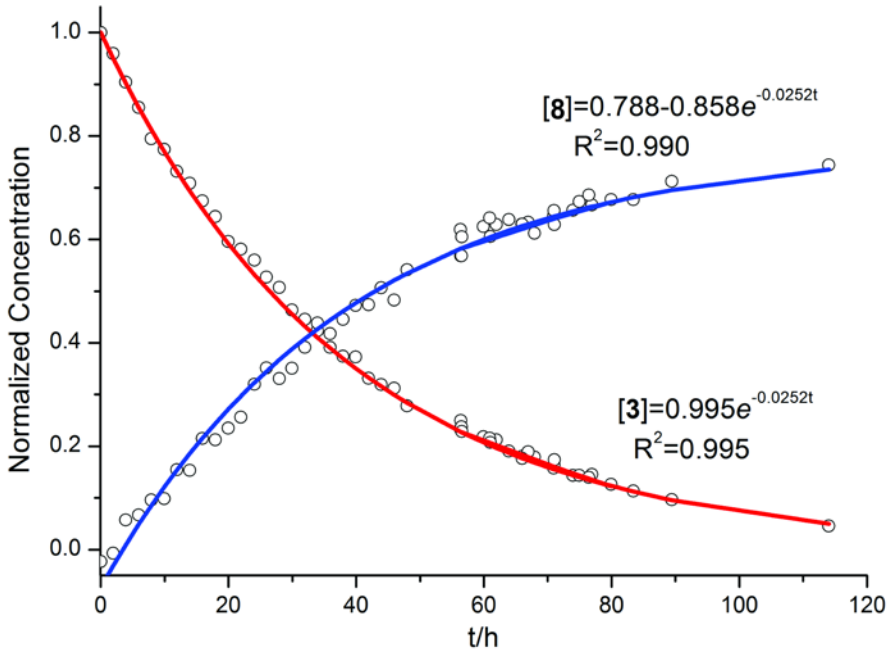

Figure S24. Representative kinetic data for the dimerization of **3** to **8** in toluene at 25 ˚C. The concentration versus time profile of starting material **3** and product **8** fit first order equations: [**3**] = Ae^{-kt} and [**8**] = $B - Ce^{-kt}$, with a rate constant k_{obs} = 0.0252 h^{-1} at 25 ˚C.

S3: X-Ray Diffraction Studies

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or by emailing data_request@ccdc.cam.ac.uk. The CCDC reference numbers for **3**, **8**, **9**, **11** and **9**-*trans*/*cis* mixture are 1026346, 1026345, 1026347, 1026349, and 1026348, respectively.

X-ray crystal structure of 3: Yellow crystals of **3** were obtained from a saturated *n*-hexane solution stored at –20 °C.

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{27}H_{36}N_2OP_2$
Formula weight	466.55 g/mol
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5186(12)
b/Å	12.9781(15)
c/Å	21.293(3)
α/°	90
β/°	95.781(4)
γ/°	90
Volume/Å^3	2617.0(6)
Z	4
ρ_{calc}g/cm^3	1.1841
μ/mm^{-1}	0.187
F(000)	1001.2
Crystal size/mm^3	0.477 × 0.183 × 0.129
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.96 to 61.2
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 18, -30 ≤ l ≤ 30
Reflections collected	35771

Independent reflections	7819 [R_{int} = 0.0296, R_{sigma} = 0.0223]
Data/restraints/parameters	7819/1/432
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0957
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.1042
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.29

X-ray crystal structure of 8: Yellow crystals of **8** were obtained from a saturated acetonitrile / diethyl ether solution via slow evaporation.

Table S2. Crystal data and structure refinement for **8**.

Empirical formula	$C_{53}H_{72}N_4OP_4$
Formula weight	905.02 g/mol
Temperature/K	105.0(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.86749(18)
b/Å	15.8674(3)
c/Å	18.6581(4)
α/°	68.043(2)
β/°	77.0428(17)
γ/°	73.5767(17)
Volume/$Å^3$	2575.71(10)
Z	2
ρ_{calc}g/cm^3	1.167
μ/mm^{-1}	0.187
F(000)	972
Crystal size/mm^3	0.28 × 0.21 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.686 to 65.138

Index ranges	$-14 \le h \le 14, -23 \le k \le 24, -26 \le l \le 28$
Reflections collected	82945
Independent reflections	17517 [R_{int} = 0.0320, R_{sigma} = 0.0272]
Data/restraints/parameters	17517/0/682
Goodness-of-fit on F^2	1.08
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1228
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1274
Largest diff. peak/hole / e $Å^{-3}$	1.12/-0.47

X-ray crystal structure of 9: Yellow crystals of **9** from the *trans* / *cis* isomer mixture (ratio is about 2:1) were obtained from a saturated *n*-hexane solution stored at –20 °C.

Table S3. Crystal data and structure refinement for **9** (only trans form).

Empirical formula	$C_{33}H_{46}N_2OP_2$
Formula weight	548.66 g/mol
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.0689(11)
b/Å	11.5642(12)
c/Å	14.5238(16)
α/°	84.273(3)
β/°	72.479(3)
γ/°	76.618(3)
Volume/$Å^3$	1568.1(3)
Z	2
ρ_{calc}g/cm^3	1.162
μ/mm^{-1}	0.166
F(000)	592
Crystal size/mm^3	0.26 × 0.23 × 0.19

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.592 to 52.882
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	42934
Independent reflections	6422 [R_{int} = 0.0246, R_{sigma} = 0.0125]
Data/restraints/parameters	6422/0/527
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.0998
Largest diff. peak/hole / e $Å^{-3}$	1.12/-0.22

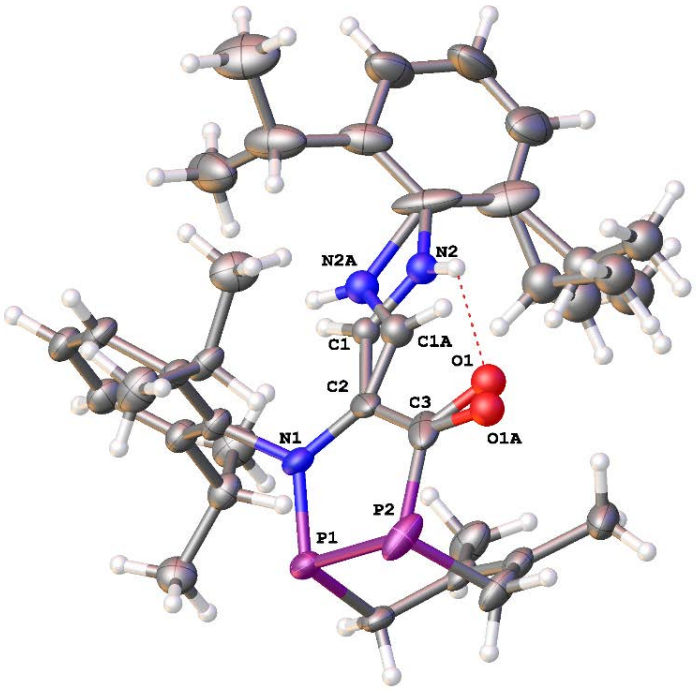

Figure S25. Molecular structure of **9**. The atom occupation percentage of C1, N2 and C1A, N2A are 0.632 and 0.368 respectively, which indicates the ratio of *trans* and *cis* isomer is around 2:1.

Table S4. Crystal data and structure refinement for **9** (*trans* and *cis* isomer mixture).

Empirical formula	$C_{33}H_{46}N_2OP_2$
Formula weight	548.66
Temperature/K	100.8
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.3904(5)
b/Å	20.3999(9)
c/Å	13.5469(6)
α/°	90
β/°	93.823(3)
γ/°	90
Volume/Å^3	3140.8(2)
Z	4
ρ_{calc}g/cm^3	1.160
μ/mm^{-1}	1.453
F(000)	1184.0
Crystal size/mm^3	0.2 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.846 to 127.874
Index ranges	-12 ≤ h ≤ 13, -22 ≤ k ≤ 22, -15 ≤ l ≤ 15
Reflections collected	18428
Independent reflections	4958 [R_{int} = 0.1557, R_{sigma} = 0.0836]
Data/restraints/parameters	4958/0/351
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0774, wR_2 = 0.1725
Final R indexes [all data]	R_1 = 0.1001, wR_2 = 0.1881

Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.50

X-ray crystal structure of 11: Yellow crystals of **11** were obtained from a saturated acetonitrile / diethyl ether solution via slow evaporation.

Table S5. Crystal data and structure refinement for **11**.

Empirical formula	$C_{63}H_{65}N_3OP_2$
Formula weight	942.12
Temperature/K	100.7
Crystal system	triclinic
Space group	P-1
a/Å	17.7901(14)
b/Å	18.7231(16)
c/Å	19.1169(16)
α/°	73.099(3)
β/°	63.618(3)
γ/°	71.027(3)
Volume/$Å^3$	5313.5(8)
Z	4
$\rho_{calc}g/cm^3$	1.178
μ/mm^{-1}	0.126
F(000)	2008.0
Crystal size/mm^3	0.21 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.246 to 56.71
Index ranges	-23 ≤ h ≤ 23, -24 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	243043

Independent reflections	26447 [R_{int} = 0.0932, R_{sigma} = 0.0409]
Data/restraints/parameters	26447/3199/1239
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0640, wR_2 = 0.1680
Final R indexes [all data]	R_1 = 0.0850, wR_2 = 0.1827
Largest diff. peak/hole / e $Å^{-3}$	1.04/-0.99

S4: Theoretical Details

We performed density functional calculations with the Turbomole[3] (versions 6.3.1 and 6.5) and Gaussian[4] (version 09, Revision C.1) program packages. In the Turbomole calculations we employed Ahlrichs' def2-SVP and def2-TZVP basis set[5,6]. The BP86[7,8] and PBE[9,10] (in combination with the resolution of the identity (RI) technique) as well as the hybrid functionals PBE0[11] and B3LYP[12-14] were chosen. Furthermore, second-order Møller-Plesset (MP2) calculations were performed with the def2-TZVPP[6] basis set. Since similar relative energies have been obtained for the different quantum-chemical methods, we only discuss the BP86 energies explicitly. The convergence criterium for the self-consistent-field single-point calculations was set to an energy difference of 10^{-7} hartree between the two last energy iterations and structure optimizations were considered converged when the length of the geometry gradient was below 10^{-4} hartree/bohr. In the Gaussian calculations we employed BP86[8,9] with the TZVP basis set. We used the default convergence criteria (scfconv=tight, which means that the energy difference between two iteration steps was less than 10^{-8} hartree, and optimizations were considered converged when the root mean square force was below 3×10^{-4} a.u.). We located the transition-state structures (TS) by performing a constrained optimization scan with Gaussian, selecting the highest-energy structure, calculating the vibrational frequencies and following the lowest-eigenvalue mode with the trust-radius image based eigenvector-following procedure implemented in Turbomole. A preoptimization was carried out with def2-SVP basis set and on the converged structure we performed a TS calculation with def2-TZVP basis set. We performed a vibrational analysis on every structure with vanishing gradient, in order to verify that the structure is a minimum or transition state. The intrinsic reaction coordinates have been calculated with Gaussian

to verifiy that the transition-state structure between the correct local minima has been found. Molecular structures were visualized with PyMOL.[15]

The BP86 energy difference between the OCP^- and PCO^- products amounts to 18 kcal/mol (see Figure S26).

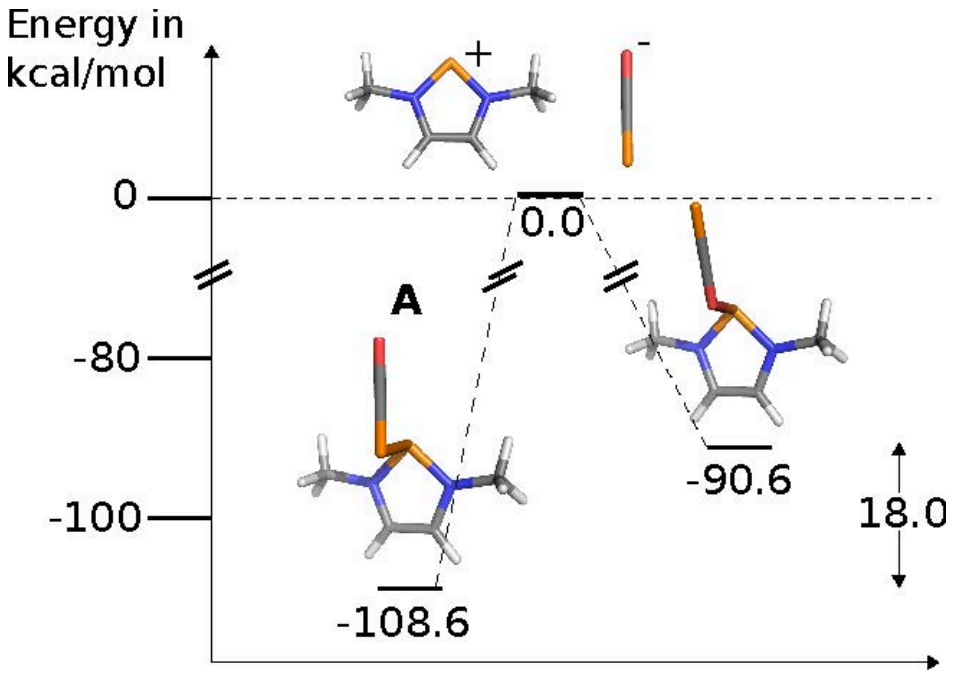

Figure S26. The BP86/def2-TZVP energy difference between structure $(HC)_2(NMe)_2P$-P=C=O (**A**) and the oxy-phosphaalkyne isomer $(HC)_2(NMe)_2P$-O-C≡P. Element color code: gray, C; red, O; blue, N; white, H; orange, P.

The optimization of structure **A** led to two local minimum-energy structures, where the P-C-O group is rotated around the P-P bond. One conformer is by 1–2 kcal mol^{-1} higher in energy (called $\mathbf{A_{rot}}$) than the other one (**A**). The BP86 and B3LYP reaction energy pathways from structure **A** to **I** are shown in Figure S27.

By performing a constrained optimization scan along the C-C bond, which is formed in the transition from $\mathbf{A_{rot}}$ to **I**, as well as a quadratic synchronous transit approach (QST3), we obtained

two different transition states, **TS^1** and **TS^2**. The intrinsic reaction coordinates calculated for both, **TS^1** and **TS^2**, confirmed that the transition between **A$_{rot}$** and **I** proceeds directly through one transition state and not through several TSs, i.e., either over **TS^1** or **TS^2**. **TS^1** appears to be slightly lower in energy. Although it cannot be excluded that more reaction pathways than the reported two exist, the energy of **TS^1** may serve as an upper limit for the transition barrier.

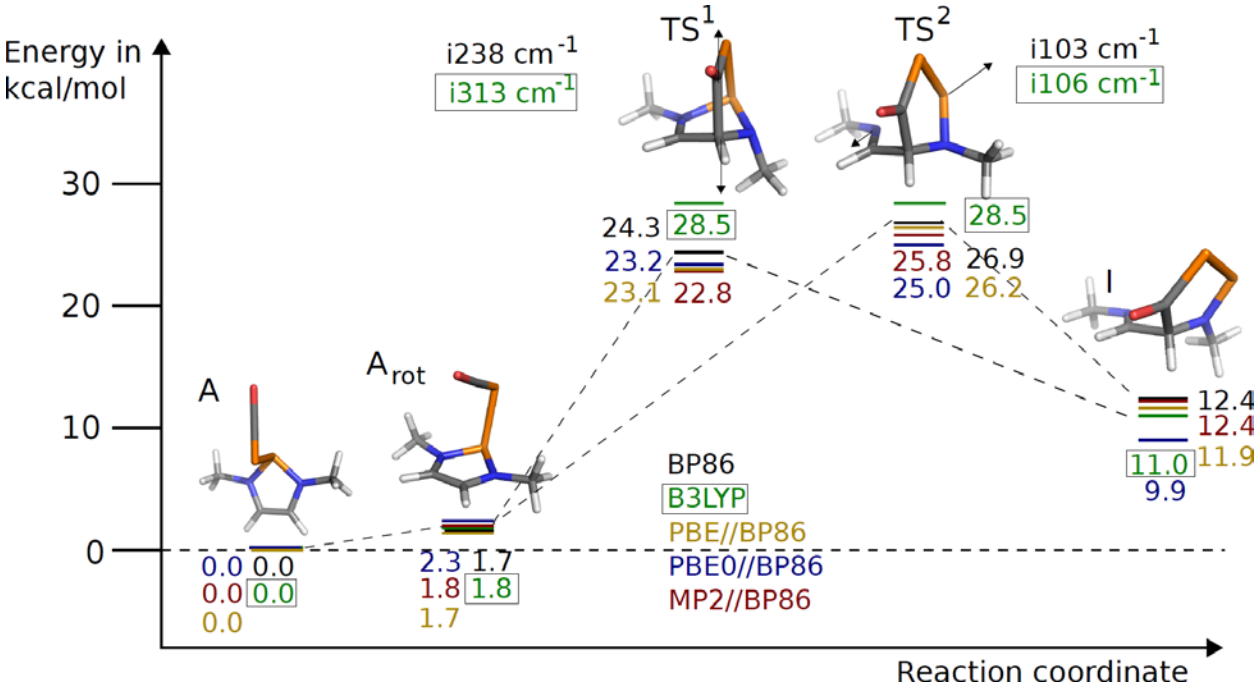

Figure S27. BP86/def2-TZVP and B3LYP transition path from structure **A** to **I**. The PBE, PBE0 and MP2 single-point energies on the BP86/def2-TZVP optimized structures (denoted by e.g. PBE//BP86) are also reported. Element color code: gray, C; red, O; blue, N; white, H; orange, P.

Noteworthy, the CO dissociation energy from **A** is by 4.6 kcal/mol more endothermic than the reaction barrier between **A** and **I**. The dimerization pathway of structures **A** and **I** to **C** is reported in Figure S28.

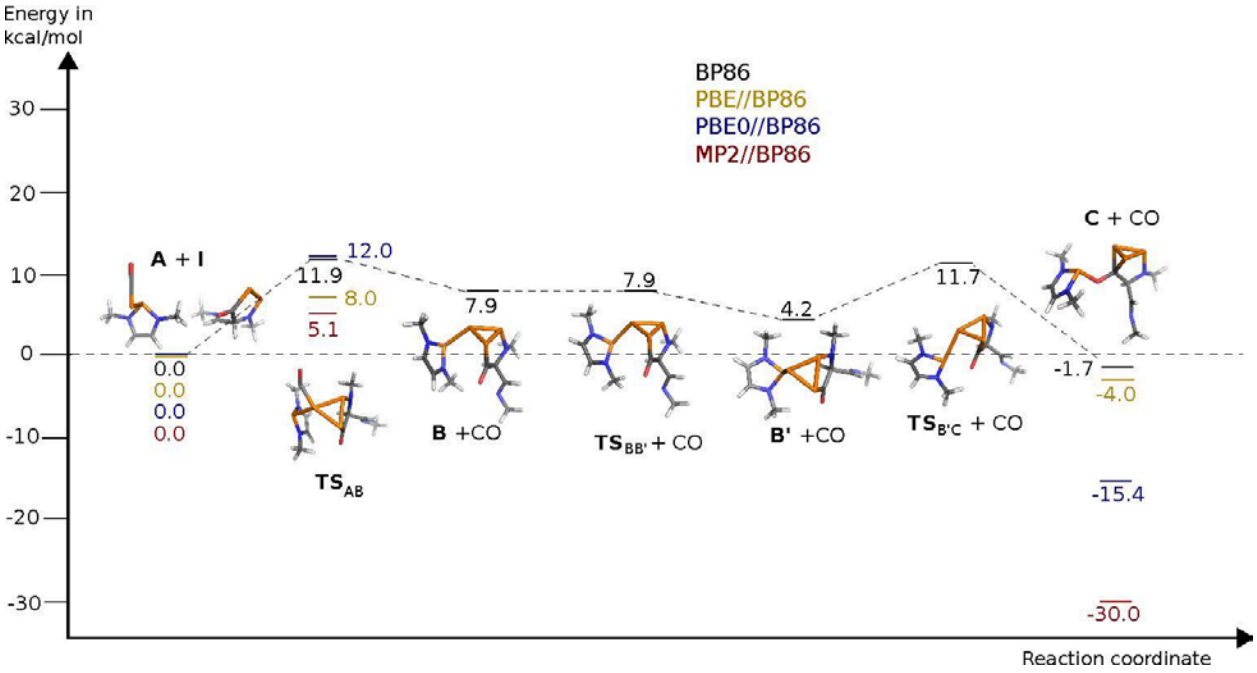

Figure S28. BP86/def2-TZVP transition path from structures **A** and **I** to the dimer **C** and CO. The PBE, PBE0 and MP2 single-point energies on BP86/def2-TZVP optimized structures (denoted by e.g., PBE//BP86) are reported for several intermediates. Element color code: gray, C; red, O; blue, N; white, H; orange, P.

The reaction pathway of the Diels-Alder reaction between **I** and 2,3-DMB is reported in Figure S29.

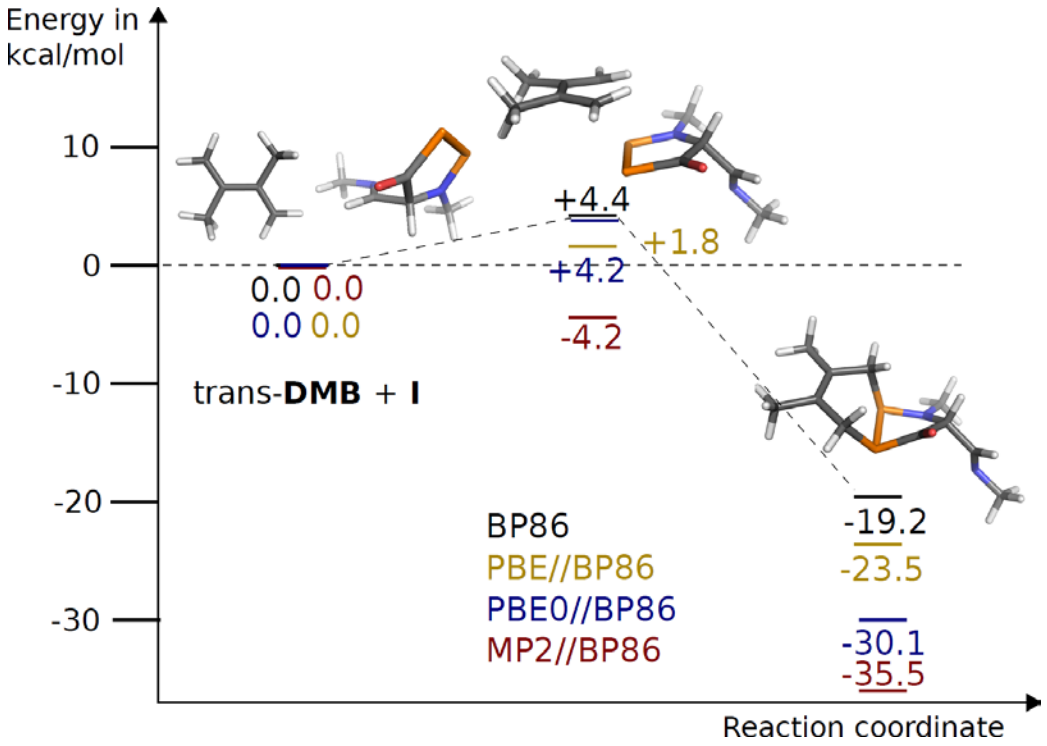

Figure S29. BP86/def2-TZVP Diels-Alder reaction path of **I** with 2,3-trans-DMB. The PBE, PBE0 and MP2 single-point energies on the BP86/def2-TZVP optimized structures (denoted by e.g. PBE//BP86) are also reported. Element color code: gray, C; red, O; blue, N; white, H; orange, P.

From the analysis of the highest-occupied and lowest-unoccupied molecular orbitals of the reactants (cf. Figure S30), we conclude that a normal Diels-Alder reaction occurs and not an inverse one.[16]

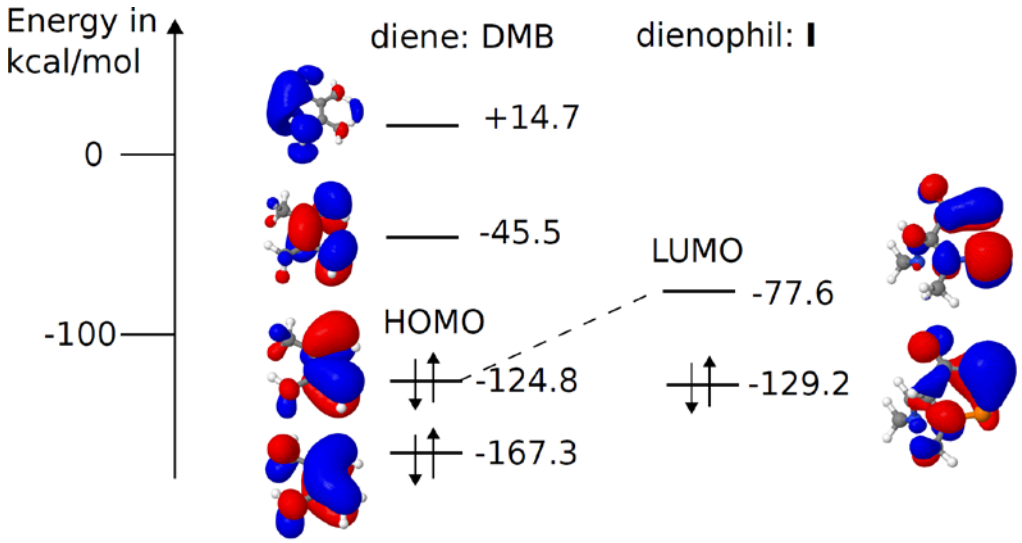

Figure S30. BP86/ def2-TZVP energies of the highest occupied and lowest unoccupied molecular orbitals of **I** and cis-DMB.

In Figures S31 and S32 possible BP86/def2-TZVP transition paths of structure **A** with tetramethylcyclopentadienone **M** (and tetraphenylcyclopentadienone **P**) are displayed. The potential energy surface of this system (**A** and **M**) is probably quite flat, because several minimum-energy structures have been found, which are very close on the Born-Oppenheimer potential energy surface. Several side reactions are possible, because the PCO fragment can migrate to different positions of the dienone 5-ring.

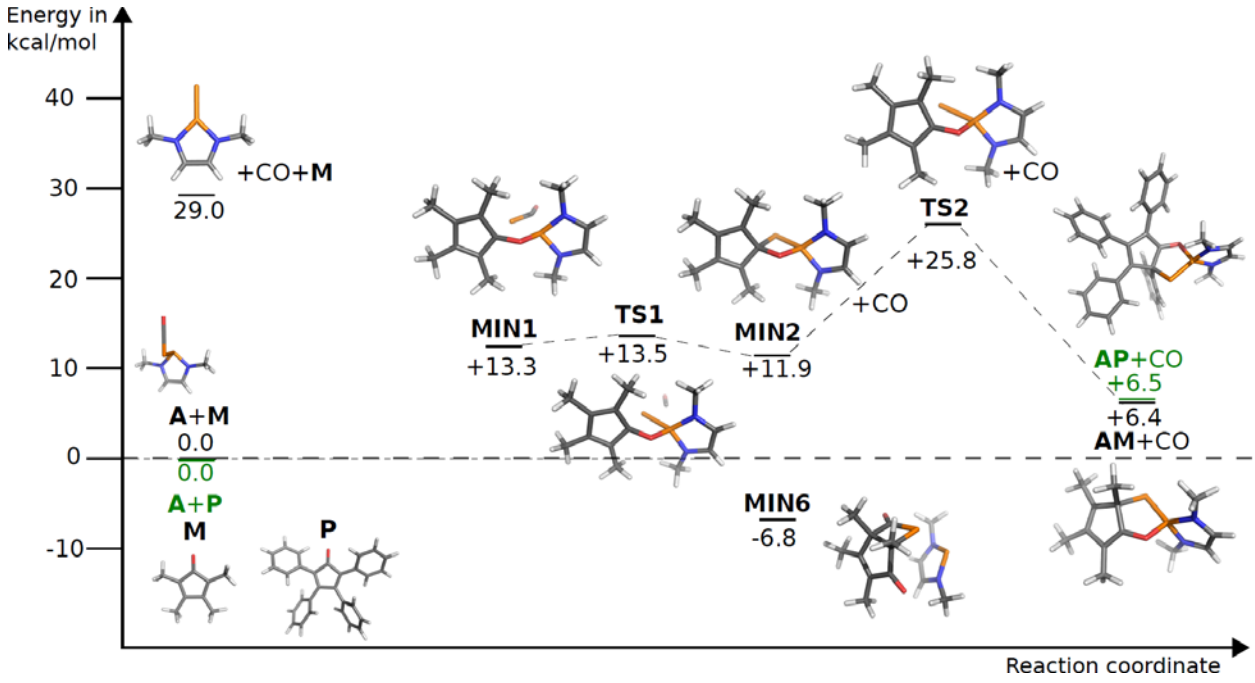

Figure S31. Part I: Possible intermediates of the transition path from structures **A** and **M** to **AM** and CO calculated with BP86/def2-TZVP. For comparison, we also report the energy difference between the educt and product for the reaction of **A** with **P** to **AP**. Element color code: gray, C; red, O; blue, N; white, H; orange, P.

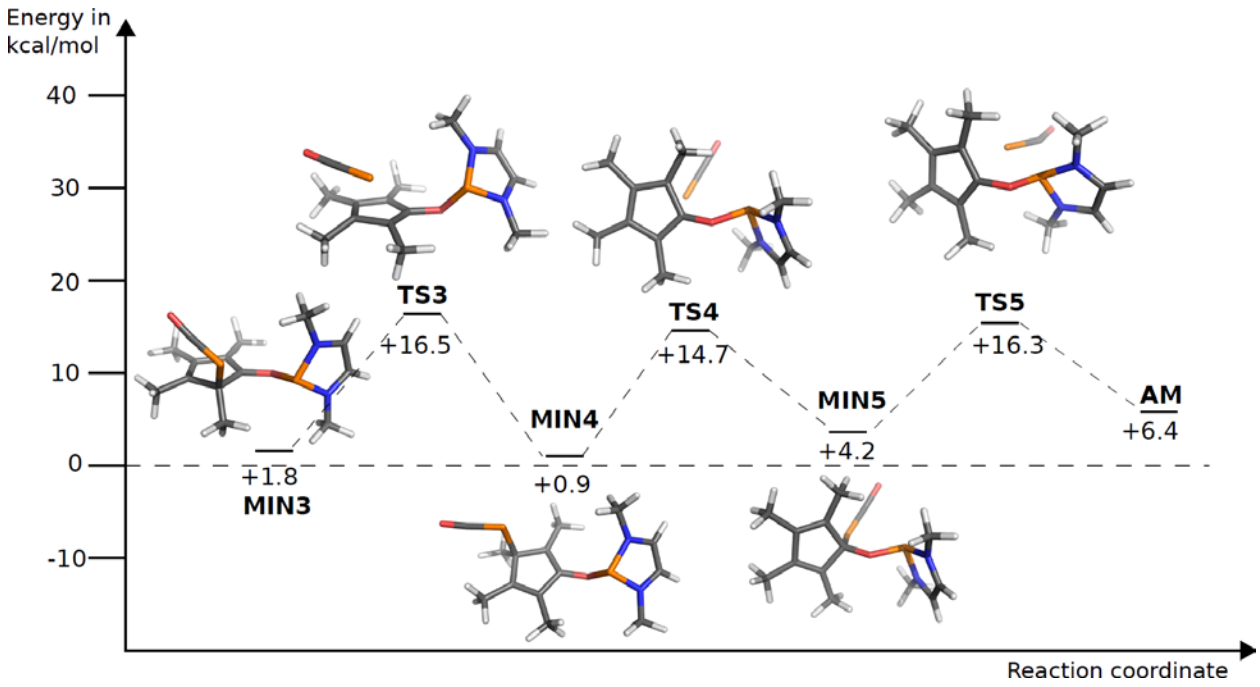

Figure S32. Part II: Possible intermediates of the transition path from structures **A** and **M** to **AM** and CO calculated with BP86/def2-TZVP. Element color code: gray, C; red, O; blue, N; white, H; orange, P.

Coordinates of all calculated Structures

The Cartesian coordinates of the BP86/def2-TZVP optimized structures of all above reported minima and TS structures are given in XYZ format in the following:

Figure S27:

A:

18

C 2.23350 -0.24855 -1.65258

N 1.67157 -0.16714 -0.31136

P 2.53348 -0.73719 1.06593

P 4.20559 1.05584 1.29872

C 5.38858 -0.08259 1.52634

O 6.24312 -0.87709 1.68938

C 0.67823 0.75463 0.01973

C 0.45095 0.79258 1.35609

N 1.27029 -0.09998 2.04714

C 1.35194 -0.10536 3.50123

H 2.90200 0.60149 -1.86597

H 2.81093 -1.17657 -1.75100

H 1.42171 -0.26766 -2.39287

H 1.91956 0.76034 3.88051

H 0.33962 -0.09124 3.92805

H 1.85368 -1.02229 3.83606

H -0.29112 1.38318 1.88483

H 0.15792 1.30829 -0.75609

A_{rot}:

18

C 2.15805 -0.22727 -1.67309

N 1.60762 -0.17689 -0.32551

C 0.49512 0.60106 -0.00567

C 0.27186 0.63563 1.33031

N 1.21311 -0.11600 2.03335

C 1.29630 -0.08833 3.48714

P 2.52320 -0.63333 1.05251

P 4.38501 0.97849 1.32539

C 3.54366 2.39421 1.11761

O 3.00892 3.43747 0.97682

H 2.68674 0.70473 -1.93035

H 2.86920 -1.05990 -1.74596

H 1.35014 -0.39933 -2.39760

H 1.72136 0.86092 3.85074

H 0.29512 -0.22710 3.91804

H 1.93717 -0.90967 3.83222

H -0.53244 1.14221 1.85486

H -0.09108 1.07373 -0.78771

TS^1 :

18

C -1.50908 -2.36555 0.46718

N -1.11717 -0.94814 0.40772

P -2.34770 0.21506 0.03638

P -0.99566 1.94359 -0.16203

C 0.17501 1.26696 0.98683

O 1.24980 1.53463 1.44658

C -0.51491 -0.43695 1.62153

C -1.52468 0.03872 2.50821

N -2.63693 0.38858 1.88068

C -3.70904 1.17991 2.45550

H -1.37430 0.27871 3.56345

H 0.36970 -0.94936 2.00209

H -0.60273 -2.98439 0.53621

H -2.16379 -2.60802 1.32607

H -2.03051 -2.62843 -0.46242

H -3.67409 2.20048 2.03953

H -4.68236 0.73513 2.20869

H -3.60393 1.23609 3.54668

TS^2:

18

C 3.09975 -0.73395 0.33635
N 1.77436 -0.15896 0.32076
P 0.05612 0.51175 -1.44320
P -1.03872 -1.25135 -1.17887
C -1.26838 -0.88473 0.65094
O -1.90158 -1.55021 1.44647
C 0.99382 -0.17555 1.32198
C -0.40025 0.37410 1.10874
N -0.30490 1.34660 0.04357
C -1.37831 2.34192 -0.02412
H 3.15476 -1.51635 -0.43575
H 3.83391 0.03957 0.06925
H 3.36694 -1.17012 1.31435
H -1.20543 2.99407 -0.89124
H -2.38519 1.89511 -0.12587
H -1.35475 2.96384 0.88302
H -0.83383 0.78301 2.03123
H 1.24471 -0.64477 2.28664

I:

18

P 1.53112 1.62871 1.49507
P 0.24281 0.35910 2.51097

N -1.02329 0.22503 1.41330

C -2.23027 -0.53876 1.71648

H -2.14382 -0.95003 2.73040

H -2.34366 -1.36312 0.99879

H -3.12023 0.11046 1.67553

C 0.33048 1.81757 0.07756

O 0.49036 2.58122 -0.85889

C -0.92506 0.88877 0.13701

C -0.82937 -0.03873 -1.06362

H -1.79521 1.55531 -0.01556

N -0.81803 -1.30263 -0.96443

H -0.73868 0.50533 -2.02453

C -0.67723 -2.08336 -2.18212

H 0.21563 -2.71970 -2.09243

H -1.54003 -2.75926 -2.27810

H -0.59293 -1.46981 -3.09859

Figure S28:

TS_{AG}:

18

C 2.34207 -0.28188 -1.56352

N 1.71341 -0.15118 -0.26288

C 0.71976 0.77288 0.02113

C 0.42684 0.84047 1.34861

N 1.18502 -0.03339 2.11223

C 1.24060 0.00558 3.56139

P 2.36098 -0.88847 1.16671

P 4.35803 -0.86390 1.62534

C 4.80505 -2.96138 1.82463

O 5.85594 -3.37493 2.11328

H 3.02889 0.55746 -1.76627

H 2.92555 -1.21031 -1.59131

H 1.57679 -0.32266 -2.35209

H 1.95511 0.76754 3.91869

H 0.24244 0.22739 3.96341

H 1.56565 -0.96949 3.94501

H -0.35747 1.43190 1.81228

H 0.21311 1.29720 -0.78393

G:

16

C 2.22081 -0.26617 -1.65612

N 1.76280 -0.02468 -0.29739

P 2.45026 -0.80094 1.06465

N 1.35549 0.04901 2.06958

C 1.33032 -0.10632 3.51513

C 0.73196 0.85049 0.02908

C 0.50188 0.89200 1.36541

H 2.60084 0.65989 -2.11273

H 3.03568 -1.00098 -1.61547

H 1.40811 -0.67133 -2.27738

H 1.54217 0.85010 4.01617

H 0.35364 -0.48459 3.85200

H 2.10635 -0.83148 3.79342

H -0.24082 1.48673 1.88765

H 0.21290 1.40536 -0.74612

P 3.86376 -2.09092 1.34811

TS_{AB}:

36

C -6.22601 1.49721 -0.33963

N -4.92421 1.03467 -0.78645

C -4.07929 0.68901 0.09754

C -2.68612 0.23503 -0.27193

C -1.65520 1.28314 0.24851

P -0.40877 0.67828 1.47944

P -0.96799 -1.41991 1.13818

P 0.73175 -0.70387 -0.24341

P 2.80092 0.24771 -0.98834

N 2.49920 1.93238 -1.01709

C 1.49749 2.54380 -1.88753

N -2.41504 -1.08804 0.27981

C -3.08939 -2.19806 -0.39214

O -1.69531 2.44252 -0.14319

N 3.92239 0.52214 0.28143

C 4.59497 -0.56566 0.97812

C 3.91252 1.82786 0.76318

C 3.10935 2.62820 0.01841

H -6.36066 1.46694 0.75888

H -6.37260 2.53072 -0.68841

H -7.00808 0.88830 -0.81772

H -4.30028 0.70363 1.18487

H -2.61203 0.23765 -1.37563

H -2.83862 -3.13634 0.12071

H -2.78616 -2.28276 -1.45107

H -4.18025 -2.05910 -0.35763

H 5.61105 -0.25761 1.26031

H 4.04190 -0.86610 1.88220

H 4.66808 -1.43476 0.31247

H 4.51291 2.10564 1.62402

H 2.92728 3.69046 0.14880

H 0.55893 2.73182 -1.34381

H 1.28587 1.86734 -2.72462

H 1.88498 3.48867 -2.29311

C 1.35337 -2.32662 -1.08478

O 1.14506 -3.47226 -1.13639

B:

34

C -4.68298 2.43549 -1.12847

N -3.43010 1.70758 -1.03111

C -3.30103 0.86420 -0.08825

C -2.01238 0.11616 0.13011

C -1.19507 0.79304 1.28295

P -0.21450 -0.36931 2.41998

P -1.01660 -2.13332 1.33826

P 0.99845 -1.34795 0.81941

P 1.89131 0.28512 -0.97923

N 1.25017 1.87027 -0.93249

C 0.17673 2.35231 -1.79895

N -2.24095 -1.28539 0.41936

C -2.77338 -2.04888 -0.71144

O -1.17536 2.00011 1.42450

N 3.17871 0.83371 0.01801

C 4.28156 -0.00938 0.46257

C 2.95962 2.10310 0.54537

C 1.86248 2.69215 0.01035

H -5.43137 2.14128 -0.36788

H -4.47832 3.51213 -1.02709

H -5.10943 2.28682 -2.13213

H -4.10446 0.65437 0.64672

H -1.38657 0.25197 -0.77816

H -2.89288 -3.09953 -0.41213

H -2.11063 -2.01029 -1.59894

H -3.75992 -1.65912 -1.00372

H 5.23223 0.53543 0.36160

H 4.15130 -0.32657 1.50764

H 4.33064 -0.90731 -0.16476

H 3.63068 2.51021 1.29581

H 1.44426 3.66449 0.25020

H -0.72812 2.59958 -1.22712

H -0.07751 1.57344 -2.52837

H 0.51743 3.24107 -2.35160

$TS_{BB'}$:

34

C -4.42603 2.54568 -0.36254

N -3.15942 1.86456 -0.56661

C -3.05242 0.66873 -0.14903

C -1.75931 -0.09696 -0.26793

C -1.08288 -0.20658 1.13927

P -0.17323 -1.82653 1.52249

P -0.80022 -2.66405 -0.43419

P 1.22233 -1.77305 -0.21930

P 1.87843 0.54555 -1.19497

N 1.68069 1.82121 -0.07535

C 0.57073 2.77339 -0.07505

N -1.96446 -1.41457 -0.83546

C -2.37340 -1.40826 -2.24148

O -1.13053 0.70430 1.94385

N 3.50706 0.39543 -0.66274

C 4.43483 -0.60307 -1.17799

C 3.76346 1.11260 0.50307

C 2.72858 1.91948 0.84038

H -5.19818 1.91891 0.12348

H -4.25351 3.43966 0.25573

H -4.80507 2.89968 -1.33305

H -3.88387 0.12561 0.34433

H -1.06817 0.51894 -0.88555

H -2.48006 -2.44561 -2.58841

H -1.64272 -0.89287 -2.89568

H -3.34594 -0.90585 -2.35312

H 5.44701 -0.17651 -1.23190

H 4.45137 -1.50539 -0.54813

H 4.13342 -0.89430 -2.19196

H 4.70919 0.99584 1.02385

H 2.65879 2.59434 1.68786

H -0.04932 2.66380 0.82402

H -0.06659 2.59991 -0.94972

H 0.96543 3.79897 -0.13316

B':

34

C 2.70574 -1.68322 -1.80027

N 1.97269 -0.87910 -0.82486

P 0.70592 -1.70245 0.04224

P 0.40939 -0.17108 1.60059

C 2.04732 0.67611 1.11169

O 2.52754 1.57177 1.78111

C 2.76044 0.14712 -0.16098

C 3.02680 1.30181 -1.10256

N 4.20765 1.69952 -1.35079

C 4.37104 2.83032 -2.24737

P 1.31154 -2.14679 2.15565

P 3.71888 -1.65096 2.70673

N 3.54968 -1.31399 4.37983

C 3.57941 -2.46848 5.16752

C 3.95670 -3.55678 4.45687

N 4.22231 -3.24079 3.11996

C 4.47849 -4.26160 2.11626

C 3.04624 -0.03936 4.87777

H 3.74194 -0.23268 0.19266

H 2.12534 1.76068 -1.55801

H 3.35835 -2.41432 6.22912

H 4.11363 -4.56641 4.82389

H 3.11625 -1.04092 -2.59367

H 3.54628 -2.24367 -1.34571

H 2.01746 -2.40426 -2.26287

H 5.04179 2.54243 -3.07076

H 3.42046 3.21215 -2.66721

H 4.87221 3.64402 -1.70150

H 4.94328 -3.80120 1.23477

H 5.17687 -5.00926 2.51689

H 3.55231 -4.77080 1.79920

H 1.95234 -0.05967 5.01109

H 3.52190 0.19590 5.84034

H 3.28939 0.75542 4.16173

TS_{BC}:

34

C 0.50853 3.36334 2.13751

N 0.87913 2.25635 1.25949

C 1.99059 1.43952 1.72905

C 1.45429 0.37458 2.66092

N 1.77827 0.33428 3.88989

C 1.19908 -0.71590 4.70942

P 0.87772 2.58019 -0.45373

P 3.04350 2.45320 -0.98066

P 1.74989 0.63446 -1.06170

C 2.70899 0.76712 0.54249

O 3.74512 0.03989 0.77351

P 5.39571 1.50525 0.26814

N 6.49470 2.62670 -0.50109

C 6.33958 4.06426 -0.32327

N 6.25534 0.27233 -0.58574

C 6.03598 -1.17311 -0.45228

C 7.23050 0.72627 -1.44742

C 7.36817 2.08282 -1.40247

H 2.73575 2.03581 2.28953

H 0.74436 -0.34331 2.20094

H 7.78084 0.02734 -2.07056

H 8.04669 2.69591 -1.99025

H 0.22942 2.97369 3.12777

H 1.32816 4.09611 2.27603

H -0.36078 3.88666 1.71598

H 0.66510 -0.26010 5.55718

H 0.50433 -1.38100 4.16041

H 2.01093 -1.32382 5.13731

H 5.97520 4.53464 -1.24862

H 5.60385 4.24645 0.47042

H 7.29322 4.52418 -0.02786

H 6.10686 -1.64137 -1.44323

H 6.79924 -1.60877 0.20814

H 5.04114 -1.34410 -0.03259

C:

34

P 0.51122 2.43626 0.75966

P 2.69908 0.34827 -0.82697

P 2.32760 -0.64422 -2.76388

P 1.32472 1.31377 -2.28946

O 0.06169 0.82375 0.23809

N 1.08295 -1.71406 -2.20220

N 0.12304 2.29614 2.41934

N -0.91477 3.35868 0.55788

N -0.83914 -2.75484 0.30274

C 0.19627 -2.07217 0.02240

C 0.22348 -1.13511 -1.16378

C -1.76885 3.32052 1.67003

C 0.77752 0.24877 -0.80692

C -1.17694 2.71940 2.72596

H -0.81318 -1.02358 -1.53104

H 1.14928 -2.16183 0.58424

H -2.76538 3.74787 1.61913

H -1.58908 2.55933 3.71761

C 0.41147 -2.57507 -3.17358

H -0.07287 -3.41191 -2.64927

H -0.36154 -2.04278 -3.76026

H 1.15464 -2.98969 -3.86798

C -0.76521 -3.68152 1.41838

H -1.00276 -4.69523 1.06103

H 0.22125 -3.69948 1.92124

H -1.53942 -3.41814 2.15487

C 0.96385 1.60235 3.38126

H 0.60761 0.57818 3.57885

H 1.98753 1.53991 2.98922

H 0.99559 2.15668 4.33139

C -1.28277 4.02508 -0.68125

H -2.10966 3.50849 -1.19493

H -1.58247 5.06610 -0.48544

H -0.41647 4.03627 -1.35592

$TS_{B'C}$:

34

C 0.50853 3.36334 2.13751

N 0.87913 2.25635 1.25949

C 1.99059 1.43952 1.72905

C 1.45429 0.37458 2.66092

N 1.77827 0.33428 3.88989

C 1.19908 -0.71590 4.70942

P 0.87772 2.58019 -0.45373

P 3.04350 2.45320 -0.98066

P 1.74989 0.63446 -1.06170

C 2.70899 0.76712 0.54249

O 3.74512 0.03989 0.77351

P 5.39571 1.50525 0.26814

N 6.49470 2.62670 -0.50109

C 6.33958 4.06426 -0.32327

N 6.25534 0.27233 -0.58574

C 6.03598 -1.17311 -0.45228

C 7.23050 0.72627 -1.44742

C 7.36817 2.08282 -1.40247

H 2.73575 2.03581 2.28953

H 0.74436 -0.34331 2.20094

H 7.78084 0.02734 -2.07056

H 8.04669 2.69591 -1.99025

H 0.22942 2.97369 3.12777

H 1.32816 4.09611 2.27603

H -0.36078 3.88666 1.71598

H 0.66510 -0.26010 5.55718

H 0.50433 -1.38100 4.16041

H 2.01093 -1.32382 5.13731

H 5.97520 4.53464 -1.24862

H 5.60385 4.24645 0.47042

H 7.29322 4.52418 -0.02786

H 6.10686 -1.64137 -1.44323

H 6.79924 -1.60877 0.20814

H 5.04114 -1.34410 -0.03259

Figure S29:

TS Diels Alder:

34

C -2.00832 -0.64419 1.61756

N -0.84552 0.20002 1.36905

P -0.63957 0.97577 -0.12653

C 0.19207 -0.90487 -1.58756

C 0.97301 -0.37410 -2.60138

C 0.35910 -0.19110 -3.96668

C 0.15925 0.30779 2.39391

C 1.40006 1.11202 1.89473

O 2.40983 1.17991 2.58086

C -0.29222 0.97610 3.68196

N -1.45778 1.44545 3.85499

C -1.74612 2.10382 5.11752

P 1.23225 1.91773 0.22783

C 2.84743 0.13338 -1.09891

C 2.29081 0.15738 -2.35538

C 2.99211 0.91872 -3.45566

H -2.68427 -0.58033 0.75400

H -2.54642 -0.29704 2.51133

H -1.71700 -1.70093 1.75313

H 0.55975 -0.69095 2.66343

H 0.51159 1.03961 4.44253

H -2.06094 3.13843 4.91434

H -2.59810 1.60224 5.60047

H -0.88981 2.11958 5.81854

H -0.77961 -1.33356 -1.83400

H 0.64117 -1.26730 -0.66436

H 3.81221 0.60383 -0.90968

H 2.49178 -0.53194 -0.31597

H 3.13713 0.29551 -4.35132

H 2.41570 1.80223 -3.77563

H 3.97879 1.26365 -3.12411

H -0.64487 -0.62991 -4.01331

H 0.27830 0.87438 -4.23763

H 0.97401 -0.66394 -4.74792

trans-DMB:

16

C -0.26129 -0.00000 -0.10001

C 0.05805 0.00000 1.21120

C -1.05267 0.00000 2.23623

C 1.45367 0.00000 1.70143

C 2.61464 0.00000 0.72289

C 1.72453 -0.00000 3.02381

H -1.30482 -0.00000 -0.41658

H 0.48113 -0.00000 -0.89603

H 2.75471 -0.00000 3.38421

H 0.94650 -0.00000 3.78505

H -2.03299 -0.00000 1.74434

H -0.99742 -0.88493 2.88838

H -0.99742 0.88493 2.88838

H 2.30137 0.00000 -0.32547

H 3.24688 0.88590 0.87568

H 3.24688 -0.88590 0.87568

Figures S31, S32:

M:

22

C 3.49518 3.83475 2.90252

C 3.22882 5.15274 3.03748

C 4.01963 5.62833 4.23144

C 4.77224 4.44041 4.78263

C 4.46004 3.38793 3.99383

C 4.93703 1.97811 4.09861

H 5.61888 1.84022 4.94639

H 5.46686 1.66550 3.18387

H 4.09463 1.27812 4.22301

C 2.96241 2.89652 1.87269

H 2.38569 2.07857 2.33554

H 3.77647 2.41678 1.30532

H 2.30611 3.41025 1.15944

C 2.35406 6.06777 2.24507

H 1.28505 5.83247 2.37236

H 2.57238 6.02434 1.16739

H 2.50604 7.10195 2.58400

C 5.66101 4.54955 5.97315

H 6.48438 5.25765 5.78878

H 6.09784 3.58185 6.25263

H 5.10960 4.94250 6.84161

O 4.04981 6.76958 4.66877

P:

50

C 3.47419 4.03673 2.93637

C 3.41698 5.49134 3.35615

C 4.27791 5.62684 4.40703

C 4.93628 4.29069 4.70707

C 4.46194 3.34026 3.84948

C 4.68783 1.89362 3.80104

C 4.74699 1.22158 2.56220

C 4.94224 -0.15878 2.50849

C 5.07201 -0.90143 3.68462

C 5.00156 -0.25059 4.92088

C 4.81118 1.12805 4.97963

H 4.73958 1.62256 5.94846

H 5.08665 -0.82253 5.84632

H 5.21951 -1.98141 3.63992

H 4.99003 -0.65747 1.53903

H 4.63797 1.79038 1.64019

C 5.93125 4.10357 5.77607

C 7.16316 3.47961 5.49825

C 5.68046 4.53563 7.09274

H 4.73246 5.01969 7.32903

H 7.37252 3.14741 4.48087

C 8.11067 3.29438 6.50343

C 6.62257 4.32984 8.10115

H 6.40373 4.65818 9.11824

H 9.06359 2.81911 6.26617

C 7.84227 3.71370 7.81046

H 8.58248 3.56350 8.59760

C 4.56534 6.85656 5.16412

C 5.88724 7.29682 5.36963

H 6.71681 6.71603 4.96562

C 6.14372 8.47979 6.06390

H 7.17379 8.81282 6.19897

C 5.08932 9.23096 6.58936

H 5.29214 10.14999 7.14086

C 3.77260 8.79592 6.40742

H 2.94379 9.37268 6.82048

C 3.51178 7.62568 5.69647

H 2.48406 7.29099 5.55142

C 2.64009 6.48961 2.61735

C 3.15336 7.77772 2.35729

H 4.14929 8.03953 2.71481

H 2.83499 9.69766 1.43864

C 2.41376 8.71000 1.63335

C 1.14369 8.38089 1.14805

H 0.56631 9.11165 0.57983

C 0.62534 7.10617 1.38840

H -0.36179 6.83665 1.00963

C 1.36418 6.16752 2.10924

H 0.95557 5.17346 2.28369

O 2.84233 3.52133 2.02911

AM:

38

N 3.47601 3.80402 2.92475

P 3.36774 5.47197 3.18823

N 4.49412 5.34040 4.45069

C 4.79984 4.01252 4.76892

H 5.44566 3.78716 5.61134

C 4.22377 3.14146 3.91043

H 4.29849 2.05931 3.90716

C 2.80829 3.09822 1.84011

C 5.02990 6.47968 5.17765

O 1.93413 5.89630 3.96703

C 1.18562 6.64920 3.06031

P 3.42783 6.76236 1.55813

C 1.88518 7.70893 2.26940

C 0.85016 8.05188 1.21950

C -0.28697 7.33607 1.47143

C -0.07215 6.42046 2.61192

C -1.03937 5.38716 3.09416

C -1.58904 7.39249 0.73089

C 1.08152 9.10902 0.18760

C 2.30621 8.94288 3.08762

H -0.59453 4.77857 3.89237

H -1.95862 5.84463 3.49430

H -1.35171 4.71252 2.28067

H -1.86319 6.40735 0.31933

H -2.41526 7.69636 1.39423

H -1.55462 8.10214 -0.10563

H 0.22231 9.21589 -0.48778

H 1.26432 10.09723 0.64366

H 1.96351 8.88094 -0.43283

H 2.90660 9.62991 2.47509

H 1.41913 9.48467 3.45385

H 2.91637 8.64675 3.95152

H 6.08987 6.30913 5.41307

H 4.96065 7.36943 4.53673

H 4.47820 6.66906 6.11183

H 1.96243 2.49880 2.21081

H 2.43682 3.84156 1.12255

H 3.51867 2.43653 1.32320

AP:

66

C 3.99880 3.85915 2.36578

C 3.76942 5.19557 2.70766

C 4.02946 5.65976 4.00315

C 4.53047 4.75031 4.94990

C 4.75037 3.41357 4.61387

C 4.48532 2.96133 3.31776

C 3.83814 7.12260 4.41276

C 5.16055 7.87279 4.49566

C 5.30277 8.38651 5.76816

C 4.11185 8.07152 6.58377

C 3.28922 7.32405 5.78924

P 2.50271 8.09632 3.36450

P 1.04142 7.57246 4.75871

N -0.21879 6.45540 4.60133

C -1.43891 6.94931 5.07538

C -1.34951 8.24515 5.44968

N -0.05553 8.75377 5.25111

C 0.30479 10.12970 5.57471

C 6.45808 9.15858 6.27329

C 6.95170 10.26937 5.56457

C 8.04380 10.99428 6.04170

C 8.66732 10.62485 7.23702

C 8.18433 9.52691 7.95420

C 7.08762 8.80531 7.48124

C 3.77053 8.58689 7.91884

C 4.06100 9.91418 8.29394

C 3.69397 10.39996 9.54945

C 3.03214 9.57380 10.46232

C 2.73728 8.25486 10.10486

C 3.10246 7.76693 8.84988

C 6.15740 7.84311 3.41352

C 5.78121 8.06538 2.07390

C 6.72046 8.02432 1.04290

C 8.06213 7.75389 1.32246

C 8.45220 7.52030 2.64464

C 7.51406 7.56156 3.67490

O 1.97116 6.96878 6.03385

C -0.04063 5.09636 4.10881

H 8.40879 11.85442 5.47780

H 6.46632 10.56230 4.63276

H -2.13267 8.88402 5.84292

H 6.71503 7.95081 8.04832

H 4.74785 5.09897 5.96110

H 4.57085 10.57174 7.59011

H 7.82738 7.35978 4.69911

H 3.36762 5.88763 1.96622

H 4.73996 8.29716 1.84053

H 5.13150 2.72281 5.36798

H 8.79697 7.72001 0.51684

H 4.65773 1.91701 3.05296

H 2.75111 9.95387 11.44559

H 2.22522 7.59832 10.81043

H 2.87760 6.73429 8.58157

H -2.31562 6.31023 5.09374

H 9.52196 11.19149 7.60962

H 8.66252 9.23113 8.88950

H 3.92759 11.43224 9.81539

H 6.40100 8.20891 0.01589

H 9.49468 7.29418 2.87532

H 3.79393 3.52152 1.34842

H 0.93199 5.02454 3.60447

H -0.06334 4.36416 4.93014

H -0.82748 4.85114 3.38137

H 1.31434 10.32383 5.19114

H -0.39557 10.82495 5.09048

H 0.29513 10.29910 6.66148

MIN1:

40

C -1.40096 -0.60025 -1.86057

C -0.11808 -0.15184 -1.33708

C 0.42154 0.89611 -2.19311

C -0.56789 1.16041 -3.14009

C -1.68757 0.24081 -2.93569

O 0.69396 -0.96031 -0.52244

P 0.64646 -0.54235 1.10403

P -0.76593 1.10479 0.66412

C 1.76388 1.54230 -2.03032

C -0.54595 2.22437 -4.19961

C -2.94136 0.25661 -3.76299

C -2.21391 -1.73232 -1.30935

N 0.34442 -1.89404 2.09896

C -0.94214 -2.57370 2.18632

N 2.22097 -0.41588 1.74654

C 3.15435 0.65511 1.41859

C 1.46234 -2.26867 2.86538

C 2.51843 -1.43541 2.66811

H 2.62233 1.44062 0.84921

H 3.55853 1.11327 2.34451

H 3.99693 0.28391 0.79844

H 3.50576 -1.47557 3.14173

H 1.40334 -3.13499 3.53366

H -0.90968 -3.57101 1.70021

H -1.71156 -1.96253 1.67774

H -1.24318 -2.69551 3.24688

H 2.55054 0.79452 -1.79317

H 2.07561 2.06444 -2.95677

H 1.78068 2.30508 -1.21625

H 0.43892 2.72868 -4.26073

H -1.30643 3.01669 -4.01547

H -0.76936 1.81083 -5.20761

H -3.53346 1.18711 -3.61018

H -2.72087 0.20708 -4.85200

H -3.60823 -0.59464 -3.52128

H -2.82838 -1.43807 -0.42634

H -2.92042 -2.12949 -2.06583

H -1.56610 -2.57664 -0.99047

C -0.82538 1.56489 2.38007

O -1.19814 2.22158 3.28384

MIN2:

38

C 1.01146 7.06763 3.37404

C 1.64152 8.02272 2.39028

C 0.79840 8.14204 1.33162

C -0.35228 7.21533 1.50602

C -0.21146 6.53124 2.67142

O 1.94195 6.00285 3.86189

P 1.89414 6.36673 5.46577

N 1.60919 4.97923 6.40191

C 2.74482 4.53059 7.08717

C 3.78995 5.37268 6.92940

N 3.45639 6.46758 6.12288

P 0.58458 7.92523 5.09821

C 4.37261 7.57587 5.89827

H 3.80709 8.41800 5.47993

H 4.81795 7.89578 6.85149

H 5.17671 7.30290 5.19773

H 4.78566 5.28573 7.35134

H 2.70979 3.61219 7.66378

C 0.32148 4.31002 6.50948

H 0.29945 3.37548 5.92825

H -0.45630 4.98411 6.12922

H 0.10098 4.08460 7.56299

C 2.94773 8.69846 2.62877

H 3.74760 7.96099 2.80468

H 3.24504 9.31428 1.77028

H 2.90703 9.35018 3.51689

C 0.93640 9.04134 0.14290

H 1.86068 9.63127 0.18053

H 0.09300 9.74808 0.07212

H 0.94237 8.46807 -0.79839

C -1.46090 7.10935 0.50602

H -1.98935 8.06973 0.38740

H -1.07936 6.83765 -0.49171

H -2.20313 6.35565 0.79622

C -1.07713 5.46050 3.24015

H -1.53450 5.77683 4.19206

H -1.88608 5.18710 2.55044

H -0.49323 4.54900 3.44822

MIN3:

40

C -2.59431 0.76701 -0.26561

C -2.36784 1.51432 0.85637

C -0.93044 1.57508 1.14558

C -0.27046 0.85681 0.18913

C -1.25148 0.26497 -0.78888

C -3.38888 2.20121 1.71053

C -0.30586 2.29736 2.29604

O 1.08243 0.72722 0.13721

C -0.98363 0.62094 -2.25873

P -1.19491 -1.66906 -0.61523

P 1.96500 -0.55177 -0.68262

N 2.75416 -1.39838 0.57765

C 2.17101 -2.51517 1.30609

C -3.87593 0.56440 -1.01133

N 3.42073 0.31451 -0.93540

C 3.57584 1.33372 -1.95977

C 4.35707 0.14285 0.09321

C 3.97990 -0.82850 0.95322

H 3.38509 2.34772 -1.57120

H 2.86798 1.14046 -2.77678

H 4.59310 1.29962 -2.37795

H 5.25902 0.74628 0.12418

H 4.50709 -1.18083 1.83437

H 1.92779 -2.23837 2.34479

H 1.24130 -2.82204 0.81113

H 2.86244 -3.37167 1.31922

H -0.65602 1.90104 3.26341

H -0.55146 3.37183 2.28777

H 0.78623 2.19764 2.26392

H -3.24795 3.29426 1.69883

H -4.41236 1.99353 1.37495

H -3.30787 1.88571 2.76274

H -3.95582 1.24484 -1.87728

H -3.96881 -0.45997 -1.40308

H -4.74642 0.75459 -0.36978

H -0.96759 1.71580 -2.37038

H -1.76719 0.21268 -2.91118

H -0.01686 0.22413 -2.59854

C -2.46596 -1.79688 0.49382

O -3.29810 -2.11592 1.25457

MIN4:

40

C 0.03464 7.22443 1.06736

C 0.49446 6.06019 1.92456

C 1.72852 6.57728 2.63678

C 1.93594 7.85239 2.20430

C 0.89766 8.26335 1.23810

C -0.57221 5.48732 2.85976

C 2.48986 5.82219 3.67339

O 2.92181 8.69592 2.64182

P 4.35436 8.96473 1.65456

N 5.63125 8.11502 2.41395

C 6.00041 6.74643 2.08914

C 0.86882 9.61824 0.60733

C -1.19573 7.16648 0.22378

N 4.89625 10.37876 2.45216

C 5.83119 10.12105 3.46317

C 6.24950 8.83573 3.44694

C 4.24626 11.67195 2.31325

H 6.14646 10.91452 4.13385

H 6.96536 8.35904 4.10945

H 3.32673 6.42807 4.04485

H 1.85662 5.56431 4.53931

H 2.89252 4.87125 3.28565

H -0.18449 4.63636 3.43506

H -0.88808 6.26913 3.56830

H -1.46111 5.14734 2.31070

H -1.16208 6.32114 -0.48236

H -2.10515 7.03660 0.83444

H -1.32445 8.08367 -0.36525

H 1.78132 9.79817 0.01607

H 0.00669 9.74131 -0.05994

H 0.82421 10.40939 1.37234

H 4.99456 12.47801 2.34676

H 3.73865 11.72230 1.34124

H 3.49828 11.84667 3.10341

H 5.71631 6.04052 2.88641

H 5.48564 6.44348 1.16800

H 7.08550 6.66965 1.91968

P 1.29221 4.75628 0.70553

C -0.09452 3.88792 0.32835

O -1.00612 3.21079 0.03382

MIN5:

40

C -2.73681 1.25327 -1.00236

C -2.03943 0.11695 -0.73965

C -0.59192 0.50936 -0.48952

C -0.58431 2.01951 -0.56315

C -1.83941 2.42845 -0.89238

C -2.49756 -1.29779 -0.64037

O -0.06745 -0.05068 0.68044

P 1.44886 -0.90187 0.75615

N 1.63471 -0.82222 2.46057

C 1.98534 0.39668 3.17012

P 0.16456 -0.14758 -2.22766

C 1.76849 0.35292 -2.15251

O 2.90055 0.63710 -2.27447

C 0.63006 2.83389 -0.27601

C -2.30873 3.82877 -1.13465

C -4.18857 1.37237 -1.34737

N 1.08072 -2.56732 0.93565

C 0.86052 -2.95634 2.26334

C 1.17664 -1.96297 3.12557

C 0.96912 -3.50612 -0.17042

H 1.12553 -1.98371 4.21004

H 0.48673 -3.94839 2.49807

H -2.26143 -1.71154 0.35347

H -3.57997 -1.38693 -0.79990

H -1.99657 -1.94570 -1.38053

H -4.68576 0.39470 -1.36762

H -4.72328 2.00708 -0.62255

H -4.32730 1.83928 -2.33605

H -2.64167 3.96431 -2.17702

H -3.16851 4.08403 -0.49467

H -1.51756 4.56457 -0.94348

H 0.38271 3.89755 -0.16327

H 1.11368 2.50035 0.65617

H 1.38755 2.75598 -1.07275

H 2.62314 0.16118 4.03511

H 2.55440 1.05717 2.50275

H 1.09454 0.94227 3.52211

H -0.05044 -3.91679 -0.24736

H 1.19542 -2.98522 -1.10916

H 1.67744 -4.34056 -0.04870

Min6:

40

C -1.37405 -1.13895 -0.98229

C -2.22702 -0.56051 0.11744

C -2.20866 0.80235 0.11629

C -1.38525 1.29202 -1.00231

C -0.86167 0.09884 -1.78625

C -2.88403 -1.45217 1.11576

C -2.86662 1.74495 1.07469

O -1.16997 2.47599 -1.27875

C -1.15371 0.21814 -3.27775

P 0.96634 -0.36191 -1.38063

P 2.60423 1.08762 0.10933

N 2.60427 0.08738 1.49613

C 3.17519 -1.25850 1.50581

C -1.99812 -2.29713 -1.75976

N 1.71657 2.25094 0.98174

C 1.34005 3.55202 0.43264

C 1.22189 1.76234 2.18839

C 1.72486 0.53471 2.47640

H 0.32157 3.53021 0.01687

H 2.03895 3.81620 -0.37140

H 1.41697 4.31644 1.21835

H 0.55253 2.36469 2.79464

H 1.53283 -0.06989 3.35735

H 2.41557 -2.00884 1.23281

H 4.00534 -1.30263 0.78895

H 3.57570 -1.47870 2.50496

H -2.28547 1.84263 2.00676

H -3.87770 1.41746 1.35362

H -2.93186 2.74357 0.62157

H -3.34687 -0.88951 1.93584

H -3.66043 -2.07510 0.64267

H -2.13865 -2.14927 1.53350

H -2.95494 -2.00446 -2.21679

H -1.32286 -2.63838 -2.55637

H -2.17818 -3.14968 -1.09095

H -2.23824 0.23785 -3.47147

H -0.71155 -0.61060 -3.84579

H -0.73439 1.16036 -3.65642

C 0.02406 -1.54158 -0.36532

O 0.25132 -2.41092 0.46577

TS1:

40

C -0.16069 6.46429 2.59167

C 1.06281 6.98131 3.24972

C 1.68012 7.94971 2.31220

C 0.78630 8.13886 1.29240

C -0.35369 7.21827 1.46514

O 1.94318 6.01248 3.90714

P 1.88496 6.38443 5.50137

P 0.55370 7.95911 5.06772

C 3.00239 8.60562 2.53173

C 0.87907 9.12012 0.16504

C -1.52131 7.18077 0.52836

C -1.01111 5.36842 3.14143

N 1.58248 5.01289 6.43889

C 0.29466 4.33786 6.53008

N 3.43524 6.50312 6.15993

C 4.35577 7.60674 5.91962

C 2.69414 4.61084 7.19370

C 3.73884 5.45118 7.03662

H 3.81338 8.42123 5.42458

H 4.75000 7.98428 6.87400

H 5.19361 7.29687 5.27724

H 4.71644 5.39701 7.50341

H 2.63711 3.72393 7.81556

H 0.31168 3.37037 6.00659

H -0.47365 4.97328 6.07353

H 0.02707 4.17610 7.58412

H 3.79111 7.86111 2.72641

H 3.30838 9.18982 1.65408

H 2.98351 9.29287 3.39522

H 1.82243 9.68058 0.18707

H 0.05783 9.85580 0.19788

H 0.81029 8.61956 -0.81451

H -2.07106 8.13678 0.52554

H -1.20058 7.00243 -0.51107

H -2.23503 6.39163 0.79666

H -1.51551 5.66717 4.07676

H -1.79179 5.07288 2.42826

H -0.41173 4.47143 3.36739

C 0.46853 8.45029 7.03042

O -0.05693 9.24380 7.69685

TS2:

38

C 0.82336 -0.10638 -0.55473

C 1.71721 -1.20847 -0.57323

C 2.96828 -0.70428 -0.17930

C 2.89898 0.70854 0.01915

C 1.59505 1.14371 -0.28413

O -0.47367 -0.13647 -1.14854

P -1.44861 0.08550 0.19185

N -2.73866 1.11974 -0.18593

C -3.95159 0.44570 -0.37436

C -3.84458 -0.87150 -0.08875

N -2.54842 -1.21036 0.31212

P 0.15488 0.55427 1.44176

C -2.18981 -2.54781 0.75966

H -1.19272 -2.50906 1.21743

H -2.90524 -2.90071 1.51670

H -2.16866 -3.26209 -0.07775

H -4.62361 -1.62607 -0.12991

H -4.83462 0.98857 -0.69484

C -2.63102 2.56729 -0.29980

H -2.60081 2.89309 -1.35130

H -1.71108 2.89100 0.20401

H -3.48590 3.04494 0.19955

C 1.32578 -2.63471 -0.78883

H 0.48358 -2.71269 -1.49119

H 2.15836 -3.22229 -1.20123

H 1.01855 -3.13082 0.15028

C 4.19492 -1.52585 0.07647

H 4.14510 -2.50230 -0.42343

H 4.33238 -1.71735 1.15459

H 5.10381 -1.01222 -0.27125

C 4.04284 1.58756 0.43235

H 4.42500 1.33516 1.43548

H 4.89731 1.50464 -0.26033

H 3.74527 2.64456 0.45557

C 1.20730 2.52288 -0.72806

H 1.31900 3.26849 0.07216

H 1.84182 2.83966 -1.57228

H 0.16522 2.54814 -1.06795

TS3:

40

C -4.64273 5.21929 -1.03697

C -5.22382 5.31835 0.26255

C -4.57176 6.34516 0.96749

C -3.57155 6.91890 0.13372

C -3.54369 6.26513 -1.11034

C -6.35584 4.47667 0.76434

C -4.83525 6.77468 2.37529

O -2.75583 7.94017 0.54931

C -3.02010 6.84525 -2.39387

P -2.48615 4.26767 -0.95396

P -1.01037 7.72648 0.52879

N -0.56431 7.35355 2.13867

C -0.50143 5.99994 2.66751

C -5.37422 4.71144 -2.24430

N -0.59512 9.35480 0.84625

C -0.68731 10.41571 -0.14302

C -0.39722 9.62030 2.20839

C -0.38247 8.48711 2.94486

H -1.63823 10.96840 -0.07194

H -0.61620 9.98314 -1.14952

H 0.14585 11.12388 -0.01952

H -0.26091 10.64030 2.55451

H -0.24594 8.39167 4.01769

H -0.60478 5.28418 1.84103

H 0.46485 5.82097 3.16412

H -1.31092 5.80440 3.38926

H -4.28119 7.69284 2.60685

H -4.52707 5.99958 3.09608

H -5.90581 6.96142 2.54957

H -6.73038 4.85327 1.72482

H -7.20213 4.46263 0.05916

H -6.05305 3.42677 0.91420

H -6.18135 5.41532 -2.51330

H -4.71529 4.60077 -3.11375

H -5.84446 3.73745 -2.04795

H -3.77821 7.49821 -2.85859

H -2.74889 6.07076 -3.12466

H -2.12424 7.45111 -2.20685

C -3.55878 3.04894 -0.53012

O -4.25866 2.14622 -0.23159

TS4:

40

C -2.85869 1.31059 -0.34518

C -1.49039 1.65960 -0.26597

C -0.75381 0.47009 -0.46596

C -1.74459 -0.67713 -0.59896

C -3.01924 -0.09043 -0.55984

C -0.89316 3.01827 -0.07405

O 0.52332 0.43869 -0.85261

P 1.84146 -0.54043 -0.03523

N 2.98104 -0.32200 -1.29671

C 2.87790 -0.99603 -2.58223

P -1.06030 -0.55264 1.71431

C -0.50179 -2.12358 1.80408

O -0.09415 -3.22402 1.92685

C -1.38963 -2.00672 -1.18601

C -4.32796 -0.81936 -0.60589

C -3.99077 2.27428 -0.18496

N 2.73185 0.58889 0.88822

C 3.71711 1.26362 0.15962

C 3.85659 0.74195 -1.08163

C 2.47555 0.88972 2.29193

H 4.55585 1.04607 -1.85469

H 4.26850 2.08651 0.60364

H 0.17747 2.99791 -0.31854

H -1.36860 3.77023 -0.72305

H -0.99231 3.38084 0.96300

H -3.68259 3.30639 -0.39963

H -4.83585 2.02036 -0.84092

H -4.37639 2.25810 0.84895

H -4.77289 -0.93734 0.39772

H -5.06832 -0.28699 -1.22238

H -4.21474 -1.82567 -1.03067

H -2.05247 -2.80385 -0.82251

H -1.48306 -1.97094 -2.28468

H -0.35688 -2.29630 -0.95090

H 3.88020 -1.24069 -2.96276

H 2.32381 -1.93544 -2.45777

H 2.35090 -0.37847 -3.32691

H 2.22712 1.95389 2.42547

H 1.62084 0.29347 2.63647

H 3.35508 0.64760 2.90736

TS5:

40

C -0.10385 7.30396 1.40069

C 0.26610 6.27914 2.31972

C 1.35271 6.79059 3.04523

C 1.68844 8.12228 2.59693

C 0.75990 8.41496 1.55996

C -0.37801 4.93586 2.46899

O 2.10265 6.07921 4.01132

P 3.42641 5.34213 3.37616

N 4.61621 5.35634 4.56860

C 5.26259 6.55731 5.08571

P 3.38539 6.46298 1.50847

C 4.83498 5.58442 1.02332

O 5.77085 5.32792 0.36457

C 2.57797 9.10766 3.29012

C 0.67601 9.73228 0.84363

C -1.23952 7.18468 0.42772

N 3.39643 3.65578 3.39735

C 4.24243 3.11245 4.37838

C 4.93228 4.06926 5.03327

C 2.66237 2.82114 2.45154

H 5.66306 3.94406 5.82513

H 4.28758 2.03822 4.52223

H 0.06971 4.37015 3.29832

H -1.45511 5.02569 2.68709

H -0.29801 4.31922 1.55674

H -1.19672 6.24156 -0.14125

H -2.22027 7.20167 0.93409

H -1.24017 8.00759 -0.30024

H 0.18633 9.63350 -0.13584

H 0.10262 10.48632 1.41217

H 1.67370 10.16107 0.66461

H 3.19502 9.68087 2.58049

H 1.99173 9.83980 3.87218

H 3.25767 8.61279 3.99803

H 6.34613 6.39253 5.16652

H 5.09544 7.38753 4.38893

H 4.86084 6.83623 6.07096

H 1.86531 2.25906 2.95910

H 2.20793 3.46103 1.68611

H 3.34647 2.11796 1.95530

S5: References

1. F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H. F. Grützmacher and H. Grützmacher, *Angew. Chem. Int. Ed.*, 2011, 50, 8420–8423.
2. S. Burck, D. Gudat, M. Nieger and W. W. Du Mont, *J. Am. Chem. Soc.*, 2006, 128, 3946–3955.
3. R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett., 1989, 162, 165–169.
4. M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, Gaussian 09, Revision A.1 edn., 2009.
5. A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.,* 1994, 100, 5829–5835.
6. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, 7, 3297–3305.
7. A. D. Becke, *Phys. Rev. A*, 1988, 38, 3098–3100.
8. J. P. Perdew, *Phys. Rev. B,* 1986, 33, 8822–8824.
9. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett*., 1996, 77, 3865-68.
10. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*,1997, 78, 1396.
11. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, 110, 6158-69.
12. A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652.
13. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.*, 1994, 98, 11623–11627.
14. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, 37, 785–789.

15. DeLano, W. L. DeLano Scientific: San Carlos, CA, 2002.

16. R. Sustmann, R. Schubert, *Angew. Chem. Int. Ed*., 1972, 11, 840.